UNIVERSITÀ DELLA CALABRIA

UNIVERSITA' DEGLI STUDI DELLA CALABRIA
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TESI PER IL CONSEGUIMENTO DEL TITOLO DI
DOTTORE DI RICERCA IN FISICA, FIS/03

Proprietà elettroniche e vibrazionali di strati sottili adsorbiti su substrati metallici

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Electronic and vibrational properties of
adsorbed layers on metallic substrates

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Riassunto

La comprensione delle proprietà catalitiche, elettroniche e di adsorbimento di interface metallo/metallo è uno dei principali scopi della scienza delle superfici. Infatti, attraverso la manipolazione delle caratteristiche del substrato è possible ottenere catalizzatori più selettivi e dispositive elettronici più efficienti.

Il presente lavoro di tesi è basato sullo studio delle proprietà vibrazionali ed elettroniche di vari sistemi metallo/metallo, investigate tramite la spettroscopia ad alta risoluzione di perdita di energia di elettroni. Innanzitutto, sono stati investigate l'adsorbimento di metalli alcalini e il loro coadsorbimento con CO, O e gruppi OH su superfici di metalli di transizioni e di metalli nobili. Gli atomi di metalli alcalini adsorbono su superfici metalliche come particelle neutre ma polarizzate. L'adsorbimento di CO induce la ionizzazione del metallo alcalino. L'interazione a corto raggio tra coadsorbati è predominante nei sistemi di coadsorbimento dei metalli alcalini. L'ossidazione dei metalli alcalini è più facilmente ottenuta tramite l'adsorbimento e la dissociazione di CO che tramite esposizioni dirette a ossigeno. La stabilizzazione del sito di adsorbimento sotto la superficie è stata raggiunta per superfici di Cu(111) derogate con piccolo quantità di metalli alcalini, mentre su superfici di metalli di transizione modificate dall'adsorbimento di alcalini gli atomi di ossigeno rimangono in siti sopra la superficie. In quest'ultimo caso il legame tra substrato e ossigeno si indebolisce nella fase coadsorbita. Inoltre, abbiamo studiato le reazioni chimiche che avvengono su superfici bimetalliche (in presenza e in assenza di drogaggio con metalli alcalini) formate dalla deposizione di un monostrato di argento su Ni(111) e Cu(111).

L'analisi delle eccitazioni elettroniche collettive può dare importanti informazioni sulle superfici e le interfacce metalliche. La dispersione del plasmone di superficie è stata studiata in sistemi metallo/metallo in cui esistono elettroni confinati. Gli effetti di schermaggio dinamico sono incrementati dal confinamento elettronico ed esiste una correlazione tra la densità di stati ad elettrone libero del sistema, la sua reattività chimica e i processi di schermaggio dinamici. Sono state anche effettuate misure su strati sottili cresciuti sia strato dopo strato sia nano strutturati in isole. La risposta elettronica dipende fortemente dalla modalità di crescita del sistema.

I risultati presentati nella presente tesi hanno implicazioni dirette sulla comprensione dei processi che avvengono presso le interfacce metallo/metallo, con conseguenti potenziali applicazioni tecnologiche.

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UNIVERSITA' DEGLI STUDI DELLA CALABRIA
DIPARTIMENTO DI FISICA

THESIS FOR THE ATTAINMENT OF THE PHYLOSOPHIAE DOCTOR
DEGREE IN PHYSICS, FIS/03

Electronic and vibrational properties of adsorbed layers on metallic substrates

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Abstract

Understanding the adsorption, catalytic, and electronic properties of metal/metal interfaces is one of the foremost aims of surface science. In fact, through the tailoring of the characteristics of the substrate it should be possible to obtain more selective catalysts and more effective electronic devices.

This thesis is focused on the vibrational and electronic properties of various metal/metal systems, studied by high-resolution electron energy loss spectroscopy. Firstly, alkali adsorption and their coadsorption with CO, O, and OH on transition-metal and noble-metal surfaces have been investigated. Vibrational measurements demonstrated that alkalis adsorb as neutral and polarized adatoms on metal surfaces. The adsorption of CO induces alkali ionization. Short-range effects dominate in alkali coadsorption systems. Alkali oxidation is more readily achieved upon CO adsorption or dissociation than by direct exposures to oxygen. The stabilization of subsurface O was obtained on alkali-doped Cu(111), while on alkali-modified transition-metal catalysts O adatoms remain in on-surface sites. In the latter case a softening of the O-substrate bond occurs. Moreover, we studied chemical reactions at clean and alkali-doped bimetallic surfaces obtained by depositing monolayers of silver on Ni(111) and Cu(111).

Important information on the metal surfaces and interfaces could be provided also by the analysis of collective electronic excitations. Surface plasmon dispersion was investigated in metal/metal systems exhibiting electron quantum confinement. Screening effects are enhanced by the presence of quantum well states and a direct correlation between the free-electron density of states of the system, the chemical reactivity, and dynamical screening processes exists. Measurements have been performed on both flat thin films and films nanostructured in islands in order to shed light on the influence of the growth mode on the electronic response of the system.

The knowledge gained herein has far-reaching implications to the general understanding of processes at metal/metal interfaces.

Keywords: chemisorption, alkali metals, carbon monoxide, oxygen, metallic thin films, silver, bimetallic surfaces, electronic excitations, electron energy loss spectroscopy, surface chemical reactivity, charge transfers, electron confinement.

Preface

The thesis is divided into two parts. The first part represents an introductory section, with the aim of giving the reader a background to the subject. The second part contains the papers which this thesis is based on.

Published or accepted papers included in the thesis:

1. *High resolution energy loss measurements of Na/Cu(111) and H_2O/Na/Cu(111): Dependence of water reactivity as a function of Na coverage*
   Politano A. , Agostino R. G. , Colavita E. , Formoso V. , Chiarello G.
   Journal of Chemical Physics, 2007, Vol. 126, n. 24, pp. 244712-1-244712-5.

2. *Influence of CO adsorption on the alkali-substrate bond studied by high-resolution electron energy loss spectroscopy*
   Politano A. , Formoso V. , Agostino R. G. , Colavita E. , Chiarello G. ,
   Physical Review B, 2007, Vol. 76, n. 23, pp. 23340-23340.

3. *Electronic properties of self-assembled quantum dots of sodium on Cu (111) and their interaction with water*
   Politano A. , Agostino R. G. , Colavita E. , Formoso V. , Chiarello G.
   Surface Science, 2007, Vol. 601, n. 13, pp. 2656-2659.

4. *Purely quadratic dispersion of surface plasmon in Ag/Ni(111): the influence of electron confinement*
   Politano A. , Agostino R. G. , Colavita E. , Formoso V. , Chiarello G. ,
   Physica status solidi RRL - Rapid Research Letters, 2008, Vol. 2, n. 2, pp. 86-88.

5. *Electronic properties of (3/2x3/2)-Na/Cu(111)*
   Politano A. , Agostino R. G. , Colavita E. , Formoso V. , Chiarello G.
   Journal of electron spectroscopy and related phenomena, 2008, Vol. 162, n. 1, pp. 25-29.

6. *Evidences of alkali-induced softening of the oxygen-substrate bond*
   Politano A. , Formoso V. , Agostino R. G. , Colavita E. , Chiarello G.
   The Journal of Chemical Physics, 2008, Vol. 128, pp. 074703-1-074703-5.

7. *Vibrational measurements of Na/Ni(111) and (Na+CO)/ Ni(111)*
   Politano A. , Agostino R. G. , Colavita E. , Formoso V. , Tenuta L. , Chiarello G.
   Journal of Material Science, 2008, Vol. 43, pp. 3447-3451.

8. *Short-range interactions in Na coadsorption with CO and O on Ni(111)*
   Politano A., Agostino R. G., Formoso V., Chiarello G.
   ChemPhysChem, 2008, Vol. 9, pp. 1189-1194.

9. *Collective excitations in nanoscale thin alkali films: Na/Cu(111)*
   Politano A., Agostino R. G., Colavita E., Formoso V., Chiarello G.
   Journal of Nanoscience and Nanotechnology, 2008, doi:10.1166/jnn.2008.SBN28.

10. *The nature of the alkali-surface bond at low coverages investigated by vibrational measurements*
    Politano A., Agostino R. G., Colavita E., Formoso V., Tenuta L.,Chiarello G.
    The Journal of Physical Chemistry C, 2008, Vol. 112, pp. 3977-3980.

11. *Temperature effects on alkali-promoted CO dissociation on Ni(111)*
    Politano A, Formoso V., Chiarello G.
    Surface Science, 2008, Vol. 602, pp. 2096-2100.

12. *Alkali adsorption on Ni(111) and their coadsorption with CO and O*
    Politano A., Formoso V., Chiarello G.,
    Applied Surface Science, 2008, Vol. 254, pp. 6854-6859.

13. *Unexpected alkali-promoted CO dissociation on Cu(111) at room temperature*
Politano A., Formoso V., Chiarello G.
The Journal of Chemical Physics, 2008, Vol. 129, pp. 164703.

14. *Dispersion and damping of gold surface plasmon*
Politano A., Formoso V., Chiarello G.
Plasmonics, 2008, Vol. 3, pp. 165-170.

15. *Mechanisms leading to alkali oxidation on metal surfaces*
Politano A., Formoso V., Chiarello G.
The Journal of Physical Chemistry C, 2008, Vol. 112,pp. 17772-17774**.**

16. *Dispersion and damping of surface plasmon in Ag thin films grown on Cu(111) and Ni(111)*
Politano A., Formoso V., Chiarello G.
Superlattices and Microstructures, doi:10.1016/j.spmi.2008.10.017**.**

17. *Chemical reactions at clean and alkali-doped mismatched metal/metal interfaces*
Politano A., Formoso V., Chiarello G.
The Journal of Physical Chemistry C, in press**.**

18. *Interference effects in the excitation of collective electronic modes in nanoscale thin Ag films*
Politano A., Formoso V., Chiarello G.
Superlattices and Microstructures, doi:10.1016/j.spmi.2008.10.003**.**

19. *Effects of O adsorption on the Na+CO coadsorption system*
Politano A., Formoso V., Chiarello G.
Superlattices and Microstructures, in press**.**

Submitted papers included in the thesis:

1. *Alkali-promoted stabilization of subsurface oxygen on Cu(111)*
Politano A., Formoso V., Chiarello G.

2. *Comparative vibrational study on alkali coadsorption with CO and O on Ni(111) and Cu(111)*
Politano A., Formoso V., Chiarello G.

3. *Chemical interface damping in thin Ag films*
Politano A., Formoso V., Chiarello G.

4. *CO-promoted formation of the alkali-oxygen bond on Ni(111)*
Politano A., Formoso V., Chiarello G.

5. *Probing collective electronic excitations in ultrathin Ag layers grown on Cu(111)*
Politano A., Formoso V., Chiarello G.

6. *Tuning the lifetime of the surface plasmon upon sputtering*
Politano A., Formoso V., Chiarello G.

7. *Annealing effects on the plasmonic excitations of metal/metal interfaces*
Politano A., Formoso V., Chiarello G.

8. *Collective electronic excitations in nanoscale thin silver layers*
Politano A., Formoso V., Chiarello G.

Related papers, not included in the thesis:

1. *Plasmon of Shockley surface states in Cu(111): a high resolution electron energy loss spectroscopy study*
Politano A. , Chiarello G. , Formoso V. , Agostino R. G. , Colavita E.
Physical Review B, 2006, Vol. 74, n. 8, pp. 081401(R)-081404(R).
Selected for *Virtual Journal of Nanoscale Science and Technology,* Vol. 14, n. 7.

2. *Collective electronic excitations in systems exhibiting quantum well states*
Politano A., submitted to *Surface Review and Letters* (Review Paper)

Introduction

The adsorption of chemical species onto metallic substrates has attracted considerable interest in recent years for both fundamental interest and technological applications [1-4]. The presence of adsorbed atoms significantly changes the physical and chemical properties of the substrate. Understanding the electronic properties of surfaces and interfaces would imply the tailoring of more selective catalysts and an improvement of electronic devices.

Despite the progress in surface science during last decades, there are still important unsolved questions regarding atomic adsorption, charge transfers at surfaces, and the emerging field of electron confinement.

Atoms or simple molecules adsorbed on metal single crystals and, moreover, flat ultrathin films deposited onto metallic substrates are model systems currently used by both experimentalists and theoreticians.

The hybridization between the bonding and anti-bonding molecular states and the metal d-states would lead to the activation of charge transfers which strongly influence the occurrence of the dissociation of the molecules and the formation of other chemical species [5]. Quantum confinement of electrons in quantum well states play a key role in these phenomena as it was demonstrated that confined electrons may mediate charge transfer [6].

The best description of quantum well states can be achieved using an extended phase accumulation model that takes into account scattering of electron waves on the film–substrate boundary [7-9]. Alternatively, in substrates exhibiting energy gaps within the projected bulk band structure adsorbates may induce states within the energy gap [10-12]. Electrons occupying such states are confined at the top layer of the bulk sample and form a two-dimensional nearly free-electron gas. Even though both kinds of systems are characterized by the existence of confined electronic states, their character differs substantially. In fact, quantum wells are characterized by standing wave patterns only in the presence of a gap in the substrate [13]. Such significant dissimilarities in the electronic properties of apparently similar bimetallic surfaces should imply a quite different catalytic activity.

On the other hand, collective electronic oscillations are localized within the metal/metal interface [14, 15]. The confinement of collective charge oscillations influences electronic dynamics and electron-phonon coupling [16]. They also enhance the local electromagnetic field, so as to lead to high sensitivity in the surface-enhanced Raman scattering spectroscopy [17].

Furthermore, novel properties in metallic systems may emerge also with the reduction of the dimensionality. One well-known example is gold which is inert in its bulk form while gold nanoparticles are excellent catalysts in CO oxidation [18, 19]. Also the electronic properties are notably affected by the reduced dimensionality, as evidenced by the various colours that gold nanoparticles may assume, depending on the size.

The oscillation of charge within nanoparticles may support a Mie plasmon [20-22]. It could be excited by both light and electrons. In principle, Mie plasmons could be used as a very sensible sensor of gas adsorption. In general, it is quite expected that the growth mode and the geometrical properties of the system could influence the occurrence of chemical reactions.

In this thesis, we used high-resolution electron energy loss spectroscopy (HREELS) to investigate both the vibrational and electronic properties of metal/metal systems and the interaction of these interfaces with reactive species such as carbon monoxide, oxygen, and water. As concerns the vibrational measurements, we studied alkali adsorption and their coadsorption with reactive species on Ni(111) and Cu(111) surfaces and on bimetallic surfaces obtained adsorbing single layers of silver on these substrates.

Our results indicated that alkali adsorption is well described within the framework of the covalent model. The adsorption of CO has a dramatic effect on the vibrational properties of alkalis as it induces the ionization of alkali adatoms and enhances the efficiency of alkali oxidation, i.e. the formation of a direct alkali-oxygen bond. On alkali-modified transition-metal surfaces, the O-substrate bond is weakened in the coadsorbed phase. Instead, on copper substrates alkali doping reverses the energetic conditions for oxygen adsorption, so as to render energetically favourable the subsurface site.

Moreover, the dispersion and damping relation of collective electronic excitations in flat sodium, silver, and gold films grown on metal surfaces were investigated in order to find the relationship between electron quantum confinement and dynamic screening processes.

In addition, we carried out similar measurements on nanostructured sodium and silver films which put in evidence the influence of the growth mode on the electronic response of metal/metal systems. A joint analysis of vibrational and electronic properties revealed that supported metal clusters allow a remarkable charge transfer between coadsorbates compared with flat films.

The first part of the thesis presents an introductory section, where the physical background is given to the second part which contains the papers.

Experimental

In Figure 1 is shown the UHV chamber (with a base pressure of $5 \cdot 10^{-9}$ Pa) used for our experiments. It is equipped with an electron analyser (Phoibos 100, Specs), a high-resolution electron energy loss spectrometer (Delta 0.5, Specs), an apparatus for low-energy electron diffraction, a quadrupole spectrometer, and an ion gun for sputtering. Leak valves are used for controlled gas inlet in the UHV chamber.

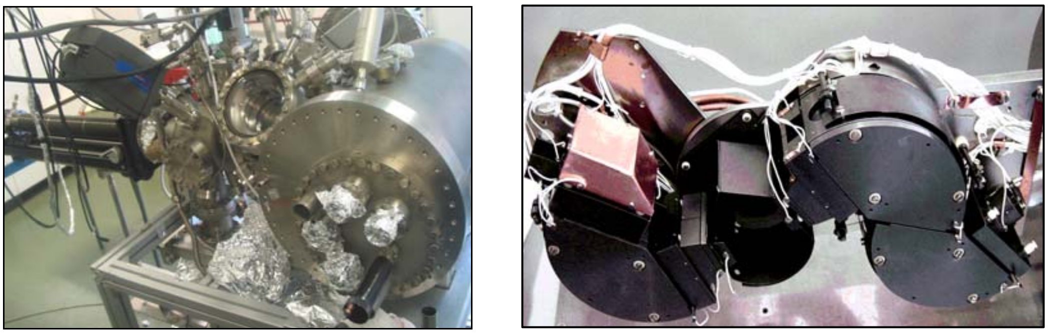

Figure 1: (left panel) UHV chamber used for experiments (right panel) HREELS spectrometer in the straight-trough position. It has a double-step monochromator and a single-step analyzer. Its ultimate energy resolution is 0.5 meV.

Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) were used as control techniques for checking the cleanliness of the order of the surface.

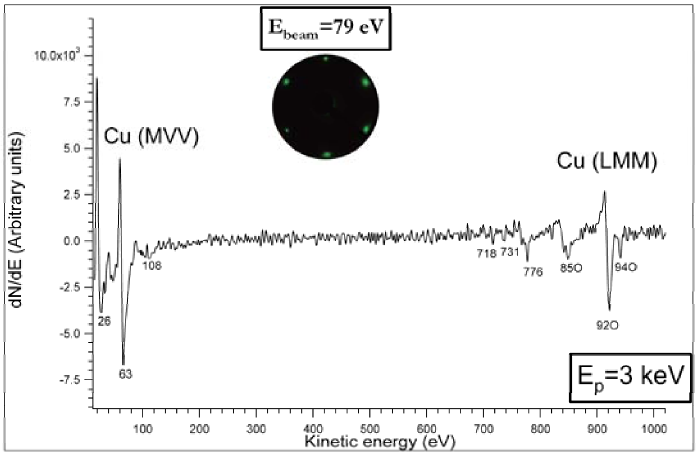

Figure 2: AES spectrum of the clean Cu(111) surface. The correspondent LEED pattern is also shown.

In HREELS experiments, a primary electron beam impinges with energy E_p onto a surface and the back-scattered beam emerges with energy E_p-E_{loss} where E_{loss} is the loss energy, that is the energy lost by electrons by exciting phonons, single-particle transitions, vibrations of atoms or molecule adsorbed onto the surface or plasmons [23-25].

Conservation of both energy and momentum leads to:

$$\begin{cases} E_{loss} = E_i - E_S \\ \hbar \vec{q}_{\parallel} = \hbar(\vec{k}_i \sin\theta_i - \vec{k}_S \sin\theta_S) \end{cases}$$

From the above equations, it is possible to calculate the parallel momentum transfer $q_{\parallel}$:

$$q_{\parallel} = \frac{\sqrt{2mE_i}}{\eta}(\sin\theta_i - \sqrt{1 - \frac{E_{loss}}{E_i}}\sin\theta_S)$$

In most cases, the inelastic event occurs far from the surface. This process is called “dipole scattering” as the long-range electric field of primary electrons interacts with the fluctuating dipolar field associated with the induced surface charges.

The scattering intensity is peaked at angles in the close nearness of the specular direction. For calculating the cross section, the dipole approximation allows neglecting the electron-substrate interaction.

On the other hand, if the loss occurs during the impact of impinging electrons with the ion cores (impact scattering), a fully microscopic calculation is required for theoretically describing the cross section.

A complete description of EELS theory can be found in Ref. 23-27.

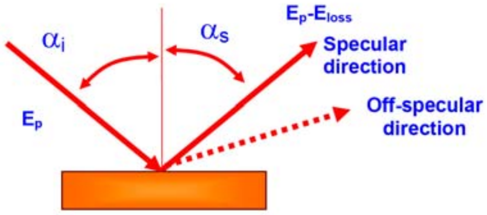

Figure 3: Scattering geometry in HREELS experiments

Adsorption on metallic surfaces

The surface science approach to heterogeneous catalysis is based on the step-by-step investigation of reaction pathways (adsorption, surface diffusion, chemical transformation and desorption of the adsorbed species). A chemisorbed atom, locally influencing the surface electronic structure, may affect the bond between the substrate and other coadsorbates. Adsorbates are used for tailoring the catalytic properties of substrates. They may behave as promoters or inhibitors of chemical reactions. Alkalis are generally promoters as they enhance the chemical reactivity of the system. Moreover, due to their simple electronic structure [28-30], they are used as model for chemisorption. Alkalis did not complicate the theoretical treatment by intermixing with the substrate (except for Al surfaces [31]) but they adsorb in over-surface sites [32]. Accordingly, several studies were performed for alkalis adsorbed on single-crystal surfaces and coadsorbed with reactive species as CO, O, and OH [30]. Alkalis often activate charge transfers (direct [33] or substrate-mediated [34]) between coadsorbates. For example, their peculiar electronic structure enhance the back-donation processes [35, 36] whenever coadsorbed with CO, so as to weaken the C-O bond (Figure 4).

Despite the considerable effort, several issues remained unresolved. The main challenge about alkali adsorption is to establish whether the alkali-substrate bond at low coverages has ionic [37], covalent [28, 29] or metallic character . The behaviour of the alkali-substrate vibration frequency as a function of the alkali coverage could provide important information on this point. However, the experimental findings disagree [38-48] with calculations [29]. As concerns the alkali coadsorption systems, recently more and more works [49-52] are invoking the predominant influence of nonlocal effects even though a short-range and local interaction of alkalis with coadsorbates had been taken for granted in most previous studies [53-55].

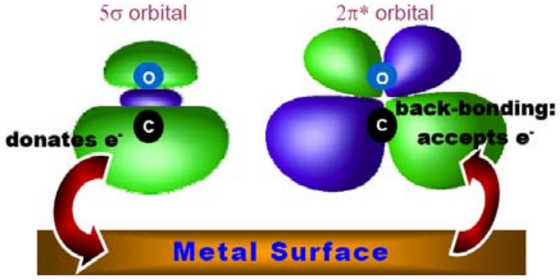

Figure 4: The mechanism for CO adsorption on metal substrates, which implies a back-donation process [35, 36] from 5σ to anti-bonding 2π* orbitals of CO, so as to weaken the intramolecular bond of CO molecules.

Furthermore, while alkali effects on coadsorbates have been widely investigated, the influence of coadsorbates on the vibrational properties of alkalis has been completely disregarded. Such approach could in principle show up novel effects that may lead to a decisive advancement in understanding adsorption processes at metal surfaces.

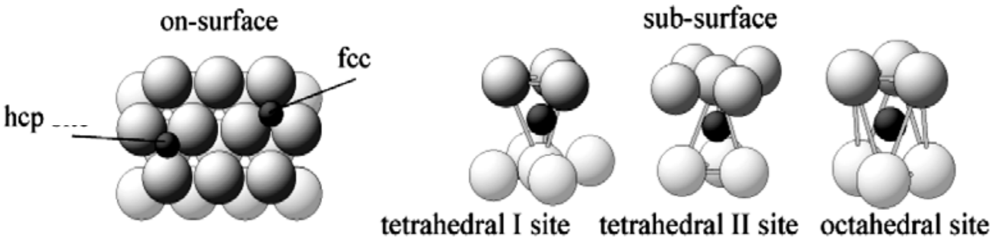

Figure 5: On-surface and subsurface adsorption sites [58]

In addition, alkalis may reverse the sign of the adsorption energy of chemisorbed species and stabilize metastable species, such as subsurface oxygen, whose pivotal role in many surface chemical reactions has been recently demonstrated [55-59].

Collective electronic excitations at metal surfaces

Surface plasmons are the normal modes of charge fluctuation at a metallic surface excited by an external electromagnetic field. They are localized at the surface and, like their bulk counterpart, are longitudinal modes. Collective electronic excitations have been experimentally investigated over a variety of different systems by means of different spectroscopic techniques [24, 25].

Time-dependent density-functional theory reasonably describes collective electronic excitations in simple metals. However, the available theoretical models are not able to completely describe more complex systems. In particular, the presence of d electrons and the subsequent s-d polarization [25] has a strong influence on the dynamical response at the surface.

Important information on the surface response is given by the dispersion relation of the surface plasmon. According to the Feibelman's model [60-63], the position of the surface screening charge relative to the jellium edge has to be considered to correctly describe the surface plasmon dispersion. Simple metals (alkalis, aluminium, alkaline-earth metals) exhibit an initial negative dispersion curves as the position of the centroid of the induced charge lies outside the surface. However, in the presence of a polarizable medium, as d-electrons in silver, the centroid is pushed well inside the geometrical surface and, thus, the initial dispersion of the surface plasmon became positive. It should be noticed that according to another model proposed by Liebsch [64], the centroid lies always outside the geometrical surface.

$$\omega_s(q_{||}) = \omega_s[1 - \frac{1}{2}q_{||}Re(d(\omega_s)) + O(q_{||}^2)]$$

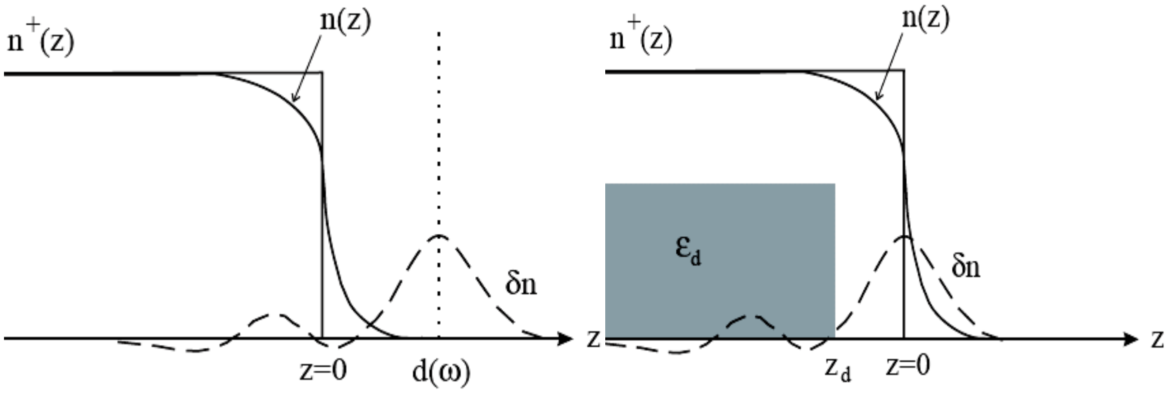

Figure 6: Position of the centroid of the dynamical screening charge $d(\omega_s)$ with respect to the geometric surface. $n^+(z)$ represent the positive jellium background, $n(z)$ the negative charge density and δn the induced density. In the left panel the centroid of the induced charge lies outside the geometrical surface ($z>0$). But in the presence of a polarizable medium, represented by ε_d, the centroid is shifted inside the bulk (right panel).

Summary of the papers

The papers summarized below treat vibrational and electronic properties of various metal/metal interfaces:

- Alkalis/Ni(111)

In paper I the vibrational properties of alkali adatoms were investigated. Measurements taken on very clean alkali layer revealed that the alkali adatoms adsorbs on Ni(111) in a neutral charge state, being the alkalis essentially polarized towards the surface. This was argued by the behavior of the alkali-substrate vibration energy as a function of the alkali coverage, which agrees with theoretical predictions within the framework of the covalent model. The adsorption of carbon monoxide leads to the ionization of the alkali adatoms. Moreover, a softening of the alkali-substrate bond was revealed in the alkali+CO coadsorbed phase (Paper II and III), in agreement with structural studies. Alkalis enhance the dissociation rate of CO molecules. A temperature-dependent critical alkali precoverage for CO dissociation was found to exist on Ni(111) (Paper IV). Contrary to all previous experimental findings, CO desorption is non-coincident with that of alkali (Paper IV and V).

As concerns alkali coadsorption with oxygen, alkalis promote the population of O 2 p_z antibonding orbitals, so as to weaken the O-Ni bond (Paper VI). Local effects were found to dominate alkali coadsorption with reactive species (Paper VII). Oxygen adsorption onto a CO-modified Ni(111) surface causes a blue-shift of the C-O stretching frequency (Paper VIII). On the other hand, alkali oxidation is more readily achieved upon CO adsorption (Paper IX) or CO dissociation (Paper X) than by direct exposures to oxygen.

-Alkalis/Cu(111)

Charge-density waves were suggested to occur on a single layer of Na on Cu(111) (Paper XI and XII). Increasing Na coverage beyond the monolayer, Na self-assembled quantum dots appeared. Mie plasmons exist within Na supported clusters (Paper XIII). They were found to be significantly reactive towards OH groups. For thicknesses higher than two layers, the film is flat and the ordinary surface plasmon was observed. Its dispersion relation is quite different from that of thick alkali films. We argue that this is a consequence of screening effects enhanced by electron quantum confinement in Na quantum well states (Paper XIV).

A softening of the alkali-substrate bond in the alkali+CO coadsorbed phase was recorded also on Cu(111) (Paper XV). On Cu(111), CO adsorption is dissociative also at the lowest alkali precoverages, due to the enhanced short-range character of the alkali-CO interaction on copper substrates (Paper XVI). Moreover, even small amounts of alkali doping reverses the energetic conditions for O adsorption, so as to stabilize subsurface O (Paper XVII).

-Silver ultrathin films on Ni(111)

A purely quadratic dispersion of the surface plasmon was measured for thin Ag films. As a consequence of the enhanced free-electron density of states due to the presence of Ag 5 sp-derived quantum well states, the position of the centroid of the induced charge lies less inside the geometrical surface compared with other Ag systems (Paper XVIII). The damping processes of the surface plasmon are enhanced in thin films and, moreover, the first experimental evidence of chemical interface damping of the surface plasmon in the presence of reactive species was reported (Paper XIX). Furthermore, the intensity of the surface plasmon underwent to a nonmonotonous behaviour as a function of the impinging energy, thus revealing interference effects between the incoming and the reflected field (Paper XX). The occurrence of Ag multipole surface plasmon is discussed in Paper XXI. It is excited only under very stringent kinematic conditions enhancing surface sensitivity. A similar excitation was observed also for Ag and Au films grown on Cu(111).

-Silver ultrathin films on Cu(111)

For two layers of Ag on Cu(111), the surface plasmon was not excited in the long-wavelength limit. At higher momenta a dispersionless surface plasmon was observed, in agreement with s-d polarization theory for ultrathin films (Paper XXII). For higher coverages, Ag islands appear on the flat bilayer. Surface plasmon is confined within Ag grains (Paper XXII and XXIII). Annealing removes the

confinement of surface plasmon and induces a negative linear term of the dispersion curve (Paper XXIII).
The lifetime of the surface plasmon could be tuned upon sputtering (Paper XXIV).
A comparative investigation between Ag films on Cu(111) and Ni(111) was reported in Paper XXV.

-Alkali-doped bimetallic surfaces: Ag/Cu(111) and Ag/Ni(111)
A giant increasing of the CO dissociation rate was obtained for the alkali-doped Ag/Ni(111) interface (Paper XXVI). A different behavior was found on the alkali/Ag/Cu(111) system. For higher Ag thickness (ten Ag layers), the alkali-modified bimetallic surface was found to be strongly reactive towards water molecules.

-Gold thin films on Cu(111)
In analogy with silver, a positive dispersion of the Au surface plasmon was observed (Paper XXVII). Damping processes of the Au surface plasmon are enhanced with respect to the case of Ag.

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PAPER I

The nature of the alkali-surface bond at low coverages investigated by vibrational measurements

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Nature of the Alkali Surface Bond at Low Coverages Investigated by Vibrational Measurements

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High-resolution electron energy loss spectroscopy has been used to study the nature of the Na/Ni(111) and K/Ni(111) bond at very low coverages. Measurements taken for very clean alkali layers provided, for the first time, the expected behavior of the alkali −substrate stretching energy as a function of the alkali coverage. Moreover, we found that the Na −Ni (K−Ni) bond was dramatically influenced by coadsorbed CO molecules causing a red shift of the Na −Ni (K−Ni) vibrational frequency. We argue that this effect could be at the base of discrepancies existing between the calculated and measured behavior of the vibrational energies as a function of the alkali coverage.

Introduction

Alkali metals are simple systems and efficient promoters of many surface chemical reactions[1−3] such as promoted oxidation of metals and semiconductors, hydrolysis, and carbon monoxide dissociation in the Fischer−Tropsch process. Previous studies aimed at revealing the nature of the alkali−substrate (A−S) bond at very low coverages led to controversial results.[4]

For a long time the adsorption properties of alkali atoms on metal surfaces were explained assuming for granted the Langmuir−Gurney model.[5] It predicted a donation of charge from the alkali metal atoms to the substrate and the formation of an ionic bond at low coverages. However, recent calculations[6,7] demonstrated that even in the low alkali coverage regime the adatoms are essentially in a neutral charge state implying a covalent bond. Photoemission measurements[8] confirmed these predictions. However, subsequent theoretical works[9,10] did not confirm the covalent model and suggested that the adsorption of alkali metals is always accompanied by a charge transfer to the metal surface. Experimentally, measurements of core-level binding energies[11,12] provided conflicting information on the charge transfer as a function of alkali coverage. To date, the main controversy concerns the determination of the A−S bond at very low coverages. There is a great effort to establish whether the adatom is partly ionic or it is neutral but strongly polarized. For the sake of truth, the new paradigm is that the A−S bond must contain an element of both these extreme ªmodelº situations.[4] The answer to this point has profound implications in our understanding of the surface chemical bond and catalytic reactions.

Whereas the electronic properties of the alkali metals on metal surfaces have been extensively studied, their vibrational properties have been measured only for a few systems.[13−24] On the other hand, the energy of the measured vibrational modes directly reflects the nature of the adsorbate−substrate bond. The decreasing adsorption energy of the alkali metal atoms with increasing coverage[25,26] should imply a decrease in the A−S stretching frequency, as a consequence of the bond weakening. Aside from the expectations of the Ishida's covalent model[6,7] of alkali adsorption on metal surfaces, predicting a softening of the A−S bond as a function of coverage, theoretical calculations for Na/jellium[27] and K on Cu(100)[28] found coverage-dependent downshifts of the A−S stretching energy.

High-resolution electron energy loss spectroscopy (HREELS) measurements of alkalis (Li, Na, K) adsorbed onto copper surfaces[13−16] and for Na/Mo(100)[23] observed a nearly coverage-independent A−S stretching frequency. Moreover, recent density functional theory[29] results for Na submonolayers on Cu(111) reported an A−S stretching mode at 22 meV whose energy was constant with coverage.

On the contrary, for Li/Cu(111) Lindgren[20] et al. measured an upshift of the Li−Cu vibration as a function of Li coverage. Likewise, for Cs/Ru(0001),[21] K/Pt(111),[22] and Li/Mo(110),[24] the A−S stretching energy was found to increase as a function of coverage. The upward shift of the A−S stretching was tentatively ascribed to the combined effects of many factors, such as dipole−dipole interactions,[15,20−22] the response of the substrate surface layer,[16] and an increase of the curvature of the potential-energy surface.[21]

To date, no experimental evidence reporting the expected[6,7,27,28] decreasing behavior of the A−S stretching energy as a function of coverage exists.

Here HREELS has been used to obtain information on the nature of the A−S bond of alkalis (Na, K) adsorbed onto the Ni(111) surface and coadsorbed with CO molecules on the same substrate. Loss measurements taken on very clean alkali layers provided the expected[6,7,27,28] behavior of the A−S stretching energy as a function of the alkali coverage in contrast to previous experimental studies[13−24] on similar systems. Moreover, we found that the A−S bond was dramatically influenced by coadsorbed CO molecules. The Na−Ni (K−Ni) vibration frequency shifted to lower frequencies in the presence of even small amounts of coadsorbed CO. We show that this effect changes the behavior of the A−S vibration energy as a function of coverage. Our results prepare the grounds for more sophisticated theoretical models about adsorption and coadsorption of alkalis with other molecular species.

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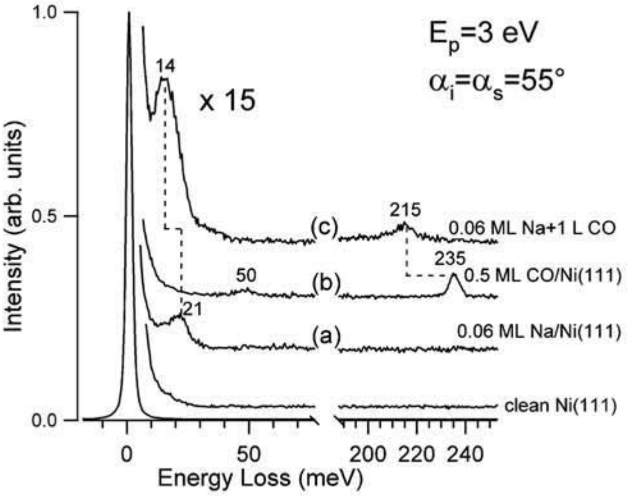

Figure 1. HREEL spectra of (a) 0.06 ML Na deposited at 400 K onto the Ni(111) surface; the loss spectrum was acquired at the same temperature, (b) 0.5 ML CO/Ni(111) dosed at room temperature, (c) 0.06 ML Na coadsorbed with CO at room temperature. All spectra were multiplied by the same factor.

Experimental Methods

Loss measurements were performed using a HREEL spectrometer (Delta 0.5, SPECS) mounted in an ultrahigh vacuum chamber with a base pressure of 5×10^{-9} Pa. Loss spectra were acquired in the specular geometry (incident angle of 55° with respect to the sample normal) using a primary electron beam of 3 eV and an energy resolution of 2 meV. The Ni(111) surface was prepared by repeated cycles of ion sputtering (E_p = 1.5 keV) and annealing at 1000−1200 K. Low-energy electron diffraction (LEED) and Auger electron spectroscopy were used to check surface order and cleanliness, respectively. Na and K atoms were deposited onto the surface by a dispenser (SAES GETTERS), which was carefully degassed for several days at a pressure of $2-4 \times 10^{-8}$ Pa. Before each deposition, the dispenser was held at a fixed temperature in order to reach a constant evaporation rate. Heating currents between 5.3 and 6.0 A for Na and 4.8 and 5.5 A for K were used. CO molecules were admitted in the chamber by means of a precise leak valve. Alkali coverages were estimated from the exposure time, taking as reference the coverage of well-known LEED structures: $p(2 \times 2)$ K and $(\sqrt{3} \times \sqrt{3})R30°$ Na. The coverage θ is given as the ratio between the number of adsorbed atoms and the number of atoms of the topmost layer of the Ni(111) substrate.

Results and Discussion

Figure 1 shows HREEL spectra taken for 0.06 ML Na/Ni(111), 0.5 ML CO/Ni(111), and for the coadsorbed phase (Na + CO), respectively. Spectra a and b show the characteristic vibrational modes for Na/Ni(111) and CO/Ni(111). Spectrum c shows that Na and C−O stretching vibrations are mutually influenced upon coadsorption of the two species. We associate the 21 meV loss peak with Na atoms vibrating perpendicular to the substrate. Upon coadsorption, the Na stretching frequency shifted from 21 down to 14 meV and the internal C−O vibration shifted from 235 down to 215 meV. The softening of the Na−Ni stretching well agrees with the increased bond length found in the alkali+CO coadsorbed phase.[30,31] An elongated A−S bond length should imply a weaker A−S vibration energy.

Moreover, CO exposure was found to cause a remarkable increase of the intensity of the Na−Ni peak. Such findings suggest the occurrence of a local charge transfer between coadsorbed species, i.e., a CO-induced ionization of the alkali adatom. In fact, the intensity of vibrational modes is expected to be higher for ionized species rather than for strongly polarized but essentially neutral adatoms.[35] Figure 2 shows the same CO-induced weakening of the A−S bond for K (θ_K = 0.030 ML) and for another Na coverage (θ_{Na} = 0.025 ML). The C−O stretching was revealed at 224 and 215 meV, respectively. The alkali-induced shift of the C−O stretching energy has been observed and interpreted so far.[32,33] However, it was argued that the adsorption properties of alkali metals were not influenced by CO molecules. Present loss measurements demonstrated that as Na and K affect the bond properties of CO, likewise CO molecules alter the adsorption properties of alkali-metal atoms. We suggest that this effect never revealed before could have masked the true interpretation of previous experimental results concerning the nature of the bond between alkali metals and metallic surfaces. As the adsorption of small amount of CO dramatically affect the vibrational properties of alkalis, and thus the A−S bond, we dedicated much care to prepare very clean alkali layers to perform vibrational measurements with an unprecedented precision. In fact, it is well-known that alkali layers are extremely reactive and that their deposition is often accompanied by the adsorption of atomic and molecular species arising from residual gases in the chamber.[22,36,37]

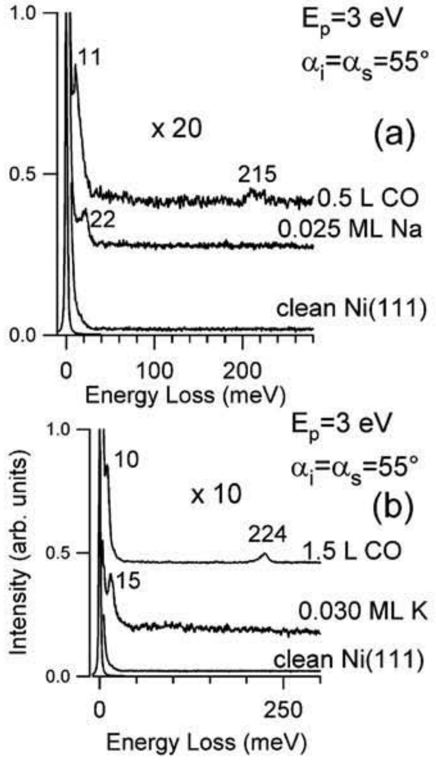

Figure 2. HREEL spectra of Na (panel a) and K (panel b) deposited on Ni(111) at 400 K and after the exposure of the alkali layer to CO at room temperature.

Alkali layers free of any contamination and particularly without traces of CO could be obtained with the sample held at 400 K during both deposition and measurements; moreover, each loss spectrum was acquired in a few minutes (less than 5 min) to limit as more as possible any influence of residual gases on the loss spectra.

Loss spectra for selected coverages of Na deposited on Ni(111) at 400 K are reported in Figure 3a. At the lowest coverage (0.01 ML) the Na−Ni stretching vibration was revealed at 25 meV. For greater Na coverages, this peak shifted down to 21−22 meV, and it remained at a constant energy for coverages above 0.05 ML as reported in the inset of Figure 3a. At higher

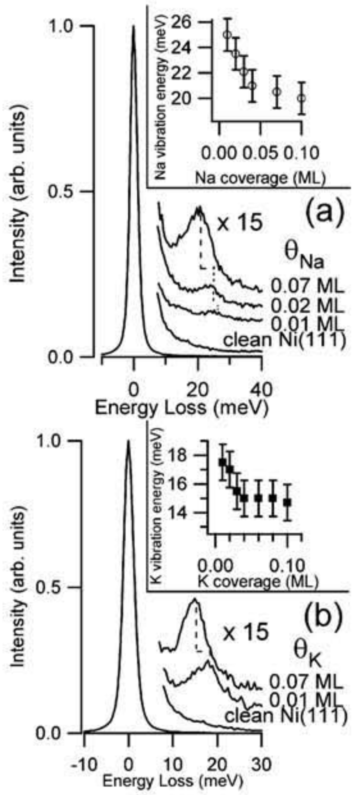

Figure 3. (a) HREEL spectra of low Na coverages deposited on Ni(111) at 400 K (loss spectra were acquired at the same temperature). Loss peaks are due to the Na−Ni stretching vibration. The inset shows the behavior of the Na−Ni vibration as a function of Na coverage. (b) The same for panel a but for K.

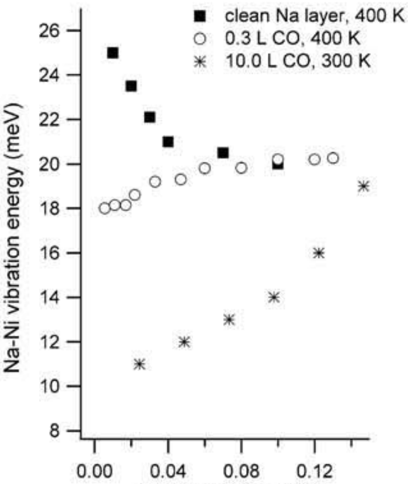

Figure 4. Behavior of the Na−Ni stretching energy for a clean Na adlayer and for Na dosed onto a CO-modified Ni(111) surface at 400 and 300 K, respectively.

coverage, the closer distances between Na adatoms cause the overlayer to be completely metallized, and as a consequence, dipole fluctuation are screened very efficiently by the two-dimensional electron gas so that the excitation of adatom vibrations perpendicular to the surface is no longer feasible.[34] A similar behavior of the A−S stretching as a function of coverage was found also for K deposited onto the Ni(111) at 400 K (Figure 3b). The K−Ni stretching energy shifted from 18 down to 15 meV with increasing coverage, thus indicating the occurrence of a K−Ni bond weakening.

In Figure 4 we compare the behavior of the Na−Ni vibration in clean Na layers grown on Ni(111) and in Na deposited onto a Ni(111) surface precovered with 0.3 L of CO at 400 K and with 10 L CO at room temperature, respectively. The presence of preadsorbed CO molecules changes the Na−Ni vibration energy especially at the lowest Na coverages. In particular, it was observed that the Na−Ni frequency depends on the CO/Na ratio. Higher is such ratio, lower is the Na−Ni vibration energy. The behavior of the curves obtained for Na adsorbed onto the CO-precovered Ni(111) surface as a function of the alkali coverage are similar to those reported in previous investigations of Li/Cu(111),[20] Cs/Ru(0001),[21] K/Pt(111),[22] and Li/Mo(110).[24] It is worth to notice that authors of ref 22 found that K “reacts with residual water molecules to form KOH”. The effects of contamination-induced changes of the A−S bond were not taken into account.

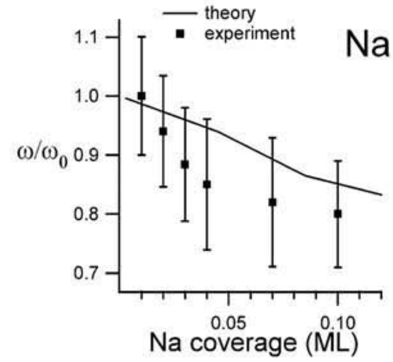

Figure 5. Comparison between the theoretical behavior of the A−S stretching vibration (data taken from ref 27, with permission) and the experimental curve for Na reported in Figure 3a. The frequency of the A−S stretching, ω, was normalized to its value for the lowest alkali coverage, ω_0.

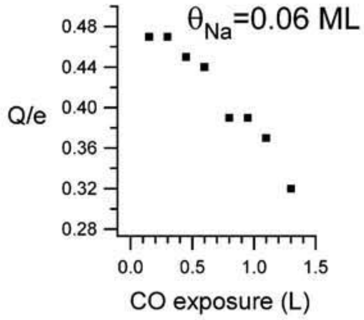

Figure 6. The dynamic dipole charge Q/e (e is the electron charge) of Na as a function of CO exposure.

The experimental results obtained in the present study were compared to calculation performed by Ishida and Morikawa[27] for Na/jellium. The comparison between present experimental data for Na and theoretical prediction[27] is rather good (Figure 5), thus confirming the reliability of our measurements.

To gain more information on the microscopic mechanisms determining the A−S bond, we reported in Figure 6 the behavior of the dynamical charge of Na as a function of CO exposure. The dynamical dipole moment μ of Na could be evaluated from the measured intensity and energy of the Na−Ni loss peak using the dipole scattering theory.[35] The effective charge Q can be then calculated from $\mu = (\hbar/2M_r\omega)^{1/2}$, with M_r being the reduced mass. Here a rigid Ni substrate is assumed, i.e., $M_r = M_{Na}$, and the following experimental parameters are used: the incidence angle (55°), the half-angle of acceptance (1.0°), and the primary energy of 3 eV. As the amount of CO deposited on the surface increased, the dynamical charge Q of Na decreased almost linearly, giving hints on the charge status of alkali atoms.

Hence, present loss measurements provided novel results, which may definitively elucidate on the nature of the A−S bond.

Direct evidence is reported that the bond is stronger at low coverages and becomes weaker as the alkali coverage is increased (Figure 3). This finding is in excellent agreement with the results predicted by the covalent model introduced by Ishida.[6,7,27] Moreover, spectra showed in Figures 2 and 3 indicate that the coadsorption of Na (K) with CO is accompanied by a dramatic weakening of the Na−Ni (K−Ni) bond. The lowering of the A−S vibration is assigned to a charge transfer from the alkali atoms to the antibonding $2\pi^*$ orbitals of CO.[38,39] As a matter of fact, the population of an antibonding orbital weakens the C−O bond causing the observed red shift of the C−O stretching vibration.

The transition from the covalent to the metallic state occurs at very low coverages (Figure 3). This is a further evidence of the neutral charge state of alkali atoms adsorbed on the clean Ni(111) surface. In the absence of strong dipole−dipole repulsive interactions, the alkali atoms are led to condensate in small islands with a high local coverage. By contrast, the finding of an increasing A−S stretching frequency with alkali coverage by previous experimental results[20−22] led to the conclusion that the metallization should start only at higher coverages.[21] Moreover, present measurements support a picture in which the ionization of alkali metal atoms occurs only whenever they are coadsorbed with CO (Figure 6).

Conclusions

In conclusion, we have presented loss measurements providing, for the first time, a full agreement with Ishida's model (refs 6, 7, 27) and photoemission measurements (ref 8). The coadsorption of CO molecules influences the A−S bond, causing a dramatic lowering of the Na−Ni (K−Ni) stretching frequency. Accordingly, alkalis adsorbed on Ni(111) are essentially in a neutral charge state with no donation of charge to the substrate. On the contrary, the coadsorption of alkali atoms with CO molecules is accompanied by a charge transfer from Na (K) to the $2\pi^*$ orbitals of CO. This leads to the ionization of alkali atoms. Present results claim for more accurate theories about alkali coadsorption with CO molecules.

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PAPER II

Influence of CO adsorption on the alkali-substrate bond studied by high-resolution electron energy loss spectroscopy

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Influence of CO adsorption on the alkali-substrate bond studied by high-resolution electron energy loss spectroscopy

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The coadsorption of Na/CO on Ni(111) has been investigated using high-resolution electron energy loss spectroscopy. Loss measurements showed that coadsorbed CO molecules dramatically affect the vibrational properties of Na adatoms. The Na-Ni vibration energy at 22 meV measured on the Na/Ni system shifted down to 12 meV for the CO/Na/Ni surface. This result was ascribed to a charge transfer from Na to CO. On the contrary, no appreciable shift of the Na-Ni stretching frequency was observed for the coadsorption of Na with oxygen.

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The knowledge of chemical reactions at surfaces is one of the main aims of surface science studies in ultrahigh-vacuum conditions. Alkali-metal atoms are promoters of a wide variety of catalytic reactions such as oxidation of metal and semiconductor surfaces and dissociation of various molecules (CO, N_2, NO).[1–4] Because of its fundamental and technological importance, the alkali+CO system received a great attention.

High-resolution electron energy loss spectroscopy (HREELS) and infrared reflection absorption spectroscopy (IRAS) measurements revealed a significant lowering of the C-O stretching frequency in the alkali+CO coadsorbed phase.[5,6] To date, many effects are supposed to be responsible for the softening of the C-O internal bond: Electrostatic interactions,[7–10] surface states,[11] direct,[12] and indirect (substrate-mediated)[13] chemical interactions. A recent theoretical work suggests that the shift of the C-O energy vibration is caused by an enhanced alkali-induced electronic polarizability of the metal surface.[14]

Despite the wealth of efforts, the achieved results have not yet been conclusive and new experimental investigations are needed to shed more light on this area and, in general, on the microscopic mechanisms governing the surface reactivity. So far, many of the previous experimental studies[2,5,6] on the alkali-CO coadsorption were performed within a common approach; that is, first, alkali atoms were deposited onto the metal surface and only successively the surface was exposed to CO molecules. This procedure was based on the assumption, taken for granted, that preadsorbed alkalis change the electronic properties of the underlying surface and, as a consequence, the adsorption properties of CO molecules. Accordingly, the softening of the C-O bond was mainly ascribed to the action of preadsorbed alkali atoms. Theoretical investigations were performed within the same assumption.[14] As a matter of fact, all previous studies were focused on the alkali-induced shift of the C-O stretching vibration, whereas any effect of CO on the alkali-substrate bond was completely disregarded. As alkali atoms affect the vibrational properties of CO, likewise CO molecules should influence the nature of the alkali-substrate bond. So far, the effects of CO on the vibrational properties of alkali atoms have not been investigated.

In this Brief Report, we show that CO molecules dramatically affect the chemical bond of alkali-metal atoms with the substrate. The Na-Ni stretching mode measured in the presence of coadsorbed CO molecules was found to shift to lower energies by about 10 meV with respect to the Na-Ni stretching energy (22 meV) measured for Na adsorbed on the clean Ni(111) surface. Same results were obtained for the coadsorption of K and CO. By contrast, the Na-Ni vibration was slightly reinforced for Na coadsorbed with oxygen atoms. Our results suggest that the basic mechanisms of the catalytic promotion of alkali atoms are still poorly understood and claim for new theoretical approaches.

HREEL measurements were performed using a spectrometer (Delta 0.5, SPECS) operating at a base pressure of 5×10^{-9} Pa. Loss spectra were acquired in the specular geometry (incidence angle of 55°) using a primary electron beam energy of 3 eV and an energy resolution of about 2 meV. The Ni(111) surface was prepared by repeated cycles of ion sputtering ($E_p = 1.5$ keV) and annealing at 1000–1200 K. Low energy electron diffraction (LEED) and Auger electron spectroscopy were used to check surface order and cleanliness, respectively. Na (K) atoms were deposited onto the Ni(111) surface by a well degassed dispenser (SAES GETTERS). Preadsorbed alkali layers free of any contamination could be obtained only by keeping the Ni(111) surface at 400 K during deposition. Alkali, CO, and oxygen coverages were estimated from the exposure time taking as reference the coverage of well-known LEED structures; that is, $(\sqrt{3} \times \sqrt{3})R30°$-Na, $p(2\times 2)$-K, $c(4\times 2)$-CO, and $p(2\times 2)$-O, respectively. The coverage θ is given as the ratio between the number of adsorbed atoms and the number of atoms of the topmost layer of the Ni(111) substrate. Furthermore, a clear $(3/2\times 3/2)$-Na LEED pattern appeared at full Na monolayer coverage, i.e., 0.44 ML.

First, the vibrational spectra of alkalis, CO, and oxygen separately adsorbed on the Ni(111) surface were recorded in order to have well-established reference data. As known, CO molecules occupy threefold hollow sites on Ni(111) and at the coverage of 0.5 ML they form a $c(4\times 2)$ LEED structure.[15] For this phase, the CO-Ni mode and the C-O stretching energy were observed at 50 and 235 meV, respectively.[16] As far as oxygen atoms, they form a $p(2$

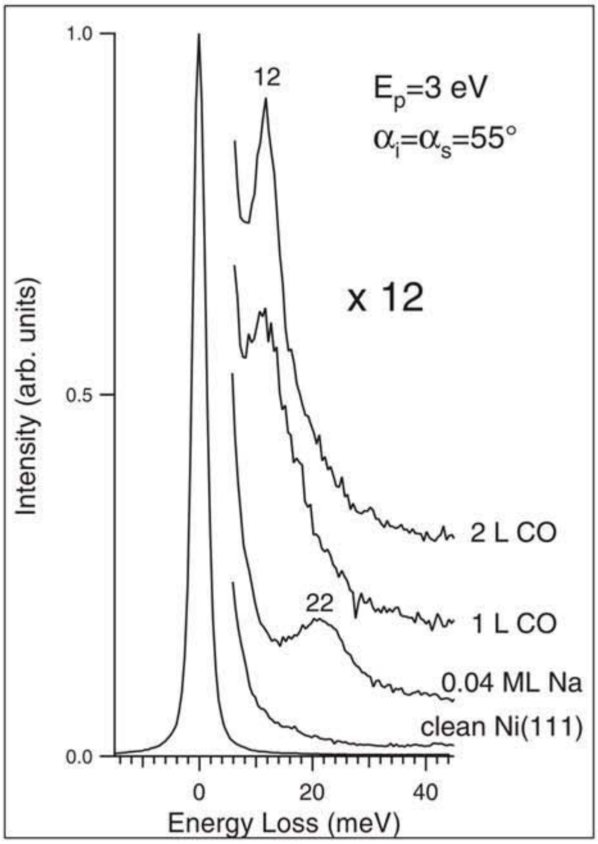

FIG. 1. Electron energy loss spectra of 0.04 ML of Na deposited at 400 K onto the Ni(111) surface and after CO exposures. After CO exposures, the Na-Ni vibration energy shifted from 22 meV down to 12 meV.

$\times 2$) structure and the O-Ni vibration was found at 70 meV.[17] As concerns the adsorption of Na, the Na-Ni stretching energy assumed values between 25 meV (for Na coverage less than 0.01 ML) and 22 meV (for Na coverage above 0.04 ML).

The loss spectrum of 0.04 ML of Na deposited on Ni(111) showed the Na-Ni stretching energy at about 22 meV (Fig. 1). The latter result is in excellent agreement with loss measurements[18] and calculations[19] performed on Na/Cu(111) and it provides a direct evidence that the differences between the electronic structure of Ni(111) and Cu(111) play only a negligible role on the Na-substrate bonding. The Na-Ni stretching energy shifted from 22 meV down to 12 meV upon CO exposure (Fig. 1); moreover, the Na-Ni loss peak became narrower than that measured on the Ni(111) clean surface. The behavior of the Na-Ni and C-O stretching energies for 0.08 ML of preadsorbed Na as a function of CO exposure is shown in Fig. 2. The Na-Ni vibration was observed to continuously shift towards lower energies while the C-O stretching energy initially remained at 208 meV (0.3 L of CO) and then shifted upward to 218 meV for 1.6 L of CO (highest CO coverage and saturation). Interestingly, both the Na-Ni and the C-O vibration energies were mutually affected upon coadsorption. The energy shift of the Na-Ni and C-O vibrations was found to be dependent on the Na/CO ratio. Similar results were obtained by coadsorbing K and CO on the same surface.

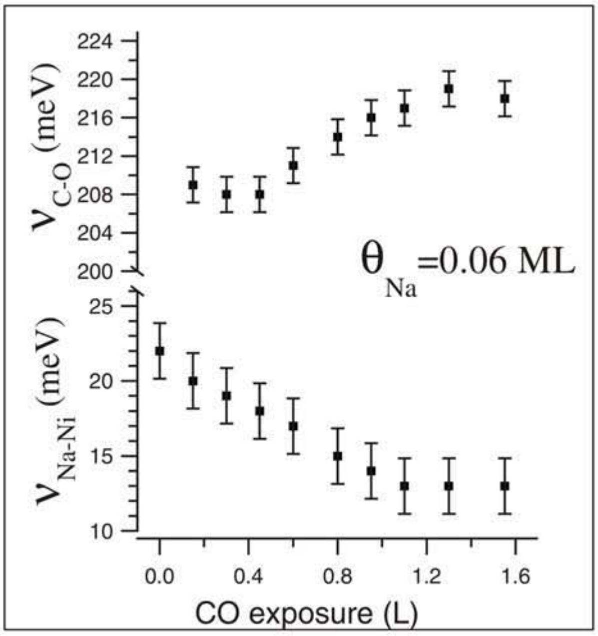

FIG. 2. Behavior of the C-O internal stretching and the Na-Ni vibration energies as a function of CO exposure. The Na layer was prepared at 400 K, whereas CO exposures were made at room temperature.

More details on the Na-CO interaction could be obtained by adsorbing Na on the $c(4\times 2)$-CO/Ni(111) surface. The $c(4\times 2)$ structure was prepared by exposing the surface to 1 L of CO at 200 K. The CO-Ni and the C-O vibrational modes were measured at 50 meV and 235 meV, respectively (Fig. 3). Such modes were significantly affected by Na deposition (at 200 K). The CO-Ni vibration strengthened and shifted to higher loss energies up to 72 meV; moreover, a new feature arose at 220 meV, close to the C-O stretching vibration. Both modes at 220 and 235 meV evolved with the alkali deposition and merged into a single feature at 220 meV for a Na coverage of 0.22 ML. The Na-Ni stretching energy for the CO/Na phase was observed between 12 meV and 14 meV (Na coverages above 0.22 ML). As regards the structural side of the investigation, the initial $c(4\times 2)$-CO LEED pattern slightly degraded with the Na deposition but no new ordered structures were observed. The existence of two distinct C-O frequencies for Na coverages between 0.07 and 0.13 ML indicated the presence of two different species of adsorbed CO molecules; the former was essentially unaffected being the C-O stretching energy at 235 meV; the latter, instead, interacted with Na atoms and moved to 220 meV. The interaction between sodium and carbon monoxide influenced also the CO-Ni loss as its line shape appeared broadened. At the highest Na coverage (0.22 ML), a uniform layer with about one atom of Na for each two CO molecules should exist on the surface and only a single C-O stretching energy at 220 meV was observed in the loss spectrum.

Loss measurements taken for the Na/CO coadsorbed phase (Figs. 1–3) showed a simultaneous weakening of the Na-Ni and C-O bonds and a strengthening of the CO-Ni bond. The weakening of the Na-Ni bond caused by CO mol-

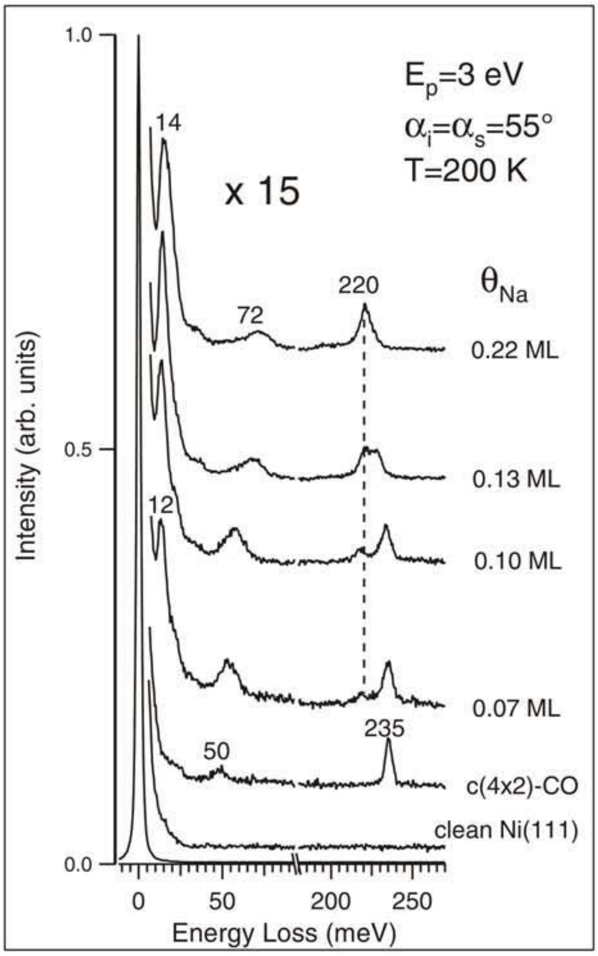

FIG. 3. Electron energy loss spectra of $c(4\times2)$-CO prepared at 200 K and after deposition of different amounts of Na at the same temperature.

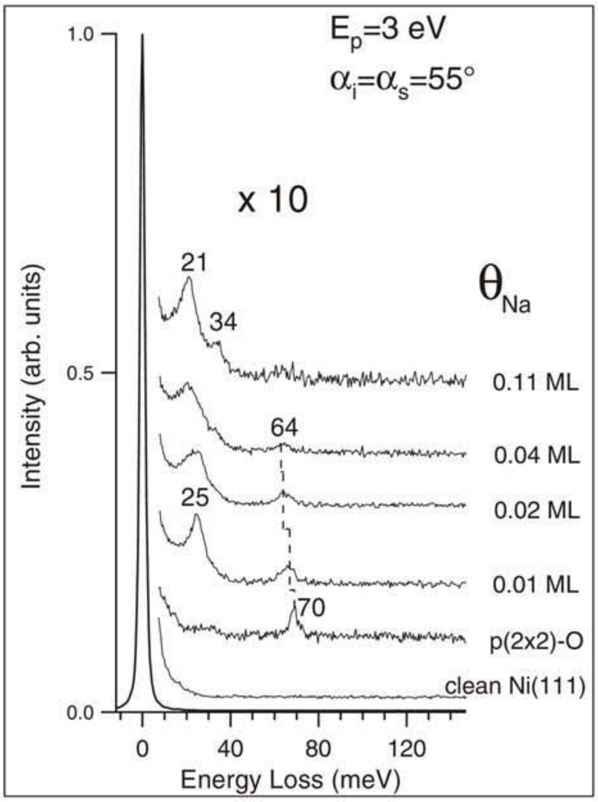

FIG. 4. Electron energy loss spectra of $p(2$-$2)$-O prepared at 400 K and after deposition of different amounts of Na at the same temperature.

ecules was unexpected and never observed before. During the investigation of the structural properties of K/CO on Ni(111) and on Ni(100),[20,21] a significant increasing of the alkali-substrate bond length was revealed with respect to the case of K/Ni(111) and K/Ni(100). Such finding was not completely understood, but it is in excellent agreement with the weakening of the Na-Ni bond reported in this work.

The bond of CO with metal surfaces is explained within the donation-backdonation model.[22,23] The stretching frequency of CO strongly depends on the population of the $2\pi^*$ orbitals as occupied antibonding orbitals weakens the C-O bond.[24] On the other hand, the CO-Ni bond depends on the electron donation from the CO-5σ orbitals to the Ni surface and the back-donation from the substrate into the $2\pi^*$ orbitals of CO.[24] The alkali-induced lowering of the C-O stretching frequency has been ascribed to an enhanced back-donation from the substrate into the $2\pi^*$ molecular states promoted by alkalis.[25,26] Nevertheless, the physical mechanisms describing the charge donation are very different one from each other. He and Jacobi[27] studied CO/Cs on Ru(0001) and assumed a two-step process: Preadsorbed alkalis donate their charge to the metal surface and then such charge is back-donated to coadsorbed CO molecules. Their measurements were interpreted assuming a long-range interaction between CO and Cs. Instead, calculations by Wimmer *et al.*[25] led to a picture of alkali *s* electrons polarized towards the surface. The alkali-induced dipole layer causes a shift of all electronic states of CO towards the Fermi level, favoring a charge transfer from the metal surface into the $2\pi^*$ orbitals. In others "electrostatic models,"[9,28] the electric field causing the enhanced electron back-donation was assumed to be arising from alkali atoms adsorbed in a full ionic state. Recently, Stolbov and Rahman[14] showed that the softening of the internal bond in diatomic molecules, such as CO and O_2 adsorbed on Cu(111) and Pd(111), was caused by an enhancement of the surface electronic polarizability induced by preadsorbed K atoms (nonlocal model). Unfortunately, in all these studies the vibrational properties of alkali atoms were not considered either before or after the coadsorption with molecular species.

Our loss spectra provide direct evidences that the shifts of the Na-Ni and C-O stretching frequencies are related to each other and we suggest that they are correlated to the charge state of both CO molecules and Na atoms. The adsorption of CO on the Ni(111) surface precovered with Na and vice versa is accompanied by a significant donation of charge from Na atoms into CO molecules. Moreover, the strengthening of the CO-Ni bond (Fig. 3) confirms experimentally the alkali-induced charge transfer from CO-5σ to the metal surfaces induced by alkali atoms, as found by Wimmer *et al.*[25] and by Jenkins and King.[26] Present measurements indicated that Na and CO should be in close contact on the metal surface for charge transfer to take place. Accordingly, we suggest that the action of CO on the Na adatoms is a local effect. The similar Na+CO/Cu(111) system studied by Svensson[29] exhibited an analogous behavior, i.e., the action of Na on CO molecules was found to be very local, in disagreement with the nonlocal electron transfer process (Wimmer and Stolbov models).

In order to ascertain whether the same mechanisms, i.e., charge transfer processes, apply for other systems, we investigated the coadsorption of Na with oxygen. Carbon monoxide and oxygen are both electronegative species with respect to Na atoms and they could behave in the same way. A $p(2\times2)$-O structure was prepared at 400 K and several coverages of Na were deposited on this phase at the same temperature. The loss spectrum of the $p(2\times2)$-O showed the O-Ni mode at 70 meV and an induced phonon at 30 meV (Fig. 4). After the deposition of Na on the oxygen layer, the Na-Ni stretching appeared at 25 meV while the O-Ni vibration shifted from 70 meV down to 64 meV. For Na coverages between 0.04–0.11 ML, a new feature appeared at 34 meV and the Na-Ni peak shifted to 21 meV. The feature at 34 meV was assigned to the O-Na stretching mode. The weakening of the O-Ni bonding may be due to the formation of Ni-oxygen-Na bonds or a charge transfer from the metal surface to the antibonding states of adsorbed oxygen atoms, as found for K/O/Rh(111).[30] No other changes were observed for higher Na coverages. Hence, present results unambiguously indicated that Na atoms donate charge to CO molecules, but they do not donate any charge to oxygen atoms.

In conclusion, we have presented loss measurements providing direct evidences of a dramatic lowering of the Na-Ni stretching frequency in the presence of coadsorbed CO. The effect was ascribed to a local charge transfer between the coadsorbed species. Such charge donation is responsible of the weakening of the C-O and Na-Ni stretching vibrations and of the strengthening of the CO-Ni bond. Calculations including the effects reported here (the CO-induced weakening of the Na-Ni mode) are needed to clarify the basic mechanisms of the alkali-CO bond and alkali promotion effects.

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PAPER III

Vibrational measurements of Na/Ni(111) and (Na+CO)/ Ni(111)

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Vibrational measurements of Na/Ni(111) and (Na + CO)/Ni(111)

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Abstract The vibrational properties of Na atoms and of Na coadsorbed with CO on Ni(111) have been studied by high-resolution electron energy loss spectroscopy. Loss measurements showed a significant weakening of the alkali–substrate bond as a function of the alkali coverage. Moreover, we found that coadsorbed CO molecules dramatically influence the vibrational properties of Na adatoms. The Na–Ni stretching frequency (22 meV) measured on the Na/Ni(111) system shifted down to 13 meV for the (Na + CO)/Ni(111) surface. This unexpected result was ascribed to a charge transfer from Na to CO. Present findings give new insights on the nature of the alkali–substrate and alkali–CO bond.

Introduction

The adsorption and coadsorption properties of alkali metals on metal surfaces have motivated the experimental and theoretical research aimed at providing new insights into the alkali–substrate [1] and alkali–adsorbate interactions [2]. The alkali-metal atom is regarded as the prototype system for modeling chemisorption and coadsorption. Such processes are of great interest in several applications such as heterogeneous catalysis, corrosion, and oxidation [3, 4]. Despite the great effort, the nature of the alkali–substrate bond is still under investigation and no conclusive results have been reached. In the Gurney model [5], the alkali atoms transfer their valence charge to the substrate and the bonding is ionic; on the contrary, at higher coverages the alkali–alkali interaction dominates over the alkali–substrate interaction, and the overlayer assumes a metallic character. However, Ishida [6, 7] questioned the ionic model and demonstrated that, regardless of the coverage, the alkali–substrate bond has essentially a covalent character. Ishida's predictions were confirmed by the photoemission measurements [8]. Nonetheless, the covalent model was not accepted.

The coadsorption of CO with alkali metals on transition metal surfaces has also been extensively investigated [9]. High-resolution electron energy loss spectroscopy (HREELS) and infrared reflection absorption spectroscopy measurements revealed a notable lowering of the C–O stretching frequency in the CO-alkali coadsorbed phase [10, 11]. Such finding stimulated a great interest and several investigations aimed at understanding the chemical and physical origins of the softening of the C–O vibration were performed. The weakening of the C–O bond favors the dissociation and the reactions of CO with other species, i.e., the Fischer–Tropsch process. To date, many effects had been considered as responsible of the softening of the C–O stretching: electrostatic interactions [12, 13], surface states [14], direct [15], and indirect chemical interactions mediated by the substrate [16]. Furthermore, a recent [17] theoretical work reported that such lowering is caused by the alkali-induced electronic polarizability of the metal surface.

However, the achieved results have not yet been conclusive and new experimental investigations are needed to clarify the adsorption properties of alkali atoms on metal surfaces and the alkali–CO interaction.

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In this study, HREELS measurements taken for Na adsorbed on Ni(111) and for the (Na + CO)/Ni(111) coadsorbed phase are reported. First, the Na–Ni stretching vibration was measured as a function of the alkali coverage and, successively, we focused our attention on the effects of CO on the vibrational properties of Na atoms. This point is particularly important, as previous studies of the coadsorption of alkali atoms with CO were focused exclusively on the shift of the C–O vibration, while the effects caused by CO on the vibrational properties of alkali atoms were completely disregarded.

The Na–Ni stretching energy was found to decrease as a function of the alkali coverage. Moreover, the Na–Ni mode measured in the presence of coadsorbed CO molecules was unexpectedly found to downshift by about 10 meV with respect to the Na–Ni vibration measured for Na adsorbed on the clean Ni(111) surface (22 meV).

Experimental

High-resolution electron energy loss measurements were performed using a spectrometer (Delta 0.5, SPECS) operating at a base pressure of 5×10^{-9} Pa. Loss spectra were acquired in the specular geometry (incidence angle of 55°) using a primary electron beam of 3 eV and an energy resolution between 2.0 and 3.0 meV. The Ni(111) surface was prepared by repeated cycles of ion sputtering (E_p = 1.5 keV) and annealing to 1,000 K. Low energy electron diffraction (LEED) and Auger electron spectroscopy were used to check surface order and cleanliness, respectively. Na atoms were deposited onto the Ni(111) surface by a dispenser, which was carefully degassed for several days at a pressure of $2–4 \times 10^{-8}$ Pa. CO molecules were admitted in the chamber by means of a precise leak-valve. Alkali and CO coverages were determined from the exposure time taking as reference the coverage of well-known LEED structures: c(4 × 2)-CO and ($\sqrt{3} \times \sqrt{3}$)R30°-Na.

Results and discussion

Loss spectra of Na deposited on Ni(111) at 400 K are shown in Fig. 1a. The Na–Ni stretching vibration was revealed at about 25 meV for a very low coverage (0.01 ML). Increasing Na coverages (0.06 ML), this peak shifted down to 21–22 meV (Fig. 1b). No further variation of the Na–Ni stretching energy was observed for higher coverages. Previous loss measurements [18] and calculations [19] performed on Na/Cu(111) as a function of the Na coverage found a constant energy of 21–22 meV for the Na–Cu mode. During these measurements, we noticed that the presence of even small amounts of CO had a dramatic influence on the Na–Ni stretching vibration. Accordingly, much care was devoted to avoid any contamination of the surface. Very clean layers of alkali metals could be obtained with the Ni(111) surface held at 400 K during both deposition and measurements.

In order to accurately investigate the effects of CO molecules on the vibrational properties of Na, clean layers of Na were exposed to CO at room temperature. Unexpectedly, the loss spectrum of Na/Ni(111) changed upon CO exposure (Fig. 2). The Na–Ni stretching frequency shifted from 22 down to 13 meV and, moreover, the line

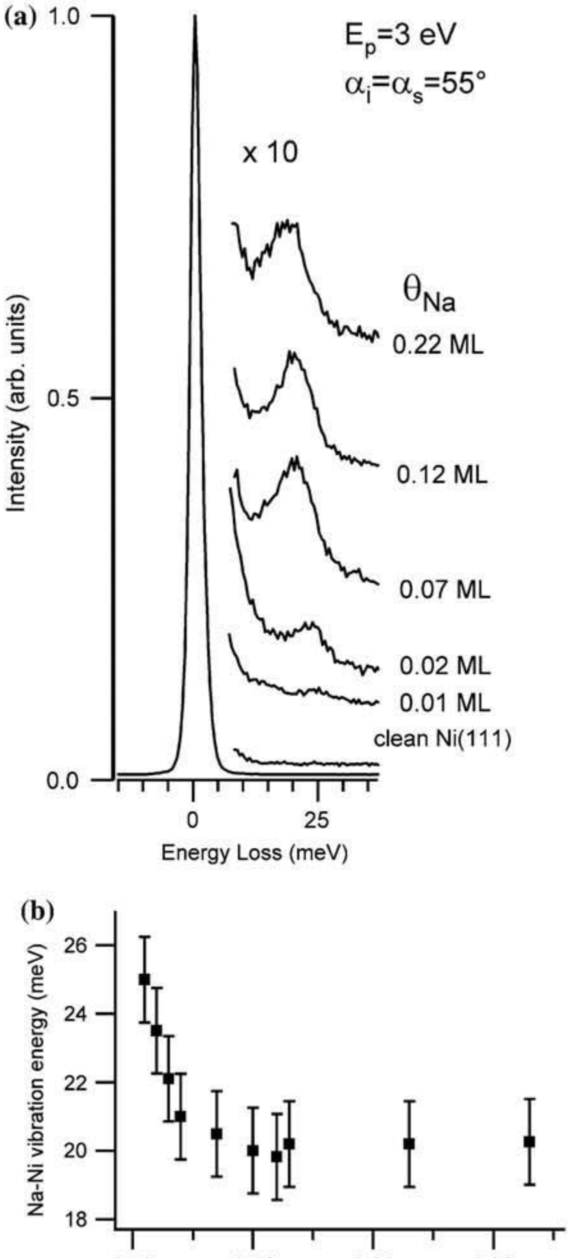

Fig. 1 (**a**) HREEL spectra of Na deposited at 400 K onto the Ni(111) surface as a function of the alkali coverage. (**b**) Na–Ni vibration energy as a function of the Na coverage

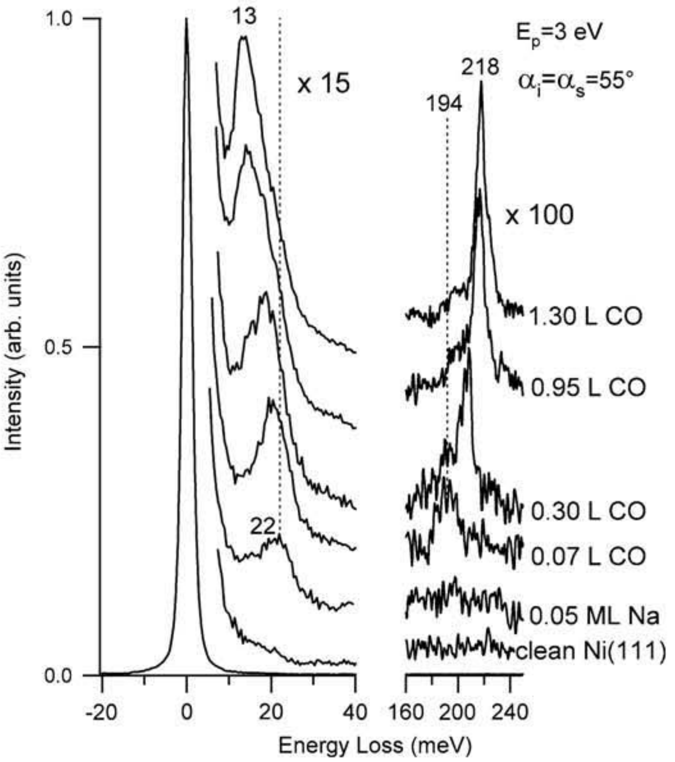

Fig. 2 HREEL spectra for 0.05 ML Na/Ni(111) at 400 K for different CO exposures at room temperature

shape of such peak became narrower. The C–O stretching energy, initially at 194 meV (0.07 L of CO), shifted upward to 218 meV (for higher CO exposure). As a comparison, the C–O stretching frequency is 235 meV for c(4 × 2)-CO/Ni(111) (0.5 ML of CO) [20]. Interestingly, the coadsorption process affected both the Na–Ni and the C–O vibrations and their frequencies were found to depend on the Na/CO ratio. We suggest that the energy shift of the Na–Ni mode induced by CO molecules should be taken into account in any realistic model describing the coadsorption of alkali and CO on metal surfaces.

The weakening of the Na–Ni bond induced by CO molecules was not previously reported and its observation may be the key to understand the basic mechanisms of the catalytic activity of alkali atoms. A remarkable increasing of the alkali–substrate bond length in the coadsorbed phase was observed in the investigation of the structural properties of K/CO on Ni(111) and K/CO on Ni(100) [21, 22]. This finding was not completely understood; nonetheless, it is in excellent agreement with the weakening of the alkali–substrate bond reported in this work.

The stretching frequency of CO adsorbed on metal surfaces is strictly related to the electronic population of the $2\pi^*$ orbitals as the occupation of such antibonding orbitals weakens the C–O bond. Most existing models interpreted the lowering of the C–O stretching frequency induced by the alkali coadsorption in the above framework. Nevertheless, the physical mechanisms leading to the charge back-donation into the empty $2\pi^*$ orbital of CO are very different from each other. He and Jacobi [23] studied the coadsorption of Cs with CO on Ru(0001) and assumed a two-step process: pre-adsorbed alkalis donate their charge to the metal surface and then such charge is back-donated to CO coadsorbed molecules. Instead, calculations by Wimmer et al. [12] led to a picture of alkali s electrons polarized toward the surface. The alkali-induced dipole layer causes a shift of all CO electronic states toward the Fermi level favoring an enhanced charge transfer from the surface metal to the $2\pi^*$ orbital. In other "electrostatic models", alkali atoms were assumed to be in an ionic state. A recent model explaining the softening of the C–O bond was proposed by Stolbov and Rahman [17]. It is based on an alkali-induced enhancement of the surface electronic polarizability. These authors showed that the strong electronic polarizability of Cu(111) and Pd(111) surfaces induced by the pre-adsorbed K atoms (0.25 ML) causes a red shift in the C–O and O–O stretching frequencies. Unfortunately, the effects of coadsorbed CO molecules on the vibrational properties of K atoms were not considered also in that study.

In order to investigate whether others effects (e.g., screening effects among coadsorbates) could be at the origin of the lowering of the Na–Ni vibration frequency, the (Na + CO)/Ni(111) surface was exposed to oxygen (Fig. 3). It is evident that oxygen atoms did not influence the Na–Ni stretching vibration.

Furthermore, in order to verify the possibility of the occurrence of alkali-induced promotion effects, the Na/Ni(111) surface was exposed to CO at 400 K (Fig. 4). We found the existence of a critical alkali-metal coverage for the CO dissociation. A partial dissociation of CO occurred at both 400 K and room temperature provided that the alkali coverage was sufficiently high.

For a CO exposure of only 0.20 L ($1 \text{ L} = 1 \times 10^{-6}$ mbar s), the critical alkali precoverage for carbon monoxide dissociation at 400 K was 0.10 ML as revealed (Fig. 4) by the appearance of the Na–O vibration at 33 meV. For $\sqrt{3} \times \sqrt{3}R30° - \text{Na}$ (0.33 ML) such vibration was found at 36 meV, while at the saturation of the first Na layer (0.44 ML) its loss energy shifted up to 38 meV. The presence of such vibrational mode unambiguously demonstrated the partial dissociation of carbon monoxide into atomic oxygen and carbon. Very likely, sodium atoms essentially interact with highly electronegative oxygen atoms rather than with carbon atoms, thus explaining the absence of a carbon-substrate vibrational mode. The presence of the Na–O bond did not influence the Na–Ni stretching energy, as any shift of Na vibration was measured. The direct alkali–oxygen interaction was found to reduce the dissociation barrier [9]

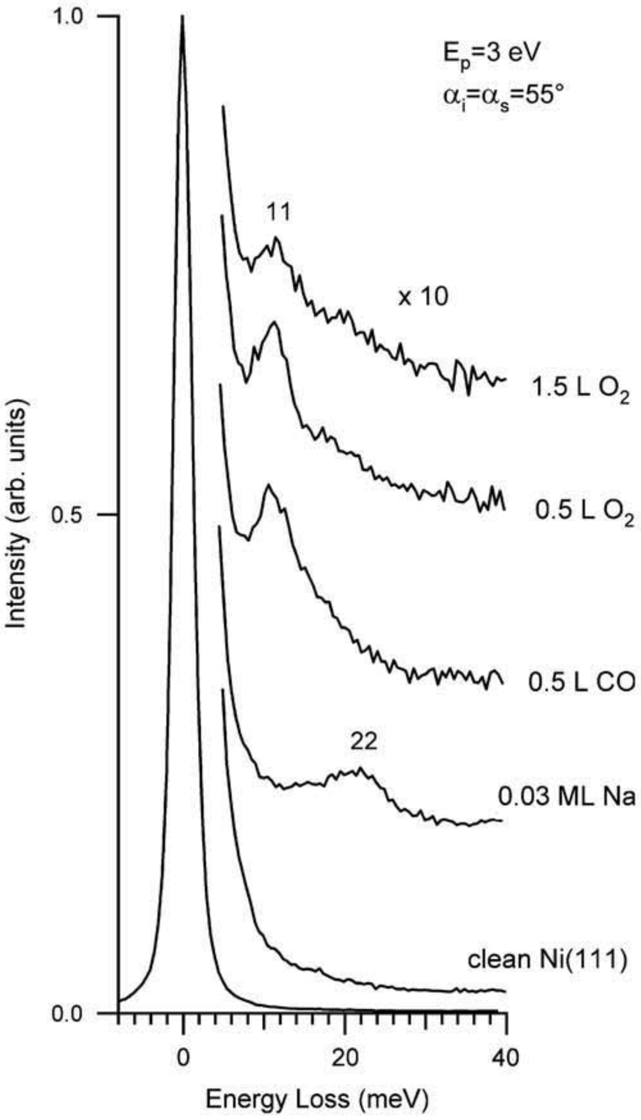

Fig. 3 HREEL spectra for 0.03 ML Na/Ni(111) exposed at room temperature to CO and successively to O$_2$

and was suggested to be the main physical origin of alkali-promoted CO dissociation.

Present loss measurements may simultaneously elucidate on the nature of the alkali–substrate and alkali–CO bond. The alkali–substrate bond is stronger at low coverages and becomes weaker as the alkali coverage was increased (Fig. 1). Such behavior is rather different from that reported in previous studies. For K on Pt(111) [24] and Na and K deposited on copper surfaces [18], the alkali-metal stretching energy was found to increase as a function of the alkali coverage. No convincing explanations were given for this unexpected finding. Instead, our results are in excellent agreement with Ishida's covalent model [6, 7]. As a matter of the fact, the adsorbate–substrate interaction dominated at low coverages and became less important as the alkali coverage increased. Moreover, the presence of CO molecules affected the Na–Ni stretching energy, which shifted toward lower energies. The energy shifts of the Na–Ni and C–O stretching vibrations were strictly related to each other (Fig. 2). We suggest that the shift of the alkali–substrate and C–O modes are correlated to the charge state of CO molecules and Na atoms. A significant charge transfer from Na atoms to CO molecules accompanied the adsorption of CO onto the Na-precovered Ni(111) surface. Loss measurements indicate that alkali atoms form a covalent bond at low coverages and a metallic bond at higher coverages. Strong support to this picture arises from the results of Figs. 1 and 2 which directly prove that initially the alkali atoms are almost in a neutral charge state and that their ionization occurs only if coadsorbed with CO. The transition from the covalent state to the metallic one occurs at very low coverages.

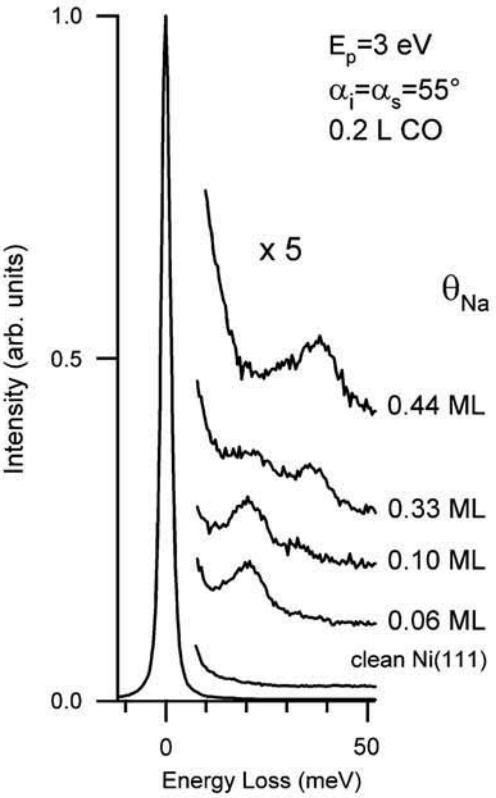

Fig. 4 HREEL spectra of 0.20 L of CO dosed at room temperature on different Na sub-layers prepared at 400 K on Ni(111)

Concluding remarks

In conclusion, we have presented loss measurements providing direct evidence of a dramatic lowering of the Na–Ni stretching frequency in the presence of coadsorbed CO. Alkalis adsorbed on clean Ni(111) donate almost no charge to the substrate (covalent bond). On the contrary, a charge transfer from Na to CO was found to occur in the (Na + CO) coadsorbed phase. Calculations including the new effects reported here (the weakening of the Na–Ni mode)

PAPER IV

Temperature effects on alkali-promoted CO dissociation on Ni(111)
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Temperature effects on alkali-promoted CO dissociation on Ni(1 1 1)

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ABSTRACT

Temperature effects on the alkali-induced CO dissociation on Ni(1 1 1) were studied by high-resolution electron energy loss spectroscopy. Measurements showed that CO adsorption on an alkali-precovered Ni(1 1 1) surface is partially dissociative in a temperature range up to 400 K and completely dissociative for higher sample temperatures. Depending on temperature an alkali critical precoverage for CO dissociation was found to exist, in agreement with theoretical calculations. Moreover, loss measurements demonstrated that Na and CO desorption are non-concurrent, in contrast with results obtained using thermal desorption spectroscopy for similar systems.

1. Introduction

Alkali promotion effects in heterogeneous catalysis have been widely studied with a variety of techniques as alkali metals significantly enhance the rate of many catalytic reactions [1–4]. CO dissociation is particularly important being one of the fundamental steps in the Fisher–Tropsch reaction [5]. This process is strongly influenced by alkali metals which are added as promoters to transition-metal catalysts [6–9].

The co-adsorption of alkali metal atoms and carbon monoxide molecules on single-crystal metal surfaces is characterized by a large decrease of the C–O stretching frequency [10,11], an increase in the heat of adsorption of both alkali metal and carbon monoxide [12,13], and changes in core and valence level binding energies of CO [14,15]. The general picture of the promotion effect is that the intramolecular C–O bond is weakened, while the metal–CO bond becomes stronger in the presence of alkali metals [11,16]. The detailed description of the above effect involves various models including substrate-mediated charge transfers [17,18], direct bond through complex formation [19], electrostatic interactions [20–22], and the non-local alkali-induced enhancement of the electronic surface polarizability [23].

The weakening of the C–O bond often leads to the enhancement of the CO dissociation probability on some metal substrates [24,25] and it can be detected by CO intermolecular isotope scrambling [25–27].

However, no clear picture has emerged yet to fully explain the alkali-induced dissociation. For example, the adsorption of CO on low-index copper surfaces modified by sub-monolayers of alkali metals is not dissociative [28–34], while CO dissociation was observed on stepped copper [7,35].

Recent density-functional theory calculations [36] found that the alkali promotion in CO dissociation strongly depends on the distance between the alkali adatom and the dissociating carbon monoxide molecule. Whenever the average distance between alkali and CO is long, the interaction between them is mainly electrostatic. Increasing alkali coverage, the average distance became shorter (2–3 Å) and a direct bond between co-adsorbates occurs, which reduces the reaction barrier for CO dissociation [36]. Accordingly, a strong dependence of the CO dissociation rate on alkali precoverage is expected.

One of the most important parameter in CO dissociation and alkali–CO interaction is the temperature. Its role is quite intriguing as annealing can significantly modify the bonds between co-adsorbates and the substrate through changes in bond length. However, systematic studies of temperature-induced effects on alkali promotion phenomena are still lacking.

With the aim of investigating the role of the temperature and alkali precoverage on the alkali promotion effects, high-resolution electron energy loss spectroscopy (HREELS) measurements on Na + CO/Ni(1 1 1) were performed.

CO dissociation was found to be strongly dependent on alkali coverage, and therefore on the average Na–CO distance, in excellent agreement with recent theoretical calculations [36]. Depending on temperature an alkali critical precoverage for CO dissociation was found to exist. At room temperature such critical coverage was found to be 0.40 ML and at 400 K 0.10 ML. Instead, CO adsorption on a Na-modified Ni(1 1 1) surface is always dissociative for temperatures higher than 430 K.

Moreover, in contrast with all previous measurements, Na and CO desorption was found to be non-concurrent.

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2. Experimental

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single-crystal of Ni(1 1 1) with a purity of 99.9999%. The surface was cleaned by repeated cycles of ion sputtering and annealing at 900 K. Surface cleanliness and order were checked using Auger electron spectroscopy and low-energy electron diffraction (LEED), respectively. The Ni(1 1 1) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium and potassium were deposited onto the Ni(1 1 1) surface by evaporating from a well-outgassed commercial getter source. The occurrence of the $(3/2 \times 3/2)$-Na and $p(2 \times 2)$-K LEED pattern was used as the calibration point of $\theta_{Na} = 0.44$ ML and $\theta_K = 0.25$ ML, respectively. The calibration procedure was repeated for different temperatures. Moreover, LEED examinations revealed the formation of a clear $\sqrt{3} \times \sqrt{3}R30°$-Na superstructure for $\theta_{Na} = 0.33$ ML. A constant sticking coefficient was assumed to obtain other desired alkali coverage. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of our spectrometer ranged from 2 to 3 meV.

3. Results and discussion

Loss measurements were performed at different temperatures, dosing CO on the Ni(1 1 1) surface precovered with selected amounts of Na and vice versa.

A 0.08 ML Na/Ni(1 1 1) surface prepared at different temperatures was exposed (at the same preparation temperature) to 0.4 L ($1 \text{ L} = 1.33 \times 10^{-6}$ mbar s or 1×10^{-6} Torr s) of CO (Fig. 1). A partial dissociation of CO was found to occur at 400 K, as indicated by the appearance of the O–Ni vibration at 63 meV [37]. The Na–O vibration at 32 meV [37] is a further evidence of CO dissociation. The presence of the C–O stretching at 197 meV indicates that only a part of CO molecules dissociates. However, at higher temperatures, i.e. $T \geqslant 430$ K, all CO molecules dissociate, as indicated by the disappearance of the C–O stretching vibration. Interestingly, the Na–Ni stretching continuously shifted from 12 to 23 meV as a function of temperature. Recently, it has been demonstrated [11] that the Na–Ni bond weakens upon CO exposure as a consequence of a mutual Na–CO interaction causing a lengthening of the Na–Ni bond. On the basis of such finding, we suggest the occurrence of a temperature-induced shortening of the Na–Ni bond length in the Na + CO co-adsorbed phase. At 430 K and 470 K all CO molecules dissociated and the Na–Ni stretching frequency assumed the same values (about 20–23 meV) as on the Ni(1 1 1) clean surface. Moreover, at this temperature oxygen atoms arising from the dissociating CO interact with the substrate but not with the Na adlayer.

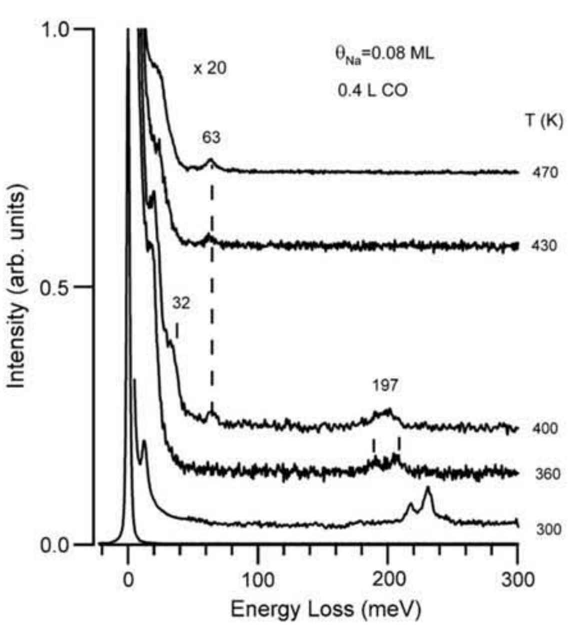

Fig. 1. HREEL spectra of 0.08 ML Na/Ni(1 1 1) exposed to 0.4 L CO as a function of the sample temperature. Na deposition and CO exposure were made at the same temperature. CO adsorption was found to be partly dissociative at 400 K and completely dissociative for temperatures higher than 430 K. The intensity of all peaks was normalized to the intensity of the elastic peak. All spectra were multiplied by the same factor.

Two C–O stretching peaks were observed at 300 and 360 K. This is ascribed to different local [Na]:[CO] stoichiometries. In fact, not all CO molecules can adsorb in the close vicinities of alkali adatoms. As a consequence, different environments for CO molecules exist, thus implying different shifts of the C–O stretching. The C–O stretching peaks were measured at 217 and 231 meV at room temperature and 190 and 206 meV at 360 K. They merged into a single feature at 197 meV at 400 K, as a consequence of the annealing-induced almost homogenous local distribution of Na and CO over the surface, and disappeared for higher temperatures. It is worth mentioning that at 360 K the CO sticking coefficient is lower than at 300 K, as evidenced by the higher alkali-induced energy shift of the C–O stretching at 360 K (the C–O mode measured for $c(4 \times 2)$-CO/Ni(1 1 1) is 235 meV [11]). As the Na coverage was for both cases 0.08 ML, the CO/Na ratios would be quite different in the two cases. As expected, for a higher CO/Na ratio (300 K) the alkali-induced shift of the C–O stretching is much less effective than for a lower CO/Na ratio (360 K).

More insights into temperature-induced effects on Na–CO interaction and alkali promotion phenomena could be obtained by reversing the order of adsorption. HREELS measurements on 0.50 ML of Na deposited onto a $c(4 \times 2)$-CO/Ni(1 1 1) surface prepared at 200 K were performed (Fig. 2). The loss spectrum of $c(4 \times 2)$-CO was dominated by the CO–Ni vibration at 50 meV and the C–O intramolecular stretching at 235 meV [11]. The adsorption of 0.50 ML of Na caused a shift of the C–O loss down to 202 meV, as found in other alkali–CO co-adsorbed systems [11,38]. Moreover, a shoulder at 33 meV due to the O–Na vibration arose in the loss spectrum. Such mode is a clear indication of the alkali-promoted CO dissociation at 200 K. By increasing sample temperature up to 300 K, the intensity of the latter feature increased so as to become a well distinct peak. We noticed that while the intensity of the Na–Ni vibration increased, the full-width at half maximum of its line-shape decreased. This result was ascribed to a CO-induced ionization of the alkali adatom [11]. In fact, the intensity of vibrational modes is expected to be higher for ionized species rather than for strongly polarized but essentially neutral adatoms, such as alkalis adsorbed on clean metal surfaces [39–41]. Another thing that we observed was the absence of the O–Ni vibration in spectra in Fig. 2. Thus, contrary to the results of Fig. 1, oxygen interacted only with alkali adatoms.

Unexpectedly, CO molecules and oxygen atoms were found to desorb at lower temperatures with respect to Na. Na vibration was still present in the loss spectrum even with the sample kept at 600 K, while the C–O and the O–Na stretching modes disappeared. This is in strong contrast with results reported in literature which generally assumed that a coincident desorption of both alkalis and CO occurs [12,13,28,42–46]. However, spectra in Fig. 2 unambiguously ensure that Na and CO desorption are not at all coincident and thus this common thought should be revised. The

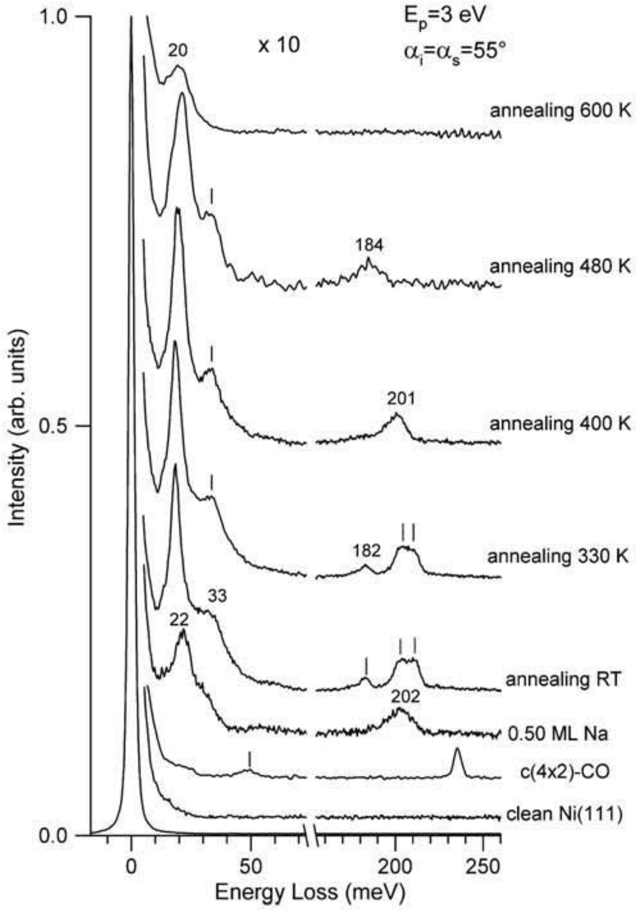

Fig. 2. HREEL spectra of 0.50 ML Na/c-(4 × 2)-CO/Ni(1 1 1) at 200 K. Annealing at progressively higher sample temperature caused CO dissociation and the desorption of CO molecules and O-derived species.

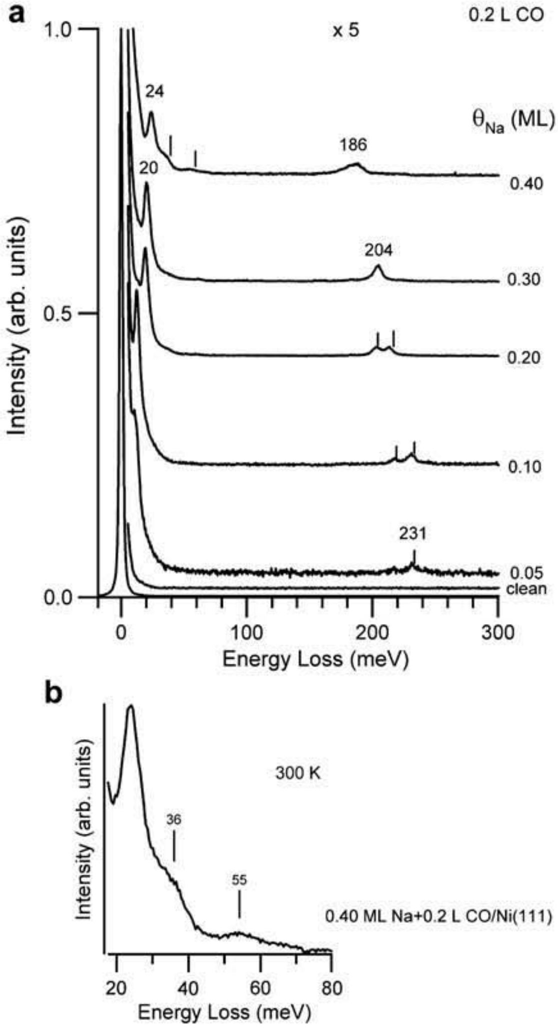

Fig. 3. (a) HREEL spectra of various coverages of Na deposited onto the Ni(1 1 1) surface at 300 K and exposed to 0.2 L of CO at the same temperature; (b) Magnification of the spectrum of 0.40 ML Na/Ni(1 1 1). Two loss features at 36 meV (O–Na) and 55 meV (C–Na) were recorded.

reduced intensity of the Na–Ni vibration at 600 K may indicate a partial desorption of Na atoms. However, the decreased intensity of the Na–Ni vibration could arise from a change of the ionic character of Na after desorption of CO. Both effects should be considered and it is quite difficult to establish whether is dominating.

Annealing induces a higher mobility of CO molecules and Na atoms and thus, depending on temperature, Na + CO overstructures having different local [Na]:[CO] stoichiometries exist, as also indicated by the appearance of a feature at 182 meV which disappears upon annealing at 400 K.

The C–O bond softened as a function of temperature. An energy shift of the C–O stretching from 201 down to 184 meV was observed for temperatures between 400 and 480 K. Hence, there is a direct evidence that the C–O bond weakens before CO desorption.

It is worth to study the dependence of the dissociation rate on the average Na–CO distance in order to experimentally verify the theoretical predictions reported in [36]. It is expected that a critical precoverage for CO dissociation exists and in principle it should diminish with increasing sample temperature. However, no previous dedicated study addressed this problem.

With this in mind, different Na precoverages were exposed to 0.2 L CO at room temperature (Fig. 3). The Na–Ni stretching peak shifted from 10 to 24 meV as a function of Na coverage. The C–O stretching continuously shifted down to 186 meV as a consequence of the increasing Na/CO ratio.

At the highest Na coverage loss spectra revealed the occurrence of a partial CO dissociation at 0.40 ML Na even at room temperature. In fact, a close inspection of the corresponding loss spectrum (Fig. 3b) revealed two new loss feature at 36 (Na–O vibration) and 55 meV. The peak at 55 meV is assigned to a C-derived vibration [8].

The direct CO–Na bond enhances the efficiency of CO dissociation on Ni(1 1 1), as revealed by examining CO dissociation at different Na coverages, and therefore at different average Na–CO distances. This finding is in excellent agreement with theoretical calculations [36]. A possible explanation for the existence of a critical Na coverage for CO dissociation can be given assuming an important role for lateral Na–CO interactions which weaken the C–O stretching bond up to dissociation. Very likely, several Na atoms are involved in this process. At low coverages, Na atoms are expected to be uniformly spread over the surface because of the repulsion due to their large dipole moments. Whenever the distance is long only electrostatic interaction exists, which was found to be not predominant in alkali promotion effects [36]. At higher coverages, each Na atom is obliged to get closer to each other, so that each CO molecule can interact with more than one alkali metal atom.

In order to investigate the dependence on the alkali precoverage for CO dissociation at 400 K, different Na precoverage were exposed to 0.2 L CO at this temperature. In these conditions, the critical alkali precoverage for CO dissociation at 400 K was 0.10 ML as revealed (Fig. 4) by the appearance of the Na–O vibration at 33 meV [37]. For $\sqrt{3} \times \sqrt{3}$-NaR30° (0.33 ML) this vibration energy was found at 36 meV, while at the saturation of the first Na layer, i.e. 0.44 ML, it shifted up to 38 meV. At the highest coverages all Na atoms form a bond with oxygen arising from CO dissociation. No C-derived mode was observed, indicating that sodium atoms mainly interact with the highly electronegative oxygen atoms.

The shift of the Na–O stretching energy as a function of Na coverage may be related to a charge transfer from Na atoms to oxygen. A similar result was found for Na co-adsorbed with OH groups in Na + OH/Cu(1 1 1) [47,48]. The Na–OH vibration energy shifted from 36 to 50 meV as a function of alkali coverage. It was suggested that Cu(1 1 1) surface states and Na quantum well states strongly influence the Na–OH bond. Likewise, Ni(1 1 1) Shockley states [49,50] could mediate the charge transfer occurring in Na + O/Ni(1 1 1).

For the sake of a comparison, we extended the measurements of Fig. 4 to potassium. The critical potassium precoverage for CO dissociation at 400 K was found to be 0.15 ML (Fig. 5). For 0.17 ML K a clear and well-resolved K–O vibration at 28 meV appeared (Fig. 5). For 0.40 ML K, the K–O vibration was recorded at 29 meV. Very likely, the charge transfer between O and K is not efficient. Moreover, even at the saturation of the first alkali layer, the K–Ni vibration was measured. It is well known that for increasing alkali metal depositions on single-crystal surfaces, the intensity of the alkali–substrate vibration gets lower because of the growing surface metallization. On the other hand, CO molecules co-adsorbed with alkali atoms inhibit the metallization. Such effect is evidently enhanced for K + CO with respect to Na + CO.

In conclusion, our experiments demonstrated that CO adsorption on an alkali-precovered Ni(1 1 1) flat surface is partially dissociative for temperatures lower than 430 K and completely dissociative for higher ones. The reduction of the alkali–CO average bond distance obtained by increasing alkali coverage was found to strongly enhance the dissociation rate of CO. A temperature-dependent alkali critical precoverage was found to exist. Moreover, CO desorbs before of Na, in contrast with all previous measurements reporting instead a concurrent desorption of both species. A temperature-induced shortening of the Na–Ni bond length was also suggested to occur.

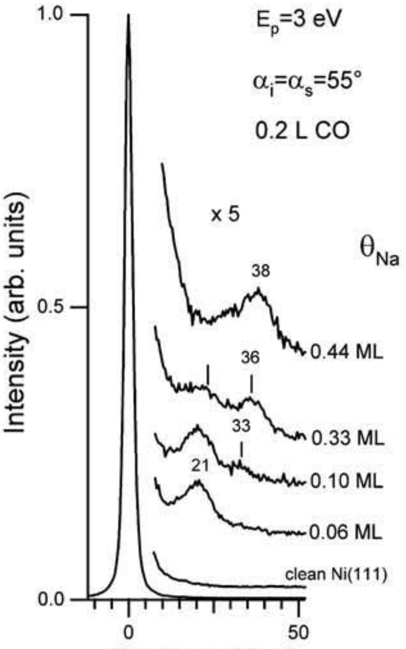

Fig. 4. HREEL spectra of various coverages of Na deposited onto the Ni(1 1 1) surface at 400 K and exposed to 0.2 L of CO at room temperature.

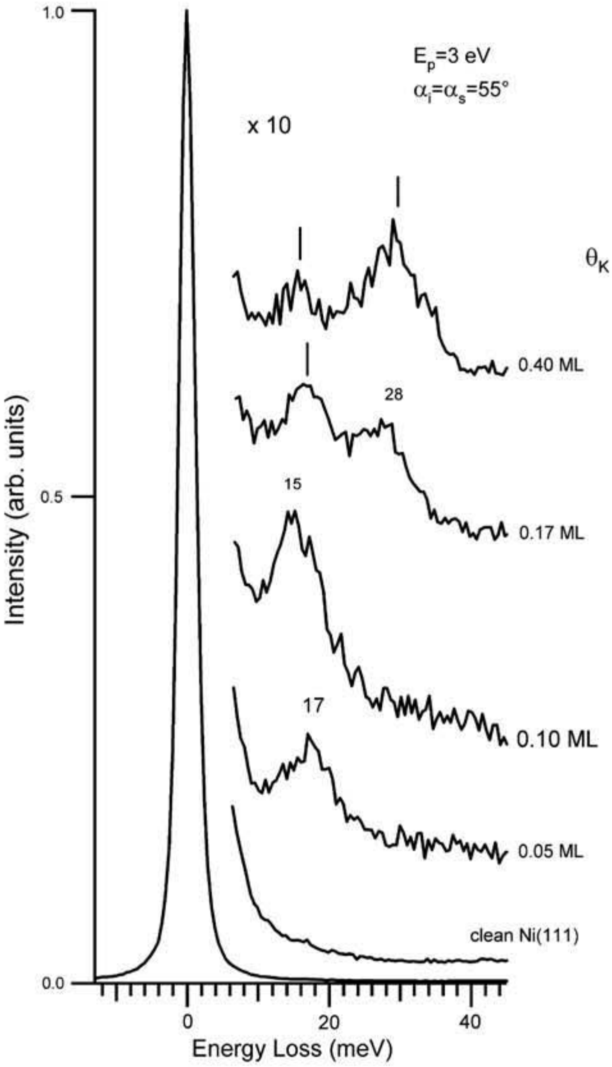

Fig. 5. HREEL spectra of various coverages of K deposited onto the Ni(1 1 1) surface at 400 K and exposed to 0.2 L of CO at room temperature.

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PAPER V

Alkali adsorption on Ni(111) and their coadsorption with CO and O

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Alkali adsorption on Ni(1 1 1) and their coadsorption with CO and O

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ABSTRACT

The adsorption of alkalis (Na, K) on Ni(1 1 1) and their coadsorption with CO and O were studied by high-resolution electron energy loss spectroscopy. Loss measurements of clean alkali adlayers provided the expected behaviour of the alkali-substrate vibration energy as a function of the alkali coverage. This result was achieved by eliminating any trace of CO contamination from the alkali adlayer. As a matter of fact, a significant softening of the alkali–Ni vibration energy was revealed in the alkali + CO coadsorbed phase. Moreover, alkali coadsorption with oxygen caused a weakening of the O–Ni bond and a strengthening of the alkali–Ni bond.

1. Introduction

The study of the adsorption and the coadsorption of alkali-metal atoms on single-crystal metal surfaces is a topic of surface science, both for the importance of technological applications (promotion of catalytic reactions, enhanced electron emission rates, and oxidation rate) and for fundamental interest [1–6]. Alkalis are used as a model system for understanding the properties of adsorption on metal surfaces [7–11] as it was demonstrated that the adatom would not complicate the system by intermixing with the substrate (except for Al surfaces [12]), but would stay in over-surface adsorption sites [13].

For a long time, alkali adsorption on metal surfaces was explained in the framework of the Langmuir–Gurney model [7]. It involves a donation of charge from the alkali-metal atoms to the substrate and the formation of an ionic bond at low coverages, followed by a back-donation of some of this charge to alkali adatoms at higher coverages. However, this model was questioned on the basis of some experimental [14] and theoretical [8,9] studies showing evidences for a covalent character of the alkali-substrate (A–S) bond, thus suggesting the occurrence of the polarization of adatoms. Successively, other theoretical calculations re-proposed the occurrence of charge transfers [15,16]. Nonetheless, there is still a debate to establish whether the adatom is partly ionic or it is neutral but strongly polarized. It was argued that very likely the A–S bond must contain an element of both these extreme ‘model’ situations [4]. The answer to this point would imply a great advancement in our understanding of the surface chemical bond and of catalytic reactions occurring whenever alkalis are coadsorbed with other chemical species. Hence, systematic studies of coadsorption systems are essential for a more complete understanding of heterogeneous catalysis [17]. In particular, the coadsorption of CO with alkali metals on transition-metal surfaces has been extensively investigated from both experimentalists [18–25] and theoreticians [26–32]. The main alkali promotion effects on CO are: a significant increase in the thermal desorption temperature of CO molecules [20–25,33–38], changes of work function of the surfaces [39–42], shifts in CO core- and valence-level binding energies [43], and an enhancement of the CO dissociation probability [44].

Moreover, infrared reflection absorption spectroscopy (IRAS) and high-resolution electron energy loss spectroscopy (HREELS) revealed a remarkable softening of the C–O stretching energy in the alkali + CO coadsorbed phase [18,19,26–32]. The weakening of

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the C–O bond was ascribed to: electrostatic interactions [26–28], surface states [29], direct [30] and indirect (substrate-mediated) [31] interactions, and the alkali-induced enhancement of the surface electronic polarizability of the metal surface [32]. Nevertheless, any effect of CO on the vibrational properties of the coadsorbed alkali atoms was completely disregarded. As a matter of fact, all previous works [18,19,28–32] were focused on the alkali-induced shift of the C–O stretching vibration. As alkali atoms affect the vibrational properties of carbon monoxide, likewise CO molecules are expected to affect the properties of the alkali atoms. Hence, any contamination of the alkali adlayer during the sample preparation should lead to significant modifications of the A–S bond. As alkalis are very reactive, much effort should be dedicated to this point in order to eliminate any influence of coadsorbed CO molecules on the A–S bond.

Contrary to the alkali + CO system, the coadsorption of alkalis with oxygen received less attention and only few dedicated spectroscopic studies have been carried out over the years in order to address the electronic, vibrational, and bonding properties of alkalis coadsorbed with oxygen. Thus, a clear picture has not emerged yet. Theoretical calculations [2] found a K-induced increasing of the O-substrate bond length. To the best of our knowledge, no experimental evidence supporting this model exists.

Nickel is a suitable substrate for such studies as it is extensively used in heterogeneous catalytic processes and thus the interaction of alkali-metal atoms with nickel surfaces and with coadsorbed species is of considerable interest in understanding the catalytic mechanisms. Earlier IRAS vibrational measurements on K + CO/Ni(1 1 1) [34] were focused only on the alkali-induced shift of the C–O stretching mode, while the A–S vibration could not be investigated due to experimental limitations. The structural investigations of the K + CO phase on Ni(1 1 1) [45] revealed that the K atoms retain the atop site but with an increased K–Ni bond length in the coadsorbed phase. Also for CO molecules (in the three-fold hollow adsorption site), no site change was observed. On the other hand, no structural study exists for alkali coadsorbed with oxygen on nickel surfaces.

Whereas the electronic properties of the alkali metals on metal surfaces have been extensively studied, their vibrational properties have been measured only for a few systems [46–56] providing a behaviour of the A–S vibration energy as a function of alkali coverage that disagrees with theoretical predictions [8–10].

In this article, we report HREEL measurements taken for Na and K deposited onto the Ni(1 1 1) surface and for their coadsorption with CO and O on the same surface with the aim to obtain information on the nature of the A–S bond and to investigate the effects of CO (oxygen) on the vibrational properties of alkali atoms. These systems were not widely investigated and the present measurements allow us to obtain new and interesting results.

In particular, we found that in contrast to expectations, the A–S bond is influenced by coadsorbed CO molecules and O atoms. The Na–Ni (K–Ni) vibration frequency dramatically red-shifted in the presence of even small amounts of coadsorbed CO. This finding was ascribed to a local charge transfer between coadsorbed species. By contrast, the Na–Ni bond was found to strengthen for increasing O/Na ratio. This finding suggests a shortening of the Na–Ni bond length. A weakening of the O–Ni bond was revealed for the Na + O coadsorbed phase, in agreement with the electrostatic model presented in ref. [2], by assuming an alkali-induced filling of the O $2p_z$ antibonding orbitals.

On the basis of the above findings, we carried out measurements on very clean alkali layers revealing for the first time the expected [8–10] behaviour of the A–S stretching energy as a function of the alkali coverage in contrast to previous experimental studies [46–56] on similar systems.

2. Experimental

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Ni(1 1 1) with a purity of 99.9999%. The surface was cleaned by repeated cycles of ion sputtering and annealing at 1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy measurements and low-energy electron diffraction (LEED), respectively. The Ni(1 1 1) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium and potassium were deposited onto the substrate by evaporating from well-outgassed commercial getter sources.

Pre-adsorbed alkali layers free of any contamination could be obtained only by keeping the Ni(1 1 1) surface at 400 K during both deposition and measurements. Nonetheless, measurements were performed in a few minutes in order to avoid any residual contamination. Carbon monoxide and oxygen were admitted through precise leak valves. Alkali, carbon monoxide, and oxygen coverages (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate) were estimated from the exposure time taking as reference the coverage of well-known LEED structures, that is: $\left(\sqrt{3} \times \sqrt{3}\right)$ R30°-Na, $p(2 \times 2)$-K, $c(4 \times 2)$-CO, and $p(2 \times 2)$-O. A constant sticking coefficient was assumed to obtain other desired coverage. Coverages were calibrated for different substrate temperature. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of the spectrometer ranged from 2 to 3 meV.

3. Results and discussion

3.1. Na and K adsorption on clean Ni(1 1 1)

Loss spectra of Na deposited on Ni(1 1 1) at 400 K are shown in Fig. 1a. The Na–Ni stretching vibration shifted (Fig. 1b) from about 25 meV for a very low coverage (0.01 ML) down to 21–22 meV for increasing Na coverages (0.06 ML). No further variation of the Na–Ni stretching energy was observed for higher coverages, at which the adlayer undergoes a metallization because of the closer distances between Na adatoms. As a consequence, dipole fluctuation is screened very efficiently by the two-dimensional electron gas and the excitation of adatom vibrations perpendicular to the surface is no longer observable [57].

Theoretical studies [58] and HREELS measurements performed for alkalis (Li, Na, K) adsorbed onto copper surfaces [46–49] and for Na/Mo(1 0 0) [52] revealed a nearly coverage-independent A–S stretching frequency. On the contrary, for Li/Cu(1 1 1) Lindgren et al. [53] measured an up-shift of the Li–Cu vibration as a function of Li coverage. Likewise, for Cs/Ru(0 0 0 1) [54], K/Pt(1 1 1) [55], and Li/Mo(1 1 0) [56] the A–S stretching energy was found to increase as a function of coverage.

On the contrary, total-energy calculations [10] found a decreasing of the A–S stretching frequency as a function of the alkali coverage. In addition, the alkali-metal adsorption energy decreases largely with coverage [59,60], thus implying a bond weakening for increasing coverage. The observed behaviour of the A–S stretching was tentatively ascribed to the combined effects of many factors, such as: dipole–dipole interactions [48,49,53], the

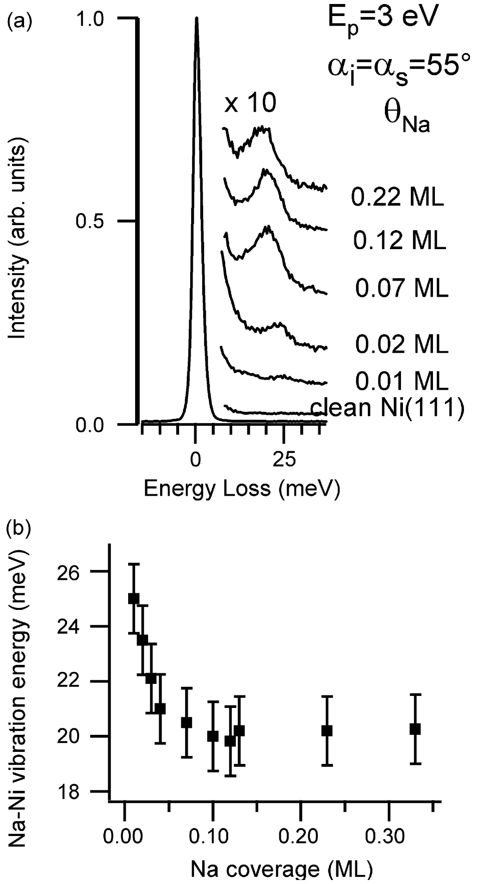

Fig. 1. (a) HREEL spectra of Na layers deposited on Ni(1 1 1) at 400 K (loss spectra were acquired at the same temperature). Loss peaks are due to the Na–Ni stretching vibration (b) behaviour of the Na-substrate vibration as a function of Na coverage.

response of the substrate surface layer [49], and an increase of the curvature of the potential-energy surface [54].

Similar conclusions were reached for K deposited onto the Ni(1 1 1) substrate. K–Ni vibration energy was found to shift from 18 down to 15 meV as a function of alkali coverage (Fig. 2).

During these measurements we noticed that the presence of even small amounts of CO had a dramatic influence on the Na–Ni stretching vibration. Accordingly, much care was devoted to avoid any contamination of the surface. Very clean layers of alkali metals could be obtained with the Ni(1 1 1) surface held at 400 K during both deposition and measurements [61]. Moreover, all spectra were recorded in a few minutes to further reduce contamination. Very likely, the influence of coadsorbed CO on the A–S bond would be enhanced at low alkali coverage, i.e. at a low Na/CO ratio. It is worth noticing that measurements of the A–S vibration frequency as a function of the alkali coverage performed with the sample kept at room temperature (and with some CO contamination) provided the same behaviour reported in previous experimental works [46–56].

3.2. Na and K coadsorption with CO on Ni(1 1 1)

In order to carefully investigate the effects of CO molecules on the vibrational properties of Na, clean layers of Na (deposited at 400 K) were exposed to CO at room temperature. Unexpectedly, the loss spectrum of Na/Ni(1 1 1) changed upon CO exposure (Fig. 3). The Na–Ni stretching frequency shifted from 22 down to 13 meV. The C–O stretching energy, initially at 194 meV for 0.07 L of CO (1 L = 1 L = 10^{-6} Torr s or 1.33×10^{-6} mbar s), shifted

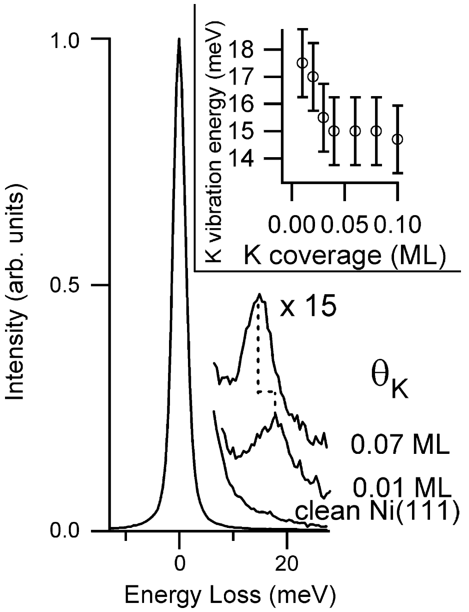

Fig. 2. HREEL spectra of K layers deposited on Ni(1 1 1) at 400 K (loss spectra were acquired at the same temperature). The inset shows the behaviour of the K-substrate vibration as a function of K coverage.

upward to 218 meV (for higher CO exposure). As a comparison, the C–O stretching frequency is 235 meV (0.5 ML of CO) for CO on Ni(1 1 1) [61]. Interestingly, the coadsorption process affected both the Na–Ni and the C–O vibrations and their frequencies were found to depend on the Na/CO local ratio. The CO-induced weakening of the Na–Ni bond was not previously reported and its observation may help to elucidate the basic mechanisms of the catalytic activity of alkali atoms. Likewise, the K–Ni stretching energy was found to shift from 15 down to 10 meV (Fig. 4) upon CO exposure.

This finding is in excellent agreement with the observed increasing of the A–S bond length in the K + CO coadsorption on Ni(1 1 1) and Ni(1 0 0) [62,63].

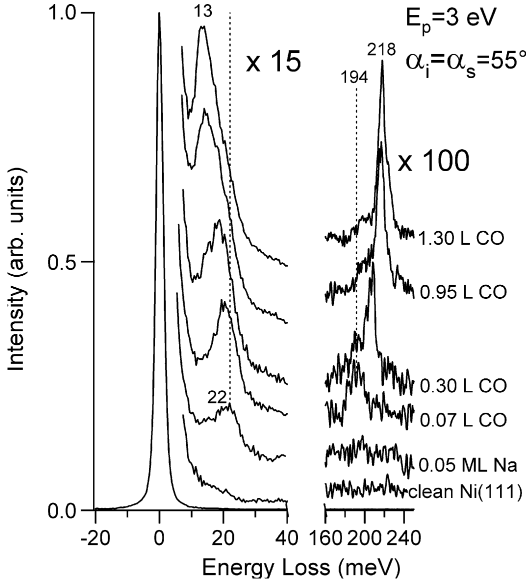

Fig. 3. HREEL spectra for 0.05 ML Na/Ni(1 1 1) deposited at 400 K for different CO exposures made at room temperature. Both the Na–Ni and C–O vibrational modes are shown.

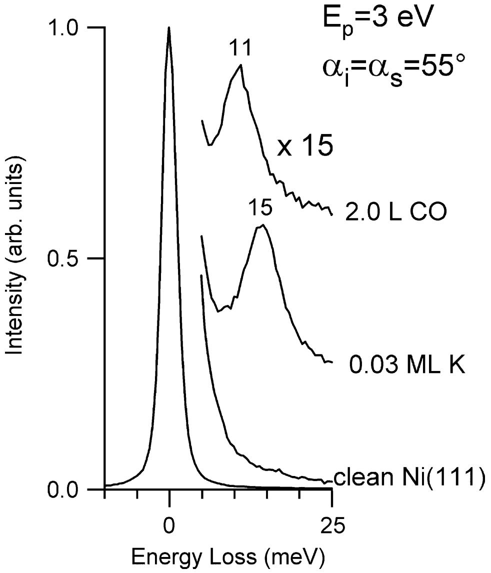

Fig. 4. HREEL spectra for 0.03 ML K/Ni(1 1 1) deposited at 400 K. The K adlayer was successively exposed to CO at room temperature.

The stretching frequency of CO adsorbed on metal surfaces is strictly related to the electronic population of the $2\pi^*$ orbitals as the occupation of such antibonding orbitals weakens the C–O bond. However, the physical mechanisms leading to the charge donation into the empty $2\pi^*$ orbital of CO are very different from each other. He and Jacobi [64] argued that preadsorbed alkalis donate their charge to the metal surface and then such charge is backdonated to CO coadsorbed molecules. By contrast, Wimmer et al. [26] suggested the occurrence of the polarization of the alkali adatom causing a shift of all CO electronic states towards the Fermi level. This implies an enhanced charge transfer from the surface metal to the $2\pi^*$ orbital. In other "electrostatic models", alkali atoms were assumed to be in an ionic state. On the other hand, according to the recent model proposed by Stolbov and Rahman [32], the enhanced alkali-induced polarization is responsible of the red-shift of the C–O stretching frequency. Unfortunately, also this study did not consider the effects of coadsorbed CO molecules on the vibrational properties of alkali atoms.

The Na–CO interaction could be investigated with more details by adsorbing Na on the $c(4 \times 2)$-CO/Ni(1 1 1) surface. The $c(4 \times 2)$ structure was prepared by exposing the surface to 1 L of CO at 200 K and its formation was checked by LEED. The loss spectrum of this phase is showed in Fig. 5. The CO–Ni and the C–O modes were measured at 50 and 235 meV, respectively. The CO–Ni mode strengthened and shifted to higher loss energies up to 72 meV, while a new feature arose at 220 meV close to the C–O vibration. Both modes (at 220 and 235 meV) merged into a single feature at 220 meV for a Na coverage of 0.22 ML. Increasing Na coverage up to 0.37 ML caused the shift of such peak down to 205 meV. Contrary to the adsorption of Na on the clean Ni(1 1 1) surface (Fig. 1a), the Na–Ni stretching energy was observed at 12 meV (for Na depositions up 0.13 ML) and shifted to 21 meV for higher Na coverages (0.37 ML). As regards the structural side of the investigation, we did not observe any new LEED feature related to Na depositions, but we noticed that the initial $c(4 \times 2)$ phase degraded slightly with the Na coverage.

The existence of two distinct C–O frequencies for Na coverages between 0.07 and 0.13 ML indicated the presence of two different species of adsorbed CO molecules; the former is essentially unaffected being the C–O energy at 235 meV, the latter, instead, interacted with Na atoms and moved to 220 meV. The line shape of the CO–Ni loss broadened as a consequence of the occurring Na–CO interaction. At a Na coverage of 0.22 ML, a uniform layer with about one atom of Na for each two CO molecules should exist on the surface. As a matter of fact, the interaction between Na and CO is unique as only one C–O stretching energy at 220 meV was observed.

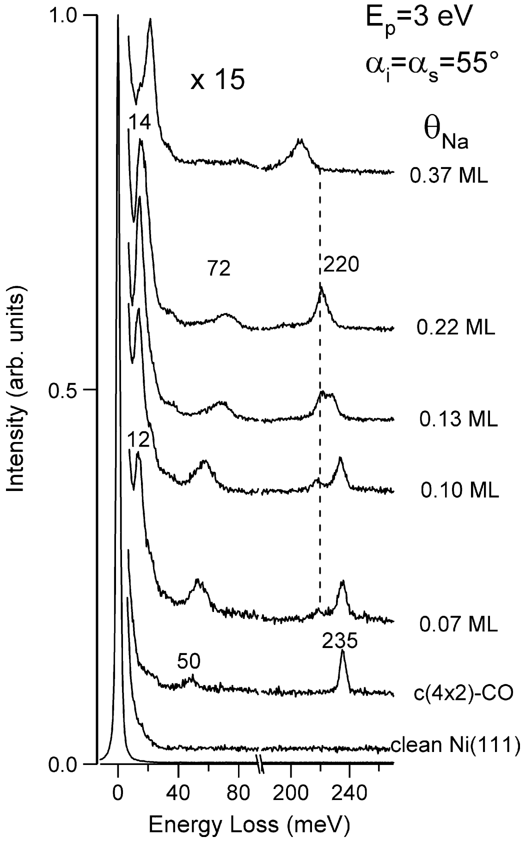

Fig. 5. HREEL spectra of $c(4 \times 2)$-CO prepared at 200 K and after deposition of different amounts of Na at the same temperature.

3.3. Na coadsorption with oxygen on Ni(1 1 1)

In order to ascertain whether the same mechanisms, i.e. charge transfer processes, apply for other systems, we investigated the coadsorption of Na with oxygen. CO and oxygen are both electronegative species with respect to Na atoms and might behave in the same way.

Fig. 6a shows HREEL spectra of 0.02 ML Na/Ni(1 1 1) exposed to small quantities of O_2. The Na–Ni stretching vibration was found to shift from 21 to 26 meV after an O_2 exposure of only 3×10^{-3} L. Further oxygen exposures did not cause remarkable changes in the HREEL spectrum. Such finding is a fingerprint of a notable strengthening of the Na-Ni bond and it could be ascribed to a shorter Na–Ni bond distance, caused by the presence of oxygen atoms. As the technique does not allow direct evidences of changes in bond distances, accurate structural studies are needed to further support this suggestion. An explanation in the framework of the electrostatic model has to be excluded. In fact, the O–Ni bond is largely covalent and, thus, the O-induced electrostatic field should be relatively small and it would have only little effects on the Na–Ni bond.

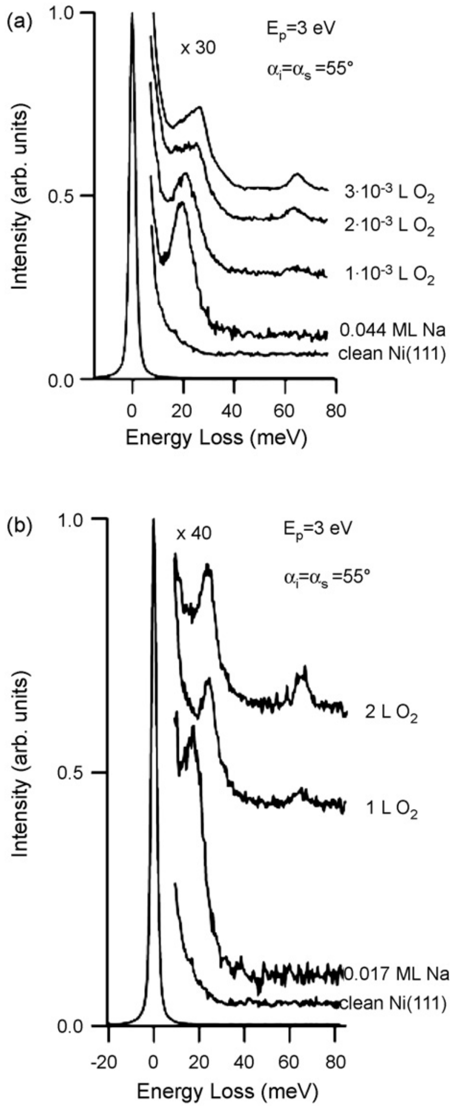

Fig. 6. (a) HREEL spectra for 0.044 ML Na/Ni(1 1 1) as a function of O_2 exposures. Upon O adsorption, the Na–Ni vibration energy shifted from 21 to 26 meV. (b) Similar HREEL spectra for a lower Na precoverage, i.e. 0.017 ML.

A small blue-shift of the alkali-substrate vibration energy upon oxygen exposure was also revealed for Cs/Ru(0001) [57]. The Cs–Ru vibration shifted from 8 to 10 meV. However, the authors did not discuss such finding. The Ru–O bond length was found to increase for Cs + O/Ru(0 0 0 1) as a function of Cs coverage [64] and such result well agrees with the softening of the oxygen-substrate bond observed in the present study.

Interestingly, the O–Ni stretching energy was revealed at 63–65 meV in the O + Na coadsorbed phase and at 70 meV for $p(2\times2)$-O/Ni(1 1 1) [61,65]. This finding implies the occurrence of a weaker interaction between O and Ni in the presence of coadsorbed Na.

The weakening of the O–Ni bond may be interpreted as due to a charge transfer from the metal surface to the antibonding states of adsorbed oxygen atoms, as found by theoretical calculations for the K + O/Rh(1 1 1) system [2], which revealed that the O-substrate bond length increases in the presence of K. The electric field by alkali adatoms would affect the O-substrate bond by shifting electronic states. In particular, the antibonding orbitals with O $2p_z$ character become partially occupied in the presence of coadsorbed alkalis. Support to this picture comes from the finding that even at the lowest alkali precoverages the O–Ni bond was weakened and this is a clear indication of the predominant influence of alkali-induced electrostatic fields.

It should be noticed that the two coadsorbed species (O and Na) do not interact each others, but directly with the substrate, even for higher oxygen exposures. This finding is quite surprising as oxygen and alkalis are expected to strongly interact each other, especially for high oxygen or alkali precoverages.

In previous studies [66,67] of the coadsorption of oxygen and alkalis, oxygen was assumed to migrate underneath the alkali layer. However, according to this model, the A–S vibration should disappear because of the intralayer of oxygen atoms. On the contrary, it was always present and, accordingly, our measurements indicated that a more complex model is needed to describe the coadsorption process. We suggest that for submonolayers of alkalis both species are coplanar, as found for similar systems [68], and only a weak bond, not evidenced in loss spectra, exists between them.

To the best of our knowledge, no experimental investigation supporting theoretical findings reported in ref. [2] exists. In the HREELS study of the K + O coadsorption on Ni (1 1 1) [69], potassium layers were affected by the presence of "spurious CO" on the surface and no weakening of the O–Ni bond was revealed. Hence, only measurements taken on very clean alkali layers may reveal the occurrence of the alkali-induced softening of the O–Ni bond. The results shown in Fig. 6b demonstrated that a similar mechanism occurs with a higher Na precoverage.

To investigate whether the CO-induced lowering of the Na–Ni vibration frequency occurs even in a O-modified surface, the Na + O/Ni(1 1 1) surface was exposed to CO (Fig. 7). CO exposure cause a red-shift from 26 meV and a splitting of the Na–Ni vibration peak into two components at 12 and 19 meV. Two peaks assigned to the C–O stretching appeared at 216 and 227 meV. Such findings may be taken as an evidence of a local interaction between Na and CO. Not all CO molecules can adsorb in close vicinity of the preadsorbed Na atom. Accordingly, a splitting of both the C–O and Na–Ni modes is expected. The similar Na + CO/Cu(1 1 1) system studied by Svensson [70] exhibited an analogous behaviour, i.e. the action of Na on CO molecules was found to be very local, in disagreement with the nonlocal electron transfer process (Wimmer and Stolbov models).

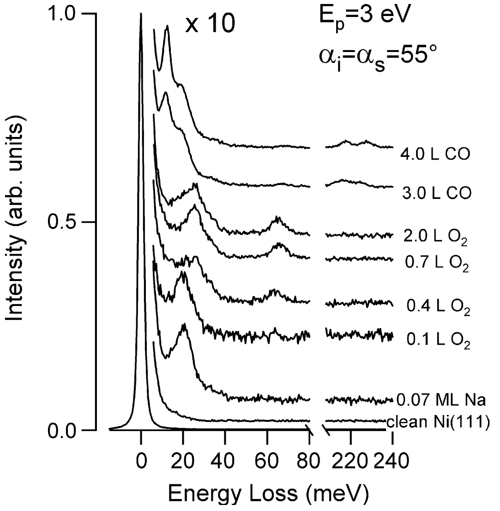

Fig. 7. HREEL spectra for 0.07 ML Na/Ni(1 1 1) as a function of O_2 exposure (at 400 K) and of successive CO exposure (at room temperature).

4. Conclusions

We have presented loss measurements providing, for the first time, a full agreement with Ishida's model Ref. [8–10] and photoemission measurements Ref. [14]. The coadsorption of CO molecules influences the A-S bond, causing a dramatic lowering of the Na–Ni (K–Ni) stretching frequency. Accordingly, alkalis adsorbed on Ni(1 1 1) are essentially in a neutral charge state with no donation of charge to the substrate. On the contrary, the coadsorption of alkali atoms with CO molecules is accompanied by a local charge transfer from Na (K) to the $2\pi^*$ orbitals of CO. Such effect is responsible of the weakening of the C–O and Na–Ni stretching vibrations and of the strengthening of the CO–Ni bond. This leads to the ionization of alkali atoms. Moreover, our vibrational measurements provided the first evidence of a softening of the O–Ni bond and of a strengthening of the Na–Ni bond in Na + O coadsorbed phase. According to the electrostatic model, the alkali-induced filling of the O $2p_z$ orbital was ascribed to be responsible of the weakening of the O–Ni bond. Similar results were obtained in K + O coadsorption on Ni(1 1 1). The strengthening of the alkali-substrate bond was explained with a reduced bond distance occurring whenever alkalis are coadsorbed with O. Present results well reproduce for the first time theoretical calculations in ref. [2] and, moreover, are in excellent agreement with structural studies on similar systems.

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PAPER VI

Evidences of alkali-induced softening of the oxygen-substrate bond

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Evidences of alkali-induced softening of the oxygen-substrate bond

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The interaction of oxygen with alkalis (Na, K) on Ni(111) was studied by high-resolution electron energy loss spectroscopy. Loss measurements revealed for the first time a softening of the O–Ni bond and, simultaneously, a strengthening of the alkali-Ni bond in the alkali+O coadsorbed phase, in perfect agreement with recent theoretical calculations. The weakening of the O–Ni bond was ascribed to the alkali-induced filling of the O $2p_z$ antibonding orbitals. Different physical mechanisms were discussed for explaining the strengthening of the alkali-substrate bond whenever alkalis are coadsorbed with O adatoms. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2835597]

INTRODUCTION

Alkalis and oxygen coadsorption on metal surfaces has been extensively studied for both basic and practical reasons.[1] For example, alkali atoms are used for oxidation of metal and semiconductor surfaces. Alkali-metal oxides are widely used as additives for obtaining low work-function surfaces for photocathodes[2] or for improving catalytic reactivity, such as, e.g., ammonia synthesis.[3] From a fundamental point of view, alkali-metal coadsorption with oxygen is a very challenging subject because of the great variety of chemical and physical phenomena involved in the reaction. Despite the remarkable interest, only few dedicated spectroscopic studies have been conducted over the years in order to address the electronic, vibrational, and bonding properties of coadsorbed alkalis and oxygen and, thus, a clear picture has not emerged yet.

Density functional theory (DFT) calculations by Liu and Hu[4] revealed that the O-substrate bond length increases in the presence of K. This implies an alkali-induced weakening of the bond between oxygen and the substrate. The nature of the K–O interaction was found to be dependent on their mutual distance. As a matter of fact, their interaction is electrostatic when K is farther away from the O adatom (4–5 Å). On the contrary, for closer configurations a direct bond occurs. Accordingly, a dependence on alkali coverage is expected. The role of the alkali precoverage is quite intriguing as the adsorption of alkali-metal adatoms can significantly modify the bonds between coadsorbates and the substrate. Moreover, depending on the alkali-metal precoverage, different scenarios exist for the structural evolution of the alkali +O coadsorption system.[5]

To the best of our knowledge, no experimental investigation supporting theoretical findings reported in Ref. 4 exists. Recent experimental studies[6] demonstrated that CO adsorption significantly influences the alkali-substrate bond. Moreover, in the high-resolution electron energy loss spectroscopy (HREELS) study of the K+O coadsorption on Ni (111),[7] potassium layers were affected by the presence of "spurious CO" on the surface and no weakening of the O–Ni bond was revealed. Hence, measurements taken on very clean alkali layers are needed in order to verify experimentally the predicted alkali-induced softening of the O–Ni bond.

In the alkali+O coadsorption the competition among different bonds occurs.[8] In fact, both species strongly interact with the substrate, but nevertheless strong lateral and attractive interactions between the opposite dipoles alkali substrate and oxygen substrate are expected. In addiction, direct chemical bonds between alkali metal and oxygen atoms may be formed.

A substrate-mediated charge transfer from the alkali atom to the oxygen molecule was revealed for the coadsorption of K and O_2 on graphite.[9] Similar results were obtained for Cs coadsorption with O on Ru(0001).[10] Previous experimental studies on the alkali+O coadsorption were performed within a common approach, that is, first, alkali atoms were deposited onto the metal surface and only successively the surface was exposed to O_2 molecules. This procedure was based on the assumption, taken for granted, that preadsorbed alkalis change the electronic properties of the underlying surface. Any effect of O on the alkali-substrate bond was completely disregarded. Moreover, previous experimental works were focused mainly on the formation of a direct bond between coadsorbates. As a consequence, the possible occurrence of alkali-induced modifications of O-substrate bond, very likely overshadowed by contamination due to the high reactivity of alkali layers, was not taken into account.

HREELS is a suitable technique which offers the opportunity to distinguish between indirect (substrate mediated) and direct charge transfers.

With the aim of shedding light on the nature of the bond in alkali+oxygen coadsorption and, moreover, of verifying the model presented by Liu and Hu,[4] a HREELS study on the coadsorption of alkalis (Na, K) and oxygen on Ni(111) was performed. This is an excellent system to study the nature of surface chemical bond. Oxygen molecules adsorb dissocia-

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tively at threefold hollow sites and may form ordered $p(2\times 2)$ and $(\sqrt{3}\times\sqrt{3})R30°$ ordered structures.[11]

A weakening of the O–Ni bond was revealed for the Na+O coadsorbed phase, in agreement with DFT calculations.[4] The O–Ni stretching energy was observed to shift from 70 down to 63 meV. Such finding was explained in the framework of the electrostatic model, by assuming an alkali-induced filling of the O $2p_z$ antibonding orbitals. By contrast, the Na–Ni bond was found to strengthen for increasing O/Na ratio. This finding suggests a shortening of the Na–Ni bond length. The same results were obtained in O+K coadsorption.

EXPERIMENTAL

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Ni(111) with a purity of 99.9999%. The surface was cleaned by repeated cycles of ion sputtering and annealing at 900 K. Surface cleanliness and order were checked using low energy electron diffraction (LEED) and Auger electron spectroscopy measurements, respectively. The Ni(111) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium and potassium were deposited onto the substrate by evaporating from well-outgassed commercial getter sources. Preadsorbed alkali layers free of any contamination could be obtained only by keeping the Ni(111) surface at 400 K during both deposition and measurements. Nonetheless, measurements were performed in a few minutes in order to further reduce the contamination. Oxygen was admitted through a precise leak valve. Alkali and oxygen coverages (the coverage of one monolayer (ML) is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate) were estimated from the exposure time taking as reference the coverage of well-known LEED structures, that is, $(\sqrt{3}\times\sqrt{3})R30°$-Na, $p(2\times 2)$-K, and $p(2\times 2)$-O. A constant sticking coefficient was assumed to obtain other desired coverage. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of the spectrometer ranged from 2 to 3 meV. The angular acceptance α of our electron analyzer was ±1°.

RESULTS AND DISCUSSION

Figure 1 shows HREEL spectra of 0.02 ML Na/Ni(111) exposed to small quantities of O_2. The Na–Ni stretching vibration was found to shift from 21 to 26 meV after an O_2 exposure of only 3×10^{-3} L (1 L$=1\times 10^{-6}$ mbar s). Further oxygen exposures did not cause remarkable changes in the HREEL spectrum. Such finding is a fingerprint of a notable strengthening of the Na–Ni bond and it could be ascribed to a shorter Na–Ni bond distance, caused by the presence of oxygen atoms. As the technique does not allow direct evidences of changes in bond distances, accurate structural studies are needed to further support this suggestion. An explanation in the framework of the electrostatic model has to be excluded. In fact, the O–Ni bond is largely covalent and, thus, the O-induced electrostatic field should be relatively small and it would have only little effects on the Na–Ni bond.

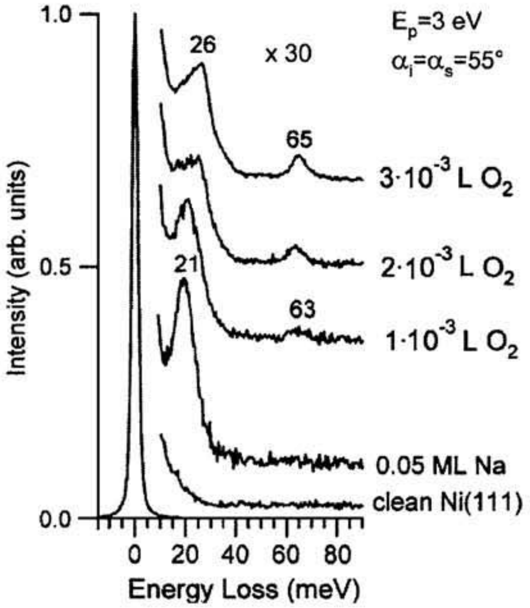

FIG. 1. HREEL spectra for 0.05 ML Na/Ni(111) as a function of O_2 exposures. Upon O adsorption, the Na–Ni vibration energy shifted from 21 to 26 meV.

A small blueshift of the alkali-substrate vibration energy upon oxygen exposure was also revealed for Cs/Ru(0001).[12] The Cs–Ru vibration shifted from 8 to 10 meV. However, the authors did not discuss such finding.

In addition, a broadening of the peak of the Na vibration was observed in our spectra, and this suggests the occurrence of a disordered Na+O phase. Support to this picture was given by the analysis of the LEED pattern, which slightly degraded with oxygen exposures.

Interestingly, the O–Ni stretching energy was revealed at 63–65 meV in the O+Na coadsorbed phase and at 70 meV for $p(2\times 2)$-O/Ni(111).[11] This finding implies the occurrence of a weaker interaction between O and Ni in the presence of coadsorbed Na.

The Ru–O bond length was found to increase for Cs+O/Ru(0001) as a function of Cs coverage,[10] and such result well agrees with the softening of the oxygen-substrate bond observed in the present study.

The weakening of the O–Ni bond may be interpreted as due to a charge transfer from the metal surface to the antibonding states of adsorbed oxygen atoms, as found by theoretical calculations for the K/O/Rh(111) system.[4] In fact, the electric field by alkali adatoms would affect the O-substrate bond by shifting electronic states. In particular, the antibonding orbitals with O $2p_z$ character become partially occupied in the presence of coadsorbed alkalis. A further support to this picture comes from the finding that even at the lowest alkali precoverages the O–Ni bond was weakened, thus suggesting the predominant influence of alkali-induced Coulombian fields.

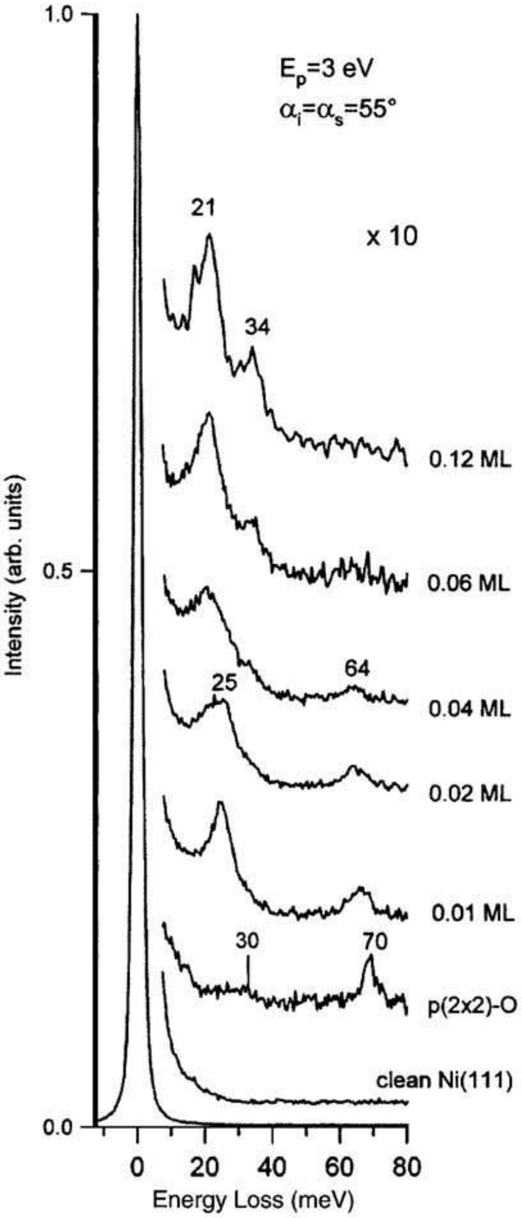

FIG. 2. Electron energy loss spectra of $p(2\times2)$-O prepared at 400 K and after deposition of different amounts of Na at the same temperature.

It should be noticed that the two coadsorbed species do not interact each others, but directly with the substrate, even for higher oxygen exposures. This finding is quite surprising as oxygen and alkalis are expected to strongly interact each other, especially for high oxygen or alkali precoverages.

In previous studies[13,14] of the coadsorption of oxygen and alkalis, oxygen was assumed to migrate underneath the alkali layer. However, according to this model, the alkali-substrate vibration should disappear because of the intralayer of oxygen atoms. On the contrary, it was always present and, accordingly, our measurements indicated that a more complex model is needed to describe the coadsorption. We suggest that for submonolayers of alkalis both species are coplanar, as found for similar systems,[15] and only a weak bond, not evidenced in loss spectra, exists between them.

It is worth to verify if the same mechanism occurs with a reversed order of adsorption. With this in mind, we exposed Na on an O-precovered surface.

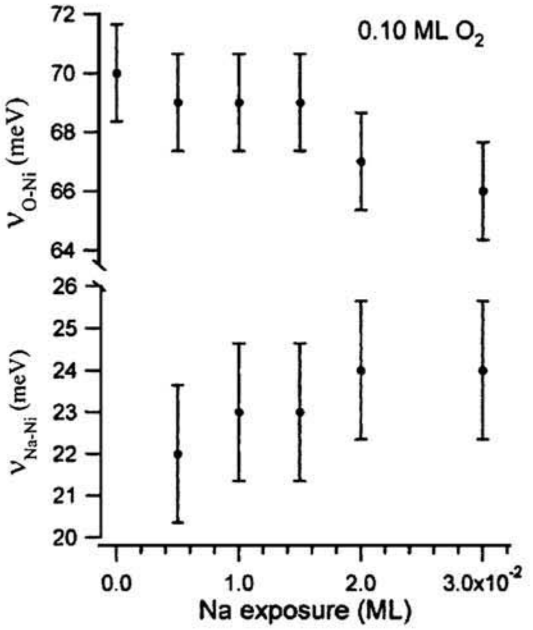

FIG. 3. Behavior of the O–Ni and the Na–Ni vibration energies as a function of Na exposure for an initial O-precoverage of 0.10 ML.

A $p(2\times2)$-O structure was prepared at 400 K and several coverages of Na were deposited on this phase at the same temperature. The loss spectrum of the $p(2\times2)$-O showed the O–Ni mode at 70 meV and an induced phonon at 30 meV (Ref. 11) (Fig. 2). The presence of such mode is typical of very ordered oxygen overlayers. After the deposition of sodium on the O-modified surface, the Na–Ni stretching appeared at 25 meV while the O–Ni vibration shifted from 70 down to 64 meV. For Na coverages between 0.11 and 0.30 ML, a new feature appeared at 34 meV and the Na–Ni peak shifted to 21 meV. The feature at 34 meV was assigned to the Na–O stretching mode. Accordingly, a direct interaction between O and Na arose with the formation of a bond between coadsorbates. No other relevant changes were observed for higher Na coverages.

The appearance of the peak at 34 meV for a Na coverage of 0.11 ML is simultaneous with the shift of the Na–Ni vibration energy from 25 down to 21 meV. This finding can be taken as an evidence of the formation of Na–O–Ni bonds.

Similar results were obtained even for a lower O precoverage, i.e., 0.10 ML (Fig. 3).

Interestingly, we noticed that whenever alkalis were adsorbed first, the alkali-O bond was not formed while reversing the order of the adsorption, i.e., oxygen first of alkalis, the O-alkali vibration arose in spectra. We do not have a fully convincing explanation for such finding. However, when CO was coadsorbed with alkalis, the alkali-O vibration appeared upon oxygen exposures. We tentatively suggest that the system alkali/Ni(111) is less reactive toward oxygen compared to O/Ni(111) toward alkalis. Instead, the reactivity of the alkali/Ni(111) toward oxygen is enhanced whenever alkalis are coadsorbed with CO. The bond with the substrate may play an important and decisive role in understanding this unexpected behavior as a function of the order of adsorption between Na and O. Only more accurate and dedicated theoretical studies may shed the light on such finding.

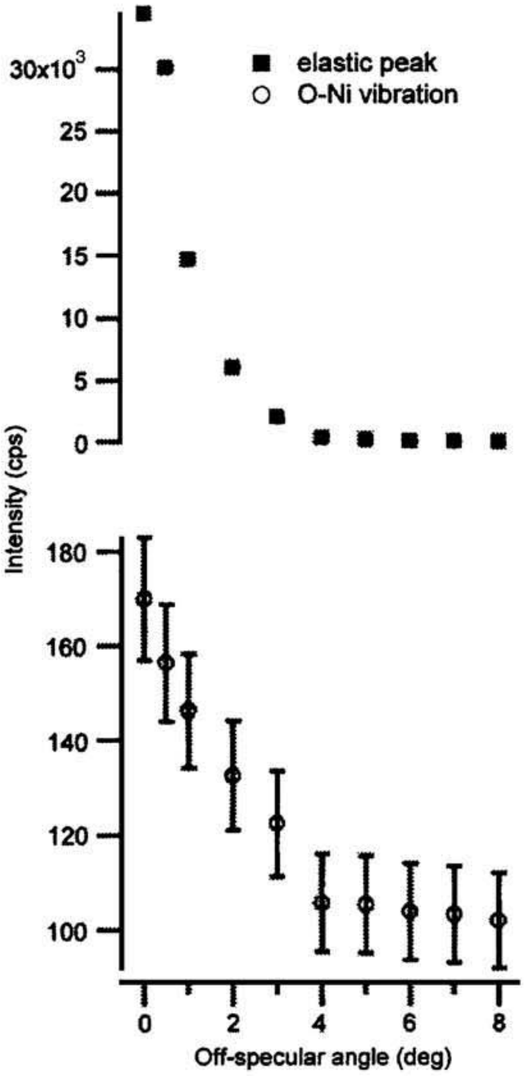

FIG. 4. Behavior of the intensity of the elastic beam and of the vibrational loss of oxygen as a function of the off-specular angle suggesting the dipolar character of the O–Ni peak.

The dynamical dipole moment μ of O–Ni stretching energies as a function of Na exposure could be evaluated from the measured intensity and energy of their loss peaks using the dipole scattering theory.[16] In principle, an impact component could be present for either specular and off-specular measurements. The intensity of the O–Ni loss recorded for off-specular scattering geometry decreased as the intensity of the elastic peak (Fig. 4). This behavior suggests the dipolar nature of such excitation, in excellent agreement with results on similar systems.[17]

An effective charge Q can be then calculated from $\mu=(h/4\pi M_r\omega)^{1/2}$, with M_r being the reduced mass. Here a rigid Ni substrate is assumed, i.e., $M_r=M_{\mathrm{O}}$, and the following experimental parameters are used: the incidence angle (55°), the half-angle of acceptance (1.0°), and the primary energy of 3 eV.

The dynamical charge of O–Ni was found to exponentially decrease as a function of Na exposure (Fig. 5). The best curve that fits the data of Fig. 5 is

$$Q/e=A+B^{*}e^{-C\theta},$$

where $A=0.29$, $B=0.28$, $C=67$, and θ is Na coverage.

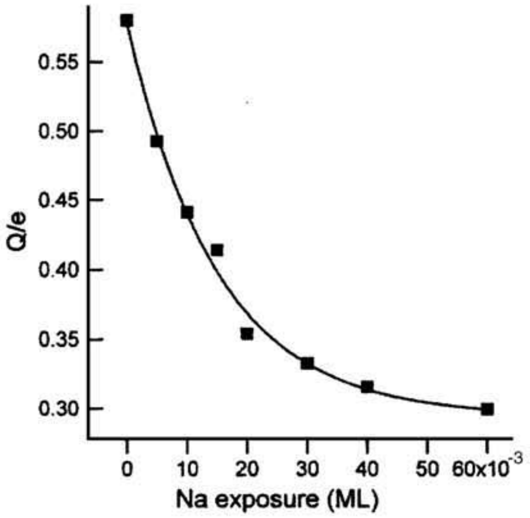

FIG. 5. The dynamic dipole charge Q/e (e is the electron charge) of O as a function of Na exposure.

A link between the exponential behavior of this empirical relation with the progressive filling of the O $2p_z$ antibonding orbitals may be tentatively suggested.

Likewise, similar results should be obtained even depositing an other alkali metal, e.g., potassium, instead of sodium. HREEL spectra taken for 0.10 ML O/Ni(111), for 0.03 ML K/Ni(111), and for the coadsorbed phase 0.10 ML O+0.03 ML K on the same substrate are reported in Fig. 6. The latter shows how the K–Ni and O–Ni stretching vibrations change upon coadsorption of the two species. We associate the 15 meV loss peak with K atoms vibrating perpendicular to the substrate. Upon coadsorption, the K stretching energy shifted from 15 to 18 meV and the O–Ni vibration shifted from 70 down to 66 meV.

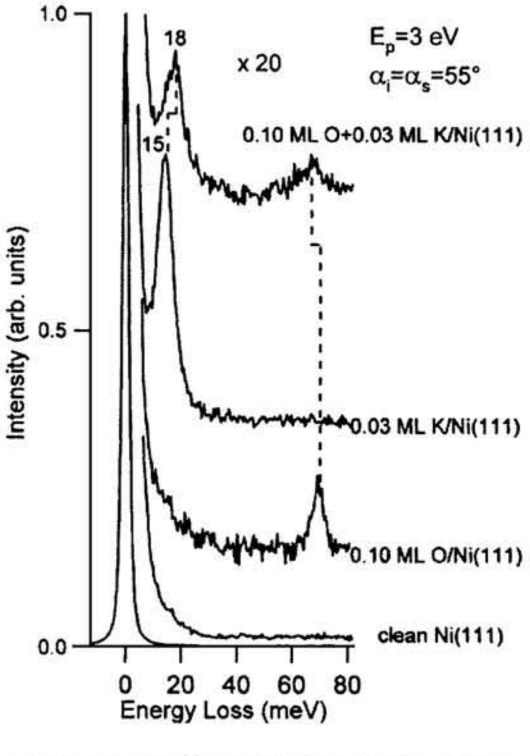

FIG. 6. HREEL spectra of (a) 0.03 ML of K deposited at 400 K onto the Ni(111) surface, (b) 0.10 ML O/Ni(111) at the same temperature, (c) 0.03 ML K coadsorbed at 400 K with 0.10 ML of O on the Ni(111) surface.

In conclusion, our vibrational measurements provided the first evidence of a softening of the O–Ni bond and of a strengthening of the Na–Ni bond in Na+O coadsorbed phase. According to the electrostatic model, the alkali-induced filling of the O $2p_z$ orbital was ascribed to be responsible of the weakening of the O–Ni bond. The dynamical charge Q/e of O–Ni stretching exponentially decreased as a function of Na exposure. A direct Na–O bond was formed only whenever oxygen was preadsorbed. Similar results were obtained in K+O coadsorption on Ni(111). The strengthening of the alkali-substrate bond was explained with a reduced bond distance occurring whenever O and alkalis are coadsorbed. Our measurements well reproduce for the first time theoretical calculations in Ref. 4 and, moreover, are in excellent agreement with structural studies in similar systems.

ACKNOWLEDGMENTS

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PAPER VII

Short-range interactions in Na coadsorption with CO and O on Ni(111)
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Short-Range Interactions in Na Coadsorption with CO and O on Ni(111)

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The coadsorption of Na with CO and O on Ni(111) is studied by high-resolution electron energy loss spectroscopy. Experimental evidence for a very short-range interaction between Na and coadsorbates is reported, in contrast with recent theoretical predictions overestimating nonlocal alkali-induced effects. Loss spectra show distinct features, as a consequence of different local [CO]:[Na] and [O]:[Na] stoichiometries.

1. Introduction

The addition of alkali-metal atoms as promoters of catalytic reactions on metal surfaces is widespread in heterogeneous catalysis.[1–4] For this reason, alkali coadsorption with reactive species, such as oxygen adatoms and CO molecules, on a catalytic metal surface has been extensively studied over the years. A systematic study of coadsorption systems is essential for understanding the nature of interactions among neighbouring species. Such interactions significantly affect the physical and chemical properties of adsorbates and consequently the occurrence of reactions.

Both experimental[5–9] and theoretical[10–16] works have highlighted the factors influencing the interactions between alkalis and coadsorbed species on transition-metal surfaces. Nevertheless, the microscopic mechanisms of the interactions poisoning or promoting catalytic reactions are not well understood yet. As a consequence, a renewed interest has recently re-emerged.[7,8,16] There is particular attention towards the local/nonlocal character of electronic interactions, that is, about the range of such interactions. The answer to this point would imply a significant advancement in our understanding of the surface chemical bond and catalytic reactions occurring whenever alkalis are coadsorbed with other chemical species.

To date, four types of alkali-coadsorbate interactions have been proposed to explain alkali-induced effects: a very short-range (ca. 3 Å) direct orbital overlap between the adsorbate and the alkali atom;[5,17] a short-range (about 4 Å) electrostatic interaction of the alkali-induced electric field with the adsorbate-substrate bond;[2,11,12,18–22] a long-range indirect interaction mediated by surface electrons;[15] and a nonlocal and long-range alkali-induced enhancement of the surface electronic polarizability.[16] However, for a long time the promotion effect of alkalis on metal surfaces was assumed to have predominantly a local and short-range character.[1,27–29]

The properties of CO chemisorbed with alkalis were explained within the framework of the Blyholder model, based on a local concept of hybridization.[23,24] The surface potential is locally lowered by alkali adatoms so that charge from the 5σ orbital of CO is donated to the metal surface which back-donates some charge into the anti-bonding 2π^* orbital of CO. This charge redistribution weakens the internal C–O bond, as found by infrared reflection absorption spectroscopy and high-resolution electron energy loss spectroscopy (HREELS).[5–7] Other studies suggested a model based on a very local and direct interaction between the alkali-metal atoms and the CO molecules through the formation of a surface complex.[25,26]

Nonetheless, recently the occurrence of a predominant long-range character of the alkali-induced effects has been more and more invoked. He and Jacobi[9,30] found a significant weakening of the C–O stretching energy even if CO is adsorbed on the Ru(0001) surface far from the Cs atoms. They discussed the long-range or nonlocal effects in the following picture: the CO outside of the (Cs + 2 CO)-2×2 islands reduces the amount of charge back-donated to the CO within the island. Moreover, in the coadsorption of K and CO on Ru(0001) an upward shift of the C–O mode for increasing CO exposures was revealed[31] and attributed to a long-range substrate-mediated interaction between coadsorbates. Long-range effects were invoked also for explaining the energy shift as a function of CO coverage of different bands ascribed to the C–O stretching for K coadsorbed with CO onto the Pt(111) surface.[32,33] Both short and long-range interactions were proposed for the coadsorption of Li with CO and N_2 on Ru surfaces.[34,35] In particular, the red-shift of the C–O stretching was ascribed to a long-range effect, occurring especially at lower alkali metal coverages because of the absence of complexes.[34] Long-range effects were suggested to occur also in Na + CO/Ni(111) at low sodium coverages,[36] as indicated by subtle changes in desorption activation energies and in vibrational frequencies. Infrared reflection absorption spectroscopy measurements on K + CO/Ni(111) found a mixture of long-range and short-range interactions.[37] Furthermore, Brown et al.[38] had to introduce a long-range electronic perturbation in the vicinity of alkali-ad-

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sorbed metal surface for explaining the alkali-promoted hydrogen dissociation. Finally, very recently the long-range enhancement of the polarizability of the metal surfaces upon alkali adsorption has been ascribed to be ultimately responsible for facilitating surface reactions.[16] Such significant nonlocal effects were suggested to be responsible of the softening of the C–O stretching in the alkali + CO coadsorbed phase, so as to seriously question the results of most previous theoretical and experimental works.[1,29]

On the basis of the above discussion, it is essential to provide accurate and dedicated measurements aimed at unambiguously establish the range of the electronic interactions between alkalis and coadsorbed species on transition-metal surfaces.

Herein we demonstrate how the joint analysis of Na-substrate and C–O stretching vibrations as a function of the Na/CO ratio, that is, the local [Na]:[CO] stoichiometry, may give unambiguous information about the range of the Na–CO interaction. It is worth to mention that most of previous experimental studies investigating the alkali + CO and alkali + O coadsorption were performed within a common approach, that is: first, alkali atoms were deposited onto the metal surface and only successively the surface was exposed to CO (O_2) molecules. This procedure was based on the assumption, taken for granted, that pre-adsorbed alkalis induce important changes in the electronic properties of the underlying surface and as a consequence in the reactivity of coadsorbates. On the contrary, the effects of CO (O) on the alkali-substrate bond have been always neglected.

We report HREELS measurements of Na coadsorbed with CO and O on Ni(111). Nickel is a suitable substrate to investigate such processes. It is extensively used in heterogeneous catalytic processes and thus the coadsorption of alkali-metal atoms with carbon monoxide and oxygen on these surfaces is of considerable interest in understanding the catalytic mechanisms involved in the reactions. The HREELS technique offers the opportunity to distinguish between indirect (substrate-mediated) and direct charge transfer and, thus, between short and long-range interactions.

Contrary to all previous measurements, we focus essentially on the coadsorbates-induced effects on the Na-substrate vibrational mode. Measurements provide direct evidence of local interactions between Na and coadsorbates (CO, O).

The most evident effect of short-range and local interactions is the occurrence in the loss spectra of features arising from local Na–CO interactions and other features characteristic of Na and CO not interacting with each other. The same mechanism (short-range interaction) was found to be predominant for Na coadsorption with O, as predicted by Liu and Hu.[2]

Present results demonstrate that in alkali coadsorption systems local interactions play a major role and the nonlocal effects of the alkali-induced enhancement of the surface electronic polarizability in ref. [16] have been probably overestimated.

2. Results and Discussion

First, the vibrational spectra of Na, CO, and oxygen separately adsorbed on the Ni(111) surface are recorded in order to have well-established reference data. As known, CO molecules occupy three-fold hollow sites on Ni(111) and at the coverage of 0.5 ML they form a c(4×2) LEED structure.[39] For this phase, the CO–Ni mode and the C–O stretching energy are observed at 50 and 235 meV, respectively.[7] The oxygen atoms form a p(2×2) structure and the O–Ni vibration occurs at 70 meV.[7,40] Concerning the adsorption of Na, the Na–Ni stretching energy is found between 25 meV (for Na coverage less than 0.01 ML) and 19 meV (for Na coverage above 0.10 ML).

In order to investigate interactions between CO and Na, a 0.08 ML Na/Ni(111) is exposed to CO at room temperature (Figure 1 a). The effects of CO on the Na–Ni stretching are discussed elsewhere.[7] The Na–Ni stretching vibration, observed at 20 meV for the clean Na/Ni(111) surface, clearly splits into two components upon CO exposures. Likewise, two different C–O stretching modes are revealed. The appearance of a second Na–Ni and C–O mode with increasing CO exposure is interpreted as due to a very local and mutual interaction between coadsorbates. As a matter of fact, not all CO molecules can adsorb in close vicinity of the pre-adsorbed Na adatom, and vice versa.

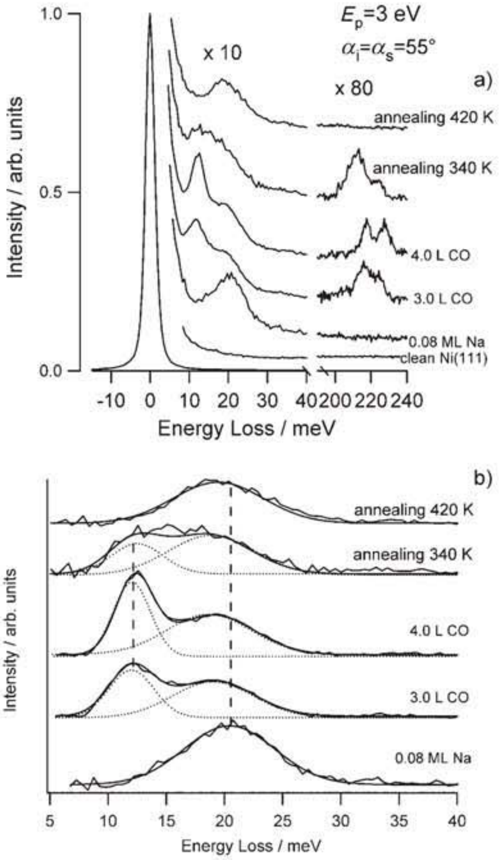

Figure 1. a) HREEL spectra of 0.08 ML Na/Ni(111) exposed to CO molecules at room temperature and successively annealed. Na was deposited at 400 K. b) Each curve is obtained by subtracting an exponential background and by fitting the resulting spectrum with Lorentzian lineshapes.

For a better analysis of loss spectra, an exponential background is subtracted from each of the spectra in Figure 1 a. The loss features thus obtained are fitted by a Lorentzian curve (Figure 1 b). We observe that upon CO exposure a new Na–Ni peak arises at 12 meV and its intensity increases as a function of CO coverage. On the contrary, the intensity of the Na–Ni peak at 19 meV gradually decreases. However, it is worth to notice that in principle HREELS intensities can be affected by several external factors. Beside depolarization effects caused by coadsorbates,[41] further problems can originate, for example, from the changes in reflectivity due to the different surface conditions (temperature, adsorbate coverage and consequent work-function changes, angle of incidence of the electron beam, etc.).[42]

The feature at 12 meV is assigned to Na adatoms in close contact with CO molecules. Conversely, the Na–Ni vibration at 19 meV is due to Na adatoms far from CO molecules. The absence of an energy shift of the latter peak upon CO exposures is further evidence of a local interaction between Na and CO. The red-shift of the Na–Ni peak in the Na+CO coadsorbed phase is ascribed to a CO-induced lengthening of the Na–Ni bond.[7] Studies concerning the structural properties of K+CO on both Ni(111) and Ni(100)[43,44] exhibit a significant increasing of the alkali-substrate bond length with respect to the case of K/Ni(111) and K/Ni(100). This result is in excellent agreement with the weakening of the Na–Ni bond in the Na+CO coadsorbed phase.

The presence of two different Na–Ni peaks and the lack of any defined LEED pattern suggest the occurrence of a disordered Na+CO phase. Zones with different local [Na]:[CO] stoichiometries coexist on the Ni(111) surface.

As concerns the C–O stretching, a peak at 216 meV with a shoulder at 225 meV arises after an exposure of 3 L ($1\,L=1\times10^{-6}$ torr s) of CO. Further CO exposure allows a better separation of such features. Two well distinct losses are recorded at 217 and 227 meV. The presence of two C–O features is ascribed to different environments for CO molecules and is indicative of different local [Na]:[CO] stoichiometries.

A local charge transfer is suggested for the similar Na+CO/Cu(111) system.[45] At low Na coverage (0.06 ML) and low CO coverage, CO adsorbed essentially unperturbed onto the Cu(111) surface while at higher CO coverage part of the CO in close contact with Na is strongly perturbed, that is, the action of Na on the CO adsorbate is found to be local. Similar results are obtained for Cs+CO/Pt(111)[32] and K+CO/Pt(111).[28,32] A short-range attractive interaction between the alkali-metal atoms and CO molecules is suggested on the basis of the finding that C–O stretching frequency changed as a function of the local [CO]:[alkali] stoichiometry. However, in all these studies the Na–Ni vibration is not investigated.

Moreover, very recently a theoretical analysis[46] of the variation of CO bond lengths, the charge-density redistribution, and the energy shift of molecular levels performed for K+CO coadsorbed onto the Ni(111) surface indicates that the K-induced effect is short-ranged. The alkali-induced energy shift of the molecular levels causes the $2\pi^*$ states to be partially occupied.

Annealing the sample up to 340 K causes the desorption of the CO molecules which are weakly bonded to the surface (Figure 1 a). As a consequence, the C–O stretching peak at higher energy disappears. After further annealing up to 420 K, CO molecules completely desorb from the surface. Instead, only a part of Na adatoms desorbed, as indicated by the overall diminishing of the integral of the Na–Ni peaks. However, Na–Ni vibration is still present in the HREEL spectrum even with the sample kept at 600 K. As expected, after the desorption of CO molecules the energy of the Na–Ni peak returns to 19 meV. Upon annealing, the component at 12 meV decreases in intensity (Figure 1 b) and finally disappears.

These findings disagree with previous results. In fact, it was generally assumed that a coincident desorption of both alkalis and CO occurs.[25,47–51] However, the presence of the Na–Ni stretching in the absence of any CO-derived mode ensures that Na and CO desorption are not at all coincident.

The role of the alkali precoverage is quite intriguing as the adsorption of alkali-metal adatoms can notably modify the bonds between coadsorbates and the substrate. In particular, it would be interesting to investigate low alkali coverages for which some authors have proposed the formation of chainlike nuclei in CO+Cs/Pt(111),[32] CO+K/Ru(0001),[33] and CO+K/Pt(111).[38] Similar structures may in principle occur also for CO+Na/Ni(111). Accordingly, 0.04 ML Na/Ni(111) is exposed to CO molecules (Figure 2 a). However, no indication for such structures emerges from the analysis of the LEED pattern of the Na+CO coadsorbed phase and, therefore, we can argue that instead 2D-islands are formed from the very beginning. Our findings are in agreement with those of Murray et al.,[52] who used scanning tunnelling microscopy to observe a dense network of small K+CO islands on Ni(100), without chain formation. Similar conclusions are also reached for the CO+Cs/Ru(0001) system.[9,53]

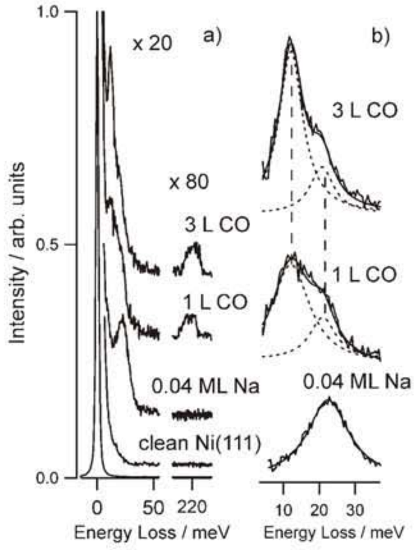

Figure 2. a) HREEL spectra of Ni(111) and 0.04 ML Na/Ni(111) exposed to CO molecules at room temperature. b) Each curve is obtained using the same procedure as Figure 1 b.

After the subtraction of the background of Figure 2a, the spectrum clearly shows the coexistence of two Na–Ni losses at 12 and 19 meV (Figure 2b).

It is worth noticing that at high Na/CO ratios, almost all CO molecules are perturbed by Na adatoms. Accordingly, an unique C–O stretching peak is expected. Likewise, for a very high CO/Na ratio, only one Na–Ni feature should exist.

More details on the locality of the Na–CO interaction are obtained by adsorbing Na on the c(4×2)–CO/Ni(111) surface, that is, by reversing the order of adsorption. Such measurements allow one to observe the evolution of the C–O stretching as a function of Na exposures and can be decisive for establishing the range of the Na–CO interaction. A nonlocal Na–CO interaction would imply a continuous red-shift of the C–O stretching even at a very low Na/CO ratio, while the appearance of a second C–O stretching due to Na-perturbed CO molecules together with the not perturbed C–O stretching would provide unambiguous evidence of the strong local character of the Na–CO interaction.

The c(4×2) structure was prepared by exposing the surface to 1 L of CO at 200 K. The CO–Ni and the C–O vibrational modes are measured at 50 meV and 235 meV, respectively (Figure 3). Such modes are significantly affected by Na deposition at the same temperature. The CO–Ni vibration peak increases in intensity and shifts to higher loss energies up to 72 meV. Furthermore, a new feature arises at 220 meV. Both modes at 220 and 235 meV evolve with the alkali deposition and merge into a single feature at 220 meV for a Na coverage of 0.22 ML. The Na–Ni stretching energy for the CO+Na coadsorbed phase is observed between 12 meV and 14 meV (Na coverages above 0.22 ML). The existence of two distinct C–O frequencies for Na coverages between 0.07 and 0.13 ML indicate the presence of two different species of adsorbed CO molecules; the former, being the C–O stretching at 235 meV, is essentially unaffected; the latter, however, interacts with Na atoms and moves to 220 meV. For a Na coverage of 0.13 ML, all CO molecules are influenced by Na adatoms, as suggested by the disappearance of the not perturbed C–O stretching at 235 meV. However, the coadsorbed Na+CO phase is very disordered as confirmed by LEED analysis and therefore different local [CO]:[Na] stoichiometries exist. As a consequence, two different C–O stretching modes at 220 and 228 meV are recorded. At the highest Na coverage (0.22 ML), a uniform layer with about one atom of Na for each two CO molecules exists on the surface and a unique C–O stretching energy at 220 meV is observed in the loss spectrum. Interestingly, no Na–Ni vibration peak at 20 meV (unperturbed Na) is revealed under these conditions. This result ensures the mixing of Na and CO within Na–CO islands so as to exclude the occurrence of a phase separation between coadsorbates. Data reported in Figure 3 represent a clear and unambiguous fingerprint of a very short-range interaction between Na and CO.

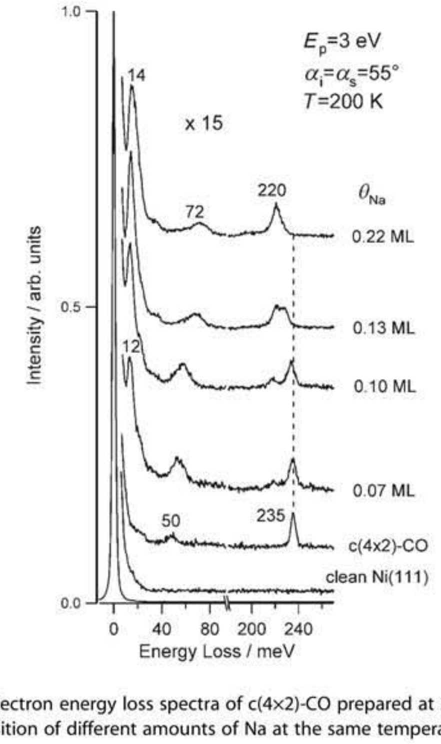

Figure 3. Electron energy loss spectra of c(4×2)-CO prepared at 200 K and after deposition of different amounts of Na at the same temperature.

In order to ascertain whether the same local mechanisms apply for other systems, we investigate the coadsorption of sodium with oxygen. Carbon monoxide and oxygen are both electronegative species with respect to Na atoms and they could behave in the same way.

Figure 4a shows HREEL spectra of 0.16 ML Na/Ni(111) exposed to small amounts of O_2. The clean 0.16 ML Na/Ni(111) shows only a feature at 19 meV. Upon O_2 exposures, two different Na–Ni stretching vibrations are revealed at 19 and 25 meV. The peak at 25 meV is assigned to Na adatoms interacting with oxygen. Probably oxygen adsorption induces a notable strengthening of the Na–Ni bond.[8] Increasing oxygen exposure, the number of Na atoms in close contact with oxygen gradually increases causing a decreasing of the intensity of the component at 19 meV and an increasing of the peak at 25 meV (Figure 4b). The Ni–O vibration at 63 meV[8] is also recorded.

By reducing the O/Na ratio with respect to the spectra in Figure 4, it should be possible, in principle, to observe an energy shift of the peak at 25 meV. It is quite intuitive that a change in Na–Ni bond length should be almost continuous as a function of the O/Na ratio. With this in mind, we exposed a 0.05 ML Na/Ni(111) surface to small quantities of O_2 (Figure 5a). A second component of the Na–Ni peak arises also in this case. Upon oxygen exposure, the energy of the second Na–Ni vibration shifts from 23 up to 26 meV. This result is a fingerprint of the gradual strengthening of the Na–Ni bond and it is ascribed to a shorter Na–Ni bond distance, caused by the presence of oxygen atoms. Further oxygen exposures do not cause remarkable changes in the HREEL spectrum.

Our findings for the Na+O phase agree well with the theoretical prediction by Liu and Hu,[2] who suggest the occurrence of a short-range alkali-induced filling of the O $2p_z$ orbitals (electrostatic model). Moreover, it is worth noticing the absence of any Na–O chemical bond (the Na–O mode is expected at about 36 meV).[8] On the contrary, an interpretation

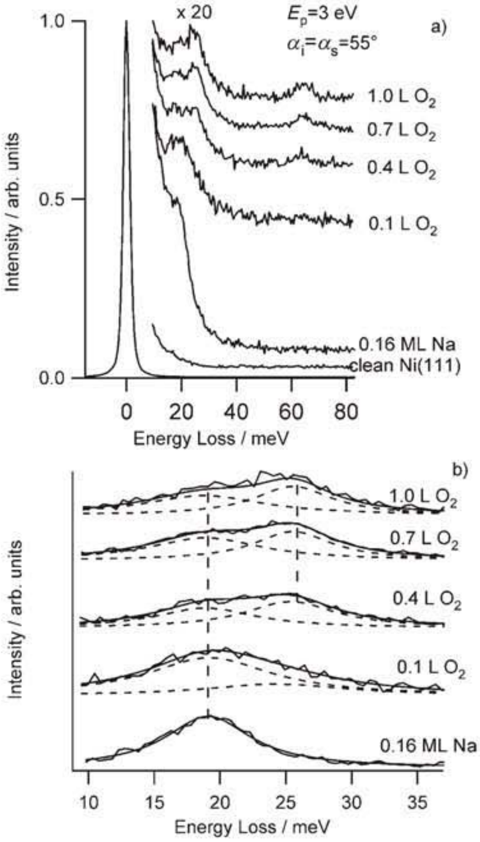

Figure 4. a) HREEL spectra of Ni(111) and 0.16 ML Na/Ni(111) exposed to O_2 molecules at 400 K. b) Each curve is obtained using the same procedure as Figure 1 b.

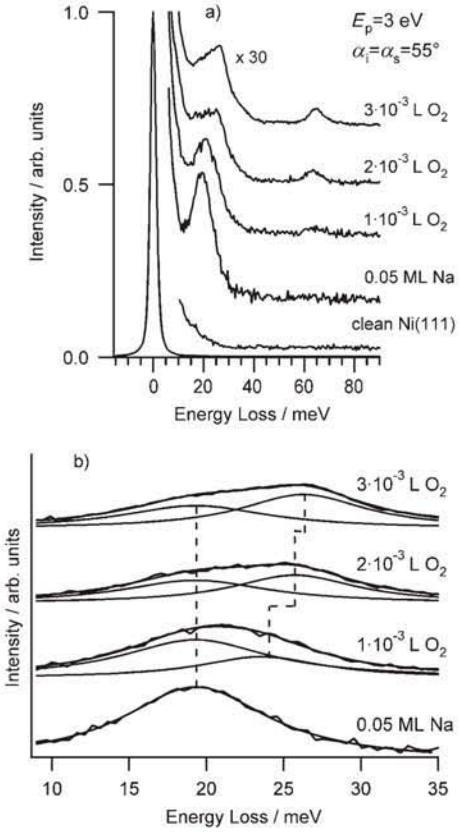

Figure 5. a) HREEL spectra of Ni(111) and 0.05 ML Na/Ni(111) exposed to O_2 molecules at 400 K. b) Each curve is obtained using the same procedure as Figure 1 b.

based on nonlocal effects reported by Stolbov and Rahman[16] also for alkali coadsorption with oxygen has to be excluded.

3. Conclusions

We have shown that loss measurements provide unambiguous evidences for a local and mutual interaction between alkalis and coadsorbates species. The range of the interaction is suggested to be not more than 3–4 Å. Two different Na–Ni and C–O stretching frequencies were observed in the Na+CO coadsorbed phase, as a consequence of different local [CO]:[Na] stoichiometries. A similar short-range mechanism of interaction was observed to occur for Na+O. On the basis of the present findings, we argue that the nonlocal effects of alkali-induced enhancement of the surface electronic polarizability reported in ref. [16] are overestimated. If existing, long-range interactions would have negligible effects on the Na–Ni and C–O vibrational frequencies. Moreover, annealing does not cause a coincident desorption of Na and CO, in contrast with previous measurements.

Experimental Section

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Ni(111) with a purity of 99.9999%. The surface was cleaned by repeated cycles of ion sputtering and annealing at 900–1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy and low-energy electron diffraction (LEED) measurements, respectively. The Ni(111) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium was deposited onto the substrate by evaporating from well-outgassed commercial getter sources.

Pre-adsorbed alkali layers free of any contamination could be obtained only by keeping the Ni(111) surface at 400 K during both deposition and measurements. Nonetheless, measurements were performed in a few minutes in order to further reduce the contamination. Carbon monoxide and oxygen were admitted through a precise leak valve. Sodium, carbon monoxide, and oxygen coverages (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate) were estimated from the exposure time taking as reference the coverage of well-known LEED structures, that is: $(\sqrt{3}\times\sqrt{3})R30^\circ$-Na, c(4×2)-CO, and p(2×2)-O. A constant sticking coefficient was assumed to obtain other desired coverages. Coverages were calibrated for different substrate temperatures. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of the spectrometer ranged from 2 to 3 meV.

Keywords: chemisorption · oxygen · sodium · surface analysis · vibrational spectroscopy

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PAPER VIII

Effects of O adsorption on the Na+CO coadsorption system

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PAPER IX

Mechanisms leading to alkali oxidation on metal surfaces

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Letter

Mechanisms Leading to Alkali Oxidation on Metal Surfaces

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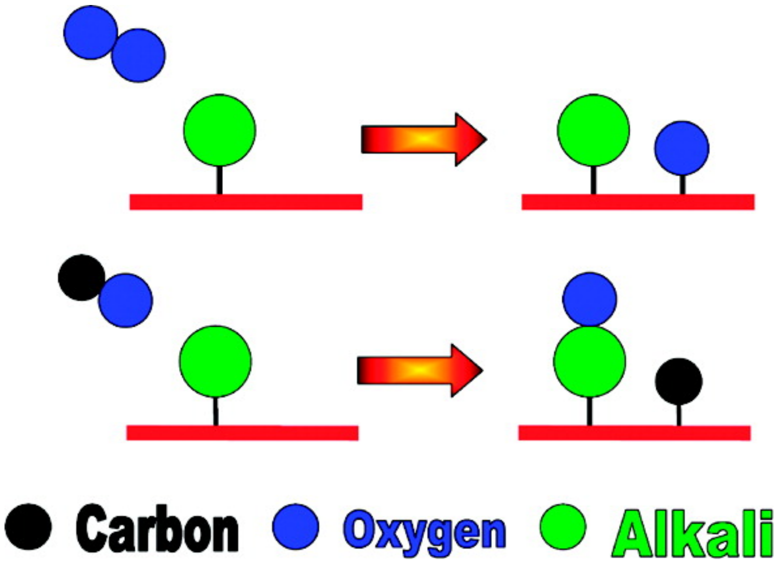

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Mechanisms Leading to Alkali Oxidation on Metal Surfaces

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The coadsorption of alkalis with CO and O on Cu(111) and Ni(111) was studied by vibrational measurements. Unexpectedly, we found an enhanced alkali oxidation rate for alkali + CO compared with alkali + O. Such finding was ascribed to the short-range alkali−CO interaction which lowers the barrier for CO dissociation and favors a giant alkali oxidation. Surprisingly, no alkali-O bond was formed for O/alkalis.

The metal−oxygen bond plays an important role in many biological and synthetic reactions.[1] Moreover, oxidation processes of metal and semiconductor surfaces are of primary importance in electronic-device technology. On the other hand, alkali metals are widely used in the chemical industry as promoters of chemical reactions at surfaces. They catalyze processes such as manganation,[2,3] zincation,[4−7] ammonia synthesis,[8] Fischer−Tropsch,[8] and epoxidation processes.[9−11] At the fundamental level, alkalis are employed as model systems for understanding their promotional role and the nature of the chemical bond with the substrate and with other coadsorbed species.

Using high-resolution electron energy loss spectroscopy (HREELS) measurements of alkali (Na, K) coadsorption with CO and O on Cu(111) and Ni(111), we provide direct evidence that the oxidation of alkali atoms is more efficient if promoted by the dissociation of CO molecules than by direct exposures of alkalis to O_2.

It is well-known that, when coadsorbed with CO, alkalis cause a weakening of the intramolecular C−O bond[8,12] and a strengthening of the metal−CO bond.[8,12] In some cases, depending on substrate, temperature, and alkali coverage, the dissociation of CO molecules has been observed. On the other hand, alkalis were demonstrated to weaken the O-substrate bond.[13,14]

At room temperature, Na on Cu(111) forms a disordered phase up to the formation of the (3/2 × 3/2) structure[15] (0.44 ML) with Na atoms occupying 3-fold hollow sites.[16] On the contrary, on Ni(111) a $(\sqrt{3} \times \sqrt{3})$R30°-Na structure has also been recently revealed for intermediate coverages[17] (0.33 ML). Instead, on both surfaces potassium forms a p(2 × 2) structure[15] (0.25 ML) with atoms in atop sites. On Ni(111) oxygen molecules adsorb dissociatively forming p(2 × 2) and $(\sqrt{3} \times \sqrt{3})$R30° ordered structures[15] at room temperature.

Experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were cleaned by repeated cycles of ion sputtering and annealing at 900−1100 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) measurements and low-energy electron diffraction (LEED), respectively. Na and K were deposited onto the substrate by evaporating from well-outgassed getter sources. Carbon monoxide and oxygen were admitted through precise leak valves. Alkali, CO, and O coverages (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate) were estimated from the exposure time taking as reference the coverage of well-known LEED structures, that is: (3/2 × 3/2)-Na, p(2 × 2)-K, c(4 × 2)-CO, and p(2 × 2)-O. A constant sticking coefficient was assumed to obtain other desired coverage. Similar results were achieved by calibrating using AES. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The use of low-energy impinging electrons ensures of the absence of irradiation-induced CO dissociation. The energy resolution of the spectrometer ranged from 2 to 3 meV. All deposition and measurements were carried out at room temperature. A particular care was dedicated to avoid any contamination of the alkali adlayer.

Figure 1 shows HREEL spectra acquired for (3/2 × 3/2)-Na (top panel) and p(2 × 2)-K (bottom panel) deposited on Cu(111) and Ni(111) exposed to CO (0.4 L, 1 $L = 10^{-6}$ torr · s) at room temperature. Loss spectra show several features giving unambiguous information on the chemical reactions occurred at the investigated surfaces. In particular, we observe peaks at 19−24 meV for Na (top panel) and 15 meV for K (bottom panel), assigned to the alkali vibration against the substrate.[17] Loss features recorded in the range 169−197 meV were assigned to the intramolecular C−O stretching vibration. The internal C−O frequency is red-shifted with respect to its value recorded on the clean surfaces[8] as a consequence of the alkali-CO interaction. Interestingly, we observed features at 36 meV and at 24−29 meV. These losses are due to O−Na[18] and O−K[18] vibrations, respectively. This finding is a unambiguous and direct evidence of the dissociation of a part of CO molecules. Carbon

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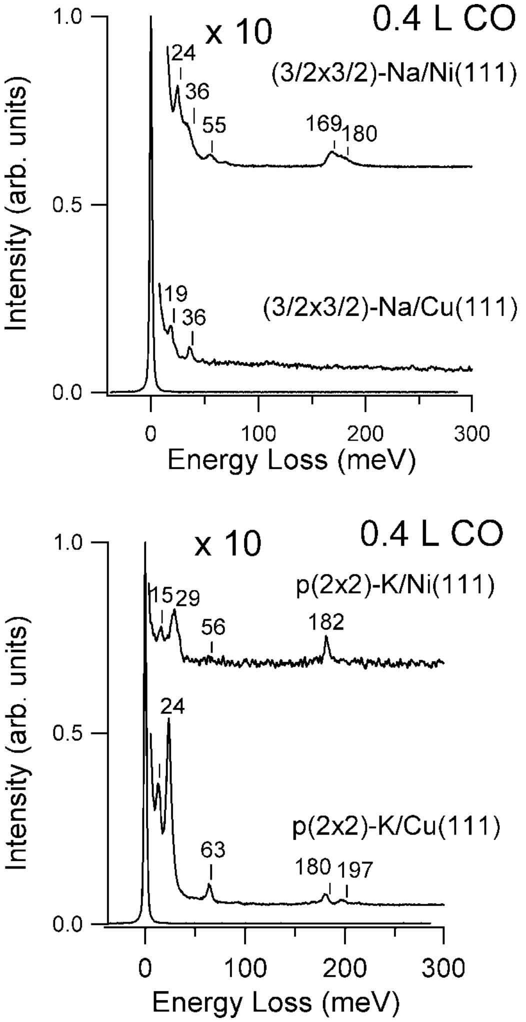

Figure 1. HREEL spectra acquired at 300 K (at a fixed CO exposure of 0.4 L) for: (top panel) (3/2 × 3/2)-Na/Cu(111) and (3/2 × 3/2)-Na/Ni(111); (bottom panel) p(2 × 2)-K/Cu(111) and p(2 × 2)-K/Ni(111). All spectra were normalized to the intensity of the elastic peak and multiplied by the same factor.

monoxide adsorption is partially dissociative for all above systems, except for Na/Cu(111), for which it is fully dissociative as indicated by the absence of C−O stretching losses. Moreover, carbon-derived modes at 55−56 meV (arising from CO dissociation) were observed for alkalis/nickel but not for alkalis/copper.

Hence, loss measurements indicate that Na and K oxidation is promoted by CO dissociation. Moreover, it is worth noticing that for K/Cu(111) part of the oxygen arising from CO dissociation migrates underneath the surface, as suggested by the occurrence of the feature at 63 meV[19] (atomic oxygen in subsurface sites). On the contrary, no oversurface O was present as deduced by the absence of its vibration against Cu(111) expected at 46 meV.[20]

The same alkali-precovered surfaces of Figure 1 were exposed to O_2. In these spectra (Figure 2), besides alkali−substrate vibrations (21−25 meV for Na[13] and 16−17 meV for K[17]), there are additional peaks assigned to oxygen-substrate stretching vibrations. In particular, the feature at 66 meV is due to the O−Ni vibration (red-shifted by the presence of alkalis[12,14]). On alkali-modified Cu(111), we observe peaks due to oxygen adatoms in oversurface (45−46 meV feature[20]) and in subsurface sites (62 meV,[19] only for K).

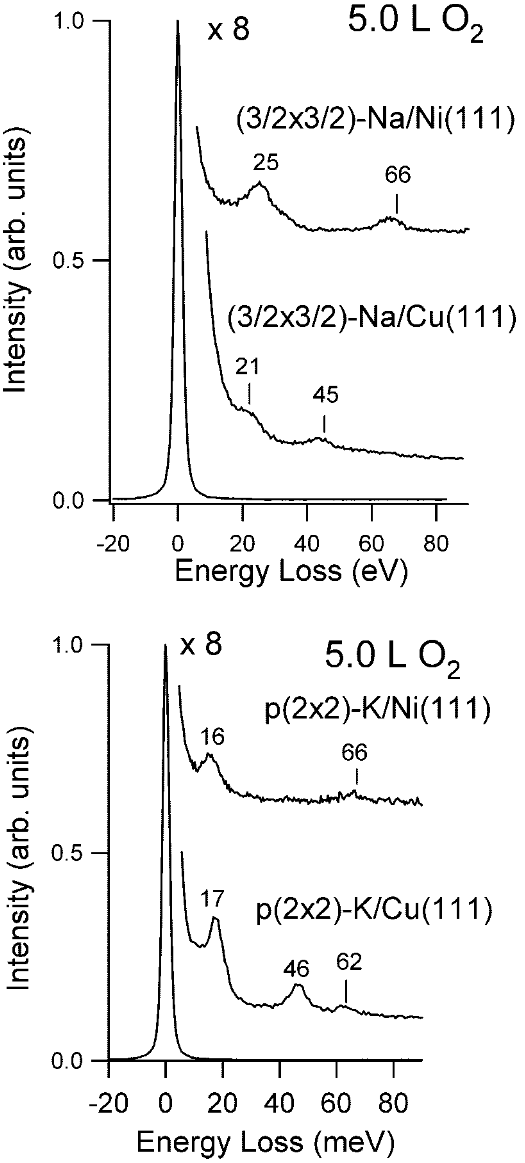

Figure 2. HREEL spectra (at a fixed O_2 exposure of 5.0 L) for (top panel) (3/2 × 3/2)-Na/Cu(111) and (3/2 × 3/2)-Na/Ni(111); (bottom panel) p(2 × 2)-K/Cu(111) and p(2 × 2)-K/Ni(111).

Unexpectedly, the direct exposure of the alkali-doped surface to O_2 does not lead to alkali oxidation (Figure 2), as indicated by the absence in loss spectra of vibrational modes assignable to O−Na (36 meV[18]) and O−K (24−29 meV[18]), respectively.

We suggest that the local and short-range interaction between alkali atoms and CO molecules enhances the CO dissociation rate and thus the efficiency of alkali oxidation (alkali-O bond). For CO adsorbed in sites directly adjacent to alkali adatoms, the lowered electrostatic potential stabilize the electronegative adsorbate and activate a charge transfer from the surface to the 2 π* antibonding orbital, so as to facilitate CO dissociation.[14] In agreement with present findings, experiments performed for K+CO/Co($10\bar{1}0$)[21] revealed the existence of a direct K−O bond. On the other hand, short-range interactions have been unambiguously demonstrated to be predominant in alkali coadsorption with CO.[13,14,22]

The alkali oxidation rate is enhanced for Cu(111), as suggested by spectra in Figure 1. In fact, the ratio between the intensity of the vibrational mode of the alkali-O bond with respect to that of molecular CO (C−O intramolecular stretching) is higher for alkali/Cu(111) than for alkali/Ni(111). This finding

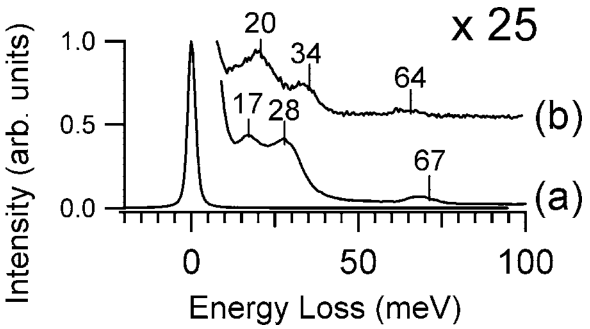

Figure 3. HREEL spectrum acquired for 0.10 ML K deposited onto a 0.10 ML O-modified Ni(111) surface (spectrum a). Reversing the order of adsorption, the alkali−O bond is formed. Similar results were obtained by substituting K with Na (spectrum b).

is well described within the framework of a local and short-range interaction between alkali and CO. As a matter of fact, on clean copper surfaces the sticking coefficient for CO molecules at 300 K is extremely reduced with respect to transition-metal catalysts (Ni, Pt, Ru). The saturation coverage for CO molecules on clean copper was found to be about zero for temperatures higher than 200 K,[23] while for Ni(111) the surface was found to be fully covered by CO molecules at 300 K even for small CO exposures.[24] Accordingly, it is quite expected that CO adsorption on alkali-modified copper substrates might occur only in the close vicinity of alkali adatoms.

We expect that the distances between alkali-metal atoms and reactants are quite short, i.e., about 3 Å,[14] so as to allow the orbital overlap and the formation of a direct bond.[14] Hence, in these conditions oxygen atoms arising from CO dissociation interact essentially with alkali atoms and less with the substrate.

As regards results reported in Figure 2 (direct O_2 exposures), it is quite surprising that the two coadsorbed species (alkali adatoms and atomic oxygen) do not interact with each other but directly with the substrate, even for higher oxygen exposures than 5.0 L. Very likely, in the alkali + O coadsorbed phase on Ni(111) and Cu(111), the distance between O and the alkali adatom should always be higher than 3 Å.[14] Weak electrostatic interactions between alkalis and O already dominate (without the occurrence of alkali oxidation) for distances of 4 Å.[14]

Measurements were also performed by reversing the order of the adsorption, i.e. oxygen first of alkalis. In these conditions, alkali oxidation is readily observed, as suggested by the appearance of the O−K (28 meV[18]) and O−Na (34 meV[18]) in spectra (Figure 3). The direct bond of atomic oxygen with the substrate, which modifies the electronic properties of the system, should be responsible for this behavior.

Our results highlight the general features of the mechanisms of alkali oxidation. For alkali-precovered surfaces, a giant alkali oxidation is achieved upon CO adsorption and dissociation. This is ascribed to the short-range interaction between alkalis and CO, which lowers the CO dissociation barrier. On the contrary, no alkali oxidation occurs for oxygen exposures on alkali-precovered Ni(111) and Cu(111) surfaces. However, by changing the adsorption order (oxygen first of alkalis), the alkali-O bond was formed. We argue that this is a consequence of the modification of the surface reactivity through the adsorption of an electronegative species.

Present results open new effective pathways for alkali oxidation and should provide a decisive advancement of the understanding of the heterogeneous catalysis at metal surfaces.

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PAPER X

CO-promoted formation of the alkali-oxygen bond on Ni(111)

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CO-promoted formation of the alkali-oxygen bond on Ni(111)

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High-resolution electron energy loss spectroscopy was used to study the coadsorption of alkalis (Na, K) and oxygen on clean and CO-modified Ni(111) surfaces. We unambiguosly show that on an alkali-precovered surface the alkali-O bond was not formed upon O_2 exposure. On the contrary, the alkali-O bond was readily observed by exposing to O_2 the Ni(111) surface precovered with an alkali+CO phase. This enhanced oxidation rate of alkalis in the presence of CO molecules was ascribed to the short-range CO-induced modification of the electronic charge of alkali adatoms.

Introduction

Alkali coadsorption with oxygen has attracted a remarkable attention[1-5] as the oxidation rate of metal and semiconductor surfaces is notably affected by the presence of alkali adatoms. Moreover, such studies have important applications in the chemical industry. As a matter of fact, alkali oxides are widely used for obtaining low work-function surfaces and as promoters in Fischer-Tropsch, Haber-Bosch, and ethylene epoxidation[6,7] processes.

Several spectroscopic studies have been performed to investigate the interaction of oxygen codsorbed with alkalis on solid surfaces[8-15]. Most of these works have been carried out on nickel substrates due to the great interest attracted by the oxidation of Ni substrates[5,14-17] (material processing, surface magnetism, surface chemical reactions[18,19]). On clean Ni(111) surfaces the adsorption of both oxygen and alkalis has been widely investigated and the vibrational and structural properties have been well characterized. In particular, it is worthwhile mentioning that at room temperature oxygen molecules adsorb dissociatively forming p(2x2) and (√3x√3)R30° over-structures[15,20,21].

Nonetheless, many aspects of the catalytical oxidation processes are not at all clarified. Unexpectedly, no direct oxygen-alkali bond was formed at low alkali precoverages[5,22]. Furthermore, measurements taken on very clean alkali layers revealed that the presence of alkali atoms causes a softening of the O-Ni bond in the coadsorbed phase[16], in excellent agreement with calculations performed within the framework of the electrostatic model[23]. This finding was ascribed to the alkali-induced population of the O $2p_z$ antibonding orbitals[16,23]. On the other hand, in the presence of a significant contamination by CO molecules such bond weakening was not observed in a similar investigation[24].

Very recently, a local charge transfer from alkalis to carbon monoxide molecules has been demonstrated to occur on Ni(111)[15], leading to the ionization of alkali adatoms. It is worth studying in details how oxygen adsorb on a surface whose properties are modified by a preadsorbed alkali+CO phase. This problem is quite intriguing as tuning the surface reactivity by modifying the charge density profile trough doping the substrate with electronegative species is one of the foremost aims of surface science. In particular, studying the coadsorption of CO and O in the presence of alkalis allows to follow step-by-step the reaction pathways for the formation of carbonates[26] or carbon dioxide[27].

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on alkali (Na, K) coadsorption with oxygen on clean and CO-modified Ni(111) surfaces. We show that in the presence of CO molecules the oxidation of alkali atoms occurs even in the limit of very low precoverages. We argue that this finding is due to the change of the electronic structure of alkalis induced by CO molecules. In other words, while neutral alkali atoms do not bond with oxygen, polarized or partially ionized alkalis become highly reactive towards oxygen.

Experimental

HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Sodium and potassiun were deposited onto the substrate from well-outgassed commercial getter sources. Oxygen and carbon monoxide molecules were dosed through a leak valve. Alkali and O coverage (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate) was estimated from the exposure time taking as reference the coverage of well-known LEED structures, that is, (√3x√3)R30°-Na (0.33 ML), p(2x2)-K (0.25 ML) and p(2x2)-O (0.25 ML). It is worth mentioning that at the saturation of the first Na layer (0.44 ML), the 3/2x3/2-Na structure was also observed in LEED experiments. A constant sticking coefficient was assumed to obtain other desired coverage. Similar results were achieved by using AES. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. The energy resolution of the spectrometer ranged from 2 to 3 meV. All measurements and exposures were carried out at room temperature. A particular care was dedicated to avoid any contamination of the alkali adlayer.

Results and Discussion

Figure 1 shows HREEL spectra acquired for 0.10 ML of atomic oxygen adsorbed onto a Ni(111) surface precovered with 0.04 ML of Na (spectrum b) and 0.04 ML of K (spectrum c). Loss spectra show several features assigned to the alkali-substrate vibrations (Na-Ni and K-Ni at 23 and 16 meV, respectively[28]) and the O-Ni stretching (65 meV). Interestingly, the O-Ni loss energy is red-shifted by 5 meV with respect to its value recorded for oxygen/Ni(111)[24] (spectrum a). No evidences of alkali-O bonds are present, as indicated by the absence of alkali-O stretching features in the vibrational spectra (such vibrations are expected at 36 meV for Na-O and 27 meV for K-O, respectively[25]).

In order to investigate the effects induced by CO adsorption on the surface chemical bonds of Na and O, oxygen was coadsorbed with Na onto a CO-modified Ni(111) surface. The substrate was firstly predosed with 1.0 L (1 L=$1.33\cdot10^{-6}$ mbar·s) of CO (Figure 2) and in these conditions the C-O vibration was recorded at 226 meV. The coadsorption of Na atoms (third spectrum of Figure 2) caused a softening of the C-O stretching energy down to 197 meV. An oxygen exposure of 8.0 L caused remarkable changes in the vibrational spectrum, thus suggesting the occurrence of striking modifications of surface chemical bonds. The appeareance in the loss spectrum of a feature at 35-36 meV indicated the formation of the Na-O bond. In the meantime, the energy of the C-O stretching shifted from 197 to 209 meV. Further O_2 exposures cause a shift of the C-O peak up to 214 meV.

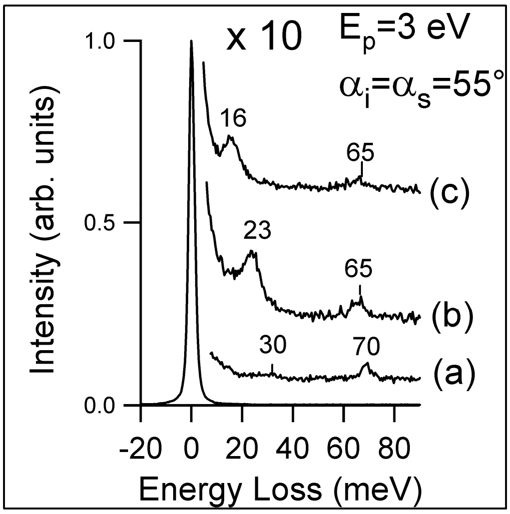

Figure 1: HREEL spectra for: (a) p(2x2)-O/Ni(111); (b) 0.04 ML Na coadsorbed with 0.10 ML of atomic O; (c) 0.04 ML K coadsorbed with 0.10 ML of atomic O. All spectra were normalized to the intensity of the elastic peak and multiplied by the same factor.

It is well known that the C-O intramolecular bond is softened in the alkali+CO coadsorbed phase[29-33], as a consequence of the alkali-induced occupation of the 2 π^* antibonding orbitals of CO[34,35]. Increasing the number of oxygen atoms on the surface, the number of Na atoms directly interacting with CO decreases and the charge for each CO molecule which is available for being donated by alkali atoms is reduced. The presence of a shoulder in the last spectrum of Figure 2 (O_2 exposure of 14.0 L) that remained at 199 meV indicates that not all CO molecules interact with oxygen. Hence, two different environments exist for CO molecules. Most of them interacts with both O and Na atoms, while the remaining molecules are influenced only by the presence of sodium. The Na-Ni vibration broadened upon O adsorption and shifted from 20 down to 18 meV.

For a CO-modified Ni(111) surface (by predosing the substrate with the same CO exposure of 1.0 L), the C-O stretching energy as a function of O_2 exposure was found to follow a power law (figure 3) depending on the initial Na precoverage:

$$\nu_{C\text{-}0}=E_0+A^*(O_2\ \exp)^B$$

where E_0, A, and B are coefficients determined by the fit procedure.

As expected, the energy of the C-O loss peak is strictly related to the Na/CO ratio. Exposing to O_2 a 0.20 ML Na/CO/Ni(111) surface, the formation of carbonates CO_3^{2-} occurs, as inferred by the appearance of loss peaks at 92 and 108 meV[26] (not shown).

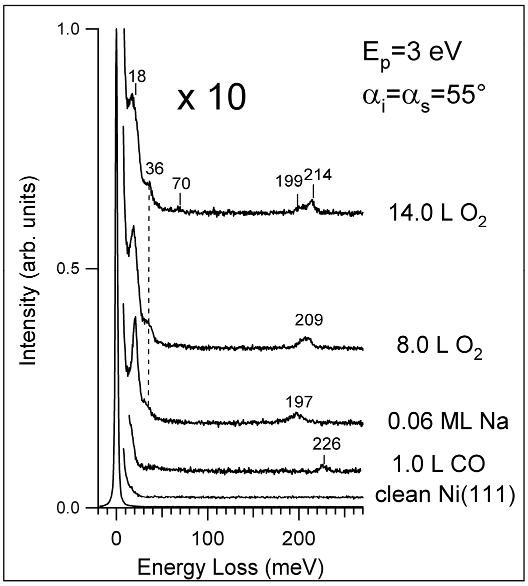

Figure 2: HREEL spectra for Na coadsorption with O onto a Ni(111) surface modified by the adsorption of 1.0 L of CO. In this case the Na-O bond was formed, as revealed by the appearance of the feature at 36 meV. In a CO-modified surface, the O-Ni stretching was revealed at 70 meV.

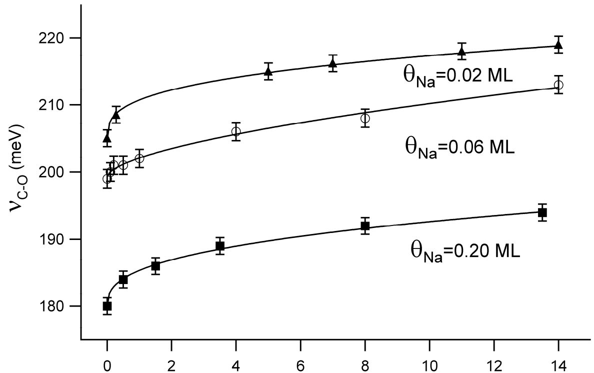

Figure 3: Behavior of the C-O stretching energy as a function of the O_2 exposure for different Na precoverages.

Similar results were obtained by changing Na with K (Figure 4). In the coadsorption of K and O onto a CO-modified surface, the O-Ni bond was not softened (O-Ni stretching at 70 meV, as in spectrum a of Figure 1). Accordingly, it could be suggested that the presence of CO molecules inhibits the population of the O 2 p_z antibonding orbitals. The intensity of the O-K vibration at 27 meV gradually increased as a function of the O_2 exposure. The C-O stretching blue-shifted from 201 to 209 meV.

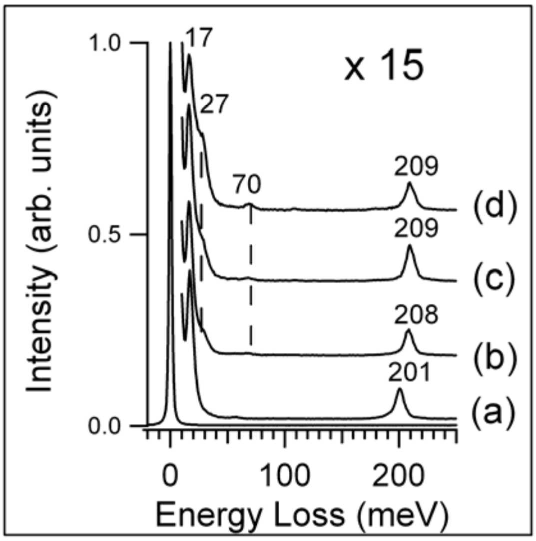

Figure 4: HREEL spectra for (a) 0.03 ML K adsorbed onto a Ni(111) modified by the exposure of 1.0 L of CO. Successively, the surface was exposed to oxygen: (b) 0.2 L; (c) 0.5 L; (d) 2.0 L.

Thus, alkali oxidation could be readily achieved by dosing oxygen on alkali-precovered Ni(111) surfaces in the presence of CO (Figures 2 and 4). This is a direct consequence of the CO-induced change of the electronic charge of alkali adatoms. Such results indicate that oxygen interacts strongly with charged alkali species and less with neutral adatoms. Furthermore, it should be noticed that also the CO-induced blocking of the population of O 2 p_z antibonding orbitals in the alkali+O coadsorbed phase may play a key role in the microscopical mechanisms leading to alkali oxidation.

An alternative explanation about the enhanced reactivity of charged alkalis towards oxygen could involve the possible hybridization between the electronic states of alkali and O atoms coadsorbed on Ni(111). Such hybridization leads to the formation of an alkali-O bond. Unfortunately, to date no experimental and theoretical studies have been performed on the dispersion and energy of electronic states of Na atoms coadsorbed with CO. Hence, present results claim for dedicated calculations. A large hybridization, and very likely an efficient charge transfer, is possible only whenever the distance between the reactants is short-ranged[36].

In order to understand the CO-induced enhancement of the alkali oxidation rate, we studied also the mutual Na-CO interaction by exposing 0.05 ML Na/Ni(111) to CO at room temperature. The Na-Ni stretching frequency shifted from 22 meV down to 13 meV (Figure 5) and, moreover, the lineshape of such peak became narrower. The C-O stretching energy, initially at 194 meV (0.07 L of CO), shifted upward to 218 meV (for higher CO exposure). As a comparison, the C-O stretching frequency is 235 meV (0.5 ML of CO) for CO on Ni(111)[25]. Moreover, CO exposure was found to cause a remarkable increase of the intensity of the Na-Ni peak. Such finding is a clear fingerprint of the occurrence of a local charge transfer between coadsorbed species, i.e. a CO-induced partially ionization of alkali adatoms. In fact, the intensity of vibrational modes is expected to be higher for ionized species rather than for strongly polarized but essentially neutral adatoms.

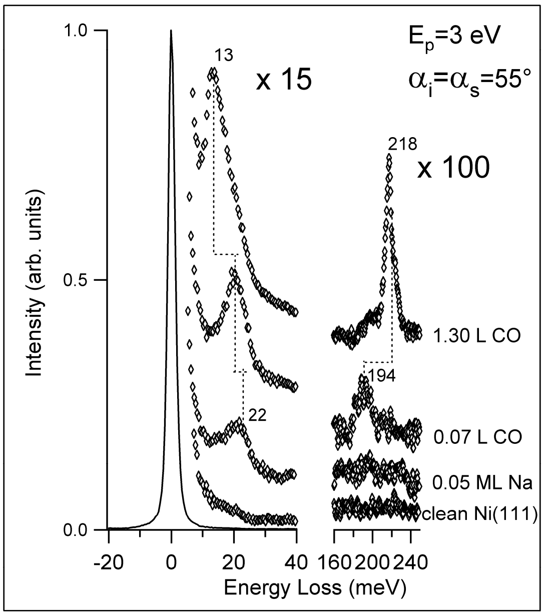

Figure 5: HREEL spectra for 0.05 ML Na/Ni(111) at 400 K for different CO exposures at room temperature.

Likewise, the K-Ni stretching energy was found to shift from 15 down to 11 meV (figure 6) upon CO exposure.

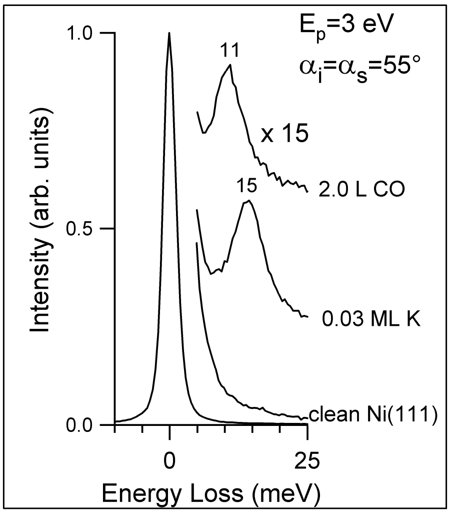

Figure 6: HREEL spectra for 0.03 ML K/Ni(111) deposited at 400 K. The K adlayer was successively exposed to CO at room temperature.

With the aim of achieving more details on the microscopic mechanisms determining the CO-promoted charging of the alkali adatoms, we reported in Fig. 7 the behavior of the dynamical charge of Na as a function of CO exposure. The dynamical dipole moment μ of Na could be evaluated from the measured intensity and energy of the Na-Ni loss peak using the dipole scattering theory[37]. The effective charge Q can be calculated from $\mu = \left(\eta / 2M_r\omega\right)^{1/2}$, with M_r being the reduced mass. Here a rigid Ni substrate is assumed, i.e. M_r=M_{Na}, and the following experimental parameters are used: the incidence angle (55°), the half-angle of acceptance (1.0°), and the primary energy of 3 eV. As the amount of CO deposited on the surface increased, the dynamical charge Q of Na decreased almost linearly, giving hints on the charge status of alkali atoms.

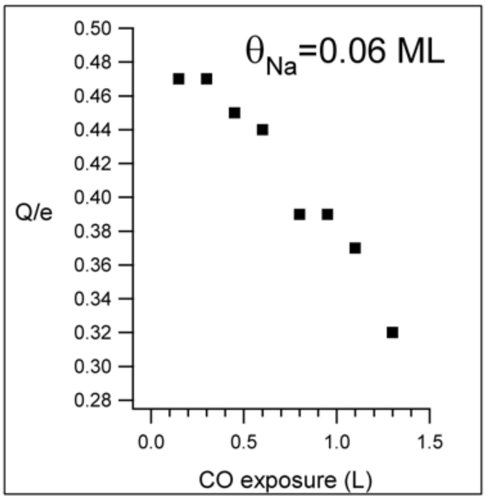

Figure 7: The dynamic dipole charge Q/e (e is the electron charge) of Na as a function of CO exposure.

Measurements were also performed (in the absence of CO) by reversing the order of the adsorption, i.e. oxygen adsorbed before of alkalis. In these conditions, alkali oxidation is readily observed, as suggested by the appearance of the O-K (28 meV) and O-Na (34 meV) vibrational modes in HREEL spectra (Figure 8). The direct bond of atomic oxygen with the substrate modifies the electronic properties of the system and it should be responsible of the observed behaviour. Very likely, the charge status of O atoms plays a decisive role.

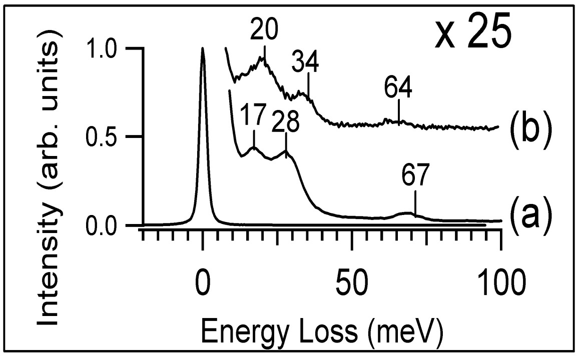

Figure 8. HREEL spectrum acquired for 0.10 ML K deposited onto a 0.10 ML O-modified Ni(111) surface (spectrum a). Reversing the order of adsorption, the alkali-O bond is formed. Similar results were obtained by substituting K with Na (spectrum b).

Conclusions

Our results elucidate the general mechanisms for the formation of an alkali-oxygen bond on Ni(111) surfaces. For alkali-precovered surfaces, a giant alkali oxidation is achieved only upon CO adsorption. This is ascribed to the short-range interaction between alkalis and CO, which activate a charge transfer between coadsorbates leading to the ionization of the alkali adatoms. Oxygen interacts with charged alkali species leading to the formation of a direct chemical bond. On the contrary, no alkali oxidation occurs in the absence of CO. However, upon changing the adsorption order (oxygen first of alkalis), the alkali-O bond was formed. We argue that this is a consequence of the modification of the surface reactivity through the adsorption of an electronegative specie.

Present results open new effective pathways for alkali oxidation and should provide a decisive advancement in understanding the promotional role of alkalis in heterogeneous catalysis at metal surfaces.

Notes and references

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PAPER XI

Electronic properties of (3/2x3/2)-Na/Cu(111)

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Electronic properties of (3/2 × 3/2)-Na/Cu(1 1 1)

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Abstract

High-resolution electron energy loss spectroscopy was used to study the electronic properties of (3/2 × 3/2)-Na/Cu(1 1 1) at room temperature. Loss spectra showed two-well distinct losses at 114 and 180 meV assigned to not dispersive charge density waves. Mechanisms to explain their existence are proposed. Moreover, the expected 2D plasmon of the Na quantum well state was not observed. The strong influence of the underlying Cu substrate may be responsible for the absence of such mode.

Keywords: Electron energy loss spectroscopy (EELS); Alkali metals

1. Introduction

Electronic confinement may occur in clean surfaces and metallic adlayers deposited on selected substrates. It occurs when electronic states are localised between the vacuum barrier at one side and a local band gap at the other side. This phenomenon is very interesting from a fundamental point of view since it influences a variety of physical properties such as diffusion and adsorption [1–5].

The Cu(1 1 1) surface has a partially occupied band of Shockley surface states lying in an electron pocket of the projected bulk band structure centred at the $\bar{\Gamma}$ point of the surface Brillouin zone [6]. Na atoms adsorbed on Cu(1 1 1) also give rise to a confined quantum well state (QWS) derived from $3p_z$ orbitals with a parabolic dispersion running along the wide energy gap of the projected bulk band structure. This state was found at 0.1 eV below the Fermi energy at $\bar{\Gamma}$ [7–9]. Electrons in Na-induced QWS, as well as in Shockley surface states, can be regarded as a quasi-2D nearly free-electron gas [6,10].

The properties of the Na/Cu(1 1 1) have been widely studied by different experimental techniques and theoretical methods. However, due to the complexity of this system, some open questions on elementary excitations in the Na adlayers are still to be clarified. In this work the electronic excitations of the (3/2 × 3/2)-Na/Cu(1 1 1) surface at room temperature were studied. This phase occurs for a coverage of 0.44 ML (saturation coverage) [11,12] and is characterised by Na–Na distances which are close to the first neighbours distances of bulk sodium. In principle this surface phase offers the possibility to investigate electronic excitations in a quasi-two-dimensional free-electron gas because the interaction with the Cu substrate should be negligible. For the present aim high resolution electron energy loss spectroscopy (HREELS) was used, as it is a very suitable technique to study collective electronic excitations of valence electrons in a metallic overlayer.

Early infrared reflection absorption spectroscopy (IRAS) measurements carried out on the (3/2 × 3/2)-Na/Cu(1 1 1) surface at 92 K [13] found a resonance at 105 meV which was assigned to a pinned surface charge density wave (CDW). This excitation is a peculiarity for the Cu(1 1 1) surface and it was also revealed for the K/Cu(1 1 1) surface, but not for Na/Cu(100). However, angle resolved photoemission spectroscopy did not reveal any gap opening in the Fermi surface [8,14]. On the other hand, the presence of this energy gap is thought to be a necessary condition for the existence of CDWs.

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Our loss spectra showed two peaks at 114 and 180 meV which did not exhibit any energy dispersion as a function of the scattering angle. These experimental results led us to interpret the loss peaks as gapless and not dispersive CDWs rather than plasmons in the Na metallic layer. Moreover, we found that the Na layer strongly reacts with residual water molecules forming a Na–OH complex. In agreement with previous results obtained in similar systems, we suggest that water contamination is responsible of the appearance of CDWs in this system.

2. Experimental

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa equipped with standard facilities for surface characterization. The HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The angular acceptance (α) of the electron analyser was $\pm 1^\circ$. The sample was a single crystal of Cu(1 1 1) with a purity of 99.9999% oriented along the $\bar{\Gamma} - \bar{M}$ direction. The Cu(1 1 1) surface was cleaned by means of Ar^+ sputtering at 1 keV. Surface cleanliness and order were checked by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) carried out by using a hemispherical analyzer (Phoibos 100, SPECS). The Cu(1 1 1) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium was evaporated from a well-outgassed commercial getter source (SAES getters, Italy). The pressure during evaporation stayed in the low 10^{-8} Pa. The occurrence of the (3/2 × 3/2) LEED pattern was used as the calibration point of $\theta_{\mathrm{Na}} = 0.44$ ML and a constant sticking coefficient was assumed to obtain other desired Na coverages. The angle of incidence was 55° with respect to the surface normal. A primary electron beam energy of 20 eV was used with energy resolution of 8 meV in order to increase the signal-to-noise ratio for off-specular spectra. All measurements were made at room temperature.

3. Results and discussion

The HREEL spectrum of the clean Cu(1 1 1) surface showed no peak, but two well distinct losses at 114 and 180 meV appeared in the spectrum (Fig. 1) after the deposition of $\theta_{\mathrm{Na}} = 0.44$ ML (completion of the first layer). No other feature up to 1 eV was revealed. Interestingly, the two losses gradually disappeared for increasing Na coverages. We are aware of the high reactivity of alkali metals towards residual gases in the UHV chamber and, thus, on purpose, the sample surface was exposed to some of the most common contaminants such as CO, CO_2, H_2O, O_2. The intensity, lineshape, and loss energy of the observed features were essentially unchanged upon gas exposure. Moreover, we carried out selected measurements at different Na submonolayers because the peak at 180 meV could be assigned to the intramolecular vibration of CO. Its energy is known to move from 255 meV for adsorption on clean Cu(1 1 1) surfaces to lower energies in presence of coadsorbed alkali metals [15]. Although the loss energy of the CO intramolecular stretching energy is quite sensible to the initial alkali precoverage [15], no shift of the 180 meV peak was observed thus excluding that assignment.

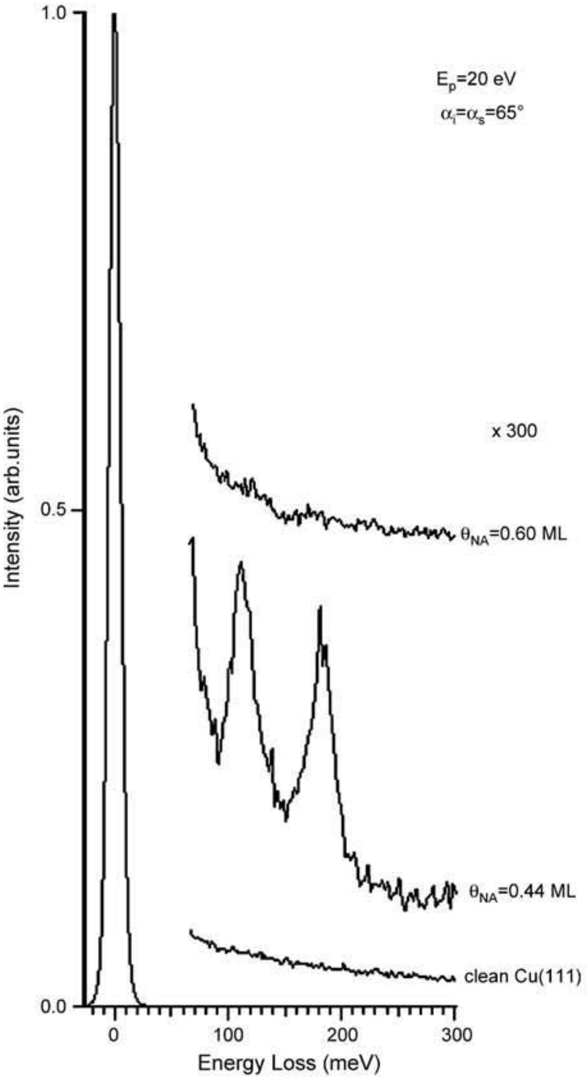

Fig. 1. Electron energy loss spectra of Na/Cu(1 1 1) as a function of the Na coverage.

On the basis of these results, the final assignment of the two loss features of Fig. 1 is carried out excluding the presence of contaminants. In principle, both losses could be interpreted as single-particle transitions involving Na-induced QWS but their widths were so narrow that are not compatible with that interpretation. On the other hand, both photoemission [8,14] and scanning tunnelling spectroscopy [9,16,17] experiments showed broad features with the full width at half maximum (FWHM) much larger than that of the present loss features. Moreover, we are not able to interpret the observed loss peaks at 114 and 180 meV within the electronic band structure of Na/Cu(1 1 1) surface [18].

Angular resolved measurements put also in evidence that the observed peaks at 114 and 180 meV do not follow the behaviour expected for a dipole transition cross-section.

The effect of temperature on the energy loss spectra is shown in Fig. 2. They further support the above conclusions. Annealing the sample at 330 K caused a marked increase of the intensity of

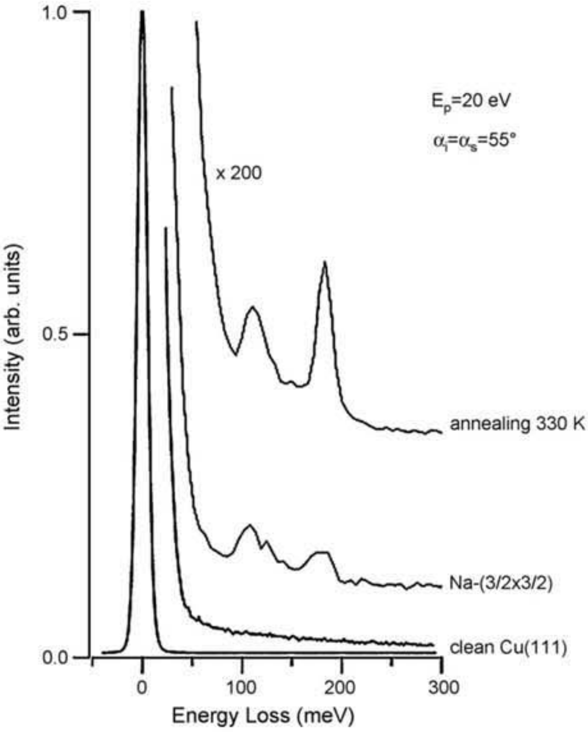

Fig. 2. Electron energy loss spectra for clean Cu(1 1 1) and for (3/2 × 3/2)-Na/Cu(1 1 1) at 300 K and after a flash annealing at 330 K.

the two losses. Interestingly, their widths exhibited a simultaneous narrowing, suggesting at first an ordering of the Na adlayer, but a further temperature increase produced a rapid decrease of the intensity of both peaks because of Na desorption [19]. As single adatom contaminants cannot explain the above results, the suggestion that the losses of Figs. 1 and 2 may be Na-induced becomes appealing and plausible.

The two losses of Figs. 1 and 2 could be interpreted as collective excitations (plasmons) localized at the interface between the Na adlayer and the substrate, as suggested by Tosatti [20]. For the sake of truth, we remind that the excitation of a two-dimensional collective mode with a square root-like surface plasmon dispersion was found in $(\sqrt{3} \times \sqrt{3})$-Ag/Si(1 1 1)$(7 \times 7)$ using electron backscattering measurements [21]. The Ag overlayer of the semiconducting substrate was assumed to form a nearly free electron-like band, which was well separated from the silicon bulk band. Although 2D plasmons could be similarly predicted for Na QWS formed on Cu(1 1 1), nevertheless the behaviour of the angular dispersion of such surface excitations (Fig. 3) induces us to exclude the occurrence of a 2D plasmon. In fact, the loss energy of each peak did not change as a function of the scattering angle, so that their plasma autofrequency would not disperse versus the parallel momentum transfer $\boldsymbol{q}_{||}$. This behaviour is quite different from the square root dispersion expected for a two-dimensional collective mode [21]. Furthermore, such collective excitation should be characterized by a rapid increase of the line width as a function of $\boldsymbol{q}_{||}$, while in the present case the FWHM of each loss did not change. As last but not least remark, the cross-section increased as a function of the collection angle suggesting the occurrence of an impact mechanism.

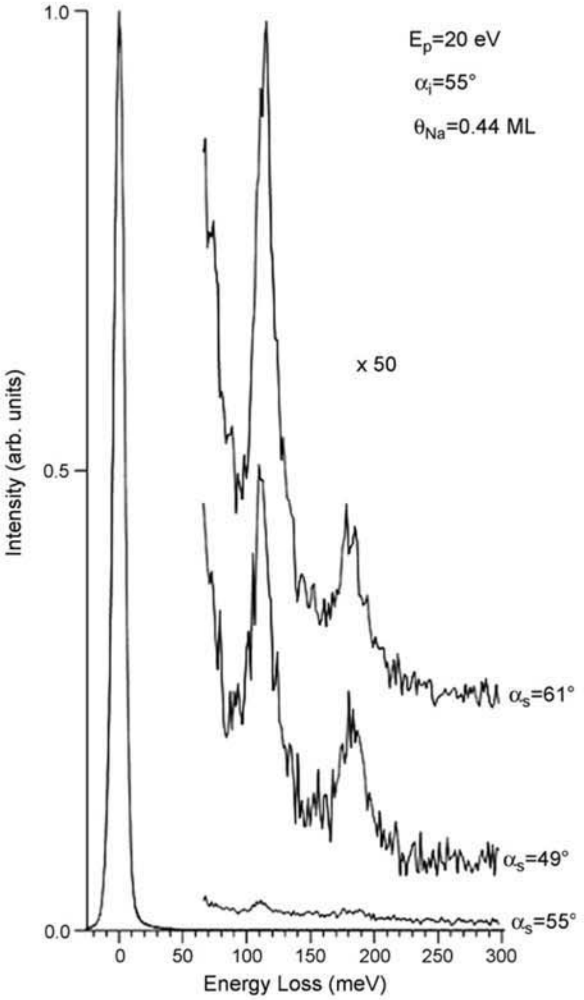

Fig. 3. Electron energy loss spectra of Cu(1 1 1) at different scattering angles α_s. The incident beam energy E_p is held constant at 20 eV and all spectra were recorded at an incident angle of $\alpha_i = 55°$ with respect to the sample normal.

It would be very interesting to understand why a Na QWS does not support the excitation of a 2D plasmon. We tentatively suggest that the metallic substrate might dump and screen the electric field associated to the 2D plasmon more efficiently than a semiconductor surface. On the other hand, Shockley surface states of the clean Cu(1 1 1) surface do not support two-dimensional plasmons too [22]. Probably, the tail of the wave function of Na QWs extends into the substrate overlapping Cu bulk states, as reported in Ag/Ge(1 1 1) [23]. Also in our case a strong hybridization between substrate and surface states of the film is present, as evidenced by the character of Na-induced QWS which is Na-like as well as Cu-like [20]. In our opinion, this hybridization might be responsible for the dumping or screening of the two-dimensional plasmonic modes.

Similarly to Na/Cu(1 1 1) IRAS measurements [13] which showed a charge density wave resonance at about 105 meV, we tentatively interpret the loss feature at 114 meV as a CDW mode. Furthermore, the FWHM of that CDW resonance in ref. [13] is comparable with the widths of the losses at 114 and 180 meV of our experiments. CDWs characterised by impact behaviour and by no dispersion as a function of the parallel transfer momentum have been observed in the Sn/Ge(1 1 1) system [24]. However, the existence of an energy dispersing CDW was reported for another phase of the same system.

Finally, although CDWs are more common at low temperatures, we remind that there are experimental evidences for their existence also at room temperature [25–29].

As far as the physical mechanism at the base of the CDW, the spatial modulation of both the electron density and the lattice of ion cores [30] might be driven in the Na/Cu(1 1 1) system by a strong electron–phonon (e-ph) coupling. The increased e–ph coupling strength in Na/Cu(1 1 1), which is significantly larger than the bulk coupling constants of Na and Cu, is very likely due to the low dimensionality of Na-induced QWS [31]. In fact, the e–ph coupling in the overlayer and in the interface region was found to be the main contribution to the lifetime broadening of photoemission peaks [32,33].

CDW instabilities driven by partly filled surface states or QWS have been advocated in various systems [20]. In fact, whenever there are partly filled electronic confined states on a solid surface, the system seems to be unstable and the surface structure develops a tendency to rearrange. Overhauser [34] demonstrated that a 2D electron gas will have a greater tendency to form a CDW than will a 3D electron gas.

CDWs may be instable and give rise to a rearrangement of the surface. As a matter of fact, the adsorption site for Na on Cu(1 1 1) has not been reported yet. A photoelectron diffraction investigation of the Na $(3/2 \times 3/2)$/Cu(1 1 1) performed by our group led to inconclusive results, probably due to a complicated surface reconstruction. This instability observed in various systems was ascribed to the presence of partly filled surface states or QWS [20]. Recently, it has been found that a surface CDW may also be due to the Fermi-surface nesting of a nearly-free-electron-like sp surface resonance band [30]. Indeed, charge density waves have been claimed for Li on Cu(1 0 0) [35] and Ni(1 0 0) [35,36] and for Na on Ag(1 0 0) [35].

The existence of the CDW in the framework of a band picture would imply the formation of a gap, with the gap pinned at the Fermi energy; however, ARPES data for Na/Cu(1 1 1) [8,14] excluded this situation. Very recently, Barnett et al. [37] have demonstrated the coexistence of gapless excitations and CDWs in the 2H transition metal dichalcogenides. Thus, a CDW without a gap opening on the Fermi surface might occur in this system too.

The loss peak at 180 meV may have an interpretation similar to that at 114 meV. This result is not surprising and as a matter of fact, the coexistence of two CDWs was already found in NbS_3 [38].

Finally, we would briefly discuss an alternative effect which may be at the origin of the existence of the CDWs in the Na/Cu(1 1 1) system. A series of loss spectra acquired after the exposition of the $(3/2 \times 3/2)$-Na/Cu(1 1 1) surface to water vapour gave clear evidence that the two losses at 114 and 180 meV were not affected by water adsorption as discussed above. However, a small peak at 32 meV arose for an exposure of only 0.01 L of H_2O ($1\,L = 1 \times 10^{-6}$ mbar s). The same peak moved to higher loss energies for increasing water adsorption and reached 37 meV for an exposure of 0.09 L of water vapour becoming very intense (about 2% of the elastic peak). This loss feature was attributed to the vibration of Na against OH in agreement with literature data [39,40]. In our opinion, even small water contamination of this system could have dramatic effects on the surface structure and should be taken into account in spectroscopy measurements. We can not at all exclude that this small amount of water contamination may be at the base of the CDWs of the present system, as found in similar systems [41].

In conclusion, although we are not able to provide a direct proof of the existence of CDWs by energy loss measurements, all experimental evidences agree with such assignment. More theoretical and experimental studies are certainly needed for a better characterization of the electronic properties of this system. Particularly, it would be interesting to know why two-dimensional plasmons and CDWs are driven by partly filled QWS or surface states in the presence of an underlying metal substrate. While HREEL experiments on electrons confined on metallic and semiconductor substrates are currently underway in our laboratory, these present findings provide the grounds for more accurate experimental studies taking into account the unavoidable water contamination.

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PAPER XII

Electronic properties of self-assembled quantum dots of sodium on Cu (111) and their interaction with water

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Electronic properties of self-assembled quantum dots of sodium on Cu(1 1 1) and their interaction with water

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Abstract

The electronic properties of thin films of Na on Cu(1 1 1) and their interaction with water have been investigated at room temperature by high resolution electron energy loss spectroscopy. The first Na layer is characterized by two features tentatively assigned to charge density waves. The second Na layer grows as small islands. The loss spectrum of this layer shows a feature at 3.0 eV identified as a Mie resonance. Increasing alkali coverage, Na islands form a continuous film, as indicated by the appearance of a Na surface plasmon and by the disappearance of the Mie resonance. Water vapour strongly interacts with Na layers as shown by the OH–Na vibration whose frequency shifts from 36 meV to 53 meV as a function of alkali coverage.

Keywords: Electron energy loss spectroscopy (EELS); Alkali metals

1. Introduction

Electronic excitations in thin alkali metal films have attracted much attention from both theoreticians and experimentalists [1]. Gaspar et al. [2] performed electron energy loss measurements and dynamical response calculations for Na and K on Al(1 1 1). They found that the alkali-metal undergoes a transition from a quasi two-dimensional to three-dimensional free electron gas as a function of coverage. In recent years an increasing attention has been devoted to the investigation of Na on noble metal substrates with particular emphasis towards the (1 1 1) surface.

The (1 1 1) surface of Cu exhibits a large confined gap within the projected bulk band structure, centred at the $\bar{\Gamma}$ point of the surface Brillouin zone [3]. Shockley surface states exist within the energy gap. It is well known that surface states have strong influence on a variety of physical phenomena occurring at surface such as adsorption and diffusion [4,5]. Electronic states, called quantum well states (QWS), appear in the energy gap when Na is adsorbed on Cu(1 1 1) [3]. Electrons occupying these states are confined by the work function on one side and by the energy band gap on the other side. Na-induced QWS were measured by photoemission spectroscopy (PES) [6,7] and by scanning tunnelling spectroscopy (STS) [8–10].

Scanning tunnelling microscopy measurements show that after the completion of the first layer (the first monolayer saturates for $\theta_{\mathrm{Na}} = 0.44$ ML yielding a $(3/2 \times 3/2)$ diffraction pattern[1] [11]), additional Na deposition at room temperature causes the growth of self-assembled small islands called quantum dots (QDs). Electronic states of Na QDs have been measured by STS [12] and calculated by density functional theory (DFT) [13]. The reactivity of Na QDs towards CO was studied by first principle calculations [14]. The chemisorption properties of supported thin metal films exhibiting electron confinement is a very attractive topic for scientific research as demonstrated by recent studies [15–17].

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[1] Na coverage, θ_{Na}, is given as the ratio between the number of adsorbed atoms and the number of atoms of the Cu(1 1 1) surface.

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In this paper we present high resolution electron energy loss (HREEL) measurements of Na films prepared at room temperature on Cu(1 1 1) and ranging from 0.44 ML (first physical layer) up to 1.20 ML. To our best knowledge, this is the first experimental investigation of collective excitations in supported self-assembled quantum dots of sodium on Cu (1 1 1). Loss spectra were acquired in a wide energy loss range (up to 6 eV) with the aim to study both low-energy and collective excitations in Na adlayers. Furthermore, we probed the reactivity of Na layers for low exposures of water.

2. Experimental

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Cu(1 1 1) with a purity of 99.9999%. The Cu(1 1 1) surface was cleaned with standard procedures. Surface cleanliness and order were controlled by Auger electron spectroscopy and low energy electron diffraction (LEED). The Cu(1 1 1) surface showed an excellent LEED pattern characterized by sharp spots and a very low background. Sodium was evaporated from a well outgassed commercial getter source. The occurrence of the $(3/2 \times 3/2)$ LEED pattern was used as the calibration point for $\theta_{\mathrm{Na}} = 0.44$ ML. Loss spectra were taken in specular geometry with an incident angle of 55° with respect to the surface normal. We used a primary electron beam energy of 20 eV and an energy resolution between 8 and 12 meV. All measurements were made at room temperature.

3. Results and discussion

Fig. 1 shows the HREEL spectra of clean Cu(1 1 1) surface and covered with $\theta_{\mathrm{Na}} = 0.44$ ML deposited at room temperature. The spectrum of the clean Cu(1 1 1) surface does not show any peak in the low-energy loss region, but shows a pronounced jump at about 2.1 eV, which is the onset of single-particle excitations of valence electrons. Interestingly, Na deposition causes the rising of two features at 114 meV and at 180 meV and, moreover, a slight intensity increase at about 3.0 eV. Since alkali layers are known to react rapidly with any residual gas present in the chamber, we exposed the surface to different gases (CO, H_2O, etc.) to exclude any influence of contaminants on our loss spectra. We found that these two peaks were not influenced by gas exposures.

In previous experimental studies on $(3/2 \times 3/2)$-Na/Cu(1 1 1) surface, the same Na-induced state was observed at different energies: −97 meV [7], −110 meV [6] and −127 meV [8] with respect to Fermi energy and assigned to QWS. Calculations performed by Butti et al. [18] for the $(3/2 \times 3/2)$-Na phase found QWS at −173 meV with respect to Fermi energy. We are not able to interpret the observed loss peaks at 114 meV and 180 meV within the electronic band structure of Na/Cu(1 1 1) surface. Really, the loss peak at 114 meV could be analogous to the result obtained for Na/Cu(1 1 1) by Infrared Reflection Absorption Spectroscopy [19]. These measurements show an antiabsorption resonance at 105 meV with a very narrow line-width, as in our case. This feature was assigned to a Charge Density Wave (CDW) of the alkali metallic states. The interpretation of IRAS measurements was questioned by Tosatti [20] who suggested that the excitation at 105 meV could be due to a 2D plasmon mode.

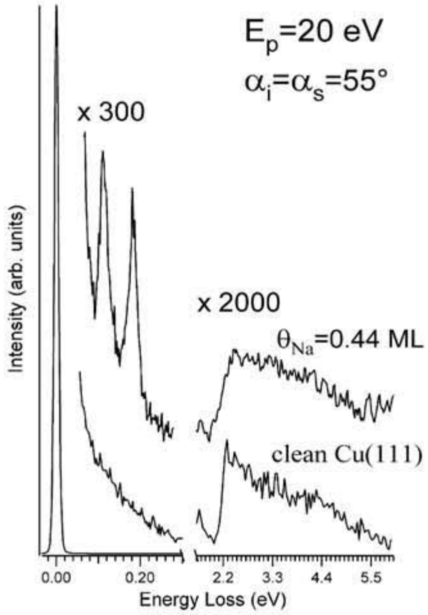

Fig. 1. HREEL spectra of the Cu(1 1 1) clean surface and for $\theta_{\mathrm{Na}} = 0.44$ ML.

To better characterise the loss features at 114 meV and 180 meV, we performed angular resolved measurements which will be published elsewhere [21]. Both features exhibit a strong intensity increase for off-specular spectra. This behaviour indicates the occurrence of impact, rather than dipole scattering which is instead expected for 2D plasmons [22]. Furthermore, the loss energy and the Full Width at Half Maximum (FWHM) of both features remain almost constant as a function of the collection angle ruling out that such losses could be assigned to two-dimensional plasmons. In fact, they are characterised [22] by a square root-like dispersion as a function of the parallel transfer momentum $\boldsymbol{q}_{\parallel}$ and, moreover, by an increasing FWHM as a function of $\boldsymbol{q}_{\parallel}$.

All these considerations are compatible with the assignment of a CDW at 114 meV. As regards the feature at 180 meV, the interpretation is still unclear although it may be another CDW. The strong electron–phonon (e–ph) coupling existing in this system may be the reason for the occurrence of CDWs, i.e. a standing spatial modulation of both the conduction-electron density and the lattice of ion cores [23]. Electron standing waves scattered by defects were already imaged by Kliewer and Berndt [24] in this

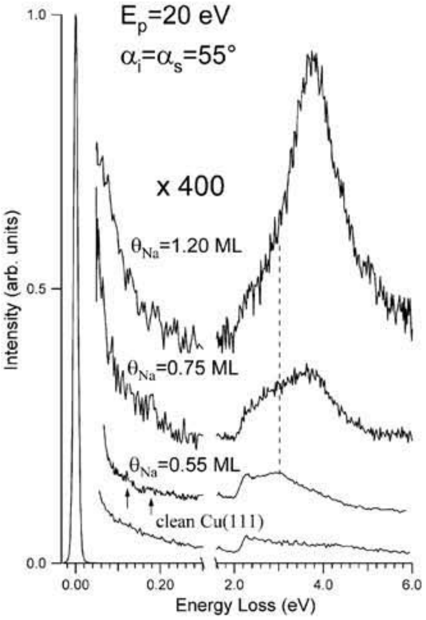

Fig. 2. HREELS spectra of the Cu(1 1 1) surface and for $\theta_{Na} = 0.55$, 0.75 and 1.20 ML.

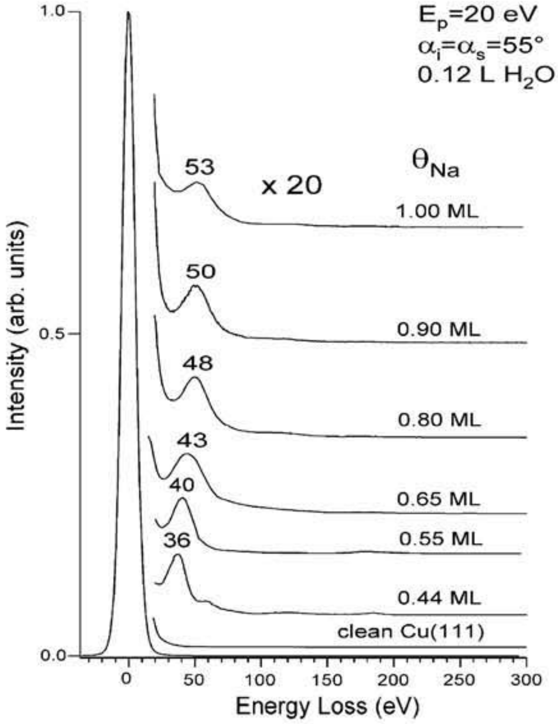

Fig. 3. HREEL spectra of 0.12 L of water vapour adsorbed at room temperature on different amounts of Na/Cu(1 1 1) surface.

system. Moreover, the coexistence of two CDWs was found in NbS_3 [25] too.

Fig. 2 shows loss spectra for increasing alkali coverages. For $\theta_{Na} = 0.55$ ML the peaks at 114 meV and 180 meV are not visible any more and a new feature at 3.0 eV arises. By a comparison with the calculations reported for Na clusters [26], we assign this peak to a Mie resonance, that is a plasmonic mode confined in the cluster and, thus, occurring within the self-assembled supported Na QDs. The interpretation is also based on previous topographical investigations of this system [10,12,24]. For nonspherical supported metal clusters, the Mie resonance should exhibit two distinct modes corresponding to electronic oscillation which is parallel (1, 1) and perpendicular (1, 0) to the substrate [27], respectively. However, only the perpendicular mode is expected to be efficiently excited by a dipole mechanism. The spectrum measured for coverages beyond two layers is dominated by a peak at 3.9 eV assigned to the Na surface plasmon [28]. Its occurrence can be taken as an evidence that the surface morphology of the sample is making a transition from an island-shaped to a continuous film. For $\theta_{Na} = 0.75$ ML, the Na surface plasmon and the Mie resonance coexist in Na islands. This finding indicates that the appearance of surface plasmons is preceded by Mie resonances in films following Stranski–Krastanow growth mechanism [29].

In order to investigate the reactivity of Na QWS and QDs, the Cu(1 1 1) surface precovered with increasing amounts of Na was exposed to 0.12 L ($1\ \text{L} = 1 \times 10^{-6}$ Torr × s) of water vapour. The corresponding loss spectra are presented in Fig. 3. For $\theta_{Na} = 0.44$ ML, water exposure causes the rise of a strong loss peak at 36 meV and of a tine shoulder at 58 meV. In addition, a weak peak was observed at 448 meV (not shown). We assign the peak at 36 meV to the stretching vibration of OH groups against Na atoms while the feature at 448 meV is due to the O–H stretching. Increasing Na coverage, the peak at 36 meV shifts towards higher loss energies and for $\theta_{Na} = 1.00$ ML the OH–Na vibration is at 53 meV. This is exactly the loss energy of the OH–Na vibration in matrix isolated NaOH molecules [30].

In conclusion, the electronic properties of Na layers on the Cu(1 1 1) surface and their interaction with water show a strong dependence on the Na coverage. The first Na layer is characterized by two peaks in the low-energy region tentatively assigned to CDWs. Na QDs are characterized by a Mie resonance at 3.0 eV. The Na surface plasmon becomes the dominant peak for $\theta_{Na} = 1.20$ ML indicating a morphologic transition of the surface from an island-shaped to a continuous alkali film. The OH–Na stretching vibration shows a dramatic dependence on the amount of the Na precoverage.

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PAPER XIII

High resolution energy loss measurements of Na/Cu(111) and H_2O/Na/Cu(111): Dependence of water reactivity as a function of Na coverage

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High resolution electron energy loss measurements of Na/Cu(111) and H_2O/Na/Cu(111): Dependence of water reactivity as a function of Na coverage

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Collective electronic excitations occurring in Na layers grown on Cu(111) and in H_2O/Na/Cu(111) have been investigated at room temperature by high resolution electron energy loss spectroscopy. Loss spectra taken for a coverage between 0.55 and 0.70 ML of Na are characterized by a feature at 3.0 eV assigned to a Mie resonance. Further increasing the Na coverage leads to the appearance of the Na surface plasmon at 3.9 eV. Water molecules dissociate on Na layers as shown by the appearance of the OH–Na vibration. Upon water adsorption, relevant effects on both electronic excitations and vibrational modes were observed as a function of Na coverage. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2748385]

INTRODUCTION

Electronic excitations in thin alkali metal films have attracted much attention from both theoreticians and experimentalists.[1] Alkali metals deposited on Al surfaces have been extensively studied because of the simple electronic structure of both substrate and adsorbate. Gaspar *et al.*[2] performed electron energy loss measurements and dynamical response calculations for Na and K on Al(111). They found that the alkali-metal free-electron gas made a transition from quasi-two-dimensional to three-dimensional as a function of coverage.

In recent years, an increasing attention has been devoted to the investigation of alkalis deposited on the Cu(111) surface.[3,4] This surface is characterized by the presence of a large confined gap within the projected bulk band structure, centered at the $\bar{\Gamma}$ point of the surface Brillouin zone.[5] Electronic states of different origin can exist in this gap. They may be Shockley surface states, or states induced by adsorbates (quantum wells). Electrons occupying these states are confined in a quasi-two-dimensional space at the surface plane.

Scanning tunneling microscopy measurements[6] performed for Na deposited at room temperature on Cu(111) showed that an additional Na deposition on the first Na layer[7,8] caused the growth of self-assembled small islands called quantum dots (QDs). Electrons in Na QDs are confined in all three dimensions. Recent investigations have provided a clear evidence that surface states and electron confinement may influence the surface chemical reactivity. As a matter of fact, a clear relationship between electronic confinement, the density of states at the Fermi level, and the chemical reactivity has been demonstrated for different systems.[9–11]

Single-particle excitations of Na QDs have been measured by scanning tunneling spectroscopy[6] (STS) and calculated by density functional theory.[12] Moreover, the reactivity of Na QDs towards CO was studied by first principle calculations.[13] It has been argued that when CO molecules are close to the surface, some charge may be transferred from the QD to the antibonding $2\pi^*$ orbital of CO.

However, the collective excitations (Mie plasmons) and the reactivity of Na QDs have not been experimentally investigated yet. On the other hand, the electronic structure and the chemical activity of nanostructured materials is a topic of great importance as these properties may affect their stability and growth mode.

With the aim to address the above points, high resolution electron energy loss (HREEL) measurements of Na/Cu(111) and H_2O/Na/Cu(111) for Na coverages ranging from 0.44 ML (first physical layer) up to 1.30 ML were carried out. Water was chosen to probe the reactivity of the Na/Cu(111) model system since the knowledge of the mechanisms of water interaction with solid surfaces is useful for understanding a wealth of physical and chemical phenomena such as heterogeneous catalysis, energy production, pollution, and corrosion. Moreover, understanding how water molecules interact with Na QDs may provide new insights on the role of confined electrons on the chemical activity of self-assembled nanostructures.

We have found that, depending on the Na coverage, loss spectra are characterized by different excitations. Particularly, for coverages between 0.55 and 0.66 ML, spectra showed a feature at 3.0 eV interpreted as a Mie resonance in QDs; at higher coverages the ordinary surface plasmon (3.9 eV) of a continuous Na film appeared. Moreover, the energy of the Mie plasmon was found to be strongly influenced by the adsorption of OH groups which, on the con-

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trary, had little effect on the surface plasmon. This different behavior was ascribed to the confinement of electrons in Na QDs.

EXPERIMENT

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Cu(111) with a purity of 99.9999%. The Cu(111) surface showed an excellent low energy electron diffraction (LEED) pattern characterized by sharp spots against a very low background. Sodium was deposited onto the Cu(111) surface by means of evaporations from a well-outgassed commercial getter source. The occurrence of the $(3/2\times 3/2)$ LEED pattern was used as the calibration point for $\theta_{\mathrm{Na}}=0.44$ ML; a constant sticking coefficient was assumed in order to obtain any other desired Na coverage. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 20 eV was used; the energy resolution ranged between 8 and 12 meV. The Na/Cu(111) surface was exposed to water vapor and no traces of impurities were detected by a mass spectrometer. All exposures and measurements were made at room temperature.

RESULTS AND DISCUSSION

Loss spectra for both clean and Na-exposed Cu(111) surfaces are shown in Fig. 1 for Na layers ranging from 0.40 to 1.30 ML. The loss spectrum of the clean surface showed a pronounced and sharp jump at about 2.1 eV, representing the onset of single-particle transitions of valence electrons.[14,15] The deposition of $\theta_{\mathrm{Na}}=0.44$ ML caused only slight changes in the loss spectrum, but as soon as the coverage was increased up to 0.55 ML, a feature at 3.0 eV arose in the loss spectrum. A further increase of Na coverage (0.66–0.70 ML) caused the development of a new peak at 3.9 eV. For Na coverages greater than 0.80 ML, the loss spectrum did not evolve further.

The LEED structure progressively degraded with increasing the amount of the adsorbed Na and for the highest coverage only a diffuse background was observed. Our measurements indicate that the loss spectrum is dominated by two different features: one at 3.0 eV which is predominant at lower Na coverages and the other at 3.9 eV which is the main peak at the highest Na coverage. The peak at 3.9 eV can be assigned to the Na surface plasmon in agreement with several previous investigations performed on both thick[16,17] and thin[17,18] Na layers deposited on other metal substrates. A possible explanation of the feature at 3.0 eV may be searched in the structural properties of the Na film at lower coverages, for which the growth of small islands have been imaged.[6] It is well known that collective excitations of valence electrons confined inside clusters may occur in isolated metallic clusters.[19] These modes are called Mie resonances. Particularly, for Na clusters of 1.2 nm the Mie plasmon occurs at about 3.0 eV.

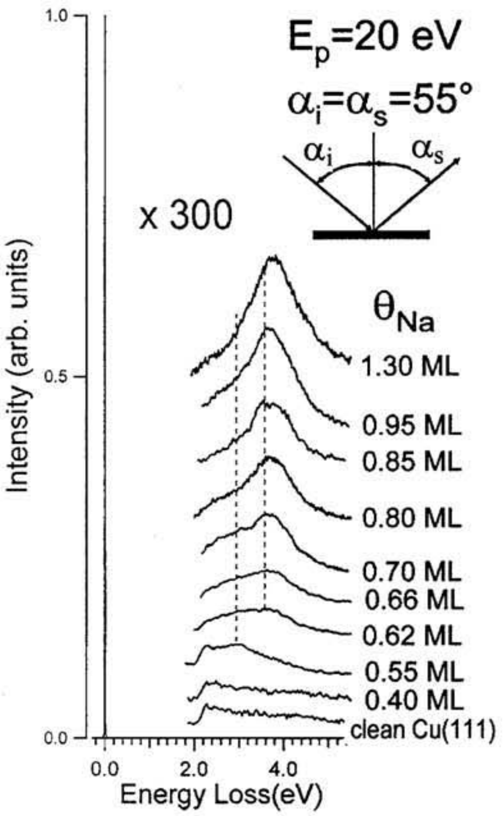

FIG. 1. HREEL spectra of Cu(111) and of Na-covered Cu(111) for several sodium coverages.

At the light of these findings, we assign the loss feature at 3.0 eV to a Mie resonance within supported self-assembled Na QDs. Actually, nonspherical supported metal clusters should exhibit two distinct Mie resonances corresponding to electronic oscillations parallel, i.e., the so called (1,1) mode, and perpendicular, i.e., the (1,0) mode, to the substrate,[20] respectively. Only the perpendicular mode is expected to be efficiently excited by dipole scattering and, thus, the peak at 3.0 eV can be attributed to the (1,0) mode.

Although the observation of Mie resonances for unsupported alkali clusters is rather common,[21–23] we are not aware of the occurrence of Mie resonances for supported Na clusters. For submonolayer of Na deposited onto Al(111) surfaces, a loss peak was observed between 2.5 and 3.0 eV. It was interpreted as a single-particle transition from the Fermi level to unoccupied Na 3*p* orbitals.[24] In our case, we exclude this possibility because for Na coverages higher than one layer adatom-adatom interactions dominate over the adatom-substrate interactions[1] and the occurrence of electronic collective excitations within the overlayer are expected to dominate over single-particle transitions. The finding that a Mie resonance with the same energy was found for both supported and unsupported Na clusters is indicative of a weak cluster-substrate interaction. Very likely, the absence of a Mie resonance in other alkali-metal systems may be due to the different growth mechanism that characterizes Na on Cu(111) at room temperature. In fact, for most alkali overlayers, the formation of a second layer needs low-temperature depositions.[1] However, for the sake of truth we should note that the interpretation of our loss spectra is based

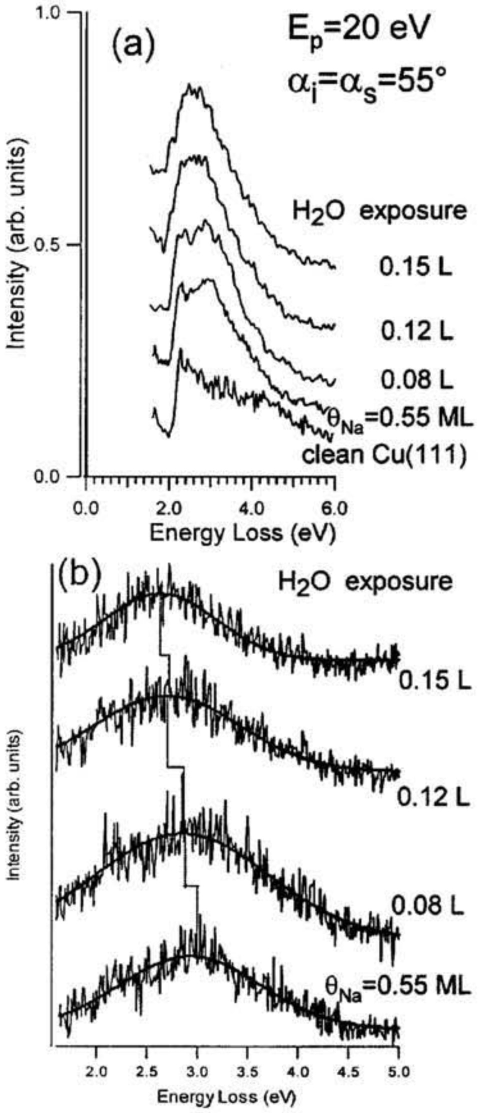

FIG. 2. (a) HREEL spectra of Cu(111) and of θ_{Na}=0.55 ML/Cu(111) exposed to water vapor. Na Mie resonance is at 3.0 eV. (b) Each curve was obtained by subtracting the background and the copper contribution. The resulting curve was fitted by a Gaussian line shape.

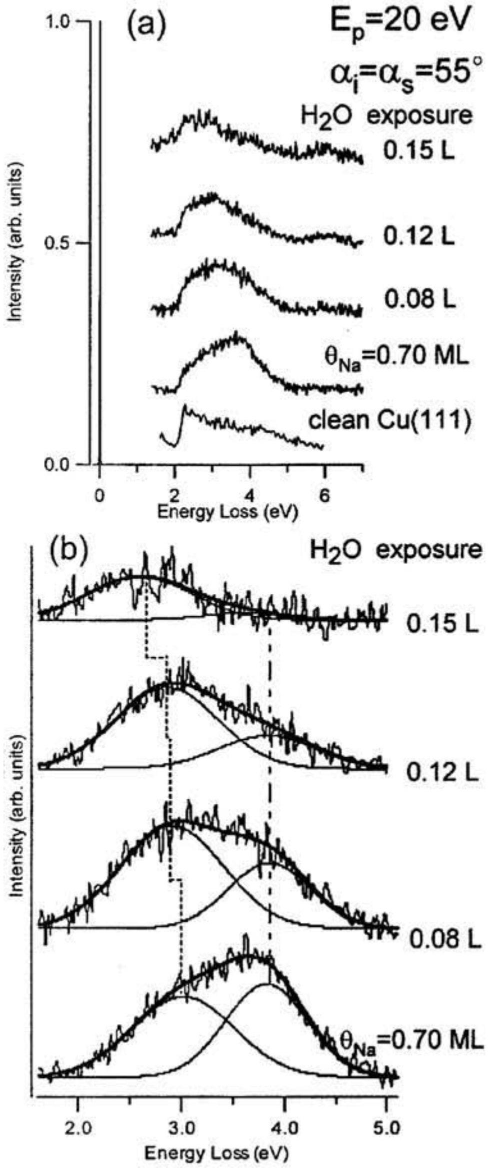

FIG. 3. (a) HREEL spectra of Cu(111) and of θ_{Na}=0.70 ML/Cu(111) exposed to water vapor. (b) Each curve was obtained following the same procedure of Fig. 2(b).

on previous topographical results because our technique does not allow the investigation of the dependence of the Mie resonance on the size and shape of Na clusters.

The rise of the surface plasmon for Na coverages beyond θ_{Na}=0.90 ML indicates that sodium film changes its morphology from isolated Na clusters to a continuous layer. We suggest that alkali metal films, as Na on Cu(111) at room temperature, following the Stranski-Krastanow growth mechanism[25] may be characterized by a Mie resonance at lower coverages and by the surface plasmon at higher coverages.

Alkali metals strongly interact with many atomic and molecular species. The presence of small amounts of alkalis may have a tremendous effect on the surface chemical activity and on the rearrangement of surface layers.

In order to verify the stability and reactivity of Na layers, we exposed the surface to small amounts of water vapor at room temperature [Fig. 2(a)]. For a better analysis of our loss spectra, the background and the contribution of the copper substrate were subtracted from each spectrum of Fig. 2(a). The loss feature thus obtained was fitted by a Gaussian curve [Fig. 2(b)]. We observe that the energy of the Mie plasmon shifted from 3.0 eV down to 2.6 eV as 0.15 L ($1\ \text{L}=1\times10^{-6}$ Torr s) of H$_2$O were dosed. This energy shift indicates that a direct or indirect (via substrate) charge transfer from the alkali QDs to adsorbed species occurs. The same procedure was applied to the loss spectrum of 0.70 ML Na/Cu(111) [Fig. 3(a)]. After the subtraction of the background and of the copper contribution [Fig. 3(b)], the spectrum clearly showed the coexistence of Mie resonance (3.0 eV) and the Na surface plasmon (3.9 eV). Upon water exposure, the energy of the Mie plasmon shifted to lower values while its intensity remained almost constant. On the contrary, the intensity of the Na surface plasmon rapidly decreased with water exposure.

Interestingly, a new loss peak at 6.1 eV arose for increasing water exposures. Its interpretation may be related to the presence of OH groups on the surface. In fact, photo-

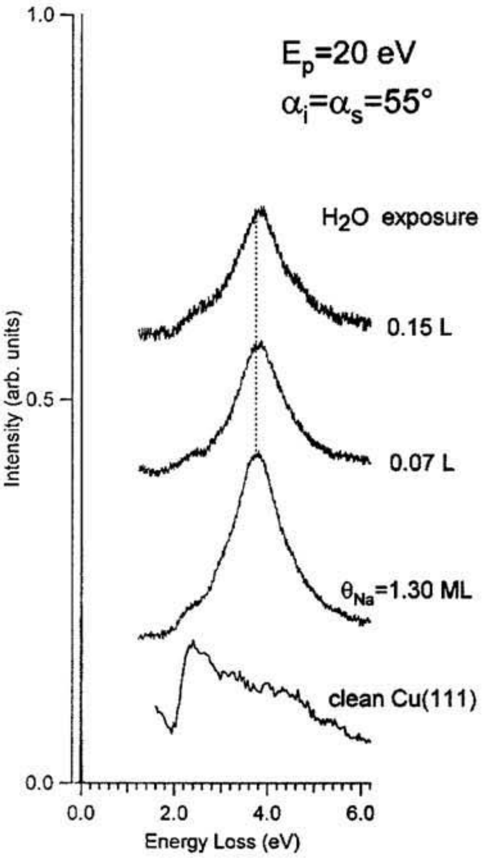

FIG. 4. HREEL spectra of Cu(111) and of $\theta_{Na}=1.30$ ML/Cu(111) exposed to water vapor.

emission spectroscopy experiments carried out by Claesson *et al.*[26] on (2×2)-Li/Cu(111) exposed to water and oxygen molecules showed a peak at a similar energy. These authors interpreted this peak as due to single-particle transitions involving oxygen $2p$-derived orbitals. Water exposures affected the energy of Mie resonance but not that of the surface plasmon of a thin Na film (i.e., $\theta_{Na}=1.30$ ML, Fig. 4). All LEED observations revealed a negligible influence of water exposures on the order status of the overlayer. Thus, loss measurements unambiguously indicated that Na QDs and thin continuous Na films react differently to OH groups.

More insights into the nature of the chemical bond between water and Na layers can be obtained investigating also the vibrational modes of 0.12 L $H_2O/Na/Cu(111)$ (Fig. 5). For $\theta_{Na}=0.44$ ML, water exposure caused the rise of a strong and sharp loss peak at 36 meV in the EEL spectrum, as well as its replica at 73 meV and a weak peak at 450 meV (not shown in Fig. 5). The peak at 36 meV was assigned to the stretching vibration of OH groups against Na atoms and the feature at 450 meV to the O–H stretching mode in OH.[27] Both peaks indicated that water molecules dissociate upon adsorption on Na layers. Increasing Na coverage, the OH–Na peak at 36 meV shifted towards higher loss energies and for $\theta_{Na}=0.90$ ML such vibration reached 50 meV. Interestingly, this value is close to the frequency of the OH–Na stretching vibration in matrix isolated NaOH molecules.[28] Moreover, OH–Na vibrational peak significantly broadens with Na coverage.

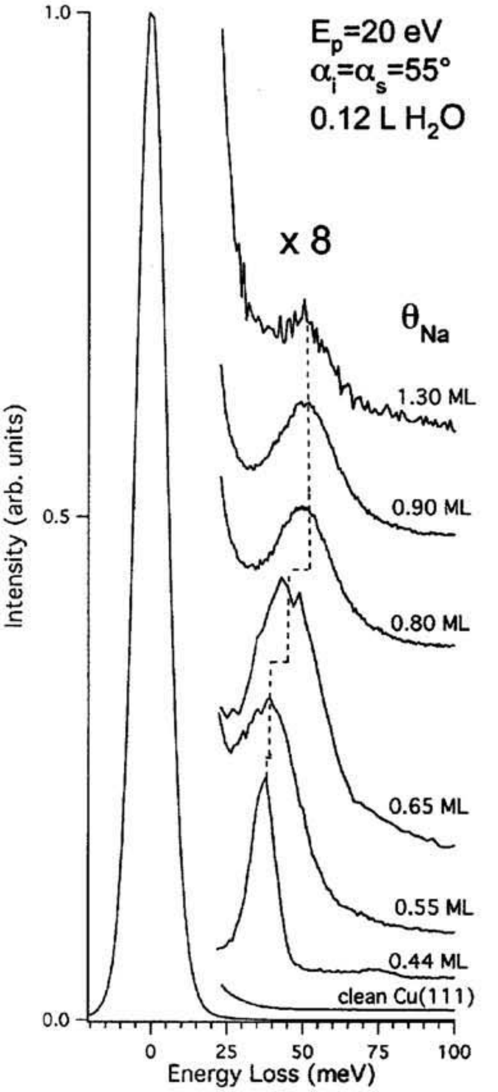

FIG. 5. HREEL spectra of Cu(111) and of Na-covered Cu(111) for several coverages. Each coverage was exposed to 0.12 L of water vapor at room temperature.

The adsorption of water on submonolayers of Na deposited on Cu(111) has been studied by Lindgren *et al.*[29] They found a single vibrational mode at 36 meV for low Na coverages and two vibrations at 31 and 36 meV for higher alkali coverages. The mode at 31 meV was assigned to a vibration of water molecules and that at 36 meV to the Na–OH stretching.

The presence of H_2O molecules on the surface can be easily recognized and thus, as far as all the Na coverages investigated in the present study, we exclude any evidence of molecular water.

Vibrational spectra of Fig. 5 completely support the conclusions drawn from the measurements of the collective electronic modes (Figs. 2–4). The strong dependence of the OH–Na bonding on the Na coverage was ascribed to the different Na–Cu(111) bonding as well as to the different morphology of the Na film with respect to the coverage. For $\theta_{Na}=0.44$ ML, Na atoms form a uniform layer which exhibits an occupied Na p_z-derived quantum well state at about 100 meV below the Fermi level.[30–33] Increasing the coverage, metallic QDs self-assemble on Cu(111) and electrons become confined in these small islands. For higher Na coverages, these islands get closer to each other to form a continuous film for which the Na–Na bonding very likely dominates upon the Na–Cu bonding.

Electron confinement must have a strong influence on the chemical bond as demonstrated for CO on Cu/fcc Fe/Cu(100),[11] CO on Ag(111),[34] and for O_2/Mg/W(110).[10] The main effects observed in the present investigation may be explained within this framework. At low Na coverages, OH species formed by water dissociation interact very strongly with the alkali film and a charge transfer from Na particles to OH occurs. Such charge transfer is responsible of the energy shift of the Mie plasmon and of Na–OH stretching vibration. These findings suggest that Cu(111) surface states and Na quantum well states strongly influence the Na–OH bonding for low Na coverage. On the contrary, at the highest Na coverages, the charge transfer between Na and OH is less important because the density of states at the Fermi level is lower according to the observed poor reactivity and to STS experiments[6,33] which did not find Na occupied quantum well states crossing the Fermi level.

CONCLUSIONS

Present measurements provide several hints to understand the microscopic mechanism of the sodium adsorption on the Cu(111) surface. The formation of Na QDs on Cu(111) is characterized by the loss feature at 3.0 eV which was visible for Na coverages ranging from 0.55 up to 0.66 ML. For higher Na depositions, a collective oscillation at 3.9 eV arose and developed increasing with coverage up to $\theta_{Na}=1.30$ ML. This feature is the surface plasmon of the Na adlayer and its energy is in good agreement with the surface plasmon of thick Na layers deposited on several substrates. The rise of the Na surface plasmon indicates a morphological change from isolated Na clusters to a continuous alkali film. The chemical reactivity of the Na/Cu(111) surface was probed by the adsorption of OH groups. Both the energy shift of the Mie collective mode and the Na–OH stretching indicate a charge transfer from the Na film towards OH groups. On the contrary, for higher Na coverages, the formation of a Na–OH bond did not influence the electronic properties of the Na layer. Although theoretical calculations are needed and claimed for interpreting underlying microscopic mechanisms, we suggest that Cu(111) surface states, Na-induced quantum well states, and electron quantum confinement into Na QDs are at the base of present experimental results.

ACKNOWLEDGMENT

We would like to thank S. Abate and G. Desiderio for their technical support.

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PAPER XIV

Collective excitations in nanoscale thin alkali films: Na/Cu(111)

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Collective Excitations in Nanoscale Thin Alkali Films: Na/Cu(111)

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The relationship between electron quantum confinement and the energy dispersion of the surface plasmon in nanoscale thin Na layers adsorbed on Cu(111) at room temperature have been studied by high resolution electron energy loss spectroscopy. Screening effects due to electron quantum confinement occurring in this system cause the lowering of the surface plasmon frequency and, moreover, make the energy range of its dispersion curve larger than in thick alkali films. Landau damping of the plasma excitation was unexpectedly very efficient at small momenta. The dispersion curve of the Na surface plasmon was found to depend on the primary electron beam energy. Multipole surface plasmon at 4.70 eV was observed only for higher impinging energies.

Keywords: Nanoscale Thin Films, Surface Plasmon, Alkali Metals, Electron Energy Loss Spectroscopy, Dynamic Screening.

1. INTRODUCTION

Nanoscale films are becoming increasingly prevalent in microelectronic, optic, and structural applications. Physical properties are expected to vary, often dramatically, with thickness. In fact, as the thickness of a film is reduced to the nanometer scale, the overall electronic structure of the film modifies because of the occurrence of physical phenomena such as quantum size effects and electron quantum confinement. As a matter of fact, recent experimental studies[1–6] have demonstrated that the electronic density of states, electron-phonon coupling, chemical reactivity, superconductivity, magnetism, surface energy, and thermal stability change with the film thickness.

In the last few years much effort has been devoted to the investigation of the electronic collective excitations in alkali metal films deposited on solid surfaces. The surface plasmon (SP) dispersion and the nature of the collective excitations in thick alkali-metal films are well understood and there exists full agreement between experimental results[7–11] and theoretical predictions.[7, 10, 12] On the other hand, details of the nature and dispersion of the collective excitations in nanoscale thin alkali-metal films[7–12] remain uncertain.

High resolution electron energy loss spectroscopy (HREELS) measurements have been reported for two layers of alkali metals deposited on Al(111),[8] for K on Ni(111),[13] and for Cs on Si(111).[14] Two different surface modes (the monopole SP and the multipole SP) have been observed and studied in great detail.[15,16] However, any comparison of experimental results with calculations for thin alkali films has been inconclusive. Moreover, the influence of electron quantum confinement on the electronic collective excitations in nanoscale thin alkali film has not been investigated yet. This is a topic of a great importance and recent studies[17–20] found that electron confinement plays an important role on the physical and chemical properties of nanoscopic thin films. A clear relationship between electronic confinement, the density of states at the Fermi level, and the chemical reactivity has been demonstrated for different systems.[17–20]

The (111) surface of noble metals (Cu, Ag, Au) exhibits a large confined gap within the projected bulk band structure centered at the $\overline{\Gamma}$ point of the surface Brillouin zone.[21] Electronic states of different origin can exist in this gap. They may be Shockley surface states or states induced by adsorbates (quantum well states, QWS). The adsorption of Na on Cu(111) has been extensively investigated recently. The existence of Na $3p_z$-derived confined electron states has been well established.[22, 23] Electrons occupying QWS are confined at the top layer of the bulk sample and form a two-dimensional nearly free-electron gas. Thus, Na/Cu(111) is a suitable model system for investigating the relationship between electron confinement and the nature and dispersion of collective electronic excitations. Multilayers of alkali metals are easily grown on

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Cu(111) even at room temperature (RT) while in other systems the growth of a second alkali layer is possible only at liquid nitrogen temperature.[24] A study reporting the dispersion curve of the SP in alkali thin layers at RT is still lacking.

To address these problems, we performed angle-resolved HREELS measurements for two layers of Na deposited onto the Cu(111) surface at RT.

Our results clearly show that the collective excitations in nanoscale thin Na layers grown on Cu(111) are influenced by several effects such as: dynamical screening enhanced by electron quantum confinement, changes in probing depth as a function of the primary electron beam energy, and coupling between confined electronic states and the underlying three-dimensional bulk states.

2. EXPERIMENTAL DETAILS

Measurements were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Cu(111) with a purity of 99.9999%. The surface was cleaned by repeated cycles of ion sputtering and annealing at 800 K. Surface cleanliness and order were checked using low energy electron diffraction (LEED) and Auger electron spectroscopy. The Cu(111) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium was deposited onto the Cu(111) surface by evaporating from a well outgassed commercial getter source. The occurrence of the $(3/2 \times 3/2)$ LEED pattern was used as the calibration point of $\theta_{\mathrm{Na}} = 0.44$ ML; a constant sticking coefficient was assumed to obtain other desired Na coverage. Loss spectra were taken for both the specular (angle of 55° with respect to the surface normal) and off-specular geometries. A primary electron beam energy of 20 eV and 100 eV was used. The energy resolution of the spectrometer was degraded to 12 meV so as to increase the signal-to-noise ratio for off-specular spectra. The angular acceptance α of our electron analyzer was $\pm 1°$. Dispersion of the collective mode, i.e., $\mathrm{E}_{\mathrm{loss}}(q_{\parallel})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. The sample was oriented along the $\overline{\Gamma} - \overline{M}$ direction. Each loss spectrum was acquired in few minutes in order to minimize the interaction of the Na layers with residual gases in the UHV chamber. All exposures and measurements were made at room temperature.

3. RESULTS AND DISCUSSION

HREEL spectra of Na adsorbed at RT on Cu(111) as a function of coverage are shown in Figure 1. For the clean Cu(111) surface, the onset of collective excitations of valence electrons could be detected at 2.1 eV.[25, 26] A broad loss feature, peaked at 3.70 eV and assigned to the Na SP, gradually arose in the spectrum as a function of Na coverage.

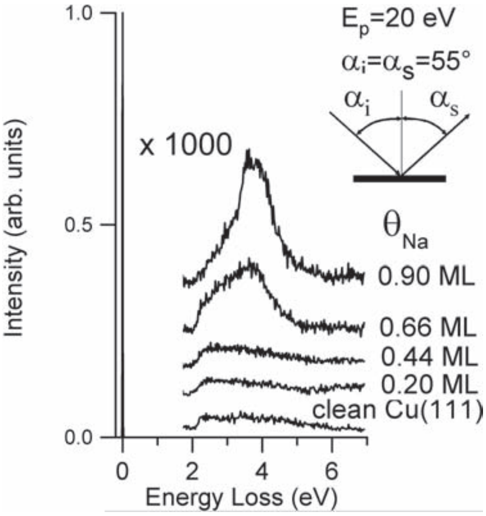

Fig. 1. HREEL spectra of Na/Cu(111) as a function of the alkali coverage. The incident beam energy E_p was 20 eV.

To measure SP dispersion, values for the parameters E_p, impinging energy, and θ_i, the incident angle, were chosen in order to obtain the best compromise among surface sensitivity, the highest cross section for mode excitation, and $q_{\parallel}$ resolution.

As

$$\hbar \vec{q}_{\parallel} = \hbar(\vec{k}_i \sin\theta_i - \vec{k}_S \sin\theta_S) \tag{1}$$

the parallel momentum transfer, $q_{\parallel}$ depends on E_P, E_{loss}, θ_I, and θ_S according to:

$$q_{\parallel} = \frac{\sqrt{2mE_p}}{\hbar}\left(\sin\theta_i - \sqrt{1 - \frac{E_{\mathrm{loss}}}{E_P}}\sin\theta_S\right) \tag{2}$$

where E_{loss} is the energy loss and θ_S is the electron scattering angle.[15]

Accordingly, the integration window in reciprocal space is:[27, 28]

$$\Delta q_{\parallel} \cong \frac{\sqrt{2mE_P}}{\hbar}\left(\cos\theta_i + \sqrt{1 - \frac{E_{\mathrm{loss}}}{E_P}}\cos\theta_S\right) \cdot \delta\theta_S \tag{3}$$

where $\delta\theta_S$ is related to the angular acceptance α of the apparatus.

Loss spectra in Figure 2 show the SP of two layers of Na/Cu(111) as a function of the scattering angle for $E_P = 20$ eV. The spectrum recorded in the specular geometry is centered at 3.70 eV and it exhibits clear energy dispersion for off-specular angles.

One advantage of EELS technique is that changing the primary beam energy of the electrons, it is possible to modify their mean free path in the solid and so their penetration length.[29] This allows a direct control of the surface

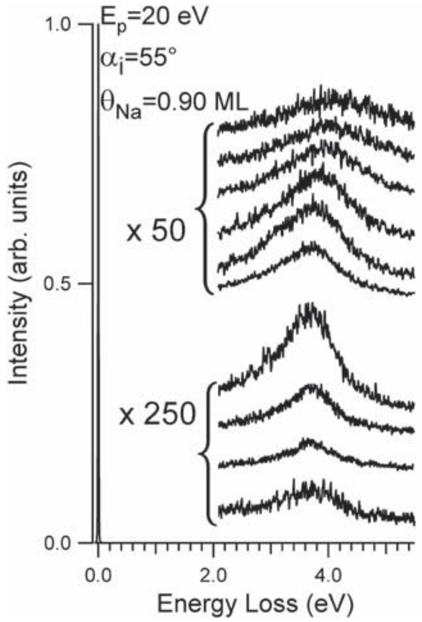

Fig. 2. Electron energy loss spectra of 0.90 ML Na/Cu(111) at different scattering angles θ_s. The incident beam energy E_p was held constant at 20 eV and all spectra were recorded at an incident angle of $\theta_i = 55°$ with respect to the sample normal.

sensitivity. Moreover, the modification of the electron penetration would imply, according to random-phase approximation calculations,[30] a change in the position of the reflection plane at which probing electrons are scattered within the extended electron-density distribution. On the basis of the above result, a strong dependence of dynamic screening processes on impinging energy is expected especially for systems in which electrons are confined into a two-dimensional space. Hence, spectra were acquired also for a higher primary energy, i.e., 100 eV, in order to reveal such behavior.

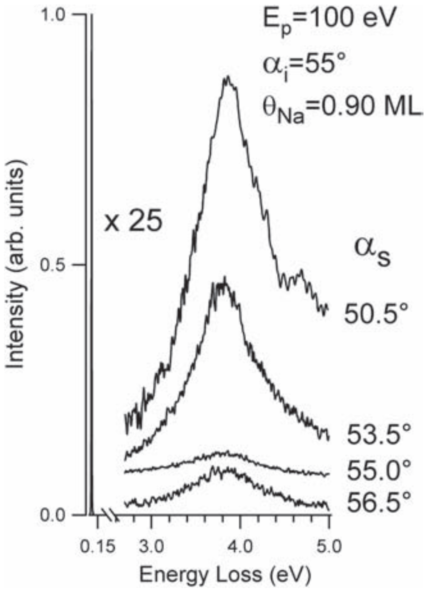

Fig. 3. Electron energy loss spectra of 0.90 ML Na/Cu(111) at different scattering angles θ_s, recorded with a primary electron beam energy of 100 eV.

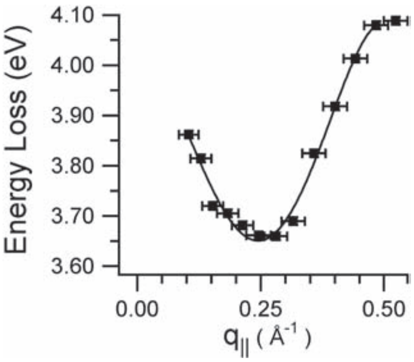

Fig. 4. Na SP energy as a function of $q_{\|}$ ($E_p = 20$ eV).

Multipole SP in Na/Cu(111) became quite evident in spectra taken with $E_p = 100$ eV behind 3 degrees off-specular (Fig. 3). Its energy was found to be 4.70 eV, in excellent agreement with the value reported for bulk Na by Tsuei et al.,[11] i.e., 4.67 eV. However, the multipole mode was not revealed for lower impinging electron beam energies, thus suggesting the existence of a threshold primary beam energy.

The measured dispersion curve $E_{\text{loss}}(q_{\|})$ for $E_p = 20$ eV reported in Fig. 4 was fitted by a fourth-order polynomial[15] given by:

$$E_{\text{loss}}(q_{\|}) = a + bq_{\|} + cq_{\|}^2 + dq_{\|}^3 + eq_{\|}^4$$

where $a = 3.99$ eV, $b = 0.70$ eV · Å, $c = -29.53$ eV · Å^2, $d = 113.14$ eV · Å^3, and $e = -112.31$ eV · Å^4.

The slope of the dispersion curve is negative up to 0.25 Å^{-1}, then the loss energy of the SP increases with increasing $q_{\|}$ and the dispersion becomes definitively positive. Interestingly, the value of the parallel momentum transfer corresponding to the minimum of the dispersion curve is anomalous with respect to the common value found in others similar investigations, i.e., 0.15 Å^{-1}.[13, 25, 27] However, a physical interpretation of the minimum of a dispersion curve of a SP does not exist and we have not a convincing explanation for this finding.

It should be noticed that the SP was not damped into single-particle transitions until $q_{\|} = 0.53$ Å^{-1}, while the critical wavevector of alkali SPs was found to be around 0.30 Å^{-1} both in thin[13] and thick[10] alkali films.

Furthermore, no loss features were revealed for the lowest values of parallel momentum transfer (below 0.10 Å^{-1}). A similar result was found by Zielasek et al.[14] in Cs/Si(111)-(7 × 7) in which the SP was suppressed for small wave vector. These findings are in agreement with Liebsch's calculations[12] which predicted that for two layers of alkali metals the spectral weight of the SP is vanishing at $q_{\|} = 0$. In other words, at $q_{\|} = 0$ only the excitation of the so called multipole SP is possible. In this regard, we notice that the Na/Cu(111) system behaves differently from K/Ni(111)[13] for which the excitation of the SP was found to be possible.

The energy dispersion of the SP of two Na layers was 430 meV, while it was 130 meV for thick Na films. Such finding could be explained by screening effects that push the position of the induced charge density centroid more outside the substrate jellium edge than in thick Na films. The energy dispersion of the SP may be written[31] as a function of two surface response functions, $d_\perp(\omega)$ and $d_\parallel(\omega)$, which embody the position and power spectrum of a surface with respect to the normal and parallel electric fields, respectively:

$$\omega_{SP}(q_\parallel)=\omega_{SP}(0)\left\{1-\frac{1}{2}\left[d_\perp(\omega_{SP})-d_\parallel(\omega_{SP})\right]q_\parallel+\mathrm{O}(q_\parallel^2)\right\}$$

In particular, the parameter $d_\perp(\omega)$ is the position of the centroid of the screening density charge induced by a uniform field normal to the surface.

We propose that electron quantum confinement in Na QWS may be the responsible of such result. In fact, the electron confinement of Na electrons on Cu(111) was found[32] to drastically change the dynamical screening properties of this system. The occurrence of electron confinement in Na QWS, moreover, modifies the electron charge-density distribution. Hence, the reflection of external charges at different distances from the surface[30] should affect the electronic response of this system.

The dispersion curve of the SP, measured using a primary electron beam of 100 eV (Fig. 5) is quite different from that in Figure 4. The energy dispersion of the SP is lower (70 meV vs. 430 meV). On the basis of the above considerations, a relationship between electron confinement and the observed dependence on impinging energy could be suggested.

The measured dispersion curve $E_{\mathrm{loss}}(q_\parallel)$ for $E_p=100$ eV was fitted by a fourth-order polynomial[15] given by:

$$E_{\mathrm{loss}}(q_\parallel)=a+bq_\parallel+cq_\parallel^2+dq_\parallel^3+eq_\parallel^4$$

where $a=3.84$ eV, $b=-0.79$ eV · Å, $c=6.22$ eV · Å^2, $d=-17.98$ eV · Å^3, and $e=-20.99$ eV · Å.^{4}

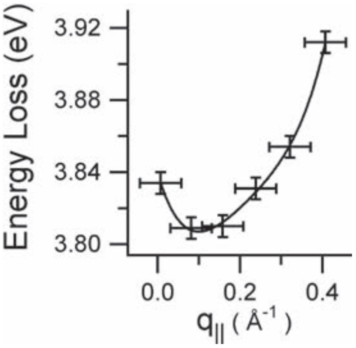

Fig. 5. Na SP energy as a function of $q_\parallel$ ($E_{\mathrm{p}}=100$ eV).

It showed an initial negative behavior that became positive above 0.15 Å^{-1}, in analogy with the dispersion curve of SPs of other simple metals.

It should be noticed that for $E_p=100$ eV the SP could be excited even at small momenta. This is a combined effect of the higher dipole/impact scattering ratio of the excitation (see Fig. 10 and its discussion) and of the increased integration window (3) in reciprocal space. The latter implies the collection of a finite range of momenta of the outgoing electron.

A dispersion curve not dependent on the primary electron beam energy is expected only for the case of pure sheet plasmons,[33] i.e., two-dimensional plasmons strictly confined to the surface and with a square root-like dependence on $q_\parallel$. However, our measurements revealed that the dispersion curve depends on the impinging energy. When the thickness of the film gets smaller, the tail of the wave function of the QWS can reach and interact with the substrate. The main effect is a hybridization interaction between overlayer and substrate states. Recently, such hybridization was unambiguously revealed in an angle-resolved photoemission spectroscopy study for Ag QWS on Ge(111)[34] and it became evident especially for ultrathin Ag film. We suggest that the occurrence of such interactions between overlayer states and substrate ones may lead to the observed differences in the two dispersion curves.

Figure 6 shows a comparison between the dispersion curve obtained for two layers of Na on Cu(111) and the dispersion curve of the SP of a thick Na film.[10] The plasmon energy for a nanoscale thin Na film is lower because screening effects make lower the induced average charge-density and thus the SP energy, as found in two layers of K on Ni(111).[13] The differences in the critical wavevector of the SP for each dispersion curve are quite evident, thus suggesting strong differences about damping processes.

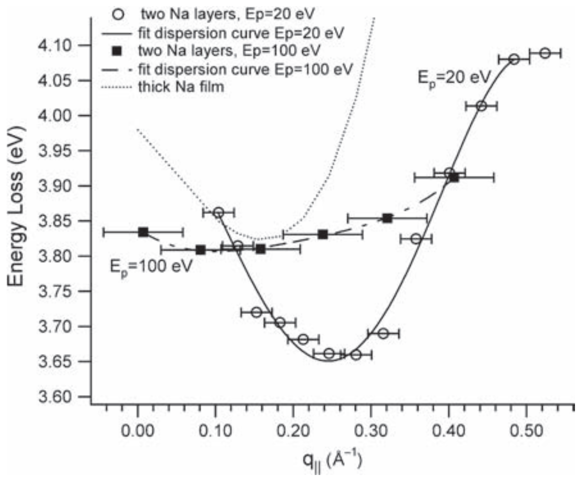

Fig. 6. The surface plasmon dispersion versus the parallel momentum $q_\parallel$ for: (■) two Na layers, $E_p=100$ eV; (○) two Na layers, $E_p=20$ eV; (-) thick Na film (data taken from Ref. [10]).

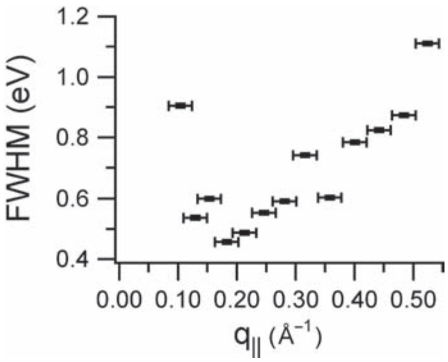

Fig. 7. FWHM of the Na SP peak as a function of $q_\|$ ($E_p = 20$ eV).

The damping of the plasmon excitation is clearly revealed by the trend of the full width at half maximum (FWHM) versus $q_\|$, as shown in Figure 7 for $E_p = 20$ eV. The width of the Na plasmon initially decreased, followed by a steep increase as a function of $q_\|$. Experimentally, a similar behavior was also observed for a variety of metal surfaces such as Ag(110),[35, 36] Mg(0001),[37] Al(111),[38] and Cu(111).[25] On the contrary, the FWHM of the SP in thick films of Na and K[10] increases for increasing $q_\|$, while it was almost constant in two layers of K on Ni(111).[13]

Existing theories predict that, with increasing of the momentum $q_\|$ parallel to the surface, the width of the SP rapidly increases due to the decay into electron–hole pairs (Landau damping). However, for real surfaces the SP peak is generally considerably wider than that predicted by calculations[39] because of short-range many-body exchange-correlation effects and of interband transitions. The behavior shown in Figure 7 could arise from a more efficient disexcitation channel of the SP by single-particle transitions at small momenta. Such assumption could explain a so high critical wavevector (0.53 Å^{-1}) of the plasmonic excitation too.

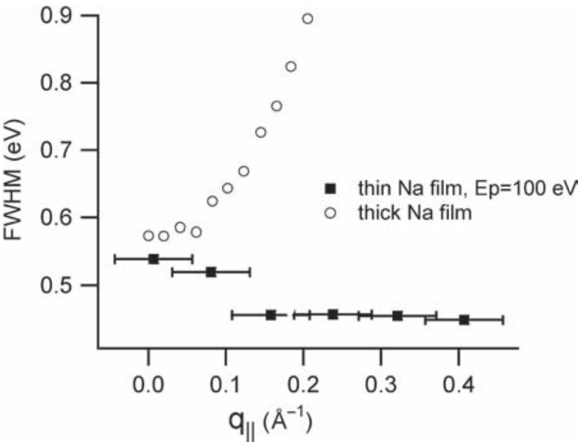

Fig. 8. FWHM of the Na SP peak as a function of $q_\|$ for (■) 0.90 ML Na/Cu(111), $E_p = 100$ eV and for (○) thick Na film (data taken from Ref. 10).

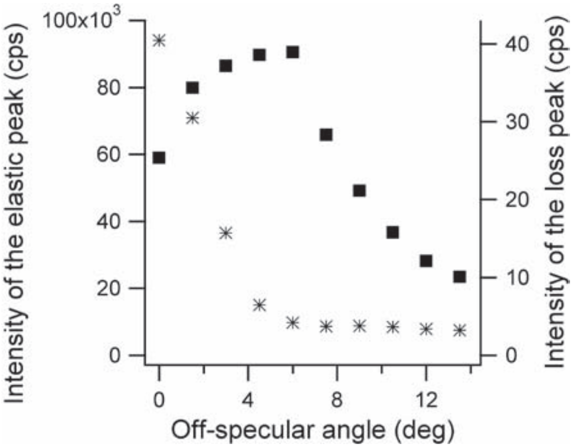

Fig. 9. Intensity of the SP (■) and of the elastic peak (*) as a function of the off-specular angle ($E_p = 20$ eV).

The FWHM of the SP for $E_p = 100$ eV was characterized by a negative dispersion versus $q_\|$ (Fig. 8). To the best of our knowledge, it is the first time that a FWHM was found to have a similar behavior which disagrees with existing theories. Such finding suggests a strong dependence of the dynamical response of electrons and of screening effects as a function of the impinging energy. Interestingly, the FWHM for thick Na films[10] has the opposite trend as a function of the parallel momentum transfer. This experimental result is a clear evidence that understanding of the broadening mechanisms of a SP requires a careful analysis of the band structure of the system.

The intensity of the SP versus the off-specular angle for $E_p = 20$ eV (Fig. 9) clearly demonstrates that such collective mode was excited by impact mechanism because it is peaked at six degrees off-specular,[15] while a dipolar loss would have the same behavior of the elastic peak as a function of the off-specular angle. Instead, the intensity of the SP for $E_p = 100$ eV exhibited a maximum around 1.5 degrees off-specular. Thus, the SP excited by a higher primary beam energy has a substantially dipole character while the same mode with a lower impinging energy

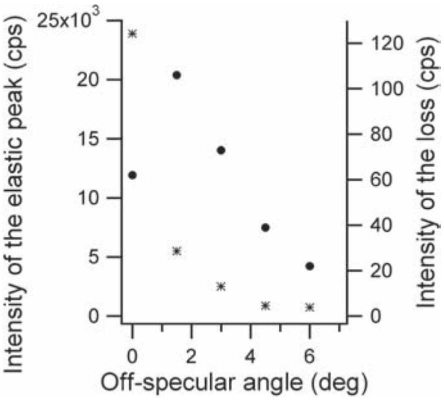

Fig. 10. Intensity of the SP (•) and of the elastic peak (*) as a function of the off-specular angle ($E_p = 100$ eV).

exhibits a notable impact character. The dependence of the dipole/impact scattering ratio in SP excitation as a function of primary beam energy is still an unexplored research field.

4. SUMMARY AND CONCLUSIONS

Loss measurements taken at $E_p = 20$ eV revealed only the ordinary SP, while at $E_p = 100$ eV the multipole plasmon at 4.70 eV was also observed.

A strong dependence of the dispersion curve on the energy of the primary beam was observed. Screening effects enhanced by electron quantum confinement and interactions between overlayer states and substrate states are suggested to be at the basis of the above results. The FWHM of two Na layers behaves very differently with respect to that reported for a Na thick film. These differences were ascribed to different Landau damping mechanisms of the plasmonic mode in the two cases.

These findings provide the grounds for theoretical studies aimed at characterizing of the nature and dispersion of the excitation modes in nanoscale thin alkali films exhibiting confined electron states.

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PAPER XV

Comparative vibrational study on alkali coadsorption with CO and O on Ni(111) and Cu(111)

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Comparative vibrational study on alkali coadsorption with CO and O on Ni(111) and Cu(111)

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Abstract

High-resolution electron energy loss spectroscopy was used to investigate alkali (Na, K) coadsorption with CO and O on Cu(111) and Ni(111). A CO-induced weakening of the alkali-substrate bond was revealed on both substrates. The effect is more pronounced on Ni(111) as on Cu(111) a notable dissociation rate for CO exists. Submonolayers of alkalis were found to promote the preferential population of the subsurface site for O/Cu(111)

1. Introduction

The adsorption of alkali-metal atoms on single-crystal metal surfaces [1-8] and their coadsorption [9-14] with reactive species is a topic of surface science, both for fundamental interest in understanding the mechanisms of heterogeneous catalysis and for technological applications (promotion of catalytic reactions, oxidation rate, and enhanced electron emission rates).

In particular, the coadsorption of CO with alkali metals on noble-metal and transition-metal surfaces has been widely investigated from both experimentalists [15-22] and theoreticians [23-29]. The chief effects of coadsorbed alkali-metal atoms on CO molecules are: a notable increase in the thermal desorption temperature of CO molecules [16, 20-22], changes of work function of the surfaces [30], shifts in CO core- and valence-level binding energies [31], and an enhancement of the CO dissociation probability [32].

Moreover, infrared reflection absorption spectroscopy (IRAS) and high resolution electron energy loss spectroscopy (HREELS) revealed a significant weakening of the C-O bond in the alkali+CO coadsorbed phase [15, 17]. Several models have been made in order to explain such softening of the C-O stretching frequency, involving electrostatic interactions [23-25], surface states [26], direct [27] and indirect (substrate-mediated) [28] interactions, and the alkali-induced enhancement of the surface electronic polarizability of the metal surface [29].

Recently, CO molecules have been demonstrated to induce a significant weakening of the alkali-substrate bond [18, 19] on Ni(111). By contrast, all previous research activities were focused on the shift of the C-O stretching vibration, whereas any effect of CO on the vibrational properties of the co-adsorbed alkali atoms was completely disregarded. The shifts of the Na-Ni and C-O stretching frequencies are related each other. CO molecules locally affect the electronic properties of the Ni(111)surface and "activate" a lengthening of the Na-Ni bond. However, it should be essential a comparative study on a different substrate in order to establish the general validity of such effect.

On the other hand, the electronic, vibrational, and bonding properties of alkalis coadsorbed with oxygen have been scarcely investigated [33-35]. As alkalis are used as catalysts in epoxidation chemistry [36-38], alkali doping may in principle affect the adsorption energy for subsurface adsorption sites for oxygen. A systematic study carried out on different alkali-modified substrates may clarify the conditions for the migration of oxygen adatoms underneath the surface, which is a reaction pathway whose pivotal importance has been demonstrated in many chemical reactions.

Nickel and copper are suitable substrate for such studies as they have a quite different catalytic activity. Such comparative investigations could provide interesting information for understanding the catalytic mechanisms.

As concerns structural investigations, the structural investigations of the K+CO phase on Ni(111) [39] revealed that the K atoms retain the atop site but with an increased K-Ni bond length in the coadsorbed phase. Also for CO molecules (in the three-fold hollow adsorption site), no site change was observed. On the other hand, no structural study exists for alkali coadsorbed with oxygen on nickel or copper surfaces.

High-resolution electron energy loss spectroscopy (HREELS) is a suitable experimental technique for such aims as it allows to follow charge transfer and to individuate adsorption sites of coadsorbates.

Herein we report on HREELS measurements performed on alkali (Na, K) coadsorbed with CO and O on both Ni(111) and Cu(111). The CO-induced softening of the alkali-substrate bond was revealed on both Ni and Cu substrates. Moreover, on alkali-modified copper surfaces the subsurface site for O is energetically favourable with respect to over-surfaces sites. On the contrary, for alkali+O/Ni(111) no subsurface species were revealed.

2. Experimental

Experiments were carried out in a UHV chamber operating at a base pressure of $5x10^{-9}$ Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were single-crystal surfaces of Ni(111) and Cu(111) with a purity of 99.9999%. The surfaces were cleaned by repeated cycles of ion sputtering and annealing at 900 K. Surface cleanliness and order were checked using Auger electron spectroscopy and low-energy electron diffraction (LEED), respectively. Both samples showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium and potassium were deposited onto the substrate by evaporating from a well-outgassed commercial getter source. The occurrence of the (3/2x3/2)-Na and p(2x2)-K LEED pattern was used as the calibration point of θ_{Na}=0.44 ML and θ_K=0.25 ML, respectively. Very clean alkali adlayers could be obtained at 400 K, as demonstrated elsewhere [8, 18, 19, 33]. Nonetheless, measurements were carried out in a few minutes in order to further reduce the contamination. A constant sticking coefficient was assumed to obtain other desired alkali coverage. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of our spectrometer ranged from 2 to 3 meV.

3. Results

3.1 Na coadsorption with CO

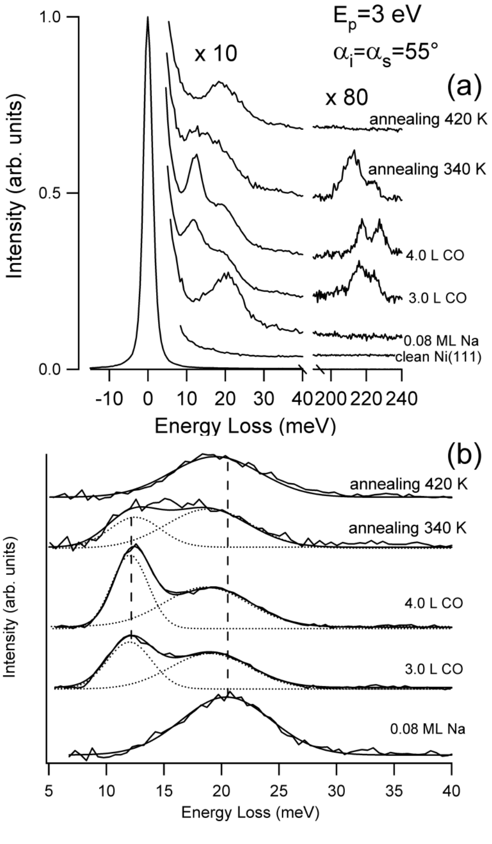

Figure 1. (a) HREEL spectra of 0.08 ML Na/Ni(111) exposed to CO molecules at room temperature and successively annealed. Na was deposited at 400 K. (b) Each curve was obtained by subtracting an exponential background. The resulting curve was fitted by two Lorentzian line-shapes.

HREEL spectra of 0.08 ML Na/Ni(111) exposed to CO molecules at room temperature are shown in Figure 1. A CO-induced splitting of the Na-Ni stretching vibration, observed at 20 meV for the clean Na/Ni(111) surface, was observed. Likewise, two different C-O stretching modes were revealed. A very local and mutual interaction between coadsorbates should be responsible of the appearance of a second Na-Ni and C-O mode upon CO exposure. In fact, not all CO molecules can adsorb in close nearness of the pre-adsorbed Na adatom, and vice versa.

An exponential background was subtracted from each spectra of Fig. 1a for a better analysis of the spectra. The loss features thus obtained were fitted by a Lorentzian curve (Fig. 1b). Upon CO exposure a new Na-Ni peak arose at 12 meV and its intensity increased as a function of CO coverage, while the intensity of the Na-Ni peak at 19 meV gradually diminished.

The feature at 12 meV was assigned to Na adatoms in close contact with CO molecules. Instead, the Na-Ni vibration at 19 meV was due to Na adatoms far from CO molecules. The absence of an energy shift of the latter peak upon CO exposures is a further evidence of a local interaction between Na and CO. The red-shift of the Na-Ni peak in the Na+CO coadsorbed phase was ascribed to a CO-induced lengthening of the Na-Ni bond [18, 19]. Studies concerning the structural properties of K+CO on both Ni(111) and Ni(100) [40, 41] exhibited a significant increasing of the alkali-substrate bond length with respect to the case of K/Ni(111) and K/Ni(100). Such finding is in excellent agreement with the weakening of the Na-Ni bond in the Na+CO coadsorbed phase.

As concerns the C-O stretching, a peak at 216 meV with a shoulder at 225 meV arose after an exposure of 3 L (1 L=$1.33 \cdot 10^{-6}$ mbar·s) of CO. Further CO exposure allows a better separation of such features. Two well distinct losses were recorded at 217 and 227 meV. The presence of two C-O features is ascribed to different environments for CO molecules and it is indicative of different local [Na]:[CO] stoichiometries.

Such results well agree with a recent theoretical analysis [42] of the variation of CO bond lengths, the charge density redistribution, and the energy shift of molecular levels performed for K+CO coadsorbed onto the Ni(111) surface. Such calculations indicated that the K-induced effect is short-ranged. The alkali-induced energy shift of the molecular levels causes the $2\pi^*$ states to be partially occupied.

The CO molecules less bonded to the surface desorbed upon annealing at 340 K (Fig. 1a). As a consequence, the C-O stretching peak at higher energy disappeared. After a further annealing up to 420 K, CO molecules completely desorbed from the surface. Instead, only a part of Na adatoms desorbed, as indicated by the overall diminishing of the integral of the Na-Ni peaks [43]. However, Na-Ni vibration was still present in the HREEL spectrum even with the sample kept at 600 K. As expected, after CO desorption the energy of the Na-Ni peak returned at 19 meV. Upon annealing the component at 12 meV decreased in intensity (Fig. 1b) and finally disappeared.

These findings disagree with previous results. In fact, it was generally assumed that a coincident desorption of both alkalis and CO occurs [21, 44-46]. However, the presence of the Na-Ni stretching in the absence of any CO-derived mode ensures that Na and CO desorption are not at all coincident.

With the aim of verifying if similar effects occur also on a noble-metal substrate, we carried out measurements on Na+CO/Cu(111).

The Na-Cu feature shifted from 22 to 19 meV. Interestingly, HREEL spectra recorded on Na-modified Cu(111) indicated a fully dissociative CO adsorption. No other peak was revealed except the O-Na vibration at 36 meV, due to CO dissociation. The weakening of the Na-substrate bond is more effective in the presence of molecular CO, as in the case of Na+CO/Ni(111).

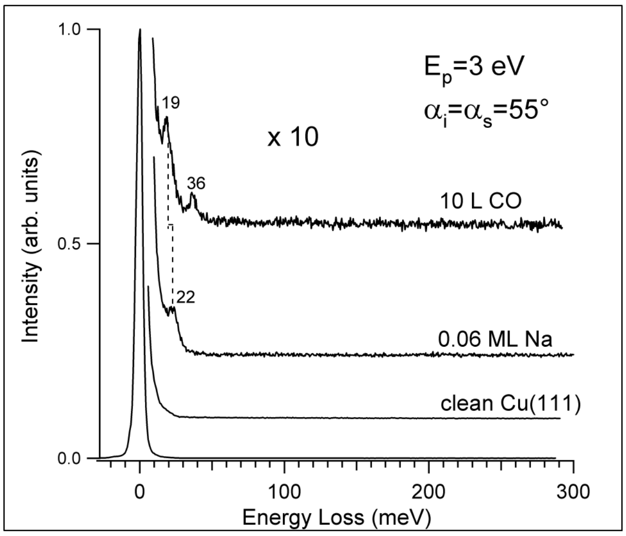

Figure 2: HREEL spectra for 0.06 ML Na/Cu(111) exposed to CO molecules at room temperature.

The enhanced CO dissociation rate on alkali-modified copper surfaces with respect to nickel substrates may be ascribed to the different reactivity of such surfaces towards CO adsorption. It is worth noticing that the sticking coefficient for CO molecules on copper surfaces at 300 K is extremely reduced compared with on transition-metal surfaces (Ni, Pt, Ru). In fact, the saturation coverage for CO molecules on clean copper coverage was found to be about zero for temperatures higher 200 K [47], while for Ni(111) the surface was found to be fully covered by CO molecules at 300 K even for small CO exposures [48, 49]. Accordingly, it is quite expected that CO adsorption on alkali-modified copper substrates might occur only in the close vicinity of alkali adatoms. As confirmed by the analysis of HREEL spectra acquired for several Na coverages on Cu(111) exposed to 0.4 L of CO (Figure 3), no critical precoverage for CO dissociation exists.

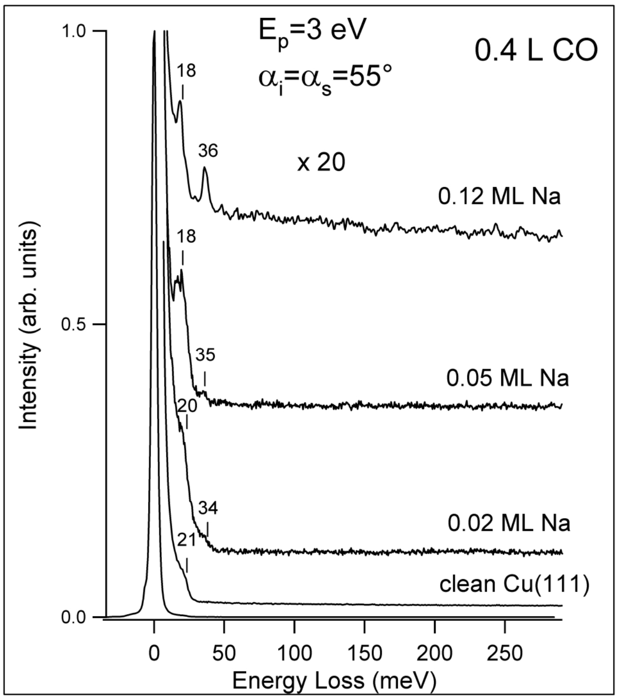

Figure 3: HREEL spectra for different amounts of Na deposited onto the Cu(111) surface and successively exposed to 0.4 L of CO. No critical precoverage for CO dissociation exists. The peak at 21 meV recorded for the clean Cu(111) surface is assigned to the copper optical phonon [50].

On the contrary, on alkali-precovered Ni(111) surfaces CO adsorption was molecular at room temperature up to a critical precoverage, i.e. the saturation of the first layer (Figure 4). The Na-Ni stretching peak shifted from 10 to 24 meV as a function of Na coverage. The C-O stretching continuously shifted down to 186 meV as a consequence of the increasing Na/CO ratio.

At the highest Na coverage loss spectra revealed the occurrence of a partial CO dissociation at 0.40 ML Na even at room temperature. In fact, a close inspection of the corresponding loss spectrum (Fig. 4b) revealed two new loss feature at 36 (Na-O vibration) and 55 meV. The peak at 55 meV is assigned to a C-derived vibration [51].

A possible explanation for the existence of a critical Na coverage for CO dissociation on Ni(111) can be given assuming an important role for lateral Na-CO interactions which weaken the C-O stretching bond up to dissociation. Very likely, several Na atoms are involved in this process. At low coverages, Na atoms are expected to be uniformly spread over the surface because of the repulsion due to their large dipole moments. Whenever the distance is long only electrostatic interaction exists, which was found to be not predominant in alkali promotion effects [52]. At higher coverages, each Na atom is obliged to get closer to each other, so that each CO molecule can interact with more than one alkali metal atom. However, the Na-CO distance has to be closer on Cu(111) as CO can adsorb only in sites directly adjacent to the alkali adatoms.

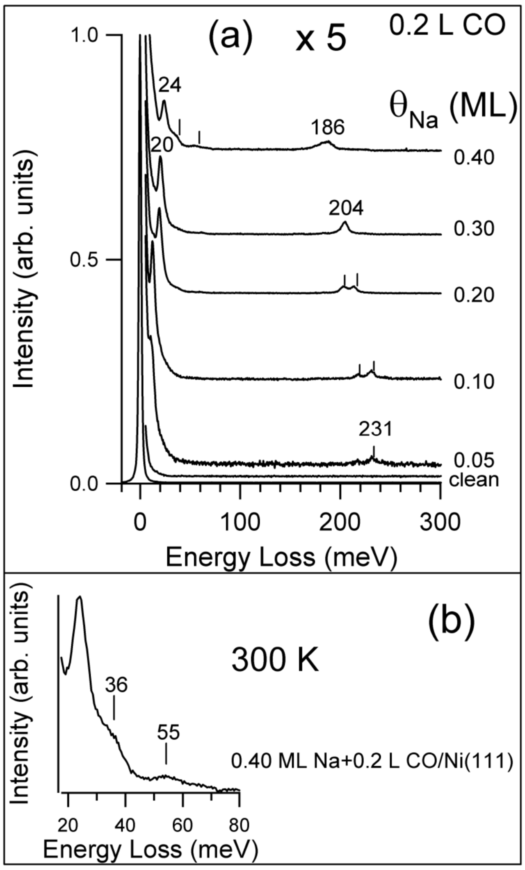

Figure 4: (a) HREEL spectra of various coverages of Na deposited onto the Ni(111) surface at 300 K and exposed to 0.2 L of CO at the same temperature; (b) Magnification of the spectrum of 0.40 ML Na/Ni(111). Two loss features at 36 meV (O-Na) and 55 meV (C-Na) were recorded.

3.2 K coadsorption with CO

Similar findings were found also substituting Na with K A molecular CO adsorption was revealed for K+CO/Ni(111) (Figure 5). On the contrary, on Cu(111) CO molecules dissociated.

Figure 6 shows HREEL spectra acquired for 0.05 ML K/Cu(111) and for the same surface exposed to 0.4 L of CO. The K-Cu vibration was measured at 15 meV for the clean K/Cu(111), in agreement with previous measurements for K adsorbed on copper surfaces [53, 54]. Upon CO exposure, a partial CO dissociation was revealed as indicated by the appearance of a well distinct O-K peak at 23 meV. The observation of the C-O stretching at 180 and 197 meV indicates that only a part of CO molecules dissociates. The presence of two C-O features is ascribed to different local [K]:[CO] stoichiometries. As a consequence, different environments for CO molecules exist, thus implying different shifts of the C-O vibration compared with the value of C-O stretching on clean copper surfaces, i.e. 255-258 meV [55, 56]. It is worth noticing that K-Cu vibration red-shifted down to 13 meV in the K+CO coadsorbed phase, as a consequence of the CO-induced lengthening of the alkali-substrate bond [40, 41]. The increased intensity of the K-Cu vibration in the K+CO coadsorbed phase is ascribed to the CO-derived depolarization effect [57], as a consequence of the enhanced ionic character of the alkali-substrate bond upon coadsorption with CO [8].

It should be noticed that also a peak at 64 meV appeared upon CO exposure. Such peak may be ascribed (see also the discussion of spectra for Na+O/Cu(111) in Figure 8) to a vibration arising from O adatoms in subsurface sites [58-60].

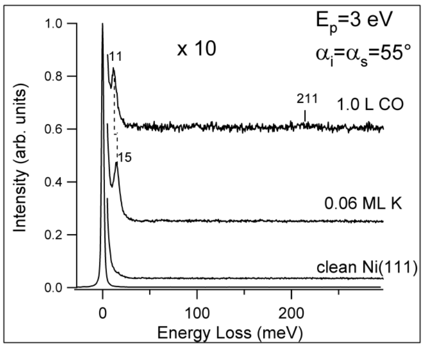

Figure 5: HREEL spectra for 0.03 ML K/Ni(111) exposed to 2 L CO at room temperature. The CO-induced shift is of only 4 meV, so as not to allow the separation of the two K-Ni features due to the not sufficient experimental resolution.

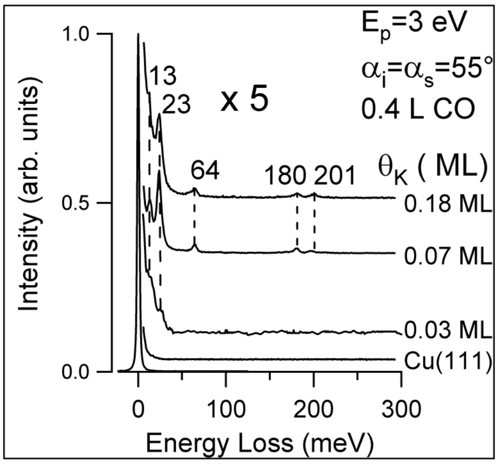

FIG. 6. HREEL spectra for various coverage of K deposited at 400 K on Cu(111) and exposed to CO at 300 K. Measurements were carried out at 300 K. A partial CO dissociation was argued by the presence of O-related modes.

3.3 Na coadsorption with O

Figure 7 shows HREEL spectra of 0.05 ML Na/Ni(111) exposed to small quantities of O_2. A splitting of the Na-Ni vibration was revealed upon small O_2

exposures. Further oxygen exposures did not cause remarkable changes in the HREEL spectrum. The appearance of a higher energy component for Na-Ni stretching could be ascribed to an O-induced shortening of Na-Ni bond. As the technique does not allow direct evidences of changes in bond distances, accurate structural studies are needed to further support this suggestion. An explanation in the framework of the electrostatic model has to be excluded. In fact, the O-Ni bond is largely covalent and, thus, the O-induced electrostatic field should be relatively small and it would have only little effects on the Na-Ni bond.

A small blue-shift of the alkali-substrate vibration energy upon oxygen exposure was also revealed for Cs/Ru(0001) [57]. The Cs-Ru vibration shifted from 8 to 10 meV. However, the authors did not discuss such finding.

The O-Ni vibration shifted from 70 meV, recorded for p(2x2)-O/Ni(111) [19, 33, 61], to 63 meV. The O-Ni bond is softened in the alkali+O coadsorbed phase, in agreement with theoretical calculations suggesting a short-range alkali-induced population of O 2 p_z anti-bonding orbitals.

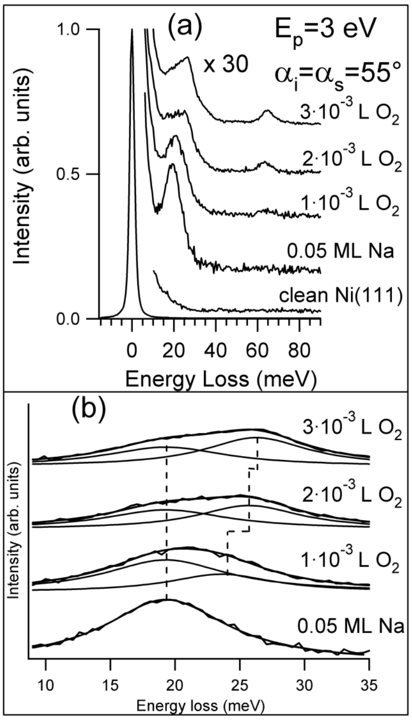

Figure 7: HREEL spectra of Ni(111) and 0.16 ML Na/Ni(111) exposed to O_2 molecules at 400 K. (b) Each curve was obtained following the same procedure of Fig. 1b.

A similar experiment was carried out on Cu(111). Loss spectra for 0.06 ML of Na on Cu(111) and for (Na+O) are reported in Fig. 8. The loss peak observed at 22 meV was assigned to the Na-Cu vibration, as also for K adsorbed on other metal substrates[17]. For small O_2 exposures a loss feature at 58 meV arose in the spectrum.

Previous HREELS studies on O/Cu(111) [62] found the O-Cu vibration at 46 meV. As concerns the adsorption of molecular oxygen [62], it is allowed on Cu(111) only up to 230

K, as indicated by the presence of vibrations related to bridged peroxo and atop species at 77 and 108 meV, respectively.

As regards the peak at 58 meV, its vibration energy suggests the occurrence of atomic oxygen adsorption on subsurface sites. As expected, the presence of O in a higher coordination site leads to the appearance of a feature with higher vibration energy in the loss spectrum. On silver surfaces, O adsorption in the octahedral subsurface sites was argued from the presence of a loss peak at 53-59 meV [58-60]. However, on Ag the subsurface site for O is metastable [58-60], i.e. it is accessible only after the complete occupation of available on-surface sites. Similar conclusions were reached by theoretical results for O adsorption on clean Cu(100) [63, 64]. On the contrary, for Na-doped Cu(111) the energetic conditions are completely reversed, as shown in Figure 1. In the first stage of O adsorption, only subsurface sites are occupied. Such finding deserves particular attention for potential applications as subsurface oxygen have been widely demonstrated to play an important role in activating chemical reactions [37, 38, 65-69].

No trace of O adsorption on the clean Cu(111) surface was recorded even after prolonged O_2 exposures for temperatures between 300 and 500 K.

It is worth mentioning that also the occurrence of a Na-promoted formation of Cu_2O has to be excluded, for the lack in the loss spectrum of the infrared-active mode at 79 meV [70] indicative of the oxidation of the copper surface.

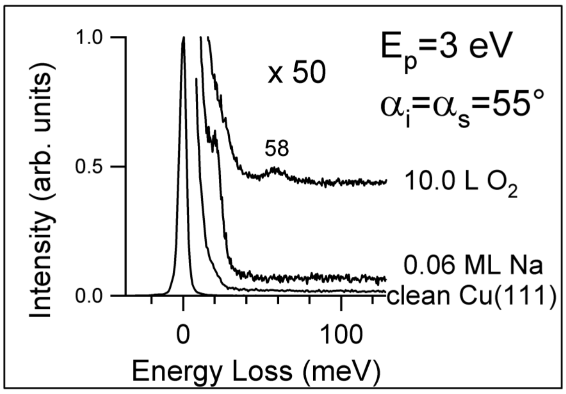

Figure 8: HREEL spectra for O/0.06 ML Na/Cu(111).

3.4 K coadsorption with O

For O+K/Cu(111), besides subsurface oxygen (peak at 57-61 meV), also over-surface O vibration against Cu(111) was observed at 46 meV (Figure 9). As for subsurface O on clean silver surfaces, annealing caused the disappearance of the subsurface species.

As regards K+O/Ni(111), no significant differences with respect to Na+O/Ni(111) were observed (Figure 10). No subsurface species were revealed for Ni, as also found on rhodium [71]. Such findings suggest a general different behavior of noble-metal and transition-metal catalysts.

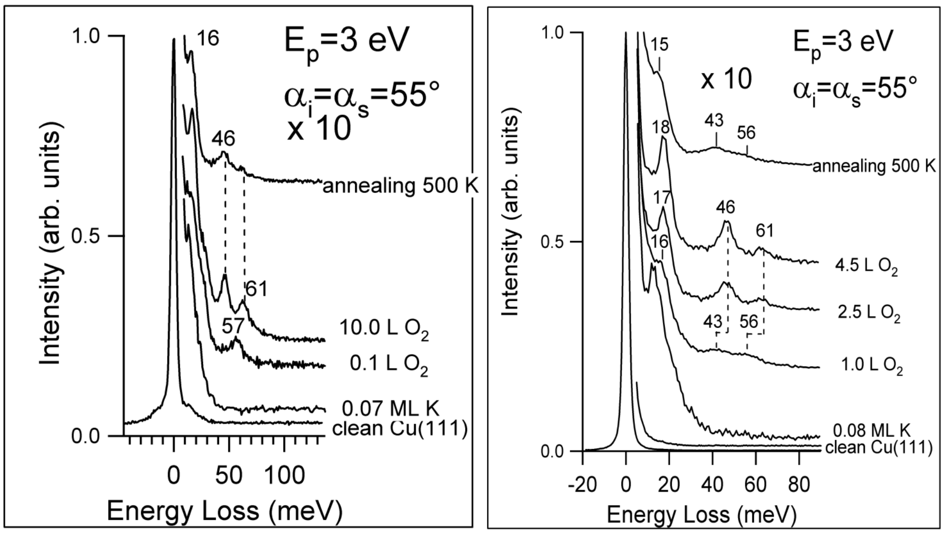

Figure 9: (left panel) HREEL spectra for 0.07 ML K/Cu(111) as a function of O_2 exposure. In the first stage, only subsurface site was populated by oxygen adatoms; (right panel) the same, but for a different K/O ratio. At the saturation the intensity of over-surface O-Cu vibration dominates.

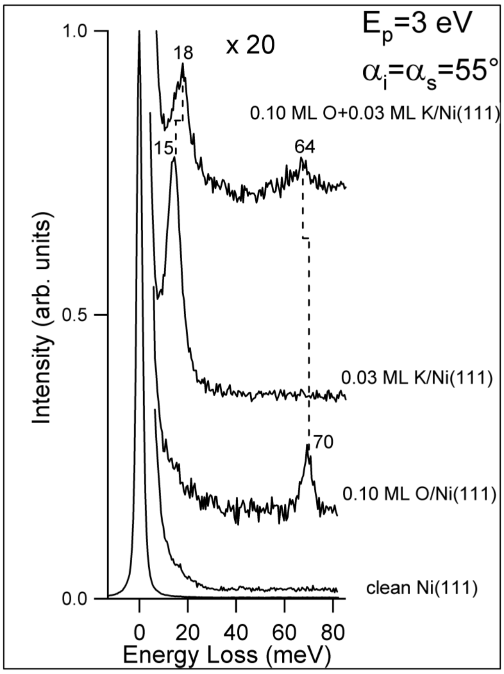

Figure 10: HREEL spectra of: (a) 0.03 ML of K deposited at 400 K onto the Ni(111) surface (b) 0.10 ML O/Ni(111) at the same temperature (c) 0.03 ML K coadsorbed at 400 K with 0.10 ML of O on the Ni(111) surface.

3.5 Alkali oxidation

Loss measurements provided direct evidences of a more efficient alkali oxidation rate (finely controlled via the formation of the alkali-O bond) in alkali coadsorption with CO with respect to alkali+O. Unexpectedly, no alkali-O bond was revealed for O/alkalis. On the contrary, alkali oxidation was easily achieved by CO exposures. We suggest that the very local interaction between alkali and CO could enhance the CO dissociation rate and the alkali oxidation efficiency (alkali-O bond), in agreement with density-functional calculations [52]. Such effect is even more evident on Cu(111), which is less reactive towards CO adsorption compared with Ni(111).

Figure 11 shows HREEL spectra for alkalis (Na, K) on both Cu(111) and Ni(111) acquired after an exposure to 0.4 L of CO at room temperature. The formation of alkali-O bonds was revealed by the appearance of features at 36 meV for CO/(3/2x3/2)-Na on both Cu(111) (spectrum a) and Ni(111) (spectrum b) and at 24-29 meV for CO/p(2x2)-K on both Cu(111) (spectrum c) and Ni(111) (spectrum d). CO adsorption is partially dissociative for all such systems, except for Na/Cu(111), for which it is fully dissociative as suggested by the absence of C-O stretching features (recorded for the other systems in the range 169-197 meV). Carbon-derived modes at 59 meV [51] (arising from CO dissociation) were observed only for alkalis/nickel.

It is worth noticing that for K/Cu(111) part of the oxygen arising from CO dissociation does not bond with alkali adatoms but instead migrates underneath the surface in subsurface adsorption sites, as suggested by the occurrence of the feature at 57 meV [58-60].

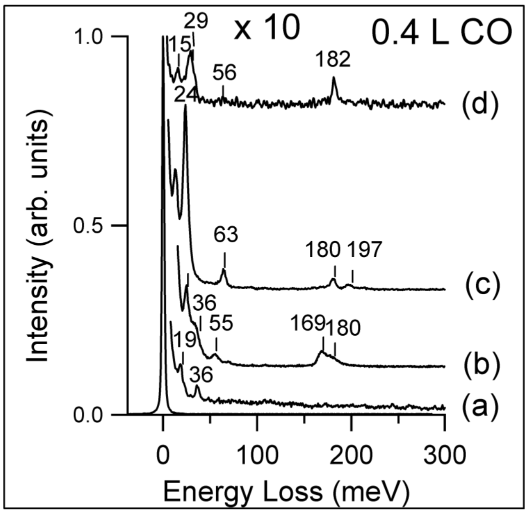

Figure 11: HREEL spectra at 300 K (at a fixed CO exposure of 0.4 L) for: (a) (3/2x3/2)-Na/Cu(111); (b) (3/2x3/2)-Na/Ni(111); (c) p(2x2)-K/Cu(111); (d) p(2x2)-K/Ni(111).

Unexpectedly, for O_2 exposures no alkali-O bond was formed (Figure 12). Besides alkali-substrate vibrations (23 meV for Na and 16-18 meV for K), only O-related features were revealed. The appearance of O-Ni at 65 meV (red-shifted by the presence of alkalis [33, 52], spectra a and b) indicates the O remains on surface on Ni(111), while for O/K/Cu(111) (spectrum d) oxygen adatoms are both in over-surface (46 meV feature [62]) and in subsurface sites. Interestingly, in spectrum c, acquired for a CO-modified Na/Ni(111) surface (by pre-dosing 0.2 ML of CO on the clean surface), the Na-O bond was formed (loss at 33 meV), thus indicating the pivotal role of CO in alkali oxidation.

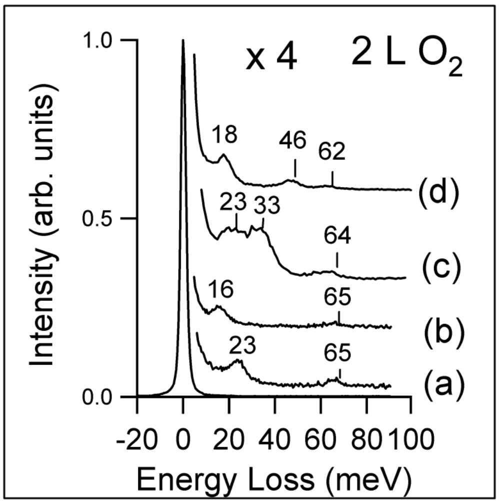

Figure 12: HREEL spectra (at a fixed O_2 exposure of 2 L) for (a) 0.1 ML Na/Cu(111); (b) 0.1 ML K/Ni(111); (c) (√3x√3)R30°-Na/0.2 ML CO/Ni(111); (d) p(2x2)-K/Cu(111).

Present results for CO-promoted alkali oxidation are well interpreted within the framework of the electrostatic model. For CO adsorbed in adsorption sites directly adjacent to alkali adatoms, the lowered potential stabilize the electronegative adsorbate and activate a charge transfer from the surface to 2 π^* anti-bonding orbitals, so as to facilitate CO dissociation. It is worth mentioning that the formation of a direct bond between the alkali adatom and the O atom of the CO molecule was invoked by Bonzel [72] to explain isotope exchange occurring in alkali coadsorption with CO. Moreover, K-O π resonances were revealed in the oxygen K-edge for K+CO/Co(10-10) [15]. On the other hand, short-range interactions have been unambiguously demonstrated to be predominant in alkali coadsorption with CO [73].

Accordingly, the real alkali promotion effects should be associated to a geometrical configuration in which the distances between alkali-metal atoms and reactants are quite short, i.e. about 3 Å, so as to allow the orbital overlap and the formation of a direct bond [52]. We are led to suggest the existence of a geometry of the alkali+CO coadsorbed phase that favours the direct bonding between alkalis and the O atoms of the CO molecules.

On the contrary, it is quite unexpected the lack of alkali oxidation in O/alkalis. It is quite surprising that the two coadsorbed species do not interact each others, but directly with the substrate, even for higher oxygen exposures (not shown). In fact, oxygen and alkalis are expected to strongly interact each other, especially for high oxygen or alkali precoverages. Very likely in the alkali+O coadsorbed phase on Ni(111) and Cu(111) the distance between O and the alkali adatom should be always higher than 4 Å. In fact, theoretical calculations [52] demonstrated that a direct O-alkali bond forms only for very close distances, i.e. 3 Å, due to the direct overlap of orbitals. Weak electrostatic interactions between alkalis and O dominate (without the occurrence of alkali oxidation) also for distances of 4 Å.

4. Conclusions

HREELS measurements reported here provided direct evidences of a substrate-independent weakening of the alkali-substrate bond in the alkali+CO coadsorbed phase. Moreover, CO was found to efficiently promote alkali oxidation much more than O_2. Short-range effects dominated the alkali interaction with coadsorbates (CO, O). No critical precoverage for CO dissociation was found on Cu(111), in contrast with results obtained for Ni(111). Alkali induced a softening of the O-Ni bond well described within the framework of the electrostatic model. On the contrary, such mechanism is not efficient for copper, where alkali doping renders negative the adsorption energy of subsurface site for O. Present results should open new pathways in understanding heterogeneous catalysis on metal surfaces.

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PAPER XVI

Unexpected alkali-promoted CO dissociation on Cu(111) at room temperature

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Alkali-promoted CO dissociation on Cu(111) and Ni(111) at room temperature

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The coadsorption of alkalis (K, Na) and CO on Cu(111) was investigated by high-resolution electron energy loss spectroscopy. Measurements performed at room temperature showed that CO adsorption is partially dissociative on a potassium-precovered Cu(111) surface and fully dissociative for Na/Cu(111). Carbon monoxide molecules occupy adsorption sites directly adjacent to those of alkali adatoms, as suggested by the absence of a threshold alkali precoverage for CO dissociation. On the contrary, for alkali+CO/Ni(111) a threshold alkali precoverage for CO dissociation was found to exist. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2996133]

I. INTRODUCTION

The understanding of heterogeneous catalysis, which is the foundation of the chemical industry, and the tailoring of more selective catalysts are the main motivations for studying chemical reactions at surfaces. Alkali promotion effects in heterogeneous catalysis have been widely studied with a variety of techniques as alkali metals strongly enhance the rate of many catalytic reactions.[1–5] As a matter of fact, the adsorption of alkali-metal atoms changes the electronic structure of the surface, thus inducing strong modifications in the catalytic properties of the substrate.[6,7]

In particular, the dissociation of CO in the Fischer–Tropsch process[8] is a key catalytic reaction step, which is notably influenced by alkali metals added as promoters to transition-metal catalysts.[9–15] Experimental evidence of CO dissociation caused by alkali doping has been reported for many of the Fischer–Tropsch metal-catalyst surfaces.[16–19]

On the contrary, no clear picture has emerged yet to fully explain the alkali-induced dissociation on noble-metal surfaces. The adsorption of CO on low-index copper surfaces modified by submonolayers of alkali metals is not dissociative,[20–28] while CO dissociation was observed on stepped copper surfaces in the presence of potassium.[29–32] From these measurements, it was suggested that the CO dissociation process primarily occurs at the steps. In fact, the presence of steps would cause an electric field with a lateral component which induces a quite high occupation of the antibonding $2\pi^*$ orbitals so as to cause the dissociation of CO molecules in the close vicinities of step.[29]

The alkali promotion effects on CO dissociation were found to be related to both the short-range electrostatic interaction and the direct orbital overlap.[14] In particular, the direct CO-alkali bond significantly enhances the efficiency of CO dissociation. Accordingly, the dissociation barrier is lowered only for short alkali-CO distances (2–3 Å).

Previous measurements reporting a nondissociative CO adsorption on alkali-doped flat copper surfaces[20–28] were performed at temperatures ranging from 100 to 180 K. A study at room temperature is still lacking. On the other hand, the increased temperature could imply strong modifications of the bonds between coadsorbates so as to facilitate CO dissociation.

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on alkali (Na, K) coadsorption with CO on the Cu(111) and Ni(111) surfaces. Contrary to the common expectations, we found that the dissociation barrier for CO molecules is lowered on alkali-modified Cu(111) surfaces compared with an alkali-doped transition-metal substrate. In the case of Cu(111), the CO dissociation occurs for all alkali coverages investigated; on the contrary, on Ni(111) CO dissociation at room temperature is allowed only when the substrate is covered by a monolayer of alkalis.

The coadsorption of alkali-metal atoms and carbon monoxide molecules on copper surfaces (and, in general, on single-crystal metal surfaces) is characterized by a large decrease in the C–O stretching frequency,[33,34] an increase in the heat of adsorption of both alkali-metal and carbon monoxide,[35,36] and changes in core and valence level binding energies of CO.[37,38] The general picture of the promotion effect is that the intramolecular C–O bond is weakened, while the metal-CO bond becomes stronger in the presence of alkali metals.[33,39] The detailed description of the above effect involves various models including substrate-mediated charge transfers,[40,41] direct bond through complex formation,[42] electrostatic interactions,[43–45] and the nonlocal alkali-induced enhancement of the electronic surface polarizability.[46] As concerns the structural investigations, alkali adsorption on copper surfaces was found to induce a rearrangement of the substrate via relaxation, reconstruction,

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and faceting, as suggested by scanning tunneling microscopy and low-energy electron diffraction (LEED).[47] For alkali coadsorbed with CO on copper surfaces the formation of a CO-alkali complex was reported.[20,22,25] A direct interaction between alkalis and CO was observed by ultraviolet photoemission spectroscopy[22] and HREELS.[20] Moreover, the CO adsorption site was found to change upon coadsorption.[20,25] The CO desorption temperature increased,[20] as a consequence of the coadsorption-induced mutual stabilization of both alkalis and CO.

II. EXPERIMENTAL

Experiments were carried out in an UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were single-crystal surfaces of Cu(111) and Ni(111) with a purity of 99.9999%. The substrate was cleaned by repeated cycles of ion sputtering and annealing at 800 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and LEED measurements, respectively. The Cu(111) and Ni(111) surfaces showed an excellent LEED pattern characterized by sharp spots against a very low background. Potassium and sodium atoms were deposited onto the substrate by evaporating from a well-outgassed commercial getter source. Very clean alkali layers could be obtained by keeping the sample at 400 K during depositions. The necessity of such a procedure in order to avoid contamination of the alkali layer was demonstrated elsewhere.[7,39] Alkali coverages were estimated by both AES and LEED (the coverage of 1 ML is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate). Loss spectra were taken in the specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of our spectrometer ranged from 2 to 3 meV. Measurements and CO exposures were carried out at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows HREEL spectra acquired for 0.05 ML K/Cu(111) and for the same surface exposed to 0.4 L of CO ($1\ \mathrm{L}=1.33\times10^{-6}$ mbar s). The K–Cu vibration was measured at 15 meV for the clean K/Cu(111), in agreement with previous measurements.[48,49]

Upon CO exposure, a partial CO dissociation was revealed as indicated by the appearance of a very intense O–K peak at 23 meV and a feature at 63 meV due to subsurface oxygen species[50–52] arising from CO dissociation [oversurface O vibration against Cu would be found at 46 meV (Ref. 53)]. The latter assignment is supported by HREELS measurements (not shown herein) for alkalis coadsorbed with O on Cu(111). The observation of the C–O stretching at 180 and 197 meV indicates that only a part of CO molecules dissociates. The presence of two C–O features is ascribed to different local [K]:[CO] stoichiometries. As a consequence, different environments for CO molecules exist, thus implying different shifts of the C–O vibration compared with the value of C–O stretching on clean copper surfaces, i.e., 255–258 meV.[54,55] We argue that dissociating CO molecules are in close contact with alkalis. Instead, CO molecules adsorbed far from alkalis exhibit only a weakened C–O bond without dissociation. It is worth noticing that K–Cu vibration redshifted down to 12 meV in the K+CO coadsorbed phase, as a consequence of the CO-induced lengthening of the alkali-substrate bond.[56,57] The increased intensity of the K–Cu vibration in the K+CO coadsorbed phase is ascribed to the CO-derived depolarization effect,[58] as a consequence of the enhanced ionic character of the alkali-substrate bond upon coadsorption with CO.[59]

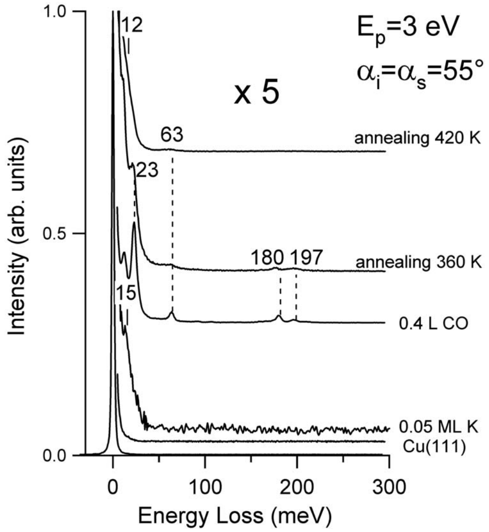

FIG. 1. HREEL spectra for 0.05 ML K deposited at 400 K on Cu(111) and exposed to CO at 300 K. Measurements were carried out at 300 K. All spectra were multiplied by the same factor. The intensity of all peaks was normalized to that of the elastic peak.

Annealing the surface up to 360 K caused a decreasing in the intensity of all vibrational peaks. Further annealing up to 420 K caused the desorption of most CO molecules. On the other hand, the vibrational modes of K atoms and subsurface O are still present in the HREEL spectrum.

The analysis of HREEL spectra acquired for several K coverages on Cu(111) exposed to 0.4 L of CO (Fig. 2) indicates that no threshold precoverage for CO dissociation exists. For 0.18 ML K, almost all alkali adatoms are bonded with oxygen coming from CO dissociation, as suggested by the reduced intensity of K–Cu vibration at 13 meV compared with that of O–K stretching at 23 meV. Similar conclusions were reached substituting K with Na (Fig. 3). The O–Na vibration at 34–36 meV was revealed even at the lowest Na precoverages. Interestingly, no subsurface oxygen was observed for Na+CO/Cu(111), thus suggesting a major role of potassium in inducing the migration of oxygen adatoms coming from CO dissociation underneath the substrate with respect to sodium.

The investigation of the dependence of the alkali promotion effects on the average alkali-CO distance has been recently studied by density-functional theory calculations for K+CO/Rh(111) by Hu and Liu.[14] They found that the alkali promotion in CO dissociation strongly depends on the dis-

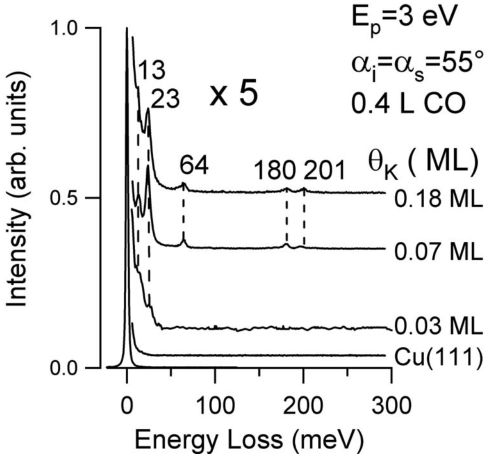

FIG. 2. HREEL spectra for various coverages of K deposited at 400 K on Cu(111) and exposed to CO at 300 K. Measurements were carried out at 300 K. A partial CO dissociation was argued by the presence of O-related modes.

tance between the alkali adatom and the dissociating CO molecule. Whenever the average distance between alkali and CO is long, the interaction between them is mainly electrostatic. If the average distance is shorter (2–3 Å), a direct bond between coadsorbates occurs, which reduces the dissociation barrier for CO molecules.[14]

However, it is worth mentioning that the sticking coefficient for CO molecules on copper surfaces at 300 K is extremely reduced compared with transition-metal surfaces (Ni, Pt, Ru). In fact, the saturation coverage for CO molecules on clean copper coverage was found to be about zero for temperatures higher than 200 K,[60] while for Ni(111) the surface was found to be fully covered by CO molecules at 300 K even for small CO exposures.[61,62] Accordingly, it is quite expected that CO adsorption on alkali-modified copper substrates might occur only in the close vicinity of alkali adatoms. Results reported in Figs. 2 and 3 fully confirm the picture proposed in Ref. 14.

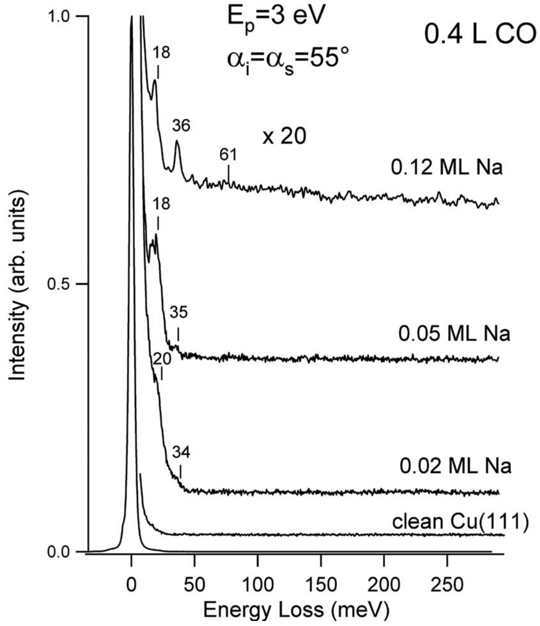

FIG. 3. HREEL spectra for various amounts of Na deposited at 400 K on Cu(111) and exposed to CO at 300 K. The absence of C–O stretching ensures that all CO molecules dissociated. Loss features recorded at 34–36 meV are assigned to the vibration of Na against O adatoms arising from CO dissociation.

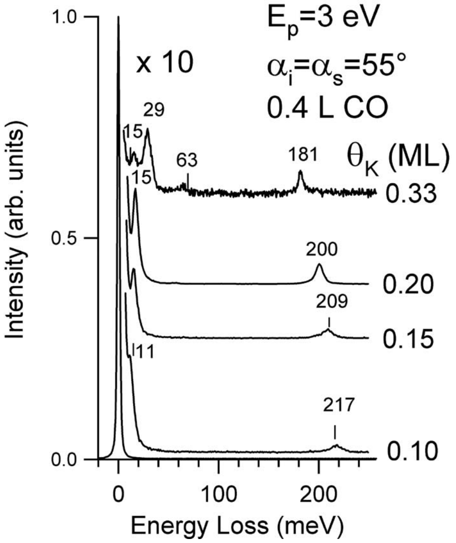

FIG. 4. HREEL spectra of various coverages of K deposited onto the Ni(111) surface at 300 K and exposed to 0.4 L of CO at the same temperature. The appearance of loss features at 29 and 63 meV, ascribed to the O–K and the O–Ni vibrations, respectively, indicates the partial dissociation of CO molecules.

Another factor that should be considered is the surface diffusion of CO molecules, that has been demonstrated to influence catalytic reactivity[63,64] even for low temperatures (35–53 K). The importance of such process is surely enhanced at room temperature, so as to allow diffusing CO molecules to reach alkali adatoms and form a direct alkali-CO bond, leading to CO dissociation.

For the sake of a comparison, we studied the CO adsorption on alkali-modified Ni(111) surfaces as a function of the alkali (K, Na) precoverage. Interestingly, a strong dependence on alkali precoverage was found to exist in this case. The threshold precoverages for CO dissociation are 0.33 and 0.40 ML for K (Fig. 4) and Na [Fig. 5(a)], respectively. In fact, for 0.33 ML K/Ni(111) the K–O stretching appeared at 29 meV upon CO exposure (last spectrum of Fig. 4). Likewise, a close inspection of the loss spectrum of the CO-exposed 0.33 ML Na/Ni(111) surface [Fig. 5(b)] revealed two new loss features at 36 (O–Na vibration) and 55 meV. The peak at 55 meV is assigned to a C-derived vibration.[65]

As concerns the C–O intramolecular bond, the C–O stretching shifted from 217 down to 181 meV as a function of K coverage (Fig. 4). Likewise, a redshift of the C–O stretching from 231 down to 186 meV was recorded in the Na+CO coadsorbed phase (Fig. 5). As in Figs. 1 and 2, the two C–O stretching peaks revealed for intermediate Na coverages (0.10–0.20 ML) were ascribed to different [Na]:[CO] local stoichiometries.[66,67] For higher coverages, these features merged into a single C–O stretching, thus suggesting the occurrence of a quite homogeneous Na/CO ratio along the surface.

Present measurements reveal striking differences toward CO dissociation on alkali-modified Cu(111) and Ni(111) surfaces. On alkali-doped Cu(111), CO dissociation occurs re-

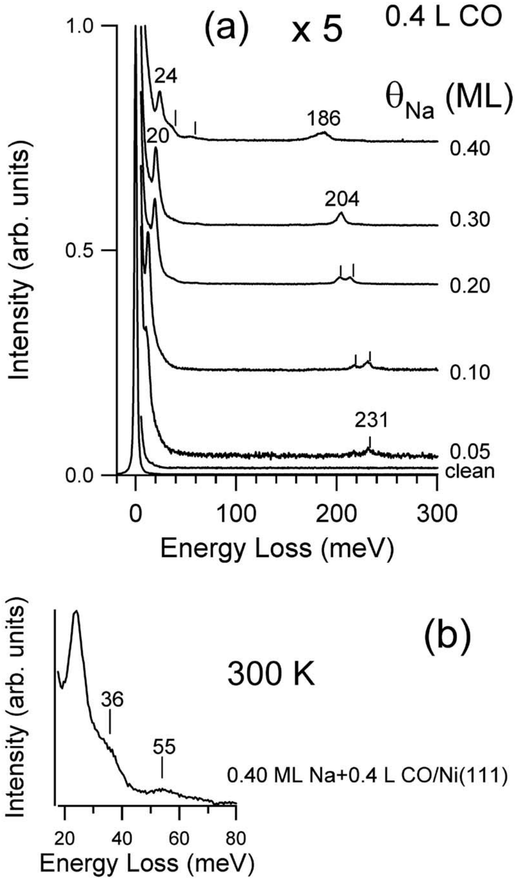

FIG. 5. (a) HREEL spectra of various coverages of Na deposited onto the Ni(111) surface at 300 K and exposed to 0.4 L of CO at the same temperature. (b) Magnification of the spectrum of 0.40 ML Na/Ni(111). Two loss features at 36 meV (O–Na) and 55 meV (C–Na) were recorded.

gardless of the alkali precoverage. On the contrary, on Ni(111) CO dissociation was observed only after deposition of about a complete monolayer of alkalis. We suggest that very likely this behavior arises from the higher dissociation barrier for CO molecules on Ni(111) due to the larger adsorption energy of CO on Ni compared to Cu. Hence, a threshold alkali coverage is needed on Ni(111) in order to allow CO dissociation at room temperature.

On the Ni(111) surface CO can adsorb also far from the alkali adatoms as a consequence of the great reactivity of transition-metal surfaces[61,62] toward CO adsorption with respect to noble-metal substrates.[60] If the alkali-CO distance is more than 4 Å only electrostatic interaction exists, which was found to be not predominant in alkali promotion effects.[14]

Experiment carried out at 400 K revealed that the threshold Na precoverage for CO dissociation is reduced to 0.10 ML. Likewise, the threshold K precoverage at 400 K was found to be 0.15 ML, i.e., lower than at room temperature.

In conclusion, HREELS measurements reported here provided direct evidences of the occurrence of CO dissociation also on alkali-modified Cu(111) surface at room temperature. Carbon monoxide dissociates even at the lowest alkali (K, Na) precoverages on Cu(111), as a consequence of the local alkali-CO interaction causing a drastic reduction in the dissociation barrier for CO molecules. On the contrary, a threshold alkali precoverage for CO dissociation was found for alkalis/Ni(111). We suggest that this different behavior toward CO adsorption between these two alkali-modified surfaces could be interpreted assuming for the alkali/Cu(111) a more effective direct and short-range alkali-CO interaction, very likely favored by CO diffusion.

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PAPER XVII

Alkali-promoted stabilization of subsurface oxygen on Cu(111)

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Alkali-promoted stabilization of subsurface oxygen on Cu(111)

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The coadsorption of alkalis (Na, K) with O on Cu(111) and Ni(111) was studied by vibrational measurements. We found that even small amounts of alkali doping reverse the energetic conditions for oxygen adsorption on Cu(111), so as to render energetically favourable the population of subsurface sites. Such mechanism is not effective for the clean Cu(111) substrate and for clean and alkali-modified Ni(111) surfaces.

Recently, subsurface species have been demonstrated to activate several important chemical reactions on catalyst surfaces [1-5]. In particular, it has been shown that subsurface oxygen plays a key role in the partial oxidation of methanol to formaldehyde [6], selective CO oxidation in the presence of H_2 [7], ethylene [8] and propylene [9] epoxidation. Several dedicated studies were performed on silver surfaces [8, 10-12] with the aim to understand the enhanced reactivity of such substrates towards epoxidation chemistry. The reactivity of Ag surfaces originates from the existence of subsurface O species which induce an up-shift of the centroid of the d-band of the Ag surface [13]. The presence of subsurface oxygen reduces the activation energy for oxametallacycle (OMC) formation and increases the OMC-surface interaction [8]. On the other hand, the OMC is thought to be an intermediate in the reactive formation of ethylene epoxide. Very recently the interest in epoxidation chemistry is moving from silver to copper surfaces. Studies [13-15] carried out on single-crystal Cu surfaces demonstrated that oxygenated copper is intrinsically a much more selective epoxidation agent with respect to oxygenated silver, especially at low oxygen coverage. It seems that the main practical limitation to the use of Cu as an epoxidation catalyst arises from the stability of the epoxide. Therefore, the preparation of stabilizing epoxidation agents, and in particular subsurface O in metastable adsorption sites, is a grand challenge that remains still elusive. From a fundamental point of view, it is also essential to establish the nanoscopic conditions needed for the migration of O atoms underneath the surface.

Alkali-metal doping is a powerful tool to manipulate the physical and chemical properties of surfaces and it is widely used for tailoring new catalysts [16-21]. Alkalis are used to promote ethylene [22] and propylene [9] epoxidation. Nonetheless, their promotional role in such reactions is not well understood.

In this Communication we demonstrate that K (Na) doping of the O/Cu(111) system causes the stabilization of the metastable subsurface adsorption site for O atoms. The over-surface oxygen was revealed only after saturation of subsurface sites. The preferential occupation of subsurface site for O was observed for K+O/Cu(111) but not for O/Cu(111), O/Ni(111), and O+K/Ni(111). Similar results were obtained substituting potassium with sodium.

We argue that the presence of very small amounts of alkalis reverses the energetic conditions for oxygen adsorption on the Cu(111) surface, so as to render negative the adsorption energy for subsurface oxygen. On the contrary, in the case of clean copper surfaces and clean and alkali-modified nickel surfaces, the subsurface site was found to be energetically unfavourable. These findings suggest an enhanced reactivity of alkali-doped oxygenated copper and claim for accurate investigations on this system from both experimentalists and theoreticians.

Experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were cleaned by repeated cycles of ion sputtering and annealing at 900 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) measurements and low-energy electron diffraction (LEED), respectively. Na and K were deposited onto the substrate by evaporating from well-outgassed getter sources. During alkali depositions, the sample was kept at 400 K in order to avoid contamination of the alkali adlayer [23-25]. Oxygen molecules were admitted through precise leak valves. Alkali coverages (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate) were estimated from the exposure time taking as reference the coverage of well-known LEED structures, that is: (3/2x3/2)–Na and p(2x2)-K. A constant sticking coefficient was assumed to obtain other desired coverage. Similar results were achieved by calibrating using AES. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of the spectrometer ranged from 2 to 3 meV. A particular care was dedicated to avoid any contamination of the alkali adlayer.

Loss spectra for 0.07 ML of K on Cu(111) and for (K+O) are reported in Fig. 1. The loss peak observed at 16 meV was assigned to the K-Cu vibration, in agreement with studies performed for K deposited on other metal substrates [23]. For small O_2 exposures ($1\ L=1.33x10^{-6}$ mbar·s) a loss feature at 57 meV arose in the spectrum. For further O_2 exposures, such peak shifted from 57 to 61 meV and a new loss appeared at 46 meV. After an annealing of the surface at 500 K the intensity of the higher energy peak decreased.

Previous HREELS studies on O/Cu(111) [24] found the O-Cu vibration at 46 meV. As concerns the adsorption of molecular oxygen [26], it is allowed on Cu(111) only up to 230 K, as indicated by the presence of vibrations related to bridged peroxo and atop species at 77 and 108 meV, respectively. On the basis of such results [26], we assign the feature at 46 meV to over-surface O vibrating against Cu(111).

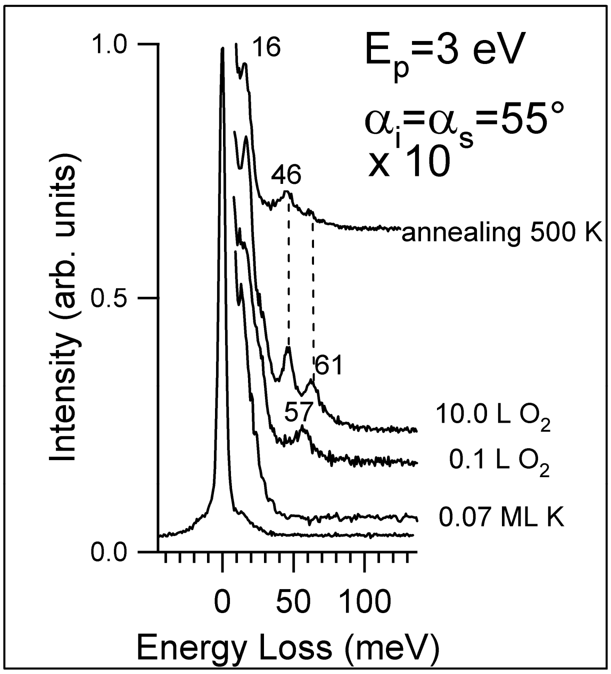

Figure 1. HREEL spectra of 0.07 ML of K deposited on Cu(111) at 400 K and successively exposed to O_2. Both O_2 exposures and measurements were carried out at 400 K. All spectra were multiplied by the same factor.

As concerns the feature at 57-61 meV, its vibration energy suggests the occurrence of atomic oxygen adsorption on subsurface sites. As expected, the presence of O in a higher coordination site leads to the appearance of a feature with higher vibration energy in the loss spectrum. On silver surfaces, O adsorption in the octahedral subsurface sites was argued from the presence of a loss peak at 53-59 meV [11, 27, 28]. The population of subsurface sites in oxygenated Ag abruptly decreased upon annealing. All these findings for O on silver surfaces fully support our assignment. However, on Ag the subsurface site for O is metastable [11, 27, 28], i.e. it is accessible only after the complete occupation of available on-surface sites. Similar conclusion were reached by theoretical results for O adsorption on clean Cu(100) [29, 30]. On the contrary, for K-doped Cu(111) the energetic conditions are completely reversed, as shown in Figure 1. In the first stage of O adsorption, only subsurface sites are occupied. At the saturation, also over-surface sites could be populated.

Moreover, spectra in Figure 1 show that the effect of alkali adatoms on the stability of subsurface oxygen is reduced once oxygen atoms adsorb also in over-surface sites. Probably this is a consequence of the formation of a direct O-K bond. In fact, upon annealing at 500 K the intensity of the feature assigned to subsurface oxygen drastically decreased. By contrast, only a slight variation in the amplitude of the O-Cu vibration at 46 meV was recorded.

In the absence of alkali doping, no trace of O adsorption on Cu(111) was revealed even after prolonged O_2 exposures for temperatures between 300 and 500 K.

It is worth mentioning that also the occurrence of a K-promoted formation of Cu_2O has to be excluded, for the lack in the loss spectrum of the infrared-active mode at 79 meV [31] indicative of the oxidation of the copper surface.

Loss measurements performed on alkali-doped Cu(111) at 300 K gave similar results.

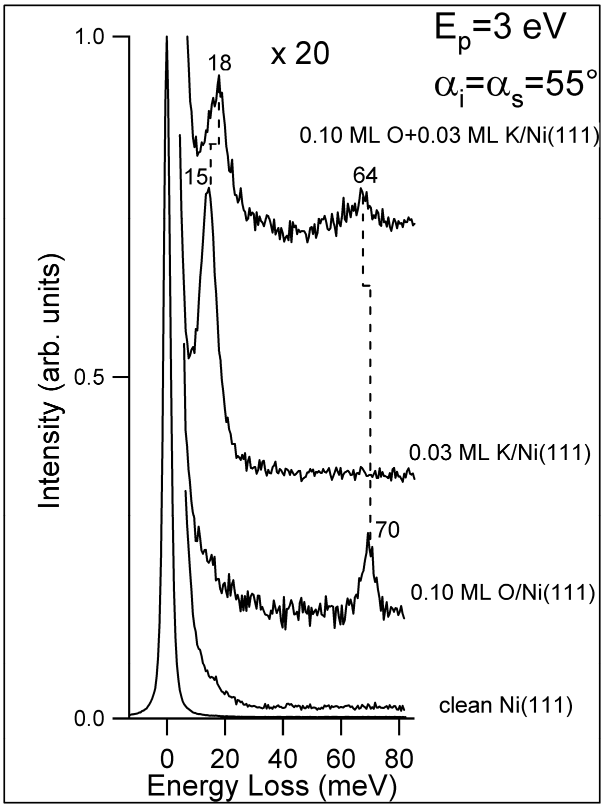

Figure 2. HREEL spectra of: (a) 0.03 ML of K deposited at 400 K onto the Ni(111) surface; (b) 0.10 ML O/Ni(111) at the same temperature; (c) 0.03 ML K coadsorbed at 400 K with 0.10 ML of O on the Ni(111) surface.

With the sake of a comparison, we studied the coadsorption of O and K on the Ni(111) surface (Figure 2) in order to verify if the same K-induced stabilization of the subsurface site for O occurs on a transition-metal catalyst. For O/Ni(111), a loss feature at 70 meV was observed for all coverages and assigned to over-surface O adsorbed on three-fold hollow sites, in agreement with all previous experimental studies [24, 32]. In the K+O coadsorbed phase, a slight shift of the O-Ni peak was revealed from 70 down to 64 meV as a function of the K/O ratio, as theoretically predicted [33] within the framework of the electrostatic model. However, no subsurface O was found (for subsurface O in Ni, a feature at energies higher than 70 meV should have been revealed in the loss spectrum). Occupation of subsurface sites is not energetically allowed also in O+K/Rh(110) [34], thus suggesting striking substrate-dependent differences on O adsorption in alkali-modified surfaces.

Likewise, subsurface oxygen was revealed in Na+O/Cu(111) (Figure 3) but not on Na+O/Ni(111) (Figure 4).

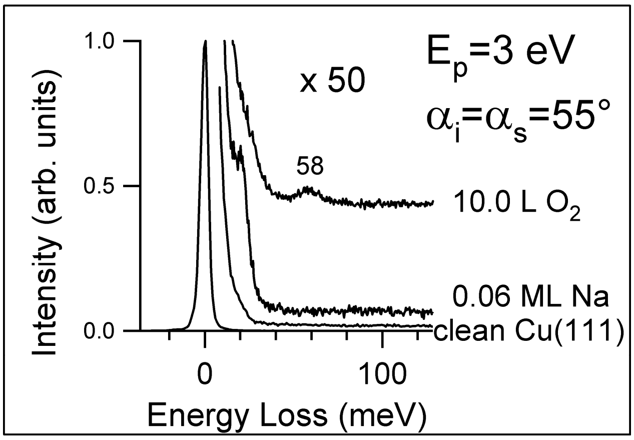

Figure 3. HREEL spectra of Na-doped Cu(111) surface and of Na+O/Cu(111). The loss feature at 22 meV is ascribed to Na-Cu vibration [23]. In Na+O/Cu(111) the presence of subsurface O is argued from the appearance of the 58 meV peak. No on-surface species were revealed for Na-doped oxygenated copper.

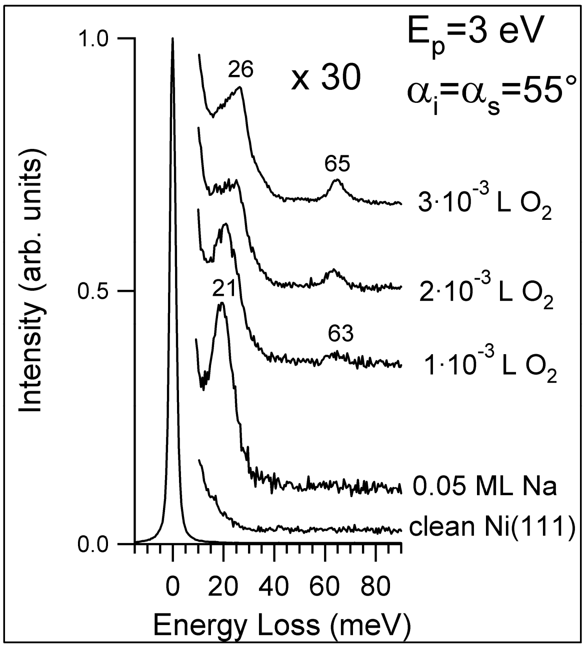

Figure 4. HREEL spectra for Na-doped Ni(111) surface: as for K+O/Ni(111) no subsurface oxygen was revealed.

In conclusion, we have reported direct evidences that alkali adsorption opens effective pathways leading to the occupation and stabilization of subsurface sites for O on Cu(111). Such mechanism is not effective for alkali+O coadsorption on transition metals, for which only on-surface O was found.

Notes and references

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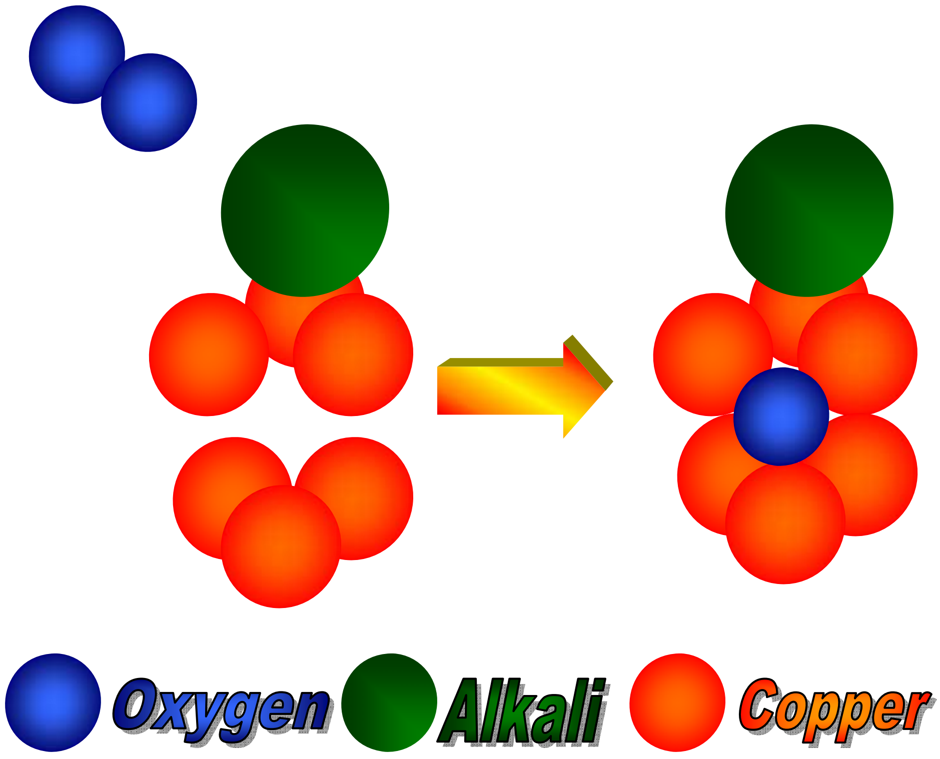

PAPER XVIII

Purely quadratic dispersion of surface plasmon in Ag/Ni(111): the influence of electron confinement

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Purely quadratic dispersion of surface plasmon in Ag/Ni(111): the influence of electron confinement

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Surface plasmon dispersion in nanoscale thin Ag films deposited onto the Ni(111) surface was investigated by angle-resolved electron energy loss spectroscopy. We found that the dispersion curve contains only the quadratic term. The vanishing of the linear term was ascribed to the presence in the film of Ag 5sp-related quantum well states. Screening effects enhanced by electron confinement in Ag quantum well states push the position of the centroid of the induced charge of the surface plasmon less inside the interface compared to other Ag systems, rendering null the linear coefficient of the dispersion curve.

1 Introduction Collective electronic excitations in semi-infinite media (surfaces), thin films, embedded particles, and supported clusters have been widely studied [1–3], as plasmonic excitations are essential for understanding dynamic screening processes and, hence, the response of the electronic gas at surfaces and interfaces. Nevertheless, many questions remained unresolved and recently a renewed interest in this topic has re-emerged [4–6]. In particular, thin films can exhibit electronic properties markedly different from the bulk counterpart as physical phenomena such as quantum size effects and electron quantum confinement may occur. It is now well established that electron quantum confinement influences many physical properties such as chemical reactivity, magnetism, superconductivity, electron–phonon coupling [7, 8]. Nevertheless, the influence of electron quantum confinement on the dispersion relation of electronic collective excitations in nanoscale thin films has not been investigated yet.

Ag surfaces are characterized by a strong lowering of the surface plasmon (SP) energy. Contrary to alkali-metal systems [1], the dispersion of Ag SP was found positive [1–3, 9–15]. Such behavior was ascribed to the presence of filled d bands. Moreover, the magnitude of this positive slope differs for different Ag crystal faces [1] and it is anisotropic for the (110) face [13]. Great efforts have been devoted to solve the controversy concerning the quadratic versus linear form of the dispersion curve. The conclusion of this long debate is that the dominant coefficient of the SP dispersion for small momenta is always linear. On the other hand, quadratic terms become important at higher values of the parallel transfer momentum $q_{\|}$. However, quadratic terms are nearly absent for Ag(100). For the sake of truth, a purely quadratic dispersion was previously invoked by Suto et al. [13] for Ag(110) and Ag(111). However, these results were questioned by successive measurements on the same systems [2, 10, 12–15].

While Ag surfaces were extensively studied [1–3, 9–15], experimental studies on low-dimensional Ag systems, such as ultrathin films on metal substrates (only studies on Si(111) exist [16, 17]), nanowires or quantum dots are still lacking.

In this Letter we present high-resolution electron energy loss spectroscopy (HREELS) measurements on SP dispersion in thin Ag layers on Ni(111). Photoemission measurements of Ag/Ni(111) [18] revealed the existence of Ag 5sp-derived quantum well states (QWS) for film thickness from 0 to 15 layers. This implies the occurrence of an enhanced sp density of states at the Fermi level that modifies the electron charge-density distribution, thus causing significant changes in the dynamical screening properties of this system. A similar behaviour was found for Na QWS on Cu(111) [19].

Measurements show that the SP exhibits a purely quadratic dispersion. We argue that this is a consequence of the dynamic screening properties of the Ag adlayer enhanced by electron quantum confinement.

2 Experimental Measurements were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Ni(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 1000 K. Surface cleanliness and order were checked using low-energy electron diffraction (LEED) and Auger electron spectroscopy measurements, respectively. Silver was deposited onto the Ni(111) surface by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈0.05 ML/min). The occurrence of the p(1 × 1)-Ag LEED pattern was used as the calibration point of $\theta_{Ag} = 1.0$ ML. A constant sticking coefficient was assumed to obtain other desired Ag coverage. Loss spectra were acquired with a primary electron beam energy of 40 eV. The energy resolution of the spectrometer was degraded to 7 meV so as to increase the signal-to-noise ratio for off-specular spectra. The measured angular acceptance α of our electron analyzer was ±0.5°. Dispersion of the collective mode, i.e. $E_{loss}(q_\parallel)$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. The sample was oriented along the $\bar{\Gamma} - \bar{M}$-direction. All depositions and measurements were made at room temperature.

3 Results and discussion Selected HREEL spectra for 10 ML of Ag as a function of the scattering angle are shown in Fig. 1. The Ag SP energy dispersed from 3.751 up to 3.880 eV.

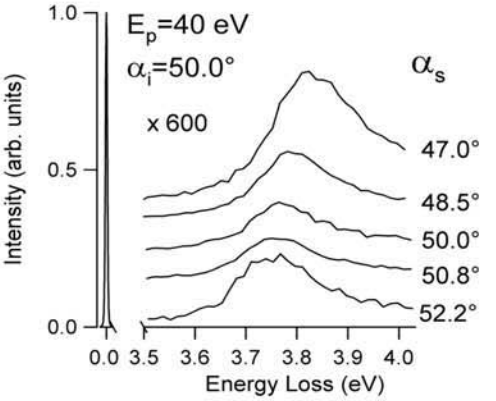

Figure 1 HREEL spectra as a function of the scattering angle for 10 ML Ag/Ni(111) at $T = 300$ K.

To measure plasmon dispersion, values for the parameters E_p, impinging energy, and θ_i, the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, $E_p = 40$ eV, provided, in fact, the best compromise among surface sensitivity, the highest cross-section for mode excitation, and $q_\parallel$ resolution. As

$$\hbar \boldsymbol{q}_\parallel = \hbar(\boldsymbol{k}_i \sin\theta_i - \boldsymbol{k}_s \sin\theta_s),$$

the parallel momentum transfer $\boldsymbol{q}_\parallel$ depends on E_p, E_{loss}, θ_i and θ_s according to

$$q_\parallel = \frac{\sqrt{2mE_p}}{\hbar}\left(\sin\theta_i - \sqrt{1-\frac{E_{loss}}{E_p}}\,\sin\theta_s\right),$$

where E_{loss} is the energy loss and θ_s is the electron scattering angle [1].

The measured dispersion curve $E_{loss}(q_\parallel)$ in Fig. 2 was fitted by a second-order polynomial given by

$$E_{loss}(q_\parallel) = A + Bq_\parallel + Cq_\parallel^{\,2},$$

where $A = (3.751 \pm 0.002)$ eV, $B = (0.000 \pm 0.004)$ eV Å, and $C = (1.57 \pm 0.04)$ eV Å^2.

Hence, the dispersion curve for 10 ML Ag/Ni(111) reported in Fig. 2 is purely quadratic, as the linear coefficient B is null. Similar results were obtained for slightly different Ag thicknesses (Fig. 2) for which QWS were also observed to exist by photoemission spectroscopy [18]. At higher thicknesses at which the discrete electronic structure of quantum well states [18] is vanishing, the dispersion curve deviates from being purely quadratic. As expected [1, 16, 17], the energy of the SP changed with Ag coverage.

According to Feibelman's model [20] of the SP dispersion, a direct relation between the linear coefficient of the

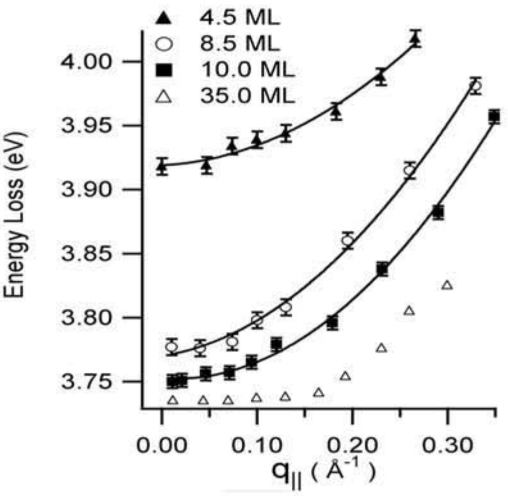

Figure 2 SP dispersion as a function of the parallel transfer momentum for 4.5, 8.5, 10.0, and 35.0 ML Ag/Ni(111) at $T = 300$ K. The solid line indicates the best-fit curve for experimental data.

Table 1 Best-fit values *A*, *B*, and *C* for different Ag surfaces [15], 10 ML Ag/Ni(111) (our data), and 10 ML Ag/Si(111) [17]. The values of $d_\perp$ were calculated by using Eq. (4) of Ref. [10]. The values for Ag surfaces were reported in the same references.

	A	*B*	*C*	$d_\perp$ (Å)
10 ML Ag/Ni(111)	3.751	0.00	1.57	–0.6
Ag(110), $\langle 1\bar{1}0\rangle$	3.683	0.14	3.60	–0.7
10 ML Ag/Si(111)	3.796	0.35	2.56	–0.9
Ag(111)	3.684	0.45	3.40	–1.3
Ag(110), $\langle 001\rangle$	3.681	0.65	3.10	–1.9
Ag(100)	3.690	1.40	0.06	–2.6

dispersion curve and the position of the centroid of the induced charge, $d_\perp$, may be found [10]. In Ag such centroid lies inside the geometrical surface ($z < 0$). The values of the dispersion coefficients and of the calculated position of $d_\perp$ for Ag single-crystal surfaces, 10 ML Ag/Ni(111), and 10 ML Ag/Si(111) are reported in Table 1. As the linear coefficient B increased, $d_\perp$ became more negative. On the contrary, no particular relationship involving the quadratic coefficient *C* exists.

Feibelman [21] considered the relation between the SP dispersion and the 4d–5s excitations induced by the field of the SP. He argued that the linear coefficient is increased in Ag(100) because the 4d electrons lie closer to the centroid of the oscillating free-electron charge. On the basis of these results, we suggest that for 10 ML Ag/Ni(111) the linear coefficient is null as the centroid of the induced charge of the SP lies much farther with respect to 4d electrons compared to other Ag systems. We ascribe this effect to screening processes [19] enhanced by the existence of Ag QWS [18]. The presence of confined electronic states in the adlayer modifies the shape of the potential barrier that becomes smoother. Very likely, dynamic screening would be more efficient for Ag thin films deposited onto metal substrates with respect to semiconductor surfaces. As a matter of fact, for Ag/Si(111) the linear coefficient of the SP dispersion was decreasing with thickness but it was always different from zero [17]. Moreover, hybridization effects should also be taken into account, as recently found for Ag films on Ge(111) with thickness up to 9 ML [22]. Their influence should be different for different substrates. Reflection (phase shifts) of the QWS wave functions depends on the interfacial hybridization with the electronic states of the substrate, thus influencing the dynamic screening properties and the electronic response of the Ag/Ni(111) interface.

4 Conclusions

Our results demonstrated that the dominant coefficient of SP dispersion for thin Ag films on Ni(111) presenting QWS is quadratic even at small $q_\parallel$, in contrast with previous measurements on Ag semi-infinite media and Ag thin films deposited on Si(111). We suggest that this behavior is due to screening effects enhanced by electron confinement in the Ag/Ni(111) shifting the position of the centroid of the induced charge less inside the geometrical surface compared to Ag surfaces and Ag/Si(111). This work provides the grounds for more accurate theoretical studies taking into account the influence of electron quantum confinement and the hybridization between adsorbate and substrate states on the electronic response of surfaces and interfaces.

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PAPER XIX

Chemical interface damping in thin Ag films
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Chemical interface damping in thin Ag films

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Abstract

The damping of electronic collective excitations of Ag/Ni(111) was studied by high-resolution electron energy spectroscopy. Loss spectra showed the usual Ag surface plasmon at 3.8 eV and a broad peak at 7.5 eV, which was assigned to the Ag multipole surface plasmon. The behaviour of the damping of the Ag surface plasmon was reported as a function of Ag thickness, primary electron beam energy, Ag surface plasmon energy, and parallel momentum transfer. The strong thickness dependence of the full-width at half maximum of the Ag surface plasmon can be associated to the presence of quantum well states in the direction perpendicular to the surface. The damping of the Ag surface plasmon was found to be related to 5sp-5sp indirect transitions, for which a critical wave vector of 0.2 Å^{-1} exists. Moreover, we reported the first evidence of the occurrence of chemical interface damping in thin films, upon K adsorption on thin Ag films deposited onto the Ni(111) surface. The significant plasmon broadening was ascribed to new channels for decay into electron-hole pairs at the K/Ag interface.

PACS: 73.20.Mf; 79.20.Uv; 79.60.Dp

Keywords: A. Thin Films; D. Plasmons; E. Electron energy loss spectroscopy

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1. **Introduction**

Plasmonic excitations in metals in either forms, semi-infinite media (surfaces), nanoscale thin layers, embedded particles, and supported clusters have been widely studied, as collective excitations have a key role in understanding the response of the electronic gas at surfaces and interfaces.

In particular, thin films can exhibit an electronic structure markedly different from the bulk counterpart. Physical properties are expected to vary, often dramatically, with thickness and physical phenomena such as quantum size effects and electron quantum confinement occur. As a matter of fact, recent experimental[1-6] studies have demonstrated the existence of variations with film thickness for properties such as the electronic density of states, electron-phonon coupling, chemical reactivity, superconductivity, magnetism, surface energy, and thermal stability.

The different distribution of occupied and unoccupied electronic states in thin films with respect to surfaces would imply enhanced damping mechanisms for collective excitations by creating electron-hole pairs.

Ag surfaces are characterized by a strong lowering of the surface plasmon (SP) energy, which follows a positive dispersion as a function of the parallel momentum transfer. Such behavior was ascribed to the presence of filled d bands[7,8]. However, experimental studies on low-dimensional Ag systems, such as ultrathin films on metal substrates (only as studies on Si(111) exist[9,10]), nanowires or quantum dots are still lacking.

Recent theoretical results[11] found that an additional broadening of the Ag Mie plasmon in nanoparticles in contact with reactive adsorbates with respect to those immersed in inert noble gas matrices exists. It is caused by the transfer of the excitation energy into adsorbate-induced levels located above the Fermi level. Accordingly, the enhanced broadening of the Mie plasmon was ascribed to such increased density of states at the Fermi level. This model, called chemical interface damping (CID), was in excellent quantitative agreement with experiments carried out on Ag nanoparticles[12]. A similar mechanism may occur for SP resonance in Ag thin film in the presence of reactive adsorbates, such as potassium. To date, to the best of our knowledge no experimental evidence of CID in thin films has been reported.

Ag on Ni(111) is a suitable system for such scopes. Moreover, it offers the possibility of investigating the relationship between quantum electron confinement and the damping of collective excitations in ultrathin films as confined electron states in the Ag adlayer exist. As a matter of fact, photoemission measurements[13] revealed the occurrence of Ag quantum well states for films with thickness from 0 to 15 layers. It is expected that the presence of quantum well states should influence the damping mechanism of the SP in Ag thin films. Furthermore, this system presents an enhanced sp density of states at the Fermi level that could ensure the conditions for the existence of the multipole surface plasmon, predicted by theoretical calculations[14].

High resolution electron energy loss spectroscopy (HREELS) is the major tool for such aims as it permits to easily follow the damping dependence of the SP on various parameters, such as Ag thickness, primary electron beam energy, Ag surface plasmon energy, and parallel momentum transfer.

In this Communication, we report on the damping of Ag SP in thin Ag films grown at room temperature on Ni(111) and, moreover, on the CID existing on K/Ag/Ni(111). Both SP energy and full width at half maximum (FWHM) of the Ag SP were found to follow a linear relation as a function of the inverse of the primary electron beam energy, thus suggesting a strong dependence on the penetration length. The loss width notably grows beyond an energy of 3.80 eV. A critical wave vector of 0.2 Å^{-1} exists. Accordingly, damping of the Ag SP is ascribed mainly to indirect 5sp-5sp indirect transition between Ag 5sp-derived quantum well states. The significant damping dependence on the Ag thickness further supports such assignment. Moreover, our measurements on K/Ag/Ni(111) provided the first evidence of CID in thin films. The SP energy red-shifted while its line shape broadened as a function of K coverage. The remarkable plasmon broadening is due to new channels for decay into electron-hole pairs at the K/Ag interface.

2. Experiment

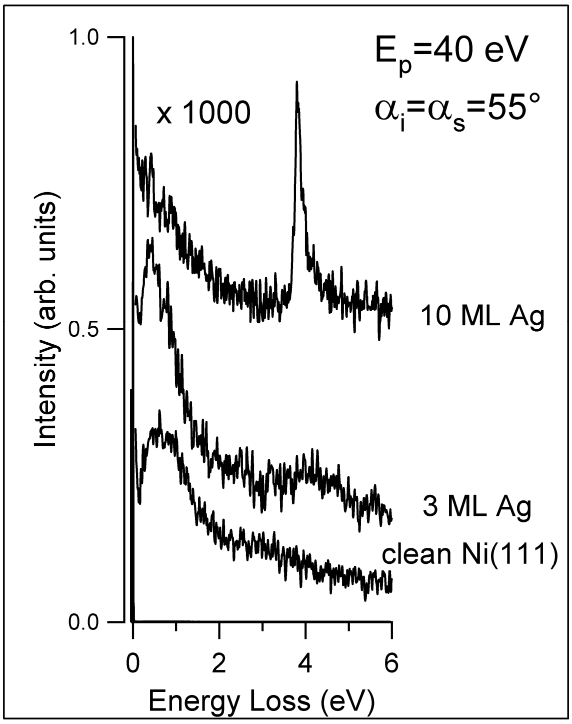
Measurements were carried out in a UHV chamber operating at a base pressure of 5x10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Ni(111) with a purity of 99.9999%. The surface was cleaned by repeated cycles of ion sputtering and annealing at 1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy measurements and low energy electron diffraction (LEED), respectively. The Ni(111) surface showed an excellent LEED pattern characterized by sharp spots against a very low background. Silver was deposited onto the Ni(111) surface by evaporating from a resistively heated drop on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈0.05 ML/min). Potassium was evaporated in the UHV chamber by means of a well outgassed dispenser (Saes Getters). The occurrence of the p(1x1)-Ag and p(2x2)-K LEED patterns was used as the calibration point of θ_{Ag}=1.0 ML and θ_K=0.25 ML, respectively. A constant sticking coefficient was assumed to obtain other desired Ag and K coverage. Loss spectra were acquired with a primary electron beam energy of 40 eV. The energy resolution of the spectrometer was degraded to 7 meV so as to increase the signal-to-noise ratio for off-specular spectra. The angular acceptance α of our electron analyzer was ±1°. All depositions and measurements were made at room temperature.

3. **Results and Discussion**

Figure 1 shows HREEL spectra for thin Ag layers on Ni(111) as a function of Ag coverage. The spectrum of the Ni(111) surface is characterized by a broad peak at 1.0 eV. For less than 2 ML of Ag, the spectrum is extremely broad without a well-defined peak. A broad Ag SP at 4.2 eV arose for Ag coverages above 2 ML. However, its plasma energy was considerably higher than that of the SP of semi-infinite Ag, as also found for Ag/Si(111)[9,10]. As the Ag coverage is increased, the energy of the plasmonic mode reduced and its line shape became sharper.

Such finding has to be ascribed to the s-d polarization. For thin Ag films, the overall screening of the plasmon via the polarizable d electron medium diminishes and a higher SP frequency occurs[8]. Moreover, the spill-out region not affected by s-d polarization becomes more important, causing a further blue-shift of the SP frequency.

For a thinner film, extra decay channels exist as compared with a thicker film. As a matter of fact, sp-sp interband transitions were found[16] to be more efficient in thinner films rather than in thicker ones.



One advantage of EELS technique is that changing the primary beam energy of the electrons, it is possible to modify their mean free path in the solid and thus their penetration length[15]. This allows direct control of the surface sensitivity. The energy loss position of the Ag SP was found to shift as a function of the primary electron beam energy (fig. 2a). This could be ascribed at the combined effect of the dispersion in the parallel transfer momentum and changes in the penetration length of the primary electrons. It is worth to mention that even for the thickness of the Ag film for which spectra were acquired, i.e. 10 ML, quantum well states were found to exist[13].

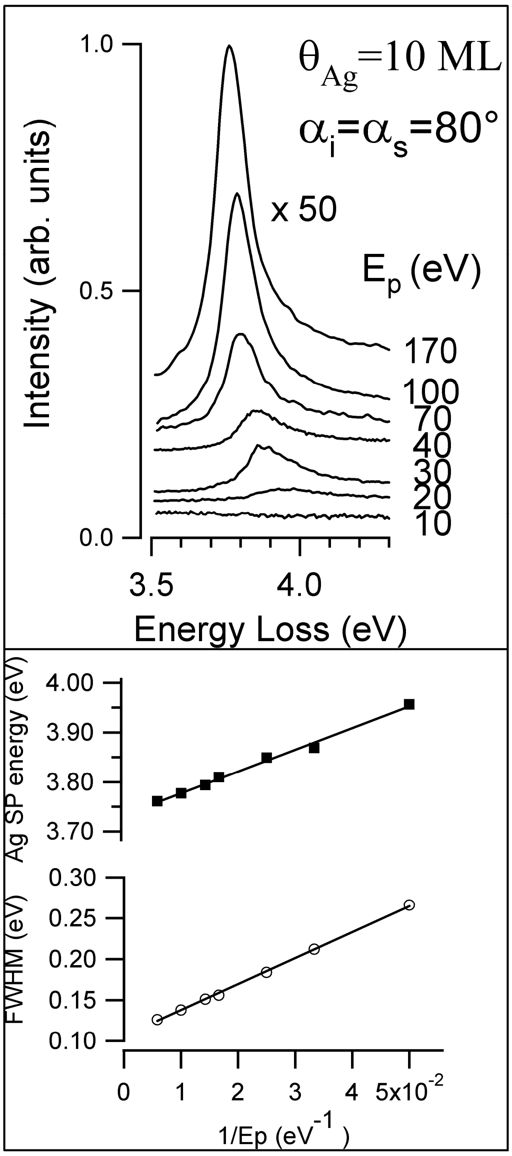
Interestingly, both the Ag SP energy ω_{sp} and the full width at half maximum (FWHM) follow a linear relation as a function of the inverse of the primary beam energy E_p (fig. 2 b).

$$\omega_{sp}=a+b^*(1/E_p)$$

$$\text{FWHM}= c+d^*(1/E_p)$$

where a=3.73 eV; b= 4.39 eV^2; c=0.11 eV; and d= 3.18 eV^2.

Increasing the kinetic energy of incident electrons from 20 to 170 eV caused a 200 meV shift of the energy loss position. Furthermore, the FWHM decreased by 140 meV for increasing primary energy. The FWHM of the Ag SP is associated with the damping of the SP, as a results of its decaying into single-particle excitations (Landau damping) through 5sp-5sp or 4d-5sp band transitions.



The FWHM of the SP peaks is plotted as a function of Ag SP energy in Fig. 3a. The FWHM was found to continuously increase a function of Ag SP energy and no minimum exists (figure 3a). The loss width notably grows beyond 3.80 eV (empty circles, primary beam energy fixed) indicating the opening of a new efficient decay channel. However, the same plot obtained by changing the impinging beam energy (filled squares) did not present such critical energy. This result was ascribed to effects caused by differences in penetration length of the impinging electrons.

As

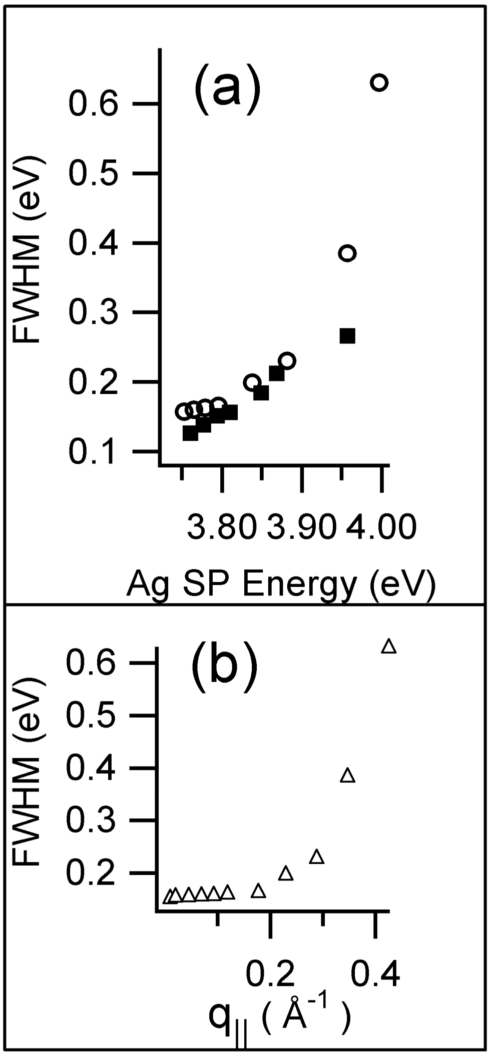
$$\hbar\vec{q}_{\parallel} = \hbar(\vec{k}_i \sin\theta_i - \vec{k}_S \sin\theta_S)$$

the parallel momentum transfer $q_{||}$ depends on E_p, E_{loss}, θ_i and θ_s according to[7]:

$$q_{\parallel} = \frac{\sqrt{2mE_p}}{\eta}(\sin\theta_i - \sqrt{1-\frac{E_{loss}}{E_p}}\sin\theta_S) \quad (1)$$

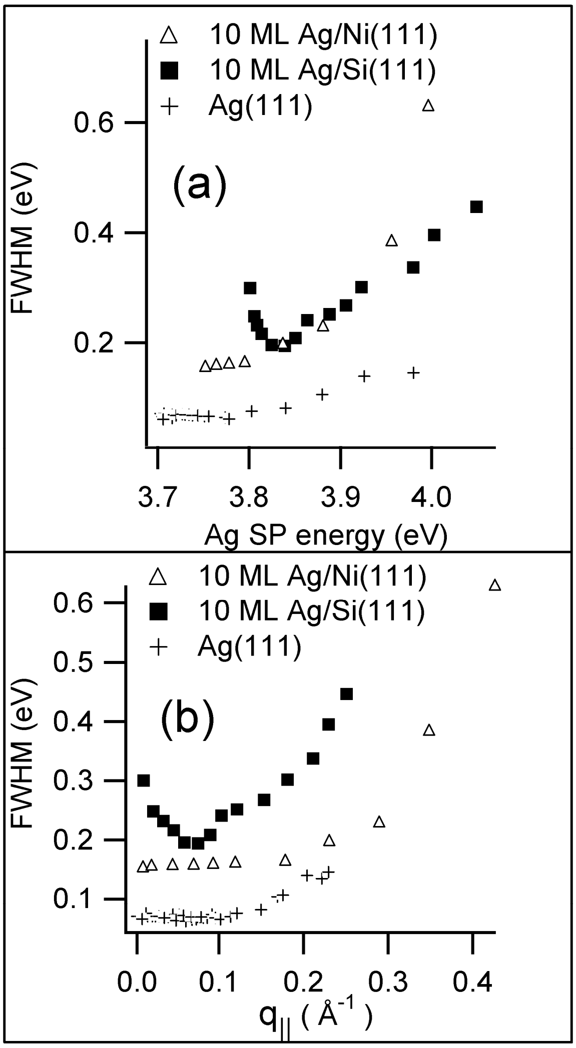
where E_{loss} is the energy loss, θ_i is the electron incident angle, and θ_s is the electron scattering angle.

The behavior of the FWHM as a function of the parallel transfer momentum $q_{||}$ (figure 3b) demonstrated that for $q_{||}$>0.2 Å^{-1} electrons may be promoted from occupied to unoccupied electronic states such that the corresponding plasmon peak would broaden considerably until decaying into the single-particle excitation continuum.

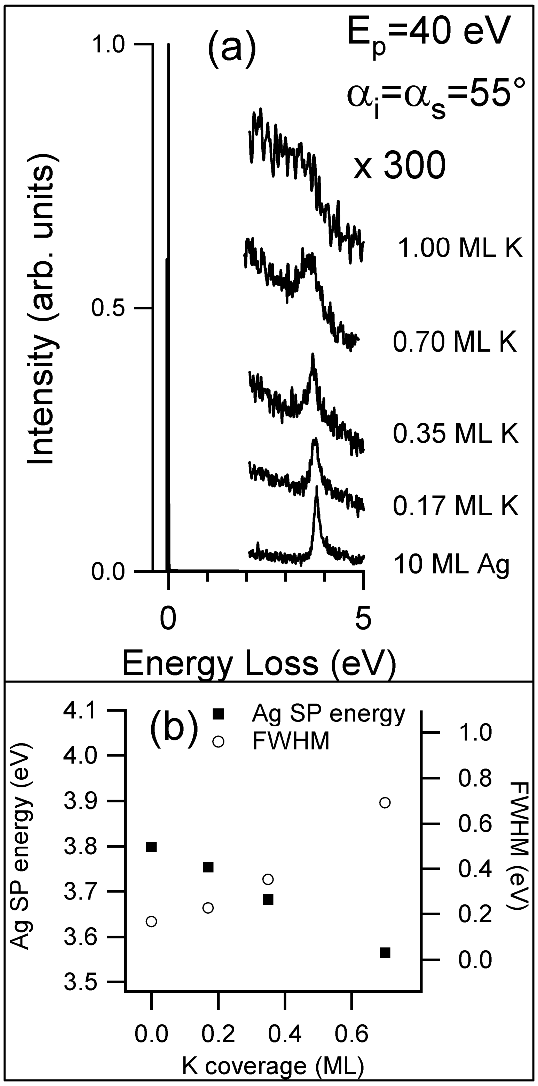


The width of the surface plasmon peak at $q_{||}$=0 is a sensitive function of the lattice potential, i.e. it is influenced by the periodic potential of the bulk. Such decay mechanisms can be direct or mediated by the exchange of reciprocal lattice vectors or phonons[7]. However, at larger values of $q_{||}$ the plasmon lifetime becomes less sensitive to the bulk lattice potential and the increasing of the damping is then caused by electron-hole pair excitations in the surface region. In real systems the lifetime of the plasmon is further limited by the scattering against crystallographic defects.

A comparison of the behavior of the FWHM of the Ag SP in 10 ML Ag/Ni(111), 10 ML Ag/Si(111), and Ag(111) is reported in Figure 4. Panel (a) shows the FWHM dependence on the Ag SP energy, while panel (b) on the parallel transfer momentum. For 10 ML Ag/Si(111), Yu et al.[10] found for different thicknesses an initial decrease of the FWHM as a function of the Ag SP energy, followed by an abruptly increasing. Such abrupt increase was ascribed to the opening of a new damping channel, i.e. intraband transitions between Ag 5sp-derived quantum well states. The initial decrease of FWHM was associated with the increased surface barrier due to the ionic pseudopotential of the crystal. On the contrary, the FWHM of Ag SP in 10 ML Ag/Ni(111) has an initial flat dependence on both Ag SP energy and $q_{||}$ and a stronger dependence beyond a critical value of both Ag SP energy and $q_{||}$. The notable difference existing in the behavior of the FWHM of Ag SP in 10 ML Ag deposited on Si(111) and on Ni(111) may be tentatively ascribed to substrate effects. As a matter of fact, it should be noticed that hybridization effects between Ag quantum well states and substrate states may also occur, as recently found for Ag films on Ge(111) with thickness up to 9 ML[17]. The tail of the wave function of the Ag quantum well states may reach and interact with the substrate, thus modifying the electronic response of the interface. The FWHM of the Ag SP in Ag(111)[16] has, in analogy with 10 ML Ag/Ni(111), an initial flat dependence on both Ag SP energy and $q_{||}$. The critical values of Ag SP and $q_{||}$ were found to be 3.78 eV and 0.15 Å^{-1}, respectively. Beyond such values, the FWHM significantly increased. It is worth to stress that the FWHM of the Ag SP in Ag(111) was always notably lower than that of Ag SP in thin films. This finding is ascribed to enhanced damping processes via 5sp-5sp indirect transitions, due to the different electronic properties of thin films with respect to surfaces.



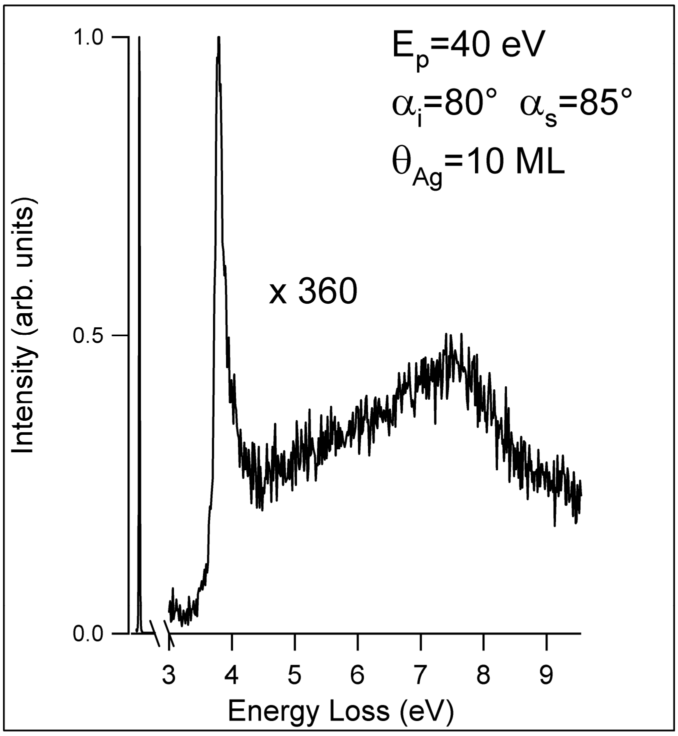
If the surface is exposed to chemically reactive atoms or molecules, the distribution of occupied and unoccupied electronic states changes. Accordingly, differences in damping processes and in the energy of the plasmonic excitation are quite expected. Rather than considering the new overlayer plasmon, we investigated the overlayer-induced modification of the substrate plasmon. Figure 5a shows Ag surface excitation spectra for increasing amounts of adsorbed K. At low K coverages, the Ag SP peak is only weakly affected. As the K coverage approaches one monolayer, the FWHM of the SP increased from 0.17 (clean Ag layers) up to 0.70 eV. Moreover, upon K adsorption the plasma energy of the Ag SP shifted from 3.80 down to 3.56 eV. The redshift of the Ag SP energy may be ascribed to a charge transfer from the Ag substrate to the adsorbates. Vibrational measurements indicated that water contamination occurs. Hence, we suggest that the redshift of the plasmon energy may be water-induced, as found for H_2O/Na/Cu(111)[18]. It is more correct to describe the plasmonic excitation as the K/Ag interface plasmon rather than a redshifted Ag SP. New adsorbate-induced electronic states arose at the interface. Hence, the significant plasmon broadening is due to new channels for decay into electron-hole pairs at the K/Ag interface. The interband transitions involving the overlayer-induced band below the Fermi level thus influences the surface plasmon energy and gives rise to a redshift of the surface plasmon energy.



Such SP broadening is ascribed to CID. It was observed in absorption spectra of small metal particles embedded in a reactive matrix[12], but it is the first experimental evidence of its occurrence in thin films.

Interestingly, loss spectra taken in grazing incidence showed also the presence of a broad peak at 7.5 eV (figure 6). Calculations based on s-d polarization by Liebsch[14] predicted the existence of the Ag MP near $\omega=0.8\cdot\omega_p=7.2$ eV (ω_p =9.0 eV is the s-electron bulk plasma energy) as the density profile at the surface has predominantly s-electron character. The line width of such feature is in excellent agreement with the predictions. Accordingly, we assign it to the Ag multipole surface plasmon. In contrast to all simple metals, this mode appeared above rather below bulk plasma frequency. The physical reason for this behavior is that the multipole surface plasmon is an intrinsic property of the s-electron density profile. Previous angle and energy resolved photo-yield measurements performed for Ag(100) and Ag thin films found no evidences for the existence of such mode[19].

However, the novel excitation mode presented here is currently under investigation and the results will be published in a forthcoming paper[20].



5. Conclusions

Damping processes were found to be more efficient for thinner films rather than for thicker one. Such finding suggests the occurrence of damping through indirect 5sp-5sp transition between Ag 5sp-derived quantum well states confined in the Ag adlayer, in the direction perpendicular to the surface. The width of the SP peak significantly broadened beyond ω_{SP}=3.80 eV and a critical parallel transfer momentum of 0.2 Å^{-1} exists. Both SP energy and FWHM were found to follow a linear relation as a function of the inverse of the primary electron beam energy, thus suggesting a strong dependence on the penetration length. Moreover, our measurements on K/Ag/Ni(111) provided the first evidence of CID in thin films. The SP energy red-shifted while its line shape broadened as a function of K coverage. Such remarkable plasmon broadening may be associated to the occurrence of overlayer-induced electronic states that offer new channels for decay of the Ag SP into electron-hole pairs at the K/Ag interface. A peak revealed at 7.5 eV was assigned to the Ag multipole surface plasmon.

Acknowledgments

We would like to thank S. Abate and G. Desiderio for their technical support.

Figure captions

Figure 1: HREEL spectra for Ag/Ni(111) as a function of Ag coverage.

Figure 2: (a) HREEL spectra for 10 ML Ag/Ni(111) as a function of the primary electrons beam energy. (b) (■) Loss energy and (○) FWHM as a function of the inverse of the kinetic energy of primary electrons.

Figure 3: (a) FWHM of the Ag SP peak for 10 ML Ag/Ni(111) as a function of the energy of the Ag SP, as obtained in different experimental conditions (■) $\theta_i = \theta_S$ =55° fixed and E_p varying (○) θ_i =55°, Ep =40 eV fixed and θ_S varying. (b) FWHM of the SP peak for 10 ML Ag/Ni(111) as a function of the parallel momentum transfer $q_{||}$, calculated using equation 1 with the following experimental parameters: θi =55°, Ep =40 eV. The abrupt increase of the FWHM beyond $q_{||}$=0.2 Å^{-1} indicates that an extra decay channel due to indirect single-particle transition between surface electronic states opens up.

Figure 4: (a) FWHM of the Ag SP peak as a function of the energy of the Ag SP for (Δ) 10 ML Ag/Ni(111); (■) 10 ML Ag/Si(111) (data taken from ref. 10); and (+) Ag(111) (data taken from ref. 16). (b) FWHM of the SP peak as a function of the parallel momentum transfer $q_{||}$ for (Δ) 10 ML Ag/Ni(111); (■) 10 ML Ag/Si(111) (data taken from ref. 10); and (+) Ag(111) (data taken from ref. 16).

Figure 5: (a) HREEL spectra for K/10 ML Ag/Ni(111) as a function of K exposure. (b) (■) Ag SP energy and (○) FWHM as a function of K coverage.

Figure 6: HREEL spectrum of 10 ML Ag/Ni(111) for θ_i=80° and θ_s=85°.

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PAPER XX

Interference effects in the excitation of collective electronic modes in nanoscale thin Ag films

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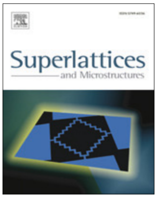

Interference effects in the excitation of collective electronic modes in nanoscale thin Ag films

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ABSTRACT

The surface plasmon in nanoscale thin Ag films deposited on Ni(111) was studied as a function of the impinging electron beam energy and of the scattering angle. The nonmonotonous behavior of the amplitude of the Ag surface plasmon suggests the occurrence of interference effects between the incoming and the outgoing field. Such interference phenomena occur whenever the scattering plane is in the close vicinities of the jellium edge. An alternative explanation involves diffraction effects.

The investigation of the surface plasmon (SP) continues to attract a considerable attention due to the fundamental interest in understanding dynamic screening processes at metal surfaces and for practical applications [1–6]. The role of the penetration depth by impinging electrons and of its influence on the intensity of collective electronic excitations was previously studied by random-phase approximation (RPA) calculations [7]. However, no dedicated experimental work assessing theoretical conclusions was performed. In particular, the SP amplitude was predicted to follow a nonmonotonous behavior as a function of the penetration, as a consequence of interference phenomena between the incident and the reflected beam whenever the scattering plane is in the nearness of the jellium edge.

One advantage of high-resolution electron energy loss spectroscopy (HREELS) technique is that by changing the primary beam energy of the electrons, it is possible to modify their mean free path in the solid and thus their penetration length [8]. This allows a shift of the reflection plane at which impinging electrons are scattered so as to obtain direct control of the surface sensitivity.

In this paper, we report on EELS measurements on thin Ag layers deposited on Ni(111) at room temperature. We report the first experimental confirmation of the model proposed by Nazarov [7] on dynamical screening of an incident charge reflected inside the extended electron-density distribution

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at a metal surface. As concerns the structural properties of the investigated system, Ag on Ni(111) is an example of film growth in large (16%) mismatched materials. Such a large misfit determines the silver film to have the crystalline structure of bulk silver even for ultrathin Ag layers [9]. Moreover, the small solubility of Ag into Ni prevents the dissolution of the silver layer into the nickel substrate [10, 11]. As a matter of fact, the formation of a surface alloy was not reported for this system [12,13]. For coverages higher than three layers, a reconstruction of the silver overlayer was reported [9], which exhibits a 7 × 7 moiré structure [10].

1. Experimental

HREELS experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The Ni(111) surface was cleaned by repeated cycles of ion sputtering and annealing at 1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy measurements and low-energy electron diffraction (LEED), respectively. Silver was deposited onto the Ni(111) surface by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates ($\approx$0.05 ML/min). LEED measurements ensured of the layer-by-layer growth of the Ag adlayer and reproduced results reported in previous structural studies of this system [10]. In particular, the absence of a plateau in the SP dispersion curve reported elsewhere [4] is a fingerprint of a layer-by-layer growth for Ag on Ni(111) at room temperature in the investigated film thickness range (0–10 ML), as also confirmed by photoemission results reported for the same substrate temperature and deposition rate [14]. For the first Ag layer, LEED pattern showed spots characteristic of the p(1 × 1) silver structure and of the Ni(111) substrate. For higher coverages only the Ag(111) pattern was observed. This means that the Ni(111) substrate is fully covered by Ag. When the Ag coverage reached three layers, a clear 7 × 7 reconstruction was revealed by the analysis of the LEED pattern. The occurrence of the p(1 × 1)-Ag LEED pattern was used as the calibration point of $\theta_{\mathrm{Ag}} = 1.0$ ML (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate). A constant sticking coefficient was assumed to obtain other desired Ag coverage. The energy resolution of the spectrometer was degraded to 7 meV so as to increase the signal-to-noise ratio for off-specular spectra. All depositions and measurements were made at room temperature.

2. Results and discussion

HREEL spectra acquired in specular geometry for 10 ML Ag/Ni(111) as a function of the primary electron beam energy are showed in the left panel of Fig. 1. For the sake of comparison we show the results obtained for the case of 60 ML Au/Cu(111) (Fig. 1, right panel). For both systems, the SP intensity increases with the impinging energy, E_p. However, a careful analysis of loss spectra shows that a decrease in intensity occurs at about 40 and 100 eV per Ag and Au, respectively. The existence of such behavior for two different systems ensures that these effects have a general validity. A careful investigation on the SP intensity around $E_p = 40$ eV was performed for Ag/Ni(111). An increase of the SP amplitude for E_p in the range 35–39 eV occurs, which is followed by a sudden decrease (minimum at 41 eV). Then, the SP intensity monotonously increases again with E_p (Fig. 2, left).

Such behavior may be understood within the framework of Nazarov's model [7]. The amplitude of the SP is nonmonotonous with penetration. Whenever the scattering plane is beyond the jellium edge, the intensity grows as a function of E_p. Increasing the impinging energy, the scattering plane moves the closeness of the jellium edge. The decreasing intensity of the SP is related to the decay of the external potential near the edge due to the interference between the incident and the reflected beam. We argue that such interference is also responsible of the sudden increase of the SP amplitude revealed for $E_p = 37$ eV (Fig. 2, left). For higher primary energies (beyond $E_p = 45$ eV) the scattering plane moves inside the bulk and the intensity of the SP increases once again. The influence of interference effects on SP amplitude was invoked also in Refs. [15,16].

It is worth noticing that such phenomena should be related to the surface sensitivity. Hence, changing the specular scattering geometry from grazing (left panels of Figs. 1 and 2) to nongrazing

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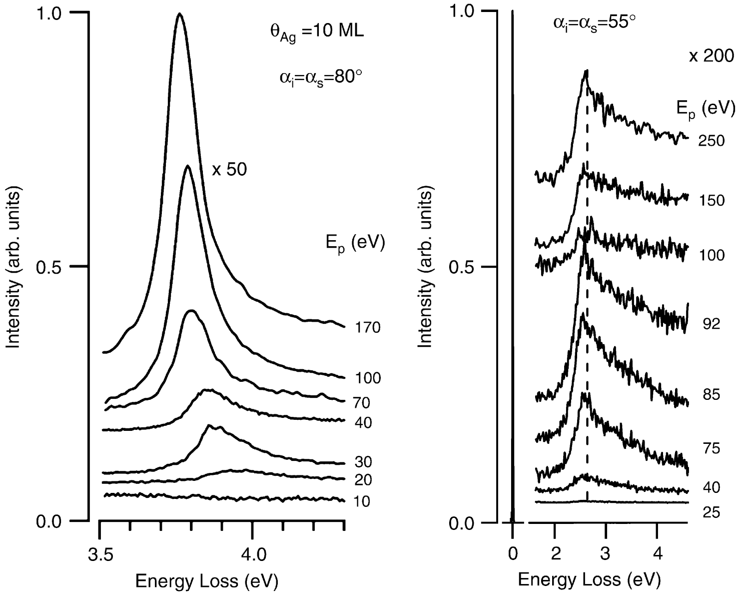

Fig. 1. (Left) HREEL spectra for 10 ML Ag/Ni(111) acquired for different primary energies. A nonmonotonous behavior was revealed around 40 eV; (Right) HREEL spectra for 60 ML Au/Cu(111) for different impinging energies. For Au a minimum was found around 100 eV. All angles are measured with respect to the surface normal.

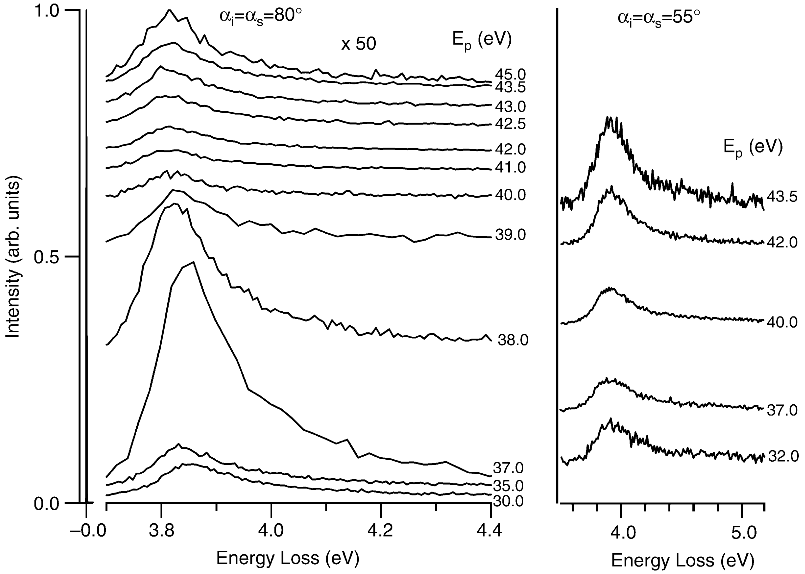

Fig. 2. (Left) Magnification of left panel of Fig. 1 around $E_p = 40$ eV (Right) HREEL spectra for 10 ML Ag/Ni(111) for different primary energies for a scattering geometry far from grazing conditions.

(55° with respect to the surface) should significantly reduce the interference effect. Spectra reported in the right panel of Fig. 2 demonstrated that in nongrazing geometry the nonmonotonous behavior of the SP amplitude is much less evident. However, an alternative explanation involves diffraction

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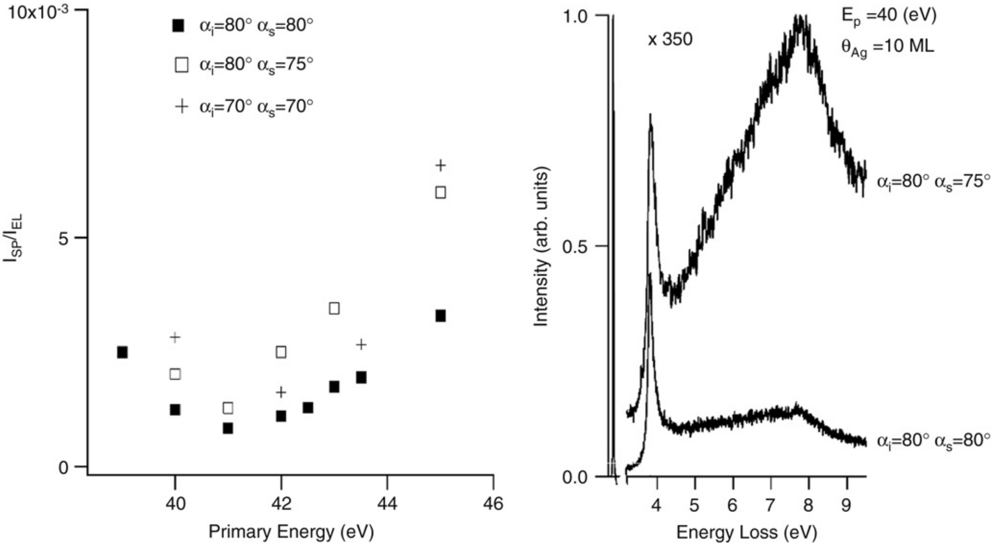

Fig. 3. (Left): Behavior of the intensity of the SP peak as a function of the impinging energy for different scattering geometries in grazing conditions. All intensities were normalized to that of the elastic peak. (Right) Besides the ordinary surface plasmon, a loss feature at 7.5 eV was excited in spectra recorded at grazing incidence. Its enhanced intensity in off-specular spectra ensures its impact character.

effects as being responsible of present findings. Dedicated calculations could shed the light on this phenomenon.

A nonmonotonous behavior was found to exist also for different scattering geometries in grazing-incidence conditions (Fig. 3, left panel). Interestingly, in correspondence of the minimum of the SP intensity ($E_p = 41$ eV, Fig. 3), an enhancement of the intensity of a broader peak recorded at 7.5 eV (Fig. 3, right panel) was revealed. This peak was observed also in other Ag systems and was assigned to a single-particle transition [17,18], the Ag multipole surface plasmon [19] or the ordinary surface plasmon [20]. However, experiments aimed at investigating the nature of such a peak in detail, whose intensity notably increased in off-specular spectra, are currently under way.

3. Conclusions

We have reported the first experimental evidence of interference effects caused by the coupling between electron charge in its outgoing trajectory with the electric field excited in the medium by impinging electrons. The nonmonotonous dependence of the behavior of the SP intensity on penetration was observed for both Ag/Ni(111) and Au/Cu(111). Our results provide grounds for more accurate theoretical calculations taking into account such phenomena.

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PAPER XXI

Collective electronic excitations in nanoscale silver films
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Plasmonic modes confined in nanoscale thin silver films deposited onto metallic substrates

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Collective electronic excitations in nanoscale thin Ag layers adsorbed on Cu(111) and Ni(111) at room temperature have been investigated by high-resolution electron energy loss spectroscopy. Surface plasmon was found to be confined within grains on Ag thin films on Cu(111) nanostructured in islands. Annealing removed surface plasmon confinement and induced a negative linear term of the dispersion relation. On the other hand, on flat thin films on Ni(111) the dispersion of Ag surface plasmon was found to be fully quadratic. Landau damping processes of the plasmonic excitation were found to be dependent on the growth mode. Ag multipole surface plasmon at 7.7 eV was observed only under stringent kinematic conditions enhancing surface sensitivity.

Keywords: Nanoscale Thin Films, Surface Plasmon, Silver, Electron Energy Loss Spectroscopy, Dynamic Screening.

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1. INTRODUCTION

Nanoscale thin metallic films have received considerable attention in recent years as they show physical properties well distinct from their bulk counterpart as a consequence of quantum size effects and electron quantum confinement[1-9]. They are a unique class of nanosystems, whose electronic properties can be easily tuned upon controlling the thickness of the film at the atomic level. This interest is accounted for, on the one hand, the lack of information on such systems compared with bulk crystals, and, on the other, the broad potential application of nanoscopic structures in nanoelectronics. Moreover, it has been demonstrated that metallic nanostructures may enhance the local electric field[10], so as to lead to sub-diffraction limit imaging[11,12], efficient optical mixing[13,14], and single-molecule Raman scattering[15,16].

Among metallic thin films, much effort has been devoted to the investigation of the electronic collective excitations in silver films deposited on solid surfaces[17-22]. In fact, silver is widely used in plasmonics due to its superior response to visible light. Moreover, studies on noble-metal systems are particularly motivated by fundamental interest in understanding their electronic response. The presence of localized d electrons makes unrealistic the jellium model, usually applied for describing dynamic screening of simple metals. Hence, several attempts have been undertaken in order to include band-structure effects in theoretical models[22,23].

The surface plasmon (SP) dispersion and the nature of the collective excitations in single-crystal Ag surfaces are well understood and there exists full agreement between experimental results[23-28] and theoretical predictions[29-32]. The interaction between s and d electrons shifts the energy of the Ag SP from 6.50 down to 3.70 eV. Furthermore, contrary to simple metals the dispersion of

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Ag SP was found positive[23-32]. A negative dispersion on Ag systems was reported only for modified Ag single-crystal surfaces, i.e. Cl/Ag(111)[33], O/Ag(100)[34], and the sputtered and nanostructured Ag(100)[35]. However, some issues are still unresolved. Currently, the main debate on the dielectric properties of silver systems is focused on the nature of a peak at 7-8 eV that was ascribed to a bulk plasmon[36], the multipole surface plasmon (MP)[37], another SP[36,38], or an interband transition[39]. Interestingly, this feature was revealed in some energy loss measurements[19,39,40], but it was not excited in other experimental conditions[28] and, moreover, in photoyield measurements[41,42].

Furthermore, details on the nature and dispersion of the collective excitations in nanoscale thin silver films[17,18] deposited on metal substrates are not at all well understood. In these systems well-defined Ag 5sp-derived quantum well states (QWS) are present within the adlayer[43-49]. Hence, they are characterized by an enhanced sp density of states at the Fermi level which modifies the electron charge-density distribution, so as to cause remarkable changes in the dynamical screening properties[50] with respect to the case of single-crystal surfaces. Hybridization between Ag QWS and the substrate[51] may also influence the electronic response of the interface.

Ag films grown on copper and nickel surfaces are suitable systems for such aims as silver does not form alloys with these substrates[52-57] at room temperature. Ag/Cu(111) and Ag/Ni(111) represent an example of film growth in large mismatched (16% and 13%, respectively) materials. Such a large misfit determines the silver film to have the crystalline structure of bulk silver even for ultrathin Ag layers[58]. However, due to the absence of a gap in Ni(111), the character of the QWS in such two systems differs substantially[59]. QWS on Ag/Cu(111) are typified by standing wave patterns, whose formation instead is not allowed on Ag/Ni(111). Furthermore, on Ag/Cu(111) the interfacial transmittivity is suppressed, with an enhanced specular reflectivity. The opposite occurs for Ag on Ni(111). Such dissimilarities in the electronic properties should imply quite different dynamic screening processes at these metal/metal interfaces.

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements performed on Ag/Cu(111) and Ag/Ni(111) at room temperature. For Ag on Cu(111), which follows the Stranski-Krastanov growth mode[45] (islands appear on the flat Ag adlayer for coverages higher than two layers[60,61]), the SP was found to be confined within Ag grains. SP confinement was removed by annealing at 400 K. The linear term of the SP dispersion curve measured after the annealing was slightly negative, as a consequence of the enhanced free-electron character of QWS upon annealing[1]. On the other hand, on flat Ag films on Ni(111)[49,62] a purely quadratic SP dispersion was recorded. Measurements provided direct evidence of the strict surface nature of the loss peak at 7-8 eV, thus excluding its assignation to a bulk plasmon or an interband transition. Instead, on the basis of present experimental findings, we ascribe this excitation to the Ag MP, in agreement with theoretical predictions[37].

2. EXPERIMENTAL DETAILS

Measurements were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were single-crystal surfaces of Cu(111) and Ni(111) with a purity of 99.9999%. Surfaces were cleaned by repeated cycles of ion sputtering and annealing at 800-900 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) measurements and low-energy electron diffraction (LEED), respectively. Silver was deposited onto the Cu(111) and Ni(111) surfaces by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈0.05 ML/min). The occurrence of the p(1x1)-Ag LEED pattern was used as the calibration point of θ_{Ag}=1.0 ML, respectively (the coverage of one monolayer, ML, is defined as the ratio between the number of the atoms of the adsorbate and that of the topmost layer of the substrate). A constant sticking coefficient was assumed to obtain other desired coverage. A calibration procedure using AES gave similar results.

As concerns Ag/Cu(111), around each spot of the p(1x1)-Ag, LEED measurements showed also the occurrence of a (9.5x9.5) reconstruction for the first Ag layer and of a (9x9) reconstruction in correspondence of θ_{Ag}=2.0 ML, in excellent agreement with previous structural studies on this system[60,61]. As regards Ag/Ni(111), the LEED pattern of the first Ag layer showed spots characteristic of the p(1X1) silver structure and of the Ni(111) substrate. When the Ag coverage reached three layers, a clear (7x7) reconstruction was revealed by the analysis of the LEED pattern, as previously reported[52].

The energy resolution of the spectrometer was degraded to 7 meV so as to increase the signal-to-noise ratio for off-specular spectra. The angular acceptance α of our electron analyzer was ±0.5°.

Dispersion of the collective mode, i.e. $E_{loss}(q_{||})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. The sample was oriented along the $\overline{\Gamma}-\overline{M}$ direction.

The values of E_p, impinging energy, and θ_i, the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, E_p=40 eV, provided, in fact, the best compromise among surface sensitivity, the highest cross-section for the plasmonic excitation, and $q_{||}$ resolution. As

$$\hbar\overrightarrow{q_{||}} = \hbar\left(\overrightarrow{k_i}\sin\theta_i - \overrightarrow{k_s}\sin\theta_s\right)$$

the parallel momentum transfer $q_{||}$ is determined by the values of E_p, E_{loss}, θ_i and θ_s:

$$q_{||} = \frac{\sqrt{2mE_p}}{\hbar}\left(\sin\theta_i - \sqrt{1-\frac{E_{loss}}{E_p}}\sin\theta_s\right)$$

where E_{loss} is the energy loss and θ_s is the electron scattering angle[23,63].

Hence, it is possible to estimate the integration window in reciprocal space:

$$\Delta q_{||} \approx \frac{\sqrt{2mE_p}}{\hbar} \left(\cos\theta_i + \sqrt{1 - \frac{E_{loss}}{E_p}} \cos\theta_s \right) \cdot \alpha$$

where α is the angular acceptance of the apparatus[23]. Under our experimental conditions, $\Delta q_{||}$=0.012 Å^{-1}, much less than the scanned range in the reciprocal space.

All depositions and measurements were made at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows HREEL spectra recorded for different Ag coverages on Cu(111). The SP energy underwent to a red-shift from 3.97 to 3.82 eV as a function of the coverage. However, its plasma energy was considerably higher than that of the SP of semi-infinite Ag, as also found for Ag/Si(111)[17,18]. As the Ag coverage is increased, the energy of the plasmonic mode reduced and its line shape became sharper.

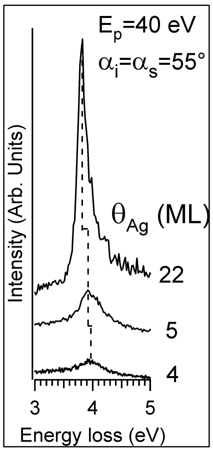

Figure 1: HREEL spectra of Ag/Cu(111) as a function of Ag coverage. As the thickness of the Ag film increases, the cross-section for SP excitation increases.

Such finding has to be ascribed to the s-d polarization. For thin Ag films, the overall screening of the plasmon via the polarizable d electron medium diminishes and a higher SP frequency occurs[22]. A similar dependence of the surface plasmon on thickness was obtained for Ag/Ni(111) (Figure 2). The spectrum of the Ni(111) surface is characterized by a broad peak at 1.0 eV. For less than 2 ML of Ag, the spectrum is extremely broad without a well-defined peak. A broad Ag SP at 4.2 eV arose for Ag coverages above 2 ML.

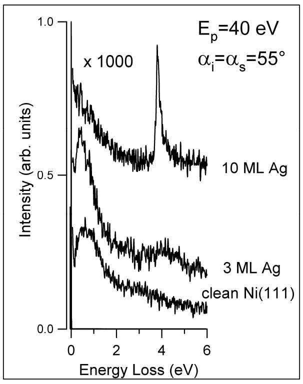

Figure 2: HREEL spectra of Ag/Ni(111) as a function of Ag coverage.

Important information on the nature of plasmonic excitations in metal systems is given by their dispersion relation. Selected HREEL spectra for 22 ML of Ag on Cu(111) as a function of the parallel transfer momentum are showed in Figure 3.

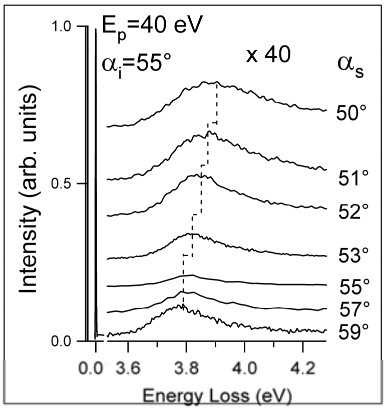

Figure 3: HREEL spectra for 22 ML Ag/Cu(111).

In contrast with previous experimental works on Ag single-crystal surfaces[22,23,26-28] and layer-by-layer Ag films on Si(111)[18], the frequency of the SP did not increase as a function of the parallel transfer momentum. Similar results were obtained varying Ag thickness (Figure 4).

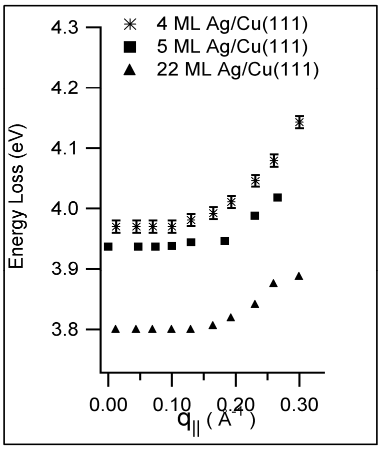

Figure 4: Dispersion of the SP energy for different Ag coverages. The lack of a dispersion before a critical wave-vector indicates that the SP is confined within Ag grains.

The behavior of the SP dispersion suggests that the as-deposited film is made up of Ag grains. The lack of a dispersion of the SP frequency below a critical wave vector, i.e. 0.15-0.18 A^{-1}, indicates that the s electrons oscillate independently in the single (111)-oriented grains. The propagation of the SP can occur only for modes whose wavelength is smaller than the diameter of the single grain.

The occurrence of SP confinement was reported also for Ag thin films nanostructured in islands on Si(111)[17]. The critical wave vector was suggested[17] to be related to the average island size through the relation:

$$q_c=2\pi/d$$

From the above equation, we estimate the grain size in Ag/Cu(111) to be about 30-40 Å.

The behavior of the SP dispersion well agrees with the Stranski-Krastanov growth mode of this system[43-46]. The increasing strain caused by adsorbed layers destabilizes the film and induces clustering[64].

It is worth noticing that the grain size is already too high for allowing the excitation of Mie plasmons at 3.1 and 3.9 eV, which instead occurs on Ag nanoparticles deposited on metal-oxide surfaces[65,66]. As concerns metal/metal interfaces, the occurrence of Mie plasmons was invoked only for Na quantum dots on Cu(111)[9] but only for a very restricted alkali thickness range. Mie plasmon merged into the ordinary SP already for two nominal Na layers[9].

SP confinement was removed upon annealing the film at 400 K (Figure 5). The annealing process caused notable changes in the dispersion curve and, moreover, it induced a higher degree of ordering, as suggested by the analysis of the LEED pattern. The measured dispersion curve $E_{loss}(q_{||})$ of the annealed film, reported in the inset of Fig. 5, was fitted by a second-order polynomial given by:

$$E_{loss}(q_{||})=A+Bq_{||}+Cq_{||}^2$$

($A=3.791\pm0.006$ eV; $B=-0.60\pm0.09$ eV·Å; and $C=3.4\pm0.3$ eV·Å^2)

The linear coefficient was found to be slightly negative, as a consequence of the increased sp density of states existing in thin Ag films, due to the presence of QWS. Enhancing the free-electron character of the QWS by annealing[1] should imply the occurrence of a negative linear term, as in modified Ag single-crystal surfaces[33-35].

Nonetheless, the value of the linear coefficient is still enough higher than the linear coefficient of the SP dispersion curve of alkalis[67], aluminum[68], or alkaline-earth metals[69]. Such finding leads us to suggest that the centroid of the induced charge lies in the close vicinity of the jellium edge[22,70,71] in contrast with all other Ag systems[18,22-28,72], but not outside as for simple metals[67-69]. Interestingly, the quadratic coefficient coincides with that of SP dispersion in Ag(111)[72], i.e. the surface with the same crystallographic orientation.

On the other hand, for layer-by-layer thin Ag films on Ni(111), a fully quadratic SP dispersion was recorded (Figure 6), without the occurrence of SP confinement, as indicated by the lack of a critical wave-vector in the SP dispersion curve as in Figure 4.

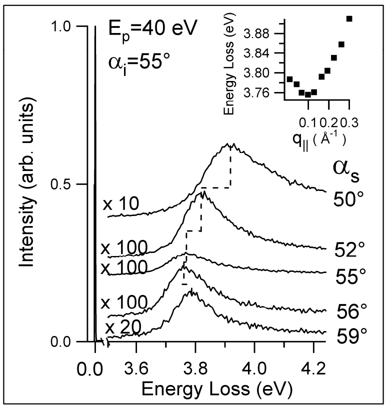

Figure 5: HREEL spectra for 22 ML Ag/Cu(111) as a function of the scattering angle after an annealing at 400 K. In the inset the dispersion relation of the Ag SP energy is shown. The initial flat behavior reported in Figure 4 abruptly changed upon annealing and an initial negative dispersion appeared .

The absence of the linear term is ascribed to the existence of Ag QWS confined within the flat adlayer. Interestingly, the linear term was null for all investigated coverages for which well-defined QWS exist[49]. Hence, the different growth modes of the Ag adlayer reflect into different dispersion of the SP (Figures 3, 4, and 6). In particular, using equation 4 of Ref. 27 we could estimate the position of the centroid of the induced charge to be located at -0.6 Å with respect to the jellium edge, less inside the geometrical surface with respect to other Ag systems[18,72]. For the sake of a comparison, its value for Ag(100) and Ag(111) is -2.6 and -1.3 Å, respectively.

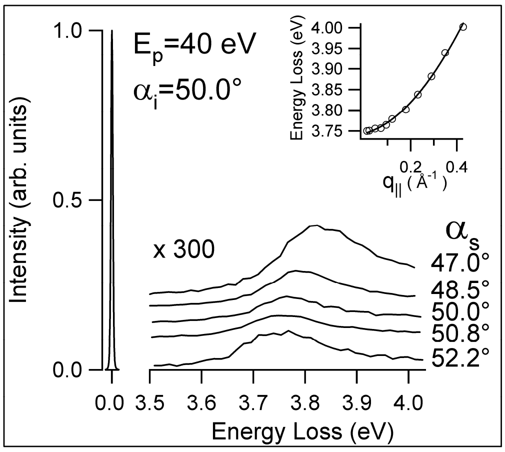

Figure 6: HREEL spectra for as-deposited 10 ML Ag/Ni(111) as a function of the scattering angle. In the inset the dispersion relation of the Ag SP energy is shown. A purely quadratic dispersion was found.

It is quite expected that the different distribution of occupied and unoccupied electronic states in thin films with respect to surfaces would imply enhanced damping mechanisms for collective excitations by creating electron-hole pairs. On the other hand, Landau damping and the lifetime of surface plasmons have been demonstrated to strongly influence plasmon-mediated dynamic processes and, moreover, the field enhancement and the sensitivity of surface-enhanced Raman spectroscopy[21].

Figure 7 shows the thickness-dependence of the full-width at half maximum (FWHM) as a function of the parallel momentum transfer for Ag/Cu(111). An initial negative behavior of the FWHM was found for ultrathin films, while for higher coverages (22 ML) the behavior is substantially dispersionless. This behavior of the FHMM is well described by a theoretical model recently proposed[21] on plasmon lifetime in free-standing Ag layers. The dispersion relation of the FWHM was found to be characterized by a negative behavior of the line-width for small momenta up to a critical wave-vector. This finding was ascribed[21] to the splitting between symmetric and anti-symmetric excitation modes and the enhanced electron-hole pair excitation at small $q_{||}$ [73]. For higher values of $q_{||}$, a linear increase of the line-width was reported.

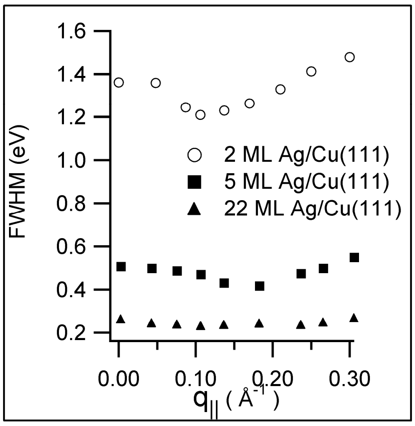

Figure 7: Behavior of the FWHM of the Ag SP as a function of Ag thickness on Cu(111).

On the other hand, the behavior of the FHWM for single-crystal Ag surfaces is positive[23,72] and it was recovered by annealing the Ag film (not shown).

The FWHM of Ag SP notably increases for reduced thicknesses. For a thinner film extra decay channels exist as compared with a thicker film. Such finding suggests the occurrence of damping through indirect 5sp-5sp transitions between Ag 5sp-derived QWS confined in the Ag adlayer, in the direction perpendicular to the surface. In fact, sp-sp interband transitions were found[18] to be more efficient in thinner films rather than in thicker ones. It is worth noticing that the value of the FWHM is always much higher than for Ag semi-infinite media (for Ag(111) the FWHM at small momenta is 69 meV[72]).

In order to investigate whether Landau damping processes of the SP[74] are influenced by the growth mode of the film, we report the behavior of the FWHM of the SP for Ag flat layers on Ni(111). In this case, as the SP frequency changes with $q_{||}$ (Figure 6), it is also possible to plot the FWHM also as a function of the Ag SP (Figure 8a). Combined with its dependence on $q_{||}$ (Figure 8b), this joint approach could identify the single-particle transition leading to SP broadening. The FWHM was found to continuously increase a function of Ag SP energy and no minimum exists. The loss width notably grows beyond 3.80 eV (empty circles, primary beam energy fixed) indicating the opening of a new efficient decay channel. However, the same plot obtained by changing the impinging beam energy (filled squares) did not present such critical energy. This result was ascribed to effects caused by differences in penetration length of the impinging electrons[75-76].

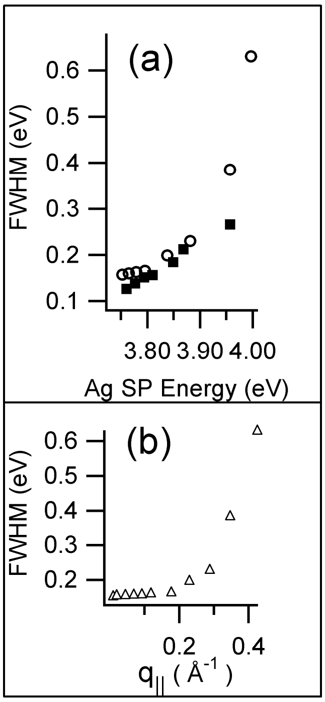

Figure 8: (a) FWHM of the Ag SP peak for 10 ML Ag/Ni(111) as a function of the energy of the Ag SP, as obtained in different experimental conditions (■) $\theta_i = \theta_s = 55°$ fixed and Ep varying (○) $\theta_i = 55°$, $E_p = 40$ eV fixed and θ_s varying. (b) FWHM of the SP peak for 10 ML Ag/Ni(111) as a function of the parallel momentum transfer $q_{||}$, calculated with the following experimental parameters: $\theta_i = 55°$, $E_p = 40$ eV. The abrupt increase of the FWHM beyond $q_{||} = 0.2$ Å^{-1} indicates that an extra decay channel due to indirect single-particle transition between surface electronic states opens up.

The behavior of the FWHM as a function of the parallel transfer momentum $q_{||}$ demonstrated that for $q_{||} > 0.2$ Å^{-1} electrons may be promoted from occupied to unoccupied electronic states so that the corresponding plasmon peak would broaden considerably until decaying into the single-particle excitation continuum.

The different behavior with respect to the case of Ag/Ni(111) should be ascribed to differences in both the growth mode and in the nature of QWS[59]. Such significant dissimilarities between these two bimetallic surfaces should in principle imply quite different Landau damping processes of the plasmonic excitation.

Interestingly, a broader peak recorded at 7.7 eV (Figure 9) was revealed for both Ag/Cu(111) and Ag/Ni(111). As mentioned above, this peak was observed also in other Ag systems[19,39,40] and its nature is still unclear. A shoulder at about 12 eV was also revealed on both systems and it was ascribed to a combination mode of the Ag SP and the feature at 7.7 eV. For Ag/Cu(111) also a peak at about 16 eV was recorded.

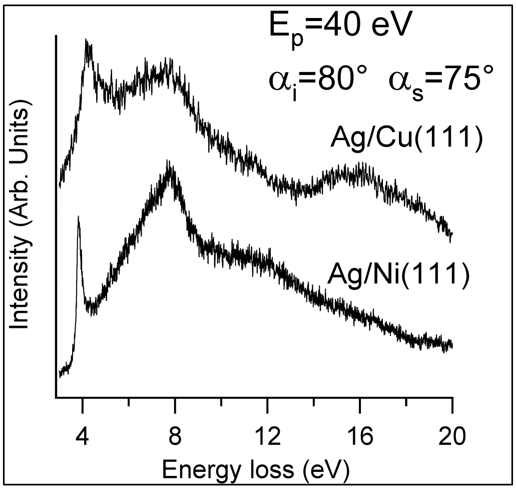

Figure 9: HREEL spectra of 10 layers of Ag on Ni(111) and Cu(111). The incident beam energy E_p was held constant at 40 eV and all spectra were recorded at an incident angle of θ_i=80° with respect to the sample normal and with a diffusion angle of θ_s=75°.

Interestingly, the mode at 7.7 eV was measured only in experimental conditions enhancing the surface sensitivity, i.e. at low impinging energies and grazing incidence (Figure 10). These findings unambiguously exclude the assignation of this mode to a bulk plasmon[36] or to a single-particle transition[39], which should not have such a strict surface nature.

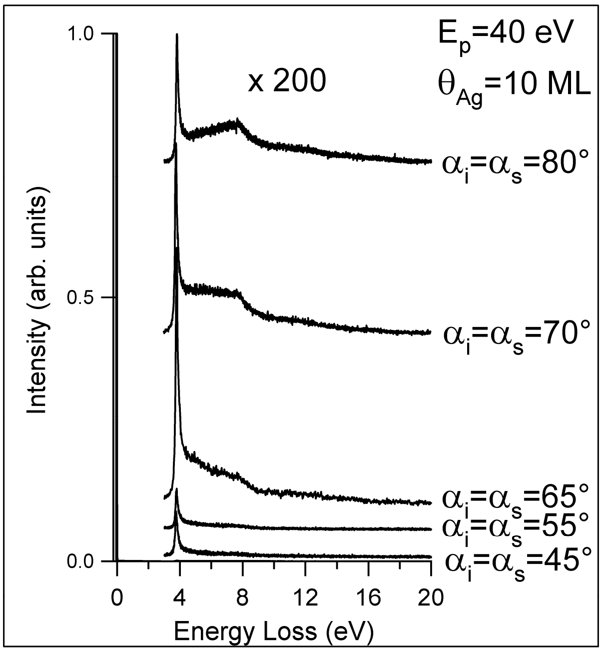

Figure 10: HREEL spectra of 10 ML Ag/Ni(111) as a function of the scattering geometry. Each spectrum was acquired in specular geometry.

This behavior leads us to suggest that this peak could be ascribed to the MP[37], which is characterized by a strong surface character. It should be noticed that according to Liebsch's calculations[37], this broad feature should have spectral contributions (not separable, even though at higher momenta MP should predominate) from both MP and the free-electron Ag SP. A SP at similar frequencies has been invoked also in Ref. 36 and 38. Moreover, Ag MP has an intrinsically free-electron nature[37] and electron quantum confinement in Ag 5sp-derived QWS[43-49] should in principle enhance the cross-section for Ag MP excitation in Ag thin films compared with Ag single-crystal surfaces.

The intensity of the MP (normalized to that of the elastic peak) versus the off-specular angle (figure 11) clearly demonstrates that such collective mode was excited by impact mechanism because it is peaked at seven degrees off-specular[23], while a dipolar loss would have the same behavior of the elastic peak as a function of the off-specular angle. Likewise, the intensity of SP exhibited a maximum around 8 degrees off-specular.

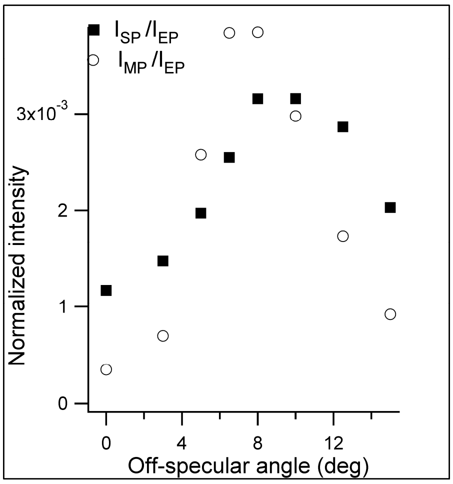

Figure 11: Behavior of the ratio of the intensity of the SP with respect to that of the elastic peak, I_{SP}/I_{EL}, and of the ratio of the intensity of the MP with respect to that of the EP peak, I_{MP}/I_{EP},as a function of the off-specular angle. A maximum for both quantities was found around seven-eight degrees off-specular. For such angle, the intensity of MP was higher than that of the SP peak.

As a consequence of its strictly surface nature, the excitation of a MP should strongly depend on the state of the surface, much more with respect to the ordinary SP. As extremely amounts of coadsorbed water notably influence the electronic properties by inducing peaks in the loss spectrum[9,77], the adsorption of water molecules could be the best probe to test the surface sensitivity of Ag MP. However, water molecules adsorb onto noble-metal surfaces at room temperature only in the presence of submonolayers of alkalis. Thus, we adsorbed 0.15 ML of K onto the Ag film in order to enhance the reactivity towards water molecules. Vibrational spectra (not shown) revealed the presence of partially dissociated water as contamination coming from residual gas in UHV chamber, as suggested by the presence of O-H stretching peaks at 435 meV (water molecules) and 450 meV (OH groups)[78,79] As a matter of fact, the critical K-precoverage for water dissociation on Ag(111) is 0.17 ML[80]. Another clear fingerprint of molecular water adsorbed is the appearance of HOH bending at 199 meV[81,82].

The energy of the ordinary SP shifted by about 100 meV after potassium exposure (figure 12). Such red-shift indicates a charge transfer from Ag to adsorbates. The MP disappeared and two new loss features appeared at 5.7 and 9.9 eV. Photoemission spectroscopy experiments carried out on $H_2O/(2x2)$-Li/Cu(111)[77] and HREELS measurements on H_2O/Na/Cu(111)[9] showed a peak at a similar energy. These authors interpreted a peak at 5.9-6.0 eV as due to single-particle transitions involving oxygen 2*p*-derived orbitals. Likewise, these loss features may be assigned to single-particle transitions occurring between orbitals of water molecules (or OH groups). In particular, the peaks at 5.7 and 9.9 eV could be ascribed to transitions starting from the $1b_1$ and $3a_1$ orbitals of water molecules, respectively. Further support to such assignment arises from the finding that these losses did not follow any dependence on the scattering geometry and the primary electron beam energy. Hence, any relationship between such two features and the MP has to be excluded.

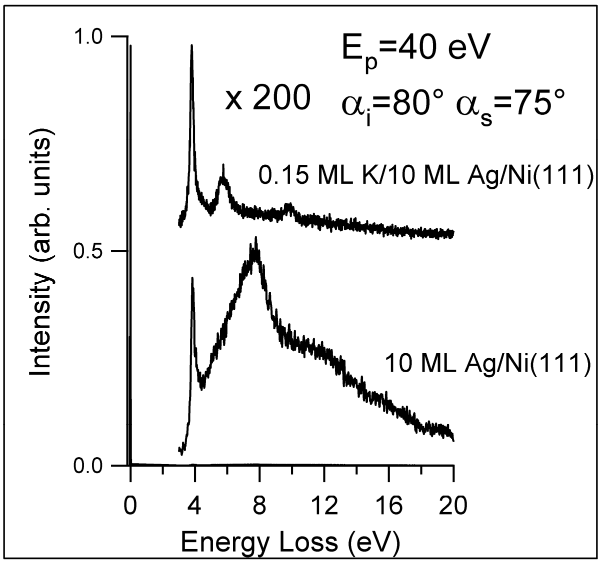

Figure 12: HREEL spectra of 10 ML Ag/Ni(111) after the exposure of 0.15 ML of K at room temperature. MP disappeared and new loss features due to water contamination arose in spectrum.

Interestingly, such an enhanced surface-sensitivity was not found for other electronic modes confined at surfaces, such as acoustic plasmon[83], which instead was revealed even in the presence of a remarkable oxygen contamination, and Shockley plasmon[63].

Results reported in Figure 9-12 suggest that the MP is a general property of the optical response for Ag and presumably for all metal surfaces. Its existence should be essential for potential applications as it affects significantly the high-frequency optical properties. For example, it is expected to strongly influence the production of hot electrons by photons, whenever the frequency matches that of the MP[84].

4. SUMMARY AND CONCLUSIONS

Growth mode was found to strongly affect collective electronic excitations in nanoscale thin Ag films. SP was found to be confined within grains for Ag/Cu(111). Annealing at 400 K removes SP confinement and induces a negative linear term in the SP dispersion relation. On Ag flat films on Ni(111) a fully quadratic dispersion was found to occur. This implies that the centroid of the induced charge lies less inside the geometrical surface compared with other Ag systems, as a consequence of the presence of Ag 5 sp-derived QWS. Landau damping processes were found to be dependent on the growth mode too, as indicated by the different dispersion relation of the FWHM in the two systems. The broadening of the Ag SP is enhanced for thinner films due to 5sp-5sp transitions.

Moreover, we report direct evidences of the existence of a mode at 7.7 eV which is excited only in conditions enhancing surface sensitivity. It disappeared upon coadsorption with reactive species. We suggest that this excitation could be ascribed to the MP, in agreement with theoretical predictions in Ref. 37.

These findings provide the grounds for theoretical studies aimed at characterizing the dependence of the nature and dispersion of collective excitations in nanoscale thin silver films on the growth mode and on the electron quantum confinement within the adlayer.

FIGURE CAPTIONS

Figure 1: HREEL spectra of Ag/Cu(111) as a function of Ag coverage. As the thickness of the Ag film increases, the cross-section for SP excitation increases.

Figure 2: HREEL spectra of Ag/Ni(111) as a function of Ag coverage.

Figure 3: HREEL spectra for 22 ML Ag/Cu(111).

Figure 4: Dispersion of the SP energy for different Ag coverages. The lack of a dispersion before a critical wave-vector indicates that the SP is confined within Ag grains.

Figure 5: HREEL spectra for 22 ML Ag/Cu(111) as a function of the scattering angle after an annealing at 400 K. In the inset the dispersion relation of the Ag SP energy is shown. The initial flat behavior reported in Figure 4 abruptly changed upon annealing and an initial negative dispersion appeared .

Figure 6: HREEL spectra for as-deposited 10 ML Ag/Ni(111) as a function of the scattering angle. In the inset the dispersion relation of the Ag SP energy is shown. A purely quadratic dispersion was found.

Figure 7: Behavior of the FWHM of the Ag SP as a function of Ag thickness on Cu(111).

Figure 8: (a) FWHM of the Ag SP peak for 10 ML Ag/Ni(111) as a function of the energy of the Ag SP, as obtained in different experimental conditions (■) $\theta_i=\theta_s$ =55° fixed and Ep varying (○) θi =55°, E_p =40 eV fixed and θ_s varying. (b) FWHM of the SP peak for 10 ML Ag/Ni(111) as a function of the parallel momentum transfer $q_{||}$, calculated with the following experimental parameters: θ_i =55°, E_p =40 eV. The abrupt increase of the FWHM beyond $q_{||}$=0.2 $Å^{-1}$ indicates that an extra decay channel due to indirect single-particle transition between surface electronic states opens up.

Figure 9: HREEL spectra of 10 layers of Ag on Ni(111) and Cu(111). The incident beam energy E_p was held constant at 40 eV and all spectra were recorded at an incident angle of θ_i=80°

with respect to the sample normal and with a diffusion angle of θ_s=75°.

Figure 10: HREEL spectra of 10 ML Ag/Ni(111) as a function of the scattering geometry. Each spectrum was acquired in specular geometry.

Figure 11: Behavior of the ratio of the intensity of the SP with respect to that of the elastic peak, I_{SP}/I_{EL}, and of the ratio of the intensity of the MP with respect to that of the EP peak, I_{MP}/I_{EP},as a function of the off-specular angle. A maximum for both quantities was found around seven-eight degrees off-specular. For such angle, the intensity of MP was higher than that of the SP peak.

Figure 12: HREEL spectra of 10 ML Ag/Ni(111) after the exposure of 0.15 ML of K at room temperature. MP disappeared and new loss features due to water contamination arose in spectrum.

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Tuning the lifetime of the surface plasmon upon sputtering

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Abstract

The lifetime of the surface plasmon in sputtered Ag nanoscale thin films on Cu(111) was investigated by high-resolution electron energy loss spectroscopy measurements. The line-width of the surface plasmon was found to follow a square-root dependence on the fluence. Such finding allows the tuning of the lifetime of the plasmonic excitation upon sputtering and has general implications in plasmon-based spectroscopies and in plasmon-mediated processes across the films and at their surfaces.

Plasmonic resonances in metallic systems have been widely studied in recent years [1-3] as they can be applied to alter light–matter interaction. It has been shown that supported metal nanostructures can dramatically enhance the local electrical field by concentrating electromagnetic energy into sub-wavelength volumes [1]. This could lead to many applications, ranging from sub-diffraction limit imaging [4] to efficient optical mixing [5]. In particular, surface plasmons (SPs) in thin films have a direct implication in light and electron transmission across the film [6, 7], sensing of chemisorbed atoms or molecules on the surface of the film, SP-coupled emission, and light scattering and absorption.

A key factor in the relaxation processes is the lifetime of the SP, which is limited by the decay into electron-hole pairs (Landau damping). The lifetime of SP has been demonstrated to strongly influence plasmon-mediated dynamic processes and, moreover, the field enhancement and the sensitivity of surface-enhanced Raman spectroscopy (SERS) [8] and surface-enhanced fluorescence [9].

Tuning the SP lifetime, i.e. SP line-width, is a grand challenge to date still elusive, for both fundamental and technological interest. In fact, it should imply a significant advancement for plasmon-based applications such as chemical and biological sensors, waveguides, photonic circuits, molecular rulers, optical tweezers [10] and all-optical switching devices [11].

The damping processes of the SP are well understood for both bulk crystals [12] and nanoparticles [13]. However, information on the Landau damping in thin films is still lacking. Recent calculations [14] for Ag nanoscale thin films have found that Landau damping behaves very differently in thin films with respect to their bulk counterpart.

For example, damping processes are enhanced in the long-wavelength limit while for bulk crystals an opposite behavior has been reported [15].

On the other hand, the use of sputtering techniques for obtaining ultrathin and nanostructured metallic films for SP-based applications has been recently demonstrated [16]. In particular, silver films are essential in optical devices [17, 18].

Herein we report on high-resolution electron energy loss (HREELS) measurements on plasmonic excitations in Ag thin films grown on Cu(111) which were sputtered by Ar^+ ions at room temperature and in normal incidence. We found that the line-width of the SP follows a square-root-like behavior on the fluence. This finding offers an unique possibility of controlling the SP lifetime.

Measurements were carried out in a UHV chamber operating at a base pressure of $5 \cdot 10^{-9}$ Pa. The sample was a single crystal of Cu(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 700-800 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Silver was deposited onto the Cu(111) surface by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈0.05 ML/min). The occurrence of the p(1x1)-Ag LEED pattern was used as the calibration point of θ_{Ag}=1.0 ML. Similar results were obtained by a calibration procedure using AES. A constant sticking coefficient was assumed to obtain other desired Ag coverage. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). Loss spectra were acquired with a primary electron beam energy of 40 eV. The incident angle with respect to the sample normal was fixed at 55.0°. All spectra were acquired in the specular geometry. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio of loss peaks. All depositions and measurements were made at room temperature. The sputtering of the Ag film was performed also at room temperature, using Ar^+ ions with an impinging energy of 1 keV and in normal incidence. It should be mentioned that the temperature of the substrate and the angle of incidence of the ions can be used to select the final surface morphology [19]. For sputtering at normal incidence and at room temperature, diffusion dominates and the surface achieves a morphology that resembles the crystallographic symmetry of the underlying substrate [20, 21].

The Ar^+ flux was 10^{13} ions·cm^{-2}·sec^{-1}. The fluence (flux·time) was varied by changing the sputtering time at fixed flux. The values of the SP frequency and of the full-width at half maximum (FWHM) were obtained by subtracting a polynomial background and fitting the resulting spectrum by a Gaussian line-shape. The excellent LEED pattern and the good reflectivity of the surface suggest the occurrence of ion-induced long-range periodic modulations of the adlayer, i.e. ripples [20, 21], as observed for sputtered Ag single-crystal surfaces.

The left panel of Figure 1 shows the HREEL spectra recorded for ten layers of Ag for different values of the fluence. For the as-deposited Ag film, the loss spectrum presents only the ordinary SP at 3.79 eV, which is shifted to 3.89 eV (regardless of fluence) in the sputtered film.

Interestingly, the line-width of the SP peak increases with fluence (Figure 1, right panel).

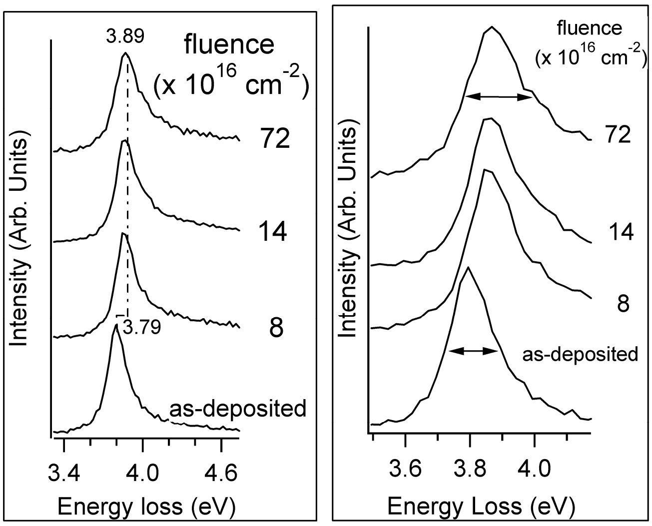

Figure 1: (left panel) HREEL spectra for 10 layers of Ag/Cu(111). The SP energy shifted from 3.79 eV (as-deposited film) to 3.89 eV, regardless of fluence. On the other hand, the FWHM of the SP peak broadened upon sputtering; (right panel) HREEL spectra after the subtraction of a polynomial background, presented in a restricted energy range. The arrows indicate the value of the FWHM, which increased from 164 to 235 meV upon increasing the fluence.

The analysis of the right panel of Figure 1 reveals that also the line-shape of the SP changed by sputtering. The SP peak became progressively asymmetric, as indicated by the increasing of the skewness [22], i.e. the third standardized momentum [23, 24], from 0.74 (as-deposited film) to 1.23 (last spectrum of Figure 1) upon sputtering.

The increasing value of the FWHM upon sputtering signals the onset of inelastic processes which shorten the SP lifetime. They should be ascribed to the enhanced Landau damping via “phase-breaking” scattering events. Very likely, the collisions of electrons with lattice defects in the sputtering-modified film are responsible of the progressive broadening of the SP line-width. However, it should be noticed that an accurate evaluation of the line-width of a long-lived excitation such as the Ag SP poses a nontrivial problem to theory [25].

Figure 2 shows the behavior of the FWHM as a function of the fluence. The FWHM is characterized by a power-law dependence on the fluence (F):

$$\mathrm{FWHM}=\Delta_0+A\cdot F^{pow}$$

where Δ_0= (164±3) meV; A= (8±2) meV·cm, and pow=0.50±0.06

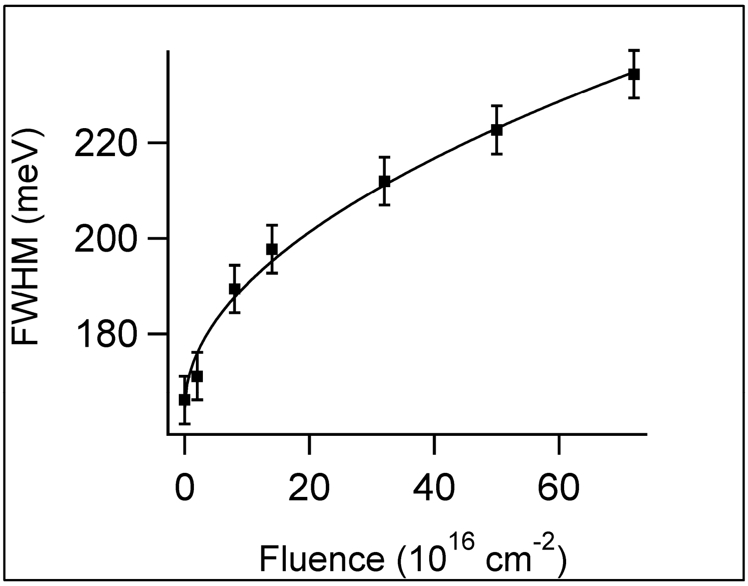

Figure 2: Behavior of the FWHM as a function of the fluence of the Ar^+ ion beam.

Interestingly, a square-root dependence exists between the FWHM and the fluence. Accordingly, by varying the fluence it is possible in principle to obtain any desired value of the FWHM, i.e. the SP lifetime. As discussed above, such finding has many potential applications and claim for dedicated investigations from both theoreticians and experimentalists. In fact, the SP lifetime is a key factor in many phenomena such as relaxation processes [26] and the propagation of SP polariton in SP sub-wavelength optics [27]. Moreover, it affects the functioning of "superlenses" [28].

In conclusion, we have demonstrated that the lifetime of the SP can be tuned upon sputtering as the FWHM follows a square-root dependence on fluence. On the other hand, the SP frequency is blue-shifted in sputtered films compared with as-deposited Ag layers. The possible technological implications of present findings were also discussed.

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PAPER XXII

Probing collective electronic excitations in ultrathin Ag layers grown on Cu(111)

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Probing collective electronic excitations in an Ag bilayer grown on Cu(111)

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Abstract

The nature and the dispersion of the electronic collective excitations in ultrathin Ag layers deposited onto the Cu(111) surface were investigated by angle-resolved high-resolution electron energy loss spectroscopy. For two Ag layers we found a nearly-flat behavior of the surface plasmon energy (absence of dispersion) as a function of the parallel momentum transfer, in good agreement with theoretical calculations performed within the framework of the s-d polarization model. However, the same agreement was not found for higher coverages, for which surface plasmon is confined in Ag grains.

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Keywords:

Collective electronic excitations in nanoscale systems have been widely studied in recent years[1–7]. In particular, the behavior of the surface plasmon (SP) dispersion in ultrathin films deposited on metal and semiconductor surfaces has been the subject of several theoretical[1,7–9] and experimental[3–5,10,11] investigations. Ultrathin films usually exhibit physical and chemical properties markedly different from their bulk counterpart as quantum size effects and electron quantum confinement may occur[12,13].

In the case of simple metals it has been demonstrated that the nature of collective electronic excitations occurring in two layers is very different from that in multilayers. For alkali bilayers, the jellium model predicts that at small momenta the SP has a vanishing weight[1,7] and in this limit only bulk plasmon (BP) and multipole plasmon exist[1]. Increasing the coverage above two layers, the excitation of SP becomes possible also in the long-wavelength limit (small momenta).

In silver samples, considering its s electron density, the energy of the SP is expected to be 6.50 eV, but due to the interaction between s and d electrons it is lowered to 3.70 eV. Moreover, contrary to alkali-metal systems[1,4,10,11], the dispersion of Ag SP was found positive[1,2,14–16]. A negative dispersion on Ag systems was reported only for modified Ag single-crystal surfaces, i.e. Cl/Ag(111)[17], O/Ag(100)[18], and the sputtered and nanostructured Ag(100)[19]. While Ag semi-infinite media have been extensively investigated[2,14–16], a very few experimental studies on low-dimensional Ag systems, such as ultrathin films on metal[5] and semiconductor substrates[20–22], nanowires[23], nanoparticles[24,25], and quantum dots exist. On the other hand, it would be extremely useful to study dynamic screening processes in the case of Ag bilayers deposited on metallic substrates. In fact, two layers are commonly accepted as a borderline between interface physics and thin-films physics[1,10,11]. Such coverage constitutes the minimal thickness necessary to observe in loss spectra well-distinct features assignable to collective excitations, while the very broad loss features observed from 0 to 2 ML are assigned to single-particle transitions[11]. Increasing the coverage, the nature and the dispersion of the collective excitations in the Ag thin film approach those of bulk Ag. The excitation spectra of Ag films deposited onto an aluminum substrate were calculated by Liebsch using the s-d polarization model[1]. As expected, the nature and dispersion of the collective excitations calculated for two layers deviated substantially from those reported for multilayers[5]. However, to the best of our knowledge, no experimental study for Ag/metal interfaces supporting such theoretical findings[1] exists. On the other hand, experiments carried out on ultrathin Ag films grown on Si(111)[21,22] reported a positive behavior of the SP dispersion and, moreover, the collective excitation observed at small momenta was assigned to the ordinary SP. These findings are in contrast with theoretical expectations[1] performed for Ag/Al, thus indicating the existence of strong differences in the electronic response between Ag layers deposited onto metallic and semiconductor substrates. Hence, further experimental work aimed at investigating the nature of the collective excitations in metal/metal interfaces is needed. Such studies should provide a significant advancement in understanding dynamic screening processes in the limit of ultrathin metallic layers, especially for the quite intriguing case of two layers.

Herein we present high-resolution electron energy loss spectroscopy (HREELS) measurements shedding light on the nature and the dispersion of the collective excitations in ultrathin Ag layers on Cu(111). This system represents an example of film growth in large (13 %) mismatched materials. As the surface energy of Ag and the stress energy at the interface are lower than the Cu substrate energy, the Ag ultrathin films grows layer-by-layer up to two layers[26,27]. Further increasing Ag coverage, three-dimensional Ag islands are formed. Scanning tunnelling microscopy and low-energy electron diffraction (LEED) measurements showed that the two Ag layers form a (9x9) reconstruction[26,27]. Moreover, it is worth mentioning that photoemission measurements of Ag/Cu(111)[28–31] revealed the existence of well-defined Ag 5sp-derived quantum well states (QWS) even for rather high film thickness. This implies the occurrence of an enhanced sp density of states at the Fermi level that modifies the electron charge-density distribution, and thus significant changes in the dynamical screening properties[32] with respect to the case of single-crystal surfaces are expected. Hybridization between Ag QWS and the substrate[33] may also influence the electronic response of the interface and it should be enhanced for very reduced thicknesses, i.e. 2 ML. Loss measurements reported here demonstrated that in two Ag layers the excitation of SP is not allowed at small momenta. The excitation at $q_{||} \sim 0$ is assigned to the ordinary BP. Moreover, for $q_{||} > 0.087 \mathring{A}^{-1}$ the SP energy did not exhibit a positive dispersion. Such finding demonstrated that an excellent agreement with theoretical calculations performed for two layers of Ag on Al[1] exists.

Experiments have been carried out in ultrahigh vacuum (at a base pressure of $5 \cdot 10^{-9}$ Pa) on a Cu single crystal cut within 0.1 ° along the (111) direction. The sample is a 9 mm diameter disk which was delivered from MaTecK GmbH. It was cleaned by cycles of 1.5 keV sputtering with Ar ions followed by annealing for 30 minutes to 800-900 K. The structure of the Ag adlayer was analyzed by low-energy electron diffraction (LEED) measurements, showing the characteristic[26,27] diffraction pattern of the reconstructed (9x9) structure in correspondence of the adsorption of the flat bilayer. Ag was evaporated from a heated wire, while the crystal was kept at room temperature. The amount of evaporated Ag was calibrated with Auger electron spectroscopy (AES) and LEED measurements. The energy loss spectra were recorded with an Ibach-type spectrometer at a crystal temperature of 300 K. For the present experiment the momentum resolution was 0.012 Å^{-1}, while the energy resolution was tuned to 10 meV to improve the signal-to-noise ratio of the losses.

Selected HREEL spectra for 2 of Ag/Cu(111) as a function of the parallel momentum transfer are showed in Figure 1a. Instead, the energy of the loss features as a function of the parallel momentum transfer is shown in Figure 2. To obtain the energies of loss peaks plotted in Figure 2, a polynomial background was subtracted from each spectrum. The resulting spectra were fitted by a Gaussian line-shape (not shown).

From Figure 1a it can be observed that at the smallest momenta ($q_{||} = 0.024 \AA^{-1}$ and $0.051 \AA^{-1}$) a loss peak with a very reduced intensity was revealed at about 4.15 eV. The intensity of the loss peak increased notably with $q_{||}$ while its energy underwent a sudden red-shift down to 3.96 eV. For $q_{||} > 0.087 \AA^{-1}$, the energy of the latter loss peak remained almost constant. We assign the feature at about 4.15 eV to the BP in two Ag layers. Instead, the dispersionless feature at 3.96 eV is assigned to the SP in two Ag layers. The significant energy step existing between small and high momenta is due to the different nature of the excitation, i.e. BP and SP, respectively, and not to a rapid change of the SP dispersion. On the other hand, the existence of two well-distinct plasmonic excitations for extremely reduced thicknesses well agrees with the current theoretical picture of collective electronic excitations in thin films[1,8,9]. Both features are strongly blue-shifted by s-d screening[1] compared to their respective values in Ag semi-infinite media, i.e. 3.80 and 3.70 eV, respectively. The blue-shift of the SP frequency was previously observed in thin Ag films on Si(111)[20–22] and Ni(111)[5] and it is fully described within the framework of the s-d polarization model[1]. As the thickness of the Ag film is reduced, the overall screening of the charge associated to the SP via the polarizable d electronic medium diminishes, giving higher plasmon energy[1]. As regards the blue-shift of the BP, it is shifted by s-d screening at a frequency $\omega_p* = \omega_p/\varepsilon_d$, where ε_d is the local dielectric function and ω_p is the s-p BP frequency[1]. The real part of the dielectric function decreases as the film thickness is reduced, as a direct consequence of the occurrence of a less sharp onset of transitions involving d states in thin films compared to bulk Ag[1]. The lack of the SP excitation at $q_{||}=0$ was reported also for ultrathin alkali layers, from both theoreticians[1] and experimentalists[3]. In this case, the surface response function in the long-wavelength limit (small momenta) is peaked at the BP frequency as the overlayer SP has a vanishing weight[1]. On the contrary, in ultrathin and flat Ag layers on Si(111)[21] the SP was excited even at small momenta. Such evidence should be taken as a fingerprint of very different screening processes between 2.5 ML Ag/Si and 2 ML Ag/Cu. The SP was excited at $q_{||} \approx 0$ also for Ag layers on Si(111) nanostructured in islands[20]. However, increasing Ag coverage, i.e. 5 ML (Figures 1b and 2) the SP was excited also at small values of $q_{||}$, as generally found for thick alkali layers[34]. This result suggests that no substantial differences in the electronic response between Ag/Cu and Ag/Si exist for a sufficiently high thickness, so as to reduce the influence of the underlying substrate. As regards the SP dispersion for 2 ML Ag/Cu(111) ($q_{||} > 0.087 \mathring{A}^{-1}$), it was not positive (Figure 2) in contrast with all previous measurements on unmodified Ag surfaces[2,14–16] and Ag/Si(111)[21] exhibiting, instead, a positive and quadratic dispersion. In Figure 3 we compare the SP dispersion for different Ag systems. We notice that strong differences in both energy and dispersion behavior exist for the different cases. Interestingly, the results of present measurements for 2 ML well agree in dispersion with the theoretically predicted behavior[1] (Figure 3a).

Increasing the Ag thickness beyond the bilayer, the Ag film becomes granular[28–31]. Spectra for 5 ML are shown in Figure 1b. The analysis of the dispersion relation (Figure 2) reveals that SP is confined within Ag grains, as indicated by the absence of dispersion below a critical wave vector[20], i.e. 0.18 $\mathring{A}^{-1}$. While the lower energy of the SP has to be ascribed to the increased thickness[21], the changes in growth mode are responsible of the dissimilarities in the SP dispersion relation. Similar results were obtained for slightly similar coverages.

It should be noticed that in the theoretical investigation for 4 ML Ag/Al[1], the SP was excited only for momenta higher than $0.05 \mathring{A}^{-1}$, while for experimental studies on 5 ML Ag deposited on both Si(111)[20–22], Ni(111)[5], and Cu(111) the SP was excited even at the smallest momenta, thus suggesting that the thickness dependence of the behavior of the SP dispersion is not appropriately described by s-d polarization model[1] (Figure 3b).

Important information on collective electronic excitations at metal surfaces could be provided by the dispersion relation of the full-width at half maximum (FWHM). An initial negative behavior of the FWHM was found for both 2 and 5 ML Ag/Cu(111) (Figure 4), but beyond a critical wave-vector the dispersion became positive. This is well described within the framework of a recently proposed[7] theoretical model on plasmon lifetime in free-standing Ag layers. The initial negative behavior was ascribed[7] to the splitting between symmetric and anti-symmetric excitation modes and to the enhanced electron-hole pair excitation at small $q_{||}$. The increased value of the FWHM for 2 ML compared with 5 ML suggests that damping processes of the SP through indirect 5sp-5sp transition between Ag 5sp-derived QWS confined in the adlayer are more efficient for thinner films.

In conclusion, our results demonstrated that the SP dispersion in an Ag bilayer on Cu(111) is not positive, in contrast with all previous measurements on Ag semi-infinite media. At small momenta, at which the SP has a vanishing weight, the feature observed in loss spectra was assigned to the BP, in agreement with theory and with previous results on alkali ultrathin layers. Significant differences found between 2 and 5 ML of Ag/Cu(111) are a clear experimental evidence of the changes occurring in screening processes as Ag thickness increases, and also of changes in the growth mode. However, the s-d polarization model did not accurately describe the thickness dependence of the SP dispersion relation.

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Figure Captions

FIG. 1: Selected HREEL spectra as a function of the parallel momentum transfer for 2 ML Ag/Cu(111) (top panel) and 5 ML Ag/Cu(111) (bottom panel) at T=300 K.

FIG. 2: SP dispersion relation for 2 ML and 5 ML of Ag on Cu(111) at T=300 K.

FIG. 3: (a) Behavior of the dispersion curve of the Ag SP for 2 ML Ag/Cu(111) (our data, filled squares), 2 ML Ag/Al (theory, continuous line)[1], and Ag(111) (dashed-dotted line)[16]. (b) Behavior of the dispersion curve of the Ag SP for 5 ML Ag/Cu(111) (our data, filled squares), 4 ML Ag/Al (theory, continuous line)[1], and Ag(111) (dashed-dotted line)[16].

FIG. 4: Behavior of the FWHM for plasmonic excitations on 2 and 5 ML of Ag/Cu(111).

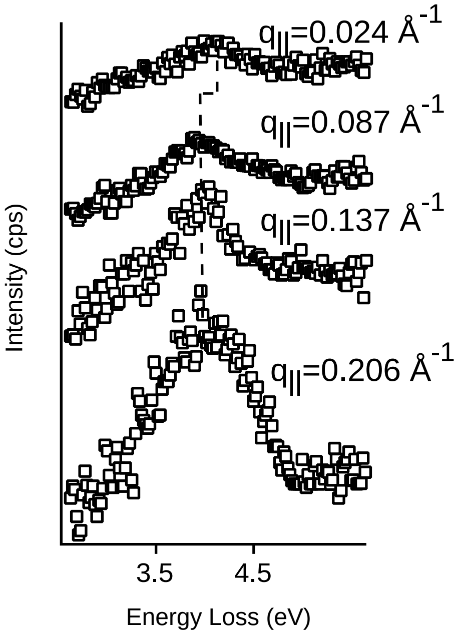

Figure 1a BUJ1093 24Sep2008

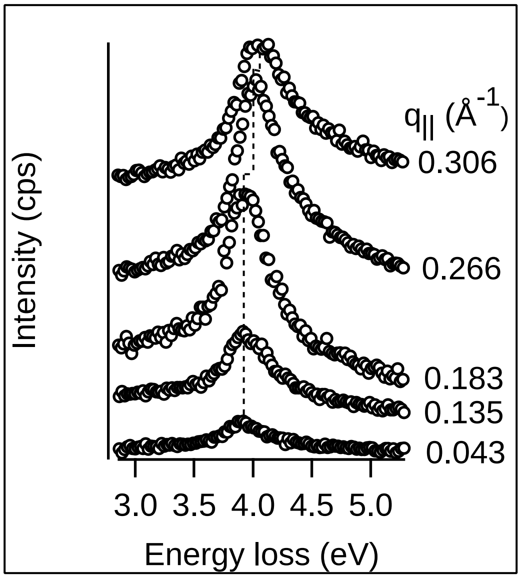

Figure 1b BUJ1093 24Sep2008

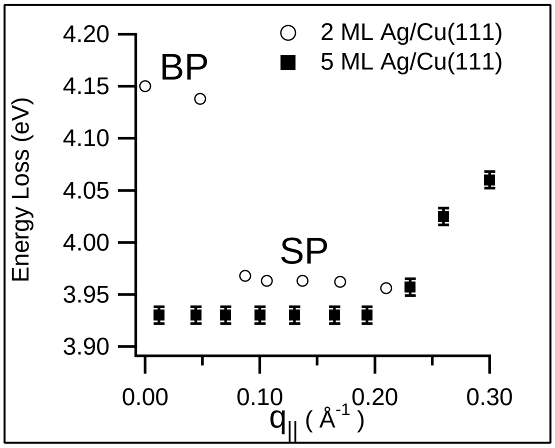

Figure 2 BUJ1093 24Sep2008

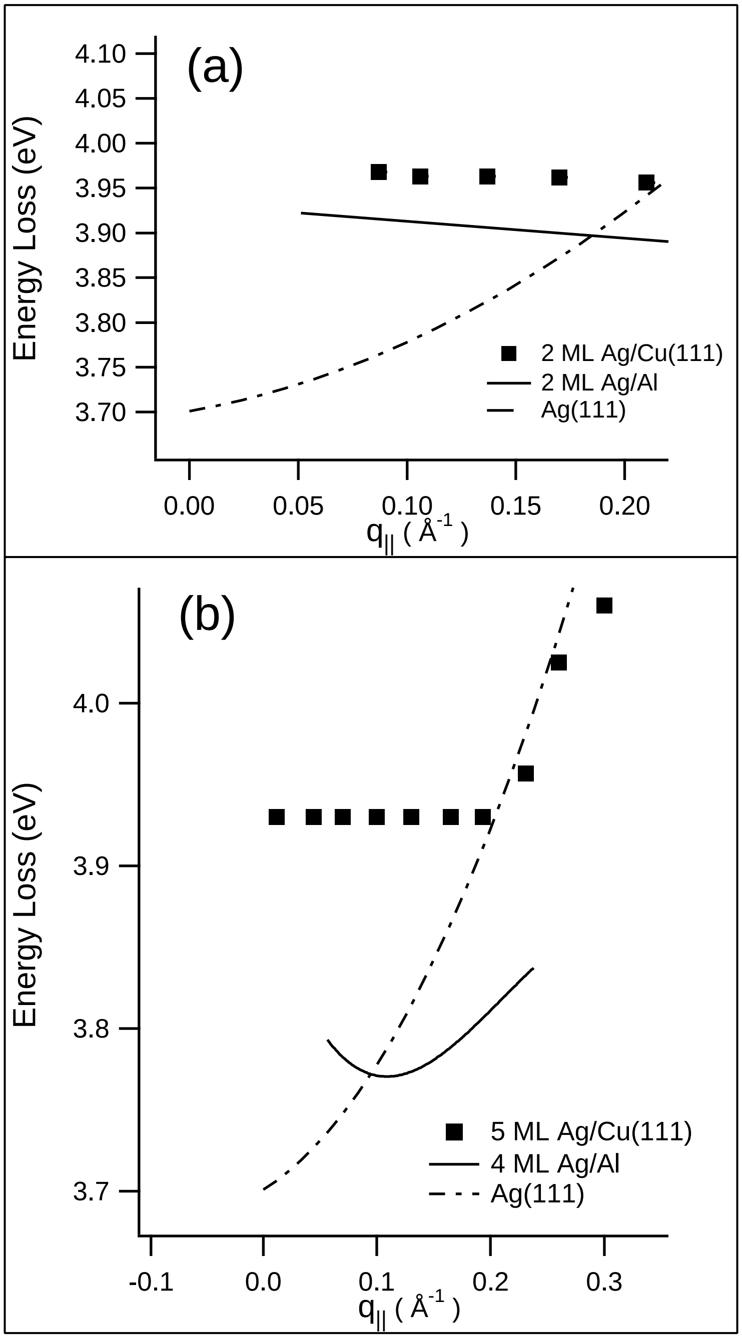

Figure 3 BUJ1093 24Sep2008

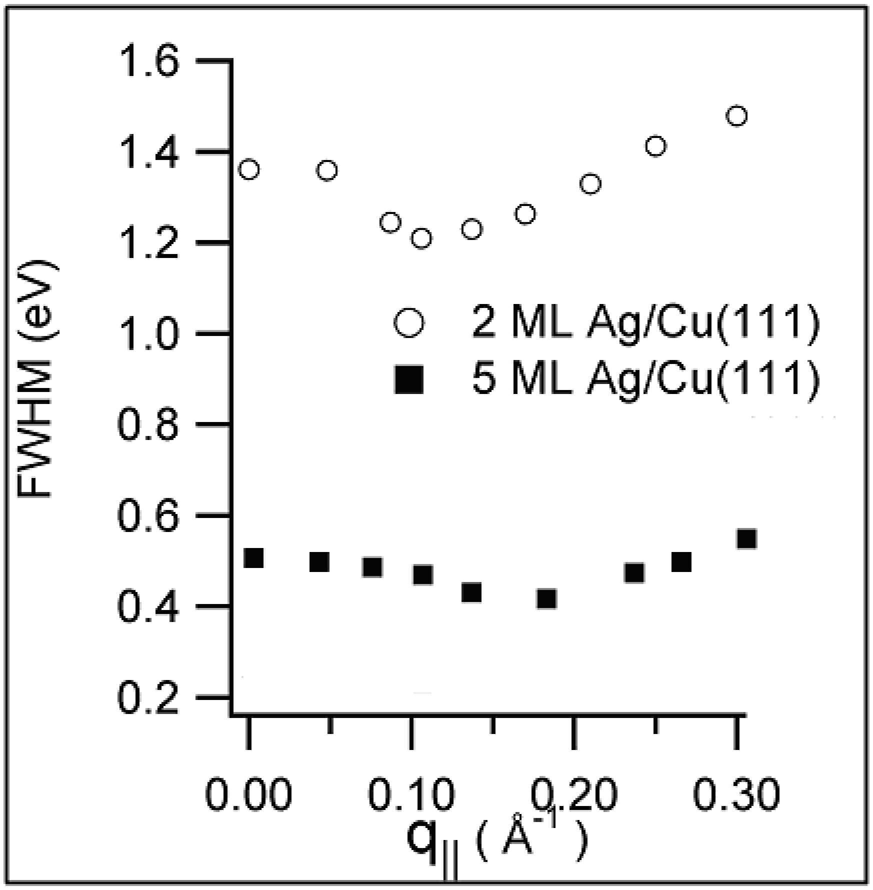

Figure 4 BUJ1093 24Sep2008

PAPER XXIII

Dispersion and damping of Ag surface plasmons in annealed and sputtered thin films

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Dispersion and damping of Ag surface plasmon in annealed and sputtered thin films

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The dispersion of surface plasmon in as-deposited and modified Ag thin films on Cu(111) was investigated by angle-resolved high-resolution electron energy loss spectroscopy. Loss measurements revealed that for the as-prepared film the surface plasmon is confined within Ag grains. The confinement of the surface plasmon was removed upon annealing. The linear coefficient of the dispersion became slightly negative for the annealed film and this effect was ascribed to the enhancement of the free-electron density of states. On the contrary, on the sputtered Ag film the quadratic term dominates, as found for the sputtered Ag(100) surface.

PACS numbers: 73.20.Mf, 79.20.Uv, 79.60.Dp

I. INTRODUCTION

The growth of thin metallic films continues to attract a great interest for both fundamental and technological reasons[1,2]. Thin films exhibit novel physical and chemical properties, as a consequence of the presence of quantum well states (QWS)[3,4], whose wave function describes electrons confined within the adlayer. Such states have been observed in a great variety of systems and, in particular, in thin films grown on the Cu(111) surface[4,5] which presents a large energy gap at the $\bar{\Gamma}$ point of the projected bulk band structure. Recently, the dispersion of QWS has been found to change by annealing the adlayer[2]. Angle-resolved photoemission experiments showed that Ag QWS on Au(111) have flat in-plane dispersion in a disordered film and a nearly free-electron-like dispersion in an annealed and well-ordered film. Accordingly, the sp density of states of the film may be finely tuned by annealing. Moreover, the possibility of nanostructuring surfaces by ion bombardment was demonstrated by scanning tunnelling microscopy[6,7]. The surface morphology is determined by the interplay between the sputtering and the surface diffusion. Ion-induced nanostructures were observed on Ag(110)[7], Cu(110)[8,9], and Ag(001)[6]. The angle of incidence of the ions can also be used to select the final surface morphology[10]. For sputtering at normal incidence, diffusion dominates and the surface morphology resembles the crystallographic symmetry of the underlying substrate: ripples form on Ag(110) and Cu(110) and a checkerboard structure of pits and hills on Ag(001). The application of ion sputtering techniques in producing novel nanoscale structures may be of great interest for future applications[11].

Further information on the physical and chemical properties of such manipulated nanostructured films can be obtained from their electronic excitations and, in particular, from the dispersion relation of the collective modes. A drastic change in the dispersion curve of Ag surface plasmon (SP) was reported[12] for a sputtered Ag(100) surface. Upon sputtering, the linear coefficient of the dispersion changed from positive to negative, while the quadratic term increased so as to recover the value of the quadratic term of bulk plasmon. However, dynamic screening properties of annealed and sputtered Ag films have not been investigated yet. On the other hand, screening effects are of fundamental importance in understanding the electronic response of systems exhibiting confined electrons[13].

Herein we present a high-resolution electron energy loss spectroscopy (HREELS) study aimed at investigating the SP dispersion in thin Ag layers on Cu(111). Photoemission measurements of Ag/Cu(111)[14–17] revealed the existence of well-defined Ag 5sp-derived QWS even for quite high film thickness. This implies the occurrence of an enhanced sp density of states at the Fermi level that modifies the electron charge-density distribution, thus causing significant changes in dynamical screening properties[18]. At room temperature Ag layers grow on Cu(111) in the Stranski-Krastanov growth mode. The layer-by-layer growth of Ag film stops at the completion of the first two layers, characterized by the occurrence of a (9x9) reconstruction[19,20]. Further increasing Ag coverage, three-dimensional islands grow on the flat silver bilayer. Annealing caused changes in the photoemission spectra and in the morphology of the film[16] and, moreover, silver dissolution into the substrate occurred[21,22].

Loss measurements reported here demonstrate that SP is confined within Ag grains in as-deposited Ag layers. Annealing removed SP confinement and, moreover, induced the occurrence of a negative value of the linear coefficient of the SP dispersion, as a consequence of the enhanced free-electron character of Ag QWS upon annealing[2]. For the sputtered film, the quadratic term of the dispersion was found to be predominant, as for the sputtered Ag(100) surface[12].

II. EXPERIMENTAL

Measurements were carried out in a UHV chamber operating at a base pressure of $5\text{x}10^{-9}$ Pa, equipped with standard facilities for surface characterizations. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Cu(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 700-800 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Silver was deposited onto the Cu(111) surface by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈0.05 ML/min). The occurrence of the p(1x1)-Ag LEED pattern was used as the calibration point of θ_{Ag}=1.0 ML. Around each spot of the p(1x1)-Ag, LEED measurements showed also the occurrence of a (9.5x9.5) reconstruction for the first Ag layer and of a (9x9) reconstruction in correspondence of θ_{Ag}=2.0 ML, in excellent agreement with previous structural studies on this system[19,20]. A constant sticking coefficient was assumed to obtain other desired Ag coverage. All depositions and measurements were made at room temperature. The sputtering of the Ag film was performed at room temperature, using Ar$^+$ ions with an impinging energy of 1 keV and in normal incidence. We worked at a sputtering flux of 10^{13} ions cm^{-2} sec and a fluence of 1.7x10^{15} ions cm^{-2}. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio for off-specular spectra. The measured angular acceptance α of our electron energy analyzer was 0.5 °. Dispersion of the collective mode, i.e., E$_{loss}(q_{||})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. The sample was oriented along the $\bar{\Gamma}-\bar{\mathrm{K}}$ direction. The incident angle with respect to the sample normal was fixed at 55 °. To measure plasmon dispersion, values for the parameters E_p, impinging energy, and θ_i , the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, E_p=40 eV, provided, in fact, the best compromise among surface sensitivity, the highest cross-section for mode excitation, and $q_{||}$ resolution. As

$$\hbar\overrightarrow{q_{||}} = \hbar\left(\overrightarrow{k_i}\sin\theta_i - \overrightarrow{k_s}\sin\theta_s\right),$$

the parallel momentum transfer, $q_{||}$ depends on E_p, E_{loss}, θ_i, and θ_s according to[23,24]:

$$q_{||} = \frac{\sqrt{2mE_p}}{\hbar}\left(\sin\theta_{\mathrm{i}} - \sqrt{1-\frac{E_{loss}}{E_p}}\sin\theta_s\right)$$

where E$_{loss}$ is the energy loss and θ_s is the electron scattering angle. Under the conditions in the present experiment, we estimate the integration window in the reciprocal space[23,24] to be $\Delta q_{||}$=0.012 $\mathrm{\AA}^{-1}$, much less than the scanned range in the reciprocal space.

III. RESULTS AND DISCUSSION

Selected HREEL spectra for as-deposited Ag layers as a function of the scattering angle are showed in Figure 1. The granularity of the as-deposited film is argued from the behavior of the dispersion of the SP. The absence of dispersion below a critical wave vector, i.e. 0.18 $\mathring{A}^{-1}$ (Figure 2), indicates that the plasmon is localized within each single (111)-oriented grain. Similar results were reported for Ag/Si(111)[25] nanostructured in islands (Ag films on Si(111) in the work by Yu et al.[26] were instead characterized by a layer-by-layer growth and no SP confinement occurs). The propagation of the SP can occur only for modes whose wavelength is smaller than the diameter of the single grain. Interestingly, the Ag grains behave like isolated clusters with respect to the plasmonic excitation. The behaviour of the SP well agree with the Stranski-Krastanov growth mode of this system. The increasing strain caused by adsorbed layers destabilizes the film and induces clustering[27]. This behavior arises from the large lattice mismatch between Ag and Cu (13 %). The existence of Ag islands for coverages higher than 2 ML is in agreement with previous structural studies[16,19,20]. It is worth noticing that we have no evidences for the existence of Mie plasmons within Ag islands. Two well-distinct Mie plasmons at 3.1 and 3.9 eV were revealed only for Ag deposited on metal-oxide surfaces[28,29] and not for three-dimensional islands on Si(111)[25]. As concerns metal/metal interfaces, the occurrence of Mie plasmons was invoked only for Na quantum dots on Cu(111)[4,30] but only for a very restricted alkali thickness range. Mie plasmon merged into the ordinary SP already for two nominal Na layers.

In the Ag film the energy of the SP for small momenta was found to be 100 meV higher than that reported for bulk Ag. This is in excellent agreement with calculations within the framework of the s-d polarization model[13] and with previous experimental studies[25,26,31,32]. In order to remove SP confinement, an annealing of the film at 400 K was performed. Loss spectra in figure 3 provided evidences for drastic morphological changes in the film that may be ascribed to a re-ordering of the film. LEED measurements indicated that a flattening of the Ag adlayer has occurred without the formation of an AgCu alloy (also confirmed by AES).

The dispersion curve changed significantly upon annealing and, moreover, the SP confinement was lost. The measured dispersion curve $E_{loss}(q_{||})$ of the annealed film, reported in fig. 2, was fitted by a second-order polynomial given by:

$$E_{loss}(q_{||}) = A + Bq_{||} + Cq_{||}^2$$

(A=3.791±0.006 eV; B=-0.60±0.09 eV·$\mathring{A}$; and C=3.4±0.3 eV·$\mathring{A}^2$)

The linear coefficient was found to be slightly negative. Recently, it has been found to be null on layer-by-layer Ag films grown on Ni(111)[32]. This finding was ascribed to the enhanced sp density of states existing in thin Ag films, as a direct consequence of the presence of QWS. Increasing the free-electron character of the QWS by annealing[2] should imply the occurrence of a negative linear term. Nonetheless, the value of the linear coefficient is still enough higher than the linear coefficient of the SP dispersion curve of alkalis, aluminium, or alkaline-earth metals[24,34]. In contrast with all other Ag systems[24,26,35] in which the centroid of the induced charge is well inside the geometrical surface[36], in annealed Ag films it lies in the close vicinity of the jellium edge[24,33,34], but not outside as for simple metals. Interestingly, the quadratic coefficient coincides with that of SP dispersion in Ag(111)[35], i.e. the surface with the same crystallographic orientation.

Significant differences exist between spectra acquired for annealed (figure 3) and sputtered films (figure 4). The dispersion curve measured in a sputtered Ag film and reported in figure 2 shows that the quadratic term is predominant:

(A=3.760±0.004 eV; B=-0.08±0.06 eV$\cdot \mathring{A}$; and C=2.5±0.2 eV$\cdot \mathring{A}^2$).

Accordingly, an increased linear coefficient and a decreased quadratic term were obtained by fit procedure. Contrary to the sputtered Ag(100) surface[12] the bulk value of 6 eV$\cdot \mathring{A}^2$[37] was not recovered for the quadratic term . Probably, the link proposed in Ref. 12 between the value of the quadratic term of the SP dispersion and that of the bulk plasmon, related to bulk properties, should be revised. The occurrence of an increased linear coefficient suggests that sputtering induces a significant shift of the position of the centroid of the induced charge associated to the SP compared to the case of annealed films. The analysis of the SP dispersion curve seems to exclude the occurrence of SP confinement and, thus, the formation of islands. It is worth mentioning that ion bombardment of a growing film was found to produce both bombardment-induced segregation normal to the film surface and an advancing nanoscale subsurface diffusion zone[38]. Both of such phenomena should be considered in theoretical studies on the electronic response of sputtered thin films. Moreover, our results provide the grounds for angle-resolved photoemission experiments shedding light on the sputtering-induced modifications of the QWS.

Important information about collective electronic excitations at metal surfaces could be provided by the behavior of the full-width at half maximum (FWHM). For the as-deposited Ag film, the initial dispersion of the FWHM is negative (Figure 5). The behavior became positive after a critical wave-vector (0.10 Å^{-1}). This finding is in agreement with results for Ag/Si(111)[26] and with recent theoretical calculations for free-standing Ag slabs[39]. It was ascribed to the splitting between symmetric and anti-symmetric excitation modes at small $q_{||}$[39]. However, the behavior of the FHWM for single-crystal Ag surfaces is positive[24,35] and was recovered by annealing the Ag film. It is worthwhile noticing that in all cases (as-deposited, annealed, and sputtered Ag film), the value of the FWHM is higher than for Ag semi-infinite media (for Ag(111) the FWHM at small momenta is 69 meV[35]). In fact, the different distribution of occupied and unoccupied electronic states in thin films with respect to surfaces would imply enhanced damping mechanisms for collective excitations by creating electron-hole pairs.

In conclusion, loss measurements provided evidences that SP is confined within islands in as-deposited Ag layers on Cu(111). The annealing of the Ag adlayer causes the loss of SP confinement and determines an enhancement of the free-electron density of states, which renders slightly negative the linear coefficient of the dispersion relation. On the other hand, sputtering induces an increasing of the linear term and a decreasing of the quadratic term.

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Figure Captions

FIG. 1: HREEL spectra for as-deposited 22 ML Ag/Cu(111). All spectra were normalized to the intensity of the elastic peak and multiplied by the same factor. It should be noticed that the normalized intensity of the surface plasmon is higher for off-specular spectra, as expected for not purely dipolar excitations.

FIG. 2: SP dispersion for as-deposited, annealed, and sputtered Ag films (22 ML) on Cu(111).

FIG. 3: HREEL spectra for 22 ML Ag/Cu(111) after an annealing at 400 K. Measurements were carried out at 300 K.

FIG. 4: HREEL spectra for a sputtered 22 ML Ag/Cu(111) surface.

FIG. 5: Behavior of the FWHM for as-deposited, annealed, and sputtered Ag films (22 ML) on Cu(111).

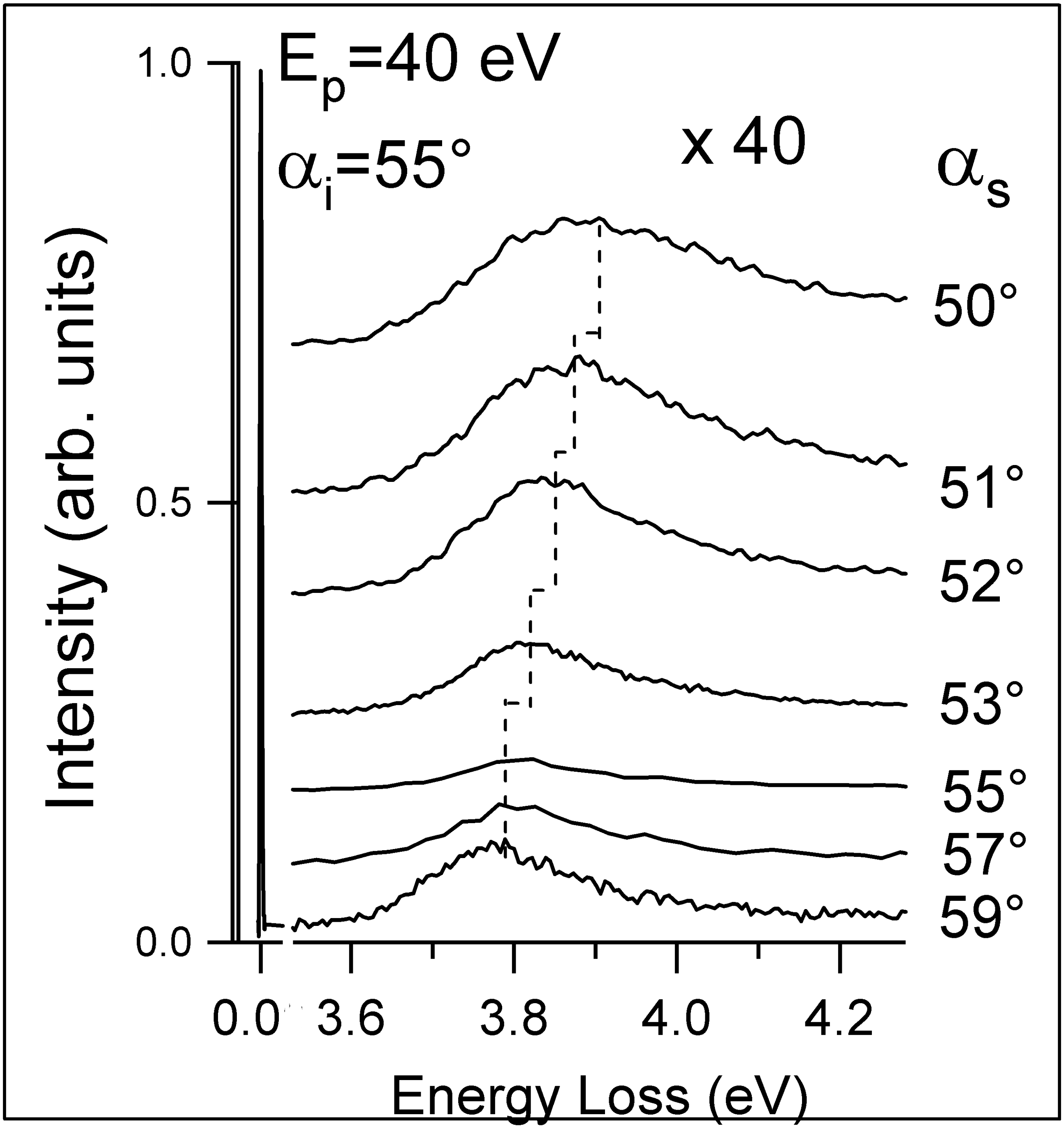
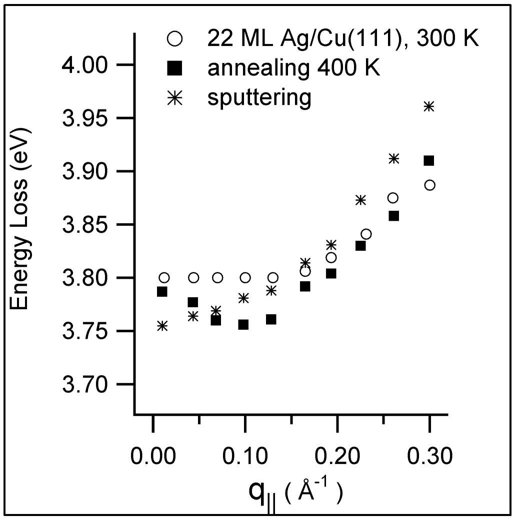


Figure 1 BS11023 15Sep2008



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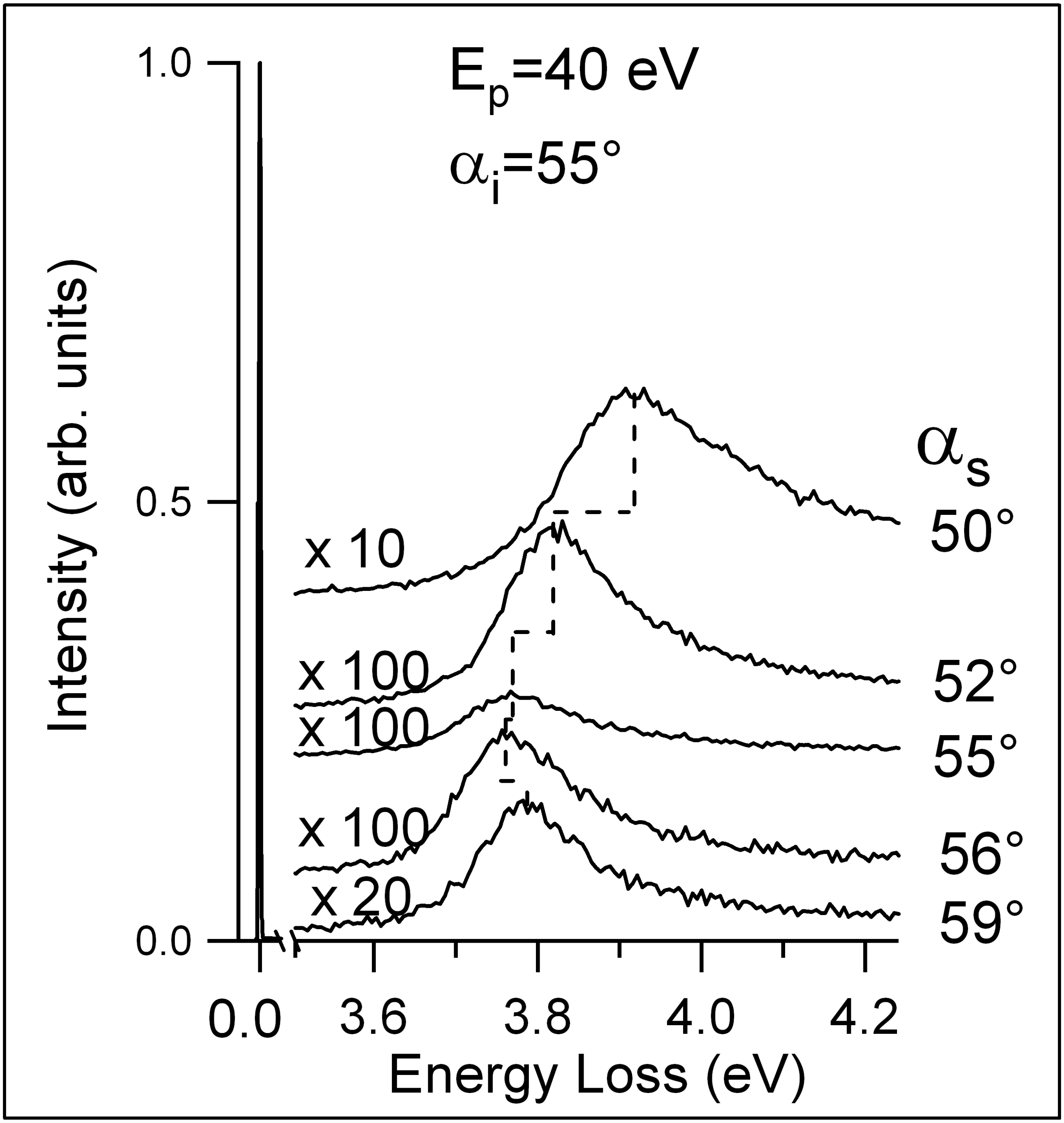

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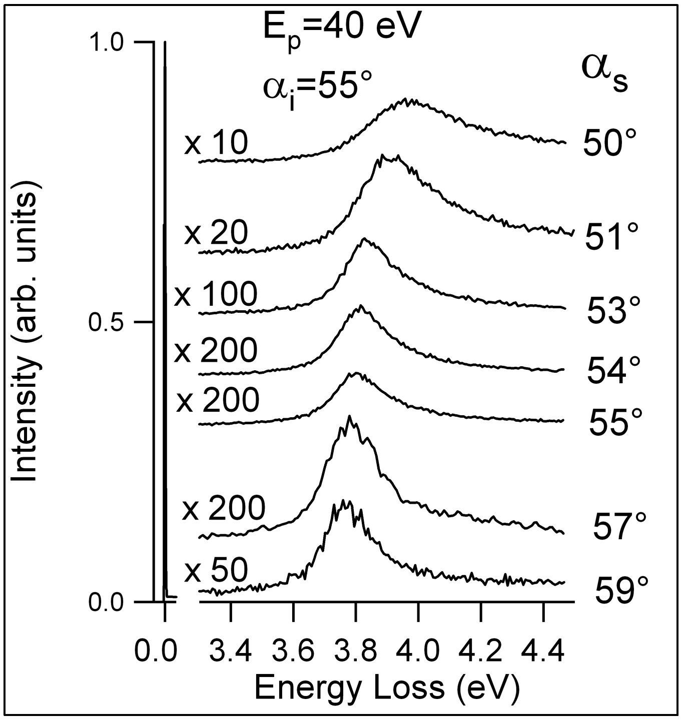

Figure 4 BS11023 15Sep2008

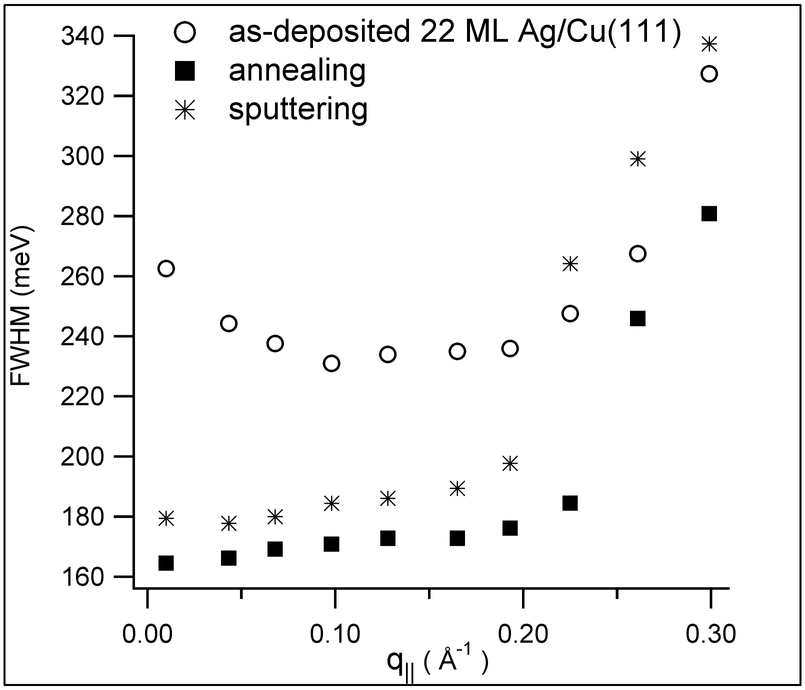

Figure 5 BS11023 15Sep2008

PAPER XXIV

Dispersion and damping of surface plasmon at metal/metal interfaces: Ag/Cu(111) and Ag/Ni(111)

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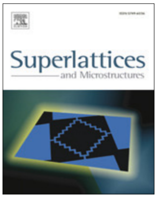

Dispersion and damping of surface plasmon in Ag thin films grown on Cu(111) and Ni(111)

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ABSTRACT

We present high-resolution energy loss spectroscopy measurements on the dispersion and damping of collective electronic excitations in ultrathin Ag films grown on Cu(111) and Ni(111). For Ag/Cu(111) the surface plasmon was found to be confined within grains but confinement was removed by annealing. On the other hand, a purely quadratic dispersion was observed for the layer-by-layer Ag film deposited onto the Ni(111) surface.

Recently, collective electronic excitations on thin metal films have attracted a considerable attention due to the fundamental interest in understanding dynamic screening processes at metal/metal interfaces and for potential applications [1–5]. In particular, while Ag semi-infinite media (surfaces) have been extensively studied [6], experimental studies on Ag thin films deposited onto metallic substrates are less common. Ag films grown on copper and nickel surfaces are suitable systems for such aims as silver does not form alloys with these substrates at room temperature.

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on the dispersion and damping of surface plasmon (SP) in thin Ag films deposited on Cu(111) and Ni(111). For Ag on Cu(111), which follows the Stranski–Krastanow growth mode [7] (islands appear on the flat Ag adlayer for coverages higher than two layers), the SP was confined within Ag grains. The SP confinement was removed upon annealing at 400 K. The linear term of the dispersion curve measured in the annealed film was found to be slightly negative, as a consequence of the enhanced free-electron character of quantum well states upon annealing [8]. On the other hand, on layer-by-layer Ag films on Ni(111) a purely quadratic dispersion was recorded.

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1. Experimental

Experiments were carried out in an ultra-high vacuum chamber with a base pressure of 5×10^{-9} Pa. The Cu(111) and Ni(111) surfaces were cleaned by repeated cycles of ion sputtering and annealing at 800–900 K. The cleanliness and order of both the substrate and the Ag overlayer were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Silver was deposited onto the Cu(111) and Ni(111) surfaces by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates ($\approx$0.05 ML/min). The occurrence of the $p(1 \times 1)$-Ag LEED pattern was used as the calibration point of $\theta_{\mathrm{Ag}} = 1.0$ ML. As concerns Ag/Cu(111), around each spot of the $p(1 \times 1)$-Ag, LEED measurements showed also the occurrence of a (9.5×9.5) reconstruction for the first Ag layer and of a (9×9) reconstruction in correspondence of $\theta_{\mathrm{Ag}} = 2.0$ ML, in excellent agreement with previous structural studies on this system [9,10]. Similar results were achieved by a calibration procedure using AES. As regards the Ag/Ni(111) system, the absence of a plateau in the SP dispersion reported elsewhere [4] is a fingerprint of a layer-by-layer growth for Ag on Ni(111) at room temperature in the investigated film thickness range (0–10 ML), as also confirmed by photoemission results reported for the same substrate temperature and deposition rate [11]. For the first Ag layer, LEED pattern showed spots characteristic of the $p(1 \times 1)$-Ag overstructure and of the Ni(111) substrate. When the Ag coverage reached three layers, a clear (7×7) reconstruction was revealed by the analysis of the LEED pattern. The incident angle with respect to the sample normal was fixed at 55.0°. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS), whose energy resolution was degraded to 10 meV so as to increase the signal-to-noise ratio for off-specular spectra. The kinetic energy of the impinging electrons was 40 eV. The measured angular acceptance α of our electron analyzer was $\pm 0.5°$. The integration window in the reciprocal space [6] was estimated to be 0.02 Å^{-1}. All depositions and measurements were made at 300 K.

2. Results and discussion

Selected HREEL spectra measured for 5 ML Ag/Cu(111) are showed in the left panel of Fig. 1. The loss feature recorded at 3.93 eV was assigned to the Ag SP. Its loss energy is significantly blue-shifted with respect to the value found on single-crystal Ag surfaces [6]. This effect was ascribed to the reduced screening of the charge associated with the Ag SP via the polarizability of the d-electron medium [12, 13]. The SP energy did not shift up to a critical wave-vector of about 0.19 Å^{-1}.

The presence of such critical value of the parallel momentum transfer indicates that Ag s electrons oscillate independently in the single grains. Similar results were reported for Ag/Si(111) [12]. The critical wave vector was suggested [12] to be related to the average island size through the relation:

$$q_c = 2\pi / d.$$

From the above equation, the grain size in Ag/Cu(111) is estimated to be about 30–40 Å.

The propagation of the SP can occur only for modes whose wavelength is smaller than the diameter of the single grain. Interestingly, in this system the Mie plasmon was not revealed, probably due to the large extension of Ag islands with respect to Ag nanoparticles in which it is usually observed [6]. The behavior of the SP agrees well with the Stranski–Krastanov growth mode of this system [7].

The SP confinement was removed by annealing at 400 K (left panel of Fig. 2) that, evidently, induced both a re-ordering and a flattening of the Ag film. The SP dispersion curve was found to be quadratic, with a slightly negative linear coefficient (−0.6 eV Å). Nonetheless, the value of the linear coefficient is still enough higher than the linear coefficient of the SP dispersion curve of alkalis, aluminum, or alkaline-earth metals [6]. Such a finding leads us to suggest that, according to the Feibelman's model [14] of Ag SP dispersion, the centroid of the induced charge lies in the close vicinity of the jellium edge, in contrast with all other Ag systems [6,15], but not outside as for simple metals. Interestingly, the quadratic coefficient (3.4 eV Å^2) coincides with that of SP dispersion in Ag(111) [15], i.e. the surface with the same crystallographic orientation.

On the other hand, for layer-by-layer Ag films on Ni(111), no trace of SP confinement was revealed as the dispersion curve of SP was found to be purely quadratic (Fig. 2, right panel). The absence of the

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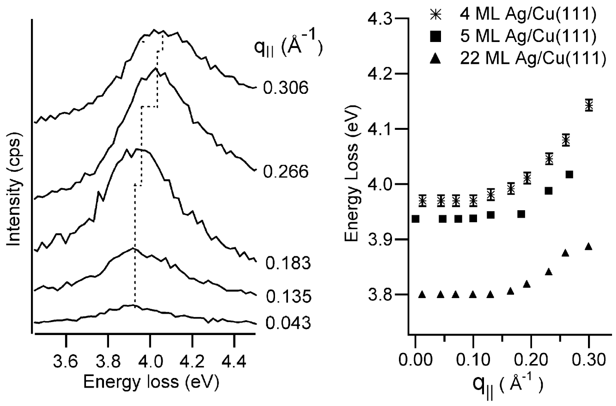

Fig. 1. (left) HREEL spectra for 5 ML Ag/Cu(111) (right) Dispersion of the SP energy for different Ag coverages. The lack of a dispersion before a critical wave-vector indicates that the SP is confined within Ag grains.

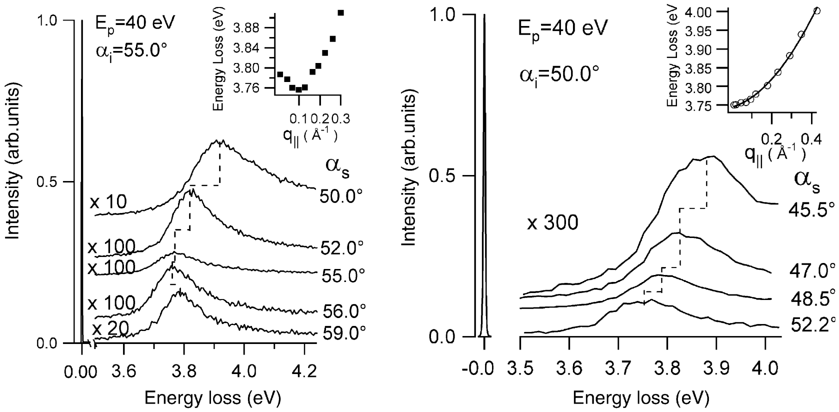

Fig. 2. (left) HREEL spectra for 22 ML Ag/Cu(111) as a function of the scattering angle after an annealing at 400 K. In the inset the dispersion relation of the Ag SP energy is shown. The initial flat behavior reported in the right panel of Fig. 1 abruptly changed upon annealing and an initial negative dispersion appeared. The intensity of each spectrum was normalized to that of the elastic peak; (right) HREEL spectra for as-deposited 10 ML Ag/Ni(111) as a function of the scattering angle. In the inset the dispersion relation of the Ag SP energy is shown. A purely quadratic dispersion was found: $A + B \cdot q_{\|} + C \cdot q_{\|}^2$ with $A = (3.751 \pm 0.002)$ eV, $B = (0.000 \pm 0.004)$ eV Å, and $C = (1.57 \pm 0.04)$ eV Å^2.

linear term is ascribed to the existence of Ag quantum well states confined within the adlayer [11]. Hence, the different growth modes of the as-deposited Ag adlayer reflect into different dispersion of the SP (Fig. 1, left and Fig. 2, right).

Fig. 3 (left panel) shows the thickness-dependence of the full-width at half maximum (FWHM) as a function of the parallel momentum transfer for Ag/Cu(111). An initial negative behavior of the FWHM was found for ultrathin films, while for higher coverages (22 ML) the behavior is substantially dispersionless. By comparing the dispersion of the FWHM of the SP for 5 ML Ag/Cu(111) and 5 ML Ag/Si(111) [5], we found (Fig. 3, right panel) that beyond a critical wave-vector the dispersion became positive for Ag films. However, the value of the turning point differs in 5 ML deposited on Cu(111) and Si(111) (0.19 and 0.08 Å^{-1}, respectively).

This behavior of the FHMM is well described by a theoretical model recently proposed [16] on the SP lifetime in free-standing Ag layers. The dispersion relation of line-width of the Ag SP was found to be characterized by a negative behavior of the line-width for small momenta up to a critical wave-vector. This finding was ascribed [16] to the splitting between symmetric and anti-symmetric

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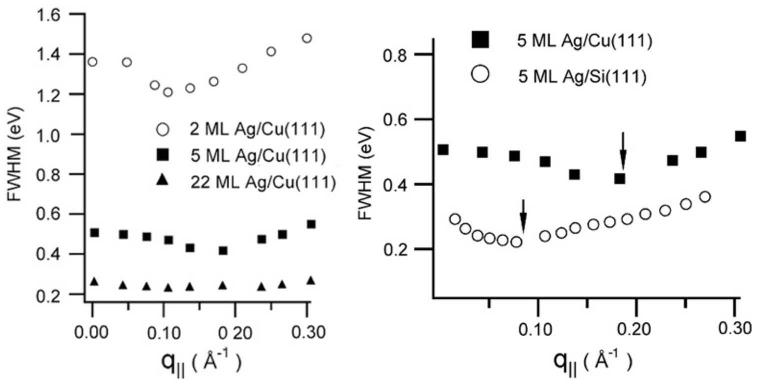

Fig. 3. (left) Behavior of the FWHM of the Ag SP for different thicknesses of the Ag film on Cu(111). (right) Comparison between the dispersion of the FWHM of the Ag SP for 5 ML Ag/Cu(111) (our data) and 5 ML Ag/Si(111) (data taken from Ref. [5]) The arrows indicate the turning point [16] in the dispersion of the FWHM. The uncertainty on the FWHM is 10 meV.

excitation modes and the enhanced electron-hole pair excitation at small $q_{\|}$. For higher values of $q_{\|}$, a linear increase of the line-width was reported.

3. Conclusions

HREEL measurements performed on Ag/Cu(111) showed that SP is confined within Ag grains. The SP confinement is removed upon annealing at 400 K. A slightly negative coefficient of the dispersion relation was found for the annealed film. On the contrary, a purely quadratic dispersion was observed in the layer-by-layer Ag film on Ni(111).

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PAPER XXV

Chemical reactions at clean and alkali-doped mismatched metal/metal interfaces

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Chemical reactions at clean and alkali-doped mismatched metal/metal interfaces

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ABSTRACT

High-resolution electron energy loss spectroscopy has been used to study CO adsorption on clean and alkali-modified Ag single layers deposited on Ni(111) and Cu(111) surfaces. An increasing of the CO dissociation rate was obtained for the alkali-doped Ag/Ni(111) interface. On the contrary, for a monolayer of Ag on Cu(111) alkali adsorption causes an increasing of the CO dissociation barrier. For higher Ag thickness (ten layers), the alkali-modified surface strongly reacts with water molecules.

KEYWORDS Bimetallic surfaces~ Alkali metals~ Carbon monoxide ~ Silver

INTRODUCTION

Recently, chemical reactions at bimetallic surfaces have attracted a notable interest [1-7] for both fundamental interest and technological applications (fuel cells, heterogeneous catalysis, chemical sensors, pollution). Metal/metal interfaces exhibit novel physical and chemical properties, as a consequence of the occurrence of electron quantum confinement and of the modified electronic properties at the interface [8, 9].

Both the Ag/Cu(111) and Ag/Ni(111) systems are characterized by the existence of quantum well states (QWS) within the Ag adlayer [10-13]. However, due to the absence of a gap in Ni(111), the character of the QWS in such two systems is substantially different [14]. QWS on Ag/Cu(111) are characterized by standing wave patterns, which on the contrary are not supported on Ag/Ni(111).

Such significant dissimilarities in the electronic properties between these two bimetallic surfaces could in principle lead to quite different catalytic properties. Accordingly, they may be used as model systems for a comparative study on the chemical reactivity of bimetallic surfaces.

Moreover, Ag on Ni(111) and Cu(111) offers the opportunity to study the chemical activity of mismatched metal/metal interfaces. Silver grows unstrained on such substrates along the [111] direction due to the remarkable lattice mismatch (16 and 13% for Ag/Ni and Ag/Cu, respectively). This mismatch causes the formation of an incommensurate or reconstructed interface. Such a large misfit determines the silver film to have the crystalline structure of bulk silver even for ultrathin Ag layers [15]. It is worth mentioning that Ag/Cu and Ag/Ni do not form alloys at room temperature [16, 17].

On the other hand, alkali-metal doping is a powerful tool to manipulate the physical and chemical properties of surfaces and it is widely used for tailoring new catalysts. For these reasons, the study of alkali promotional effects on surfaces and interfaces continues to be one of the main topics of surface science [18-23]. In particular, the dissociation of CO is a key catalytic reaction step in the Fischer-Tropsch process, which is strongly influenced by alkali metals added as promoters to transition-metal catalysts. The alkali promotional role on CO dissociation was found to be related to both short-range electrostatic interactions and the direct orbital overlap [24]. The general picture of the promotional effect is that the intramolecular C–O bond is weakened, while the metal-CO bond becomes stronger in the presence of alkali metals. In particular, the direct CO-alkali bond notably enhances the efficiency of CO dissociation. Accordingly, the dissociation barrier is significantly reduced only for short alkali-CO distances (2-3 Å) [24].

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on CO adsorption on clean and alkali-modified Ag layers grown on Ni(111) and Cu(111). A significant enhancement of the CO dissociation rate was revealed for alkali-doped Ag/Ni(111). On the other hand, the presence of the Ag monolayer blocks the migration of oxygen underneath the surface on the alkali-doped Ag/Cu(111) interface, in contrast with the alkali-modified Cu(111) surface. Moreover, the surface obtained by doping with alkalis ten layers of Ag was found to be strongly reactive towards residual water molecules.

EXPERIMENTAL SECTION

Measurements were carried out in a UHV chamber operating at a base pressure of $5x10^{-9}$ Pa, equipped with standard facilities for surface characterizations. HREELS experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were single-crystal surfaces of Ni(111) and Cu(111) with a purity of 99.9999% purchased from MaTecK GmbH. Surfaces were cleaned by repeated cycles of ion sputtering and annealing at 800-1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) measurements and low-energy electron diffraction (LEED), respectively. Silver was deposited onto the Ni(111) and Cu(111) surface by evaporating from an Ag wire (purity 99.999%) wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈0.05 ML/min). Alkalis (Na, K) were evaporated in the UHV chamber by means of a well-outgassed dispenser (Saes Getters). The occurrence of the p(1x1)-Ag, (3/2x3/2)-Na, and p(2x2)-K LEED patterns was used as the calibration point of θ_{Ag}=1.0 ML, θ_{Na}=0.44 ML, and θ_{K}=0.25 ML, respectively. Similar results were achieved by calibrating using AES. LEED measurements ensured of the layer-by-layer growth of the Ag monolayer and reproduced results reported in previous structural studies of Ag/Ni(111) [25] and Ag/Cu(111) [26, 27]. For the first Ag layer, LEED pattern showed spots characteristic of the p(1x1) silver structure and of the substrate. For higher coverages only the Ag(111) pattern was observed. This means that the substrate is fully covered by Ag. A clear (7x7) [25] and (9.5x9.5) reconstruction [26, 27] was revealed by the analysis of the LEED pattern of Ag/Ni(111) and Ag/Cu(111), respectively. A constant sticking coefficient was assumed to obtain other desired coverage. The energy resolution of the spectrometer ranged from 2 to 4 meV. All depositions and measurements were made at room temperature.

RESULTS AND DISCUSSION

3.1 Clean Ag/Cu(111) and Ag/Ni(111) interfaces

Carbon monoxide was dosed (0.4 L, 1 L=1.33 10^{-6} mbar·s) at room temperature on the clean Cu(111) and Ni(111) substrates and on the bimetallic surfaces obtained by depositing 1 ML Ag on Cu(111) and Ni(111). At room temperature, CO does not adsorb on Cu(111) and on a single Ag layer deposited on both Cu(111) and Ni(111), as indicated by the absence of CO-related vibrations in HREEL spectra (Figure 1, spectra b, c, and d). However, the Ni(111) surface (spectrum a of Figure 1) is highly reactive towards CO adsorption and the C-O stretching was revealed at 230 (three-fold site [28]) and 250 meV (on-top [28]). Hence, it worth studying CO adsorption at the interface Ag/Ni(111) for submonolayers of Ag.

The presence of 0.15 ML Ag does not significantly modify the reactivity towards CO of the Ni(111) surface (spectrum c of Figure 2). Only C-O modes at 231 and 250 meV were revealed, thus implying the presence of CO molecules in three-fold and on-top adsorption sites.

Upon oxygen exposure (8.0 L) new loss features arose at 83, 95, and 176 meV (spectrum d). Their appearance is indicative of carbonate formation [29]. The formation of CO_3 on silver surfaces is extremely interesting in epoxidation chemistry as it stabilizes subsurface oxygen [29]. Moreover, silver carbonate plays an important role in heterogeneous catalysis as it is used as a reagent in organic synthesis such as the Koenigs-Knorr reaction. While its formation on single-crystal Ag surfaces is well described [30], to the best of our knowledge no experimental studies on thin Ag films have been performed yet.

The key role of silver in this reaction is demonstrated by the absence of CO_3 modes in coadsorption of O and CO on clean Ni(111). In fact, dosing 2.0 L of O_2 (T=240 K) onto a CO-modified Ni(111) surface (pre-dosed with 1.0 L of CO), we recorded losses due to a phonon activated by oxygen at 32 meV [31], the CO-Ni vibration at 56 meV [32], and the O-Ni vibration at 70 meV [31] (spectrum b of Figure 2). Interestingly, only on-top sites for CO exist in the absence of Ag, as indicated by the presence of the feature at 256 meV.

3.2 Alkali-doped Ag monolayers on Ni(111) and Cu(111)

In order to verify the effects of the adsorption of submonolayers of alkalis on the chemical reactivity of the above bimetallic surfaces, 0.06 ML of Na deposited on a single layer of Ag on Ni(111) were exposed to 0.4 L of CO (Figure 3, spectrum d). For the sake of a comparison, the same experiment was performed for 0.06 ML of Na deposited onto the clean Ni(111) and Cu(111) substrates (Figure 3, spectra a and c). Peaks at 19-24 meV were assigned to Na-Ni vibration [21]. For a sufficiently high CO/Na ratio, the Na-Ni bond softened (Na-Ni loss at 9 meV, spectrum c) as a consequence of the CO-induced lengthening of the alkali-substrate bond [21].

The occurrence of CO dissociation was found for 0.06 ML Na/1 ML Ag/Ni(111) (Figure 3, spectrum d) while only molecular CO adsorption was observed on 0.06 ML Na/Ni(111) (spectrum c). The partial dissociation of CO molecules was inferred from the appearance of the stretching vibration of Na against O atoms at 36 meV coming from dissociating CO molecules. Furthermore, a shoulder at 55 meV [33] due to the C-Ni stretching was also recorded. As concern the C-O internal vibration, its energy was recorded at 215 and 232 meV for 0.06 ML Na/Ni(111) (spectrum c) and at 186 meV in the 0.06 Na/1 ML Ag/Ni(111) (spectrum d), respectively. Interestingly, at a fixed Na precoverage (0.06 ML) the C-O bond is much more softened in the bimetallic surface with respect to the clean Ni(111) substrate. The weakening of the C-O bond leads to CO dissociation and to chemical reactions of the derived species, i.e. the Fisher-Tropsch process, CO oxidation, carbonate formation and so on. Hence, such finding may have important implications in heterogeneous catalysis.

On the other hand, for Na+CO coadsorption on clean Ni(111), CO dissociation was not revealed for alkali precoverages below 0.40 ML Na. For such coverage two loss features at 36 and 55 meV appeared (Figure 3, spectrum b), thus indicating the occurrence of CO dissociation.

Na doping determines the activation of a local charge transfer from the Ag/Ni(111) interface to the 2π* antibonding orbitals of CO leading to a softening of the C-O bond up to the dissociation of CO molecules. We suggest that such charge transfer is due to the hybridization between the CO 2 π* states and the QWS of Na-promoted Ag/Ni(111). It is worthwhile mentioning that small amounts of alkali doping have been widely demonstrated to have a dramatic effect on the dispersion of QWS [34-38]. Unfortunately, to date no experimental and theoretical studies have been performed on alkali-modified bimetallic surfaces and hence no data are available for a comparison. A large hybridization, and very likely an efficient charge transfer, is possible only whenever the Na-CO distance is short, as also found in theoretical calculations performed for CO adsorption on Na quantum dots on Cu(111) [39]. Moreover, recent theoretical results performed for CO adsorption on Al/Fe(100) [40] have demonstrated that the activation barrier for CO dissociation is strongly reduced in the bimetallic surface with respect to the clean Fe(100) surface. On the basis of the latter result, we argue that the joint action of alkali doping and the existence of a bimetallic Ag/Ni(111) interface should further reduce the activation barrier so as to produce an enhanced CO dissociation rate. On the other hand, CO adsorption is fully dissociative on Na/Cu(111) (Figure 3, spectrum a), as evidenced by lack of the C-O mode in the HREEL spectrum and by the existence of the O-Na feature at 36 meV. It should be noticed that CO adsorption on alkali-modified copper substrates might occur only in the close vicinity of alkali adatoms, as a consequence of the reduced reactivity of copper towards CO adsorption at room temperature (Figure 1). In fact, the electrostatic potential is lowered in sites directly adjacent to the alkali-adatom, so as to stabilize CO adsorption [41-43]. As a consequence, only very short-range promotion effects occur, i.e. direct orbital overlap between alkalis and CO. Accordingly, the short-range character of the alkali-CO interaction, which was demonstrated to play a pivotal role in CO dissociation [24], is notably enhanced. A similar phenomenon could also be suggested to occur for bimetallic surfaces, as discussed above.

However, substituting Na with K, part of the oxygen atoms arising from CO dissociation migrates underneath the surface as suggested by the feature at 64 meV [29, 44] (atomic oxygen in subsurface sites) in spectrum a of Figure 4 for 0.06 ML K/Cu(111). Instead, no over-surface O was present as deduced by the absence of its vibration against Cu(111) at 46 meV [45]. The presence of subsurface oxygen deserves particular attention as it has been recently demonstrated to activate many industrially important chemical reactions [46-50]. Interestingly, for 0.06 ML K/1 ML Ag/Cu(111) the presence of the Ag monolayer inhibits the subsurface diffusion of O atoms (Figure 4, spectrum b) in the bimetallic surface. The ratio between the intensity of the O-K vibration (recorded at 27-29 meV) with respect to the C-O stretching indicates that in the K-doped Ag/Cu(111) surface the activation barrier for CO dissociation is higher than on K/Cu(111). Instead, for K-doped clean Ni(111) surfaces, CO adsorption is molecular for precoverages below 0.33 ML K (spectrum c, 0.06 ML K, and d, 0.33 ML K).

The remarkable differences towards the promotion of CO dissociation in alkali-modified Ag/Cu(111) with respect to the case of alkali-doped Ag/Ni(111) could be ascribed to the different electronic properties of these two systems. Due to the absence of a gap on Ni(111), hybridization effects between QWS and substrate states are enhanced on Ni(111). This effect is very important for a single layer of Ag [51]. Such hybridization enhances the efficiency of the charge transfer to 2 π^* antibonding orbitals of CO, so as to soften the C-O bond and decrease the activation barrier for CO dissociation.

It should be noticed that a fully dissociative CO adsorption at room temperature was revealed for both Na/Cu(111) and Na/1 ML Ag/Cu(111). For 0.02 ML Na-doped 1 ML Ag/Cu(111) (Figure 5), besides the Na-Ni stretching at 19 meV, also the O-Ag stretching at 30 meV [52] was recorded even for small

CO exposures (0.3 L). Na doping cause CO dissociation but not all O atoms migrate in subsurface sites as both over-surface (30 meV) and subsurface (64 meV) were revealed. Further increasing CO exposure, a new feature appeared at 36 meV, thus suggesting the formation of the Na-O bond. No C-O stretching was recorded for spectra in Figure 5 (not shown). This finding ensures of the complete dissociation of impinging CO molecules, as also found for CO/Na/Cu(111) (Figure 3, spectrum a). It should be noticed that alkalis are extremely mobile on noble-metal surfaces at room temperature and, then, also Na diffusion has to be taken into account as it could play a key role in Na oxidation. Subsurface oxygen (peak at 64 meV) does not have a particular role in the reaction of CO-promoted alkali oxidation as no changes were revealed in the intensity as well as in its loss energy.

On the other hand, the surface obtained by depositing 0.15 ML of potassium on 10 ML Ag/Ni(111) was found to be strongly reactive towards water molecules arising from residual gas in the UHV chamber. Vibrational spectra (figure 6) revealed the adsorption of partially dissociated water, as suggested by the presence of O-H stretching peaks at 435 meV (water molecules) and 450 meV (OH groups) [53, 54]. As a matter of fact, the critical K-precoverage for water dissociation on Ag(111) is 0.17 ML [51]. Another clear fingerprint of adsorbed molecular water is the appearance of HOH bending at 199 meV [55, 56]. Interestingly, water adsorption was not allowed for alkali-modified 1 ML Ag on both Cu(111) and Ni(111) substrates. The enhanced reactivity of the alkalis/bimetallic surfaces towards water adsorption could be ascribed to the presence of well-defined Ag 5sp-derived QWS within the adlayer for 10 ML compared to 1 ML [13]. In fact, water reactivity was found to be enhanced in systems exhibiting electron quantum confinement [9, 57]. Such finding may be of great interest as water interaction with solid surfaces is useful for understanding a wealth of physical and chemical phenomena such as pollution, corrosion, energy production, and heterogeneous catalysis.

CONCLUSIONS

Herein we have reported a comparative study on the chemical activity of clean and alkali-doped bimetallic surfaces. Submonolayers of silver deposited on Ni(111) promote carbonate formation. A remarkable difference in promoting CO dissociation was found for alkali-doped single layers of Ag on Ni(111) and Cu(111). At a fixed amount of alkali doping, the activation barrier for CO dissociation is notably reduced in the bimetallic 1 ML Ag/Ni(111) surface with respect to the clean substrate. Instead, it is increased on the K-doped 1 ML Ag/Cu(111) with respect to the K-modified Cu(111) surface. Such opposite behavior was ascribed to the different nature of the QWS in these systems. Increasing the thickness of the Ag adlayer up to ten layers, the alkali-modified bimetallic surface exhibited a remarkable reactivity towards water.

FIGURE CAPTIONS

Figure 1, HREEL spectra acquired after having exposed 0.4 L CO at room temperature on: (a) clean Ni(111); (b) 1 ML Ag/Ni(111); (c) clean Cu(111); (d) 1 ML Ag/Cu(111).

Figure 2, (a) clean Ni(111); (b) 2.0 L O_2+2.0 L CO on Ni(111); (c) 2.0 L CO on a 0.15 ML Ag/Ni(111) surface; (d) 8.0 L O_2 added on spectrum (c).

Figure 3, HREEL spectra acquired after having exposed 0.4 L CO at room temperature on: (a) 0.06 ML Na/Cu(111); (b) 0.40 ML Na/Ni(111); (c) 0.06 ML Na/Ni(111); (d) 0.06 ML Na/1 ML Ag/Ni(111).

Figure 4, HREEL spectra acquired after having exposed 0.4 L CO at room temperature on: (a) 0.06 ML K/Cu(111); (b) 0.06 ML K/1 ML Ag/Cu(111); (c) 0.06 K/Ni(111); (d) 0.33 ML K/Ni(111).

Figure 5, HREEL spectra acquired for 0.02 ML Na/1 ML Ag/Cu(111) as a function of CO exposures at 300 K.

Figure 6, HREEL spectra acquired for 0.15 ML K deposited onto 10 ML Ag/Ni(111) at room temperature.

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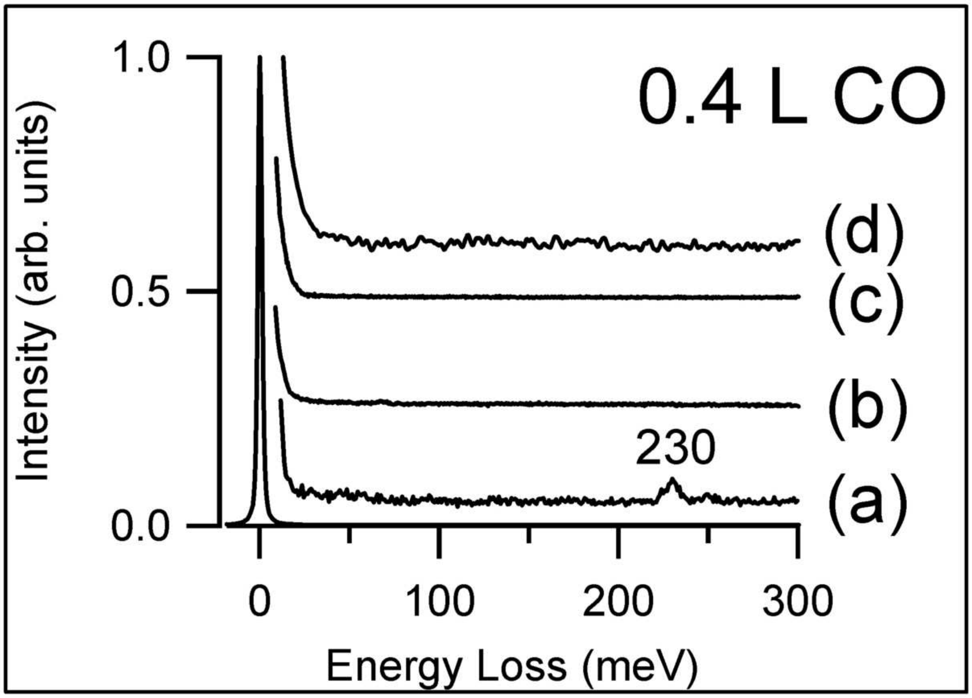

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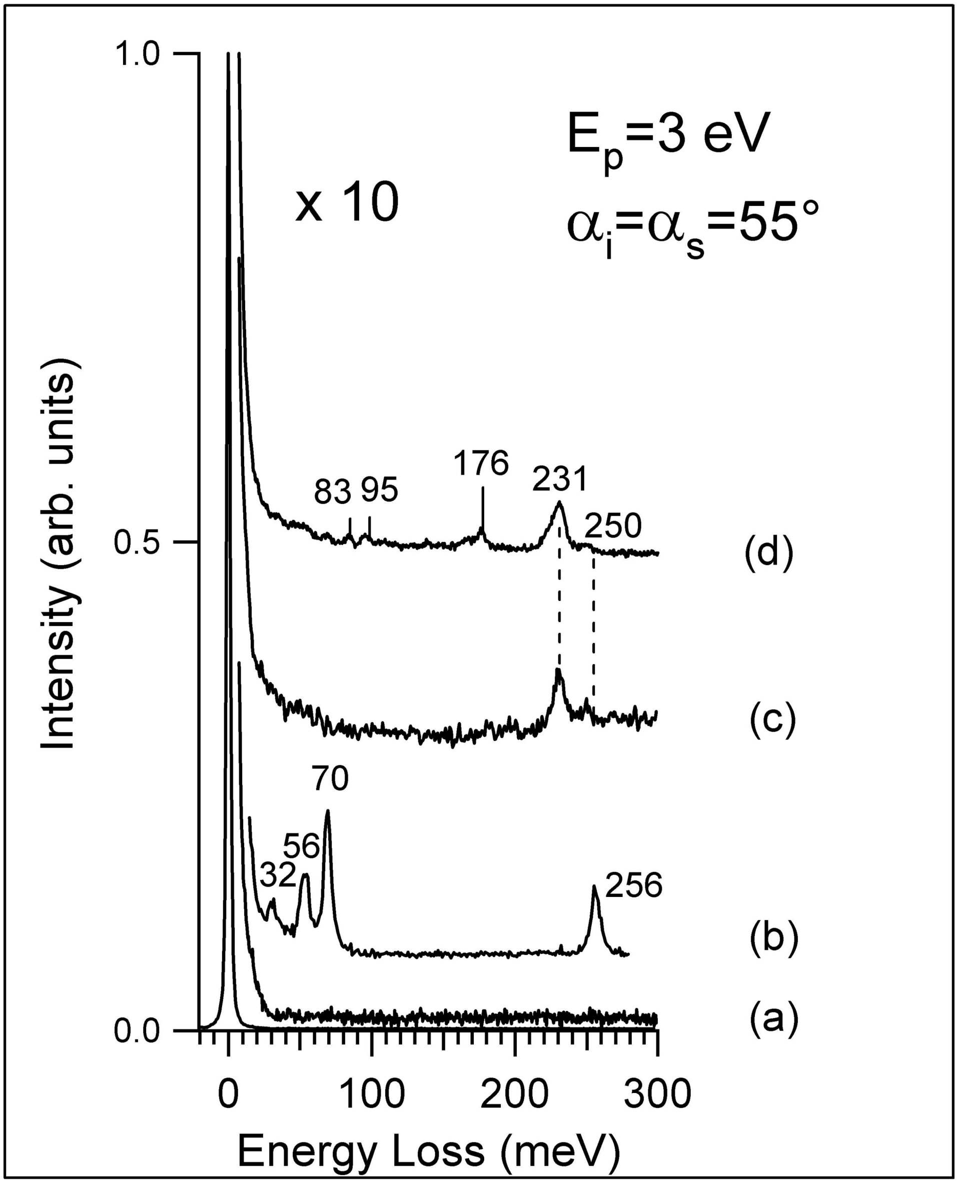

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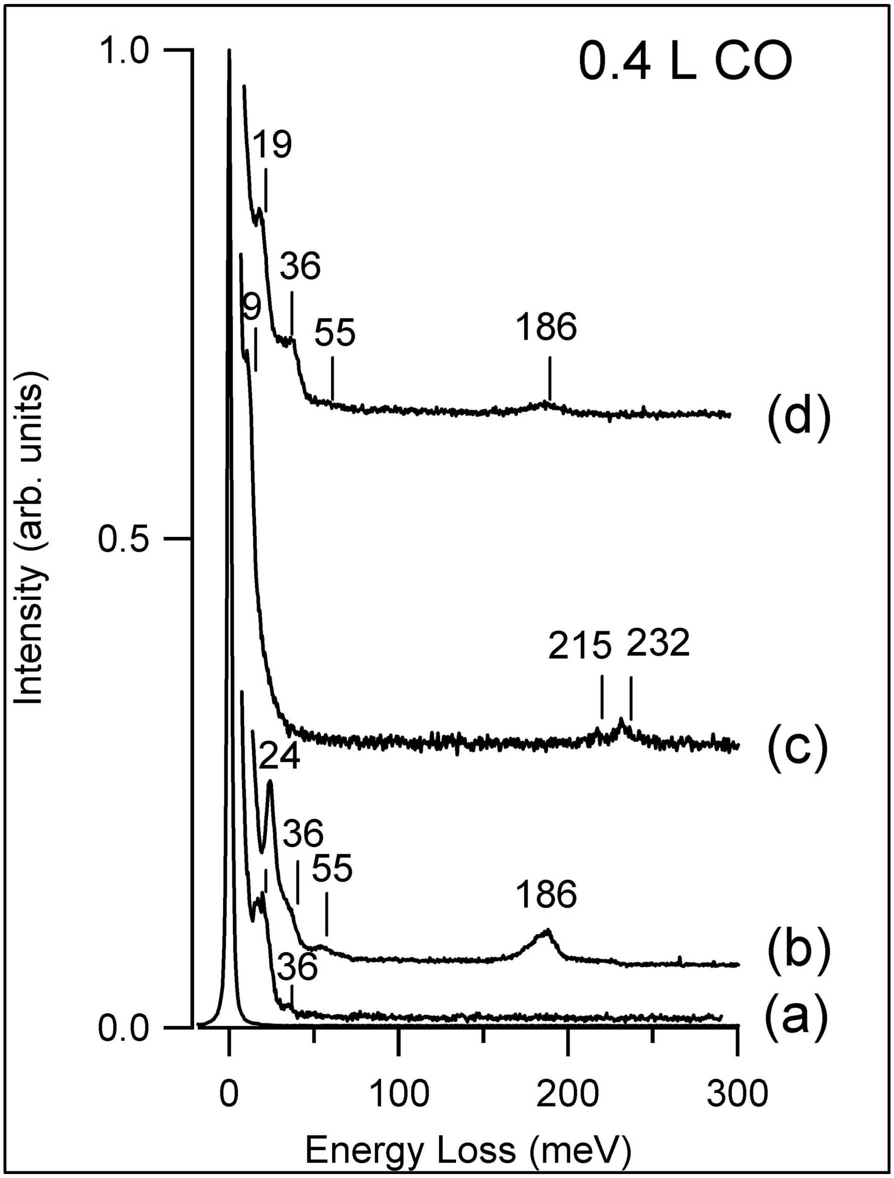

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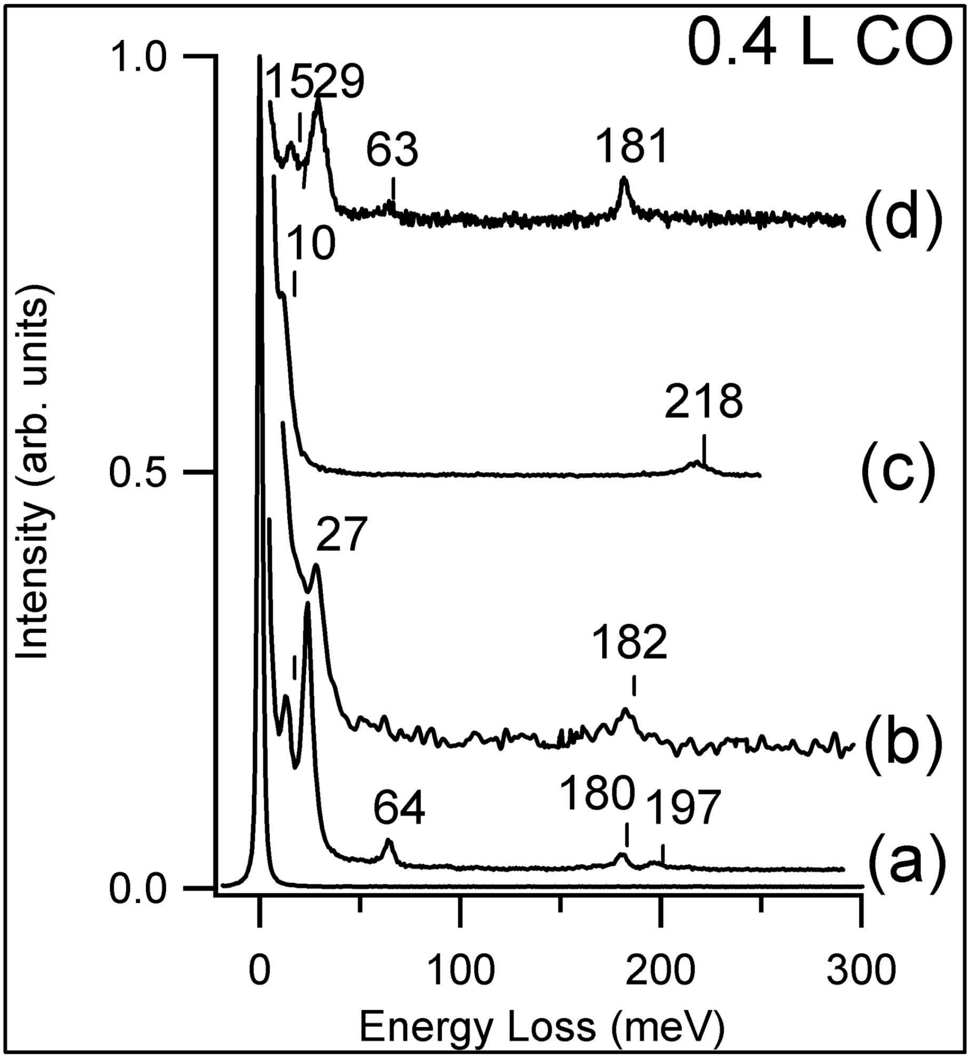

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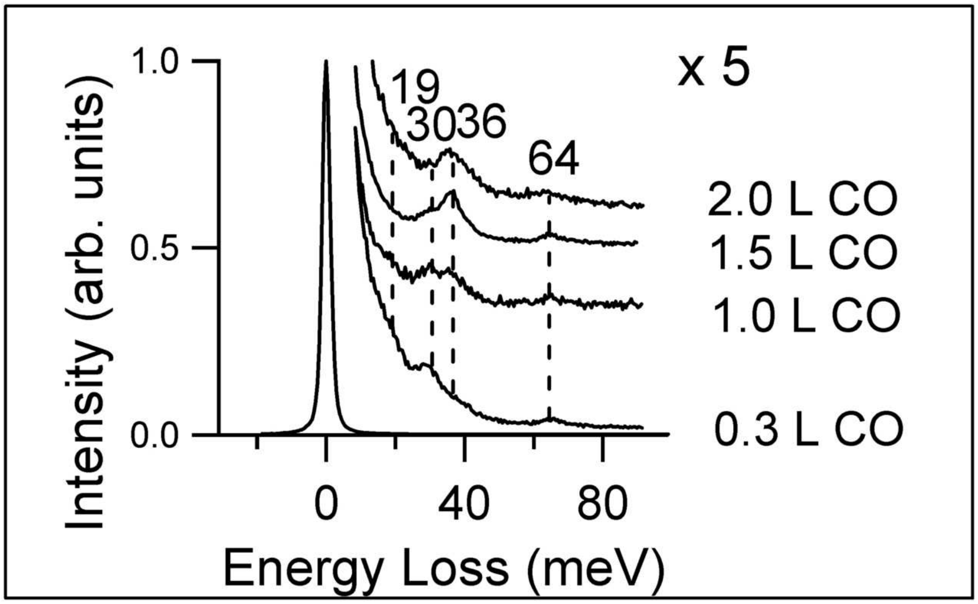

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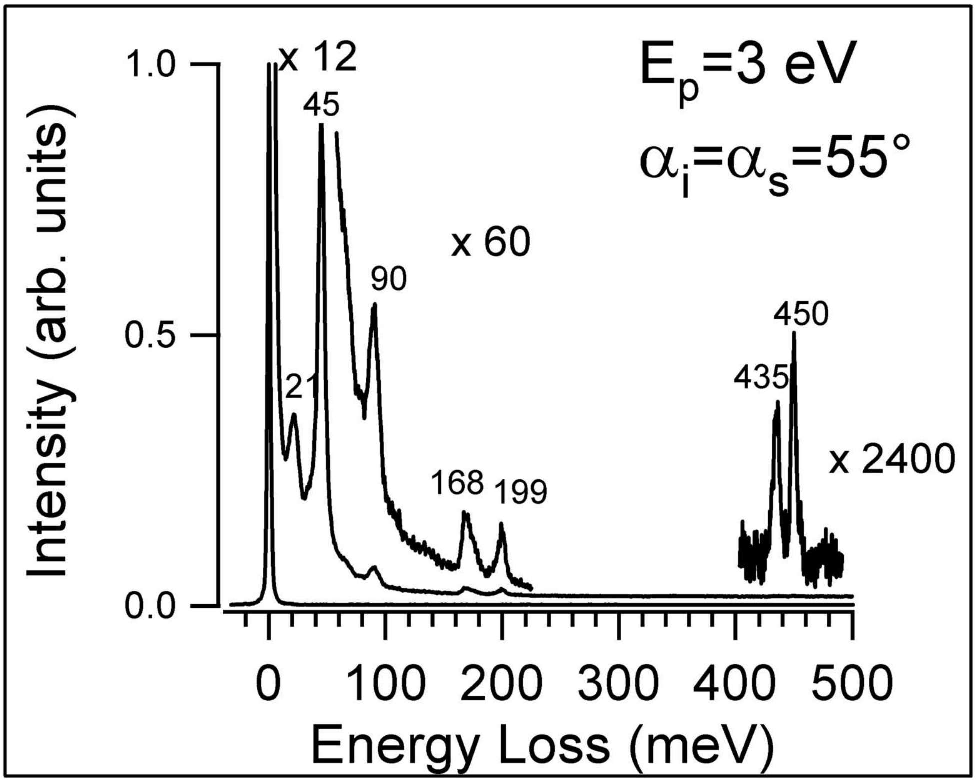

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PAPER XXVI

Dispersion and damping of Au surface plasmon
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Dispersion and Damping of Gold Surface Plasmon

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Abstract High-resolution electron energy loss spectroscopy was used to investigate the surface plasmon dispersion in (111)-oriented Au films grown on Cu(111). The measured dispersion of the plasmon mode was positive, as found for Ag. The centroid of the induced charge associated to the plasmon field lies well inside the jellium edge. The damping relation of the Au surface plasmon presented a critical wave vector of 0.11 Å^{-1}. For higher values of the parallel momentum transfer, the line width of Au surface plasmon considerably increased as a consequence of the opening of a new decay channel via single-particle transitions.

Keywords Surface plasmons · Electron energy loss spectroscopy (EELS) · Gold · Dynamic screening

Introduction

Collective electronic excitations in metallic systems influence many physical and chemical phenomena, such as catalytic processes, epitaxy, charge transfers at interfaces, and dynamical processes [1–4] and, hence, they have been widely studied in recent years [5–11]. In particular, investigations on noble-metal surfaces are motivated by fundamental interest in understanding the electronic response of such systems. As a matter of fact, the jellium model, usually applied for describing screening properties in simple metals, is not realistic in this case as a consequence of the presence of localized d electrons [12]. Accordingly, several attempts have been undertaken in order to include band-structure effects in theoretical models [3, 13, 14]. For Ag, the s–d polarization model [14] correctly reproduces the main experimental findings.

The excitation of surface plasmons (SP) has been investigated using many spectroscopic techniques such as electron energy loss spectroscopy (EELS) [15], optical absorption and transmission [16], photoemission and inverse photoemission [17], surface-enhanced Raman spectroscopy [18], scanning tunnelling spectroscopy (STS) [19], and energy-filtered low-energy electron microscopy [9].

While silver was extensively investigated [7, 14, 20, 21–24], by contrast gold systems, such as semi-infinite media [25], thin films [26], quantum wires [27, 28], and nanoparticles [29] have attracted relevant interest only in recent years as a consequence of the discovery that Au is a selective catalyst for a variety of important chemical reactions [30–39].

Optical [40–43] and STS measurements [25, 44] observed the surface plasmon of Au at about 2.6 eV. However, the investigation of both the dispersion and the damping relation of SP with an adequate resolution in the reciprocal space is accessible only by EELS and, to date, no measurements addressing this problem exist. On the other hand, understanding the behavior of Au collective excitations is a necessary step towards the tailoring of Au-based catalysts [30–39].

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Herein, we report on high-resolution EELS measurements performed with the aim to investigate the dispersion and the damping of SP in thin Au films deposited at room temperature on Cu(111). The thickness of the Au film chosen for our investigation, i.e., 60 ML, was high enough in order to avoid any influence of quantum size effect, layer-dependent hybridization, and electron quantum confinement on the SP dispersion [7, 45, 46].

It is worth mentioning that no surface alloy formation takes place in the Au/Cu(111) system at room temperature [47].

Experimental

Measurements were carried out in an ultra-high-vacuum chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterizations. High-resolution electron energy loss spectroscopy (HREEL) experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The sample was a single crystal of Cu(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 900 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Gold was deposited onto the Cu(111) surface by evaporating from a Au wire wrapped on a tungsten filament. Well-ordered Au films could be obtained at very low deposition rates (≈0.05 ML/min). The occurrence of the p(1×1)-Au LEED pattern was used as the calibration point of $\theta_{\mathrm{Au}}=1.0$ ML. A constant sticking coefficient was assumed to obtain other desired Au coverage. Similar results were achieved by calibration using AES. The incident angle with respect to the sample normal was fixed at 55.0°. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio for off-specular spectra. The measured angular acceptance α of our electron analyzer was ±0.5°. Dispersion of the collective mode, i.e., $E_{\mathrm{loss}}(q_{\|})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. To measure plasmon dispersion, values for the parameters E_{p}, impinging energy, and θ_{i}, the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, E_{p}=40 eV, provided, in fact, the best compromise among surface sensitivity, the highest cross-section for mode excitation, and $q_{\|}$ resolution.

As

$$\hbar\overrightarrow{q_{\|}} = \hbar\left(\overrightarrow{k_{\mathrm{i}}}\sin\theta_{\mathrm{i}} - \overrightarrow{k_{\mathrm{s}}}\sin\theta_{\mathrm{s}}\right),$$

the parallel momentum transfer, $q_{\|}$ depends on E_{p}, E_{loss}, θ_{i}, and θ_{s} according to:

$$q_{\|} = \frac{\sqrt{2\mathrm{m}E_{\mathrm{p}}}}{\hbar}\left(\sin\theta_{\mathrm{i}} - \sqrt{1-\frac{E_{\mathrm{loss}}}{E_{\mathrm{p}}}}\sin\theta_{\mathrm{S}}\right)$$

where E_{loss} is the loss energy and θ_{s} is the electron scattering angle [15].

Accordingly, the integration window in reciprocal space is

$$\Delta q_{\|} \approx \frac{\sqrt{2\mathrm{m}E_{\mathrm{p}}}}{\hbar}\left(\cos\theta_{\mathrm{i}} + \sqrt{1-\frac{E_{\mathrm{loss}}}{E_{\mathrm{p}}}}\cos\theta_{\mathrm{s}}\right)\alpha$$

where α is the angular acceptance of the apparatus. The integration window in the reciprocal space was estimated to be 0.022 Å^{-1}, much less than the scanned range in the reciprocal space.

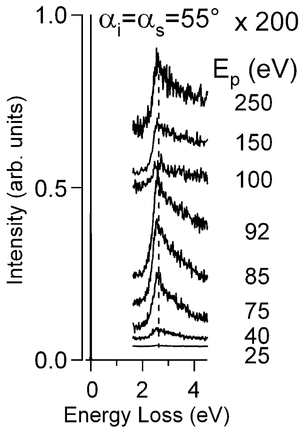
All depositions and measurements were made at room temperature.

Results and discussion

Figure 1 shows electron energy loss spectra acquired for 60 ML Au/Cu(111) as a function of the impinging energy. Loss spectra show a peak at 2.5 eV assigned to the Au SP. It is worth mentioning that for a jellium surface with a density rs=3, i.e., the effective radius for Au, the SP should have an energy of about 6.4 eV [46]. The presence of d electrons shifts the SP energy down to 2.5 eV. The energy of the Au SP did not change with E_{p} while its intensity showed a nonmonotonous behavior.

Changing the primary energy of electrons offers the opportunity to investigate the dependence of the EEL spectrum as a function of the penetration depth of electrons [48] within the extended electron-density distribution at the interface.

Fig. 1 HREEL spectra of the Au(111) film for different values of the primary electron beam energy. All spectra were acquired in the specular geometry and were normalized to the intensity of the elastic peak



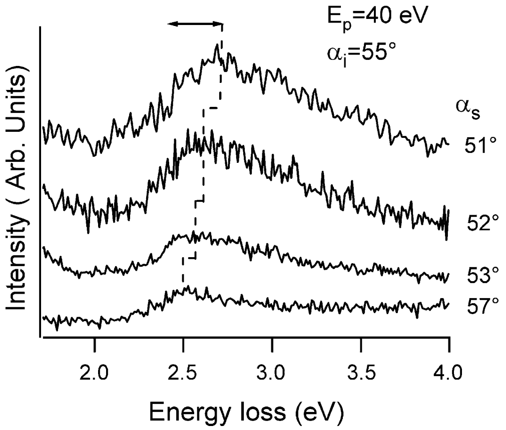


Fig. 2 HREEL spectra of the Au(111) film as a function of the scattering angle. A clear dispersion of energy of the broad loss peak, assigned to the Au SP, exists, as indicated by the *arrow*

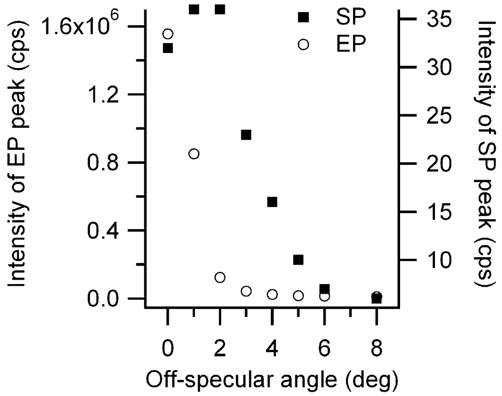


Fig. 4 Intensity of the SP and of the elastic peak (*EP*) as a function of the off-specular angle

The nonmonotonous behavior of the SP intensity is in excellent agreement with random-phase approximation calculations [49] of the dynamical screening of an incident charge. As a matter of fact, the intensity of the SP is generally increasing as a function of the primary electron beam energy and, thus, of the penetration depth. However, whenever the reflection plane is located in the nearness of the jellium edge, interference effects between the incident and the reflected field lead to a decrease of the external potential, so as to induce a lowering of the SP amplitude. Further increasing the penetration of the impinging electrons so as to allow the scattering plane to reach the bulk increases SP intensity again as a consequence of the rising of the external potential [49]. On the basis of the above theoretical findings, we suggest that, for impinging energies between 90 and 150 eV, the Au SP is excited by electron scattering at a reflection plane located in the close vicinity of the jellium edge, as revealed by the nonmonotonous behavior of the SP amplitude as a function of the impinging energy in such range.

Selected HREEL spectra for Au layers as a function of the scattering angle are shown in Fig. 2. The Au SP energy shifted from 2.53 to 3.05 eV.

The dispersion of the SP was found (Fig. 3) to be positive. Likewise, a similar result was reported for Ag systems [7, 15, 21, 22, 50, 51]. According to the Feibelman's model [52, 53, 54] of the SP dispersion, this implies that the position of the centroid of the induced charge, $d_\perp$, lies inside

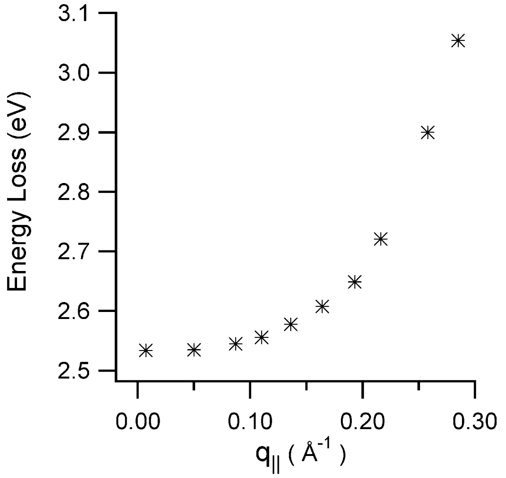


Fig. 3 Dispersion of the Au SP energy as a function of the parallel momentum transfer

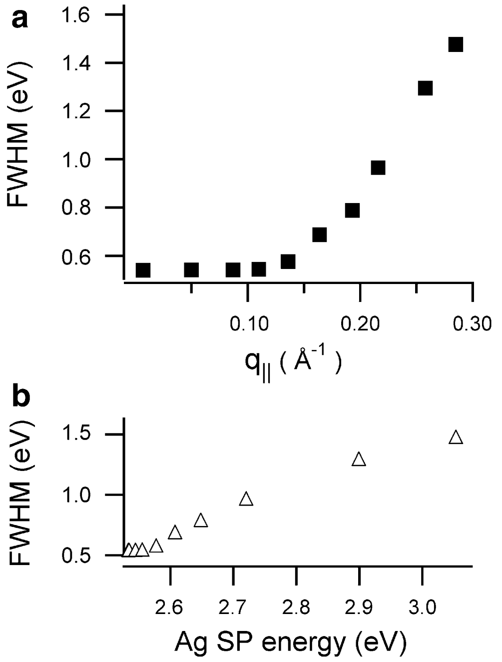


Fig. 5 **a** (*top panel*) FWHM of the Au SP peak as a function of the parallel momentum transfer; **b** (*bottom panel*) FWHM of the Au SP peak as a function of the energy of the Au SP

the geometrical surface ($z<0$), as for Ag [55]. On the other hand, according to another theoretical model on Ag SP dispersion proposed by Liebsch [56, 57], the position of the centroid of the induced charge is always external with respect to the jellium edge. Hence, the positive dispersion of the SP is due to the stronger influence of the polarizable medium when the penetration depth of the surface plasmon is larger.

No polynomial fit of the Au SP dispersion is possible, in contrast with SP on both simple and not simple metals [15].

The dispersion relation of Au SP should be in principle strongly influenced by band-structure effects due to the presence of d electrons. Besides the above-mentioned frequency shift, the dispersion relation should also be affected, as previously demonstrated for Mg [3], Al [58], and Ag [59].

The behavior of the intensity of the Au SP as a function of the off-specular angle ensures the dipolar nature of the excitation (Fig. 4). In fact, it is peaked only 1–2° off specular. However, the presence of a reduced but existing impact component can be argued from the deviation by the purely dipolar behavior of the intensity of the elastic peak [15].

Important information on the collective electronic excitations at metal surfaces is provided by the analysis of their damping processes. On the other hand, Landau damping and the lifetime of SPs strongly influence plasmon-mediated dynamic processes and, moreover, the field enhancement and the sensitivity of surface-enhanced Raman spectroscopy.

The dispersion of the full-width at half maximum (FWHM) as a function of the parallel transfer momentum $q_{\|}$ (Fig. 5a) was found to be positive with also the existence of a critical wave vector which indicates the opening of a new decay channel via interband transitions. For $q_{\|}>0.11$ Å^{-1}, electrons may be promoted from occupied to unoccupied electronic states so as to broaden considerably the SP peak. The FWHM of the SP peak continuously increased as a function of Au SP energy (Fig. 5b). In particular, the loss width notably grows beyond 2.56 eV.

The positive behavior of the FWHM of the SP for Au agrees with findings for Ag [15] and thick alkali films [60], but it is in contrast with results on Al(111) [61], Mg(0001) [62], and graphite [63]. The value of the FWHM at small momenta is 540 meV. It should be remembered that the width of the surface plasmon peak at $q_{\|}=0$ is a sensitive function of the lattice potential, i.e., it is influenced by the periodic potential of the bulk. At larger values of $q_{\|}$, the plasmon's lifetime becomes less sensitive to the bulk lattice potential and the increase of damping is then caused by electron–hole pair excitations in the surface region. Such enhanced line width of the SP excitation in Au (for a comparison, the initial value of the FWHM in Ag(111) is 69 meV [64]) could be also due to a particularly significant contribution of d electrons to the screening of electron–electron interaction [65, 66] occurring for gold.

In conclusion, loss measurements reported here provided evidence for a positive dispersion of Au SP. Electronic coupling between s and d electrons should have an important role in shifting the centroid of the induced charge associated to the SP inside the geometrical surface, as found for Ag. The intensity of the SP excitation showed a nonmonotonous behavior as a function of primary energy. The Au SP was found to be much broader than Ag SP. A critical wave vector of 0.11 A^{-1} for the damping of the Au SP was found, thus indicating the opening of a decay channel via interband transitions. While HREEL experiments on other Au systems are currently under way, these findings claim for theoretical studies aimed at investigating the influence of d electrons on the dispersion and damping relation of the Au SP.

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Annealing effects on the plasmonic excitations of metal/metal interfaces

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Abstract

The effects of the annealing procedure at 400-450 K on the electronic properties of nanoscale thin films of Ca, Au and Ag grown on Cu(111) at room temperature were probed by high-resolution electron energy loss spectroscopy measurements. Ca surface plasmon underwent to a significant red-shift upon annealing, due to the oxidation of the topmost Ca layer. Water strongly interacted with the CaO interface at room temperature. Au surface plasmon disappeared upon annealing the gold film, as a consequence of the formation of an Au-Cu alloy. Ag surface plasmon red-shifted both in the annealed adlayer and with increasing temperature compared with the frequency recorded for the as-deposited silver film.

Introduction

The study of bimetallic surfaces [1-4] and thin films [5-9] is attracting a considerable attention in recent years for both fundamental interest and potential technological applications. Metal/metal interfaces exhibit novel physical and chemical properties, as a consequence of the occurrence of electron quantum confinement and of the modified electronic properties of these systems [10, 11]. The investigation of collective electronic excitations could provide important information so as to lead to the tailoring of more effective electronic devices and more selective catalysts.

Temperature has been demonstrated to be a key factor affecting the energy and the line-width of the surface plasmon (SP). On Ag(100) the Ag SP frequency was found to decrease with increasing temperature due to the thermal expansion of the crystal [12]. Similar results have been reported for graphite [13].

However, to date the effects of the temperature on plasmonic excitations have been investigated only for single-crystal surfaces but not for nanoscale thin films or bimetallic surfaces. Temperature drives several phenomena occurring in these systems such as surface metal-insulator transitions [14, 15], enhanced oxidation processes [16], the formation of alloys [17-20], the structural rearrangement of the film [21], the desorption [22] of the adlayer and changes in the character of the quantum well states (QWS) confined in the film [23].

The influence of temperature on plasmonic excitations of metal/metal interfaces could be efficiently probed by a systematic and comparative study on nanoscale thin layers of different metals grown on the same substrate.

Herein we present high-resolution electron energy loss spectroscopy (HREELS) measurements shedding light on the effects of temperature on collective excitations in nanoscale thin films of Ca, Au, and Ag on Cu(111).

The (111) surface of noble metals (Cu, Ag, Au) exhibits a large confined gap within the projected bulk band structure centred at the $\bar{\Gamma}$ point of the surface Brillouin zone [24]. Electronic states of different origin can exist in this gap. They may be Shockley surface states or states induced by adsorbates (QWS). In particular, photoemission spectroscopy measurements demonstrated the existence of well-defined Ag 5sp-derived QWS [21, 25-27] in Ag/Cu(111). The presence of QWS has been revealed also for alkaline-earth thin films on the same substrate [28]. This implies the occurrence of an enhanced sp density of states at the Fermi level that modifies the electron charge-density distribution, causing significant changes in the dynamical screening properties of these systems [29] with respect to the case of single-crystal surfaces. Hybridization between QWS and the substrate [30] may also influence the electronic response of the interface.

Loss measurements indicated that the effects of the temperature on the electronic properties change on going from a metal/metal system to another. Temperature induces a surface metal-insulator transition on Ca/Cu(111), leading to the formation of CaO thin layers which are highly reactive towards water molecules.

The Au SP decreased in intensity in the Au-Cu alloy formed upon annealing the Au/Cu(111) interface at 450 K. A red-shifted SP was recorded for Ag films kept at 400 K during measurements or upon annealing at the same temperature, in agreement with results for single-crystal surfaces. However, we have no evidence of formation of the Ag-Cu alloy for temperatures ranging up to 400-500 K.

1. Experimental

Experiments were performed in ultra-high vacuum (UHV) conditions at a base pressure of $5 \cdot 10^{-9}$ Pa. The Cu(111) surface was cleaned by repeated cycles of ion sputtering and annealing at 1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Calcium was evaporated by a heated tungsten basket containing Ca grains. Silver and gold were deposited onto the Cu(111) surface by evaporating from Ag and Au wires wrapped on a tungsten filament, respectively. Coverages were calibrated using AES. Temperature was monitored using a K (chromel-alumel) thermocouple spot-welded near the sample.

HREEL measurements were carried out by using an Ibach-type spectrometer (Delta 0.5, Specs). The incident angle with respect to the sample normal was fixed at 55.0°. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio of loss peaks. All depositions and measurements were made at 300 K.

2. Results and discussion

2.1 Ca on Cu(111)

Contrary to beryllium and magnesium, calcium is characterized by sharp features in the density of states due to d-like states. In fact, the electronic structure of Ca is complicated by the presence of 3d orbitals (empty in the free atom) lying in the close proximity of the valence 4s orbitals [31]. Interestingly, density-functional calculations found that d_{xz} and d_{yz} bands are occupied in Ca ultrathin films [32].

Hence, the electronic response of the Ca/Cu(111) interface should be strongly influenced by 3d-4s hybridization. The presence of the polarizable medium represented by d electrons shifts the position of the SP, which the jellium model is expected at 6.5 eV. Instead, transmittance and reflectance measurements on ultrathin films found that Ca SP lies at about 3.6 eV [33].

The spectrum a of Figure 1 shows that for 2 ML Ca/Cu(111) the Ca SP is at an energy of about 3.3 eV. Upon an annealing at 450 K, the loss spectrum exhibited considerable changes (spectrum b). The Ca SP red-shifted down to 2.1 eV. Moreover, a loss peak at 5.7 eV was recorded. Its intensity notably increased in off-specular conditions (spectrum c), thus ensuring of its impact character.

The red-shift of the SP energy could be ascribed to a reduced surface conductivity, so as to suggest the occurrence of a surface metal-insulator transition, i.e. the formation of a CaO layer. In fact, the plasma frequency is directly proportional to the surface conductivity [34-36]. Moreover, a red-shifted SP has been predicted [37] to occur on a MgO single layer adsorbed onto a Mg substrate. As regards the peak at 2.1 eV, its plasmonic nature is ensured by both its line-shape and its energy shift up to 2.4 eV revealed in off-specular scattering geometry (spectrum c).

Very likely, the annealing procedure dramatically increased the oxidation rate of the Ca film, which strongly reacted with residual oxygen in the UHV chamber. On the other hand, in UHV conditions the contamination by O atoms was revealed only after several hours from the deposition for both Mg [38] and Ca (present work) thin films.

Interestingly, the feature at 5.7 eV observed in the spectra b and c of Figure 1 is a fingerprint of water adsorption coming from residual gas. In fact, photoemission spectroscopy experiments carried out on H_2O/(2x2)-Li/Cu(111) [39] and HREELS measurements on H_2O/Na/Cu(111) [6] showed a peak at a similar energy, assigned to single-particle transitions involving the $1b_1$ orbitals of water molecules [40].

Vibrational measurements related to spectra b and c of Figure 1 showed several loss features that unambiguously indicate the formation of a CaO adlayer (Figure 2).

The vibrational spectrum of CaO films is dominated by the presence of the Wallis mode, a microscopic phonon corresponding to the vibration of O-atoms of the utmost CaO layer against the Ca sublattice. It was recorded at 63 meV, in excellent agreement with results by Savio et al. [41] for MgO thin films. Moreover, a shoulder at 50 meV was ascribed to the Fuchs-Kliever mode (FK), a macroscopic surface optical phonon corresponding to the vibration of the Ca and O sublattices one against the other. It was detected at the same energy on CaO crystals [42-44].

The peaks at 126 and 189 are broadened replica of the Wallis mode.

Losses at 160 and 227, they can be tentatively assigned to other dipole-active modes of the CaO layer.

The occurrence of a single O-H stretching at 452 meV [40] indicates that water adsorption is mainly dissociative.

As many important CaO devices [45-49] work in air, the occurrence of water contamination has a key importance as it is essential to determine their chemical stability. Moreover, it should be mentioned that the interaction of water with films and surfaces of metal oxides is attracting a remarkable interest in recent years [50-55] as it has been demonstrated to be an important factor in environmental protection, atmospheric chemistry, gas sensor, corrosion, heterogeneous catalysis, and geology. At room temperature ideal alkaline-earth metal-oxide surfaces are quite inert towards water dissociation, which is allowed only on defect sites [41, 56, 57]. A hydroxilated monolayer was formed only upon high-pressure exposures [58] but not for low-pressure water exposures [59].

On the contrary, present findings (Figures 1 and 2) demonstrate that CaO ultrathin films are highly reactive towards hydrolysis at room temperature.

2.2 Au on Cu(111)

Many experimental studies have been performed on Au alloying with copper substrates [60-62]. However, collective electronic excitations of the Au-Cu alloy have not been investigated yet.

As regards the Au SP, it was revealed at 2.5-2.6 eV in HREELS [63, 64], scanning tunnelling spectroscopy [65, 66] and optical [67-70] measurements.

The formation of an Au-Cu alloy upon annealing at 450 K was demonstrated by AES measurements (Figure 3). In fact, both Cu and Au contributions are present in the AES spectrum. As regards the electronic spectrum (Figure 4a), the Au SP, recorded at 2.60 eV in the as-deposited film, decreased in intensity. Several other features arose upon the formation of the Au-Cu alloy, as evidenced by the analysis of the difference spectrum (Figure 4b). They are ascribed to interband transitions in the alloy located at about 4 eV with respect to the Fermi level. Moreover, an interband transition at 1 eV was observed in the alloy.

2.3 Ag on Cu(111)

In silver, considering its s electron density, the energy of the SP is expected to be 6.50 eV, but due to the interaction between s and d electrons it is strongly red-shifted [37]. While Ag bulk crystals have been widely studied [37, 11, 71], only a very few experimental studies exist for Ag ultrathin film on metal [7] and semiconductor [72-74] substrates. On the other hand, silver thin films have many potential applications [75]. They are essential for most optical devices owing to their high reflectance over a wide spectral range [76, 77].

The Ag SP energy for the as-deposited film (22 ML) was found to be 3.80 eV (Figure 5). It shifted down to 3.76 eV in annealed film, regardless of the annealing temperature. The SP energy was found to be 3.74 eV with the sample kept at 400 K during measurements. The decreased energy upon annealing could be ascribed to the flattening of the film. Instead, the decreasing frequency with the increased temperature may be in principle due to the thermal expansion of the adlayer lattice, as for single-crystal surfaces [12].

The effects of annealing on the SP frequency were found to be reversible (Figure 6). In fact, upon sputtering the Ag films with Ar^+ ions the SP energy returned to its value for the as-deposited Ag layer, i.e. 3.80 eV. However, upon a new annealing of the film the SP shifted again to 3.74 eV. This finding demonstrates that the modifications of the electronic properties upon sputtering and annealing of the adlayer may be finely controlled, so as to tune the electronic response of the interface.

Likewise, the inspection of the wide spectrum (Figure 7) reveals that the intensity of spectral features at 8.00 and 16.67 eV are recovered upon the second annealing, while an intense and broad peak at 11.48 eV appears only by annealing the sputtered film. The sputtering procedure induces the arising of a low-energy peak at 1.16 eV, whose intensity is not changed by annealing. On the other hand, the intensity of all other loss peaks except the ordinary SP is vanishing in the sputtered film.

3 Conclusions

We have presented loss measurements providing direct evidences of the effects of temperature on the plasmonic excitations in nanoscale thin layers of Ca, Au and Ag on Cu(111). A CaO layer (highly reactive towards hydrolysis at room temperature) was formed upon annealing, while for the Au film the formation of an Au-Cu alloy was observed by both HREELS and AES measurements. On the contrary, upon annealing up to 500 K the Ag-Cu alloy was not formed. The SP frequency in annealed Ag layers is redshifted with respect to the as-deposited film. The perfect reversibility of the annealing/sputtering modifications of the electronic properties of the Ag adlayer was demonstrated, so as to obtain readily tunable dielectric properties.

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Figure captions:

Figure 1: HREEL spectra for (a) as-deposited Ca film (b) annealed Ca film in specular geometry ($\theta_i=\theta_s=55.0°$); (c) annealed Ca film in off-specular geometry ($\theta_i=55.0°$ $\theta_s=45.0°$).

Figure 2: Vibrational spectrum of the annealed Ca film.

Figure 3: AES spectrum for the Cu(111) substrate, 10 ML Au/Cu(111) and the Au-Cu alloy.

Figure 4: (a) HREEL spectra for 10 ML Au/Cu(111) and the Au-Cu alloy; (b) Difference spectrum

Figure 5: HREEL spectra for 22 ML Ag/Cu(111) for the as-deposited and the annealed film. The utmost spectrum was recorded at 400 K.

Figure 6: HREEL spectra for the as-deposited, annealed and sputtered Ag films (22 ML). All spectra were acquired at room temperature.

Figure 7: HREEL spectrum of annealed and sputtered 22 ML Ag/Cu(111) in a wide loss energy range.

Figure 1

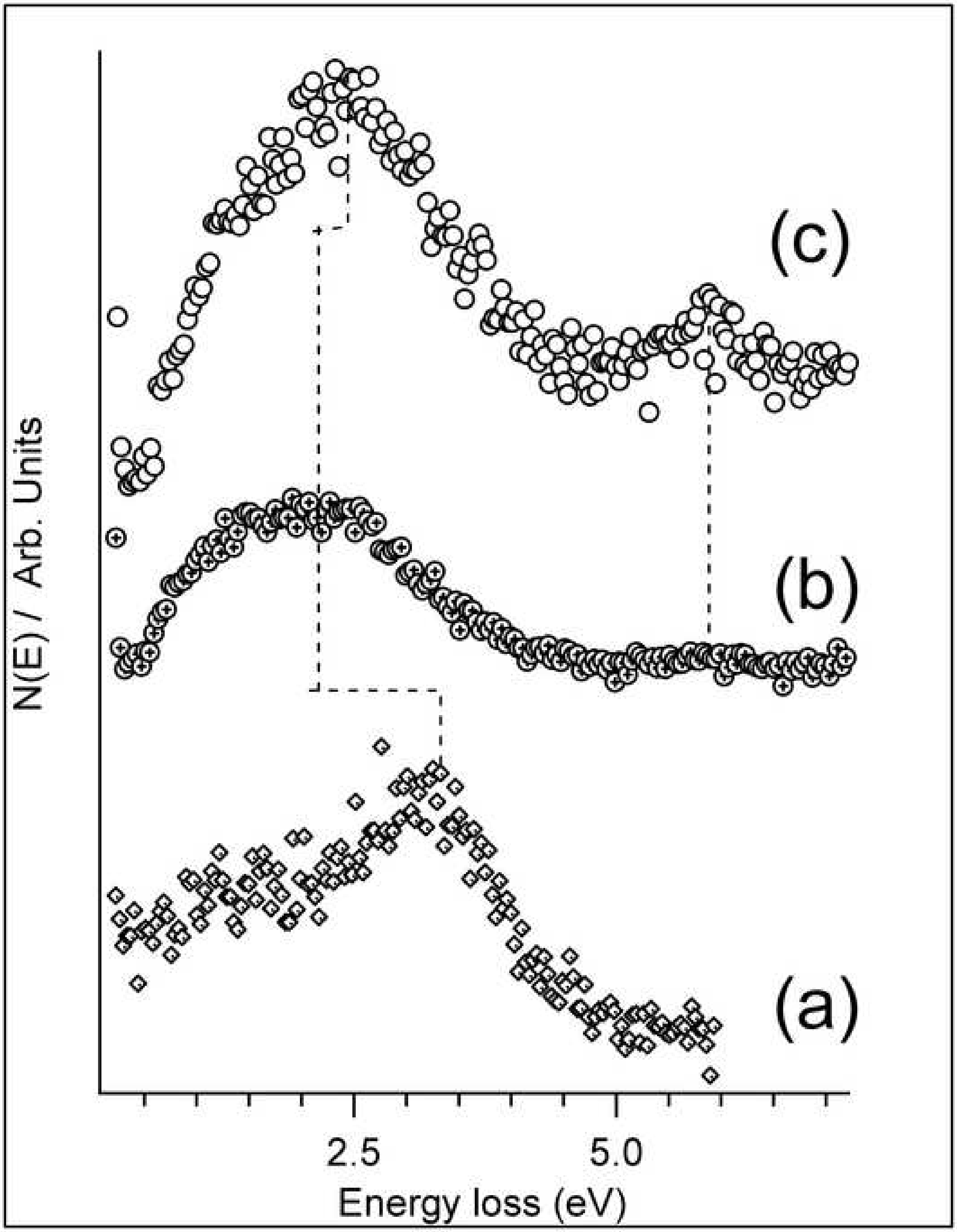
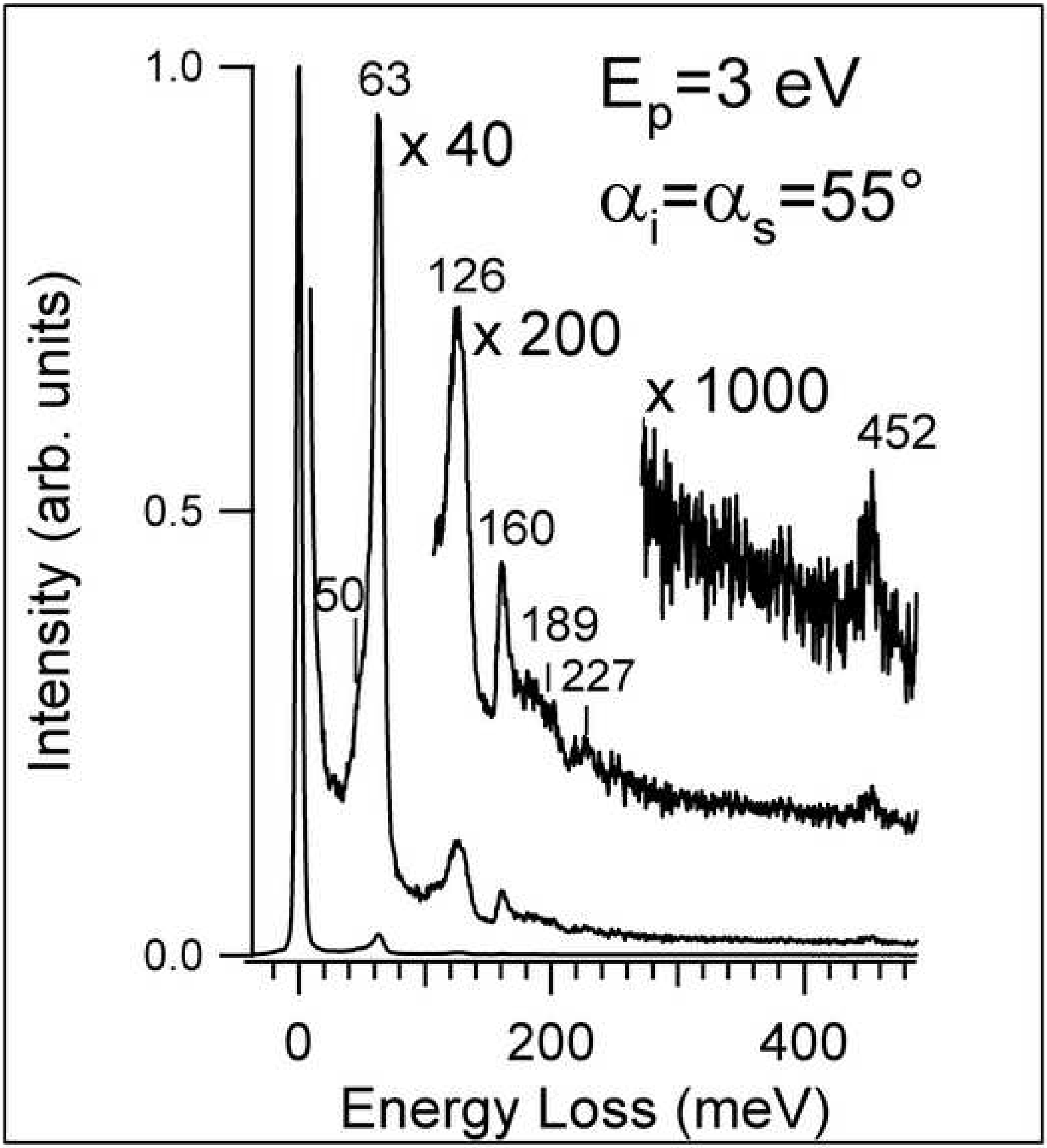


Figure 2



1.0
0.5
0.0
63
x 40
E_p=3 eV
α_i=α_s=55°
126
x 200
x 1000
452
160
50
189
227
Intensity (arb. units)
0
200
400
Energy Loss (meV)

Figure 3

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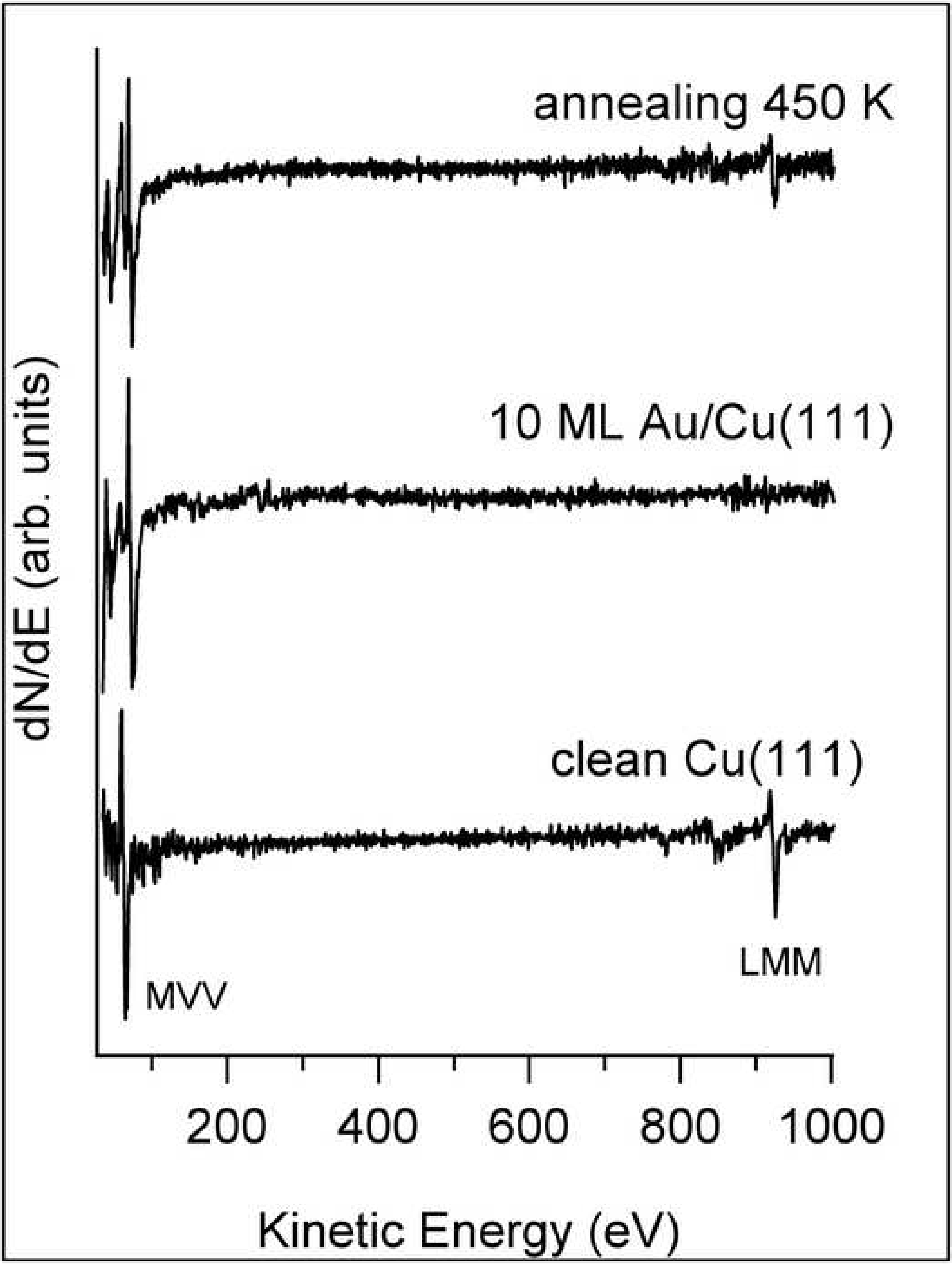

Figure 4

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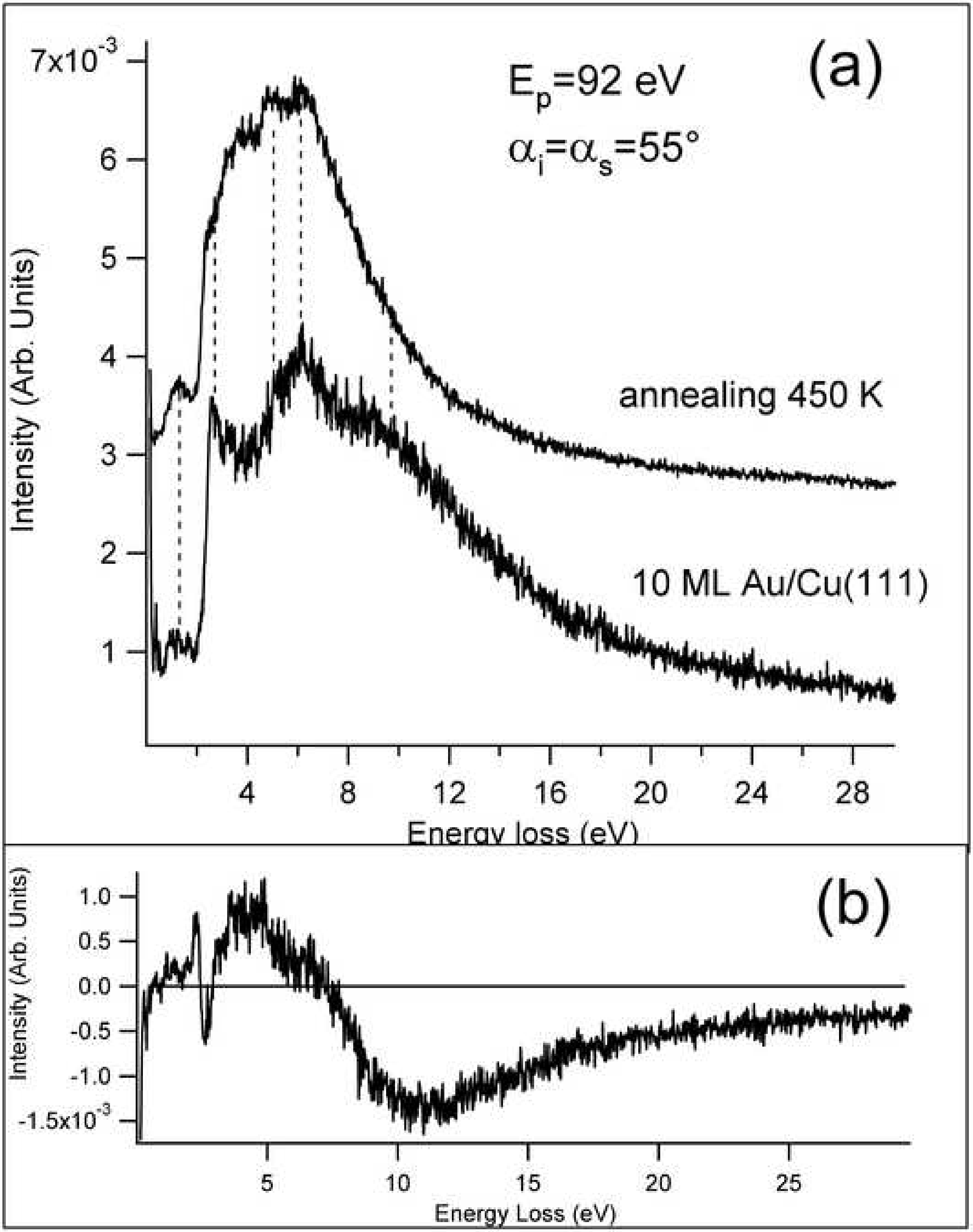

Figure 5

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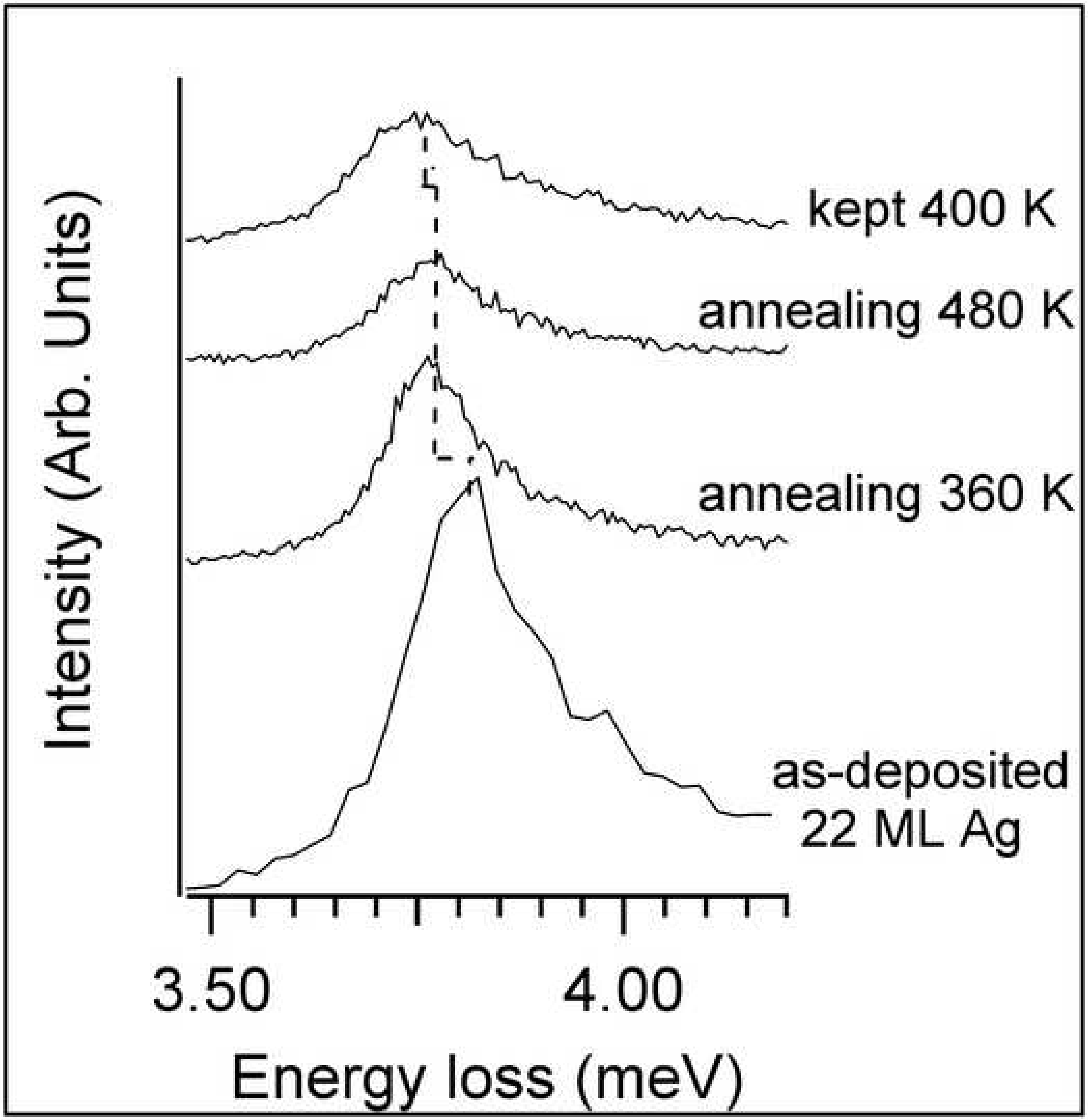

Figure 6

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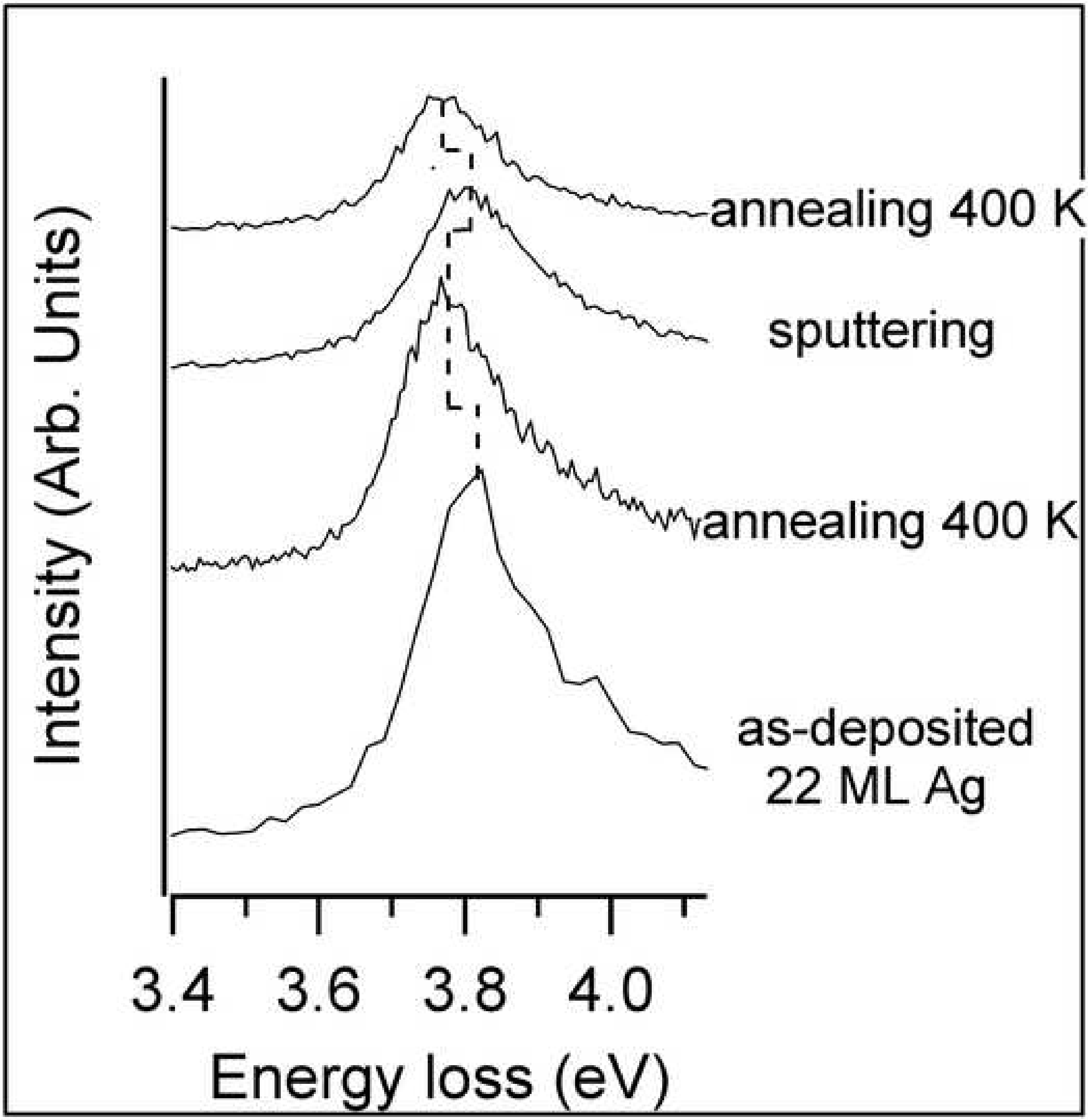
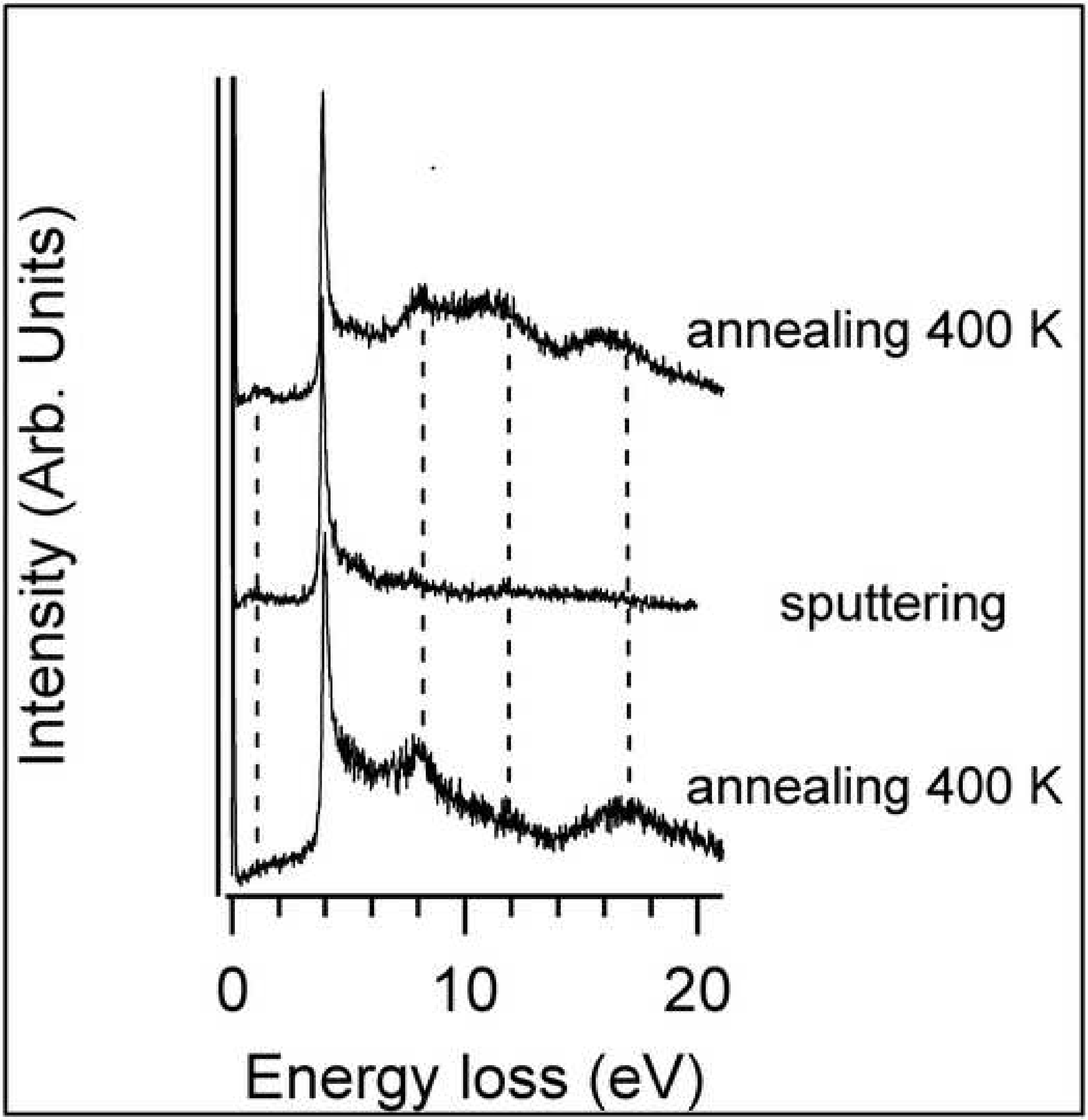


Figure 7


Intensity (Arb. Units)
annealing 400 K
sputtering
annealing 400 K
0
10
20
Energy loss (eV)