Elementary Excitations in Alkali-Metal Overlayers Probed by Electron-Energy-Loss Spectroscopy: Quantum-Mechanical Effects

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The spectrum of electronic excitations of Na and K overlayers adsorbed on Al(111) has been studied by means of electron-energy-loss-spectroscopy experiments, and self-consistent, dynamical-response calculations. Losses are observed in two distinct energy and coverage domains. The loss observed during the formation of the second atomic layer shows novel features, which are traced to the intrinsic quantum-mechanical nature of the excitations being probed, and their spatial confinement by the overlayer.

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The spectrum of elementary excitations of alkali-metal atom overlayers adsorbed on metal surfaces has been a subject of inquiry for many years [1–16], and some trends of its coverage dependence have been established. In this Letter we report a joint experimental and theoretical study for Na and K overlayers adsorbed on Al(111) which reveals new features of the basic physics of these excitations. Since the spatial confinement of the conduction electrons by the overlayer plays an important role, we expect our findings to have a bearing on other confined-geometry systems as well.

The experimental probe used is high-resolution, energy-resolved, electron-energy-loss spectroscopy (EELS); the theoretical work is based on a self-consistent computation of the loss spectrum for an electron-gas model. For the most part, we center our attention on coverages between one and two monolayers, for which the overlayer is metallic. This coverage regime (for which the current controversy about the nature of the alkali-metal atom-surface bond [17] does not apply) is of particular interest, since it allows us to investigate in a controlled fashion the transition from quasi-two-dimensional to quasi-three-dimensional electronic behavior for a prototype system.

For both overlayer systems our EELS data reveal the abrupt formation of an intense electron-gas loss at the completion of the first atomic layer. The behavior of this loss as a function of coverage is novel, as is its interpretation. The loss is shown to be dominated by a switchover from an electron-hole-pair excitation regime into a plasmonlike regime that takes place as the second layer forms.

The experiments were performed in a UHV chamber typically operated in the 10^{-11}-torr range. The chamber was equipped with LEED optics, a quadrupole mass spectrometer, and a Leybold-Heraus ELS-22 spectrometer. The Al crystal was prepared in the usual fashion, and the alkali metals were evaporated from SAES getters [2,18]. The energy resolution was 20 and 60 meV for measurements on K and Na overlayers, respectively. The incident beam energy used in both cases was $E_0=30$ eV, with incidence angle $=60°$. The loss spectra were recorded in the specular geometry, with an angular resolution of $\pm 1°$.

The coverage was calibrated via low-energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS). The coverage of Na relative to the number of atoms at the Al(111) surface is defined as $\theta=\frac{1}{3}$ when the $(\sqrt{3}\times\sqrt{3})R30°$ Na pattern is most intense. At a higher dosage a (2×2) LEED pattern was observed, which is most likely formed from three domains of a Na(2×1) structure [19]. This is consistent with the exposure time and the area of the thermal desorption peak, and gives a coverage $\theta=\frac{1}{2}$ for the (2×2) LEED pattern. This coverage corresponds to a full monolayer whose density equals 90% of the density of the bulk Na(110) planes.

The structure of K/Al(111) was determined by LEED studies. A clear $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern is observed; the same saturates in intensity with the completion of the first layer, as observed via TDS. If, as in the case of Na, the $(\sqrt{3}\times\sqrt{3})R30°$ structure is assumed to realize for $\theta=\frac{1}{3}$, the density of a full K monolayer corresponds to 91% of the bulk K(110) planes. For higher coverages a well developed $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern is still observed, but with a background whose intensity increases with coverage, indicating that the second layer grows disordered on top of the first one for $\theta>\frac{1}{3}$. It was found that annealing was necessary in order to produce an epitaxial K film, even at submonolayer coverage [18]. All the data reported here correspond to films annealed to 240 K.

The scattering probability per unit frequency, $I(\omega)$, for a process in which an electron is backscattered in the specular direction with energy loss $\hbar\omega$ [20] is given by the equation

$$I(\omega)=\frac{2e^2v_z^2}{\pi\hbar}|R_l|^2\int d^2q_\parallel\frac{P(\mathbf{q}_\parallel;\omega)}{[v_z^2q_\parallel^2+(\omega-\mathbf{v}_\parallel\cdot\mathbf{q}_\parallel)^2]^2}\,, \quad (1)$$

in which the physics of the overlayer response, and the coupling to the long-range dipolar fields which dominate the loss process, enter via the surface energy-loss function $P(\mathbf{q}_\parallel;\omega)$, defined by the equation [20]

$$P(\mathbf{q}_\parallel;\omega) = -2\hbar e^2 \int dz \int dz' e^{-q_\parallel(z+z')} \times \mathrm{Im}\chi(\mathbf{q}_\parallel;\omega+i\eta|zz'), \quad (2)$$

where $\mathbf{q}_\parallel$ is a two-dimensional wave vector in the plane of the surface (the x-y plane). The kinematics of the loss process in the trajectory approximation [20] enters Eq. (1) through the factor multiplying the loss function (in which v_z and $\mathbf{v}_\parallel$ are the components of the electron velocity normal to the surface and in the plane of the surface). The density response function $\chi(\mathbf{x},\mathbf{x}'|\omega)$ [21] is obtained by solving an integral equation of the form $\chi=\chi^0+\chi^0 V\chi$, where the electron-electron interaction $V(\mathbf{x},\mathbf{x}')$ includes many-electron effects in the local-density approximation, and $\chi^0(\mathbf{x},\mathbf{x}'|\omega)$ is the irreducible polarizability [21].

For coverages up to one monolayer (ML) we use the chemisorption model proposed by Serena *et al.* [22], in which the width d of the jellium slab for the overlayer is given by $d(\theta_{\mathrm{ML}})=d_{\mathrm{ion}}+(b-d_{\mathrm{ion}})\theta_{\mathrm{ML}}$, where d_{ion} is twice the alkali-metal ionic radius, b is the interplanar spacing for the (110) planes in the bulk, and θ_{ML} measures the coverage in numbers of (110) layers. Thus, $\theta_{\mathrm{ML}}=1$ corresponds to one monolayer whose areal density equals that of the (110) planes in the bulk, $\theta_{\mathrm{ML}}=2$ corresponds to two such layers, etc. For Na/Al(111) we have that $\theta_{\mathrm{ML}}=(0.9/0.5)\theta$, and for K/Al(111) $\theta_{\mathrm{ML}}=(0.91/0.33)\theta$, where θ is the experimental coverage as defined above. This model provides a very good account of the work function changes induced by alkali-metal adsorption. We simulate the growth of the second layer ($\theta_{\mathrm{ML}}>1$) according to $d(\theta_{\mathrm{ML}})=b\theta_{\mathrm{ML}}$, which corresponds to keeping the density of the jellium slab for the second layer fixed, and yields a work function that remains equal to its saturation value, as observed experimentally [23]. It is to be noted that a model of second-layer growth with a variable jellium density was ruled out since it gives rise to a pronounced dip in the work function, and a downward jump in the energy of the loss peak at the start of the second layer. Both features of that model are in conflict with the experimental observations.

Our EELS data show losses in two distinct frequency and coverage domains. A lower-frequency loss is first observed for submonolayer coverage. The abrupt onset of a higher-frequency loss at the start of the second atomic layer is apparent in the data for the energy position of the loss peak shown in Fig. 1 for both overlayer systems. This feature of the data (which has not been reported before for similar adsorption systems) is vividly underscored in Fig. 2 by the related feature of the abrupt jump undergone by the linewidth of the loss at the completion of the first layer for Na/Al.

The lower-frequency loss has been discussed before

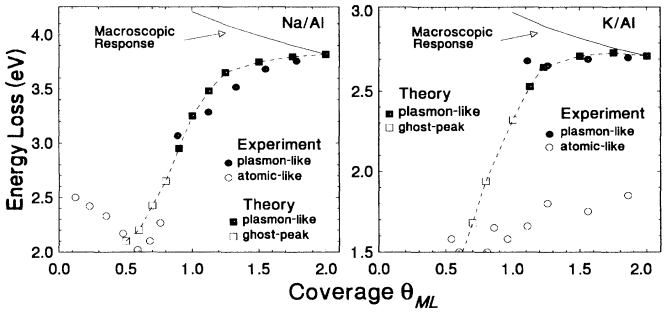

FIG. 1. Energy position vs coverage θ_{ML} of the loss peak for Na/Al(111) (left panel) and K/Al(111) (right panel). The peak positions extracted from the EELS data for $E_0=30$ eV and from $I(\omega)$ calculated via microscopic response theory are shown. The dashed line is a guide to the eye through the theoretical points. As noted in the text, for $E_0=30$ eV the ghost peak—open squares—is a very weak loss feature, and was not observed experimentally. The solid line refers to the peak position for a macroscopic response model.

[8,18]. It involves atomic transitions which are outside the electron-gas model. We thus turn our attention to the loss observed with the formation of the second layer. The main features of that loss are striking: In addition to its abrupt onset just noted, its energy shows a pronounced dependence on coverage for Na/Al(111) but not for K/Al(111). Now, given the fact that for two monolayers the loss occurs for $\omega\sim\omega_p/\sqrt{2}$, it proves instructive to attempt a preliminary understanding in terms of a macroscopic model—often used in the analysis of experiments—in which both substrate and overlayer are described by frequency-dependent dielectric functions. In this model [20],

$$P(q_\parallel;\omega)=\frac{2\hbar q_\parallel}{\pi}\,\mathrm{Im}\left[\frac{(-1)}{1+\varepsilon_{\mathrm{eff}}(q_\parallel;\omega)}\right], \quad (3)$$

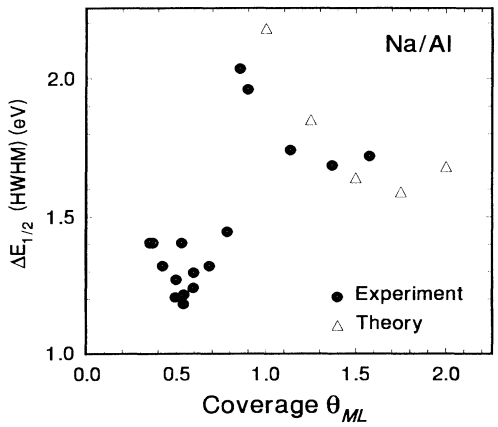

FIG. 2. Half width at half maximum of the loss peak for Na/Al(111) (see Ref. [28]).

where ε_{eff} is the effective dielectric function of the adsorbate-substrate system. Equation (3) yields a loss spectrum which corresponds to excitation of a "classical" plasmon for *all coverages*, and which, as seen in Fig. 1, is in *qualitative* disagreement with experiment.

Before discussing the predictions of the microscopic theory, a few technical details are in order. Since the density response function for the electron gas depends on $\mathbf{q}_\parallel$ only through its magnitude $q_\parallel$, Eq. (1) can be reduced to a one-dimensional integral of the form

$$I(\omega)=\int_0^{q_{\parallel\max}} dq_\parallel K(q_\parallel;\omega)P(q_\parallel;\omega)\,,$$

where $K(q_\parallel;\omega)$ is the *kinematic factor*, whose explicit definition has been given by Camley and Mills [24]. The finite angle subtended by the spectrometer is taken into account via the definition $q_{\parallel\max}=\Delta\Theta(2mE_0)^{1/2}/\hbar$. The computation of $I(\omega)$ was performed for a substrate which is sufficiently thick that spurious low-energy peaks, present for thinner slabs, are eliminated [25]. For easy comparison with experiment the theoretical spectra were shifted so that for two monolayers the energy of the loss agrees with experiment. This (downward) shift amounts to 0.5 eV (0.36 eV) for the case of Na (K), and it basically models the core-polarization process responsible for the difference between $\omega_p/\sqrt{2}$ and the measured value of the surface-plasmon frequency for the corresponding alkali metal.

The microscopic theory reproduces the main trends of the higher-frequency experimental loss accurately, as seen in Fig. 1. Insight into the physics of this loss is gained from Fig. 3, which shows the loss function for a wave vector representative of the $q_\parallel$'s which contribute to $I(\omega)$ for $E_0=30$ eV ($q_\parallel=0.05$ Å^{-1}). For $\theta_{\text{ML}}<1$ the loss function for Na/Al is featureless, except for its low-energy dropoff; it corresponds to incoherent electron-hole-pair excitation. For K/Al it can be best described as corresponding to excitation of a severely overdamped plasmon, the damping being due to electron-hole-pair decay (Landau damping). With increasing coverage the response gradually becomes coherent or plasmonlike [26], the switchover between both response regimes occurring for $\theta_{\text{ML}}\sim 1$ [27]. Since the frequency of the loss at the completion of the second layer ($\sim\omega_p/\sqrt{2}$) is basically determined by macroscopic physics, we have that the overall shape of the curve for the peak position versus coverage during the formation of the second atomic layer reflects the transition between the two electron-gas-response regimes that occur for $\theta_{\text{ML}}\sim 1$.

In addition, it is important to note that the microscopic theory (which we have implemented in the collisionless regime) provides a natural mechanism for the narrowing of the loss peak [28] observed during second-layer formation (Fig. 2). In effect, this narrowing is consistent with the reduction in the efficiency of Landau damping associated with the switchover we have just identified between one-electron and collectivelike elementary excitations.

Thus the coverage dependence of the loss is traced to a nontrivial effect, namely, the enhancement of the importance of the quantum-mechanical process of electron-hole-pair decay which is induced by the spatial confinement of the overlayer electrons. This enhancement, meant to be relative to the case of the metal-vacuum interface, explains why Eq. (3) fails, *despite the small wave-vector transfers involved in the loss process.*

The abrupt onset of electron-gas response implied by the data of Figs. 1 and 2 at the start of the second layer can be understood as follows. The loss spectrum $I(\omega)$ is given by (an integral over) the product of the loss function and the kinematic factor, and not just by the former. Figure 4 shows how for large E_0 a loss may develop for submonolayer coverage as a result of two competing effects: (i) The loss function (which is indeed a smooth function of coverage, see Fig. 3) drops off for small-energy transfers, but is quite constant for higher energies, and (ii) the kinematic factor favors small-energy transfers, suppressing large-energy transfers. The resulting loss feature (open squares in Fig. 1) does not reflect an underlying coherent electronic response, and has a similar origin to what in the literature has been called a "ghost peak" [29]. Now, because of the nature of the kinematic factor, the intensity of this feature decays rapidly with decreasing E_0. For the energy used in our experiments, $E_0=30$ eV, the ghost peak becomes a much weaker feature (see Fig. 4), which is consistent with the fact that it is not observed experimentally, leading to an abrupt on-

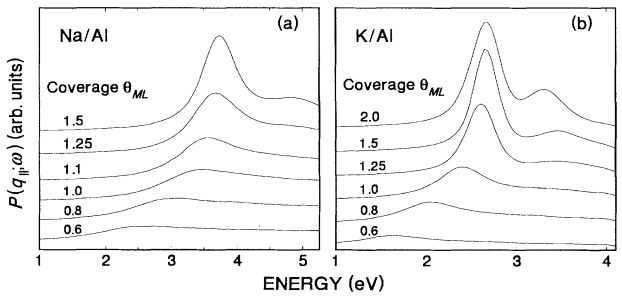

FIG. 3. (a) Surface energy-loss function for Na/Al for $q_\parallel=0.05$ Å^{-1} for several values of the coverage θ_{ML}. (b) Same as (a), but for K/Al.

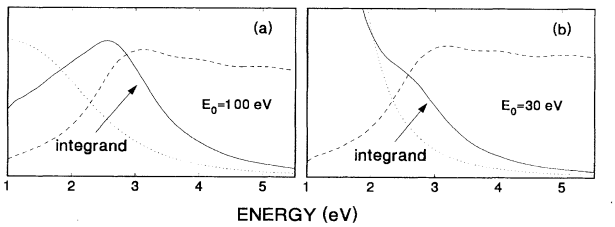

FIG. 4. Solid line: the integrand of $I(\omega)$ for Na/Al for $\theta_{\text{ML}}=0.6$, and for the values of E_0 and $q_\parallel$ shown in each panel. The angle of incidence is 45°. Dashed line: surface energy-loss function. Dotted line: kinematic factor.

set of the electron-gas loss in the EELS data.

In conclusion, our combined experimental/theoretical investigation has led us to a novel physical picture of the spectrum of electronic excitations in the Na/Al(111) and K/Al(111) adsorption systems. The loss observed during second-layer formation provides a signature of the inherent quantum-mechanical nature of the excitations being probed. Our results can also be visualized as involving a transition from the quasi-two-dimensional response embodied by the loss function for monolayer coverage to the quasi-three-dimensional response that realizes for two-layer coverage.

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[1] A. U. MacRae *et al.*, Phys. Rev. Lett. **22**, 1048 (1969); S. Andersson and U. Jostell, Surf. Sci. **46**, 625 (1974); Faraday Discuss. Chem. Soc. **60**, 255 (1975); J. Cousty, R. Riwan, and P. Soukiassian, J. Phys. (Paris) **46**, 109 (1985).

[2] A. Hohlfeld, M. Sunjic, and K. Horn, J. Vac. Sci. Technol. A **5**, 679 (1987); A. Hohlfeld and K. Horn, Surf. Sci. **211/212**, 844 (1989).

[3] B. N. J. Persson and L. H. Dubois, Phys. Rev. B **39**, 6249 (1989).

[4] S. Å. Lindgren and L. Walldén, Phys. Rev. Lett. **59**, 3003 (1987); **59**, 2894 (1987); Phys. Rev. B **38**, 3060 (1988).

[5] K. Horn *et al.*, Phys. Rev. Lett. **61**, 2488 (1988).

[6] D. Heskett, K.-H. Frank, E. E. Koch, and H.-J. Freund, Phys. Rev. B **36**, 1276 (1987).

[7] S. Å. Lindgren and L. Walldén, Phys. Rev. B **38**, 10044 (1988).

[8] D. Heskett, K.-H. Frank, K. Horn, E. E. Koch, H.-J. Freund, A. Baddorf, K.-D. Tsuei, and E. W. Plummer, Phys. Rev. B **37**, 10387 (1988).

[9] J. W. Gadzuk, Phys. Rev. B **1**, 1267 (1970); D. M. Newns, Phys. Lett. **39A**, 341 (1972).

[10] A. G. Eguiluz and D. A. Campbell, Phys. Rev. B **31**, 7572 (1985).

[11] H. Ishida and M. Tsukada, Surf. Sci. **169**, 225 (1986).

[12] R. Fuchs and W. Ekardt, J. Phys. Condens. Matter **1**, 4081 (1989).

[13] N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978).

[14] L.-A. Salmi and M. Persson, Phys. Rev. B **39**, 6249 (1989).

[15] J. P. Muscat and I. P. Batra, Phys. Rev. B **34**, 2889 (1986).

[16] P. Nordlander and J. C. Tully, Surf. Sci. **211/212**, 207 (1989).

[17] G. M. Lamble, R. S. Brooks, and D. A. King, Phys. Rev. Lett. **61**, 1112 (1988); D. M. Riffe, G. K. Wertheim, and P. H. Citrin, *ibid.* **64**, 571 (1990); H. Ishida, Phys. Rev. B **39**, 5492 (1989); B. N. J. Persson and H. Ishida, *ibid.* **42**, 3171 (1990); E. Wimmer *et al.*, *ibid.* **28**, 3074 (1983); M. Scheffler *et al.*, Physica B (to be published).

[18] K.-D. Tsuei, Ph.D. thesis, University of Pennsylvania, 1990 (unpublished); K.-D. Tsuei *et al.*, J. Vac. Sci. Technol. (to be published).

[19] J. O. Porteus, Surf. Sci. **41**, 55 (1974).

[20] D. L. Mills, Surf. Sci. **48**, 59 (1975); W. L. Schaich, Phys. Rev. B **24**, 686 (1981).

[21] A. G. Eguiluz, Phys. Rev. B **31**, 7472 (1985); Phys. Scr. **36**, 651 (1987).

[22] P. A. Serena, J. M. Soler, N. García, and I. P. Batra, Phys. Rev. B **36**, 3452 (1987).

[23] The success of this model in the description of the dynamics may be indicative of second-layer island formation [which would be consistent, e.g., with the fact that the loss peak for K/Al(111) shifts very little with coverage].

[24] R. E. Camley and D. L. Mills, Phys. Rev. B **29**, 1695 (1984).

[25] The substrate width used in the calculations corresponds to at least 25 Al(111) layers.

[26] The loss that develops in Fig. 3 for $\theta_{ML} > 1.5$ corresponds to the dipole surface plasmon recently observed by K.-D. Tsuei *et al.* for thick alkali metal slabs [Phys. Rev. Lett. **64**, 44 (1990)]; its behavior as the coverage grows from two monolayers to a thick slab is discussed in A. G. Eguiluz and J. A. Gaspar, in Lectures in Surface Physics, edited by M. Cardona and F. Ponce (Springer, Heidelberg, to be published). See also A. Liebsch, following Letter, Phys. Rev. Lett. **67**, 2858 (1991).

[27] For K/Al the theoretical loss for $\theta_{ML}=1$ actually includes both coherent-response and ghost-peak features.

[28] The theoretical points in Fig. 2 have been shifted *upwards* (by about 1 eV) so that for $\theta_{ML}=2$ the theoretical linewidth agrees with the extrapolated value of the experimental linewidth. (That the experimental linewidth is larger than that of the electron-gas loss was to be expected; however, the key issue is the narrowing of the loss with increasing coverage.)

[29] R. E. Palmer, J. F. Annett, and R. F. Willis, Phys. Rev. Lett. **58**, 2490 (1987).