Photoinduced plasmon excitations in alkali-metal overlayers

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Collective surface excitations in alkali-metal overlayers are observed using photoyield spectroscopy. Spectra for Na and K on Al(111) reveal a multipole surface plasmon and bulklike overlayer plasmon. In contrast, Li on Al exhibits only the multipole mode. In the submonolayer regime, all three alkali metals provide evidence for the threshold excitation. Time-dependent density-functional calculations for realistic alkali-metal overlayers agree well with these observations. [S0163-1829(98)07408-6]

The study of electronic excitations in thin alkali-metal films provides an ideal testing ground for the theoretical description of many-body effects in solids, since these systems represent quasi-two-dimensional electron gases whose average density and thickness can be varied over a wide range. Also, alkali-metal overlayers are of interest because of phenomena such as large work function changes, surface reconstruction, catalytic promotion, and metal-insulator transitions.[1] Nevertheless, the experimental identification of the various types of collective modes and their variation with coverage is far from complete. Electron energy loss measurements are difficult to analyze because these modes can have very different spectral weights and because of limited momentum resolution,[2,3] while photoyield data, ideally suited for this purpose, were mostly recorded at fixed (low) photon energies.[4]

To elucidate the nature of overlayer-induced electronic excitations, we have carried out systematic photoyield measurements of three alkali metals (Na, K, and Li) on Al(111) over a wide range of coverages. The photon energies range from below 3 to beyond 15 eV, so that all important modes can be detected. For Na and K, we observe the threshold excitation in the submonolayer regime, evolving towards a doublet of collective modes in the multilayer regime. The latter correspond to the multipole surface plasmon and bulklike overlayer plasmon. These findings are in excellent agreement with theoretical predictions.[5,6] The Li photoyield spectra, however, differ strikingly from those of Na and K since beyond two monolayers only one collective mode appears. With the aid of dynamical response calculations for three-dimensional Li overlayers we identify the observed peak as the Li multipole surface plasmon and show that the bulklike overlayer mode is greatly reduced due to lattice-induced single-particle transitions.

The Li data are particularly surprising since available spectra on clean metal surfaces suggest that the multipole surface plasmon is a fragile surface excitation readily weakened by interband transitions. While nearly-free-electron metals such as Na, K, Al, and Mg show the multipole mode,[7–12] metals exhibiting substantial lattice effects such as Li,[10] Ag,[13] and Hg (Ref. 14) do not reveal any clear evidence of it. Thus, large pseudopotentials, occupied *d* bands, or shallow core levels appear to annihilate this excitation. Our experimental and theoretical results demonstrate instead that the Li multipole mode exists *in spite of* strong lattice effects. As we discuss below, the origin of this remarkable behavior is connected with the location of the multipole charge. Since it is confined to the overlayer-vacuum interface, the multipole mode is largely decoupled from interband transitions.

The measurements were carried out at the 1 m Seya-Namioka beamline at the BESSY (Berliner Elektronen-Speicherring-Gesellschaft für Synchrotronstrahlung) storage ring using a commercial angle-resolving electron spectrometer at a base pressure of 6×10^{-11} mbar. A prepolished Al(111) crystal was cleaned by repeated sputtering and heating cycles. The substrate temperature during deposition was 100 K. We define one monolayer ($c=1$) as a fully occupied (110) plane in the alkali-metal bulk crystal. Thus, one layer corresponds to $\Theta_K\approx0.45$, $\Theta_{Na}\approx0.53$, and $\Theta_{Li}\approx0.77$, where $\Theta=1$ refers to the underlying Al(111) structure.[15] Coverages were calibrated on the basis of existing literature data by the characteristic variation of the work function,[16,17] the core-level line shape in the case of K,[15,18] and deposition time. At low coverages, Na/Al(111) exhibits a $(4/3\times4/3)$ low-energy electron diffraction (LEED) pattern, above which an epitaxial (1×1) growth is observed.[17] For K/Al(111), a $(\sqrt{3}\times\sqrt{3})$R30° structure is initially formed, with K atoms occupying on top sites, while for higher coverages the growth is not epitaxial. For the thickest Li/Al(111) layers, no LEED spots were observed, indicating nonepitaxial growth. A layer-by-layer film growth was established from the attenuation of the substrate signal. Also, surface roughness was

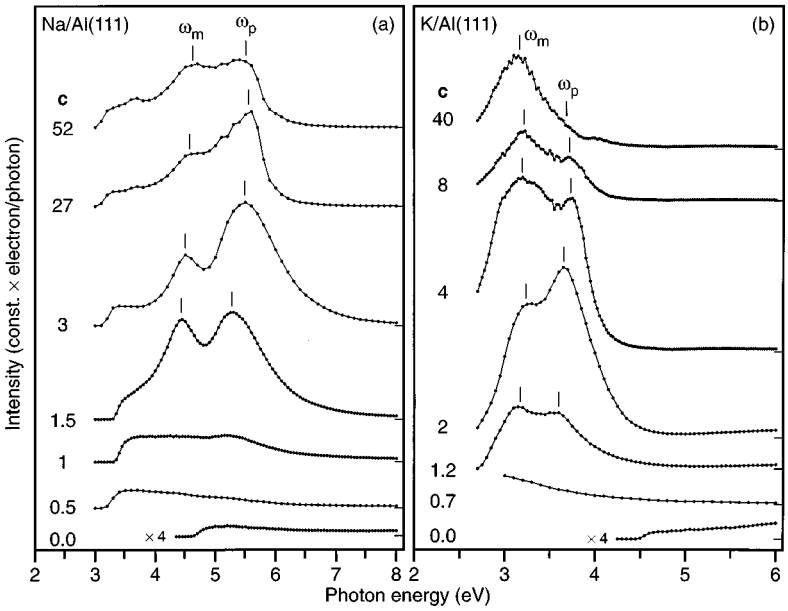

FIG. 1. Photoelectron yield spectra for (a) Na and (b) K overlayers on Al(111) at different coverages. ω_m and ω_p indicate the multipole surface and bulk-like plasmons. The vertical bar denotes the intensity scale.

negligible since the monopole surface plasmon was never observed. The photoyield spectra were measured in the energy and angle resolved mode by recording the intensity near the Fermi level E_F.[8] The data were collected in normal emission with p-polarized light incident at 45°. The intensity was measured in the constant initial state mode at binding energies 0.1 eV (K) and 0.3 eV (Na and Li) below E_F. The data were normalized by measuring the photon flux using a gold mesh and (at low photon energies) a GaAsP diode, taking into account the decrease of photon flux with time. Corrections were carried out for higher-order light and analyzer transmission function. The same intensity scale is used in all spectra.

The salient multielectron excitations in photoyield spectra of alkali metal overlayers can be discussed in terms of the Na and K data shown in Fig. 1. For $c \leqslant 1$, there is a gradual intensity increase towards the work function cutoff. (For K the cutoff is below the energy range of the monochromator.) Beyond $c=1$, the spectra show a dramatic increase in intensity with the appearance of two well-resolved peaks: for Na at 4.5 and 5.3 eV; for K at 3.2 and 3.6 eV. With increasing coverage, the upper peaks shift towards the Na and K bulk plasma frequencies at 5.8 and 3.8 eV, respectively, and their intensity diminishes. Similar spectra for K on Al were independently observed by Kim *et al.*[3]

The Na and K spectra agree very well with results of dynamical response calculations based on the time-dependent local density approximation (TDLDA)[19] (see Fig. 3 in Ref. 5 and Figs. 8 and 10 in Ref. 6). As shown in Ref. 6, lattice effects in these spectra are very weak, even at low coverages where the induced density exhibits appreciable atomic corrugation. Thus, the jellium model for alkali-metal adsorption[16] is adequate. The only spectral feature for $c < 0.5$ is the threshold excitation, corresponding to transitions from near E_F to the vacuum level. For $c \geqslant 2$, the density in the overlayer is rather flat, so that a bulklike plasma oscillation (ω_p) is feasible. This mode is analogous to the antisymmetric collective mode of a finite slab. Its frequency differs slightly from that of the $q=0$ bulk plasmon because of the spatial confinement in the normal direction and the smoothness of the density profile at the adsorbate interfaces. At the adsorbate-vacuum interface, the density is similar to that at the semi-infinite alkali metal, giving rise to the multipole surface plasmon (ω_m) at 4.5 eV (Na) and 3.2 eV (K). For $c \approx 1$, it is not possible to distinguish the adsorbate interfaces. Hence, the bulklike and multipole surface modes become very broad. The measured Na and K spectra confirm all of these theoretical predictions.

As illustrated in Fig. 2, the yield spectra for Li overlayers on Al(111) differ fundamentally from the Na and K spectra. For $c \leqslant 1$, there is again a gradual intensity increase towards the work function cutoff. Beyond $c=1$, however, the spectra are dominated by only a single peak near 5.3 eV accompa-

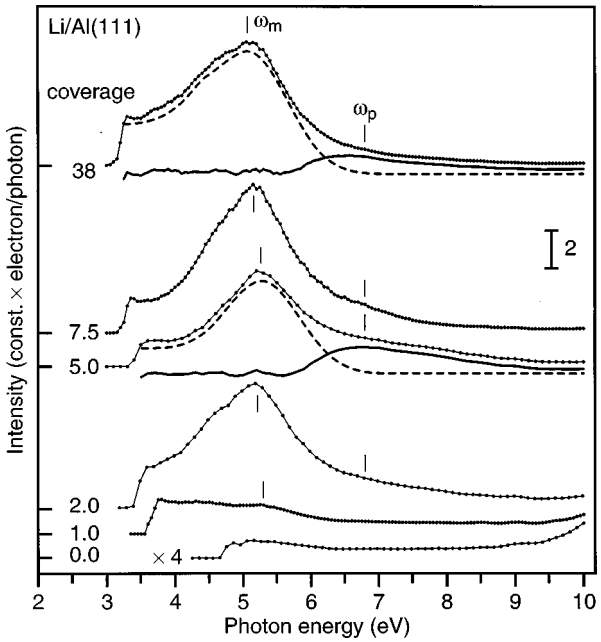

FIG. 2. Photoelectron yield spectra for Li overlayers on Al(111) at different coverages. The $c=5$ and 38 spectra are decomposed into a peak at 5.3 eV (dashed line) and a high-frequency hump (solid line) around 6.8 eV (see text). The vertical bar denotes the intensity scale.

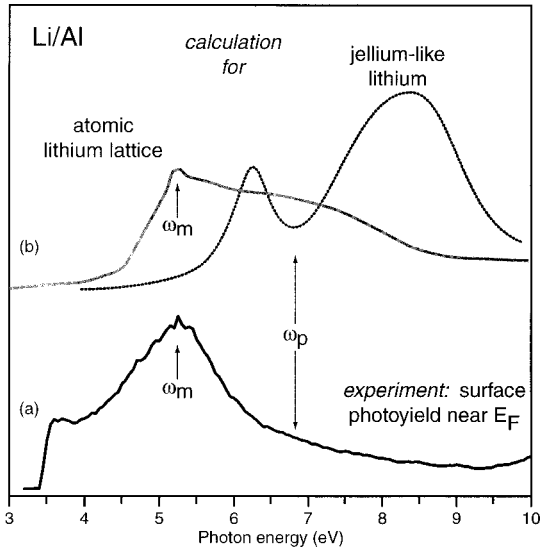

FIG. 3. Comparison of (a) measured $c=2$ Li/Al photoyield spectrum with (b) calculated TDLDA excitations spectrum for $c=2$ Li(110) on jellium substrate corresponding to Al (solid curve). Dotted curve: spectrum for equivalent jellium overlayer. The frequency of the Li multipole surface plasmon is $\omega_m \approx 5.2$ eV, that of the bulk plasmon $\omega_p = 6.7$ eV. The corresponding jellium values are 6.2 and 8.0 eV, respectively.

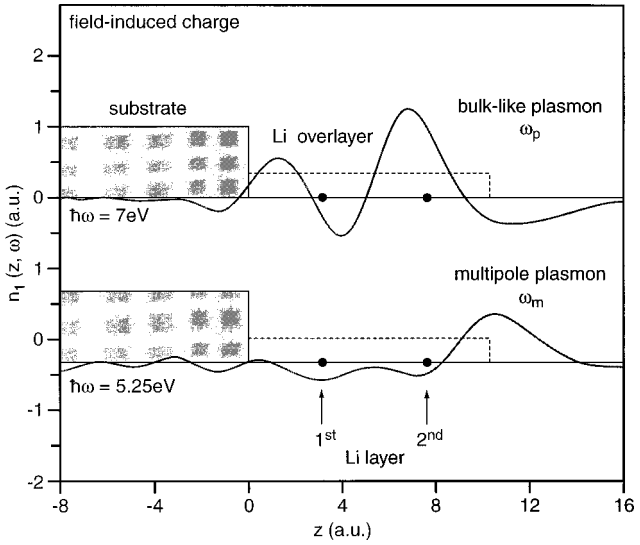

FIG. 4. Laterally averaged fluctuating charge density $n_1(z,\omega)$ (real part) for two Li(110) layers. Upper curve: standing wave associated with bulk-like overlayer plasmon; lower curve: multipole surface plasmon. The dots denote the positions of the Li atomic planes. The shaded areas indicate schematically the location of the substrate ($z \leqslant 0$) and of the overlayer ($0 \leqslant z \leqslant 10a_0$).

nied by a broad shoulder extending up about to 9 eV. In order to ascertain the approximate position and shape of this shoulder, the 5.3 eV peak was fitted with a Gaussian and a background accounting roughly for the substrate yield. The remnant is a broad hump around 6.8 eV, whose intensity diminishes at large coverages. Comparing Figs. 1 and 2, it is evident that the Li spectra cannot be understood within the jellium model. In particular, the nature of the main peak for $c \geqslant 2$ is not obvious.

To analyze the Li spectra, we have performed TDLDA calculations for realistic Li overlayers on jellium corresponding to Al. The method is the same as described in Ref. 6 except that the partial-core correction to the exchange-correlation potential[20] is incorporated in the ground-state and response calculations. We consider Li(110) and Li(001) atomic planes whose spacing a is the same as in the bulk ($a_{110}=2.47$ Å, $a_{001}=1.75$ Å). The distance d between the first Li layer and the Al jellium edge is determined by minimizing the total energy. We find $d_{110}=1.64$ Å and $d_{001}=1.48$ Å. Below, we focus on Im $d_\perp(\omega)$ which represents the main contribution to the surface photoabsorption.[11] Since transitions to internal and external final states give similar peak positions,[21] Im $d_\perp(\omega)$ can be taken as representative of the emitted photoyield. We have also investigated the photoabsorption due to parallel surface currents induced by interband transitions within the Li overlayer. We neglect this contribution here since it is more than one order of magnitude weaker than the absorption due to the many-body screening processes associated with the normal component of the electric field.

Figure 3 compares the measured $c=2$ Li spectrum with the calculated surface photoabsorption for two Li(110) layers on Al. Li(001) layers give similar results. The theoretical spectra exhibit a peak near 5.2 eV and a ~ 3 eV wide shoulder on the high-frequency side, centered around 7 eV. In contrast, the analogous spectrum for the equivalent jellium overlayer has two peaks, just as in the case of Na and K. Evidently, the ionic potential has a significant influence on the adsorbate excitations. The multipole peak is redshifted, but its strength and width are roughly unchanged. The bulklike Li mode, however, is not only redshifted but strongly broadened. In fact, the damping of this mode is so large that it is reduced to a shoulder on the high-energy side of the multipole plasmon. The frequency and width are consistent with those of the $q=0$ volume plasmon of Li ($\omega_p=6.7$ eV, $\Gamma_p=2.5$ eV).[22] Similar theoretical spectra are obtained for $c=3$.

We have also performed TDLDA calculations for a one-dimensional cosine potential in the overlayer, with parameters chosen to represent the main Fourier component of the Li potential. In this case, the spectrum is intermediate between the jellium and three-dimensional spectra shown in Fig. 3. The bulklike Li plasmon is considerably broader and weaker than for jellium, but not as much as for realistic Li. Hence, electron-hole pair creation induced by the lateral density corrugation contributes significantly to the spectral distribution. The multipole mode is only weakly affected by the one-dimensional cosine potential. This systematic evolution of the calculated overlayer modes with increasing strength of the Li potential gives us confidence that our peak assignment of the Li spectra is correct, i.e., the peak at 5.3 eV is the multipole surface plasmon while the shoulder on the high-frequency side is the damped bulklike plasmon. We conclude therefore that, despite the strong Li potential, the multipole surface plasmon is a well-defined collective excitation. In electron energy loss spectra[10] it was not possible to detect this mode since it is hidden in the tail of the monopole surface plasmon. The multipole mode should, however, be observable in photoyield spectra of single-crystal Li(110) and Li(001) surfaces.

What is the origin of the different lattice effect on the Li

overlayer modes? As illustrated in Fig. 4, this difference is associated with the location of the fluctuating plasmon charge relative to the lattice potential. The bulklike mode corresponds to a standing wave in the overlayer and is fully exposed to the potential. Our results show that the single-particle transitions created by only two Li layers make this mode surprisingly similar to the Li volume plasmon. The multipole charge, on the other hand, has its main weight near the adsorbate-vacuum interface. Since it couples less well to the lattice, decay via interband excitations is much weaker. This qualitative difference of the location of the Li overlayer modes is even more evident in the calculations for $c=3$.

Our calculations for the (001) geometry reveal a slightly larger damping of the Li bulklike mode than for (110). This is plausible since the interplanar spacing and distance from the jellium edge are shorter. Thus the (001) overlayer is more compact, implying stronger decay of the bulklike mode at the boundaries. On the other hand, the shape of the multipole peak is similar for both geometries since it is less affected by the lattice potential. The fine-strucure in the calculated Li spectra in Fig. 3 is presumably caused by interband transitions. Similar structure was found in yield spectra for a one-dimensional, semi-infinite corrugated potential.[23]

As noted above, the intensity of the bulklike excitation of all three alkali-metal overlayers diminishes with increasing coverage. This is to be expected since the alkali metals eventually become transparent at ω_p. The surface photoyield then exhibits the characteristic minimum that was observed on several systems.[7,8,11]

The analysis of the Li overlayer modes leads us to an interesting speculation concerning the possible existence of the Ag multipole surface plasmon. Since the use of photons suppresses the ordinary monopole plasmon and the bulk plasmon is not yet fully developed in a thin overlayer (the interband onset is less sharp than in the bulk), it might be feasible to observe the multipole mode in photoyield spectra of Ag overlayers. Presumably, its frequency lies *above* the bulk plasma frequency (3.8 eV) near $0.8\times 9.0=7.2$ eV, where 9.0 eV is the bulk plasma frequency of the $5s$ electrons. Such a feature might be difficult to separate from single-particle excitations. It would be interesting to perform photoyield measurements for Ag and Ag overlayers in this energy range.

In summary, TDLDA calculations provide an unambiguous identification of coverage-dependent collective excitations in adsorbed alkali-metal films. Surprisingly, the Li multipole surface plasmon exists despite strong lattice effects, whereas the bulklike mode is suppressed. In contrast, the Na and K overlayers exhibit well-defined multipole surface and bulklike plasmon excitations. At submonolayer coverages, the spectra of all three alkali metals support the existence of the threshold excitation.

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