Electronic Excitations in Adsorbed Alkali-Metal Layers

A. Liebsch
Institut für Festkörperforschung, Forschungszentrum, 517 Jülich, Germany

(Received 10 May 1991)

A new concept for the electronic excitations in adsorbed alkali-metal layers is presented. It explains how these excitations evolve with coverage from below one monolayer to thick multilayers, and it establishes a direct relation of these overlayer collective modes to those of clean alkali-metal surfaces.

PACS numbers: 73.20.Mf, 79.20.Kz

The electronic excitation spectra of chemisorbed alkali-metal layers have been studied for more than 20 years [1-10]. At coverages c up to about one monolayer, the spectra appear to show evidence for atomiclike transitions and the coverage dependence of the observed excitation frequencies resembles that of the work function. At $c > 1$ collective excitations dominate. The momentum dispersion of these modes, however, deviates significantly from that of the surface plasmons observed at clean alkali metals. Until now, most of these observations are not understood. In particular, the nature of the collective modes at coverages beyond one monolayer is not known and no clear physical picture exists for the transition from these excitations to the surface-plasmon modes of thicker samples.

This situation is quite different from that of the clean simple-metal surfaces where recently a consistent picture of the electronic excitations as observed in various surface spectroscopies was achieved [11]. Two surface-induced collective modes are seen on a variety of systems: the ordinary surface plasmon which shows a negative dispersion [12] at small wave vectors $q \equiv |\mathbf{q}_{\parallel}|$ and then goes through a minimum, and the so-called multipole surface plasmon which disperses upwards at small q. The term "multipole" here refers to the fact that this peak of the surface response function can be related to a pole in the complex frequency plane at which the density fluctuation has dipolar character normal to the surface in contrast to the monopole character of the usual surface plasmon. The multipole mode also gives rise to the well-known local-field enhancement [13] observed in surface photoemission on simple metals [14] and to the enormous enhancement of the second-harmonic intensity from adsorbed alkali-metal overlayers [9].

The most detailed calculation of the electronic excitations in alkali-metal overlayers was carried out by Eguiluz and Campbell [8]. They used Lang's jellium model [15] for the electronic properties of Na layers on a Al slab and treated the electronic response within the random-phase approximation. The frequencies of the calculated modes, however, were much higher than those observed [2,4,5]. Also, no interpretation of the excitations at small q was given.

The aim of this paper is to elucidate the nature of the electronic excitations of thin alkali-metal overlayers, to explain their systematic variation with coverage, and to relate them to the known collective modes found at clean alkali-metal surfaces [11]. We have carried out calculations for Na, K, and Cs overlayers adsorbed on Al at various coverages since these systems have now been studied extensively experimentally [4,5]. We also employ Lang's jellium model to determine the ground-state electronic properties of these systems. The Al substrate, however, is here taken to be semi-infinite rather than a slab. We found this to be crucial for the correct interpretation of the excitations in the small-q region since we then can establish a direct connection to the known alkali-induced spectral features in the long-wavelength limit [9,10]. The electronic response is treated within the time-dependent local-density approach [16,17]. Obviously, atomiclike transitions are not included in the jellium model. Nevertheless, those quantities which depend on lateral averages (such as the work function [15] or the induced dynamic dipole moment in the $q=0$ limit [18]) are described remarkably well within this model, even at coverages as low as $c \approx \frac{1}{4}$. We can therefore expect this model to be qualitatively correct also at not too large q.

The physical picture that emerges from this work differs fundamentally from previous models of overlayer-induced electronic excitations [6-8]. Our results are summarized in Fig. 1 where the dispersion of the over-

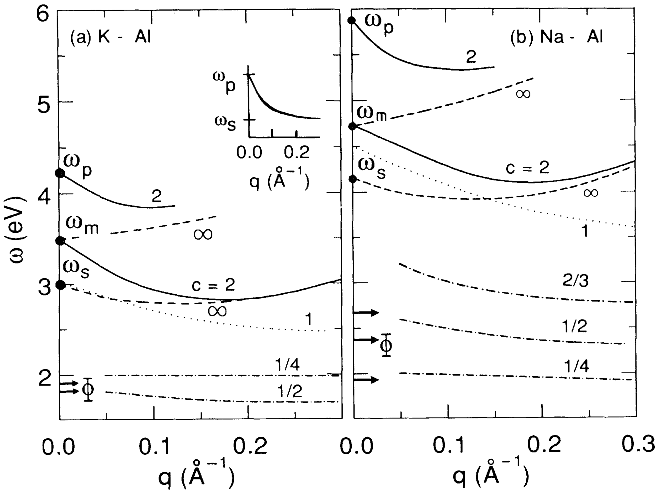

FIG. 1. Calculated dispersion of electronic excitations for K and Na overlayers on Al at various coverages. Solid curves: $c=2$; dotted curves: $c=1$; dash-dotted curves: $c<1$; dashed curves: $c=\infty$, i.e., dispersion of collective modes at clean K and Na surfaces (from Ref. [11]). The arrows indicate the work functions for $c<1$. Inset: Dispersion of double-layer mode from local optics.

layer modes for K and Na on Al are compared to those of clean K and Na surfaces. Three coverage regions can be identified which exhibit distinct electronic excitation mechanisms (a denotes the overlayer thickness).

(i) For $c=2$, two overlayer collective modes are found at small q: one near $\omega_p \equiv \omega_p(\text{ads})$ corresponding to the excitation of a volume plasmon in the adsorbate and the other near $\omega_m \approx 0.8\omega_p$ due to the multipole surface plasmon at the adsorbate-vacuum interface. At larger q, these two adsorbate modes undergo a transition towards the collective modes of clean alkali-metal surfaces: The overlayer multipole surface plasmon at small q turns into the usual monopole surface plasmon at large q, whereas the overlayer volume plasmon at small q becomes the clean surface multipole plasmon at large q [19]. The transition is complete when the quantity $\exp(-2qa)$, which characterizes the electrostatic coupling between the adsorbate-vacuum and adsorbate-substrate interfaces, is less than $\approx 5\%$.

This remarkable behavior may be understood as follows. In the local optics picture, the coupling between the adsorbate-vacuum and adsorbate-substrate interfaces gives a single overlayer mode which coincides with ω_p in the $q=0$ limit and which disperses towards $\omega_s = \omega_p/\sqrt{2}$ at large q (see inset in Fig. 1). As a result of nonlocal screening and spatial dispersion, a new mode arises at the overlayer-vacuum interface, namely, the multipole surface plasmon mode at ω_m. Since both modes couple to electron-hole pairs, they may hybridize. In order to avoid the crossing of these two modes, a "hybridization gap" opens up in the excitation spectrum. It then becomes evident that the multipole mode does not disperse upwards as on the clean surface, but downwards and finally turns into the ordinary surface plasmon at large q. For the same reason, the overlayer volume plasmon at small q disperses towards the clean surface multipole mode.

From this behavior it is now straightforward to predict the dispersions at multilayer coverages: They will be similar to those for $c=2$ except that the transition between the small and large wave-vector regimes will occur at progressively smaller q (near $q \approx 1.5/a$). Thus, in the limit of large a this transition occurs at $q \approx 0$, so that the clean alkali-metal surface modes evolve naturally within this concept [20].

We point out that the only monopole surface plasmon that exists at $q=0$ (in the absence of retardation), is determined by the condition $\epsilon(\omega) = -1$, where $\epsilon(\omega)$ is the dielectric function of the substrate. In the present case, this yields a mode at 11 eV, the surface plasma frequency of Al. Of course, at small q, there is no electronic excitation near ω_s, the surface plasmon of clean alkali metals.

(ii) For $c=1$, the ground-state electron density does not show a plateau in the overlayer region, in contrast to the double-layer case discussed above. Thus, the overlayer volume plasmon mode is heavily broadened due to decay into electron-hole pairs. Moreover, since it is no longer possible to distinguish two separate adsorbate-vacuum and adsorbate-substrate interfaces, the overlayer multipole mode is also less sharp. Both modes therefore greatly overlap so that only one broad asymmetric spectral peak is found in the electron-energy-loss (EEL) function. As can be seen in Fig. 1, this peak lies below the double-layer multipole plasmon mode.

(iii) For $c < 1$, the average density in the overlayer decreases which leads to a rapid lowering of the excitation frequencies. More importantly, the density profile differs more and more from that of the clean alkali-metal surface. Instead, it begins to resemble that of the substrate with only a weak amplification of the outer tail in the overlayer region. Thus, the excitations near the overlayer volume and multipole surface plasmons disappear until, in the range $\frac{1}{4} < c < \frac{1}{2}$, a new excitation mechanism sets in which is governed by electronic transitions from the Fermi energy to the vacuum level. Thus, the loss function is dominated by a peak near the work function Φ. As shown in Fig. 1, this peak exhibits very little dispersion with q.

The above results for the adsorbate-induced electronic excitations show that the wave-vector dispersion of these modes exhibits a characteristic trend from very low to very high coverages, and that it is uniquely related to the dispersion of the surface modes of clean alkali metals. Moreover, we now have for the first time a detailed understanding of the transition from the macroscopic to the microscopic picture of these excitations.

The results in Fig. 1 were obtained from the maxima of the electron-energy-loss function which is given by the imaginary part of the reflection amplitude

$$g(q,\omega) = \int dz\, e^{qz} \delta n(z,q,\omega)\,, \tag{1}$$

where δn is the self-consistently screened electron density induced at the surface by the external electric potential

$$\phi_{\text{ext}}(\mathbf{r},t) = -(2\pi/q)\exp(i\mathbf{q}_{\parallel}\cdot\mathbf{r}_{\parallel} + qz - i\omega t)\,.$$

Figure 2 shows the loss function for K on Al. For $c=2$ the multipole mode first shifts down and then it disperses upwards. The volume excitation also shifts initially downwards. At larger q, it rapidly loses weight since the external potential penetrates the overlayer less efficiently. The loss function for $c=\frac{1}{2}$ shows only one peak near Φ almost independent of q.

For the above assignment of the overlayer collective excitations, the detailed understanding of the small-q behavior of these modes is essential. In this region, the loss function has the expansion [13]

$$g(q,\omega) = \sigma(\omega)[1 + qd(\omega)]/[1 - qd(\omega)\sigma(\omega)]\,, \tag{2}$$

where $\sigma(\omega)$ is the total weight of the surface charge in the $q=0$ limit and $d(\omega)$ is its centroid position measured from the substrate jellium edge [21]. Thus, the small-q behavior of the loss function is governed by the frequency dependence of $d(\omega)$. These spectra are shown in Fig. 3

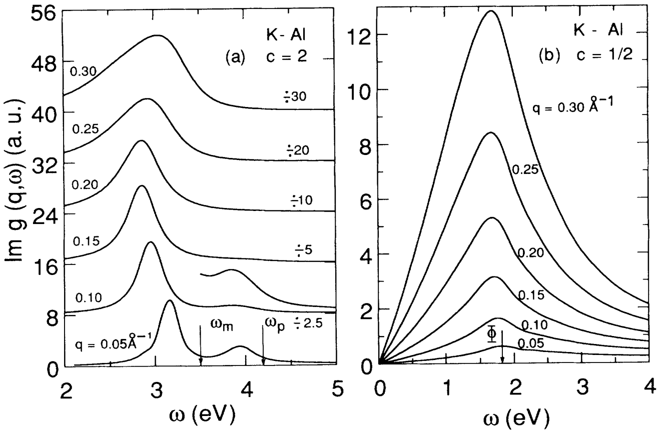

FIG. 2. Electron-energy-loss function $\mathrm{Im}g(q,\omega)$ for K on Al at various wave vectors. (a) $c=2$; (b) $c=\frac{1}{2}$.

for K on Al. For $c \leq \frac{1}{2}$, $\mathrm{Im}d(\omega)$ has only one broad peak near $\omega \approx \Phi$. Towards $c=1$ this peak is gradually replaced by a stronger peak slightly below ω_m with a shoulder near ω_p. The multipole mode arises since the density profile at the adsorbate-vacuum interface resembles that at the clean alkali-metal surface but one monolayer is too thin to sustain a well-defined mode at ω_p. For $c>1$ these two modes become progressively sharper and they are clearly resolved at $c \geq \frac{3}{2}$, the mode at ω_p being the analog of the classical overlayer mode at $q=0$. Since the full results obtained for $\mathrm{Im}g(q,\omega)$ are in excellent agreement with the small-q expansion given in Eq. (2), we are confident that our interpretation of the nature of the overlayer collective modes is in fact correct.

In the dipole scattering regime the probability for creating electronic excitations is proportional to $\mathrm{Im}g(q,\omega)$ [22]. The analysis of EEL data, however, can be complicated since the kinematic factor that describes the scattering geometry varies rapidly with q and ω. Nevertheless, it is evident that the essential features of the results discussed above are in agreement with recent EEL spectra for alkali-metal layers adsorbed on Al. The experimental details are discussed in Refs. [4] and [5]. As shown in Fig. 4, for Na and K double layers, a negative dispersion is observed at small q with a slope that is steeper than that of the clean alkali-metal surface plasmon. Since according to Fig. 1 the lowest overlayer-induced mode starts at ω_m and then disperses down towards the minimum of the surface plasmon of the clean alkali-metal, our results provide a clear physical explanation of this steeper slope. Moreover, near $q=0$ the observed loss peak shows a broad shoulder on the high-energy side [5]. This might well be caused by the double-layer mode near ω_p.

In these experiments the actual density within the Na and K overlayers was about 90% of the bulk density. For a comparison with the surface modes of the clean metals, the overlayer excitation frequencies should therefore be scaled upwards by about 5%, i.e., at $q=0$ they would appear at 3.0 eV for K and 4.0 eV for Na. If we take for ω_s the values measured at $q=0$ (2.73 eV for K and 4.0 eV for Na), the expected overlayer multipole mode in the $q=0$ limit would be at 3.1 eV for K and 4.5 eV for Na. Thus, the K data are consistent with the theoretical prediction, while the Na overlayer mode is 0.5 eV too low. This could be related to the much larger width of the Na loss peaks (1.6 eV as compared to 0.6 eV for K) and a correspondingly greater importance of the kinematic factor.

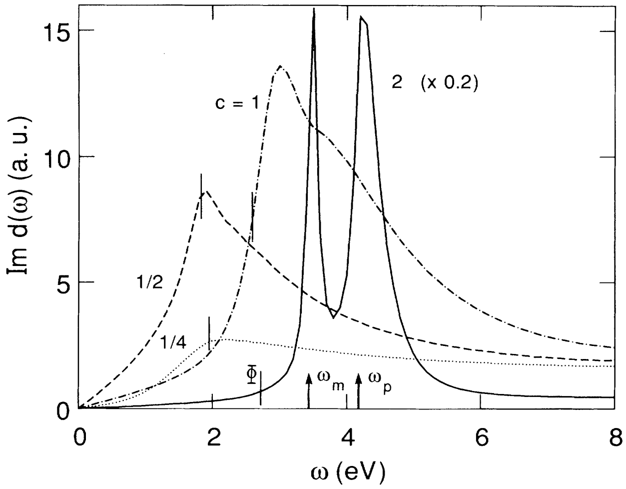

FIG. 3. $\mathrm{Im}d(\omega)$ for K on Al at various coverages. The vertical dashes denote the work functions.

According to Fig. 1 the overlayer mode for $c \leq 1$ shifts rapidly to lower ω. For Na on Al, such a shift is also seen experimentally [4]. On the other hand, near the work function minimum, the loss energy should be ap-

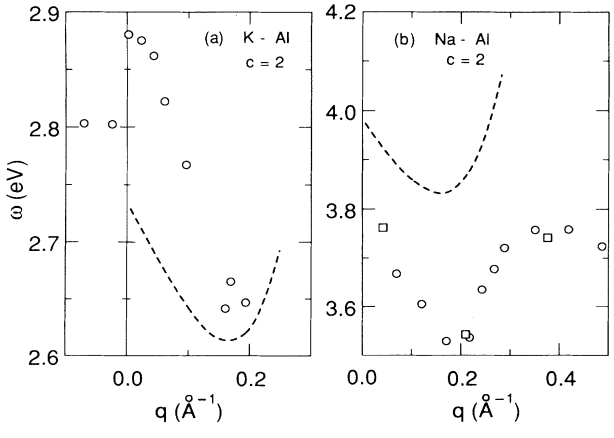

FIG. 4. Measured dispersion of electronic excitations for K and Na double layers on Al [open circles; the open squares in (b) are obtained for negative q; from Ref. [5]]. Dashed curves: measured dispersion of the ordinary surface plasmons for clean K and Na (from Ref. [11]).

proximately related to the coverage dependence of Φ. The comparison of EEL spectra and work function data for Na on Al [4,5] provides convincing evidence for the validity of this excitation mechanism. This correlation between loss energy and work function has been observed in several other experiments on adsorbed alkali-metal layers [1-3]. Of course, for $c < \frac{1}{4}$ the jellium model becomes inappropriate so that we cannot expect this correlation to hold at very low coverages. Realistic calculations for three-dimensional alkali-metal overlayers at low c are presently under way [18].

Although the electronic excitations discussed here were derived for alkali metals adsorbed on Al, they show a striking relation to the early loss measurements by Anderson and Jostell [2] for alkali adsorption on Ni. In the case of a Na double layer on Ni, the EEL spectra show a peak at 3.9 eV near $q = 0.1$ Å^{-1} which disperses upwards to 4.3 eV near $q = 0.5$ Å^{-1}. This dispersion agrees remarkably well with the results shown in Fig. 1, in particular, if we recall that the jellium model overestimates the Na plasma frequency by about 5% due to the neglect of core polarization, etc. Apparently, in this range of q, the nature of the substrate does not play any longer a crucial role. Unfortunately, the resolution in this experiment was not sufficiently high to detect the minimum in the dispersion curve.

In conclusion, a systematic understanding of the electronic excitations in adsorbed alkali-metal layers has been achieved. The variation of these modes with coverage is consistent with the expected limits both at small and large coverages, and with the dispersion of the collective surface modes at clean alkali metals. It is demonstrated how the classical picture is modified by the incorporation of microscopic effects. For adsorbed double layers, the excitation spectrum exhibits a hybridization gap, whereas, for $c < 1$, the overlayer excitations follow the coverage dependence of the work function. These theoretical results are consistent with electron-energy-loss measurements on adsorbed alkali-metal layers.

---

[1] For a review, see T. Aruga and Y. Murata, Prog. Surf. Sci. **31**, 61 (1989).

[2] S. Andersson and U. Jostell, Faraday Discuss. Chem. Soc. **60**, 255 (1975).

[3] S. A. Lindgren and L. Wallden, Phys. Rev. B **4**, 5967 (1980); J. Cousty, R. Riwan, and P. Soukiassian, J. Phys. (Paris) **46**, 1693 (1985); T. Aruga, H. Tochihara, and Y. Murata, Phys. Rev. B **34**, 8237 (1986).

[4] 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 (1989).

[5] K.-D. Tsuei, Ph.D. thesis, University of Pennsylvania, 1990 (unpublished); K.-D. Tsuei, D. Heskett, A. P. Baddorf, and E. W. Plummer, J. Vac. Sci. Technol. A **9**, 1761 (1991). See also J. A. Gaspar, A. G. Eguiluz, K.-D. Tsuei, and E. W. Plummer, preceding Letter, Phys. Rev. Lett. **67**, 2854 (1991).

[6] J. W. Gadzuk, Phys. Rev. B **1**, 1267 (1970).

[7] D. Newns, Phys. Lett. **39A**, 341 (1972); J. E. Inglesfield and E. Wikborg, J. Phys. F **5**, 1706 (1975); H. Ishida and M. Tsukada, Surf. Sci. **169**, 225 (1986); K. Kempa and W. L. Schaich, Solid State Commun. **61**, 357 (1987); R. Fuchs and W. Ekardt, J. Phys. Condens. Matter **1**, 4081 (1989).

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

[9] A. Liebsch, Phys. Rev. B **40**, 3421 (1989).

[10] A. Liebsch, G. Hincelin, and T. López-Ríos, Phys. Rev. B **41**, 10463 (1990).

[11] K.-D. Tsuei, E. W. Plummer, A. Liebsch, K. Kempa, and P. Bakshi, Phys. Rev. Lett. **64**, 44 (1990).

[12] K.-D. Tsuei, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **63**, 2256 (1989).

[13] P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).

[14] H. J. Levinson, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **43**, 952 (1979).

[15] N. D. Lang, Phys. Rev. B **4**, 4234 (1971).

[16] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).

[17] A. Liebsch, Phys. Rev. B **36**, 7378 (1987); K. Kempa and W. L. Schaich, Phys. Rev. B **37**, 6711 (1988).

[18] H. Ishida and A. Liebsch, Phys. Rev. B **42**, 5505 (1990); (to be published).

[19] Note that, at real ω, the "monopole" and "multipole" character is partially lost due to decay into electron-hole pairs.

[20] Such a behavior has been found in recent calculations by A. G. Eguiluz and J. A. Gaspar, in Lectures in Surface Physics, edited by M. Cardona and F. A. Ponce (Springer, Heidelberg, to be published).

[21] We ignore here the small correction due to $d_{\parallel} \ll a$.

[22] A. A. Lucas and M. Sunjic, Phys. Rev. Lett. **26**, 229 (1971).