

Correlation between electron loss and inverse photoemission measurements of alkali metals on metal surfaces

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(Received 14 March 1988)*

We have used the techniques of electron loss spectroscopy (ELS) and inverse photoemission spectroscopy (IPES) to study the adsorption of Na on Al(111) as a function of coverage. We find a strong correlation between the energy of the primary loss feature in ELS and the unoccupied Na $3p$ level in IPES. This correlation allows us to interpret the ELS peak as an electronic transition for an Na coverage of less than one monolayer. For coverages greater than one Na layer, we observe an attenuation of the unoccupied $3p$ level and a conversion of the ELS feature into an electronic excitation (a surface or interfacial plasmon mode).

The electronic properties of alkali metals and alkali-metal overlayers have been studied both experimentally and theoretically for many years.¹⁻¹² In some of the early measurements of alkali-metal overlayer systems, Andersson and Jostell^{2,5} observed loss peaks in the 2-4-eV energy range for Na, K, and Rb adsorbed on Ni(100). These features all exhibited a similar coverage-dependent behavior: an initial decrease in energy as a function of increasing coverage, a minimum at intermediate coverage, and then an increase to saturation at the corresponding alkali-metal surface plasmon energy at the completion of the first one or two alkali-metal layers. This qualitative behavior of alkali-metal-induced electron-loss spectroscopy (ELS) features has since been observed for a number of other systems, including Na, Cs/Cu(111) (Ref. 1), K/Cu(100) (Ref. 6), Cs/Al(111) (Refs. 7 and 8), Na/Ru(001) (Ref. 9), and Cs/W(100), Mo(100).¹⁰ Explanations for these loss features include collective plasmon modes,^{1,11,12} s - p transitions within the alkali-metal layer,^{2,6,7,9} and excitations involving substrate electrons.^{6,10,11} In the present study, we will present ELS measurements of Na/Al(111) which show a strong correlation with corresponding inverse photoemission measurements of the same system. The combination of these two techniques allows us to more critically evaluate these models and suggest an alternative explanation.

The electron-loss measurements presented here were

performed using a Leybold-Heraeus ELS-22 spectrometer with an incident electron energy of 30 eV and a resolution of ~ 50 meV. The angle of incidence was 60° and most spectra were recorded in the specular geometry. The inverse photoemission measurements were carried out in a separate system. Emitted photons at 9.5 eV were detected by a Geiger-Müller tube equipped with an SrF₂ window and yielding an overall energy resolution of ~ 0.4 eV. The movable electron gun, which has an angular resolution of $\sim \pm 3^\circ$, was fixed at normal incidence to the crystal for the measurements reported here. The Al(111) crystal was cleaned routinely by sputtering and annealing. Cleanliness was checked by Auger and inverse photoemission spectroscopy (IPES) or high-resolution electron energy-loss spectroscopy. The Na was evaporated from a commercial SAES getter source onto the crystal at room temperature. The Na coverages were determined by evaporation times and calibrated to thermal desorption, low-energy electron-diffraction (LEED), and work-function measurements.

In Fig. 1 are displayed spectra from our ELS measurements of Na/Al(111) as a function of Na coverage. When sodium is evaporated onto the Al surface, a loss feature at 2.5-3.0 eV is observed at a coverage of 0.07, as shown in Fig. 1. (For low Na coverages, two possible loss peak positions are indicated on the spectra in Fig. 1 and the plot of the data in Fig. 2 due to an ambiguity in the

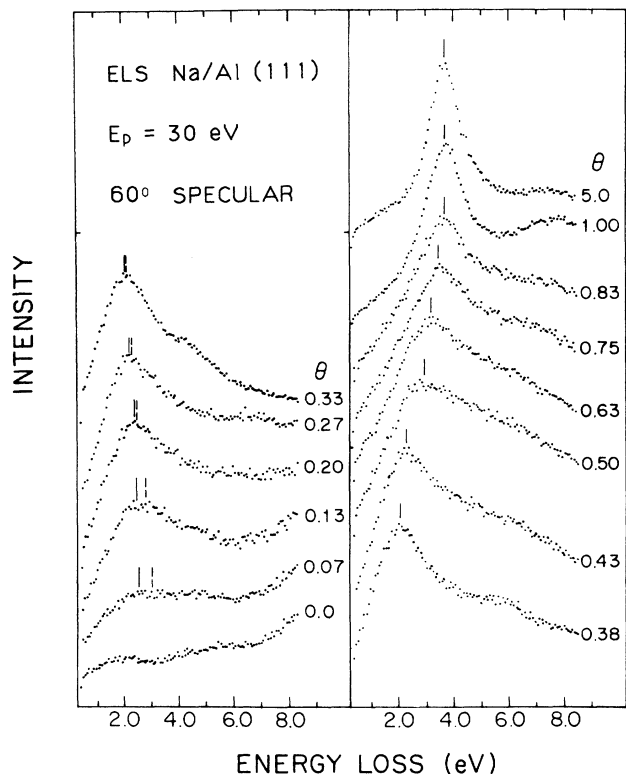


FIG. 1. Electron-loss spectroscopy measurements of Na/Al(111) as a function of Na coverage. Tic marks indicate the ELS features discussed in the text and plotted in Fig. 2.

choice of backgrounds for low coverages.) As the coverage is increased, this loss increases in intensity and decreases in energy, reaching a minimum of ~ 2.0 eV at a coverage of $\frac{1}{3}$, where a well-ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ is observed; then it increases sharply to 3.1 eV at a coverage of $\frac{1}{2}$, which corresponds to the completion of the first Na layer [(2x2) ordered overlayer]. In the second Na layer, this peak shifts to 3.6 eV, continues to increase in intensity, and, at the completion of the second layer, reaches a value of ~ 3.8 eV, which is equal to the energy of the surface plasmon of sodium.¹ These results are plotted in Fig. 2 and are discussed in more detail in another publication.¹³

Analogous coverage-dependent measurements of Na/Al(111) by inverse photoemission are presented in Fig. 3 and plotted in Fig. 2 on a shifted scale. For the clean Al(111) surface, a peak in IPES is observed at ~ 3.7 eV above E_F . As discussed elsewhere,¹⁴ we assign this to an image-induced surface resonance of the clean surface. The addition of small amounts of Na causes a rapid quenching of this resonance along with the appearance of several Na-induced features. At low Na coverage, a peak is observed at 2.1 eV above E_F , as shown in Fig. 3 and plotted in Fig. 2. As the Na coverage is increased, this peak decreases in energy, reaching a minimum at an energy of 1.1 eV at a coverage of $\frac{1}{3}$. The addition of more Na causes this peak to increase in intensity and energy to 1.8 eV at the completion of the first Na layer ($\theta = \frac{1}{2}$). Since this is the lowest unoccupied Na level, we

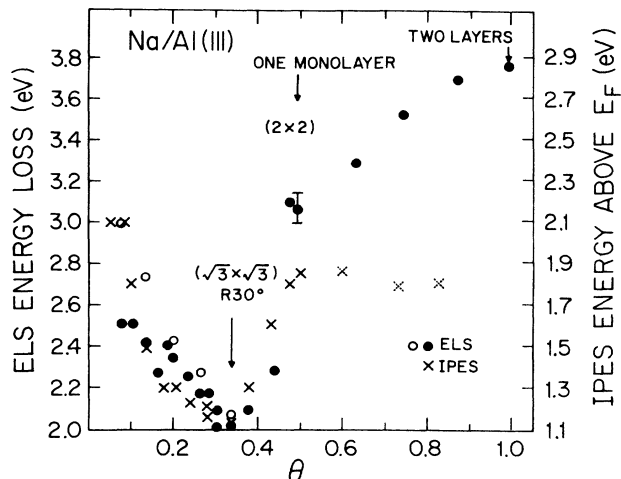


FIG. 2. Correlation of ELS (\times) and IPES (\circ, \bullet) measurements of Na/Al(111) as a function of Na coverage. Note shifted scale by 0.9 eV between the two spectroscopies.

assign this peak to the Na 3p level. This assignment is supported by dispersion measurements of this system reported elsewhere.¹⁵ When the Na coverage is further increased, corresponding to the growth of the second layer, the energetic position of the 3p level remains fixed while

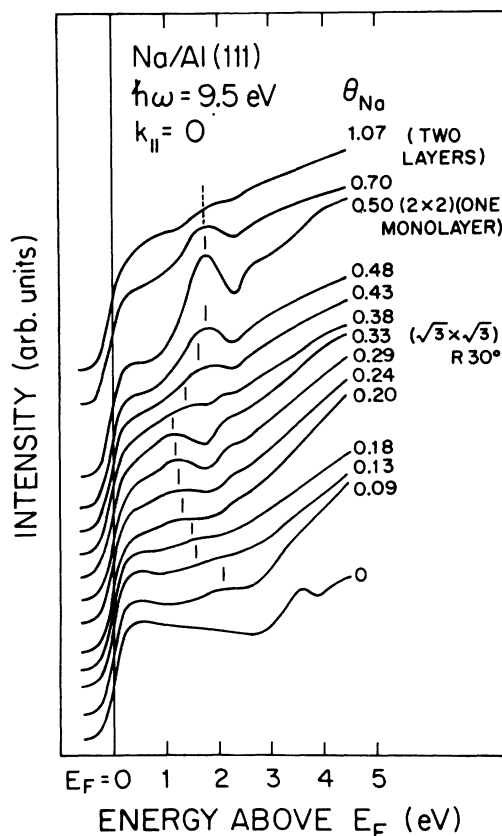


FIG. 3. Inverse photoemission spectroscopy measurements of Na/Al(111) as a function of Na coverage. Tic marks indicate the positions of the Na 3p level as discussed in the text and plotted in Fig. 2.

its intensity decreases. By the completion of the second layer, this peak has been completely attenuated, even though the (2×2) LEED pattern from the first Na layer ($\theta = \frac{1}{2}$) is still observed at a somewhat weaker intensity, probably due to a greater surface sensitivity of the IPES measurements compared to LEED.

The behavior of the ELS peak of Na/Al(111) as a function of coverage shown in Figs. 1 and 2 is characteristic of most alkali-metal overlayer systems studied so far.^{1,2,5-10} The similarity between the present and previous results demonstrates that the origin of these loss feature and their coverage dependence are substrate and alkali independent and, in addition, since aluminum has no d bands, that substrate d bands do not play a significant role. The coverage dependence of the loss feature in ELS correlates quite well with the energy of the Na $3p$ level for coverages less than one Na layer ($\theta = \frac{1}{2}$). The breakdown in the correlation at this coverage coupled with the discontinuous jump in loss energy at $\theta = \frac{1}{2}$ (see Fig. 2), the anomalous broadening in the width of the loss exactly at this coverage¹³ (see the corresponding spectrum in Fig. 1), and finally the qualitative differences in ELS dispersion for submonolayer versus higher coverage¹³ all indicate a transition in the nature of the loss feature at the completion of the first Na layer. In other words, our results suggest that the correct explanation for the Na-induced loss feature in ELS involves *not one mechanism but two, depending on the coverage.*

What are these two different mechanisms? The similarity of the coverage dependence of the Na ELS peak to the position of the unoccupied Na $3p$ level (Fig. 2) suggests that for submonolayer coverages the loss peak is due to an *electronic transition* from a coverage-independent initial state in the Na/Al(111) system into the previously unoccupied Na $3p$ level. For higher coverages, the fact that the energy of the Na loss feature saturates after approximately two layers at the value of the Na surface plasmon, the distinct differences in dispersion measurements of this peak at high versus low coverage,¹³ and a comparison to theoretical calculations¹⁶ suggests that the ELS peak is dominated by a *collective excitation*, i.e., a surface or interfacial Na/Al(111) plasmon, for coverages greater than one Na overlayer.

Turning back to the ELS peak in the submonolayer coverage regime, assuming this is due to an electronic transition into the Na $3p$ level, then we still must identify the initial state, which must be *coverage independent*. The degree of ionicity and type of bonding between adsorbed alkali atoms and metal surfaces is still a matter of substantial debate;^{2-4,10} however, no theory predicts a lack of shift in the energetic position of the alkali valence s level (the $3s$ in the case of Na) as a function of coverage. The measured shift in the energy of the unoccupied Na $3p$ level versus coverage by ~ 1 eV [similar changes have also been reported for the corresponding unoccupied p levels of K,Cs/Al(111) (Ref. 17) and K/Ag(110) (Ref. 18)] supports the idea that the s -level position must also vary significantly in energy with coverage. If this is the case, our results show that the ELS loss cannot be, strictly

speaking, an Na $3s$ - $3p$ transition, since we require a coverage-independent initial state to account for the correlation we have observed between our ELS and IPES measurements, as displayed in Fig. 2.

Since our ELS results of Na/Al(111) are qualitatively similar to analogous measurements of most other systems, this initial state for electronic excitations must be both alkali-metal and substrate independent. We propose that this loss originates from electrons at the Fermi level of the overlayer system. This will involve charge mainly from the Na $3s$ level (in our case) but also some contribution perhaps from the substrate as well. We further suggest that the 0.9 eV shift necessary to bring the ELS and IPES data into quantitative agreement (note the shifted scales in Fig. 2) is due to differences in screening in the two processes. [Preliminary ELS and IPES measurements of Cs/Al(111) as a function of coverage indicate a similar energetic shift of ~ 0.8 eV.¹⁷] In particular, in inverse photoemission, an extra electron is added to the system, creating a negative-ion final state. In electron loss, the final state is neutral, but involves the excitation of an electron from its ground state to an excited state. We believe that these two final states will couple differently to the screening excitations in the Na/Al(111) system, resulting in an apparent relative shift in the energies of the measured levels. We await theoretical calculations in order to more fully understand this screening process.

In summary, the correlation of electron loss and inverse photoemission measurements of Na/Al(111) as a function of coverage allow us to more critically evaluate previous models for ELS measurements of alkali overlayers. We propose as an alternative picture that the loss peaks originate from two distinct mechanisms, depending on the alkali coverage. For submonolayer coverages, the ELS peak is due to electronic excitations from the Fermi level (primarily Na $3s$ electrons) into the previously unoccupied Na $3p$ level, which is detected by IPES. We assign the 0.9 eV shift between our ELS and IPES measurements to screening effects associated with the different measurement techniques. For Na coverages greater than one layer, the nature of the loss peak changes to the collective electronic excitation of a surface or interfacial plasmon mode. We see evidence for a rather abrupt transition between these two mechanisms at the completion of the first Na layer; however, a more precise description of these results should involve a determination of the *relative* importance of the two excitation mechanisms in the different coverage regimes. We hope future experimental and theoretical work will clarify this and other issues addressed in this paper.

We would like to acknowledge useful discussions with Professor R. P. Messmer, Professor E. Mele, Professor A. Eguluz, and Dr. M. Hybertsen. This work has been partially supported by the Bundesministerium für Forschung und Technologie (BMFT) under Contract No. 05363FAB, and by the National Science Foundation under Grant No. DMR-8610491.

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- ¹S. A. Lindgren and L. Wallden, *Phys. Rev. B* **22**, 5967 (1980).
- ²S. Andersson and U. Jostell, *Surf. Sci.* **46**, 625 (1974); *Faraday Disc. Chem. Soc.* **60**, 255 (1970).
- ³J. P. Muscat and D. M. Newns, *Surf. Sci.* **84**, 262 (1979).
- ⁴N. D. Lang, *Phys. Rev. B* **4**, 4234 (1971).
- ⁵U. Jostell, *Surf. Sci.* **82**, 333 (1979).
- ⁶T. Aruga, H. Tochiara, and Y. Murata, *Phys. Rev. B* **34**, 8237 (1986).
- ⁷A. Hohlfeld, M. Sunjic, and K. Horn, *J. Vac. Sci. Technol. A* **5**, 679 (1987).
- ⁸A. Hohlfeld, Ph.D. thesis, Freie Universitat, Berlin, 1986 (unpublished).
- ⁹L. Surnev, G. Rangelov, E. Bertel, and F. P. Netzer (unpublished).
- ¹⁰P. Soukiassian, R. Riwan, J. Lecante, E. Wimmer, S. R. Chubb, and A. J. Freeman, *Phys. Rev. B* **31**, 4911 (1985).
- ¹¹A. Eguluz and D. A. Campbell, *Phys. Rev. B* **31**, 7572 (1985).
- ¹²H. Ishida and M. Tsukada, *Surf. Sci.* **169**, 225 (1986).
- ¹³K.-D. Tsuei, A. P. Baddorf, D. Heskett, and E. W. Plummer (unpublished).
- ¹⁴K. H. Frank (unpublished).
- ¹⁵D. Heskett, K.-H. Frank, E. E. Koch, and H.-J. Freund, *Phys. Rev. B* **36**, 1276 (1987).
- ¹⁶Gaspar and Eguluz (unpublished).
- ¹⁷K.-H. Frank, A. Hohlfeld, K. Horn, E. E. Koch, D. Heskett, and H.-J. Freund (unpublished).
- ¹⁸W. Jacob, E. Bertel, and V. Dose, *Phys. Rev. B* **35**, 5910 (1987).