Observation of a discontinous nonmetal-to-metal disorder-to-order transition in an alkali overlayer

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We report measurements of the coverage-dependent electronic and structural properties of submono-layer Li films, grown on Be(0001). We observe a structural phase transition from a disordered state at low coverages to an ordered hexagonally close-packed structure at high coverages. This structural transition is accompanied by a nonmetal-to-metal transition in the overlayer. The Li overlayer structure was determined using low-energy electron diffraction, while angle-resolved photoemission, inverse photoemission, and core-level spectroscopy were employed to characterize the electronic transformation. For the disordered, low-coverage phase the spectroscopies show only one Li-induced electronic state. This level is centered 3.1 eV above E_F and is completely unoccupied at the lowest coverages studied. At the completion of the first Li adlayer, the overlayer band is metallic.

While there is controversy regarding how to describe the bonding of an alkali atom to a metallic substrate at low coverages, the different theories agree well in their predictions for the energies, and coverage dependence, of the electronic states.[1-3] We refer to these predictions for the coverage-dependent electronic states as the "conventional picture." In the conventional picture of alkali adsorption on metal surfaces the *s* valence level of an isolated alkali atom lies above the Fermi level and is broadened through interactions with the electronic states of the substrate.[1-3] The tail of the *s* resonance extends below the Fermi level and is partially occupied. The alkali adatom and its induced image charge result in a dipole that lowers the work function. At low coverages, the overlayer structure is determined by the repulsive dipole-dipole interactions of the adatoms. In the original formulation of this model, with increasing coverage, these dipole-dipole interactions continuously shift the *s* resonance to lower energies thereby increasing its occupation.[1] At the completion of the first atomic layer, the overlayer is neutral. This picture has been very successful in describing the dramatic, coverage-dependent, work-function change induced by alkali-metal adsorbates.

Recently, there have been several reports in the literature questioning the validity of the conventional picture. In particular, there are studies that indicate that the energy of the alkali *s* resonance may not be a continuous function of the coverage. In 1986, using low-energy electron diffraction (LEED), Aruga, Tochihara, and Murata observed a structural transition for K on Cu(001) from a disordered phase at low coverages to an ordered, condensed phase at higher coverages.[4] It was speculated that this condensation was probably "closely connected with the ionic-to-neutral change in the adsorbates." Such a

condensation transition is supported by a recent density-functional calculation that shows that for alkali metals adsorbed on Al(111), the adatoms may undergo both a site change and a condensation into islands with increasing coverage.[5] For K/Al(111), Horn et al. using angle-resolved photoemission observed the onset of an occupied K-induced feature at a coverage corresponding to the minimum in the work function.[6] They suggested that the coverage dependence of this feature was "indicative of a transition from strongly ionic to metallic bonding," but concluded that the K *s* resonance was partially occupied at low coverages. Based on their photoemission measurements for K/Ag(001), Nielsen et al. reported that the K *s* resonance was completely unoccupied at low coverages and that the "ionic-to-neutral transition is abrupt."[7] An abrupt transition in the electronic properties of an alkali overlayer found support in the electron-energy-loss measurement of K and Cs adsorption on Ag(001), which showed a "striking coverage dependence" of the loss function.[8] While these and other data indicate that there may be problems with the traditional picture, it is still widely accepted.

This paper reports on the measurement of the structure, electronic states, and the excitation spectra of the Li/Be(0001) system. Using LEED, we observe a condensation transition in the Li overlayer from a low-coverage, disordered phase, to a densely packed hexagonal phase. The combination of a variety of techniques enables us to follow the electronic properties through the condensation transition. We find that the Li *s* resonance is completely unoccupied in the disordered phase. At the completion of the first Li layer, the overlayer band is partially occupied and is observed to disperse across the Fermi level.[9] Furthermore, the transition to a metallic overlayer is

strongly discontinuous. This nonmetal-to-metal transition in the overlayer coincides with the condensation transition. We believe that these electronic and structural changes are manifestations of the same phase transformation and propose that the attractive alkali-alkali interaction in the metallic regime is responsible for stabilizing the condensed phase. Some of the data have appeared previously. In particular, the effect of the vacuum potential on the inverse-photoemission spectra appears in Ref. 10, while a complete description of the core-level spectra may be found in Ref. 11.

Two separate UHV chambers were used in this study.[12] The Li coverage was determined by the evaporation time, calibrated by work-function measurements and by the observation of $(\sqrt{3} \times \sqrt{3})R\,30°$ LEED spots. The coverage corresponding to the completion of the first Li adlayer, defined as 1 ML, has a density of 0.48 Li atoms per Be surface atom. At low coverages, we observe no Li features in LEED, indicating that the Li is disordered. The first observable Li-induced LEED structure is the $(\sqrt{3} \times \sqrt{3})R\,30°$ structure. Weak $(\sqrt{3} \times \sqrt{3})R\,30°$ LEED spots are initially observed at 0.42 ML. This is considerably lower than the coverage corresponding to a complete $(\sqrt{3} \times \sqrt{3})R\,30°$ structure, 0.69 ML, and indicates that island formation is taking place. At coverages greater than 0.69 ML, the LEED pattern is consistent with a hexagonal Li overlayer that is compressed relative to the $(\sqrt{3} \times \sqrt{3})R\,30°$ overlayer.

Unlike most other metals, bulk Be has a low density of states near the Fermi level. It is an ideal substrate for measuring small, alkali-induced changes near E_F. In Fig. 1, we show photoemission and inverse-photoemission spectra for clean Be(0001) and for low coverages of Li on Be(0001). The peak at 2.8 eV below E_F in the clean photoemission spectrum is the Be surface state.[13] It shifts to lower energies as the Li coverage increases and is observed 4.0 eV below E_F at the completion of the first Li adlayer.[9] The peak at ~ 11 eV below E_F is a bulk Be band.[14] In the inverse-photoemission spectra shown in Fig. 1(b), it is obvious that the only Li-induced structure lies 3.1 eV above E_F and has a full width at half maximum of ~ 1.5 eV.[10] This feature is completely unoccupied, it has no weight at the Fermi level, and disperses to higher energies with increasing wave vector parallel to the surface. For a single Li atom adsorbed on $r_s = 2$ jellium, Lang and Williams calculated the Li s resonance to be centered 1.6 eV above E_F with a width of 2–2.5 eV.[2] *The data shown here do not support the conventional picture of alkali adsorption at low coverages.*

The coverage dependence of this Li-induced feature is shown in Figs. 2(a) and 2(c). Below 0.40 ML, the Li-induced peak is observed to shift toward the Fermi level with increasing coverage. In the extrapolated single-atom limit, this feature lies 3.4 eV above E_F. At 0.40 ML, the Li-induced peak is centered 0.6 eV above E_F and has a full width of 0.5 eV. It is located well above the Fermi level and is still completely unoccupied. As the coverage increases further, this peak does not continue to shift towards the Fermi level, but instead broadens slightly and loses intensity. In this same coverage range, a Li-induced peak first becomes observable in the photoemis-

sion. At the coverage corresponding to the sharpest $(\sqrt{3} \times \sqrt{3})R\,30°$ LEED spots, the Li-induced peak is no longer visible in inverse photoemission at $k_{\parallel} = 0$.

Our data show that the peak observed in inverse photoemission does not cross the Fermi level in a continuous manner with coverage. It is observed either well above or below E_F, and is never observed at the Fermi level. The transformation from an unoccupied state or nonmetallic band, to a partially occupied or metallic band is strongly discontinuous. The assignment of the electronic transition as first order is further supported by the observation of coexistence of the two phases for coverages near the transition.

The LEED data show that Li forms two structural phases on the Be(0001) surface: a low-coverage disordered phase, and a high-coverage hexagonal phase. In our data, the weak $(\sqrt{3} \times \sqrt{3})R\,30°$ LEED spots are observed at a coverage below that expected for a $(\sqrt{3} \times \sqrt{3})R\,30°$ overlayer, indicating that there is island formation and again coexistence of two phases over a coverage range from 0.42 to 0.69 ML. This is almost exactly the same range that coexistence is observed between the unoccupied and the occupied valence structure. It is natural to associate the unoccupied Li-induced peak with the low-coverage disordered phase and the occupied feature with the condensed phase. *The electronic and*
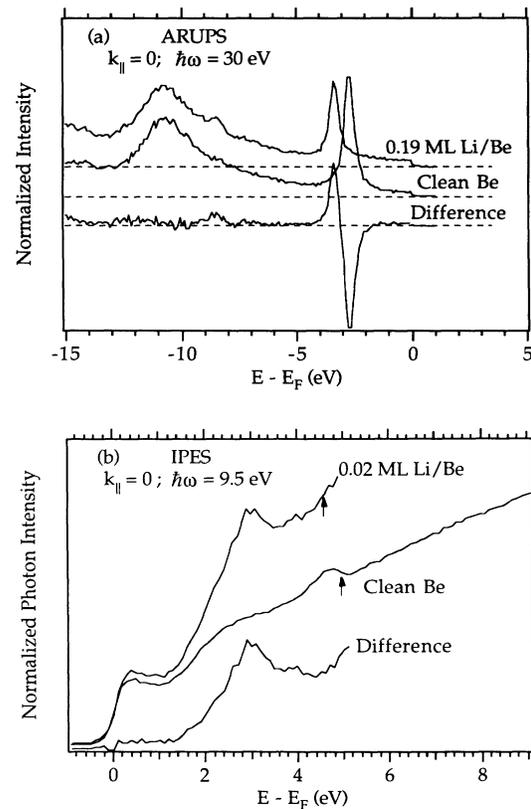
FIG. 1. Normalized photoemission (a) and inverse-photoemission (b) spectra for clean and Li-covered Be(0001). In (b), the arrows indicate the position of the vacuum level. The slight increase in emission evident in the difference spectra is understood as due to reduced momentum conservation in the presence of the disordered overlayer.
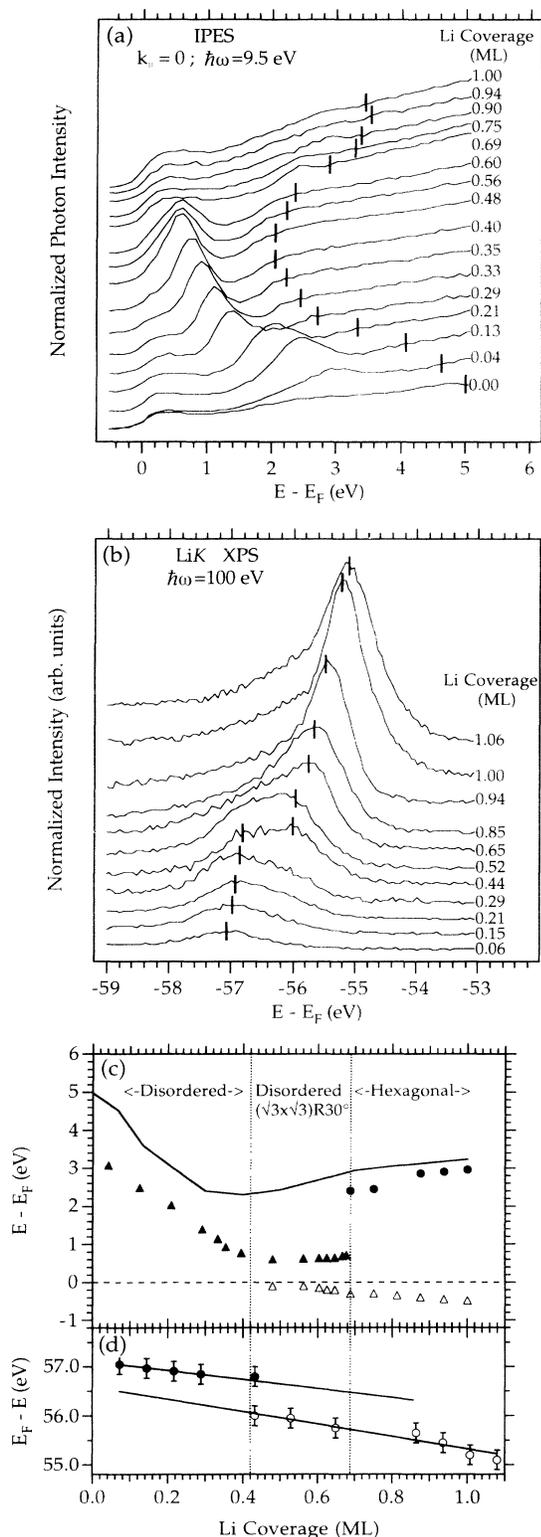
FIG. 2. (a) Normalized inverse-photoemission spectra for various coverages of Li on Be(0001). (b) Li 1s core-level spectra for various Li coverages on Be(0001). (c) Peak positions from inverse-photoemission and photoemission spectra as a function of coverage (symbols) and measured work function (solid line). The observed LEED patterns are indicated. (d) Measured 1s binding energy as a function of coverage. Lines are linear fits in each phase.

structural transitions are manifestations of the same phase transformation. We refer to the low-coverage phase as the dispersed phase, and the ordered, high-coverage phase as the condensed or metallic phase.

This phase transformation is also observed in the Li 1s core-level spectra shown in Fig. 2(b). In Fig. 2(d), the Li 1s core-level binding energy is shown as a function of Li coverage. The dispersed and condensed phases can be clearly differentiated, and the transition between the two occurs in the expected coverage range. For the coverage range in which coexistence is observed in the valence structure, it is difficult to uniquely fit two peaks to the core-level spectra. However, for these coverages, there are well-pronounced shoulders in the core-level spectra indicative of coexistence.[11] This transition in the core-level binding energy is in the direction one would expect for a transition to a metallic overlayer state.

Based on a tight-binding calculation, Ishida and Palmer have suggested that the structural phase transition observed for K on graphite may be related to the semimetallic nature of the substrate.[15] Beryllium is far from a free-electron metal, since the density of states at the Fermi energy is only 0.054 states/eV atom, compared to the free-electron value of 0.21. On the other hand, the nearly-free-electron surface states on the Be(0001) increase the surface density of states at E_F to 0.23, very close to the free-electron value.[16] More importantly, the picture presented here is consistent with previous results for alkali adsorption on metal substrates. At low coverages, alkali-induced features are typically observed 2.5–3.5 eV above E_F.[7,17–19] In addition, the data of Frank, Sagner, and Heskett for K on Al(111) show that the unoccupied K-induced feature loses intensity at the same coverage that the K-induced feature appears below the Fermi level.[17] Nielsen *et al.* have used photoemission to show that the filling of the K overlayer band on Ag(100) is abrupt rather than gradual.[7] Furthermore, electron-energy-loss spectroscopy measurements have indicated a discontinuous change in the electronic structure of K and Cs overlayers on Ag(100).[8,20]

While the electronic transformation is associated with a structural transition from a disordered to an ordered state, it is not an Anderson transition: the overlayer state in the disordered low-coverage phase is not partially occupied. Rather, there is a redistribution of charge from states that are predominantly substrate derived in the dispersed phase to a partial occupation of the overlayer band in the condensed phase. The fact that the electronic and structural properties are intimately related is obvious. However, until recently, coverage-dependent calculations of the electronic properties of alkali overlayers on metals have not allowed for structural changes.[21] Furthermore, our work shows that experimental measurements of the electronic properties of alkali overlayers must include a careful characterization of the atomic structure.

At present, our understanding of the electronic properties of alkali overlayers on metal substrates is rooted in the Gurney model of a partially occupied atomic s resonance.[1] In contrast, it has been pointed out that many alkali-induced features could be explained in terms of the

phase-analysis model of image states.[22] While the model of Lindgren and Walldén only applies for coverages greater than that corresponding to the work-function minimum, it is natural to ask if the Li features discussed here are just the image states of the clean substrate, shifted in energy by the changing work function. In Fig. 1(b), a feature can be seen for the clean Be surface at ~ 0.4 eV below the vacuum level. We ascribe this feature to the image potential.[10] The coverage dependence of the Li feature shown in Figs. 2(a) and 2(c) extrapolates to an energy of 1.6 eV below the vacuum level at zero coverage. This implies that the state is Li induced and is not simply a shifted image-potential feature. In their inverse-photoemission spectroscopy data for Na on Ni(111), Tang and Heskett found that they could observe the development of a Na-induced peak at ~ 3.75 eV above the Fermi level while the image state was being quenched.[18] These data indicate that the presence of the alkali core potential is necessary to produce these states.

These features do not fit into the conventional picture of an alkali s resonance either. In particular, the energy of these features is consistently higher than those predicted by local-density approximation (LDA) calculations for an alkali s resonance at low coverages.[2,3] One possibility considered by others is that these features are alkali p resonances.[17,18] Our data disagree with this assignment in both the coverage dependence and the dispersion.[3] These discrepancies suggest that LDA calculations may not be able to describe the electronic structure of alkali adsorption at low coverages. Since LDA calculations do not reproduce the image potential at a surface a possible improvement may come from a proper treatment of exchange and correlation at the surface.[23]

In this paper, we present a complete experimental study of the structural and electronic properties of an alkali-metal adsorbate on a metallic substrate, including measurements of the atomic structure, the occupied and unoccupied alkali-induced states, and the core-excitation spectra. For low coverages of Li on Be(0001), we have shown that the dominant Li-induced feature is observed 3.1 eV above the Fermi level and is completely unoccupied. This appears to be a general property of alkali adsorption on metal substrates. At the completion of the first Li adlayer, the Li overlayer band is metallic, as expected. However, we show that the development of the metallic state is strongly discontinuous. This phase transformation involves a change in the electronic structure as well as a structural change from a disordered phase at low coverages to an ordered, condensed phase at high coverages and highlights the importance of the atomic structure on the electronic properties of alkali overlayers.

Since the submission of this work, we have become aware of a recent study of Na adsorption on Cu(111) that shows results remarkably similar to ours.[24]

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