

Two-Dimensional Band Structure of a Li Layer: Li/Be(0001)

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Angle-resolved photoemission and inverse photoemission have been used to measure the two-dimensional dispersion of the energy bands of a single dense layer of Li grown on Be(0001). These two techniques show excellent agreement for both the Fermi-level crossing and the effective mass of the Li valence band. This band is parabolic, with an effective mass (m^*/m) of 1.8, which is larger than that predicted for an isolated atomic layer. The large effective mass may be due to hybridization with the substrate bands. An avoided band crossing of the Li band and the Be surface state is observed.

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Thin films have proven to be very interesting, because their physical properties can be radically different from their thick film (or bulk) counterparts, and because these properties develop with film thickness. For example, the following behavior has been observed for metallic monolayers: anomalous magnetic properties,^{1,2} structure and lattice spacings different from the bulk,^{1,3} and two-dimensional electronic states.¹ The electronic response of thin metal films is reported to be governed by single-particle rather than collective excitations (i.e., plasmons).⁴ In contrast, the many-body corrections to the single-particle bands should be larger in two dimensions than in three.⁵ The area in which there has been considerable theoretical effort is that of the simple alkali metals grown on different substrates.⁶⁻⁸ While there is still a controversy over the nature of the bonding of alkali metals on simple metal substrates in the low coverage regime,⁶ for a single dense layer the theoretical picture is clear: The alkali s band is metallic and has an effective mass close to 1.

In contrast to the theoretical work on alkali overlayers, there have been relatively few experimental results published on the dispersion of the two-dimensional bands for alkali overlayers. A recent Letter has shown that the K $4s$ band could be seen⁹ on Al(111) in a region of k space in which there should be strong mixing with the substrate bulk bands. The data showed several interesting, but not explained, features. First, the effective mass of the authors fit to the K-induced structure is approximately 4, compared to the theoretical prediction of 0.9 for both an isolated K film¹⁰ and for K on Al.⁷ In addition, there is no clear sign of a Fermi-level crossing in the published results. In a related paper, Heskett *et al.*⁴ compared electron-energy-loss spectra (EELS) to measured energy levels for Na on Al(111). For Na coverages less than a close-packed monolayer, they attributed a loss seen in the EELS spectra to a transition from the Fermi level to the unoccupied Na $3p$ level. Surprisingly,

the loss energy was 0.9 eV larger than what was deduced from inverse-photoemission spectroscopy (IPES). This discrepancy is in the wrong direction to be explained by standard screening arguments. *These studies indicate that for alkali overlayer films there are fundamental questions which need to be addressed, concerning both the basic physics of overlayer electronic bands and the applicability of the single-particle picture for the different spectroscopies used.*¹¹

While the low cross section for s bands has been used to explain the lack of photoemission data for the valence bands of alkali overlayers, the emission of bulk features from the substrate can also obscure the alkali valence structure. As noted by Horn *et al.*,⁹ measurements of alkali-induced features are difficult even on substrates with a small cross section for emission such as Al. This is due to bulk band transitions in the same energy range as the alkali state as well as possible mixing with the bulk bands. The importance of using a substrate where the alkali levels are in a bulk band gap is illustrated by the data of Lindgren and Walldén, in which the first clear observations of alkali-induced levels were reported, for Na and Cs on Cu(111).¹² The alkali levels appeared in the bulk band gap responsible for the neck of the Cu Fermi surface. We chose to examine Li on Be(0001) using angle-resolved ultraviolet photoemission spectroscopy (ARUPS) to measure the occupied electronic bands and IPES to measure the unoccupied bands. Be(0001) was picked for the substrate since it is a simple metal (i.e., no d electrons), and has a large projected bulk band gap extending 4.25 eV below the Fermi level at $\bar{\Gamma}$.^{13,14} Since the best estimate of the occupied bandwidth of bulk Li is 3.45 eV for the ground state and 2.84 eV for the quasi-particle bandwidth,¹⁵ the Li valence band should lie entirely in the Be bulk band gap.

The experiments were performed in standard UHV vacuum chambers with base pressures of 1.5×10^{-10} Torr. Photoelectrons were analyzed with a hemispheri-

cal analyzer with an acceptance angle of $\pm 2^\circ$.¹⁶ The total energy resolution of the system was better than 250 meV. The IPES measurements were carried out in the isochromat mode with a photon energy of 9.5 eV. The electron gun was mounted on a two-axis goniometer and had an angular resolution of $\pm 3^\circ$.⁴ The total energy resolution of the IPES system was 350 meV.⁴ Sample preparation will be described elsewhere.¹⁷

Saturation coverage of the first layer of Li was determined by LEED and corresponds to a density of 1.0×10^{15} Li atoms/cm² as determined from the Li $\bar{\Gamma}$ - \bar{M} - $\bar{\Gamma}$ ' distance observed in ARUPS assuming a single Li atom per unit cell. This is slightly less than the 1.3×10^{15} atoms/cm² one might expect using the nearest-neighbor separation of bulk Li to form a hexagonal layer. LEED showed a twelfold pattern suggesting that the Li overlayer forms two hexagonal domains, one aligned to the substrate and one rotated by 30° . A complete description of the ARUPS and IPES as a function of Li coverage will be presented elsewhere.¹⁷ The results presented here are for a saturated layer of Li on Be(0001).

Figure 1 shows the projection of the theoretical Be bulk bands¹⁴ (shaded) onto the hexagonal surface Brillouin zone (SBZ) of Be(0001). In this figure, $\bar{\Gamma}$ is the center on the SBZ and \bar{M} is the center of one edge. Note the large bulk band gap mentioned above. The Li Λ_1 band created by one layer of Li is shown by the triangles and, except for a small region of the unoccupied band, lies entirely in the Be band gap. It has both s and

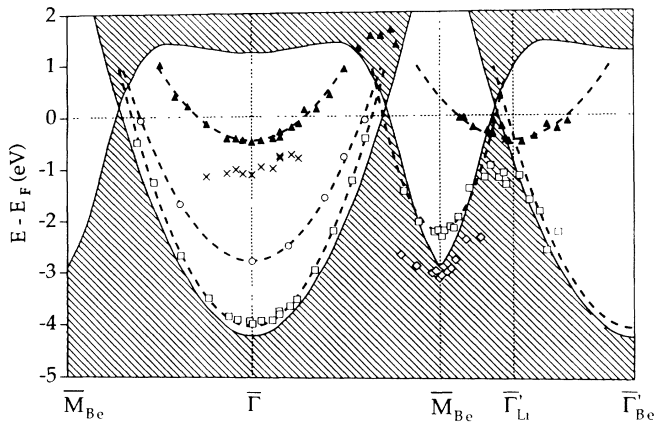


FIG. 1. Two-dimensional dispersion for both clean Be(0001) and a saturated monolayer of Li on Be(0001). The measured dispersion of the clean Be SS (surface state) is shown by the circles while the squares (triangles) show the measured dispersion of the Be SS (Li band) for the Li-covered surface. Dashed lines are fits to the data in the first Brillouin zones. Dashed lines in the second Brillouin zones represent fits in the first Brillouin zones shifted by the appropriate reciprocal-lattice vector. The $\bar{\Gamma}$ - \bar{M} distance for Be is 1.58 \AA^{-1} . The photon energy was 40 eV for the ARUPS and 9.5 eV for the IPES measurements.

p_z symmetry in the overlayer. The admixture of p_z is due to the difference between the vacuum and substrate potentials. At $\bar{\Gamma}$ the Li band has an initial-state energy of -0.47 eV and a width, after deconvolution of the experimental resolution, of 120 meV. The Li band disperses parabolically upwards towards the Fermi energy with increasing k_{\parallel} . This band is observed to cross the Fermi energy at 0.47 \AA^{-1} in both photoemission and inverse photoemission. Both ARUPS and IPES show the same value of the Fermi-level crossing and the same effective mass for this two-dimensional band. *These data indicate that the many-body effects in photoemission and inverse photoemission are similar for these two-dimensional systems.* Yet the effective mass, 1.8, derived from both techniques is considerably larger than predicted for an isolated film.¹⁰

Upon evaporation of Li, the energy of the Be surface state at $\bar{\Gamma}$ was seen to shift continuously from -2.8 eV, for clean Be, to -4.0 eV at the completion of the first Li layer. This is well below the bottom of the bulk Li s band suggesting that for thick films this state would be an interface state.¹⁸ The measured dispersion of the Be surface state (Be SS) for the clean surface is shown in Fig. 1 by circles while for a saturated overlayer of Li the Be SS is shown by squares. For the saturated surface, the Be SS lies on the bottom edge of the bulk band gap. This state penetrates far into the bulk, has the wavefunction character of the bulk wave function at Γ_3^+ , and decays exponentially into the Li layer. Be has two surface states at \bar{M} .¹⁹ For clean Be, these states have initial-state energies of -1.8 and -3.0 eV. For the surface with the Li overlayer, these states have initial-state energies of -2.3 and -3.1 eV, respectively. In Fig. 1, the dispersion of the lower Be surface state at \bar{M} is shown by diamonds and the upper by squares for the Li-covered surface.

It should be pointed out that the Li overlayer is incommensurate with the Be substrate. In principle, states which extend into both the substrate and the overlayer have no periodicity. Because of the lack of periodicity, the dispersion of these states poses an interesting theoretical problem. It can be seen in Fig. 1 that to a first approximation the substrate structure does not affect the dispersion of the Li valence band and the overlayer structure does not affect the dispersion of the Be bands. This is evidence that the Be surface-state wave function lies almost entirely in the substrate and suggests that the Li band is well confined to the overlayer. For simplicity, we refer to separate Brillouin zones for the Li overlayer and the Be substrate.

Since in both photoemission and inverse photoemission the component of the electron's momentum parallel to the surface is conserved, dispersion of two-dimensional electronic states can be mapped out by moving the analyzer (or electron gun) off the crystal normal. Figure 2 shows a series of spectra for both ARUPS and IPES at different angles for k_{\parallel} along $\bar{\Gamma}$ - \bar{M} . The Li-induced peak,

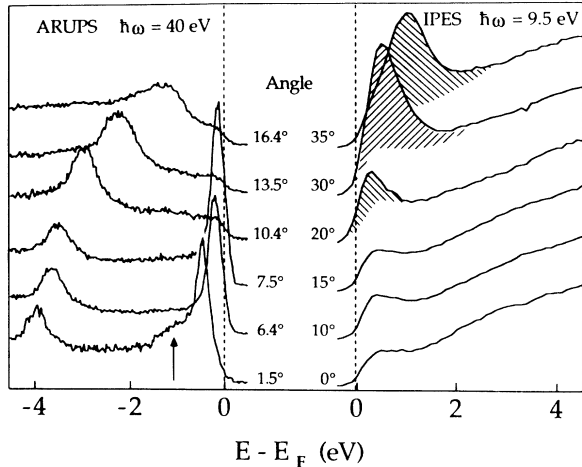


FIG. 2. Unsmoothed ARUPS and IPES spectra for various emission (ARUPS) and incident (IPES) angles for a saturated layer of Li on Be(0001), and k_{\parallel} is along $\bar{\Gamma}$ - \bar{M} . The kinetic energy of the Fermi edge is 35.56 eV for the ARUPS and 6.3 eV for the IPES.

with -0.47 eV initial-state energy at $\bar{\Gamma}$, is seen to disperse to higher energy with increasing k_{\parallel} . It crosses the Fermi level at which point it becomes visible in the IPES spectra. In addition to the emission from the Li valence band, a second, weaker Li-induced peak with an initial-state energy of -1.1 eV can also be seen at $k_{\parallel}=0$ (shown by the arrow in Fig. 2). This Li-induced structure does not disperse significantly but decreases in intensity as k_{\parallel} increases. This peak is shown in Fig. 1 by the crosses. While this peak may be a loss satellite of the main Li-induced peak at -0.47 eV, we believe it is due to an umklapp process from states with larger k_{\parallel} . This will be discussed further below.

In order to clearly see the Fermi-level crossings in ARUPS, the analyzer was set to detect electrons at E_F . To probe states with finite k_{\parallel} , the analyzer was rotated away from the crystal normal. The count rate peaked when a state crossed E_F . Figure 3 shows the Fermi-level crossings of the Be SS for the clean surface (circles), the Be SS (squares), and Li-induced peak (triangles) at Li monolayer saturation along $\bar{\Gamma}$ - \bar{K} . The Li state crosses at $\theta=8.9^\circ$ which corresponds to $k_{\parallel}=0.47 \text{ \AA}^{-1}$. The occupied charge for a Λ_1 band is given by twice the occupied area divided by the total area of the two-dimensional Brillouin zone, where the factor of 2 accounts for spin. The occupied charge of the Li state is $0.33e$ per Li atom. The two-dimensional Fermi surface of the Be SS clearly expands in the presence of Li. The increase in charge for this state is $0.37e$ per Li atom.

In the simplest picture, where the interaction of the Li layer with the Be substrate is visualized to take place through the overlap of the Be surface state with the Li band, there is a problem with charge neutrality. In this picture, all of the Li s electrons cannot be accounted for and the Li layer would appear to be partially ionic. It is

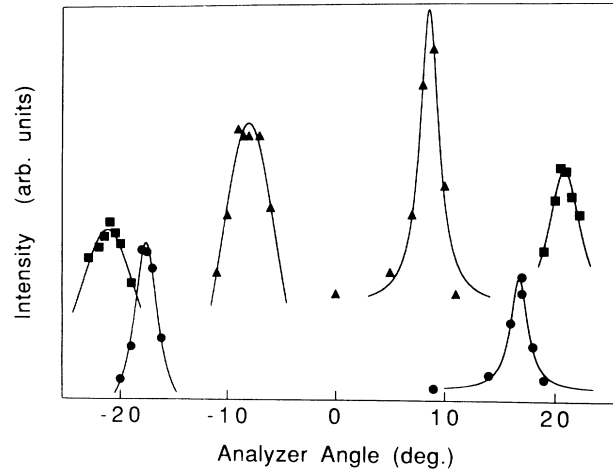


FIG. 3. Fermi-level crossings of the Be SS for the clean (circles) and Li-covered (squares) surfaces, as well as the Li band (triangles) for the saturated Li monolayer. The Fermi-level crossings are measured along $\bar{\Gamma}$ - \bar{M} for a photon energy of 40 eV.

commonly agreed that a dense layer of an alkali is neutral and our core-level spectra support this idea. The problem with this simple picture of the bonding is that it ignores the importance of the hybridization of the Be bands near the surface with the isolated two-dimensional film. Theoretical calculations for single-layer (neutral) films of Na and K on Al predict that only $0.4e$ to $0.6e$ is found in the alkali s bands^{7,8} due to the mixing of overlayer and substrate bands.

In Fig. 1, the dashed lines are fits to the data for the Li band and Be SS's. The three dashed lines beyond the Be \bar{M} point are a fit to the data for the upper Be surface state at \bar{M} , a fit to the dispersion of the Be SS in the first SBZ shifted by a Be reciprocal-lattice vector, and a fit to the Li-induced data in the first Li Brillouin zone shifted by a Li reciprocal-lattice vector. If these states did not mix, then the Be SS should disperse up across the Fermi level and back down again. The Be surface state does not cross E_F but has been pushed to lower energies, in the region in which the states would be expected to cross, while the Li band has been distorted and pushed to higher energies. *This is an avoided band crossing, and is a clear indication that hybridization occurs between the Li Λ_1 band and the Be surface state.* Regions of k space in which there is strong mixing of overlayer and substrate bands, such as this, are obvious candidates for accounting for the remaining Li charge. The lower band in the region of the avoided band crossing has an initial-state energy close to -1.1 eV. It could be folded back by a Li reciprocal-lattice vector (see Fig. 1) to produce the anomalous peak mentioned earlier at $\bar{\Gamma}$.

The effective mass for the bulk Li Λ_1 band from a local-density calculation is 1.40.¹⁵ For an isolated layer of Li the local-density approximation¹⁰ (LDA) value of the effective mass is also 1.40. The self-energy correc-

tion for bulk Li in the GW approximation increases the effective mass to 1.67.¹⁵ The effective mass of the Li band shown in Fig. 1 is 1.8, considerably larger than expected from either a single-particle picture or many-body effects. Two possible explanations for the large effective mass are hybridization of the Li band with the substrate bands or an enhanced self-energy correction due to the two-dimensional nature of the Li film. The relative importance of these possibilities cannot be determined here.

The effective mass of the Be SS in the $\bar{\Gamma}$ - \bar{M} direction changes from 1.27,²⁰ for clean Be, to 1.03 at Li monolayer saturation. As the Be SS shifts towards the edge of the bulk band gap it penetrates further into the bulk and becomes more bulklike in character. As seen in Fig. 1, for the Li-covered surface the dispersion of the Be SS closely follows the theoretical bulk band edge. At Li saturation, the effective mass of the Be SS is governed by the dispersion of the nearby bulk bands.

While alkali-induced overlayer bands have historically been difficult to observe, the large bulk band gap of the Be(0001) substrate has made it possible to clearly observe the Li A_1 band both above and below the Fermi level. No anomalous effects were observed in the screening of ARUPS and IPES which could explain the unexpected results reported for Na on Al(111).⁴ The effect of substrate interactions on the Li valence band is clearly observed in an avoided band crossing and explains the depletion of charge in the Li band from the isolated layer value of one electron per Li atom. The effective mass for the Li band is 1.8, significantly larger than expected from LDA calculations.

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