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Unoccupied electron band structure of Na overlayers on Al(111)

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Using the technique of inverse photoemission spectroscopy in the isochromat mode, we have determined the unoccupied part of the electron band structure of Na/Al(111) for two ordered overlayers: $(\sqrt{3}\times\sqrt{3})R30°$, $\Theta_{Na}=\frac{1}{3}$ monolayers (ML) and (2×2), $\Theta_{Na}=\frac{1}{2}$ ML. At normal incidence, we find peaks at energies 1.1 and 2.1 eV above the Fermi energy E_F for the low-coverage phase and 1.8 and 2.7 eV for the high-coverage phase. These peaks disperse away from E_F as a function of increasing parallel momentum of the incident electron. At larger angles a new state is observed in each phase which disperses toward E_F. We assign these peaks to unoccupied p and d levels of the Na/Al(111) overlayers and compare our measurements to a recent band-structure calculation of isolated alkali-metal monolayers.

The past few years have witnessed a revival of interest in the properties of alkali metals adsorbed on metal surfaces.[1-3] This is partially the result of recent experimental and theoretical investigations of the coadsorption of alkali metals with atoms and molecules on surfaces,[2,4] which have significant technological applications in promoting certain catalytic reactions. Many of the important issues in previous studies regarding the properties of alkali-metal adsorption have been obscured by the use of d-band metals as substrates.[5,6] The interaction between an alkali metal and the d bands of a metal is not well known and is difficult to model theoretically; in addition, the presence of the substrate d bands in the spectra of photoemission and other spectroscopies has made the identification of alkali-induced features often difficult or impossible.[1,5,6] In the present study of Na/Al(111) we have eliminated these problems by the choice of an s-p metal as substrate. In addition, Al(111) is perhaps the optimum choice as a substrate for purposes of comparison to jellium-model calculations, which have been extensively appled to alkali-metal overlayers.[6-8] Finally, the choice of inverse photoemission to investigate this system is partially motivated by the fact that most of the valence levels of a monolayer film (or bulk) of an alkali metal are *unoccupied.*

The experiments reported below were carried out in an ultrahigh-vacuum (UHV) chamber with a base pressure of 1×10^{-10} mbar, equipped with standard surface-science analysis equipment. The inverse-photoemission spectroscopy (IPES) measurements were performed in the isochromat mode, detecting 9.5-eV photons with a Geiger-Müller-type tube equipped with a SrF_2 window. The electrostatically focused electron gun[9] with BaO cathode was mounted on a goniometer which makes it possible to vary the angle of incidence of the incoming electrons without changing the angle relative to the photon detector. The electron-beam divergence was 3°, resulting in an uncertainty of the wave vector $k_\parallel$ of about $\Delta k_\parallel=0.06$ Å^{-1}. The overall system energy resolution was better than 0.4 eV.

The Al(111) crystal was cleaned by argon-ion sputtering and annealing. Cleanliness was checked by Auger and IPES measurements. Na was deposited from a commercial getter source[10] onto the sample at room temperature. Approximately two monolayers were initially deposited, then the crystal was annealed to appropriate temperatures to produce the ordered overlayers determined by low-energy electron diffraction (LEED) and reported below.

Figure 1(a) shows a typical IPES spectrum of the clean Al(111) surface taken at normal incidence of the electron beam ($k_\parallel=0$). The Fermi energy E_F is determined by the onset of detected photons. We assign the peak at 3.70 eV above E_F (0.54 eV below the vacuum level[11]) as an image-potential surface state[12] of the clean Al surface. This will be discussed in more detail elsewhere.[13] When $\frac{1}{3}$ monolayer (ML) of Na is deposited onto the Al(111)

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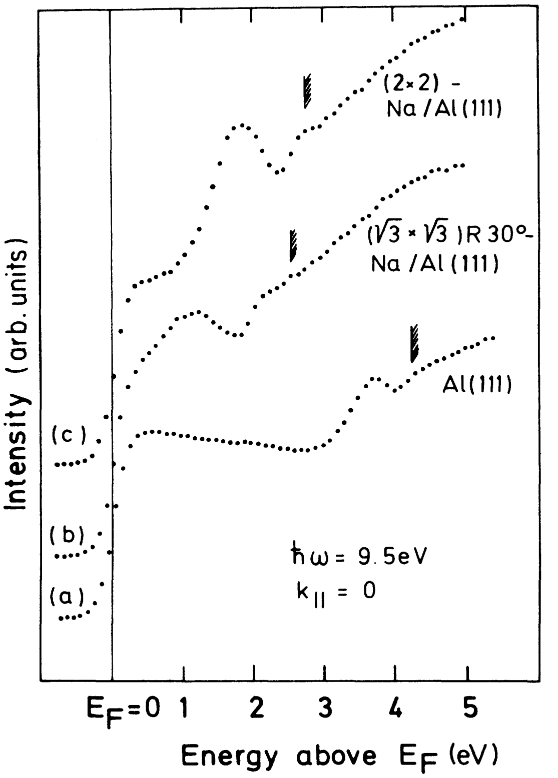

FIG. 1. Inverse photoemission spectra at normal incidence of (a) the Al(111) surface, (b) the $(\sqrt{3}\times\sqrt{3})R30°$-Na overlayer on Al(111) ($\Theta_{Na}=\frac{1}{3}$ ML), and (c) the (2×2)-Na/Al(111) system ($\Theta_{Na}=\frac{1}{2}$ ML). The hatched marks indicate the vacuum levels of clean Al(111), $\phi=4.24$ eV (Ref. 11), and the overlayer systems. These values were deduced from the Na-induced work-function changes measured by the onset edge of the sample current (biased at -10 V) as a function of the gun cathode voltage.

substrate at room temperature, a well-ordered $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern (also referred to as the $\sqrt{3}$ pattern) is observed, as has been reported previously.[14,15] The corresponding IPES spectrum of this Na overlayer is presented in Fig. 1(b). The image state has been completely quenched and two new Na-induced features are observed at normal incidence—a well-defined peak at 1.1 eV above E_F and a shoulder at 2.1 eV. Both features disperse as a function of polar angle θ. In Fig. 2 inverse-photoemission spectra of the $(\sqrt{3}\times\sqrt{3})R\,30°$-Na/Al(111) overlayer system are displayed as a function of θ along the $\bar{\Gamma}\bar{K}$ azimuth of the surface Brillouin zone (SBZ) of the Na overlayer. The upper peak (2.1 eV) can only be followed out to an incident angle of $\theta=12.5°$ before it disappears. The lower peak (1.1 eV) appears to broaden in the angular range of 15°–25°, but then sharpens up again at higher angles. Simultaneously, a new peak appears at lower energies (~ 1.75 eV) and disperses toward E_F as θ is further increased. We have observed two weak features at higher incident angles in the IPES spectra of clean Al(111) (not shown). One disperses toward the Fermi level and crosses E_F at $\theta\sim 50°$.[13] The second Al(111) structure at $E_F+4.5$ eV is almost independent of θ. Therefore the spectra in the high-angle regime ($\theta > 30°$) of the Na/Al(111) system may consist of a superposition of substrate and Na-induced features. Particularly the dispersion of the low-lying peak at $\theta > 30°$ may be modified. The IPES spectra measured along the $\bar{\Gamma}\bar{M}$ azimuth are not shown. They resemble the spectra of the $\bar{\Gamma}\bar{K}$ azimuth apart from a turning back at the $\bar{M}$ point. The dispersion of all these Na-induced peaks is plotted in Fig. 3 as a function of $k_\parallel$ along the symmetry lines of the SBZ of the $(\sqrt{3}\times\sqrt{3})R30°$ Na overlayer.

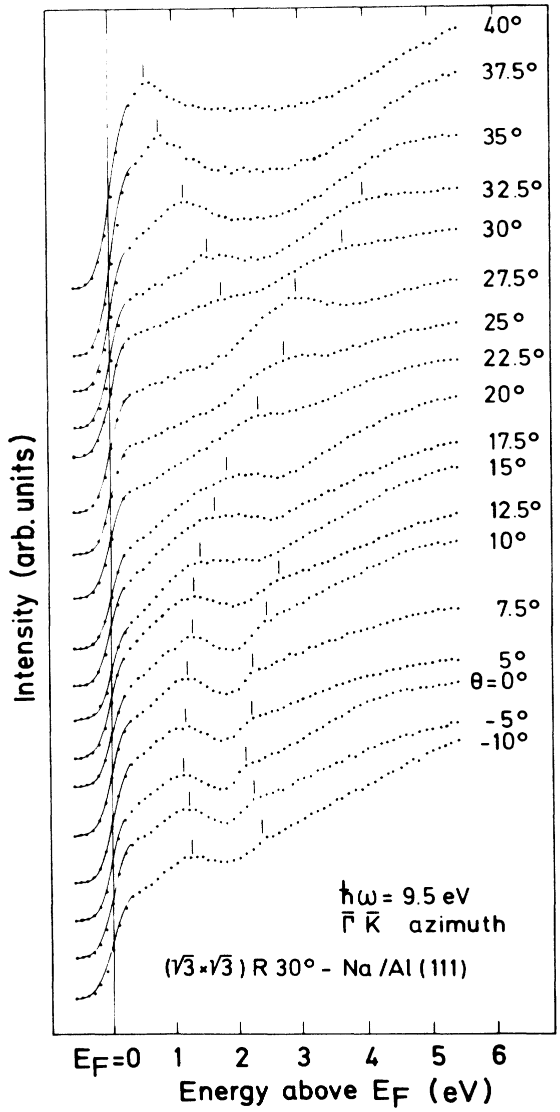

FIG. 2. Isochromat spectra ($h\nu=9.5$ eV) for electrons incident at different polar angles θ along the $\bar{\Gamma}\bar{K}$ azimuth of the $(\sqrt{3}\times\sqrt{3})R30°$-Na/Al(111) overlayer.

If the Na coverage on Al(111) is increased to 0.5 monolayer (saturation of the first Na layer), a well-ordered (2×2) LEED pattern is observed.[14,15] The corresponding IPES spectrum at normal incidence is presented in Fig. 1(c). An intense peak is observed at 1.8 eV above E_F and

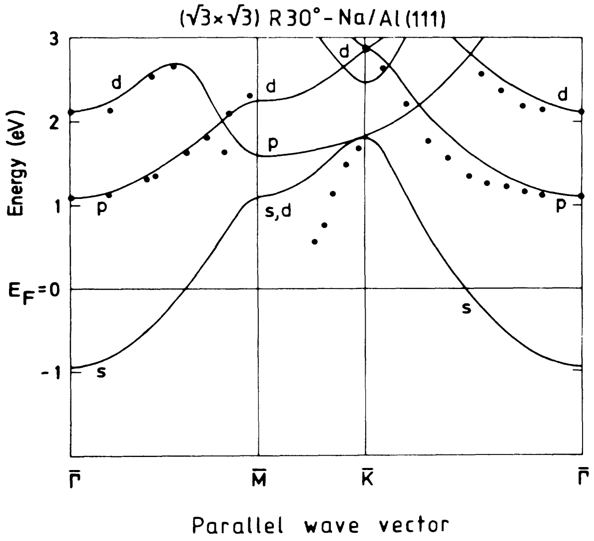

FIG. 3. Dispersion of the IPES structures of the $(\sqrt{3}\times\sqrt{3})R30°$ Na overlayer on Al(111) (4.85 Å) compared to a band-structure calculation of a hexagonal monolayer of rubidium (full lines) by Wimmer (Ref. 16) with a similar nearest-neighbor spacing (4.84 Å). The labels s,p,d denote the main character of the Rb bands, according to Wimmer.

a shoulder at 2.7 eV, qualitatively similar to the IPES spectrum of the $\sqrt{3}$ phase [Fig. 1(b)], but with the maxima at different energies. The dispersion is measured along the $\bar{\Gamma}\bar{M}$ azimuth of the Al(111) substrate. The lower peak disperses as a function of $k_{\parallel}$, as plotted in Fig. 4. The 2.7-eV shoulder can be observed out to a polar angle of $\theta=7.5°$. As in the previous $\sqrt{3}$ case, the first peak broadens at intermediate angles and then sharpens at larger angles, with a new structure appearing closer to E_F and dispersing downwards. Unfortunately, the structure of the (2×2) overlayer is not known in detail, and may consist of several (2×1) domains[14] or more than one atom per unit cell.[15] As a result, we are unable to specify the direction or directions probed in reciprocal space for this overlayer.

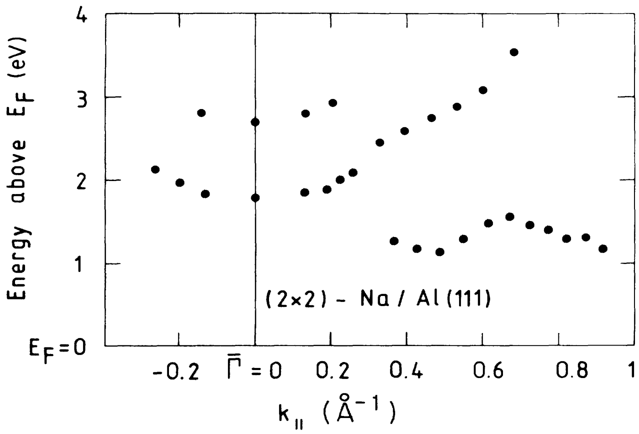

FIG. 4. Dispersion of the Na-derived unoccupied two-dimensional bands of the (2×2) Na overlayer on Al(111).

We assign the energy band located closest to E_F at $\bar{\Gamma}$ in our IPES spectra of each coverage phase to the unoccupied $3p$ state of the Na overlayer, since this is the first unoccupied level. We were unable to experimentally determine the symmetry of the observed bands; however, our assignment is supported and the identification of the other experimental features is aided by a comparison to a band-structure calculation of isolated alkali-metal monolayers by Wimmer.[16] For an isolated hexagonal Na monolayer, but with a significantly different nearest-neighbor spacing (3.66 Å) than for the $\sqrt{3}$-Na/Al(111) overlayer measured here (4.95 Å), Wimmer finds the bottom of the upwardly dispersing p_z band of Na at 0.65 eV above E_F, compared with 1.1 eV measured experimentally. At approximately 2 eV higher in energy at $\bar{\Gamma}$ (2.7 eV above E_F), a hybridized s-d band appears in the calculation. We associate this band with the shoulder observed experimentally which disperses from 2.1 eV at $\bar{\Gamma}$ for the $\sqrt{3}$ overlayer. In addition, Wimmer finds downwardly dispersing s and p bands along the $\bar{K}\bar{M}$ direction starting at 2.4 eV at $\bar{K}$. We assign these bands, or probably more precisely the p band which should have a higher cross section, to the band observed at ~1.75 eV above E_F at $\bar{K}$, and which disperses downward to E_F along $\bar{K}\bar{M}$. Its dispersion (Fig. 3) may be modified by an underlying Al(111) feature as discussed above. In our experimental spectra we detect no sign of the Na s band which is occupied at $\bar{\Gamma}$ and should cross into the unoccupied region somewhere along $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$. We attribute this fact to the comparatively low cross section expected for an s level.

The qualitatively similar IPES results for the $(\sqrt{3}\times\sqrt{3})R30°$- and (2×2)-Na/Al(111) overlayers lead us to similar peak assignments in the higher-coverage phase. In particular, we assign the 1.8-eV peak at $\bar{\Gamma}$ to the p_z band, the shoulder at 2.7 eV at $\bar{\Gamma}$ to an s-d level, and the downward-dispersing peak at larger $k_{\parallel}$ values to a p_x-p_y state. A determination of the surface structure of this overlayer is necessary before a further comparison to theory can be made. The increase in energy above E_F of the p_z level from the $\sqrt{3}$ to the (2×2) phase by 0.7 eV is consistent with a corresponding increase in loss energy detected in a recent electron-energy-loss study of this same system,[17] and which will be discussed in more detail in a future publication.[18] We should also like to mention that Jacob, Bertel, and Dose[19] have observed a similar peak in their IPES investigation of K/Ag(110) and have likewise assigned it to an unoccupied p level of the alkali-metal overlayer. It should be pointed out that the explanation of the high-lying features at $\bar{\Gamma}$ (see Fig. 1) as image-potential surface states of the ordered Na/Al(111) overlayer systems cannot be ruled out, although their binding energies (0.4 and 1.0 eV) with respect to the vacuum level would be unusually low. In addition, similar structures do not appear in the normal-incidence spectra of the ordered Cs/Al(111) overlayers.[18]

Because of the significantly different Na-Na spacing between the experimental situation for the $\sqrt{3}$ phase and the calculation of Na by Wimmer, we do not expect the energy positions (position of the bands, bandwidths, etc.)

to be in particularly good agreement. In our view, it is certainly good enough to justify the assignments discussed above. Somewhat fortuitously, the interatomic spacing of 4.84 Å used in Wimmer's calculation of an Rb overlayer is quite close to the $\sqrt{3}$-Na/Al(111) spacing (4.95 Å). We find it useful to directly compare our measurements to this calculation and we display this comparison in Fig. 3. It was necessary to shift the Rb monolayer band structure to higher energies by 0.45 eV to compare it with our experimental results. Aside from this change, the agreement is surprisingly good, particularly considering that the calculation was performed for a different alkali metal than that studied experimentally. An examination of Fig. 3 confirms our original assignments and also enables us to understand the broadening of the p_z level in our IPES spectra at intermediate incident angles. It is at approximately this region in reciprocal space (below the $\overline{K}$ point) that the upward-dispersing p_z band in Fig. 3 crosses a downward-dispersing *d* band. We suggest that this band crossing and possible hybridization (induced by the influence of the substrate) causes the observed broadening. A similar behavior is observed at $\frac{3}{4}\overline{\Gamma}\overline{M}$.

Since the extent of the Rb and Na wave functions must be quite different it is highly unlikely that a similar calculation of Na with the appropriate lattice spacing could produce as good agreement as we find for Rb in Fig. 3, specifically in regard to both bandwidths and level separations. This suggests that either the calculational method is inadequate or, more likely, the influence of the Al substrate must be included to correctly describe the measurements. The possibility that the substrate is important receives support from a model Hamiltonian calculation of Muscat and Newns,[7] in which they have predicted strong Na *s*-*p* hybridization and a shift upwards in the energy of the Na p_z level by 0.5–1 eV for a *strongly interacting* Na-jellium system. In their model, strong interaction implies a Na *s*-*p* energetic separation similar to that in the isolated atom (2.1 eV),[7] and a rather short Na-jellium bond distance (~2.7–3.0 Å). In fact, separate LEED studies of Na/Al(100) (Ref. 20) derived independently a relatively short Na—Al bond length of ~2.9 Å. We do not expect this result to vary too much for Na/Al(111). Thus at least one of Muscat and Newns' criteria for a strongly interacting system appears to be met in Na/Al(111). In addition, the upward shift in energy of the p_z level predicted by Muscat and Newns (0.5–1 eV) is similar to that (0.45 eV) needed to bring Wimmer's band calculation and our measurements into good agreement. We hope that the work reported here will stimulate new theoretical calculations of alkali-metal overlayers using jellium (or aluminum) as a substrate in an attempt to resolve some of the issues raised above, and will lead to a better general understanding of the properties of alkali- and other metal overlayers on metal surfaces.

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