

## Layer-by-Layer Band Structure of Physisorbed Xe on Al(111)

T. Mandel, G. Kaindl, M. Domke, W. Fischer, and W. D. Schneider<sup>(a)</sup>  
*Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany*  
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The dispersion of Xe-5*p* valence-band states is studied layerwise for multilayers of Xe physisorbed on Al(111) by means of the layer-dependent shifts of photoelectron energies due to screening of the photohole. While the bilayer band structure is essentially the sum of two single-layer band dispersions, Xe bulk bands begin to form with the third layer. Nondispersive peaks are also observed in the photoemission spectra, and are assigned to indirect transitions from critical points in the Xe surface Brillouin zone.

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In the last few years, extensive theoretical work has been devoted to the study of multilayer slabs of transition metals, and the electronic properties were calculated in a layer-by-layer way.<sup>1</sup> Comparison with experiment, however, has been limited to the outermost layer, which may be studied experimentally by surface-sensitive techniques. Even though in photoemission (PE) experiments of solid surfaces the outermost two layers of atoms may be distinguished in favorable cases by their different core-electron ionization potentials,<sup>2</sup> the dispersion of valence bands has not yet been experimentally accessible in a layer-dependent way. The only relevant studies so far were connected with the development of the electronic structure in metal overlayers with increasing thickness of the layers.<sup>3</sup>

The present paper reports on the first—to our knowledge—experimental study of layer-by-layer band dispersion. For experimental reasons, we studied a van der Waals solid, namely ordered multilayers of Xe physisorbed on Al(111), using angle-resolved photoemission spectroscopy (ARPES). As previously found, photoelectrons and Auger electrons from weakly adsorbed multilayers allow a labeling of the first two or three layers through layer-dependent line shifts due to screening of the photohole.<sup>4</sup> Here, this effect is utilized to follow separately the dispersion of the Xe-5*p*-derived valence bands in the  $\Gamma M$  direction across the surface Brillouin zone (SBZ) for the first two layers of an adsorbed bilayer of Xe. Previously, adsorbate band structure had been studied only for monolayers,<sup>5,6</sup> particularly those of rare gases, and exhibited essentially two-dimensional character. The present work is also the first study of the effects of a final-state photohole on the experimental valence bands. We find that the experimental valence-band dispersion in the second layer of a physisorbed Xe bilayer is almost identical to that in the first layer, but shifted to higher binding energies by  $\approx 0.50$  eV as a result of the layer-dependent hole-screening effect. These essentially two-dimensional bands are well described by the band-structure calculation of Hermann, Noffke, and Horn<sup>7</sup> for an unsupported Xe monolayer. With forma-

tion of the third layer, additional features appear in the PE spectra, which—by comparison with the (111) surface of a bulk Xe single crystal<sup>8</sup>—are identified as due to a beginning of three-dimensional band dispersion. In all spectra, less intense nondispersive peaks are observed that can be assigned to indirect transitions from critical points of the Xe SBZ.

The ARPES measurements were performed in a VG-ADES-400 spectrometer with use of unpolarized He I (21.2 eV) and He II (40.8 eV) radiation, with an overall system resolution of better than 0.1 eV (FWHM) and a base pressure of  $1 \times 10^{-10}$  Torr. The Al(111) crystal, cleaned by repeated cycles of Ne-ion sputtering and annealing, could be cooled to 40 K with use of a liquid-He flow cryostat or it could be resistively heated to 500 °C. Monolayers, bilayers, and thicker layers of Xe were prepared by suitable choices of gas exposure and sample temperature,<sup>4</sup> and their structure was studied by LEED. We find that the hexagonal-close-packed Xe layers with a nearest-neighbor Xe distance of  $4.38 \pm 0.03$  Å are well aligned but incommensurate with the substrate, independent of the number of Xe layers studied (up to 3); accordingly, multiple-diffraction LEED peaks were observed.

In Fig. 1 the normal-emission PE spectra of Xe/Al(111) are shown for different Xe-layer configurations. In the monolayer spectrum five peaks can be clearly identified: Three of them are due to direct PE from Xe-5*p*<sub>1/2</sub>- and Xe-5*p*<sub>3/2</sub>-derived valence-band states at the  $\Gamma$  point, and the other two peaks are assigned to indirect transitions from critical points in the Xe SBZ (see below). The assignment of the direct PE lines follows from theoretical band-structure calculations for ordered Xe monolayers<sup>7,9</sup> and is identical to the one given in earlier studies of monolayer-Xe-adsorbate systems.<sup>5,10</sup> The PE spectrum of the Xe bilayer [Fig. 1(b)] can be decomposed into almost identical single-layer contributions from the first and the second Xe layer, separated by a binding energy shift of 0.50 eV. As previously shown,<sup>4</sup> this layer-dependent shift is mainly due to differences in the image-charge screening of the photohole in the first and second adsorbate layer. It should be noted here that almost

identical layer-dependent shifts have been observed in angle-integrated Xe- $5p$  PE spectra of Xe bilayers on Pd(100)<sup>4</sup> and Al(111),<sup>11</sup> while the bilayer splittings observed for Xe- $4d$  core lines were found to be  $\approx 25\%$  larger.<sup>4</sup>

For Xe coverages exceeding two layers, substantial changes occur in the PE spectrum, which cannot be explained by the addition of another single-layer contribution to the bilayer spectrum. In the 2.5-layer spectrum [Fig. 1(c)], only the two main peaks of second-layer Xe can be identified as indicated by the dashed bar diagram, whereas the extra structures not due to single-layer contributions become dominant upon completion of the third layer [Fig. 1(d)]. Upon adsorption of more Xe, these new structures remain essentially unchanged, except for an increase in the intensity of peak A. The same structures A, A' have been observed for bulk Xe(111),<sup>8</sup> and were ascribed to

emission from the band edges of the  $5p_{1/2}$ -derived bulk-Xe band. The present results thus clearly show that three-dimensional Xe bands are already formed in a 2.5-layer-thick Xe configuration [Fig. 1(c)].

This conclusion is confirmed by normal-emission PE spectra taken at different photon energies. Accordingly, a strong shift of the peak positions with photon energy is observed in the 2.5-layer spectrum [Fig. 2(b)], which reflects a dispersion of the band states with the momentum component normal to the surface,  $k_{\perp}$ , as expected for three-dimensional bands. On the other hand, such a dispersion is clearly absent in the Xe-bilayer spectra [Fig. 2(a)], which again proves the two-dimensional character of the Xe bands in this case.

For monolayers and bilayers of Xe/Al(111), we have also studied the ARPES spectra as a function of the polar electron-emission angle,  $\theta$ , which is the angle between the surface normal and the direction of electron emission in the  $(1\bar{1}0)$  plane (corresponding to the

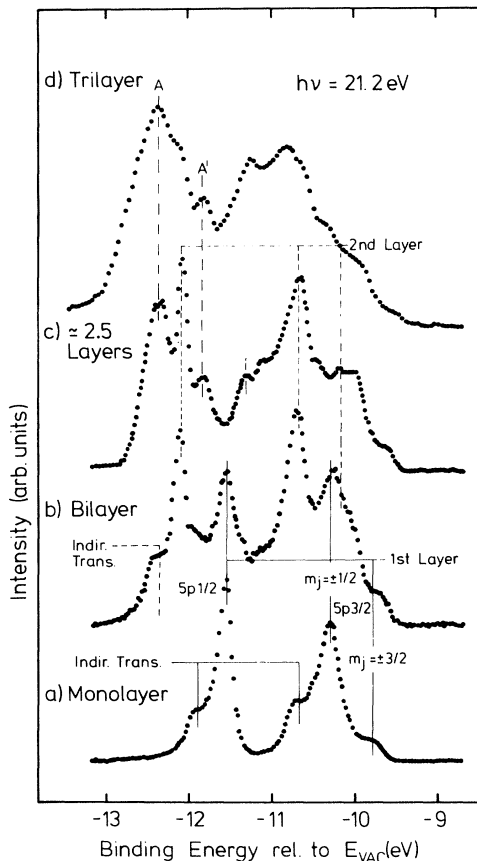


FIG. 1. Normal-emission PE spectra of (a) a monolayer, (b) a bilayer, (c)  $\approx 2.5$  layers, and (d) a trilayer of Xe/Al(111). The contributions due to direct as well as indirect transitions from the first (second) layer are indicated by solid (dashed) bar diagrams. In the 2.5-layer and trilayer spectra, the peaks labeled A and A' were identified as bulk-Xe features.

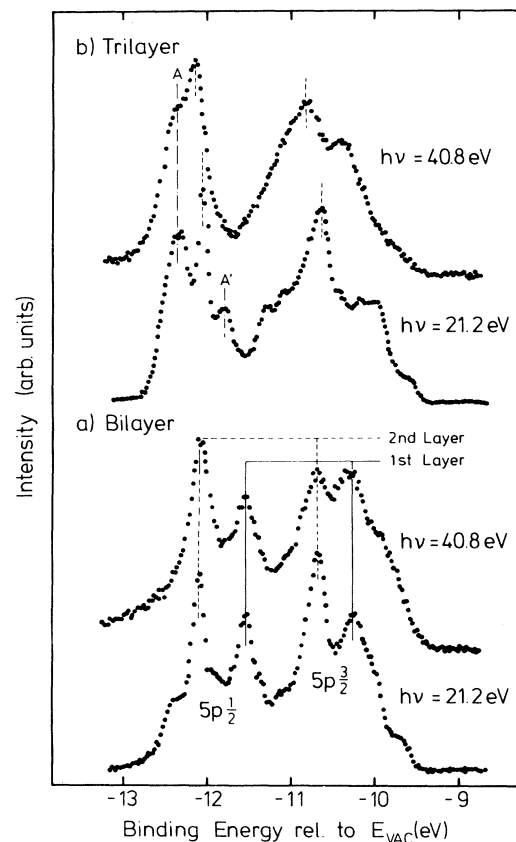


FIG. 2. Normal-emission PE spectra of (a) a bilayer and (b)  $\approx 2.5$  layers of Xe adsorbed on Al(111) for different photon energies ( $h\nu = 21.2$  and  $40.8$  eV). For notations see Fig. 1. Note that dispersion with photon energy is clearly absent for a bilayer of Xe, but substantial for thicker-layer configurations.

[112] azimuth). Some representative spectra are summarized in Fig. 3. We can clearly distinguish between the direct PE peaks which disperse with  $\theta$  and the non-dispersing features from indirect transitions, which are situated at the low-energy band edges, i.e., due to emission from the Brillouin zone edges.

Since  $k_{\parallel}$  is conserved in direct PE transitions, experimental band dispersions along  $\Gamma M$  of the Xe SBZ may be derived by use of the well-known relation  $k_{\parallel} = (2\pi/h)(2m_e E)^{1/2} \sin\theta$ ; here,  $E$  is the kinetic energy of the photoelectrons. The results of this analysis are presented in Fig. 4 for the monolayer and bilayer configurations. Obviously, the experimental band dispersions for the first (filled circles) and the second Xe layers (open circles) are well described by the theoretical curves of Ref. 7. These were calculated with a linear rigorous cellular method for an unsupported Xe monolayer with nearest-neighbor Xe distances as determined in the present LEED measurements. This agreement means that the assumption of negligible interaction between substrate and Xe overlayer is well fulfilled in the present case. It should be noted that the agreement with a simple tight-binding calculation<sup>9</sup> is much less satisfactory. In the bilayer case [Fig. 4(b)], the second-layer band-dispersion curves (dashed) are rigidly shifted to higher binding energies by 0.50 eV relative to the first-layer curves

(solid). A close look at Fig. 4(b) shows that the dispersion of the experimental second-layer  $j = \frac{1}{2}$ -derived band seems to be slightly smaller than that of the first layer. This effect—if real—would indicate a small deviation from a description of the electronic structure of bilayer Xe/Al(111) as a simple sum of two single-layer two-dimensional band dispersions.

The close similarity between the first- and second-layer band-dispersion curves [Fig. 4(b)] underlines the following points: (i) The adsorbate-substrate interactions seem to be small even for first-layer Xe atoms on Al(111). (ii) Differences in image-charge screening with respect to the metal surface are smaller than  $\approx 0.2$  eV. Such differences are expected to be particularly observable at the  $\Gamma$  point, where the  $j = \frac{3}{2}$ ,  $m_j = \pm \frac{1}{2}$  ( $j = \frac{3}{2}$ ,  $m_j = \pm \frac{3}{2}$ ) states have predominantly  $5p_z$  ( $5p_{x,y}$ ) character. This would lead—by the influence of the photohole—to a distortion of the experimentally observed first-layer band dispersion as compared to the initial-state dispersion (calculated theoretically); for the second layer such effects are expected to be negligible.

The present results represent the first experimental study of the effects of the final-state photohole on ex-

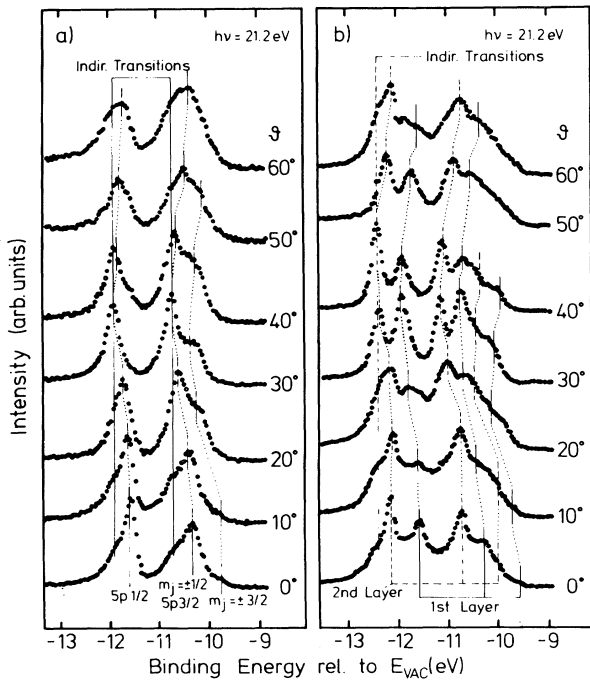


FIG. 3. Polar-angle dependence of PE spectra from (a) monolayer and (b) bilayer Xe/Al(111). The dispersions of the various peaks are traced along the  $\Gamma M$  direction in the Xe SBZ.

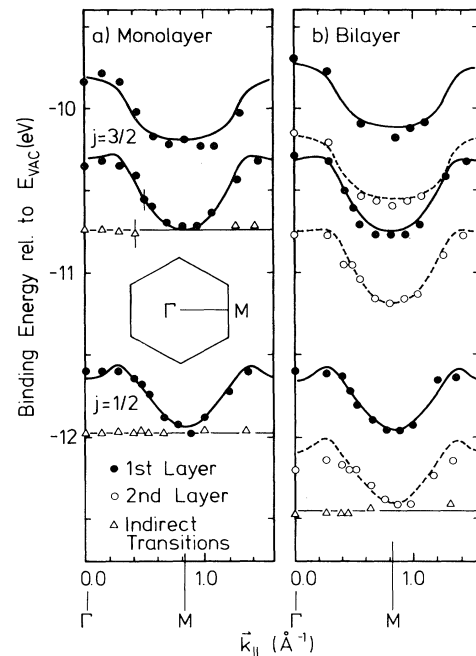


FIG. 4. Experimental band dispersions along  $\Gamma M$  for the monolayer-Xe and bilayer-Xe configurations. The solid (first layer) and dashed (second layer) curves, drawn through the data points, represent the theoretical single-layer band-dispersion curves of Ref. 7, displaced by layer-dependent binding-energy shifts. Indirect transition peaks are denoted by triangles.

perimental band dispersions. Even though the system studied here is rather simple, we may anticipate that such effects do also exist in more complicated ones; they should be taken into account when comparing experimental PE band-dispersion curves with the results of band-structure calculations. A similar suggestion has recently been made on the basis of x-ray photoemission spectroscopy studies of core levels and valence-band states in dilute alloys.<sup>12</sup>

Finally, we comment on the nondispersive peaks assigned to indirect transitions from critical points of the Xe SBZ. In cases where the  $k_{\parallel}$  conservation is not valid, peaks from regions with a high density of states are observed. Indirect-transition peaks have previously been observed for incommensurate Xe layers on Pd(100)<sup>13</sup> and Cu(110),<sup>10</sup> and were explained as a consequence of photoelectron scattering at the incommensurate substrate (substrate umklapp). Recently, indirect transitions were also found in the case of commensurate Xe overlayers,<sup>14</sup> suggesting other mechanisms for this partial breakdown of  $k_{\parallel}$  conservation. In particular, phonon-induced processes and/or local disorder in the adsorbate structures must be considered.<sup>15</sup> An extensive study of these effects will be the subject of a forthcoming paper.<sup>14</sup>

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<sup>(a)</sup>Present address: Institut de Physique, Université de Neuchâtel, Rue A.L. Bregut 1, CH-2000 Neuchâtel, Switzerland.

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