

## Surface effects on energies of Auger electrons from Xe(111)

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The Xe  $N_{4,5}O_{2,3}O_{2,3}$  Auger spectrum of a Xe crystal grown on Pd(111) is found to consist of two atom-like subspectra from surface and bulk Xe atoms, respectively, separated by  $\Delta^A = 0.79 \pm 0.05$  eV. This surface Auger-electron shift is three times as large as the simultaneously studied surface shift of the Xe 4*d* core-level photoemission lines. We explain these surface shifts in terms of a reduced dielectric screening of the positive hole states in surface atoms as compared with the bulk.

Surface effects on core-level binding energies have been studied quite extensively in recent years both experimentally<sup>1,2</sup> and theoretically.<sup>3,4</sup> Soon after the first report on such effects<sup>5</sup> it was realized that the reduced coordination of surface atoms will generally affect core-hole binding energies measured in photoemission experiments. Shifts to both higher and lower binding energies have been observed depending on specific electronic and structural properties of bulk and surface atoms. For a theoretical understanding of surface core-level shifts, initial-state potential-energy effects, as well as final-state hole-screening shifts, must be considered. The two contributions, however, have not been separated experimentally up to now.<sup>6</sup>

On the other hand, surface effects on Auger-electron energies have not been reported to date, even though they should occur, considering the initial one-hole and final two-hole states of Auger transitions. In many solids essentially atomlike Auger transitions are observed,<sup>7,8</sup> which should make an observation of surface effects feasible, particularly for low-energy Auger transitions providing high surface sensitivity. The present paper reports on the first observation of surface shifts of Auger-electron energies from a study of photon-excited Xe *NOO* Auger spectra of a Xe(111) crystal surface.

We find that the Xe  $N_{4,5}O_{2,3}O_{2,3}$  Auger spectrum from the (111) surface of a Xe crystal grown on Pd(111) is made up of two rigidly shifted atomlike Auger spectra. The subspectrum originating from the outermost surface layer is shifted by  $\Delta^A = 0.79$  eV to lower kinetic energies as compared with the one from bulk Xe. Surface effects on Xe 4*d* core-level binding energies, as derived from high-resolution Xe 4*d* photoemission spectra of the same Xe surface, are found to be smaller by a factor of 3. This agrees with an interpretation of these surface shifts in terms of a reduced dielectric screening of the hole states at the surface. We show that the observation of both surface Auger-electron energy shifts and surface core-level shifts allows their separation into potential-energy and hole-screening contributions.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin with the use of a toroidal-grating monochromator in combination with a double-cylindrical mirror analyzer in an ultrahigh vacuum system with a base pressure of  $5 \times 10^{-11}$  Torr. Xe layers with variable thickness were grown on a cooled Pd(111) surface cleaned by Ar-ion sputtering and annealing. The temperature of the Pd crystal could be varied continuously between 40 and about 1100 K. Xe monolayers were prepared by deposition of slightly thicker layers at a substrate temperature of 40 K and subsequent annealing at a higher temperature where second-layer Xe atoms desorb. This process could be followed quantitatively via the well-separated core-level peaks for first- and second-layer Xe atoms.<sup>8</sup> A thick Xe layer (about 16 layers) was prepared by an appropriate Xe exposure at 40 K.

Figure 1 shows angle-integrated Xe *NOO* Auger spectra excited by 90-eV photons for a Xe monolayer and a 16-layer-thick Xe crystal on Pd(111). Xe grows epitaxially on most metal substrates,<sup>9</sup> and in the present case a Xe(111) surface is formed. As noted previously,<sup>8</sup> the Auger spectrum of a Xe monolayer is atomlike and is well described by the gas-phase Xe-Auger spectrum<sup>10</sup> indicated by the short-dashed bar diagram in Fig. 1(a). The solid line is the result of a least-squares fit of this gas-phase spectrum to the data points (assuming Lorentzian line shapes for the individual components) plus a linear background. The Auger spectrum obtained from the Xe(111) crystal surface [Fig. 1(b)] is well described by a superposition of two atomlike Auger spectra rigidly shifted against each other by  $\Delta^A = 0.79 \pm 0.05$  eV. As outlined in more detail below, we interpret the subspectrum with the smaller kinetic energies (dotted) as due to Xe atoms in the outermost surface layer, while the other one (long-dashed) originates from deeper-lying bulk Xe layers.  $\Delta^A$  then represents a surface-induced shift of Auger-electron energies.

We have also carefully looked for surface effects on Xe 4*d* core-level binding energies. The pertinent photoemission spectra taken at  $h\nu = 90$  eV from the same two Xe config-

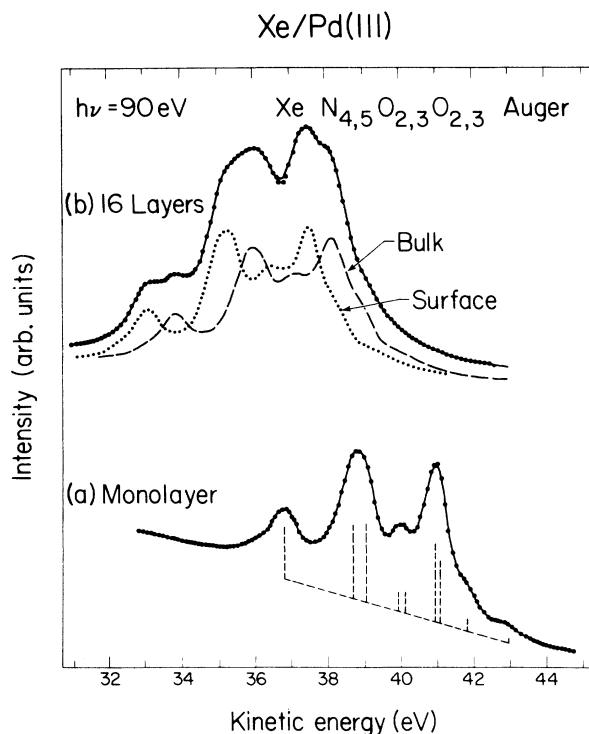


FIG. 1. Xe  $N_{4,5}O_{2,3}O_{2,3}$  Auger spectra for (a) a monolayer of Xe and (b) a 16-layer-thick Xe(111) crystal grown on Pd(111). The kinetic energies are relative to the vacuum level of the adsorbate-covered substrate.

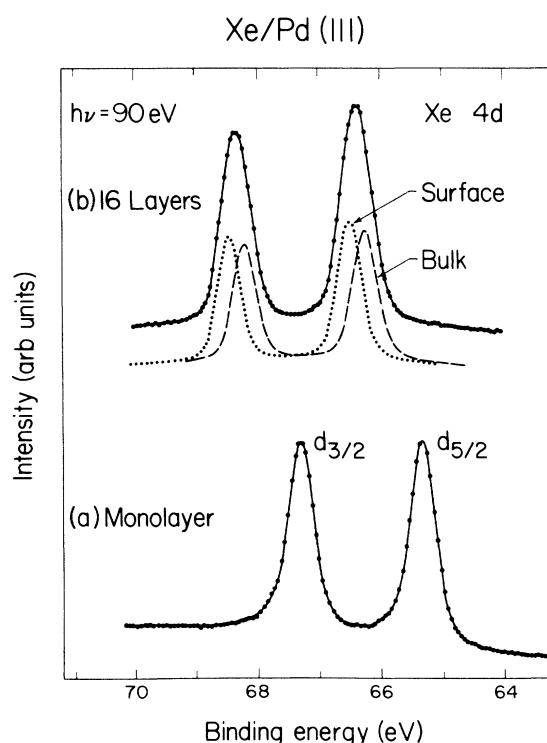


FIG. 2. Xe 4d core-level photoemission spectra for the same two Xe/Pd(111) configurations as in Fig. 1. The binding energies are relative to the vacuum level of the adsorbate-covered substrate.

urations are presented in Fig. 2, together with the results of a least-squares-fit analysis based on Lorentzian line shapes convoluted by a Gaussian for instrumental resolution. The monolayer Xe 4d spectrum is a well-resolved doublet with the free-atom spin-orbit splitting.<sup>8</sup> The spectrum from the Xe(111) crystal surface, on the other hand, consists of two much broader peaks, which are well described by a superposition of two such doublets separated by  $\Delta^c = 0.25 \pm 0.05$  eV. In agreement with the Auger case, the doublet with higher binding energy (dotted) is assigned to emission from surface atoms, and the other one to bulk emission. Note that the magnitudes of  $\Delta^d$  and  $\Delta^c$  differ by a factor of 3.

We have simultaneously measured the vacuum levels ( $E_v$ ) of the two Xe configurations on Pd(111) by recording the total widths of the photoelectron distributions (at  $h\nu = 28$  eV). Therefore the electron-kinetic energies can be

properly referenced with respect to  $E_v$  and compared with the values for gas-phase Xe.<sup>10,11</sup> Table I gives a summary of the resulting Xe 4d binding-energy shifts  $\Delta E_B$  and Xe NOO Auger kinetic-energy shifts  $\Delta E_k$  relative to gas-phase Xe. In the last column of Table I the ratio  $\Delta E_k/\Delta E_B$  is also listed, which is very close to 3 in each case. As discussed previously in connection with distance-dependent shifts<sup>8</sup> this implies that the shifts are predominantly due to screening of the localized one- and two-hole states in the electron emission process. Since the screening energy will be proportional to the square of the localized-hole charge, a three times as large energy shift is expected for Auger electrons (with a one-hole initial and a two-hole final state) as compared with core-level photoelectrons (with a neutral initial and a one-hole final state).

The  $\Delta E_B$  and  $\Delta E_k$  shifts observed for monolayer Xe are

TABLE I. Summary of results for Xe 4d binding-energy shifts  $\Delta E_B$  and Xe NOO Auger kinetic-energy shifts  $\Delta E_k$  relative to gas-phase Xe for a monolayer of Xe and a 16-layer-thick Xe(111) crystal grown on Pd(111). The energies are referenced against the vacuum level of the adsorbate-covered substrate and are given in eV, with estimated error bars of  $\pm 0.05$  eV.

Xe/Pd(111)	Layer	$\Delta E_B^a$	$\Delta E_k^a$	$ \Delta E_k/\Delta E_B $
Monolayer	First	-2.23	7.10	3.18(10)
Thick layer ( $\approx 16$ )	Bulk	-1.32	4.05	3.07(15)
	Surface	-1.07	3.26	3.05(15)

<sup>a</sup> With  $E_B(4d_{5/2}) = 67.55$  eV (Ref. 11) and  $E_k(^1S_0) = 29.73$  eV (Ref. 10) for gas-phase Xe.

mainly caused by metallic screening of the hole states through conduction electrons of the metal substrate, and have been studied extensively both theoretically<sup>12</sup> and experimentally.<sup>8,13,14</sup> They depend on the distance of the core hole from the substrate surface<sup>8</sup> and should be negligibly small for the few outer layers of the 16-layer-thick Xe(111) crystal contributing to the Auger and photoemission spectra. Therefore the Pd(111) substrate can be neglected in the thick-layer case.

The observed shifts for bulk Xe atoms ( $\Delta E_B = -1.32$  eV;  $\Delta E_k = 4.05$  eV) are caused by dielectric screening of the positive hole states due to polarization of the neighboring Xe atoms. At the surface this screening is reduced due to incomplete coordination of surface atoms. The observed shifts for surface Xe atoms ( $\Delta E_B = -1.07$  eV;  $\Delta E_k = 3.26$  eV) correspond to approximately 80% of the values for bulk Xe. A simple lattice-sum calculation assuming polarizable Xe atoms results in a reduction of the dielectric screening for Xe(111) surface atoms to about 66% of its bulk value. This qualitative agreement supports the proposed model and the given assignment.

The separation into surface and bulk subspectra is also supported by the ratio of their spectral intensities,  $I_S/I_B$ , resulting from the least-squares fits. With the electron-escape depth  $l$  we arrive at  $I_S/I_B = \exp(d/l) - 1$ , where  $d$  is the interplanar spacing ( $d_{111} = 3.54$  Å). With  $I_S/I_B = 1.07$  in the Auger case we obtain  $l \approx 4.8$  Å for electrons with an average kinetic energy of  $\approx 36$  eV. This is in agreement with  $l$  values derived from the relative intensities of subspectra for individual layers in adsorbed bilayers and trilayers of Xe.<sup>8,14</sup> In the Xe 4d spectrum of Fig. 2(b) the surface contribution is slightly reduced ( $I_S/I_B = 1.02$ ) as a result of a larger electron escape depth at average electron kinetic energies of  $\approx 23$  eV.

The observation of separate Auger signals from surface and bulk Xe atoms in the present work is closely related to the fact that the  $N_{4,5}O_{2,3}O_{2,3}$  Auger spectra from solid Xe, as well as from adsorbed multilayers of Xe, are atomic-like.<sup>8,14</sup> This is expected since the Coulomb interaction of the two holes in the final state ( $U \approx 10$  eV) is much larger than the one-hole bandwidth  $W$  ( $\approx 0.5$  eV) of the Xe 5p

valence bands.<sup>15</sup> The kinetic-energy distribution of Auger electrons is determined by the local two-hole density of states, which for  $U \gg 2W$  is dominated by a narrow bound state causing an atomiclike Auger spectrum.<sup>7</sup>

Since atomiclike Auger spectra have been observed for many solids,<sup>7</sup> surface effects must be anticipated for several other low-energy Auger spectra with sufficient surface sensitivity. They should always be considered when quantitative conclusions are drawn from detailed line-shape analyses of Auger lines, since their presence can strongly change the observed line shapes. Previously noted discrepancies between theoretical and experimental Auger line shapes, as, e.g., in the case of the Si  $L_{1,2,3}V$  Auger spectrum,<sup>16</sup> might be due to unresolved surface shifts.

Finally, we want to point out that a simultaneous observation of surface Auger-electron shifts and surface core-level shifts allows a separation of surface shifts into potential-energy ( $p$ ) and core-hole-screening ( $h$ ) contributions. Potential-energy effects are expected to contribute in the same way to  $\Delta^c$  and  $\Delta^A$ , while core-hole-screening shifts will be three times larger in the Auger case. This leads to the following equations:  $\Delta^c = \Delta_p^c + \Delta_h^c$  and  $\Delta^A = -(\Delta_p^c + 3\Delta_h^c)$ . In this way a negligible small potential-energy contribution of  $\Delta_p^c = -0.02$  eV is obtained for Xe(111), in agreement with the assumption that dielectric screening effects are dominant in this case.

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