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[2] For a review of isoelectronic traps in zinc-blende semiconductors, see W. Czaja, in *Festkörperprobleme IV,* edited by O. Madelung (Pergamon, New York, 1971), p. 65.

[3] The band gap of GaP is not accurately known, while the position of the 1*S* free exciton is. Effective-mass theory gives a binding energy of 17 meV, if the 2 meV splitting due to the electron-mass anisotropy is neglected: N. O. Lipari and A. Baldereschi, Phys. Rev. B 3, 2497 (1971); N. O. Lipari and M. Altarelli, to be published. In the present Letter we refer all energies to the 0°K band gap, assumed to be 2.345 eV, 17 meV above the 1*S* free-exciton level.

[4] Lipari and Baldereschi, Ref. 3.

[5] Lipari and Altarelli, Ref. 3.

[6] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. 17, 312 (1966).

[7] *P*-like excited states of acceptors have been extensively reported. The data are reviewed and compared with theory in A. Baldereschi and N. O. Lipari, Phys. Rev. B 9, 1524 (1974).

[8] R. A. Faulkner and P. J. Dean [J. Lumin. 1, 2, 552 (1970)] report selective excitation measurements on excitons bound to NN_1 and Bi in GaP. They used a monochromator for excitation and a broad-band filter to monitor the fluorescence. They found two of the NN_1 lines reported here, but their interpretation differs from ours. Their $NN_1{}^*$ and $NN_1{}^{**}$ correspond to our 2*S* and 3*S*.

[9] C. J. Frosch, J. Electrochem. Soc. 111, 180 (1964).

[10] R. J. Elliott, Phys. Rev. 108, 1384 (1957). The transition probability is proportional to $|\Psi(0)|^2$, which varies as n^{-3} for nS states and is zero for all others.

[11] In Ref. 8 this line is reported not to split under stress, which leads to some difficulties in interpretation. It can be seen from the splitting pattern (inset to Fig. 1) that the split-off lines might easily be overlooked, especially if the exciting light happened to be predominantly σ polarized.

[12] A. Baldereschi and N. O. Lipari, Phys. Rev. B 8, 2697 (1973).

[13] M. Altarelli and N. O. Lipari, unpublished.

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Photoemission for Xe Physisorbed on W(100): Evidence for Surface Crystal-Field Effects

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Photoemission spectra at $h\nu = 21.2$ eV reveal two $5p$ levels for xenon physisorbed on a tungsten (100) surface. The spin-orbit splitting of the two levels and their intensity ratio correspond closely to gas-phase measurements, while the $5p_{3/2}$ peak is significantly broadened with respect to the $5p_{1/2}$. We interpret the broadened structure as an unresolved doublet resulting from splitting the Xe $5p_{3/2}$ states in the tungsten-surface crystal field.

One of the most challenging problems confronting surface science is understanding the adsorption of gases on the surfaces of transition metals, whose properties are intimately connected with catalytic and other chemical processes. A prototype system for studying the interaction of atoms with a metal surface is provided by rare-gas physisorption. This system is particularly interesting since the interaction energies involved are at least an order of magnitude smaller than those for chemisorbed species, and the Van der Waals forces responsible for the interaction are reasonably well understood.[1] Physisorption thus offers the possibility of delineating some of the mechanisms governing the interaction of an adsorbate with a metal surface whereas chemisorption, with its much stronger forces, involves competing effects which generally preclude unambiguous identification of structure observed in photoemission spectra. In this communication we report ultraviolet photoelectron spectroscopy (UPS) measurements for xenon physisorbed on a tungsten (100) surface. Specifically, we observe two well-defined peaks arising from the Xe $5p$ levels; the $5p_{3/2}$ peak is appreciably broadened with respect to its spin-orbit companion, and we suggest that the broadening results from splitting of the Xe $5p_{3/2}$ states in the tungsten-surface crystal field. To our knowledge this is the first UPS evidence for surface-crystal-field effects.

A description of the photoemission apparatus employed in these investigations has been given

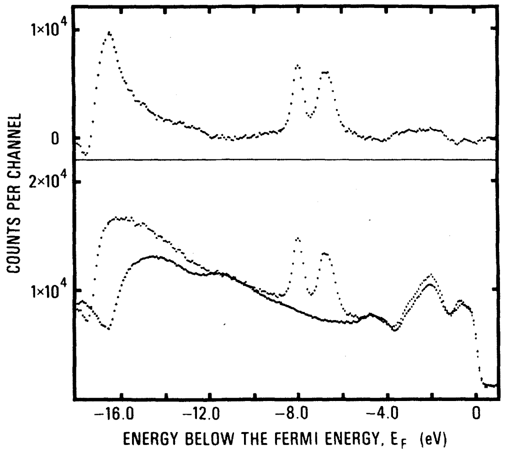

FIG. 1. Photoelectron energy distributions. The lowermost curve is for W(100) at a temperature of ~ 80 K, and directly above it is the distribution after exposure to 5 Langmuirs of xenon. The difference of the two distributions is given at the top of the figure.

elsewhere.[2] Data were collected for a photon energy of 21.2 eV and an electron-energy-analyzer resolution of approximately 0.25 eV. Usual ultrahigh-vacuum techniques were used to obtain a base pressure in the vacuum chamber of 10^{-8} Pa ($\sim 10^{-10}$ Torr) or less.

The lower two curves of Fig. 1 are the photoelectron distribution for a clean tungsten (100) surface at a temperature of ~ 80 K and the distribution after exposure to 5 Langmuirs (5×10^{-6} Torr sec $\sim 7\times10^{-4}$ Pa sec) of xenon. Subtraction of the width of the "clean" distribution from the photon energy yields a work-function value of 4.65 ± 0.03 eV, which compares well with other published values.[3] The increased width of the "exposed" distribution shows that the work function decreases to 3.66 ± 0.03 eV. The pronounced peaks at − 6.8 and − 8.1 eV are due to emission from the two spin-orbit–split Xe $5p$ levels. We note that the structure at − 0.5 eV, which has been identified[4] as a surface state, persists even after exposure to the rare gas, whereas exposure to gases such as H_2, O_2, N_2, and CO, which chemisorb on tungsten, is known[4] to suppress the structure. This is another indication of the weakness of the forces responsible for physisorption.

Figure 2 shows an enlargement of the difference spectrum given at the top of Fig. 1, together with an inset displaying the photoelectron distribution[5] for gas-phase Xe at the same photon energy. For gaseous Xe the binding energies of the $5p_{1/2}$ and $5p_{3/2}$ electrons are 13.4 and 12.1 eV, respectively, and the spin-orbit splitting is consequently 1.3 eV. The $5p_{3/2}$:$5p_{1/2}$ intensity ratio is 1.6:1 instead of the statistical ratio 2:1; this reflects the different radial wave functions for the two states in that it arises from the different overlap between the two bound orbitals and the continuum states. For physisorbed xenon the spin-orbit splitting remains 1.3 eV, and the areas beneath the two peaks are in essentially the same ratio[6] as for the gas phase. Because the partial-cross-section ratio is practically unaffected by physisorption, the interaction between the xenon and the surface produces no drastic modification of one orbital with respect to the other. It is apparent from Figs. 1 and 2, however, that the $5p_{3/2}$ peak is significantly broadened with respect to the $5p_{1/2}$ peak. If one attempts to account for this selective broadening by, say, an inequivalent mixing of the two states with the substrate bands, then one is hard pressed to explain the unchanged spin-orbit splitting and partial-cross-section ratio. We suggest that the broadened structure is in fact an unresolved doublet; if we assume that it is comprised of two peaks having the same width as the $5p_{1/2}$ peak, their separation is approximately 0.3 eV. The crystal field of the tungsten substrate offers a possible mechanism for such a splitting, as the following simple model demonstrates.

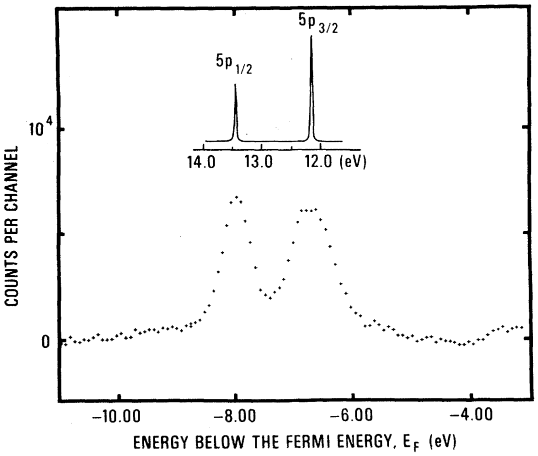

FIG. 2. Expanded view of the two Xe $5p$ peaks from the difference spectrum of Fig. 1. The inset is the photoelectron distribution for gaseous Xe (Ref. 5).

A physisorbed Xe atom lies partially within the dipole layer formed by electrons from the outermost orbitals of the tungsten substrate atoms, so that in the immediate vicinity of the adsorbate the tungsten-ion cores are incompletely shielded. The simplest approximation which preserves the lattice symmetry is to replace the partially screened ions by point charges of magnitude $Z|e|$. We assume that the Xe atoms occupy fourfold sites at the centers of the square mesh formed by the ions of the (100) surface, so that there are four nearest-neighbor ions in the first plane and one in the second plane directly below a Xe atom. An elementary first-order perturbation calculation[7] shows that the $5p_{3/2}$ hole state ($^2P_{3/2}$ in spectroscopic notation) splits into two doubly degenerate levels whose separation Δ is

$$\Delta = \frac{4\sqrt{2}}{5} Ze^2 \frac{\langle r^2\rangle_{3/2}}{a^3} \times \left\{ \frac{2(3\cos^2\alpha - 1)}{(2h^2/a^2+1)^{3/2}} + \frac{1}{[\sqrt{2}h/a + 1/\sqrt{2}\,]^3} \right\}. \qquad (1)$$

The point charge in the second plane produces the second term within the brackets of Eq. (1), and we have arbitrarily assigned it a charge $Z|e|$ as well (although a smaller Z should probably be used for this more distant ion). $\langle r^2\rangle_{3/2}$ is the expectation value of r^2 for the Xe $5p_{3/2}$ orbital ($\langle r^2\rangle_{3/2} = 1.8$ Å^2 from a relativistic Hartree-Fock calculation[8] for Xe), a is the W lattice constant ($a = 3.16$ Å), h is the distance of the Xe nucleus from the first plane ($h \sim 2.8$ Å using 1.4 and 2.2 Å for "hard core" W and Xe radii, respectively), and $\tan\alpha \equiv a/\sqrt{2}h$. To first order a $p_{1/2}$ hole state ($^2P_{1/2}$) will not split in any crystal field because the charge density associated with it is spherically symmetric. The substrate crystal field, therefore, provides a mechanism which at least qualitatively accounts for the preferential broadening of the $5p_{3/2}$ peak. With the values of a, h, and $\langle r^2\rangle_{3/2}$ given above, $Z \sim 0.5$ leads to $\Delta \sim 0.3$ eV. (The point charge in the second plane contributes ~25% of the splitting.)

Finally, we observed that both the decrease in work function and the areas of the $5p$ peaks varied linearly with Xe exposures up to ~0.5 L (Langmuir), and essentially reached saturation at ~2 L. For any exposure up to ~10 L, however, the two peaks remained fixed in energy below E_F; i.e., the binding energy relative to the Fermi level is independent of Xe coverage, while that relative to the vacuum zero decreases with increasing rare-gas exposure. At saturated coverage the binding energies of the $5p$ electrons for physisorbed Xe decreased by 1.6 eV compared to the gas phase.[5] This is to be compared with the 2.1-eV shift of the Xe $3d_{5/2}$ level observed by Yates and Erickson[9] for Xe physisorbed on W(111). The disparity between the two shifts stems principally from the different work functions [in Ref. 9 a work-function value of 3.3 eV was observed for Xe on W(111)], although it is possible that the screening of the spatially more extensive $5p$ hole is somewhat different from that of the highly localized $3d$ hole.

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[4] B. J. Waclawski and E. W. Plummer, Phys. Rev. Lett. 29, 783 (1972); B. Feuerbacher and B. Fitton, Phys. Lett. 29, 786 (1972).

[5] D. W. Turner, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, New York, 1970), p. 42.

[6] The $5p_{3/2}$:$5p_{1/2}$ intensity ratio for the physisorbed case varies between 1.4:1 and 1.6:1 depending on the manner in which the background is estimated for unfolding. As has been seen from other work (E. W. Plummer, B. J. Waclawski, T. V. Vorburger, and C. E. Kuyatt, to be published), caution must be exercised in utilizing difference curves. In subtracting a "clean" distribution from one obtained after adsorption, it is tempting to assume that the "clean" distribution underlying the structure of interest remains unaffected by the adsorbate.

[7] P. V. S. Rao and J. T. Waber [Surf. Sci. 28, 299 (1971)] have performed similar calculations for p and d orbitals but did not include spin-orbit effects.

[8] Courtesy of Professor I. Lindgren and Dr. R. E. Watson.

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