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Experimental observation of adsorbate orbital splitting at single-crystal metal surfaces

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Splitting of the $5P_{3/2}$ component of the photoexcited Xe ion doublet is observed on the (110) planes of several metal surfaces. This effect is shown to originate from a true "crystal-field" effect, not as a consequence of adatom-adatom interactions. The splitting therefore provides a probe of local fields at the screened ion.

One of the more important parameters associated with surface phenomena is the local potential. Recent efforts to more thoroughly understand local surface potentials include calculations of the orbital splitting of atoms approaching a metal surface,[1] studies of dipole moments and polarizabilities of adsorbed atoms[2] (both ground-state effects), and analysis of charge transfer and screening effects at metal surfaces which accompany various photon and electron excitation phenomena.[3-5] One particular focus of work on this problem has involved excitation properties of rare-gas atoms[6-13] on metal surfaces, i.e., systems which have well-defined ground states.

Waclawski and Herbst[6] conducted one of the first photoemission investigations of a rare-gas monolayer on a metal surface. They reported significant broadening of the $5P_{3/2}$ component of the spin-orbit split $5p$ level of Xe physisorbed on W(100), and attributed the broadening to unresolved splitting resulting from the surface crystal field. This interpretation stimulated several model calculations[7-9] and additional experiments[10] aimed at testing the hypothesis of surface crystal fields in more detail. These calculations, and subsequent experiments,[10,12] which were conducted under more carefully controlled conditions, have shown that the broadening of the $5P_{3/2}$ line observed by Waclawski and Herbst at full monolayer coverages was not due to crystal-field or image charge effects.[7,8] In this case, the line broadening resulted from Xe-Xe interactions as shown by angle-resolved photoemission determination of the Xe-band dispersion throughout the surface Brillouin zone and comparison with results of simple tight-binding calculations.

More recent experiments by Opila and Gomer[13] have again raised the issue of surface image dipole or crystal-field effects in relation to the photoemission spectra of physisorbed rare-gas atoms on metal surfaces. In these carefully conducted experiments a very convincing case is presented in support of the existence of a mechanism, unrelated to adatom-adatom interactions, which splits the $5P_{3/2}$ line of rare-gas atoms on W(110). This result is in contrast to the null result obtained by Erskine[10] under similar experimental conditions for Xe on W(100).

We have recently conducted extensive photoemission studies of physisorbed rare-gas atoms on single crystal NiAl alloy surfaces[14] to investigate surface stoichiometry and local work functions as probed by the photoemission of adsorbed xenon (PAX) technique.[15] During this study we observed splitting of the $5P_{3/2}$ component of photoexcited Xe atoms on the NiAl(110) surface, but not on the (100) surface of the same ordered alloy. The splitting was observed using experimental conditions under which Xe-Xe interactions are negligible (i.e., low coverages), leading to the conclusion that the splitting is similar in nature to that reported by Opila and Gomer. We have conducted additional experiments on Ni(110) and Ni(100) surfaces which yield the same result, i.e., that the lower-symmetry surface produces splitting of the $5P_{3/2}$ line. The purpose of the present Brief Report is to present these results which suggest that splitting of the $J=\frac{3}{2}$ component of photoexcited Xe atoms physisorbed at low coverage on (110) surfaces results from the lower coordination symmetry of the adsorption site.

Experiments reported here were conducted using an Auger-photoelectron spectrometer[10] equipped with low-energy electron diffraction (LEED) optics and a cold stage manipulator capable of sample temperatures ranging from 1200 to below 30 K. The $\frac{3}{8}$-in.-diam × $\frac{1}{16}$-in.-thick NiAl(110) samples were aligned to $\pm 1°$ using x-ray Laue techniques, and spark cut and mechanically polished using alumina powder to 0.05-μm grit. *In situ* cleaning using Ne ion sputtering (500 eV, 10 μA/cm^2) and annealing to 800 °C yielded clean, well-ordered surfaces. Auger analysis of the clean surfaces, our work[14] in which work-function changes were studied, and chemisorption experiments[16] involving CO indicate that the well-annealed NiAl(110) surfaces exhibit a stoichiometry (ratio of Ni to Al) equal to the bulk value (i.e., 1 to 1). Recent LEED studies of this surface suggest a reconstruction involving atomic rippling,[17] which consists of small displacement of the surface atoms (~ 0.08 Å) perpendicular to the surface. Extensive angle-resolved photoemission studies[18] of the NiAl(110) surface using synchrotron radiation have yielded bulk band structure in good agreement with calculations. These experiments constitute additional characterization of the NiAl(110) surface.

Our interpretation of the splitting of the $5P_{3/2}$ peak in terms of local-substrate-related fields rather than adsorbate-adsorbate coupling relies on accurate knowledge of the surface conditions, including substrate order and composition, which was just discussed, as well as adatom coverage and spatial distributions. Adatom concentration was accurately calibrated at integral monolayer coverages by analysis of multipeak spectra resulting from layer-dependent *NOO* Auger energy shifts,[10] and checked using $5P$ valence level shifts observed in photoemission spectra. Uniform Xe layers of $n=1$, 2, and 3 monolayers could be obtained by adsorption followed by carefully monitored annealing. Submonolayer coverages were determined from work-function changes, which are roughly linear in the 0–0.5-ML range, and from the intensity of the angle-integrated photoemission peaks relative to the NiAl d bands measured in the same configuration used in calibration experiments. Sample temperatures during and after adsorption were maintained below 40 K to ensure low surface mobility of the adsorbed rare gases. No evidence of island or cluster formation of Xe atoms was observed in photoemission (i.e., $k_{\parallel}$ dispersion of peaks) or by LEED analysis at these temperatures. Weak halos having sixfold symmetry were observed in LEED studies of low coverage Xe films only after annealing to ~ 100 K, indicating that temperatures in this range are required to induce island formation.

Figure 1 displays angle-resolved electron energy distribution curves (EDC's) for various coverages of physisorbed Xe on NiAl(110) at $T \sim 30$ K. Various features[18] of the d bands of NiAl along the Λ direction of the three-dimensional Brillouin zone are apparent in the energy range within 5 eV of the Fermi energy, E_F. Submonolayer Xe spectra exhibit two primary peaks corresponding to the $5P_{1/2}$, $5P_{3/2}$ states of the ion. Spectra for coverages greater than one monolayer exhibit two additional peaks which increase in strength with coverage. These are the second layer peaks, which are shifted to higher binding energy due to less effective screening of the ion (relaxation shifts), and which were used in thickness calibration.

Close inspection of the $5P_{3/2}$-derived peaks corresponding to low coverage reveals that it is not symmetric as is the $5P_{1/2}$ peak at equal coverage. Figure 2 illustrates, on an expanded scale, the two peaks for equal coverages of Xe on NiAl(110) and on NiAl(100). One does not expect to be able to resolve the actual crystal-field splitting of the $P_{3/2}$ level because the *intrinsic* broadening of the lines due to relaxation mechanisms related to the presence of the metal surface is approximately equal to the splitting. The inset of Fig. 2 compares results of curve fitting the two EDC's using three Gaussian functions, assuming that the $5P_{3/2}$ component in each case is composed of two Gaussians having the same width as the $5P_{1/2}$ component. This analysis shows that splitting of the $5P_{3/2}$ line is approximately 0.35 eV.

There are no detectable shifts in peak positions as a function of Xe coverage at low coverages. This coverage independence suggests that splitting of the $5P_{3/2}$ line results from coupling between the screened ion and the substrate rather than with neighboring Xe atoms. The annealing experiments which established the temperature at which islands did form also eliminated the possibility that the independence of binding energy with coverage resulted from islands or clusters of constant density at all coverage.

We have carried out corresponding experiments involving low coverage Xe layers on Ni(100) and Ni(110). These experiments yield a similar splitting of the $5P_{3/2}$ peak for Xe on the Ni(110) surface but not on the Ni(100) surface. Close inspection of experimental results of Jacobi and Rotermund,[19] which were obtained under similar experimental conditions, also reveals a split $5P_{3/2}$ level for low coverages of Xe on Ni(110), in agreement with our results. Our previous search for crystal-field splitting on the W(100) surface revealed no splitting of the $5P_{3/2}$ level,[10] but photoemission studies of Xe of Opila and Gomer on the W(110) surface exhibit splitting of this level.[19] Based on these experimental data,[7] it appears that the splitting of the $5P_{3/2}$ state could be related to the reduced symmetry of the adsorption site on the (110) surfaces.

To validate this possibility, one must be convinced that the (110) and the (100) faces of W, Ni, and β-NiAl can and probably do yield qualitatively different local environments

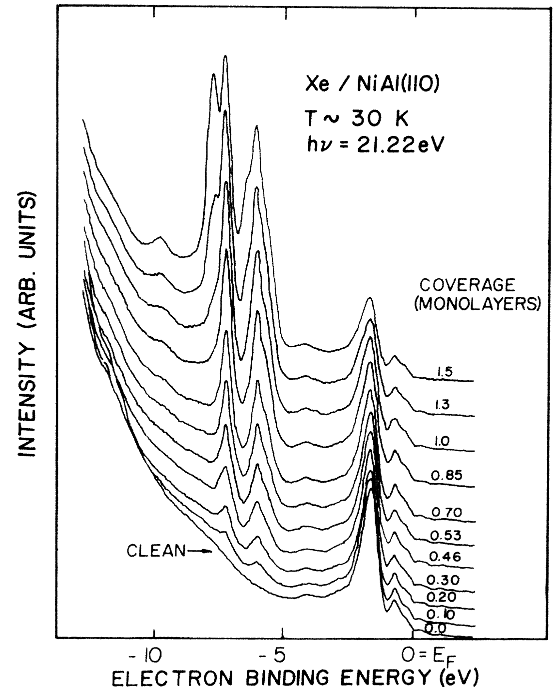

FIG. 1. Angle-resolved photoemission spectra for Xe adsorbed on NiAl(110) as a function of Xe coverage.

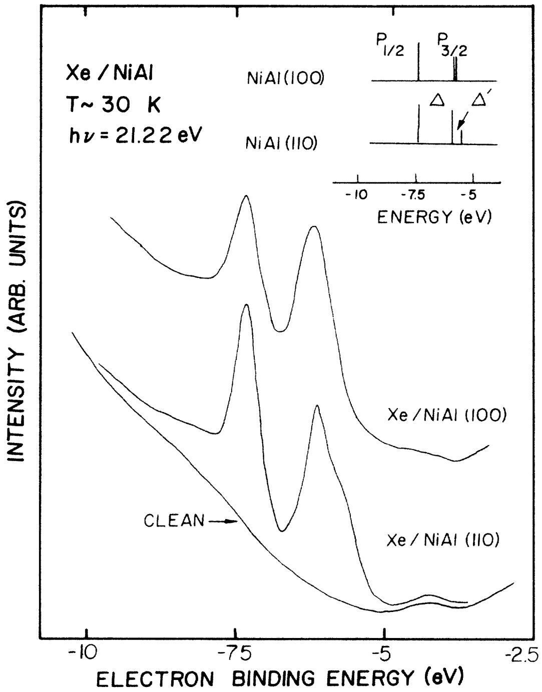

FIG. 2. Expanded scale of angle-resolved photoemission spectra for Xe adsorbed on NiAl(110) and NiAl(100) surfaces. Inset, line intensities as determined by Gaussian fitting of the data. Values of the splitting are Xe on NiAl(110), $\Delta = 1.22 \pm 0.04$ eV, $\Delta' = 0.37 \pm 0.4$ eV; Xe on NiAl(100), $\Delta = 1.20 \pm 0.04$ eV, $\Delta' = 0.06 \pm 0.06$ eV.

TABLE I. Polar-angle dependence of $5P_{1/2}$ and $5P_{3/2}$ linewidths of photoemission spectra for Xe adsorbed on NiAl(110). Photon energy $h\nu = 21.22$ eV, sample temperature $T \sim 30$ K. Angle is measured from the sample normal along the [1$\bar{1}$0] direction; center and width energies are in eV. Angular resolution ±4°.

	$5P_{1/2}$		$5P_{3/2}$	
Polar angle	Center (below ϵ_F)	Width	Center (below ϵ_F)	Width
0°	7.05	0.54	5.83	0.75
10°	7.05	0.53	5.83	0.70
20°	7.05	0.52	5.83	0.67
30°	7.05	0.50	5.83	0.63
40°	7.05	0.50	5.83	0.63

for adsorbed Xe. For physisorbed atoms, at *low coverage*, the preferred site will most likely be the deepest hollow sites in a surface unit cell. For bcc W(100), Xe should physisorb at the C_{4v} fourfold hollow site; for W(110) the corresponding site has C_{2v} symmetry. In the case of fcc Ni, again, the preferred surface site on the (100) face will have C_{4v} symmetry, and C_{2v} symmetry on the (110) face. The crystal structure of β-NiAl is the CaF_2 (cubic) structure. Here again, the (100) surface offers only C_{4v} sites, whereas the (110) surface offers C_{2v} sites. Qualitatively, the argument of a symmetry based origin of the splitting appears valid.

Herbst[9] has investigated theoretically the angular dependence of photoelectrons from atoms adsorbed on metal surfaces, taking into account the effects of the substrate atoms. Although none of the specific results obtained by Herbst apply directly to Xe adsorbed in the C_{2v} site on NiAl, one of the general characteristics of the model should apply. This characteristic is that the polar-angle variation of photoelectron emission associated with component lines of a crystal-field split level will be different.

Table I illustrates the experimentally determined polar angle dependence of the $5P_{1/2}$, $5P_{3/2}$ linewidths for Xe on NiAl(110). The intrinsic broadening is too large to clearly resolve the $5P_{3/2}$ state splitting (as shown in Fig. 2). However, two features are clear from our polar-angle-variation data. First, the binding energies of the $5P_{1/2}$ and $5P_{3/2}$ states are independent of polar angle, confirming that lateral interactions (which would produce band dispersion) are not present. Second, the $5P_{1/2}$ linewidth is nearly constant, whereas the $5P_{3/2}$ linewidth changes significantly, as would be expected if the intensity ratio of the component lines changed. This constitutes additional evidence of a local crystal-field origin of the splitting.

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[1] P. V. S. Rao and J. T. Waber, Surf. Sci. **28**, 299 (1971).
[2] T. C. Chiang, G. Kaindl, and D. E. Eastman, Solid State Commun. **41**, 661 (1982).
[3] N. D. Lang, Phys. Rev. Lett. **46**, 842 (1981).
[4] N. C. Giles and C. M. Varma, Phys. Rev. B **23**, 5600 (1981).
[5] N. D. Lang and A. R. Williams, Phys. Rev. B **16**, 2408 (1977).
[6] B. J. Waclawski and J. F. Herbst, Phys. Rev. Lett. **35**, 1594 (1975).
[7] P. R. Antoniewicz, Phys. Rev. Lett. **38**, 374 (1977).
[8] J. A. D. Matthew and M. G. Devey, J. Phys. C **9**, L413 (1976).
[9] J. F. Herbst, Phys. Rev. B **15**, 3720 (1977).
[10] J. L. Erskine, Phys. Rev. B **24**, 2236 (1981).
[11] K. Horn, M. Scheffler, and A. M. Bradshaw, Phys. Rev. Lett. **41**, 822 (1978).
[12] M. Scheffler, K. Horn, A. M. Bradshaw, and K. Kambe, Surf. Sci. **80**, 69 (1979).
[13] R. Opila and R. Gomer, Surf. Sci. **127**, 569 (1983).
[14] M. Onellion and J. L. Erskine (unpublished).
[15] K. Wandelt, J. Vac. Sci. Technol. A **2**, 802 (1984).
[16] W. K. Ford (private communication).
[17] H. L. Davis and J. R. Noonan, Phys. Rev. Lett. **54**, 566 (1985).
[18] W. K. Ford, E. W. Plummer, J. L. Erskine, and D. Pease, Bull. Am. Phys. Soc. **29**, 523 (1984).
[19] K. Jacobi and H. H. Rotermund, Surf. Sci. **116**, 435 (1982).