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Photoionization Line Shape of the Surface State on W(100)

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Surface-state photoemission from W(100) is observed for photon energies up to 40.8 eV, contrary to previous measurements. The linewidth of this feature shows an excitation-energy dependence, which extrapolates to the field-emission value. Asymmetric broadening occurs at higher photon energies and is interpreted in terms of many-body effects associated with a heavy-hole state, implying a relaxation shift of the energetic position of the surface state.

A strongly surface-sensitive feature is observed in photoemission[1-3] and field-emission[4,5] spectra from tungsten and molybdenum (100) crystal faces at an energetic position 0.4 eV below the Fermi level, E_F. This feature has been attributed[6] to a surface state located in the uppermost d-band spin-orbit gap, based on the prediction of similar states in the sp-d hybridization gap[7] at much lower energies. Recent calculations[8] support this view. However, subsequent studies[9-11] raised doubts as to the detailed nature of the origin of the observed peak. The intensity of this peak has been found to be substantial for photon energies from 7.7 to 16.8 eV,[12] in agreement with the assignment to a surface state. However, Waclawski and Plummer[1] (WP) reported a sharp decrease in intensity at a photon energy of 21.2 eV, extrapolating to zero surface-state emission at around 23 eV. In a subsequent paper, Egelhoff, Linnett, and Perry[13] (ELP) interpreted their results at 16.8- and 26.8-eV photon energy as indicative of surface-state photoemission occurring only at photon energies below the bulk plasmon frequency of about 23 eV for tungsten. This leads to the conclusion that the intensity of surface-state excitation is critically dependent upon the degree to which the dynamic polarization screening of the local photon field at the surface allows photoionization to occur via the $\vec{p}\cdot\vec{A}$ term of the operator in the photoexcitation matrix element.

In this Letter we report the result of a study of the photoexcitation-energy dependence of the *intensity* of the surface-state feature on W(100) and show that emission continues to be observed for photon energies up to 40 eV. In addition the *width* of the peak is observed to increase asymmetrically with photon energy, extrapolating smoothly to the field-emission value for energies below E_F. The excitation-energy dependence of the line-shape asymmetry is interpreted as arising from many-body effects associated with the creation of a heavy-surface-state hole in the pho-

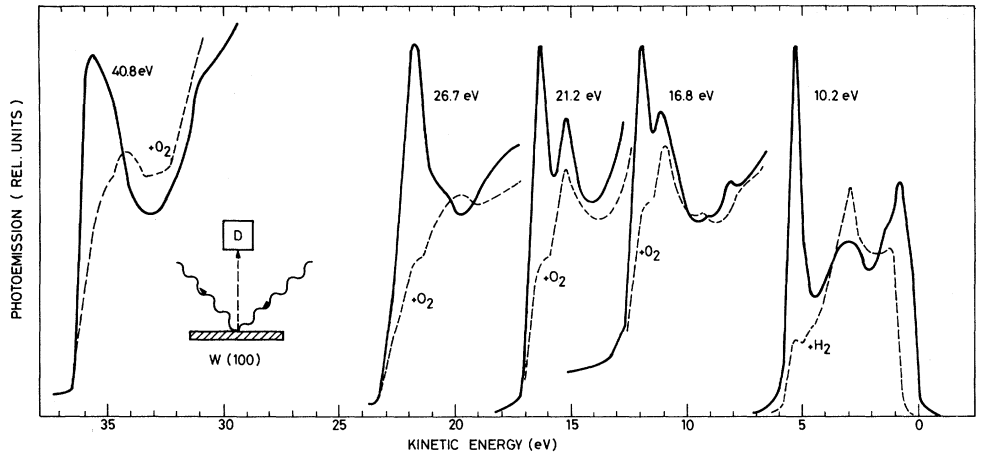

FIG. 1. Energy distribution spectra of photoelectrons emitted normal to a (100) surface of tungsten for various photon energies (only high-kinetic-energy part shown for $\hbar\omega > 10.2$ eV). Full curves, clean spectra; dashed curves, spectra after saturation coverage of O_2 or H_2. The curves are normalized to the surface-state feature, which is the pronounced peak at the high-energy edge of the clean spectra.

toionization process, analogous to photoemission from tightly bound core levels discussed by Gadzuk and Šunjić.[14] The implication is that the observed hole state is subject to a relaxation shift, such that its energetic position does not coincide with the electron-state energy of the surface state prior to excitation. This would suggest that the origin of the W(100) surface state is not necessarily located in the uppermost ("relative") spin-orbit gap, but could arise in the lower ("absolute") d-band spin-orbit gap[15] or even the sp-d hybridization gap, depending on the magnitude of the relaxation shift involved.

The measurements were performed in an angle-resolved electron spectrometer[15] accepting electrons emitted normal to a W(100) surface within a $2° \times 2°$ angle. Energy analysis was performed by means of a 127° electrostatic-deflection analyzer with a theoretical resolution of 1% at a fixed band-pass energy of 10 eV. Photoemitted electrons were retarded or accelerated between crossed slits to ensure minimum transmission change within a spectral scan. The light, incident at 45° onto the sample, was generated in a dc capillary-discharge resonance light source sealed with a 1000-Å thick aluminum window, so the vacuum in the experimental chamber could be maintained in the 10^{-10} Torr range. The results are presented in Fig. 1, where the highest-kinetic-energy part of the spectra measured at photon energies between 10.2 and 40.8 eV is shown for the clean surface and after saturation adsorption of O_2 or H_2. All data are normalized with respect to the amplitude of the surface-state emission, which is the dominant peak in the "clean" curves at 0.4 eV below the cutoff. This structure is strongly attenuated in the spectra taken after gas adsorption. Figure 1 shows that emission from the surface state is clearly defined for excitation photon energies up to 40.8 eV.

The data shown in Fig. 1 would appear to be in conflict with previously published results of other workers.[1,13] WP observed a sharp decrease in the photoemission yield of the surface state relative to the bulk at an excitation energy of 21.2 eV, which extrapolated to zero intensity for photon energies exceeding 23 eV. This prompted ELP to interpret their spectra, simultaneously obtained at 16.8- and 26.7-eV photon energy, as evidence for vanishing photoionization cross section for surface-state emission at 26.7 eV photon energy. While the absolute cross section for the ionization of the surface state cannot be determined from the present photoemission measurements, a measure of the yield from the surface state relative to the bulk yield as a function of photon energy can be obtained by comparing the area difference under the peak for the clean spectrum with that following gas adsorption for an energy range of ± 1 eV about the peak maximum of $E - E_F \sim -0.4$ eV.[1] By use of this procedure, the present results (Fig. 1) show agreement with the behavior previously observed for photon energies of 16.8 eV and below.[1,13] However, the relative photoionization cross section remains at a value close to unity at 21.2 eV photon energy, in contrast to the value of approximately 0.15 found by WP but in agreement with observations of Egel-

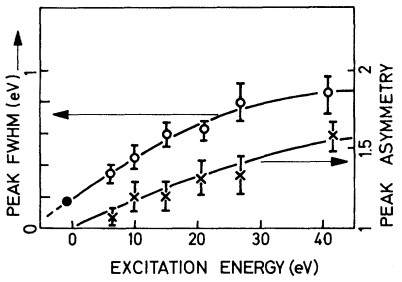

FIG. 2. Full width at half-maximum (top curve, left scale) and line asymmetry (lower curve, right scale) of the surface-state peak as observed using different excitation energies. Line shapes are evaluated from the difference between clean and adsorbate covered spectra. The value for -0.4 eV (full circle) is taken from field-emission spectroscopy (Ref. 18).

hoff, Lennett, and Perry,[16] and other work.[17] The relative cross section at 40.8 eV is close to 0.5 so that significant emission intensity is still observed at photon energies *above* the bulk-plasmon frequency of tungsten.

An interesting feature of the spectra displayed in Fig. 1 is the fact that the surface-state peak increases in width with increasing photon energy, developing an asymmetric shape with a low-energy tail at high excitation energies. The half-width of the peak has been evaluated from the difference between the clean and gas-covered curves, and the result is plotted in Fig. 2, together with the observed asymmetry, i.e., the ratio of the low-energy half-width to the high-energy half width. A remarkable feature of this result is that the decrease of peak width with decreasing photon energy extrapolates to the value observed by Plummer and Bell[18] in field-emission spectroscopy, where the surface-state peak is only 0.2 eV wide and shows no asymmetry. The large discrepancy between the peak width observed in photoemission or field emission has long been a puzzle,[8,15,17] for which the present results possibly give a clue to a solution.

Many effects may act to broaden sharp structure in low-energy photoemission spectra from solids. The mere presence of the surface removes the periodicity normal to it, giving rise to a relaxation of the bulk k-vector selection rule. This "momentum broadening" is present in solids independent of the hot-electron lifetime. A short electron mean-free path, or electron lifetime, leads to "lifetime broadening." Both momentum and lifetime broadening smear sharp structure arising from the k-vector selection rule in the joint density of states, so that the maximum width that can be caused by such effects is limited to the initial-state bandwidth. However, the bandwidth of the W(100) surface state appears to be quite small. Its dispersion *normal* to the (100) surface plane is less than 0.2 eV as revealed by field-emission measurements[18] which effectively integrate over normal-k-vector values. Recent photoemission measurements of the variation of the energetic position of the surface-state peak with polar emission angle[15] indicate a dispersion of the band *parallel* to the surface plane to be less than 0.2 eV; the peak is well defined only over a limited range of $\vec{k}_{\parallel} < 0.5$ Å^{-1} of the surface-Brillouin-zone dimensions. Therefore, the bandwidth is such that broadening mechanisms affecting the k-vector selection rule cannot explain a peak width (full width at half-maximum) of the order of 0.5 to 1 eV as observed here for higher photon energies (Fig. 2). An asymmetric line shape may be produced by inelastic losses of the excited electron by interaction with the Fermi sea, giving rise to electron-hole pair production and plasmon excitation. It is difficult to assess the magnitude of broadening introduced by such a process for this special case of emission from a surface state, where losses to the bulk are likely to be small. Some indication of such effects should be apparent from results of low-energy electron scattering experiments. Electrons of about 25 eV reflected from a tungsten surface indeed exhibit an asymmetric line shape with a low-energy tail, but the observed width of the elastic peak is only of the order of 40 meV which is negligible compared to the widths observed in Fig. 1.

The above field-emission[18] and photoemission[15] measurements are indicative of emission from a narrow, flat, band state. The observed broadening could therefore be due to many-body effects associated with the relaxation of the *heavy* hole left behind in the photoemission process, as predicted[19] and observed[20] for x-ray emission from core levels. Here a "sudden" photoionization event leaves the emitter and the hole in an excited state, which subsequently relaxes to its ground state. The low-energy excited states of a metal are electron-hole pairs created across the Fermi surface. Electrons emitted with the highest kinetic energy correspond to the fully relaxed hole state, and an asymmetric tail of lower-energy electrons arises from these excited states of the metal plus hole, in complete analogy to "shake-up" structure observed in atomic photoionization. If the ionization process can be re-

garded as "adiabatic," such that at low excitation energies the system can adjust to the slow change in potential due to the creation of a hole, a sharp photoelectron line is observed at the fully relaxed position, i.e., the highest possible kinetic energy. The photoemission line shape is therefore excitation-energy dependent, as discussed by Gadzuk and Šunjić,[14] who have also shown that the adiabatic-sudden transition cannot be observed in most core-level spectroscopies since the energy of the excited electron is usually far enough above threshold that the sudden approximation always applies. The present data, Fig. 2, would indicate a transition from the extreme adiabatic limit of slow tunneling in field emission, up to the sudden limit operating at excitation energies of 40 eV and above. The field-emission experiment consequently observed the line unbroadened and symmetric at the fully relaxed position, whereas the photoemission spectrum exhibits asymmetric line broadening due to "shake-up" processes at the emitter Fermi surface.

A most interesting consequence implicit in such an interpretation is that of an associated relaxation shift in the energetic position of the surface-state feature. Shake-up processes are intimately related to relaxation shifts, a fact that may be quantified by a sum rule.[21] With no relaxation the emitter is left in the hole ground state (even in the sudden approximation), so no low-energy tail is observed. The observation of an excitation-energy-dependent asymmetric line shape therefore is an indication of a many-body relaxation shift. This, in turn, implies that the initial-state energy of the surface state, derived by subtracting the photon energy from the observed electron kinetic energy, is the relaxed hole-state energy rather than the occupied electron-state energy. The same holds for the state observed in field-emission spectroscopy. The associated electron state will therefore have a higher binding energy than is apparently observed, i.e., a lower initial-state energy. The actual magnitude of relaxation shift cannot directly be observed. In principle sum rules[21] should allow the initial-state energy corresponding to Koopman's theorem to be determined, but the presence of a low-energy secondary-electron cascade makes their evaluation difficult in ultraviolet photoemission spectra. The present results would suggest, however, that the relaxation shift amounts to at least a few tenths of an eV, sufficient to move the surface-state energy from a position in the upper, relative, spin-orbit gap near the Fermi level[22] to the lower, absolute, spin-orbit gap. If surface-plasmon satellites could be detected at higher excitation energies, this would indicate an even larger relaxation shift, placing the surface state at lower energies, perhaps right into the sp-d hybridization gap, where it was originally postulated.[7]

The present results would indicate that the detailed study of the line shapes of similar sharp photoemission features, using synchrotron radiation as a continuous light source, could help to identify the degree of localization of surface states or adsorbate-induced states at surfaces. Such measurements would provide an estimate of the magnitude of possible relaxation shifts, depending on the degree of localization of the emitter hole state. The effects observed here are expected to be much weaker for surface states having a large bandwidth parallel to the surface, as, for example, on the (111) face of silicon.

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Nonuniqueness of Freezing Temperature of Spins in Binary Alloys

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Small-angle neutron scattering measurements on *Au*Fe alloys containing 10 and 13 at.% Fe are reported. These show a series of q-dependent freezing temperatures [sharp discontinuities in the forward scattering intensity $I(q)$ as a function of T] in contrast to a unique freezing temperature (sharp cusp) observed in the low-field magnetic susceptibility of the alloys.

Spin-glasses or binary alloys such as *Cu*Mn, *Au*Fe consisting of a small concentration of magnetic atoms (e.g., Mn, Fe) distributed substitutionally and randomly in a nonmagnetic metallic matrix (e.g., Cu, Au) have been the subject of renewed theoretical interest recently since the discovery of sharp cusps in their low-field magnetic susceptibility[1] which provide additional support to the "sharp transitions" observed in their Mössbauer hyperfine spectra.[2]

There is a growing tendency to interpret the sharp cusp as indicating a magnetic phase transition and indeed several apparently successful theoretical attempts have been made in this direction.[3] There remain, nevertheless, unexplained complexities, such as the specific heat which shows a broad maximum instead of a sharp, λ-type anomaly predicted theoretically.[4] The idea of a sharp magnetic phase transition in a system consisting of spins distributed randomly and interacting via the long-range oscillatory Ruderman-Kittel-Kasuya-Yosida exchange interaction is physically not very obvious, and other interpretations of the observed physical properties could also be considered.

Magnetic susceptibility data on many spin-glasses, such as *Au*Fe for example, show that the spins are correlated to a certain degree into superparamagnetic clusters well above the freezing temperature.[5] This is an important characteristic of spin-glasses in general which may be explained in simple terms. Within a random substitutional solid-solution system there are wide, statistical fluctuations in concentration of solute atoms over a suitably chosen microscopic scale. Spins within the more concentrated regions become correlated, in general without particular directional order, when their interaction energy $H_{\rm int}$ becomes comparable to or greater than the thermal energy kT. Such regions of correlated spins evolve progressively in size with decreasing temperature as more distant spins also become correlated resulting in an increase of the anisotropy energy E_a of the magnetic clusters which will be related in some way to the total number of spins within them. At any finite temperature the spin system may be considered as subdivided into interacting regions of correlated spins, or magnetic clusters, of various sizes. In the framework of the Néel theory of superparamagnetism,[6] the relaxation time of a particle consisting of a number of correlated spins varies exponentially with its anisotropy energy E_a and the inverse temperature $1/T$ as given by the formula

$$\tau = \tau_0 \exp(E_a/kT), \tag{1}$$

where τ_0 is some characteristic relaxation rate of the spins and k the Boltzmann constant.

As in the case of superparamagnetic particles, when the relaxation time τ becomes long compared with the "measurement time" the magnetic clusters will appear frozen, such that the magnetic susceptibility, for example, will no longer follow the Curie-Weiss behavior. This idea has been applied previously to a discussion of magnetic properties of *Au*Fe alloys[7] and more recently in a semiqualitative theory of spin-glasses by Smith.[8]

The above arguments lead us to expect a whole