Energy dependence of cross sections in inverse photoemission

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Two general types of energy-dependent cross-section variations are demonstrated for inverse photoemission: (i) an atomic effect based on the spatial extent of the wave function and (ii) a solid-state effect caused by peaks in the Fourier spectrum of bandlike states. As examples, data are shown on the photon-energy dependence of (i) the $5d$- to $4f$-intensity ratio in Gd and (ii) the intensity of broken-bond states on Si(111).

I. INTRODUCTION

Inverse photoemission (or bremsstrahlung spectroscopy) has been used in a manner similar to photoemission for obtaining the energy and momentum distributions of unoccupied electronic states.[1,2] Tunable photon energy can be used as an additional parameter. In the following, we are concerned with the photon-energy dependence of the cross section for inverse photoemission which has rarely been utilized because of a lack of tunable photon detectors. From photoemission work with tunable synchrotron radiation it is known that several interesting and useful effects exist. They can be classified into two groups pertaining to angle-integrated and angle-resolved measurements, respectively.

Different trends in the angle-integrated excitation cross section versus photon energy[3–8] have been utilized to separate states with different orbital symmetry. For example, the very localized $4f$ states in the rare-earth series have an appreciable overlap with the wave function of the outgoing photoelectron not until about 50—100 eV above threshold where the wave function of the photoelectron starts penetrating into the region of the $4f$ wave function.[3,4] The $5d$ states, despite their proximity to the $4f$ states in energy, are spatially more extended and turn on right above the photoemission threshold. Similar conditions exist for the $5f$ and $6d$ states in actinides.[5] Special resonance phenomena, such as autoionization and resonant Auger processes, can be very valuable in identifying orbital symmetries as well. Resonances at core-level thresholds have also been observed in inverse photoemission[9] but will not be considered in detail here.

In angle-resolved photoemission[10] with single crystals, momentum conservation plays an important role in determining which states are seen. Even when no strict momentum selection rules exist, such as for the momentum perpendicular to the surface ($k^{\perp}$) of two-dimensional states at surfaces, there can be strong cross-section variations due to approximate selection rules which make surface states almost invisible in certain excitation energy regions.[11–14] Angular symmetries can have a similar effect via dipole selection rules[15] near symmetry points in momentum space but approximate angular selection rules[16] have been found far away from symmetry points, too.

The matrix element governing inverse photoemission is very similar to the photoemission matrix element.[17] Thus, all the cross-section phenomena described above are expected to occur in inverse photoemission. Their potential has not been realized since tunable photon detectors became available for inverse photoemission only recently.[18,19] This work is a first step in demonstrating that photon-energy dependences exist in the inverse photoemission intensity and that they can be understood qualitatively in terms of atomic and solid-state wave-function overlap.

II. EXPERIMENTAL ARRANGEMENT

The details of the experimental setup are described elsewhere.[19] The tunability of the photon energy is provided by a Seya-type grating monochromator. A loss in the photon acceptance solid angle of two to three orders of magnitude compared with fixed photon-energy detectors is made up by parallel detection of about 100 photon-energy channels with a position-sensitive detector. Other significant features include a Pierce-type electron gun with a BaO cathode. The energy resolution of the system is determined by the electron-energy spread (0.25 eV) at low energies and by the monochromator resolution (5 Å) at high energies. The angular spread is determined mainly by the thermal velocity distribution of the electrons normal to the beam axis and gives 0.1-Å^{-1} momentum resolution.

Gadolinium thin films were evaporated in 10^{-10}-Torr vacuum onto tungsten foils. Annealing up to 600 °C had little influence on the spectra.

The Si(111)-(7×7) surfaces were prepared by etching the oxide film from the surface of wafers and subliming residual suboxides at 1000 °C *in situ*. In order to estimate the bulk contribution to the spectra, the surface states were quenched by an exposure to 1000 L [1 langmuir (L)$\equiv 10^{-6}$ Torr sec] of O_2 which leaves about 1.5 layers of chemisorbed oxygen.[20] The energies were measured with respect to the Fermi level E_F and were referenced to the conduction-band minimum E_c using $E_c - E_F = 0.49$ eV from Ref. 21.

III. ATOMIC CROSS SECTIONS

The photon-energy dependence of an atomiclike inverse photoemission cross section is demonstrated for a case

where theory[3,4] predicts large effects. The $4f$ states have very low cross section near threshold and exhibit a strong peak in the cross section about 200 eV above threshold. By contrast, the $5d$ states turn on rather quickly and start decaying already 30 eV above threshold. This behavior is shown in the ratio of the $4f$ to the $5d$ cross sections calculated[3] for Au in Fig. 1. Since inverse photoemission probes unoccupied states we had to choose an element with partially filled $5d$ and $4f$ shells to demonstrate the effect. Gd metal has approximately the configuration $4f^7 5d 6s^2$ and the inverse photoemission is expected to be dominated by electrons filling the seven $4f$ holes and nine $5d$ holes (see Fig. 1 inset). As Fig. 1 shows, there is very little intensity due to $4f$ states (located about 4.3 eV above E_F) at low initial-state energies, but they dominate[22] at high E_i. For $E_i = 20$ eV we can barely detect $4f$ emission on top of the large $5d$ (not shown) emission. Therefore, we give only an upper limit for the $4f$ intensity at this energy (Fig. 1, right). The $5d$ emission is expected to extend up to about 6 eV above the Fermi level using band-structure calculations and measurements.[23] In our data, the upper edge of the $5d$ states is difficult to locate due to the $4f$ states and to photons produced by electrons that have suffered energy losses before radiatively dropping into an empty $5d$ state. The width of the $4f$ states is ~ 1.2 eV for all energies. In order to obtain a rough estimate of the partial cross sections (here we are not concerned with a quantitative comparison but rather with demonstrating an effect) we have used the intensity of the emission at particular energies as shown in Fig. 1. The quantitative comparison of the measured $4f$- to $5d$-intensity ratios of Gd with the calculation for Au in Fig. 1 suffers from several other uncertainties: The atomic potentials for Au and Gd differ significantly (compare the calculations for Eu versus Au in Ref. 3). No $5d,4f$ cross-section calculations appear to be available for the rare earths over a sufficient energy range. The occupation numbers and binding energies of $5d$ and $4f$ electrons (holes) are different between Au and Gd (10 $5d$ electrons centered around $E_F - 4$ eV and 14 $4f$ electrons around $E_F - 85$ eV in Au; 9 $5d$ holes around $E_F + 2$ eV and 7 $4f$ holes around $E_F + 4.3$ eV in Gd). For the difference in $4f$ binding energy we have corrected somewhat by shifting the calculated Au $4f$ cross-section curve down in energy by 80 eV. Furthermore, the continuumlike $6p$ (and higher) states have been disregarded. Nevertheless, the trend in the ratio of the $4f$ to the $5d$ cross section with E_i can be explained by existing calculations.

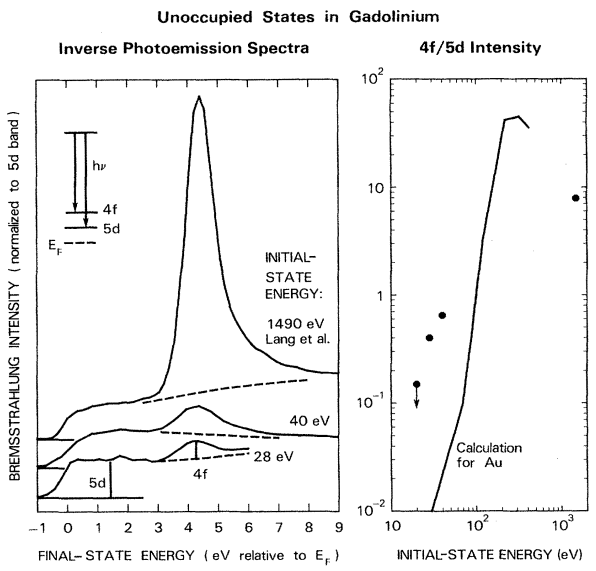

FIG. 1. Inverse photoemission spectra of unoccupied $5d$ and $4f$ states in gadolinium taken at various initial-state energies E_i (see inset) are shown on the left (the $h\nu = 1490$-eV spectrum is from Ref. 22). The $4f$ intensity increases dramatically relative to the $5d$ intensity with increasing initial-state energy. This is due to atomic matrix-element effects as one can see from a qualitative comparison with the calculation for Au (taken from Ref. 3 with the $4f$ threshold shifted down by 80 eV).

IV. SOLID-STATE EFFECTS

In a single-crystal solid, momentum selection rules can strongly modify atomic cross-section variations. The data from polycrystalline Gd are momentum averaged and exhibit mostly atomic effects. The strongest realization of momentum selection rules lies in the concept of direct interband transitions in the bulk whereby only discrete states in momentum space contribute to the photon emission at any given energy and momentum of the incoming electron. This feature has been used for mapping unoccupied energy bands (see Refs. 1 and 2). Here, we are concerned with cross-section variations in the absence of strict selection rules. Substantial intensity variations with

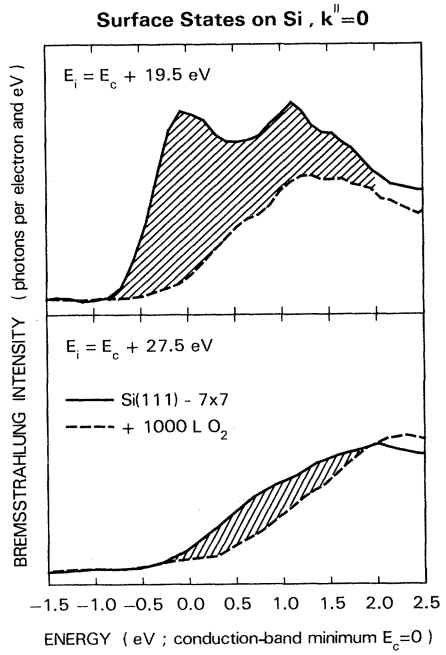

FIG. 2. Momentum-resolved inverse photoemission spectra show surface states on Si(111)-(7×7) (cross-hatched areas). The surface-state intensity depends strongly on the initial-state energy due to an approximate selection rule for the momentum perpendicular to the surface.

photon energy (more than an order of magnitude) have been seen for photoemission from surface states[11–14] where the selection rule for the momentum perpendicular to the surface $k^{\perp}$ is released. With Si(111) we have chosen a system where such effects have been observed for the broken-bond–like surface states near the top of the valence band.[11,24] Analogous unoccupied surface states exist near the bottom of the conduction band,[2,25] because a broken bond represents a half-filled orbital. In Fig. 2, angle-resolved inverse photoemission spectra are shown which allow an estimate of the surface-state emission by subtracting the spectra of an adsorbate-covered surface where the broken bonds are saturated. Two sets of spectra are taken with different initial-state energies E_i but with the momentum parallel to the surface $\vec{k}^{\parallel}$ kept the same ($\vec{k}^{\parallel}=\vec{0}$) thereby not altering the momentum selection rules. Only the $k^{\perp}$ of the initial state is changed by varying the initial-state energy. Relative to the bulk (and on our absolute scale, too) the surface-state emission decreases dramatically when going from $E_i=19.5$ eV to $E_i=27.5$ eV. The same trend has been observed for the occupied surface states with photoemission,[11,24] although not equally strong. The explanation lies in the assumption that the unoccupied surface states are split off from bulk states near the conduction-band minimum and carry mostly Fourier components in their wave function with $k^{\perp}$ similar to these bulk states. For $\vec{k}^{\parallel}=\vec{0}$ the conduction-band minimum is located at the L point (L_1 at $E_c+1.1$ eV; $E_c=$ absolute conduction-band minimum) on Si(111). At $E_i=19.5$ eV and $\vec{k}^{\parallel}=0$ one is close to the L point assuming a nearly-free-electron–like initial state.[11,24] Therefore, the matrix element[12,17] between the initial state and the surface state is large. At $E_i=27.5$ eV one is already halfway towards the Γ point and the Fourier components do not match as well.

In conclusion, we have shown that there exist strong cross-section variations with initial-state energy (and photon energy) in inverse photoemission. Certain states become virtually invisible over a range of initial-state energies. With a tunable photon detector one can utilize these cross-section variations to enhance emission from selected states, or suppress emission from unwanted states.

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