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Directional Photoemission from Three Tungsten Single-Crystal Faces

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Energy distribution spectra have been measured for photoelectrons emitted normal to three tungsten single-crystal faces, namely (100), (110), and (111), for photon energies between 7.7 and 11.7 eV. The spectra show marked differences for the different faces, in agreement with the assumption that the electrons originate from states along different symmetry lines in the Brillouin zone. Structure in the spectra is interpreted in terms of emission due to direct optical interband transitions and surface photoelectric emission.

Photoelectron energy-distribution spectra have generally been measured using energy analyzers which integrate over large emission angles, although a few attempts have been made to resolve the angular distribution.[1-6] Most of these measurements have been interpreted in terms of the bulk electronic structure. In this Letter we present results of measurements of energy distribution spectra of photoelectrons emitted into a narrow cone normal to the emitting surface, which was chosen to be a low-index symmetry plane of a single crystal. Such spectra should be related to the properties of mainly those electrons which have k vectors along that symmetry line in k space that corresponds to the emitting symmetry face, on the assumption that the component of the k vector parallel to the surface is conserved during electron emission[7] (this means $k_{\parallel} = 0$ in the present configuration), and that multiple-scattering effects can be neglected. Since band-structure calculations usually are shown along symmetry lines, the method used here allows a simple and direct comparison of the experimental results with theoretical predictions. Furthermore, the number of observable direct optical transitions is limited in the present experiment, since general points in the Brillouin zone are excluded. Experimental identification of direct optical transitions is possible from the variation of the initial-state energy of the observed photoelectrons with varying photon energy. Therefore, the present method opens up the possibility to distinguish between photoelectron emission due to direct interband transitions and other emission mechanisms.

In this Letter are presented energy distribution spectra of photoelectrons emitted normal to the (100), (110), and (111) faces of tungsten. Measurements have been taken for various photon energies between 7.7 and 11.7 eV. The results are compared with theoretical band-structure calculations. An interpretation of the spectra is attempted in terms of bulk direct interband transitions involving a three-step photoemission process and surface photoelectric emission.

The photoemission spectra were measured using a 127° electrostatic analyzer[8] with a theoretical resolution of 2%. The acceptance angle of the analyzer was 12°, centered normal to the sample surface to within about 1°. Tungsten single crystals were cut along the respective face to within 3°. A low-energy electron-diffraction Auger system within the experimental chamber allowed the sample surfaces to be checked *in situ* for cleanliness and structure. Measurement times and the vacuum in the chamber were such that during one scan the sample exposure time was equivalent to less than 0.05 of a monolayer time. A clean surface was restored after exposure by resistive heating to about 2500°C for several seconds.

The energy-distribution spectra of photoelectrons emitted normal to the three single-crystal surfaces of tungsten are shown in Fig. 1. Each of the three parts of this figure shows a set of spectra obtained for emission normal to the crystal surface indicated in the part. The curves are shifted vertically such that the photon energy at which the spectrum was taken may be read from the right-hand scale. From the measured elec-

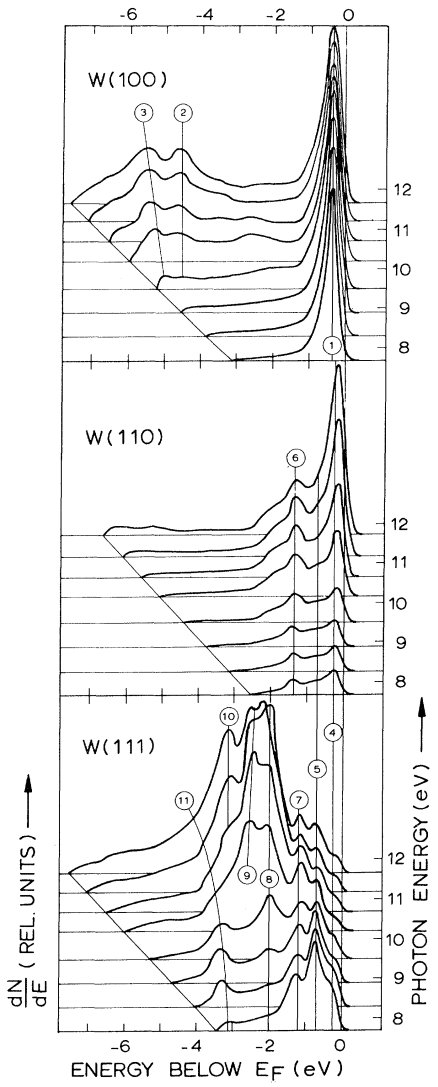

FIG. 1. Energy-distribution spectra of photoelectrons emitted normal to three single-crystal faces of tungsten. Photon energies may be read from the right-hand scale.

tron energies the photon energy has been subtracted and the work function added, so the energies on the horizontal scale refer to initial-state energies relative to the Fermi level. Within each part of Fig. 1 the relative size of the curves is scaled such that the integral is proportional to the total photoelectric yield from the respective surface at the photon energy where the measurement was taken. The relative size of curves from different faces is arbitrarily chosen to facilitate presentation.

The spectra from the three faces look very different, a fact that is in agreement with the idea

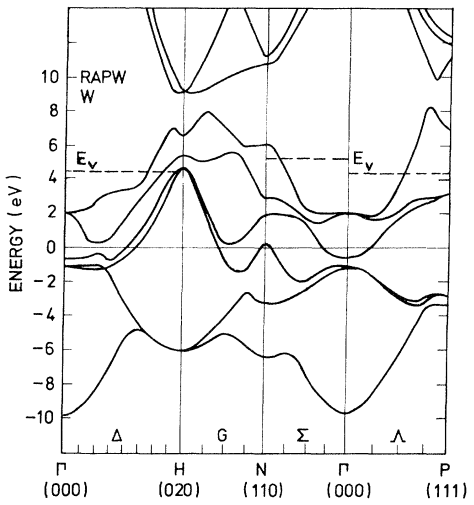

FIG. 2. Band structure of tungsten as calculated by a relativistic augmented-plane-wave method by Christensen (Ref. 9).

that they should carry information from different regions of the Brillouin zone. The various structures will now be discussed with the aid of a theoretical band-structure calculation shown in Fig. 2, which has been obtained by Cristensen[9] from a relativistic augmented-plane-wave calculation. This band structure gives a much better fit to the experimental data than earlier calculations[10,11] even along the ΓH symmetry line, where theoretical data including the relativistic splitting[12,13] were available.

The spectra of photoelectrons emitted normal to the (100) face are dominated by a strong peak about 0.4 eV below the Fermi level, that is nearly independent of photon energy in position and size. This peak, labeled No. 1, has been discussed in terms of emission from surface states in an earlier paper.[14] The assignment to surface-state emission was mainly based on its behavior following gas adsorption, in agreement with the interpretation of field-emission[15] and other photoemission measurements.[16] For photon energies above 9.5 eV, two other structures, No. 2 and No. 3, are emerging. While structure No. 2 is observed to originate from a constant initial-state energy, peak No. 3 is moving to lower energies with increasing photon energy, in a way characteristic for electrons emitted after excitation by direct interband transitions. These structures are consistent with what one would expect from electrons originating from states along the ΓH symmetry line. Here no final states above the vacuum level E_v are available for di-

rect transitions from initial states between the Fermi level and about -4 eV. For photon energies above 9.5 eV, direct transitions are possible from states along the two nearly degenerate lower Δ bands, decreasing in energy with increasing photon energy, in agreement with the observed behavior of structure No. 3. The stationary peak No. 2 is likely to arise from the high density of states associated with the maximum in the lowest Δ band. The electrons in this peak could be emitted by a nondirect excitation mechanism as proposed by Spicer.[17] However, if k was not an important selection rule, high density-of-states regions along other symmetry directions (e.g., near P) should also contribute to the electron emission normal to the (100) face, which apparently is not the case.[18] Therefore structure No. 2 is assigned to surface emission. This assignment becomes more evident from the spectra taken normal to the (110) face, shown in the middle part of Fig. 1. For the symmetry line ΓN, which corresponds to this face, the band structure (Fig. 2) indicates that no direct transitions are possible because of the lack of final states within about 5 eV above the vacuum level E_v. The spectra from the (110) face in fact do not show structure moving in initial-state energy. The absence of final band states means that no Bloch states are available to transport electrons excited in the bulk to the surface with the proper k vector. Therefore it is proposed that the photoelectrons emitted in this case are due to a surface photoelectric effect with excitation directly into the ionization continuum.

A striking feature of the spectra taken normal to the (110) face is the fact that very few electrons are observed from states between -2.5 and -5 eV. This is in agreement with the band structure, which at those energies shows a band gap along the ΓN direction that may be the origin of this lack of photoelectrons. High density-of-states areas, which are present for other directions, do not contribute electrons in this region. This supports the assumption that multiple-scattering effects may be neglected in the present photoemission spectra.

Assuming that the emission normal to the (110) face is a surface photoelectric effect,[19-21] it should be related to the density of states[22] at the surface, which is probably close to the bulk density of states. This, of course, applies also for those regions along other symmetry lines for which no final states are available for direct optical transitions. Comparing the (110) and the (111) face, one finds that the structures No. 4 and No. 5 coincide in these spectra. Structure No. 4, which does not coincide with No. 1,[23] is probably due to the cutoff of occupied states by the Fermi level and therefore a trivial coincidence. The common structure No. 5 is likely to be due to a critical point of the fourth band at Γ common to the two faces. The structures No. 6 and No. 7, however, do not line up. This is in agreement with the band structrure, noting that a density-of-states peak[22] in the third band is expected along ΓN slightly below the critical point at Γ.

For lower initial-state energies, direct transitions are possible from three initial bands along ΓP. Those might be responsible for the strong emission normal to the (111) face, structures No. 8 to No. 11. Except for No. 11, these peaks move very little with photon energy, probably because the initial bands are rather flat and the final band is steep. Some of these structures [e.g., No. 8] are also observed at low photon energies. If the present interpretation in terms of surface and volume photoemission is correct, this would mean that some structure in the surface density of states is rather close to the bulk density-of-states structure.

The observation of peaks due to direct transitions with conservation of the k vector normal to the surface leads to the conclusion that such structure arises from transitions not confined to the surface of the crystal. A lower limit for the penetration depth of the emitted electrons may be estimated from the width of these peaks. On the other hand, emission is observed for directions where no final states are available, which leads to the conclusion that this emission has to be attributed to a surface photoelectric effect. It therefore appears that directional photoemission experiments can permit the separation of the volume and surface contributions to the photoelectric emission.

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Bilinear Dynamics of a CaF_2 Electret*

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The measured strong space-charge electret equilibrium polarization in high-purity CaF_2 follows the form predicted for stored charge in a Schottky barrier. The electret decay obeys simple bilinear dynamics with a thermally activated rate constant. The formation of the electret as well as its decay is directly governed by the sample's bulk ionic conductivity.

This Letter concerns the strong ionic space-charge thermoelectret state in Harshaw optical quality (high-purity) CaF_2. In remarkable contrast with the exceedingly complicated behavior reported for other space-charge electrets,[1,2] we report for the first time, to our knowledge, a strong ionic electret in which the complete decay dynamics can be simply described and a single source mechanism unambiguously identified. Since Bucci and Fieschi[3] introduced their ionic-thermoconductivity method, the impurity-vacancy weak dipolar electrets, which follow linear decay kinetics, have been studied intensively. The extreme complexity of the much stronger space-charge electrets appears, however, to have discouraged all but a few recent research efforts. We have found no theoretical work on bilinear depolarization dynamics of the form we report here. There has, however, been substantial treatment, notably in the work of Perlman and Meunier,[4] Creswell and Perlman,[5] Gross,[6,7] and others,[8-10] of systems showing linear response.

Our experiments used an evacuated ($\sim 10^{-5}$ Torr) metal Dewar capable of spanning the temperature range from 77 to ~5000°K. CaF_2 crystals were cleaved along the (111) plane to a cross section of 1×1 cm^2 and a thickness of 0.8 mm. A polarizing electrode, which can be connected either to a dc power supply or to ground, is placed on one crystal face, and a measuring electrode, which is grounded through an electrometer, is placed on the other face. Inside the Dewar, the sample-electrode structure is electrically in-