Photoemission from (110) Faces of Noble Metals: Observation of One-Dimensional Density of States*

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Photoelectron distribution curves of (110) single-crystal faces of the noble metals Cu, Ag, and Au obtained at photon energies of 16.85 and 21.22 eV show strong contributions which cannot be accounted for by direct k-conserving transitions. Instead we observed a surprisingly good correlation between the measured spectra and the one-dimensional density of states of the bulk band structure. It is supposed that surface photoemission is responsible for the observed effect.

Ultraviolet photoelectron spectroscopic (UPS) studies of single-crystal faces of tungsten by Feuerbacher and Christensen[1] have established the influence of the surface on the photoemission process in several ways. (i) Important contributions in their electron distribution curves (EDC's) were attributed to structures of the local density of surface states, which is characteristically modified compared with the bulk density of states of the corresponding symmetry direction. (ii) It had to be concluded that because of the presence of the surface, transitions are allowed to final states which lie in a gap of the bulk band structure.[2] (iii) A surface resonance was observed. Keeping in mind these results it seems surprising that recent angle-resolved UPS investigations of copper[3,4] and gold[5,6] could essentially be understood by merely considering direct $\vec{k}$-conserving transitions between $E(\vec{k})$ curves of the bulk band structure. Only Gartland and Slagsvold have thoroughly discussed a surface state of the (111) face of Cu.[7]

In this Letter we report on high-resolution measurements of the (110) faces of Cu, Ag, and Au at photon energies of 16.85 and 21.22 eV, where for the first time considerable contributions to angle-resolved EDC's of the noble metals were identified, which cannot be explained by bulk $\vec{k}$-conserving transitions. Instead we found strong correlation of the observed structures with the one-dimensional density of states of the *bulk* band structure. Our observations and conclusions are also different from those reported by Feuerbacher and Christensen,[1] because no definite modification of the bulk density of states near the surface is seen, nor do absolute gaps exist at the relevant final-state energies. Furthermore, no experimental evidence was found for the existence of surface states attributable to these faces. It is important to note that direct transitions were clearly analyzed in our UPS results of the (100) and (111) single crystals of the noble metals, where they are dominant processes.[8] We assume our observations, obtained from Cu(110), Ag(110), and Au(110), to be related to surface photoemission.

The EDC's have been measured by means of a high-resolution photoelectron spectrometer.[9] The samples were prepared from high-purity single crystals; they were cleaned *in situ* by repeated cycles of argon-ion bombardment and subsequent heating. The photoelectrons were measured within a mean cone angle of $\pm 5^\circ$ normal to the surface; the angle of incidence of the light was 80°. The resolution was better than 0.06 eV. The intensity distributions were corrected for the transmission function of the analyzer and normalized. The experimental results are shown in the upper parts of Figs. 1–3. Previous and comparable investigations of these faces have been reported by Nilsson and Ilver for Cu using the same photon energies[3] and for Au at 16.8 eV.[5] Their experimental results are roughly in agreement with ours; the fine structure details of their spectra appear less resolved, especially for Cu.

The most striking result of our experimental data of Cu(110) (Fig. 1) is the full agreement between EDC's obtained at different photon energies. Since other faces of Cu do show distinct direct-transition behavior corresponding to the band structure of the symmetry direction in question, we conclude from the experiment that bulk $\vec{k}$-conserving processes cannot be responsible for the measured structures. This point will be discussed later in more detail. We tentatively related the main features, namely peaks d and a, to transitions from high-density-of-states regions at the X point of the Brillouin zone.

Our qualitative interpretation was then supported by calculations of the one-dimensional density of optical states (DOS) along the ΓKX direction and of angle-resolved EDC's assuming a direct-

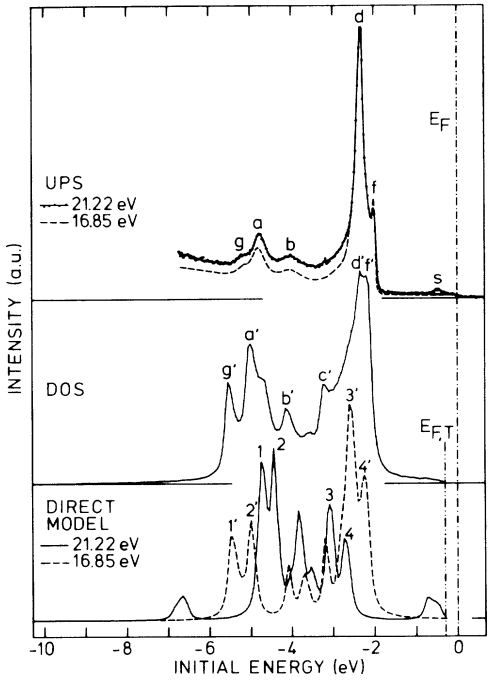

FIG. 1. Comparison among measured EDC's, calculated one-dimensional DOS, and calculated EDC's of Cu(110) (Ref. 10). The calculations are based on the band structure of Ref. 11.

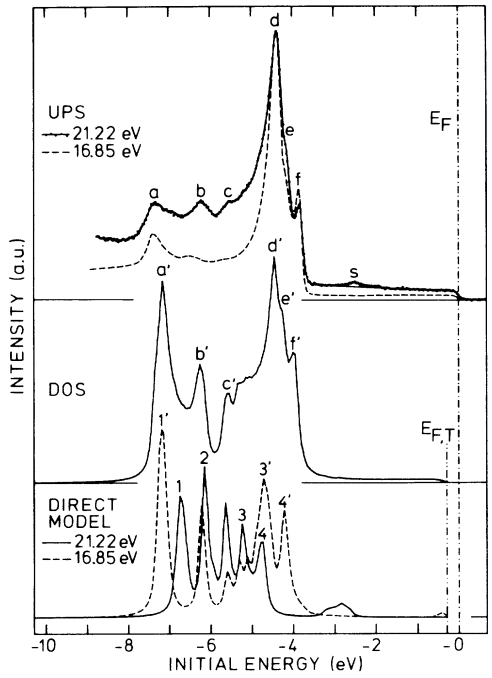

FIG. 2. Comparison among measured EDC's, calculated one-dimensional DOS, and calculated EDC's of Ag(110) (Ref. 10). The theoretical curves, which are based on the band structure of Ref. 12, are shifted to lower energies by 0.2 eV.

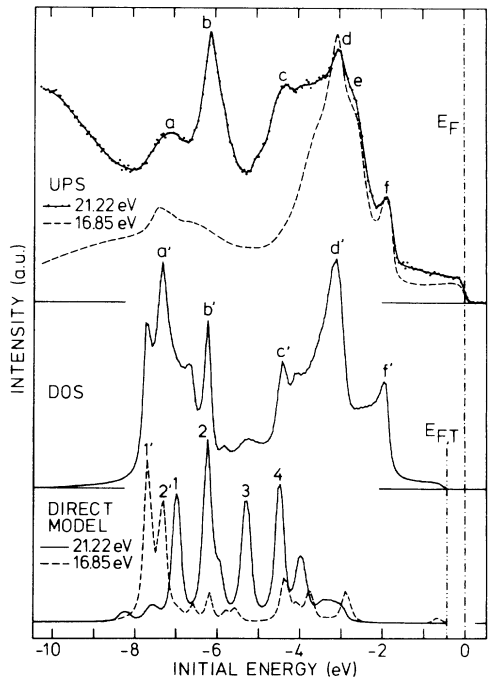

FIG. 3. Comparison among measured EDC's, calculated one-dimensional DOS, and calculated EDC's of Au(110) (Ref. 10). The theoretical curves, which are based on the band structure of Ref. 13, are shifted to lower energies by 0.4 eV.

transition model. The results are shown in the middle and lower parts of Fig. 1. Our calculations were performed under simplifying assumptions by using Burdick's band structure[11] of Cu taking into account the finite angular acceptance of the spectrometer, but neglecting matrix element effects. Nevertheless, we expected the theoretical curves to reveal the general trends of our observations. In fact, the one-dimensional density of states shows surprisingly good correspondence to the experimental EDC's; only the intensity ratio of high- to low-energy structures is somewhat different. It has to be mentioned that the theoretical curves are shifted by 0.3 eV to lower energies, so that the main peaks of DOS and the experimental EDC's approximately coincide.[14] On the other hand, the calculated EDC's show characteristic shifts of peaks upon changing the photon energies (1-1′, 2-2′, 3-3′, and 4-4′). Such shifts are certainly absent in our measured spectra. It is interesting to note that the calculated EDC for 16.85-eV photon energy is also similar to the corresponding experimental spectrum. This fact can be understood, since the possible direct transitions accidentally originate at the same locations in $\vec{k}$ space, where the density of initial states is high.[15]

For the (110) face of Ag the general agreement between the measured EDC's and DOS is even better (Fig. 2) than for Cu, although some minor contributions due to direct transitions might be present. Structures *b* and *c* are slightly different in the EDC's obtained at 21.22 and 16.85 eV; this fact could be understood in principle by considering the corresponding structures in the calculated EDC's.

Our results obtained for Au(110) (Fig. 3) also show contributions which cannot be explained by $\vec{k}$-conserving processes, especially at the high-energy part of the *d*-band region and below the Fermi level, where pronounced emission from the *sp* band is observed. It has to be remarked that emission from the *sp* bands is also clearly visible for Ag and may still be seen for Cu. This observation cannot be accounted for by the calculated EDC's but is to be expected according to the one-dimensional density of states. Direct transitions may eventually be recognized in the 21.22-eV EDC of Au(110), for example, *b* and *c*; however, these structures have counterparts in both the theoretical DOS and the calculated EDC's. More experimental work with intermediate photon energies is needed to clarify the origin of these structures.

We now summarize our knowledge on mechanisms which might be responsible or which have to be excluded, respectively, for the interpretation of our observations. (i) Because of self-energy effects, the participating high-lying conduction bands might become so broadened that the corresponding EDC's should reflect rather closely the density of initial states alone.[16] We rule out this effect, since our results of other faces of the noble metals do show pronounced direct transitions and self-energy effects are not expected to behave so differently for the individual crystal faces. (ii) Our observations can formally be described by the "nondirect" photoemission model previously proposed by Berglund and Spicer.[17] However, we did not find experimental evidence for such contributions to EDC's of other single-crystal faces and *vice versa*. We therefore conclude that "nondirect" transitions cannot be responsible for the observed effect. (iii) With use of photon energy of 11.83 eV, where the probing depth is appreciably increased, the (110) faces also reveal direct transitions.[8] We therefore assume that the measured EDC's at higher photon energies are mainly determined by *surface photoemission* from bulk initial states, which extend directly into the surface region, to free-electron-like states outside the crystal. Because of the matching conditions of the wave functions, these states have to be described as surface states within the crystal, which are degenerate with bulk Bloch-like states. This interpretation is further supported by our special geometry of incidence of the light, where the vector potential of the photon field has strong components normal to the surface and therefore favors surface emission.[18]

The fact that striking similarities between one-dimensional density of states and EDC's are seen so strongly on the (110) faces and not the (100) and (111) faces might be related to the participation of reciprocal lattice vectors in direct transitions. According to Ref. 18 direct transitions are expected to appear with maximum intensity when the vector potential of the light lies parallel to that reciprocal lattice vector which is assisting the direct transition in question in the extended zone scheme. Actually this seems to be the case for the (100) and (111) faces but not for the (110) faces, where the appropriate $\vec{G}(220)$ reciprocal lattice vector is not invoked in energetically possible direct transitions. It has to be mentioned, however, that such behavior was derived for nearly free-electron-like materials and might not be adequate for the noble metals. We therefore believe that a satisfactory explanation of the observed effect can only be obtained by a detailed calculation of momentum matrix elements taking into account the properties of the incident photon field.

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[10]Structures of the measured EDC's (above) are labeled with letters; the label *s* is used for peaks due to a satellite line of the gas discharge lamp. The primed labels of DOS have been chosen to show possible relations to structures of the experimental EDC's. Peaks of the calculated EDC's are denoted with primed (16.85 eV) and unprimed (21.22 eV) numbers; equal numbers mean origin of the peaks from the same initial band. The calculated distribtuions have been folded with a Lorentzian of full width at half-maximum equal to 0.15 eV.

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Exactly Soluble Spin-Glass Model

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An exactly soluble model for a spin-glass phase transition is presented. It is essentially a mean-field theory; but instead of "bond" randomness of the exchange interaction (as used by other authors), a "site" randomness is assumed. This enables one to calculate the "quenched" free energy without any uncertain mathematical procedures. Typical results are given for a variety of interesting cases.

There is considerable experimental evidence[1] that in certain magnetically dilute solid solutions ("spin-glasses") a new kind of phase transition takes place. In this spin-glass phase, the moments are frozen into a disordered arrangement with no or little long-range order present. There is now a reasonable model for these transitions[2] due to Edwards and Anderson. The Edwards-Anderson model is essentially a mean-field approximation in which the exchange interaction between different pairs of spins is treated as a random variable. The model, in spite of its clear physical basis, suffers from the fact that in order to solve it, one is reduced to rather complicated and questionable mathematical procedures (the "replication" methods).

In this note another mean-field type of model is proposed which, I believe, is as reasonable physically as the Edwards-Anderson model, but still exactly soluble. The model shows all the essential features of the experiment. As usual, we begin with the following Hamiltonian:

$$\mathcal{H} = -\tfrac{1}{2}\sum_{i,j} J_{ij} s_i s_j - \mu_0 H \sum_i s_i, \tag{1}$$

where $s_i = \pm 1$ gives the spin orientation of the ith spin, J_{ij} is the exchange interaction between the ith and jth spins, H is the external magnetic field, and μ_0 is the magnetic moment of each spin. (For simplicity we are assuming an Ising model for the spins, although this is not at all necessary.) The J_{ij} are random variables to be specified later. The partition function $Z[J]$ will depend on all the J_{ij}'s and is given by

$$Z[J] = \sum_{\{s_i\}} \exp(-\beta\mathcal{H}). \tag{2}$$

The corresponding free energy $F[J]$ is

$$F[J] = -\beta^{-1} \ln Z[J]. \tag{3}$$

For this problem, good physical arguments[1] suggest that it is the "quenched" free energy