structure which is closely related to that of the radial distribution function.

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Thermally Induced Breakdown of the Direct-Transition Model in Copper

R. S. Williams, P. S. Wehner, J. Stöhr, and D. A. Shirley
Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

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A strong temperature dependence has been observed for the first time in angle-resolved photoemission (ARP) spectra of the valence band of a crystalline solid. This spectral behavior confirms predictions of a model suggested by Shevchik. A controversial point in the interpretation of ARP spectra at x-ray energies is resolved by this model. Moreover, it dictates the choice of photon energy and sample temperature for future ARP studies of valence-band electronic structure.

Shevchik[1] has suggested that thermal broadening leads to a more complete sampling of the first Brillouin zone (BZ) in angle-resolved x-ray photoemission than would be expected from a rigorous direct-transition model. He expressed the angle-resolved photoemission cross section as the sum of a k-conserving direct-transition term and an atomic term, with the relative contributions of the two being governed by the Debye-Waller factor, which we shall write as

$$f = \exp[-\langle(\vec{q}\cdot\Delta\vec{r}_T)^2\rangle], \tag{1}$$

where $\vec{q} = \vec{k}_f - \vec{k}_i - \vec{k}_{h\nu}$ ($\vec{k}_f$ and $\vec{k}_i$ are the final and initial electron momentum and $\vec{k}_{h\nu}$ is the photon momentum) and $\Delta\vec{r}_T$ is the instantaneous thermal displacement of an atom in the lattice.

The energy distribution function for photoelectrons *inside* a crystal is given by[2]

$$N(E_f,\vec{k}_f,h\nu) \propto \sum_{\vec{k}_i}^{\vec{k}_i\subset\mathrm{BZ}} \sum_{E_j(\vec{k}_i)}^{E_j<E_\mathrm{F}} |\langle E_f(\vec{k}_f)|\vec{A}\cdot\vec{p}|E_j(\vec{k}_i)\rangle|^2 \delta[E_f(\vec{k}_f) - E_j(\vec{k}_i) - h\nu]. \tag{2}$$

where the summations are over the initial momentum states ($\vec{k}_i$) in the first BZ and all occupied energy levels. If electron transport and surface transmission do not alter N significantly, an experimental energy distribution curve (EDC) can be obtained by summing Eq. (2) over the final energy and momentum states (E_f and $\vec{k}_f$) allowed by the finite angular resolution of the measurement and the uncertainty in the component of crystal momentum perpendicular to the sample surface. If we assume a tight-binding initial state and plane-wave final state,[3] the matrix element of Eq. (2) demonstrates a temperature dependence similar to x-ray diffuse scattering theory[4]; i.e.,

$$\begin{aligned}&|\langle\exp(i\vec{k}_f\cdot\vec{r})|\vec{A}\cdot\vec{p}|E_j(\vec{k}_i)\rangle|^2\\ &\quad\propto \cos^2\gamma f \sigma_{ij}(\vec{k}_f)\{\delta(\vec{q}-\vec{G}) + [1-\delta(\vec{q}-\vec{G})][k_\mathrm{B}T(|\vec{q}|^2/|\vec{q}-\vec{G}|^2)\varphi_1 + (k_\mathrm{B}T)^2|\vec{q}|^4\varphi_2(\vec{q}) + \dots]\}.\end{aligned} \tag{3}$$

Here γ is the angle between the electric field polarization vector and $\vec{k}_f$, $\sigma_{ij}(\vec{k}_f)$ is the atomic cross section,[5] $\vec{G}$ is a reciprocal-lattice vector, k_B is the Boltzmann constant, and φ_1 and $\varphi_2(\vec{q})$ involve sums over phonon modes familiar from first- and second-order x-ray temperature diffuse scattering.[4] In Eq. (3) it is assumed that the temperature is high enough that equipartition holds for the phonon modes. From the expectations of low-energy-electron-diffraction (LEED) theory, Eq. (3) will be complicated by multiple-scattering events (i.e., a LEED-type final state) for the photoelectrons which may obscure the simple temperature dependence predicted above.[6] However, the overall trend in the temperature dependence of photoemission peak intensities will obey Eq. (3).

According to Eq. (3) there are two contributions to the photoemission spectrum; one from direct transitions ($\vec{q}-\vec{G}=0$) and one from a phonon-assisted indirect transition process. With increasing *temperature* or *photon energy* this latter process will increase in importance relative to the former. For room-temperature photoemission studies the direct-transition process should dominate in most metals at ultraviolet photoemission (UPS) energies, while the phonon-assisted process is expected to contribute most of the spectral intensity at x-ray photoemission (XPS) energies.[1] This can explain why the direct-transition model fits experiment at low energies[7,8] while a model based on the atomic cross section $\sigma_{ij}(\vec{k}_f)$ in Eq. (3) works better at high energy.[5,9] Shevchik noted that either of these limiting cases might be altered by varying the temperature, i.e., cooling in the XPS case to remove thermal disorder and emphasize direct transitions or heating in UPS to decrease f and emphasize phonon-assisted transitions. We have chosen the latter approach to test the predictions of Eq. (3). The recently discovered "s-p band" resonance[8] in normal photoemission from Cu(110) at $h\nu=45$ eV was employed because of its very high sensitivity to the exact portion of the BZ being sampled, as shown in Fig. 1. This resonance actually arises as the sixth valence band approaches E_F between Γ and K, where band 6 has mostly d character. Accordingly, we shall call it the band-6 resonance.

A single crystal of copper was cut with a (110) surface orientation and cleaned as described previously.[8] It was heated with a button heater mounted on a two-axis manipulator. Spectra taken in the experimental geometry of Ref. 8 at 25°C, 200°C, 400°C, 600°C, and 800°C are shown in Fig. 2. A total of three heating cycles were carried out, with two different heaters and manipulators. The spectral variations with temperature were reversible and reproducible. Several possible sources of systematic error were tested and eliminated. Of most concern was the angular sensitivity of the resonance. The button heater was noninductively wound: Magnetic fields induced by the heater and leads were calculated to deflect the electrons by less than 1°. Spectra taken at high temperatures but with the heater off proved the influence of the heater current to be undetectable. That the observed effect was not due sim-

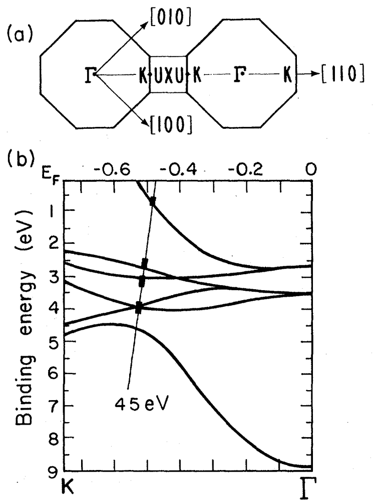

FIG. 1. (a) (001) projection of the three-dimensional Brillouin zone of an fcc lattice in the repeated-zone scheme. (b) Band structure of Cu along K-Γ. Bars indicate observed peak positions in normal photoemission from Cu(110) at $h\nu=45$ eV and $T=25$°C (see Fig. 2).

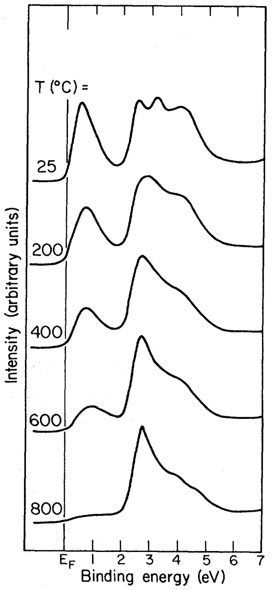

FIG. 2. Temperature dependence of the normal photoemission spectrum from a Cu(110) crystal at $h\nu=45$ eV.

ply to dimensional variations with temperature (i.e., rotation of the sample) was confirmed both by visual inspection of the sample during heating and by varying the sample orientation at high temperatures.

The band-6 resonance at 0.5-eV binding energy is an extremely sensitive indicator of the direct-transition channel, because this peak arises only through transitions from a band that goes through E_F steeply between Γ and K (cf., Fig. 1). As phonon-assisted processes become more important with increasing temperature, this peak decreases dramatically in intensity, as expected. In Fig. 3(a) we have plotted the band-6 resonance intensity versus temperature. Also shown are plots of f^n ($n = 1, 2, 3$), where the values of $\langle \Delta r_x^2 \rangle$ used were bulk mean-square displacements for copper measured by x-ray temperature diffuse scattering.[10] The effective mean-square displacement seen in photoelectron spectra will be larger than the bulk value, due to the short photoelectron mean free path (≈ 5 Å[11] at 45 eV). For Cu the (110) interplanar spacing is 1.3 Å (half the nearest-neighbor distance), which indicates the photoelectron spectra of Fig. 2 are only sensitive to four (110) planes. Calculations for a (110) surface of Ni[12] have shown that mean-square displacements normal to the surface for a surface layer are as much as three times the bulk value, and decay exponentially to the bulk value by the fifth layer. Further calculations[13] indicate that the ratio of surface to bulk mean-square displacements increases with increasing temperature. Our data are consistent with these expectations; Fig. 3(a) shows the decrease in the band-6 resonance intensity corresponds to $2 > n > 1$ near room temperature and $n > 2$ at elevated temperatures.

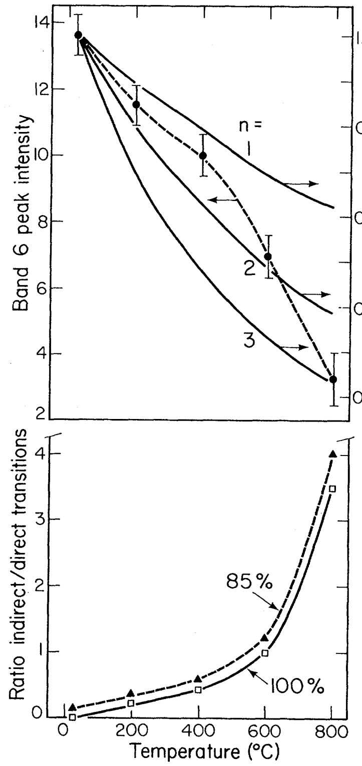

FIG. 3. (a) Experimental intensity of the peak at ~0.5-eV binding energy in Fig. 2 (band-6 resonance) as a function of temperature (full circles connected by a dashed line) as compared to the Debye-Waller factor f^n (solid lines). The different curves for f^n correspond to calculations assuming a mean-square displacement of n times the bulk value. (b) Ratio of indirect to direct transitions as derived from the spectra in Fig. 2 vs temperature. For the data points shown as squares and triangles we have assumed that at room temperature the main d-band peak is composed of 100% and 85% direct transitions, respectively.

Another noteworthy change with temperature occurs in the main d-band peak itself. At room temperature this peak shows at least three components, corresponding to the band energy positions at $k_x = k_y \approx -0.5$ in the BZ.[8] At high temperatures the d-band peak becomes asymmetric, with more intensity at the top of the bands, until, at 800°C, the spectrum resembles that of polycrystalline copper for $h\nu = 40-50$ eV.[14] For copper, a single electron-phonon interaction can change the final-state electron wave vector from the Γ point to anywhere within the BZ with no more than a 30 meV[15] change in the electron energy, thus allowing more of the k states in the BZ to be sampled without greatly disrupting their energy distribution. In Fig. 3(b) the ratio of indirect to direct transitions is plotted as a function of temperature, assuming two different values for the ratio at room temperature. This plot bears out the *temperature* dependence predicted by Eq. (3). It is noteworthy that the total integrated valence-band intensity in the spectra in Fig. 2 is nearly (within 5%) constant with temperature, indicating that f and the power series governing the indirect-transition channels balance each other.

Additional spectra at two other photon energies are completely consistent with this interpretation. For $h\nu = 80$ eV at room temperature the bands sampled are near Γ.[8] There is thus no intensity in the "s-p band" region, $0 < E_B < 2$ eV. At high temperatures, however, thermal broadening facilitates sampling over more of the BZ and the familiar "s-p band" plateau appears. At $h\nu = 140$

eV the situation is very similar to that at 45-eV photon energy. The "s-p band" region is initially unusually intense, because band 6 is again being sampled (this time at $k_x = k_y \approx 0.5$).

We note that Eq. (3) does not fully account for the differences observed in the room-temperature spectra for transitions from the band-6 region at $h\nu = 45$ and 140 eV[8] since the magnitudes of $\vec{q}$ are the same for both transitions. Rather, these differences arise because at higher photon energies $k_\parallel$ is broadened more due to the finite angular resolution of the analyzer and, more importantly $k_\perp$ is defined less accurately due to the shorter electron mean-free path at 140 eV relative to 45 eV (see Ref. 8).

We have not found any high-temperature LEED studies of the Cu(110) surface in the literature to confirm that the changes in the photoemission spectra of Fig. 2 are not due to surface reordering. However, this possibility is unlikely due to the continuous nature of the changes in the spectra with temperature. Furthermore, Ni(110) surfaces are stable to temperatures exceeding 800°C,[16] indicating there are no strong thermodynamic forces to cause Cu(110) to facet. Thus, we are confident the spectral changes we observe are not due to structural rearrangement.

The effect of thermal disorder on photoemission spectra is now established. Previous observations of temperature dependence in photoemission by Lapeyre, Huen, and Wooten[17] and by Bauer, Lin, and Spicer[18] show that thermal disorder is important for a large range of materials. The These earlier studies did not utilize the crystalline-disorder mechanism to interpret their data, however. More work is required to test its range of applicability. However, the many uses that can be made of this effect to elucidate atomic properties in solids are quite evident. Thermal disorder is clearly an essential ingredient in understanding the transition of angle-resolved photoemission spectra from UPS energies to the XPS limit. Finally, we emphasize that angle-resolved photoemission spectra at UPS energies should preferably be collected at temperatures below the surface Debye temperature of the substance under study in order to successfully interpret photoemission spectra in terms of a direct-transition model.

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