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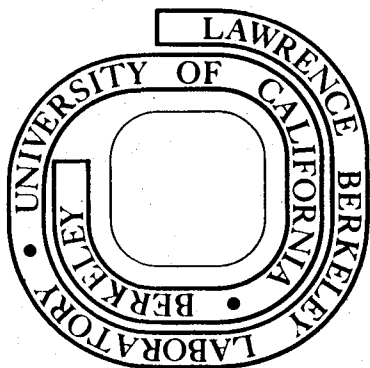# DISCLAIMER

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THERMALLY INDUCED BREAKDOWN OF THE DIRECT-TRANSITION MODEL IN COPPER*

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ABSTRACT

A strong temperature dependence has been observed for the first

time in the valence-band photoemission spectrum of a crystalline solid.

As copper is heated in increments to 800°C, dramatic changes are observed

in the angle-resolved photoemission (ARP) spectrum of the d-bands taken

at $h\nu$ = 45 eV normal to the (110) face. This confirms predictions of

a model suggested by Shevchik. It also resolves a controversial point

in the interpretation of ARP spectra at x-ray energies. Most important,

it bears strong implications for all high-energy and high-temperature

ARP studies.

Shevchik has suggested[1] 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

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

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 <u>inside</u> a crystal is given by[2]

$$N(E_f,\vec{k}_f,h\nu) \propto \sum_{\substack{\vec{k}_i \\ \vec{k}_i \supset BZ}} \sum_{\substack{E_j(\vec{k}_i) \\ E_j < E_F}} \left| \left\langle E_f(\vec{k}_f) \left| \vec{A}\cdot\vec{p} \right| E_j(\vec{k}_i) \right\rangle \right|^2 \times$$

$$\delta\left(E_f(\vec{k}_f) - E_j(\vec{k}_i) - h\nu \right) \quad , \tag{2}$$

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 in some unknown way, 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 a measurement. 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 diffuse scattering theory;[4] i.e.,

$$|\langle e^{i\vec{k}_f \cdot \vec{r}}|\vec{A}\cdot\vec{p}|E_j(\vec{k}_i)\rangle|^2 \propto \cos^2\gamma \ f \ \sigma_{ij}(\vec{k}_f) \left\{ \delta(\vec{q}-\vec{G}) + \right.$$

$$\left. \left(1-\delta(\vec{q}-\vec{G})\right)\left[(k_BT)\frac{|\vec{q}|^2}{|\vec{q}-\vec{G}|^2}\phi_1 + (k_BT)^2|\vec{q}|^4 \phi_2(\vec{q}) + \ldots\right]\right\} \qquad (3)$$

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 $\phi_2(\vec{q})$ involve sums over phonon modes familiar from first- and second-order temperature diffuse scattering.[4] In Eq. (3) it is assumed that the temperature is high enough that equipartition holds for the phonon modes.

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[6,7] while a model based on the atomic cross section $\sigma_{ij}(\vec{k}_f)$ in Eq. (3) works better at high energy.[5,8] 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[7] 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. This resonance actually arises as the 6th valence band approaches E_F between Γ and K, where Band 6 has mostly d-character. Accordingly we shall refer to it as the Band 6 resonance.

A single crystal of copper was cut with a (110) surface orientation and cleaned as described previously.[7] It was heated with a button heater mounted on a two-axis manipulator. Spectra taken in the experimental geometry of Ref. 7 at 25°C, 200°C, 400°C, 600°C, and 800°C are shown in Fig. 1. 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 non-inductively 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 to be independent of the heater current. That the observed effect was not due simply to dimensional variations with temperature (i.e., rotation of the sample) was confirmed both by visual inspection 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. As phonon-assisted processes become more important with increasing temperature, this peak decreases dramatically in intensity, as expected. In Fig. 2a we have plotted the Band 6 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 deviations for copper measured by temperature diffuse scattering.[9] Calculations for a (110) surface have shown[10] that mean-square deviations normal to the surface for a surface layer are three times the bulk value, and decay exponentially to the bulk value by the fifth layer. The inelastic mean free path for 45 eV electrons at room temperature is ≈5Å.[11] Since fcc (110) planes are separated by half the nearest-neighbor distance; i.e., 1.3Å for Cu, the effective mean-square displacement seen in the photoelectron spectrum should be larger than the bulk value. Our data are consistent with this expectation: they agree best with n > 1. The fast decrease of the Band 6 peak intensity between 600°C and 800°C is not understood.

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 $k_x = k_y \cong - 0.5$ in the BZ.[7] 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.[12] For copper, an electron-phonon interaction can change the

electron wave vector from the Γ point to anywhere within the BZ with

no more than a 30 meV[13] 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. 2b 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 underlined temperature dependence predicted by Eq.(3). It is noteworthy

that the total integrated valence-band intensity in the spectra in

Fig. 1 is nearly (within 5%) constant with temperature, indicating

that f and the power series governing the indirect transition inten-

sity balance each other.

Additional spectra at two other photon energies are completely

consistent with this interpretation. At $h\nu$ = 80 eV, at room tempera-

ture the bands are being sampled near Γ.[7] 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 reverse occurs.

The "s-p band" region is initially unusually intense, mainly because

Band 6, which gives rise to the resonance at $h\nu$ = 45 eV, is being

sampled on the other side of the BZ $(k_x = k_y \cong + 0.5)$.

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 eV and 140 eV,[7] since the magnitudes of $\vec{q}$ are the

same for both transitions. The spectra at these two photon energies

should differ only because of differences in energy and momentum

resolution in the experiments. However, these differences are too

small to explain the apparent decrease in direct transition amplitude at 140 eV. We believe that mixing of final states by the crystal potential becomes important at these higher final-state energies.[5] This would suggest that XPS spectra of cooled samples may still be dominated by directionally-dependent atomic cross sections: i.e., final-state mixing may lead to sampling throughout the BZ.

The effect of thermal disorder on photoemission spectra is now established. More work is needed to test its range of applicability. It is already clear, however, that many uses can be made of this effect to elucidate atomic properties in solids. It is also clear that thermal disorder is an essential ingredient in understanding the transition of ARP spectra from UPS energies to the XPS regime.
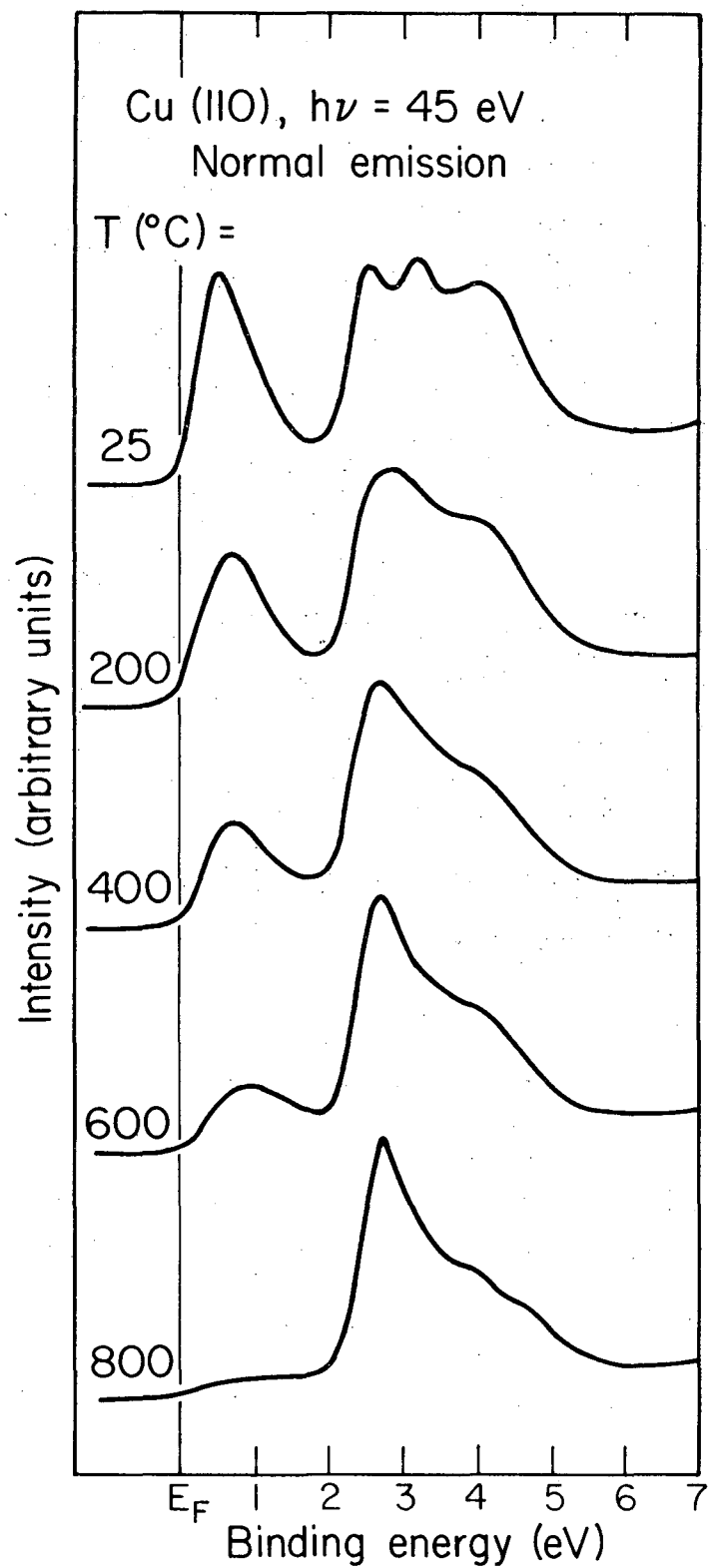
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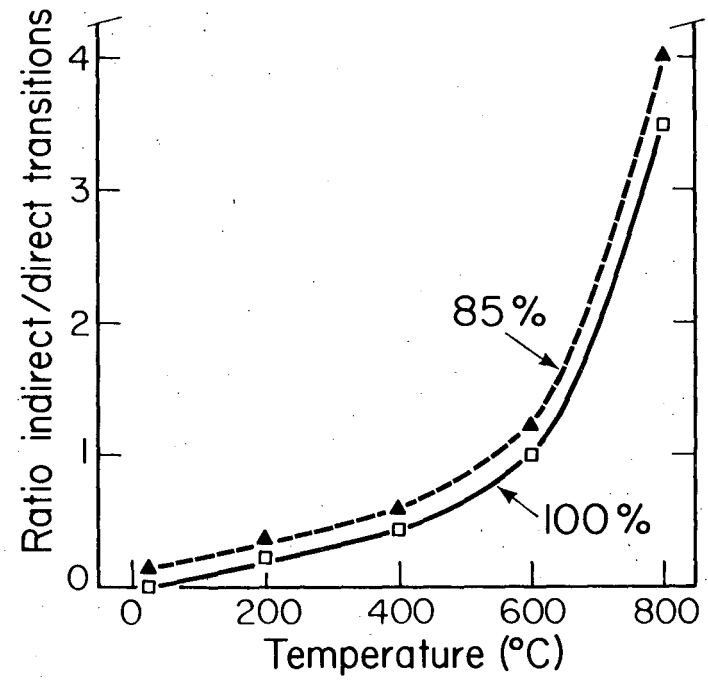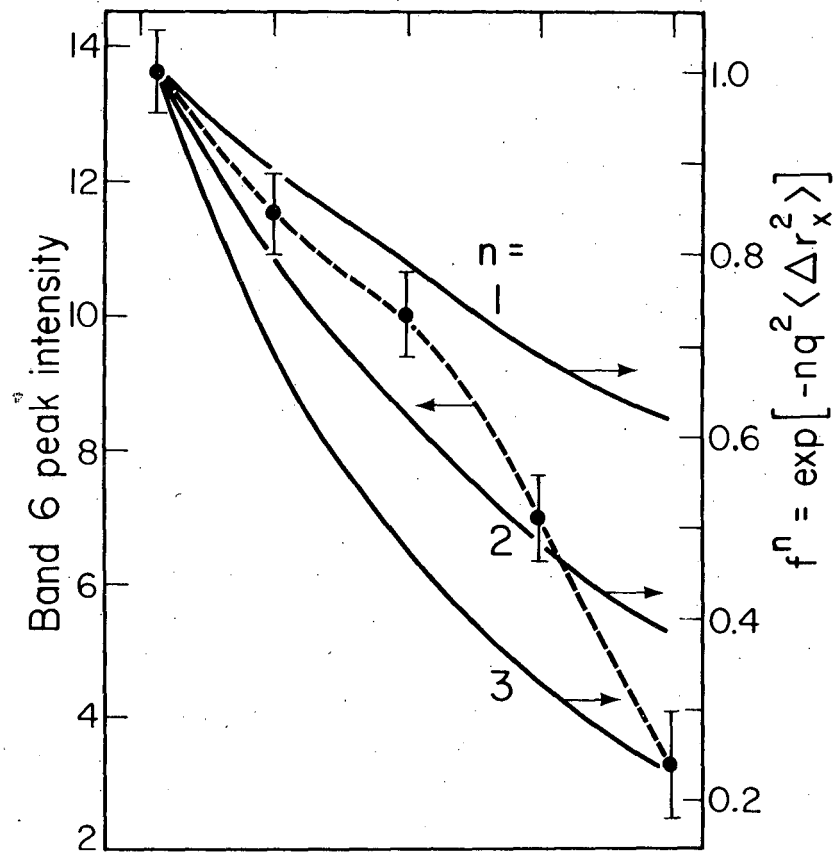   M. K. Wilkinson, Phys. Rev. 164, 922 (1967).

FIGURE CAPTIONS

Fig. 1. Temperature dependence of the normal photoemission spectrum

from a Cu(110) crystal at $h\nu$ = 45 eV.

Fig. 2. a) Experimental intensity of the peak at $\sim$0.5 eV binding energy

in Fig. 1 (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 dis-

placement of n times the bulk value.

b) Ratio of indirect to direct transitions as derived from

the spectra in Fig. 1 versus 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.

Fig. 1

XBL 774-818

Fig. 2

XBL 774-819