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[12]As in all photoelectron experiments the recorded energy spectrum corresponds to the hole state. Thus in fact we measure hole dispersion and, only by inference, the electron dispersion in the initial state. This approximation is essentially Koopmans's theorem.
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Direct Determination of Lifetime and Energy Dispersion for the Empty Δ_1 Conduction Band of Copper

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We present an accurate determination of the energy dispersion (E vs k) and the first direct determination of the energy-dependent lifetime $\Gamma(E)$ of well-defined excited Bloch states in a crystal. Using angle-resolved photoemission for Cu(100), we find that the lifetime broadening increases from $\Gamma = 1.2$ eV (6×10^{-16} sec) to 1.8 eV (4×10^{-16} sec) for Δ_1 conduction-band states ranging 10.5 to 13.5 eV above the Fermi level. The measured dispersion (~2% accuracy) shows a reduced effective mass ($m^*/m_0 = 0.90$–0.94) which is related to self-energy effects.

X-ray and ultraviolet photoelectron spectroscopy studies have yielded substantial information about occupied energy bands—e.g., densities of states—in the last decade. Indeed, angle-resolved studies at low photon energies $\hbar\omega \lesssim 100$ eV have recently yielded rather accurate energy dispersions (E vs k) for occupied valence bands,[1-5] and promise an even better future. However, much less is known about the energy-band dispersions of empty conduction bands well above the Fermi level E_F. Usually, it has been necessary to assume either that specific theoretical one-electron models are valid[3] or that a simple nearly-free-electron–band picture is valid.[4]

Even less is known about the lifetime of electrons in excited states well above E_F. These lifetimes are important since they determine such basic quantities as the electron mean free path (i.e., spatial escape depth) and the momentum broadening δk, which determines the limiting momentum resolution of angle-resolved photoemission.[6] The principal sources of information about lifetimes have been escape-depth measurements of electron attenuation through an overlayer.[7] Such measurements have determined energy-dependent mean free paths which are averaged over many crystal directions, since polycrystalline samples have been used. Also, there are often serious questions of inaccuracies due to inhomogeneities—e.g., island growth—because very thin overlayer films must be used.[7]

In this paper, we present an accurate determination of the energy dispersion E vs k as well as a direct determination of the lifetime broadening $\Gamma(E)$ for excited Bloch states in the lowest empty conduction band along Δ in Cu. Using angle-resolved normal photoemission from Cu(100) with continuum synchrotron radiation, we have directly determined the spectral distribution [i.e., Lorentzian distribution of width $\Gamma(E)$] of these excited Bloch states. For this method, the only required assumption is that there exists a smooth E-vs-k dispersion relation for the final states involved. For energies between 10.5 and 13.5 eV above E_F, we find that the energy broadening Γ increases from 1.2 eV FWHM (full width

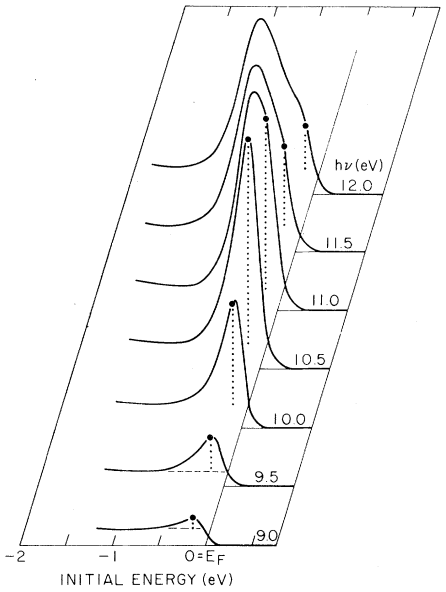

FIG. 1. Angle-resolved energy distributions for normal emission from Cu(100) showing the onset of $\Delta_1 \rightarrow \Delta_1$ interband transitions. The vertical dotted lines depict the interband transition intensity at an initial energy $E_i = -0.13$ eV.

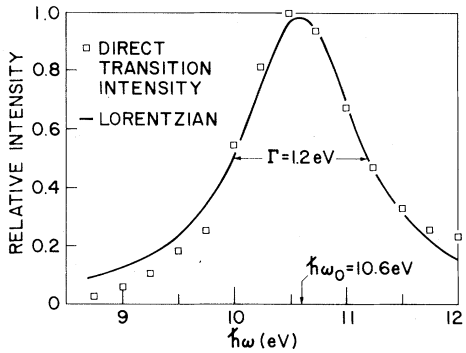

FIG. 2. Interband ($\Delta_1 \rightarrow \Delta_1$) transition intensity vs $\hbar\omega$ for an initial energy $E_i = -0.13$ eV for normal emission from Cu(100). The theoretical Lorentzian spectral density distribution is discussed in the text.

at half-maximum) (lifetime of 6×10^{-16} sec) to 1.8 eV (lifetime of 4×10^{-16} sec). Using measured group velocities $\partial E/\partial k$, the corresponding electron mean free path decreases from ~15 Å at 10.5 eV to ~11 Å at 13.5 eV. The experimentally determined energy dispersion of the empty Δ_1 conduction band is best described using a reduced effective mass ($m^*/m_0 = 0.90$–0.94) and is found to be in excellent agreement with an $X\alpha$ calculation[8] ($\alpha = 0.77$, $\lambda = 0.08$) that was based on a fit to Fermi-surface data, optical data, and the position of the occupied Cu d bands.

Experimentally, we have used an angle-resolving CMA (cylindrical-mirror analyzer) double-pass photoelectron spectrometer system with an energy resolution of ~150 meV (electrons + photons) angular acceptance of $\delta\theta = 4°$ (full angle) together with synchrotron radiation from the 240-MeV storage ring at the Synchrotron Radiation Center at the University of Wisconsin. Single crystals of Cu(100) were prepared by Ar-ion etching and annealing to ~(700–800)°K in the usual manner, checked for cleanliness using Auger spectroscopy, and measured in a working vacuum in the 10^{-11}-Torr range.

A set of angle-resolved energy distribution curves (AREDC's) for normal emission from Cu(100) is presented in Fig. 1 which shows the onset of direct interband transitions from the occupied Δ_1 s-p valence band just below E_F into the lowest empty Δ_1 conduction band ($\Delta_1 \rightarrow \Delta_1$ excited with p polarization). The vertical dotted lines show the intensity of the interband transition from an initial energy $E_i = -0.13$ eV into the empty conduction band. This transition is superimposed on a small smooth background of "indirect" transitions (e.g., surface emission, etc.). The $\hbar\omega$-dependent spectral intensity for interband transitions from this initial state into the empty Δ_1 conduction band is shown in Fig. 2. As we will show, the width $\Gamma = 1.2$ eV (FWHM) and center ($\hbar\omega_0 = 10.6$ eV) of this curve directly give the lifetime and final-state energy of the Δ_1 conduction band at the initial-state momentum k_i. This can be shown using a three-step model for angle-resolved photoemission, which is valid if the electron mean free path is long compared to the interlayer spacing. For this case, the emission intensity $N(E_i,\omega)$ can be written as the product of the excitation probability times the escape probability times the analyzer acceptance[6,9]:

$$N(E_i,\omega) \propto \left(\frac{(\Gamma/2)}{(\hbar\omega-\hbar\omega_0)^2+(\Gamma/2)^2}\,|\vec{p}_{fi}(\omega+E_i)|^2\right)\left(\frac{\alpha(\omega)l(\omega+E_i)}{1-R(\omega)}\right)(\omega+E_i-\varphi), \quad (1)$$

where the first term contains the Lorentizian spectral density function of the final state with a lifetime $\Gamma(\omega+E_i)$ and interband matrix element $\vec{p}_{fi}$, $\hbar\omega_0 = E_i(k_i) - E_i(k_i)$ is the interband transition energy, $\alpha(\omega)$

is the optical absorption coefficient, l is the electron mean free path, R is the reflectivity, $\omega + E_i - \varphi$ is proportional to the k-space acceptance solid angle of the spectrometer, and $\varphi = 4.8$ eV is the Cu(100) work function. Using a two-orthogonalized-plane-wave (OPW) approximation for our simple case, we can approximate $N(E_i,\omega)$ as[6,9]

$$N(E_i,\omega) \propto \left(\frac{\Gamma/2}{(\hbar\omega - \hbar\omega_0)^2 + (\Gamma/2)^2}\right)\left(\frac{V_{200}}{\omega + E_F}\right)^2 \left(\frac{(\omega + E_F)^{1/2}}{\omega^{3/2}}\right)(\omega + E_i - \varphi), \tag{2}$$

where V_{200} is the two-OPW pseudopotential (its magnitude is irrelevant to our analysis). Examination of Eq. (2) in view of the data in Fig. 2 indicates that we can simply write

$$N(E_i,\omega) \propto \frac{\Gamma(E_f)/2}{(\hbar\omega - \hbar\omega_0)^2 + [\Gamma(E_f)/2]^2}, \tag{3}$$

an expression which can be used to determine the lifetime Γ with an accuracy of $\lesssim 10\%$ and the transition energy $\hbar\omega_0$ with an accuracy of $\sim 1\%$. Equation (3) is plotted in Fig. 2 for $\hbar\omega_0 = 10.6$ eV and $\Gamma = 1.2$ eV and is seen to describe the overall line shape [the asymmetry can be understood using Eq. (2)]. For this transition with $E_i = -0.13$ eV, the corresponding momentum k_i is accurately given[8] from the known Fermi surface, i.e., $k_i/k_{BZ}^{\langle 100\rangle} = 0.82 \pm 0.01$ Å^{-1}, where $k_{BZ}^{\langle 100\rangle} = 1.74$ Å^{-1} for Cu. Thus, we have directly determined the lifetime $\Gamma = 1.2$ eV and energy $E_f = \hbar\omega_0 - E_i = 10.5$ eV for the Δ_1 conduction band at a reduced-zone momentum of $k/k_{BZ}^{\langle 100\rangle} = 0.82$.[10]

Using the data in Fig. 1, together with similar data at higher $\hbar\omega$'s for several initial states E_i, we have determined the energy-dependent lifetime broadening $\Gamma(E)$ shown in Fig. 3. Also shown in Fig. 3 are the corresponding energy-dependent mean free path $l(E)$ and momentum broadening (FWHM), $\Delta k \equiv 1/l$, where $l(E)$ is determined by the relation $l(E) = (\partial E/\partial k)(1/\Gamma)$ with the experimental group velocity $\partial E/\partial(\hbar k) = 17.2 \pm 0.4$ eV Å/$\hbar$ (to be discussed).[11]

In comparison with past work for the energy range $E \lesssim 40$ eV, the only relevant measurements for noble metals appear to be electron transmission measurements for Au and Cu and photoemission escape-depth measurements for Ag.[7] Our results for Cu(100) are consistent both in magnitude and energy dependence with these previous measurements. Over the limited energy range of our measurements, $\Gamma(E)$ can be described by a power law $\Gamma \propto E^{\beta}$ with $\beta = 1.3$; this is consistent with an estimate based on the random-k approximation with a free-electron model for s-p band e^--e^- scattering.[9]

We have also determined the E-vs-$\vec{k}$ relation for final states along the Δ line above $\hbar\omega_0 = 10.6$ eV as shown in Fig. 4. Here normal-emission

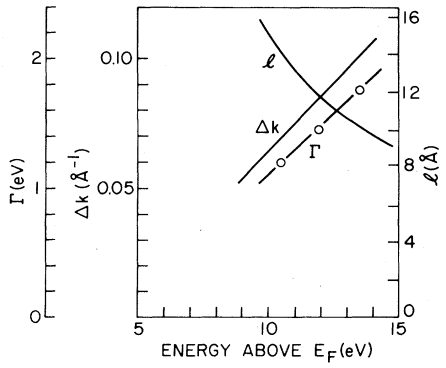

FIG. 3. Experimental energy-dependent energy width (lifetime) $\Gamma(E)$, electron mean free path $l(E)$, and momentum broadening $\Delta k(E)$ for Δ_1 conduction-band states of Cu.

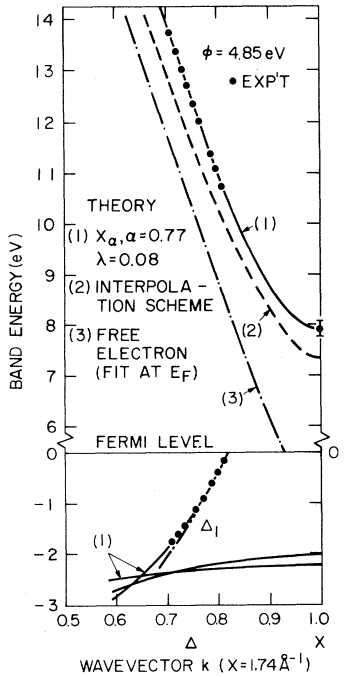

FIG. 4. Experimental E-vs-k dispersion for the Δ_1 conduction band of Cu and comparison with three theoretical models.

AREDC's have been used to determine the energies, and the corresponding momenta are accurately given by the initial-state dispersion along Δ near E_F, which is known from analyses[8,12] of the Fermi-surface data together with Cu d-band photoemission (in Fig. 4, the $X\alpha$[8] and interpolation-scheme[12] calculations agree within ± 0.1 eV and ± 0.01 Å^{-1} for these Δ_1 states). In Fig. 4, three theoretical models are compared with experiments: (1) a self-consistent $X\alpha$ calculation[8] with a self-energy correction $\lambda = 0.08$ which was fitted to the Fermi surface, optical data, the d-band position, and angle-averaged photoemission data; (2) a mixed-basis $(s+d)$ interpolation-scheme calculation[12] which was fitted to Burkick's APW calculation; and (3) a free-electron model which was shifted to pass through the Fermi energy at the known value $k_F^{\langle 100\rangle}/k_{BZ}^{\langle 100\rangle} = 0.82$.

Comparison of experiment with the $X\alpha$ calculation shows excellent agreement—better than might have been expected since accurate conduction-band data were not available. Also, the agreement between our experimental X_1 critical point (7.9 eV; determined from $X_5 \rightarrow X_1$ transitions) and the calculated X_1 point is excellent. Comparison with the interpolation-scheme model[12] shows that the calculated band lies too low in energy. This is consistent with the $X\alpha$ calculation, which gives a similar result if the ~8% reduction in effective mass (i.e., self-energy parameter $\lambda = 0.08$) is omitted. Comparison with the free-electron bands shows a large discrepancy; this is expected since important s-d orthogonalization and pseudopotential effects are not accounted for.

The experimental average group velocity is $\partial E/\partial(\hbar k) = 17.2 \pm 0.4$ eV Å$/\hbar$ for energies between 11 and 14 eV above E_F. The group velocity for the free-electron model with $k = 0.75 k_{BZ}^{\langle 111\rangle}$ is $\partial E/\partial(\hbar k) = 7.62 \hbar k/m^*$; if this is equated to experiment, one obtains an effective mass of $m^* \simeq 0.95$. The use of a two-OPW model with a further reduced effective mass would improve the fit of E vs k to experiment. In summary, comparison of experiment with such two-OPW models fit to experiment as well as with the $X\alpha$ calculation indicates that an effective mass $m^*/m_0 = 0.90$–0.94 is needed to fit the Δ_1 conduction band. This value is significantly less than unity and indicates that self-energy effects exist.[8]

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[10]We have assumed that the initial-state broadening is much smaller than the final-state broadening; this is valid for initial states at or near E_F compared to the final state involved.

[11]The direct-transition line shapes in Fig. 1 are largely determined by the final-state lifetime, together with the initial- and final-state group velocities $\partial E_i/\partial(\hbar k)$ and $\partial E_f/\partial(\hbar k)$. For a final-state broadening of Γ, it is seen using Eq. (2) and the known energy dispersions $\partial E/\partial k$ that the width $\bar{\Gamma}$ of the direct-transition peak in the AREDC is approximately given by $\bar{\Gamma}(E_i) \simeq \Gamma(E_i + \omega) \times (\partial E_i/\partial k)/(\partial E_f/\partial k)$ for $\hbar\omega > \hbar\omega_0 = 10.6$ eV. For the Δ_1 bands involved, $\bar{\Gamma} \simeq 0.55\Gamma$; thus the linewidth for the uppermost AREDC in Fig. 1 is estimated to be $\bar{\Gamma} \simeq 0.7$ eV (experimentally, $\bar{\Gamma} = 0.6$ eV). Below the threshold of $\hbar\omega_0 = 10.6$ eV, the measured line shape is roughly approximated by a single-sided Lorentzian, with a width of $\sim\bar{\Gamma}/2$ (this is the case, as the measured width Γ).

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