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PHOTOEMISSION PROPERTIES OF CESIATED COPPER*

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New measurements of the photoelectron energy distributions from cesiated Cu reveal structure not seen in previous data. The behavior of this new structure on varying the photon energy is characteristic of direct transitions. Theoretical calculations are presented which lend support to this conclusion.

An outstanding landmark in the photoemission investigation of metals was the observation of the *d* bands in Cu and Ag by Berglund and Spicer.[1] They found, however, that their results could not be reconciled with conventional theory of direct transitions. New measurements on Cu are reported here which indicate that some of these difficulties may be experimental in origin.

The failure of direct transitions appeared to lie in the behavior of structure in the photoelectron energy-distribution curves (EDC's) on varying the photon energy, $\hbar\omega$. Structure was found to remain stationary or to move in energy with increments equal to the increments in $\hbar\omega$. Direct transitions, it was argued,[1] should give rise to structure which moves in a peculiar way on varying $\hbar\omega$; in addition, peaks in the EDC might be expected to vary markedly in strength and to disappear and reappear in a rather abrupt fashion because of the gaps between the bands. Calculations on Cu, however,[2] have indicated that the equal-increment behavior is not inconsistent with direct transitions, at least for clean Cu in the range $\hbar\omega \lesssim 11$ eV. The same calculations indicated that the characteristic behavior peculiar to direct transitions was expected to occur at energies below the vacuum level of clean Cu. In other words, it is necessary to lower the work function, for example by cesiation, in order to see these effects. This was the motivation which led to the experimental reinvestigation of photoemission from cesiated Cu described here. Since sample preparation and vacuum techniques had improved over the intervening years, there was hope that it might be possible to resolve clearer structure than had been seen in the previous data of Berglund and Spicer.[1]

The Cu sample used in these new measurements was prepared by evaporation in a stainless-steel ultrahigh-vacuum system. The pressure rose to 5×10^{-10} Torr during the evaporation but dropped quickly to 1.5×10^{-10} Torr afterwards. The sample was then covered with a thin layer of cesium in order to lower the work function. The pressure did not rise above 2×10^{-9} Torr during the cesiation. Berglund and Spicer used cesiated samples prepared in a glass system in which pressures somewhat lower than 10^{-8} Torr could be attained. Our new results differ in some respects from those of Berglund and Spicer. The origin of the differences is not clear, although it is presumably associated with the overall vacuum conditions or the details of the cesiation. The role of Cs on the surface, or any surface contaminant for that matter, is very imperfectly understood. Also the general improvement in sample preparation technique over the last few years has been accompanied by an improvement in photoemission data, the work on nickel[3] being a good example.

The new and most noteworthy information has been obtained in the photon energy range 6.5 to 8.2 eV, and so we will concentrate our discussion on this region. The EDC's of photoemitted electrons are shown in Fig. 1 for photon energies between 6.5 and 8.2 eV. The horizontal scales have been shifted so that each curve is plotted against $E-\hbar\omega+e\varphi$, where E is the electron kinetic ener-

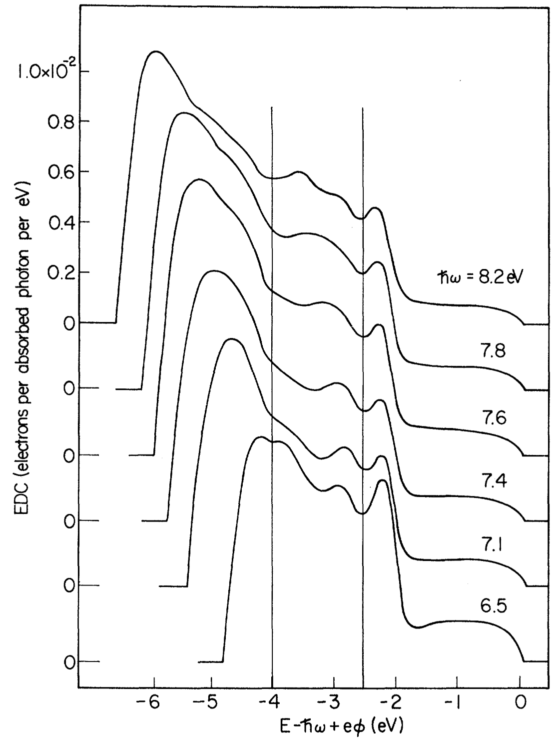

FIG. 1. Experimental photoelectron energy-distribution curves for cesiated Cu in the photon energy range 6.5 to 8.2 eV. The curves are plotted against initial-state energy with the zero of energy taken at the Fermi level.

gy in vacuum, $\hbar\omega$ is the photon energy, and $e\varphi$ is the work function. This choice of scale refers the electrons to their initial states and places the zero of energy at the Fermi level. At about −2.3 eV we see a peak due to transitions from the uppermost d band. There is additional structure at lower energies associated with the lower lying bands. Here lies the main difference between the present work and that of Berglund and Spicer.[1] Their samples revealed a broad peak in this lower d-band region which did not change on varying the photon energy.

A significant feature of the new structure seen in the present data is the way the profile of the EDC changes with photon energy. Let us focus attention on the behavior in the energy range −4.0 to −2.6 eV, indicated by the vertical lines in Fig. 1. At $\hbar\omega = 6.5$ eV we have two peaks in this region. As the photon energy is increased the left-hand peak fades away. While this is happening, the right-hand peak broadens by shifting its low-energy edge downwards, until at $\hbar\omega = 7.8$ eV, there is one broad piece of structure filling the whole range. On going to $\hbar\omega = 8.2$ eV this broad peak then splits into a doublet. This kind of qualitative behavior is characteristic of direct (i.e., $\vec{k}$-conserving) transitions. In fact, Berglund and Spicer searched specifically for such effects in just this energy region. Since their samples did not exhibit these effects, they were led to propose a nondirect model which has been quite successful in Cu and other materials.[4]

Theoretical calculations of the EDC's have been performed assuming direct transitions and constant matrix elements. When optical transitions are direct, the initial and final states lie at the same point in $\vec{k}$ space in the reduced-zone scheme. If $\mathcal{E}_i(\vec{k})$ and $\mathcal{E}_f(\vec{k})$ denote the energies in an initial band i and a final band f, then the transitions at photon energy $\hbar\omega$ are restricted to lie on the surface given by

$$\Omega_{fi}(\vec{k}) = \mathcal{E}_f(\vec{k}) - \mathcal{E}_i(\vec{k}) - \hbar\omega = 0. \tag{1}$$

The relevant property of the band structure for our present purpose is the energy distribution of the joint density of states (EDJDOS) defined by

$$\mathfrak{D}(\mathcal{E},\hbar\omega) = (2\pi)^{-3}\sum_{f,i}\int' d^3k\,\delta(\Omega_{fi}(\vec{k}))\,\delta(\mathcal{E}-\mathcal{E}_i(\vec{k})). \tag{2}$$

The prime on the integral denotes that the integration is to be performed only over those portions of $\vec{k}$ space for which $\mathcal{E}_i < E_F < \mathcal{E}_f$, where E_F is the Fermi energy. In a constant-matrix-element approximation, the EDJDOS represents the energy distribution of photoexcited electrons referred to initial-state energy.

The EDJDOS has been calculated numerically for Cu from Eq. (2) by sampling $\vec{k}$ space at more than 10^5 points in the primitive 1/48 of the zone. Calculations of this kind were first performed by Brust.[5] The band structure used here was the combined interpolation scheme of Hodges, Ehrenreich, and Lang[6] with its parameters fitted to the augmented plane-wave calculation of Burdick.[7] The EDJDOS was then converted to an EDC by multiplying by appropriate threshold and escape factors.[1] The curves were also broadened by convolving them with a Lorentzian whose width at half-maximum was 0.3 eV.

The theoretical EDC's calculated in this way for photon energies between 6.5 and 8.2 eV are shown in Fig. 2. Let us examine the trends in the energy range −4.0 to −2.6 eV again indicated by vertical lines. At $\hbar\omega = 6.5$ eV we have two peaks. On increasing the photon energy, the left-hand peak fades away, then makes a comeback. At $\hbar\omega = 7.8$ eV, there is a single broad piece of structure which splits into a doublet on going to

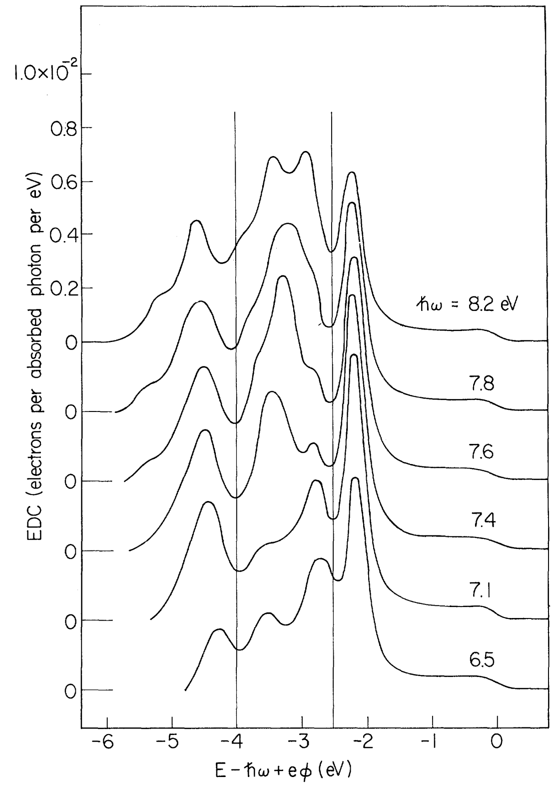

FIG. 2. Theoretical photoelectron energy-distribution curves for cesiated Cu calculated on the basis of direct transitions. The curves are plotted against initial-state energy with the zero of energy taken at the Fermi level.

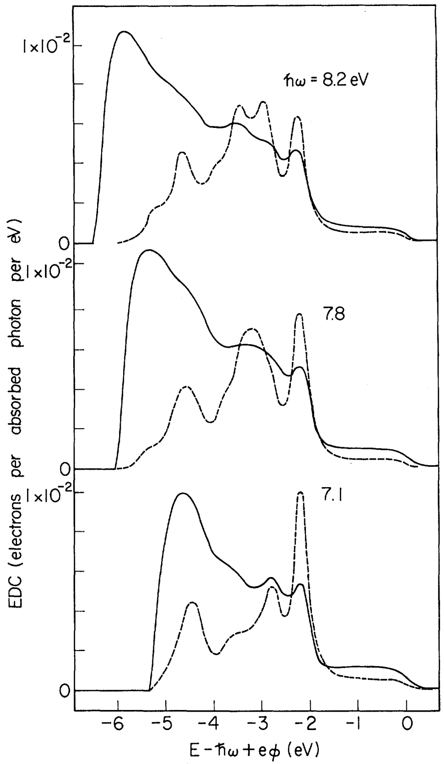

FIG. 3. Comparison of the theoretical (dashed curves) and the experimental (full curves) photoelectron energy-distribution curves for cesiated Cu at three different photon energies.

$\hbar\omega = 8.2$ eV. The similarity of these trends to those shown by the experimental data in Fig. 1 is striking, and would seem to lend further support to a direct-transition interpretation.

In Fig. 3 the experimental and theoretical curves are compared on the same scale for three photon energies. As far as the existence and energy location of structure is concerned, the agreement is reasonable. The experimental EDC's all have a large low-energy contribution which we attribute to electrons which have undergone an inelastic scattering but are still sufficiently energetic to escape from the metal.

Let us consider very briefly the experimental behavior at other photon energies. Roughly speaking, the new EDC's at high photon energies ($\hbar\omega > 9$ eV) are in fair agreement with those of Krolikowski and Spicer[8] on clean Cu. A comparison of this clean-Cu data with calculations of the EDJDOS has been reported by Smith and Spicer.[2] At low photon energies ($\hbar\omega > 5$ eV) the new results agree with those of Berglund and Spicer.[1] In particular, we still observe photoelectrons at the Fermi energy cutoff, even for photon energies below the $L_2' \rightarrow L_1$ threshold ($\lesssim 4$ eV). The calculations confirm that there are no direct transitions in bulk Cu to account for these photoelectrons. In fact, this was one of the main arguments of Berglund and Spicer in favor of a nondirect interpretation. These transitions would certainly be worthy of further study.

In conclusion, it has been found that some of the transitions from the Cu *d* bands can be unambiguously identified as direct on the basis of experiment alone. Direct-transition calculations are found to work quite well for these and other transitions.

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INTENSITY DISTRIBUTION IN THE SIDEBAND SPECTRUM OF NO_3^- IN KI

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The 1400-cm^{-1} absorption band of the nitrate impurity in potassium iodide shows at 4.2°K a considerable amount of fine structure. The intensity distribution of this fine structure is governed by the anharmonic coupling of the internal vibration of the nitrate ion with nearly unperturbed phonons. This distribution can be calculated satisfactorily by first-order perturbation theory.

It is known that the intensity distribution in sideband spectra must contain information about interactions in crystals. Therefore it is important to look for the weight factor that determines the contributions of the combinations to the total absorption. Thus far, consideration to this weight factor has only been given for the sideband spectra of an electronic transition[1] and of the absorption due to *U* centers.[2] The lack of details in the reported[3,4] sideband spectra of internal vibrations of complex ions in solid solutions made consideration of a weight factor inopportune.

We present here high-resolution spectra of the sideband absorption of the ν_3 internal vibration of the nitrate ion as an impurity in potassium iodide recorded at 4.2°K. The spectra show enough details to allow a comparison with a simple theory describing the coupling between internal vibration and lattice phonons.

Single crystals of KI doped with nitrate were grown from the molten salt. The length of the crystals used in our experiments was about 15 mm, with nitrate concentrations in the range of 10^{17} to 10^{18} cm^{-3}. Figure 1 shows the infrared absorption spectrum of such a crystal in the 1400-cm^{-1} region obtained with a Perkin-Elmer E14 spectrometer, resolution = 0.2 cm^{-1}. For the consideration of the interaction between internal vibration and undisturbed phonon spectrum some features of the experimental spectrum have to be disregarded. In the first place there is a relatively strong absorption peak with some very sharp sidebands at about 1423 cm^{-1} that arises from an overtone of the ν_4 vibration

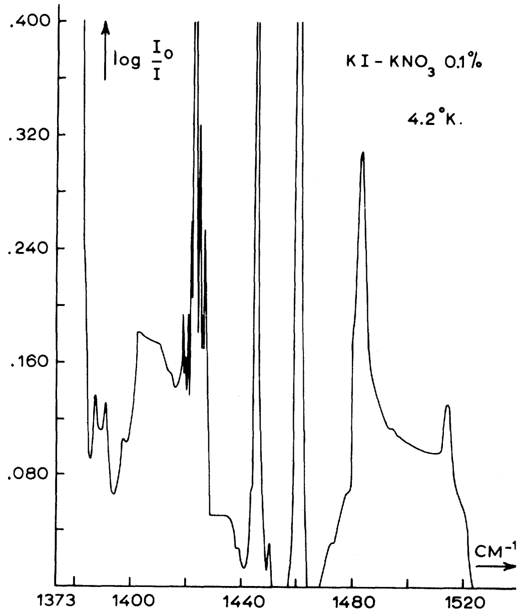

FIG. 1. The sideband spectrum of the ν_3 internal vibration of NO_3^- in a KI single crystal.