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Matrix Element Dependence of Optical Excitation and Auger Decay of $5d$ Core Holes in Bi_2Te_3†

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The spectral dependence of the Auger component of the uv photoemission and the far–uv reflectance show that the optical excitation of $5d$ core states cannot be described in terms of simple density of states indicating that matrix element effects must be included.

We report ultraviolet-photoelectron-spectroscopy data (24 eV $< h\nu <$ 30 eV) for Bi_2Te_3 which contain information on optical transitions from $5d$ core states to conduction band states below the direct emission threshold. The emission in this photon energy region has a strong component resulting from energetically allowed Auger decay of core holes. Similar to previously reported works on other solids, the spectral dependence of Auger emission is found to exhibit the same features as the optical-reflectance spectra.[1] The central issue of this Letter is the evidence that the structure in both Auger and reflectance spectra cannot be explained in terms of a simple density-of-states model despite the fact that the initial state can be considered a core state. That is, the structure in the two spectra does not reflect directly the spin-orbit splitting of the $5d_{5/2}$ and $5d_{3/2}$ core states, a fact which indicates the effect of matrix elements on core excitation. This finding should also be of importance to soft-x-ray absorption spectroscopy.

A detailed description of the photoemission spectrometer, which utilizes the UWPSL 240-MeV storage ring, has been given elsewhere.[2] The overall energy resolution and the signal-to-noise ratio were better than 0.2 eV and 100 : 3, respectively. Rhombohedral (space group D_{3d}^{5}) single crystals[3] of Bi_2Te_3 were grown from the 99.9999% purity elements using a previously described technique.[4] Bi_2Te_3 is a strongly anisotropic semiconductor (band gap $E_g \sim 0.15$ eV) of layered structure which results in excellent quality of *in situ* ($\sim 5 \times 10^{-10}$ Torr) cleaved surfaces.

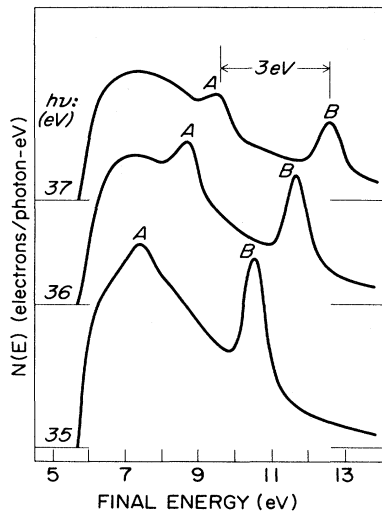The photoemission energy distribution curves (EDC's) are first used (Fig. 1) to determine the

FIG. 1. The low-energy part of the photoemission energy distribution curves for Bi_2Te_3 showing the direct emission from the $5d$ core states.

FIG. 2. The energetics of the optical transitions and of the Auger decay related to the $5d$ core states in Bi_2Te_3.

split-orbit splitting and the binding energies E_{co} of bismuth $5d_{3/2}$ (peak A) and $5d_{5/2}$ (peak B) core states. The binding energies, with respect to the valence band (VB) maximum, are $E_{co} = -24.4 \pm 0.2$ eV and -27.4 ± 0.2 eV, respectively, giving the spin-orbit splitting of 3.0 ± 0.2 eV (Fig. 2).

The threshold for core state *excitation* is then determined as the energy separation between the conduction band (CB) minimum and the core (i.e., $E_g - E_{co}$), yielding values of 24.55 and 27.55 eV for the $5d_{5/2}$ and $5d_{3/2}$ states, respectively. The threshold energy for direct *emission* from the cores is, on the other hand, $E_T - E_{co}$, yielding in this case values of 30.2 and 33.2 eV, respectively. (The vacuum level E_T is ~ 5.8 eV for Bi_2Te_3.) When the photon energy $h\nu$ is larger than the threshold for excitation (24.55 eV), but smaller than the threshold for the emission (30.2 eV), no direct photoemission from the core is possible. The core holes, however, can decay via interaction with the VB producing Auger electrons excited above the vacuum level E_T. The features observed in the Auger emission in the above spectral region (24.5 to 30.2 eV) are the main issue of this Letter.

The EDC's in this region are shown in Fig. 3. While the high-energy regions of the EDC's (right-hand sides about 5 eV wide) are directly related to primary emission from the VB's and will be discussed elsewhere,[5] we will concentrate here on the low-energy (left-hand) sides of the EDC's. The magnitude of these portions of the
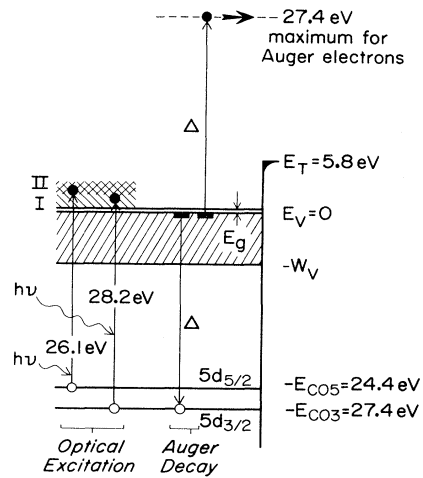
EDC's is *not* a smooth function of $h\nu$ but exhibits fluctuating values with two maxima at $h\nu \sim 26.1$ and 28.2 eV. To study this $h\nu$ variation of amplitude in detail, one could measure a large number of EDC's at closely spaced intervals of $h\nu$ and analyze their relative amplitudes. However, the synchrotron continuum greatly facilitates this study, since one can measure directly the number of electrons emitted at a constant final energy E_f, while varying the photon energy. Such a curve, which is referred to as a constant-final-state energy spectrum (CFS) (Figs. 3, 4) is measured simply by fixing the pass energy of the
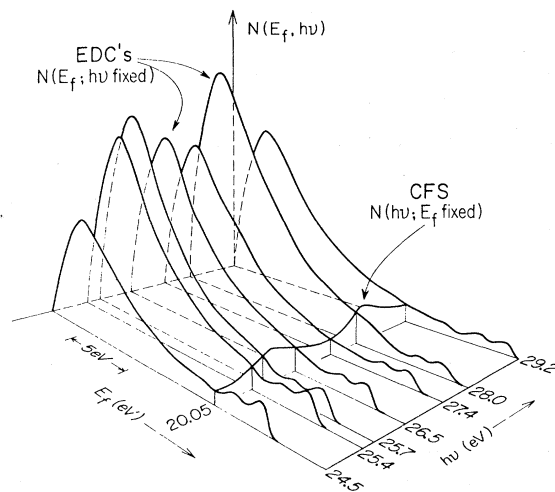

FIG. 3. The photoemission EDC's for Bi_2Te_3 for $h\nu$ between 24 and 30 eV, normalized per incident photon flux. The relation of the EDC's to the CFS's is also shown.
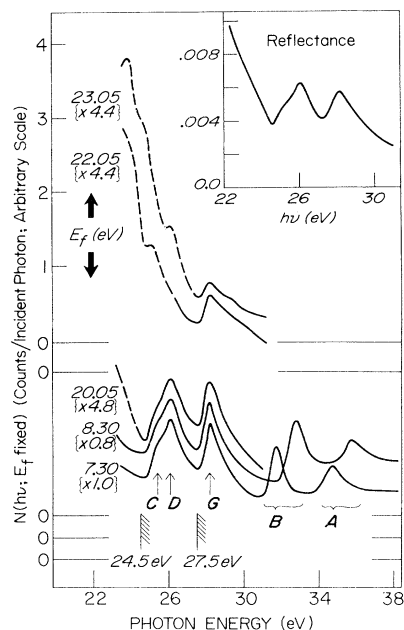
FIG. 4. The CFS's for Bi_2Te_3 measured at different values of the final energy E_f. In the bracket underneath each E_f value, the relative amplitude of each spectrum is shown. Each spectrum is vertically displaced for clarity. The parts that are dashed contain direct emission from the valence bands which obscures the Auger maximum energy edge. The insert shows the far-uv reflectance spectrum at near normal incidence.

analyzer and scanning the wavelength of the exciting radiation.[6]

The CFS's for Bi_2Te_3, normalized to the photon flux, are shown in Fig. 4. Peaks A and B are clearly due to primary emission from the $5d$ core states and correspond to the two core peaks in the EDC's of Fig. 1. In addition to peaks A and B, a shoulder C and two peaks D and G are observed in the CFS's of Fig. 4 at $h\nu = 25.4$, 26.1, and 28.2 eV, respectively. Unlike peaks A and B, these structures are observed at the same photon energy independent of the final energy E_f. That is, we observe in the CFS's peaks for a broad range of final energies from the threshold up to ~ 24 eV, which do indeed correspond to magnitude variations of the low-energy regions of the EDC's in Fig. 3. Since this emission enhancement represented by peaks D and G (Fig. 4) cannot, by reason of elementary energetics, be due to the direct emission from the CB maxima nor direct emission from the core states, we associate this structure with electrons emitted as a result of Auger decay of the Bi $5d$ core holes.

While there may be in general other causes of increased emission at a particular value of $h\nu$, our assignment of these structures to the Auger decay is based primarily on (i) the perfect matching between the *threshold* for each Auger peak and the *threshold* for the excitations of each core state which are identified by the flags at 24.5 and 27.6 eV in Fig. 4, and (ii) the overall matching of the structure in the uv reflectance spectrum (Fig. 4, insert) with the CFS's. The strong enhancement of the Auger emission at the two particular photon energies is due to two maxima in the optical transition strengths $(\omega^2 \epsilon_2)$ which correspond to increased formation of core holes at these photon energies.[7] Such a linear relationship between the Auger emission and the optical absorption has been previously established both theoretically and experimentally through the similarity between the frequency-dependent photoyield and the optical absorption coefficient,[1] and is the basis of "yield spectroscopy".[8]

The most relevant feature of the Auger component of the emission (i.e., of the CFS's in Fig. 4) and of the reflectance spectrum is immediately obvious. Despite the fact that the initial states for these optical transitions are core states, the spin-orbit splitting of 3.0 eV does not show up in the optical and Auger spectra, where the two peaks, D and G, are separated by 2.1 eV only. This indicates that the optical transitions from the core to the CB cannot be in general described in a simple density-of-states model, but require the inclusion of the effect of matrix elements. This fact is relevant in the interpretation of soft-x-ray absorption spectra.

In the particular case of Bi_2Te_3 the two final states, corresponding to the peaks D and G in Fig. 4, are associated with two very flat regions of the (spin-orbit-split) conduction band, as obtained in a relativistic pseudopotential band-structure calculation.[9] In view of the well-defined symmetries of the $5d$ core wave functions, the matrix elements should then depend on the *total* angular momentum (spin included) rather than on the orbital angular momentum.[10] It is interesting to note in this context that the separation of the *shoulder* C and the peak G in the Auger and optical spectra is approximately equal to the spin-orbit splitting of the cores; that is, the shoulder C is an indication of an optical transition supressed by the above effect of matrix elements.

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Cyclotron Resonance in a Molecular Crystal—Anthracene

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Cyclotron resonance of holes orbiting in the *a-b* plane of an anthracene crystal has been observed. This represents the first time that this phenomenon has been observed in a molecular crystal. From these experiments, the hole effective mass is determined to be $11m_e$ where m_e is the free-electron mass. The hole scattering time at 2°K was measured in two different crystals and found to be $\sim 7 \times 10^{-11}$ sec in one crystal and 4×10^{-10} sec in the other.

Cyclotron-resonance experiments have been extremely important for the elucidation of band structure and mobile-charge scattering mechanisms in covalent,[1] ionic,[2] and metallic crystals.[3] In this paper I report the first successful application of this technique to charge carriers in a molecular crystal, specifically to holes in highly purified anthracene crystals. The extension of this technique to molecular crystals is of particular importance because of the absence, at the present time, of any other experimental method capable of unambiguously unraveling detailed band-structure information and carrier-scattering quantities.

The experimental technique used to detect cyclotron resonance is similar in principal to methods used previously.[1] The anthracene crystal is placed in a microwave cavity at a position of maximum electric field. The magnetic field is perpendicular to the microwave electric field and is slowly scanned from 0 to 25 kOe. If ω_c is the fixed microwave frequency, m^* the effective mass of the holes being investigated, and H the variable magnetic field strength, microwave power will be absorbed in the cavity whenever the well-known resonance condition

$$\omega_c = eH/m^*c \qquad (1)$$

is satisfied. Scattering by phonons and impurities will tend to broaden the resonance signal. In fact a distinct resonance maximum cannot be observed unless $\omega_c \tau \gtrsim 1$, where τ is the carrier-scattering time. To maximize τ, one works at as low a temperature as possible, in this experiment 2°K, and with highly purified anthracene crystals.