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Electronic Structure and Scattering Properties of KI: Photoemission*

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Synchrotron radiation is used to obtain energy distributions of photoemitted electrons from KI above and below the threshold for hole-electron pair creation by the excited electrons. Because the inelastic scattering lengths are short ($\lesssim$15 Å) above the threshold and long (>100 Å) below, the energy distribution of secondary electrons due to pair creation replicates the conduction-band density of states.

We report the first high-resolution ultraviolet photoemission spectroscopy (UPS) study of alkali halides over an optical spectral range large compared to band gap E_g. The results reported here, based on data from KI, are typical of the alkali iodides and potassium halides studied. The experiments were performed with sychrotron radiation which allowed the examination of data below as well as above the hole-electron pair-creation scattering threshold. The three-step model, which has not previously been applied to emitted energy-distribution data both above and below a scattering threshold, is found to be an adequate description of the scattering phenomena observed. Because of the characteristics of the excited electron's scattering length above and below the threshold, one is able to obtain, from the energy distribution of secondary electrons that escape with energies less than the threshold, a replica of the conduction-band density of states (CB DOS). The above observation has not been reported before and it is a consequence of the small ratio of the electron affinity to E_g.

The data were obtained in an ultrahigh-vacuum photoemission spectrometer operated with the electron storage ring at the University of Wisconsin's Physical Science Laboratory.[1] The energy distribution curves (EDC's) of the emitted electrons were measured with a three-stage electrostatic energy analyzer of the co-cylindrical mirror type. The analyzer resolution was a constant of $\simeq$0.2 eV, full width at half-maximum. A typical optical band pass was 4 Å. The spectrometer base pressure was 5×10^{-10} Torr and rose to 2×10^{-8} Torr during vapor deposition of the films at rate of ~10 Å/sec.

A set of EDC's is shown in Fig. 1. The EDC's are plotted as a function of initial-state energy, $E_i = E_K - h\nu + E_T$, where E_K is the kinetic energy in the vacuum, $h\nu$ is the photon energy, and $E_T = 7.6 \pm 0.15$ eV is the emission threshold. Because synchrotron radiation is a continuous spectrum with weak spectral dependence, the EDC's per unit storage-ring current are approximately normalized to the light flux for small spectral intervals. The primary emission from the valence bands (VB's) forms the two peaks in the EDC's for $-2.4 \lesssim E_i < 0$ eV. The closed p-like shell of the anion forms three VB's which the spin-orbit interaction splits by 1.35 ± 0.15 eV into a pair of bands and a single band with widths of 1.2 ± 0.2 and 0.7 ± 0.15 eV, respectively. Each spin-orbit-split peak shows a complex shape attributed to

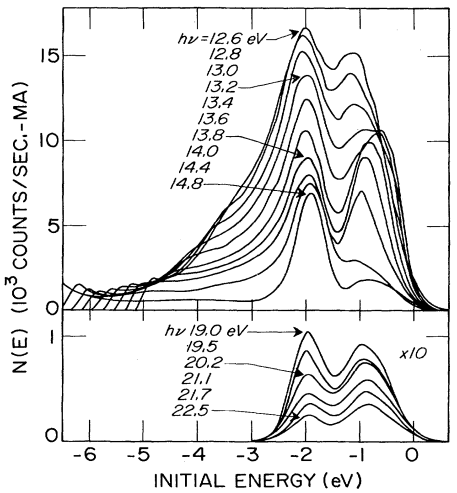

FIG. 1. EDC's from KI film A. For $h\nu > 19$ eV the portion of the EDC's less than -5 eV are deleted.

crystal-field effects. Data obtained by other investigators for $h\nu < 12$ eV are in agreement with the present work for $h\nu < 12$ eV.[2] The details of the primary emission for $h\nu < 21$ eV will be discussed elsewhere. Note that the strengths of the double-band and single-band emission do not show a 2:1 ratio for $h\nu < 21$ eV. Above $h\nu \simeq 21$ eV the strength ratio is about 2:1, suggesting that final-state effects are weak and that the primary distribution represents the VB DOS.

The electrons that are observed in the EDC's with energies less than the primaries ($E_i < -2.4$ eV) are secondaries produced by inelastic scattering processes since the core states are >10 eV below the VB's. Two kinds of secondary electrons are observed which are classified by their energetics as low-energy secondaries (LES) and the high-energy secondaries (HES). The LES result from the intrinsic scattering process which creates a hole-electron pair in the bands and thus have energies $E_i < -E_g$. The HES, appearing at energies $-E_g < E_i \lesssim -2.4$ eV, are attributed to extrinsic scattering processes. The LES characteristics are discussed first.

The effects of inelastic scattering are manifested in the emission data in two ways: (1) The primary electrons are attenuated, and (2) the secondary electrons may be emitted. The attenuation of the double-band peak observed in the EDC's of Fig. 1 for $h\nu \lesssim 13$ eV is due to the onset of scattering by pair production. As shown in Fig. 2, this attenuation occurs abruptly at a fixed final-state energy near 13 eV. The attenuation by scattering is distinct from the overall general decrease in amplitude of the primary emission for $12 \lesssim h\nu \lesssim 13.0$ eV (see Fig. 1). The latter decrease is attributed to matrix-element and DOS effects and produces an attenuation in the spectral distribution of the quantum yield (area of EDC) that is somewhat stronger than that produced by pair scattering. A yield attenuation in this spectral range was observed by earlier investigators[3] and was attributed to scattering effects only; nonscattering effects were not recognized.

According to the three-step model for photoemission,[4,5] the dominant factor in the probability for the primaries to escape *without* inelastic scattering is $\alpha L(\alpha L + 1)^{-1}$, where α is the absorption coefficient and L is the inelastic scattering length. The results of a computation for this escape probability are shown in the inset of Fig. 2. The computations used a measured value for α.[6] The values for L were calculated using the

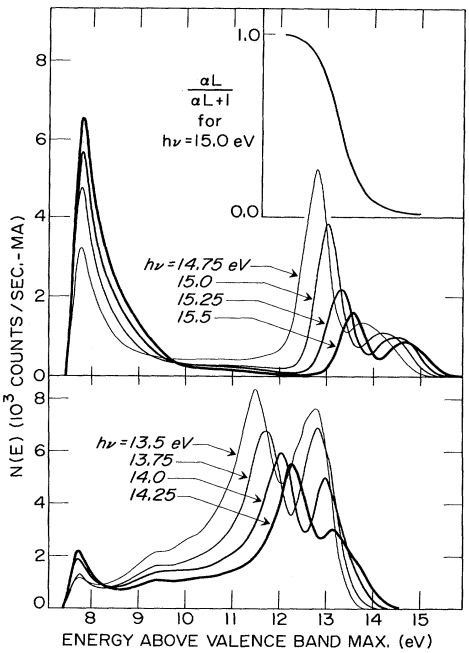

FIG. 2. EDC's from KI film D (about thickness of film A). Inset: A calculation of $\alpha L(\alpha L+1)^{-1}$ plotted on the EDC's energy axis. L is the inelastic scattering length and α is the absorption coefficient.

theory obtained in the three-step model.[4] The latter calculations assume the scattering matrix elements and group velocities to be constant,[4,5] and use the CB DOS obtained from band theory[7] (shown in Fig. 3) and the VB DOS from the present data. The value of L at one energy was used as a free parameter. The value was selected to

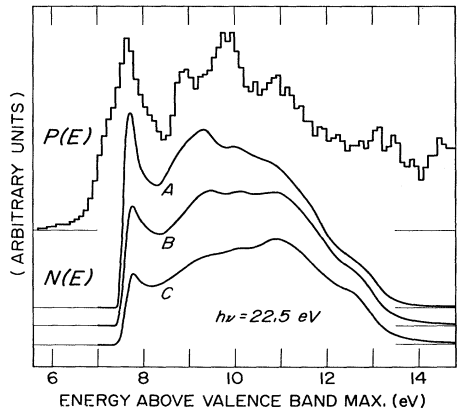

FIG. 3. The portion of the EDC's containing the secondary electrons from KI films A, B, and C with approximate thicknesses of 900, 140, and 80 Å, respectively. The histogram shows the conduction-band density of states obtained from band calculations (see Ref. 7).

be 16 Å at 14 eV above the VB maximum by fitting $\alpha L/(\alpha L+1)$ to the data in Fig. 2. While the model describes the scattering edge well it is too primitive to describe properly the emission strength of the primaries above the scattering edge.

Comparison of the data below the pair-creation threshold where the primaries' escape depth is more than 100 Å with data above the threshold where the depth is $\lesssim 15$ Å suggests that the VB electron energies in those unit cells very near the surface are not significantly shifted by surface effects from the values for electrons which originate much deeper in the solid.

The LES are emitted for $h\nu \gtrsim 14$ eV and appear as the low-E_K electrons in the EDC's since the electron affinity is much less than E_g (see Fig. 2). The maximum E_K of the LES increases with increasing energy of the primaries, and hence also with $h\nu$. Figure 3 shows the low-E_K portion of the EDC's obtained at $h\nu = 22.5$ eV for a sample of different thickness.[8] The LES are well separated from the primaries which are deleted in Fig. 3. The EDC's obtained for $32 < h\nu < 40$ eV are very similar to those in Fig. 3. Secondaries created with energies above 13 eV are also attenuated by pair production which gives an upper edge to the scattered electrons that have a high probability of escape. The LES portion of the EDC's have structures—shoulders and peaks—at energies independent of $h\nu$. The latter structures, except for the pair production edge, replicate the structure in the CB DOS. The replication is predicted by the elements of the three-step model where the resulting description of the energy distribution of secondaries can be viewed as the product of three functions: (1) CB DOS, (2) the probability for an electron to be scattered into E, and (3) the probability of escape without scattering.[4] The probability of scattering is a "smooth" function of energy since it is described by double integrations of DOS products.[4] The observation of LES structure in the alkali halides appears to be a consequence of a long inelastic scattering length below the pair-production edge. The lack of structure in the secondary distribution of other types of solids may be related to short scattering lengths which govern their emission properties. One may expect to find CB structures in the secondary distribution of other classes of solids which have electron affinities smaller than E_g.[9]

Figure 3 compares the data with CB DOS obtained from a relativistic-mixed-basis band calculation.[7] The agreement is very good. Both data and calculations show a triplet preceded by a strong minimum and followed by a shoulder at high energy. The low-energy edge in the data of Fig. 3 is a result of the sample's surface barrier.

Onset of the attenuation by pair production occurs at ≈ 13 eV, a value which is larger than twice E_g. Reported values for E_g are 5.8 to 6.3 eV.[2,6,7] Inspection of Fig. 3 appears to resolve this discrepancy when one notes how small the CB DOS is for energies near the band minimum.

We now comment on the second kind of secondary electrons that are observed in the EDC's, the HES. The HES are emitted with energies between the primaries and the LES, $-5.5 < E_i < -2.4$ eV. A different scattering mechanism produces the HES compared with the LES since the energy loss in HES creation is less than E_g. Several properties of HES are evident from the data: (1) By noting the number of HES as the primaries encounter the pair-production threshold one sees that they are closely correlated with the number of primaries from each segment of the VB's (Figs. 1 and 2); (2) secondaries are observed which have lost over 2 eV of energy; (3) the ratio of the number of HES to the number of primaries increases with sample thickness (not shown); (4) the HES distribution reflects the CB DOS (note the shoulder at $E \cong 9.5$ eV in Fig. 2). The HES have been observed in the previous UPS studies done for $h\nu < 12$ eV, in which only properties (3) and (4) were obtained.[3,10] The third property implies that the scattering mechanisms producing HES are in the interior of the sample rather than at the surface. As noted by property (2), examination of the EDC'S with the aid of property (1) shows that many of the electrons excited from the upper double-band portion of the VB's suffer an energy loss greater than 2 eV. Because of the small value for phonon energies ($\lesssim 12$ meV),[11] phonon scattering cannot account for such a large loss. These considerations suggest that scattering by imperfections in the interior is an important mechanism for HES production. A natural, but speculative, choice for the scattering centers are color centers.

Subtle modulation in the shapes of the primary peaks in the EDC's tend to support the interpretation that $\vec{k}$-conserving transitions play an important role in the optical excitations in KI.[2,10] A definitive test however is difficult to make because of the narrow VB widths and the complicated strong structure found in the CB DOS. Further, many of the curves have a shoulder near

$E_i = -0.6$ eV in addition to a peak near -1.3 eV, suggesting that the two highest filled bands are split near the edge of the Brillouin zone; such splitting would support the use of Bloch functions in the description of the VB states.[10]

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[9]Direct emission of the K^+ $3p$ core is seen for $h\nu > 23$ eV. At $h\nu = 22.5$ eV some core holes could give Auger emission into $10.5 < E < 14$ eV. In NaI and LiI at $h\nu \simeq 4E_g$, where no Auger processes exist, similar LES properties exist. Thus correction for Auger emission is not made.

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Phonon Instabilities in $TmVO_4$

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The lattice instability of $TmVO_4$ near its cooperative Jahn-Teller phase transition is shown to be a competitive process involving distortions of B_{1g} and B_{2g} symmetry. In order to understand the soft-mode behavior, we must consider the spin-lattice coupling of the entire $J = 6$ ground multiplet of the Tm^{3+} ion. Axial magnetic fields are found to affect dramatically the soft acoustic-mode behavior.

In this Letter we report experimental and theoretical results concerning the dynamic behavior of acoustic phonons near the tetragonal-to-orthorhombic cooperative Jahn-Teller phase transition in $TmVO_4$ ($T_c = 2.1$°K). The crystallographic point group for $T > T_c$ is D_{4h}, and the Tm^{3+} site symmetry is D_{2d}. Our principal findings are these: (1) The soft acoustic mode [with strain $e(B_{2g}) \equiv e_{12}$ transforming as xy, and elastic constant c_{66}] exhibits considerable structure in its temperature dependence for $T \simeq 40T_c$. This structure is found to be a consequence of the Jahn-Teller interaction of the strain with an excited doublet with E symmetry ($2\Delta \simeq 138$ cm^{-1}) of the Tm^{3+} ground multiplet ($J = 6$). (2) The acoustic mode corresponding to the $e(B_{1g}) \equiv (e_{11} - e_{22})/2$ strain transforming as $x^2 - y^2$ [elastic constant $(c_{11} - c_{12})/2$] competes with the B_{2g} strain to determine the space group of the distorted low-temperature phase. This elastic constant [$(c_{11} - c_{12})/2$] softens by 18.6% (in absolute value as much as c_{66}) as the transition is approached from above. However, at T_c the crystal becomes unstable to the B_{2g} strain and consequently distorts according to a B_{2g} strain. This distortion stabilizes the B_{1g} mode, thereby arresting the softening of $(c_{11} - c_{12})/2$, which is then found in the distorted phase to be both temperature and magnetic field independent. (3) Because the Zeeman splitting of the ground doublet by axial magnetic fields of a few kilo-oersteds is comparable to the Jahn-Teller splitting of this doublet, the elastic properties are found to be extremely sensitive to fields of this type. In particular, c_{66} is zero along the phase boundary in the H-T plane, and $(c_{11} - c_{12})/2$ exhibits a sharp kink at the phase boundary. (4) Elastic modes for which the spin-phonon interaction has no nonvanishing matrix elements