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Excitonic shifts of quasiatomic optical core to conduction-band transitions in PbI_2 and BiI_3

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Optical transitions from cation $5d$ core levels in PbI_2 and BiI_3 are studied with uv photoemission secondary yield techniques and are compared to theoretical calculations for energies up to ~ 6 eV above threshold. Sharp structures associated with quasiatomic cation $5d \rightarrow 6p$ transitions allow one to determine the relative energy position of the theoretical one-electron absorption spectrum with respect to the experimentally measured spectra. The transitions for PbI_2 appear at 1.8 eV smaller energy than the calculated structures whose energy positions are estimated from the Pb $5d$ binding energy. A similar shift is found for BiI_3. Electron–core-hole interactions provide a reasonable explanation for the observed rigid shift of the entire spectrum.

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The rather important and widely discussed[1-7] issue of possible core-hole–electron interaction effects in noninsulators has not yet been clarified satisfactorily. For silicon a large excitonic shift of the $L_{2,3}$ edge has first been denied,[1,2] however, it has more recently been supported[3,4] on the basis of different experimental data. Similarly controversial is the core-exciton issue for III-V compounds.[5,6] In the case of lead chalcogenides Martinez *et al.*[7] have identified an excitonic shift of ~ 0.8 eV in the reflectivity of the Pb $5d$ edge. As first pointed out in Ref. 7, the determination of the edge position is usually complicated due to spin-orbit effects in the conduction bands and the associated dipole selection rules for transitions from $5d_{5/2}$ levels. From the studies in Ref. 7 and also the present work, it follows that only carefully calculated one-electron absorption spectra, taking into account spin-orbit and band-structure effects, allow one to determine the existence of any excitonlike effects. Furthermore, none of the earlier experiments[1,3-7] has given clear information on excitonic effects *above* the threshold except within the effective-mass appproximation which is valid for small excitonic shifts.

In the present work we have employed a uv photoemission technique to analyze the optical transitions from the cations $5d$ core levels to states 0–6 eV above the conduction-band minimum in PbI_2 and BiI_3. These transitions are of quasiatomic character corresponding to the $5d \rightarrow 6p$ excitation of the cation atoms.[8] Four sharp structures have been found for PbI_2 due to spin-orbit splitting both initial and final states and to a partial violation of atomic dipole selection rules. Their positions in energy are in complete agreement with the theoretical spectrum after a rigid shift of about 1.8 eV. The shift is attributed to electron–core-hole interactions which seem to be energy independent and it conserves the structure of the one-electron spectrum. Similar results for BiI_3 give an excitonic shift of 1.6–1.8 eV for the Bi $5d \rightarrow 6p$ transitions. We thus present in this note clear experimental evidence for the existence of excitonic effects at and above core-level thresholds in noninsulators.[9]

The experiment consists of exciting the samples with photons of energy $\hbar\omega$ and of counting the number of photoemitted electrons with a kinetic energy $E = \hbar\omega +$ const; thus both electron and photon energies are varied synchronously. This photoemission technique is known as constant-initial state (CIS) spectroscopy.[10] Its main purpose usually is to study final-state effects in the primary photoionization process since initial-state energies are kept constant in this technique. Additional structures are often produced in the CIS spectra by several secondary mechanisms consisting of an optical excitation followed by some Auger process.[10] In this Auger process the optical excitation energy or part of it is used to excite a valence band electron to a state above the vacuum level whereby it may be able to leave the sample. CIS peaks arising from these secondary processes can be distinguished from primary peaks since they appear at constant *photon* energy $\hbar\omega$, rather than at constant photoelectron kinetic energy E.

In the present case we have taken CIS curves on freshly cleaved PbI_2 and BiI_3 samples under ultrahigh vacuum conditions (pressure $\lesssim 1.5 \times 10^{-9}$ Torr) using monochromatized photons with either s or p polarization emitted by the University of Wisconsin storage ring. Figure 1 shows the results for PbI_2 for both photon polarizations and for three different

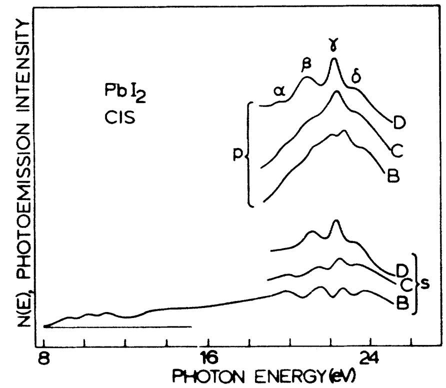

FIG. 1. Constant-initial-state (CIS) curves of PbI_2 for both photon polarizations. Each curve corresponds, to a different initial-state energy for primary photoionization processes, $E-\hbar\omega$. The initial state has been selected to coincide with one of the peaks of the valence band density of states (Ref. 15). For each CIS curve the corresponding valence band density-of-states peak is indicated by the capital letter at its right following the convention of Ref. 15. The initial state energy is 2, 3.2, and 3.8 eV below the top of the valence band for curves B, C, and D, respectively. The four structures α, β, γ, and δ appear at constant photon energies in different curves.

values of the energy difference $E-\hbar\omega$. The corresponding initial states for primary photoionization processes are 2, 3.2, and 3.8 eV below the top of the valence band E_v, for curves B, C, and D, respectively. The s-polarization curve B has been extended in Fig. 1 to low photon energies to show some constant kinetic energy structure which will be discussed elsewhere.[11]

Four structures can be observed whose photon energy positions do not change more than ± 0.4 eV for the different curves. The four peaks α, β, γ, and δ are found at $\hbar\omega = 19.9 \pm 0.3$, 21.1 ± 0.4, 22.4 ± 0.3, and 23.6 ± 0.3 eV, respectively. For reasons stated above these peaks are clearly due to structures in the absorption coefficient. The transitions start from the Pb $5d$ doublet ($5d_{3/2}$-$5d_{5/2}$) with a spin-orbit splitting of 2.5 ± 0.1 eV, measured by uv photoemission, which coincides with the α-γ and β-δ separation. Also with uv photoemission we have have measured the separation between the top of the valence band E_v and the two doublet components, $5d_{3/2}$ and $5d_{5/2}$, obtaining 18.3 ± 0.2 and 20.8 ± 0.2 eV, respectively. Since the PbI_2 energy gap is about 2.56 eV,[12] the use of the UPS binding energies yields a Pb $5d$ threshold of 20.86 ± 0.2 eV. Thus, at least one of the observed structures in Fig. 1, peak α at $\hbar\omega = 19.9 \pm 0.3$ eV, corresponds to a transition energy *below* the calculated threshold. More refined analysis, presented in the following paragraph, in fact seems to indicate the presence of a core excitonic shift of ~1.8 eV which is common to all four peaks α, β, γ, and δ.

As mentioned above, the existence and magnitude of excitonic shifts in the optical absorption spectrum can only be ascertained, if the experiment is compared to a one-electron absorption spectrum whose shape is calculated taking fully into account band-structure and spin-orbit coupling effects.

The band structure of PbI_2 has been studied previously by the pseudopotential method with and without spin-orbit coupling effects.[8] Wave-function analysis reveals that the lowest conduction bands are strongly composed of cation p levels (Pb $6p$). These findings are in fact necessary to explain the anomalous behavior of the band-gap exciton at ~2.5 eV.[12] Moreover, strong atomiclike optical transitions are thus expected between the Pb $5d$ core levels and the conduction band edge in PbI_2. In an atomic zero-order model, which neglects band-structure effects, transitions take place between the spin-orbit split $5d_{3/2}$, $5d_{5/2}$ and $6p_{1/2}$, $6p_{3/2}$ Pb levels. With spin-orbit splittings of $\Delta E_{5d} = 2.5$ eV and $\Delta E_{6p} = 1.2$ eV one obtains four transitions at energies of E_0, $E_0 + 1.2$, $E_0 + 2.5$, and $E_0 + 3.7$ eV. The lowest transition at E_0, however, is dipole forbidden in this model since it connects the $5d_{5/2}$ and $6p_{1/2}$ levels. These atomic selection rules are expected to be relaxed in the solid due to band-structure effects. To account for these effects we have calculated the conduction-band band structure of PbI_2 in a tight-binding scheme considering only Pb $6p$ orbitals. Overlap matrix elements up to third nearest neighbors are included and empirically determined by fitting the band structure at 13 high-symmetry $\vec{k}$ points to the results of empirical pseudopotential calculations. The same pseudopotentials as given in Ref. 8 have been used. The 6×6 tight-binding matrix has been evaluated at 196 $\vec{k}$ points in $\frac{1}{12}$ of the hexagonal Brillouin zone of PbI_2 and the imaginary part $\epsilon_2(\omega)$ of the dielectric function has been calculated according to

$$\epsilon_2(\omega) \sim \sum_i \int d\vec{k}\, |\langle i\, |\vec{\nabla}|\, \vec{k}\rangle|^2 \delta(\hbar\omega - E_i + E(\vec{k})) \,,$$

where both initial (i) and final ($\vec{k}$) states are combinations of atomic spin orbitals. While the initial $5d$-core states are quantized in the atomic central field, the final states are quantized in the translational invariant crystal field. The initial-state binding energies E_i have been taken, as mentioned before, from UPS and optical spectroscopic data.

Theory and experiment are compared in Fig. 2. The dashed curve is the calculated ϵ_2 spectrum for PbI_2 (broadened by 0.1 eV) *shifted downwards in energy by 1.8 eV* with respect to the UPS Pb $5d$

binding energy to obtain good alignment with the solid curve which is an average of several experimental CIS curves corrected for a smooth background. Note that the absorption coefficient for the "forbidden" $d_{5/2}$-$p_{1/2}$ transition is finite due to crystal field mixing and corresponds to the weakest experimental structure α. In general the experimental peak intensities are not expected to agree quantitatively with the calculated ϵ_2 spectrum since they are influenced by details of the Auger process and of the photoelectron escape process.[13] The very good agreement between experimental and theoretical peak positions in Fig. 2, however, is a strong indication that the Pb $5d \rightarrow 6p$ transitions are indeed influenced by electron-core hole interactions which merely result in a rigid shift of 1.8 eV for the entire spectrum. Before accepting this conclusion we would like to briefly comment on possible relaxation effects. The calculated one-electron ϵ_2 spectrum has been placed in its position on the photon energy scale by measuring with uv photoemission the binding energy of the Pb 5d doublet with respect to the top of the valence band E_v. These measurements are influenced by intra- and interatomic relaxation of the surrounding electronic clouds upon appearance of the core or valence band hole. Since the measurements emit the photoelectron, no excitoniclike effects are expected in these experiments. On the other hand, optical transitions from Pb 5d states to states below the vacuum level are affected by electron-hole interactions in addition to core-hole relaxation effects. The question remains to what extent differential relaxation energies for transitions to states respectively below and above the vacuum level can contribute to the observed 1.8-eV shift. In an attempt to clarify this situation, we have carefully searched for changes in the measured energy difference between the Pb 5d levels and the valence band edge E_v while changing the photon energy, i.e., the final-state energy. No changes could be observed for final-state energies ranging from the vacuum level to about 40 eV above it. On the other hand, we have observed the 1.8-eV shift as described above, for all transitions from Pb 5d states into states below the vacuum level including peak δ whose final-state energy falls only ~1.2 eV below the vacuum level. Since relaxation energies are not expected to change by an amount of 1.8 eV over a range of only 1–2 eV we therefore believe some form of electron-core-hole interaction to be the only reasonable explanation for the overall 1.8-eV shift.

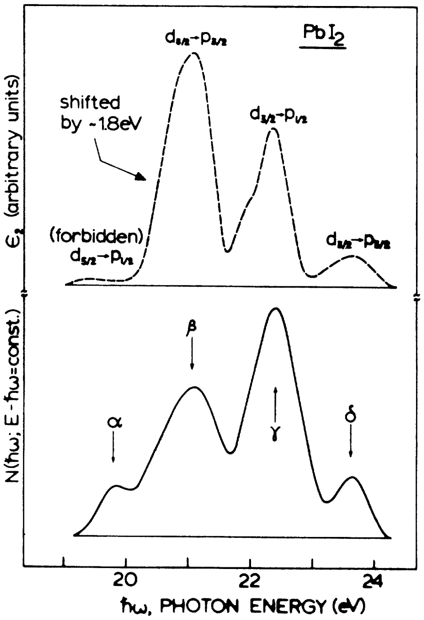

FIG. 2. Solid line: average of several PbI$_2$ CIS curves corrected for a smooth background. Dashed curve: theoretical PbI$_2$ absorption coefficient in the photon energy region where the transitions from Pb 5d to the conduction band prevail. The theoretical curve has been shifted by 1.8 eV to lower photon energies to obtain the best alignment of the four peaks α, β, γ, and δ.

In conclusion we find that all the quasiatomic Pb $5d \rightarrow 6p$ optical transition energies are affected by the same core excitonic correction of 1.8 ± 0.4 eV. We have extended our investigation to BiI$_3$ whose chemical bonds have somewhat less ionic character than those of PbI$_2$. Figure 3 shows the BiI$_3$ CIS curves which exhibit only *three* constant-photon-energy structures, peaks β, γ, and δ. The photon energies for these peaks are $\hbar\omega = 26.9 \pm 0.2$, 28.6 ± 0.2, and 29.7 ± 0.2 eV, respectively. Moreover, the separation of 2.8 ± 0.1 eV between β and δ coincides with the measured Bi $5d_{3/2}$-$5d_{5/2}$ splitting of 3.0 ± 0.2 eV within the experimental un-

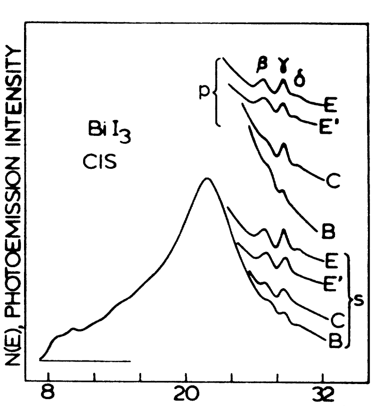

FIG. 3. Constant-initial-state curves of BiI$_3$. The initial-state energy for primary photoionization processes is 1.8, 3.8, 6.6, and 10.8 eV below the top of the valence band for curves B, C, E', and E, respectively.

certainty. Peaks β, γ, and δ are consistent with the three parity-allowed transitions between the Bi $5d$ and the Bi $6p$ doublet components if one assumes a Bi $6p_{1/2}$-$6p_{3/2}$ spin-orbit splitting of 1.1 eV. The atomic selection rule which forbids the $d_{5/2} \rightarrow p_{1/2}$ low-energy transition seems to be more strictly satisfied in the case of BiI_3 than in the case of PbI_2. Comparing as above the measured transition energies of peaks β, γ, and δ and the theoretical energies gives a rigid excitonic shift of 1.6–1.8 eV for BiI_3. We observe that the present core excitonic shifts for PbI_2 and BiI_3 roughly appears of intermediate size between those of the order of ~10 eV found for ionic insulators such as LiF,[14] and those of the order of ~1 eV found for more covalent materials such as silicon,[1-4] III-V compounds[6] and IV-VI compounds.[7]

In summary, secondary yield photoemission techniques have been used to investigate the threshold for optical transitions from d-core levels in PbI_2 and BiI_3. Comparison of the measured PbI_2 spectra with calculated one-electron absorption spectra reveals strong excitonic shifts. Surprisingly, the entire absorption spectrum of about 5 eV width seems to be rigidly shifted downwards in energy due to electron–core-hole interaction. No or little deformation of the one-electron spectra is observed which may suggest that differential or final-state-dependent relaxation effects could be involved. Careful search for such effects on the binding energy of the $5d$ core levels, using uv photoemission with 0–40 eV kinetic energy electrons gave negative results. The observed shifts are thus believed to be due to excitoniclike interactions, possibly interfering with differential hole relaxation effects.

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