RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 17 15 JUNE 1987-I

Bremsstrahlung-isochromat studies of conduction-band states in SnS_2 and $SnSe_2$

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(Received 5 March 1987)

Bremsstrahlung-isochromat spectra of SnS_2 and $SnSe_2$ measured with a photon energy of 1486.6 eV reveal the distribution of the conduction-band density of states within ~15 eV of E_F. The results are in agreement with the theoretical predictions of pseudopotential calculations and with photoemission data, while significant discrepancies exist with respect to optical data.

Layer compounds in the IV-VI and III-VI families have been extensively used as test cases for novel experimental and theoretical techniques in solid-state physics. They are particularly helpful when the techniques explore the unoccupied electronic states, since their quasimolecular character results in sharp structure in the density of unoccupied states. Recently, bremsstrahlung-isochromat spectroscopy (BIS) has emerged as an excellent probe of the electronic state above the Fermi level. We performed a BIS study of SnS_2 and $SnSe_2$, and assessed the quality of its results by comparing them with other experimental and theoretical data. We found good agreement with the theoretical density-of-states curves derived with pseudopotential methods and with photoemission results. However, we found significant discrepancies with respect to core-level optical reflectivity data, which we attributed to matrix-element distortion of the line shape and, tentatively, to the creation of Frenkel excitons.

Tin disulfphide and tin diselenide are layered semiconductors with the CdI_2 crystal structure.[1] Because of their prototypical character, these materials have been extensively studied with a variety of experimental and theoretical techniques.[2] Their band structures have been calculated with pseudopotential[3-8] and tight-binding[9-11] methods. From the calculations, the nature of the chemical bonds and the atomic-orbital character of the bands have been identified. It is generally agreed that near the valence-band maximum the anion $p_{x,y}$ states dominate, whereas the conduction-band minimum is mainly cation s-like. Photoemission[12-23] and x-ray emission spectroscopy[8,24,25] have produced detailed information about the valence-band states. In contrast, the information on the conduction band, primarily obtained from optical[10,26,27] and photoemission experiments,[16,17,20] is rather limited.

Our BIS measurements were performed with a photon energy of 1486.6 eV. We explored the energy region 0-17 eV above the Fermi level, E_F, including the region below the vacuum level, which is not accessible with photoemission and is the most likely to be affected by large excitonic effects in core-level optical spectroscopy. The experiments were performed in a four-chamber system whose base pressure is $\sim 5\times10^{-11}$ Torr in each chamber. The 1×5-mm^2 incident beam was emitted by a custom-designed Pierce electron gun.[28] The typical beam current was 15 μA. Photons with the appropriate energy, 1486.6 eV, were filtered by a 0.5-m Rowland-circle quartz grating monochromator and detected with a microchannel plate. At this energy modulation by matrix elements is negligible.[29] The final-state energies above the Fermi level were scanned by ramping the accelerating voltage of the electron gun. The overall energy resolution of the spectrometer was approximately 0.7 eV, as determined from the width of the leading edge of the Pt BIS curves. A detailed description of the experimental system will be given in Ref. 28.

The SnS_2 and $SnSe_2$ samples, prepared with the vapor-transport technique,[30] were cleaved *in situ* at 5×10^{-11} Torr. During the BIS measurements, the pressure rose to 1.6×10^{-10} due to electron-stimulated desorption.[28] Energy scanning and data acquisition were controlled by a Compupro computer. Typical count rates ranged from 2 sec^{-1} (dark counts) to 10 sec^{-1}. The total time required to scan the initial-state energy range 1482-1512 eV (measured from E_F) was 10 h. The spectral features were reproducible from cleave to cleave, and we found no evidence of contamination, consistent with the inert nature of these compounds.[12]

Figure 1 shows the BIS curves of SnS_2, $SnSe_2$, and the Pt reference sample. The latter was electrically connected to the measured samples and was used to establish the position of the Fermi level. Because of the high energy of the initial state in the deexcitation process, the effects of the initial density of states and the transition probability are negligible, and the BIS curves primarily reflect the final density of states, i.e., the density of unoccupied states in the lower conduction-band region. The SnS_2 results reveal two sharp features 3.5 and 7.2 eV above E_F, peak A and B. The band-structure calculations indicate that peak A has predominantly cation s character with some anion $p_{x,y}$ contribution. Peak B has mainly cation p_{xy} and p_z character.[6] For energies higher than ~9 eV above E_F, the calculations predict delocalized states without distinct

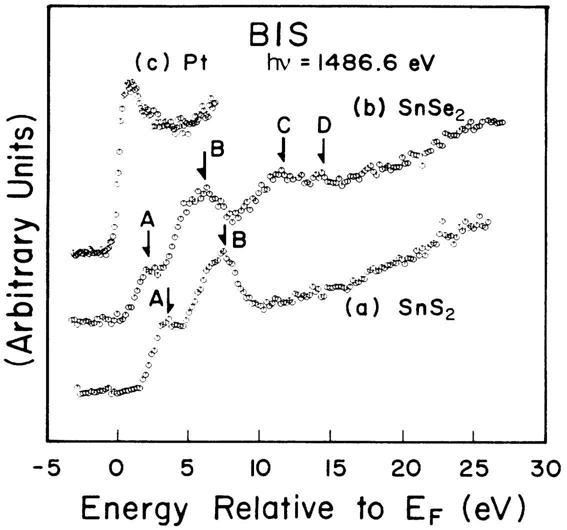

FIG. 1. Bremsstrahlung isochromat spectroscopy curves for (a) cleaved SnS_2, (b) cleaved $SnSe_2$, and (c) an air exposed Pt sample. The curves were taken at a photon energy $h\nu = 1486.6$ eV. The energy scale is referenced to the Fermi level E_F of the Pt reference. The conduction band minima are identified.

atomic-orbital character.[16] This is consistent with the absence of structure in the BIS curve, which is dominated in that region by the background due to radiative decay of secondary electrons.[31] The conduction-band minimum, E_c, is found by linear extrapolation of the leading edge to be 1.3 eV above E_F. This is consistent with the optical gap of 2.1 eV.[32]

In Fig. 2 we compare the BIS results with other experimental and theoretical estimates of the SnS_2 conduction-band density of states. Curve (b) is the result of a pseudopotential calculation by Margaritondo, Rowe, Schluter, and Kasper, reported in Ref. 16. Curve (c) is the conduction-band density of states derived from constant-initial-state (CIS) photoemission spectra taken with synchrotron radiation.[16] Curve (d) is a reflectivity spectrum, corresponding to optical transitions from the Sn 4*d* core level which is 24.4 eV below the valence-band maximum.[10,33]

The overall agreement among the BIS, theoretical, and CIS curves is evident. The good agreement of the pseudopotential results with the experimental data is in sharp contrast with the poor agreement of tight-binding results.[11,15] The tight-binding calculation, on the other hand, does provide a reasonable picture of the valence-band density of states. Notice that peak *A* in the BIS curve falls below the vacuum level and is not accessible with the CIS technique.

The reflectivity spectrum of Fig. 2(d) has only a weak shoulder in the energy region corresponding to the BIS peak *A*. This is due to the fact that the lower conduction band is primarily derived from Sn 5*s* states, to which transitions from the Sn 4*d* states are dipole forbidden. The reflectivity spectrum has a prominent peak 3.5 eV above E_c which has been associated with transitions to Sn 5*p* states.[10] This peak appears related to peak *B* in BIS spectrum, but there is a large discrepancy, ~2.4 eV, between the two peak positions. In principle, many-body effects in the BIS curves could contribute to this discrepancy. However, the agreement between photoemission and BIS curves indicates that the discrepancy originates primarily from the optical data. We tentatively attribute it to the creation of excitons, most likely highly localized Frenkel excitons. Unusually large core-excitonic shifts have been observed in the layer compounds.[2]

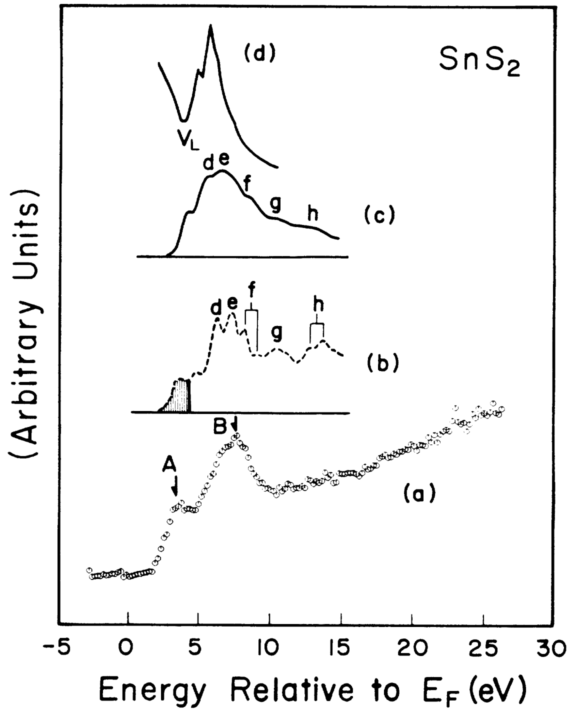

FIG. 2. Comparison among (a) a SnS_2 BIS curve, (b) the conduction-band density of states derived with pseudopotential calculations (Ref. 16), (c) the conduction-band density of states deduced from CIS measurements (Ref. 16), and (d) the reflectivity spectrum corresponding to transitions from the Sn 4*d* core level (Ref. 10).

The BIS curve of $SnSe_2$ is similar to that of SnS_2 in the lower 7 eV of the conduction band, and the two peaks *A* and *B* have similar atomic orbital character as the corresponding peaks for SnS_2. The conduction-band edge E_c was found to be 0.5 eV above E_F, consistent with the optical gap of 0.97 eV.[32] It can be seen in Fig. 1 that the $SnSe_2$ BIS spectrum exhibits additional structures, peaks *C* and *D* at 10.8 and 13.5 eV above E_F, in the region where no structure was observed for SnS_2. The identification of the corresponding conduction bands is difficult because the current calculations do not include states more than 8 eV above E_c, and also because these states are delocalized with no strong atomic-orbital character. It seems reasonable, however, to assume that peaks *C* and *D* are related to Se 4*d* states. In SnS_2 there is no evidence of localized S 3*d* states up to 10 eV above E_c.[16]

In Fig. 3 we compare our $SnSe_2$ BIS curve with the theoretical conduction-band density of states obtained from pseudopotential calculations [curve (b)],[6] and with

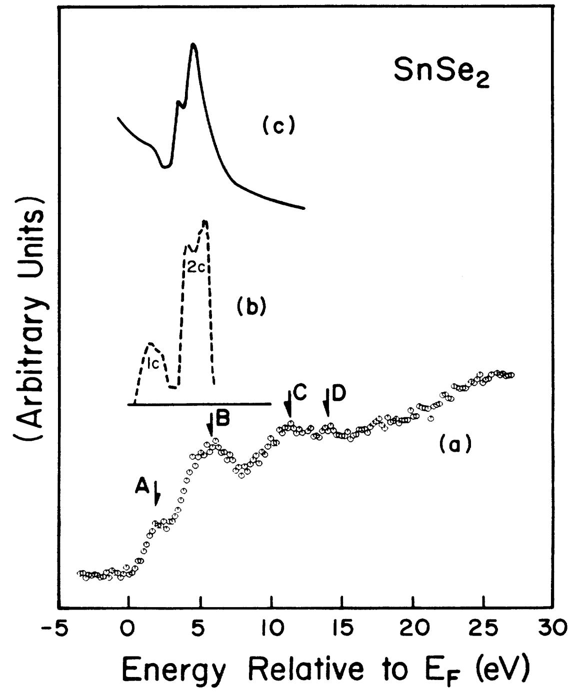

FIG. 3. Comparison among (a) a SnSe$_2$ curve, (b) the conduction-band density of states derived with pseudopotential calculations (Ref. 6), and (c) the reflectivity spectrum corresponding to transitions from the Sn 4*d* core level (Ref. 10).

the reflectivity spectrum corresponding to transitions from the Sn 4*d* core level, 25.5 eV below the valence-band maximum [curve (c)]. As for SnS$_2$, there is a large discrepancy between the BIS peak *B* and main reflectivity peak. On the contrary, peak *B* is close in energy to three conduction-band features, 5.1, 5.5, and 5.9 eV above E_c, deduced from the analysis of valence-band photoemission spectra in Ref. 20.

In conclusion, we found good agreement between our BIS results and the prediction of pseudopotential calculations. We also found good agreement with the results of photoemission measurements which, however, could not explore the region between the bottom of the conduction band and the vacuum level. Large discrepancies were found with respect to core-level reflectivity curves due to matrix element effects and, possibly, to unusually large core-exciton shifts. Our study shows that BIS provides a more spectrally complete picture of the unoccupied density of states than CIS spectroscopy and a more reliable one than core-level optical data.

This work was supported by the National Science Foundation under Grants No. DMR-86-10837 (Minnesota) and No. DMR-84-21212 (Wisconsin). We gratefully acknowledge the critical efforts of M. Grioni, K. Riggs, and S. Krahn in the development of the bremsstrahlung-isochromat spectroscopy spectrometer which was constructed with support from the Office of Naval Research under Grant No. N00014-83-G-0164.

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