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Bremsstrahlung-isochromat study of the layered compounds InSe, $TiSe_2$, $SnSe_2$, SnS_2, and Bi_2Te_3

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We present bremsstrahlung-isochromat spectra (BIS) for the layered compounds InSe, $TeSe_2$, SnS_2, SnS_2, $SnSe_2$, and Bi_2Te_3 at a photon energy of 1486.6 eV. The spectra exhibit several sharp peaks in the lower conduction bands. These spectral features are compared with theoretical calculations of the density of states and with optical data. In several cases, discrepancies between the BIS spectra and the optical spectra confirm that large core excitonic shifts occur for layered compounds.

Compounds crystallizing in layered structures, because of their quasi-two-dimensional character, are a very active area of solid-state research.[1] The interest in this area was enhanced by the recent discovery that some quaternary layered materials exhibit superconductive properties at high temperatures. This is only one example of the different kinds of instabilities prompted by quasi-two-dimensionality. Charge density waves are another important example. The general understanding of these instabilities requires a detailed knowledge of the electronic properties of layered materials.

Such properties have been extensively studied with a variety of experimental methods, as well as with theoretical approaches.[1] The experimental results have produced important insight into the electronic states—except for those that fall in the lower conduction band. These lower conduction bands fall in an energy region which is below the vacuum level, and they cannot be explored with the synchrotron-radiation photoemission technique known as constant-initial-state (CIS) spectroscopy.[2] Optical experiments do explore the lower conduction bands, but in the case of layered compounds they are often affected by very large core excitonic shifts.[1]

This gap in the knowledge of the electronic structure of layer materials can be eliminated by using bremsstrahlung-isochromat spectroscopy (BIS) to explore the lower conduction-band states. In this article, we report on BIS results for several different layered compounds which exhibit different transport properties and different structures involving a variety of polytypes. The data discussed here were taken on InSe, $TiSe_2$, Bi_2Te_3, $SnSe_2$, and SnS_2. A preliminary description of the results on the tin dichalcogenides was reported in Ref. 3, and the data on InSe are discussed in light of previous BIS results on GaSe, another compound in the same family.[4]

The BIS experiments were performed in a four-chamber ultrahigh-vacuum system at the University of

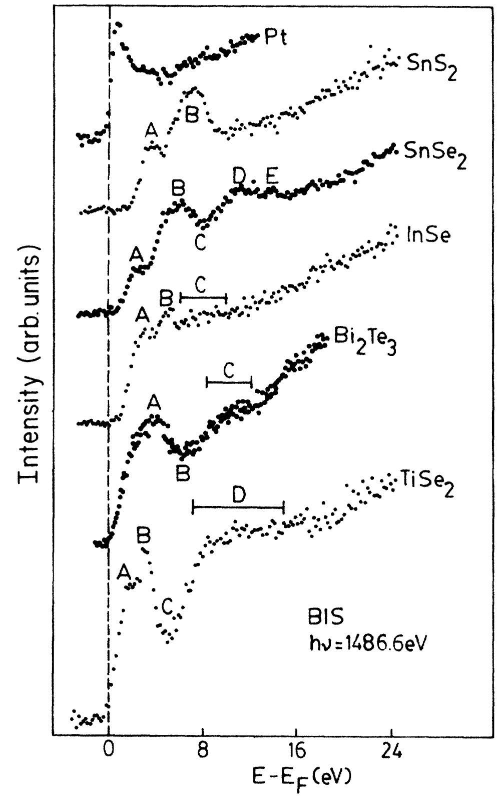

FIG. 1. BIS spectra taken at a monochromator setting of 1486.6 eV for different layer compounds. A spectrum of Pt is also shown, from which we derived the position of the Fermi level, E_F. The spectra are aligned with respect to E_F. The position of the Fermi level, 1484.56 eV, is in good agreement with the experimentally determined work function of the electron gun, 2.1 eV (Ref. 5). The positions in energy of the spectral features are listed in Table I.

TABLE I. Positions in energy of the spectral features of Fig. 1. The positions are given with respect to the experimentally determined position of the Fermi level, E_F and with respect to the valence-band maximum (VBM). The VBM position was estimated from the numerical value of the optical gap E_g and the experimentally determined position of the conduction-band minimum (CBM).

Material, Gap	Feature	Type	$E-E_F$ (eV)	$E-E_{\mathrm{VBM}}$
$TiSe_2$	*A*	shoulder	1.9	a
$E_g=-0.18$ eV[b]	*B*	peak	3.4	a
	C	valley	5.4	a
	D	broad band	7–15	a
Bi_2Te_3	CBM		0.1	0.1[c]
$E_g=0.15$ eV[d]	*A*	peak	3.5	3.5
	B	valley	6.0	6.0
	C	broad band	7.5–12	7.5–12
InSe	CBM		1.0	1.2
$E_g=1.24$ eV[e]	*A*	peak	3.0	3.2
	B	peak	5.1	5.3
	C	broad band	5.8–10	6.0–10
$SnSe_2$	CBM		0.5	1.0
$E_g=0.97$ eV[f]	*A*	peak	2.2	2.7
	B	peak	5.9	6.4
	C	valley	8.1	8.6
	D	peak	11.3	11.8
	E	peak	14.0	14.5
SnS_2	CBM		1.3	2.1
$E_g=2.1$ eV[f]	*A*	peak	3.5	4.3
	B	peak	7.2	8.0

[a] Semimetal or narrow-gap semiconductor.
[b] Reference 21.
[c] E_F is located 0.03 eV above the VBM (Ref. 22).
[d] Reference 23.
[e] Reference 24.
[f] Reference 25.

Minnesota. Each chamber can be isolated from the others, and each has a base pressure of $\sim 5\times 10^{-11}$ Torr. The first three chambers house the electron gun, the x-ray monochromator (used for inverse photoemission at high energies) and the uv monochromator (used for inverse photoemission at low photon energies). The fourth is the sample chamber which includes the instrumentation for low-energy electron diffraction, overlayer growth, cleaving, and sputtering. The 1×5 mm^2 incident electron beam is provided by a custom-designed Pierce electron gun.[5] During the present measurements, the typical beam current was 150 μA.

The incident electrons occupy states of energy E_i in the solid before a fraction of them decay to unoccupied states of energy E_f emitting photons of energy $h\nu=E_i-E_f$. The photon energy, 1486.6 eV, is selected by the 0.5-m quartz grating monochromator and the photons are detected with a microchannel plate detector. The final-state energy is scanned by ramping the accelerating voltage of the electron gun. At BIS energies, the measured photon yield as a function of initial-state energy primarily reflects the density of unoccupied states. The overall resolution of the spectrometer is about 0.7 eV, as determined by the width of the leading edge of the BIS spectrum of Pt. A detailed description of our spectrometer is given in Ref. 5.

The samples were thin platelets prepared with different techniques.[6] Electrical contact was obtained with a Ga-In eutectic, in addition to a conducting epoxy (Ohmex) which connected the sample to the Al sample holder. Each sample was cleaved in the measurement chamber at a pressure of 1×10^{-10} Torr. BIS spectra were measured in the incident electron energy range $1482\le E_i\le 1502$ eV, where E_i is referred to the Fermi level of the sample, E_F. The electron gun ramping and data accumulation were controlled by a Compupro computer. Typical count rates ranged from 2 s^{-1} below the onset (dark counts) to 10 s^{-1} a few eV above the conduction-band minimum. The typical time required to measure one spectrum was ~ 10 h. The spectral features were reproducible from cleave to cleave and showed no evidence of contamination, consistent with the inert nature of these layered compounds.

Figure 1 shows BIS spectra for SnS_2, $SnSe_2$, InSe, Bi_2Te_3, $TiSe_2$, and a Pt standard. The position of the Fermi level was determined from the BIS edge of a Pt specimen in electrical contact with the sample. The positions of the main features of our spectra are listed in Table I, referred to the valence-band maximum (VBM) and to E_F. We derived the VBM from the known gaps and from the position of the conduction-band minimum (CBM), which in turn was derived by linear extrapolation from the spectral edge. In the case of $TiSe_2$, whose semiconducting or semimetallic nature is still controversial,[1] we used the Fermi level as the only reference.

All compounds show one or two sharp peaks in the range up to 8 eV above the Fermi level. In general, these sharp peaks are followed by a minimum and by a broader feature at 8–15 eV. At higher energies, the primary signal is superimposed onto a large background of secondaries which obscure the information on the upper conduction bands. This background is the counterpart of the secondary-electron signal found in conventional photoemission spectra.[7]

Figure 2 shows a BIS spectrum for InSe, together with other experimental and theoretical density-of-states curves.[8,9] There is a reasonable correspondence between our BIS peaks *A* and *B* and the peaks observed in the L_2 and L_3 optical-absorption thresholds [Fig. 2(b)].[8] On the contrary, in the case of GaSe we observed large discrepancies between BIS and optical data.[4] Considering the similarity of the two materials, the reason for this different behavior is not clear. We emphasize that the discrepancies observed in the case of GaSe cannot be entirely attributed to core excitonic shifts[1] and that the electron self-energy in the BIS process appears to play an important role.[4]

The identification of the optical and BIS InSe peaks with the theoretical features shown in Fig. 2 is not straightforward, since this theoretical density of states (DOS), as well as other tight-binding results, predict a peak close to the CBM, which is not found in our spectra. The BIS peak *B* is primarily due to the upper structure in the theoretical DOS, formed by states with strong In $p_{x,y}$ character. The corresponding feature is weaker in the optical absorption. This corroborates the identification of the corresponding states as *p*-like, since they correspond to forbidden transitions for the $L_{2,3}$ edge. The upper group of peaks in the theoretical DOS is separated from the lower peaks by a gap. This is largely an artifact of the tight-binding approach. Pseudopotential calculations show instead an intermediate group of bands, generated mostly by empty Se 5*s* orbitals.[10] These states are close in energy to the BIS peak *A*.

Figure 3 compares our BIS data for $TiSe_2$ with two theoretical DOS curves [Figs. 3(c) and 3(d)] (Refs. 11 and 12) and with an optical *K*-edge absorption threshold curve [Fig. 3(b)].[13] Notice, that, since this material is known to be either a semimetal or a semiconductor with very narrow gap, we aligned the leading edge of the optical-absorption curve, rather than the midpoint, with the experimentally determined Fermi level. There is a reasonably good correspondence of the peaks of all curves in this figure. In particular, the BIS curve shows the fine structure of the lower peak, which is not resolved in the optical-absorption spectrum. The existence of this fine structure is consistent with the theoretical DOS data, the curves of Figs. 3(c) and 3(d), which exhibit four narrow peaks, mainly Ti *d*-like. At higher energies, the minimum in the spectral curves corresponds to a gap predicted in Ref. 14.

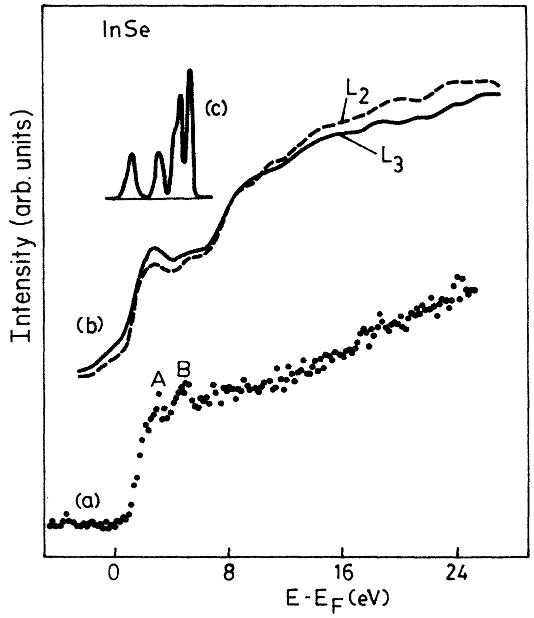

FIG. 2. (a) BIS spectrum of InSe. (b) In L_2 and L_3 optical-absorption edges of InSe from Ref. 8. (c) Theoretical DOS of InSe, from Ref. 9.

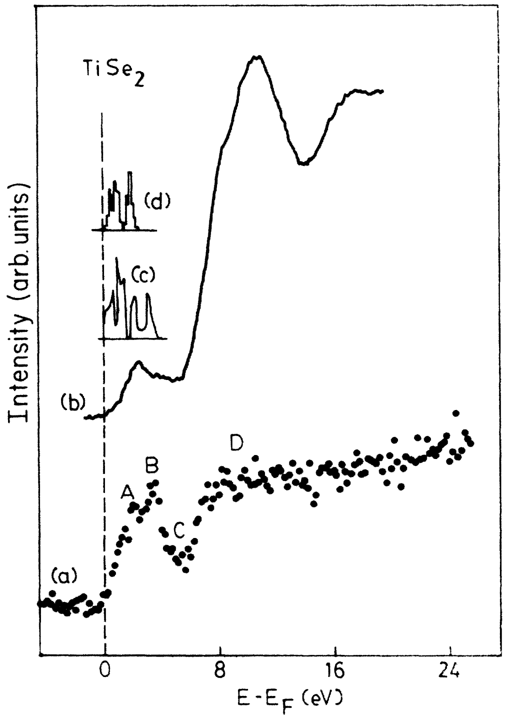

FIG. 3. (a) BIS spectrum of $TiSe_2$. (b) Titanium *K* optical-absorption edge of the same compound, from Ref. 13. (c) and (d) are theoretical DOS curves from Refs. 11 and 12.

Figures 4 and 5 compare our data with previous theoretical and experimental studies for SnS_2 and $SnSe_2$.[15–17] A preliminary discussion of these results is reported in Ref. 3. The most important point concerning Fig. 4 is that there is a good correspondence between the BIS peaks and the peaks in the theoretical DOS data and in the experimental CIS curve. On the contrary, the peak in the optical-absorption spectrum which corresponds to the BIS peak *B* is shifted to lower energies by approximately 1.5 eV. This suggests that the discrepancy in this case is primarily due to core excitonic effects in the optical data. Likewise, there is a 1.0-eV discrepancy between BIS and optical data in the case of peak *B* for $SnSe_2$.

The theoretical calculations of Refs. 18–20 for Bi_2Te_3 do not include DOS results and it is difficult to compare them directly with our BIS data. In essence, the lower-conduction-band BIS data show only a broad feature which corresponds to a variety of theoretical conduction bands.

One important issue concerning our BIS data is to what extent they provide a picture of the conduction-band density of states. This is a crucial issue since, for layer compounds, the traditional core-level optical-absorption experiments can be affected by unusually large core excitonic shifts. Thus, one cannot rely entirely on optical data to establish the energy positions of the lower conduction-band structure. One cannot, on the other hand, assume *a priori* that the BIS curves provide a reliable picture of the DOS features. The final state of the BIS process is that of the system under investigation plus one electron. Many-body effects can cause discrepancies between the BIS spectral features and the corresponding DOS peaks of the system. There is no easy way to identify these effects and make the necessary corrections. However, our data indicate that the BIS features do, in most cases, provide a good picture of the conduction-band DOS. This conclusion is reached by systematically comparing BIS, optical and theoretical curves. Among the latter, those derived with advanced pseudopotential techniques appear, as expected, more reliable than the tight-binding results. Perhaps the most significant results are those obtained for SnS_2. They show good agreement between BIS, CIS, and theoretical curves, and a substantial discrepancy with respect to the optical data. In this case, it is safe to conclude that BIS provides a more reliable picture of the conduction-band DOS than the optical data.

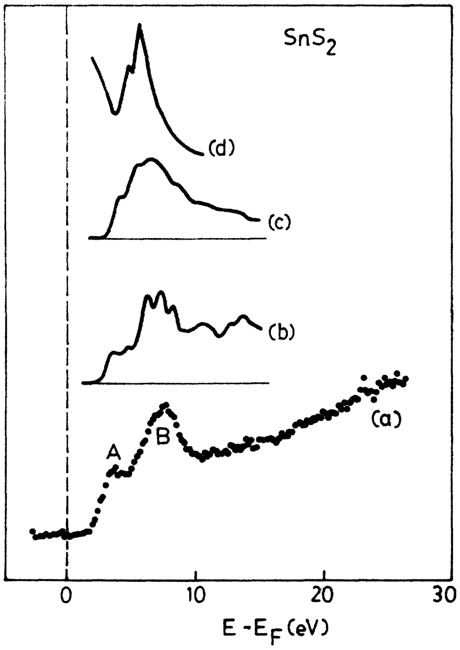

FIG. 4. (a) BIS spectrum of SnS_2. (b) Theoretical conduction-band DOS of the same compound, from Ref. 17. (c) CIS spectrum from Ref. 17. (d) Reflectivity spectrum in the photon energy region corresponding to transitions from the Sn 4*d* core level to the lower-conduction-band states (from Ref. 16).

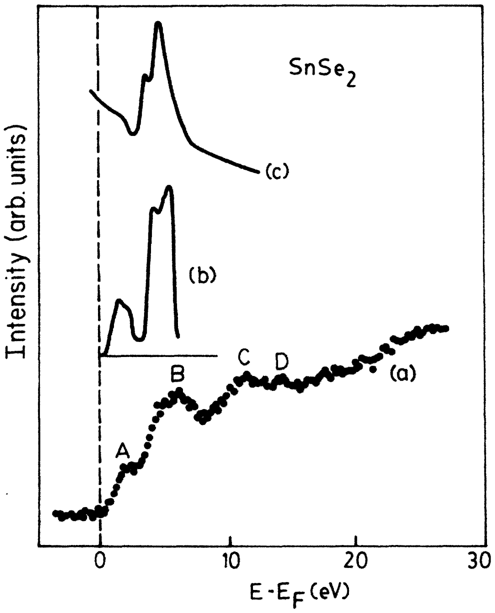

FIG. 5. (a) BIS spectrum of $SnSe_2$. (b) Theoretical DOS from Ref. 15. (c) Reflectivity spectrum in the photon energy region corresponding to transitions from the Sn 4*d* core level to the lower-conduction-band states (from Ref. 16).

For Bi_2Te_3, the BIS curves do not have enough structure for a direct test of the theoretical calculations. The reliability of BIS appears very good in the case of InSe and $TiSe_2$. For both of these materials, there is agreement between the BIS data and the optical-absorption data for deep core levels. This result is particularly significant for InSe for two reasons. First, it is known that optical data at lower photon energies are affected by particularly strong core excitonic effects.[1] Second, InSe is in the same family as GaSe, for which self-energy corrections strongly affect the BIS curves.[4] On the contrary, these effects do not appear important in the case of InSe.

In conclusion, our data dissipate some of the questions raised by the results of Ref. 4 on the use of BIS to study the conduction-band structure of layer compounds. This does not imply that BIS can automatically be assumed to provide a good picture of the DOS. A prudent approach should always include a parallel use of BIS and optical techniques because their combined use substantially increases the reliability of their results.

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[1] See, for example, *Electronic Structure and Electronic Transitions in Layered Materials,* edited by V. Grasso (Riedel, Dordrecht, 1986), and references therein.

[2] G. Margaritondo, *Introduction to Synchrotron Radiation* (Oxford University Press, London, in press).

[3] Y. Gao, B. Smandek, T. J. Wagener, J. H. Weaver, F. Lévy, and G. Margaritondo, Phys. Rev. B **35**, 9357 (1987).

[4] Y. Gao, B. Smandek, M. Nikaido, J. H. Weaver, F. Lévy, and G. Margaritondo, Solid State Commun. (to be published).

[5] Y. Gao, M. Grioni, B. Smandek, J. H. Weaver, and T. Tyrie (unpublished). The electron gun was manufactured by Kymball Physics, Inc.

[6] F. Lévy, Nuovo Cimento B **38**, 359 (1977).

[7] V. Dose, Prog. Surf. Sci. **13**, 225 (1983).

[8] F. Antonangeli, M. L. Apicella, A. Balzarotti, L. Incoccia, and M. Piacentini, Physica B + C **105B**, 25 (1981).

[9] J. Robertson, J. Phys. C **12**, 4777 (1979).

[10] Y. Depeursinge, Nuovo Cimento B **64**, 111 (1981).

[11] Y. Yoshida and K. Motzuki, J. Phys. Soc. Jpn. **49**, 898 (1980).

[12] H. W. Myron and A. J. Freeman, Phys. Rev. B **9**, 481 (1974).

[13] B. R. Davies and F. C. Brown, Phys. Rev. B **25**, 2997 (1982).

[14] Alex Zunger and A. J. Fecince, Phys. Rev. Lett. **40**, 1155 (1978).

[15] M. Schlüter and M. L. Cohen, Phys. Rev. B **14**, 424 (1976).

[16] J. Bordas, J. Robertson, and A. Jacobsson, J. Phys. C **12**, 1907 (1979).

[17] G. Margaritondo, J. E. Rowe, M. Schlüter, and H. Kasper, Solid State Commun. **22**, 753 (1977).

[18] F. Borghese and E. Donato, Nuovo Cimento B **53**, 283 (1968).

[19] S. Katsuki, J. Phys. Soc. Jpn. **26**, 58 (1969).

[20] R. Togei and G. R. Miller, in *The Physics of Semimetals and Narrow Gap Semiconductors,* edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1970), p. 349.

[21] A. Zunger and A. J. Freeman, Phys. Rev. B **17**, 1839 (1978).

[22] A. Balzarotti, E. Burattini, and P. Picozzi, Phys. Rev. B **3**, 1159 (1971).

[23] D. L. Greenaway and G. Harbecke, J. Phys. Chem. Solids **16**, 1585 (1965).

[24] M. Piacentini, E. Doni, R. Girlanda, V. Grasso, and A. Balzarotti, Nuovo Cimento B **54**, 269 (1979).

[25] R. Domingo, R. S. Itago, and C. R. Kannewuf, Phys. Rev. **143**, 536 (1966).