Lawrence Berkeley National Laboratory

Recent Work

Title

WAVELENGTH MODULATION SPECTRA and ELECTRONIC BAND STRUCTURE OF SnS and SnSe

Permalink

<https://escholarship.org/uc/item/8m48w21p>

Author

Camassel, J.

Publication Date

1975-12-01

WAVELENGTH MODULATION SPECTRA AND
ELECTRONIC BAND STRUCTURE OF SnS_2 AND SnSe_2

J. Camassel, M. Schlüter, S. Kohn, J. P. Voitchovsky,
Y. R. Shen, and Marvin L. Cohen

December 1975

RECEIVED
LAWRENCE
BERKELEY
LABORATORY

MAY 14 1978

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-4571

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 6 0 4 4 0 7 9 3 8

UNIVERSITY OF CALIFORNIA

Lawrence Berkeley Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

WAVELENGTH MODULATION SPECTRA AND ELECTRONIC BAND STRUCTURE
OF SnS_2 AND SnSe_2

J. Camassel^{*}, M. Schlüter[§], S. Kohn
J.P. Voitchovsky[§], Y.R. Shen and Marvin L. Cohen[§]

Physics Department, University of California
Berkeley, California

December 1975

WAVELENGTH MODULATION SPECTRA AND ELECTRONIC BAND STRUCTURE
OF SnS_2 AND SnSe_2

by

J. Camassel^{*}, M. Schlüter[§], S. Kohn,[§]
J.P. Voitchovsky[§], Y.R. Shen and Marvin L. Cohen[§]

Department of Physics, University of California, and
Materials and Molecular Research Division
Lawrence Berkeley Laboratory, Berkeley, California 94720

ABSTRACT

We present the first detailed reflectivity and differential reflectivity measurements performed on the layer compounds SnS_2 and SnSe_2 for energies ranging from 2 eV to 6 eV. The results are discussed on the basis of existing band structure calculations. The main structures in the optical response of SnS_2 and SnSe_2 are found to result from excitations from the top most anion p-type valence states (crystal field split p_z - and p_{xy} -type levels) into the lowest conduction band (anion and cation s- and p-type levels). The location of these structures in k-space is found to be very close to symmetry determined "special k points" for SnS_2 .

I - INTRODUCTION

Because of a close admixture of two-dimensional and three-dimensional character, the optical properties of layer compounds have attracted a considerable interest¹⁻³. In this paper, we report the first systematic attempt to analyse the reflectivity and first order derivative reflectivity spectra of SnS_2 and SnSe_2 in terms of electronic interband transitions.

SnS_2 and SnSe_2 crystallize in a hexagonal closed packed CdI_2 -type structure. Within one layer, a plane of metal atoms is sandwiched between two planes of chalcogenides such that each metal atom is octahedrally surrounded by six chalcogen atoms as shown in Fig. 1. From optical absorption measurements⁴⁻⁸, the fundamental absorption has been found to be indirect in both compounds and forbidden for polarisation perpendicular to the C axis. The band edge energies are about 2 eV for SnS_2 and 1 eV for SnSe_2 . In the range of interband reflectivity spectra, very little work has been done: i) room temperature reflectivity⁴ has been reported for SnS_2 in the range 1 eV to 12 eV and, ii) room temperature and liquid nitrogen temperature reflectivity⁹ have been reported for SnSe_2 in the range 1.5 - 5 eV. The reproducibility of the results in this case, obtained on different samples, is somewhat questionable.

In this work we present highly resolved experimental data for an energy range extending from 2 eV to 6 eV. From the measurements of different samples, we find the results are reproducible and we compare our data with the results of two independent three dimensional band structure calculations^{10,11} based on the empirical pseudopotential method (EPM).

II - EXPERIMENTS

All samples used in this experiment were grown by iodine transport technique. As usual, the samples were flat with their large surface ($\sim 1 \text{ cm}^2$) perpendicular to the C axis. Their thickness was only a few tenth of a millimeter, which prevented any attempt to polish them and to perform measurements in the configuration E//C. Consequently, our measurements are restricted to the standard configuration E $\perp$ C. Due to the good quality of the natural faces of the crystals, we used them "as grown". No difference between the spectra obtained in these conditions and a spectrum obtained on a freshly cleaved face was found.

The wavelength spectrometer used in this experiment has been described elsewhere¹². We operate the system in the configuration which gives experimental spectra of $R(\lambda)$ and $(dR/d\lambda)/R$ simultaneously. In order to compare with the calculated spectra, we digitize the data and convert them on a computer to $R(E)$ and $(dR/dE)/E$. Typical spectra are given in Figs. 2 to 5.

Fig. 2 represents the experimental reflectivity spectra of SnS_2 at room temperature and at liquid helium temperature. As usual, the structures shift to higher energy and become much sharper when the temperature lowers. This is clearly seen on the differential reflectivity spectra of Fig. 3. As will be seen in more detail in Sec. III, the structures in our reflectivity spectrum are mainly due to transitions from a group of six top valence bands to the lowest conduction band.

Many fine structures appear at low temperature and correspond to transitions at specific critical points and lines in the Brillouin Zone.

Around 2 eV, a rapid change in reflectivity appears in SnS_2 which is indicative of the absorption edge. However, it is difficult to believe that the strong structure seen in differential reflectivity in Fig. 3 is only due to indirect forbidden transitions^{4,5,7,8}; one has probably in the same range of energy a close superposition of direct and indirect transitions. In Table I, we compare the indirect gap energies found in our derivative spectra with those reported in absorption measurements.

Fig. 4 displays the reflectivity spectra of SnSe_2 from 1.5 eV to 6 eV at 300° K and 5° K. The wavelength modulated spectra are given on Fig. 5. Comparison with the SnS_2 spectra shows the following:

i) There is a shift of the overall structure to lower energies by about 1 eV. This is reminiscent of the shift (0.8 eV) observed on $\text{GaS}_{1-x}\text{Se}_x$ alloys³ for optical transitions with a large charge concentration on anion sites. Total charge density maps, previously published for SnSe_2 ¹⁴, suggest a similar situation for the present case.

ii) The large structure around 4 eV is considerably broader than in SnS_2 (4.9 eV) and displays many more fine structures. The detailed analysis is also given in Sec. III. The lowest structure, seen around 2 eV in Fig. 4 correlates well with previously reported absorption data⁸. The fundamental absorption edge at 1.24 was out of our range of investigation.

The precise position of structures is obtained from the derivative spectra. We list them in Table II for SnS_2 and in Table III for SnSe_2 together with the results of previous investigations and their theoretical assignments discussed in Sec. III.

III - DISCUSSION

a) SnS₂

As already mentioned, SnS₂ (and also SnSe₂) is a material with a strong indirect gap whose energy has been reported in absorption at about 2.40 eV at 80°K⁴. EPM band structure calculations^{10,11} on SnS₂ also reveal a strong indirect gap between the states Γ_2^- and M_1^+ at about 2.2eV. Group theoretical arguments show that this indirect transition is forbidden for polarization $E \perp C$ which is in accord with experimental findings. Although the two band structures of Ref. 10 and 11 show reasonable overall agreement and also quantitative agreement in the immediate vicinity of the fundamental gap, they differ somewhat for higher energy optical transitions. We thus base the following discussion on the band structure of SnS₂ of Ref. 10 and on the band structure of SnSe₂ of Ref. 11. The two band structures are shown in Fig. 6 and k-space locations of the main transitions are indicated.

The first structure found in the differential reflectivity (Fig. 3) appears around 2.5 eV. The richness of structure suggests a close mixing of several direct and indirect transitions in the same range of energy. The situation is quite similar to an observation on SnSe₂^{2,8} where three gaps, two indirect forbidden and one direct allowed, have been reported within one eV. Our suggestion seems also to be in agreement with the high level of absorption ($\sim 10^3 \text{ cm}^{-1}$) found in experiment⁴ for energies only 0.2 eV higher than the first indirect forbidden transition. An inspection of the band structure (Fig. 6) further supports the suggestion.

The next set of structures found in differential reflectivity is located around 2.8 eV (2.61, 2.70, 2.81, 2.90, 2.95). It corresponds to a small structure seen in reflectivity around 3 eV and is attributed to some transitions between bands 8 and 9 (topmost valence band and lowest conduction band) around the points M and L in the Brillouin zone. According to the theoretical results of Fig. 6 these transitions are direct and forbidden. Another set of weak, broad peaks in the reflectivity appears around 3.37 and 3.80 eV. The peak at higher energy is resolved into structures at 3.61, 3.80, and 3.92 eV in the differential reflectivity and corresponds to the structure previously reported at room temperature by Greenaway et al.⁴; our room temperature measurements give the structure at 3.57 eV. According to the band structure, these transitions take place along the line Σ between bands 8 and 9.

So far we were concerned with structure of relatively low intensity which is due either to small transition matrix elements (indirect transitions, forbidden transitions) or to small joint density-of-states contributions. In contrast to this, the next higher energy transitions correspond to the two strong maxima of reflectivity found at 4.98 eV and 5.85 eV at 5°K, displayed in Fig. 2. Around the lower peak, our differential reflectivity spectrum reveals at low temperature four structures which are seen as weak shoulders in the reflectivity. They are located at 4.17 eV and 4.53 eV on the low energy side and at 5.32 eV on the high energy side of the 4.98 eV peak. At room temperature the dominant structure is found at 4.89 eV. The second main peak in the

reflectivity at higher energies (5.8 eV at 5°K) shows only one shoulder at its low energy side (5.58 eV) in the differential reflectivity.

As indicated in Table II, the structures forming the main peak around 4.98 eV correspond to transitions (marked Z1, Z2, in the band structure of Fig. 6), which take place along the lines T and P, including the high symmetry points K and H between the topmost valence bands (they are degenerate along P) and the lowest conduction band. Inspection of the corresponding calculated charge density maps shows that these transitions excited electrons from sulphur P_z -like orbitals into sulphur and tin S- and P-like orbitals. In contrast to these transitions, the second big peak in the reflectivity at 5.85 eV corresponds to transitions in which electrons from sulphur P_{xy} like orbitals are promoted into sulfur and tin S- and P-like orbitals. These transitions are marked XI in Fig. 6 and take place along the lines Σ (and S) between lower valence bands (6) and the first conduction band. The theoretical and experimental findings are summarized in Fig. 7 where a calculated reflectivity based on the band structure of Ref. 19 and the measured reflectivity are compared. The strong disagreement in amplitude for the 4.98 eV structure is probably due to the existence of excitonic character of these transitions⁴. We have investigated the temperature dependence of the differential reflectivity spectra (Fig. 8) and we found that most of the temperature dependence of the broadening parameter occurs between 100°K and 300°K. This supports a characteristic temperature of exciton-phonon interaction in SnS_2 ¹⁵: $\theta \sim 100^\circ\text{K}$ which is in close agreement with the value recently reported for the layer compound MoS_2 ¹⁶ and which suggests a large reduced mass for

the exciton. More experimental studies are however necessary before a conclusive interpretation can be given.

We have seen that the dielectric response of SnS_2 , up to about 6 eV, consists mainly of two peaks. Roughly speaking one can attribute these two main peaks to transitions from sulphur P-like states into sulphur and tin S- and P-like states. The splitting of about 0.9 eV between the two peaks is caused by the anisotropic crystal field splitting of the sulphur P-like levels. Similar splittings with the P_{xy} -like levels at lower energy than the P_z -like levels have also been found in other layer compounds like GaSe or GaS^3 . These two main peaks originate from transitions which take place at locations in k -space which are close to "special k -points" as it has also been found for GaSe^3 . These special k -points are symmetry determined and represent an optimum zero order approximation for evaluating quantities which require k -space integration¹⁶. In other words, a reasonable approximation to the dielectric response of SnS_2 can be obtained by evaluating the band structure at just two "special k -points".

b) SnSe_2

The interpretation of the SnSe_2 spectra results in similar conclusions as obtained for the SnS_2 spectra. Mainly there are two large peaks in the reflectivity between 2 and 6 eV which can roughly be assigned to transitions from the crystal-field split selenium P_z and P_{xy} -like levels to the selenium and tin S- and P-like levels. The difference from the SnS_2 spectra however is the appearance of more fine-structure and more spreading out of the first main peak, coupled to a decrease in intensity.

To clarify the discussion we shall present for this compound charge density contour maps of initial and final states involved in typical transitions.

In addition, we present an optical transition function

$F(\mathbf{r}) = \psi_i(\mathbf{r})P\psi_f(\mathbf{r})$, where P is the momentum operator defined in Ref. 3, which illustrate the character of transitions. The additional information obtained by examining the real-space localization of optical transitions, may be used to discern between atomic-like (intra-ionic), charge-transfer-like, (inter-ionic) or bond-like (bonding-antibonding) transitions.

SnSe_2 has an indirect, forbidden band gap like SnS_2 around 1 eV (see Table III). The theoretical value is close to this value within 0.1 eV. A second indirect forbidden transition has been reported at about 0.3 eV higher energies⁸. Theoretically these transitions could correspond to final states between M and L in the Brillouin zone (see Fig. 6).

The first experimental structure found in our work is at 1.92 eV. This structure is clearly seen on the reflectivity spectra of Fig. 4 and agrees well in position with the first direct transition reported in absorption⁸. The peak however is broad which may indicate contributions from different points in the Brillouin zone. Even with first order differential spectroscopy it was not resolved accurately. Theoretically, the first direct (forbidden) transitions occur at about 1.7 eV between M_2^+ and M_1^+ . The next structure around 2.0 eV is also seen in reflectivity, but not resolved in any previous work. Theoretically these weak transitions occur between M and Γ in the Brillouin zone.

The first large structure is observed between 3.5 and 4.5 eV and obviously corresponds to the first main structure around 5.0 eV in SnS_2 . In SnSe_2 , however, this structure is broad and extends over about 1 eV and features up to five resolved transition peaks in reflectivity (3.6 eV,

3.75 eV, 3.9 eV, 4.2 eV and 4.45 eV). Many fine-structures are found in differential reflectivity and compiled in Table III, together with some tentative theoretical assignments.

In Fig. 9, we compare an experimental spectrum with the calculated spectrum based on the band structure of Ref. 11. To visualize the statements made, about transitions between crystal field split selenium p-like levels and selenium and tin S- and P-like levels, we present in Fig. 10 and 11 charge density contour maps of initial and final states together with contour maps of the transition function $F(r)$ for two representative transitions. The contours are displayed in a (110) plane extending over two half layers with the inter-layer region in the middle of the figures. The atoms are indicated in the figures, the densities are given in units of electrons per unit cell and the transition function is given in atomic units. As a representative transition, we take the transition labelled Z1 in Figs. 6, 9 and Table III as a transition between a selenium P_z -like orbital and selenium and tin S- and P-like orbitals (Fig. 10). As seen from the transition function (Fig. 10c), the optical transition is strongly localized around the anions and exhibits E // C polarization dependence. Note the strong, clear selenium P_z -like character of the valence-band wave function.

As another representative transition, we take the M_{8-10} transition which occurs at slightly higher energy than the experimental X4 peak (see Fig. 9). Both, the T_{7-9} transition which corresponds probably to the X4 peak, and the M_{8-10} transition are of comparable character, with the latter being more pronounced. In Fig. 11, charge density contour maps of

initial and final states are displayed together with the corresponding transition function. The optical transition is also strongly localized around the anions, but now exhibits $E \perp C$ polarization dependence. Note the strong, clear selenium P_{xy} -like character of the valence-band wave function. In contrast to Fig. 10, where the conduction band of the M_{8-10} transition shows some tin P_z -like contributions. These differences, however are unessential in the context of the present discussion, since the optical transition is strongly localized around the anions.

IV - CONCLUSIONS

We presented the first detailed reflectivity and differential reflectivity measurements for the two layer compounds SnS_2 and SnSe_2 . In both compounds the reflectivity spectrum between 2 eV and 6 eV consists of two main peaks. The contributing transitions can be identified on the basis of existing band structure calculations. The two main peaks correspond to transitions from crystal field split anion P_z^- and P_{xy} -like levels respectively into anion and cation S- and P-like levels. The hexagonal crystal field splits the anion P-levels by about 1 eV which roughly corresponds to the separation between the two main peaks in the observed spectra. The corresponding transitions are strongly anion-like which explains the shift of about 1 eV comparing the spectra of SnS_2 and SnSe_2 . The k-space location of the main transitions is close to "special k-points" as defined in Ref. 17. This applies in particular to SnS_2 ; in SnSe_2 the spectrum is more spread out and shows more structures which cannot be so easily generated by two "special k-points".

ACKNOWLEDGEMENTS: We thank Dr. Levy and H. Berger from the Laboratoire de Physique Appliquee, Ecole Polytechnique Federale, Lausanne, for the growth and supply of the samples used in this experiment.

Work performed under the auspices of the U. S. Energy Research and Development Administration.

REFERENCES

- * Supported by a N.A.T.O. fellowship. Permanent adress : CEES - USTL,
34060 - MONTPELLIER-CEDEX - FRANCE.
- § Supported in part by the National Science Foundation, Grant DMR 72-03206-A02.
- o Present adress : Bell Laboratories, Murray Hill, N.J. 07974.
- £ Swiss National Science Foundation Fellow.
- 1 - J.A. Wilson and A.D. Yoffe, Adv. Phys. 18, 193, 1969.
- 2 - A.D. Yoffe, Proc. of the "12th Int. Conf. On the Physics of Semiconductors"
Stuttgart 1974, p. 611.
- 3 - M. Schlüter, J. Camassel, S. Kohn, J.P. Voitchovsky, Y.R. Shen, and M.L. Cohen
Phys. Rev. in press.
- 4 - D.L. Greenaway and R. Nitsche
J. Phys. Chem. Solids. 26, 1445, 1965.
- 5 - G. Domingo, R.S. Itoga and C.R. Kannewurf
Phys. Rev. 143, 536, 1966.
- 6 - P.A. Lee and G. Said
Brit. J. Appl. Phys., J. Phys. D 1, 837, 1968.
- 7 - P.A. Lee, G. Said, R. Davis and T.H. Lim
J. Phys. Chem. Solids, 30, 2719, (1969).
- 8 - B.L. Evans, and R.A. Hazelwood
Brit. J. of Appl. Physics, J. of Physics D2, 1507, 1969.
- 9 - V.V. Sobolev and V.I. Donetskich
Physica Status Solidi, 42, K 53, 1970.
- 10 - C.Y. Fong and M.L. Cohen
Phys. Review, B.5, 3095, 1972.
- 11 - I. Ch. Schlüter and M. Schlüter
Phys. Stat. Sol. B. 57, 145, 1973.

- 12 - R. Zucca and Y.R. Shen
Applied Optics 12, 1293,
also see Y.R. Shen, Surf. Sciences, 37, 522, 1973.
- 13 - R.B. Murray and R.H. Williams
J. Phys. C. Solid State Physics, 6, 3643, 1973.
- 14 - E. Mooser, I. Ch Schlüter and M. Schlüter
J. Phys. Chem. Solids 35, 1269, 1974.
- 15 - Y. Toyozawa
Progress of Theoretical Physics, 20, 53, 1958.
- 16 - E. Fortin and F. Raga
Proc. of the "12 th. Int. Conf. Phys. of Semiconducteurs".
Stuttgart, 1974, p. 647.
- 17 - A. Baldereschi,
Phys. Rev. B7, 5212, (1973)
D.J. Chadi and M.L. Cohen, Phys. Rev. B.7, 692, (1973).

TABLE CAPTION

TABLE I :

SnS_2 : Comparison of the low energy structure obtained in differential reflectivity with the indirect forbidden edge reported in absorption.

TABLE II :

Listing of experimental energies for the main structures in the reflectivity spectrum of SnS_2 (300° K , 5° K) and results of previous experiments. The theoretical assignment, k -space location, and band numbers of the prominent transitions are also listed.

TABLE III :

Listing of experimental energies for the main structures in the reflectivity spectrum of SnSe_2 . We give also the results of previous experiments for comparison. The theoretical assignment, k -space location, and band number of the prominent transitions are also listed.

TABLE I

:	:	:	:	:	:
:	SnS ₂	:	Diff. Reflectivity	:	Absorption
:	:	:	:	:	:
:	Reference	:	(This work)	:	(a) (b) (c)
:	:	:	:	:	:
:	300° K	:	2.32 eV	:	2.21 2.07 2.22
:	5° K/77° K	:	2.50 eV	:	~ 2.40 - -
:	:	:	(5° K)	:	(77° K)
:	:	:	:	:	:
:	:	:	:	:	:

a) - Ref. 4

b) - Ref. 5

c) - Ref. 7

TABLE II : SnS_2

: <u>This work</u> : 300° K	: 2.32	: 2.82	: 3.32	: 3.57	: 4.37	: <u>4.89</u>	: 5.09	: <u>5.74</u>	: 6.04	:	:
:	:	:	:	:	:	:	: 5.41	:	:	:	:
: <u>Previous work</u> : 300° K	: 2.21	:	:	: 3.8	:	: 4.9	:	: 5.8	:	: 6.9	:
: (a)	:	:	:	:	:	:	:	:	:	:	:
: <u>This work</u> : 5° K	: 2.5	: 2.61	: 3.37	: 3.61	: 4.17	: <u>4.98</u>	: 5.22	: 5.58	:	:	:
:	:	: 2.70	:	: 3.80	: 4.53	:	: 5.32	: <u>5.85</u>	:	:	:
:	:	: 2.81	:	: 3.92	:	:	:	:	:	:	:
:	:	: 2.90	:	:	:	:	:	:	:	:	:
:	:	: 2.95	:	:	:	:	:	:	:	:	:
: Label	:	:	:	:	: Z1	: Z2	:	: X1	:	:	:
: <u>Theory</u> : Energy	:	: 2.7	:	: 3.9	: 4.49	: 4.65	: 5.40	: 5.91	:	:	:
: Assignment	:	: M, L ₈₋₉	:	: Σ_{8-9}	: T ₈₋₉	: K ₈₋₉	: H ₇₋₉	: Σ, S_{6-9}	:	:	:
					Sulphur (P _Z)			Sulphur (P _{xy})			
					Sulphur (S), tin (S)			Sulphur (S), tin (S)			

a) Ref. 4.

FIGURE CAPTIONS

- FIGURE 1 : Schematic view of the CdI_2 -type layer-structure in which SnS_2 and SnSe_2 crystallize. The octahedral coordination of the tin atoms within one layer is shown.
- FIGURE 2 : Reflectivity spectrum of SnS_2 at 5°K and room temperature between 2 eV and 6 eV.
- FIGURE 3 : Wavelength modulated reflectivity spectrum of SnS_2 at 5°K and room temperature.
- FIGURE 4 : Reflectivity spectrum of SnSe_2 at 5°K and room temperature between 2 eV and 6 eV.
- FIGURE 5 : Wavelength modulated reflectivity spectrum of SnSe_2 at 5°K and room temperature.
- FIGURE 6 : Band structure of SnS_2 (Ref. 10) and SnSe_2 (Ref. 11) along some high symmetry lines in the hexagonal Brillouin zone. The locations of some of the main optical transitions are indicated. The notation corresponds to that used in tables II and III and figs. 7 and 9.
- FIGURE 7 : Comparison of the experimental (5°K) and calculated (Ref. 10) reflectivity spectra of SnS_2 .
- FIGURE 8 : Temperature dependence of the experimental differential reflectivity spectra of SnS_2 .
- FIGURE 9 : Comparison of the experimental (5°K) and calculated (Ref. 11) reflectivity spectra of SnSe_2 .

TABLE III		SnSe ₂	
1	2	3	4
5	6	7	8
9	10	11	12
13	14	15	16
17	18	19	20
21	22	23	24
25	26	27	28
29	30	31	32
33	34	35	36
37	38	39	40
41	42	43	44
45	46	47	48
49	50	51	52
53	54	55	56
57	58	59	60
61	62	63	64
65	66	67	68
69	70	71	72
73	74	75	76
77	78	79	80
81	82	83	84
85	86	87	88
89	90	91	92
93	94	95	96
97	98	99	100

[illegible]

a) - Ref. 5
b) - Ref. 7
c) - Ref. 8
d) - Ref. 9.

FIGURE 10 : Charge density contour plots of valence band state (b) and conduction band state (a) at the line Σ in the Brillouin zone of SnSe_2 . The transition between these states, which gives rise to the Z1, Z2 structures indicated in Fig. 10 and in Table III, is chosen as representative for anion P_z -like transitions. The transition function F_z (c) which indicates the real space location (around the anions) of the transition is defined in the text. All contour plots are displayed in a (110) plane extending over two half layers of SnSe_2 . The charge density contours are given in units of electrons per unit cell. The transition function contours are given in atomic units.

FIGURE 11 : Charge density and transition function contour plots for the transition X5 between states in bands 8 and 10 around the point M in the hexagonal Brillouin zone. The transition is chosen representative for anion P_{xy} -like transitions. Units are as in fig. 10.

Fig 1

Fig 2

Fig. 3

Fig. 4

Fig. 7

Fig 7

Fig 9

Fig. 10

Fig. 11

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720