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DICHALCOGENIDES

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MODULATION SPECTROSCOPY OF SEMICONDUCTING

GROUP IV-A AND IV-B DICHALCOGENIDES

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ABSTRACT

We have measured the optical properties of HfS_2 , SnS_2 and SnSe_2 at 5°K and 300°K , in the range $2 \text{ eV} - 6 \text{ eV}$. We report a large number of new structures and discuss the main transitions in light of recent band structure calculations. We have also investigated the indirect absorption edge of the 3 compounds by means of additional piezotransmission measurements at 80°K .

INTRODUCTION

The group IV-A and IV-B dichalcogenides crystallise in the CdI_2 layer structure. A typical layer is shown in Fig. 1. It consists of a plane of metal atoms sandwiched between two planes of chalcogens. In the layer, the coordination of a metal atom relative to the 6 neighbouring chalcogens is octahedral. From simple chemical bonding considerations, and from the saturation of anions p orbitals in one formula unit, one expects these compounds to be semiconductors. Experimental results⁽¹⁾⁽²⁾ and band structure calculations⁽³⁻⁵⁾ confirm this expectation.

We have measured both the normal reflectivity R and wavelength derivative reflectivity $1/R \cdot dR/dE$ of HfS_2 , SnS_2 and SnSe_2 at 5° K and 300° K , in the range 2 eV-6eV. On the basis of existing band structure calculations, we discuss the main features of their optical response. We report additional piezotransmission measurements, in order to clear-out the fine structure of their indirect absorption edge.

EXPERIMENTAL RESULTS AND DISCUSSION

All crystals used in this experiment had natural faces of about 1 cm x 0.5 cm and were grown by an iodine transport method. As usual, the C axis was perpendicular to the large faces of the platelets and our optical measurements were restricted to the standard configuration $E \perp C$. We used "as grown" the natural faces of the platelets. The experimental apparatus for simultaneous measurements of the reflectivity and logarithmic derivative of the reflectivity (W.M.R.) is described in Ref. 6, the stress modulation technique in Ref. 7.

A) Sn S_2

Fig. 2-1 is a plot of our experimental results at 5° K and 300° K . The fundamental absorption region is found at low temperature around 2.5 eV. A second set of transitions appears between 3 and 4 eV. It corresponds with excitations from the top most valence band to the lowest conduction band (8-9) at different points of the Brillouin zone. A detailed analysis of the spectra and assignment of the transitions has been given elsewhere⁽⁸⁾ which shows that, in this range of energy, most of the transition matrix elements and /or joint density of states are small. Due to this special character, many structures found in this work were not resolved in previous experiments (see Table 1).

The main structures at 4.98 and 5.85 eV (at 5° K) come from an excitation of sulphur p-like states in the top-most valence bands. The splitting of about 0.9 eV between the two peaks is caused by the anisotropic crystal field : a p_z - like level appear first⁽⁸⁾, followed by 2 p_{xy} - like levels. This is in good agreement with the general structure of the valence band expected in the family⁽⁹⁾. However, the relative ordering of levels may be dependent on the compound : is is identical in Sn-Se_2 , but appears reversed in Hf S_2 .

Our next results concern the indirect absorption edge. At room temperature, three different investigations^(1,2,10) report an indirect gap around 2.2 eV, but no definite assignment or associate phonon energy or low temperature data have been published. Even the nature of the indirect gap is under discussion: Ref. 1 reports an indirect allowed transition ($\alpha \sim E^2$) around 2.21 eV and Ref. 2 report an indirect forbidden transition ($\alpha \sim E^3$) at 2.07 eV with a direct forbidden transition ($\alpha \sim E^{3/2}$) at 2.88 eV. The band structure calculation of Ref. 8 supports an indirect absorption edge $\Gamma_{2-} \rightarrow M_1+$ with an intermediate state Γ_1+ . The transition $\Gamma_{2-} \rightarrow \Gamma_1+$ is forbidden for polarisation $E \perp C$ and all phonons involved must have M_1+ symmetry. The compatibility relations for D_{3d} space group show that there are only 2 M_1+ phonons (optical modes). The corresponding vibrational modes at Γ (see Table 2) are the two Raman active modes A_{1g} (327 cm^{-1}) and E_g (166 cm^{-1}).

Fig. 3-1 is a plot of our piezotransmission data. The differential transmission coefficient $\Delta T/T$ is simply the first order derivative $\Delta\alpha$ of the absorption coefficient versus deformation and we expect to find a characteristic lineshape depending on the critical point (c.p.) investigated. On table 3, we summarized the different possible lineshapes for a 2- or 3- dimensional M_0 c.p., direct or indirect, allowed or forbidden, but neglecting all excitonic effects. Note the same linear dependence of $\Delta\alpha$ versus energy for i) a 3- dimensional indirect allowed transition and ii) a 2- dimensional indirect forbidden transition. According to the results of Table 3, we give a possible decomposition on Fig. 3-1. We find A) a linear variation $\Delta\alpha$ starting at about 2,255 eV but no phonon replica, B) the structure around 2,38 eV is more likely associated with an impurity - induced absorption and C) $\Delta\alpha$ goes to infinity as the wavelength comes closed to the first strong W.M.R. structure at about 2.5 eV.

B) Sn Se₂

A plot of our reflectivity and W.M.R. data is given on Fig. 2-2. We find again 2 broad peaks (3.91 and 4.91 eV at 5° K) associated with excitations from the

Selenium p-like valence states to the lowest conduction states. The crystal field splitting is almost the same as in SnS_2 (~ 1 eV). The main difference with our SnS_2 spectra is the appearance of more fine structure, spreading out of the first main peak, coupled to a decrease in intensity. Qualitatively speaking, this spreading out, the decrease in bandgap by about 1 eV from SnS_2 to SnSe_2 and the shift of the main interband transitions (also ~ 1 eV), all correlate with the shift of p - type atomic levels for Selenium compared with Sulphur ($\sim + 0.8$ eV⁽¹¹⁾). Decreasing their energy separation with the Tin sp^3 levels which constitute the conduction band, one decreases the main interband transitions. Last, increasing the coupling between chalcogen and metal levels, one get wider valence and conduction bands. A similar set of results were recently reported for $\text{GaS}_x\text{Se}_{1-x}$ alloys⁽¹²⁾. At 5° K, our W.M.R. data result in 20 structures listed in Table 4. A detailed analysis is given in Ref. 8.

At 80° K, we have also investigated the indirect absorption edge using the stress modulation technique. A previous investigation⁽¹³⁾ gives at 77° K :
 i) two forbidden indirect transitions accross energy gaps of about 1.03 and 1.30 eV, and ii) an allowed direct transition accross an energy gap of 1.97 eV. The band structure calculations^(4,8) also support an indirect gap similar to SnS_2 : transition $\Gamma_2^- \rightarrow M_1^+$ with a forbidden intermediate state Γ_1^+ . The phonon spectrum of SnSe_2 is not known but, according to the simple mass scaling found for the Raman active modes of IV-B transition metals dichalcogenides⁽¹⁵⁾ :

$$\frac{h\nu(\text{M S}_2)}{h\nu(\text{M Se}_2)} = \sqrt{\frac{m(\text{Se})}{m(\text{S})}} \sim 1.57$$

we expect 2 phonons of energies ~ 26 and 13 meV to participate in that transition.

Fig. 3-2 is a plot of our experimental spectrum between 0.9 and 1.4 eV. (We do not find any significant signal below 0.9 eV). The two lowest structures appear at 1.08 and 1.13 eV. According to the theoretical results of Table 3, they are not likely associated with an indirect forbidden absorption edge but, provided the transition had some excitonic character, with an indirect allowed absorption edge. In this case α is proportional to $E^{1/2}$, $\Delta\alpha$ to $E^{-1/2}$, and the structure appears more pronounced. The phonon energy ~ 25 meV is in good agreement with our expected value for a $\Gamma_1^+ \rightarrow M_1^+$ diffusion process. The next structure also is not likely associated with an indirect forbidden transition but rather with a direct allowed transitions whose point density of states and / or transition matrix element

are small. Last $\Delta T/T$ goes to infinity as the photon energy comes closer to the first strong W.M.R. structure around 1.92 eV.

Compared with the results of Ref. 13, our experimental energies of transition are in good agreement. We do not find 2 indirect forbidden absorption edge as previously reported but i) an indirect allowed absorption edge at 1.105 eV (80° K) assisted by a 25 meV M_1+ phonon and ii) a small intensity direct allowed absorption edge at slightly higher energy : 1.31 eV.

C) Hf S₂

One expect to find the same electronic structure for the valence band of IV-B transition metal dichalcogenides as for the Tin compounds. Indeed, we have again a transfert of 4 electrons from Hafnium to Sulphur to fill up the 6 p - type atomic orbitals of Sulphur. The anisotropic crystal field splits the 6 p-like levels in 2 p_z - and 4 p_{xy} - type and the conduction band is mainly built of empty (5d - 6s) states.

Fig. 2-3 is a plot of our experimental reflectivity data. At room temperature, we find a good overall agreement with the results of Greenaway et al⁽¹⁾ (see Table 5). The main discrepancy between our work and the work of Ref. 1 is in the magnitude of the structure seen above 4 eV. At 5° K, our W.M.R. spectrum exhibits many fine structures. They are listed on Table 5 and compared with the values reported in transmission on thin cello-tape cleaved samples by Beal et al⁽¹⁶⁾. A detailed analysis and comparison with a theoretical reflectivity spectrum obtained from an E.P.M. band structure calculation was reported elsewhere⁽⁵⁾. Most of the structures come from transitions between the top-most valence band (p_{xy} -like) and the lowest conduction band. Opposite to the Tin dichalcogenides, the p_z -like valence band lie at lower energy and does not participate in interband transitions in our range of energy. The different structures around 3 eV comes from transitions between band 8- 9 at different points of the Brillouin zone. For example the strong structures at 2.83 and 3.35 eV respectively, at 5° K come from volume effects near Δ (line Γ -A) and R (line L-A) respectively. These points are interesting to outline in light of the systematics found in different investigations on the family i) the main features repeat in the optical response through the entire family⁽¹⁶⁾

and ii) these features have been tentatively assigned to possible transitions at specific points of the Brillouin zone and used to adjust empirical band structure calculation⁽¹⁷⁾.

The lowest absorption edge of Hf S₂ was also investigated with our piezo modulation technique. According to the experimental finding of Ref. 1, one expect an indirect gap at about 1.96 eV (300° K). The band structure calculations^(5, 15) indicate either a $\Gamma_2^- \rightarrow M_1^+$ or a $\Gamma_2^- \rightarrow L_1^+$ absorption edge. Both minima of the conduction band are found in the calculation within 0.1eV, and the 2 transitions have identical selection rules. For a virtual Γ_3^+ intermediate state, 3 different phonons modes (2 M₁⁺ and 1 M₂⁺) are possible. The corresponding Raman active modes have energies of about 42 and 32 meV (see Table 2).

Fig. 3-3 shows an experimental $\Delta I/T$ spectrum at 80° K. We find first a linear variation of $\Delta\alpha$ versus $h\nu$, compatible with an indirect allowed phonon assisted transition. It starts around 1.75 eV (80° K) but no clear phonon replica permits to ascertain the band gap. The next two structures are not clearly understood. Their energy separation is about 2 times the TO phonon mode in Table 2 and they could be associated with a second indirect absorption edge at slightly higher energy. More investigation along this path is needed before we get a conclusive evidence.

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TABLE 1 : Listing of interband transitions for SnS_2 .

PREVIOUS WORKS (300° K)		THIS WORK (300° K) (5° K)		ASSIGNEMENT (from Ref. 8)
(a)	(b)			
2.21	2.07		2.255 (c)	$\Gamma_{2-} \rightarrow M_1^+$
		2.32	2.50	
			2.61 ; 2.70	
	2.88	2.82	2.81 ; 2.90 ; 2.95	M, L (8→9)
		3.32	3.37	
3.8		3.57	3.61 ; 3.80 ; 3.92	Σ (8→9)
		4.37	4.17 ; 4.53	T (8→9)
4.9		<u>4.89</u>	<u>4.98</u>	K (8→9)
		5.09 ; 5.41	5.22 ; 5.32	H (7→9)
5.8		<u>5.74</u>	5.58 <u>5.85</u>	S (6→9)
5.9		6.04		
7.6				

a) Ref. 1

b) Ref. 2

c) Piezotransmission (80° K).

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TABLE II : Symmetries, energies and selection rules for the vibrational modes in Group IV dichalcogenide

PHONON (Γ)	ENERGY (cm^{-1})			VIBRATIONAL MODE AT $K = 0$		SELECT. RULE	CORRESPONDING AT M, L
	SnS ₂ (a)	SnSe ₂ (b)	Hf S ₂ (c)	Optic	Acoustic		
$\Gamma_1^+ (A_{1g})$	327	~ 208	337	X		R.A.	M_1^+
$\Gamma_3^+ (E_g)$	166	~ 106	253	X		R.A.	$M_1^+ + M_2^+$
$2 \Gamma_2^- (A_{2u})$				X	X	I.R. Active (E // C)	$2 M_2^-$
$2 \Gamma_3^- (E_u)$			$\begin{cases} \text{LO : 315} \\ \text{TO : 160} \end{cases}$	X	X	I. R. active (E $\perp$ C)	$2 (M_1^- + M_2^-)$

a) Ph. Schmid, Private Communication

b) Estimate from SnS₂ see text.

c) Ref. 15.

TABLE 3 : Dependence of α and $d\alpha/dE$ versus energy for i) a 3- dimensional isotropic critical point and ii) 2-dimensional layer structure. Spectral dependence for α obtained from Ref. 10
The results for an impurity induced absorption are also given for comparison.

TRANSITION	3 - DIMENSIONAL c.p.		2 - DIMENSIONAL c.p.		IMPURITY	
	α	$d\alpha$	α	$d\alpha$	α	$d\alpha$
Direct allowed	$(E - E_g)^{1/2}$	$(E - E_g)^{-1/2}$	E independent step	$\delta(E)$	$\delta(E)$
Direct forbidden	$(E - E_g)^{3/2}$	$(E - E_g)^{1/2}$	$(E - E_g)$	E independent step		
Indirect allowed	$(E - E_g + E_{ph})^2$	$(E - E_g + E_{ph})$	$(E - E_g + E_{ph})$	E independent step		
Indirect forbidden	$(E - E_g + E_{ph})^3$	$(E - E_g + E_{ph})^2$	$(E - E_g + E_{ph})^2$	$(E - E_g + E_{ph})$		

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TABLE IV : Listing of interband transitions for SnSe_2

PREVIOUS WORKS			THIS WORK		ASSIGNMENT (from Re
<u>300° K</u>	<u>77° K</u>		<u>300° K</u>	<u>5° K</u>	
(a)	(b)	(c)			
0.97	1.03			1.105 (d)	
	1.30			1.30 (d)	
1.62	1.97	1.7 ; 1.8 ; 2.0 2.3	1.92	1.92	
		2.8 ; 3.2	2.88	3.05	
		3.6	3.52	3.60 ; 3.66	
				3.75	Σ (8 +9)
		3.9	<u>3.79</u>	3.88 ; <u>3.91</u> ; 3.95	Γ , K (8 +9)
				3.99 ; 4.05	R, U (6 +9)
			4.09	4.19 ; 4.30	R, U (6 +9)
		4.5	4.27 ; 4.46	4.45 ; 4.55	Γ (7 +9)
		4.9	<u>4.76</u> ; 5.06	<u>4.91</u> ; 5.06	M (8 +10)
		6	5.58	5.29 ; 5.71	
		7.1			
		9.6			

a) Ref. 2

b) Ref. 13

c) Ref. 14

d) Piezotransmission (77° K)

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TABLE V : Listing of interband transitions for Hf S₂

PREVIOUS WORK		THIS WORK		THEORETICAL ASSIGNMENT (from Ref. 5)
300° K	5° K	300° K	5° K	
a)	(b)			
36			1.75 (c) 2.10 (c)	$\Gamma_2^- \rightarrow M_1^+$
9	2.88	2.81	2.83	Δ (8 → 9)
	3.03 ; 3.07		2.94 ; 2.95	$L_3 \rightarrow L_1$; $A_3 \rightarrow A_1^+$
	3.2		3.17	$L_2 \rightarrow L_1$
35	3.23	3.22	3.3	(8 → 9) Volume effect.
		3.3	3.5	$M_1 \rightarrow M_1^+$
		3.5	3.8	(8 → 9 ; 7 → 9) volume effect.
0		4.8	4.9	(7 → 10) volume effect.

a) Ref. 1

b) Ref. 16

c) piezotransmission (80° K).

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FIGURE CAPTIONS

FIGURE 1 : Perspective view of arrangement of atoms within one layer.

FIGURE 2 : Reflectivity (R) and derivative reflectivity ($1/R \cdot dR/dE$) of
a) SnS_2 ; b) SnSe_2 ; c) HfS_2 at 300°K and 5°K .

FIGURE 3 : Differential transmission spectra of a) SnS_2 ; b) SnSe_2 and
c) HfS_2 at 80°K .

The diagram illustrates a crystal lattice structure, possibly a graphite intercalation compound. It features a central metal atom (M) surrounded by carbon atoms (C) in a hexagonal arrangement. The structure is composed of several interconnected hexagonal rings. The central metal atom (M) is positioned within a hexagonal ring formed by carbon atoms (C). The diagram shows various bonds and angles, with labels 'M' and 'C' indicating the respective atoms. The structure is symmetrical and shows a clear hexagonal pattern.

a)

b)

Fig 2

c)

a)

b)

ig 3

c)

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