Turk J Phys
26 (2002) , 341 – 347.
© TÜBİTAK

Dispersion Analysis of SnS and SnSe

Haluk ŞAFAK
Department of Physics, Faculty of Arts and Sciences, Selcuk University, 42031 Kampüs, Konya-TURKEY
Mustafa MERDAN
Department of Electronics and Communications, Faculty of Engineering and Architecture, Süleyman Demirel University, 32260 Isparta-TURKEY
Ö. Faruk YÜKSEL
Department of Physics, Faculty of Arts and Sciences, Selcuk University, 42031 Kampüs, Konya-TURKEY

Received 05.12.2001

Abstract

The reflectance spectra of single crystals of SnS and SnSe were measured at normal incidence by unpolarized light. The refractive indices of speciemens were calculated by Kramers-Kronig Analysis. On the basis of the Wemple diDomenico single oscillator model, the dispersion parameters were determined. It is found that the parameters obtained by unpolarized light are, in general close to those reported for polarized cases. Morever, a close similarity were observed with E//b polarization for SnS.

PACS codes/Key Words: 78.20.Ci, 78.40.Fy/IV-VI semiconductors, optical constant, dispersion analysis

1. Introduction

Tin sulfide and the isomorphous tin selenide belong to IV-VI compounds. These semiconductors crystallize in layer-type character, and they show a strong anisotropy for most properties.

SnS has the lattice constants a=0.399 nm, b=0.434 nm and c=1.120 nm [1] and SnSe has a=0.419 nm, b=0.446 nm and c=1.157 nm [2]. The core excitons and conduction band structures [3], infrared and raman spectra [1,2], electron-energy-loss spectroscopy [4] and energy band structure [5] have been investigated for SnS and SnSe. Also, the optical absorption edge in SnS [6] and SnSe [7,8], electroreflectance and thermoreflectance spectra for SnS [9] and SnSe [10], and temperature dependence of the optical gap in SnSe [11] have been studied. The direct and indirect band gap energies of SnS were given as E_{dir}=1.60 eV [5] and E_{ind}=1.076 eV [12] for $\vec{a}$ polarization and E_{dir}=1.296 eV and E_{ind}=1.049 eV [12] for $\vec{b}$ polarization respectively. On the other hand, the direct and indirect band gaps of SnSe have been reported as E_{dir}=1.238 eV and E_{ind}=0.898 eV for $\vec{a}$ polarization and E_{dir}=1.047 eV and E_{ind}=0.903 eV for $\vec{b}$ polarization, respectively [12].

Due to the anisotropical character of SnS and SnSe, the optical and electrical measurements on these materials have usually performed been by polarized light. This is reasonable and also necessary to characterize the behavior of optical and electrical properties at certain directions. But there are also a number of studies that have used unpolarized light [13,14].

In this study, the reflectance spectra of SnS and SnSe single crystals, with unpolarized light in 0.5–2.5 eV energy range have been investigated. The results obtained have been analyzed in the frame-fork of the single oscillator Wemple diDomenico dispersion model.

2. Theory

The optical properties of a solid are usually described in terms of the complex dielectric function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$. The real part ε_1 and imaginary part ε_2 of this description are both frequency-dependent quantities, which include all the desired response information. The complex dielectric constant ε_2 is thought to contain many useful physical information about the material.

In the analysis of experimental optical spectra, many different contributions can be observed, contributions that need to be separated for any complete analysis. Separation is usually done by using various models describing both the material under investigation and the experimental parameters.

It is well known that $\varepsilon_2(\omega)$ can be considered to be superimposed from many independent contributions by interband transitions at energies $E \gg E_g$, by interband transitions near the absorption edge, by free carrier absorption and by optical phonon absorption [15]. Namely, there are four terms that contribute to the real part of the dielectric constant. In the transparency region, k has very small value and are negligible and therefore all above terms result in normal dispersion.

According the to single-oscillator model [16,17], the only contribution to the dispersion of dielectric constant is due to interband transitions and it is assumed that each electron behaves as an oscillator. So, the real part of dielectric constant is expressed as

$$\varepsilon_1(\omega) = 1 + \omega_p^2 \sum_n \frac{f_n}{\omega_n^2 - \omega^2}. \tag{1}$$

Here, ω_p is the plasma angular frequency, f_n is the electrical dipole oscillator strength for the transitions at frequency ω_n. For $\omega < \omega_n$, the sum over the oscillators can be separated into two parts, the first being a single strong oscillator $f_1/(\omega_1^2 - \omega^2)$ and the second including the remaining higher order terms:

$$\sum_{n \neq 2} \frac{f_n}{\omega_n^2}(1 + \frac{\omega^2}{\omega_n^2}). \tag{2}$$

Then the dielectric constant becomes

$$\varepsilon_1(\omega) = 1 + \omega_p^2 \left\{ \frac{f_1}{\omega_1^2 - \omega^2} + \sum_{\mathrm{n} \neq 1} \frac{f_n}{\omega_n^2}(1 + \frac{\omega^2}{\omega_n^2}) \right\}. \tag{3}$$

Wemple and diDomenico [17] have proposed that, by including the higher order terms in Eq. (3) into the first resonant strong oscillator, the dielectric constant can be written as

$$\varepsilon_1(\omega) = 1 + \frac{F}{E_0^2 - (\hbar\omega)^2}. \tag{4}$$

In this single-oscillator approximation, E_0 and F are parameters dependent on f_n strengths and ω_n frequencies of oscillators. In the original Wemple di-Domenico model, the parameter F is expressed as $F = E_d E_0$, E_d is defined as dispersion energy and E_0 as a single oscillator energy. Finally, the dielectric constant for any material have been given as

$$\varepsilon_1(\omega) = n^2(\omega) - 1 = \frac{E_d E_0}{E_0^2 - (\hbar\omega)^2} = \frac{E_d}{E_0}\left[1 - \frac{(\hbar\omega)^2}{E_0^2}\right]^{-1} \tag{5}$$

by means of these dispersion parameters.

The dispersion energy E_d is a measure of the strength of interband optical transitions and can be considered as a parameter having very close relation with the charge distribution within unit cell and therefore with the chemical bonding. This parameter is given by

$$E_d = \beta N_c Z_a N_e, \tag{6}$$

where N_c is the nearest-neighbour cation coordination number, Z_a is the formal anion valency, N_e is the effective number of valence electrons per anion and β is a constant whose value depends on the chemical bonding character of material. It was declared that the constant β can assume two values: $\beta_i = 0.26$ eV for ionic compounds and $\beta_c = 0.39$ eV for covalent compounds [16,17].

The other dispersion parameter, E_0, has usually been considered as an "average" energy gap and is empirically related to the lowest direct band gap E_g as

$$E_0 \cong 1.5 E_g. \tag{7}$$

The dispersion parameters, E_0 and E_d, are usually described by means of the r^{th} moment of the $\varepsilon_2(E)$ optical spectrum. It is known that the r^{th} moment of the $\varepsilon_2(E)$ spectrum is defined as

$$M_r = \frac{2}{\pi}\int_{E_t}^{\infty} E^r \varepsilon_2(E) dE, \tag{8}$$

where $E = \hbar\omega$ and E_t is the absorption threshold energy. On the other hand, the real and imaginary parts of dielectric constant can be related to each other by a Kramers-Kronig transformation as [18-22]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\int_0^{\infty} \frac{\omega'\varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'. \tag{9}$$

This equation can be written in the form

$$n^2(\omega) - 1 = \frac{2}{\pi}\int_0^{\infty} \frac{\varepsilon_2(\omega')}{\omega'} \frac{d\omega'}{1 - \omega^2/\omega'^2}. \tag{10}$$

By expanding Eq. (9) into the powers of ω^2 and multiplying by $\hbar$, we obtain

$$n^2 - 1 = \frac{2}{\pi}\int_0^{\infty} \varepsilon_2(\omega')\left[\frac{1}{\hbar\omega'} + \frac{\hbar^2\omega^2}{\hbar^3\omega'^3} + \frac{\hbar^4\omega^4}{\hbar^5\omega'^5} + \frac{\hbar^6\omega^6}{\hbar^7\omega'^7} + \cdots\right] d(\hbar\omega'). \tag{11}$$

Similarly, if Eq. (5) has been expanded into the power of E_0^2, we find

$$n^2(\omega) - 1 = \frac{E_d}{E_0}\left\{1 + \frac{(\hbar\omega)^2}{E_0^2} + \frac{(\hbar\omega)^4}{E_0^4} + \frac{(\hbar\omega)^6}{E_0^6} + \cdots\right\}. \tag{12}$$

From a comparison between Eqs. (11) and (12), one can develop some relationships between the dispersion parameters and the $\varepsilon_2(\omega)$ spectrum via

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \tag{13}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}}. \tag{14}$$

It is known that static dielectric constant of any substance is defined as

$$\varepsilon_r(0) = \underset{E=0}{lim} n^2(E) = n_0^2. \tag{15}$$

If Eq. (5) is considered, it would be seen that the static dielectric constant can be written in terms of dispersion parameters simply as

$$n_0^2 = \varepsilon_r(0) = 1 + \frac{E_d}{E_0}. \tag{16}$$

So, the knowledge of dispersion parameters allows us to determine the static dielectric constant of materials.

3. Experimental Method

SnS and SnSe compound single crystals were prepared by Bridgman technique. For reflectance measurements, thin samples were obtained by cleavage along {001} planes. The crystallographic $\vec{a}$ and $\vec{b}$ axes lie in the cleavage plane and the thickness of samples so obtained were about 150 μm.

The reflection measurements by unpolarized light performed by a Jasco Model V-570 UV/VIS/NIR spectrophotometer in the 220-2200 nm wavelength range.

4. Result and Discussion

Figure 1 shows the measured reflectance spectra of SnS and SnSe at 0.5-2.5 eV range by unpolarized light. These spectra have a similar variation to those obtained by polarized light [4,23,24]. Especially, the similarity with $\vec{E}//\vec{b}$ reflectance curves for SnS are more apparent. Elkorashy [23] has reported that the reflectance spectral response for SnS shows a decrease above the fundamental edge at 1.8 eV for the $\vec{b}$-axis and no similar decrease for the $\vec{a}$-axis. In Figure 1 of Ref. [9], the thermoreflectance curve for a SnS single crystal with $E//\vec{b}$ polarization has shown an apparent decreasing structure at nearly 1.8 eV for both 100 K and 320 K. We have observed the same behaviour here too (see Figure 1). This is interesting, because we have performed measurements by unpolarized light. The spectral reflectance variation of SnSe for $\vec{a}$ and $\vec{b}$ axis are already very close to each other at this energy interval [4].

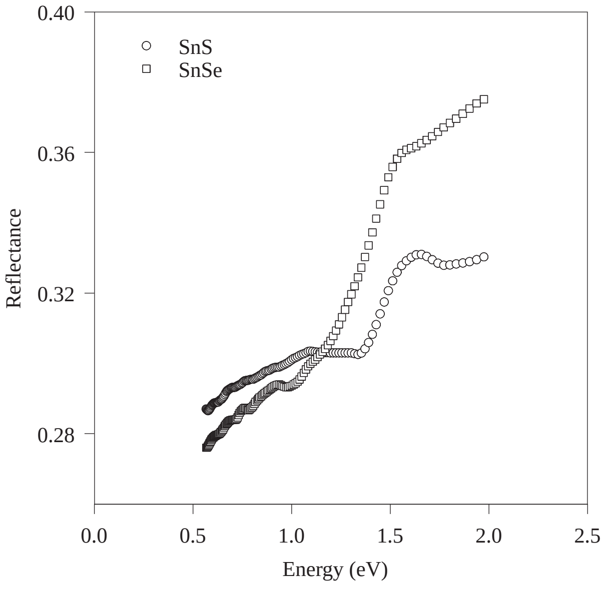

Figure 1. The measured reflectance spectra of SnS and SnSe.

Refractive indices n of both specimens were calculated by Kramers-Kronig analysis and given at Figure 2. The graphs of n versus energy curves have very similar trends to reflectance curves as expected. At the energy interval which the measurements were performed, the obtained n values lies in the range 3.3–3.7 range for SnS and in the range 3.2–4.0 range for SnSe. These results have also shown that the refractive indices were closer to those obtained for $\vec{b}$-axis for both specimens [23,24]. But here, the $n(E)$ variation does not show exactly the same trend as in Ref. [23] and exhibits a decrease or dip at nearly the fundamental band gap for SnS. This dip structure may most probably be due to the surface roughness. The roughness at the sample surface can give rise to an appreciable negative dip in some measured optical properties, such as absorption coefficient or reflectivity, and hence in the calculated quantities based upon them [25,26].

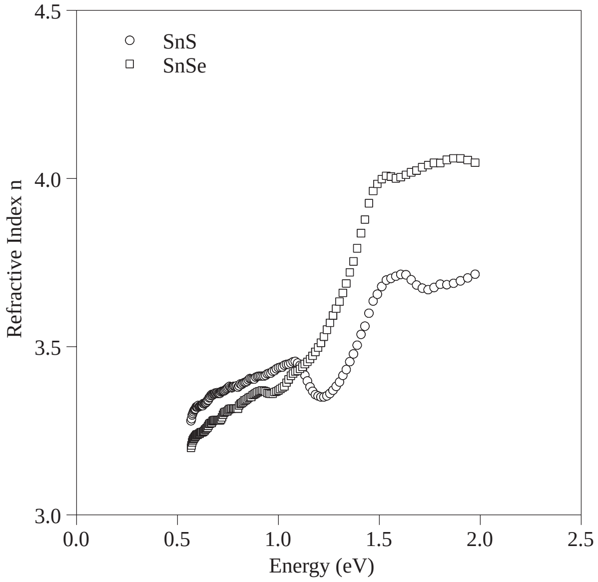

Figure 2. The spectral variation of the calculated refractive indices for SnS and SnSe.

To determine the dispersion parameters E_0 and E_d, the graphs of $(n^2\text{-}1)^{-1}$ versus E^2 were plotted and fitted to a straight line, as shown in Figure 3 for both specimens. Finally, the E_0, E_d dispersion parameters obtained by this fit procedure, together with M_{-1} and M_{-3} moments of $\varepsilon(E)$ spectrum calculated by using Eqs. (13) and (14) are listed in Table 1.

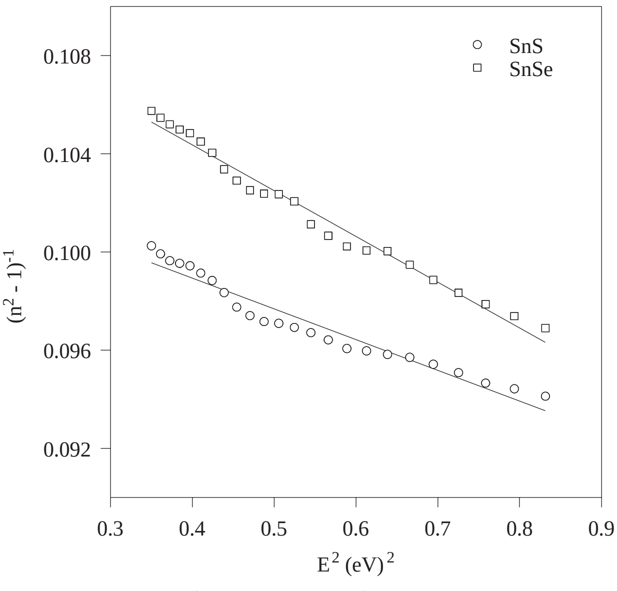

Figure 3. $(n^2\text{-}1)^{-1}$ versus E^2 for SnS and SnSe.

Table 1. Single oscillator parameters calculated by the reflectance for SnS and SnSe.

	SnS (Present)	SnS Ref.[22] (E//b)	SnSe
Eo (eV)	2.88	2.25	2.45
Ed (eV)	27.75	24.03	21.90
M_{-1}(dimensionless)	9.62	12.23	8.94
$M_{-3}(eV^{-2})$	1.16	3.17	1.49

For SnS and SnSe, effective number of valence electrons per anion is $N_e = 4 + 6 = 10$ and formal anion valency is $Z_a = 2$. Another parameter which required determination of β by means of Eq. (6) is N_c, the coordination number of cation nearest-neighbor to the anion.

It was known that SnS and SnSe have layered structures in which atoms are arranged in two adjacent double layers orthogonal to the largest cell dimension [27]. Within either double layer, each atom has three nearest neighbors and two next nearest neighbors. Sixth next nearest neighboring atom lies in the other double layer and provides the band between the double layers. Therefore, if the layered structure has been taken account, the coordination number N_c would be 3. On the other hand, SnS and SnSe single crystals belongs to the group of orthorombic semiconductor compounds with a distorted rocksalt structure of form AX, where A is Sn and X is either S or Se [9]. So, if this deformed rocksalt structure is considered, N_c would be 6. Therefore, there is an uncertainty about the coordination number of these materials and two different values can be used for it. This case has also been pointed out by Elkorashy [23].

We calculated β values for both $N_c = 3$ and $N_c = 6$. The results have been given in Table 2 for SnS and SnSe. As seen from the table, there is not enough discrimination among β values to be certain about the binding character of the materials. Elkorashy have interpreted these different β values as that the binding is partly ionic and partly covalent [23]. This can be true. But, utilizing different N_c values ($N_c = 3$ or $N_c = 6$) would give rise to a different β value, and therefore to a different result, and it seems to be a somewhat inexplicit case. Assuming $N_c = 3$ inevitably would cause a larger β value, namely to a case closer to the covalent binding. A similar situation also holds true for $N_c = 6$. Consequently, before one decides about the binding character of this materials, one must be certain about the coordination number.

Table 2. Values of the parameter β for SnS and SnSe.

	SnS (Present)	SnS Ref.[22] (E//b)	SnSe
N_c=3	0.46	0.40	0.37
N_c=6	0.23	0.20	0.18

Finally, have calculated the static dielectric constants of SnS and SnSe, by means of Eq. (16), using the dispersion parameters listed in Table 1. $\varepsilon_r(0) = 10.62$ and $\varepsilon_r(0) = 9.94$ values have been found for SnS and SnSe respectively. These values are smaller than those reported by Elkorashy [23,24].

References

[1] J. M. Chamberlain, P. M. Nicolić, M., Merdan, P. Mihailović, *P., J. Phys.,* **C 9**, (1970), L637.

[2] H. R. Chandrasekhar, R. G. Humpreys, U. Zwicki, M. Cardona, *Phys. Rev.,* **B 15**, (1977) 2177.

[3] M. Taniguchi, R. L. Johnson, J. Ghijsen, M. Cardona, *Phys. Rev.*, **B 42**, (1990), 3634.

[4] R. Eymard, A. Otto, *Phys. Rev.*, **B 16**, (1972), 1616.

[5] G. Valiukonis, D. A. Guseinova, G. Krivaitė, A. Šileika, *Phys. Stat. Sol.*, **B 135**, (1986), 299.

[6] A. P. Lambros, D. Geraleas, N. A. Economou, *J. Phys. Chem. Solids,* **35**, (1974), 537.

[7] F. Lukes, E. Schmidt, J. Humlicek, P. Dub, F. Kosek, *Phys. Stat. Sol.*, **B 137**, (1986), 569.

[8] D. A.Guseinova, G. Krivaité, M. M. Mamedov, *Sov. Phys. Semiconductors,* **19(8)**, (1985), 923.

[9] F. Lukes, J. Humlicek, E. Schmidt, *Solid State Commun.,* **45**, (1983), 445.

[10] G. Valiukonis, F. M. Gashimzade, D. A. Guseinova, G. Krivate, M. M. Mamedov, A. Šileika, *Phys. Stat. Sol.* **B 122**, (1984), 623.

[11] A. M.Elkorashy, *J. Phys. Chem. Solids,* **50**, (1989), 893.

[12] M. Parenteau and C. Carlone, *Phys. Rev.*, **B 41**, (1990) 5227.

[13] W. Albers, C. Haas, F.Van der Maesen, *J. Phys. Chem. Solids,* **15**, (1960), 306.

[14] W. Albers, C. Haas, H. Ober, G. R. Schodder, J. D. Wasscher, *J. Phys. Chem. Solids,* **23**, (1962), 215.

[15] K. H. Hermann, V. Melzer, U. Müller, *IR Phys.*, **34**, (1993), 117.

[16] S. H. Wemple, M. DiDomenico, *Phys. Rev.*, **B 1**, (1970), 193.

[17] S. H. Wemple, M. DiDomenico, *M., Phys. Rev.*, **B 3**, (1971), 1338.

[18] J. A. Bardwell, M. J. Dignam, *J. Chem. Phys.,* **83**, (1985), 5468.

[19] R. K. Ahrenkiel, *J. Opt. Soc. Ame.,* **61**, (1971), 1651.

[20] A. E. Tshmel, V. I. Vettegren, *Spectrochemica Acta,* **29A**, (1973), 1681.

[21] H. W. Verluer, *J. Opt. Soc. Ame.,* **58**, (1968), 1356.

[22] P. P. Kircheva, G. B. Hadjichristov, *J. Physics,* **B 27**, (1994), 3781.

[23] A. M. Elkorashy, *Semicond. Sci. Tech.,* **4**, (1989), 382.

[24] A. M. Elkorashy, *J. Phys. Chem. Solids,* **51**, (1990), 289.

[25] K. Jezierski and J. Misiewicz, *J. Opt. Soc. Ame.*, **B 1**, (1984), 850.

[26] K. Jezierski and J. M. Pawlikowski, *Acta Physica Polonica,* **A67**, (1985), 447.

[27] R. Car, G. Ciucci, L. Quartapelle, *Phys. Stat. Sol.,* **B 86**, (1978), 471.