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FUNDAMENTAL OPTICAL ABSORPTION IN SINGLE CRYSTAL GeS_2

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The transmission and reflectivity spectra of single crystal GeS_2 are measured at various temperatures in the spectral range from 300 nm to 450 nm using polarised light. The energy gap and temperature coefficients of energy gap values are obtained for two directions of polarisation $E \,||\, a$ and $E \,||\, b$.

1. Introduction

The germanium disulphide is semiconducting compound with layer structure whose optical properties are subject of large interest in the last few years. A large number of papers which deal with optical properties of this compound in amorphous state, is recently published and in connection with this apply of this compound as optical material in the infrared spectral region from 8 do 12 μm is announced[1]. Very little information is available concerning the optical properties of single crystal GeS_2 in the fundamental absorption edge region. The position of absorption edge of GeS_2 was found for the first time in 1962[2] that it lies about 350 nm at room temperature and shifted to 330 nm at temperature of liquid nitrogen. Sobolev and Donetskih[3] found out, from nonpolarised reflectivity spectra of single crystal GeS_2 that the peaks on the reflectivity spectra at 3.4 eV and 3.65 eV are correspondent to the smallest width of forbidden zone of this compound at 300 K and 77 K, respectively. In our previous paper[4] from nonpolarised transmission spectra of GeS_2 we estimated value of energy gap of $E_g = 3.425$ eV at room temperature. In the present work we present, for the first time, the absorption spectra of GeS_2 single crystal measured with polarised and nonpolarised light at temperatures of 300 K, 77 K and 4.2 K. From these spectra we obtained the corresponding values of energy gap as well as the values of temperature coefficients of energy gap.

2. *Experimental details*

Single crystal of GeS_2 which are used in this work are obtained using a Bridgman procedure, whose details were published elsewhere[4]. The samples for transmission measurements with thicknesses ranging from 20 to 80 μm were obtained by cleavage from single crystals with sticking tape. The specimens were then oriented using X-ray back reflection Laue method and the transmission coefficient was measured using a *Cary*-17 spectrophotometer. The samples were mounted in a cryostat designed so that their temperature could be mainted at any given value in the range between 4.2 and 300 K. The measurements were made only along the a - and b - axis, because measurements along c - axis were not possible due to the easy shear of the crystal along (001) planes.

3. *Results and discussion*

The nonpolarised reflectivity spectra of GeS_2 at 300 K is shown in Fig. 1a. Nonpolarised and polarised transmission spectra of GeS_2 at 300 K, 77 K and 4.2. K are given in Fig. 1b. The absorption coefficient of GeS_2 as a function of photon energy at different temperatures which are shown on Fig. 2 are calculated from transmission and reflectivity spectra from Fig. 1 using equation:

$$T = (1 - R)^2 \exp(- ad), \qquad (1)$$

where T, R and a are coefficients of transmission, reflectivity and absorption, respectively, and d is thickness of the sample.

As it is known[5] absorption coefficient a as a function of photon energy in absorption edge region can be described with equation:

$$a \cong A\,(h\nu - E_g)^n, \qquad (2)$$

where A is a slowly varying function which we regard as a constant over the observed narrow range and n is a number which depends on the nature of energy transition from valence to conduction band.

The first derivative of equation (2) gives:

$$\frac{\mathrm{d}a}{\mathrm{d}\,(h\nu)} = A \cdot n\,(\mathrm{h}\nu - E_g)^{n-1} = \frac{1}{2}\,\frac{A}{\sqrt{(h\nu - E_g)}} \quad (\text{for } n = 1/2). \qquad (3)$$

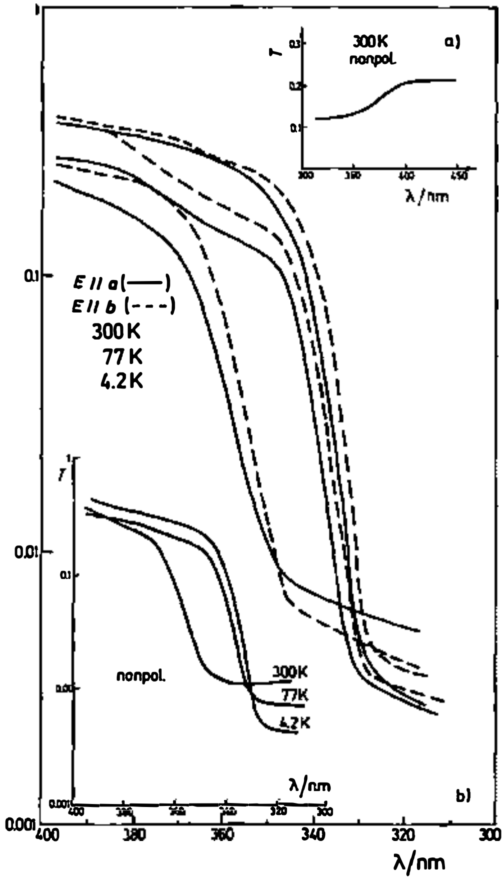

Fig. 1. Nonpolarised reflectivity (R) spectra at 300 K (a) and polarised and nonpolarised transmission (T) spectra of GeS_2 single crystal at 300 K, 77 K and 4.2. K (b).

In the case of direct energy gap for which $n = 1/2$, equation (3) has a sharp maximum at $h\nu = E_g$.

Using this derivative procedure we obtained the energy gap values of GeS_2 which are shown in Table 1.

TABLE 1.

	E_g/eV			$-\Delta E_g/\Delta T$/eV/K $\times 10^4$	
	300 K	77 K	4.2 K	(300—77 K)	(77—4 K)
$E \| \| a$	3.444	3.626	3.658	8.161	4.38
nonpol.	3.454	3.652	3.685	8.879	4.52
$E \| \| b$	3.464	3.658	3.696	8.699	5.2

The energy gap as well as the temperature coefficient of energy gap of GeS_2 at different temperatures.

We can compare presented values of energy gap of GeS_2 (Tab. 1) with previously published ones only in the case of nonpolarised light at room temperature. The values of $E_g = 3.454$ eV which is obtained in this work for energy gap value of GeS_2 in the case of nonpolarised light at 300 K is in good agreement with previously published values[2-4].

The value of width of forbidden band of GeS_2 of 3.65 eV, which is determined from reflectivity spectra at 77 K[3] is in very good agreement with value of $E_g =$ $= 3.65$ eV, which is obtained in this work (Tab. 1.) The other values which are given in Tab. 1 could not be compared with the ones from literature, because, as far as we know, neither polarised spectra of fundamental absorption of GeS_2 nor nonpolarised spectra of fundamental absorption of GeS_2 at temperatures lower than room temperature, were not published by now.

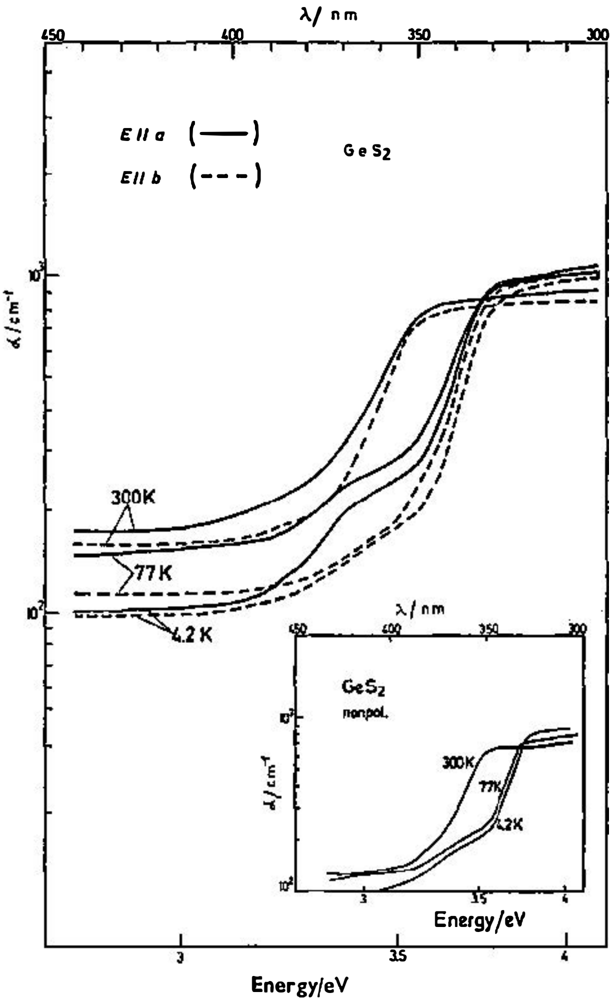

Fig. 2. Coefficient of absorption of GeS_2 as function of photon energy at 300 K, 77 K and 4.2 K for $E \mid\mid a$ and $E \mid\mid b$ polarisation of light.

The values $\Delta E_g/\Delta T$ given in Table 1 are almost the same as the corresponding values in other germanium chalcogenides (GeS[6], $GeSe$[7], $GeSe_2$[5], Sn (Pb) GeS_3[8]).

On the absorption spectra at 77 K and 4.2 K from Fig. 2 the sharper changes of slope are noticed. These changes of slope in the absorption spectra might correspond to transitions between band-localized states (impurity or defect levels which lie deep in the forbidden zone). Identification of these levels would probably be possible using photoluminiscence measurements. This work is in progress.

At the end, it is interesting to notice that similar change of slope of absorption coefficient is noticable in the case of Sn (Pb)GeS_3[8] — compounds at which tetrahedra's surroundings of germanium atoms by sulphur atoms are exactly the same as in the case of GeS_2.

References

1) A. Feltz, B. Voigt, L. Senf and G. Dresler, Wiss. Zeitschr. Friedrich Schiller-Univer. Jena. Math. Nat. R **28** (1979) 327;
2) K. F. Lider and L. E. Soloveev, Fizika Tverd. Tela **4** (1962) 161;
3) V. V. Sobolev and A. Doneskih, Izv. Akad. Nauk. SSSR, Ser. Neorg. Mater **8** (1972) 688;
4) P. M. Nikolić and Z. V. Popović, J. Phys. C. **12** (1979)1151;
5) Z. V. Popović and P. M. Nikolić, J. Engineer Phys. **16** (1977) 39;
6) J. Wiley, D. Thomas, E. Schönherr and A. Breitschwerdt, J. Phys. Chem. Solids **41** (1980) 801;
7) S. V. Vlachos, A. P. Lambros and N. A. Economou, Solid St. Communications **19** (1976) 749;
8) U. V. Alpen, J. Fenner and E. Gmelin, Mat. Res. Bull. **10** (1975) 175.

FUNDAMENTALNA OPTIČKA APSORPCIJA MONOKRISTALNOG GeS_2

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Spektri transmisije i refleksije monokristalnog germanijum disulfida mereni su pri različitim temperaturama u spektralnom opsegu od 300 nm do 450 nm polarisanom svetlošću. Određene su vrednosti energetskog procepa kao i vrednosti koeficijenta temperaturske promene energetskog procepa.