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OPTICAL PROPERTIES OF GERMANIUM DISELENIDE

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The optical properties of $GeSe_2$ were studied in the range from 400 nm to 600 nm, at the temperatures of 300 K, 77 K and 4.2 K. In the absorption spectra, two different regions were noticed, which correspond to the direct and indirect transition. The stepped dependence of absorption coefficient in the region of the indirect transition indicates absorption, that is emission of phonons in the indirect transition. The parameters, characterizing the direct and indirect transition were determined.

1. Introduction

Germanium diselenide is a layer semiconducting compound, that crystallizes in an monoclinic system with parameters of the unit cell: $a = 0.7019$ nm; $b = 1.6864$ nm; $c = 1.1814$ nm; $\beta = 90.65°$, $Z = 16$, the space group $P_{2_1/c}$ [1]. Atoms of the germanium are tetrahedraly surrounded by Se atoms so the structure of one $GeSe_2$ layer can be presented by $GeSe_4$ tetrahedra, interconnected via a common edge, or a common corner. In an unit cell of $GeSe_2$ there are two such layers that spread normally to the $\vec{c}$ axis. Within one layer, chemical bonds in $GeSe_2$ are of the covalent type, while the layers bounding has been achieved by the van der Waals forces. Inter-layer forces in $GeSe_2$ are about 100 times weaker than intra-layer forces [1], and this fact explains an expressive cleavage of this material and the anisotropy of many of its properties.

Though the layered semiconducting compounds have been intensively studied for the last few years, properties of $GeSe_2$ are still mainly unknown. The reason for that lies probably in the fact that it is very difficult to obtain $GeSe_2$ in the single crystal form of satisfactory quality and dimensions.

The so far studies of optical and electric properties of this compound have also hinted its eventual application. Recently, an optical-memory-switching effect has been noticed in $GeSe_2$ [2], and from the Ge_xSe_{1-x} alloy, doped by silver, some photo-resistors of considerable photosensitivity have been made [3].

Optical properties of $GeSe_2$ in the visible spectral region have been studied [4-7] without a more detailed analysis of the band structure of this compound.

In this work there will be presented the spectra of $GeSe_2$ on the base of which the values of a direct and indirect band gap will be calculated. Besides, on the base of stepped dependence of the absorption coefficient on the energy, energies of the phonons which involve in the indirect transition have been determined.

2. *Experimental method and results*

The samples used in this measurements were cleaved from a single-crystal bulk sample of $GeSe_2$, grown by Bridgman technique [1]. Freshly cleaved bulk samples were used for the reflectivity measurements. The specimens used for transmission measurements were obtained by cleavage, too. A crystal was held on both sides with a sticking tape, so that pulling appart resulted in trisecting it. The middle part was used. The thickness of these samples ranged from 10 to 300 μm. The surfaces of all samples were free of cleavage-steps over areas of at least 0.5 cm^2. An IR viewer was used to verify that the thicker samples contained no internal cracks, voids, incipient cleavages or other visible defects.

The samples were mounted in a variable-temperature cryostat, and transmission measurements were performed at 4.2 K, 77 K and 300 K, using a Cary model 17 spectrophotometer.

Figures 1a and 1b show the transmission and reflection coefficients as functions of photon energy at 300 K, 77 K and 4.2 K.

Using the relation:

$$T = \frac{(1 - R)^2 \, e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}},$$

where T and R are the transmission and reflectivity coefficients, respectively, and d the thickness of the sample, the absorption spectra of $GeSe_2$ were obtained. These spectra are shown in Fig. 2.

3. *Discussion*

The reflectivity spectra of $GeSe_2$ shown in Fig. 1b, in the spectral range from 450 nm to 600 nm, is a slowly varying function with the saddling point at about 525 nm. The existence of the saddling point on the reflection curve is related to

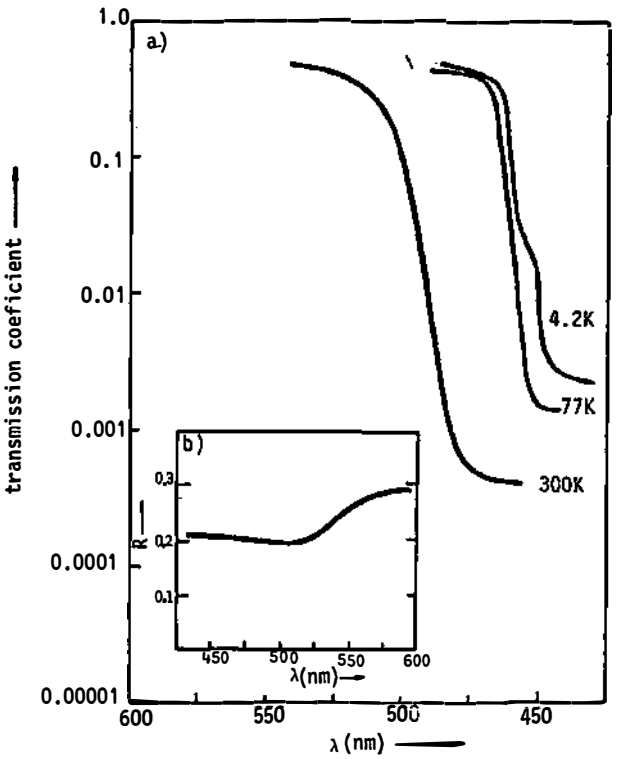

Fig. 1. Transmission (a) and reflectivity (b) spectra of $GeSe_2$.

electron transition from the valence band to the conduction band. The position of the saddling point corresponds the position of the absorption edge. The reflectivity spectra of $GeSe_2$ has been shown by now only in the Ref. 8. The value of $E = 2.35$ eV [8] accords with the saddling point position from Fig. 1b.

Since the reflectivity coefficient of $GeSe_2$ in the spectral range under 500 nm is almost constant and makes about 20%, the constant value of $R = 0.2$ was taken for calculation of the absorption coefficient at 77 K and 4.2 K.

In the absorption spectra of $GeSe_2$ shown in Fig. 2, two spectral regions can be observed: over 10^3 cm^{-1} and under 10^3 cm^{-1}, which, as it is known, correspond to the direct, that is indirect energy gap of semiconducting materials. Particularly noticeable is the existence of fwo spectral regions from the absorption curve of $GeSe_2$ at 4.2 K.

For a case of direct energy gap, the dependence of the absorption coefficient α on the photon energy, can be presented by the relation:

$$\alpha = A \cdot (h\nu - E_g)^n \qquad (1)$$

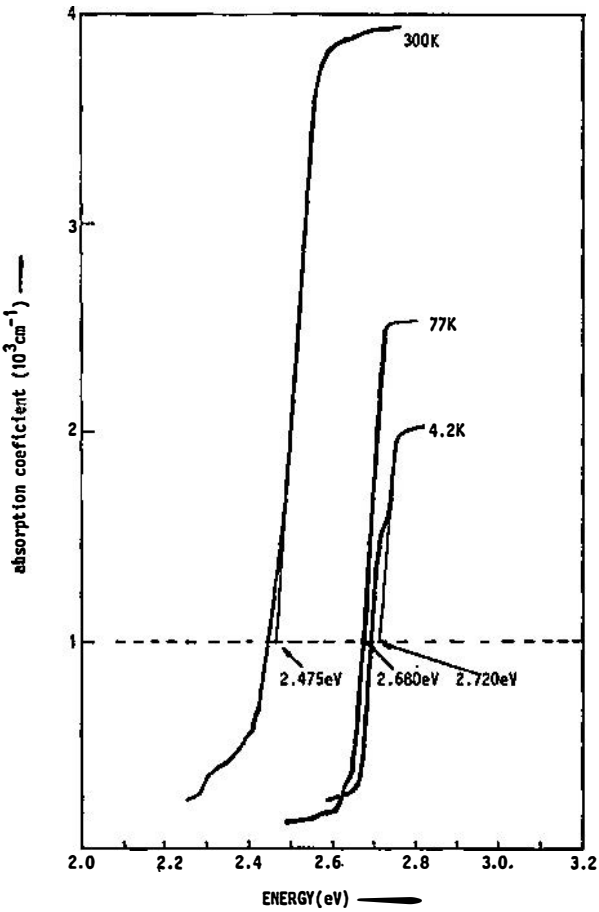

Fig. 2. Spectral variation of the absorption coefficient for $GeSe_2$ at 300 K, 77 K and 4.2 K.

where A is the slowly varying function, which can be regarded as a constant over the observed narrow spectral range, and n is the number which depends on the nature of the energy transition of electrons between the valence and conduction bands. As it was shown in Ref. 9, for the case of direct transition of layered semiconducting materials, $n = 1$. Drawing $\alpha\,(h\,\nu)$ and by means of extrapolation of the straight part of this curve with the line up to the section with the abscis axis (for $\alpha = 10^3\ \mathrm{cm}^{-1}$), we obtained values of the direct energy gap of $E_g = 2.475$ eV (300 K); 2.680 eV (77 K) and 2.720 eV (4.2 K).

The values of the energy gap at 300 K and 77 K are in good agreement with those ones previously published[4,7]. Value of direct energy gap of the $GeSe_2$ at 4.2 K had not been known by now. The values of E_g at 0 K $E_{g0} = 2.690$[4] and $E_{g0} = 2.772$ (2.782)[5] for $E \parallel a\,(E \parallel b)$ polarization were previously determined. However, these values were not determined correctly, because, as it was shown in Ref. 2, the exciton peak at 2.854 eV was stated at 4.2 K, which means that energy

gap at 0 K must be bigger than this value. Besides, we have recently[10] determined the energy gap at 0 K, using the Urbach's rule $E_{g0} = 2.870$ eV (2.900 eV) for $E \parallel a\,(E \parallel b)$ polarization, discussing these differences in more details. The fact that the exciton peak was stated at 2.854 eV at 4.2 K (for the absorption coefficient $> 10^4$ cm^{-1}), led us to the conclusion that the saddling-shaped part of the curve α in Fig. 2 should be ascribed to the change of the transition mechanism and not, for instance, to transition from a lower valence zone into a higher conduction zone, and similarly.

The dependence of the absorption coefficient α on the photon energy in a case of indirect transition is given by the relation:

$$\alpha = A' \cdot (h\nu - E_g \pm E_p)^n$$

where $n = 2$ for the case of indirect transition, and E_p is energy of the phonons which are emitted or absorbed in transition.

Drawing the dependence $\alpha^{1/2}\,(h\nu)$ and by means of extrapolation of the straight part of the curve up to the section with the abscis axis ($\alpha = 0$ cm^{-1}), values of the indirect energy gap were determined. This process is depicted in Fig. 3. The following values of the indirect energy gap were obtained: $E_g = 2.356$ eV (300 K); 2.605 eV (77 K) and 2.650 eV (4.2 K).

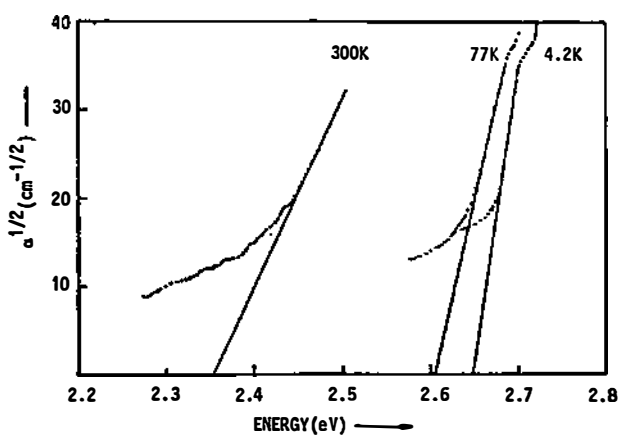

Fig. 3. Absorption coefficients $\alpha\,(h\nu)^{1/2}$ for $GeSe_2$ at 300 K, 77 K and 4.2 K.

As it can be seen in Fig. 3, the absorption coefficient shows a steeped dependence on the photon energy $h\nu$. This dependence is shown in Fig. 4 to a larger extent. The steeped dependence of the absorption coefficient on the energy in the indirect transition region results from the phonon-photon interaction, and the number of steps determining the number of phonons which involve in the transition. In our case (Fig. 4), a bigger number of steps was noticed, symmetrically distributed in relation to the indirect energy gap value of $E_g = 2.356$ eV.

TABLE 1

	$h\nu_1$	$h\nu_2$	$h\nu_3$	$h\nu_4$	$h\nu_5$	$h\nu_6$	$h\nu_7$	$h\nu_8$	$h\nu_9$	$h\nu_{10}$	$h\nu_{11}$	$h\nu_{12}$	$h\nu_{13}$	$h\nu_{14}$	$h\nu_{15}$	$h\nu_{16}$
E_i (meV)	2.222	2.261	2.268	2.291	2.300	2.304	2.314	2.344	2.369	2.400	2.410	2.414	2.424	2.453	2.460	2.497
E_p (meV)	137.6	99.5	92.5	66.5	57	53	43	12.5	13	44	54	58	68	97	104	141

Phonon energies of $GeSe_2$.

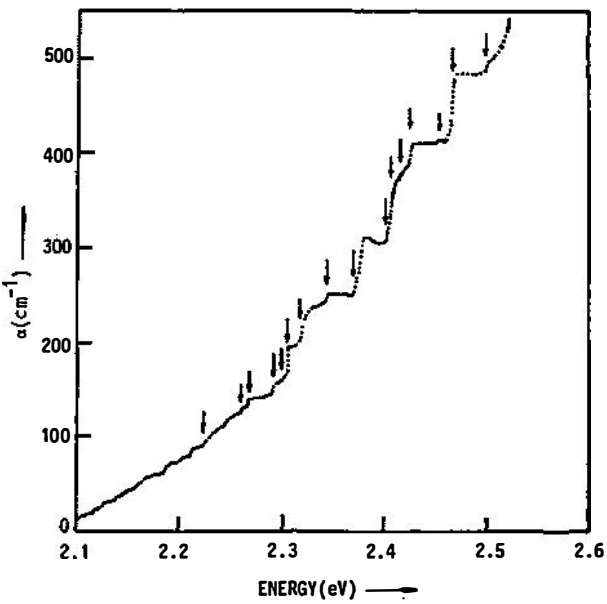

Fig. 4. The variation of the absorption coefficient at the indirect absorption edge indicates a step function dependence, followed by a plateau.

The energy values at which occurs the changing of steps at the absorption curve (Fig. 4), are given in Table 1. Using these values, by means of the formula $E_p = (h\nu_t - h\nu_{n-1})/2$ or $E_p = E_t - E_g$, energies of the phonons were determined. According to the data given in Table 1, it can be seen that the indirect transition involve 8 phonons, whose energies are 13; 44; 54; 58; 68; 97; 104; 141 meV. The energies of the first two phonons correspond the phonon energies of $GeSe_2$ which were determined by analysis of lattice vibrations of this material, given in the Ref. 1.

4. *Conclusions*

Studying of optical spectra of the layered compound $GeSe_2$ the existence of direct and indirect energy gap were determined. The values of direct (2.425 eV; 2.680 eV and 2.720 eV) and indirect energy gap (2.356 eV; 2.605 eV and 2.650 eV) at the temperatures of 300 K, 77 K and 4.2 K, respectively, were obtained. It was also shown that the indirect transition is performed by absorption, that is emission of the phonons whose energies are 13; 44; 54; 68; 97; 104; 141 meV.

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OPTIČKE OSOBINE GERMANIJUM DISELENIDA

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Originalni naučni rad

Optičke osobine $GeSe_2$ proučavane su u opsegu od 400 nm do 600 nm pri temperaturama od 300 K, 77 K i 4.2 K. U apsorpcionom spektru uočene su dve različite oblasti koje odgovaraju direktnom i indirektnom prelazu. Stepenasta zavisnost koeficijenta apsorpcije u oblasti indirektnog prelaza uslovljena je apsorpcijom odnosno emisijom fonona pri indirektnom prelazu. Određeni su parametri koji karakterišu direktni i indirektni prelaz.