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Optical Absorption in  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> Single Crystals

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The difference between the defect semiconductor compounds  $A_2^{III}B_3^{VI}$ , to which  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> refers, and other semiconductors lies, in particular, in the fact that their absorption spectra do not reveal a sharp edge and a line structure at the fundamental absorption edge and their reflection spectra do not show sharp reflection peaks /1 to 3/. This is associated with the presence of a great number of stoichiometric vacancies in the lattice of the  $A_2^{III}B_3^{VI}$  compounds, which lead to a strong blurring of the band edges and a smoothing of the Van Hove features. The stoichiometric vacancies impede, in particular, the process of exciton creation and their migration in the crystal lattice /3/.

At present the absorption edge of the Ga<sub>2</sub>S<sub>3</sub> compound is poorly investigated and the data reported in the literature are ambiguous.

In the present note experimental results on the fundamental absorption edge of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> single crystals, grown by the closed tube chemical transport method, are described /4/. The measurements were made at temperatures between 1.6 and 293 K by means of a common technique /1/.

At low temperatures in the absorption spectrum of Ga<sub>2</sub>S<sub>3</sub> a structure consisting of two bands, which lie immediately at the fundamental absorption edge, has been observed for the first time (as has been already reported in /5/). At 1.6 K the bands are situated at 3659 and 3621 Å, the half-width of the intense band ( $n = 1$ ) being equal to 9 Å. The short-wavelength band ( $n = 2$ ) is wider and weaker than the first band. A rise in temperature leads to a smooth shift of bands to the long-wavelength range of the spectrum and causes their broadening. At  $T > 200$  K the bands are not observed.

Fig. 1 shows one of the typical transmission curves of the  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> single crystal at 1.6 K (the sample thickness is 25 μm). The short-wavelength band, clearly seen in the spectrogram, is weakly delineated in the figure because of its low intensity. Its position in the spectrum is marked by an arrow. The location of the bands on the

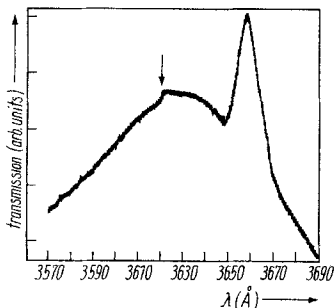


Fig. 1. Transmission spectrum of an  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> single crystal at 1.6 K

wavelength scale at various temperatures is shown in Table 1.

The absorption coefficient in the maximum of the intense band at 77 K reaches the value of  $1250 \text{ cm}^{-1}$

By assuming the bands to be due to impurity absorption and using the well-known Fan formula /6/, we have estimated the impurity level concentrations, necessary for the appearance of an absorption band of such an intensity. The value obtained is in many orders higher than the concentration of equilibrium carriers in Ga<sub>2</sub>S<sub>3</sub> at 293 K. Consequently, the observed absorption bands are unlikely to be of impurity nature. This is also evidenced by the exceptional reproducibility of the results of measurements in the range of the observed absorption bands made on crystals of various thicknesses grown under different conditions.

Besides, at 1.6 K we have observed a peak in the reflection spectrum of Ga<sub>2</sub>S<sub>3</sub> at  $\lambda \approx 3660 \text{ \AA}$ , that is, in the energy where the intense absorption band ( $n = 1$ ) is located. In view of the high absorption in the band ( $\alpha > 10^3 \text{ cm}^{-1}$ ) and low reflectivity ( $R \approx 15\%$ ) the peak in the reflection spectrum is weakly expressed.

The above mentioned properties of the absorption bands, along with the peak in the reflection spectrum give ground to affirm that the structure observed near the fundamental absorption edge is related to the basic lattice of the  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> crystal rather than to its defects or deviations from stoichiometric composition, and is of excitonic character.

By assuming that the exciton satisfies the Wannier-Mott-type model and that the absorption bands correspond to the ground ( $n = 1$ ) and first ( $n = 2$ ) excited exciton states, the values of the band gap  $E_g$ , the effective Rydberg constant  $R_y$ , the reduced mass of the hole-electron pair  $\mu$ , and the effective Bohr radius  $a_{ex}$  of the exciton, are estimated by the position of the absorption bands on the energy scale /7/. The values obtained are given in Table 1.

The long-wavelength wing of the absorption band at various temperatures is analysed. The absorption coefficient in this energy range follows the well-known

Table 1

line number	T (K)	$\lambda(\text{\AA})$	$E_g(\text{eV})$	$R_y(\text{meV})$	$\mu/m_o$	$a_{ex}(\text{\AA})$	$dE_g/dT(\text{eV/K})$
1	1.6	3659	3.438	47.5	0.413	13.95	$-3.8 \times 10^{-4}$
2		3621					
1	4.2	3660	3.437	47.3	0.411	14.00	$-1.8 \times 10^{-4}$
2		3622					
1	77	3674	3.424	47.1	0.410	14.06	
2		3636					

exponential dependence /8/:

$$\alpha = \alpha_o \exp[-S(\hbar\omega_o - \hbar\omega)] , \quad (1)$$

where  $S$  is the slope of the absorption edge,  $\alpha_o$  and  $\hbar\omega_o$  are constants equal to  $3.6 \times 10^4 \text{ cm}^{-1}$  and 3.486 eV, respectively (see Fig. 2).

If the exponential absorption edge is due to the exciton-phonon interaction, the absorption is known to be described by the relation (1) and the slope of the edge is dependent upon temperature /9/:

$$S = \frac{\sigma}{kT} = \frac{2\sigma_o}{\hbar\omega} \text{th} \frac{\hbar\omega}{2kT} , \quad (2)$$

where  $\hbar\omega$  is the mean energy of phonons forming the absorption edge. If the exponential edge is due to transitions between the "tails" of the state densities, which appear in the band gap in view of the existence and fluctuations of random internal microfields and as a result of band edge distortions caused by the charge impurities etc., then a significant lowering of the edge slope is experimentally observed and in this case  $S$  depends only upon the concentration of crystal imperfections rather than on temperature /10 to 12/.

In our case the slope of the absorption edge of  $\alpha\text{-Ga}_2\text{S}_3$  changes with temperature within  $26$  and  $15 \text{ eV}^{-1}$  in the temperature range between 77 and 293 K, this

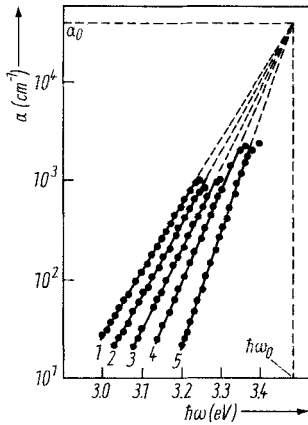


Fig. 2. Temperature dependence of the absorption coefficient. (1) 293, (2) 230, (3) 180, (4) 115, (5) 77 K

being in agreement with the mechanism of exciton-phonon interaction /9/. From a comparison between the experimental curve and the family of theoretical curves describing the  $\sigma$  dependence, the values of  $\sigma_0$  and  $\hbar\omega$  are found to be equal to 0.42 and 32 meV, respectively. The calculation gives, however, S values ranging from 80 and 45 eV<sup>-1</sup>, that means in the case of exciton-phonon interaction the experimental values of the edge slope for  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> crystals, as well as for A<sup>II</sup>B<sup>VI</sup> semiconductors /13, 14/, appear to be lower than the theoretical ones.

This lowering of the slope may be accounted for in terms of the theory of disordered systems /10 to 12/ as resulting from the action of random internal electric fields, causing the potential relief of the crystal. The optical phonons, impurities, dislocations, and other crystal imperfections might be the main source of the existence of local fields.

$\alpha$ -Ga<sub>2</sub>S<sub>3</sub> grown by the closed tube chemical transport method contains in addition to those mentioned above a lot of "intrinsic" defects, associated with the existence of stoichiometric vacancies (SV) in the lattice. The electric microfields caused by SV, seem to lead to an effective lowering of the slope of the absorption edge. We have obtained the magnitude of the characteristic impurity field  $E_i \approx 10^5$  V/cm for given S values in the case of a Coulomb field of charged centres /15/. A rather high electric field appears to be due to the potential relief and probably to the significant ionicity of the chemical bond of the Ga<sub>2</sub>S<sub>3</sub> compound /1/.

Thus, the analysis of the long-wavelength branch of absorption shows the formation of the fundamental absorption edge of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> which is affected by the exciton-phonon interaction, as well as by the potential relief of the crystal.

The isoabsorption curves taken from Fig. 2, for various values of  $\alpha$ , converge in the point  $\hbar\omega_0 = 3.486$  eV, which is positioned on the short-wavelength side of the excitonic peak, this being characteristic of free excitons /16/. Beyond the

boundary of the convergence of excitonic bands the absorption is described by the  $(\alpha\hbar\omega)^2 = f(\hbar\omega)$  dependence, this being indicative of the occurrence of direct allowed optical transitions at  $K = 0$  in this energy range.

The information presented above gives evidence that qualitatively new results on the absorption edge of the monoclinic  $\alpha$ -modification of the defect compound  $\text{Ga}_2\text{S}_3$  are obtained. These results will contribute to further investigations of the presently insufficiently explored energy band structure of the defect compounds  $\text{A}_2^{\text{III}}\text{B}_3^{\text{VI}}$  and primarily of  $\text{Ga}_2\text{S}_3$ . Taking into account that, according to literature data, the absorption edge of  $\text{Ga}_2\text{S}_3$  at 77 K lies at  $\lambda \approx 4320 \text{ \AA} / 2, 3, 17/$ , the results obtained in this work seem to be of principle importance.

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