Excitonic and intraatomic absorption in Nd_2S_3-activated $TlGaS_2$ single crystals

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Observations reveal a mutual effect of the excitonic and intraatomic absorption components in $TlGaS_2$ single crystals activated with the compound neodymium sesquisulfide (Nd_2S_3). A model is proposed for the appearance of local Nd^{3+} formations in $TlGaS_2$.

A red luminescence with a complex fine structure has been observed previously[1] in pure $TlGaS_2$ single crystals at 1.8 K. A detailed further study has now established that the ESR observed in real, undoped $TlGaS_2$ crystals in the temperature interval 3.8–8.2 K is directly associated with paramagnetic Tl^{2+} centers (in a concentration $\sim 10^{18}\,cm^{-3}$) of low-temperature luminescence. With this as a starting point, we carried out a study of the absorption spectra of $TlGaS_2$ single crystals activated with the compound neodymium sesquisulfide (Nd_2S_3) over broad ranges of the energy (1.7–2.8 eV) and the temperature (77–300 K). We are reporting the results of this study in the present letter.

The $TlGaS_2$–Nd_2S_3 crystals were grown by the Bridgman–Stockbarger method. The lattice constants were determined by x-ray structural analysis. The maximum $TlGaS_2$ concentration was $\sim 10^{19}$ cm^{-3}. The $TlGaS_2$ single crystals crystallized in a tetragonal structure (of space group C_2^4; Refs. 2 and 3) with the lattice constants $a = b = 7.29$ Å, $c = 29.9$ Å and with $z = 16$. The Nd_2S_3 sample is yellowish-green with an n-type conductivity and a resistivity $\rho = 1.6 \times 10^{10}$ $\Omega \cdot cm$. The fundamental absorption edge is at $\lambda = 4750$ Å and coincides with that of $TlGaS_2$. Correspondingly, the band gap is $E_g = 2.61$ eV at 77 K. The red part of the absorption spectrum [4] contains clearly defined absorption lines associated with interatomic $4f$–$4f$ electron transitions between the $^4I_{9/2}$ ground state and the $^2G_{7/2}$ and $^4G_{5/2}$ excited states of the Nd^{3+} ion. A DFS-24 grating monochromator was used to study the absorption spectra.

The experimental results are shown in Fig. 1 as a plot of the absorption coefficient K versus the energy E at temperatures of 300 K and 77 K in $TlGaS_2$ crystals with various Nd_2S_3 concentrations. Here are the most characteristic features of the absorption of these crystals.

1. Excitonic absorption lines of the $TlGaS_2$ crystal and a wide absorption band associated with intracenter transitions of Nd^{3+} are observed.

2. As the temperature is lowered to 77 K, we observe (a) shifts of the edge and of the absorption band in opposite directions, in the long-wavelength and short-wavelength directions, respectively, and (b) a change in the relative intensities of the ab-

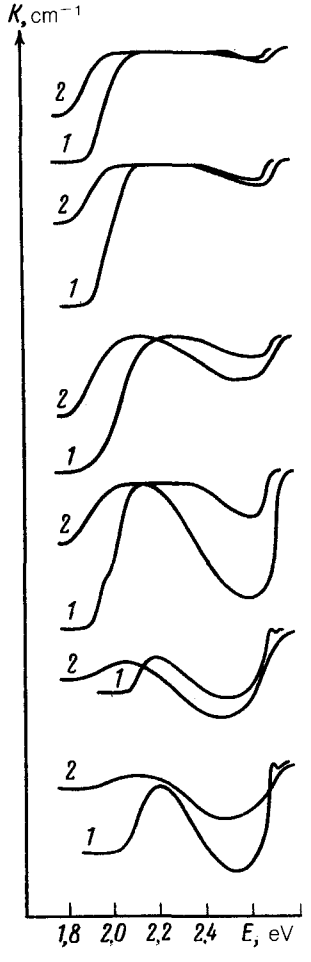

FIG. 1. Absorption spectra of $TlGaS_2$ with various Nd_2S_3 concentrations. The concentration increases from bottom to top. *1*—77 K; *2*—300 K.

sorption lines. In the experiments, these changes are accompanied by changes in the color of the single crystal. A dark green sample becomes bright red at 77 K.

3. The absorption coefficient exhibits a strong concentration dependence. As the Nd_2S_3 concentration is increased, (a) the relative intensity of the absorption line in the low-frequency part of the spectrum clearly increases, and (b) the energy distance between the absorption lines increases from 2.1–2.3 eV to 2.0–2.5 eV at 77 K.

To explain these experimental results, we suggest the following model for $TlGaS_2$–Nd_2S_3. This model gives a self-consistent description of the red luminescence and the absorption; these two properties of the crystal are intimately related to each other. A diagram of this model is shown in Fig. 2. The following series of processes occurs in this system: When the rare-earth compound Nd_2S_3 is added to the $TlGaS_2$, the Nd^{3+} ion localizes at Tl^{1+} vacancies (10^{18} cm^{-3}), with weak bonds to six S^{2-} ions (two of the sulfur ions are in the upper layer of the stack, and four in the lower

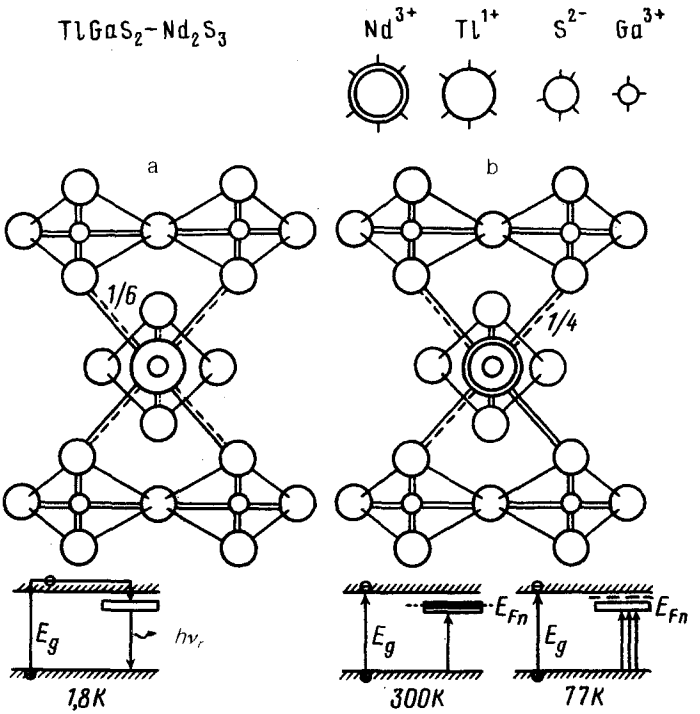

FIG. 2. a—Fragment of the crystal structure of $TlGaS_2$ in the plane perpendicular to the C optic axis; b—fragment of the crystal structure of $TlGaS_2$–Nd_2S_3. Energy diagrams are shown at the bottom.

layer). It forms a weak covalent bond with two sulfur ions in different layers, while it forms an ionic bond with the other four sulfur ions. This circumstance means that the interstack and interlayer interactions in the crystal are intensified and correspond to a decrease in the number of defective stackings associated with a relative displacement. Occurring in parallel with the incorporation of the Nd_2S_3 is another process: a healing of the defects due to sulfur vacancies. Experimental confirmation of this healing comes from the intensification of the excitonic absorption line and the observation of an edge luminescence due to the recombination radiation of free excitons.

This model and the energy diagrams in Figs. 2a and 2b agree qualitatively with the experimental results on $K(E)$.

The conditions under which the experiments, which lead to conclusions of this sort, were carried out do not permit a definitive determination of the topology of the resulting structure. A specific interpretation of the results will require ESR spectra and further, multifaceted experiments at low temperatures.

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