Optical Properties of the Cr_5S_6 Single Crystal

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Abstract—Results of the investigation of optical density spectra of Cr_5S_6 single crystals in the infrared region have been presented. A comparative analysis of the temperature dependences of the magnetization and the light absorption has been performed. Physical mechanisms to explain the specific features of the spectral and temperature dependences of the optical density have been proposed.

1. INTRODUCTION

In the Cr−S system, the Cr_5S_6 compound has attracted attention due to its interesting magnetic properties. The crystal structure of this compound belongs to the trigonal type (space group $P\bar{3}1c$ (D_{3d}^2)) with ordered vacancies in every second chromium layer [1]. There is the following sequence of magnetic structures at an increased temperature [2]: an antiferromagnetic screw-type spiral structure at $T < T_1 \approx 158$ K, a collinear ferrimagnetic structure in the range from T_1 to $T_2 \approx 305$ K (spontaneous magnetization is very small in the ferrimagnetic state), and a paramagnetic structure at $T > T_2$. Features of the magnetic state manifest themselves in the temperature dependences of the ferrimagnetic resonance line width [3], magnetization [4, 5], X-ray magnetic circular dichroism spectra [6], and electrical resistivity [7].

Measurements were mainly performed on polycrystalline samples due to the difficulties in growing Cr_5S_6 single crystals, since there is a very narrow region in the Cr−S phase diagram where this compound exists [1]. We know only two works [4, 7] dedicated to the study of Cr_5S_6 single crystals. The optical properties of this compound were not investigated.

The aim of this work is to study the light absorption in the Cr_5S_6 single crystal in the IR region. Special attention is paid to interrelation between the magnetic state and optical properties.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The plates of Cr_5S_6 single crystals with dimensions of 1.2×1.2 mm and a thickness of $d = 75$ μm were produced by the method of chemical transport reactions using polycrystalline Cr_5S_6 and iodine as a transporting agent based on the technology described in [4]. We did not determine the crystallographic indices of faces because of the small sizes of the crystals.

The visual inspection of the plates suggests that the crystals grow mainly in directions perpendicular to the *c* axis.

The temperature dependences of magnetization in the range $T = 80−300$ K were measured using a vibrating-sample magnetometer with eight plates glued onto a mica substrate. These results were published in [4]. Figure 1 presents $M(T)$ curves, since the analysis of the optical data requires taking into account the results of magnetic measurements.

Light transmission *t* was measured using a highly sensitive IR setup in the wavelength range $1 \leq \lambda \leq 8$ μm in the temperature range from 80 to 300 K. The coefficient of specular reflection was not measured because of small sizes of the crystals and the uneven surface of the plates. So, we calculated only the optical density from $D = \ln(1/t)$. Temperature dependences of D were measured under heating conditions at a rate of $\sim 1−4$ K/min.

3. RESULTS AND DISCUSSION

The temperature dependences of the magnetization $M(T)$ measured at perpendicular magnetic field orientations (Fig. 1, curve *1*) and parallel to the plane of the plates (curve *2*) are significantly different from each other. In the first case, there is nothing special on the curve $M(T)$. When a magnetic field is applied parallel to the plane of the plates, the magnetization sharply grows in the range $T = 154−168$ K. Therefore, the transition from antiferromagnetic to ferrimagnetic state is not pronounced even for single-crystal samples. With a further increase in temperature, the mag-
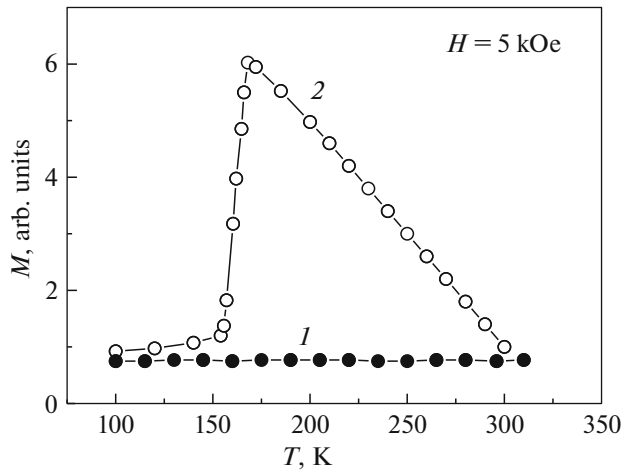
Fig. 1. Temperature dependence of the magnetization at $H = 5$ kOe oriented (*1*) perpendicular and (*2*) parallel to the surface of the Cr_5S_6 single-crystal plates.

Fig. 2. Spectra of optical density D measured for the Cr_5S_6 single crystal at 80 and 295 K. Solid lines indicate the calculated spectra of D.

netization gradually decreases and, at a temperature of about 300 K (near the transition to the paramagnetic state), the difference between these curves disappears.

Figure 2 shows the spectra of optical density $D(E)$ measured at 80 and 295 K. Light propagated along the *c* axis, so that the electric wave vector was in the same plane as magnetic moments. For all the energy values, the optical density is greater than 2.9, which indicates a large number of defects and can be the contribution of free carriers. Together with this, a strong growth of absorption is observed at $E > 0.21$ eV. This behavior is typical of heavily doped semiconductors. The difference between the curves measured at $T = 80$ and 295 K is caused not by the "blue" shift, as might appear from the figure, but by an increase in the "background" with an increase in the temperature, since these curves practically match together, if one shifts the lower curve up by 0.17. This total increase in absorption with temperature cannot be caused by free carriers, since the resistance of Cr_5S_6 increases as temperature increases [7]; therefore, the appropriate contribution to the absorption must decrease. In the region $E > 0.25$ eV, the absorption is well described by the following relationship:

$$D(E) = D_0 + C(E - E_0)^{1/2}$$

(solid lines in Fig. 2), where $E_0 = 0.23$ eV, $C = 3.1$ eV$^{-1/2}$, $D_0 = 2.77$ at $T = 80$ K, and $D_0 = 2.94$ at $T = 295$ K. Such dependence $D(E)$ indicates the transitions involving closely located wide bands. This conclusion is supported by the results of [8], where authors believe that a wide (~8 eV) valence band is formed by *d* states of chromium and *p* states of sulfur.

The optical density slightly increases at $E < 0.21$ eV. This increase cannot be associated with the phonon absorption, since phonon bands in sulfides appear only at lower frequencies (for example [9]). The above
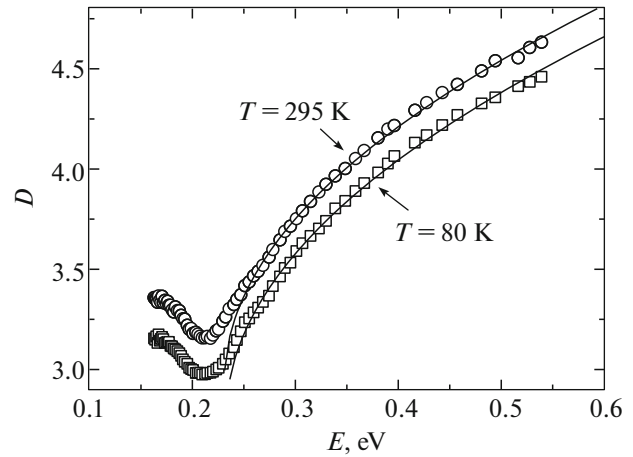
is the reason why the absorption of free carriers cannot also be decisive. It remains to assume that this increase is caused by $d-d$ transitions between the states of Cr^{2+} and Cr^{3+} ions.

Let us consider the temperature dependence of the optical density shown in Fig. 3. The measurements were performed at an energy $E = 0.27$ eV (wavelength $\lambda = 4.6$ μm). The optical density increases almost linearly with an increase in the temperature in the range $T = 77-196$ K. The absorption decreases in the range $T = 196-225$ K and the optical density at $T > 225$ K increases again up to the temperature of transition to the paramagnetic state. Both the antiferromagnetic–ferrimagnetic transition region ($T = 154-168$K) and the transition to the paramagnetic state are not pronounced, despite the fact that, in such magnetic semiconductors as EuO, $HgCr_2Se_4$, $CdCr_2Se_4$, and others,
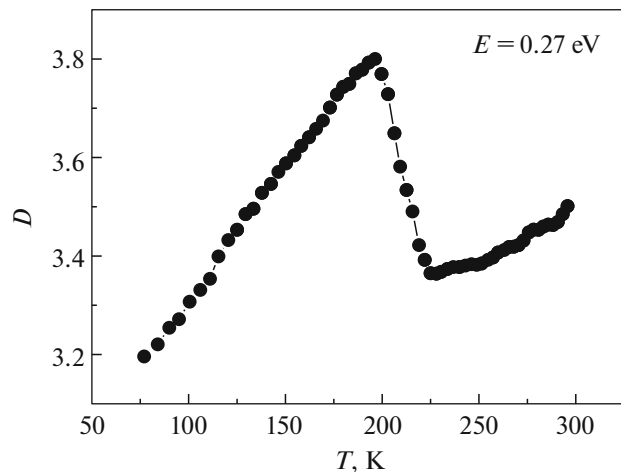

Fig. 3. Temperature dependence of the optical density of Cr_5S_6 at $\lambda = 4.6$ μm.

the appearance of spontaneous magnetization leads to clearly pronounced peculiarities in the temperature dependence of the absorption edge [10−12]. The absence of such peculiarities in the case of Cr$_5$S$_6$ can be due to the extremely small spontaneous magnetic moment.

The maxima and minima in the curve $D(T)$ are not associated with a magnetic transition; hence, the reason for the appearance of these extrema remains unclear. It should be noted that the width of the ferromagnetic resonance line and the effective g factor in the Cr$_5$S$_6$ single crystal reach maxima at temperatures being within the region of the existence of the ferromagnetic phase far from its boundaries [3]. According to [3], these peculiarities can be explained by the energy absorption during the hopping of valence electrons between ions with different valences: Cr^{2+} and Cr^{3+}. Such energy absorption takes place under the condition that the hopping time of electrons, which is a function of temperature, is comparable with the time of the magnetic precession. The formation of the observed temperature dependence of the optical absorption is probably also associated with the hopping of electrons between the Cr^{2+} and Cr^{3+} ions.

4. CONCLUSIONS

The optical absorption spectra of the Cr$_5$S$_6$ single crystals were investigated for the first time in the IR region at $T = 80-300$ K. The optical density and the temperature dependences of the magnetization of Cr$_5$S$_6$ were analyzed. It was assumed that the fundamental absorption edge at energies $E > 0.25$ eV resulted from the transitions from the wide valence band formed by d states of Cr and p states of S. The increase in the optical density at $E < 0.21$ eV is caused by $d-d$ transitions between Cr^{2+} and Cr^{3+} ion states. The peculiarities of the temperature dependence of the optical density cannot be explained by magnetic transitions.

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