

Luminescence of the ferromagnetic semiconductor CdCr_2Se_4

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1. It is known that the compound CdCr_2Se_4 crystallizes in a "normal" spinel structure, has an energy gap ~ 1.3 eV at 300°K , and is a ferromagnet up to $T_c \approx 130^\circ\text{K}$. The upper valence band and the lower conduction band in CdCr_2Se_4 is formed by the strongly-interacting $2p$ and $4s$ states, while the α and f states of the Cr^{3+} electrons form localized states or narrow bands (see, e. g., ^[1]). One can expect the presence of ferromagnetism and of

strongly localized states of Cr^{3+} to lead to interesting luminescent properties of this material.

2. We obtain single crystals of CdCr_2Se_4 from solution in the melt. The initial materials were cadmium, selenium, and anhydrous CrCl_3 , in a molar ratio 2:2:1, were loaded in quartz containers evacuated to 10^{-5} mm Hg. The containers with the initial components were

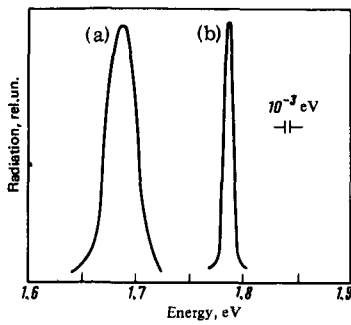


FIG. 1. Luminescence of CdCr_2Se_4 at 300°K (a) and 77.3°K (b).

heated to a temperature on the order of 900°C, then cooled at a rate 2–4 deg/hr to 500°C. The CdCr_2Se_4 crystals, separated from the CdCl_2 , were octahedra with mirror faces; the crystal dimensions reached 4 mm.

3. We investigated the luminescence of the CdCr_2Se_4 single crystals in the temperature interval 77.3–300°K and in magnetic fields up to 30 kG. The luminescence was excited by the second harmonic of a Q-switched neodymium laser (exciting-photon energy 2.34 eV, pulse duration ~35 nsec, photon flux density up to 10^{15} cm^{-3} , pulse repetition frequency ~1 Hz). We used in the experiments an MDR-2 monochromator (4 nm/mm), an FEU-62 photomultiplier, and a pulsed synchronous detector. The luminescence spectrum was registered on the chart of an automatic recorder, and the luminescence kinetics was displayed on a long-persistence oscilloscope screen. The samples were mounted on the cold finger of a cryostat placed between the poles of a magnet.

4. Figure 1 shows the CdCr_2Se_4 emission spectra in the absence of a magnetic field. We see that the crystal radiation is concentrated in a narrow region of the spectrum, with maxima 1.79 and 1.69 eV at 77.3 and 300°K, respectively. The line half-widths were $\sim 10^{-2}$ and $\sim 4 \times 10^{-2}$ eV, respectively. It was noted that the luminescence band of certain samples has a fine structure. According to a highly approximate estimate, the radiation luminance is not less than 10^3 – 10^4 nit at 77.3°K and is approximately one order of magnitude lower at 300°K (at the same value of the exciting-light

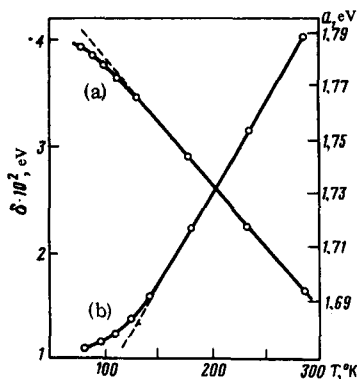


FIG. 2. Temperature dependence of the position of the maximum luminescence (a) and of the emission line half-width (b).

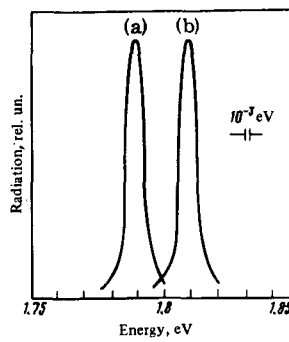


FIG. 3. Luminescence spectrum of CdCr_2Se_4 at 77.3°K a—no applied magnetic field; b—magnetic field ~30 kG.

photon flux density, $\sim 10^{15} \text{ cm}^{-3}$). An investigation of the radiation kinetics has shown that the radiation pulse duplicates exactly the laser pulse, both at 77.3 and at 300°K, i. e., the pulse duration does not exceed 35 nsec.

At 77.3°K, the position of the maximum emission of the CdCr_2Se_4 crystal practically coincides with the emission line of the ruby laser (1.78 eV). It appears that this equality is not an accident, inasmuch as in CdCr_2Se_4 , just as in ruby, the luminescence center is obviously the Cr^{3+} ion in an octahedral surrounding of the anion atoms. On the other hand, the strong difference between the Cr^{3+} concentrations in Al_2O_3 (ruby) and CdCr_2Se_4 (1:100) leads to a difference between the emission linewidths of these materials (1:1000), and the states of Cr^{3+} in CdCr_2Se_4 seem to merge into narrow bands. We note also that in CdCr_2Se_4 , unlike in ruby, the luminescence transitions of Cr^{3+} do not fall in the transparency region of the medium. Naturally, under these conditions the radiation is produced by only a thin surface layer of the crystal (the thickness of which is determined by the absorption coefficient in the region $1.8 \text{ eV} \gg 10^3 \text{ cm}^{-2}$)^[2] and by the emission intensity. We note that the luminescence peak experiences a monotonic temperature shift, in the entire interval 77–300°K, in the same direction as the shift of the edge of absorption and photoconductivity of CdCr_2Se_4 at a temperature above the Curie point.^[3] The reversal in the sign of the temperature shift of the absorption edge below the Curie point^[3] is due to the appearance, in the band structure of CdCr_2Se_4 at $T < T_c$, of a transition that is responsible in particular for the photoferromagnetic effect.^[4, 5]

Figure 2 shows the changes in the position of the maximum of the luminescence band (a) and its half-width (b) with changing temperature. Curves a and b show distinct inflection points in the region of the Curie temperature, evidencing an influence of the magnetic order on the luminescent properties CdCr_2Se_4 .

5. In the investigation of the luminescence of CdCr_2Se_4 in magnetic fields, we observed a phenomenon that can be called optical magnetic memory of semiconductors (OMMS). This phenomenon consists in the following. When a CdCr_2Se_4 crystal is placed in a magnetic field at a temperature $T < T_c$, the maximum of the emission line shifts towards the short-wave side; the subsequent operations, such as reversal of the direction of the magnetic field, turning off the field for a short time, and heating the sample to $T \approx T_c$ or somewhat higher, do

not change the position of the emission maximum. The OMMS is observed several dozen hours after the magnetic field is turned off; during this time, the maximum of the emission line returns gradually to the initial position.

In the first experiments on the observation of the OMMS they used magnetic fields of ~ 30 kG, and the ensuing shift of the emission-line maximum reached $(1.7-2) \times 10^{-2}$ eV (Fig. 3). It was found later on that fields of much lower intensity suffice for the observation of noticeable shifts and of the OMMS phenomenon.

We note that the shift of the emission maximum in a magnetic field is close in order of magnitude to the corresponding shift of the absorption-band edge,^[6] but is of opposite sign. A possible explanation is that the position of the absorption edge $T < T_c$ is governed by the appearance of an additional transition, which is not connected directly with the observable luminescence.

It is natural to relate the OMMS phenomenon with the orientation of the magnetic domains and with the preservation of this orientation after the field is turned off,

but further research is necessary to explain the mechanism of the phenomenon in detail.

It can be assumed that the results reported here can find use in the development of narrow-band light sources controlled by a magnetic field, and for the development of elements for optical magnetic memory.

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