Luminescence of ferromagnetic semiconductor HgCr₂Se₄ with quantum energy exceeding the width of the forbidden band

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It is found that in HgCr₂Se₄ the cathodoluminescence and photoluminescence spectra lie much higher than the absorption edge. The results obtained indicate that the distribution of excited electrons within the conduction band is essentially a nonequilibrium distribution.

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Luminescence spectra of semiconductors generally lie near or below the characteristic absorption edge. This is atributable to the fact that the thermalization time for nonequilibrium charge carriers within the limits of the corresponding bands ($\sim 10^{-12}$ s) is much shorter than their lifetime ($\gtrsim 10^{-9}$ s).

The radiative properties of magnetic semiconductors differ considerably due to the particular features of their electronic spectrum, which is characterized by the presence of strongly localized $4f$ or $3d$ electrons of the transition element, in addition to collectivized electrons. Thus the cathodoluminescence (CL) spectra of specimens of EuO, EuS, EuSe, CdCr₂Se₄, and HgCr₂Se₄ Refs. 1–3 and the photoluminescence (PL) spectra of CdCr₂Se₄ (Ref. 4) contained lines whose energies are considerably higher than the absorption edge (by 0.05–1 eV). In europium chalcogenides, as well as ferromagnetic semiconductors CdCr₂Se₄, these emission lines are related to intracenter f-f and d-d transitions of the Eu²⁺ and Cr³⁺ ions (Ref. 1, 2, and 4), respectively, while in HgCr₂Se₄, according to Ref. 3, Cl is associated with interband transitions from the narrow d-band (formed by $3d$ electrons of chromium), which lies above the bottom of the wide s conduction band (formed by the s and p states), to the valence band.[1] In this case, it was assumed that the nonequilibrium electrons are "held up" in the d band during thermalization. Other models of the electron transitions in HgCr₂Se₄ can also be suggested; for example, it may be assumed that the absorption edge is determined by transitions from the valence band to the unfilled d band, while Cl is due to transitions from the s band (which lies above the d band) to the d conduction band. Since at present there is no generally accepted model of the band structure of the ferromagnetic semiconductor HgCr₂Se₄, it is important to clarify the mechanism of the radiative transitions in this compound not only from the point of view of confirming the specific model but also in order to solve fundamental problems associated with the study of band structure. With this goal in mind, we investigated the PL spectra of HgCr₂Se₄ with excitation by wavelength-tunable radiation (YAG) laser and parametric generator of light).

We investigated single crystals of $HgCr_2Se$, whose size did not exceed 3 mm. These single crystals were obtained by the method of spontaneous crystallization out of a solution in a melt and by chemical transport reactions. In particular, the specimen annealed in a mercury atmosphere had a high electron mobility (1100 cm^2/V s) at $T = 5.2$ K (in Ref. 3, only specimens obtained by the method of chemical transport reactions were investigated).

The investigations were performed in the temperature range 80–300 K. The PL was excited by YAG laser radiation (photon energy 1.17 eV, pulse duration 40 ns, pumping pulse power (I) up to 5 mW/cm^2, repetition frequency 12.5 Hz) and by a parametric light generator based on the potassium niobate crystal (with wavelength tuning from 1 to 1.6 μm).[7] The cathodoluminescence was investigated with the same electron-beam parameters as in Ref. 3 (the energy of the electrons was up to 40 keV, the current density (j) up to 20 A/cm^2, pulse duration was 100 ns, and the repetition frequency was 50 Hz). A MDR-2 monochromator (resolution 4 nm/mm) and a S7-12 stroboscopic oscillograph were used in the experiments, a LFD-2 (or FD-10G) photodiode served as a photodetector.

Figures 1a and 1b show the PL (with pumping by a YAG laser) and CL spectra, respectively. In contast to CL, the PL spectra have a weakly resolved structure which, in our opinion, is related to the two radiative transitions. In this case, as the temprature decreases, there is a gradual redistribution of the luminescence intensity from the short-wavelength transition to a long-wavelength transition and the luminescence is quenched as the Curie temperature of 106 K is approached (Fig. 2). The characteristic feature of the luminescence in $HgCr_2Se_4$ is that the peak in the emission spectrum lies above the absorption edge by 0.05–0.08 eV at $T = 300$ K and by 0.3 eV at $T = 100$ K.[8] The effect of reabsorption on the CL spectrum was investigated in this connection. The data obtained are shown in Figs. 2 and 3, from which it follows that at $T < 200$ K,
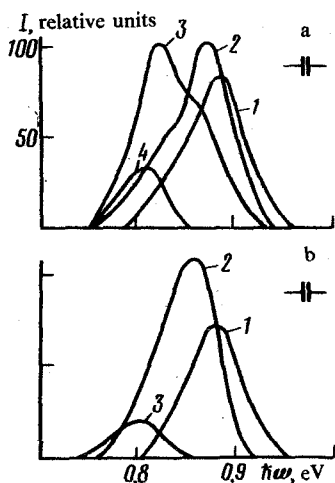

FIG. 1. (a) Photoluminescence spectrum of $HgCr_2Se_4$ $I = 1.6$ MW/cm^2, T, K: 1—300, 2—273, 3—188, 4—133; (b) cathodoluminescence spectra of $HgCr_2Se_4$ $j = 14$ A/cm^2, T, K: 1—300, 2—180, 3—93.

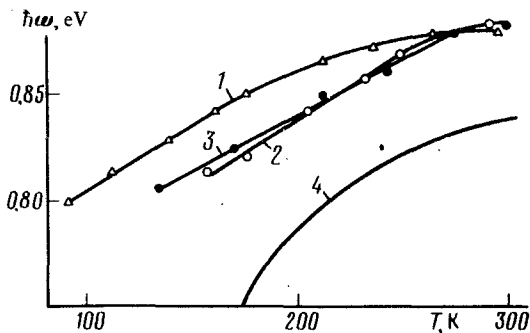FIG. 2. Dependence of the peak in the luminescence spectrum on the temperature of the cathodoluminescence. j, A/cm^2; φ, deg (φ is the angle at which the electrons reach the surface of the specimen): 1—14, 70–90, 2—19, 20–40; 3—FL, $I = 1.6$ MW/cm^2; 4) dependence of the position of the absorption edge, according to Ref. 8.

reabsorption leads to a decrease in the CL intensity and to a displacement of the peak in its spectrum to the long-wavelength region [due to the dispersion $\alpha(\omega)$]. In this case, as the temperature decreases, the coefficient of absorption in the spectral region of CL increases from 10^3 cm^{-1} at $T = 300$ K[9] up to $\sim 10^4$ cm^{-1} at $T = 100$ K. According to very rough estimates, the external quantum yield was 10^{-7} for PL and $\sim 10^{-5}$ for CL. An investigation of the luminescence kinetics showed that the characteristic decay times of the radiation do not exceed 10^{-7} s. Investigation of the PL spectra (at $T = 300$ K) with excitation by a parameter light generator ($\hbar\omega = 1$–1.24 eV) and radiation of the second harmonic of the YAG laser ($\hbar\omega = 2.34$ eV) showed that the spectrum and the luminescence intensity were essentially independent of the wavelength of the pumping radiation.

Thus the investigation of PL with selective excitation showed that the radiation in HgCr$_2$Se$_4$ is associated with transitions from states lying above the bottom of the conduction band to the valence band (or, which is less likely, from the conduction
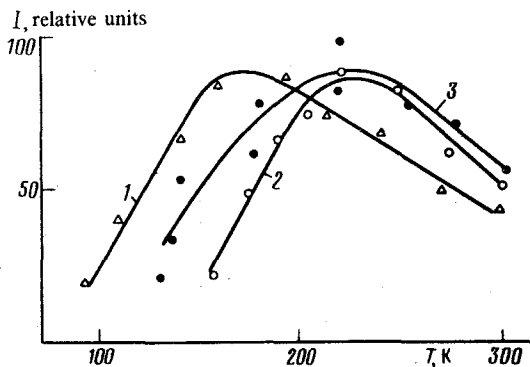

FIG. 3. Dependence of the luminescence intensity on the temperature of CL j, A/cm^2, φ, deg: 1—14, 70–90, 2—19, 20–40; 3—FL, $I = 1.6$ MW/cm^2.

band to states situated below the top of the valence band). This indicates that the distribution of nonequilibrium electrons in the conduction band does not conform to Fermi statistics, i.e., the distribution within the band is a nonequilibrium distribution (in the opposite case, as the temperature decreases from 300 to 100 K, the luminescence intensity must decrease by 12 orders of magnitude). Thus the characteristic energy relaxation time of nonequilibrium electrons in $HgCr_2Se_4$ must be comparable to the radiative lifetime ($\gtrsim 10^{-9}$ s) and, for this reason, it is much higher than the corresponding values in nonmagnetic semiconductors ($\sim 10^{-12}$ s). Such high intraband relaxation times are apparently attributable to the fact that in $HgCr_2Se_4$ the conduction band is formed both by external electrons and by internal $3d$ electrons of chromium.[3] This proposition agrees with the calculations of the band structure of chromium chalcogenide spinels,[10] according to which in $HgCr_2Se_4$ the narrow d conduction band and the wide s conduction band overlap. The long intraband relation times can be explained on the basis of the many-electron description of the electron spectrum.[5] According to this work, as a result of hybridization of overlapping narrow d and wide s conduction bands, these bands split into subbands and the luminescence is caused by transitions from the upper subbands to the valence band. As the temperature is decreased, the width of the energy gaps between the subbands decreases and, therefore, the energy relaxation time and the intensity of the luminescence decrease.

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[1] The energy of the lower excited state of the Cr^{3+} ion[5] is two times higher than the quantum energy of cathodoluminescence of $HgCr_2Se_4$.[3]

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