Characteristics of the photoconductivity of lightly and heavily doped *n*-type $CdCr_2Se_4$ single crystals

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The spectral dependences of the photoresistance R and photomagnetoresistance were investigated experimentally in a wide range of temperatures and magnetic fields applied to lightly doped (with Ga) $CdCr_2Se_4$ single crystals. It was found that two transitions were responsible for the photoresistance maximum in the region of the Curie point T_C: these corresponded to 1.1 and 1.7 eV. The temperature and field dependences of the photomagnetoresistance were complex. Thus, when temperature increased in the region of T_C, a deep minimum of the negative photomagnetoresistance was followed by a range of positive values and a maximum. These features were explained on the basis of the ferron hypothesis. A giant photoconductivity of $CdCr_2Se_4$ single crystals heavily doped with In was observed at low temperatures.

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We investigated earlier[1] the photoconductivity of $CdCr_2Se_4$ single crystals doped lightly with Ga. We found that the photoresistance R of a sample illuminated with white light was maximal in the region of the Curie point T_C, whereas the dark resistance R_d had no such maximum and there was only a kink of the $\log R_d(T^{-1})$ plot in the region of T_C. A giant negative photomagnetoresistance was observed in the vicinity of the Curie point.

In the present study we were concerned with the spectral dependences of the photoresistance $R(E)$ and photomagnetoresistance in a wide range of temperatures and magnetic fields applied to $CdCr_2Se_4$ single crystals doped lightly with Ga; moreover we detected a giant photoconductivity at low temperatures in the case of $CdCr_2Se_4$ single crystals heavily doped with In. The samples and contacts were prepared as described in detail earlier.[1,2]

The earlier study[1] of $CdCr_2Se_4$ single crystals doped lightly with Ga revealed a high photoconductivity in the ferromagnetic region. For example, when the illumination intensity was $\sim 10^3$ lx, the resistivity fell by two or three orders of magnitude.

The photoconductivity was measured under dc conditions. A sample was illuminated with unmodulated light and its resistance was measured by the voltmeter–ammeter method. The use of this method was necessary because of the long rise and relaxation times of the photocurrent, so that modulated illumination could not be employed. Heating of a sample by illumination was avoided by limiting the illumination intensity to $\sim 10^2$ lx, which was kept constant at all the wavelengths in the investigated range.

The spectral dependences of the photoresistance exhibited a number of special features. By way of example, Fig. 1 shows the dependences of the photoresistance R on the photon energy E for a $Cd_{0.98}Ga_{0.02}Cr_2Se_4$ sample, typical of the crystals doped lightly with Ga. The $R(E)$ curves are given for temperatures throughout the investigated range, both below and above T_C. We can clearly see two wide maxima A and C above the Curie point and a minimum B disappearing at $T > 136$ °K. At high temperatures the minimum B degenerates into a shoulder which then splits into two components. The

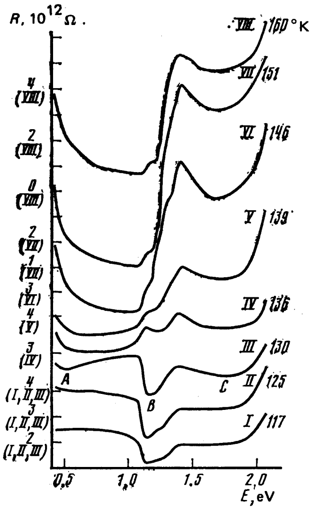

FIG. 1. Low-temperature dependences of the photoresistance of $Cd_{0.98}GA_{0.02}Cr_2Se_4$ on the photon energy.

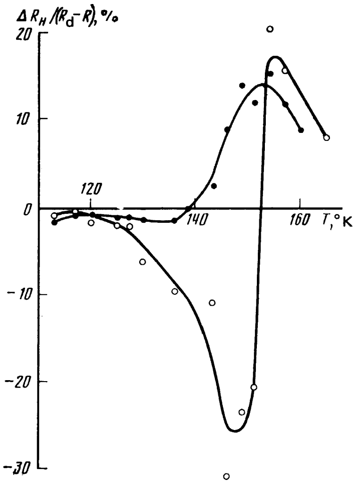

FIG. 2. Temperature dependence of the photomagnetoresistance of $Cd_{0.98}Ga_{0.02}Cr_2Se_4$ and the minima A (•) and C (○) in a field of 5 kOe.

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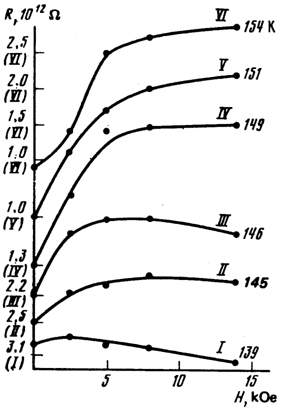

FIG. 3. Dependences of the photoresistance of $Cd_{0.98}Ga_{0.02}Cr_2Se_4$ on the magnetic field at temperatures corresponding to the positive photomagnetoresistance.

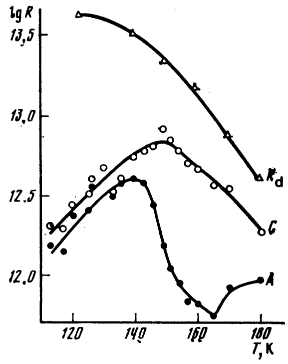

FIG. 4. Temperature dependences of the dark resistance R_d and photoresitance of $Cd_{0.98}Ga_{0.02}Cr_2Se_4$ at the minima A and C.

position of the peak C is practically independent of temperature. The shoulder B splits into two components at temperatures $T > 140$ °K and their positions depend weakly on temperature. The minima A and B exhibit a red shift at low temperatures, and the depth of the minimum A decreases as a result of cooling.

Figure 2 shows the photomagnetoresistance of the same sample recorded in the region of the minima A and C. It is clear from Fig. 1 that the photomagnetoresistance is negative in the ferromagnetic temperature range and that it passes through a minimum in the region of T_C; a further increase in temperature alters its sign to positive. This positive photomagnetoresistance passes through a maximum in the region of ~150 °K. The maximum positive magnetoresistance is anomalously large, amounting to ~17% in a field of 5 kOe. Figure 3 shows the dependences of R on the magnetic field in the range of temperatures corresponding to the positive photomagnetoresistance ($E \approx 1.1$ eV). It is clear that in weaker fields the resistance increases with the field (positive photomagnetoresistance), but in stronger fields at temperatures $T < 149$ °K it begins to fall (negative photomagnetoresistance). At higher temperatures in fields up to 14 kOe the photomagnetoresistance is positive.

In the earlier study of $CdCr_2Se_4$ crystals lightly doped with Ga we found a photoresistance maximum in the region of the Curie point, but the dark resistance showed no such maximum. The present investigation of the spectral sensitivity of R showed that this maximum was largely due to the transitions A and C. This is clear from Fig. 4, which shows the temperature dependence of the dark resistance and photoresistance at the minima A and C.

Investigations of the photoconductivity[4,5] and luminescence,[6] and of the absorption and reflection of light[7,8] by pure and indium-doped $CdCr_2Se_4$ crystals have established the presence of several absorption and luminescence peaks. A peak at ~1.8 eV is usually attributed to interband transitions. Our results confirm this attribution; for example, the width of the minimum C in the spectral sensitivity experiments is quite considerable (Fig. 1), whereas the transition B is clearly associated with local levels or with a narrow band because its width is considerably less than that of C.

The steep photoresistance maximum near T_C may be explained by the ferron hypothesis assuming that ferromagnetic microregions (ferrons), formed around nonionized donors because of a gain in the s–d exchange energy,[9] represent potential wells for photoelectrons. The depth of these wells is maximal near T_C and then nonionized donors become photoelectron traps. The trapping of a photoelectron converts a donor from an analog of the hydrogen atom to an analog of the hydrogen ion. The possibility of trapping, by a nonionized donor, of a second electron near T_C was demonstrated by Grigin and Nagaev.[10] Kovalenko and Nagaev[11] showed that the application of a magnetic field reduces the energy of impurity ferrons because of orientation of their moments along the field and also because of an increase in these moments. Lowering of the energy of these ferrons (clusters) makes them more difficult to ionize. On the other hand, the application of a magnetic field splits the bottom of the conduction band, so that the minimal energy of the conduction electrons also decreases but its field dependence is different than that of the electrons localized in a cluster. As a result of competition between these two factors, a positive photomagnetoresistance predominates in weak fields and the negative effect in stronger fields, as observed experimentally in our study. In weak fields the mobility increases slightly and, therefore, the value of R rises on increase in the field when the field is weak because there is a reduction in the carrier density. Consequently, in weak fields we should observe a positive photomagnetoresistance, whereas in strong fields the effect should be negative, exactly as found experimentally.

In the case of crystals with small amounts of In the low-temperature behavior of the dark resistance $R_d(T)$ is unusual. Its value is affected very strongly by illumination and magnetic fields. The data plotted for a sample of $Cd_{0.487}In_{0.513}Cr_2Se_4$ in Fig. 5 include the magnetization curves $\sigma(T)$, dark resistance dependences $R_d(T)$, and (dashed curve) the photoresistance $R(T)$ observed on illumination with white light whose intensity on the sample surface was ~5.5×10^3 lx. It is clear from this figure that the dark resistance has a maximum in the region of T_C and cooling produces a mini-

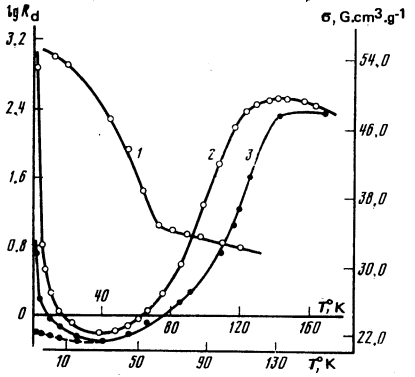

FIG. 5. Temperature dependences of the spontaneous magnetization σ(1), $\lg R_d$ in $H=0$ (2) and in $H=67$ kOe (3) for $Cd_{0.487}In_{0.513}Cr_2Se_4$. The dashed curve shows the photoresistance R.

mum in the vicinity of 40–60 °K followed by a rapid rise. Illumination with white light destroys practically completely this rapid rise of the resistance below 40 °K but has hardly any effect on the rest of the $R_d(T)$ curve.

The application of an external magnetic field $H=67$ kOe has hardly any effect on the photoresistance throughout the investigated temperature range. On the other hand, the dark resistance is affected considerably by this magnetic field although there is no suppression of the rise of $R_d(T)$ below 40 °K. Thus, at 2 °K the application of the field H = 67 kOe reduces R_d by more than two orders of magnitude which is considerably greater than the reduction in the vicinity of the Curie point. Similar effects of illumination and magnetic fields were observed by us also for the compositions $Cd_{0.9}In_{0.1}Cr_2Se_4$ and $Cd_{0.42}In_{0.58}Cr_2Se_4$.

Figure 5 shows also the temperature dependence of the spontaneous magnetization σ; we can see that the transition at T_C is broad and the Curie point (~85 °K) is less than T_C of the pure material (130 °K). The giant low-temperature negative magnetoresistance can clearly be explained as follows. Since the indium impurities are distributed at random, the case of n-type conduction between impurities approaches the process of conduction in a disordered medium because in both cases an electron moves in a nonperiodic force field. In this case the energy gap between the conduction and valence bands may change into a continuous density of states where the electron mobility is $\mu=0$ at $T=0$ °K (Ref. 12). The range of energies where the density of states is finite but the mobility is zero is known as the mobility gap. The width of this gap increases on increase in the degree of disorder in a crystal. The absence of saturation of the $\sigma(H)$ curves in fields up to 5–8 kOe observed in our study and the reduction in the exchange interaction compared with the undoped material suggest nonferromagnetic ordering near the in ions.

We can thus see that the disorder in our crystals has the electrostatic (fluctuations of the potential) and magnetic (fluctuations of the magnetic order) components. The application of an external magnetic field which increases the degree of ferromagnetic ordering near the In ions suppresses the magnetic disorder and, therefore, it reduces the mobility gap transferring current-free electron states to the conduction band. This is the reason for the giant magnetoresistance. Illumination of a sample with white light clearly allows us to excite electrons from the valence band and from the current-free states located in the band gap.

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