Electric and magnetic properties of $CdCr_2Se_4$ single crystals doped with indium

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We have investigated the temperature dependence of the electro- and magnetoresistance, and also of the magnetization and of the paramagnetic susceptibility of single crystals of $Cd_{1-x}In_xCr_2Se_4$ ($0.004 \leq x \leq 0.378$). We have observed that the maximum of the resistivity increases with increasing doping. Besides the giant negative magnetoresistance in the region of the Curie point, we have observed a positive magnetoresistance in the paramagnetic region. These phenomena are explained.

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We have investigated the temperature dependence of the electric resistance and the magnetoresistance, as well as the magnetization and the paramagnetic susceptibility of single crystals of $Cd_{1-x}In_xCr_2Se_4$ ($0.004 \leq x \leq 0.378$). Anomalies of the electric properties were observed in the region of the Curie temperature and above it.

The single crystals were grown by solution in the melt. The samples were regular octahedra with edge

Composition	Ratio of $\ln\rho$ at the maximum to $\ln\rho$ at 77°K	Activation energy in the paramagnetic region, eV
0.004	1	0.37
0.007	1.15	0.26
0.013	1.64	0.34
0.017	1.83	0.25

dimensions from 0.3 to 1 mm. Homogeneity was verified by x-rays with accuracy to 2.5%. The gallium content was determined by the atomic absorption method. The ohmic contacts were produced by fusing-in indium; their resistance was less than 10% of the sample resistance.

The sample magnetization was determined with a vibration magnetometer. The ferromagnetic Curie point Θ_f, was determined from the magnetization curves by the thermodynamic-coefficient method.[1] It turned out that Θ_f was independent of the composition and was located in the region 139–141 °K. In practice, Θ_f was the same as for the undoped single crystal (139.5 °K).

The paramagnetic susceptibility was determined by a torsion-balance method with electromagnetic compensation in the temperature region 293–700 °K.

The electric resistance was measured by volt-ammeter method with an electrostatic voltmeter, since the resistance R of the samples was of the order of $10^8\,\Omega$ in some cases. The current indicator was a picovoltmeter-nanoammeter of type TR-1452. The accuracy with which R was measured was better than 6%, and in the paramagnetic region, where the positive magnetoresistance (to be described below) was observed, the accuracy was better than 2.5%. Since the single-crystal dimension decreases rapidly with increasing indium additive, and the deposition of the contacts becomes more complicated, we were able to study the electric properties for compositions with $x \leq 0.017$.

We have also investigated the photoconductivity of the four compositions listed in the table, in a manner similar to that used earlier for gallium-doped $CdCr_2Se_4$ single crystals.[2] However, the photoconductivity in

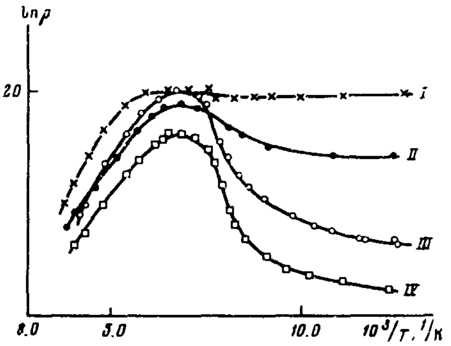

FIG. 1. Temperature dependence of the natural logarithm of the dark resistivity ρ of compositions with x equal to 0.004 (I), 0.007 (II), 0.013 (III), and 0.017 (IV).

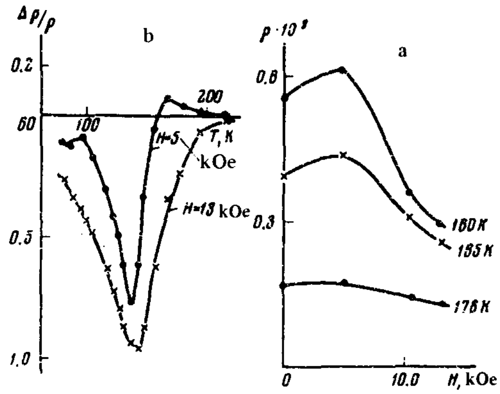

FIG. 2. Composition with $x = 0.013$: a—dependence of ρ on the magnetic field at the temperatures at which positive magnetoresistance is observed; b—temperature dependence of the magnetoresistance.

the case of indium doping turned out to be low; thus, for $x = 0.004$ at $T = 77$ °K the resistance decreased under the influence of the light by a factor of only 0.2.

Figure 1 shows the temperature dependence of the logarithm of the dark resistivity ρ of the investigated compositions. It is seen that the plot of $\ln\rho$ against $1/T$ has a maximum in the region of the Curie point. The value of this maximum, however, depends essentially on the degree of doping (see the table). It is seen from Fig. 1 and the table that for a composition with minimum indium additive ($x = 0.004$) this maximum is barely noticeable, whereas for the composition with the maximum additive ($x = 0.017$) the ratio of $\ln\rho$ at the maximum to $\ln\rho$ at 77 °K is of the order of ~1.83.

Figure 2 shows the magnetoresistance of the composition with $x = 0.013$ as a function of the temperature and of the magnetic field. In the region of the Curie point one can see the large negative magnetoresistance typical of n-type $CdCr_2Se_4$,[4] but above the Curie point, in the region 140–200 °K, the magnetoresistance is positive in a certain range of magnetic fields. The dependence of the positive magnetoresistance on the temperature has a maximum. For compositions with $x = 0.07$ and $x = 0.17$ we have observed no such positive magnetoresistance.

A calculation by Amith and Friedmann[4] for In-doped $CdCr_2Se_4$ has shown that at $x = 1$ an impurity band of indium can be formed, i.e., the semiconductor becomes degenerate. Nagaev and Grigin have shown[5] that in degenerate ferromagnetic semiconductors the fluctuations Δn of the carriers give rise to fluctuations ΔM of the magnetic moment, owing to the gain in the s-d exchange energy, and these fluctuations lead in turn to further growth of the fluctuations Δn. This effect is more pronounced the greater the disturbance to the long-range magnetic order, i.e., in the region of Θ_f. The resistance is due in this case to the carrier scattering by the fluctuations ΔM, and goes through a maximum in the region of Θ_f. The relative magnitude of the resistance peak depends on the degree of doping of the crystal: it first increases with increasing carrier density, and then begins to decrease.

It appears that in our case compositions with $x = 0.01$ are degenerate semiconductors. As seen from the table, the relative value of the resistance peak in the region of Θ_f increases with increasing x, in agreement with the theoretical deductions of[5].

The temperature dependence of the paramagnetic susceptibility of all the compositions obeys the Curie-Weiss law in the investigated temperature region from 293 to 700 °K. The paramagnetic Curie temperature Θ_p is practically independent of the composition and is equal to the value of Θ_p of the undoped $CdCr_2Se_4$. Our measurements of the paramagnetic susceptibility above room temperature allow us to conclude that the fluctuations ΔM vanish below 293 °K, for otherwise they would contribute to the paramagnetic susceptibility and would increase the paramagnetic Curie temperature, just as in the case of copper-doped $CdCr_2Se_4$ and $CdCr_2S_4$.[6,7]

In the region of Θ_f we have observed in all the investigated samples a giant negative magnetoresistance ($\Delta\rho/\rho \sim 1$). For the composition with $x = 0.004$, the magnetoresistance is somewhat smaller than ~ 0.2 in a field 6.65 kOe. In the paramagnetic region (160–200 °K), however, in a certain interval of magnetic fields, positive magnetoresistance of order 0.06 at the maximum is observed for the compositions with $x = 0.004$ and $x = 0.13$.

An external magnetic field in the region of Θ_f preserves the long-range magnetic order and by the same token decreases the fluctuations ΔM, meaning also the scattering by them. It is therefore that the negative magnetoresistance is observed in the region of Θ_f. However, as shown by Nagaev,[8] in the paramagnetic region, where the long-range order is already destroyed, the magnetic field can maintain the fluctuations ΔM and by the same token decrease the scattering by them, giving rise to a positive magnetoresistence, but we have apparently not observed this fact.

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