Singularities of electric, photoelectric, and magnetic properties of $CdCr_2Se_4$ single crystals with large amounts of In added

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We investigate the temperature dependence of the resistivity $\rho(T)$, photoconductivity, magnetoresistance, magnetization, and paramagnetic susceptibility of single crystals of $Cd_{1-x}In_xCr_2Se_4$ ($0.047 \leq x \leq 0.58$). Magnetic measurements reveal a decrease of the exchange interaction, a fact attributed to disturbance of the ferromagnetic order near the In^{3+} ions. It is shown that although the $\rho(T)$ curves are in fact similar in shape to the corresponding curves for the nondegenerate case, they are smoother and have a less clearly pronounced maximum in the region of the Curie point and a minimum in the region 40–60 K, a lower activation energy in the spin-wave and paramagnetic regions, and a lower value of ρ. For a narrow range of impurity concentrations with $x = 0.378$, a low-temperature metal-semiconductor transition is observed, and is explained on the basis of the ferron hypothesis. It is observed that in the spin-wave region the value of ρ is very strongly influenced by the magnetic field and by light. Thus, a field of 67 kOe decreases ρ by two orders of magnitude, whereas exposure of the sample surface to an illumination $\sim 10^3$ lux decreases ρ by three orders of magnitude. The action of the magnetic field is attributed to the decrease of the mobility gap: the zero-current states of the carriers on the tail of the density in the forbidden band are converted into current states because of the change of the magnetic order near the In^{3+} ions.

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The present paper deals with the temperature dependence of the resistivity ρ, of the photoconductivity, of the magnetoresistance, of the magnetization, and of the paramagnetic susceptibility of single crystals of $Cd_{1-x}In_xCr_2Se_4$ ($0.047 \leq x \leq 0.580$). The production of the samples, their analysis, and the attachment of the contracts to them are described in Ref. 1. The sample resistance was measured by a potentiometer method. The procedure of measuring ρ at low temperatures and in fields produced by a superconducting solenoid is described in Ref. 2. The magnetization was measured with a vibration magnetometer, and the paramagnetic susceptibility with an electromagnetically compensated torsion balance. The sample was illuminated with white light from a 3.5 W incandescent lamp placed in a well at a distance 10 cm from the sample. To study the spectral sensitivity of the photoconductivity, the sample was placed in a cryostat with optical windows and illuminated with an MDR-2 monochromator.

We have previously investigated the electric and the magnetic properties of $CdCr_2Se_4$ crystals with small additions of In and Ga ($x < 0.047$).[2-4] In contrast, in single crystals with large additions of In the indicated properties reveal a number of singularities. Figure 1 shows the temperature dependence of the resistivity of $Cd_{1-x}In_xCr_2Se_4$ samples with compositions $x = 0.047$, 0.051, 0.1, 0.378, 0.513, 0.580. The same figure (see the inset) shows a plot for a composition with a small addition $x = 0.012$. A comparison of curves 1–6 with curve 7 reveals the following: Although the shapes of the $\rho(T)$ curves are similar, the corresponding values of ρ differ greatly in order of magnitude. Thus, ρ of the highest-resistivity sample with $x = 0.047$ is smaller by approximately three orders of magnitude than for the composition with $x = 0.012$. Furthermore, the $\rho(T)$ curves for samples with large additions of In are smoother than the curve for $x = 0.012$, with the maximum and minimum less pronounced. This manifests itself in a drastic decrease of activation energy in the spin-wave and paramagnetic temperature regions, as is well seen from the comparison of the table, which lists these activation energies for all the investigated compositions, with the analogous table of Ref. 2. Thus, as seen from Fig. 1 and from the table, with increasing In content the $\rho(T)$ curves become smoother: the difference between the resistivities at the maximum and the minimum decreases, the activation energy in the spin wave and paramagnetic regions decreases, the maximum in the region of T_c almost disappears gradually, and the resistance at the minimum first decreases to $\sim 10^2$ cm for $x = 0.378$ and then begins to increase for the composition with $x = 0.513$. It appears that one can

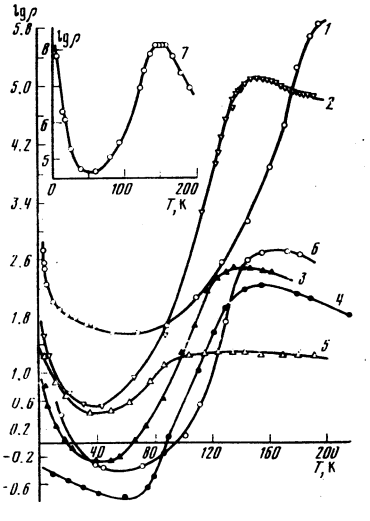

FIG. 1. Temperature dependence of log ρ for the system of single crystals $Cd_{1-x}In_xCr_2Se_4$: curve 1—$x = 0.047$, 2—0.51, 3—0.513, 4—0.378, 5—0.58, 6—0.1; curve 7—$x = 0.012$.

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TABLE I. Activation energy of $Gd_{1-x}In_xCr_2Se_4$ samples.

x	Spin-wave region	Paramagnetic region
0.051	$6.83\cdot10^{-4}$	$2.0\cdot10^{-1}$
0.100	$14.0\cdot10^{-4}$	$0.40\cdot10^{-1}$
0.378	$2.66\cdot10^{-5}$	$0.65\cdot10^{-1}$
0.513	$4.69\cdot10^{-4}$	$0.46\cdot10^{-1}$
0.580	$3.69\cdot10^{-4}$	$0.085\cdot10^{-1}$

speak of a low-temperature metal-semiconductor transition in a sample with $x=0.378$. As seen from Fig. 1, this transition takes place only in a narrow interval of impurity concentrations, in agreement with the theoretical papers of Nagaev.[5]

In crystals with large amounts of In, the behavior of $\rho(T)$ in the spin-wave region turns out to be unusual. The value of ρ is greatly influenced here by the magnetic field. Figure 2 shows by way of example a plot of $\rho(T)$ for a sample with $x=0.513$ in a magnetic field 67 kOe in the absence of a field. It is seen that the action of the magnetic field is very large here: thus, at 2 K application of a magnetic field $H=67$ kOe decreases ρ by more than two orders of magnitude. This is much more than the result of the action of the field on ρ in the region of T_c, and is in general a record figure for $CdCr_2Se_4$ samples doped with In and Ga.

The action of light is even stronger: turning on an incandescent lamp that produces on the sample surface an illumination 5.5×10^3 lux decreases ρ by almost three orders of magnitude (Fig. 2). A study of the spectral dependence of the photoconductivity at 19 K has shown that this gigantic photoconductivity is due mainly to the red light with an energy 1.8 eV that coincides apparently with the width of the forbidden band. At the same time, the light has practically no effect on ρ in other temperature regions. A similar action of light and of the field was observed by us also for compositions with $x=0.1$ and 0.58.

Figure 2 shows, for the sample with $x=0.513$, the dependence of the magnetization σ on the temperature, while Fig. 3 shows $\sigma(H)$ curves for different temperatures. It is seen from Fig. 3 that the saturation of the magnetization in the spin-wave region, where light and

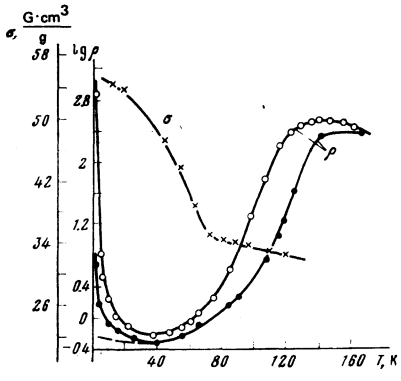

FIG. 2. Temperature dependence of log ρ and of the magnetization σ for the composition $Cd_{0.487}In_{0.513}Cr_2Se_4$. Curves of log $\rho(T)$: ○—at $H=0$, ●—at $H=67$ kOe; dashed curve—for an illuminated sample.

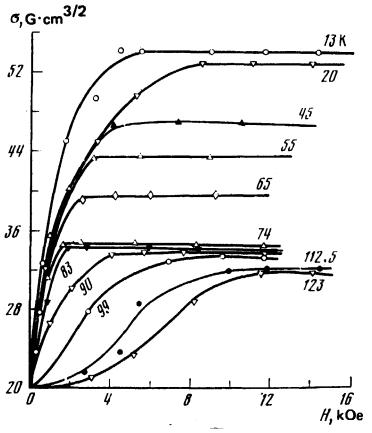

FIG. 3. Magnetization curves as functions of the field of the sample $Cd_{0.487}In_{0.513}Cr_2Se_4$ at various temperatures.

the field exert a strong effect on ρ, is reached only in fields 5–8 kOe. Yet it is known that the compound $CdCr_2Se_4$ is a magnetically soft material with anisotropy energy $\sim10^3$ erg/cm³. It is quite possible that introduction of the In ions in the lattice changes the magnetic order in their vicinity, thereby producing a magnetic inhomogeneity. Further in this assumption is the following. It is known[6,7] that normal spinels $A^+_{0.5}A^{3+}_{0.5}Cr_2X_4$

(A^+=Li, Cu, Ag; A^{3+}=In, Ga; X=S, Se)

are antiferromagnets, with the exception of $Ag_{0.5}In_{0.5}Cr_2Se_4$, whereas measurements show that there is no long-range magnetic order in $Ga_{2/3}Cr_2S_4$. As seen from Fig. 2, the shape of the magnetization curve of the sample with $x=0.513$ differs from the Brillouin shape and comes close to a linear $\sigma(T)$ dependence in the regions 30–60 K. The Curie point determined by extrapolation of this line to the temperature axis lies in the region of 85 K, which is much lower than $T_c=130$ –140 K for $CdCr_2Se_4$. The decrease of the exchange interaction with increasing In content is confirmed also by the lowering of the magnetic Curie point Θ with increasing x in the $Cd_{1-x}In_xCr_2Se_4$ system:

x	0.007	0.013	0.0135	0.020	0.047	0.214	0.378	0.513	0.58
Θ:	270	245	236	225	220	188	284	210	200

It can therefore be assumed that the superexchange interaction is lowered near the In^{3+} ion.

It appears that the gigantic negative magnetoresistance in the low-temperature region can be explained in the following manner. Since the indium impurity has a disordered distribution, the situation with the electronic conduction over the impurities approaches here that of conduction in a disordered medium, inasmuch as in either case the electron moves in a nonperiodic force field. In this case, instead of an energy gap between the conduction and valence bands, we may have a continuous density of localized states, where the electron mobility is $\mu=0$ at $T=0$.[8] The energy interval in which the state density is finite and the mobility is equal to zero is customarily called the mobility gap. Its width is larger the higher the degree of disorder of the crystal. The absence of saturation on the $\sigma(H)$ curves in fields up to 5–8 kOe and the decrease of the exchange interaction compared with the undoped material suggest

that nonferromagnetic order exists near the In ions.

Thus, the disorder of the crystal consists of an electrostatic component (i.e., of potential fluctuations) and a magnetic component (i.e., of fluctuations of the magnetic order). Application of an external magnetic field, which increases the ferromagnetic order near the In ions, eliminates the magnetic disorder and therefore decreases the mobility gap, and transfers the zero-current electron states to the conduction band.

As indicated above, for the composition with $x=0.378$ we have observed a metal-semiconductor transition. It differs from the other known transitions of this type in that in this case the low-temperature phase is conducting and the high-temperature phase is insulating. Up to now, EuO with an oxygen deficit was the only ferromagnetic semiconductor in which a metal–insulator temperature transition was found.[9] This raises the natural question whether this effect is due to specific properties of the compound in question, and in particular to the doubly charged donors (oxygen vacancies) contained in it. In our present study we observed such a transition in the ferromagnetic semiconductor $Cd_{1-x}In_xCr_2Se_4$ with $x=0.378$, where In^{3+} is a single charged donor, and have shown by the same token that a metal–semiconductor transition is possible also in ferromagnetic semiconductors with singly charged donors. Here, however, the transition is more smeared out than in EuO, possibly because of the greater deviation of the crystal structure from periodic.

The metal-semiconductor transition observed in the present study can apparently be interpreted as follows. Owing to the random distribution of the In in the crystal, fluctuations occur in both the electrostatic potential and in the superexchange between the magnetic atoms. The electrostatic fluctuations lead to fluctuations of the electron density even at $T=0$. The degree of the magnetic order at finite temperatures is determined by the sum of the indirect exchange via the conduction electrons, an exchange determined by the local electron density, and the superexchange. The order is maximal in those regions where the total exchange is maximal. With increasing temperature, the difference between the average magnetization of the crystal and the local magnetization in the regions with maximum exchange increases. The s–d exchange attraction of the conduction electrons in the regions with maximal exchange therefore becomes stronger, and the growth of the electron density in them, in turn, increases the summary exchange. Starting with a certain temperature, the electrons turn out to be gathered in individual ferromagnetic regions separated by intermediate regions with decreased magnetic order. Thus, the crystal changes from the conducting to the insulating state. The ferromagnetic microregions (ferrons) produced in this manner above T_c are generally speaking not bound to the In donor ions, but are located in those parts of the crystal where the free energy goes through minima because of fluctuations of the electrostatic potential and of the exchange integral.

Attention is called to the gigantic magnetization "tail," which amounts to more than half of σ at 4.2 K and extends above T_c (Fig. 2). In the region of the tail the magnetization curves have bends (Fig. 3) that are very similar to those observed by us for doped $CdCr_2Se_4$ crystals or those with a deficit of Se,[10] which we have ascribed to the field-produced impurity ferrons. It appears that in the case of strong doping, as is the case in the present study, localized ferron states are produced in those places where the fluctuations of the exchange strengthen the ferromagnetic coupling compared with its mean value.[5]

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