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Translated by A. Tybulewicz

Electrical properties of copper-doped $CdCr_2Se_4$

K. P. Belov, L. I. Koroleva, and M. A. Shalimova

M. V. Lomonosov Moscow State University
(Submitted 2 January 1978)
Zh. Eksp. Teor. Fiz. **74**, 2244–2249 (June 1978)

The temperature dependence of the Hall emf and the electrical resistance of single crystals of $Cd_{1-x}Cu_xCr_2Se_4$ ($x = 0.04$; 0.07; 0.14) is studied. It is found tht the Normal Hall coefficient is maximal in the vicinity of 150 K, while the anomalous coefficient is maximal in the vicinity of 130 K (the Curie point of this compound). The carrier concentration passes through a minimum in the vicinity of 150 K, whereas the mobility is maximal in this temperature region. The mobility decreases, while the carrier-number concentration increases, with increase of the copper admixture in $CdCr_2Se_4$. The character of the dependence of the electrical resistivity ρ on temperature T varies from the semiconductor type for $x = 0.04$ to the semimetallic type for $x = 0.14$, the ρ(T) curve for the compound with $x = 0.07$ being nonmonotonic with a maximum in the vicinity of the Curie point.

PACS numbers: 72.20.My, 72.20.Jv, 72.80.Jc, 72.60.+g

In the present paper we study the temperature dependence of the Hall emf and the resistivity, ρ, of single crystals of $Cd_{1-x}Cu_xCr_2Se_4$ ($x = 0.04$; 0.07; 0.14). Measurements with direct current were performed by a null method on rectangular plates cut from the crystals; the Hall-effect and ρ measurements were carried out simultaneously on one and the same sample. The preparation of the samples and the ohmic contacts with them, as well as the magnetic properties of these compounds are described in our earlier paper.[1] According to our measurements, the transverse magnetoresistance in this material is small (not more than 2%). It was positive in the paramagnetic region and negative in the ferromagnetic region.

The magnetization curves of the $Cd_{1-x}Cu_xCr_2Se_4$ system have a complex character because of the complexity of the properties of the magnetic impurity state. This is manifested especially clearly in the region of temperatures above the Curie point (130 K). In this temperature interval the magnetization in high fields cannot be represented as consisting of two simple contributions: spontaneous magnetization and the magnetization of the para-process, since the effects connected with the presence of magnetic impurity states (ferrons) are stronger than the effects of the para-process by not less than an order of magnitude.[2] Therefore, for the computation of the normal Hall coefficient R_0 and the anomalous Hall coefficient R_1 we used the standard formula for the Hall emf, U_x, in ferromagnets without allowance for the para-process:

$$U_x = (R_0 H + R_1 M) I/d, \qquad (1)$$

where M is the magnetization at the given temperature T and field intensity H, I is the current flowing through the sample, and d is the sample dimension in the direction of the magnetic field.

It should be emphasized that, because of the complexity of the processes occurring in the vicinity of the Curie point, the formula (1) is only a crude approximation and the constants R_0 and R_1 are some effective parameters. The normal Hall coefficient was determined from the slope of the $U_x(H)$ curve for fields higher than the saturation field, when the second term in Eq. (1) is a constant. The anomalous component of the Hall emf was determined by extrapolating the $U_x(H)$ curve to the ordinate axis from the high-field region. The saturation magnetization (M_s) data necessary for the computation of R_1 were taken from Ref. 1.

In Figs. 1 and 2 we show the temperature dependence of the quantities R_0, R_1, for ρ for all the compositions studied. As can be seen from Figs. 1 and 2, the anom-

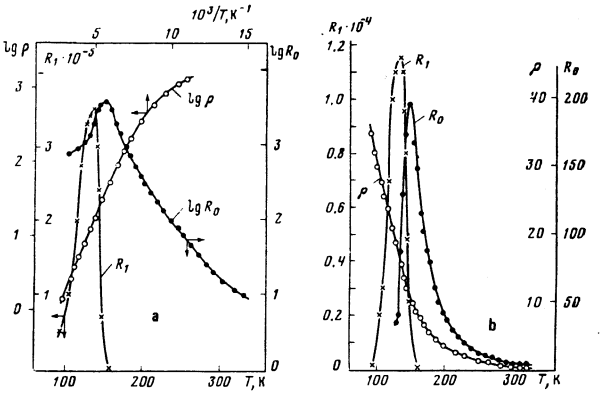

FIG. 1. Dependence of the anomalous Hall coefficient, R_1, the normal Hall coefficient, R_0, and the resistivity, ρ, on temperature for the compounds: a) $Cd_{0.96}Cu_{0.04}Cr_2Se_4$; b) $Cd_{0.93}Cu_{0.07}Cr_2Se_4$; R_1 and R_0 are given in cm^3/C; ρ, in Ω-cm.

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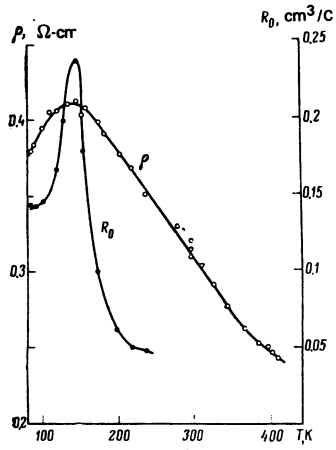

FIG. 2. Dependence of the normal Hall coefficient, R_0, and the resistivity, ρ, on temperature for the compound $Cd_{0.86}Cu_{0.14}Cr_2Se_4$.

alous Hall coefficient, R_1, decreases with increasing x, while for $x=0.14$ it is, on the whole, zero within the limits of accuracy of our measurements (the sensitivity of our apparatus was 10^{-4} mV/mm). The $R_1(T)$ curves have a maximum at 130 K, the Curie point, whereas the maximum on the $R_0(T)$ curves is observed at a temperature of 150 K, where the anomalous Hall effect is virtually equal to zero. From the sign of the thermo-emf at 300 K we determined which p-types of carriers there were in all the investigated samples.

Assuming one type of carrier, we computed the Hall mobility $\mu = R_0/\rho$ and the hole concentration $p = 1/R_0 e$ (e is the electron charge). As an example, in Fig. 3 we show the temperature dependence of μ and p for the compound with $x=0.07$. For the two other investigated compositions the $\mu(T)$ and $p(T)$ curves have a similar shape, but μ decreases, while p increases, with increasing x (see Table I). As can be seen from Fig. 3, the hole concentration has a minimum, while the mobility has a maximum, at 150 K.

The data obtained by us on the temperature dependence of R_0, R_1, μ, and p agree with the data obtained by

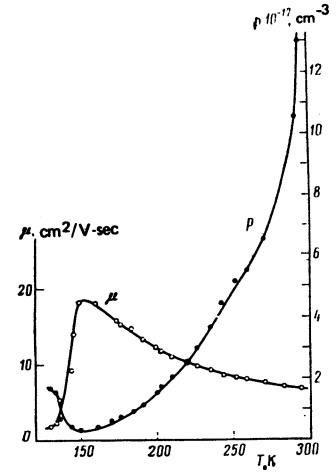

FIG. 3. Dependence of the concentration, p, of the holes and of their Hall mobility, μ, on temperature for the compound $Cd_{0.93}Cu_{0.07}Cr_2Se_4$.

TABLE I.

Parameter	x			Note
	0.04	0.07	0.14	
R_1, cm³/C	$3.5\cdot10^5$	$1.15\cdot10^4$	0	At $T=130$ K
R_0, cm³/C	$4\cdot10^3$	$2\cdot10^3$	0.24	At $T=150$ K
μ, cm²/V-sec	42	18.5	0.58	»
p, cm⁻³	$1.5\cdot10^{15}$	$3.1\cdot10^{16}$	$2.6\cdot10^{19}$	»

Lehmann[3] on polycrystalline samples of $CdCr_2Se_4$ doped with silver. It is shown in Ref. 3 that the coefficients R_1 and R_0 decrease as the Ag-impurity concentration is increased and that the curve $R_0(T)$ has a maximum at 150 K. It follows from the data of this work on $R_0(T)$ and $\rho(T)$ that $p(T)$ has a minimum and $\mu(T)$ a maximum at a temperature of 150 K.

In Figs. 1 and 2 we show the temperature dependence of the resistivity, ρ, of each of the investigated compositions. For $x=0.04$ the conductivity is of the semiconductor type, the straight line $\lg\rho = f(1/T)$ exhibiting a kink in the vicinity of the Curie point. For the two other compositions $\rho(T)$ has a nonmonotonic character. We investigated the temperature dependence of ρ for several samples of each composition. It turned out that the character of the $\rho(T)$ curve is very sensitive to the magnitude of ρ even within the limits of one composition.

Figure 4 shows the $\rho(T)$ curves obtained by us for all the investigated samples with $x=0.07$ and 0.14. It can be seen from the figure that for samples with higher ρ the $\rho(T)$ curves have in the vicinity of T_c a maximum whose height depends nonmonotonically on ρ, attaining its largest value for a sample with $\rho_{300} \approx 0.6$ Ω-cm. The position of the maximum shifts towards the region of higher temperatures as the sample resistivity, ρ, decreases. For samples with $\rho_{300} < 0.6$ Ω-cm the peak height decreases, and for the sample with $\rho = 0.06$, instead of a peak, we observe only an inflection on the $\rho(T)$ curve; for this sample the conductivity is of the metallic type. It is interesting that after the sample with $x=0.14$ has been heated to 430 K the metallic-type conductivity is replaced by a nonmonotonic dependence with a maximum in the vicinity of 150 K with a simultaneous increase in the resistivity from 0.21 Ω-cm to 0.31 Ω-cm at 300 K.

The ρ measurements carried out by us in the various crystallographic directions of a sample indicated the

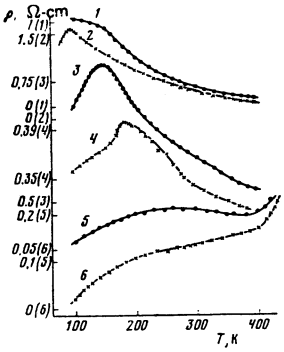

FIG. 4. Dependence of the resistivity on temperature for the compounds $Cd_{1-x}Cu_xCr_2Se_4$ with x equal to 0.07 (the curves 1–4) and 0.14 (the curves 5 and 6).

virtual absence of crystallographic anisotropy in ρ for all the compositions.

As is well known, the anomalous Hall effect is due to the spin-orbit interaction of the carriers during their scattering on (thermal, magnetic) fluctuations. The Hamiltonian of the spin-orbit interaction can be schematically represented in the form

$$H^{so}=H_1^{so}+H_2^{so}, \qquad (2)$$

where H_1^{so} takes account of the interaction of the orbit of the carrier with the intrinsic spin and H_2^{so} is the Hamiltonian of the interaction of the orbit of the carrier with the spins of the magnetic atoms. The first term in the Hamiltonian (2) takes account of the contribution of the thermal fluctuations of the lattice; the second term, the contribution of the fluctuations of the magnetization of the long-range magnetic order. The temperature 130 K is the Curie point, T_c, for the system $Cd_{1-x}Cu_xCr_2Se_4$. The maximum at 130 K is evidently due to the fluctuations in the magnetization of the long-range order, which have a maximum at the magnetic-phase-transition point. It is known that $R_1 \sim \rho$, and since ρ decreases with increasing x, it is in order for R_1 to decrease with increasing x. At the same time the existence of a strong anomalous Hall effect in the samples with $x=0.04$ and $x=0.07$ remains incomprehensible, since, according to Nagaev and Sokolova's theoretical investigation,[4] this effect should be comparatively weak in magnetic semiconductors.

In Ref. 1 a band-structure model is proposed for the $Cd_{1-x}Cu_xCr_2Se_4$ compound. For small x there exists an acceptor copper level, and ferrons—regions with an enhanced degree of ferromagnetic order, that have been theoretically predicted for magnetic semiconductors[5-7]—are produced near the non-ionized copper ions because of the s-d exchange with the surrounding Cr^{3+} ions. At higher impurity concentrations the level smears out into a band. Then as has been shown by Nagaev, there can arise near the impurity atoms regions of enhanced electron density, which produce around themselves, as a result of the s-d exchange, regions of enhanced ferromagnetic order, which, in their turn, sustain the electron-density fluctuations.[8,9] These are the so-called collective ferron states. The $\rho(T)$ peak that occurs at a temperature slightly higher than the Curie point is explained by the capture of the current carriers both by the ionized impurities (the formation of ferron states) and by the non-ionized impurities (i.e., by the ferrons),[10] since ferron production is most probable precisely in this temperature region. Another cause of the ρ peak near T_c is the transition of the current carriers into the nonconduction states at the density tail extending into the forbidden band. The above-indicated causes of the $\rho(T)$ maximum give rise to a minimum in the current-carrier concentration in the vicinity of T_c. The ρ peak in the vicinity of the Curie point can also be caused by the scattering of the current carriers on the magnetic moments of the ferrons[8]; in this case a mobility minimum should be observed in this temperature region. At a still higher doping level the impurity band overlaps the upper part of the valence band, and the collective ferron states disappear.

For all the three investigated compounds R_0 has a maximum at 150 K. At this temperature the anomalous Hall effect disappears, i.e., the fluctuations in the long-range magnetic order vanish. In Ref. 2 we give indirect evidence to show that in the vicinity of 150 K the generation of fluctuations in the short-range magnetic order, induced by the s-d exchange, is the most probable in $Cd_{1-x}Cu_xCr_2Se_4$. This is also attested by the fact that the ρ peak manifests itself best at precisely this temperature (Fig. 4). The minimum that occurs in p in the vicinity of 150 K is, apparently, responsible for the ρ peak in those samples in which it is observed. The $p(T)$ minimum observed by us may be due to some or all of the above-indicated causes, namely, the capture of the carriers by ionized and non-ionized acceptors and the transition into the nonconduction states at the density tail extending into the forbidden band.

At the same time the cause of the mobility peak at 150 K is not clear. It is clear that this mobility peak reduces appreciably the height of the $\rho(T)$ peak in the vicinity of T_c, and for the compound with $x=0.04$ such a ρ peak is not even observed, in spite of the $p(T)$ minimum. If we take into consideration the proposed band-structure model for $Cd_{1-x}Cu_xCr_2Se_4$, then the decrease of the mobility with increasing x becomes comprehensible. For small x the conduction is effected by thermally-excited holes at the top of the broad valence band, their mobility being relatively high. For higher x the conduction has a complex character; it is, apparently, effected mainly by holes on the impurity band with a lower mobility, although the conduction by the thermally-excited holes at the top of the valence band remains.

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Translated by A. K. Agyei