

Semiconducting Properties of Ferromagnetic  $\text{CdCr}_2\text{Se}_4$ 

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(Received 5 June 1967)

Measurements of the electrical conductivity, the Seebeck effect, and the Hall effect were performed on hot-pressed  $\text{CdCr}_2\text{Se}_4$  between 77 and 300°K. The conductivity of  $n$ -type  $\text{CdCr}_2\text{Se}_4$  (In-doped) shows a sharp minimum at 150°K. The increase of the conductivity at lower temperatures is due to an increasing mobility and an increasing carrier concentration. This increasing carrier concentration is explained in terms of a strong red shift of the absorption edge due to magnetic ordering. The conductivity of  $p$ -type  $\text{CdCr}_2\text{Se}_4$  (Ag-doped) shows a change of the slope of  $\log\sigma$ -versus- $1/T$  curve and a maximum of the normal Hall coefficient at 150°K. This fact is interpreted as being due to the onset of impurity conduction.

## I. INTRODUCTION

**F**ERROMAGNETISM has been found recently in several ternary chromium compounds crystallizing in the spinel structure.<sup>1,2</sup> These new compounds are unique in that they are both semiconducting and ferromagnetic with relatively high Curie temperatures. Most other known ferromagnets are either metallic like Fe, Ni, MnBi, or  $\text{CrO}_2$ , or insulating with relatively low Curie temperatures like EuO or the chromium trihalides. Ferrimagnetic ferrites show semiconductor behavior, but for those for which the electrical properties have been studied so far the mobility is very small ( $\mu \leq 5 \text{ cm}^2/\text{V sec}$ ). Table I shows a summary of recent measurements of electrical properties of  $3d$ -transition metal compounds. It is seen that with the exception of MnSb, which shows an unusually high Hall mobility for a transition-metal compound, the Hall mobilities in oxides are usually smaller than  $1 \text{ cm}^2/\text{V sec}$ , whereas in sulfides, selenides, and tellurides, mobilities of the order of 1 to  $10 \text{ cm}^2/\text{V sec}$  are found. As an exception to this general rule, it must be pointed out that  $\text{SrTiO}_3$  has a Hall mobility of  $3000 \text{ cm}^2/\text{V sec}$  at 4°K.<sup>3</sup> The Hall mobility in  $3d$ -transition metal compounds seems to be determined by the narrow  $3d$  bands and is not very much different in different structures. Table I indicates that the Hall mobility is increasing with increasing covalency. The occurrence of ferromagnetism in chromium chalcogenide spinels offers, therefore, a unique opportunity to study the interaction of magnetic and electrical properties in a ferromagnetic semiconductor. A relatively high mobility should be expected in these compounds because of their covalent character. It is the purpose of this paper to report on the electrical properties of  $\text{CdCr}_2\text{Se}_4$  as a typical example of this new class of compounds. The electrical conductivity of undoped  $\text{CdCr}_2\text{Se}_4$  was described in an earlier report.<sup>4</sup>

## II. EXPERIMENTAL

$\text{CdCr}_2\text{Se}_4$  crystallizes in the spinel structure with a lattice constant of  $10.755 \text{ \AA}$ .<sup>2</sup> It becomes ferromagnetic below 130°K, and the saturation magnetization at 4.2°K is  $5.7\mu_B$ , which is close to the theoretically predicted value of  $6\mu_B$ . The preparation of the compound is described elsewhere.<sup>2</sup>  $\text{CdCr}_2\text{Se}_4$  can be readily "doped" with Ag and In by substitution for Cd. As will be discussed later, the Ag-doped material shows  $p$ -type conductivity while the In-doped materials show  $n$ -type conductivity. In this paper only measurements on materials with up to 1.5% substitution will be discussed. A detailed account of the range of substitutions possible and an x-ray study will be published later. All percentage values of substitution given in this paper refer to the amount of Cd substituted by Ag or In, respectively.

All measurements reported in this paper were made on hot-pressed polycrystalline samples. The single-phase powders were pressure sintered at 800°C and  $1.4 \times 10^8$  atm. in vacuum for 1 h. With this method it was possible to achieve densities of 99.9% of the x-ray density. X-ray diffractometry of the surface of the hot-pressed pellets (1.2 cm diam) did not reveal a second phase. Microscopic evaluation of polished and etched surfaces did not reveal any second phases either. The main impurities detected by emission spectroscopy were Al, Fe, Cu, and Si. The transition-metal impurities originate from the Cr metal used for the preparation of the compound. The total impurity level was approximately 500 ppm. At the temperature of hot-pressing (800°C) the vapor pressure of Se over  $\text{CdCr}_2\text{Se}_4$  is considerable, and a certain loss of Se cannot be avoided while pressing the samples in vacuum. Therefore, the hot-pressed  $p$ -type samples are usually highly compensated owing to Se vacancies. If these samples are annealed in a Se atmosphere for 24 h at 450°C, these vacancies can be removed.

The homogeneity of the hot-pressed pellets was evaluated. After grinding off the outer surface, samples were cut in different locations and along different orientations. The conductivity was found to vary less than a factor of 2 over the whole pellet. Bar-shaped samples ( $6 \times 1.3 \times 0.5 \text{ mm}$ ) with 4 small sidearms were prepared ultrasonically from wafers cut from the hot-

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<sup>1</sup> P. K. Baltzer, H. W. Lehmann, and M. Robbins, *Phys. Rev. Letters* **15**, 493 (1965); N. Menyuk, K. Dwight, R. J. Arnott, and A. Wold, *J. Appl. Phys.* **37**, 1387 (1966).<sup>2</sup> P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, *Phys. Rev.* **151**, 367 (1966).<sup>3</sup> H. P. R. Frederickse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* **134**, A442 (1964).<sup>4</sup> H. W. Lehmann and M. Robbins, *J. Appl. Phys.* **37**, 1389 (1966).

TABLE I. Electrical conductivity and Hall mobility of 3d-transition metal compounds at 298°K.

Sample	Structure	Form <sup>a</sup>	Conductivity type	Conductivity $\sigma$ [ $\Omega\text{cm}$ ] <sup>-1</sup>	Hall mobility $\mu$ [ $\text{cm}^2/\text{V sec}$ ]	Magnetic ordering <sup>b</sup>	Reference
NiO: 0.2% Li	NaCl	sc	<i>p</i>	$3 \times 10^{-3}$	0.27	antiferro	c
NiO: 0.01% Li	NaCl	pc	<i>p</i>	$6.7 \times 10^{-4}$	0.3	antiferro	d
FeS	NiAs	sc	<i>p</i>	$2.2 \times 10^3$	0.16	antiferro	e
FeTe	NiAs	sc	<i>p</i>	$1.5 \times 10^3$	3.2	para	e
NiTe	NiAs	sc	<i>n</i>	$1.4 \times 10^4$	0.49	antiferro	e
MnTe	NiAs	sc	<i>p</i>	$10^{-2}$	5	antiferro	f
MnSb	NiAs	sc	<i>p</i>	$1.7 \times 10^4$	200	ferro	g
TiO	NaCl	pc	<i>n</i>	$3 \times 10^3$	1	Pauli para	h
TiO <sub>2</sub>	rutile	sc	<i>n</i>	$2 \times 10^{-6}$	1	para	i
SrTiO <sub>3</sub>	perovskite	sc	<i>n</i>	2.8	6	para	j
Fe <sub>3</sub> O <sub>4</sub>	spinel	sc	<i>n</i>	250	0.45	ferri	k
FeCr <sub>2</sub> S <sub>4</sub>	spinel	sc	<i>p</i>	1	10	ferri	l
CuCr <sub>2</sub> Se <sub>4</sub>	spinel	sc	<i>p</i>	$3 \times 10^3$	25	ferro	m

<sup>a</sup> sc: single crystal, pc: polycrystalline.

<sup>b</sup> Data from J. B. Goodenough, *Magnetism and the Chemical Bond* (John Wiley & Sons, New York, 1963), p. 98 ff.

<sup>c</sup> M. Roilos and P. Nagels, *Solid State Commun.* **2**, 285 (1964).

<sup>d</sup> A. J. Bosman, H. J. van Daal, and G. F. Knuvers, *Phys. Letters* **19**, 372 (1965).

<sup>e</sup> S. Fujime, M. Munakami and E. Hirahara, *J. Phys. Soc. Japan* **16**, 183 (1963).

<sup>f</sup> J. D. Wasscher, A. M. J. H. Seuter, and C. Haas, in *Proceedings of the 7th International Conference on the Physics of Semiconductors, Paris, 1964*, edited by M. Hulín (Academic Press Inc., 1964), Vol. 1, p. 1269.

<sup>g</sup> M. Nogami, M. Sekinobu, and H. Doi, *Japan. J. Appl. Phys.* **3**, 572 (1964).

<sup>h</sup> A. A. Samokhalov and A. G. Rustamov, *Fiz. Tverd. Tela* **5**, 1202 (1963) [English transl.: *Sov. Phys. Sol. State* **5**, 877 (1963)].

<sup>i</sup> J. H. Becker and W. R. Hosler, *Phys. Rev.* **137**, A1872 (1965).

<sup>j</sup> H. P. R. Frederickse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* **134**, A442 (1964).

<sup>k</sup> J. M. Lavine, *Phys. Rev.* **114**, 482 (1959).

<sup>l</sup> G. Haacke and L. C. Beegle, *Phys. Rev. Letters* **17**, 427 (1966).

<sup>m</sup> F. K. Lotgering, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1965), p. 533.

pressed pellets. These were mounted on ceramic sample holders provided with six narrow contact strips. Contact between the sample and these contact strips was obtained by ultrasonically applying In. These contacts proved to be Ohmic and of very good mechanical quality at low temperatures. However, before applying these contacts, the samples have to be etched in a 1:1 mixture of HCl and ethanol to dissolve any oxide layer.

The electrical conductivity and the Hall effect were measured by a standard dc 4-probe method. A constant current supply was used for measurement on high-conductivity samples, whereas batteries had to be used for samples with conductivities lower than  $10^{-3}$  ( $\Omega\text{ cm}$ )<sup>-1</sup>. The voltages across the sample were measured with either a Keithley 150A microvoltmeter or a Keithley 610 Electrometer depending on the impedance of the sample. Two different techniques were used to determine the Hall coefficient. In the region where the Hall voltage is a linear function of magnetic field, the Hall coefficient was determined by measuring the Hall voltage at one or two different values of magnetic field. However, in the temperature range where the Hall voltage is not a linear function of the magnetic field, it was plotted directly as a function of magnetic field on an X-Y recorder in order to get a sufficient number of points to calculate the normal and anomalous Hall coefficient. Conventional current and field-reversal procedures were used in both cases with magnetic field strengths of up to 10 kOe in order to subtract contributions due to the rather large magnetoresistance in this material.

Magnetization measurements using a vibrating sample magnetometer were performed on the same samples used for transport measurements in order to account for demagnetizing fields due to the particular shape of the sample. The small substitution level (1% Ag or In for Cd) did not measurably alter the magnetic properties of CdCr<sub>2</sub>Se<sub>4</sub>.

Seebeck measurements were performed by applying a constant thermal gradient between 2 copper blocks across a bar-shaped sample (10×4×3 mm) cut from the hot-pressed pellet. The temperature of the blocks were measured with a copper-constantan thermocouple. The thermoelectric voltage was measured between the two copper leads of the thermocouples.

Most of our measurements were done between liquid-nitrogen and room temperature. Hall measurements on materials with rather small Hall coefficients and large activation energies of the conductivity require good temperature control. A simple but effective temperature controller was built for this temperature range. Its operation will be described elsewhere.<sup>5</sup> The temperature can be kept constant to better than  $\pm 0.05^\circ\text{C}$  over the period of a measurement, which is about 10 min.

### III. RESULTS

#### A. Electrical Conductivity

The electrical properties of a number of "pure" and substituted samples have been studied. "Pure" CdCr<sub>2</sub>Se<sub>4</sub>

<sup>5</sup> H. W. Lehmann, *J. Sci. Instr.* (to be published).

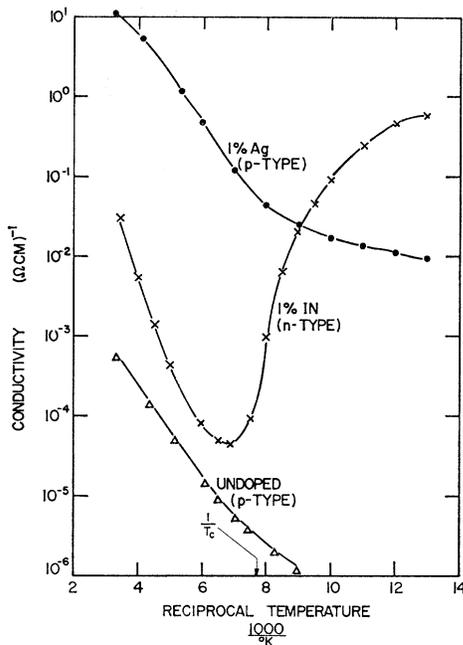


FIG. 1. Electrical conductivity  $\sigma$  of 3 different samples of  $\text{CdCr}_2\text{Se}_4$  as a function of reciprocal temperature.

prepared in the usual way is always  $p$ -type with an average carrier density of  $10^{16} \text{ (cm)}^{-3}$  at room temperature. Substitution of Ag or Au for part of the Cd increases the  $p$ -type conductivity, whereas substitution of In changes the conductivity to  $n$ -type. Therefore,  $\text{CdCr}_2\text{Se}_4$  is in general similar to II-VI compounds and, in particular, to CdTe which can also be made  $n$  or  $p$  type by doping with In or Ag, respectively.<sup>6</sup> It has been established that the amount of Ag substituted for Cd is roughly proportional to the carrier density at room temperature within the investigated range. The carrier densities of the 0.1, 0.5, 1, and 1.5% Ag-substituted samples at room temperature are  $3.6 \times 10^{17}$ ,  $1.9 \times 10^{18}$ ,  $3.6 \times 10^{18}$ , and  $4.6 \times 10^{18} \text{ cm}^{-3}$ , respectively. However, it has to be pointed out that this proportionality is only observed after the samples have been properly annealed as described earlier.

In the following we will report about the sample  $\text{CdCr}_2\text{Se}_4:1\% \text{ Ag}$  and  $\text{CdCr}_2\text{Se}_4:1\% \text{ In}$ , respectively, as typical examples of  $p$ - and  $n$ -type  $\text{CdCr}_2\text{Se}_4$ . Figure 1 shows the electrical conductivity of 3 different samples of  $\text{CdCr}_2\text{Se}_4$  as functions of reciprocal temperature between 77 and 300°K. It is obvious that the temperature dependences of  $n$ - and  $p$ -type  $\text{CdCr}_2\text{Se}_4$  are strikingly different. The conductivity of the  $n$ -type material shows a minimum at 150°K and increases sharply with further decreasing temperature. It has a maximum at 50°K (not shown in the figure) and drops to  $5 \times 10^{-2} \text{ (}\Omega \text{ cm)}^{-1}$  at 4.2°K. The change of the conductivity with temperature is greatest around the Curie

temperature ( $T_c = 130^\circ\text{K}$ ). The conductivity of the  $p$ -type material shows only a change of the slope in the neighborhood of the Curie temperature and decreases steadily with further decreasing temperature.

### B. Seebeck Effect

Figure 2 shows the Seebeck coefficient  $Q$  of the same 3 samples as a function of temperature. In  $p$  type as well as in  $n$ -type  $\text{CdCr}_2\text{Se}_4$ , the thermoelectric coefficient first increases slightly with decreasing temperature. It reaches a maximum at 160 and 240°K, respectively, and then decreases with further decreasing temperature. It changes sign at 100°K in the  $p$ -type material, whereas it shows a discrete peak at the Curie temperature in the  $n$ -type material. The temperature dependence of  $Q$  of undoped  $\text{CdCr}_2\text{Se}_4$  gives strong indication that this sample is still partially compensated.

### C. Hall Effect

Figure 3 shows the Hall coefficient  $R_0$  and the corresponding Hall mobility  $\mu$  of  $p$ -type  $\text{CdCr}_2\text{Se}_4$  in the paramagnetic range. The measurements above room temperature were performed in vacuum. Under these conditions the material starts to undergo irreversible changes of the conductivity at temperatures above 700°K. Therefore, no attempt was made to find the transition from extrinsic to intrinsic behavior.

Figure 4 shows the Hall coefficients and the corresponding Hall mobility of  $n$ -type  $\text{CdCr}_2\text{Se}_4$  in the paramagnetic range. In this case,  $\log R_0$  is a linear function of  $1/T$ , which indicates that electrons are supplied to the conduction band by a single-donor level. The mobility of electrons at room temperature is smaller by a factor of  $10^2$  than the mobility of holes. This is rather unusual in semiconductors. However, there are other

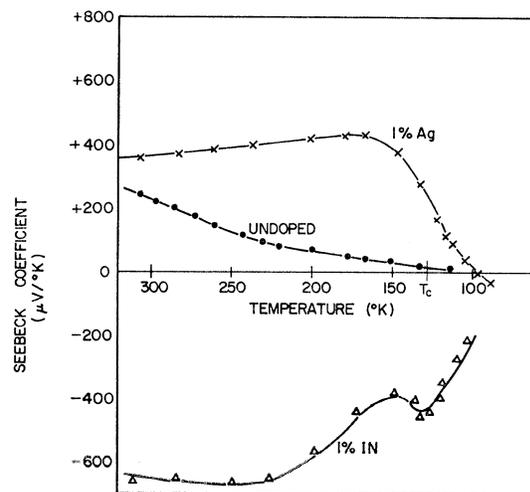


FIG. 2. Seebeck coefficient  $Q$  of 3 different samples of  $\text{CdCr}_2\text{Se}_4$  as a function of temperature.

<sup>6</sup> D. deNobel, Philips Res. Repts. 14, 361 (1959).

known materials which show the same effect; for example, sulfur<sup>7</sup> and realgar (As<sub>4</sub>S<sub>4</sub>).<sup>8</sup>

It is well established<sup>9</sup> that in the ferromagnetic range the Hall voltage is given by the following expression:

$$U_H = (R_0H + R_1M) (I/t) v, \quad (1)$$

where  $H$  is the magnetic field in oersted,  $R_0$  the normal Hall coefficient in [V cm/ A Oe],  $R_1$  the anomalous Hall coefficient in [V cm/A G],  $M$  the magnetization of the sample in gauss,  $I$  the sample current in amperes, and  $t$  the sample thickness in cm. Using this notation,  $R_0$  is related to the carrier concentration  $n$  in the following way:

$$10^8 \times |R_0| = 1/ne, \quad (2)$$

where  $10^8$  is the conversion factor from practical to cgs units, and  $e$  is the electronic charge in Coulomb. Equation (2) can only be applied for a one-carrier model.  $R_0$  and  $R_1$  were obtained in the following way: From the Hall voltage versus magnetic field curves, an average Hall voltage  $U_H$  was obtained for magnetic fields from 4 to 10 kOe in 1 kOe steps. If the magnetization

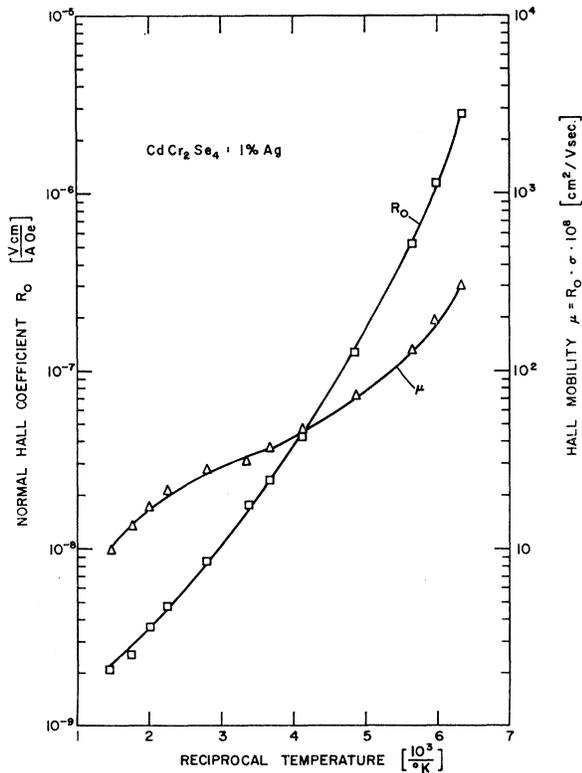


FIG. 3. Normal Hall coefficient  $R_0$  and Hall mobility  $\mu$  of  $\text{CdCr}_2\text{Se}_4$ : 1% Ag as a function of reciprocal temperature.

<sup>7</sup> D. J. Gibbons and W. E. Spear, *J. Phys. Chem. Solids* **27**, 1917 (1966).

<sup>8</sup> G. B. Street and W. D. Gill, *Phys. Status Solidi* **18**, 601 (1966).

<sup>9</sup> J. M. Lavine, *Phys. Rev.* **114**, 482 (1959).

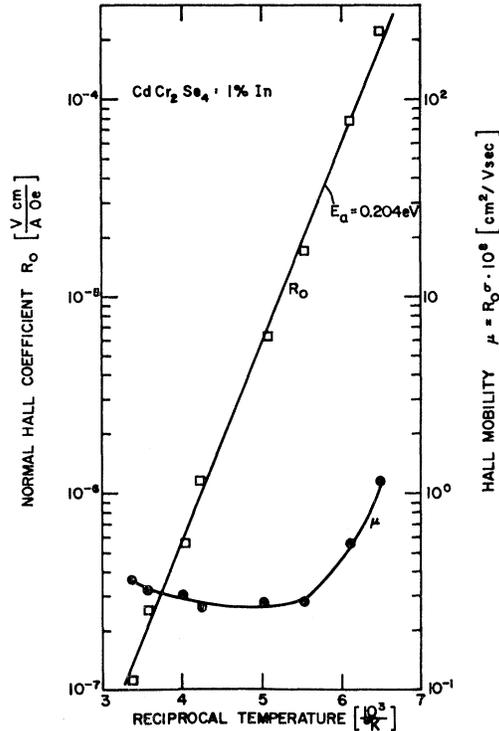


FIG. 4. Normal Hall coefficient  $R_0$  and Hall mobility  $\mu$  of  $\text{CdCr}_2\text{Se}_4$ : 1% In as a function of reciprocal temperature.

$M$  is known,  $R_0$  and  $R_1$  can be calculated as follows:

$$\rho_H = U_H t / I, \quad (3)$$

$$R_0(H_n, H_m) = \frac{\rho_H(H_n)M(H_m) - \rho_H(H_m)M(H_n)}{H_n M(H_m) - H_m M(H_n)}, \quad (4)$$

$$R_1(H_n, H_m) = \frac{\rho_H(H_n)H_m - \rho_H(H_m)H_n}{H_n M(H_m) - H_m M(H_n)}. \quad (5)$$

These equations are only valid if  $R_0$  and  $R_1$  are independent of magnetic field.

With seven values of Hall voltage in the range from 4 to 10 kOe, a total of 21 values for  $R_0$  and  $R_1$  were calculated with the help of a computer. From these, an average value and the root-mean-square error were calculated for  $R_0$  and  $R_1$ . The value of  $R_0$  could only be determined to an accuracy of about  $\pm 10\%$ , whereas  $R_1$  could be determined to  $\pm 1\%$ . The rather poor accuracy in the determination of  $R_0$  is probably due to the fact that the Hall voltage and the magnetization were not always measured at exactly the same temperature. Therefore, an interpolation had to be used to find the corresponding magnetization values.

Figure 5 shows the temperature of the normal and anomalous Hall coefficient  $R_0$  and  $R_1$ , respectively, for two Ag-substituted  $p$ -type  $\text{CdCr}_2\text{Se}_4$  samples in the vicinity of  $T_c$ . For reasons of clarity, the results on the 1% Ag-substituted sample were omitted from the graph.

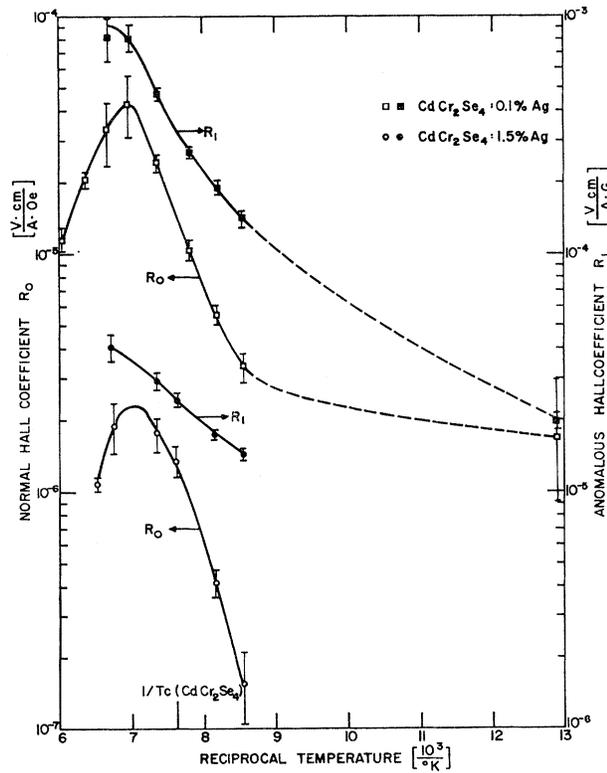


FIG. 5. Normal and anomalous Hall coefficient  $R_0$  and  $R_1$  of  $\text{CdCr}_2\text{Se}_4$ : 0.1% Ag and  $\text{CdCr}_2\text{Se}_4$ : 1.5% Ag as function of reciprocal temperature.

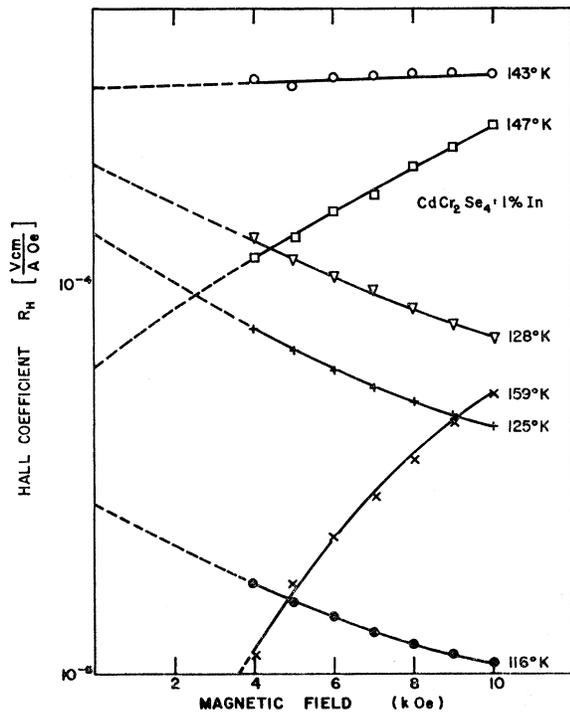


FIG. 6. Hall coefficient  $R_H$  of  $\text{CdCr}_2\text{Se}_4$ : 1% In as a function of magnetic field at different temperatures.

The general trend is the same as for the two other samples. It can be seen that  $R_0$  has a maximum at approximately  $140^\circ\text{K}$  and then decreases rather rapidly with further decreasing temperature.  $R_1$  decreases all the way with decreasing temperature. It is to be noted, however, that  $R_1$  can only be determined in a temperature range when  $M(H)$  is a sufficiently nonlinear function of  $H$ . In the paramagnetic temperature range, the denominator in Eqs. (4) and (5) is zero and  $R_0$  and  $R_1$  are not determined.

In the ferromagnetic temperature range, the Hall voltage of  $n$ -type  $\text{CdCr}_2\text{Se}_4$  is also strongly nonlinear as a function of magnetic field. However, its field dependence can apparently not be described by Eq. (1). Figure 6 shows the magnetic field dependence of the

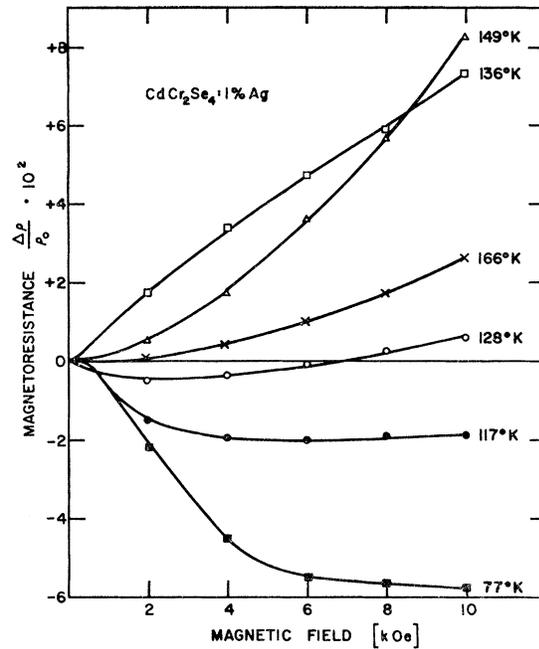


FIG. 7. Transverse magnetoresistance  $\Delta\rho/\rho_0$  of  $\text{CdCr}_2\text{Se}_4$ : 1% Ag as a function of magnetic field at different temperatures.

Hall coefficient  $R_H$  which was calculated with the usual expression

$$R_H = U_{Ht}/H \times I. \quad (6)$$

The curves drawn through the data points represent only a smooth fit and do not have any physical significance. The measurements were not extended to lower fields because of problems with demagnetizing fields. It can be clearly seen that  $R_H$  is increasing as a function of magnetic field at temperatures above  $143^\circ\text{K}$  and decreasing with field below this temperature. This trend continues to the lowest measured temperature,  $77^\circ\text{K}$ . It is noteworthy that the temperature at which the slope at  $R_H$  versus  $H$  changes is equal to the temperature where the conductivity reaches its minimum.

### D. Magnetoresistance

The transverse magnetoresistance of *p*-type  $\text{CdCr}_2\text{Se}_4$  is shown in Fig. 7 as a function of magnetic field with temperature as parameter. At the highest temperature measured ( $166^\circ\text{K}$ ),  $\Delta\rho/\rho_0$  is positive and proportional to  $H^2$ , as one would expect from ordinary transport theory. As the temperature is lowered, no simple relationship between  $\Delta\rho/\rho_0$  and  $H$  can be observed. At sufficiently low temperatures, the transverse magnetoresistance becomes negative and shows a saturation effect at the lowest measured temperature ( $77^\circ\text{K}$ ).

Figures 8 and 9 show the transverse magnetoresistance of *n*-type  $\text{CdCr}_2\text{Se}_4$  as a function of magnetic field and reciprocal temperature, respectively. Note that  $\Delta\rho/\rho_0$  is always negative and has a maximum at  $T_c$  ( $130^\circ\text{K}$ ).

## IV. DISCUSSION AND CONCLUSIONS

Zener<sup>10</sup> originally predicted that ferromagnetism could only occur in compounds with metallic conductivity. The discovery of ferromagnetism in europium chalcogenides<sup>11</sup> and also in chromium trihalides<sup>12</sup> was a first

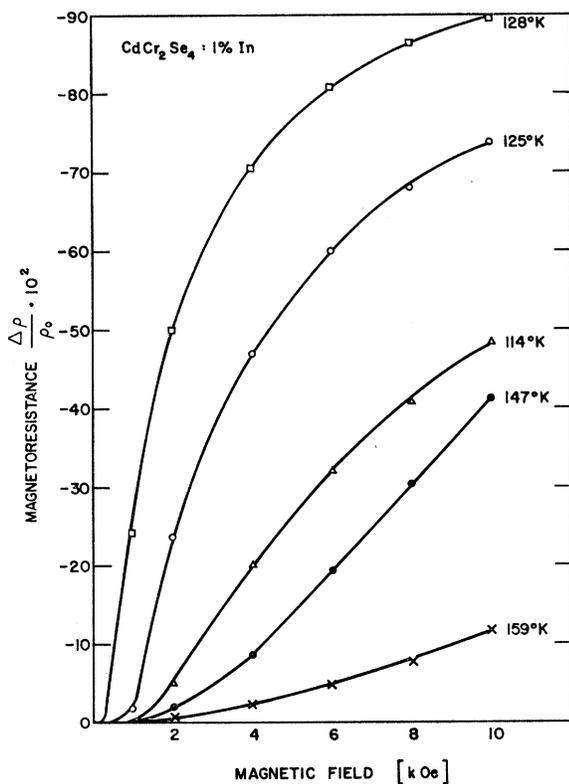


FIG. 8. Transverse magnetoresistance  $\Delta\rho/\rho_0$  of  $\text{CdCr}_2\text{Se}_4$ : 1% In as a function of magnetic field at different temperatures.

<sup>10</sup> C. Zener, Phys. Rev. **82**, 403 (1951).

<sup>11</sup> B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck, Phys. Rev. Letters **7**, 160 (1961).

<sup>12</sup> I. Tsubokawa, J. Phys. Soc. Japan **15**, 1664 (1960).

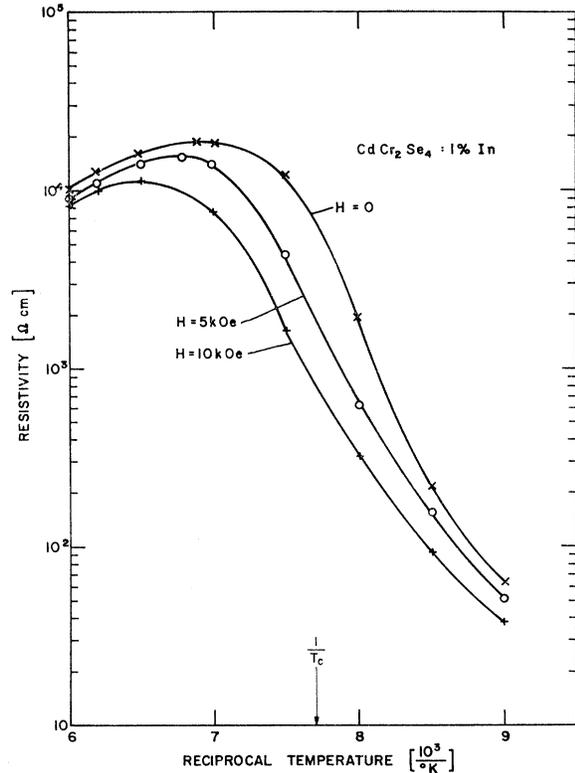


FIG. 9. Transverse magnetoresistance  $\Delta\rho/\rho_0$  of  $\text{CdCr}_2\text{Se}_4$ : 1% In as a function of reciprocal temperature at different magnetic fields.

indication that metallic conductivity is not a necessary condition for ferromagnetism. Both classes of compounds mentioned are insulators if they are sufficiently pure. EuS can be made semiconducting by doping with La.<sup>13</sup> It shows a maximum of the resistance around the Curie temperature. EuSe can also be doped with  $\text{Gd}^{3+}$  and the resulting compound is also semiconducting.<sup>14</sup> It shows an unusually large negative magnetoresistance effect around the Curie temperature.  $\text{CdCr}_2\text{Se}_4$  is at the same time a ferromagnet and a semiconductor with a hole mobility which is much larger than in most other  $3d$ -transition metal compounds. The fact that  $\text{CdCr}_2\text{Se}_4$  can be obtained as either *n* or *p* type makes the material even more interesting, but on the other hand, also more complex, for a theoretical treatment due to additional complications when a two-band model has to be used.

In the following discussion we will concentrate first on the temperature and magnetic field dependence of the optical band edge as determined by Harbeke and Pinch.<sup>15</sup> This discussion will help us to understand the rather unusual electrical properties in the ferromagnetic

<sup>13</sup> R. R. Heikes and C. W. Chen, Physics **1**, 159 (1964).

<sup>14</sup> S. von Molnar and S. Methfessel, J. Appl. Phys. **38**, 959 (1967).

<sup>15</sup> G. Harbeke and H. Pinch, Phys. Rev. Letters **17**, 1090 (1966).

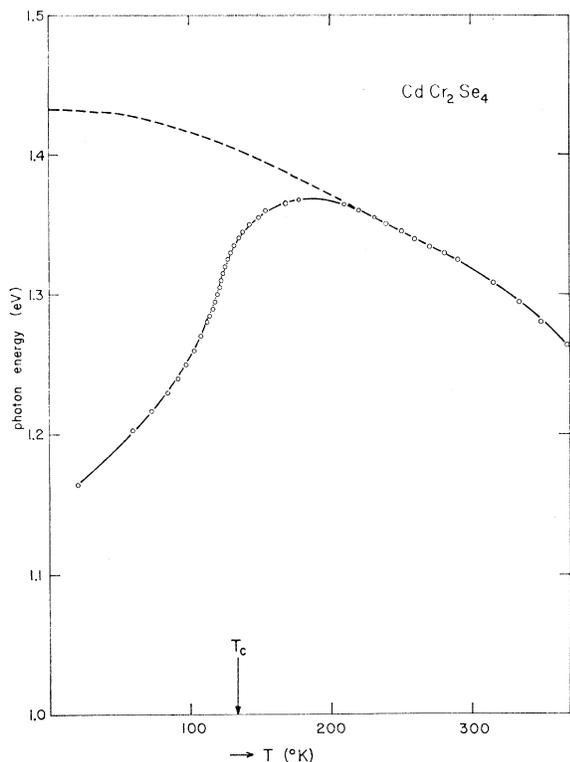


FIG. 10. Band edge of  $\text{CdCr}_2\text{Se}_4$  single crystals as a function of temperature [after Harbeke and Pinch (Ref. 17)].

range. Then we will discuss the semiconducting properties of  $n$  type and  $p$  type  $\text{CdCr}_2\text{Se}_4$  separately.

#### A. Temperature and Magnetic Field Dependence of the Band Edge

In Fig. 10 the temperature dependence of the band edge measured on single crystals of  $\text{CdCr}_2\text{Se}_4$  is shown as reported by Harbeke and Pinch.<sup>15</sup> Busch and co-workers<sup>16</sup> obtained essentially the same results by diffuse reflectance measurements on  $\text{CdCr}_2\text{Se}_4$  powder. In the paramagnetic range, the temperature dependence of the band edge follows the usual linear temperature dependence found in most nonmagnetic semiconductors (i.e.,  $\text{CdTe}$ <sup>17</sup>). The dashed line is an extrapolation to lower temperatures based on the assumption of a similar behavior as in II-VI compounds. Approaching  $T_c$  the edge shifts strongly towards lower energies as has also been found in  $\text{EuO}$ <sup>18</sup> and  $\text{EuSe}$ .<sup>19</sup> The application of a magnetic field in the ferromagnetic range results in a further red-shift.

<sup>16</sup> G. Busch, B. Magyar and P. Wachter, Phys. Letters **23**, 438 (1966).

<sup>17</sup> G. D. Mahan, J. Phys. Chem. Solids **25**, 751 (1965).

<sup>18</sup> G. Busch, P. Junod, and P. Wachter, Phys. Letters **12**, 11 (1964).

<sup>19</sup> B. E. Argyle, J. C. Suits, and M. J. Freiser, Phys. Rev. Letters **15**, 822 (1965).

#### B. $n$ -Type $\text{CdCr}_2\text{Se}_4$

In the paramagnetic temperature range, the conductivity  $\sigma$  decreases with decreasing temperature. However, it reaches a minimum at 150°K and rises sharply as the material becomes magnetically ordered. The Hall coefficient  $R_0$  increases with decreasing temperature in the paramagnetic range. The activation energy  $E_a$  deduced from Fig. 4 gives some indication as to the ionization energy of the donor level.

It is not possible to calculate the ionization energy exactly, due to lack of knowledge of the concentration of acceptor centers ( $N_A$ ) in these samples. For the two limiting cases we have

$$n \gg N_A, \quad E_a = \frac{1}{2}(E_c - E_D), \quad (7)$$

$$n \ll N_A, \quad E_a = E_c - E_D, \quad (8)$$

where  $n$  is the free electron concentration and  $E_c - E_D$  the donor ionization energy. Therefore, the ionization energy must lie between 0.2 and 0.4 eV. To date, we do not have any definite indication as to the nature of the donor level, although we have an indication that it is due to  $\text{Cr}^{2+}$ . Berger and Pinch<sup>20</sup> have made magnetization and magnetocrystalline anisotropy measurements on In-substituted and slightly Se-deficient  $\text{CdCr}_2\text{Se}_4$ . The magnetization decreases and the anisotropy increases with increasing In substitution or Se deficiency. These facts are explained by the presence of  $\text{Cr}^{2+}$ , with its moment aligned antiparallel to the  $\text{Cr}^{3+}$  moments.  $\text{Cr}^{2+}$  also acts as a charge compensator. An extra electron in the lattice is therefore most likely to be found on a  $B$  site by forming a  $\text{Cr}^{2+}$  state.

The conductivity of  $n$ -type  $\text{CdCr}_2\text{Se}_4$  seems to be very much influenced by magnetic ordering (see Fig. 1). The origin of this change in the conductivity can be due either to a large increase of the mobility as has been observed in  $\text{EuSe}$ <sup>14</sup> or to an increase of the carrier concentration. From the results shown in Fig. 6, we have to conclude that in  $n$ -type  $\text{CdCr}_2\text{Se}_4$ , the mobility, as well as the carrier concentration, is affected by magnetic ordering. As has been mentioned earlier, we were not able to separate the observed Hall coefficient into normal and anomalous Hall coefficient. Von Molnar and Methfessel<sup>14</sup> have made a similar observation in  $\text{EuSe}$ . They claim that the Hall voltage is a linear function of the magnetic field, which means that only the normal Hall coefficient  $R_0$  could be observed. For the following discussion we assume that the anomalous Hall coefficient is much smaller than the normal Hall coefficient and must not be taken into account for the following considerations. If we use Eq. (6) and extrapolate  $R_H$  to zero magnetic field, we find that  $R_H$  has a maximum at about 143°K. This corresponds to a minimum of the carrier concentration in a simple one-band

<sup>20</sup> S. B. Berger and H. L. Pinch, presented at Second International Conference on Solid Compounds of Transition Elements, at Enschede (Holland), 1967 (unpublished).

model. If we assume that the Hall mobility  $\mu$  in this range is still given by  $\mu = R_H \sigma$  and if we use the same graphic extrapolations for  $R_H$  as above, we find that  $\mu$  rises rapidly with decreasing temperature. At 116°K it reaches a value of 35 cm<sup>2</sup>/V sec.

The order of magnitude and the temperature dependence of the mobility  $\mu$  in the paramagnetic range give some indication that a hopping process involving a transfer of electrons from Cr<sup>2+</sup> to Cr<sup>3+</sup> might be responsible for charge transport in *n*-type CdCr<sub>2</sub>Se<sub>4</sub>. However, the high mobility in the ferromagnetic range indicates a collective electron behavior. At present it is not understood why the magnetic ordering induces a change from hopping to collective electron behavior.

The rise of the carrier concentration can best be explained by the strong red-shift of the band edge. If we assume that the donor level stays approximately constant with respect to the valence band and that the observed red-shift is mainly due to a shift of the conduction band edge, then the shift of the band edge will decrease the depth of the donor level. Therefore, the donor levels will release more and more electrons into the conduction band as the temperature is lowered.

As has been mentioned before, the application of a magnetic field results in a further red-shift of the band edge which again decreases the depth of the donor levels and increases the number of conduction electrons. At 130°K the band edge is shifted by 0.007 eV by the application of a magnetic field of 8.5 kOe.<sup>15</sup> This decrease of the donor ionization energy would result in an increase of the number of free carriers by a factor of 2. Calculating the same ratio from the Hall measurements shown in Fig. 6, one obtains a factor of 2.3, which is reasonably close to the value calculated from the shift of the band edge. It is therefore reasonable to conclude that the magnetic field dependence of the Hall coefficient actually reflects a field dependence of the free carrier concentration.

Using the same argument, one can also understand the large negative magnetoresistance of *n*-type CdCr<sub>2</sub>Se<sub>4</sub>. The application of a magnetic field not only increases the concentration of free carriers as shown above but also increases the magnetic ordering of the spin system. This results in a decrease of the spin scattering and therefore in an increasing mobility as a function of increasing magnetic field.

### C. *p*-Type CdCr<sub>2</sub>Se<sub>4</sub>

The conductivity  $\sigma$  of *p*-type CdCr<sub>2</sub>Se<sub>4</sub> (see Fig. 1) does not show any drastic changes around  $T_c$  in contrast to *n*-type CdCr<sub>2</sub>Se<sub>4</sub>. Only a slight change of the slope of  $\log \sigma$  versus  $1/T$  can be seen at  $T_c$ . As shown in Fig. 3,  $\log R_0$  is not a linear function of  $1/T$ . This could be due to a freeze-out of carriers to acceptor levels that differ slightly in ionization energy.

The *p*-type CdCr<sub>2</sub>Se<sub>4</sub> has a rather high hole mobility for a 3*d*-transition metal compound (see Fig. 3). It is

of the same order of magnitude as the hole mobility reported for CdTe ( $\mu_h = 65$  cm<sup>2</sup>/V sec)<sup>6</sup> and CdSe ( $\mu_h = 50$  cm<sup>2</sup>/V sec).<sup>21</sup>

The Hall measurements on *p*-type CdCr<sub>2</sub>Se<sub>4</sub> in the ferromagnetic range can best be described using Eqs. (4) and (5). From these equations one obtains the normal Hall coefficient  $R_0$ , which is inversely proportional to the carrier concentration and the anomalous Hall coefficient  $R_1$ . Although the exact physical significance of  $R_1$  is still a matter of controversy, it seems to be well established that it has its origin in the spin-orbit coupling of the conduction electrons.

So far, theoretical<sup>22-24</sup> and experimental studies of the Hall effect in ferromagnetic materials have mainly been performed on metals like Fe or Ni<sup>25-27</sup> and also on some ferromagnetic compounds with metallic conductivity like CrTe<sup>28</sup> and MnSb.<sup>29</sup> Comparatively few experimental papers have described the Hall effect in magnetic semiconductors, mainly in ferrites.<sup>9,30-33</sup> Abel'skii and Irkhin<sup>31</sup> have made some calculations of the Hall effect in magnetic semiconductors. Using the same method as was previously applied to metals<sup>22</sup> and taking into account the differences in the statistics of carriers, they found that the anomalous Hall coefficient  $R_1$  in semiconductors should be proportional to the resistivity  $\rho$  (it is expected to be proportional to  $\rho^2$  in metals<sup>22</sup>) and inversely proportional to the mobility  $\mu$  and the effective mass  $m^*$ :

$$R_1 = -\frac{E_{so}}{4\pi\Delta^2} \times \frac{\mu_B c}{1 + \frac{3}{5}\phi/kT} \times \frac{m}{m^*} \times \frac{\rho}{\mu M_s^0}, \quad (9)$$

where  $E_{so}$  is the spin-orbit energy,  $\Delta$  is the energy separation between the bands for which the spin-orbit interaction is taken into account, using perturbation theory,  $\mu_B$  is the Bohr magneton,  $c$  the velocity of light,  $\phi$  the mean impurity-scattering potential, and  $M_s^0$  the

<sup>21</sup> M. Itakura and H. Toyoda, Japan. J. Appl. Phys. **4**, 560 (1965).

<sup>22</sup> R. Karplus and J. M. Luttinger, Phys. Rev. **95**, 1154 (1954).

<sup>23</sup> J. Kondo, Progr. Theoret. Phys. (Kyoto) **27**, 772 (1962).

<sup>24</sup> Yu. Kagan and L. A. Maksimov, Fiz. Tver. Tela **7**, 530 (1965) [English transl.: Soviet Phys.—Solid State **7**, 422 (1965)].

<sup>25</sup> E. M. Pugh and N. Rostoker, Rev. Mod. Phys. **25**, 151 (1953).

<sup>26</sup> S. Foner and E. M. Pugh, Phys. Rev. **91**, 20 (1953).

<sup>27</sup> S. Soffer, J. A. Dreesen, and E. M. Pugh, Phys. Rev. **140**, A668 (1965).

<sup>28</sup> I. K. Kikoin, E. M. Buryak, and Yu. A. Muromkin, Dokl. Akad. Nauk SSSR **125**, 1011 (1959) [English transl.: Soviet Phys.—Doklady **4**, 386 (1959)].

<sup>29</sup> M. Nogami, M. Sekinobu and H. Doi, Japan J. Appl. Phys. **3**, 572 (1964).

<sup>30</sup> K. P. Belov and E. P. Svirina, Zh. Eksperim. i Teor. Fiz. **37**, 1212 (1959) [English transl.: Soviet Phys.—JETP **10**, 862 (1960)].

<sup>31</sup> Sh. Sh. Abel'skii and Yu. P. Irkhin, Zh. Eksperim. i Teor. Fiz. **44**, 230 (1963) [English transl.: Soviet Phys.—JETP **17**, 158 (1963)].

<sup>32</sup> E. P. Svirina, Fiz. Tver. Tela **6**, 3378 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2702 (1965)].

<sup>33</sup> E. P. Svirina, O. A. Malikova, and M. A. Malikova, Fiz. Tver. Tela **8**, 1599 (1966) [English transl.: Soviet Phys.—Solid State **8**, 1269 (1966)].

spontaneous magnetization at  $T=0^\circ\text{K}$ . According to their assumptions, this theory should be valid for a nondegenerate semiconductor with one type of carrier. They further predict that  $R_1$  should have the same sign as  $R_0$ . Svirina<sup>32</sup> finds reasonable agreement between his experimental results on single crystals of  $\text{MnFe}_2\text{O}_4$  and the theory of Abel'skii and Irkhin.<sup>31</sup>

Our experimental results on  $p$ -type  $\text{CdCr}_2\text{Se}_4$  are obviously only in agreement with the theory of Abel'skii and Irkhin as to the relative signs of  $R_0$  and  $R_1$ . However,  $R_1$  decreases with decreasing temperature whereas the resistivity  $\rho$  is increasing in the same temperature range. The maximum of the normal Hall coefficient  $R_0$  at  $150^\circ\text{K}$  and the sharp decrease with further decreasing temperature indicate that in this temperature range the single-band model description of the electrical properties of  $p$ -type  $\text{CdCr}_2\text{Se}_4$  probably breaks down and that a two-band approach has to be used. Therefore, the theory of Abel'skii and Irkhin would not be applicable in this temperature range.

Considering the maximum of the normal Hall coefficient  $R_0$ , the change in slope of the conductivity  $\sigma$  in all Ag-substituted samples and the rather high doping level, we suggest that the conductivity below  $150^\circ\text{K}$  is due to impurity conduction. Our experimental results are very similar to results obtained; i.e., on silicon<sup>34</sup> and germanium,<sup>35</sup> for impurity conduction at very low temperatures. If we assume that the conduction is due to two noninteracting conduction mechanisms, the electrical conductivity  $\sigma$ , the normal Hall coefficient  $R_0$ , and the Seebeck coefficient  $Q$  are given by

$$\sigma_{\text{tot}} = \sigma_h + \sigma_i = pe\mu_h + ne\mu_i, \quad (10)$$

$$R_0 = -[c^2n - p/e(cn + p)^2], \quad c = \mu_i/\mu_h \quad (11)$$

$$Q = (Q_h\sigma_h + Q_i\sigma_i)/\sigma_{\text{tot}}, \quad (12)$$

where  $\sigma_h$  is the electrical conductivity due to holes in the valence band and  $\sigma_i$  is the electrical conductivity due to impurity conduction. Impurity conduction in Si and Ge is only observed at very low temperatures

because the mobility  $\mu_h$  of valence-band holes is very high and the carrier concentration  $p$  varies relatively slowly as a function of temperature due to the rather shallow acceptor levels. Therefore, the first term in Eq. (10) is dominant over most of the temperature range and the second term becomes only important at very low temperatures. In  $\text{CdCr}_2\text{Se}_4$ , however, the mobility is much lower and the ionization energy of the acceptor level is bigger by a factor of 10. Therefore, one would expect that the second term in Eq. (10) becomes important at much higher temperatures. A similar observation has recently been made in NiO by Bosman and Crevecoeur.<sup>36</sup> They claim that below  $140^\circ\text{K}$  the conductivity is due to impurity conduction. The Seebeck coefficient  $Q$  of NiO is rapidly decreasing with temperature in the range of impurity conduction. We find a very similar temperature dependence of  $Q$  in  $\text{CdCr}_2\text{Se}_4$  below  $170^\circ\text{K}$ . If we assume that the Seebeck coefficient in the impurity conduction region can be described by Eq. (12), then the observed rapid decrease of  $Q$  with temperature is a further indication of impurity conduction. Further experiments have to be performed to decide whether the onset of impurity conduction at  $150^\circ\text{K}$  is related to the onset of magnetic short-range order or not.

The magnetoresistance  $\Delta\rho/\rho_0$  of  $p$ -type  $\text{CdCr}_2\text{Se}_4$  is positive and proportional to  $H^2$  at sufficiently high temperatures. At lower temperatures the magnetic field dependence becomes more and more complicated. Any interpretation would have to take into account the combination of effects due to impurity conduction and magnetic ordering.

#### ACKNOWLEDGMENTS

The author wishes to express his thanks to M. Robbins, who prepared the powders, R. Arlett, who did most of the hot-pressing, and to E. Lopatin, who performed the magnetization measurements. It is also a pleasure to acknowledge the many helpful discussions with P. K. Baltzer, A. Amith, L. Friedman, and R. S. Crandall.

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