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Mixed-Conduction Model for Charge Transport in *n*-Type $CdCr_2Se_4$

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A model consisting of a conduction band and a subsidiary hole band is presented and applied to explain recently published transport data on $CdCr_2Se_4$ – a chalcogenide spinel semiconductor which becomes ferromagnetic below $T_C \approx 130$ °K. The crucial feature of the data, which describe the behavior of ρ, R_0, and Q from 300 to 4.2 °K, is the coincidence of maxima in ρ and in $|R_0|$ with a minimum in $|Q|$, at 150 °K. The data cannot be explained in terms of a single conduction band, even if the spin splitting of the band and the effect of spin-disorder scattering are included, nor in terms of two-electron conduction bands. The present two-band model, wherein one band is the *n*-type conduction band and the other is a subsidiary hole band in the band gap, is the simplest one which can account for the data in a consistent manner. As T is lowered from 300 to 150 °K, electrons freeze out onto the donors while the hole concentration increases; below 150 °K the hole concentration decreases while the electron concentration increases rapidly, because of the reduction of the donor ionization energy. These effects are due to temperature-dependent changes of the above interband energies associated with the assumed relative motions of the bands as the temperature is lowered below 186 °K - an effect due to intra-atomic exchange. Evidence for localized transport at very low temperatures is discussed briefly.

I. INTRODUCTION

The compound $CdCr_2Se_4$ is one of the chalcogenide spinels which are both semiconducting and ferromagnetic.[1] The transport properties of this[2,3] and of other ferromagnetic semiconductors have been the subject of a number of recent studies.[4] Doping $CdCr_2Se_4$ with indium or galium renders it *n* type, whereas silver or gold doping renders it *p* type. Electrical measurements on both types have been reported.[2] The optical band gap has been found[5] to increase slowly from 1.320 eV at 300 °K to 1.354 eV at 186 °K, and thence to decrease rapidly to 1.162 eV at 20 °K. The decrease has been assumed to be associated with magnetic ordering.[6,7]

Recent measurements on a series of indium-doped samples of $CdCr_2Se_4$ have been reported [3] in which the temperature dependences of the electrical resistivity ρ, the normal Hall coefficient R_0, and the Seebeck coefficient Q behaved in an anomalous manner. The salient features of this anomalous behavior were that in the temperature region from 300 to 150 °K, where ρ and R_0 indicated a decrease in carrier concentration, the absolute value $|Q|$ decreased; whereas in another region, from 150 to 125 °K, where ρ and R_0 indicated an increase in the carrier concentration, the absolute value $|Q|$ increased.

The present paper is concerned with understanding these features of charge transport in *n*-type $Cd_{1-x}In_xCr_2Se_4$. A band model is developed which accounts for the behavior of ρ, R_0, and Q from room temperature down into the ferromagnetic region below the Curie temperature[8] T_C ($T_C \approx 130$ °K).

In Sec. II, the principal features of the experimental data[3] relevant to the proposed model are reviewed. In Sec. III, it is first pointed out that the temperature dependences of ρ, R_0, and Q described above cannot be reconciled on the basis of a simple one-band model which had been proposed earlier[2]; the simplest model which accounts for the data in a consistent manner is one in which an *n*-type and a *p*-type band contribute jointly to the transport. This model is described in some detail and is used to interpret the data. It is assumed that the *n*-type band is the material's intrinsic conduction band, whereas the *p*-type band is subsidiary and lies well above the intrinsic valence band. It is finally suggested briefly that the applicability of the band theory does not extend to the transport data at low temperatures, and that below about 60 °K the transport is thermally activated, hopping among magnetic ions in which the short-range magnetic order plays an essential role.

In Sec. IV, a number of other relevant effects are discussed, and it is demonstrated that they are incapable of explaining the data. First, the possibility of the appearance of a subsidiary conduction band is dismissed. It is then shown, in more detail, that the effects of spin-disorder scattering on ρ and Q cannot account for the large temperature variations in these quantities. Finally, the effects of possible spin splitting of the conduction band[7] for $T \lesssim T_C$ are shown to be inadequate to explain the Seebeck data over an extended temper-

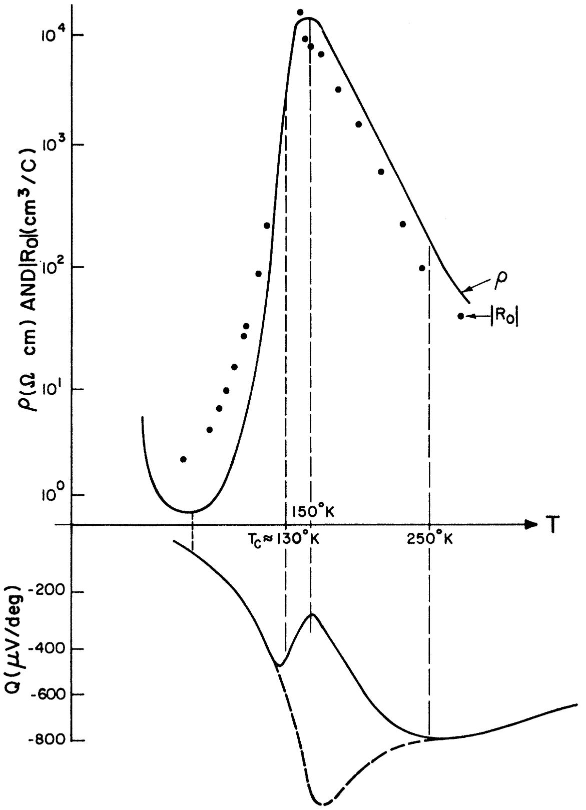

FIG. 1. Sample $Cd_{0.99}In_{0.01}Cr_2Se_4$. Top part: experimental resistivity and normal Hall coefficient (absolute value). Bottom part: solid curve is the experimental Seebeck coefficient. Dashed curve is the value which the Seebeck coefficient would have had if the single-band model had been applicable (see text).

ature range, though they may explain part of the sharp structure in Q near T_C. In Sec. V, there is speculation, based on experimental evidence, for the atomic origins of the various bands, and additional experimental tests of the model are suggested. The conclusions are summarized in Sec. VI.

II. SUMMARY OF EXPERIMENTAL DATA

The ferromagnetic semiconductor of interest in the present paper is the chalcogenide spinel $CdCr_2Se_4$. The data were taken on hot-pressed unannealed samples and have been verified since on single crystals. As such, the material is deficient in selenium.[9] At 4.2°K, each missing selenium ion is charge compensated by the formation of two Cr^{2+} ions from the host Cr^{3+}. In addition, the samples had been rendered n type by doping with indium. The indium is assumed to substitute for Cd^{2+} ions on the A sites[9] and contributes one excess electron to the system.

In Fig. 1, we reproduce data from Ref. 3 on the temperature dependences of the electrical resistivity ρ, the normal Hall coefficient[10,11] R_0, the Hall mobility $\mu_H \equiv R_0\rho^{-1}$, and the Seebeck coefficient Q for the $Cd_{1-x}In_xCr_2Se_4$ sample in which $x = 0.01$. The data for samples with $x = 0.005$ and $x = 0.02$ show the same temperature dependences, differing only in magnitude. The salient features of the data are the following: The resistivity increases exponentially with an activation energy 0.23 eV as T is lowered from 300 to 150 °K, where it exhibits a maximum; this is shown explicitly in Fig. 2 where $\ln\rho$ is plotted versus T^{-1}. Upon further decrease in temperature to about 60°K, ρ decreases by approximately four orders of magnitude. As the temperature is decreased below 60 °K, the resistivity rises again with an activation energy of about 1.7 meV.

The normal Hall coefficient R_0 is negative and increases in absolute value at approximately the same rate as does ρ in the temperature from 300 to 150 °K as seen in Figs. 1 and 2. This is consistent with the contention that the resistivity increase in this range is due to a variation in carrier concentration, rather than to a mobility variation.[12] For $T < 150$ °K, $|R_0|$ decreases monotonically with decreasing temperature even below 60 °K, where ρ begins to rise again. The magnitude of the Hall

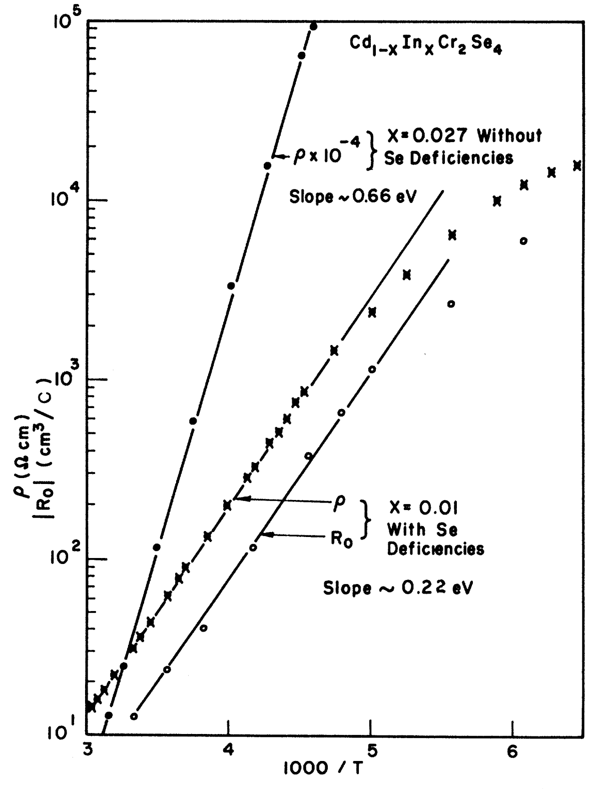

FIG. 2. Behavior of $\ln\rho$ and of $\ln|R_0|$ versus T^{-1} for a sample with Se deficiencies; and the behavior of $\ln\rho$ versus T^{-1} for a stoichiometric sample.

mobility is between 0.1 and 10 cm^2/V sec; it is relatively temperature insensitive for $T > 150$ °K; it peaks near T_C and decreases as the temperature is lowered below 100 °K.

The above interpretation of the Hall data is not straightforward and requires some elaboration. In Ref. 3, it was noted that from 30 to 100 °K, the Hall field E_H is linear with H only above about 3 kOe, R_0 being taken from the high-field slope. Above 150 °K, E_H is superlinear in H. The reasons for this are not understood. In this regime, R_0 was taken from the low-field data.

In general, the Hall field is written

$$E_H = R_0 H_i + R_1 M(H_i, T),$$

where H_i is the internal field, M the sample magnetization, R_0 the normal Hall coefficient, and R_1 the ferromagnetic Hall coefficient. Also,

$$H_i = H_a - NM,$$

where H_a is the applied field and N is the demagnetizing factor. Thus, one may write

$$E_H = R_0 H_a + (R_1 - NR_0)M,$$

from which it follows that the high-field slope in the saturation range (above 3 kOe) gives R_0. In the paramagnetic regime $(T > T_C)$, one has

$$M = \chi H_i,$$

where χ is the magnetic susceptibility, so that

$$R_{\mathrm{expt}} \equiv E_H/H_a = R_0 + (R_1 - NR_0)\chi/(1 + N\chi).$$

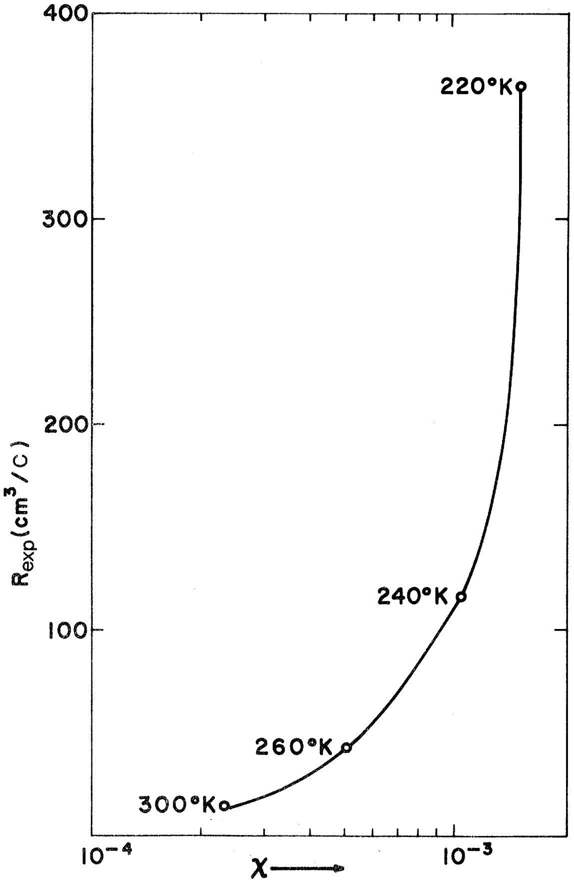

FIG. 3. Measured Hall coefficient R_{expt} versus susceptibility χ in the paramagnetic regime.

A plot of the above expression as a function of χ is presented in Fig. 3. ($\chi \ll 1$ over the entire range, so that the $N\chi$ correction is negligible.) It shows that R_{expt} is strongly nonlinear and, in fact, superlinear in χ. (In the Curie-Weiss expression for χ, we took $C_M = 3.82$ mole^{-1}, and $\theta = 204$ °K.[8]) Thus, R_0, R_1, or both must be temperature dependent. The temperature dependence of R_0 alone and its parallel behavior with ρ is consistent with carrier freeze-out; the alternative could be that R_1 alone is temperature dependent. However, the latter would require that R_1 be strictly linear in ρ through the mobility μ; in such a case, however, the logarithmic dependence on χ should be apparent for $T \gtrsim \theta$ and result in R_{expt} not being parallel to ρ. Furthermore, this interpretation is not consistent with the high-temperature Q data above 250 °K, which shows $|Q|$ increasing approximately as T^{-1}. It is this evidence which leads us to conclude that we are seeing carrier freeze-out at high temperatures.

The Seebeck coefficient Q, like the Hall coefficient, is negative at all temperatures. As shown in Fig. 1, its absolute value $|Q|$ increases as T decreases to about 250 °K, where it starts decreasing, and exhibits a local minimum at 150 °K. From there down to 125 °K, it increases, having a local maximum at that temperature. At still lower temperatures, it decreases monotonically toward zero.

III. MODEL OF n AND p BANDS

The experimentally determined temperature dependences of ρ, R_0, and Q cannot be explained in a consistent way by a model in which it is assumed that conduction takes place in a single band.[2] The expressions for the transport coefficients for such a case, wherein the band is parabolic and the statistics are nondegenerate, are[13]

$$\rho = (ne\mu)^{-1} = (Ne\mu)^{-1} e^{(E_C - E_F)/kT}, \qquad (1)$$

$$R_0 = -1/nec = -(1/Nec) e^{(E_C - E_F)/kT}, \qquad (2)$$

$$Q = -\frac{k}{e}\left(\frac{E_C - E_F}{kT} + \alpha\right) = -\frac{k}{e}(\ln N_C - \ln n + \alpha), \qquad (3)$$

where we assume the single band to be an n-type conduction band. The band edge and the Fermi level are at E_C and E_F, respectively; n is the electron concentration, $N_C = 2(2\pi m^* kT/\hbar^2)^{3/2}$ is the conduction band's density of states, and m^* is its effective mass; μ is the carrier mobility, k is Boltzmann's constant, T is the absolute temperature, e is the magnitude of the electron charge, and c is the velocity of light; α is a scattering factor (or "kinetic-energy" term) which, for the case of classical statistics, is a function only of the energy dependence of the scattering time of the carriers. In Eq. (2), it has been assumed that the single-band Hall and drift mobilities are equal.

If we neglect the temperature dependence of μ in comparison with that of n, then ρ is proportional to n^{-1}, just as $|R_0|$ is. The value of Q is also seen to diminish as n gets larger, though more slowly.

Figure 2 shows that from 300 to 150 °K, both ρ and $|R_0|$ increase in a manner which is characteristic of carrier freeze-out at a constant value of $(E_C - E_F)$. One might have expected, on the basis of such a simple picture, that in the same temperature range $|Q|$ would have been proportional to T^{-1} [see Eq. (3)] and reached a maximum at 150 °K. The decrease in $|Q|$ from about 250 to 150 °K is clearly inconsistent with this. Furthermore, the sharp drop in ρ and in $|R_0|$ from 150 °K down indicates a fast increase in the concentration of electrons, and thus a decrease in $(E_C - E_F)/kT$ which, in turn, may be related to magnetic ordering.[6,7] The increase in $|Q|$ from 150 °K down to a little below the Curie temperature, is again inconsistent with the rise in carrier concentration. Only between 125 and 60 °K and above 250 °K are the behavior of ρ, R_0, and Q consistent with one another.

The simplest model which reconciles the temperature dependences of ρ and R_0, on the one hand, with that of Q on the other, is one which postulates the presence of a p band in addition to the n-type conduction band. Such a model will be shown to explain the rise in ρ and in $|R_0|$ and the decrease in $|Q|$, and also the coincidence of a peak in ρ and in $|R_0|$, with a minimum in $|Q|$.

The transport coefficients for the case of mixed conduction (of electrons and holes) are[13]

$$\rho^{-1} = \rho_n^{-1} + \rho_p^{-1}, \tag{4a}$$

$$R_0 = (R_n \rho_n^{-2} + R_p \rho_p^{-2})\rho^2, \tag{4b}$$

$$Q = (Q_n \rho_n^{-1} + Q_p \rho_p^{-1})\rho, \tag{4c}$$

wherein the subscripted coefficients refer to the individual n and p bands, respectively. Thus,

$$\rho = [e(n\mu_n + p\mu_p)]^{-1}, \tag{5a}$$

$$R_0 = -(1/ec)[(n\mu_n^2 - p\mu_p^2)/(n\mu_n + p\mu_p)^2], \tag{5b}$$

$$Q = \{-(k/e)[(E_C - E_F)/kT + \alpha_n]n\mu_n + (k/e) \times [(E_F - E_p)/kT + \alpha_p]p\mu_p\}\,(n\mu_n + p\mu_p)^{-1}. \tag{5c}$$

The salient feature of this mixed-conduction model is that in the vicinity of 150 °K it allows for a relatively large contribution of holes. This contribution lowers the values which ρ, $|R_0|$, and $|Q|$ would have had otherwise: In the case of ρ this is due simply to the additive contribution of the free holes to the conductivity; in the cases of R_0 and of Q it is due to the fact that the partial contributions of the holes have signs opposite to the partial contributions of electrons. It is clear that the hole band cannot be the material's intrinsic valence band; the valence band lies much too far below the conduction band (the room-temperature optical band gap is 1.32 eV) to account for any free holes. The postulated hole band, then, must lie in the forbidden band gap well above the valence-band edge. It will be argued later (Sec. V) that such a subsidiary band may be due to the combined effects of the added indium impurities and intrinsic defects.[9] The reasons for the similarity between the temperature dependence of $|R_0|$ and ρ, but not $|Q|$, is shown in Eqs. (18) and (19) below.

We proceed to consider the effect which the subsidiary hole band has on the position of the Fermi level.[14] The lower edge of the intrinsic conduction band is designated by E_C, and the upper edge of the hole band is designated by E_p. The densities of states in the conduction band and in the hole band are N_C and N_p, respectively, and the total concentration of donors is N_D. The Fermi level is E_F and the donor level is E_D. Nondegenerate statistics are applied.

The concentrations of electrons in the conduction band and of holes in the p bands are, respectively,

$$n = N_C e^{-(E_C - E_F)/kT}, \quad p = N_p e^{-(E_F - E_p)/kT}. \tag{6}$$

The concentration of un-ionized donors (i.e., the concentration of electrons on donors) is

$$N_D^0 = N_D/[1 + \tfrac{1}{2}e^{-(E_F - E_D)/kT}]. \tag{7}$$

The condition of electrical neutrality is

$$n = p + N_D - N_D^0. \tag{8}$$

Combination of Eq. (8) with Eqs. (6) and (7) results in an equation which is cubic in the quantity $e^{E_F/kT}$.[15]

In the special case where there is no hole band, but only a conduction band and donors, the equation for $e^{E_F/kT}$ is quadratic. In the limit of low T and/or high N_D/N_C, the solution for the Fermi level assumes the simple and well-known form[14]

$$E_F = \tfrac{1}{2}(E_C + E_D) + \tfrac{1}{2}kT\,\ln\,(N_D/2N_C). \tag{9}$$

The full equation which is cubic in $e^{E_F/kT}$ is quite complex,[15] but it is simplified in the low-T and/or high-donor density approximation, where

$$(\overline{N}_D/N_C)e^{(E_C-E_D)/kT} \gg 1, \tag{10}$$

wherein $\overline{N}_D$ is an "effective" concentration of donors,

$$\overline{N}_D = N_D[1 + 2(N_p/N_D)e^{-(E_D-E_p)/kT}]. \tag{11}$$

The solution of the simplified cubic equation which yields an acceptable solution (i.e., positive $e^{E_F/kT}$) becomes

$$E_F = \tfrac{1}{2}(E_C + E_D) + \tfrac{1}{2}kT\ln(N_D/2N_C) + \tfrac{1}{2}kT\ln[1 + 2(N_p/N_D)e^{-(E_D-E_p)/kT}]. \tag{12}$$

The preceding expression for the Fermi level in the presence of the subsidiary hole band has the same form as that in Eq. (9), only now there appears an effective density of donors [Eq. (11)] instead of the density of donors itself. The position of the Fermi level is raised by the presence of the hole band, and consequently the concentration of electrons n in the conduction band is larger than it would have been otherwise:

$$n = N_C e^{-(E_C-E_F)/kT} = (\tfrac{1}{2}N_C\overline{N}_D)^{1/2}e^{-(E_C-E_D)/2kT}, \tag{13a}$$

$$p = N_p e^{-(E_F-E_p)/kT} = N_p(2N_C/\overline{N}_D)^{1/2}e^{-(E_C+E_D-2E_p)/2kT}. \tag{13b}$$

The ratio of the concentrations of electrons and holes is

$$n/p = 1 + (N_D/2N_p)e^{(E_D-E_p)/kT}. \tag{14}$$

At 300 °K, we have $n \gg p$, $(E_C - E_F) < (E_F - E_p)$. The freeze-out of electrons onto donors is given by (13a) with $(E_C - E_D) \approx 0.44$ eV.

We now consider the behavior of the various transport coefficients at 150 °K for the sample $\mathrm{Cd_{0.99}In_{0.01}Cr_2Se_4}$. At that temperature $Q = -260\ \mu\mathrm{V/deg}$, $\rho = 1.6 \times 10^4\ \Omega\,\mathrm{cm}$, and $kT = 1.29 \times 10^{-2}$ eV. We deduce, from Eqs. (4c) and (5c), that at 150 °K

$$-2.43 \times 10^{-7}\ \mathrm{eV}(\Omega\,\mathrm{cm})^{-1} = -[E_C - E_F + 1.29 \times 10^{-2}\alpha_n]\rho_n^{-1} + [E_F - E_p + 1.29 \times 10^{-2}\alpha_p]\rho_p^{-1}, \tag{15}$$

which becomes

$$\frac{E_F - E_p + 1.29 \times 10^{-2}\alpha_p}{E_C - E_F + 1.29 \times 10^{-2}\alpha_n} = \frac{-2.43 \times 10^{-7}}{(E_C - E_F + 1.29 \times 10^{-2}\alpha_n)pe\mu_p} + \frac{n\mu_n}{p\mu_p}. \tag{16}$$

Estimating $(E_C - E_F) \sim 0.22$ eV, the first term of (16) is negligible compared with the second term. Thus,

$$\frac{E_F - E_p + 1.29 \times 10^{-2}\alpha_p}{E_C - E_F + 1.29 \times 10^{-2}\alpha_n} \approx \frac{n\mu_n}{p\mu_p} = \frac{\mu_n}{\mu_p} \times \left(1 + \frac{N_D}{2N_p}e^{(E_D-E_p)/kT}\right). \tag{17}$$

The large and negative value of R_0 requires that

$$n\mu_n^2/p\mu_p^2 = (\mu_n^2/\mu_p^2)[1 + (N_D/2N_p)e^{(E_D-E_p)/kT}] > 1. \tag{18}$$

The conditions of Eqs. (17) and (18) can be satisfied simultaneously. If the bracketed term of Eqs. (17) and (18) is approximately unity, then the conditions are satisfied if $\mu_n/\mu_p > 1$. If the bracketed term is much larger than unity, then the two mobilities can be comparable. In either case, satisfaction of the condition Eq. (18) requires that

$$(E_F - E_p + kT\alpha_p)/(E_C - E_F + kT\alpha_n) > 1, \tag{19}$$

which is rewritten as

$$[2E_F - (E_C + E_p) + kT(\alpha_p - \alpha_n)]/(E_C - E_F + kT\alpha_n) > 0 \tag{20}$$

or, since $E_F < E_C$,

$$E_F > \tfrac{1}{2}(E_C + E_p) + \tfrac{1}{2}kT(\alpha_p - \alpha_n). \tag{21}$$

Since the individual scattering factors lie between 2 and 4 for a variety of scattering mechanisms, and since, furthermore, α_n and α_p are likely to be comparable,[13] the second term is negligible. All that is required, then, is that at 150 °K the Fermi level be above the midpoint between the conduction band and the subsidiary p band. This condition is consistent with that of Eq. (12). It is just this condition which allows a large cancellation to occur for Q, but a negligible cancellation to occur in R_0.

We now turn to inspect the requirements which are imposed by the simultaneous occurrence of the maxima of ρ and of $|R_0|$, and the minimum of $|Q|$ at 150 °K.

The condition of the resistivity extremum is

$$\frac{d\rho}{dT} = 0, \quad \frac{d\rho^{-1}}{dT} = 0. \tag{22}$$

Since the conductivity of the two bands in parallel is the sum of their individual partial conductivities, it follows that at the extremum

$$\frac{d\rho_n^{-1}}{dT} = -\frac{d\rho_p^{-1}}{dT}. \tag{23}$$

The occurrence of the Hall-coefficient maximum at 150 °K requires that at this temperature

$$\frac{dR_0}{dT} = 0. \tag{24}$$

The derivative of Eq. (24) is developed by using

Eqs. (5a) and (5b) together with the conditions of Eqs. (22) and (23). We assume that the temperature dependences of the mobilities as well as the densities of states can be neglected in comparison with the temperature dependences of the carrier concentrations. Thus we obtain

$$\frac{dR_0}{dT}=\rho^2\mu_p(\mu_n+\mu_p)\frac{dp}{dT}=\rho^2\mu_p(\mu_n+\mu_p)p\frac{d}{dT}\left(\frac{E_p-E_F}{kT}\right). \tag{25}$$

In order for Eq. (24) to be satisfied, it follows that

$$\frac{d}{dT}\left(\frac{E_p-E_F}{kT}\right)=0, \tag{26}$$

which means that $dp/dT=0$ at 150 °K.

The occurrence of the extremum in the Seebeck coefficient at 150 °K requires, likewise, that

$$\frac{dQ}{dT}=0. \tag{27}$$

The derivative of Eq. (27) is developed by using Eqs. (4c) and (5c), together with the conditions of Eqs. (22) and (23):

$$\frac{dQ}{dT}=\rho\left[\rho_n^{-1}\frac{d}{dT}Q_n+\rho_p^{-1}\frac{d}{dT}Q_p+(Q_p-Q_n)\frac{d}{dT}\rho_p^{-1}\right]. \tag{28}$$

We assume that the temperature dependences of the mobilities, of the scattering factors α_n and α_p, and of the densities of states are all negligible. Then Eq. (28) becomes

$$\frac{dQ}{dT}=k\rho\mu_p p\left[\frac{E_C-E_p}{kT}-(\alpha_n+\alpha_p-2)\right]\frac{d}{dT}\left(\frac{E_p-E_F}{kT}\right). \tag{29}$$

The condition of Eq. (27) can be satisfied in two ways. The first way is $E_C-E_p=kT(\alpha_n+\alpha_p-2)$. This represents a very narrow separation between the two bands, since the dimensionless scattering factors α_n and α_p are[13] between 2 and 4. The temperature dependences of ρ and of R_0 near 300 °K give ample indication that the separation between the two bands has to be much wider. Hence we discard this possibility.

The other condition which will make the derivative dQ/dT vanish is identical to that given by Eq. (26). This is precisely the condition that the hole density given by Eq. (5b) no longer continue to increase with decreasing temperature below 150 °K. This is consistent with the model as described previously and the kinematics of the band changes with temperature shown in Fig. 4. The latter is expected to be relatively independent of the doping concentration, as is the position of the Fermi level given by Eq. (12). Thus, the occurrence of the maxima of ρ and of $|R_0|$, and of the local minimum of $|Q|$ at the same temperature are consistent with the model.

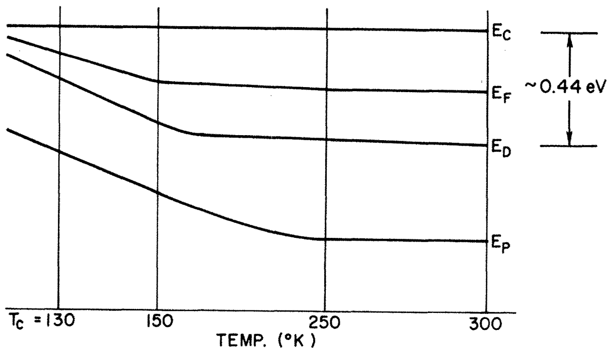

FIG. 4. *n*- and *p*-band model. The temperature dependence of the band edges, the donor level, and the Fermi level, all *relative* to the conduction-band edge.

The proposed model is sketched in Fig. 4. At room temperature, we find, in order of increasing energy, the intrinsic valence band at E_V, a higher-lying subsidiary valence band at E_p, a donor level at E_D, the Fermi level at E_F, and the conduction band at E_C. The above energies indicate the respective band edges; the bandwidths are not included. The energy scale, deduced from the high-temperature activation energies of R_0 and ρ, is indicated in the figure.

The present model, then, exhibits the following behavior as function of temperature. From 300 to about 250 °K, the Fermi level is approximately midway between E_C and E_D, characteristic of an extrinsic semiconductor in the high-impurity concentration, low-temperature limit [see Eq. (9)]. Upon decreasing the temperature below 300 °K, the usual carrier freeze-out from the conduction band onto donor sites occurs. The rise in ρ, $|Q|$, and $|R_0|$ is consistent with this interpretation. The conduction band and donor level continue to move together down to 150 °K so as to maintain a constant ionization energy, but from 250 to 150 °K, the distance E_F-E_p decreases so that p increases as T is lowered while, at the same time, n continues to decrease because of freeze-out onto the donors. Consequently, as T approaches 150 °K, $\ln|R_0|$ and $\ln\rho$ are no longer linear as functions of T^{-1} but rather increase much less rapidly (see Fig. 2). At 150 °K the hole concentration has become significant in comparison with the electron density and $|R_0|$ as well as ρ are lower by about a factor of 10 from what they would have been otherwise. At the same time, the hole contribution to the Seebeck coefficient has substantially cancelled a major part of the electrons's contribution.

At 150 °K, the rates of change of p and of n as function of T become zero. Both partial conductivities, then, have zero temperature dependences at that temperature. From 150 down to about

130 °K, the reduced ionization energy $(E_C - E_D)/kT$ decreases rapidly, resulting in an increase in n. At the same time, $(E_F - E_p)$ either remains constant or decreases slowly so that $(E_F - E_p)/kT$ increases. The hole concentration p then becomes very rapidly insignificant in comparison with the electron concentration n.

Since the E_D and E_p levels approach each other from 250 to 105 °K and then separate slightly, it would be reasonable to suppose that the wave functions of the donors and of the p band have the same symmetry character, resulting in their mutual repulsion when the two levels get close to each other. As will be discussed later, it is plausible that they both have s-like characters. The decrease in the concentration of holes below 150 °K accounts for the increase in $|Q|$ down to about 130 °K, whereas below 130 °K, the decrease in $|Q|$ is due to the continuing increase in n with further lowering of T. As discussed below, the initial sharp drop in Q just at T_C may also be due to the spin splitting of the conduction band. The shape of the Q curve below 150 °K is then the result of two competing effects: the increase in the negative value of Q due to the diminishing contribution of holes, and the decrease in the negative value of Q due to the increasing concentration as n increases toward degeneracy. In Fig. 1 is shown, in dotted line, the temperature dependence which Q would have had in the absence of the hole band: From 300 to 150 °K, $|Q|$ would have increased due to the exponential decrease in the concentration of electrons which freeze onto the donors, whereas below 150 °K, $|Q|$ would have decreased because of the rapid increase in n. The solid line in Fig. 1 shows the actual behavior of Q. The decrease in $|Q|$ from 250 to 150 °K is due to the relative increase in the partial contribution of the holes; the increase in $|Q|$ from 150 to 125 °K is governed by the rapid separation of E_p from E_F, and below 125 °K, the dominant mechanism is the increasing electron concentration.

It will be recalled that the minimum in $|Q|$ at 150 °K is due to the cancellation of a large part of the term $Q_n\rho_n^{-1}$ of Eq. (4c) by the term $Q_p\rho_p^{-1}$. At this temperature, p is a maximum. If, in going from 150 °K to $T_C = 130$ °K it be assumed that $(E_F - E_p)/kT$ increases sufficiently that p, given by Eq. (5a), becomes negligibly small at T_C, then ρ and Q are determined by the electrons alone. From Fig. 1 we see that ρ decreases by approximately a factor of 10 in going from 150 °K to T_C. From (13a) and (13b), neglecting the temperature variation in mobility from 150 to 130 °K, we have

$$\left(\frac{13}{15}\right)^{3/2} \exp\left\{-\left[\left(\frac{E_C - E_F}{kT}\right)_{130\,^\circ\mathrm{K}} - \left(\frac{E_C - E_F}{kT}\right)_{150\,^\circ\mathrm{K}}\right]\right\} \cong 10.$$

With $(E_C - E_F)_{150} = 0.22$ eV, we calculate $(E_C - E_F)_{130} = 0.17$ eV as the reduced value of ionization energy at T_C.

Thus, at 130 °K, $(E_C - E_F)/kT$ is smaller by a factor of ln 10 = 2.3 than it would be if E_C and E_F moved rigidly to lower energy. Since Q is directly proportional to the above quantity (in the absence of holes at 130 °K), it follows that $|Q|$ at T_C should be smaller than the value extrapolated to T_C from high temperatures ($T > 300$ °K) by just the above numerical factor. This is in approximate quantitative agreement with the data of Fig. 1.

For $T < T_C$, the onset of long-range order will result in a splitting of the conduction band into spin-up and spin-down polarized bands. This splitting can account for the initial rapid decrease in $|Q|$ just at T_C (see Sec. IV). The continued decrease in $|Q|$ for temperatures far below T_C must, however, be due to other factors: in particular, the onset of carrier degeneracy. We may assume that at these temperatures the holes no longer play any role and the transport is due to electrons only.

The low-temperature transport behavior is not treated in the present paper. However, the following features are cited. First, it has been proposed[9] that at low temperatures (4.2 °K) the excess electrons due to the added indium and lack of stoichiometry are localized on chromium B sites, reducing the ion to Cr^{2+} ions which are antiferromagnetically coupled to the host Cr^{+3} spins.[9] Second, between 60 and 4.2 °K, the resistivity is rising with decreasing temperature with an activation energy of about 1.7 meV, while $|R_0|$ continues its monotonic decrease. This behavior is characteristic of impurity conduction with the added feature that the magnetic ordering plays an essential role: The excess electron on a Cr^{2+} site can transfer to a neighboring Cr^{3+} site only if the two Cr^{3+} cores's spins are not antiparallel.[16] This requires an energy of activation which approximates the exchange energy (i.e., $\sim kT_C$). This will be treated in a future paper.

IV. ROLE OF MAGNETIC EFFECTS

In this section, we consider the roles which certain effects, associated with the magnetic properties of the material, have upon the transport phenomena previously discussed.

Presence of a Subsidiary Conduction Band

It was shown, at the beginning of Sec. III, that the reported transport data could not be reconciled on the basis of a single conduction band. However, in the vicinity of room temperature, as well as some distance below 150 °K, such a model coincides with the one proposed in this paper. Since some of the constituents of the compound have narrow d bands above the lower s bands, the possibility exists that at some temperatures the two bands are sufficiently close to one another that electrons in both contribute to transport. In the brief discussion which follows, it will be demonstrated that such a model does not explain the data.

The model supposes that in addition to the main conduction band, labeled I, there exists a subsidiary conduction band, labeled II. If the distance between the two band edges is designated by δ

$$\delta = (E_{C_{\text{II}}} - E_{C_{\text{I}}})/kT > 0, \tag{30}$$

then in the low-T and/or high-density of donors approximation, it is readily verified that the Fermi level is[15] given by the same expression as in Eq. (9) where N_C has been replaced by

$$N_{C_{\text{I}}}[1 + (N_{C_{\text{II}}}/N_{C_{\text{I}}})\, e^{-\delta}]. \tag{31}$$

The appearance of the higher-lying conduction band has the effect of depressing the Fermi level from where it would have been otherwise; this results in the ionization of additional donors and the liberation of electrons which are needed to occupy states in the upper band. The Seebeck coefficient of each band is given by an expression such as in Eq. (3), and the two are related in the following manner:

$$Q_{\text{II}} = Q_{\text{I}} + (k/e)(\alpha_{\text{I}} - \alpha_{\text{II}}) - (k/e)\delta \approx Q_{\text{I}} - (k/e)\delta, \tag{32}$$

where, for simplicity, we have taken $\alpha_{\text{I}} \approx \alpha_{\text{II}}$. It is noteworthy that Q_{I} is larger in magnitude than it would have been in the absence of the higher-lying subsidiary band, owing to the latter's effect in lowering E_F. The total Seebeck coefficient for the two bands conducting in parallel is given by an expression analogous to Eq. (4c) and it becomes

$$Q = Q_{\text{I}} - (k/e)\delta(\rho/\rho_{\text{II}}). \tag{33}$$

Since Q_{I} is negative, it is clear from Eqs. (32) and (33) that

$$|Q_{\text{II}}| > |Q_{\text{I}}| \tag{34a}$$

and that

$$|Q| > |Q_{\text{I}}|. \tag{34b}$$

The appearance of a higher-lying n-type band then results in making the measured (total) Seebeck coefficient more negative than it would have been otherwise. It is obvious that this model cannot reconcile the large increase in ρ from 300 to 150 °K, with the considerable decrease in $|Q|$ over the same temperature range.

Spin Disorder Scattering

The analysis of Sec. II has ascribed the temperature dependence of the transport properties entirely to variations in carrier concentration. By comparison, the scattering times were assumed to be much more slowly varying functions of temperature. While this is reasonable for conventional lattice and ionized impurity scattering,[13] the scattering by spin disorder must be considered more carefully, particularly as it may affect the Seebeck coefficient.

The scattering of electrons by spin disorder was first considered by de Gennes and Friedel.[17] The local exchange between the itinerant electron spin and the spins of the localized moments is treated in the Born approximation. In the high-temperature limit ($T \gg T_C$), they obtain a temperature-independent scattering rate due to random fluctuations of the ion spins, given by

$$\tau_0^{-1} = c(hk_0/m)\sigma_0, \tag{35a}$$

with $$\sigma_0 = (1/4\pi)(m^*G/h^2)^2 S(S+1). \tag{35b}$$

Here, hk_0 is the electron momentum, c is the concentration of magnetic ions, G is the magnitude of the above-mentioned exchange interaction, and S is the magnitude of the ion spin. For $T < T_C$ and short electron wavelengths, the scattering rate τ^{-1} decreases with decreasing temperature, tending to zero as $T \to 0$, where the exchange interaction assumes the periodicity of the lattice. In the case of semiconductors, however, electrons whose thermal deBroglie wavelengths are large in comparison with the interion spacing are scattered by correlated motions of the ions and experience enhanced scattering in the vicinity of T_C. This is contained in the expression

$$\tau^{-1} = \tau_0^{-1}\frac{1}{4}\int_0^2 dx\, x^3 \bigg/ \left(1 - \frac{1}{t}\,\frac{\sin k_0 ax}{k_0 ax}\right), \tag{36}$$

where a is the lattice spacing and $t = (T/T_C)$ is the reduced temperature.

The various transport integrals over the above relaxation time are intractable. We therefore consider only the change in ρ and Q due to spin disorder, from $t \gg 1$ to $t \gtrsim 1$. The integration is facilitated by noting that

$$k_0^{\text{th}}\, a = (2m^*kT/\hbar^2)^{1/2} a \cong 0.2\ , \tag{37}$$

taking $T = 150$ °K, $m^* = m$, and $a =$ Cr-Cr distance[8] $= 3.8$ Å, where k_0^{th} is the thermal average electron momentum. The integrand can then be expanded for small $(k_0 a)$ and the integration taken straightforwardly. The result is

$$\tau^{-1} \cong \tau_0^{-1}\,(3!/2)t(k_0a)^{-2}[1-\ln(1+\beta)/\beta], \tag{38a}$$

where $\beta=(4/3!)[1/(t-1)](k_0a)^2$. (38b)

It is readily verified that Eq. (35) is recovered in the high-temperature limit $\beta \ll 1$ (arbitrarily large values of k_0a are precluded by the Boltzmann factor). In the opposite limit $\beta \gg 1$, in which T approaches T_C from above, one obtains

$$\tau^{-1}=(3!/2)ct(h/m^*a)\sigma_0(k_0a)^{-1}\,. \tag{39}$$

From Eqs. (35) and (39), the mobilities are calculated straightforwardly from the Einstein relation. The results are

$$\mu=\frac{4}{\pi^{1/2}}\,\frac{1}{c(h/m^*a)\sigma_0}\,\frac{1}{(k_0^{\text{th}}a)} \qquad \text{for } t\gg 1, \tag{40}$$

$$\mu=\frac{2}{\pi^{1/2}}\,(3!)\frac{1}{c(h/m^*a)\sigma_0}\,t(k_0^{\text{th}}a) \quad \text{for } t\gtrsim 1. \tag{41}$$

Thus,

$$\frac{\mu(t\gtrsim 1)}{\mu(t\gg 1)}=\frac{3!}{2}\left(\frac{2m^*k_\beta T_Ca^2}{h^2}\right)\left(\frac{T}{T_C}\right)^{1/2}$$

$$\cong 0.12\left(\frac{T}{T_C}\right)^{1/2} \tag{42a}$$

$$\text{and}\quad \frac{\mu(130\,^\circ\text{K})}{\mu(300\,^\circ\text{K})}=0.17. \tag{42b}$$

Not only is this insufficient to account for the four order-of-magnitude variation in resistivity shown in Fig. 1, but it predicts a maximum in ρ at T_C, contrary to the data.

Finally, the scattering factor α_s for the Seebeck coefficient [Eq. (3a)] is obtained. For a scattering mechanism characterized by

$$\tau \sim k_0^p\,, \tag{43}$$

this is given by[18]

$$\alpha_s=\tfrac{5}{2}+\tfrac{1}{2}p. \tag{44}$$

Hence, from Eqs. (35) and (39), α_s increases from $\alpha_s=2$ when $t\gg 1$ to $\alpha_s=3$ when $t\sim 1$.

Thus, the variation in the scattering factor predicts an additional increase in $|Q|$ of $1\times(k/e)=86\ \mu\text{V}/^\circ\text{K}$ in going from $T\gg T_C$ to $T\sim T_C$. Although this may account for part of the increase at T_C, it is clearly insufficient to account for the total increase shown in Fig. 1. In addition, it does not explain the decrease in $|Q|$ from 250 to 150 °K. Furthermore, it has already been noted that this decrease in $|Q|$ is incompatible with the temperature dependencies of ρ and R_0 in a single-band model. Hence, we conclude that the inclusion of spin-disorder scattering within a single-band model cannot, by itself, explain our data.

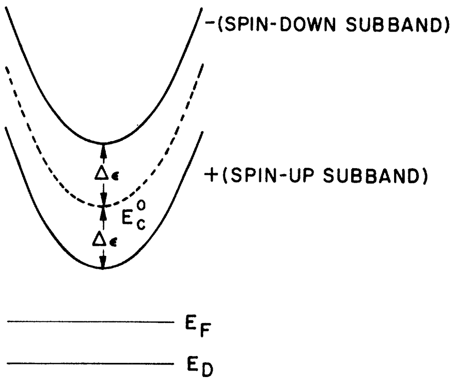

FIG. 5. Spin splitting of the conduction band.

Effect of Exchange Splitting of Conduction Band on Transport Properties

An essential feature of the present model is the shift of the energy bands, and therefore interband energies, with magnetic order.[6,7] With the onset of long-range order below T_C, the conduction band will, in addition, be split into spin-up and spin-down polarized subbands[7] shown in Fig. 5. In the present section, we show very briefly that while the splitting may account for the rapid decrease in $|Q|$ just below T_C, it otherwise cannot account for the data.

The first-order energy splitting is given by[7]

$$\Delta E^{\pm}=\mp\tfrac{1}{2}SJ(M/M_0), \tag{45}$$

where (+, −) refer to the splitting of the (lower, upper) subbands relative to the unperturbed band, S is the magnitude of the ion spin, J is the exchange integral, and (M/M_0) is the relative magnetization.

It may be easily verified that dependence of the Fermi level on the splitting is given by replacing true density of states by an effective density of states:

$$N_C^{(\text{eff})}=N_C^\circ\cosh(\Delta E/kT). \tag{46}$$

$$\text{Thus,}\quad E_F=E_F^\circ-\tfrac{1}{2}kT\ln\cosh(\Delta E/kT), \tag{47}$$

where E_F^0 is the Fermi level in the absence of splitting. It is seen that E_F decreases with magnetic order; for $\Delta\epsilon>kT$, E_F decreases at half the rate of the band splitting so as to stay midway between the lower (+) subband and donor level,[19] as it must.

Substituting the partial carrier densities

$$n^{\pm}=\tfrac{1}{2}N_C^0\exp[-(E_C^0\mp\Delta\epsilon-E_F)/kT] \tag{48}$$

into the standard two-band expressions for Q, we obtain

$$Q=Q^0+Q^s+Q(\Delta\epsilon), \tag{49}$$

where Q^0 is the unperturbed part of Q exclusive of the scattering factor, Q^s is a part depending on the scattering factors of the individual subbands, and

$$Q(\Delta\epsilon) = -\frac{k}{e}\left(\tfrac{1}{2}\ln\cosh\frac{\Delta\epsilon}{kT} - \frac{\Delta\epsilon}{kT}\frac{n^+\mu^+ - n^-\mu^-}{n^+\mu^+ + n^-\mu^-}\right) \qquad (50)$$

is the part explicitly dependent on magnetic order, where $\mu^\pm$ are the mobilities of the respective subbands.

The scattering rates within the subbands may be written as a part due to exchange scattering plus a part due to unspecified but spin-independent processes. Now, if the former process were dominant, the mobility of the lower subband, which contains nearly all the carriers below T_C, would be expected to rise precipitiously in this temperature range. On the contrary, our data[3] show that μ_H rises slowly from 4.2 °K to T_C. Thus, nonmagnetic scattering processes must dominate, and $\mu^+ \cong \mu^- \equiv \mu_0$. Equation (50) then reduces to

$$Q(\Delta\epsilon) \simeq -(k/e)[\tfrac{1}{2}\ln\cosh(\Delta\epsilon/kT) - (\Delta\epsilon/kT)]. \qquad (51)$$

This quantity is zero at $\Delta\epsilon/kT = 0$, increases to *positive* values, saturating at

$$Q(\Delta\epsilon_{\text{sat}}) = +(k/e)(\Delta\epsilon_{\text{sat}}/2kT + \tfrac{1}{2}\ln 2) \qquad (52)$$

for $(\Delta\epsilon/kT) \gg 1$. For representative values of the parameters ($T_C = 130$ °K, $S=\frac{1}{2}$, $J = 0.2$ eV),

$$Q(\Delta\epsilon_{\text{sat}}) \sim +10k/e. \qquad (53)$$

This decrease in the magnitude of the negative electronic Seebeck coefficient just at T_C is in agreement with the lower curve of Fig. 1. However, since the magnetization is fully saturated[7] just a few degrees below T_C, it follows from (45) and (52) that the above decrease in $|Q|$ at T_C should be completed within this same narrow temperature range. However, Fig. 1 shows a monotonic decrease in $|Q|$ extending toward zero temperature. This must then reflect other factors, such as the onset of carrier degeneracy as the donor level approaches the conduction band. Furthermore, the spin splitting does not occur in the temperature range above T_C where anomalous behavior of Q is also observed.

V. ATOMIC ORIGINS OF THE BANDS

In this section, we first discuss what experimental evidence is available for the atomic origins of the relevant energy bands.

In the absence of any band-structure calculations or optical determinations of the band structure, we can only speculate on the atomic origins of the bands consistent with experimental information. We would reasonably assume that the valence band is constructed mainly from the 4*p* orbitals of the selenium anions. The principal conduction band is likely an admixture of the 4*s* orbitals on the Cd, with the 3*d* or 4*s* states of Cr. The latter is needed in order to have sufficient intra-atomic exchange to account for the substantial red shift of the optical energy gap, *if* it is assumed that the latter is a band-to-band transition.[20]

The evidence for the assignment of the donor level is more definite. Namely, it is thought that the donor levels arise not from In ions, but from the selenium deficiencies. As shown by the upper curve in Fig. 2, when the sample is annealed in a selenium atmosphere, the resistivity increases by about four orders of magnitude as indicated. In addition, it continues to increase monotonically with decreasing temperature with an activation energy which is very near one-half the optical energy gap. The marked decrease in resistivity about the Curie temperature is absent in the defect-free samples. This evidence strongly suggests that annealing in the selenium atmosphere removes the extrinsic sources of carriers, leaving only intrinsic excitation from the valence band (or perhaps, the subsidiary-hole band).

Furthermore, it is noted that the above behavior for the defect-free sample obtains in spite of the presence of 2.7 at. % of indium. This suggests that indium does not act like a donor in the usual way, but, rather, lies in the gap, below the selenium defect level. Thus, it should be possible to have *n*-CdCr_2Se_4 due to selenium defects alone. That this is in fact the case is shown in Fig. 6 which shows resistivity data taken on a vacuum-annealed sample (i.e., containing selenium deficiencies) but with no indium. The high-temperature activation energy was indeed ~0.21 eV. The Seebeck coefficient was negative, indicating *n*-type conduction. For $T \lesssim 150$ °K, the resistance saturated to a new small activation energy. This is consistent with the proposed model since, as indicated immediately below, in the absence of the indium, there is no reason for the donor activation energy or resistance to decrease. The low-temperature behavior may be interpreted as impurity conduction among the electrons localized about selenium deficiencies.

This interpretation suggests a possible origin for the postulated, subsidiary *p* band. Namely, in the selenium-deficient but indium-free sample, there would be two electrons per missing selenium ion arising, perhaps, from the 4*s* electrons of the chromium. Upon doping with indium, if it be assumed that the indiums overlap sufficiently to form an impurity band, such a band would be just half filled. Some of the empty states could, however, be filled by electrons about the missing selenium sites, resulting in a more-than-half-filled band

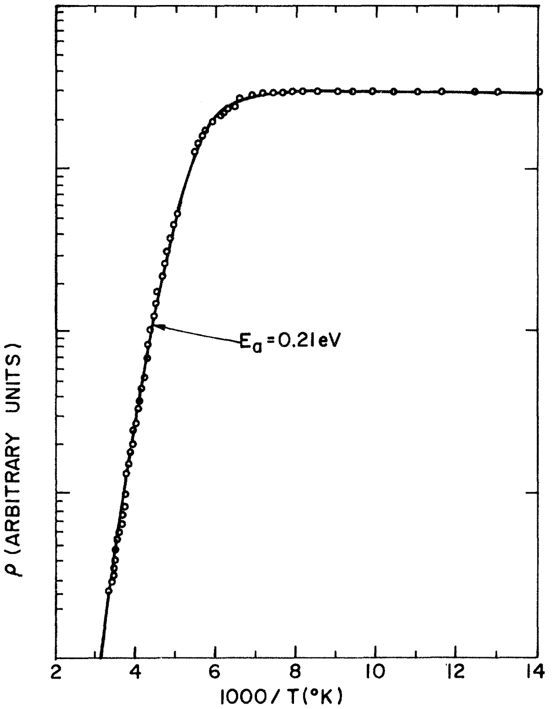

FIG. 6. Resistivity versus T^{-1} for a Se-deficient sample undoped (intrinsic). E_a is the thermal activation energy for the resistivity.

with p-like behavior. At the $x = 0.01$ doping level, the mean indium separation is $d = (3/4\pi N_{\text{In}})^{1/3} \sim 40$ Å where $N_{\text{In}} = 3.6 \times 10^{18}$ cm^{-3} is the indium concentration. The Bohr radius of an s electron about a In^{3+} impurity, treated in a hydrogenic model, is $a_B = 0.53\epsilon(m/m^*)$ Å, where $\epsilon_0 > 9$ is the dielectric constant,[21] and m and m^* are the free-electron and effective masses, respectively. In the absence of any band structure or optical determinations of m^*, let us assume that $(m^*/m) = 0.2$. In this case, $a_B \gtrsim 25$ Å and $(d/a_B) \lesssim 1.6$, which is in the impurity-banding regime. On the other hand, if $(m^*/m) = 1$, $(d/a_B) \lesssim 8$, which is more likely in the impurity-hopping regime. Thus, the effective mass must be sufficiently small so that an impurity band results, in order that the above behavior obtain.

This interpretation of the roles of the indium and selenium defects is further corroborated by the following: In all the samples investigated which did not contain selenium defects, the Seebeck coefficient was positive, regardless of whether or not they were doped with indium. On the other hand, once they were vacuum annealed, thereby introducting selenium defects, not only did the resistivity-versus-temperature curves change drastically as already indicated, but the sign of the Seebeck coefficient became negative. This was true even for the selenium-deficient sample without any indium shown in Fig. 6.

VI. CONCLUSIONS

A two-band model consisting of an n-type and a p-type band has been proposed to explain and reconcile the temperature dependences of the electrical resistivity, the Hall, and the Seebeck coefficients of n-type $\text{Cd}_{1-x}\text{In}_x\text{Cr}_2\text{Se}_4$ from room temperature to below the Curie temperature. The fact that both the high-temperature resistivity and the absolute value of the Hall coefficient increase with decreasing temperature with essentially identical activation energies is strong evidence that the changes in transport coefficients are due to carrier-density variations rather than to mobility variations. In this connection, it has been shown that spin-disorder scattering, expected to be the dominant scattering mechanism in the vicinity of the Curie temperature, cannot account for the large variations in resistivity and Seebeck coefficient. Furthermore, it has been shown that both a single-band model and one involving two n-type bands are inapplicable; nor can the spin splitting of the conductance band account for the transport data. Thus, the proposed model, while not unique, is the simplest multiband model capable of accounting for the data. Verification of the model must await band-structure calculations, providing information on the orbital character of the energy-band levels, effective masses, etc. In the meantime, there are a number of experimental tests of the model as well as experiments to obtain the detailed temperature dependences of the characteristic interband energies. Among these are

(a) following both $(E_C - E_D)$ and $(E_C - E_p)$ by optical absorption in the near to far infrared as the temperature is decreased from 300 °K to T_C (see Fig. 4);

(b) detecting the lower-lying valence band E_p in detailed optical-absorption, reflectivity, or tunneling experiments;

(c) determination of the relative positions of the conduction and p-bands by photoinjection from a metal contact. This technique has been applied successfully to study the detailed structure of the narrow conductivity bands of crystalline anthracene.[22]

(d) The model predicts that the bandlike behavior at high temperatures goes over into localized transport among the Cr ions for $T \lesssim 50$ °K. A larger fraction of the excess electrons will therefore get transferred from the conduction band to the d levels with decreasing temperature. Since the Cr^{2+} ions so formed are antiferromagnetically coupled[9] to the host Cr^{3+}, a decrease in sample moment should be observed with decreasing temperature, for a fixed indium concentration.

(e) More detailed studies of the effect of annealing in a selenium atmosphere are clearly called for. The effect of annealing on the high- and low-temperature activation energies of the resistivity (as well as its magnitude) should be examined. The Seebeck anomaly as well should be studied for various selenium concentrations.

ACKNOWLEDGMENT

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