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Spin-disorder Scattering and Band Structure of the Ferromagnetic Chalcogenide Spinels

Abstract: Magnetic semiconductors are characterized by the presence of charge carriers and magnetic moments. The interaction between the charge carriers and the magnetic moments leads to a spin splitting of the energy bands, and to spin-disorder scattering of the charge carriers. The result is a strong influence of magnetic properties on the transport properties. The theory of these effects is discussed in the first part of this paper. In the second part two models for the band structure of $CdCr_2Se_4$ are discussed, and compared with experimental data on the optical properties and the transport properties.

Introduction

The chalcogenide spinels show a large variety of magnetic and electrical properties.[1,2] They are either metallic or semiconducting, and one finds in this class of materials ferromagnets, antiferromagnets, ferrimagnets and pauli-paramagnetism.

Some chalcogenide spinels, e.g. $CdCr_2S_4$, $CdCr_2Se_4$, $HgCr_2S_4$ and $HgCr_2Se_4$, are ferromagnetic semiconductors.[3] In these compounds the magnetic properties have a large influence on the transport properties. It was found, for example, that the electrical resistivity and the magneto-resistance show pronounced maxima at the Curie temperature.[4-8] Although these effects have been studied by various authors, the interpretation of the data is by no means clear at present. This is due partly to difficulties in preparing good quality single crystals, and to deviations of stoichiometry.[9]

However, there are also more fundamental problems. Little is known with certainty about the band structure of ferromagnetic semiconductors of the chalcogenide-spinel type. Rehwald[10] has calculated qualitatively the band structure of $CdIn_2S_4$; unfortunately it is not possible to calculate in a similar way the position of the d-bands in compounds such as $CdCr_2Se_4$. Moreover, there is no quantitative theory for the transport properties of narrow-band electrons in magnetic materials,[11] so that experimental data are of little help in making decisions about the type of charges carriers.

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In this paper no final answer can be given to these questions. We will rather give a description of the present situation.

The theory of the influence of localized magnetic moments on the electronic energy levels[12,13] and the transport properties[13] of magnetic semiconductors has been worked out in considerable detail; a survey of this theory is given in the next section. In the last section some experimental data on the optical and the transport properties of ferromagnetic semiconductors of the chalcogenide-spinel type are discussed and compared with models for the band structure that have been proposed in the literature.

Band structure and spin-disorder scattering

In this section we discuss the influence of the magnetic properties on the band structure and the transport properties of ferromagnetic semiconductors. The discussion is given for a simple model, a crystal containing one type of magnetic atom with spin S and magnetic moment $g\mu_B S$. At low temperature all magnetic moments are aligned parallel to one another by an exchange interaction among these magnetic moments. In addition to the magnetic moments, the crystal contains a relatively small number of charge carriers, occupying the states of a broad conduction band. There will exist an exchange interaction between the spin of a charge carrier and the spins of the magnetic atoms. This interaction is written as

$$H^1 = -\sum_n J(|\mathbf{r} - \mathbf{R}_n|)\mathbf{s}\cdot\mathbf{S}_n, \qquad (1)$$

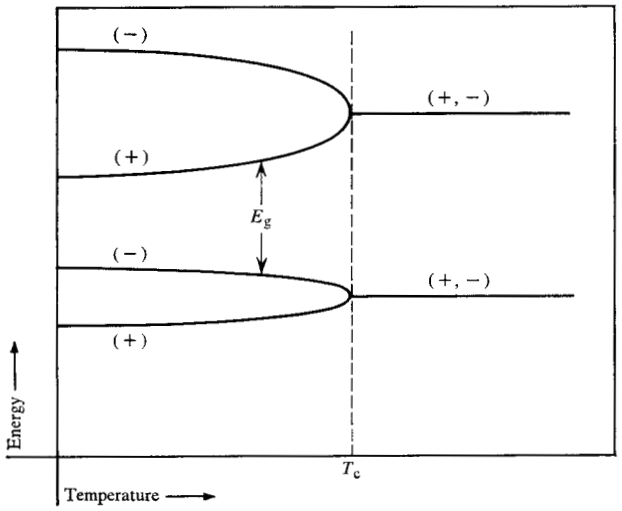


Figure 1 Spin splitting of conduction and valence bands in a ferromagnetic semiconductor. The energy gap is E_g.

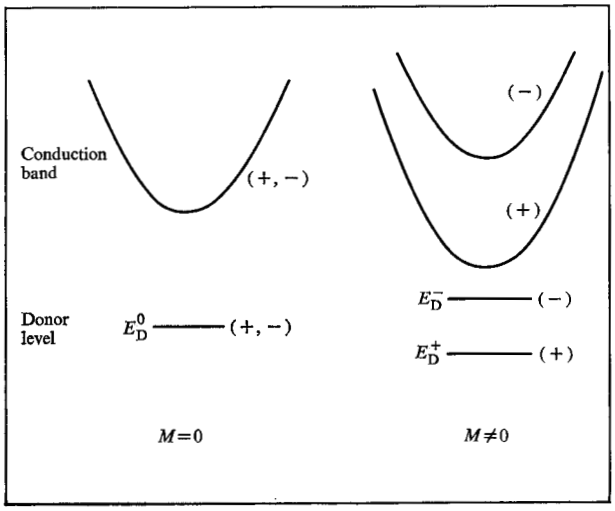


Figure 2 Spin splitting of conduction band and donor level, leading to a change of the donor ionization energy.

where $J(|\mathbf{r} - \mathbf{R}_n|)$ gives the interaction as a function of the distance $|\mathbf{r} - \mathbf{R}_n|$ between a charge carrier with spin $\mathbf{s}$ at $\mathbf{r}$, and a magnetic atom with spin $\mathbf{S}_n$ at $\mathbf{R}_n$. The sum is over all magnetic atoms, the total magnetization of the magnetic atoms is $\mathbf{M} = \sum_n g\mu_B \mathbf{S}_n$.

An interaction of this type has been used frequently in the literature to discuss the interaction between magnetic moments and conduction electrons; it is for example, the basis of the Rudermann-Kittel-Kasuya-Yosida theory for indirect exchange via conduction electrons.[14] More recently the interaction was used to discuss the spin splitting of energy bands[12,13] and spin-disorder scattering[13] in magnetic semiconductors.

The interaction of Eq. (1) causes a different energy for conduction electrons with spin parallel (+) and antiparallel (−) to the magnetization $\mathbf{M}$. A simple calculation with first-order perturbation theory gives for this spin splitting of the conduction band

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

where $J = N \int |u(\mathbf{r})|^2 J(|\mathbf{r} - \mathbf{R}_n|)\, dv(\mathbf{r})$, $M_0 = Ng\mu_B S$, N is the number of magnetic atoms per cm^3 and $u(\mathbf{r})$ is the periodic part of the Bloch functions $\phi_k = u(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r})$ describing the conduction electrons. Figure 1 shows this spin splitting of the conduction and valence bands. Because M depends on T, the spin splitting depends also on T, and this fact results in an anomalous temperature dependence of the energy gap E_g.[15]

Donor and acceptor atoms in semiconductors form localized states falling in the energy gap between valence and conduction bands. Electrons in these localized states will also experience exchange interactions with the spins of magnetic atoms. A quantitative discussion of these effects is quite complicated and depends on the nature of the donor or acceptor levels.[16–18] Generally, however, donor (and also acceptor) states will split into separate energy levels for electrons with (+) and (−) spins:[7,13]

$$E_D^{\pm} = E_D^0 \mp \tfrac{1}{2}\gamma JS(M/M_0), \tag{3}$$

where γJ is a measure of the splitting. If the splitting of the donor state is different from the splitting of the conduction band (i.e. if $\gamma \neq 1$), the donor ionization energy will change with M (Fig. 2). This effect can lead to an anomalous temperature dependence of the charge-carrier concentration.

In nonmagnetic semiconductors charge carriers are scattered by impurities and lattice vibrations. In many magnetic crystals these effects are dominated by spin-disorder scattering, that is, the scattering of charge carriers at the disorder in the spin system.[19,20] Except at $T = 0$°K, the spins are not completely aligned, and the fluctuations or deviations of spins from the average orientation cause a strong scattering of the charge carriers. This spin-disorder scattering is also a consequence of the exchange interaction [Eq. (1)] between charge carriers and atomic spins.

On the basis of Eq. (1) it is possible to calculate the mobility of the charge carriers, using perturbation theory.[13] The result for a non-degenerate ferromagnetic semiconductor is

$$\mu^{\pm} = \frac{8(2\pi)^{1/2}(Ng\mu_B)^2 e\hbar^4}{3m^{*5/2}J^2(k_B T)^{3/2}} \times \int_0^{\infty} \frac{te^{-t}\, dt}{\chi^z + 2f^{\pm}\chi^x[1 \mp (\delta/t)]^{1/2}}, \tag{4}$$

where k_B is the Boltzmann constant, m^* the effective mass of the carriers, and $\delta = SJM/M_0 k_B T$ is a measure of the

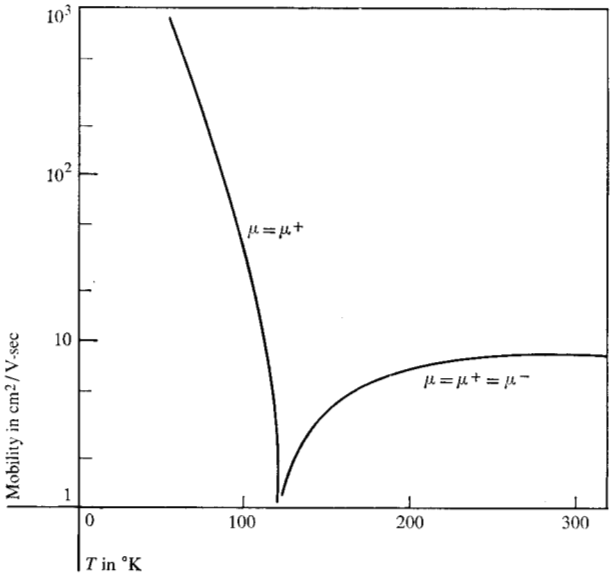


Figure 3 Calculated mobility as a function of temperature for a ferromagnetic semiconductor (with $S = 3/2$, $J = 0.5$ eV).

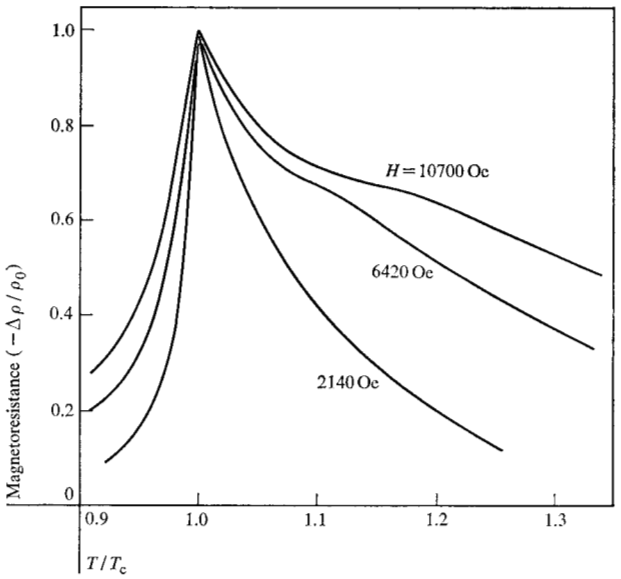


Figure 4 Calculated magnetoresistance, assuming that the carrier concentration is field independent (with $S = 3/2$, $J = 0.5$ eV).

spin splitting of the conduction band. J is the same exchange constant, used above to express the spin splitting of the conduction band and $f^{\pm}$ is a constant with value 1 for $[1 \mp (\delta/t)]^{\frac{1}{2}}$ real, and with value 0 for imaginary values of $[1 \mp (\delta/t)]^{\frac{1}{2}}$. The mobilities of electrons in the (+) and (−) subbands are given by μ^+ and μ^- respectively. χ^z and χ^x are the magnetic susceptibilities for fields parallel and perpendicular to the magnetization **M**.

For a degenerate ferromagnetic semiconductor, the mobilities are given by

$$\mu^{\pm} = \frac{2\pi\sqrt{2}(Ng\mu_B)^2 e\hbar^4(\epsilon_F^{\pm})^{\frac{1}{2}}}{m^{*5/2}J^2k_BT} \times\left\{\left(\frac{\hbar^2}{8m^*A_z}\right)\ln\left[1 + (8m^*A_z\chi^z\epsilon_F^{\pm}/\hbar^2)\right] + 2\alpha\left(\frac{\hbar^2}{8m^*A_x}\right) \times\ln\left[\frac{1 + (2m^*A_x\chi^x/\hbar^2)[\epsilon_F^{\pm} + \epsilon_F^{\mp} + 2(\epsilon_F^{\pm}\epsilon_F^{\mp})^{\frac{1}{2}}]}{1 + (2m^*A_x\chi^x/\hbar^2)[\epsilon_F^{\pm} + \epsilon_F^{\mp} - 2(\epsilon_F^{\pm}\epsilon_F^{\mp})^{\frac{1}{2}}]}\right]\right\}^{-1}. \quad (5)$$

In this expression ϵ_F^+ and ϵ_F^- are the Fermi energies in the (+) and (−) subbands with respect to the minima of these subbands; α is a constant with value 1 if both ϵ_F^+ and ϵ_F^- are positive, and with value 0 if either ϵ_F^+ or ϵ_F^- is negative.

The magnetic susceptibilities occur in these equations because the fluctuations of the magnetization with wave vector **k** can be expressed in terms of generalized susceptibilities $\chi^z(\mathbf{k})$ and $\chi^x(\mathbf{k})$.[21] For small values of **k**, one has $1/\chi^z(\mathbf{k}) = (1/\chi^z) + A_zk^2$ and $1/\chi^x(\mathbf{k}) = (1/\chi^x) + A_xk^2$, where χ^z and χ^x are the normal magnetic susceptibilities for homogeneous magnetic fields. In nondegenerate semiconductors the terms A_zk^2 and A_xk^2 in the susceptibilities can be neglected (except at temperatures very close to T_c, where $1/\chi^z$ and $1/\chi^x$ are very small); this approximation has been used to obtain Eq. (4). For a degenerate semiconductor with a large charge-carrier concentration, this approximation is not valid, and the full expression [Eq. (5)] should be used. For simple cubic lattices (as in EuS or $CdCr_2Se_4$), and assuming exchange interactions of only one type between magnetic moments separated by a distance b, one finds[22]

$$A_z = A_x = \frac{k_BT_cb^2}{2N(g\mu_B)^2S(S+1)}. \quad (6)$$

The terms with χ^z and χ^x in Eqs. (4) and (5) represent the effects of scattering within one subband [without change of spin: (+)→(+) or (−)→(−)], and between subbands [spin-flip scattering (+)→(−) or (−)→(+)], respectively.

The result of a calculation of the mobility of charge carriers in a non-degenerate ferromagnetic semiconductor, using Eq. (4), is shown in Fig. 3. The calculations[13] are for $S = 3/2$, $J = 0.5$ eV and $m^* = m_0$. In the ferromagnetic region $T < T_c$, the spin splitting of the bands is large compared to k_BT, and practically all carriers will occupy states of the lower-subband (+), so that $\mu = \mu^+$. Above T_c there is no spin splitting, and $\mu^+ = \mu^- = \mu$. The calculated mobility shows a pronounced minimum at T_c. This is due to the fact that long-range fluctuations of the magnetization are large at T_c (critical fluctuations),

and it is these long-range fluctuations in particular which are responsible for the scattering of the charge carriers in semiconductors.

A direct consequence of spin-disorder scattering is that one expects a large influence of magnetic fields on the mobility. This is due to the fact that the susceptibilities, occuring in the expressions for the mobility, are field dependent. Moreover, the distribution of charge carriers between the two subbands is influenced by the magnetic field.[13] A third contribution to the magnetoresistance may come from the change of the carrier concentration by a magnetic field; this effect is a direct consequence of the dependence of the donor ionization energy on the magnetization.[7] Results of calculations of these contributions to the magnetoresistance are given in Figs. 4 and 5.

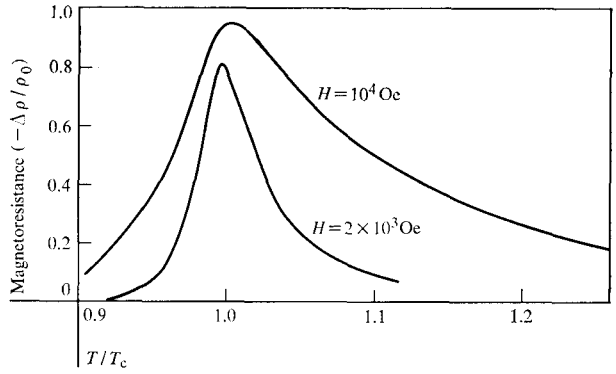


Figure 5 Calculated magnetoresistance, assuming a field independent mobility. The calculation is for a donor level (with $E_D^0 = 0.2$ eV, $\gamma = 1/2$, $S = 3/2$ and $J = 0.5$ eV).

Band structure and transport properties of ferromagnetic semiconductors of the chalcogenide-spinel type

Several ferromagnetic semiconductors of the chalcogenide-spinel type are known; the Curie temperatures[3] and energy gaps[5,23–25] are given in Table 1. Except for $CdCr_2S_4$, the edge absorption shows no pronounced structure, and its shape does not change with temperature. The position E_g of the absorption edge shows a large shift to longer wavelength (red shift) below the Curie temperature. For $CdCr_2S_4$ the temperature dependence of the edge absorption is quite different; the shape of the absorption curve changes with temperature and the edge shifts to shorter wavelength (blue shift) at low temperature.[24]

Various interpretations of the edge shift have been proposed in the literature. Callen[26] proposed an explanation in terms of a magneto-elastic coupling, but recent measurements[5,27] indicate that this effect is too small to account for the observed shift.

Goodenough[28] has discussed the energy levels of chalcogenide spinels. The model he proposed for $CdCr_2S_4$ and $CdCr_2Se_4$ (Fig. 6) is based on the following arguments. The mobility of holes in $CdCr_2S_4$ and $CdCr_2Se_4$ is quite large, that of electrons is much smaller.[4] This indicates that the holes are charge carriers in a broad valence band. Consequently the $Cr^{3+}(^4A_{2g})$ levels, which presumably form a rather narrow band, lie below the top of the valence band. According to Goodenough, the low mobility of electrons indicates conduction in a narrow d-band, i.e., a band consisting of Cr^{2+} d levels, which should then be situated below the bottom of the broad conduction band. For a Cr^{2+} ion with d^4 configuration, one expects the high-spin ^5E_g state to be rather close to the low-spin $^3T_{1g}$ state. The difference between the edge absorption spectra of $CdCr_2S_4$ and $CdCr_2Se_4$ is explained by assuming that, in $CdCr_2S_4$, the $Cr^{2+}(^5E_g)$ state lies below the $Cr^{2+}(^3T_{1g})$ state, whereas the two states have approximately the same energy in $CdCr_2Se_4$. The edge absorption in $CdCr_2S_4$ would then be due to a transfer of electrons from the lower subband (+) of the spin-split valence band to $Cr^{2+}(^5E_g)$. The transition from the higher subband (−) is spin forbidden; the weak absorption below the edge in $CdCr_2S_4$ [24] might be due to magnon-assisted transitions of this type. In $CdCr_2Se_4$ the edge absorption is due to a transfer of electrons from the upper subband (−) to $Cr^{2+}(^3T_{1g})$; this transition is not spin forbidden, because in the $^3T_{1g}$ state there is one electron with antiparallel spin. The shift of the absorption edge is attributed in this model to the spin splitting of the valence band.

Another possibility is that the broad conduction band lies below the Cr^{2+} states, and that the spin splitting of the conduction band is responsible for the red shift of the edge in all semiconducting chalcogenide spinels except $CdCr_2S_4$.[6] In this model (Fig. 7) the small mobility and the large magnetoresistance of n-type $CdCr_2Se_4$ are explained in terms of spin-disorder scattering of the charge carriers, using a spin splitting of the conduction band of about 0.75 eV. This value is about the spin splitting required to explain the red shift of the edge if it were due mainly to the spin splitting of the conduction band. The much larger mobility and the small magnetoresistance of p-type $CdCr_2Se_4$ indicate indeed a weak interaction between

Table 1 Ferromagnetic semiconductors of the chalcogenide spinel type.

	Curie temperature T_c *(in °K)*	*Energy gap* E_g *at 300°K (in eV)*
$CdCr_2S_4$	84	1.57
$HgCr_2S_4$	36	1.42
$CdCr_2Se_4$	130	1.32
$HgCr_2Se_4$	106	0.84

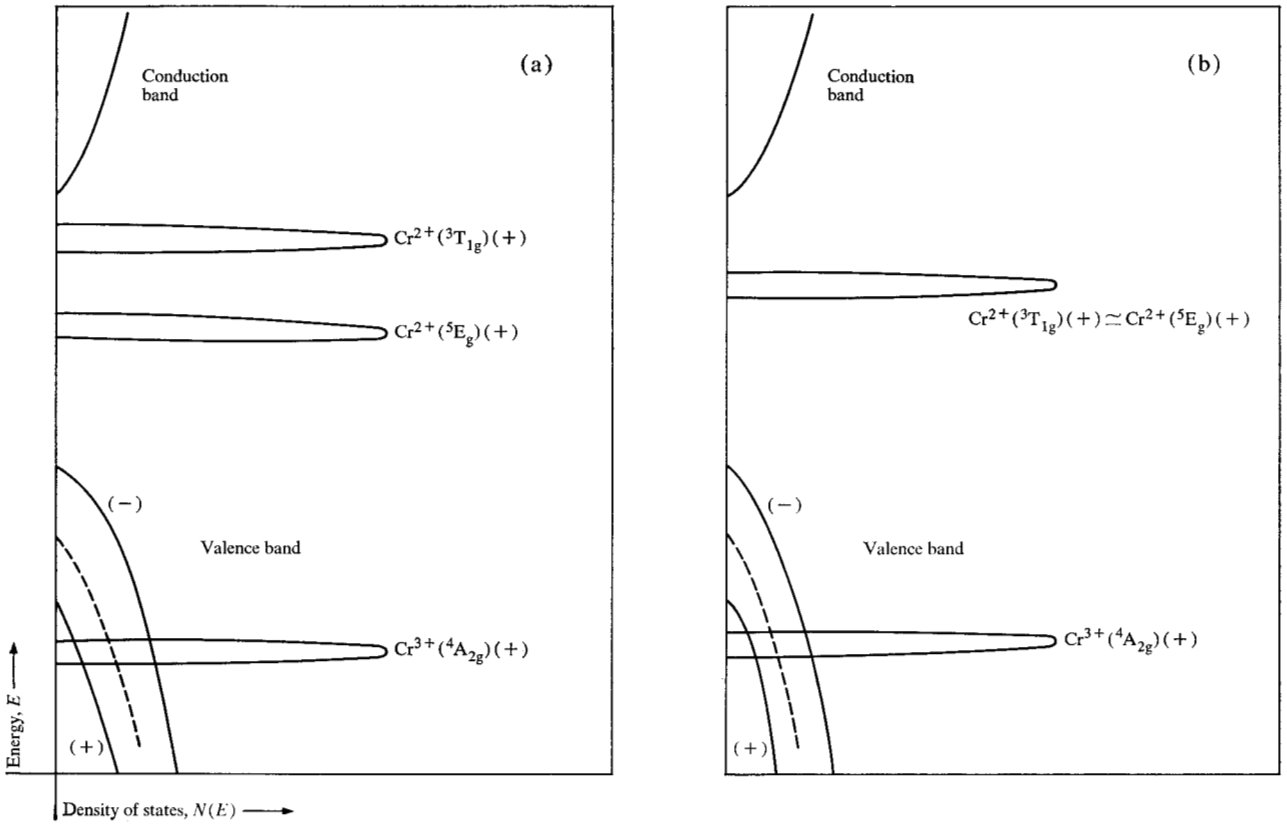


Figure 6 Schematic energy level diagram [energy E vs density-of-states $N(E)$] for (a) $CdCr_2S_4$ and (b) $CdCr_2Se_4$ at $T < T_c$, according to Ref. 28. The position of the valence band at $T > T_c$ is indicated by the dashed line.

holes in the valence band and magnetic moments, and consequently a small spin splitting of the valence band.

The states of the conduction band are primarily 4s-orbitals of Cr^{3+} (excess electrons will presumably have a high density on atoms of high positive charge). For electrons of this type one expects a spin splitting somewhat smaller than the intra-atomic exchange splitting of 0.9 eV between the $S = 2$ and $S = 1$ states of a free Cr^{2+} ion with configuration $3d^3(^4A_{2g})4s$. The top of the valence band consists of non-bonding p-orbitals of the anion.[10] For states of this type one expects indeed a small intra-atomic exchange interaction with magnetic moments of Cr^{3+}. Thus the spin splitting of the valence band is expected to be small.

Recent magneto-optical data on $CdCr_2Se_4$ have been discussed in terms of this model.[7] The polar Kerr effect of $CdCr_2Se_4$ shows a spectrum with three sign reversals of the Kerr rotation (Fig. 8). Each sign reversal corresponds to a strong magneto-optical transition. Transitions 1, 2 and 3 are assigned to transitions of electrons from the valence band to the conduction band (1), from $Cr^{3+}(^4A_{2g})$ levels to the conduction band (2), and to a charge transfer transition Se $\rightarrow$ Cr from the valence band to a $Cr^{2+}(d^4)$ level (3). This assignment places the $Cr^{2+}(d^4)$ level at about 1.5 eV above the bottom of the conduction band, and the Cr^{3+} level at about 0.6 eV below the top of the valence band.

Both models for the energy levels (Figs. 6 and 7) leave some problems unsolved. In our opinion the spin splitting of the valence band, assumed by Goodenough, is too large for a band of states having only a small density on the magnetic atoms. On the other hand, the alternative model (Fig. 7) does not explain the observed blue shift of the edge in $CdCr_2S_4$.

Recent publications, however, have opened two ways to understand a blue shift of the absorption edge even in the case of an energy level diagram as shown in Fig. 7. For direct transitions one expects a red shift due to the spin splitting of the bands. However, if the edge absorption is due to indirect transitions, an apparent blue shift, caused by the change of the shape of the absorption curve with temperature, is possible.[29] Secondly, a comparison of the spectra of $CdCr_2S_4$ with spectra of $CdIn_2S_4$, doped with Cr, indicates that the edge in $CdCr_2S_4$ is not the semiconductor band edge, but rather the wing of the $^4A_2 \rightarrow {}^4T_2$ crystal field transition.[30]

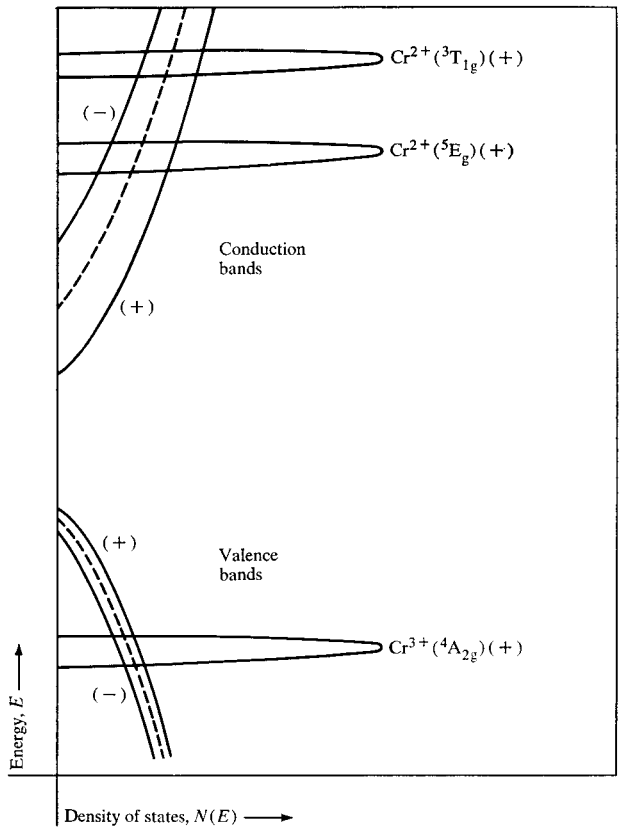


Figure 7 Alternative energy level diagram for $CdCr_2Se_4$ at $T < T_c$. Conduction and valence bands at $T > T_c$ are indicated by dashed lines.

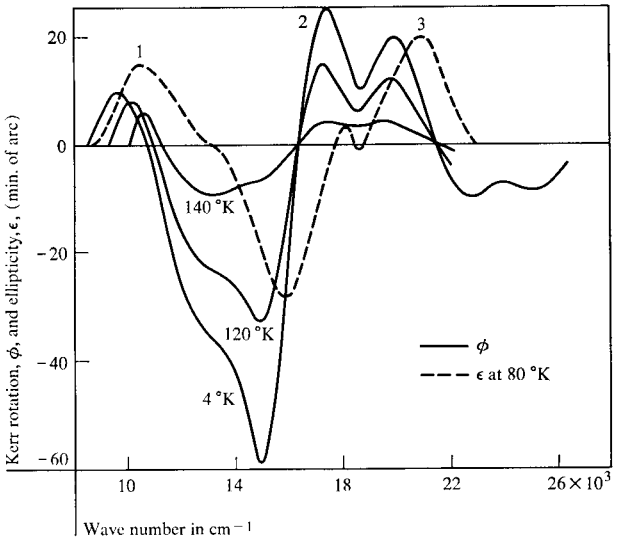
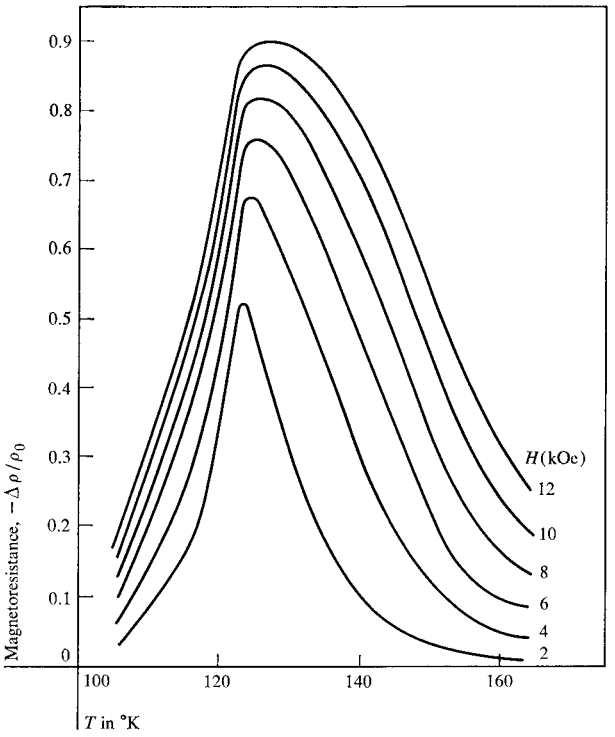


Figure 8 Magneto-optical polar Kerr effect of $CdCr_2Se_4$: rotation ϕ and ellipticity ϵ, according to Ref. 7.

Figure 9 Magnetoresistance of n-type $CdCr_2Se_4$ (2% Ga-doped), according to Ref. 6.



In a band structure of the type shown in Fig. 7, conduction electrons occupy states in a broad band. This makes it possible to apply the theory of spin-disorder scattering to this case. The magnetoresistance observed for $CdCr_2Se_4$ (Fig. 9), shows indeed a remarkable resemblance to the calculated curves (Fig. 4 or 5). The agreement with Fig. 4 is especially gratifying since for the calculations of the curves in this figure no adjustable parameters were used. The only parameter involved, the exchange interaction J, was taken from optical data on the shift of the absorption edge. Unfortunately this agreement is not a conclusive proof that charges carriers in n-type $CdCr_2Se_4$ do indeed occupy states in a broad conduction band. Since a quantitative theory of the transport properties of narrow-band electrons in magnetic materials has not been given so far, one does not know whether the experimental data would agree with such theory for electrons in a narrow d-band. The calculations of spin-disorder scattering, however, show at least that low values of the mobility do not necessarily indicate conduction in a narrow band, but might very well be due to strong, critical spin-disorder scattering.

A single-band model, with charge carriers of only one type, is perhaps not sufficient to explain all data on the electrical properties of $CdCr_2Se_4$. The complicated behavior of the Seebeck effect has been considered as an indication of the presence of charge carriers of several types.[8] These effects are probably due to contributions of impurity band conduction.

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