

Spin-Disorder Scattering and Magnetoresistance of Magnetic Semiconductors

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The consequences of a simple type of exchange interaction between free charge carriers in a broad energy band and localized magnetic moments are discussed. The interaction causes a splitting of the energy bands into bands for the two spin directions. It also leads to spin-disorder scattering of the charge carriers. The temperature dependence of the mobility is calculated for ferromagnetic and antiferromagnetic semiconductors. Expressions are given for the magnetoresistance of ferromagnetic semiconductors.

INTRODUCTION

THE electrical resistivity of nonmagnetic metals and semiconductors is due to the scattering of charge carriers by impurities and lattice vibrations. In magnetic materials, scattering due to a disorder of the magnetic moments is also possible. The importance of this mechanism is indicated by an abrupt change of slope, or even a peak, at the Curie temperature in the resistivity-versus-temperature curve.

The simplest calculations of this effect consider an exchange interaction between the free charge carriers, occupying states in a broad energy band, and localized magnetic moments responsible for the magnetic properties. Calculations of the resistivity as a function of the temperature, based on this model, have been given by several authors.¹⁻⁴

More complicated scattering mechanisms have been considered also. One of these is the so-called *s-d* scattering, i.e., the scattering of an electron from a state of a broad *s* band to a state of a narrow *d* band.^{5,6} Related to this is the resonance scattering in metals.⁷ These effects, however, are specific to metals, and not relevant to semiconductors.

This paper discusses the consequences of the simplest type of exchange interaction between free charge carriers in a broad band of a semiconductor and localized magnetic moments. The interaction mentioned causes a splitting of the energy band and an anomalous temperature dependence of the energy gap. These effects were discussed recently also by Rys *et al.*⁸ The temperature dependence of the mobility of charge carriers in ferromagnetic and antiferromagnetic semiconductors will be calculated. Finally, calculations are presented for the magnetoresistance of a ferromagnetic semiconductor.

The calculations given in this article are not valid at very low temperatures, i.e., far below the Curie temperature. This is because the quasistatic approximation, used here, is not valid at very low temperatures. For calculations in this temperature region, spin-wave theory should be used.

CHARGE CARRIERS AND LOCALIZED SPINS

For the calculations, it will be assumed that there are two distinct types of electronic states in the crystal. On the one hand, there are states derived mainly from the outer *s* and *p* orbitals of the atoms. These states overlap strongly, and are properly described by energy-band theory, just as in nonmagnetic semiconductors. The charge carriers in the magnetic semiconductors are assumed to occupy states in a broad energy band of this type.

In *3d* transition-metal compounds, there are also electronic states derived mainly from *3d* orbitals. Because of the much smaller extension of these orbitals, overlap is much smaller, and correlation energies are more important than for the states of the broad energy bands. Electrons in these *d* states are more localized, and are assumed to be responsible for the localized magnetic moments present in the magnetic semiconductor.

The electronic energy bands can be derived from a one-electron Hamiltonian⁹ \mathcal{H}_0 :

$$\begin{aligned} \mathcal{H}_0 \varphi_{b\mathbf{k}}(\mathbf{r}) &= [\mathbf{p}^2/2m + V_0(\mathbf{r})] \varphi_{b\mathbf{k}}(\mathbf{r}) \\ &= \epsilon_{b\mathbf{k}}^0 \varphi_{b\mathbf{k}}(\mathbf{r}). \end{aligned} \quad (1)$$

Here $V_0(\mathbf{r})$ is the periodic potential, $\epsilon_{b\mathbf{k}}^0$ the energy, and \mathbf{p} the momentum operator. The eigenfunctions $\varphi_{b\mathbf{k}}(\mathbf{r})$ are Bloch functions which can be written as $u_{b\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$, where \mathbf{k} is the wave vector and b a subscript labelling the various energy bands. The functions are normalized in unit volume, i.e.,

$$\int |\varphi_{b\mathbf{k}}(\mathbf{r})|^2 d^3v(\mathbf{r}) = 1.$$

$u_{b\mathbf{k}}(\mathbf{r})$ is a periodic function, invariant for translations which leave the crystal lattice unchanged.

⁹ See, for example, J. M. Ziman, *The Principles of the Theory of Solids* (Cambridge University Press, London, 1964).

¹ T. Kasuya, *Progr. Theoret. Phys. (Kyoto)* **16**, 58 (1956); **22**, 227 (1959).

² P. G. de Gennes and J. Friedel, *J. Phys. Chem. Solids* **4**, 71 (1958).

³ T. van Peski-Tinbergen and A. J. Dekker, *Physica* **29**, 917 (1963).

⁴ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **27**, 772 (1962).

⁵ N. F. Mott, *Proc. Phys. Soc. (London)* **47**, 571 (1935); *Proc. Roy. Soc. (London)* **153**, 699 (1936).

⁶ D. A. Goodings, *Phys. Rev.* **132**, 542 (1963).

⁷ Y. A. Rocher, *Advan. Phys.* **11**, 233 (1962).

⁸ F. Rys, J. S. Helman, and W. Baltensperger, *Physik Kondensierten Materie* **6**, 105 (1967).

For simplicity, it will be assumed that there is only one type of magnetic atom in the crystal. The coordinates of these atoms are \mathbf{R}_n , the spins \mathbf{S}_n , and the magnetic moments $-g\mu_B\mathbf{S}_n$. The interactions between the spins \mathbf{S}_n are given by a Hamiltonian \mathcal{H}_s . The eigenfunctions of \mathcal{H}_s , describing the orientation of all spins \mathbf{S}_n , are called α , and the corresponding energies ϵ_α , so that $\mathcal{H}_s\alpha = \epsilon_s\alpha$.

At a given temperature, there is a certain probability w_α for a state α to occur. Thus, the statistical average, for example, of the value of the spin of the atom at \mathbf{R}_n , is given by

$$\langle \mathbf{S}_n \rangle = \sum_{\alpha} w_{\alpha} \langle \alpha | \mathbf{S}_n | \alpha \rangle,$$

where $\langle \alpha | \mathbf{S}_n | \alpha \rangle$ is the expectation value of \mathbf{S}_n for the state α .

The generalized spin susceptibility $\chi^{ij}(\mathbf{k})$, which is a useful quantity for later calculations, can be expressed in terms of the spin correlations¹⁰:

$$\chi^{ij}(\mathbf{k}) = [(g\mu_B)^2/k_B T] \sum_n \sum_m \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)] \times (\langle S_{ni} S_{mj} \rangle - \langle S_{ni} \rangle \langle S_{mj} \rangle). \quad (2)$$

The brackets indicate statistical averages as defined above, $i, j = x, y, z$, and k_B is the Boltzmann constant. For small values of \mathbf{k} , a dependence on \mathbf{k} is to be expected of the form

$$1/\chi^{ij}(\mathbf{k}) = 1/\chi^{ij} + A_{ij}k^2. \quad (3)$$

In this expression, χ^{ij} is the susceptibility for homogeneous fields, defined as $\chi^{ij} = \partial M_i / \partial H_j$, where $\mathbf{M} = -g\mu_B \sum_n \langle \mathbf{S}_n \rangle$ is the total magnetization per unit volume and H the magnetic field.¹¹ The susceptibility defined in this way depends on H . The values of the constants A_{ij} can be calculated by using a method given by de Gennes and Villain.¹²

The interaction between an electron at a position \mathbf{r} and the spins \mathbf{S}_n is written as

$$V = - \sum_n J(\mathbf{r} - \mathbf{R}_n) \mathbf{s} \mathbf{S}_n, \quad (4)$$

where \mathbf{s} is the spin of the electron and $J(\mathbf{r} - \mathbf{R}_n)$ an exchange interaction, depending on the distance $\mathbf{r} - \mathbf{R}_n$ of the electron from the spin \mathbf{S}_n .

We assume that the interaction V is sufficiently weak to be treated as a perturbation. Because only semiconductors with a small number of charge carriers are considered, the interaction of the spins with the charge carriers will give only a negligible contribution to the exchange interaction between the spins.

¹⁰ P. G. de Gennes, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, p. 115.

¹¹ Strictly speaking, the susceptibilities χ^{ij} of Eq. (3) differ from the static susceptibilities by corrections due to demagnetizing fields. However, for the case of interest, i.e., not too close to T_c , these corrections are small.

¹² P. G. de Gennes and J. Villain, *J. Phys. Chem. Solids* **13**, 10 (1960).

ENERGY BANDS

Consider an electron in an unperturbed band state $\varphi_{b\mathbf{k}}(\mathbf{r})$, with energy $\epsilon_{b\mathbf{k}}^0$. The first-order energy change, due to V , is given by $\langle \varphi_{b\mathbf{k}}(\mathbf{r}) X \alpha | V | \varphi_{b\mathbf{k}}(\mathbf{r}) X \alpha \rangle$, where X is the spin function of the electron. Since in the band theory only the periodic part contributes to the energy of the band states in first order, the expression given above must be averaged over all spin states α , giving, for the first-order energy change,

$$\Delta \epsilon_{b\mathbf{k}}^1 = \sum_{\alpha} w_{\alpha} \langle \varphi_{b\mathbf{k}}(\mathbf{r}) X \alpha | V | \varphi_{b\mathbf{k}}(\mathbf{r}) X \alpha \rangle. \quad (5)$$

Substituting V and $\varphi_{b\mathbf{k}}(\mathbf{r})$, one finds

$$\Delta \epsilon_{b\mathbf{k}}^1 = - \sum_n \int |u_{b\mathbf{k}}(\mathbf{r})|^2 J(\mathbf{r} - \mathbf{R}_n) dv(\mathbf{r}) \langle X | \mathbf{s} | X \rangle \times \sum_{\alpha} w_{\alpha} \langle \alpha | \mathbf{S}_n | \alpha \rangle. \quad (6)$$

Only colinear spin arrangements will be considered, so that the average values $\sum_{\alpha} w_{\alpha} \langle \alpha | \mathbf{S}_n | \alpha \rangle$ are all parallel to a common direction, called the z axis. This makes it possible to choose spin functions X^+ and X^- , with the spin of the electron parallel and antiparallel to the z axis, for which nondiagonal matrix elements vanish.

Because all magnetic atoms are equivalent, one can write

$$\int |u_{b\mathbf{k}}(\mathbf{r})|^2 J(\mathbf{r} - \mathbf{R}_n) dv(\mathbf{r}) = J_{b\mathbf{k}}/N, \quad (7)$$

where N is the number of magnetic atoms per unit volume.

In all following considerations, only one single, non-degenerate energy band is considered, and interband matrix elements are neglected; the band subscript b will be omitted.

For the first-order energy change of electrons with spin parallel (+) and antiparallel (-) to the z axis, we then find

$$\Delta \epsilon_{\mathbf{k}}^{1,\pm} = \mp \frac{1}{2} S J_{\mathbf{k}} (M/M_0), \quad (8)$$

where $M_0 = -Ng\mu_B S$.

If only states near the band extrema (maximum of the valence band, or minimum of the conduction band) are considered, the effective-mass approximation can be used.⁹ In this approximation, the dependence of $u_{\mathbf{k}}(\mathbf{r})$ on \mathbf{k} is disregarded: $u_{\mathbf{k}}(\mathbf{r}) = u_0(\mathbf{r})$. For the states of a conduction band with minimum energy ϵ_e^0 at \mathbf{k}_{\min} , one obtains

$$\epsilon_{e\mathbf{k}} = \epsilon_e^0 + \sum_{j=1}^3 (\hbar^2 k_{ej}^2 / 2m_{ej}^*), \quad (9)$$

where k_{ej} is the j component of the wave vector with respect to the conduction-band minimum \mathbf{k}_{\min} , and m_{ej}^* is the effective mass for the direction j . The directions $j=1, 2, 3$ are chosen along the main axes of the energy ellipsoid in k space. A similar expression is found for the states near the top of the valence band.

In the effective-mass approximation, $J_k = J$, and the first-order energy change is independent of \mathbf{k} :

$$\Delta\epsilon_{\mathbf{k}}^{1,\pm} = \mp \frac{1}{2} SJ(M/M_0). \quad (10)$$

This result is sketched in Fig. 1. For a ferromagnetic semiconductor below T_c , the band splits into a band for spin parallel (+) and one for spin antiparallel (-)

to the magnetization. Above T_c , M is zero, and there is no splitting of the band. In an applied magnetic field, band splitting will also occur above T_c . In an antiferromagnetic semiconductor, band splitting occurs only in an applied magnetic field.

The second-order contribution to the change of the energy levels is given by

$$\Delta\epsilon_{\mathbf{k}}^{2,\pm} = \sum_{\alpha} \sum_{\alpha'} \sum_{\mathbf{k}'} w_{\alpha} \left\{ \frac{\langle \mathbf{k} \pm \alpha | V | \mathbf{k}' \pm \alpha' \rangle \langle \mathbf{k}' \pm \alpha' | V | \mathbf{k} \pm \alpha \rangle}{\epsilon_{\mathbf{k}}^{1,\pm} + \epsilon_{\alpha} - \epsilon_{\mathbf{k}'}^{1,\pm} - \epsilon_{\alpha'}} + \frac{\langle \mathbf{k} \pm \alpha | V | \mathbf{k}' \mp \alpha' \rangle \langle \mathbf{k}' \mp \alpha' | V | \mathbf{k} \pm \alpha \rangle}{\epsilon_{\mathbf{k}}^{1,\pm} + \epsilon_{\alpha} - \epsilon_{\mathbf{k}'}^{1,\mp} - \epsilon_{\alpha'}} \right\}, \quad (11)$$

where $\epsilon_{\mathbf{k}}^{1,\pm} = \epsilon_{\mathbf{k}}^0 + \Delta\epsilon_{\mathbf{k}}^{1,\pm}$.

For reasons of simplicity, the matrix elements $\langle \varphi_{\mathbf{k}}(\mathbf{r}) X^{\pm\alpha} | V | \varphi_{\mathbf{k}'}(\mathbf{r}) X^{\mp\alpha'} \rangle$ are written as $\langle \mathbf{k} + \alpha | V | \mathbf{k}' - \alpha' \rangle$, etc.

For the evaluation of Eq. (11), the quasistatic approximation^{2,10} will be used. This corresponds to neglecting $\epsilon_{\alpha} - \epsilon_{\alpha'}$ in the denominator. This approximation is justified because the excitation energies $\hbar\omega_{\mathbf{k}}$ of the spin system are much smaller than the electronic energies for the same value of k . Furthermore, one can write

$$\sum_{\alpha} w_{\alpha} \sum_{\alpha'} \langle \alpha | V | \alpha' \rangle \langle \alpha' | V | \alpha \rangle = \sum_{\alpha} w_{\alpha} \langle \alpha | V V | \alpha \rangle = \langle V V \rangle;$$

and with

$$S_n^{\pm} = S_n^x \pm i S_n^y$$

and

$$J_{\mathbf{k}\mathbf{k}'} = N \int u_{\mathbf{k}}^*(\mathbf{r}) u_{\mathbf{k}'}(\mathbf{r}) J(\mathbf{r} - \mathbf{R}_n) \exp[i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{r} - \mathbf{R}_n)] d\mathbf{v}(\mathbf{r}),$$

one finds

$$\Delta\epsilon_{\mathbf{k}}^{2,\pm} = \sum_{\mathbf{k}'} \left(\frac{J_{\mathbf{k}\mathbf{k}'}}{2N} \right)^2 \sum_n \sum_m \exp[i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{R}_n - \mathbf{R}_m)] \left(\frac{\langle S_n^z S_m^z \rangle}{\epsilon_{\mathbf{k}}^{1,\pm} - \epsilon_{\mathbf{k}'}^{1,\pm}} + \frac{\langle S_n^{\mp} S_m^{\pm} \rangle}{\epsilon_{\mathbf{k}}^{1,\pm} - \epsilon_{\mathbf{k}'}^{1,\mp}} \right). \quad (12)$$

Using Eq. (2), and $\chi^{xy} = 0$, $\chi^{xx} = \chi^x$, etc.,

$$\Delta\epsilon_{\mathbf{k}}^{2,\pm} = \sum_{\mathbf{q}} \left(\frac{J_{\mathbf{k},\mathbf{k}+\mathbf{q}}}{2N g \mu_B} \right)^2 (k_B T) \left(\frac{\chi^z(\mathbf{q})}{\epsilon_{\mathbf{k}}^{1,\pm} - \epsilon_{\mathbf{k}+\mathbf{q}}^{1,\pm}} + \frac{\chi^x(\mathbf{q}) + \chi^y(\mathbf{q})}{\epsilon_{\mathbf{k}}^{1,\pm} - \epsilon_{\mathbf{k}+\mathbf{q}}^{1,\mp}} \right). \quad (13)$$

In the effective-mass approximation, $u_{\mathbf{k}}(\mathbf{r}) = u_0(\mathbf{r})$, independent of \mathbf{k} . The function $J(\mathbf{r} - \mathbf{R}_n)$ is strongly localized around \mathbf{R}_n ; the extension b_0 is of the order of the radius of the orbitals of the electrons causing the magnetic moment on atom \mathbf{R}_n . For semiconductors, rather small values of k and k' are of interest, so that kb_0 and $k'b_0$ are much smaller than one. Therefore one can write as a good approximation $J_{\mathbf{k}\mathbf{k}'} = J$. For antiferromagnets and for ferromagnets in the paramagnetic region, the first-order splitting vanishes. In that case, the summation over \mathbf{q} for an isotropic conduction band with $\epsilon_{\mathbf{k}}^{1,\pm} = \epsilon^0 + (\hbar^2 k^2 / 2m^*)$ gives

$$\Delta\epsilon_{\mathbf{k}}^{2,\pm} = - \frac{J^2 k_B T m^*}{16\pi N^2 g^2 \mu_B^2 \hbar^2 k} \left(\frac{2 \arctan(4k^2 A_x \chi^x)^{1/2}}{A_x} + \frac{\arctan(4k^2 A_z \chi^z)^{1/2}}{A_z} \right). \quad (14)$$

For a ferromagnet below the Curie temperature, the contribution of the interband term χ^x and χ^y is strongly reduced because of the appearance of the first-order splitting in the energy denominator. Below T_c (but not too close to T_c), the contribution of these terms can be neglected if the first-order splitting is large.

The temperature dependence of $\Delta\epsilon_{\mathbf{k}}^{2,\pm}$ is sketched in Fig. 2 for a ferromagnet, using a molecular-field theory to calculate χ^x and χ^z as a function of T . The values of A_x and A_z were calculated by the method of de Gennes and Villain.¹² The result given in Fig. 2 is for a ferromagnet with spinel structure, and magnetic atoms only on B sites (CdCr_2Se_4). If only nearest-

neighbor interactions are taken into account, one finds

$$A_x = A_z = a^3 k_B T [256 g^2 \mu_B^2 S(S+1)]^{-1},$$

where a is the lattice parameter.

The first- and second-order changes of the energy levels can be used to explain the observed anomalous temperature dependence of the energy gap in CdCr_2Se_4 ^{13,14} and EuSe .¹⁵

¹³ G. Busch, B. Magyar, and P. Wachter, Phys. Letters **23**, 438 (1966).

¹⁴ G. Harbeke and H. Pinch, Phys. Rev. Letters **17**, 1090 (1966).

¹⁵ G. Busch and P. Wachter, Physik Kondensierten Materie **5**, 232 (1966).

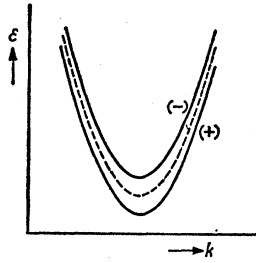


FIG. 1. Splitting of the conduction band into sub-bands for spin parallel (+) and antiparallel (-) to the magnetization. ---, band in paramagnetic region; —, sub-bands in ferromagnetic region.

Reservations should be made about the validity of the perturbation theory for the calculation of the shift of the energy levels. For a ferromagnetic crystal near T_c , the expression given above diverges for small values of k , which means that a perturbation expansion does not converge properly in this case. Related to this is the possibility of self-trapping of charge carriers due to a polarization of the spin system. These magnetic polaron effects are expected to be quite strong at temperatures near T_c , where the magnetic susceptibility is very large, and at small kinetic energies of the charge carrier (small k). In these cases, an intermediate or strong-coupling theory similar to that used for ordinary polarons¹⁶ should be used instead of the perturbation theory discussed above. A consequence of these considerations is that Eq. (14) may be expected to describe the change in the energy levels only at temperatures not too close to T_c .

The conclusions of this section are similar to those obtained by Rys *et al.*⁸; in his paper, calculations are also given for the critical region and spin-wave region.

ELECTRICAL RESISTIVITY

The nonperiodic part of the interaction V causes a scattering of the charge carriers. To calculate this spin-disorder resistivity, we must know the transition probabilities for an electron going from a state \mathbf{k} to a state \mathbf{k}' in the same band, both with or without change of spin, whereas the spin system changes its state

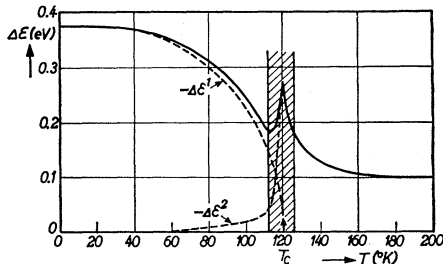


FIG. 2. Change of energy levels in a ferromagnetic semiconductor. $\Delta\epsilon = \Delta\epsilon^1$ [Eq. (10)] + $\Delta\epsilon^2$ [Eq. (14)]. The following values were used: $J = 0.5$ eV; $ka = 1$; $a = 10^{-7}$ cm; $T_c = 120^\circ\text{K}$, $N = 16/a^3$, $S = \frac{3}{2}$, m^* = free-electron mass. Results in hatched region are doubtful.

¹⁶ F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).

¹⁷ As a general reference for transport theory, see, for example, J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960).

from α to α' . These transition probabilities are given by¹⁷

$$P(\mathbf{k}\pm\alpha, \mathbf{k}'\pm\alpha') = (2\pi/\hbar) |\langle \mathbf{k}\pm\alpha | V | \mathbf{k}'\pm\alpha' \rangle|^2 \times \delta(\epsilon_{\mathbf{k}\pm\alpha} + \epsilon_{\alpha} - \epsilon_{\mathbf{k}'\pm\alpha'} - \epsilon_{\alpha'}), \quad (15)$$

$$P(\mathbf{k}\pm\alpha, \mathbf{k}'\mp\alpha') = (2\pi/\hbar) |\langle \mathbf{k}\pm\alpha | V | \mathbf{k}'\mp\alpha' \rangle|^2 \times \delta(\epsilon_{\mathbf{k}\pm\alpha} + \epsilon_{\alpha} - \epsilon_{\mathbf{k}'\mp\alpha'} - \epsilon_{\alpha'}). \quad (16)$$

If $f_{\mathbf{k}\pm}$ is the probability of a state $\mathbf{k}\pm$ being occupied, then the change of $f_{\mathbf{k}\pm}$ with time, due to the scattering, is given by

$$\begin{aligned} (\partial f_{\mathbf{k}^+}/\partial t)_{\text{scatt}} = & \sum_{\alpha} \sum_{\alpha'} \sum_{\mathbf{k}'} w_{\alpha'} [f_{\mathbf{k}'^+} (1 - f_{\mathbf{k}^+}) \\ & \times P(\mathbf{k}'^+ \alpha', \mathbf{k} + \alpha) + f_{\mathbf{k}'^-} (1 - f_{\mathbf{k}^+}) P(\mathbf{k}'^- \alpha', \mathbf{k} + \alpha)] \\ & - \sum_{\alpha} \sum_{\alpha'} \sum_{\mathbf{k}'} w_{\alpha} [f_{\mathbf{k}^+} (1 - f_{\mathbf{k}'^+}) P(\mathbf{k} + \alpha, \mathbf{k}'^+ \alpha') \\ & + f_{\mathbf{k}^+} (1 - f_{\mathbf{k}'^-}) P(\mathbf{k} + \alpha, \mathbf{k}'^- \alpha')], \quad (17) \end{aligned}$$

and a similar expression for $(\partial f_{\mathbf{k}^-}/\partial t)_{\text{scatt}}$.

The electrons are accelerated in an electric field \mathbf{F} , so that $\hbar(\partial \mathbf{k}/\partial t) = e\mathbf{F}$, and this induces a change

$$(\partial f_{\mathbf{k}\pm}/\partial t)_{\text{field}} = (\partial f_{\mathbf{k}\pm}/\partial \epsilon_{\mathbf{k}\pm}) (\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}\pm}) (e/\hbar) \mathbf{F}, \quad (18)$$

or, for a parabolic band $\epsilon_{\mathbf{k}\pm} = \epsilon_0 \pm \sum_i (\hbar^2 k_i^2 / 2m_i^*)$,

$$(\partial f_{\mathbf{k}\pm}/\partial t)_{\text{field}} = \sum_i (e\hbar/m_i^*) (k_i F_i) (\partial f_{\mathbf{k}\pm}/\partial \epsilon_{\mathbf{k}\pm}). \quad (19)$$

In the stationary state, one has

$$(\partial f_{\mathbf{k}\pm}/\partial t)_{\text{field}} + (\partial f_{\mathbf{k}\pm}/\partial t)_{\text{scatt}} = 0. \quad (20)$$

The equilibrium distribution $f_{0\mathbf{k}\pm}$ is given by $f_{0\mathbf{k}\pm} = [1 + \exp(\epsilon_{\mathbf{k}\pm} - \zeta)/k_B T]^{-1}$, where ζ is the Fermi level.

The calculations are carried out, making use of the following approximations: (a) The field \mathbf{F} is assumed to be weak, so that the distribution function $f_{\mathbf{k}\pm}$ differs only slightly from $f_{0\mathbf{k}\pm}$. It is convenient to write $f_{\mathbf{k}\pm} = f_{0\mathbf{k}\pm} + (\partial f_{0\mathbf{k}\pm}/\partial \epsilon_{\mathbf{k}\pm}) g_{\mathbf{k}\pm}$. For small fields, only linear terms in $g_{\mathbf{k}\pm}$ must be taken into account. (b) It is assumed that the electrical current has little influence on the spin system, so that w_{α} can be taken equal to the equilibrium distribution. This corresponds to neglecting magnon drag.^{18,19}

Using the fact that there should be detailed balance for all processes in the equilibrium situation (i.e., for $g_{\mathbf{k}\pm} = 0$ and $\mathbf{F} = 0$), one can express $w_{\alpha'}$ in terms of w_{α} , $f_{0\mathbf{k}\pm}$, and $f_{0\mathbf{k}'\pm}$. This is possible without making any assumptions about the properties of the spin system. Elimination of $w_{\alpha'}$ gives

$$\begin{aligned} (\partial f_{\mathbf{k}^+}/\partial t)_{\text{scatt}} = & \sum_{\alpha} \sum_{\alpha'} \sum_{\mathbf{k}'} w_{\alpha} \left(\frac{\partial f_{0\mathbf{k}^+}}{\partial \epsilon_{\mathbf{k}^+}} \right) \\ & \times \left[P(\mathbf{k} + \alpha, \mathbf{k}' + \alpha') \left(\frac{1 - f_{0\mathbf{k}'^+}}{1 - f_{0\mathbf{k}^+}} \right) (g_{\mathbf{k}'^+} - g_{\mathbf{k}^+}) \right. \\ & \left. + P(\mathbf{k} + \alpha, \mathbf{k}' - \alpha') \left(\frac{1 - f_{0\mathbf{k}'^-}}{1 - f_{0\mathbf{k}^+}} \right) (g_{\mathbf{k}'^-} - g_{\mathbf{k}^+}) \right]. \quad (21) \end{aligned}$$

¹⁸ M. Bailyn, Phys. Rev. **126**, 2040 (1962).

¹⁹ J. D. Wasscher and C. Haas, Phys. Letters **8**, 302 (1964).

The quasistatic approximation will be used. Making use of some results of the preceding sections, one finds

$$\sum_{\alpha} \sum_{\alpha'} w_{\alpha} P(\mathbf{k}+\alpha, \mathbf{k}'+\alpha') = (2\pi/\hbar) \delta(\epsilon_{\mathbf{k}^+} - \epsilon_{\mathbf{k}'^+}) \times (J/2N)^2 [k_B T / (g\mu_B)^2] \chi^z(\mathbf{k}' - \mathbf{k}), \quad (22)$$

$$\sum_{\alpha} \sum_{\alpha'} w_{\alpha} P(\mathbf{k}+\alpha, \mathbf{k}'-\alpha') = 2(2\pi/\hbar) \delta(\epsilon_{\mathbf{k}^+} - \epsilon_{\mathbf{k}'^-}) \times (J/2N)^2 [k_B T / (g\mu_B)^2] \chi^x(\mathbf{k}' - \mathbf{k}). \quad (23)$$

In semiconductors the relevant values of \mathbf{k}' and \mathbf{k} are indeed small, so that one can write approximately $\chi^i(\mathbf{k}' - \mathbf{k}) \simeq \chi^i$. This approximation is not valid for a ferromagnet close to T_c , where the term $A |\mathbf{k}' - \mathbf{k}|^2$ of Eq. (3) is no longer small compared with $1/\chi$. In metallic conductors it is necessary to take into account explicitly the \mathbf{k} dependence of χ . Using approximate expressions for the spin correlations, the temperature dependence of the resistivity of metals has been calculated by de Gennes and Friedel.²

It is possible to solve the transport equation (20), with

$$g_{\mathbf{k}^{\pm}} = e\hbar\tau_{\mathbf{k}^{\pm}} \sum_i (k_i F_i / m_i^*), \quad (24)$$

$$1/\tau_{\mathbf{k}^{\pm}} = (2\pi/\hbar) (J/2N g\mu_B)^2 (k_B T) \times [\chi^z \sum_{\mathbf{k}'} \delta(\epsilon_{\mathbf{k}^{\pm}} - \epsilon_{\mathbf{k}'^{\pm}}) + 2\chi^x \sum_{\mathbf{k}'} \delta(\epsilon_{\mathbf{k}^{\pm}} - \epsilon_{\mathbf{k}'^{\mp}})]. \quad (25)$$

For parabolic bands, the sums are easily evaluated, giving

$$\frac{1}{\tau_{\mathbf{k}^{\pm}}} = \frac{(m_1^* m_2^* m_3^*)^{1/2} (k_B T)}{2\pi\sqrt{2}\hbar^4} \left(\frac{J}{N g\mu_B} \right)^2 \times [\chi^z (\epsilon_{\mathbf{k}^{\pm}} - \epsilon_0^{\pm})^{1/2} + 2\chi^x (\epsilon_{\mathbf{k}^{\pm}} - \epsilon_0^{\mp})^{1/2}]. \quad (26)$$

The mobility of the charge carriers is given by¹⁹

$$\mu_{i^{\pm}} = \left(\frac{e\hbar^2}{m_i^*} \right) \frac{\sum_{\mathbf{k}} k_i^2 (\partial f_{0\mathbf{k}^{\pm}} / \partial \epsilon_{\mathbf{k}^{\pm}}) \tau_{\mathbf{k}^{\pm}}}{\sum_{\mathbf{k}} f_{0\mathbf{k}^{\pm}}} \quad (27)$$

for conduction in a direction i , chosen along one of the main directions of the energy ellipsoid in \mathbf{k} space. The equations given above make it possible to calculate the electrical resistivity if the values of χ and J are known. Explicit equations will be given for the mobility of charge carriers in ferromagnetic and antiferromagnetic semiconductors. Because the susceptibilities and the band energy change with an applied magnetic field, it is also possible to calculate the magnetoresistance.

If the charge carriers are nondegenerate, i.e., if $f_{0\mathbf{k}^{\pm}} \sim \exp[-(\epsilon_{\mathbf{k}^{\pm}} - \zeta)/k_B T]$, one finds, for the mobility in an antiferromagnetic semiconductor with $\epsilon_0^+ = \epsilon_0^-$,

$$\mu_i = \frac{8(2\pi)^{1/2} (N g\mu_B)^2 e\hbar^4}{3m_i^* (m_1^* m_2^* m_3^*)^{1/2} J^2 (k_B T)^{3/2}} (\chi^z + 2\chi^x)^{-1}. \quad (28)$$

Thus the mobility is proportional to the inverse of the average susceptibility $\frac{1}{3}(\chi^z + 2\chi^x)$. The anisotropy of the mobility is due only to the anisotropy of the effective mass.

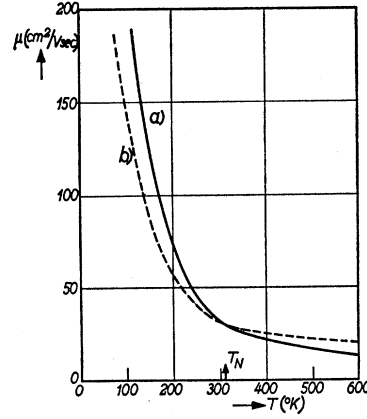


FIG. 3. Mobility of charge carriers in an antiferromagnetic semiconductor: (a) nondegenerate; (b) degenerate.

For a degenerate antiferromagnetic semiconductor (i.e., with $\epsilon_0 - \zeta \gg k_B T$), the result is

$$\mu_i = \frac{2\pi\sqrt{2} (N g\mu_B)^2 e\hbar^4}{m_i^* (m_1^* m_2^* m_3^*)^{1/2} J^2 (k_B T) E_F^{1/2}} (\chi^z + 2\chi^x)^{-1}, \quad (29)$$

where E_F is the Fermi energy with respect to the bottom of the band ($E_F + \epsilon_0^{\pm} = \zeta$).

The temperature dependence of μ for an antiferromagnetic semiconductor is shown in Fig. 3. (For the calculation, the following values were used: $m_1^* = m_2^* = m_3^* =$ free-electron mass; $J = 0.5$ eV; $E_F = 0.05$ eV; $N = 2 \times 10^{22}$ cm⁻³, $E_F = 0.05$ eV, $g = 2$, $T_N = 310^\circ\text{K}$; for the susceptibility, the experimental values of MnTe²⁰ were used.)

In a ferromagnetic semiconductor, the situation is complicated by the band splitting.

The number of carriers in the two sub-bands are n^+ and n^- , their mobilities μ^+ and μ^- . The electrical conductivity is $1/\rho = ne\mu = n^+e\mu^+ + n^-e\mu^-$, with $n = n^+ + n^-$.

For a nondegenerate ferromagnetic semiconductor, the result is

$$\mu_{i^{\pm}} = \frac{8(2\pi)^{1/2} (N g\mu_B)^2 e\hbar^4}{3m_i^* (m_1^* m_2^* m_3^*)^{1/2} J^2 (k_B T)^{3/2}} \times \int_0^\infty \frac{te^{-t} dt}{\chi^z + 2f^{\pm}\chi^x [1 \mp (\delta/t)]^{1/2}}. \quad (30)$$

If δ is positive, then $f^- = 1$; $f^+ = 1$ for $t > \delta$; $f^+ = 0$ for $t < \delta$; and δ is a measure of the band splitting

$$\delta = (\epsilon_0^- - \epsilon_0^+) / k_B T = (SJ/k_B T) (M/M_0). \quad (31)$$

The ratio of n^+ and n^- is $n^+/n^- = e^{\delta}$. The terms with χ^z and χ^x in Eq. (30) are due to scattering within one sub-band (without change of spin: $+\rightarrow+$ or $-\rightarrow-$) and between two sub-bands (spin flip: $+\rightarrow-$ or $-\rightarrow+$), respectively. (See Fig. 4.)

²⁰ T. Komatsubara, M. Murakami, and E. Hirahara, J. Phys. Soc. Japan **18**, 356 (1963).

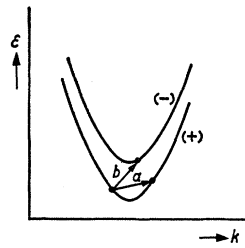


FIG. 4. Spin-disorder scattering in a ferromagnetic semiconductor: (a) scattering without spin flip; (b) scattering with spin flip.

For a degenerate ferromagnetic semiconductor,

$$\mu_i^{\pm} = \frac{2\pi\sqrt{2}(N g \mu_B)^2 e \hbar^4}{m_i^* (m_1^* m_2^* m_3^*)^{1/2} J^2 (k_B T)} \times [\chi^2 (E_F^{\pm})^{1/2} + 2\chi^2 (E_F^{\mp})^{1/2}]^{-1}. \quad (32)$$

In this equation, E_F^+ and E_F^- are the Fermi energies in the + and the - bands with respect to the minima of these bands ($E_F^+ + \epsilon_0^+ = E_F^- + \epsilon_0^- = \zeta$).

Figure 5 shows the temperature dependence of μ^+ and μ^- for a nondegenerate ferromagnetic semiconductor. [The curve is calculated with $J=0.5$ eV, $S=\frac{3}{2}$, $m_1^*=m_2^*=m_3^*$ =free-electron mass, $N=1.3 \times 10^{22}$ cm $^{-3}$, $g=2$; the susceptibilities are calculated by using a molecular-field model with $T_c=120^\circ$ K (see Appendix); these values are characteristic of CdCr $_2$ Se $_4$.²¹]

In many cases, one expects $J \gg k_B T_c$, in which case the band splitting in the ferromagnetic region is much larger than $k_B T_c$ (except for temperatures very close to T_c). Then practically all carriers are in the lowest sub-band, and $1/\rho = ne\mu^+$. (For example, if $J=0.5$ eV, $S=\frac{3}{2}$, $T_c=120^\circ$ K, this is not the case only in the region $118 < T < 120^\circ$ K. However, it is precisely in this region very close to T_c that the equations are not valid anyway.)

The mobility in ferromagnetic semiconductors is expected to have a pronounced minimum at T_c , provided, of course, that the coupling J is strong, so that the influence of spin disorder dominates.

Maxima in the resistivity at T_c have been observed in n -type CdCr $_2$ Se $_4$ ²² and in Eu $_{1-x}$ Gd $_x$ Se.^{23,24} A maximum of this type does not occur in antiferromagnetic semiconductors.

MAGNETORESISTANCE

The magnetoresistance of nonmagnetic semiconductors is usually quite small; it is due to the influence which a magnetic field has on the energy bands.⁹ In ferromagnetic semiconductors, much larger effects have been observed near the Curie temperature (Eu $_{1-x}$ Gd $_x$ Se^{23,24} and n -type CdCr $_2$ Se $_4$ ²²).

²¹ C. Haas, A. M. J. G. van Run, P. F. Bongers, and W. Albers, *Solid State Commun.* **5**, 657 (1967).

²² H. W. Lehmann and G. Harbeke, *J. Appl. Phys.* **38**, 946 (1967).

²³ S. Methfessel, *Z. Angew. Phys.* **18**, 414 (1965).

²⁴ S. von Molnar and S. Methfessel, *J. Appl. Phys.* **38**, 959 (1967).

In magnetic semiconductors, a magnetic field changes the spin disorder, and this influences the resistivity. This effect will be calculated in this section. The normal magnetoresistance effects, occurring also in nonmagnetic semiconductors, are neglected.

A contribution to the magnetoresistance may also come from a change of the carrier concentration induced by a magnetic field. This will be the case if the ionization energies of donors or acceptors change with a magnetic field.

As an example, consider an n -type semiconductor, containing N_D donor atoms, with ionization energy E_D . The charge-carrier concentration (for an uncompensated crystal, without acceptors) is given by²⁵

$$n = (g_1 N_D N_c / g_0)^{1/2} \exp[-(E_D / 2k_B T)] \quad (33)$$

if $n \ll N_D$; $N_c = 2(2\pi m_d^* k_B T / \hbar^2)^{3/2}$ is the effective density of states of the conduction band, m_d^* being the density-of-states effective mass [for a single parabolic band, $m_d^* = (m_1^* m_2^* m_3^*)^{1/3}$]. The degeneracies of occupied and unoccupied donor states are g_0 and g_1 , respectively.

In a ferromagnetic semiconductor, there is a splitting of the conduction band into two sub-bands $\epsilon_c^{\pm} = \mp \frac{1}{2} S J (M / M_0)$ (see Fig. 6). The donor states will also split into levels for + and - spin, with energy $E_D^{\pm} = E_D^0 \mp \frac{1}{2} \gamma S J (M / M_0)$.

In the ferromagnetic region, the charge-carrier concentration is given by

$$n = \left(\frac{g_1 N_D N_c}{g_0} \right)^{1/2} \exp\left(- \frac{E_D^0 + \frac{1}{2}(\gamma - 1) S J (M / M_0)}{2k_B T} \right) \quad (34)$$

for the case where the splitting of the conduction band and that of the donor level are both large compared to $k_B T$. This corresponds to an apparent gradual change of the donor ionization energy due to the temperature dependence of M (Fig. 7). Because M also depends on

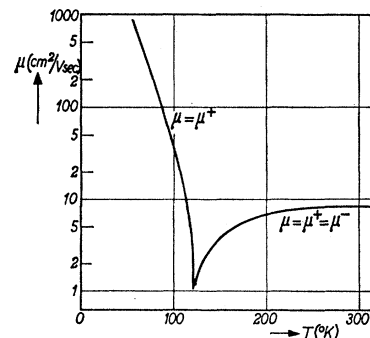


FIG. 5. Mobility of charge carriers in a nondegenerate ferromagnetic semiconductor ($T_c=120^\circ$ K).

²⁵ For general reference about the application of Fermi statistics in semiconductors, see R. A. Smith, *Semiconductors* (Cambridge University Press, London, 1959).

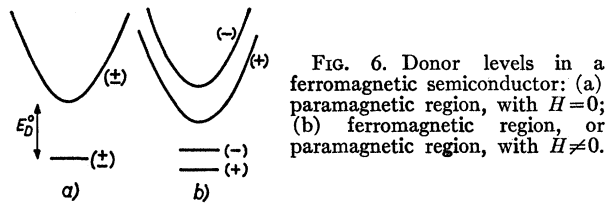


FIG. 6. Donor levels in a ferromagnetic semiconductor: (a) paramagnetic region, with $H=0$; (b) ferromagnetic region, or paramagnetic region, with $H \neq 0$.

H , there will be a change of the carrier concentration with H , which can be calculated directly from Eq. (34).

In the paramagnetic region, the splitting of donor levels and bands is small, and proportional to H . One finds for the relative change of the number of free charge carriers (for the case that $n \ll N_D$)

$$\frac{n(H)}{n(0)} = \left\{ \frac{\cosh[SJM(H)/2M_0k_B T]}{\cosh[\gamma SJM(H)/2M_0k_B T]} \right\}^{1/2} \quad (35)$$

A change of n of course contributes directly to the magnetoresistance. The effect will have a maximum at T_c , because there, χ has the largest value.

For shallow donors the effect is small, because in that case, γ will be about one. This can be understood as follows. The wave function of an electron in a donor state with a small ionization energy (a shallow donor) consists in most cases of a combination of only slightly perturbed conduction-band wave functions.²⁶ A consequence is that the change of the donor energy E_D with a magnetic field will be the same as that of the corresponding band states, i.e., $\gamma \simeq 1$. For deeper donors, there is no reason why γ should be about one, and appreciable magnetoresistance effects due to a change of the carrier concentration are possible.

The magnetoresistance of a ferromagnetic semiconductor due to a change of the mobility, i.e., assuming a constant carrier concentration, can be calculated from the equations give before. Below the Curie temperature, $n^+ \gg n^-$, $\delta \gg 1$, and $1/\rho = n^+ e \mu^+$. From

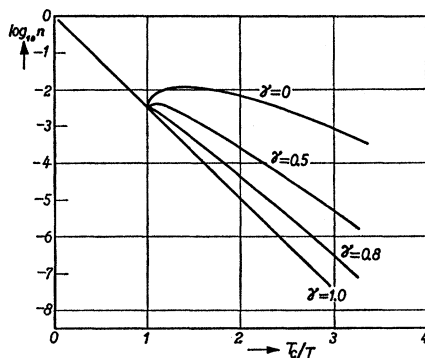


FIG. 7. Free-carrier concentration n (arbitrary units) in an extrinsic ferromagnetic semiconductor. The curves are calculated from Eq. (34), with $E_D^0=0.125$ eV; $SJ=0.15$ eV; $T_c=120^\circ\text{K}$.

²⁶ W. Kohn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. V, p. 258.

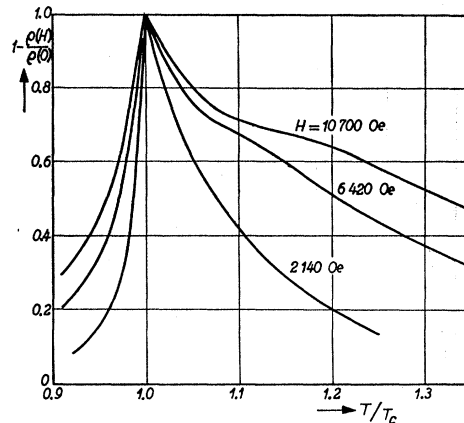


FIG. 8. Magnetoresistance of a ferromagnetic semiconductor as a function of temperature.

Eq. (30) one finds

$$\rho(H)/\rho(0) = \chi^z(H)/\chi^z(0). \quad (36)$$

The band splitting in this case is large compared with $k_B T$, so that only scattering between the states of the lowest sub-band is important. The expected magnetoresistance in this region does not depend on the strength of the coupling between localized spins and conduction electrons, provided, of course, that it is large enough for spin-disorder scattering to dominate. Curves of the magnetoresistance as a function of temperature and field are given in Figs. 8 and 9; the field dependence of the susceptibility was calculated with the molecular-field theory for a ferromagnet, with $S = \frac{3}{2}$.

Above T_c carriers are present in both sub-bands; the ratio $n^+/n^- = \exp[SJM(H)/M_0k_B T]$. Moreover, the mobilities are different, and depend on the field. From Eq. (30) one can calculate the magnetoresistance, if again the field dependence of the susceptibilities is known. Figures 8 and 10 give the result of calculations for $S = \frac{3}{2}$ and $J = 0.5$ eV. A comparison of calculations

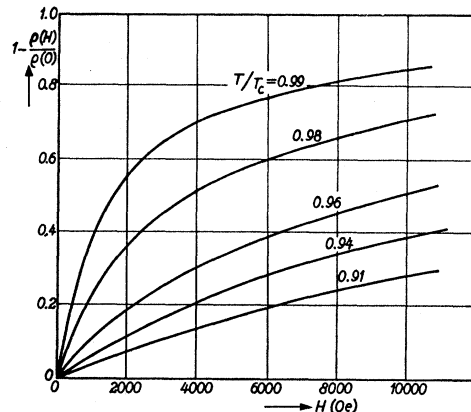


FIG. 9. Magnetoresistance of a ferromagnetic semiconductor as a function of the field for $T < T_c$.

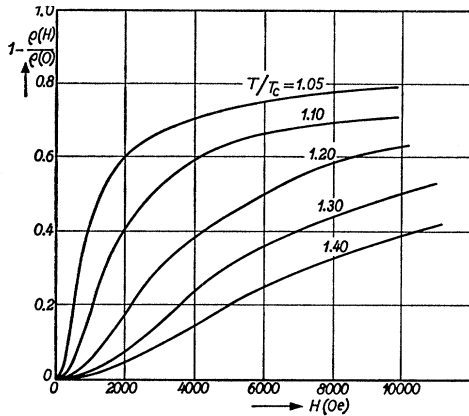


FIG. 10. Magnetoconductance of a ferromagnetic semiconductor as a function of the field for $T > T_c$.

of this type with experimental data on n -type CdCr_2Se_4 was given recently.²¹

The origin of the magnetoconductance above T_c is somewhat different from that below T_c . Upon the application of a field, the number of carriers in the lower sub-band increases. At the same time, the mobility of these carriers increases because spin-flip scattering decreases, leading to a lower resistivity.

DISCUSSION

Assuming a simple type of exchange coupling between charge carriers and spins, the change of the energy levels, the electrical resistivity, and the magnetoconductance were calculated for magnetic semiconductors, using perturbation theory.

Experimental evidence is available only for a few cases. The resistivity-versus-temperature curve of MnTe ¹⁹ is in qualitative agreement with the calculations, although the decrease of the resistivity below the Neel temperature is stronger than predicted. This may be due to the influence of magnon drag, which is probably appreciable in this compound.^{19,27,28}

For the ferromagnetic semiconductors $\text{Eu}_{1-x}\text{Gd}_x\text{Se}$ ^{23,24} and n -type CdCr_2Se_4 ,^{21,22} a pronounced maximum in the resistivity has been observed at T_c , and also a large magnetoconductance effect. The data for CdCr_2Se_4 are in reasonable agreement with the theory.²¹ The situation in $\text{Eu}_{1-x}\text{Gd}_x\text{Se}$ is more complicated, because the presence of the charge carriers strongly influences the magnetic interactions between the localized spins.

Some reservations about the results obtained are necessary. The calculated mobilities are quite small, particularly near and above the Curie temperature. It is well known that in such a situation of very strong scattering, a simple perturbation theory becomes less

reliable. Some of the consequences were already briefly mentioned.

For an increased but not too strong coupling between charge carriers and spins, the moving charge carriers perturb the spin system from its normal isotropic equilibrium in such a way that an energy current in the spin system is dragged along by an electrical current of the charge carriers. This magnon-drag effect has been described elsewhere.^{19,27,28}

If the coupling becomes very strong, magnetic self-trapping of the charge carriers may occur, leading to a magnetic polaron.²⁴ In this case, a cloud of magnetization surrounds the carrier, and prevents its unhindered motion through the lattice. This corresponds to an apparent increase of the effective mass (polaron mass), and is related to the effects discussed by Wolfram and Callaway.²⁹ No theory has yet been given for the conductivity of magnetic polarons.

APPENDIX

The susceptibilities χ^x and χ^z do not include the effects of Bloch wall motions, i.e., they describe the change of the magnetization M of a single domain. χ^x and χ^z can be defined in the following way: If a sample with magnetization \mathbf{M} parallel to a field \mathbf{H} along the z axis is subjected to a small extra field $\delta\mathbf{H}$, then the change of the magnetization is given by $\delta M_z = \chi^z \delta H_z$, $\delta M_x = \chi^x \delta H_x$, and $\delta M_y = \chi^y \delta H_y$. The susceptibilities defined in this way depend on the field H .

In the molecular-field approximation for a ferromagnet, the magnetization is given by

$$\mathbf{M} = M_0 \mathbf{u} B_s(g\mu_B S | \mathbf{F} | / k_B T), \quad (\text{A1})$$

if the influence of anisotropy can be neglected. Here B_s is the Brillouin function and \mathbf{u} is a unit vector parallel to the molecular field \mathbf{F} acting on the spins. \mathbf{F} is given by $\mathbf{F} = \lambda \mathbf{M} + \mathbf{H}$, where λ is the molecular-field constant equal to

$$\lambda = 3k_B T_c / N g^2 \mu_B^2 S(S+1).$$

From Eq. (A1) the change $\delta\mathbf{M}$ induced by a small field $\delta\mathbf{H}$ can easily be calculated, and from this the susceptibilities χ^z and χ^x :

$$1/\chi^z(H) = H/M, \quad (\text{A2})$$

$$1/\chi^x(H) = [M_0(\partial B_s / \partial F)]^{-1} - \lambda. \quad (\text{A3})$$

From Eqs. (A1)–(A3) one can calculate numerically χ^x and χ^z as a function of temperature and field.

The molecular-field theory can be used only to obtain a crude estimate of the susceptibilities. For a more accurate calculation, the effect of short-range order above T_c and the influence of the magnetic anisotropy should be taken into account.

²⁷ G. Zanmarchi and C. Haas, J. Appl. Phys. (to be published).

²⁸ G. Zanmarchi and C. Haas (to be published).

²⁹ T. Wolfram and J. Callaway, Phys. Rev. **127**, 1605 (1962); **130**, 45 (1963).