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SPIN-DEPENDENT SCATTERING AND RESISTIVITY OF MAGNETIC METALS AND ALLOYS

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Synopsis

The purpose of this paper is to review and extend the explanation of the resistivity anomalies observed in certain magnetic metals and alloys in terms of spin-dependent scattering of the conduction electrons. For this purpose, the usual theory of electrical conductivity has been extended to include inelastic collisions with and without spin flip. Assuming the existence of an exchange interaction between the conduction electrons and unpaired electrons localized on particular atoms, the resistivity has been calculated for scattering by (i) isolated magnetic ions, (ii) pairs of exchange-coupled magnetic ions and (iii) spin-disorder in a ferromagnetic lattice. For models (i) and (ii) the magnetoresistance has also been investigated.

1. *Introduction.* Two different theories have been put forward to explain the electrical behaviour of transition metals and their alloys. On the one hand, there is the band theory of Mott[1]) for nickel, palladium and their alloys, in which it is assumed that the abnormal behaviour of these metals is due to transitions from the *s*-band (which carries most of the current) to the *d*-band under influence of lattice vibrations. The consequences of this theory have been tested by Schindler[2])[3]) and coworkers, by Allison and Pugh[4]), by Pugh and Ryan[5]) and others. From this work it appears that *s*–*d*-scattering is indeed responsible for the relatively high resistivity of these metals and for the greater part of the anomalies near the Curie temperature.

On the other hand, it seems fairly certain that in the rare earth metals, and probably also in iron, the unpaired electrons are localized on particular atoms; the same situation is encountered in a number of dilute alloys of transition elements in copper, silver and gold. Thus, it has been suggested by Kasuya[6]) and by De Gennes and Friedel[7]) that the resistivity of the rare earth metals is determined to a large extent by an exchange interaction between the conduction electrons and the localized spins in these materials. If this interaction is sufficiently strong, disorder of the spin system will produce an appreciable contribution to the resistivity in the form of a spin-

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*) During the course of publication of this paper the sad news was received of the sudden death of Mrs. T. van Peski-Tinbergen.

disorder term. For a review of spin-disorder effects in the electrical resistivities of metals and alloys we refer to Coles[8]).

The electrical resistivity of noble metal alloys containing traces of transition elements has been measured by Gerritsen and Linde[9]) and others. Some of these alloys exhibit a minimum in the resistivity at some low temperature; typical examples are dilute alloys of iron in copper[10]). Others, such as manganese in copper, show a minimum in the resistivity followed by a maximum at a still lower temperature. Correlated with the resistivity anomalies in these alloys is an anomalous magnetoresistance[11]) and magnetic behaviour[12]). Several attempts have been made[13]) to explain these properties, but the occurrence of a maximum and (or) a minimum in the resistivity as a function of temperature remained rather puzzling for a number of years. However, from the work of Brailsford and Overhauser[14]) and Dekker[15]) it seems fair to conclude that the resistivity anomalies may be attributed to the scattering of conduction electrons by the exchange-coupled magnetic ions. In particular, these authors considered the scattering of the conduction electrons by pairs of exchange-coupled magnetic ions, on the assumption that there exists an exchange interaction between the conduction electrons and the ionic spins. The pair-model had been introduced earlier by Dekker[16]) in an effort to understand the magnetic behaviour of alloys such as Cu–Mn. This model must be considered a rather crude approximation to the actual situation encountered in dilute magnetic alloys. In fact, from the work of Blandin and Friedel[17]) we now know that the electron density (corresponding to a given spin direction) around a magnetic impurity is determined by an oscillating function with an amplitude which decreases relatively slowly with the distance from the ion. Since this function is different for the two possible spin directions of the conduction electrons, there results an indirect exchange interaction between the magnetic ions, which may range over relatively long distances. In the resistivity of these alloys there will thus occur a term due to the exchange interaction between the conduction electrons and the system of magnetic ions which are indirectly coupled among themselves. The calculation of the resistivity poses a difficult statistical problem*).

A strongly simplified approximation to this state of affairs in dilute magnetic alloys consists of the following: if the actual long-range indirect exchange forces between the magnetic impurities are replaced by short-range forces, the system of magnetic atoms may be considered to consist of isolated atoms and of pairs of nearest neighbours; in sufficiently dilute alloys, larger clusters may then be neglected. In this case, the impurity resistivity would be determined by the scattering produced by the isolated magnetic atoms and by the pairs of exchange-coupled atoms. Since the

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*) An elegant approximation is being worked out by Miss T. Béal (Orsay, France; private communication).

latter indeed may produce anomalies of the kind observed, one may expect similar anomalies to occur for a more sophisticated model in which the long range of the exchange forces is taken into account. Obviously, the pair model does not allow a quantitative comparison between theory and experiment. It is believed, however, that the pair-model exhibits the essential features of the actual situation in a qualitative way.

In the present paper we give a unified treatment of the electrical resistivity produced by

(i) isolated magnetic atoms
(ii) pairs of exchange-coupled magnetic atoms
(iii) spin-disorder in pure ferromagnetic metals with localized spins.

In all these cases we assume that there exists an exchange interaction between the conduction electrons and the localized unpaired electrons of the magnetic atoms. From what has been said above, it will be evident that this paper constitutes partly a review of previous work; in other respects it contains an extension thereof. Thus, because the actual transport theory including inelastic spin-dependent collisions has received relatively little attention in the earlier papers, section 2 is devoted to this subject; this section unifies the treatment of the three models discussed in sections 3 through 5. For models (i) and (ii) we have also investigated the effect of a magnetic field on the resistivity. Our results on the resistivity produced by spin-disorder in a ferromagnetic model, differ somewhat from those obtained by Kasuya[6]) and by De Gennes and Friedel[7]), as mentioned in section 5. Finally, we believe that the formula for the resistivity produced by pairs of magnetic atoms as originally published by Brailsford and Overhauser[14]), should have preference over their "corrected" formula published later[18]) (see section 4).

2. *Transport theory for electrons which suffer inelastic and elastic collisions.* In the following sections we shall be concerned with calculating the resistivity of a metal resulting from various kinds of scattering processes. Assuming that the matrix elements for these processes are known, it will be necessary to have available a general expression for the relaxation time of the conduction electrons in terms of these matrix elements; such an expression will be derived in the present section.

Apart from the usual type of elastic scattering of the conduction electrons by foreign charge distributions, we shall be interested in scattering processes which are governed by an exchange interaction between the conduction electrons and magnetic impurities. The perturbation hamiltonian in such cases depends on the relative orientation of the spins of the incident electron and the scattering center. Collisions of this type may or may not be elastic, depending in general on whether the collision proceeds without or with spin flip. Thus, in deriving a general expression for the relaxation time, one should take into account any energy transfer between the scattered electrons and the scattering centers. Also, spin-dependent scattering will in general lead to different relaxation times for conduction electrons with magnetic spin quantum number $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. It will therefore be necessary to consider the "plus" and "minus" electrons separately.

The wave vector of an electron will be denoted by $\boldsymbol{k}$ and we shall consider a single conduction band for which the energy as a function of $\boldsymbol{k}$ is assumed to be of the form $E_0 + \hbar^2k^2/2m$, where m is an effective mass. In the presence of some uniform effective magnetic field, the constant E_0 may be different for electrons with $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$; we shall choose the zero of energy such that $E_\pm(\boldsymbol{k}) = \pm\Delta E + \hbar^2k^2/2m$ for $m_s = \pm\frac{1}{2}$. The number of possible states per unit volume corresponding to an element $\mathrm{d}\boldsymbol{k}$ in $\boldsymbol{k}$-space equals $(1/8\pi^3)\,\mathrm{d}\boldsymbol{k}$ for each of the two types of electrons. In thermal equilibrium and in the absence of electric or non-uniform magnetic fields, the fraction of states occupied by electrons is given by the Fermi-Dirac distribution function

$$f_{0\pm}(E_\pm) \equiv f_{0\pm}(\boldsymbol{k}) = \left[\exp\left\{\left(\frac{\hbar^2k^2}{2m} \pm \Delta E - E_F\right)\bigg/ k_BT\right\} + 1\right]^{-1}$$

for $m_s = \pm\frac{1}{2}$; E_F is the Fermi energy and k_B is Boltzmann's constant. The electron densities $n_\pm$ may easily be shown to differ from $\frac{1}{2}n$ (n = total electron density) only by a term of the order $\Delta E/E_F$, which is negligible for our purposes. The electron densities $n_\pm$ are not affected by the occurrence of collision processes involving spinflip, as long as the whole system (electrons + scattering centers) is in thermal equilibrium.

In a state of steady electric current under influence of an electric field F_x along the x-axis, let the densities of electrons corresponding to $\mathrm{d}\boldsymbol{k}$ be given by $(1/8\pi^3)\,f_\pm(\boldsymbol{k})\,\mathrm{d}\boldsymbol{k}$. If e represents the charge of an electron, the rate of change of $f_\pm(\boldsymbol{k})$ produced by the field F_x equals

$$[\partial f_\pm/\partial t]_{\text{field}} = -(eF_x\hbar k_x/m)(\partial f_{0\pm}/\partial E_\pm) \tag{2-1}$$

If the rate of change of $f_\pm$ due to scattering processes can be described by a relaxation time $\tau_\pm(\boldsymbol{k})$, we may write

$$[\partial f_\pm/\partial t]_{\text{coll.}} = -(f_\pm - f_{0\pm})/\tau_\pm \tag{2-2}$$

In the steady state the sum of (2-1) and (2-2) must vanish, so that

$$f_\pm - f_{0\pm} = -(eF_x\hbar k_x\tau_\pm/m)(\partial f_{0\pm}/\partial E) \equiv g_\pm(\boldsymbol{k}) \tag{2-3}$$

which defines the quantities $g_\pm$ to be used later. Once the relaxation times $\tau_\pm$ are known, the electrical conductivity, σ_e, follows directly from $\sigma_e = \sigma_{e+} + \sigma_{e-}$ and from the well-known expression for the current density J_x:

$$\sigma_{e\pm} \equiv J_{x\pm}/F_x = (e/F_x)\int(1/8\pi^3)\,\mathrm{d}\boldsymbol{k}(f_\pm - f_{0\pm})(\hbar k_x/m) =$$
$$= -(e^2/6\pi^2m)\int k^3\tau_\pm(\partial f_{0\pm}/\partial E_\pm)\,\mathrm{d}E_\pm. \tag{2-4}$$

In order to calculate τ_+ in terms of the relevant matrix elements, consider the quantity $(\partial f_+/\partial t)_{\text{coll.}}$; the calculation of τ_- proceeds in exactly the same manner. The collision processes involving no spin flip will be denoted by a subscript i or i'; those for which spin flip does occur will carry a subscript j or j'. Although usually only collisions involving spin flip may be inelastic, we shall assume for generality that in collisions of type i (or j) the electron *gains* an energy ε_i(or ε_j); ε_i is simply a difference in kinetic energy, whereas ε_j contains, in addition, a term $\mp 2\Delta E$, depending upon the change in magnetic quantum number $\Delta m_s = \mp 1$ of the electron. The transition probabilities for the various processes will be denoted by $P_i(\boldsymbol{k}_+ \to \boldsymbol{k}'_+)$, $P_j(\boldsymbol{k}_+ \to \boldsymbol{k}'_-)$, etc. Extending the standard procedure19) for our purpose, we may write

$$\begin{aligned}(\partial f_+/\partial t)_{\text{coll}} = (1/8\pi^3) \int \mathrm{d}\boldsymbol{k}'_+ [- \sum_i P_i(\boldsymbol{k}_+ \to \boldsymbol{k}'_+)\, f_+(1 - f'_+) + \\ + \sum_{i'} P_{i'}(\boldsymbol{k}'_+ \to \boldsymbol{k}_+)\, f'_+(1 - f_+)] + \\ + (1/8\pi^3) \int \mathrm{d}\boldsymbol{k}'_- [- \sum_j P_j (\boldsymbol{k}_+ \to \boldsymbol{k}'_-)\, f_+ (1 - f'_-) + \\ + \sum_{j'} P_{j'}(\boldsymbol{k}'_- \to \boldsymbol{k}_+)\, f'_-(1 - f_+)] \end{aligned} \tag{2-5}$$

Here, we have introduced the abbreviation $f(\boldsymbol{k}') = f'$, etc. Detailed balance in the absence of fields for the system in thermal equilibrium requires

$$\sum_{i'} P_{i'}(\boldsymbol{k}'_+ \to \boldsymbol{k}_+) = \sum_i P_i(\boldsymbol{k}_+ \to \boldsymbol{k}'_+)\, \frac{f_{0+}(1 - f'_{0+})}{f'_{0+}(1 - f_{0+})} \tag{2-6}$$

and

$$\sum_{j'} P_{j'}(\boldsymbol{k}'_- \to \boldsymbol{k}_+) = \sum_j P_j(\boldsymbol{k}_+ \to \boldsymbol{k}'_-)\, \frac{f_{0+}(1 - f'_{0-})}{f'_{0-}(1 - f_{0+})} \tag{2-7}$$

Furthermore, up to linear terms in g, defined in (2–3), the following relations hold:

$$\frac{f'_+(1 - f_+)}{f'_{0+}(1 - f_{0+})} - \frac{f_+(1 - f'_+)}{f_{0+}(1 - f'_{0+})} = \frac{g'_+}{f'_{0+}(1 - f'_{0+})} - \frac{g_+}{f_{0+}(1 - f_{0+})} \tag{2-8}$$

$$\frac{f'_-(1 - f_+)}{f'_{0-}(1 - f_{0+})} - \frac{f_+(1 - f'_-)}{f_{0+}(1 - f'_{0-})} = \frac{g'_-}{f'_{0-}(1 - f'_{0-})} = \frac{g_+}{f_{0+}(1 - f_{0+})} \tag{2-9}$$

Note that on the right hand side of these equations, the first term contains only primed quantities and the second term only unprimed quantities, whereas the left hand sides are mixed. Making use of the last four equations, (2-5) may be written as follows

$$(\partial f_+/\partial t)_{\text{coll.}} = (1/8\pi^3) \int \mathrm{d}\boldsymbol{k}'_+ \sum_i P_i(\boldsymbol{k}_+ \to \boldsymbol{k}'_+)\, f_{0+}(1 - f'_{0+}) \left[\frac{g'_+}{f'_{0+}(1 - f'_{0+})} - \right.$$

$$- \frac{g_+}{f_{0+}(1 - f_{0+})}\Bigg] + (1/8\pi^3) \int \mathrm{d}\boldsymbol{k}'_- \sum_j P_j(\boldsymbol{k}_+ \to \boldsymbol{k}'_-)\, f_{0+}(1 - f'_{0-}) \cdot$$
$$\cdot \left[\frac{g'_-}{f'_{0-}(1 - f'_{0-})} - \frac{g_+}{f_{0+}(1 - f_{0+})} \right] \qquad (2\text{-}10)$$

Furthermore,

$$f_{0\pm}(1 - f_{0\pm}) = -k_B T \left(\frac{\partial f_{0\pm}}{\partial E_\pm} \right) \qquad (2\text{-}11)$$

and

$$f_{0+}(1 - f'_{0+}) = -k_B T \frac{\partial f_{0+}}{\partial E_+} \frac{1}{1 - f_{0+}\{1 - \exp(-\varepsilon_i/k_B T)\}}$$
$$f_{0+}(1 - f'_{0-}) = -k_B T \frac{\partial f_{0+}}{\partial E_+} \frac{1}{1 - f_{0+}\{1 - \exp(-\varepsilon_j/k_B T)\}} \qquad (2\text{-}12)$$

where $\varepsilon_i = E'_+ - E_+ = (\hbar^2/2m)(k'^2_+ - k^2_+)$ and $\varepsilon_j = E'_- - E_+ = -2\Delta E + (\hbar^2/2m)(k'^2_- - k^2_+)$. Employing (2–3), (2-11) and (2-12) one obtains for (2-10) the following expression

$$\frac{\partial f_+}{\partial t} = -g_+ \Bigg[(1/8\pi^3) \int \mathrm{d}\boldsymbol{k}'_+ \sum_i P_i(\boldsymbol{k}_+ \to \boldsymbol{k}'_+)(1 - k'_x/k_x) \cdot$$
$$\cdot \frac{1}{1 - f_0\{1 - \exp(-\varepsilon_i/k_B T)\}} +$$
$$+ (1/8\pi^3) \int \mathrm{d}\boldsymbol{k}'_- \sum_j P_j(\boldsymbol{k}_+ \to \boldsymbol{k}'_-)(1 - \tau_- k'_x/\tau_+ k_x) \cdot$$
$$\cdot \frac{1}{1 - f_0\{1 - \exp(-\varepsilon_j/k_B T)\}} \Bigg] \equiv -g_+/\tau_+. \qquad (2\text{-}13)$$

Note that the relaxation time τ_+ contains a term which depends on the ratio τ_-/τ_+, as a consequence of collisions involving spin flip.

We now make the usual assumption that the transition probabilities depend only on the magnitudes k' and k, and on the angle of scattering θ. Furthermore, we write the transition probabilities in terms of the matrix elements, M_i, corresponding to a single scattering center of type i as follows:

$$P_i(k_+ \to k'_+, \theta) = (2\pi/\hbar)\, |M_i(k_+ \to k'_+, \theta)|^2\, N_i \delta(E'_+ - E_+ - \varepsilon_i) \qquad (2\text{-}14)$$

N_i is the number of scattering centers producing a particular collision process; the delta function takes care of energy conservation.

Finally, we write for a volume element $\mathrm{d}\boldsymbol{k}'$ in k-space $2\pi \sin\theta\, \mathrm{d}\theta\, k'^2\, \mathrm{d}k' = (2\pi m/\hbar^2)\, k' \sin\theta\, \mathrm{d}\theta\, \mathrm{d}E'$. Expression (2-13) then takes the form

$$1/\tau_+ = (mk/2\pi\hbar^3) \Bigg[\sum_i \int_0^\pi N_i\, |M_i(k_+ \to k'_+, \theta)|^2\, (1 - \cos\theta) \sin\theta\, \mathrm{d}\theta \cdot$$
$$\cdot \frac{1}{1 - f_{0+}\{1 - \exp(-\varepsilon_i/k_B T)\}} +$$

$$+ \sum_j \int_0^\pi N_j \, |M_j(k_+ \to k'_-, \theta)|^2 \{1 - (\tau_-/\tau_+) \cos\theta\} \sin\theta \, \mathrm{d}\theta \cdot$$

$$\cdot \left. \frac{1}{1 - f_{0+}\{1 - \exp(-\varepsilon_j/k_B T)\}} \right]. \tag{2-15}$$

A similar expression holds for $1/\tau_-$.

In order to obtain the conductivity, (2-15) must be substituted into (2-4); the resulting expression for $\sigma_{e\pm}$ then contains an integral of the type

$$I = -\int G(E) \frac{\partial f_0}{\partial E} \, \mathrm{d}E = G(E_F) + \frac{\pi^2}{6} (k_B T)^2 \left[\frac{\mathrm{d}^2 G}{\mathrm{d}E^2}\right]_{E_F} + \dots \tag{2-16}$$

In the usual theory of electrical conductivity where one deals with quasi-elastic scattering, so that the change in energy of the electrons during a collision is small compared to $k_B T$, and hence the numerators $1 - f_0\{1 - - \exp(-\varepsilon/k_B T)\}$ in $1/\tau$ may be omitted, it is common practice to neglect the second and higher terms in (2-16) because they are assumed to be smaller than the first term by powers of $k_B T/E_F$ (this is correct if the derivatives of $|M_{i(j)}|^2$ with respect to E are of the order $|M_{i(j)}|^2/E^p (p \geq 1)$, which seems plausible). In our case, this procedure would be valid when $\varepsilon_{i(j)} \ll k_B T$, i.e. at sufficiently high temperatures.

On the other hand, at very low temperatures the factors $(k_B T)^{2n}$ seem at first sight to provide a rapid convergence of the series. However, due to the special form of the function $G(E)$, the $2n$-th derivative of G contains a part with the factor $(k_B T)^{-2n}$, cancelling the $(k_B T)^{2n}$ in the $(n+1)$-th term in (2-16); this might possibly give rise to a non-negligible contribution to I under certain circumstances, originating in charge transport by electrons having not exactly the Fermi energy. Fortunately, it turns out that the first term of (2-16) is still a sufficiently good approximation for the integral I; one can show, in fact, that the terms under consideration still go to zero for $T \to 0$ and we feel justified in neglecting all terms in (2-16) beyond $G(E_F)$. (We shall return to this point in section 4 in connection with the work of Brailsford and Overhauser[18]).

Following the procedure outlined above, we obtain from (2-4) the well-known formula

$$\sigma_{e\pm} = (n_\pm e^2/m) \, \tau_{F\pm} \tag{2-17}$$

where τ_F is the relaxation time for electrons with the Fermi energy.

Note that if the matrix elements in (2-15) are independent of θ, i.e. if the scattering is isotropic, the term containing (τ_-/τ_+) disappears upon integration. Thus, for *isotropic* scattering, the relaxation times $\tau_{F\pm}$ are given by

$$1/\tau_{F\pm} = (mk_F/\pi\hbar^3) \left[\sum_i N_i \, |M_i(k_\pm \to k'_\pm)|^2 \frac{2}{1 + \exp(-\varepsilon_i/k_B T)} + \right.$$

$$+ \sum_j N_j \, |M_j(k_\pm \to k'_\mp)|^2 \frac{2}{1 + \exp(-\varepsilon_j/k_B T)} \Big]. \qquad (2\text{-}18)$$

In this formula, the quantities $k_{F\pm}$ satisfying $E_F = \pm \Delta E + (\hbar^2 k^2_{F\pm}/2m)$ have been replaced by $k_F = \sqrt{2mE_F/\hbar^2}$, from which they differ only by an amount of order $\Delta E/E_F$.

3. *Scattering of conduction electrons by isolated magnetic ions.* In this section we shall consider the resistivity ρ_i resulting from scattering of the conduction electrons by isolated magnetic ions. The magnetic ions will be characterized by a spin angular momentum operator $\boldsymbol{S}$ (expressed in units $\hbar$), a spin quantum number S and a magnetic spin quantum number M_s, which runs from $-S$ to $+S$. If $u(S, M_s)$ represents a spin eigenfunction, the following relations hold:

$$\begin{aligned} \boldsymbol{S}^2 u(S, M_s) &= S(S+1)\, u(S, M_s) \\ S_z u(S, M_s) &= M_s u(S, M_s) \end{aligned} \qquad (3\text{-}1)$$

Similarly, the electron spin operator is $\boldsymbol{s}$ and the eigenvalues of $\boldsymbol{s}^2$ and s_z are $s(s+1)$ and m_s respectively, where $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$.

Choosing the origin of our coordinate system at the center of a magnetic ion, we shall assume that the Hamiltonian for an electron at $\boldsymbol{r}$ interacting with the ion consists of the following two parts:

$$\mathscr{H}_0 = \frac{p^2}{2m} + U(\boldsymbol{r}) + g\beta S_z H + 2\beta s_z H$$

and (3-2)

$$\mathscr{H}_1 = V(\boldsymbol{r}) - 2J(\boldsymbol{r})\, \boldsymbol{s}\cdot\boldsymbol{S}.$$

Here, $\boldsymbol{p}$ and m are the momentum and effective mass of the conduction electron; $U(\boldsymbol{r})$ is the periodic potential of the crystal lattice; the third and fourth terms in $\mathscr{H}_0$ represent the energy of the ion and the electron in a magnetic field H pointing along the z direction, with $\beta = e\hbar/2mc$ representing the Bohr magneton, and g and 2 the spectroscopic splitting factors of ion and electron, respectively. $V(\boldsymbol{r})$ describes the usual spin independent interaction between the electron and the ion, whereas the term containing $J(\boldsymbol{r})$ stands for the exchange interaction between them; V and J are real.

The eigenvalues of $\mathscr{H}_0$ are

$$E(k, M_s, m_s) = \frac{\hbar^2 k^2}{2m} + g\beta M_s H + 2\beta m_s H. \qquad (3\text{-}3)$$

From the assumed form of the exchange interaction it follows immediately that in the scattering processes the quantities S, s and $(M_s + m_s)$ remain unchanged, because the operators $\boldsymbol{S}^2$, $\boldsymbol{s}^2$ and $(S_z + s_z)$ all commute with the Hamiltonian $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$. The initial state of the system electron plus ion will be characterized by the quantum numbers M_s and m_s, and by the wave vector $\boldsymbol{k}$ of the electron. In the Born approximation, the scattering processes leading to transitions of the electron from $\boldsymbol{k}$ to $\boldsymbol{k}'$ are then governed by matrix elements (cf. (2-14))

$$M_{i(j)}(k(m_s), k'(m_s'), \theta) = \langle m_s', M_S' \,|\, \textstyle\int \mathscr{H}_1(\boldsymbol{r})\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r} \,|\, m_s, M_S\rangle \tag{3-4}$$

where the integration over $\boldsymbol{r}$ extends over unit volume of the crystal. $\boldsymbol{q} \equiv \boldsymbol{k} - \boldsymbol{k}'$, and m_s', M_S' define the final spin state of the system. Performing the integration over $\boldsymbol{r}$, (3-4) becomes

$$\langle m_s', M_S' \,|V(q) - 2J(q)\{s_zS_z + \tfrac{1}{2}(s_+S_- + s_-S_+)\}|\, m_s, M_S\rangle \tag{3-5}$$

where, as usual, the dependence of

$$V(\boldsymbol{q}) \equiv \textstyle\int V(\boldsymbol{r})\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r} \quad \text{and} \quad J(\boldsymbol{q}) \equiv \textstyle\int J(\boldsymbol{r})\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r}$$

upon the direction of $\boldsymbol{q}$ is neglected; $S_\pm = S_x \pm iS_y$. The relevant non-vanishing spin-matrix elements are

$$\langle m_s, M_S\, |s_zS_z|\, m_sM_S\rangle = m_sM_S \tag{3-6}$$

$$\begin{aligned}\langle m_s + 1, M_S - 1\, |s_+S_-|\, m_s, M_S\rangle &= \\ &= \{(s - m_s)(s + m_s + 1)(S + M_S)(S - M_S + 1)\}^{\frac{1}{2}}\end{aligned} \tag{3-7}$$

$$\begin{aligned}\langle m_s - 1, M_S + 1\, |s_-S_+|\, m_s, M_S\rangle &= \\ &= \{(s + m_s)(s - m_s + 1)(S - M_S)(S + M_S + 1)\}^{\frac{1}{2}}\end{aligned} \tag{3-8}$$

The matrix element (3-6) gives rise to scattering without spin flip, whereas (3-7) and (3-8) correspond to collisions with spin flip. Note that (3-7) automatically vanishes for $m_s = +\frac{1}{2}$ as it should, because in this state the electron can make a transition only to $m_s' = -\frac{1}{2}$. Similarly, (3-8) vanishes automatically if $m_s = -\frac{1}{2}$. Also note that (3-7) and (3-8) vanish, respectively, if $M_S = -S$ and if $M_S = +S$; these cases are thus automatically excluded in a summation over M_S from $-S$ to $+S$. The collisions without spin flip may be considered elastic. In a collision with spin flip, the electron absorbs an energy

$$\varepsilon_j \equiv \frac{\hbar^2k'^2}{2m} - \frac{\hbar^2k^2}{2m} \mp 2\Delta E;$$

here $\Delta E = \beta H$, so that by (3-3) $\varepsilon_j = \mp g\beta H$ for $m_s = \pm\frac{1}{2}$, because the total energy of scattering center plus electron must remain constant.

Substituting the above information into expression (2-15) for the relaxation times, we obtain

$$\frac{1}{\tau_\pm} = \frac{mkN_i}{2\pi\hbar^3} \sum_{M_s=-S}^{+S} p_{M_s} \left[\int_0^\pi |V(q) \mp J(q)\, M_S|^2 \sin\theta\, \mathrm{d}\theta (1 - \cos\theta) + \right.$$

$$+\int_0^{\pi} |J(q)|^2\,(S \mp M_s)(S \pm M_s + 1)\cdot$$

$$\cdot\sin\theta\,\mathrm{d}\theta\left(1-\frac{\tau_-}{\tau_+}\cos\theta\right)\frac{1}{1-f_{0\pm}\left\{1-\exp\left(\dfrac{\pm g\beta H}{k_BT}\right)\right\}}\Bigg] \qquad (3\text{-}9)$$

The upper signs refer to electrons with $m_s = +\frac{1}{2}$; the lower signs refer to $m_s = -\frac{1}{2}$. The quantity P_{M_s} represents the probability for a given magnetic scattering center to be in the state M_s; N_i is the number of isolated scattering centers per unit volume.

If $V(q_F)$ and $J(q_F)$ are independent of θ (isotropic scattering at the Fermi level), the value of τ at the Fermi level is, according to (2-18), given by

$$\frac{1}{\tau_{F\pm}}=\frac{mk_FN_i}{\pi\hbar^3}\sum_{M_s=-S}^{+S}p_{M_s}\Bigg[(V\mp JM_s)^2+J^2(S\mp M_s)(S\pm M_s+1)\cdot$$

$$\cdot\frac{2}{1+\exp\left(\pm\dfrac{g\beta H}{k_BT}\right)}\Bigg] \qquad (3\text{-}10)$$

where $V \equiv V(q_F)$ and $J \equiv J(q_F)$

If there are no internal or external magnetic fields, $\varepsilon_j = 0$; in that case, $p_{M_s} = 1/(2S+1)$ and all collisions are elastic. Under these circumstances, the two relaxation times will be equal and the part of the resistivity under consideration becomes

$$\rho_i=\left(\frac{m}{ne^2}\right)\left(\frac{1}{\tau_F}\right)_i=\frac{m^2k_F\,N_i}{\pi ne^2\hbar^3}\,[V^2+J^2S(S+1)] \qquad (3\text{-}11)$$

Thus, the resistivity produced by the exchange interaction is proportional to $S(S+1)$.

Magnetoresistance. In the presence of a uniform internal or external field H, we have

$$p_{M_s}=\frac{\exp(-\alpha M_s)}{D}\ \text{where}\ \alpha=\frac{g\beta H}{k_BT}\ \text{and}\ D=\sum_{M_s=-S}^{+S}\mathrm{e}^{-\alpha M_s} \qquad (3\text{-}12)$$

and the following relations hold

$$\left.\begin{aligned}
&\Sigma\,p_{M_s}=1\\
&\Sigma\,M_sp_{M_s}=-\frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}\alpha}=-\left(\frac{2S+1}{2}\right)\coth\left\{\frac{(2S+1)\,\alpha}{2}\right\}+\tfrac{1}{2}\coth\frac{\alpha}{2}\\
&\Sigma\,M_s^2p_{M_s}=\frac{1}{D}\frac{\mathrm{d}^2D}{\mathrm{d}\alpha^2}=S(S+1)-\left(\frac{2S+1}{2}\right)\coth\left\{\frac{(2S+1)\alpha}{2}\right\}\coth\frac{\alpha}{2}+\\
&\qquad+\tfrac{1}{2}\coth^2\frac{\alpha}{2}=S(S+1)-\frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}\alpha}\coth\frac{\alpha}{2}
\end{aligned}\right\} \qquad (3\text{-}14)$$

The summations over M_s run from $-S$ to $+S$. Expression (3-10) may then be put in the following form

$$\frac{1}{\tau_{F\pm}} = \frac{mk_F N_i}{\pi \hbar^3}\left[V^2 + J^2\left\{S(S+1) - \frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}\alpha}\tanh\frac{\alpha}{2}\right\} \pm 2VJ\frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}\alpha}\right] \equiv \frac{1}{\tau_{F0}} - \frac{1}{\tau_1} \pm \frac{1}{\tau_2} \qquad (3\text{-}15)$$

Here, τ_{F0} represents the relaxation time in the absence of a magnetic field (cf. (3-11)); τ_1 and τ_2 are a consequence of the magnetic field and are defined by the corresponding terms containing D in (3-15). From the additivity of the conductivities $\sigma_{e\pm}$ one readily finds for the ratio of the impurity resistivities with and without magnetic field

$$\frac{\rho_i(H)}{\rho_i(0)} = \frac{2\tau_{F0}}{\tau_{F+} + \tau_{F-}} = 1 - \frac{\tau_{F0}}{\tau_1} - \left(\frac{\tau_{F0}}{\tau_2}\right)^2 \frac{\tau_1}{\tau_1 - \tau_{F0}}. \qquad (3\text{-}16)$$

If we limit the discussion of the magnetoresistance to relatively small magnetic fields, we may write $\tanh(\alpha/2) \approx \alpha/2$ and $\mathrm{d}\ln D/\mathrm{d}\alpha \approx S(S+1)\alpha/3$. In that case

$$\frac{1}{\tau_1} \approx \frac{mk_F N_i}{6\pi\hbar^3} J^2 S(S+1)\,\alpha^2$$

$$\frac{1}{\tau_2} \approx \frac{2mk_F N_i}{3\pi\hbar^3} VJS(S+1)\,\alpha$$

and one finds from (3-16)

$$\frac{\rho_i(H)}{\rho_i(0)} \approx 1 - \left(\frac{g\beta H}{k_B T}\right)^2 \left[\frac{J^2}{V^2 + J^2 S(S+1)}\,\tfrac{1}{6}\,S(S+1) + \left\{\frac{2VJ}{V^2 + J^2 S(S+1)}\,\tfrac{1}{3}S(S+1)\right\}^2\right] \qquad (3\text{-}17)$$

where terms in H with a power larger than two have been neglected. Thus, isolated magnetic atoms produce a negative magnetoresistance, as one should expect because a magnetic field tends to order the system of atomic spins.

4. *Scattering of conduction electrons by nearest neighbour pairs of magnetic ions.* If the scattering by nearest neighbour pairs of magnetic ions is considered, pair energy levels enter into the calculation and more differentiated types of scattering arise, even in the absence of a magnetic field. For instance, in the latter case elastic collisions may occur with electron spin flip corresponding to a change in direction, but not in magnitude, of the total spin of an ion pair. Also, inelastic collisions may occur without electron spin flip (or,

illustratively said, with double electron spin flip) accompanying a change in magnitude, though not in z-component, of the total ion pair spin.

The Hamiltonian for an electron at $\boldsymbol{r}$ with spin $\boldsymbol{s}$ interacting with a nearest neighbour pair of solute magnetic ions at 0 and $\boldsymbol{R}$, with spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ respective- ly, is taken to be the sum of (cf. (3-2))

$$\mathscr{H}_0 = \frac{p^2}{2m} + U(\boldsymbol{r}) - W\boldsymbol{S}_1\cdot\boldsymbol{S}_2 + g\beta(S_{1z} + S_{2z}) + 2\beta s_z H$$

and

$$\begin{aligned}\mathscr{H}_1 = V(\boldsymbol{r}) + V(\boldsymbol{r}-\boldsymbol{R}) - 2J(\boldsymbol{r})\,\boldsymbol{s}\cdot\boldsymbol{S}_1 - 2J(\boldsymbol{r}-\boldsymbol{R})\,\boldsymbol{s}\cdot\boldsymbol{S}_2 &= \\ = V(\boldsymbol{r}) + V(\boldsymbol{r}-\boldsymbol{R}) - \{J(\boldsymbol{r}) + J(\boldsymbol{r}-\boldsymbol{R})\}&\cdot \\ \{\boldsymbol{s}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2)\} - \{J(\boldsymbol{r}) - J(\boldsymbol{r}-\boldsymbol{R})\}\{\boldsymbol{s}\cdot(\boldsymbol{S}_1-\boldsymbol{S}_2)\}& \qquad (4\text{-}1)\end{aligned}$$

where W is the effective exchange interaction between nearest neighbour magnetic ions; the fourth and fifth terms in $\mathscr{H}_0$ represent the energy of the ion pair and the electron in a magnetic field H, pointing, as before, in the z-direction.

The eigenvalues of $\mathscr{H}_0$ are

$$E(k, I, M, m_s) = \frac{\hbar^2 k^2}{2m} + W_I + g\beta MH + 2\beta m_s H \qquad (4\text{-}2)$$

where $I\,(I+1)$, M and m_s are the eigenvalues of $(\boldsymbol{S}_1+\boldsymbol{S}_2)^2$, $S_{1z}+S_{2z}$ and s_z respectively ($I = 0, 1, \ldots, 2S; M = -I, -I+1, \ldots, +I; m_s = -\frac{1}{2}, +\frac{1}{2}$), and

$$W_I = \tfrac{1}{2}W\{2S(S+1) - I(I+1)\} \qquad (4\text{-}3)$$

are the eigenvalues of

$$-W\boldsymbol{S}_1\cdot\boldsymbol{S}_2 = \tfrac{1}{2}W\{\boldsymbol{S}_1^2 + \boldsymbol{S}_2^2 - (\boldsymbol{S}_1+\boldsymbol{S}_2)^2\}$$

The probability that a pair state (I, M) is occupied reads

$$p_{I,M} = \frac{\exp\{-(W_I + g\beta MH)/k_BT\}}{\sum\limits_{I'=0}^{2S}\ \sum\limits_{M'=-I'}^{+I'} \exp\{-(W_{I'} + g\beta M'H)/k_BT\}} \qquad (4\text{-}4)$$

For zero magnetic field this becomes

$$p_I = \frac{\exp(-W_I/k_BT)}{\sum\limits_{I'=0}^{2S} (2I'+1)\exp(-W_{I'}/k_BT)} \qquad (4\text{-}4a)$$

The scattering processes under consideration are governed by matrix elements

$$M_{i(j)}(k(m_s), k'(m_s'), \theta) = \langle m_s', I', M' | \textstyle\int \mathscr{H}_1 \exp(i\boldsymbol{q}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} |\, m_s, I, M\rangle \qquad (4\text{-}5)$$

(cf. (2-14)) in analogy to (3-4). The integration over $\boldsymbol{r}$ involves

$$\int \mathscr{H}_1 \exp(i\boldsymbol{q}\cdot\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = (1 + \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{R}}) \int [V(\boldsymbol{r}) - J(\boldsymbol{r})\{\boldsymbol{s}\cdot(\boldsymbol{S}_1 + \boldsymbol{S}_2)\}\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r} -$$
$$- (1 - \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{R}}) \int J(\boldsymbol{r})\{\boldsymbol{s}\cdot(\boldsymbol{S}_1 - \boldsymbol{S}_2)\}\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r} =$$
$$= (1 + \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{R}})[V(q) - J(q)\{\boldsymbol{s}\cdot(\boldsymbol{S}_1 + \boldsymbol{S}_2)\}] - (1 - \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{R}})\, J(q)\{\boldsymbol{s}\cdot(\boldsymbol{S}_1 - \boldsymbol{S}_2)\} \quad (4\text{-}6)$$

where, as usual, the dependence of

$$V(\boldsymbol{q}) = \int V(\boldsymbol{r})\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r} \quad \text{and} \quad J(\boldsymbol{q}) = \int J(\boldsymbol{r})\, \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r}$$

upon the direction of $\boldsymbol{q}$ is neglected.

The relevant non-vanishing spin-matrix elements are found from general considerations on angular momentum operators[20]), providing as selection rules

for $\boldsymbol{S}_1 + \boldsymbol{S}_2$: $\Delta I = 0, \Delta M = 0, \pm 1$; for $\boldsymbol{S}_1 - \boldsymbol{S}_2$: $\Delta I = \pm 1, \Delta M = 0, \pm 1$; in processes with $\Delta M = 0$ the electron spin does not reverse; with $\Delta M = \pm 1$ it does.

With each process, we indicate the amount of energy absorbed by the electron.

$$\langle m_s, I, M\, |s_z(S_{1z} + S_{2z})|\, m_s, I, M\rangle = m_s M;\quad \varepsilon_i = 0$$

$$\langle m_s \mp 1, I, M \pm 1\, |s_\mp(S_{1\pm} + S_{2\pm})|\, m_s, I, M\rangle =$$
$$= \{(s \mp m_s)(s \pm m_s + 1)(I \mp M)(I \pm M + 1)\}^{\frac{1}{2}};\quad \varepsilon_j = \mp g\beta H$$

$$\langle m_s, I, M\, |s_z(S_{1z} - S_{2z})|\, m_s, I - 1, M\rangle =$$
$$= m_s \left\{ (I + M)(I - M)\, \frac{(2S + 1)^2 - I^2}{4I^2 - 1} \right\}^{\frac{1}{2}};\quad \varepsilon_i = WI$$

$$\langle m_s \mp 1, I, M\, |s_\mp(S_{1\pm} - S_{2\pm})|\, m_s, I - 1, M \mp 1\rangle =$$
$$= \left\{ (s \mp m_s)(s \pm m_s + 1)(I \pm M)(I \pm M - 1)\, \frac{(2S + 1)^2 - I^2}{4I^2 - 1} \right\}^{\frac{1}{2}};$$
$$\varepsilon_j = WI \mp g\beta H$$

$$\langle m_s, I - 1, M\, |\, s_z\, (S_{1z} - S_{2z})\, |\, m_s, I, M\rangle = m_s \left\{ (I + M)(I - M)\, \frac{(2S+1)^2 - I^2}{4I^2 - 1} \right\}^{\frac{1}{2}};$$
$$\varepsilon_i = -\, WI$$

$$\langle m_s \mp 1, I - 1, M \pm 1\, |s_\mp(S_{1\pm} - S_{2\pm})|\, m_s, I, M\rangle =$$
$$= \left\{ (s \mp m_s)(s \pm m_s + 1)(I \mp M - 1)(I \mp M)\, \frac{(2S + 1)^2 - I^2}{4I^2 - 1} \right\}^{\frac{1}{2}};$$
$$\varepsilon_j = -WI \mp g\beta H$$

The interference factors $|1 \pm \exp(i\boldsymbol{q}\cdot\boldsymbol{R})|^2$ which occur in the expressions for the relaxation times as a consequence of (4-6), must be averaged over all orientations of $\boldsymbol{R}$ relative to $\boldsymbol{q}$, which is best done by integration

$$\frac{1}{4\pi}\iint|1 \pm \mathrm{e}^{iqR\cos\chi}|^2 \sin\chi\,\mathrm{d}\chi\,\mathrm{d}\varphi = 2\left(1 \pm \frac{\sin qR}{qR}\right) \tag{4-8}$$

Substitution of the matrix elements (4-4) into (2-15) by means of (4-5), (4-6) and (4-7) yields, with N_p the number of nearest neighbour ion pairs per unit volume,

$$\begin{aligned}
\frac{1}{\tau_\pm} = \frac{mk}{\pi\hbar^3} N_p \sum_{I=0}^{2S}\sum_{M=-I}^{+I}\Bigg[& p_{I,M}\int_0^\pi\left(1+\frac{\sin qR}{qR}\right) \\
& \cdot|V(q) \mp \tfrac{1}{2}MJ(q)|^2\,(1-\cos\theta)\sin\theta\,\mathrm{d}\theta + \\
& + p_{I-1,M}\int_0^\pi\left(1-\frac{\sin qR}{qR}\right)|J(q)|^2\,\tfrac{1}{4}(I+M)\,(I-M)\cdot \\
& \cdot\frac{(2S+1)^2-I^2}{4I^2-1}\;\frac{(1-\cos\theta)\sin\theta\,\mathrm{d}\theta}{1-f_0\{1-\exp(-WI/k_BT)\}} + \\
& + p_{I,M}\int_0^\pi\left(1-\frac{\sin qR}{qR}\right)|J(q)|^2\,\tfrac{1}{4}(I+M)(I-M)\cdot \\
& \frac{(2S+1)^2-I^2}{4I^2-1}\;\frac{(1-\cos\theta)\sin\theta\,\mathrm{d}\theta}{1-f_0\{1-\exp(WI/k_BT)\}} + \\
& + p_{I,M}\int_0^\pi\left(1+\frac{\sin qR}{qR}\right)|J(q)|^2\,\tfrac{1}{4}(I \mp M)(I \pm M+1)\cdot \\
& \cdot\left(1-\frac{\tau_\mp}{\tau_\pm}\cos\theta\right)\sin\theta\,\mathrm{d}\theta\,\frac{1}{1-f_0\{1-\exp(\pm g\beta H/k_BT)\}} + \\
+ p_{I-1,M\mp1} & \int_0^\pi\left(1-\frac{\sin qR}{qR}\right)|J(q)|^2\,\tfrac{1}{4}(I \pm M)(I \pm M-1)\,\frac{(2S+1)^2-I^2}{4I^2-1}\cdot \\
& \left(1-\frac{\tau_\mp}{\tau_\pm}\cos\theta\right)\sin\theta\,\mathrm{d}\theta\;\frac{1}{1-f_0\left\{1-\exp\left(\dfrac{-WI \pm g\beta H}{k_BT}\right)\right\}} + \\
+ p_{I,M} & \int_0^\pi\left(1-\frac{\sin qR}{qR}\right)|J(q)|^2\,\tfrac{1}{4}(I \mp M-1)(I \mp M)\,\frac{(2S+1)^2-I^2}{4I^2-1}\cdot \\
& \cdot\left(1-\frac{\tau_\mp}{\tau_\pm}\cos\theta\right)\sin\theta\,\mathrm{d}\theta\;\frac{1}{1-f_0\left\{1-\exp\left(\dfrac{WI \pm g\beta H}{k_BT}\right)\right\}}
\end{aligned} \tag{4-9}$$

(N.B. In the second and fifth terms between the square brackets in (4-9), one starts from states other than (I, M), still retaining the same summation limits; it is easily seen, though, that the terms omitted or added are all zero).

We shall first consider the situation for $H = 0$, which is less complicated and still brings out the main features; this is also the case treated by Brailsford and Overhauser[14]). All states with the same I but different M become equally probable (cf. (4-4*a*)), and in (4-9) the terms linear in M vanish upon summation over M from $-I$ to $+I$. The two equations for τ_+ and τ_- coincide into one equation for τ, as expected physically from the absence of a preferred direction. In analogy with (3-11) we find for the "pair resistivity"

$$\rho_p = \frac{m}{ne^2}\left(\frac{1}{\tau_F}\right)_p = \frac{m^2 k_F N_p}{\pi n e^2 \hbar^3}\{A + \beta(T)\, B + \gamma(T)\, C\} \tag{4-10}$$

with

$$\left.\begin{aligned} \beta(T) &= \tfrac{1}{4}\sum_I p_I I(I+1)(2I+1) \\ \gamma(T) &= \sum_I p_I I\,\frac{(2S+1)^2 - I^2}{\exp\dfrac{WI}{k_B T} + 1} \end{aligned}\right\} \tag{4-11}$$

$$\left.\begin{aligned} A &= \int_0^\pi \left(1 + \frac{\sin q_F R}{q_F R}\right) |V(q_F)|^2\,(1 - \cos\theta)\sin\theta\,\mathrm{d}\theta \\ B &= \int_0^\pi \left(1 + \frac{\sin q_F R}{q_F R}\right) |J(q_F)|^2\,(1 - \cos\theta)\sin\theta\,\mathrm{d}\theta \\ C &= \int_0^\pi \left(1 - \frac{\sin q_F R}{q_F R}\right) |J(q_F)|^2\,(1 - \cos\theta)\sin\theta\,\mathrm{d}\theta \\ D &= \int_0^\pi \left(1 + \frac{\sin q_F R}{q_F R}\right) 2V(q_F)\,J(q_F)(1 - \cos\theta)\sin\theta\,\mathrm{d}\theta \end{aligned}\right\} \tag{4-12}$$

(The integral D enters only in the presence of a magnetic field).

The temperature dependence of ρ_p is contained in the coefficients $\beta(T)$ and $\gamma(T)$. Following Brailsford and Overhauser[14]) we find their asymptotic values for small and large T:

$k_B T \ll |W|$

$$\text{if } W > 0 \quad \beta(T) \approx \tfrac{1}{2}S(2S+1) - S\,\frac{4S-1}{4S+1}\exp\left(-\frac{2WS}{k_B T}\right)$$

$$\gamma(T) \approx 2S\exp\left(-\frac{2WS}{k_B T}\right) \tag{4-13}$$

$$\text{if } W < 0 \quad \begin{aligned} \beta(T) &\approx \tfrac{3}{2} \exp\left(\frac{W}{k_B T}\right) \\ \gamma(T) &\approx 4S(S+1) \exp\left(\frac{W}{k_B T}\right) \end{aligned} \tag{4-13}$$

$k_B T \gg |W|$

$$\begin{aligned} \beta(T) &\approx \tfrac{1}{2} S(S+1) \left\{ 1 + \frac{WS(S+1)}{3k_B T} \right\} \\ \gamma(T) &\approx \tfrac{1}{2} S(S+1) \left\{ 1 - \frac{WS(S+1)}{3k_B T} \right\} \end{aligned} \tag{4-14}$$

If we assume that $V(q_F)$ and $J(q_F)$ are independent of the scattering angle and we write $V \equiv V(q_F)$ and $J \equiv J(q_F)$, the "high" temperature behaviour of ρ_p takes the form

$$\rho_p = \frac{m^2 k_F N_p}{\pi n e^2 \hbar^3} \left[A + 2J^2 S(S+1) \left\{ 1 + F(k_F R)\, W \frac{S(S+1)}{3k_B T} \right\} \right] \tag{4-15}$$

where the function

$$F(x) \equiv \frac{2x \sin 2x + (1 - 2x^2) \cos 2x - 1}{2x^4}$$

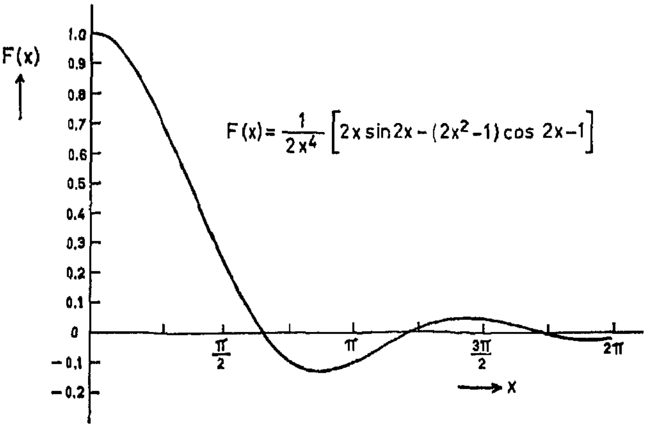

Fig. 1. The interference function F(x).

comes from integration of the terms $(\sin q_F R)/q_F R$ in (4-12). In terms of this function, expression (4-10) takes the form

$$\rho_p = \frac{2m^2 k_F N_p}{\pi n e^2 \hbar^3} [V^2\{1 + F(k_F R)\} + J^2 \beta(T)\{1 + F(k_F R)\} + \\ + J^2 \gamma(T)\{1 - F(k_F R)\}] \tag{4-16}$$

It is clear from (4-15) that the total resistivity (magnetic impurity + phonon resistivity) as a function of T exhibits a minimum only if $WF(k_F R) > 0$. The values of $k_F R$ for which this occurs for a given sign of W

may be read from figure 1. In the case of ferromagnetic coupling between neighbouring solute ions ($W > 0$) such a minimum is followed by a maximum at lower temperatures if $F(k_FR) < (4S + 3)/(12S + 1)$, as can be shown by an analysis of (4-13). If the coupling is antiferromagnetic ($W < 0$), a minimum is always followed by a maximum.

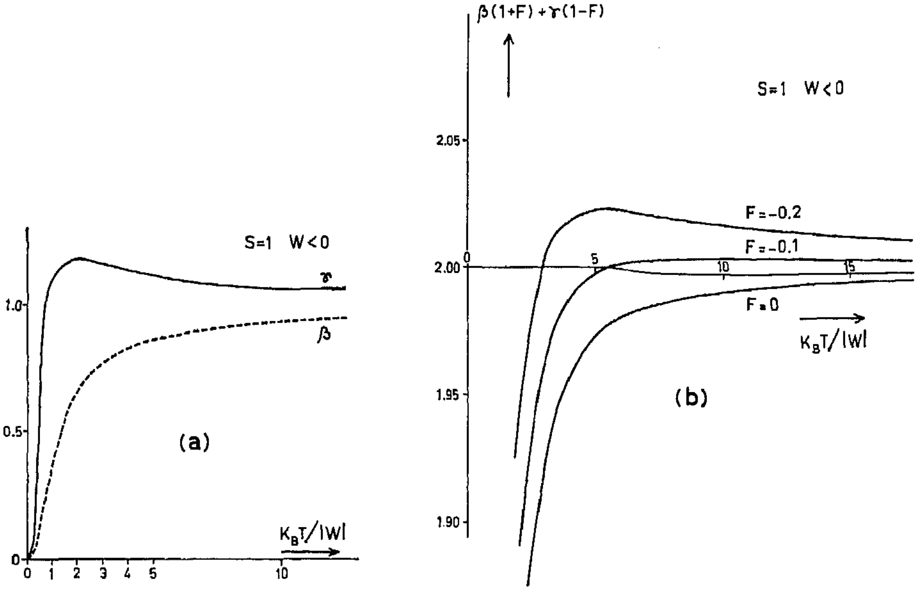

Fig. 2. (*a*) The temperature dependence of β and γ for the special case $S = 1$ and antiferromagnetic coupling between the partners of a pair; (*b*) gives the corresponding temperature dependent part of the pair-resistivity for three values of F.

In figure 2*a* we show the temperature dependence of $\beta(T)$ and $\gamma(T)$ for the special case $W < 0$ and $S = 1$; figure 2*b* gives the corresponding temperature dependence of the resistivity calculated for three values of $F(k_FR)$.

As to the "corrected" formula of Brailsford and Overhauser[18]), we may remark that these authors met with a convergence problem similar to the one mentioned toward the end of section 2; they got around it by using a different integration procedure, which makes their corrected result look better at small T than the original one. Nevertheless, the procedure is not wholly justified, as they make use from the beginning of a constant a which already contains a relaxation time taken at the Fermi level (ref. 18, eq. (2)), to be compared with our formula (2-3)). The actual integral involved is much more complicated, but, as was mentioned in section 2, the correction terms in it tend to zero for $T \to 0$, contrary to the conclusion from their partial approximation.

Magnetoresistance. The application of a small magnetic field

($g\beta H \ll k_BT$) causes in general a decrease of ρ_p (negative magnetoresistance); under certain circumstances, however, i.e. if the pairs are strongly antiferromagnetically coupled and the cross-term D is sufficiently small, ρ_p may increase slightly. This is indeed what one expects from physical arguments.

5. *Resistivity of a ferromagnetic metal.* The exchange scattering of conduction electrons in a ferromagnetic metal with localized spins has been treated by Kasuya[6]) and by De Gennes and Friedel[7]). These authors assumed that the scattering results from the departure of each ion spin from the mean ion spin σ. Approximating the ferromagnetic coupling between ion spins by a molecular field model, we may apply the formulae already found for the scattering of conduction electrons by isolated magnetic ions in a magnetic field by introducing two alterations:

(*a*) Replacing $g\beta \boldsymbol{S}\cdot\boldsymbol{H}$ by the energy $-\gamma\boldsymbol{S}\cdot\boldsymbol{\sigma}$ of an ion spin in the molecular field, due to the total magnetization of the crystal lattice; the molecular field coupling constant γ is connected with the Curie temperature T_c by

$$\gamma = 3k_BT_c/S(S+1)$$

(*b*) Transferring a term $V(\boldsymbol{r}) - 2J(\boldsymbol{r})\,\boldsymbol{s}\cdot\boldsymbol{\sigma}$ from $\mathscr{H}_1$ to $\mathscr{H}_0$; this merely means inclusion of the periodic part of the electron-ion exchange interaction in the unperturbed Hamiltonian, leaving $\boldsymbol{S} - \boldsymbol{\sigma}$ for each ion to govern the electron scattering.

Thus, (3-2) becomes

$$\mathscr{H}_0 = \frac{p^2}{2m} + U(\boldsymbol{r}) + V(\boldsymbol{r}) - 2J(\boldsymbol{r})\,s_z\sigma - \gamma S_z\sigma$$

and \hfill (5-1)

$$\mathscr{H}_1 = -2J(\boldsymbol{r})\,\boldsymbol{s}\cdot(\boldsymbol{S}-\boldsymbol{\sigma}) = -2J(\boldsymbol{r})\{s_zS_z - s_z\sigma + \tfrac{1}{2}(s_+S_- + s_-S_+)\} \tag{5-1}$$

Here, the z-direction is taken to be that of spontaneous magnetization.

We shall assume that the added $\boldsymbol{s}$-dependent potential in $\mathscr{H}_0$ is sufficiently accounted for by a shift $\pm\Delta E$ (corresponding to $m_s = \pm\frac{1}{2}$) in the bottom of the conduction band, where ΔE is now proportional to σ (but of different sign); a more painstaking approximation would not be consistent with our simple model.

Just as in section 3 we may neglect the differences between $n_\pm$ and $\frac{1}{2}n$, and between $k_{F\pm}$ and k_F, (being of the order of $\Delta E/E_F$), at least as long as σ is not too large ($\sigma \ll S$); that is to say, we exclude the low temperature region ($T \lesssim \frac{1}{2}T_c$, say) where our model is not satisfactory anyway and should be supplemented by consideration of spin waves.

Application of section 3 is straightforward; with

$$\langle m_s, M_s\,|s_zS_z - s_z\sigma|\,m_s, M_s\rangle = m_s(M_s - \sigma)$$

and the other matrix elements remaining unchanged, it yields

$$\frac{1}{\tau_{F\pm}} = \frac{mk_F N}{\pi\hbar^3} \sum_{M_s=-S}^{+S} p_{M_s} \Big[J^2(M_s - \sigma)^2 + + J^2(S \mp M_s)(S \pm M_s + 1) \frac{2}{1 + \exp\left(\mp \frac{\gamma\sigma}{k_B T}\right)} \Big] \tag{5-2}$$

where N is the number of ions per unit volume and the scattering is taken to be isotropic.

Taking into account that

$$\sigma = \sum_{-S}^{+S} p_{M_s} M_s$$

$$p_{M_s} = \frac{\exp(\gamma\sigma M_s/k_B T)}{\sum_{-S}^{+S} \exp(\gamma\sigma M_s'/k_B T)}$$

$$\sum_{-S}^{+S} p_{M_s} M_s^2 = S(S+1) - \sigma \coth(\gamma\sigma/k_B T) = = S(S+1) \mp \sigma \frac{1 + \exp(\mp\gamma\sigma/k_B T)}{1 - \exp(\mp\gamma\sigma/k_B T)}$$

(5-2) simplifies into

$$\frac{1}{\tau_{F\pm}} = \frac{mk_F N}{\pi\hbar^3} J^2 \{S(S+1) - \sigma^2 - \sigma \tanh(\gamma\sigma/2k_B T)\} \tag{5-3}$$

Note that no difference is found between the two relaxation times. This means that the resistivity becomes simply

$$\rho = \frac{m^2 k_F N}{\pi n e^2 \hbar^3} J^2 [S(S+1) - \sigma^2 - \sigma \tanh\{3T_c\sigma/2TS\,(S+1)\}] \tag{5-4}$$

Although our assumptions are essentially the same as those introduced by Kasuya6), our formula differs from his result in that the term $-\sigma \tanh(\gamma\sigma/2k_B T)$ in (5-4) has been replaced by $-\sigma$. Whereas Kasuya's formula leads to an infinite value of $d\rho/dT$ immediately below the Curie temperature, (5-4) predicts a finite positive value which is in better agreement with experiment.

In their discussion of the spin-disorder resistivity, De Gennes and Friedel7) concluded that for temperatures not too far below T_c, the collisions between the conduction electrons and the spin-lattice can be considered elastic. In this approximation they find for the dependence of ρ on the average spin σ the following formula

$$\rho(\sigma)/\rho(0) = 1 - \sigma^2/\{S(S+1)\} \tag{5-5}$$

We note that this formula can be obtained from (5-4) by omitting the last term.

In figure 3 we give a comparison between the formulae of Kasuya, De Gennes and Friedel and our formula (5-4) for the case $S = 7/2$. It should be pointed out that actually none of these formulae can be applied to the region of low temperatures.

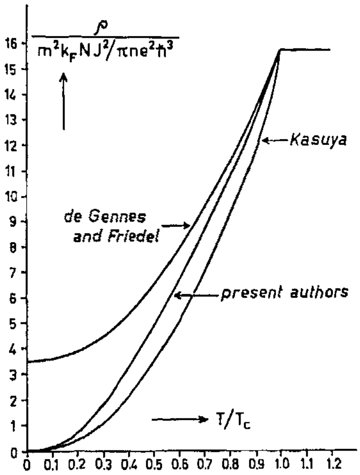

Fig. 3. Comparison between the theoretical formulae of Kasuya[6]), De Gennes and Friedel[7]) and the present authors for $S = 7/2$. It must be emphasized that none of these formulae actually applies in the low temperature region.

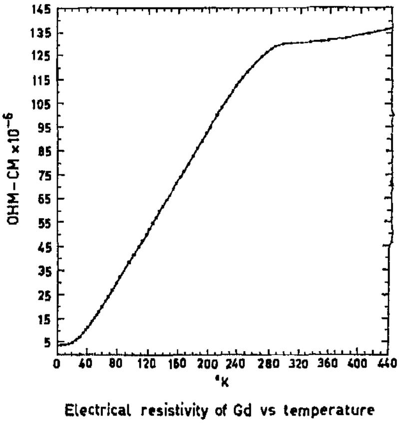

Fig. 4. The resistivity of gadolinium as a function of temperature according to Colvin, Legvold and Spedding[21]).

In figure 4 we reproduce for comparison an experimental curve for the resistivity of gadolinium ($S = 7/2$) as obtained by Colvin, Legvold and Spedding[21]). We note that the shape of this curve in the vicinity of the critical temperature deviates from that obtained from a simple molecular field model. It is likely that short-range order plays a role in that temperature region; De Gennes and Friedel[7]) have discussed certain aspects of this problem.

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