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THE RESISTIVITY OF DILUTE MAGNETIC ALLOYS *)

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The resistivity of dilute magnetic alloys is discussed in terms of a model which assumes an exchange energy only between magnetic atoms which are nearest neighbours. The perturbing potential produced by the magnetic atoms is assumed to consist of a spin-independent and a spin-dependent part. It is shown that the elastic scattering resulting from nearest-neighbour pairs of magnetic atoms contains a temperature-dependent term. It is suggested that this model might explain the occurrence of a maximum followed by a minimum in the resistivity versus temperature curve observed for some alloys.

1. *Introduction.* It is well-known that the electrical resistivity of the rare-earth metals drops rapidly below the ferro- or antiferromagnetic transition temperature. Elliott [1]) has discussed this behaviour in terms of a spin-independent interaction between the conduction electrons and the ion cores under the assumption that a fraction of the ions is excited as a result of the crystalline Stark effect. Kasuya [2]) and more recently de Gennes and Friedel [3]) considered the resistivity in these materials as arising from the exchange interaction between the conduction electrons and the localized spins of the ions. A review of the effects resulting from spin-disorder in metals and alloys has been given by Coles [4]).

In magnetic alloys with localized spins one expects contributions to the resistivity from atomic disorder as well as from an exchange coupling between the conduction electrons and the magnetic ions. Of particular interest are dilute magnetic alloys of transition elements in metals such as copper, silver and gold. Gerritsen and Linde [5]) observed that dilute alloys of manganese in copper exhibit anomalous resistivity behaviour at low temperatures; this behaviour has been confirmed by Schmitt and Jacobs [6]). These alloys also show an interesting magnetic behaviour [6])[7]). In the earlier work [6])[7]), the magnetic properties of dilute magnetic alloys have been discussed in terms of a molecular-field model, employing assumptions very similar to those used in the Curie-Weiss and Néel theories of cooperative magnetic phenomena. As a result of a certain amount of

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dissatisfaction with such a treatment, in particular for dilute alloys, the author [8]) discussed the magnetic susceptibility of such alloys from a different point of view in which the distribution of magnetic atoms plays an essential role. Objections to the molecular-field model for alloys were raised independently by Sato and Arrott [9]), who discussed the statistical aspects of the problem at some length. In view of the results obtained in this work, one may express doubt concerning the validity of calculations of the electrical resistivity of dilute magnetic alloys based on a magnetic model involving a molecular-field treatment [6])[7])[10]). In the present paper, therefore, some aspects of the electrical resistivity of dilute magnetic alloys will be discussed on the basis of a magnetic model which is rather similar to that used earlier by the author [8]), and in the pair-approximation of the cluster-variation method in the work of Sato and Arrott [9]).

2. *The model of a dilute magnetic alloy.* Consider a dilute alloy of A-atoms of spin 1/2 and non-magnetic B-atoms. We shall assume that there exists an exchange interaction only between A-atoms which are nearest neighbours. An A-atom which has only B-atoms as nearest neighbours will be referred to as a "single" A-atom; magnetically, it behaves as a free spin. Similarly, two nearest neighbour A-atoms constitute a "pair" if they are surrounded by B-atoms only. For a pair of nearest neighbours with spin configuration A^+A^+ or A^-A^- let the exchange energy be $-J/2$; for a pair A^+A^- let it be $J/2$. We shall consider both ferromagnetic ($J > 0$) and antiferromagnetic ($J < 0$) interactions.Let there be N_s single A-atoms per unit volume and N_{AA} pairs of A-atoms. Assuming for a moment that the A and B-atoms are distributed ar random one has

$$N_s = Nc(1 - c)^v \tag{1}$$

where c is the atomic concentration of A, N is the number of lattice sites per unit volume and v is the coordination number of the lattice. The number of AA pairs per unit volume, surrounded by B-atoms only, is equal to

$$N_{AA} = (1/2)Nvc^2(1 - c)^{2v-v'-2} \tag{2}$$

Here, v' represents the number of nearest neighbours common to both atoms constituting the pair; for a f.c.c. lattice, for example, $v' = 6$. The fraction of A-atoms incorporated in clusters of three or more is presumably given by

$$f = (Nc - N_s - 2N_{AA})/Nc \approx vc^2(2v - v' - 2) \tag{3}$$

where the approximation involves the assumption $c \ll 1$. For a face-centered cubic lattice, $f \approx 192c^2$. It will be assumed that c is sufficiently small that only effects arising from single A-atoms and AA-pairs have to be taken into account.

For later use it will be convenient to introduce the following densities of single A-atoms and AA-pairs corresponding to the various possible spin orientations:

spin configuration: A^+ A^- A^+A^+ A^-A^- A^+A^- A^-A^+
density: N_s^+ N_s^- N_p^+ N_p^- $(1/2)N_a$ $(1/2)N_a$

In the absence of an applied magnetic field statistical arguments give

$$N_s^+ = N_s^- = (1/2)N_s \tag{4}$$

$$N_p^+ = N_p^- = \frac{(1/2)N_{AA}}{1 + e^{-x}} \text{ where } x = J/kT \tag{5}$$

$$N_a = \frac{N_{AA}}{1 + e^{x}} \tag{6}$$

In the presence of an applied field H, let the energy of a "plus" spin in the field be $-\beta H$, and that of a "minus" spin $+\beta H$; β is a Bohr magneton. The discussion will be limited to those cases for which $\beta H \ll kT$. Introducing the quantity $\alpha = \beta H/kT$ one then finds in the presence of H, to a first approximation:

$$N_s^+ = (1/2)N_s(1 + \alpha);\ N_s^- = (1/2)N_s(1 - \alpha) \tag{7}$$

$$N_p^+ = (N_{AA}/2)\frac{1 + 2\alpha}{1 + e^{-x}};\ N_p^- = (N_{AA}/2)\frac{1 - 2\alpha}{1 + e^{-x}} \tag{8}$$

$$N_a = \frac{N_{AA}}{1 + e^{x}} \tag{9}$$

3. *The elastic scattering cross section for single A-atoms.* For the purpose of calculating the resistivity resulting from the presence of the magnetic atoms we shall assume that the conduction electrons can be treated as free, with an effective mass m. The wave vector of an electron at the Fermi level before scattering will be denoted by $\boldsymbol{k}_0$ and after scattering by $\boldsymbol{k}$. We shall introduce the vector $\boldsymbol{K} = \boldsymbol{k} - \boldsymbol{k}_0$. Since we consider elastic scattering only, $|\boldsymbol{k}| = |\boldsymbol{k}_0|$ and also $|\boldsymbol{K}| = 2k_0 \sin(\theta/2)$, where θ is the scattering angle. We shall assume that the scattering by a single atom located at $\boldsymbol{R}_i$ results from a perturbing potential which can be separated into a spin-independent and a spin-dependent part:

$$V_i(\boldsymbol{r}) = V_a\delta(\boldsymbol{r} - \boldsymbol{R}_i) + V_b\delta(\boldsymbol{r} - \boldsymbol{R}_i)\sigma_{ei} \tag{10}$$

Here, $\boldsymbol{r}$ gives the position of the conduction electron and $\sigma_{ei} = 4\boldsymbol{S}_e \cdot \boldsymbol{S}_i$ where $\boldsymbol{S}_e$ and $\boldsymbol{S}_i$ represent the spin of the conduction electron and the ion at $\boldsymbol{R}_i$, respectively. Thus $\sigma_{ei} = \pm 1$ depending on the relative orientation of $\boldsymbol{S}_e$ and $\boldsymbol{S}_i$. The quantities V_a and V_b are constants describing the spin-independent and spin-dependent coupling between the electron and the ion.

The delta-functions are introduced mainly because they are convenient for the discussion of the scattering by pairs, as we shall see in the next section. They represent undoubtedly a strong simplification of the problem, but it is believed that the main purpose of this paper is not impaired by the use of these functions. Delta-function potentials have also been used by de Gennes and Friedel [3]) in their discussion of the resistivity of the rare-earth metals.

In the Born approximation the differential cross-section for scattering by the single ion at $\boldsymbol{R}_i$ is given by

$$q_i(\theta) = 2\pi(m/2\pi\hbar^2)^2 \, | \int V_i(\boldsymbol{r}) \, e^{i\boldsymbol{K}.\boldsymbol{r}} \, \mathrm{d}\boldsymbol{r}|^2. \tag{11}$$

Substitution of (10) into (11) yields

$$q_i(\theta) = 2\pi(m/2\pi\hbar^2)^2 \, (V_a{}^2 + V_b{}^2 + 2V_aV_b\sigma_{ei}). \tag{12}$$

The transport cross section which determines the resistivity resulting from scattering by the total of N_s single A-atoms per unit volume is then equal to

$$Q_s = \sum_{i=1}^{i=N_s} \int q_i(\theta)(1 - \cos\theta) \sin\theta \, \mathrm{d}\theta =$$

$$= 4\pi(m/2\pi\hbar^2)^2[N_s(V_a{}^2 + 3V_b{}^2) + 2V_aV_b \sum_{i=1}^{N_s} \sigma_{ei}]. \tag{13}$$

Making use of (4) and (7) one thus obtains for the cross-section in the presence of an applied magnetic field

$$Q_{s\pm}(H) = (m^2/\pi\hbar^4)N_s[V_a{}^2 + 3V_b{}^2 \pm 2 \, V_aV_b\alpha] \tag{14}$$

Here, the $\pm$ sign refers to the two possible orientations of the spin of the conduction electron. For $H = 0$, $\alpha = \beta H/kT = 0$.

4. *The elastic cross-section resulting from AA-pairs.* Consider a pair of nearest-neighbour A-atoms located at $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$. We shall introduce the vector $\rho = \boldsymbol{R}_i - \boldsymbol{R}_j$. In analogy with the scattering by a single A-atom, we assume that the pair produces a perturbing potential

$$V_{ij}(\boldsymbol{r}) = V_a[\delta(\boldsymbol{r} - \boldsymbol{R}_i) + \delta(\boldsymbol{r} - \boldsymbol{R}_j)] +$$
$$+ V_b[\sigma_{ei}\delta(\boldsymbol{r} - \boldsymbol{R}_i) + \sigma_{ej}\delta(\boldsymbol{r} - \boldsymbol{R}_j)]. \tag{15}$$

Substitution into the Born approximation (11) yields for the differential cross section of the pair

$$q_{ij}(\theta) = 2\pi\left(\frac{m}{2\pi\hbar^2}\right)^2 [(V_a + V_b\sigma_{ei})^2 + (V_a + V_b\sigma_{ej})^2 +$$
$$+ 2(V_a + V_b\sigma_{ei})(V_a + V_b\sigma_{ej}) \cos(\boldsymbol{K}\cdot\rho)]. \tag{16}$$

Since we are interested in the cross section averaged over all directions of

incidence, we shall replace $\cos(\boldsymbol{K}\cdot\boldsymbol{\rho})$ by the value obtained by averaging over all directions of $\boldsymbol{K}$,

$$\langle\cos(\boldsymbol{K}\cdot\boldsymbol{\rho})\rangle_{\boldsymbol{K}} = \frac{\sin K\rho}{K\rho}. \tag{17}$$

The transport cross section corresponding to the pair under consideration is given by

$$Q_{ij} = \int q_{ij}(\theta)(1 - \cos\theta)\sin\theta\,\mathrm{d}\theta. \tag{18}$$

For brevity we shall introduce the function

$$F(k_0\rho) = (1/2)\int \frac{\sin K\rho}{K\rho}(1 - \cos\theta)\sin\theta\,\mathrm{d}\theta =$$
$$= (1/2\,k_0{}^4\rho^4)\,[2k_0\rho\sin(2k_0\rho) - (2k_0{}^2\rho^2 - 1)\cos 2k_0\rho - 1] \tag{19}$$

where the last equality follows from the fact that $K = 2k_0\sin(\theta/2)$. A summation of the Q_{ij} over all AA-pairs thus leads for elastic cross section per unit volume resulting from pairs to the expression

$$Q_p = \sum_{\text{pairs}} Q_{ij} = (2m^2/\pi\hbar^4)\,[N_{AA}(V_a{}^2 + 3V_b{}^2) +$$
$$+ V_aV_b\sum_{\text{pairs}}(\sigma_{ei} + \sigma_{ej}) + F(k_0\rho)\,\{N_{AA}V_a{}^2 +$$
$$+ V_aV_b\sum_{\text{pairs}}(\sigma_{ei} + \sigma_{ej}) + V_b{}^2\sum_{\text{pairs}}(\sigma_{ei}\sigma_{ej})\}]. \tag{20}$$

Note that the term containing $F(k_0\rho)$ arises from interference of the waves scattered by each of the atoms constituting a pair. A term of this kind has not been taken into account in earlier work on alloys.

From (8) and (9) it follows that

$$\sum_{\text{pairs}}(\sigma_{ei} + \sigma_{ej}) = \pm 2(N_{p+} - N_{p-}) = \pm\frac{4N_{aa}\alpha}{1 + e^{-x}} \tag{21}$$

$$\sum_{\text{pairs}}\sigma_{ei}\sigma_{ej} = N_{p+} + N_{p-} - N_a = N_{aa}\left(\frac{1}{1 + e^{-x}} - \frac{1}{1 + e^{x}}\right) \tag{22}$$

where the upper sign in (21) refers to a conduction electron with a "plus" spin, and the lower sign to one with a "minus" spin. Expression (22) holds for conduction electrons with both spin directions. From the last three equations, one thus obtains for the transport cross section resulting from AA-pairs in the presence of an applied field H

$$Q_{p\pm}(H) = (2m^2/\pi\hbar^4)N_{AA}\left[V_a{}^2 + 3V_b{}^2 \pm \frac{4V_aV_b\alpha}{1 + e^{-x}} +\right.$$
$$\left. + F(k_0\rho)\left\{V_a{}^2 \pm \frac{4V_aV_b\alpha}{1 + e^{-x}} + V_b{}^2\left(\frac{1}{1 + e^{-x}} - \frac{1}{1 + e^{x}}\right)\right\}\right] \tag{23}$$

5. *The concentration dependence of the resistivity of dilute non-magnetic*

alloys. If there is no spin-dependent scattering, $V_b = 0$ in expressions (14) and (23). In terms of the model adopted here, this would correspond to a non-magnetic dilute alloy. The total elastic transport cross section obtained from (14) and (23) for this case is given by

$$Q_{\text{elastic}} \approx (Ncm^2V_a^2/\pi\hbar^4)\left[1 + \frac{2N_{AA}}{Nc}\,F(k_0\rho)\right] \tag{24}$$

where we have written $N_s + 2N_{AA} \approx Nc$. According to (2), the coefficient of $F(k_0\rho)$ is proportional to c, so that (24) predicts an impurity resistivity consisting of two terms: one proportional to the concentration and another proportional to c^2.

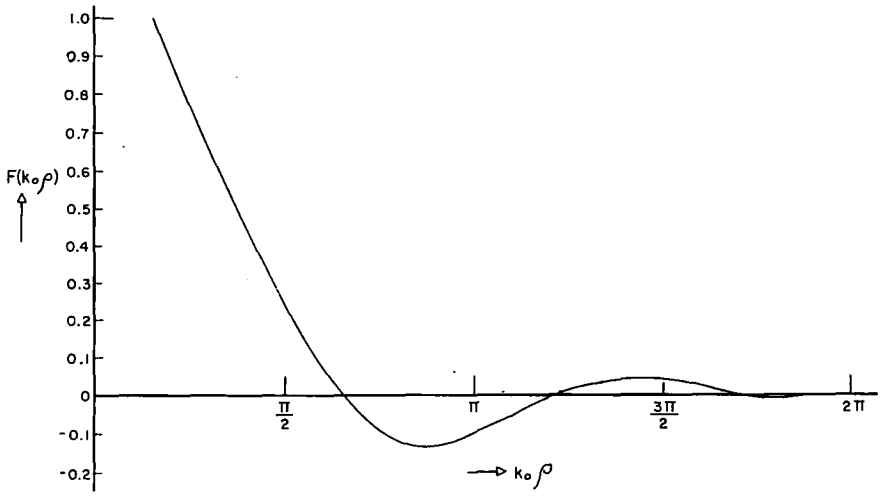

Fig. 1. The function $F(k_0\rho)$

The function $F(k_0\rho)$ is shown in Fig. 1. For a monovalent host metal of face-centered cubic structure, the free electron approximation leads to $k_0\rho \approx 1.1\pi$, corresponding to $F(k_0\rho) \approx -0.1$. Since $2N_{AA}/Nc$ according to (2) is of the order of $10c$ for dilute alloys, the interference effects arrising from scattering by pairs of impurity atoms amounts to relative deviations from linearity of the order of c.

6. *Temperature dependence of the resistivity of dilute magnetic alloys*. In the absence of a magnetic field, the total elastic cross section per unit volume is obtained from (14) and (23) by putting $\alpha = 0$. This leads to

$$Q_{\text{elastic}} = (m^2/\pi\hbar^4)\,[Nc(V_a^2 + 3V_b^2) + \\ + 2N_{AA}F(k_0\rho)\,\{V_a^2 + V_b^2\,f(J/kT)\}] \tag{25}$$

where

$$f(J/kT) = f(x) = \frac{1}{1 + e^{-x}} - \frac{1}{1 + e^{x}}$$

and where we have assumed $N_s + 2N_{AA} = Nc$. Expression (25) holds for both spin directions of the conduction electrons, and corresponds to a temperature-dependent impurity resistivity. The function $f(x)$ is represented in Fig. 2. Whether the resistivity increases or decreases with increasing temperature depends on the sign of $F(k_0\rho)$ as well as on the sign of J. In

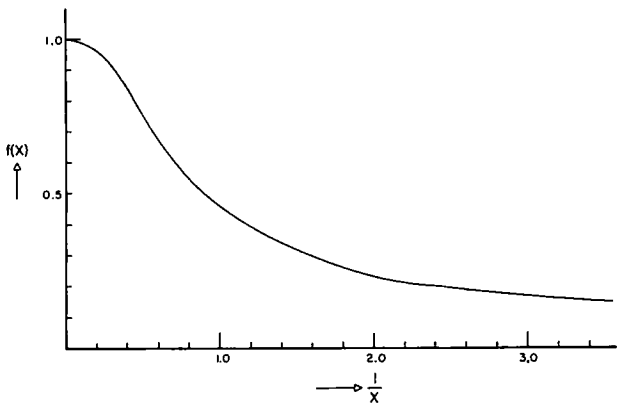

Fig. 2. The function $f(x)$ where $x = J/kT$ in the text

fact, the possible temperature dependence of the elastic cross-section may be summarized as follows:

$$\mathrm{d}Q/\mathrm{d}T > 0 \text{ for } \begin{cases} F(k_0\rho) > 0 \text{ and } J < 0 \text{ (antiferromagnetic)} \\ F(k_0\rho) < 0 \text{ and } J > 0 \text{ (ferromagnetic)} \end{cases}$$

$$\mathrm{d}Q/\mathrm{d}T < 0 \text{ for } \begin{cases} F(k_0\rho) > 0 \text{ and } J > 0 \text{ (ferromagnetic)} \\ F(k_0\rho) < 0 \text{ and } J < 0 \text{ (antiferromagnetic)} \end{cases}$$

The total impurity resistivity is of course determined by the elastic as well as the inelastic cross sections. In the present model inelastic collisions would occur between conduction electrons and AA-pairs in which the spin of the conduction electron and the spin of one of the A-atoms were reversed. Thus, the following types of inelastic collisions would occur for a conduction electron with plus spin:

$$e^+ + A^-A^- \rightarrow e^- + A^+A^-$$
$$e^+ + A^-A^+ \rightarrow e^- + A^+A^+$$

In the first case, the electron would loose an amount of energy J; in the second case it would gain J. Conduction electrons with a minus spin would suffer similar inelastic collisions. In this model, as in many others in which the scattering centers have two or more possible energy levels, the cross section for inelastic scattering decreases with decreasing temperature, becoming zero at $T = 0$. The reason is that the probability for scattering is proportional to the probability for the final state to be unoccupied and

to the probability of finding the scattering center in the proper initial state. At low temperatures, absorption processes become unlikely because there are few scattering centers in an excited state; emission processes become unlikely because the final electron states are nearly all occupied. For the present model the temperature dependence of the inelastic scattering cross section would be given by an expression of the form

$$Q_{\text{inelastic}} = N_{AA} \frac{Q_{\text{abs}} + (1/2)Q_{\text{em}}}{(1 + e^{-x})(1 + e^{x})} \quad (H = 0) \tag{26}$$

where $x = J/kT$, and Q_{abs} and Q_{em} are a measure of the cross section for absorption and emission processes. For $T = 0$, this expression becomes zero. Similar arguments have been used in previous work to explain the drop of the resistivity with decreasing temperature observed in some dilute magnetic alloys. However, some dilute magnetic alloys exhibit a maximum and subsequent minimum in the resistivity versus temperature curve. It is suggested that the present model, which provides the possibility of a negative temperature coefficient for the elastic cross section, might explain these observations, as well as the negative temperature coefficient of the resistivity of certain alloys observed at high temperatures.

It should be emphasized that in the model employed here, J is independent of the concentration of the alloy. In a model which relies on the molecular field treatment, the effective field acting at the position of a particular atom does depend on concentration. In principle, the effects discussed here are not limited to the low-temperature region; depending on the magnitude of J, they might occur at high temperatures as well.

7. *Influence of a magnetic field on the resistivity.* From equations (14) and (23), and from an extension of equation (26) for the case of a non-vanishing magnetic field it follows that the total scattering cross-sections for electrons with plus and minus spin can be written in the general form

$$Q_{e+} = Q_0 + \gamma H$$
$$Q_{e-} = Q_0 - \gamma H$$

where for a given temperature and concentration both Q_0 and γ are constants. Since the conductivities of the two kinds of conduction electrons are additive, this leads to a reduction of the impurity resistivity upon application of a magnetic field.

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