Effect of Short-Range Spin Correlation on the Electrical Resistivity of Dilute Magnetic Alloys

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The *s-d* exchange-interaction model has been widely used to explain many properties of magnetic metals and alloys. In particular, it has been suggested that the short-range order of the spins in a dilute magnetic alloy may give rise to the resistivity minimum effect. This paper gives a general discussion of the effect of spin correlation on the resistivity. The short-range correlation of the spins is investigated by the cluster expansion method. For dilute manganese-copper alloys where the Mn spins are believed to be coupled by the indirect exchange mechanism, the predicted variation in resistivity around the temperature where the minimum occurs is about 2 orders of magnitude smaller than the observed value. Hence, this model does not seem to explain the resistivity minimum phenomenon.

I. INTRODUCTION

MANY dilute alloys exhibit the resistivity minimum phenomenon.[1] The recent experiment of Gold *et al.*[2] makes it seem certain that this phenomenon is caused by the transition metal impurities. As a summary of the experimental findings, one observes that the minimum resistivity is roughly proportional to the impurity concentration, and the temperature T_0 at which the minimum occurs depends on the impurity concentration x through the power law

$$(T_0)^n \propto x, \tag{1}$$

where $n = 5\text{-}6$. These materials are also found to have negative magnetoresistance and anomalously large thermoelectric power. In some alloys the resistivity also has a maximum at a somewhat lower temperature.

One explanation of the resistivity minimum was put forward by Korringa and Gerritsen,[3] who postulated that the scattering between the electrons and the transition metal ions undergoes a resonance when the electron nearly has the Fermi energy. This model seems to explain the phenomenon quite well, even though the basic mechanism for the scattering interaction is not understood. Recently Hedgcock and Muir[4] found further evidence for the resonant scattering from deHaas-van Alphen measurement on zinc-manganese alloys.

Another model that has been rather popular lately is the *s-d* exchange interaction model. The basic postulate is that there is a spin-dependent interaction between the conduction electrons and the impurity ions.

Yosida[5] showed that this interaction can account for the negative magnetoresistance of these materials. If the coupling between the impurity spins is approximated by an effective field, the eventual drop in resistivity of some alloys at low temperatures can also be understood. Brailsford and Overhauser[6] suggested that the resistivity minimum may be due to the ferromagnetic interaction between the spins. They showed that when a pair of closely spaced spins are ferromagnetically coupled, they tend to scatter the electrons more strongly than two uncoupled spins. The extra resistivity has roughly the observed temperature dependence and is proportional to the square of the impurity concentration. A very similar model was also discussed by Dekker.[7]

The result of Brailsford and Overhauser seems to suggest that the resistivity is sensitive to the short-range order of the spins. The present paper investigates this possibility in a general way. It is assumed that the spins are coupled by the most general type of long-range interaction. The short-range correlation between the spins is investigated by the cluster expansion method. The resistivity is calculated by solving the Boltzmann equation. The result is that the resistivity due to spin scattering can be expressed in the form

$$\rho_s = \rho_0 + a/T + O(1/T^2), \tag{2}$$

where ρ_0 is proportional to the impurity concentration x, and a is proportional to x^2. Under suitable conditions a can be positive, so ρ may increase upon lowering the temperature and, when combined with the phonon-scattering contribution, give rise to a minimum. These conclusions are in qualitative agreement with Brailsford and Overhauser. However, if one tries to fit the experimental curves by Eq. (2), one finds that a should be roughly proportional to x for most dilute alloys. Hence, the short-range effect does not seem to satisfactorily explain the minimum. Moreover, if one takes the spin

[1] For reviews of the problem, see J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 344; F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 200; D. K. C. MacDonald, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 137. For recent publications not covered by these reviews, see the references listed in R. R. Hake, D. H. Leslie, and T. G. Belincourt, Phys. Rev. **127**, 170 (1962).

[2] A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. **5**, 765 (1960).

[3] J. Korringa and A. N. Gerritsen, Physica **19**, 457 (1953).

[4] F. T. Hedgcock and W. B. Muir, Phys. Rev. **129**, 2045 (1963).

[5] K. Yosida, Phys. Rev. **107**, 396 (1957).

[6] A. D. Brailsford and A. W. Overhauser, J. Phys. Chem. Solids **15**, 140 (1960).

[7] A. J. Dekker, Physica **25**, 1244 (1959).

coupling to be the Ruderman-Kittel-Kasuya-Yosida coupling,[8-10] as commonly assumed, one finds that the size of the short-range effect in these alloys is also too small to play a role.

II. BASIC FORMULATION

The model system is described by a total Hamiltonian H which consists of the unperturbed Hamiltonian for the Bloch electrons H_0, the spin Hamiltonian H_s, and the interaction Hamiltonian H_I. Explicitly,[9,10]

$$H_0 = \sum_{ks} \epsilon_k c_{ks}^* c_{ks}, \tag{3}$$

$$H_s = -\sum_{(i,j)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{4}$$

$$H_I = \frac{I}{2N} \sum_{k,k'} \sum_j [S_j^z(c_{k'\uparrow}^* c_{k\uparrow} - c_{k'\downarrow}^* c_{k\downarrow})$$
$$+ S_j^+ c_{k'\downarrow}^* c_{k\uparrow} + S_j^- c_{k'\uparrow}^* c_{k\downarrow}] e^{i(k-k')\cdot R_j}. \tag{5}$$

Here c_{ks}^*, c_{ks} are the creation and annihilation operators of an electron in the state of momentum $\mathbf{k}$ and spin s, ϵ_k is the energy of this state; $\mathbf{R}_j$ and $\mathbf{S}_j$ are the position and spin of the jth ion; I is the matrix element of the s-d interaction; N is the total number of ions in the sample. In the spherical-band approximation, ϵ_k depends only on the size of k. The coupling constant J_{ij} is a function of the vector distance $\mathbf{R}_{ij}$ of the two spins. The interaction H_I should also contain a spin-independent part. However, since this part gives rise to a temperature-independent resistivity and since there is no cross-product term between the spin-independent and the spin-dependent interactions when there is no long-range order, one may ignore the spin-independent interaction in the present discussion. The matrix element I should normally be a function of the initial and final momenta $\mathbf{k}$ and $\mathbf{k'}$. It is simplified here to facilitate the calculation.

The electrical resistivity due to the interaction H_I is calculated by the Boltzmann equation method. For general scatterings the Boltzmann equation has the form[11]

$$(\partial f_\kappa/\partial t)_{\text{drift}} + (\partial f_\kappa/\partial t)_{\text{coll}} = 0, \tag{6}$$

where f_κ is the distribution function for the electron state κ; κ designates both the momentum $\mathbf{k}$ and the spin s. The two terms in Eq. (6) are defined by ($\hbar = 1$)

$$(\partial f_\kappa/\partial t)_{\text{drift}} = -e\mathbf{E} \cdot \nabla_k f_\kappa^0, \tag{7}$$

$$\left(\frac{\partial f_\kappa}{\partial t}\right)_{\text{coll}} = \sum_{\kappa'} [W_{\kappa'\kappa} f_{\kappa'}(1-f_\kappa) - W_{\kappa\kappa'} f_\kappa(1-f_{\kappa'})], \tag{8}$$

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[8] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).
[9] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).
[10] K. Yosida, Phys. Rev. **106**, 893 (1957).
[11] P. N. Argyres, J. Phys. Chem. Solids **19**, 66 (1961). This special form of the transport equation is used because it seems to be the correct equation that can be derived from quantum mechanics.

where f_κ^0 is the unperturbed distribution function $f_\kappa^0 = [e^{\beta(\epsilon_k - \epsilon_F)} + 1]^{-1}$, $\beta = 1/k_B T$. The transition rate $W_{\kappa\kappa'}$ is given by

$$W_{\kappa\kappa'} = \sum_\alpha \rho_\alpha \sum_{\alpha'} 2\pi |\langle \alpha'\kappa' | H_I | \alpha\kappa \rangle|^2$$
$$\times \delta(E_\alpha + \epsilon_k - E_{\alpha'} - \epsilon_{k'}), \tag{9}$$

where α, α' label the spin states such that

$$H_s|\alpha\rangle = E_\alpha|\alpha\rangle,$$
$$\rho_\alpha = \langle \alpha | \rho | \alpha \rangle = \langle \alpha | e^{-\beta H_s} | \alpha \rangle / \sum_\alpha \langle \alpha | e^{-\beta H_s} | \alpha \rangle. \tag{10}$$

ρ is the density matrix for the spins, and the states $|\alpha\rangle$ form a complete orthonormal set. Using the identity

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\zeta x} d\zeta,$$

one can readily write

$$W_{\kappa\kappa'} = \sum_\alpha \rho_\alpha \sum_{\alpha'} \int_{-\infty}^{\infty} e^{i(\epsilon_k - \epsilon_{k'})\zeta} \langle \alpha'\kappa' | e^{-i\zeta H_s} H_I e^{i\zeta H_s} | \alpha\kappa \rangle$$
$$\times \langle \alpha\kappa | H_I | \alpha'\kappa' \rangle d\zeta.$$

Defining $(H_I)_{\kappa'\kappa} = \langle \kappa' | H_I | \kappa \rangle$, one finds after some simple manipulations

$$W_{\kappa\kappa'} = \int_{-\infty}^{\infty} e^{i(\epsilon_k - \epsilon_{k'})\zeta} d\zeta$$
$$\times \text{Tr}[e^{-i\zeta H_s}(H_I)_{\kappa'\kappa} e^{i\zeta H_s} \rho (H_I)_{\kappa\kappa'}], \tag{11}$$

where the trace is taken over all the eigenstates of the spin system. The quantity $W_{\kappa'\kappa}$ can be found by exchanging the indices κ and κ' in Eq. (11). Next, one evaluates $(H_I)_{\kappa'\kappa}$ from Eq. (5) and substitutes the result into Eq. (11). This gives

$$W_{k\uparrow k'\uparrow} = \frac{I^2}{4N^2} \int_{-\infty}^{\infty} e^{i(\epsilon_k - \epsilon_{k'})\zeta} d\zeta$$
$$\times \text{Tr}[\sum_{ij} e^{-i\zeta H_s} S_i^z e^{i\zeta H_s} \rho S_j^z] e^{i(k-k')\cdot R_{ij}},$$

and similar expressions for $W_{k\uparrow k'\downarrow}$, etc. The trace has the form of a two-time correlation function of the spins because, if one defines

$$\mathbf{S}_i(\zeta) = e^{i\zeta H_s} \mathbf{S}_i e^{-i\zeta H_s},$$

one finds

$$\text{Tr}[\sum_{ij} e^{-i\zeta H_s} S_i^z e^{i\zeta H_s} \rho S_j^z] e^{i(k-k')\cdot R_{ij}}$$
$$= \sum_{ij} \langle S_j^z(\zeta) S_i^z(0) \rangle e^{i(k-k')\cdot R_{ij}},$$

where $\langle \ \rangle$ denotes a thermal average. Putting these results into Eq. (8) and averaging over the spin states

of the incoming electron, one obtains

$$\left(\frac{\partial f_k}{\partial t}\right)_{\text{coll}} = \frac{I^2}{4N^2}\sum_{k'}\int_{-\infty}^{\infty}e^{i(\epsilon_k-\epsilon_{k'})\zeta}d\zeta\sum_{ij}\{\langle \mathbf{S}_i(0)\cdot \mathbf{S}_j(\zeta)\rangle$$

$$\times f_{k'}(1-f_k)-\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_i(0)\rangle f_k(1-f_{k'})\}$$

$$\times e^{i(\mathbf{k}-\mathbf{k}')\cdot \mathbf{R}_{ij}}. \quad (12)$$

Hence, the calculation of the resistivity depends on the evaluation of the two-time correlation functions of the spins.

III. EVALUATION OF THE CORRELATION FUNCTIONS

In this section the correlation functions that appeared in Eq. (12) are evaluated by the cluster expansion method. This method is useful in studying dilute systems because it will be shown that for a random system the cluster expansion is equivalent to a density expansion.

The general cluster expansion for the partition function was first discussed by Kubo.[12] A very similar method will be used here for the correlation functions. The calculation is illustrated by expanding $\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_i(0)\rangle$ for $i\neq j$. One defines

$$H_2(ij)=-J_{ij}\mathbf{S}_i\cdot \mathbf{S}_j,$$

$$H_3(ijk)=-J_{ij}\mathbf{S}_i\cdot \mathbf{S}_j-J_{ik}\mathbf{S}_i\cdot \mathbf{S}_k-J_{jk}\mathbf{S}_j\cdot \mathbf{S}_k,$$

and, in general,

$$H_n(ijk\cdots)=-\sum_{(ij)}J_{ij}\mathbf{S}_i\cdot \mathbf{S}_j, \quad (13)$$

where the sum is taken over all interacting pairs of the n spins. Next one defines the n-spin density matrix

$$\rho_n(ijk\cdots)=e^{-\beta H_n(ijk\cdots)}/\text{Tr}e^{-\beta H_n(ijk\cdots)}, \quad (14)$$

where the trace is taken over all the eigenstates of $H_n(ijk\cdots)$. Then one defines the functions F_n by

$$F_2(ij)=\text{Tr}[\rho_2(ij)e^{i\zeta H_2(ij)}\mathbf{S}_je^{-i\zeta H_2(ij)}\cdot \mathbf{S}_i],$$

$$F_3(ij|k)=\text{Tr}[\rho_3(ijk)e^{i\zeta H_3(ijk)}\mathbf{S}_je^{-i\zeta H_3(ijk)}\cdot \mathbf{S}_i],$$

and

$$F_n(ij|kl\cdots)=\text{Tr}[\rho_ne^{i\zeta H_n}\mathbf{S}_je^{-i\zeta H_n}\cdot \mathbf{S}_i], \quad (15)$$

and the functions G_n by

$$G_2(ij)=F_2(ij),$$

$$G_3(ij|k)=F_3(ij|k)-G_2(ij),$$

and

$$G_n(ij|kl\cdots)=F_n(ij|kl\cdots)-\sum_{(n-1)}G_{n-1}(ij|kl\cdots)$$

$$-\sum_{(n-2)}G_{n-2}(ij|kl\cdots)-\cdots$$

$$-\sum_k G_3(ij|k)-G_2(ij). \quad (16)$$

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[12] R. Kubo, J. Phys. Soc. Japan **17**, 1100 (1962).

The symbol $\sum_{(n-m)}$ means a sum over all clusters of $n-m$ spins that can be formed out of i, j and any set of $n-m-2$ of the remaining $n-2$ spins. Then the two-time correlation function has the cluster expansion

$$\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_i(0)\rangle=G_2(ij)+\sum_k G_3(ij|k)$$

$$+\sum_{(kl)}G_4(ij|kl)+\cdots. \quad (17)$$

The proof for this expansion is very simple. It is clear that

$$\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_i(0)\rangle=F_{N_0},$$

where N_0 is total number of spins. From the definition of G_{N_0}, one can write

$$G_{N_0}=F_{N_0}-\sum_{(N_0-1)}G_{N_0-1}-\sum_{(N_0-2)}G_{N_0-2}\cdots$$

$$-\sum_k G_3(ij|k)-G_2(ij).$$

The result in Eq. (16) follows by transposition. The cluster property of the expansion is also easy to establish. If the spin k does not interact with any of the rest, then it is clear that

$$H_3(ijk)=H_2(ij)$$

and

$$H_n(ijkl\cdots)=H_{n-1}(ijl\cdots).$$

So

$$F_3(ij|k)=F_2(ij),$$

$$F_4(ij|kl)=F_3(ij|l),$$

etc. Hence,

$$G_3(ij|k)=F_2(ij)-F_2(ij)=0,$$

$$G_4(ij|kl)=F_3(ij|l)-G_3(ij|l)-G_2(ij)=0,$$

and, in general,

$$G_n(ij|kl\cdots)=0,$$

for every n. The proof can be extended to show that if the spins can be divided into two noninteracting groups, then any G_n which contains members from both groups is identically zero. In other words, Eq. (17) is a linked cluster expansion.

In a similar manner one can expand $\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_j(0)\rangle$ into a cluster expansion whose leading terms are

$$\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_j(0)\rangle=S(S+1)$$

$$+\sum_i\{\text{Tr}[\rho_2(ij)e^{i\zeta H_2(ij)}\mathbf{S}_je^{-i\zeta H_2(ij)}\cdot \mathbf{S}_j]$$

$$-S(S+1)\}+\cdots. \quad (18)$$

Therefore,

$$\sum_{ij}\langle \mathbf{S}_j(\zeta)\cdot \mathbf{S}_i(0)\rangle e^{i(\mathbf{k}-\mathbf{k}')\cdot \mathbf{R}_{ij}}=N_0S(S+1)$$

$$+\sum_{ij}\{\text{Tr}[\rho_2(ij)e^{i\zeta H_2(ij)}\mathbf{S}_je^{-i\zeta H_2(ij)}\cdot \mathbf{S}_j]-S(S+1)\}$$

$$+\sum_{ij}\text{Tr}[\rho_2(ij)e^{i\zeta H_2(ij)}\mathbf{S}_je^{-i\zeta H_2(ij)}\cdot \mathbf{S}_i]e^{i(\mathbf{k}-\mathbf{k}')\cdot \mathbf{R}_{ij}}$$

$$+\text{higher order terms}. \quad (19)$$

In a polycrystalline random alloy one should average the result of Eq. (19) over the positions of the spins and the relative orientation of the pairs. This gives

$$\sum_{ij} \langle \mathbf{S}_j(\zeta) \cdot \mathbf{S}_i(0) \rangle e^{i(\mathbf{k}-\mathbf{k}')\cdot \mathbf{R}_{ij}} = N_0 S(S+1) + N_0 x$$
$$\times \sum_j \{ \mathrm{Tr}[\rho_2(0j) e^{i\zeta H_2(0j)} \mathbf{S}_0 e^{-i\zeta H_2(0j)} \cdot \mathbf{S}_0] - S(S+1) \}$$
$$+ N_0 x \sum_j \mathrm{Tr}[\rho_2(0j) e^{i\zeta H_2(0j)} \mathbf{S}_0 e^{-i\zeta H_2(0j)} \cdot \mathbf{S}_j]$$
$$\times \mathcal{S}(qR_j) + O(x^2), \quad (20)$$

where $\mathcal{S}(qR_j) = \sin(qR_j)/qR_j$, $q = |\mathbf{k}-\mathbf{k}'|$, x is the density of the impurities N_0/N, 0 is any convenient reference point in the lattice, R_j is measured from 0, and the sums are now taken over the whole lattice. The higher order terms of the expansion involve the interaction of more than two spins, they are proportional to higher powers of the density.

The method of evaluation of the various terms in Eq. (20) is illustrated below for $S = \frac{1}{2}$. The identity

$$\exp(a\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) = \tfrac{1}{4}(1 - \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) e^{-3a} + \tfrac{1}{4}(3 + \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) e^a, \quad (21)$$

where a is any number and $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$ are Pauli matrices, will be very useful. For example, the two-spin partition function

$$\mathrm{Tr}(e^{-\beta H_2(0j)}) = \mathrm{Tr}[\exp(\tfrac{1}{4}\beta J_{0j} \boldsymbol{\sigma}_0 \cdot \boldsymbol{\sigma}_j)]$$
$$= \tfrac{1}{2} e^{-(3/4)\beta J_{0j}} + \tfrac{3}{2} e^{(1/4)\beta J_{0j}}$$

because $\mathrm{Tr}(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) = 0$ and $\mathrm{Tr}(1) = 2$. Since

$$\mathbf{S}_0 e^{-i\zeta H_2(0j)} = e^{-i\zeta H_2(0j)} \mathbf{S}_0 + [\mathbf{S}_0, e^{-i\zeta H_2(0j)}],$$

using Eq. (21) and the multiplication rules of the spinors, one can find

$$[\mathbf{S}_0, e^{-i\zeta H_2(0j)}] = \tfrac{1}{4} i (\boldsymbol{\sigma}_0 \times \boldsymbol{\sigma}_j)[e^{-(3/4)\zeta J_{0j}} - e^{i(1/4)\zeta J_{0j}}].$$

Therefore,

$$e^{i\zeta H_2(0j)} \mathbf{S}_0 e^{-i\zeta H_2(0j)} = \mathbf{S}_0 + e^{i\zeta H_2(0j)}[\mathbf{S}_0, e^{-i\zeta H_2(0j)}]$$
$$= \mathbf{S}_0 + \tfrac{1}{4}(\mathbf{S}_0 - \mathbf{S}_j)(e^{i\zeta J_{0j}} + e^{-i\zeta J_{0j}} - 2)$$
$$- \tfrac{1}{2} i (\mathbf{S}_0 \times \mathbf{S}_j)(e^{i\zeta J_{0j}} - e^{-i\zeta J_{0j}}),$$

where Eq. (21) is again used to expand the product. It is now a simple matter to calculate the traces in Eq. (20). One finds that

$$\mathrm{Tr}[\rho_2(0j) e^{i\zeta H_2(0j)} \mathbf{S}_0 e^{-i\zeta H_2(0j)} \cdot \mathbf{S}_0]$$
$$= S(S+1) + \tfrac{1}{2}(\tfrac{3}{4} - [\mathbf{S}_0 \cdot \mathbf{S}_j])[\cos(\zeta J_{0j}) - 1]$$
$$- i[\mathbf{S}_0 \cdot \mathbf{S}_j] \sin(\zeta J_{0j}),$$
$$\mathrm{Tr}[\rho_2(0j) e^{i\zeta H_2(0j)} \mathbf{S}_0 e^{-i\zeta H_2(0j)} \cdot \mathbf{S}_j]$$
$$= [\mathbf{S}_0 \cdot \mathbf{S}_j] - \tfrac{1}{2}(\tfrac{3}{4} - [\mathbf{S}_0 \cdot \mathbf{S}_j])[\cos(\zeta J_{0j}) - 1]$$
$$+ i[\mathbf{S}_0 \cdot \mathbf{S}_j] \sin(\zeta J_{0j}),$$

where

$$[\mathbf{S}_0 \cdot \mathbf{S}_j] = \mathrm{Tr}[\rho_2(0j) \mathbf{S}_0 \cdot \mathbf{S}_j]$$
$$= 3(e^{(1/4)\beta J_{0j}} - e^{-(3/4)\beta J_{0j}})/$$
$$4(e^{-(3/4)\beta J_{0j}} + 3e^{(1/4)\beta J_{0j}}).$$

Also

$$\tfrac{3}{4} - [\mathbf{S}_0 \cdot \mathbf{S}_j] = 2[\mathbf{S}_0 \cdot \mathbf{S}_j] \coth(\tfrac{1}{2}\beta J_{0j}).$$

Putting these results into Eq. (20), one obtains

$$\sum_{ij} \langle \mathbf{S}_j(\zeta) \cdot \mathbf{S}_i(0) \rangle e^{i(\mathbf{k}-\mathbf{k}')\cdot \mathbf{R}_{ij}} = \tfrac{3}{4} N_0$$
$$+ N_0 x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j] \mathcal{S}(qR_j)$$
$$+ N_0 x \sum_j F(0j)[1 - \mathcal{S}(qR_j)] + O(x^2), \quad (22)$$

where

$$F(0j) = [\mathbf{S}_0 \cdot \mathbf{S}_j]\{[\cos(\zeta J_{0j}) - 1] \coth(\tfrac{1}{2}\beta J_{0j})$$
$$- i \sin(\zeta J_{0j})\}. \quad (23)$$

For general S the result can be written down in terms of the Clebsch-Gordan coefficients.

To summarize this section, a cluster expansion is developed for the two time-correlation functions in Eq. (12). The leading terms of the expansion are explicitly calculated for $S = \frac{1}{2}$ case. In a dilute random alloy the cluster expansion is shown to be a density expansion. The convergence of this series of x is very difficult to establish. One is more or less guided by physical intuition to expect that the properties of a dilute system at a finite temperature can be approximated by a finite number of terms of the expansion. In the present problem, the lowest order collective effect of the spins is given by the pair interaction terms.

IV. CALCUATION OF THE RESISTIVITY

In this section the resistivity is calculated by finding an approximate solution of the transport equation, Eq. (6). Using the result of Eq. (23), one can write the collision term Eq. (12) as, for $S = \frac{1}{2}$

$$\left(\frac{\partial f_k}{\partial t}\right)_{\mathrm{coll}} = \frac{2\pi I^2}{4N^2} \sum_{k'} \{[A(\epsilon_k, \epsilon_{k'})$$
$$+ \sum_j B_j(\epsilon_k, \epsilon_{k'}) \mathcal{S}(qR_j)] f_{k'}(1 - f_k)$$
$$- [A(\epsilon_{k'}, \epsilon_k) + \sum_j B_j(\epsilon_{k'}, \epsilon_k) \mathcal{S}(qR_j)] f_k(1 - f_{k'})\}, \quad (24)$$

where

$$A(\epsilon_{k'}, \epsilon_k) = \tfrac{3}{4} N_0 \delta(\epsilon_k - \epsilon_{k'})$$
$$+ N_0 x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j] \left\{ \frac{1}{e^{\beta J_{0j}} - 1} \delta(\epsilon_k - \epsilon_{k'} + J_{0j}) \right.$$
$$+ \frac{e^{\beta J_{0j}}}{e^{\beta J_{0j}} - 1} \delta(\epsilon_k - \epsilon_{k'} - J_{0j}) - \coth(\tfrac{1}{2}\beta J_{0j}) \delta(\epsilon_k - \epsilon_{k'}) \left. \right\},$$

and

$$B_j(\epsilon_{k'}, \epsilon_k) = N_0 x [\mathbf{S}_0 \cdot \mathbf{S}_j] \left\{ [1 + \coth(\tfrac{1}{2}\beta J_{0j})] \delta(\epsilon_k - \epsilon_{k'}) \right.$$
$$- \frac{1}{e^{\beta J_{0j}} - 1} \delta(\epsilon_k - \epsilon_{k'} + J_{0j})$$
$$- \frac{e^{\beta J_{0j}}}{e^{\beta J_{0j}} - 1} \delta(\epsilon_k - \epsilon_{k'} - J_{0j}) \left. \right\}. \quad (25)$$

The transport equation is solved by the ansatz[13]

$$f_{\mathbf{k}} = f_k{}^0 + k_z c(\epsilon_k) \partial f_k{}^0 / \partial \epsilon_k,$$

$$f_{\mathbf{k}'} = f_{k'}{}^0 + k_z' c(\epsilon_{k'}) \partial f_{k'}{}^0 / \partial \epsilon_{k'},$$

where the z axis is chosen to be the direction of the external field. The unknown function $c(\epsilon_k)$ is assumed to be a smooth function of the energy. Using the following relations:

$$\delta(\epsilon_k - \epsilon_{k'})[f_{k'}{}^0(1 - f_k{}^0) - f_k{}^0(1 - f_{k'}{}^0)] = 0,$$

$$\delta(\epsilon_k - \epsilon_{k'} + J_{0j})[e^{\beta J_{0j}} f_{k'}{}^0(1 - f_k{}^0) - f_k{}^0(1 - f_{k'}{}^0)] = 0,$$

$$\delta(\epsilon_k - \epsilon_{k'} - J_{0j})[f_{k'}{}^0(1 - f_k{}^0) - e^{\beta J_{0j}} f_k{}^0(1 - f_{k'}{}^0)] = 0,$$

one can readily verify that

$$[A(\epsilon_k, \epsilon_{k'}) + \sum_j B_j(\epsilon_k, \epsilon_{k'}) \mathcal{S}(qR_j)] f_{k'}{}^0(1 - f_k{}^0)$$

$$- [A(\epsilon_{k'}, \epsilon_k) + \sum_j B_j(\epsilon_{k'}, \epsilon_k) \mathcal{S}(qR_j)] f_k{}^0(1 - f_{k'}{}^0) = 0.$$

Hence, the zeroth-order term vanishes. If one also neglects the products of c's, one obtains a linear expression in c.

$$\left(\frac{\partial f_{\mathbf{k}}}{\partial t}\right)_{\text{coll}} = \frac{2\pi I^2}{4N^2} \sum_{\mathbf{k}'} \left\{ D(\epsilon_k, \epsilon_{k'}) k_z' c(\epsilon_{k'}) \frac{\partial f_{k'}{}^0}{\partial \epsilon_{k'}} \right.$$

$$\left. - D(\epsilon_{k'}, \epsilon_k) k_z c(\epsilon_k) \frac{\partial f_k{}^0}{\partial \epsilon_k} \right\},$$

where

$$D(\epsilon_k, \epsilon_{k'}) = [A(\epsilon_k, \epsilon_{k'}) + \sum_j B_j(\epsilon_k, \epsilon_{k'}) \mathcal{S}(qR_j)](1 - f_k{}^0)$$

$$+ [A(\epsilon_{k'}, \epsilon_k) + \sum_j B_j(\epsilon_{k'}, \epsilon_k) \mathcal{S}(qR_j)] f_k{}^0$$

$$= \tfrac{3}{4} N_0 \delta(\epsilon_k - \epsilon_{k'}) + N_0 x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j] \mathcal{S}(qR_j)$$

$$\times \delta(\epsilon_k - \epsilon_{k'}) + N_0 x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j][1 - \mathcal{S}(qR_j)]$$

$$\times \left\{ \frac{f_k{}^0}{f_{k'}{}^0} \cdot \frac{1}{e^{\beta J_{0j}} - 1} \right.$$

$$\times [\delta(\epsilon_k - \epsilon_{k'} + J_{0j}) + e^{\beta J_{0j}} \delta(\epsilon_k - \epsilon_{k'} - J_{0j})]$$

$$\left. - \coth(\tfrac{1}{2}\beta J_{0j}) \delta(\epsilon_k - \epsilon_{k'}) \right\}.$$

Now one averages over the angles of $\mathbf{k}'$. It can be verified that

$$\langle \mathcal{S}(qR_j) \rangle_{\Omega'} = L(kR_j),$$

$$\langle k_z' \mathcal{S}(qR_j) \rangle_{\Omega'} = M(kR_j) k_z,$$

where

$$L(\xi) = (1/2\xi^2)(1 - \cos 2\xi),$$

$$M(\xi) = (1/2\xi^4)[\xi^2 + 1 + (\xi^2 - 1)\cos 2\xi - 2\xi \sin 2\xi].$$

[13] See A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1954), p. 268.

Then one may carry out the summation on $\mathbf{k}'$ by using the results

$$\sum_{\mathbf{k}'} \delta(\epsilon_k - \epsilon_{k'}) = \tfrac{1}{2} N(\epsilon_k),$$

$$\sum_{\mathbf{k}'} \delta(\epsilon_k - \epsilon_{k'} \pm J_{0j}) = \tfrac{1}{2} N(\epsilon_k \pm J_{0j}),$$

where $N(\epsilon_k) = mkV/\pi^2$ is the density of electron states at ϵ_k. Ordinarily $J_{0j} \ll \epsilon_k$ for $\epsilon_k \cong \epsilon_F$, so one may take $N(\epsilon_k \pm J_{0j}) \cong N(\epsilon_k)$ since $N(\epsilon_k)$ is a smooth function. Since it is assumed that $c(\epsilon_k)$ is also a smooth function, so $c(\epsilon_k \pm J_{0j}) \cong c(\epsilon_k)$. Then one can write

$$\left(\frac{\partial f_{\mathbf{k}}}{\partial t}\right)_{\text{coll}} = -\frac{2\pi I^2}{4N^2} k_z c(\epsilon_k) \frac{\partial f_k{}^0}{\partial \epsilon_k} \times \tfrac{1}{2} N(\epsilon_k) F(\epsilon_k),$$

where

$$F(\epsilon_k) = \tfrac{3}{4} N_0 + N_0 x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j][L(kR_j) - M(kR_j)]$$

$$+ N_0 x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j][1 - L(kR_j) + M(kR_j)]$$

$$\times \left\{ \frac{1}{e^{\beta J_{0j}} - 1} \left[e^{\beta J_{0j}} \frac{f^0(\epsilon_k + J_{0j})}{f_k{}^0} + \frac{f^0(\epsilon_k - J_{0j})}{f_k{}^0} \right] \right.$$

$$\left. - \coth(\tfrac{1}{2}\beta J_{0j}) \right\}.$$

From Eq. (7) one finds that the drift term is

$$\left(\frac{\partial f_{\mathbf{k}}}{\partial t}\right)_{\text{drift}} = -eE \frac{\partial f_k{}^0}{\partial k_z} = -eE \frac{k_z}{m} \frac{\partial f_k{}^0}{\partial \epsilon_k}.$$

Putting these results into Eq. (6) one obtains

$$[c(\epsilon_k)]^{-1} = -\pi m I^2 N(\epsilon_k) F(\epsilon_k) / 4N^2 eE. \qquad (26)$$

The current density is

$$j = \frac{2e}{V} \sum_{\mathbf{k}} v_z f_{\mathbf{k}} = -\frac{2e}{m(2\pi)^3} \int k_z \left(f_k{}^0 + k_z c(\epsilon_k) \frac{\partial f_k{}^0}{\partial \epsilon_k} \right) d^3k$$

$$= -ek_F{}^3 c(\epsilon_F) / 3\pi^2. \qquad (27)$$

Therefore, the resistivity is

$$\rho(T) = \frac{E}{j} = -\frac{3\pi^2 E}{ek_F{}^3} [c(\epsilon_F)]^{-1}$$

$$= 3\pi^3 m I^2 N(\epsilon_F) F(\epsilon_F) / 4N^2 e^2 k_F{}^3.$$

Hence,

$$\rho = \rho_0 \{ 1 + \tfrac{4}{3} x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j][L(k_F R_j) - M(k_F R_j)]$$

$$- \tfrac{4}{3} x \sum_j [\mathbf{S}_0 \cdot \mathbf{S}_j][1 - L(k_F R_j) + M(k_F R_j)]$$

$$\times \tanh(\tfrac{1}{2}\beta J_{0j}) \}, \qquad (28)$$

where

$$\rho_0 = 9\pi^3 mN(\epsilon_k)N_0/16N^2e^2k_F{}^3$$
$$= 9\pi m^2 I^2 V_0 x/16e^2k_F{}^2. \qquad (29)$$

V_0 is the volume of the unit cell.

It is interesting to note that de Gennes and Friedel[14] and Rocher[15] studied a similar problem, the effect of short-range order on the high-temperature resistivity of ferro- or antiferromagnetic metals, by the "elastic scattering approximation." The method essentially ignores the energy transfer between the spin system and the conduction electron. Or equivalently, one approximates

$$\langle \mathbf{S}_j(\zeta)\cdot\mathbf{S}_i(0)\rangle = \langle \mathbf{S}_j\cdot\mathbf{S}_i\rangle. \qquad (30)$$

As a result the collision term Eq. (12) consists only of elastic scatterings and the transport equation is easy to solve. The resistivity as found this way is

$$\rho(T) = \rho_0 \left\{ 1 + x \sum_i \frac{\langle \mathbf{S}_0\cdot\mathbf{S}_j\rangle}{S(S+1)}[L(k_FR_j) - M(k_FR_j)] \right\}, \qquad (31)$$

where

$$\rho_0 = 3\pi m^2 I^2 V_0 x S(S+1)/4e^2 k_F{}^2$$

for general spin S. The approximation in Eq. (30) is obviously a good one when S is very large. For $S=\frac{1}{2}$, one may compare Eq. (28) and Eq. (31) at high temperatures. To the first order of β, it can be verified that

$$\langle \mathbf{S}_0\cdot\mathbf{S}_j\rangle \cong [\mathbf{S}_0\cdot\mathbf{S}_j] \cong \tfrac{3}{16}\beta J_{0j},$$
$$\tanh(\tfrac{1}{2}\beta J_{0j}) \cong \tfrac{1}{2}\beta J_{0j}.$$

So the last term in the bracket of Eq. (28), which is the contribution of inelastic collisions, is of the order β^2. Therefore, to the order β, only the elastic scatterings need to be considered and Eqs. (28) and (31) agree. This conclusion should also hold for higher spins.

V. DISCUSSION

The result of Eqs. (28) and (31) shows that at high temperatures where the spin correlation is negligible, the resistivity is ρ_0. At lower temperatures where the collective effect of the spins becomes significant, the modification to the resistivity is at least of the order x^2. These conclusions are in agreement with Brailsford and Overhauser. To the lowest order of βJ_{0j}, one finds

$$\rho(T) = \rho_0 + a/T + O(\beta^2, x^2),$$

where

$$a = \rho_0 x S(S+1) \sum_j J_{0j}[L(k_FR_i) - M(k_FR_i)]/3k_B \qquad (32)$$

and k_B is the Boltzmann constant. If the sum in the

[14] P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).
[15] Y. A. Rocher, J. Phys. Radium 22, 367 (1961).

expression for a is positive, then the resistivity tends to rise when the temperature is lowered. The total resistivity of the material is $\rho(T)$ plus a phonon contribution, i.e.,

$$\rho_t(T) = \rho(T) + bT^5$$
$$\cong \rho_0 + a/T + bT^5.$$

It is apparent that if $a>0$, $\rho_t(T)$ can have a minimum at a temperature T_0 such that

$$T_0 = (a/5b)^{1/6} \propto x^{1/3}, \qquad (33)$$

since a is proportional to x^2. Therefore, the concentration dependence of T_0 disagrees with the experimental law, Eq. (1), for most alloys.

In dilute alloys where the spins are on the average rather far apart, the coupling mechanism between the spins has been shown to be due to the second order effect of the s-d exchange interaction.[8-10] The coupling energy J_{0j} is given by

$$J_{0j} = -v_0(2k_FR_j)^{-4}[2k_FR_j\cos(2k_FR_j) - \sin(2k_FR_j)]$$

and $v_0 = 9\pi I^2 Z^2/4\epsilon_F$, Z is the valence of the solvent ion. The summation in the expression for a will involve lattice sums of $\sin(2k_FR_j)/R_j{}^\alpha$ and $\cos(2k_FR_j)/R_j{}^\beta$ and their products. Since the sine and cosine function are rapidly oscillatory, one may approximate them and their products by the average values, i.e.,

$$\cos(2k_FR_j) \cong \sin(2k_FR_j) \cong 0,$$
$$\cos(2k_FR_j)\sin(2k_FR_j) \cong 0,$$
$$\cos^2(2k_FR_j) \cong \sin^2(2k_FR_j) \cong \tfrac{1}{2}.$$

This gives

$$\sum_j J_{0j}[L(k_FR_j) - M(k_FR_j)] \cong v_0 \sum_j \frac{1}{16k_F{}^5R_j{}^5}.$$

Therefore, a is, indeed, positive. If one approximates the lattice sum by an integral, one finds

$$\sum_j \frac{1}{R_j{}^5} \cong \frac{1}{V_0} \int_c^\infty \frac{4\pi R^2 dR}{R^5} = \frac{2\pi}{c^5},$$

where $c = (V_0)^{1/3}$ is the linear dimension of the unit cell. From these results one finally obtains

$$a \cong \pi \rho_0 x S(S+1) v_0/24 k_B(k_Fc)^5.$$

It is now possible to make a numerical estimate of a. The solutions of manganese in copper is used as an example. The commonly accepted value for the s-d exchange-interaction constant $|I|$ is about 0.5 eV.[10] Taking $S=2$ and the effective mass ratio to be unity, one finds for a 0.03% alloy

$$\rho_0 \cong 0.6\times 10^{-8}\ \Omega\text{-cm},$$

which is comparable to the observed minimum resistivity $2.2\times 10^{-8}\ \Omega$-cm.[16] The spin-coupling constant

[16] A. Kjekshus and W. B. Pearson, Can. J. Phys. 40, 98 (1962).

v_0 is estimated to be about 4×10^{-13} erg. Using $2k_F c \cong 2\pi$, one finds that for two spins at a distance c apart, the interaction energy is roughly 12°K. The resistivity minimum occurs at about 12°K. Hence, it is safe to use the high-temperature expansion at around this temperature because the average nearest neighbor distance is much larger than c. One then finds that for $x = 0.03\%$ the change in resistivity from 8 to 12°K is roughly

$$\Delta\rho = 5 \times 10^{-13} \ \Omega\text{-cm}.$$

However, the observed variation is of the order of 10^{-10} Ω-cm.[16] This shows that the spin correlation effect does not explain the resistivity minimum phenomenon. At the present moment the resonant scattering theory seems to be more satisfactory because it is supported by another experiment.

Gap Equation and Current Density for a Superconductor in a Slowly Varying Static Magnetic Field

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The energy gap equation and the current density expression for a superconductor in a slowly varying static magnetic field are derived on the basis of a generalization of Nambu's Green's function formalism to finite temperatures. In the integral equation for the quasiparticle Green's function $G^A(\mathbf{R}; \mathbf{r})$, expansions of G^A, the self-energy part Σ, and the vector potential $\mathbf{A}$, about the center-of-mass coordinates $\mathbf{R}$, are introduced. The integral equation is solved by iteration, and the contributions of all orders in the gap $\phi(\mathbf{R})$ are summed up. With the help of G^A, the generalized Ginzburg-Landau-Gor'kov (GLG) equations, valid at all temperatures for slowly varying $\mathbf{A}(\mathbf{R})$ and $\phi(\mathbf{R})$, are derived. For temperatures near T_c, correction terms to the coefficients of the GLG equations occur which are proportional to powers of $|\beta\phi|^2$. For temperatures near 0°K, the function multiplying the term $(\nabla + 2ie\mathbf{A})^2\phi$ behaves like $\exp(-|\beta\phi|)$. The first-order correction to the term proportional to A^2 is found to be proportional to $\xi_0^2 H^2$, for T near T_c and near 0°K (H = magnetic field strength, ξ_0 = coherence length). Our results are consistent with the formula of Nambu and Tuan for the reduction of the gap at 0°K in the London region.

I. INTRODUCTION

EQUATIONS for the superconducting energy gap in the presence of a magnetic field on the basis of the Bardeen-Cooper-Schrieffer[1] (BCS) and Bogoliubov microscopic theory have been derived by Gor'kov.[2] The validity of these equations is restricted to temperatures T, such that $T_c - T \ll T_c$, and to the local or London region where $q\xi_0 \ll 1$. Here T_c is the transition temperature, ξ_0 is the coherence length, and the q are the wave numbers of the field. By defining a wave function proportional to the energy gap, Gor'kov was able to transform his equations into the Ginzburg-Landau[3] phenomenological equations. In the following, the Gor'kov version of the Ginzburg-Landau equations is referred to as the GLG equations.

The GLG approach has been used to estimate the magnetic field dependence of the gap.[4] One finds good agreement between theory and experiment down to temperatures of about 0.7 T_c. However, one expects that at the lower temperatures corrections to the GLG equations will become significant. The aim of this paper is to generalize the GLG equations to all temperatures, under the assumption that the vector potential $\mathbf{A}(\mathbf{R})$ and the gap $\phi(\mathbf{R})$ vary slowly over the distance of a coherence length ξ_0. Our main concern is to establish the connection between the first generalized GLG equation and the equation of Nambu and Tuan[5] for the reduction of the energy gap at zero temperature in the local region. A characteristic point of their result is that the reduction of the gap depends only on the magnetic field strength.

Gor'kov has derived his equations with the help of integral equations for the quasiparticle Green's function. These integral equations were solved by iteration in powers of the gap, and only terms up to the fourth order in the gap were kept. This latter approximation is the origin of the restriction $T_c - T \ll T_c$. Our calculation is based on a generalization of Nambu's[6] two-component Green's function formalism to finite temperatures which has been developed in a previous paper.[7] Under the integral of the integral equation for

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[2] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [translation: Soviet Phys.—JETP **9**, 1364 (1959)].

[3] V. L. Ginzburg and D. L. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

[4] See, for instance, D. H. Douglass, Jr., Phys. Rev. Letters **6**, 346 (1961); **7**, 14 (1961); Phys. Rev. **124**, 735 (1961).

[5] Y. Nambu and S. F. Tuan, Phys. Rev. **128**, 2622 (1962).

[6] Y. Nambu, Phys. Rev. **117**, 648 (1960).

[7] L. Tewordt, Phys. Rev. **128**, 12 (1962).