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VIRIAL EXPANSION FOR MAGNETIC IMPURITIES IN METALS

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The method proposed in a previous paper by the same authors[1] is used to investigate the temperature dependence of the resistance, of the superconducting transition temperature, and of the line shape of the impurity EPR. The results obtained are applicable in the domain of not too low temperatures, when one can restrict oneself to the first virial terms.

1. INTRODUCTION

THE properties of alloys with paramagnetic impurities have been extensively investigated in recent times both theoretically and experimentally. The interest in these alloys is due to the low temperature anomalies of kinetic (conductivity, thermoelectric e.m.f.) and of thermodynamic (susceptibility, heat capacity) quantities.

Such anomalies can be due to two causes—the change in the amplitude of the scattering of an electron by an impurity (the Kondo effect) and the interaction between the impurities themselves. In metals the principal interaction between the impurities is the indirect exchange via the conduction electrons (the Kittel-Ruderman interaction[2]). This interaction falls off slowly with distance and therefore can turn out to be significant even at a low concentration of the impurities.

In[1], a study was made of the effect of the interaction between the impurities on the thermodynamic functions of the alloy. It was shown that at sufficiently high temperatures a virial expansion is valid for the thermodynamic functions and corrections were calculated quadratic in the concentration of the impurities. Analogous corrections are found below for the resistance, for the temperature of transition into the superconducting state and for the line shape of impurity paramagnetic resonance. The relative order of magnitude of these corrections is the same as for the thermodynamic quantities—they are small if the temperature exceeds the energy of the interaction between two impurities at an average distance between them (for a given concentration).

However, there exist a number of phenomena for which the position of the energy levels is significant, for example the inelastic scattering of neutrons and the hyperfine structure. In these cases the virial expansion contains instead of the temperature another, usually a much smaller, energy parameter—the transfer of energy in neutron scattering or the magnitude of the hyperfine splitting—and for this reason the expansion is in practice inapplicable.

Just as in[1], we shall not take into account the influence of the Kondo effect. This is valid when $T \gg T_K$. As will be shown below, a number of our results is valid over a wider temperature range.

2. THE VIRIAL EXPANSION FOR THE SPIN CORRELATION FUNCTION

In order to calculate the corrections to the resistance and to the temperature of the superconducting transition it is necessary to know both the time (K) and the temperature ($\mathscr{K}$) correlation functions for the spin of an individual impurity:

$$K(\omega)=\int_{-\infty}^{+\infty} dt e^{i\omega t}\langle \mathrm{S}_1(0)\mathrm{S}_1(t)\rangle, \tag{1}$$

$$\mathscr{K}(\omega_m)=\int_0 d\tau e^{i\omega_m\tau}\langle \mathrm{S}_1(0)\mathrm{S}_1(\tau)\rangle, \tag{2}$$

$$\omega_m=2\pi mT,\quad \beta=1/T.$$

The angular brackets denote averaging according to Gibbs for a given distribution of the impurities, $\mathbf{S}_1$ is the operator for the spin of the first impurity. Naturally, after averaging over the position of the impurities the result does not depend on the number of the impurity. The quantities $\mathbf{S}_1(t)$ and $\mathbf{S}_1(\tau)$ are given by the formulas

$$\mathrm{S}_1(t)=e^{i\mathscr{H}t}\mathrm{S}_1e^{-i\mathscr{H}t},\quad \mathrm{S}_1(\tau)=e^{\mathscr{H}\tau}\mathrm{S}_1e^{-\mathscr{H}\tau}, \tag{3}$$

where

$$\mathscr{H}=\sum_{ij}V(R_{ij})\mathrm{S}_i\mathrm{S}_j \tag{4}$$

is the Kittel-Ruderman Hamiltonian, R_{ij} is the distance between the i-th and the j-th impurities,

$$V(R)=V_0\frac{\cos 2p_0R}{R^3}\text{ for } p_0R\gg 1, \tag{5}$$

p_0 is the Fermi momentum. We shall carry out all the intermediate calculations only for K.

In the zero order approximation with respect to the impurity concentration we can leave out of consideration their interaction, so that

$$K_0(\omega)=2\pi S(S+1)\delta(\omega). \tag{6}$$

Here S is the spin of the impurity.

In order to evaluate the term K_1 linear in the impurity concentration n we shall find the addition to K for the case when in the volume $\mathscr{V}$ in addition to the first impurity there is also present another impurity, and we shall multiply it by the total number of impurities $N = n\mathscr{V}$. Then we have

$$K_1(\omega) = N\int_{-\infty}^{+\infty} dt e^{i\omega t}\overline{[\langle S_1(0)S_1(t)\rangle_2 - S(S+1)]}. \tag{7}$$

Taking into account the fact that the energy levels of the Hamiltonian for two impurities depend only on their total angular momentum J and are equal to $V(R_{12})\,[\epsilon_J - S(S+1)]$, $\epsilon_J = J(J+1)/2$, we obtain

$$\langle S_1(0)S_1(t)\rangle_2 = \Big[\sum_{J=0}^{2S}(2J+1)\exp\{-\beta V(R_{12})\varepsilon_J\}\Big]^{-1} \tag{8}$$

$$\times\sum_{JJ'=0}^{2S}(2J+1)A_{JJ'}\exp\{-V(R_{12})\,[\beta\varepsilon_J + it(\varepsilon_J - \varepsilon_{J'})]\}.$$

Here we have introduced the notation

$$A_{JJ'} = \sum_{M'}|\langle JM|S_1|J'M'\rangle|^2 \tag{9}$$

and we have taken into account the fact that $A_{JJ'}$ does not depend on M. The expression for $A_{JJ'}$ in terms of the 6j-symbols is given in the Appendix.

In future we shall consider $K(\omega)$ at frequencies $\omega \sim T$. Therefore in averaging over the position of the impurities the significant values of R will turn out to be $R \sim (T/V_0)^{1/3} \gg p_0^{-1}$ and, thus, the averaging over R will be conveniently carried out in two stages. First we average over the argument of the cosine (cf., formula (5)), and then we average the smooth function so obtained over R. Thus, for an arbitrary function f we have

$$\overline{f\left(\frac{V(R)}{T}\right)} = \frac{1}{\mathscr{V}}\int d\mathbf{R}\int_{-\pi}\frac{d\varphi}{2\pi}f\left(\frac{V_0}{TR^3}\cos\varphi\right). \tag{10}$$

Interchanging the order of integration we obtain

$$\bar{f} = f(0) + \frac{4}{3}\frac{V_0}{T\mathscr{V}}\int_{-\infty}^{+\infty}\frac{dy}{y^2}[f(y) - f(0)]. \tag{11}$$

Utilizing (7), (8) and (11) we obtain the final formula

$$K(\omega) = S(S+1)\Big\{2\pi\delta(\omega) + \frac{8\pi}{3}\frac{nV_0}{T}\int_{-\infty}^{+\infty}\frac{dy}{y^2}\Big[\frac{P(\omega,y)}{Z(y)} - \delta(\omega)\Big]\Big\}, \tag{12}$$

where

$$P(\omega, y) = \sum_{JJ'=0}^{2S}(2J+1)A_{JJ'}e^{-y\varepsilon_J}\delta[\omega - Ty(\varepsilon_J - \varepsilon_{J'})], \tag{13}$$

$$Z(y) = S(S+1)\sum_{J=0}^{2S}(2J+1)e^{-y\varepsilon_J}. \tag{14}$$

Similarly for $\mathscr{K}(\omega_m)$ we have

$$\mathscr{K}(\omega_m) = \beta S(S+1)\Big\{\delta_{m0} + \frac{4}{3}\frac{nV_0}{T}\int_{-\infty}^{+\infty}\frac{dy}{y^2}\Big[\frac{Q(\omega_m, y)}{Z(y)} - \delta_{m0}\Big]\Big\}, \tag{15}$$

where

$$Q(\omega_m, y) = -\sum_{JJ'=0}^{2S}(2J+1)\frac{y(\varepsilon_J - \varepsilon_{J'})A_{JJ'}}{(2\pi m)^2 + y^2(\varepsilon_J - \varepsilon_{J'})^2}[e^{-y\varepsilon_J} - e^{-y\varepsilon_{J'}}]. \tag{16}$$

The values for $J = J'$ are taken in the limit $J \to J'$ and are proportional to δ_{m0}.

Carrying out the integration in (12) taking into account (13) we obtain for $\omega \neq 0$ the following formula:

$$K(\omega) = \frac{8\pi}{3}\frac{nV_0}{\omega^2}S(S+1)\sum_{J=1}^{2S}J(2J+1)A_{J,J-1}$$
$$\times\left\{\frac{\exp\{-\beta\omega(J+1)/2\}}{Z(\beta\omega/J)} + \frac{\exp\{\beta\omega(J-1)/2\}}{Z(-\beta\omega/J)}\right\}. \tag{17}$$

The expression (17) satisfies the well-known relation

$$K(-\omega) = e^{\beta\omega}K(\omega). \tag{18}$$

In the limiting cases we obtain

$$K(\omega) = \frac{8\pi}{3}\frac{nV_0}{\omega^2}\begin{cases}\dfrac{2}{(2S+1)^2}\displaystyle\sum_{J=1}^{2S}J(2J+1)A_{J,J-1}, & \beta\omega S \ll 1\\ S(S+1)e^{-\beta\omega}, & \beta\omega \gg 1\end{cases} \tag{19}$$

The function $K(\omega)$ determines the spectral distribution of neutrons inelastically scattered by the impurities. Distances $R \sim (V_0/\omega)^{1/3}$ give contributions to the result (17). Therefore the expression obtained above can be utilized only if the average distance between the impurities is greater than $(V_0/\omega)^{1/3}$.

3. RESISTANCE

The kinetic equation for the distribution function f_p for the conduction electrons scattered by the impurities has the form

$$e\mathbf{E}\frac{\partial f_{\mathbf{p}}}{\partial\mathbf{p}} = \int\frac{d\mathbf{p}'}{(2\pi)^3}\{W_{\mathbf{pp}'}[(1-f_{\mathbf{p}})f_{\mathbf{p}'} - f_{\mathbf{p}}(1-f_{\mathbf{p}'})]$$
$$+ w_{\mathbf{pp}'}[f_{\mathbf{p}'}(1-f_{\mathbf{p}}) - e^{\beta(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'})}f_{\mathbf{p}}(1-f_{\mathbf{p}'})]\}. \tag{20}$$

Here $W_{pp'}$ is the probability for elastic scattering without spin flip, while $w_{pp'}$ is the probability of scattering with spin flip, which may be inelastic. The solution of equation (20) is facilitated by the circumstance that the exchange scattering is weaker than the ordinary scattering. Linearizing (20) with respect to **E**, taking into account the fact that the first term in the collision term reduces to the form $-(f_p - f_p^0)/\tau_{tr}$ (f_p^0 is the equilibrium Fermi function), and solving the equation so obtained with an accuracy linear in $w_{pp'}$, we obtain for the resistance ρ the expression

$$\rho = \rho_0 + \frac{m^2}{e^2Tn_0}\int w_{\mathbf{pp}'}(\mathbf{v} - \mathbf{v}')\mathbf{v}(1 - f_{\mathbf{p}}^0)f_{\mathbf{p}'}^0\frac{d\mathbf{p}\,d\mathbf{p}'}{(2\pi)^6}, \tag{21}$$

where ρ_0 is the resistance without taking the exchange scattering into account, m and e are the mass of the electron and its charge, n_0 is the electron density.

In order to determine $w_{pp'}$ we write the Hamiltonian for the exchange interaction between the electrons and the impurities in the form

$$\mathscr{H}_{int} = \sum_{\mathbf{k},\mathbf{p},i}I(\mathbf{k})S_i\sigma_{\alpha\beta}a_{\mathbf{p}\alpha}^{+}a_{\mathbf{p}-\mathbf{k}\beta}e^{i\mathbf{k}\mathbf{R}_i}, \tag{22}$$

where $\mathbf{R}_i$ is the coordinate of the i-th impurity, σ are the Pauli matrices, $a_{p\alpha}^{+}$ and $a_{p\alpha}$ are the creation and annihilation operators for an electron in the state **p**, α. We note that this Hamiltonian has already been utilized in deriving the Kittel-Ruderman interaction, the constant V_0 of which is related to $I(\mathbf{k})$ by the equation

$$V_0 = mp_0|I(2p_0)|^2/4\pi^3. \tag{23}$$

The transition probability $w_{pp'}$, related to the Hamiltonian (20), is given by the formula

$$w_{\mathbf{pp}'} = 2n\,|I(\mathbf{p}-\mathbf{p}')|^2 \int_{-\infty}^{+\infty} dt\, e^{i(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'})t} \langle S_1(0)\, S_1(t)\rangle = 2n\,|I(\mathbf{p}-\mathbf{p}')|^2 K(\varepsilon_p - \varepsilon_{\mathbf{p}'}). \qquad (24)$$

Combining (12), (13) and (22) and taking into account the fact that for the Fermi functions $f_{\mathbf{p}}^0$ we have

$$\int d\varepsilon\, d\varepsilon' f^0(\varepsilon')\,[1-f^0(\varepsilon)]\,\delta(\varepsilon-\varepsilon'+T\alpha) = \Phi(\alpha) = T\alpha/(e^\alpha - 1), \qquad (25)$$

we obtain the final expression for the resistance

$$\rho = \rho_0 + \rho_S(1 - a_S n V_0 / T), \qquad (26)$$

where ρ_S is the part of the resistance linear in the impurity concentration which is due to the exchange scattering,

$$a_S = \frac{4}{3}\int_{-\infty}^{+\infty} \frac{dy}{y^2}\left[1 - \frac{T(y)}{Z(y)}\right], \qquad (27)$$

$$T(y) = \sum_{JJ'=0}^{2S} (2J+1) \times e^{-y\varepsilon_J} A_{JJ'}\Phi\,[y(\varepsilon_J - \varepsilon_{J'})]. \qquad (28)$$

Numerically the a_S are equal to

$$a(1/2) = 1{,}12,\quad a(1) = 1{,}53,\quad a(3/2) = 1.85,\ a(2) = 2.12,\ a(5/2) = 2{,}35,$$
$$a(3) = 2{,}54,\ a(7/2) = 2{,}70,$$
$$a(4) = 2{,}84.$$

The integrand in (27) describing the contribution to the resistance made by a pair of impurities at a fixed distance for the case S = ½ coincides with the one obtained in[3].

From (26) it can be seen that the interaction between the impurities leads to a reduction in the resistance as the temperature is reduced. The reason for this is the fact that the interacting impurities possess a system of energy levels, and with the reduction in temperature the scattering processes accompanied by a transition from one level to another one are frozen out.

4. THE TEMPERATURE OF TRANSITION INTO THE SUPERCONDUCTING STATE

Without taking into account the interaction between magnetic impurities the equation for the order parameter Δ has been derived by Abrikosov and Gor'kov[4]. The interaction between the impurities leads to the exchange scattering being inelastic. Repeating the calculations of Abrikosov and Gor'kov taking this fact into account we obtain a system of equations for determining Δ:

$$\omega_n \sin\varphi_n - \Delta\cos\varphi_n = -\frac{1}{2\tau_S}\sum_m \frac{\mathcal{K}(\omega_m)}{S(S+1)}\sin(\varphi_{m+n}+\varphi_n), \qquad (29)$$

$$\Delta = \lambda T\sum_n \sin\varphi_n,\quad \omega_n = \pi T(2n+1),\quad \omega_m = 2\pi m T. \qquad (30)$$

We note that in the Born approximation the superconducting properties are expressed in terms of the correlation function for the impurity spins $\mathcal{K}(\omega_m)$. The virial expansion (15) has been obtained for $\mathcal{K}(\omega_m)$.

In order to find the transition temperature T_c we let $\Delta \to 0$. Then $\cos\varphi_n = \operatorname{sign}\omega_n$. Evaluating with the aid of (29) $\sin\varphi_n$ in the approximation linear in terms of the increment to the virial and substituting it into (30) we obtain an equation for T_c:

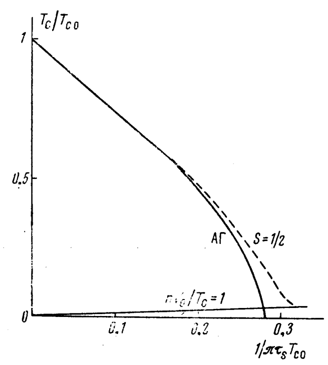

FIG. 1

$$\ln\frac{T_{c0}}{T_c} = \psi\left(\frac{1}{2}+\frac{\rho}{2}\right) - \psi\left(\frac{1}{2}\right) + \sum_m \frac{\mathcal{K}_1(\omega_m)}{S(S+1)}\cdot \sum_n \left\{\frac{\operatorname{sign}\omega_n \operatorname{sign}\omega_{m+n}}{(|2n+1|+\rho)^2} + \frac{1}{(|2n+1|+\rho)(|2n+2m+1|+\rho)}\right\}, \qquad (31)$$

where $\rho = (\pi\tau_S T_c)^{-1}$, $\psi(z) = \Gamma'(z)/\Gamma(z)$. We note that the virial parameter nV_0 is related to τ_S by the equation

$$nV_0 = 1/4\pi^2\tau_S S(S+1). \qquad (32)$$

For small impurity concentrations the transition temperature can be represented in the form of a series in the concentrations

$$T_c = T_{c0}\left\{1 - \frac{\pi}{4\tau_S T_{c0}} - \frac{1}{(T_{c0}\tau_S)^2}\left[\frac{\pi^2}{32} - \frac{7}{4\pi^3}\zeta(3) - \frac{16}{9\pi^3}b(S)\right]\right\}. \qquad (33)$$

The last term in brackets represents a correction due to the interaction between the impurities b(½) = 0.21, b(1) = 0.10, b(3/2) = 0.066, b(2) = 0.047. For numerical reasons (the factor $1/4\pi^2$ in formula (32)) the correction turns out to be small, and the interaction can be neglected everywhere except for the region of the lowest temperatures. In Fig. 1 curves are given for the function $T_c(n)$: the one obtained by Abrikosov and Gor'kov[4] and the one calculated by means of formula (31) in the case S = ½. The small differences between the functions are associated with the numerical factor referred to above. This difference becomes even smaller in the case of large spins.

5. IMPURITY PARAMAGNETIC RESONANCE

The intensity and the line shape of paramagnetic resonance are determined by the quantity

$$\chi''(\omega) = -\operatorname{Im}\chi(\omega) = \frac{\mu^2\omega}{4T}N\int_{-\infty}^{+\infty}\langle S_+(t)S_-(0)\rangle e^{-i\omega t}\,dt, \qquad (34)$$

where $\mathbf{S} = \Sigma\,\mathbf{S}_i$ is the total spin of the system. Here

$$S(t) = e^{i\mathcal{H}t}Se^{-i\mathcal{H}t},$$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int} - \mu\mathbf{SH},$$

$\mathcal{H}_0$ is the sum of the Kittel-Ruderman Hamiltonians and the kinetic energy of the electrons, while the Hamiltonian for the interaction between the impurities and the electrons $\mathcal{H}_{int}$ is given by formula (22). Here H is the external magnetic field, while μS is the magnetic moment of the impurities. The interaction of the conduction electrons with the magnetic field is omitted, and this is allowable if the electron and the impurity resonances do not overlap. When $\mathcal{H}_{int}$ is neglected we have

$$\chi''(\omega) = \mu H\chi(0)\delta(\omega - \mu H)/2\pi, \qquad (35)$$

where $\chi(0)$ is the static susceptibility, the virial correction to which has been evaluated in[1]:

$$\chi^{-1}(0)=\frac{3(T+c_S nV_0)}{N\mu^2 S(S+1)}, \tag{36}$$

$$c_S=\frac{4}{3}\int\frac{dy}{y^2}\left[1-\frac{M(y)}{Z(y)}\right], \tag{37}$$

$$M(y)=\frac{1}{2}\sum_{J=0}^{2S}J(J+1)(2J+1)e^{-y\varepsilon_J}. \tag{38}$$

The numerical values of c_S are equal to:

$c(^1/_2)=0{,}667,\quad c(1)=0{,}85,\quad c(^3/_2)=0{,}984,\quad c(2)=1{,}09,$

$c(^5/_2)=1{,}17,\quad c(3)=1{,}25,\quad c(^7/_2)=1{,}31,\quad c(4)=1{,}36.$

We note that the value of T^* given in[1] is incorrect. The correct value is equal to $T^*_{1/2}=0.667nV_0$. Moreover, in all the formulas of[1], with the exception of formula (2), one should replace V_0 by $V_0/2$.

The Kittel-Ruderman interaction does not by itself lead either to a shift of the frequency of paramagnetic resonance or to its broadening. This is associated with the fact that the Kittel-Ruderman Hamiltonian commutes with the total spin of the impurities. The finite width of the resonance line arises due to the interaction of the impurities with the thermal electrons. Taking this interaction into account the virial expansion for $\chi''(\omega)$ can be written in the form

$$\chi''(\omega)=\frac{\mu^2\omega}{4T}N\int dte^{-i\omega t}\Big\{\langle S_+(t)S_-(0)\rangle_1+N\overline{\left[\frac{1}{2}\langle S_+(t)S_-(0)\rangle_2-\langle S_+(t)S_-(0)\rangle_1\right]}\Big\},$$

where $\langle S_+S_-\rangle_1$ and $\langle S_+S_-\rangle_2$ denote respectively the correlation functions for the spin of one and the total spin of two impurities for a fixed distance between them. The bar as before denotes averaging over the different mutual positions of the impurities.

The equation for the operator S_+ in the interaction representation has the form

$$\frac{d}{dt}S_+-i\omega_0 S_+=\int_0^t dt'[\mathcal{H}_{int}(t)[\mathcal{H}_{int}(t')S_+(t')]],$$

where $\omega_0=\mu H$ is the frequency of the resonance, while $\mathcal{H}_{int}(t)=e^{i\mathcal{H}_0 t}\mathcal{H}_{int}e^{-i\mathcal{H}_0 t}$. The equation for the operator S_+ averaged over the electron distribution is obtained by means of averaging the product $\mathcal{H}_{int}(t)\mathcal{H}_{int}(t')$. After this averaging it becomes clear that the significant values of $t-t'$ are $t-t'\sim T^{-1}$ and, therefore, for times t which are of the order of magnitude of the relaxation time and large compared to T^{-1} one can replace the lower limit in the integral by $-\infty$. For the same reason the operator $S_+(t')$ can be replaced by $S_+(t)$ and one need not take into account the interaction with the electrons in the time dependence of the operators $\mathbf{S}_1(t')$ and $\mathbf{S}_2(t')$ which appear in $\mathcal{H}_{int}(t')$. Finally the equation for the operator $S_+(t)$ averaged over the electron distribution has the form

$$\begin{aligned}\frac{d}{dt}S_+-i\omega_0 S_+=\int\frac{d\mathbf{p}\,d\mathbf{p}'}{(2\pi)^6}\int_{-\infty}^{+\infty}dt'\,e^{i(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'})t'}\cdot\{&\mathbf{S}_1S_+(t)\mathbf{S}_1(t')f_{\mathbf{p}}^0(1-f_{\mathbf{p}'}^0)\\ &-\mathbf{S}_1\mathbf{S}_1(t')S_+(t)f_{\mathbf{p}'}^0(1-f_{\mathbf{p}}^0)+\mathbf{S}_2S_+(t)\mathbf{S}_2(t')f_{\mathbf{p}}^0(1-f_{\mathbf{p}'}^0)-\\ &-\mathbf{S}_2\mathbf{S}_2(t')S_+(t)f_{\mathbf{p}'}^0(1-f_{\mathbf{p}}^0)\}.\end{aligned} \tag{39}$$

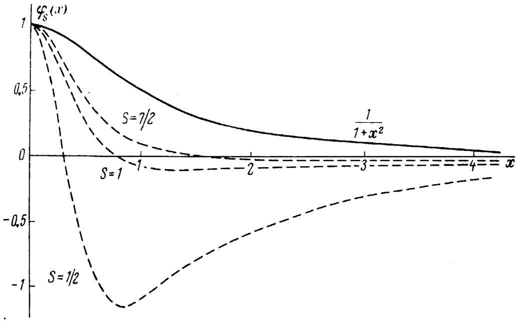

FIG. 2

We seek the solution of this equation in the form

$$S_+(t)=S_+\sum_{J=1}^{2S}\hat{P}_J a_J(t)e^{i\omega_0 t}. \tag{40}$$

Here $\hat{P}_J$ is the projection operator unto a state with the total angular momentum of the two spins J, and $a_J(t)$ are unknown functions. Taking into account the fact that

$$e^{i\hat{\mathcal{H}}_0 t}=\sum_{J=0}^{2S}e^{i\varepsilon_J V_{12}t}\hat{P}_J,$$

we obtain a system of $2S$ equations for a_J:

$$\frac{d}{dt}a_J=-\frac{1}{\tau}\sum_{J'}M_{JJ'}a_{J'}, \tag{41}$$

where $\tau^{-1}=m^2p_0^2T\int d\Omega\,|I(\theta)|^2/4\pi^2$ is the relaxation time for a free spin, while

$$TM_{JJ'}=2B_{JJ'}\Phi_{JJ'}-2\delta_{JJ'}\sum_{J''}A_{JJ''}\Phi_{JJ''}.$$

The quantities $A_{JJ'}$ and $\Phi_{JJ'}$ are defined by equations (9) and (25), $B_{JJ'}$ is defined by the equation

$$\sum_{i=1,2}\mathbf{S}_i\hat{P}_{J'}S_+\mathbf{S}_i=2S_+\sum_J B_{JJ'}\hat{P}_J. \tag{42}$$

$B_{JJ'}$ is expressed in terms of the 6j-symbols in the Appendix.

The unsymmetric matrix $M_{JJ'}$ has the eigenvalues λ_i and the corresponding right hand and left hand eigenvectors $x_J^{(i)}$ and $\tilde{x}_J^{(i)}$. In the representation of these eigenvectors the solution of the equation for a_J taking into account the initial conditions $a_J(0)=1$ has the form

$$a_J(t)=\sum_i D_{iJ}e^{-\lambda_i t/\tau},\qquad D_{iJ}=x_J^{(i)}\sum_{J'}\tilde{x}_{J'}^{(i)}. \tag{43}$$

Substituting (43) into (40), and the resulting expression into (39), we write the final result for the line shape taking into account the first virial correction:

$$\chi''(\omega)=\frac{N}{6T}\mu^2\omega_0\tau S(S+1)\left\{\frac{1}{1+(\omega-\omega_0)^2\tau^2}+\frac{nV_0}{T}d_S\varphi_S[(\omega-\omega_0)\tau]\right\} \tag{44}$$

$$d_S\varphi_S(x)=\frac{4}{3}\int_{-\infty}^{+\infty}\frac{dy}{y^2}\left[\frac{R(y;x)}{Z(y)}+\frac{1}{1+x^2}\right], \tag{45}$$

$$R(y,x)=\sum_{Ji}e^{-y\varepsilon_J}(2J+1)D_{iJ}\frac{\lambda_i}{\lambda_i^2+x^2}. \tag{46}$$

The quantities d_S which determine the magnitude of the corrections at the centre of the line are equal to

$d(^1/_2)=0{,}437,\quad d(1)=3{,}91,\quad d(^3/_2)=10{,}5,$

$d(2)=20{,}6,\quad d(^5/_2)=34{,}6,\quad d(^7/_2)=75{,}7.$

For large values of S we have $d_S \approx 7S^2$. The functions $\varphi_S(x)$ are given in Fig. 2 for $S = 1/2$, $S = 1$ and $S = 7/2$.

As has been noted above the integral of expression (44) is proportional to the susceptibility, the relative virial correction to which is given by formula (36). This correction is negative and in the classical limit ($S \to \infty$, $S^2V_0 \to$ const) tends to zero as $\ln S/S^2$ [1]. This means that the integral of $\varphi_S(x)$ over x is negative and for large values of S tends to zero as $\ln S/S^2$. The relative correction to the intensity of the resonance at the centre of the line is positive and in the classical limit ($V_0S^2 \to$ const, $S \to \infty$) remains finite. Thus, taking spin correlation into account leads to a narrowing of the resonance line. The reason for this is the effective reduction of the interaction of the impurities with the conduction electrons noted above.

6. CONCLUSION

In the majority of cases discussed above the interaction between the impurities led only to a change in the temperature dependence of the different quantities. However, there exist effects which would be absent completely if there were no interaction between the impurities. The inelastic scattering of neutrons mentioned above can serve as an example. Another effect which is also related to the existence of levels in a system of interacting impurities is the energy relaxation of the electrons.

The scattering of electrons by nonmagnetic impurities, and by magnetic impurities without taking into account the interaction between them, is elastic. Thermal equilibrium in the electron system is established relatively slowly as a result of their interaction with phonons. The relaxation time for the relaxation of energy via the interacting impurities is in order of magnitude equal to $T\tau_S/nV_0$ for $\beta nV_0 \ll 1$. At low temperatures and for a sufficiently high impurity concentration this relaxation time can be much lower than the phonon relaxation time. We note that under these conditions the time for the establishment of thermal equilibrium between electrons and phonons is increased. It becomes proportional to the total specific heat of the electrons and the impurities.

We discuss the approximations made above. One of them consists of the fact that the Kittel-Ruderman Hamiltonian was considered independently of the exchange interaction of spins with the conduction electrons. In our case such an approximation is valid since the exchange Hamiltonian was utilized for the evaluation of the kinetic quantities determined by the electrons in the narrow range $\sim T$ near the Fermi-limit. These electrons make a small contribution to the Kittel-Ruderman interaction which is determined by electrons in the energy interval $v_F(T/V_0)^{1/3} \gg T$. For the same reason we did not take into account the dependence of the interaction on the magnetic field, on the temperature and on the electron mean free path.

Both in the evaluation of the kinetic effects and in the derivation of the Kittel-Ruderman Hamiltonian the interaction of the impurities with the electrons was taken into account in the Born approximation. Usually the exchange interaction is weak. However, the corrections to the Born amplitude for the scattering of thermal electrons increase with decreasing temperature as $\ln(\epsilon_F/T)$ (Kondo effect). The non-Born corrections to the Kittel-Ruderman interaction turn out to be smaller and are of two types. The first of these are not described by the exchange of a single electron-hole pair and lead to an interaction which falls off with distance faster than R^{-3}. At significant distances the contribution of these corrections is negligibly small. For analogous reasons one can also neglect the non-pair exchange interaction between impurities. Corrections of the other type are associated only with the scattering amplitude becoming more complicated in deriving the expression for the Hamiltonian for the indirect exchange. Taking these corrections into account one can in formula (5) replace with logarithmic accuracy V_0 by the effective value V. The corresponding Kondo logarithms are equal to $\ln p_0R$. For significant values of $R \sim (V_0/T)^{1/3}$ these logarithms are smaller than the logarithms $\ln(\epsilon_F/T)$ mentioned above in the corrections to the amplitude for the scattering of thermal electrons.

When the corrections to the Born amplitude are not small the results obtained above are applicable with logarithmic accuracy if we replace the parameters I and V_0 by effective quantities which vary slowly with the temperature. The new parameters will no longer be related by equation (23) in view of the difference in the corresponding logarithms mentioned above. The logarithmically accurate results are applicable at all temperatures if $I < 0$. But if $I > 0$, then the results for the kinetic coefficients and for the temperature of the superconducting transition are applicable only for $T > T_K$ (T_K is the Kondo temperature). The results for the contribution of the impurities to the thermodynamic quantities are also applicable for lower temperatures $T > V_0(T_K/v_F)^3$.

We discuss the behavior of the virial additions to the different quantities in the limiting case of large spins $S \gg 1$. One should regard βnV_0S^2 as the expansion parameter in this case, but, as can be seen from the results obtained above, in the susceptibility, conductivity and the temperature of transition into the superconducting state the leading terms in S cancel. The virial corrections to the shape of the EPR line, like the corrections to the specific heat, remain finite in the classical limit ($S \to \infty$, $S^2V_0 \to$ const).

The virial expansion is not applicable to the study of the domain of low temperatures $T \lesssim nV_0$. One can only assert that the dependence on the concentration, just as in the case of the thermodynamic quantities, is determined by some functions of the parameter nV_0/T. For example, the resistance can be expressed in terms of an unknown function of one parameter $\rho(T) - \rho(0) = n\varphi(nV_0/T)$, while the shape of the paramagnetic resonance line is expressed in terms of the function of two parameters $\chi'' = \chi''(nV_0/T, \omega\tau)$. Formulas (26) and (44) yield the first terms in the expansions of these functions in series in terms of the parameter nV_0/T. The coefficients in this high temperature expansion are found without additional unjustified assumptions. Therefore, in addition to their independent interest, these results are useful for checking the different approximate theories which lay claim to describing phenomena at arbitrary temperatures.

The inapplicability of the method of the self-consistent field was discussed in[1]. Particularly clearly the inapplicability of this method can be seen in the example of impurity EPR. As could be seen from section 4, the resonance frequency does not depend on the impurity concentration. But in the theory of the self-consistent field such a dependence arises. Another widely used method proposed by Marshall, Klein and Brout[5] has been developed and is applied only to the Ising model. But even in this model such a method gives an incorrect high temperature expansion. In particular, in reference[6] a nonzero high temperature correction to the susceptibility is obtained. In actual fact the high temperature expansion for the susceptibility of impurities interacting according to Ising is given by the formula

$$\chi=\frac{N\mu^2}{2T}\left\{1-n\int d\mathbf{R}\,\mathrm{th}\frac{V}{T}\right\}. \tag{47}$$

The integral appearing on the right hand side is equal to zero since in the integrand we have the odd function $\cos 2p_0R$, and the term quadratic in the concentration does not appear in the susceptibility. Thus, the method mentioned above leads to an incorrect result in the high temperature limit, and therefore its applicability appears to be doubtful also at low temperatures.

For comparison with experiment it is useful to keep in mind the fact that only one adjustable parameter V_0 enters into the virial corrections to the different quantities. With the aid of relations (23), (32), (33) this parameter can also be estimated from the width of the EPR line and the decrease in T_c. For the Cu(Mn) alloy one can obtain from the data of[7] the values of the parameter $V_0 = 5\times10^{-36}$ erg cm^3 both from the data on the susceptibility and also from the measurements of the magnetic moment in a strong field. For other substances the nature of the dependences qualitatively coincides with the one described in the present paper and in[1]. The data on the susceptibility give, for example, $V_0 = 2.2\times10^{-37}$ erg cm^3 for Au(Mn) and $V_0 = 1.3\times10^{-36}$ erg cm^3 for Au(Cr). However, for a detailed quantitative comparison between theory and experiment it would be useful to know the results of measurements of different physical quantities on the same samples and to verify whether the values of the parameter V_0 obtained from different experiments coincide.

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APPENDIX

We express the coefficients $A_{JJ'}$ and $B_{JJ'}$ in terms of the 6j-symbols. We consider an expression of the form

$$\sum_{i=1,2}\langle JM|\mathbf{S}_iP_{J'}\hat{f}_{kq}\mathbf{S}_i|JM\rangle=C_{JJ'}\langle JM|\hat{f}_{kq}|JM\rangle,$$

where the operator $\hat{f}_{kq}$ is a tensor of the k-th rank with the spherical component q and conserves the total angular momentum of the two impurities. Writing $\mathbf{S}_i\,\mathbf{S}_i$ in terms of the spherical components and expressing the matrix elements of the tensors in terms of the 3j-symbols, we obtain

$$C_{JJ'}i^k(-1)^{J-M}\begin{pmatrix} J & k & J\\ -M & q & M\end{pmatrix}\langle J|\hat{f}_k|J\rangle$$
$$=\sum_i\sum_{mM'M''}i^{2+k}(-1)^{J'-M-M'-M''+1-m},$$
$$\times\begin{pmatrix} J & 1 & J'\\ -M & -m & M'\end{pmatrix}\begin{pmatrix} J' & k & J'\\ -M' & q & M'\end{pmatrix}\begin{pmatrix} J' & 1 & J\\ -M'' & m & M\end{pmatrix}|\langle JS|S_i|J'S\rangle|^2$$
$$\times\langle J'|\hat{f}_k|J'\rangle.$$

Utilizing the relation between the 3j- and the 6j-symbols (formula (108.4) in[8]) and the symmetry properties of the 3j-symbol we have

$$C_{JJ'}=(-1)^{J+J'+k+1}\frac{\langle J'|\hat{f}_k|J'\rangle}{\langle J|\hat{f}_k|J\rangle}\begin{Bmatrix} J & 1 & J\\ J' & 1 & J'\end{Bmatrix}$$
$$\times\sum_i|\langle JS|S_i|J'S\rangle|^2.$$

We must now express the matrix element of S_i involving functions of two spins in terms of the single spin matrix element

$$C_{JJ'}=(-1)^{J+J'+k+1}\frac{\langle J'|\hat{f}_k|J'\rangle}{\langle J|\hat{f}_k|J\rangle}|\langle S|S|S\rangle|^2$$
$$\times\begin{Bmatrix} J & k & J\\ J' & 1 & J'\end{Bmatrix}\begin{Bmatrix} S & J & S\\ J' & S & 1\end{Bmatrix}^2 2(2J+1)(2J'+1). \tag{A.1}$$

In order to evaluate $A_{JJ'}$ we must set $\hat{f} = 1/2$, and for $B_{JJ'}$ we must set $\hat{f} = \mathbf{J}/2$. Evaluating now the irreducible matrix elements and substituting them into (A.1) we obtain finally

$$A_{JJ'}=(2J+1)(2J'+1)\left(\frac{2J'+1}{2J+1}\right)^{1/2}S(S+1)(2S+1)$$
$$\times\left|\begin{Bmatrix} 0 & J & J'\\ 1 & J' & J\end{Bmatrix}\right|\begin{Bmatrix} S & S & J\\ 1 & J' & S\end{Bmatrix}^2, \tag{A.2}$$

$$B_{JJ'}=(2J+1)(2J'+1)\left[\frac{J'(J'+1)(2J'+1)}{J(J+1)(2J+1)}\right]^{1/2}S(S+1)(2S+1)$$
$$\times\left|\begin{Bmatrix} 1 & J & J'\\ 1 & J' & J\end{Bmatrix}\right|\begin{Bmatrix} S & S & J\\ 1 & J' & S\end{Bmatrix}^2. \tag{A.3}$$

In the last formulas the 6j-symbols are reduced to the form convenient for utilizing table 10 from[8]. The sign of the 6j-symbol is exactly compensated by the phase factor in formula (A.1), thereby guaranteeing the positive nature of $A_{JJ'}$ and $B_{JJ'}$.

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[1] A. I. Larkin and D. E. Khmel'nitskiĭ, Zh. Eksp. Teor. Fiz. 58, 1789 (1970) [Sov. Phys.-JETP 31, 958 (1970)].

[2] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

[3] M. T. Beal-Monod, Phys. Rev. 178, 874 (1964).

[4] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 1782 (1960) [Sov. Phys.-JETP 12, 1243 (1961)].

[5] W. Marchall, Phys. Rev. 118, 1519 (1960). M. W. Klein and R. Brout, Phys. Rev. 132, 2412 (1963).

[6] M. W. Klein, Phys. Rev. 173, 552 (1968).

[7] J. Souletie and R. Tournier, J. Low Temp. Phys. 1, 95 (1969).

[8] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963, p. 468 [Addison-Wesley, 1965].

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