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Thermodynamic and Kinetic Properties of Dilute Ferromagnetic Alloys

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The effect of fluctuations in the distribution of impurities on the thermodynamic and kinetic properties of dilute ferromagnetic alloys at temperatures much less than and much greater than the ordering temperature T_c is investigated. It is assumed that the interaction between the impurities falls off exponentially with distance. Owing to the presence of fluctuations in which the molecular-field energy is less than T_c, in impurity ferromagnets the contribution of local impurity spin flips to the thermodynamic and kinetic quantities for $T \ll T_c$ is much greater, and falls off with temperature much more slowly, than in ordered ferromagnets, and may compete with the spin-wave contribution. For $T \gg T_c$, the interaction in pairs of closely spaced impurities causes a slow decrease of the corrections to the thermodynamic and kinetic quantities with increasing temperature. The results of the theory agree well with the experimental data on dilute PdFe alloys.

1. INTRODUCTION

At the present time, a number of paramagnetic metals (Pd, Pt) are known which become ferromagnetic at small concentrations of the magnetic impurities (Fe, Co, Mn)[1]. If the impurity distribution is random, as it is natural to assume when their concentration is small, the ferromagnetic character of the ordering is evidence that their exchange interaction potential has positive sign. The low-temperature properties of an ordered ferromagnet are determined by the spin waves, since a local spin flip requires energy of the order of the Curie temperature T_c. In an impurity ferromagnet, the situation, generally speaking, is different. As a consequence of the random impurity distribution, fluctuations of the molecular field occur. At an impurity separated from its neighbors by a distance greater than the average, the acting molecular field H is less than the molecular field H_c at impurities spaced at the average distance apart. Even at low temperatures, a spin flip is possible for such isolated impurities.

The molecular-field distribution function W(H), which is the probability density that the value of the molecular field lies in the interval (H, H + dH), is proportional, for $H \ll H_c$, to the probability of fluctuations in which one of the impurities is separated from the others by a distance greater than the average. Since the potential is of constant sign, W(H) decreases with H and tends to zero as $H \to 0$. On the other hand, the contribution of an impurity at which the molecular field $H > T/\mu_e$ (μ_e is the effective magneton) to the thermodynamic quantities is proportional to $\exp(-\mu_e H/T)$ and increases with decreasing H. Therefore, the main contribution, proportional to $\exp[-\mu_e H_{opt}(T)/T]$, is given by impurities situated in a certain optimal field $H_{opt} \ll H_c$, which is determined by the form of the function W(H) (i.e., the potential) and by the temperature. The contribution of impurities with the average spacing is proportional to $\exp(-\mu_e H_c/T)$ and is therefore small, despite the fact that there are many of them. Thus, in an impurity ferromagnet at temperatures that are not too low, but small compared with T_c, and at low impurity concentrations, along with the spin waves local excitations with an impurity-spin flip may also be important. Fluctuations in the distribution of impurities are also important at high temperatures $T \gg T_c$, since there are pairs of closely spaced impurities whose interaction energy $V(r) \gtrsim T$.

The effect of fluctuations in the impurity distribution on thermodynamic and kinetic phenomena in impurity ferromagnets is considered in the present paper. We assume that the exchange interaction of the impurities is described by the Heisenberg Hamiltonian

$$\mathscr{H} = -\frac{1}{2}\sum_{ij} V(\mathbf{r}_{ij})\mathbf{S}_i\mathbf{S}_j, \tag{1}$$

where $\mathbf{S}_i$ is a spin localized at the point $\mathbf{r}_i$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and

$$V(\mathbf{r}) = V_0 e^{-r/R}. \tag{2}$$

Such an interaction potential, of constant sign, describes well the properties of PdFe alloys in a wide range of Fe impurity concentrations. This follows both from theoretical considerations[2], and from the analysis of the concentration dependence of the Curie temperature $T_c \approx \mu_e H_c$ in this alloy carried out in Sec. 6 of this article. The distribution function W(H) has been determined by a method which is well-known from the theory of random walks[3] and which has been applied by Klein and Brout[4] to the Ising model with a potential of alternating sign. By means of this function, the magnetization, specific heat and kinetic coefficients have been calculated. The principal temperature and concentration dependences of these quantities are determined by the factor $\exp[-\nu \ln^3(SV_0/T)]$. Here, $\nu = 4\pi nR^3/3$ is the average number of impurities in the interaction radius R; n is the concentration of impurities. We shall assume that $\nu \ll 1$. In all the quantities considered, except the magnetization, there are also pre-exponential factors, which are large in the most interesting cases and increase with increasing ν and decreasing T.

An analysis of the experimental data on the alloy PdFe for $T \ll T_c$ confirms the conclusion that the contribution of local spin flips to the thermodynamic and kinetic quantities may compete with the corresponding contribution of the spin waves. It has been found that, at iron concentrations with c < 1%, the local impurity-spin flips determine the magnetic part of the specific heat and, apparently, give a contribution to the resistance comparable with that of the spin waves.$^{1)}$

The thermodynamic and kinetic properties for $T \gg T_c$ can be investigated by means of the virial expansion in powers of the impurity concentration.[6] The specific heat, the temperature-dependent part of the resistance and other phenomena absent in an ordered ferromagnet are connected with the system of magnetic levels of pairs of closely spaced impurities. These same pairs give the main contribution to the concentration correction to the Curie law for the susceptibility. For the interaction (2) treated in the present article, the correction to the susceptibility proportional to n^2 depends on the temperature, for $T \ll V_0$, according to the law $\ln^3(V_0/T)$, i.e., the Curie-Weiss law does not hold.

2. THE MOLECULAR-FIELD DISTRIBUTION FUNCTION

We shall consider the temperature region $T \ll T_c$. In the molecular-field approximation, in place of (1) we have

$$\mathcal{H} = {}^1\!/_2\mu_e \sum_i \mathbf{H}_i\langle \mathbf{S}_i\rangle - \mu_e \sum_i \mathbf{H}_i\mathbf{S}_i, \tag{3}$$

where the molecular field is

$$\mathbf{H}_i = \mu_e^{-1} \sum_j V(\mathbf{r}_i - \mathbf{r}_j)\langle \mathbf{S}_j\rangle, \tag{4}$$

and $\langle S_j\rangle$ is the average spin. In going from (1) to (3), we have discarded thermodynamic fluctuations of the spins, which, as is well-known, lead to spin waves. It follows from (3) that the free energy of the impurities (the z-axis is the magnetization direction) is

$$\begin{gathered} F = \frac{1}{2}\mu_e \sum_i H_i\langle S_i^z\rangle + \sum_i F_i, \\ F_i = -T\ln\frac{\operatorname{sh}[(S+{}^1\!/_2)\mu_e H_i/T]}{\operatorname{sh}(\mu_e H_i/T)}. \end{gathered} \tag{5}$$

From the condition that the free energy be a minimum with respect to the distribution of molecular fields, $\partial F/\partial H_i = 0$, it follows that the magnetization is

$$M = \mu_e \sum_i B_S\left(\frac{H_i}{T}\right), \tag{6}$$

where $B_S(H/T)$ is the Brillouin function, and the specific heat of the magnetic system is

$$\begin{aligned} C_M = \sum_i C_i(H_i) = \sum_i \left(\frac{\mu_e H_i}{T}\right)^2 \bigg\{ \frac{1}{4}\operatorname{sh}^{-2}\frac{\mu_e H_i}{2T} \\ - \left(S+\frac{1}{2}\right)^2 \operatorname{sh}^{-2}\left[\left(S+\frac{1}{2}\right)\frac{\mu_e H_i}{T}\right]\bigg\}. \end{aligned} \tag{7}$$

Replacing the summation over the sites by averaging over the values of the molecular field H with the distribution function W(H), we obtain for the specific heat and the magnetization per unit volume

$$M = n\mu_e \int_0^\infty W(H) B_S\left(\frac{H}{T}\right) dH, \tag{8}$$

$$C_M = n\int_0^\infty W(H)C(H)\,dH. \tag{8a}$$

According to[3], the distribution function, normalized to unity, has the form

$$W(H) = \frac{1}{v^N}\int \delta\Big(H - \frac{1}{\mu_e}\sum_{j=1}^N V(\mathbf{r}_{ij})S\Big) d^3r_1\ldots d^3r_N, \tag{9}$$

where N is the total number of impurities and v is the volume of the system. In the right-hand side of (9), $\langle S_j\rangle$ has been replaced by S, since for $T \ll T_c$ most of the spins are almost completely saturated. By making use of the integral representation of the δ-function, we obtain

$$\begin{aligned} W(H) &= \frac{1}{2\pi v^N}\int_{-\infty}^{\infty} d\rho \int \exp\Big\{-i\rho\Big(H - \frac{1}{\mu_e}\sum_{j=1}^N V(r_j)S\Big)\Big\}\, d^3r_1\ldots d^3r_N \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\rho\, e^{-iH\rho}\left[\frac{1}{v}\int d^3r \exp\left(\frac{iV(r)S\rho}{\mu_e}\right)\right]^N. \end{aligned}$$

In the limit $N \to \infty$, $N/v = \text{const}$, we have

$$W(H) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\rho\, e^{-iH\rho - D(\rho)}, \tag{10}$$

$$D(\rho) = n\int d^3r\left(1 - \exp\left(\frac{iV(r)S\rho}{\mu_e}\right)\right).$$

Substituting into this the expression for the potential and integrating by parts, we obtain

$$D(\rho) = \frac{i\nu S V_0 \rho}{\mu_e}\int_0^1 dx \ln^3 x \exp\left(\frac{i\rho V_0 S x}{\mu_e}\right). \tag{11}$$

To calculate averages by means of the function W(H), its explicit form, as we shall see in the next Section, will not be required. It is sufficient to know its Fourier transform, i.e., the function $e^{-D(\rho)}$. But in order to make the following results more visualizable, it is useful to study the properties of the function W(H) in detail. We shall give a simple estimate for W(H) for

$$H \ll H_c = \frac{V_0 S}{\mu_e}\exp\left\{-\frac{r_c}{R}\right\},$$

where $r_c \approx n^{-1/3}$. Since the molecular field has the same direction at each impurity, in order that the molecular field at a given impurity not exceed H it is necessary (but not sufficient) that there be no other impurities at a distance $r = R\ln(V_0S/\mu_e H) \gg r_c$ from it. Therefore, using the nearest-neighbor distribution function $w(r) = 4\pi r^2\exp(-4\pi n r^3/3)$[3], we have

$$W(H) < \frac{1}{H}3\nu\ln^2\frac{V_0S}{\mu_e H}\exp\left(-\nu\ln^3\frac{V_0S}{\mu_e H}\right). \tag{12}$$

From (12) follows the obvious result W(0) = 0, which is true for any finite extended potential V(r) of constant sign. The function W(H) for fields greater than H_c but smaller than $\mu_e^{-1}V_0S$ can be calculated by expanding the integrand function in (10) in powers of $D(\rho)$:

$$W(H) = \frac{3\nu}{H}\ln^2\frac{V_0S}{\mu_e H} - \frac{3\nu^2}{H}\ln^5\frac{V_0S}{\mu_e H} + \ldots. \tag{13}$$

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[1] In the paper by Kitchens and Trousdale[5], the Mössbauer effect was investigated for $T < T_c$ in the framework of a fluctuating-molecular-field model. The authors of this paper assumed that $\nu \gg 1$ and, consequently, W(H) has a Gaussian form. Since the value of R in PdFe is close to the lattice constant (cf. See 6), this inequality cannot be fulfilled. Besides, at large impurity concentrations, the temperature dependence of the magnetization is determined not by fluctuations of the molecular field, but by the spin waves.

As can be seen from (13), the expansion is taken in powers of the parameter $\nu \ln^3(V_0S/\mu_e H)$, i.e., it is valid for $H_c \ll H \ll \mu_e^{-1} SV_0$. With increasing H, the function W(H) in this region of the fields falls off slowly. It is clear that the maximum of W(H) is attained at $H \approx H_c$.

The relation (13) is, essentially, an expansion in powers of the concentration. The first two terms in (13) can be interpreted as the contribution to the molecular field from interactions with one and two nearest neighbors, separated from the impurity with molecular field H by a distance considerably less than the average distance between the impurities. By means of the virial expansion, we obtain, for example, the first term $W_1(H)$ in (13). In order that the value of the molecular field lie in the interval from H to H + dH, it is necessary that the distance between the impurities in the pair lie between $r = R \ln(V_0S/\mu_e H)$ (at these r, the energy $V(r)S = \mu_e H$) and $r + dr = r - R\,dH/H$. The quantity $W_1(H)dH$ is equal to twice the number of such pairs, i.e.,

$$W_1(H) = 4\pi n r^2 |dr/dH| = \frac{3\nu}{H} \ln^2 \frac{V_0 S}{\mu_e H}.$$

Since the potential (2) is bounded, the field $\mu_e H > V_0 S$ is created by a large number of closely spaced impurities (we neglect correlation in the distribution of impurities). Therefore, for such fields, the virial expansion is inapplicable. We shall show that, for $\mu_e H > V_0S$, the function W(H) falls off more rapidly than any power of H. For this, we calculate the moments of the function W(H)

$$\overline{H^m} = \int_0^\infty H^m W(H)\,dH, \quad m = 1, 2 \ldots .$$

Substituting W(H) from (10) into this, we represent $\overline{H^m}$ in the form

$$\overline{H^m} = \frac{i^m}{2\pi} \int_0^\infty dH \int_{-\infty}^\infty d\rho\, e^{-D(\rho)} \frac{d^m}{d\rho^m} e^{-i\rho H} d\rho.$$

Integrating by parts m times, and using the fact that $D(\rho) \to \infty$ as $\rho \to \infty$, we obtain

$$\overline{H^m} = (-i)^m \frac{d^m}{d\rho^m} e^{-D(\rho)} \Big|_{\rho=0}.$$

Carrying out the differentiation to terms of first order in ν, we find, finally,

$$\overline{H^m} = \frac{6\nu}{m^3} \left(\frac{V_0 S}{\mu_e} \right)^m. \tag{14}$$

The existence of all the moments proves the assertion made above. It can be seen from (14) that the main contribution to all the moments is made by impurities at which the molecular field is of order $\mu_e^{-1} V_0 S$. Such fields are created by fluctuations consisting of pairs with distance between impurities of order R. The probability of these fluctuations is of order ν. The large contribution of such fluctuations is connected with the slow falling off of the distribution function W(H) at large fields $H_c < H < V_0S$.

3. THE MAGNETIZATION AND SPECIFIC HEAT AT LOW TEMPERATURES

According to (8), the average spin per impurity is

$$\sigma = \int_0^\infty W(H) \left[\left(S + \frac{1}{2}\right) \operatorname{cth} \left(S + \frac{1}{2}\right) \frac{\mu_e H}{T} - \frac{1}{2} \operatorname{cth} \frac{\mu_e H}{2T} \right] dH. \tag{15}$$

We shall consider the integral

$$A_\gamma = \gamma \int \left(\operatorname{cth} \frac{\gamma \mu_e H}{T} - 1 \right) W(H)\,dH, \quad \gamma > 0. \tag{16}$$

We represent $\coth(\gamma\mu_e H/T)$ in the form of a series in powers of $\exp(-2\gamma\mu_e H/T)$. The calculation of A_γ is reduced to the calculation of integrals of the type

$$\Phi(\alpha) = \int_0^\infty e^{-\alpha H} W(H)\,dH.$$

It can be seen from (10) that the Fourier component of the function W(H) is $e^{-D(\rho)}$. Using the connection between the Fourier component of a function and its Lapla Laplace transform, and taking into account that W(−H) = 0, we obtain

$$\Phi(\alpha) = e^{-D(i\alpha)}.$$

Thus,

$$A_\gamma = \gamma \sum_{k=1}^\infty \exp\left[-D\left(\frac{2ik\mu_e\gamma}{T} \right) \right]. \tag{17}$$

According to (11),

$$D\left(\frac{ik\gamma\mu_e}{T}\right) = -\frac{\nu V_0 S k\gamma}{T} \int_0^1 dx \ln^3 x \exp\left(-\frac{\gamma V_0 S k x}{T} \right).$$

To within the exponentially small terms $\exp(-V_0S/T)$, in this integral we can replace the upper limit by ∞. We then obtain

$$D\left(\frac{ik\gamma\mu_e}{T}\right) = \nu f\left(k \frac{\gamma S V_0}{T}\right). \tag{18}$$

Here, the function

$$f(x) = \ln^3 x + 3C \ln^2 x + (3C^2 + \pi^2/2) \ln x + C(C^2 + \pi^2/2) - \psi''(1), \tag{19}$$

where C is Euler's constant, and ψ is the logarithmic derivative of the gamma function. Since $\sigma = S + A_{S+1/2} - A_{1/2}$, we have, according to (17) and (18),

$$\sigma = S + \left(S + \frac{1}{2}\right) \sum_{k=1}^\infty \exp\left\{ -\nu f\left(\frac{(2S+1) V_0 S k}{T} \right) \right\} - \frac{1}{2} \sum_{k=1}^\infty \exp\left\{ -\nu f\left(\frac{S V_0 k}{T} \right) \right\}. \tag{20}$$

From the condition $\delta\sigma \equiv S - \sigma \ll 1$, which was used in deriving the distribution function W(H), it follows that the relation (20) is valid for low temperatures satisfying the inequality $\nu \ln^3(SV_0/T) \gg 1$. On the other hand, as will be seen from Sec. 5, the high-temperature virial expansions are applicable for $\nu \ln^3(V_0S/T) \ll 1$. Therefore, we should expect that a phase transition occurs when $\nu \ln^3(V_0S/T) \approx 1$, i.e., at temperature $T_c \approx \mu_e H_c \sim \exp(-1/an^{1/3})$, where $a \approx R$. We note that earlier[8,9], the Curie temperature was incorrectly identified with the average energy of the spins in the molecular field, this energy being proportional to the impurity concentration (cf. (14)).

If[2)] $3\nu \ln^3(V_0S/T) > 1$, we can discard the first sum in formula (20) and retain only the term with k = 1 in the second sum. This means that the optimal molecular field $H_{opt} \gg T/\mu_e$. Then,

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[2)] The quantity $3\nu \ln^2(SV_0/T)$ has the meaning of the average number of impurities positioned in a layer of thickness R at a distance R $\ln(V_0S/T)$ from an impurity with molecular field $\mu_e H \approx T$.

$$\sigma = S - {}^{1}\!/\!{}_{2}\exp[-\nu f(SV_0/T)]. \tag{21}$$

It can be seen from (21), (19) and (12) that the temperature dependence of the magnetization is closely connected with the form of the distribution function W(H) for small molecular fields. At not too low temperatures, the magnitude of $\nu \ln^2(V_0S/T)$ in a sufficiently broad temperature range is of order unity and depends weakly on T. Since

$$\exp\left(-\nu\ln^3\frac{V_0S}{T}\right) \equiv \left(\frac{T}{V_0S}\right)^{\nu\ln^2(V_0S/T)},$$

the temperature dependence of σ can be described in this case by a power function with exponent close to unity. If $3\nu\ln^2(V_0S/T) \ll 1$, but $\nu\ln^3(V_0S/T) \gg 1$ as before, then many terms in the sums in (20) make a contribution. Going over from the summation to integration over k, we find

$$\sigma = S - (S + {}^{1}\!/\!{}_{2})\exp\left\{-\nu\ln^3\left(\frac{SV_0}{T}\right)\right\}. \tag{22}$$

It is interesting that, in this region of temperature, $\delta\sigma$ falls off with temperature more slowly than linearly. Thus, the presence of fluctuations in which $H \ll H_c$ leads to the result that the contribution of the molecular field to $\delta\sigma$ in impurity ferromagnets is much greater and falls off with temperature much more slowly than in ordered ferromagnets. Moreover, in certain ranges of concentration and temperature, the magnitude of $\delta\sigma$, described by (20), falls off with temperature more slowly than indicated by the Bloch law.

We proceed to calculate the magnetic part of the specific heat. The integral in (8a) can be calculated similarly to the integral (15). We obtain

$$C_M = n\sum_{k=1}^{\infty}\frac{1}{k}\,\frac{d^2}{d\gamma^2}\,\exp\left[-\nu f\left(\frac{\gamma SV_0k}{T}\right)\right]\Bigg|_{\gamma=1} - n\sum_{k=1}\frac{(2S+1)^2}{k}\,\frac{d^2}{d\gamma^2}$$
$$\times\exp\left[-\nu f\left(\frac{\gamma SV_0k}{T}\right)\right]\Bigg|_{\gamma=2S+1}. \tag{23}$$

If $3\nu\ln^2(V_0S/T) > 1$, then the second sum in (23) can be discarded and we can confine ourselves to one term in the first sum. Then,

$$C_M = n\nu\left[f_1(1+\nu f_1) - 6\left(\ln\frac{SV_0}{T} + C\right)\right]\exp\left[-\nu f\left(\frac{SV_0}{T}\right)\right],$$
$$f_1 = 3\ln^2\frac{SV_0}{T} + 6C\ln\frac{SV_0}{T} + \frac{\pi^2}{2} + 3C^2. \tag{24}$$

We see that, in contrast to $\delta\sigma$, the specific heat contains an additional large pre-exponential factor, which increases with decreasing temperature. Therefore, the specific specific heat decreases with temperature more slowly than the magnetization. Consequently, the role of local impurity-spin flips turns out to be even more important in the specific heat than in the magnetization. The temperature dependence of the specific heat at different impurity concentrations, calculated from the formulas (24), is shown in Fig. 1.

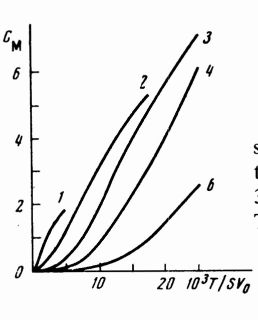

FIG. 1. Temperature dependence of the specific heat for different impurity concentrations: 1) $\nu = 10^{-2}$, 2) $\nu = 2 \times 10^{-2}$, 3) $\nu = 3 \times 10^{-2}$, 4) $\nu = 4 \times 10^{-2}$, 6) $\nu = 6 \times 10^{-2}$. The specific heat is in arbitrary units.

If $3\nu\ln^2(SV_0/T) \ll 1$, then the summation over k in (23) can be replaced by integration, and

$$C_M = 3n\nu\ln(2S+1)\ln^2\frac{SV_0}{T}\exp\left\{-\nu\ln^3\frac{SV_0}{T}\right\}. \tag{25}$$

Both the deviation of the average spin from saturation and the magnetic specific heat decrease rapidly with increasing impurity concentration. Therefore, at high concentrations, spin waves must play the principal role.

4. KINETIC PHENOMENA AT LOW TEMPERATURES

The kinetic phenomena in ferromagnetic metals below the transition point possess a number of features connected with the s-d interaction. These phenomena in ordered ferromagnets were investigated by Kasuya[7] within the framework of molecular-field theory. To calculate the kinetic coefficients in our case, we must average the probability of scattering of electrons by a localized spin, obtained by Kasuya[7], with W(H). We shall assume that the s-d-interaction constant I is small compared with the non-exchange interaction constant U. In this case, all the kinetic coefficients of interest to us are proportional to the s-d-scattering probability, i.e., we can average directly the expressions for the kinetic coefficients calculated by Kasuya[7] for a fixed value of the molecular field.

We shall confine ourselves in this section to temperatures for which $3\nu\ln^2(SV_0/T) > 1$. After averaging with W(H), which is performed analogously to the averaging of the thermodynamic quantities, we obtain for the resistivity ρ, the thermal e.m.f. α and the thermal conductivity κ:

$$\frac{\Delta\rho}{\rho_0} = \left(\frac{I}{U}\right)^2\int_0^\infty W(H)\left\{\langle S_z^2\rangle + 2\langle S_z\rangle\frac{\mu_eH}{T}\left[\exp\left(\frac{\mu_eH}{T}\right) - 1\right)^{-1}\right\}dH$$
$$= 6S\left(\frac{I}{U}\right)^2\nu\ln^2\frac{SV_0}{T}\exp\left[-\nu f\left(\frac{SV_0}{T}\right)\right], \tag{26}$$

$$\alpha = \frac{2}{e}\left(\frac{I}{U}\right)^3\int_0^\infty\langle S_z\rangle[S(S+1) - \langle S_z(S_z+1)\rangle]\left(\frac{\mu_eH}{T}\right)^2$$
$$\times\left[1 - \exp\left(-\frac{\mu_eH}{T}\right)\right]^{-1}W(H)\,dH$$
$$= \frac{6S^2}{e}\left(\frac{I}{U}\right)^3\nu\ln^2\frac{SV_0}{T}\left(1 + 3\nu\ln^2\frac{SV_0}{T}\right)\exp\left[-\nu f\left(\frac{SV_0}{T}\right)\right]$$

$$\frac{\Delta\varkappa}{\varkappa_0} = \frac{\Delta L}{L_0} - \frac{\Delta\rho}{\rho_0} = -2\left(\frac{I}{U}\right)^2\int\langle S_z\rangle\frac{\mu_eH}{T}\left[1 + \frac{1}{\pi^2}\left(\frac{\mu_eH}{T}\right)^2\right]$$
$$\times\exp\left(-\frac{\mu_eH}{T}\right)\left[1 - \exp\left(-\frac{\mu_eH}{T}\right)\right]^{-2}W(H)\,dH \tag{27}$$

$$= -6S\left(\frac{I}{U}\right)^2\nu\ln^2\frac{SV_0}{T}\left[1 + \frac{1}{\pi^2}\left(1 + 3\nu\ln^2\frac{SV_0}{T}\right)\right.$$
$$\left.\times\left(2 + 3\nu\ln^2\frac{SV_0}{T}\right)\right]\exp\left[-\nu f\left(\frac{SV_0}{T}\right)\right]; \tag{28}$$

where ρ_0 and κ_0 are respectively the resistivity and thermal conductivity associated with the non-exchange scattering of electrons by impurities, $\Delta\rho = \rho - \rho_0$, $\Delta\kappa = \kappa - \kappa_0$, L is the Lorentz number, L_0 is the Sommerfeld value of L, and $\Delta L = L - L_0$. As can be seen from formulas (26)—(28), all the calculated kinetic coefficients decrease with temperature and with increasing impurity concentration more slowly than the magnetization, owing to the large pre-exponential factors. Thus, local impurity-spin flips are as important for the kinetic phenomena as for the thermodynamic properties of impurity ferromagnets.

5. HIGH TEMPERATURES. THE VIRIAL EXPANSION IN POWERS OF THE CONCENTRATION

Fluctuations in the distribution of impurities give rise to unusual properties of an impurity ferromagnet compared with an ordered ferromagnet, not only below the transition temperature, but also above it. At temperature $V_0 \gg T \gg \mu_e H_c \approx T_c$, the main role is played by pairs of impurities, whose interaction energy $V(r) \gtrsim T$. The distance between impurities in such pairs is

$$r(T) \lesssim R \ln\frac{V_0}{T}, \quad R \ll r(T) \ll r_c,$$

and their number is of order $\nu \ln^3(V_0/T) \ll 1$. The system of magnetic levels in these pairs affects the thermodynamic and kinetic properties of the impurity ferromagnet. In the work of Larkin, Mel'nikov and Khmel'nitskiĭ[6], a virial-expansion method has been developed for magnetic impurities in metals, when the Rudermann-Kittel-Kasuya-Yosida (RKKY) indirect exchange gives rise to an interaction between impurities, oscillating with distance. This method is also completely applicable in the present case of the positive potential (2).

According to[6], the first virial correction to the free energy per unit volume is

$$F = -T\frac{n^2}{2}\int d^3r\varphi\left(\frac{V(r)}{2T}, \frac{\mu_e h}{T}\right),$$

$$\varphi(y, z) = \ln\sum_{j=0}^{2S}\frac{\operatorname{sh} z(j+{}^1\!/_2)}{\operatorname{sh}(z/2)}\exp\left\{y\left[S(S+1)-\frac{1}{2}j(j+1)\right]\right\} - 2\ln\frac{\operatorname{sh} z(S+{}^1\!/_2)}{\operatorname{sh}(z/2)} \tag{29}$$

where h is the external magnetic field. For the correction to the magnetic susceptibility due to the interaction of the impurities, it follows from (29) and (2) that

$$\Delta\chi = -3\nu\chi_0\int_0^{V_0/2T}\frac{dx}{x}\ln^2\frac{xT}{V_0} \tag{30}$$

$$\times\left\{1-\sum_{j=0}^{2S}j(j+1)(2j+1)\exp(x\varepsilon_j)/2S(S+1)\sum_j(2j+1)\exp(x\varepsilon_j)\right\},$$

where $\epsilon_j = {}^1\!/_2 j(j+1)$, and $\chi_0 = n\mu_e^2 S(S+1)/3T$. If $T \ll V_0/2$, then, integrating by parts and confining ourselves to the leading term in $\ln(V_0/T)$, we obtain

$$\Delta\chi = \frac{S}{S+1}\chi_0\nu\ln^3\frac{V_0}{T} \tag{31}$$

This correction is small when $\nu\ln^3(V_0/T) \ll 1$, as it should be. The physical nature of the result (31) lies in the following. Two non-interacting impurities with spin S make a contribution proportional to 2S(S + 1) to the susceptibility. If there is ferromagnetic interaction between the impurities, and the first excited level of the pair differs from the ground level by an amount of order T or greater, then this pair gives the same contribution to the magnetic susceptibility as one impurity with spin 2S. It is proportional to 2S(2S + 1). The number of pairs with interaction energy $V(r) \gtrsim T$ is of order $n^2R^3\ln^3(V_0/T)$. Therefore, $\Delta\chi \sim \nu n \ln^3(V_0/T)$. It is interesting that, according to (31), the temperature dependence of the susceptibility for $T_c \ll T \ll V_0/2$ differs from the Curie-Weiss law. The molecular-field method, within the framework of which this law is usually obtained, is not applicable here, because impurities whose interaction is important are spaced at distances much less than r_c. In the case of the RKKY interaction, the virial expansion leads to the antiferromagnetic Curie-Weiss law[6]. The negative sign of the correction in this case follows naturally from the alternating sign of the interaction and from the random distribution of the impurities, while the form of the temperature dependence is connected with the fact that $V_{RKKY} \sim r^{-3}$.

For $T \gg V_0/2$, we can expand the exponential in (30) in powers of x. Then

$$\Delta\chi = S(S+1)\chi_0\nu V_0/T. \tag{32}$$

Formula (32), in contrast to (31), gives a Curie-Weiss law for the magnetic susceptibility, with constant $\theta = S(S+1)\nu V_0$. This difference is explained by the fact that, for $T \gg V_0$, the main contribution at all temperatures is given by pairs with distance between the impurities of order R. We note that the paramagnetic Curie-Weiss temperature θ, unlike the transition temperature T_c, is proportional to the impurity concentration. For the magnetic part of the specific heat per unit volume, it follows from (29) that

$$C_M = \frac{3}{16}\nu n\int_0^{V_0/2T}dx\,x\ln^2\frac{xT}{V_0}\sum_{jj'}\exp[x(\varepsilon_j+\varepsilon_{j'})](2j+1)(2j'+1)$$

$$\times(j-j')^2(j+j'+1)^2\left[\sum_{j''}(2j''+1)\exp(x\varepsilon_{j''})\right]^{-2}. \tag{33}$$

For $T \ll V_0$, to within terms of order $\ln^{-1}(V_0/T)$, we obtain

$$C_M = {}^3\!/_2 A\nu n\ln^2(V_0/T). \tag{34}$$

For $S = {}^1\!/_2$, the quantity $A = \ln(4/3)$. For large S, the factor A does not depend on S and is of order unity.

It is not difficult to understand why the specific heat is of order $\nu\ln^2(V_0/T)$. Impurity pairs whose interaction energy does not differ too much from T give a contribution to the specific heat. The distance between such impurities can differ from $R\ln(V_0/T)$ by not more than the order of magnitude of R; therefore, the number of such pairs is of order $\nu n\ln^2(V_0/T)$. The corrections to all quantities due to transitions between levels have the same temperature dependence (cf., e.g., the correction to the Lorentz number (37) below). For $T \gg V_0$, the specific heat $C_M \sim n\nu(V_0/T)^2$. It can be seen from (24) and (34) that the specific heat has a maximum at a certain temperature of order T_c.

We shall examine the effect of interaction between the impurities on the kinetic phenomena. We shall assume the interaction between the electrons and the impurities to be a point interaction. Then the scattering cross-section does not depend on the scattering angle, so that we can introduce a relaxation time into the kinetic equation. By making use of the expression for the impurity-spin correlator from[6], we obtain for the relaxation time associated with the presence of pairs, for $S = {}^1\!/_2$,

$$\tau^{-1}(\varepsilon)=\frac{9}{4\pi^2}n\nu I^2(2m^3\varepsilon)^{1/2}\int_0^{V_0/2T}\frac{dx}{x}\ln^2\frac{Tx}{V_0}$$

$$\times\left\{\frac{1+e^x}{1+3e^x}\frac{f_0(\xi+x)f_0(\xi-x)}{f_0^2(\xi)}-\frac{1}{2}\right\}, \tag{35}$$

where ϵ is the electron energy, $\xi = (\epsilon - \epsilon_F)/T$, and $f_0(\xi)$ is the Fermi function. Since the scattering described by the relaxation time (35) is inelastic, it leads to a deviation of the Lorentz number from the Sommerfeld value. The virial corrections to the resistivity and Lorentz number have the form (for $T < V_0/2$)

$$\frac{\Delta\rho}{\rho}=-\frac{3}{16\pi}\nu\left(\frac{I}{U}\right)^2\ln^3\frac{V_0}{T}, \tag{36}$$

$$\frac{\Delta L}{L}=\frac{3}{8\pi}\left[1+\frac{2}{\pi^2}{}_1F_1\left(-\frac{1}{3},3,1\right)\right]\nu\left(\frac{I}{U}\right)^2\ln^2\frac{V_0}{T}. \tag{37}$$

Here, ${}_1F_1$ is the confluent hypergeometric function. The interaction of the impurities makes an impurity-spin flip in the scattering more difficult. Therefore, the correction (36) to the resistivity is negative. With increase of temperature, the role of the interaction is decreased, so that, in an impurity ferromagnet, the magnetic part of the resistivity increases with temperature for $T \gg T \gg T_c$ also.

6. IMPURITY FERROMAGNETISM OF Pd ALLOYS

The theory developed above can be applied to explain the properties of dilute alloys of Pd with Fe and Co. The interaction of the impurity spins in Pd is realized by means of indirect exchange of d-band holes.[2] Because of the strong correlation in a narrow d-band, this interaction, apart from the usual part oscillating with the distance between the impurities, contains a positive part which falls off with distance according to the law $V(r) = r^{-1}e^{-r/R}$ and is greater than the oscillating part at not too great distances.[2] It is this ferromagnetic interaction which leads to the result that Pd alloys with magnetic impurities, unlike alloys of the CuMn type, go over into the ferromagnetic state at low temperatures. As already noted in Sec. 4, we should expect that, in the case of the potential (2), this transition should occur at temperatures satisfying the condition $\nu\ln^3(SV_0/T) \approx 1$, i.e., at temperatures of the order of the interaction energy of spins situated at distances of the order of the average distance from each other. In this case, the tr transition temperature T_c should depend on the impurity concentration like

$$\ln T_c = \ln V_c - 1/an^{1/3}, \tag{38}$$

where $V_c \approx zV_0$, z is the average number of impurities whose interaction energy with a given impurity is of order T_c, and $a \approx R$. In Fig. 2, we show the dependence of $\ln T_c$ on $n^{-1/3}$, constructed from the experimental data of Crangle and Scott[10], who determined T_c as the point at which the magnetization goes to zero. It can be seen that, in a wide range of concentrations, the dependence (38) is very well fulfilled with a = 4 Å and V_c = 900°K. The transition temperature T_c found by Williams and Loram[11] from the discontinuity in the electrical resistivity $\rho(T)$ also obeys (38), but with slightly different parameters V_c and a. The good agreement of (38) with experiment is evidence that the potential (2), which, for $r > R$, is close to $r^{-1}e^{-r/R}$ obtained in[2], correctly describes the interaction of iron impurities in Pd.

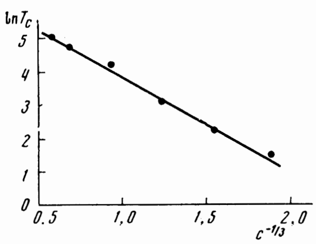

FIG. 2. Dependence of T_c on the impurity concentration c in %, according to the data of [10] for PdFe alloys.

In a number of papers[12,13], the magnetic part of the specific heat in PdFe alloys with Fe concentrations of 0.1% and higher has been measured. The magnetic part of the specific heat as a function of temperature displays a maximum at temperatures T_m close to T_c. At temperatures below T_m, the specific heat falls off rapidly with the temperature and decreases with increase of impurity concentration. These features in the dependence of the magnetic specific heat on temperature and concentration agree qualitatively with our theory. Detailed quantitative data[12,13] are given only for temperatures in the range 1.4–4.2°K. The temperature dependence of the magnetic part of the specific heat for samples with concentration $c > 1\%$, according to the experimental data[12,13], is well described by spin-wave theory in the indicated temperature range, and for $c < 1\%$ falls off more slowly than the spin-wave contribution, which is proportional to $T^{3/2}$. We have calculated the contribution of the molecular field to C_M by the formula (24). By selecting the parameters R and SV_0 (R = 2.5 Å and SV_0 = 170°K), we can match the calculated specific heat with the experimental specific heat[12] in the whole of the indicated temperature range for a sample with c = 0.72% (Fig. 3). In this case, $\nu = 3.1 \times 10^{-2}$. The value obtained for R is close to the R found from neutron measurements[14] (R ≈ 3 Å), and close to the value a = 4 Å found by means of Fig. 2. The magnitude of the parameter SV_0 agrees reasonably with the value of V_c/z, if we assume that z is of the order of several units. For c = 1.52%, the values of C_M at low temperatures, calculated with these parameters, are several times smaller than the experimental values, indicating, in accordance with[12], the important contribution of the spin waves. The increasing role of spin waves with increase of the concentration is connected with the fact that the specific heat (23) falls off almost exponentially with increase of ν. For c = 0.36%, formula (23) is applicable only for $T \leq 1.5$°K; it can be seen from Fig. 3 that, at this temperature, the calculated value of the specific heat is close to the experimental value. At yet lower concentrations, the region of applicability of formula (23) lies below 1.4°K. For a sample with c = 0.09%, the specific heat C_M, according

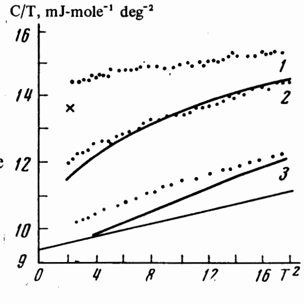

FIG. 3. Specific heat of PdFe. The points are the experimental results of [12] for samples with Fe concentrations c = 0.36% (1), c = 0.72% (2), c = 1.52% (3). The straight line is the measured specific heat of pure Pd. The curves are the calculated values of the specific heat; X is the calculated specific heat for c = 0.36% and T = 1.4°K.

to[12], in the interval 1.4–4.2°K lying above T_c, decreases with increasing T. This temperature dependence can be well described by the law $\ln^2(V_0/T)$ (cf. (34)).

The kinetic phenomena in PdFe alloys are determined by the s-electrons. The resistivity of PdFe samples for $T \ll T_c$ and with impurity concentration in the range 0.1–1% was measured by Williams and Loram[11]. According to[11], the resistivity $\Delta\rho$ is proportional to $n^{-1}T^{3/2}$. In the framework of standard spin-wave theory, which Williams and Loram[11] use to interpret their results, $\Delta\rho \sim n^{-1/2}T^{3/2}$. On the other hand, one can show that the temperature dependence of the resistance $\Delta\rho$ calculated from formula (26) in the ranges of temperature and concentration corresponding to the experimental conditions in[11] is close to $T^{3/2}$. But the concentration dependence is found to be stronger than n_0^{-1}. Apparently, the experimentally observed temperature and concentration dependences of the resistivity are a consequence of the fact that the spin waves and local excitations with a spin flip give a commensurate contribute to the resistivity. The difference between the specific heat and the resistivity in this respect is connected with the fact that the specific heat (24) contains a larger pre-exponential factor than does the resistivity (26). We should therefore expect that the electron-scattering mechanism considered in the present paper will turn out to be even more important for the thermal e.m.f. and thermal conductivity than for the resistivity.

CONCLUSION

As already noted, the indirect-exchange energy in metals with strong correlation over distances greater than a certain $r_0 \gg R$ is a function of the distance with alternating sign. Therefore, for sufficiently low concentrations, when $r_c > r_0$, such alloys should not go over into the ferromagnetic state even at T = 0. Their properties should, in this case, resemble the properties of alloys of the CuMn type. It does not appear to be possible to estimate the quantity r_0 reliably. The lower limit of the concentrations for which ferromagnetic ordering can appear has not been discovered experimentally.

The alternating-sign part of the potential does not affect the results obtained above, if the impurities contributing to the quantities under consideration are se separated from their neighbors by a distance less than r_0, i.e., if $\mu_e H_{opt}(T) \approx T3\nu \ln^2(SV_0/T) > V(r_0)$. At lower temperatures, those impurities for which the alternating-sign part of the potential aligns the spins both along and against the magnetization become important. Because of the collinear orientation of the spins, this leads to the result that $W(0) \neq 0$ and, correspondingly, to a contribution to the specific heat that is linear in the temperature.

We have nowhere taken into account the influence of the Kondo effect. For $T \ll T_c$, the Kondo effect is suppressed by the molecular field. One can show that the Kondo effect has no influence on the indirect interaction at high temperatures also. However, the effective magneton in (30) is a function of the temperature[15]. The influence of the Kondo effect on the corrections to the resistivity that are quadratic in the concentration reduces to replacing the scattering amplitude of the electrons by its exact value at the Fermi surface. Consequently, the temperature dependence of the resistivity, given by formula (36), is valid with logarithmic accuracy in the case $I < 0$, both for $T \gg T_K$, and for $T \ll T_K$, while if $I > 0$, it is valid only for $T \gg T_K$ (T_K is the Kondo temperature). The formulas for the thermal conductivity and Lorentz number are applicable for $T \gg T_K$.

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