SOVIET PHYSICS JETP VOLUME 31, NUMBER 5 NOVEMBER, 1970

VIRIAL EXPANSION FOR MAGNETIC IMPURITIES IN METALS

A. I. LARKIN and D. E. KHMEL'NITSKIĬ

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

Submitted December 1, 1969

Zh. Eksp. Teor. Fiz. 58, 1789–1793 (May, 1970)

An expansion of the thermodynamic functions in a series in powers of the density of impurities is constructed for a system of magnetic impurities in a metal. In a weak magnetic field such a series is simultaneously a high-temperature expansion. In a sufficiently strong field the obtained expressions are valid at all temperatures.

THE interaction of magnetic impurities in a normal metal is achieved by means of indirect exchange via the conduction electrons. This interaction slowly decreases with distance between the impurities and therefore may exert a substantial influence on the thermodynamics even for small impurity concentrations. After averaging over the conduction electrons the effective Hamiltonian of the impurities may be written in the form[1,2]

$$\mathscr{H}=\sum_{ij}V_{ij}\mathbf{S}_i\mathbf{S}_j-\mu\mathbf{H}\sum_i\mathbf{S}_i, \tag{1}$$

where **H** denotes the magnetic field, μ denotes the gyromagnetic ratio, and the interaction between spins at large distances is given by

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

The interaction influences the thermodynamic functions if it is not small in comparison with the temperature, $V(R)\gtrsim T$. Therefore, the volume in which the interaction is significant is inversely proportional to the temperature. For large temperatures and small concentrations the probability of finding two impurities in such a volume is small, and the thermodynamic functions may be obtained by an expansion in powers of the density of impurities.

The distribution of the impurities in a metal does not depend on the temperature. Therefore, it is necessary to calculate the thermodynamic functions for a given position, and then to average with respect to the various mutual positions of the impurities.

The free energy of N impurities is determined by the formula

$$F_{1,2\ldots N}=-T\ln\operatorname{Sp}\left\{\exp\left[-\frac{1}{T}\left(\sum_{ij}^{N}V_{ij}\mathbf{S}_i\mathbf{S}_j-\mu\mathbf{H}\sum_i^N\mathbf{S}\right)\right]\right\}. \tag{3}$$

In order to obtain a virial expansion it is convenient to introduce quantities f defined by the recurrence relation

$$f_i=F_i,$$
$$F_{ij\ldots n}=\sum_k f_k+\sum_{kr}f_{kr}+\ldots\sum_{kr\ldots m}f_{kr\ldots m}+f_{ij\ldots n}, \tag{4}$$

where the summation is carried out over different sets of the indices ij ... n. The function f vanishes if the distance between any two impurities tends to infinity. For example,

$$f_{ij}=F_{ij}-(F_i+F_j). \tag{5}$$

Averaging expression (4) over the distribution of the impurities and going to the thermodynamic limit N → ∞, we obtain an expansion of the free energy in powers of the density. For the first term in formula (4) we obtain the expression

$$F^{(1)}=-NT\frac{\operatorname{sh}\{\mu H(S+{}^1/{}_2)/T\}}{\operatorname{sh}\{\mu H/2T\}}. \tag{6}$$

In order to calculate the subsequent terms in the expansion, it should be noted that those impurities are essential when the distance between them is determined by the condition V ~ T. At not too high temperatures these distances are large in comparison with interatomic distances, and the distribution of the impurities can be regarded as independent. Therefore, for the second term of formula (4) we obtain

$$F^{(2)}=-TN\frac{n}{2}\int d\mathbf{R}\varphi\left[\frac{V(R)}{T};\frac{\mu H}{T}\right],$$
$$\varphi(y;z)=\ln\left\{\sum_{J=0}^{2S}\frac{\operatorname{sh}z(J+{}^1/{}_2)}{\operatorname{sh}(z/2)}\exp\left[y\left(S(S+1)-\frac{1}{2}J(J+1)\right)\right]\right\}-2\ln\frac{\operatorname{sh}z(S+{}^1/{}_2)}{\operatorname{sh}(z/2)}. \tag{7}$$

Here n denotes the impurity concentration, and the interaction V(R) is determined by expression (2) and is the product of the smooth function R^{-3} times the rapidly oscillating function $\cos 2p_0R$. Therefore, it is convenient to carry out the integration in formula (7) by first averaging the integrand over the period of the oscillations. Changing the order of averaging and integration, we obtain

$$F^{(2)}=-\frac{4}{3}NnV_0\int\frac{dy}{y^2}\varphi\left(y,\frac{\mu H}{T}\right). \tag{8}$$

For large values of y this integral diverges logarithmically. It is necessary to cut if off at distances of the order of interatomic distances:

$$F^{(2)}=-\frac{4}{3}NnV_0\left[S(2S+1)\ln\frac{V_0n}{T(a^3n)}+\Phi_2\left(\frac{\mu H}{T}\right)\right]. \tag{9}$$

All physical quantities are obtained by differentiation of the free energy with respect to temperature or field and do not depend on the cutoff parameter a. The integrals which appear upon averaging the next terms in formula (4) converge at small distances. After averaging over the distribution of impurities we obtain

$$F^{(m)}=-NT\left(\frac{nV_0}{T}\right)^{m-1}\Phi_m\left(\frac{\mu H}{T}\right). \tag{10}$$

The dependence of the interaction V(R) on the temperature, impurity concentration, and magnetic field was not taken into consideration in the derivation of formulas (7) and (10). Such a dependence arises at distances comparable with v_F/T, the mean free path and the Larmor radius, $v_F/\mu H$. In the ranges of temperatures, fields, and concentrations under consideration these distances are large in comparison with the average distance between impurities, and they are not essential for calculations of the thermodynamic functions. The exchange interaction of the conduction electrons with the impurities is usually small, and in the derivation of formula (2) it has been taken into account in the Born approximation. This is valid if the temperature T or the magnetic energy μH are larger than the Kondo temperature.

Indirect exchange via conduction electrons not only leads to the pair interaction (2) of impurities, but it also leads to various unpaired forces. Over atomic distances these forces are smaller than the pair forces within reasonable limits for the smallness of the exchange interaction between the conduction electrons and the impurities. In addition, these forces fall off more rapidly with distance than the pair forces do. Therefore, the unpaired forces are unessential for a determination of the thermodynamic functions.

Summing all of the $F^{(m)}$ we obtain

$$F=-NT\Phi\left(\frac{nV_0}{T},\frac{\mu H}{T}\right). \tag{11}$$

Thus, in the range of temperatures under consideration, smaller than V_0 but larger than the Kondo temperature, the free energy does not depend on the three parameters n, H, and T, but only on their ratios. Such a result was obtained in[3] by a different method. The approach set forth above is convenient in that it makes it possible to find the free energy in the form of a series in powers of the first argument. In the case $\mu H \lesssim T$ this series gives a high-temperature expansion of the free energy.

For $\mu H \gtrsim T$ the series represents an expansion in terms of the parameter $nV_0/\mu H$. In a sufficiently strong field, when this parameter is small, a sum of the first terms of the series correctly describes the thermodynamic functions at arbitrarily low temperatures. The free energy is given by formula (6) to first order in the impurity density. Let us consider the quadratic term in more detail. Differentiating expression (9), we find the heat capacity when the magnetic field is equal to zero:

$$C=-T\frac{\partial^2 F}{\partial T^2}=\frac{4}{3}N\frac{nV_0}{T}S(2S+1). \tag{12}$$

The obtained formula is valid for $nV_0 \ll T$. From Eq. (12) it is clear that the heat capacity increases upon a reduction of the temperature. According to Nernst's theorem the heat capacity vanishes at quite low temperatures. Therefore the function C(T) has a maximum at a temperature of the order of nV_0.

If, in agreement with experiment, it is assumed that the heat capacity depends on the temperature linearly for $T < nV_0$, then in order of magnitude the coefficient can be found from the condition for matching with formula (12):

$$C \sim NT/nV_0. \tag{13}$$

At low temperatures the heat capacity does not depend on the concentration of impurities, and for a weak interaction V_0 it is much larger than the heat capacity of the conduction electrons.

For $\mu H \gg T$ with logarithmic accuracy we have

$$\Phi_2=-S(2S+1)\ln(\mu H/T). \tag{14}$$

Substituting (14) into formula (9) we verify that in this limit the free energy $F^{(2)}$ does not depend on the temperature. Differentiating (6) and (9) with (14) taken into account, we obtain the following expression for the magnetic moment in a strong field:

$$M=\mu SN\left[1-\frac{4}{3}\frac{V_0 n}{\mu H}(2S+1)\right]. \tag{15}$$

Formula (15) is applicable when the second term inside the square brackets is a small correction.

For spin S = 1/2 we present the dependence of $F^{(2)}$ on temperature and field for an arbitrary relation between them. In this case the function Φ_2 in formula (9) is given by

$$\Phi_2=\operatorname{Re}\psi\left[\frac{1}{2}-\frac{i}{2\pi}\ln\left(1+2\operatorname{ch}\frac{\mu H}{T}\right)\right]. \tag{16}$$

Here $\psi(x)$ denotes the logarithmic derivative of the Γ-function. The remaining thermodynamic quantities can be obtained by differentiation of the free energy. For example, for the heat capacity in a strong field, $\mu H \gg T$, $\mu H \gg nV_0$, we obtain the formula

$$C=4\pi^2 NnV_0T/\mu^2H^2. \tag{17}$$

Thus, in a strong field the heat capacity depends on the temperature linearly and falls with increasing magnetic field.

In a weak field the susceptibility may be written in the form

$$\chi^{-1}=\frac{3}{N\mu^2S(S+1)}(T+T^*), \tag{18}$$

$$T^*=\frac{8}{3}nV_0\int\frac{dy}{y^2}\left\{1-\frac{A}{B}\right\}, \tag{19}$$

$$A=\sum_{J=0}^{2S}J(J+1)(2J+1)\exp\left\{-\frac{y}{2}J(J+1)\right\},$$

$$B=2S(S+1)\sum_{J=0}^{2S}(2J+1)\exp\left\{-\frac{y}{2}J(J+1)\right\}.$$

Formula (18) is applicable at not too low temperatures, $T \gg T^*$. For the case of spin S = 1/2

$$T_{1/2}^*=\frac{16}{9\pi}nV_0\operatorname{Im}\psi'\left[\frac{1}{2}-i\frac{\ln 3}{2\pi}\right]\cong 0.044nV_0. \tag{20}$$

This expression may be obtained by differentiation of the free energy (16) with respect to the field. For the case of large spin

$$T_S^*={}^8/_9\,nV_0\ln S. \tag{21}$$

We note that in the classical limit, when $S\to\infty$, μS = const., V_0S^2 = const, the second term on the right hand side of (18) vanishes.

Expressions similar to formula (18) may be obtained by the method of a self-consistent field. The quantity T^*, obtained by this method, corresponds to the first term of an expansion of formula (19) in powers of the interaction and is proportional to the integral of the interaction potential. In such an integral the region of small distances of the order of interatomic distances is important. In the exact expression (19), for not too high temperatures, $a^3V_0 \gg T$, such distances are not important. This difference is associated with the fact that the self-consistent field method does not take spin correlations into account, which are large for small distances between the impurities, where $V \gg T$. Therefore many of the results obtained by the method of the self-consistent field appear doubtful to us. In particular, conclusions about the ferromagnetism of such a system at low temperatures are unconvincing.

An additional reason concerning the absence of impurity ferromagnetism arises upon analysis of formula (15). Usually in ferromagnetics at zero temperature the magnetic moment reaches saturation even in a weak field. From formula (15) it is clear that the moment of an impurity at zero temperature does not reach saturation even in a strong field. By considering the system placed in an inhomogeneous magnetic field, in similar fashion we convince ourselves that a transition to a helical structure with a nominal spin is not possible. It is impossible, however, to regard a transition into a ferromagnetic or antiferromagnetic state with non-nominal spin as excluded. A phase transition would be indicated by the presence of a singularity in the function Φ in formula (11). It appears more plausible to us that the ground state of a system of magnetic impurities is paramagnetic. On this, apparently, the indications are that a singularity in the temperature dependence of the thermal conductivity is not observed experimentally (see, for example,[3]). Only a smooth maximum is observed in this dependence, which was explained above without including any arguments about magnetic ordering.

In connection with a comparison with experiment, it is necessary to keep in mind that in addition to the values of the spin and magnetic moment of the impurity the theory only contains one adjustable parameter V_0. The temperature dependence of the heat capacity and of the susceptibility has been studied experimentally, and also the dependence of the moment on the magnetic field.[3] Formulas (12), (15), (18), and (19) obtained above describe the experimental results well.

The authors thank I. E. Dzyaloshinskiĭ for helpful discussions.

---

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

[2] Kei Yosida, Phys. Rev. **106**, 893 (1957).

[3] I. Souletie and R. Tournier, Journal of Low Temperature Physics 1, 95 (1969).

Translated by H. H. Nickle
216