Interaction between quadrupole centers in antiferromagnetic substances and the magnetic properties of an impurity system

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The properties are considered of a system of interacting impurity centers located symmetrically between magnetic sublattices of an antiferromagnet. Interaction between impurity spins occurs via exchange of virtual spin waves and can be described by a Hamiltonian of the xy model (z is the matrix antiferromagnetism axis). In metamagnetic substances the impurity interaction potential is of the ferromagnetic type and at sufficiently low temperatures leads to spontaneous magnetization of the impurities. At small momenta the magnon impurity spectrum is linear. It is shown that even low concentrations of impurities of this type may cause in this case the whole matrix to go over to the ferromagnetic state. In weakly anisotropic antiferromagnets the sign of the interaction potential alternates or the potential is of the antiferromagnetic type and hence there is no spontaneous moment in the low-temperature phase of the impurity system. The concentration and temperature dependences of the thermodynamic quantities are found in both cases.

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Studies of the properties of disordered magnetic systems are presently vigorously pursued. Particular interest is attached to systems with low concentration of the magnetic atoms, for in this case the perfectly random disposition of the magnetic centers makes their properties quite different from those of systems in which the magnetic atoms form a crystal lattice. The only presently known example of strongly-diluted magnetic systems are alloys of nonmagnetic metals with magnetic impurities. The interaction of the impurity spins is effected in them via indirect exchange of the conduction electrons of the matrix, and is of the Heisenberg type. The form of the potential depends on the properties of the matrix. In weakly paramagnetic metals, the indirect exchange of s electrons leads to the well known Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, the potential of which at distances larger than interatomic is of the form $V_{\mathrm{RKKY}} \sim r^{-3}\cos 2k_{\mathrm{F}}r$ (k_{F} is the Fermi momentum).[1] The fact that this potential is of alternating sign and the random disposition of the impurities produces in alloys of the CuMn type peculiar magnetic structures called magnetic glasses.[2,3]

In nearly-magnetic metals such as Pd, owing to the presence of a strong correlation of the matrix d electrons, the potential of the interaction between the impurities is ferromagnetic and falls off exponentially with distance.[4] The properties of dilute ferromagnetic alloys of the PdFe type were investigated in[5,6].

In this paper we consider, for the first time, systems of another type, in which it is possible to realize dilute disordered magnets, namely antiferromagnets with magnetic impurities disposed symmetrically relative to the sublattices of the matrix. The molecular field at such impurities is equal to zero, and they therefore interact with the matrix only via virtual emission and absorption of spin waves. In the one-impurity approximation this leads, as shown in[7,8], to an impurity spectrum that coincides with the spectrum of a quadrupole in an external electric field. In this paper we obtain the interaction Hamiltonian of such quadrupole impurities and consider the effects brought about by this interaction.

The interaction Hamiltonian obtained by us for two impurity spins I_1 and I_2 localized at the points r_1 and r_2 is of the form

$$H_{12} = -V_{\alpha_1\alpha_2}(\mathbf{r}_1-\mathbf{r}_2)\,(I_1^x I_2^x + I_1^y I_2^y). \tag{1}$$

The subscripts α_i determine the possible nonequivalent positions of the impurities in the elementary magnetic cell (see the figure). The z axis is directed along the antiferromagnetism axis. It is seen from (1) that the interaction corresponding to the so-called xy model has a strong magnetic anisotropy. $V_{\alpha_1\alpha_2}(\mathbf{r})$ turns out to depend strongly on the angles between $\mathbf{r}$ and the crystallographic axes.

The concrete form of the potential is determined by the relation between the parameter of the magnetic anisotropy of the matrix and the exchange integrals between the sublattices. In "classical" antiferromagnets, where the anisotropy parameter is much less than the exchange integrals, at not too large distances $r < a$ (with a determined by the anisotropy parameter) we have $V_{\alpha_1\alpha_2} \sim r^{-2}$, and the dependence of this potential on the angle causes its positive and negative values to be equally probable at a given $|\mathbf{r}|$. In this respect, our potential is analogous to the potential V_{RKKY}, which is proportional to r^{-3}, and the equal probabilities of the positive and negative values follow from the rapid spatial oscillations of the cosine. The fact that the potential is of alternating sign and the random distribution of the impurities cause the low-temperature phase of the impurity system to be magnetic glass in this case.

Distances smaller than a are of importance if the impurity concentration n is larger than a^{-3}. At $n < a^{-3}$ the potential $V_{\alpha_1\alpha_2}(\mathbf{r})$ is either negative or of alternating sign, and an important role is played by $r > a$ for which $V_{\alpha_1\alpha_2}(\mathbf{r}) \sim r^{-1}e^{-r/a}$. In the low-temperature phase, just as in the preceding case, the spontaneous moment is obviously zero, and the orientation of the spins is determined by the configuration of the impurities. However, owing to the exponential character of the potential, the concrete properties of the low-temperature phase can be significantly different. The characteristic temperature T_0 of the transition to the magnetic-glass phase is of the order of $|V_{\alpha_1\alpha_2}(r_c)|$, where $r_c \sim n^{-1/3}$ is the average distance between impurities. It turns out as a result that $T_0 \sim n$ when $n > a^{-3}$ and $T_0 \sim \exp(-\gamma/n^{1/3}a)$ when $n < a^{-3}$ (γ is a constant of the order of unity).

At high temperatures $T \gg T_0$, the thermodynamics of the impurity system was investigated by using a virial expansion in powers of the concentration. The first virial corrections $\delta\chi_{zz}$ and $\delta\chi_{xx}$ to the susceptibilities of the free spins turned out to be negative, i.e., antiferromagnetic in character. If $T \gg |V_{\alpha_1\alpha_2}(a)|$, then $\delta\chi \sim T^{-2}$ and the temperature dependence of the susceptibility can be described by the antiferromagnetic Curie-Weiss law. On the other hand, if $T_0 \ll T \ll |V_{\alpha_1\alpha_2}(a)|$, then $\delta\chi \sim \ln^3(|V_{\alpha_1\alpha_2}(a)|/T)$ and the Curie-Weiss law does not hold. It should be noted that already at $T \gg T_0$ the impurity susceptibility and the specific heat can become larger than the corresponding quantities for the matrix.

In metamagnets, where the anisotropy parameter is larger than the exchange integral between the planes, the interaction potential is positive and leads at sufficiently low temperatures to ordering in the xy plane. It is shown that the magnon dispersion law in the impurity subsystem at small momenta is linear. The concentration dependences of the Curie temperature and of the magnon velocities were obtained at different ratios of n and $a^{-2}d^{-1}$ (2d is the distance between the planes of the metamagnet).

The quadrupole character of the spectrum in the one-impurity approximation causes the ground state of an impurity with half-integer spin to be a doublet with $m = \pm 1/2$, as against a nonmagnetic singlet for an integer spin. Owing to the large radius of the potential, the impurity-interaction energy in the metamagnet at $n > n_1 \sim a^{-2}d^{-1}\ln(a/d)$ is larger than the energy of the quadrupole splitting. Therefore the quadrupole systematics of the centers is disturbed and the moment of the impurities is no longer quenched. As a result, at a sufficiently high concentration, a spontaneous moment is produced also in a system of impurities with integer spin. In this case, regardless of the value of I, the saturation moment of each impurity depends on the concentration.

It is also interesting to note that as a result of the peculiarities of the xy model the magnetic susceptibility of the impurity system along the impurity magnetization axis is different from zero even at T = 0; it can greatly exceed the susceptibility of the matrix. A similar situation obtains also in the case of magnetic glasses.

Quadrupole impurities were observed in the metamagnet $FeCl_2$.[9] Their concentration, however, was very slight, so that no interaction effects were observed.

1. INTERACTION HAMILTONIAN OF QUADRUPOLE CENTERS

The Hamiltonian of a uniaxial antiferromagnet with two sublattices can be written, in the presence of magnetic impurities, in the form

$$H=H_0+H_1, \tag{2}$$

where H_0 is the Hamiltonian of the ideal matrix

$$H_0=\sum_{\substack{pp'\\ ll'}}\{-J_{ll'}^{pp'}\mathbf{S}_{pl}\mathbf{S}_{p'l'}+\beta_{ll'}^{pp'}S_{pl}^zS_{p'l'}^z\},$$

and H_1 describes the interaction of the impurities with the matrix

$$H_1=\sum_{\substack{l\\ s\alpha}}J_{pls\alpha}\mathbf{S}_{pl}\mathbf{I}_{s\alpha}.$$

Here S_{pl} is the spin operator of an atom of the p-th sublattice in the l-the unit cell; $J_{ll'}^{pp'}$ and $\beta_{ll'}^{pp'}$ are the exchange integrals and the anisotropy parameters inside and between the sublattices; $I_{s\alpha}$ is the spin operator of an impurity in the s-th cell. The subscript α labels the possible positions of the impurity in the magnetic unit cell. The summation is carried out, naturally, only over the interstices occupied by impurities.

We consider temperatures much lower than the Néel temperature of the matrix T_N. We can then go over in the usual manner from S_{pl} to the spin-wave operators c_{nk},[10] which diagonalize H_0:

$$H_0=\sum_{n,\mathbf{k}}\omega_k c_{n\mathbf{k}}{}^+c_{n\mathbf{k}}, \qquad n=1.2$$

$$\omega_{\mathbf{k}}=(A_{\mathbf{k}}^2-B_{\mathbf{k}}^2)^{1/2}, \qquad B_{\mathbf{k}}=-2SJ^{12}(\mathbf{k}), \tag{3}$$

$$A_{\mathbf{k}}=2S[J^{11}(0)-J^{11}(\mathbf{k})-J^{12}(0)+\beta^{12}(0)-\beta^{11}(0)].$$

$J^{pp'}(\mathbf{k})$ and $\beta^{pp'}(\mathbf{k})$ are the Fourier transforms of the corresponding exchange integrals and anisotropy parameters. It must be borne in mind that $J^{11}(0) > 0$, $J^{12}(0) < 0$, and the condition that the z axis be the antiferromagnetism axis is that the quantity $\beta^1 = \beta^{12}(0) - \beta^{11}(0)$ be positive.

The impurity part of the Hamiltonian H_1 is expressed in terms of the spin-wave operators in the following manner[7]:

$$\begin{aligned}H_1=&-\sqrt{\frac{2S}{N}}\sum_{\mathbf{k},s,\alpha}I_{s\alpha}^x[J_\alpha^+(\mathbf{k})\hat{\gamma}_{2,\mathbf{k}}^+ + J_\alpha^-(\mathbf{k})\hat{\gamma}_{1\mathbf{k}}^+]\exp(i\mathbf{k}\mathbf{r}_{s\alpha})\\ &-i\sqrt{\frac{2S}{N}}\sum_{k,s,\alpha}I_{s\alpha}^y[J_\alpha^+(\mathbf{k})\hat{\gamma}_{1,\mathbf{k}}^- + J_\alpha^-(\mathbf{k})\hat{\gamma}_{2\mathbf{k}}^-]\exp(i\mathbf{k}\mathbf{r}_{s\alpha})+\sum_{s,\alpha}J_\alpha^-(0)I_{s\alpha}^z.\end{aligned} \tag{4}$$

In (4) we used the following notation:

$$\hat{\gamma}_{n,\mathbf{k}}^{\pm}=(u_{\mathbf{k}}\pm v_{\mathbf{k}})(c_{n,\mathbf{k}}\pm \overset{+}{c}_{n,-\mathbf{k}}),$$

$$u_{\mathbf{k}}=\left(\frac{A_{\mathbf{k}}+\omega_{\mathbf{k}}}{2\omega_{\mathbf{k}}}\right)^{1/2}, \qquad v_{\mathbf{k}}=\left(\frac{A_{\mathbf{k}}-\omega_{\mathbf{k}}}{2\omega_{\mathbf{k}}}\right)^{1/2}, \tag{5}$$

$$J_\alpha^{\pm}(\mathbf{k})=1/2[J_{2\alpha}(\mathbf{k})\pm J_{1\alpha}(\mathbf{k})], \qquad J_{p\alpha}(\mathbf{k})=\sum_l J_{pls\alpha}\exp(i\mathbf{k}(\mathbf{r}_{pl}-\mathbf{r}_{s\alpha})),$$

N is the number of unit cells in the crystal, and $\mathbf{r}_{s\alpha}$ is the radius vector of the impurity. The last term of (4) has the meaning of a molecular field acting on the impurity spin. For impurities that are arranged symmetrically between the sublattices, $J_\alpha^- = 0$ and this term drops out.

Let us calculate the effective Hamiltonian H_{eff} of the impurity system under the assumption that the impurities are weakly coupled with the matrix, i.e.,

$$J_\alpha^{\pm}(0)\ll\max[J^{11}(0), -J^{12}(0)].$$

In second order of perturbation theory in H_1 we can obtain the following expression for H_{eff}:

$$H_{\mathrm{eff}}=\langle H_1(E-H_0)^{-1}H_1\rangle=A\sum_{s,\alpha}[(I_{s\alpha}^z)^2-I(I+1)]$$

$$-\sum_{\substack{ss'\\ \alpha\alpha'}}V_{\alpha\alpha'}(\mathbf{r})[I_{s\alpha}^xI_{s'\alpha'}^x+I_{s\alpha}^yI_{s'\alpha'}^y]; \tag{6}$$

$$A=\sum_k B_{\alpha\alpha}(\mathbf{k}),\qquad V_{\alpha\alpha'}(\mathbf{r})=\sum_{\mathbf{k}}B_{\alpha\alpha'}(\mathbf{k})e^{i\mathbf{kr}},$$

$$B_{\alpha\alpha'}(\mathbf{k})=\frac{S}{4N\omega_{\mathbf{k}}}\{(u_{\mathbf{k}}-v_{\mathbf{k}})^2J_\alpha^+(\mathbf{k})J_{\alpha'}^+(-\mathbf{k})+(u_{\mathbf{k}}+v_{\mathbf{k}})^2J_\alpha^-(\mathbf{k})J_{\alpha'}^-(-\mathbf{k})\}, \tag{7}$$

$\mathbf{r}=\mathbf{r}_{s\alpha}-\mathbf{r}_{s'\alpha'}$. The first term in (6) is the Hamiltonian of the one-impurity problem, first obtained in[7]. It coincides with the Hamiltonian of a quadrupole in an external electric field, and this is why the impurities in question were named quadrupole impurities.[7] Since $A > 0$, the ground state for impurities with half-integer spin is doubly degenerate in the one-impurity approximation. For integer spins, the ground state is a nonmagnetic singlet. We consider in the main impurities with half-integer spin. The influence of the inter-impurity interaction on the singlet quadrupole centers is discussed in Sec. 3. As seen from (6), the interaction of the impurities is described by the so-called xy model.

We proceed to calculate the potential $V_{\alpha\alpha'}(\mathbf{r})$. It turns out to depend essentially on the ratio of the anisotropy parameter to the exchange integral between the sublattices.

We consider two limiting cases.

1) Weakly anisotropic antiferromagnet $\beta'(0) \ll |J^{pp'}(0)|$. We carry out the calculation using as an example a crystal with the unit cell shown in the figure. The magnetic atoms of the sublattices are marked a and b. The impurities lie on the edges and are marked by crosses. They can occupy two nonequivalent positions ($\alpha = 1$ or 2). Assuming that the impurities interact only with the nearest magnetic neighbors of the matrix, we obtain from (5) and (7)

$$V_{\alpha\alpha'}(\mathbf{r})=\frac{J_1^2S}{N}\sum_{\mathbf{k}}e^{i\mathbf{kr}}\left\{\frac{\cos^2k_zd}{A_{\mathbf{k}}+B_{\mathbf{k}}}+(-1)^{\alpha+\alpha'}\frac{\sin^2k_zd}{A_{\mathbf{k}}-B_{\mathbf{k}}}\right\}. \tag{8}$$

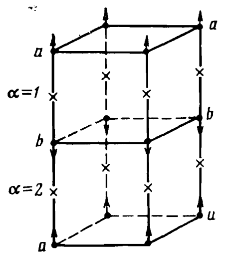
Here J_1 is the exchange integral between the impurity and the nearest atom of the matrix, d is the distance between them. At $kd \ll 1$, expanding A_k and B_k in (3) in terms of the momenta, we can readily obtain

$$A_k-B_k=2S[\beta'+w_\perp(k_\perp d)^2+w_z(k_zd)^2],$$
$$k_\perp^2=k^2-k_z^2. \tag{9}$$

Substitution of (9) in (8) leads to the following expression for the potential at $r \gg d$:

$$V_{\alpha\alpha'}(\mathbf{r})=(-1)^{\alpha+\alpha'}v_0V_0e^{-R/a_0}R^{-1}\left[\left(1-3\frac{r_z^2}{R^2}\right)\left(\frac{1}{R^2}+\frac{1}{a_0R}\right)-\frac{1}{a_0^2}\frac{r_z^2}{R^2}\right];$$
$$a_0^2=d^2\frac{w_z}{\beta'}\gg d^2,\qquad R^2=\frac{w_z}{w_\perp}r_\perp^2+r_z^2,\qquad V_0=\frac{J_1^2}{8\pi w_\perp}. \tag{10}$$

Here v_0 is the volume of the unit cell, while $r_\perp$ and r_z are the projections of the vector $\mathbf{r}$ on the xy plane and on the z axis.



We note that the potential (10) is determined by the second term in (8), since the contribution of the first term decreases exponentially over distances on the order of the lattice constant. It follows from (10) that

$$V_{\alpha\alpha'}(\mathbf{r})=(-1)^{\alpha+\alpha'}v_0V_0\begin{cases}R^{-3}\left(1-3\dfrac{r_z^2}{R^2}\right) & \text{for}\quad R<a_0,\\ -\dfrac{r_z^2}{R^3a_0^2}e^{-R/a_0} & \text{for}\quad R>a_0.\end{cases} \tag{11}$$

For crystals with more than one possible impurity position in the unit magnetic cell, the interaction potential is a quantity of alternating sign, regardless of the form of the unit cell, and all its essential singularities are given by formula (10). On the other hand if there is only one position of the quadrupole impurity in the cell, then the potential takes the form (10) but without the coefficient $(-1)^{\alpha+\alpha'}$.

2. The second limiting case is that of strongly anisotropic ferromagnets. We consider layered metamagnets with $-J^{12}(0) < \beta' \ll J^{11}(0)$. The spin-wave approximation used by us is valid for layered magnets at $T \ll T_N$ as a result of the stabilizing role played by the interplanar interaction and as a result of the anisotropy.[11]

In this case we can neglect B_k in comparison with A_k in (8), and A_k takes the form

$$A_{\mathbf{k}}=2S(\beta'+w_\perp k_\perp^2d^2).$$

The interaction potential of impurities lying in one interplanar layer is then equal to

$$V_{11}(\mathbf{r})=V_1K_0(r/a_1);$$
$$V_1=V_0v_0/2d^3,\qquad a_1^2=d^2w_\perp/\beta', \tag{12}$$

while for impurities lying in neighboring layers we have

$$V_{12}(\mathbf{r})={}^1\!/_2V_1K_0(r_\perp/a_1). \tag{13}$$

Here $K_0(x)$ is a cylindrical function. The interaction potential of impurities from more remote layers is equal to zero in the assumed approximation. Allowance for the dispersion of the spin waves in the z direction, or allowance for the interaction of impurities with matrix atoms that are more remote would lead to the appearance of a weak interaction of impurities from more remote layers, which falls off rapidly and is of no importance to us. The coefficient in ½ which is present in (13) but not in (12) is due to the fact that the indirect exchange of neighboring-layer impurities is effected via atoms of one plane of the matrix, and the impurities of one layer interact via atoms of two planes of the matrix.

As seen from (12) and (13), the interaction of the quadrupole centers in the metamagnet has a ferromagnetic character and leads at sufficiently low temperatures to the appearance of a spontaneous moment that is oriented in the xy plane perpendicular to the antiferromagnetism axis of the matrix. In weakly-anisotropic ferromagnets the situation is much more complicated. The potential (10) is an alternating-sign function of the indices and of the angle between the z axis and r. We shall use an analysis of this situation as the starting point for the examination of the effects due to the interaction of quadrupole centers.

2. QUADRUPOLE CENTERS IN WEAKLY ANISOTROPIC ANTIFERROMAGNETS

As seen from (11) at $R < a_0$ the potential is $V_{\alpha\alpha'}(r) \sim R^{-3}$ and positive as well as negative values of the potential are equally probable at fixed R. As already noted, in this respect our potential is similar to the potential V_{RKKY}. The question of the low-temperature phase of systems for which positive and negative values of the interaction potential are equally probable is still open at present (regardless of the law governing the decrease of the potential). It appears that such systems do not have a spontaneous moment in the ground state.[2,3] but at sufficiently low temperatures the spins are quenched and their directions are determined by the impurity configuration. Systems of this type, for example alloys of the CuMn type, were called magnetic glasses. It follows from the foregoing that at $n < a_0^{-3}$, when the characteristic distances are $r_c \sim n^{-1/3} \ll a_0$, the system of quadrupole centers in antiferromagnets also has the properties of magnetic glasses.

At $n < a_0^{-3}$ the significant distances r between the impurities are larger than a_0. At such distances, as seen from (11), $V_{\alpha\alpha'}(r) \sim R^{-1}\exp(-R/a_0)$. If the impurity can occupy several positions in the unit magnetic cell, then the potential is of alternating sign, as before, On the other hand, if there is only one nonequivalent position, then the potential $V_{\alpha\alpha'}(r)$ from (11) is negative. It appears that no spontaneous magnetization occurs in these cases. The direction of the spins is determined by the configuration and therefore varies in random fashion, so that the resultant low-temperature phase can in these cases be called magnetic glass. The concrete properties of this phase, however, can depend on the form of the potential. In particular, if the potential is exponential the impurity spins can be collinear in sufficiently large volumes, on the order of $r_c^3(na_0^3)^{-1/3}$.

At high temperatures, much higher than the characteristic temperature T_0 of the transition to the magnetic-glass phase, the influence of the interimpurity interaction on the thermodynamic functions can be considered with the aid of a virial expansion in powers of the concentration. The principal role is played in this case by impurity pairs whose interaction energy is $V_{\alpha\alpha'}(r) \gtrsim T$; the distance between impurities in such pairs is much less than the average distance between impurities if $T \gg T_0$.

The system of magnetic levels in such pairs determines the impurity heat capacity, the increment to the susceptibility of the free spins, etc., For impurities interaction with a potential V_{RKKY}, a similar calculation was carried out by Larkin, Mel'nikov, and Khmel'nitskiĭ.[12] The first virial correction to the free-energy density is of the form[12]

$$F=-T\frac{n^2}{2}v_0\sum_{\mathbf{r}}\Big(\ln\sum_i\exp(-\beta E_i(\mathbf{r}))-2\ln\sum_i\exp(-\beta E_i(\infty))\Big), \tag{14}$$

where $\mathbf{r}_{s\alpha}-\mathbf{r}_{s'\alpha'}$, $E_i(\mathbf{r})$ are the energy levels of the pairs of impurities separated by a distance $\mathbf{r}$, $E_i(\infty)$ is the energy of the noninteracting impurities, and $\beta = T^{-1}$.

Unless specially stipulated, we shall consider henceforth only impurities with half-integer spin. For these impurities, the upper excited levels are separated from the doublet with the magnetic quantum number $m = \pm 1/2$ by an energy A equal, in order of magnitude, the interaction energy of the impurities located in the neighboring cells. At low impurity concentrations the value of A is therefore much larger than T and in a wide temperature interval, $A \gg T \gg T_0$, we can disregard the excited levels of the isolated quadrupole impurities. In the spectrum of a pair of such impurities there are four levels. If the external magnetic field h is directed along the z axis, then

$$\begin{gathered}E_i(\mathbf{r})=E_{jM}=-{}^1/_2 g_z\mu_B Mh-V(\mathbf{r})\,[j(j+1)-M^2+1],\\ V(\mathbf{r})=V_{\alpha\alpha'}(\mathbf{r})\,(I+{}^1/_2)^2,\qquad j=0,\ 1,\qquad |M|<j.\end{gathered} \tag{15}$$

Here g_Z is the effective g-factor in the z direction,[8] and μ_B is the Bohr magneton. But if h lies in the xy plane, then the wave functions of the pair are not classified with respect to M. In this case the spectrum takes the form

$$\begin{gathered}E_1=V(\mathbf{r}),\qquad E_2=0,\\ E_{3,4}=-{}^1/_2[V(\mathbf{r})\pm(V^2(\mathbf{r})+4g_\perp{}^2\mu_B{}^2h^2)^{1/2}],\end{gathered} \tag{16}$$

where $g_\perp$ is the effective g factor in the transverse direction.[8]

Differentiating the expression for the free energy, we can find with the aid of formulas (14)–(16) the specific heat of the impurity system and the magnetic susceptibilities:

$$\begin{gathered}C=n^2\int d^3\mathbf{r}\,x^2\,\mathrm{ch}^{-2}x,\\ \chi_{zz}=\chi_{zz}^{(0)}\left[1-n\int d^3\mathbf{r}\,\mathrm{th}^2x\right],\qquad \chi_{zz}^{(0)}=\frac{(g_z\mu_B)^2n}{4T},\\ \chi_{xx}=\chi_{xx}^{(0)}\left[1-n\int d^3\mathbf{r}\,(1-x^{-1}\,\mathrm{th}\,x)\right],\qquad \chi_{xx}^{(0)}=\frac{(g_\perp\mu_B)^2n}{4T},\\ x={}^1/_2\beta V(\mathbf{r}).\end{gathered} \tag{17}$$

It is seen from (17) that the concentration increments to the susceptibility, just as for the potential V_{RKKY}, are negative.

The heat capacity is determined by the energies $|V(r)| \sim T$, and the susceptibility by the energies $|V(r)| \gtrsim T$. Therefore if $T \gg T^* = V_0v_0a_0^{-3}$, so that $R > a_0$, then we can use the asymptotic form (11) of $V_{\alpha\alpha'}(r)$ at short distances. We then have:

$$\begin{gathered}C=\frac{\pi^2}{14\zeta(3)}n\frac{T_1}{T},\\ \frac{\chi_{xx}^{(0)}-\chi_{xx}}{\chi_{xx}^{(0)}}=\frac{1}{2}\frac{\chi_{zz}^{(0)}-\chi_{zz}}{\chi_{zz}^{(0)}}=\frac{T_1}{T};\\ T_1=nv_0V_0\cdot 56\zeta(3)\,(I+{}^1/_2)^2w_\perp/3^{7/2}\pi w_z,\end{gathered} \tag{18}$$

where $\zeta(x)$ is the zeta function. It is seen from (18) that the virial expansion is in this case in terms of the parameter T_1T^{-1}, and is consequently valid at $T \gg T_1$. If the impurity concentration exceeds $a^{-3} = a_1^{-1}a_0^{-2}$, then the inequality $T_1 \gg T^*$ holds and we can use the asymptotic form of the potential at small r throughout the region of applicability of the virial expansion. The transition into the magnetic-glass phase takes place at temperatures on the order of $T_1 \sim nV_0v_0$.

The temperature dependences (18) coincide, naturally, with those obtained by Larkin et al.[12] However, as a consequence of the magnetic anisotropy of the Hamiltonian (6), the relative correction to the longitudinal susceptibility has turned out to be twice as large as the correction to the transverse susceptibility. (In[12], where the Hamiltonian is of the Heisenberg type, the relative corrections are the same.) The temperature dependences of the susceptibilities (18) are described by the Curie-Weiss antiferromagnetic law.

If $n \ll a^{-3}$, and hence $T_1 \ll T^*$, then formulas (18) no longer hold at $T \approx T^*$; the viral correction are still small in this case. In the temperature range $T_0 \ll T \ll T^*$ we can replace $V_{\alpha\alpha'}(\mathbf{r})$ by its asymptotic form at $R > a_0$ from (11). Then the dependence of the potential on $\mathbf{r}$ is determined mainly by the exponential, so that we take the potential in the form

$$V_{\alpha\alpha'}(\mathbf{r}) = (-1)^{\alpha+\alpha'} V' r_z^2 R^{-2} \exp(-R/a_0). \tag{19}$$

Substituting (19) in (17) we get

$$\begin{gathered} C = 3 \ln 2 \cdot n\nu \ln^2 (V'/T), \\ \frac{\chi_{xx}^{(0)} - \chi_{xx}}{\chi_{xx}^{(0)}} = \frac{\chi_{zz}^{(0)} - \chi_{zz}}{\chi_{zz}^{(0)}} = \nu \ln^3 \frac{V'}{T}, \end{gathered} \tag{20}$$

where $\nu = (4/3)\pi n a^3$ is the number of impurities in the radius of the potential. Only the highest-order terms in $\ln(V'/T)$ have been retained in the expressions of (20).

The virial corrections (20) decrease quite slowly with increasing temperature. The reason for the different powers of the logarithm in the expressions for C and χ is that the contribution to the heat capacity is made by pairs with $|V_{\alpha\alpha'}(\mathbf{r})| \gtrsim T$, while the pairs contributing to the susceptibility have $|V_{\alpha\alpha'}(\mathbf{r})| \gtrsim T$. Unlike in the preceding case, the temperature dependence of the susceptibility, determined by (20), is not described by the Curie-Weiss law, and the relative corrections to the susceptibilities χ_{xx} and χ_{zz} turn out to be equal.

The parameter of the virial expansion (20) is $\nu \ln^3 (V'/T) \ll 1$. One can therefore expect the transition to the low-temperature phase to occur when this parameter becomes of the order of unity, i.e.,

$$T_0 \sim V' \exp[-\gamma / n^{1/3} a], \tag{21}$$

where γ is a number of the order of unity. Relation (21) shows that the transition to the low-temperature phase occurs when the temperature becomes equalized with the energy of the interaction of the impurities located at medium distances from one another. Thus, the linear dependence of T_0 on n gives way to the exponential one (21) with decreasing concentration.

It is seen from (18) and (20) that at sufficiently low temperatures but still higher than T_0 the heat capacity and the magnetic susceptibilities of the impurity subsystem can exceed the corresponding characteristics of the matrix. The total heat capacity at a temperature on the order of T_0 can have a maximum.

3. IMPURITY FERROMAGNETISM OF QUADRUPOLE CENTERS IN LAYERED METAMAGNETS

In layered metamagnets, where the exchange interaction between the planes $-J^{12}(0)$ is smaller than the anisotropy β' (but $\beta' \ll J^{11}(0)$), the energy of the quadrupole splitting is

$$A = {}^1\!/_2 V_1 \ln (W_\perp / \beta'). \tag{22}$$

It is easy to verify that (22) is valid at $J_1^2 / J^{11}(0)\beta' \ll 1$. The interaction Hamiltonian of the impurities takes the form (6), and the potential is determined by formulas (12) and (13). This potential is positive at arbitrary r, and therefore at sufficiently low temperatures it leads to an impurity ferromagnetism of the quadrupole centers.

Inasmuch as the interaction Hamiltonian (6) contains only the x and y components of the spins, the spontaneous moment of the impurity system is oriented in the xy plane perpendicular to the antiferromagnetism axis. At large distances, the potential decreases exponentially ($K_0(x) = (\pi/2x)^{1/2} e^{-x}$ at $x \gg 1$), and at short distances it depends slowly on the coordinates ($K_0(x) = -C_E - \ln x$ at $x \ll 1$, where C_E is the Euler constant). Therefore the properties of the considered system depend essentially on the ratio of the radius a_1 of the potential and the average distance $r_C \sim (2dn)^{-1/2}$ between the impurities lying in one interplanar layer. If $n \ll n_1 = (8\pi a_1^2 d)^{-1}$, then $r_C \gg a_1$. Most impurities have a nearest neighbor at a distance on the order of r_C, and owing to the exponential decrease of the potential they interact effectively only with the nearest neighbor. The Curie temperature is of the order of the interaction energy of such impurities

$$T_C \sim V_1 \exp(-\gamma_1 / (nd)^{1/2} a_1), \tag{23}$$

where γ_1 is a coefficient on the order of unity. This dependence can also be obtained by equating to unity the virial-expansion parameter. We note that for a ferromagnet with a three-dimensional random disposition of the impurities and with an exponential potential the dependence of T_C on n at low concentrations was obtained earlier[5]; the phase transition in dilute ferromagnets was investigated also by using the ideas of percolation theory.[6]

In the case under consideration the value of A is much larger than the characteristic interaction energy $V_1 K_0(r_C/a_1)$, and therefore the ferromagnetism appears only for quadrupole impurities with half-integer spin and the saturation moment is equal to $(2I + 1)/4$.

The most characteristic features of the quadrupole impurities in metamagnets appear at $n \gg n_1$. We consider first temperatures $T \ll T_C$. The Hamiltonian (6) in the molecular-field approximation takes the form (the x axis is directed along the magnetization axis):

$$\begin{gathered} H_{\text{eff}} = A \sum_i [(I_i^z)^2 - I(I+1)] - \sum_i H_i I_i^x + \frac{1}{2} \sum_i H_i \langle I_i^x \rangle, \\ H_i = 2 \sum_j V(\mathbf{r}_i - \mathbf{r}_j) \langle I_j^x \rangle. \end{gathered}$$

The subscripts i and j label the impurities.

The slow logarithmic dependence of $V(\mathbf{r})$ on r at $r \ll a_1$ causes each impurity to interact at $n > n_1$ with many neighbors. Therefore, despite the random disposition of the impurities in the layers, $\langle I_i^x \rangle$ and H_i fluctuate weakly and they can be replaced by values averaged over the impurity distribution, and equal respectively to $\langle I^x \rangle$ and

$$H = 2nV_1 \langle I_i^x \rangle / n_1. \tag{24}$$

In the cases considered earlier, the interaction energy was lower than A and did not change the systematics of the quadrupole centers. In particular, no spontaneous moment appeared for impurities with integer spin. It is seen from (22) and (24) that in this case the interaction energy can be larger than A, and this leads to an significant change in the properties of the system. For example, for integer spins a sufficiently strong molecular field causes a restructuring of the ground state of the quadrupole centers. An "admixture" of functions with $m \neq 0$ appears in the wave function of the ground state, and as a result a spontaneous moment appears in the system. Thus, for I = 1 a simple calculation shows that the spontaneous moment appears if $n > n_{cr} = {}^1\!/_8 n_1 \ln(W_\perp / \beta')$. Its value is

$$M=ng_\perp\mu_B\langle I^x\rangle=(1-(n_{cr}/n)^2)^{1/2}ng_\perp\mu_B. \qquad (25)$$

The dependence of $\langle I^x\rangle$ on the concentration has near the critical concentration x_{cr} a square-root singularity that is typical of second-order phase transitions in the molecular-field approximation. The Curie temperature of the impurity system is in this case equal to

$$T_C=A\ln^{-1}\frac{2n_{cr}+n}{n-n_{cr}} \qquad (26)$$

and at $n \gg n_{cr}$ we have

$$T_C=4nV_1/3n_1.$$

The last formula coincides with the usual result of the theory of the molecular field with spin $I = 1$. Our calculation and formulas (25) and (26) are valid, strictly speaking, only at $n \gg n_1$, when all the H_i can be replaced by H. The values of n_1 and n_{cr} are of the same order. However, the existence of a critical concentration n_{cr} and the singularity it introduces in the dependence of $\langle I^x\rangle$ on n are not connected with the spatial averaging performed by us.

For centers with half-integer spin there is also an appreciable change in the ground state of the quadrupole centers. The molecular field "unquenches" the moment of the impurity, as a result of which it changes smoothly from the value $(2I + 1)/4$ at $n \ll n_{cr}$ to the value I at $n \gg n_{cr}$. The Curie temperature at $n \gg n_{cr}$, whether the spin is integer or half-integer, is equal to

$$T_C=2nI(I+1)V_1/3n_1.$$

We proceed now to the question of the magnon spectrum in the impurity system at $T = 0$. In the case of large concentration $n \gg n_1$, when the molecular-field fluctuations are small, it is possible to develop for the Green's functions of the transverse components a consistent perturbation theory in n_1/n (similar to what was done in[13]). The magnon spectrum of first order in this parameter is given by

$$\begin{aligned}\omega(\mathbf{q})&=nn_1^{-1}[J(0)(J(0)-J(\mathbf{q}))]^{1/2},\\ J(\mathbf{q})&=IV_1\beta'(1+\cos 2q_zd)(\beta'+w_\perp q_\perp^2d^2)^{-1}.\end{aligned} \qquad (27)$$

Examination of the higher orders of perturbation theory shows that the magnon damping at $qr_C \ll 1$ is small. At small momenta the dispersion law has an acoustic character with strong anisotropy, and at $q_\perp \gtrsim a_1^{-1}$ it assumes a limiting value equal to InV_0/n_1. The acoustic character of the spectrum at small q is due to the absence of magnetic anisotropy in the xy plane, and the non-activation linear dispersion law is preserved in any order of perturbation theory in n_1/n. It can therefore be assumed that the acoustic character of the spectrum at small q is preserved also at $n < n_1$. The magnon velocity s depends in this case on the concentration in the same manner as the Curie temperature (23)

$$s\sim\exp(-\gamma_1n^{-1/2}d^{-1/2}a_1^{-1}),$$

so that the limiting energy of the magnons is of the order of T_C.

In concluding this section we note that when the concentration of the impurities between the planes of a metamagnet is high enough, these impurities cause the entire matrix to go over into a ferromagnetic state with magnetization axis along z. The onset of ferromagnetic orientation of the planes leads at $T = 0$ to an exchange-energy loss $4|J^{12}(0)|S^2$. At the same time, on the other hand, there is produced at the impurities a molecular field that magnetizes them along the z axis, and this leads to an energy gain equal to $2nv_0SI|J_1|$. As a result, the ferromagnetic state of the impurities becomes energywise favored at a relative impurity concentration

$$c>c_{\text{flip}}=2\frac{S}{I}\left|\frac{J^{12}(0)}{J_1}\right|.$$

The energy of the quadrupole splitting A and the interaction energy of the impurities are much smaller than J_1, and therefore have no effect on the value of c_{flip}.

4. LONGITUDINAL SUSCEPTIBILITY AT ZERO TEMPERATURE

It will be shown in this section that for a system of interacting quadrupole centers the susceptibility along the magnetization axis (the x axis) differs from zero even at $T = 0$ and is sufficiently large. We consider first the case of high concentration of the quadrupole centers in a metamagnet, when the molecular-field theory is valid. The magnetic field directed along the x axis leads to an increase of the magnetic moment as a result of the nonzero off-diagonal matrix elements of the operator I^x between the different quadrupole states (in analogy with the well-known Van Vleck susceptibility). For impurities with $I = 1$, the corresponding magnetic susceptibility is given by

$$\begin{aligned}\chi_{xx}&=\frac{2n_{cr}}{A(1-n/n_{cr})}, \quad n<n_{cr},\\ \chi_{xx}&=\frac{2n_{cr}}{A(n^2/n_{cr}^2-1)}, \quad n>n_{cr}.\end{aligned} \qquad (28)$$

Our calculation, just as in the derivation of (25)—(27), is valid only at $n \gg n_1 \sim n_{cr}$. Formulas (28) contain, besides the presence of the singularity, the correct asymptotic form at $n \gg n_{cr}$ and as $n \to 0$. For half-integer I the susceptibility of the type in question has no singularities and decreases with increasing n.

At low concentrations, for impurities with half-integer spin, the most important is the susceptibility of the other type. It takes place independently of the type of matrix, and its presence is connected with the anisotropy of the xy model, which describes the interaction of the impurity spins. In the xy model, the value of the saturation moment $\langle I^x\rangle$ is smaller than $(2I + 1)/4$, since the x and y projections of the total moment do not commute with the Hamiltonian of the xy model (6). The external magnetic field directed along the axis magnetizes additionally the spins of the impurities, and this leads to a nonzero susceptibility.

To estimate this susceptibility, we consider a pair of impurities whose interaction with the neighbors is much smaller than their interaction with each other (for the sake of argument, we consider impurities in a weakly-anisotropic antiferromagnet). If $n < a^{-3}$, then the potential falls off exponentially and only the interaction with the nearest neighbor is of significance to us. The probability that impurities located at a distance r are nearest neighbors is equal to $\exp(-\frac{4}{3}\pi nr^3)$.[14] Differentiating the expression for the ground-state energy of this pair in a transverse magnetic field (16), we obtain the susceptibility of the pair in the xy plane:

$$\begin{aligned}\chi_\perp(\mathbf{r})&=0, \text{ if } V_{\alpha\alpha'}(\mathbf{r})<0,\\ \chi_\perp(\mathbf{r})&=2/V(\mathbf{r}), \text{ if } V_{\alpha\alpha'}(\mathbf{r})>0.\end{aligned}$$

Averaging $\chi_\perp(r)$ over all the possible pairs, we get

$$\chi_\perp = \frac{n}{4}\int \chi_\perp(\mathbf{r}) \exp\left(-\frac{9}{4}\pi n r^3\right)\cdot 4\pi n r^2\, dr$$
$$= \frac{32(2\pi)^{1/2}}{729}\frac{(g_\perp \mu_B)^2}{T^*}(na_0^3)^{-3/4}\exp\left[\frac{8}{27}(na_0^3)^{-1/2}\right]. \qquad (29)$$

The concentration dependence of the susceptibility (29) is determined by the exponential factor, with $\chi_\perp$ increasing sharply with decreasing concentration.

Similar estimates for complexes made up of a large number of atoms yield the same concentration dependence of the argument of the exponential for $\chi_\perp$, as in (29), so that we can assume

$$\chi_\perp \sim \exp[\delta(na_0^3)^{-1/2}], \qquad (30)$$

where δ is a numerical factor no smaller, in any case, than $8/27$. The concentration dependence of the pre-exponential factor can, of course not be obtained from these estimates.

For quadrupole impurities in metamagnets we can show that

$$\chi_{xx} \sim \exp(\delta_1 n/n_1), \qquad (31)$$

where x is the direction of the spontaneous moment of the impurities. The concentration dependence differs from (30) because of the layered character of the impurity distribution. Formulas (29)–(31) are valid at sufficiently low temperatures, when the obtained susceptibilities are lower than the Langevin susceptibility.

In the case of low concentrations $n \ll n_0$ and $n \ll n_1$, the Van Vleck quadrupole susceptibility, which is proportional to A^{-1}, is negligibly small in comparison with χ given by (30) and (31). The susceptibility along the z axis at low concentrations depends on n in the same manner as χ_{xx}, but the numerical coefficients in the argument of the exponential can be different. Impurities with integer spins at low concentrations constitute Van Vleck paramagnets even at $T = 0$, with a transverse susceptibility equal to $2(g_\perp \mu_B)^2 A^{-1}$ for $I = 1$.

CONCLUSION

An investigation of the quadrupole centers in antiferromagnets is of interest from two points of view. From the point of view of the theory of disordered systems, quadrupole impurities are a new class of disordered magnets with a unique interaction law. In weakly-anisotropic antiferromagnets, by varying the concentration of the quadrupole centers, it is possible to change the form of the $V_{\alpha\alpha'}(r)$ dependence at characteristic distances, retaining an alternating-sign potential. Therefore an experimental investigation of quadrupole centers in antiferromagnets would make it possible to ascertain, in particular, whether the basic property of magnetic glasses of the CuMn type, namely the finite character of the density of states at zero energy[2], is due to the concrete character of the decrease of the potential ($V_{RKKY} \sim r^{-3}$), or whether it is due only to the fact that the potential is of alternating sign. This would be all the more interesting because there is at present no consistent theory of magnetic glasses.

We note also that in certain matrices there can occur a new type of interaction, namely an antiferromagnetic exponentially-decreasing potential. The properties of such systems can differ significantly from the properties of other disordered magnets.

On the other hand, as already shown, doping with quadrupole centers makes it possible to change significantly the properties of the antiferromagnetic matrix. The corresponding concentration and temperature dependences have a clearly pronounced anomalous character and therefore can be observed in experiment relatively easily.

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36