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ANTIFERROMAGNETISM DUE TO SPIN-PHONON INTERACTION

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It is shown that spin-spin interaction via the phonon field leads to an antiferromagnetic state when magnetic dipole-dipole interactions are taken into account. A number of experimental facts are explained on the basis of this model.

1. INTRODUCTION

THERE is a large group of magnetic substances which, although they undergo phase transitions from a paramagnetic to a ferro- or anti-ferromagnetic state, have such small exchange interactions between the magnetic particles that it is difficult to explain the emergence of spin ordering. Thus, for example, in the well known experiments on the adiabatic demagnetization of potassium-chrome and iron-ammonium alums (see, e.g., [1]) it was established that at very low temperatures these salts made a transition to an antiferromagnetic state with transition temperatures of 0.004 and 0.03° K, respectively. The exchange interactions of the Cr^{3+} and Fe^{3+} ions in these crystals are evidently insignificant, and therefore it is usual to consider that the phase transition is caused in this case by magnetic dipole-dipole interactions.[2] However, the facts show that it is not so simple. In the majority of paramagnetic ions in a crystalline electric field of cubic symmetry the lowest energy level has only spin degeneracy. In a weak field of lower symmetry (usually axial, described by the Hamiltonian DS_z^2, where S is the ionic spin), this degeneracy is removed down to the Kramers doublets. O'Brien[3] has shown, in a theoretical investigation of the nature of the antiferromagnetism of potassium-chrome alum, that dipole-dipole interactions can lead to antiferromagnetism in the special case when the Kramers doublet $|\pm 3/2\rangle$ lies lowest (sign of D negative). Apparently, the sign was identified with the sign of D of chromium-methylamine alums, which has been determined by paramagnetic resonance[4] (in the paper there is a corresponding citation). However, in ammonium alums of chromium the sign of D is positive,[5] and the question of the sign of D and consequently of the nature of the antiferromagnetism in potassium-chrome alums (and likewise iron-ammonium alums) remains an open one. Also unexplained is the great difference in the transition temperatures of the chromium and iron alums (approximately 10 times). Besides, in many cases in which the spin ordering is attributed to indirect exchange, the calculations of this interaction are so complicated that many assumptions are made, decreasing the reliability of these calculations.

Hence, it would be of interest to consider whether the magnetic ordering could be brought about by means of an interaction with the phonon field, which has been thoroughly studied recently in connection with the theory of superconductivity. The mechanism of the interaction of the spins of paramagnetic ions via the phonon field is essentially different from that of conduction electrons. Estimates of the magnitude of this interaction were first made for the iron-group ions by Sugihara[6] and for the rare-earth group in papers by Aminov, Morocha, and Khabibullin.[7] A general investigation of spin-spin interaction via the phonon field was given by Aminov and the present author;[8] in the case for which retardation effects can be neglected, a pair-interaction operator is obtained.

2. THE INTERACTION HAMILTONIAN

In an attempt to make a direct application of the operator of the spin-spin interaction given in [8], it became immediately clear that no magnetic ordering of the spins could arise. The reason is simple. The most significant part of the interaction of the ionic spins with the phonons is electrical in nature; hence, according to Kramers' theorem, states with spin components m and − m have the same energy, and consequently no magnetic ordering arises. This is expressed formally by saying that the matrix elements of the spin interaction obey quadrupolar selection rules. This situation, however, changes significantly in the presence of a magnetic field or some anisotropy field of magnetic character. The magnetic dipole-dipole interaction can always play the role of such a field. Thus, the problem arises of obtaining the operator for the spin-spin interaction via the phonon field, taking dipole-dipole interactions into account.

We shall write the Hamiltonian of two particles in a phonon field as follows:

$$\mathcal{H} = \sum_{j=1,2} \mathcal{H}^j_{\mathrm{cr}} + \mathcal{H}_{\mathrm{ph}} + \mathcal{H}^{12}_{\mathrm{dd}} + \sum_{j=1,2} \mathcal{H}^j_{\text{s-ph}}, \qquad (1)$$

where $\mathcal{H}^j_{\mathrm{cr}}$ is the Hamiltonian of the j-th spin describing the splitting of the spin levels in the crystalline electric field, $\mathcal{H}_{\mathrm{ph}}$ is the Hamiltonian of the phonon field, $\mathcal{H}_{\mathrm{dd}}$ is the Hamiltonian of the magnetic dipole-dipole interactions (we will write $\mathcal{H}^{12}_{\mathrm{dd}} = P^{12}_{ik}S^1_iS^2_k$; i, k = x, y, z), and $\mathcal{H}^j_{\text{s-ph}}$ is the Hamiltonian of the spin-phonon interaction.

In the case $S > 1/2$, this last can be represented by the formula

$$\mathcal{H}_{\text{s-ph}} = G_{ikst}Q_{ik}e_{st}, \quad i, k, s, t = x, y, z. \qquad (2)$$

In Eq. (2) $Q_{ik} = (1/2)(S_iS_k + S_kS_i)$, $\mathbf{e}$ is the tensor of the lattice deformation, and $\mathbf{G}$ is a tensor of the fourth rank characterizing the magnitude of the spin-phonon interaction.

It is easy to see that in the case of cubic symmetry of the surroundings of the paramagnetic ion the tensor can be defined by only two independent constants.[9,10] Neglecting retardation effects, which are insignificant in concentrated magnetic substances,[8] we obtain the interaction in the framework of perturbation theory. We shall assume that the degeneracy in direction of the spins is removed by the electric field and the temperature is such that all the particles are in the states of the lower Kramers doublet (these states will be symbolized by the letters m, n, and the excited ones by μ, ν). Hence it is necessary to write the effective spin Hamiltonian of the interaction only for this doublet.

To this end it is convenient to use the operator variant of perturbation theory for degenerate levels, as employed by Bogolyubov.[11] Taking $\mathcal{H}_{\mathrm{cr}}$ and $\mathcal{H}_{\mathrm{ph}}$ as the unperturbed Hamiltonian and transforming to the representation of the second quantization, we obtain in third approximation

$$\begin{aligned}\mathcal{H}_{\mathrm{ss}} = \sum_{\substack{\mathbf{q}p\\ mm'nn'}} & \frac{\hbar\omega_{qp}}{8\rho V v^2} e^{i\mathbf{q}\mathbf{r}_{12}} G_{ikst}G_{i'k's't'}P^{12}_{i''k''}(\varkappa_s\lambda^p_t + \lambda^p_s\varkappa_t)\\ & \times(\varkappa_{s'}\lambda^p_{t'} + \lambda^p_{s'}\varkappa_{t'})\left\{\sum_{\mu\nu}\frac{1}{\Delta_\nu(\hbar\omega_{qp}+\Delta_\mu)}[(Q^2_{ik})_{m\mu}(S^1_{i''})_{\mu m'}\right.\\ & \times(Q^2_{i'k'})_{n\nu}(S^2_{k''})_{\nu n'} + \text{к. с.}]\\ & + \sum_\mu\left(\frac{1}{\Delta_\mu\hbar\omega_{qp}} + \frac{1}{(\Delta_\mu+\hbar\omega_{qp})\hbar\omega_{qp}}\right)\\ & \times[\langle Q^1_{ik}\rangle(S^1_{i''})_{mm'}((Q^2_{i'k'})_{n\mu}(S^2_{k''})_{\mu n'} + \text{к. с.})\\ & + \langle Q^2_{i'k'}\rangle(S^2_{k''})_{nn'}((Q^1_{ik})_{m\mu}(S^1_{i''})_{\mu m'} + \text{к. с.})]\\ & \left. + \frac{2}{(\hbar\omega_{qp})^2}\langle Q^1_{ik}\rangle\langle Q^2_{i'k'}\rangle\langle S^1_{i''}\rangle_{mm'}\langle S^2_{k''}\rangle_{nn'}\right\}\overset{+}{a}_{1m}a_{1m'}\overset{+}{a}_{2n}a_{2n'};\end{aligned}$$

$$\sum_m \overset{+}{a}_m a_m \approx 1. \qquad (3)$$

where $\mathbf{q}$ is the wave vector of a phonon, κ is its unit vector, λ^p is the unit vector of the wave polarization, p is the number of the normal mode, v is the speed of sound, ρ is the density of the crystal, V is its volume, $\mathbf{r}_{12}$ is the radius vector from spin 1 to spin 2, and $\Delta_\nu = E_\nu - E_m$ is the magnitude of the splitting of the energy levels. In addition, we consider that $(Q_{ik})_{mm'} = 0$ for $m \neq m'$ and denote $(Q_{ik})_{mm} = (Q_{ik})_{m'm'}$ by Q_{ik}.

We shall write down the result of the summation over q and p for an axial crystalline field and cubic environment for the paramagnetic ion. If $\Delta \ll \hbar v/r_{12}$ (which is true for almost all the ions of the iron group) and $D > 0$, then the largest part of the Hamiltonian (which corresponds to the first sum in curly brackets in Eq. (3), since the second sum is small if the paramagnetic ions form a lattice of high symmetry) has the form

$$\begin{aligned}\mathcal{H}_{\mathrm{ss}} &= 2J_1\sigma^1_z\sigma^2_z + J_2(\sigma^1_+\sigma^2_- + \sigma^1_-\sigma^2_+);\\ J_1 &= \tfrac{1}{2}AG^2_{44}(2-3\cos^2\vartheta),\\ J_2 &= \tfrac{1}{8}A(\tfrac{9}{16}G^2_{11} + G^2_{44})[S(S+1) + \tfrac{1}{4}](1-3\cos^2\vartheta)^2,\\ A &= g^2\beta^2[S(S+1) - \tfrac{3}{4}]^2/\pi\Delta\rho v^2 r^6_{12}, \end{aligned} \qquad (4)$$

where σ is the effective spin (σ = 1/2), $\sigma_\pm = \sigma_x \pm i\sigma_y$, ϑ is the angle between $\mathbf{r}_{12}$ and the axis of symmetry of the electric field (z), and G_{11} and G_{44} are components of the tensor $\mathbf{G}$ in Voigt symbols (used in elasticity theory). We have not written out that part of the Hamiltonian which gives a contribution to the average energy only in second order.

If $D < 0$, the factor $[S(S+1) - 3/4]^2$ appearing in J_1 in Eq. (4) must be replaced by $S^2(2S-1)^2$ and $J_2 = 0$ for $S > 3/2$.

In case $\Delta > \hbar v/r_{12}$, valid for the majority of rare-earth ions, we have for the principal part of the Hamiltonian (the lower doublet is $|\pm S\rangle$)

$$J_1 = \frac{3\beta^2S^4(2S-1)^2G^2_{11}}{8\pi^2\hbar\rho v^3 r^5_{12}}(1-3\cos^2\vartheta)^2, \quad J_2 = 0. \qquad (5)$$

In the case of the rare-earth ions, we must replace the spin S by the total moment J.

3. THE GROUND STATE

Let us emphasize first that in all the cases considered for the majority of crystal structures

$J_1 > 0$, which means that the interactions considered here will evidently always lead to antiferromagnetic ordering.

As an example of a substance containing iron-group ions, we shall take potassium chrome alum. The elementary cell of the alum contains four non-equivalent Cr^{3+} ions, the crystalline-field symmetry axes of which are directed along the cube diagonals. Transforming J_1 and J_2 to the cubic axes, we obtain that for the nearest neighbors in each sublattice $J_2 = 0$ and $J_1 = 1/2\, AG_{44}^2$. Hence, neglecting the action of the sublattices on each other and the direct effect of the dipole-dipole interactions, we can compute the magnetization by the molecular field method. The calculation is trivial and shows that as the temperature is lowered each of the sublattices undergoes a phase transition to the antiferromagnetic state such that the spins σ of each of them are oriented along the body diagonals of the cube. The transition temperature is $T_t = (9/2) J_1$.

$$T_t = \frac{9}{2} J_1.$$

Let us make a numerical estimate. The magnitude of G_{44} has been measured for Cr^{3+} in MgO, and equals 6.5 cm^{-1}.[12] In estimating a figure for alum, we take into account that the relaxation time of Cr^{3+} in MgO, where the relaxation is due to one-phonon processes (and proportional to G^{-2}), is 200 times longer than in the alum;[13] thus we have $G_{44} \approx 100\ cm^{-1}$. Utilizing further the constants $\rho = 2$, $v = 2 \times 10^5$ cm/sec, $r_{12} = 1.2 \times 10^{-7}$ cm, $S = 3/2$, $g = 2$, and $\Delta = 0.3\ cm^{-1}$,[14] we obtain $T_t \approx 0.001°$ K, which agrees with experiment in order of magnitude. In the case of the iron alum, $S = 5/2$ and Δ is 10 times smaller; this gives a value for T_t that is an order of magnitude higher than that for the chrome alum, which agrees well with the experimental results.

We now present an example from the rare-earth group. We estimate the transition temperature of metallic cerium with the close-packed cubic structure. The lower level of Ce^{3+} in a crystalline field (ground state $^2F_{5/2}$) is a doublet the wave functions of which are a mixture of the states $| \pm 3/2 \rangle$ and $| \pm 5/2 \rangle$. Hence, T_t can be estimated as $T_t \sim J_1$, with the substitution $S = 5/2$ in Eq. (5). We estimate the constant G from the following considerations: since in the rare-earths the electric field acts directly on the total moment of the ion, we obtain the spin-phonon interaction by expanding the Coulomb interaction of the particles in a power series in the coordinates of the f-electrons and their relative displacements. Thus $G \approx \alpha q^2 \overline{r^2}/r_{12}^3$, where q is the charge on the ion, $\overline{r^2}$ is the mean square distance of the f-electrons from the nucleus, and α is a transformation coefficient from electronic coordinates to spin operators [for Ce^{3+} we have $\alpha = -(2/35)$[14]]. Using the values $q = 2.5e$ (e the electronic charge), $\overline{r^2} = 0.5 \times 10^{-16}\ cm^2$, $r_{12} = 3.6 \times 10^{-8}$ cm, and $v = 4 \times 10^5$ cm/sec, we obtain a magnitude of a few degrees for T_t. The experimental value is 12° K.[15]

The foregoing evidently permits the assertion that in a whole group of substances the antiferromagnetic transition is determined by spin-spin interactions via the phonon field.

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