SPIN-SPIN INTERACTION VIA A PHONON FIELD IN PARAMAGNETIC CRYSTALS

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Spin coupling via a phonon field is treated by the methods of quantum field theory. The energy of paired spin interaction is written in operator form for cases in which retardation can be neglected. The effect of this interaction on the shape of the resonance lines is estimated.

SPIN-SPIN interaction in paramagnets is usually considered to be of two types: exchange and magnetic dipole-dipole. The first is an interaction that is essentially of the contact type; the second acts through a photon field, neglecting retardation, i.e., in the approximation of an instantaneous interaction. It is clear, however, that the presence of a spin coupling with a phonon field, like an interaction with a photon field, will lead to additional coupling between the spins in crystals, which in some cases can be extremely effective. In this paper we shall carry through a calculation of the interaction of spins via a phonon field, which in the main will be analogous to the investigation of the interaction between two charges in quantum electrodynamics.

We shall write the Hamiltonian of the spins and phonons in the form

$$H = H_0 + H_1, \qquad H_0 = \sum_{m,i} E_m a_{mi}^+ a_{mi} + \sum_{k} \hbar \omega_k b_k^+ b_k,$$

$$H_1 = i \sum_{imnq} G_{imn}^{q} a_{mi}^+ a_{ni} (b_q e^{i q r_i} - b_q^+ e^{-i q r_i}). \qquad (1)$$

Here E_m is the energy of a spin in state m, a_{mi}^+ and a_{mi} are creation and annihilation operators for the i-th spin in state m; and $\hbar \omega_k$, b_k^+, and b_k are the corresponding quantities pertaining to a phonon with wave vector k.

The matrix of the interaction of two spins is obtained by selecting those components of the second-order scattering matrix in which a neutralization over the states of the phonons is effected:

$$S_{ij}^{(2)} = - \frac{\pi i}{\hbar^2} \sum_{mnm'n'q} G_{imn}^{q} G_{jm'n'}^{q} a_{mi}^+ a_{ni} a_{m'j}^+ a_{n'j}$$

$$\times \left\{ n_q e^{-i q r} \zeta \left(\frac{\omega_q^2 - \omega_{mn}^2}{2\omega_q} \right) \right.$$

$$\left. + (1 + n_q) e^{i q r} \zeta \left(\frac{\omega_q^2 - \omega_{mn}^2}{-2\omega_q} \right) \right\} \delta(\omega_{mn} + \omega_{m'n'}).$$

Here n_q is the number of phonons in state q, r is the distance between the i-th and j-th lattice points, $\delta(x)$ is the usual δ-function. Representing the energy of the spin-phonon interaction in the form

$$H_1^i = \sum_{\alpha} \varepsilon_\alpha Q_\alpha^i F^\alpha (\mathsf{S}_i), \qquad (2)$$

we have

$$G_{imn}^{q} = \sum_{\alpha} \varepsilon_\alpha (\hbar \omega_q / M)^{1/2} (R/v) a_{\alpha q}^{i} F_{mn}^{\alpha}. \qquad (3)$$

In Eqs. (2) and (3), Q_α^i are the normal vibrations of the complex surrounding the i-th spin, $F^\alpha(\mathsf{S}_i)$ are some spin functions, ε_α is a constant characterizing the magnitude of the spin-phonon interaction, M is the crystal mass, R is the size of the complex, v is the speed of sound, which we consider to be constant for all types of vibration, and $a_{\alpha q}^i$ are functions of the unit vectors of polarization and of the wave vector of phonon q; besides this, we here make use of the assumption that the phonon wavelength $\lambda \gg R$.

We obtain further, by changing the summation over the wave vectors of the phonons to an integration

$$S_{ij}^{(2)} = - 2\pi i \sum_{mnm'n'\alpha\beta} a_{mi}^+ a_{ni} a_{m'j}^+ a_{n'j} F_{imn}^{\alpha} F_{jm'n'}^{\beta} \{ A_{\alpha\beta}(r)$$

$$+ i (2n_\omega + 1) B_{\alpha\beta}(r) \} \delta(\omega_{mn} + \omega_{m'n'}),$$

$$A_{\alpha\beta}(r) = \frac{\varepsilon_\alpha \varepsilon_\beta R^2}{2\pi\hbar\rho v^2} \left(p_{\alpha\beta} \frac{\omega_{mn}^2}{v^2 r} \cos\varphi + q_{\alpha\beta} \frac{\omega_{mn}}{vr^2} \sin\varphi + s_{\alpha\beta} \frac{1}{r^3} \cos\varphi \right),$$

$$B_{\alpha\beta}(r) = \frac{\varepsilon_\alpha \varepsilon_\beta R^2}{2\pi\hbar\rho v^2} \left(p_{\alpha\beta} \frac{\omega_{mn}^2}{v^2 r} \sin\varphi + q_{\alpha\beta} \frac{\omega_{mn}}{vr^2} \cos\varphi + s_{\alpha\beta} \frac{1}{r^3} \sin\varphi \right),$$

$$\varphi = \omega_{mn} r / v. \qquad (4)$$

Here p, q, and s are all functions of r/r, and their order of magnitude is unity, and ρ is the density of the crystal. As a result the perturbation

energy U_{ij}, which is related, according to [1] to $S_{ij}^{(2)}$ by the equality

$$S_{ij}^{(2)} = - 2\pi i U_{ij} \, \delta \, (\hbar\omega_{mn} + \hbar\omega_{m'n'}),$$

turns out to be complex, because the spin levels are non-stationary.

The dependence of the spin interaction on the spacing between spins is not completely determined from Eq. (4), since the phonon can be scattered in the path between spins either by another phonon or by some kind of obstruction. In connection with this it is necessary to supplement Eq. (4) with the condition $r < l_{ph}$, where l_{ph} is the free path of a phonon of frequency ω_{mn}.

If l_{ph} is small (e.g., at high temperatures, in crystals with a large number of defects, etc.), then the retardation part of the interaction of spins via the phonon field can be neglected; in this case it is possible to speak of the potential energy of a direct pair interaction, which can be written down in explicit form.

We shall write the energy operator of the direct interaction between spins for the most widely distributed case, when the paramagnetic particle is situated in an octahedral site:

$$U_{ij}^{ph} = A r_{ij}^{-3} \sum_{\alpha, \beta=1}^{6} s_{\alpha\beta} \varepsilon_\alpha \varepsilon_\beta F^\alpha (S_j) F^\beta (S_i), \quad A = R^2 (2\pi\rho v^2)^{-1};$$

$$s_{11} = s_{24} = 0, \quad s_{12} = \sqrt{2} s_{23} = \sqrt{3/2} (X^2 - Y^2),$$

$$s_{13} = \sqrt{2} s_{22} = -\sqrt{2} s_{33} = \sqrt{2} s_{44} = \sqrt{1/2} (1 - 3Z^2),$$

$$s_{14} = \sqrt{2} s_{34} = \sqrt{8/3} s_{56} = \sqrt{6} XY,$$

$$s_{15} = \sqrt{8/3} s_{25} = -\sqrt{8} s_{35} = \sqrt{8/3} s_{46} = \sqrt{6} XZ,$$

$$s_{16} = -\sqrt{8/3} s_{26} = -\sqrt{8} s_{36} = \sqrt{8/3} s_{45} = -\sqrt{6} YZ,$$

$$s_{55} = \frac{1}{2} (1 - Y^2), \quad s_{66} = \frac{1}{2} (1 - X^2). \tag{5}$$

Here $X = x_{ij}/r_{ij}$, $Y = y_{ij}/r_{ij}$, and $Z = z_{ij}/r_{ij}$. The summation limits are imposed by the fact that the spin-phonon interaction is determined by the symmetrical normal vibrations of the complex (cf. [3]), of which there are six for an octahedron.* We note that one of the terms in Eq. (5) with the factor s_{22} for $Z = 1$ was obtained by Sugihara.[2] The constants ε_α and the functions of the spin variables $F^\alpha(S)$ are determined by the kind of paramagnetic particles and were given for iron group ions in the review by Al'tshuler, Kochelaev, and Leushin.[4] We shall indicate only the gen-

eral properties of these quantities. If the paramagnetic ion has a spin $S = \frac{1}{2}$, then the constants ε_α are proportional to the intensity of the magnetic field H, which arises from the fact that the Kramers doublet can be split only by a magnetic field (see [3]). In this case $U_{ij}^{ph} \sim H^2$. It is obvious that the functions $F^\alpha(S)$ are linear in the spin projections. If $S > \frac{1}{2}$, then U_{ij}^{ph} does not depend on the magnetic field and the functions $F^\alpha(S)$ are usually quadratic in the spin variables.

The estimate of the order of magnitude of the interactions considered is made much clearer by a comparison with the usual spin-spin interactions, e.g., dipole-dipole U_{ij}^{d-d}. For comparison we consider the effect of both types of interaction on the width of a paramagnetic resonance line. For the sake of simplicity, we select a paramagnetic ion with spin $S = \frac{1}{2}$, e.g., Cu^{2+}, in a crystalline field of tetragonal symmetry, in which the symmetry axis is directed along one of the four-fold axes of the oxtahedral complex (OZ). The external magnetic field is directed perpendicular to this axis (in this case the spin-phonon interaction is a maximum [4]), along the other four-fold axis (OX). Then the reduced second moment of the paramagnetic resonance absorption curve, for a direction of the alternating magnetic field perpendicular to the constant field, equals

$$\langle (\Delta v)^2 \rangle = \frac{A^2 \varepsilon_2^4}{432\pi^2\hbar^2} \sum_i' \frac{(1 - 3Z^2)^2}{r_{ij}^6},$$

$$\varepsilon_2 = -\frac{12}{7} \left(\frac{ee'}{R^2}\right) \left(\frac{\lambda g\beta H}{\Delta\delta}\right) \left(3 \frac{\overline{r_0^2}}{R^2} + \frac{25}{12} \frac{\overline{r_0^4}}{R^4}\right), \tag{6}$$

where we have made use of Eq. (2) of [5]. Here e and e' are the charges on the electron and on the particle closest to the paramagnetic ion, λ is the spin-orbit coupling constant, $\overline{r_0^2}$ and $\overline{r_0^4}$ are the mean square and fourth degree separation of the d electron from the nucleus of the paramagnetic ion, and Δ and δ are the splittings of the orbital levels in electric fields of cubic and tetragonal symmetry respectively. Using $\lambda = 700$ cm^{-1}, $\delta = 1400$ cm^{-1}, $\Delta = 12\,000$ cm^{-1}[6], and H = 10 kOe we obtain for a cubic lattice with parameter $a = 10^{-7}$ cm

$$\langle (\Delta v)^2 \rangle^{1/2} \approx 2 \cdot 10^7 \text{ cps.}$$

This is one or two orders less than the width of the resonance line caused by magnetic dipole-dipole interactions. We obtain just such an approximate result for the majority of the ions of the iron group elements. However, this group contains paramagnetic ions whose spin interac-

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*Usually the term in H_1^i, which includes the wholly symmetrical vibration Q_1 is discarded, since it is assumed that the terms linear in the vibrations of the complex are bound to the Jahn-Teller effect and Q_1 does not contribute to this effect. However, it seems more natural to explain the presence of linear terms by the difference in the equilibrium configurations of the complex when the spin is in the ground or excited states. In this case the term in Q_1 should be retained.

tion with the phonon field is anomalously large. Ti^{3+} is an example of such an ion. In order to estimate the magnitude of the spin-spin interaction we are considering, it is necessary in this case to replace $\Delta\delta$ in Eq. (6) by δ^2 (see [4]). Hence it can be seen that U_{ij}^{ph} is of the same order as U_{ij}^{d-d} and larger. A similar result is also obtained for salts of elements of the rare-earth group.

At low temperatures, when the phonon scattering is not large, the retardation part of the spin-spin interaction $S_{ij}^{(2)}$ begins to play an important role. The distinguishing features of this part are the strong dependence on the magnitude of the spin splittings (for the first term in Eq. (4) $S_{ij\ ret}^{(2)} \sim \omega^4$ for $S = \frac{1}{2}$ and $S_{ij}^{(2)} \sim \omega^2$ for $S > \frac{1}{2}$) and action at a distance (of order $1/r$). With decreasing concentration of paramagnetic centers, because of the latter property, $S_{ij\ ret}^{(2)}$ inevitably will begin to dominate the interaction between spins at some value of their concentration. It is curious to note that the more perfect the crystal, the more significant the role of $S_{ij\ ret}^{(2)}$.

In conclusion we emphasize the obvious circumstance that there exists an additional coupling energy between ions in a crystal, caused by the interaction of the orbital moments of the bound electrons via the phonon field. If the splitting of the orbital levels is less than the Debye temperature Θ, then the coupling energy will be extremely significant. The calculation procedure for this interaction is similar to that presented above, the only difference being that in case $\Delta < k\Theta$ it is significantly simpler.

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