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THE INFLUENCE OF CRYSTAL DEFECTS ON SPIN-LATTICE RELAXATION

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1. Recently, intensive study has been devoted to the spin-lattice interaction in paramagnetic crystals. In this connection, serious discrepancies have appeared between theory and experiment; apparently, these can be explained if defects of the crystal lattices are taken into account. Experimental investigations are carried out for the most part on crystals that are strongly diluted magnetically. This means that paramagnetic ions have been introduced into a diamagnetic crystal in place of some atoms, and defects have thereby been created artificially. Defects of other types may also play an essential role, for example microcracks that arise when crystals are cooled to the temperature of liquid helium.

It is well known that the spin-lattice interaction is determined by how strongly the distances between the paramagnetic center and the surrounding atoms change under the influence of lattice vibrations. In the existing theory of spin-lattice relaxation, the relative displacements of neighboring atoms are calculated under the assumption that the crystal is ideal and that its vibrations are described by Debye waves. Scattering of waves by defects of the crystal, while causing small changes in the amplitude of the vibrations, may, however, lead to the creation of relative displacements of the nearest atoms much larger than the displacements caused by Debye waves. In our calculations we use the theory of vibrations of nonideal lattices of I. M. Lifshitz (1,2).

2. The operator of the spin-lattice interaction is a function of the coordinates of the spin and of the displacements of the atom carrying the spin relative to the surrounding particles. Since for spin-lattice relaxation in most cases only symmetric vibrations are important, it is necessary to know only the relative displacements of particles situated symmetrically with respect to the paramagnetic center. We shall take into account only the nearest particles.

Let us suppose that a monatomic crystal lattice has a defect at the point with radius vector $\mathbf{R}^*$. Then the amplitude of the relative displacement of two particles, caused by a plane wave with wave vector $\mathbf{k}$ and by the corresponding scattered wave, according to (1,2), in the case of small values of k, is equal to

$$\varphi_\sigma(\mathbf{R}_1) - \varphi_\sigma(\mathbf{R}_2) \approx \frac{2\pi a \cos\gamma}{|\mathbf{R}_0 - \mathbf{R}^*|^2 \Omega} e^{ik|\mathbf{R}_0 - \mathbf{R}^*|} \sum_t \frac{C^t_\sigma(kn)}{v_t^2} + \varepsilon; \tag{1}$$

$$C^t_\sigma(\vec{x}) = \sum_{\sigma_1 \sigma_l k l} \Lambda^{\sigma_k \sigma_l}_{R_k R_l} \lambda^t_{\sigma_k}(\vec{x}) \lambda^t_\sigma(\vec{x}) \lambda_{\sigma_l}(\mathbf{k}), \qquad \sigma = x, y, z.$$

Notation: $\mathbf{R}_0$, $\mathbf{R}_{1,2}$ are the radius vectors of the paramagnetic atom and of the nearest particle; a is the distance between their equilibrium positions; γ is the angle between the vectors $\mathbf{R}_0 - \mathbf{R}^*$ and $\mathbf{R}_1 - \mathbf{R}_2$; $\mathbf{n} = (\mathbf{R}_0 - \mathbf{R}^*)/|\mathbf{R}_0 - \mathbf{R}^*|$; Ω is the volume of a cell of the reciprocal lattice; t is the number of a vibration branch; v_t is the corresponding sound velocity; $\lambda^t(\mathbf{k})$ is the polarization vector; $\Lambda^{\sigma_k \sigma_l}_{R_k \mathbf{R}_l}$ is the matrix describing the change, introduced by the defect, in the interaction coefficients between atoms; ε denotes terms proportional to the length of the wave vector $\mathbf{k}$ and to higher powers of $1/|\mathbf{R}_0 - \mathbf{R}^*|$. Here the following assumptions have been used: the perturbation introduced by the defect is small; the dimensions of the inhomogeneity are small compared with the wavelength; the vibration frequency does not depend on the direction of $\mathbf{k}$, i.e. $\omega_t^2 = v_t^2 k^2$.

The influence of crystal defects on spin-lattice relaxation will be determining if the condition

$$\frac{2\pi a \cos\gamma}{|\mathbf{R}_0 - \mathbf{R}^*|^2 \Omega} \sum_t \frac{C^t_\sigma(kn)}{v_t^2} > k. \tag{2}$$

is satisfied.

It is easy to see that for two-phonon processes the influence of defects may be insignificant, since the largest contribution to the probability of a relaxation transition is made by vibrations with a large value of the wave vector. However, for direct processes condition (2) will be fulfilled almost always because of the smallness of the frequency of the "spin quantum" (of the order of 10^{-3}–$1\ \text{cm}^{-1}$). For simplicity let us assume that the "defectiveness" of the crystal consists in the fact that, for one of the atoms, all the interaction coefficients have changed by some amount ξ. Then the matrix $\Lambda^{\sigma_k \sigma_l}_{R_k \mathbf{R}_l}$ will take the form:

$$\Lambda^{\sigma_1 \sigma_2}_{R_k \mathbf{R}_l} = \xi \left\{ -z \delta_{R_k \mathbf{R}^*} \delta_{R_l \mathbf{R}^*} + \sum_m \left(\delta_{R_k \mathbf{R}^*} \delta_{R_l \mathbf{R}_m} + \delta_{R_k \mathbf{R}_m} \delta_{R_l \mathbf{R}^*} \right) \right\}, \tag{3}$$

where $\mathbf{R}_m$ is the radius vector of a particle nearest to the paramagnetic atom, and z is the number of these particles.

Let us consider a concrete example: relaxation of the ion Cr^{3+} in an octahedral environment. The operator of the spin-lattice interaction is (3)

$$\mathcal{H}_{c-p} = \varepsilon_1 \left(\mathcal{H}^{(2)}Q_2 + \mathcal{H}^{(3)}Q_3\right) + \varepsilon_2 \left(\mathcal{H}^{(4)}Q_4 + \mathcal{H}^{(5)}Q_5 + \mathcal{H}^{(6)}Q_6\right); \quad (4)$$

$$\mathcal{H}^{(2)} = \sqrt{3}\,(S_y^2 - S_x^2), \qquad \mathcal{H}^{(3)} = (3S_z^2 - S(S+1)), \qquad \mathcal{H}^{(4)} = (S_{xS}y + S_{yS}x),$$

$$\mathcal{H}^{(5)} = (S_{xS}z + S_{zS}x), \qquad \mathcal{H}^{(6)} = (S_{yS}z + S_{zS}y);$$

$$\varepsilon_1 = 9\sqrt{3}\left(\frac{\lambda}{\Delta}\right)^2 \left(\frac{eE}{a^2}\right) \frac{\overline{r^4}}{a^4}, \qquad \varepsilon_2 = \frac{486}{25}\left(\frac{\lambda}{\Delta}\right)^2 \left(\frac{eE}{a^2}\right) \left(\frac{\overline{r^2}}{a^2} + \frac{5}{36}\frac{\overline{r^4}}{a^4}\right).$$

Here S_x, S_y, S_z are the operators of the spin projections on the cubic axes; Q_k is the normal coordinate of the octahedron; λ is the spin-orbit coupling constant; Δ is the splitting of the orbital level in the cubic field; E is the charge of the particle neighboring the Cr^{3+} ion; r is the distance from the center of the nucleus to the $3d$-electron.

The probability of a relaxation transition with the creation of one phonon is determined by the usual formula:

$$A_{pq} = \frac{2\pi}{\hbar^2}\rho_\omega \left|\langle p, n|\mathcal{H}_{c-p}|q, n+1\rangle\right|^2, \quad (5)$$

where ρ_ω is the spectral density of the oscillators of the lattice; n is the quantum number of the oscillator; p, q are spin levels.

Using (1), (3) and averaging over all directions of the relative position of the Cr^{3+} ion and the defect, we obtain:

$$A_{pq} = \frac{96\pi^4}{\hbar} \frac{a^2\xi^2\omega}{|\mathbf{R}_0 - \mathbf{R}|^4\Omega^2\rho v^7} \frac{\exp(\hbar\omega/kT)}{\exp(\hbar\omega/kT) - 1} W_{pq}; \quad (6)$$

$$W_{pq} = \varepsilon_1^2\left[|\mathcal{H}_{pq}^{(2)}|^2 + |\mathcal{H}_{pq}^{(3)}|^2\right] + \varepsilon_2^2\left[|\mathcal{H}_{pq}^{(4)}|^2 + |\mathcal{H}_{pq}^{(5)}|^2 + |\mathcal{H}_{pq}^{(6)}|^2\right],$$

where ω is the frequency of the "spin quantum" ; ρ is the density of the crystal; $v_1 = v_2 = v_3 = v$.

The principal difference between formula (6) and the usual one, obtained under the assumption of an ideal crystal (3), is as follows: the transition probability depends on the distance from the paramagnetic atom to the defect, as a result of which the relaxation time becomes dependent on the concentration of paramagnetic centers; for $\hbar\omega \ll kT$ the dependence on the frequency of the "spin quantum," and consequently on the magnetic-field strength, disappears, whereas in work (3) $A_{pq} \sim \omega^2$.

The case in which the defect is the paramagnetic atom itself is somewhat more complicated, since one cannot use the asymptotic expression (1). However, returning to the general formula (2.9) of work (1), one may observe that the part of the relative displacement that does not contain the factor k vanishes. Thus, when condition (2) is fulfilled, the relative displacements will be determined by the influence of another, nearest paramagnetic atom. In this case one may use formula (6) approximately.

3. Before proceeding to a discussion of formula (6), let us note that we do not consider the case of such low temperatures that the heat capacity of the lattice becomes so small that spin relaxation is determined by the outflow of energy to the thermostat.

As already noted, in experimental studies of spin-lattice relaxation at low temperatures, where one-phonon processes should predominate, regularities have been found (an increase of the relaxation time τ with decreasing concentration of paramagnetic centers, and an anomalous dependence on the strength of the external magnetic field) that cannot be explained within the framework of the existing theory. Let us turn to experiments with Cr^{3+} ions. A. M. Prokhorov and A. A. Manenkov (4) found that, in experiments on saturation of the paramagnetic resonance of the Cr^{3+} ion in corundum at a temperature of 4.2° K, τ depends on the ion concentration as x^{-1}–x^{-2} in the range of variation of x from $6.5 \cdot 10^{-3}$ to $5.3 \cdot 10^{-4}$ (x is the ratio of the number of Cr^{3+} ions to the number of Al^{3+} ions). This dependence disappears at room temperature. If we assume that the "defectiveness" of corundum consists mainly in the presence of Cr^{3+} ions, then the relaxation time, according to (6), turns out to depend on the concentration as $x^{-1/3}$. This dependence disappears at room temperature, since in two-phonon processes, according to the considerations given above, the influence of defects will not be determining. It is easy to see that, at a sufficiently low concentration, condition (2) will not be fulfilled. Then the relaxation time will be determined by ordinary one-phonon processes (3), and the dependence of τ on x disappears. For corundum this should occur at $x \sim 10^{-5}$. (The coupling constant of the Cr^{3+} ion with its environment in corundum is 1/3 larger than that of Al^{3+} ions, which can be roughly estimated from spectroscopic data.) The cessation of the dependence of τ on x was found in $K_3Cr_xCo_{1-x}(CN)_6$ at $x = 5 \cdot 10^{-3}$ (5). It should be taken into account that the mean distance between vacant sites for the Cr^{3+} ion in cobalt cyanide is greater than in corundum.

The influence of crystal defects on the spin-lattice relaxation of nuclear spins should be especially significant, since the magnitude of k in one-phonon processes should be 10^3 times smaller than for electron spins. From this point of view the following experiment (6) can be explained: the relaxation time of J^{127} in KJ was measured by the saturation method at at temperatures of 2–20° K. It was found that in the interval 14–20° K the dependence of τ on T and its magnitude are well explained by two-phonon processes, with τ being the same for the powder and the single crystal. But in the temperature interval 2–4° K, τ for the powder is more than 10 times shorter than for the single crystal and does not depend on the magnetic-field strength. This is in full agreement with formula (6), since in the crystallites of the powder there are many more defects; moreover, the influence of the surface may be manifest. It remains unclear, however, why there is no dependence of τ on T in this interval, whereas according to (6) it is linear.

In conclusion, we note that special experiments are required for a final clarification of the role of defects in the process of spin-lattice relaxation.

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