MAGNETIC RELAXATION OF NUCLEI IN CRYSTALS CONTAINING MAGNETIC IMPURITIES

G. R. KHUTSISHVILI

Physics Institute, Academy of Sciences, Georgian S.S.R.

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The "sphere of influence" model proposed by Jeffries to explain the experimental data on proton relaxation in dilute paramagnetic salts is analyzed critically. The effect of heating of the dipole-dipole reservoir of the magnetic ion system on nuclear relaxation is considered. A qualitative analysis indicates that when a certain inequality is satisfied, dipole-dipole reservoir heating can be neglected during nuclear relaxation, irrespective of the impurity-concentration. If the inverse inequality holds, then, at intermediate concentrations of the magnetic impurity, heating of the dipole-dipole reservoir significantly slows down relaxation of the nuclei.

1. THE question of nuclear relaxation in an ionic crystal containing a magnetic impurity has acquired great interest in connection with the progress of the method of dynamic polarization. Theoretical analysis shows that spin diffusion plays an essential role in the relaxation of the nuclei (of the host lattice) (see our review paper[1]).

Comparison of the diffusion theory of nuclear relaxation with experiment shows that there is satisfactory agreement between them when temperatures are not very low and impurity concentrations are sufficiently small. However, at helium temperatures and sufficiently high impurity concentrations (greater than about 0.5%), the agreement between experiment and theory (developed in the review[1]) is unsatisfactory. Under these conditions $\delta \gg b$ and $\tau_l \gg \tau_s$ (δ is the radius of the diffusion barrier, b is a characteristic length, τ_l and τ_s are the spin-lattice and spin-spin correlation times of the magnetic ion, respectively). If one substitutes the quantity τ_s for the correlation time τ of the z components of the spin of the magnetic ion in the formula for the relaxation time T_n of the magnetic moment of the sample, one obtains values of T_n that are two orders of magnitude smaller than the measured ones. But if τ_l is substituted for τ (this substitution, however, is illogical, since when $\tau_l \gg \tau_s$, we have $\tau = \tau_s$), we find values of T_n that are three orders of magnitude too large.

In recent papers,[2,3] Jeffries proposed the so-called sphere of influence model to explain the experimental data on the relaxation of protons in dilute paramagnetic salts.

In this paper we shall make some remarks in connection with this model of Jeffries. Then we analyze the results of Buishvili's work,[4] in which the role of the dipole-dipole reservoir of magnetic ions in nuclear relaxation is considered.

2. Let us consider a sphere with its center in the magnetic ion and of radius R (R is the radius of a sphere which fits over one magnetic ion). Symbolizing the distance from a point to the magnetic ion by r, we divide the sphere into three regions (see Fig. 1): $0 < r < r_m$ (r_m is the distance from the magnetic ion to the nearest nucleus), $r_m < r < \delta$ and $\delta < r < R$. Let us assume that $r_m \ll \delta \ll R$ and, in addition, that $\delta \gg b$. The overwhelming majority of nuclei are in region III, whereas region I contains none, in general.

Internal equilibrium of the nuclear spin system is quickly established in region III because of spin diffusion. Jeffries[2,3] assumes that in region II it is possible to introduce an average (over r) proba-

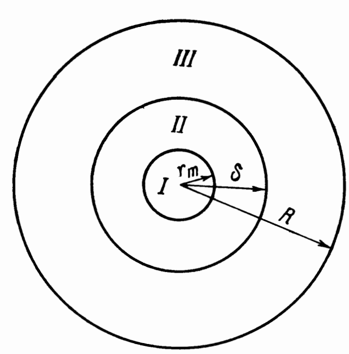

FIG. 1. Sphere of influence.

bility of nuclear relaxation; further, he supposes that the nuclei of region III have thermal contact with the magnetic ion only via the nuclei of region II and introduces the corresponding cross-relaxation time. Setting up the rate equations for the polarization of nuclei of regions II and III and solving these equations approximately, we find that the relaxation time of the total nuclear moment (which may be considered the same as the relaxation time of the nuclei in region III) is given by the formula

$$T_{\mathrm{II}}^{-1} = \langle T_{\mathrm{неп}}^{-1}(r)\rangle_{r_m,\delta}(\delta/R)^3. \qquad (1)$$

In this formula $\langle T_{\mathrm{dir}}^{-1}(r)\rangle_{r_m,\delta}$ is the average value of the probability of direct relaxation for the interval (r_m, δ). The factor $(\delta/R)^3$ gives the ratio of the heat capacities of the nuclei of regions II and III.

In our opinion, the introduction of a cross-relaxation between the nuclei of regions II and III is a dubious procedure. However, since the cross-relaxation time disappears from the final result, this assumption does not play an essential role.

A weak point of the Jeffries model is the introduction of an average relaxation probability for the nuclei of region II. Actually, in typical circumstances, $\delta/r_m = 2$ to 4, and the direct relaxation times at the distances r_m and δ differ very strongly.

Spin diffusion plays an important role in region III, whereas it is suppressed in region II. Hence, a definite role is played by the value of the direct relaxation time at the boundary between regions II and III, i.e., $T_{\mathrm{dir}}(\delta)$, in the relaxation of nuclei in region III. Therefore, instead of (1), it is more correct to write

$$T_{\mathrm{n}}^{-1} = T_{\mathrm{dir}}^{-1}(\delta)(\delta/R)^3. \qquad (2)$$

Substitution of $T_{\mathrm{dir}}(\delta)$ into (2) leads to Eq. (5.26b) in our review paper.[1]

3. In [1] we assumed that, in the case $\tau_s < \tau_l$, when a nuclear spin is reoriented, its Zeeman energy goes into the energy of the dipole-dipole reservoir of the magnetic ions. It is necessary, however, to take into account that at a sufficiently low concentration of the magnetic impurity, the energy of the dipole-dipole reservoir is less than the energy of the nuclear Zeeman interactions. As a result, the "magnetic ion dipole-dipole reservoir-to-lattice" portion may turn out to be the bottleneck in the process of energy transfer from the nuclear spins to the lattice.

In Buishvili's work,[4] the relaxation of nuclei in a crystal with a magnetic impurity was considered with the possibility of heating the dipole-dipole reservoir taken into account. In doing this, the author limited himself to a treatment of the homogeneous problem (the nuclear magnetization was assumed to be independent of position) and of the high temperature approximation. In order to further analyze the question of the role of the dipole-dipole reservoir in nuclear relaxation, we need to recall some of Buishvili's results.[4]

The Hamiltonian of the system is chosen in the form

$$\mathcal{H} = \mathcal{H}_I + \mathcal{H}_d + \mathcal{H}_l + \mathcal{H}_{Id} + \mathcal{H}_{dl}, \qquad (3)$$

where $\mathcal{H}_I$, $\mathcal{H}_d$, and $\mathcal{H}_l$ are respectively the Hamiltonians of the Zeeman system of the nuclei, the magnetic ion dipole-dipole reservoir, and the lattice (the Zeeman degrees of freedom of the magnetic ions are assumed to be in equilibrium with the lattice), $\mathcal{H}_{Id}$ is the Hamiltonian of the interaction of the spins of the nuclei and the magnetic ions, and $\mathcal{H}_{dl}$ is the Hamiltonian of the interaction of the spins of the magnetic ions with the lattice.

Symbolizing by β_I, β_d, and β_l the inverse temperatures of the nuclear Zeeman system, the dipole-dipole reservoir, and the lattice, respectively, we obtain (the dot indicates time differentiation)

$$\dot{\beta}_I = -\frac{\beta_I - \beta_l}{T_I} + \frac{\beta_d - \beta_l}{T_{Id}},$$
$$\dot{\beta}_d = \frac{\beta_I - \beta_l}{T_{dI}} - \frac{\beta_d - \beta_l}{T_d}, \qquad (4)$$

where $(\epsilon \to +0)$

$$\frac{1}{T_I} = \frac{1}{T_{Id}} + \frac{1}{T_{Il}}, \quad \frac{1}{T_d} = \frac{1}{T_{dI}} + \frac{1}{T_{dl}}, \qquad (5)$$

$$\frac{1}{T_{Id}} = -\frac{(2I+1)^n}{\mathrm{Sp}\,\mathcal{H}_I^2}\int_{-\infty}^{0} e^{\epsilon t}\langle K_I K_d(t)\rangle\,dt,$$
$$\frac{1}{T_{dI}} = -\frac{(2S+1)^N}{\mathrm{Sp}\,\mathcal{H}_d^2}\int_{-\infty}^{0} e^{\epsilon t}\langle K_d K_I(t)\rangle\,dt; \qquad (6)$$

N and n are the concentrations of the magnetic ions and nuclei, and $\langle A\rangle = \mathrm{Sp}\,A/\mathrm{Sp}\,1$.

Further, T_{Il} is obtained from T_{Id} by replacing $K_d(t)$ by $K_l(t)$, and T_{dl} is obtained from T_{dI} by replacing $K_I(t)$ by $K_l(t)$; K(t) means the operator K in the Heisenberg representation. Finally, the operators K_I, K_d, and K_l are defined by the formulas

$$K_I = -i[\mathcal{H}_I, \mathcal{H}_{Id}], \quad K_l = -i[\mathcal{H}_l, \mathcal{H}_{dl}],$$
$$K_d = -i[\mathcal{H}_d, \mathcal{H}_{Id} + \mathcal{H}_{dl}]. \qquad (7)$$

From (6) it follows that

$$T_{dI}/T_{Id} = c_d/c_I, \qquad (8)$$

where c_I and c_d are the heat capacities of the

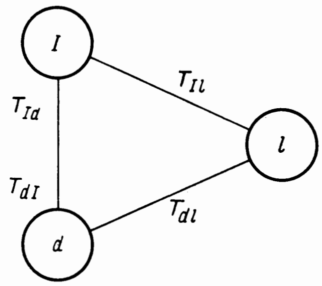

FIG. 2. Schematic picture of relaxation. I represents the Zeeman system of the nuclei, d the dipole-dipole reservoir of the magnetic ions, and l the lattice.

nuclear Zeeman system and the dipole-dipole reservoir, respectively.[1)]

The relaxation pattern is sketched out schematically in Fig. 2.

Assuming that the correlator of the z component of the spin of a magnetic ion is an exponential with correlation time τ, we obtain

$$\frac{1}{T_I} = C\sum_k r_{ik}^{-6} = C\frac{N}{n}\sum_i r_{ik}^{-6}, \tag{9}$$

where r_{ik} is the distance from the i-th nucleus to the k-th magnetic ion, and the quantity C is given by Eq. (2.9) in [1].

The relaxations of β_I and β_d are described by sums of two exponentials $\exp(-\lambda + t)$ and $\exp(-\lambda - t)$, $\lambda_+ > \lambda_-$. We consider only three special cases:[4,5]

Case I: $T_{Id} \gg T_{Il}$. The quantity β_I relaxes with relaxation time λ^{-1}, where

$$\lambda_- = 1/T_I = 1/T_{Il}. \tag{10}$$

Case II. $T_{dI} \gg T_{dl}$. The quantity β_I relaxes with relaxation time λ^{-1}, where

$$\lambda_- = 1/T_I = 1/T_{Id} + 1/T_{Il}. \tag{11}$$

Case III: $T_{Id} \ll T_{Il}$, $T_{dI} \ll T_{dl}$, $T_{dI} \ll T_{Id}$.

For slow relaxation of β_I we obtain

$$\lambda_- = \frac{c_d}{c_I}\frac{1}{T_{dl}} + \frac{1}{T_{Il}}. \tag{12}$$

4. We now consider what kind of results can be obtained using Buishvili's work.[4]

The relaxation process is described by four quantities with the dimensions of time T_{dI}, T_{Id}, T_{dl}, T_{Il}. Equation (9) gives us an expression for T_I. For a complete solution of the problem it is necessary to calculate Eq. (6) and the analogous expressions for T_{Il} and T_{dl}. However, let us see what kind of general conclusions can be extracted.

The quantity T_{dl} is independent of N. It is likewise known[6] that $\tau_{dl} \approx \tau_l$. Considering (8) and the fact that $c_d \propto N^3$ (see [7]), we obtain $T_{dI}/T_{Id} \propto N^3$. From this it is possible with almost complete certainty to conclude that T_{dI} increases with increasing N (the quantity T_{Id}, of course, decreases with increasing N, but there is sufficient reason to believe that this decrease is slower than N^{-3}).

As N increases, T_{Il}/T_{Id} increases. In fact, for sufficiently small N (when $\tau_s > \tau_l$), the nuclear relaxation process does not affect the dipole-dipole reservoir, and hence $T_{Il} < T_{Id}$; for sufficiently large N, on the other hand, this condition no longer holds.

Further, T_l is so small that it is always possible to consider that the condition $T_{dl} \ll T_{Il}$, T_{Id} is fulfilled. In all the experiments that have been done the concentration of the magnetic ions is so small that the condition $c_d \ll c_I$ is satisfied. According to (8), we find that $T_{dI} \ll T_{Id}$.

In further analysis the values of T_{Il}/T_{Id} and T_{dl}/T_{dI} play an important role.

Let N_1 and N_2 be the solutions respectively of the equations $T_{Il} = T_{Id}$ and $T_{dl} = T_{dI}$. The quantities N_1 and N_2 are functions of the temperature and the external field. In addition, they depend strongly on the type of magnetic impurity in the host lattice. Considering all of this we have

$$T_{Il} < T_{Id} \text{ when } N < N_1, \quad T_{dl} > T_{dI} \text{ when } N < N_2,$$
$$T_{Il} > T_{Id} \text{ when } N > N_1, \quad T_{dl} < T_{dI} \text{ when } N > N_2.$$

Let $N_2 < N_1$. Then when $N < N_1$ we have case I, and when $N > N_1$, case II.[2)] Thus if $N_2 < N_1$ there is no range of N in which heating of the dipole-dipole reservoir plays a significant role in nuclear relaxation. This result is easy to understand. In region I the nuclear relaxation is independent of the dipole-dipole reservoir; in region II the dipole-dipole reservoir has a very large heat capacity and so does not heat up.

Now let $N_1 < N_2$. Then when $N < N_1$ we have case I, when $N_1 < N < N_2$, case III, and when $N > N_2$, case II. Thus if $N_1 < N_2$, heating of the dipole-dipole reservoir plays a significant role in nuclear relaxation for intermediate values of N. We note that in region III the coupling of the nuclei with the dipole-dipole reservoir is stronger than the coupling of

1)In case $T_{Il} = T_{dl} = \infty$, Eqs. (4) give $\dot\beta_I = (\beta_d - \beta_I)/T_{Id}$, $\dot\beta_d = (\beta_I - \beta_d)/T_{dI}$; considering (8), we obtain, as of course we should, $c_I\dot\beta_I + c_d\dot\beta_d = 0$.

$$c_I\dot\beta_I + c_e\beta_d = 0.$$

2)More accurately, when $N < N_2$ we have case I and not case II; when $N_2 < N < N_1$ we have cases I and II simultaneously; finally when $N > N_1$ we have case II and not case I.

the nuclei with the lattice and the coupling of the dipole-dipole reservoir with the lattice.

Finally, all these considerations make sense only if N_1 and N_2 are sufficiently small, since the entire theory is valid only for sufficiently small concentrations of the magnetic impurity.

5. The diffusion theory of nuclear magnetic relaxation (in the form given in [1]) agrees rather well with many experiments performed at sufficiently low magnetic impurity concentrations (see our review[1] and Goldman's paper[8]).

The theory does not agree mainly with those low-temperature measurements in which relatively high magnetic impurity concentrations are used. The discrepancy evidently exists because it is necessary to take the possibility of heating the dipole-dipole reservoir of the magnetic ions into account in the theory. For this one needs to calculate the quantities T_{Id}, T_{dI}, T_{Il}, T_{dl} and after this make a quantitative analysis based on the treatment presented in Sec. 4 (in case $\delta < b$, it is necessary, however, to include spin diffusion in the calculations).

The disagreement of theory with experiment in the case of helium temperatures and large N is probably due to another cause, namely that in these cases the quantity δ/R is insufficiently small and one of the criteria of applicability of the diffusion treatment is destroyed. It is also possible that the disagreement is partially due to not considering the anisotropy of the diffusion barrier. We remark also that under conditions when $\delta > b$ or $\tau_s < \tau_l$ it is difficult to make a comparison of the absolute values of the calculated and measured values of T_n, since δ and τ_s are known only to an order of magnitude.

We observe, finally, that in the theory the distribution of the magnetic ions is assumed to be uniform. Non-uniformity of distribution of the ions leads in the case of large N to a reduction of the effective concentration, which in turn leads to an increase in the relaxation time.

All of the above points up the desirability of having more experimental determinations of the dependence of T_n on temperature, external field, crystal orientation, and magnetic impurity concentration.

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