Low-temperature relaxation of nuclear spins caused by a paramagnetic impurity

T. L. Buishvili and N. P. Fokina

Tbilisi State University
(Submitted 3 January 1989)
Zh. Eksp. Teor. Fiz. **95**, 2135–2139 (June 1989)

Low-temperature nuclear relaxation involving a reservoir of local fields of a paramagnetic impurity is analyzed. The anomalously fast relaxation of the nuclei at ultralow temperatures which has been observed by several investigators is explained on the basis of a temperature-independent term in the expression for the rate of the nuclear relaxation due to the interaction with this reservoir. This term becomes predominant at ultralow temperatures.

INTRODUCTION

The spin–lattice relaxation of nuclei associated with the presence of a paramagnetic impurity has been the subject of theoretical and experimental research for a long time now.[1-3] In recent years this research has been extended to low and ultralow temperatures,[4,5] where several descrepancies have been found between theory and experiment. In particular, at ultralow lattice temperatures ($T_L \lesssim 0.1$ K) the nuclear relaxation time T_I increases with decreasing temperature far more slowly than predicted by the theory.

In an effort to explain the anomalously rapid nuclear relaxation at ultralow temperatures, Waugh and Slichter[6] pointed out that the hyperfine interaction contains, in addition to terms proportional to the z component of the electron spin, S_i^z, terms which are proportional to $S_i^{\pm}$. The latter are usually ignored since they contribute a small factor to the probabilities for transitions involving nuclei. At low temperatures, however, the terms $V_{im}^{\pm z} I_m^{\pm} S_i^z$ lead to a strong dependence of T_I on the lattice temperature,

$$T_I \propto (1-p_0^2)^{-1}, \quad \text{where} \quad p_0 = \text{th}(\omega_s/2T_L)$$

(ω_s is the electron Zeeman frequency, $\hbar = 1$, and $k_B = 1$), while the terms $V_{im}^{\pm\pm} I_m^{\pm} S_i^{\pm}$, do not contribute such a factor, as was shown in Ref. 6. Calculating the nuclear relaxation time to second order in the electron spin-lattice and hyperfine interactions, we find[1]

$$T_I^{-1} = (T_I')^{-1} + (T_I'')^{-1}. \tag{1}$$

Here

$$(T_I')^{-1} = \tau_c^{-1} \frac{1-p_0^2}{4} f \frac{|V^{+z}|^2}{\omega_I^2},$$
$$(T_I'')^{-1} = \frac{\pi L(\omega_I)}{4} f \frac{|V^{++}|^2 + (V^{+-})^2}{\omega_s^2}, \tag{2}$$

τ_c is the correlation time of the z component of the electron spin (which is the same in this nuclear relaxation mechanism as the electron spin–lattice relaxation time T_{SL}), ω_I is the nuclear frequency,

$$|V^{\alpha\beta}|^2 = N_I^{-1} \sum_{im}{}' |V_{im}^{\alpha\beta}|^2, \tag{3}$$

N_I is the number of nuclear spins, f is the dilution of paramagnetic centers, the prime on the summation sign means summation over all sites accessible to the paramagnetic centers, and $L(\omega)$ is the Fourier transform of the lattice correlation function, which is given by the following expression in the case of a one-phonon relaxation process:

$$L(\omega) = \frac{3\omega^3 \mathscr{A}}{4\pi^2 \bar{u}^3} \text{ctg} \frac{\omega}{2T_L}. \tag{4}$$

Here $\mathscr{A}$ is the spin–lattice relaxation time, and $\bar{u}$ is the average phonon velocity. The second term in (1) describes the nuclear relaxation mechanism which was proposed by Waugh and Slichter.[6] According to that mechanism, an electron spin undergoes virtual transitions from a lower level to an upper level and back because of (for example) a process caused by the $S_i^+ I_m^{\pm}$ interaction and the spin–lattice interaction $S_i^- L^+$, while the nuclear spin undergoes a real flip, exchanging energy directly with phonons. Since the electron transitions are virtual, they do not make the nuclear relaxation rate temperature-dependent. To compare (3) with the estimate given by Waugh and Slichter,[6] we express $(T_I'')^{-1}$ in terms of $T_{SL}^{-1} = \pi L(\omega_s)$, finding

$$(T_I'')^{-1} = T_{sL}^{-1} \left(\frac{\omega_I}{\omega_s}\right)^4 \frac{f}{4} \frac{|V^{++}|^2 + (V^{+-})^2}{\omega_I^2} \frac{p_0}{\omega_s/2T_L}. \tag{5}$$

Expression (5) differs from the estimate in Ref. 6 in the presence of a factor $p_0/(\omega_s/2T_L)$, which arises because of the exact incorporation of the electron polarization and which may be far smaller than unity at ultralow temperatures. It follows from (5) that $(T_I'')^{-1}$ falls off with decreasing temperature far more slowly than $(T_I')^{-1}$. With decreasing lattice temperature, $(T_I'')^{-1}$ dominate $(T_I')^{-1}$ at a temperature T_L^* determined by the condition

$$1 - p_0^2 = \left(\frac{\omega_I}{\omega_s}\right)^4 \frac{p_0}{\omega_s/2T_L}. \tag{6}$$

The value found for T_L^* from (6) is smaller than that given in Ref. 6.

Waugh and Slichter[6] proposed a mechanism which explained the results of Ref. 4, where the impurity concentration in the sample was extremely low. However, when Eq. (6) is used to evaluate the temperature T_L^* at which the $T_I(T_L)$ dependence changes slope (this slope change was observed in Ref. 5; curve III.11), it leads to results which are too low [$T_L^* = 0.016$ and 0.106 K at values $H_0 = 3.84$ and 25 kG, respectively, of the static magnetic field, while we have $(T_L^*)_{\text{expt}} \approx 0.08$ and ≈ 0.27 K]. In order to explain the results of Ref. 5, we should thus seek another nuclear relaxation mechanism, which depends weakly on T_L. The samples

0038-5646/89/061235-03$04.00

used in Ref. 5 had a fairly high concentration of paramagnetic centers (16×10^{19} spins/cm^3), and their ESR line was inhomogeneously broadened. Under such conditions, cross relaxation processes lead to the formation of a reservoir of local fields,[7,8] which can participate in nuclear relaxation.[9] A relationship between nuclei and the reservoir of local fields under the conditions of Ref. 5 is also indicated by the fact that the dynamic polarization of nuclei which was observed in Ref. 5 was successfully interpreted there as the result of nucleus–reservoir contact.

Our purpose in the present study is to systematically analyze the relaxation of nuclei involving a reservoir of local fields at low temperatures.

STATEMENT OF THE PROBLEM

The Hamiltonian of the problem is

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}',\quad \mathscr{H}_0=\mathscr{H}_s+\mathscr{H}_I+\mathscr{H}_{LF},\quad \mathscr{H}'=\mathscr{H}_{Is}+\mathscr{H}_{CR},\tag{7}$$

where

$$\mathscr{H}_s=\omega_s S^z,\quad \mathscr{H}_I=-\omega_I I^z,\quad \mathscr{H}_{LF}=\sum_i \Delta_i S_i^z+\mathscr{H}_d',$$

$$\mathscr{H}_d'=\frac{1}{2}\Big\{\sum_{i,j,n,n'} A_{ij}S_{in}^zS_{jn'}^z+\sum_{i,j,n} B_{ij}S_{in}^+S_{jn}^-\Big\}.$$

Here $\mathscr{H}_s$ and $\mathscr{H}_I$ are the Zeeman energies of the electron and nuclear spins; $\mathscr{H}_{LF}$ is the Hamiltonian of the reservoir of local fields,[7] which consists of "difference" terms ($\Delta_i = \omega_i - \omega_s$) and a secular part corresponding to a dipole–dipole interaction, $\mathscr{H}_d'$ (we are assuming that the inhomogeneous width Δ^* of the ESR line is much greater than the average quantum of the dipole–dipole interaction); i, j are the indices of the sites occupied by paramagnetic centers; n, n' are the indices of spin packets with frequencies ω_n and ω_n'; and a "spin packet" is to be understood as a set of spins with approximately equal frequencies within which an equilibrium is established far more rapidly than over the entire homogeneously broadened line.

In the hyperfine interaction $\mathscr{H}_{Is}$ and in the cross relaxation interaction $\mathscr{H}_{CR}$ we retain the terms of interest for the analysis below:

$$\mathscr{H}_{Is}=\frac{1}{2}\sum_{i,n,m}\{V_{im}^{+z}I_m^+S_{in}^z+V_{im}^{+-}I_m^+S_{in}^- +V_{im}^{++}I_m^+S_{in}^++\text{H.a.}\},\tag{8}$$

$$\mathscr{H}_{CR}=\frac{1}{2}\sum_{\substack{i,j,n,n'\\(n\neq n')}}\{B_{ij}S_{in}^+S_{jn'}^-+C_{ij}S_{in}^zS_{jn'}^++C_{ij}^*S_{in}^zS_{jn'}^-\};$$

explicit expressions for the coefficients A, B, C, and V can be found in Ref. 10, among other places.

INTERACTION OF NUCLEI WITH THE RESERVOIR OF LOCAL FIELDS

We assume that in the course of the nuclear relaxation the electron system is in equilibrium with the lattice. In calculating the relaxation rate we assume that the paramagnetic centers are distributed randomly in the crystal and that the spectral functions describing their cross relaxation are much narrower than the Gaussian inhomogeneous ESR line $g(\omega-\omega_s)$, whose width satisfies $\Delta^*>\omega_I$. We assume $\omega_I \gg \tau_c^{-1}$, where τ_c is the correlation time of the function

$$\langle\delta S_{in}^z(t)\,\delta S_{in}^z\rangle/\langle(\delta S_{in}^z)^2\rangle,$$

$$\delta S_{in}^z=S_{in}^z-\langle S_{in}^z\rangle,\tag{9}$$

which we will be discussing below. Under these conditions, which are the most common conditions experimentally, we find the following expression for the rate of the relaxation due to the interaction of nuclei with the reservoir of local fields in second-order perturbation theory:

$$T_{Id}^{-1}=\tau_c^{-1}\frac{1-p_0^2}{4}f\frac{|V^{+z}|^2}{\omega_I^2}+\pi f_s(\omega_s)f\{|V^{++}|^2+(V^{+-})^2\}$$
$$+\frac{\pi^{1/2}}{16}(1-p_0^2)f^2\frac{B^2}{\Delta^*}\frac{|V^{+z}|^2}{\omega_I^2}\exp\left(\frac{-\omega_I^2}{4\Delta^{*2}}\right)+\frac{\pi}{8}g(\omega_s)f^2\left(\frac{\omega_I}{\omega_s}\right)^2$$
$$\times B^2\frac{|V^{++}|^2+(V^{+-})^2}{\omega_I^2}+\frac{\pi^{1/2}}{8}f^2\left(\frac{\omega_I}{\omega_s}\right)^2$$
$$\times\frac{C^2}{\Delta^*}\frac{|V^{++}|^2+(V^{+-})^2}{\omega_I^2}\exp\left(\frac{-\omega_I^2}{\Delta^{*2}}\right),\tag{10}$$

where

$$B^2=\sum_j{}' B_{ij}^2,\quad C^2=\sum_j{}' |C_{ij}|^2,$$

the function $f_s(\omega)$ describes the frequency distribution in the spin packet, and the last three terms correspond to second-order of perturbations in $\mathscr{H}'$.

Let us examine the physical meaning of each term in (10). The first describes a process in which a set of flip–flop transitions within a packet creates at the nuclei an alternating field which has a nonzero component at the nuclear frequency. The second term describes the relaxation coupling of nuclei with the reservoir through simultaneous flips of the electron and nuclear spins caused by the interaction $S_{in}^{\pm}I_m^{\mp}$ and $S_{in}^{\mp}I_m^{\pm}$. The third term stems from the electron-nucleus cross relaxation, a discrete process in which the elementary event is the simultaneous flip of two electron spins with frequencies ω_n and $\omega_{n'}$ where $|\omega_n-\omega_{n'}|=\omega_I$, and of the nuclear spin. The fourth and fifth terms have a physical meaning similar to that described in Ref. 6, with the distinction that the lattice is not involved here. The fourth term results from two pairs of interactions which flip spins: $S_{in}^+S_{jn'}^-$ and $S_{in}^-I_m^{\pm}$, where the transitions caused by S_{in}^+ and S_{in}^- are virtual, and those caused by $S_{jn'}$ and $I_m^{\pm}$ are real. The fifth term describes a process in which an electron spin which has undergone a virtual transition, while a nuclear spin has undergone a real transition (the process due to the term $S_{in}^+I_m^{\pm}$), undergoes the inverse transition by means of the process described by the term $S_{in}^-S_{jn'}^z$.

To evaluate the contributions to the relaxation rate of the various terms in expression (10), we need to estimate τ_c. As was shown in Ref. 11, when the broadening is significantly inhomogeneous ($\delta_{sp}\ll\Delta^*$, where δ_{sp} is the width of the spin packet), the t dependence in (9) is determined by Hamiltonian $\mathscr{H}_d'$. Evaluating τ_c with $\mathscr{H}_d'$ by the method of moments under the condition $f\ll1$, we find

$$\tau_c^{-1} \approx \frac{\pi}{4\times 3^{1/2}} f \frac{\delta_{sp}}{\Delta^*} B. \tag{11}$$

The same quantity was calculated by the method of moments in Ref. 3, where the complete secular interaction with respect to $\Sigma_{in} S^z_{in}$, was used in place of $\mathscr{H}'_d$. This result is

$$\mathscr{H}_{dd} = \mathscr{H}_d' + \frac{1}{2} \sum_{\substack{i,j,n,n' \\ (n\neq n')}} B_{ij} S_{in}^+ S_{jn'}^-,$$

$$\tau_c^{-1} \approx \frac{\pi}{4\cdot 3^{1/4}} \frac{fB}{(B'^4/B^4 + 2\Delta^{*2}/B^2)^{1/4}}; \quad B'^4 = \sum_j{}' B_{ij}^4. \tag{12}$$

Substituting (11) into (10), we note that in our analysis the interaction $\mathscr{H}_{dd}$ gives rise to two additive contributions to the expression for the nuclear relaxation rate. Of the two, one is a consequence of flip–flop transitions of spins within the packet [the first term in expression (10)], while the other is due to electron-nucleus cross relaxation (the third term). Since the relation $\delta_{sp} \ll B$ holds in dilute paramagnets, the third term is always greater than the first. In Ref. 3, T_{Id}^{-1} was formally like the first term in (10), but with τ_c^{-1} given by (12). If we adopt $\Delta^* \gg B$ in (12), the resulting expression for T_{Id}^{-1} agrees to within a numerical factor of order unit with the electron–nucleus cross relaxation term in (10), which was found without the assumption $\Delta^* \gg B$. In practice, that condition does not hold for dilute paramagnets. Consequently, the imperfect use of the method of moments makes the result of Ref. 3 correct only under the assumption $\Delta^* \gg B$, which does not hold in practice, while the valid assumption $\Delta^* \gg \delta_{sp}$ was used in the calculation of the third term in (10).

We turn now to the terms proportional to $|V^{++}|^2$ and $|V^{+-}|^2$. Of them, the second and fourth contain small factors $f_s(\omega_s)$ and $g(\omega_s)$, so the largest of the temperature-independent terms in expression (10) is the last, which should dominate at ultralow temperatures. In Ref. 5, the high-temperature part of the $T_I(T_L)$ curve was described by as functional dependence of approximately $T_I \propto (1 - p_0^2)^{-1}$. A function of this sort comes from the third term in (10). Comparing it with the temperature–independent last term, we find that the transition from one mechanism to another should occur under the condition

$$1 - p_0^2 = (\omega_I/\omega_s)^2. \tag{13}$$

From this condition we find the crossing temperatures $T_L^* = 0.04$ and 0.23 K, for $H_0 = 3.84$ and 25 kG, respectively. These values agree with the experimental values, to within the experimental error.

A plot of $T_I(H_0)$ at constant values of T_L was also constructed in Ref. 5. It has a transition to a weaker field dependence in strong fields. Using (13) to calculate the particular field at which this transition occurs, we find agreement with experiment.

CONCLUSION

By estimating the contributions of the various terms in expression (10) and making a comparison with experimental data, we can draw the following conclusions: 1) The thermal interaction of nuclei with the reservoir of local fields at high concentrations of paramagnetic centers is determined by two terms in expression (10), specifically, the electron–nucleus cross relaxation term, which has a temperature dependence $(1 - p_0^2)$, and the last term, which is independent of the temperature. This last term should be dominant at ultralow temperatures. 2) The results calculated for the temperature at which the transition occurs from one mechanism to another agree with the experimental results of Ref. 5.

We wish to thank V. A. Atsarkin for a discussion of the results and for calling our attention to the role played by electron–nucleus cross relaxation in the relaxation of the nuclear subsystem.

[1)] Here and below, we are using the high–temperature approximation in the nuclear polarization. That approximation is valid for the relaxation of nuclei after their saturation[4] and also after a dynamic polarization, if not too effective.

[1] G. P. Khutsishvili, Usp. Fiz. Nauk **87**, 211 (1965) [Sov. Phys. Usp. **8**, 743 (1965)].

[2] L. L. Buishvili *et al.*, Phys. Status Solidi (b) **48**, 851 (1971).

[3] M. Goldman, S. F. J. Cox, and V. Bouffard, J. Phys. C **7**, 2940 (1974).

[4] P. L. Kuhns *et al.*, Phys. Rev. B **35**, 4591 (1987).

[5] W. De Boer, Thesis University of Technology. Delft, 1974; W. De Boer and T. O. Niinikovski, Nuclear Instrum. Methods **114**, 495 (1974).

[6] J. S. Waugh and Ch. P. Slichter, Phys. Rev. B **37**, 4337 (1988).

[7] S. Clough and C. A. Scott, Proc. Phys. Soc. **1**, 919 (1968).

[8] M. I. Rodak, Zh. Eksp. Teor. Fiz. **61**, 831 (1971) [Sov. Phys. JETP **34**, 443 (1971)].

[9] N. S. Bendiashvili, L. I. Buishuili, and M. D. Zuiadedze, Zh. Eksp. Teor. Fiz. **58**, 597 (1970) [Sov. Phys. JETP **31**, 321 (1970)].

[10] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford Univ. Press, London, 1961 (Russ. Transl. Izd-vo inostr. lit., Moscow, Ch. 4, 1963).

[11] L. L. Buishvili, I. M. Metreveli, and N. P. Fokina, Zh. Eksp. Teor. Fiz. **80**, 678 (1981) [Sov. Phys. JETP **53**, 341 (1981)].

Translated by Dave Parsons