Low-temperature nuclear relaxation of the first kind through a paramagnetic impurity

L. L. Buishvili, T. L. Buishvili, and N. P. Fokina
I. Dzhavakhishvili Tiflis State University

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Under certain conditions, the nuclear relaxation mechanism of the first kind, which results from a modulation of the hyperfine interaction constant by lattice vibrations, can play a decisive role in nuclear relaxation at ultralow temperatures.

Nuclear relaxation in solid paramagnets is determined[1,2] by fluctuations of the z component of the electron spin, S^z, which is involved in a hyperfine interaction (hfi) of nuclei with paramagnetic centers of the type $V^{\pm z}_{mn} I^{\pm}_{m} S^{z}_{n}$. In the terminology of Ref. 1, this is a relaxation of the second kind. The rate (T_I^{-1}) of the relaxation due to fluctuations in S^z is proportional to the factor $(1-p_0^2)$, where $p_0 = \tanh(\hbar\omega_s/2k_B T_L)$ (ω_s is the ESR frequency, and T_L is the lattice temperature), which "freezes" the nuclear relaxation at ultralow temperatures ($p_0 \simeq 1$). On the other hand, significantly larger relaxation rates were observed in the experiments of Ref. 3. In an attempt to explain the experimental results of Kuhns *et al.*,[3] Waugh and Slichter[4] have proposed and evaluated a nuclear relaxation mechanism, which operates in second-order perturbation theory in the hyperfine interaction of the form $V^{\pm\pm}_{mn} I^{\pm}_{m} S^{\pm}_{n}$. The nuclear relaxation rate which we have calculated for relaxation by the mechanism of Ref. 4 is

$$T_I^{-1} = \frac{f}{4}\frac{1}{T_{sL}}\frac{[|V^{++}|^2 + (V^{+-})^2]\omega_I^2}{\hbar^2\omega_s^4}\frac{p_0}{\hbar\omega_s/2k_B T_L}, \qquad (1)$$

where

$$|V^{\gamma\delta}|^2 = N_I^{-1}\sum_{mn}{}' |V^{\gamma\delta}_{mn}|^2, \quad \gamma, \delta = +, -, z.$$

The summation over n is over all sites accessible to paramagnetic centers, N_I is the number of nuclear spins, f is the dilution of the electron spins, T_{sL} is the electron spin-lattice relaxation time (the direct process), and ω_I is the nuclear Zeeman frequency. The rate given by (1) falls off slowly with decreasing temperature, but it contains a small factor $(\omega_I/\omega_s)^2$. It is known,[1] however, that paramagnetic relaxation can be caused by fluctuations of the spin-spin coupling constant (a relaxation of the first kind[1]). Since the corresponding relaxation rate should not contain this small factor, one might suggest that a modulation of the hyperfine interaction constant by lattice vibrations of the type $V^{\pm z}_{mn} I^{\pm}_{m} S^{z}_{n}$ leads to an effective relaxation of nuclei at ultralow temperatures. To calculate the rate T_I^{-1} corresponding to this mechanism in the Hamiltonian of the hyperfine interaction,

$$\mathcal{H}_{\rm hfi} = \frac{1}{2}\sum_{mn}(V^{+z}_{mn} I^{+}_{m} + V^{-z}_{mn} I^{-}_{m}) S^{z}_{n}$$

we take the approach of Ref. 5, expanding the constants $V_{mn}^{\pm z}$ in series in the displacements of the atoms from their equilibrium positions. We restrict the analysis to first order. The effective nuclear spin-phonon interaction can then be described by

$$\mathcal{H}' = \sum_{mn\alpha\beta} G_{\alpha\beta}^{mn} e_{\alpha\beta} \quad (\alpha, \beta = x, y, z), \tag{2}$$

where

$$e_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial \beta} + \frac{\partial u_\beta}{\partial \alpha}\right)$$

is the strain tensor (u_α are components of the displacement vector),

$$G_{\alpha\beta}^{mn} = \frac{1}{4}\left(\frac{\partial V_{mn}^{+z}}{\partial R_\alpha} R_\beta + \frac{\partial V_{mn}^{+z}}{\partial R_\beta} R_\alpha\right) I_m^+ S_n^z + \text{c.c.}, \tag{3}$$

and the vector $\mathbf{R}$ connects the equilibrium positions of atoms. We then expand $e_{\alpha\beta}$ in normal coordinates of the lattice:

$$e_{\alpha\beta} = \frac{i}{2} \sum_{\mathbf{k}j} \sqrt{\frac{\hbar\omega_{\mathbf{k}j}}{2M\bar{v}^2}} \{a_{\mathbf{k}j}^+ \exp(2\pi i \mathbf{k}\mathbf{R}) - a_{\mathbf{k}j} \exp(-2\pi i \mathbf{k}\mathbf{R})\} (\lambda_\alpha f_\beta + \lambda_\beta f_\alpha), \tag{4}$$

where M is the mass of the crystal, the operator $a_{\mathbf{k}j}^+$ creates a phonon j, of the branch with wave vector $\mathbf{k}$ and frequency $\omega_{\mathbf{k}j}$, λ_α and f_α are the direction cosines of the photon polarization vector and of the vector $\mathbf{k}$, respectively, and $\bar{v}$ is the average phonon velocity. Calculating the nuclear relaxation rate from (2)–(4), we can use the high-temperature approximation for the nuclear spins, and we can also use the estimate

$$\left|\sum_{mn\alpha\beta}\left(\frac{\partial V_{mn}^{+z}}{\partial R_\alpha} R_\beta + \frac{\partial V_{mn}^{+z}}{\partial R_\beta} R_\alpha\right)(\lambda_\alpha\lambda_\beta + \lambda_\beta f_\alpha)\right|^2 \sim f N_I |V^{+z}|^2 .$$

We then find

$$T_I^{-1} \sim 10^{-2} f \frac{\omega_I^2 |V^{+z}|^2 k_B T_L}{\hbar^2 \rho \bar{v}^5}, \tag{5}$$

where ρ is the density of the crystal. The rate given by (5), like that given by (1), depends only weakly on the temperature, but it differs from (1) in that it does not contain a small factor $(\omega_I/\omega_s)^2$. Let us compare (5) and (1). Their ratio, c, is given in order of magnitude by

$$c \sim 10^{-2} \frac{T_{sL} \hbar \omega_s^5}{\rho \bar{v}^5 p_0}. \tag{6}$$

Substituting into (6) data for phosphorus-doped silicon[6] at $T_L = 1.25$ K ($\omega_s = 2\pi \times 0.84 \times 10^{10}$ rad/s, $T_{sL} \sim 3.8 \times 10^4$ s), and using the estimates $\rho \sim 10^3$ kg/m^3 and $\bar{v} \sim 3 \times 10^3$ m/s, we find $c \sim 10^2$ (we have in mind the relaxation of Si^{29} nuclei, which are not enveloped by an s-state electron orbital). In the case of Kramers ions, such as Cu^{2+} in $Cu_xZn_{1-x}(NH_4)_2(SO_4)_2\cdot 6H_2O$ (Ref. 7), the rate of nuclear relaxation due to the process under consideration here can reach the same value as that for the mechanism proposed by Waugh and Slichter[4] or even exceed it.

In summary, modulation of the hyperfine constant $V_{mn}^{\pm z}$ by lattice vibrations provides a nuclear relaxation mechanism which, while ineffective at high temperature ($p_0 \ll 1$), plays a major role at ultralow temperatures ($p_0 \sim 1$).

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