

## Mechanism of nuclear spin-lattice relaxation in insulators at very low temperatures

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Nuclear spin-lattice relaxation by paramagnetic impurities in insulating crystals is expected in conventional theory to be frozen out in the millikelvin temperature region owing to the freezing of the electron-spin orientation into the lowest-energy spin state in the presence of a static field. Experimental relaxation times are much shorter than the conventional theory predicts. The authors show that by extending the normal relaxation theory to include the slight change in electron-spin quantization arising from a nuclear spin flip, the electron effectively gains a new degree of freedom, which we call wobble, which takes much less energy to excite than a complete electron-spin flip. The electron-spin orientation is, therefore, effectively unfrozen even at millikelvin temperatures. This new mechanism is expected to dominate in high field at temperatures of tens of millikelvin and below.

Recently, systematic measurements of  $^{19}\text{F}$  spin-lattice relaxation in  $\text{CaF}_2$  crystals were reported<sup>1</sup> which extended to considerably lower temperatures (8 mK) than the lowest previously employed (70 mK).<sup>2</sup> It was found that, at very low temperatures,  $T_1$  increased far more slowly than expected: Indeed, at 8 mK  $T_1$  was roughly nine orders of magnitude shorter than would have been predicted by standard relaxation theory. Qualitative observations by others also suggest the existence of anomalously rapid relaxation at low temperatures.<sup>3</sup>

The usual theory<sup>4</sup> focuses attention on a single nuclear spin  $I$  (Larmor frequency  $\omega_n$ ) coupled to a single electronic impurity spin  $S$  (Larmor frequency  $\omega_e$ ) by a tensor interaction, e.g., dipolar

$$\mathcal{H}_{en} = \mathbf{S} \cdot \mathcal{D} \cdot \mathbf{I} . \quad (1)$$

$S$  is assumed to have some interaction with the lattice which induces electronic spin flips and thus to an electronic relaxation time  $T_{1e}$ : To put it another way,  $\langle S_z(t) \rangle$  when undisturbed, fluctuates about its equilibrium value with correlation time  $T_{1e}$ . The local field arising from  $S_z(t)$ , now regarded as a classical random variable, causes spin flips of the nucleus through terms of the type  $S_z I_{\pm}$  contained in Eq. (1). The rate of these flips defines a nuclear relaxation time  $T_{1n}$ : in the limit  $\omega_n T_{1e} \gg 1$  and at temperatures above a few K

$$T_{1n}^{-1} = T_{1e}^{-1} \left( \frac{\omega_{en}}{\omega_n} \right)^2 , \quad (2)$$

where  $\omega_{en}$  is the "size" of the relevant part of  $\mathcal{H}_{en}$ . The overall relaxation of a crystal containing many nuclei is then brought about, in a way difficult to analyze in detail, by a combination of this direct process, for nuclei near  $S$ , and nuclear spin diffusion<sup>5</sup> for nuclei remote from  $S$ .

Equation (2) is valid only at high temperatures  $k_B T \gg \hbar \omega_e$ : Otherwise, the upward and downward elec-

tronic spin-flip rates must be weighted by the equilibrium populations of the electronic Zeeman levels. The result is to replace Eq. (2) by

$$T_{1n}^{-1} = T_{1e} \left( \frac{\omega_{en}}{\omega_n} \right)^2 (1 - P_e^2) , \quad (3)$$

where  $P_e = \tanh(\hbar \omega_e / 2k_B T)$  is the equilibrium electronic polarization. It is in fact this detailed-balance requirement which is responsible for the predicted astronomical increase in  $T_{1n}$  at low temperatures: when  $P_e \rightarrow 1$ ,  $1 - P_e^2 \rightarrow \exp(-\hbar \omega_e / k_B T)$ . For electrons in a field of 1 T this factor reaches  $10^{-57}$  at 10 mK.

The difficulty can be removed by recognizing that detailed balance is required by "real" electronic transitions  $\alpha \leftrightarrow \beta$  at equilibrium but is irrelevant to "virtual transitions," i.e., to purely quantum mechanical mixing of electron spin states. Such mixing is in fact required by Eq. (1). To first order in perturbation theory the eigenstates  $|en\rangle$  of the coupled system are

$$\begin{aligned} |1\rangle &= a\alpha - b^* \alpha\beta - c_1^* \beta\alpha - c_2^* \beta\beta , \\ |2\rangle &= b\alpha\alpha + a\beta - c_0^* \beta\alpha - c_1^* \beta\beta , \\ |3\rangle &= c_1\alpha\alpha + c_0\alpha\beta + \beta\alpha + b^* \beta\beta , \\ |4\rangle &= c_2\alpha\alpha + c_1\alpha\beta - b\beta\alpha + \beta\beta . \end{aligned} \quad (4)$$

The mixing coefficients arise from the various terms in  $\mathcal{H}_{IS}$  as follows:

$$\begin{aligned} S_z I_{\pm} : |b| &\approx \omega_{en} / \omega_n , \\ S_{\pm} I_{\mp} : |c_0| &\approx \omega_{en} / (\omega_e - \omega_n) , \\ S_{\pm} I_z : |c_1| &\approx \omega_{en} / \omega_e , \\ S_{\pm} I_{\pm} : |c_2| &\approx \omega_{en} / (\omega_e + \omega_n) , \end{aligned} \quad (5)$$

and have different angle dependences. Now consider the situation at temperatures so low that only  $|3\rangle$  and  $|4\rangle$  are populated. The electron spin is coupled to the lattice by a perturbation which can be represented semiclassically in terms of a fluctuating field  $\mathbf{B}_{el}(t)$ :

$$\mathcal{H}_{el} = \gamma_e \mathbf{B}_{el}(t) \cdot \mathbf{S} , \quad (6)$$

which causes transition between  $|3\rangle$  and  $|4\rangle$ . The relevant matrix elements are, to lowest order in the mixing coefficients

$$\begin{aligned} \langle 3 | S_z | 4 \rangle &\approx 0 , \\ \langle 3 | S_{\pm} | 4 \rangle &\approx c_0^* + c_2 . \end{aligned} \quad (7)$$

(Note that  $c_0$  and  $c_2$  have different angle dependences and so cannot cancel one another.) Now let us approximate  $c_0 \approx c_1 \approx c_2 = \omega_{en}/\omega_e$ . The  $|3\rangle \leftrightarrow |4\rangle$  transitions are accompanied by nuclear spin flips and thus lead to nuclear relaxation.

One may gain physical insight into the process as follows. The coefficient  $b$  represents the fact that the effective field acting on the nucleus is the vector sum of the applied field and the field due to the electron. As a result, the nuclear quantization direction depends on the orientation of the electron spin. This is a well-known phenomenon in electron spin resonance where it gives rise to nuclear spin transitions accompanying electron spin flips and the appearance of so-called "forbidden transitions."<sup>6</sup> The  $b$  term is unimportant in our case since the electron spin is confined to one eigenstate at low temperatures. The terms involving the  $c$  coefficients represent the corresponding fact that when a nuclear spin flips, the magnitude and direction of the effective field acting on the electron changes. Consequently the electron quantization undergoes a slight change when a nucleus flips. This gives the electron spin a slight degree of freedom, which we might call a wobble, at much lower energy cost than a complete electron spin flip, an important fact at very low temperatures. The fact that flipping a nucleus wobbles the electron has as a reciprocal process the fact that wobbling the electron can flip a nucleus. In short, at low temperatures one freezes out electron flips but not electron wobble. Thus, it still remains true that a fluctuating field acting on the electron can flip a nucleus.

Since (7) is the same coupling and  $S_{\pm}$  the same operator which lead to electronic relaxation, one supposes that the rate of nuclear relaxation will be just  $T_{1e}^{-1}$ , except for (i) reduction by a factor  $\sim (\omega_{en}/\omega_e)^2$  arising from the small mixing coefficients and (ii) the fact that the energy exchanged with the lattice is  $\hbar\omega_n$  rather than  $\hbar\omega_e$ . If the electrons relax by the direct process<sup>4</sup> (absorption and emission of single phonons) a factor representing the relative phonon densities of states  $\rho(\omega_n)/\rho(\omega_e) \sim (\omega_n/\omega_e)^2$

needs to be introduced: Making these changes we find

$$T_{1n}^{-1} \approx T_{1e}^{-1} \left( \frac{\omega_{en}}{\omega_e} \right)^2 \left( \frac{\omega_n}{\omega_e} \right)^2 . \quad (8)$$

Equation (8) is supposed to describe the relaxation of a particular nucleus, so located with respect to a paramagnetic impurity that its coupling is  $\omega_{en}$ . To proceed further with the calculation of  $T_{1n}$  in a crystal containing many nuclei we would need to worry about (a) contributions of (8) to nuclear neighbors at different distances from the impurity, (b) propagation of nuclear magnetization between this local region and remote parts of the crystal, (c) the actual value of  $T_{1e}$ . Without attempting this task, we can at least observe that it arises in exactly the same way in both the standard theory and the mechanism considered here. By comparing (3) and (8) it is clear that the crossover between the two mechanisms must occur when

$$1 - P_e^2 = \left( \frac{\omega_n}{\omega_e} \right)^4 , \quad (9)$$

independent of the value of  $\omega_{en}$ . For  $^{19}\text{F}$  spins relaxed by electrons in a field of 1 T this crossover occurs at  $T \sim 50$  mK, satisfactorily accounting for the fact that "anomalously" small values of  $T_{1n}$  are observed only in the millikelvin regime. At very low temperatures where the proposed mechanism is dominant,  $T_{1n}$  has only the relatively weak temperature dependence of  $T_{1e}$ .

The validity of (8) might in principle be tested by measuring both  $T_{1n}$  and  $T_{1e}$  in the regime where the classical mechanism is eliminated. Then we predict  $T_{1n}/T_{1e} \propto B_0^2$ , independent of temperature. Such experiments would be laborious. Moreover, the discussion leading to (8) assumes (a) that the bottleneck in relaxation of the system of many  $I$  spins in the direct relaxation through (6) of those  $I$  spins near an impurity, and (b) that  $T_{1e}$  arises from the one-phonon mechanism. In fact a Raman process<sup>4</sup> may govern the rate of the low frequency  $|3\rangle, |4\rangle$  transitions even though it is probably not important for the high ( $\omega_e$ ) frequency transitions leading to normal electronic relaxation at large  $B_0/T$ .

What of lattice temperatures so extraordinarily low that the equilibrium nuclear polarization  $P_n \rightarrow 1$ ? Since the measurement of  $T_1$  requires driving  $\langle I_z \rangle$  far from equilibrium, the detailed-balance considerations governing equilibrium fluctuations do not apply: If (8) is valid at all, it should prevent huge increases in  $T_{1n}$  even to arbitrarily low temperatures.

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<sup>1</sup>P. Kuhns, P. C. Hammel, O. Gonen, and J. S. Waugh, *Phys. Rev. B* **35**, 4591 (1987).

<sup>2</sup>B. T. Beal and J. Hatton, *Phys. Lett.* **15**, 210 (1965).

<sup>3</sup>R. Richardson, N. Sullivan, and M. Chapellier (private communications).

<sup>4</sup>For a general discussion of this subject, see A. Abragam, *Principles of Nuclear Magnetism* (Oxford Univ. Press, New

York, 1961), Chap. 9; also A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Oxford Univ. Press, New York, 1982), Chap. 6.

<sup>5</sup>N. Bloembergen, *Physics* **15**, 386 (1949).

<sup>6</sup>C. P. Slichter, *Principles of Magnetic Resonance*, 2nd ed. (Springer, New York, 1980), pp. 314–315.