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Direct Observation of a Nuclear Spin Diffusion Barrier*

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Experiments are reported which measure the relaxation properties of nuclei near a paramagnetic impurity. For $Y(C_2H_5SO_4)_3 \cdot 9H_2O{:}Yb^{3+}$, nuclei as close as 3 Å to the Yb ion are in strong thermal contact with the bulk spins, contradicting the traditional notions of the diffusion barrier. I present evidence that impurity-induced diffusion and interaction with the electron spin-spin reservoir are important processes which act to reduce the barrier dimension.

It is well established that abundant spin-$\frac{1}{2}$ nuclei in a paramagnetically doped insulator reach thermal equilibrium with the lattice via interaction with paramagnetic impurities. The theoretical foundation for this nuclear relaxation process was formulated by Bloembergen[1] in 1949 and has since formed the basis for interpreting voluminous experimental data.[1,2] Bloembergen postulated that nuclear spins *near* the ion are relaxed by fluctuations in the magnetic field of the impurity (direct relaxation) and that *bulk* spins are relaxed by diffusion of Zeeman energy to near nuclei (spin diffusion). Diffusion among bulk nuclei is an energy-conserving process with typical diffusion constant $D_0 \simeq 10^{-12}$ cm^2/sec for abundant F^{19} or H^1 spins. At low temperatures, the static component of the local field can shift the NMR resonance of a near nucleus well outside the bulk NMR linewidth, so it was postulated that spin diffusion should be greatly inhibited inside a certain "radius" from the ion,

$$b \simeq (3\mu_e/\mu_n)^{1/4}a, \qquad (1)$$

known as the diffusion-barrier radius.[1,3-7] Here μ_e and μ_n are the impurity and nuclear moments, respectively, and a is the distance between nuclei. This is the radius at which the difference in impurity fields at two adjacent nuclei equals the NMR linewidth. The common theoretical description of the bulk nuclear relaxation process is to assume $D = 0$ inside the sphere of radius b, and $D = D_0$ outside.[8] The principal drawbacks of this macroscopic model are the assumptions of a continuum nuclear polarization and a spherical barrier, where in fact spins at discrete lattice sites and an anisotropic local field are involved.

In a recent experiment with a ytterbium-doped yttrium-ethyl-sulfate (YES:Yb) crystal,[9] it was demonstrated that one could actually detect the resonances of near nuclei, as well as measure their individual relaxation rates. In the course of this work, a straightforward experiment has been devised to determine precisely which protons are inside the *actual* diffusion barrier, where here we use the operational definition that a spin is *inside* the barrier if it is in stronger thermal contact with the lattice phonons than with the bulk spins. This microscopic study of the nuclear relaxation process in YES:Yb has uncovered the existance of a strong thermal contact between the bulk spins and near nuclei well within the above radius b.

The thermal-equilibrium near-proton spectrum is shown in Fig. 1(a). The eighteen protons $H1W7$,

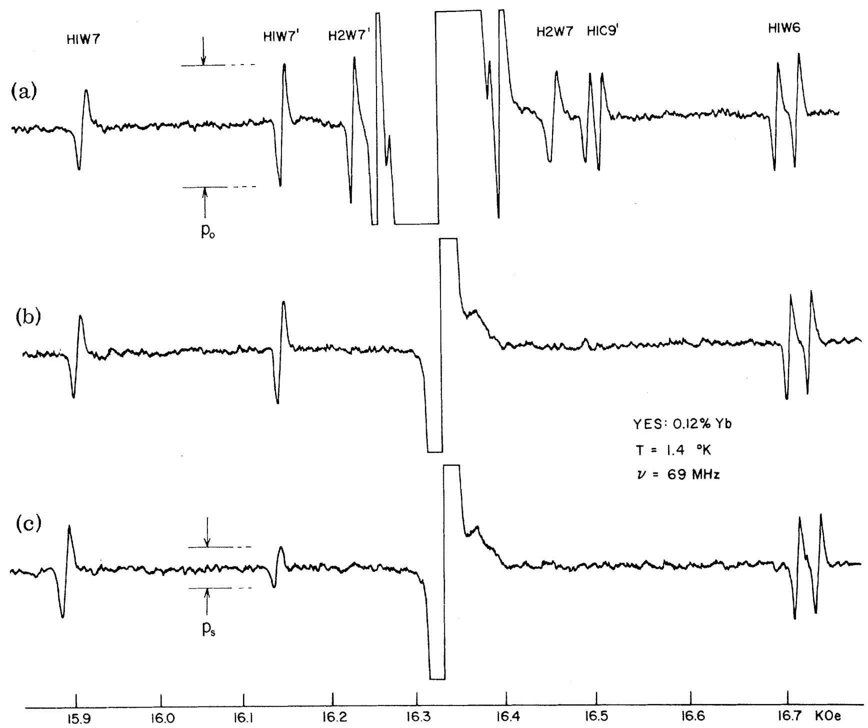

FIG. 1. (a) Thermal-equilibrium near-proton signals for $H \| c$ axis. Labeled lines correspond to protons within 6.2 Å of a Yb^{3+} impurity; the bulk NMR at 16.33 kOe is 1000× off scale. An illustration of the proton positions appears in Ref. 9, Fig. 1. (b) Two to six minutes after the bulk NMR was saturated with radio frequency, showing the strong coupling between many near protons and the bulk. (c) After 100 minutes only the twelve protons $H1W7$ and $H1W6$ remain at the lattice temperature. This trace is close to the steady-state spectrum with $T_b = \infty$.

$H2W7$, and $H1W6$ are located about 3 Å from the Yb ion; however, the resonant field of $H2W7$ is much closer to the bulk resonance than that of $H1W7$ and $H1W6$ as a result of the anisotropy of the local dipole field. The protons $H1W7'$ and $H2W7'$ occur in the next unit cell at 5.2 and 6.2 Å. The dilution of Yb:Y is determined to be 0.12% from the integrated intensities of the near-proton signals. Equation (1) gives $b = 12$ Å for $a = 1.6$ Å, corresponding to a sphere of 400 protons.

After the thermal-equilibrium signals were recorded, the bulk spin resonance at 16.33 kOe was briefly saturated with radio frequency. The bulk polarization remained small throughout the successive field sweeps [Figs. 1(b) and 1(c)] because of the long bulk relaxation time T_{1n} of several hours. The striking result is that nearly all of the near protons quickly come into thermal equilibrium with the bulk at $T_b \simeq \infty$. Only the twelve protons $H1W7$ and $H1W6$ at 3 Å remain close to the lattice temperature, in stark contrast to the prediction of Eq. (1). Indeed, one of the protons with the fastest *direct* relaxation rate, $H2W7$, is actually in much stronger contact with the bulk spins than the lattice. By performing a lattice sum of the direct relaxation rates w_1 for all protons outside the barrier (i.e., excluding $H1W7$, $H1W6$), we find that the inclusion of $H2W7$ outside the barrier increases the predicted *bulk* relaxation rate by a factor of 7, illustrating the importance of this hole in the traditional barrier.

In order to determine the nature of this strong bulk-to-near-proton contact, we measured the temperature dependences, Figs. 2 and 3, of p_s/p_0 and the relaxation rate T_{1n}^{-1} for the intermediately located $H1W7'$ proton, where p_0 and p_s are the steady-state derivative signal heights for $T_b = T_{\text{lattice}}$ and $T_b = \infty$, respectively. In this crystal, the electron relaxation rate[10,11] $T_{1e}^{-1} = 0.0135T^9 + (7\times10^{11})\exp(-60/T)$ sec^{-1} varies over 6 orders of magnitude between 1.3 and 4.2°K, which makes Yb^{3+} a particularly good probe of the diffusion processes.[12] When the bulk spins are saturated, the inverse temperature β of $H1W7'$ is most simply described by

$$\dot{\beta} = -w_1(\beta - \beta_l) - w_d(\beta - 0), \tag{2}$$

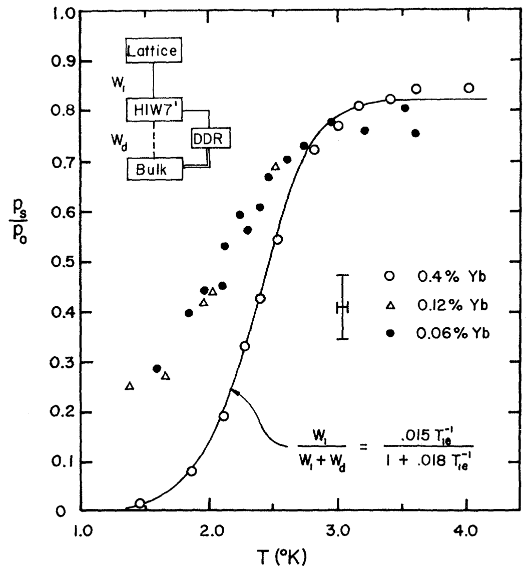

FIG. 2. Temperature dependence for $H1W7'$ of p_s/p_0, defined in Fig. 1. Solid curve, formula derived in the text. The two lower concentration crystals show a marked decrease in the bulk-to-$H1W7'$ contact, suggesting the importance of the spin-spin interaction reservoir of the Yb ions.

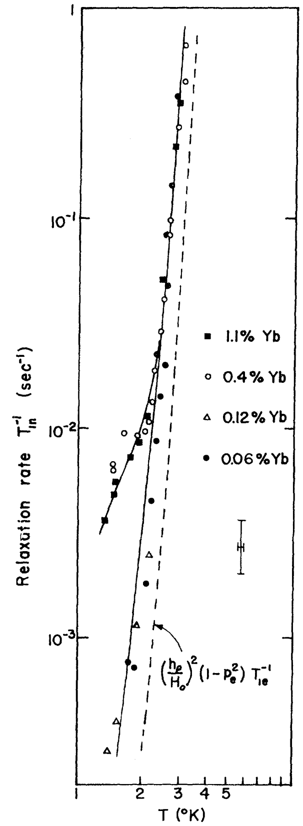

FIG. 3. Temperature dependence of the relaxation rate of $H1W7'$, showing also a large Yb-concentration dependence at low temperatures. Solid curves, the function $T_{1n}^{-1} = (1-p_e^2)\{C_1 + 0.0058T_{1e}^{-1}\}$, with $C_1 = 0$ and 0.016; dashed line, predicted direct relaxation w_1 using $h_\rho = 122$ Oe, $H_0 = 16.21$ kOe, and T_{1e} measured at 5 kOe.

where $w_1 = \sigma T_{1e}^{-1}$ is the direct relaxation rate and w_d describes the contact between $H1W7'$ and the bulk spins, which we loosely term diffusion. A more exact analysis must also include the effects of other near protons. The steady-state condition implies $p_s/p_0 = \beta/\beta_l = w_1/(w_1+w_d)$. This expression fits the data remarkably well for the 0.4% crystal, provided w_d has the form $\alpha + \gamma T_{1e}^{-1}$, discussed below. The 0.06 and 0.12% crystals show a marked decrease in the $H1W7'$-to-bulk contact at the lower temperatures. This concentration-dependent contact is also strongly reflected in the temperature dependence of the $H1W7'$ relaxation rate, Fig. 3, where the more concentrated crystals display a relatively T-independent process at the lower temperatures, characteristic of cross relaxation or spin diffusion.

The concentration-dependent contact between bulk and $H1W7'$ spins extends also to other near protons and indicates the profound influence of the impurity dipole-dipole reservoir (DDR) in the nuclear relaxation process. Redfield[13] and Provotorov[14] have shown the existence of a spin temperature in the DDR distinct from the electronic Zeeman temperature, and recent dynamic nuclear polarization experiments[15-18] on bulk nuclei indicate that the DDR is strongly coupled to the bulk spins. Thus, when the bulk spins are saturated, $\beta_{DDR} \simeq \beta_b = 0$, and the near protons, which are also strongly coupled to the DDR, are affected. Effectively, the DDR short circuits the traditional barrier, as suggested in the inset of Fig. 2. This process is represented by the rate α, which does not depend explicitly on T_{1e} and therefore dominates the relaxation rate at the lowest temperatures. While it should be possible to fit the low-concentration data by adjusting α, the fit at low temperatures is poor, perhaps because of the simplifying assumptions implicit in Eq. (2).

The necessity of a diffusion term γT_{1e}^{-1} follows from an examination of Fig. 2. Between 2.7 and 4.0°K, p_s/p_0 remains constant at about 0.82 while T_{1e} (and hence w_1) varies by 3 orders of magnitude. This implies $w_1/w_d \simeq 4.5$, a constant above 3°K. This result suggests an impurity-induced diffusion process, such as proposed by Horvitz.[19] Here the fluctuations in the impurity field cause mutual spin flips between $H1W7'$ and a neighboring proton, labeled i and coupled to $H1W7'$ by the nuclear-nuclear dipole field d_{1i}^z. For two well-resolved near protons at resonant fields h_1 and h_i, we find the probability for a mutual spin flip is $[d_{1i}^z/(h_1-h_i)]^2(1-p_e^2)T_{1e}^{-1}$, with p_e the Yb polarization.[20] By summing this over all lattice protons, we calculate $\gamma = 10^{-4}-10^{-3}$ for $H1W7'$, depending sensitively on exact proton positions. This is in general agreement with the measured rates. Uncertainties in the radial local-field component h_ρ, the nuclear positions, and T_{1e} at high field may partially account for the discrepancy between the data of Fig. 3 and w_1(calc) above 2°K. In particular, it seems probable that T_{1e} contains an unexpected field dependence.

These experiments display for the first time the counterplay of direct relaxation and diffusion for particular near nuclei. It is apparent that such a microscopic approach is required to explain the complicated process of nuclear relaxation; for YES:Yb and no doubt many other systems at low temperature, the continuum model employed extensively in the past is a vast oversimplification. I have found a dominant thermal contact between the bulk spins and many near nuclei which is attributed to impurity-induced diffusion and intervention of the impurity spin-spin reservoir. I wish to thank C. D. Jeffries for active support and criticism of this work and A. R. King and H. Engstrom for assistance in the early stages.

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