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Model for nonexponential nuclear relaxation in highly doped magnetic glasses

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NMR measurements on rare-earth metaphosphate glasses, made over a wide temperature range, have shown that nuclear relaxation is not governed by a single exponential in these systems. A model that incorporates spin diffusion ideas has been developed to explain the results. For the highly doped paramagnetic glass systems, it appears that nuclear spins contributing to the NMR signal are found in distinct regions, which are distinguished by the presence or absence of spin diffusion amongst the nuclear spins. The model satisfactorily accounts for the observations and should be applicable to other paramagnetic systems. Information on the rare-earth-ion spin dynamics may be obtained from the NMR measurements using expressions derived from the model. [S0163-1829(97)51938-2]

The rare-earth R^{3+} metaphosphate glasses $R(PO_3)_3$ (REMG) have highly novel magnetic and magneto-optical properties with potential applications in laser and optoelectronics technology. These glasses incorporate rare earth ions in extremely large concentrations, rather than at the low dopant levels usually employed in devices. Structural studies employing the complementary probes EXAFS and x-ray diffraction have shown¹⁻³ that the trivalent rare-earth R^{3+} ions occupy sites with an average coordination number $6 \le N \le 8$ inside a skeleton comprised of PO₄ tetrahedra; there is no evidence for R-R correlations within the short range order, a result particularly pertinent to the magnetic and magneto-optical properties. There is evidence^{1,4,5} that the point symmetry for rare-earth ions in such glasses is predominantly trigonal symmetry, C_{3v} as in the corresponding sesquioxide crystals, with small distortions to triclinic symmetry, C_1 . NMR studies have now been carried out on well characterized REMG of high optical quality on which structural determination and systematic studies of the optical, magnetic, and nonlinear acoustic properties have previously been made.^{6,7} The ³¹P nuclei serve as probes of rare-earthion dynamical behavior.

The results presented here were obtained from measurements on a REMG doped with 1%(mol) Er³⁺ and buffered with La^{3+} to achieve the metaphosphate concentration. ³¹P NMR measurements were made using a conventional coherent pulsed NMR spectrometer,⁸ operating at 19.25 MHz. Nonexponential nuclear spin-lattice relaxation (NSLR) in solids may, in many cases, be analyzed using the stretched exponential or "Kohlrausch curve,"

$$1 - \frac{M(\tau)}{M(\infty)} = \exp\left[-\left(\frac{\tau}{T_1}\right)^{\alpha}\right],\tag{1}$$

where M denotes the signal amplitude, τ is the time following saturation of the nuclear spin system, T_1 is the nuclear spin-lattice relaxation time, and α is a fitting parameter. This curve is often used to describe glassy relaxation,9-12 including relaxation in systems with random free energies, such as spin glasses.¹³ It has been suggested¹⁴ that nonexponential relaxation in glasses may be the result of a distribution of relaxation times within the sample. Rammal¹⁵ has derived a stretched exponential expression to describe glassy relaxation on fractals and percolation structures. Narayanan et al.¹⁶ have described the characterization of nonexponential relaxation in solids, with reference to NSLR due to fixed paramagnetic impurities. They give α typically equal to 1 or 0.5.

Figure 1 shows time-domain NMR spin echo signals for different delays, τ , following an inversion pulse. The inset shows corresponding frequency-domain waveforms. Close to the site of a magnetic ion (Er^{3+}) , the average of the magnetic field due to the ion, B_{loc} , causes shifts in the nuclear resonance frequency. Adjacent nuclei communicate through spin diffusion only if their resonance frequencies are sufficiently close together; i.e., if the resonance frequencies differ by less than the natural nuclear linewidth $\Delta \omega$. This condition is sat-



FIG. 1. NMR data for a 1% Er REMG at 20 K: time-domain and frequency-domain (inset) spin echo signals for different delays, τ , following an inversion pulse.

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isfied when $a_0[dB_{loc}/dr]_{r=b_0} = \Delta \omega$, where a_0 is the internuclear spacing. The radius b_0 defines a sphere, the diffusion barrier, inside which spin diffusion is inoperative. The magnitude of $b_0(T)$ is given by

$$b_0(T)^{-4} = \frac{k_B T \Delta \omega}{3 a_0 \gamma_s \gamma_s^2 \hbar^2 S^2 B}, \quad \text{for } \tau_e \ll T_2, \qquad (2)$$

where *T* is the absolute temperature, τ_e is the electron correlation time, γ_I and γ_s are the nuclear and electron magnetogyric ratios, respectively, *B* is the applied magnetic field, *S* is the electron spin quantum number, and T_2 is the nuclear spin-spin relaxation time.

Samples are therefore composed of diffusive and nondiffusive regions of nuclear spins. In dilute systems nuclei in diffusive regions dominate the observed signal. Nuclei contained within nondiffusive regions have significantly shifted resonance frequencies and therefore contribute on short time scales to the echo or free induction decay (FID) waveforms, while nuclei in diffusive regions contribute over a longer time. From Fig. 1 it can be seen that the nondiffusive nuclei relax faster than nuclei in diffusive regions. Nuclear magnetization recovery data obtained at any point on the echo may be fitted using the Kohlrausch curve, with α varying between 0.6 (near the peak) and 0.9 (in the wings).

Nuclear relaxation in insulating glasses of this type proceeds through coupling of the electronic and nuclear spins. The theory of NSLR due to fixed, isolated paramagnetic centres in magnetically dilute crystals^{17–22} has been extended to describe nuclear relaxation in this highly paramagnetic system. In finding expressions for the average nuclear spin lattice relaxation time T_1 , NSLR both in the presence and in the absence of spin diffusion is considered. In either case, it is assumed that the 4f electrons of the magnetic ions are closely coupled to the lattice so that the nuclear-electron relaxation time may be taken as the nuclear spin lattice relaxation time.

Within diffusive regions, spin diffusion establishes a spatially homogeneous nuclear spin temperature. Nuclei in these regions relax following

$$S(t) = \exp(-t/T_1), \qquad (3)$$

where

$$\frac{1}{T_1} = \frac{4\pi}{3} n_s C^{1/4} D^{3/4} \tag{4}$$

in the diffusion limited [DL] case and

$$\frac{1}{T_1} = \frac{4\pi}{3} \frac{n_s \gamma_I^{3/2}}{(\gamma_I \gamma_S \hbar)^{3/2} S^{3/2}} C \left(\frac{\Delta \omega}{\omega_n}\right)^{3/4} \left(\frac{k_B T}{3a_0}\right)^{3/4}$$
(5)

in the rapid diffusion [RD] case, with

$$C = \frac{2}{5} (\gamma_I \gamma_S \hbar)^2 S(S+1) \frac{\tau}{1+\omega_n^2 \tau_e^2}.$$
 (6)

D is the nuclear spin diffusion coefficient, n_s is the magnetic ion concentration, and ω_n is the nuclear Larmor frequency.²⁰ The local symmetry of the rare-earth ions shows only small deviations from the crystalline trigonal symmetry. It is there-

fore expected that there will be only a small distribution of spectroscopic splitting factors for the ions and it is reasonable to assume a single exponential correlation function, leading to the simple form of the spectral density used in Eq. (6).

Expressions for nuclear relaxation without spin diffusion have been derived for systems where spin diffusion can be suppressed (i) by rotating frame experiments,²³ and (ii) by considering a dilute nuclear system with a vanishingly small spin diffusion coefficient.²⁴ For high dopant concentrations, or at sufficiently low temperatures, it is possible that the spheres defined by the diffusion barrier will overlap. In this case the bulk of the nuclear spins will lie in regions where spin diffusion is not operative. The volume in which nuclear resonance frequencies are shifted such that the nuclei are no longer seen in measurements is defined by some critical radius ρ_c which will be significantly smaller than b_0 . It arises from the same mechanism as b_0 and follows the same temperature dependence. Relaxation in the absence of spin diffusion with multiple sinks is of the form²³

$$S(t) = \int_{v-v_c} \exp\left[-\sum_{j=1}^{N} W_j t\right] dv , \qquad (7)$$

where W_j is the transition probability for a nuclear spin flip at position r due to an electron at dopant site j. Tse and Hartmann²³ have argued that ρ_c has an angular dependence but for a glassy system it becomes necessary to use angular averages. Using a suitable change of variables²⁵ it can be shown that nuclei in nondiffusive regions relax following

$$S(t) = \exp[t/T_1']^{1/2},$$
 (8)

where

$$\frac{1}{T_1'} = \left(\frac{3n_s}{4\pi}C^{1/2}[C^{1/2}\rho_c^3\exp(-Ct\rho_c^{-6}) + \sqrt{\pi}\phi_1(\sqrt{Ct\rho_c^{-6}})]\right)^2.$$
(9)

 ϕ_1 is the standard error function. In the limit $\sqrt{Ct\rho_c^{-6}} \ge 1$ Eq. (9) reduces to

$$\frac{1}{T_1'} = \frac{9}{4} n_s^2 C \,. \tag{10}$$

Figure 2 shows plots of $-\ln(1-M(\tau)/M_0)$ versus τ and versus $\tau^{1/2}$ for data obtained from the peak (squares) and from the wings (circles) of the time-domain waveforms. The straight lines illustrate that measurements taken at any point on the line shape include contributions from both diffusive and nondiffusive nuclei.

Nuclear magnetization recovery in systems containing both diffusive and nondiffusive regions may be described by an expression of the form

$$\frac{M(\tau)}{M_0} = 1 - 2\nu \left[f \exp\left(\frac{-\tau}{T_1}\right) + (1 - f) \exp\left(\frac{-\tau}{\lambda T_1}\right)^{1/2} \right], \qquad (11)$$

where ν is a scaling factor, introduced because the degree of nuclear saturation is not known precisely, and *f* is the diffusive fraction. The first and second terms describe NSLR in diffusive and nondiffusive regions, respectively. The relax-





FIG. 2. NMR data for a 1% Er REMG at 20 K: plots of $-\ln(1-M(\tau)/M(\infty))$ versus τ (filled) and versus $\tau^{1/2}$ (open), respectively obtained from the peak (squares) and from the wings (circles) of the time-domain waveforms. The straight lines highlight the nonlinearity of the data.

ation rate for nondiffusive regions has been expressed in the form $T'_1 = \lambda T_1$ for convenience, where

$$\lambda = \frac{16\pi}{27} \frac{1}{n_s} \left(\frac{D}{C}\right)^{3/4} \tag{12}$$

in the diffusion limited case and

$$\lambda = \frac{4\pi}{3} \frac{\gamma_I^{3/2}}{n_s(\gamma_I \gamma_S \hbar)^{3/2} s^{3/2}} \left(\frac{\Delta \omega}{\omega_n}\right)^{3/4} \left(\frac{k_B T}{3a_0}\right)^{3/4}$$
(13)

in the rapid diffusion limit. The temperature dependence of λ in Eq. (12) arises from the temperature dependence of τ in *C* [Eq. (6)]. Calculation of λ is complicated by a lack of detailed knowledge of the symmetry of the paramagnetic ion sites, the exact paramagnetic ion concentration, the angular dependence of the critical radii (b_0 and ρ_c), and the width and shape of the spectrometer passband. In the diffusion-limited case prior knowledge of the electronic relaxation rates is required.

Figure 3 shows a family of recovery curves measured at four different points on the time-domain waveform from the peak (top) down to the wings (bottom). The fitted curves were obtained by fitting the four data sets simultaneously using Eq. (11), and provide strong support for the two-component model. From the fits it was found that the diffusive fraction increases from f>0 at the peak to f<1 in the wings of the resonance line. The parameters obtained were: $T_1=1.41(5)\times10^{-2}$ s; $\lambda=0.26(2)$. Nuclear relaxation data for this system over the temperature range 4 K to 100 K have been analyzed using Eq. (11). The data were described consistently by the model.

A plot of the nuclear spin-lattice relaxation rate T_1^{-1} and λ versus T^{-1} for the 1% Er-doped sample is shown in Fig. 4. The T_1^{-1} results correspond to regions in which spin diffusion operates and have been analyzed using Eq. (4) [DL] and Eq. (5) [RD]. The peak in the data corresponds to $\omega_n \tau_e = 1$.



FIG. 3. Recovery data for a 1% Er REMG at 20 K, measured at different points on the time-domain waveform from the peak (top curve) down to the wings (bottom curve) of the FID signal. The curves represent the best simultaneous fits to the data of Eq. (11).

The data are well described by the [RD] expression above 20 K, and the [DL] expression at lower temperatures. At high temperatures λ decreases with decreasing temperature as predicted by Eq. (13), but with less than the expected $T^{3/4}$ dependence. In the region of the peak in the T_1^{-1} data estimates of ρ_c indicate that the condition $\sqrt{Ct\rho_c^{-6}} \ge 1$ no longer holds so Eq. (10) cannot be used, and the temperature dependence of λ is difficult to predict. Below 7 K the experimental values of λ increase much less sharply than Eq. (12) predicts. Linewidth data suggest that over this temperature range local electronic fields are large and increase dramatically at low temperatures, so that b_0 and ρ_c are large, and may overlap at sufficiently low temperatures. The measured nuclear relaxation rates for the diffusive and nondiffusive regions may thus be determined by nuclei situated close to the diffusion barrier, and λ may therefore change less rapidly than expected. A more detailed analysis of this effect, including discussion of the measured linewidths, will be published elsewhere.



FIG. 4. A plot of T_1^{-1} (•) and λ (Δ) versus T^{-1} for a 1% Er REMG. The curves represent the best fits to the data of the [RD] and [DL] expressions.

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Parameters obtained from fitting the nuclear relaxation expressions suggest that the Orbach process²⁶ dominates electronic relaxation over the whole temperature range. For the 1% Er sample, the crystal field splitting is found to be $\Delta = 102(5)$ K. Glasses containing other rare-earth ions have been studied using similar methods, and the results will be published elsewhere.

The present measurements on rare-earth-doped paramagnetic phosphate glass systems containing high concentrations (1% to 25%) of magnetic ions suggest that nuclei in distinct regions in a given sample contribute in separate ways to the

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The two regions are characterized by the presence or absence of nuclear spin diffusion amongst the nuclei, respectively. The nuclear spin-lattice relaxation times are governed by the spin-lattice relaxation time of the paramagnetic ions which, in turn, is determined by the various phonon processes which can occur. A model incorporating these ideas has been developed and is able to describe nuclear relaxation over a large range of temperatures and rare-earth-dopant concentrations in a consistent way.

observed NMR spectrum and magnetization recovery curves.

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