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Nuclear Spin-Lattice Relaxation in Amorphous Materials: B_2O_3

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The temperature and frequency dependence of the nuclear spin-lattice relaxation in amorphous B_2O_3 has been investigated and a T_1 minimum with unusual properties has been discovered at ~ 300 K. The relaxation is described in detail by Raman-like processes involving the two-level disorder modes and phonons characteristic of glassy materials.

A direct comparison of the nuclear spin-lattice relaxation rates of solids in their vitreous and crystalline forms has been made in only few materials. Rubinstein and Taylor¹ studied and compared the relaxation rates of crystalline and amorphous As_2S_3 , and reported a much faster relaxation rate in the glass. Earlier, Haupt and Müller-Warmuth² found that the relaxation rate of protons in some organic glasses is much faster than in their crystalline counterparts. These results strongly indicate that defects which are intrinsic to the glassy state of matter are very effective sinks for nuclear-spin-excitation energy.

Recently Szeftel and Alloul³ examined the nuclear spin-lattice relaxation in glassy and crystalline B_2O_3 , among other samples. These authors report that T_1 (the spin-lattice relaxation time) in crystalline B_2O_3 was much longer than in glassy B_2O_3 and that the temperature dependence of the relaxation time is $T_1 \propto T^{-1.3}$ in the temperature range 1.2 to 90 K.

We report on measurements of the spin-lattice relaxation time of ^{11}B in crystalline and amorphous B_2O_3 in the temperature range 150 to 500 K, and nuclear resonance frequencies ranging from 10 to 30 MHz. We find a minimum in T_1 as a function of temperature in the vicinity of 300 K, and an increase in T_1 with increasing temperature thereafter. Our data agree with those of

Szeftel and Alloul in the small range of temperature overlap between the two experiments. Our values of T_1 are found to be practically independent of Larmor frequency ω_L at temperatures both above and below the T_1 minimum, in contrast to the predictions of the Bloembergen, Purcell, and Pound⁴ motional-narrowing theory. The temperature at which the minimum occurs is only weakly dependent on ω_L , and the value of T_1 at the minimum is nearly independent of ω_L . The measured line shape (due to random distribution of electric-field-gradient axes with respect to the applied magnetic field which broadens the ^{11}B nuclear-resonance line because of the sizable quadrupole moment of this nucleus) does not change at all in the temperature range we have covered, indicating that melting of the glass is not involved at these temperatures.⁵ We have made extensive studies of many B_2O_3 glasses containing widely different paramagnetic impurity concentrations and absorbed water content which show that the spin relaxation is unrelated to these extraneous impurities.⁶

The T_1 measurements were made on the central $-\frac{1}{2}$ to $+\frac{1}{2}$ component of the quadrupole-split resonance line with a Bruker SXP pulsed spectrometer using both the saturating-comb and the repetition-rate techniques. Both types of measurements gave identical results for T_1 . The resulting temperature dependence of T_1 in B_2O_3 is

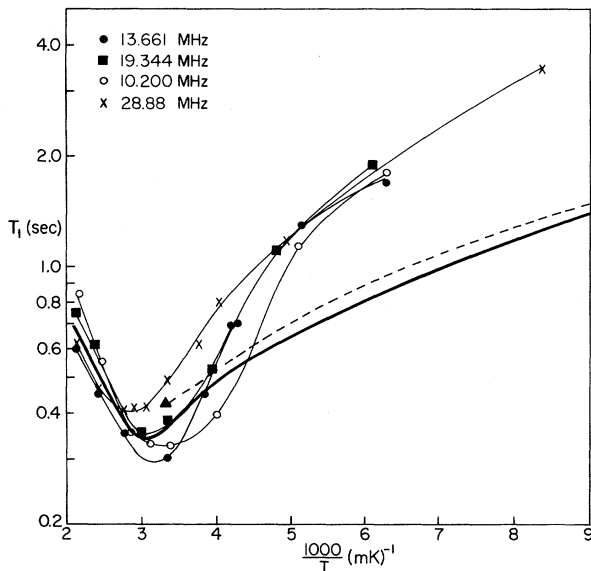


FIG. 1. Spin-lattice relaxation time versus $1000/T$ at 10.2, 13.1, 19.3, and 28.9 MHz. Dashed line represents $T_1 \propto T^{-1.3}$, valid at low temperatures, and solid triangle is room-temperature datum point of Ref. 3. Heavy solid line is the theoretical fit to the data. Light solid lines are a guide to the eye.

drawn in Fig. 1, where measurements taken at $\sim 10, 20,$ and 30 MHz are shown. The nearly linear dependence of T_1 on T , found by Szeftel and Alloul to be valid at low temperatures, is shown by a dashed line; note that only one of their data points (300 K) appears in the temperature range shown in Fig. 1. The theoretical temperature dependence, discussed below, is drawn in a broader line. Values of T_1 in polycrystalline B_2O_3 are a factor of ~ 30 larger than in vitreous B_2O_3 , and will be discussed in a later publication. The variation of the T_1 -minimum temperature with Larmor frequency is a small, but real, effect.

We describe spin-lattice relaxation in amorphous materials using a model for these materials introduced by Anderson, Halperin, and Varma⁷ and by Phillips,⁸ which has successfully explained many of the anomalous thermal and ultrasonic properties of glass. In this model the excitations consist of phonons plus a series of two-level systems (which we call "disorder modes") with a distribution of energy splittings which is continuous in energy and whose levels are separated by a relatively high potential barrier (see Fig. 2). Such a two-level mode is thought to arise from a group of atoms which can sit in two

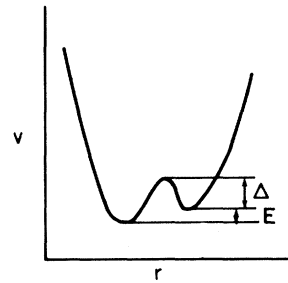


FIG. 2. Schematic diagram of potential energy of single disorder mode versus a generalized separation coordinate where E is the energy difference between the two mode configurations, and Δ is the potential-barrier height between them.

configurations separated by a small energy difference.⁷

The relaxation of the nuclear spin states is caused by the usual coupling of the lattice to the nuclear quadrupole moment Q ,

$$\mathcal{H}_Q = \sum_{m=-2}^{m=+2} Q_m V_m, \quad (1)$$

where V_m are the matrix elements of the electric field gradient at the nucleus and Q_m are irreducible tensor operators of the nuclear spin at, or near, a defect site. V_m is expanded in the coordinates of phonons and disorder modes of the system.⁹ The resulting relaxation is transmitted throughout the glass by rapid spin diffusion.⁶ The dominant processes which cause changes in the nuclear-spin states are Raman processes involving two modes and are shown schematically in Fig. 3. The direct decay of the nuclear spin into

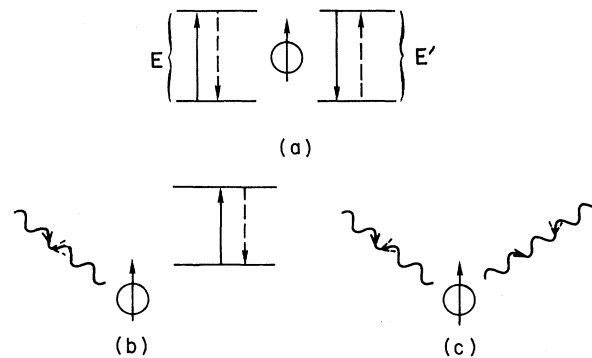


FIG. 3. Processes in which nuclear spin state changes from m to m' ; (a) involves excitation of a disorder mode of energy E , and de-excitation of a disorder mode of energy E' , (b) a phonon and a disorder mode, and (c) two phonons.

a single disorder mode or phonon gives a negligible contribution to T_1 .¹⁰ Process (a) involves a nucleus which is acted on by two overlapping disorder modes; such a pair of modes involves two different disorder modes, each of which produces an electric field gradient at the nucleus. Process (b) is decay via a phonon and a disorder mode and was suggested by Szeftel and Alloul.³ Process (c) is decay via two phonons.¹⁰ Each

process is mediated by thermally activated hopping.

The contributions to T_1 from the processes in Fig. 3 are now obtained. For $T \geq T_{\min}$, the temperature at which the minimum in T_1 occurs, the intrinsic lifetimes of the states (especially the disorder modes) must be included. Using a generalization of the density-matrix formalism, we obtain for the contribution of process (a) to the relaxation rate

$$(T_1)^{-1} = \frac{2Q_m^2}{\hbar^2} \langle [V\lambda]^2 \rangle \rho^2 \times \int_0^{E_m} \int_0^{E_m} dE dE' \left\{ \frac{2\tau_a}{1 + \hbar^{-2}(E - E' \pm \hbar\omega_L)^2 \tau_a^2} \right\} \times \{ [1 + \exp(E'/k_B T)]^{-1} [1 + \exp(-E/k_B T)]^{-1} + [1 + \exp(-E'/k_B T)]^{-1} [1 + \exp(E/k_B T)]^{-1} \}. \quad (2)$$

Here $\langle [V\lambda]^2 \rangle$ is an averaged electric-field-gradient matrix element and overlap integral for process (a); τ_a is a combined lifetime for the two disorder modes; ρ is the density in energy of disorder modes (which is taken to be a constant), E_m is their maximum energy; and ω_L is the nuclear Larmor frequency ($\hbar\omega_L/E_m \ll 1$). There are similar contributions for processes (b) and (c).

For $T \ll T_{\min}$, process (a) accounts for available experimental results.³ There $\tau(T)$ becomes very long, and the factor in the first curly brackets of Eq. (2) becomes an energy-conservation δ function. Taking the energy density of disorder modes to be constant, process (a) gives $T_1 \propto T^{-1}$ in the low-temperature limit. Processes (b) and (c) give contributions proportional to T^{-4} and T^{-7} , respectively, at low temperatures. The low-temperature data of Ref. 3 show that mechanism (a) dominates below ~ 100 K. The observed deviation of the exponent of T from unity at low T may arise from a weak energy dependence of the disorder-mode density of states.

For $T > T_{\min}$, on the other hand, $\tau(T)$ becomes small and T_1 once again becomes large. The minimum in T_1 near room temperature can be understood from the form of Eq. (2). Changing variables to the sum and difference of E and E' , and performing one integration gives for the integrals in T_1

$$\int_{-\gamma/2}^{+\gamma/2} dy \left\{ \frac{E_m \tau_a(T) \hbar^{-1}}{1 + \gamma^2 [y \pm (\hbar\omega_L/k_B T)]^2 [E_m \tau_a(T) \hbar^{-1}]^2} \right\} F_T(y), \quad (3)$$

$$F_T(y) = [e^{2y} - 1]^{-1} \ln[(e^{\gamma+y} + 1)/(e^\gamma + e^y)],$$

where $\gamma = (E_m/k_B T)$ and $y = (E - E')/k_B T$. We assume that the dominant contribution to $\tau_a(T)$ for T in the neighborhood of room temperature and higher comes from the disorder modes decaying and nuclei hopping over potential barriers, which has the form¹¹

$$\tau_a(T) = \tau_0 \exp(\Delta/k_B T). \quad (4)$$

We neglect the contributions to τ from barrier-tunneling and scattering processes which we expect to be much smaller at these temperatures. The function $F_T(y)$ is a smoothly varying function of y for all temperatures. For temperatures such that $E_m \hbar^{-1} \tau_a(T) \sim O(1)$, the term in curly brackets in Eq. (3) is a rapidly varying function. T_1 has a minimum at a τ given by the solution of

$$(E_m + \hbar\omega_L) \hbar^{-1} \tau_a(T_{\min}) = g(T_{\min}), \quad (5)$$

where the function $g(T)$ arises from the T dependence of $F_T(y)$ and $g(T_{\min}) \approx 10$ for B_2O_3 . Processes (b) and (c) give expressions similar to (5).

By using (4) in (3) and noting that $(\hbar\omega_L/E_m) \ll 1$, we see that the temperature at which the minimum in T_1 occurs is weakly dependent on $(\hbar\omega_L/E_m)$ and that the magnitude of T_1 at the minimum is virtually independent of ω_L . Both of these observations are in agreement with experiment.

The integrals for T_1 have been evaluated numerically using (4) for $\tau_a(T)$, and estimates of the several parameters have been obtained. When $T \gg T_{\min}$, $T_1(T) \propto \exp(-\Delta/k_B T)$, and from the slope of the data we find $\Delta \approx 2000$ K. Fitting the shape of T_1 to experiment over all T gives $E_m \approx 800$ K. Using $T_{\min} = 300$ K in Eq. (5) gives

$E_m \bar{h}^{-1} \tau_0 \approx 10 \exp(-\Delta/300)$; this yields $\tau_0 \approx 1.2 \times 10^{-16}$ sec. The overall magnitude of T_1 is scaled to agree with experiment near the minimum, and the curve for the above parameters is shown in Fig. 1.

In summary, we have discovered the existence of a T_1 minimum in vitreous B_2O_3 at ~ 300 K, well below its melting point of 730 K. We have developed a theory which explains the experimental properties of the longitudinal relaxation time in the vicinity of the minimum, as well as both the low- and high-temperature behavior. At low temperatures, Raman-like processes involving two-level disorder modes and acoustic phonons are dominant; at high temperatures thermally activated relaxation involving two-level defects dominates. Thus, the anomalous nuclear spin-lattice relaxation in glasses is caused by the same defects which are now believed to be responsible for their anomalous thermal and ultrasonic properties.

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Field-Induced Charge-Carrier Trapping in the Photoconduction of a Quasi One-Dimensional System: Phenanthrene-Pyromellitic Acid Dianhydride

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A field-dependent charge-carrier trapping process has been observed in the photoconduction mechanism of phenanthrene-pyromellitic acid dianhydride. This effect can be observed at electric field strengths exceeding 10^3 V/cm. A calculation on the basis of a hopping model shows that field-induced charge-carrier trapping occurs in a three-dimensional system at critical field strengths well above 10^6 V/cm. In a one-dimensional model, however, the critical field strength can be as low as 1 V/cm.

Organic charge-transfer crystals belong to the class of solids which exhibit quasi one-dimensional properties. This one-dimensionality is due to a characteristic packing of the molecules in the solid state. In phenanthrene-pyromellitic acid dianhydride (-PMDA), which belongs to the class of weak charge-transfer crystals, the molecules form stacks of alternating donors and acceptors. The molecular planes are parallel or close to parallel and have a spacing which is close to 3.5 Å.¹ Consequently, the intermolecular interaction

along the stack axis is considerably larger than the interaction perpendicular to the stack axis. This gives rise to an anisotropy of those physical properties which are governed by the overlap of molecular wave functions (short-range interaction) such as triplet-exciton energy transfer² and charge-carrier transport.^{3,4}

In this Letter we report a specific charge-carrier-trapping phenomenon which has to our knowledge not been reported in the field of photoconduction of organic solids: field-induced charge-