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Low-temperature nuclear-spin–lattice relaxation in glasses

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We show that recent measurements of nuclear-spin–lattice relaxation in glasses at low temperatures are accounted for by a Raman-like process involving the excitation and deexcitation of the low-energy modes typical of glasses. Using this analysis of the above measurements, we obtain new information about the density of these modes for energies up to 100 K.

Recent detailed measurements of the nuclear-spin–lattice relaxation time T_1 for temperatures $1.2 < T < 100$ K in glasses have given $T_1 \propto T^{-\alpha}$. Szeftel and Alloul[1] find $\alpha = 1.3$ in amorphous B_2O_3 and $\alpha = 1.4 \pm 0.1$ in amorphous $(NaO_2)_{0.3} \cdot (SiO_2)_{0.7}$, and they report finding similar results for $Na_2B_4O_7$. Earlier, Rubinstein and Taylor[2] reported an estimate of $\alpha \simeq 2$ for As_2S_3; it is doubtful, however, that these authors have sufficient data to distinguish $\alpha \simeq 2$ from the values reported in Ref. 1.

These data for the temperature dependence of T_1 provide detailed new information about the relaxation mechanisms in glasses over a wide range of energies up to 100 K; in order to obtain this information, however, it is necessary to identify the relaxation mechanism. We show here that the processes suggested by these authors are not consistent with the data; the data are however accounted for by a Raman-like process involving the excitation and deexcitation of the low-lying disorder modes known to be typical of glasses.[3-5] Using this analysis, new information about the density of these modes for energies up to 100 K is obtained; the density of the disorder modes for energies $\gtrsim$ 3K has not been investigated in detail before.[3]

There is now considerable evidence that a universal feature of glasses is the existence of a distribution of modes special to that state (in addition to phonons) which have a density nearly independent of energy. They have been observed in detail for energies between 0.05 and 2 K by heat-capacity measurements.[4,5] A model of glasses employing two-level modes with a continuous distribution of energy splittings and an appreciable potential barrier between the two levels has been proposed by Anderson, Halperin, and Varma and by Phillips[6]; the modes are thought to arise from the motion of groups of atoms which can occupy two configurations of nearly equal energy (see Fig. 1). We shall refer to these modes as "disorder modes." This model has been used successfully to describe the heat capacity,[6] thermal conductivity,[6] ultrasonic attenuation,[6,7] variation of the velocity of sound[8] and other properties of glasses at low T ($\lesssim 10$ K). We shall use this model of glasses to describe nuclear-spin–lattice relaxation.

The nuclei studied by Szeftel and Alloul and by Rubinstein and Taylor couple to the lattice primarily through their quadrupole moments. This interaction is written in the usual form

$$H_I = \sum_m Q_m V_m ,$$

where Q_m are the tensor components of the quadrupole moment and V_m are the matrix elements of the electric field gradient at the nucleus. Variations of V_m at the nucleus cause its spin state to decay; these variations are caused either by phonons modulating the positions of nearby atoms or by nearby atoms changing from one to the other position in a disorder mode. We expand V_m in the coordinates of the phonons and disorder modes

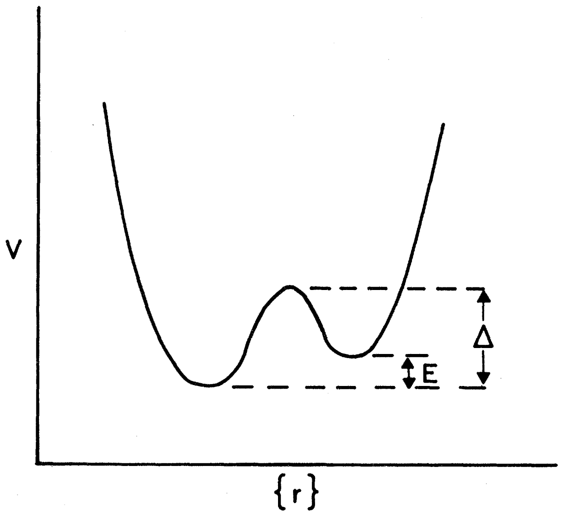

FIG. 1. Schematic diagram of potential energy of a disorder mode vs generalized coordinate. E is the excitation energy splitting and Δ is the potential barrier.

which gives terms in V_m like $(V_{i,j})\sigma_i^{\pm}\sigma_j^{\pm}$, $(V_{k,l})\sigma_k^{\pm}\vec{U}_l$, and $(V_{m,n})\vec{U}_m\vec{U}_n$, where $\sigma^{\pm}$ are the Pauli operators for the two level disorder modes, and $\vec{U}_m$ is the strain[9] at site m; the V's are the matrix elements of the electric field gradient for these processes. Note that nuclear decay into a single mode (either phonon or disorder mode) gives a negligible contribution to T_1 because the density of such states is restricted by the nuclear spin energy.[9] The first two processes above are shown schematically in Fig. 2; the third process gives the usual Raman scattering of a phonon.[10]

Consider first the contribution of process (a), Fig. 2, to the temperature dependence of T_1 at low T. This process involves the excitation and deexcitation of disorder modes both of which interact with the nuclear spin.[11] Its contribution to the transition rate T_1^{-1} is given in lowest order perturbation theory by

$$T_1^{-1} = 2 \times \frac{2\pi}{\hbar^2} \int_0^{E_m} Q_m^2 \, |V_{i,j}|^2 \rho_D^2(E) \times \left[1 + \cosh\left(\frac{E}{k_B T}\right) \right]^{-1} dE. \tag{1}$$

ρ_D is the density of disorder modes, E is their energy splitting [see Fig. 2(a)] and E_m is the maximum energy of the splittings. The small nuclear-spin energy has been neglected compared to E, E'. $\rho_D(E)$ has been studied for $T < 3\text{K}$ where it has been found to be nearly independent of energy.[4,5] We choose $\rho_D(E) = \rho_{D,0}E^{\eta}$, where η is positive and considerably less than unity to give a weak increase of $\rho_D(E)$ with increasing E in the range $2 < E/k_B < 100$ K. We assume that $V_{i,j}$ is independent of E, and then evaluating Eq. (1) at low T ($k_B T \ll E_m$) gives

$$T_1 \propto T^{-\alpha}, \quad \alpha = 1 + \eta. \tag{2}$$

E_m has been estimated to be $\gtrsim 400$ K,[6,12] and therefore Eq. (2) should give the temperature dependence of process (a) well throughout the range of T in these experiments.

The contributions to T_1 from other processes must now be considered. The contribution of optic phonons to process (b), Fig. 2, will be exponentially small at low T, and we neglect it. The contribution of acoustic phonons to process (b), Fig. 2, is obtained in a manner similar to that in Eq. (1) by using a Debye density of phonon states and again taking $\rho_D(E) = \rho_{D,0}E^{\eta}$. Care must be taken in obtaining the energy dependence of the matrix element of the strain operator.[9] The contribution of this process at low T($k_B T \ll E_m$, Debye energy) goes as

$$T_1 \propto T^{-4-\eta}.$$

Note that the Debye temperatures of all of the materials studied in Ref. 1 and 2 exceeds 150 K.[4] Szeftel and Alloul have used process (b) evaluated for $k_B T \gg E_m$, Debye energy, to account for their data; because E_m,[6,12] and the Debye energies,[4] are estimated to be considerably higher than any temperature in their experiment, this evaluation does not seem to be justified. Lastly, consider the contribution to T_1 at low T from the Raman process in which the nucleus decays by scattering a phonon: this is known to give $T_1 \propto T^{-7}$ for $k_B T \ll$ Debye energy.[10]

We have shown that the processes contributing to T_1 have markedly different temperature dependences at low T; only process (a) can be important at $T \lesssim 10$ K. Furthermore, this process accounts well for all of the experimental data up to $T \simeq 100$ K. Process (b), which was suggested by Szeftel and Alloul, varies too strongly with T to account for their data. Rubinstein and Taylor use the result of Bloembergen, Purcell, and Pound,[13]

$$T_1^{-1} \cong V^2\tau/(1 + \omega_S^2\tau^2) \cong V^2/\omega_S^2\tau$$

(ω_S the nuclear-spin frequency and τ a characteristic relaxation time) evaluated for $\omega_S\tau \gg 1$; Szeftel and Alloul have pointed out that this result predicts a strong ω_S dependence of T_1 which is not observed in any of the materials which they studied.[14] The conclusion that process (a) accounts for T_1 in the range of T studied along with the fact that it is widely believed that disorder modes are a universal feature of glasses[3-5] suggests that the dependence of T_1 on T reported in Ref. 1 and 2 will be a universal feature of glasses.

The fact that process (a) accounts for the temperature dependence of T_1 for $T \lesssim 100$ K and that the other possible processes give markedly different temperature dependences shows that these measurements of $T_1(T)$ probe quite directly the density of disorder modes over this broad range of energies. Specifically, these measurements suggest that a nearly constant density of disorder modes exists for energies between 2 and 100 K; this is a region of energies for which the disorder

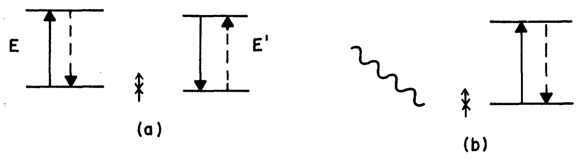

FIG. 2. Schematic representation of processes causing nuclear-spin–lattice relaxation in glasses at low T. Process (a) involves the excitation and deexcitation of disorder modes of energies E, E'; (b) involves absorption (emission) of a phonon with disorder mode excitation (deexcitation).

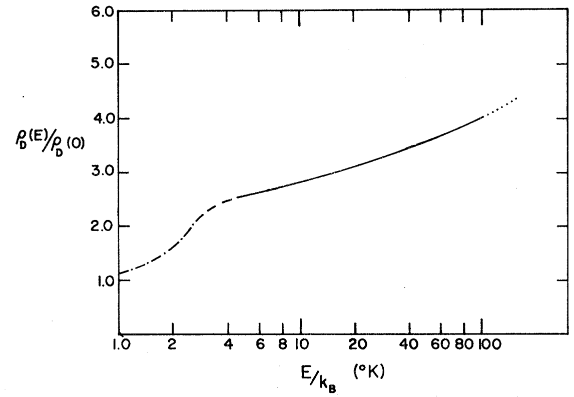

FIG. 3. Disorder mode density of states $\rho_D(E)$ vs energy E for amorphous B_2O_3. The chain curve is an estimate from Ref. 5 from heat-capacity measurements. Solid curve is result obtained here from nuclear spin-lattice relaxation measurements. The dashed curve joins the above two curves smoothly, and the dotted curve indicates modes at higher energies which have not yet been studied in detail.

mode density of states has not been measured in detail before.[3] Furthermore, these measurements give specific information about the E dependence of $\rho_D(E)$ in this range. For $T \lesssim 2\text{K}$, heat capacity measurements[5] give the estimate $\rho_D \cong a + bE^2$, where b/a is small[15]; for higher energies, however, it is difficult to separate the disorder mode contribution from the much larger phonon term in heat capacity measurements. Using the result for $T_1(T)$ in Eq. (2) (where the matrix element was assumed to be independent of energy), we immediately obtain from the results of Szeftel and Alloul the estimate $\rho_D(E) \cong \rho_{D,0} E^{\eta}$ with $\eta \cong 0.15$ for amorphous B_2O_3 and $\eta \cong 0.2$ for $(NaO_2)_{0.3} \cdot (SiO_2)_{0.7}$ for $2 < E/k_B < 100$ K. The energy dependence of $\rho_D(E)$ for B_2O_3 is shown in Fig. 3 where the estimate of Refs. 5 and 15 is shown for $E/k_B \lesssim 3$ K and the estimate obtained here is shown for $5 < E/k_B < 100$ K.[16] One caution should be noted with regard to obtaining a quantitative measure of the E dependence of $\rho_D(E)$ from $T_1(T)$: the matrix element $V_{i,j}$ in process (a), Fig. 2 might have some E dependence which would affect the value of α; this matrix element is not presently known in detail for the coupling to the disorder modes of glasses.

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[11] This process can be pictured by using the atomic-configuration interpretation of disorder modes given in Ref. 6. Two "different" groups of atoms (which might have some atoms in common) each have two nearly equivalent energy levels. Energy is given to the nucleus by the deexcitation of one group and absorbed from the nucleus in the excitation of the other.

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[14] It should be noted that As_2S_3, which was studied by Rubinstein and Taylor, was not among the materials studied by Szeftel and Alloul, and that Rubinstein and Taylor were experimentally restricted to a single ω_S and therefore could not study the ω_S dependence of T_1.

[15] This result for $\rho_D(E)$ is obtained in Reference 5 by subtracting the contribution of the Debye phonon density of states from that obtained from heat-capacity measurements.

[16] The two curves are joined somewhat arbitrarily at $E/k_B = 3.5$ K.