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Nuclear Spin-Lattice Relaxation Associated with Low-Energy Excitations in Glasses

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The nuclear T_1 has been measured between 1.2 and 300 K on ^{11}B, ^{23}Na, ^{29}Si, and ^{77}Se in amorphous B_2O_3, $(Na_2O)_{0.3}(SiO_2)_{0.7}$, $Na_2B_4O_7$, and Se. The measured rates, which for spins $I > \frac{1}{2}$ are much greater than those observed in corresponding crystalline materials, are nearly field independent and vary as T^{α} with $\alpha \sim 1.3$. Such a quadrupolar relaxation might be explained by a model involving the distribution of two-level systems, as describes the anomalous thermal and ultrasonic-wave properties of similar materials.

Recent measurements of specific heat and thermal conductivity[1] have revealed the existence of low-energy excitations in all insulating glasses so far investigated. One of the models proposed[2,3] to explain this effect assumes the existence of two-level excitations, whose energy splittings are widely distributed.[3] Later experimental results, namely a nonlinear ultrasonic attenuation[4] and an increase in the sound velocity[5] at temperatures below 10 K, can also be understood in this model. Such low-energy excitations might induce relaxation of the nuclear magnetization. The nuclear-quadrupole relaxation was indeed found to be faster in amorphous As_2S_3 than in the corresponding crystalline phase between 1.2 and 300 K.[6]

This Letter deals with measurements of the nuclear spin-lattice relaxation time T_1 performed on glasses in which the specific-heat anomaly has already been observed.[1] The results confirm that $(T_1)^{-1}$ is always much higher in the glassy state than in the crystalline. The data further enable us to conclude that the relaxation mechanism involves low-temperature motional excitations rather than paramagnetic centers. The observed frequency dependence of T_1^{-1} will be shown to disagree with the models usually proposed to explain the relaxation through motions in solids. A model for the relaxation process which involves the distribution of two-level systems and might explain the data will be suggested.

Pulsed NMR measurements have been carried out on amorphous samples of B_2O_3, $(Na_2O)_{0.3}$-$(SiO_2)_{0.7}$, $Na_2B_4O_7$, and pure Se. The experimental data obtained at $T = 4.2$ K and in an external field $H_0 \sim 20$ kG will be given first as they enable us to draw straightforward conclusions. The measured T_1 for ^{11}B and ^{23}Na nuclei ($I = \frac{3}{2}$) were always found to be extremely short (~2 min) when compared with values of several hours generally found for the same nuclei in crystalline insulating materials.[7] A direct comparison is possible with crystalline samples for boron oxide and for soda silica. In B_2O_3 T_1 was found to be 20 times longer in crystalline samples (the measured T_1 values were not critically dependent on the preparation procedure for either phase, and this ratio of T_1's was obtained for a sample on which data were first taken in the crystalline state and then after vitrifying). The difference is even larger in soda silica, with T_1 at least 2 orders of magnitude greater in the crystal than in the glass. On the contrary, ^{77}Se $(I=\frac{1}{2})$ in amorphous selenium and ^{29}Si $(I=\frac{1}{2})$ in vitreous soda silica exhibited very long T_1, more than 5 h. The result for ^{29}Si can be compared with the T_1 of ^{23}Na which is equal to 80 sec in the same sample. If the relaxation mechanism was of magnetic nature as it would be, for instance, for paramagnetic centers present either as impurities or as dangling bonds, the ratio of more than 200 between the T_1 values of ^{23}Na and of ^{29}Si could not be accounted for by the different gyromagnetic ratios and spin factors.[8] As ^{77}Se and ^{29}Si do not bear any quadrupole moment, it can be concluded by comparing the data for ^{77}Se and ^{29}Si on one hand, and for ^{11}B and ^{23}Na on the other, that the relaxation mechanism specific to glasses consists of the modulation of the quadrupole coupling.

Complete investigations of the nuclear relaxation for $3 < H_0 < 60$ kG and $1.2 < T < 300$ K were then performed for these nuclei. It is worth pointing out here that the quadrupole effects broaden the NMR spectra in all the observed systems. In all cases only the $(-\frac{1}{2}+\frac{1}{2})$ transition is sampled by a spin-echo technique. As the quadrupole splittings are known to be at most of about 1 MHz, measurements were taken by saturating the whole spectrum with a frequency-modulated comb of pulses. The magnetization recovery was always found to be slightly nonexponential. In a plot of $\log(M-M_0)$ versus time the initial slope (referred to as T_1 in this Letter) was found to be about 2 times steeper than the long-time slope corresponding to about 30% of the magnetization, in all the materials investigated. Such a nonexponential decay might be linked either with the different transition probabilities for $\Delta m = 1$ and $\Delta m = 2$,[10] or with a distribution of relaxation times over the sample. A more systematic study of the shape of the magnetization recoveries obtained when the spin system is prepared in different initial states has been performed, and details will be given in a later publication. Anyhow these effects did not influence the frequency and temperature dependences of the initial slope, though slightly modifying its value. From the data given in Fig. 1 it can be seen that in all materials T_1 varies over the whole temperature range as $T^{-\alpha}$, with α equal to 1.3 and 1.4 ± 0.1, respectively, for ^{11}B in B_2O_3 and for ^{23}Na in $(Na_2O)_{0.3}(SiO_2)_{0.70}$. Similar results were observed for both ^{11}B and ^{23}Na in $Na_2B_4O_7$. The frequency dependence of T_1 has been found very weak at 4.2 K (Fig. 1) since T_1 increases slightly in low fields by a factor which does not exceed 1.8 over the whole field range. Similarly weak dependences are observed at higher temperatures. In all these glasses the quadrupole relaxation shows the same major features as is the case for the specific heat and thermal conductivity. The relaxation processes which might explain such experimental results will now be considered.

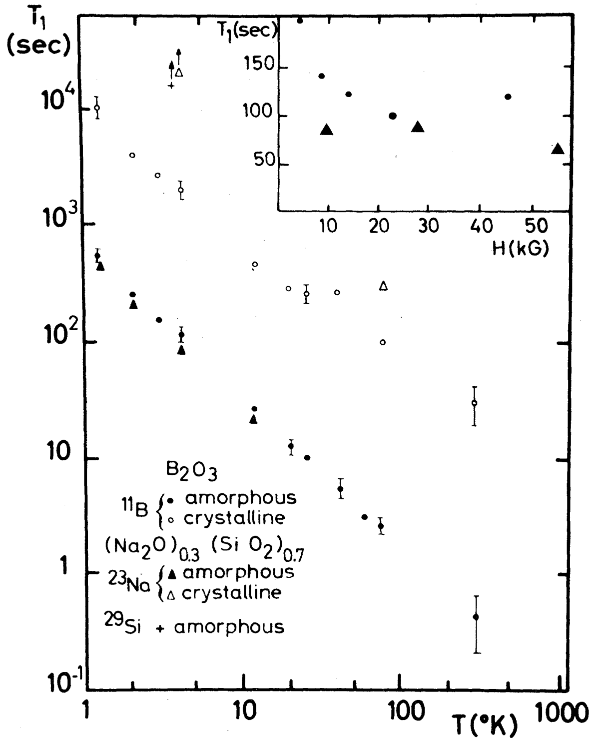

FIG. 1. Relaxation times of ^{11}B, ^{23}Na, and ^{29}Si at about 10 MHz in the amorphous and crystalline states of B_2O_3 and $(Na_2O)_{0.3}(SiO_2)_{0.7}$ versus temperature. The insert gives the field dependences of T_1 at 4.2 K. Only lower limits for the relaxation times of ^{23}Na in crystalline and ^{29}Si in amorphous soda silica are given as the saturation magnetization was not reached in 24 h.

Using standard notations,[11] the quadrupole Hamiltonian can be written for a nucleus as

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

where Q_m involves only spin operators and V_m stands for the electric-field-gradient Hamiltonian. These terms can be expanded with respect to the relative atomic displacement r_i of first-nearest-neighbor sites of the nucleus considered:

$$V_m = V_m{}^0 + \sum_i V_{mi}{}^{(1)} r_i + \sum_{ij} V_{mij}{}^{(2)} r_i r_j + \dots . \qquad (2)$$

In crystalline materials at temperatures below the melting point the quadrupolar relaxation is usually due to a two-phonon Raman process,[11] obtained by applying first-order perturbation theory to the third term of Eq. (2). An enhancement in the density of low-energy phononlike excitations as proposed in Ref. 2 would yield a decrease of T_1 at low temperatures as compared with crystalline materials. In such a case T_1 would vary as T^{-2} for temperatures greater than the highest energy kT_{max} of the phononlike excitations, and would have a steeper temperature dependence below T_{max}, as in crystalline materials where the Debye temperature is assigned to T_{max}. Unlike Rubinstein and Taylor[6] who actually observed a T^{-2} dependence for T_1 of ^{75}As in amorphous As_2S_3, such a behavior failed to appear over our whole range of investigation, which shows that such a model cannot describe the present results. As such a T^{-2} dependence was not found in crystalline B_2O_3 (Fig. 1), it might even be claimed that some disorder still remains in crystalline B_2O_3 (which has never been produced in single-crystal form).

Alternatively let us consider the possibility that the low-energy excitations consist of two-level systems, such as the tunneling states proposed by various authors.[3] In such a model some atoms or group of atoms could tunnel between two equilibrium positions and then give rise to a fluctuating part in the quadrupole interaction, mainly on first neighbors. Such a modulation of the quadrupole interaction is well known to be a relaxation process, and is usually treated according to the Bloembergen-Purcell-Pound approach.[12] If τ is the relaxation time of a given tunneling state,[13] the transition probabilities for the nearest neighbors are

$$W_1 \propto \tau(1+\omega^2\tau^2)^{-1}, \quad W_2 \propto \tau(1+4\omega^2\tau^2)^{-1}, \tag{3}$$

for $\Delta m = 1$ and $\Delta m = 2$, respectively. Here ω is the resonance frequency, and spin-diffusion processes yield $T_1^{-1} = \langle W_1 \rangle + \langle W_2 \rangle$, where the brackets mean an average over all tunneling states and nuclei. Since the data depend very weakly upon the magnetic field and thus upon ω, such results would require that $\omega\tau \ll 1$ for most tunneling states. In such conditions T_1^{-1} would be a certain average of τ over all the tunneling states. Since τ decreases with increasing T, T_1 would increase at high temperature, which disagrees with our results. Rubinstein and Taylor reached the opposite conclusion by making the assumption that $\omega\tau \gg 1$, which they could not check since nuclear quadrupole resonance experiments do not enable one to measure the frequency dependence of T_1. In such a case a strong increase of T_1 with the external field would be expected. It can then be concluded that such a relaxation process is not efficient enough to explain our data.

Now consider a nuclear spin in the vicinity of an atom (or a group of atoms) which can tunnel between states $|\beta\rangle$ and $|\gamma\rangle$. As $V_m^{(1)}$ has nonzero matrix elements between such states, the nuclear relaxation can proceed through a scattering of a phonon of energy $\hbar\omega_i$ by a tunneling state of energy E. The difference $|E - \hbar\omega_i|$ is equal to the Zeeman energy $\hbar\omega$ which is neglected as compared to most tunneling state energies. Then the second term of Eq. (2) will yield in a rapid diffusion regime a mean relaxation rate

$$T_1^{-1} \simeq 2\frac{2\pi}{\hbar}c\sum_{mi\alpha}\int_E\int_U \langle Q_m\rangle^2 |\langle\beta|V_{mi\alpha}{}^{(1)}|\gamma\rangle|^2 |\langle 1|r_{i\alpha}|0\rangle|^2 [\sinh(E/kT)]^{-1}\rho_\varphi(E)\rho_T(E,U)\,dE\,dU, \tag{4}$$

where the factor 2 comes from the crude assumption $W_1 \simeq W_2$, c is the concentration of tunneling states, the factor $\langle Q_m\rangle^2$ is a spin-matrix element, α represents the three spin coordinates, $|1\rangle$ and $|0\rangle$ are respectively one- and zero-phonon states of energy E, $\rho_\varphi(E)$ is the phonon density of states, and $\rho_T(E,U)$ is a normalized function, describing the distribution of the two-level systems which depends on their energy E and barrier height U. Equation (4) does not involve ω, which is consistent with the experimental absence of field dependence. The factor $[\sinh(E/kT)]^{-1}$ which comes from the thermal populations of phonons and tunneling states is the only one which depends on temperature. Hence, for kT greater than the highest tunneling state energy kT_{max}, T_1 should vary like T^{-1}, whereas a steeper dependence would occur for $kT \ll kT_{\text{max}}$. As $\rho_T(E,U)$ is expected to vanish for $E/k \gtrsim 400$ K,[3,13] the experimental T dependence is not inconsistent with the model. An exact computation of $T_1(T)$ would require us to assume a microscopic description of the two-level systems, as $\langle\beta|V_{mi\alpha}|\gamma\rangle$ actually depends on E and U. Anyhow, a fit of this model with the present experimental results implies that the nuclear relaxation proceeds mainly through low-energy tunneling states. This would happen whether $\rho_T(E,U)$ vanishes for $E/k \gtrsim 1$ K or if $\langle\beta|V_{mi\alpha}|\gamma\rangle$ enhances the contribution of low-energy tunneling states.

In conclusion, in the present work experimental evidence of a strong quadrupole relaxation process in inorganic amorphous materials has been presented. It has been shown that this general, very pronounced effect should be associated with the anomalous low-temperature properties of glasses. A relaxation mechanism has been proposed, which might explain the T and H dependence of T_1 in terms of a broad distribution of two-level systems which has been introduced previously to explain both the thermal properties and ultrasonic-wave experiments in amorphous materials. Further NMR experiments at lower temperatures together with other measurements might help us to obtain a better description of the two-level systems.

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Theoretical Analyses of the Angular-Dependent Photoemission from GaAs†

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A simple method, based on the direct transition model, has been developed for analyzing angular–energy-dependent photoemission data. Applying it to a pseudopotential band structure for GaAs all major structure in the experimental results from the (110) face can be accounted for and the wave vectors of the initial states are accurately determined. It is found that the umklapp scattering involving surface reciprocal-lattice vectors is important and that this mechanism may account for peaks previously attributed to surface states.

It has long been anticipated[1-3] that measurements of the angular dependence of photoelectron energy distribution curves (EDC's) would yield considerably more information than conventional experiments regarding the detailed structure of electron states in solids. The recent measurements by Smith and Traum[3,4] confirm this expectation by revealing much structure in the angular dependence of the EDC's from several single crystals. Until now however, because of the complex geometrical relation between the band structure and the photocurrent, no detailed theoretical analysis has been made. In this Letter we report a numerical method for calculating the angular-dependent EDC's and apply it to GaAs using a pseudopotential band structure.[5] We also present a numerical scheme for determining the origin in the Brillouin zone (BZ) corresponding to each experimental peak. Our results indicate that even at photon energies as high as 10.2 eV