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β -NMR investigation of dynamic and structural properties of lithium borate glass

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Abstract. With the method of β -radiation-detected nuclear magnetic resonance/relaxation (β -NMR) nuclear spin relaxation, resonance signals and reorientation in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ glass were investigated using the probe nuclei ^8Li and ^{12}B . The non-exponential relaxation found for both probes can be described by an $\exp(-\sqrt{t/T_{\text{inh}}})$ law and is explained by inhomogeneous polarization averaging over the isolated nuclei. The temperature dependence of the corresponding relaxation rate T_{inh}^{-1} shows two regions of different characteristics: below 200 K the coupling to relaxation centres typical of glasses dominates the relaxation. Above room temperature the relaxation of ^8Li and ^{12}B is due to Li diffusion in the glass. Linewidth and nuclear spin re-orientation measurements corroborate earlier results from ^7Li and ^{11}B NMR on the electric field gradients at the respective probe sites.

1. Introduction

The $\text{Li}_2\text{O}\text{-B}_2\text{O}_3$ glass system has been subjected to numerous investigations of its ion-conducting [1-3] and structural properties [4]. Various spectroscopic methods such as light scattering and ultrasonic techniques were applied for the investigation of glass transition phenomena and low-temperature properties. Nuclear magnetic resonance (NMR) measurements have become a versatile tool for investigating such structural properties as atomic coordination and chemical bonding on the one hand and dynamical processes as atomic motions on the other. Most of the NMR experiments were done with the nuclei ^6Li and ^7Li [5, 6] and also broad-line continuous-wave NMR measurements on ^{10}B and ^{11}B [7, 8] were reported. In this paper spin-lattice relaxation (SLR) measurements on β -active ^8Li (lifetime $\tau_\beta = 1.2$ s, nuclear spin $I = 2$) and ^{12}B ($\tau_\beta = 29$ ms, $I = 1$) with the method of β -radiation detected NMR (β -NMR) for the investigation of motional processes are presented and compared with earlier results of SLR measurements on the corresponding stable nuclei. In addition information on the structure of the probe site environment was obtained from lineshape measurements

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on ^8Li and the investigation of the nuclear reorientation of ^{12}B . In the latter case the magnetic field dependence of the nuclear polarization is used to determine the size of the quadrupole interaction of the ^{12}B probe.

2. Experimental details

The spectrometer used for our measurements was the in-beam β -NMR spectrometer S6 at the High Flux Reactor of the Institut Laue-Langevin, Grenoble. The details of the method are outlined elsewhere [9, 10] and only a brief description will be given here. Polarized β -active probe nuclei, here ^8Li and ^{12}B , are produced in the sample by capture of polarized neutrons. The sample is placed in the external magnetic field B_0 . The β -decay radiation is asymmetric with respect to B_0 and proportional to the nuclear polarization P . Monitoring the β -asymmetry after neutron activation pulses yields directly the transient behaviour of P . The nuclear polarization is influenced by two effects: nuclear reorientation in static internal or external fields and SLR due to coupling to fluctuating internal fields. As the lifetimes of the β -active nuclei are long compared to their precession periods about the magnetic field, nuclear reorientation cannot be resolved in β -NMR. Only the time-averaged effect is accessible via the initial polarization value P_0 at the end of a neutron activation pulse. Spin-lattice relaxation leads to the decay of the nuclear polarization and can be observed between the neutron activation pulses. Under continuous neutron activation and irradiation of radiofrequency (RF) fields on the sample, NMR spectra can be recorded by measuring the β -asymmetry.

Specific properties of β -NMR, important for measurements in glasses are the following:

(i) The nuclear polarization stems from a nuclear reaction and is independent of a Boltzmann factor. Thus a wide range of external magnetic fields is easily accessible.

(ii) The SLR measurements do not require RF pulses for a polarization inversion. The problem of saturating a broad distribution of resonance frequencies does not arise.

(iii) The radioactive probe nuclei are extremely diluted (typically 10^{-18}) and spin diffusion is prevented. β -NMR is therefore basically different from the general case of NMR, where a spin temperature is established via resonant spin flips. Inequivalent sites of the probe nuclei, expected for disordered materials, should affect the SLR behaviour observed by NMR and β -NMR in different ways, e.g. the single-exponential polarization decay $P(t) \propto \exp(-t/T_1)$, found in NMR in the presence of spin temperature, is not generally to be expected in β -NMR.

(iv) The β -lifetime τ_β of the probe nuclei used in β -NMR measurements limits accessible SLR times T_1 to the range $0.01\tau_\beta \leq T_1 \leq 100\tau_\beta$ since the repetition time of the neutron activation pulses has to be of the order of magnitude of τ_β for an appropriate signal/noise ratio.

In the measurements presented here the asymmetry of ^8Li and ^{12}B was observed. Both probe nuclei were produced simultaneously in the sample. The β -radiation of the two ensembles cannot be discriminated with respect to their energy, since both ^8Li and ^{12}B have endpoint β -energies of about 13 MeV. However, by timing the neutron activation and subsequent observation periods appropriate to the β -lifetimes the β -asymmetries of ^8Li and ^{12}B could be measured separately.

The sample with the nominal composition $\text{Li}_2\text{O} \cdot 2.86\text{B}_2\text{O}_3$ was produced from isotopically pure $^7\text{Li}_2\text{CO}_3$ and $^{11}\text{B}_2\text{O}_3$. Isotopically pure material was used in order to

prevent parasitic neutron capture by ^6Li and ^{10}B in the measurements. The starting materials were melted in a Pt crucible. Dry oxygen was passed through the melt for two hours to minimize the moisture content. The melt was quenched and tempered in order to remove residual stresses. Measurements of the electrical conductivity σ were performed and no deviation from the law

$$\sigma(T) = \frac{\sigma_0}{T} \exp(-E_A^{\text{COND}}/kT) \quad (1)$$

was found. An activation energy $E_A^{\text{COND}} = 0.78$ eV and a prefactor $\sigma_0 = 1.3 \times 10^5 \text{ k}\Omega^{-1} \text{ cm}^{-1}$ were obtained [11]. These values are compatible with the results of other measurements of Li triborate glass [12].

3. Results and discussion

3.1. Lineshape measurements of the ^8Li resonance

Under continuous neutron activation, lineshape measurements of the ^8Li resonance were performed. The quadrupolar coupling of the ^8Li nuclei to electric field gradients (EFG) leads to a NMR spectrum consisting of four lines. In a glass these lines are broadened due to non-uniform EFG parameters. Irradiation of a sharp RF would depolarize only nuclei with resonance frequencies within a line and reduce the β -asymmetry by only 5%. Much stronger signals can be obtained by depolarizing several lines simultaneously while scanning an additional one. This is achieved by shifting a broadly modulated RF band over the frequency region around the Larmor frequency ν_L [13]. The lineshape thus obtained for a spectrum of four lines is depicted in the inset of figure 1. In the $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ glass the lines are broadened and the step-shaped resonance signal is smeared out as shown in figure 1. The full curve is the fit of a Gaussian distribution function $g(q) = \frac{1}{\sqrt{2\pi}\bar{q}} \exp(-q^2/2\bar{q}^2)$ of the EFG q at the inequivalent Li sites in the glass. The integral line shape was measured for temperatures in the range $5 \leq T/\text{K} \leq 290$. No narrowing of the linewidth with increasing T was observed. This indicates that motional processes are not effective in this T range. The value for the mean ^8Li quadrupole coupling constant at $T = 290$ K is $\frac{e^2\bar{q}Q}{h} = 101(8)$ kHz. This is compatible with the value obtained from the width of the quadrupolar spin echo using ^7Li -NMR in this glass [14].

3.2. Reorientation of ^{12}B

For temperatures above room temperature, where the SLR of ^8Li and ^{12}B is dominated by Li diffusion (see section 3.3), the reorientation behaviour of ^{12}B was investigated. At low values of the external B_0 field the nuclear spins do not precess about B_0 but primarily about EFGs, resulting in a loss of nuclear polarization. As B_0 rises, the nuclear spins are decoupled from the EFGs and P_0 increases to a saturation value $P_{0,\infty}$. The proper description of the reorientation behaviour of nuclear polarization in electromagnetic fields is given by the solution of the Liouville equation. In β -NMR only the average of the nuclear polarization is measured, since the β -lifetime is long compared with a nuclear precession period. The time-averaged polarization behaviour for the case $I = 1$ is given by [13]:

$$P_0 = P_{0,\infty} [1 + (3/2\nu_L^2)(eQ/h)^2(-V_1V_{-1} + V_2V_{-2})]^{-1}. \quad (2)$$

Here $V_{\pm m}$ are the irreducible EFG tensor components. Assuming statistically distributed EFG parameters, which accounts for the random network character of the borate glass, it follows that

$$P_0 = P_{0,\infty} \int \left[1 + \frac{3}{2\nu_L^2} \left(\frac{eQ}{h} \right)^2 (-\nu_1\nu_{-1} + \nu_2\nu_{-2}) \right]^{-1} \frac{2\Gamma}{\pi^3} (\Gamma^2 + |\nu|^2)^{-3} d\nu_{-2} \dots d\nu_2 \quad (3)$$

with $\Gamma = \frac{\pi^2}{12} eq$. Here eq is the EFG at the site of a ^{12}B probe nucleus. The result of the integral is given in [13].

The measured B_0 dependence of P_0 for $T = 448$ K is plotted in figure 2. The full curve is a fit of $P_0(B_0)$ (3) and yields for the ^{12}B quadrupole coupling constant $\frac{e^2qQ}{h} = 1.0(4)$ MHz. NMR measurements on ^{10}B in Li triborate glass yield for about 70% of the ^{10}B sites a quadrupole coupling constant of about 5.5 MHz, which was assigned to boron nuclei in planar BO_3 units [7]. Taking into account the ratio of the quadrupole moments of ^{12}B and ^{10}B ($Q(^{12}\text{B})/Q(^{10}\text{B}) \simeq 0.16$ [15]) the value for the quadrupole coupling constant obtained from reorientation data of ^{12}B is compatible with the result for ^{10}B -NMR.

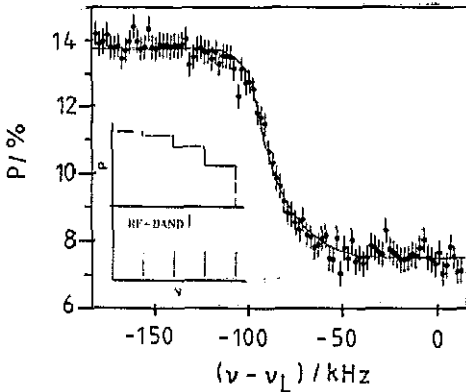


Figure 1. Line shape of ^8Li in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ glass at $T = 11$ K: a RF band with 100 kHz frequency modulation centred at ν is shifted over the Larmor frequency $\nu_L = 1890$ kHz. The inset shows the lineshape for sharp lines. In a glass the pattern is smeared out due to distribution of the EFG q . The full curve is a fit of a Gaussian distribution of q .

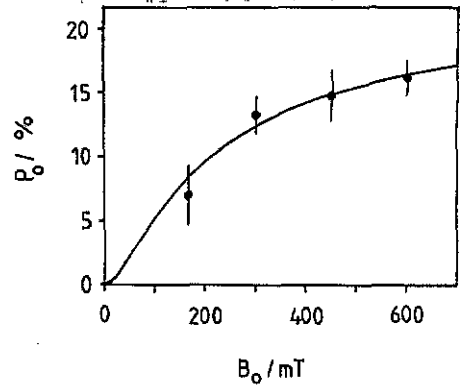


Figure 2. Decoupling curve of ^{12}B in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ at $T = 448$ K.

3.3. SLR measurements

3.3.1. Time dependence of nuclear polarization. By time-resolved recording of the β asymmetry the SLR behaviour of ^8Li and ^{12}B was studied for $5 \leq T/\text{K} \leq 480$ and $190 \leq T/\text{K} \leq 490$, respectively. The values of the external field B_0 in the ^8Li measurements ranged from 37 mT to 600 mT, the ^{12}B measurements were preferentially done at

$B_0 = 300$ mT and 600 mT. The nuclear polarization P of both probe nuclei decays non-exponentially and can be described by the stretched exponential

$$P(t) = P_0 \exp[-(t/T_{1\text{inh}})^\alpha]. \quad (4)$$

The ^8Li transients are best described by $\alpha = 0.52(1)$ for T below 200 K and all B_0 values. For ^8Li at high temperatures ($T > 300$ K) and ^{12}B a trend for somewhat smaller α values was observed. But due to the statistical error in the data and the restriction of the time window of the transients to the order of magnitude of τ_β no exact values can be given. All transients of ^8Li and ^{12}B were thus described by the law

$$P(t) = P_0 \exp(-\sqrt{t/T_{1\text{inh}}}). \quad (5)$$

For the evaluation of $T_{1\text{inh}}$ from the β -asymmetry transients the relaxation already occurring during the preceding neutron activation pulse was taken into account. This correction, which is not necessary for single-exponential relaxation behaviour, is essential for a proper description of the transients in the case of non-exponential relaxation behaviour [16]. A similar behaviour of the nuclear spin polarization was already found in earlier β -NMR measurements of the ^8Li relaxation in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass [17] and can be explained by inhomogeneous polarization averaging over the the isolated probe nuclei [18]. The arguments are summarized below. The relaxation of each probe nucleus is due to coupling to fluctuating dipolar or quadrupolar fields caused by nearby relaxation centres. These fluctuations are described by spectral densities $j(\omega, \tau_i)$, where τ_i denotes the correlation time of the motion of relaxation centre i . If the motions are not correlated, the individual decay behaviour of a probe nucleus k can be characterized by a time constant $T_1^{(k)}$ which is given by

$$1/T_1^{(k)} = \sum_i a_{ik}(r) j(\omega, \tau_i) \quad (6)$$

where a_{ik} denotes the coupling constant of the nuclear moment to the fluctuating field. The assumption of single-exponential relaxation with the rate $1/T_1^{(k)}$ is a simplification since the relaxation of a nucleus with $I = 2$ is expected to be two-exponential with both prefactors and rates depending on spectral densities $j_1(\omega, \tau)$ and $j_2(\omega, \tau)$ [19]. Non-exponential correlation functions have been shown not to affect the exponential decay behaviour of the polarization for the high-field regime ($\omega\tau \gg 1$) [20]. Possible angular dependences of the coupling constant are neglected and a simple power law

$$a_{ik}(r) = a_0 \left(\frac{r_0}{r_{ik}} \right)^m \quad (7)$$

is assumed, where r_0 denotes the nearest distance between relaxation centre and probe nucleus and a_0 is the corresponding coupling constant. The β asymmetry is given by the inhomogeneous average over all probe nuclei [18]:

$$P_{\text{inh}}(t) = \langle P_0 \exp(-t/T_1^{(k)}) \rangle_k = P_0 \exp[-(t/T_{1\text{inh}})^{3/m}]. \quad (8)$$

with

$$T_{1\text{inh}}^{-3/m} = \frac{4\pi}{3} r_0^3 a_0^{3/m} \Gamma\left(1 - \frac{3}{m}\right) \int (j(\omega, \tau))^{3/m} n_\tau(\tau) d\tau \quad (9)$$

where $n_r(\tau) d\tau$ is the number density of relaxation centres with correlation times in the range $\tau, \dots, \tau + d\tau$. For $m = 6$ the observed $\exp(-\sqrt{t/T_{1\text{inh}}})$ law follows.

The finding of non-exponential polarization transients in β -NMR measurements on isolated ^8Li and ^{12}B contrasts with the results of T_1 measurements on ^7Li in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ glass by classical NMR, where single-exponential decay of the magnetization is observed [21, 22]. This behaviour can be ascribed to homogeneous polarization averaging over the probe nuclei which are coupled due to rapid spin diffusion.

3.3.2. Temperature and magnetic field dependence of spin-lattice relaxation. The following discussion will be focussed on the T and B_0 dependence of $T_{1\text{inh}}^{-1}$. For ^8Li and ^{12}B different $T_{1\text{inh}}^{-1}(T)$ characteristics in different T regimes were observed. A weak increase of $T_{1\text{inh}}^{-1}$ with T at low temperatures is followed by a sharp rise for T above room temperature, which is due to the onset of long-range Li^+ diffusion. The two regions of different T dependences of the SLR rate were also found in T_1 measurements of series of alkali oxide glasses [6].

At very high temperatures long-range Li^+ motion may take the role of spin diffusion. In this case the polarization of the β probe nuclei would be given by homogeneous averaging and should follow an $\exp(-t/T_{1\text{hom}})$ law, i.e. α in (4) should increase. In the data, however, no indication for such a behaviour was found. The displacement of a ^8Li probe nucleus due to long-range diffusive motion can be estimated from electrical conductivity data and the Nernst-Einstein relation. At the highest temperature applied in our measurements this displacement is still three orders of magnitude below the average ^8Li - ^8Li distance. The β -active probe nuclei can still be regarded as being isolated and the polarization decay follows the $\exp(-\sqrt{t/T_{1\text{inh}}})$ law.

The B_0 dependence of $T_{1\text{inh}}^{-1}$ was studied in detail with ^8Li . The two regions of different T dependences of the relaxation rate also exhibited different $T_{1\text{inh}}^{-1}(B_0)$ characteristics. The two temperature regimes will be discussed separately.

Below 200 K the T dependence of the ^8Li relaxation rate can be described by the power law $T_{1\text{inh}}^{-1} \propto T^\gamma$ with $\gamma = 0.4, \dots, 0.9$ for the external B_0 field increasing from 37 mT to 600 mT as illustrated by figure 3. A similar behaviour of the exponent γ of the T dependence for different B_0 was found in earlier β -NMR measurements of ^8Li in the glass $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$, where γ ranged from 0.8 to 1.2 for B_0 between 30 mT and 338.5 mT [17]. The B_0 dependence of $T_{1\text{inh}}^{-1}$ consequently has different characteristics at different temperatures: the exponent β in the power law $T_{1\text{inh}}^{-1} \propto B_0^{-\beta}$ decreases from $\beta = 1.6$ to $\beta = 0.9$ when T increases from 5 K to 150 K for the $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ glass. In the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass β ranges from 1.1 to 0.7 as T increases over the same T range [17].

SLR measurements of ^7Li in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ revealed the power laws

$$T_{1\text{hom}}^{-1} \propto T^\gamma \quad T_{1\text{inh}}^{-1} \propto B_0^{-\beta} \quad (10)$$

with $\gamma \simeq 1.2$ and $\beta \simeq 0.8$ [5]. This behaviour of $T_{1\text{inh}}^{-1}$ could be explained in terms of a Raman process involving excitation and de-excitation of two two-level systems (TLS), which act on the nuclear moments [23, 24]. By rapid spin diffusion the nuclear relaxation is transmitted throughout the glass and the observed single-exponential magnetization decay results. Using an extended expression of Rubinstein *et al* [25] for $T_{1\text{inh}}^{-1}$, which involves the density of states of the TLS, the maximum energy difference between the TLS and the strength of the TLS nucleus coupling, the measured exponents γ and β can be explained according to [5].

In the present case of β -NMR, spin diffusion is inhibited and SLR can proceed only via direct coupling to TLS or other relaxation centres in the vicinity of the probe nuclei. The T and B_0 dependence of $T_{1\text{inh}}^{-1}$ in the observed $\exp(-\sqrt{t/T_{1\text{inh}}})$ law for the polarization cannot be explained quantitatively by the two-TLS Raman process mentioned above. The exponents γ , β in (10) reflect the energy dependence of the number density of the TLS and the maximum energy difference between the TLS and should therefore also apply to the present β -NMR results. But here the exponent γ of the T dependence is different for different B_0 values (see figure 3). However, with B_0 rising to the values used in the ^7Li SLR measurements, γ approaches the value found there.

The expression for $T_{1\text{inh}}^{-1}$ in (7) can be evaluated with simplifying assumptions for the T dependence of the correlation time τ and the spectral density j [18]. The assumptions are similar to those made in the calculation for the two-TLS Raman mechanism. The correlation time τ of the process dominating SLR is assumed to obey an Arrhenius-like temperature dependence $\tau = \tau_0 e^{E/kT}$. The density of relaxation centres $n_\tau(\tau)$ then corresponds to a distribution function $n_E(E)$ of activation energies. Further assumptions are that $n_E(E)$ is broad and has no sharp maxima and that the spectral density $j(\omega, \tau_i)$ of the relaxation centres can be described by the Bloembergen-Purcell-Pound (BPP) approximation [26], i.e.

$$j(\omega, \tau_i) = \frac{2\tau_i}{1 + (\omega\tau_i)^2} \quad (11)$$

Then three regions of different B_0 dependences of $T_{1\text{inh}}^{-1}$ and $T_{1\text{hom}}^{-1}$ are expected:

$$T_{1\text{inh}}^{-1}, T_{1\text{hom}}^{-1} \propto \begin{cases} B_0^0 & \text{for high T} \\ B_0^{-1} & \text{for intermediate T} \\ B_0^{-2} & \text{for low T} \end{cases} \quad (12)$$

The boundaries between these regions may be specified by comparing T with E_{max}/k , where E_{max} denotes the energy where $n_E(E)$ takes its maximum. The T dependence of the exponent β in the power law $T_{1\text{inh}}^{-1} \propto B_0^{-\beta}$ for ^8Li does indeed show the corresponding behaviour.

The B_0 dependence of the SLR rate of ^{12}B in the $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ glass was studied less systematically and the T dependence of $T_{1\text{inh}}^{-1}$ of ^{12}B was investigated only for $T > 190$ K, because at lower T the relaxation time became too long compared with the β -lifetime of ^{12}B . The T dependence can be characterized by the power law $T_{1\text{inh}}^{-1} \propto T^{1.5}$ for T below 400 K. To our knowledge there are no ^{11}B relaxation data for the $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ glass available for direct comparison, whereas SLR of ^{11}B in the pure B_2O_3 glass has been measured by two groups [25, 27]. Szeftel and Alloul [27] found a $T_1^{-1} \propto T^{1.3}$ dependence for T between 1.2 K and 300 K. The T_1^{-1} measurements on ^{11}B of Rubinstein *et al* [25] covered temperatures between 120 K and 500 K. Contrary to the results of [27] their data follow a $T_1^{-1} \propto T^2$ law in the T range $120 \text{ K} < T < 200 \text{ K}$ and were explained by a two-phonon Raman process [28].

Above 300 K $T_{1\text{inh}}^{-1}$ of ^8Li shows a steep increase with T which is due to the onset of Li^+ diffusion. For ^{12}B a similar sharp rise with T was found above 400 K. The maximum of the peak in $T_{1\text{inh}}^{-1}(T)$, expected for diffusion-induced SLR, and its high- T side lying above the glass transition temperature were not reached in our measurements. From the slope of the $\ln(T_{1\text{inh}}^{-1})$ vs $1/T$ plot (figure 4), the same apparent activation

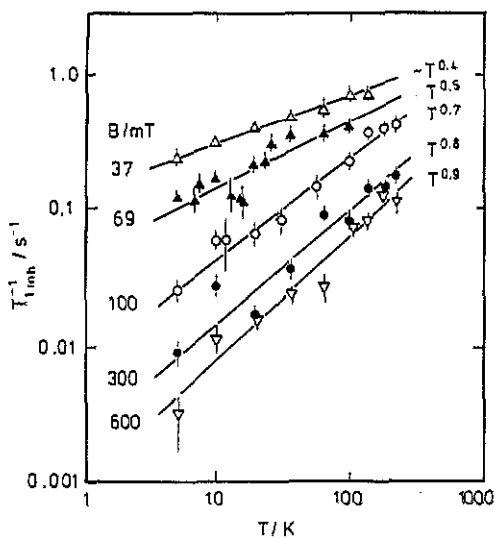


Figure 3. T dependence of $T_{1\text{inh}}^{-1}$ in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ for different external B_0 fields in the low- T range: power laws $T_{1\text{inh}}^{-1} \propto T^\gamma$ with γ as indicated are obtained.

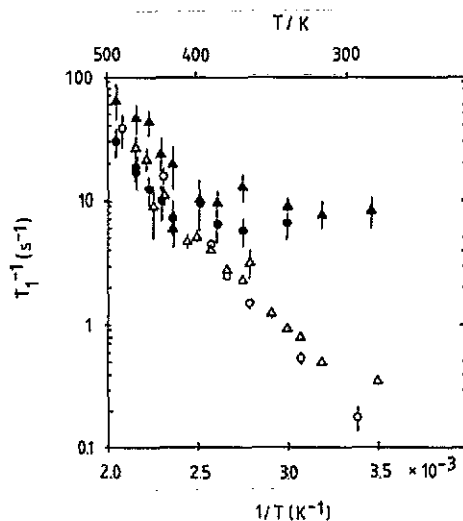


Figure 4. T dependence of $T_{1\text{inh}}^{-1}$ of ^8Li (open symbols) and ^{12}B (full symbols) in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ for $B_0 = 300$ mT (triangles) and $B_0 = 600$ mT (circles) in the T range of the ^8Li diffusion. From the slope for $T > 350$ K the apparent activation energy is obtained as $E_A^{\text{SLR}} = 0.35$ eV.

energies $E_A^{\text{SLR}} \approx 0.35$ eV were obtained from the ^8Li and ^{12}B data. E_A^{SLR} is only about half of the value of the activation energy E_A^{COND} of the electrical conductivity ($E_A^{\text{COND}} = 0.78$ eV), which is due to long-range Li^+ diffusion.

The B_0 dependences of the SLR rates of ^8Li and ^{12}B are weaker than the dependence $T_{1\text{inh}}^{-1} \propto B_0^{-2}$ predicted by the classical model for diffusion-induced SLR [26]. T_1 measurements with ^7Li also yield $E_A^{\text{SLR}} \approx 0.5E_A^{\text{COND}}$ and a weak B_0 dependence ($T_{1\text{inh}}^{-1} \propto B_0^{-0.7}$) [5]. Possible explanations for these findings, which all invoke an irregular diffusive Li motion in the glass, are summarized in [29]. However, in a recent paper [30] SLR even in the T range discussed here is considered to be due to two-level systems. The authors present a new interpretation of the activation energies E_A^{SLR} and E_A^{COND} on the basis of the coupling model of conductivity relaxation in glassy ionic conductors [31].

The SLR behaviour of ^{12}B at high temperatures is also dominated by the Li diffusion. The boron nucleus itself remains at rest in the B_2O_3 network. A similar observation of Li-diffusion-dominated SLR of nuclei at rest in a glassy network was made in ^{19}F T_1 measurements in the triborate glass $(0.1\text{Li}_2\text{F}_2\cdot 0.9\text{Li}_2\text{O})\cdot 3\text{B}_2\text{O}_3$, where the fluorine atom becomes part of the network like the oxygen. Above room temperature a sharp rise of T_1^{-1} of ^{19}F similar to that of T_1^{-1} of the diffusing ^7Li nuclei is observed [32], whereas the ^{19}F resonance line itself does not show narrowing effects [14].

4. Summary

We have presented β -NMR measurements on ^8Li and ^{12}B in $\text{Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ glass, which comprised measurements of the line shape of the ^8Li resonance, the nuclear spin-lattice

relaxation of both probe nuclei and the reorientation behaviour of ^{12}B . The values for the quadrupole coupling constants of ^8Li and ^{12}B deduced from the line shape and the reorientation behaviour, respectively, are consistent with data from classical NMR.

The spin-lattice relaxation behaviour of the β probe nuclei contrasts with the relaxation behaviour of the stable nuclei. The polarization transients of the β -active probe nuclei are non-exponential whereas the magnetization of ^6Li and ^7Li in the T_1 measurements by classical NMR shows single-exponential decays. This finding was ascribed to the inhibition of spin diffusion of the β -NMR probe nuclei, whereas in the classical NMR measurement generally rapid spin diffusion occurs. The $\exp(-\sqrt{t/T_{1\text{inh}}})$ law for the polarization transients of the β -NMR probes was explained via an inhomogeneous polarization average over the isolated nuclear spins. Each probe nucleus relaxes single-exponentially with a rate determined by the coupling to nearby relaxation centres. The disorder in the glass was accounted for by a distribution of correlation times of these centres.

The T dependence of the obtained relaxation rate $T_{1\text{inh}}^{-1}$ of ^8Li and ^{12}B showed two different regimes. A weak T dependence at low T with $T_{1\text{inh}}^{-1}$ increasing with T is followed by a steep rise with T above room temperature which is ascribed to the onset of long-range Li diffusion. These two regions of different $T_{1\text{inh}}^{-1}(T)$ characteristics were also found in the B_0 dependence of $T_{1\text{inh}}^{-1}$. The B_0 dependence of $T_{1\text{inh}}^{-1}$ at low T can be qualitatively described by (9) with a broad distribution of correlation times and a BPP-like *ansatz* for the spectral densities. At high T the B_0 dependence is weaker than predicted by the classical model for diffusion-induced SLR.

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