

Exchange-mediated spin–lattice relaxation of Fe^{3+} ions in borate glasses

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Abstract

Spin–lattice relaxation times (T_1) of two borate glasses doped with different concentrations of Fe_2O_3 were measured using the Electron Spin-Echo (ESE) technique at X-band (9.630 GHz) in the temperature range 2–6 K. In comparison with a previous investigation of Fe^{3+} -doped silicate glasses, the relaxation rates were comparable and differed by no more than a factor of two. The data presented here extend those previously reported for borate glasses in the 10–250 K range but measured using the amplitude-modulation technique. The T_1 values were found to depend on temperature (T) as T^n with $n \sim 1$ for the 1% and 0.1% Fe_2O_3 -doped glass samples. These results are consistent with spin–lattice relaxation as effected by exchange interaction of a Fe^{3+} spin exchange-coupled to another Fe^{3+} spin in an amorphous material.

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1. Introduction

The origin of spin–lattice relaxation (SLR) in glassy materials, characterized by disordered random network, is more complex than that in a crystal characterized by a regular phonon spectrum due to lattice vibrations. In these materials, no two spin probe sites are identical. All sites therefore possess triclinic point symmetry, such that the spin-Hamiltonian parameters and principal-axis orientations are all random quantities. Thus, a full spectroscopic characterization of EPR spectrum in a glass is achieved only with simplifying global assumptions. Knowledge of the spin–lattice relaxation time (T_1) for spin probes in glasses as a function of temperature provides clues to the mechanism responsible for the spin–lattice relaxation. It must be realized that at any value of the magnetic field used for measurement, one is obtaining a local average measure

of T_1 , as the contributions to relaxation result from a number of different Fe^{3+} sites with different spin-Hamiltonian parameters and orientations of the molecular ‘cage’. However, if the relaxation mechanism is not very dependent on magnetic field and other spectral parameters, then the ‘average’ T_1 will be a good measure of the true relaxation time.

Recently, SLR data in several Pilkington glasses doped with the S-state Fe^{3+} ions in the temperature range 2–8 K was obtained using the electron spin-echo (ESE) technique of inversion recovery. These materials provided very strong spin-echo amplitudes over the entire range of 2000–6000 Gauss at 9.630 GHz at or near the temperature of liquid helium [1]. The data confirmed that the mechanism of SLR was predominantly due to the exchange interaction between Fe^{3+} ions as revealed by the temperature dependence and magnitude of T_1 times [2].

This report presents yet another study on SLR times of Fe^{3+} ions as determined in two borate glasses doped with Fe^{3+} ions at liquid-helium temperatures. This has provided

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an opportunity to compare these data with those due to silicate glasses [1]. As well, the data also afford the opportunity to extend SLR measurements on these samples to much lower temperatures than those reported previously by Zinsou et al. [2] as measured by the amplitude-modulation technique in the range 10–250 K. The primary aim was to confirm the mechanism responsible for the spin–lattice relaxation process in these samples, which was not interpreted convincingly in [2] as these results were published well before the mechanism of relaxation due to the exchange interaction to describe T_1 times in these samples was pointed out in Ref. [3]. In [2], the observed linear temperature dependence of the SLR rate in the 25–100 K range was interpreted as being effected by TLS (tunneling level states) centers and/or electron-nuclear dipolar interaction via phonon modulation of the Fermi-contact interaction. However, as discussed in [1], the relaxation rates, in the range $(2–20) \times 10^6 \text{ s}^{-1}$, were rather fast, and therefore much more likely to have been effected by the exchange interaction.

2. Experimental

The two borate glass samples are described by the chemical formula $(1-x)[0.4\text{B}_2\text{O}_3, 0.6\text{Li}_2\text{O}_3] \cdot x\text{Fe}_2\text{O}_3$; $x = 0.001$ and 0.01 . Light, colored glass samples were prepared by melting appropriate amounts of B_2O_3 , Li_2O_3 , and Fe_2O_3 at a temperature of about 1000°C in a crucible made of an alloy of gold, platinum, and rhodium, followed by rapid air cooling. The glassy nature of the samples was verified by X-ray diffraction [4]. The details of the low temperature arrangement, using Oxford Instruments CF935 Helium Flow Cryostat, and temperature measurement are described in [1].

All EPR CW and pulsed experiments were carried out using a Bruker ESP380E FT/CW EPR spectrometer at Monash University. Whilst Continuous Wave (CW) EPR spectra are observable at room temperature, pulsed experiments were only possible in the liquid-helium temperature range. The spectrometer software is pre-programmed for pulse sequences for standard longitudinal or spin–lattice relaxation measurements and Echo-Detected EPR measurements.

The Echo-Detected EPR spectra, obtained from monitoring the peak intensity of two-pulse Hahn echoes as a function of magnetic field, were very broad, extending from 2000 G to 6000 G for the two samples at liquid-helium temperatures. For example, Fig. 1 shows the Echo-Detected EPR spectrum for the sample doped with 1.0 wt% Fe_2O_3 . (See [1] for more details of the ESE technique.) In particular, it is noted that there are four bumps in the spectrum with decreasing intensity as the magnetic field increases. These represent, in fact, the powder average of a typical Fe^{3+} single-crystal EPR spectrum averaged over distributions of spin-Hamiltonian tensors [5].

The value of the external magnetic field (B) for relaxation-time experiments was set close to the peak intensity

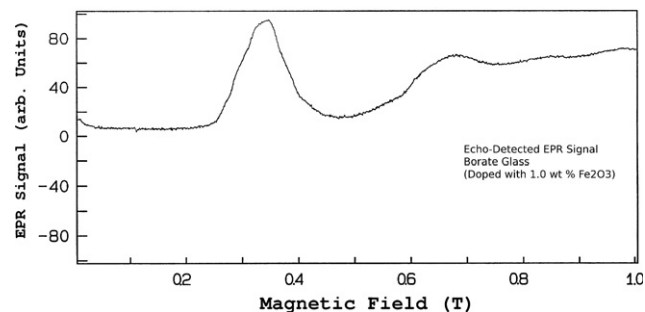


Fig. 1. Echo-detected EPR signal (arbitrary units) in the borate glass sample doped with 1.0 wt% of Fe_2O_3 at 4.2 K at X-band (9.630 GHz) plotted against the magnetic field.

of the spectrum, in particular, at 3480 G. Echoes disappeared or became weak above 6 K, so that the measurements of SLR times could be performed only over the range 2–6 K.

Fitting of the magnetization recovery curves was carried out using the in-built software on the ESP380E spectrometer. The analysis of the recovery curves used two-exponential fits except that in the case of the 1% Fe_2O_3 -doped borate data they automatically converged to a single exponential fit. The 0.1% Fe^{3+} -doped borate data required two exponentials, with one component representing an initial rapid rise with short T_1 values which are not reliable enough to be reported here. The longer T_1 values were then taken as representing the exchange-mediated relaxation times. The SLR rates as estimated for the two borate glass samples are exhibited as functions of temperature in Fig. 2. It is clear from Fig. 2 that, within the experimental error, the relaxation rates measured here in the temperature range 2–6 K can be satisfactorily accounted for by a fit to T^n , with $n \sim 1$, for both 1.0 wt% Fe_2O_3 :Borate ($n = 0.8 \pm 0.2$) and 0.1 wt% Fe_2O_3 :Borate glass ($n = 0.7 \pm 0.3$)

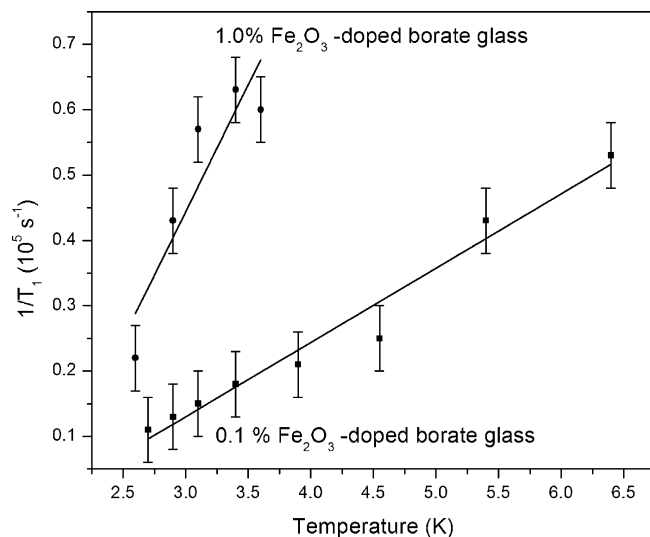


Fig. 2. Plot of the spin–lattice relaxation rate (T_1^{-1}) in the samples doped with 1.0, and 0.1 wt% of Fe_2O_3 in the temperature range ~ 2.5 –6 K. The continuous straight lines show linear fits to the temperature (T).

samples. Although very low temperatures were not achievable, the two plots appear to project back close to the origin within experimental errors. This is consistent with the temperature dependence predicted by exchange-effected relaxation with the values of the maximum exchange constant $|J_0| \leq 0.3$ K in the various samples as discussed in Section 3, similar to that found for silicate glasses [1].

3. Results and discussion

The role played by the exchange interaction, described here as $\mathbf{JS}_1 \cdot \mathbf{S}_2$, between two spins \mathbf{S}_1 and \mathbf{S}_2 , in effecting spin–lattice relaxation (SLR) in amorphous materials was discussed in detail by Misra [3]. The spin–lattice relaxation mechanisms effective in amorphous materials have been reviewed in [6]. They are based on the mechanisms discussed by Altshuler [7] (transition probability), Gill [8], Dalton et al. [9] (averaging of exchange coupling over a broad distribution), and Stevens [10] (calculation of transition probability leading to SLR). An analysis along these lines was successfully applied to explain the published SLR data on Cr^{3+} in $\text{Cu}_{2+x}\text{Cr}_{2x}\text{Sn}_{2-2x}$ spinel and dangling bonds in amorphous silicon [3]. While the Cr^{3+} ion has its orbital angular momentum (L) partially quenched, dangling bonds do not possess any angular momentum. This is similar to the case studied here where the Fe^{3+} ion does not possess any orbital angular momentum ($L = 0$) being an S-state ion.

For an amorphous material, it was found that the SLR rate T_1^{-1} , where T_1 is the SLR time, can be expressed as [1]:

$$T_1^{-1} \propto \frac{1}{v^5} I_{\text{ex}}, \quad (1)$$

where v is the velocity of sound in the sample, and

$$I_{\text{ex}} = \frac{4\pi}{\xi^3} \int_0^{J_0} \frac{[J \ln(J/J_0)]^2 dJ}{\{\exp(J/kT) - 1\}}, \quad (2)$$

where k is Boltzmann's constant. In Eq. (1) the velocity of sound dependence has been explicitly retained in case the comparative results from the silicate and borate glasses shed some light on its role. The form (2) was obtained by substituting the dependence of the exchange interaction on distances r_{ij} between paramagnetic ions in the amorphous material as [3,9]: $J = -J_0 \exp(-\xi r_{ij})$, and integrating over all values of r_{ij} . In particular, it was found in [3] that, depending on the absolute maximum value of the exchange interaction constant (J_0) between adjacent spins in an amorphous material, the SLR rate depended on the temperature (T) as T^n with n depending on the value of J_0 as listed in Table [1]. In particular, it is easily seen that when $J \ll kT$, the integral given by (2) is proportional to T ($n = 1$), i.e. for $J \leq 0.3$.

It is the assumption of the present paper that the dominant SLR mechanism responsible for the Fe^{3+} relaxation in both silicate and borate glasses is that mediated by exchange coupling between pairs of Fe^{3+} ions because of rather fast relaxation rates observed here, similar to those in Pilkington glasses [1]. Noting the dependence of the

SLR rate to be characterized by the temperature power dependence $n \sim 1$ as seen in Section 2, the effects of the following four mechanisms are insignificant in the present case: (i) The two-level tunneling-state (TLS) models of Anderson, Halperin and Varma [11] and Phillips [12,13] which lead to a combined temperature and frequency dependence of the SLR rate as $T^n \nu^{-\beta}$ where n lies in the range 1–2. It is not applicable here because the predominant naturally abundant isotope of Fe^{3+} does not experience any hyperfine interaction, on which this mechanism is based, due to not possessing any nuclear magnetic moment. (ii) Cross-relaxation, which produces an SLR rate proportional to T^2 [14], is not consistent with the results reported in this paper. (iii) Spin diffusion, which is highly important for spins in solution, but irrelevant in the present case, since Standley and Vaughan [14] point out that cross-relaxation and spin diffusion would lead to temperature independent relaxation processes, which is not the case here. (iv) Spectral diffusion, where spectral information is transferred between neighboring spin packets, appears unlikely to be of great interest in borate glasses given the nature of the glassy state and the relative isolation of the Fe^{3+} ions.

The comparison with the relaxation rates observed previously for commercial silicate glasses [1] shows that the average relaxation rates are comparable in the silicate and borate glasses, at best being larger by a factor of two in the latter. Thus, the velocities of sound (v) in the borate and silicate glasses as revealed by the relaxation rates are about the same taking into account their v^{-5} dependence as exhibited by (1), and that there may be other factors that affect the velocity of sound in the host material. When compared with the relaxation rates reported in borate glasses in the 10–250 K range by Zinsou et al. [2], it turns out that for the 1.0% Fe_2O_3 -doped sample, the only common one to the present study, the rates are $\sim 20.0 \times 10^5 \text{ s}^{-1}$ at 10 K in [2] and $\sim 0.6 \times 10^5 \text{ s}^{-1}$ at 6.4 K here. Thus, the measurements reported here using the echo technique extrapolate well to those reported in [2] at ~ 10 K using the amplitude-modulation technique.

4. Conclusions

The salient features of the experimental results and their interpretation presented here are as follows.

- (i) The SLR rates estimated here extrapolate well those reported previously in the 5–250 K range [2]. Further, in contrast to the conclusion made in [2], it is concluded here that most likely it is the exchange interaction that is responsible for spin–lattice relaxation in borate glasses.
- (ii) The spin–lattice relaxation study on the Fe^{3+} -doped borate glass samples with two rather different concentration of Fe^{3+} ions presented here confirm the broad conclusions reached for the commercial (Pilkington) silicate glasses [1] that the Fe^{3+} ions are, on the whole, distributed in close enough proximity to other

Fe^{3+} ions to participate meaningfully in the exchange-mediated relaxation process. Accordingly, in the case of the borate glasses reported here the SLR rates exhibit an approximately linear dependence on T in the 2–6 K temperature range (T^n with $n \sim 1$), implying the maximum absolute value of the pair exchange to be $|J_0| \leq 0.3$ K.

- (iii) The velocities of sound (v) in the borate and silicate glasses as revealed by the relaxation rates are about the same.

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