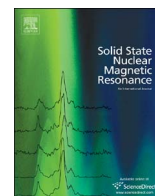




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## Solid State Nuclear Magnetic Resonance

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# Recoupling dipolar interactions with multiple $I=1$ quadrupolar nuclei: A $^{11}\text{B}\{^6\text{Li}\}$ and $^{31}\text{P}\{^6\text{Li}\}$ rotational echo double resonance study of lithium borophosphate glasses<sup>☆</sup>

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## ABSTRACT

The case of rotational echo double resonance (REDOR) experiments on the observe nuclei  $^{11}\text{B}$  and  $^{31}\text{P}$  interacting with multiple  $I=1$  quadrupolar nuclei is analyzed in detail by SIMPSON simulations and experimental studies. The simulations define the region within the parameter space spanned by nutation frequency, quadrupolar coupling constant and spinning frequency where the parabolic analysis of the initial REDOR curve in terms of dipolar second moments has validity. The predictions are tested by experimental studies on the crystalline model compounds lithium diborate and lithium pyrophosphate, which are subsequently extended to measure dipolar second moments  $M_2(^{11}\text{B}\{^6\text{Li}\})$  and  $M_2(^{31}\text{P}\{^6\text{Li}\})$  in three borophosphate glasses. The data indicate that the lithium cations interact significantly more strongly with the phosphate than with the borate species, despite the formally anionic character of four-coordinate boron and the formally neutral character of the ultraphosphate ( $\text{P}^{(3)}$ ) units to which they are linked.

## 1. Introduction

Rotational echo double resonance (REDOR) experiments in which the magnetic dipole-dipole interactions between an observe nucleus  $S$  and another nucleus  $I$  are re-coupled enjoy widespread popularity in different fields of scientific endeavor [1–5]. While initially conceived (and predominantly used) for distance measurements between pairs of spin-1/2 nuclei in doubly labeled biological solids [2,3,6], during the past 15 years the scope of applications has broadened considerably, including disordered crystals, glasses, and inorganic-organic nanocomposites [4,5]. Most of the latter applications involve the measurement of multi-spin interactions comprising different numbers of interacting nuclei over widely spread-out distance ranges. As has been previously shown by us, the dipolar coupling within such ill-defined and distributed spin systems are described most effectively by average second moments, which can be measured rather conveniently from the initial data range ( $\Delta S/S_0 \leq 0.2-0.3$ ) of the REDOR curve [6]. Additional inherent complications concerned with REDOR measurements of inorganic systems arise when quadrupolar nuclei (nuclei having spin quantum numbers larger than 1/2) are involved. One aspect is the occurrence of the dephaser nuclei in different Zeeman states, which produce  $S$ -nucleus dephasing of different magnitudes. A further

complication arises from strong first-order quadrupolar splittings encountered with half-integer quadrupolar nuclei. In this case the magnitude of the REDOR effect of the observe nucleus is compromised by off-resonance irradiation of those dephaser nuclei that are in the non-central Zeeman states. A number of experimental strategies, among them the RESPDOR technique [7] have been designed to deal with such complications [7–12]. The less-common case, namely that of dipolar recoupling to nuclei with integral spin quantum numbers has been discussed for spin-1/2 - spin-1 pairs by various authors [12,13], however, to the best of our knowledge no application to disordered inorganic multiple-spin systems can be found in the literature. Such situations may occur, for example, in glasses enriched with the  $^6\text{Li}$  isotope ( $I=1$ ), which is frequently introduced as a convenient probe of chemical bonding and ion dynamics in solid electrolyte materials [14–16].

In the present contribution, we have introduced this isotope with the objective of measuring the magnetic dipole-dipole interactions between the network-modifying lithium ions and the network former species boron and phosphorus in lithium borophosphate glasses by rotational echo double resonance. The glasses under consideration are characterized by strong network former mixing effects on various bulk properties, indicating the formation of new medium-range structures

<sup>☆</sup> Dedicated to Professor Jean-Paul Amoureux on the occasion of his 70th birthday.

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not represented in the binary systems  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  and  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5$ . Standard  $^{11}\text{B}$  and  $^{31}\text{P}$  MAS-NMR spectra, supported by  $^{11}\text{B}\{^{31}\text{P}\}$  rotational echo double resonance reveal the distinct preference of the boron atoms to occur in the four-coordinated state ( $\text{B}^{(4)}$  units) having the maximum number of B-O-P linkages that is possible for a given glass composition, i.e.  $(\text{B}(\text{OP})_4)$  units. In the borophosphate glass literature these are denoted as  $\text{B}^{(4)}_{\text{AP}}$  species, where the superscript denotes the number of bridging oxygen atoms linked to other network former species, whereas the subscript denotes the number of B-O-P linkages [17]. Even though the  $\text{B}^{(4)}_{\text{AP}}$  species have a negative formal charge, bond valence considerations suggest that these anionic charges are actually dispersed onto the non-bridging oxygen atoms of the phosphate species to which these  $\text{B}^{(4)}$  units are linked [17]. Indeed in sodium borophosphate glasses this view has been supported by a comparative analysis of  $^{31}\text{P}\{^{23}\text{Na}\}$  and  $^{11}\text{B}\{^{23}\text{Na}\}$  magnetic dipole interactions [18]. To examine the question whether this behavior is a general feature of alkali borophosphate glasses and independently test the conclusions of reference [18] on a different system, we decided to carry out an analogous double resonance study of lithium borophosphate glasses. At natural abundance, 92.4% of the lithium atoms contain the nuclear isotope  $^7\text{Li}$ , but the close proximity of its nuclear Zeeman frequency to those of  $^{11}\text{B}$  and  $^{31}\text{P}$  requires special hardware set up for double resonance studies [19], and makes the quantification of dipolar interactions rather difficult. As an alternative we have turned to the study of  $^6\text{Li}$  enriched glasses, which is more straightforward to carry out experimentally, but requires appropriate attention to the effects of dipolar interactions to the quadrupolar spin-1 nuclei. In the present contribution we report our simulations and experimental results concerning the measurement of heteronuclear dipolar second moments characterizing the interaction of  $^{11}\text{B}$  and  $^{31}\text{P}$  with multiple  $^6\text{Li}$  spins ( $I=1$ ) in lithium borophosphate glasses and the crystalline model compounds  $\text{Li}_2\text{B}_4\text{O}_7$  and  $\text{Li}_4\text{P}_2\text{O}_7$ .

## 2. Experimental

### 2.1. Sample preparation and characterization

Table 1 summarizes the compositions and physical properties of the glasses under investigation. The starting materials, anhydrous  $\text{Li}_2\text{CO}_3$  (Sigma Aldrich, 95 atom%  $^6\text{Li}$ ) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (Acros, 99.9%) were pre-dried for 48 h at 120 °C.  $\text{B}_2\text{O}_3$  (Acros, 99%) was heated for 2 h at 900 °C in a platinum crucible and the resulting melt was quenched to form a glass. It was immediately stored in an argon filled glovebox and powdered only immediately before glass preparation. 1–3 g batches of the mixtures (see Table 2) were degassed and melted in a platinum crucible inside a Thermoconcept muffle furnace at 1000–1200 °C for 15 min. Melts were quenched by placing the crucible onto a copper plate held at room temperature. To limit exposure to ambient moisture and ensure sample quality over a long period of time, glass samples were stored in an argon filled glove box. All glasses were found to be homogenous and transparent. Excess mass losses were less than or equal to 3%. Thermal analyses were carried out with a Netzsch Phoenix differential scanning calorimeter using a heating rate of 10 K min<sup>-1</sup> and glass transition temperatures were determined from the onset region of the observed thermal event by the tangent intersection method. A LabRAM HR Raman microscope spectrometer from Jobin

**Table 1**  
Glass Compositions and glass transition temperatures,  $T_g$ , obtained in the present study.

Composition	$\text{Li}_2\text{O}:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$	Mole% $\text{Li}_2\text{O}$	Mole% $\text{B}_2\text{O}_3$	Mole% $\text{P}_2\text{O}_5$	$T_g/\text{K}$ ( $\pm 5$ K)
B	1.0:1.0:2.0	25.0	25.0	50.0	714
C	1.0:0.5:1.5	33.3	16.7	50.0	662
D	1.0:2.0:0.0	33.3	66.7	–	764

Yvon Horiba was used to collect the Raman spectra from smooth sample regions. The spectra were recorded using a 532 nm laser focused with a 50× objective, a 1800 1/mm grating and a CCD-detector operated at an acquisition time of 10 s. 50–100 scans were averaged to enhance the signal-to-noise ratio. The  $^6\text{Li}$  enriched model compounds  $^6\text{Li}_2\text{B}_4\text{O}_7$  and  $^6\text{Li}_4\text{P}_2\text{O}_7$  were obtained by crystallization of the corresponding stoichiometric glasses, at annealing temperatures and annealing times of 550 °C, 20 h and 830 °C, respectively, for 10 min prior to slow cooling at a rate of 13 K h<sup>-1</sup>. The phase purity of these crystalline compounds was ascertained by X-ray powder diffraction, using a FR 552 Guinier-camera from Enraf-Nonius.

### 2.2. Solid state NMR

All experiments were conducted at room temperature on a Bruker-Avance-III 300 MHz spectrometer, a Bruker-Avance-DSX-400 spectrometer and a Bruker-Avance-DSX-500 spectrometer, equipped with fast MAS capabilities. To minimize radio frequency amplitude inhomogeneity all the REDOR experiments were conducted with rotors that were only filled in the center 1/3 of their total volumes. The  $^{11}\text{B}$ -MAS-NMR spectra were recorded at 7.05 and 11.74 T in 4 mm MAS probes operated at a spinning frequency of  $\nu_r=13.0$  kHz and pulse lengths of 1.0  $\mu\text{s}$  were used at a nutation frequency of 26 kHz on a liquid sample (22.5° flip angle). For the three-coordinate  $^{11}\text{B}$  nuclei this corresponded to selective excitation conditions. To ensure complete relaxation, signal averaging required recycle delays of 5 s. The  $^{31}\text{P}$ -MAS-NMR spectra were recorded at 7.05 T using a 2.5 mm MAS probe operated at a spinning frequency 28.0 kHz. Recycle delays of 1000 s were required.  $^7\text{Li}$  single pulse experiments were conducted at 9.4 T (155.5 MHz), using a 4 mm MAS probe operated at a spinning speed of 2.5 kHz. Short excitation pulses of 0.5  $\mu\text{s}$  were used and recycle delays were set to 1–20 s. The Fourier transformed phased signals were analyzed using the Dmfit 2011 program package [20]. The specific measurement conditions selected for the various heteronuclear  $I - S$  double resonance experiments are summarized in Table 2. They were conducted with a saturation comb ensuring reproducible initial conditions. Lithium pyrophosphate ( $\text{Li}_4\text{P}_2\text{O}_7$ ) and lithium diborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) were used as reference and calibration materials. All the REDOR experiments used the standard sequence of Gullion and Schaefer [1] using XY-4 phase cycles [21] on the recoupling  $\pi$ -pulses. In the case of the  $^{11}\text{B}\{^6\text{Li}\}$  REDOR studies, two separate series of experiments were done, optimizing the respective 180° pulse conditions for the observation of the rotorsynchronized spin echoes arising from the three- and four-coordinate  $^{11}\text{B}$  nuclei. While the three-coordinate boron units were observed in the limit of selective excitation of the  $m = 1/2 \leftrightarrow m = -1/2$  transition, this was not the case for the four-coordinate boron units. Simulations of  $^{31}\text{P}\{^6\text{Li}\}$  REDOR experiments were conducted on two-spin systems, considering the effects of nutation frequency, MAS rotor frequency,  $^6\text{Li}$  nuclear quadrupolar interaction strength, as well as heterodipolar interaction strength, using the SIMPSON program [22].

**Table 2**  
Measurement conditions for the double resonance experiments conducted in the present study.

Experiment	$B_0 / \text{T}$	$\nu_r / \text{kHz}$	$t_p^c (\pi) / \mu\text{s}$ (obs.)	$t_p^c (\pi) / \mu\text{s}$ (non-obs.)	$D_1^d / \text{s}$
$^{11}\text{B}\{^6\text{Li}\}$ REDOR	9.4	13.0	6.2 <sup>a</sup> , 4.7 <sup>b</sup>	24.4	5–10
$^{31}\text{P}\{^6\text{Li}\}$ REDOR	11.7	10.5–14.0	11.7	28.3–37.0	240

<sup>a</sup> for four-coordinate boron

<sup>b</sup> for three-coordinate boron

<sup>c</sup> pulse length

<sup>d</sup> relaxation delay

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