NQR Studies of the Structure of Glasses and Crystalline Compounds*

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Pure nuclear quadrupole resonance (NQR) spectroscopy at low frequencies (down to 275 kHz) has been used to investigate a number of borate, aluminate, and vanadate crystalline compounds and borate glasses. The values of the quadrupole coupling constants ($Q_{cc}$) and asymmetry parameters ($\eta$) are obtained with error limits that are one or two orders of magnitude less than those for values obtained from NMR spectra. New sites, not resolved in NMR spectra, have been detected for boron in borate glasses.

Introduction

A Robinson-type [1, 2] regenerative spectrometer has recently been developed [3, 4] that is very sensitive at relatively low frequencies (currently down to about 250 kHz). This instrument is being used to detect the NQR spectra of various elements (e.g. B, Al, Sc, V, Ga) in glasses and crystalline solids. Initial and recent results of these studies are reported in the following section. All of the data were obtained at 77 K unless otherwise noted.

Polycrystalline Solids

The $^{11}$B NQR response for crystalline $\text{B}_2\text{O}_3$ at 77 K is displayed in Figure 1. The resonance, located at 1351.5 ± 0.1 kHz, has a signal-to-noise ratio (S/N) of more than 100. Since the spin of $^{11}$B is 3/2, there is only one resonance, located at

$$v = \frac{Q_{cc}}{2} \sqrt{1 + \frac{\eta^2}{3}},$$

where $Q_{cc}$ is the quadrupole coupling constant $e^2\eta Q$ and $\eta$ is the asymmetry parameter. The small response above 1400 kHz is one of the $^{10}$B responses, and is shown in greater detail in Figure 2. The latter spectrum was obtained by running the spectrometer with a much larger gain setting than that used in obtaining the spectrum in Figure 1. Since the spin of $^{10}$B is $I = 3$, there can be as many as 13 NQR responses [5] from $^{10}$B in a single site in a boron-containing solid (see Figure 3). The natural isotopic abundance of $^{10}$B is 18.8% as compared to 81.2% for $^{11}$B.

![Fig. 1. Boron NQR spectrum for crystalline $\text{B}_2\text{O}_3$.](image)

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Fig. 2. The features of Fig. 1 displayed with a greatly expanded vertical scale.

Fig. 3. $^{10}$B (spin $I = 3$) NQR frequencies (in units of $Q_{cc}$).

Since (1) involves both $Q_{cc}$ and $\eta$ in the expression for the single transition frequency, values of the two parameters cannot be obtained from the $^{11}$B resonance. But the observed transitions for $^{10}$B (see the examples in Figs. 2 and 4) can be used with the data displayed in Fig. 3 to obtain those values. For $^{11}$B in crystalline $B_2O_3$ one finds [4] at 77 K that $Q_{cc}(^{11}B) = 2701.1 \pm 0.2$ kHz and $\eta = 0.0669 \pm 0.0004$. The values at 300 K are $2682.6 \pm 0.5$ and $0.071 \pm 0.001$ [6]. (Note that $Q_{cc}(^{10}B)/Q_{cc}(^{11}B) = 2.084 \pm 0.002$ [4].)

The boron atoms in crystalline $B_2O_3$ are in the center of planar triangles of oxygens [7–9]. The known range of $Q_{cc}$ values for this configuration is $2.4 \leq Q_{cc} \leq 2.9$ MHz with $\eta$ values generally smaller than 0.2 if the triangles are symmetric (e.g. the three oxygens are each bonded to a boron outside the triangle as in crystalline $B_2O_3$) and larger than 0.4 if the triangles are asymmetric (e.g. having one or two non-bridging oxygens).

The detection of many of the $^{10}$B NQR transitions in a borate material is illustrated by the case of calcium metaborate [6]. Figure 5 displays eleven $^{10}$B responses that are consistently present in repeated acquisitions of the NQR spectra. A fit of these resonance frequencies to the data displayed in Fig. 3 yields $Q_{cc}(^{10}B) = 5406.5 \pm 1$ kHz, $Q_{cc}(^{11}B) = 2594.3 \pm 0.5$ kHz, and $\eta = 0.515 \pm 0.001$. The boron atoms in this material are in asymmetric $BO_3$ triangles having two bridging and one non-bridging oxygen (Fig. 6), which gives rise to the large asymmetry parameter.

The structural units in crystalline borates (Fig. 7) are made up of $BO_3$ triangles and $BO_4$ tetrahedra; in the latter case, the boron atom is in the center of the tetrahedron of oxygens. For the four-coordinated borons, the values of $Q_{cc}$ are low because of the tetrahedral symmetry. All of the previously reported values are such that $0 \leq Q_{cc}(^{11}B) \leq 800$ kHz. A value of $527 \pm 6$ kHz, with $\eta = 0.53 \pm 0.04$ has recently been deduced [4] from combined NMR and NQR $^{11}$B data for $^{11}$B in the tetrahedral site (see Fig. 7) in lithium diborate ($Li_2O \cdot 2B_2O_3$). An unusual case is that of the compound PbO $\cdot 2B_2O_3$ (lead diborate) which is known [10, 11] to contain only $BO_4$ units. The $^{11}$B
Fig. 5. $^{11}$B and $^{10}$B NQR spectra of CaO–B$_2$O$_3$ at 77 K, the $^{11}$B line is driven off scale in order to show the $^{10}$B lines.

Fig. 6. A portion of the (B$_2$O$_4$)$^{5-}$ chain in calcium metaborate; the non-bridging oxygen is negatively charged.

NQR spectrum (Fig. 8) contains two responses, showing that there are two different boron sites in this material. NMR spectra for the narrow $^{11}$B resonance in this material provide additional information on the quadrupolar interaction [6]. Together, the NQR and NMR data yield the values shown in Table 1. A search for $^{10}$B responses in a $^{10}$B-enriched sample may yield much more accurate values of $Q_{cc}$ and $\eta$. (Most of the
Boroxol

Pyroborate

Vv

[B_0 B_{-1}]

Pentaborate

[B_0 B_{-1}]

Triborate

[B_{-1}]

Tetraborate

[B_{-1}]

Orthoborate

[B_{-1}]

Metaborate

Diborate

Fig. 7. Structural groupings for alkali borate compounds and glasses.

Table 1. $^{11}$B quadrupole parameters for crystalline PbO·2B$_2$O$_3$.

<table>
<thead>
<tr>
<th>BO$_4$</th>
<th>$Q_{ee}$ (kHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>805 ± 5</td>
<td>0.90 ± 0.03</td>
</tr>
<tr>
<td>Site 2</td>
<td>960 ± 5</td>
<td>0.05 ± 0.03</td>
</tr>
</tbody>
</table>

$^{10}$B NQR responses for borates are below the $^{11}$B resonance (Fig. 3) and are difficult to detect when the $^{11}$B response is at a low frequency.) $^{11}$B and $^{27}$Al share the characteristic of being impossible or extremely difficult to detect with pulsed NQR spectrometers, apparently because of extremely
Fig. 8. $^{11}$B NMR of PbO$-2$B$_2$O$_3$ at 77 K.

Fig. 9. $^{27}$Al NQR response for corundum ($\alpha$-Al$_2$O$_3$) at 77 K.

Table 2. $^{27}$Al quadrupole parameters for corundum ($\alpha$-Al$_2$O$_3$).

<table>
<thead>
<tr>
<th>Studies</th>
<th>$Q_{cc}$ (MHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NQR study</td>
<td>2.386 ± 0.002</td>
<td>0.034 ± 0.016</td>
</tr>
<tr>
<td>NMR study</td>
<td>2.40 ± 0.03</td>
<td>0</td>
</tr>
</tbody>
</table>

short relaxation times. But $^{27}$Al is just amenable as $^{11}$B to detection with CW NMR instruments. Figure 9 displays the two NQR responses expected for this spin $I = 5/2$ nucleus in the single site in corundum ($\alpha$-Al$_2$O$_3$). The signals are strong, even at 360 kHz, and yield the values of $Q_{cc}$ and $\eta$ displayed in Table 2. Included in Table 2 are the parameters found in an earlier NMR study [12]. Since the visible quadrupolar effects in an $^{27}$Al NMR spectrum are generally of second-order, the spectrum is relatively insensitive to all but large changes in $Q_{cc}$ and $\eta$. Clearly, much more accurate values can be obtained from the NQR responses. It is, in fact generally true that NQR can provide an increase in accuracy by an order of magnitude or more over $Q_{cc}$ and $\eta$ values obtained from the first-order or second-order effects of the quadrupolar interaction on the NMR spectrum.

NQR spectra have recently been obtained [13] for $^{27}$Al in the three crystalline forms of Al$_2$SiO$_5$ or (Al$_2$O$_3$ · SiO$_2$). Figure 10 displays the responses for the AlO$_4$ and AlO$_6$ sites in sillimanite. The frequencies yield the values given in Table 3. Similar accuracy has been attained [13] in the quadrupolar parameters for the 5- and 6-coordinated aluminum sites in andalusite and the four 6-coordinated sites in kyanite.
Table 3. $^{27}$Al quadrupolar parameters for sillimanite at 77 K.

<table>
<thead>
<tr>
<th>Site</th>
<th>$Q_{cc}$ (MHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlO$_4$</td>
<td>6.7867 ± 0.0030</td>
<td>0.5254 ± 0.0011</td>
</tr>
<tr>
<td>AlO$_6$</td>
<td>8.7409 ± 0.0020</td>
<td>0.4884 ± 0.0006</td>
</tr>
</tbody>
</table>

The quadrupolar parameters for $^{51}$V in a number of metavanadates have previously been obtained from NMR spectra [14]. More accurate values are now available from NQR measurements [6, 15]. Figure 11 displays two of the three $^{51}$V responses expected for this spin $I=7/2$ nucleus in ammonium metavanadate (NH$_4$VO$_3$). A search at higher frequencies has not detected the third response, which may then be in the 250–300 kHz region. Modification of the spectrometer will be required for satisfactory operation in that frequency region. All of the responses have been detected in the sodium and potassium metavanadates. Table 4 summarizes the data for the three compounds studied.

Included in Table 4 are values of $Q_{cc}$ and $\eta$ previously determined [14] from a $^{51}$V NMR study. The large improvement in accuracy achieved using NQR is apparent. (The lower accuracy of NQR-derived values for NH$_4$VO$_3$ reflects the fact that only two NQR responses were detected.)

**Glasses**

NMR has been used for some 35 years to investigate the studies of glasses [16], with much attention...
focusing on $^{11}$B and $^{10}$B spectra for borate glasses [17]. But low-frequency NQR studies can now yield quadrupolar parameters of much higher accuracy and obtain data not available from NMR studies (e.g. $Q_{cc}$ and $\eta$ for borons in tetrahedral BO$_4$ units for which $0 \leq Q_{cc} \leq 800$ kHz.)

Figure 12 displays the two $^{11}$B responses for vitreous boron oxide (B$_2$O$_3$). The responses are unexpectedly narrow (widths $\leq 30$ kHz) in light of the broad distribution in the values of the electric field gradient (EFG) components and $Q_{cc}$ values expected for glasses. (The single feature most commonly used to describe the difference between crystalline and vitreous states of matter is the random arrangements of atoms and chemical bonds in glasses.) The only previous NQR study [18] of glasses involved $^{75}$As in arsenic chalcogenides revealed linewidths of 7 MHz or more, precluding resolution of resonances from different sites. In contrast to the distribution in $Q_{cc}$ values of 10% in $^{75}$As$_2$S$_3$, the distribution smaller than 2% in borate glasses.

The larger of the two responses in Fig. 12 is quite near the location of the single $^{11}$B response for crystalline B$_2$O$_3$ (see Fig. 1) and is believed to arise from BO$_3$ units in boroxol structural groupings (see Fig. 7), which have been identified by some investigators [19, 20] as the principal structural groupings in the glass. The smaller response may arise from BO$_3$ in other borate structural groupings (see Figure 7).

The pioneering explorer of borate structures by infrared spectroscopy, Jan Krogh-Moe [21] proposed a structural model of borate glasses as consisting of mixtures of the structural groupings (Fig. 7) from the crystalline compounds. This is a significant modification of the conventional random network model which would envision a random arrangement of BO$_3$ and BO$_4$ units in the glass. The current NQR studies of borate glasses are focused on assessing the validity of the Krogh-Moe model. Figure 13 displays the $^{11}$B spectrum [22, 23] for a glass of molar composition 0.15Na$_2$O–B$_2$O$_3$, along with the spectrum from Fig. 12 for pure vitreous B$_2$O$_3$. There are clearly at least three peaks in the sodium borate glass, of which two may be the same as those found in vitreous B$_2$O$_3$. [One would not expect to find exact agreement of the frequencies for BO$_3$ units in structural groupings common to the crystalline compounds (e.g. boroxol, tetraborate, diborate; see Fig. 7) and the glasses. The randomness in the glass structure would arise from random bondings among the various structural
groupings in a glass, giving rise to some alterations in the EFG's (and thus the $Q_{cc}$ values) for the borons in the groupings. This would produce the distributions of $Q_{cc}$ values in the glasses (which produce the wider lines in the glasses as compared to the crystals; compare Figs. 1 and 12) and could produce shifts in the peak frequencies comparable to the linewidths for the glasses. Earlier NMR studies [24] of lithium borate glasses by NMR, with analysis of the spectra based on the Krogh-Moe model, would predict the presence of boroxol, tetraborate, and diborate groupings in the 0.15 Na$_2$O–B$_2$O$_3$ glass. NQR spectra for glasses spanning the region of glass formation in the Na$_2$O–B$_2$O$_3$ and Li$_2$O–B$_2$O$_3$ systems, and for all of the crystalline compounds in those systems, are currently being secured, so that comparisons of the $^{11}$B resonance frequencies for the glasses and crystals can be made. If the degree of correspondence favors the Krogh-Moe model, the $^{10}$B spectra for $^{10}$B-enriched samples will be secured for a comparison of the highly accurate values of $Q_{cc}$ and $\eta$.

Figure 14 displays $^{11}$B NQR responses for BO$_3$ in a sodium pyroborate glass (2Na$_2$O · B$_2$O$_3$). The Krogh-Moe model would predict the pyroborate structural grouping to be dominant in this glass, with some orthoborate and metaborate groupings. $Q_{cc}$ for the orthoborate grouping is known [25] to be larger than the $Q_{cc}$ values for other groups. One tentatively assigns, then, the lower frequency response to the pyroborate grouping and the one above 1400 kHz to the orthoborate.

The $^{11}$B response from BO$_3$ units reflects the observation that $2.4 \leq Q_{cc} \leq 2.9$ MHz for all borates investigated by NMR and NQR. NQR responses can occur, then, in the region from about 1200 to 1675 kHz (see (1)). The NQR spectra for BO$_4$ units may provide an even more accurate identification of structural groupings in glasses since the accumulated NMR data yield $0 \leq Q_{cc} \leq 800$ kHz for BO$_4$ units in borate structural groupings. With the detection of the $^{11}$B NQR responses in the 400–500 kHz region for crystalline PbO · B$_2$O$_3$ (Fig. 8), this range is appropriately ex-
tended so that $0 \leq Q_{cc} \leq 1100 \text{ kHz}$. This broad range presumably reflects the sensitive dependence of the quadrupolar parameters to distortions (asymmetries) of the BO$_4$ tetrahedra. Those distortions can vary strongly among BO$_4$ units in different structural groupings. The $^{11}$B NQR response near 275 kHz for the BO$_4$ units in crystalline Li$_2$O : 2 B$_2$O$_3$ is shown in Figure 15. Modifications of the NQR spectrometer (currently in progress) to achieve greater sensitivity at low frequencies should yield spectra down to or below 150 kHz.

The range of values for $Q_{cc}$ in BO$_4$ units must apparently be extended to even larger values based on the recent discovery [26, 27] of a $^{11}$B resonance at 687 kHz in vitreous lithium metaborate (Figure 16). (The other possible responses in Fig. 16 may arise from $^{10}$B.) From (1), the $Q_{cc}$ value for this response lies between 1190 and 1374 kHz. Identification of the unit responsible for this resonance has not been made, but there are reasons to postulate a BO$_4$ unit with a non-bridging oxygen, which would constitute an exception to the general Krogh-Moe model.