

NQR Studies of Atomic Arrangements and Chemical Bonding in Glasses*,^a

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A very high sensitivity continuous wave NQR spectrometer was developed to detect pure NQR transitions at low frequencies (down to 200 kHz). A signal-to-noise ratio of more than 100 to 1 has been achieved at about 1.36 MHz for crystalline B_2O_3 . Two large ^{11}B responses have been found in vitreous B_2O_3 (NMR detected only one site) with linewidths of less than 30 kHz. ^{27}Al NQR spectra were obtained for $\alpha-Al_2O_3$ (Corundum), the mineral andalusite (a form of $Al_2O_3 \cdot SiO_2$), and a glass having the composition of anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$).

Introduction

The structure of glasses has been studied by many techniques such as X-ray [1], Raman [2], Infrared [3], Mössbauer [4], Electron Spin Resonance (ESR) [5], and Nuclear Magnetic Resonance (NMR) [6] spectroscopy. In this laboratory, NMR [7] has been used extensively for more than 30 years to study glass structure (i.e. atomic arrangements, coordinations, chemical bonding, presence of particular structural groupings). The perturbations of the NMR Zeeman levels by the nuclear quadrupole interaction is one of the most useful tools for gathering data on glass structure. But that interaction is usually seen only as a second-order effect, and values of the quadrupole coupling constant e^2qQh^{-1} and the asymmetry parameter η are not measurable with high accuracy. Here we show that NQR studies can be carried out for many glasses, yielding much more accurate values of e^2qQh^{-1} and η and revealing sites in glasses and crystalline powders not detected by NMR.

Most NQR frequencies of both borate and aluminate glasses are predicted to be in the 200 to 4000 kHz region. These low frequencies, and the relatively broad linewidths expected for glasses, could make detection of the NQR responses difficult or impossible. Further – with rare exceptions – no NQR spectra have been

detected in solids for boron and aluminum using pulsed spectrometers. Several boron [8, 9] and aluminum [10] NQR responses have been reported using the double resonance technique. This technique requires the presence in the sample of nuclei having high values of the gyromagnetic ratio, in most cases hydrogen atoms, to obtain an adequate S/N (signal-to-noise ratio). However, many compounds and glasses of interest do not contain significant amounts of hydrogen.

Recently, a low-frequency regenerative continuous wave (CW) NQR spectrometer has been constructed in this laboratory. A Robinson type oscillator [11] and Zeeman modulation have been used for this instrument. The advantages of Zeeman modulation over other modulation techniques are explained elsewhere [12, 13]. This spectrometer is very sensitive and can operate at frequencies as low as 200 kHz.

Sample Preparation

In this work both ^{11}B and ^{10}B NQR spectroscopy have been performed on vitreous and crystalline samples, and ^{27}Al NQR has been carried out on crystalline materials.

Crystalline B_2O_3 was produced using a procedure described by Kline et al. [14]. Crystalline $Li_2O \cdot 2B_2O_3$ was prepared by melting a mixture of the appropriate amounts of H_3BO_3 and Li_2CO_3 in a platinum crucible at 1100°C for 15 minutes, and then holding the melt at 500°C for about 8 h. A polycrystalline material of composition $Na_2O \cdot 4B_2O_3$ was prepared by melting a mixture of the appropriate amounts of H_3BO_3 and Na_2CO_3 in a platinum

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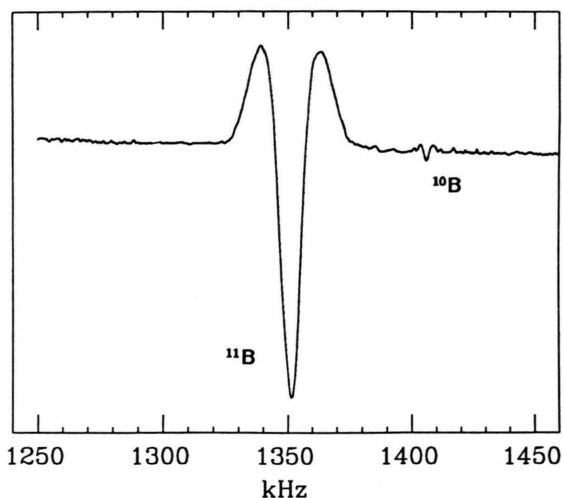
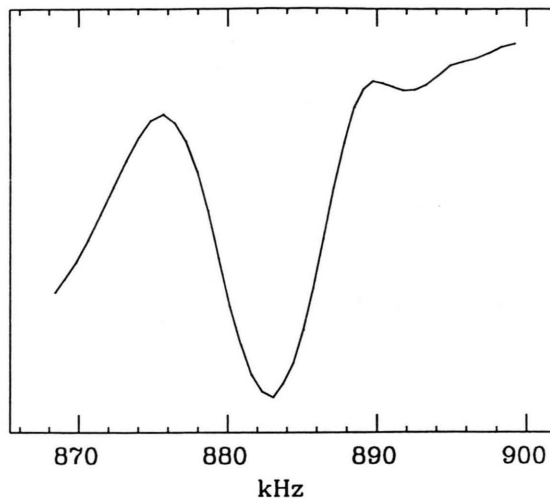
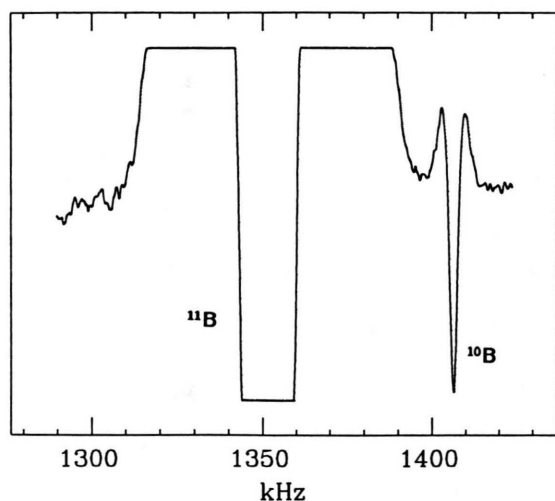
Fig. 1a. Boron NQR spectrum for crystalline B_2O_3 .Fig. 2. A ^{10}B response from crystalline B_2O_3 .

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

crucible at 1100°C for 15 min, and then holding the melt at 500°C for 12 h. All of the glasses were prepared by melting a mixture of the appropriate amounts of H_3BO_3 , Li_2CO_3 , and Na_2CO_3 in a platinum crucible at 1100°C for about 15 min and pouring the melt into a carbon mold which was preheated to about 200°C to prevent cracking of the glass as it cooled.

$\alpha\text{-Al}_2\text{O}_3$ was purchased from Fisher Scientific Co. The mineral andalusite (Al_2SiO_5) came from White Mountain, Mono County, Calif., USA, and was pulverized. All the powder samples were put in 29 ml glass vials whose background boron responses were

negligible, and the solid vitreous samples were wrapped in teflon tape to prevent hydration. The NQR was carried out at liq. N_2 temperature since S/N is inversely proportional to temperature.

NQR Results

1. Boron NQR Studies of Borate Glasses and Crystalline Compounds at Liquid N_2 Temperature

The boron NQR spectrum obtained from crystalline B_2O_3 is shown in Figure 1. By x-ray diffraction [15] and NMR [16], the structure of crystalline B_2O_3 has been shown to consist of BO_3 units. The ^{11}B nucleus in this three-coordinated boron site gives rise to the transition at 1351.5 kHz in Figure 1. (The spectrum shown in Fig. 1b was obtained from a separate run using a different time constant that is one of the acquisition parameters, which provided a greatly expanded vertical scale.) Other transitions at 883 kHz (Fig. 2) and 1406 kHz (in Figs. 1a and 1b) arise from ^{10}B nuclei. ^{11}B has a nuclear spin of $3/2$ and yields only one transition frequency, so that e^2qQh^{-1} and η cannot be determined from ^{11}B data alone. ^{10}B , however, has a spin of 3 and for nonzero η there are 13 transition frequencies [17] allowing measurement of both e^2qQh^{-1} and η . (For $\eta=0$, there are three transition frequencies, again allowing the determination of both e^2qQh^{-1} and η .) Since the ratio [18] $e^2qQh^{-1}(^{10}B)/e^2qQh^{-1}(^{11}B)$ is known independently, the parameters for ^{11}B can be determined. The values of e^2qQh^{-1} and η for ^{11}B were determined to

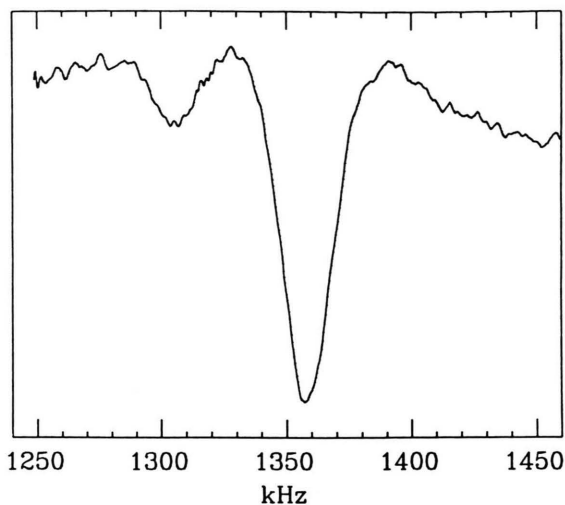


Fig. 3. ^{11}B responses from vitreous B_2O_3 .

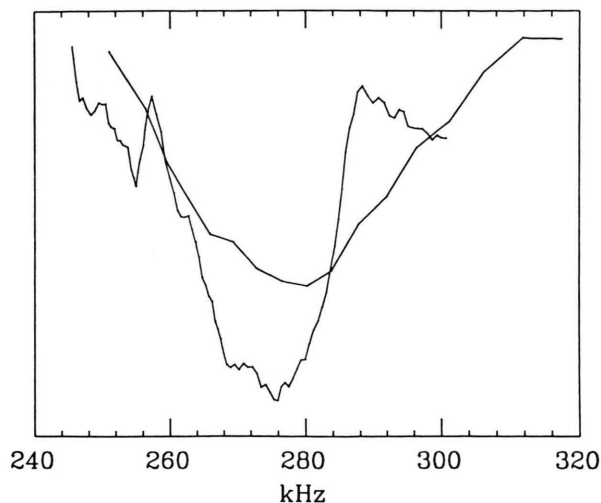


Fig. 5. Two ^{11}B NQR spectra for four-coordinated borons in crystalline $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$.

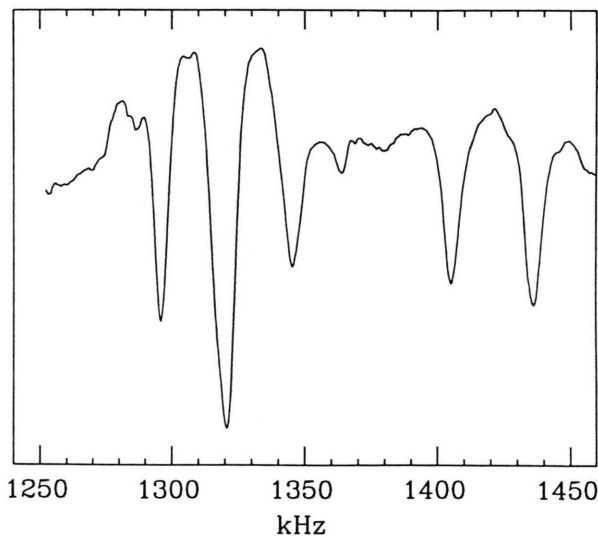


Fig. 4. ^{11}B responses from a polycrystalline sample having the sodium tetraborate composition ($\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$).

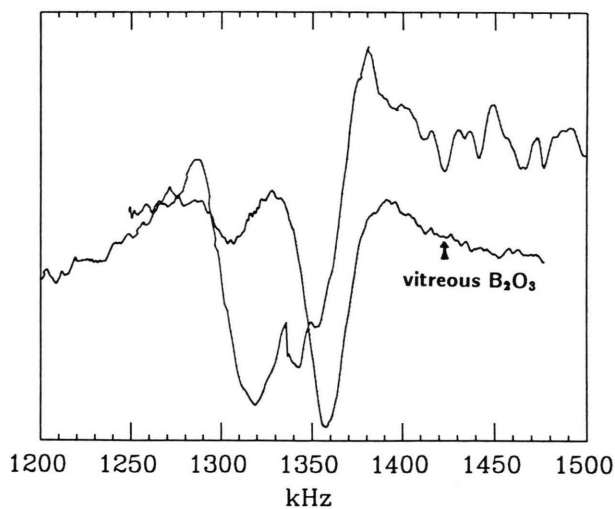


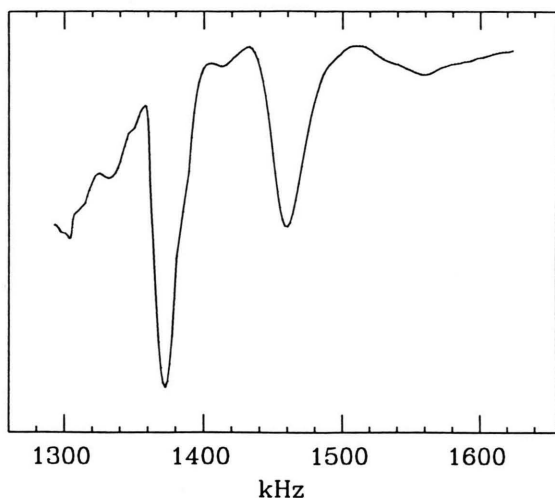
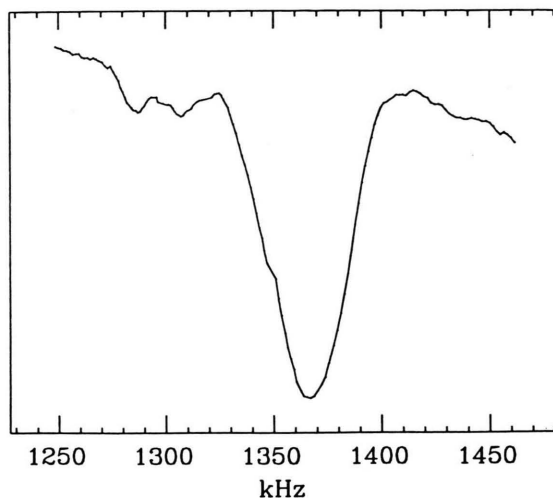
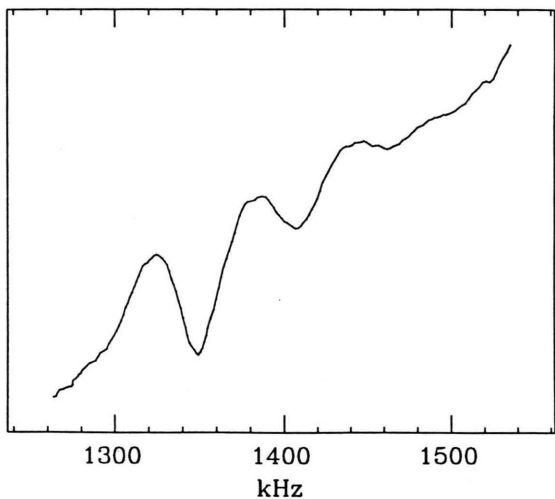
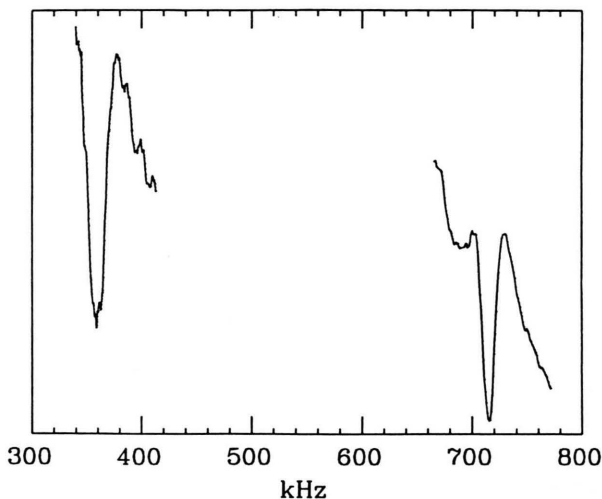
Fig. 6. ^{11}B NQR for a glass of composition $0.15\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ referenced to vitreous B_2O_3 .

be 2701.10 ± 0.16 kHz and 0.0667 ± 0.00036 respectively for crystalline B_2O_3 from the present experimental results.

Responses from two types of BO_3 units in vitreous B_2O_3 are clearly resolved in the NQR spectrum shown in Figure 3. The responses are surprisingly narrow (≤ 30 kHz). No other structural studies have reported this. Boron atoms in the site corresponding to the higher frequency are calculated to compose about 85% of the total boron atoms. We believe that the

1358 kHz response probably arises from ^{11}B in boroxol groups, and the 1305 kHz response from ^{11}B not contained in boroxol groups. The structure of the latter structural grouping is not yet determined.

In a polycrystalline material prepared with the sodium tetraborate composition ($\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$), six sites are resolved by ^{11}B NQR (Figure 4). X-ray diffraction shows the material to be a mixture of sodium borate compounds. The spectrum of Fig. 5 then shows how sensitive the ^{11}B response from BO_3 units is to

Fig. 7a. ^{11}B NQR for crystalline $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$.Fig. 8. Boron NQR for vitreous $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$. No assignment of the responses to ^{10}B or ^{11}B has yet been made.Fig. 7b. ^{11}B NQR for vitreous $\text{Na}_2\text{O}-2\text{B}_2\text{O}_3$.Fig. 9. ^{27}Al NQR responses for $\alpha\text{-Al}_2\text{O}_3$ (corundum).

the different structural groupings of the various sodium borate compounds in which the BO_3 units are contained.

Figure 5 displays two ^{11}B NQR spectra for BO_4 units in crystalline $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$. The two runs were carried out using different settings of the spectrometer parameters (radio-frequency voltage, modulation amplitude, etc.). ^{11}B and ^{10}B NQR frequencies from BO_4 units are expected to occur at low frequencies (≤ 400 kHz) because of the near tetrahedral symmetry about the boron atom in the BO_4 unit.

Figure 6 shows the ^{11}B NQR spectrum for a glass of composition $0.15 \text{ Na}_2\text{O}-\text{B}_2\text{O}_3$, referenced to vit-

reous B_2O_3 . The three lines between 1310 and 1360 kHz correspond to BO_3 units in at least three different structural groupings.

In Figs. 7a and 7b, ^{11}B NQR spectra for crystalline and vitreous $2\text{Na}_2\text{O}-\text{B}_2\text{O}_3$, respectively, are shown. These compounds are known from x-ray diffraction studies to have pyroborate groupings (separated BO_3^{-3} units each having three non-bridging oxygens. A bridging oxygen links [i.e. is bounded to] two boron atoms; a non-bridging oxygen has a formal negative charge and is bonded to only one boron atom). Figure 8 shows the spectrum obtained from vitreous $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$. The predominant structural grouping is

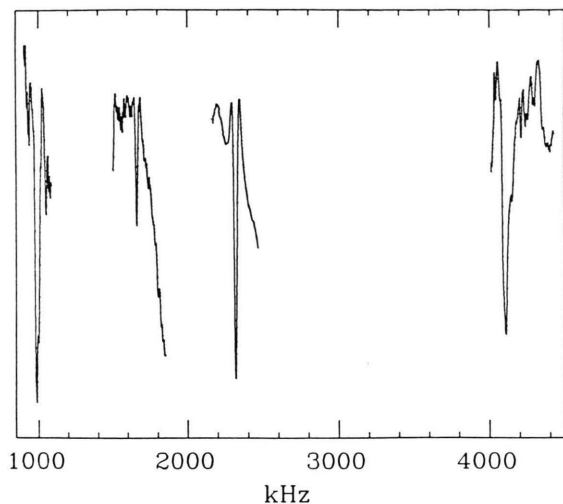


Fig. 10. ^{27}Al NQR responses for the mineral andalusite (Al_2SiO_5).

presumably the metaborate chain of BO_3^{-1} -type units, each unit having two bridging oxygens and one non-bridging oxygen.

2. Aluminum NQR Studies of Crystalline Compounds at Liquid Nitrogen Temperature

Although ^{27}Al MAS NMR studies may resolve responses from three aluminum-oxygen coordinations (four, five and six-coordinated aluminum sites) by chemical shift differences [19], Magic angle spinning (MAS) reduces quadrupole effects and may eliminate information gained from the quadrupole interaction. Knowledge of the electric field gradient components obtained from ^{27}Al NQR can give information about the geometry and chemical bonding of aluminum atoms in the various sites.

Table 1. ^{27}Al quadrupole parameters for the mineral andalusite (Al_2SiO_5). The values of e^2qQh^{-1} and η for two different aluminum-oxygen coordinations (i.e. five- and six-coordinations) obtained from this NQR work are compared with those obtained from an NMR study [21] of a single crystal. The second and third columns are the e^2qQh^{-1} and η values obtained from the five-coordinated aluminum site, and the fourth and fifth columns those obtained from the six-coordinated aluminum site.

Studies	e^2qQh^{-1}	η	e^2qQh^{-1}	η
NQR Study	5.696 ± 0.018	0.3978 ± 0.0083	14.112 ± 0.095	0.3003 ± 0.0193
NMR Study	5.9	0.7	15.6	0.08

Figure 9 displays ^{27}Al responses for $\alpha\text{-Al}_2\text{O}_3$ (corundum). The frequencies are 361.6 and 715.5 kHz yielding $e^2qQh^{-1} = 2389$ kHz and $\eta = 0.0913$. η is different from zero obtained from NMR studies [20]. NQR resonances from both the five-coordinated and six-coordinated aluminum sites are shown in Fig. 10 for the mineral andalusite (Al_2SiO_5). The two lower frequencies correspond to the five-coordinated aluminum site, and the two higher frequencies to the six-coordinated aluminum site. Values of e^2qQh^{-1} and η obtained from the NQR responses are compared in Table 1 with those obtained from NMR study [21] of a single crystal. The second and third columns in Table 1 are the e^2qQh^{-1} and η values obtained from the five-coordinated aluminum site, and the fourth and fifth columns those obtained from the six-coordinated aluminum site. There are significant disagreements, but it should be noted that the polycrystalline sample used in the NQR studies was not of good quality, containing obvious inclusions of other material. Several ^{27}Al responses have also recently been detected for vitreous anorthite ($\text{CaO-Al}_2\text{O}_3-2\text{SiO}_2$).

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