

The Configuration of Three-Coordinated Boron in Vitreous and Crystalline Boron Oxide

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The nuclear magnetic resonance spectrum of ^{11}B has been investigated in glassy and crystalline substances. From a comparison of the values of the quadrupole coupling constants with those of crystalline compounds of known structure, a planar structure of three-fold symmetry has been proposed for the BO_3 -group in vitreous as well as in crystalline B_2O_3 , which contradicts the structure previously reported for crystalline B_2O_3 . The observation of a shorter relaxation time and higher degree of thermal motion in the B_2O_3 samples than for the borates is also taken as a support for this structural interpretation.

Since the first observation of quadrupole effects in the NMR signal of the ^{11}B -resonance, this resonance has been used fruitfully in the study of the structures of boron-containing glasses. Several crystalline compounds have also been investigated, but it is striking that new structural information has been obtained mainly from the glassforming systems.¹⁻³

Polycrystalline and vitreous substances give comparatively smooth spectral patterns, from which the primary broadening parameters are difficult to determine. The uncertainties due to this fact constitute the main limitations of these investigations. The spectra obtained from glassforming substances have consequently been compared with those of crystalline compounds of known structure, and in the case of agreement between the spectra conclusions have been drawn concerning the structure of the glasses.

A similar comparison between crystalline and vitreous borates is presented in this paper (Table 1), including both previously published results and the results of a series of new investigations. Attention has been focused upon the broad spectral line assigned to three-coordinated boron. Since the shape of this line is determined mainly by the quadrupole coupling, the size of this effect can be examined with a good relative accuracy even for powdered samples. This is not, however, the case for the narrow spectral line assigned to four-coordinated boron, and information concerning the structure of the BO_4 -group cannot be expected to be obtained in a similar way.

Previous NMR investigations have indicated that the BO_3 -group in B_2O_3 glass is planar.¹ The structure of crystalline B_2O_3 as determined by Berger⁴ may be described in terms of a three-dimensional network built up of BO_3O pyramids, in which one of the boron-oxygen distances is longer than the other three. A very close similarity between the spectra of vitreous and crystalline B_2O_3 has also, however, been observed.⁵ This latter fact tends to substantiate the assumption of a structural similarity between the two modifications which is in contradiction to the previously proposed structures. The present investigation has been undertaken in order to explore the cause of the divergence.

EXPERIMENTAL

Spectra were recorded with a Varian-4250 Wide line spectrometer, stabilized at 16.000 Mc/s by the clock frequency from a digital counter. The magnetic scan was calibrated using the normal sideband technique. Samples were prepared in accordance with the procedures described in the structure references given in Table 1. Crystalline B_2O_3 was supplied by Professor J. Krogh-Moe for an earlier study.⁵ The spectra of the boric acids were difficult to detect. The deuterated samples were pressed in order to obtain a sufficient filling factor. To make the signal detectable it was, furthermore, necessary to register the spectra under conditions which probably implied partial saturation and modulation broadening of the signal, although both doped and gamma irradiated samples were studied. Under the conditions used an appreciable background signal was obtained originating from three-coordinated boron in the glass tubings of the coil holder and the test tube. The values of the peak-to-peak separations thus determined are rather uncertain, as is indicated in Table 1.

It should also be mentioned that results deviating from those presented in Table 1 were obtained from the first measurements performed. The setting of the spectrograph happened to be chosen using the sample of vitreous B_2O_3 showing the largest intensity for the broad spectral line assigned to three-coordinated boron. This resulted in the use of a comparatively large h.f. field, and whereas the spectrum of B_2O_3 was registered under reasonable conditions, those of the alkali borates were registered under conditions that implied partial saturation. The area under the spectral line differed, namely, considerably from zero, in the latter cases, which is indicative of such conditions as has been demonstrated in dispersion mode experiments.⁶ These findings are of interest as they indicate a shorter relaxation time for the pure B_2O_3 samples than for the alkali borates, a fact of great importance in the structural interpretation of the measurements. The data submitted in Table 1 has been taken from spectra recorded with a h.f. field only one tenth of that employed in the first measurements.

DISCUSSION

The factors influencing the line width and line shape of quadrupole-broadened resonance lines of powdered samples have previously been reported in detail.^{1,7-9} Factors of importance for the interpretation of appropriate spectra of the BO_3 -group are summarized below to facilitate a closer study of the geometry of the group.

Since the quadrupole interaction is comparatively large, only the central line representing the transition $m = -\frac{1}{2} \rightarrow m = +\frac{1}{2}$ is observed, whereas the so-called satellites representing the transitions $m = \pm 3/2 \rightarrow \pm 1/2$ are broadened beyond observation for powdered samples.³ The quadrupole interaction gives rise to a shift of the resonance frequency of the spectral lines. In

the theoretical calculation the resonance frequencies are expressed as a power series of the parameter eqQ/ν_0 , where eqQ denotes the quadrupole coupling constant, and ν_0 the frequency of the unshifted resonance. The theory shows that the frequency shift of the central line contains the even order terms only, and that since the first term in the series, quadratic in eqQ/ν_0 , heavily dominates the others, it provides a good approximation of the frequency shift. The random orientation of the local principal axes of the electric field gradient tensor of a powdered sample gives rise to a continuous distribution of frequency shifts, generating a powder pattern characteristic of the field gradient tensor in cases in which the quadrupole broadening is large compared with the superimposed dipolar broadening. The shape of the powder pattern has been calculated for some different values of the asymmetry parameter η of the field gradient tensor.^{1,7-9} The shape of the experimentally recorded derivative curve has also been calculated for a narrow superimposed dipolar broadening function.^{2,9} For $\eta=0$ this curve shows a characteristic pattern with large intensities only at the extremes of the quadrupole perturbed frequency shifts, where the absorption line displays sharp cut-off and infinities. The spectrum could be regarded as being composed of a high and a low field component line, from the peak-to-peak separation of which the value of eqQ could be determined.^{2,7} For $\eta>0$ the powder pattern is broadened and in the derivative curve large intensities occur at the points of sharp cut-off and infinities of the absorption line. For η in the interval $0<\eta<0.10$ the infinity points are displaced somewhat from the cut-off points towards the centre of the spectrum. In the case of a superimposed narrow dipolar broadening function the increase of η from zero results in an increased width of the derivative curve and in a broadening of the component lines. The change in spectral line shape caused by the growth of η from 0 to about 0.10 is demonstrated by the spectra shown in Figs. 1 and 2. The spectrum of pure B_2O_3 has a shape very similar to that characteristic for $\eta=0$. The spectrum of the alkali borate glass containing 16 mole % K_2O has a shape approaching that of $\eta=0.10$, a conclusion drawn from the similarity of the spectrum with that of deuterated

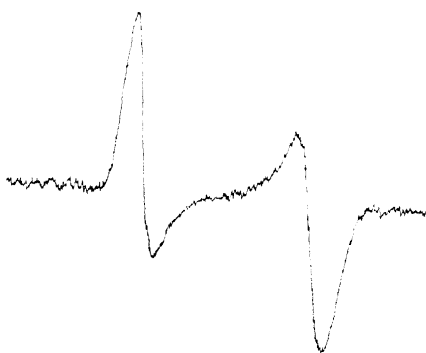


Fig. 1. ^{11}B resonance of vitreous B_2O_3 , $\nu_0=16.00$ Mc/s.

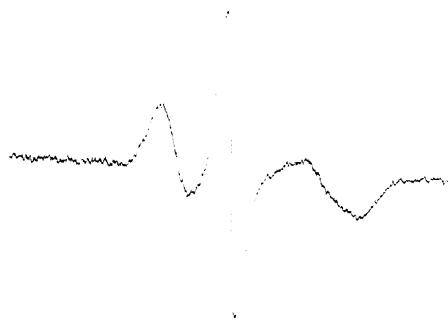


Fig. 2. ^{11}B resonance of a potassium borate glass containing 16 mole % K_2O , $\nu_0=16.00$ Mc/s.

polycrystalline borax, ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{D}_2\text{O}$) for which single crystal NMR studies have shown that $\eta \approx 0.09$ ¹⁰ and that only one type of three-coordinated boron is present.¹¹ If the BO_3 -group exhibits a three-fold rotational axis orientated perpendicular to the plane through the O-atoms, a sharp spectrum characteristic for $\eta=0$ is to be expected. As long as this symmetry requirement is fulfilled, the shape of the spectrum is not dependent upon whether the boron atom is located in the plane of the O-atoms or whether it is somewhat displaced from the plane. On the other hand, the value of the quadrupole coupling constant and thus the width of the spectrum is strongly influenced by the puckering of the BO_3 -group.

The compounds investigated may be divided into two groups, the first including substances with eqQ around 2.74 Mc/s and the second substances with eqQ around 2.54 Mc/s. The first group comprises vitreous and crystalline B_2O_3 , orthorhombic boric acid (H_3BO_3), metaboric acid (HBO_2), and lanthanum orthoborate (LaBO_3). All these substances display spectra of the form characteristic for $\eta=0$. From crystal structure determinations it is also known that orthorhombic boric acid, metaboric acid, and lanthanum orthoborate contain planar symmetrical BO_3 -groups.¹²⁻¹⁴ Compounds of the second group include all the alkali and alkaline earth borate glasses investigated and the related crystalline compounds which give spectra of a type indicating a value of η between 0.05 and 0.10, owing to distortions of the BO_3 -group from three-fold symmetry.

The valence electrons on the boron atom may be presumed to be equivalent for these different compounds since the electronegativity difference between boron and hydrogen is very small. This is further confirmed by the fact that even the metaboric acids display spectra of the form characteristic for $\eta=0$. The valence electrons on the three-coordinated boron must thus be equivalent although some of the oxygen atoms are bonded to the boron atom and some to the hydrogen atoms.

To facilitate a closer study of the structure of the BO_3 -group we will try to estimate the quadrupole coupling constant, eqQ , as a function of the geometry of the group. The BO_3 -group is planar in most compounds and as the bond angles of the boron atom are approximately 120° , it can be assumed that three sp^2 -hybridized σ -bonds are formed between the boron atom and the surrounding oxygen atoms. The bond angles at the oxygen atoms are also approximately 120° , so that even the atomic orbitals of the oxygen atom can be assumed to approach sp^2 -hybridization. Since the planes through the O—B—O and B—O—B groups of neighbouring boron and oxygen atoms coincide in most cases, we have further assumed that the π -electrons of the oxygen atoms are transferred to some degree to the empty p_z -orbitals of the boron atoms, thus forming conjugated systems. Spectroscopic evidence for such a partial transference exists,¹⁵⁻²⁰ and the BO distance for three-coordinated boron has moreover been interpreted as indicating approximately 20% double bond character.^{21,22} This corresponds to a π -electron charge density on the boron atom of about one half the unit charge, which is also in fairly close agreement with the charge density calculated for some representative conjugated borate groups using the usual methods, the size of the resonance integral being estimated from the electronegativity difference between boron

and oxygen.²³ The π -electrons must then be regarded as having a considerable effect on the value of eqQ , and we have estimated that the value of eqQ will be reduced by approximately 0.6–0.8 Mc/s by transference of π -electrons from the oxygen atoms. As the observed value of eqQ is around 2.7 Mc/s for boron atoms in planar, symmetrical BO_3 -groups, we may suppose that the σ -electrons give a contribution to eqQ of approximately 3.3–3.5 Mc/s in such groups. The structure previously proposed for crystalline B_2O_3 may then be tested against the NMR measurements. For a first approximate calculation of the contribution to eqQ from the σ -electrons, we will use the simplified theory of Towns and Dailey²⁴ in which only the atomic orbitals on the boron atom are considered. The effect on eqQ of puckering the BO_3 -group so as to preserve the three-fold symmetry has been studied by Das and Hahn²⁵ who give the value of the field gradient at the B nuclei as a function of the angle θ between the BO bond and the three-fold symmetry axis. The field gradient shows a maximum for the planar group ($\theta=90^\circ$), and is reduced by 17.3 % for the puckered group with $\theta=70.5^\circ$. Since the valence orbitals of boron approach one another as the group is puckered, their p -character increases. The value of the quadrupole coupling constant, however, diminishes, as the contribution to eqQ from the p -orbitals aligned along the BO bond greatly decreases with the puckering. The value of eqQ for a puckered BO_3 -group in accordance with the proposed structure of crystalline B_2O_3 would then be of the order of 2.5–3.0 Mc/s, assuming that the boron atom forms three normal σ -bonds to the three nearest oxygen atoms. It has been assumed that the lone-pair electrons of the fourth oxygen atom are more or less donated to the boron atom in this structure, and that the boron atom has a quasi-tetrahedral configuration. The value of eqQ would, in this case, be considerably less than that calculated for the conjugated planar or the puckered BO_3 -group containing purely three-coordinated boron. It is thus apparent that the quasi-tetrahedral structure cannot be brought into agreement with the NMR measurements. These arguments also show, however, that the NMR data do not give sufficient information, to allow us to distinguish between the planar conjugated and the puckered BO_3 -group of purely three-coordinated boron. We are, however, of the opinion that the NMR measurements should be interpreted in terms of a planar, three-fold symmetrical BO_3 -group in crystalline as well as in vitreous B_2O_3 . The reasons for this are as follows:

The agreement in eqQ between the boric acids and the two forms of B_2O_3 seems to support the existence of planar BO_3 -groups in the B_2O_3 samples as it must be regarded as being rather unlikely that two structures so widely different as the planar conjugated and the puckered BO_3 -groups could give rise to such similar eqQ values.

The shorter relaxation time observed for the B_2O_3 samples than for the alkali borates indicates that the degree of thermal motion is much higher in the pure B_2O_3 systems than in the borates. This is all in agreement with previous knowledge concerning the glass systems. The B_2O_3 glass has been characterized as a Stewart-type liquid consisting of more or less branched macromolecules with only weak intermolecular forces. The description is grounded on experimental evidence including molar refractivity,²⁶ melting point, low temperature specific heat,^{26,27} thermal expansivity, surface tension,

viscosity, mechanical damping,²⁸ and the diamagnetic anisotropy of drawn fibers.²⁹ By addition of alkali oxides some of the boron atoms become four-fold coordinated^{3,5} resulting in the formation of a three-dimensional B—O skeleton which strengthens the structure. As a result the melting point is increased and the thermal expansivity decreased. A low degree of thermal motion can thus be expected in these systems and consequently a long relaxation time. These experimental facts have been interpreted as indicating a planar structure of the BO_3 -group in the B_2O_3 glass, since a conjugated structural group cannot permit the formation of a four-dimensional skeleton. The NMR measurements now indicate that the same should apply to the crystalline form of B_2O_3 , and it is quite obvious that a large relaxation time is to be expected for the previously proposed structure of this substance. The necessity of using the powder diffraction method in the X-ray analysis of crystalline B_2O_3 , and the high thermal vibration of this compound, probably not found in other borates, may explain the uncertainty of the X-ray determination.

The effect of deviations from three-fold symmetry on the NMR spectrum must also be considered. It is convenient to study eqQ as a function of the degree of distortion for a group in which the angle θ of the three BO bonds is kept constant. The contributions to eqQ from the p -orbitals are not influenced by the degree of distortion in such a case, whereas the p -character of the hybrids is greatly affected. Calculations show, however, that the p -character of the different hybrids changes in such a way that eqQ remains practically constant under distortions of the order of magnitude observed for the BO_3 -group in crystalline solids. The distortion of the BO_3 -group from three-fold symmetry as reported in the previously proposed structure of crystalline B_2O_3 will thus not affect the arguments given above. An asymmetry of this order will, however, greatly affect the shape of the spectrum and give rise to a spectrum in which the high and low field component lines are very broad and of at least the same width as those of the crystalline alkali borates. The NMR measurements may thus further be interpreted as indicating that the BO_3 -group in vitreous as well as in crystalline B_2O_3 has a structure of almost three-fold symmetry.

Further support for this structural model may be obtained by inspecting the line width of the high and low field component lines of the spectra of the two modifications of B_2O_3 and of lanthanum orthoborate. In order to observe the true line width of the component lines, it was necessary to use a very low h.f. field and a small modulation amplitude. Under these conditions the signals of most other boron containing compounds could not be distinguished from the background noise of the spectrograph.

The shape of the derivative curve has been calculated for $\eta=0$ together with appropriate values of eqQ and a superimposed dipolar broadening function of gaussian shape with an rms width of 1.3 kc/s, as previously estimated from the B_2O_3 -system.² From the observed spectra of the samples of B_2O_3 , the low field component line is found to be about 15 % broader and the high field component line about 50 % broader than that calculated. This indicates some variation of eqQ or η over the nuclei in the sample. As the spectra of vitreous and crystalline B_2O_3 are, however, identical, the NMR measurements may furthermore be interpreted as being indicative of a high degree of short range

order in the glassy phase, with only small variations in the bond angles at the boron atom. The extra broadening observed may be due to variations in the angles owing to intense thermal motion within the solids. The out of plane vibration of the boron atom, which does not affect the asymmetry parameter η , cannot, for reasonable amplitudes, account for the broadening. The fact is that eqQ shows a very small variation with θ for values of θ around 90° .²⁵ The bending vibration, which greatly affects θ , is likely to be responsible for the broadening effect. The equations for calculating the cut-off and infinity points of the absorption curve⁹ show that even small deviations of θ from zero will cause a considerable broadening. These equations also predict a larger extra broadening of the high field component line than of the low field component line for variations in η . Extrapolating linearly from the broadening observed in the spectra of the alkali borates, which is caused by a value of $\eta=0.1$ and a bending of approximately 3° , the extra broadening observed in the spectra of B_2O_3 indicates a bending amplitude of 1° . In the spectrum of lanthanum orthoborate, on the other hand, the component lines are narrow and of the same width.³⁰ This indicates the presence of a rigid lattice with a long relaxation time, which is also borne out by the fact that the spectrum of the compound could only be observed after irradiating the sample with hard γ -rays.

The peak-to-peak separations between the maxima of the derivative curve fall in the region 2.60 to 2.75 Mc/s for all compounds of the second group of Table 1. The spectra here display a form from which a value of the asymmetry parameter η in the range 0.05 to 0.10 may be estimated. Using the formulae given earlier¹ for the calculation of the peak-to-peak separation of the spectrum as a function of eqQ and η , a value of eqQ around 2.5–2.6 could be determined for these compounds. These values seem to be in agreement with the more accurate values of eqQ determined for single crystals. Structure determinations of the crystalline compounds of this group indicate that the BO_3 -group is planar though somewhat distorted from three-fold symmetry. It thus seems as if eqQ is affected by distortions from three-fold symmetry and that the constant is about 10 % smaller in the distorted case than in the symmetric one. This is in contradiction to what was found by applying the simplified theory of Towns and Dailey. The result constitutes, since the difference in eqQ between the two groups of compounds is rather small, a further proof of the planar structure of the BO_3 -group in vitreous as well as in crystalline B_2O_3 . This is of importance as the signal strengths of the spectra of the boric acids are rather poor and conclusions drawn solely from a comparison between these spectra and those of the two modifications of B_2O_3 must be regarded as resting on rather weak experimental evidences.

The variation of the value of eqQ between the two groups of substances that are summarized in Table 1 remains to be explained. To treat these finer details we have to apply the complete theory in which the charges outside the valence orbitals of the boron atom are taken into consideration. The theory of Towns and Dailey gives, in fact, a rather poor approximation when used to calculate the eqQ of a BO_3 -group in which the bonding electrons are rather heavily displaced towards the oxygen atoms. The variation of eqQ with the puckering of this BO_3 -group, as discussed above, still, however,

Table 1. Experimental NMR data for the broad spectral line assigned to three-coordinated boron.

Compounds	<i>eqQ</i> Mc/s as determined directly from the peak-to-peak separation	<i>eqQ</i> Mc/s estimated from powder patterns	η	<i>eqQ</i> Mc/s determined from single crystals	η	NMR ref. powder pattern	NMR ref. single crystal	Structure ref.
<i>Group I. eqQ</i> ~ 2.70 Mc/s, $\eta \sim 0.0$ Known structures with planar, three-fold symmetrical BO_3 -groups.								
Orthorhombic boric acid, H_3BO_3	2.60 ± 0.15	2.60 ± 0.20	0.0	—	—	2^a	—	12
Metaboric acid HBO_2 , monoclinic	2.62 ± 0.20	2.66 ± 0.25	0.0	—	—	2^a	—	13
Metaboric acid HBO_2 , orthorhombic	2.62 ± 0.20	2.66 ± 0.25	0.0	—	—	2^a	—	13, 41
Lanthanum orthoborate, LaBO_3	2.74 ± 0.05	2.74 ± 0.05	0.0	—	—	30^a	—	14
<i>Group I. eqQ</i> ~ 2.75 Mc/s, $\eta \sim 0.0$ Unknown structures.								
B_2O_3 -glass	2.76 ± 0.02	2.76 ± 0.02	0.0	—	—	$1, 2, 30^a$	—	—
B_2O_3 -crystal	2.76 ± 0.02	2.76 ± 0.04	0.0	—	—	$1, 2, 30^a$	—	4
<i>Group II. eqQ</i> ~ 2.55 Mc/s, $\eta \sim 0.05$ — 0.10 Known structures with planar, nonsymmetrical BO_3 -groups								
Potassium pentaborate tetrahydrate, $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$	2.51 ± 0.10	2.47 ± 0.06	0.05 — 0.10	2.536 ± 0.003 2.521 ± 0.003	0.212 ± 0.004 0.195 ± 0.005	30^a	35	42, 43

holds true as long as the shape of the charge cloud of the oxygen atoms is preserved. Under such conditions the value of eqQ then decreases somewhat more rapidly than calculated above when puckering the group, whereas it still remains unaffected by small deviations from three-fold symmetry. It seems to be justified to take into account only the charges on the neighbouring oxygen atoms, as the positive charges on the cations and the corresponding negative charges on the BO_4 -groups of the borates cannot appreciably influence the value of eqQ . Each of the groups of substances in Table 1 contains compounds with greatly varying numbers of neighbouring cations and BO_4 -groups of the studied three-coordinated boron atoms. It could then be concluded also that these surrounding atom groups do not influence the electron charge density close to the boron atoms so as to affect the value of eqQ .

The observed difference of the value of eqQ between the two groups seems then to be correlated with the symmetry of the BO_3 -group. It could be assumed that the observed decrease in the value of eqQ when going from the compounds containing BO_3 -groups of three-fold symmetry to those containing distorted groups should be attributed to changes of the charge densities accompanying the distortion of the boron-oxygen skeleton. The boron oxygen bonds of the distorted structures could be assumed to be strained and less ideal than those of compounds containing BO_3 -groups of three-fold symmetry. The observation of a shorter relaxation time for the samples of pure B_2O_3 than for the borates strongly supports this assumption. In the borates of known structures very large variations in the OBO and BOB angles are observed. In most cases occurring conjugated groups are further distorted somewhat from perfect planarity. Whereas the effect of such distortions on the σ -electron charge densities are not so easily calculated, the effect could be predicted on the π -electron charge densities of the boron atoms. This charge density could be expected to decrease with the distortion as the size of the resonance integrals between neighbouring boron and oxygen atoms are reduced, whereas the π -electron Coulomb integrals are left invariant, upon such structural changes. A decrease in the π -electron density at the boron atom gives rise to an increase in eqQ , and as the reversed effect is observed, we will conclude that the structural changes occur in such a way that the resonance integrals are not too drastically reduced. As, further, the σ -electrons are responsible for the major contribution to the value of eqQ , it is quite natural to assume that variations in the σ -electron densities are also responsible for the major part of the variation in the value of eqQ between the two groups of compounds, and that the variations in the π -electron densities only counterbalance these effects to some degree.

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