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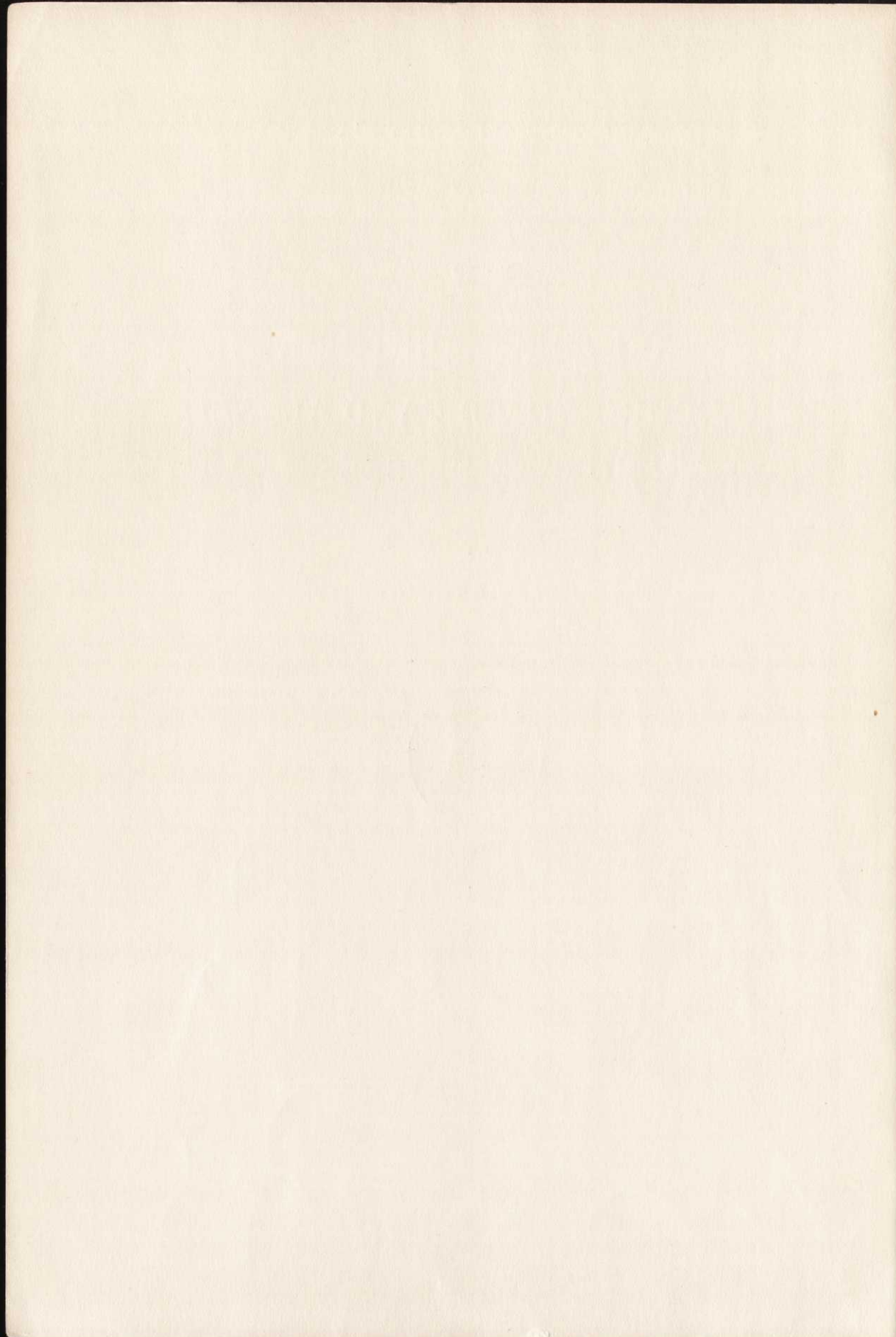GÖTEBORGS UNIVERSITETSBIBLIOTEK

ON THE STRUCTURE
OF BORON OXIDE AND ALKALI
BORATE GLASSES

BY

JAN KROGH-MOE

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Preface

During the last two years the author has published the results of an extensive investigation relating to the structure of alkali borate glasses and melts. The present paper will discuss the main aspects of this work, based on the following eight communications by the author:

I Some new compounds in the system cesium oxide-boron oxide. Arkiv för Kemi *12*, 247 (1958).
II The infrared spectra of some vitreous and crystalline borates. Arkiv för Kemi *12*, 475 (1958).
III Electron microscope studies of borate glasses. Arkiv för Kemi *14*, 1 (1959).
IV An X-ray study of lithium borate glasses. Arkiv för Kemi *14*, 31 (1959).
V The cation distribution in some crystalline and vitreous cesium borates. Arkiv för Kemi *14*, 451 (1959).
VI The crystal structures of potassium pentaborate, $K_2O \cdot 5B_2O_3$, and the isomorphous rubidium compound. Arkiv för Kemi *14*, 439 (1959).
VII On the structural relationship of vitreous potassium pentaborate to the crystalline modifications. Arkiv för Kemi *14*, 553 (1959).
VIII The relation of structure to some physical properties of vitreous and molten borates. Arkiv för Kemi *14*, 567 (1959).

These communications will in the following be referred to by the Roman numerals given above.

Nomenclature

Different systems of nomenclature for the crystalline borates are in use. The following table gives a comparison of the notation employed in this work with that recently recommended by the International Union of Pure and Applied Chemistry (1).

Formula	Notation used in this work	Notation recommended by IUPAC
$3 Na_2O \cdot B_2O_3$	Sodium orthoborate	Trisodium borate
$2 Na_2O \cdot B_2O_3$	Sodium pyroborate	Tetrasodium diborate
$Na_2O \cdot B_2O_3$	Sodium metaborate	Sodium borate
$Na_2O \cdot 2 B_2O_3$	Sodium diborate	Disodium tetraborate
$Na_2O \cdot 3 B_2O_3$	Sodium triborate	Sodium triborate
$Na_2O \cdot 4 B_2O_3$	Sodium tetraborate	Disodium octaborate
$Na_2O \cdot 5 B_2O_3$	Sodium pentaborate	Sodium pentaborate

the average closest cesium–cesium separation did not depend upon the cesium oxide content of the glass up to 20 mole per cent. The lithium borate system was studied with the purpose of determining the coordination of boron. The results indicate that the boron atoms in boron oxide glass are essentially three-fold coordinated by oxygen. No significant deviation in magnitude or position form the boron–oxygen peak in boron-oxide glass could be detected in lithium borate glasses containing 18 and 50 mole per cent lithium oxide. Because of the insensitivity of the method, this result was not taken to exclude a coordination change of boron.

The infrared absorption spectra

The infrared spectra of some lithium, sodium, potassium and cesium borates have been determined (II, VII). The samples were obtained by fusing pro analysi chemicals in a platinum crucible, and prepared for the spectroscopical measurements by the potassium bromide disc technique. To avoid contamination with water, the samples were exposed to the atmosphere as briefly as possible during the preparation. In the case of boron oxide, which is rather hygroscopic, the sample was prepared in a dry box. The spectra were recorded with a double beam Perkin Elmer 21 infrared spectrophotometer.

It was found that the spectra of glass and crystalline phases of the same chemical composition show a considerable resemblance. Furthermore the spectra of different alkali borates with the same alkali content resemble each other. It is concluded that the spectra are characteristic not so much of the BO_3 triangles, BO_4 tetrahedra, and non-bridging oxygens, as of how these structure elements are interlinked and distributed in the structure.

The crystal structure investigations

The crystal structures of potassium pentaborate and rubidium pentaborate have been solved in detail (VI). The cation positions in three crystalline phases in the cesium borate system, cesium enneaborate, cesium pentaborate and cesium triborate, have also been determined (V). The unit cells, space groups and experimental intensities were obtained from single crystal Weissenberg exposures. The intensities were measured visually and the appropriate corrections for the Lorenz and polarization factors were introduced. Cation positions were determined by two dimensional Patterson synthesis in projections along the shortest cell edges. The computations were in some cases carried out with Lipson Strips. For most of the numerical work an Alwac III-E electronic digital computer was available. The computer was used for both Fourier synthesis and structure factor calculations.

The crystal structures of rubidium and potassium pentaborate were solved by two-dimensional projections and a complete three-dimensional Fourier synthesis. The pentaborate is shown to consist of two intermeshing three-dimensional networks, where the basic structural unit is a double ring (cf. Fig 2f). For the cesium borate systems, the closest cesium-cesium separations were found to be 3.90 Å in the triborate, 4.90 Å in the pentaborate and 7.86 Å in the enneaborate.

The phase relationship investigations

Preliminary to the crystal structure studies mentioned above, an approximate melting point diagram was determined for the cesium borate system in the concentration range from 7 to 26 mole per cent cesium oxide (I). The phase relationships were established by equilibrating the melts at constant temperatures in a temperature-controlled electric furnace. Crystallization was detected by visual inspection. 5 previously unknown crystalline phases were found and identified.

The electron microscope studies

A RCA electron microscope, model EMU 2, in conjunction with a replica technique was used to study phase separations in lithium borate glasses containing 20 mole per cent lithium oxide or less (III). Replicas of fresh fracture surfaces of the glass were made by shadowing with platinum and depositing a thin layer of carbon on the surface. The ensuing replica film could easily be detached from the glass by immersion of the sample in water.

The micrographs revealed two kinds of phase separations. Usually a moderate annealing of the glass led to a crystallization. Submicroscopic crystallinity, not affecting the optical transparency to a noticeable degree, was demonstrated. The size of the crystals increased with the annealing time. In one case the electron micrograph appeared to show a phase separation in two liquid phases.

Discussion of the glass structure and properties

The structure of boron oxide

Pure boron oxide glass was pictured by Zachariasen as a random network of planar, triangular BO_3 groups, interlinked by sharing corners (4). A schematic representation of the structure is given in Fig. 1 a. Warren, Krutter and Morningstar supported this structure on the basis of an X-ray investigation of the glass (5). Several later X-ray studies seem to confirm that most of the boron atoms in boron oxide glass are threefold coordinated by oxygen (IV).

Dissenting opinions on the structure of boron oxide glass have appeared in the literature, however, Fajans and Barber suggested that the glass consists of B_4O_6 molecules in analogy with the known P_4O_6, As_4O_6 and Sb_4O_6 molecules (6). Each boron in a free molecule of this kind lies on the apex of a flat tetrahedron and is thus coordinated by three oxygens. To explain the low vapour pressure of the glass, a strong interaction of the boron atom of one molecule with an additional fourth oxygen belonging to an adjacent molecule was assumed. The boron atoms thus become four-fold coordinated by oxygen. This resembles a theory by Grjotheim and Krogh-Moe, where the boron in boron oxide glass are assumed to be essentially four-fold coordinated (7). The glass structure was described as a disordered version of the crystal structure of hexagonal boron oxide with boron–oxygen bonds of different strength. A section of the boron–oxygen network in this crystalline modification is shown on Fig. 1b. The figure is based on the crystal structure determination by Berger (8). Attention is drawn to the fact that all the boron atoms in this modification are four-fold coordinated by oxygen. There are two different kinds of BO_4
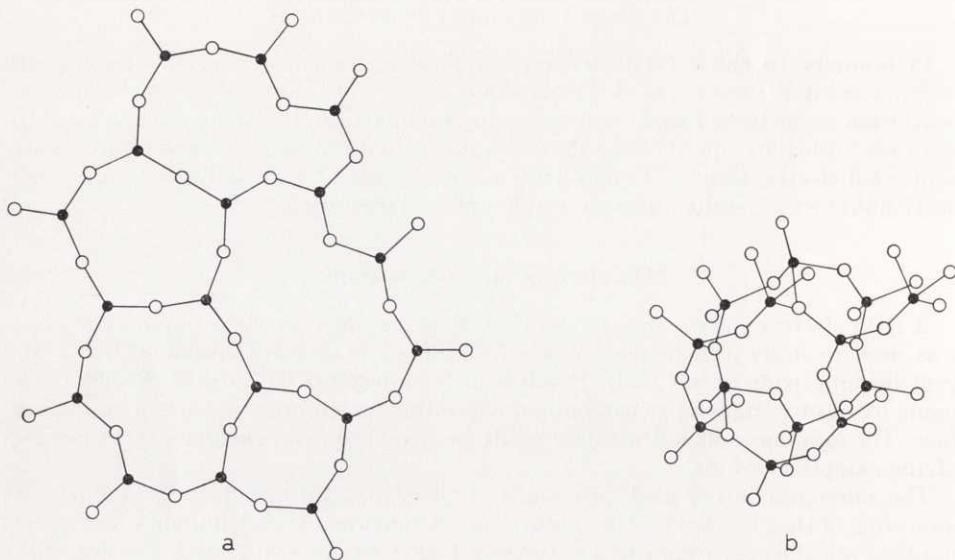
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Fig. 1. Boron oxide structures. Open circles indicate oxygen atoms, filled circles indicate boron atoms. a) Schematic two-dimensional representation of the structure of vitreous boron oxide according to Zachariasen. b) Section of the crystal structure of hexagonal boron oxide according to Berger.

tetrahedra, neither of which are regular. The one kind of tetrahedra has been described as a hybrid between three-fold and four-fold coordination since one of the boron–oxygen bonds is appreciably longer than the other three (8).

The Raman spectrum of boron oxide glass seems to show that boroxol rings are predominant in the structure (9, II). The boroxol group is a planar six-membered ring such as is shown in Fig. 2b. The six-membered ring appears to be a stable configuration in borates, since it occurs commonly in borate structures. A non-planar six-membered ring exists in hexagonal boron oxide, as can be seen in Fig. 1b. Other examples of six-membered rings, planar or puckered, can be seen in Fig. 2.

The low temperature heat capacity curve of boron oxide glass is consistent with a chain structure, according to Tarasov and Stroganov (10). The authors suggest that the chains are built in an analogous manner to the double chains in orthorhombic antimony trioxide.

Zachariasen's theory for the structure of boron oxide glass is still accepted by most workers in this field. Nuclear magnetic resonance data (11) and X-ray glass scattering data (IV) show that within the experimental accuracy the boron atoms in boron oxide glass are really three-fold coordinated by oxygen, as required by Zachariasen's theory. The precision of these results is not so high as to exclude the presence of a certain amount of boron in four-fold coordination, however. This is particularly true if one of the boron–oxygen bonds in the BO_4 group is longer than the other three, i.e. a hybrid coordination such as is observed in hexagonal boron oxide. It should be realized that the glass is a thermodynamically unstable phase, and that the arrangement indicated in Fig. 2b with four-fold coordinated borons represents
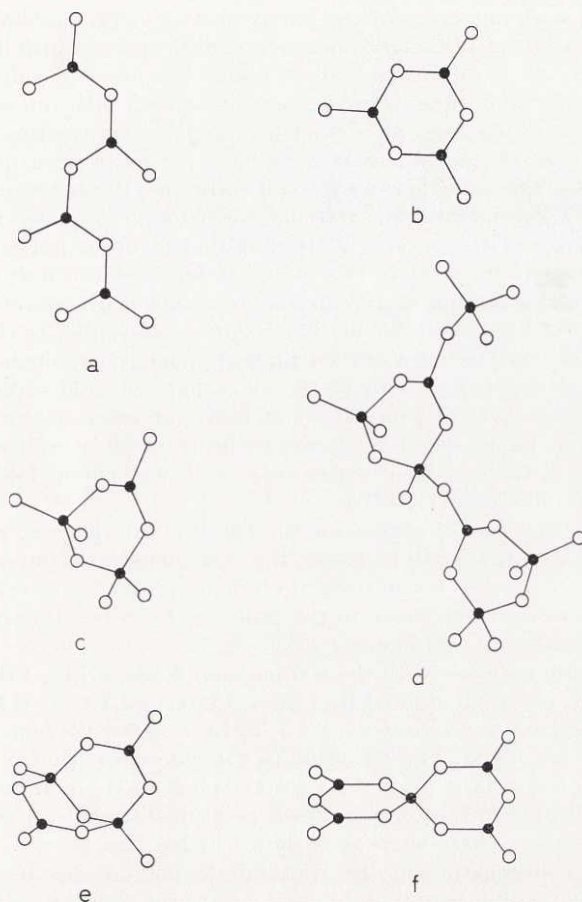
Fig. 2. The borate polyions in some crystalline borates. Open circles indicate oxygen atoms (and in some cases hydroxyl groups), filled circles indicate boron atoms. a) The borate chain in calcium metaborate. b) The boroxol group in sodium and potassium metaborate. c) The polyion in inyoite. d) The borate chain in colemanite. e) The polyion in borax. f) The polyion in potassium penta-borate.

an energetically favoured state under appropriate conditions. The existence of a limited amount of four-fold coordinated boron in the glass, as suggested by the author (VIII), should therefore hardly be surprising. (The reason for introducing the hypothesis of a limited four-fold coordination will be discussed in a later section of this paper).

Review of some borate structures

The first structural picture of the alkali borate glasses is due to Biscoe and Warren (12). These authors studied the system sodium oxide–boron oxide by means of X-ray scattering. Their results were taken to indicate that the boron atoms in the alkali

borate glass are partly in triangular and partly in tetrahedral coordination by oxygen. The fraction of the latter coordination was assumed to increase with increasing sodium oxide content of the glass until a limit of about 15 mole per cent sodium oxide is reached. Below this limit each oxygen atom introduced with the sodium oxide will convert two boron atoms from three-fold to four-fold coordination.

The X-ray results of Biscoe and Warren have generally been quoted as a proof of the coordination change of boron by alkali additions. It has been shown, however, that the current X-ray methods of studying the structure of glass are too inaccurate to prove the theory of Biscoe and Warren (IV). But other indications in support of the coordination change exist. The mere existence of the four-fold coordinated boron in the crystal structure of anhydrous potassium pentaborate (VI) shows that this configuration of boron is stable under circumstances similar to those encountered in the glass. Moreover, recent work on nuclear magnetic resonance absorption of boron in borate glasses is in favour of the view that four-fold coordinated boron is formed in the glass (11). The formation of four-fold coordinated boron by alkali additions to boron oxide therefore seems to be reasonably well established. (For melts and glasses in the system of boron oxide with water, four-fold coordination of boron appears less likely (VIII, 13).)

To see which structures to expect for the alkali borate glasses, a review of some pertinent crystal structures will be made. Fig. 2 demonstrates important features in the arrangement of the boron and oxygen atoms in a number of crystalline borates. Almost all the borates of relevance to the problem, for which the structure has been solved, are represented in this figure.

A series of borate minerals with the composition $2CaO \cdot 3B_2O_3 \cdot xH_2O$, where x can be 5, 7, 9 and 13, has been studied by Christ, Clark and Evans (14, 15, 16, 17). In those with the highest water content, $x = 7, 9, 13$, isolated polyions of the composition $B_3O_3(OH)_5^{2-}$ are found. The structure of this polyion is shown in Fig. 2c. (Hydrogen atoms, not shown in the figure, are attached to the non-bridging oxygens.) By partial dehydration to the compound where x equals 5, known as colemanite, the polyions condense to a chain such as is shown in Fig. 2d.

An analogous condensation of the pentaborate polyion has been noted by the author (VI). In potassium pentaborate octahydrate the isolated polyion $B_5O_6(OH)_4^-$, shown in Fig. 2f, is present (18). On the complete dehydration of the octahydrate, these groups polymerize to three-dimensional networks (VI). Thus anhydrous potassium pentaborate is built up from groups identical to the one shown in Fig. 2f.

Even in the sodium diborates a similar polymerization process can be conceived. In sodium diborate decahydrate (borax), isolated polyions of the composition $B_4O_5(OH)_4^{2-}$ exists (19). This polyion, shown in Fig. 2e, can be derived by adding a BO_3 triangle to the polyion in Fig. 2c. There are indications that the fibrous tetrahydrate (kernite) has a chain structure which can be derived by a polymerization of the polyions in the decahydrate (20). The analogy with the potassium pentaborates suggests that the structure of anhydrous crystalline sodium diborate consists of a three-dimensional network obtained from a polymerization of groups as shown in Fig. 2e. In such a structure all the oxygens are shared between two borons. One half of all the borons are four-fold coordinated by oxygen.

The glass structure at the diborate composition is closely related to the crystal structure of anhydrous sodium diborate. It will be recalled that there is a pronounced correspondence of the infrared spectrum of the crystalline and vitreous modifications in this case (II). The discussion above therefore suggests that the formation of

four-fold coordinated borons in alkali borate glasses proceeds until at least 33 mole per cent alkali oxide has been added and 50 per cent of the borons converted to four-fold coordination. This result agrees well with nuclear magnetic resonance measurements of sodium borate glasses (11). The infrared spectra show that the same borate network exists in all the alkali borates (II, VII).

A coordination change in the glass back to three-fold coordination of boron possibly takes place in the concentration range from the diborate to the metaborate composition. (That is between 33 and 50 mole per cent alkali oxide.) Thus the crystal structures of calcium metaborate (21), sodium metaborate (22) and potassium metaborate (23) have all the borons in three-fold coordination. The metaborate polyions are shown in Fig. 2a and b. Neither the potassium nor the sodium metaborate can be obtained as a glass, whereas this is possible for the lithium metaborate by rapid quenching of the melt. X-ray work indicates three-fold coordinated boron in lithium metaborate glass (IV). A metastable crystalline modification of anhydrous lithium metaborate, on the other hand, has recently been reported to have the α-cristobalite structure, i.e. with all the borons in four-fold coordination (24). The difference in energy (and thus stability) of the two different coordinations of boron is therefore likely to be small.

In conclusion one can say that the groups shown in Fig. 2c, e, and f probably occur in the alkali borate glasses. Less is yet known about the manner in which these and possibly other groups are connected to a network in the glass structure. Much work remains to be done before this part of the borate chemistry has been thoroughly explored.

The chemically induced coordination change of boron

The coordination change of boron by alkali additions to boron oxide glass offer an interesting example of a case where a simple electrostatic theory proves inadequate in explaining the process. This will be apparent from the following discussion.

Warren attempted to explain the coordination change by considering the screening demand of the alkali ion. He argues as follows (25): "If a small amount of sodium oxide is added to boron oxide and all of the borons remain in three-fold coordination, there will be two kinds of oxygens, namely, those bonded to two borons and those bonded only to one boron. The sodium ions will try to surround themselves by unsaturated single-bonded oxygens. The number of sodium ions and of unsaturated oxygens is too small at small sodium oxide content, and they are consequently too widely separated for this to be accomplished effectively. On the other hand, if as many as possible of the borons change to tetrahedral coordination, there will be four times as many unsaturated oxygens and therefore a much better possibility for the sodium ions to surround themselves by unsaturated oxygens".

This argument fails to consider the more important screening demand of the boron atom. The screening demand of the boron atom in an electrostatic description of the system should be emphasized at the expense of the sodium atom because of the high field strength of the B^{3+} ion compared with the Na^+ ion. By doing this, a conclusion, differing from that of Warren, is obtained. Weyl has pointed out that a cation will usually try to lower its coordination number, if possible, when the coordinating atoms are replaced by more polarizable ones (26). The more polarizable atoms will provide a better screening, thereby permitting a reduction of the number of screeners. Several

examples can be given to support this rule (26). Applied to the alkali borate system, this rule requires that alkali additions should not increase the coordination number of boron, because more polarizable oxygen atoms now become available (7). Thus a simple electrostatic description of the system is obviously inadequate, since it leads to an erroneous conclusion.

By taking into account quantum mechanical principles, however, the coordination change can be explained (VIII). The boron atom in the ground state of its valency shell has two electrons in s orbitals and one electron in a p orbital. An s electron is easily excited to give the sp^2 valency state characterized by a planar, triangular configuration. This is the usual configuration around the boron atom in its compounds. If, however, the boron atoms can aquire one negative charge in excess, the sp^3 hybrid may be formed. This hybrid is characterized by a tetrahedral configuration leading to a fairly stable four-fold coordination of boron, with a complete octet of electrons in the valency shell. An example of this is the tetrahedral borofluoride ion, BF_4^-. Limited alkali additions to boron oxide will also provide a number of the boron atoms with one negative charge. The doubly charged oxygen ion, O^{2-}, entering with the alkali may be incorporated in the network as a bridge between two BO_3 groups, thus forming two BO_4^- groups. These groups are then free to dissociate, leaving two isolated BO_4^- tetrahedra. Each BO_4 tetrahedron will have one surplus negative charge as required to stabilize the group by quantum mechanical hybridization.

Warren believed that no boron tetrahedra are formed beyond about 13 per cent sodium oxide additions in the sodium borate system (25). This theory was elaborated by Abe (27), who postulated that "BO_4 tetrahedra cannot be bonded to each other and that each BO_3 triangle cannot be bonded to more than one BO_4 tetrahedron". If these limitations are imposed, a maximum BO_4 content will be reached at 16.7 mole per cent alkali additions. 20 per cent of the borons will then be tetrahedrally coordinated.

The idea of a maximum in BO_4 groups at about 15 mole per cent alkali oxide has been adopted by a majority of the workers in the field to explain the boron oxide anomaly, i.e. the occurrence of maxima and minima in physical properties as a function of the alkali concentration. Nuclear magnetic resonance data (11), as well as the structural data discussed in a previous section of this paper, render this theory improbable, however. The presence of maxima and minima in the property-composition curves does not support the theory substantially. In all cases of such anomalies, reported so far, it is impossible to exclude other explanations. Alternative explanations for the boron oxide anomaly have actually been proposed for a number of properties (VIII). The following part of this paper will be devoted to some structural aspects of borate glasses and melts, which provide a basis for an explanation of some of the anomalous properties.

The mechanically induced coordination change of boron

The author has postulated that a certain degree of four-fold coordination exists or can easily be induced in pure boron oxide glass by external forces (VIII). (This "mechanical" coordination change should be distinguished sharply from the "chemical" coordination change resulting from the additions of alkali oxide to boron oxide.) The discussion of boron oxide structures in a previous section of this paper has brought out the possibility of such a coordination change. In the language of electrostatics one would explain the ease of a coordination change in pure boron oxide by

noting that the boron atoms in this compound are not well screened by three oxygen atoms when the oxygens are strongly contrapolarized by other boron atoms. The deficiency in polarizable oxygens will tend to promote a four-fold coordination of boron. The ability to change coordination is expected to be most prominent in pure boron oxide and diminish when alkali oxide is added, since this addition increases the average oxygen polarizability.

The reason for introducing this concept of the variable coordination of boron is that it offers a basis for understanding some peculiar properties exhibited by boron oxide and by the systems of boron oxide with other oxides. The difficulties in explaining several properties of boron oxide by means of a two-dimensional or three-dimensional network structure has been recognized for some time (6). An example of this difficulty is the low viscosity of boron oxide as compared with the viscosity of silicon oxide. At 1260°C, for instance, the viscosity of boron oxide is smaller than that of silica by a factor of $10^{-11.6}$ (6), even though the strength of the boron–oxygen bond equals that of the silicon–oxygen bond (28). The viscous flow in molten boron oxide therefore cannot involve the complete rupture of the strong boron–oxygen bonds. The flow can proceed, however, with a lower activation energy through a continuous coordination change. A boron atom can change its position by becoming temporarily four-fold coordinated and then switching back to three-fold coordination, choosing another three of the available four oxygens. In a quite analogous manner the oxygens could move about, thereby contributing to a viscous flow. According to our previous comments, alkali additions would tend to provide the boron atom with more polarizable oxygens, thereby making the coordination changes less probable. This would increase the viscosity. Simultaneously the normal weakening of the structure by alkali additions will reduce the viscosity. The combined result of these effects can explain the occurrence of maxima and minima in the viscosity curves of the alkali borates (VIII).

The volume–composition curves of the borates do not exhibit anomalies, contrary to what is often assumed (VIII). In pure boron oxide the lower density of the vitreous modification compared with the crystalline modifications may be due partly to a higher degree of four-fold coordination in the latter modifications. The situation is then somewhat analogous to the relation of the low density graphite (three-fold coordinated carbon) to the high density diamond (four-fold coordinated carbon). If boron oxide glass is subjected to pressure, it follows from the volume–coordination relationship suggested above that four-fold coordination of boron is induced. Since four-fold coordinated boron is present in the crystalline modification, it is understandable that the glass crystallizes much more readily under pressure (29). Moreover, the low energy required for the coordination change explains the high compressibility of vitreous boron oxide compared with that of vitreous silicon oxide, even though the atoms in vitreous boron oxide are denser packed in advance (VIII). Our theory assumes that the ability of boron to change coordination number becomes smaller when alkali is added. This makes it understandable that the compressibility drops by such additions (30).

The thermal expansion of sodium borate glasses run through a minimum at about 15 mole per cent sodium oxide (31). This minimum has played a considerable role in the discussion of the boron oxide anomaly. It has been taken as the point where the chemically induced coordination change of boron reverses its direction (25). The relation between structure and thermal expansion is unfortunately very complex. Even in cases where the structure is known, it has been exceedingly difficult to

make good predictions of the coefficients of thermal expansion. The uncertain correlation of thermal expansion with structure therefore leaves room for several explanations of the minimum in thermal expansion. Thus a tentative explanation on the basis of the present theory has been given (VIII).

Other properties of the borate system which are influenced by the mechanically induced coordination change can be conceived. The mechanical strength of boron oxide glass, for instance, may be related to the release of stresses by coordination changes. Most properties, however, are too complicated functions of the structure to allow unequivocal interpretations. Moreover, other aspects of the structure can dominate in other cases, so that the coordination changes of boron are not the only structural principle to be reckoned with, as the following discussion will show.

The cation distribution

For compositions with less than 20 mole per cent alkali oxide, there exists evidence of a non-uniform cation distribution in alkali borates (III, V). The cations are not randomly distributed among the holes of sufficient size in the structure, as is claimed by a number of workers. On the contrary the coordination requirements of the cations are fairly strict. Firstly these ions will always be located in the neighbourhood of those borate groups which have an excess negative charge. Secondly they will tend to attract and share other such negatively charged groups in order to screen themselves more efficiently. The latter process amounts to an accumulation of the cations in regions of basic composition. In the extreme case the clustering will develop to a phase separation. This process will be favoured by the presence of cations which have a high field strength. Thus for molten barium borates, liquid immiscibility is observed from about 2 to 17 mole per cent barium oxide (32).

Among the alkali borates, the lithium system is expected to show the greatest clustering effects. Actually an electron microscope investigation of lithium borate glasses indicates that this system is on the verge of a phase separation (III). The smallest effect is expected for the cesium borates. Even here, however, an X-ray investigation has shown that the cesium atoms are not randomly distributed, inasmuch as each cesium atom has at least one neighbour at a fairly fixed distance down to low alkali concentrations (V). This reminds one of the results on fused silver borates, where an interpretation of thermodynamic data has shown that the silver atoms are ideally distributed in pairs at concentrations below 15 mole per cent silver oxide (VIII).

Undoubtedly the cation clustering must have an effect on several physical properties of the system. A case where the clustering may possibly play an important role is in the bulk electrical conductivity of the glass or melt (VIII). The cations are the main carrier of the electric current in these systems because the anions are condensed to large, fairly immobile polyions. The clusters provide the cations with regions where the flow of electricity can proceed by the well-known Grotthus mechanism (33). This explains the increase in equivalent conductance of the borates with increasing alkali content. At about 20 mole per cent alkali oxide, the equivalent conductance starts rising faster (33), possibly due to the merging of the clusters to a continuous structure.
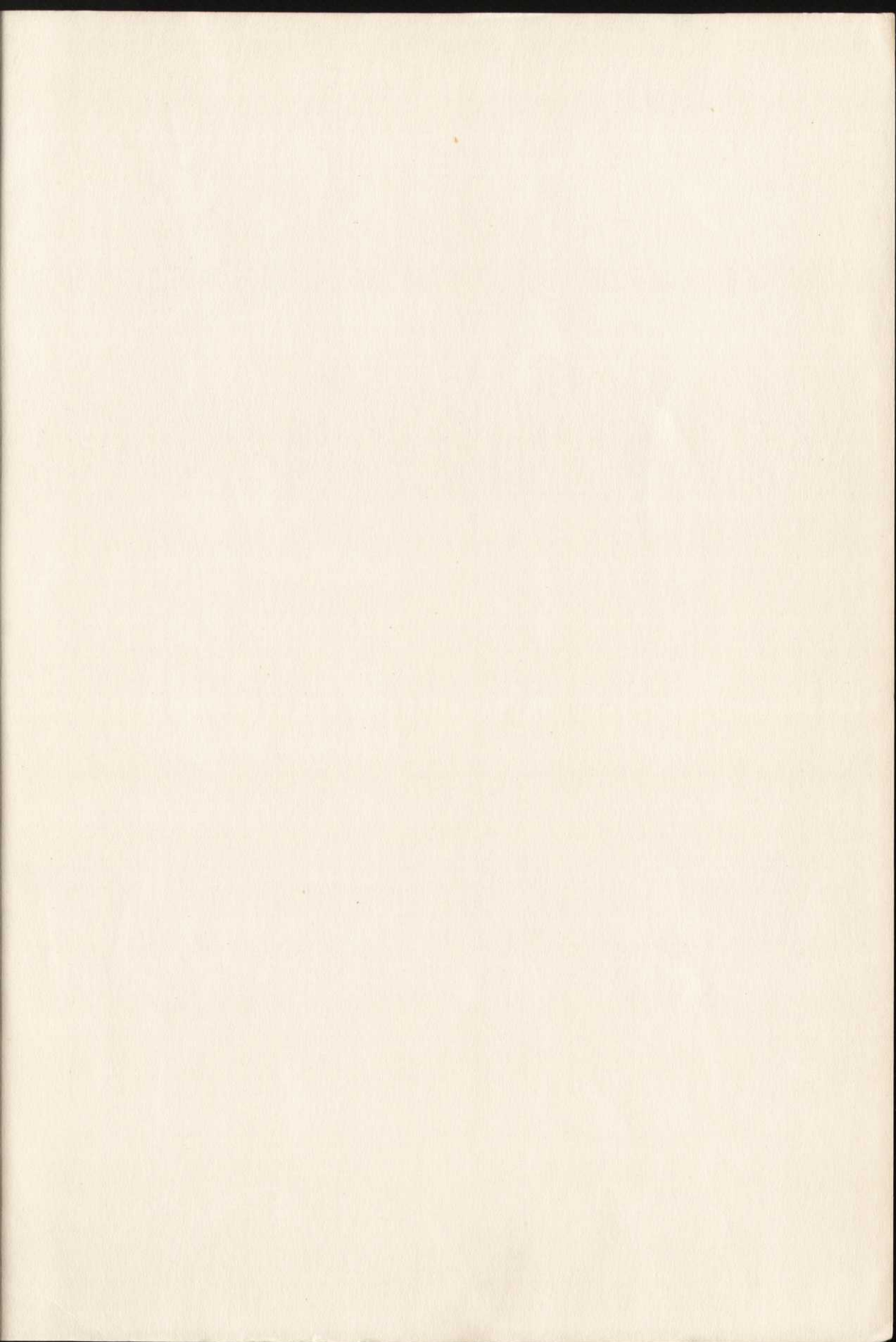
Another example of a property where the clustering conceivably should be taken into account, is the viscosity. Unfortunately our knowledge about the cation distribution is too vague to do us much good when it comes to estimates of a quantitative nature. It is therefore impossible at present to judge the effect of the clustering on most properties of the borates.

ACKNOWLEDGEMENTS

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