

## Structure, defects and properties of some refractory borides

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*Abstract* - Structural defects in some refractory borides are reviewed. The  $Ru_7B_3$ -type borides display fewer defects than the closely related  $M_7C_3$  carbides. Monoborides often crystallize in domains of variable size. Point defects are common among boride structures belonging to the  $AlB_2$  structure family. Mechanisms behind the composition changes in the homogeneity ranges of hexaborides are discussed.

### INTRODUCTION

The refractory borides display several unique properties, which have been the subject of fundamental studies for a long period of time (ref. 1). The borides are characterized by high melting points, great hardness and, most of them, good electrical and thermal conductivity. Further characteristics are a fair corrosion resistance, chemical inertness, good wear resistance and a thermal shock resistance much better than that of oxide ceramics. Many of these properties are of great interest for technical applications.

Although it was possible in early structural research to determine the positional parameters of the metal atoms with satisfactory accuracy, atomic coordinates and possible fractional occupancies could not be obtained with good result. Rather the boron atoms were placed in the structure from space filling considerations. This situation has changed radically during the last 10-20 years, and furthermore, some borides have been studied using transmission electron microscopy and electron diffraction techniques. It is the purpose of the present contribution to review boride structures, whose defects (mainly point defects) have been investigated in detail and/or whose properties in the homogeneity range have been studied relatively well.

### STRUCTURAL FUNDAMENTALS

The boride structures cover a very wide range of compositions, namely from the ternary, metal-rich  $Nd_2Fe_{14}B$ -type structure (ref. 2) to the boron-rich  $YB_{66}$ -type structure (ref. 3). Within this composition range the crystal structures of the borides display structural features, which depend strongly on the Me/B ratio. Structures with metal-rich composition are characterized by a good space filling, although the structures frequently contain interstitial holes, which are of sufficient size for the accommodation of boron atoms but which do not contain any boron atoms (ref. 4). The following structural features distinguish the boride structures from those of other refractory compounds (in particular those of the carbides and nitrides).

#### a. The occurrence of short boron-boron contacts

The tendency towards formation of short boron-boron contacts (1.7-1.9 Å) is displayed already in  $Me_2B$  compositions (2.1 Å in  $Mn_2B$ ), but it is more definite in phases of composition  $Me_5B_3$  and  $Me_3B_2$ . The formation of one-, two-, and three-dimensional boron networks is illustrated schematically in Figs. 1-3. More than one of the boron arrangements, shown in the Figs. 1-3 may occur in a specific boride structure. In ternary phases other boron aggregates may also occur. The formation of a three-dimensional boron framework from the structural building units in Fig. 3 requires a metal/boron ratio smaller than or equal to 0.25. It is also interesting to note that several of the structural elements, displayed in Fig. 3, are common to the stable boranes and carboranes as pointed out by Lipscomb (ref. 5).

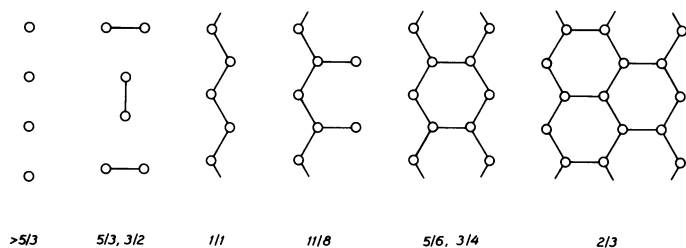


Fig. 1. Boron arrangements in metal-rich borides. The metal/boron ratio is indicated.

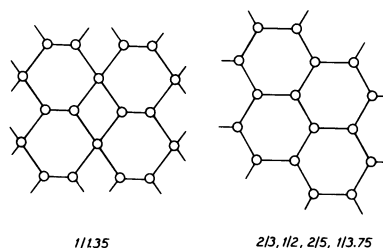


Fig. 2. Two-dimensional boron arrangements. The metal/boron ratio is indicated.

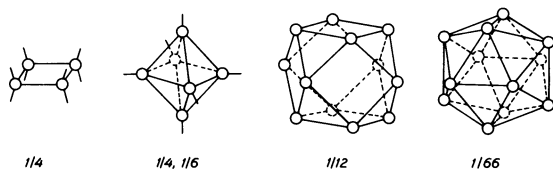


Fig. 3. Structural units of boron atoms, forming three-dimensional networks. The metal/boron ratio is indicated.

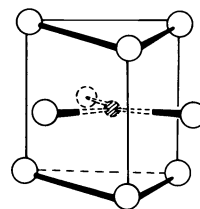


Fig. 4. Trigonal prismatic arrangement of metal atoms around boron.

#### b. The trigonal prismatic environment of boron

In a boride structure of a composition more metal-rich than  $\text{MeB}_4$  the preferred coordination polyhedron of a boron atom is a trigonal prism with metal atoms at the corners (Fig. 4). Metal neighbours (0-3) may also occur outside the rectangular faces of the prism.

In contrast to this carbon and nitrogen atoms prefer octahedral coordination. In a few structures the boron atoms have a non-prismatic environment, for instance in  $\text{PtB}$  and  $\text{Rh}_5\text{B}_4$  (ref. 6), where the coordination is octahedral or  $\text{Mn}_2\text{B}$ , where the boron atom is surrounded by an Archimedean anti-prism of metal atoms.

#### c. Transition from close-packed to open structures

As mentioned above the space-filling principle is relatively well satisfied in metal-rich boride structures. As the boron content of the boride increases, however, more boron-boron contacts form. Furthermore, the directionality of the boron-boron bonds increase leading to very open structures. The space-filling parameter of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  is 73% while it is only 40% for  $\text{YB}_{66}$  (as calculated with Goldschmidt radii for the metals and 0.88 Å for boron).

### SOME PROPERTIES AND APPLICATIONS

Most bulk properties of a material are sensitive to the details of crystal structure, microstructure and chemical composition, although the degree of sensitivity is frequently unknown. Since the borides often require very high temperatures for their synthesis and at least one of the components is very reactive (boron) at these temperatures, a close control of the purity, chemical composition, defects and microstructure is very difficult to achieve. Physical and chemical properties of a boride, which has not been characterized completely as to atomic arrangement, chemical composition, defects and microstructure may vary considerably.

The series of hexaborides, formed by calcium, strontium, barium and most of the lanthanoids (Ln), is one of the most interesting groups of borides as regards physical properties. It displays an amazing diversification in magnetic and electrical properties: there are diamagnetic, Pauli-paramagnetic, anti-ferromagnetic, ferromagnetic and more complex spin-ordered hexaborides as well as normal electrical conductors, superconductors and semiconductors. Some of the hexaborides (in particular  $\text{LaB}_6$ ) have a very low work function for thermionic electron emission and this property together with a low rate of evaporation makes  $\text{LaB}_6$  very attractive as a filament material. Most of the magnetic

and electrical properties mentioned can be regarded as very sensitive to the number of valence electrons available in the valence band. A strong dependence of the properties on stoichiometry and impurities of the  $\text{LnB}_6$  phase is therefore anticipated. It is, however, not easy to establish the homogeneity range of a hexaboride (*vide infra*) and considering this it seems very likely that discrepancies among the numerous reported electrical and magnetic investigations of hexaborides are partly due to differences in composition arising from the conditions of preparation. As an example the influence of carbon on the magnetic and electrical properties of  $\text{EuB}_6$  may be mentioned (ref. 7 and refs. therein).

Most mechanical properties are influenced by point defects, e.g. vacancies within a homogeneity range and interstitial atoms. Although microhardness is a complex property of a material, it can be regarded as a very convenient probe to study shifts in the mechanical properties of brittle, refractory compounds, provided cracking around the indentation is avoided. Microhardness measurements were recently used to demonstrate that a refractory material like  $\beta$ -rhombohedral boron can be solution hardened by dissolving transition metals interstitially (ref. 8). In fact, microhardness can be used as a qualitative indicator of the mechanical strength of a material and also of the strength of the chemical bonding, provided the material is brittle so that no significant work-hardening effect occurs.

#### BORIDES OF COMPOSITION $\text{Me}_7\text{B}_3$

Borides of the composition  $\text{Me}_7\text{B}_3$ , crystallize in the hexagonal  $\text{Ru}_7\text{B}_3$ -type structure (refs. 9,10), illustrated in Fig. 5a

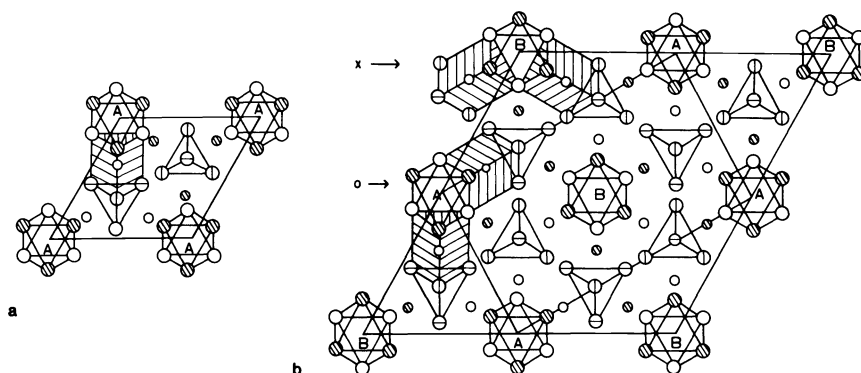


Fig. 5. The structures of (a)  $\text{Ru}_7\text{B}_3$  and (b)  $\text{Cr}_7\text{B}_3$ .

Note two different environments of the octahedra in (b).

The structure is closely related to that of  $\text{Me}_7\text{B}_3$  (ref. 11, Fig. 5b). Both structure types contain metal tetrahedra, metal octahedra, arranged with shared faces along the  $c$  axis, and trigonal prisms, which accommodate boron atoms. The structures differ as regards the arrangement of the octahedral and trigonal prisms as shown in Fig. 5b (A,B). The octahedra in  $\text{Ru}_7\text{B}_3$  are equivalent, while those in the  $\text{Cr}_7\text{B}_3$  structure are situated in two different positions (A and B in Fig. 5b), which are shifted by  $c/2$  along the  $c$  direction.

The  $\text{Me}_7\text{C}_3$  carbides have recently been investigated using electron microscopy and diffraction techniques (refs. 12-14). The results confirm the orthorhombic unit cell proposed by Fruchart and Rouault (ref. 11). Orthorhombic domains, separated by (1100) twins and anti-phase boundaries, occur frequently in  $\text{Me}_7\text{B}_3$  carbides. The domains can be ordered or disordered but the typical local environment of the orthorhombic cell (A,B) is always conserved. The experimental results reported (ref. 14) were recently interpreted in terms of an atom-cluster model (ref. 15).

Studies of  $\text{Ru}_7\text{B}_3$  using electron microscopy and diffraction have demonstrated that the hexagonal unit cell is correct (ref. 16). The structure of  $\text{Ru}_7\text{B}_3$  also generally contains a smaller number of defects than the carbides (refs. 16,17). A contribution to the present conference, however, presents evidence for the occurrence of inversion boundaries in borides, which separate domains with their six-fold axes in opposite directions (ref. 18).

The hot hardness of solid solutions  $(\text{Fe,Cr})_7\text{C}_3$  carbides does not seem to be influenced by the possible disorder (ref. 19).

## MONOBORIDES

The structures of monoborides were determined a long time ago and the structural similarities have also been discussed (refs. 20-22). Let us begin this section, however, with a description of the CrB-, FeB- and MoB-type structures. They are illustrated in Fig. 6. It is seen that the boron zig-zag chains run perpendicular to the picture plane in the FeB- and CrB-type structures. The

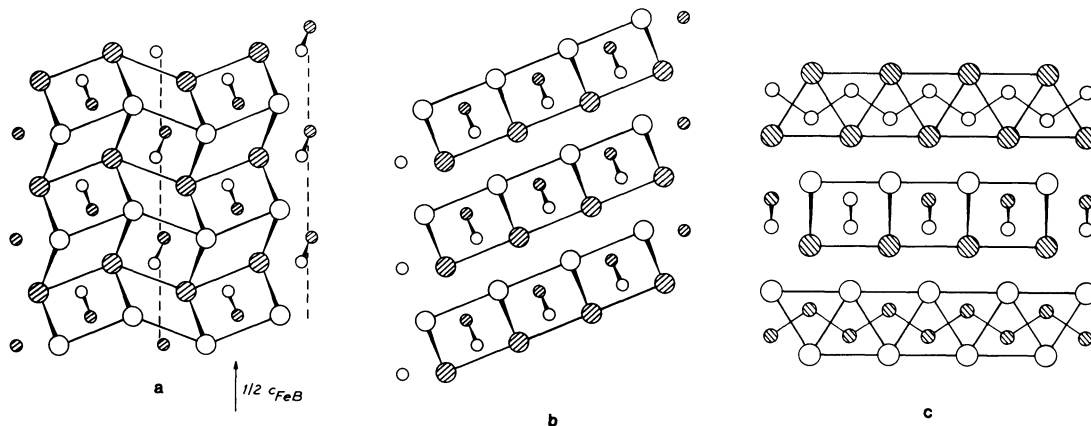


Fig. 6. The crystal structures of (a) FeB (b) CrB and (c) MoB.

CrB-type structure can be obtained from the FeB-type structure by a translation ( $c_{FeB}/2$ ) of identical structural slabs (dashed lines in Fig. 6a) in the  $c$  direction. In the MoB-type structure there are two sets of parallel boron chains perpendicular to each other. This structure can also be regarded as a transposition (shift  $\vec{a}/2 + \vec{b}/2$ ) structure.

Several monoborides have been reported to crystallize in two structure types, depending on temperature, or to display some type of disorder. These monoborides have been collected in Table 1. The low-temperature modifications of MnB and FeB were suggested to be built up of domains of variable size. These domains are very small and according to the suggestion the low-temperature phase consists of a phase mixture. The model seems plausible due to a small free-energy difference between the two phases and a low interfacial energy between them (structural similarity). Alternative explanations have, however,

TABLE 1. Dimorphous phases among the monoborides.

Compound	Structure type at		Ref.
	low T	high T	
FeB	CrB? + FeB	FeB	23,24
MnB	CrB? + FeB	FeB	23,25
CrB	MoB	CrB	25,23
MoB	MoB	CrB	26
WB	MoB	CrB	21

been advanced (refs. 24,25). According to Šmid and Rogl (ref. 24) the diffraction pattern of "low-temperature" FeB, consisting of sharp and diffuse lines, can be interpreted on the basis of an FeB-type unit cell only. The material is assumed to crystallize in a domain structure, which causes the line broadening. The undisturbed regions in the structure are approximately 80 Å. The observations of Papesch *et al.* (ref. 25) indicate that an excess of boron is required to obtain the low-temperature CrB-like MnB phase. The dimorphism of WB was discussed in terms of systematic stacking faults (ref. 21).

It was noted that the magnetic properties of the high- and low-temperature phase of FeB were very similar (ref. 23) and at least in this case the defect structure does not influence the property significantly.

STRUCTURES OF THE  $AlB_2$  FAMILY

It is convenient to present structures related to the  $AlB_2$ -type structure by regarding the structures as built up from a stacking of metal and boron layers (refs. 4,8). The structures contain close-packed metal atoms (A,B), defective metal layers (A',B') and three types of boron layers (H,H',K'), which are displayed in Fig. 7. A boron layer of type K (Fig. 7) was earlier suggested to occur, but it has never been corroborated experimentally. The K and K' layers are slightly puckered. The stacking sequences in the  $c$  direction are the following for some of the structure types:

$AlB_2$	AH AH...
" $Mo_2B_{5-x}$ " ( $x=1.0$ )	AHAK'BHBK'CHCK'A...
$Mo_{1-x}B_3$ ( $x=0.20$ )	A'HB'HA'H...
" $W_2B_{5-x}$ " ( $x=1.0$ )	AHAK'BHBK'A...
$ReB_2$	AK'BK'AK'...
$Ru_2B_3$	AH'AK'BH'BK'AH'...

The width of the homogeneity range has frequently not been determined in detail. The structure of some of the layers have, however, been established recently.

In a single-crystal X-ray diffraction investigation (refinement to  $R=2.6\%$ ) Dr I. Higashi has demonstrated that a boron-rich composition of  $Mo_2B_5$  does not contain boron layers of the K type but rather of the K' type (ref. 27). The crystal used was boron-rich with the cell dimensions  $a=3.0152(8)$  Å and  $c=20.971(7)$  Å. The chemical analyses gave the composition  $MoB_{1.92}$ . Similar results were earlier reported for  $WB_{2.0}$  (ref. 4). Consequently it has been shown that no K layers occur in boron-rich " $Mo_2B_{5-x}$ " and " $W_2B_{5-x}$ " phases and it seems very plausible that these phases do not accommodate more boron than corresponding to the composition  $MeB_{2.0}$ .

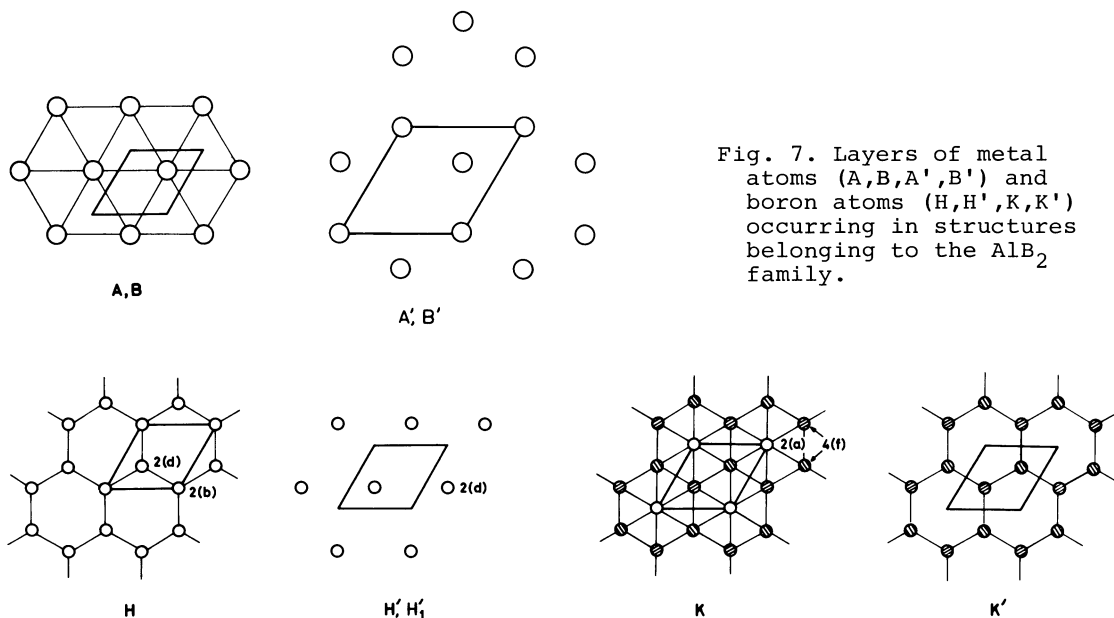


Fig. 7. Layers of metal atoms (A,B,A',B') and boron atoms (H,H',K,K') occurring in structures belonging to the  $AlB_2$  family.

The most molybdenum-rich molybdenum boride (ref. 28),  $Mo_{1-x}B_3$  ( $x=0.20$ ), contains vacancies at the metal positions as shown in layers A' and B' in Fig. 7. Every third metal atom has been removed and in addition, the occupancy of one of the remaining 2-fold positions is only 80%. This position is never filled completely, since the very small shifts in the cell dimensions indicate a very small homogeneity range. The boride seems to be the most boron-rich boride, which does not contain a three-dimensional boron network.

The diborides of niobium and tantalum crystallize in the  $AlB_2$ -type structure and have both a wide homogeneity range. It extends from 65 to 70 at.% boron for  $NbB_2$  and from 66 to 73 at.% boron for  $TaB_2$ . The microhardness at room temperature (ref. 29) displays an increase with boron content for both borides.

By the use of calculated density of states curves for  $ZrB_2$  (refs. 30,31) the observed relationship between microhardness and composition could be discussed in terms of chemical bond strength. A considerable number of valence electrons can be anticipated to enter anti-bonding states in the diborides of the group V transition elements. An increase of the boron/metal ratio, however, involves a decrease in valence electron concentration (irrespective of the mechanism responsible for the composition shift) and, consequently, a smaller number of electrons in anti-bonding states, which in turn leads to increased bond strength and microhardness.

#### HEXABORIDES

Earlier experimental results on homogeneity ranges of hexaborides were reviewed by Spear (ref. 32). The composition variations and the mechanisms behind these have not been studied in detail for most of the hexaborides, and only for  $LaB_6$  has the single-phase composition been measured as a function of temperature.

Several difficulties are associated with the study of hexaboride homogeneity ranges, namely

- a. Observed shifts in cell dimensions may originate from substitutional solid solutions of small non-metal atoms, introduced during synthesis. Carbon may easily dissolve, if the specimen is prepared (ref. 7) using the "carbothermic" method. It has been shown that substitutions of approximately 3.4% carbon in  $EuB_6-xC_x$  ( $x=0.2$ ) decreases the a axis by 0.36%, which corresponds to the whole variation within the regime of homogeneity. Other impurities might have a similar influence. In earlier studies carbon was often used during preparation.
- b. The impossibility to distinguish quantitatively between free boron and chemical bound boron in chemical analyses. The possibility of amorphous, very fine-grained boron might escape detection in X-ray powder diffraction studies and disturb density measurements.
- c. The rigid three-dimensional boron network complicates the interpretation of cell dimension measurements. In current theories (ref. 32) a certain number of electrons must be transferred from each metal position to the boron network in order to stabilize this. The number of electrons is according to theory two per metal position but, since potassium hexaboride exists as a relatively stable compound, the number should be lower. Let us, however, assume the number is two and that all metal positions are filled. Then each metal atom contributes two electrons to the boron network. If only two thirds of the metal positions are filled, then each metal atom must contribute on the average three electrons to the boron network. Due to this transfer of electrons and the stability of +2 or +3 valency of the metal atoms an observed cell dimension variation cannot be interpreted in a straight-forward manner in terms of metal vacancies.

From these observations one comes to the conclusion that the homogeneity ranges of hexaborides should be investigated using accurate X-ray and neutron diffraction techniques and high resolution transmission electron microscopy along with density and cell dimension measurements.

Thorium hexaboride must be mentioned in this context, since it was studied using neutron diffraction technique (ref. 33). Boride samples with B/Th ratios ranging from 6 to 24 were prepared and subsequently, the cell dimensions, X-ray and neutron diffraction intensities and the density were measured as a function of composition. The results all supported a structure model with no change in the boron network but with a decrease in thorium occupancy from 100% to 78% with increasing boron content. The cell dimensions increased slightly with increasing boron content.

Lanthanum hexaboride and its homogeneity range has been studied intensely during the last few years, partly depending on the increased industrial use of the hexaboride as a high-performance thermionic emitter in electron beam instruments. Early reports on the homogeneity range of lanthanum hexaboride were conflicting (ref. 34). Johnson and Daane (ref. 35) found that the homogeneity range extends from  $LaB_{6.0}$  to  $LaB_{7.8}$ , using microscopy and density measurements. They did not observe any cell dimension variation within the range of homogeneity but a change in colour of  $LaB_6$  was noted. The hexaboride is purple for stoichiometric composition and blue for boron-rich compositions. All later investigators have also failed to establish any significant cell dimension variation (refs. 36,37) with boron content for lanthanum hexaboride.

Russian scientists revealed the occurrence of finely dispersed amorphous boron in boron-rich compositions within the homogeneity range (refs. 38,39) and came to the conclusion that the homogeneity regime of lanthanum hexaboride is very small. Storms and Mueller (ref. 37) associated the blue lanthanum hexaboride with a new phase of composition  $\text{LaB}_9$  using Knudsen activity studies, differential thermal measurements and the colour. It was, however, not possible to distinguish between  $\text{LaB}_6$  and  $\text{LaB}_9$  using neutron and X-ray diffraction investigations. Recently the composition of the blue phase was changed to  $\text{LaB}_{6.13 \pm 0.03}$  (ref. 40) as a result of structural investigations of arc-melted  $\text{LaB}_9$  samples using high-resolution electron microscopy, and analytical techniques including backscattered electron imaging, electron microprobe analysis and nuclear magnetic resonance. According to this study (ref. 40) the homogeneity range extends from  $\text{LaB}_6$  to  $\text{LaB}_{6.13}$  through the formation of vacancies at the lanthanum positions. The colour is claimed to change from purple to blue roughly at  $\text{LaB}_{6.07}$ .

Three crystals of  $\text{LaB}_6$ , prepared from an aluminium melt containing excess boron ( $\text{LaB}_9$ ) or excess lanthanum ( $\text{LaB}_5$ ), were recently investigated using single-crystal diffractometry (refs. 41,42). The structures were refined to final conventional R-values of 1.10% - 1.36%. In none of the crystals were vacancies established at the metal position. The occupancy of the boron position was, however, 96.4(7)%, 97.2(5)% and 98.2(5)% (st.dev. in parentheses), respectively, indicating a deficient boron sub-lattice for all three crystals. In this connection it must also be mentioned that Ito and Higashi (ref. 43) have carried out a charge density distribution study of  $\text{CaB}_6$  (final R-value for the free atom refinement 1.34%). They found a partial occupancy of 97.5% for the boron position in that hexaboride as well.

A significant anisotropy was found in the thermal vibrations of the boron atoms in  $\text{LaB}_6$  (Fig. 8).

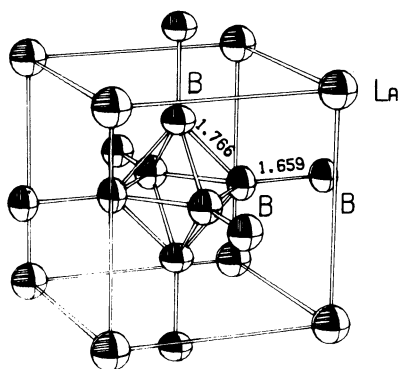


Fig. 8 The crystal structure and thermal vibration ellipsoids of  $\text{LaB}_6$ .

The *inter*-octahedral thermal vibrations are smaller than the *intra*-octahedral ones in agreement with values of the measured force constants (ref. 44).

The results available today permit the following conclusions as regards the homogeneity range of lanthanum hexaboride. The homogeneity range is very narrow, approximately 2% in the boron/metal ratio, although it widens significantly above 2000 K. The narrow homogeneity range explains the extremely small variation in cell dimensions, a variation that can be estimated to be less than 0.02% from published data. Available single-crystal X-ray diffraction data indicate vacancies at the boron position, although NMR seems to favour the occurrence of vacancies at the lanthanum position. Possibly both types of defects are involved.

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