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A New Criterion for Explaining the Polar and Reticular Microhardness Anisotropy of Tetra- and Hexaborides of Lanthanides and Actinides

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Knoop microhardness measurements were made on single crystals of hexa- and tetraborides of lanthanides and actinides prepared by the solution-melt method. Polar and reticular anisotropy of the microhardness was established ($P=20$ g). The highest polar anisotropy was observed for NdB_6 (410 kg/mm^2) and for SmB_4 (760 kg/mm^2). The highest reticular anisotropy was observed for SmB_6 (620 kg/mm^2) and for HoB_4 (1120 kg/mm^2). To explain the microhardness anisotropy, a new criterion of inverse density of atoms in a layer within a unit cell (unit volume of identity in the crystal structure or in a block of layers in the crystal structure) was proposed. It was found that the inverse density of metal or boron atoms in a layer correlates with the reticular and polar microhardness anisotropy of hexa- and tetraborides of lanthanides and actinides.

INTRODUCTION

The microhardness of single crystals of hexa- and tetraborides of lanthanides and actinides has been studied insufficiently. The reticular microhardness was measured on zone-melted LaB_6 single crystals (1). Polar microhardness was measured on the cube faces of single crystals of metal hexaborides MB_6, where M stands for Ca, Sr, Ba, La, Ce, Pr, Nd, Sm, and Eu (2). Recently we performed systematic studies on the microhardness of the whole series of isostructural hexa- and tetraborides of rare earth elements, Th, and U (3). Knoop microhardness measurements were made on single crystals prepared by the solution-melt method. For all compounds considerable reticular (on faces of different type) and polar (on the same face in different directions) anisotropies of microhardness were established.

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Until now a few approaches have been proposed to account for the nature of the microhardness anisotropy. They can be referred to as the crystal-chemical (4), physical (5, 6), and crystallographic (7) approaches. In our opinion, the simplest and the most convenient is the crystallographic or structural approach. It is based on the calculation of the reticular density of atoms on the crystal's faces with different indices, i.e., in different crystallographic directions. However, by this approach only the reticular (but not the polar) microhardness anisotropy can be accounted for and this can be done only for elementary substances. In what follows, it will be shown that for compounds, such as hexa- and tetraborides, this approach is insufficient. In the present paper we propose for calculations of the density of atoms to use, instead of a single atomic plane, a set of such planes which is limited by an elementary volume of the crystal structure.

EXPERIMENTAL

Single crystals of hexa- and tetraborides of lanthanides and actinides were prepared by the solution-melt method employing Al as a solvent. A detailed description of the experimental procedure is given elsewhere (3). Chemical composition of the crystals was determined by wet chemical analysis (gravimetric and spectrophotometric) and by EDAX method. Crystal system and lattice parameters were determined by single-crystal X-ray diffractometry on an automated CAD 4 diffractometer. In the natural faceting of hexaborides crystals cube faces {001}, rhombododecahedron faces {011}, and very rarely octahedron faces {111} were found (8). Single crystals of tetraborides displayed faces of two tetragonal prisms {011} and {100}, bipyramide {111}, and pinacoid {001} (8).

Microhardness measurements were made with the microhardness tester PMT-3 employing diamond Knoop

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pyramid as indenter. Before measurements, single crystals were subjected to a special cleaning procedure of: (i) treating the crystals with dilute nitric acid (1:5–1:10) for 10–40 s, depending on the nature and the size of the crystals; (ii) washing the crystals in distilled water four to five times; and (iii) drying the crystals at 60–70°C for 2 h. For microhardness measurements the crystals were fixed in the following manner: on the surface of a metal disk covered with plasticine an aluminium foil (one or two layers with a thickness of 0.01 mm) was placed and leveled off with a mineralogical press; the crystals were then placed on top of the foil and "embedded" into the foil with the mineralogical press to a depth of 50–90 μm. This arrangement made it easy to turn the crystal with a desirable face up and thus enabled the measurements of reticular microhardness for one and the same crystal. For determining the reticular anisotropy, microhardness was measured on the cube faces and on the rhombododecahedron faces of hexaborides' crystals and on the faces of the prism, of the bipyramide, and of the pinacoid of the tetraborides' crystals. For determining the polar anisotropy, microhardness measurements were made on the chosen crystal face at different orientations of the long diagonal of the Knoop pyramid relative to the face edges. The long diagonal was oriented at angles of 0°, 45°, and 90° relative to the face edge (on the cube faces of hexaborides and on the pinacoid and prism faces of tetraborides). On the rhombododecahedron faces of hexaborides and on the prism faces of tetraborides the intermediate orientation of the long diagonal differed from 45°.

It should be mentioned that in a few cases we did not succeed in measuring the microhardness on some faces, e.g., on octahedron faces of hexaboride single crystals because of the extremely small area and the low perfection of such faces. Single crystals of some compounds (CeB_6, YB_6, ThB_6, YB_4, YbB_4) were of very small size (less than 0.2 mm) and some of their faces were not perfect. Due to these reasons the microhardness measurements on these crystals were performed only with a load of $P = 20$ g.

RESULTS AND DISCUSSION

The microhardness measurements with a load of $P = 20$ g on the single crystals of hexa- and tetraborides of lanthanides and actinides confirmed the considerable reticular (e.g., for HoB_4 up to $\sim 1120\ kg/mm^2$; for SmB_6 up to $\sim 620\ kg/mm^2$) and polar (e.g., for SmB_4 up to $\sim 760\ kg/mm^2$; for NdB_6 up to $\sim 410\ kg/mm^2$) microhardness anisotropy which was established earlier with higher loads (3).

In our opinion, it is of special interest to explain this anisotropy. We employed the conventional criterion of reticular density of atoms (7) and calculated these values for different crystal faces of LaB_6 and ErB_4 (see Table 1). Comparing these values of reticular density with the corresponding microhardness values one can see that for the consecutive faces there is no successive proportionality, since, as mentioned above, in case of compounds atoms of different kinds occur in different crystallographic directions. For example, there are only boron atoms on the prism faces of ErB_4, while on the cube faces of LaB_6 and on the pinacoid faces of ErB_4 there are only metal atoms (see Figs. 1 and 3). Therefore, we propose to consider the reticular density of atoms within a certain volume of the crystal structure, in which the structural motif is contained. We suggest to designate such volume as a unit volume of identity (V_i). This volume is the most representative part of the crystal structure of any element or compound. It will provide for a more objective base for comparing the density of atoms of different kinds on different crystal faces as well as on one face in different directions. Since the density of

TABLE 1
Inverse Density of Atoms and Reticular Density of Atoms on Different Faces of LaB_6 and ErB_4 Single Crystals

	LaB_6		ErB_4	
	Cube {001}	Rhombododecahedron {011}	Pinacoid {001}	Prism {100}
Area of one layer (Å^2)	17. 281	24.435	49.999	28.284
Total number of layers	5	6	5	15
Number of layers with metal atoms	2	2	2	4
Number of layers with boron atoms	3	6	3	11
Total number of atoms in the layers	La–8	La–8	Er–8	Er–8
	B–6	B–8	B–22	B–22
ρ_{inv} (Å^2/atom)	La–4.320	La–6.109	Er–12.500	Er–14.142
	B–8.641	B–0	B–6.818	B–14.142
Reticular density of atoms (atom/Å^2)	La–0.058	La–0.041	Er–0.019	Er–0
	B–0	B–0	B–0	B–0.034

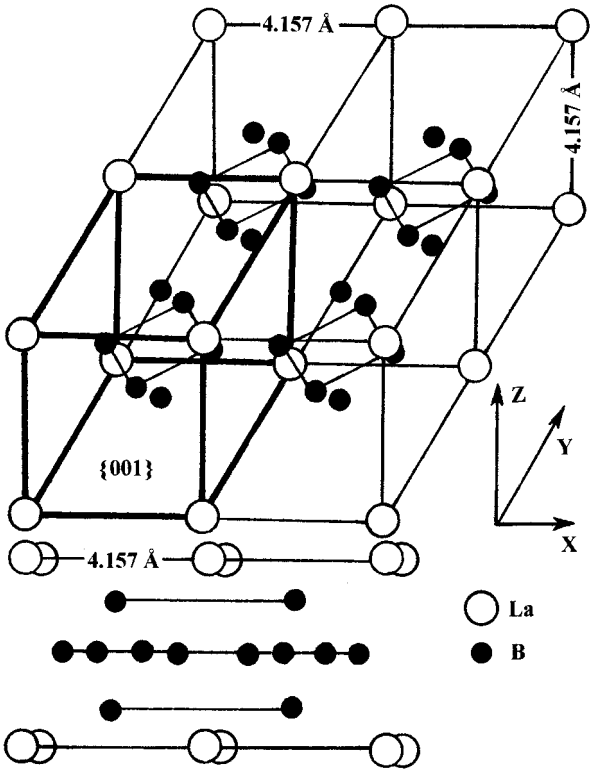

FIG. 1. Schematic view of LaB_6 lattice for the cube habit form {100}. The unit volume of identity (it coincides with the unit cell) is shown by heavy lines. At the bottom the succession of atomic layers parallel to the (001) face is shown.

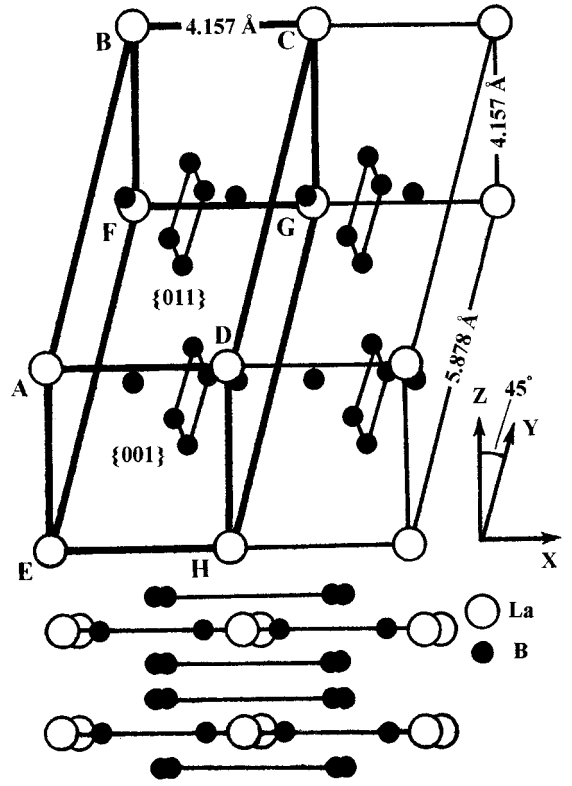

FIG. 2. Schematic view of LaB_6 lattice for the rhombododecahedron habit form {011}. The unit volume of identity is shown by heavy lines. At the bottom the succession of atomic layers parallel to the (011) face is shown.

atoms will be calculated for a set of planes within this volume of identity, it is expected that the values obtained will better characterize the special features of a given crystal structure.

As a criterion of the density of atoms, to be used for an evaluation of the microhardness anisotropy, we introduce the notion of the inverse density of atoms (ρ_{inv});

$$\rho_{inv} = \sum S_i / \sum n_i,$$

where $\sum S_i$ is the sum of the areas of planes parallel to the face of a given crystal form and lying within the unit volume of identity, and $\sum n_i$ is the total number of atoms of the same kind occurring on this set of planes.

For the sake of convenience we shall count the atoms on the edges and on the vertices of a given face as whole atoms. Whole atoms are more convenient to count when considering the polyhedrons within the crystal structures. To calculate ρ_{inv} for different faces one should determine the number of planes within V_i which are parallel to these faces and contain atoms of the same kind. Thus, we obtain a sort of "volume" inverse density of atoms within the V_i corresponding to different crystal forms.

The unit volumes of identity for the cube and rhombododecahedron faces of LaB_6 and for the pinacoid and prism faces of ErB_4 are shown in Figs. 1–3 by heavy lines. In the lower part of these figures a set of planes parallel to the corresponding faces (except for the pinacoid for ErB_4) and lying within V_i is shown schematically. As an example, the calculation of ρ_{inv} for the cube face of LaB_6 (Fig. 1) is presented. From the lower part of Fig. 1 one can see that within the V_i there are five planes parallel to the cube face: two planes contain only La atoms (eight atoms) and three planes contain only boron atoms (six atoms). For the cube face the area $S_i = a^2 = (4.157\ \text{Å})^2 = 17.281\ \text{Å}^2$. Thus, $\rho_{inv}(\text{La}) = 2S_i/8 = 4.320\ \text{Å}^2/\text{atom}$; $\rho_{inv}(\text{B}) = 3S_i/6 = 8.641\ \text{Å}^2/\text{atom}$. The calculated ρ_{inv} values for different faces of LaB_6 and ErB_4 crystals are presented in the Table 1 (in the series of isostructural hexa- and tetraborides the values of ρ_{inv} will vary proportionally with the variation of the lattice parameters of the series' members). One can see that for LaB_6 the character of variation of ρ_{inv} for both types of faces is the same as the character of variation of the conventional reticular density of atoms. However, for ErB_4 there is no such resemblance, since in this case it is not possible to compare the reticular density of atoms of the same kind on different

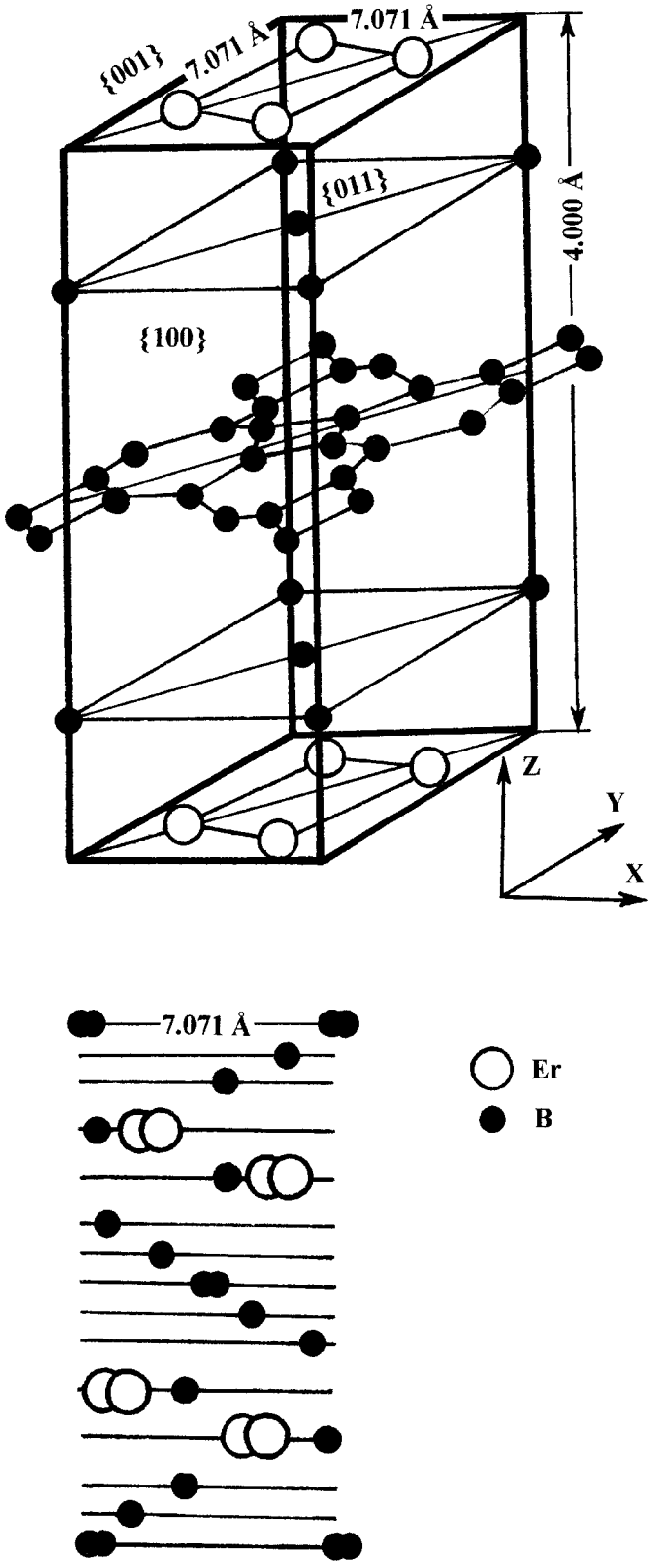

FIG. 3. The unit volume of identity in the crystal structure of ErB_4. For the pinacoid (001) and prism (100) and (110) it corresponds to the unit cell (the scale of the z axis is enlarged). At the bottom the succession of atomic layers parallel to the (100) prism face is shown.

types of crystal faces. One can also note that, in accordance with the variation of ρ_{inv}, for LaB_6 the cube form is harder than the rhombododecahedron, and for ErB_4 the pinacoid is harder than the prism. This observation holds for all hexaborides studied (3), while for tetraborides there are some exceptions. These exceptions may originate from experimental errors, but they can be due to other reasons, too (see below).

When measuring the polar microhardness, the long diagonal of the Knoop pyramid oriented along different directions (0°, 45°, 90°) on a given face meets under its base different sets of atoms within the V_i, which accounts for the different microhardness values in these directions. These sets of atoms lie within V_i on the planes normal to the face under consideration and normal to the direction of the long diagonal of Knoop's pyramid on this face. It follows that ρ_{inv}, for any polar direction on a given crystal face, can be calculated by dividing the area of the plane (S_i) normal to this direction by the number of atoms of the same kind lying on this plane (n): $\rho_{inv} = S_i/n$.This ρ_{inv} represents the inverse reticular density of atoms in the normal direction calculated according to rules proposed in the present paper.

As an example, the calculation of ρ_{inv} normal to the three directions (0°, ~45°, 90°) on the rhombododecahedron face of LaB_6 is presented (because the rhombododecahedron face is not square but rectangular, the intermediate angle is approximately 45°). First we estimate the area of planes within V_i normal to these directions, i.e., the area of planes ABFE, ADHF, and ACGE in Fig. 2. These planes contain only La atoms (4 atoms in every plane) and there are no B atoms. The areas of ABFE and ADHF are equal ($S_i = a^2 = (4.157\ Å)^2 = 17.281\ Å^2$). The area of ACGE is determined by the sum of two equal triangles, ACE and ECG, and $S_i = 24.435\ Å^2$. Thus, $\rho_{inv} = 17.281\ Å^2/4$ atoms = $4.320\ Å^2$/atom for the plane ABEF, i.e., for the direction 0°. The same value has $\rho_{inv}(90°)$, and $\rho_{inv}(\sim 45°) = 24.435\ Å^2/4$ atoms = $6.109\ Å^2$/atom.

The calculated ρ_{inv} values for the studied faces of LaB_6 and ErB_4 are presented in the Table 2 together with the microhardness data. One can see a good correlation between ρ_{inv} and H_K for all directions on both types of faces of LaB_6 and on the pinacoid face of ErB_4 (i.e., the smaller the ρ_{inv} value, the higher the H_K value). This correlation holds for other hexa- and tetraborides and for H_K values measured at different loads (3). The exceptions are SmB_6 (the variation of H_K on the rhombododecahedron face at $P =$ 50 g differs from that for other hexaborides) and tetraborides SmB_4, DyB_4, HoB_4, and UB_4 (the variation of H_K on the pinacoid face differs from that for other tetraborides). The occurrence of these exceptions may be due to the poor quality of crystal faces as well as due to the deviation in the orientation of the long diagonal of Knoop's pyramid from the direction 45°. One can easily see from Fig. 4 that for the pinacoid face of tetraborides even a small deviation in the

TABLE 2
Inverse Density of Atoms and Microhardness ($P = 20$ g) in Different Directions on the Faces of LaB_6 and ErB_4 Single Crystals

	0°	45°	90°
	LaB_6, cube {001}		
N^a	La–4	La–4	La–4
	B–0	B–2	B–0
ρ_{inv} (Å/atom)	La–8.640	La(>)–8.640	La–8.640
	B–0	B–17.281	B–0
H_K (kg/mm^2)	2350	2160	2350
CeB_6	2460	2130	2460
PrB_6	2460	2220	2460
NdB_6	2460	2050	2460
SmB_6	2120	1950	2120
EuB_6	2330	2100	2330
YbB_6	2330	2200	2330
ThB_6	1830	1710	1830
	LaB_6, rhombododecahedron {011}		
N^a	La–4	La(≫)–4	La(>)–4
	B–0	B–0	B–0
ρ_{inv} (Å/atom)	La–12.217	La(≫)–12.217	La(>)–12.217
	B–0	B–0	B–0
H_K (kg/mm^2)	2350	2160	2250
SmB_6	1600	1740	1500
YbB_6	2140	1860	1740
	ErB_4, pinacoid {001}		
N^a	Er–0	Er–0	Er–0
	B–4	B–6	B–4
ρ_{inv} (Å/atom)	Er–0	Er–0	Er–0
	B–25.000	B–16.666	B–25.000
H_K (kg/mm^2)	1790	2140	1790
SmB_4	2710	1950	2710
GdB_4	1740	2190	1740
TbB_4	1830	2220	1830
DyB_4	2140	2050	2140
HoB_4	2070	1600	2070
UB_4	2260	2190	2260
	ErB_4, prism {100}		
N^a	Er–4	Er–0	Er–0
	B–0	B–0	B–4
ρ_{inv} (Å/atom)	Er–12.500	Er–0	Er–0
	B–0	B–0	B–12.500
H_K (kg/mm^2)	2570	2800	2330
SmB_4	2530	2700	2140
GdB_4	2480	2520	2200
TbB_4	2050	2580	1950
DyB_4	1910	2220	1740
HoB_4	2500	2720	2050
TmB_4	2280	2420	1950
LuB_4	2150	2200	1950
ThB_4	2050	2140	1740

[a] Number of atoms in the plane normal to the direction of the long diagonal of the Knoop's pyramid.

orientation of the long diagonal from the direction 45° may lead to a considerable increase in H_K since the plane under the diagonal will now contain not only boron atoms but also two metal atoms. Such deviation is very likely to occur when working on pinacoid faces having an extremely small area and poor shape.

Attention should be paid to the occurrence of maximum H_K in the direction ~45° on the prism face of all tetraborides at all loads (3), while $\rho_{inv} = 0$ for both the boron and the metal atoms. The following explanations can be proposed: (i) due to the minute deviations from the direction ~45° in the orientation of the long diagonal the plane under the pyramid (which is normal to the prism face and normal to the direction ~45°) will now include at least two boron atoms (situated very close to the "ideal" plane, see Figs. 3 and 4); (ii) the plane normal to the direction ~45° is also normal to the network of boron atoms made up from the boron atoms of the octahedron's base and two additional boron atoms (see Fig. 4); therefore the direction of the action of the Knoop's pyramid is normal to the direction of chemical bonds between many boron atoms. Both factors contribute to the considerable increase in polar microhardness (direction ~45°) on the prism faces of tetraborides.

For the prism faces of tetraborides another interesting feature was observed: H_K in the direction 0° is higher than in the direction 90° (3). This can be explained by the fact that different kinds of atoms occur in these directions: only metal atoms occur in the direction 0° and only boron atoms occur in the direction 90°. The values of ρ_{inv} for each kind of atoms are the same in both cases. Therefore, one can conclude that it is the metal atoms that contribute to the higher microhardness values. Comparison and analyses of ρ_{inv} values can be made for both kinds of atoms. This becomes a necessity when the atoms of only one kind occur in all directions (e.g., only boron atoms on the prism faces and only metal atoms on the pinacoid faces of tetraborides, see Table 2).

Comparing the data presented in Tables 1 and 2, one can make another interesting observation. The value of ρ_{inv} (calculated without taking into account the polarity, Table 1) on the pinacoid faces of tetraborides is lower than the ρ_{inv} on the prism faces. Hence, H_K values on the pinacoid face should be higher than on the prism face. However, if one calculates ρ_{inv} taking into account the polarity, there is a good correlation with the H_K values; i.e, the prism faces are harder than the pinacoid faces (see Table 2). This correlation holds for six of eight studied tetraborides, including the previously published data (3). Therefore, it should be emphasized that, when comparing the microhardness values of single crystals, one should always indicate the direction on the face in which the measurements were made (this is especially so when employing Knoop's pyramid). Unfortunately, this is not always the case with

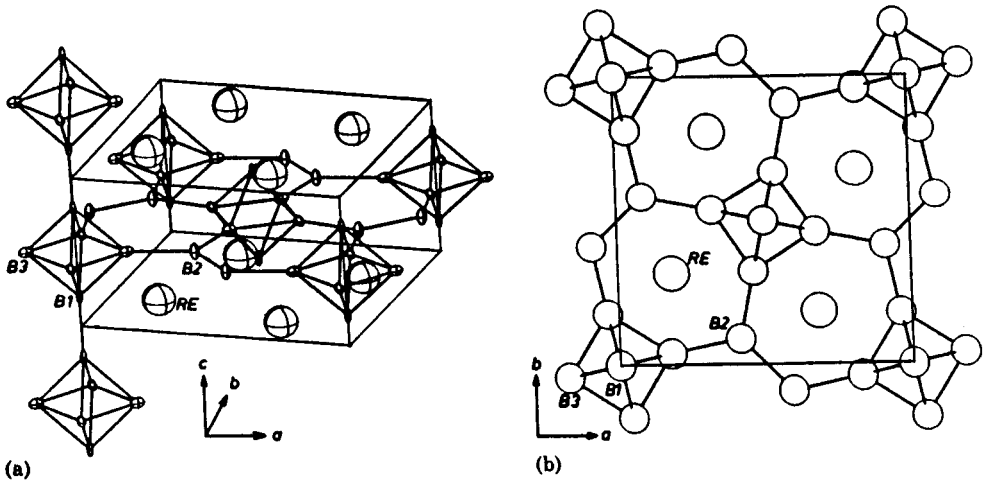

FIG. 4. Crystal structure of tetraborides (9): (a) three-dimensional view; (b) projection onto the pinacoid plane (001).

some data presented in the literature: e.g., for LaB_6 single crystals the H_K values on different faces are given without the indication of the directions in which they were measured (1).

To summarize, the proposed criterion and conditions for its application help to explain and to give a prognosis for the microhardness variation on different types of faces as well as within one face of single crystals of refractory compounds. In the isostructural series of hexa- and tetraborides, ρ_{inv} will vary in the same manner as the lattice parameters of the members of each series.

CONCLUSIONS

The unit volume of identity and the inverse density of atoms are new objective structural characteristics for any element or compound.

Employing these notions, the reticular and polar microhardness anisotropy of hexa- and tetraborides of lanthanides and actinides can be accounted for by the variation of the inverse density of atoms within the respective unit volumes of identity.

Employing the criterion of inverse density of atoms, one can predict the character of variation in the properties (like microhardness) for the series of isostructural compounds provided that these properties depend on the ρ_{inv} within the unit volume of identity.

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