– Type $SnCl_2$ ($PbCl_2$–PbClBr–$PbBr_2$): on observe un prisme tricapé (environnement neuf). L'atome métallique est déplacé par rapport au centre du prisme, vers les atomes X formant les liaisons les plus courtes. Le déplacement peut être imputé au rôle de la paire non engagée qui est alors dirigée vers les atomes les plus éloignés de façon à minimiser les répulsions.

– Type SnClI: on observe un prisme bicapé (environnement huit) MX_4Y_4. L'atome métallique est alors déplacé vers les quatre atomes les plus lourds et la paire non engagée est vraisemblablement dirigée dans la 9^e direction du prisme tricapé, direction dans laquelle se trouve un atome Y très éloigné ($M-Y = 4{,}5$ Å).

– Type PbClI: on retrouve un environnement neuf (prisme tricapé), mais cette fois l'atome de plomb est très peu déplacé par rapport au centre du prisme, ce qui rendrait compte d'une faible activité de la paire non engagée.

– Type SnClF (PbF_2): pour ces deux composés, si l'environnement à courte distance est le même, celui à plus longue distance est différent. Dans SnClF, on observe un environnement huit, MX_3Y_5, mais le polyèdre obtenu est très déformé. Pour PbF_2, on observe sept distances comprises entre 2,41 et 2,69 Å et deux distances de 3,03 Å, ce qui définit un environnement (7 + 2), le prisme tricapé étant très déformé.

En conclusion, les composés mixtes $SnXX'$ et $PbXX'$ cristallisent tous dans le système orthorhombique, groupe spatial *Pnma*, avec des paramètres proches les uns des autres, la dilatation de la maille rendant compte de l'augmentation de la taille des halogènes. L'observation plus détaillée des structures montre cependant des différences dans l'environnement à courtes et longues distances des cations Sn^{2+} et Pb^{2+}. En effet, si les halogènes se disposent toujours aux mêmes positions, formant une cage de huit ou neuf entités, suivant la nature de ceux-ci, les cations Sn^{2+} ou Pb^{2+} sont déplacés vers l'un ou l'autre des sommets de cette cage, en restant dans le miroir situé à $y = \frac{1}{4}$ ou $y = \frac{3}{4}$.

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The Ordering of Boron and Carbon Atoms in the LaB_2C_2 Structure

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Abstract

The crystal structure of LaB_2C_2 has been determined by X-ray diffraction with an automatic diffractometer and Mo $K\alpha$ radiation. The structure consists of two planar, infinite layers which alternate along the c axis. Within the (ordered) B—C network, each atom is bonded to three other atoms so as to form aromatic-like, fused four- and eight-membered rings. Each four-membered ring contains two B and two C atoms

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in opposite positions, each eight-membered ring contains four B and four C atoms. The La atoms are located in the interstices between the eight-membered rings. The structure is tetragonal with the space group $P\bar{4}2c$; the lattice parameters are: a = 3·8218 (6), c = 7·9237 (12) Å, Z = 2. Bond distances are: La—B 2·885 (5), La—C 2·831 (4), B—C 1·628 (19), C—C 1·321 (13), and B—B 1·725 (13) Å; bond angles are: C—B—B 130·0 (5), B—C—C 140·0 (5)°. Least-squares refinement of diffractometrically recorded intensities gives a final R value of 3·8%.

Introduction

The existence of ternary lanthanide–boron–carbon phases, LnB_2C_2, has been known for several years. Post, Moskowitz & Glaser (1956) were possibly the first to observe these phases (which they called LnB_x), which have tetragonal symmetry, while attempting to prepare lanthanoid borides by the reaction of sesquioxides with boron and carbon. A similar preparation of YB_x was reported by Binder (1956) who also suggested that carbon was needed to stabilize this phase (Binder, 1960). Smith (1964) and Smith & Gilles (1967) have characterized a number of LnB_2C_2 phases (Ln = Nd, Gd, Tb, Dy, Ho, Er, and Yb) as members of an isostructural series with tetragonal symmetry. They have established that the previously reported LnB_x phases (Ln = La, Pr, Gd, Er, Yb, and Y) are also members of this series. Later works by Nordine, Smith & Johnson (1964), Fishel & Eick (1969), Bauer & Nowotny (1971), Bauer & Debuigne (1972) and Bezruk & Markovskii (1972) have established that all the rare-earth metals (except Eu) and the pseudo-rare-earth metal yttrium form this phase. Very recently in our laboratory we have prepared the diboride dicarbides of europium (Schwetz, Hörle & Bauer, 1979) and calcium (Bréant, Pensec, Bauer & Debuigne, 1978) by annealing mixtures of the elements in sealed Mo bombs. X-ray powder diffraction analyses showed that EuB_2C_2 and CaB_2C_2 also possess the tetragonal symmetry common to the other members of the LnB_2C_2 series. The existence of CaB_2C_2 proves that this borocarbide can also be formed with divalent cations. In addition, the lattice parameters of EuB_2C_2 and YbB_2C_2 indicate that the metals in these two compounds are (at least partially) divalent.

Previously reported structures

The X-ray powder diffraction patterns for these diboride dicarbides were indexed by all the authors on the basis of a small tetragonal cell containing one LnB_2C_2 formula unit. Powder intensity calculations (Smith, 1964; Bauer & Nowotny, 1971) and also single-crystal data for TbB_2C_2 (Smith, 1964) indicated clearly the metal position at 0,0,0 and the B–C network along $z = \frac{1}{2}$. As pointed out by Hoard & Hughes (1967), the geometry of these B–C networks – four- and eight-membered rings – can easily be derived from the cubic LnB_6 arrangement. A boron network consisting of fused four- and eight-membered rings (B_4 squares and B_8 octagons) is present in every cube face of the LnB_6 structure. By selecting one set of parallel networks or cube faces and eliminating the connecting interplanar B atoms – those that convert B_4 squares into B_8 octahedra – we obtain a stratified (hypothetical) LnB_4 structure of tetragonal symmetry. Substitution, in an alternating pattern, of C for half the B atoms in the ring system then gives the B–C networks and the structure type of the rare-earth borocarbides, LnB_2C_2. Unfortunately, the accuracy of the structure determination of TbB_2C_2 (Weissenberg equi- and anti-equi-inclination techniques) was insufficient to determine the ordering of the B and C atoms within these networks.

In the small tetragonal cell observed, the two C and two B atom sites may be adjacent (onefold axis) or opposite (twofold axis); as in the high-angle photographs and single-crystal studies 'splitting' of lines or spots (indicating lower symmetry than a fourfold axis) was never observed, the small unit cell can only be considered as a first approach. So, in spite of the fact that no superlattice lines indicating a larger unit cell were observed, the cell had to be doubled in a rather speculative way.

On the basis of general bonding considerations, bond distances, electronic requirements and similarities to boride and carbide structures, Smith (1964) discussed a number of possibilities for the arrangement of the light atoms in an enlarged unit cell. He proposed a new unit cell with $a' = a\sqrt{2}$ and $c' = c$; the space group is $P4/mbm$ (No. 127), with the metal atoms at 2(a). The four B atoms are positioned at 4(h) with $x_B = 0{\cdot}352$. The four C atoms are also located in the 4(h) positions

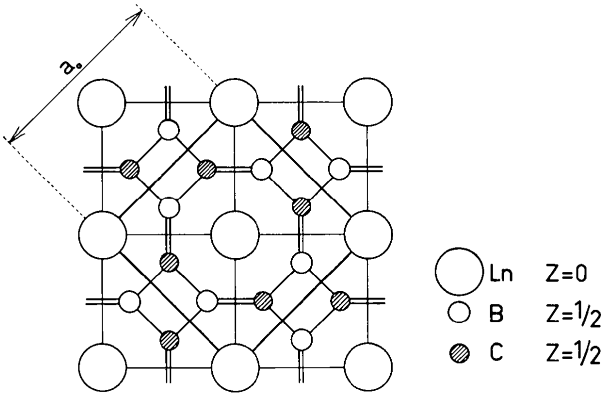

Fig. 1. Ordering of B and C atoms in the LnB_2C_2 structure as proposed by Smith (1964).

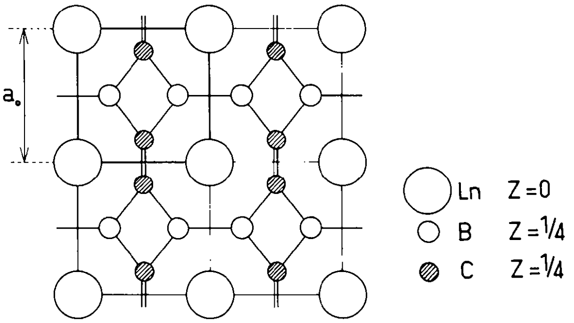

Fig. 2. Ordering of B and C atoms in the LnB_2C_2 structure as proposed by Bauer & Nowotny (1971). For clarity only one half of the cell is shown. For $z = \frac{3}{4}$ the B–C network is rotated by 90°.

with $x_C = 0{\cdot}148$ ($x_C = \frac{1}{2} - x_B$). This gives a planar B–C network composed of regular octagons and squares with alternating B and C atoms as shown in Fig. 1. There is only one B–C distance in the structure (1·58 Å in the case of HoB_2C_2) and there is no difference between the *M*–C and *M*–B distances which are 2·70 Å. The bond angles inside the planar polygons are 135 and 90°. This might produce some angular strain for either sp^2 or sp^3 hybridization and therefore Fishel & Eick (1969) proposed the possibility of a 'puckered' light-atom ring. However, there was no experimental proof for this proposition either.

On the other hand, Bauer & Nowotny (1971) proposed another model for the B–C ordering in YB_2C_2. In this case the unit cell is doubled in the direction of the *c* axis. The space group is $P\bar{4}2c$, the metal atoms are positioned at 2(*e*), four B atoms at 4(*i*), $y = 0{\cdot}232$, and four C atoms at 4(*h*), $x = 0{\cdot}168$. In this case the light atoms are in opposite positions in the small subcell, but they are rotated about a $\bar{4}$ axis to give the next sheet, thus conserving the tetragonal symmetry which has always been observed. The bond angles are no longer fixed at 135 and 90°, but they depend on the C–C and B–B bond distances. This is shown in Fig. 2.

From these two propositions results the somewhat troubling fact that in the literature the basically very simple LnB_2C_2 structure appears with two different unit cells. To clarify this problem we have determined the crystal structure of LaB_2C_2.

Experimental

Homogeneous samples of lanthanum diboride dicarbide were obtained from reactions of stoichiometric mixtures of the elements. The starting materials were 99·5% pure lanthanum, 99·999% boron and 99·9999% carbon. The blended stoichiometric mixture (2 g) was compacted to pellets of 8 mm diameter in a hardened steel die. The pellet was melted, turned over and remelted three times on a water-cooled copper hearth in a 25 kW 500 kHz high-frequency furnace. The protective atmosphere was highly purified argon. After the last melting, the sample was annealed at 2273 K for 24 h. The sample was then crushed and examined by X-ray analysis, micrographic and SEM techniques.

X-ray powder photographs were taken with 114·6 mm Debye–Scherrer cameras with Ni-filtered Cu radiation yielding powder diagrams of very good quality with sharp lines, which were well resolved for $K\alpha_1$ and $K\alpha_2$ wavelengths in the back-reflection region. Precise lattice parameters and their standard deviations were calculated from the powder diagrams applying the Bradlay & Jay extrapolation to the high-angle reflections. For the crystal structure analysis a single crystal of size 50 × 20 × 9 μm was isolated from the crushed sample and analysed on a computer-controlled four-circle diffractometer. The intensity data were collected with a Nonius CAD-4 automatic diffractometer using the ω–2θ scan technique and a peak-scan interval $\Delta\omega = (1{\cdot}2 + 0{\cdot}3 \tan \theta)^\circ$. The maximum time spent on a reflection was 70 s. Graphite-monochromatized Mo $K\alpha$ radiation was used ($\lambda = 0{\cdot}7093$ Å) and in one octant of reciprocal space all reflexions with $2^\circ < \theta \leq 45^\circ$ were measured. Intensities were corrected for Lorentz and polarization effects, but no extinction or absorption corrections were applied (the crystal was very small). Symmetry-related reflexions were averaged in the Laue-symmetry group $4/mmm$ to give 174 F_o values. The atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The calculated Patterson function yielded coordinates for the lanthanum atoms at 0,0,0. Difference Fourier syntheses enabled us to localize the light-atom positions and also to distinguish between the B and C atoms. The intensities of the peaks attributed to the C atoms were 1·15 times greater than those of the B atoms. Refinements were calculated by full-matrix least squares (Prewitt, 1966) for the different previously reported possible structures. The weighting scheme was $w = (w_c^{-1} + p^2|F_o|^2)^{-1}$, where w_c depends on counting statistics and the instrument instability factor p was taken as 0·02.*

Structure results

As several propositions for the structure had been advanced, all compatible with the observed Laue symmetry, we carried out least-squares refinements for the following hypotheses:

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35149 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional and thermal parameters of* LaB_2C_2 (*space group* $P\bar{4}2c$)

Numbers in parentheses are e.s.d.'s in the least significant digits. Debye–Waller temperature factors are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; equivalent isotropic thermal parameters B_{eq} are in Å^2.

		x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La	2(*e*)	0	0	0	0·27	0·0044 (5)	0·0044 (5)	0·0012 (2)	0	0	0
B	4(*h*)	0·5	0·226 (5)	0·250	0·47	0·008 (5)	0·004 (4)	0·003 (4)	0	0·002 (4)	0
C	4(*i*)	0·173 (5)	0·5	0·250	0·54	0·008 (5)	0·010 (6)	0·002 (4)	0	0	−0·001 (4)

(*a*) Using the small tetragonal cell with $a = 3{\cdot}8218$, $c = 3{\cdot}9618$ Å, and $Z = 1$, in the space group $P422$, we tested a statistical distribution of the light atoms in the positions $(x,\frac{1}{2},\frac{1}{2})$, $(\bar{x},\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},x,\frac{1}{2})$, $(\frac{1}{2},\bar{x},\frac{1}{2})$. Refinement of the atomic positions was possible [$x = 0{\cdot}203$ (5), $R = 4{\cdot}2\%$, $R_w = 5\%$], but the isotropic temperature factors yielded unacceptable values. In addition, a wide solid-solution range of the LnB_2C_2 phases was not observed, thus eliminating random filling of these positions. For these two reasons the hypothesis of random distribution can be eliminated.

(*b*) Refinement of the structure in the space group *Pmmm*, still using the small tetragonal cell, with the B atoms at the 2(*p*) positions and the C atoms at the 2(*l*) positions, yielded acceptable thermal parameters, the conventional R value of 4·7% also being quite good, but in this case the interatomic distances were not acceptable. We obtained shorter B—B than C—C distances. The bond angles were nearly equal to 135°, very unlikely for the proposed aromatic-like rings. This model had to be eliminated too, and it was necessary to double the unit cell.

(*c*) We tried a refinement in the space group *P*4/*mbm* with the doubled cell and the atomic positions proposed by Smith (1964). The structure could not be refined at all: the refinement was diverging. This model also had to be eliminated.

(*d*) Finally we refined the structure in the space group $P\bar{4}2c$ in conformity with the structure proposed by Bauer & Nowotny (1971) described above. The refinement has shown that this proposition was consistent with the experimental data. The final R value was 3·8% ($R_w = 4{\cdot}5\%$). The observed interatomic distances are in good agreement with those measured in related compounds. The thermal parameters have plausible values. Positional and thermal parameters are given in Table 1. The positional parameters of the B and C atoms are only slightly different from those calculated on a geometrical basis for YB_2C_2.

Discussion

A comparison of the interatomic distances in the present compound with the analogous distances in the lanthanum carbides and borides confirms their close bonding relationships.

Atoji (1961) determined the bond distances in LaC_2 by neutron diffraction techniques. According to this work, the La—C distance in LaC_2 is 2·857 (7) Å; in LaB_2C_2 we measured 2·831 (4) Å.

The C—C distance in LaC_2 is 1·303 (12) Å compared with 1·321 (13) Å in LaB_2C_2. It was assumed (Nowotny, Boller & Zwilling, 1972, and references therein) that in the rare-earth dicarbides there are two different carbon—carbon bonds, a C—C triple bond (acetylene) and a C—C double bond (ethylene). The C—C distances in ethylene and acetylene are 1·33 and 1·20 Å respectively. Compared with our measured C—C distance, we can assume that there is a double bond between the adjacent C atoms in the B–C network.

The observed B—B distance, 1·725 (13) Å, is the average value of the B—B inter- and intraoctahedral distances in LaB_6, 1·659 (3) and 1·764 (2) Å (Hoard & Hughes, 1967). This value is also comparable to the B—B distances between adjoining icosahedra in the $B_{13}C_2$ structure, 1·723 (7) Å (Will & Kossobutzki, 1976).

The La—B distance of 2·885 (5) Å in LaB_2C_2 is somewhat shorter than that in LaB_6 (3·05 Å). This can be understood when we assume that the La atoms are slightly elongated in the direction of the c axis, as indicated by the variation of the c/a values as the atomic number increases through the lanthanides.

Finally, the B—C distance is in very good agreement with the analogous distance in $B_{13}C_2$: Will & Kossobutzki (1976) measured a distance of 1·610 (5) Å between the icosahedra and the C atoms in the CBC chain; in the LaB_2C_2 structure the C atoms are bonded to two B atoms at 1·628 (19) Å.

It is more difficult to compare the bond angles, but it is noteworthy that in the orthorhombic ScB_2C_2 structure, which is composed of fused five- and seven-membered rings of B and C atoms with the Sc atoms in the interstices of the seven-membered rings, one finds the same angles (within experimental error) as in the structure of LaB_2C_2.

It should be noted that superstructure lines or spots, due to the doubling of the small tetragonal cell, with $l =$ odd were never observed. The intensities of these lines are too weak to be observed on powder photographs, but in the single-crystal study they were not observed

Table 2. *Corrected unit-cell parameters of the tetragonal diboride dicarbide phases*

	a (Å)	*c* (Å)	Reference
LaB_2C_2	3·8218 (6)	7·9237 (12)	(1)
CeB_2C_2	3·817 (1)	7·704 (2)	(2)
PrB_2C_2	3·81	7·62	(3)
NdB_2C_2	3·803 (8)	7·588 (18)	(4)
SmB_2C_2	3·796 (1)	7·392 (2)	(2)
EuB_2C_2	3·801 (1)	7·602 (1)	(5)
GdB_2C_2	3·792 (1)	7·280 (2)	(4)
TbB_2C_2	3·784 (2)	7·182 (2)	(4)
DyB_2C_2	3·781 (1)	7·118 (1)	(6)
HoB_2C_2	3·780 (1)	7·074 (2)	(4)
ErB_2C_2	3·778 (1)	7·016 (2)	(4)
TmB_2C_2	3·776 (11)	6·954 (16)	(2)
YbB_2C_2	3·775 (1)	7·120 (2)	(4)
LuB_2C_2	3·762 (5)	7·102 (10)	(2)
YB_2C_2	3·796 (10)	7·124 (10)	(7)
CaB_2C_2	3·7921 (3)	7·3966 (5)	(8)

References: (1) This work. (2) Fishel & Eick (1969). (3) Post, Moskowitz & Glaser (1956). (4) Smith & Gilles (1967). (5) Schwetz, Hörle & Bauer (1979). (6) Bauer & Debuigne (1972). (7) Bauer & Nowotny (1971). (8) Bréant, Pensec, Bauer & Debuigne (1978).

either. This may be because the separation of 3·96 Å between subsequent layers is too great for bonds to occur between the light atoms in different sheets, so stacking faults, diminishing these already very weak intensities, can appear.

Conclusions

The aim of this work was to show the ordering of B and C atoms in the LnB_2C_2 structure and to decide between the different possible ring conformations. The experimental results confirm the structure proposed by Bauer & Nowotny (1971).

Although a complete crystal structure determination was carried out only for LaB_2C_2, we can, on the basis of structural similarities between the rare-earth borides and carbides, extend these results to the other lanthanides. For the ordered arrangement of the light atoms in the B–C networks, the *c* axis of the small tetragonal cell has to be doubled. Table 2 shows the corrected unit-cell parameters of these phases.

It has already been shown that there is a lower size limit for the tetragonal diboride dicarbide structure since ScB_2C_2 is not a member of the isostructural series (Smith, Johnson & Nordine, 1965). If we consider that all the metals which form CaB_6-type hexaborides can also form tetragonal diboride dicarbides, the upper size limit should be for BaB_2C_2.

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