

Ternary rare earth metal boride carbides containing two-dimensional boron–carbon network: The crystal and electronic structure of R_2B_4C ($R = Tb, Dy, Ho, Er$)

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Received 28 August 2007; received in revised form 10 October 2007; accepted 14 October 2007

Available online 22 October 2007

Abstract

The ternary rare earth boride carbides R_2B_4C ($R = Tb, Dy, Ho, Er$) have been synthesized by reacting the elements at temperatures between 1800 and 2000K. The crystal structure of Dy_2B_4C has been determined from single-crystal X-ray diffraction data. It crystallizes in a new structure type in the orthorhombic space group $Immm$ ($a = 3.2772(6) \text{ \AA}$, $b = 6.567(2) \text{ \AA}$, $c = 7.542(1) \text{ \AA}$, $Z = 2$, $R1 = 0.035$ ($wR_2 = 0.10$) for 224 reflections with $I_o > 2\sigma(I_o)$). Boron atoms form infinite chains of fused B_6 rings in [100] joined with carbon atoms into planar, two-dimensional networks which alternate with planar sheets of rare earth metal atoms. The electronic structure of Dy_2B_4C was also analyzed using the tight-binding extended Hückel method.

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Keywords: Rare earth metals boride carbide; Crystal structure; Electronic structure

1. Introduction

The structures of the ternary rare earth metal boride carbides $R_xB_yC_z$ display a variety of different arrangements with boron–carbon substructures ranging from zero-dimensional units to one- and two-dimensional (2D) networks alternating with metal atom sublattices. Nearly a dozen structural types have been reported so far for the most electron-rich compounds, i.e., those containing finite quasi-molecular entities [1–3]. These units embedded in the voids of the metal atom matrix can have different lengths ranging from 2 to 13 non-metal atoms, in which chain-like units of different sizes as well as isolated C atoms can coexist. In the second category, the non-metal atoms form infinite one-dimensional planar or nearly planar ribbons made of zigzag chains of boron atoms to which carbon atoms are attached [1,4]. In the third family, the boron and carbon atoms form infinite, planar 2D networks which alternate with sheets of

metal atoms [1]. To this family belong the structures of the compounds RB_2C_2 (LaB_2C_2 and ScB_2C_2 types of structures) [5–7], RB_2C (YB_2C , ThB_2C , $\alpha\text{-}UB_2C$ types) [8–11], and $R_2B_3C_2$ ($Gd_2B_3C_2$) [12]. In the tetragonal LaB_2C_2 -type structure the B and C atoms form planar nets of four- and eight-membered rings stacked directly above one another with the cations occupying positions between the eight-membered rings. In orthorhombic ScB_2C_2 the B/C layers consist of fused five- and seven-membered rings with the cations occupying positions between the larger rings. In both B/C networks all atoms are three-connected. Three structural types have been reported for the RB_2C phases. While the structure type of ThB_2C [10] is found with the early actinoid metals (Th, U, Pu) [13] so far, CeB_2C [14] is the only rare earth compound with ThB_2C structure containing fused hexagonal and nine-membered rings. The boride carbides of the smaller rare earth metals, (Sc, Tb–Lu) B_2C , adopt the tetragonal YB_2C -type based on four- and seven-membered rings [8,9].

New structural representatives were recently discovered during our investigations of the Dy–B–C system. In this

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paper we report the synthesis, new crystal structure type, and electronic structures of R_2B_4C ($R = Tb, Dy, Ho, Er$).

2. Experimental

2.1. Synthesis and analysis

The samples R_2B_4C ($R = Tb, Dy, Ho, Er$) were prepared from commercially available pure elements: rare earth metals with a claimed purity of 99.99 at%, Alfa-Aesar, Johnson Matthey Company, sublimed bulk pieces; crystalline boron powder, purity 99.99 at%, H.C. Starck, Germany; graphite powder, purity 99.98 at%, Aldrich. Before use, the graphite and boron powders were outgassed overnight at 950 °C, $p < 10^{-5}$ mbar. Mixtures of powders were compacted in stainless steel dies. The pellets were arc-melted under purified argon atmosphere [15] on a water-cooled copper hearth. The alloy buttons of 1g were turned over and remelted three times to improve homogeneity. The samples appeared with shiny metallic luster pellets. Subsequent heating just above the melting point was carried out in a high-frequency furnace on a water-cooled copper hearth, TIG-10/300, Hüttinger, FRG, under purified argon atmosphere for 12 h at 1830, 1870, 2000 and 2030 K for the Tb, Dy, Ho and Er samples, respectively. The annealing temperatures were determined using a digital pyrometer Metis MS/MI (Sensortherm GmbH, Germany) with instrumental errors of ± 4 K for the temperature range 1570–2170 K. The compounds are quite stable in air, yet sample handling was carried out under argon atmosphere in a glove box or through the Schlenk technique. Our attempts to synthesize the R_2B_4C with Y, Gd, Tm, Yb, Lu were not successful.

The samples were characterized by energy-dispersive X-ray spectroscopy analyses (EDX) on polished pellets and single crystals in a scanning electron microscope, TESCAN 5130MM with Oxford Si detector. EDX analyses confirmed terbium, dysprosium, holmium, erbium, carbon, and boron as the only components in the samples.

2.2. X-ray diffraction and structure refinement

Small irregularly shaped single crystals were selected from the crushed samples and sealed under argon atmosphere in glass capillaries. These crystals were first examined by the Buerger precession technique in order to establish their suitability for the subsequent data collection. Single-crystal reflection data of Dy_2B_4C were collected at room temperature on a STOE IPDS II image plate diffractometer with monochromatized $MoK\alpha$ radiation. A numerical absorption correction was made on the basis of the crystal shape [16]. All relevant crystallographic data are listed in Table 1. The starting atomic parameters were derived via direct methods using the program SIR97 [17]. These were subsequently refined with the program SHELX-97 [18] within the WinGX program package [19] (full matrix least-squares on F^2) with anisotropic atomic

Table 1
Crystal data and structure refinement for Dy_2B_4C

Empirical formula	Dy_2B_4C
Crystal system	Orthorhombic
Space group	$Immm$ (No. 71)
Pearson symbol	$oI14$
Formula per unit cell, Z	2
Lattice parameters	
a (Å)	3.2772(6)
b (Å)	6.567(2)
c (Å)	7.542(1)
Unit cell volume (Å ³)	162.31(6)
Calculated density (g/cm ³)	7.78
Absorption coefficient (1/cm)	45.391
Crystal size (mm ³)	$0.12 \times 0.10 \times 0.06$
Radiation and wavelength (Å)	$MoK\alpha$, 0.71069
Diffractometer	STOE IPDS II
Refined parameters	17
Refinement	F^2
$2\theta_{max}$ and $(\sin \theta/\lambda)_{max}$	73.5, 0.768
h, k, l	$-5 < h < 4$ $-10 < k < 10$ $-11 < l < 12$
Collected reflections	1260
Independent reflections	224 ($R_{int} = 0.093$)
Reflections with $I_o > 2\sigma(I_o)$	222 ($R_\sigma = 0.040$)
Final R_1^a indices (R_1^a all data)	0.035 (0.095)
Weighted wR_2^b factor (wR_2^b all data)	0.037 (0.10) ^c
Goodness-of-fit on F^2	1.2
Extinction coefficient	0.062(11)
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	$-4.78/5.01$

$$^a R_1(F) = [\sum(|F_o| - |F_c|)] / \sum |F_o|$$

$$^b wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$$

$$^c [w^{-1} = \sigma^2(F_o^2) + (0.056P)^2 + 12.60P], \text{ where } P = (F_o^2 + 2F_c^2)/3$$

displacements for Dy atoms. The refinements converged well, and the light atoms could be located from the difference Fourier maps. The final ΔF synthesis was flat, and the refinement of the occupancy factors gave no evidence for partial occupations. The atomic coordinates and thermal parameters are listed in Table 2, selected interatomic distances and bond angles are reported in Table 3. All atoms could be refined anisotropically. Drawings of the structure were prepared with the program DIAMOND [20].

The calculated X-ray powder diffraction patterns recorded on samples sealed in capillaries under dry argon were found to be in good agreement with the experimental patterns collected on a STOE STADI P with $MoK\alpha_1$ radiation. The unit cell parameters for all investigated compounds R_2B_4C ($R = Tb, Dy, Ho, Er$), refined with the CSD program package [21], are given in Table 4. The correct indexing of the X-ray patterns was ensured through intensity calculations using the atomic positions from the single-crystal refinement.

2.3. Theoretical calculations

The density of states (DOS) and the crystal orbital overlap population (COOP) [22] curves were computed

Table 2
Atomic coordinates and atom displacement^a parameters (in Å²) for Dy₂B₄C

Atom	Site	x	y	z	U _{eq}	U ₁₁	U ₂₂	U ₃₃
Dy	4i	0	0	0.2343(1)	0.0040(4)	0.0033(5)	0.0038(5)	0.0050(6)
C	2b	1/2	0	0	0.004(3)	–	–	–
B1	4g	1/2	0.133(3)	1/2	0.009(3)	–	–	–
B2	4h	1/2	0.770(2)	0	0.006(3)	–	–	–

$$^a U_{23} = U_{13} = U_{12} = 0.$$

Table 3
Selected interatomic distances (*d*, Å) and angles (°) with multiplicities for Dy₂B₄C

Atoms	Multiplicity	<i>d</i>	Atoms	Multiplicity	<i>d</i> /angle
Dy–Dy	2	3.277(7)	Dy–B1	2	2.99(2)
Dy–Dy	1	3.534(1)	C–B2	2	1.51(1)
Dy–Dy	4	3.677(2)	B1–B1	1	1.75(3)
Dy–Dy	1	4.008(1)	B1–B2	2	1.87(1)
Dy–C	4	2.410(3)	B2–C–B2	2	180.0
Dy–B2	2	2.676(9)	B1–B1–B2	2	118.8(6)
Dy–B1	4	2.732(7)	B2–B1–B2	2	122.3(1)
Dy–B2	4	2.844(7)	C–B2–B1	2	118.8(6)

Table 4
Unit cell parameters for some boride carbides R₂B₄C^a

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Tb ₂ B ₄ C	3.2877(9)	6.569(1)	7.593(2)	164.0(1)
Dy ₂ B ₄ C	3.2712(9)	6.552(1)	7.528(2)	161.3(1)
Ho ₂ B ₄ C	3.266(1)	6.551(1)	7.462(2)	159.7(1)
Er ₂ B ₄ C	3.2528(4)	6.5462(7)	7.4048(8)	157.7(1)

^aX-ray powder data.

Table 5
Extended Hückel parameters [23,32,33]

	Orbital	<i>H_{ii}</i> (eV)	ζ ₁ ^a	ζ ₂	<i>C₁</i> ^a	<i>C₂</i>
Dy	6s	–6.73	1.47			
	6p	–4.18	1.47			
	5d	–6.33	2.778	1.2415	0.7123	0.4640
B	2s	–15.2	1.30			
	2p	–8.5	1.30			
C	2s	–21.4	1.625			
	2p	–11.4	1.625			

^aExponents and coefficients in a double ζ expansion of the *d* orbital.

using the tight-binding extended Hückel method (EH) [23,24] with 512 K points in the irreducible wedge of the Brillouin zone. The used EH parameters are listed in Table 5.

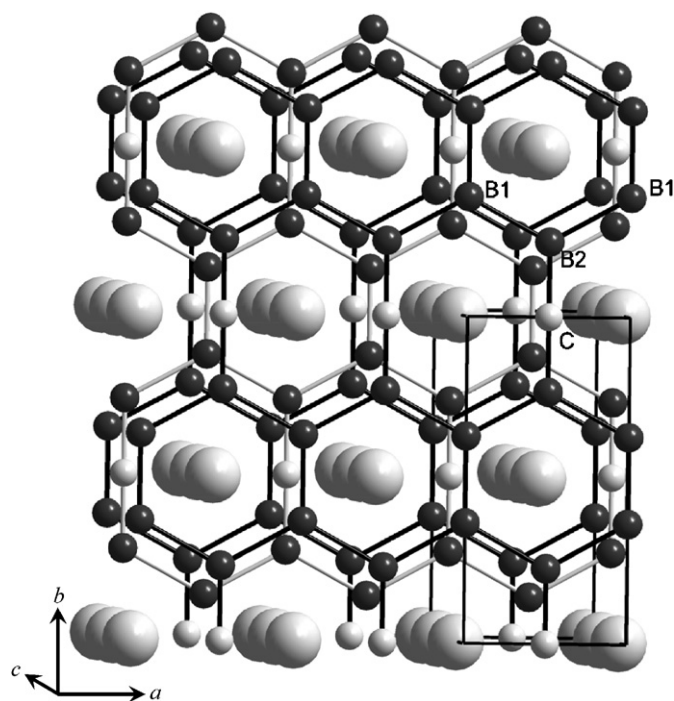


Fig. 1. Crystal structure of Dy₂B₄C.

3. Results and discussion

3.1. Crystal structure

The crystal structure of Dy₂B₄C (Fig. 1) represents a new type. It is, however, closely related to the crystal structures of other ternary rare-earth metal boride carbides containing planar 2D networks formed of the boron and carbon atoms which alternate with planar sheets of metal atoms (Fig. 2) such as in structures with compositions RB₂C₂, RB₂C and R₂B₃C₂. In the structure of Dy₂B₄C the planar 6³ nets formed by dysprosium atoms alternate with planar non-metal atom layers. The boron atoms form hexagons fused to straight chains along [100]. Neighboring chains are interconnected via C atoms. The 2D non-metal atom layer is thus composed of B₆ and B₆C₂ rings. The boron atoms occupy the approximate centers of fused Dy₆ trigonal prisms. Carbon atoms occupy the centers of rectangular

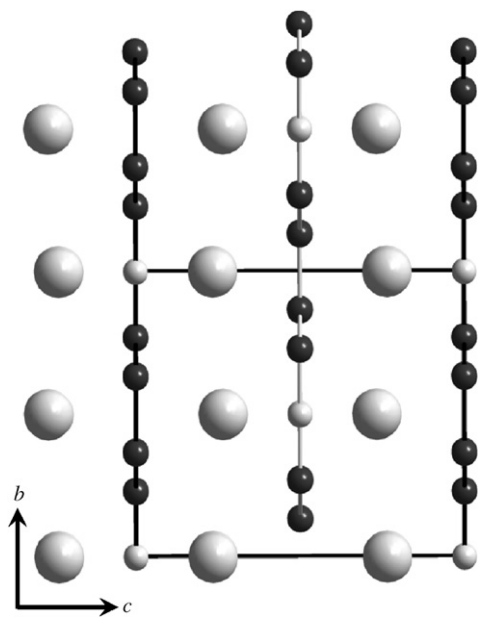


Fig. 2. Projection of the crystal structure of $\text{Dy}_2\text{B}_4\text{C}$ along the a -axis.

by pyramids formed by four dysprosium atoms (in planar coordination) and two additional boron atoms at the apices of octahedron $\text{C}[\text{Dy}_4\text{B}_2]$. There are no direct C–C contacts in the structure. The shortest Dy–Dy distance, $d_{\text{Dy-Dy}} = 3.277(7) \text{ \AA}$, corresponds to the length of the a -axis. Other Dy–Dy distances in the structure range from $3.534(1)$ to $4.008(1) \text{ \AA}$. The Dy–C distances, $2.410(3) \text{ \AA}$, are close to average distances in $\text{Dy}_5\text{B}_2\text{C}_5$, 2.443 and 2.463 \AA [25]. The Dy–B distances range from $(2 \times) 2.676(9) \text{ \AA}$ to $(4 \times) 2.732(7) \text{ \AA}$ (Table 3) in good agreement with the distances in DyB_2 , 2.701 \AA , and DyB_2C_2 , 2.732 \AA [26,27]. The corresponding Dy–B distances for the metal atoms above and below the eight-membered B_6C_2 rings are slightly larger and range from $(4 \times) 2.844(7) \text{ \AA}$ to $(2 \times) 2.99(2) \text{ \AA}$. The alternate stacking of the B hexagons and B_6C_2 rings above and below the Dy layer is the reason for the many different Dy–B distances.

Within the non-metal atom layer each B1 atom is bonded to three other boron atoms with distances of $d_{\text{B1-B2}} = 1.87(1) \text{ \AA}$ and $d_{\text{B1-B1}} = 1.75(3) \text{ \AA}$ (angles $\varphi_{\text{B1-B1-B2}} = 118.8(6)^\circ$ and $\varphi_{\text{B1-B2-B1}} = 122.3(1)^\circ$), while the

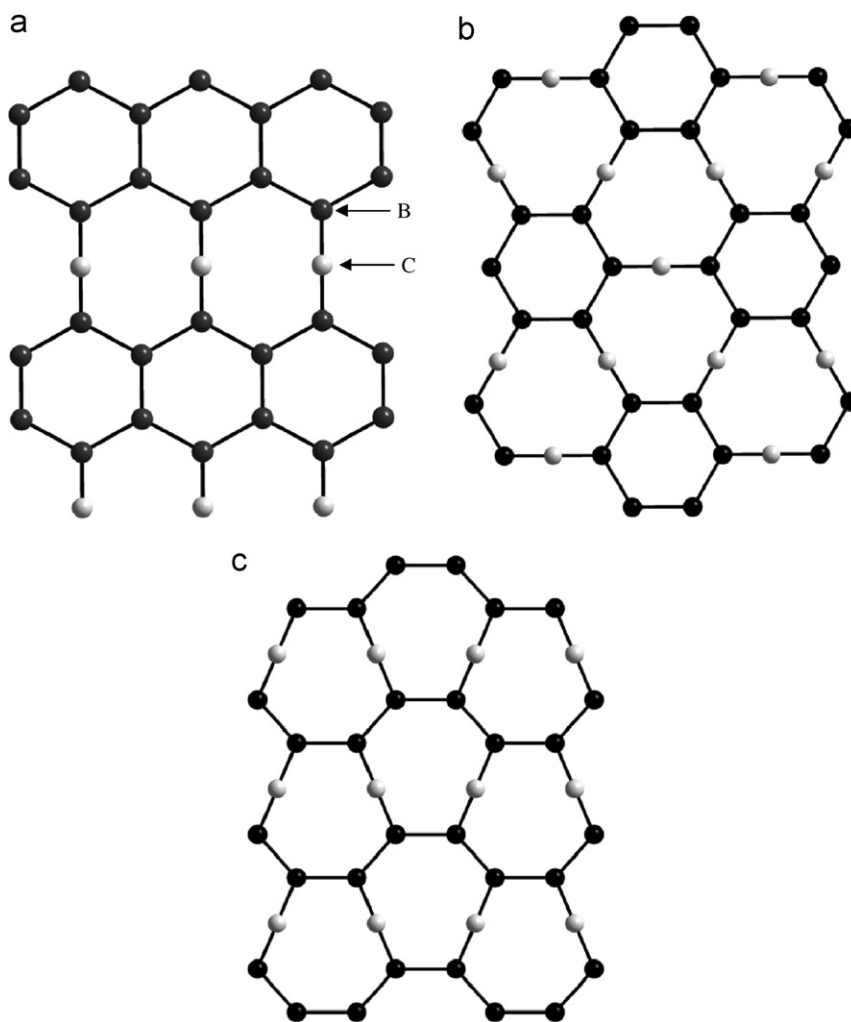


Fig. 3. Layers of boron and carbon atoms in the structures of $\text{Dy}_2\text{B}_4\text{C}$ (a) ThB_2C (b) and $\alpha\text{-UB}_2\text{C}$ (c).

B2 atom is bonded to two B1 and one C atom ($d_{\text{B2-C}} = 1.51(1) \text{ \AA}$, $\varphi_{\text{B2-C-B2}} = 180.0(4)^\circ$). The distances indicate a stronger bonding parallel to b (B2–C–B2, B1–B1) compared to a (B1–B2).

The characteristic non-metal atom layers in the structure of $\text{Dy}_2\text{B}_4\text{C}$ show similarities with motifs in related boride carbides as illustrated in Fig. 3. Both $\text{Dy}_2\text{B}_4\text{C}$ and ThB_2C contain B_6 hexagons; however, they interconnect in a different way. Whereas the connection of hexagons via opposite edges and via B–C–B bridges involving opposite corners in (a) $\text{Dy}_2\text{B}_4\text{C}$ leads to a layer of condensed B_6 and B_6C_2 rings with two-fold symmetry, the interconnection of the hexagons via B–C–B bridges involving all six corners preserves the hexagonal symmetry, $d_{\text{B-B}} = 1.847 \text{ \AA}$ in the crystal structure of (b) ThB_2C (and the isotypic $\beta\text{-UB}_2\text{C}$). The layers in the ThB_2C structure are hence composed of condensed B_6 and B_6C_3 rings. B_6C_3 rings are the only structural motifs in the layers found in (c) $\alpha\text{-UB}_2\text{C}$ [11].

3.2. Electronic structure

Similar to many other known rare earth boride carbides [1,12], the valence electron concentration (VEC) per non-metal atom in $\text{Dy}_2\text{B}_4\text{C}$ is $(2 \times 3 + 4 \times 3 + 4)/(4 + 1) = 4.4$ thus slightly larger than 4. Since all boron atoms are three-connected and carbon two-connected, they can be assigned as sp^2 and sp hybridized, respectively. Anticipating that $\text{Dy}_2\text{B}_4\text{C}$ is a normal valence compound as a first approximation the electron partition can be assigned as $(\text{Dy}^{3+})_2(\text{B}^-)_4\text{C}^{2-}$ which corresponds to a closed-shell configuration. The $(\text{B}^-)_4$ part in the formula is isoelectronic to polyacene, and the electronic structure would support a planar boron ribbon. The polyacene-like entity has also been found in other compounds such as Ta_3B_4 , whose electronic structure has been analyzed in detail by Minyaev and Hoffmann [28]. However, because the distance of B1–B1 (1.75 \AA) is close to that of a B–B double bond, B2–B2 (1.87 \AA) to a B–B single bond, and C–B2 (1.51 \AA) to a C–B partial double bond, a more accurate assignment is $(\text{Dy}^{3+})_2(\text{B}_4\text{C})^{6-}$. The $(\text{B}_4\text{C})^{6-}$ part has therefore a quinoidic form with alternating single and double bonds [29]. This assignment is also in agreement with a linear $(\text{B}_2\text{C})^{4-}$ moiety whose electronic structure has been analyzed by Witek et al [30]. The assignment of a mesomeric system $(\text{B}_2\text{C})^{4-}$ with lone-pair configuration at B and C [29] also avoids a bent conformation required by the otherwise two lone pairs at the C^{2-} center. Fig. 4 shows the calculated EH DOS and COOP curves of various atomic contacts in the structure. The solid curve in panel (a) represents the total

DOS, the shaded areas and dashed curves correspond to the contribution from Dy and its integrated value, respectively. It shows that the above descriptions are approximations as the Dy d states penetrate below the

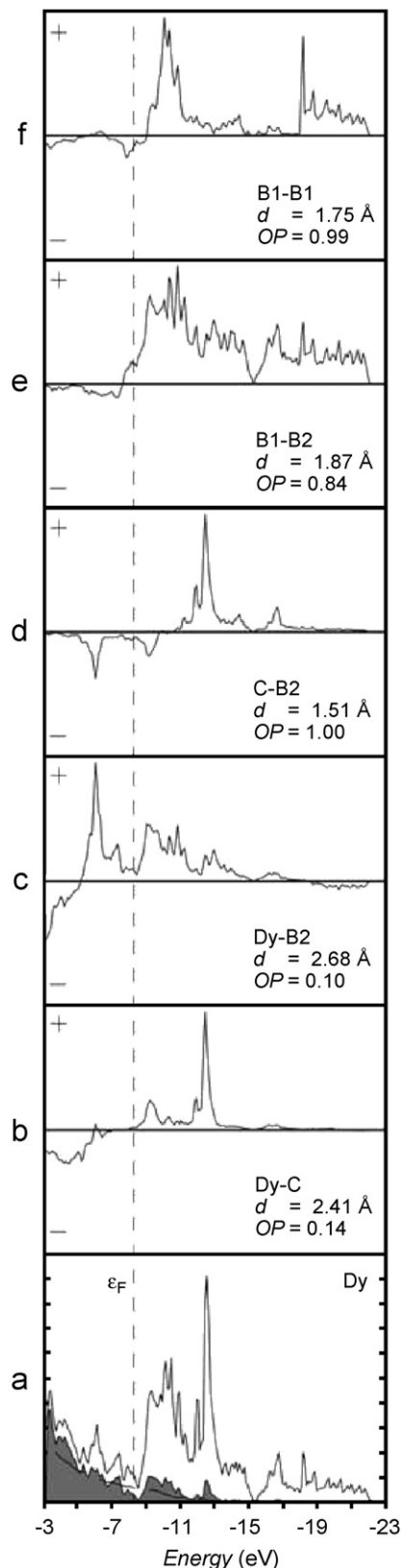


Fig. 4. Calculated EH DOS and COOP for $\text{Dy}_2\text{B}_4\text{C}$. (a) DOS. The solid curves represent the total DOS, the shaded areas and dashed curves correspond to the contribution from Dy and its integrated value, respectively. The vertical dotted line indicates the Fermi level. (b–f) COOP curves of representative atomic contacts in $\text{Dy}_2\text{B}_4\text{C}$. The + region is the bonding area and the – region the antibonding area. The bond type, distance (d) and integrated overlap population up to the Fermi level (OP) are indicated in each panel.

Fermi level and are partially occupied, resulting in approximately 1.0 electron accumulating at each Dy center as estimated by the EH method. Panels (b–f) confirm the nearly closed-shell electron configuration. Except for some weak Dy–B antibonding feature, all occupied states contribute to Dy–B, Dy–C, B–B and B–C bonding. This feature is a result of strong B–B bonding at the expense of weak Dy–B antibonding, typical of a non-metal network interacting with rare earth metal hosts.

Because of the linear configuration around the Wyckoff position *2b*, calculations with the identical VEC = 4.4 for structures with all B and C atoms always resulted in more electron accumulation at this position. For the experimental structure, there are 1.8 electrons more than in the *4g* and *4h* positions of the B atoms. With only B atoms in all three positions, 0.2 more electrons, and with only C atoms, 0.5 more electrons accumulate in the position *2b*. According to a coloring theory [31] the more electronegative atom carbon should occupy the *2b* position in agreement with the structure refinement and differentiation of interatomic distances.

4. Conclusion

Dy₂B₄C prepared from pure elements by melting and subsequent heating at 1870 K is a new member of the rare earth metal boride carbide series in which the boron and carbon atoms form infinite, planar 2D networks which alternate with sheets of rare earth metal atoms. Isostructural analogues with Tb, Ho and Er have also been characterized. Dy₂B₄C crystallizes with a new structure type where planar 6³-Dy metal atom layers alternate with planar non-metal layers consisting of ribbons of fused B₆ hexagons bridged by carbon atoms.

Supplemental information

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49)7247-808-666; E-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CSD- 418403.

Acknowledgments

The authors gratefully thank M. Babizhetskyy for the sample preparation and Dr. C. Hoch for X-ray intensity data collection.

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