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Preparation, properties and crystal structures of the thorium chromium borides $ThCrB_4$ and $ThCr_2B_6$; structure refinements of $CeCr_2B_6$, ThB_4 and ThB_6

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Abstract

The new polyborides ThCrB₄ and ThCr₂B₆ were prepared by arc melting of the elemental components, and their crystal structures were determined from single-crystal X-ray data. ThCrB₄ has a YCrB₄-type structure: *Pbam*, a = 605.8(1) pm, b = 1171.2(2) pm, c = 364.0(1) pm, R = 0.024 for 714 structure factors and 26 variable parameters. ThCr₂B₆ is isotypic with CeCr₂B₆: *Immm*, a = 315.8(1) pm, b = 659.1(1) pm, c = 836.4(2) pm, R = 0.030 (415 F values, 14 variables). The structures of the borides CeCr₂B₆, ThB₄ and ThB₆ were refined from single-crystal X-ray data. The B–B bonds between the B₆ octahedra of ThB₄ and ThB₆ are considerably shorter than those within the octahedra. ThCrB₄, ThCr₂B₆ and CeCr₂B₆ are metallic conductors and Pauli paramagnetic.

Keywords: Polyborides; Crystal structures; Metallic conductors; Pauli paramagnets

1. Introduction

Some 100 ternary polyborides with the composition ATB_4 are known [1], in which the A components are rare earth elements or actinoids and the T components are transition metals of groups 5 (vanadium) to 10 (nickel). They crystallize with two related structure types first determined for YCrB₄ [2] and ThMoB₄ [3]. The compound ThCrB₄ reported in this paper is formed peritectically and, apparently for that reason, was missed in earlier investigations. This is also true of ThCr₂B₆, which crystallizes with a CeCr₂B₆-type structure, that has also been reported for the three isotypic borides $PrCr_2B_6$, $NdCr_2B_6$ and $SmCr_2B_6$ [4,5]. We report the results of structure refinements for $CeCr_2B_6$, ThB_4 and ThB_6 from single-crystal X-ray data. The structure of CeCr₂B₆ has been determined previously from single-crystal film data [4], while those of ThB₄ and ThB₆ have been obtained from powder data [6,7].

2. Sample preparation and lattice constants

The starting materials were ingots of thorium (Kelpin) and cerium (Kelpin) and chromium powder (Riedel de Haën), all with nominal purities of greater than 99.9%, and boron powder (Heraeus, purity better than 99.5%). Filings of cerium and thorium were prepared under dry (Na) paraffin oil. The oil was dissolved with dry *n*-hexane, and the hexane was removed under vacuum. The filings were stored under vacuum and were only briefly exposed to air prior to the reactions. For the preparation of $ThCrB_4$, the starting ratio was Th: Cr: B = 1:2:4; for all other compounds the ideal starting ratios were used. Coldpressed pellets of the elements were arc melted in an atmosphere of purified argon. After wrapping the samples in tantalum foil, they were enclosed in evacuated silica tubes and annealed for 10 days at 900°C, followed by quenching in cold water.

The samples were characterized by their Guinier powder patterns using Cu K α_1 radiation and α -quartz (a = 491.30 pm, c = 540.46 pm) as internal standard. The lattice constants (Table 1) were obtained from

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Table 1						
Crystal dat	a for	ThCrB ₄ ,	ThCr ₂ B ₆ ,	CeCr ₂ B ₆ ,	ThB_4	and ThB ₆ ^a

	ThCrB ₄	ThCr ₂ B ₆	CeCr ₂ B ₆	ThB₄	ThB ₆
Structure type	YCrB ₄	CeCr ₂ B ₆	CeCr ₂ B ₆	ThB₄	CaB
Space group	<i>Pbam</i> (No. 55)	Immm (No. 71)	Immm (No. 71)	P4/mbm (No. 127)	$Pm\bar{3}m$ (No. 221)
a (pm)	605.7(1)	315.8(1)	310.5(1)	725.6(1)	409.31(3)
<i>b</i> (pm)	1171.2(2)	659.1(1)	656.2(2)	_	
<i>c</i> (pm)	364.0(1)	836.4(2)	834.1(1)	411.18(9)	
$V(nm^3)$	0.2582	0.1741	0.1699	0.2165	0.06857
Formula units per cell	Z = 4	Z = 2	Z = 2	Z = 4	Z = 1
Formula weight	327.3	400.9	309.0	275.3	296.9
Calculated density ($g \text{ cm}^{-3}$)	8.42	7.65	6.04	8.45	7.19
Crystal dimensions (mm ³)	$30 \times 30 \times 40$	$20 \times 20 \times 100$	$22 \times 22 \times 110$	$22 \times 22 \times 110$	$44 \times 44 \times 44$
Range in k, k, l	±12, ±23, 0-7	$0-6, \pm 13, \pm 16$	±15, ±19, 0-7	±13, ±13, 0-7	$\pm 8, \pm 8, \pm 8$
$\theta/2\theta$ scans up to	$2\theta = 95^{\circ}$	$2\theta = 90^{\circ}$	$2\theta = 110^{\circ}$	$2\theta = 80^{\circ}$	$2\theta = 110^{\circ}$
Total number of reflections	5902	2002	2870	2911	4105
Highest/lowest transmission	1.28	1.28	1.19	1.52	1.59
Unique reflections	1451	436	752	437	158
Inner residual	$R_{i} = 0.038$	$R_{\rm i} = 0.030$	$R_{i} = 0.021$	$R_{i} = 0.046$	$R_{\rm i} = 0.048$
Reflections with $I > 3\sigma(I)$	714	415	420	280	86
Number of variables	26	14	14	13	5
Highest residual electron density (e $Å^{-3}$)	7.4	1.2	0.6	4.8	8.3
Their location at x, y, z	0.13, 0.35, 1	0, 0.38, 0	0, 0, 0.21	0.16, 0.34, 0	1/2, 0, 1/2
Conventional residual	R = 0.024	R = 0.030	R = 0.017	R = 0.026	R = 0.021
Weighted residual	$R_{\rm w} = 0.029$	$R_{\rm w} = 0.037$	$R_{\rm w} = 0.022$	$R_{\rm w} = 0.029$	$R_{\rm w} = 0.022$

^a Standard deviations are listed in parentheses in the place values of the last listed digits throughout the paper.

least-squares fits. The identification of the diffraction lines was facilitated by comparing the experimental patterns with the calculated patterns [8]. For these calculations, the positional parameters obtained from the single-crystal investigations were used. Energydispersive X-ray fluorescence analyses of the samples and crystals used for the structure refinements in a scanning electron microscope did not reveal any impurity elements heavier than sodium, and the ratios of the two metals for the ternary samples were within 5% of the ideal values.

3. Properties

The five borides are stable in air. The powdered samples have a dark grey colour and the crystals have a silvery lustre, except for the crystals of ThB_6 which have a shiny red colour. The electrical properties of the binary compounds ThB_4 and ThB_6 have been examined previously [9]; therefore, in this work, only the ternary compounds were investigated.

The magnetic susceptibilities of the ternary borides $ThCrB_4$, $CeCr_2B_6$ and $ThCr_2B_6$ were determined with a superconducting quantum interference device (SQUID) magnetometer at temperatures between 2 and 300 K. The compounds show essentially temperature-independent Pauli paramagnetism (Fig. 1). The upturns in the susceptibility curves at low temperature may be ascribed to paramagnetic impurities or to paramagnetic surface states of the powdered samples. The susceptibility values were fitted to the



Fig. 1. Temperature dependence of the magnetic susceptibilities of $ThCrB_4$, $ThCr_2B_6$ and $CeCr_2B_6$.

function $\chi = \chi_0 + C/(T - \Theta)$ allowing for Curie–Weiss behaviour for the temperature-dependent term. The following values were obtained for the temperatureindependent susceptibilities: $\chi_0 = 3.2 \times 10^{-9}$ m³ per formula unit (f.u.), $\chi_0 = 3.3 \times 10^{-9}$ m³ f.u.⁻¹ and $\chi_0 = 5.0 \times 10^{-9}$ m³ f.u.⁻¹ for ThCrB₄, ThCr₂B₆ and CeCr₂B₆, respectively.



Fig. 2. Electrical resistivities of $ThCrB_4$, $ThCr_2B_6$ and $CeCr_2B_6$.

The electrical conductivity behaviour of polycrystalline pieces of the ternary borides was determined with an a.c. four-probe technique in the temperature range 4-300 K. The samples were contacted with copper filaments using a silver epoxy cement. Because of the uncertainties in estimating the sizes of the contact areas, the absolute values of the electrical resistivities are estimated to be correct only to within a factor of ± 3 . The relative values for different temperatures, however, are much more reliable. The electrical resistivities of the three compounds increase with increasing temperature (Fig. 2), as is typical for metallic conductors in agreement with the magnetic behaviour of these borides.

4. Structure refinements

Single crystals of the five compounds were isolated from the annealed, crushed samples. They were investigated using Weissenberg and Buerger precession cameras to establish their suitability for intensity data collection. Intensity data were collected on a fourcircle diffractometer with graphite-monochromated Mo K α radiation and a scintillation counter with pulse height discrimination. The scans were along θ with background counts at both ends of each scan. Empirical absorption corrections were applied from psi scan data. Further details of the structure determinations are summarized in Table 1.

The structures were refined with a full-matrix leastsquares program using atomic scattering factors [10], corrected for anomalous dispersion [11]. The initial positional parameters were taken from previous structure determinations [2,4,6,7]. A parameter accounting for isotropic secondary extinction was refined and applied to the calculated structure factors. The weighting scheme accounted for the counting statistics. To check for deviations from the ideal compositions, the occupancy parameters were refined in separate least-squares cycles together with the thermal parameters. No large deviations from the ideal occupancies were found (Table 2), and in the final least-squares cycles all positions were refined with ideal occupancies. The highest residual electron densities were located at sites which were unsuitable for the placement of additional atoms. The atomic parameters and interatomic distances are listed in Tables 2–5.

5. Discussion

The metal to boron ratio of the new compounds ThCrB₄ and ThCr₂B₆ is the same (1:2); nevertheless, their boron networks are different. In ThCrB₄ the boron atoms form planar two-dimensional infinite nets consisting of five- and seven-membered rings (Fig. 3), accounting for the different sizes of the chromium and thorium atoms, which are situated above and below these rings. In contrast, the boron atoms in $ThCr_2B_6$ form a three-dimensional infinite network in which eight-, ten- and fourteen-membered, puckered rings are discernible (Fig. 4). In both compounds all boron atoms have three boron neighbours with B-B distances in the range 167-193 pm in ThCrB₄ and 176-188 pm in Th Cr_2B_6 . The thorium atoms in Th CrB_4 and ThCr₂B₆ have 14 and 16 boron neighbours respectively, and this is reflected by the average Th-B distances of 279.7 and 288.7 pm. In addition to these boron neighbours, the thorium atoms have metal neighbours. The short Th-Th distances of 315.8 pm in ThCr₂B₆ are remarkable (the metallic radius of thorium is 180 pm). In both compounds, the chromium atoms have ten boron neighbours. However, the Cr-B distances are quite different in the two compounds; in Th CrB_4 , they extend between 235 and 239 pm with an average of 236.3 pm; in $ThCr_2B_6$, they vary between 214 and 225 pm with an average of 222.4 pm. This rather large difference may be rationalized by the much shorter metal-metal bonds of the chromium atoms in ThCrB₄ (Table 3). This, in turn, indicates that the metal-metal interactions in this compound have considerable bonding character. The short Cr-Cr distance of 245.9 pm is especially noteworthy.

The three compounds CeCr_2B_6 [4], ThB_4 [6] and ThB_6 [7] have been reported previously; however, their crystal structures were determined from film data. The present structure refinements are considerably more accurate and allow a discussion of the boron-boron distances to be made. The interatomic distances of CeCr_2B_6 are similar to the distances of ThCr_2B_6 (Table 4). In ThB_4 and ThB_6 , the boron atoms form B_6 octahedra (Fig. 5). In ThB_4 , these octahedra are formed by the B2 and B3 atoms. The

Table 2 Atomic parameters of $ThCrB_4$, $ThCr_2B_6$, $CeCr_2B_6$, ThB_4 and ThB_6 "

Atom	Space group	Occupancy	x	у	Ζ.	В
	Pbam		······································		·····	
Th	4h	1.000(1)	0.37715(6)	0.34884(2)	1/2	0.170(3)
Cr	4h	0.996(5)	0.3762(3)	0.0832(1)	1/2	0.26(2)
B1	4g	0.92(4)	0.139(2)	0.0329(1)	0	0.6(1)
B2	4g	0.87(4)	0.022(2)	0.3124(9)	0	0.4(1)
B3	4g	0.76(3)	0.108(2)	0.4562(8)	0	0.3(1)
B4	4g	0.87(4)	0.219(2)	0.1830(9)	0	0.4(1)
ThCr ₂ B ₆	Immm			. ,		
Th	2a	0.9963(9)	0	0	0	0.249(3)
Cr	4j	0.972(3)	1/2	0	0.34590(9)	0.257(8)
B1	4h	0.89(2)	0	0.1423(9)	1/2	0.47(6)
B2	81	1.06(1)	0	0.2365(6)	0.3031(4)	0.40(4)
$CeCr_2B_6$	Immm					()
Ce	2a	1.0042(9)	0	0	0	0.239(3)
Cr	4j	0.969(2)	1/2	0	0.34567(6)	0.247(6)
B1	4h	0.95(1)	0	0.1438(6)	1/2	0.38(4)
B2	81	0.936(9)	0	0.2373(4)	0.3035(3)	0.43(3)
ThB₄	P4/mbm					
Th	4h	1.001(2)	0.1853(1)	1/2 + x	1/2	0.172(8)
B1	4g	0.98(7)	0.590(2)	1/2 + x	0	0.2(3)
B2	8i	0.89(6)	0.040(2)	0.176(2)	0	0.5(2)
B3	4e	0.95(4)	0	0	0.297(5)	0.6(3)
ThB ₆	Pm3m					
Th	1a	0.997(3)	0	0	0	0.902(7)
В	6f	1.15(3)	0.197(2)	1/2	1/2	1.16(9)

^a The program STRUCTURE TIDY [12] was used to standardize the positional parameters. The occupancy parameters were obtained in separate series of least-squares cycles. In the final cycles, the occupancy parameters were assumed to be ideal. The last column contains the isotropic thermal parameters *B* of the boron atoms and the equivalent isotropic thermal parameters B_{eq} (×10⁴, in units of pm²) of the metal atoms.

Table 3	
Interatomic distances (pm) in the structure of ThCrB ₄ ^a	

Th:	2B3	274.6(9)	B1:	1B3	177(2)
	2B2	276.7(9)		1 B 4	182(2)
	2B4	278(1)		1 B 1	186(2)
	2B1	278(1)		2Cr	239(1)
	2B1	282.3(9)		2Th	278(1)
	2B4	283(1)		2Th	282.3(9)
	2B2	285(1)	B2:	1B3	176(2)
	1Cr	311.1(1)		1 B 4	184(2)
	1Cr	312.6(2)		1 B4	193(2)
	1Cr	313.7(2)		2Cr	236.4(8)
	1Cr	314.5(2)		2Th	276.7(9)
	2Th	364.0(1)		2Th	285(1)
	2Th	381.2(1)	B3:	1B3	167(2)
	1Th	384.1(1)		1 B 2	176(2)
Cr:	2B3	234.6(8)		1 B 1	177(2)
	2B3	235.2(7)		2Cr	234.6(8)
	2B4	236.3(8)		2Cr	235.2(7)
	2B2	236.4(8)		2Th	274.6(9)
	2B1	239(1)	B4:	1 B 1	182(2)
	1Cr	245.9(3)		1B2	184(2)
	1Th	311.1(1)		1 B 2	193(2)
	1Th	312.6(2)		2Cr	236.3(8)
	1Th	313.7(2)		2Th	278(1)
	1Th	314.5(2)		2Th	283(1)

^a All distances shorter than 500 pm (Th–Th), 460 pm (Th–Cr), 410 pm (Th–B), 360 pm (Cr–Cr, Cr–B) and 280 pm (B–B) are listed.

Table 4 Interatomic distances in the structures of ACr_2B_6 (A = Ce, Th)^a

A = Ce	A≡Th		$A \equiv Ce$	A = Th
A: 4B1 280.6(3)	283.7(5) I	B1: 2B2	175.0(3)	176.0(4)
8B2 284.0(2)	286.7(3)	1 B 1	188.7(6)	187.6(8)
4B2 297.3(3)	297.6(4)	4Cr	222.7(2)	224.4(3)
2A 310.5(1)	315.8(1)	2A	280.6(4)	283.7(5)
4Cr 327.5(1)	329.6(1) H	B2: 1B1	175.0(3)	176.0(4)
4Cr 352.5(1)	353.9(1)	2B2	179.9(2)	182.0(3)
Cr: 2B2 212.6(3)	213.7(4)	1Cr	212.6(3)	213.7(4)
4B1 222.7(2)	224.4(3)	2Cr	222.7(2)	224.8(3)
4B2 222.7(2)	224.8(3)	2A	284.0(2)	286.7(3)
1Cr 257.5(1)	257.8(1)	1 A	297.3(3)	297.6(4)
2Cr 310.5(1)	315.8(1)			
2A 327.5(1)	329.6(1)			
2A 352.5(1)	353.9(1)			

^a All distances shorter than 470 pm (A-A, A-Cr), 360 pm (Cr-Cr, A-B, Cr-B) and 290 pm (B-B) are listed.

B-B bonds within the B_6 octahedra (B2-B3, 179 pm; B2-B2, 185 pm) are longer than most other B-B bonds. The shortest B-B bond of 167 pm is formed between two B3 atoms along the *c* direction of the tetragonal compound connecting two octahedra. This short bond may be regarded as corresponding to a classical two-electron bond as discussed previously for CaB₆ and LaB₆ [13-15]. In the structure of ThB₆, which is isotypic with CaB₆ and LaB₆, the short B-B

Table 5									
Interatomic	distances	in	the	structures	of	ThB₄	and	ThB ₆	a

			and the second se	
4B3	277.8(7)	B1:	2B2	174(2)
4B2	281(1)		1B1	184(2)
4B2	287(1)		4Th	294.8(8)
4B1	294.8(8)		2Th	309(1)
2B1	309(1)	B2:	1B1	174(2)
4Th	374.7(1)		2 B 3	179(2)
1Th	380.4(1)		2 B 2	185(3)
2Th	411.2(1)		2Th	281(1)
			2Th	287(1)
		B3:	1B3	167(3)
			4B2	179(2)
			1B3	245(3)
			4Th	277.8(7)
24B	300.4(6)	B:	1B	161(1)
6Th	409.3(1)		4B	175.7(8)
			4Th	300.4(2)
	4B3 4B2 4B1 2B1 4Th 1Th 2Th 24B 6Th	4B3 277.8(7) 4B2 281(1) 4B2 287(1) 4B1 294.8(8) 2B1 309(1) 4Th 374.7(1) 1Th 380.4(1) 2Th 411.2(1) 24B 300.4(6) 6Th 409.3(1)	4B3 277.8(7) B1: 4B2 281(1) 4B2 4B1 294.8(8) 2B1 2B1 309(1) B2: 4Th 374.7(1) 1Th 1Th 380.4(1) 2Th 2Th 411.2(1) B3: 24B 300.4(6) B: 6Th 409.3(1) B:	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

^a All distances shorter than 530 pm (Th-Th), 410 pm (Th-B) and 290 pm (B-B) are listed.



Fig. 3. Crystal structure and coordination polyhedra of ThCrB₄. All atoms are situated on mirror planes extending perpendicular to the projection direction. Atoms connected by thick (z = 1/2) and thin (z = 0) lines are at the same height. For the metal atoms, only the lower halves of the coordination polyhedra are shown.

bond between the octahedra is even shorter (161 pm), while the B-B bonds within the octahedra have a bond distance of 176 pm.

Although CaB_6 is a semiconductor [16], LaB_6 [17]



Fig. 4. The CeCr₂B₆- type structure of ThCr₂B₆. All atoms are situated on mirror planes at x = 1/2 (thick lines) and x = 0 (thin lines). In the middle part of the drawing, the three-dimensional infinite boron network is outlined. Below, this network is shown from a slightly different viewpoint.

and ThB_6 [9] are metallic conductors. ThB_6 is even superconducting [18]. Metallic conductivity has also been reported for ThB_4 [9] and this is also observed for the three ternary compounds characterized in the present investigation. ThB₄ and ThB₆ are reported to have very small, nearly temperature-independent, susceptibilities [9], indicating Pauli paramagnetism. For ThB₆, negative susceptibilities were observed, showing that the absolute value of the core diamagnetism is greater than the Pauli paramagnetism. The low values of the magnetic susceptibilities of $CeCr_2B_6$ and ThCr₂B₆ (Fig. 1) may also be ascribed to Pauli paramagnetism, as discussed above. For ThCrB₄, the upturn of the magnetic susceptibility curve at low temperatures should possibly not be dismissed entirely as being due to paramagnetic impurities or paramagnetic surface states. However, when this curve is fitted to the modified Curie-Weiss law as formulated above, a magnetic moment of only $\mu_{exp} = 0.8 \ \mu_{B}$ is obtained



Fig. 5. Crystal structures of ThB_4 and ThB_6 . Most boron atoms of ThB_4 and all boron atoms of the CaB_6 -type structure of ThB_6 form B_6 octahedra which are connected via B-B bonds, thus forming three-dimensional infinite networks. Only the lower halves of the coordination polyhedra of the thorium atoms are shown.

from the temperature-dependent part of this equation, much less than the value of 1.73 $\mu_{\rm B}$ expected for one unpaired electron per chromium atom.

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