

SmFeB₄ – A New Ternary Boride of the YCrB₄ Type

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Abstract. SmFeB₄, *Pbam*, *Z* = 4, *a* = 5.958 (5), *b* = 11.53 (1), *c* = 3.465 (4) Å, *D_c* = 6.96 (2) Mg m⁻³, μ(Mo *Kα*) = 30.6 mm⁻¹. For the first time, the B atom parameters of a YCrB₄ isotype have been established from crystallographic data. Refinement of the structure with anisotropic thermal parameters for Sm and Fe and fixed isotropic parameters for B led to a final *R* = 0.04 for 361 reflections.

Introduction. In an attempt to synthesize tetragonal ternary borides *RT₄B₄* (*R* = rare-earth metal, *T* = transition metal) containing Fe as the transition element, we have found a new orthorhombic phase in the Sm–Fe–B system. The lattice parameters and space group suggested a YCrB₄-type structure (Kuz'ma, 1970*a*) of composition SmFeB₄. The existence of such a compound was interesting because, to our knowledge, the only other YCrB₄ isotype containing Sm so far reported is SmCrB₄ (Table 1). A refinement of the structure of SmFeB₄ was desirable, since all atomic parameters of the YCrB₄ type, in particular those of the B atoms, are only known with low precision. This may be seen from the only available single-crystal study: *R* = 0.09 for 60 observed *hk0*, *R* = 0.19 for all 119 *hk0*, *R* = 0.12 for 76 observed *hkl* (Kuz'ma, 1970*a*).

A single crystal was isolated from a multiphase sample prepared by arc-melting. Integrated intensities were collected in the θ – 2θ scan mode up to a limit of $\sin \theta/\lambda = 0.70 \text{ \AA}^{-1}$ on an automatic four-circle diffractometer (Philips PW 1100, Mo *Kα* radiation, graphite monochromator). Of 400 unique reflections, 257 had *I* > 3σ(*I*). Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). Weights $w = 1/\sigma^2(F)$ were applied and the data were corrected for spherical absorption.

The refinement was performed in two steps. In the first, only the Sm and Fe atoms were considered. The parameters of YCrB₄ given by Kuz'ma (1970*a*) were used as starting values for a least-squares refinement with *CRYLSQ* of the *XRAY* system (1976). Positional

and anisotropic thermal parameters were refined, and $R = \sum |\Delta F| / \sum |F_o|$ converged at 0.09. At this point, a difference map was calculated. As can be seen from Fig. 1, this map reveals all four symmetry-independent B positions. In the second step, the positions of these atoms were refined together with Sm and Fe. Since the refined thermal parameters of two B positions were not positive definite, the isotropic thermal parameters for all B atoms were kept fixed at 0.008 Å². The final *R* was 0.04. The atomic and thermal parameters of SmFeB₄ and YCrB₄ are presented in Table 2.† A comparison of selected bond distances is given in Table 3.

† Lists of structure factors and anisotropic thermal parameters for Sm and Fe have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35423 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Ternary borides of the YCrB₄ and ThMoB₄ structure types

	V	Cr	Mn	Fe	Co	Mo	Ru	W	Re	Os
(i) YCrB ₄ type										
Sc		(a)*					(m)*			
Y	(b)	(a)	(b)	(b)*	(b)*	(c)	(m)	(c)	(c), (l)	(m)
La						(c)*	(m)*			
Ce		(e)		(d)*	†	(c)*	(m)*		(l)*	
Pr		(k)					(m)*			
Nd		(k)		(n)*			(m)*			
Sm		(k)		(p), (m)*			(m)*			
Eu										
Gd	(b)	(a)	(b)	(n)	(l)	(c)	(m)	(c)	(c)	(m)
Tb	(b)	(a)	(b)			(c)	(m)	(c)	(c)	(m)
Dy	(b)	(a)	(b)			(c)	(m)	(c)	(c)	(m)
Ho	(b)	(a)	(b)			(c)	(m)	(c)	(c)	(m)
Er	(b)	(a)	(b)			(c)	(m)	(c)	(c)	(m)
Tm		(c)					(m)		‡	(m)
Yb		(a)*								
Lu	(b)*	(a)	(b)*							
U	(g), (h)	(h)	(g)	(g), (h)	(g), (h)	(h)*		(h)*	(h)*	
(ii) ThMoB ₄ type										
U						(g)		(g)	(g)	
Th	(f)					(f)		(f)	(f)	

References: (a) Kuz'ma (1970*a*); (b) Kuz'ma (1970*b*); (c) Kuz'ma & Svarichevskaya (1972); (d) Bilonizhko & Kuz'ma (1972); (e) Kuz'ma, Svarichevskaya & Fomenko (1973); (f) Rogl & Nowotny (1974); (g) Rogl & Nowotny (1975); (h) Val'ovka & Kuz'ma (1975); (i) Chaban & Kuz'ma (1977); (k) Mikhailenko & Kuz'ma (1977); (l) Mikhailenko, Kuz'ma & Sobolev (1977); (m) Rogl (1978); (n) Chaban, Kuz'ma, Bilonizhko, Kachmar & Petriv (1979); (p) Present work.

* Preparation attempted, but no YCrB₄ phase observed.

† CeCoB₄ of unknown structure (Bilonizhko & Kuz'ma, 1974).

‡ *Structure Reports*, 41A, 122.

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Table 2. Atomic parameters (metal: $\times 10^4$, boron: $\times 10^3$) and equivalent isotropic thermal parameters ($\times 10^4$) for SmFeB₄ (present work) and YCrB₄ (Kuz'ma, 1970a)

The space group is *Pbam* (No. 55). E.s.d.'s are given in parentheses.

	SmFeB ₄	YCrB ₄	
Sm, Y 4(g)	<i>x</i>	1259 (2)	1250*
	<i>y</i>	1505 (1)	1500
	<i>z</i>	0	0
	<i>U</i> (Å ²)	63 (5)	-†
Fe, Cr 4(g)	<i>x</i>	1289 (6)	1250
	<i>y</i>	4137 (4)	4190
	<i>z</i>	0	0
	<i>U</i> (Å ²)	60 (10)	-
B(1) 4(h)	<i>x</i>	285 (5)	280
	<i>y</i>	314 (3)	315
	<i>z</i>	500	500
	<i>U</i> (Å ²)‡	8	-
B(2) 4(h)	<i>x</i>	373 (5)	340
	<i>y</i>	463 (3)	465
	<i>z</i>	500	500
	<i>U</i> (Å ²)	8	-
B(3) 4(h)	<i>x</i>	399 (5)	385
	<i>y</i>	47 (3)	50
	<i>z</i>	500	500
	<i>U</i> (Å ²)	8	-
B(4) 4(h)	<i>x</i>	479 (5)	485
	<i>y</i>	187 (3)	180
	<i>z</i>	500	500
	<i>U</i> (Å ²)	8	-

* No e.s.d.'s were given.

† No thermal parameters were given.

‡ The boron thermal parameters were assumed and kept fixed during refinement.

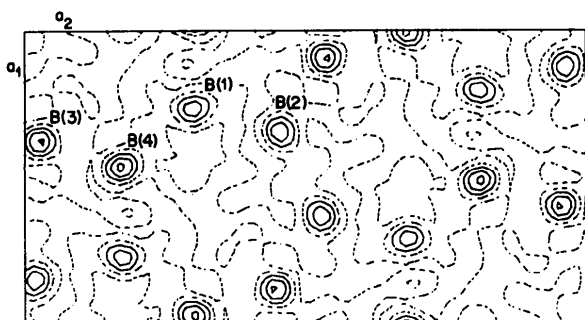


Fig. 1. Section of the difference map of SmFeB₄ at $z = \frac{1}{4}$. The contour interval is $3.5 e \text{ \AA}^{-3}$. Broken contours represent zero and negative electron densities.

Discussion. SmFeB₄ belongs to the class of borides with planar boron nets similar to ThMoB₄ and Y₂ReB₆ (Nowotny & Rogl, 1977). In YCrB₄ (and SmFeB₄), these nets consist of five- and seven-membered rings.

Each B atom has six metal atom neighbors which occupy the vertices of distorted trigonal prisms BR_4T_2 and BR_2T_4 (Kuz'ma, 1970a). Our study confirms this model. However, there are significant differences in the atomic parameters of the metal atoms and even more so of the B atoms between Kuz'ma's model and our results. Kuz'ma places the B atoms at the approximate centers of the trigonal prisms, which leads to a relatively small spread of the crystallographically non-equivalent metal–boron distances, but to a rather uneven distribution of the B–B distances within the five- and seven-membered rings. Our refinement, however, indicates that the B atoms are not centering their respective trigonal metal prisms, *i.e.* the crystallographically non-equivalent metal–boron distances show a relatively large spread. As can be seen from Table 3, the B atoms are displaced from their prism center in such a way as to achieve more equal bond distances within the planar boron nets.

Besides SmFeB₄, the only other known representative of the YCrB₄ type containing Sm is SmCrB₄ (Table 1). This is surprising because YCrB₄-type borides exist over a wide range of *T* elements with Gd and all *R* elements following it in the periodic table. On the other hand, the ThMoB₄ structure type (Rogl & Nowotny, 1975), which is an orthorhombic stacking variant of YCrB₄, also exists over a wide range of *T* elements but appears to form only in the presence of large atoms such as Th and U (Table 3). However, the absence of these two structure types with large lanthanide atoms may only be apparent. The few cases where an unsuccessful attempt to prepare RTB_4 compounds has been stated are marked with asterisks in Table 1. With Fe as the transition metal, no compounds with composition RTB_4 were found in isothermal sections of the system Ce–Fe–B at 800 K (Bilonizhko & Kuz'ma, 1972) and the systems Sm–Fe–B at 900 K and Nd–Fe–B at 900 and 700 K (Chaban, Kuz'ma, Bilonizhko, Kachmar & Petriv, 1979). In this regard, it is of interest that our sample was obtained from an arc-melted ingot, which underwent quasi quenching from the liquid state. This could indicate that SmFeB₄ is actually metastable and that the range of existence for the YCrB₄ structure may be extended toward large rare-earth ions if similar preparation conditions were employed. In view of the large number of YCrB₄- and ThMoB₄-type borides already known it would seem that neither the valence-electron concentration nor the *R/T* atom radius ratio are critical parameters for their stability. Our results rather show that the B–B interactions within the planar B nets are one of the stabilizing factors.

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Table 3. *Interatomic distances (Å) for SmFeB₄ (present work) and YCrB₄ (Kuz'ma, 1970a)*

E.s.d.'s are in parentheses.

SmFeB ₄		YCrB ₄		SmFeB ₄		YCrB ₄	
Sm-2Sm	3.465 (4)	Y-2Y	3.46	B(1)-2Sm	2.70 (2)	B(1)-2Y	2.72
2Sm	3.760 (3)	Y	3.75	2Sm	2.73 (2)	2Y	2.73
Sm	3.781 (3)	2Y	3.76	2Fe	2.28 (2)	2Cr	2.30
Fe	3.035 (5)	Cr	3.04	B(2)	1.80 (4)	B(2)	1.76
Fe	3.052 (5)	Cr	3.08	B(4)	1.82 (4)	B(4)	1.76
Fe	3.087 (5)	2Cr	3.09	B(4)	1.87 (4)	B(4)	1.97
Fe	3.097 (5)	2B(1)	2.72				
2B(1)	2.70 (2)	2B(1)	2.73	B(2)-2Sm	2.64 (2)	B(2)-2Y	2.75
2B(1)	2.73 (2)	2B(2)	2.75	2Sm	2.77 (2)	2Y	2.76
2B(2)	2.64 (2)	2B(2)	2.76	2Fe	2.33 (2)	2Cr	2.22
2B(2)	2.77 (2)	2B(3)	2.59	B(1)	1.80 (4)	B(1)	1.76
2B(3)	2.66 (2)	2B(4)	2.74	B(2)	1.73 (4)	B(2)	2.07
2B(4)	2.70 (2)	2B(4)	2.78	B(3)	1.89 (4)	B(3)	1.66
2B(4)	2.76 (2)						
Fe-Sm	3.035 (5)	Cr-Y	3.04	B(3)-2Sm	2.66 (2)	B(3)-2Y	2.59
Sm	3.052 (5)	Y	3.08	2Fe	2.25 (2)	2Cr	2.28
Sm	3.087 (5)	2Y	3.09	2Fe	2.32 (2)	2Cr	2.29
Sm	3.097 (5)	Cr	2.38	B(2)	1.89 (4)	B(2)	1.66
Fe	2.513 (5)	2B(1)	2.30	B(3)	1.62 (4)	B(3)	1.79
2B(1)	2.28 (2)	2B(2)	2.22	B(4)	1.68 (4)	B(4)	1.61
2B(2)	2.33 (2)	2B(3)	2.28				
2B(3)	2.25 (2)	2B(3)	2.29	B(4)-2Sm	2.70 (2)	B(4)-2Y	2.74
2B(3)	2.32 (2)	2B(4)	2.23	2Sm	2.76 (2)	2Y	2.78
2B(4)	2.27 (2)			2Fe	2.27 (2)	2Cr	2.23
				B(1)	1.82 (4)	B(1)	1.76
				B(1)	1.87 (4)	B(1)	1.97
				B(3)	1.68 (4)	B(3)	1.61

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