



Letter

Studies on the new UFe_2B_6 phaseM. Dias^{a,b}, P.A. Carvalho^b, O. Sologub^c, L.C.J. Pereira^a, I.C. Santos^a, A.P. Gonçalves^{a,*}^a Departamento de Química, Instituto Tecnológico e Nuclear/CFMUL, P-2686-953 Sacavém, Portugal^b Departamento de Engenharia de Materiais, Instituto Superior Técnico, Av Rovisco Pais, 1049-001 Lisboa, Portugal^c Institut für Physikalische Chemie der Universität Wien, Währingerstraße 42, A-1090 Wien, Austria

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ABSTRACT

The new UFe_2B_6 compound was synthesized by arc melting followed by crystal growth during annealing for 5 h at 1700 °C. The structure was refined down to $R=0.011$ and $wR_2=0.025$ from single crystal X-ray diffraction data. UFe_2B_6 crystallizes with the CeCr_2B_6 -type structure ($Immm$ space group no. 71, $a=0.31372(6)$ nm, $b=0.61813(11)$ nm, $c=0.82250(17)$ nm, $V=0.15950(5)$ nm³, $Z=2$, $\rho=4.316$ mg/m³). Preliminary magnetic results points to the inexistence of any magnetic anomaly down to 2 K.

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1. Introduction

Ternary intermetallic borides of AM_xB_y type ($A=f$ element and $M=d$ metal) have attracted considerable interest due to their diversity of unusual physical characteristics [1], which extend from permanent magnetism with unusually large magnetic coercive fields, like in SmCo_4B [2] and SmNi_4B [3], to unconventional magnetic ordering, as seen for UNi_4B [4]. However, in spite of such variety of physical behaviors AM_xB_y compounds are still largely unexplored.

Results on the U–Fe–B ternary system were previously reported by Valyovka and Kuzma [5,6], who identified the UFeB_4 and UFe_3B_2 compounds. Recent systematic studies on the isothermal section at 950 °C revealed the existence of two other ternary compounds: (i) UFe_4B , with a hexagonal structure closely related to the CeCo_4B -type structure ($a=0.4932(1)$ nm and $c=0.7037(2)$ nm [7]); and (ii) $\text{U}_2\text{Fe}_{21}\text{B}_6$, with a cubic Cr_{23}C_6 -type structure ($a=1.0766(4)$ nm [7]). Aiming for a comprehensive structural and physical characterization of the ternary compounds belonging to the U–Fe–B system, the study of a new intermetallic UFe_2B_6 was undertaken. Here we present its crystal structure determination and refinement, together with a preliminary magnetic characterization.

2. Experimental

A sample with U:2Fe:6B nominal composition was prepared by melting together the elements (purity >99.9 at.%) in an arc furnace equipped with a cold crucible under an argon atmosphere. The surface of uranium pieces was deoxidized in diluted nitric

acid prior to melting. In order to ensure homogeneity, the samples were melted at least three times before quenching to room temperature. No losses higher than 1 wt.% were observed. The samples were subsequently annealed at 1700 °C for 5 h.

X-ray powder diffractograms were collected at room temperature with a Philips X'Pert diffractometer using $\text{Cu K}\alpha$ radiation and with a 2θ -step size of 0.02° from 10° to 70°. The Powder Cell software package [8] was used to simulate diffractograms for comparison with experimental data.

Single crystals suitable for the X-ray measurements were isolated from the annealed sample. Data was collected on a Bruker AXS APEX CCD X-ray diffractometer equipped with an Oxford Cryosystems low temperature device at 150 K in ω and φ scans mode. Data collection, refinement and data reduction were done using the SMART and SAINT software packages [9]. A semi empirical absorption correction was carried out with SADABS [10]. The structures were solved by direct methods using SIR97 [11] and refined by fullmatrix least squares methods with the SHELX-97 [12] program using the built in atomic scattering factors and the WINGX software package [13].

Preliminary magnetization measurements were done on a fixed powder of the polycrystalline annealed U:2Fe:6B sample. The measurements were carried out using a S700X SQUID magnetometer (Cryogenic Ltd.) in the 2–300 K temperature range and under applied fields up to 5 T.

3. Results and discussion

X-ray powder diffraction showed that the annealed sample is mainly composed by the UFe_2B_6 compound. However, a significant amount of the paramagnetic UB_4 phase [14] (around 30%) is also observed.

Single crystal X-ray diffraction data indicate that the UFe_2B_6 compound adopts the CeCr_2B_6 -type structure in the $Immm$ space group (no. 71). Details on the single crystal data collection and structural refinement are listed in Table 1. The anisotropic displacement parameters (U_{xx}) for all atoms are given in Table 2. Selected interatomic distances and coordination numbers for the different atoms are presented in Table 3.

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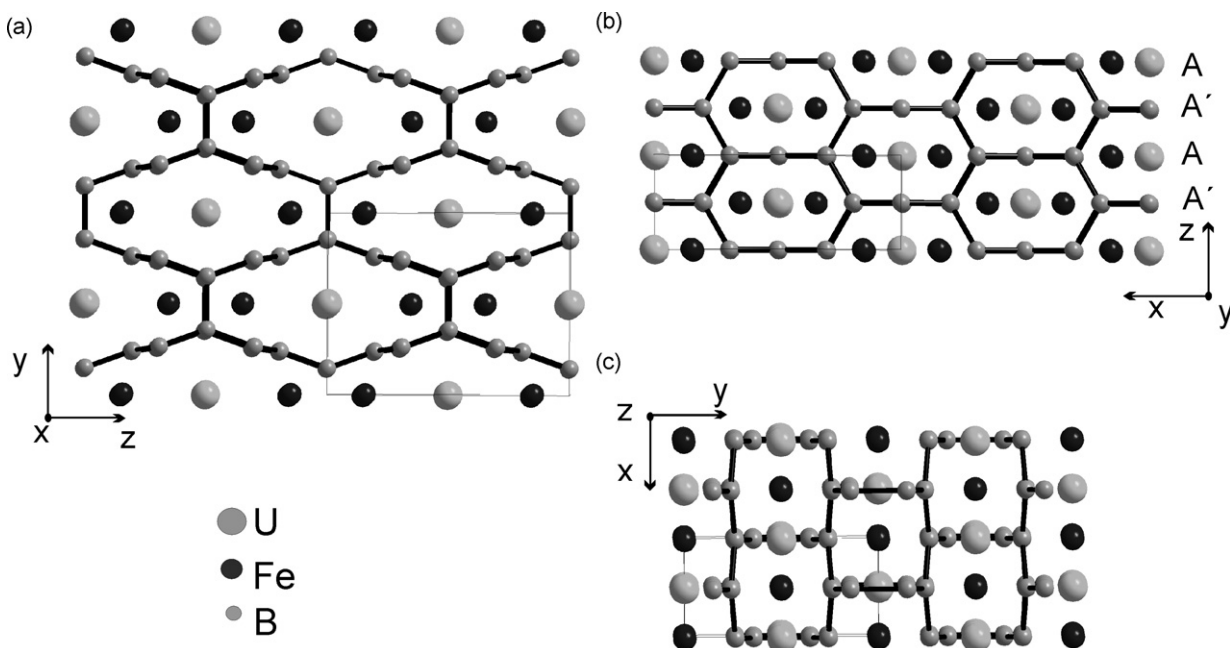
Table 1
Crystal data and structure refinement for UFe_2B_6 single crystal.

Space group	<i>Immm</i> (no. 71)
Lattice parameters (nm)	
<i>a</i>	0.31372(6)
<i>b</i>	0.61813(11)
<i>c</i>	0.82250(17)
Cell volume (nm ³)	0.15950(5)
Formula per unit cell	2
Calculated density (mg/m ³)	4.316
Temperature (K)	150(2)
Absorption coefficient (mm ⁻¹)	29.668
Data collection	CCD Mo K α , 0.71073
Theta range for data collection (°)	4.12–35.98
Data set	$-5 \leq h \leq 5$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$
Number of measured reflections	1325
Number of unique reflections	246
Number of reflections with $I > 2\sigma(I_0)$	246
Number of refined parameters	18
R_1, wR_1 ($I > 2\sigma(I_0)$)	0.0106, 0.0252
R_2, wR_2 all data	0.0106, 0.0252
Goodness of fit on F^2	1.124
Highest/lower peaks of electron density (e/Å ³)	2.377–1.990
Refinement method, software	Full matrix least squares on F^2

In the UFe_2B_6 structure the boron atoms form a three dimensional infinite network in which rings with 14-, 8-, and 10 atoms are discernible along the directions [1 0 0], [0 1 0] and [0 0 1], respectively (Fig. 1). Along the [0 1 0] direction (Fig. 1b) two types of layers, A and A', in which A' is 1/2 a shifted in relation to A, can be found.

Table 2
Atomic positions and thermal parameters (nm²) for UFe_2B_6 compound obtained from X-ray single crystal diffraction.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U ₁	2d	0	1/2	0	0.0252(8)	0.0165(8)	0.0076(8)	0.000	0.000	0.000
Fe ₁	4i	1/2	1/2	0.65308	0.0344(18)	0.0206(19)	0.0075(18)	0.000	0.000	0.000
B ₁	4h	0	0.3544(6)	1/2	0.049(12)	0.031(14)	0.013(12)	0.000	0.000	0.000
B ₂	8l	0	0.2604(5)	0.3044(3)	0.042(9)	0.034(10)	0.030(9)	-0.004(8)	0.000	0.000

**Fig. 1.** Projections of the UFe_2B_6 on along (a) [1 0 0], (b) [0 1 0] and (c) [0 0 1].**Table 3**
Selected interatomic distances (*d*, nm) for atoms in the UFe_2B_6 compound.

U ₁	4B ₁	0.2695(3)
	8B ₂	0.2764(2)
	4B ₂	0.2909(1)
	4Fe ₁	0.3257(1)
	4Fe ₁	0.3337(3)
Fe ₁	2U ₁	0.3137(2)
	2B ₂	0.2034(3)
	4B ₂	0.2186(2)
	4B ₁	0.2203(2)
	2Fe ₁	0.2518(1)
B ₁	1Fe ₁	0.3815(1)
	2U ₁	0.3256(7)
	2U ₁	0.3337(3)
	2B ₂	0.1711(3)
	1B ₁	0.1799(8)
B ₂	4Fe ₁	0.2203(2)
	2U ₁	0.2695(3)
	2B ₂	0.1810(3)
	1Fe ₁	0.2034(3)
	2Fe ₁	0.2186(2)
	1B ₁	0.1711(3)
	2U ₁	0.2764(2)
	1U ₁	0.2909(1)

The coordination polyhedra for UFe_2B_6 are shown in Fig. 2. The U atoms (Fig. 2a) occupy the 2d positions and have a coordination polyhedron composed by 16 boron, 8 iron and 2 uranium atoms. Fe atoms (Fig. 2b) occupy the 4j positions having as nearest neighbors 4 uranium, 10 boron and 3 other iron atoms. The 4h (B₂) and 4l (B₁) boron positions are represented in Fig. 2c and d respectively, with a coordination number of 9, and different atomic environments. In

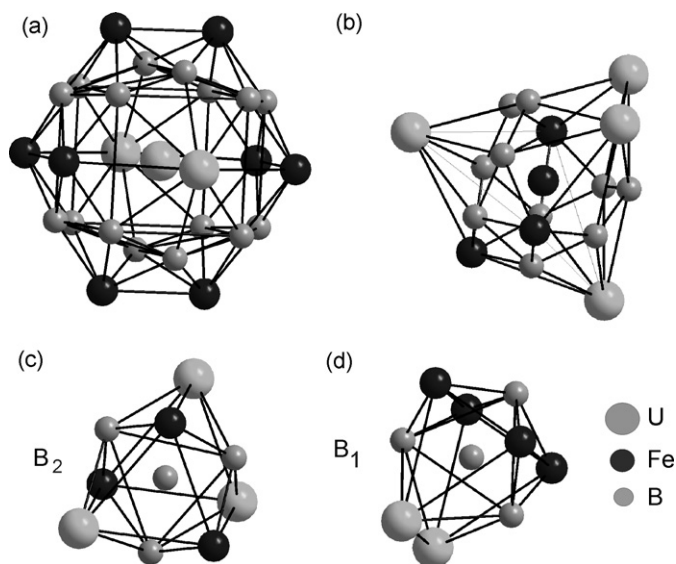


Fig. 2. Coordination polyhedra for (a) U atom, (b) Fe atom, (c) B_2 atom and (d) B_1 atom.

B_1 , the coordination polyhedron is composed by 3 boron, 2 uranium and 4 iron atoms. The environment of B_2 consists on the same number of boron atoms, but with one iron and one uranium atom less. All B atoms have therefore three boron neighbors with a B–B distance in the 0.171–0.181 nm range. The uranium atoms in UFe_2B_6 have sixteen boron neighbors and the average U–B interatomic distance is 0.278 nm, which is significantly higher than the sum of U–B radius (0.244 nm). Fe atoms have 10 boron neighbors and the Fe–B distances extent between 0.203 and 0.220 nm. It is important to note that the Fe– B_2 distance (0.203 nm) is remarkable shorter than the sum of the two radii (0.217 nm). The short Fe–Fe distance of 0.252 nm is also noteworthy, as it suggests strong metal–metal interactions and therefore points to a metallic bonding character.

The U–U distance in UFe_2B_6 is 0.314 nm, which is above the sum of metallic radii (0.304 nm). However, this value is below the Hill limit (0.34–0.35 nm), pointing to a significant 5f–5f orbital overlap and to a non-magnetic uranium nature in this compound. The isostructural $ThCr_2B_6$ boride has a Th–Th distance of 0.316 nm [15], well below the sum of metallic radii (0.360 nm), indicating a metallic bond character between the two thorium atoms. For $CeCr_2B_6$ the same situation occurs [15].

A preliminary magnetization characterization of the U:2Fe:6B sample, made between 2 and 300 K, does not show any anomaly in this temperature range, showing rather low values of susceptibility. However, these results do not allow us to make more considerations due to the high percentage of UB_4 as impurity that, in this range of temperature, shows an itinerant 5f behavior [14]. Nevertheless, it is interesting to notice that the $CeCr_2B_6$ and $ThCr_2B_6$ isostructural compounds have been reported to behave like Pauli paramagnets [15]. A more complete magnetic study will be undertaken as soon as a single phase samples would be available.

We can conclude that a new compound, UFe_2B_6 , exists in the ternary U–Fe–B system. It crystallizes in the $CeCr_2B_6$ -type structure, with the shorter U–U distances below the Hill limit. No magnetic anomaly was observed between 2 and 300 K, but the high amount of UB_4 in the sample does not allow us to make any other considerations.

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