Powder Neutron Diffraction of α-UB$_2$C (α-UB$_2$C-Type)

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The crystal structure of α-UB$_2$C (low temperature modification below $T = 1675(25)°C$) was determined from powder X-ray data (RT) and powder neutron diffraction data (at 29 K) employing the Rietveld–Young–Wiles profile analysis method. α-UB$_2$C crystallizes in the orthorhombic space group *Pmma* with $a = 0.60338(3)$, $b = 0.35177(2)$, $c = 0.41067(2)$ nm, $V = 0.0872$ nm^3, $Z = 2$. The residuals of the neutron refinement were $R_I = 0.032$ and $R_F = 0.043$. The crystal structure of α-UB$_2$C is a new structure type where planar nonregular 6^3-U-metal layers alternate with planar nonmetal layers of the type (B$_6$C$_2$)^3. Boron atoms are in a typical triangular prismatic metal surrounding with a tetrakaidekahedral coordination B[U$_6$B$_2$C$_1$], whereas carbon atoms occupy the center points of rectangular bipyramids C[U$_4$B$_2$]. The crystal structure of α-UB$_2$C derives from the high temperature modification β-UB$_2$C (ThB$_2$C-type, $R\overline{3}m$), which reveals a similar stacking of slightly puckered metal layers 6^3, alternating with planar layers B$_6 \cdot$ (B$_6$C$_3$)^2. The phase transition from β-UB$_2$C to α-UB$_2$C is thus essentially generated by carbon diffusion within the $\frac{2}{\infty}$ B$_6 \cdot$ (B$_6$C$_3$)^2 layers to form $\frac{2}{\infty}$ (B$_6$C$_2$)^3 layers. © 1991 Academic Press, Inc.

Introduction

The formation of ternary actinoid metal–boron–carbon compounds with the formulas AnBC and AnB$_2$C is a general characteristic of the early actinoid elements $An =$ Th, U, Pu, and Np (for a review see Ref. (*1*)). Among these compounds, the behavior of UB$_2$C is unique, insofar as it was found (*2*) to reveal a low- and a high-temperature modification ($T_{tr} = 1675(25)°C$) with rather distinct magnetic behavior: whereas β-UB$_2$C, which crystallizes with the ThB$_2$C-type (*3*), is a soft ferromagnet ($T_c = 85$ K), α-UB$_2$C is weakly paramagnetic (for details see Ref. (*4*)). As magnetism in the early actinoid metal compounds is primarily based on the nature of the strongly U–U distance-dependent localization or delocalization of the U-5f electrons (*5*), a close inspection of the crystal structure and bonding distances of α-UB$_2$C is the subject of the present work.

Experimental

Preparation and Characterization by X-Rays

For neutron diffraction a sample of a total amount of ca. 15 g was prepared by arc melting the elements together on a water cooled copper hearth using a nonconsum-

able thoriated tungsten electrode in a Ti/Zr-gettered 5N-argon atmosphere. The starting materials were depleted uranium in the form of platelets, 99.9% as supplied by E. Merck (Darmstadt, FRG), surface cleaned in diluted HNO_3 prior to use and compacted mixtures of carbon powder (Carbonne Lorraine, France, impurities <200 ppm) and boron powder, 98.15% ^{11}B-enriched isotope, (Centronics, UK; impurities <0.01%). To ensure homogeneity, the alloy buttons were flipped over and remelted several times; weight losses were checked to be within 1% of the original weight. To obtain the low-temperature modification, the alloy buttons were placed within a Knudsen-type graphite crucible and annealed for 180 hr at 1600°C in a tungsten sheet metal high-vacuum furnace at 10^{-4} Pa. Starting from a nominal composition 23 at% U, 47 at% B, and 30 at% C, virtually single phase and well-crystallized products were obtained. Precise lattice parameters and standard deviations were obtained by a least squares refinement of room-temperature Guinier–Huber X-ray powder data, using monochromatic $CuK\alpha_1$ radiation with an internal standard of 6N-pure Ge (a_{Ge} = 0.5657906 nm at RT).

Neutron Powder Diffraction

Neutron powder diffraction was performed at the SAPHIR-10 MW reactor (PSI, Switzerland) using the double-axis multi-counter neutron powder diffractometer with a neutron wavelength λ = 0.1706 nm (resolution $\Delta d/d \geq 4 \times 10^{-3}$; see Ref. (6)). Preferred orientation effects were minimized by powdering the sample to a grain size smaller than 30 μm. Further details concerning the experiment are summarized in Table I.

Precise atom parameters, occupation numbers, individual thermal factors, and profile parameters were derived from a least-squares powder profile refinement routine (7) including simultaneous refinement of the background. Neutron scattering lengths were taken from a recent compila-

TABLE I
EXPERIMENTAL DATA FOR α-UB_2C

Sample container	Vanadium double-cylinder, R_a/R_i = 5/4 mm
Temperature (K)	29 K
Radiation, wavelength (nm)	Neutrons, λ = 0.1706(1)
Absorption correction	μD = 0.39
Reactor	Saphir, PSI CH-Villigen
Monochromator	Germanium-(311)
Soller Slits	10'/–/12'
2θ Range (2θ)	3.0 to 134.9
Step-scan increment (2θ)	0.10
Coherent scattering lengths (fm)	U 8.417 $B[11]$ 6.646 C 6.646
Number of contributing reflections	77
Background	Background refinement (six parameters)
Preferred orientation	[001]
Number of variables	28
Largest element of correl. matrix	0.7
Maximal Δ/σ	<0.01
R values:	

$R_I = \|I_i(obs) - (1/c)I_i(calc)\|/\Sigma I_i(obs)$

$R_F = \|[I_i(obs)]^{\frac{1}{2}} - [I_i(calc)]^{\frac{1}{2}}\|/\Sigma[I_i(obs)]^{\frac{1}{2}}$

$R_P = \|Y_i(obs) - (1/c)Y_i(calc)\|/\Sigma Y_i(obs)$

$R_{WP} = [\Sigma w_i\|Y_i(obs) - (1/c)Y_i(calc)\|^2/\Sigma w_i\|Y_i(obs)\|^2]^{\frac{1}{2}}$

$R_e = \{(N - P + C)/\Sigma w_i Y_i^2(obs)\}^{\frac{1}{2}}$

$\chi^2 = \{R_{WP}/R_e\}^2$

Note. Symbols used: I_i, integrated intensity of reflection i; w_i, weighting function; Y_i, number of counts (background corrected) at 2θ; c, scale factor.

tion by Sears (8). A series of reliability measures were calculated, which are defined in detail in Table I.

When indexing the neutron data a small amount of graphite became obvious, which as an equilibrium phase is consistent with the nominal composition of the sample slightly richer in carbon, and which due to the small scattering power of the C-atoms has not been observed from previous X-ray exposures. Despite the fact that graphite was present in fairly small amounts it was decided to refine the neutron data as a two-
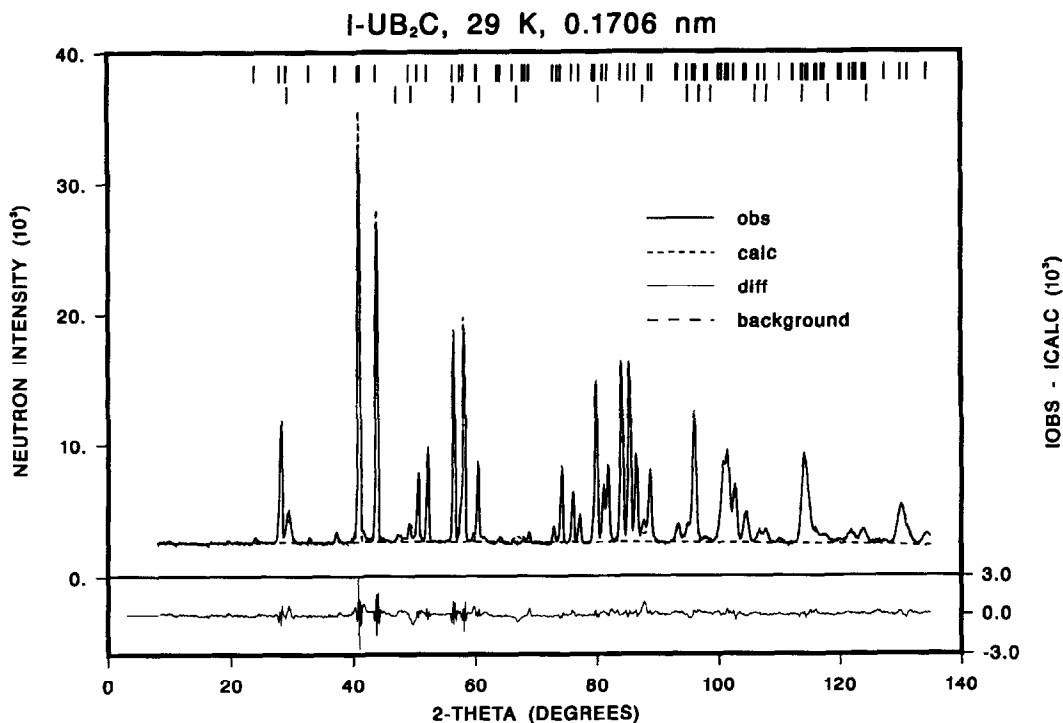
FIG. 1. Observed (solid line) and calculated (dotted line) neutron powder diffraction profile of α-UB$_2$C (λ = 0.1706 nm) at 29 K.

phase material α-UB$_2$C + C. The observed powder spectrum (corrected for ^{11}B absorption, see Table I) as used in the refinement is shown in Fig. 1.

Results and Discussion

Structure Determination

Complete indexation of the X-ray powder diagram was possible on the basis of a primitive orthorhombic unit cell found from a trial indexation by use of the automatic indexing program KOHL (9). The lattice parameters obtained at room temperature were a = 0.60363(13), b = 0.35251(2), c = 0.41091(3) nm; V = 0.08744 nm^3. A comparison of the atomic volumes with the volume of the unit cell, assuming a space filling of ca. 70%, yielded two formula units of UB$_2$C. A detailed

inspection of the X-ray intensities revealed a single set of systematic extinctions (hkO) for h = $2n$, and this observation is compatible with the following space groups: $Pmma$, $P222_1$, $Pmc2_1$, and $Pma2$.

On the basis of these results a structure model was developed in the space group with the highest symmetry $Pmma$, and satisfactory agreement between observed and calculated X-ray intensities is obtained for 2U in the (2e) sites ($\frac{1}{4}$, 0, z) with the free parameter value close to z_u = 0.30. Filling the triangular metal (U) prisms with boron atoms and the octahedral units U$_4$B$_2$, as typical for β-UB$_2$C, with carbon atoms, we obtain the following site distribution and atom parameters of the nonmetal atoms as the initial parameter set for the neutron data refinement: 4B in 4j (x $\approx$ 0.9, $\frac{1}{2}$, z $\approx$ 0.2) and 2C in 2d (0, $\frac{1}{2}$, $\frac{1}{2}$). This structure model refined satisfactorily for the neutron diffrac-

TABLE II

CRYSTALLOGRAPHIC DATA FOR α-UB$_2$C
(α-UB$_2$C-TYPE, AT 29 K)

Space group, $Pmma - D_{2h}^5$, No. 51, $Z = 2$; origin at center.

The expression for the individual isotropic temperature factor is $T = \exp\{-B(\sin\theta/\lambda)^2\}$. The standard deviations are in parentheses.

$a = 0.60338(3)$, $b = 0.35177(2)$, $c = 0.41067(2)$ nm, $c/a = 0.681$, $a/b = 1.715$, $V = 0.087165$ nm^3; the calculated density is: $\rho_x = 10.35$ M g m^{-3}.

Atom	Site	x	y	z	B (nm^2) $\times 10^2$
U	2e	$\frac{1}{4}$	0	0.2981(5)	0.21(4)
B	4j	0.9018(3)	$\frac{1}{2}$	0.1602(4)	0.42(4)
C	2d	0	$\frac{1}{2}$	$\frac{1}{2}$	0.34(4)

Note. Residuals: $R_I = 0.032$, $R_F = 0.043$, $R_P = 0.037$, $R_{WP} = 0.052$, $R_e = 0.015$, $\chi^2 = 10.2$ (for details see Table I).

TABLE III

INTERATOMIC DISTANCES FOR α-UB$_2$C
NEUTRON DIFFRACTION

U–2	U	0.4107(1)
U–2	U	0.3885(3)
U–2	U	0.3518(1)
U–2	U	0.3443(2)
U–4	B	0.2980(2)
U–4	B	0.2798(2)
U–4	B	0.2734(2)
U–4	C	0.2461(1)
B–2	U	0.2980(2)
B–2	U	0.2798(2)
B–2	U	0.2734(2)
B–1	B	0.1832(4)
B–1	B	0.1771(3)
B–1	C	0.1516(2)
C–4	U	0.2461(1)
C–2	B	0.1516(2)

tion data; the final structural and profile parameters as well as the residual values obtained from the least squares refinement including simultaneous refinement of the background (7) and of graphite as a second phase are presented in Table II. Atomic distances are shown in Table III. The occupancies of the nonmetal sites have been refined; however, no significant deviation from a full occupation was revealed. As seen from Fig. 1 and from the R values in Table II, observed and calculated neutron intensities are in excellent agreement. This is furthermore true for the X-ray powder intensity calculation employing the refined atom parameters from the neutron diffraction, thereby confirming the structure model. The unit cell dimensions obtained for graphite as the second but minor equilibrium phase were as follows (at 29 K): $a = 0.2466(2)$ and $c = 0.6736(5)$ and compare well with the data available in literature ($a = 0.2464$, $c = 0.6711$, see Ref. (10)).

Structural Chemistry

α-UB$_2$C crystallizes with a new structure type and is typical for the so-called non-

metal layer-type boron carbides usually found at a boron to metal ratio $B/M \approx 2$; for a recent review on the formation and crystal chemistry of borides including boron-rich boron-carbides see Ref. (11). In α-UB$_2$C planar 6^3-layers consisting of irreg-
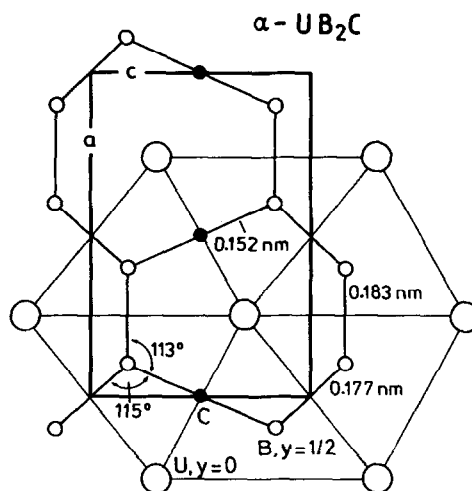

FIG. 2. Projection of the crystal structure of α-UB$_2$C along [010].

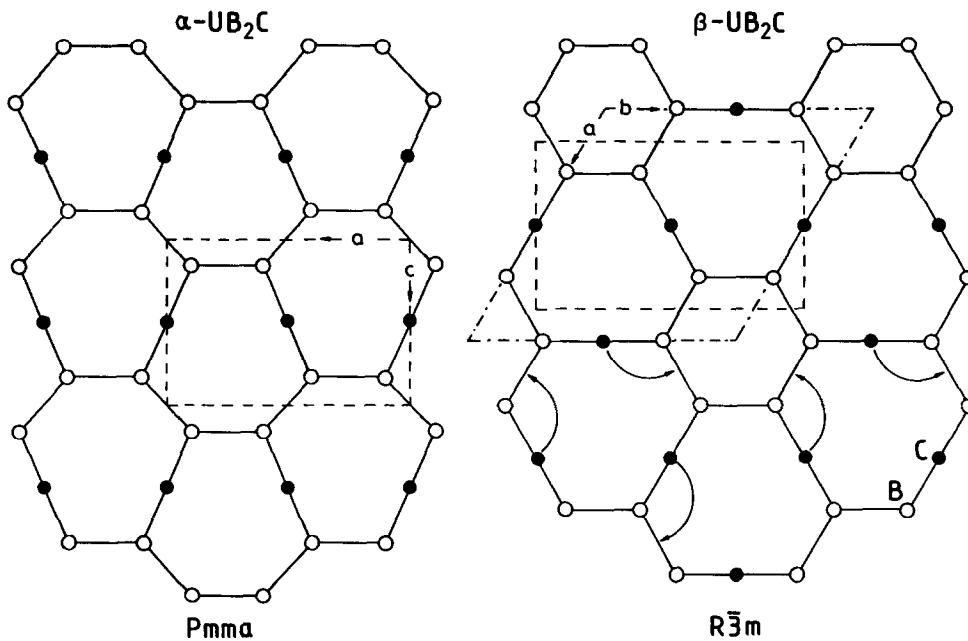FIG. 3. Comparison of the $\overset{2}{\infty}$ net type layers of boron and carbon atoms in α-UB₂C and β-UB₂C. The corresponding crystallographic units are outlined by dashed lines. The hexagonal unit cell of rhombohedral β-UB₂C is indicated by a thin solid line. The diffusion paths of the carbon atoms in the transition from β-UB₂C to the α-UB₂C type are shown by curved pointed arrows.

ular triangles whose vertices are occupied by uranium atoms alternate with planar nonmetal layers $\overset{2}{\infty}(B_6C_2)^3$ (in kagomé type notation, see also Fig. 2). As typical for most of the binary and ternary transition metal borides, boron atoms occupy the center points of the triangular metal (uranium) prisms BU_6 in tetrakaidekahedral coordination extended by two additional boron atoms and one carbon atom centering the lateral faces of the metal prism $B[U_6B_2C_1]$. Carbon atoms occupy the centers of rectangular bipyramids formed by four uranium atoms (in planar coordination) and two additional borons at the apices of the distorted octahedron $C[U_4B_2]$. Metal–nonmetal bond distances (average U–B is 0.2837 nm, U–C is 0.2461 nm) are close to the sum of radii and are within the range generally observed for actinoid

metal boroncarbides (*1*). This is particularly true for the single-bond boron–carbon distances of 0.1516 nm (*1*). The B–B–C bond angles observed are 113° and 115°, respectively. Boron atoms appear to be lined up in infinite kinked chains linked by the carbon atoms; the B–B–B bond angles within the chain are 132° and thus is close to the corresponding bond angles in a typical boron–boron zig-zag chain, i.e., as observed in UBC, a prototype boron chain type boron carbide (B–B–B, 125°, Ref. (*4*)). Among rare earth and actinoid metal boron carbides, α-UB₂C is the only representative so far and is closely related to the structure type of the β-UB₂C high temperature modification (ThB₂C-type). The introduction of a straight B–C–B unit into the common B–C net structures (see Ref. (*11*)) is the new characteristic element

of the two structure types α-UB$_2$C and ThB$_2$C. It is the formation of this structural unit, which is claimed to be responsible for the exceptional refractory properties when going from the α rhombohedral boron modification to the solid solution B$_{4-x}$C$_{1+x}$ (*12*), where a C–B–C unit is linking the B$_{12}$-icosahedra entangled in a weak three center bond in α-rhB. Despite the naturally identical structural base units, the structure types of α,β-UB$_2$C are distinctly different in the arrangement of B and C atoms within the planar nonmetal layers: there are B$_6 \cdot$ (B$_6$C$_3$)^2 type kagomé layers formed in β-UB$_2$C but (B$_6$C$_2$)^3 type layers in α-UB$_2$C. The constant average number of B and C members per nonmetal ring thus alters the local but not the average nonmetal coordination number of the U-atoms (CN$_{av}$(B,C) = 16). Though these atomic changes are rather subtle, they infer a drastic alternation from a ferromagnetic β-UB$_2$C to a weakly paramagnetic α-UB$_2$C (for details see Ref. (*4*)). From a comparison of the two structure types we see that the mechanism of the β-UB$_2$C $\rightleftharpoons$ α-UB$_2$C solid state transition at 1675(25)°C is generally performed by a diffusion of the carbon atoms within the β-UB$_2$C type $\frac{2}{\infty}$B$_6 \cdot$ (B$_6$C$_3$)^2 layers to generate the small grid $\frac{2}{\infty}$(B$_6$C$_2$)^3 layers of the α-UB$_2$C type (Fig. 3). This diffusion-activated process explains why (a) the β-UB$_2$C type phase is easily obtained from samples arc melted and radiation cooled, and (b) the production of homogeneous single phase α-UB$_2$C-type materials requires long term heat treatments just below the transition temperature.

Acknowledgments

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