JOURNAL OF SOLID STATE CHEMISTRY **26**, 275–279 (1978)

X-Ray Powder Profile Refinement of Zirconium in β-Rhombohedral Boron

BENGT CALLMER, LARS-ERIK TERGENIUS, AND JOHN O. THOMAS

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Received January 27, 1978

A Rietveld-type full-profile refinement technique, as adapted to Guinier–Hägg strictly $K\alpha_1$ monochromatized X-ray powder-film data (G. Malmros and J. O. Thomas, *J. Appl. Crystallogr.* **10**, 7–11 (1977)), has been used to refine the structure of a solid solution of zirconium in β-rhombohedral boron with composition $ZrB_{\sim 51}$. The space group is $R\bar{3}m$ (No. 166) with hexagonal cell dimensions $a = 10.9564(5)$, $c = 24.0201(13)$ Å, $V = 2497.1$ Å^3 and with 309.4 boron atoms per unit cell. The R value roughly comparable to the R_f value of single-crystal work is 0.063. Zirconium atoms partially occupy two nonequivalent holes in the β-boron structure (28% at an 18(*h*) and 18% at a 6(*c*) position).

Introduction

The β-rhombohedral polymorph of boron is invariably formed from the melt at temperatures above 1500°C. It is found to be stable down to room temperature. Appreciable amounts of metal can be dissolved in β-boron, as demonstrated in X-ray investigations of single crystals with compositions $CrB_{\sim 41}$ (*1*), $CuB_{\sim 28}$, $MnB_{\sim 23}$ (*2*), $CuB_{\sim 23}$ (*3*), $FeB_{\sim 49}$ (*4*), and $ScB_{\sim 28}$ (*5*).

The β-boron network is only slightly changed by the dissolved metal atoms. However, the unit cell expands and the microhardness increases, a maximum increase of 25% occurring for scandium and manganese (*6*).

The three largest holes in β-boron (*1*), denoted by $A(1)$, D, and E, are occupied by metal atoms in various amounts. The $A(1)$ hole is occupied by chromium, manganese, copper, and iron, and the D hole by the same atom types with the addition of scandium. The E hole is occupied by manganese, copper, and scandium. Chromium and copper thus behave differently, despite their equal atomic radii. Because of the large radius for scandium, the $A(1)$ hole is unoccupied. Scandium also occupies a position between two boron atom sites in the β-boron network, replacing these boron atoms in the structure. The present investigation, using the X-ray powder profile refinement technique, is aimed at discovering how zirconium, with the same atomic radius as scandium (1.60 Å), dissolves in β-boron.

Experiment and Refinement

Crystalline boron (H. C. Starck, Goslar, claimed purity 99·8%) and zirconium turnings (Koch-Light, Colnbrook, claimed purity 99.9% with less than 0.03% O) were melted under purified argon in an arc furnace equipped with a nonconsumable tungsten electrode and a water-cooled copper hearth. The sample, with nominal composition ZrB_{50}, was put into a zirconium diboride crucible and heat treated at 1750°C for 4 hr under 0.5 atm of argon. The sample was crushed in a steel mortar, yielding a powder suitable for the X-ray investigation.

0022-4596/78/0263-0275$02.00/0

The hexagonal unit-cell dimensions (space group: $R\bar{3}m$, $a = 10.9564(5)$, $c = 24.0201(13)$ Å, $V = 2497.1$ Å^3) were determined from a least-squares refinement of θ values obtained from a Guinier–Hägg X-ray powder film. The film was exposed with Cr$K\alpha_1$ ($\lambda = 2.289753$ Å) radiation and with silicon ($a = 5.431065$ Å) as the internal calibration.

A similar film without a calibration standard was taken to provide the profile intensity data. The data were measured with a SAAB Model 2 automatic film scanner (*7*, *8*) coupled on line to an IBM 1800 computer. The data processing and refinement were performed as described at length by Malmros and Thomas (*9*). Only some special features are referred to here. The conversion from observed transmission values to intensities was made using the expressions $I = 100D(1 + kD)$, and $D = \log_{10}(T_b/T_m)$, where T_b is the background transmission value and T_m the mean transmission value for a given revolution of the film in the scanner. The correction constant k for the nonlinear relative optical density was taken as 0.4. The data evaluation and processing, including a PLG factor correction, was made using the program PILT written by Malmros and Werner (*10*).

The refinement procedure is essentially the original method of Rietveld (*11*) for the refinement of neutron powder data adapted for use with the present form of X-ray powder data. The main difference is that the X-ray film profile is assumed to comprise a superposition of individual line profiles with a modified Lorentzian form. The original Rietveld program uses Gaussian functions.

The characteristic half-width H (in 2θ) is assumed to have a θ dependence given by $H^2 = U\tan^2\theta + V\tan\theta + W$, where U, V, and W are refinable constants. The refinement minimizes the function Δ:

$$\Delta = \sum_i w_i[y_i(\text{obs}) - K^{-1}\cdot y_i(\text{calc})]^2,$$

where w_i is the weight assigned to an individual observed net intensity $y_i(\text{obs})$, $y_i(\text{calc})$ is the intensity calculated on the basis of the above assumptions, and K is a scale factor. The parameters refined in the final refinements were

(i) *Profile parameters*

U, V, W	Half-width parameters
Z	Zero point (in 2θ)
a, c	Cell parameters
P	Asymmetry parameter

(ii) *Structure parameters*

K	Scale factor
x_j, y_j, z_j	Fractional coordinates for the jth atom
B_j	Isotropic temperature factor for the jth atom
n_j	Occupation factor for the jth atom

TABLE I

THE REFINED STRUCTURAL PARAMETERS IN $\mathrm{ZrB}_{\sim 51}$[a]

Atom	Position	x	y	z	Partial occupancy (%)
B(13)	18 (*h*)		Not refined[b]		52.8 (12)[c]
B(16)	18 (*h*)	0.0521 (23)	0.1043(47)	0.1371(26)	14.5(11)
Zr(2)	18 (*h*)	0.20108(14)	0.40215(28)	0.17628(14)	27.9(2)
Zr(3)	6 (*c*)	0	0	0.23441 (36)	18.1(2)

[a] Overall thermal parameter $B = 2.61(10)$ Å^2.

[b] Coordinates taken from $\mathrm{ScB}_{\sim 28}$ (*5*).

[c] Estimated standard deviations are given in parentheses and refer to the least significant digits of their respective values.

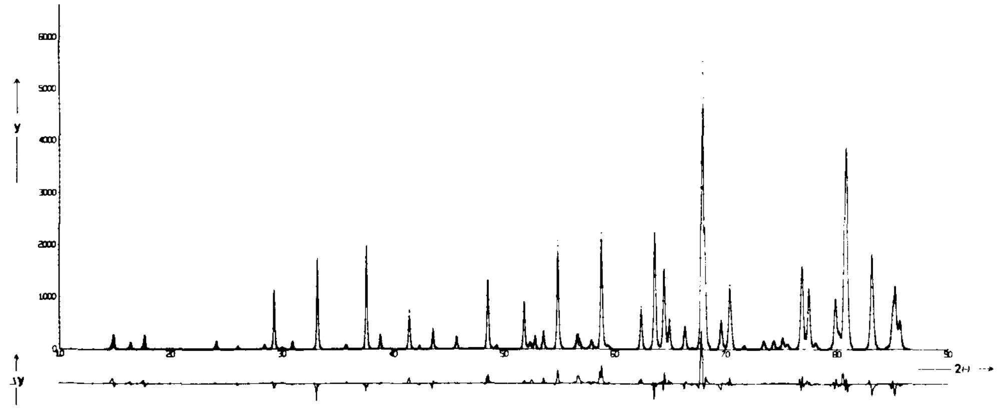

FIG. 1. X-Ray powder profile curve fit for $ZrB_{\sim51}$. Observed profile; points; calculated profile: continuous line. The lower curve plots the discrepancies on the same scale.

The start values for the positional parameters and the occupation factors were taken from a single-crystal study of $ScB_{\sim28}$ (5). No satisfactory convergence could be obtained, however, until the occupation factors were allowed to refine for the Zr atoms. In all, 1602 observed intensities with 14.7° < 2θ < 88.2° (92 reflections with a maximum of 7 overlapping reflections) were included in the refinement of 18 parameters. The final R values obtained were

$$R_I = \sum |I_o - K^{-1}I_c| / \sum I_o = 0.084,$$

$$R_{\text{profile}} = \sum |y_o - K^{-1}y_c| / \sum y_o = 0.124,$$

$$R_{\text{w, profile}} = [\sum w(y_o - K^{-1}y_c)^2 / \sum wy_o^2]^{1/2} = 0.168.$$

Here, I denotes the integrated intensity of a reflection. An R value roughly comparable to the R_f value of single-crystal work was 0.063. The final positional and thermal parameters are given in Table I, and the final profile fit is shown in Fig. 1. A list of observed and calculated structure factors is given in Table II.

Atomic scattering factors used for Zr and B were those of Hanson *et al.* (12). No correction was made for anomalous dispersion.

TABLE II

OBSERVED AND CALCULATED X-RAY STRUCTURE FACTORS FOR $ZrB_{\sim51}$

H	K	L	100*FO	100*FC	H	K	L	100*FO	100*FC
0	0	3	6968	6307	2	0	2	2540	1534
0	0	6	23276	25145	2	0	5	549	1043
0	0	9	959	868	2	0	8	7096	6485
0	0	12	15974	17233	2	0	11	5679	5591
0	1	2	5858	5647	2	1	1	10601	11072
0	1	5	4440	4609	2	1	4	4829	5134
0	1	8	527	1435	2	1	7	9034	8532
0	1	11	9528	9190	2	1	10	1369	1352
0	1	14	2196	2303	2	1	13	1064	1055
0	2	1	3567	3263	2	2	0	3274	3154
0	2	4	3689	3210	2	2	3	3539	3031
0	2	7	13946	13330	2	2	6	397	1222
0	2	10	14103	13885	2	2	9	4059	3852
0	2	13	19700	20378	2	3	2	6564	6378
0	3	0	1708	2430	2	3	5	9567	9430
0	3	3	5333	5390	2	3	8	18242	18283
0	3	6	3683	3559	2	4	1	1804	1951
0	3	9	18710	18193	2	4	4	1549	1505
0	3	12	10425	10867					
0	4	2	18520	17146	3	0	0	1708	2430
0	4	5	2303	2208	3	0	3	1961	1982
0	4	8	528	455	3	0	6	12441	12024
0	5	1	5826	5384	3	0	9	715	696
0	5	4	1382	1244	3	0	12	2627	2739
0	5	7	3901	4091	3	1	2	4460	4327
					3	1	5	2799	2610
1	0	1	6356	5464	3	1	8	4543	4589
1	0	4	2200	2966	3	1	11	6805	7068
1	0	7	8712	8182	3	2	1	13240	13685
1	0	10	7147	6577	3	2	4	21477	20201
1	0	13	5284	5029	3	2	7	11113	11099
1	1	0	4646	4244	3	3	0	15430	15208
1	1	3	7924	8221	3	3	3	10202	10212
1	1	6	3883	3657	3	3	6	116	68
1	1	9	3217	1815					
1	1	12	913	750	4	0	1	6074	5305
1	2	2	4104	4244	4	0	4	11458	10931
1	2	5	388	1138	4	0	7	3666	3887
1	2	8	1379	1109	4	0	10	11113	11738
1	2	11	3280	3056	4	1	0	393	1328
1	3	1	8156	7958	4	1	3	815	904
1	3	4	5299	4142	4	1	6	6535	6503
1	3	7	6000	6268	4	2	2	2277	2322
1	3	10	4724	4808	4	2	5	3244	3385
1	4	0	393	1328					
1	4	3	1761	1953	5	0	2	6665	6260
1	4	6	1579	1571	5	0	5	19115	18750
1	5	2	7364	7806	5	1	1	1928	1818

Discussion

The structure of β-boron and the holes which metal atoms have been found to occupy were described earlier (2, 5, 13, 14). Only the special features of $ZrB_{\sim51}$ are discussed below.

Positional parameters for only one boron atom, B(16), and the two zirconium atoms have been refined. We thus have no basis for a discussion of metal–boron and boron–boron

TABLE III

UNIT CELL DIMENSIONS FOR β-BORON $ZrB_{\sim 51}$ AND $ScB_{\sim 28}$ AS OBTAINED FROM POWDER SPECIMENS

	a	*b*
β-Boron[a]	10.9253(5) Å	23.8103(16) Å
$ZrB_{\sim 51}$	10.9564(5)	24.0201(13)
$ScB_{\sim 28}$[b]	10.9620(7)	24.0752(27)

[a] Reference (*1*).

[b] Reference (*5*).

distances. However, zirconium can be assumed to expand the β-boron network in the same way that scandium expands it, since the two metals dissolve in qualitatively similar manners. The lower metal content in $ZrB_{\sim 51}$ compared to $ScB_{\sim 28}$ is demonstrated by its smaller unit-cell dimensions; see Table III.

The metal atoms in $ZrB_{\sim 51}$ partially occupy two different crystallographic positions. The Zr(2) atoms have a 28% occupancy of the *D* holes, and have 14 or possibly 15 boron neighbors. The mean Me(2)–B distances in the earlier MeB_x structures studied are 2.40–2.44 Å. The centers of six *D* holes form a slightly puckered hexagonal ring with B(15) at its center. The distance between adjacent *D* holes is ~2.5 Å, which is too short for zirconium atoms. Only nonadjacent positions can thus be occupied; see Fig. 2. In $ScB_{\sim 28}$ and the other MeB_x structures, the boron neighbor closest to Me(2) is B(13). A high Me(2) occupancy or a large atomic radius for Me(2) seems to decrease the occupancy of the B(13) positions from 73% in β-boron to approximately 63% in $ScB_{\sim 28}$, $CuB_{\sim 28}$, and $MnB_{\sim 23}$. This effect is also seen in $ZrB_{\sim 51}$; the B(13) occupancy here is 53%.

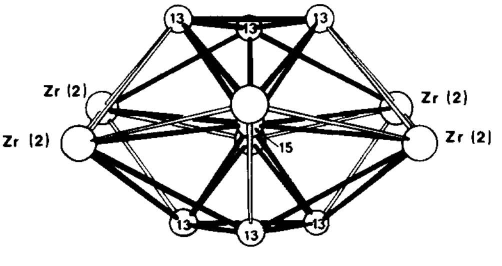

FIG. 2. A perspective view of B(15) and the surrounding B(13) and Zr(2) positions. The *c* axis is vertical in the plane of the paper and passes through B(15). Short Zr(2)–B(13) and Zr(2)–Zr(2) distances are unfilled.

The other metal atom, Zr(3), occupies the *E* hole. The Zr(3) atom has 15 boron neighbors, and the mean Me–B distances in the other structures are 2.45–2.46 Å. See Refs. (*2*, *5*) for descriptions of the β-boron structure and the metal positions.

The *A*(1) hole has been found not to be occupied by zirconium; it is clearly too small, with mean Me–B distances in other MeB_x structures of 2.15–2.16 Å.

The B(16) position is found to be occupied to 14% in $ZrB_{\sim 51}$, although it was unoccupied in $ScB_{\sim 28}$. The largest B(16) occupancy (25%) has been found for β-boron itself. Factors other than space restrictions clearly control the occupancy of this position.

In an additional refinement, the occupancy of the Zr(4) position was found to be insignificantly low (0.7(2)%). This position has been found to be occupied in the case of scandium, where the Me(4) atom is situated close to the center of the line joining two neighboring boron atoms. The two boron atoms are replaced by the metal atom at an intermediate position.

Despite the apparently low *R* value (0.063), the standard deviations obtained are large and are probably underestimated. This is due both to the limited number of reflections (92) and to the rather special character of the curve-fitting technique used here. Furthermore, no anomalous dispersion correction has been made for the zirconium atoms, a factor which could affect the refined zirconium occupancies. Nevertheless, in spite of these limitations, the method used has been shown to give a reasonably accurate result in this investigation. The accuracy, although not as high as the accuracies obtained with single-crystal methods, does represent an average taken over a much larger sample.

Acknowledgments

The authors are grateful to Professor Ivar Olovsson for all the facilities which have been placed at their disposal. The work has been supported by grants from the Swedish Natural Science Research Council.

References

1. S. ANDERSSON AND T. LUNDSTRÖM, *J. Solid State Chem.* **2**, 603 (1970).
2. S. ANDERSSON AND B. CALLMER, *J. Solid State Chem.* **10**, 219 (1974).
3. I. HIGASHI, T. SAKURAI, AND T. ATODA, *J. Less Common Metals*, **45**, 283 (1976).
4. B. CALLMER AND T. LUNDSTRÖM, *J. Solid State Chem.* **17**, 165 (1976).
5. B. CALLMER, Internal Report UUIC-B18-65, Institute of Chemistry, University of Uppsala (1977).
6. J.-O. CARLSSON AND T. LUNDSTRÖM, *J. Less Common Metals* **22**, 317 (1970).
7. S. ABRAHAMSSON, *J. Sci. Instrum.* **43**, 931 (1966).
8. SAAB, "Film Scanner Manual", SAAB AB, Datasaab, Linköping, Sweden (1967).
9. G. MALMROS AND J. O. THOMAS, *J. Appl. Crystallogr.* **10**, 7 (1977).
10. G. MALMROS AND P.-E. WERNER. *Acta Chem. Scand.* **27**, 493 (1973).
11. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
12. H. P. HANSON, F. HERMAN, J. D. LEA, AND S. SKILLMAN, *Acta Crystallogr.* **17**, 1040 (1964).
13. J. L. HOARD, D. B. SULLENGER, C. H. L. KENNARD, AND R. E. HUGHES, *J. Solid State Chem.* **1**, 268 (1970).
14. B. CALLMER, *Acta Crystallogr. B* **33**, 1951 (1977).