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Zirconium Dodecarborides ZrB_{12}. Confirmation of the B_{12} Cubooctahedral Unit

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Using powder neutron diffraction and Rietveld's method of profile refinement, the structure of ZrB_{12} was confirmed.

On the basis of steric considerations, Bertaut and Blum (*1*) proposed that the B_{12} unit in UB_{12} was in a cubeoctahedron. Post and Glaser (*2*) found that the X-ray powder pattern of ZrB_{12} was isomorphous with UB_{12}. Matkovich *et al.* (*3*) prepared a single $Fm3m$ crystal of YB_{12} and observed 37 reflections (Cu$K\alpha$ X radiation, no absorption correction applied). Using phase angles from the yttrium atoms, a subsequent electron density synthesis confirmed the cubooctahedral arrangement of boron atoms. Least-squares refinement lowered the R to 0.05(7); 0.061 [isotropic temperature factors, Y = 0.56(7); B = 1.4(3) Å^2].

A survey of MB_{12} compounds by Matkovich *et al.* (*4*) indicated (i) a cubeoctahedron for B_{12}, where M was a large atomic number element (space group $Fm3m$), and (ii) an icosahedron, where M was a low-atomic number element (space group $R\bar{3}m$).

These two lattices are related, with the body diagonal of the face-centered cube the equivalent of the c axis of the hexagonal cell. In both cases the M atom (at the faces of the cube or at the corners of the rhombohedral cell) are in equivalent positions. The difference depends on the B_{12} unit at the center of both unit cells (Fig. 1). Table I shows the relationship for powder patterns between the two cells for the same d spacings.

ZrB_{12} (Z-1032, lot number 2041, from Cerac/Pure Inc, Menomonie Falls, Wisc.; 200 mesh, 99% pure, Zr, 40.80; B, 58.21; C, 0.36; Fe, 0.22; H, 0.002; N, 0.12, O, 0.14%, X-ray pattern, 3655 matches ZrB_{12} PDS 6-590, with a trace of ZrB_{12} present) in a cadmium boat (internal dimensions, 100 mm high, 60 mm wide, 3 mm deep) was covered by aluminium foil and cemented with Araldite.

In $Fm3m$, one atom at a point symmetry mm will generate about $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, etc., a cubeoctahedron, while for $R\bar{3}m$, two atoms at point symmetry m will generate about $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, etc., an icosahedron. Using

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TABLE I

RELATIONSHIP BETWEEN TWO CELLS

*Fm*3*m* cell					$R\bar{3}m$ cell			
h	*k*	*l*	Multiplicity	*d* (Å)	*h*	*k*	*l*	Multiplicity
−1	−1	1	8	4.28	0	0	3	2
					−1	1	1	6
−2	0	0	6	3.70	−1	1	−2	6
−2	−2	0	12	2.62	−1	1	4	6
−3	−1	1	24	2.23	−1	1	−5	6
					−2	1	3	12
					−2	2	−1	6
−2	−2	−2	8	2.14	0	0	6	2
					−2	2	2	6
−4	0	0	6	1.85	−2	2	−4	6
−3	−3	−1	24	1.70	−1	1	7	6
					−2	2	5	6
					−3	2	1	12
−4	−2	0	24	1.66	−2	1	6	12
					−3	2	−2	12
−4	−2	2	24	1.51	−1	1	−8	6
					−3	2	4	12
					−3	3	0	6
−5	−1	1	24	1.43	0	0	9	2
					−2	2	−7	12
					−3	3	−3	6
					−3	3	3	6
−4	−4	0	12	1.31	−2	2	8	6
					−4	2	0	6
−5	−3	−1	48	1.25	−2	1	−9	12
					−3	2	7	12
					−4	2	−3	12
					−4	3	−1	12
−6	0	0	6	1.23	−1	1	10	6
					−3	3	6	6
−4	−4	−2	24		−3	3	−6	6
					−4	3	2	12
−6	−2	0	24	1.17	−3	2	−8	12
					−4	3	−4	12
−5	−3	−3	24	1.13	−1	1	−11	6
					−4	3	5	12
					−4	4	1	6
−6	−2	−2	24	1.12	−2	2	−10	6
					−4	2	6	12
					−4	4	−2	6
−4	−4	−4	8	1.07	0	0	−12	2
					−4	4	4	6
−5	−5	1	24	1.04	−2	2	11	6
−7	−1	−1	24		−3	3	9	6
					−3	3	−9	6
					−4	3	−7	12
					−4	4	−5	6
					−5	3	1	12
−6	−4	0	24	1.03	−3	2	10	12
					−5	3	−2	12

neutron powder diffraction, the difference will depend on multiplicity and structure factor calculations (see Fig. 2 and Table II).

The highly absorbing sample was put in the reflecting position in the stationary

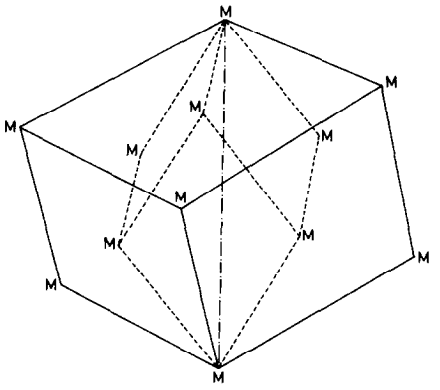

FIG. 1. Relationship between *Fm*3*m* and $R\bar{3}m$. *M* is either at the corners of a face-centered table (solid line) or a rhombohedron (dashed line).

powder mode on a neutron diffractometer (λ = 1.086 Å) attached to hole 4H1 on the Australian Atomic Energy Commission's HIFAR (DIDO type) 10-MW reactor. A blank without ZrB_{12} gave only aluminium lines (Al, *Fm*3*m*, *a* = 4.050 Å) and no cadmium ones (Cd, *P*63/*mmc*, *a* = 2.979, *c* = 5.618 Å).

The data were refined (*5*) to give in the cubic case *R* = 0.028, [0.047]; *n*, 16, [22]; *a*,

TABLE II

POWDER DATA BASED ON CUBIC CELL

h	*k*	*l*	Half-width	2θ	I_{calc}	I_{obs}
1	1	1	0.492	14.628	2,380	2,384
0	0	2	0.473	16.906	519	531
0	2	2	0.462	23.998	2,477	2,634
1	1	3	0.492	28.219	16,068	15,568
2	2	2	0.506	29.501	6,707	7,225
0	0	4	0.575	34.196	626	569
1	3	3	0.635	37.372	519	523
0	2	4	0.655	38.381	1,761	1,496
2	2	4	0.740	42.210	7,531	7,670
3	3	3	0.805	44.906	16,302	16,460
1	1	5	0.805	44.906	1,974	1,993
0	4	4	0.916	49.137	431	458
1	3	5	0.983	51.550	11,478	11,274
2	4	4	1.005	52.336	3,723	3,789
0	0	6	1.005	52.336	13,363	13,599
0	2	6	1.095	55.402	94	100

Derived Bragg *R* factor = 2.75

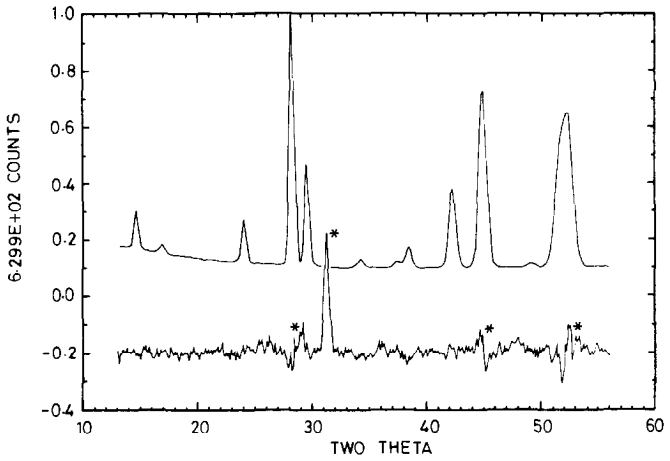

FIG. 2. I_{calc} (above) and $|I_{obs}| - |I_{calc}|$ (below) neutron diffraction spectrum for ZrB_{12} (*) Al powder lines; 111, 200, 220, 311, respectively.

7.388(3), [7.408(2)] Å, Zr B, 1.6(3), [−0.04(10)] Å^2; B y, 0.1710(6), [0.1699(18)] Å; B B, −0.075(5), [0.53(62)] Å^2, with the square brackets referring to the Post and Glaser X-ray powder data (*2*) refined by Matkovich *et al.* (*4*). The model for the hexagonal case, as calculated in the Appendix, did not refine (R = 0.112).

Appendix

Calculation of B Parameters

$V_0 - V_1 = l$ (side of icosahedron),

$V_0 - V_2 = 1.618l$,

$V_0 - V_3 = 1.902l$, (diagonal)

Hexagonal cell, a = 5.238 Å.

$$x_1 = \frac{l}{3a} = \frac{l}{3 \times 5.238} = 0.0636l; \qquad x_2 = \frac{1.618l}{3 \times 5.238} = 0.1030l$$

$x, 2x, z; -x, -2x, -z$
(inversion)

$$(1.902l)^2 = (x + x)^2 + (2x + 2x)^2a^2 + (z + z)c^2 + 2a^2(x + x)(2x + 2x)\cos(\gamma)$$

$$= 4x^2a^2 + 16x^2a^2 + 4z^2c^2 - 8x^2a^2$$

$$= 12x^2a^2 + 4z^2c^2$$

$$z^2 = \frac{(1.902l)^2 - 12x^2a^2}{4c^2}; \qquad c = 12.831 \text{ Å}$$

if $l = 1.8$

$x_1 = 0.1145$ $x_2 = 0.1854$

$z_1 = 0.1060$ $z_2 = -0.0248$

References

1. F. BERTAUT AND P. BLUM, *C. R. Acad. Sci. Paris* **229,** 666–667 (1949).
2. B. POST AND F. W. GLASER, *J. Metals* **4,** 631–632 (1952).
3. V. I. MATKOVICH, J. ECONOMY, R. F. GIESE, AND R. BARRETT, *Acta Crystallogr.* **19,** 1056–1057 (1965).
4. V. I. MATKOVICH, R. F. GIESE, AND J. ECONOMY, *Z. Krist.* **122,** 116–130 (1965).
5. A. W. HEWAT, AERE Report R 7350, Modified Rietveld Program (1975).