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The Redetermination of the Structure of Beryllium–Molybdenum $MoBe_{12}$

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Abstract. $M_r = 204{\cdot}09$, tetragonal, $I4/mmm$, $a = 7{\cdot}251\ (2)$, $c = 4{\cdot}234\ (1)$ Å, $V = 222{\cdot}6$ Å^3, $Z = 2$, $D_x = 3{\cdot}045$ Mg m^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}71073$ Å), $\mu = 2{\cdot}68$ mm^{-1}, $F(000) = 180$, $T = 295$ K, $R = 0{\cdot}012$ for 475 reflections. $MoBe_{12}$ is an intermetallic compound with four distinct atom types. Each atom type is at the center of a polyhedral array of 12 or more atoms; the Mo atom is centered among 20 Be atoms. The results confirm every principal finding of the earlier report [Raeuchle & von Batchelder (1955). *Acta Cryst.* **8**, 691–694].

Introduction. Intermetallic compounds of beryllium occur in variety and have relatively low X-ray absorption coefficients. Consequently these compounds are uniquely suited to the study of metal bonding through critical analysis of charge-density distribution as obtained from X-ray diffraction experiments. As part of a systematic study of Be alloys we have redetermined the structure of $MoBe_{12}$. The structure was first determined by Raeuchle & von Batchelder (1955) using 78 independent data obtained as visually estimated intensities from a photographic diffraction record.

Experimental. A mixture of molybdenum and beryllium in a 1:15 atomic ratio was pressed into a pellet. The pellet was then melted and remelted under an inert atmosphere in a copper-hearth tungsten-arc furnace to form an ingot containing $MoBe_{12}$. The ingot was fractured and the fragments were searched for suitable crystals.

Irregularly shaped crystal ($0{\cdot}3 \times 0{\cdot}15 \times 0{\cdot}15$ mm); computer-controlled four-circle diffractometer (Syntex $P\bar{1}$, Mo $K\alpha$ radiation); lattice parameters by least-squares refinement of the 2θ values of 15 reflections, $23° < 2\theta < 40°$. 772 intensities were measured in the two ranges $0{\cdot}0 < \sin\theta/\lambda \le 0{\cdot}8$, $0{\cdot}8 < \sin\theta/\lambda \le 1{\cdot}18$ Å^{-1}. Unique reflections were measured in the upper range and at least two reflections in each form were measured in the lower range; by a 3σ counting-statistics criterion all reflections were considered observed. Three standard reflections measured periodically were stable with an average sample deviation of 0·8%; Lorentz, polarization and empirical absorption (North, Phillips & Mathews, 1968) corrections; maximum absorption correction: 0·9992, minimum: 0·8814 (Enraf–Nonius, 1979); R_{int} (for merging equivalent reflections) = 0·022 yielding 475 unique reflections; positional and anisotropic thermal parameters refined by full-matrix least squares minimizing $\sum\omega(|F_o| - |F_c|)^2$ using *LINEX*81 (provided by E. D. Stevens; Becker & Coppens, 1975), $\omega = 1/\sigma^2(F)$; $R = 0{\cdot}012$, $R_w = 0{\cdot}016$, $S = 1{\cdot}36$; final parameter shifts $< 0{\cdot}2\sigma$. Lorentzian type-I extinction $g = 7{\cdot}2\ (5) \times 10^{-3}$. Anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) were applied to F_c during refinement but to F_o after refinement was complete.

Discussion. The final structural parameters are given in Table 1, a list of interatomic distances is given in Table 2.*

Table 1. *Atomic positions and thermal parameters* (Å^2) *for* $MoBe_{12}$

E.s.d.'s are given in parentheses. $T = \exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_ja^*_ia^*_j)$.

	Mo	Be(*f*)	Be(*i*)	Be(*j*)
x	0·0	0·25	0·3505 (2)	0·2895 (2)
y	0·0	0·25	0·0	0·5
z	0·0	0·25	0·0	0·0
U_{11}	0·00324 (3)	0·0063 (3)	0·0062 (3)	0·0081 (3)
U_{22}	$(=U_{11})$	$(=U_{11})$	0·0060 (3)	0·0046 (3)
U_{33}	0·00236 (3)	0·0050 (3)	0·0115 (4)	0·0060 (3)
U_{12}	0·0	0·0006 (2)	0·0	0·0
U_{13}	0·0	0·0008 (3)	0·0	0·0
U_{23}	0·0	$(=U_{13})$	0·0	0·0

Table 2. *Interatomic distances* (Å) *for* $MoBe_{12}$

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

Mo—4 Be(*i*)	2·541 (2)	Be(*f*)—2 Be(*f*′)	2·117 (1)
8 Be(*j*)	2·610 (1)	4 Be(*j*)	2·119 (1)
8 Be(*f*)	2·774 (1)	4 Be(*i*)	2·222 (1)
		2 Mo	2·774 (1)
Be(*i*)—Be(*i*′)	2·168 (3)	Be(*j*)—4 Be(*f*)	2·119 (1)
4 Be(*f*)	2·222 (1)	2 Be(*j*′)	2·159 (1)
2 Be(*j*)	2·348 (1)	2 Be(*i*)	2·348 (1)
2 Be(*j*′)	2·362 (1)	2 Be(*i*′)	2·362 (1)
Mo	2·541 (2)	2 Mo	2·610 (1)
4 Be(*i*″)	2·614 (1)		

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39214 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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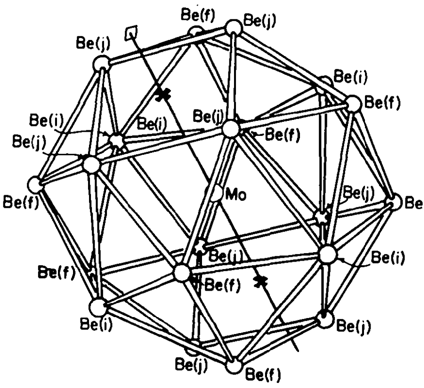

Fig. 1. The environment around the Mo atom omitting the Mo—Be bonds and showing the direction of the fourfold axis.

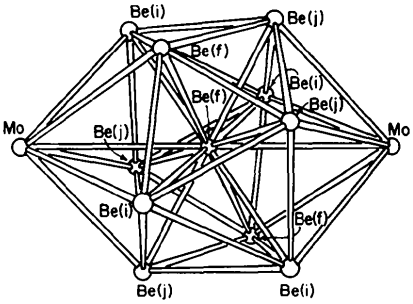

Fig. 2. The 12-neighbor environment of the Be(*f*) atom.

$MoBe_{12}$ as reported by Raeuchle & von Batchelder is of the $ThMn_{12}$-type structure (Florio, Rundle & Snow, 1952). Fig. 1 shows the environment around the Mo atom omitting bonds to the Mo for clarity. Fig. 2 shows the nearly regular icosahedral environment around the Be(*f*) atom. Be(*j*) is at the center of an irregular icosahedron. Be(*i*) has 14 nearest neighbors which are at the apices of a bicapped hexagonal antiprism, the caps lying outside the hexagonal faces. This structure description confirms every principal finding of the earlier report with a precision an order of magnitude greater. The present report also confirms by precise determination of anisotropic thermal parameters that they are near zero as was originally assumed.

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Wolframtetrabromidoxid, $WOBr_4$

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Abstract. $M_r = 519{\cdot}5$, tetragonal, $I4$, $a = 9{\cdot}002$ (5), $c = 3{\cdot}935$ (1) Å, $V = 318{\cdot}9$ (4) Å^3, $Z = 2$, $D_x = 2{\cdot}70$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 41{\cdot}9$ mm^{-1}, $F(000) = 444$, $T = 293$ K, $R = 0{\cdot}0495$ for 269 reflexions. $WOBr_4$ is isostructural with $WOCl_4$, consisting of square-pyramidal $WOBr_4$ units that are associated *via* the O atoms forming linear $\cdots W{=}O{-}W{=}O\cdots$ chains; the WO distances are 1·78 (3) and 2·16 (3) Å, respectively. This represents a slight lengthening of the W=O bond compared with monomers in the gas phase (1·70 Å).

Einleitung. Hess & Hartung (1966) haben zusammen mit der Strukturbestimmung von $WOCl_4$ auch Angaben zur Struktur des isotypen $WOBr_4$ gemacht, sie haben jedoch keine Strukturverfeinerung durchgeführt und konnten insbesondere keine Aussagen über die Lage des O-Atoms machen. Mit neuen Messdaten konnte jetzt eine genauere Strukturanalyse durchgeführt werden.

Experimentelles. Einkristalle von $WOBr_4$ wurden als Nebenprodukt bei der Synthese von WBr_4 aus WBr_5 und Al in einem abgeschmolzenen Glasrohr im

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