

DONOHUE, J. & TRUEBLOOD, K. N. (1952). *Acta Cryst.* **5**, 414.
International Tables for X-ray Crystallography (1959).
 Vol. 2, Section 2.6. Birmingham: The Kynoch Press.
 PATTERSON, A. L. (1935). *Z. Kristallogr.* **90**, 517.

SHOEMAKER, D. P. (1947). Ph.D. Thesis, Calif. Inst. of Tech.
 STADLER, H. P. (1950). *Acta Cryst.* **3**, 262.
 WASER, J. & SCHOMAKER, V. (1953). *Rev. Mod. Phys.* **25**,
 671.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1963). **16**, 202

The Structure of Dimolybdenum Carbide by Neutron Diffraction Technique*

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It is generally believed that Mo₂C has either the hexagonal C6 cadmium iodide anti-type structure or the related hexagonal L'3 structure. A neutron diffraction study showed that this is not the case. Mo₂C is only pseudohexagonal and crystallizes with an orthorhombic unit cell with $a=4.724$, $b=6.004$, and $c=5.19$, Å. The atomic arrangement of Mo₂C presents a new structure type. Space group is $D_{2h}^{14}-Pbcn$. Eight molybdenum atoms are in 8(*d*) with $x=1/4$, $y=1/8$, $z=1/12$ and four carbon atoms are in 4(*c*) with $y=3/8$. The carbon atoms in Mo₂C arrange themselves in such a way that each molybdenum atom has three nearly planar carbon neighbours.

Introduction

In the system molybdenum-carbon two carbide phases exist: The monocarbide, MoC, and the sesquicarbide, Mo₂C. The structure of the monocarbide was solved earlier by one of the authors (Nowotny, Parthé, Kieffer & Benesovsky, 1954). Recent investigations show, however, that it occurs only with a carbon defect and the formula Mo₃C₂ has been suggested for this compound (Rudy, Rudy and Benesovsky, 1962). A structure proposal for Mo₂C dates back as far as 1926. Using the X-ray diffraction technique, Mo₂C was investigated at that time by Westgren & Phragmen. Due to the small scattering factor of carbon, they could determine with certainty only the spatial arrangement of the metal atoms. They found them to be arranged in a hexagonal close packing. For each two molybdenum atoms, one carbon atom can be tentatively placed in one of the octahedral holes. One thus receives a structure proposal for Mo₂C as follows:

C6 structure type

Unit cell: Hexagonal: $a=3.002$ Å, $c=4.724$ Å

Space group: $D_{3d}^3-P\bar{3}m1$

Point position: 2 Mo in 2(*d*): $1/3, 2/3, z$; $2/3, 1/3, \bar{z}$
 with $z=1/4$

1 C in 1(*a*): 0, 0, 0

This structure is identical to the first CdJ₂(C6) structure type, except the metal and non-metal atoms have been interchanged. This type may be called, therefore, CdJ₂-antitype. However, modern crystal structure compilations (Pearson, 1958) list the Mo₂C structure as belonging to the L'3 structure type with the one carbon atom statistically distributed between two possible places.

L'3 structure type

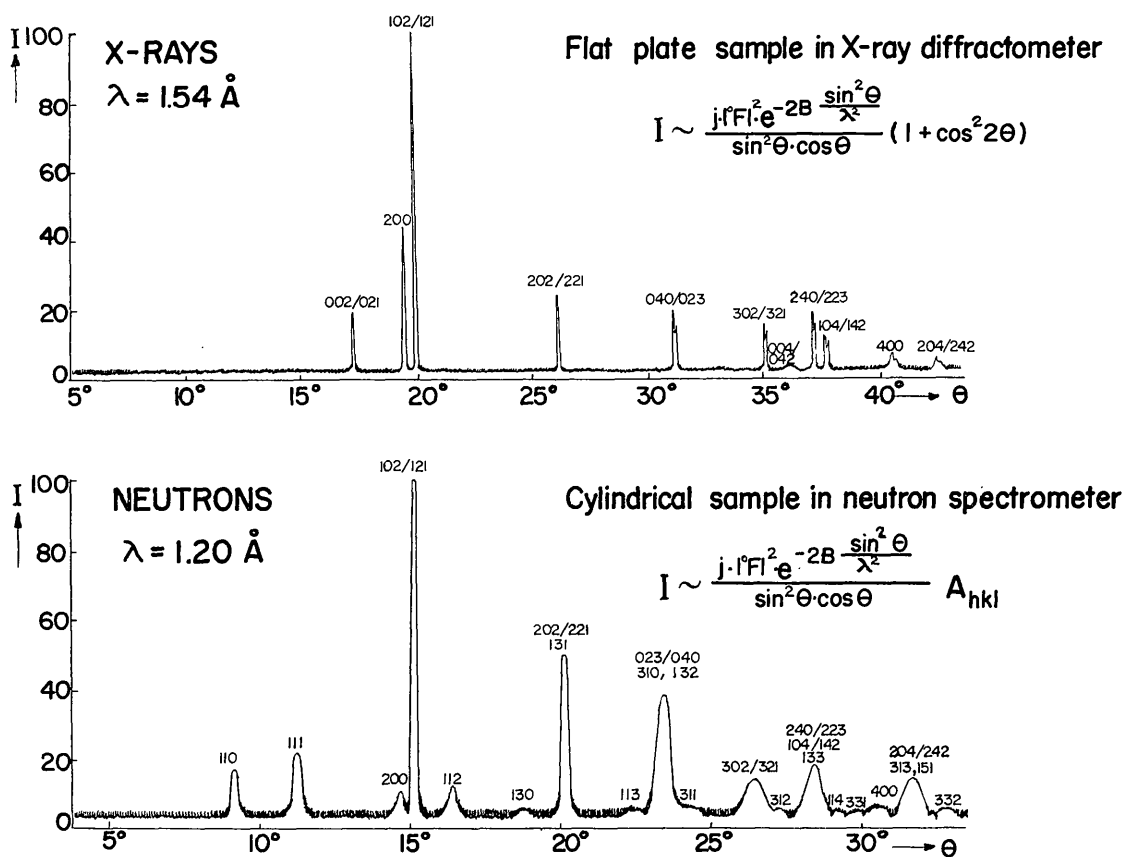
Same hexagonal unit cell dimensions as above.

Space group: $D_{6h}^4-P6_3/mmc$

Point positions: 2 Mo in 2(*c*): $1/3, 2/3, 1/4$; $2/3, 1/3, 3/4$
 1 C in 2(*a*): 0, 0, 0; 0, 0, 1/2

To reveal the true carbon atom positions in Mo₂C, a neutron diffraction study was undertaken.

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Fig. 1. Mo_2C powder patterns.

Experimental procedure

The neutron diffraction powder pattern of Mo_2C was obtained in a manner described in an earlier paper (Parthé & Sadagopan, 1962). The Mo_2C powder was a gift from the Metallwerk Plansee G.m.b.H. in Reutte, Austria, which also provided the analysis. The Mo_2C contained 33.3 a./o. bound carbon. There was also 0.8 a./o. free carbon present.

Analysis of the diffraction experiments

The neutron diffraction pattern of Mo_2C is compared with the X-ray diffraction pattern in Fig. 1. To account for the extra neutron diffraction lines, a super cell had to be sought which was based on the hexagonal unit cell determined earlier by X-ray methods. Describing the original hexagonal cell with an orthorhombic set of axes and doubling of one axes gives the desired result. If a_H and c_H are the hexagonal unit cell dimensions, then the dimensions of the new orthorhombic unit cell are given by: $a_O = c_H$, $b_O = 2 a_H$ and $c_O = a_H \cdot \sqrt{3}$. This particular setting of axes is chosen to conform with the standard setting of the orthorhombic space group of Mo_2C which is given

below. The new orthorhombic lattice parameters of Mo_2C , which account for every observed neutron diffraction line, are

$$a = 4.724, \quad b = 6.004 \quad \text{and} \quad c = 5.199 \text{ \AA}.$$

As the positions of the molybdenum atoms are known to be those of a hexagonal close-packed structure, only a limited number of possibilities exist for the positioning of the four carbon atoms. Excellent agreement between calculated and observed intensities was obtained by assuming:

Space group: $D_{2h}^{14} - Pbcn$

Point positions: 8 Mo in 8(d) with $x=1/4$, $y=1/8$, $z=1/12$.

4 C in 4(c) with $y=3/8$.

Due to the very special values of the free parameters, many lines which are allowed by the space group were calculated to have zero intensity as can be seen in Table 1. Only the symmetry elements of space group $Pbcn$ are present in the structure.

For the calculation of the integrated intensities, a temperature coefficient of $B = 0.5 \times 10^{-16} \text{ cm.}$ has been used. The absorption coefficient A_{hkl} hardly

Table 1. *Neutron intensity calculation for Mo₂C with new structure type*
 ($\lambda=1.20$ Å) and comparison between the $|^{\circ}F|$ values for neutrons and X-ray diffraction

New ortho- rhombohedral indices <i>hkl</i>	Old hexagonal indices <i>hkil</i>	<i>d</i> (Å)	$1000 \cdot \sin^2 \theta_c$	$1000 \cdot \sin^2 \theta_o$	I_c		I_o		Neutrons $ ^{\circ}F _c$	X-rays $ ^{\circ}F _c$
110		3.710	26.12	26.0		14.8		11.3	10.0	0.9
111		3.021	39.44		19.6		18.5	10.0	0.9	
020		—	39.95	39.4	0	19.6		0	0	0
002	10 $\bar{1}$ 0	(2.601)	53.26		0		—	(0)	(11.9)	
021			53.26		0		(0)	(11.9)		
200	0002	2.363	64.52	64.4		6.0	7.0	14.1	24.9	
102	10 $\bar{1}$ 1	2.278	69.39		33.3		100.0	(24.5)	(22.0)	
121			69.39	69.3	66.6		100.0	(24.5)	(22.0)	
112		2.130	79.38	79.3		7.4	8.3	10.0	0.7	
211		—	87.82	—	0	—	—	0	0	0
022		—	93.21	—	0	—	—	0	0	0
220		—	104.47	—	0	—	—	0	0	0
130		1.843	106.01	105.5		3.6	3.1	10.0	0.7	
122		—	109.34	—		0	—	0	0	0
202	10 $\bar{1}$ 2	1.749	117.78		25.8		—	(28.3)	(12.4)	
221			117.78	118.1	51.6	83.8	83.0	(28.3)	(12.4)	
131		1.736	119.32		6.4			10.0	0.7	
212		—	127.77	—		0	—	0	0	0
113		1.571	145.96	146.4		5.2	5.0	10.0	0.6	
310		1.523	155.16		2.5			10.0	0.6	
222		—	157.73	—	0			0	0	0
132	11 $\bar{2}$ 0	1.503	159.27	159.0	4.8	72.1	74.9	10.0	0.6	
040			159.27		21.6		(42.3)	(21.9)		
023		1.501	159.79		43.2			(42.3)	(21.9)	
231		—	167.71	—		0	—	0	0	0
311		1.462	168.47	168.0		4.6	5.0	10.0	0.6	
041		—	173.10	—		0	—	0	0	0
123		—	175.92	—		0	—	0	0	0
141		—	189.23	—		0	—	0	0	0
213		—	194.35	—		0	—	0	0	0
302	10 $\bar{1}$ 3	1.347	198.43	198.7	11.5	34.5	33.8	(24.5)	(17.3)	
321			198.43		23.0		(24.5)	(17.3)		
232		—	207.66	—		0	—	0	0	0
312		1.315	208.42	208.9		3.7	3.7	10.0	0.5	
004	20 $\bar{2}$ 0	(1.300)	213.05		0		—	(0)	(9.2)	
042			213.05		0		(0)	(9.2)		
240	11 $\bar{2}$ 2	1.267	224.31		3.4			(14.1)	(18.4)	
223			224.31		6.7		(14.1)	(18.4)		
133		1.263	225.85	227.7	3.4	43.5	45.8	10.0	0.5	
104	20 $\bar{2}$ 1	1.253	229.18		10.0			(24.5)	(16.4)	
142			229.18		20.0		(24.5)	(16.4)		
330		1.238	235.05	—		1.6	—	10.0	0.5	
241		—	237.62	—		0	—	0	0	0
322		—	238.38	—		0	—	0	0	0
114		1.227	239.17	238.0		3.2	3.5	10.0	0.5	
331		1.204	248.36	248.5		2.9	3.1	10.0	0.5	
024		—	253.00	—		0	—	0	0	0
400	0004	1.181	258.08	257.6		13.2	12.6	42.3	19.2	
150		1.164	265.80	—		1.4	—	10.0	0.5	
124		—	269.13	—		0	—	0	0	0
233		—	274.24	—		0	—	0	0	0
313		1.144	275.00	—	2.8			10.0	0.5	
204	20 $\bar{2}$ 2	1.139	277.57	276.1	11.0	38.5	37.5	(28.3)	(9.8)	
242			277.57		22.0		(28.3)	(9.8)		
151		1.135	279.11	—	2.7			10.0	0.5	
043		—	279.63	—		0	—	0	0	0
411		—	281.38	—		0	—	0	0	0
214		—	287.56	—		0	—	0	0	0
332		1.117	288.31	288.7		2.6	3.1	10.0	0.5	
143		—	295.76	—		0	—	0	0	0
420		—	298.03	—		0	—	0	0	0

changes at all and was assumed to be constant. The agreement between calculated and observed intensities is remarkable, although the measurement of the high angle lines due to broadening is somewhat difficult.

The X-ray and neutron diffraction patterns compared in Fig. 1 show some interesting features. The X-ray scattering factor for carbon in comparison to that for molybdenum is practically zero. Thus, as is well known, the X-ray diffraction pattern will reveal only the molybdenum partial structure, a hexagonal close-packed arrangement. Otherwise, in the case of neutron diffraction, carbon and molybdenum have exactly the same neutron scattering amplitude of $b_{\text{Mo}} = b_{\text{C}} = 0.661 \times 10^{-12}$ cm. Thus the Mo_2C structure will behave like a more complicated element structure to neutrons. This leads to the uncommon situation that some diffraction lines occur in the X-ray diffraction pattern that do not occur in the neutron diffraction pattern (002/021 and 004/042) and also vice versa (110, 111 etc.). This is illustrated in the last two columns of Table I which allow a comparison between the $|^{\circ}F|$ values for neutron- and X-ray diffraction.

Discussion of the Mo_2C structure

Mo_2C is a member of the family of interstitial or Hägg compounds as they occur with TiC , WC or MoC . Fig. 2

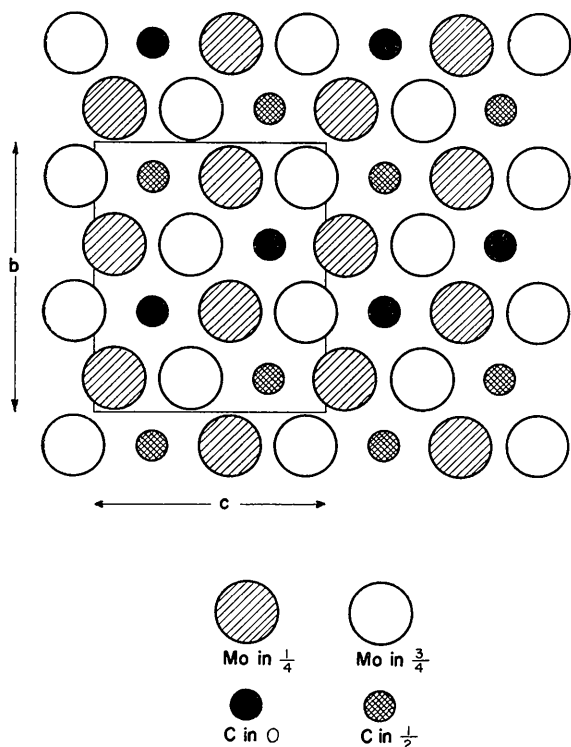
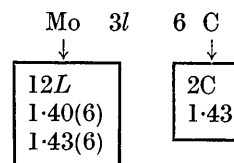


Fig. 2. Atom positions in Mo_2C .

shows the nets of the hexagonal closed-packed molybdenum atoms with the carbon atoms placed in octahedral voids. While in the CdI_2 structure proposal the carbon atoms would be in one layer only, or according to $L/3$ distributed randomly about all possible sites, the carbon atoms in Mo_2C arrange themselves in both layers (0 and $1/2$) in a systematic way. This particular arrangement lets every molybdenum atom have three equidistant carbon atom neighbours, whereby the three carbon atoms and the molybdenum atom are very nearly in one plane. The construction formula (Laves, 1956; Parthé, 1961) of Mo_2C can be calculated to be



Four carbides: V_2C , Nb_2C , Ta_2C and W_2C —and also a few nitrides like Ta_2N are known from X-ray data to be isostructural with Mo_2C . But a recent electron diffraction study on W_2C by Butorina & Pinsker (1960) has shown that W_2C has the anti-cadmium iodide structure type. It might be worthwhile to investigate W_2C and all other sesquicarbides and nitrides by neutron diffraction technique.

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References

- BUTORINA, L. N. & PINSKER, Z. G. (1960). *Soviet Physics, Crystallography*, **5**, 560.
 NOWOTNY, H., PARTHÉ, E., KIEFFER, R. & BENESOVSKY, F. (1954). *Mh. Chem.* **85**, 255.
 PARTHÉ, E. (1961). *Z. Kristallogr.* **115**, 52.
 LAVES, F. (1956). *Crystal Structure and Atomic Size in Theory of Alloy Phases*. Cleveland: American Society for Metals.
 PARTHÉ, E. & SADAGOPAN, V. (1962). *Mh. Chem.* **93**, 263.
 PEARSON, W. B. (1958). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*. New York: Pergamon Press.
 RUDY, ERWIN, RUDY, ELISABETH & BENESOVSKY, F. (1962). *Planseeberichte*, **10**, 42.
 WESTGREN, A. & PHRAGMEN, V. (1926). *Z. anorg. Chem.* **156**, 27.