

A Neutron Diffraction Investigation on a Crystal of α -Mo₂C

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The crystal structure of α -Mo₂C was refined in space group *Pbcn* (No. 60) from neutron diffraction single crystal data. The unit cell $a = 4.732(2)$ Å, $b = 6.037(3)$ Å, $c = 5.204(2)$ Å, has $Z = 4$. The carbon atoms are partly ordered in the structure. Each carbon atom is coordinated with six molybdenum atoms in an octahedron. Each molybdenum atom is coordinated with three carbon atoms arranged in a triangle with the molybdenum atom placed approximately in the centre. α -Mo₂C has a superstructure. It is most likely a modulation of the carbon sublattice that yields the superstructure.

Some of the carbides and nitrides of the group IV, V, and VI transition metals have structures with the metal atoms either in face centered cubic or in hexagonal close packings. The carbon or nitrogen atoms are placed in the octahedral holes of the structures. Two structures are known for molybdenum carbide. β -Mo₂C has a hexagonal structure with the metal atoms in a hexagonal close packing and with the carbon atoms arranged statistically in the octahedral holes of the structure. (The number of holes is twice the number of carbon atoms). The structure of α -Mo₂C is orthorhombic. The packing of the metal atoms is of the hexagonal close packing type, but is deformed to an orthorhombic symmetry, and the carbon atoms are ordered in the structure.¹ The crystal structure of α -Mo₂C was studied by Parthé and Sadagopan¹ by neutron diffraction powder techniques.

Single crystals of α -Mo₂C have been made using floating zone crystal growth methods.² A preliminary X-ray crystallographic investigation of such a single crystal showed the diffraction pattern of α -Mo₂C to have strong reflections that were indexed with an orthorhombic unit cell *abc* of the same size as that

reported previously,¹ and some rather weak reflections that were indexed with an orthorhombic unit cell with $a_s = a$, $b_s = 2b$, and $c_s = 4c$.² The compound has thus a superstructure, that is assumed to arise from a small modulation of the crystal structure.¹ This paper is concerned with the structure of α -Mo₂C and the nature of the modulation of the structure that results in the occurrence of the superstructure. This could be due to a partial ordering of the carbon atoms in the octahedral sites available, or could be due to a modulation of the atomic positions of the carbon and/or the molybdenum sublattices.

EXPERIMENTAL

The preparation of single crystals of α -Mo₂C is reported elsewhere.² A Guinier powder pattern was taken of the compound with germanium, $a = 6.6576$ Å, as an internal standard. The powder pattern was indexed with an orthorhombic unit cell with $a = 4.732(2)$ Å, $b = 6.037(3)$ Å, $c = 5.204(2)$ Å, see Table 1. No superstructure reflections could be observed in the X-ray powder pattern but were visible on Weissenberg and precession photographs.²

The neutron diffraction data were measured at an automatic four-circle diffractometer at DR3, Risø, using 1.07 Å neutrons and a standard $\omega - 2\theta$ scan technique.³ A single crystal of α -Mo₂C with a volume of 2.04 mm³ and linear dimensions in the range 0.8 to 1.8 mm was used in measuring a total of 1557 reflections. The diffraction data were reduced using a standard procedure,⁴ resulting in a total of 301 independent reflections with $I > 3\sigma(I)$. Of these reflections 87 belonged to the small cell and only 214 of the reflections were superstructure reflections. A total of 195 of the superstructure reflections had intensities between $3\sigma(I)$ and $4\sigma(I)$. The reflections were corrected for absorption ($\mu = 11.6$ cm⁻¹).

Table 1. X-Ray powder pattern of α -Mo₂C, $a = 4.732(2)$ Å, $b = 6.037(3)$ Å, $c = 5.204(2)$ Å.

d_{obs}	d_{calc}	h k l	I_{obs}
2.613	2.611	0 2 1	m
2.604	2.602	0 0 2	m
2.369	2.366	2 0 0	m
2.290	2.286	1 2 1	s
2.282	2.280	1 0 2	m
1.754	1.753	2 2 1	s
1.751	1.750	2 0 2	m
1.509	1.509	0 4 0	m
1.504	1.504	0 2 3	s
1.351	1.349	3 0 2	m
1.306	1.305	0 4 2	w
1.301	1.301	0 0 4	w
1.272	1.272	2 4 0	m
1.269	1.269	2 2 3	m
1.258	1.258	1 4 2	m
1.254	1.254	1 0 4	m
1.182	1.183	4 0 0	w

s: strong, m: medium, w: weak

The structure of Mo₂C was refined using only reflections belonging to the small cell. The program LINUS⁵ was used to compare observed and calculated intensities. The neutron scattering lengths used for Mo and C were (in units of 10⁻¹² cm) 0.688 and 0.6648, respectively.⁶

Refinement of the structure of the small cell. The observed reflections correspond to the space group *Pbcn* (No. 60). As starting values in the refinement the following set of atomic coordinates from the structure of α -Mo₂C described by Parthé and Sadagopan were used.¹ Mo1 in site 8d at (0.25, 0.125, 0.083) and C1 in

site 4c at (0, 0.375, 0.25). The number of parameters refined was: one scale factor, four positional parameters and two isotropic temperature factor parameters, giving a total of seven parameters. This model of the structure refined to a conventional *R*-value of 7.6 %, see Table 2. Fourier and difference Fourier maps phased on this model showed, however, that the structure was not completely ordered with respect to the carbon atoms but had less mass density at the atomic site listed in Table 2 than corresponding to the multiplicity 0.5 and had additional mass density at the position (0, 0.87, 0.25). A model with only partly ordered carbon atoms was introduced. A total of nine parameters was refined: one scale factor, five positional parameters, an isotropic temperature factor parameter for Mo and two multiplicity parameters for the carbon atoms. This model of the structure refined to a conventional *R*-value of 6.4 %, see Table 2. The isotropic temperature factor parameters of the carbon atoms were not refined as they were strongly correlated with the multiplicity parameters.

Refinement of the structure of the superlattice. The reflections observed for the large cell corresponds to the space group *P2₁2₁2₁* (No. 19). A Patterson function made with the superstructure reflections only showed that these reflections had scattering contributions from atoms arranged in a h.c.p. type packing that could be the atoms in the carbon sublattice. The asymmetric unit in the superstructure cell contains eight formula units. A refinement of all positional, thermal and multiplicity parameters and a scale factor would involve 145 parameters, and many of these would be strongly correlated. Refinements showed as expected that the limited number of observed intensities, 301 reflections, was insufficient for a determination of the parameter of the superstructure. Fourier maps showed, however, that the superstructure was due to a modulation of the partial ordering of the carbon atoms found for the structure described in the small cell.

Table 2. Atomic coordinates for the structure of α -Mo₂C.

Atom	Multiplicity	x	y	z	$B(\text{Å}^2)$
<i>R</i> = 7.6 %					
Mo1	1.0	0.252(5)	0.124(9)	0.083(1)	0.68(6)
C1	0.5	0	0.376(9)	0.25	0.71(9)
<i>R</i> = 6.4 % ^a					
Mo1	1.0	0.249(5)	0.130(12)	0.083(1)	0.71(7)
C1	0.10(6)	0	0.355(73)	0.25	0.70
C2	0.41(6)	0	0.866(17)	0.25	0.70

^a The list of observed and calculated structure factors is available on request.

CONCLUSION

The investigation of the crystal structure of α -Mo₂C shows that the structure is orthorhombic of the type reported previously.¹ The specimen investigated had only a partial ordering of the carbon atoms in the structure and its X-ray and neutron diffraction pattern had superstructure reflections. It is most likely that the superstructure is due to a modulation of the atomic arrangement in the carbon sublattice. The partial ordering of the carbon atoms in the structure could only be found by Fourier methods and could not be elucidated from neutron diffraction powder data.¹

The phase α -Mo₂C is obtained on cooling from the phase β -Mo₂C and an ordering of the carbon atoms in the lattice is involved in this phase transition. For the sample investigated this ordering has not been complete, and this has resulted in a crystal with a superstructure.

The interatomic distances in the structure show Mo–C distances from 2.00(2) to 2.22(2) Å.

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