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THE CRYSTAL STRUCTURE OF Mo_3Si

D. H. Templeton and Carol H. Dauben

August 24, 1949

Berkeley, California

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The Crystal Structure of Mo_3Si

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ABSTRACT

The crystal structure of Mo_3Si has been determined from powder diffraction patterns. The lattice is cubic with $\underline{a} = 4.890 \pm 0.002$. The structure is that of β- tungsten, and the compound is isomorphous with Cr_3Si and V_3Si.

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An investigation of the phase diagram of the molybdenum-silicon system has been made in this laboratory by A. Searcy and L. Brewer, who heated known mixtures of the elements and submitted them to us for x-ray examination.(1) A new phase was found whose composition corresponded to $MoSi_{0.35 \pm 0.05}$. Powder diffraction patterns were obtained using copper Kα x-rays with a 9-cm diameter powder camera and with a "Norelco" spectrometer. The density of a small sample was determined by measurement of its apparent weight in air and immersed in toluene. From these data it was possible to deduce the complete structure by a straightforward procedure depending only on the reflections of zero intensity. The result was checked by computation of the intensities of the observed lines.

The diffraction patterns corresponded to a primitive cubic lattice with $\underline{a} = 4.890 \pm 0.002$. The density measured by buoyancy was 8.4 ± 0.3, where the uncertainty is due to the weighing error of the small sample used. This value corresponds to a molecular weight of 592. The composition $MoSi_{0.35 \pm 0.05}$ deduced from the phase studies corresponds to $91 \pm 1\%$ molybdenum. Thus there are 5.6 ± 0.3, *i.e.*, 6 molybdenum atoms, and 2.1 ± 0.3, or 2 silicon atoms in each unit cell. For Mo_6Si_2 the density calculated from the x-ray measurement is 8.97 ± 0.01. The difference is not regarded as significant, because of the porous appearance

(1) A. Searcy, Ph. D. Thesis, University of California, Berkeley, 1949.

of the sample tested by buoyancy.

Reflections were observed for planes hhl only if l = 2n. Also absent were 410, 430, and 531. All other lines up to $h^2 + k^2 + l^2 = 38$ were observed. These extinctions limit the space group to O_h^3 - Pm3n and T_d^4 - P$\bar{4}$3n, which have sets of 2, 6, 8, 12, and more equivalent positions. The two-fold and six-fold special positions for these two space groups are identical, so it is sufficient to consider O_h^3. The two silicon atoms must be in 2(a): 000; 1/2 1/2 1/2. Molybdenum in 6(b): 0 1/2 1/2; 1/2 0 1/2; 1/2 1/2 0; 00 1/2; 0 1/2 0; 1/2 00 does not permit the observed reflections 210, 320, 421, and others. The two remaining sets 6(c) and 6(d) differ by the translation 1/2 1/2 1/2, and therefore give equivalent structures when combined with 2(a). Such a combination moreover requires all the observed extinctions. Therefore, the structure is:

Space group O_h^3 - Pm3n

2 Si in (a) : 000; 1/2 1/2 1/2

6 Mo in (c) : 1/4 0 1/2; 1/2 1/4 0; 0 1/2 1/4; 3/4 0 1/2; 1/2 3/4 0; 0 1/2 1/4

Intensities were calculated for this structure by the equation

$$I = p \left| F_{hkl} \right|^2 \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta} \quad 3.3 \times 10^{-5}$$

where F_{hkl} is the structure factor, p is the multiplicity, and θ is the Bragg angle. The numerical factor reduces the intensities to the arbitrary scale of the spectrometer values. The agreement of these intensities with the observed values listed in Table I confirms the structure deduced above. Reflections required to be absent by the symmetry are omitted from the table. The slightly low values observed for the first few lines are probably the result of absorption in the sample.

Table I

Diffraction Data for Mo_3Si

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.[a]	intensity visual[b]	intensity spectrometer	intensity calc.
110	0.0499	0.0497	m	22	36
200	.0994	.0994	m^-	21	25
210	.1244	.1242	vs	122	183
211	.1496	.1490	s^-	55	58
220	.1992	.1987	w	5	3
310	.2500	.2484	w^+	6	7
222	.2990	.2981	m	22	25
320	.3247	.3229	m^+	39	35
321	.3493	.3478	m^+	26	26
400	.3992	.3974	m	21	16
411,330	.4490	.4471	w	3	4
420	.4979	.4968	m^-		7
421	.5223	.5216	s		33
332	.5482	.5465	m^-		7
422	.5964	.5962	w^-		2
510,431	.6465	.6458	w^+		6
520,432	.7201c	.7198c	s^+		43
521	.7447c	.7446c	m		13
440	.7950c	.7942c	m^+		22
530,433	.8448c	.8439c	w		5
600,442	.8936c	.8935c	m		12
610	.9181c	.9183c	s^-		27
611,532	.9436c	.9432c	s		39

a $\underline{a}$ = 4.890; $CuK\alpha_1$ = 1.54050 Å

b vs = very strong; s = strong; m = medium; w = weak

c $K\alpha_1$

In this structure each Si is surrounded by 12 Mo at 2.73 Å. Each Mo has 2 Mo at 2.44 Å, 4 Si at 2.73 Å and 8 Mo at 2.99 Å.

This molybdenum silicide is isomorphous with Cr_3Si[2] and V_3Si[3]. The structure is that of β- tungsten, which has 8 W per unit cell, located in both the molybdenum and the silicon positions.[4] The compound UH_3 is similar, with 8 U in the same structure and with hydrogen in certain interstitial positions.[5]

This research was made possible by the close cooperation of A. Searcy and Professor L. Brewer. We are indebted to Dr. K. J. Palmer and Miss. M. Ballantyne of Western Regional Research Laboratory, U. S. Department of Agriculture, for the spectrometer record. Mrs. L. Jackson obtained the photographic diffraction patterns. This research was performed under the auspices of the United States Atomic Energy Commission.

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(3) H. J. Wallbaum, Z. Metallkde. 31, 362 (1939); Strukturbericht VII, 3, 98.

(4) H. Hartmann, F. Ebert, and O. Bretschneider, Z. Anorg. allg. Chem. 198, 116 (1931); Strukturbericht II, 6, 191.

(5) R. E. Rundle, J. Am. Chem. Soc. 69, 1719 (1947).

Figure 1

Structure of Mo_3Si, above, one unit cell; below, four unit cells, with atoms approximately to scale. The molybdenum atoms are shaded.

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