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The Structure of the μ-Phase Co_7Mo_6

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(*Received* 25 *August* 1961)

The μ-phase structure of Co_7Mo_6 has been confirmed by making single-crystal measurements. The atomic parameters show some significant changes when compared with those in μFe_7W_6, and the interatomic distances in Co_7Mo_6 are compared with those in other transition-metal phases. The distribution of atoms in the available sites appears to be completely ordered.

1. Introduction

The cobalt–molybdenum system has been investigated by several workers. The phase diagram in the range 0–50 at.% Mo was determined by Raydt & Tammann (1913), Takei (1928), Sykes & Graff (1935) and Haschimoto (1937). Two intermediate phases were found in this range: Co_3Mo at 25 at.% Mo and Co_7Mo_6 at 46·15 at.% Mo. Takei detected the phase Co_2Mo_3 at 60 at.% Mo, which was later confirmed by Sykes & Graff (1935) and Ham (1950). Co_2Mo_3 has a σ-phase structure (Summers-Smith, 1951; Goldschmidt, 1951).

Henglein & Kohsok (1949) showed that the intermediate phase Co_7Mo_6 was isotypic with Fe_7W_6 by comparison of their X-ray powder photographs. The structure of the latter phase had been determined by Westgren (1936) using Arnfelt's (1928) data.

The present work is concerned with the refinement of the structure of Co_7Mo_6.

2. Material

The crystal used in this work was prepared by heating pressed compacts of the two metal powders. The composition of the compacts was 58·25 wt.% Mo (i.e. 46·15 at.% Mo) and each compact was melted in an aluminium boat under 10^{-5} mm. Hg pressure using an induction heater.

Some difficulty was experienced in finding a sufficiently large single crystal and three melts had to be prepared. A few crystals of reasonable size were obtained, the habit being plate-like, with the c_{hex}-axis perpendicular to the plate. X-ray examination showed that every crystal was twinned; however, one of these crystals was successfully used for the refinement of the structure.

3. Unit cell and space group

Accurate lattice parameters were determined by the method of Farquhar & Lipson (1946). The values obtained are compared with those of Henglein & Kohsok in Table 1.

Table 1. *The lattice parameters of* Co_7Mo_6

		Henglein & Kohsok's values	
	Present investigation	58·4 wt.% Mo	Alloy at Co rich end of composition range
a_{hex}	4·762 ± 0·001 Å	4·767 ± 0·005 Å	4·725 ± 0·05 Å
c_{hex}	25·615 ± 0·005	25·65 ± 0·01	25·42 ± 0·02
a_{rh}	8·970	8·980	8·873
α	30° 47′	30° 48′	30° 53′

Laue and Weissenberg photographs were consistent with the space group $R32$, $R3m$ and $R\bar{3}m$. The last

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space group was chosen by Westgren (1936) for Fe_7W_6 and has been used for Co_7Mo_6. The subsequent refinement of Co_7Mo_6 has justified this choice.

4. Collection of intensities

Reflections of the form $0h{\cdot}l$ were collected using normal-beam, zero-layer Weissenberg photographs, and packs of five films. The radiation used was Mo $K\alpha$. Reflections out to $\sin\theta/\lambda = 1{\cdot}1$ Å^{-1} were measured by visual comparison with a scale obtained using the 02·1 reflection. The linear absorption coefficient is $\mu = 283$ cm.$^{-1}$. Absorption factors were computed for each reflection using the program devised by Wells (1960). The intensities were then corrected for Lorentz and polarization factors and allowance was made for the resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o to F_c in regions of $\sin\theta/\lambda$.

Reflections from both obverse and reverse forms of the rhombohedral cell occurred, those from the reverse component of the twinned crystal being stronger. In order to resolve the superimposed reflections—those with h a multiple of 3—, 46 non-superimposed reflections from the obverse form were measured and their intensities compared with those of the corresponding reflections from the reverse form. The twin ratio so obtained (1:6·7 in intensity) was particularly insensitive to any error in the absorption corrections as only 14 of the reflections had absorption-factors which differed for the two forms.

5. Refinement of the structure

The refinement was carried out by means of $F_o - F_c$ Fourier syntheses on the [10·0] projection using reflections from the reverse form.

The asymmetric unit chosen was half the monoclinic cell derived from the hexagonal unit cell by the matrix

$$\begin{matrix} \bar{\frac{1}{2}} & \bar{1} & 0 \\ 1 & 0 & 0 \\ \bar{\frac{1}{6}} & \bar{\frac{1}{3}} & \frac{1}{3} \end{matrix}$$

The atomic positions in the rhombohedral cell of Co_7Mo_6 are as follows:

Co_1	$1(a)$	$0, 0, 0$
Co_2	$6(h)$	x_0, x_0, z_0; x_0, z_0, x_0; z_0, x_0, x_0; $\bar{x}_0, \bar{x}_0, \bar{z}_0$; $\bar{x}_0, \bar{z}_0, \bar{x}_0$; $\bar{z}_0, \bar{x}_0, \bar{x}_0$
Mo_1	$2(c)$	x_1, x_1, x_1; $\bar{x}_1, \bar{x}_1, \bar{x}_1$
Mo_2	$2(c)$	x_2, x_2, x_2; $\bar{x}_2, \bar{x}_2, \bar{x}_2$
Mo_3	$2(c)$	x_3, x_3, x_3; $\bar{x}_3, \bar{x}_3, \bar{x}_3$

The atomic scattering factors were generated from the analytical constants for Co^{2+} and Mo^{+} proposed by Forsyth & Wells (1959). Both curves were corrected for anomalous dispersion by including the contribution $-\Delta f'$, as calculated by Dauben & Templeton (1955). The imaginary components of the scattering factors made no signifcant contribution to the magnitudes of the structure factors and this correction was not included in the calculations. The final $(F_o - F_c)$ synthesis was recalculated with the small phase shifts introduced by the imaginary components but there was no significant change in its appearance.

Initially, structure factors were calculated for a unit cell in which Co and Mo had the same coordinates as Fe and W in the structure of Fe_7W_6 proposed by Westgren. The resulting R-factor for the reflections out to $\sin\theta/\lambda = 0{\cdot}5$ Å^{-1} was 0·20. The corresponding $F_o - F_c$ synthesis showed that the most significant shifts were associated with the Mo atoms. The refinement was continued until all 165 non-zero reflections

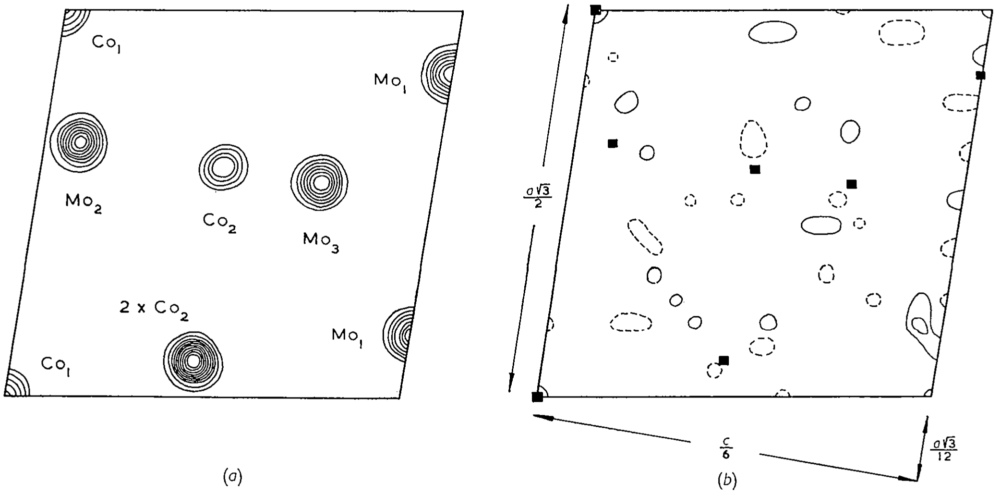

Fig. 1. Final F_o and $F_o - F_c$ [010] Fourier projections of the monoclinic asymmetric unit. (a) F_o. The contours are at equal arbitrary intervals. (b) $(F_o - F_c)$. The contour intervals are one-eighth those of the F_o map; negative contours are shown as broken lines. Squares mark the atomic sites.

out to $\sin \theta/\lambda = 1{\cdot}1$ Å^{-1} had been included and the final R-factor was $R = 0{\cdot}065$. Tabulated values of F_o and F_c will be available elsewhere (da Veiga). The final $F_o - F_c$ projection, which includes the phase changes due to anomalous dispersion, showed no significant features and is illustrated together with the final F_o synthesis in Fig. 1. There was no evidence that even the strongest reflections are affected by extinction, nor did the final difference synthesis indicate any anisotropy in the thermal vibrations of the atoms. The initial and final atomic parameters are listed in Table 2; their standard deviations were estimated from the final F_o and $(F_o - F_c)$ Fourier syntheses by the method suggested by Lipson & Cochran (1953).

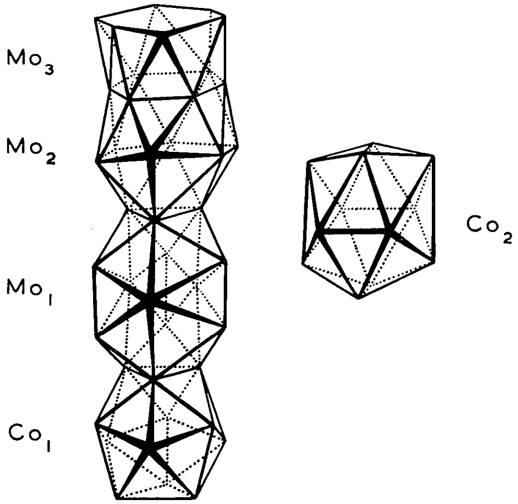

Fig. 2. Coordination polyhedra in Co_7Mo_6; the atom at the centre of each polyhedron is named. The coordination polyhedra around the Co_1, Mo_1, Mo_2 and Mo_3 atoms form an interpenetrated chain running parallel to the trigonal axis. The sequence is reversed in the top half of the unit cell by the operation of a centre of symmetry at $z = \frac{1}{2}$.

Table 2. *Initial and final atomic parameters in* Co_7Mo_6

Parameter	Initial	Final	Standard deviation
x_0	0·09	0·0895	0·0002
z_0	0·59	0·5895	0·0002
x_1	0·167	0·1655	0·0003
x_2	0·346	0·3483	0·0003
x_3	0·448	0·4518	0·0003

6. Discussion

The μ phase is known to exist in the Co–Mo, Co–W, Fe–Mo and Fe–W systems. It is structurally related to several other phases which occur between two or more transition metals: the σ phase (Fe–Cr, Co–Cr and many other systems), the P phase (Mo–Ni–Cr, Mo–Ni–Fe), the delta phase (Mo–Ni), the R phase (Mo–Co–Cr) and the χ phase (α-Mn, Mo–Fe–Cr etc.). The most obvious similarity between these phases lies in the occurrence of 12-, 14-, 15-, and 16-fold coordination polyhedra. The linkage of these polyhedra (illustrated for the μ phase in Fig. 2) is discussed by Shoemaker, Shoemaker & Wilson (1957), Frank & Kasper (1958, 1959) and Komura, Sly & Shoemaker (1960).

The structure of the μ phase is shown in Fig. 3. The diffraction data are consistent with perfect ordering of the atoms on the various sites; the smaller cobalt atoms occupy the two sites with 12-fold coordination and the molybdenum atoms occupy the 14-, 15- and 16-fold sites.

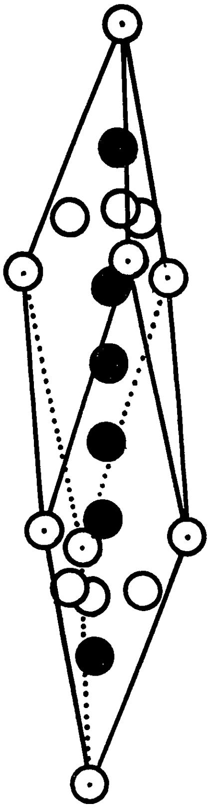

Fig. 3. The rhombohedral unit cell of Co_7Mo_6.
● Mo atoms, ⊙ Co_1 atoms, ○ Co_2 atoms.

A detailed discussion of the interatomic distances, which are listed in Table 3, must await the structure refinement of the other two binary phases, σCo_2Mo_3 and Co_3Mo (Ni_3Sn type). This work is being undertaken in the laboratory at the time of writing. The mean interatomic distances for Co_7Mo_6 and Fe_7W_6 are given in Table 4; they are very similar and are in good agreement with the generally accepted radii of the elements. There are, however, two short Mo_3–Mo contacts of 2·469 and 2·651 Å which result from the interpenetration of the 14-fold Mo_3 coordination poly-

Table 3. *Interatomic distances in* Co_7Mo_6, *together with their standard deviations*

Atom	Neighbour	Distance	Standard deviation	Other neighbours
Co_1	6 Co_2	2·408 Å	0·002 Å	
	6 Mo_2	2·776	0	
Co_2	4 Co_2	2·381	0·002	
	1 Mo_1	2·647	0·003	
	1 Mo_1	2·699	0·003	
	1 Mo_2	2·731	0·003	
	2 Mo_2	2·865	0·002	
	2 Mo_3	2·605	0·002	1 Co_1
Mo_1	3 Mo_1	2·750	0	
	3 Mo_3	3·002	0·001	
	3 Mo_3	3·026	0·001	3 Co_2, 3 Co_2
Mo_2	3 Mo_2	2·854	0·001	
	1 Mo_3	2·651	0·003	3 Co_1, 3 Co_2, 6 Co_2
Mo_3	1 Mo_3	2·469	0·003	6 Co_2, 3 Mo_1, 3 Mo_1, 1 Mo_2

Table 4. *Mean interatomic distances in* Co_7Mo_6 *and* Fe_7W_6

Type	Distance	Type	Distance
Co–Co	2·386 Å	Fe–Fe	2·38 Å
Co–Mo	2·724	Fe–W	2·72
Mo–Mo	2·858	W–W	2·88

hedron with those above and below it (Fig. 2). The same short bonds exist for the W_3 atom in Fe_7W_6, the distances being 2·68 and 2·63 Å. The occurrence of this polyhedron in the σ phase is also associated with the presence of short bonds in the same directions. They occur between the atoms on the J site (Dickins, Douglas & Taylor, 1956); these atoms form a chain parallel to the z axis at approximately $c/2$ apart. A preliminary measurement of the c dimension of σCo_2Mo_3 gives a value of $4·83_5$ Å which means that the atom occupying the J site must make two contacts whose average is 2·42 Å. A complete study will be necessary before the proportion Co:Mo in this site can be determined, but in σNb_2Al (Brown & Forsyth, 1951) the J site is filled by the larger niobium atoms giving Nb–Nb distances of 2·614 and 2·572 Å compared with the diameter of 2·85 Å in the element.

The molybdenum contents of the atomic sites in the R phase Mo–Co–Cr (Komura, Sly & Shoemaker) increase from approximately zero for coordination 12 to approximately 100% for coordination 16. The average Mo–Mo distance between the completely occupied sites is 2·861 Å, in close agreement with the value in Co_7Mo_6; the Co–Mo and Co–Co distances cannot be compared as the ordering of the Co and Cr atoms in the R phase was not determined.

This research forms part of a project supported by the Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office, under Contract No. AF 61(052)-50. Some of the equipment used was purchased with the help of a generous award from the Government Grants Committee of the Royal Society.

We wish to thank Prof. N. F. Mott and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. We are indebted to Dr M. V. Wilkes and Mr E. N. Mutch for providing time on the Edsac computer. One of us (A. da V.) also wishes to thank the Calouste Gulbenkian Foundation, Lisbon for the award of a Research Studentship.

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