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The Structure of the σ-Phase Co_2Mo_3

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The σ-phase structure of Co_2Mo_3 has been confirmed by single-crystal measurements. The structure has been refined and the interatomic distances compared with those in Co_7Mo_6 and three other σ-phases. The distribution of atoms in the available sites has been determined: cobalt occupies the 12-fold, molybdenum the 15-fold, and a mixture of Co and Mo the 14-fold co-ordinated positions.

1. Introduction

Three intermediate phases have been found in the cobalt–molybdenum system: Co_3Mo at 25 at.% Mo, μCo_7Mo_6 at 46·15 at.% Mo and σCo_2Mo_3 at 60 at.% Mo (Sykes & Graff, 1935).

The structure of the phase Co_7Mo_6 has already been refined (Forsyth & da Veiga, 1962) and the refinement of the structures of the other two phases was undertaken so that the interatomic distances in the three phases might be compared.

The phase Co_2Mo_3 was confirmed by Ham (1950); Summers-Smith (1951) and Goldschmidt (1951) showed that it has a σ-phase structure. According to Sykes & Graff (1935) 'while no precise limits could be determined from the microstructures this phase appears to extend over a very narrow range of composition'.

2. Material

The crystal used in this work was prepared by heating a pressed compact of the two metal powders. The compact, of composition 71 wt.% Mo (*i.e.* 60 at.% Mo), was melted in an alumina boat under a pressure of 10^{-5} mm Hg in an induction heater. The ingot obtained was annealed at 1400 °C in a platinum-resistance furnace under the same pressure and quenched rapidly. X-ray powder photographs showed that the ingot was a single phase and no difficulty was experienced in finding a single crystal.

3. Unit cell and space group

Accurate lattice parameters were determined by the method of Farquhar & Lipson (1946). The crystal used in the structure gave values:

$$a = 9{\cdot}2287 \pm 0{\cdot}0004,\quad c = 4{\cdot}8269 \pm 0{\cdot}0006\ \text{Å}\,.$$

Some variation about these values is possible as another crystal examined gave:

$$a = 9{\cdot}221 \pm 0{\cdot}002,\quad c = 4{\cdot}814 \pm 0{\cdot}002\ \text{Å}\,.$$

If it is assumed that the positional parameters in this crystal are the same as for the crystal investigated, these differences would give rise to a maximum change in the interatomic distances listed in Table 3 of $0{\cdot}006_5$ Å (J–J distance). However, no refinement has been carried out on this specimen.

Laue, oscillation and Weissenberg photographs were consistent with the space groups $P4_2nm$, $P\bar{4}n2$ and $P4_2/mnm$. The subsequent refinement of the structure has justified the choice of the last space group.

4. Refinement of the structure

Reflections from the zero layer of the [001] projection were collected using normal-beam Weissenberg photographs; filtered Mo $K\alpha$ radiation and a multiple-film technique were used. The reflections were measured by visual comparison with an intensity scale obtained using the 330 reflection from the same crystal. The intensities were corrected for Lorentz and polarization factors and allowance was made for resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o and F_c in regions of $\sin\theta/\lambda$; this method of scaling also makes adequate allowance for the variation of absorption in the crystal used. It was found necessary to apply to the nine strongest reflections an empirical extinction correction of the type used by Damjanovic & Black (1961).

The structure was refined using $(F_o - F_c)$ syntheses. The atomic scattering factors were generated from the analytical constants for Co^{2+} and Mo^{+} proposed by Forsyth & Wells (1959), and both curves were corrected for anomalous dispersion by including the contribution $-\Delta f'$, as calculated by Dauben & Templeton (1955).

The refinement was started with an ordered arrangement of atoms, Co in A and I_1 sites and Mo in I_2, G and J, using the σNb_2Al parameters (Brown & Forsyth, 1961), although this allocation did not correspond exactly to the formula Co_2Mo_3. The subsequent refinement indicated disordering in the 14-coordinated sites, and three possible arrangements corresponding to the formula Co_2Mo_3 were investi-

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Table 1. *Atomic parameters in* σCoCr, σNb_2Al *and* σCo_2Mo_3

Type		Site	σCoCr	σNb_2Al	σCo_2Mo_3	
				Parameters		St. dev.
2(a)	(0, 0, 0)	A				
8(i)	(x_1, y_1, 0)	I_1	x_1 = 0·0654	0·0665	0·0670	0·0003
			y_1 = 0·2596	0·2615	0·2550	0·0003
8(i)	(x_2, y_2, 0)	I_2	x_2 = 0·5373	0·5350	0·5365	0·0002
			y_2 = 0·1291	0·1280	0·1283	0·0002
4(g)	(x_3, $\bar{x}_3$, 0)	G	x_3 = 0·3984	0·3965	0·3973	0·0002
8(j)	$(x_4, x_4, z_4)_0$	J	x_4 = 0·3174	0·3180	0·3180	0·0001
			z_4 = 0·250	0·2520	0·2500	0·0001

Table 2. *Possible ordering arrangements in* σCo_2Mo_3

Arrangement	Co atoms	Mo atoms	R-factor
I	2A, 8I_1, 2J = 12	4G, 8I_2, 6J = 18	0·128
II	2A, 8I_1, 2I_2 = 12	4G, 6I_2, 8J = 18	0·128
III	2A, 8I_1, 1I_2, 1J = 12	4G, 7I_2, 7J = 18	0·077
IV	2A, 8I_1, 0·8I_2, 0·8J, 0·4G = 12	3·6G, 7·2I_2, 7·2J = 18	0·091

Table 3. *Interatomic distances in* σCo_2Mo_3, *together with their standard deviations*

Site	Atom	Neighbours	Distance	St. dev.	Other neighbours
A	Co	4J	2·664 Å	0·001 Å	
		4G	2·761	0·002	
		4I_1	2·433	0·003	
I_1	Co	2J	2·682	0·004	
		2J	2·676	0·004	
		2G	2·812	0·004	
		2I_2	2·658	0·004	
		1I_2	2·636	0·004	
		1I_2	2·659	0·004	
		1I_1	2·454	0·005	1A
I_2	$\frac{7}{8}$Mo + $\frac{1}{8}$Co	2J	2·907	0·003	
		2J	2·930	0·003	
		1G	2·557	0·003	
		2I_2	2·976	0·003	
		2I_2	2·854	0·003	
		1I_2	2·462	0·004	2I_1, 1I_1, 1I_1
G	Mo	2J	3·058	0·003	
		4J	2·982	0·003	
		1G	2·681	0·004	2I_2, 4I_1, 2A
J	$\frac{7}{8}$Mo + $\frac{1}{8}$Co	2J	2·413	0·002	1G, 2G, 2I_2, 2I_2, 2I_1, 2I_1, 1A

gated. These are given in Table 2 (arrangements I–III) together with the R-factors obtained for reflections out to $\sin\theta/\lambda = 0{\cdot}61$ Å^{-1}, which are those more sensitive to the ordering. Reflections affected by extinction were not included. Both the R-factors and the $(F_o - F_c)$ syntheses indicated that arrangement III should be chosen. The final R-factor for this arrangement was 0·056 for reflections out to $\sin\theta/\lambda = 1{\cdot}3$ Å^{-1}.

In order to determine the z_4 parameter, reflections were recorded for the zero layer of the [110] projection. In this projection 15 reflections had to be corrected for extinction. The refinement was carried out as for the [001] projection and a final R-factor of 0·052 was obtained for reflections out to $\sin\theta/\lambda = 1{\cdot}4$ Å^{-1} with the sites filled as for arrangement III.

The final syntheses for the [001] and [110] projections are shown in Figs. 1 and 2 respectively.*

The final parameters are listed in Table 1 and the interatomic distances in Table 3. The standard deviations were estimated from the final F_o and $(F_o - F_c)$ Fourier syntheses by the method suggested by Lipson & Cochran (1953).

Tabulated values of F_o and F_c will be available elsewhere (da Veiga).

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* The following corrections should be made to the paper on Nb_2Al by Brown & Forsyth (1961):
Fig. 2: projected length on z axis is $c/2$ and not $c/4$ as shown, and the occupation of the overlapped peaks on the lower edge of the asymmetric unit is $2Al_1$, $1Nb_3$ and not $2Al_1$, $2Nb_3$.
Table 2: Nb_2 atom is also in contact with a further $1Al_1$ atom previously listed.

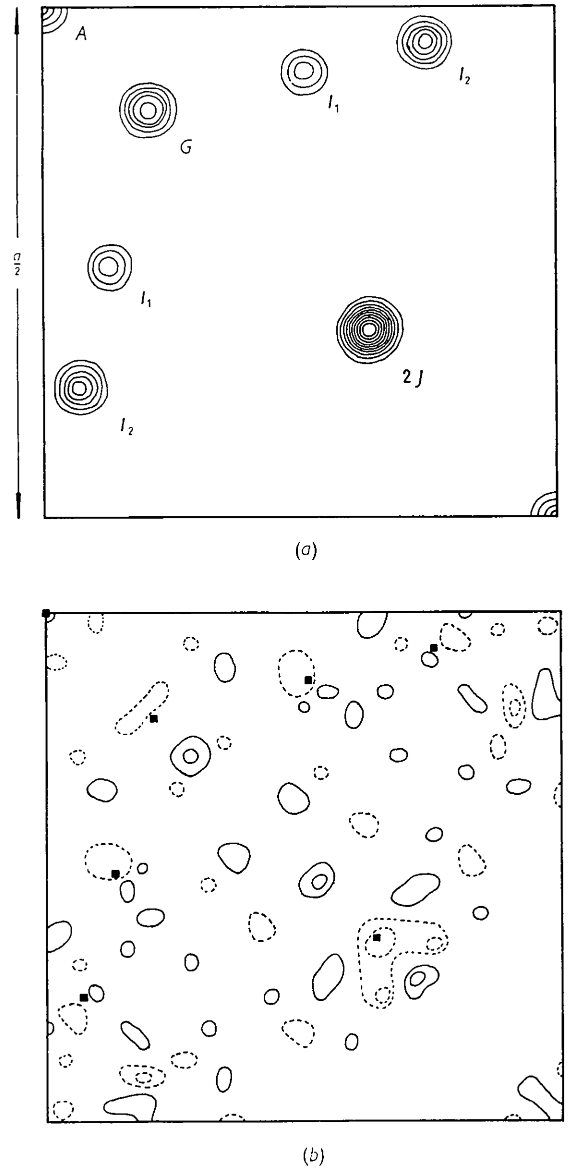

Fig. 1. Final F_o and (F_o-F_c) [001] Fourier projections. (a) F_o. The contours are at equal arbitrary intervals. (b) (F_o-F_c). The contour intervals are one-sixteenth those of the F_o; negative contours are shown as broken lines. Squares mark the atomic sites.

5. Discussion

The structure of Co_3Mo is now being refined and the interatomic distances in the three (Co–Mo) phases will be discussed in detail when this is completed. The interatomic distances in Co_2Mo_3 may, however, be compared with those in other σ-phases.

In σCo_2Mo_3, the parameter z_4 which is 0·2520 in Nb_2Al was found to be 0·2500, as in σCoCr (Dickins, Douglas & Taylor, 1956). Calculated interatomic distances with an artificial $z_4=0{\cdot}2520$ show that the distances from J atoms to others are not significantly different from those listed in Table 3, as the differences are of the same order as the standard deviations, nor can any trend in the average coordination distances be detected, even within the standard deviation, when z_4 is thus varied. On the other hand $z_4=0{\cdot}2500$ equalises the two J–J distances, *i.e.* two abnormally short Mo–Mo distances. These abnormal interatomic distances are associated with bond angles of 180°, as in Co_7Mo_6 (Forsyth & da Veiga, 1962).

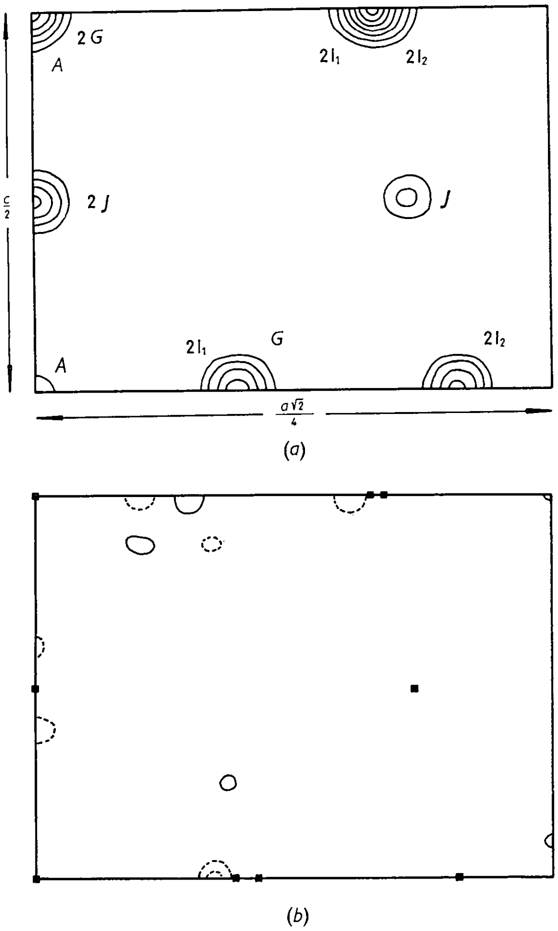

Fig. 2. Final F_o and (F_o-F_c) [110] Fourier projections. (a) F_o. The contours are at equal arbitrary intervals. (b) (F_o-F_c). The contour intervals are one-sixteenth those of the F_o; negative contours are shown as broken lines. Squares mark the atomic sites.

A and I_1 are 12-coordinated sites, I_2 and J 14-coordinated and G 15-coordinated. From size considerations it would be expected that the 2 Co atoms which cannot be accommodated in the 12-coordinated sites would share the J sites with Mo, as these sites are associated with the short interatomic distance (2·413 Å). The preference for arrangement III, in which the 2 Co are randomly distributed between the two 14-coordinated sites, suggests that coordination number is more important than size factor. The smaller cobalt atoms occupy the two 12-coordinated sites, Mo occupies the 15-coordinated, and the two 14-coordinated sites are randomly occupied by both kinds of atom. The occupation of the sites is similar to that in Co_7Mo_6 with the smaller atom occupying the lower coordinated site. The main difference is that in Co_7Mo_6 the 14-fold, as well as the 15 and 16-fold sites are occupied completely by molybdenum.

Wilson & Spooner (1963) have determined the order in the sigma phase FeMo using X-ray powder techniques. They find an ordering scheme similar to that in σCo_2Mo_3 with Fe atoms in the A and I_1 sites. However, the composition of σFeMo is approximately equiatomic and the I_2, J and G sites are occupied by 75% Mo, 25% Fe. Equal preference for cobalt atoms in the 14 and 15-fold sites in σCo_2Mo_3 does not give an equally good agreement with the observed data [see arrangement IV in Table 1]. Both the R-factor and the $(F_o - F_c)$ synthesis are worse than those for arrangement III. It is therefore suggested that, in the presence of a fairly large size difference between the constituents, partial occupation of the 15-fold sites by the smaller atom occurs only when the phase exists at a composition far removed from the ideal 'size factor' composition of 1:2, this being the ratio of 12:(14+15) fold sites. Further information on this point may result from a determination of the ordering in σ(Fe–Nb) (Goldschmidt, 1960) which is now being undertaken in this laboratory. The elements differ considerably in size (Goldschmidt radii: Fe 1·28 Å, Nb 1·47 Å) and the phase has a composition approximating to 16 Fe and 14 Nb per unit cell, even more removed from the 1:2 size ratio than σFeMo.

The mean interatomic distances were calculated in two ways between sites occupied by one kind of atom only, and between all the sites but weighting accordingly the sites shared by both kinds of atom. The results are listed in Table 4 together with those found in Co_7Mo_6. The main feature is the mean Co–Co distance which is significantly greater in Co_2Mo_3.

Table 4. *Mean interatomic distances in* σCo_2Mo_3 *and* μCo_7Mo_6

(*a*) Between sites occupied by one kind of atom only
(*b*) Including sites occupied by both kinds of atom, which were correspondingly weighted.

	σCo_2Mo_3		μCo_7Mo_6
	(*a*)	(*b*)	
Co–Co	2·437 Å	2·497 Å	2·386 Å
Co–Mo	2·778	2·722	2·724
Mo–Mo	—	2·818	2·858

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