

## Refinement of the Structure of the Phase $\text{Co}_3\text{Mo}$

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Single-crystal measurements have been used to confirm that the structure of  $\text{Co}_3\text{Mo}$  is of the type  $DO_{19}$ , and to determine the nature and extent of the distortion of the layers of atoms from the ideal close-packed configuration.

### Introduction

The phase  $\text{Co}_3\text{Mo}$  has been found at 25 at. % Mo and has a narrow range of composition (Sykes & Graff, 1935; Quinn & Hume-Rothery, 1963). Babich, Kislyakova & Umanskiy (1939) identified this phase as the compound  $\text{Co}_3\text{Mo}$  isotypic with  $\text{Ni}_3\text{Sn}$  ( $DO_{19}$  type of structure) by comparison of X-ray powder photographs of  $\text{Co}_3\text{Mo}$  and  $\text{Co}_3\text{W}$ .

The structures of the phases  $\mu\text{-Co}_7\text{Mo}_6$  and  $\sigma\text{-Co}_2\text{Mo}_3$  have already been refined (Forsyth & Alte da Veiga, 1962, 1963) and the refinement of the structure of  $\text{Co}_3\text{Mo}$  was undertaken in the first place in view of the probable interest of a comparison of the interatomic distances Co-Co and Co-Mo in the three structures.

### Material

Powder compacts of composition 35.18 wt. % Mo (*i.e.* 25 at. % Mo) were melted, with an induction heater, in an alumina boat in air at  $10^{-5}$  mmHg pressure; the ingots obtained were then annealed in a platinum resistance furnace at  $900^\circ\text{C}$  at the same pressure. Although powder photographs of the first two melts, which had been annealed for 3 and 6 days, showed they were single phase, no sufficiently large single crystal was found. A third ingot was therefore annealed for 15 days and a sufficiently large crystal was found and used for the refinement of the structure.

### Unit cell and space group

Some difficulty was experienced in determining the cell dimensions very accurately owing to the difficulty in obtaining suitable reflexions at high angles. The accuracy attained is, however, enough to obtain standard deviations of the interatomic distances of the same order as in  $\text{Co}_7\text{Mo}_6$  and  $\text{Co}_2\text{Mo}_3$  (Forsyth & Alte da Veiga, 1962, 1963). The cell dimensions, determined by the method of Farquhar & Lipson (1946), are:

$$\begin{aligned} a &= 5.1245 \pm 0.0015 \text{ \AA} \\ c &= 4.1125 \pm 0.0020 \text{ \AA} \\ 2c/a &= 1.6050 \end{aligned}$$

Laue, oscillation and Weissenberg photographs were consistent with the space groups  $P6_3mc$ ,  $P6_2c$  and  $P6_3/mmc$ . The subsequent refinement of the structure of  $\text{Co}_3\text{Mo}$  has justified the choice of  $P6_3/mmc$ , which is that also chosen for  $\text{Ni}_3\text{Sn}$  (Rahlf's, 1937).

### Refinement of the structure

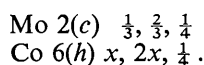
Reflexions from the zero layer of the  $[01\cdot1]$  projection were collected, normal-beam Weissenberg photographs being used; filtered Mo  $K\alpha$  radiation and a multiple-film technique were used. The reflexions were measured by visual comparison with an intensity scale obtained using the  $02\cdot0$  reflexion 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.

The  $[00\cdot1]$  projection is the one that would provide the best resolution of the atoms but it would not show any change in the  $z$  parameter which is not fixed in the space group  $P6_3mc$ . In both the other standard projections,  $[10\cdot0]$  and  $[11\cdot0]$ , Co and Mo atoms or Co and Co atoms overlap. The inclined projection  $[01\cdot1]$  provides good resolution of the atoms and the choice of space group can be made from it; this projection has allowed the determination of the atomic parameters without loss of accuracy as the only variable positional parameter of the final structure is that of the Co atoms, in  $6(h)$  sites, and atoms in these positions are confined to lines, some of which are at right angles to the axis of projection. The monoclinic unit cell chosen is derived from the hexagonal unit cell by the matrix:

$$\begin{bmatrix} 2 & 1 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{bmatrix}$$

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The atomic positions of  $\text{Co}_3\text{Mo}$  in the space group  $P6_3/mmc$  are as follows:



The structure was refined by  $F_o - F_c$  syntheses. The atomic scattering factors were generated from the analytical constants for  $\text{Co}^{2+}$  and  $\text{Mo}^{3+}$  proposed by Forsyth & Wells (1959), and were corrected for anomalous dispersion by including the contribution  $-\Delta f'$  as calculated by Dauben & Templeton (1955).

The refinement was started with the  $\text{Ni}_3\text{Sn}$  atomic parameter (Pearson, 1958, p. 202). The resulting  $R$  index for all the reflexions, out to  $\sin \theta/\lambda = 1.38 \text{ \AA}^{-1}$ , was 0.16. The corresponding  $F_o - F_c$  synthesis showed that the Co atoms should be moved from these initial positions. The refinement was continued until the  $F_o - F_c$  synthesis showed no significant features; the final  $R$  value was 0.070. There was no evidence that even the strongest reflexions were affected by extinction, nor did the final difference synthesis indicate any anisotropy in the thermal vibrations of the atoms. Tabulated values of  $F_o$  and  $F_c$  are available elsewhere

(Alte da Veiga, 1963). The final  $F_o - F_c$  and  $F_o$  syntheses are illustrated in Fig. 1. The initial parameter, and the final parameter and its standard deviation are:

Initial parameter  $x = 0.833$

Final parameter  $x = 0.8373 \pm 0.0003$

The standard deviation was estimated from the final  $F_o$  and  $F_o - F_c$  Fourier syntheses by the method suggested by Lipson & Cochran (1953).

### The interatomic distances

The structure of the phase  $\text{Co}_3\text{Mo}$  can be generated by stacking close-packed ordered layers each of which has the composition  $\text{Co}_3\text{Mo}$ . In each layer, the Mo atoms are surrounded by 6 Co atoms, and the Co atoms make contacts with 2 Mo atoms and 4 Co atoms. The stacking of the layers is such that no Mo-Mo contacts occur in the structure.

The initial atomic parameter corresponds to a close-packed layer where all the interatomic distances are equal. The final atomic parameter corresponds to a slightly distorted layer in the sense that differences occur between the interatomic distances in the layer. The cause of this distortion is most probably the difference in size between the two atoms, and the effect is to originate two sets of Co-Co distances in the layer. The interatomic distances are listed in Table 1. The distances between atoms which belong to the same layer will be considered first. The shortest Co-Co distance, 2.501 Å, is in close agreement with the proposed atomic radius for this metal (Hansen, 1958, p. 1265), but the other Co-Co distance, 2.623 Å is significantly larger. The Co-Mo distance is significantly smaller than the distance (2.65 Å) calculated from the proposed 12-fold atomic radii for the two metals. There is a compromise between the Co-Mo and the Co-Co distances, as an increase in the Co-Mo distance could only be achieved either by shortening the shorter Co-Co distance or making the long Co-Co distance even longer. The mean Co-Co distance in the layer, 2.562 Å, and the Co-Mo distance are larger than the corresponding distances between atoms which belong to different layers; as is already implied by the ratio  $2c/a = 1.605 < 1.67$ .

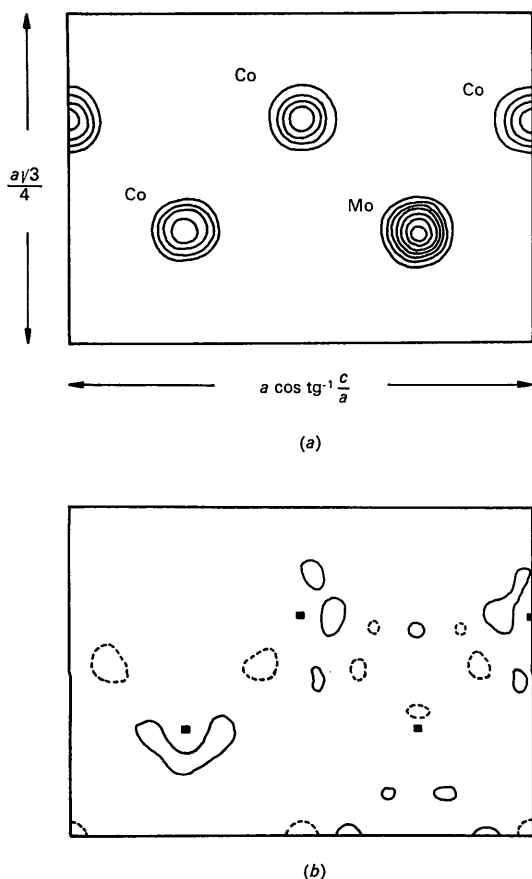


Fig. 1. Final  $F_o$  and  $F_o - F_c$  [01.1] electron-density projections. (a)  $F_o$ . The contours are at equal arbitrary intervals. (b)  $F_o - F_c$ . The contour intervals are one-eighth those of the  $F_o$  map; negative contours are shown as broken lines. Squares mark the atomic sites.

Table 1. Interatomic distances in  $\text{Co}_3\text{Mo}$ , together with their standard deviations

Atom	Neighbours	Distance	St.dev.
Mo	6 Co	2.554 Å	0.003 Å
	6 Co	2.652*	0.002
Co	4 Co	2.513	0.004
	2 Co	2.501*	0.004
	2 Co	2.623*	0.004
	2 Mo	2.554	0.003
	2 Mo	2.562*	0.002

\* Distances between atoms which belong to the same layer.

The structure of  $\text{Co}_3\text{Mo}$  is not related to those of  $\sigma\text{-Co}_2\text{Mo}_3$  and  $\mu\text{-Co}_7\text{Mo}_6$ . Mo-Mo contacts, which are the most significant feature in the last two structures (Forsyth & Alte da Veiga, 1962, 1963), do not occur in  $\text{Co}_3\text{Mo}$ . On the other hand, all Co-Mo distances are short in  $\text{Co}_3\text{Mo}$ , but not in the other two structures.

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## A Neutron and X-ray Diffraction Study of Ulvöspinel, $\text{Fe}_2\text{TiO}_4$

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Powdered specimens of ulvöspinel,  $\text{Fe}_2\text{TiO}_4$ , having lattice parameters of  $8.521 \pm 0.003$  Å and  $8.538 \pm 0.003$  Å respectively, were studied by neutron and X-ray diffraction techniques. It was confirmed that the titanium ions,  $\text{Ti}^{4+}$ , prefer to occupy the octahedral (*B*) sites rather than the tetrahedral (*A*) sites. However, the ordering was not complete and the degree of inversion was  $y = 0.92$ . Estimates of the oxygen parameter yielded  $u = 0.386 \pm 0.001$ .

### Introduction

The discovery of natural ulvöspinel by Morgensen (1946) led to a realization that this mineral may be of some significance particularly from petrological and ore dressing standpoints. A number of studies of the properties of ulvöspinel have been undertaken mainly because of its relation to rock magnetism.

Since the first synthetic specimen of ulvöspinel was prepared (Barth & Posnjak, 1932), it has been generally accepted that it is isomorphous with magnetite, that is, it has the well known spinel structure. However, the exact positions of the cations are difficult to determine accurately by X-ray diffraction because the similarity in scattering power of the iron and titanium atoms results in only small intensity differences for different cation arrangements. Moreover, the intensities are also affected by a change in the oxygen parameter. An accurate structure analysis

should be possible by neutron diffraction because the effective scattering cross-sections for neutrons of iron and titanium ions are widely different.

This paper describes a detailed structural study of two synthetic ulvöspinel specimens.

### Previous work

Ulvöspinel has a spinel structure (space group *Fd3m*) similar to magnetite (Barth & Posnjak, 1932) except that eight iron ions have been replaced by eight titanium ions in the unit cell, which contains eight molecules. If the titanium ions are considered to be tetravalent, then the addition of eight titanium ions to the magnetite structure is accompanied by the removal of eight  $\text{Fe}^{3+}$  ions and the conversion of eight  $\text{Fe}^{3+}$  ions to eight  $\text{Fe}^{2+}$  ions, so that a constant total valence of the cations is maintained. This question of the valency of the titanium ions in  $\text{Fe}_2\text{TiO}_4$  has been