

## The Crystal Structure of Cobalt Molybdate, $\text{CoMoO}_4$

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Cobalt molybdate crystallizes in the monoclinic system, space group  $C2/m$ , with 8 molecules in a cell of  $a=9.67$ ,  $b=8.85$ ,  $c=7.76$  Å,  $\beta=113^\circ 49'$ . The structure, which has a marked sub-cell exhibiting almost perfect tetragonal symmetry, was determined by Patterson and Fourier methods and refined by least-squares methods. The oxygen atoms are sixfold coordinated around both cations in a close-packed arrangement of distorted octahedra, based upon the NaCl (or CoO) type structure. However, not all the octahedral holes are filled by the cations; the cations only occupy edge-sharing octahedra in such a way that infinite chains parallel to the  $c$  axis are formed. Each chain of filled octahedra is surrounded by other chains of unfilled octahedra. Each of the two independent Co atoms is displaced from the center of its octahedron by about 0.1 Å, with Co–O distances ranging from 2.03 to 2.17 Å and from 2.01 to 2.16 Å; similarly each of the two crystallographically independent Mo atoms is displaced from the center of its octahedron by about 0.4 Å, with Mo–O distances ranging from 1.73 to 2.31 Å and from 1.72 to 2.33 Å. These displacements result in a wide range of inter-cationic distances in the structure.

### Introduction

The crystal structures of the molybdates of small cations (*e.g.* Co, Fe, Mg, Mn, Ni, Zn) are unknown although the tungstate analogues have been studied; in particular, the structure of  $\text{NiWO}_4$  has been investigated in detail (Keeling, 1957). In a previous communication (Smith, 1962) the lattice geometry of  $\text{CoMoO}_4$  as derived from single-crystal and powder diffraction data was described. The unusual lattice relationships and high degree of pseudo-symmetry present in this structure prompted the complete structure determination which is now reported here.

For the sake of completeness the crystal data and brief details of the symmetry of  $\text{CoMoO}_4$  are repeated.

System: Monoclinic.

Space group  $C2/m$ .

Cell  $a=9.666 \pm 0.008$ ,  $b=8.854 \pm 0.008$ ,

$c=7.755 \pm 0.008$  Å,  $\beta=113^\circ 49' \pm 12'$ ,

$V=607$  Å<sup>3</sup>,  $Z=8$ .

Calculated density 4.79 g.cm<sup>-3</sup>.

Highest measured density of powder material 4.69 g.cm<sup>-3</sup>.

The structure has a very marked pseudo-tetragonal sub-cell ( $a \sin \beta \times b \times \frac{1}{2}c$ ), with symmetry near to  $I4/mmm$ . The relation of this pseudo-tetragonal cell to the true monoclinic cell was illustrated earlier (Smith, 1962). In addition the intensities of reflections on the reciprocal lattice layers of constant  $l$  are related approximately to those on the layers  $(l+4)$  and  $(l+8)$  by

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$F(h-n, k, l+2n) = K F(hkl)$ ,  $n=2, 4$ , where the proportionality factor  $K$  falls off nearly as the square root of the sum of the squares of the atomic scattering factors. This relation holds approximately up to  $l=10^*$  (see Table 3).

The space groups compatible with the observed extinctions ( $hkl$ ,  $h+k$  odd) are  $C2/m$ ,  $Cm$  and  $C2$ . Space group  $C2/m$  has been assumed here, both because it is favored by the intensity statistics and because of our failure to observe a piezoelectric effect with a very sensitive apparatus.† A reasonable structure has been found on this assumption, whereas attempts to find a structure in the lower symmetry space groups have been unsuccessful.

### Experimental

A complete set of three-dimensional intensity data was collected at room temperature with Mo  $K\alpha$  radiation from one crystal. Data were recorded for the layers  $l=0$  to 10 and also for the layers  $h0l$  and  $0kl$ . Intensities were estimated visually from multiple films out to approximately  $\lambda^{-1} \sin \theta = 1$  Å<sup>-1</sup>. The intensities were reduced to  $F_0^2$  by application of the usual Lorentz-polarization corrections. The linear absorption coef-

\* Note added in proof. - The relationship of the indices of 'equivalent' reflections related by the pseudo-tetragonal symmetry, in the even  $l$  layers, is given by the continued transformation on  $hkl$  of  $-(l/2+k)$ ,  $\pm(l/2+h)$ ,  $l$ .

*e.g.* 422 → 352, 352

352 → 622, 622

622 → 152, 152

152 → 422, 422

The change of sign of the second index is permitted by monoclinic symmetry.

† We are indebted to F. Holtzberg for performing this experiment for us.

efficient of  $\text{CoMoO}_4$  for Mo  $K\alpha$  radiation is  $95.3 \text{ cm}^{-1}$ , and since the crystal employed in the analysis had approximate dimensions  $0.2 \text{ mm} \times 0.2 \text{ mm} \times 0.35 \text{ mm}$ , our neglect of an absorption correction may not be too serious. No correction has been applied for extinction. The  $|F_o|^2$  values were brought to a common scale with the use of data from the other two principal zones, and this scale was made approximately absolute by Wilson's method. The average overall isotropic temperature factor was found to be  $0.6 \text{ \AA}^2$ .

### Structure determination

Certain general features of the structure could be guessed from the peculiar intensity relationships between the various  $l$  layers. For instance the very marked intensity similarities in the even  $l$  layers, in particular, indicated that most, if not all, of the atoms must be lying in or very close to the (002) planes of the sub-cell. These planes, which are the  $(20\bar{4})$  planes of the true cell, easily give the strongest intensity, which is almost equal to the sum of the atomic scattering factors  $\sum f_i^2$ . It was also noted that  $d_{20\bar{4}} = 1.94 \text{ \AA}$  is a very likely cation–oxygen distance, while the pseudo-tetragonal symmetry indicated that the  $x$  and  $y$  coordinates of all the atoms ought to be nearly equal.

The three-dimensional Patterson map quickly confirmed these ideas and showed the distribution of the vector peaks in each sub-cell to be almost identical. It was clear that the cations were sited in (I) two sets of mirror plane positions ( $4i$ ) with (II) a further two sets on each of the twofold axes ( $4h$ ) and ( $4g$ ). The problem at this point was to distinguish which of the cations was in each of the four positions because the vector peaks arising from inter-cation vectors of like and unlike kinds were all superposed. The cation–oxygen vectors were likewise indistinguishable. Thus although it proved possible to derive four sets of cation coordinates, which gave a vector set consistent with the Patterson, it was not possible to decide whether the cations were distributed in an ordered or disordered manner over these sites. In addition to the sets of cation coordinates, three sets of oxygen coordinates were also obtained from the Patterson map (one set of which proved to be incorrect). From these atomic parameters structure factors were calculated on the assumption that the Co and Mo were randomly distributed over the four sites. The subsequent three-dimensional  $F_o$  map revealed the complete oxygen coordination, which took the form of a close-packed arrangement of octahedra. Three sets of oxygen atoms were in the general positions ( $8j$ ) with two further sets in the mirror plane ( $4i$ ). In this map, the mirror plane cation peaks were of the same weight and were very elongated in the  $z$  direction; while these features might be expected in an 'average' structure, where the signs of the weak odd  $l$  reflections are incorrect, the peak distortion could also be interpreted as disorder in the sites of these cations.

In structures possessing sub-cells the weak reflections arise from small differences in atomic content and/or sites of the sub-cells, and the assignment of correct signs to these weak superlattice reflections is always a major problem. A statistical analysis of the superlattice reflections (Mackay, 1953) for  $\text{CoMoO}_4$  yielded an average displacement from the 'ideal' structure of  $0.19 \text{ \AA}$ . Accordingly a series of structure-factor calculations was made for models incorporating several displacement values and for other models having a disordered arrangement of cations. None of these models was satisfactory. Attention was therefore concentrated on an ordered model and four trial structures were examined, each based upon a different ordered arrangement of cations that lead to the same vector set. In all these the agreement between  $F_o$  and  $F_c$  for the  $l$ -odd reflections was poor but for the  $l$ -even reflections it was good. The model which gave best agreement for the  $l$ -even reflections was chosen for refinement, and this turned out to be the proper choice.

### The refinement

Least-squares refinements were carried out on  $F$  using our local modification of the Busing–Levy ORFLS full-matrix program for the IBM 7094 computer. The scattering factors used were those for Co, O, and  $\text{Mo}^+$  tabulated by Ibers (1962), except that the  $\text{Mo}^+$  values were reduced to approximate  $\text{Mo}^0$  values by comparison with the Thomas–Fermi–Dirac values for  $\text{Mo}^+$  and  $\text{Mo}^0$ . Dispersion corrections were applied to  $F_c$  (Ibers & Hamilton, 1964), use being made of the values tabulated by Templeton (1962). The weighting scheme employed was:  $w = (150/F)^2$  for  $F > 150$ ,  $w = (F/50)$  for  $F < 50$  and  $w = 1$  for  $50 \leq F \leq 150$  electrons.

In the first series of calculations each of the nine atoms in the asymmetric unit was assigned a variable isotropic thermal parameter and refinement was carried out for the  $l$ -even reflections only. This was done because previous calculations for  $l$ -odd reflections had shown very poor agreement (conventional  $R > 50\%$ ) and it was not known whether this poor agreement resulted from an improper placement of some or all of the heavy atoms (off, for example, by  $\frac{1}{2}$  in  $z$ ) or (as it turned out) because the heavy atoms were slightly misplaced, causing the important heavy-atom contributions to these weak  $l$ -odd reflections to be incorrect. A subsequent refinement of the  $l$ -odd reflections based on the positions obtained from the  $l$ -even refinement began with an  $R$  of 18% and dropped in one cycle to 11%. From this point on all of the 1317 independent reflections were refined together, and the conventional  $R$  factor for this refinement was 0.087 and the weighted  $R$  factor 0.10. Although it seemed unlikely that this excellent agreement could be achieved if the postulated structure were not correct, a further refinement was carried out in which in addition the site occupancies of the heavy atoms were varied. This refinement yielded the same agreement factors, no significant shifts of the

Table 1. Atomic parameters for CoMoO<sub>4</sub>

Atom	Position	x	y	z	$\beta_{11}$ or $B^*$	$\beta_{22}$	$\beta_{33}$	$\beta_{13}$
Mo(1)	4(i)	0.2844 (1)†	0	0.6391 (2)	0.00078 (10)	0.00143 (10)	0.00145 (19)	-0.00013 (10)
Mo(2)	4(g)	0	0.2852 (1)	0	0.00134 (11)	0.00085 (9)	0.00111 (18)	0.00018 (10)
Co(1)	4(i)	0.3108 (2)	0	0.1555 (3)	0.00117 (18)	0.00171 (17)	0.00259 (33)	0.00020 (17)
Co(2)	4(h)	0	0.3094 (2)	$\frac{1}{2}$	0.00148 (17)	0.00131 (17)	0.00220 (29)	0.00049 (16)
O(1)	8(j)	0.5035 (9)	0.1515 (9)	0.2395 (11)	0.40 (8)			
O(2)	8(j)	0.1528 (10)	0.1656 (11)	0.0772 (13)	0.92 (11)			
O(3)	8(j)	0.1642 (10)	0.1534 (10)	0.5815 (12)	0.80 (11)			
O(4)	4(i)	0.3476 (12)	0	0.4376 (16)	0.43 (13)			
O(5)	4(i)	0.3487 (14)	0	0.9156 (18)	0.74 (15)			

\* Temperature factor expression for the heavy atoms in  $\exp\{-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl\}$ ; for the oxygen atoms the isotropic  $B$  ( $\text{\AA}^2$ ) is listed.

† Figures in parentheses are the estimated standard deviations in the preceding value.

previous parameters, and the following occupancies: Mo(1)  $1.024 \pm 0.010$ , Mo(2)  $1.001 \pm 0.009$ , Co(1)  $1.003 \pm 0.015$ , Co(2)  $0.998 \pm 0.014$ . These differ insignificantly from unit occupancy, and hence proof is provided that the structure is stoichiometric and ordered. Certain geometric features of the resultant structure were surprising; in particular each of the Mo atoms was displaced about 0.4  $\text{\AA}$  from the center of its octahedron. Refinements carried out in which the heavy atoms were re-set to the centers of the octahedra diverged, and no evidence could be found that the structure we had found was a false-minimum one. Finally attempts were made to refine a distorted version of the  $C2/m$  model in  $Cm$ . All of these calculations met with disaster, for the atoms moved toward  $C2/m$  with resultant spurious shifts from nearly singular matrices.

A difference Fourier synthesis calculated from the structure factors of the isotropic refinement with fixed occupancies of unity in  $C2/m$  showed peaks as high as  $8.9 \text{ e.\AA}^{-3}$ , about 30% of the height of an oxygen atom peak in this structure. Some of the peaks were ascribable to anisotropy of the thermal motions of the heavy atoms, and in a final series of calculations refinement was carried out with the heavy atoms allowed to vibrate anisotropically, but with the oxygen atoms restricted to isotropic motion. This refinement of 41 variables for the 1317 data converged rapidly to a conventional  $R$  factor of 0.082 and to a weighted  $R$  factor of 0.095. The improvement over the isotropic refinement, as judged by Hamilton's weighted  $R$ -factor test (Hamilton, 1965) is highly significant. The parameters obtained in this refinement are listed in Table 1, together with their standard deviations as obtained from the inverse matrix. There are no unexpected correlations between parameters; in fact, none of the correlation coefficients exceed 0.5.

In Table 2 the principal axes and orientations of the vibrational ellipsoids of the heavy atoms are listed.

In Table 3 the values of  $F_o$  and  $|F_c|$  are given. The  $|F_c|$  for unobserved reflections are not listed in Table 3 for none exceeded  $F_{\min}$  as estimated from  $I_{\min}$ .

A difference Fourier synthesis based on this anisotropic refinement showed no peaks higher than  $5 \text{ e.\AA}^{-3}$ , approximately 15% of the height of an oxygen atom in this structure.

Table 2. Root-mean-square amplitudes of vibration ( $\text{\AA}$ ) and orientation of principal axes

Atom	Axis 1	Axis 2	Axis 3	Angle 1, $a^*$
Mo(1)	0.046(4)	0.075(3)	0.080(4)	52(5)
Mo(2)	0.052(4)	0.058(3)	0.080(3)	80(6)
Co(1)	0.065(5)	0.082(4)	0.093(5)	132(8)
Co(2)	0.072(5)	0.072(5)	0.084(5)	62(20)

\* By symmetry one of the axes must be in the  $b$  direction, and this turns out to be axis 2 in each case. The angle is between axis 1 and the  $a$  axis, as measured clockwise looking down the positive  $b$  axis.

## Discussion

The structure is a close-packed arrangement of oxygen octahedra about both types of cations and can be thought of as a distorted modification of the CoO structure. The relationship between the structures can be seen from Fig. 1 where the (001) projection of CoO is shown together with the  $c$ -axis projection of CoMoO<sub>4</sub>. The  $\langle 110 \rangle$  directions of CoO are parallel to the  $a$   $\sin \beta$  and  $b$  axes of CoMoO<sub>4</sub> with the area of the ( $a \sin \beta \times b$ ) face nearly  $9/2$  times that of the (001) face

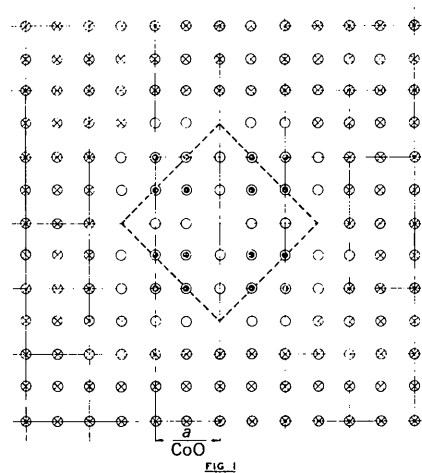


Fig. 1.  $c$ -Axis projection of CoO and CoMoO<sub>4</sub> showing relationship between the structures.

Circled crosses: Co and O sites of CoO structure.

Circled dots: Idealized cation/oxygen sites in CoMoO<sub>4</sub>.

Open circles: Idealized oxygen sites in CoMoO<sub>4</sub>.

--- Outline of unit cell of CoMoO<sub>4</sub> projected down  $c$  axis.





of  $\text{CoO}$ . However, in  $\text{CoMoO}_4$  not all of the 18 metal and 18 oxygen atom sites allowed by the  $\text{CoO}$  structure are filled. Two oxygen and ten metal atoms are omitted so that the sub-cell of  $\text{CoMoO}_4$  has the correct number of 8 metal and 16 oxygen atoms. The volume of the sub-cell of  $\text{CoMoO}_4$  is very close in value to the volume of 4 cells of  $\text{CoO}$ , whereas in the idealized structure the volume is equivalent to  $4\frac{1}{2}$  cells. This reduction in volume of the sub-cell is directly related to the change in oxygen atom content from 18 to 16.

The contraction in volume introduces some distortion of the octahedra, and the cations are off their ideal position in the centers of the octahedra (Fig. 3*b*). The effect, which is about  $0.4 \text{ \AA}$  for the Mo atoms and  $0.1 \text{ \AA}$  for the Co atoms, resembles that occurring in the structure of  $\text{NiWO}_4$ , and as in this structure the cations are off center in the opposite sense. However, the octahedral packing in  $\text{CoMoO}_4$  differs markedly from that in  $\text{NiWO}_4$  where like-filled octahedra share edges but unlike octahedra share corners only. In  $\text{CoMoO}_4$  both the like and unlike octahedra share edges to form infinite chains parallel to the  $c$  direction (Fig. 2). The sequence of pairs of cations in the  $(20\bar{4})$  plane, down the chain is  $\cdots \text{Mo}, \text{Mo}; \text{Co}, \text{Mo}; \text{Co}, \text{Co}; \text{Mo}, \text{Co}; \text{Mo}, \text{Mo} \cdots$

Each chain is surrounded by four other chains and joined to them by corner sharing of oxygen atoms, with a displacement, parallel to  $c$ , of one octahedron of the

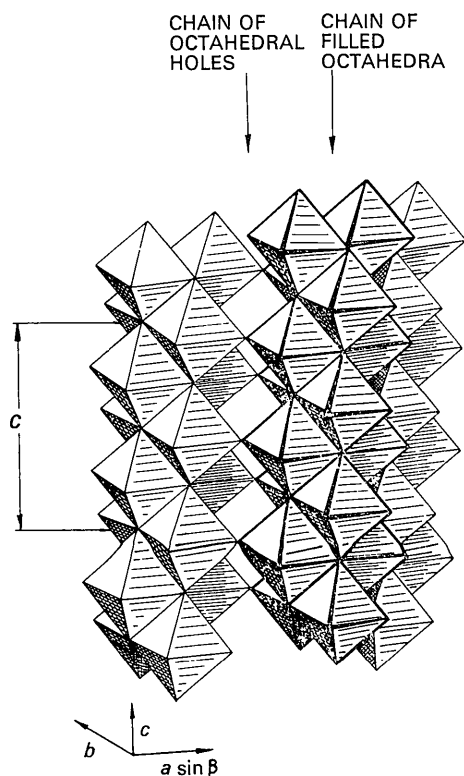


Fig. 2. Structure of  $\text{CoMoO}_4$  showing the chains of close-packed octahedra parallel to  $c$  axis. Chains of filled octahedra are joined by corner-sharing to other chains leaving unfilled octahedral holes in between.

central chain relative to its four neighbors. Between the filled chains occur chains of 'holes' of unfilled octahedra, and viewed down the  $c$  axis the structure exhibits the pseudo-tetragonal symmetry so evident in the X-ray photographs.

In Table 4 we list selected bond distances, and in Figs. 3(*a*) and (*b*) we show the principal inter-cation distances together with an indication of the directions in which these cations are displaced from the centers of their respective octahedra.

The  $\text{Co-O}$  distances for both  $\text{Co}(1)$  and  $\text{Co}(2)$  are reasonably constant and lie in the range  $2.01\text{--}2.17 \text{ \AA}$ . In contrast, the distortion arising out of the displacements of the Mo atoms leads to a much wider range for  $\text{Mo-O}$  distances. The calculated values lie between

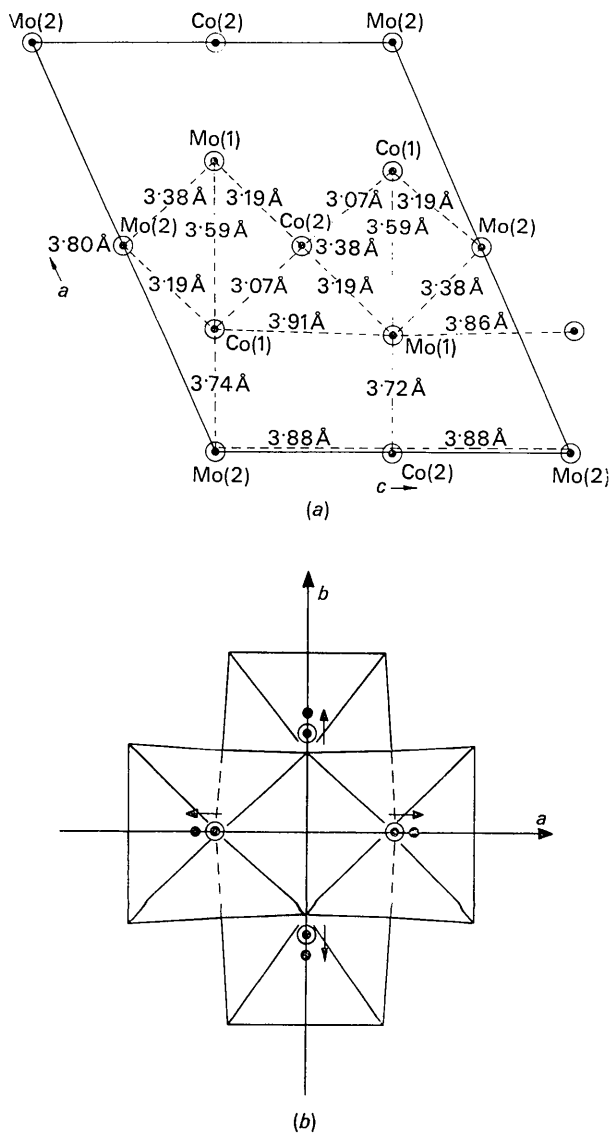


Fig. 3. (*a*)  $(010)$  projection of unit cell showing principal cation distances. (*b*)  $c$ -axis projection of octahedral chain. The off-center displacement of the cations is indicated by the arrows. Small dot: Mo atom. Circled dot: Co atom.

1.72 and 2.33 Å; the lower limit is typical of those occurring in MoO<sub>4</sub> tetrahedra but it has been reported for MoO<sub>6</sub> octahedra in the structure of sodium dimolybdate (Lindquist, 1950a).

Inter-cation distances (Table 4, Fig. 3a) also show wide variation, particularly for the edge-sharing octahedra. Distances between cations in octahedra which share corners either within a chain, *e.g.* Co(1)–Mo(1), Mo(2)–Co(2) or between chains, *e.g.* Mo(1)–Co(2) and Co(1)–Mo(2), are close to those found in the complex molybdenum oxides, Mo<sub>8</sub>O<sub>23</sub> and Mo<sub>9</sub>O<sub>26</sub> (Magnéli, 1948), though less than those reported in the complex ions (Mo<sub>7</sub>O<sub>24</sub>)<sup>6-</sup> and (Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup> (Lindquist, 1950b). On the other hand, the cation distances for the edge-sharing octahedra show a very wide range of distances. Extreme values arise between like cations: *e.g.* Mo(2)–Mo(2) = 3.80 Å compared with Co(1)–Co(2) = 3.07 Å. Other intercation distances compare favorably with those in the complex para- and tetra-molybdate ions.

Why these displacements of the cations from the centers of their octahedra occur is not known, but a study of the magnetic and electrical properties of CoMoO<sub>4</sub> might possibly provide pertinent information. There are very few well-refined complex oxide structures reported in the literature, and we believe that the displacements found here are probably more common than one would suspect on the basis of the classic oxide structures, many of which are sorely in need of redetermination or refinement.

It has been reported (Smith, 1962) that nickel molybdate is isomorphous with cobalt molybdate and simple attempts have been made to synthesize the other molybdates of small cations such as Fe, Mg, Mn, and Zn. The X-ray powder photographs of these molybdates all gave exceedingly complex patterns all differing from each other. As the valency state of the iron and manganese in the starting materials was uncertain,

the composition of the iron and manganese compounds is in doubt.

However, Young (1964) reports that at ambient pressures MnMoO<sub>4</sub> and MgMoO<sub>4</sub> give similar diffraction patterns but that ZnMoO<sub>4</sub> and FeMoO<sub>4</sub> each give unique patterns. It is also reported (Young & Schwartz, 1963) that when the small-cation molybdates are synthesized at high pressures and temperatures the stable structure is of the wolframite type with cell parameters, in each case, very close to those of the tungstate analogues; but after prolonged heating at 600°C reversion takes place to their respective structures at ordinary pressures.

The early calculations were made on a DEUCE computer, using programs written by Dr Rollett, and on an Elliott 803. Thanks are due to Mr D. J. Smith, who made the calculations, for his structure-factor program for the Elliott machine.

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### Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

*Acta Cryst.* (1965). **19**, 275

**Stannides and plumbides of Sc, Y, La and Ce with D<sub>8h</sub> structure.** By W. JEITSCHKO and E. PARTHÉ, *Metallurgy Department, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa., U.S.A.*

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#### Introduction

In the past not much attention has been paid to the alloy formation between scandium, yttrium or rare earth elements and tin or lead as second components. AB<sub>3</sub> compounds with

Cu<sub>3</sub>Au structure type were the only compounds reported which have been analyzed structurally. Partial phase diagrams have been reported for La–Pb (Cannery, 1931) and Ce–Pb (Vogel & Heumann, 1943) based mostly on metallo-