Acta Cryst. (1964). **17**, 918

The Refinement of the Crystal Structure of the Intermetallic Phase Al_4Mo

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(*Received* 19 *August* 1963)

The crystal structure of Al_4Mo has been refined by means of two-dimensional difference syntheses using visually estimated X-ray intensity data. The space group is *Cm*. The unit cell has lattice parameters $a=5{\cdot}255$, $b=17{\cdot}768$, $c=5{\cdot}225$ Å, and $\beta=100°\ 53'$ and contains 30 atoms arranged in sets of almost close-packed puckered planes. Isomorphism with Al_4W is confirmed.

Introduction

The refinement of the structure of the phase Al_4Mo forms a further part of the detailed work on the crystal structures of the aluminum-rich binary alloys with transition metals carried out under the general direction of Dr W. H. Taylor in a study of the mechanism of cohesion in transition metals and their compounds. Related theoretical studies have been reviewed recently by Mott (1962).

Numerous studies of the Al–Mo system have been made. Recent contributions are those of Sperner (1959), Schubert, Bahn, Burkhardt, Gohle, Meissner, Pötzschke & Stolz (1960), Clare (1961), Forsyth & Gran (1962), Schubert, Meissner, Pötzschke, Rossteutscher & Stolz (1962) and Pötzschke & Schubert (1962). Their results have been incorporated in a modified phase diagram published by Walford (1963, 1964).

Structural information about Al_4Mo was first given by Schubert *et al.* (1960) who published lattice parameters, and suggested, from a comparison of relative intensities, that the substance was isomorphous with Al_4W, of which the space group (*Cm*) and structure had been determined by Bland & Clark (1958). Another isomorph Al_4Tc is now known (Alte da Veiga & Walford, 1963).

Experimental

Crystals

The single crystals used were very generously supplied by Dr K. Schubert of the Max-Planck-Institut für Metallforschung in Stuttgart. The method of preparation is described in the paper by Pötzschke & Schubert (1962). The crystals occur as thick plates with the *y* axis perpendicular to the plate. No evidence for twinning was observed, although it is very prominent in the related triclinic phase Al_4Re (Alte da Veiga, 1963).

Unit cell

The accurate value of *b* was found by the method of Farquhar & Lipson (1946). Those of *a*, *c* and β were determined by Miss K. M. Adams by the method of Weisz, Cochran & Cole (1948) using a Geiger counter spectrometer. The values are:

$$a=5{\cdot}255\pm0{\cdot}005,\ b=17{\cdot}768\pm0{\cdot}005,$$
$$c=5{\cdot}225\pm0{\cdot}005\ \text{Å};\ \beta=100°53'\pm4'.$$

These values show close similarity to the corresponding values for Al_4W. The discrepancy between these values and those published by Schubert *et al.* (1960) has been removed by more accurate measurements, (Pötzschke, 1963).

Dr S. R. Nockolds, of the Department of Mineralogy and Petrology, kindly arranged for spectroscopic examination of a few of the crystals. No transition metal other than molybdenum was found in more than trace amounts. The density, measured by the displacement of bromoform, was $4{\cdot}35\pm0{\cdot}15$ g.cm^{-3}, which agrees with the calculated value, $4{\cdot}26$ g.cm^{-3}.

Intensity measurements

Consideration of the Al_4W structure showed that the [001] and [101] projections would suffer least from overlap of atoms. Intensity data were determined from zero-layer normal-beam Weissenberg photographs, two five-film packs being used for each projection. The intensities were measured by visual comparison with a standard scale. The use of filtered Mo $K\alpha$ radiation, for which Al_4Mo has a theoretical linear absorption coefficient of 52 cm^{-1}, and an approximately cubic crystal of maximum linear dimension 0·01 cm enabled serious absorption effects to be avoided; when $\mu R=0{\cdot}5$ the difference between the transmission coefficients at $\theta=0°$ and at $\theta=90°$ is only about 8% (Evans & Eckstein, 1952 — spherical approximation). This is less than the accuracy of the method of measurement of the intensities. Lorentz and polarization corrections were calculated on EDSAC 2.

The layering of the structure is so strong that marked ridges of intensity occur perpendicular to $\mathbf{y}^*$ in reciprocal space.

Refinement of the structure

The [001] projection was refined starting from the coordinates of Al_4W. For the [101] projection the $(x-z)$ coordinates of Al_4W and the refined y coordinates from the [001] projection were used. Computations were performed on EDSAC 2, using a program written by Dr M. Wells to calculate Fourier and difference syntheses and, at the predicted atomic sites, the observed electronic density and its curvatures and the difference density and its slopes.

Observed structure factors out to $\sin\theta/\lambda = 1{\cdot}3$ Å^{-1} were scaled in groups by comparison with the corresponding groups of calculated values. Eight ranges equally spaced in $\sin^2\theta/\lambda^2$ were used, giving about 28 independent reflexions per group for the [001] projection and 22 for the [101] projection after elimination of those reflexions suffering from extinction or too weak to be observed. This method of correcting F_o for the effects which are smooth functions of $\sin\theta/\lambda$ (small absorption, $\alpha_1\alpha_2$ resolution and focusing) has been discussed by Black (1955*a*). The atomic scattering factors were calculated from the analytic approximation of Forsyth & Wells (1959) with the values given in their Table 4 for Mo^+ and Al^0. The real parts of the dispersion corrections for molybdenum (Dauben & Templeton, 1955) and aluminum (Cooper, 1963, private communication) were applied. The effect of the imaginary parts was shown to be negligible for Al_8Mo_3 (Forsyth & Gran, 1962) and is even smaller for Al_4Mo.

Isotropic temperature factors of 0·4 Å^2 on Mo and 0·75 Å^2 on Al (compared with 0·27 and 0·90 respectively for the elements at the same temperature) were found to give the flattest difference maps and an F_o to F_c scaling factor which was nearly independent of $\sin\theta/\lambda$ at high angles where $\alpha_1\alpha_2$ resolution is complete. These numbers are reasonable but they cannot be interpreted directly as atomic vibrations in the sense of the Debye–Waller approximation because of other smaller uncorrected θ-dependent effects which modify the observed intensities. Both absorption and focusing act in opposition to the temperature effect. The values quoted are therefore lower limits to the true isotropic temperature factors at room temperature.

Those reflexions which were not observed although not systematically absent were excluded from the calculations. The corresponding calculated structure factors were checked to ascertain that they were always very small. The treatment of reflexions weakened by extinction is discussed later. For the purposes of the calculations these reflexions were treated as having an observed value equal to the calculated value except in the calculation of standard deviations. The validity of ignoring inaccurately observed reflexions has been discussed by Lipson & Cochran (1957, page 307). Cruickshank (1960) has shown that the standard deviation of an atomic coordinate is proportional to $(u-v)^{-\frac{1}{2}}$ where u is the number of independent reflexions used in the calculation and v is the number of independent parameters being determined. In the present example the omission of thirty reflexions would cause the standard deviation of a parameter to be increased by about 5%, assuming that the reflexions ignored are as accurate as those used.

Although the structure does not possess a centre of symmetry, the line-projection on the y axis does. In accordance with expectation, it was found that more rapid convergence was obtained by doubling the calculated shifts parallel to x but not those parallel to y. This treatment differs slightly from that suggested by Shoemaker, Donohue, Schomaker & Corey (1950) and by Buerger (1960, page 593).

The final values of the reliability index $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ were 0·063 for the [001] projection and 0·075 for the [101] projection. None of the features in the final difference syntheses is statistically significant, although the shape of the contours around the position of the atom Mo(0) in the [101] projection suggests a slightly anisotropic vibration. This effect does not occur in the [001] projection and is probably the result of ignoring certain reflexions (*cf.* Lipson & Cochran, page 307). There was no evidence for atomic disorder, partial occupation of sites or symmetry debasement.

Table 1 shows the final atomic coordinates, along

Table 1. *Atomic coordinates*

The asymmetric unit chosen was $0 \leq x \leq 1$, $0 \leq y \leq \frac{1}{4}$, $0 \leq z \leq 1$

Al(7) as originally chosen had to be moved out of this unit; hence the apparently large difference between initial and final x coordinates

Atom	Type of position and point symmetry	Initial x	Final x	$\sigma(x)$	Initial y	Final y	$\sigma(y)$	Initial z	Final z	$\sigma(z)$
Mo(0)	2(*a*)*m*	0	0	0·0002	0	0	—	0	0	0·0003
Mo(1)	4(*b*)1	0·336	0·3514	0·0002	0·137	0·1368	0·0001	0·331	0·3452	0·0003
Al(1)	2(*a*)*m*	0·125	0·1611	0·0012	0	0	—	0·491	0·5103	0·0018
Al(2)	2(*a*)*m*	0·494	0·5117	0·0015	0	0	—	0·129	0·1481	0·0020
Al(3)	4(*b*)1	0·674	0·6753	0·0013	0·076	0·0767	0·0004	0·687	0·6951	0·0018
Al(4)	4(*b*)1	0·824	0·8322	0·0013	0·118	0·1180	0·0004	0·213	0·2246	0·0018
Al(5)	4(*b*)1	0·181	0·2067	0·0016	0·129	0·1218	0·0004	0·809	0·8267	0·0020
Al(6)	4(*b*)1	0·682	0·7087	0·0015	0·232	0·2351	0·0004	0·583	0·6057	0·0019
Al(7)	4(*b*)1	0·005	0·5414	0·0013	0·245	0·2497	0·0004	0·090	0·0818	0·0018

with the initial values for comparison, and the standard deviations. These were estimated by the first of the methods given by Lipson & Cochran (1957, page 308) for non-centrosymmetric structures. No allowance has been made for the centre of symmetry in the projection onto the y axis (so that $\sigma(y)$ has been overestimated) nor for the effects of special positions (*cf.* Cruickshank & Rollett, 1953). The standard deviations are all greater than the corrections applied in the final cycle of refinement.

The final Fourier and difference syntheses are shown in Figs. 1 and 2.

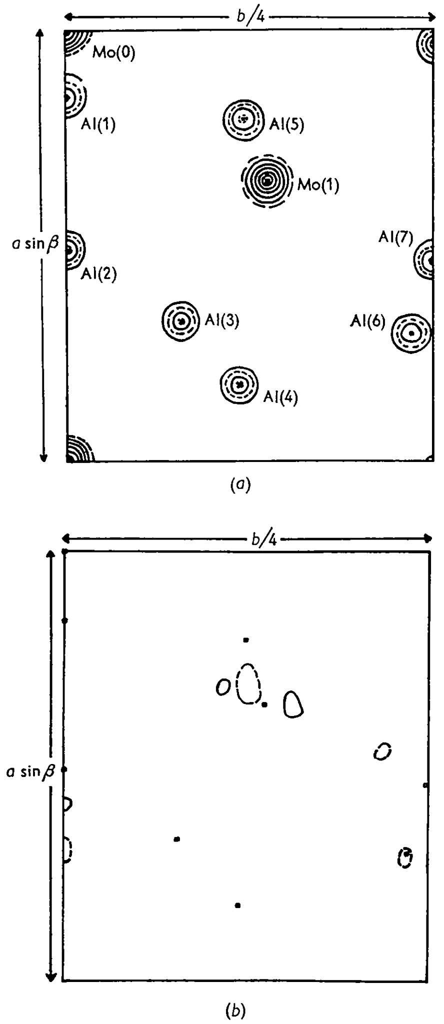

Fig. 1. (*a*) Final Fourier synthesis [001] projection. The contours around the Mo atoms are at intervals of 40 e.Å^{-2}. The contours around the Al atoms are at intervals of 20 e.Å^{-2}. Dashed contours are at half these intervals. (*b*) Final difference synthesis [001] projection. The contours are at intervals of 2 e.Å^{-2}; the zero contour is omitted. The standard deviation of the electron density is 1·8 e.Å^{-2}. Negative contours are dashed.

Full details of scaling factors and observed and calculated structure factors will be included in a thesis to be submitted to the University of Cambridge by the present author.

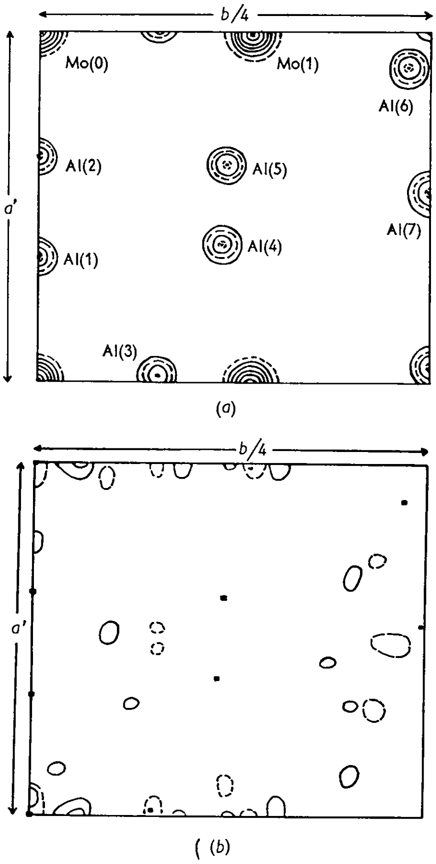

Fig. 2. (*a*) Final Fourier synthesis [101] projection. The contours around the Mo atoms are at intervals of 40 e.Å^{-2}. The contours around the Al atoms are at intervals of 20 e.Å^{-2}. Dashed contours are at half these intervals.

$$a' = ac \sin\beta / \sqrt{(a^2+c^2-2ac\cos\beta)}\ .$$

(*b*) Final difference synthesis [101] projection. The contours are at intervals of 2 e.Å^{-2}; the zero contour is omitted. The standard deviation of the electron density is 2·2 e.Å^{-2}. Negative contours are dashed.

Extinction

Reflexions suffering from extinction were identified by the fact that the calculated structure factor was consistently greater than the (scaled) observed value. As secondary extinction is a function of intensity it was assumed that above a certain value of diffracted intensity extinction effects in this crystal would cease to be negligible.

If only secondary extinction occurs Darwin (1922) showed that a graph of I_c/I_o against I_c would be a straight line (*cf.* Pinnock, Taylor & Lipson, 1956). Fig. 3 shows the strong reflexions from both projections plotted in this way. That both sets are satisfied by the same straight line shows that there is no

Table 2. *Interatomic distances*

The figures in square brackets give the number of bonds of that type when greater than one

Atom	Neighbour	Length		Already quoted	C.N.*	Mean
Mo(0)	Al(3)	2·504 Å	[2]		12	2·773 Å
	Al(4)	2·635	[2]			
	Al(1)	2·640				
	Al(2)	2·653				
	Al(5)	2·657	[2]			
	Al(2)	2·818				
	Al(1)	2·844				
	Mo(1)	3·362	[2]			
Mo(1)	Al(3)	2·489		Mo(0)	12	2·789
	Al(5)	2·684				
	Al(4)	2·702				
	Al(7)	2·727				
	Al(6)	2·731				
	Al(4)	2·738				
	Al(5)	2·776				
	Al(7)	2·786				
	Al(1)	2·825				
	Al(6)	2·826				
	Al(2)	2·830				
Al(1)	Al(5)	2·706	[2]	Mo(0)[2], Mo(1)[2]	13	2·903
	Al(2)	2·881				
	Al(4)	2·938	[2]			
	Al(3)	3·016	[2]			
	Al(3)	3·201	[2]			
Al(2)	Al(4)	2·671	[2]	Mo(0)[2], Mo(1)[2], Al(1)	13	2·895
	Al(3)	2·995	[2]			
	Al(5)	3·008	[2]			
	Al(3)	3·135	[2]			
Al(3)	Al(3)	2·726		Mo(0), Mo(1), Al(1)[2], Al(2)[2]	12	2·854
	Al(5)	2·797				
	Al(4)	2·829				
	Al(4)	2·834				
	Al(5)	2·861				
	Al(6)	2·864				
Al(4)	Al(7)	2·757		Mo(0), Mo(1)[2], Al(1), Al(2), Al(3)[2]	12	2·872
	Al(7)	2·817				
	Al(6)	3·034				
	Al(5)	3·124				
	Al(5)	3·379				
Al(5)	Al(6)	2·793		Mo(0), Mo(1)[2], Al(1), Al(2), Al(3)[2], Al(4)[2]	13	2·938
	Al(7)	2·861				
	Al(7)	3·024				
	Al(6)	3·329				
Al(6)	Al(6)	2·680	[2]	Mo(1)[2], Al(3), Al(4), Al(5)[2]	11	2·839
	Al(7)	2·724				
	Al(7)	2·768				
	Al(7)	2·804				
Al(7)	Al(7)	2·628	[2]	Mo(1)[2], Al(4)[2], Al(5)[2], Al(6)[3]	11	2·775

* C.N. = coordination number.

strongly preferred orientation for the mosaicity. The failure of the regression line to pass through $I_c/I_o=1$ when $I_c=0$ may be caused by the presence of primary extinction or by observational errors.

In view of the large number of high-angle data available, it was not considered worth while to use this graph to determine the amount of extinction occurring for each reflexion and hence a corrected value of F_o for use in the syntheses.

Description of the structure

The coordination of each atom is described in turn. Then a discussion of how these atoms fit together to form the complete structure is presented.

Individual atoms

Table 2 lists the independent interatomic distances less than 3·40 Å and Table 3 gives the standard

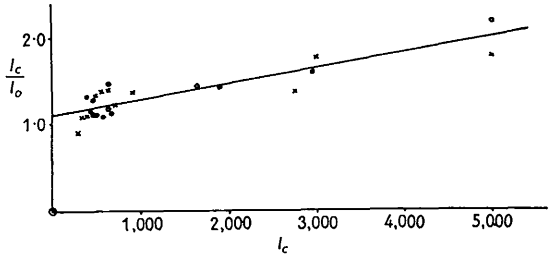

Fig. 3. Graph of I_c/I_0 against I_c for reflexions suffering from extinction.

○ = reflexions in the [001] projection;
× = reflexions in the [101] projection.

deviations for the different types of bond, estimated from those for the atomic coordinates. These are upper limits because of the overestimate of $\sigma(y)$ discussed above. The maximum length, 3·40 Å, was selected to include the Mo–Mo distance, which is almost equal to that found in Al_8Mo_3, and also because it occurred in a gap of about 0·1 Å in the otherwise almost continuous distribution of Al–Al distances. This distribution has peaks close to those lengths which would correspond to interatomic distances in a cubic close-packed material with the same mean atomic volume. It makes it difficult to describe the coordinations systematically without carrying out the very lengthy calculations demanded by the criterion of Frank & Kasper (1958). These have not been attempted. The mean interatomic distances to each atom and of each type in the complete structure are also shown in Tables 2 and 3 respectively. In the terminology of Cruickshank & Robertson (1953), the mean value of the Mo–Al distances is shorter than the sum of the Goldschmidt radii by a 'highly significant' amount. Because of the nearly continuous distribution discussed above, the mean Al–Al distance has little meaning. However about 70% of the Al–Al contacts are less than 3·0 Å and these have a mean of 2·79 Å. In the element it is 2·86 Å.

Table 3. *Bond types*

Bond type	Mean length	Standard deviation*
Mo–Mo	3·36 Å	0·002 Å
Mo–Al	2·71	0·009
Al–Al	2·89	0·012

* For an individual bond, not for the mean.

The contraction of the transition-metal–Al bond length especially in transition-metal–Al–transition-metal sequences with an interbond angle near 180° is a well-known feature of these structures (Brown, 1959). It is illustrated in this structure by the sequence Mo(0)–Al(3)–Mo(1) where the lengths are 2·50 Å and 2·49 Å respectively and the angle is 168°. Similarly, in structures of this type, transition-metal atoms tend to avoid each other as first neighbours. Here the closest approach is 3·36 Å. The relationship of this distance to the short transition-metal–Al distances is discussed in geometrical terms in the next section.

The mean bond lengths to each atom show that the Mo atoms are on the whole smaller than the Al atoms. The mean atomic volume in this structure is 16·0 $Å^3$ per atom, which is appreciably smaller than that calculated from appropriate proportions of the two elements, *viz.* 16·4 $Å^3$ per atom, or 16·5 $Å^3$ per atom if the atomic volume of molybdenum is corrected for the change from 8-fold to 12-fold coordination. The details of the variations of mean atomic volume with composition in the Al–Mo system have been given by Pötzschke & Schubert (1962). The contraction in volume has been related to the cohesive energy by Mott (1962).

In the aluminum-rich compounds of metals occurring near the beginning of each transition series, the coordination polyhedron of the transition-metal is often a regular icosahedron, *e.g.* $Al_{10}V$ (Brown, 1957). In this structure both Mo(0) and Mo(1) are 12-fold coordinated and have bonds whose directions correspond closely to those in regular icosahedral coordination. However, as the bond lengths are not all equal, a distorted structure is produced but space is more efficiently filled.

The correlations between the mean lengths of the different types of bond to a given type of atom are not significant in this structure (unlike Al_3Fe; Black, 1955*b*), with the exception of the mean Mo–Al length from an Al atom. This increases as the number of Mo neighbours increases.

The complete structure

The structure is very like Al_4W and in particular the shortest bonds are in the same positions.

As is to be expected from the geometrical properties of structures with high coordination described by Frank & Kasper (1958, 1959) and Kripyakevich (1960) and from the properties of transition-metal–Al alloys in particular (Black, 1956), the principal feature of this structure is the layering. The most prominent layers are (080), (042) and (240) in decreasing order of planarity. There are three sorts of (080) layer, one on the mirror planes at $y=0$ and $\frac{1}{2}$ consisting of Al and Mo atoms, another at $y=\frac{1}{4}$ and $\frac{3}{4}$ consisting of Al atoms only and the third at $y=\frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$ containing Al and Mo atoms and sharing an atom (Al(3)) with the layers at $y=0$ or $\frac{1}{2}$. These have been described in detail by Bland & Clark (1958). There are two sorts of (042) layer and one (240) layer. The arrangements of the atoms in all the layers form nets consisting mainly of almost equilateral triangles. A few pentagons caused by the distortion occur in the (042) and (240) layers. The interplanar spacing in all cases is 2·2 Å which is to be expected for close-packed planes in a close-packed structure of atoms of this size. These sets of planes all have very large structure factors and produce the very strong reflexions at about $\sin\theta/\lambda = 0{\cdot}23$ Å^{-1}, a phenomenon observed in most intermetallic compounds and interpreted by Jones (1934) in terms of the Brillouin zones and by Black (1955*c*) from the geometrical requirements.

The close-packed planes are arranged in the structure to intersect in six lines which would be expected to be the probable directions for the interatomic vectors. These directions correspond remarkably closely to the arrangement in cubic close-packing, as the stereograms in Fig. 4 show. Again, however, the distortions in the structure are such that the environment of individual atoms is not recognizably cubic.

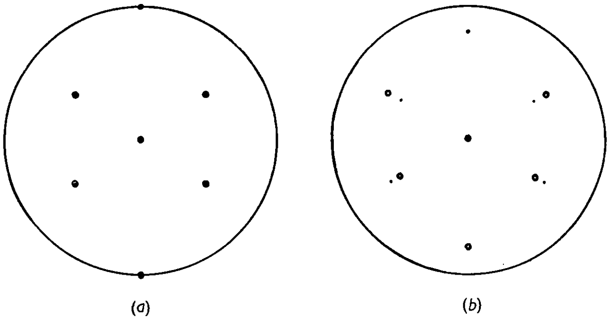
(*a*) (*b*)

Fig. 4. (*a*) Bond directions in cubic close-packing. (*b*) Directions of the intersections of the close-packed planes in Al_4Mo.

It is interesting to observe that the sequence Mo(1)–Mo(0)–Al(3)–Mo(1), in which the bond lengths are 3·36, 2·50 and 2·49 Å respectively and the angles are 167 and 168°, is roughly linear and has a total length (8·35 Å) approximately equal to the sum of the Goldschmidt radii (8·46 Å). The major distortions in the structure are thus concentrated around this row of atoms. Similar sequences exist in Al_8Mo_3 and Al_3Fe.

The relationship of this structure to Al_6Mn and $Al_{11}Mn_4$ has been described by Bland (1958) and by Bland & Clark (1958).

A final point is that the atomic arrangement in the [101] projection fits into plane group *Ccm* quite closely. Using all reflexions out to $\sin\theta/\lambda = 1{\cdot}3$ and this symmetry group, a reliability index of 0·20 was obtained.

Conclusion

The structure of Al_4Mo has been shown to have many geometrical features typical of intermetallic compounds, especially the aluminum-rich binary alloys of transition metals. The isomorph Al_4Tc and related triclinic phase Al_4Re are being studied in this laboratory at present.

This research was supported in part by the Directorate of Solid State Sciences, A.F.O.S.R., A.F.R.D. of the Air Research and Development Council, U.S.A.F., monitored by the European Office of the Air Research and Development Council under Grant No. AF-EOARDC-61-24.

I am grateful to Prof. Sir Nevill Mott and Dr W. H. Taylor for the provision of facilities and for interest and encouragement, Dr K. Schubert for supplying crystals, and Dr J. B. Forsyth, Dr M. J. Cooper and other members of this laboratory for advice and helpful criticism. Computations on the EDSAC 2 were carried out by kind permission of Dr M. V. Wilkes and Mr E. N. Mutch and with guidance and assistance from Miss J. C. Ward. For financial support I must thank St. John's College, Cambridge and the Department of Scientific and Industrial Research.

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Acta Cryst. (1964). **17**, 924

The Structures of Trioctahedral Kaolin-Type Silicates

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(*Received* 19 *June* 1963 *and in revised form* 31 *August* 1963)

From an examination of the known, fully ordered structures of trioctahedral, kaolin-type silicates, four rules are obtained which govern the way in which the layers forming the structures are stacked together. All the possible structures which may be formed in conformity with these rules are then derived. A consideration of the nature of the rules shows that the polymorphism in these silicates is unlikely to be caused by random slip occurring during the early stages of crystal formation, followed by growth around a screw dislocation.

Recent work on cronstedtite by Steadman & Nuttall (1963, 1964) has revealed eight structures of this mineral which differ from each other principally in the way in which the trioctahedral kaolin-type layers are stacked together. Polymorphism of this kind had been known previously in other minerals of this class, such as amesite and chrysotile, but these did not show such an extent of structural variety.

The present work was undertaken as an attempt to discover general principles underlying all these ordered structures, in the hope that knowledge of this kind would assist in the discovery of further structures, and, more important, would lead to an understanding of the way in which the minerals are formed. The first purpose has already been fulfilled, and details are given in an appendix.

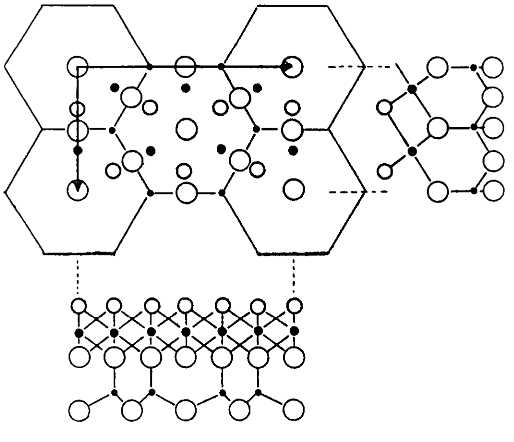

Fig. 1. The trioctahedral kaolin-type layer. The unit of structure referred to in the text is shown bounded by *a* and *b* axes, of which the *a* axis is the shorter. The smaller open circles are hydroxyl groups. The larger ones at the base of the layer are oxygen atoms, and those within the layer may be oxygen or hydroxyl.

The trioctahedral layer

The ideal structure of this layer is shown in Fig. 1. No attempt has been made to show there the departures from regularity which real layers invariably possess, since these vary from one polymorph to another. This paper will not be concerned with detailed variations of the composition or geometry of the layer, but it may be that such details do influence the structures decisively; Newnham (1961), for example, has shown how the structures of the dioctahedral minerals kaolinite and dickite appear to be determined very largely by the distortion of the layers.

The octahedral part of each layer will be referred to as being above the tetrahedral part.

Interlayer relationships

In all known structures, the layers fit together in such a manner that the oxygen atoms of one layer and the hydroxyl groups of the layer below are related in ways similar to those shown in Fig. 2(*a*) and (*b*). These again are ideal positions. The distinction is made there between the structures in which oxygen atoms fall (*a*) in triangles of hydroxyl groups which have no cation beneath them and (*b*) in triangles which do have cations beneath them. The relationships of (*a*) and (*b*) (Fig. 2) will be referred to as α and β respectively.

In the derivation of the possible structures which may exist, the structures will be regarded as being formed by stacking layers together, each layer suffer-