

high and therefore the value of I_d/I_0 falls to a low value and can hardly be distinguished from the background intensity.

Each elastic constant is evaluated from at least two different directions of the thermal wave vector. The values of the elastic constants are presented in Table 2 along with the corresponding $K[uvw]_{hkl}$. It is estimated that because of the inherent errors in the measurement of the intensity of diffuse reflexion and the direct beam, use of absorption screens and the uncertainty in the estimation of correction factors, elastic constants C_{44} , C_{55} , and C_{66} may have errors up to 5%. Evaluation of the remaining constants depends upon the accuracy of the other constants, so error may be up to 8%.

A correlation of the elastic data (Table 2) with the structure of 1,3,5-triphenylbenzene has been attempted. The crystal structure analysis shows that the molecules are arranged in two layers at approximately $x = \frac{1}{4}, \frac{3}{4}$ and are nearly parallel to the (200) planes. The diffuse spots corresponding to thermal vibrations affecting these planes signify that all the bonds in planes (200) are stronger than those normal to them. This means that C_{22} and C_{33} , a measure of resistance to expansion in layers, are greater than C_{11} , which corresponds to separation of the layers. Thermal diffuse scattering pictures also revealed transverse elastic waves of large amplitude travelling along the [100] axis such that (001) planes are strongly affected. This gives a large diffuse intensity for the reflexion 002, when the X-ray beam is parallel to [100] axis: which is presumably the cause of the small value of C_{55} .

Thanks are due to Professor Vachaspati for his kind interest and encouragement. One of us (S.C.) wishes to

Table 2. Elastic constants of 1,3,5-triphenylbenzene

Elastic constant	$K[uvw]_{hkl}$ from which the elastic constant is evaluated	Value of the elastic constant in unit of 10^{10} dynes. cm^{-2}
C_{11}	$K[100]_{206}$	0.31
C_{22}	$K[010]_{015}$	1.36
C_{33}	$K[001]_{206}$	2.33
C_{44}	$K[010]_{006}$	5.02
C_{55}	$K[100]_{002}$	0.34
C_{66}	$K[010]_{200}$	3.69
C_{12}	$K[1/2, 1/2, 0]_{200}$	-1.78
C_{23}	$K[0, 1/2, 1/2]_{006}$	0.80
C_{13}	$K[1/2, 0, 1/2]_{002}$	0.92

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Acta Cryst. (1973). A29, 28

On the Relation Between Molybdenum Trioxide and Rhenium Trioxide Type Crystal Structures

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The structural relation between MoO_3 -type and ReO_3 -type is clarified by considering layers of anions parallel to $(1\bar{3}\bar{1})_{\text{MoO}_3}$ and $(111)_{\text{ReO}_3}$. MoO_3 is then seen to be approximately cubic close-packed anions while ReO_3 is cubic close-packed anions but with one-quarter of the anion sites unoccupied. The two structures may then be interconverted by a rotation operation resembling that which links ReO_3 - and PdF_3 -type structures. Photographs of ball models are used to illustrate the relations. No compounds are known which exhibit direct transition from ReO_3 -type to either MoO_3 - or PdF_3 -type. This is probably because of the large change in volume per anion. The interface between ReO_3 and the close packed structures may be described as a *dilation* fault.

Introduction

Two groups of higher molybdenum oxides may be distinguished. The first includes MoO_3 and the structures $\text{Mo}_n\text{O}_{3n-2}$ ($n = 18$ to 22) derived from it by crys-

tallographic shear (Kihlberg, 1963a; Bursill, 1972). These occupy the composition range MoO_x ($2.8 \leq x \leq 3.00$). The second contains three subgroups, each derived from the ReO_3 structure type (Kihlberg, 1963a): Mo_4O_{11} , by the ordered omission of oxygen; Mo_8O_{23}

and Mo_9O_{26} , by crystallographic shear; Mo_5O_{14} and $\text{Mo}_{17}\text{O}_{47}$, by the formation of pentagonal bipyramids. At $x=2.8$ the MoO_3 derived structure $\text{Mo}_{18}\text{O}_{52}$ is stable below 750°C whereas the ReO_3 derived Mo_9O_{26} is stable above this temperature.

The molybdenum oxyfluorides $\text{MoO}_{3-y}\text{F}_y$ show a similar subdivision into MoO_3 - and ReO_3 -type structures (Sleight, 1969). A cubic ReO_3 -type structure was found for $0.74 \leq y \leq 0.97$ (prepared at 700°C and 3 kbar in either 48% aqueous HF or anhydrous HF) whereas a compound $\text{Mo}_4\text{O}_{11}\text{F}$ occurred at $y=0.25$. This has structure (Pierce & Vlasse, 1971) closely related to MoO_3 and $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ (Wilhelmi, 1969). Kihlborg (1963*b*) showed that Mo in MoO_3 shows a tendency towards fourfold coordination while in $\text{Mo}_{18}\text{O}_{52}$, $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ and $\text{Mo}_4\text{O}_{11}\text{F}$ the tendency is towards a more ideal octahedral coordination. Magnéli (1956) predicted that as the amount of reduced Mo increases its coordination number approaches six. On the other hand the known tungsten oxides and oxyfluorides (Magnéli, 1956; Sleight, 1969) are related to ReO_3 -type and partial substitution of W for Mo in $(\text{Mo}, \text{W})_n\text{O}_{3n-1}$ encourages the formation of homologues with $n > 9$ (Magnéli, Blomberg-Hansson, Kihlborg & Sundkvist, 1955).

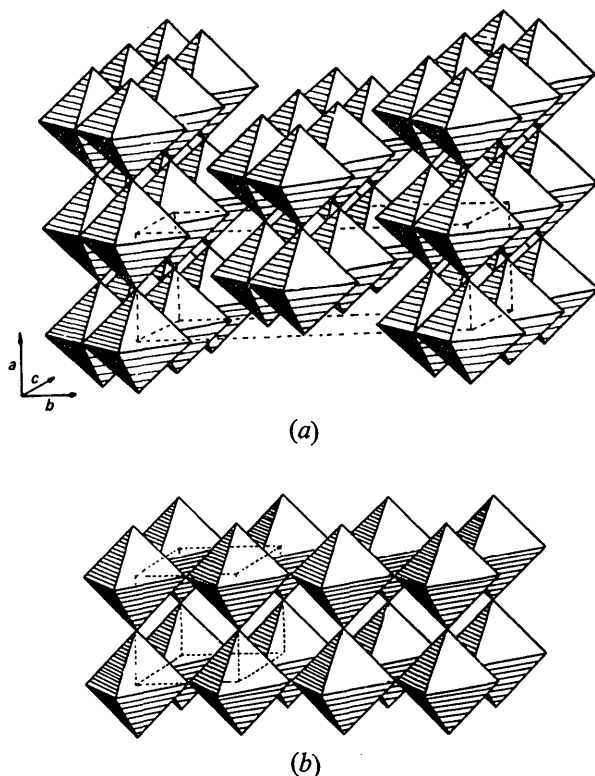


Fig. 1. Octahedral drawings of (a) MoO_3 and (b) ReO_3 , after Pierce & Vlasse (1971). Note the sheets of corner-sharing $[\text{MX}_6]$ octahedra common to both structures. These are parallel to $(010)_{\text{MoO}_3}$ and $(010)_{\text{ReO}_3}$.

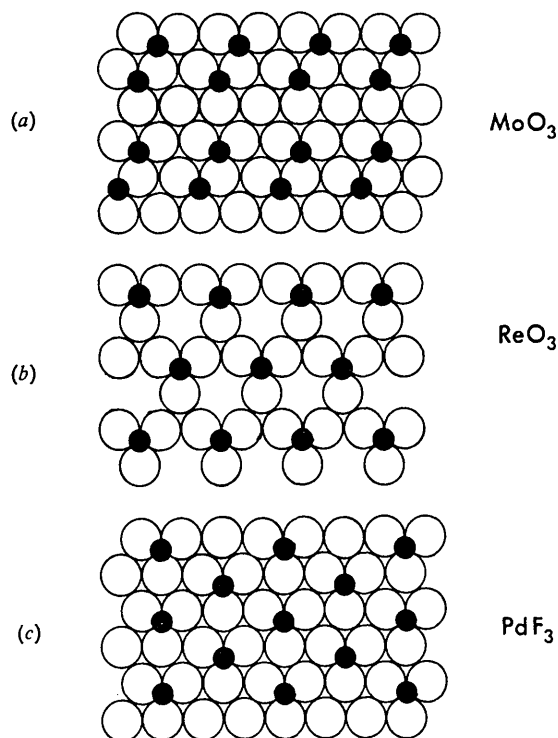


Fig. 2. (a) $(13\bar{1})_{\text{MoO}_3}$ layer consisting of close-packed anions (large balls) with metal atoms (small balls) in one third of the octahedral interstices. (b) $(111)_{\text{ReO}_3}$ layer showing a close-packed net of anions with one quarter of the sites empty and all the octahedral interstices filled with metal atoms. (c) $(111)_{\text{PdF}_3}$ layer showing close-packed anions with one third of the octahedral sites filled.

Thus the transformation of MoO_3 -type to ReO_3 -type may be accomplished by

(i) reduction of Mo^{6+} , either by reduction of anion/metal ratio or by the partial substitution of fluorine for oxygen,

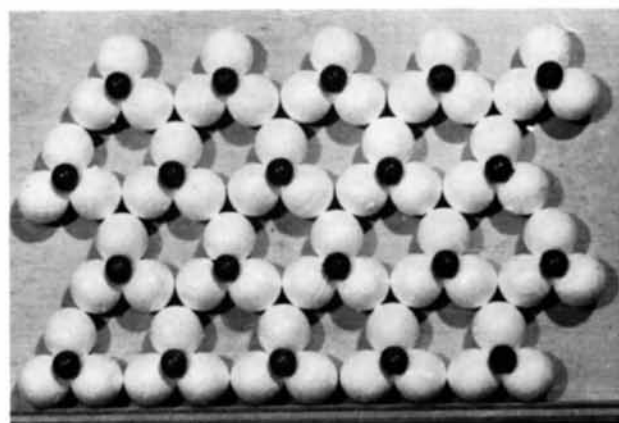
(ii) increase of temperature, e.g. at $x=2.8$, and

(iii) substitution of W for Mo.

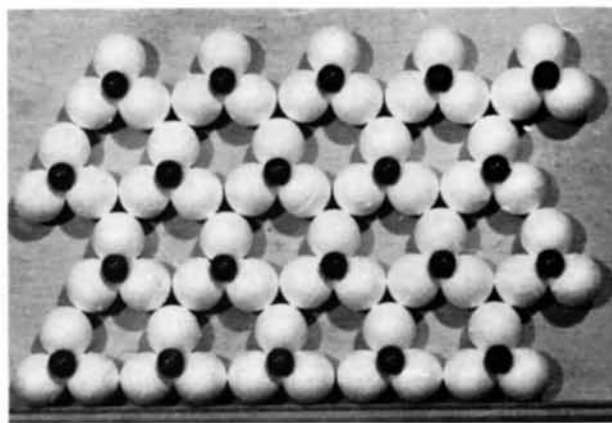
It is therefore surprising that these two basic structure types remain unrelated (Magnéli, 1956). It is the purpose of this paper to point out that a simple structural relation does in fact exist.

Relation between MoO_3 - and ReO_3 -type structures

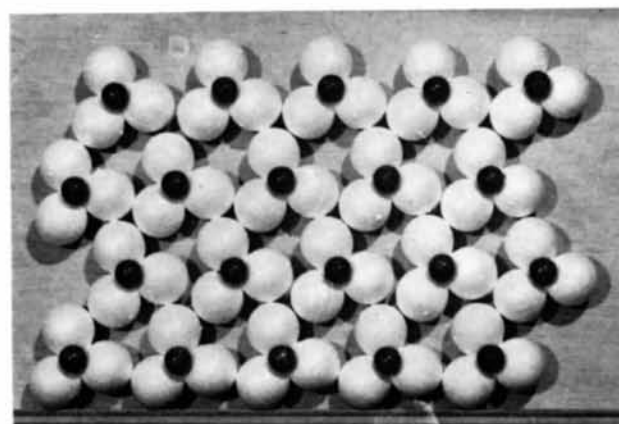
Octahedral drawings of MoO_3 and ReO_3 are shown in Fig. 1. It is apparent that the structures have in common sheets of $[\text{MoO}_6]$ octahedra joined by corners; these are parallel to $(010)_{\text{ReO}_3}$ and $(010)_{\text{MoO}_3}$. In ReO_3 these sheets are joined by further corner sharing whereas in MoO_3 pairs of sheets are fused by edge-sharing to give zigzag layers. In order to conserve stoichiometry there can be no corner-sharing between adjacent zigzag sheets. The structural relation is clarified if we compare the $(13\bar{1})_{\text{MoO}_3}$ and $(111)_{\text{ReO}_3}$ planes. The oxygen packing in MoO_3 may be idealized to cubic close-



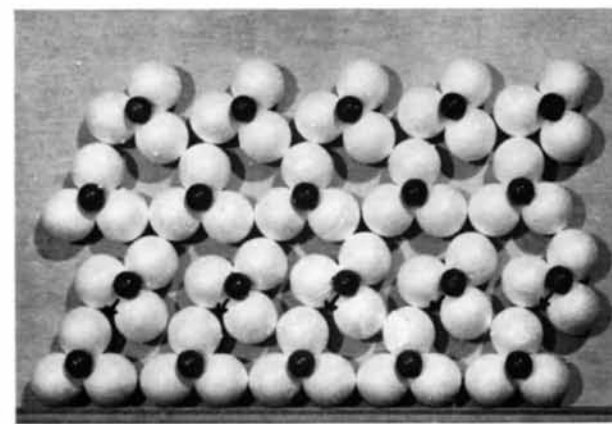
(a)



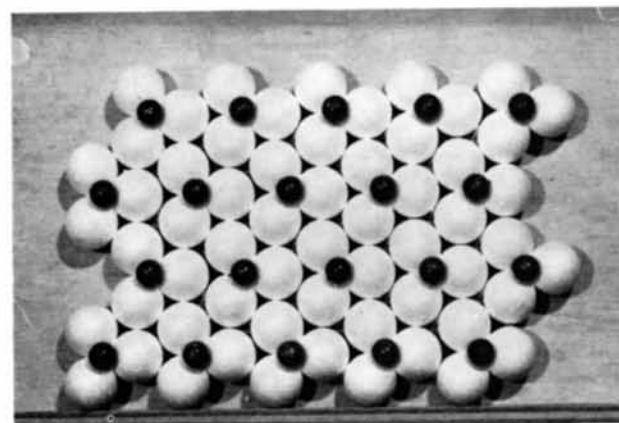
(a)



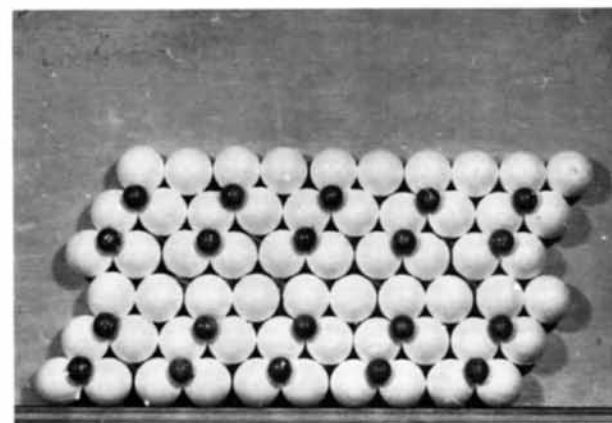
(b)



(b)



(c)



(c)

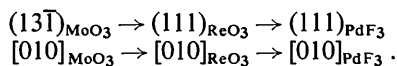
Fig.3. Three stages in a continuous transformation from $(111)_{\text{ReO}_3}$ to $(111)_{\text{PdF}_3}$. Each triangle of anions is rotated by 30° .

Fig.4. Three stages in a continuous transformation from $(111)_{\text{ReO}_3}$ to $(13\bar{1})_{\text{MoO}_3}$. Alternate rows of triangles of anions are rotated by 60° . Note the movement of metals from what become tetrahedral sites to adjacent octahedral sites in *b-c*.

packing when Mo occupy one-third of the octahedral interstices. One such close-packed layer, parallel to $(13\bar{1})_{\text{MoO}_3}$, and the arrangement of Mo sites between it and the next close-packed layer is shown in Fig. 2(a). Similarly, $(111)_{\text{ReO}_3}$ layers are arrays of close-packed anions with one-quarter of the sites unoccupied in a regular way [Fig. 2(b)]. Metal atoms now occupy all the available octahedral sites. In both MoO_3 and ReO_3 the anion layers are stacked as in cubic close-packing. Fig. 2(c) shows the metal arrangement on (111) layers of PdF_3 -type structures. The anions are again close-packed but the layers are stacked as in hexagonal close-packing (Hepworth, Jack, Peacock & Westland, 1957).

Fig. 3 shows three stages in a continuous transformation from $(111)_{\text{ReO}_3}$ to $(111)_{\text{PdF}_3}$ (rhombohedral indices). Each triangle of anions is rotated by 30° and the anion stacking changes from cubic to hexagonal close-packed. This relationship is well known (Hepworth *et al.*, 1957; Wells, 1962). The same anion movements were used by Megaw (1968) to describe the relation between LiNbO_3 (h.c.p. anions) and perovskite.

Fig. 4 shows three stages in a continuous transformation from $(111)_{\text{ReO}_3}$ to $(13\bar{1})_{\text{MoO}_3}$. Note that only every second row of triangles of anions is rotated. This is because it is unnecessary to alter the sheets of corner-shared octahedra common to $(010)_{\text{MoO}_3}$ and $(010)_{\text{ReO}_3}$ (Fig. 1). Half of these remain intact. Note that the last step *b-c* involves the cations on alternate rows apparently jumping from tetrahedral to octahedral sites. On carrying out the rotation operation on a stack of such layers it is found that these cations are naturally swept into the octahedral sites by the movement of the anions on the next layer. The orientation relationships are



Recognizing that the rotation operation is independent of the metal atoms in the interstices, provided their co-ordination requirements are met, we see that such operations provide an alternative route from cubic close packing to hexagonal close packing, regardless of the metal/anion ratio.

For the ball models there is a 25% increase in density on transforming from ReO_3 to both MoO_3 and PdF_3 . This will not necessarily follow for the real crystals. We note that the average volume per anion for $\text{MoO}_{2.4}\text{F}_{0.6}$ (ReO_3 -type) and $\text{Mo}_4\text{O}_{11.2}\text{F}_{0.8}$ (MoO_3 -type) decreases from 18.90 to 16.84 \AA^3 , a drop of 11%. Similarly the volume per anion decreases from 19.0 for $\text{Mo}_{18}\text{O}_{52}$ to 17.1 \AA^3 for Mo_9O_{26} , also about 10%. The value for MoO_3 is 16.9 \AA^3 .

There are no known polymorphs having both MoO_3 - and ReO_3 -type or both ReO_3 - and PdF_3 -type structures. The large difference in anion packing density may

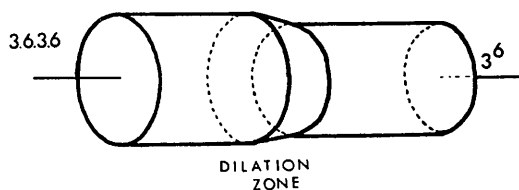


Fig. 5. Schematic diagram showing the interface between ReO_3 and either MoO_3 or PdF_3 . We call the transition zone a *dilation fault*.

explain this. If we consider the interface parallel to $(13\bar{1})_{\text{MoO}_3}$ or $(111)_{\text{PdF}_3}$ and $(111)_{\text{ReO}_3}$ we see that it must be what could be described as a *dilation fault*. There must be a transition zone (Fig. 5) between the closepacked and open nets. The possibilities for structural transitions using similar rotation operations without dilation will be considered elsewhere.

Conclusion

Although there are no known MX_3 polymorphs having both MoO_3 - and ReO_3 -type structures the above relations do link together many oxides, oxyfluorides and fluorides. This novel rotation operation relating cubic and hexagonal close packing *via* an incomplete anion lattice and the use of photographs of ball models for demonstrating such relations may have a much wider application.

The relation suggests that some ReO_3 -type structures may transform to MoO_3 -type, rather than PdF_3 -type, at high pressure. Attempts are being made to observe directly in the electron microscope the orientation relationship between $\text{Mo}_{18}\text{O}_{52}$ and Mo_9O_{26} .

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