

$$= 4\pi \int_0^{\frac{\pi}{2}} \sin \left[ \frac{A}{3} \cos \gamma (1 - 3 \sin^2 \xi) \right] \\ \times J_0 \left( -\frac{A}{2} \sin \gamma \sin 2\xi \right) \cos \xi \, d\xi.$$

Substituting in (12) gives

$$X = -4\pi \frac{c}{v} \int_{R_0}^{\infty} r^2 dr \int_0^{\frac{\pi}{2}} \sin \left[ \frac{A}{3} \cos \gamma (1 - 3 \sin^2 \xi) \right] \\ \times J_0 \left( -\frac{A}{2} \sin \gamma \sin 2\xi \right) \cos \xi \, d\xi.$$

Finally, a change in variable from  $r$  to  $u = \frac{CkR_{ss'}}{r^3} =$

$\frac{A}{3}$  gives the expression in (13).

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## Crystallographic Shear Relations between the Structure Types $\alpha$ - $\text{UO}_3$ , $\text{CaF}_2$ , $\text{La}_2\text{O}_3$ and $\text{NaCl}$ and a Correlation of some Lanthanide and Actinide Oxide Structures

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When the  $\alpha$ - $\text{UO}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{NaCl}$  structure types are idealized by a topological distortion involving only an extension or contraction of the hexagonal  $c$  axis (cubic [111]) it is clear that they are related to each other, and to the  $\text{CaF}_2$  type, by *crystallographic shear*. A number of lanthanide and actinide oxide structures are of these types, or derived superstructure types containing ordered anion 'vacancies' or 'interstitial' anions. The structural relations suggest possible reduction mechanisms.

### Introduction

A multitude of actinide and lanthanide oxides may be regarded as deriving from a very few basic structural types. The derived structures are superstructures of some of these parent types, containing ordered arrangements of 'point defects' – anion vacancies or interstitial anions. Although the structural details of many of the phases are still unknown the broad picture is quite firmly and clearly established. The basic structure types are  $\alpha$ - $\text{UO}_3$ ,  $\text{CaF}_2$  (fluorite type),  $\text{La}_2\text{O}_3$  ( $A$ -type rare earth sesquioxide) and  $\text{NaCl}$ . The derived structures are related to the first two and are summarized in Table 1. The purpose of this paper is to examine the structural relations between the basic types, and thus between the derived types also.

Previous papers (Anderson & Hyde, 1965, 1967) have discussed structural relations within various families of 'Magnéli phases', whose members are

related by so-called crystallographic shear (CS) (Wadsley, 1955). The families concerned are 'homologous series' (Magnéli, 1953) of various outer transition metal oxides in which the metal ion is octahedrally coordinated by oxygen; e.g. tungsten, molybdenum and mixed tungsten + molybdenum oxides of general formulae  $\text{M}_n\text{O}_{3n-1}$  and  $\text{M}_n\text{O}_{3n-2}$  derived from the  $\text{ReO}_3$  structure type, and titanium and vanadium oxides  $\text{M}_n\text{O}_{2n-1}$  derived from the rutile type.

A plausible dislocation mechanism was described for producing the derived phases from the parent. In reduction it involves the aggregation of anion vacancies into a disc across which the crystal then collapses and shears (the CS operation) so that the vacant sites are eliminated and the previous cation coordination [ $\text{MO}_6$ ] is restored. In oxidation a new anion plane is nucleated by aggregation of interstitial anions. Either process produces a dislocation ring which then expands by the accretion of point defects until a complete

anion plane is eliminated or generated. Recent electron microscope observations appear to substantiate the hypothesis (e.g. Amelinckx, 1964; Bursill, 1969; Bursill & Hyde, 1969).

It was stated that these principles were applicable to other systems, including those oxides in which the

cation is nominally 8-coordinated (Anderson & Hyde, 1967). Recent papers, e.g. Wallman (1964) on the transformation of curium sesquioxide from the rare earth C-type structure to the A-type and van der Walt & Louw (1968) on precipitates in arc-melted thoria, suggest that it may be useful to describe this extension.

Table 1. Structures derived from the four basic types  $\alpha$ -UO<sub>3</sub>, CaF<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> and NaCl

Basic type	Derived structure	Relationship*	Examples
$\alpha$ -UO <sub>3</sub>	low U <sub>3</sub> O <sub>8</sub> (orthorhombic)	V	
CaF <sub>2</sub>	U <sub>3</sub> O <sub>7</sub>	I	CeO <sub>2</sub> , PrO <sub>2</sub> , UO <sub>2</sub> , PuO <sub>2</sub> , CmO <sub>2</sub> , UN <sub>2</sub>
	U <sub>4</sub> O <sub>9</sub>	I	
	-	-	
	Pr <sub>12</sub> O <sub>22</sub>	V	
	Pr <sub>11</sub> O <sub>20</sub>	V	
	Pr <sub>10</sub> O <sub>18</sub>	V	
	Pr <sub>9</sub> O <sub>16</sub>	V	
La <sub>2</sub> O <sub>3</sub>	Pr <sub>7</sub> O <sub>12</sub>	V	Ce <sub>11</sub> O <sub>20</sub> , Tb <sub>11</sub> O <sub>20</sub> Ce <sub>10</sub> O <sub>18</sub> Ce <sub>9</sub> O <sub>16</sub> Ce <sub>7</sub> O <sub>12</sub> , Tb <sub>7</sub> O <sub>12</sub> , UY <sub>6</sub> O <sub>12</sub> etc. Tb <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> , Cm <sub>2</sub> O <sub>3</sub> , U <sub>2</sub> N <sub>3</sub>
	C-Pr <sub>2</sub> O <sub>3</sub>	V	
	-	-	
	B-Sm <sub>2</sub> O <sub>3</sub>	D	
	(monoclinic)	-	
NaCl	-	-	EuO, YbO, Sm(O,N), UN

\* V = ordered 'anion vacancies' in the basic structure type;  
I = ordered 'interstitial anions';  
D = slight distortion.

It should perhaps be emphasised that the 'point defects' are not defects when they are ordered on a superlattice: C-type is no more a defective fluorite type with 25% anion vacancies than sphalerite is with 50% anion vacancies or cuprite is with 75% anion vacancies.

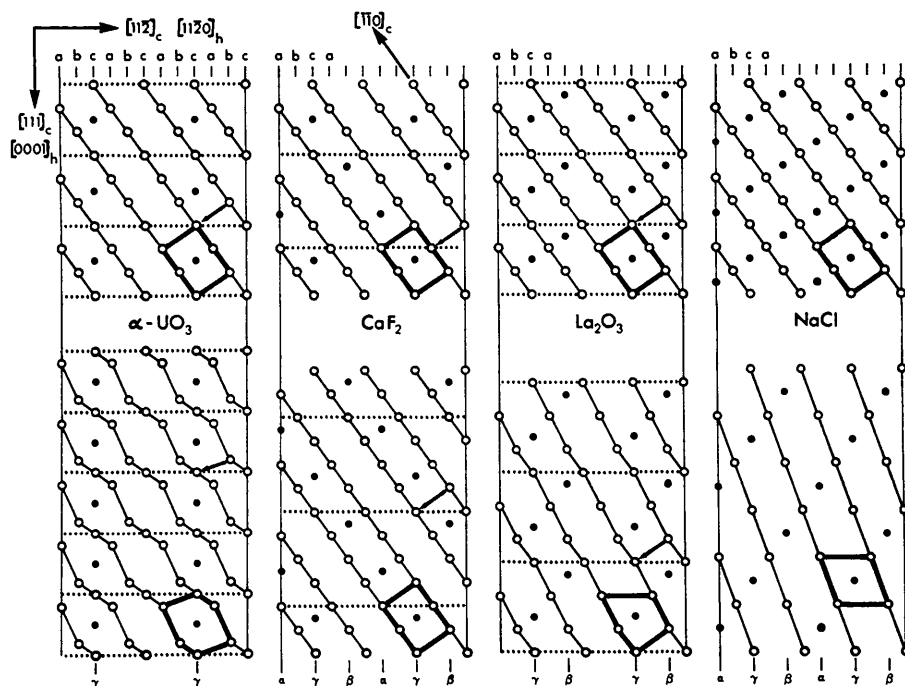


Fig. 1. Cations on a prism plane  $[(1\bar{1}00)_h = (1\bar{1}0)_c]$  and their projected anion environments. The cations are represented by filled circles and the anions by open circles. Lower: real structures; upper: idealized so that the  $[MX_8]$  coordination unit is a perfect cube. The conventional anion coordination shells are heavily outlined. The basal planes of anions that are marked with dotted lines are eliminated during reduction by CS to give the structure type adjacent on the right. The Burgers vector of the CS operation is shown by a heavy arrow.

**Formal structure relations**

The  $\alpha\text{-UO}_3$  and  $\text{La}_2\text{O}_3$  structure types are both hexagonal: fluorite and rock salt types are both face-centered cubic but, for present purposes, best considered as pseudo-hexagonal. The lower part of Fig. 1 shows corresponding planes of cations,  $(1\bar{1}00)_h$  or  $(1\bar{1}0)_c$ , (subscripts  $h$  and  $c$  denote hexagonal and cubic indices respectively) and their projected anion environments in all four structure types. The upper part of Fig. 1 shows the same structures idealized by extending or contracting the trigonal axis  $([0001]_h = [111]_c)$  so that the anion configuration around each cation is a perfect cube. Progressive reduction (from left to right in Fig. 1) involves the regular omission of a proportion of the close-packed basal planes of anions  $([0001]_h = (111)_c)$  shown dotted in Fig. 1, followed by lattice collapse and shear so that the cubic close packing sequence of anion planes ( $---abcabcabc---$ )\* and the perfect cubic coordination  $[\text{MO}_8]$  are restored. The stacking sequence of atom planes normal to the trigonal axis therefore changes in the manner shown in Table 2.

\* Although the sequence is that in cubic close packing the interplanar spacing is different (compressed by a factor of 2), so that the packing is not f.c.c.

Table 2. *The generation of the  $\text{CaF}_2$ ,  $\text{La}_2\text{O}_3$  and NaCl structure types from the  $\alpha\text{-UO}_3$  type by crystallographic shear*

The CS operation is  $\dots a(\alpha) \rightarrow b(\beta) \rightarrow c(\gamma) \rightarrow a(\alpha) \rightarrow b(\beta) \dots$ ;  $\downarrow$  = an eliminated anion layer.

$\alpha\text{-UO}_3$	$\text{CaF}_2$	$\text{La}_2\text{O}_3$	NaCl
$b$	$b$	$b$	$b$
$\gamma$	$\gamma$	$\gamma$	$\gamma$
$a$	$a$	$\downarrow$	$\downarrow$
$c$	$\downarrow$	$\downarrow$	$\downarrow$
$b - \text{CS} \rightarrow c$	$c - \text{CS} \rightarrow a$	$a$	$a$
$\gamma$	$\alpha$	$\beta$	$\beta$
$a$	$b$	$c$	$\downarrow$

Table 2 (cont.)

$\alpha\text{-UO}_3$	$\text{CaF}_2$	$\text{La}_2\text{O}_3$	NaCl
$c$	$\downarrow$	$\downarrow$	$\downarrow$
$b - \text{CS} \rightarrow a$	$\beta$	$b - \text{CS} \rightarrow a$	$c$
$\gamma$	$c$	$\gamma$	$\downarrow$
$a$	$\downarrow$	$\downarrow$	$\downarrow$
$c$	$\downarrow$	$\downarrow$	$\downarrow$
$b - \text{CS} \rightarrow b$	$\gamma$	$b - \text{CS} \rightarrow a$	$b$
$\gamma$	$a$	$\beta$	$\gamma$
$a$	$a$	$c$	$\downarrow$
$c$	$\downarrow$	$\downarrow$	$\downarrow$
$b - \text{CS} \rightarrow c$	$c$	$b - \text{CS} \rightarrow a$	$a$
$\gamma$	$\alpha$	$\gamma$	$\beta$
$a$	$b$	$\downarrow$	$\downarrow$
$c$	$\downarrow$	$\downarrow$	$\downarrow$
$b - \text{CS} \rightarrow a$	$a - \text{CS} \rightarrow a$	$a$	$c$
$\gamma$	$\beta$	$\beta$	$\alpha$
$a$	$c$	$c$	$\downarrow$
$c$	$\downarrow$	$\downarrow$	$\downarrow$
$b - \text{CS} \rightarrow b$	$b$	$b - \text{CS} \rightarrow b$	$b$
$\gamma$	$\gamma$	$\gamma$	$\gamma$

Layer sequence { anion-cubic cation-hexagonal } cubic hexagonal cubic hexagonal cubic hexagonal

The sequence of anion planes is the same in each structure in the series (*cf.* Fig. 1); only the cation sequence varies. The ideal CS displacement vectors are the same for all the transformations, being an edge of the anion cube. (In the production of the Magnéli phases it is an edge of the anion octahedron.)

The effect of the CS operations is to change corner- and edge-sharing of the  $[\text{MO}_8]$  cubes in idealized  $\alpha\text{-UO}_3$  to all edge-sharing in  $\text{CaF}_2$ ; to edge- and face-sharing in idealized  $\text{La}_2\text{O}_3$ ; to all face-sharing in idealized NaCl. A conceivable reaction mechanism is as previously described for oxides in which the cation is octahedrally coordinated: anion vacancies, produced by reduction, aggregate into a disc on the plane to be eliminated; collapse and shear across the disc eliminates the vacant sites, and eventually the complete anion plane. An element of this hypothetical process is shown in Fig. 2, in which a lamella of  $\text{La}_2\text{O}_3$  type is coherent with a fluorite type matrix, and a vacancy disc on  $(111)_c$  has collapsed with  $R = \frac{1}{2}[00a]_{\text{CaF}_2}$ .

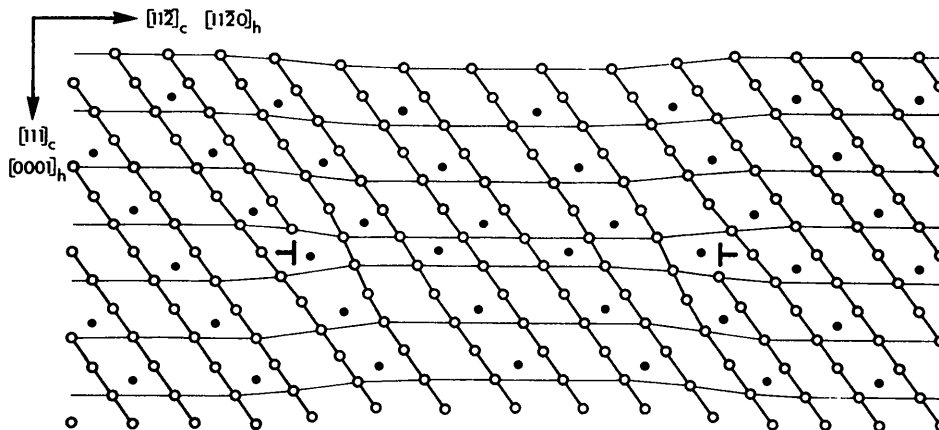


Fig. 2. A coherent lamella of A-type structure ( $\text{La}_2\text{O}_3$ ) in a fluorite type matrix.

In the case of fluorite type the real and ideal structures are identical. In  $\alpha$ - $\text{UO}_3$  the  $[\text{MO}_8]$  coordination unit is actually a dodecahedron, produced by distorting the cube mainly by contracting the



rows parallel to  $c_h$ . This reflects the presence of the uranyl groups  $\text{O-U-O}$  oriented in that direction. In both the  $\text{CaF}_2$  and  $\alpha$ - $\text{UO}_3$  structures the  $[\text{MO}_8]$  coordination is unambiguous. In contrast, the real  $\text{La}_2\text{O}_3$  and  $\text{NaCl}$  structures are produced by *extending* the ideal structures along the trigonal axes. As a result, the nominal cation coordination is reduced from  $[\text{MO}_8]$  to  $[\text{MO}_7]$  and  $[\text{MO}_6]$  respectively (see Fig. 1). This ambiguity emphasizes the difficulty sometimes experienced in assigning coordination numbers.

It is interesting to examine the distances between the close-packed cation planes [parallel to  $(0001)_h = (111)_c$ ]. In the ideal structures (Fig. 1, top) the changes on reduction follow from the successive omission of every third, fourth and third anion-only plane respectively. Consequently the ratio of the *average* cation plane separation, which we will call  $\gamma$ , to  $a_h$  is reduced at the successive steps by 33, 25 and 33% respectively. The situation is very different when the  $\gamma/a$  ratio of the real structures is examined (see Table 3.). For the conversion  $\alpha$ - $\text{UO}_3 \rightarrow \text{CaF}_2$  the change is  $\frac{2}{3}$  of the 'ideal' value: for the subsequent stages  $\gamma/a$  is very nearly constant. In other words, during the transformations  $\text{CaF}_2 \rightarrow \text{La}_2\text{O}_3$  and  $\text{La}_2\text{O}_3 \rightarrow \text{NaCl}$  oxygen planes are eliminated, and the lattice shears but remains virtually uncollapsed. Apart from a general lattice expansion due to the fall in cationic charge the volume per metal atom is almost unchanged ( $-4.5\%$ ,  $+4.5\%$ ).

#### An alternative representation

While it does not as clearly represent the CS relationship (because the CS planes are not viewed edge-on), there is another way of representing the ideal structures which emphasizes the cubic coordination  $[\text{MO}_8]$ . This shows a cation layer parallel to the face of the  $[\text{MO}_8]$  cube ( $=\{100\}_{\text{CaF}_2}$ ) together with the associated anions; a technique previously used by Eyring & Holmberg (1963) to show the relation between the  $\text{CaF}_2$  and  $\text{La}_2\text{O}_3$  structure types. The structures are represented in this way in Fig. 3. This approach emphasizes that the CS operation may in principle be equally well

achieved by the cooperative diffusion of cations through a stationary anion matrix (*cf.* Andersson & Wadsley, 1966), although this alternative is less appealing because, at least in the fluorite type structures, it is the anions that diffuse more easily. It also emphasizes that the 'ideal NaCl type structure' is in fact the CsCl type: NaCl is CsCl extended in the  $[111]_c$  direction. Viewed as pseudo-hexagonal structures the  $c/a$  ratios are 1.225 for CsCl and 2.450 for NaCl, *i.e.* the former is obtained by compressing the latter along the rhombohedral axis by a factor of 2.\*

#### Extension of the series

Two of the principal modes of accommodating stoichiometric variations are crystallographic shear and ordered 'point defects'. The above analysis suggests that these should be combined.

The behaviour may be summarized by imagining a composite family of oxides,  $\text{MO}_x$  with  $3 \geq x \geq 1$ , exhibiting all the structure types of Table 1. Starting with  $\text{MO}_3$ , reduction produces anion vacancies in its  $\alpha$ - $\text{UO}_3$  type structure, and the coordination number of some of the cations is thereby reduced. At a critical concentration the vacancies order to give regions of the  $\text{U}_3\text{O}_8$  type structure. As more oxygen is lost these regions grow until conversion to the  $\text{U}_3\text{O}_8$  type is complete. Anion vacancies then appear in the  $\text{U}_3\text{O}_8$  type structure until an intolerably high concentration is attained, when they aggregate on  $(0001)$  planes and CS eliminates the vacant sites. In this case the transformation is not, in fact,  $\alpha$ - $\text{UO}_3 \rightarrow \text{CaF}_2$  but rather  $\text{U}_3\text{O}_8 \rightarrow \text{U}_4\text{O}_9$ .† The reactant is a superstructure of  $\alpha$ - $\text{UO}_3$  with ordered 'anion vacancies'; the product may be regarded as a superstructure of the fluorite type with ordered 'interstitial anions' (Willis, 1964).

\* This has been pointed out before (*e.g.* Zintl & Brauer, 1935), although it seems not to be widely known. Wells (1962) discusses rhombohedral and other variants of the rock salt structure such as the low temperature form of KSH, but does not mention the relation to CsCl. The distortion is severe, the rhombohedral angle changing from  $60^\circ$  in NaCl to  $68^\circ$  in low KSH to  $90^\circ$  in CsCl.

† The fluorite and cadmium chloride structure types are similarly related.

† Sato's (1961) work strongly suggests that the reactant may even be a  $\text{UO}_x$  phase which is a superstructure of  $\alpha$ - $\text{UO}_3$  with an oxygen content less than that of  $\text{U}_3\text{O}_8$ . This does not affect our general argument.

Table 3. *The ratios  $c/a$  and  $\gamma/a$  for the ideal and real structures*

Structure type	Ideal structure			Real structure		
	$c/a$	$\gamma/a$	$\Delta(\gamma/a)(\%)$	$c/a$	$\gamma/a$	$\Delta(\gamma/a)(\%)$
$\alpha$ - $\text{UO}_3$	1.226	1.226		1.050	1.050	
$\text{CaF}_2$	2.450	0.817	-33	2.450	0.817	-22
$\text{La}_2\text{O}_3$	1.225	0.613	-25	1.559	0.780	-4.5
$\text{NaCl}$	1.225	0.409	-33	2.450	0.817	+4.5

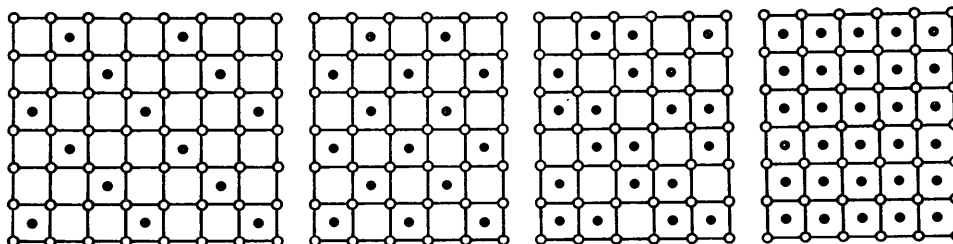


Fig. 3. Plane of cations parallel to  $(100)_c$  and the projected anion environments, idealized so that  $[MX_8]$  is a perfect cube. From left to right the structure types are  $\alpha$ - $UO_3$ ,  $CaF_2$ ,  $La_2O_3$  and  $NaCl$  ( $CsCl$ ).

Further reduction eliminates the 'interstitial anions', and fluorite type  $MO_2$  is produced.

Continued oxygen loss produces superstructures of the fluorite type with ordered arrangements of various concentrations of 'anion vacancies' (Sawyer, Hyde & Eyring, 1965) – successively  $M_{12}O_{22}$ ,  $M_{11}O_{20}$ ,  $M_{10}O_{18}$ ,  $M_9O_{16}$ ,  $M_7O_{12}$  and  $C$ -type  $M_2O_3$ . In the last, 25% of the fluorite-type anion sites in each  $\{111\}_c$  plane are vacant (Lefèvre, Brauer & Bärnighausen, 1961). At a sufficiently high temperature, or in the case of  $Cm_2O_3$  as a result of intense  $\alpha$  activity (Wallman, 1964), these 'anion vacancies' (which are ordered in groups of four on  $\{111\}_c$  planes) disorder and aggregate on every fourth  $\{111\}_c$  plane. Crystallographic shear across these (now vacant) planes eliminates all the vacant anion sites by annihilating 25% of the fluorite type  $\{111\}$  anion planes. The resulting structure (*cf.* Figs. 1 and 2) is that of  $A$ -type  $M_2O_3$  (=  $La_2O_3$  type).

It seems likely that the planar defects or precipitates recently observed in arc-melted thoria by van der Walt & Louw (1968) may be lamellae of  $La_2O_3$  type structure; perhaps unit lamellae as shown in Fig. 2. The authors interpreted their observations as arising from lamellae of  $ThO$  with the rock salt structure. The two descriptions are identical for a unit lamella.

Aggregation of the anion vacancies produced by reducing the  $La_2O_3$  structure similarly leads to a  $NaCl$ -type structure for the monoxide  $MO$ .

The complete range of behaviour described above has not been observed for any one cation  $M$ , but all parts of the full range are exhibited by various cations – particularly lanthanides and actinides (see Table 2). The increased variety and complexity, as compared with the families derived from the  $ReO_3$  and  $TiO_2$  structure types, is due to the tolerance of the lanthanide and actinide cations in the appropriate valence states

towards variation in their coordination number. This is consistent with the anion/cation radius ratios being between those values appropriate for  $[MO_6]$  and  $[MO_8]$ .

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