COORDINATION, TOPOLOGY AND STRUCTURE IN TRANSITION METAL OXIDES

RAYMOND L. MARTIN
Raymond Leslie Martin
RAYMOND LESLIE MARTIN 1926 -

Raymond Leslie Martin was born in Melbourne on 3 February 1926. His secondary education was at Scotch College, Melbourne (1932-1941), then at North Sydney Boys High School (1942). He graduated B.Sc. at the University of Melbourne in 1945, and M.Sc. (supervisor, J.S. Anderson, later Professor, and FRS) in 1947, then for the period 1947-1949 he was Senior Demonstrator in the Chemistry Department, and Senior Tutor at Queen's College, University of Melbourne. In 1949, with an 1851 Exhibition Overseas Scholarship he went to Cambridge University, where he worked with Professor H.J. Emeléus, FRS on coordination compounds of boron trifluoride, and graduated Ph.D. in 1951. Then for the period 1952-1954 he was an 1851 Senior Scholar and Research Fellow at Sidney Sussex College, Cambridge. In 1954 he returned to Australia as Senior Lecturer at the University of Technology, Sydney (later the University of N.S.W.) until 1959, when he took the position of Section Leader, Physical and Inorganic Chemistry, Central Research Laboratory, ICI (ANZ) in Melbourne. In 1962 he was appointed as the Foundation Professor and Head of the Department of Inorganic Chemistry, University of Melbourne, which position he held until 1972. During that time he spent periods of leave as Visiting Scientist, Bell Telephone Labs., Murray Hill, New Jersey (1967), and Visiting Professor at Colombia University, New York, USA (1972). In 1971 he was Dean, Faculty of Science, and Acting Dean, Faculty of Music at the University of Melbourne.

In 1972 he was appointed the Foundation Professor of Inorganic Chemistry at the Research School of Chemistry, Australian National University, acting as Dean for the period 1976-1977. In 1977 he was appointed as Vice-Chancellor and Professor at Monash University, Melbourne, which position he held for ten years, then was Professor of Chemistry at Monash University from 1987 until he retired in 1991. His research interests have been mainly in magnetochemistry, coordination chemistry, and chemistry of the solid state. During 1968-1969 he was President of the Royal Australian Chemical Institute (RACI); for the period 1988-1992 he was Chairman of the Australian Science and Technology Council (ASTEC), and between 1989-1992 was a Member of the Prime Minister's Science Council (PMSC) and the Government's Coordination Committee on Science and Technology (CCST).

In the 1980s and 1990s Ray Martin acted in various capacities in numerous institutional and national boards and committees in the Arts, Sciences, Business and philanthropic organizations. He holds Emeritus Professorships at both the Australian National University (1977-) and Monash University (1991-).

Honours and Awards (Pre-2014)

1945 Fred Walker Prize and proxime accessit Dixon Prize in the final year Chemistry, University of Melbourne
1956 FRACI (Fellow of the Royal Australian Chemical Institute)
1968 H.G. Smith Medal, RACI
1968 Sc.D., Cambridge University, UK
1971 FAA
1974 FRSC (Fellow of the Royal Society of Chemistry)
1975 Archibald D. Ollé Prize, RACI
1976 Liversidge Research Lecture, Royal Society of New South Wales
1977 Queen's Silver Jubilee Medal
1978 G.J. Burrows Medal, RACI
1978 D.Sc., Australian National University
1987 Officer Order of Australia (AO)
1989 A.E. Leighton Medal, RACI
1989 FTSE (Fellow of the Australian Academy of Technological Sciences and Engineering).
1992 L.L.D., honoris causa, Monash University
1995 D.Sc., honoris causa, University of Melbourne
2001 FAIM (Fellow of the Australian Institute of Management)

**Biographical Source**

Personal communication.

**Scientific Publications by R.L. Martin**

Between 1950 and 1999 R.L. Martin had some 176 publications on inorganic chemistry, including authorship/co-authorship of 3 book chapters.
COORDINATION, TOPOLOGY AND STRUCTURE
IN TRANSITION METAL OXIDES*

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ABSTRACT. The role of defects in the real structure of transition metal oxides which exhibit
gross departures from simple stoichiometries† is reviewed. The classical notion of a
randomized distribution of non-interacting point defects is no longer tenable being replaced by
the emerging recognition that a high level of organization into discrete clusters or more
extended assemblies of defects is an inherent feature of the real structure of defect solids. The
concept of octahedral coordination of vacant oxygen sites, taken in conjunction with
topological analysis, is shown to contribute considerable insight into the transformational and
structural relationships between defect oxides of the fluorite type.

Introduction

It is a distinction indeed to be invited by the Royal Society of New South Wales to be
their Liversidge Research Lecturer. The Lectureship honours Professor Archibald
Liversidge who profoundly influenced the development of science in Australia. During a
career of remarkable distinction he was appointed to the Chair of Chemistry and
Mineralogy in Sydney at the age of 24 and was elected to the Fellowship of the Royal
Society (London) at 34. He founded the Australasian Association for the Advancement
of Science, the Faculty of Science, and the School of Mines in the University of Sydney and
was the driving force behind the advancement of the Royal Society of New South Wales
for many decades.

The field which I wish to evaluate this evening, structural inorganic chemistry of the
solid state, has its origins in mineralogy. This is an appropriate association because
Liversidge, as Professor of Chemistry and Mineralogy, brought together the greater part of
the non-Australian mineral and geological collection at the Australian Museum in Sydney
and published a significant survey of the minerals of New South Wales in 1888.

All crystalline solids contain imperfections. Semi-conduction, thermo-electric effect
and transistor technology provide familiar examples of electronic properties which have
their origin in deviations from perfect crystalline order. Oxides of the transition metals
range from those which deviate from ideal stoichiometric composition by an amount
which is imperceptible chemically to those where departures from stoichiometry are
gross. Reduction in miniscule of TiO₂ yields TiO₁.₉₉₈₆ where the concentration of point
defects could hardly exceed 10⁻⁴ (Bursill et al., 1970); reduction in majuscule of CeO₂

*The Liversidge Research Lecture, delivered before the Royal Society of New South Wales, 15th July 1976.
†Now usually spelled ‘stoichiometries’.
yields the sesquioxide CeO$_{1.5}$ where 25% of the anion lattice sites become untenanted. Any theoretical analysis of thermodynamic equilibrium, transport and diffusion, reactivity, electronic and other properties of solids can only be based on an understanding of the structural role of defects and the nature of their interactions.

In this lecture attention will be directed to non-stoichiometric oxides which possess structures either of the rock salt (NaCl) or the fluorite (CaF$_2$) type with emphasis on the means by which quite high concentrations of point defects are assimilated by the host lattice. If one considers a regular two-dimensional array with imperfections (e.g., vacant lattice sites in Fig. 1), the essential problem is to ascertain whether these are distributed randomly or are correlated in position.

![Graph showing point defects](image)

**FIGURE 1.** Point defects (vacant sites) introduced into ordered two-dimensional lattice array (with apologies to Victor Vasarely).

**Random versus Ordered Defects**

At extremely low concentrations of point defects, the classical model (Schottky and Wagner, 1930) assumes that interactions between them are absent so that their distribution is random and the change in configurational entropy of the crystal is that for ideal mixing of the defects. However, as the concentration of randomized point defects becomes higher, an increasing proportion of defects will move into juxtaposition so that the structural and thermodynamic implications can no longer be ignored. In a real crystal, interactions between point defects is present and the tendency for them to become ordered has important structural consequences (Bursill et al., 1970). The traditional notion of randomized point defects as a basis for explaining gross departures from simple stoichiometry must be abandoned and replaced by the concept of "correlated defects" as intrinsic structure-determining elements of the defective solid.

**Ordering of Defects: Superstructure and Coherent Intergrowth**

The structural consequences of correlation between interacting defects is exemplified by the monoxides of first-row transition metals (e.g., Ti, V and Fe) which are derived from the rock salt structure. Although existence of the non-stoichiometric $\text{TiO}_{0.7}$ - $\text{TiO}_{1.25}$ has been recognized since 1939, evidence for the nature of the real defect structure of titanium oxides in this composition region was forthcoming only after a combined attack by the methods of electron microscopy, electron and X-ray diffraction
some thirty years later (Watanabe et al., 1970). Below 1000°C there are two distinct ordered phases at composition TiO$_{1.00}$ and TiO$_{1.25}$, the structures of both being super-lattices based upon the rock salt type, with every occupied lattice site assignable to a site of the parent structure (Fig. 2a). Surprisingly, the "stoichiometric" phase TiO$_{1.00}$ is grossly non-stoichiometric, the interpenetrating face-centred cubic (f.c.c.) arrays of titanium and oxygen having one-sixth of each type of atom formally missing, i.e., Ti$_{5/6}$O$_{5/6}$. The vacant cation and anion sites are octahedrally coordinated by oxygen and titanium atoms respectively, the octahedra sharing trans-apices to yield extended strings of composition $\square$Ti$_5$O$_5$ and $\square$O$\text{Ti}_5$ (Fig.2b). In the oxygen-rich TiO$_{1.25}$, the high concentration of defects (~20%) is confined solely to the cation sub-lattice, i.e., Ti$_4$O$_5$. The structure is composed of extended $\square$Ti$_5$O$_5$ strings blended with four titanium atoms giving the observed composition (Fig.2a). Interactions of point defects in both phases have led to the development of extended regions of long-range order, i.e., the generation of a super-lattice of the rock salt structure.

There is a close relationship between the structural elements of the TiO$_{1.00}$ and TiO$_{1.25}$ phases which make them dimensionally compatible so that intergrowth between them can occur coherently at a common, defect-free (120)$_\text{cub}$ planar interface (Fig. 2a). For oxides with compositions intermediate between TiO$_{1.00}$ and TiO$_{1.25}$, prolonged annealing generates lamellae comprised of alternate thin layers of the two boundary phases in the appropriate proportions.

![Figure 2](image)

**FIGURE 2.** (a) The idealized structures of ordered TiO and Ti$_4$O$_5$ coherently intergrown across a (120)$_\text{cub}$ plane of rock salt structure; (b) Vacant cation and anion sites are octahedrally coordinated by oxygen and metal atoms respectively, and occur as extended strings of composition $\square$M$_5$O$_5$ and $\square$OM$_5$ to yield Ti$_{5/6}$O$_{5/6}$.

Although the point defects are located at lattice sites of the parent rock salt structure, they are ordered geometrically so that the repeat unit of the new structure is larger than that of the parent and of lower symmetry. In a formal sense, the binary phases TiO$_{1.00}$ and TiO$_{1.25}$ can be regarded as a ternary system (anion, cation, defect), the defect being incorporated as the third component of the superstructure.
Ordering of Defects: Clusters

In the case of FeO, interactions between defects promote their organization into complex groups of correlated defects. This aggregate of defects or "cluster" becomes the new structural entity on which periodicity in the superstructure is based.

Ferrous oxide (rock salt type structure) is thermodynamically stable only above 570°C. Under ambient conditions the f.c.c. oxygen sub-lattice remains essentially complete but the cation sublattice is deficient of iron in the range Fe0.85O - Fe0.95O. To maintain electrical neutrality in the defect oxide, there are necessarily two Fe3+ ions for each vacant cation site,

$$2\text{Fe}^{2+} + 1/2\text{O}_2 = 2\text{Fe}^{3+} + \text{O}^{2-} + \square_{\text{oct}} \ldots \ldots (1)$$

Since the ligand field stabilization of energy of Fe3+ (high-spin 3d5) in an oxygen lattice is zero, it has no preference for substitutional (octahedral) as opposed to interstitial (tetrahedral) sites. Indeed, magnetic neutron scattering and X-ray crystallographic studies establish that a substantial fraction of Fe3+ cations migrate to tetrahedral interstitial sites (Koch et al., 1969),

$$\text{Fe}^{3+}_{\text{oct}} = \text{Fe}^{3+}_{\text{tet}} + \square_{\text{oct}} \ldots \ldots (2)$$

The two types of point defect, \(\square_{\text{oct}}\) and \(\text{Fe}^{3+}_{\text{tet}}\), interact strongly and coalesce to form a defect cluster comprising four tetrahedrally coordinated iron(III) atoms and thirteen octahedral vacant cation sites (Fig. 3). The \{Fe4 \(\square\) \(\square\)\} clusters being dimensionally compatible, can intergrow coherently with defect-free regions of the host rock salt structure. The structure of the cluster is much more complex than a simple aggregation of cation vacancies. It arises from both an aggregation process and a local modification of the rock salt matrix, and represents, indeed, the complete transformation of the contents of one unit cell of NaCl structure into one unit cell of zinc blende (ZnS) structure which is dimensionally compatible, both having f.c.c. anion lattices (Fig. 4).

![Diagram](image_url)

**FIGURE 3.** Fe\(_{1-x}\) Koch-Cohen cluster comprising four tetrahedral iron atoms surrounded by thirteen vacant sites in rock salt structure.
The clusters themselves tend to order under coulombic forces to develop a superstructure. The composition and configuration of this defect cluster is reminiscent of the polynuclear coordination compound, basic zinc(II) acetate, \{Zn₄O(CH₃CO₂)₆\} (Koyama et al. 1954).

Defect Elimination: Crystallographic Shear

The early transition metals in higher oxidation states (Ti⁴⁺, V⁴⁺, Nb⁵⁺, Mo⁶⁺, and W⁶⁺) preserve octahedral coordination of the central metal ion in their binary oxides. Even though reduction of the metal to a lower oxidation state involves the removal of oxygen from the parent lattice, unlike rock salt and fluorite-type oxides, vacant anion sites are not retained in the non-stoichiometric phase. Rather, the stoichiometric change is accommodated by the elimination from the crystal of a complete plane of anion sites followed by a formal structural operation, crystallographic shear (CS), which restores octahedral coordination about the metal ion (Anderson et al., 1967). There is a concomitant increase from two to three in the number of metal atoms coordinated to

\[ \text{ReO₃ structure type; (b) ReO₃ represented as apex-sharing ReO₆ octahedra and projected on the (011) plane; (c) formation of CS plane which occurs in Mo₈O₃₁.} \]
certain oxygen atoms. For example, the regular elimination of the CS plane (120) of oxygen atoms in MoO₃ (ReO₃ structure type; Fig. 5a) generates the non-stoichiometric oxide Mo₈O₂₃, the first member of the homologous series of ordered oxides MnO₃ₙ₋₁ where 8 ≤ n ≤ 12 (Fig. 5c). In the MoO₃ parent (Fig. 5b), the sequence of planes parallel to (120) is

----ABABAB----

(A = MoO₂; B = O). The regular removal of every nth B-plane of oxygen atoms from the parent structure yields the homologue of generic formula (MoO₂)ₙOₙ₋₁; i.e., MnO₃ₙ₋₁ (Fig. 5c). The elimination of anion vacancies by crystallographic shear is also common in ordered phases based on the rutile (TiO₂) structure (cf. Table 1).

### Table 1

<table>
<thead>
<tr>
<th>Parent Structure</th>
<th>Orientation of CS Plane</th>
<th>Series Formula</th>
<th>n</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO₃</td>
<td>(100)</td>
<td>MₙO₃ₙ₋₁</td>
<td>2</td>
<td>R-Nb₂O₅</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>Nb₃O₇F</td>
</tr>
<tr>
<td></td>
<td>(130)</td>
<td>MₙO₃₋₂</td>
<td>20, etc.</td>
<td>W₂O₅₈, etc.</td>
</tr>
<tr>
<td></td>
<td>(120)</td>
<td>MₙO₃ₙ₋₁</td>
<td>8 ≤ n ≤ 12</td>
<td>Mo₈O₂₃</td>
</tr>
<tr>
<td>Rutile</td>
<td>(121)</td>
<td>MₙO₂ₙ₋₁</td>
<td>4 ≤ n ≤ 9</td>
<td>Ti₄O₇ - Ti₉O₁₇</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V₄O₇ - V₉O₁₇</td>
</tr>
<tr>
<td></td>
<td>(132)</td>
<td>MₙO₂ₙ₋₁</td>
<td>16 ≤ n ≤ 36</td>
<td>Ti₁₆O₃₁ - Ti₃₆O₇₁</td>
</tr>
</tbody>
</table>

*After Anderson (1974).

### Non-Stoichiometric Oxides of Fluorite Type

In the terms of his bequest, Liversidge specified that emphasis "shall be upon recent researches and discoveries .......". Accordingly, I will now discuss some new concepts concerning the nature of defect solids of the fluorite type.

A distinguishing feature of the oxides of the early transition metals in high oxidation states, (Ti⁴⁺, V⁵⁺, Nb⁵⁺, Ta⁵⁺, Mo⁶⁺, W⁶⁺) discussed earlier, is that the MO₆ coordination polyhedron remains intact in oxides which depart from a simple stoichiometry. The oxygen lattice remains invariant in these phases and deviations in composition from the elementary MO₂ or MO₃ stoichiometry are brought about by peripheral corner- or edge-sharing of the MO₆ octahedra. As we have seen, this enables the structure of compounds with complex compositions to be illustrated with precision in two dimensions by employing the conventional projections of an idealized MO₆ octahedron (Fig. 5). Indeed, in favourable circumstances, the metal-centred octahedra are revealed directly by lattice imaging techniques in the electron microscope (Allpress, 1969) and this has produced new and deep insights into the real structure of the non-stoichiometric oxides of the early transition metals (Allpress et al., 1969).
A parallel development in the depth of our understanding of the nature of the defect oxides of the lanthanide and actinide elements and some of the larger transition metals (e.g. Hf^{4+}, Zr^{4+}) has not been forthcoming. There are a number of reasons why their structural characterization has remained elusive. Oxygen can be transferred with extraordinary ease between the MO₃ lattice and the ambient gas phase, even at relatively low temperatures (200-300°C) so that the synthesis of well-ordered crystals is inherently difficult (the remarkably high oxygen mobility inhibits the quenching-in of both composition and crystallographic order in samples equilibrated at even moderate temperatures. Of course, it is just this feature which leads to the hopeful expectation that fluorite-type oxides can be developed into successful refractory electrodes for fuel cells and other technological uses. Although very small crystals of non-stoichiometric praseodymium oxides have been grown by hydrothermal techniques, problems of crystallographic twinning, coherent intergrowth between homologous phases, absorption errors and large superstructures of low symmetry have all combined to make studies, even with single crystals, a formidable task.

The technique of lattice imaging, which has proved to be so incisive for CS structures which involve interstitial heavy metal atoms, does not produce the same marked contrast in images of the fluorite oxides. However, in the case of Tb₁₁O₂₀ periodicities imposed on the structure by oxygen vacancies appear to have been discerned in the bright field image (Kunzmann et al., 1975). The vacancies are not imaged directly but the periodicity which they impose on the potential field may be discerned in the image.

Because of these difficulties, current efforts are being directed towards the neutron profile technique and the determination of superstructure lattice parameters from electron diffraction patterns taken in a high resolution transmission electron microscope from very small single crystals (average size; 1µm). This enables the unit cell dimensions and

<table>
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<th>Table 2</th>
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<tr>
<td>Some Ordered Fluorite Type Oxides</td>
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<table>
<thead>
<tr>
<th>Composition</th>
<th>Binary Oxides</th>
<th>Ternary Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₂₀₀</td>
<td>CeO₂, PrO₂, TbO₂, HfO₂, ThO₂, PaO₂, UO₂, NpO₂, PuO₂, AmO₂, CmO₂, BkO₂</td>
<td>©-Zr₁₀Sc₄O₂₆</td>
</tr>
<tr>
<td>MO₁₈₅₇</td>
<td>©-Pr₁₂O₂₂</td>
<td></td>
</tr>
<tr>
<td>MO₁₈₃₃</td>
<td>Ce₁₁O₂₀, ℭPr₁₁O₂₀, Tb₁₁O₂₀</td>
<td>ℭ₁-CaHf₄O₉</td>
</tr>
<tr>
<td>MO₁₈₁₈</td>
<td>Ce₁₀O₁₈, ℭ-Pr₁₀O₁₈</td>
<td>ℭ₂-Ca₂Hf₇O₁₆</td>
</tr>
<tr>
<td>MO₁₈₀₀</td>
<td>Ce₉O₁₆, ℭ-Pr₉O₁₆</td>
<td>ℭ₂-Ca₆Hf₁₉O₄₄ pyrochlore, La₂Ti₂O₇, Gd₂Zr₂O₇</td>
</tr>
<tr>
<td>MO₁₇₇₈</td>
<td>Ce₇O₁₂, ℭ-Pr₇O₁₂, Tb₇O₁₂</td>
<td>UY₆O₁₂, Zr₃Sc₄O₁₂,</td>
</tr>
<tr>
<td>Zr₃Yb₄O₁₂</td>
<td>ℭ-Pr₆O₁₀</td>
<td>Sr₂UO₅, Cd₂UO₅</td>
</tr>
<tr>
<td>MO₁₆₆₇</td>
<td>ℭ-Pr₅O₁₀</td>
<td></td>
</tr>
<tr>
<td>MO₁₆₀₀</td>
<td>ℭ-Pr₄O₁₀</td>
<td></td>
</tr>
<tr>
<td>MO₁₅₅₀</td>
<td>Y₂O₃, Pr₂O₃, Sb₂O₃, ©-Bi₂O₃, bixbyite((-Mn₂O₃), In₂O₃, Te₂O₃)</td>
<td></td>
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</tbody>
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possible space groups of the intermediate phases as well as the transformation matrices to be defined in terms of the fluorite sub-structure. In defect oxides of the fluorite structure type (Table 2), the non-stoichiometry is accommodated on untenanted anion sites, the cation sub-lattice remaining essentially intact. The central problem is to ascertain the superstructural pattern which reflects the ordering of anion vacancies in order that underlying structural principles may be defined. Unfortunately, the coordination sphere of the metal atom in dioxides such as CeO₂, HfO₂ and UO₂ is comprised of a cube of oxygen anions which precludes two-dimensional projection of MO₆ octahedra along 2-, 3- and 4-fold axes which have proved to be so illuminating for TiO₂ or ReO₃ based structures. Attempts to represent the fluorite structure by the edge-sharing of MO₈ polyhedra are cumbersome (Fig. 6) and provide only limited insight into the distribution of vacancies in oxides which deviate from elementary MO₂ composition (Sawyer et al., 1965).

In an attempt to circumvent this problem, we can depart from our conventional metal-centred frame of reference and contemplate the fluorite lattice in terms of its

![Fluorite structure diagram](image)

FIGURE 6. Fluorite structure represented as edge-sharing MO₈ cubes.

anion-centred polyhedra (Martin, 1974). Examination of the MO₂ structure reveals that each oxide anion is coordinated tetrahedrally by four cations to form an octant of the fluorite cube with the composition M₀.₅O. Eight such octants arranged in juxtaposition
generate the fluorite unit cell of composition \( M_4O_8 \) and edge length \( a_F \). A single layer of octants can be represented conveniently in projection by employing the square matrix illustrated in Fig. 7c with oxygen sites envisaged at the centre of each square.

Non-stoichiometric oxides \( MO_x \) (cf. Table 2) with compositions in the range \( 1.5 \leq x \leq 2.0 \) result from the removal of oxygen from octant centres leaving vacant anion sites according to the equation:

\[
4M^{4+} + O^2-/ \square_{\text{an}} \rightarrow 4M^{4+} + 2e^-/ \square_{\text{an}} + 1/2O_2
\]

\[
\uparrow
\]

\[
2M^{4+} + 2M^{3+} + \square_{\text{an}} + 1/2O_2 \quad \ldots \ldots \quad (3)
\]

where the symbol \( \square_{\text{an}} \) denotes an anion site denuded of oxygen. For binary oxides \( (CeO_x) \) imbalance between anionic and cationic charge is accommodated by changing proportions of the two oxidation states \( Ce^{3+} \) and \( Ce^{4+} \). Kinetic barriers to configurational rearrangements in binary oxides are small since inequalities of charge can be redistributed readily by electron transfer between metal cations. On the other hand, electron hopping between aliovalent ions (i.e., solute cations of different oxidation state from the corresponding solvent cation) in ternary oxides such as \( CaO/ZrO_2 \) is precluded and the activation energy to ordering processes may be considerable. In these circumstances the distribution of aliovalent cations will pre-determine the location of the compensating defects in the anion sub-lattice.
The Coordination Defect: Topological Analysis

There are several single crystal X-ray structure determinations of fluorite type oxides which are of sufficient accuracy to confirm that every anion vacancy is circumscribed by the six nearest neighbouring oxygen atoms which are contracted inwards as though under the influence of a polarizing positive charge. In other words, the point defect □ appears to have no independent existence but, in its coordinated state □O₆ (Fig. 8a), becomes a structural entity which places effective limitations on the number of alternative ways in which a given anion deficiency can be accommodated by the parent lattice. Furthermore, by employing our unconventional anion-centred reference frame, we can now depict a vacant anion site by the conventional projection of an octahedron along its four-fold symmetry axis (Fig. 8c).

Before proceeding to explore the structural role played by the coordinated vacancy, □O₆, it is necessary to establish its topology and chemical composition. Since the cation sub-lattice remains intact, the true coordination defect (c.d.) is comprised of the seven octants illustrated in Fig. 8b which circumscribe the anion vacancy and each of its six nearest O²⁻ neighbours. The overall composition of the c.d. is M₃.₅□O₆ and its unique topology is consequent on the octahedral distribution of the six encapsulating octants.

In order to construct an oxide phase based on closest packing of c.d.s, they need to be aligned in rows parallel to the [0̅2̅1]ₕ direction (Fig. 9). Two mating holes (H) per c.d. must be incorporated in each (100)ₕ layer to enable the topological requirement of

![Diagram](image-url)
c.d.s in contiguous layers to be accommodated. The three-dimensional assembly of c.d.s is uniquely determined by their topology and since it is space filling (Fig. 8d), the overall composition of the phase is M₇O₁₂ which corresponds to ~14% of untenanted anion sites.

A number of binary and ternary oxide phases with this composition are known (e.g., ⎡-Pr₇O₁₂, Zr₃Sc₄O₁₂, Zr₃Yb₄O₁₂, ULu₆O₁₂ and UY₆O₁₂) and in each case their structure conforms with that deduced from the above topological considerations. Since each vacancy along [0T3]ₓ is related to another by the vector √2[211]ₓ, they are gathered on oblique (23T)ₓ planes and occur as metal-centred pairs in rows along the [111]ₓ direction (Fig. 8d). The detailed nature of the superstructure emerges clearly if the vacant anion sites in a (111)ₓ plane of the ⎡-Pr₇O₁₂ structure (Von Dreele et al., 1975) are delineated by their oxygen polyhedra (Fig. 10).

FIGURE 9. Idealized square-matrix representation of a (100)ₓ layer of the fluorite lattice showing the location of vacant oxygen sites in ⎡-Pr₇O₁₂ along [021]ₓ and [013]ₓ directions. Mating holes for accommodating contiguous layers are designated by H.

FIGURE 10. Section of ⎡-Pr₇O₁₂ structure perpendicular to [111]ₓ axis. Arrangements of vacant anion sites in a (111)ₓ layer is shown by their coordination octahedra.
Attempts to visualize the planar ordering of vacancies in terms of the metal-centred representation of Fig. 6 are less effective, the paired c.d. \( \text{M}_7\text{O}_{12} \Box_2 \) having to be replaced by the much larger \( \text{M}_7\text{O}_{36} \) defect cluster (Thornber et al., 1968) comprising the six \( \text{MO}_6 \) polyhedra (white cubes) which share edges with a central \( \text{MO}_6 \) polyhedron (black cube) which has a pair of vacant oxygen sites disposed across its [111] body diagonal (Fig. 11).

![Diagram of M\(_7\)O\(_{36}\) defect cluster](image.png)

**FIGURE 11.** \( \text{M}_7\text{O}_{36} \) defect cluster and the octahedrally coordinated anion vacancies \( \Box \text{O}_6 \) delineated along the same [111]\(_F\) axis.

In addition to \( \text{Zr}_3\text{Sc}_4\text{O}_{12} \), there is a second more oxidized but closely related phase, \( \odot \text{-Zr}_{10}\text{Sc}_4\text{O}_{26} \), which occurs in the \( \text{ZrO}_2\text{-Sc}_2\text{O}_3 \) system. Once again, the vacant anion sites (7%) are ordered and structural features in common emerge when the distributions of coordination defects are viewed on an \( (01\bar{1})_F \) plane (Fig. 12). In both rhombohedral structures, the vacant anion sites lie along the [111]\(_F\) direction occurring always as metal-centred pairs. The difference in composition between the two phases is seen to arise from the periodic annihilation along [111]\(_F\) of a pair of c.d.s by substitution of a pair of fluorite \( \text{Zr}_3\text{Sc}_5\text{O}_7 \) entities of identical topology which generates the composition of the \( \odot \)-phase; viz.,

\[
\text{Zr}_3\text{Sc}_4\text{O}_{12}\Box_2 + \text{Zr}_7\text{O}_{14} = \text{Zr}_{10}\text{Sc}_4\text{O}_{26}\Box_2 \quad \ldots \ldots \quad (4)
\]
Ternary oxides of the pyrochlore type (naturally occurring mineral, CaNaNb$_2$O$_6$F) also have interesting electrical, magnetic and refractory properties. This cubic $M_4O_7$ structure may be related to fluorite by deleting one-eighth of the anions in an ordered manner, the ternary oxides La$_2$Ti$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ providing examples (Table 2). Alternatively the pyrochlore composition can be achieved by incorporating one fluorite octant ($M_{0.5}O$) per c.d. into the close-packed assembly which comprises the $M_2O_{12}$ phase; viz.,

$$M_{3.5}O_6 + M_{0.5}O = M_4O_7 \quad \ldots \ldots \quad (5)$$

It is generally found that the larger $M^{3+}$ cation lies at the centre of a deformed MO$_8$-cube while the smaller $M^{4+}$ cation occupies the centre of a MO$_6$O$_2$ cube where the missing anions lie along a [111] body diagonal. The resulting ordered arrangement of vacant anion sites in a (100)$_F$ layer is illustrated in terms of c.d.s in Fig. 13.

Homologous Series and Crystallographic Shear in Lanthanide Oxides

Several rare earth elements exhibit variable valency; in particular, cerium, praseodymium and terbium form both a tervalent and tetravalent sesquioxide $M_2O_3$ and dioxide MO$_2$. In the intervening composition regions $MO_{1.5}$ - $MO_{2.0}$, the phase diagram (Fig. 14) reveals a rich variety of non-stoichiometric phenomena (Hyde et al., 1966). At higher temperatures, non-stoichiometric disordered phases of widely variable composition MO$_x$ occur. However, at lower temperatures a series of structurally ordered line phases
of quite narrow composition range develop. Their composition is well-defined conforming to the homologous series $\text{Pr}_{n}\text{O}_{2n-2}$ with $n = 6, 7, 9, 10, 11$ and 12 (cf. Table 2).

**FIGURE 13.** Pyrochlore structure $\text{M}_{8}\text{O}_{14}$. Idealized matrix representation of a $(100)_T$ layer showing location of vacant oxygen sites as c.d.s. Additional $\text{M}_{0.5}\text{O}$ octants are cross-hatched.

**FIGURE 14.** Projection of the $\text{PrO}_x$ ($1.5 \leq x \leq 2.0$) phase diagram on the temperature-composition plane. Compositions and designations of ordered phases are marked.

The detailed structural characterization of these intermediate phases has remained an elusive problem of significance in understanding the nature of fluorite related defect solids. Although the crystal structures are not known, the dimensions and symmetry of the superlattices have been obtained from high-resolution transmission electron microscopy of microcrystalline materials (Kunzmann et al., 1975). When combined with the topological restrictions imposed by the c.d., model structures can be devised which possess edge dimensions and directions which bear identical relationships to the parent fluorite structure as do the $a$, $b$ and $c$ axes of the observed unit cells.
The existence of the \( \text{Pr}_{n} \text{O}_{2n+2} \) series derives from blending \( n \) octants of composition \( \text{Pr}_{0.5}\text{O} \) with the c.d. progenitor \( \text{Pr}_{3.5}\text{O}_{6} \) to yield the homologue \( \text{Pr}_{(3.5+0.5y)}\text{O}_{6+y} \); i.e., \( \text{Pr}_{n}\text{O}_{2n+2} \) where \( n = (y+7) \). This uniform progression suggests that the homologues might be inter-related, at least formally if not mechanistically, through a process of crystallographic shear (Hoskins et al., 1976). The possibility of applying crystallographic shear to an oxygen-centred lattice is an advantage consequent on the persistence of the octahedral \( \text{O}_{6} \) entity and the invariance of the f.c.c. metal lattice in the fluorite oxides. The crystallographic shear operation can be visualized conveniently by first cutting a drawing of a \( (100)_{F} \) octant layer of \( \text{Pr}_{7}\text{O}_{12} \) along the trace \( \{01\bar{5}\}_{F} \) of a \( (1\bar{5}3)_{F} \) plane on \( (100)_{F} \) (Fig. 15a). The \( (100)_{F} \) layer is now opened up by shearing in the \( \{0\bar{1}1\}_{F} \) direction to create new oxygen sites. For example, the CS operation \( \{0\bar{1}1\}_{F} \) enables two additional \( (1\bar{5}3)_{F} \) planes of \( \text{PrO}_{2} \) (i.e., \( y = 2 \)) to be inserted coherently into the parent \( \{\text{Pr}_{7}\text{O}_{12}\} \) matrix corresponding to the formation of a sheet of \( \text{Pr}_{9}\text{O}_{16} \) (Fig. 15c). Similarly, the model which reproduces the unit cell characteristics of the \( \text{Pr}_{11}\text{O}_{20} \) phase can be generated from \( \text{Pr}_{7}\text{O}_{12} \) by the CS operation \( 2\{011\}_{F} \) as shown in Fig. 15e. In this case, four new \( (1\bar{5}3)_{F} \) planes of \( \text{PrO}_{2} \) (i.e. \( y = 4 \)) are introduced coherently into the \( \{\text{Pr}_{7}\text{O}_{12}\} \) matrix to generate the composition \( \text{Pr}_{11}\text{O}_{20} \).
The structural repeat units outlined in black in Fig. 15 can be stacked along \(a_F\) to give triclinic unit cells which reproduce the 1/2[2\(\overline{1}\)1]_F and 1/2[1\(\overline{1}\)2]_F vectors observed for the \(a\) and \(c\) axes of the super-structures respectively. Although the vacancies are grouped again as metal-centred pairs with a local [111]_F axis, the pairs now lie along [21\(\overline{1}\)]_F and [1\(\overline{1}\)2]_F directions being gathered in (15\(\overline{3}\))_F layers.

The CS operations 3/2[0\(\overline{1}\)1]_F and 5/2[0\(\overline{1}\)1]_F generate unknown triclinic polymorphs of the known monoclinic homologues \(\Sigma\)-Pr\(_{10}\)O\(_{18}\) and \(\odot\)-Pr\(_{12}\)O\(_{22}\). This suggests that the structural relationships between the odd- and even-membered phases are likely to be close. This topic has been discussed further elsewhere (Hoskins et al., 1976).

Extended Defects: Corner and Edge-Sharing of Coordination Defects

The structures of Zr\(_{10}\)Sc\(_4\)O\(_{26}\), pyrochlore and the Pr\(_n\)O\(_{2n-2}\) homologues are based on an ordered distribution of isolated coordination defects packed out with M\(_{0.5}\)O fluorite octants. The most reduced fluorite-type structure based on the close-packing of isolated c.d.s is M\(_7\)O\(_{12}\). Any further reduction inevitably leads to corner- and/or edge-sharing of c.d.s if the octahedral coordination about a vacancy is to be preserved (Hoskins et al., 1975). The structures of two ternary phases of composition MO\(_{1.667}\) (\(n = 6\)) have been reported (cf. Table 2) and both conform with the topological expectations of the c.d. model. For example, the structure of monoclinic strontium uranate (Loopstra et al., 1969) involves strings of c.d.s along [100]_F which are joined by sharing corners (Fig. 16b). The ordered vacancies are contained on every fourth (0\(\overline{1}\)1)\_F plane which has the composition [UO\(_2\)]\(_{4+}\) (cf., Fig. 16b). This ordered vacancy plane is sandwiched between

![Figure 16](image)

**FIGURE 16.** Structure of (a) pyrochlore and (b) Sr\(_2\)UO\(_5\) (or \(\odot\)-Bi\(_2\)O\(_3\)) on an (0\(\overline{1}\)1)\_F plane. The rows of c.d.s along [011]_F form “extended defects” (outlined), the anion vacancies being related by either [111]_F or [1\(\overline{1}\)2]_F metal-centred vectors.
two \((01\overline{1})_F\) intact planes of \([\text{SrO}_2]^2-\) to complete the composition of the phase \(\text{Sr}_2\text{UO}_5\). The structure of cadmium uranate (Sterns et al., 1964) is similar; the structure of \(-\text{Pr}_6\text{O}_{10}\) is not known.

Although more reduced oxide phases corresponding to \(n = 5\) have not been characterized, there are many examples of metal sesquioxides \(\text{i.e.}, n = 4\) with structures related to fluorite \(\text{cf.}\), Table 2). Examination of the cubic structures of \(\text{Bi}_2\text{O}_3\) and type 
\(\text{C-Ln}_2\text{O}_3\) (bixbyite or \(\text{Os}_2\text{O}_3\) type) has established that both are based on a f.c.c. metal lattice. Furthermore, in both structures, the 25\% anions are omitted from fluorite sites in an ordered rather than a random manner. Each vacant oxygen site is surrounded by an octahedron of oxygen atoms so that the integrity of the c.d. remains preserved in these highly reduced phases.

In the cubic \(\text{Bi}_2\text{O}_3\) structure (Gattow et al., 1964) each c.d. shares all six apices with neighbouring c.d.s to achieve the desired \(\square\text{O}_3\) stoichiometry (Fig. 17a). The resultant \(\square\text{O}_{6/2}\) infinite network is reminiscent of the metal-centred \(\text{ReO}_3\) lattice (Fig. 5a) except that the oxygen vacancies lie at the rhenium atom sites (N.B. there are actually two interpenetrating \(\text{ReO}_3\)-like sub-lattices in \(\text{Bi}_2\text{O}_3\)). If the cubic \(\text{Bi}_2\text{O}_3\) structure is viewed on \((011)_F\) planes, the arrangement of vacant anion sites is identical to that found on \((011)_F\) planes in \(\text{Sr}_2\text{UO}_5\) (Fig. 16b). Each ordered vacancy plane of composition \([\text{BiO}\square]^+\) alternates with an oxygen-intact \((011)_F\) plane of composition \([\text{BiO}_2]^+\) to generate the sesquioxide composition and structure.

![Figure 17](image)

**FIGURE 17.** Transformation of \(\text{Bi}_2\text{O}_3\) \(\Rightarrow\) type \(\text{C-M}_2\text{O}_3\). (a) arrangement of c.d.s in \((100)_F\) layer of \(\text{Bi}_2\text{O}_3\) structure; (b) \((100)_F\) layer of type \(\text{D-M}_2\text{O}_3\) generated by c/2 slip of alternate \([001]_F\) rows of c.d.s in direction arrowed in (a); (c) \((100)_F\) layer of type \(\text{C-M}_2\text{O}_3\) derived from type \(\text{D}\) by the \(b/2\) slip mechanism depicted in (b).
A close relationship between \(\textcircled{2}\)-Bi\(_2\)O\(_3\) and the cubic pyrochlore phase M\(_4\)O\(_7\) also emerges on (01\(\overline{1}\))\(_F\). The vacancy-containing (01\(\overline{1}\))\(_F\) plane in pyrochlore contains only one-half the density of vacant sites so that apex sharing between c.d.s is no longer involved (Fig. 16a). This plane of composition M\(_2\)O\(_3\) alternates with an oxygen-intact plane M\(_2\)O\(_4\) to generate the pyrochlore composition. The rows of c.d.s along [011]\(_F\) form an "extended defect" with the anion vacancies being related either by [111]\(_F\) or [\(\overline{1}\)\(\overline{1}\)1]\(_F\) vectors. (This "extended defect" was originally termed a "duplex" row of c.d.s by Martin, 1974.) These "extended defects" are also a characteristic of Sr\(_2\)UO\(_5\) except that corner-sharing between them occurs along [100]\(_F\). These transformational relationships correspond to the compositional sequence:

\[
\text{\(\textcircled{2}\)-Bi\(_2\)O\(_3\)}} \quad \text{pyrochlore} \quad \text{fluorite} \\
M_{32}O_{48}\square_{16} \quad M_{32}O_{56}\square_{8} \quad M_{32}O_{64}
\]

The type C-M\(_2\)O\(_3\) bears a different relationship to the fluorite structure. It also involves the regular omission of one-quarter of the oxygen atoms, a small distortion of the metal lattice from f.c.c., and a unit cell of b.c.c. symmetry with double the fluorite edge (Paton et al., 1965). Again, every vacant anion site is coordinated by an octahedron of nearest oxygen neighbours to yield an ordered vacancy superstructure based on c.d.s. However, unlike \(\textcircled{2}\)-Bi\(_2\)O\(_3\), each \(\square_6\) octahedron shares three of its edges with three \(\square_6\) nearest neighbours to achieve the desired stoichiometry \(\square_3\). These neighbours, and hence the edges involved, are related by a three-fold symmetry axis passing through the centrally coordinated c.d., all four c.d.'s being situated on the

\[\text{FIGURE 18. Type C-M}_2\text{O}_3. \quad \text{Arrangement of vacant anion sites on a (111)}_F \text{plane showing their coordination octahedra. The } \alpha \text{ chirality of the } \textcircled{2} \text{-shaped clusters in this plane is contrasted with the } \Delta \text{ configuration of adjoining (111)}_F \text{ planes shown in the inset.}\]
same (111)$_{F}$ plane. Effectively, each c.d. is "tris-chelated" by its three neighbouring c.d.s conferring on it the property of chirality, i.e., $\Delta$ and $\varphi$ configurations occur in equal proportions in the structure (Hoskins et al., 1975). The arrangement of vacancies on a (111)$_{F}$ plane is depicted in Fig. 18.

The chiral properties of each (111)$_{F}$ layer determine the manner in which the Y-shaped clusters link up with their neighbours in next-nearest, rather than nearest, layers. Two interpenetrating, but unconnected networks of c.d.s, each of opposite chirality, are generated throughout the type C-M$_2$O$_3$ structure, one involving the layers numbered 1,3,5 etc. ($\varphi$ chirality; Fig. 18) and the other 2,4,6 etc. ($\otimes$ chirality). The $\varphi$ network which results from edge-sharing of c.d.s between layers 1,3 and 5 is illustrated in projection on (111)$_{F}$ in Fig. 19. Layer 7 exactly overlays layer 1 of this diagram, the pattern repeating itself throughout the lattice. The corresponding projection of the even-numbered layers, i.e., those of opposite chirality, intermeshes perfectly so that the lacunae of the projection shown in Fig. 19 disappear.

The edge-sharing between c.d.s within each single (100)$_{F}$ layer of the type C structure (Fig. 17c) produces a pattern of isolated "pairs" which differs distinctively from the apex-sharing linkages of c.d.s which characterize the $\otimes$-Bi$_2$O$_3$ structure (Fig.17a). However, the relationship between the two structures is extremely close and the transformation

$$\otimes$$-Bi$_2$O$_3 \longleftrightarrow \text{type C-M}_2\text{O}_3$$

can be effected by a series of concerted oxygen/vacancy exchanges over minimal distances (of either $a/2$ or $a\sqrt{2}$): viz.,

$$\text{O}^{2-} + \Box \longleftrightarrow \Box + \text{O}^{2-} \quad \ldots \ldots \ldots (6)$$

This transformation is illustrated schematically for the single (100)$_{F}$ oxygen plane in Fig. 17a. The first step involves the translation by $a/2$ of every alternate [011]$_{F}$ string of apex-sharing c.d.s to give the precursor shown in Fig. 17b. This translation operation
1/2[01T]_{F} is similar to introducing an antiphase boundary (a.p.b.) by crystallographic shear, the composition M_{2}O_{3} remaining unchanged by the CS operation. The precursor structure differs, however, from \&-Bi_{2}O_{3} and C-M_{2}O_{3} in that it is based on a combination of apex-sharing c.d.s in trans-[001]_{F} positions and edge-sharing of c.d.s in the [\bar{1}10]_{F} direction. (This conjectural phase has not been observed experimentally and for convenience is referred to as type D-M_{2}O_{3}.)

The second translation operation 1/2[0\bar{1}0] illustrated in Fig. 17b is also a.p.b. in nature and generates a (100)_{F} plane of unchanged composition with the type C-M_{2}O_{3} structure (Fig. 17c).

Unlike the \&-Bi_{2}O_{3} and pyrochlore structures, two types of vacancy plane, A and B, occur on (01T)_{F}, for type C, there being no oxygen intact planes. These are represented in Fig. 20.

![Figure 20](image)

**FIGURE 20.** Type C-M_{2}O_{3}. Two (01T)_{F} planes, denoted A and B, which alternate in the structure. Plane A is converted to plane B by a2 slip of alternate [100]_{F} rows of c.d.s in the direction of the arrows.

both A and B having the same composition M_{4}O_{6} \square_{2}. A and B planes alternate throughout the type C structure generating the two interpenetrating sub-lattices of \Delta and \varepsilon chirality (cf., Fig. 18). Metal-centred pairing of c.d.s along [111]_{F} is evident in the B planes. An interesting feature of this beautifully ordered structure is that the sub-lattices of \Delta and \varepsilon chirality can be regarded as two independent giant extended defects which nevertheless are "paired" along <111>_{F} by six-coordinated metal atoms at the \Delta/\varepsilon interfaces.

**Conclusions**

Our concept of the real structure of a non-stoichiometric solid has changed dramatically during the past 10-15 years. The classical idea of a random distribution of
point defects has become unacceptable as a basis for explaining gross departures from simple stoichiometry. Point defects in non-stoichiometric oxide phases with either the rock salt or the fluorite structure undergo aggregation to more complex structural units which tend to be distributed throughout the host lattice in a regular periodic fashion. These may be discrete clusters or extended defects in two or three dimensions. This tendency to order when carried to completion generates a super-lattice of the parent compound which for specific cation/anion ratios frequently defines a homologous series. The "cluster" and the "extended defect" become an integral component of the superstructural pattern, so much so that it can be argued that the ordered non-stoichiometric phase is a new structure in its own right.

Recognition of the topology of the coordinated point defect enables common features of related crystal structures to be identified and their structural transformations to be better understood. This is especially important for materials such as oxides of the fluorite type where location of missing oxygen atoms by direct methods is inherently a formidable experimental task. Topological analysis of defect fluorite phases has wider implications of significance for other areas such as the magneto-optical properties of crystalline solids. For example, the green fluorescence of CaF$_2$ when doped with small amounts of uranium is observed only in the presence of oxygen and so has been attributed to U$^{6+}$ coordinated by oxygen ligands. The polarized Zeeman spectra, which differ in character from those of uranyl (UO$_2^{2+}$) compounds, establish that the electronic transition occurs at a centre with trigonal and inversion symmetry (Manson et al., 1975). These restrictions can be satisfied if the emitting centre is comprised of a metal-centred pair of c.d.s of composition UC$_6$O$_6$F$_6$\(\square_2\) (i.e., \(M_7O_{12}\) type) intergrown coherently in the host CaF$_2$ lattice (Fig. 21).

![FIGURE 21. Conjectural structure of the emitting centre responsible for green fluorescence of fluorite doped with small amounts of uranium (VI). The uranium(VI) centred pair of c.d.s has the overall composition UC$_6$O$_6$F$_6$\(\square_2\).](image)

The growing demand for new materials in high temperature and electronic technology will ensure that the complex inter-relationships between composition, structure and properties, which form the basis of research into the defect solid state, will remain a vital field of chemical endeavour.
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References