Oxide crystal structures and electron counts: The basics

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Photo by Tony Mastres
1. Brief description of oxide crystal structures (simple and complex)
   a. Ionic radii and Pauling’s rules
   b. Electrostatic valence
   c. Bond valence, and bond valence sums

   Why do certain combinations of atoms take on specific structures?

2. Counting electrons and simple electronic structures (largely avoiding transition metals)

3. d⁰ and s² configurations.
Crystal structures of simple oxides [containing a single cation site]
Crystal structures of simple oxides [containing a single cation site]

N.B.: CoO is simple, Co$_3$O$_4$ is not. ZnCo$_2$O$_4$ is certainly not! Co$_3$O$_4$ and ZnCo$_2$O$_4$ are complex oxides.

Graphs of connectivity in crystals: Atoms are nodes and edges (the lines that connect nodes) indicate short (near-neighbor) distances.

CO$_2$: The molecular structure is O=C=O. The graph is:
Each C connected to 2 O, each O connected to a 1 C

OsO$_4$: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os
Crystal structures of simple oxides of monovalent ions: $A_2O$

**Cu$_2$O**

Linear coordination is unusual. Found usually in Cu$^+$ and Ag$^+$.

**Na$_2$O (anti-fluorite)**

4-coordination for Na$^+$ and 8-coordination for O$^{2-}$ are unusual.
Crystal structures of simple oxides of divalent ions: AO

**ZnO** (wurtzite), sp$^3$

Ubiquitous for AO oxides including transition metals (distorted for CuO and NbO).

**PbO** (litharge), lone pairs

Insulators, metals (TiO), magnetic, ...

**MgO** (rock-salt)
Crystal structures of simple oxides. \( \text{Al}_2\text{O}_3 \) as an example of a sesquioxide

\( \alpha-\text{Al}_2\text{O}_3 \) (corundum)

Also the structure of \( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \).

\( \text{Ga}_2\text{O}_3 \) does funny things.

\( \text{In}_2\text{O}_3 \) is different (bixbyite).
Crystal structures of simple oxides of tetravalent ions: $\text{AO}_2$

**TiO$_2$ (rutile)**

$\text{TiO}_2$ also crystallizes as anatase and brookite.

$\text{SiO}_2$ takes on this structure, and can be quenched to it, (stishovite) under pressure.

Also the structure of $\text{ThO}_2$, and of $\text{ZrO}_2$ and $\text{HfO}_2$ at elevated temperatures.

Ordered variants abound.

**CeO$_2$ (fluorite)**
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the CdI$_2$ structure.
Crystal structures of an oxide with an octavalent ion: OsO$_4$
Shannon-Prewitt (ionic) radii

Radii assigned by systematically examining cation-anion pairs in oxides, fluorides etc.

May not work for other kinds of compounds

Be sensitive to coordination number and spin state
In brief: The cation-anion distance is the sum of cation and anion radii, and the number of anions around a cation (the coordination number) is a function of the radius ratio. Exemplified by $\text{AO}_2$ compounds below. MRR is the minimum radius ratio.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r_C$ (Å)</th>
<th>$r_C + r_O$ (Å)</th>
<th>$r_C/r_O$</th>
<th>Coordination</th>
<th>MRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2$</td>
<td>$-0.19(?)$</td>
<td>1.16 (exp.)</td>
<td>?</td>
<td>2</td>
<td>\n</td>
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<tr>
<td>$\text{TiO}_2$</td>
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<td>1.955</td>
<td>0.45</td>
<td>6</td>
<td>0.414</td>
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<tr>
<td>$\text{CeO}_2$</td>
<td>0.97</td>
<td>2.32</td>
<td>0.72</td>
<td>8</td>
<td>0.732</td>
</tr>
</tbody>
</table>

Pauling’s second rule: The electrostatic valence rule

In brief: Charges going out from cations should balance anions and *vice-versa*

Why is OsO₄ a molecule? Radius ratio + electrostatic valence

Pauling, and later Brown and Shannon, noted that the Pauling bond strength (the electrostatic valence) correlates very well with distance for many oxides: Short bonds (distances) correspond to strong bonds and vice-versa.
Electrostatic valence and bond valence

The modern bond valence relationship:

\[ s = \exp \left( \frac{R_0 - R}{B} \right) \]

Where \( s \) is the strength of the bond, \( R \) is the cation to anion distance, and \( R_0 \) and \( B \approx 0.37 \) Å are parametrized for the specific ion pair.

When all \( s \) are calculated: \( \sum_{\text{CN}} s = \text{valence of the ion} \)

For \( \text{Mn}^{2+} - \text{O}^{2-} \), \( R_0 = 1.790 \) Å, \( B = 0.37 \) Å.

This means \( R = 2.20 \) Å.

Experiment: \( 2.22 \) Å

Electrostatic valence and bond valence: Parameters for Mn

<table>
<thead>
<tr>
<th>Mn</th>
<th>2</th>
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<th>-2</th>
<th>1.790</th>
<th>0.37</th>
<th>a</th>
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<td>Cl</td>
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</table>

Crystal structures of some complex oxides [containing two or more cation sites]
The major ternary structural families (Muller and Roy, page 3, redrawn and modified)

Ternary structural families

- CaCO$_3$
- Perovskite
- Hexagonal ABX$_3$ (eg. BaNiO$_3$ in the CsCrBr$_3$ structure)
- Pyroxenes and related structures (eg. diopside CaMgSi$_2$O$_6$)
- Corundum and related structures (eg. ilmenite FeTiO$_3$)
- Zircon (ZrSiO$_4$)
- Scheelite (CaWO$_4$)
- Barite (BaSO$_4$)
- Ordered SiO$_2$ derivatives
- Ordered rutile derivatives
- K$_2$NiF$_4$ (m = 1 Ruddlesden-Popper)
- β-K$_2$SO$_4$
- Olivine (Mg$_2$SiO$_4$ and for eg. LiFePO$_4$)
- Spinel (MgAl$_2$O$_4$)
- CaFe$_2$O$_4$
- Phenacite (Be$_2$SiO$_4$)
- ABX$_2$ (eg. LiCoO$_2$ and CuFeO$_2$)
- A$_2$B$_2$X$_7$ (eg. pyrochlore Y$_2$Ti$_2$O$_7$)
- A$_2$BX$_5$
- A$_2$BX$_6$
- A$_3$BX$_5$

not listed by Muller and Roy

Will discuss compounds in highlighted boxes: Characterized by dense connectivity.
The \( \text{ABO}_3 \) structure-sorting field (from Muller and Roy)

The superscripted roman numerals indicate coordination number.
Perovskite

BaZrO$_3$

LaMnO$_3$ Pnma (Jahn-Teller distorted)

Note that the space group Pnma (#62) can be written in a variety of ways.

This is the most common perovskite space group.

In the next so many structures, BO$_6$-polyhedra are depicted.
Ordered double perovskites (elpasolites)

**Ba$_2$MgWO$_6$**

Rock-salt like ordering of dissimilar octahedra. Space group same as rock-salt: *Fm̅–3m*

**Ca$_2$MgWO$_6$**

Smaller A-ions associated with tilting as in simple perovskites.
The double perovskite field: Charge and radius

Hexagonal $\text{ABO}_3$ structures

$\text{BaNiO}_3$

Ferroelectric $\text{YMnO}_3$ ("$\text{YAI}_3$")

$\text{LiNbO}_3$ (ferroelectric $\text{R}_3\text{c}$)

Unusual 5-fold coordination (trigonal bipyramid) of $\text{MnO}_5$
Ordered rutiles (the trirutile)

CoTa$_2$O$_6$ · 3 × TiO$_2$ = Ti$_3$O$_6$; 3 × Ti$^{4+} = $ Co$^{2+} + 2 ×$ Ta$^{5+}$
The $\text{A}_2\text{BO}_4$ structure-sorting field (from Muller and Roy)

The superscripted roman numerals indicate coordination number.
$K_2NiF_4$ and Ruddlesden-Popper ($m = 1, 2, 3$) General formula $[\text{SrO}][\text{SrTiO}_3]^m$

$\text{Sr}_2\text{TiO}_4$

$\text{Sr}_3\text{Ti}_2\text{O}_7$

$\text{Sr}_4\text{Ti}_3\text{O}_{10}$

$m = 3$
Ubiquitous structure when ions have similar sizes, around 0.6 Å. A is tetrahedrally coordinated, and B octahedral (actually with a slight trigonal distortion).

In general, lower oxidation states and smaller bandwidths than in perovskites.
Spinel $\text{AB}_2\text{O}_4$

**ions on the A site**

- Li
- Mg

**ions on the B site**

- Li
- Mg

**Jahn-Teller active**

**Diamagnetic**

**High single-ion anisotropy**
Some ABO$_2$ structures: Highly dense in-plane, and frequently metallic

LiCoO$_2$ (ordered rock-salt)

111-ordered with alternating octahedral LiO$_6$ and CoO$_6$ stacking

3R–CuFeO$_2$ (delafossite)

BO$_2$ (Cdl$_2$) slabs separated by two-coordinate atoms, usually Cu$^+$ and Ag$^+$. Also unusually, Pd$^{1+}$ and Pt$^{1+}$. 
$Y_2Ti_2O_7 = Y_2Ti_2O_6\bar{O}$

6+2-coordinate A atoms and 6-coordinate B atoms.

Separately, just connecting A or just connecting B yields two interpenetrating pyrochlore lattices of corner-connected tetrahedra.
Counting electrons
Counting electrons in TiO$_2$: Assign as Ti$^{4+}$ and O$^{2-}$

Insulator, not so easy to dope.
Counting electrons in SnO\textsubscript{2}: Assign as Sn\textsuperscript{4+} and O\textsuperscript{2−} (more covalent than TiO\textsubscript{2}).

Insulator, easier to dope (TCOs).
Counting electrons in BaPbO$_3$; Assign as Pb$^{4+}$ and O$^{2-}$. An unexpected semi-metal.

Equivalent Sn$^{4+}$ compounds are insulating.
d⁰ and s² systems: Second-Order Jahn-Teller (SOJT) effects
Expand the vibronic Hamiltonian in terms of a normal coordinate $Q$:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} Q + \frac{1}{2} \hat{H}^{(2)} Q^2 + \ldots$$

where:

$$\hat{H}^{(1)} = \left( \frac{\partial \hat{H}}{\partial Q} \right)_{Q=0}; \quad \hat{H}^{(2)} = \left( \frac{\partial^2 \hat{H}}{\partial Q^2} \right)_{Q=0}$$

resulting in:

$$E = E^{(0)} + \langle 0 | \hat{H}^{(1)} | 0 \rangle Q + \frac{1}{2} \left[ \langle 0 | \hat{H}^{(2)} | 0 \rangle - 2 \sum_n \frac{\langle 0 | \hat{H}^{(1)} | n \rangle^2}{E^{(n)} - E^{(0)}} \right] Q^2 + \ldots$$

1st order (J–T)  

SOJT

d^0 systems

Seen in early transition metal oxides in their highest oxidation state. Effects strengthens with smaller ions and higher charge (i.e. with higher covalency):

<table>
<thead>
<tr>
<th></th>
<th>Sc^{3+}</th>
<th>Ti^{4+}</th>
<th>V^{5+}</th>
<th>Cr^{6+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr^{4+}</td>
<td></td>
<td>Nb^{5+}</td>
<td>Mo^{6+}</td>
<td></td>
</tr>
<tr>
<td>Hf^{4+}</td>
<td>Ta^{5+}</td>
<td></td>
<td>W^{6+}</td>
<td></td>
</tr>
</tbody>
</table>

Both JT and SOJT result in distortions, but the latter results in off-centering as well (i.e. creates a local dipole).
Countercations (other cations) play a role in determining distortion:

*P4mm* BaTiO$_3$ at room temperature with distorted TiO$_6$ octahedra.  
*Pnma* CaTiO$_3$ at room temperature with tilting and rotation, but relatively undistorted TiO$_6$ octahedra.
Cation centered lone pairs – the important cations (note the valence is 2 below the group valence):

<table>
<thead>
<tr>
<th></th>
<th>1+</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
<th>5+</th>
<th>6+</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d^{10} 4s^2$</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>$4d^{10} 5s^2$</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
</tr>
<tr>
<td>$5d^{10} 6s^2$</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sub-valent state is particularly important in the last row.

In many crystalline solids with cation-centered lone pairs, the lone pair occupies the same volume as an oxide or fluoride ion. However, the cation-lone pair distances (in Å) is much shorter than typical cation-anion distances:

<table>
<thead>
<tr>
<th>Element</th>
<th>1+</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
<th>5+</th>
<th>6+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
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<td>Ge</td>
<td>1.05</td>
<td>As</td>
<td>1.26</td>
<td>Se</td>
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<tr>
<td>In</td>
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<td>Sn</td>
<td>0.95</td>
<td>Sb</td>
<td>1.06</td>
<td>Te</td>
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<tr>
<td>Tl</td>
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<td>Pb</td>
<td>0.86</td>
<td>Bi</td>
<td>0.98</td>
<td>Po</td>
</tr>
</tbody>
</table>

*Polyhedra of anions and lone pairs must have off-centric cations.*
Cation-centered lone pairs (often with Pb\(^{2+}\) as the central cation, but also Sn\(^{2+}\) and Bi\(^{3+}\)) are important for applications requiring off-centered polyhedra and their associated dipoles:

- Ferroelectric and piezoelectric materials, actuators
- High-refractive index materials (lead crystal)
- Ionic conductors
- Multiferroic materials
- Non-linear optical materials
- Phosphors
- Semiconductor/semimetal to insulator transitions
Visualization: DFT based on the Stuttgart TB-LMTO-ASA program [O. K. Andersen, O. Jepsen etc.]


\[
\text{ELF} = \frac{1}{1 + \left( \frac{D}{D_H} \right)^2} \in (0, 1)
\]

with

\[
D = \frac{1}{2} \sum_i |\nabla \phi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}
\]

and

\[
D_H = \frac{3}{10} (3\pi^2)^{5/3} \rho^{5/3}
\]

The electron density \(\rho\) does not reveal lone pairs.
Lone pairs typically visualized with ELF values between 0.65 and 0.9

**Composition of the lone pair**

Orgel (1959): The lone pair cannot have purely $s$ character when it is *stereochemically* active; it must admix with $p$.


![Diagram](image)

- **Typical oxide (BaO)**: 
  - Anion $p$ filled
  - Cation $s$ & $p$ empty

- **Lone pair oxide (PbO)**: 
  - Cation $s$ filled
  - Anion $p$ filled
  - Cation $p$ empty

*Energy →*
A lone pair sorted structural field AQ (IV-VI semiconductors): The lone pair is not always active!

\[ \text{s}^2 \text{ systems: Lone pairs} \]

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>Se</th>
<th>Te</th>
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</tr>
<tr>
<td>Pb</td>
<td>PbS</td>
<td>PbSe</td>
<td>PbTe</td>
</tr>
</tbody>
</table>

massicot

arsenic (polar)

massicot

rock salt
When the lone pair is stereochemically active (as in GeS), cation s states are broader and are better mixed with anion p states. The mixing is intermediated by empty cation p.

Cation s states are narrow and largely unmixed with anion p in cases when the lone pair is not stereochemically active (cf. the inert pair effect).

The expression of cooperative stereochemical activity of the lone pair plays an important role in the development of polar behavior.

Even above the phase transition, the Pb$^{2+}$ ion (here, in Pb$_2$NbYbO$_6$) is not really where it is supposed to be.


Thank you

Photo by Tony Mastres