Physics of Transition Metal Oxides

Lecture 1

Introduction

This lecture course will be materials oriented

We look at various model compounds, their structure, properties, and behavior.
As a general group of compounds, we focus on transition metal oxides

Oxides:

- very wide group of compounds
- various crystal structures
- many interesting properties
- very actively studied
- many open solid state physics questions

Topics:

1. Introduction to oxides
   - Chemical aspects (oxidation states, thermodynamic stability)
   - Structures (binaries, perovskites, spinels, etc.)
   - Classification of oxides and some of the more interesting properties
2. Electronic structure of oxides
3. Insulating oxides
4. Semiconducting oxides
5. Metallic oxides
6. Superconductors
7. Magnetic oxides
8. Defects in oxides
9. Oxide crystal growth (bulk and thin films)
10. Oxide surfaces
11. Specific properties of oxide thin films

Transition metals

The transition elements are shown in Green

The d orbitals of are progressively filled as we move from left to right.
We shall mostly look at the 3d elements (Ti...Cu), but also the 4d and 5d elements.

The electron configurations shown above the columns: $[Ar]3d^24s^2$, $[Ar]3d^34s^2$, $[Ar]3d^54s^1$, $[Ar]3d^54s^2$, $[Ar]3d^64s^2$, $[Ar]3d^74s^2$, $[Ar]3d^84s^2$, $[Ar]3d^{10}4s^1$

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

What types of compounds do we look at:

The most simple case: Binary oxides, like TiO_2, Fe_3O_4, NiO, OsO_4, $Fe_{0.9}O$, ReO_3, etc.
The number of compounds is already large and we have here insulators, magnetic oxides, semiconductors, metals.

Ternary oxides, like Fe_2CoO_4, $LaNiO_3$, $PbTiO_3$, $SrTiO_3$
Dielectric materials, etc.

Complex oxides, like $YBa_2Cu_3O_7$, $Tl_2Ba_2Ca_2Cu_3O_{10}$. These examples are high-temperature superconductors.

Oxidation states

What we look at is (a somewhat arbitrary) way of assigning charges to each atom in the lattice: $Sr^{2+}Ti^{4+}O_3^{2-}$

Stoichiometry, or the precise elemental composition of a material, expressed as a chemical formula: TiO_2, $Na_{0.7}WO_3$, etc. In principle, this can be obtained from chemical analysis.

Problems:

1. Is the material a single-phase compound and not a mixture, like Fe_2O_3 + Fe_3O_4? This can be usually analyzed by x-ray diffraction. Another possibility is to do microprobe analysis in an electron microscope.

2. Do we have intrinsic nonstoichiometry, such as in *tungsten oxide bronzes* that have a general formula A_xWO_3, where A = Li, Na, Ca, Sr, U, Cd, Hf.

Lattice structures of bronzes

The name 'bronze' points to apparent similarity of Na_xWO_3 to metallic bronze.

| Bronze	Composition	Symmetry	Unit Cell Dimensions
Li_xWO_3	$0.31 < x < 0.57$	Cubic	$a \approx 3.7$Å
Na_xWO_3	$0.26 < x < 0.93$	Cubic	$a \approx 3.8$Å
Na_xWO_3	$x = 0.10$	Tetragonal	$a = 5.25, c = 3.90$Å
Cu_xWO_3	$0.26 < x < 0.77$	Orthorhombic at $x = 0.26$	$a = 3.88, b = 3.73, c = 7.74$Å
		Triclinic at $x = 0.77$	$a = 5.85, b = 6.65, c = 4.88$Å
			$\alpha = 135.7°, \beta = 91.7°, \gamma = 93.6°$
La_xTiO_3	$0.67 < x < 1.0$	Cubic	$a \approx 3.9$Å
Sr_xNbO_3	$0.7 < x < 0.95$	Cubic	$a \approx 4.0$Å

Ref:Cox92, p.8

The tungsten bronzes appear to show real nonstoichiometry, i.e. the Li, Na, etc. float in the WO_3 lattice. In other similar cases, however, it is more accurate to speak of distinct *line phases*, such as $K_{0.30}MoO_3$ and $K_{0.33}MoO_3$. These two have different structures and different electronic properties.

The only stable $x = 0$ compound of similar structure is ReO_3, a metallic binary oxide. This lattice can be viewed in several ways:
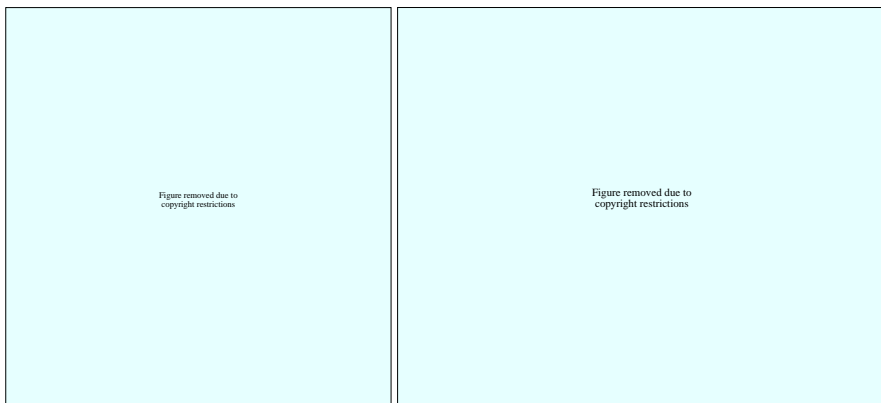 **Re-based** A cubic Re array with oxygens in the middle of each 'bond'
  O-based cubic array of oxygen octahedra with Re in the center of each octahedron
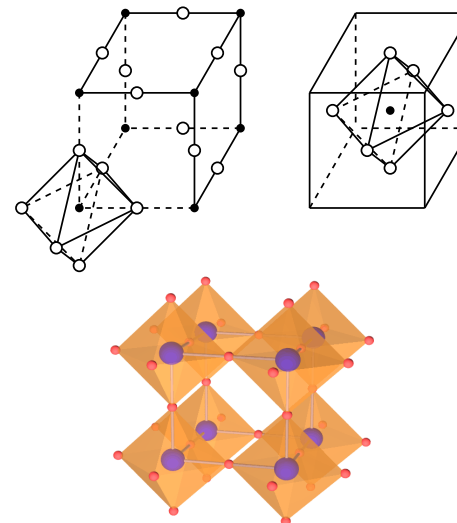
Problems (continued):

3. *Oxygen stoichiometry* is a particular problem for many oxides. Oxygen content is usually not analyzed directly. Oxygen can be easily lost or gained during synthesis and later handling. This became very clear when High-T_c superconductors were discovered. For example, the famous 1-2-3 compound, or $YBa_2Cu_3O_7$:

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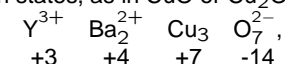Figure removed due to copyright restrictions

Ref:Poole95, p.181

9

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YBCO is tetragonal above $700^{\circ}C$ and orthorhombic below $700^{\circ}C$. In the tetragonal phase, the oxygen sites are occupied randomly and the crystal is a semiconductor. In the orthorhombic phase, the oxygens are ordered in chains along the b axis.
We will come back to these issues at a later time when discussing superconductors in greater detail.
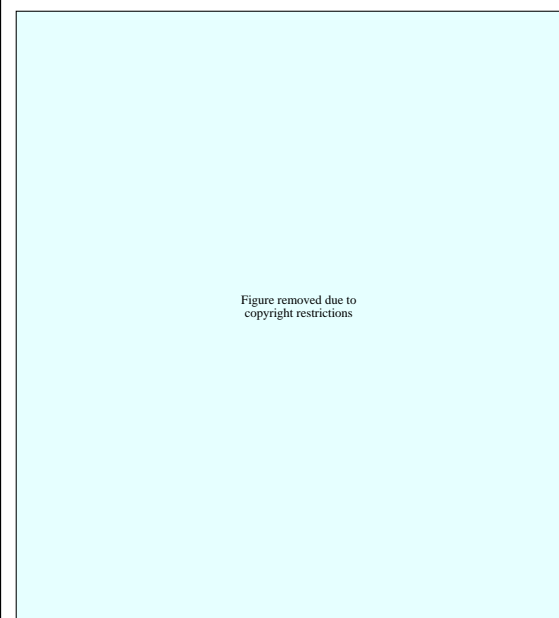
Poole95, p.185

For now, look at a composition like $YBa_2Cu_3O_7$. Copper is the only element which in a chemical sense can have various oxidation states, as in CuO or Cu_2O. What we get here is:

$$Y^{3+} \quad Ba_2^{2+} \quad Cu_3 \quad O_7^{2-},$$
$$+3 \qquad +4 \qquad +7 \quad -14$$

i.e. on average Cu is +2.33!

10

For a chemist, the *oxidation state* is a formal ionic charge. For a crystal this simple picture would apply in a purely ionic case, where each atom can gain or lose an integral number of electrons.

We would usually start by giving oxygen a fixed charge of -2.
The metals should compensate that, i.e. Ti is +4 in TiO_2.
In complex oxides we usually have some idea how to distribute charge between metals.
We always have Li^+, Sr^{2+}, La^{3+}, etc.
In $LiNbO_3$, niobium therefore has to be in the Nb^{5+} state, in $LaFeO_3$, iron is Fe^{3+}.

Things get trickier in compounds like $FeTiO_3$, because we could have either $Fe^{3+}Ti^{3+}O_3$ or $Fe^{2+}Ti^{4+}O_3$.

11

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Cox92, p.12

Oxidation states and electron configurations in the $3d$, $4d$, and $5d$ series. Each diagonal line corresponds to a d^n series.
- **B** Well-known binary oxides exist
- **T** Only found in ternaries
- **(B)(T)** Poorly characterized phases

Remarkably, there are no known oxides with $4d^7$, $4d^9$, $5d^7$ or $5d^9$ configurations, setting apart the platinum-group elements Ru, Rh, Pd, Os, Ir, and Pt.
The highest (or lowest) states may be unstable. In $BaFeO_4$, for example, not all Fe is in 6+ state due to commonly occurring oxygen deficiency.
The highest oxidation states are always found in the middle of each series.

12

Some remaining issues: *Peroxides and superoxides*

So far, we have always assigned 2- to oxygen. There are also other possibilities, such as peroxides (O_2^{2-}), as in SrO_2 and superoxides (O_2^-). Such oddities occur for example in K_3CrO_8, where it would be quite unlikely to actually have a Cr^{13+} configuration. Instead we have Cr^{5+} and O_2^{2-}.

Another interesting case is found in High-T_c superconducting oxides. As we already saw, when going from $YBa_2Cu_3O_{6.5}$ to $YBa_2Cu_3O_7$, some copper appears to be oxidized from Cu^{2+} to Cu^{3+}, which is not realistic. Instead, some of the charge is taken from the oxygens, leaving O^-.

Some remaining issues: *mixed valency*

Mixed valency traditionally has two slightly different meanings for chemists and physicists.

For chemists, iron in Fe_3O_4 would have an average oxidation state of $Fe^{2.67+}$. Structural characterization and conductivity consideartions would usually lead to an assignment of one Fe^{3+} and two Fe^{2+} ions. A phase transition occurs at 120K. Below this temperature carriers are localized and we would talk about integral Fe^{2+} and Fe^{3+}.

In physics, mixed valence refers to a case where the measured (or measurable) valence of a particular crystal site is a fractional number. This can be seen by looking at isomer shifts in NMR or Mössbauer spectra, and various other techniques.

A fractional valence state is usually associated with electron hopping between several sites. This hopping may be thermally activated. The important points are the timescales of the hopping process and the measurement process.


Electron hopping between two sites

$$
\begin{array}{ccc}
{}^{3+}\bigcirc & \Leftarrow \ominus \Rightarrow & \bigcirc^{3+} \\
{}^{2+}\odot & \Leftrightarrow & \bigcirc^{3+} \\
{}^{3+}\bigcirc & \Leftrightarrow & \odot^{2+}
\end{array}
$$
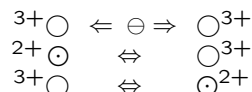
Some of the spectroscopic techniques for detecting valence states are listed below:

Technique	Phenomenon	characteristic frequency
x-ray photoelectron spectroscopy	Core electron escape	$\approx 10^{16}$ Hz
Optical absorption spectroscopy	Electron excitation	$\approx 10^{16}$ Hz
Vibrational spectroscopy	Phonon frequencies	$\approx 10^{14}$ Hz
Mössbauer spectroscopy	Nuclear decay	$\approx 10^7$ Hz
EPR spectroscopy	Electron precession rate	$\approx 10^9$ Hz
NMR spectroscopy	Zeeman precession rate	$\approx 10^8$ Hz
	Hyperfine interactions	$\approx 10^4$ Hz
NQR spectroscopy	Quadrupolar precession rate	$10^3 - 10^5$ Hz
Electrical conductivity	Average valence	
Magnetic suceptibility		
Specific heat		

XPS, UPS, and optical measurements are essentially instantaneous, we would see the presence of two distinct valence states.

Electronic configurations of the $3d$ elements (Fe):

$$\underbrace{\underbrace{\underbrace{\underbrace{1s^2}_{He}\,2s^2 2p^6}_{Ne}\,3s^2 3p^6}_{Ar}\,3d^6 4s^2}_{Fe}$$
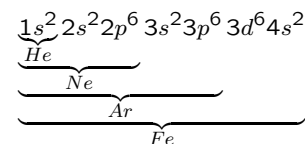
Fe is most commonly found in 2+ or 3+ states. This means that the first to go are the $4s$ and then the $3d$ electrons.

A sensitive way of detecting (local) valence state changes is to probe the existence or loss of s electrons. This can be done by looking at how the electronic shell interacts with the nucleus of the atom.

This brings us to a brief detour to *Mössbauer spectroscopy* and *chemical shifts*.

Interaction between the nucleus and the electron shell

A Hamiltonian for an atom can be written as

$$\mathcal{H} = \mathcal{H}_0 + E_0 + M_1 + E_2 + \cdots,$$

where
$\mathcal{H}$ holds all the terms that do not involve hyperfine interactions,
E_0 is the electric monopole or Coulomb interaction,
M_1 is the magnetic dipole interaction and
E_2 is the electric quadrupole interaction.
Other higher terms usually don't matter.

The Coulomb interaction causes a slight shift in the energy levels. The magnitude of the shift depends on the electronic configuration of an ataom and is therefore different in different compounds. That is where the name *chemical shift* comes from. Also known as *isomer shift*.

17

Nuclear energy levels:
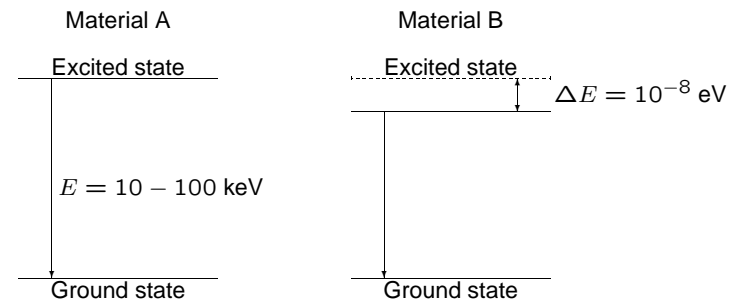
Mössbauer spectroscopy can measure the nuclear energy level shifts with very high precision (neV).

The shift of the excited state energy depends on the electronic density *at the nucleus*:

$$\delta = \text{const.} \times \left\{ |\psi_s(0)_A|^2 - |\psi_s(0)_B|^2 \right\}.$$

18

The wavefunction of an electron:

$$\psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \varphi) \exp(-iE_n t/\hbar)$$

s electrons have a nonzero probability of being located at the nucleus. Sensitivity to the chemical environment therefore is mediated by outer (or inner) s orbitals.

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19

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This example is for Eu_3S_4. Similar effects can be seen for Fe in Fe_3O_4, for example.
At low temperature hopping is slower than the characteristic time of the Mössbauer transition (9.7 ns). Two peaks are seen, corresponding to the Eu^{2+} and Eu^{3+} states. At higher temperature the hopping becomes faster than the Mössbauer probe, which sees only an average peak position, giving a 'fractional' valence for Eu.

In conclusion, oxidation states present a useful language for rough characterization of materials. Valence states should not be taken too seriously, however. Crystals are not purely ionic and charge cannot usually be divided as integers between ions.
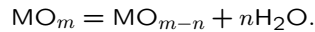
Greenwood71

20

Thermodynamic stability of oxides

The stability of a compound depends on the Gibbs free-energy change

$$\Delta G = \Delta H - T\Delta S,$$

where we have enthalpy H, temperature T, and entropy S. We look at formation and decomposition reactions, such as decomposition of MO_m to MO_{m-n}, i.e. loss of oxygen:

$$MO_m = MO_{m-n} + nH_2O.$$

Enthalpy doesn't change much in such a reaction, mostly we are interested in the entropy change (production of oxygen gas). Entropy is a function of the oxygen pressure

$$\Delta S = \Delta S^0 - (nR/2)\ln p_{O_2},$$

where R is the gas constant 8.31 $\frac{J}{Kmol}$. The Gibbs free-energy change is thus

$$\Delta G = \Delta G^0 + (nRT/2)\ln p_{O_2}.$$

This reaction can only proceed if $\Delta G < 0$, i.e. the oxygen pressure must be below a value p_d

$$\ln p_d = -2\Delta G^0/nRT.$$

21

The Ellingham diagram:
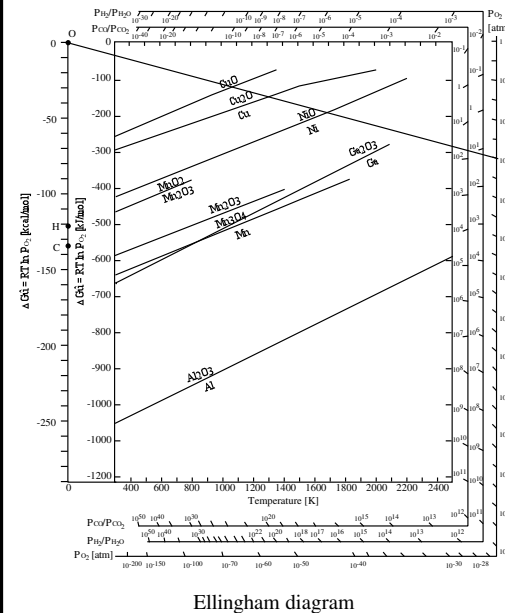
Ellingham diagram

This simply means that an oxide decomposes to another form or pure metal if the oxygen pressure is low enough. This pressure also depends on temperature, i.e. decomposition occurs at a fixed oxygen pressure if the temperature is high enough.

Very low oxygen pressures can be achieved by mixing CO and CO_2 gases due to the gas phase equilibrium reaction

$$CO_2 = CO + \frac{1}{2}O_2$$
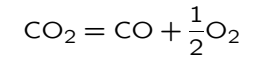
Another choice is a mixture of H_2 and H_2O in the reaction

$$H_2O = H_2 + \frac{1}{2}O_2$$
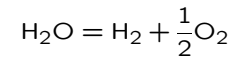
22

Ellingham diagrams give a rough idea of which oxidation state to expect. Oxides are often nonstoichiometric, however. We therefore also need more detailed phase diagrams.

There are regions with two solid phases (mixture of Fe_3O_4 and Fe_2O_3) and regions with a single (but variable composition) phase, i.e. the wüstite region in the $Fe_{0.85}O$ to $Fe_{0.96}O$ range. There are very narrow *line phases*, like Fe_2O_3. These tend to spread out at high temperature.

This figure also illustrates the phase rule:

$$F + P = C + 2.$$

P: number of phases, including gas, C: number of components, equals 2 in a binary oxide, F: number of degrees of freedom (temperature, pressure, etc.)

Cox92, p.13

23

Crystal structure of oxides

Oxides are largely ionic crystals. The nearest neighbor of a metal is always oxygen. The crystal structure and stability of a phase depends on this bonding. Specifically we are interested in *bond lengths*, *coordination number*, and *geometry*. Bond length is often compared to *ionic radius*.

Cox92, p.16

24

General rules:

1. Ionic radius decreases as electrons are removed

2. Ions with larger mass are smaller due to increased nuclear charge

3. $3d$ elements are smaller than $4d$ and $5d$.

4. Large drop of size between La and Hf, a.k.a *lanthanide contraction*, due to the filling of the f orbitals

5. Small ions (< 50 pm) are usually in tetrahedral (or square planar) sites

6. Most ions (50 to 80 pm) are in octahedral sites

7. Large ions (over 80 pm) have higher coordination numbers

The planar coordination (b) is a highly distorted case of the tetrahedral coordination (in terms of ionic radii), found in PdO.

The octahedral configuration is often distorted. Shown examples are for MoO_3 and Cu in $La_{1.85}Sr_{0.15}CuO_4$. This happens for V^{5+}, Mo^{6+} and some others. In a chemical sense the shorter Mo-O bond would look like a double bond, $Mo(=O)_2^{2+}$. These ions are too small for the octahedral configuration.

This type of distortion may also be caused by crystal field effects, or *Jahn-Teller* distortion. This happens for Mn^{3+} in $LaMnO_3$ and Cu^{2+} in La_2CuO_4.

Structural families

(a) Rock-salt: a common structure for binary oxides: MnO, CoO, NiO. Includes nonstoichiometric oxides FeO, TiO_x, VO_x. Also exists in AMO_2 type oxides where A is usually Li or another alakli earth. Li substitutes for M.

(b) Corundum M_2O_3-type oxides, like Al_2O_3, Ti_2O_3. Also some ternaries like ilmenite $FeTiO_3$, and $LiNbO_3$.

(c) Rutile Typical for TiO_2. Common for dioxides.

rhenium trioxide ReO_3 structure. Quite unusual, but parent of the *perovskite* structure.

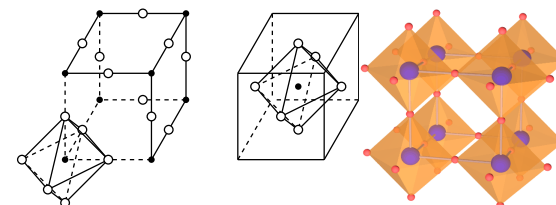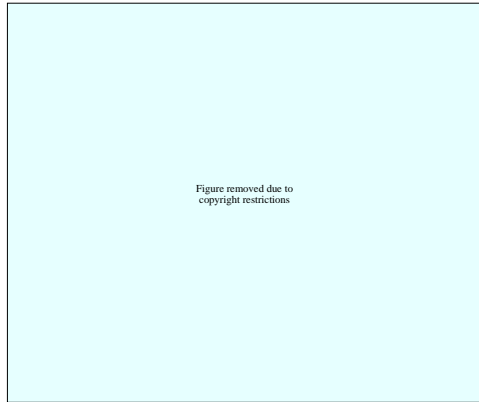It is often easier to think in terms of oxygen octahedra. Look at the ReO_3 structure again:

(a) ReO_3, (b) rutile, (c) corundum

Octahedra can be *corner*, *edge*-, or *face-sharing*. Rock-salt is edge-sharing, ReO_3 is corner-sharing, corundum is face-sharing. Rutile is a mixture of corner- and face-sharing octahedra.

More complex ternary structures:

(a) is the *perovskite* structure AMO_3, like $SrTiO_3$
(b) is a layered perovskite, the K_2NiF_4 structure
(c) is a spinel, AB_2O_4, having both octahedra and tetrahedra.

In perovskites the center metal has 12 oxygen neighbors and thus has to be a large ion, typically a pretransition metal ion, like K ($KTaO_3$) or Sr ($SrRuO_3$) or La ($LaVO_3$). Post-transition metal atoms can also be found, e.g. Pb in $PbTiO_3$.

Ideal structures are very rare. Structural distortions are usually present

29

More complex oxide structures:

Spinels form an important group. Composition is fairly simple, e.g. $MgAl_2O_4$, but the structure quite complex. Also found in some forms of binaries, such as Fe_3O_4 and Co_3O_4. All have a mixture of valence states. Also two nonequivalent metal sites, octahedral and tetrahedral.
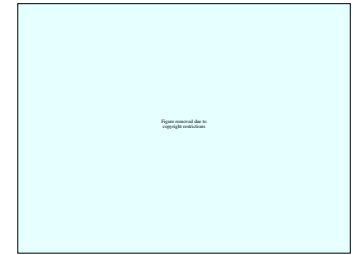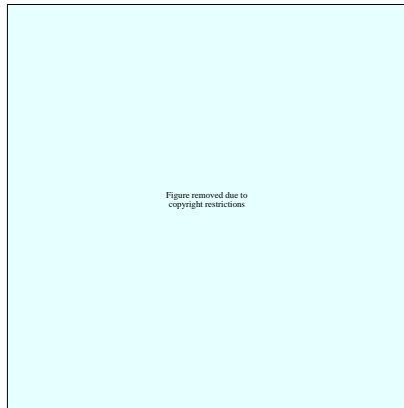
Garnets also have a complex sructure. Examples are $Ca_3Al_2Si_3O_{12}$ and $Y_3Fe_5O_{12}$ (YIG), where Fe^{3+} ions are in tetrahedral and octahedral sites and the larger Y^{3+} ions are in eight-coordinate site. YIG is an important magnetic material, while another garnet $Y_3Al_5O_{12}$ (YAG) is a well-known phosphor and laser material.
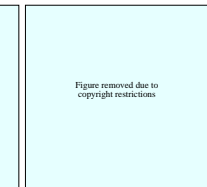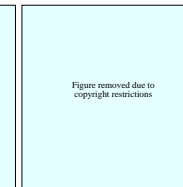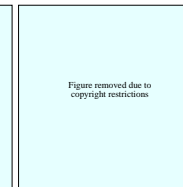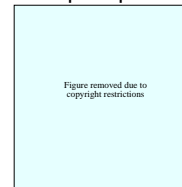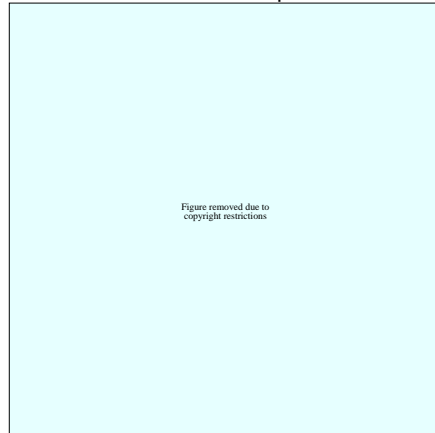
30

Some distorted lattices:

Monoclinic form of WO_3. Note the rotated octahedra, forming diamond-shaped tunnels. This type of distortion is very common in ruthenates and even titanates at low temperature.

Just to show that some oxide lattices can have very complex shapes, here is a Gatehouse tungsten bronze, or $Rb_3Nb_{54}O_{146}$
Rao98

31

Many lattices have several different metal coordination sites, for example the Hg-containing High-T_c oxides:
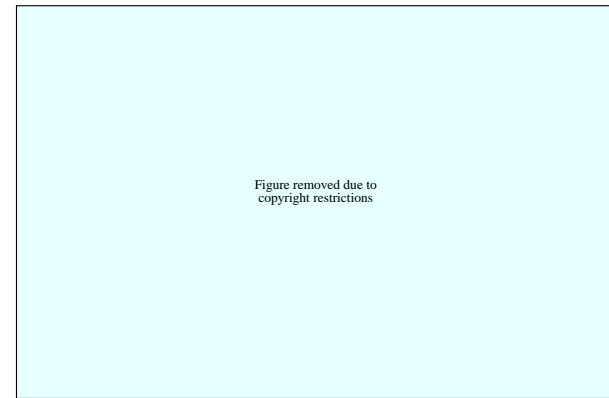
(a) $HgBa_2CuO_{4+\delta}$ (1201) (b) $HgBa_2CaCu_2O_{6+\delta}$ (1212), (c) $HgBa_2Ca_2Cu_3O_{8+\delta}$ (1223)

(Poole95)

Mercury in the form of HgO_2 in a square-planar configuration serves as a separator between the octahedral layers. The highest T_c does not always appear in a 'pure' phase, e.g. the $n = 1$ phase with a T_c=96K is $Hg_{1-x}Ba_2Cu_{1+x}O_{4-\delta}$. The extra oxygen goes into the mercury layers with $\delta \approx 0.1$.

32

Classification of oxides

Oxides exhibit a very wide range of different characteristics. Classification is therefore somewhat arbitrary, and materials may belong into several classes.
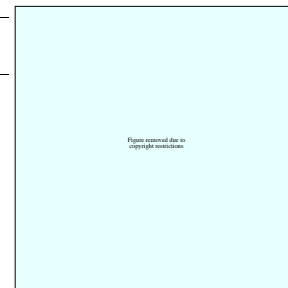
1. d^0 insulators:

- Usually stoichiometric oxides with a d^0 electronic configuration (such as $SrTiO_3$, containing Ti^{4+}).
- Band gaps are relatively large, e.g. 3.2 eV for $SrTiO_3$, over 5 ev in Zr and Hf oxides ($CaHfO_3$, $CaZrO_3$).
- Optically transparent below the band gap energy
- diamagnetic (no unpaired electrons)
- the filled levels are mostly oxygen $2p$, the transition metal $3d$ levels are empty

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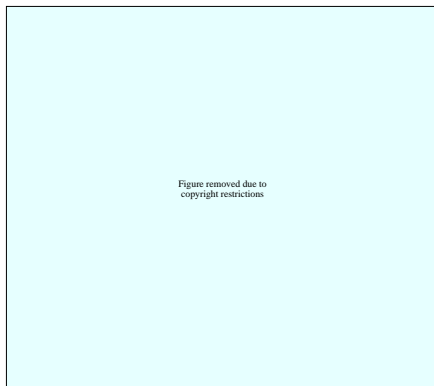
2. Other closed-shell insulators:

Compound	Electron configuration	Metal coordination	Band gap (eV)
Cu_2O	$3d^{10}$	2 (linear)	2.16
Ag_2O_2	$4d^{10}$	2 (linear)	
	$4d^8$	4 (square planar)	
PdO	$4d^8$	4 (square planar)	1
$LaCoO_3$	$3d^6$	6 (octahedral)	0.1
$LaRhO_3$	$4d^6$	6 (octahedral)	1.6

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A completely filled shell is just as good as a completely empty shell, i.e. we get an insulator because there are no electrons that could be easily delocalized.

Partially-filled shells usually result in partially-filled bands and thus also metallic conductivity.

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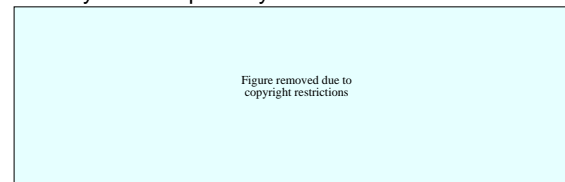
Up to now we have looked at the $3d$ electron levels as a single set. In fact, in oxides we also have to remember the presence of a crystal field, i.e. ions are not floating in vacuum.

In a crystal the d levels are split. The splitting Δ can be large enough to favor a *low spin state*.
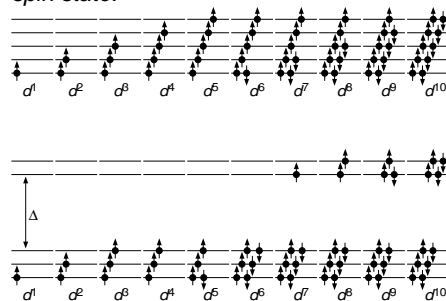
Cox92

3. d^n impurities:

Transition metal impurities often occur in various oxides (transition metal oxides and others, such as MgO or Al_2O_3). These impurities form localized states in the bandgap. Such impurities give color to various gemstones (ruby, sapphire, etc.)

4. Magnetic insulators:

This group includes some very important materials, such as yttrium-iron garnet (YIG) $Y_3Fe_5O_8$. Other magnetic oxides are NiO and Cr_2O_3. In all cases we need an unpaired electron. Magnetic order arises when d electrons interact (weakly). In most cases antiferromagnetic order arises at low temperature. The magnetic insulators can be easily turned into semiconductors by impurities or changes in oxygen stoichiometry. NiO, for example, is insulating and green when pure, but can become semiconducting and black when excess oxygen is present.

5. **Semiconductors:**

Semiconducting properties are usually seen in nonstoichiometric oxides. TiO_2, for example is a good d^0 insulator. Slightly oxygen deficient TiO_{2-x} is a semiconductor. Same happens with $Ni_{1-x}O$, and $SrTiO_{3-\delta}$.

Doping may also be done by adding other metals, such as $Li_xMn_{1-x}O$, or adding Nb into $SrTiO_3$.

6. **Transition to metallic state:**

Increasing the dopant concentration pushes the otherwise insulating parent compounds into a metallic state, e.g. 0.5 wt% doped $SrTiO_3$ is black and metallic.

7. **Simple metals:**

This is a rather small group of compounds with a partially filled conduction band. Examples are usually found among $4d$ and $5d$ elements, such as ReO_3, RuO_2, and Na_xWO_3 for $0.3 < x < 0.9$.

8. **Superconductors:**

Well known materials like $YBa_2Cu_3O_7$. Also several others, like NbO and $SrTiO_{3-\delta}$.

37

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38