Physics of Transition Metal Oxides

Lecture 9

Mixed valency in oxides

We have so far mostly looked at stoichiometric compounds. The last lecture was devoted to ruthenates, a good example of how small structural changes in a lattice can have dramatic effects on the transport and magnetic properties of oxides.

We now continue with another broad group of compounds containing a mixture of valence states. This can happen in stoichiometric compositions like Fe_3O_4 and Ti_4O_7 or in deliberately doped materials, such as $La_{1-x}Sr_xMnO_3$. The two cases that we shall cover in greater detail are the hole-doped manganese oxides (magnetic) and copper oxides (superconducting).

Doping extra carriers into an insulator can induce a metallic state, but not always. The extra carriers (electrons or holes) can get localized or we may see charge ordering.

When metallic conduction does arise, we may also see magnetic ordering due to *double exchange*.

Mixed-valent compounds are classified (in a chemical sense) based on the energy difference between the states $M_A^{n+}M_B^{(n+1)+}$ and $M_A^{(n+1)+}M_B^{n+}$. If the energy difference, $\triangle E$, is small, the valence delocalization coefficient (α) is large.

Materials can be divided into three classes with class I for small α, class II for intermediate cases and class III for large α. Metal-semiconductor boundary usually follows the class II / class III grouping. SOme examples are:

Oxide	Classification	Remarks
Pb_3O_4	I	Red lead, insulating
$BaBiO_3$	I	Insulating, Bi^{3+} and Bi^{5+}
Sb_2O_4	I	Sb^{3+} and Sb^{5+}
KCr_3O_8	I	Cr^{3+} and CrO_4^{2-}
$Li_xNi_{1-x}O$	II	Hopping semiconductor
$La_{1-x}Sr_xMnO_3$	II	Ferromagnet
$BaBi_{1-x}Pb_xO_3$	III	Superconducting
$LiTi_2O_4$	III	Superconducting
Na_xWO_3	III	metallic at high x

footnotesize Rao98 p.261

- **Class I** Distinguishable oxidation states in very different environments. Little if any charge transfer between sites.

- **Class II** Different oxidation states can be identified but transfer of charge has a very low barrier, giving a semiconductor.

  Localization may be due to potential field of defects, structural disorder or lattice interactions (polarons) in stoichiometric compounds. An example could be AgO, which could be written as $Ag^+Ag^{3+}O_2$.

- **Class III** Metal ions have essentially fractional valence states, usually metallic conductivity.

Fe$_3$O$_4$

It is obvious from the formula that this material contains both Fe^{2+} and Fe^{3+} ions (one Fe^{2+} and two Fe^{3+} per formula unit). Two different Fe-O distances: Fe^{3+}-O=1.888Å and Fe^{3+}/Fe^{2+}-O=2.058Å.
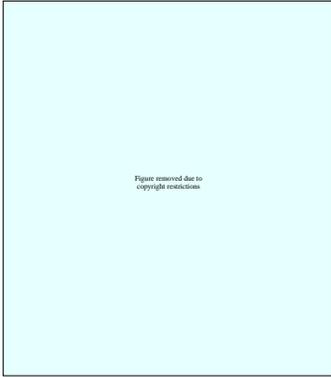
Fe$_3$O$_4$ is an *inverse spinel*. Spinels contain both tetrahedral and octahedral sites for the transition metal ions. In normal spinels, like MgAl$_2$O$_4$, the 3+ ions are in the octahedral sites. In an inverse spinel, the 2+ ions go into the octahedral sites, pushing half of the 3+ ions into the tetrahedral sites.

$$Mg^{2+}[Al_2^{3+}]O_4$$

$$Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$$
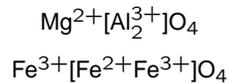
where [..] marks the octahedral ions.

The octahedral sites in Fe$_3$O$_4$ thus contain an equal number of 2+ and 3+ ions. Electrical conductivity 200$(\Omega$ cm$)^{-1}$ is due to a hopping mechanism between the 2+ and 3+ sites. Mobility is very low, around 1 cm^{2}V^{-1}s^{-1}, the mean-free path is close to the Fe-Fe distance.
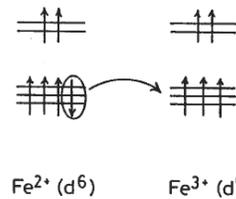
Fe ions prefer a high-spin state. In order to keep the high-spin state for the final 3+ ion, the minority spin has to move. The receiving Fe^{3+} therefore has to have a spin parallel to the original Fe ion, i.e. ferromagnetic order. Otherwise we violate the Pauli exclusion principle and would have to pay a large energy penalty by flipping the spin (eV order).

Fe^{2+} (d^6)   Fe^{3+} (d^5)

Neutron diffraction shows that the octahedral sites are indeed ferromagnetically ordered. The crystal as a whole is *ferrimagnetic* because the Fe ions in the tetrahedral sites have spins antiparallel to those in the octahedral sites. The tetrahedral sites apparently do not contribute to conductivity. The interaction between the tetrahedral and octahedral sites follows the superexchange mechanism that is very common in insulating oxides.
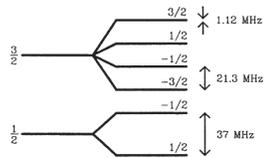
Mössbauer spectroscopy of Fe measures transitions between a spin 3/2 excited state and a spin 1/2 ground state of the Fe nucleus. Levels are split due to a hyperfine magnetic field of up to 50 T. A Total of six allowed transitions need to be considered. The absolute position of the spectrum depends on the isomer (or chemical) shift which depends on the eletronic configuration of an atom or ion. The splittings shown here are calculated for a 27 T hyperfine field. Excited state lifetime is 141 ns.

Magnetite has a peculiar transition at around 120 K, the *Verwey transition*. The high-temperature Mössbauer spectrum shows two magnetic components: low-energy sextet belongs to Fe^{3+} in the tetrahedral sites (49.1 T). The higher-energy sexted is due to Fe^{2+} and Fe^{3+} ions in the octahedral sites, average hyperfine field 45.3 T. The two valence states can not be separated on the measurement timescale of 141 ns.
At 77 K (below transition) we have two sextets with fields of 50.3 T (Fe^{3+} in tetrahedral and octahedral sites) and 48 T (Fe^{2+} in octahedral sites).

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Mössbauer measurements in external fields of $\approx$1 T can be used to determine spin orientations and show that spins in tetrahedral sites orient opposite to an external field while the octahedral sites magnetize in parallel with external fields.

The absorption peaks of the octahedral (mixed-valent) sites are broader than those of tetrahedral sites. This appears to be due to electron hopping between Fe^{2+} and Fe^{3+} at a (calculated) time scale of $\tau = 1.1$ ns.

Below transition temperature the hopping stops and the two Fe valence states can be distinguished. The crystal also becomes slightly orthorhombic and heavily twinned (c-axis can point in three directions), top plot. External magnetic field can be used during cooling to remove the c-axis twinning, leaving only an $a - b$-axis twinning (middle plot). This shows that there are *at least* 4 components for the ctahedral site Fe, two for Fe^{2+} and two for Fe^{3+}. Apparently there is partial charge ordering, with an effective unit cell doubling, but the precise structure is not known.

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The loss of magnetic order occurs over a temperature range of several tens of degrees according to Mössbauer spectroscopy. The resistive transition is always much sharper. the transport properties are also very sensitive to local disorder caused by slight stoichiometry deviations.

The plot shows resistivity for $Fe_{3(1-\delta)}O_4$ with δ values: a=-0.00053, b=-0.00017, c=0.00021, d=0.00018, e=0.00069, f=0.0017, g=0.0050, h=0.0068, i=0.0097.

In some cases it is impossible to see from the formula itself that the material has mixed-valent ions. We already saw AgO. Another example is $CaFeO_3$, a paramagnetic perovskite at room temperature.

Below 115 K $CaFeO_3$ becomes semiconducting and the Mössbauer spectrum indicates the presence of *charge disproportionation*

$$2Fe^{4+} = Fe^{3+} + Fe^{5+}$$

This reaction would need about 20 eV of extra energy in gas phase! In a crystal, this would correspond to a negative Hubbard U.

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Charge disproportionation appears to occur when the parent ion, such as Fe^{4+} has an unpaired e_g electron and the two final ionic states (like Fe^{3+} and Fe^{5+}) have a very large difference in ionic radius. $CaFeO_3$ apparently does not show a Jahn-Teller distortion, which would indicate that the e_g electron is delocalized in a band-like state. The structural distortions that should occur in $CaFeO_3$ are not well understood.

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Hole-doped manganites

This group contains compounds like $La_{1-x}A_xMnO_3$, where A is a divalent element like Sr. The doping limits are $LaMnO_3$ (Mn^{3+}) and $SrMnO_3$ (Mn^{4+}), both are antiferromagnetic insulators.

$LaMnO_3$ has an unusual cooperative Jahn-Teller distortion, giving an in-plane ferromagnetic order and an out-of-plane antiferromagnetic order, i.e. an A-type antiferromagnet.

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As Sr is aded to the compound, at about $La_{0.8}Sr_{0.2}MnO_3$, the material becomes ferromagnetic with a T_C of 300 to 400 K and at the same time the Jahn-Teller distortion disappears, i.e. the e_g electrons are no longer localized.

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$La_{1-x}Sr_xMnO_3$

Looking at the filling of d-levels, we see that the single e_g electron can hop between ferromagnetically aligned Mn sites. The t_{2g} levels behave essentially as localized core levels.

The first theoretical analysis for manganites was given by Zener. He looked at the following interactions:

The system now has both localized (t_{2g}) and mobile (e_g) electrons. Important couplings are the Hund coupling J_H, hopping t, and antiferromagnetic direct exchange J_{AF}.

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There are three basic assumptions

1. Interaction within an ion is strong, meaning that the carrier spin must be parallel with the local ionic spin.

2. Carriers do not change their spin while moving in the lattice, i.e. they can only hop from site to site if the ionic spins at these sites are parallel. If spins of neighboring ions are not parallel, a hopping electron would need extra energy, comparable to the Hund coupling.

3. Carriers participate in the ionic binding and therefore lower the total energy of the system. This is how the ferromagnetic order gets stabilized. Direct coupling between d-orbitals of metal ions is not possible due to the large distance. Direct coupling would result in antiferromagnetic order anyway (J_{AF}).

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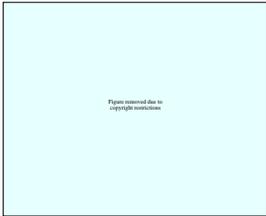
Zener originally argued that electron hopping must occur through a ligand (like oxygen) involving two electrons. the mechanism was therefore called *double exchange*.

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Spins don't always need to be exactly parallel or antiparallel. In general, the spin orientation would affect the hopping probability $t_{eff} = t \cos \frac{\theta}{2}$. This would explain the behavior of spin-canted states, which would explain the coexistence of ferromagnetic and antiferromagnetic features. This assumption is not necessarily valid if we have *phase separation*.

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Tolerance factor

Defined as

$$\Gamma = \frac{d_{A-O}}{\sqrt{2}\, d_{Mn-O}}$$

d_{A-O} is the distance between an A-site di- or trivalent ion from the nearest oxygen.
d_{Mn-O} is the distance between Mn ions and the closest oxygen.

Figure removed due to copyright restrictions

In a perfect cubic perovskite, $d_{Mn-O} = 1$ and $d_{A-O} = \sqrt{2}$. The tolerance factor is thus $\Gamma = 1$.

If the A-site ion is too small, oxygens would move closer to the cube center. In that case $\Gamma < 1$ and the Mn-O bond angle drops below $180°$. This also reduces the hopping rate (drops to zero when bond angle is $90°$). In general, $\Gamma < 1$ results in stronger charge localization due to lower mobility.

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$La_{0.75}Ca_{0.25}MnO_3$

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The magnetization is very low unless an external field is applied. This is due to domain formation, i.e. a bulk magnetic moment appears if an external field is used to wipe away all the domain boundaries. Without an external field the lattice contains many randomly oriented magnetic domains.
Strong magnetic fields (4 T) can cause a significant polarization even above the Curie point.
The resisitivity curve shows an insulating behavior above T_C. This behavior cannot be explained simply by increased scattering of e_g electrons from misaligned spins. The insulator-to-metal transition clearly occurs at the same temperature as magnetic ordering. Even at very low temperatures the conductivity of the metallic state is not very good, at around 1 mΩ cm.

The resistivity also depends on the magnetic field. As shown in the bottom plot, the magnetic field seems to affect the insulating phase more than the metallic phase. But still, around 30% magnetoresistance effect remains even at low temperatures, i.e. the ferromagnetic ordering is not ideal.

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Magnetoresistance

A fairly large magnetoresistance effect was found in $Nd_{0.5}Pb_{0.5}MnO_3$ the magnitude of the effect is comparable to the so-called giant magnetoresistance (GMR) devices (magnetic multilayers).

an even larger effect was found in $La_{0.67}Ca_{0.33}MnO_3$. If the Mr ratio is defined as

$$\frac{\Delta R}{R} = \frac{R_H - R_0}{R_H},$$

then this figure shows an effect of around 1500% at 200 K. A value of around 1000000% has been found in $Nd_{0.7}Sr_{0.3}MnO_\delta$ at 60 K in afield of 8 T. These are the colossal magnetoresistance (CMR) effect materials

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At a higher doping level the magnetic behavior is quite different

It is clear from the magnetization plot of $La_{1-x}Ca_xMnO_3$ ($x \approx 0.5$) that the crystal becomes antiferromagnetic at around 150 K. Above this temperature we see ferromagnetic behavior, which extends well above room temperature (see inset). The susceptibility of a ferromagnet should behave as

$$\chi \sim \frac{1}{T - \theta},$$

where θ is a constant. Susceptibility is related to magnetization $\chi \sim M/H$. A plot of $1/M$ should thus be a linear function $(T - \theta)$, dropping to zero at $T = \theta$. A positive θ would indicate the presence of ferromagnetism. $\theta < 0$ would be a sign of antiferromagnetism.

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The antiferromagnetic transition is very sharp and is accompanied by a change in the lattice constants, although the unit cell volume remains constant. Such a distortion can be caused by Jahn-Teller modes Q_2 and Q_3, which preserve the volume of the octahedron.
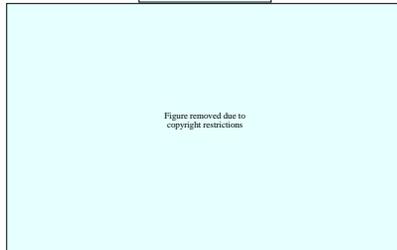
PRL 75 (1995) 4488

We thus have a simultaneus structural, magnetic, and electronic phase transition!

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$La_{1-x}Ca_xMnO_3$ magnetgic phase diagram

This material is a good ferromagnet and can be studied over a full doping range of $x = 0$ to 1. This is an intermediate bandwidth manganite.
the diagram is dominated by a metallic ferromagnetic phase at low temperature (double exchange) and a wide charge-ordered state, which appears to be orbital-ordered as well.
At low fields we get a ferromagnetic insulator (FI), a charge-ordered phase (CO), and a canted antiferromagnet (CAF) phase. The structure of the canted phase may actually consist of FM and AF phases.

Science 283 (1999) 2034

The large magnetoresistance effect occurs always at the boundaries of the metallic ferromagnetic phase

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Slide 21

$Pr_{1-x}Ca_xMnO_3$
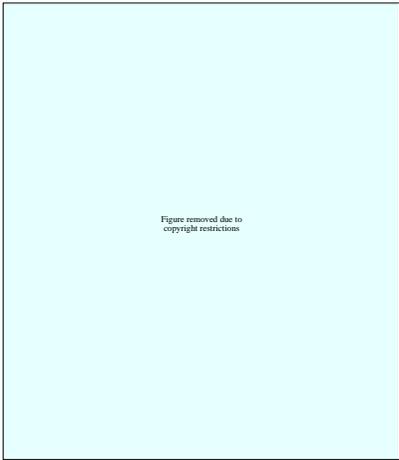
PI - paramagnetic insulator
FI - ferromagnetic insulator
AFI - antiferromagnetic insulator
COI - charge-ordered insulator
CAFI - canted antiferromagnetic insulator
This is a narrow bandwidth material. There is no stable ferromagnetic phase at low temperature. this lattice has a smaller tolerance factor and thus also a smaller hopping amplitude.
The structures of some of these phases are not well known, such as the FI, and the CAFI phases.

JAP 79 (1996) 5288

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Slide 22
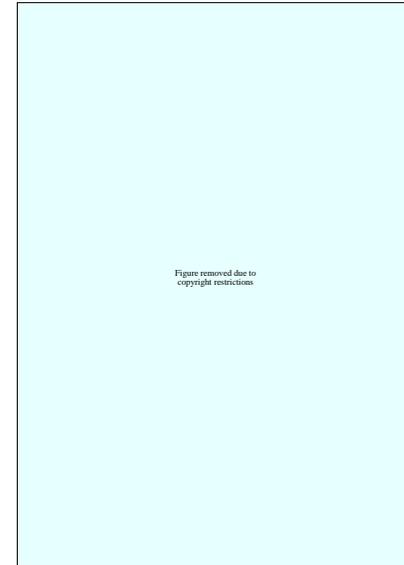
A metallic state can be created in $Pr_{1-x}Ca_xMnO_3$ if a strong external field is applied. At around 20 K the resistivity change is 10 orders of magnitude.

A similar effect is caused by apllying pressure.

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Slide 23
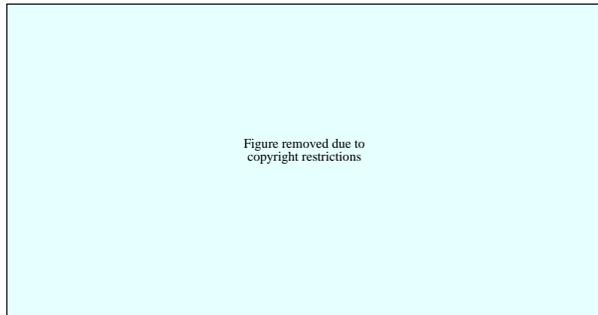
Rev. mod. Phys. 70 (1998) 1039

This plot shows how the ferromagnetic region changes with doping level and magnetic field. Significantly higher magnetic fields are needed to break the charge-ordered state close to the $x = 0.5$ doping level.

The T_C is affected by pressure, isotope substitutions, and chemical substitutions (Ca → Sr).

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Slide 24

$La_{1-x}Sr_xMnO_3$

This composition has one of the highest T_C values of up to 370 K and a representative of large bandwidth compounds. The phase diagram is dominated by a large metallic ferromagnetic region. note that above T_C there are actually two phases, one insulating, one metallic. The boundary is at around $x = 0.26$.
the antiferromagnetic state that appears xlose to $x = 0.5$ is actually ferromagnetic in-plane and antiferromagnetic in the out-of-plane direction.

Rao98 p.304
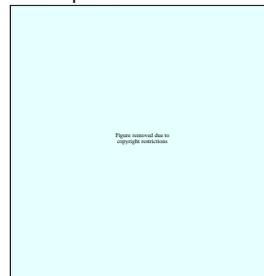
Resistivity in the $La_{1-x}Sr_xMnO_3$ system.

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Charge ordering in manganites appears to be governed by the width of the e_g band, which is determined by the average radius of the A-site cations (the tolerance factor). when r_A is large, like $La_{1-x}Sr_xMnO_3$, we get strong ferromagnetism and no CO phases. As the size drops, we first get a transition from FM to CO phase upon cooling, as in $Nd_{1/2}Sr_{1/2}MnO_3$. When r_A is very small, as in $Nd_{1/2}Ca_{1/2}MnO_3$, we get only CO and no FM phase at all.

Rao98 p.310

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One way of analyzing the magnetic structure of hole-doped systems is to consider phase separation.

This shows a transmission electron microscope image of $Nd_{1/2}Ca_{1/2}(Mn_{0.97}Cr_{0.03})O_3$ obtained from a charge-ordered lattice reflection. Bright parts are the CO phase, dark parts are the FM phase.

PRB 60 (1999) 9220

A diagram of what could happen is shown here. The black regions are the CO part. White parts are FM domains. In zero field all domains are randomly oriented. Even a small external field could orient the small domains, improving conductivity.

nature 399 (1999) 560

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Similar TEM images of $La_{5/8-y}Pr_yCa_{3/8}MnO_3$. in this case the charge-disordered ferromagnetic phase is dark. Figure (b) is showing only the CO state at low temperature. Above the ordering temperature, charge disordered domains start to appear (c).

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The shapes of nanoscale phase-separated domains are also important. A simple division of a sample into two regions is not realistic due to a huge Coulomb penalty. More realistic choices are dots or lines (stripes). The search for specific geometric ordering of domains is an active field of study.

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