Complex Ordering Phenomena in Multifunctional Oxides

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Complex ordering phenomena in multi-functional oxides

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(PhD advisor Alexander Shengelaya)

Joost de Groot (former member, PhD RWTH 2012)
Technical Approach

- Exploratory *synthesis* and crystal growth.

- **In-house characterization**
  (Diffraction, Macroscopic Properties).

- Discern detailed electronic ordering and excitations at remote *neutron/synchrotron* facilities.
Transition metal oxides

Substantial ionicity and correlation-effects provide a tendency towards localization of the electrons, which acquire "atomic-like" properties.

Electrons can hop between sites, providing interaction and facilitating charge ordering processes of degrees of freedom:

Valence e.g. $2^+/3^+$

Electrons delocalized
Transition metal oxides

Substantial ionicity and correlation-effects provide a tendency towards localization of the electrons, which acquire "atomic-like" properties.

Electrons can hop between sites, providing interaction and facilitating ordering processes of charge, orbital, spin, lattice subtle interplay.

Valence e.g. $2^+ / 3^+$

Shape of electron cloud

Magnetic moment

Scattering methods
Transition metal oxides

Substantial ionicity and correlation-effects provide a tendency towards localization of the electrons, which acquire „atomic-like“ properties.

Electrons can hop between sites, providing interaction and facilitating ordering processes of orbital spin lattice.

**Functionalities:**
- Magnetism
- Ferroelectricity
- Superconductivity
- Resistive switching
- Magnetoresistance...

**Applications:**
- Memory devices
- Signal switching
- Spintronics...
Transition metal oxides

Functionalities:
Magnetism, ferroelectricity,
Multiferroics

Magnetism: Spins

Ferroelectricity: Charge (Dipoles)

Multiferroicity: Spins and Dipoles

broken time-reversal

broken space-inversion
Multiferroics: Cross-coupling

Magnetism: **Spins**

Ferroelectricity: **Charge (Dipoles)**

**Multiferroicity: Spins and Dipoles**
MF for non-volatile memories

MRAM

Write: requires remagnetization – high currents
(slow, high power consumption)

Read with GMR

Magnetization
Write: requires remagnetization – high currents (slow, high power consumption)

Multiferroic

Read with GMR

Write with a Voltage

MF-RAM:

[M. Bibes and A. Barthélémy, Nat. Mater. 7, 425 (2008)]
Magnetism: **Spins**

Ferroelectricity: **Charge (Dipoles)**

Very small overlap!

Magnetism requires partially filled $d$-shell

Ferroelectricity (traditional mechanism) requires empty $d$-shell

Contra-indicated

[N.A. Hill (now Spaldin), *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B 104, 6694 (2000)]
Different routes to MF

independent subsystems

gen. weak electromagnetic coupling

Lone-pair FE

spin-spiral ferroelectricity

Mn → S N

P

(+ -) Dij, Js → q

Fe^{2+} Fe^{3+}

Charge-order-based

(symmetric) exchange striction
Ferroelectricity: Charge (Dipoles)

Any charge order breaking inversion-symmetry is polar.

- Can in principle lead to very large polarizations
- Spins are for free!
- same sites involved in charge and spin order
  → sizeable magnetoelectric coupling possible

Examples ????

LuFe$_2$O$_4$

CO Bilayers: charged rather than polar

Polarized Neutron Diffraction (220 K)

X-ray Magnetic Circular Dichroism

100 keV X-ray diffraction (300 K)

de Groot et al., PRL 108, 037206 (2012)
de Groot et al., PRL 108, 187601 (2012)
MF from charge order: LuFe$_2$O$_4$ is a non-example
LuFe$_2$O$_4$ is a non-example

Ferroelectricity from iron valence ordering in rare earth ferrites?
Manuel Angst
Tuning ferrites

Can a ferroelectric CO be stabilized?

*Graph showing the volume of the hexagonal cell (Å³) vs. $R^3+$ size (pm) with points for In, Lu, Yb, Er, Tm, Ho, Y, Lu, and RFe$_2$O$_4$.*

**Equations:**

- $R = Y$ (Supernova)
- $R = Yb$
- $R = Lu$ (for comparison)

**References:**

PSS RRL 7, 383 (2013)

+ layer intercalation...
Magnetite

Ancient "lodestone": oldest known magnetic material

Classical example of charge order [Verwey, Nature 144, 327 (1939)]: Verwey transition in Magnetite Fe$_3$O$_4$

Complex charge order only recently solved [Senn et al., Nature 418, 173 (2012)]: It is polar

Macroscopic indications of switching [Schrettle et al., PRB 83, 195109 (2011)]
Magnetite

Intensity modulation can be attributed to structural switching between inversion-twins:
Microscopic proof of ferroelectricity!

Intercalated intensity deviation (%)

Voltage (kV)

~12 K

(2,-2,-10)
8.5 keV

Integrated intensity deviation (%)
Different routes to MF

independent subsystems

gen. weak electromagnetic coupling

spin-spiral ferroelectricity

small polarization usually low T only

Lone-pair FE

Fe^{2+} Fe^{3+}

Charge-order-based

(symmetric) exchange striction
Hexafermites: high-\( T \) MF

Hexagonal ferrites: based on spinel-structure, but rich variation of structures by interspersing of "R-blocks" and "T-blocks"
Hexaferrites: high-$T$ MF

$\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$

$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ [Kimura et al., PRL 94, 137201 (2005)]

Block-Spin model
Hexaferrites: high-$T$ MF

Block-Spin model

$H=0$

Proposed structures, Yet to be solved!
Hexaferrites: high-\(T\) MF

Maps of circular dichroism (spin chirality)

10 K, Fe \(L_3\)

\(\pi\) in

\(\sigma\) in

\(\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}\)
Hexaferrites: high-$T$ MF

In addition, direct determination of magnetoelectric coupling in this compound is pursued by ESR/EPR/FMR techniques with electric-field modulation, at TSU.

Maps of circular dichroism (spin chirality)

→ See talk of Giorgi Khazaradze, FZJ & TSU
Parallel Session 9
(Thu afternoon, Aud. 401)

Proposed structures, Yet to be solved!

$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$
Conclusions / Outlook

Rare earth ferrites

• Contrary to expectation, LuFe$_2$O$_4$, is a non-example for CO-driven multiferroicity likely same for YbFe$_2$O$_4$

• What drives spin- & charge order (which does not minimize electron-electron repulsion)? → INS: TOF to be complemented by TAS, in progress

• Further explore ion-size effects, intercalation.

Other potential charge-order-driven multiferroics

• Magnetite is an example, as demonstrated on a microscopic level

• Further examples? (possibly including organics)

High-temperature multiferroic phases in hexaferrites

• „Classical“ Y-type hexaferrite has spin-structure compatible with „Dzyaloshinskii-Moriya“-driven ferroelectricity

• Fine-tune properties by substitutions and explore other hexaferrite structure types

• E.g. other spin-based mechanisms such as ferrotoroidicity are being studied

Other projects in multiferroicity research

Plenty of research opportunities ...
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