Magnetism and Nanoscale Electronic Properties in Transition Metal Oxides

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Cover: In these scanning tunneling microscope images of a copper oxide superconductor known as Na-CCOC, the topographical map (blue) shows the location of individual atoms on the cleaved surface. The differential conductance map (red) in the same field of view shows that the electronic states are arranged in checkerboard-like spatial patterns. As explained in the story on page 24, similar patterns have been found in other copper oxide superconductors. (Image courtesy of Séamus Davis at Cornell University and Hidenori Takagi at the University of Tokyo. Prepared by Curry Taylor.)
**Bloch's theorem** for electrons in periodic potential (crystals)

**Bloch's theorem**

Eigenfunction of a particle (electron) in a periodic potential is a product of a plane wave and a periodic Bloch function $u_{nk}(r)$ that has the same periodicity as the potential!!

$$\Psi_{nk}(r) = \varepsilon^{ikr} u_{nk}(r)$$

Symmetry of the lattice determines spatial variation of the electronic properties!!

Charge order in transition metal oxides

- **Spectacular properties**
  - High temperature superconductivity
  - Colossal magnetoresistance
  - Novel collective electronic excitations
  - Intimately coupled degrees of freedom
  - Complex phase diagrams
  - ...

- **Technical applications**
  - Problems due to intrinsic inhomogeneity
  - Self organized electronic nanostructures
  - ...

- **Challenge for solid state physics**
  - Theory: extremely complicated
  - Materials science
    (intrinsic versus extrinsic inhomogeneity)
  - Interpretation of data
  - New experimental techniques required
    (spatially res. spectroscopy, local probes)
  - ...

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STM on Bi2212 superconductors

half-doped manganites
CE-Phase,
van den Brink, PRL 1999
La$_2$CuO$_4$ is a 2d-antiferromagnet with $J/k_B \sim 1500$K. The magnetic susceptibility $\chi$ shows a peak at $T_N = 312$K. The resistivity is an insulator. The hybridisation $t$ and Coulomb repulsion $U$ play significant roles in its electronic properties.
Magnetism and Superconductivity: Cuprates

- antiferromagnetic insulator
- pseudo-gap
- conventional metal
- d-wave superconductor
- “strange” metal

Temperature vs. doping diagram.
Antiferromagnetism and Charge Mobility

Antiferromagnetism: reduced hole mobility
Hole motion: suppressed AFM

M. Hütcher et al., PRB’ 99,
M. Hütcher and B.B., PRB 06
Antiferromagnetism: reduced hole mobility
Hole motion: suppressed AFM

Cuprates with static stripes

La_{1.8-x}Eu_{0.2}Sr_xCuO_4

TN increases in metallic compounds
Antiferromagnetism and Charge Mobility

Cuprates with static stripes

La_{1.8-x}Eu_{0.2}Sr_xCuO_4

Resistivity (Ω cm)

Temperature (K)

T_N increases in metallic compounds

Striped model

Charge

Spin stripe

Charge

Charge

amag = 8 a
Antiferromagnetism and Charge Mobility

Stripe model

Charge

Spin stripe

Charge

Stripes: Compromise between hole motion and AFM?

$\Delta_{mag} = 8a$
Stripes in Cuprate Superconductors

Static Stripes in $(\text{La},\text{Nd})_{7/8}\text{Sr}_{1/8}\text{CuO}_4$

Stripes and/or neutron resonance

Tranquada et al. Nature 95

Emery et al.

Tranquada et al. Nature 04

Theory and further experiments:
Hayden et al.
Hinkov, Keimer et al.
Vojta et al.
Uhrig et al.
Seibold et al.
...
Charge order in transition metal oxides

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**Experiment** → Inhomogeneous charge and spin density

**Theory**

STM on Bi2212 superconductors
etc.

Competing interactions in doped magnets
→ Inhomogeneous charge and spin density

half-doped manganites
CE-Phase,
van den Brink, PRL 1999

J. Zaanen, Nature
Our 300mK - STM

Density of States (DOS)

- Nb-Tip on W(110) vs. Temperature
- Nb-Tip on W(110) @ 378 mK
„New“ 300mK - STM

Topography + DOS of LiFeAs

Local DOS maps

Hänke et al., PRL 2013
Resonant soft x-ray scattering

Scattering process

Intermediate state

- **Elastic process:**
  initial state=final state

- **Element specific:**
  different edges like
  O K-edge, TM L2,3-edge, RE M-edges

- **Sensitive to**
  charges, magnetism and orbitals

- **Polarization dependence:**
  Excitation of different intermediate states
O K edge in doped cuprates

Romberg, Fink et al., PRB '90

C.T. Chen et al., PRL '91
Striped order in $(\text{La}, \text{Eu})_{7/8}\text{Sr}_{1/8}\text{CuO}_4$

**Photon energy dependence**

Charge order in $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$ studied by resonant soft X-ray diffraction

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PRB (2009), PRB (2011)
Phase diagrams and stripe order in (La,Eu)$_{7/8}$Sr$_{1/8}$CuO$_4$

The wave vector of the charge correlations revealed in our experiments is in good agreement with the nesting vector of the antibonding Fermi surface sheets predicted by density functional calculations for the 123 system (34). The
“Perfect” nesting of electron- and hole-like Fermi pockets

Enhancement of instabilities

CDW and/or SDW order

Doping: “Off-tuning” of nesting

Suppression of SDW
Stripes or density waves

Long-Range Incommensurate Charge Fluctuations in (Y,Nd)Ba$_2$Cu$_3$O$_{6+x}$

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The wave vector of the charge correlations revealed in our experiments is in good agreement with the nesting vector of the antibonding Fermi surface sheets predicted by density functional calculations for the 123 system (34). The
Stripes or density waves

Rather than forming a coherent spin- and charge-modulated “striped” state, as in the 214 system [3,10–14], spin and charge order are strongly competing in YBCO$_{6+\delta}$. As a direct manifestation of this competition, we demonstrated that spinless Zn impurities substantially weaken CDW correlations in a YBCO$_{6.6}$ crystal, while at the same time nucleating incommensurate magnetic order. We further showed that an

Momentum-Dependent Charge Correlations in YBa$_2$Cu$_{3+\delta}$O$_{6+\delta}$ Superconductors Probed by Resonant X-Ray Scattering: Evidence for Three Competing Phases


PRL 2013
Incommensurate order of charge and spin

- wave vector $\epsilon$ of charge order equal to $2\delta$
- concentration dependence of $\epsilon$ is not compatible with nesting scenario

Neutron data:
Yamada et al. PRB 1998
Charge order in half doped manganites

Single layer manganite: $\text{La}_{1-x}\text{Sr}_x\text{MnO}_4$

$x = 1.5$: half-doped 50% $\text{Mn}^{3+}$ and 50% $\text{Mn}^{4+}$

CE type charge/orbital/spin order

see e.g. P. Reutler J. Cryst. Growth (2002)
ARPES on charge ordering manganites
CE type order: Nesting scenario

\( \text{Mn}^{3+} \quad \text{Mn}^{4+} \quad \text{spin} \)

**k space**

\( q_1 = \frac{a^*}{4} + \frac{b^*}{4} \)

**real space**

\( \lambda_1 = 2a + 2b \)
CE type order: Local picture

Double exchange in manganites
Orbital Polaron Ordering in Manganites

Double exchange in manganites

\[ \text{Mn}^{3+} \quad \text{e}_g \quad \text{t}_{2g} \quad \text{Mn}^{4+} \]

\[ \text{FM} \leftrightarrow \text{metallic properties} \]

hole doping: FM interactions (DE) +
destabilization of cooperative Jahn-Teller distortions
Metallic materials → tendency to ferromagnetism  

**but:**

- Magnetization
- Resistivity

**La$_{7/8}$Sr$_{1/8}$MnO$_3$**

**low temperatures:**

coexistence of ferromagnetism and insulating behavior
Phase Diagram of La$_{1-x}$Sr$_x$MnO$_3$

AFM insulating → FM metallic

FMM orthorhombic O
orthorhombic O'
triclinic triclinic

FMI FMM

canted AFI

Temperature [K]

Strontium doping $x$

FMI phase: contradicts DE model

$\rightarrow$ Orbital degrees of freedom?

Uhlenbruck et al., PRL 98
T. Niemoeller et al. EPJ B99
Klingeler et al., PRB 02
Geck et al., PRB 01
Geck et al., PRB 04
Geck et al. PRL 05
Geck et al. NJP 06
Resonant X-Ray Scattering on La$_{7/8}$Sr$_{1/8}$MnO$_3$

- Resonance at the Mn K-edge
- $\sigma\pi$-scattering
- $I \sim \sin^2\psi$

Fluorescence

(300)

$\sigma\pi$

antiferro-orbital order
Orbital Polaron Lattice in \( \text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3 \)
La$_{1-x}$Sr$_x$CoO$_3$: Rich diversity of electronic phases

Phase diagram of La$_{1-x}$Sr$_x$CoO$_3$

Co$^{3+}$ (3d$^6$)

Co$^{4+}$ (3d$^5$)

La$_{1-x}$Sr$_x$CoO$_3$: Rich diversity of electronic phases

Huge magnetic response at low T at a tiny Sr doping

La$_{1-x}$Sr$_x$CoO$_3$

$M = 15\mu_B$ per doped hole

Cannot be due to individual Co$^{3+/4+}$ in any spin state
ESR: “Easy case”: isolated spin ½ systems

Radical centers, weakly interacting half-integer spin species etc.
(chemistry, biology, semiconductor physics)

No restriction on minimal ESR frequency and field
“Difficult case”: Correlated spin systems

- Quantum spin magnets on the basis of complex oxides
  - molecular magnets
- unconventional superconductors,
  - heavy fermion and Kondo metals

→ High-Field ESR (IFW: 18T) at high frequencies (IFW: 1.2 THz)
ESR on LCO+0.2% Sr at Low T: Spin Clusters

T = 4K

Peak 1

Peak 2

Peak 3

Peak 4

Peak 5

Peak 6

Peak 7

26.9GHz

50GHz

74GHz

136GHz

155GHz

175GHz

210GHz

237GHz

265.5GHz

285GHz

380GHz

455GHz

552GHz

Attenuation (arb.u.)

B (T)
LCO+0.2% Sr: High Field ESR

Multiple gapped excitations with large $g$-factors

Big spin multiplicity
Substantial spin-orbit coupling

Response of a big spin cluster!
Molecular Magnets: “One-Molecule Spin Cluster”

Sample: B. Kersting et al. U Leipzig

![Diagram of molecular magnet structure with Ni, N, S, and bridges]

- **ESR intensity (arb. u.)**
- **Field (T)**
- **5 K**, **10 K**, **20 K**, **30 K**, **80 K**, **100 K**, **130 K**

- **DPPH marker**

**Experiment**

- **ν = 360 GHz**

- **ν = 72 Hz**

- **T_B ~ 160 mK**

- **χ_{AC} (arb. u.)**

- Temperature (K)

- Field (T)
**Ni(II)4-complex with bistable ground state**

ESR: Energy structure of the $S = 4$ multiplet resolved

$g = 2.17; D = -\Delta/7 = -0.27$ K

Negative anisotropy $D \Rightarrow$ bistable $S^z = \pm 4$

Ground state!
**Hole-induced spin state polaron due to double exchange**

The hole dynamically distributed over the cluster

Resonant state due to double exchange

Model: Energy spectrum of the spin states

\[ H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \]

\[
S = 1 \times 6 + \frac{1}{2} = \frac{13}{2}
\]

\[
g = 2.6
\]

\[
D = 101 \text{ GHz}
\]

\[
T = 4 \text{ K}
\]

\[
\theta = 50^\circ
\]
Model: Energy spectrum of the spin states

\[ H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \]

\( S = \frac{13}{2} \)
\( g = 2.6 \)
\( D = 101 \text{ GHz} \)
\( T = 4 \text{ K} \)
\( \theta = 100^\circ \)

S = 13/2
\( B \)
\( \theta = 110^\circ \)
cubic
\( \theta = 55^\circ \)
\( [001] \)
\( \theta = 0^\circ \)

\( \mathbf{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \)
Model: Energy spectrum of the spin states

Inelastic neutron scattering in magnetic field
ESR on lightly doped LaCoO$_3$: Conclusions

- Small Sr/Ca doping of LaCoO$_3$ yields extraordinary large magnetic moments
- Spectroscopic investigations evidence the occurrence of big spin clusters
- Spectrum of the spin states well understood
- Hole doping and not structural distortion is essential
- Nucleation of a spin state polaron (septamer !)
- Doping yields intrinsic magnetic inhomogeneities in LaCoO$_3$
- Spin polaron is a building block of SG and FM phases
**Orbital Polarons**

**Manganites and Cobaltates:**
- Partial delocalization of a doped hole by changing the adjacent orbital states
- Ferromagnetic nanoclusters due to (local) double exchange interaction

**Cobaltates**
- Change of spin state (IS instead of LS)
- Isolated clusters in a non-magnetic background

**Manganites**
- Orientation of orbitals changes (spin state always HS)
- Polarons coupled to AFM background → complicated magnetic state
Nanoscale Electronic Order in Transition Metal Oxides

i. Spin and Charge Stripes in two-dimensional CuO planes
   - Observing charge order by resonant soft X-ray scattering
   - Charge and spin stripes due to mobile holes in afm background
   - Stripes due to local spins and/or CDW due to nesting?

ii. Charge and Orbital Polaron Ordering in Manganites
   - CE type order: Local double exchange and/or nesting instability?
   - Ferromagnetic insulating phase due to orbital polaron

iii. Spin State Polaron in lightly doped Cobaltates
   - Doped holes in non-magnetic cobaltates
   - Ferromagnetic nanoclusters due to spin state polarons
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