NEUTRON SCATTERING AS A PROBE OF THE MAGNETIC, STRUCTURAL, AND SPIN DYNAMICAL PROPERTIES OF COLOSSAL MAGNETORESISTIVE MANGANITES

Joel Helton
Department of Physics, US Naval Academy

NCNR Summer School
“Methods and Applications of Neutron Spectroscopy”
June 9, 2015
Colossal Magnetoresistance

\[ \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \] and related materials

Phase transition between a ferromagnetic metal and a paramagnetic insulator

Applied magnetic field changes resistivity by orders of magnitude

Technological applications in commercial magnetic field sensors: hard drive read heads, etc.

La$_{1-x}$Ca$_x$MnO$_3$

- Perovskite structure
- Pseudo-cubic, $a = 3.88$ Å
- $x = 0.3$

- Average Mn oxidation:
  \[(3+x)^+\]

\[
\begin{align*}
\text{Mn}^{3+} & \quad \text{Mn}^{4+} \\
\uparrow & \quad \uparrow \\
\text{e}_g & \quad \text{t}_{2g} \\
\end{align*}
\]
Coupling between lattice, charge, and magnetic degrees of freedom

- charge ↔ magnetism
  - Zener double exchange

- Hund’s Rules
  - All electrons on a site will have aligned magnetic moments
  - $S=2$ (Mn$^{3+}$) or $S=3/2$ (Mn$^{4+}$)
  - An $e_g$ conduction electron can hop between neighboring Mn sites only if they are ferromagnetically aligned

- Zener double exchange alone can not explain the magnitude of the CMR effect
  - Millis et al., *PRL* 74, 5144 (1995)
Coupling between lattice, charge, and magnetic degrees of freedom

- Zener double exchange alone can not explain the magnitude of the CMR effect
- Electron-Phonon interaction
- Large-scale phase coexistence

- charge ↔ lattice
  - \( \text{Mn}^{3+} \) is Jahn-Teller distorting

**Polaron:** local distortion traveling with conduction electron

Coupling between lattice, charge, and magnetic degrees of freedom

Phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

- Complex phase diagram driven
- Ideal for neutron scattering!
  - Structural (nuclear)
  - Magnetic
  - Static
  - Elastic Scattering / Diffraction
- Dynamic
  - Inelastic Scattering / Spectroscopy
  - Well defined excitations as well as short-range correlations
Neutron Diffraction – Bragg’s Law

- Constructive interference when $2d \sin \theta = n\lambda$

$$\lambda = \frac{h}{p}$$

- "Where atoms are"
Ferromagnetic Order \((T < T_c)\)

Neutrons have a magnetic moment

- Sensitive to ordered magnetic moments
- Ferromagnetic order
  - Magnetic peaks on top of nuclear peaks

Ordered moment as a function of temperature

Static Polaron Correlations ($T > T_c$)

Peak at ($\frac{1}{4} \frac{1}{4} 0$) positions

- Charge ($\text{Mn}^{3+}$ vs. $\text{Mn}^{4+}$) and orbital order increases the unit cell by a factor of 4x4

- Temperature and field dependence


Polaron Peaks


Polaron melting drives CMR?

C.P. Adams, et al., *JAP* 89 6846 (2001)
Neutron Spectroscopy

- Analyze the neutron incoming and outgoing energies

\[
\text{Intensity} \propto S^{\alpha\beta}(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \int dt \, e^{-i\omega t} \frac{1}{N} \sum_{\bar{R}\bar{R}'} e^{i\vec{Q} \cdot (\bar{R} - \bar{R}')} \langle S^\alpha_{\bar{R}}(t) S^\beta_{\bar{R}'}(0) \rangle
\]
Spin Waves ($T < T_c$)

- Spin wave dispersion
  - Well defined excitations
  - $\omega$ varies with $q$
  - Gives information about exchange constants

$$\hat{H} = -\sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

- Spin wave energy softens near zone boundary
  - 4th nearest neighbor exchange need to model dispersion

- $10 \leq \hbar \omega \leq 12$ meV
- $21 \leq \hbar \omega \leq 24$ meV

Zhang, et al., JPCM 19 315204 (2007)

- $J$ is very isotropic
Spin Waves ($T < T_c$)

- Anomalous spin wave behavior


Spin wave stiffness vs. temperature

- Spin wave stiffness coefficient
  - Renormalizes at higher temperatures
  - But does not collapse at $T_c$ like most ferromagnets

Spin wave broadening at higher energies near zone boundary
Dynamic Polaron Correlations \((T > T_c)\)

- Broad features in neutron scattering experiments reveal short-range correlations

- Static and dynamic polarons observed from \(T_c\) up to 400 K
- Only dynamic polarons at higher temperatures

Paramagnetic correlations @ 265 K (1.03 $T_c$)

ARCS data
$T = 265$ K
$3 \text{ meV} \leq \hbar \omega \leq 5 \text{ meV}$

- Two components to the paramagnetic scattering
  - Rings surrounding Bragg positions
  - Ridges along (H 0 0) connecting the rings

Paramagnetic ridges

\[ h\omega = 2 \text{ meV} \]

Temperature (K)

Ridge Intensity

\[ T_c = 257 \text{ K} \]

Quasielastic magnetic scattering

La_{0.7}Ca_{0.3}\text{MnO}_3

\[ T_c = 257 \text{ K} \]

Broad temperature and magnetic field dependence

Ridge Intensity

\[ |E| \text{ (meV)} \]

S(Q,E) (arbitrary units)

\[ \mu_0H(T) \]

0 2 4 6 8 10 12

0 300 600 900 1200 1500 1800

0 0.03 0.06 0.09 0.12 0.15
• Paramagnetic ridges are consistent with short-range ferromagnetic correlations dependent on number of nearest-neighbor ‘hops’ connecting two Mn ions

\[ \langle S_i S_j \rangle \propto e^{-\frac{n}{\xi}} \quad \xi = 0.7 \text{ hops} \]

• Magnetic part of diffuse polarons
  • Conduction electron becomes self-trapped after small number of hops

J.S. Helton, et al., PRB 90 214411 (2014)
Conclusions

- The colossal magnetoresistance in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and other materials stems in part from coupling between charge, magnetic, and lattice degrees of freedom
  - Ideal for study with neutron spectroscopy
- Below $T_c$
  - Long range ferromagnetic order with well-defined spin waves
  - Spin waves anomalously broaden and soften near zone edge
- Above $T_c$
  - Short range polaron correlations
    - Static and dynamic polarons at ($\frac{1}{4} \frac{1}{4} 0$) positions
  - Magnetic ridges
    - Magnetic correlations – diffuse part of magnetic polarons
- Phase competition and coexistence at this transition may drive magnitude of the CMR effect