Magnetism in LaCoO$_3$
Bulk- and Nano-particles
David P. Belanger
Department of Physics
University of California, Santa Cruz

- Bulk system has been studied since the 1950's and yet it is not well understood.
- Nanoparticles of this system have significant practical importance, but the effect of reducing to nanometer sizes is poorly understood.
- Nanoscale particles can be used to probe the physics.
Main Collaborators and Acknowledgments outside ORNL

- Alice Durand – UCSC
- Nalini Sundaram – UCSC
- Ingrid Anderson – UCSC
- Andrew Elvin – UCSC (undergrad)
- Meghana Bhat – UCSC, Castilleja School, Palo Alto, CA
- Yu Jiang – UCSC
- Frank (Bud) Bridges – UCSC
- Corwin Booth – Lawrence Berkeley National Lab
- Thomas Proffen – LANL, now ORNL
- Shaowei Chen – UCSC
Main Collaborators and Acknowledgments from ORNL

- Feng Ye
- Jaime Fernandez-Baca
- Jane Howe
- Clarina de la Cruz
- Ashfia Huq
- Songxue Chi
- Andrey Podlesnyak
- Kai Xiao
- Tao Hong
- Andrew Payzant
Magnetic Materials

- Magnetite (loadstone or lodestone) is naturally occurring magnetic material known since ancient times: Fe$_3$O$_4$
- Materials are magnetic when they have unpaired electrons that act like tiny magnets. These can align, making a macroscopic magnetic material.
- Modern magnetic materials are very strong and stable
- Iron is magnetic – it is attracted to magnets, but has no net magnetism when not in a magnetic field
- Iron forms domains to decrease its external field
- Steel is iron with impurities – it can stay magnetic
- Heating a material will cause it to lose its magnetism
Magnetic Domains in Iron Film

0.5 micron thick films etched with 35% acetic acid for 30 seconds. Magnetic field in the plane of the film in the second image. Favorably aligned domains grow, others shrink.
The temperature is a measure of the vibrations of the lattice, which tends to disrupt the ordering.

Above Tc, the up and down spins are about equal in number, so there is no net magnetization.

Below Tc, either up or down spin should dominate, creating a net magnetization that grows as the temperature decreases.

A magnetic field in most cases assists the ordering of the spins in the direction of the field.
Susceptibility of LaCoO$_3$ – motivation for the LS, IS and HS states in the localized spin picture

Two transitions are clearly visible, one near 90K and the other near 500K. For decades, the prevalent model included three spin states, LS for T<90K, IS For 90K<T<500K, and HS For T>500K. Korotin, et al. argued that the IS is a result of a Jahn-Teller distortion.

$e_g$ and $t_{2g}$ orbitals

nanoparticle growth

Nalini Sundaram, Alice Durand, Ingrid Anderson, Meghana Bhat
UCSC

\[ 0.75 \text{La(NO}_3\text{)}_3 \times 6\text{H}_2\text{O} + 0.25 \text{Sr(NO}_3\text{)}_2 + \text{Co(NO}_3\text{)}_2 \times 6\text{H}_2\text{O} + 6\text{H}_2\text{O} + 4.75\text{NaOH}^- \]

\[ \rightarrow 0.75 \text{La(OH)}_3 + 0.25 \text{Sr(OH)}_2 + \text{Co(OH)}_2 + 12\text{H}_2\text{O} + 4.75\text{NaNO}_3 \]

adding DTPA \[ \text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10} \]

\[ 0.75 \text{La(OH)}_3 + 0.25 \text{Sr(OH)}_2 + \text{Co(OH)}_2 + 0.95\text{H}_5\text{DTPA}^- \]

\[ \rightarrow \text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_x\text{DTPA}_{0.95} + (\text{excess})\text{DTPA} + 4.75\text{H}_2\text{O} \]

DTPA is removed by heating at 350°C for 4 hours. Nanoparticles are formed in a tube furnace for 8 hours at calcination temperatures from 620°C to 1100°C.
These particles were grown by Durand and Bhat last summer. Note that the particles can be nearly isolated or they can be imbedded. The very act of choosing particles to look at can distort the actual average particle property observations.
A single crystal grain with facets.
A large area of a single crystal grain.
A closeup showing the particle edge.
High Flux Isotope Reactor – Oak Ridge National Laboratory
HB-1A triple axis spectrometer at HFIR Oak Ridge National Laboratory
Spallation Neutron Source – Oak Ridge National Laboratory

Average particle size ~19nm for this sample, but with a fairly wide range.
Figure 1: Cut-away overview of the NOMAD beam layout. A person standing on the top of the shielding gives an idea of the scale. The distance from the moderator inside the target monolith to the sample position is 19.5 m.
NOMAD in real life
Average structure of the nanoparticle powders
La$_{1-x}$Sr$_x$CoO$_3$

Co-O-Co angle vs. lattice parameter $c$.
Conclusions

- LCO bulk particles are just barely ferromagnetic at $T = 90K$ – very small fields (200Oe) destroy the ferromagnetism, which is very unusual. Usually, a magnetic field enhances ferromagnetism.

- At high fields moments disappear for bulk particles, but not for nanoparticles.

- Our model is that in very small fields, the system orders, but forms domains to minimize the external fields.

- When a field is applied, the moments in the bulk particle domains pointing along the field are happy, but the others are no longer stable and disappear – that destroys the ferromagnetic order.

- The nanoparticle surfaces act like domain walls. The magnetism within the particles easily aligns with the magnetic field. The field does not destroy the ferromagnetism in nanoparticles because all moments can align with the field easily and the moments are more stable.
Thank you!

Early work supported by the DOE
Work for past two years supported by the ORNL Summer Visitor’s Program