Cobalt: More than Just Two Steps from Manganese

Scientific Achievement

Building on a strong effort in CMR manganites, we have launched a new multidisciplinary program to study oxides of Co. The primary driver for such studies is the observation that Co^{3+} can take multiple (S=0,1,2) spin states and that the spin-lattice coupling should be different among these states. We are pursuing several different systems in this new program to map out the variety of properties unique to these materials:

- Geometrically frustrated, mixed-valent ($Co^{2+/3+}$) cobaltites $RBaCo4O_7$ have been synthesized with R=Yb,Y,Lu, and Tm. In the case of Yb, a structural phase transition breaks the geometric frustration and allows a long-range antiferromagnetic (AFM) state to develop. We have shown conclusively that the driving force for this phase transition is a rearrangement of oxide ions to satisfy a drastically underbonded Ba^{2+} ion. No evidence of charge order has been found.
- We have grownt single crystals of $La_{1-x}Sr_xCoO_3$ across the insulator-metal transition at x=0.18. Studies using small angle neutron scattering (SANS) show that this transition derives from the growth of ferromagnetic metallic droplets that eventually percolate. Inelastic neutron scattering on $LaCoO_3$ reveals coexistence of dynamic AFM and ferromagnetic (FM) correlations. Such coexistence agrees with a dynamic orbital ordered state arising from a Jahn-Teller active S=1 state. This dynamic orbital order is akin to the static ordered state found in $LaMnO_3$.

Significance

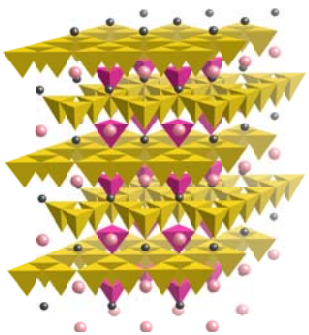
$RBaCo_4O_7$ is a new class of geometrically frustrated materials that are structurally similar to pyrochlores but present an alternative stacking topology. They thus open a new window on magnetism in these geometrically frustrated lattices. The present work (J. Solid State Chem, in press) shows that the for R=Yb^{3+} the lattice is unstable to a frustration-breaking symmetry change. Future activities are to tailor these materials chemically to prevent this phase transition from occurring, thus encouraging a magnetically frustrated state.

$LaCoO_3$ is the canonical example for which the thermally-activated population of either S=1 or S=2 states has been posited. However, the lack of a long-range structural distortion has cast doubt on the presence of the S=1, Jahn-Teller active state. The present work (D. Phelan et al, PRL **96**, 027201 (2006)) has shown that both AFM and FM interactions coexist and change with temperature. Magnetic exchange rules imply that S=0 and S=2 ions pair up antiferromagnetically. Thus, our results imply the presence of an S=1 ion. More significantly, they posit the existence of dynamic, orbitally-ordered regions formed from these S=1 ions.

Performers

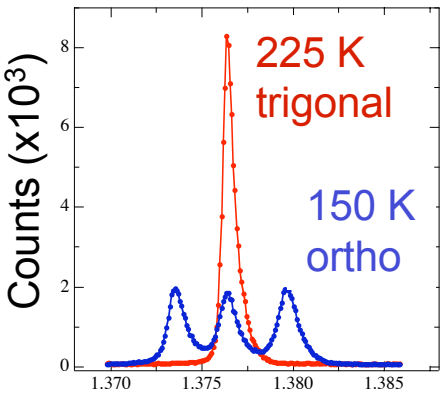
J.F. Mitchell, H. Zheng, S. Rosenkranz, R. Osborn (ANL-MSD); A. Huq (IPNS-ANL); L. Chapon, P.G. Radaelli (ISIS Facility, Rutherford Laboratory); P. Stephens (SUNY Stonybrook); J. Wu, C. Leighton (Univ. Minnesota)

Cobalt: More than Just Two Steps from Manganese

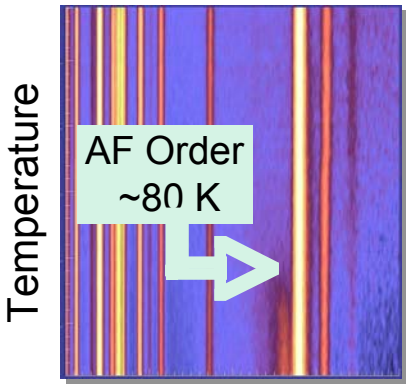


$YbBaCo_4O_7$

- Geometric frustration ~ pyrochlore
- Possible Co^{2+}/Co^{3+} charge order
- Extension of oxide physics to tetrahedra



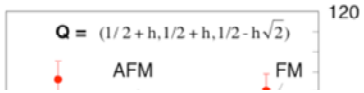
d-spacing



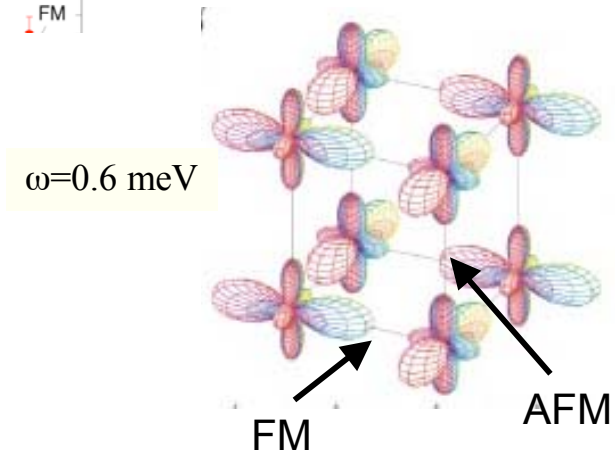
d-spacing

175 K phase transition breaks geometric frustration; yields AFM state

$La_{1-x}Sr_xCoO_3$ single crystals:



- Co spin states
- Dynamic orbital order
- Short-range magnetic order



Inelastic neutron scattering: S=1 state on Co^{3+} with dynamic orbital order

J.F. Mitchell, H. Zheng, S. Rosenkranz, R. Osborn

Materials Science Division
ARGONNE NATIONAL LABORATORY

A. Huq (IPNS); L. Chapon, P.G. Radaelli (ISIS); P. Stephens (SUNY); C. Leighton (Minnesota)