Spin-state transitions and two-phase competition in perovskite Cobaltites

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Outline

- The nature of spin state transitions in the parent compound with a non-magnetic and insulating ground state.
  - The importance of A ion in the stability of the low-spin state
- The evolution to a magnetic and conducting state and spin transitions.
  - The importance of the B ion in stabilizing the excited spin state.
- Evidence provided for the coexistence of a commensurate and an incommensurate magnetic phase below the magnetic transition with charge doping. Ca? Sr? Ba?
- Evidence provided for the induction of Jahn-Teller distortions above the transition with charge doping. Ca? Sr? Ba?
- Summary

People involved in this work:

At UVa

Danny Phelan – PhD student

Juan Yu – PhD student

Kazuya Kamazawa – powder characterization

S.-H. Lee – on the single crystal work

At NIST

Y. Qiu and J. Copley – inelastic powder measurements

At ANL

S. Rosenkranz – on the single crystal work

J. F. Mitchell – Sr single crystals

At LANL

Mike Hundley – characterization

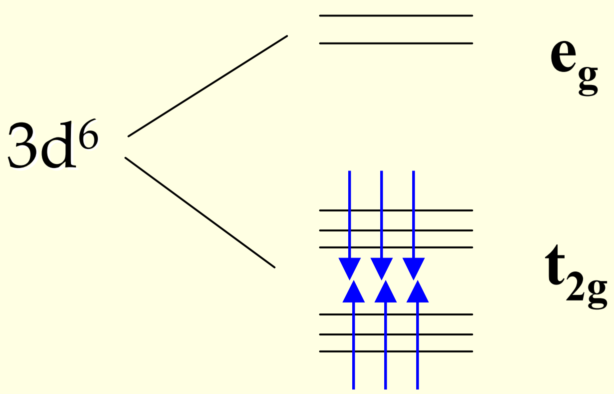
J. L. Sarrao – Sr powders

At Tohoku U.

K. Yamada – on Ba and Ca single crystal growth

Spin-state transitions

The ground state in LaCoO$_3$ is not magnetic

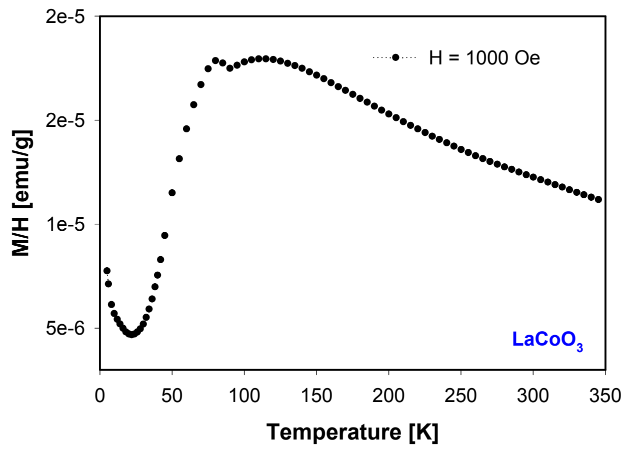


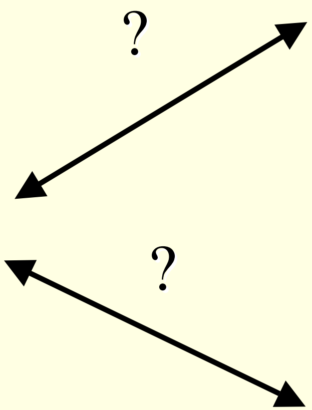
Octahedral field splitting

Co^{3+} - $3d^6$

Total spin, S = 0

Paramagnetic transition





S=0

Low spin

$t_{2g}^{6}e_{g}^{0}$

S=1

Intermediate

$t_{2g}^{5}e_{g}^{1}$

Jahn-Teller active

S=2

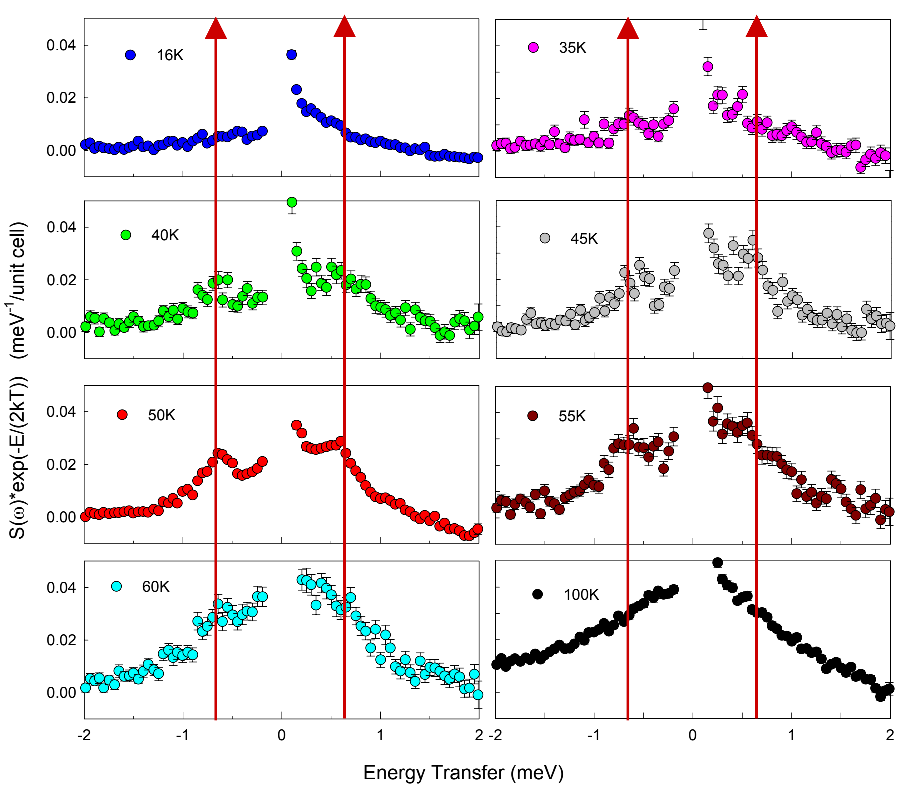
High Spin

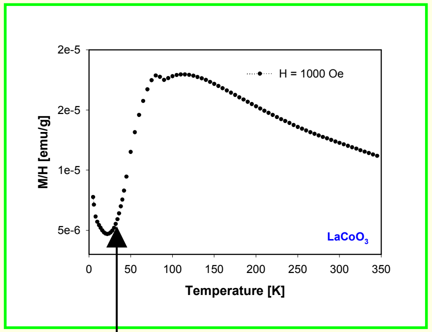
$t_{2g}^{4}e_{g}^{2}$

Proposed early on by Goodenough

Magnetic component: 3 important contributions

1) Inelastic low energy excitations



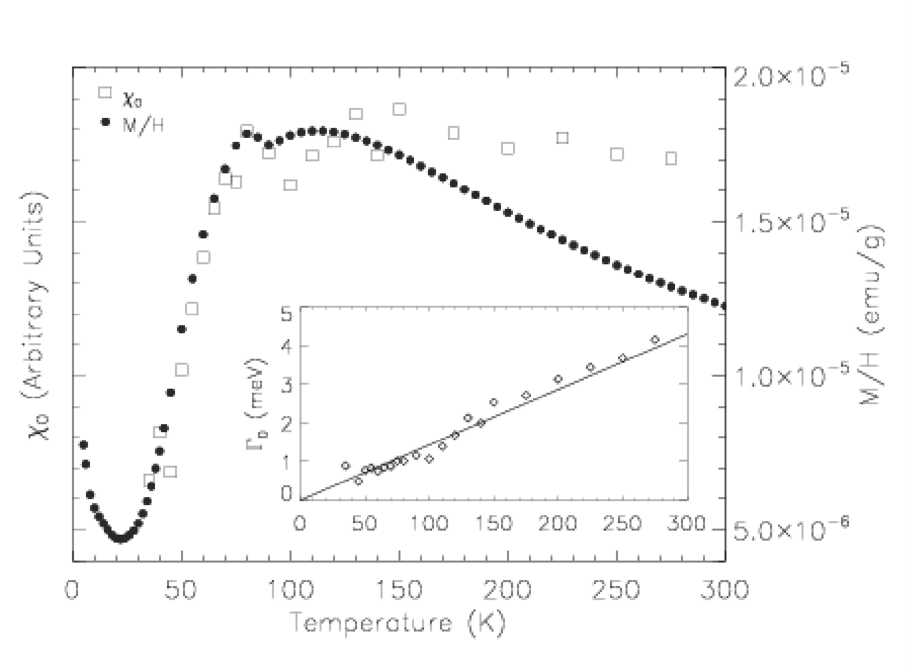


Upturn marks the onset of excitations

- Low energy magnetic excitation present. $E_{char} \sim 0.6$ meV. Single ion effect
- It is superimposed on the quasi-elastic signal corresponding to the paramagnetic state. Together, the 0.6 meV and inelastic signal are thermally enhanced.

Inelastic intensity follows χ_{bulk}

$$\chi''(\hbar\omega) = \frac{\chi_0 \Gamma_0 \omega}{\omega^2 + \Gamma_0^2} + \frac{\chi_1 \Gamma_1 |\omega \pm \omega_0|}{(\omega \pm \omega_0)^2 + \Gamma_1^2}$$



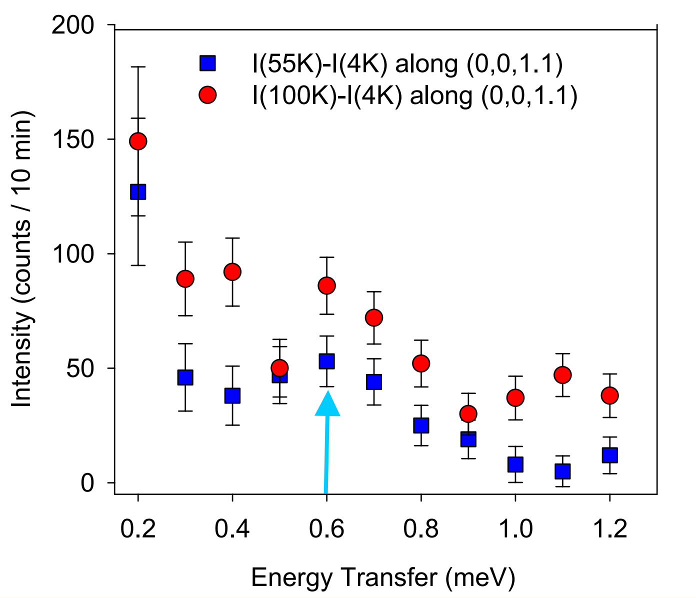
The first term (inelastic continuum intensity) contains χ_o, and is compared to the bulk susceptibility.

Origin of intensity is truly magnetic.

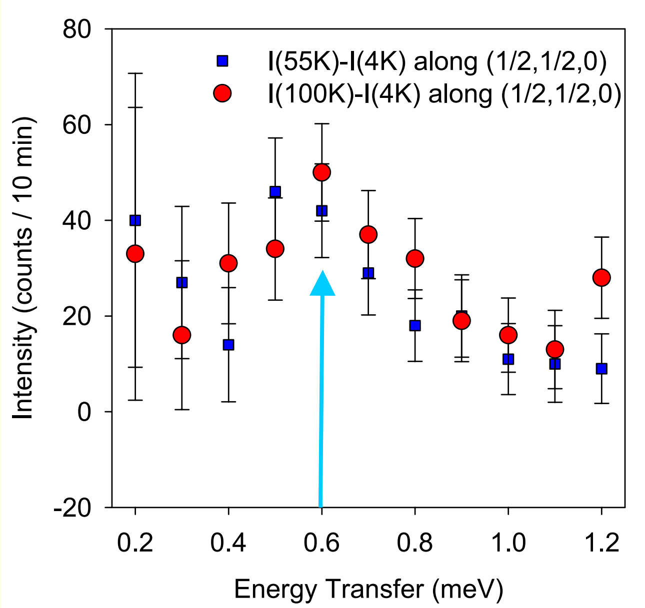
Phelan, et al., PRL **96**, 027201 (2006).

The other two components
Correlations between spins in the excited state

2) Ferromagnetic

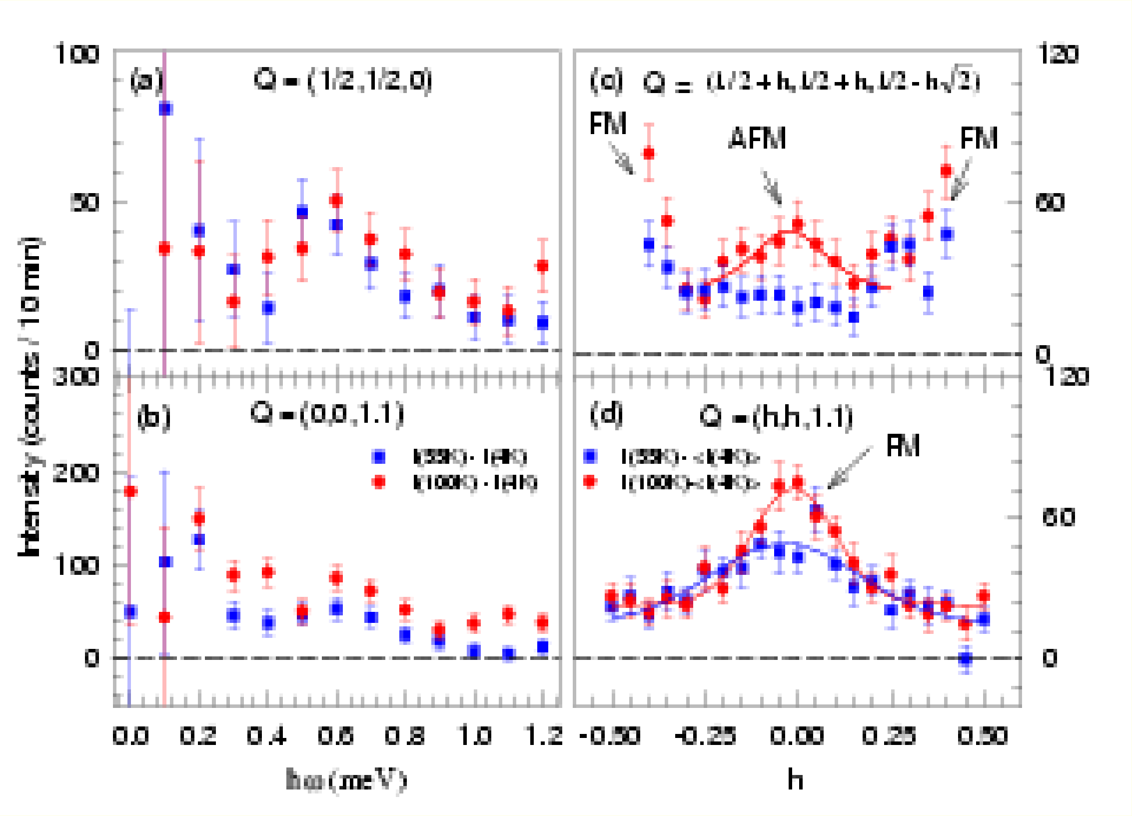


3) Antiferromagnetic!!!



- Constant Q scans at several points including (001), $\frac{1}{2}\frac{1}{2}0$ *and* $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
- The energy excitation is present even at 100 K (washed out in the powder measurement).
- Excitation present at ferromagnetic and anti-ferromagnetic points although it is stronger at (001). FM correlations were observed by Asai et al several years ago.

Strong ferromagnetism and weaker antiferromagnetism Correlations are DYNAMIC

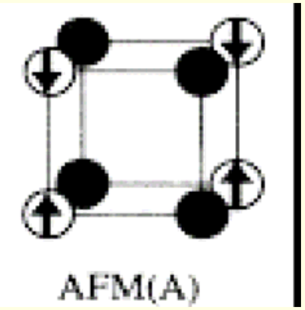


- A constant “background” is observed in both: this is a momentum transfer-independent component due to paramagnetic fluctuations
- The correlations between the ions become stronger with temperature.

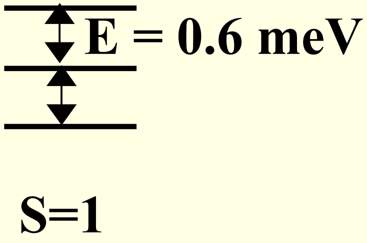
What does this mean for $LaCoO_3$?

Possible scenarios: S = 0 ground singlet splits to an S=1 or an S=2

- The FM and AFM correlations are dynamic and short ranged (characteristic $\xi = 3.6$ Å)



$LaMnO_3$

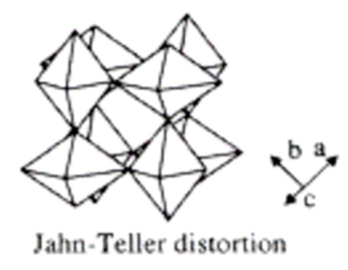


E = 0.6 meV

S=1

- Single ion transitions within the S=1 manifold
- Similar measurements by Podlesnyak et al were interpreted using the S=2.

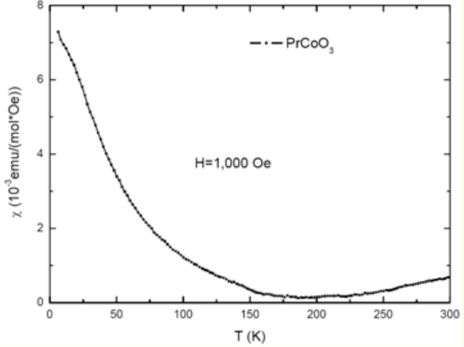
- Assumed that orbital ordering is short-range and dynamic just like the magnetic correlations



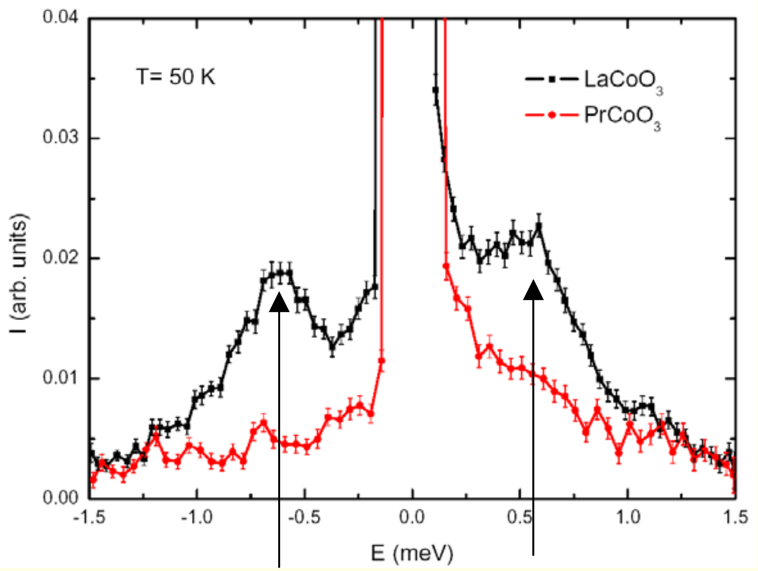
Jahn-Teller distortion

$LaMnO_3$

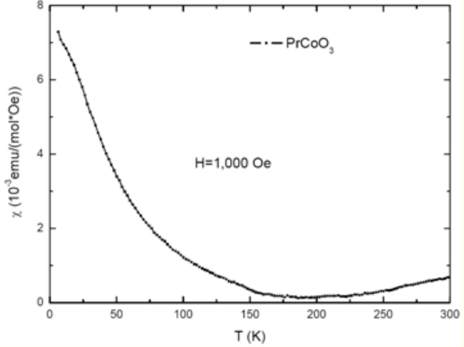
$PrCoO_3$: The critical role of oxygen



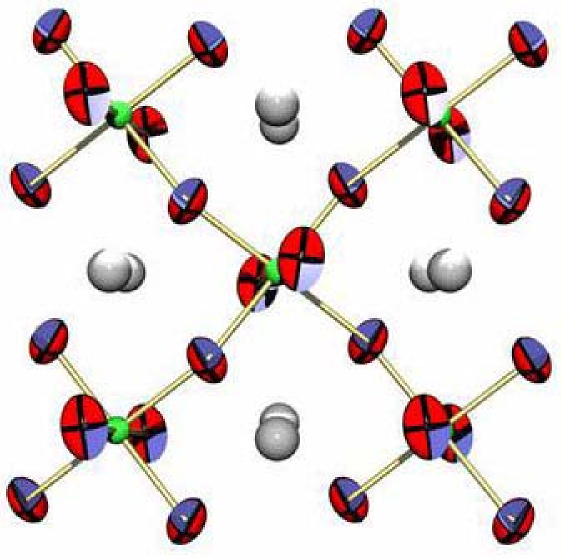
Similar measurements were performed by Goodenough's group



- The 0.6 meV excitation is absent up to 150 K!
- With Pr, the crystal symmetry changes to orthorhombic.
- Pr is a small ion that induces chemical pressure. Cooperative Oh rotations relieves the pressure. The difference in crystal field and Hund's exchange energy increases due to change in the band width.
- This might stabilize the LS state over a wider temperature range.



PrCoO$_3$: Co-O bondlengths are longer



Yan et al.

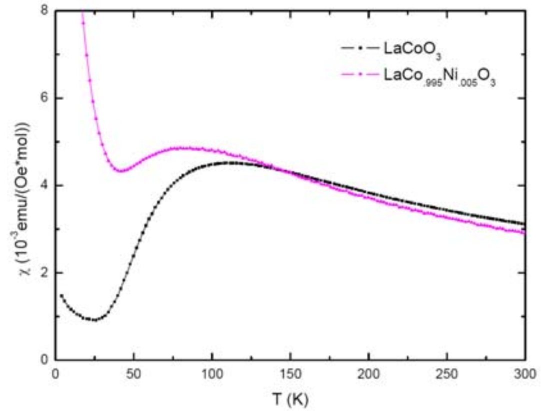
In the local structure, the Co-O bonds increase with Pr doping.

	LaCoO$_3$			PrCoO$_3$		
	Bond length (Å)	DW factor ($\times 10^{-3}$ Å^2)	R-factor	Bond length (Å)	DW factor ($\times 10^{-3}$ Å^2)	R-factor
6 model	6× 1.914(1)	4.1(2)	0.0040	6× 1.921(2)	3.5(4)	0.0056
2+4 model	2× 1.863(6) 4× 1.928(2)	4.5(8) 2.3(4)	0.0025	2× 1.886(8) 4× 1.942(4)	3.0(1.2) 2.7(6)	0.0048
Average	6× 1.906			6× 1.923		
XRD	6× 1.936(5)			6× 1.926(4)		

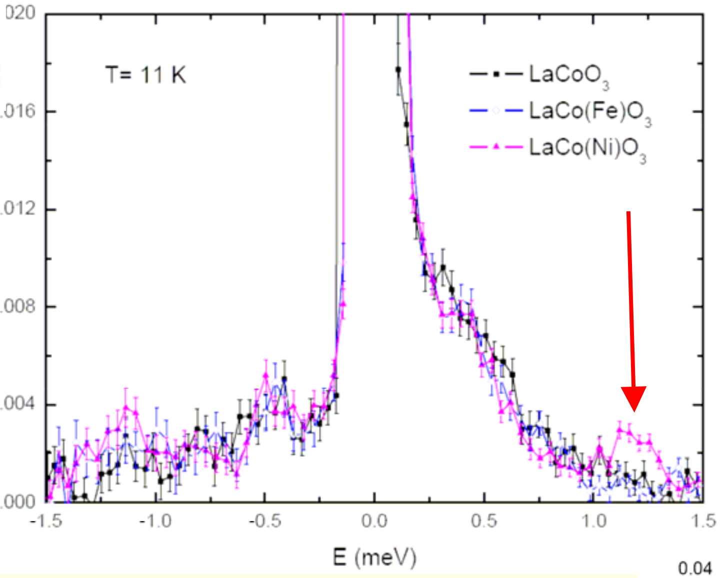
EXAFS by Pandey et al.

- Pr and oxygen hybridize more strongly than La and oxygen.
- This pulls the oxygen ions away from Co that in turn suppresses the IS state. (Yu and Louca, unpublished).

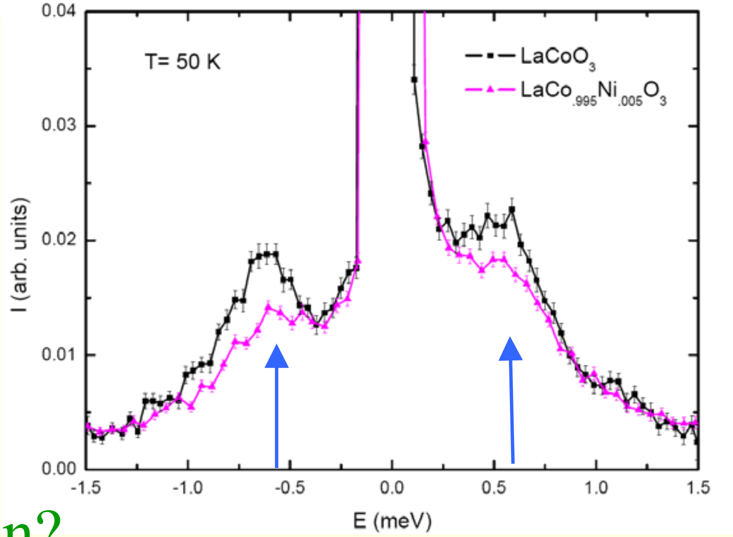
Two magnetic excitations in $La(Ni_{0.005}Co_{0.995}O_3)$



Similar transition as in $LaCoO_3$



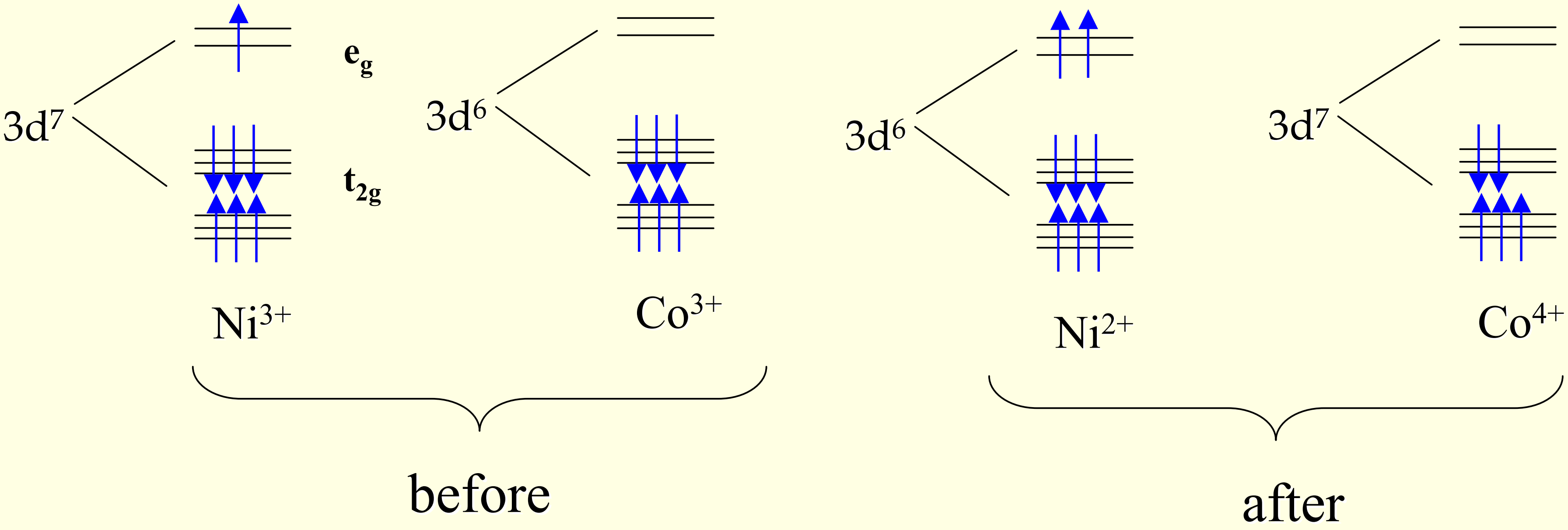
- ❖1.2 meV excitation is present only with Ni
- ❖It goes away by 35 K



At 35 K, the 0.6 meV begins to appear and shows a similar temperature dependence as in $LaCoO_3$.

Q: what is the origin of the 1.2 meV excitation?

In nickelates, charge disproportionation to Ni^{2+} and Ni^{4+} How about in Cobaltites?

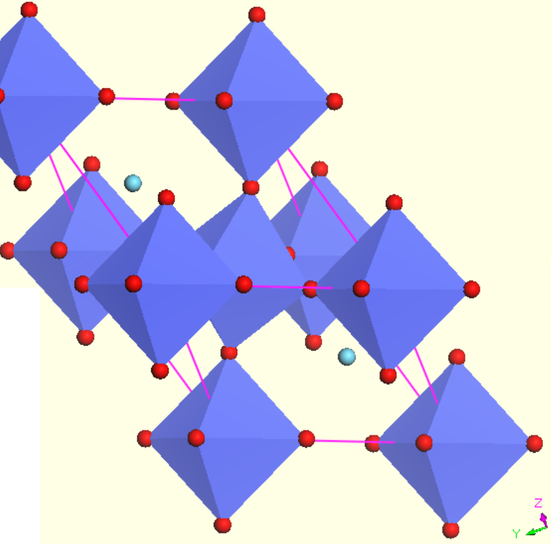


- No Jahn-Teller distortions observed in heavily doped Ni cobaltites
- Ni^{3+} might undergo a charge disproportionation to Ni^{2+} and Co^{4+} or Ni^{4+} and Co^{2+}. Could the 1.2 meV be the result of spin transitions between Ni^{3+} e_g spin and Co^{3+} empty e_g state??

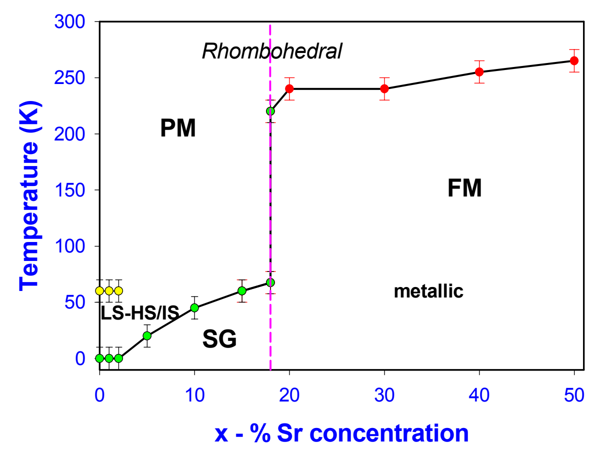
Magnetic phases

Addition of charge carriers

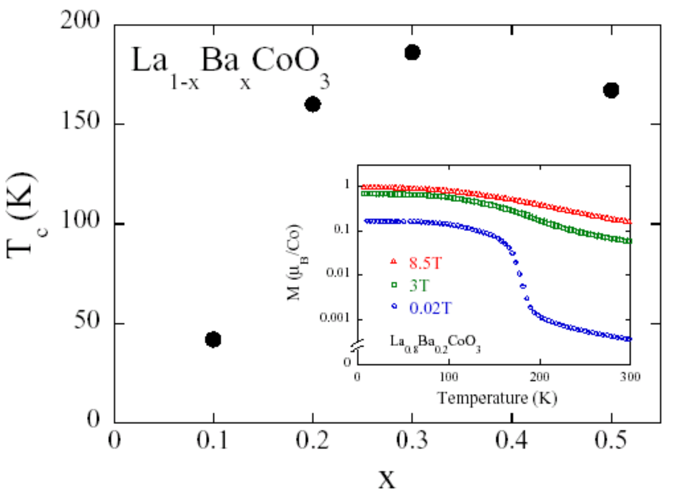
- A ferromagnetic metallic state is observed in Sr, Ba and Ca. In Sr and Ba, no symmetry change is observed.
- What happens with the spin state transitions?
- How do the orbital and lattice effects correlate with the magnetic properties?



Sr-case



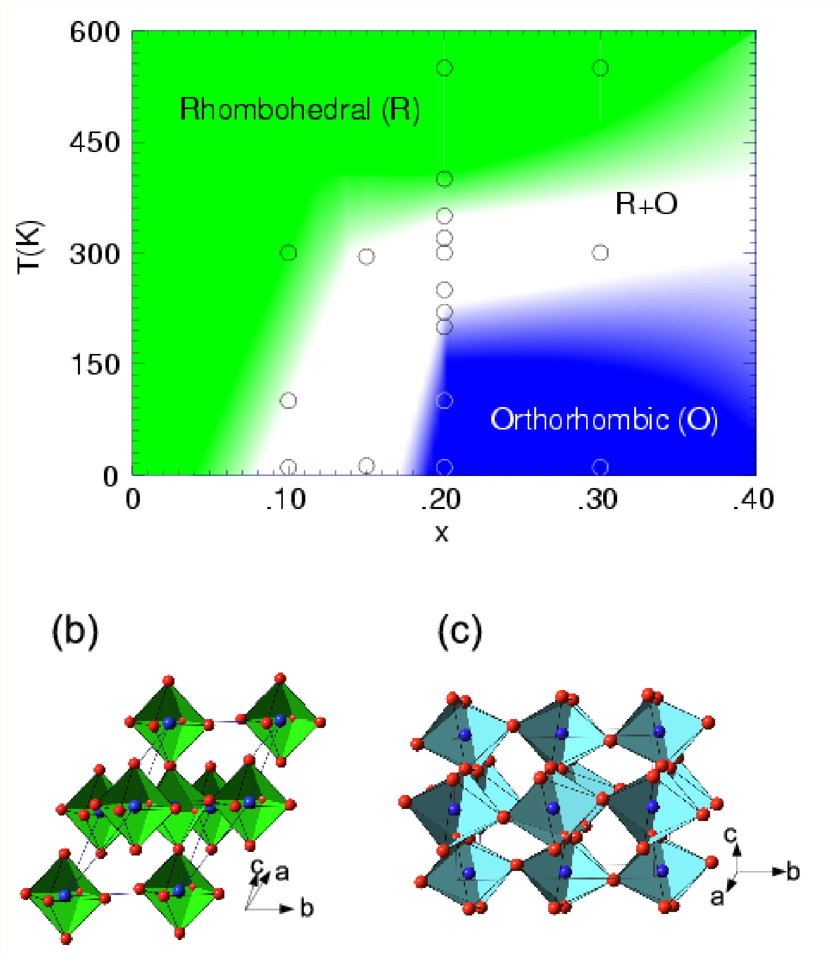
Ba-case



Louca et al., PRB **60**, R10378 (1999).

Phelan & Louca, PRB (2007)

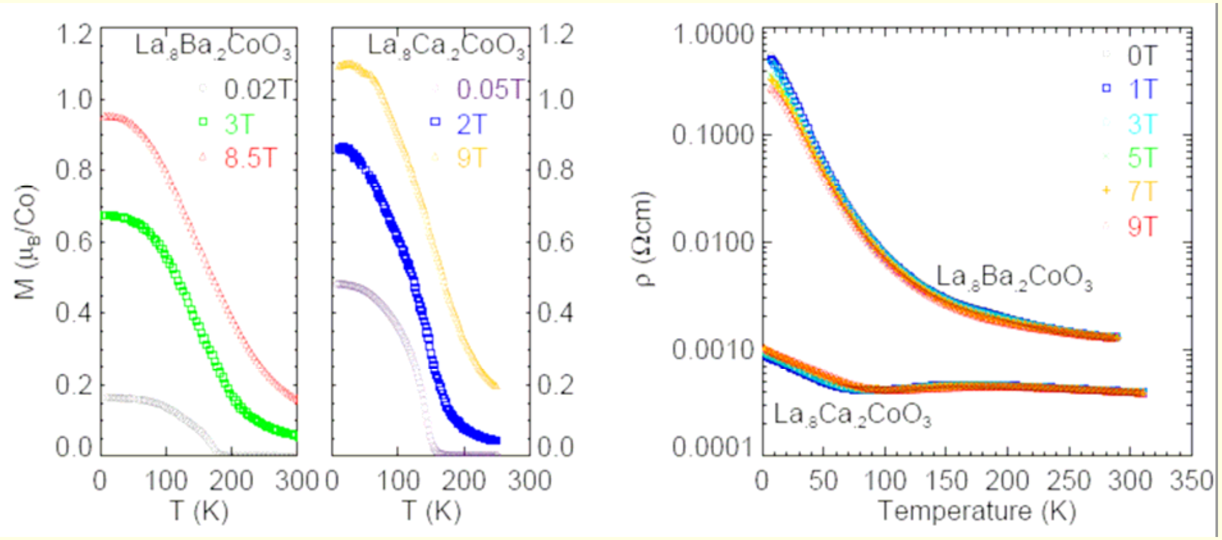
Ca-case



Phelan & Louca, PRB (2007)

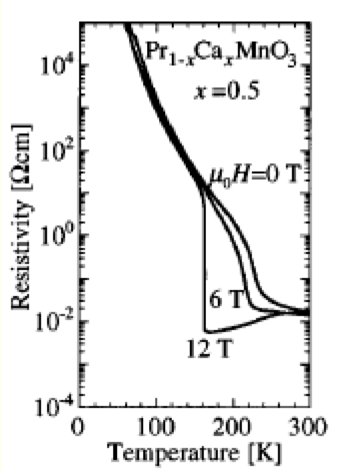
- Only the Ca compounds show a structural phase transition.
- The Co-O-Co bonds are bent even with high concentrations of Ca.
- This has important implications on the formation of the intermediate spin state. (Louca and Phelan, submitted (2007))

Low CMR effect: not a very good metal

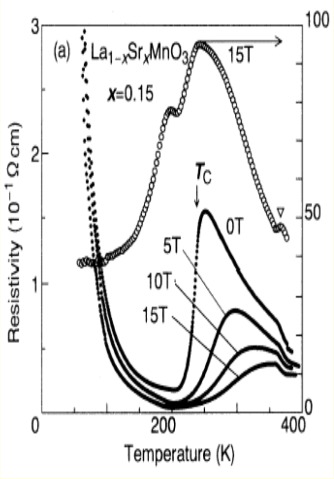


Similar to …

Only a 10 % increase in cobaltites compared to 10^6 % increase in manganites. No sharp changes observed at T_c.

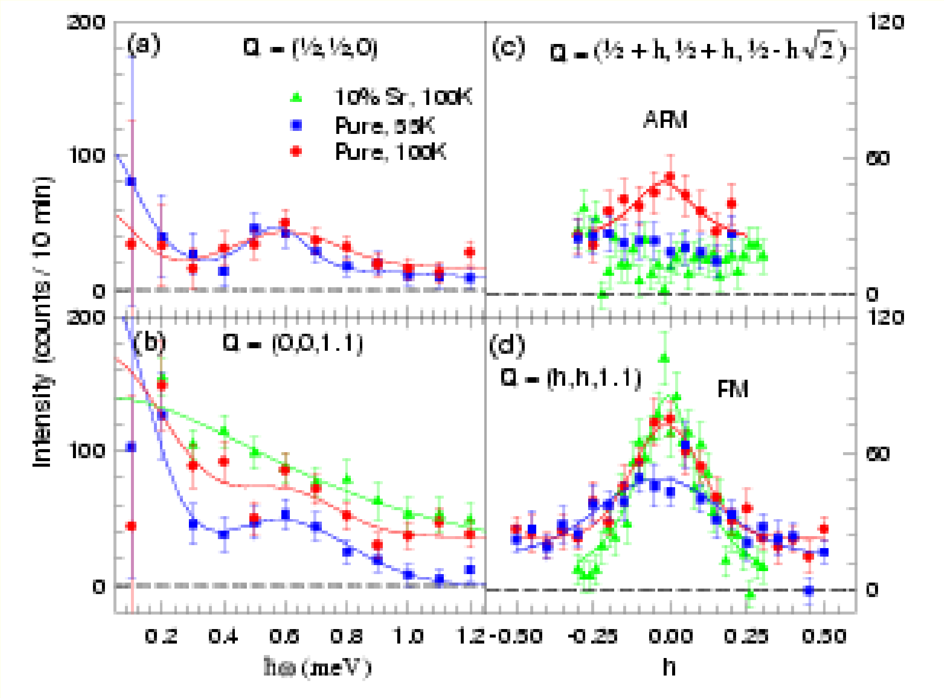


Tomioka et al., PRB 53, R1689 (1996)



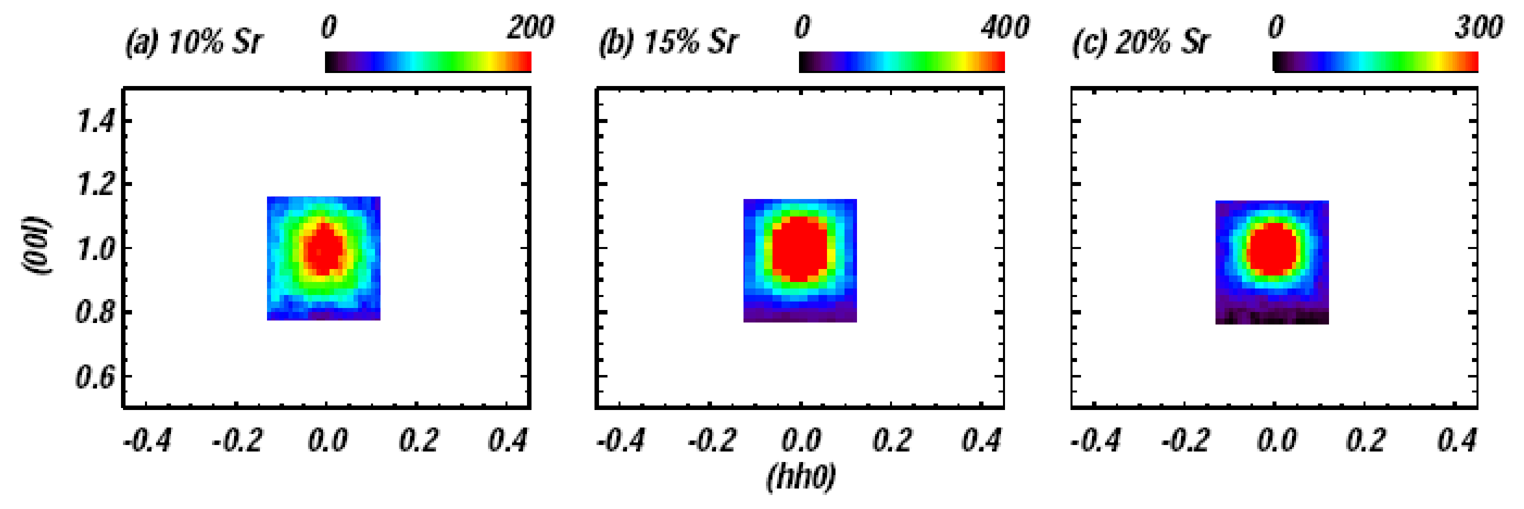
Urushibara et al., PRB 51, 14103 (1995)

Introducing charges to the lattice changes the magnetic dynamics



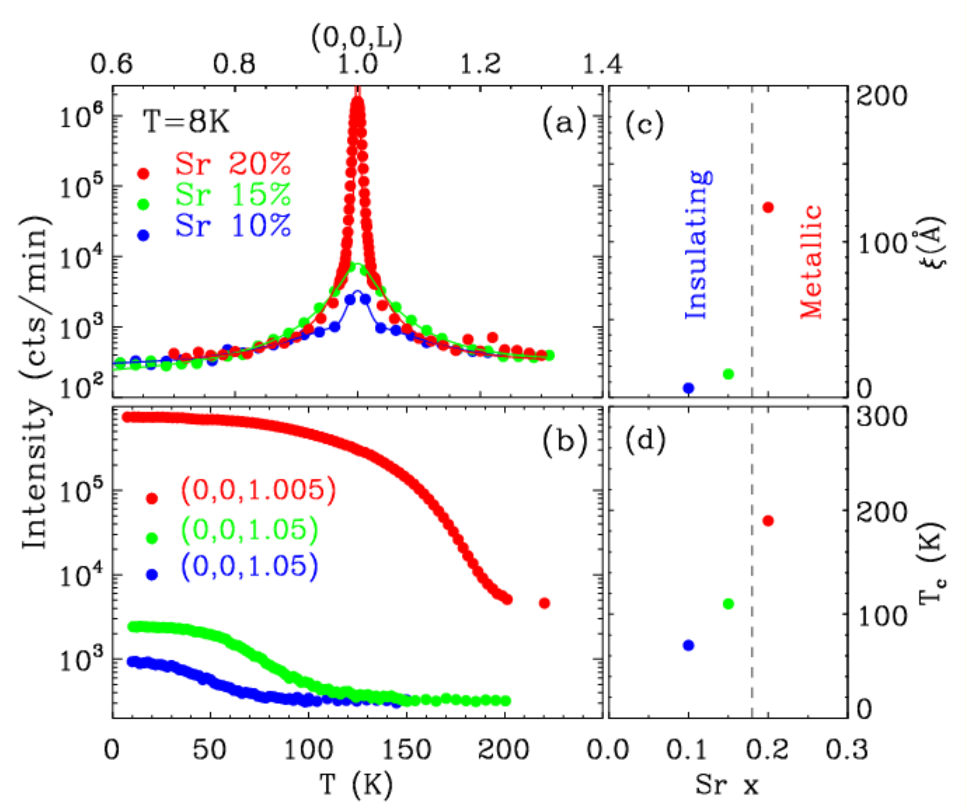
- The 0.6 meV mode (due to single ion effect) disappears with doping.
- The AFM correlations are absent.
- Dynamic FM correlations are also suppressed. However, static FM correlations appear.

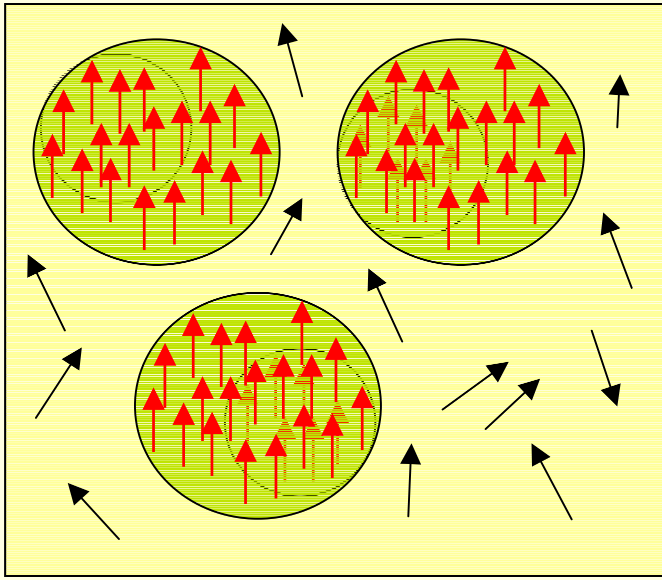
Magnetic correlations become static and spatially isotropic



- Elastic measurements around the (001) ferromagnetic point shows a circular object.
- Spatial extent of the FM correlations is isotropic for all compositions.

Correlation length increases with charge



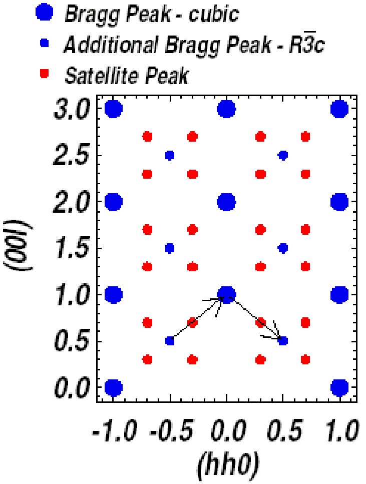


- Ferromagnetic clusters are small in the insulating phase. They grow in the metallic state. Percolation through the clusters enhances conductivity.
- At 20 %, the correlation length is finite indicating that this is not a long-range ferromagnet.

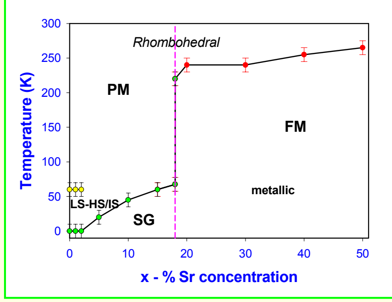
Phelan et al., PRL **96**, 027201 (2006).

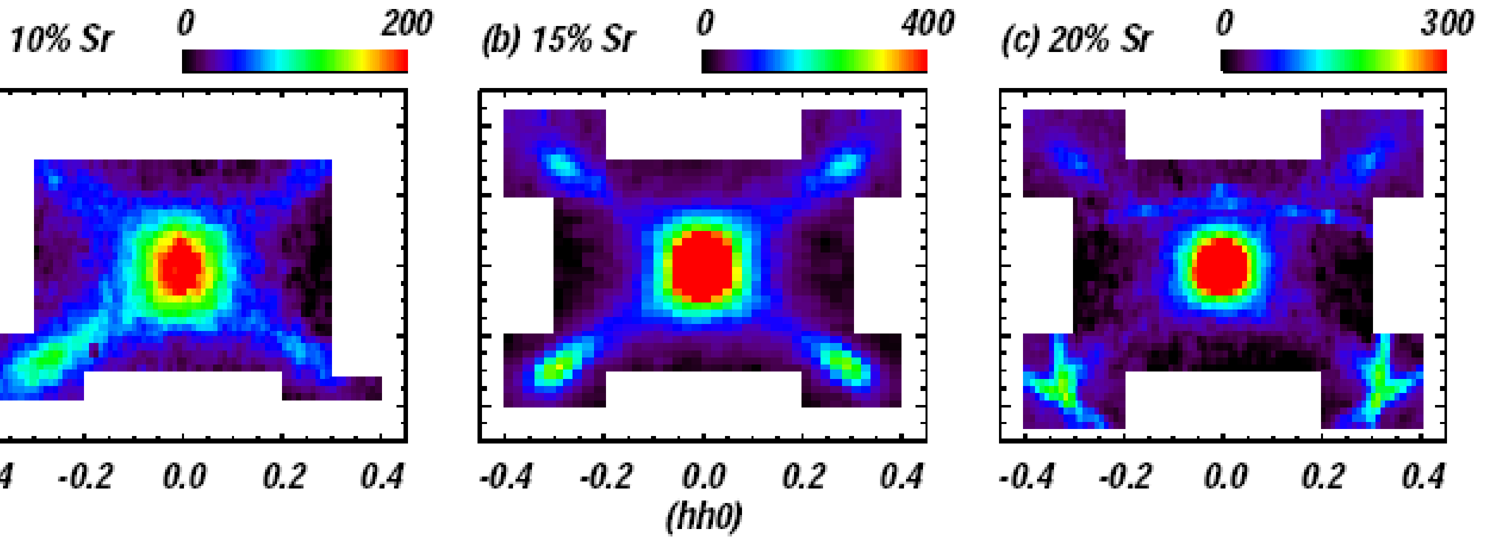
New competing state

Double exchange FM vs incommensurability



Presence of a superstructure





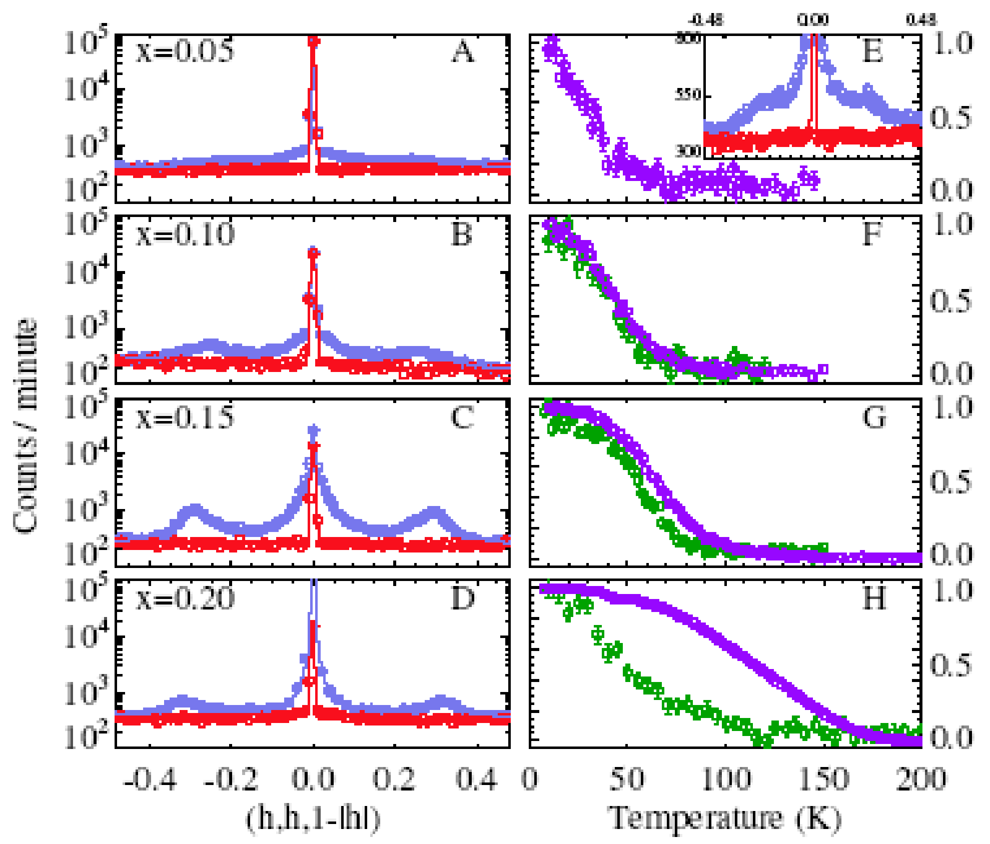
hhl scans

The isotropic feature centered at (001) due to FM correlations

- An x-shaped pattern of weak diffuse intensity
- Satellite peaks at the four corners. Superlattice reflections appear at incommensurate positions **along (111) direction**.
- The positions of the peaks change with charge doping.

Cuts along (111)

Two ordering temperatures

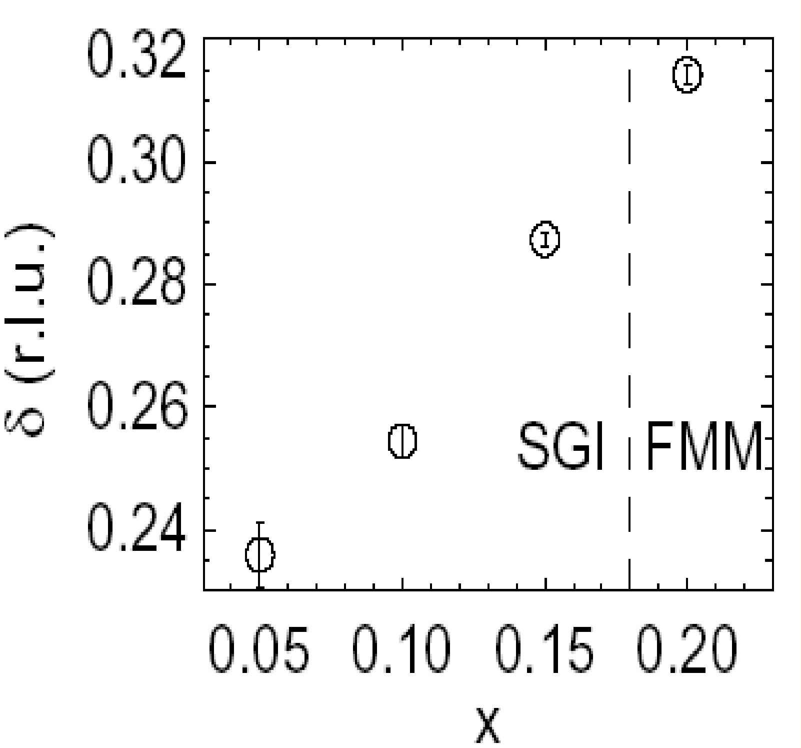


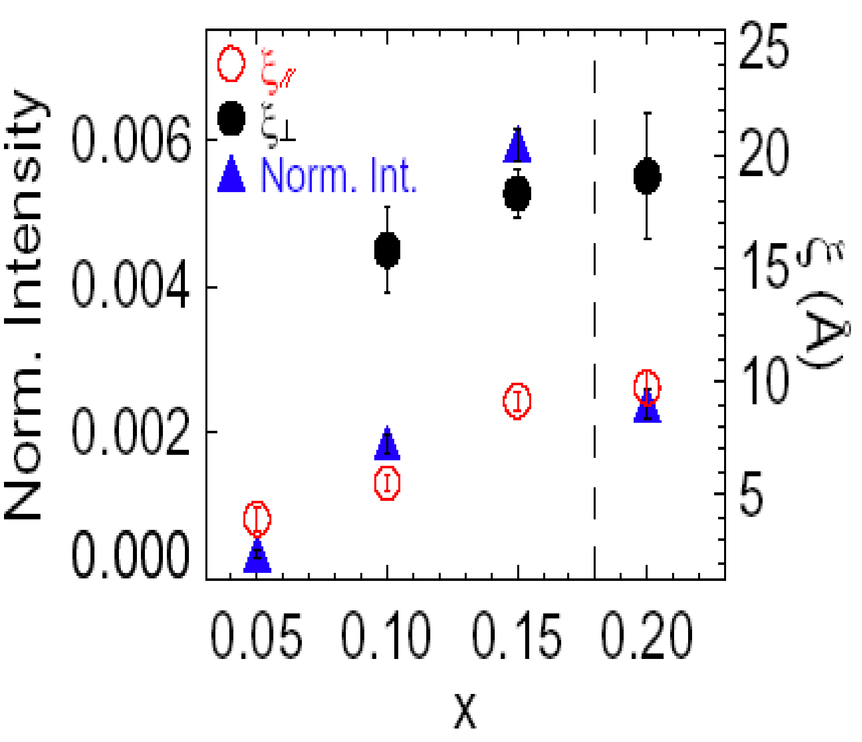
Onset temperature for FM or SG ordering occurs first

Secondary ordering follows

- Peaks are absent above the long-range transition.
- The order parameter of the secondary spin ordering deviates more with the IM transition.
- Incommensurate peaks are magnetic as they follow the form factor dependence.

How the incommensurability varies with x

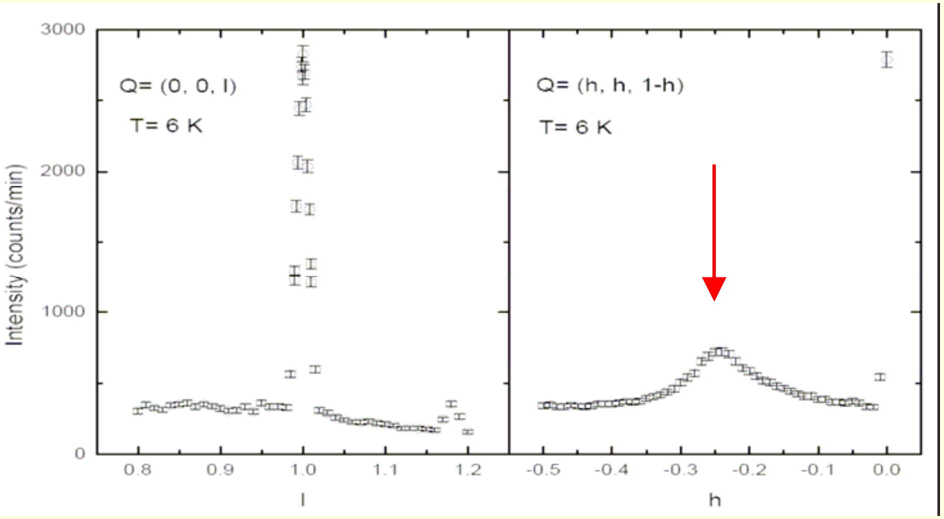


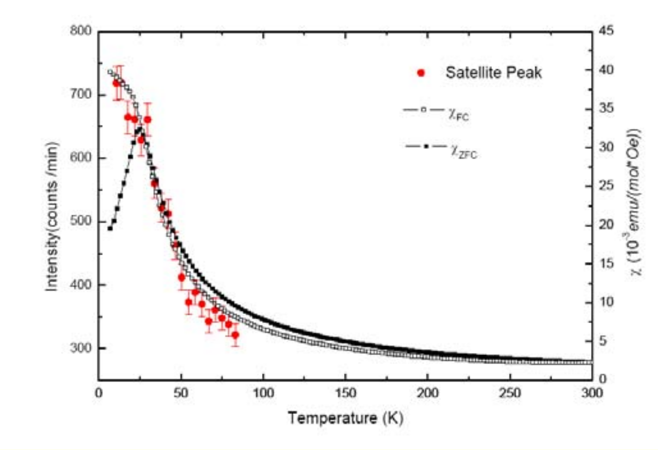


- Correlation length is longer in the perpendicular direction to (111) than in the parallel direction.
- Normalized intensity drops with the IM transition showing that peaks get weaker.

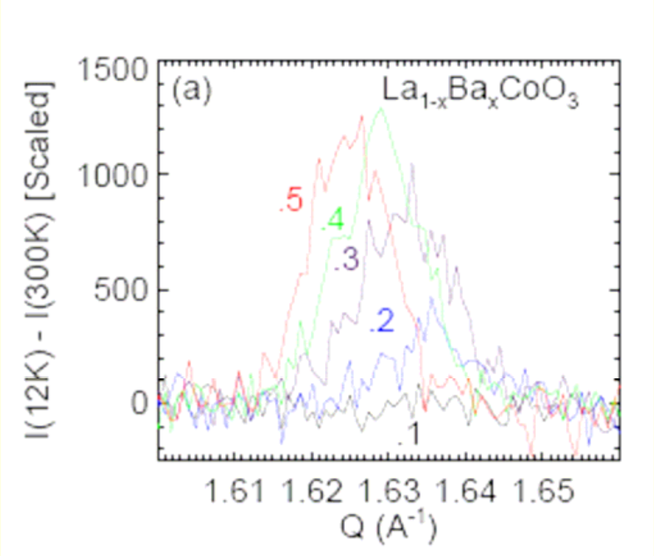
IC features in Ba!!

10 % single crystal

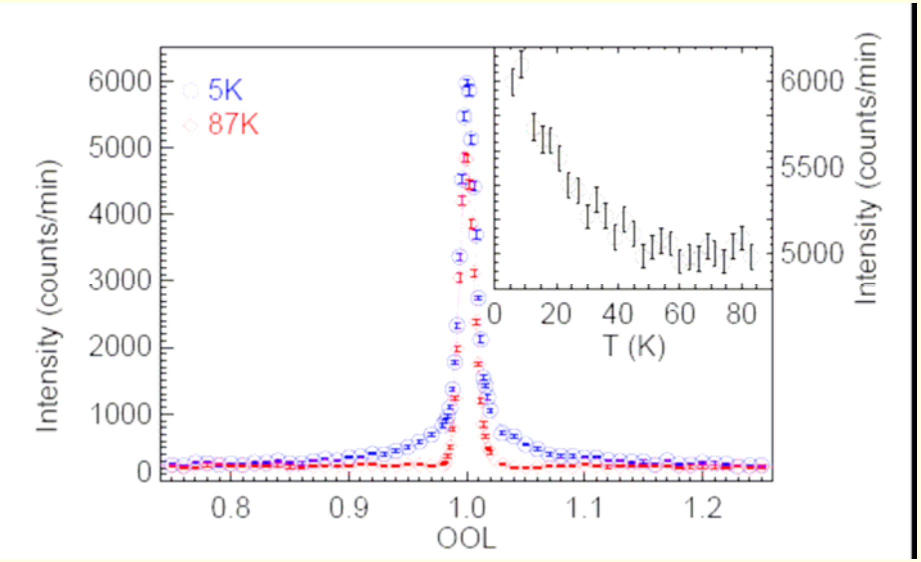




- o IC peak observed at (¼ , ¼, ¼).
- o It is more intense that in Sr 10 %.
- o Its order parameter follows the susceptibility.
- o It takes a lot more Ba to make system ferromagnetic!

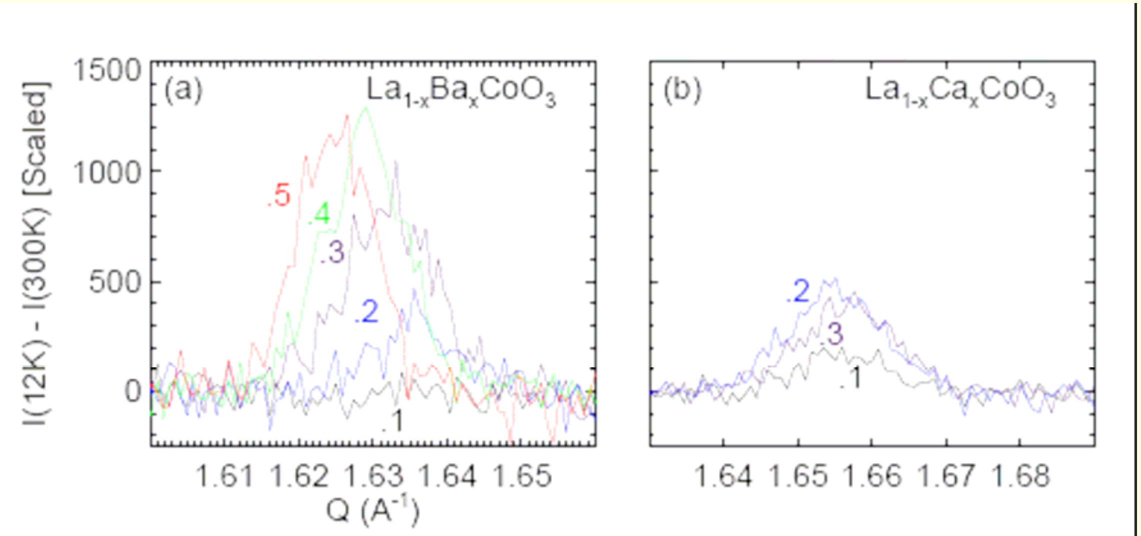


Ca-doped: no IC peaks



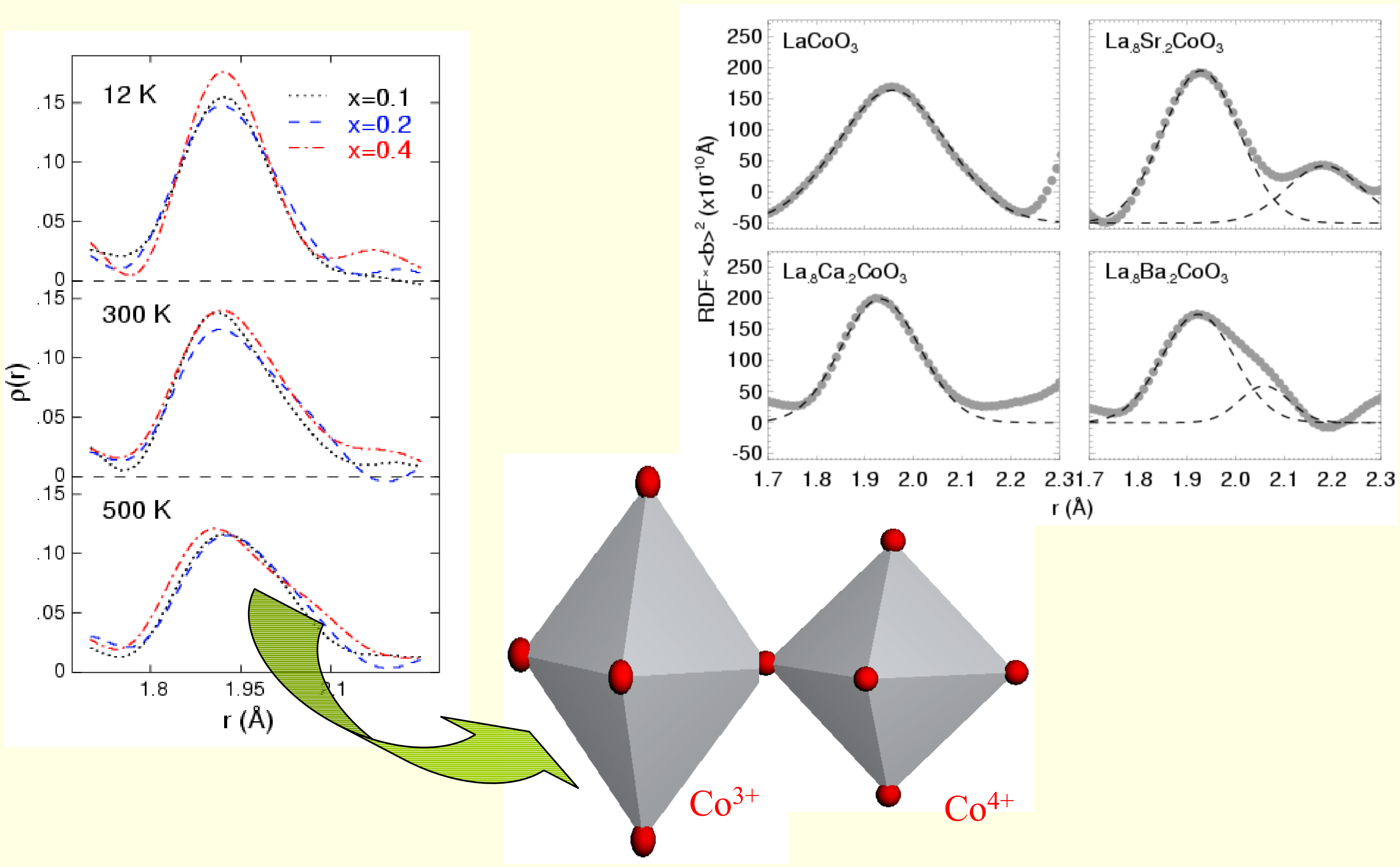
5 and 10 % single crystals showed no evidence of IC.

FM coupling does not get significantly stronger with doping.



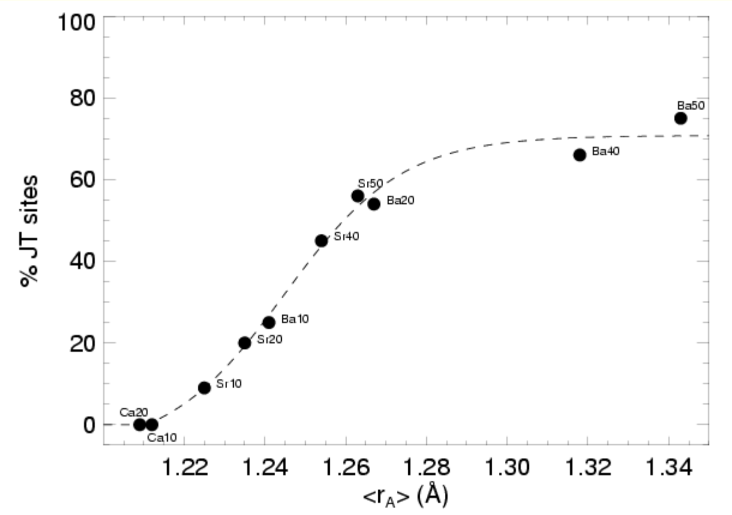
Two competing phases in the insulating state
Jahn-Teller vs low spin

Evidence for static Jahn-Teller in Ba, Sr but not Ca!



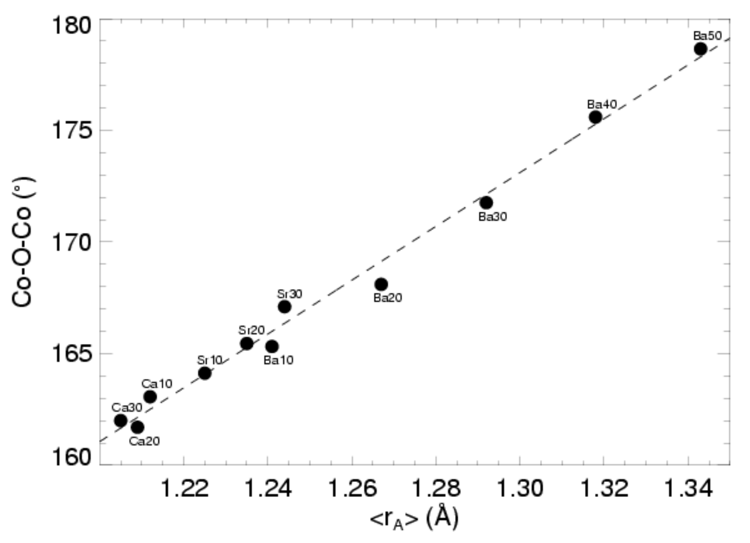
- The peak is split above the insulator to metal transition.
- Local and static JT distortions are present even as the symmetry is rhombohedral.
- Distortions are present even as the presumed band width becomes wider with Sr or Ba.

% of JT polarons with ionic radius



- Critical radius of 1.22 Å: For values above, the number of JT sites increase.
- For values below that, no JT polarons are formed.

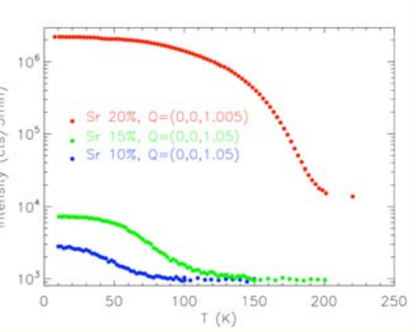
Co-O-Co bond angle

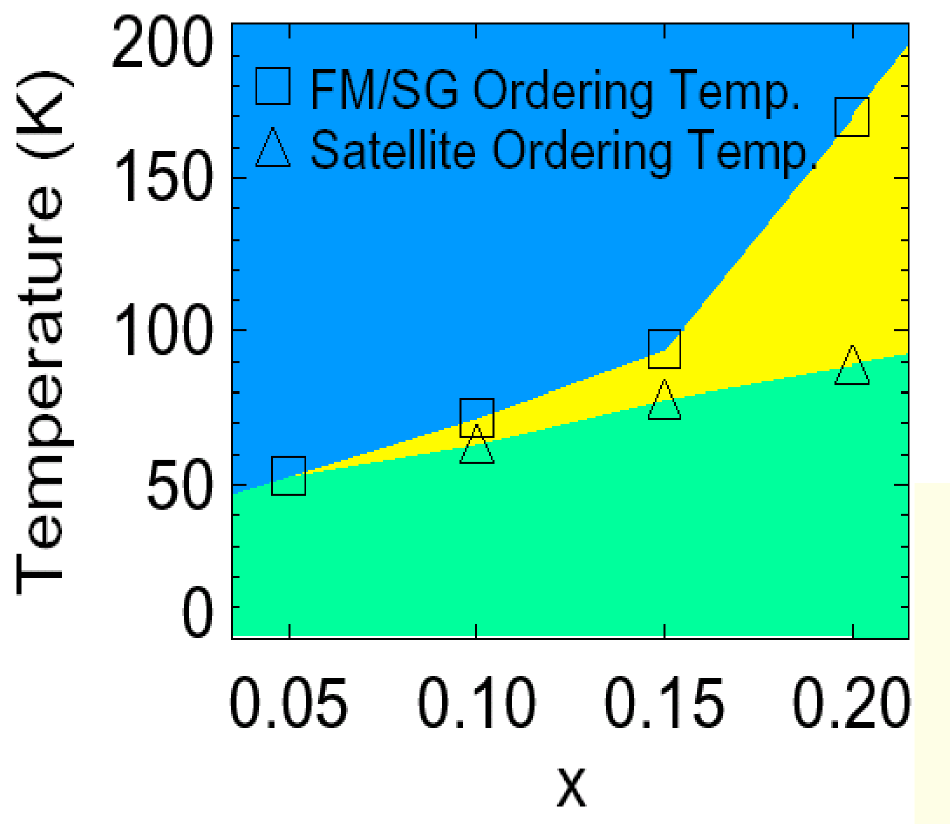


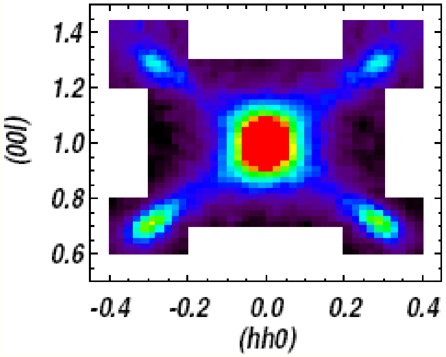
- Bond angle increases linearly above the critical radius of 1.22 Å.
- For values less than that, bond angle does not change with x.

Broadening of the bandwidth favors the excited state
The IS state is stabilized by the static Jahn-Teller distortions

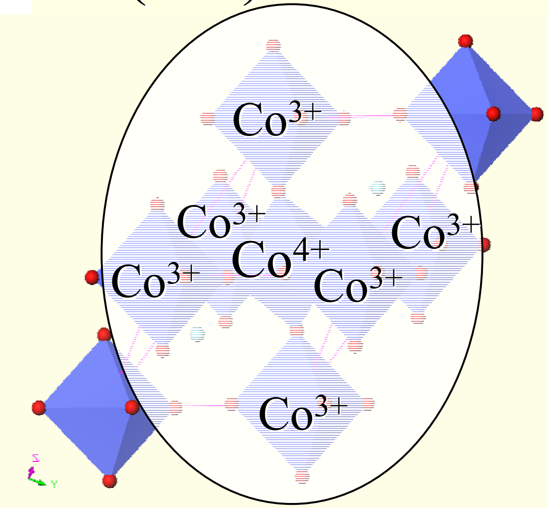
New phase diagram







7-site polarons ordering along (111)



Consequences of ordering:
-spin-charge localization
-rise in the resistivity

In conclusion

- Two magnetic phases coexist and compete in the perovskite cobaltites.
- If the competition between the two is strong, they can phase separate.
- IC peaks are present in Sr- and Ba-doped but not in Ca-doped alloys.
- The existence and organization of such structures appears to be a common feature in strongly correlated electron systems.

Support for the work is provide by the DOE