Recent Results on CMR and Multiferroic Oxides

Jeff Lynn
NIST Center for Neutron Research

University of Virginia

September 27, 2007

Outline

- Neutron Instrumentation
- Colossal MagnetoResistive (CMR) systems
  - Ferromagnetic Droplet Formation
  - Polaron Formation and Nature of the Ferromagnetic Transition
  - Polaron Glass Phase and Polaron Dynamics
  - Effect of Disorder on T_C in (La-Ba)MnO_3
  - Avalanche Behavior at low T in a Phase-Separated Material
- Multiferroics (Magnetic Ferroelectrics)
  - Ferroelectrics and Magnetic Ferroelectrics
  - How is magnetic structure coupled to ferroelectric Order?
  - Mn spin dynamics

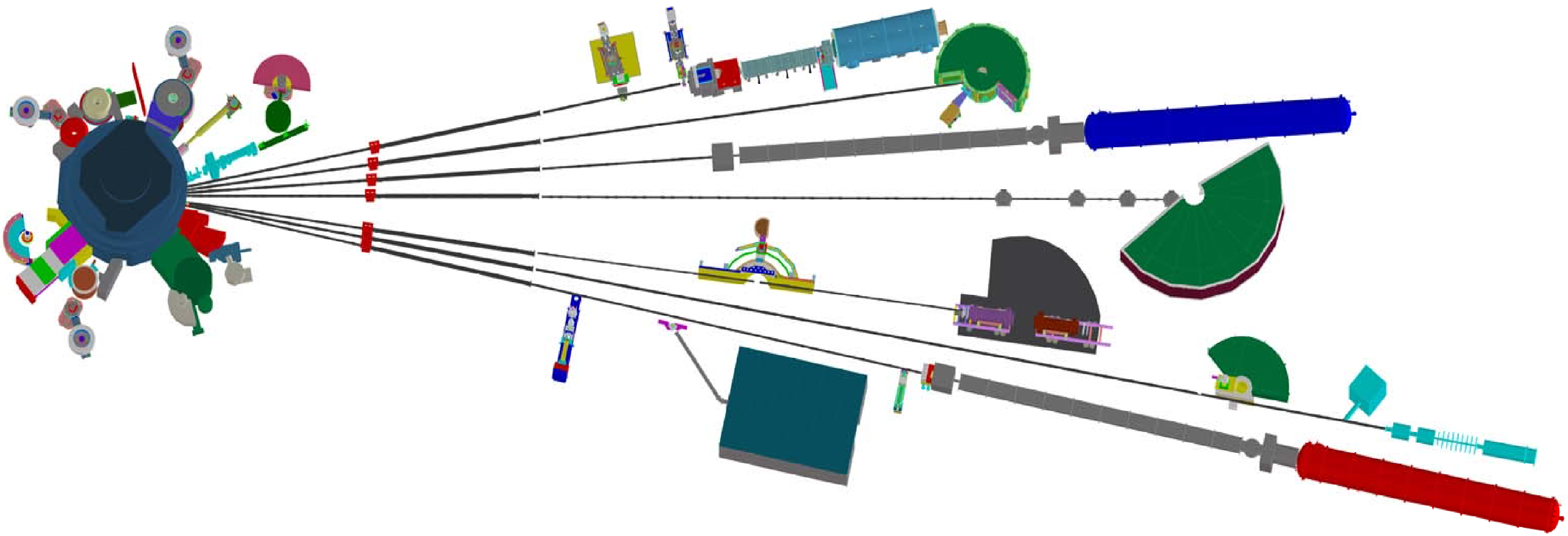
NIST Center for Neutron Research

Facilities

Structure: Diffraction (2); SANS (3); Reflectometry (3)

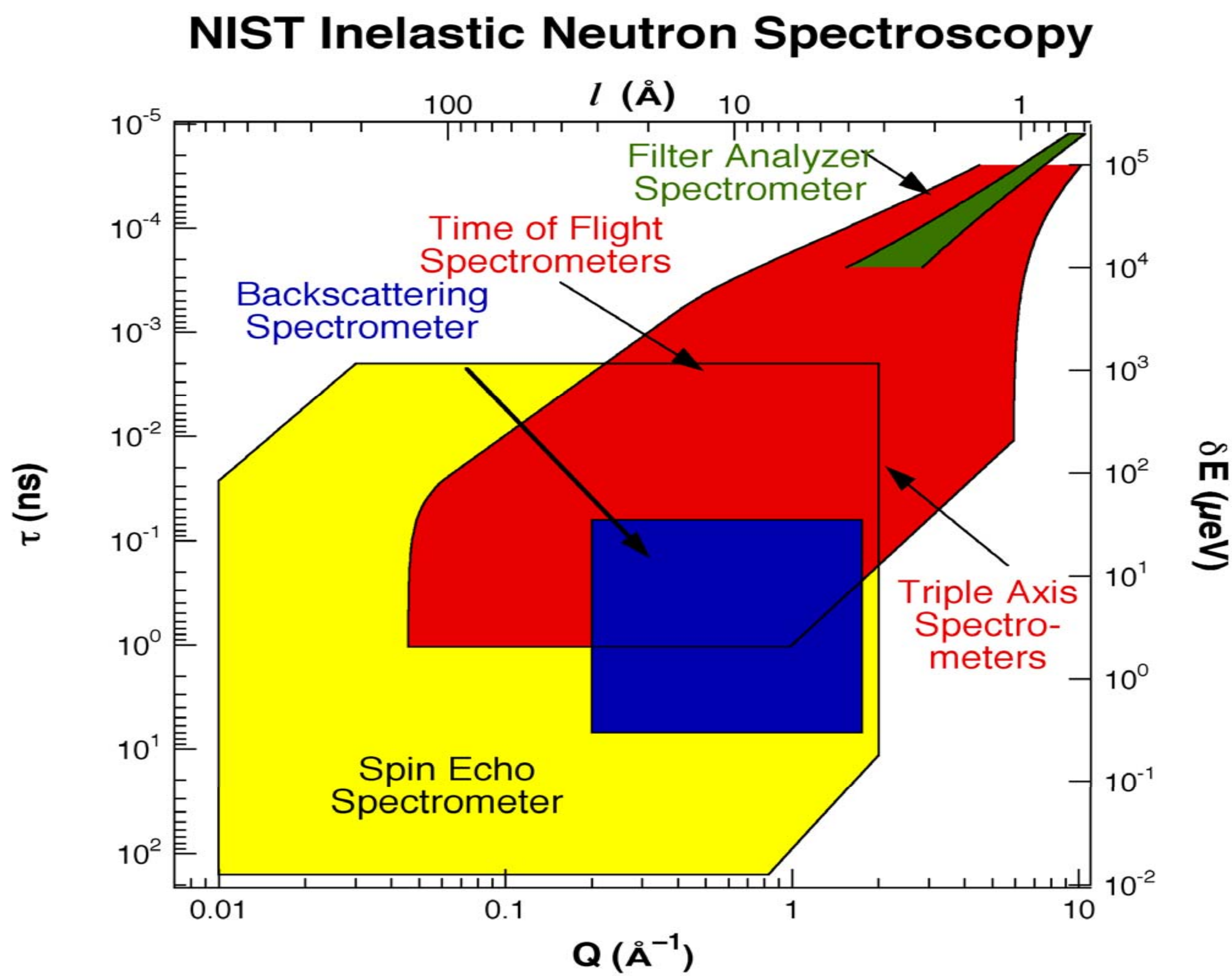
Dynamics: TAS (5+1); TOF (1); Spin Echo (1)

Prompt-γ (2); Depth Profile (2); Topography (2); Activation Analysis; Fundamental Properties (3)--Interferometry

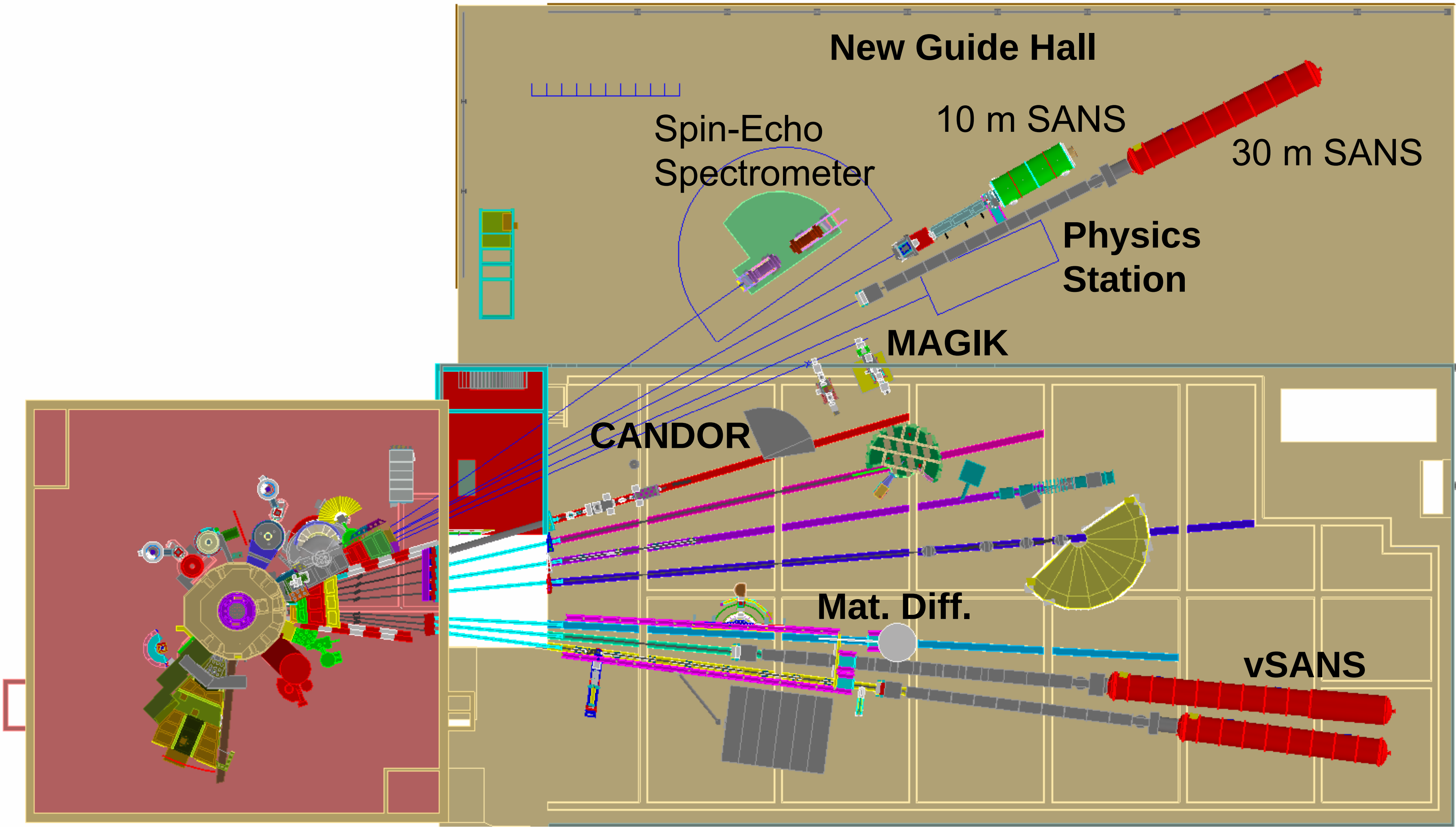


http://www.ncnr.nist.gov

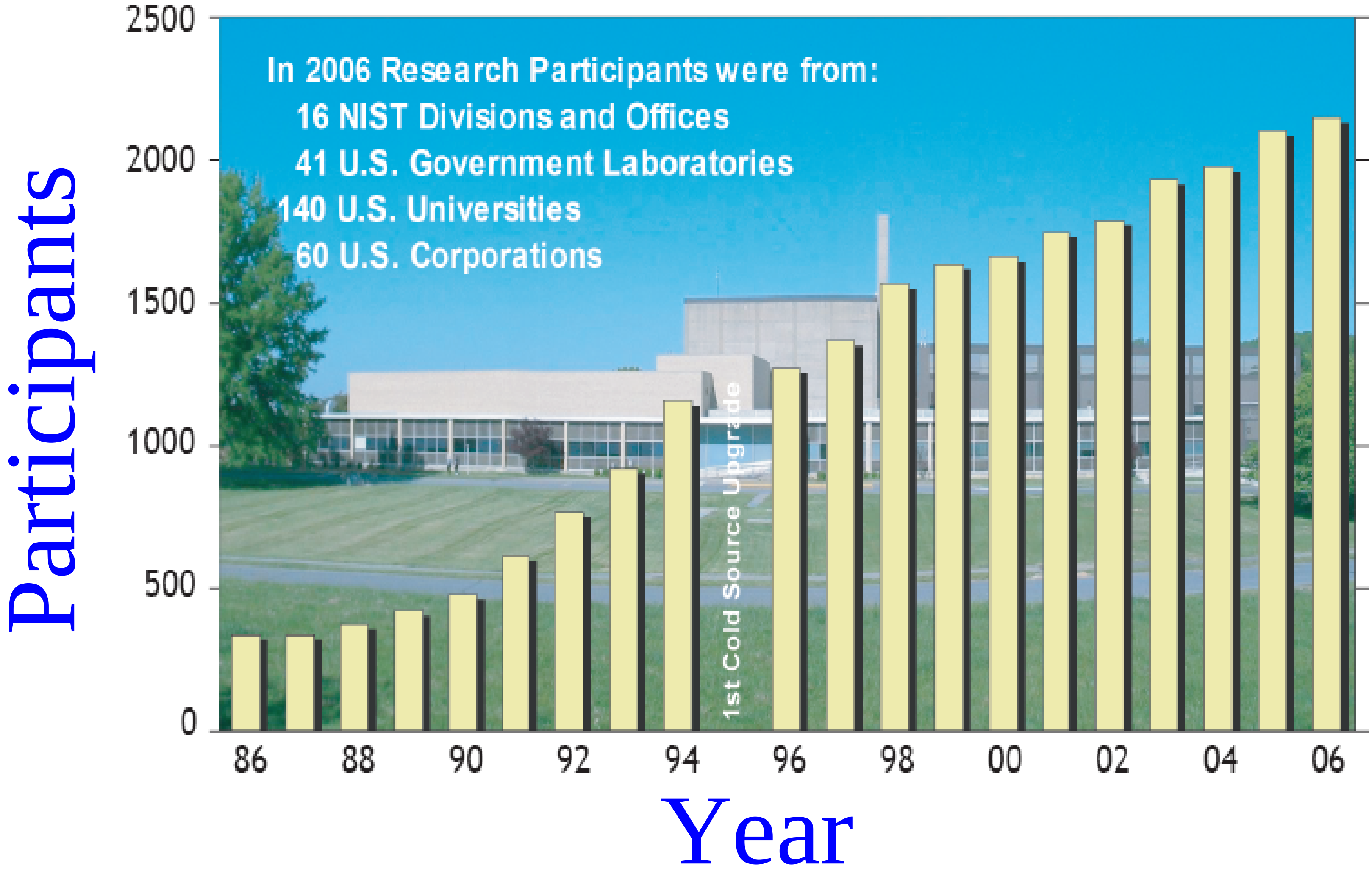
Dynamic Range



NCNR Expansion—2nd Guide Hall



http://www.ncnr.nist.gov



http://www.ncnr.nist.gov

Systems under Investigation with Neutron Scattering

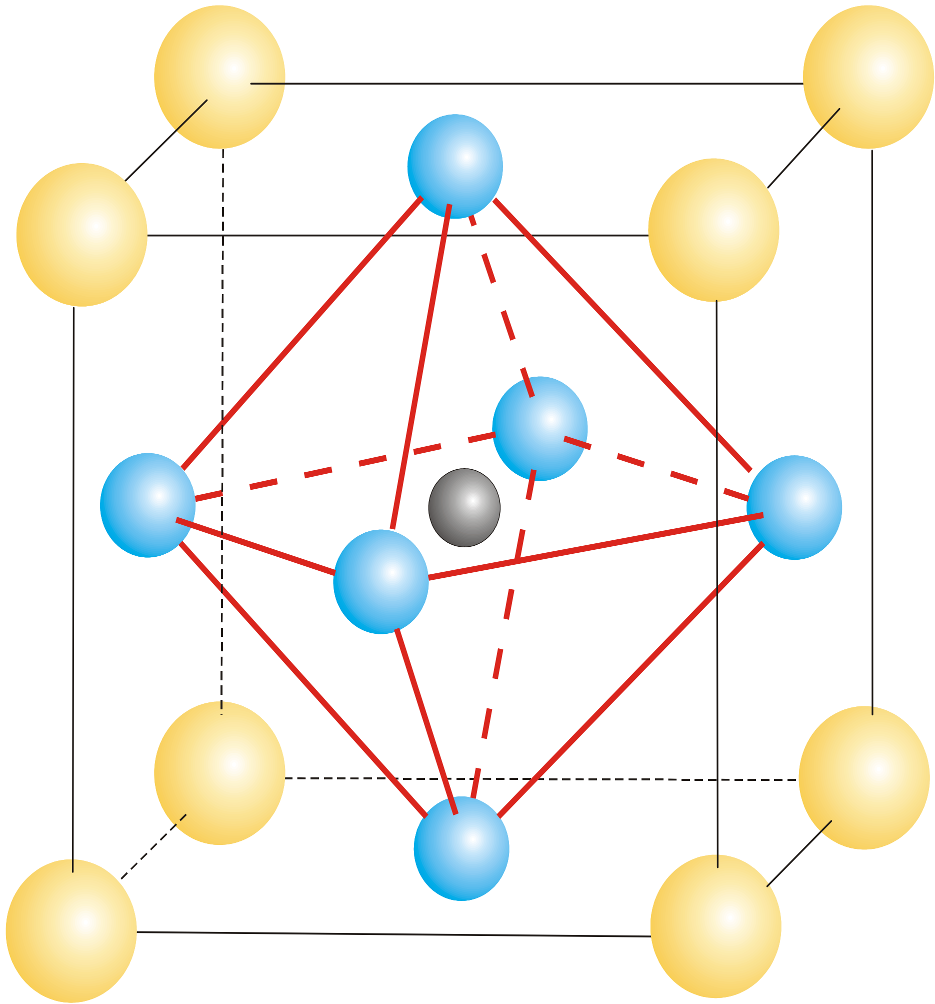
- CMR systems, Multiferroics (La-$CaMnO_3$, $HoMnO_3$)
- Magnetic Superconductors (e.g. RNi_2B_2C, $RuSr_2GdCu_2O_8$)
- Magnetic Order and Fluctuations in Cuprates (e-doped)
- Heavy Fermion Materials ($CeRhIn_5$, $PrOs_4Sb_{12}$, …)
- Non-Fermi Liquids ($UCu_{5-x}Pd_x$, $Sc_{1-x}U_xPd_3$)
- Cobaltates (Na_xCoO_2 (*just add water for Superconductivity*))
- Vortex Lattice/Melting in Superconductors (Nb, NCCO)
- Frustrated Magnets

http://www/ncnr.nist.gov/staff/jeff

CMR Systems

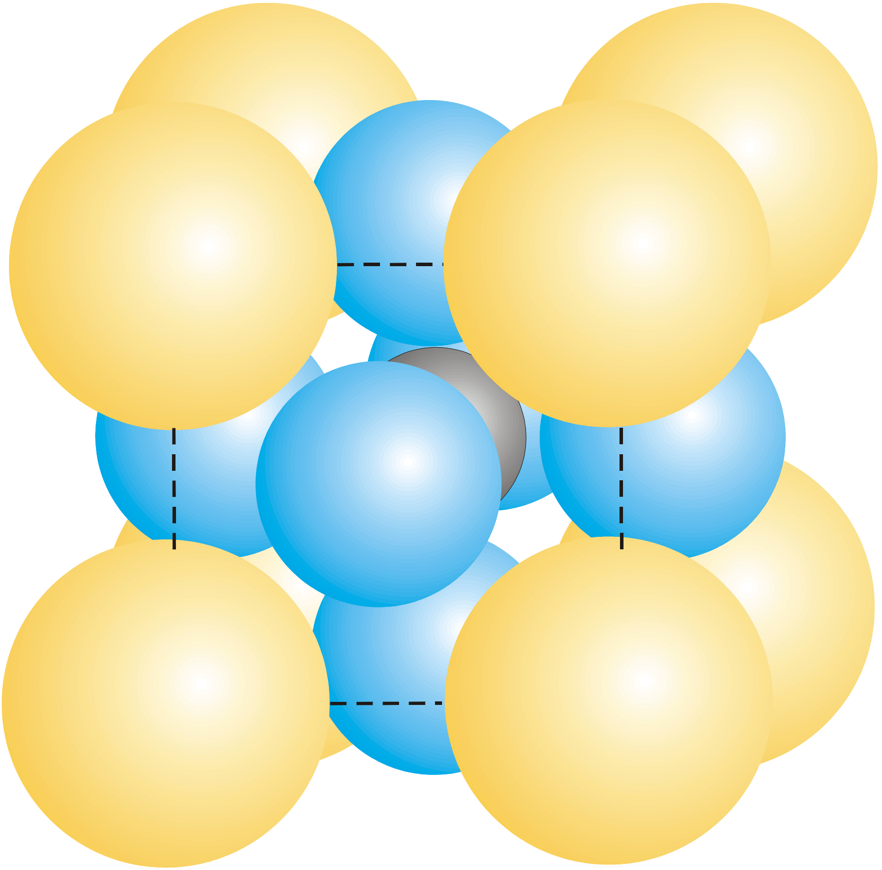
- CMR systems
  - Natural GMR System: (La-Sr)CoO_3
  - Avalanche Behavior at low T in a Phase-Separated Material
  - Ferromagnetic Droplet Formation
  - Polaron Formation and Nature of the Ferromagnetic Transition
  - Polaron Glass Phase
  - Effect of Disorder on T_C in (La-Ba)MnO_3
  - Polaron Dynamics

Ideal Perovskite Structure (Cubic)



$LaMnO_3$

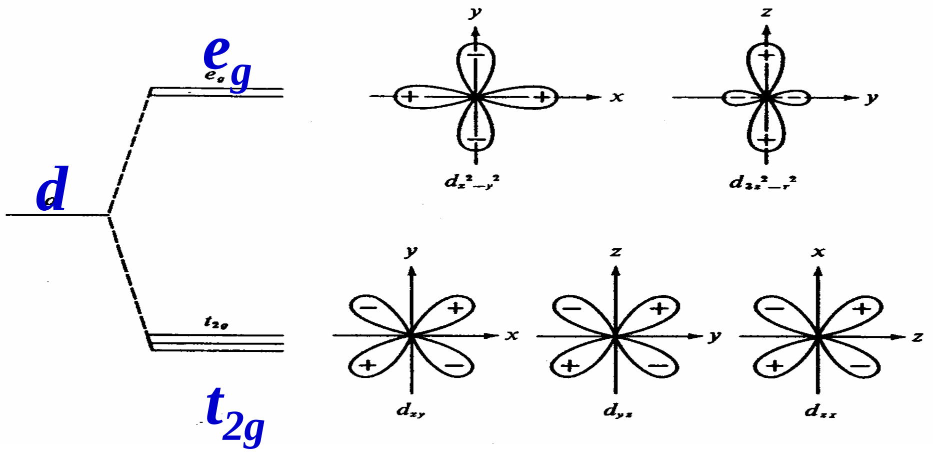
Ideal Perovskite Structure (Cubic)

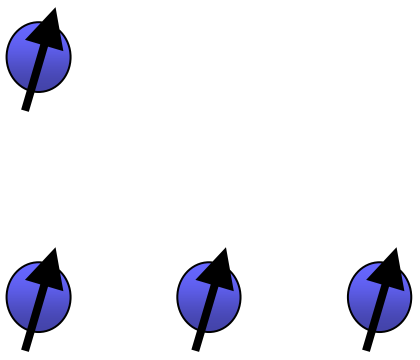


$LaMnO_3$

Basic Interactions

Mn^{3+} in $LaMnO_3$

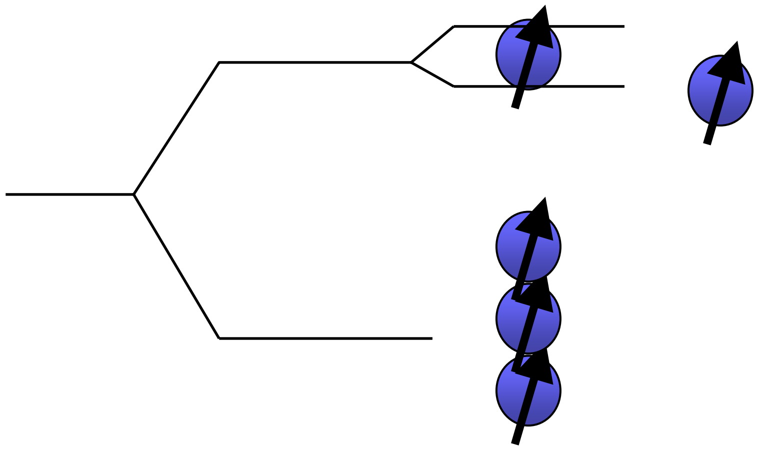




Strong Hund's Rule Coupling
(on-site electrons must be parallel)
Jahn-Teller Distortion

Basic Interactions

$LaMnO_3$

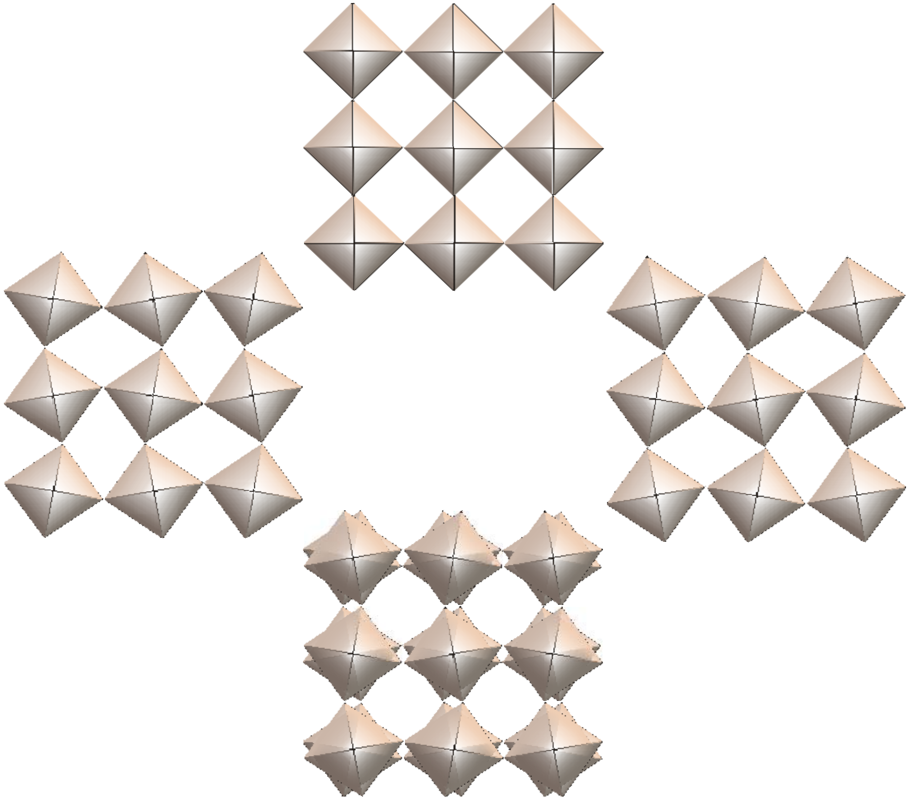


Strong Hund's Rule Coupling

(on-site electrons must be parallel)

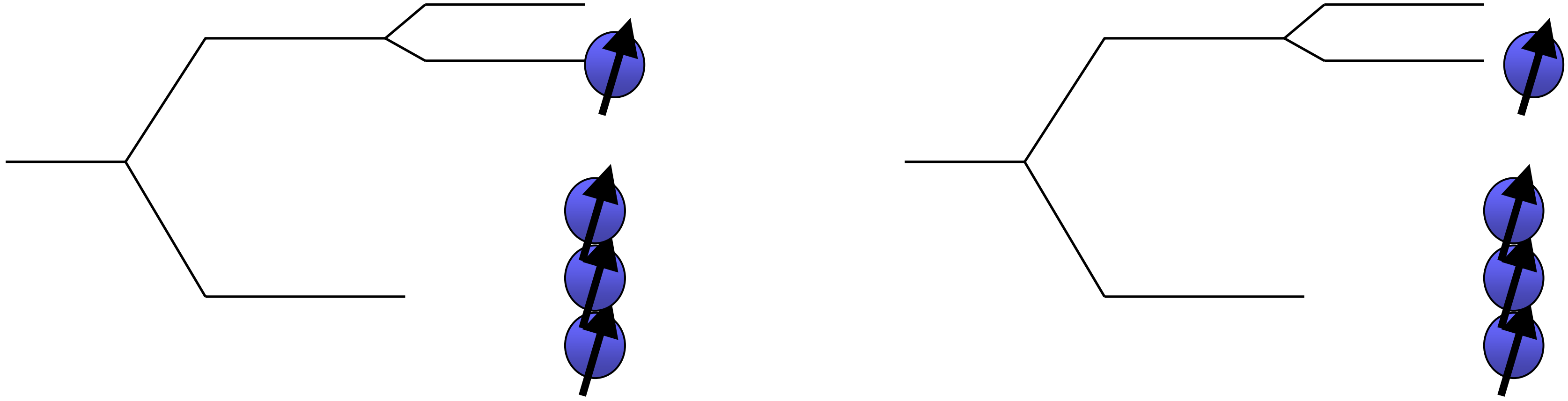
Jahn-Teller Distortion couples spins with lattice

Tiling
(Orthorhombic)



Basic Interactions

$LaMnO_3$



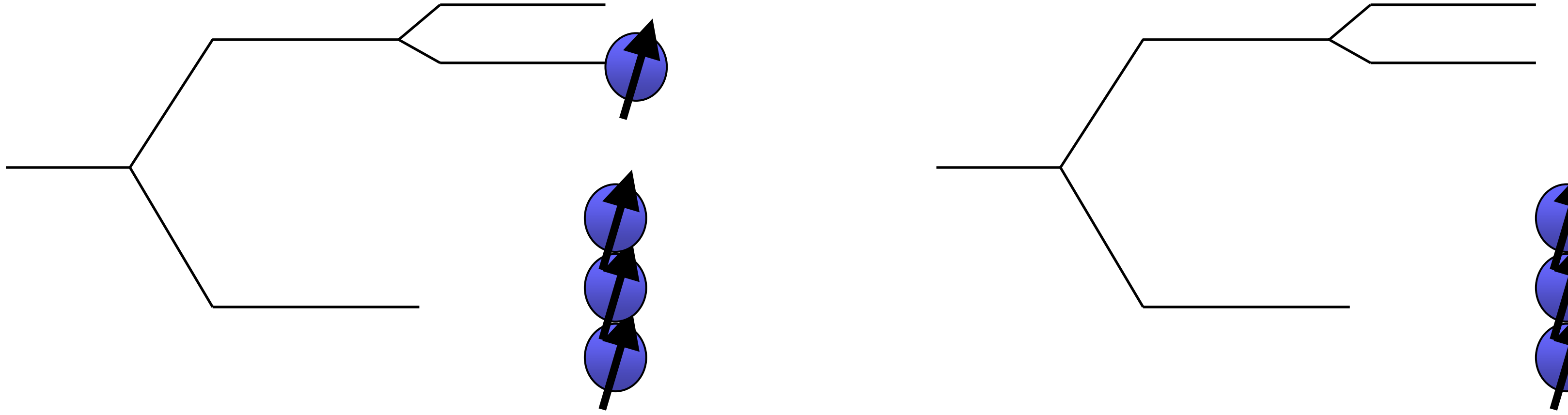
e_g electron can only hop if core spins are parallel (& an empty site)

Jahn-Teller Distortion couples spins with lattice

NCNR

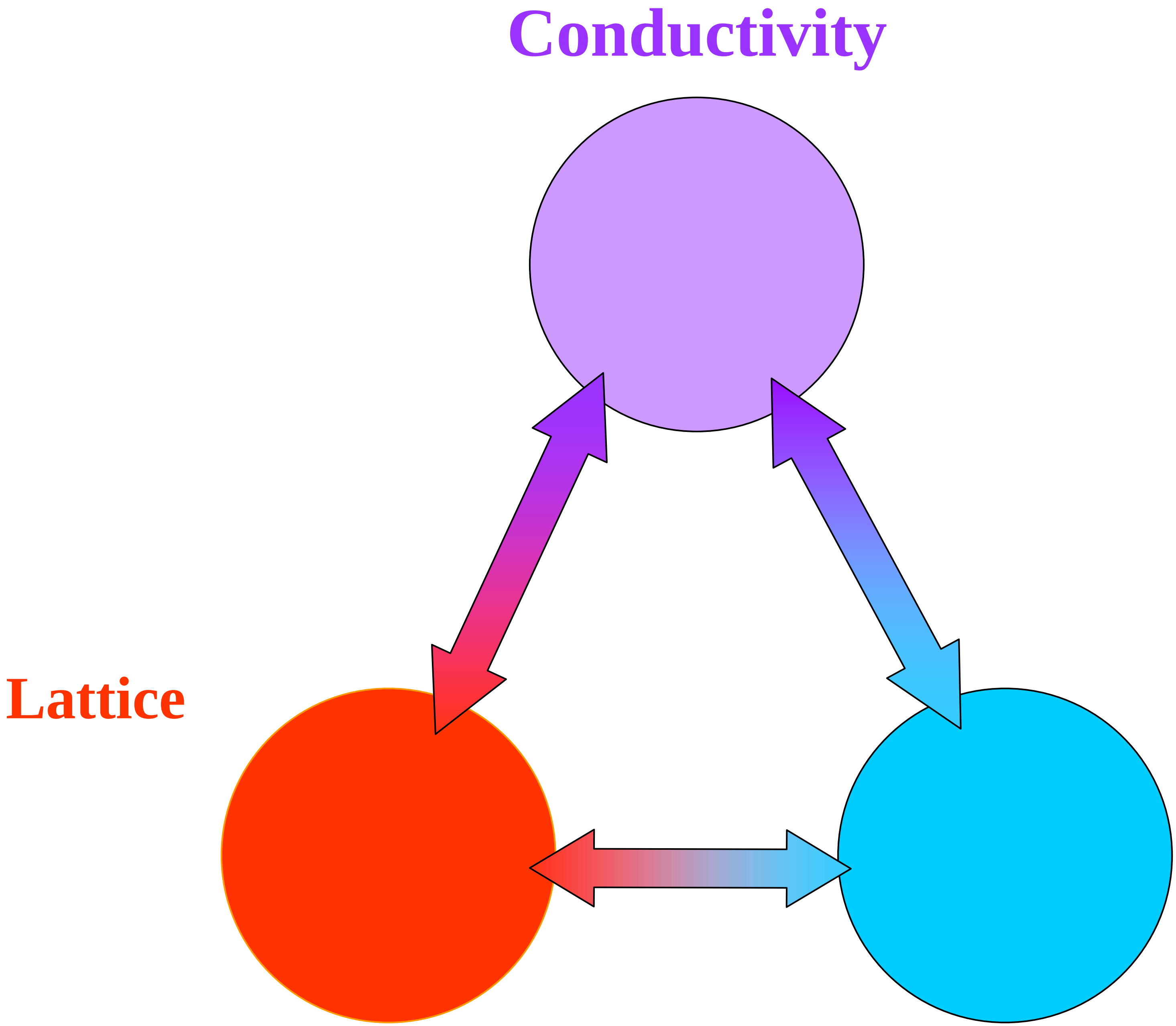
Basic Interactions

$LaMnO_3$



e_g electron can only hop if core spins are parallel (& an empty site)

Jahn-Teller Distortion couples spins with lattice

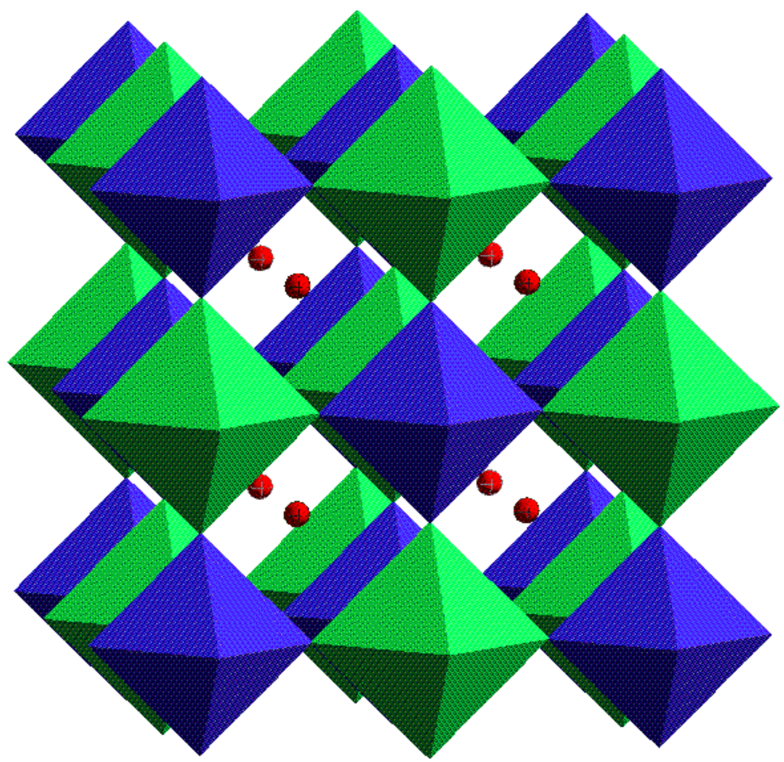

Conductivity
Lattice
Spins

Doping of Structure

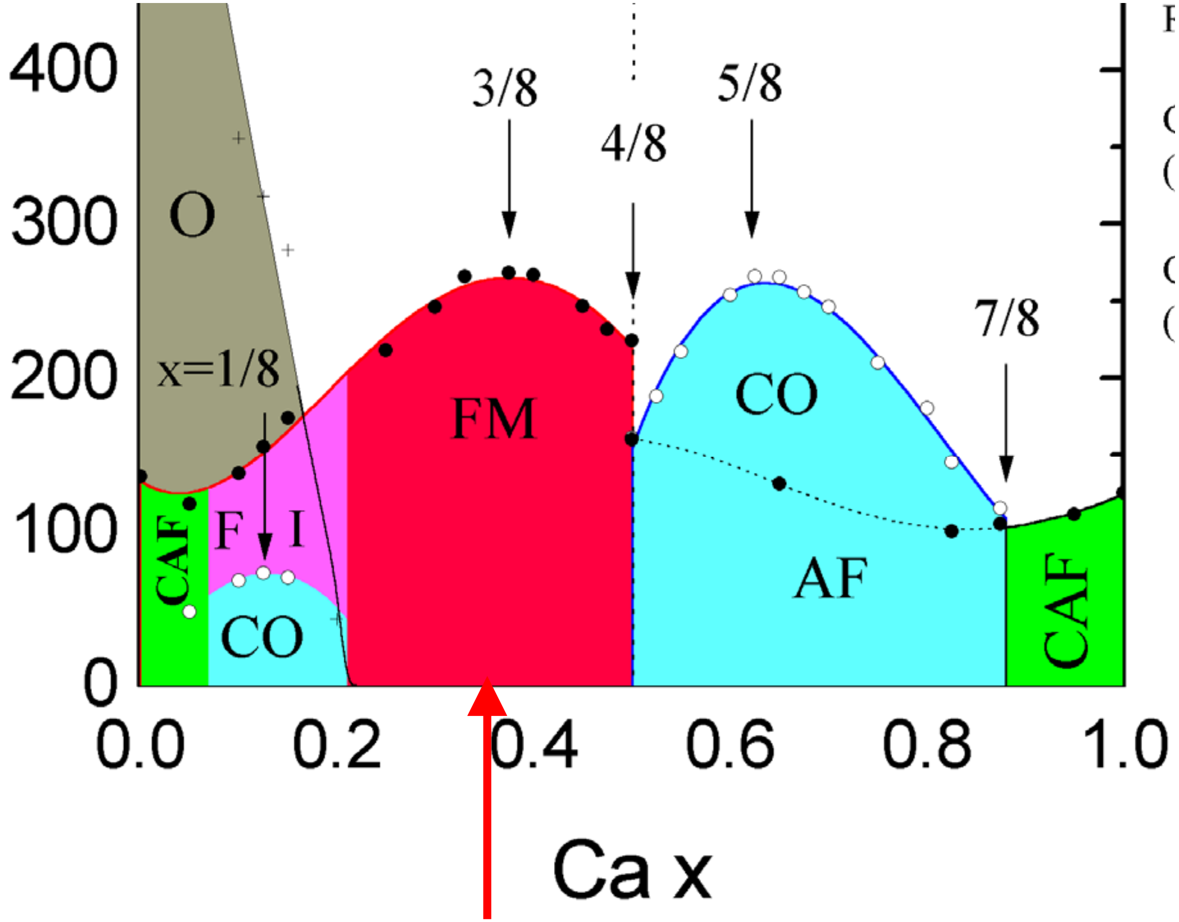
$(La\text{-}Ca)MnO_3$

$LaMnO_3$

$Ca^{2+} \rightarrow La^{3+}$ $Mn^{3+} \rightarrow Mn^{+4}$

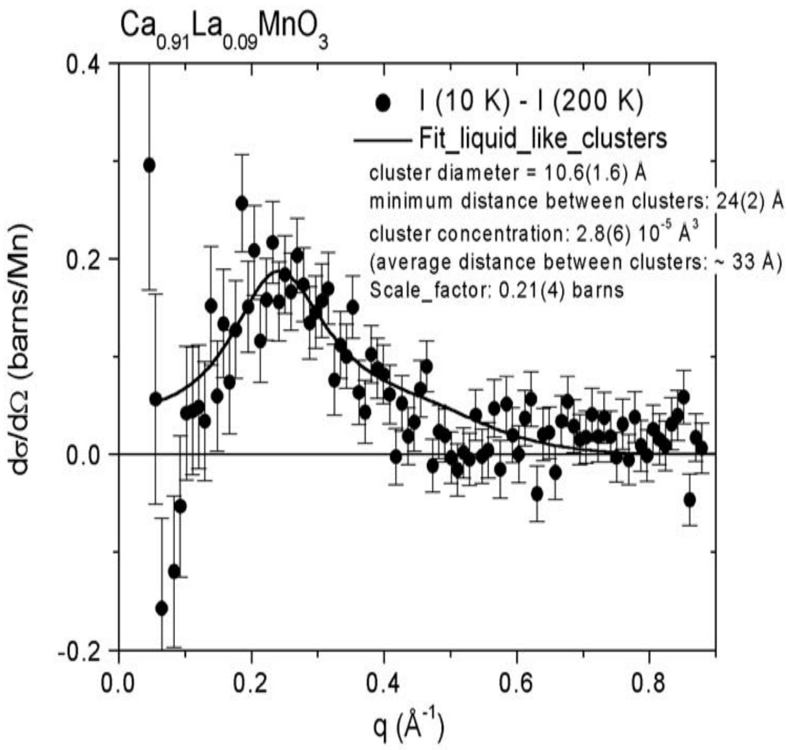


$La_{1-x}Ca_xMnO_3$



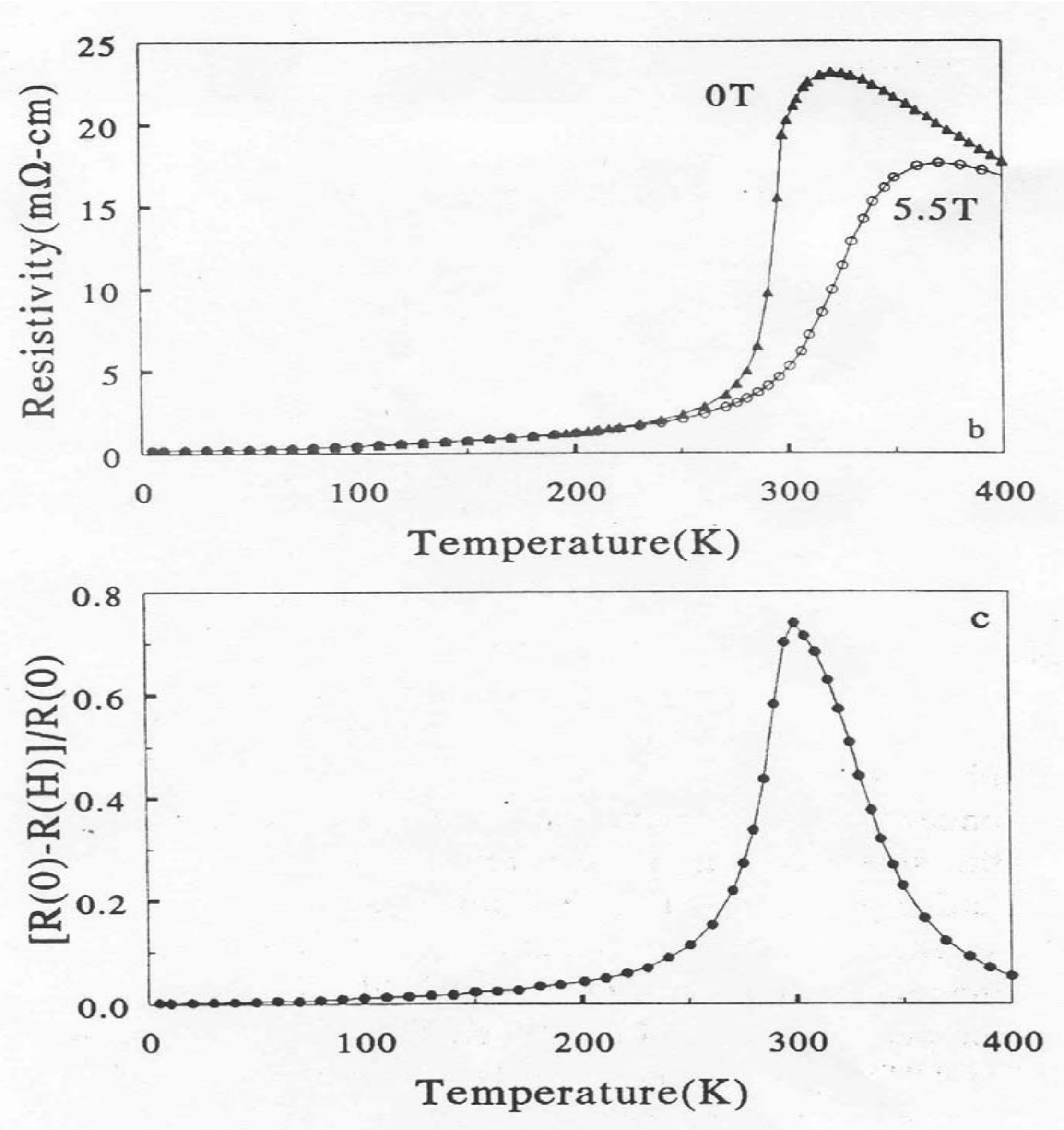
S-W. Cheong and C. H. Chen
Colossal Magnetoresistance, Charge Ordering, and Related Properties of Manganese Oxides (World Scientific, 1998), p. 241 (Ed. by Raveau and Rao)

Ferromagnetic Clusters (Electron-doped)

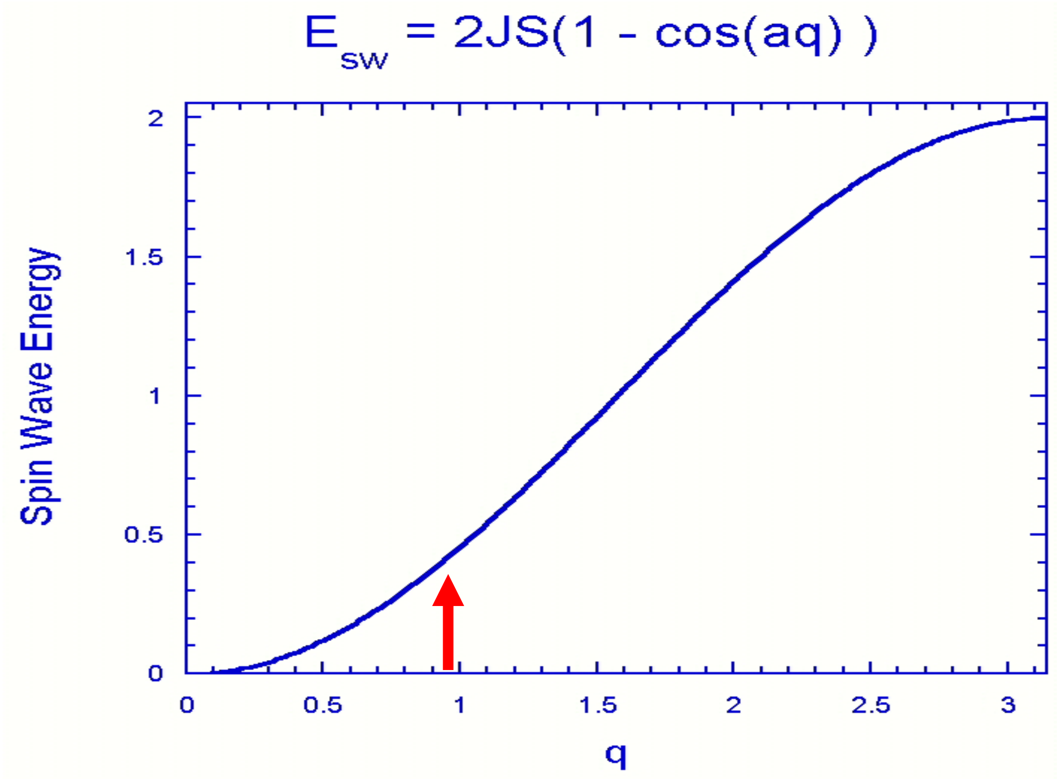


E. Granado, C. D. Ling, J. J. Neumeier, J. W. Lynn, and D. N. Argyriou, Phys. Rev. B**68**, 134440 (2003)

Magnetoresistance



Excitations

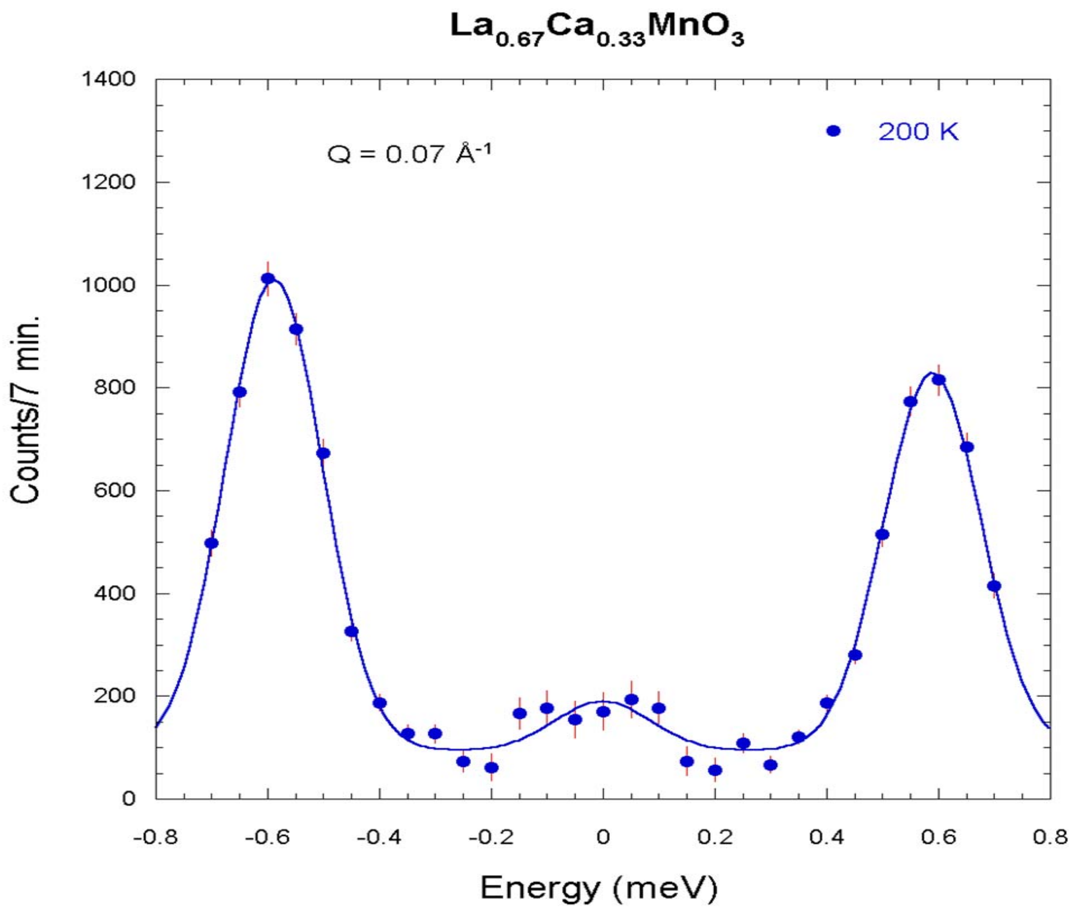


$$E_{sw} = 2JS(1 - \cos(aq)) \approx \Delta + D(T)q^2$$

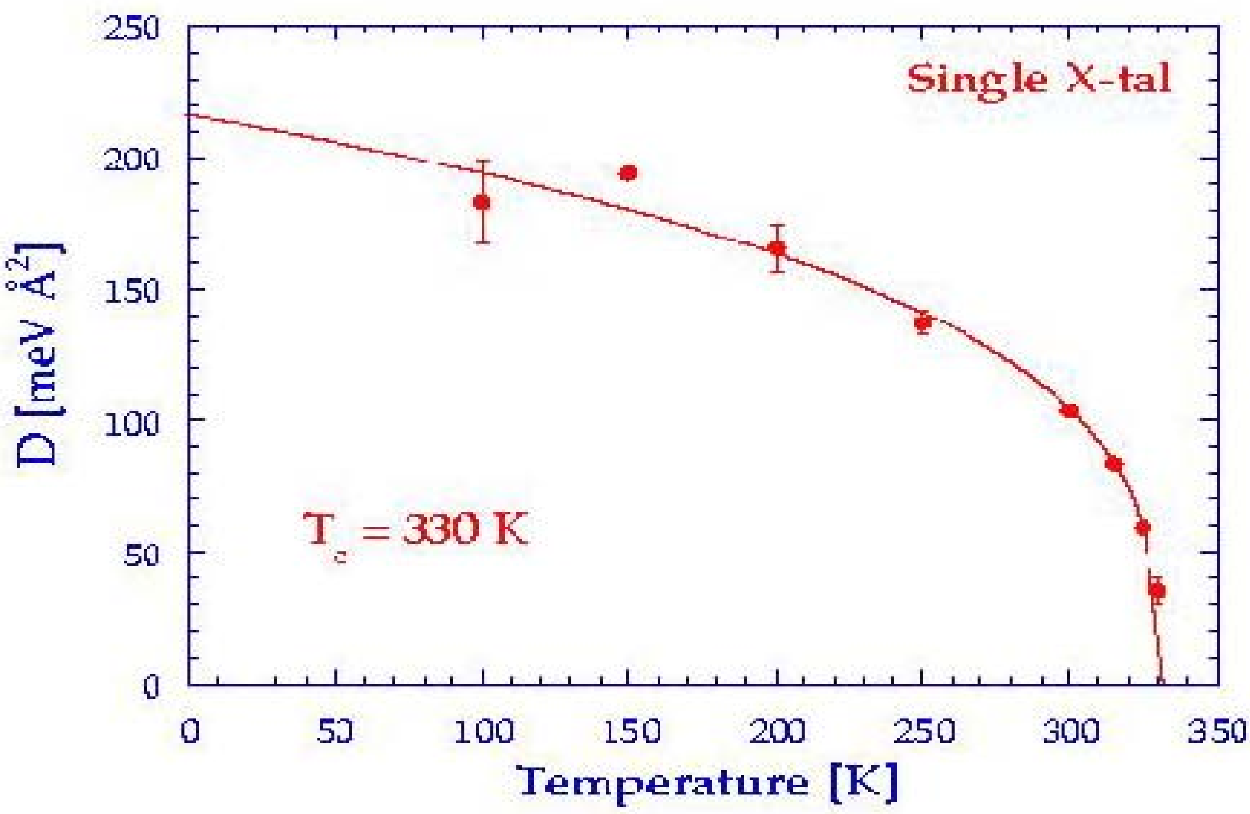
$$D(T) \sim M(T)$$

$$\Gamma \sim T^2 q^4$$

Spin Dynamics
$E_{SW} = D(T)\, Q^2$

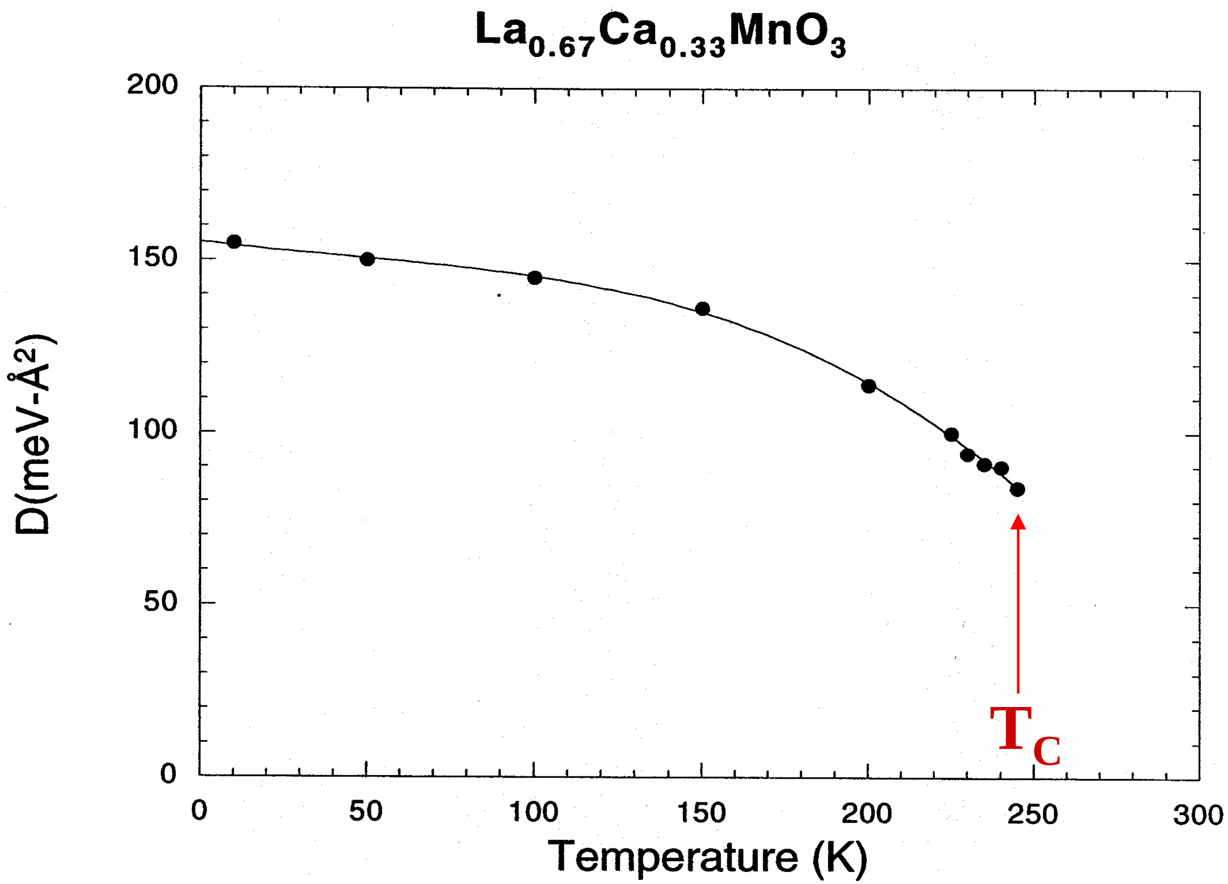


$La_{0.8}Ba_{0.2}MnO_3$ *D(T)*



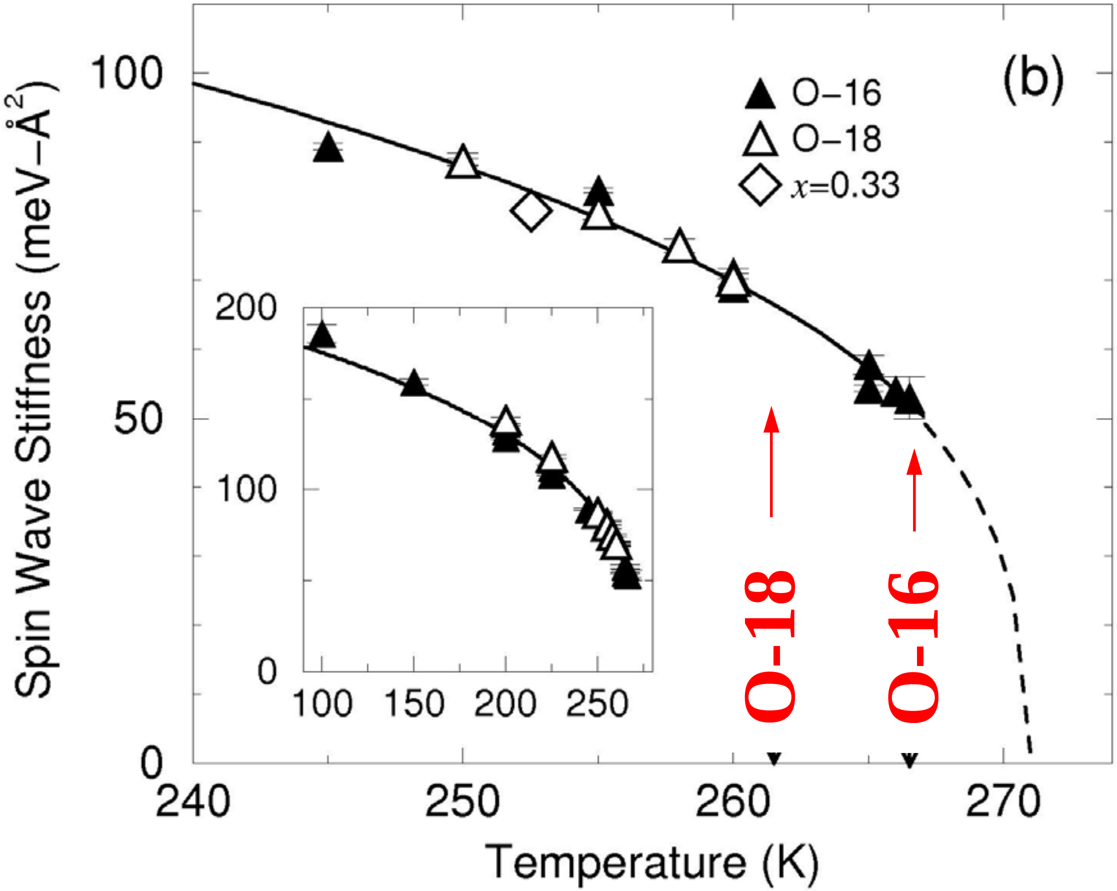
$$E_{SW} = D(T)\, Q^2$$

$La_{0.67}Ca_{0.33}MnO_3$



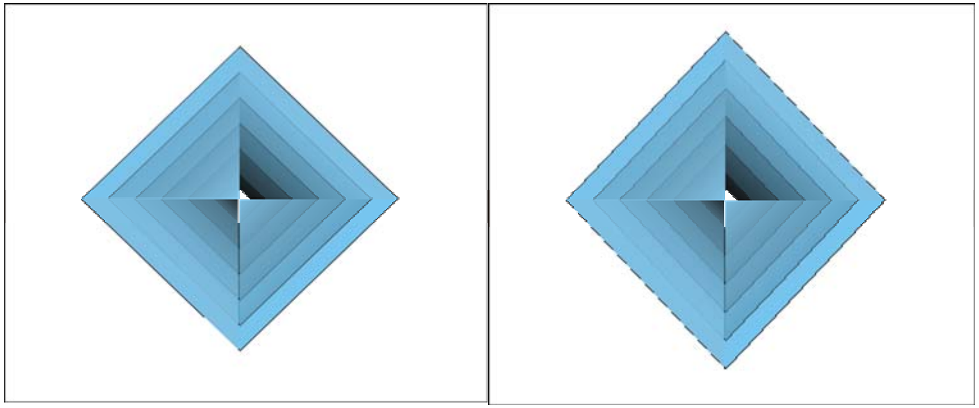
J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J. L. Peng, and Z. Y. Li, Phys. Rev. Lett. **76**, 4046 (1996).

$La_{5/8}Ca_{3/8}MnO_3$
Isotope Dependence of Spin Stiffness

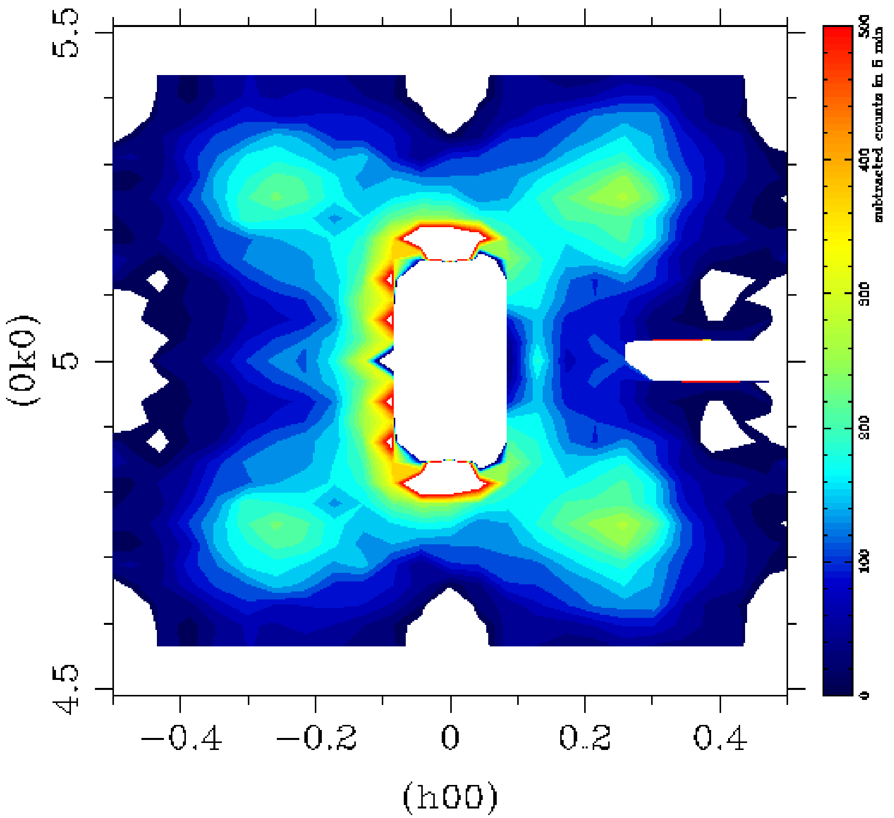


C. P. Adams, J. W. Lynn, V. N. Smolyaninova, A. Biswas, R. L. Greene, W. Ratcliff, II, S-W. Cheong, Y. M. Mukovski, and D. A. Shulyatev, Phys. Rev. B**70**, 134414 (2004)

So there is coupling to the Lattice

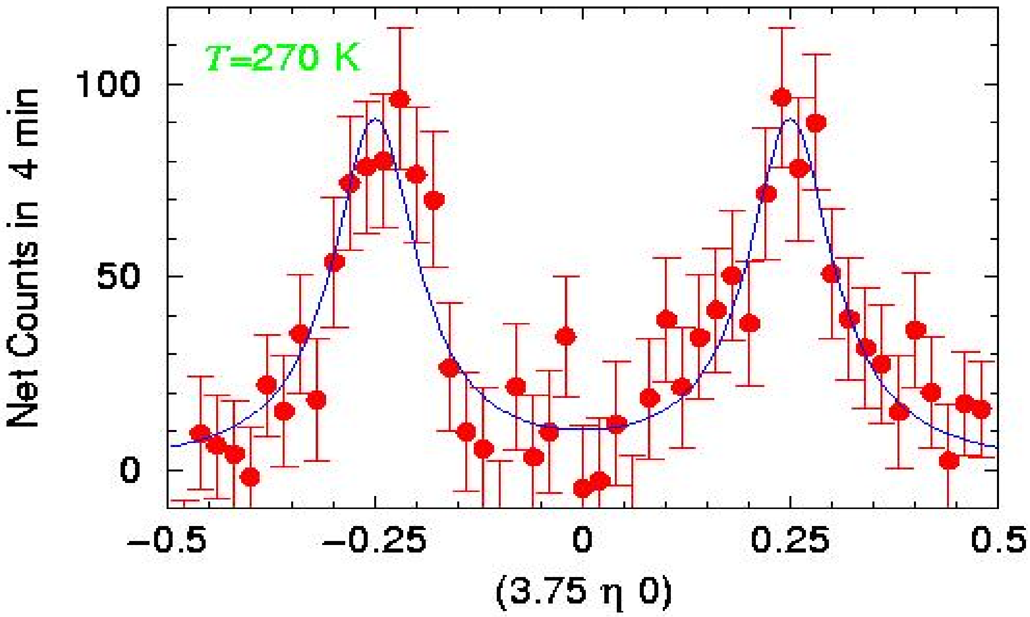


Nanoscale Correlations in CMR Manganites



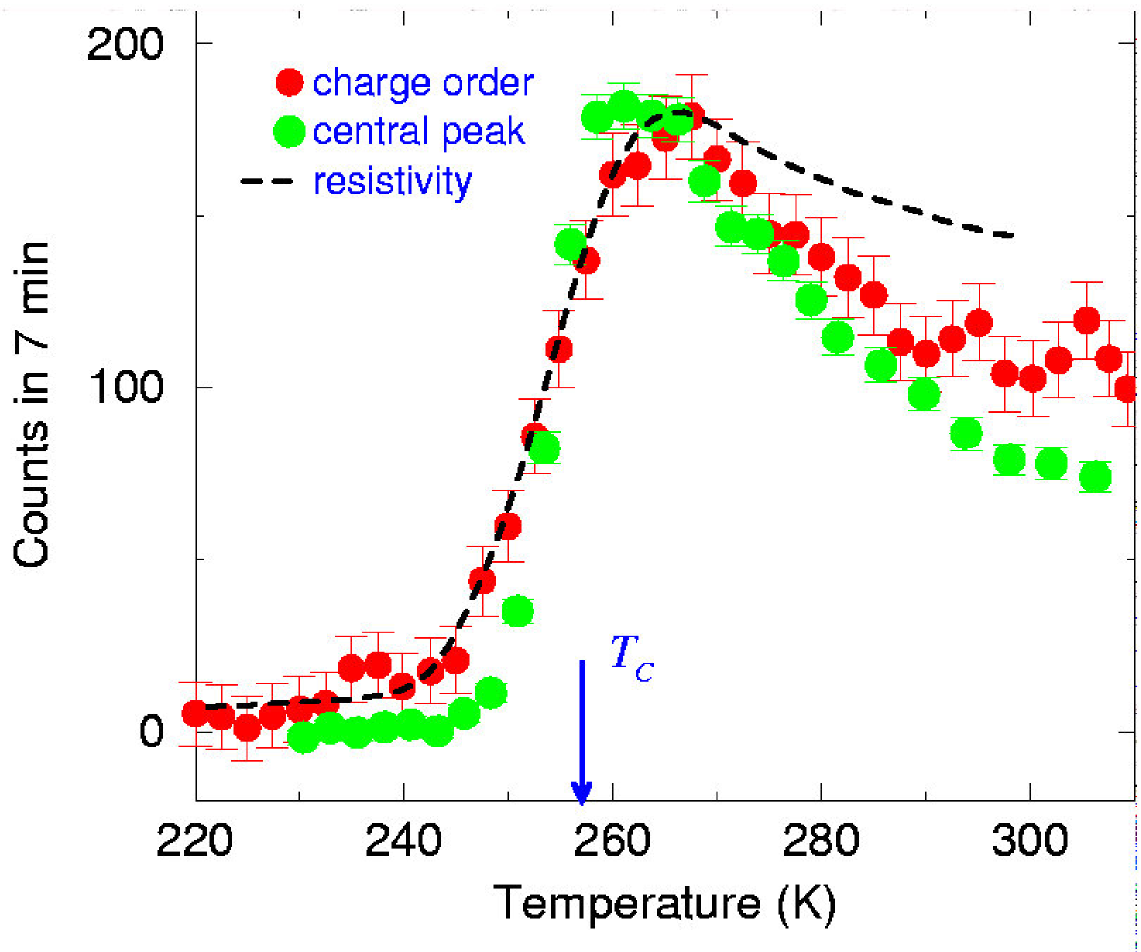
CE-type (1/4,1/4,0) peaks

Polaron Peaks

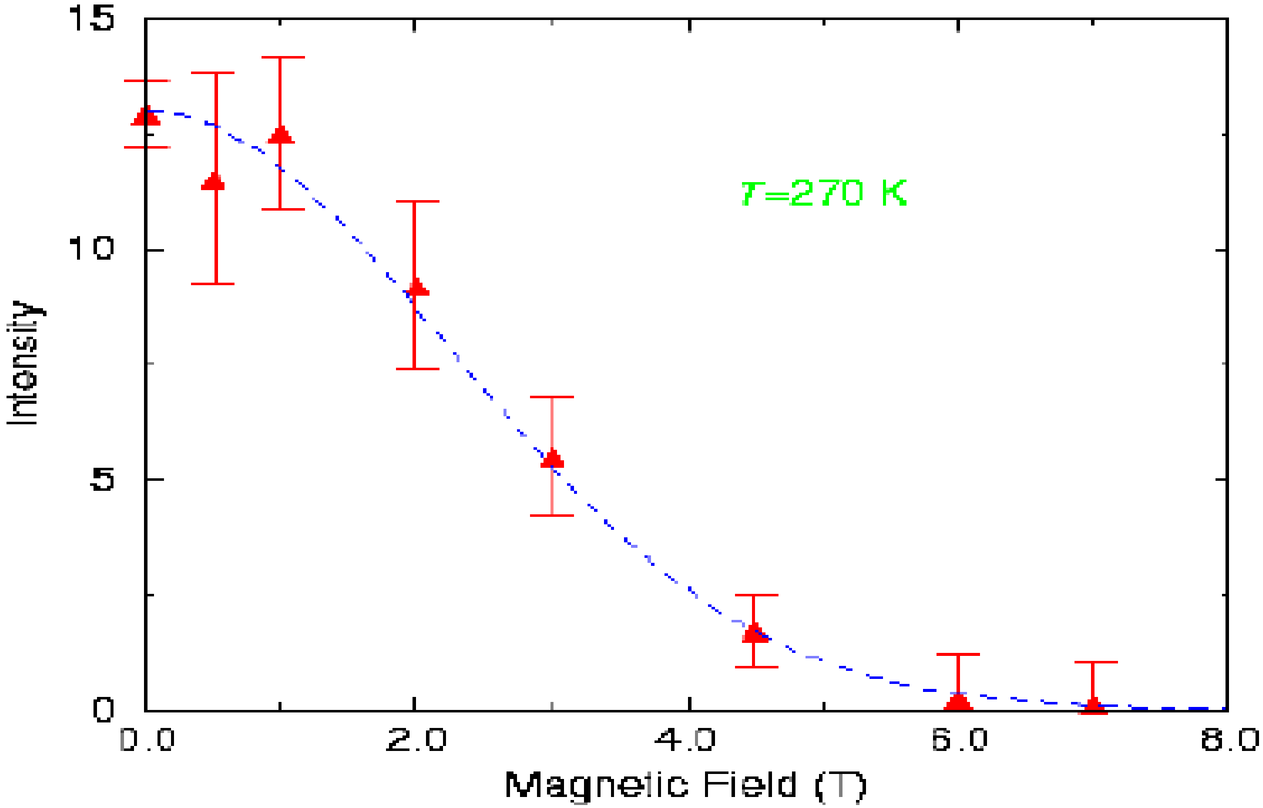


C. P. Adams, J. W. Lynn, Y. M. Mukovskii, A. A. Arsenov, and D. A. Shulyatev, Phys. Rev. Lett. **85**, 3954 (2000).

T dependence



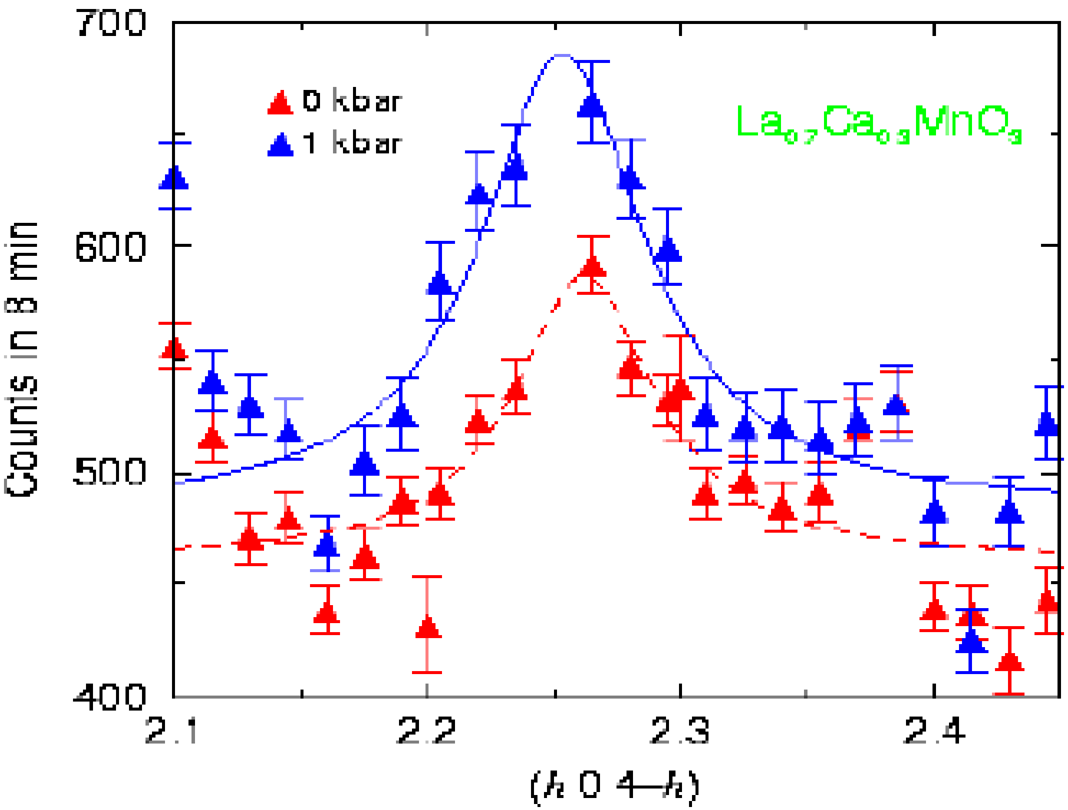
$La_{0.7}Ca_{0.3}MnO_3$ Field Dependence



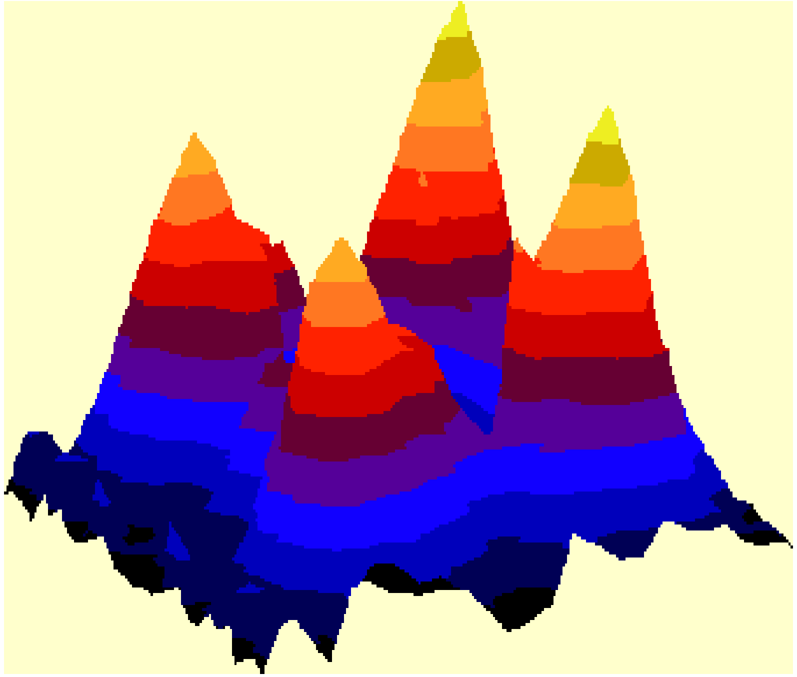
J. W. Lynn, C. P. Adams, Y. M. Mukovskii, A. A. Arsenov, and D. A. Shulyatev, J. Appl. Phys. 89, 6846 (2001).

NCNR

$La_{0.7}Ca_{0.3}MnO_3$ stress

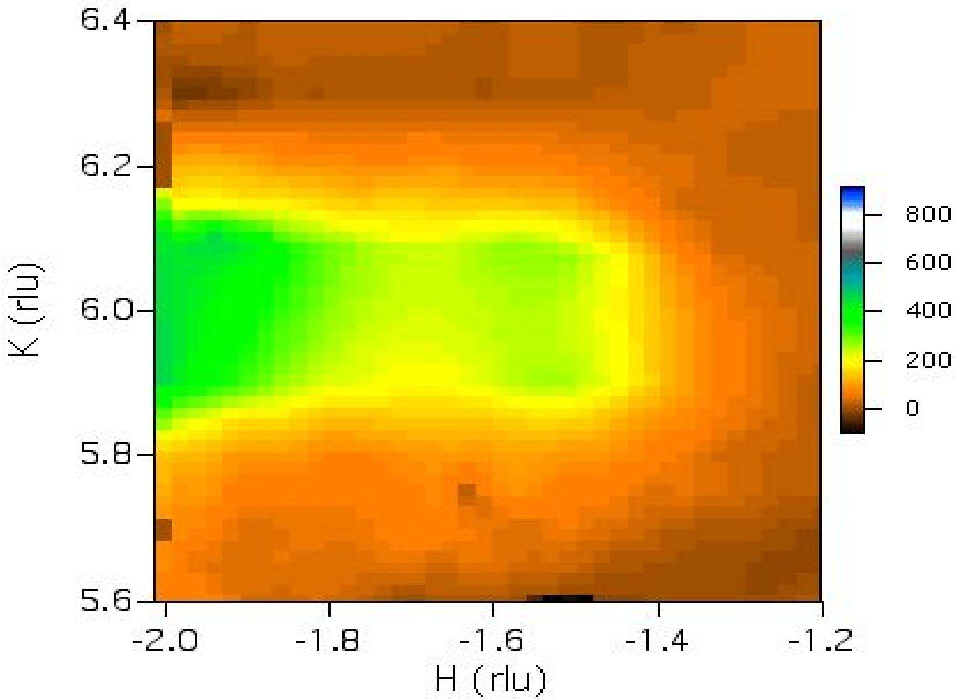


Polarons "Mountains" in CMR Manganites



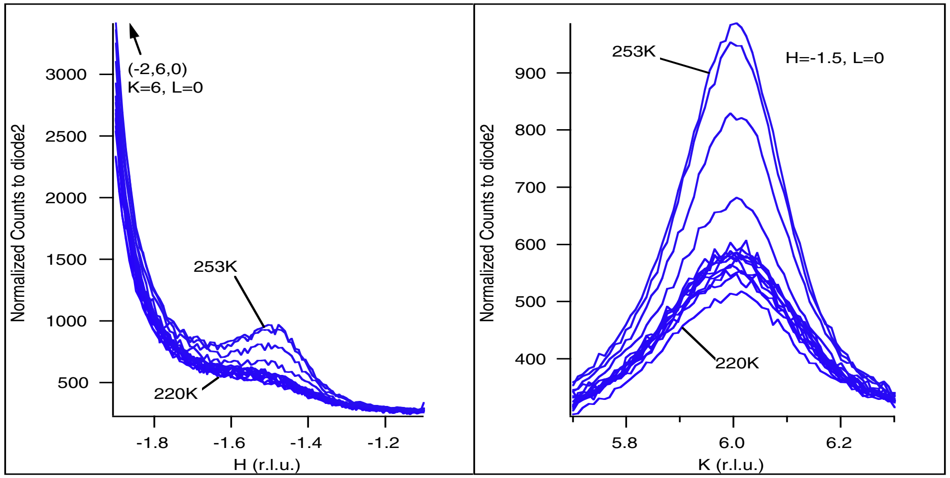
$La_{0.7}Ca_{0.3}MnO_3$
X-ray Diffuse Map

I(300 K - 220 K)



Advanced Photon Source (BESERC)
115 keV

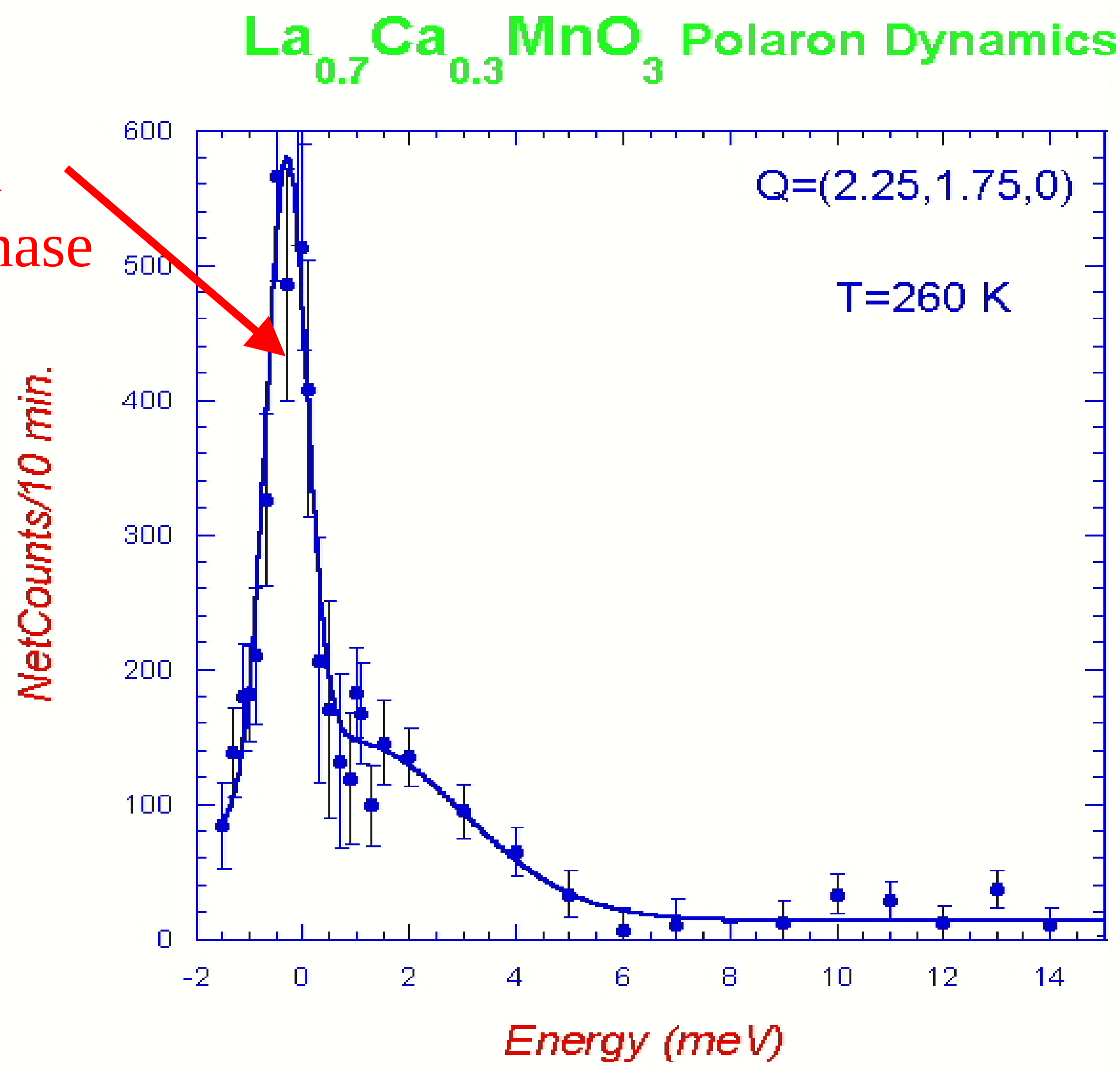
X-ray Diffuse Scattering



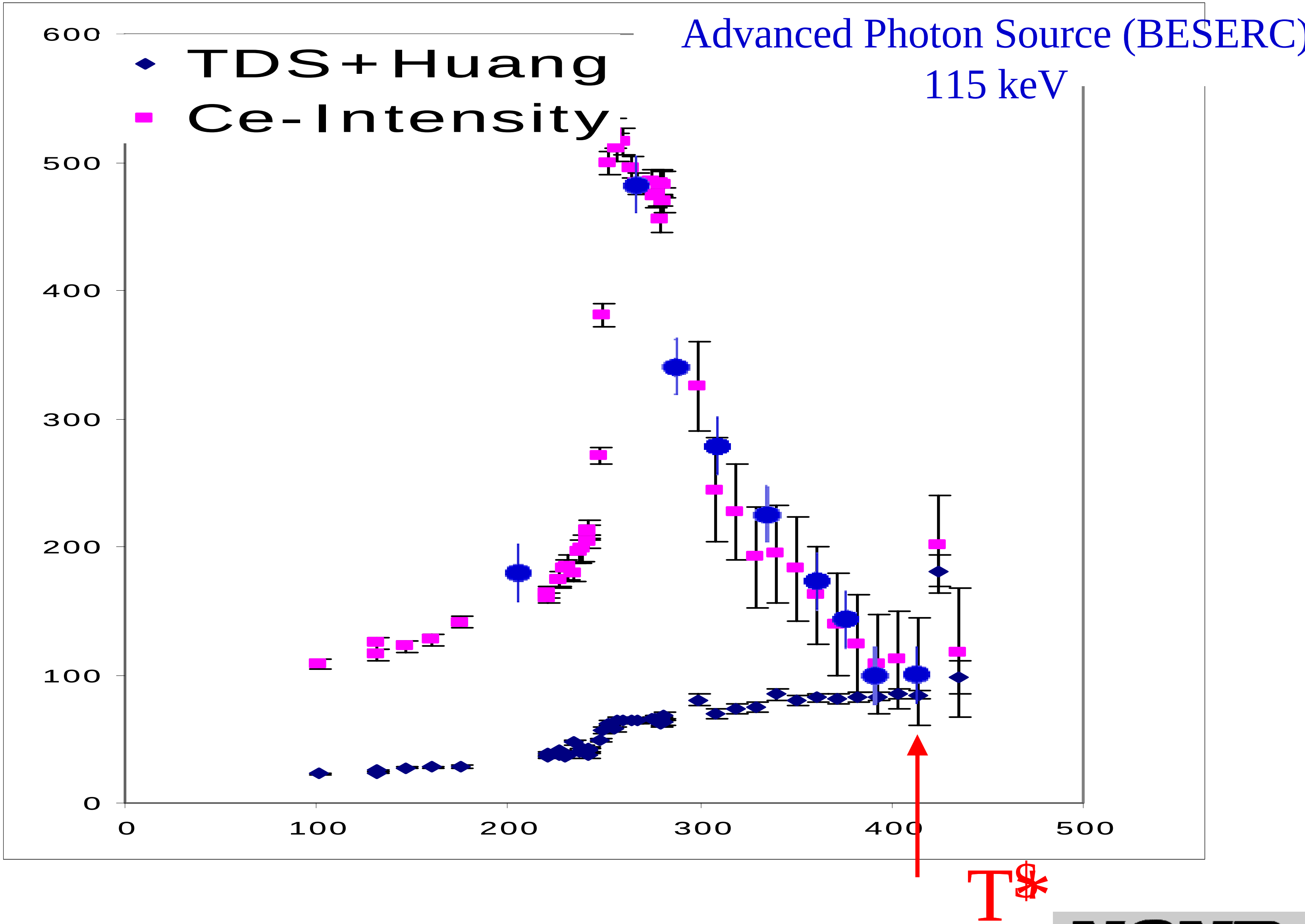
APS BESERC beam line
(with D. Argyriou, Y. Ren, Y. Mukovskii)

Polaron Dynamics

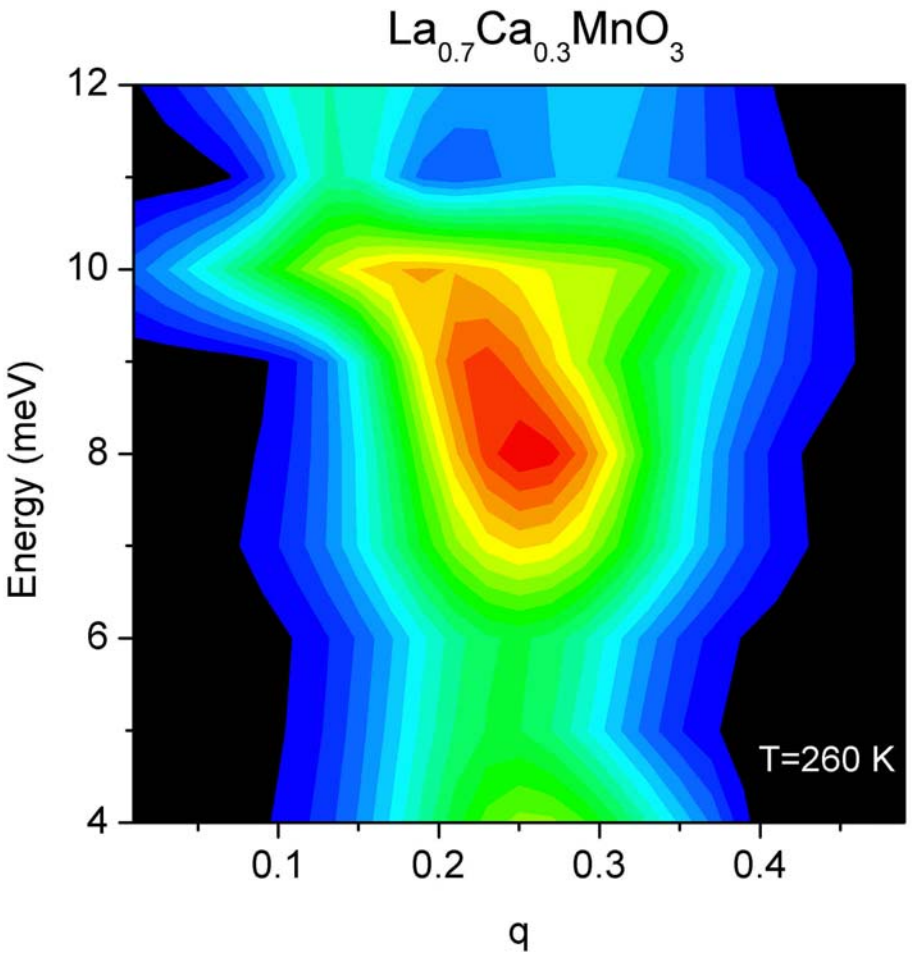
Elastic Peak
=> Glass phase

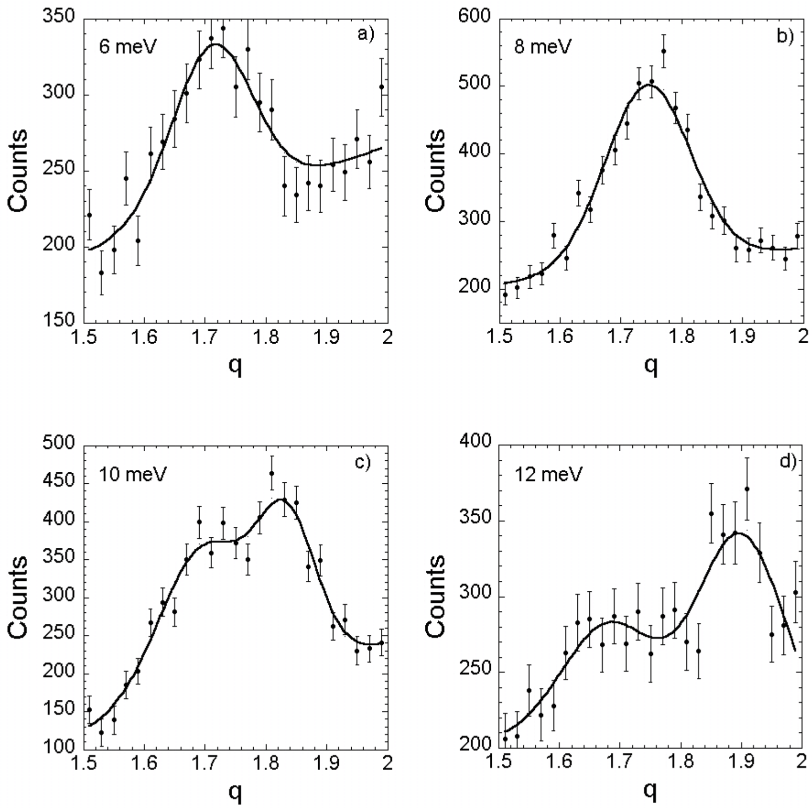


X-ray Diffuse Scattering



Polaron Dynamics

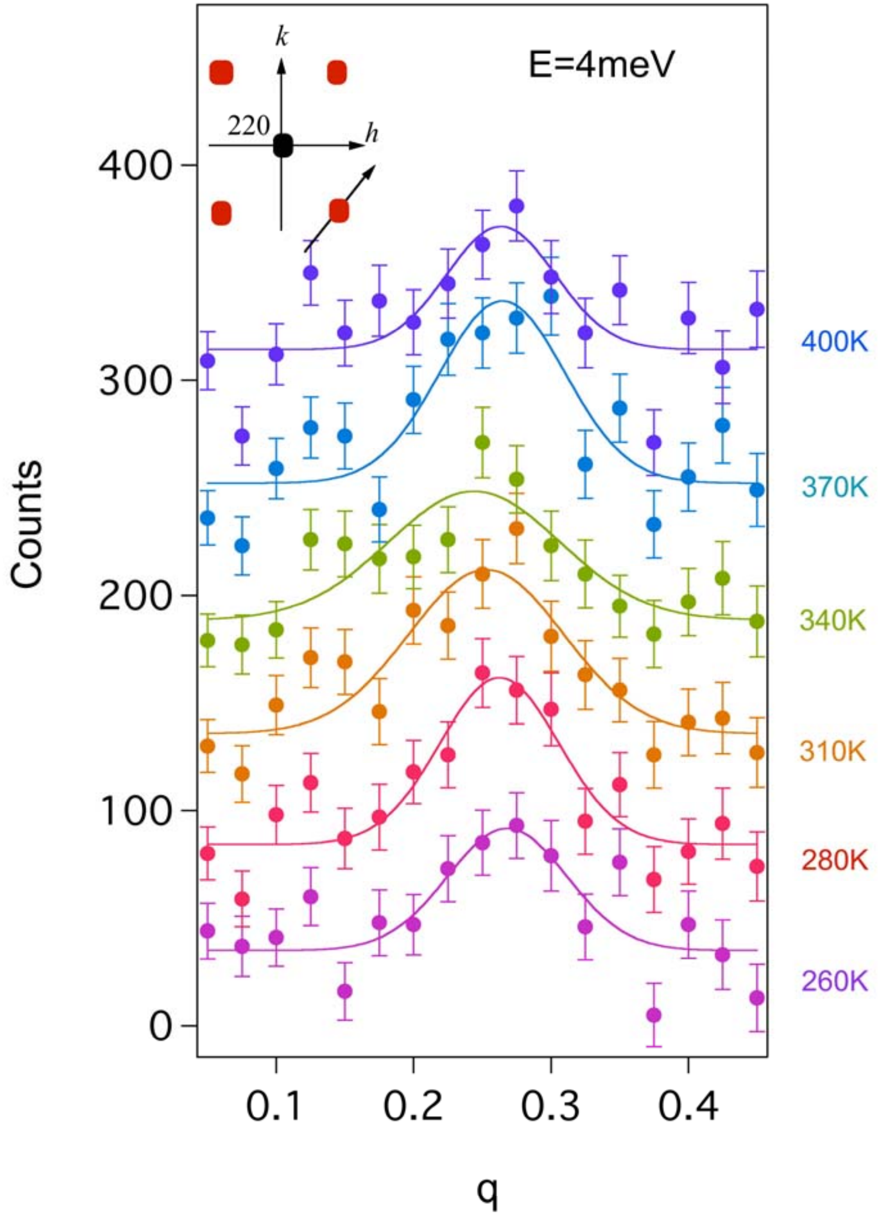




J. W. Lynn, D. N. Argyriou, Y. Ren, Y. Chen, Y. M. Mukovskii, and D. A. Shulyatev, Phys. Rev. B**76**, 014437 (2007)

NCNR

T dependence



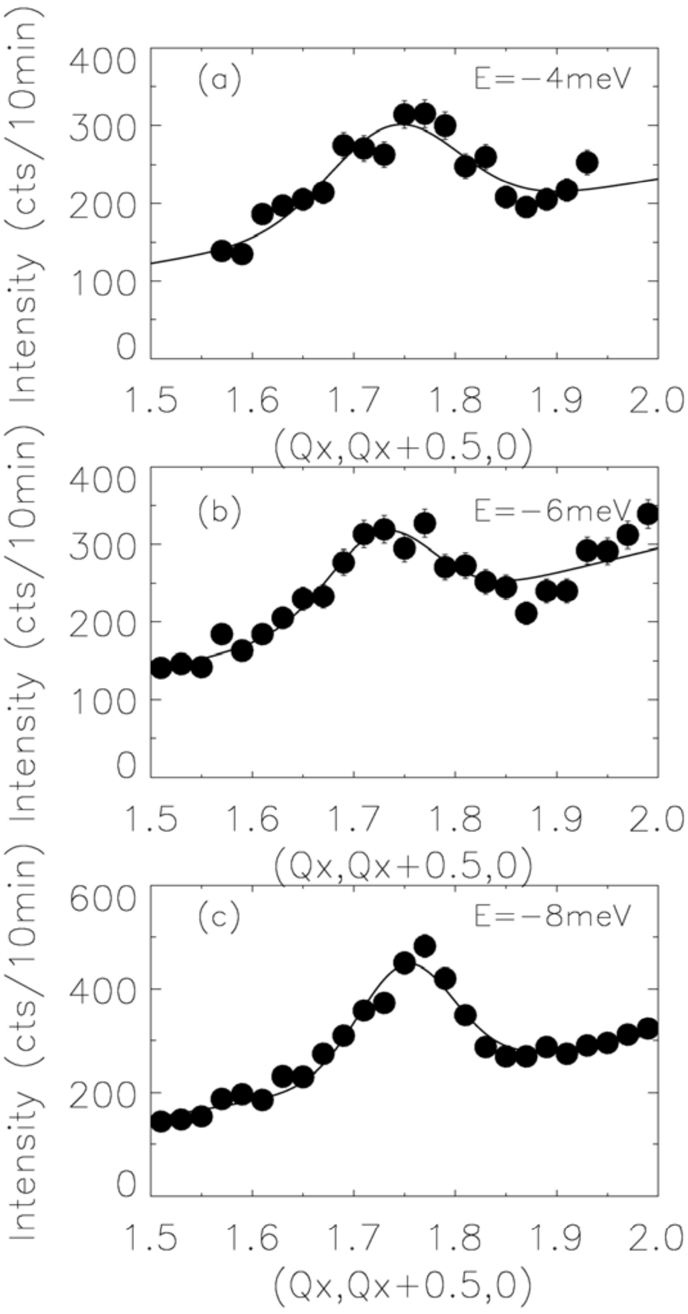
Polaron Dynamics above the Glass Transition

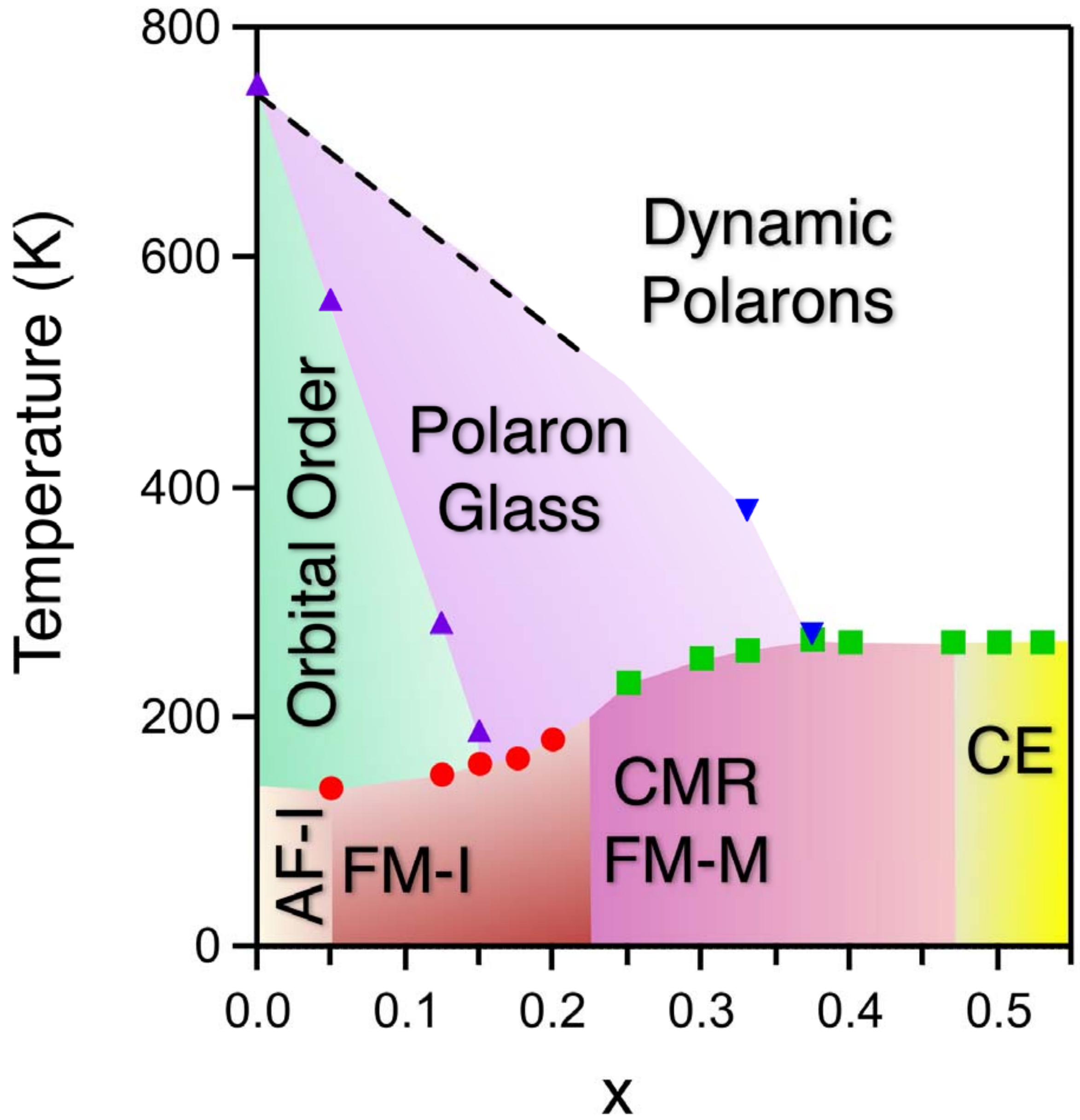
$La_{0.68}Ba_{0.32}MnO_3$

T_C=330 K

Polaron Dynamics without the Glass Transition

T=360 K





J. W. Lynn, D. N. Argyriou, Y. Ren, Y. Chen, Y. M. Mukovskii, and D. A. Shulyatev, Phys. Rev. B**76**, 014437 (2007)

NCNR

Nanoscale Correlations in Oxides

- Manganites
  - Spin, Charge, & Lattice coupled
  - *Highly* correlated electrons
  - Competing States—Delicate Balance
  - Ferromagnetic metal ⇔Polaron Glass ⇔ Polaron Fluid
- Relaxor Ferroelectrics
  - $PbTiO_3$
  - $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN)
  - Nanopolar ferroelectric droplets
- Cuprates and Nickelates
  - Charge Stripes and Spin Stripes

Multiferroics

Multiferroics are rare. Why??

- Ferroelectrics (like $BaTiO_3$, $PbTiO_3$, …)
  - Ferroelectricity comes about from atomic displacements. For standard ferroelectrics this originates from the bonding of empty d-electron orbitals with oxygen p-orbitals. Since the d-orbitals are empty, there is no magnetism.
- Need to separate the ferroelectricity and magnetism, but then, are they coupled? How?
- The interest is both fundamental, and technological (the hope is to control magnetic domains with an electric field)

Multiferroic Topics

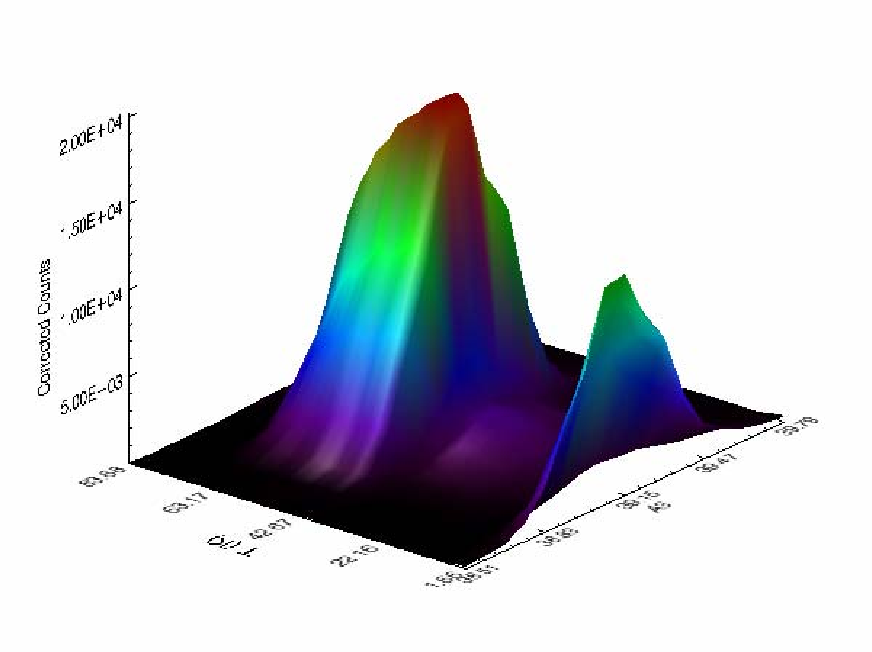
- $HoMnO_3$ and $TbMnO_3$ multiferroelectrics
  - Magnetic structure coupled to ferroelectricity
  - Low-d Mn spin dynamics
  - *Owen Vajk, Michel Kenzelmann, S. Kim & Sang Cheong, Seth Jones, Collin Broholm, Brooks Harris*
- Na doping in $(Tb\text{-}Na)MnO_3$
  - *Wen-Hsien Li, et al.*
- Kagomé Staircase systems ($Co_3V_2O_8$, $Ni_3V_2O_8$)
  - *Ying Chen, Matt Woodward, Qing Huang, Nyrissa Rogado, Bob Cava*
  - *Amnon Aharony, Brooks Harris, Ora Entin-Wohlman, Taner Yildirim, Ivelisse Cabrera, Collin Broholm, Michel Kenzelmann*
- $DyMn_2O_5$, $Tb_3Fe_5O_{12}$
  - *Willaim Ratcliff, Clarina dela Cruz (Houston), Sang Cheong*
- $BiFeO_3$ Thin Films & Single Crystals
  - *William Ratcliff, Julie Borchers, Valery Kiryukin, et al.*
- $CuFeO_2$ Multiferroic, 2D triangular magnet
  - *Feng Ye, Yeng Ren, Jaime Fernandez-Baca,Pengcheng Dai, Tsuyoshi Kimura*
- $LiMnPO_4$ Magnetic Structure and Spin Dynamics
  - *Jiying Li, Tian Wei, David Vaknin, Ying Chen*
- BSZFO hexaferrite ($Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$)
  - *Guanyong Xu, Steve Shapiro, et al.*

Magnetism in Hexagonal Ferroelectric $HoMnO_3$

Ferroelectric at 875 K (Ho sublattice)
Magnetic at 72 K (Mn)
Magnetic at 8 K (Ho)

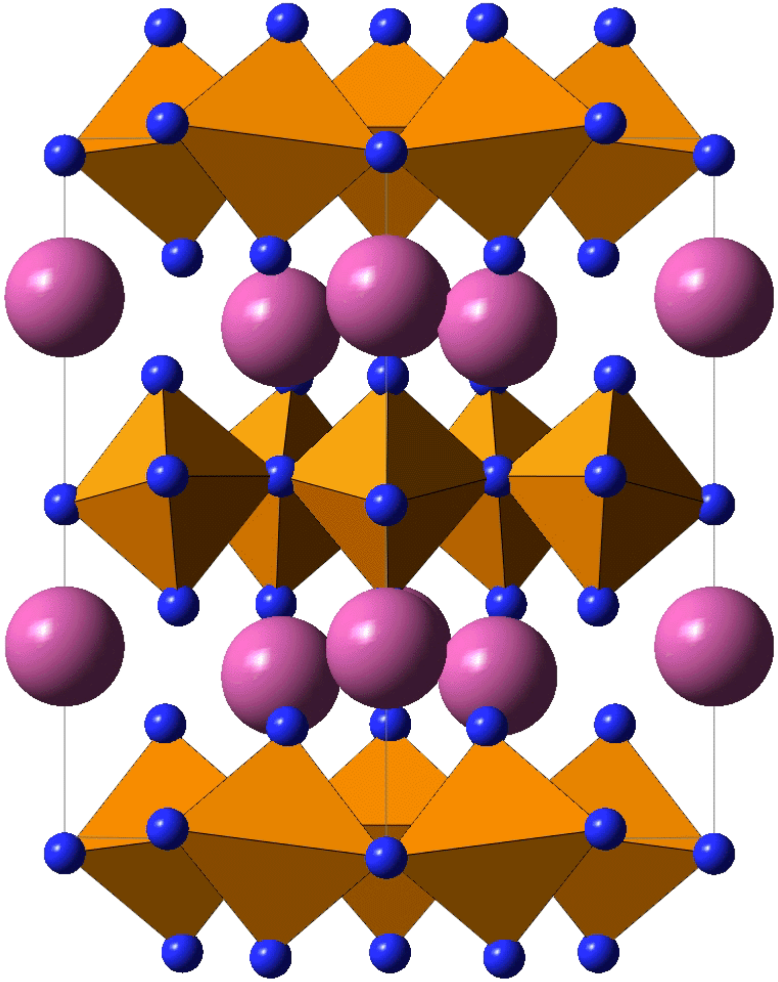
O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim and S.-W. Cheong, Phys. Rev. Lett. **94**, 087601 (2005);

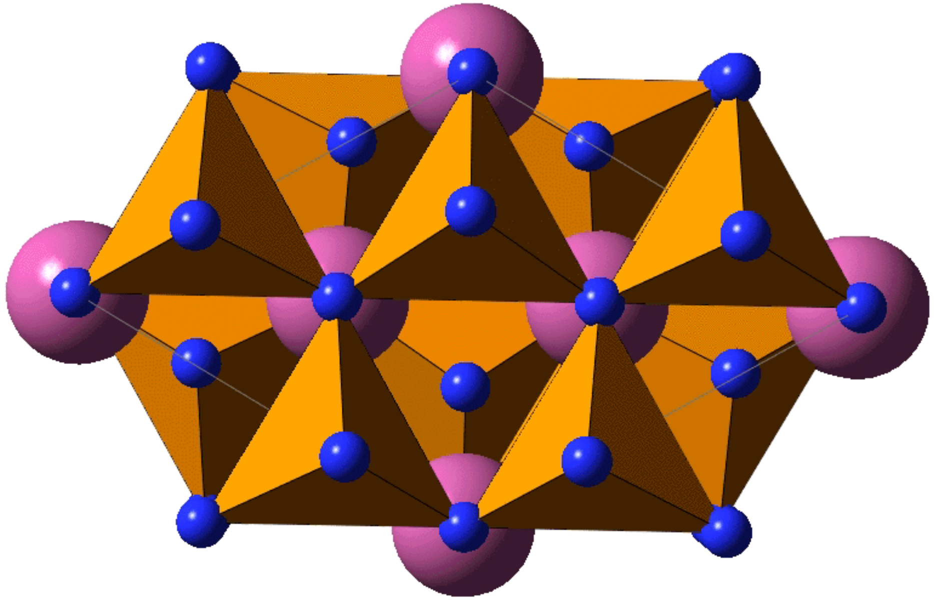
J. Appl. Phys. **99**, 08R301 (2006)



NCNR

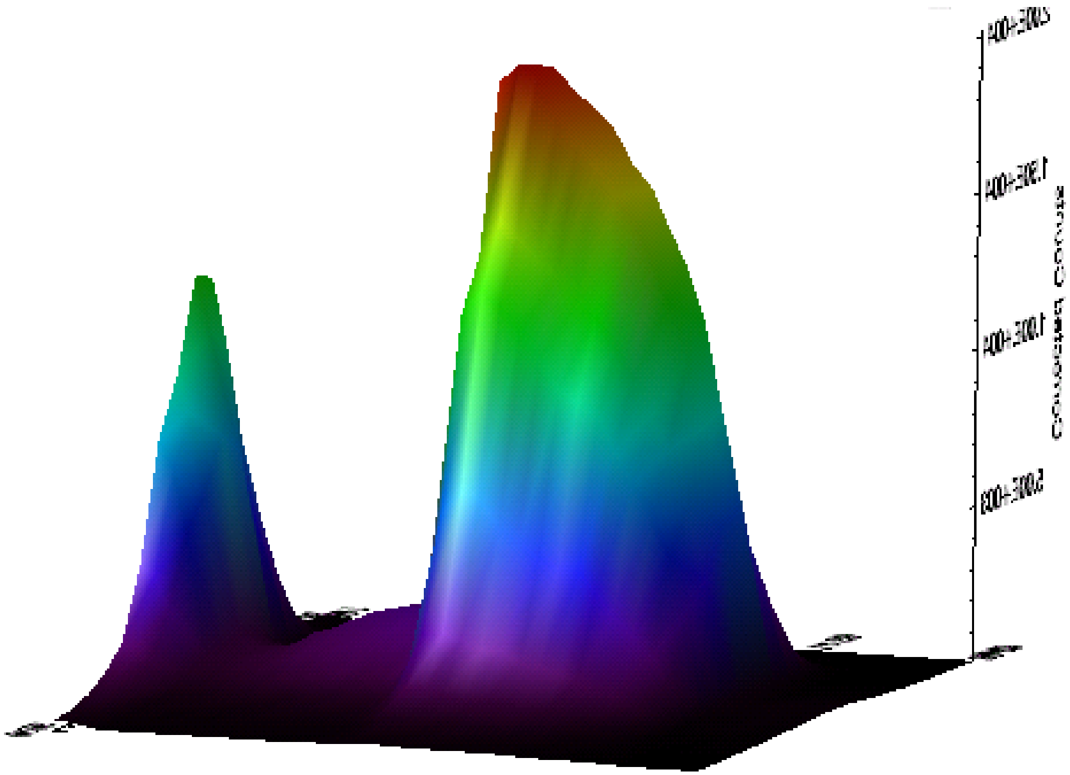
Structure of Hexagonal $HoMnO_3$





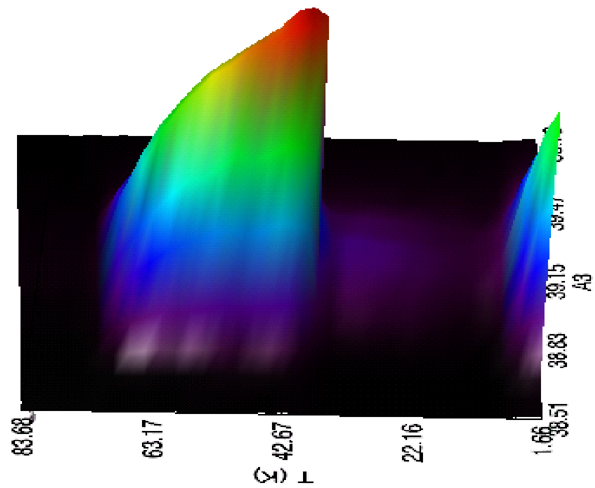
Mn^{3+} ions form triangular lattice.
2 sheets per unit cell, offset from each other

Magnetic Order Parameters

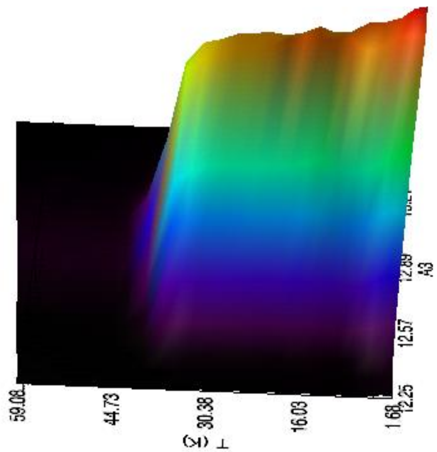


(101)

Magnetic Order Parameters

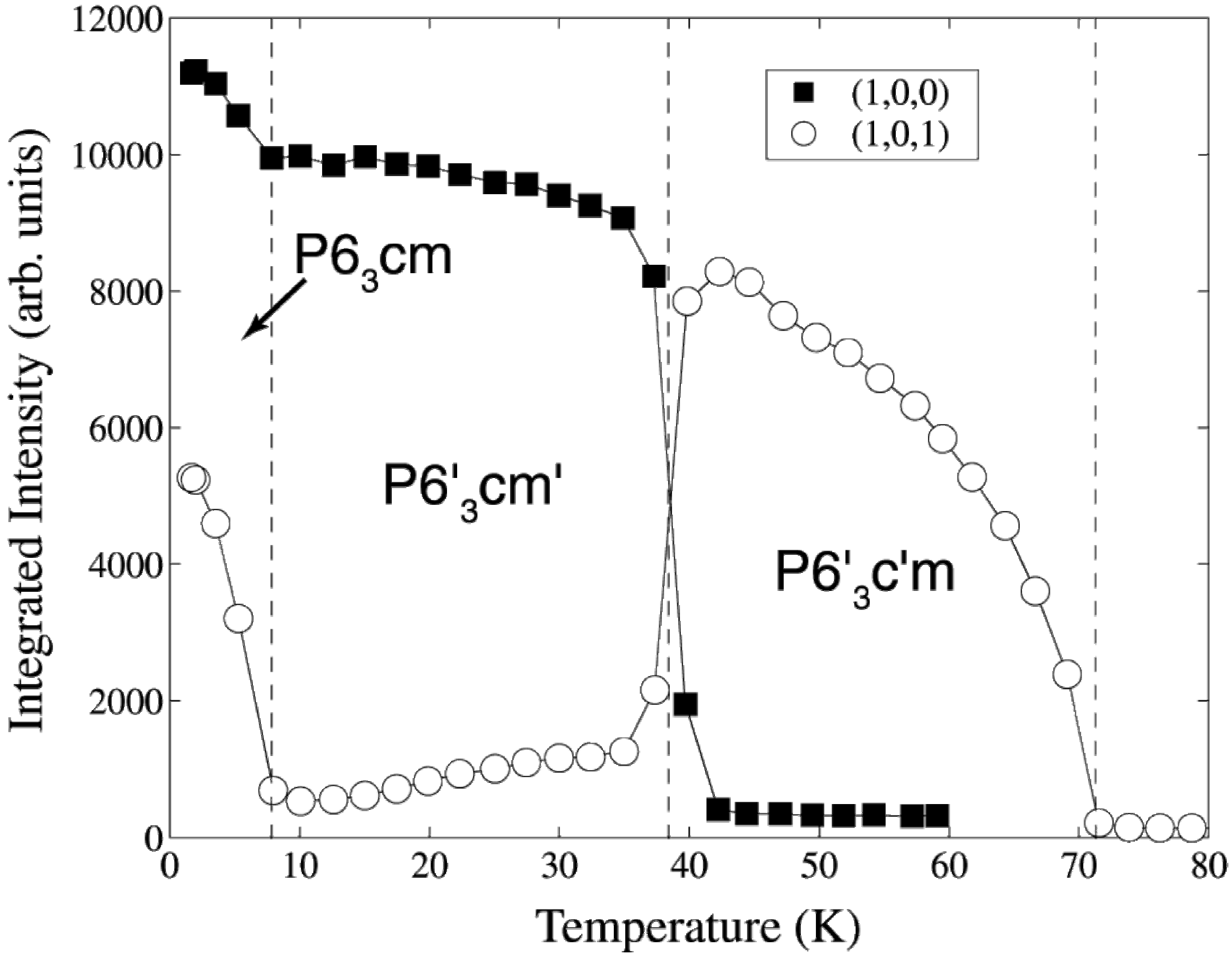


(101)



(100)

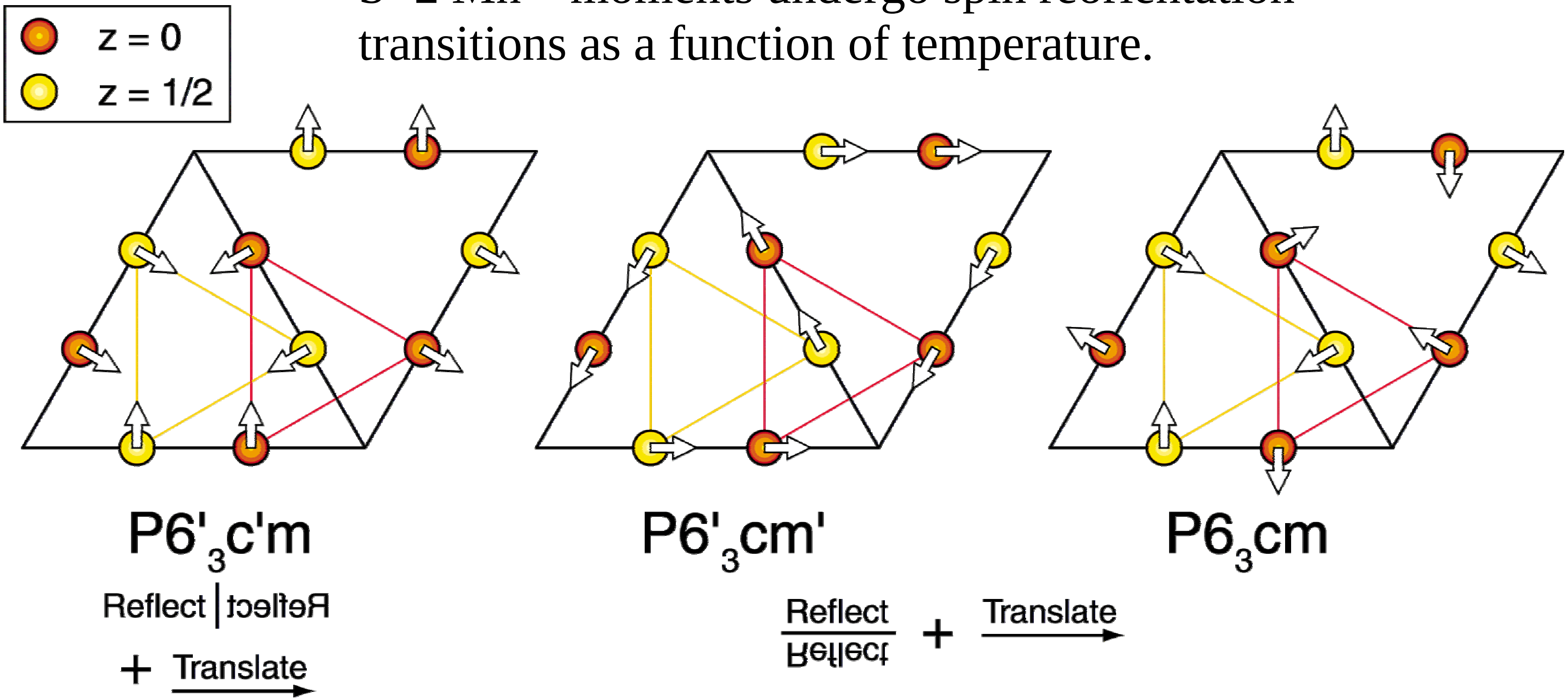
Phase Diagram from Neutron Scattering



Spin reorientation changes magnetic Bragg scattering intensities.

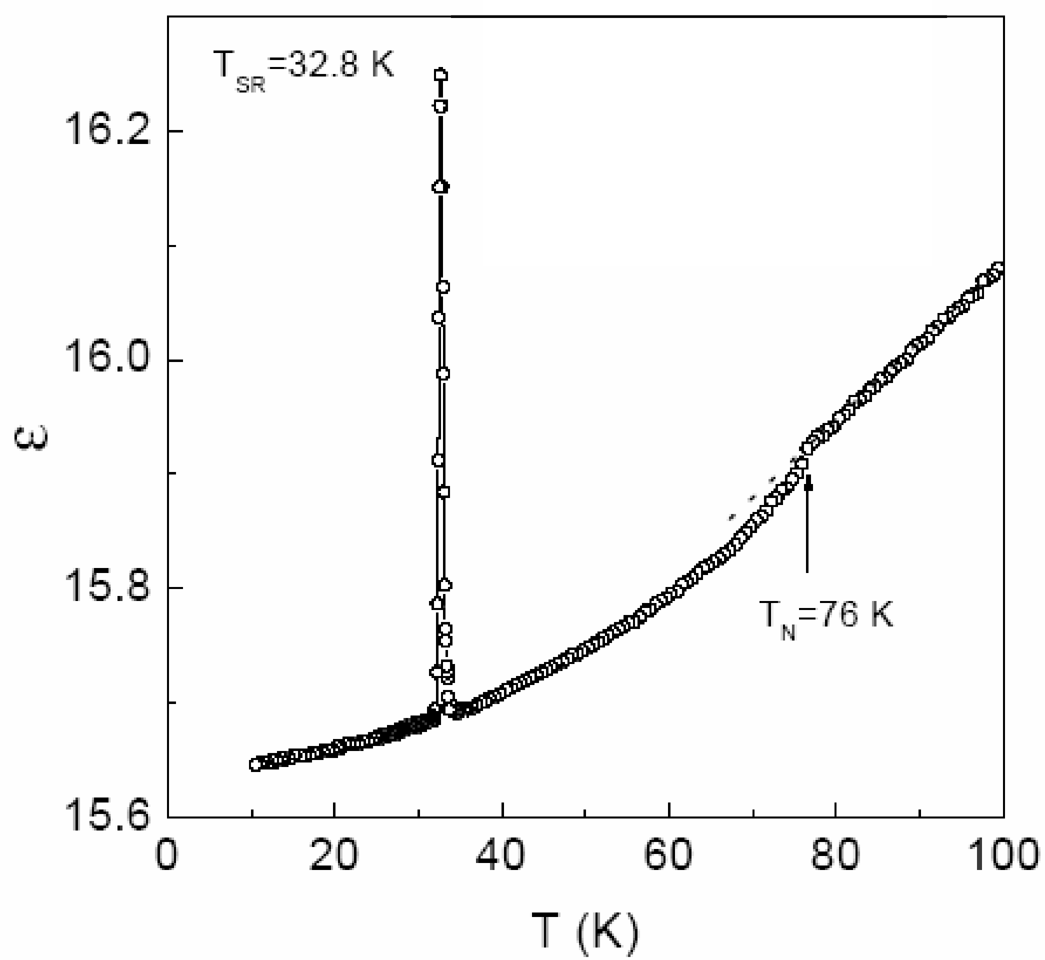
Magnetic Structure of Mn^{3+} Moments

S=2 Mn^{3+} moments undergo spin reorientation transitions as a function of temperature.



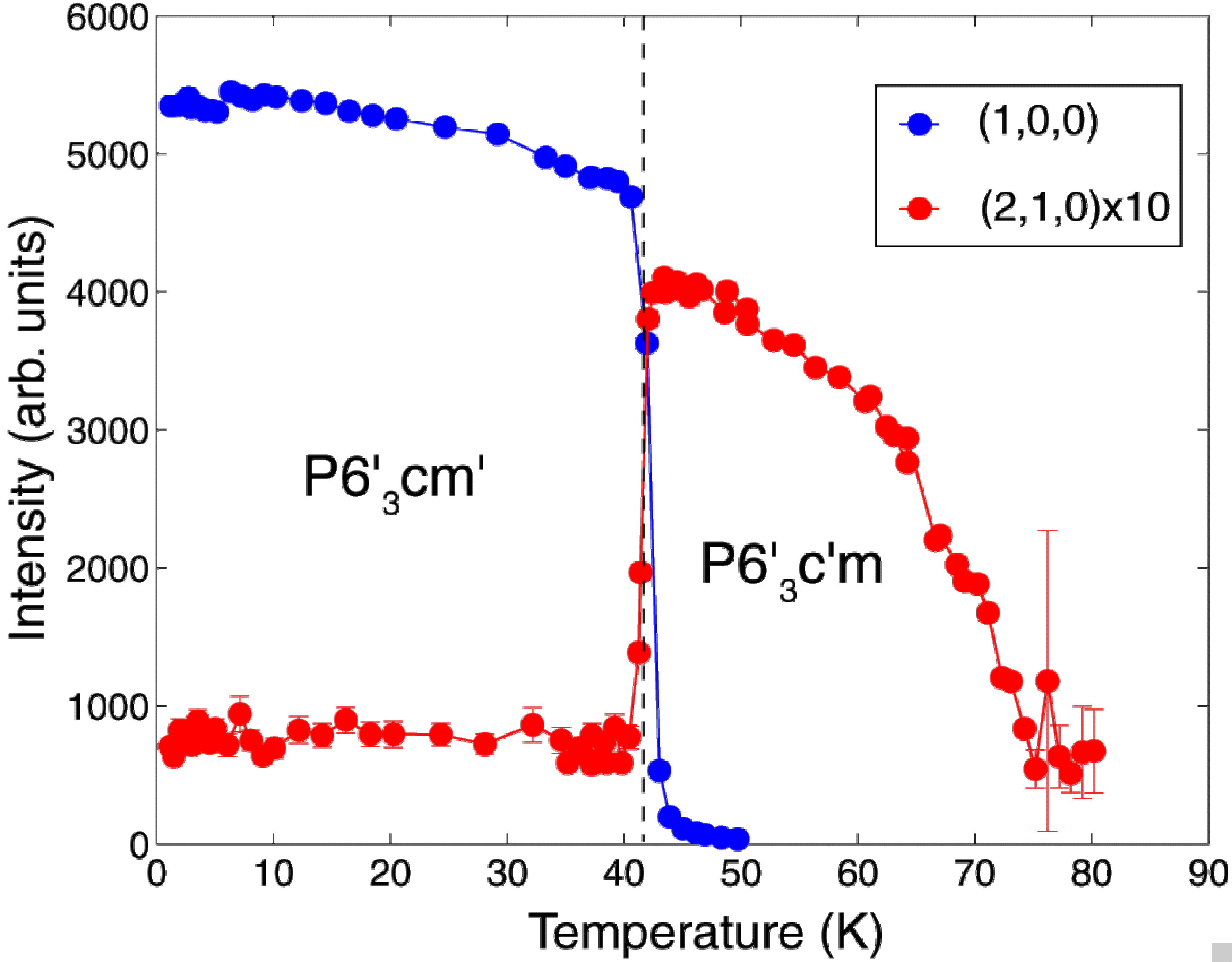
Neutron Powder studies: Lonkai, *et al.*, Appl. Phys. A**74**, S843 (2002).
Optical Spectroscopy: Fiebig, *et al.*, Phys. Rev. Lett. **84**, 5620 (2000).

Dielectric Response

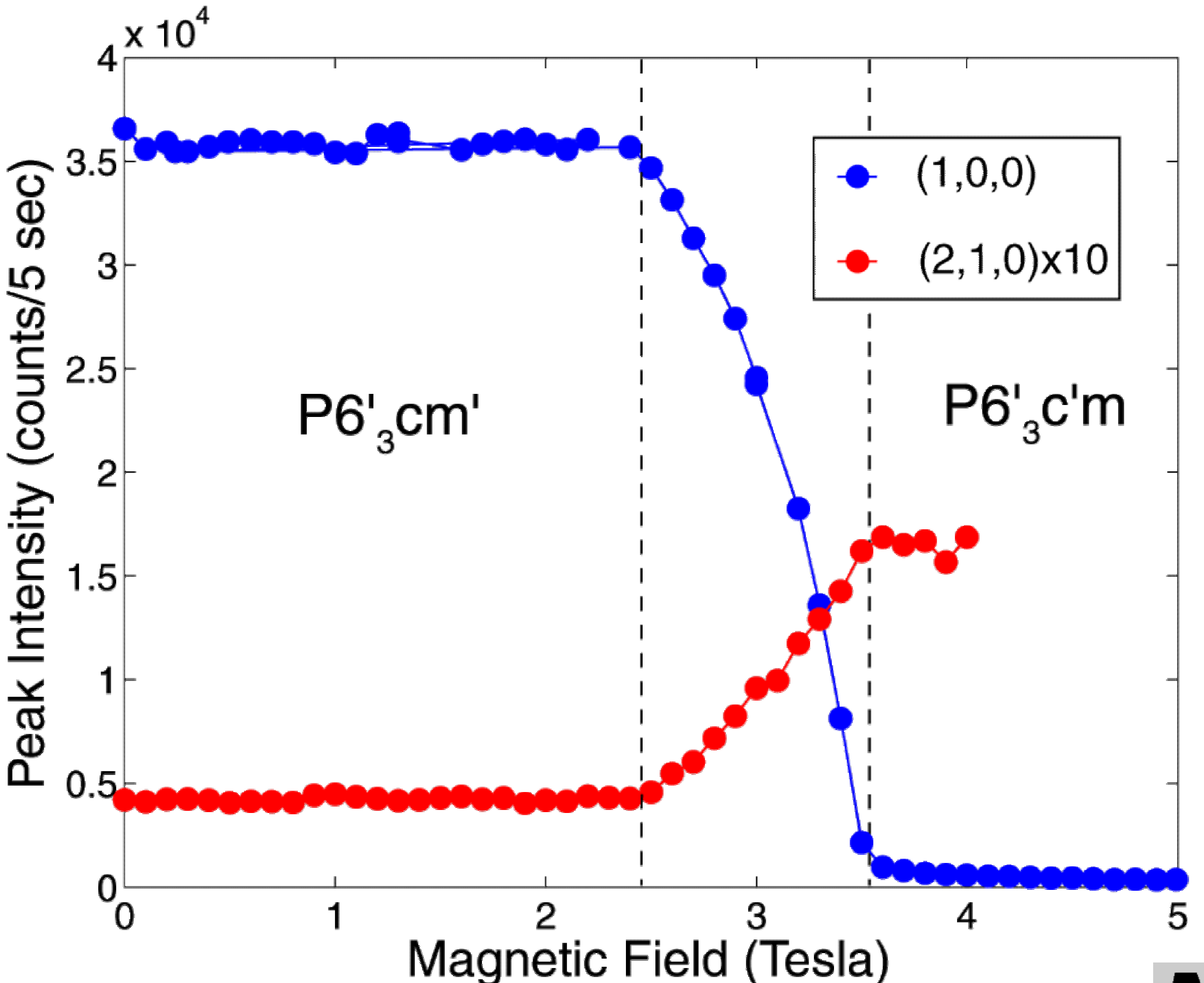


B. Lorenz, A. P. Litvinchuk, M. M. Gospodinov, and C. W. Chu, Phys. Rev. Lett. **92**, 087204 (2004).

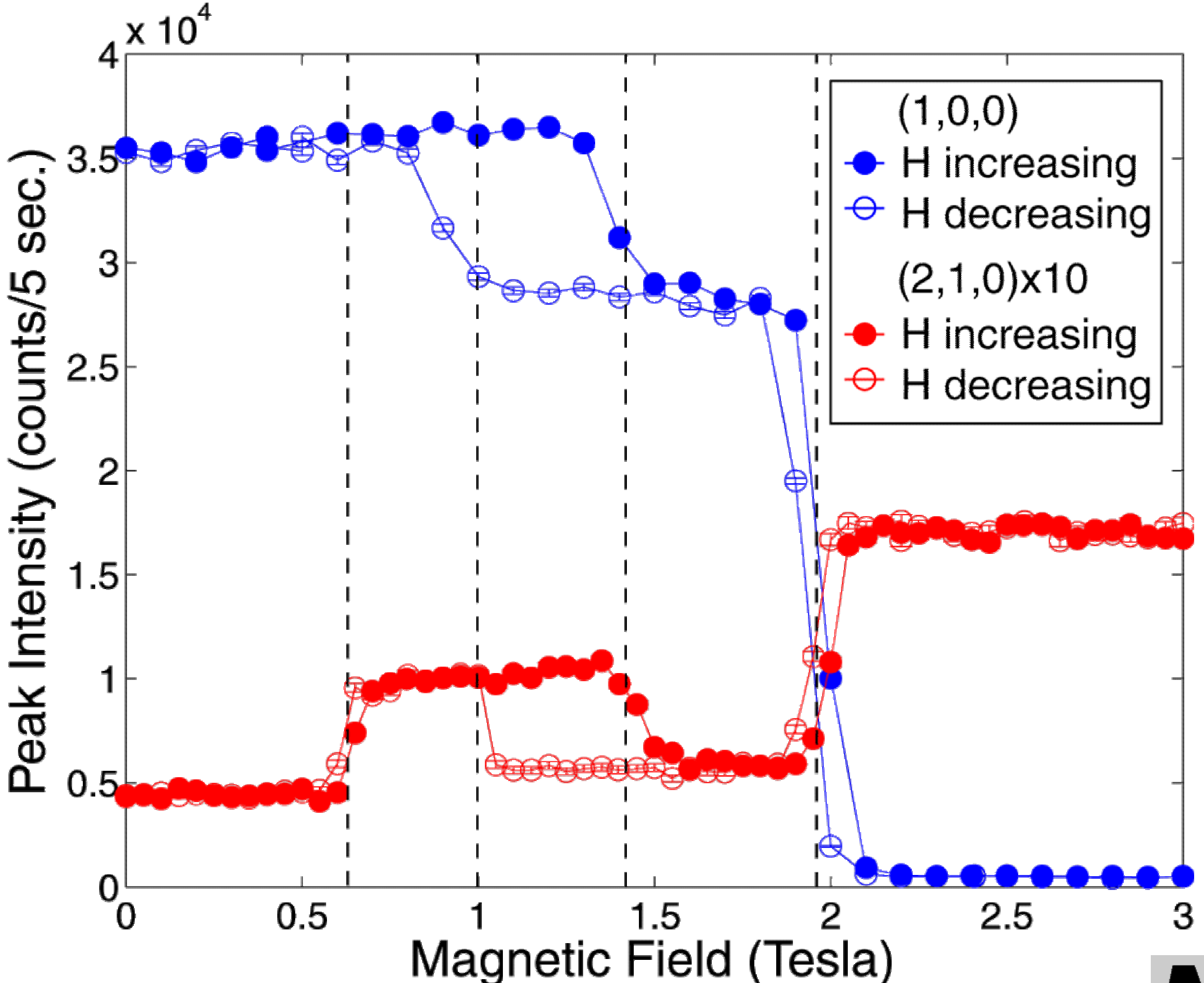
Magnetic Scattering in (H,K,0) Plane



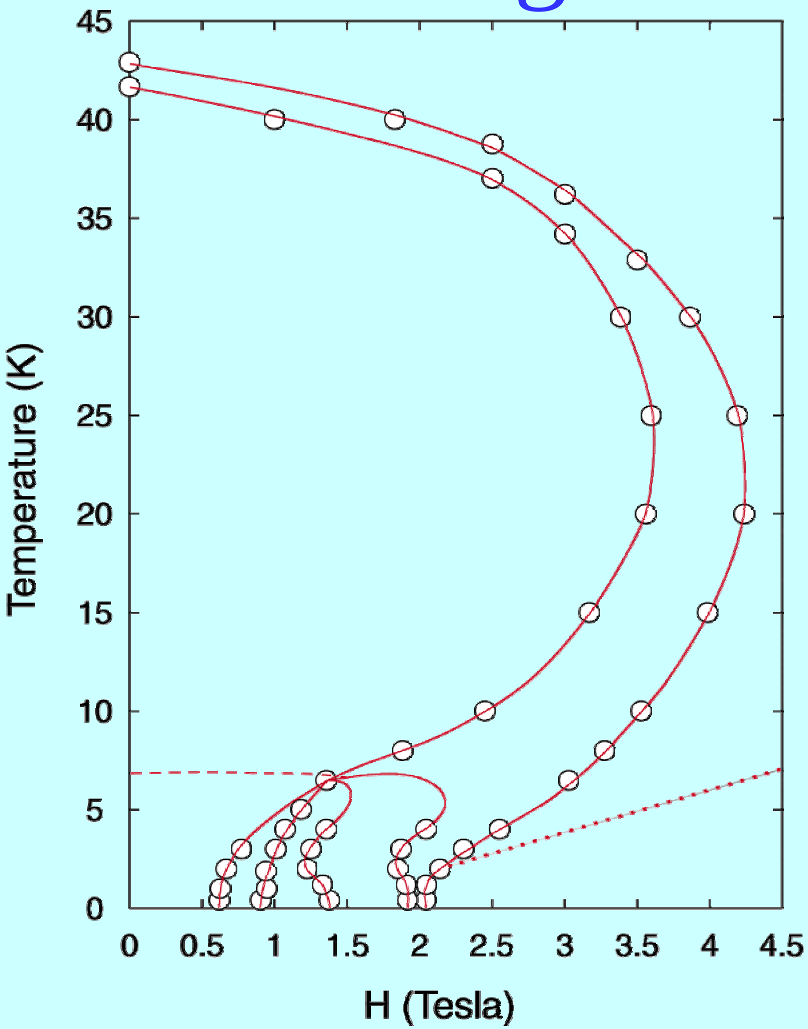
Magnetic Field Effect at 10K

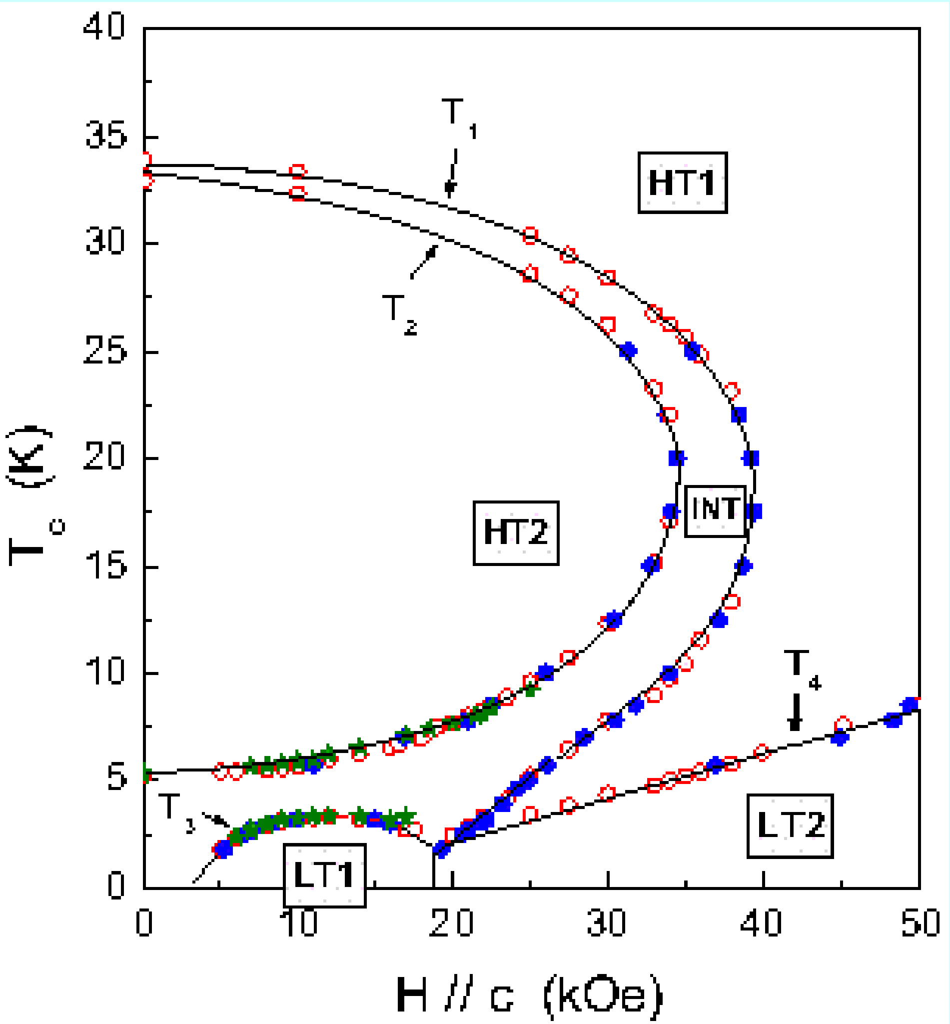


Magnetic Field Effect at ~0.4K



Magnetic Phase Diagram



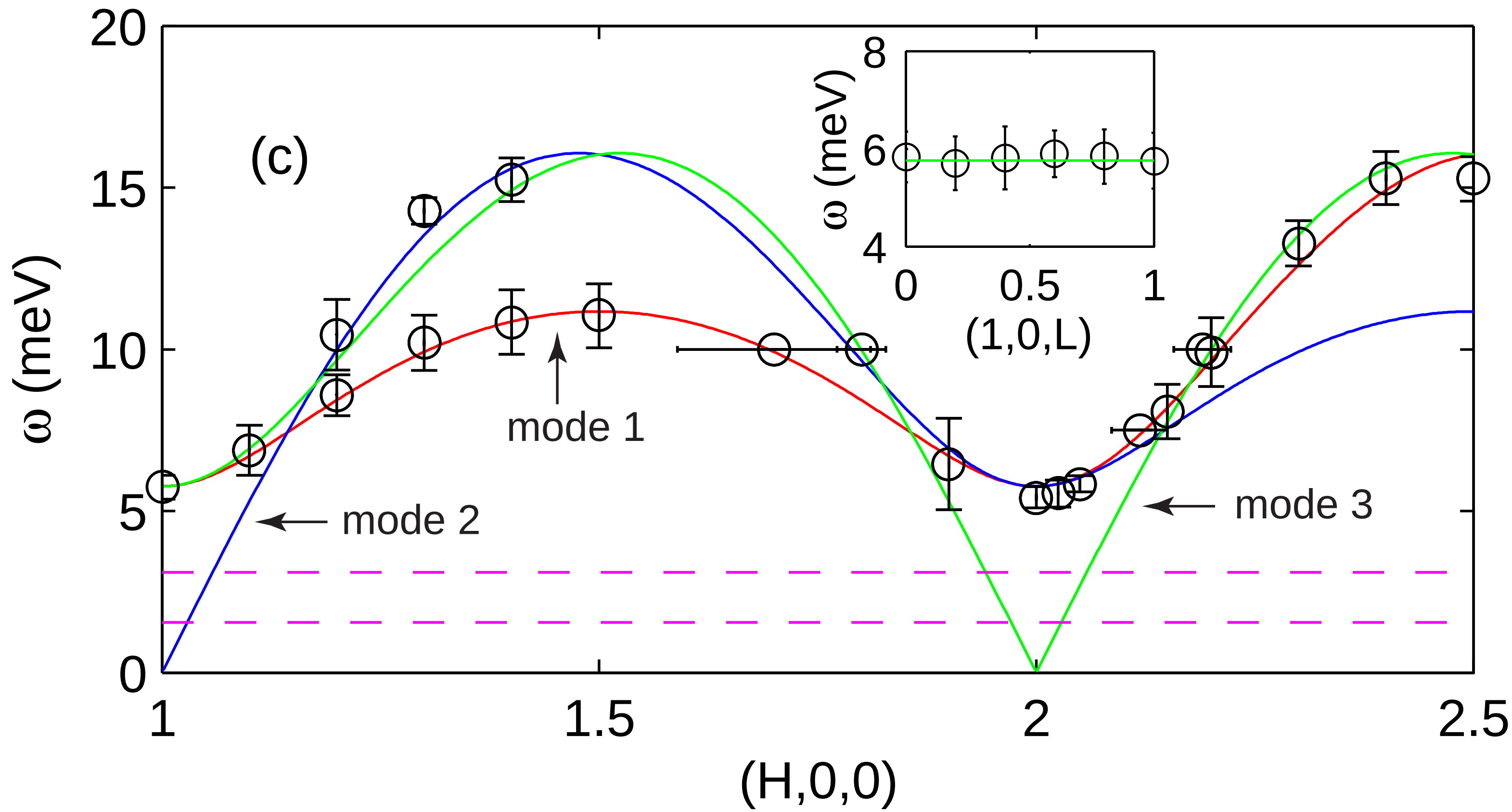


No electric field effects up to 300 kV/cm

B. Lorentz, et al., PRB71, 014438 (2005).

2-Dimensional Spin-wave Dispersion

T = 20 K

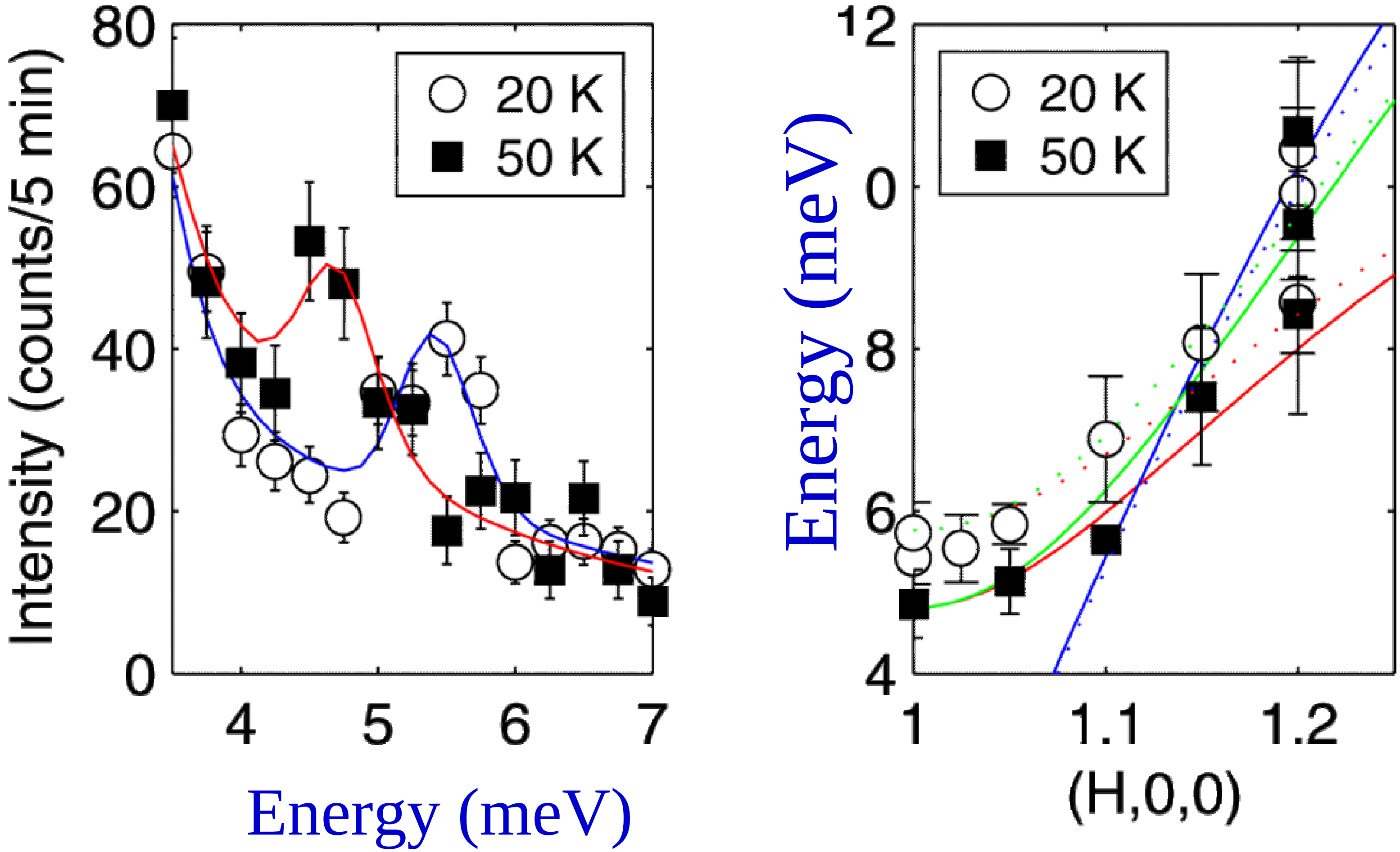


$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i S_i^z S_i^z,$$

J=2.44 meV

D=0.38 meV

Anisotropy change at Spin-Flop Transition

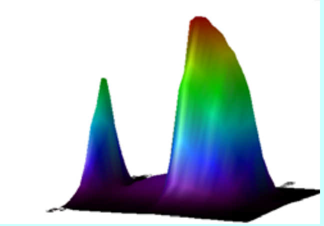


J=2.44 meV

D=0.28 meV→0.38 meV

O. P. Vajk, *et al.*, Phys. Rev. Lett. **94**, 087601 (2005).

$HoMnO_3$ Synopsis



Single-crystal samples of $HoMnO_3$ allow first measurements of spin-wave spectrum.

Spin dynamics are primarily 2D, with J ~ 2.44 meV and an anisotropy of 0.28 meV in the high T ordered phase, and increases to 0.38 meV in the spin-flop phase.

Spin reorientation transition observed as a function of H and T. Similar to Nd_2CuO_4, where the transition is caused by the coupling to the rare earth.
This transition couples to Ferroelectricity

Multiple reorientation transitions observed at low temperatures as a function of magnetic field.   No electric field effect at low T ! !

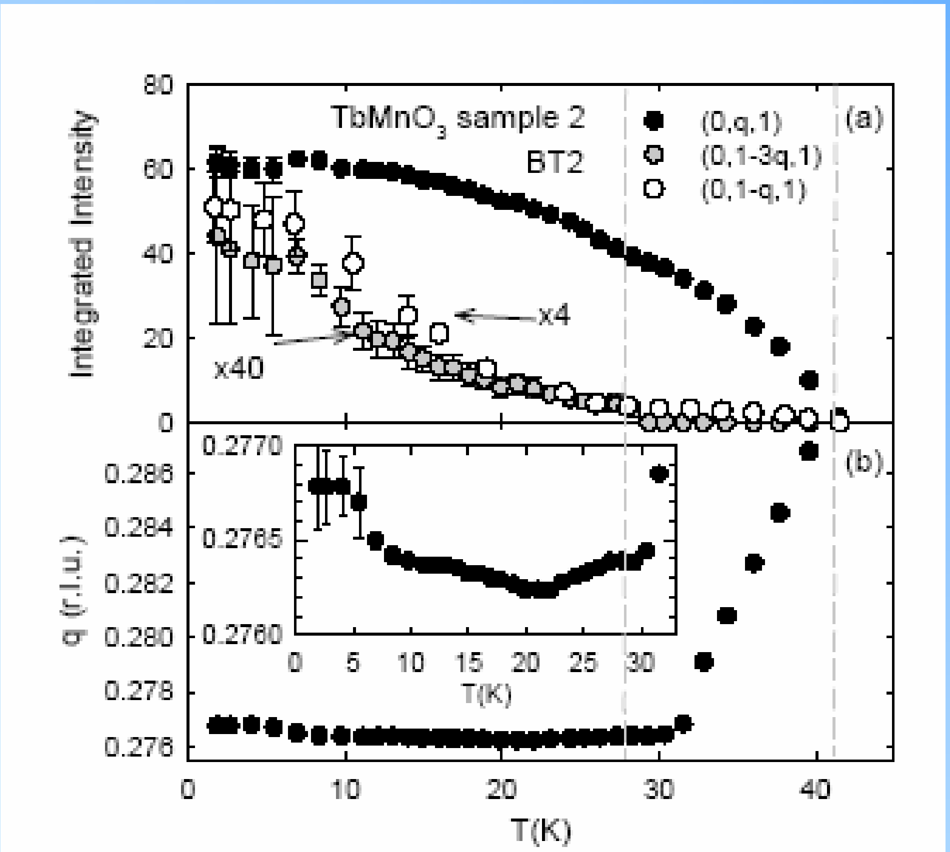
Magnetism in Orthorhombic Ferroelectric $TbMnO_3$

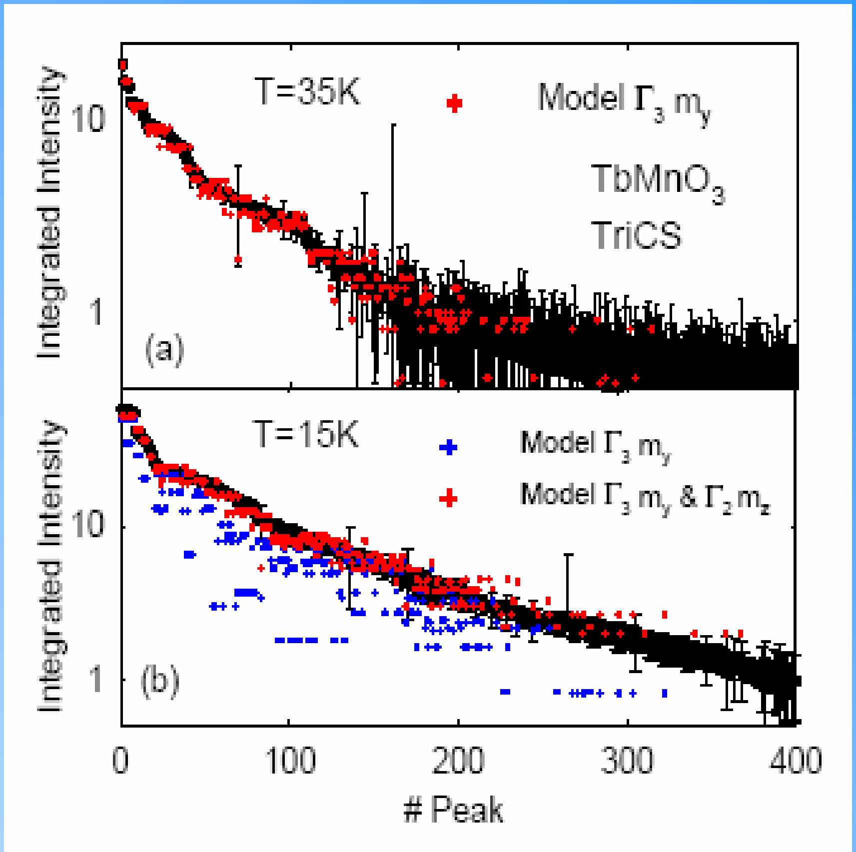
Incommensurate Spin Density wave at 41 K (Mn)

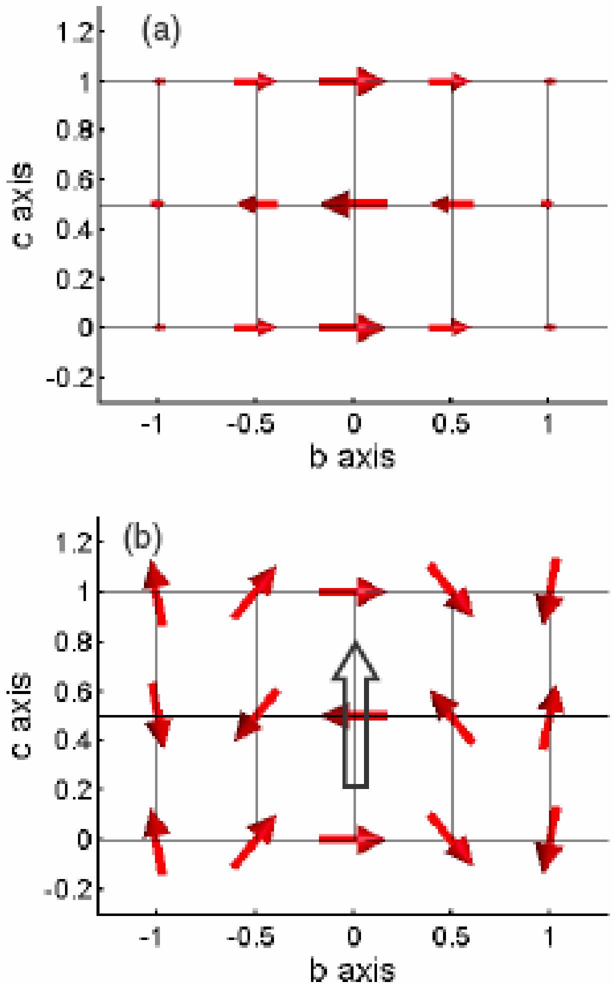
Ferroelectric at ~30 K, where the magnetic structure develops a spiral component.

M. Kenzelmann, A. B. Harris, S. Jones, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S.-W. Cheong, O. P. Vajk, & J. W. Lynn,
PRL **95**, 087206 (2005).

Magnetism in Orthorhombic Ferroelectric $TbMnO_3$

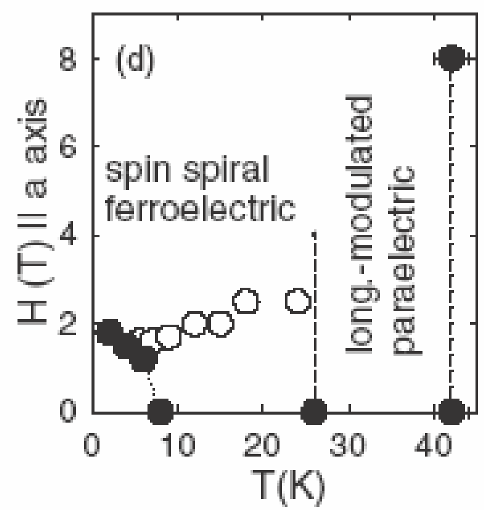






(c)

	1	2_y	m_{xy}	m_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

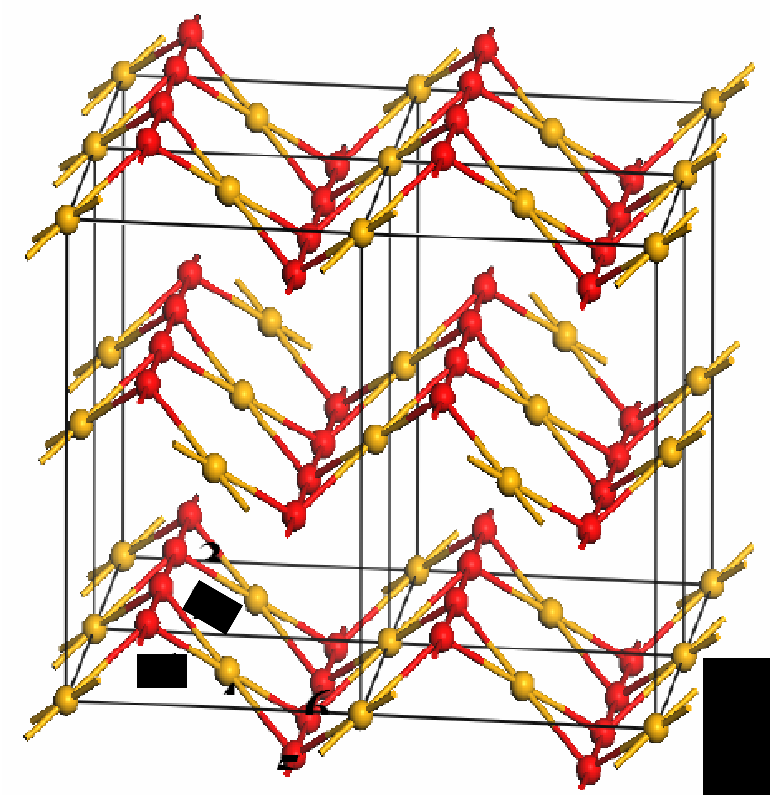


Magnetic Order in the Kagomé-Staircase System (Co,Ni)$_3$V$_2$O$_8$

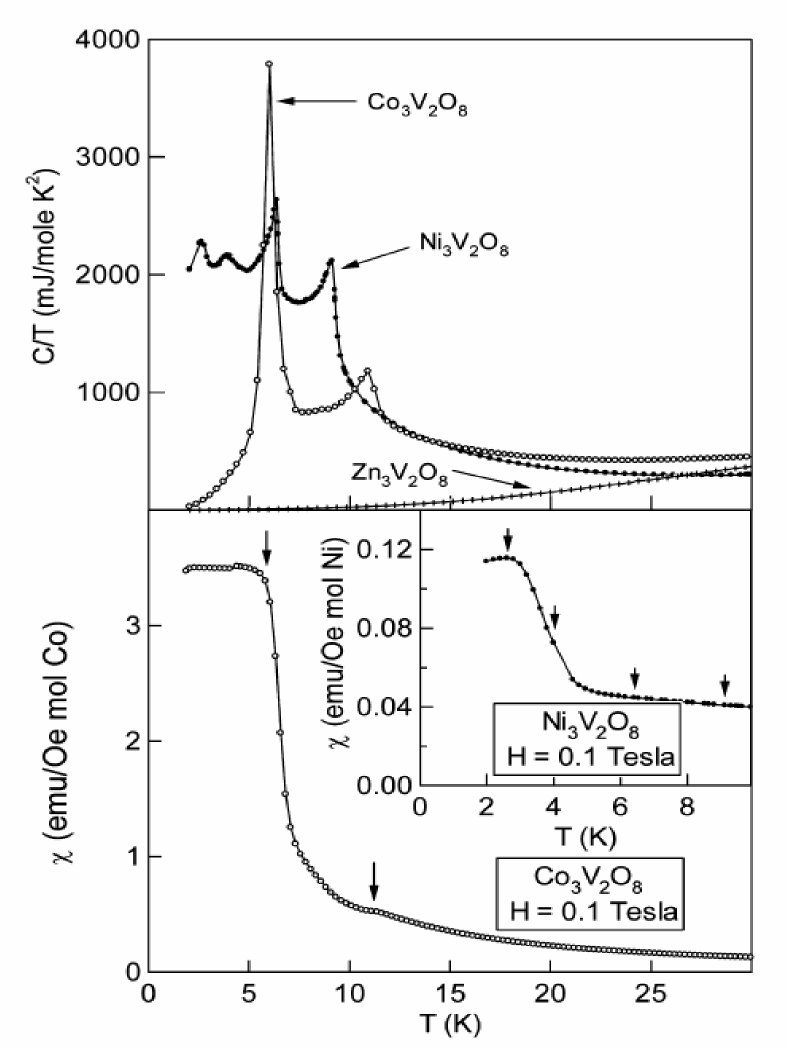
Complex Magnetic Order in the Kagome Staircase Compound $Co_3V_2O_8$,
Ying Chen, J. W. Lynn, Q. Huang, F. M. Woodward, T. Yildirim, G. Lawes, A. P. Ramirez, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, and A. B. Harris,
Phys. Rev. B ***74****, 014430 (2006).*

NCNR

Crystal Structure of $(Co,Ni)_3V_2O_8$

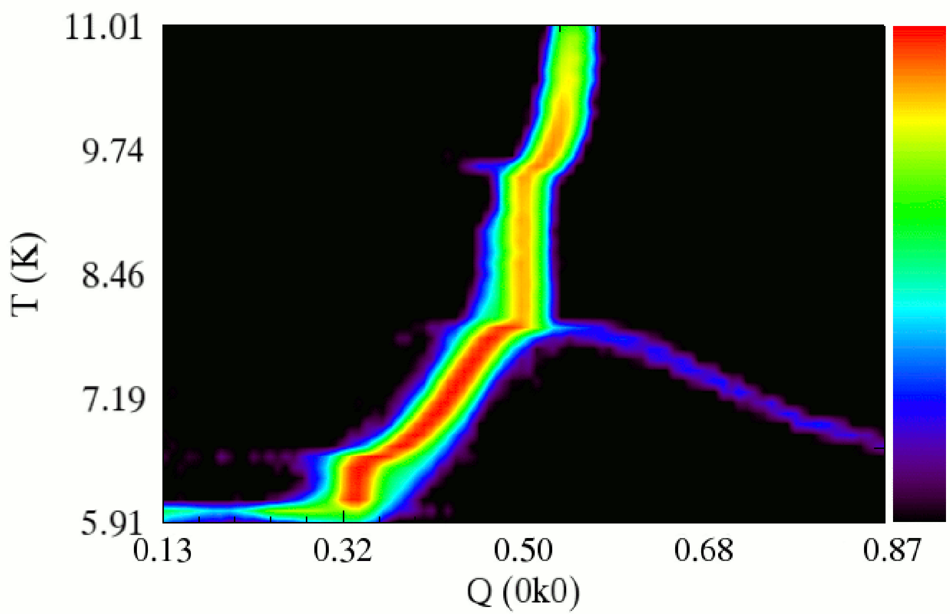


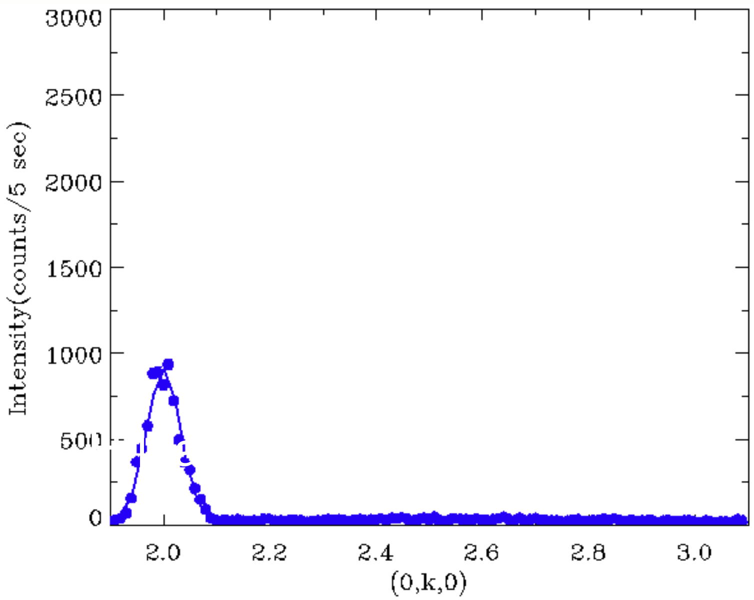
Staircase Kagome lattice



N. Rogado, G. Lawes, D.A. Huse. A.P. Ramirez and R.J. Cava, Solid State Com. 124, 229 (2002).

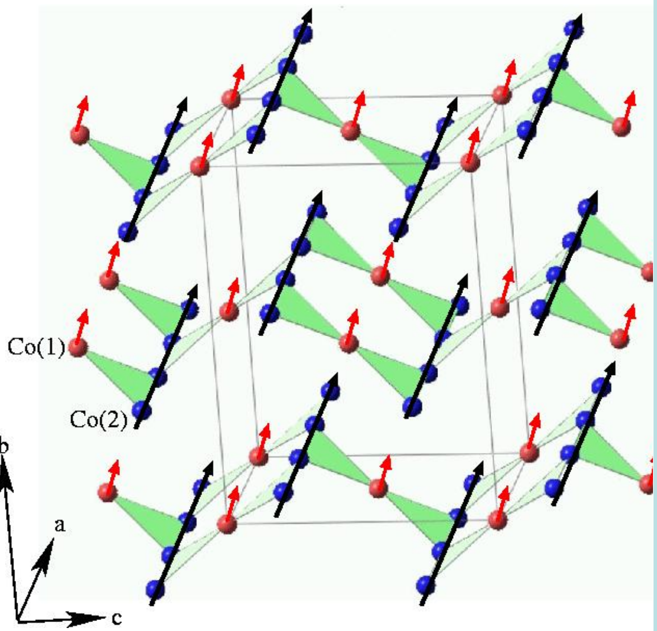
Magnetic order of $Co_3V_2O_8$





Magnetic ordered structures at H=0

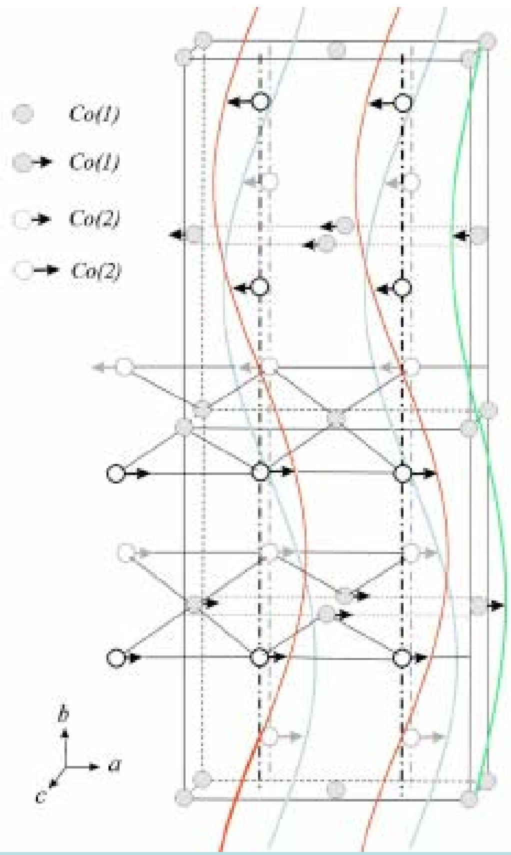
FM order (δ=0)



Chen et al. PRB 74,014430 (2006)

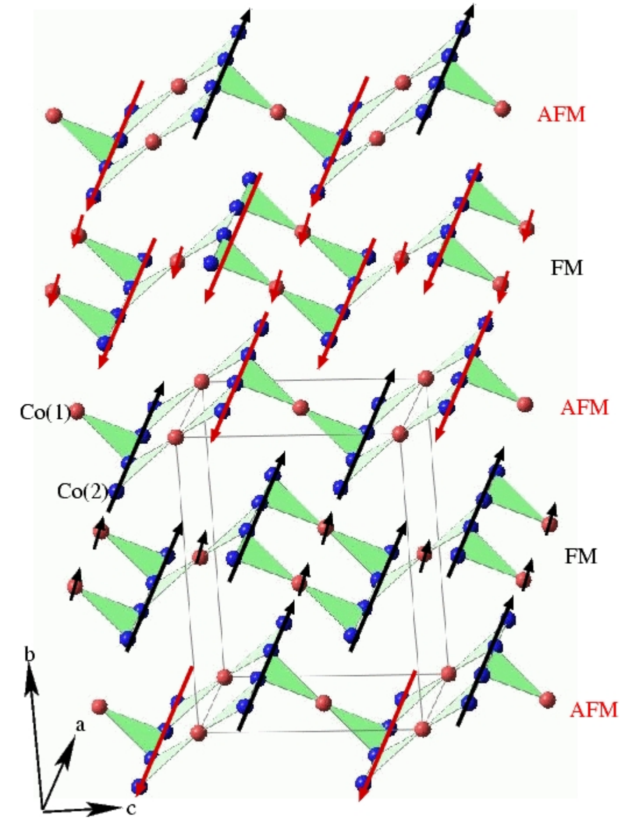
T=3.1 K
Co(1):1.54(6) μ_B
Co(2): 2.73(2) μ_B

Incommensurate Magnetic order



Transversely polarized spin density wave, wave vector along *b* axis, and spin direction along *a* axis

AFM order (δ=0.5)



T=8.4 K, FM layer:
Co(1): 1.17(6)μ_B
Co(2): 1.39(3) μ_B
AFM layer:
Co(1): 0 μ_B
Co(2): 2.55(3) μ_B

Multiferroic Summary

Coupled magnetic and Ferroelectric degrees of freedom:

Direct coupling—change in magnetic structure controls ferroelectric properties

Indirect coupling—magnetic and ferroelectric order parameters are independent to first approximation, but have higher-order coupling.

Overall Summary

CMR Polaron Formation Truncates Ferromagnetic Phase and enhances MR

Magnetic Ferroelectrics; coupling of magnetic and lattice degrees of freedom

Coupled magnetic, electronic, and structural degrees of freedom in both CMR and Multiferroic Oxides. Similarities to other oxides, such as relaxor ferroelectrics ($PbTiO_3$), cuprates, and sodium cobaltates.

Multiferroics Acknowledgments

Hexagonal $HoMnO_3$

O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim and S.-W. Cheong, Phys. Rev. Lett. **94**, 087601 (2005); J. Appl. Phys. **99**, 08R301 (2006).

Orthorhombic $TbMnO_3$

M. Kenzelmann, A. B. Harris, S. Jones, C. Broholm, J. Schefer, S.-W. Cheong, O. P. Vajk, & J. W. Lynn, PRL **95**, 087206 (2005).

RMn_2O_5 (R=Tb,Dy,Ho)

C. R. dela Cruz, F. Yen, B. Lorenz, M. M. Gospodinov, C. W. Chu, W. Ratcliff II, J. W. Lynn, S. Park, and S-W. Cheong, Phys Rev. B**73**, 100406(*R)* (2006). J. Appl. Phys. **99**, 08R103 (2006).

$Tb_{1-x}Na_xMnO_{3-x}$

C. C. Yang, M. K. Chung, W.-H. Li, T. S. Chan, Y. H. Lien, R. S. Liu, Y. Y. Chan, Y. D. Yao, and J. W. Lynn, Phys. Rev. B **74**, 094409 (2006).

$Co_3V_2O_8$

Y. Chen, J. W. Lynn, Q. Huang, F. M. Woodward, T. Yildirim, G. Lawes, A. P. Ramirez, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, and A. B. Harris, Phys. Rev. B**74**, 014430 (2006).

$CuFeO_2$

F. Ye, Y. Ren, Q. Huang, J. A. Fernandez-Baca, P. Dai, J. W. Lynn, and T. Kimura, Phys. Rev. B**73**, 220404(R) (2006)

$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$

G. Xu, S. M. Shapiro, J. W. Lynn, et al. (in preparation).

$LiMnPO_4$

J. Li, W. Tian, D. Vaknin, Y. Chen, J. W. Lynn. (in preparation).

CMR Acknowledgments

Taku Sato, Eduardo Granado, Matt Woodward, Carl Adams, (NCNR)

Bogdan Dabrowski (Northern Illinois University)

William Ratcliffe, II, Valery Kiryukhin, Sang-Wok Cheong (Rutgers University)

Vera Smolyaninova, Richard Greene (University of Maryland)

Yakov Mukovskii (Moscow)

Dimitri Argyriou, Yang Ren, Chris Ling, John Mitchell, Ray Osborn, Branton Campbell, Heloisa Bordallo (Argonne)

John Neumeier Montana State University

Jaime Fernandez-Baca, Pengcheng Dai, Feng Ye ORNL, U. Tennessee

Y. Tomioka, H. Yoshizawa, and Yoshi Tokura (U. Tokyo)

NCNR