Neutron Scattering in Transition Metal Oxides

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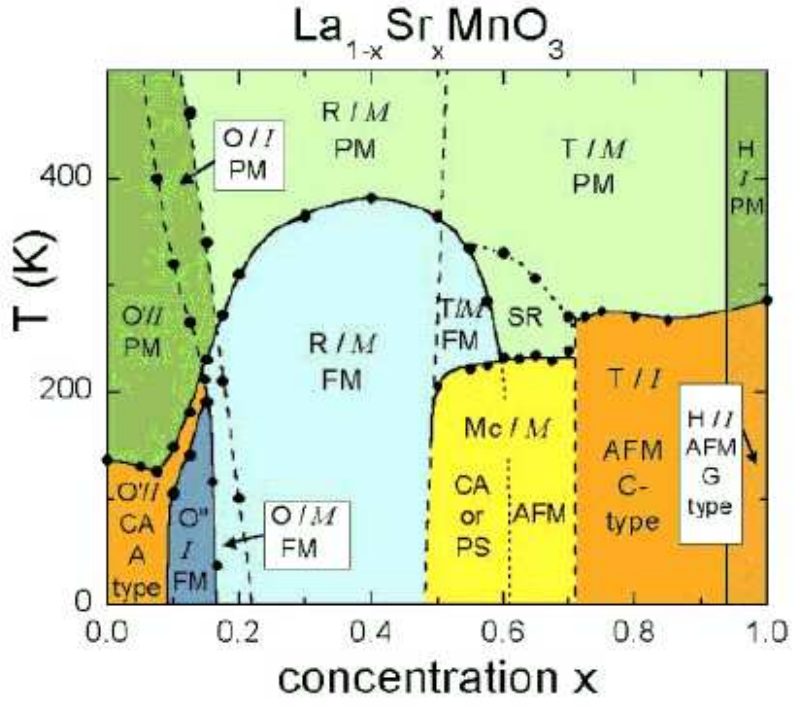
- **physics of the *3d* electrons**
- **strongly correlated electrons**
- **spin, charge, orbital degrees of freedom**

$LaMnO_3$: a material we understand today

some current frontiers:
- orbital dynamics
- colossal magnetoresistance
- high temperature superconductivity

Strongly Correlated Electrons

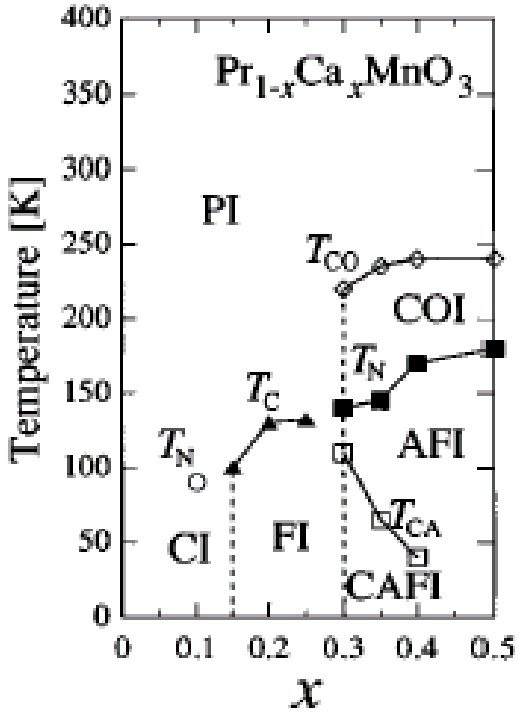
- high temperature superconductivity
- colossal magnetoresistance



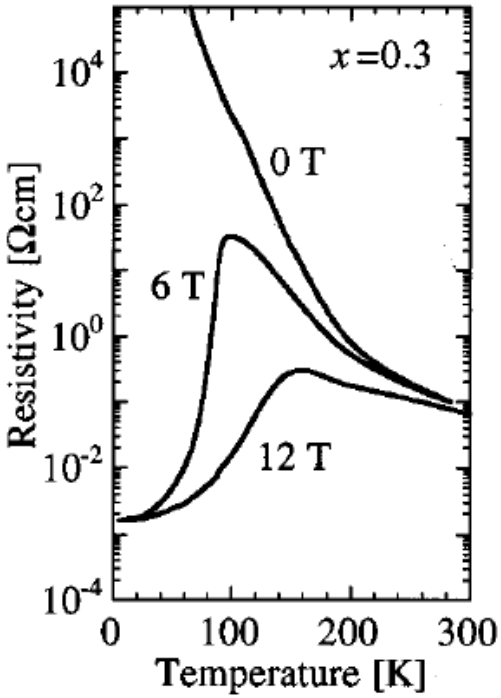
interplay between
spin, charge and orbital
degrees of freedom

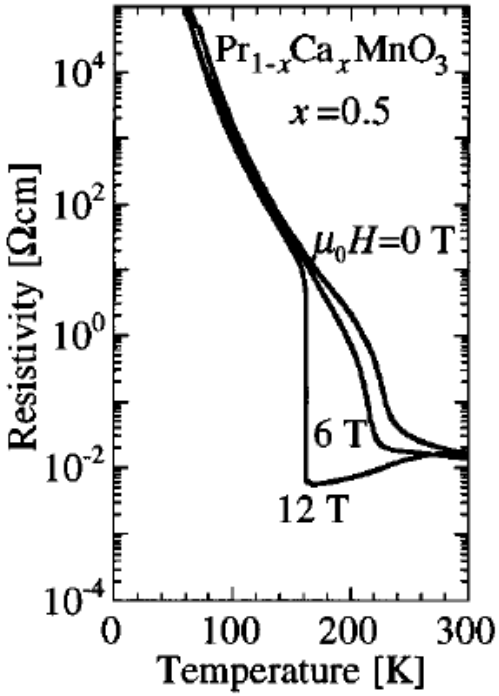
J. Hemberger *et al.*,
PRB **66**, 94410 (2002)

Colossal Magnetoresistance



Manganese oxide: $Pr_{1-x}Ca_xMnO_3$





Tomioka et al., PRB 53, 1689 (1996).

PHYSICAL REVIEW VOLUME 100, NUMBER 2 OCTOBER 15, 1955

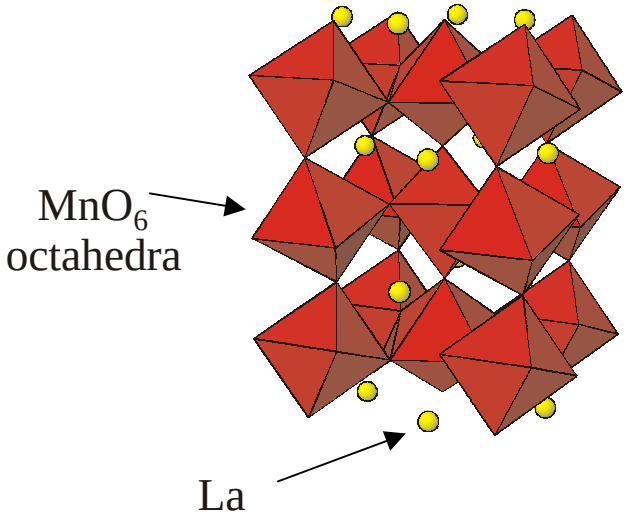
Neutron Diffraction Study of the Magnetic Properties of the Series of Perovskite-Type Compounds $[(1-x)\mathrm{La}, x\mathrm{Ca}]\mathrm{MnO}_3$†

E. O. Wollan and W. C. Koehler
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received May 9, 1955)

Theory of the Role of Covalence in the Perovskite-Type Manganites $[\mathrm{La}, M(\mathrm{II})]\mathrm{MnO}_3$†

John B. Goodenough
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts
(Received May 16, 1955)

3D - perovskite structure



$Pm\bar{3}m$ ideal cubic perovskite

Pbnm $GdFeO_3$ - type distortion

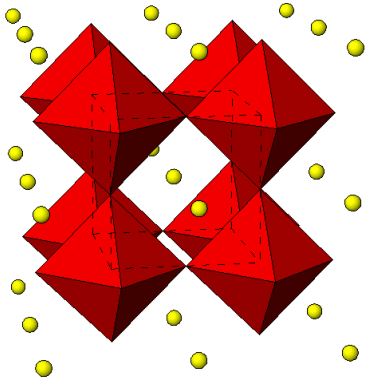
- Tilt and rotation of the TiO_6 octahedra
- Distortion of the TiO_6 octahedra

(Jahn-Teller Distortion)

$LaMnO_3$
$LaTiO_3$ / $YTiO_3$
$LaVO_3$ / YVO_3

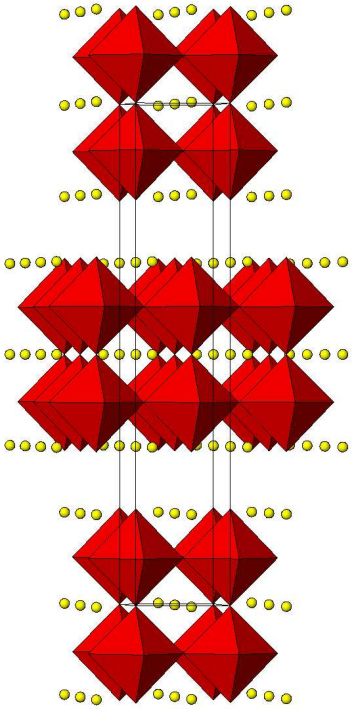
Crystal Structure: Perovskite

Ruddlesden-Popper Series



$RMnO_3$

Cubic Perovskite

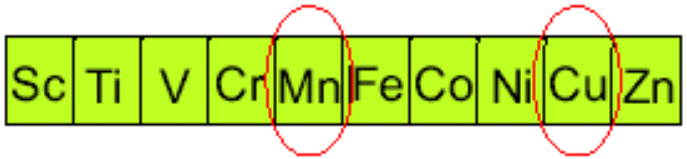


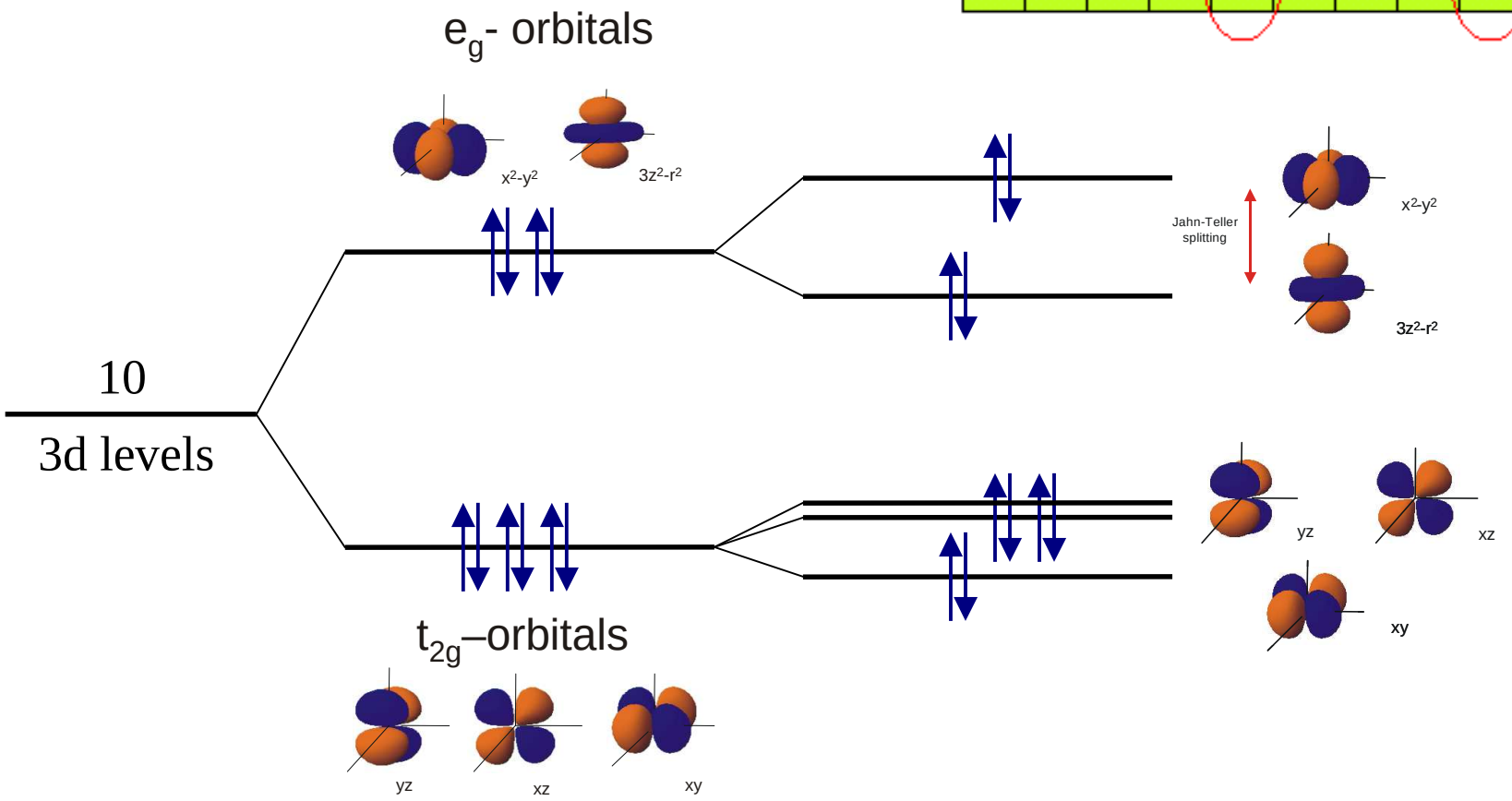
$R_3Mn_2O_7$

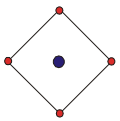
Bilayer Perovskite

Three layers

Crystal Field Splitting of the 3d levels

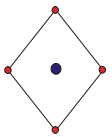




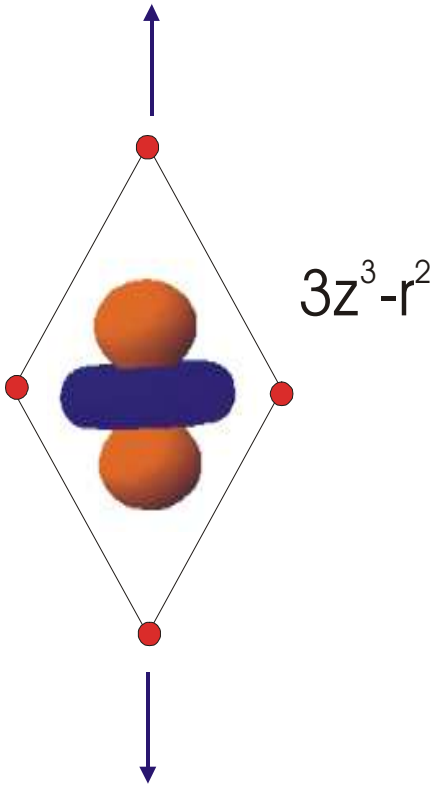


cubic splitting (octahedral)

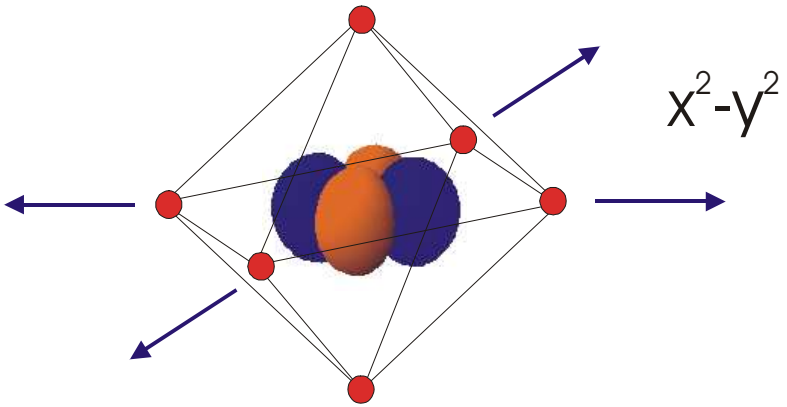
tetragonal splitting



Jahn-Teller Distortion



$3z^3-r^2$



x^2-y^2

- e_g-orbitals are bond-directional
- Coulomb repulsion from the O-atoms
- **distortion of the octahedra**

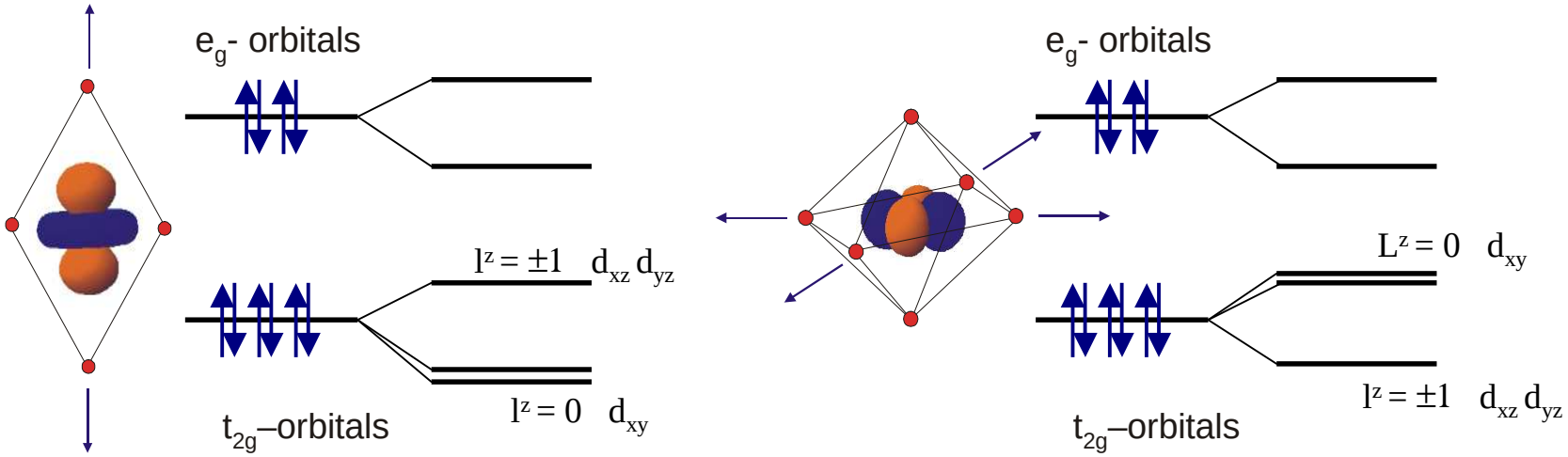
Strain versus Coulomb energy

Distortion of the MnO_6 octahedra in $LaMnO_3$ (manganites): $\Delta d = c–a \sim 0.25$ Å

Jahn-Teller Distortion

- Distortion of the octahedra
- Crystal symmetry is changed
- Lifting of degenerecy

Splitting of the electronic levels



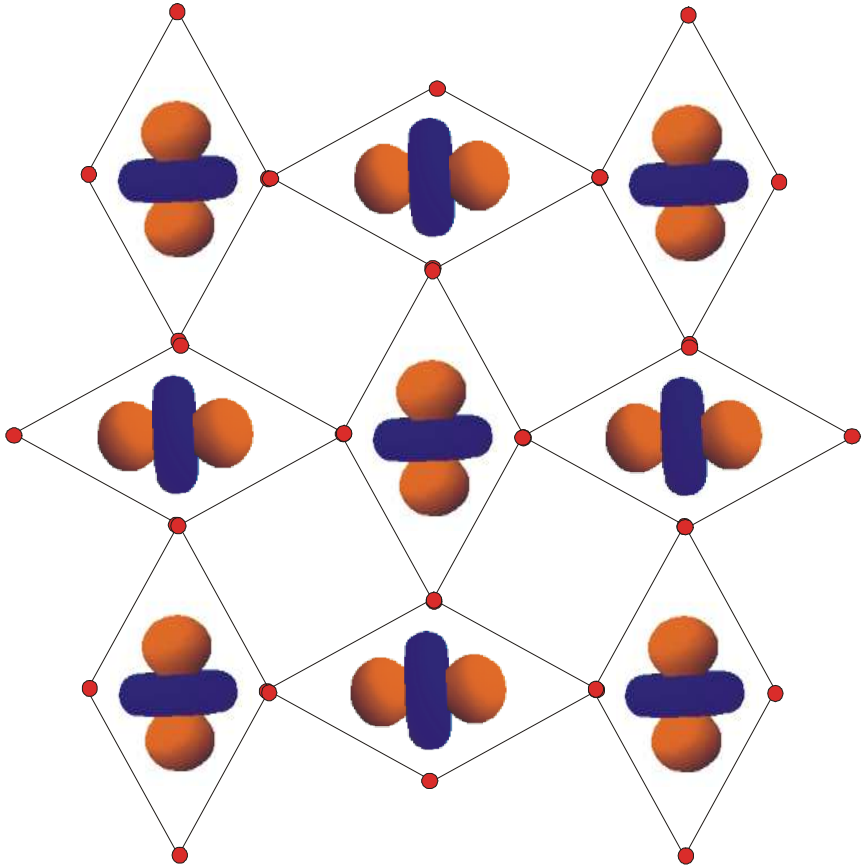
Cooperative Jahn-Teller Distortion

Distortion of the octahedra

Change in Crystal Symmetry

- Distortion
- Tilt
- Rotation

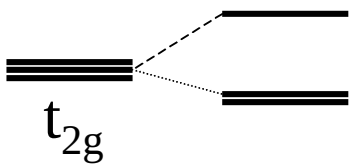
of the octahedra



The orbital degeneracy in ground state is lifted by:

- **crystal field splitting caused by lattice distortions (Jahn-Teller Effect)**

- **spin-orbit coupling**
  $\lambda \sim 20$ meV



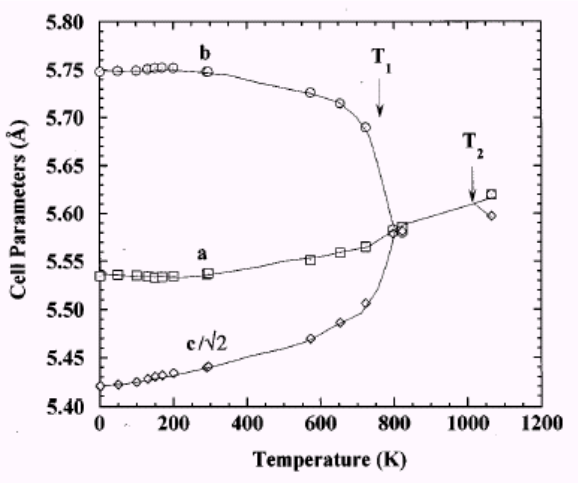
$|xz\uparrow\rangle + i\,|yz\uparrow\rangle - i\,|xy\downarrow\rangle$
$|xz\uparrow\rangle + i\,|yz\uparrow\rangle + 2i\,|xy\downarrow\rangle$
$|xz\uparrow\rangle - i\,|yz\downarrow\rangle$

  - orbital ordering with **complex** combinations of wave functions
  - **unquenched** orbital angular momentum

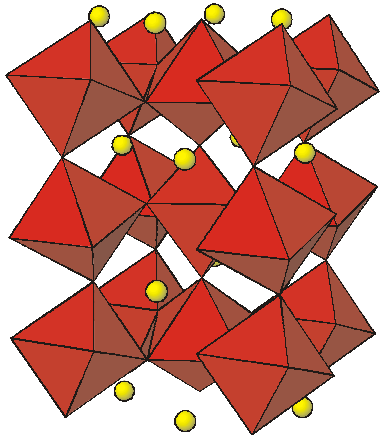
- **Superexchange Interaction**

Orbital Order in $LaMnO_3$

elastic neutron scattering

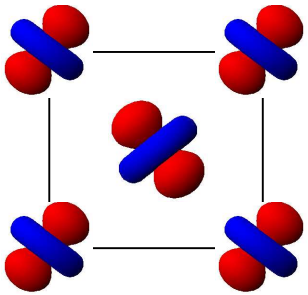


J. Rodriguez-Caravajal *et al.*,
PRB **57**, 3189 (1998)

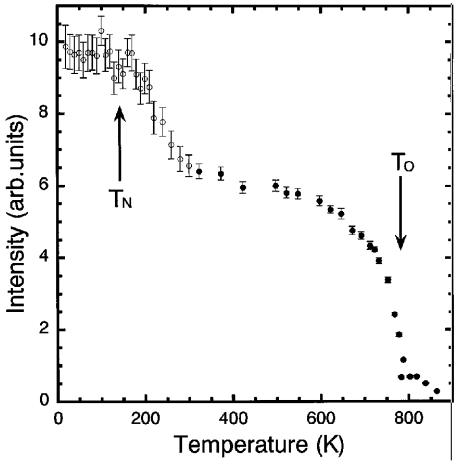


$T_{OO} = 780$ K

$T < T_{OO}$: orbital order
locks in exchange interactions



resonant X-ray scattering

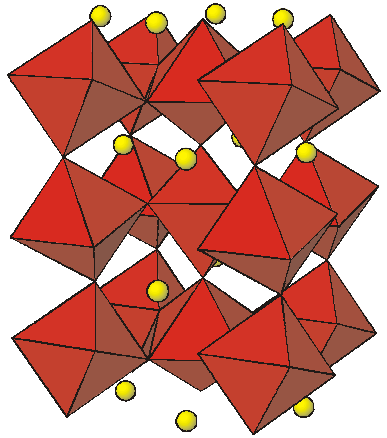


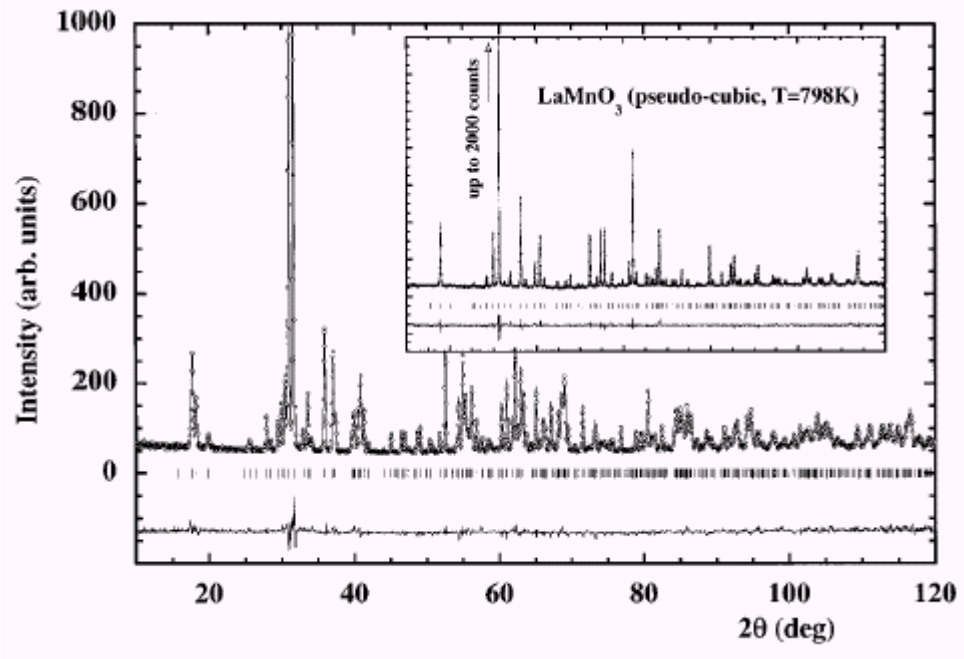
Y. Murakami *et al.*, PRL **81**, 582 (1998)

Neutron diffraction in $LaMnO_3$

TABLE I. Structural data of $LaMnO_3$ ($Pbmn$) at three selected temperatures. Data collection has been performed on the diffractometer 3T2, using a wavelength of 1.22 Å. The Jahn-Teller transition takes place at T_{JT}=750 K. Cell parameters and atomic positions from references have been put in the $Pbnm$ setting. The representative atom positions of the asymmetric unit have been converted to those used in our work. The structural parameters described in the monoclinic space group $P2_1/n$ of Ref. 15 have been used to produce a simulated neutron diffraction pattern that has been refined using the $Pbnm$ space group (see text).

	RT	T=573 K	T=798 K	RT (Ref. 11)	RT (Ref. 14)	RT (Ref. 15)	RT (Ref. 16)
a (Å)	5.5367(1)	5.5520(2)	5.5817(3)	5.537(2)	5.5392(6)	5.5365(1)	5.5358(1)
b (Å)	5.7473(1)	5.7269(2)	5.5834(2)	5.743(1)	5.6991(7)	5.7216(1)	5.7363(1)
c (Å)	7.6929(2)	7.7365(2)	7.8896(4)	7.695(2)	7.7175(9)	7.7000(1)	7.6994(2)
x (La)	−0.0078(3)	−0.0063(3)	−0.0046(9)	−0.009(1)	−0.0063(7)	−0.0069(2)	−0.0080(3)
y (La)	0.0490(2)	0.0443(2)	0.0217(3)	0.050(1)	0.0435(5)	0.0459(2)	0.0475(3)
B (La)(Å^2)	0.34(2)	0.80(2)	1.26(3)				0.62(3)
B (Mn)(Å^2)	0.21(3)	0.46(4)	0.84(4)				0.51(6)
x[O(1)]	0.0745(3)	0.0725(3)	0.0687(10)	0.071(1)	0.0733(8)	0.0754(3)	0.0752(4)
y[O(1)]	0.4874(3)	0.4885(3)	0.4890(8)	0.489(1)	0.4893(8)	0.4883(3)	0.4869(4)
B[O(1)](Å^2)	0.50(3)	1.00(4)	1.87(7)				
x[O(2)]	0.7256(2)	0.7257(2)	0.7229(6)	0.725(1)			
y[O(2)]	0.3066(2)	0.3038(2)	0.2831(5)	0.309(1)			
z[O(2)]	0.0384(2)	0.0378(2)	0.0386(4)	0.039(1)			
B[O(2)](Å^2)	0.43(3)	0.91(2)	1.67(5)				
R_p:	8.98	10.4	14.3				
R_{wp}:	9.04	10.0	11.3				
χ^2:	2.35	2.40	2.63				
R_{Nucl}(%):	5.16	5.32	4.14				

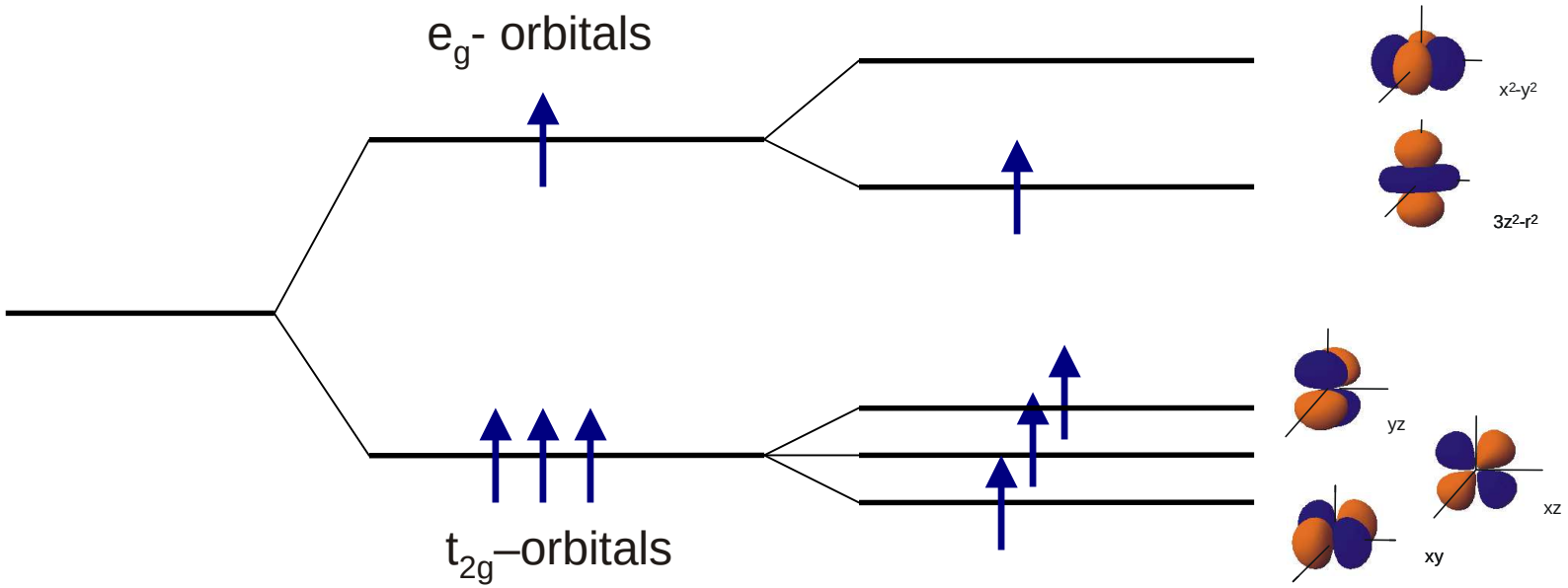




J. Rodriguez-Caravajal *et al.*,
PRB **57**, 3189 (1998)

$LaMnO_3$: high spin state $3d^4$, $t_{2g}^3\ e_g^1$ $S = 2$

$LaMnO_3$ **Mn^{3+}**

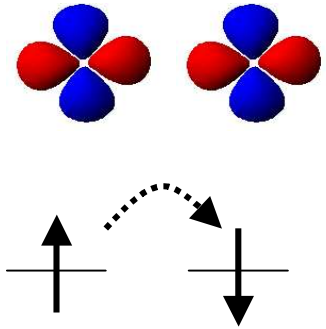


Hund´s Rules: - largest value of total spin S
- largest value of total angular momentum L
- J =| L-S| less than half filling
  J = |L+S| more than half filling

Superexchange Interaction

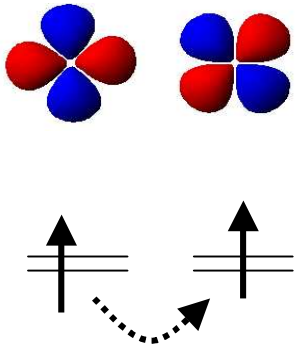
Goodenough-Kanamori Rules

strong
antiferromagnetic



electron cannot delocalize
without considering
the Pauli principle

Spin: antiferromagnetic
OO: ferromagnetic-type



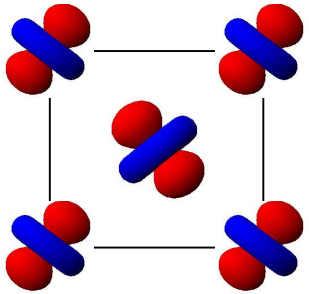
weak
ferromagnetic

intra-atomic Hund‘s
rule favors ferromagnetic
alignment in intermediate state

Spin: ferromagnetic
OO: antiferromagnetic-type

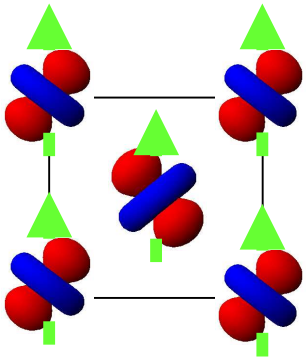
Magnetic Order in $LaMnO_3$

780 K



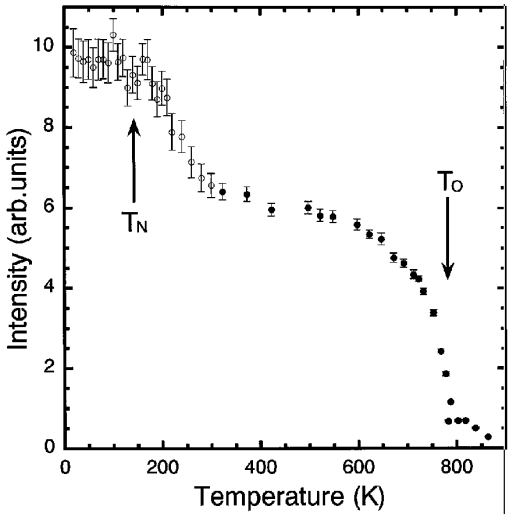
$T < T_{OO}$: orbital order
locks in exchange interactions

140 K

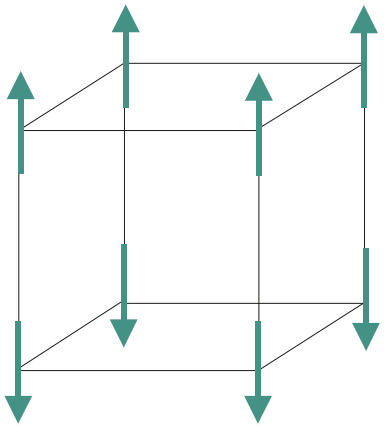


$T < T_N$: magnetic order

resonant X-ray scattering

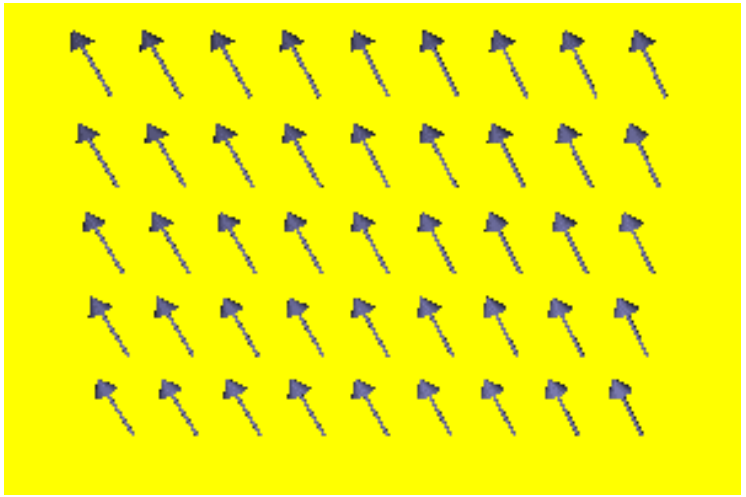


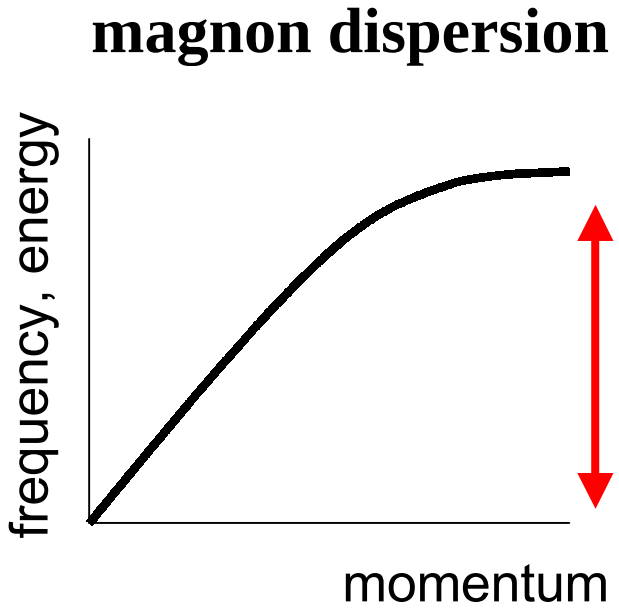
Y. Murakami *et al.*, PRL **81**, 582 (1998)



$LaMnO_3$ A-type Antiferromagnet

-ferromagnetic within the ab-plane
-antiferromagnetic along the c-axis





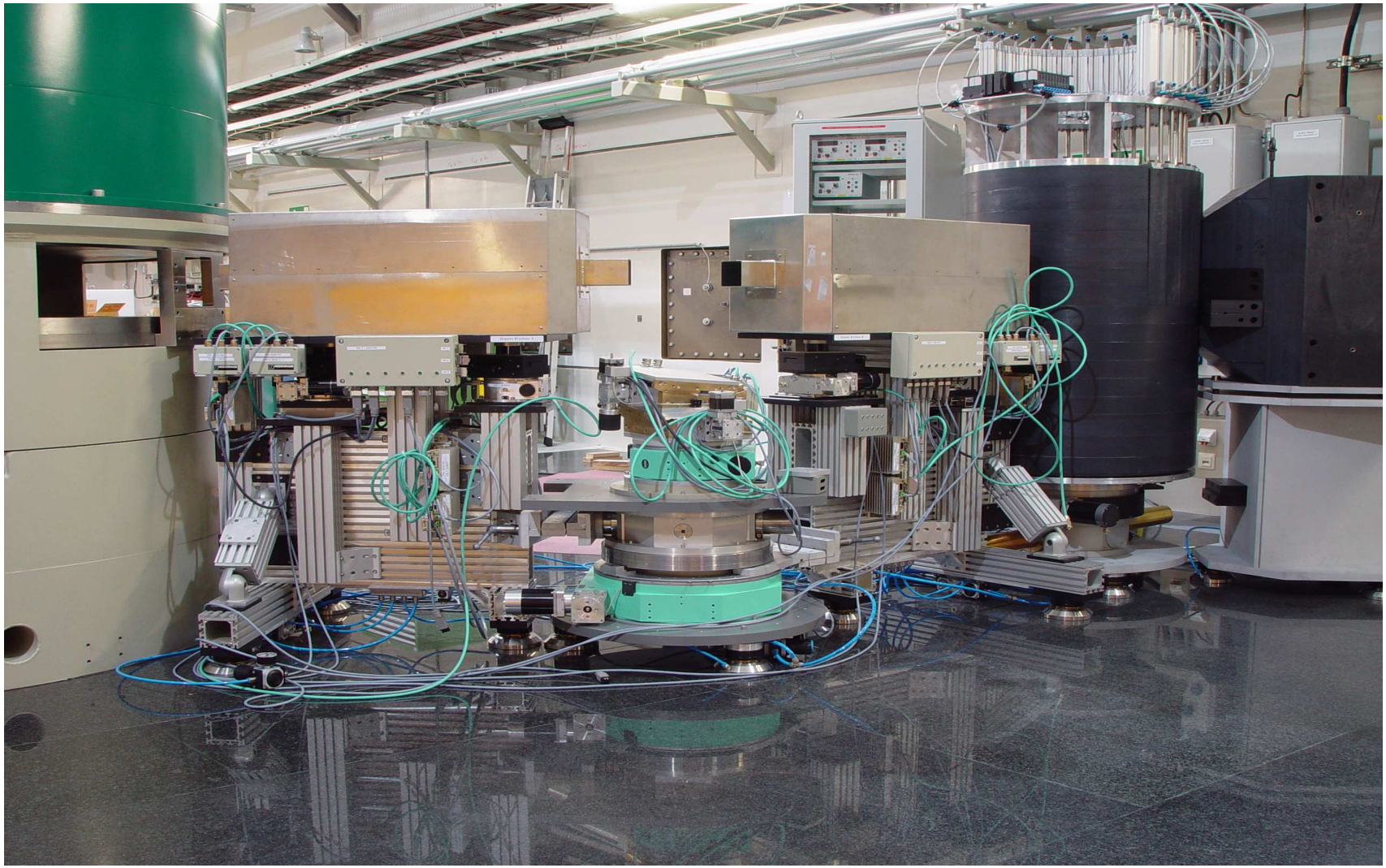
Heisenberg Hamiltonian:

$$H = \Sigma_{i\,j}\, J\, S_i \bullet S_j$$

J = exchange interaction

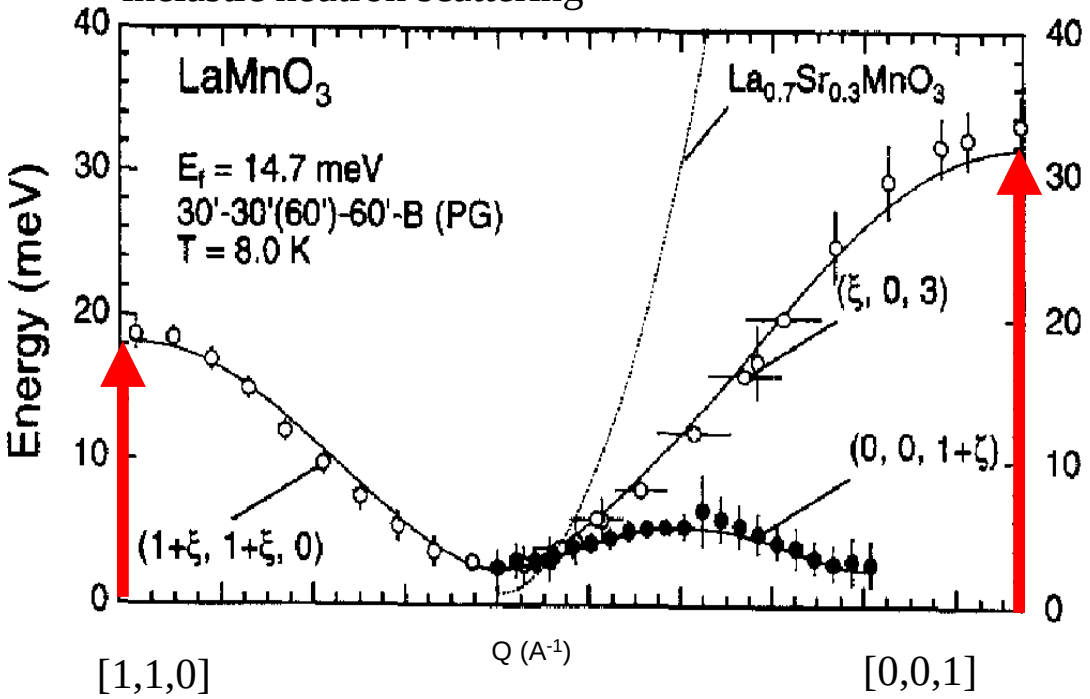
band width $\propto$ J

TRISP Spectrometer at FRM-II



Magnon Dispersion Relation in $LaMnO_3$

inelastic neutron scattering



$T < T_N$: anisotropic spin wave spectrum reflects the orbital ordering pattern

K. Hirota *et al.*, Physica B **237**, 36 (1997)

What are correlated electrons?

electron-electron Coulomb interactions

very weak → independent electrons: **ordinary metal**

very strong → electron crystal: **Mott insulator**

"strongly correlated electrons" in d- or f-electron metals:

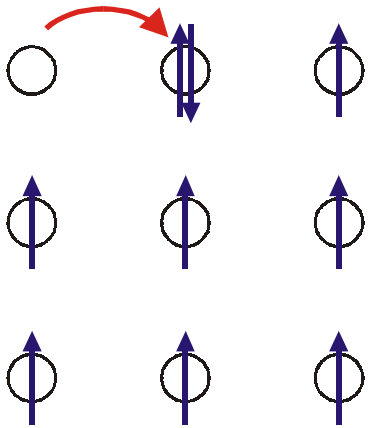
- transport dominated by electron-electron interactions, very different from ordinary metals
- new theory of metals?

Metal-Insulator Transition

Due to the screening of the outer electron shell, the intersite Coulomb interaction plays a dominant role for 3d-electrons.

Energy gain due to electron hopping is comparable to the Coulomb repulsion.

Consider a half filled conduction band:



ideal metal:

$$H = -t \sum_{\langle j,l \rangle} \sum \sigma \left(c^{\dagger}_{j\sigma} c_{l\sigma} + c^{\dagger}_{l\sigma} c_{j\sigma} \right)$$

kinetic energy due to electron-hopping

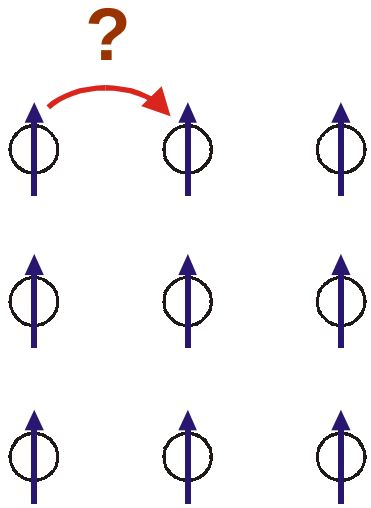
Hubbard Model

- the kinetic energy (electron hopping) wishes to delocalize the electrons

  $\Rightarrow$ metallic behavior

- the Coulomb repulsion wants to localize the electrons.

  $\Rightarrow$ insulating behavior

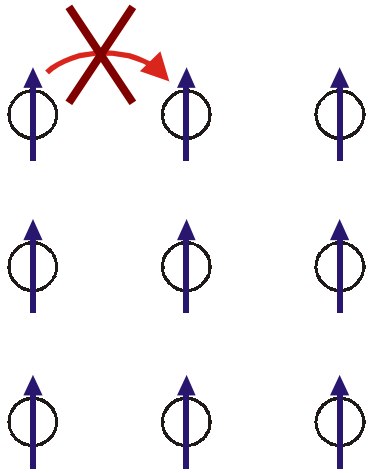


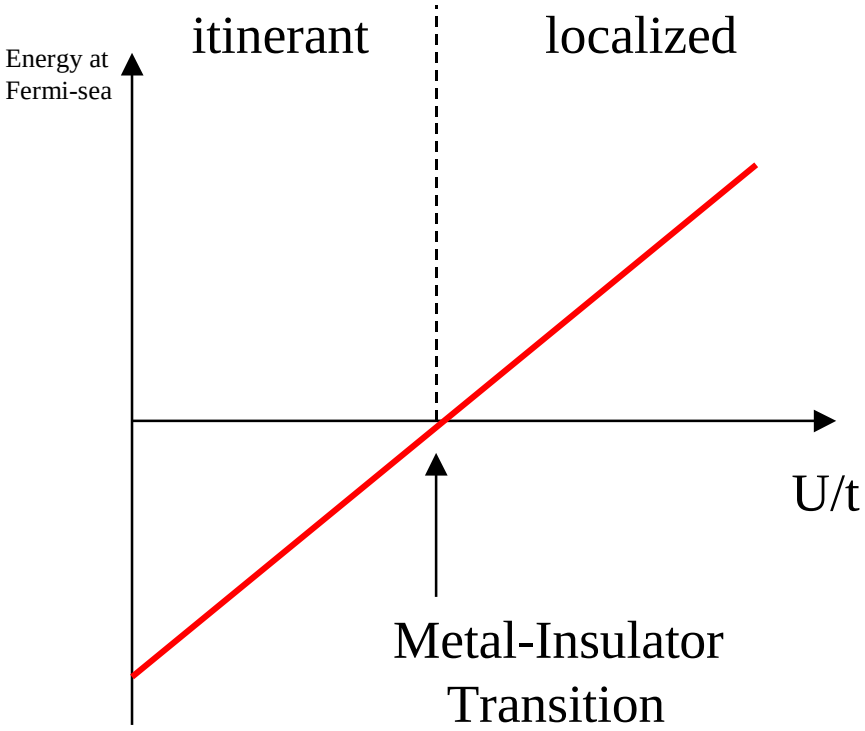
$$H = \underbrace{-t \sum_{\langle j,l \rangle} \sum \sigma \left(c^{\dagger}_{j\sigma} c_{l\sigma} + c^{\dagger}_{l\sigma} c_{j\sigma} \right)}_{Hopping} + \underbrace{U \sum_{j} \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}}_{Coulomb}$$

Mott-Hubbard Transition

Balance between:

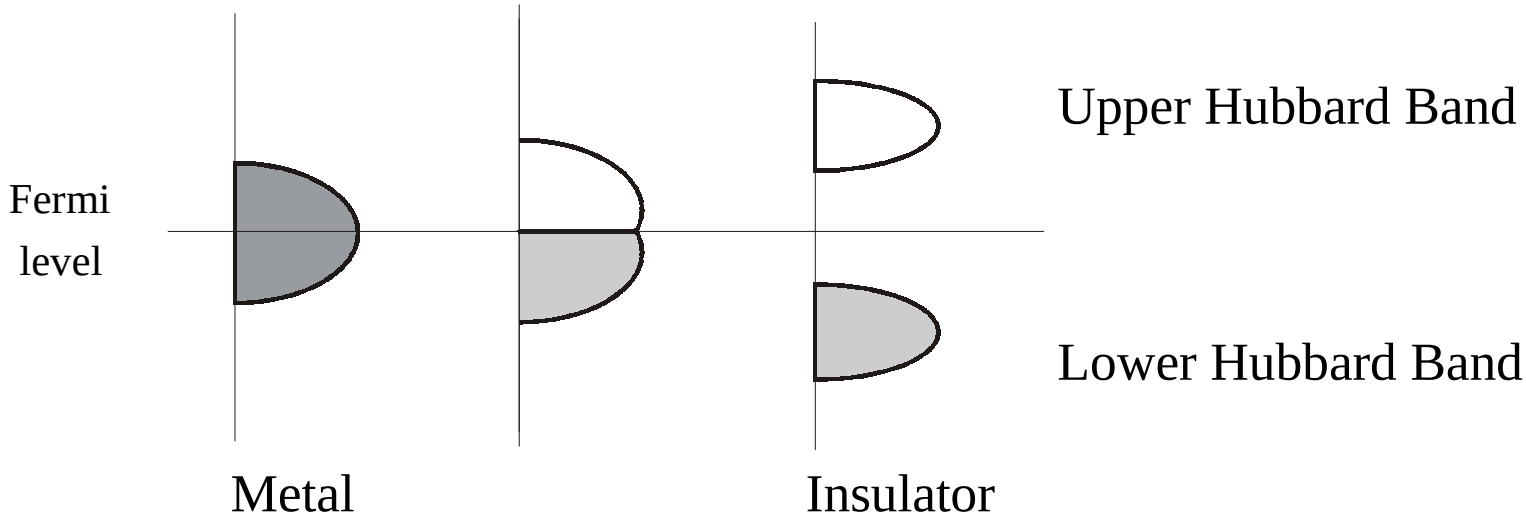
- **t** Hopping Term
- **U** Coulomb Repulsion





Metal-Insulator Transition

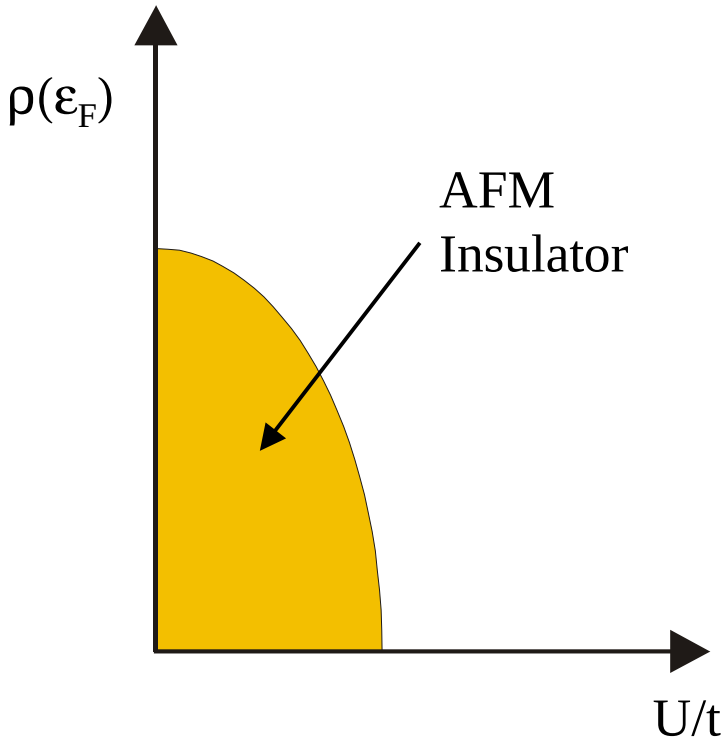
Mott-Hubbard Transition: Band Theory

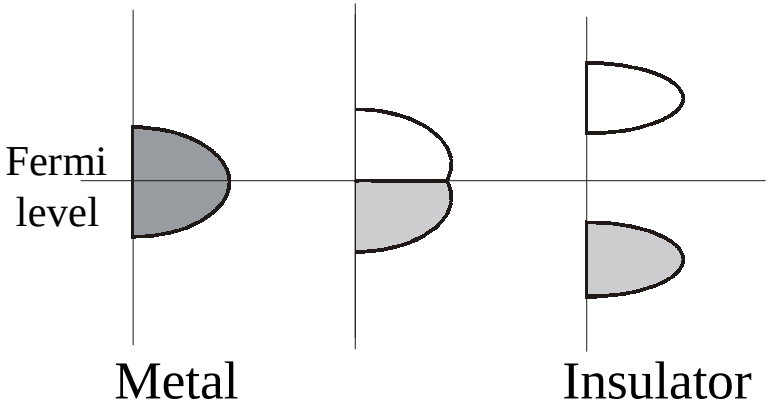


Final Step:

The localized electrons tend to order magnetically!

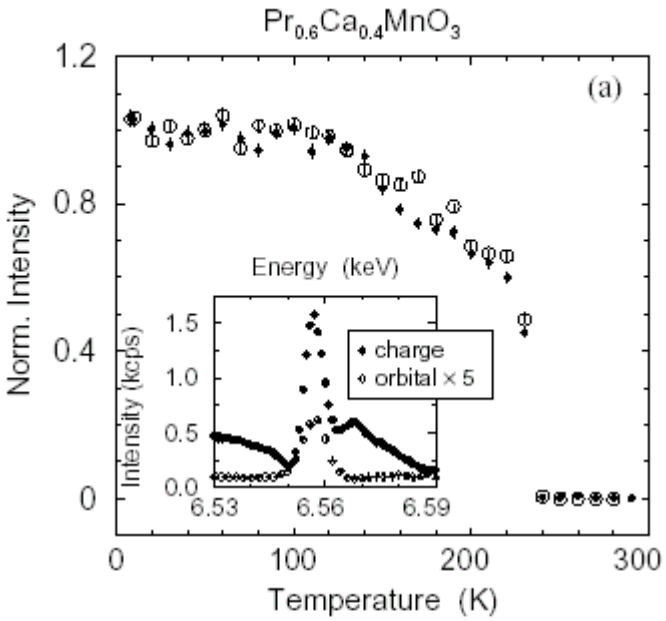
What drives the phase transition?

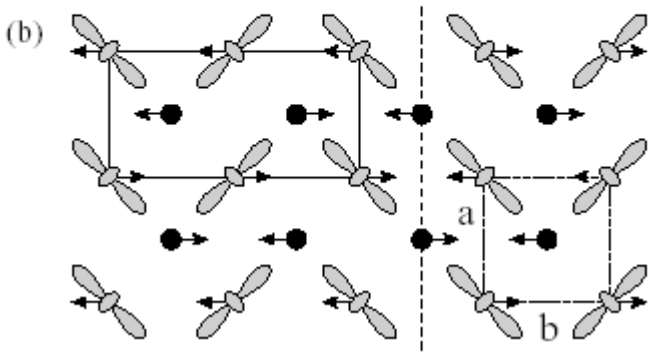




- doping
- temperature
- external parameters
  (magnetic field, stress, ...)

Charge Order





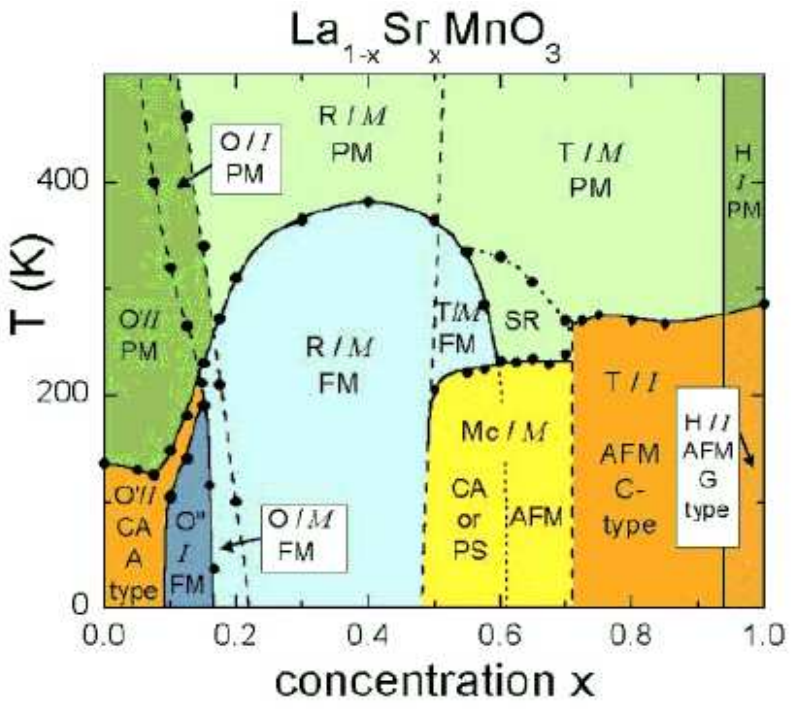
$Pr_{0.6}Ca_{0.4}MnO_3$

- Mn^{4+} (d^3)
- Mn^{3+} (d^4)

Resonant X-ray scattering of charge and orbital order

M.v. Zimmermann et al.,
PRL 83, 4872 (1999)

Spin, Charge and Orbital Order



Structural:

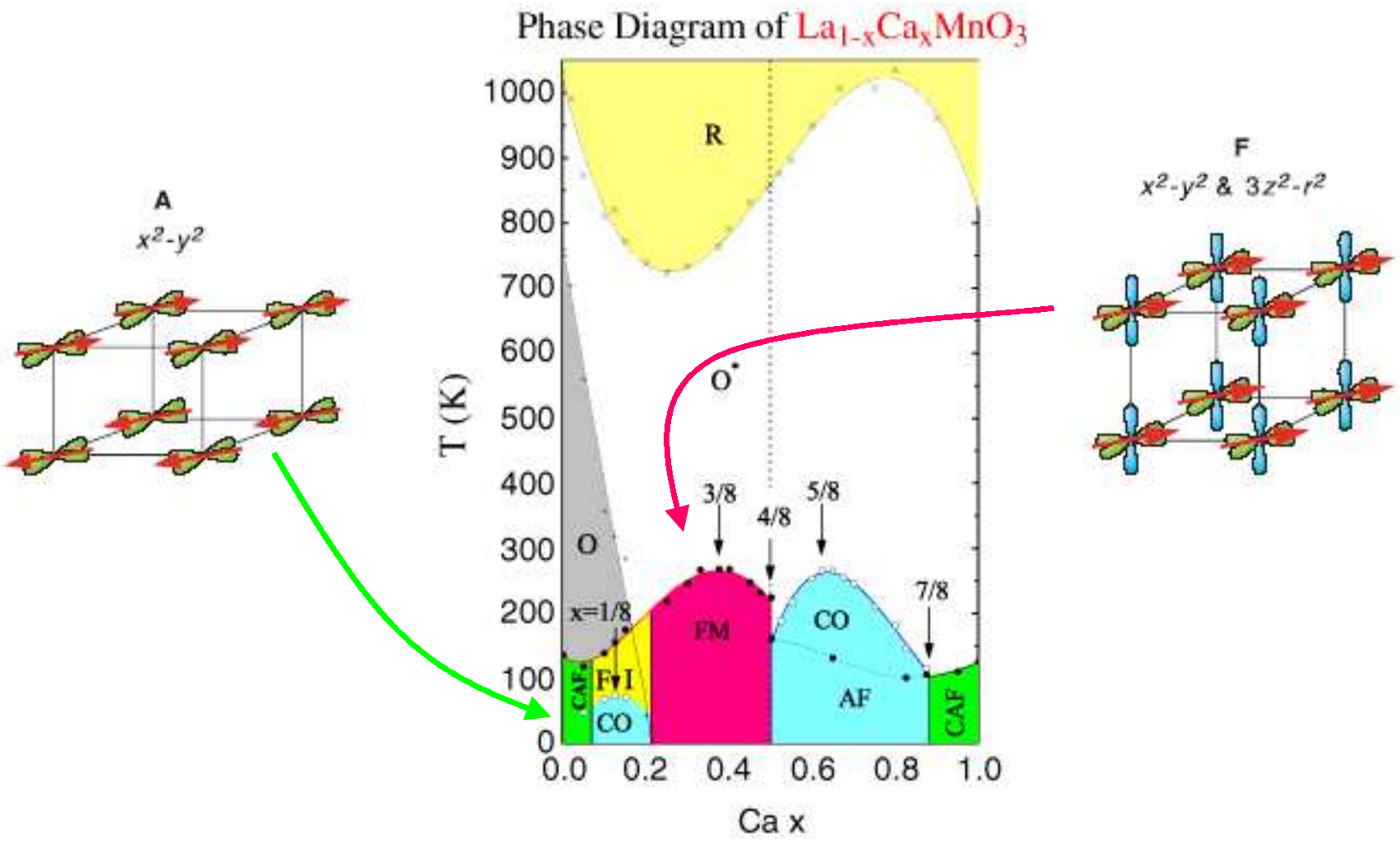
O	orthorhombic
O‘	orthorhombic Jahn-Teller
O“	orthorhombic Orbital Order
R	rhombohedral
T	tetragonal
Mc	monoclinic
H	hexagonal

PM	paramagnetic
SR	short range
CA	canted
AFM	antiferromagnetic
FM	ferromagnetic

I	insulating
M	metallic

J. Hemberger *et al.*,
PRB **66**, 94410 (2002)

Spin, Charge and Orbital Order



$LaMnO_3$ well understood!

Are Transition Metal Oxides well understood?

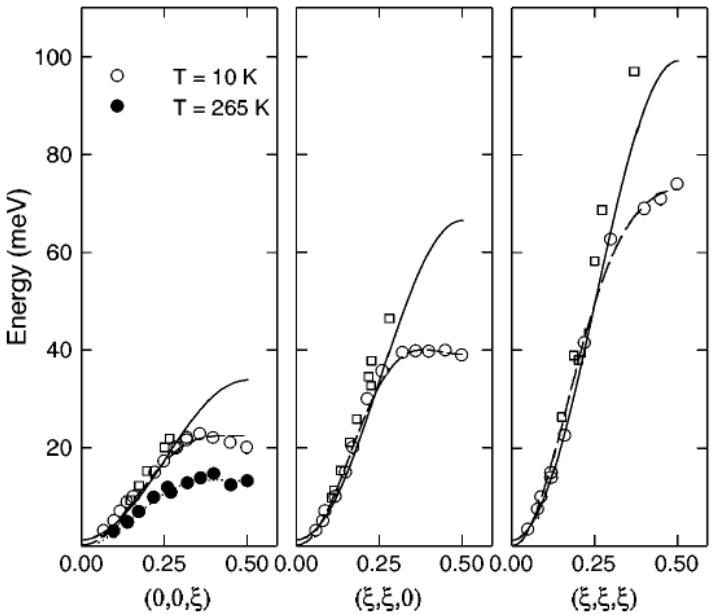
NOT AT ALL!!

- HTc superconductors (cooperates)
- Unconventional HTc superconductors
- Colossal Magnetoresistance
- Frustrated Magnets
- Quantum Magnetism
- Orbital Excitations

$LaMnO_3$: unsolved problems

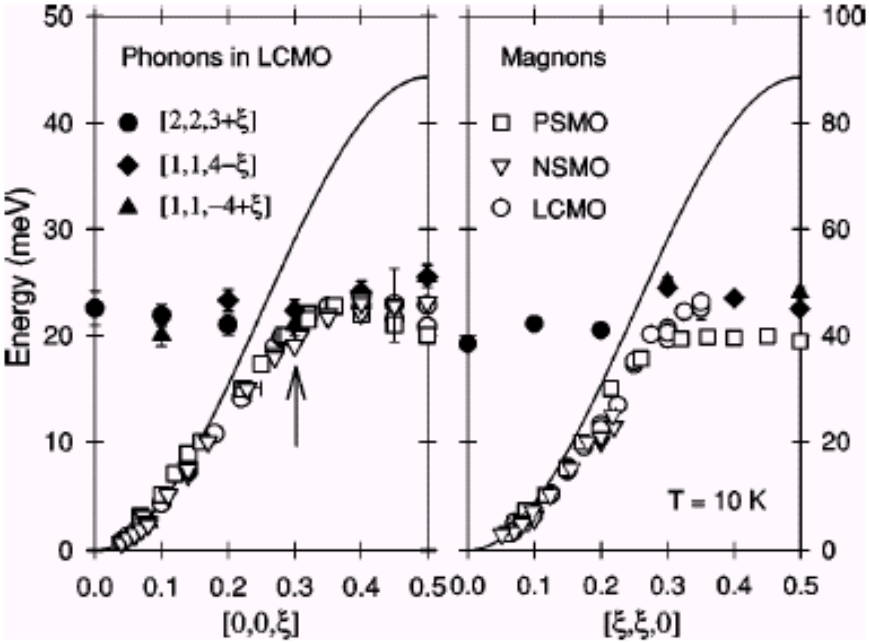
Inelastic Neutron Scattering: Spin Wave Dispersion

$Pr_{1-x}Ca_xMnO_3$



Hwang *et al.*, PRL **80**, 1316 (1998)

$Pr_{1-x}Sr_xMnO_3$ / $Nd_{1-x}Sr_xMnO_3$ / $La_{1-x}Ca_xMnO_3$

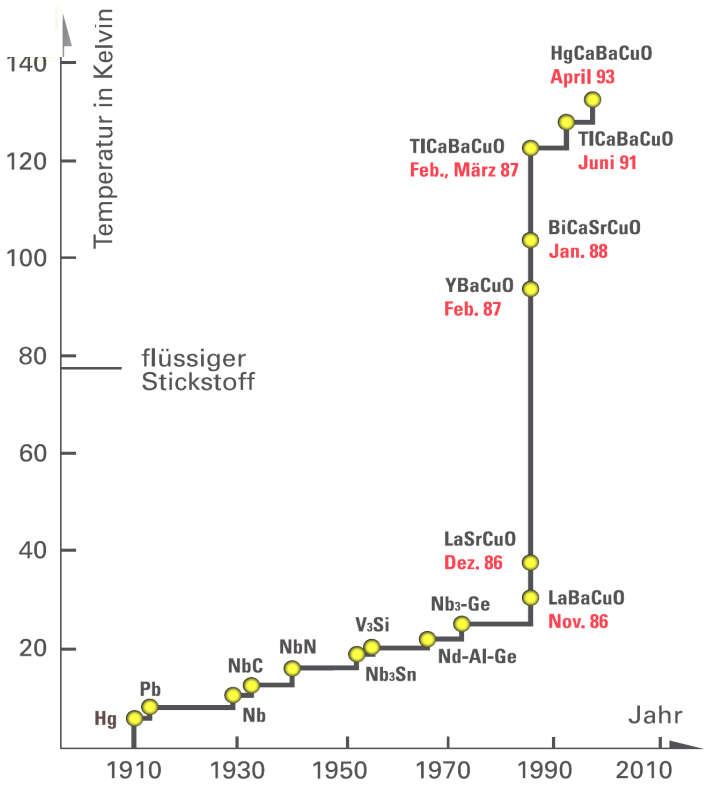


Dai *et al.*, PRB **61**, 9553 (1998)

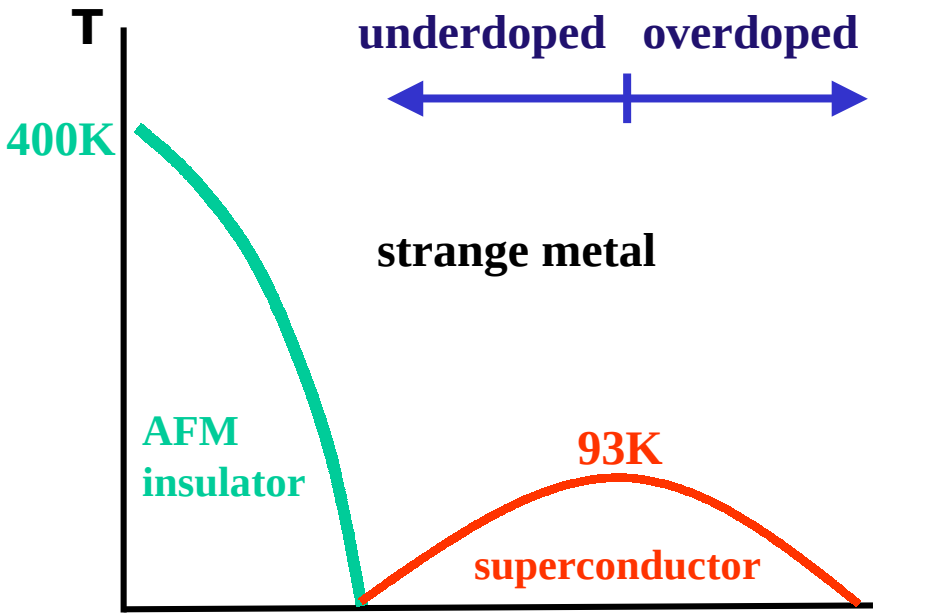
large deviations from predictions of simple Heisenberg model

→ interaction with phonons?
→ low-lying orbital excitations?

High Temperature Superconductors



HTc superconductivity

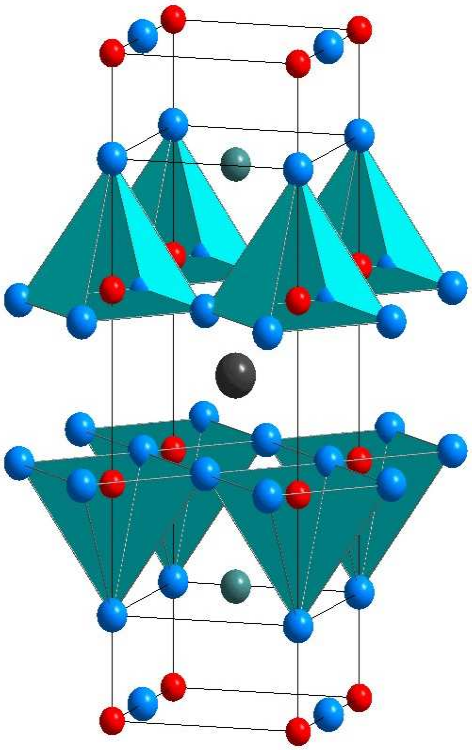


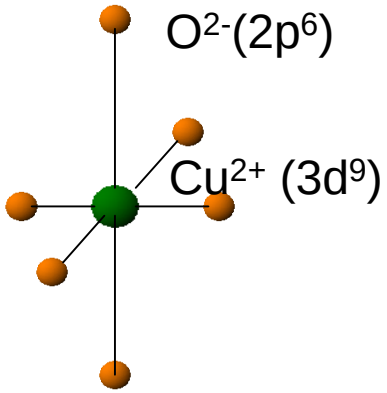
charge carrier density in CuO_2 layers

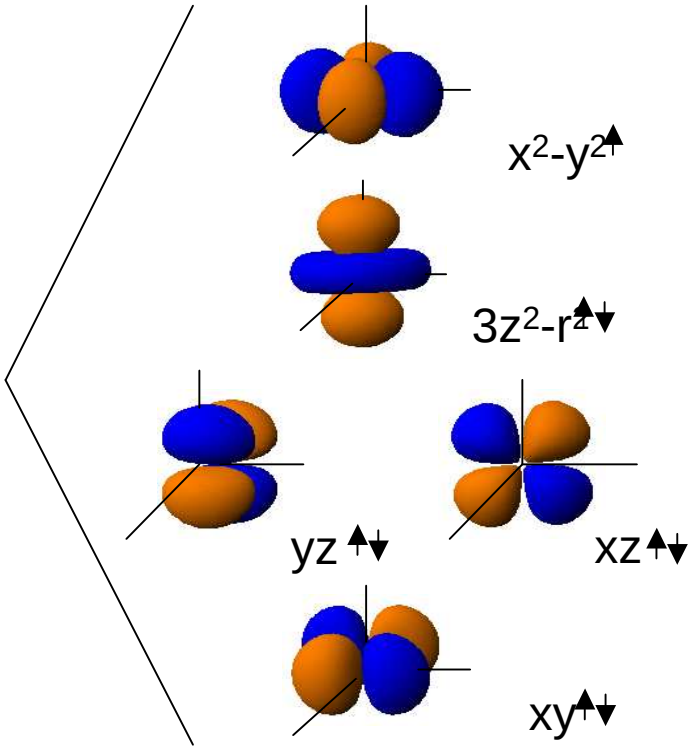
Electronic Structure of $YBa_2Cu_3O_7$

T_C = 93 K

$YBa_2Cu_3O_7$



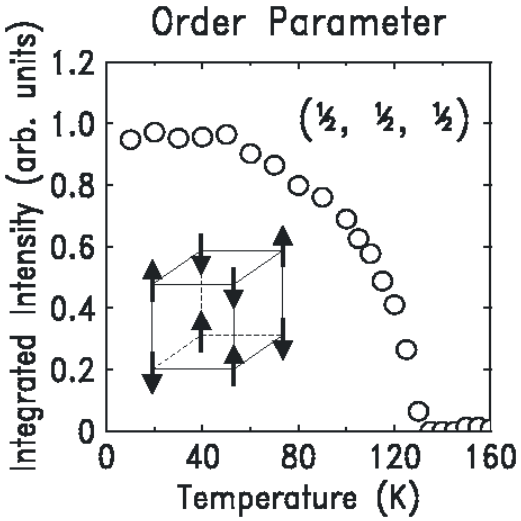




Orbital physics is more complicated!

Spin Structure in $LaTiO_3$

Ti^{3+} $3d_1$



G_x-type antiferromagnet

0.53 μ_B / Ti^{3+} ion

along the a-axis

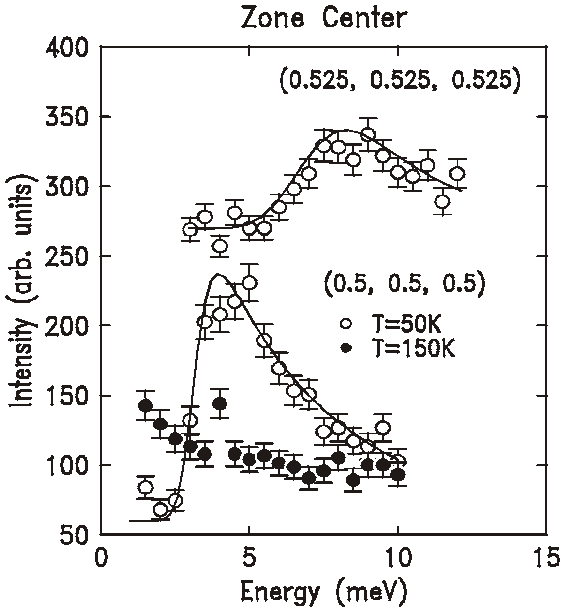
Inelastic Neutron Scattering:
Integrated intensity of the
(½ ½ ½) antiferromagnetic
Bragg reflection.
G-type spin structure.

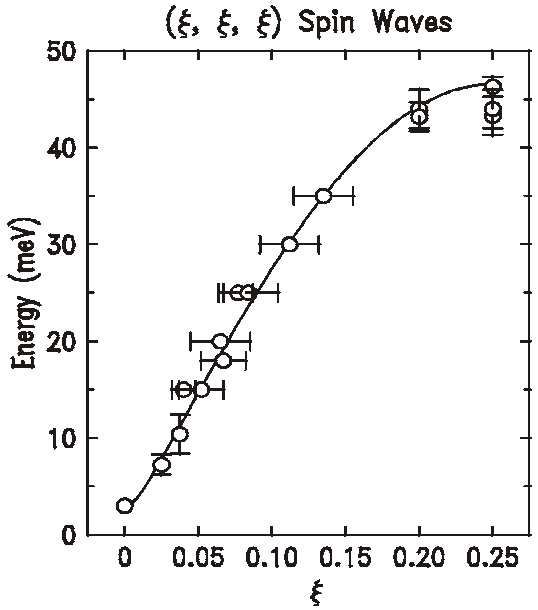
expected for a 3D Ti^{3+} ion:
$\mu_0 = 0.85\ \mu_B$ / Ti^{3+}

2D perovskite Cu^{2+}:
$\mu_0 = 0.60\ \mu_B$ / Cu^{2+}

B. Keimer *et al.*, PRL **85**, 3946 (2000).
C. Ulrich, M. Reehuis, J. Hemberger (2004).

Inelastic Neutron Scattering: Spin wave dispersion in $LaTiO_3$





J = 15.5 meV

Magnon Dispersion Relation of $LaTiO_3$ along the (1,1,1) direction.

Isotropic Heisenberg model with nearest neighbor superexchange.

J = 15.5 meV Spin Gap Δ = 3.3 meV

B. Keimer *et al.*, PRL **85**, 3946 (2000).

The Ferromagnetic Insulator $YTiO_3$

$LaTiO_3$: larger bond angle $\theta \sim 156^0$ (AFM)
$\Rightarrow$ wide band

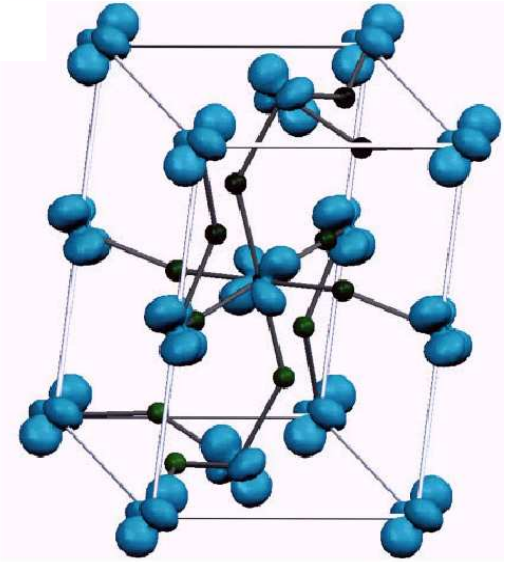
$YTiO_3$: smaller bond angle $\theta \sim 142^0$ (FM)
$\Rightarrow$ narrow band
smaller Ti-Ti hopping
weakened superexchange

- spin ferromagnetism as predicted by electronic band structure calculations
- Goodenough-Kanamori rules obeyed

Theory:
Sawada & Terakura
Mizokawa et al.

$$|\psi\rangle_{1,3} = c_1|yz\rangle \pm c_2|xy\rangle$$
$$|\psi\rangle_{2,4} = c_1|xz\rangle \pm c_2|xy\rangle$$

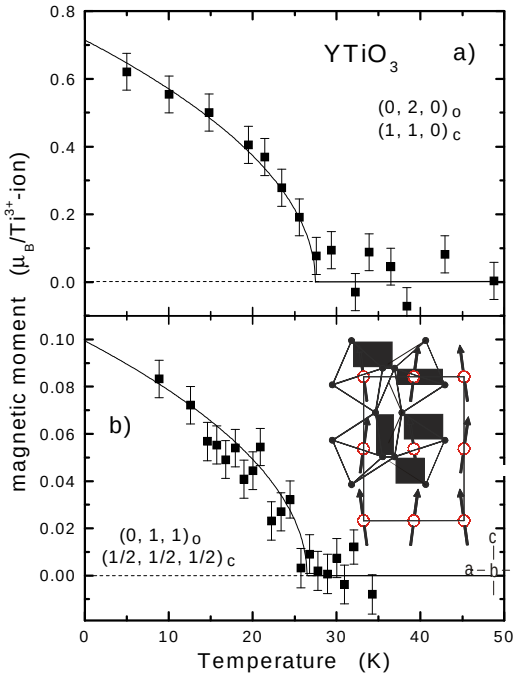
Proposed
Ti $3d^1$-orbitals

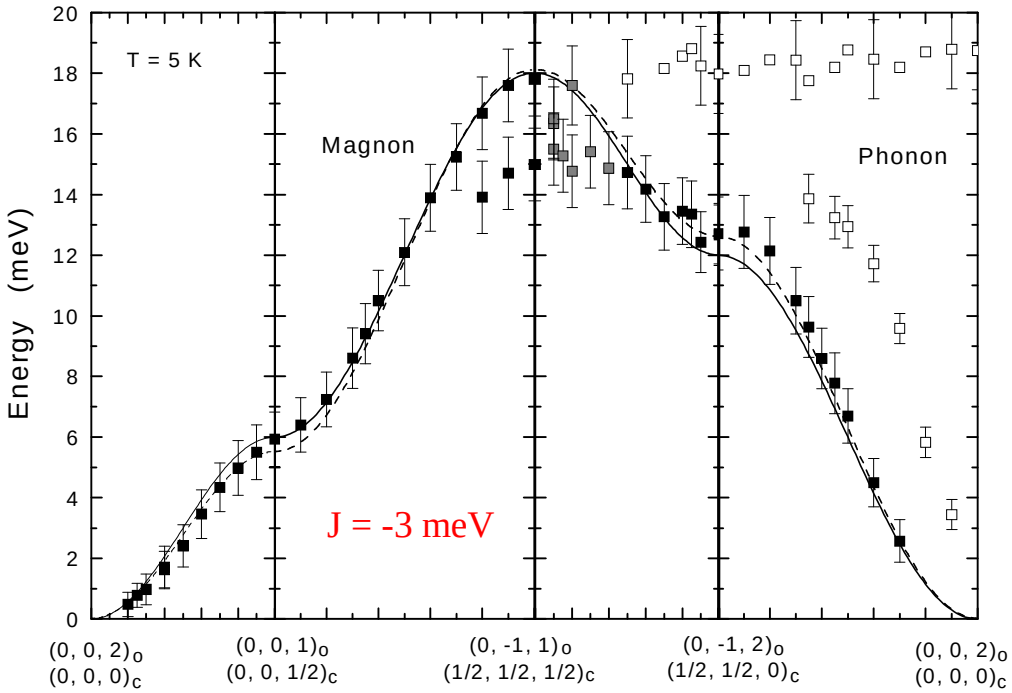


Experiment:
Akimitsu et al. (neutrons)
Itoh et al. (NMR)

$\Rightarrow$ **anisotropic spin wave spectrum expected**

Inelastic Neutron Scattering in $YTiO_3$





Ferromagnet:

$T_C = 27$ K

$\mu_0 = 0.715\ \mu_B/Ti^{3+}$

fit to a Heisenberg model with
isotropic ferromagnetic exchange

$E = 6\ S\ J\ (1 - \gamma_q)$

$J = -3.0$ meV

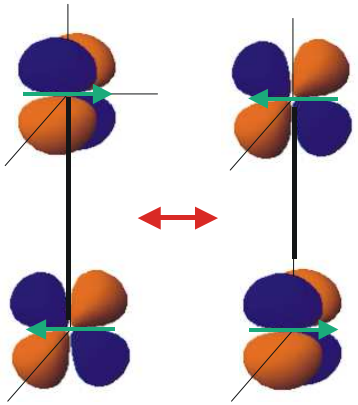
magnon gap = 0.16 meV

C. Ulrich *et al.*, PRL **89**, 167202 (2002).

Orbital Fluctuations in $LaTiO_3$

t_{2g} orbitals versus e_g orbitals

- not bond directional: JT - coupling is relatively weak
- two equivalent orbitals on every bond : quantum resonance
- large degeneracy : fluctuations are enhanced



t_{2g}-superexchange in $LaTiO_3$

c - bond :

$$\frac{4t^2}{U}\left(S_iS_j + \frac{1}{4}\right)\left(\tau_i\tau_j + \frac{1}{4}n_in_j\right)_{ab}$$

spin pseudospin on orbital doublet

Spin-orbital resonance

spin : triplet orbital: singlet	resonance ⟷	spin : singlet orbital: triplet

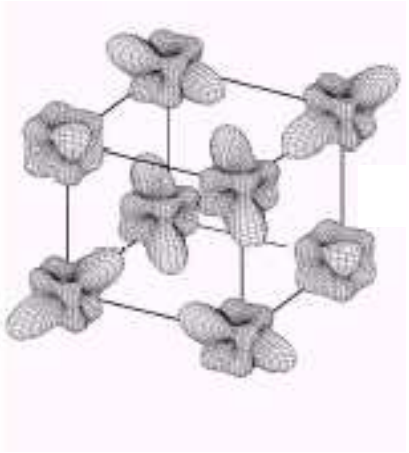
orbital fluctuations:

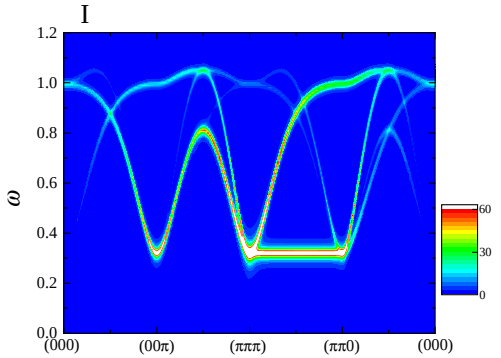
with fixed exchange parameter J = 15.5 meV from neutron scattering:
- antiferromagnetic state
- reduced magnetic moment of 0.5 μ_B
- isotropic spin dynamic with a spin gap of 3 meV

G. Khaliullin, S. Maekawa,
PRL 85, 3950 (2000).

New Orbitally Ordered States

derived from superexchange model with spin ferromagnetism imposed (Khaliullin & Okamoto, PRL 2002)





- reduced anisotropy due to strong orbital quantum fluctuations

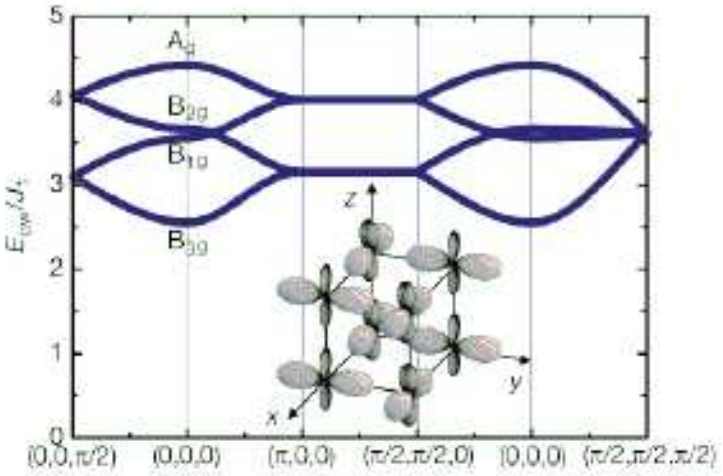
- naturally explains spatially isotropic magnon dispersions, small magnon gap

- prediction: ORBITONS (i.e. orbital wave)

Collective orbital excitations: Orbitons

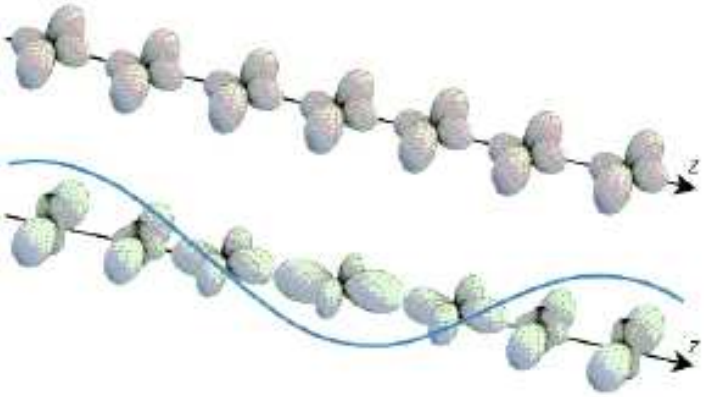
Collective orbital excitation

orbital wave



$LaMnO_3$

Dispersion
Energy gap



Observed by Raman light scattering?
E. Saitoh *et al.*, Nature **410**, 180 (2001).

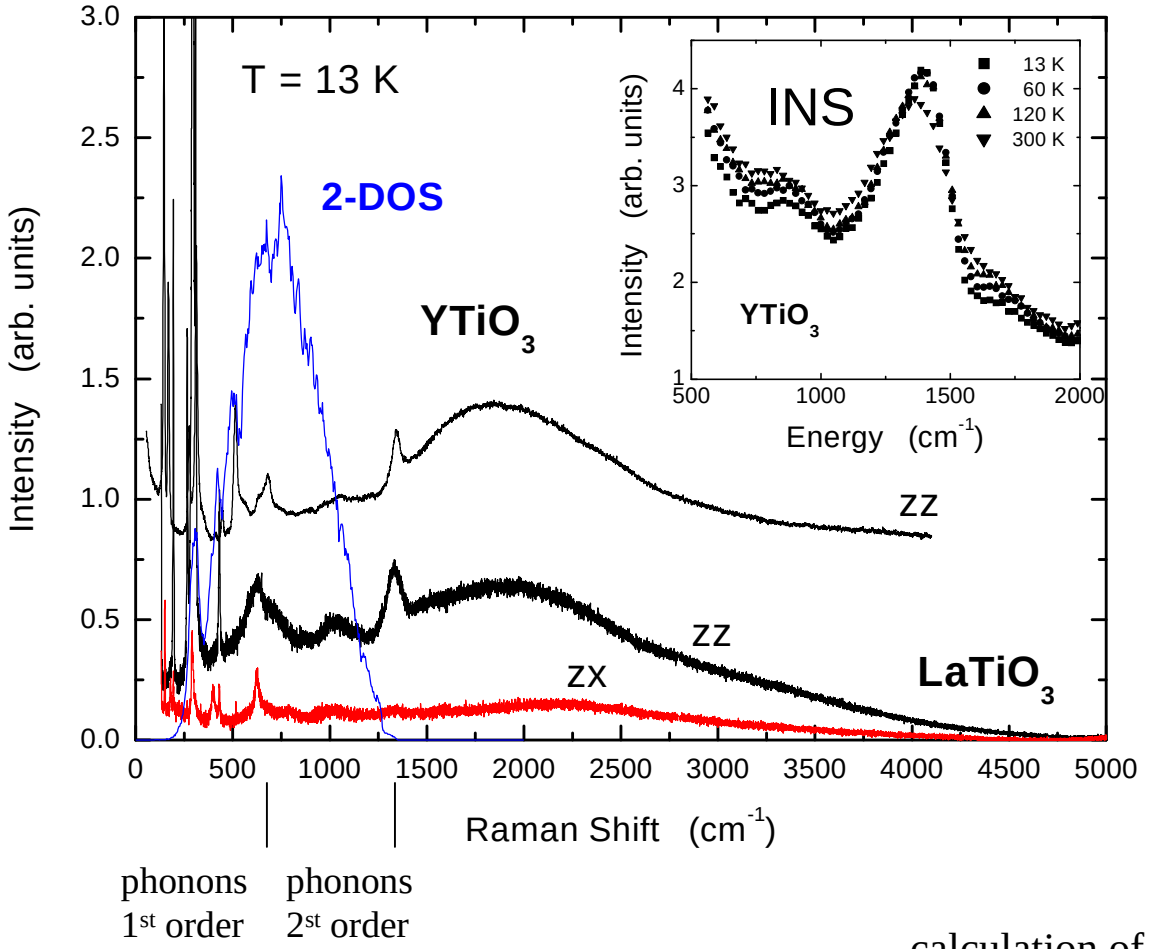
Assigned to two phonon excitations (IR)
M. Grüninger *et al.*, Nature **418**, 39 (2002).

in analogy to
magnons or phonons

Raman Scattering in $LaTiO_3$ and $YTiO_3$

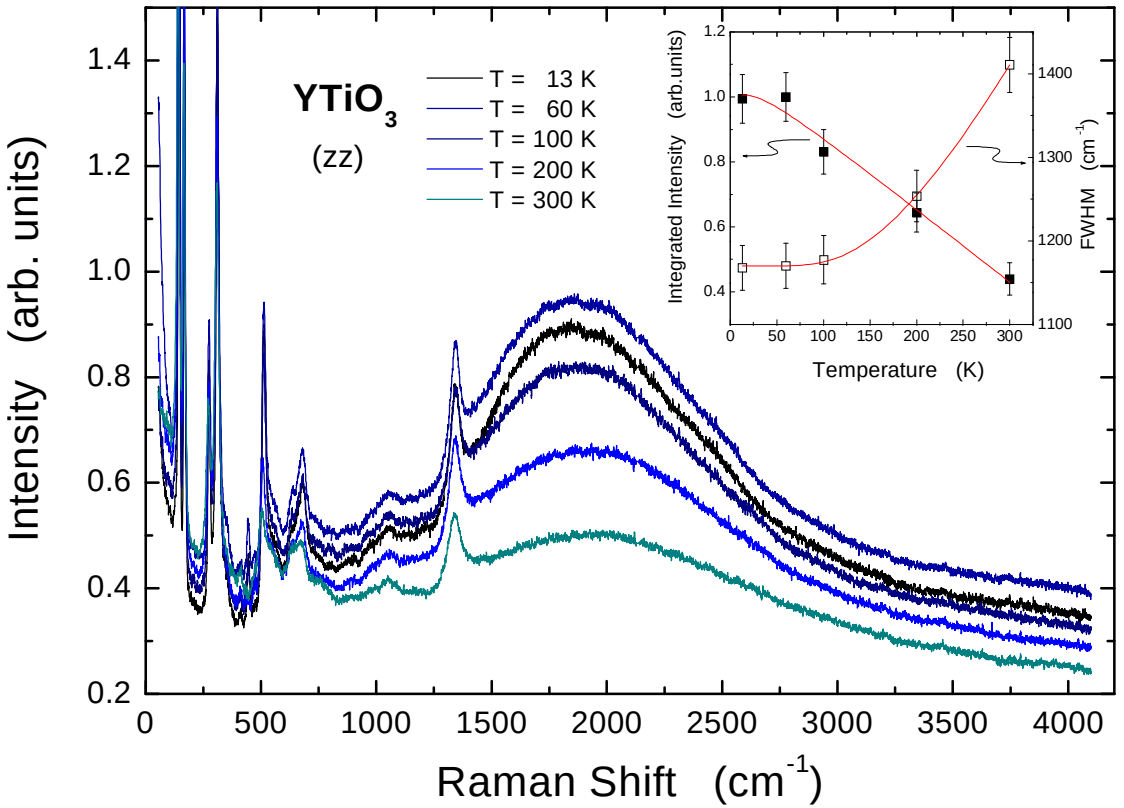
high energy Raman peak at 230 meV in $LaTiO_3$ and $YTiO_3$

possibly two-orbiton excitation



calculation of the phonon-DOS
diploma-thesis: Mael Guennou

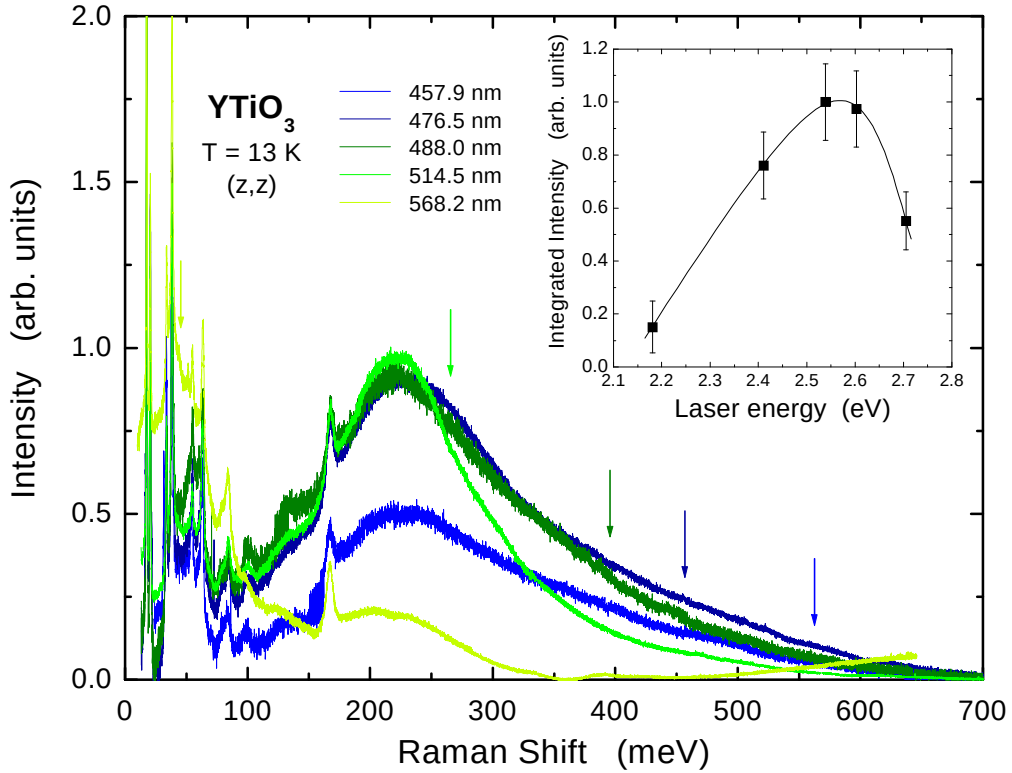
Temperature dependence of the Raman spectrum



not a two magnon excitation
not a polaron (both are insulators!)
also seen in IR transmission

(M. Grüninger, cond-mat/0503405)

Laser-Line dependence of the Raman spectrum

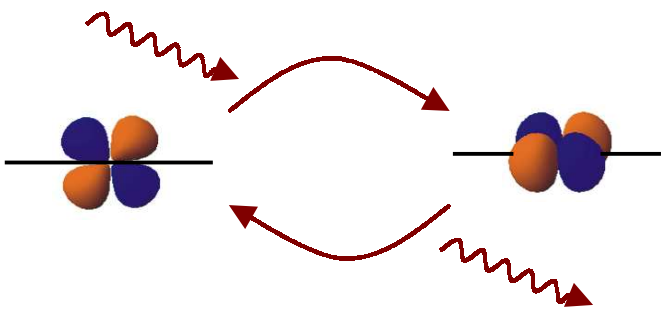


Raman resonance in the energy range of the optical d_i-d_j intersite transition

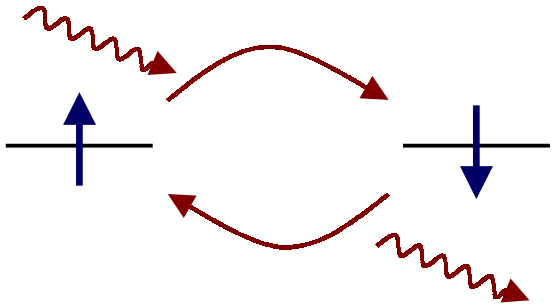
Okimoto *et al.*, PRB **51**, 9581 (1995)

Two Orbiton Raman scattering process

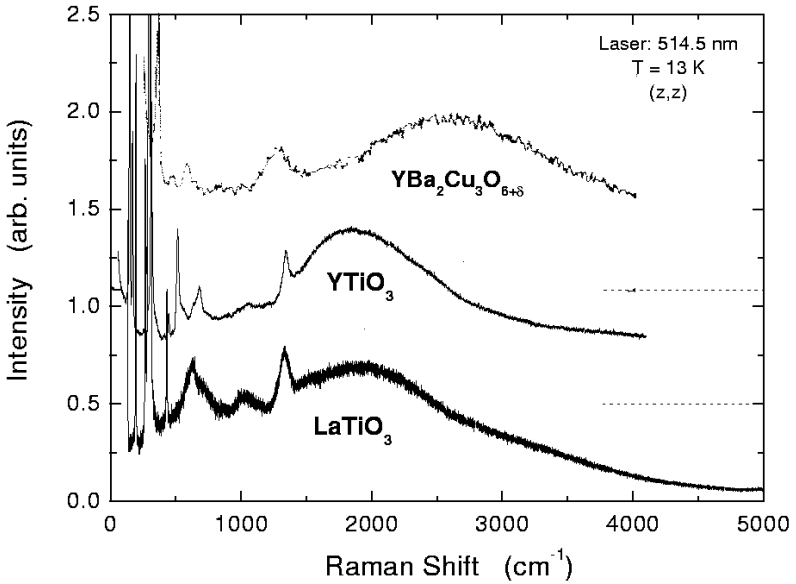
Two-orbiton process



Two-magnon process



2-orbiton excitations



$YBa_2Cu_3O_{6+\delta}$ insulating AF

K.B. Lyons *et al.*,
Phys. Rev. Lett. **60**, 732 (1987).

Conclusions

neutron scattering is an excellent technique to study the interplay between spin, charge, and orbitals

Elastic neutron scattering - Nuclear
- crystals structure
- orbital order

Elastic neutron scattering - Magnetic
- magnetic moment
- spin direction

Inelastic Neutron Scattering - Magnetic
- spin gap energies
- spin wave dispersion
- strenght of the exchange interaction

Collaborators:

Theory:

G. Khaliullin, P. Horsch, A.M. Oles,
Max-Planck-Institut FKF, Stuttgart, Germany.

S. Maekawa, S. Okamoto,
Tohoku University, Sendai, Japan.
RIKEN, Saitama, Japan.

J. Sirker,
Universität Dortmund, Germany.

Raman Light Scattering

A. Gößling, M. Grüninger
Universität zu Köln, Germany.

Crystal Growth:

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University of Tokyo, Japan.

H. Roth, M. Cwik, T. Lorenz
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J. Hemberger, F. Lichtenberg
Universität Augsburg, Germany.

ILL

Inelastic neutron scattering:

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LLB

P. Bourges, D. Reznik, Y. Sidis,
Laboratoire Léon Brillouin, Saclay, France.

NIST

J.W. Lynn,
NIST, Gaithersburg, Maryland.

HMI

Neutron diffraction:

M. Reehuis,
Hahn-Meitner-Institut, Berlin, Germany.

ESRF

Synchrotron x-ray diffraction:

P. Pattison,
ESRF, Grenoble, France.

NSLS

Resonant x-ray diffraction:

J.P. Hill, D. Gibbs, M.v. Zimmermann,
NSLS, Brookhaven National Lab., New-York.