Magnetism and Nanoscale Electronic Properties in Transition Metal Oxides

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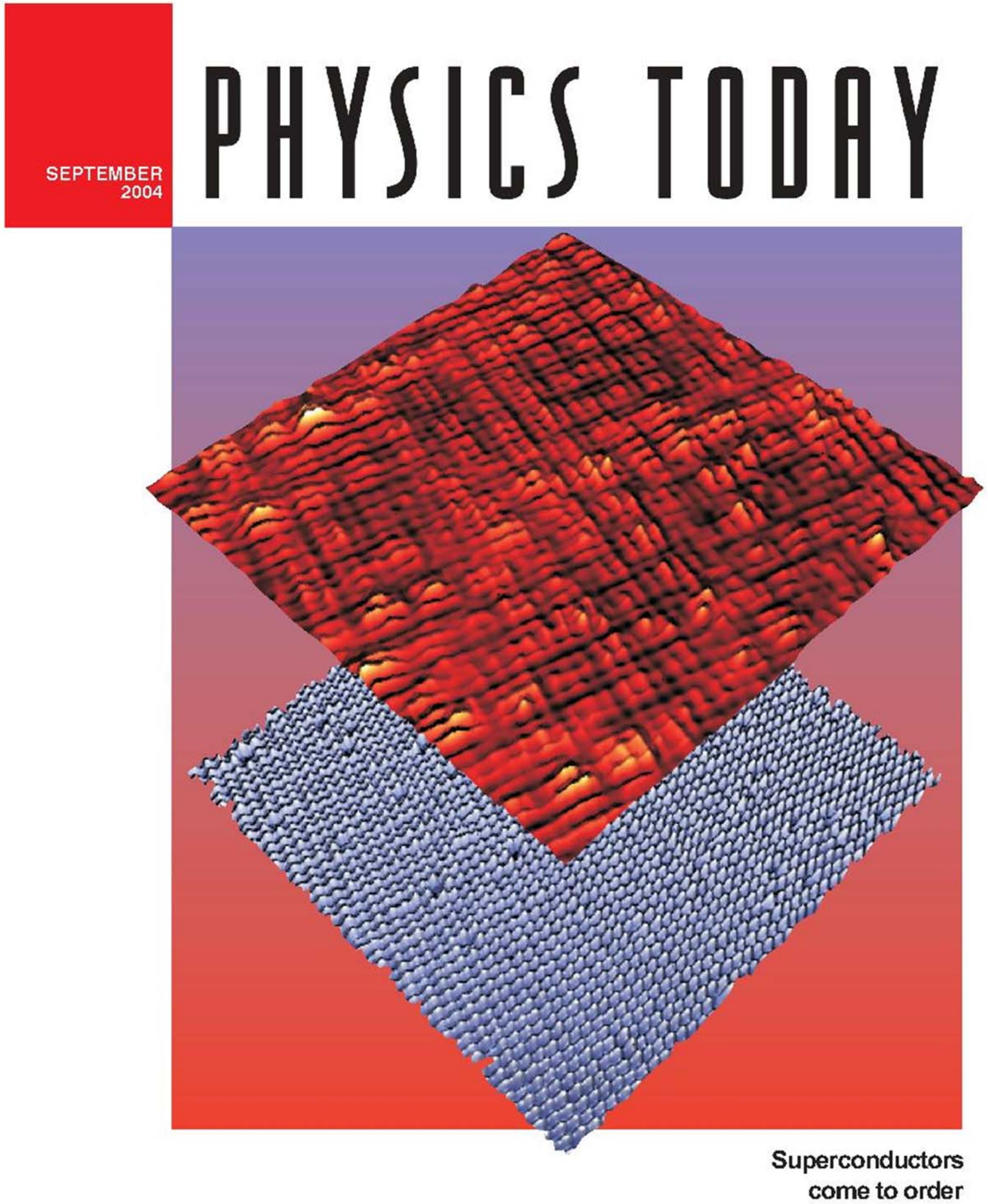
Charge Order in Cuprate Superconductors



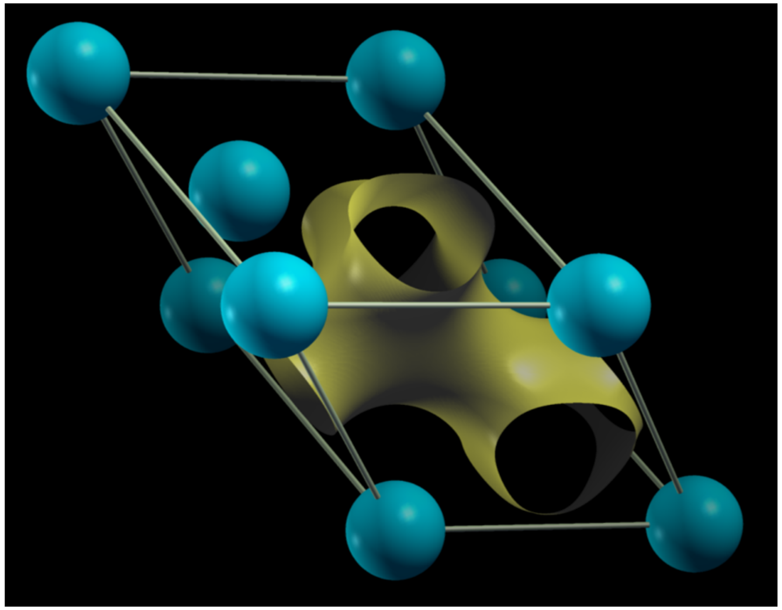
Cover: In these scanning tunneling microscope images of a copper oxide superconductor known as Na-CCOC, the topographical map (blue) shows the location of individual atoms on the cleaved surface. The differential conductance map (red) in the same field of view shows that the electronic states are arranged in checkerboard-like spatial patterns. As explained in the story on page 24, similar patterns have been found in other copper oxide superconductors. (Image courtesy of Séamus Davis at Cornell University and Hidenori Takagi at the University of Tokyo. Prepared by Curry Taylor.)

Bloch's theorem for electrons in periodic potential (crystals)

Bloch's theorem

Eigenfunction of a particle (electron)
in a periodic potential
is a product of a plane wave
and a periodic Bloch function $u_{nk}(r)$
that has the same periodicity
as the potential!!

$$\Psi_{nk}(r) = \varepsilon^{ikr} u_{nk}(r)$$



Bloch wave equipotential in silicon lattice

Symmetry of the lattice determines spatial variation of the electronic properties!!

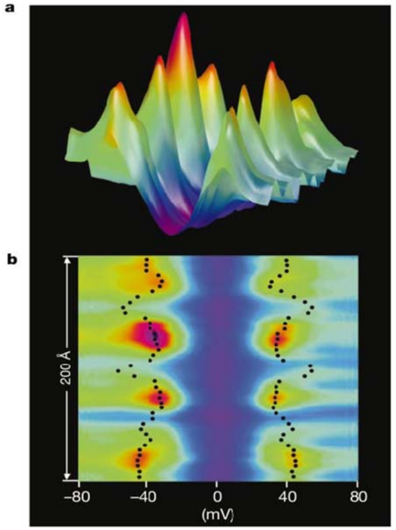
http://en.wikipedia.org/wiki/Bloch_wave or any textbook on condensed matter physics

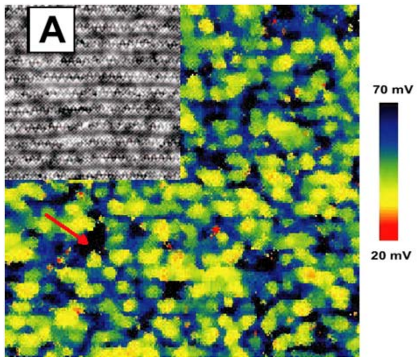
Charge order in transition metal oxides

"Experiment"

Competing interactions in doped magnets
→ Inhomogeneous charge and spin density

"Theory"





STM on Bi2212 superconductors
S.H. Pan et al. Nature (2000)
K.M. Lang et al. Nature (2002)
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etc.

- **Spectacular properties**
  - High temperature superconductivity
  - Colossal magnetoresistance
  - Novel collective electronic excitations
  - Intimately coupled degrees of freedom
  - Complex phase diagrams
  - ...
- **Technical applications**
  - Problems due to intrinsic inhomogeneity
  - Self organized electronic nanostructures
  - ...
- **Challenge for solid state physics**
  - Theory: extremely complicated
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    (intrinsic versus extrinsic inhomogeneity)
  - Interpretation of data
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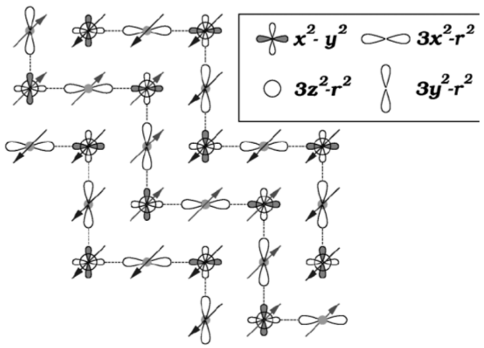
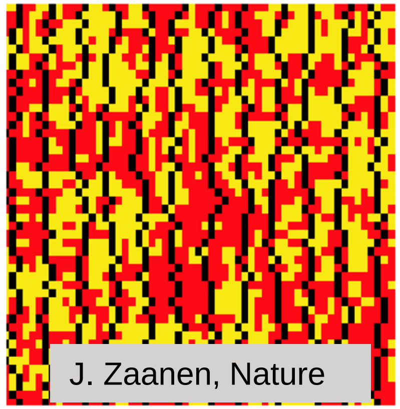
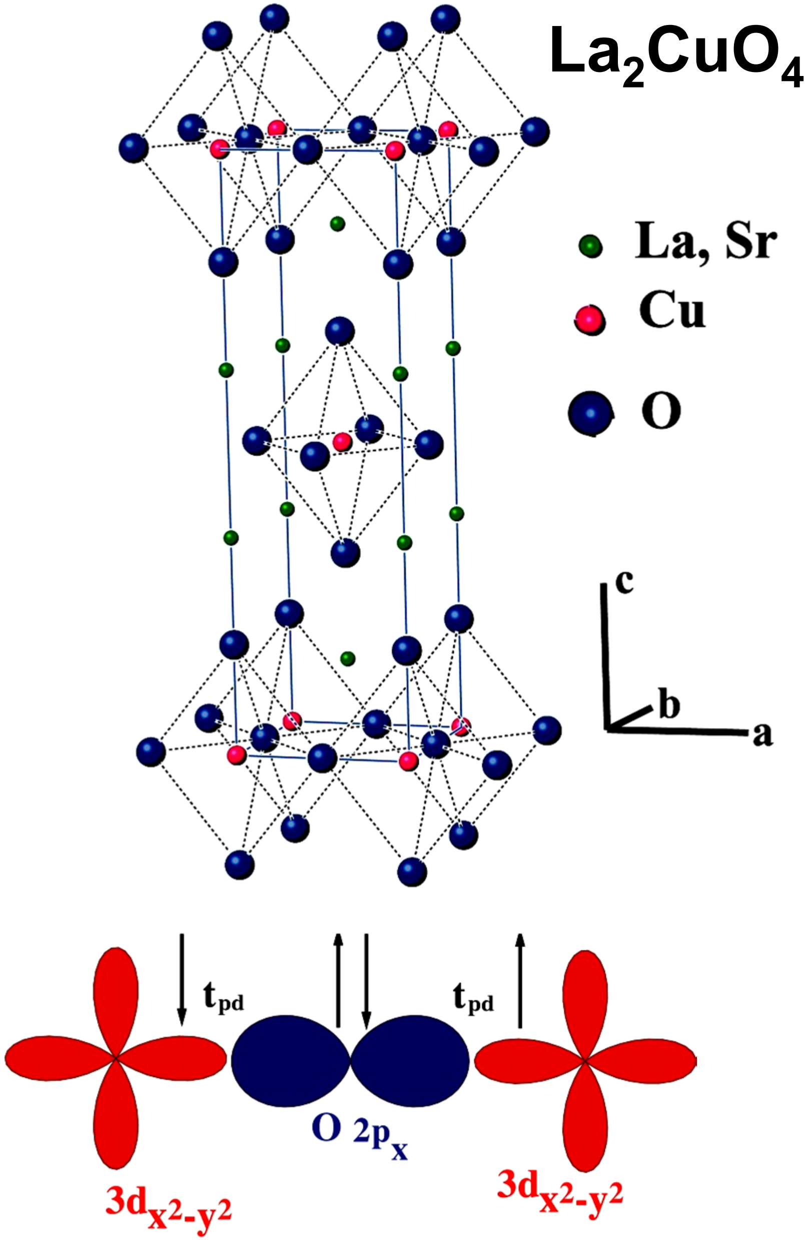


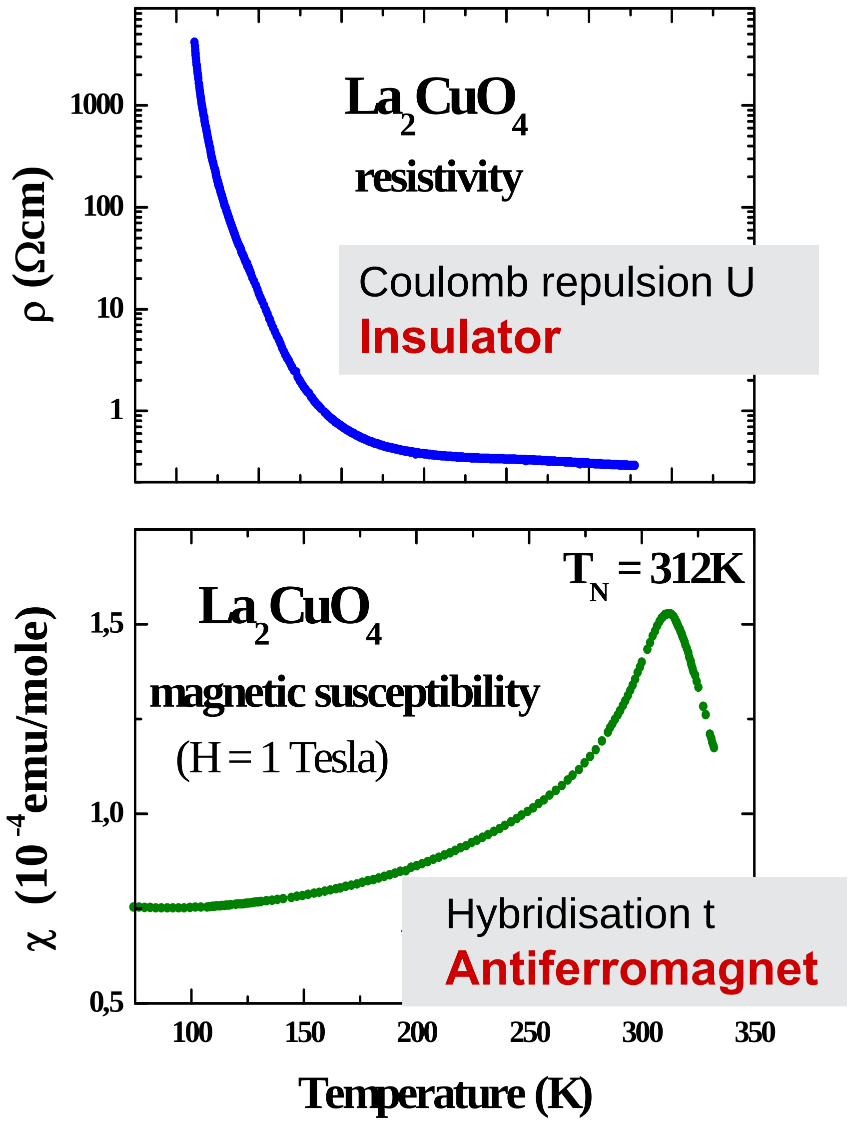
half-doped manganites
CE-Phase,
van den Brink, PRL 1999



J. Zaanen, Nature

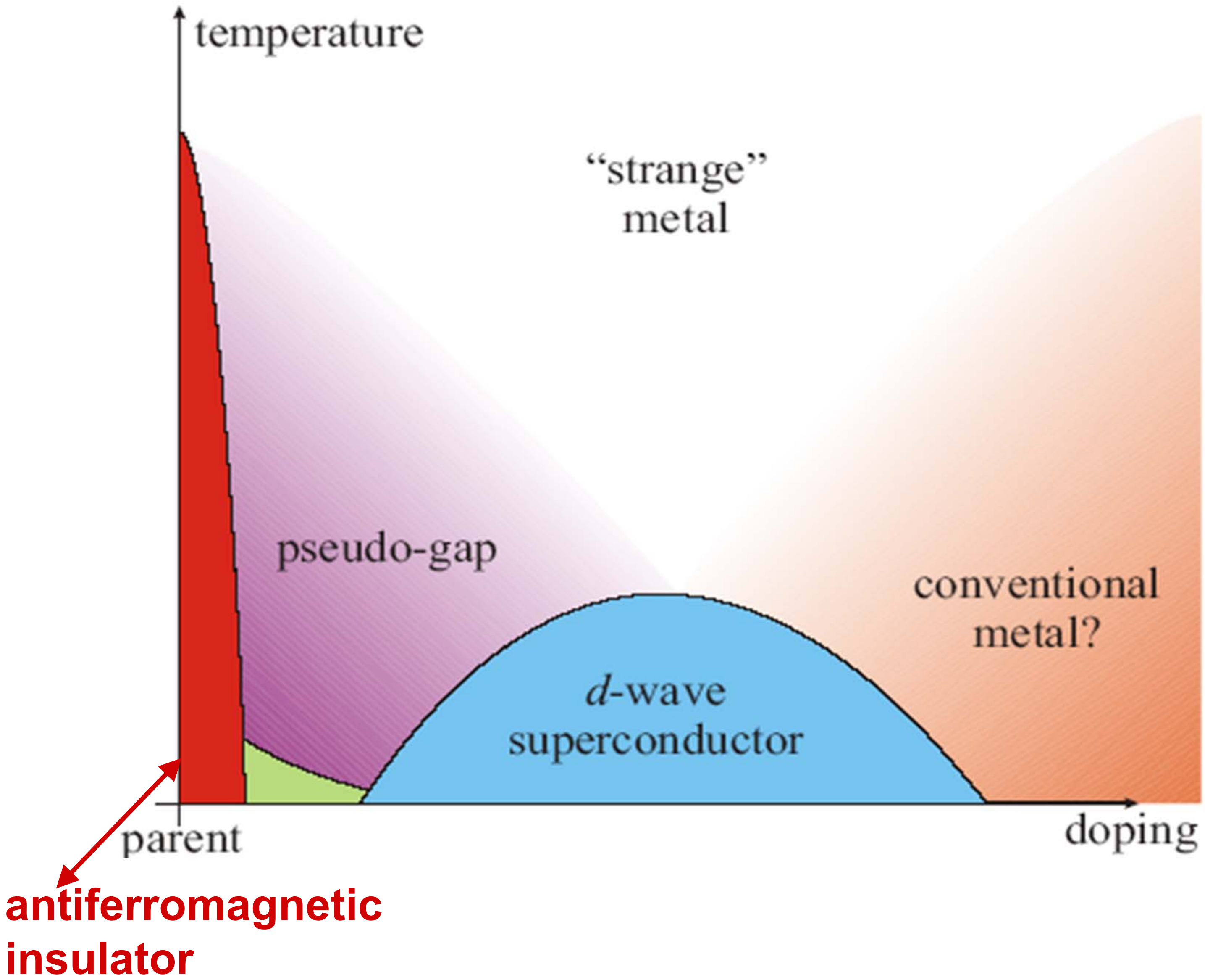
Electronic Correlations and Antiferromagnetism



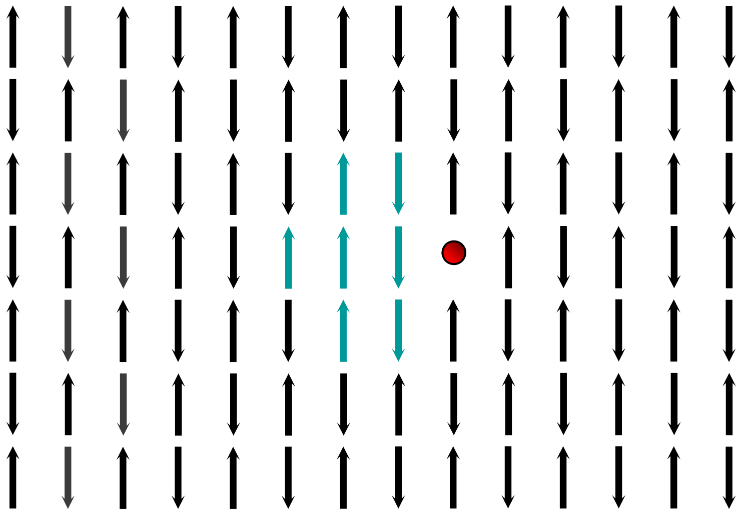


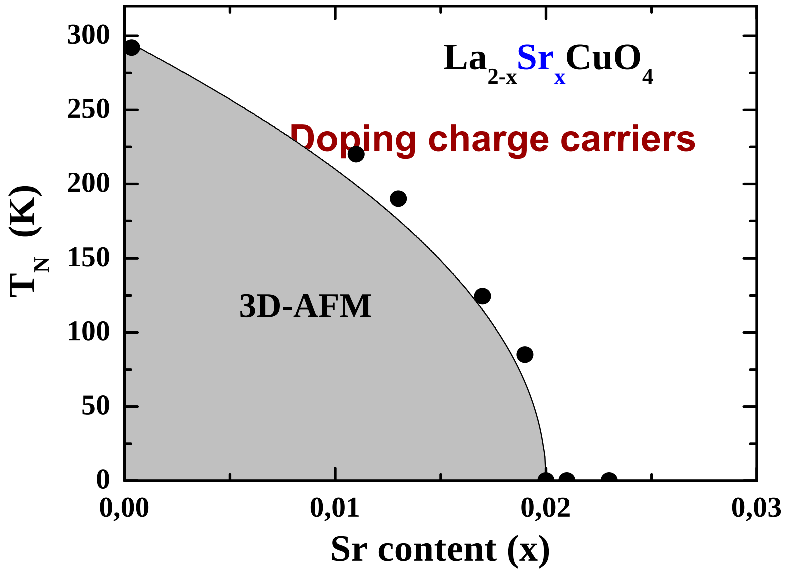
2d-antiferromagnet, $J/k_B \sim 1500K$

Magnetism and Superconductivity: Cuprates

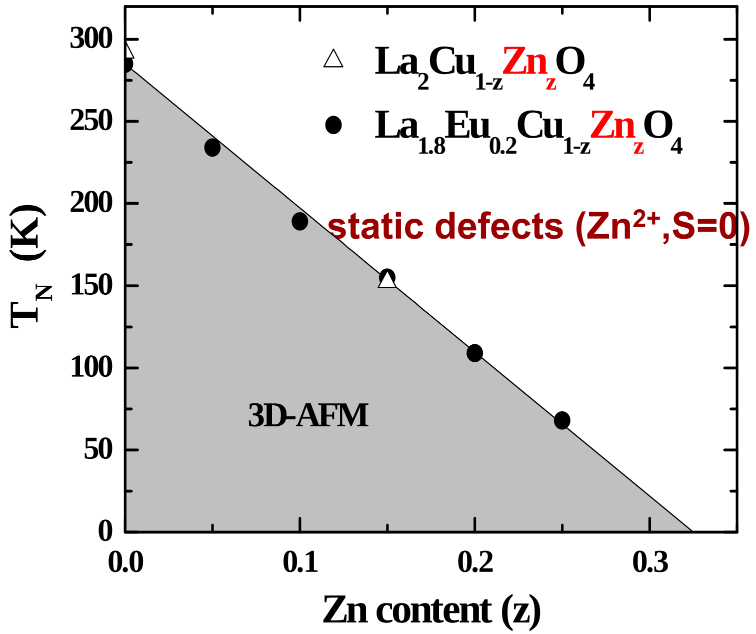


Antiferromagnetism and Charge Mobility





Antiferromagnetism:
reduced hole mobility
Hole motion:
suppressed AFM



M. Hücker et al., PRB' 99,
M. Hücker and B.B., PRB 06

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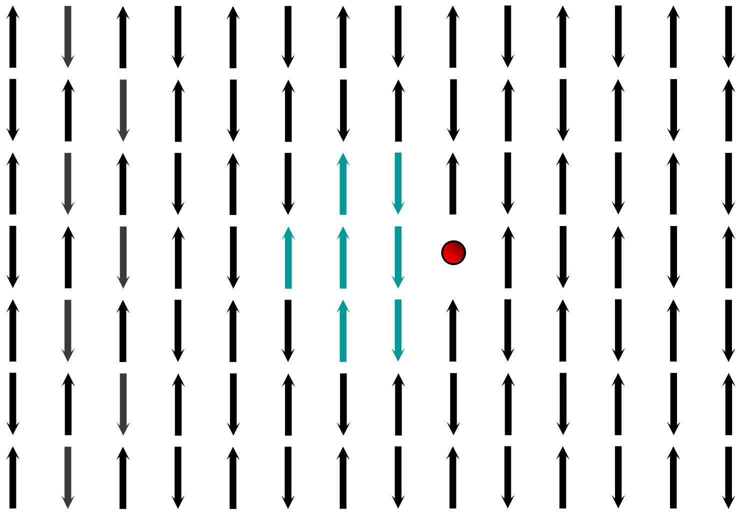

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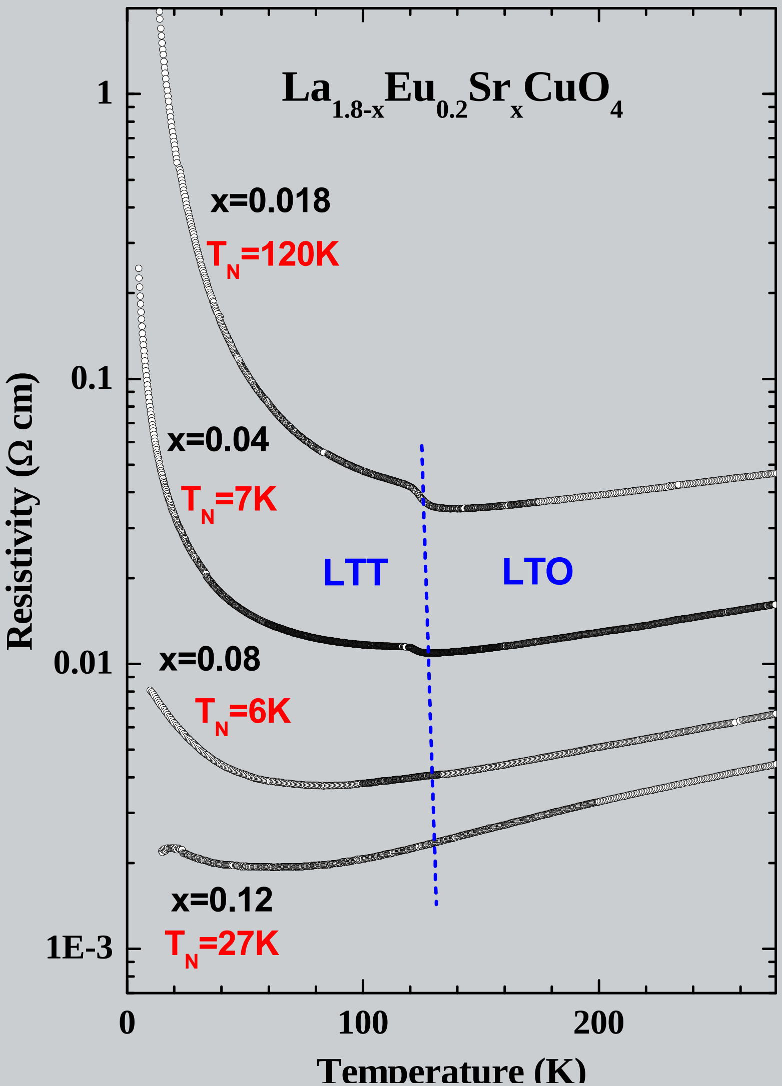
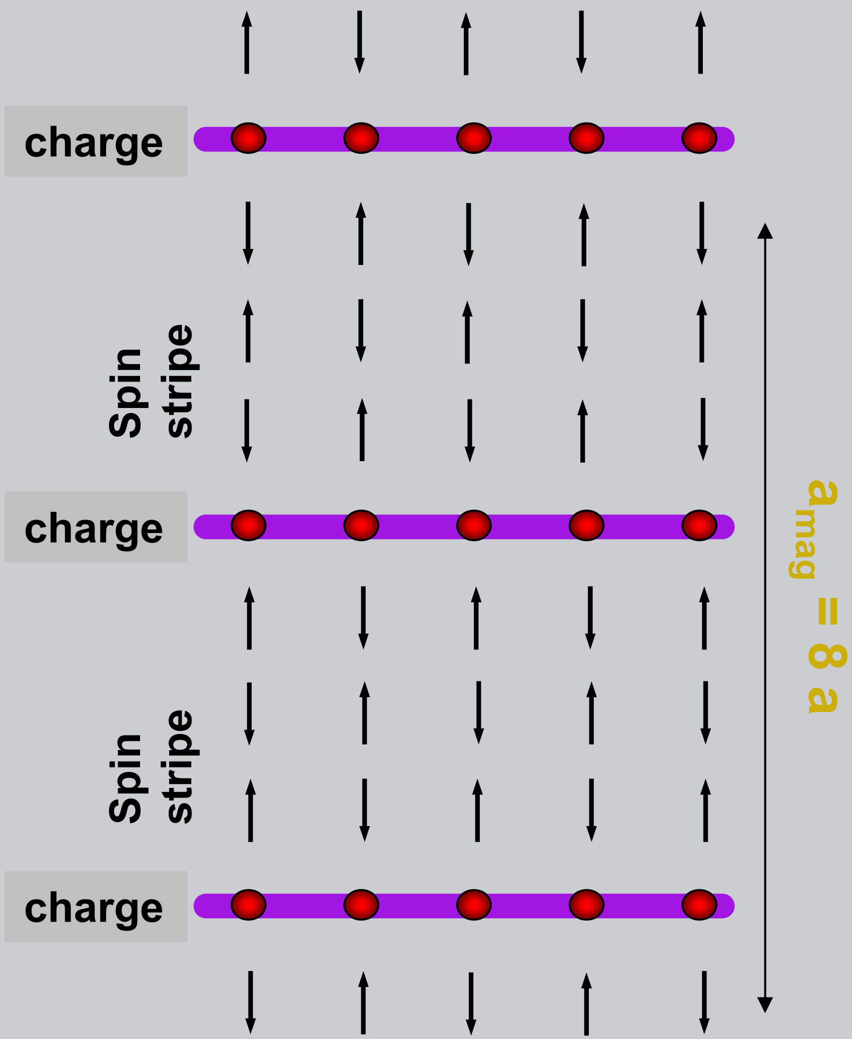
Cuprates with static stripes



T_N increases in metallic compounds

Antiferromagnetism and Charge Mobility

Stripe model



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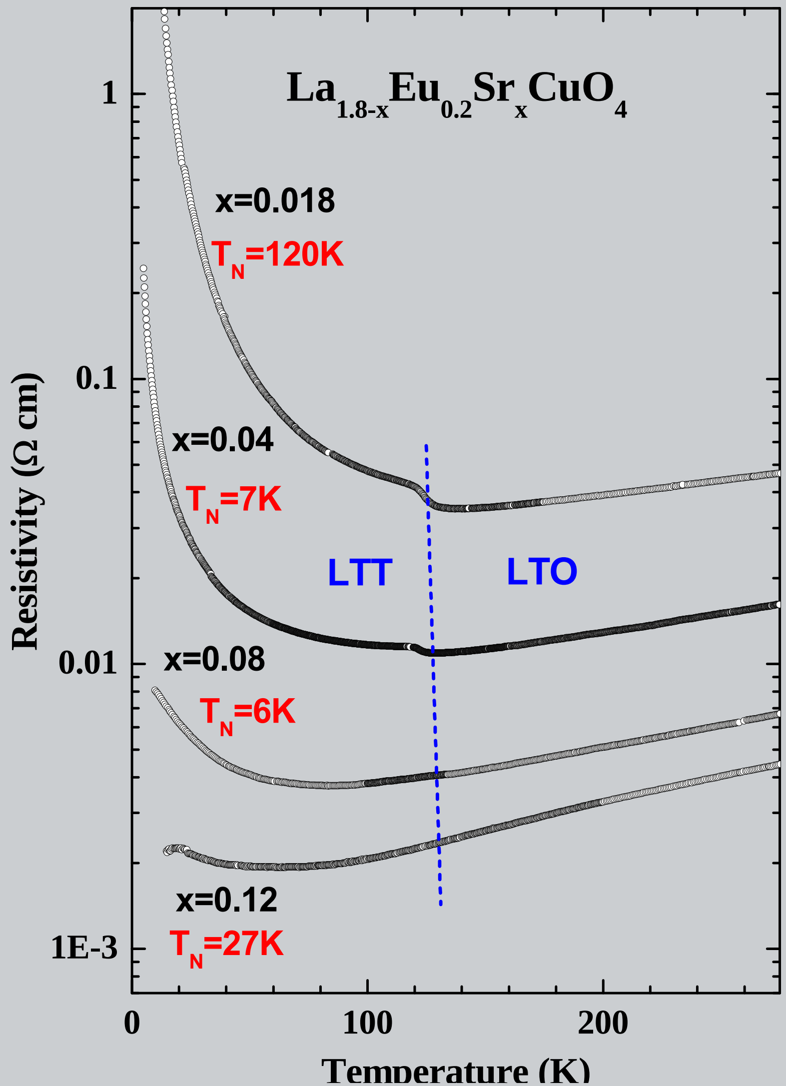

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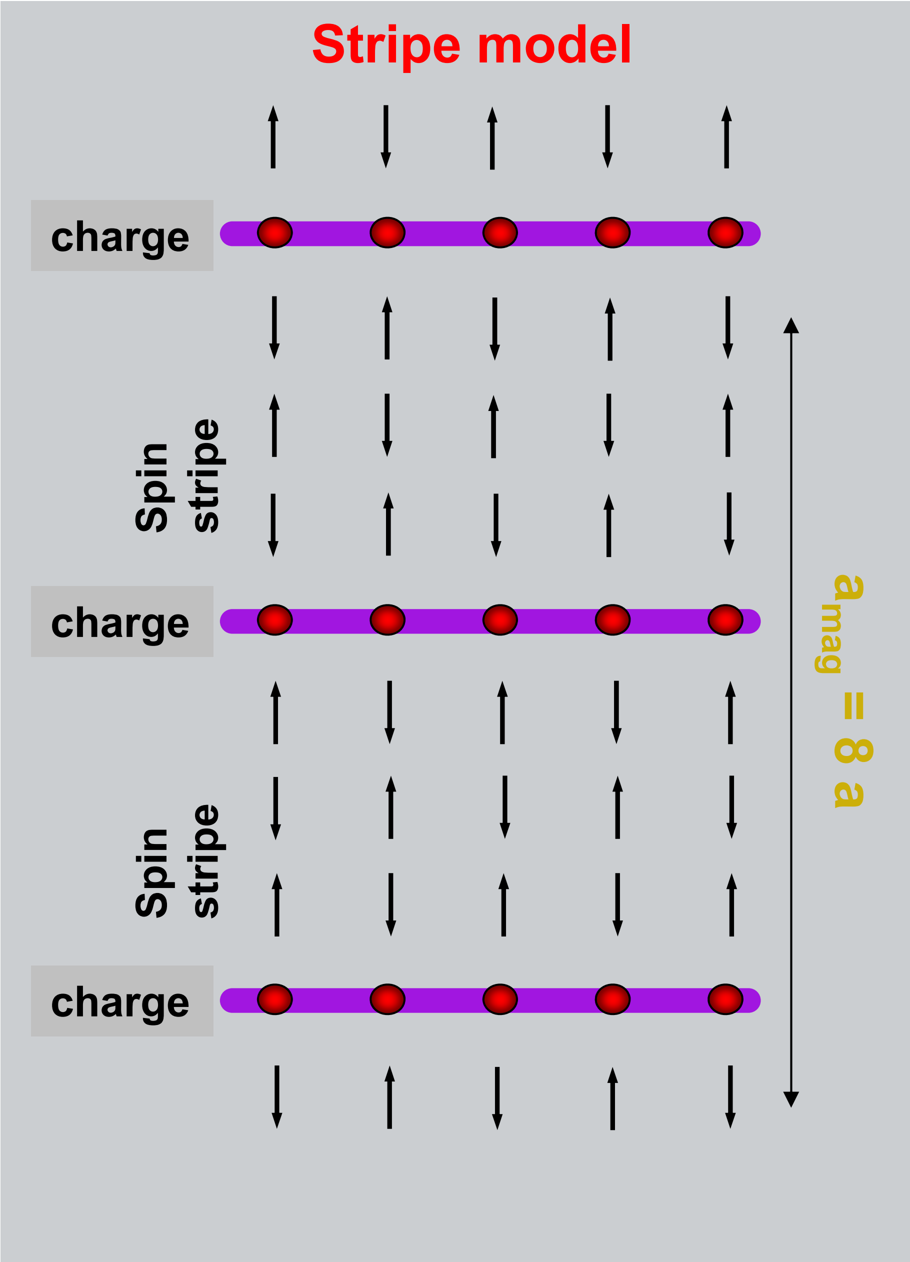
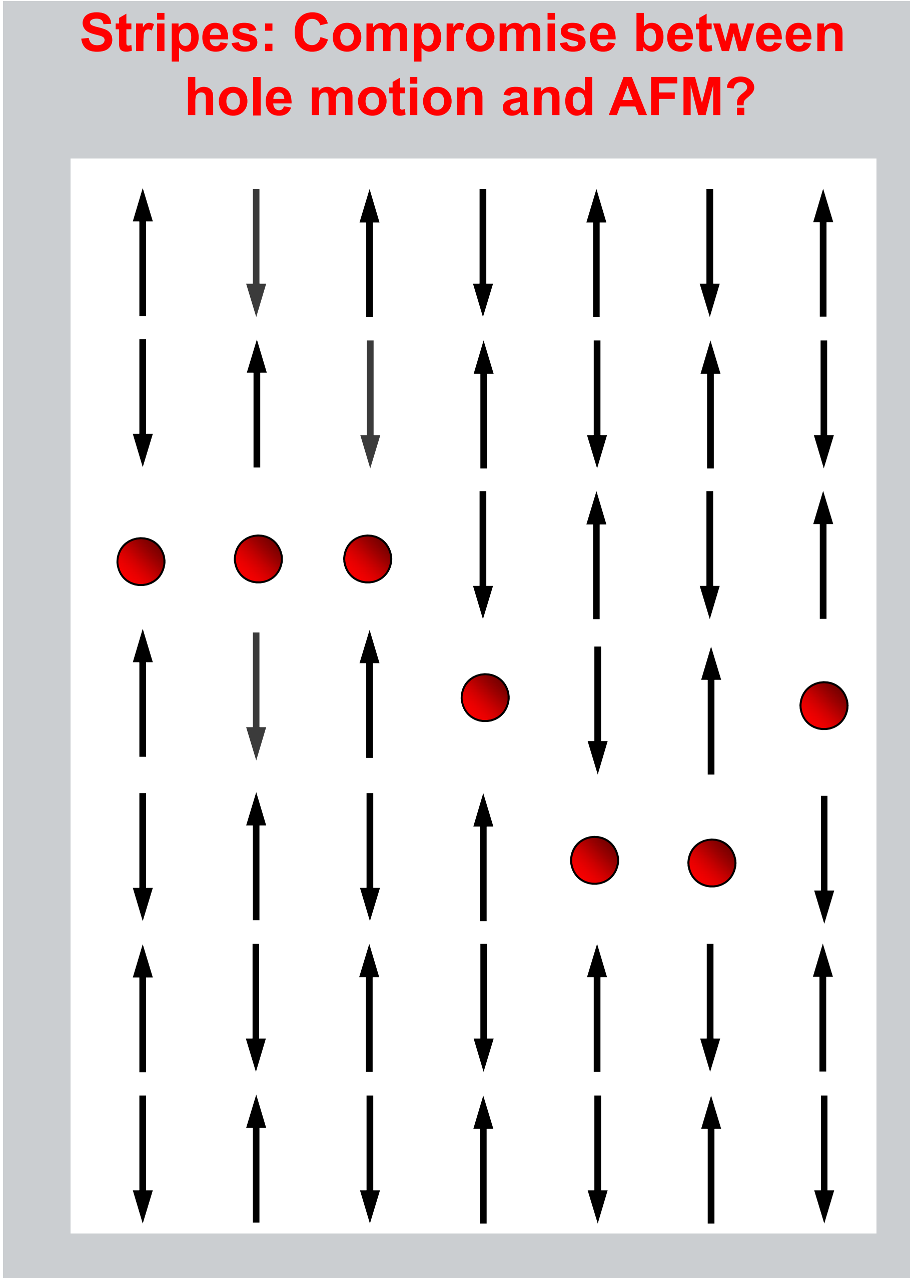
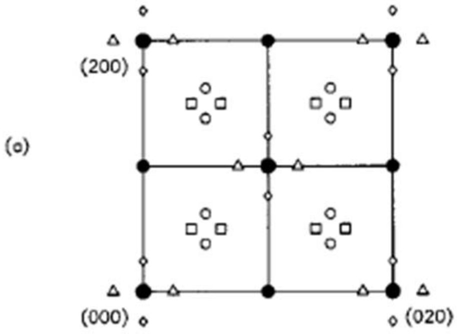
Antiferromagnetism and Charge Mobility

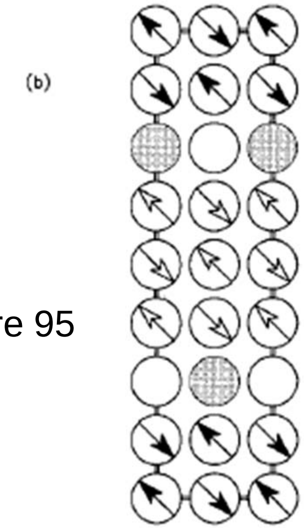




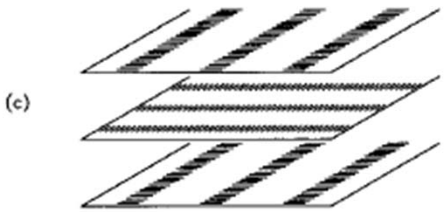
Stripes in Cuprate Superconductors

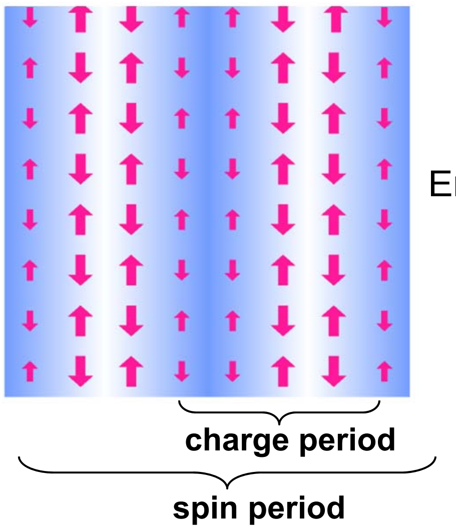
Static Stripes in $(La,Nd)_{7/8}Sr_{1/8}CuO_4$





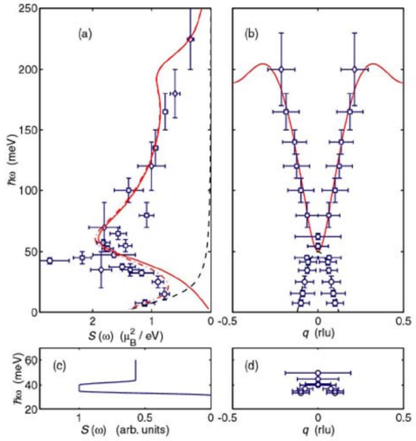
Tranquada et al. Nature 95



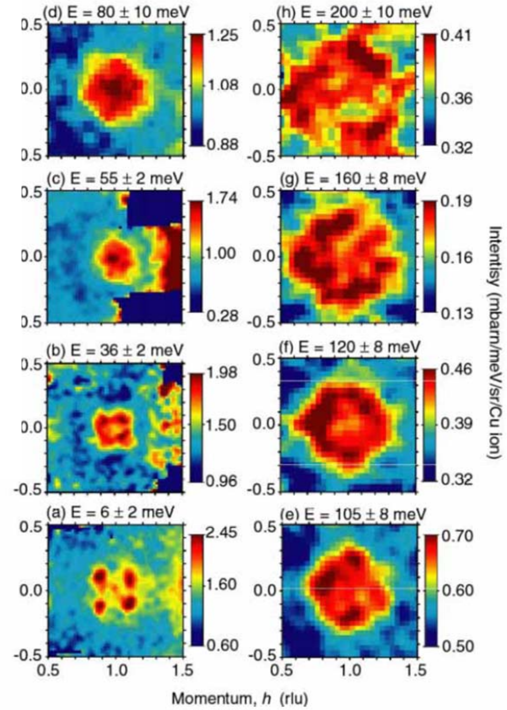


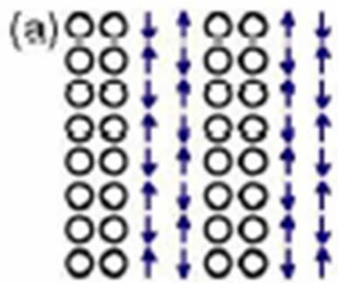
Emery et al.

Stripes and/or neutron resonance



Tranquada et al.
Nature04





Theory and further experiments:
Hayden et al.
Hinkov, Keimer et al.
Vojta et al
Uhrig et al.
Seibold et al.
...

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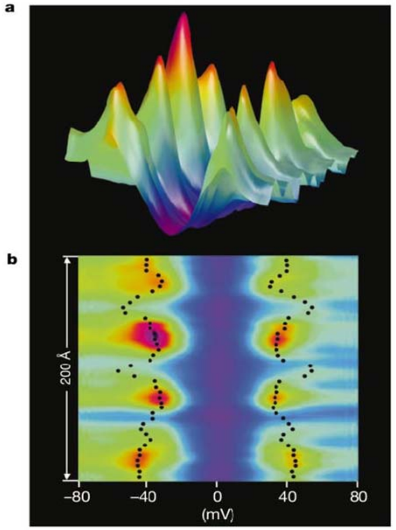

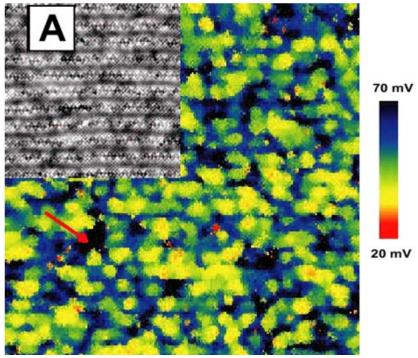

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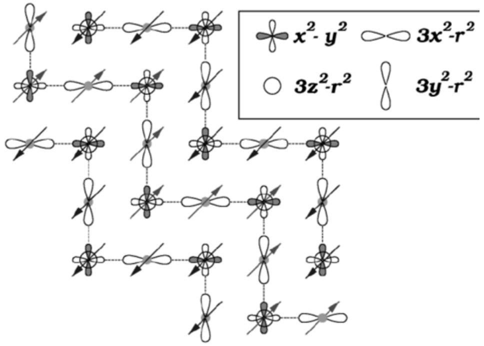

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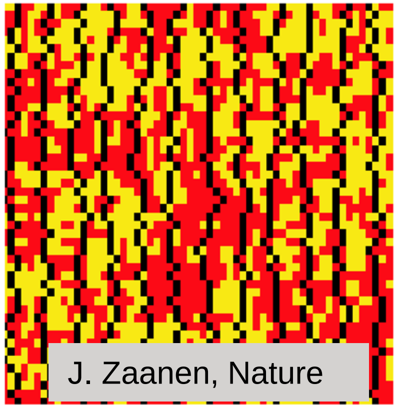
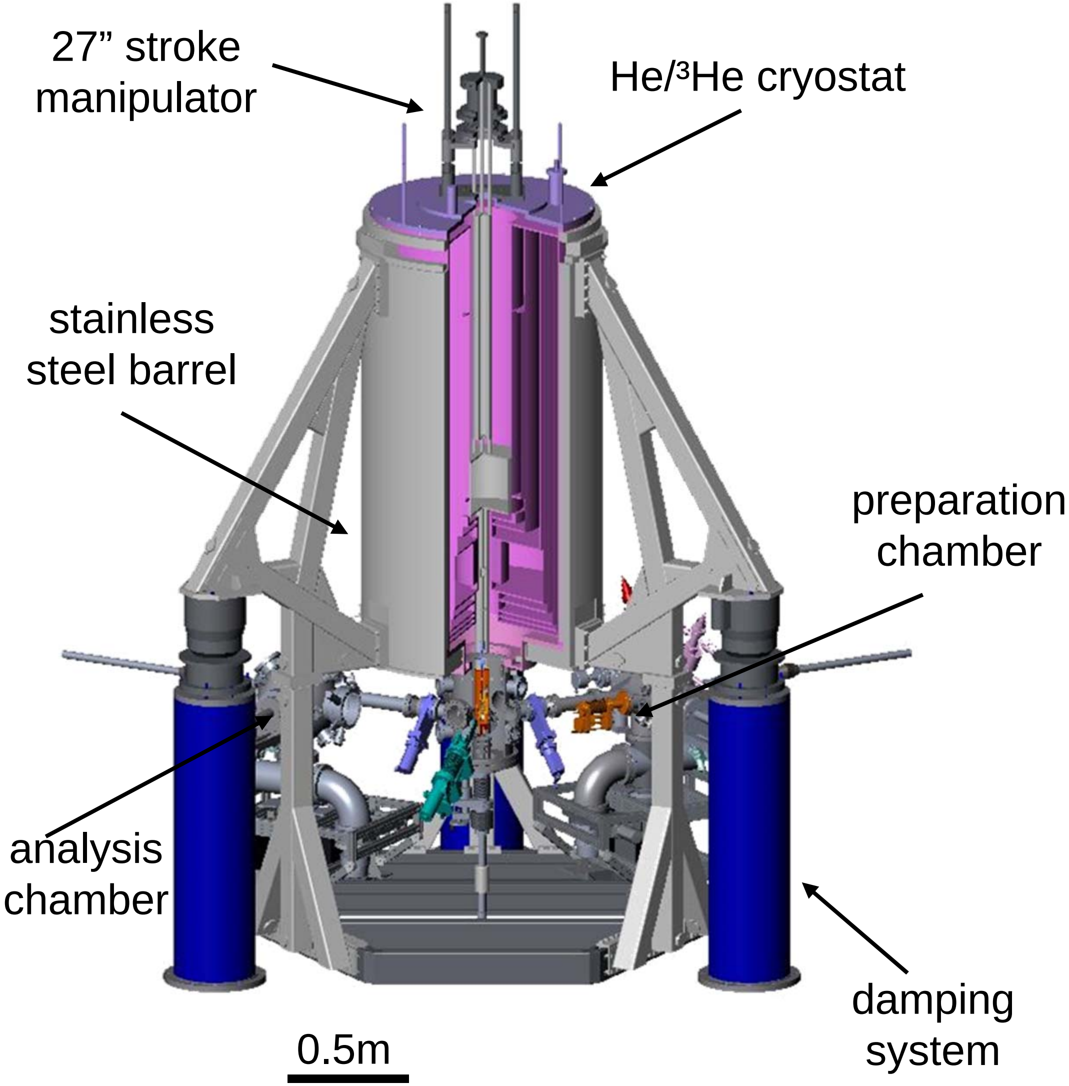
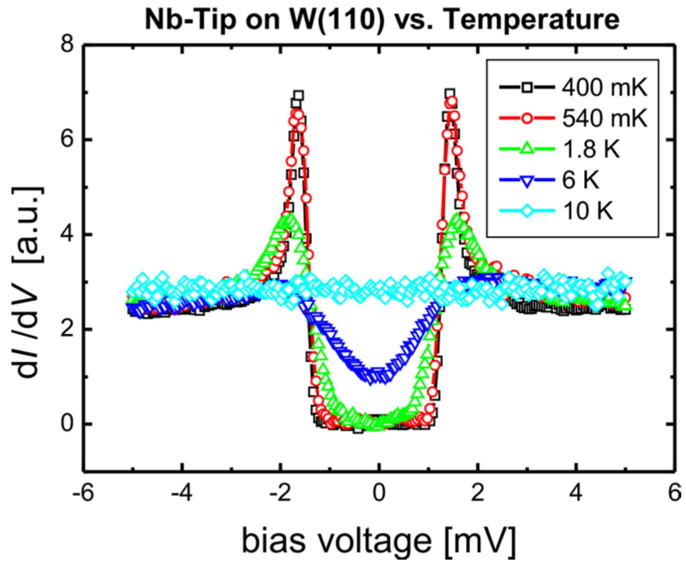
van den Brink, PRL 1999

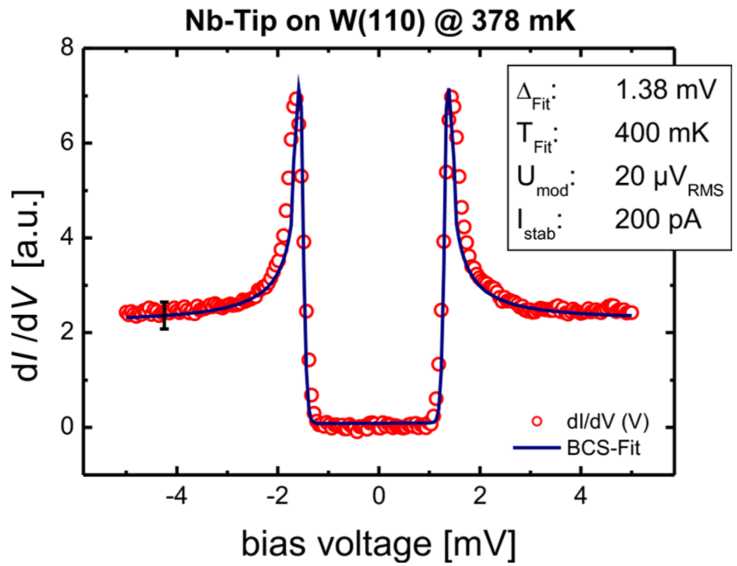


Our 300mK - STM

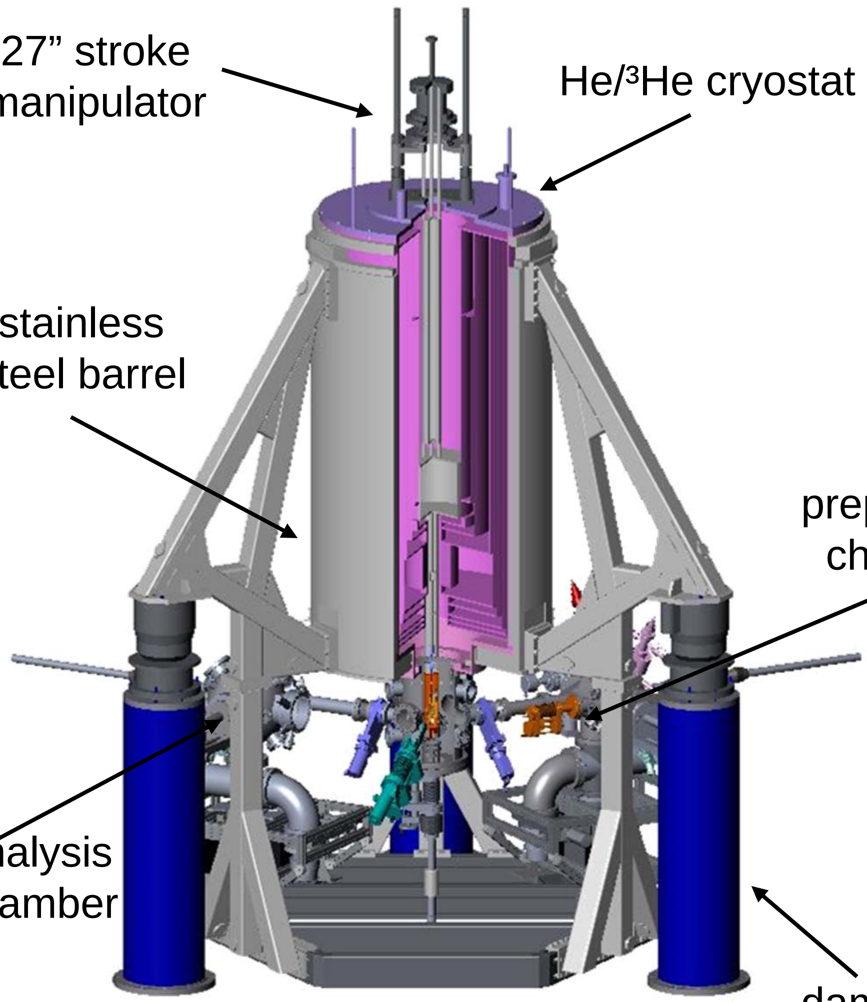


Density of States (DOS)

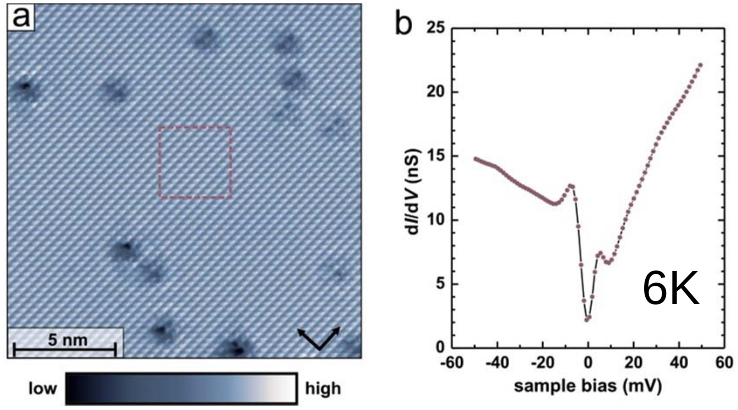




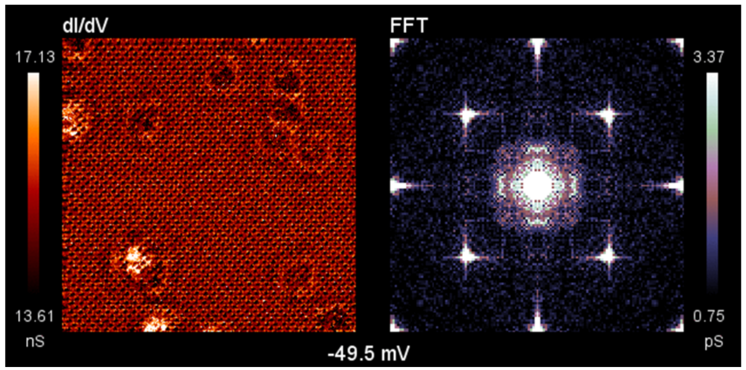
„New“ 300mK - STM



Topography + DOS of LiFeAs



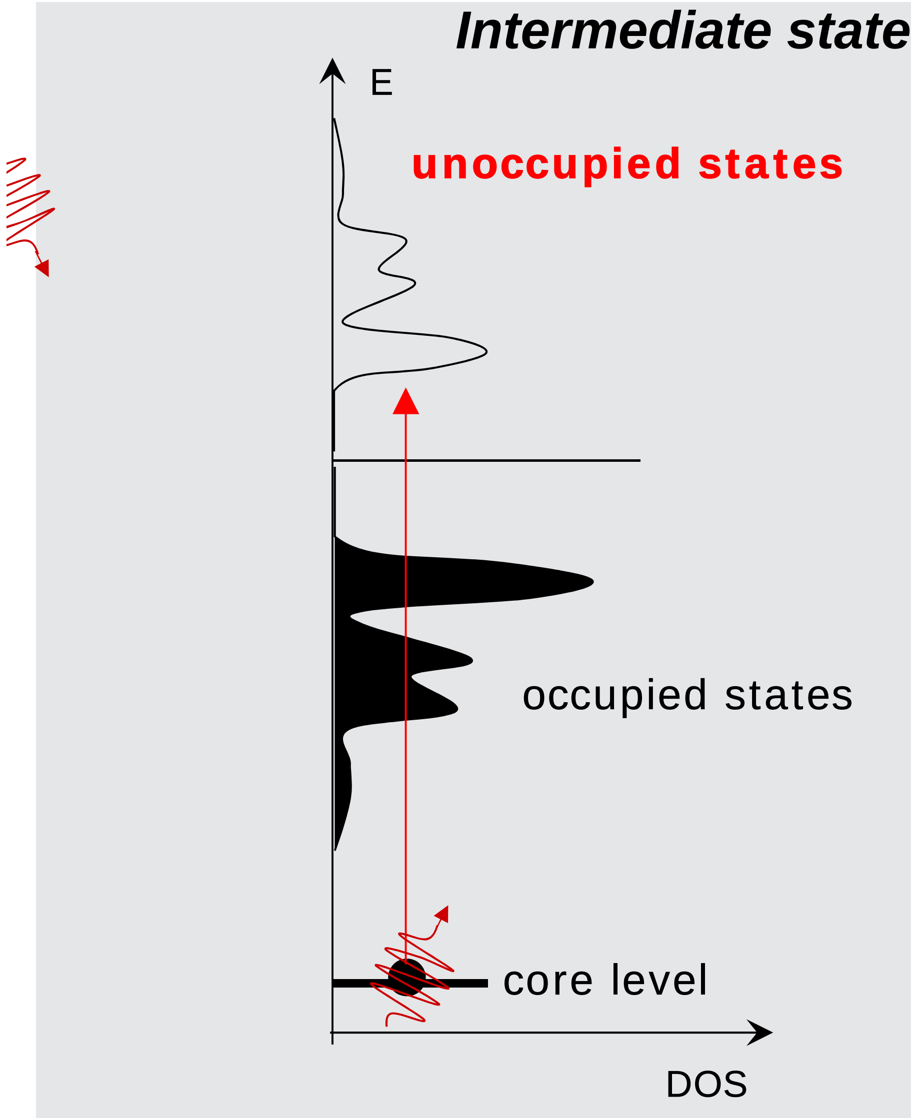
Local DOS maps



Hänke et al., PRL 2013

Resonant soft x-ray scattering

Scattering process



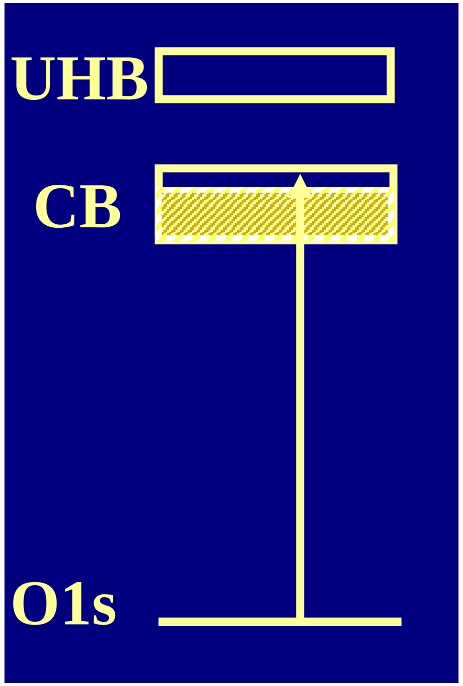
- **Elastic process:**
  initial state=final state

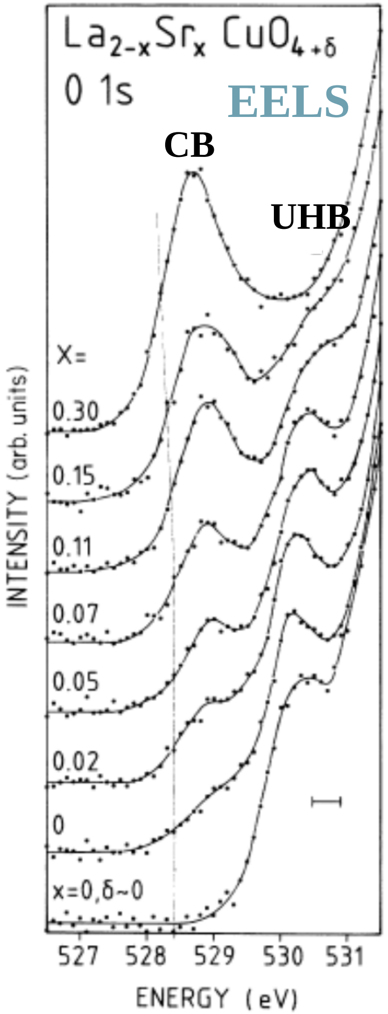
- **Element specific:**
  different edges like
  O K-edge, TM L2,3-edge, RE M-edges

- **Sensitive to**
  charges, magnetism and orbitals

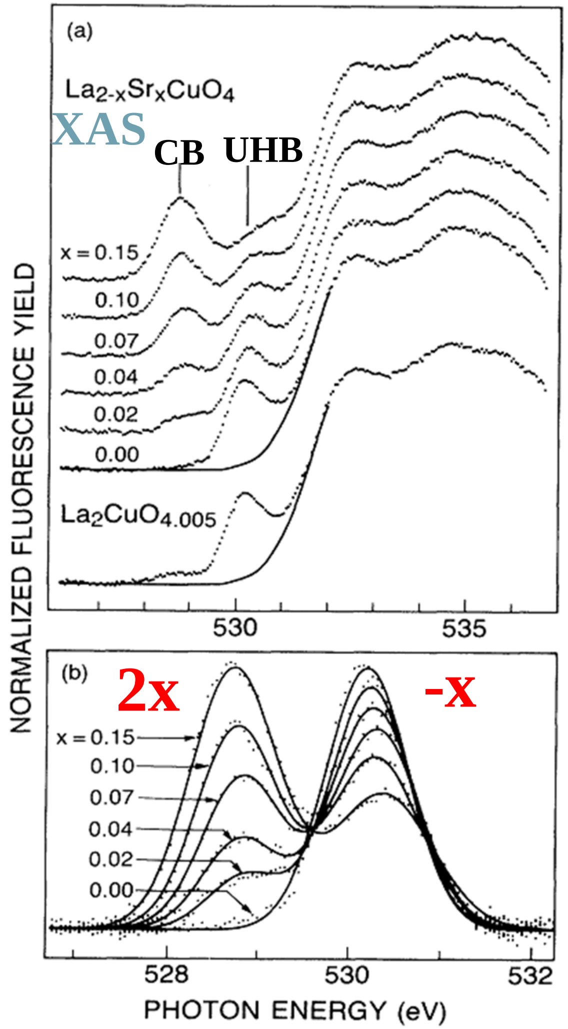
- **Polarization dependence:**
  Excitation of different intermediate states

O K edge in doped cuprates





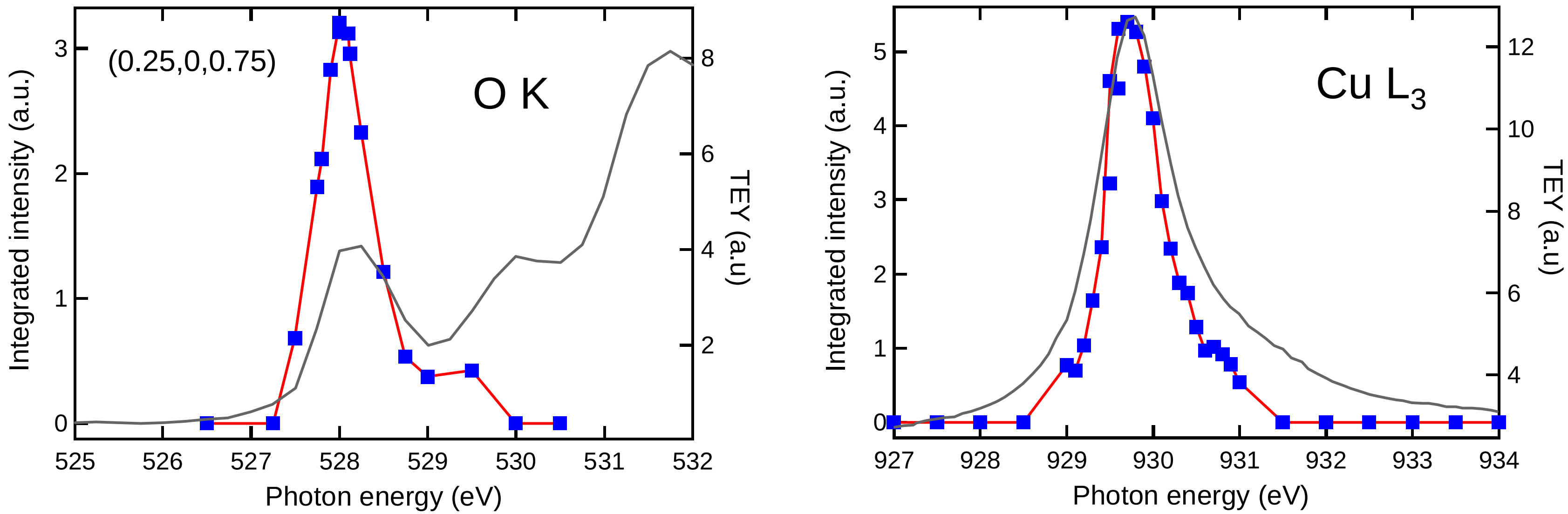
Romberg, Fink et al., PRB '90

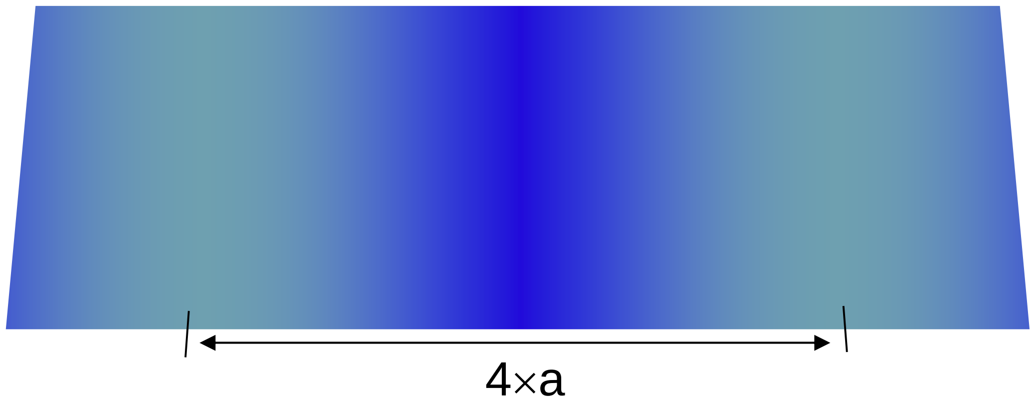


C.T. Chen *et al.*, PRL '91

Stripe order in $(La,Eu)_{7/8}Sr_{1/8}CuO_4$

Photon energy dependence



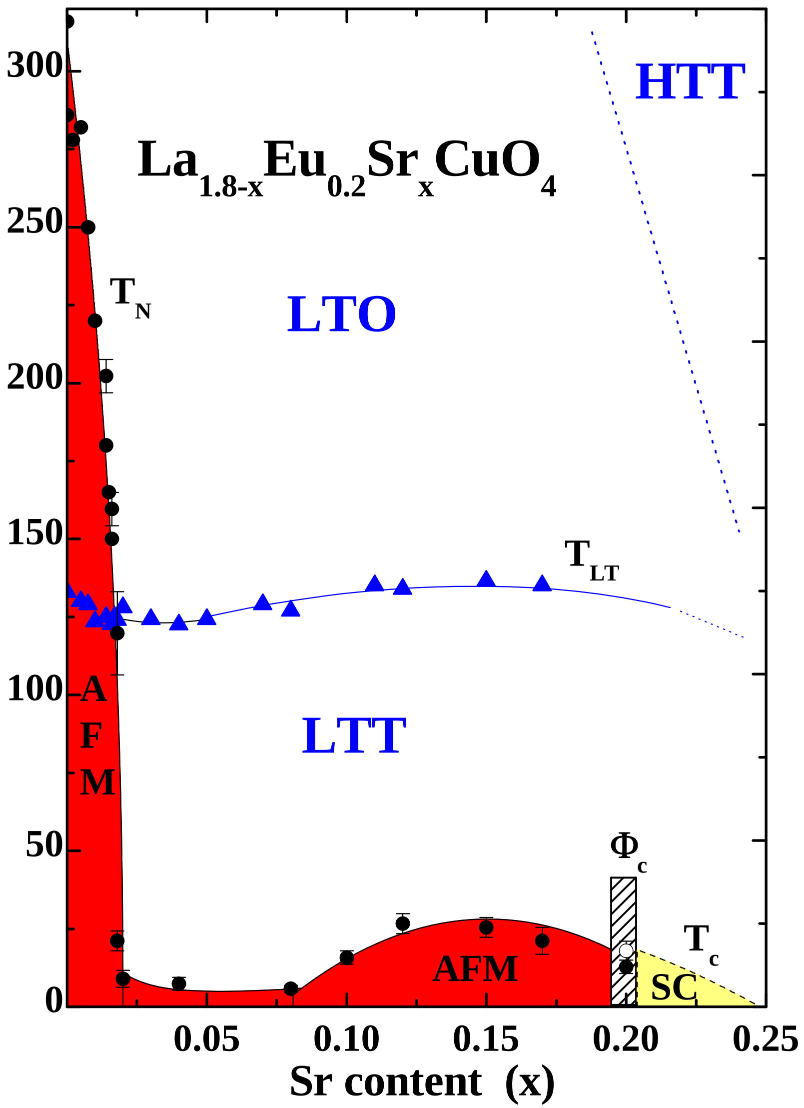


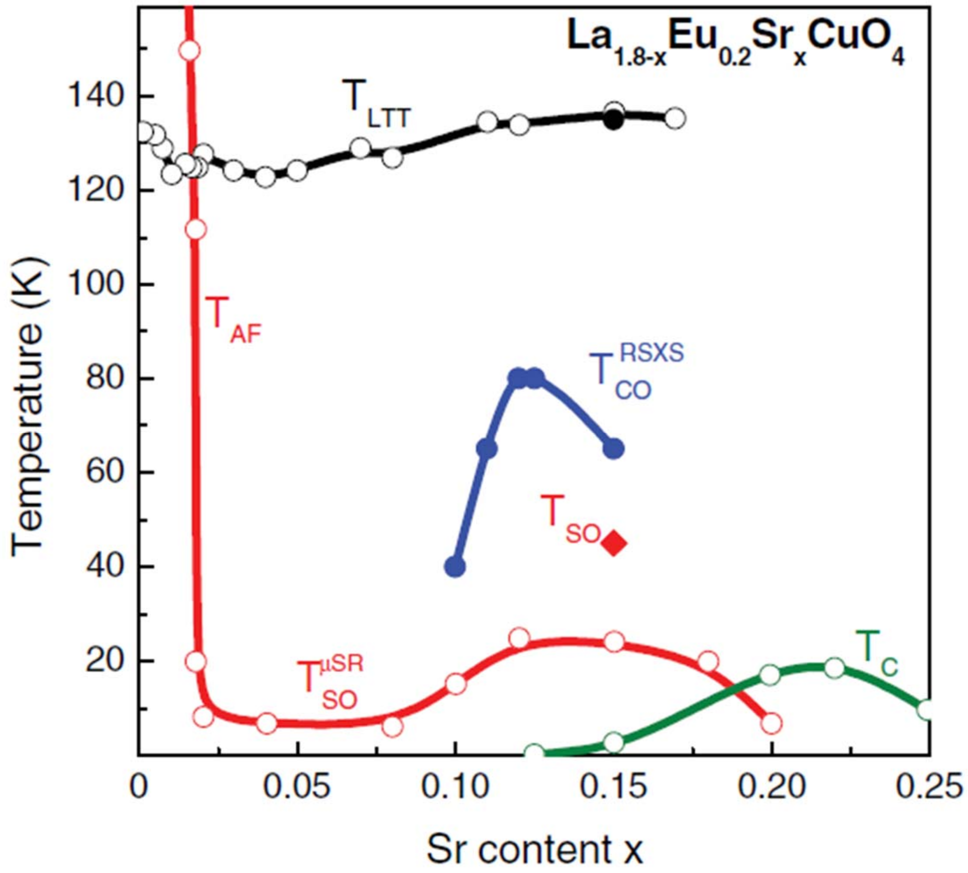
Charge order in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ studied by resonant soft X-ray diffraction

J. Fink,[1,2] E. Schierle,[3] E. Weschke,[3] J. Geck,[4] D. Hawthorn,[4] H. Wadati,[4]
H.-H. Hu,[5] H. A. Dürr,[1] N. Wizent,[2] B. Büchner,[2] G.A. Sawatzky,[4]

PRB (2009), PRB (2011)

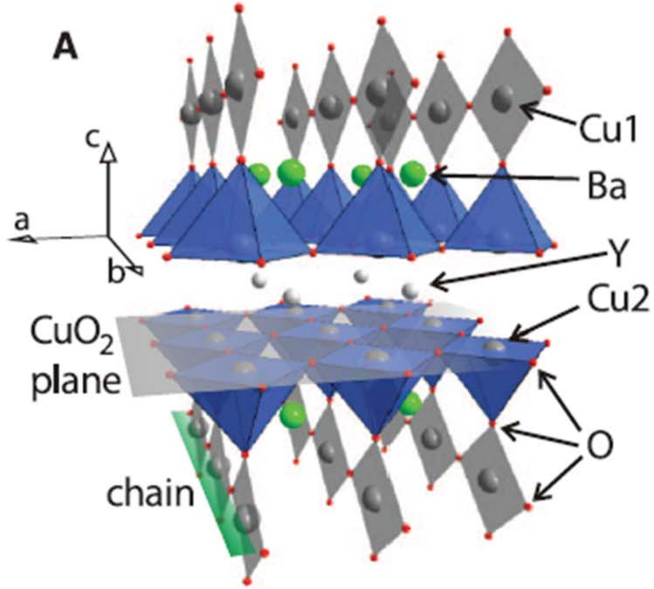
Phase diagrams and stripe order in $(La,Eu)_{7/8}Sr_{1/8}CuO_4$

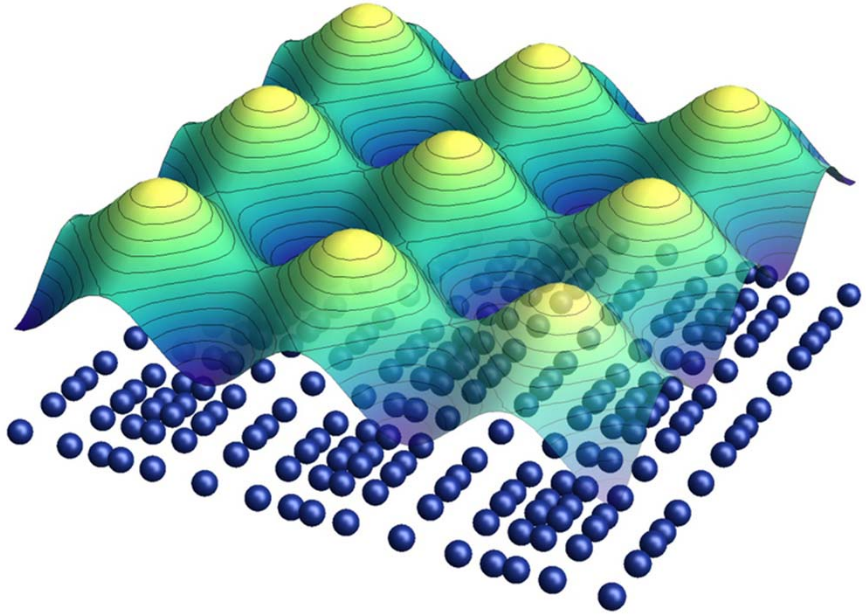


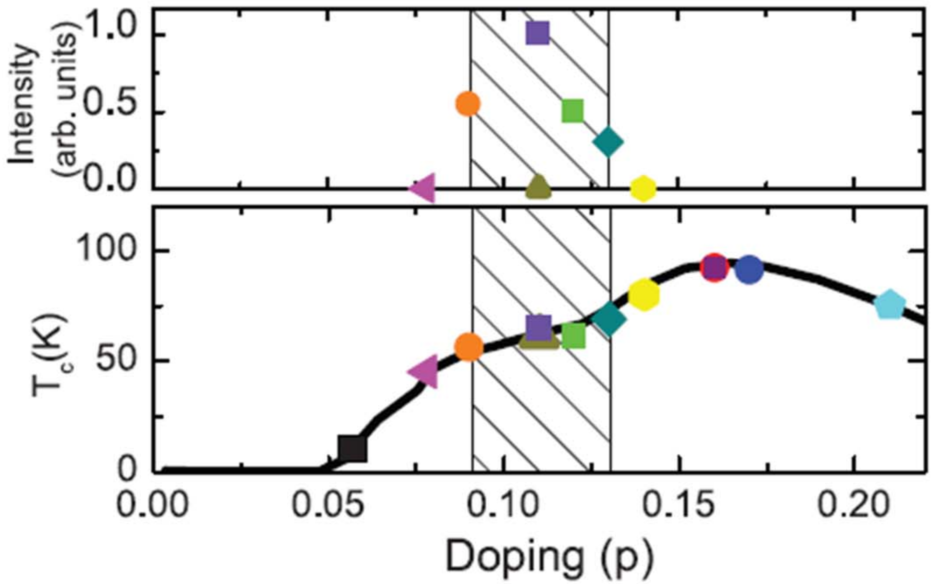


H. Klauss et al, PRL 2004; H. Grafe et al., PRL 2007; J. Fink et al. PRB (2011)

Stripes or density waves







Long-Range Incommensurate Charge Fluctuations in (Y,Nd)$Ba_2Cu_3O_{6+x}$

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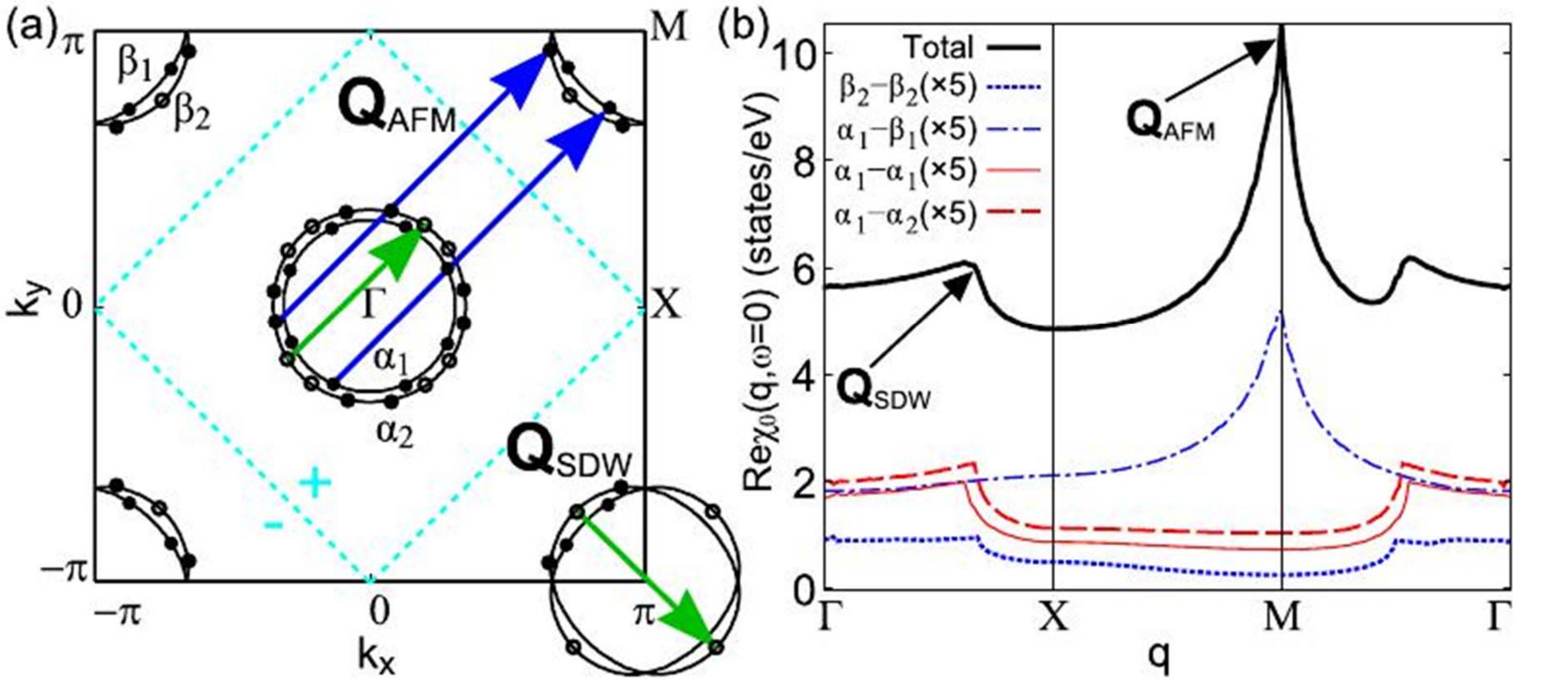
Science 2012

The wave vector of the charge correlations revealed in our experiments is in good agreement with the nesting vector of the antibonding Fermi surface sheets predicted by density functional calculations for the 123 system (*34*). The

Nesting and CDW/SDW order



Korshounov & Eremin, Phys. Rev. B **78**, 140509(R) (2008)

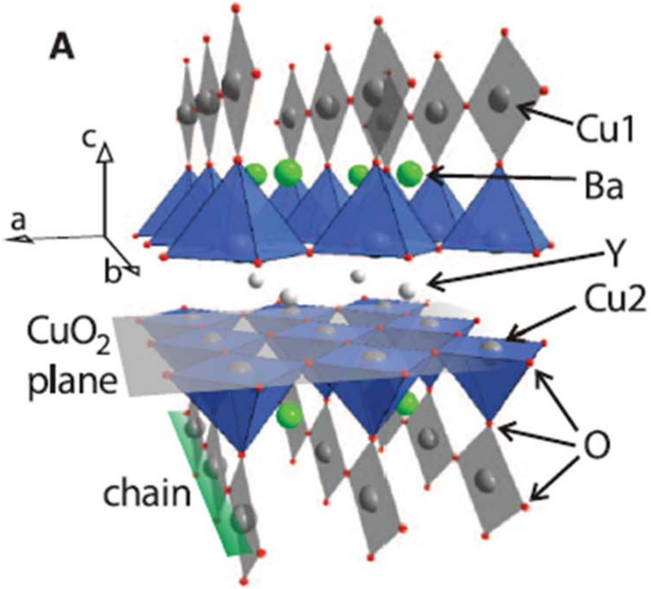
“Perfect” nesting of electron- and hole-like Fermi pockets

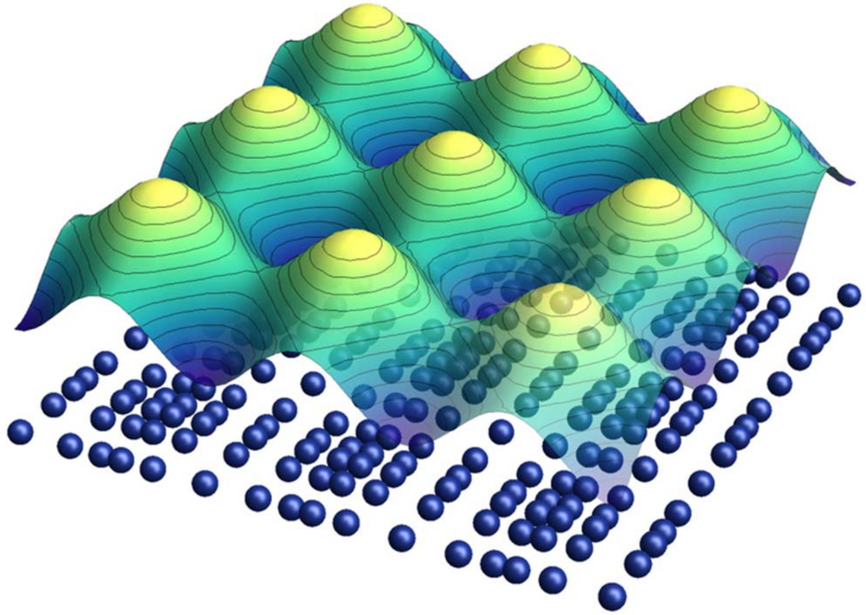
→ Enhancement of instabilities

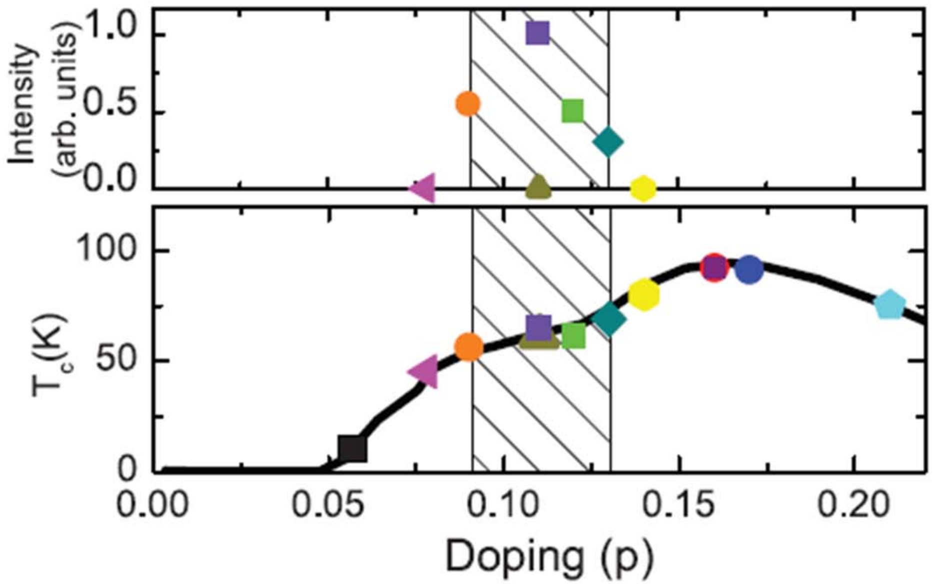
→ CDW and/or SDW order

Doping: “Off-tuning” of nesting → Suppression of SDW

Stripes or density waves







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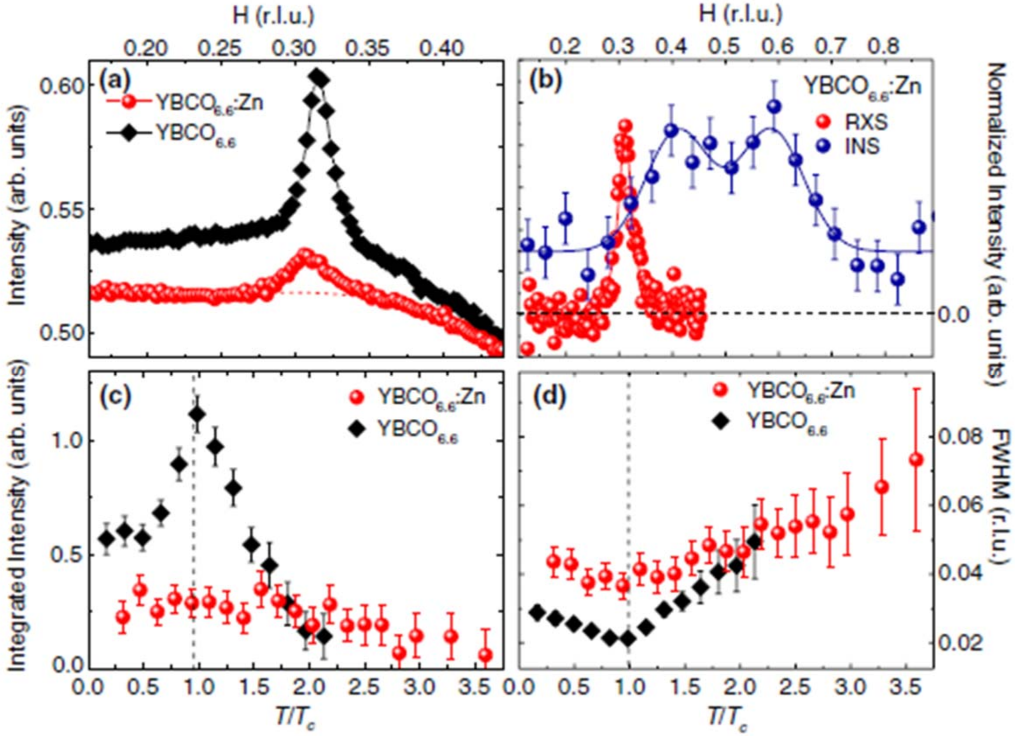

Rather than forming a coherent spin- and charge-modulated "striped" state, as in the 214 system [3,10–14], spin and charge order are strongly competing in $YBCO_{6+\delta}$. As a direct manifestation of this competition, we demonstrated that spinless Zn impurities substantially weaken CDW correlations in a $YBCO_{6.6}$ crystal, while at the same time nucleating incommensurate magnetic order. We further showed that an

Momentum-Dependent Charge Correlations in $YBa_2Cu_3O_{6+\delta}$ Superconductors Probed by Resonant X-Ray Scattering: Evidence for Three Competing Phases

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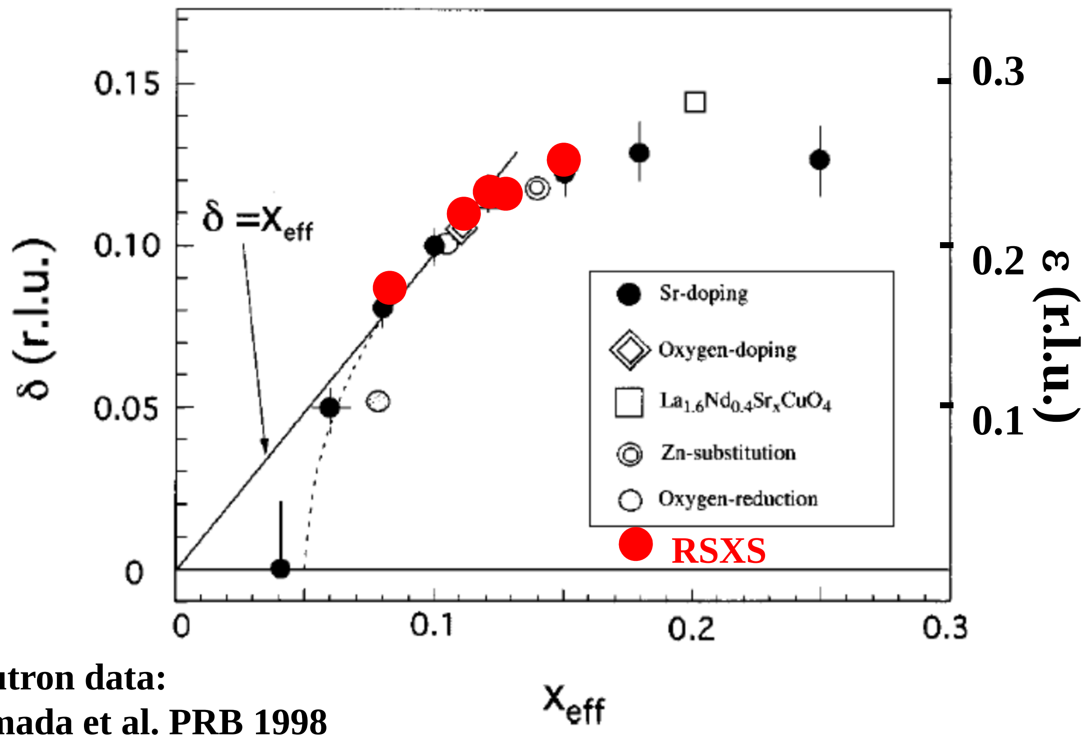
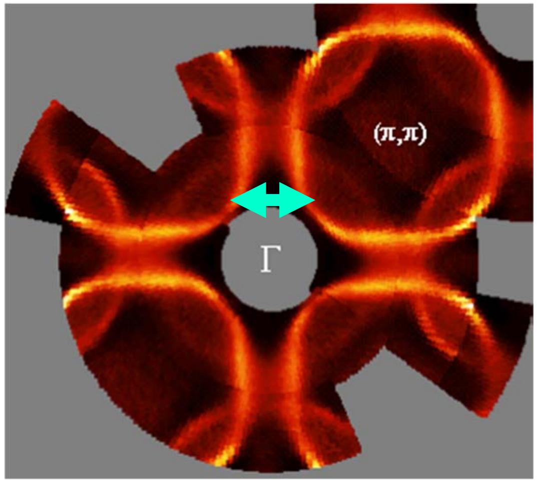
PRL 2013

Incommensurate order of charge and spin

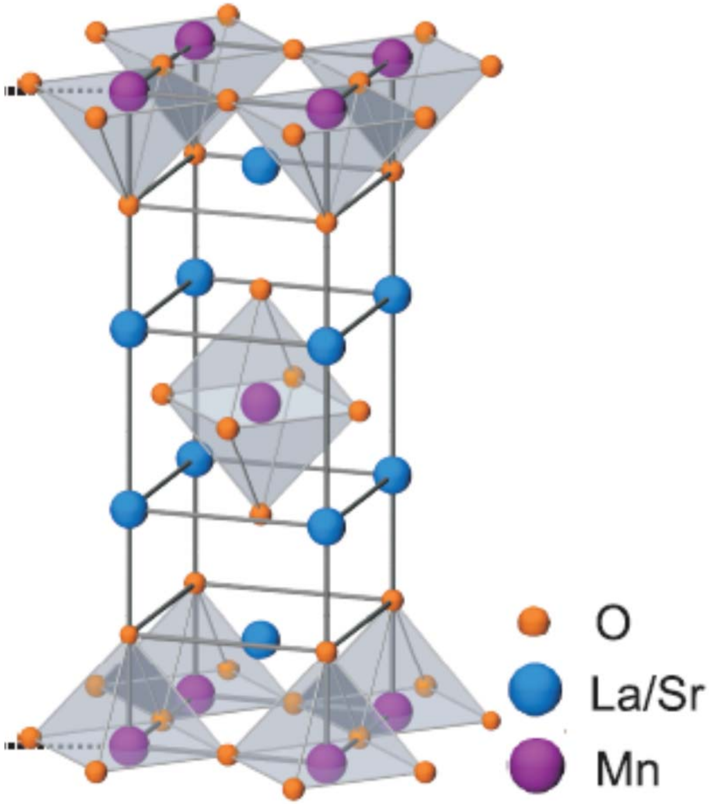


Neutron data:
Yamada et al. PRB 1998



- wave vector ε of charge order equal to 2δ of spin order of fluctuating stripes
- concentration dependence of ε is not compatible with nesting scenario

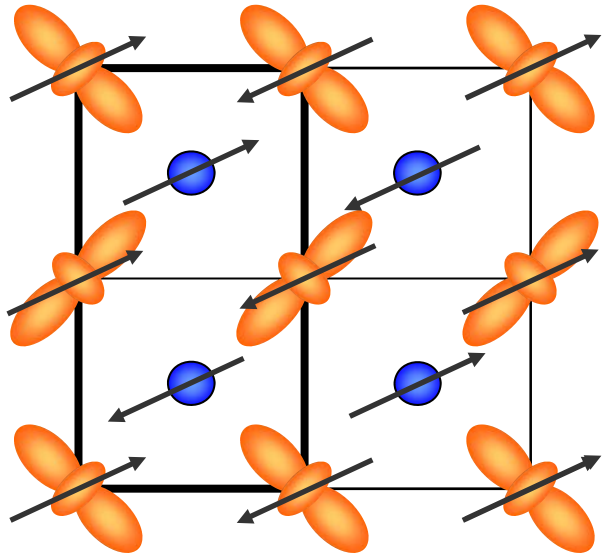
Charge order in half doped manganites

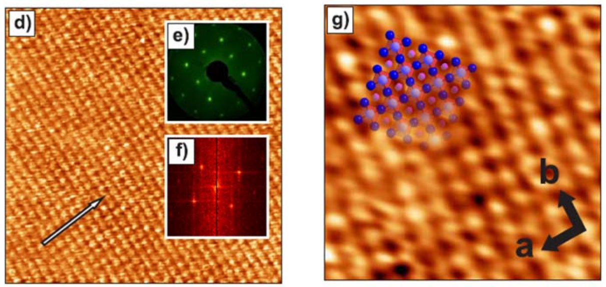


Single layer manganite: $La_{1-x}Sr_xMnO_4$

x = 1.5: half-doped 50% Mn^{3+} and 50% Mn^{4+}

CE type charge/orbital/spin order





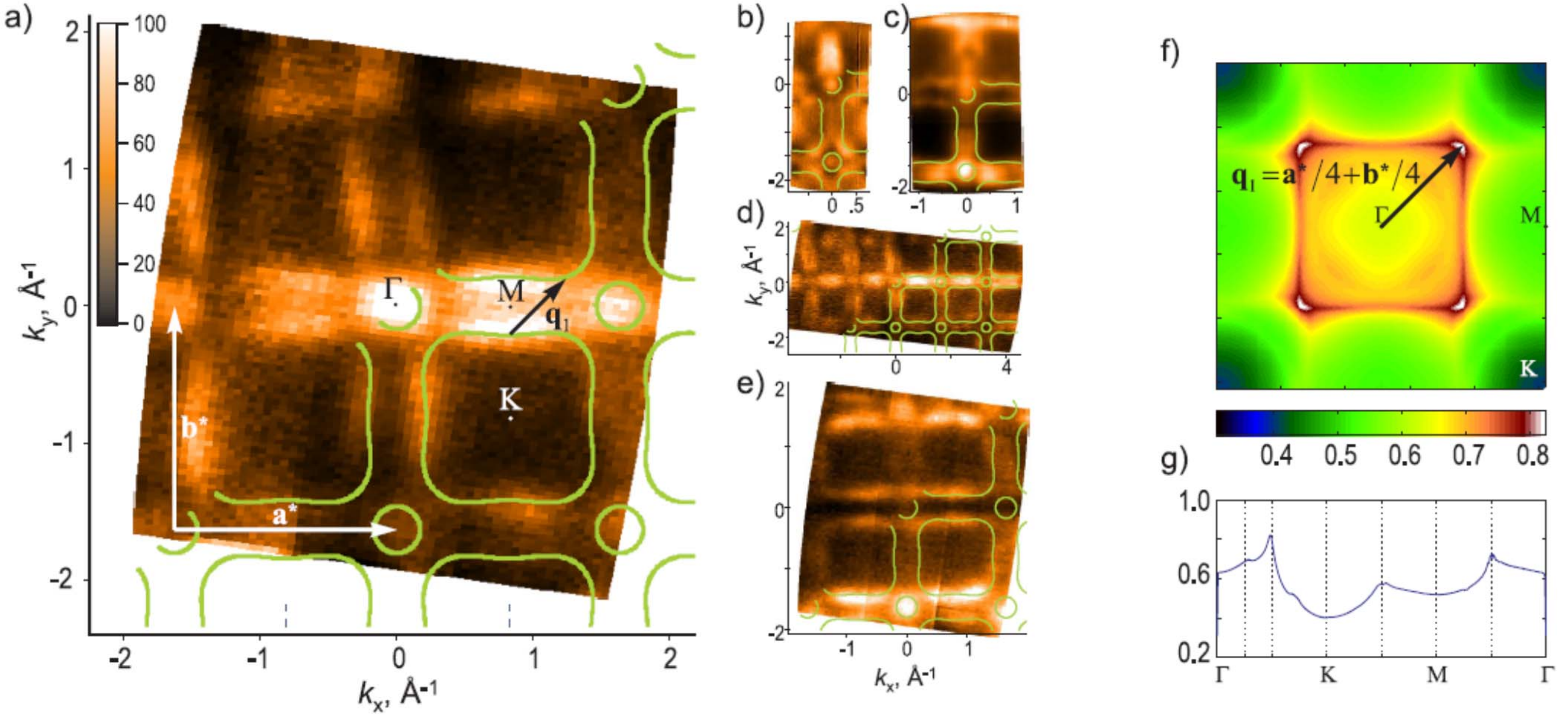
Bridging charge-orbital ordering and Fermi surface instabilities in half-doped single-layered manganite $La_{0.5}Sr_{1.5}MnO_4$

D. V. Evtushinsky,[1] D. S. Inosov,[1] G. Urbanik,[1,2] V. B. Zabolotnyy,[1] R. Schuster,[1] P. Sass,[1] T. Hänke,[1] C. Hess,[1] B. Büchner,[1] R. Follath,[3] P. Reutler,[4] A. Revcolevschi,[4] A. A. Kordyuk,[1,5] and S. V. Borisenko[1]

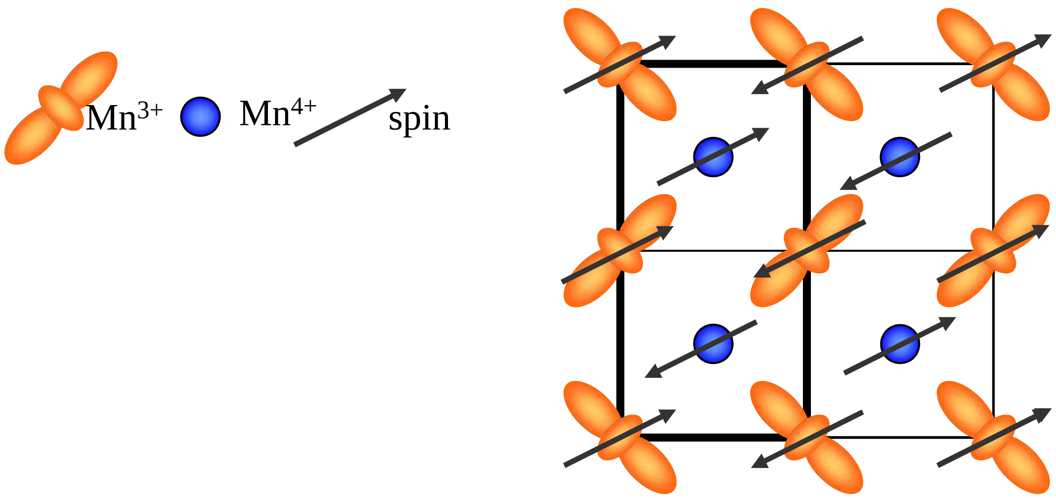
see e.g. P. Reutler J. Cryst. Growth (2002)

PRL 2009

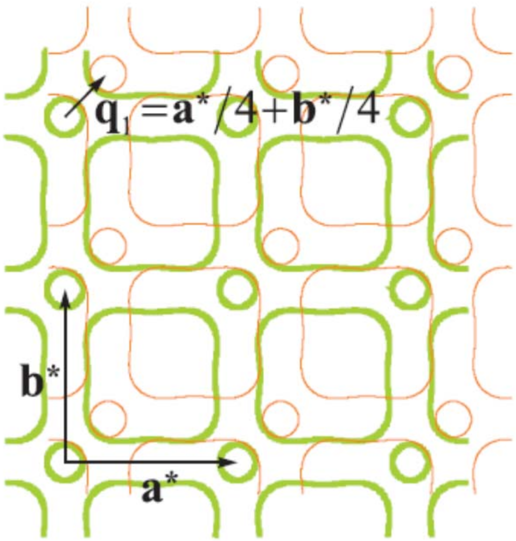
ARPES on charge ordering manganites



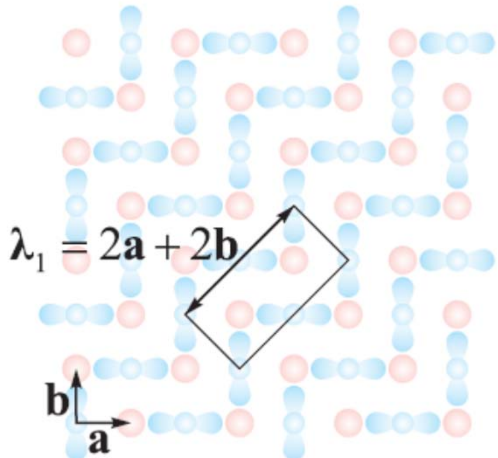
CE type order: Nesting scenario



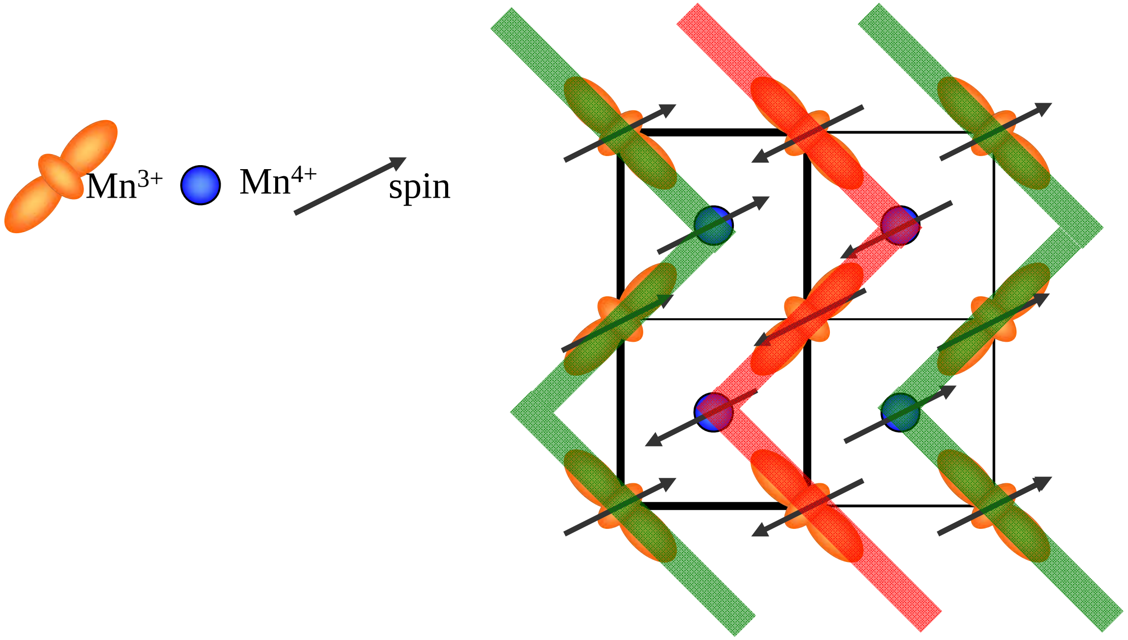
k space

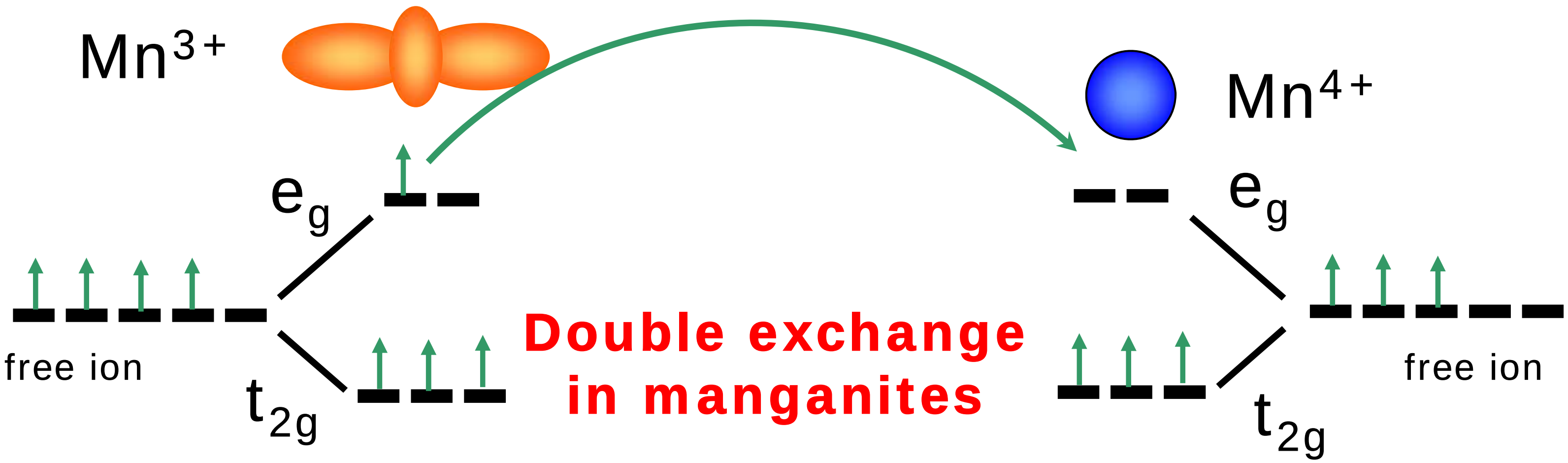


real space

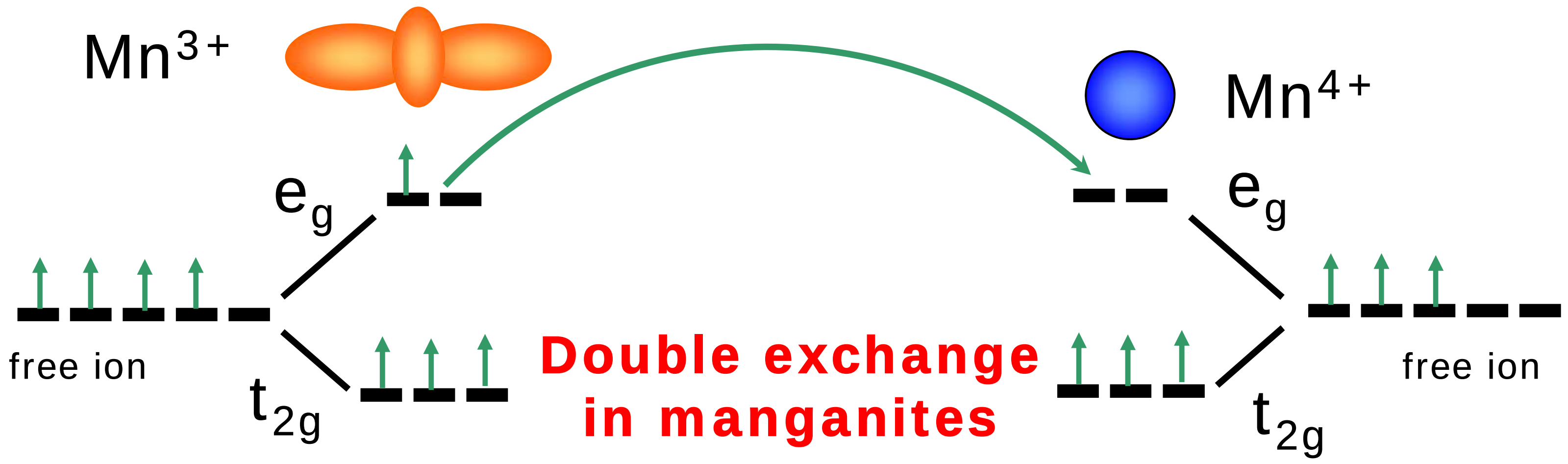


CE type order: Local picture





Orbital Polaron Ordering in Manganites



FM ↔ metallic properties

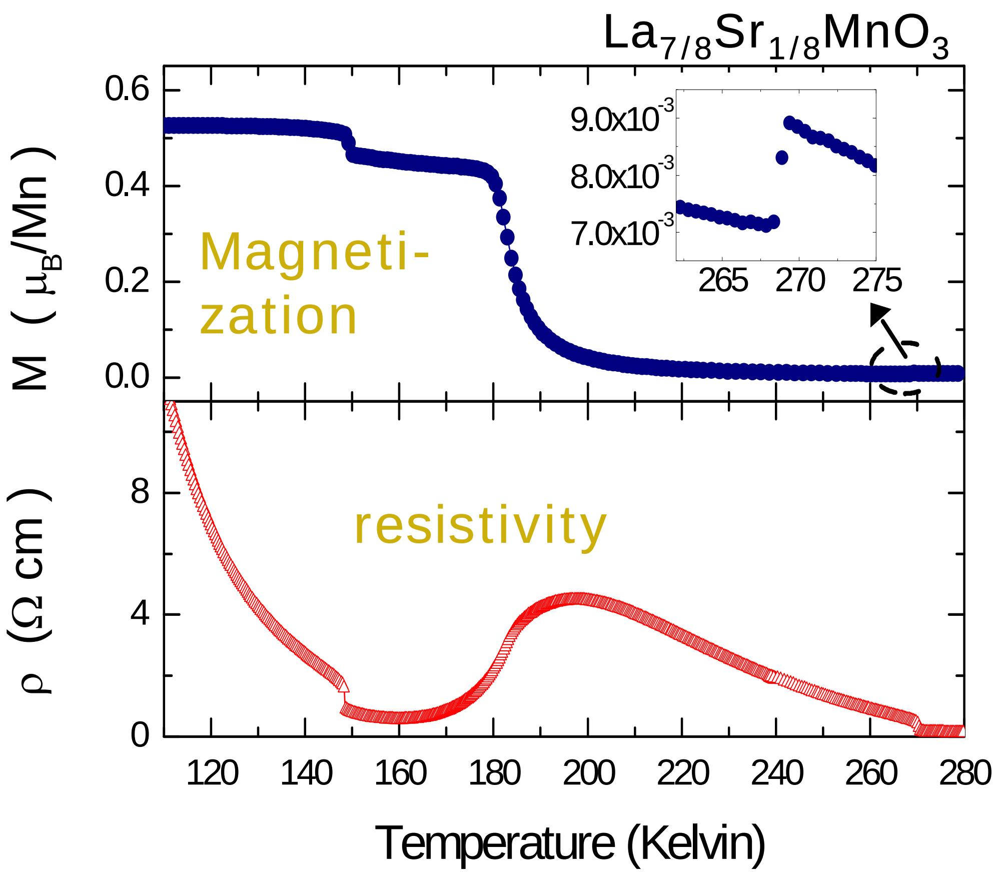
hole doping: FM interactions (DE) +

destabilization of cooperative Jahn-Teller distortions

Ferromagnetic Insulating Manganites

Metallic materials → tendency to ferromagnetism ✓

but:

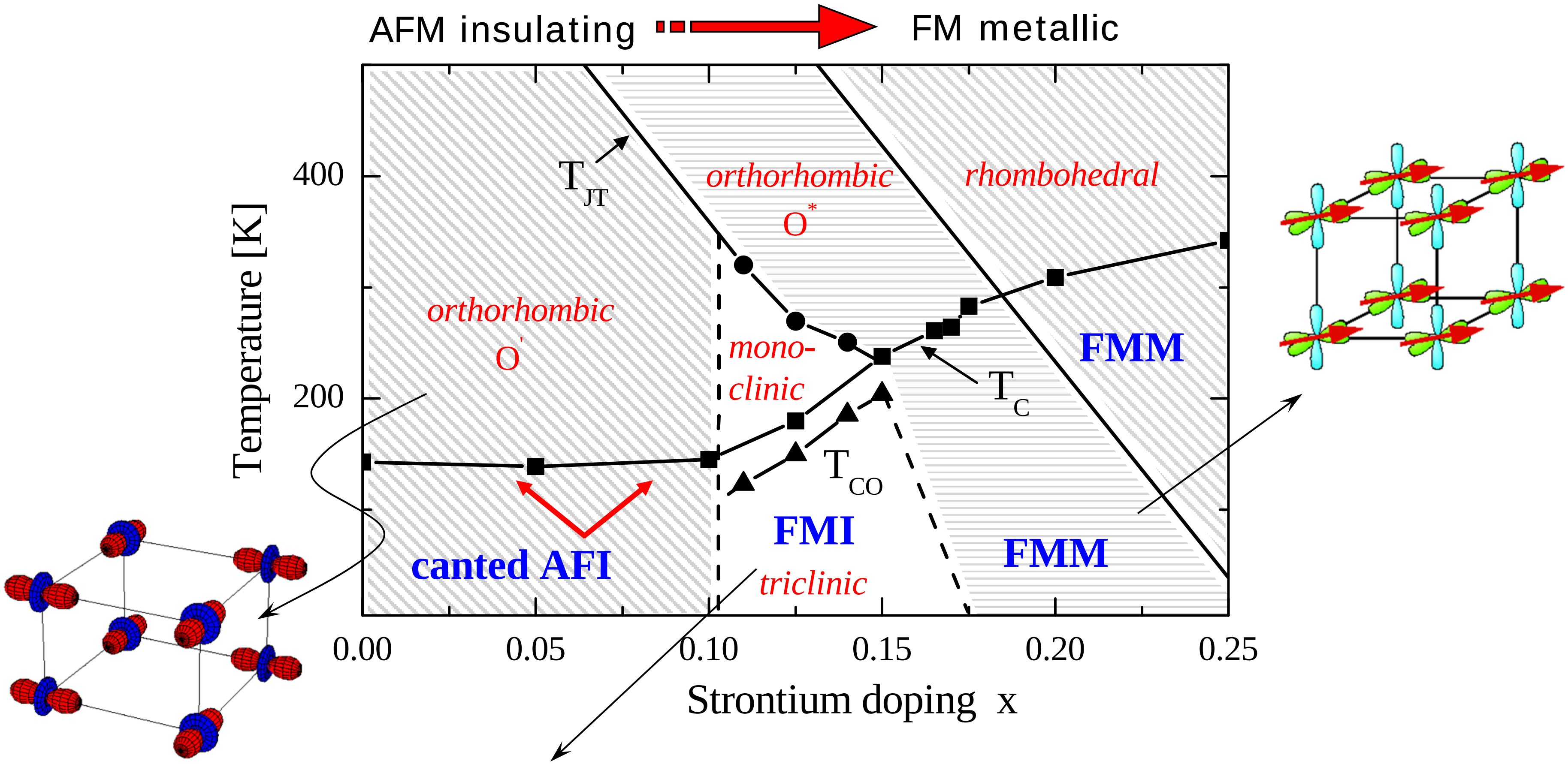


low temperatures:

coexistence of ferromagnetism and insulating behavior

?

Phase Diagram of $La_{1-x}Sr_xMnO_3$

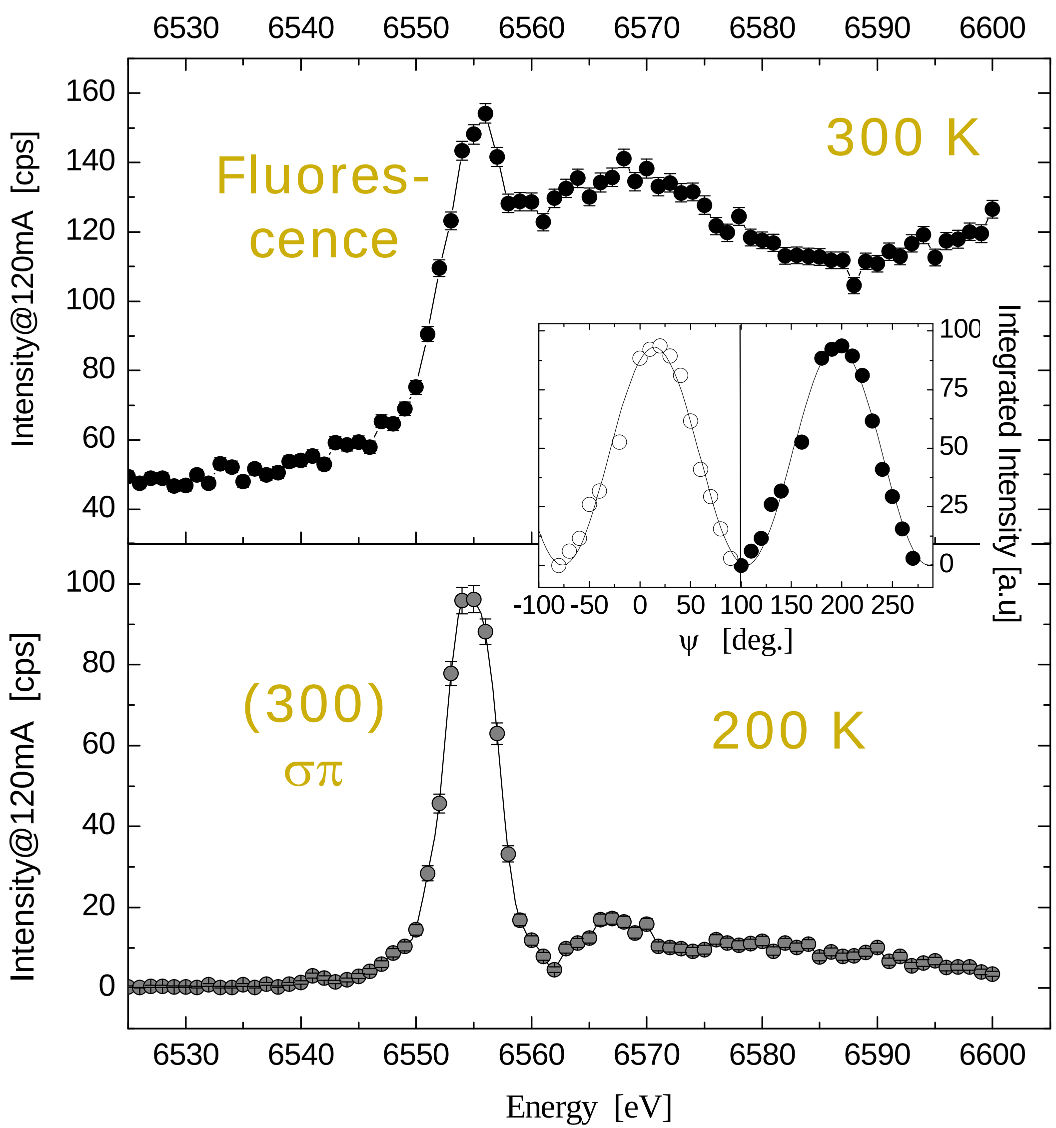


? FMI phase: contradicts DE model

→ **Orbital degrees of freedom ?**

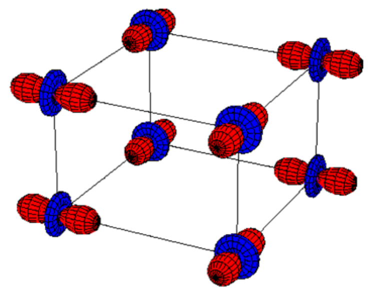
Uhlenbruck *et. al.*, PRL 98
T. Niemoeller *et. al.* EPJ B99
Klingeler *et. al.*, PRB 02
Geck *et. al.*, PRB 01
Geck *et. al.*, PRB 04
Geck et al. PRL 05
Geck et al. NJP 06

Resonant X-Ray Scattering on $La_{7/8}Sr_{1/8}MnO_3$

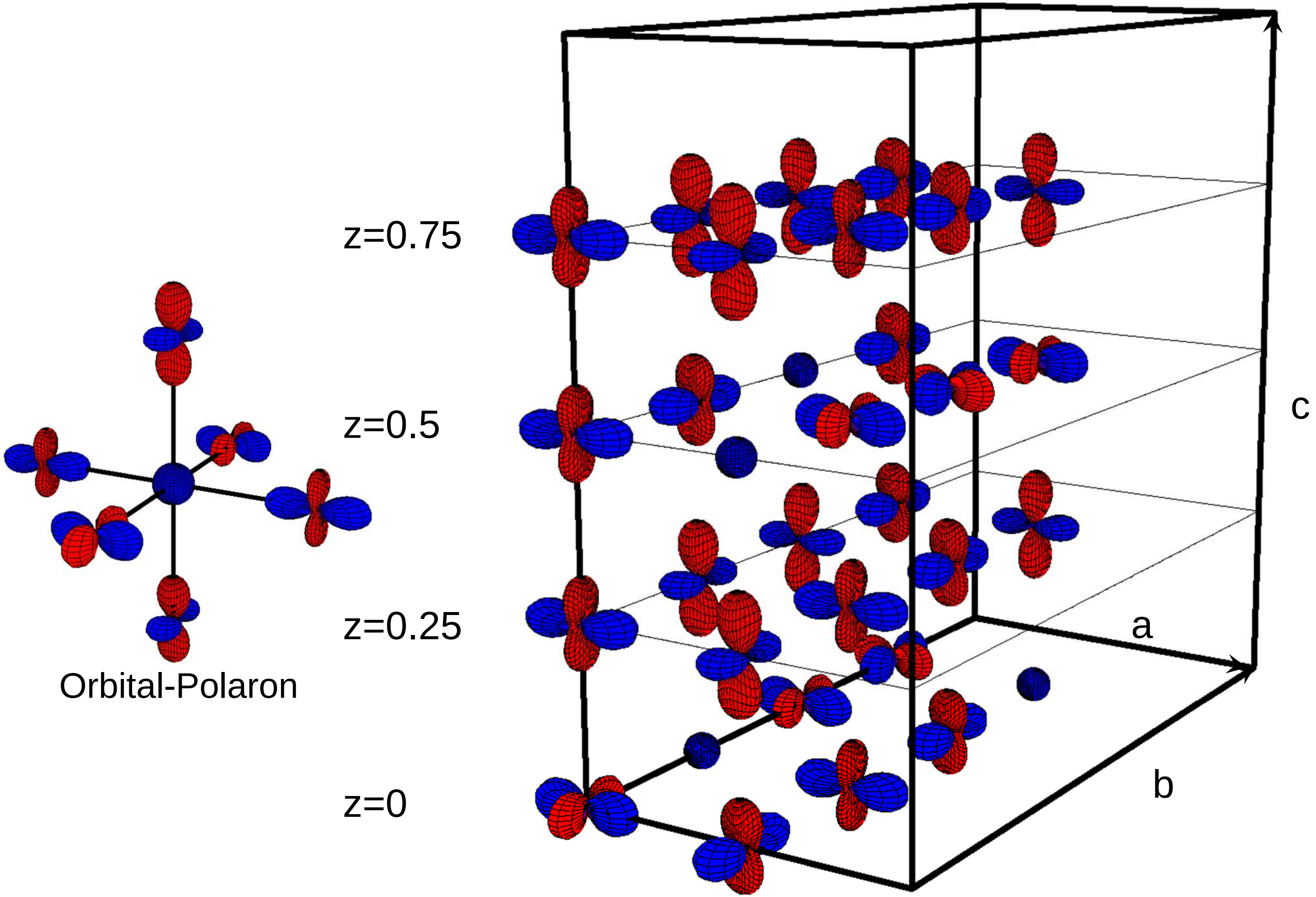


- Resonance at the Mn K-edge
- σπ-scattering
- $I \sim \sin^2\psi$

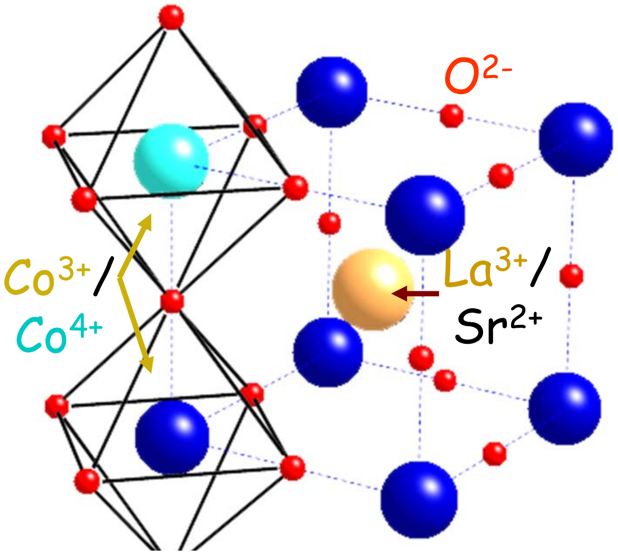
antiferro-orbital order



Orbital Polaron Lattice in $La_{7/8}Sr_{1/8}MnO_3$

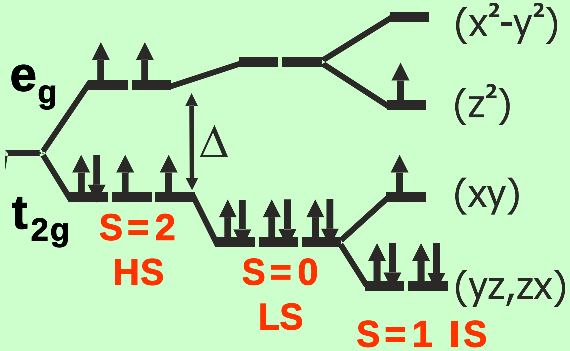


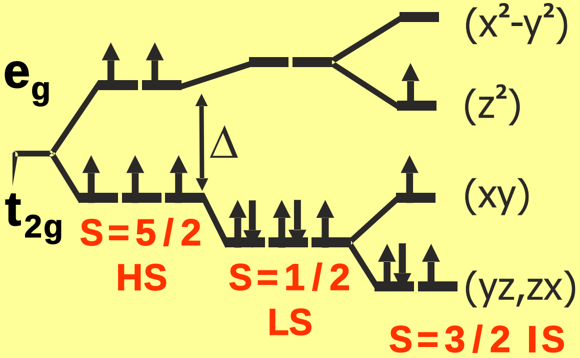
$La_{1-x}Sr_xCoO_3$: Rich diversity of electronic phases



distorted cubic perovskite structure

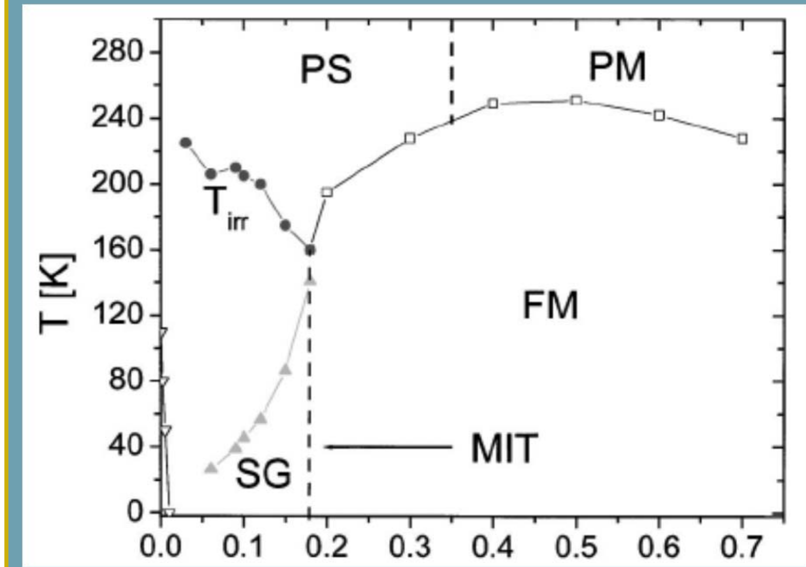
Co^{3+} (3d^6)





Co^{4+} (3d^5)

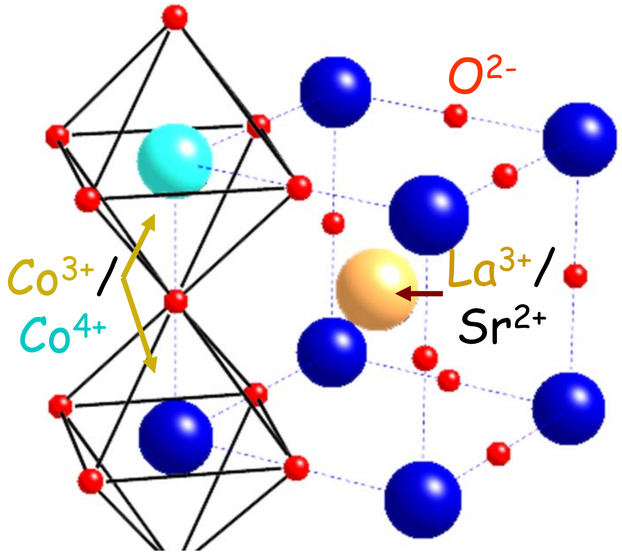
Phase diagram of $La_{1-x}Sr_xCoO_3$



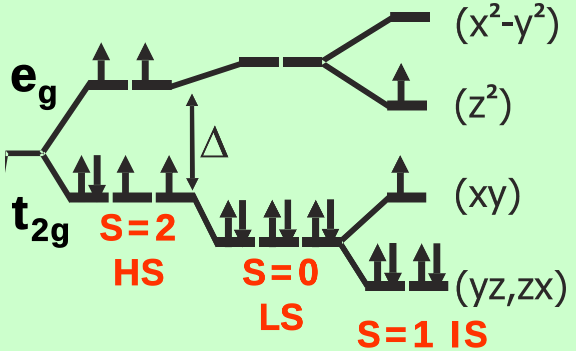
Sr, x

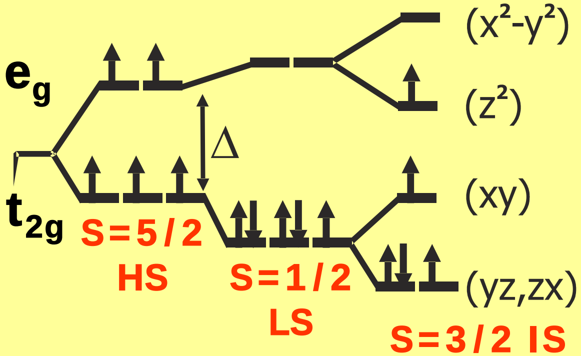
Wu and Leighton, Phys. Rev. B **67** (2003) 174408

$La_{1-x}Sr_xCoO_3$: Rich diversity of electronic phases

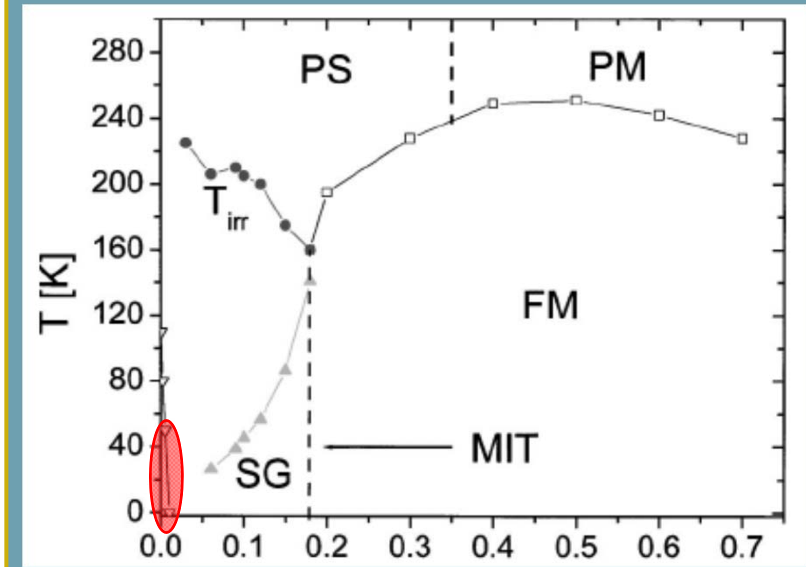


distorted cubic perovskite structure





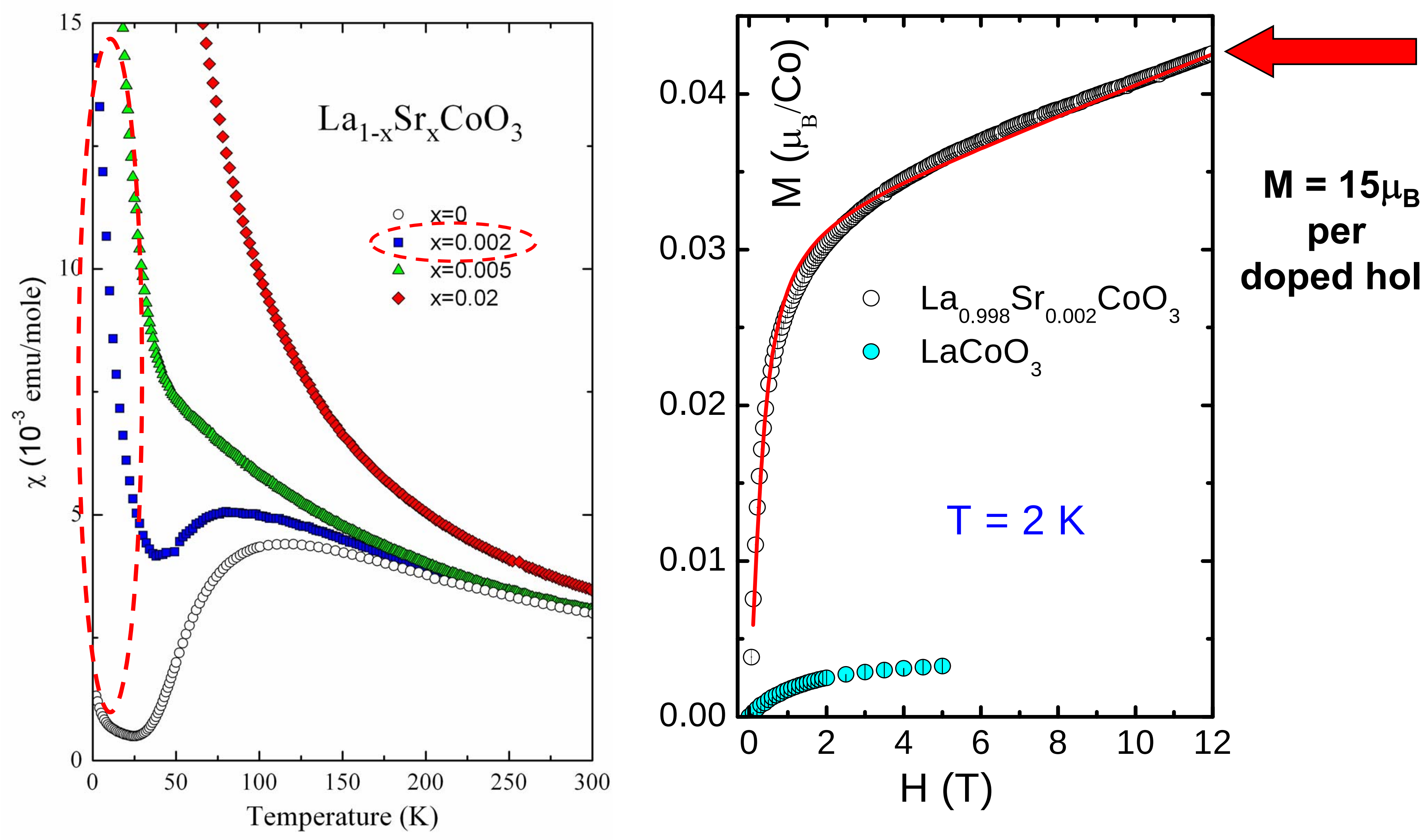
Phase diagram of $La_{1-x}Sr_xCoO_3$



Sr, x

Wu and Leighton, Phys. Rev. B **67** (2003) 174408

Huge magnetic response at low T at a tiny Sr doping

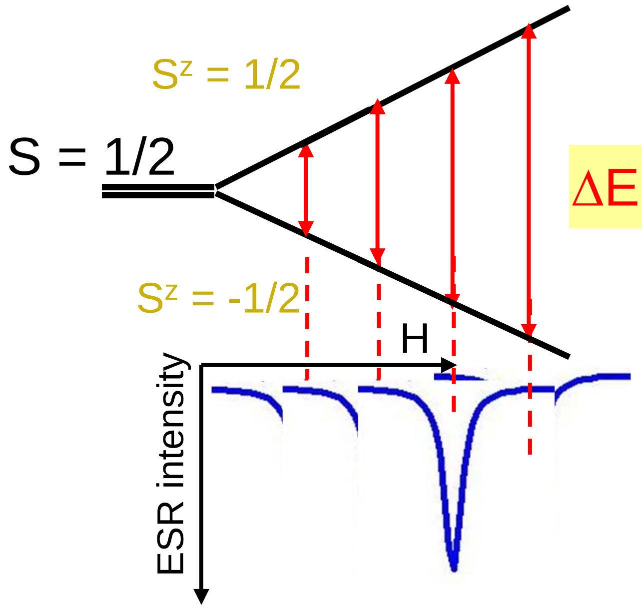


M = 15μ_B per doped hole

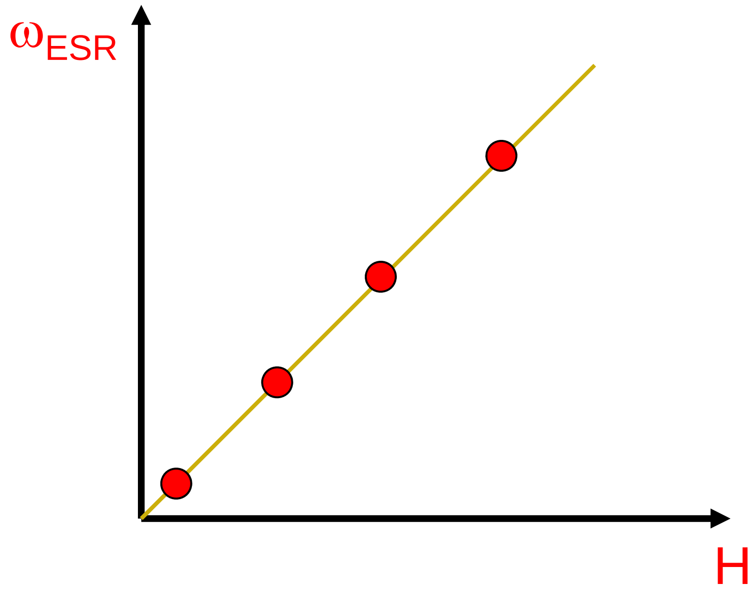
Cannot be due to individual $Co^{3+/4+}$ in any spin state

ESR: "Easy case": isolated spin ½ systems

Radical centers, weakly interacting half-integer spin species etc.
(chemistry, biology, semiconductor physics)



$\Delta E = g\mu_B H = \omega\hbar$

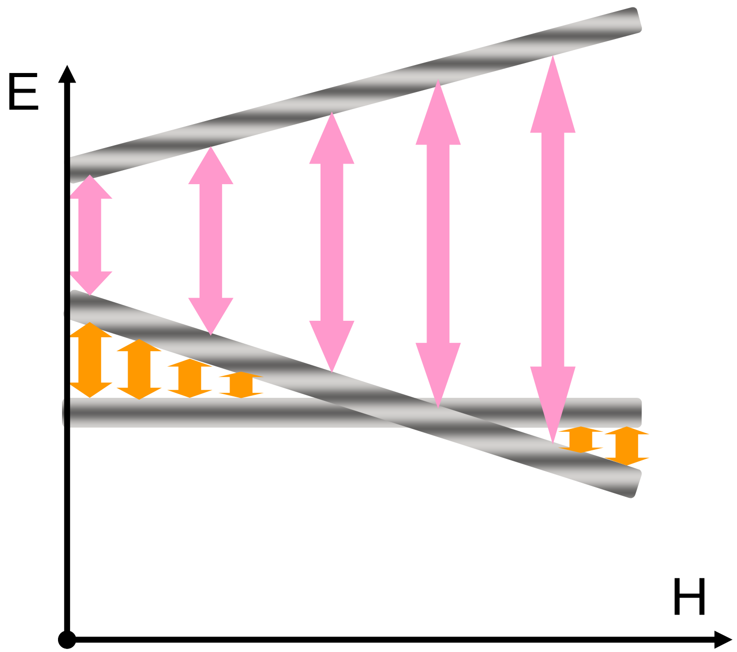


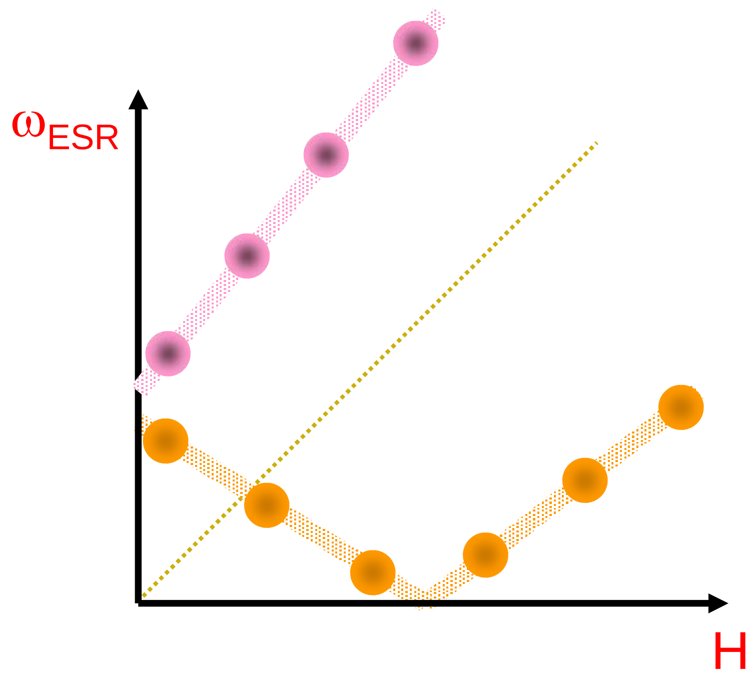
No restriction on minimal ESR frequency and field

"Difficult case": Correlated spin systems

- Quantum spin magnets on the basis of complex oxides
- molecular magnets

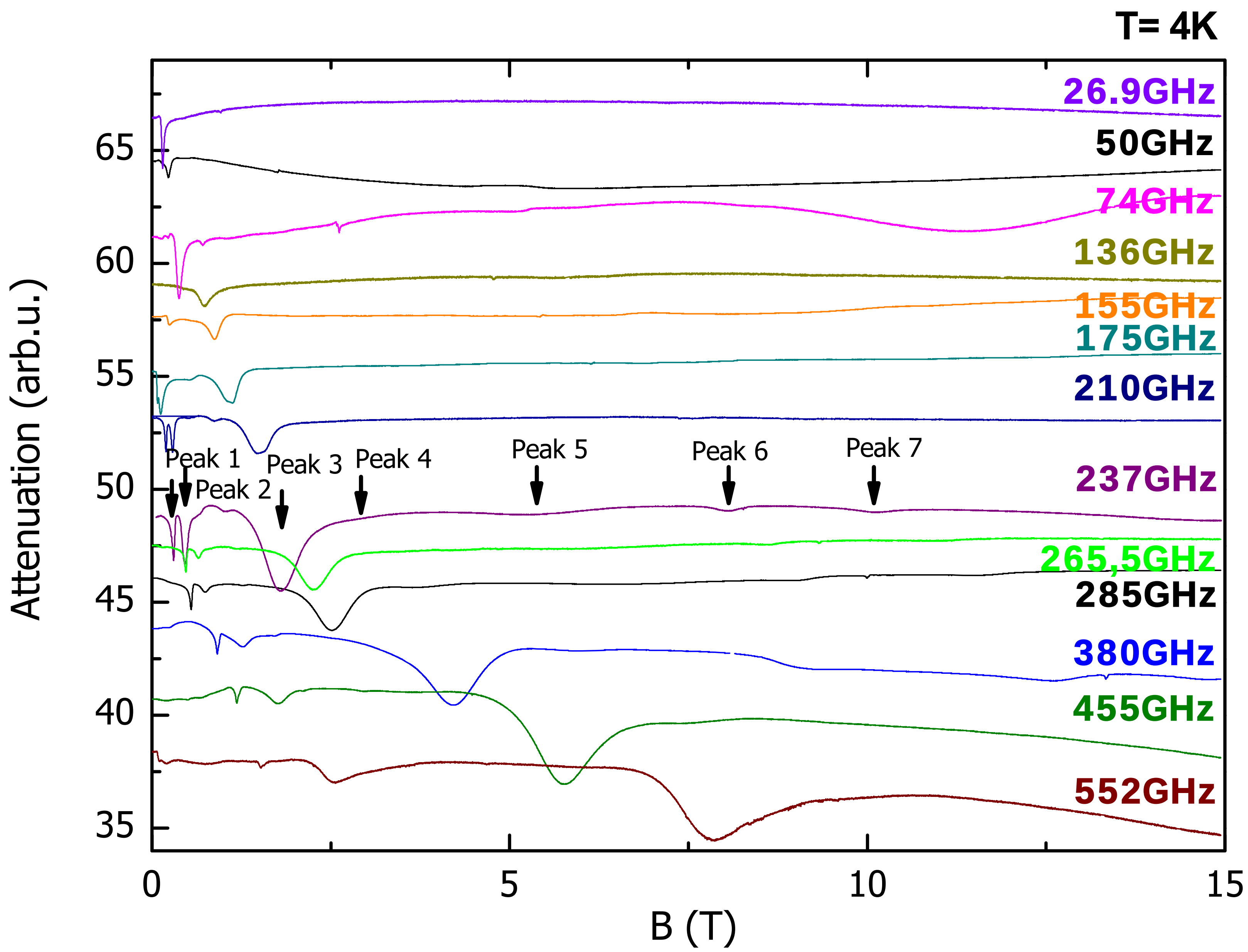
- unconventional superconductors,
- heavy fermion and Kondo metals



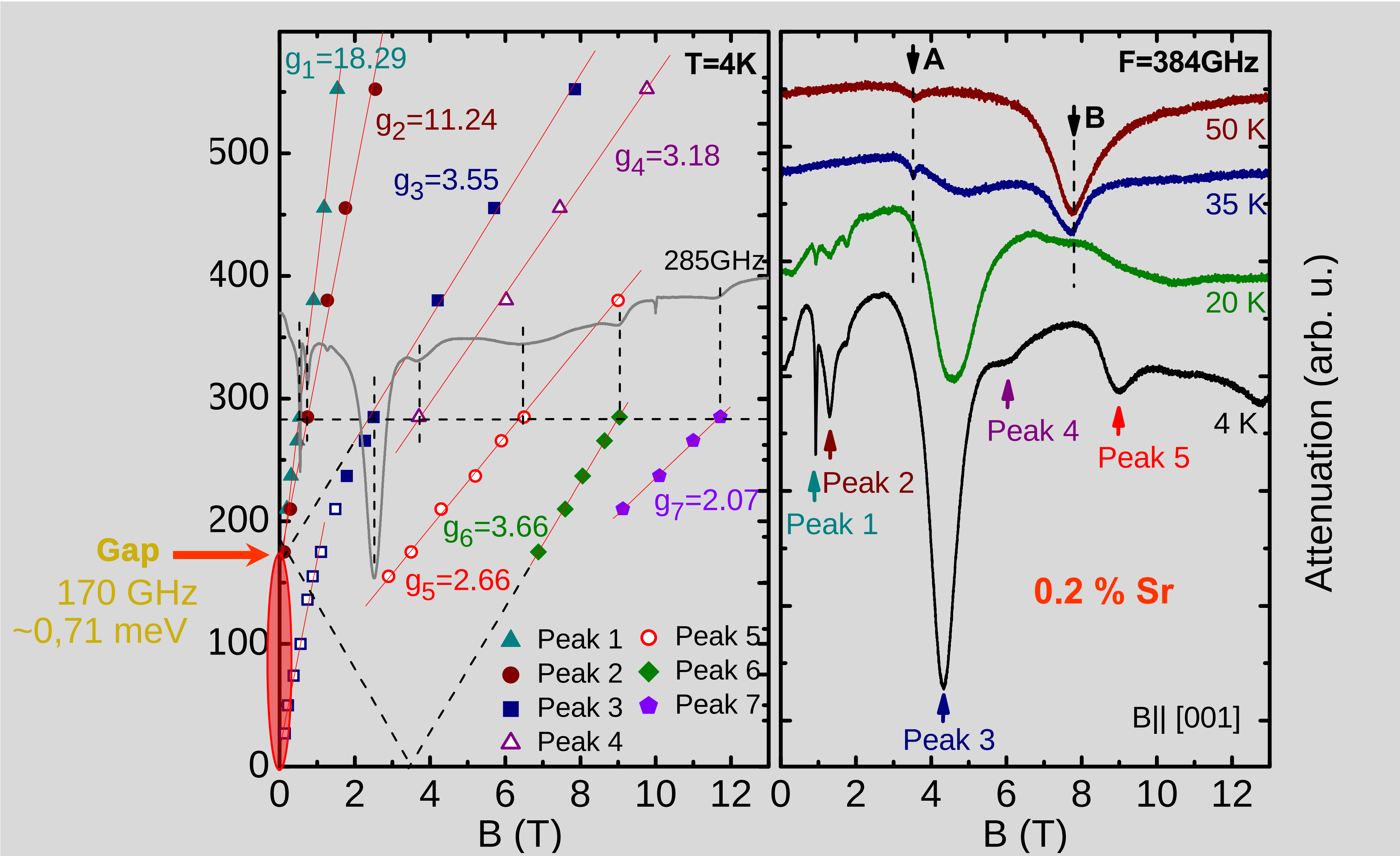


→ High-Field ESR (IFW: 18T) at high frequencies (IFW: 1.2 THz)

ESR on LCO+0.2% Sr at Low T: Spin Clusters

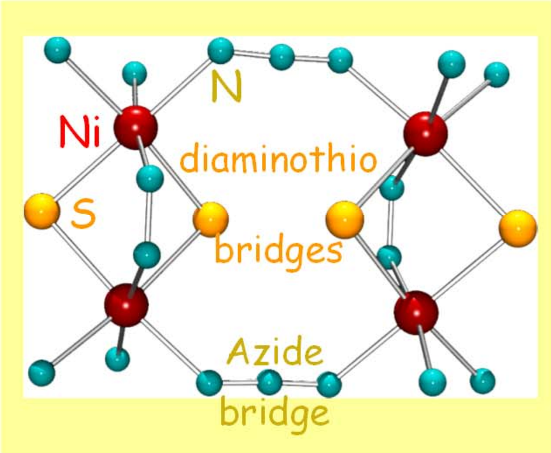


LCO+0.2% Sr: High Field ESR

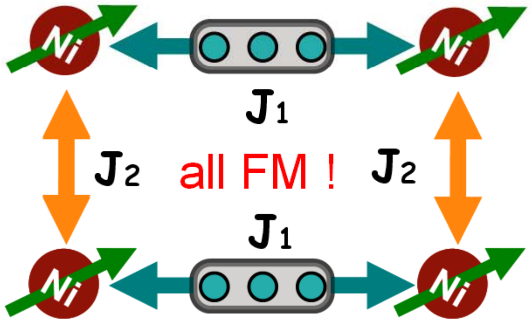


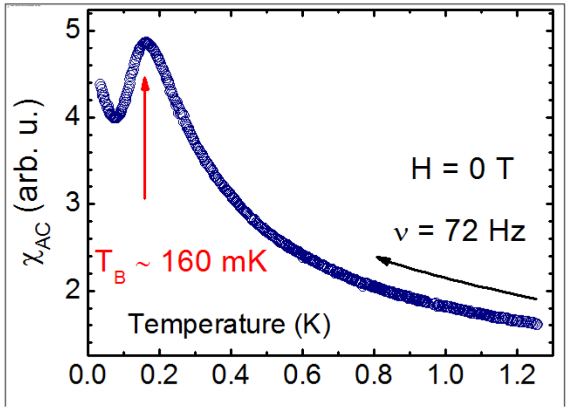
Multiple gapped excitations with large g-factors → Big spin multiplicity Substantial spin-orbit coupling → **Response of a big spin cluster!**

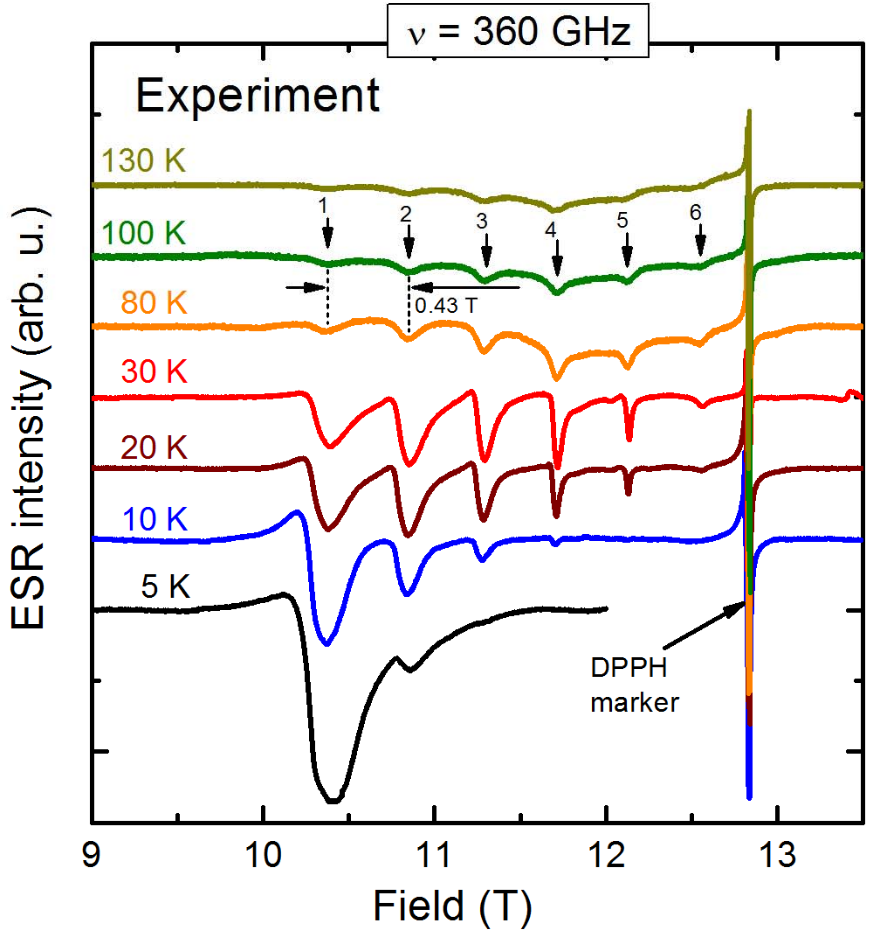
Molecular Magnets: “One-Molecule Spin Cluster”



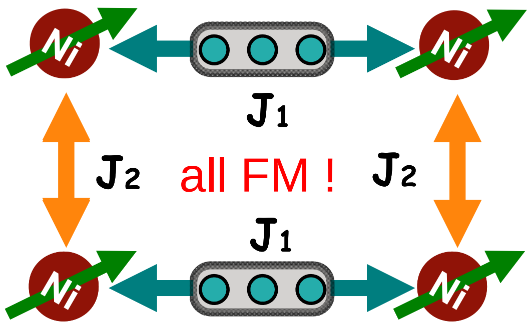
Sample: B. Kersting et al.
U Leipzig

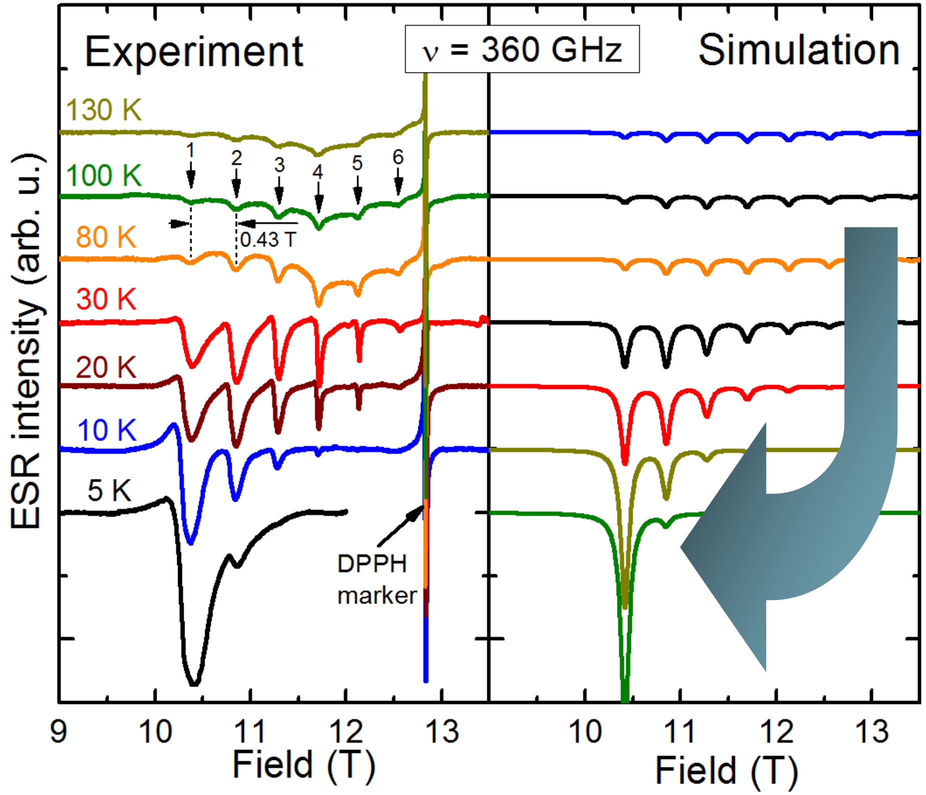






Ni(II)4-complex with bistable ground state

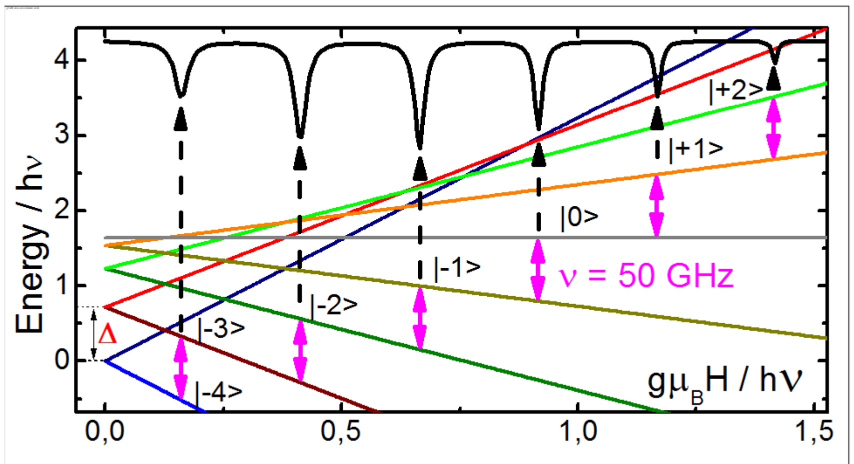




Transfer of spectral weight, D < 0

S=4 Effective Hamiltonian

$$H = D\left(S_z^2 - 20/3\right) + g\mu_B \mathbf{H}\cdot\mathbf{S}$$



ESR: Energy structure of the S = 4 multiplet resolved

g = 2.17; D = -Δ/7 = - 0.27 K

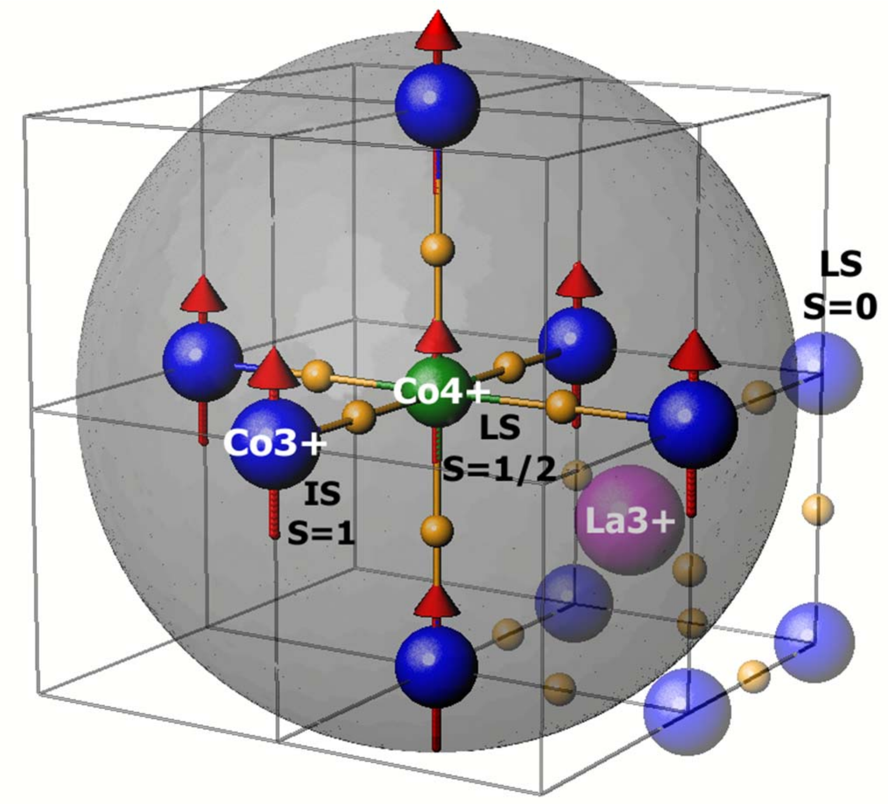
Negative anisotropy D ⇒

bistable $S^z = \pm 4$

ground state !

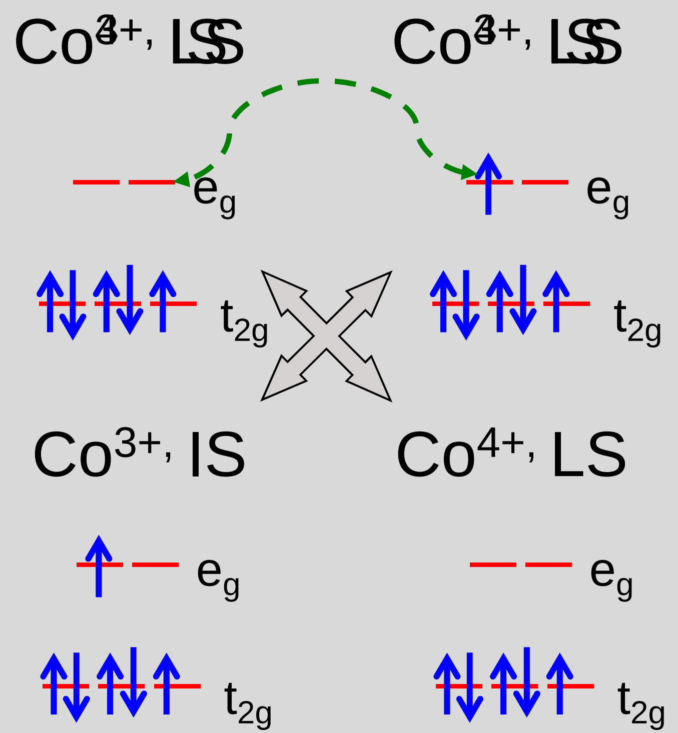
Hole-induced spin state polaron due to double exchange

The hole dynamically distributed over the cluster



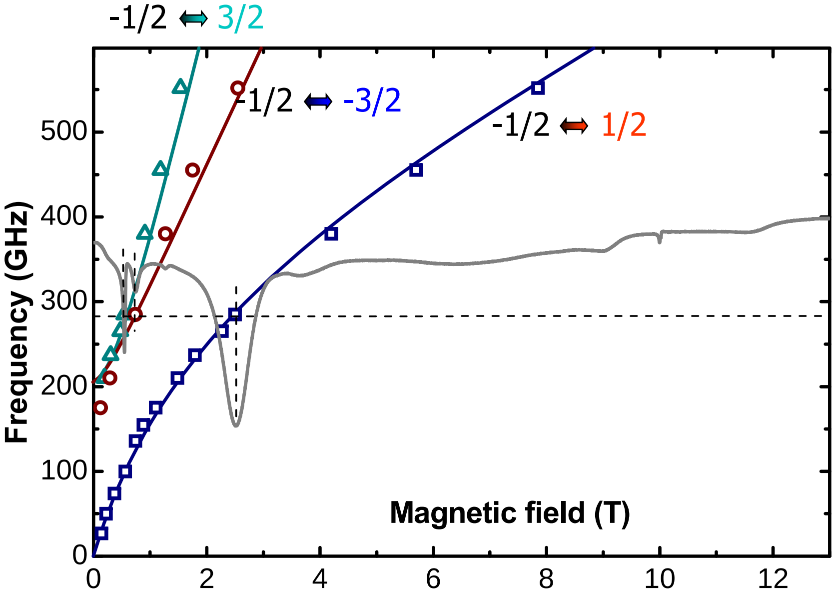
Resonant state due to double exchange

D. Louca and J. L. Sarrao, Phys. Rev. Lett. 91, 155501 (2003).

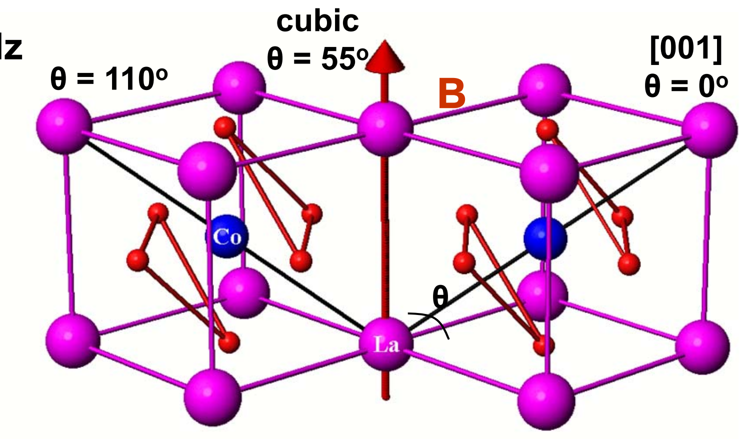


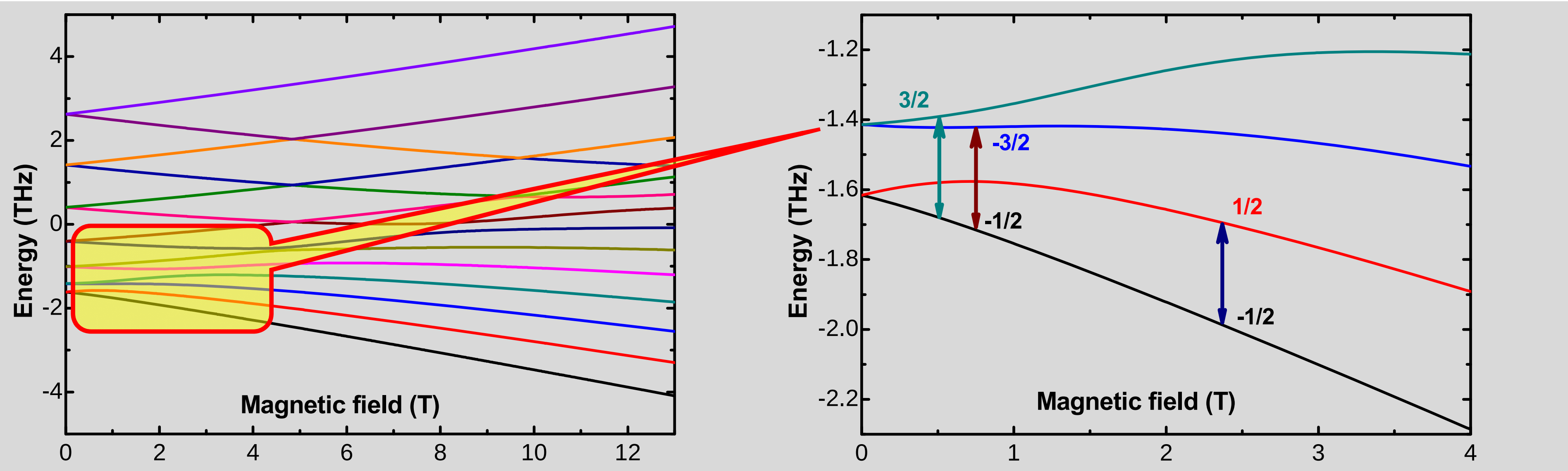
Model: Energy spectrum of the spin states

$$H = \mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}$$



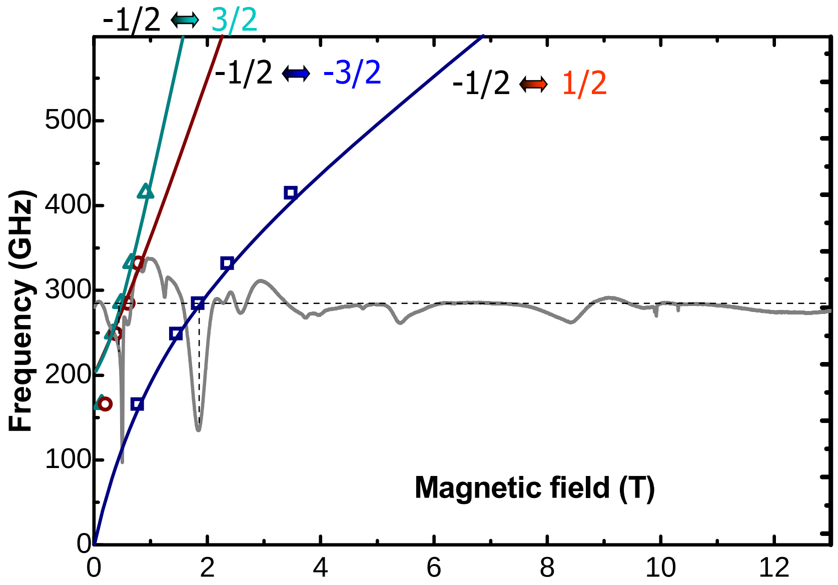
S = 1 x 6 + 1/2 = 13/2
g = 2.6
D = 101 GHz
T = 4 K
θ = 50°



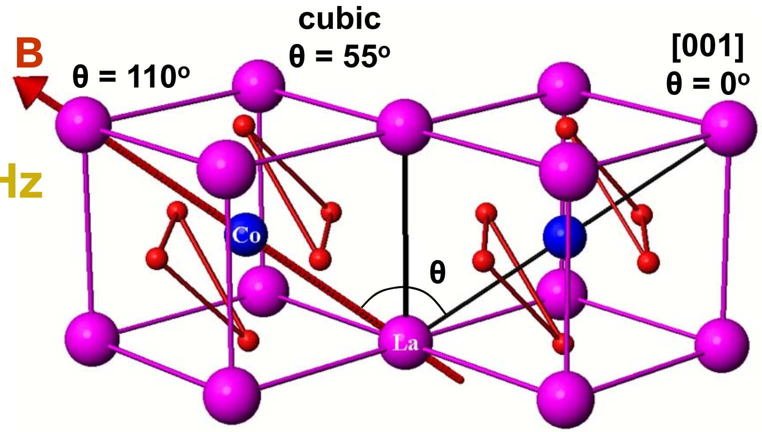


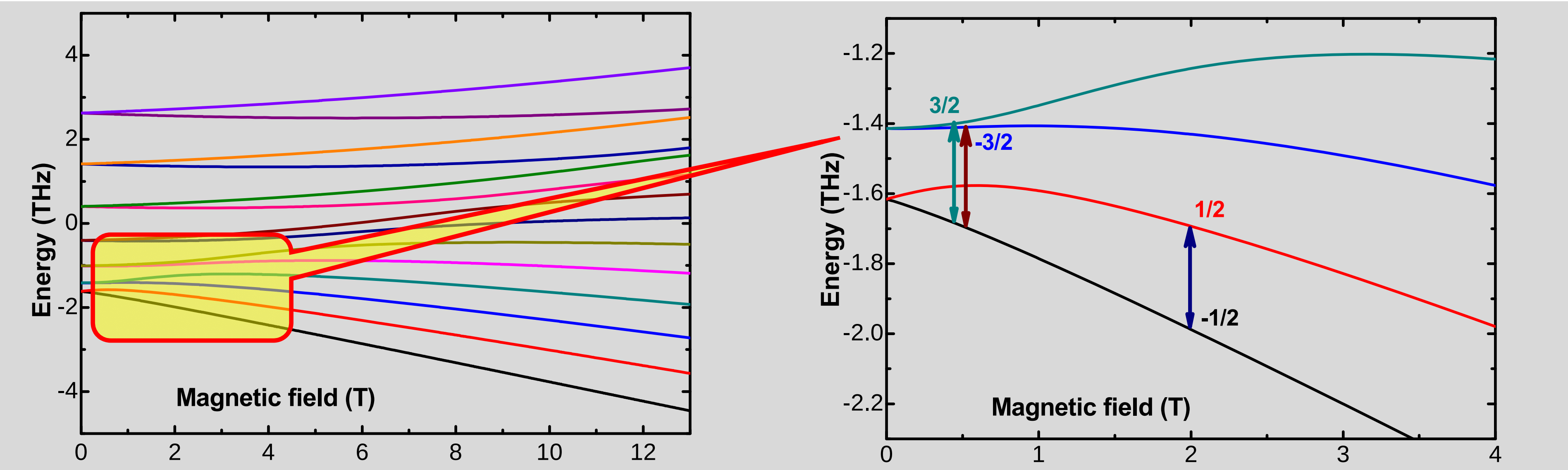
Model: Energy spectrum of the spin states

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$



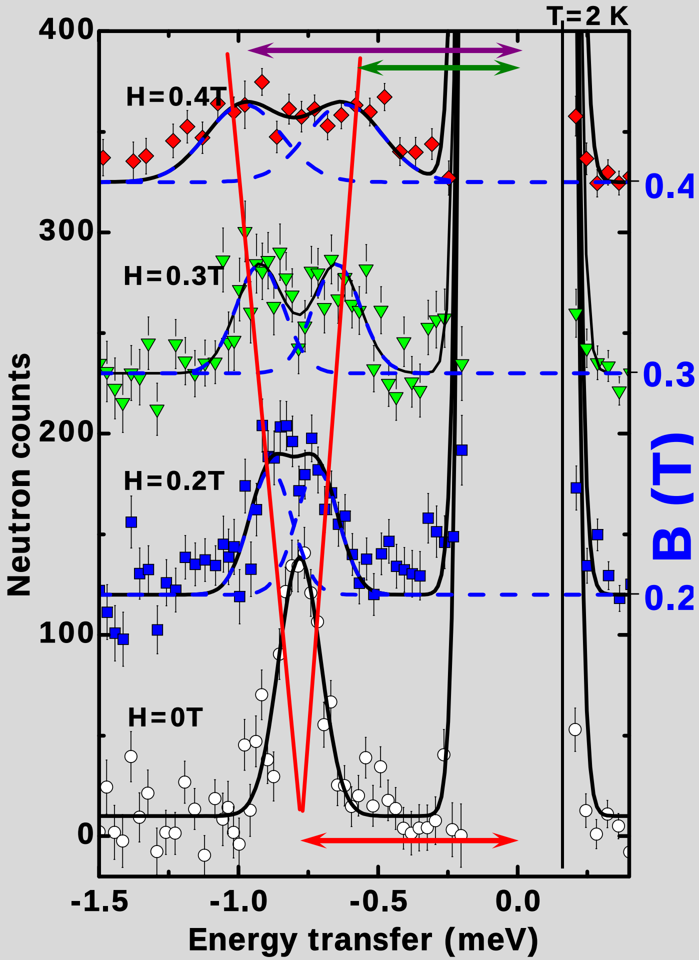
S = 13/2
g = 2.6
D = 101 GHz
T = 4K
θ = 100⁰

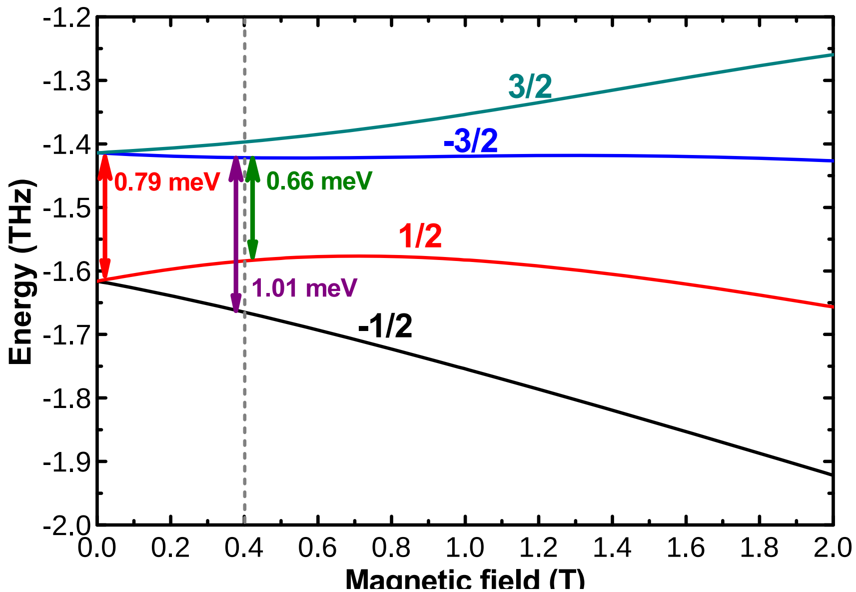




Model: Energy spectrum of the spin states

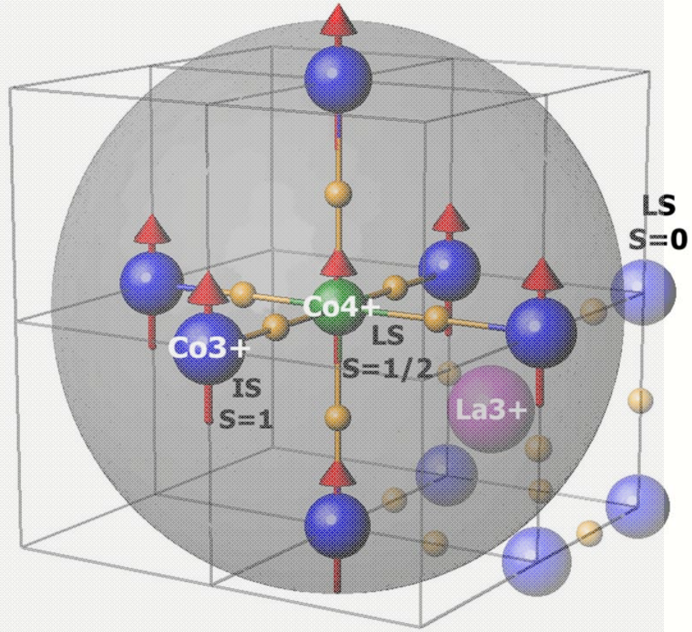
Inelastic neutron scattering
in magnetic field

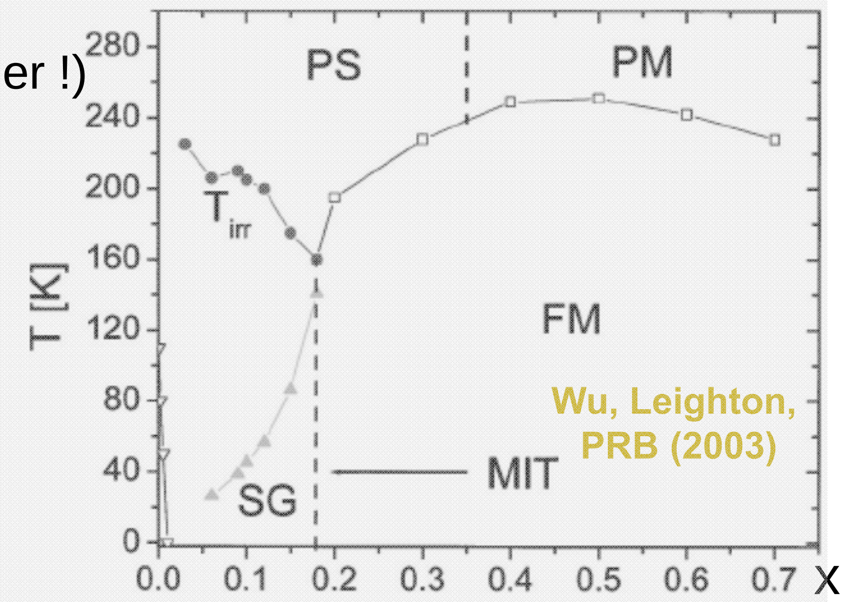




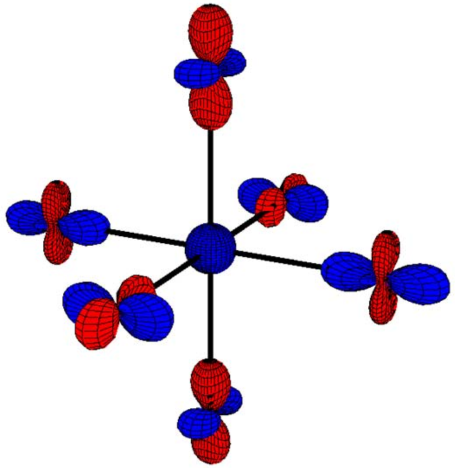
ESR on lightly doped $LaCoO_3$: Conclusions

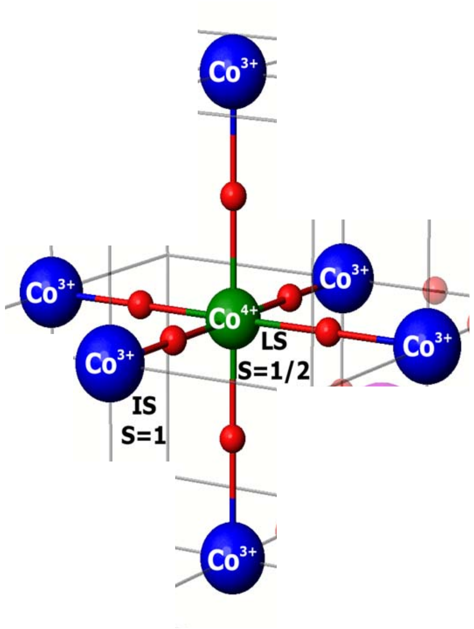
- Small Sr/Ca doping of $LaCoO_3$ yields extraordinary large magnetic moments
- Spectroscopic investigations evidence the occurrence of big spin clusters
- Spectrum of the spin states well understood
- Hole doping and not structural distortion is essential
- Nucleation of a spin state polaron (septamer !)
- doping yields intrinsic magnetic inhomogeneities in $LaCoO_3$
- spin polaron is a building block of SG and FM phases





Orbital Polarons





Manganites and Cobaltates:

- Partial delocalization of a doped hole by changing the adjacent orbital states
- Ferromagnetic nanoclusters due to (local) double exchange interaction

Cobaltates

- Change of spin state (IS instead of LS)
- Isolated clusters in a non-magnetic background

Manganites

- Orientation of orbitals changes (spin state always HS)
- Polarons coupled to AFM background→ complicated magnetic state

Nanoscale Electronic Order in Transition Metal Oxides

i. Spin and Charge Stripes in two-dimensional CuO planes

Observing charge order by resonant soft X-ray scattering

Charge and spin stripes due to mobile holes in afm background

Stripes due to local spins and/or CDW due to nesting?

ii. Charge and Orbital Polaron Ordering in Manganites

CE type order: Local double exchange and/or nesting instability?

Ferromagnetic insulating phase due to orbital polarons

iii. Spin State Polaron in lightly doped Cobaltates

Doped holes in non-magnetic cobaltates

Ferromagnetic nanoclusters due to spin state polarons

THANKS TO

J. Geck, A. Alfonsov, V. Kataev, S. Bahr R. Klingeler, P. Reutler, U. Ammerahl, T. Hänke, C. Hess S. Borisenko, V. Zabolotnyy, D. Inosov, D.S. Evtushinsky, J. Fink	IFW Dresden
H. Klauss et al.	TU Dresden
E. Schierle, E. Weschke A. Podlesnyak, M. Russina	HMI
D. Hawthorn, G. Sawatzky	UBC Vancouver
D. I. Khomskii	U Köln
A. Revcolevschi et al.	U Paris-Sud
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M. Hücker	Brookhaven
E. Vavilova	Kazan