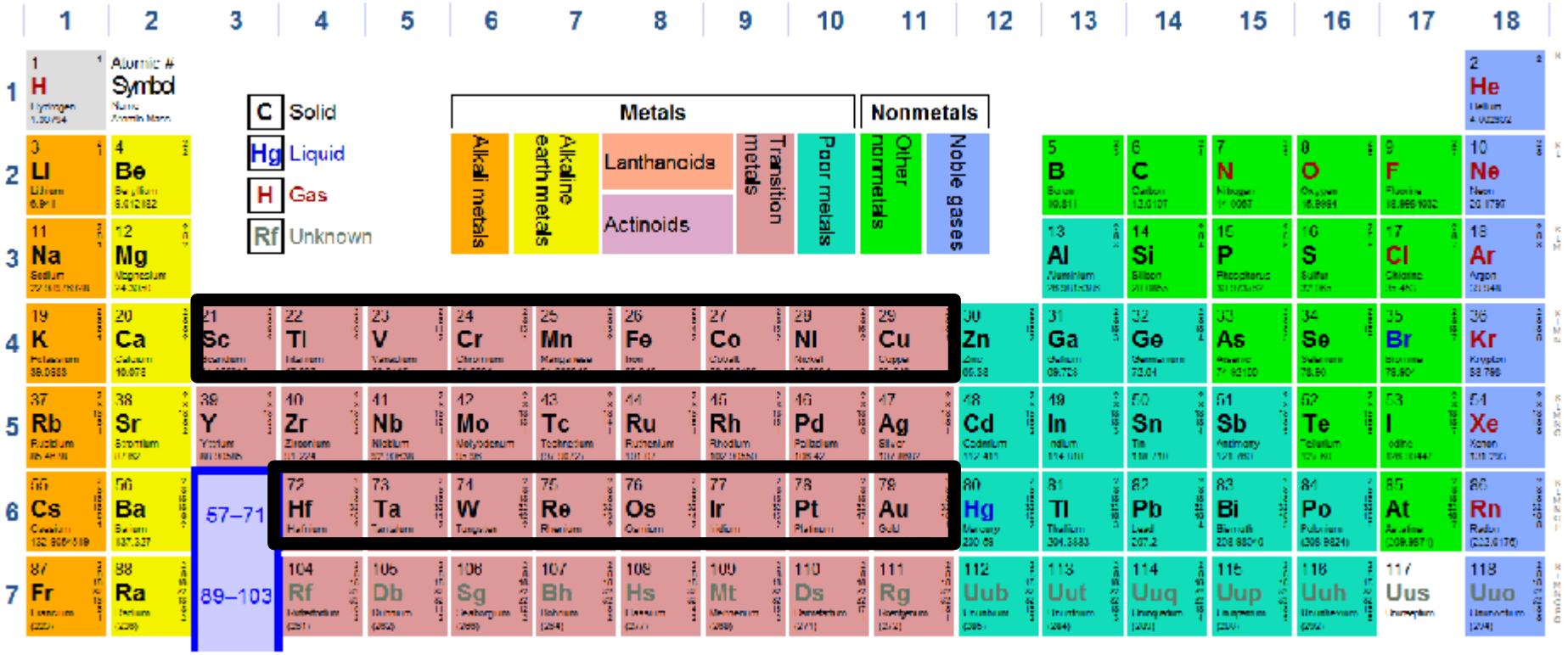
Exotic magnetism in 3d/5d ordered double perovskites

Eduardo Granado

IFGW – UNICAMP

Collaborators

- Sample synthesis: J. Gopalakrishnan and K. Ramesha (Indian Institute of Science), Marcos Tadeu D. Orlando (UFES)
- X-Ray Absorption: Julio Criginski Cesar (LNLS, ESRF), Carla Azimonte (IFGW-UNICAMP. ESRF), Andrei Rogalev, Fabrice Wilhelm (ESRF)
- Raman: Alí F. García-Flores, Alessandro F.L. Moreira, Ulisses F. Kaneko, Fábio M. Ardito, Hirotoshi Terashita, (IFGW-UNICAMP), Juan Carlos P. Campoy (UFSJ).
- Neutron Diffraction: Jeff Lynn and Qing Huang (NCNR-NIST)



3d transition metals:

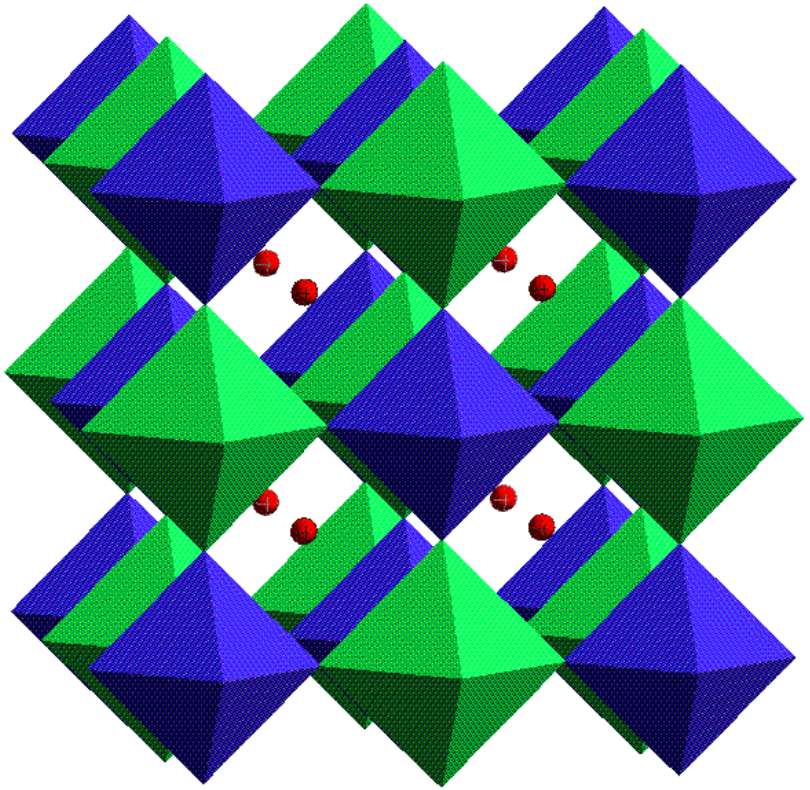
- Moderate spatial extension
- Normally magnetic
- Moderate hybridization with oxygen 2p
- Spin-orbit coupling < < crystal field splitting
- strongly correlated electrons

5d transition metals:

- Large spatial extension
- At the verge of magnetism
- Strong hybridization with oxygen 2p
- Spin-orbit coupling ~ crystal field splitting
- intermediate electronic correlation

Mixing 3d and 5d elements in a simple structure: Double Perovskites

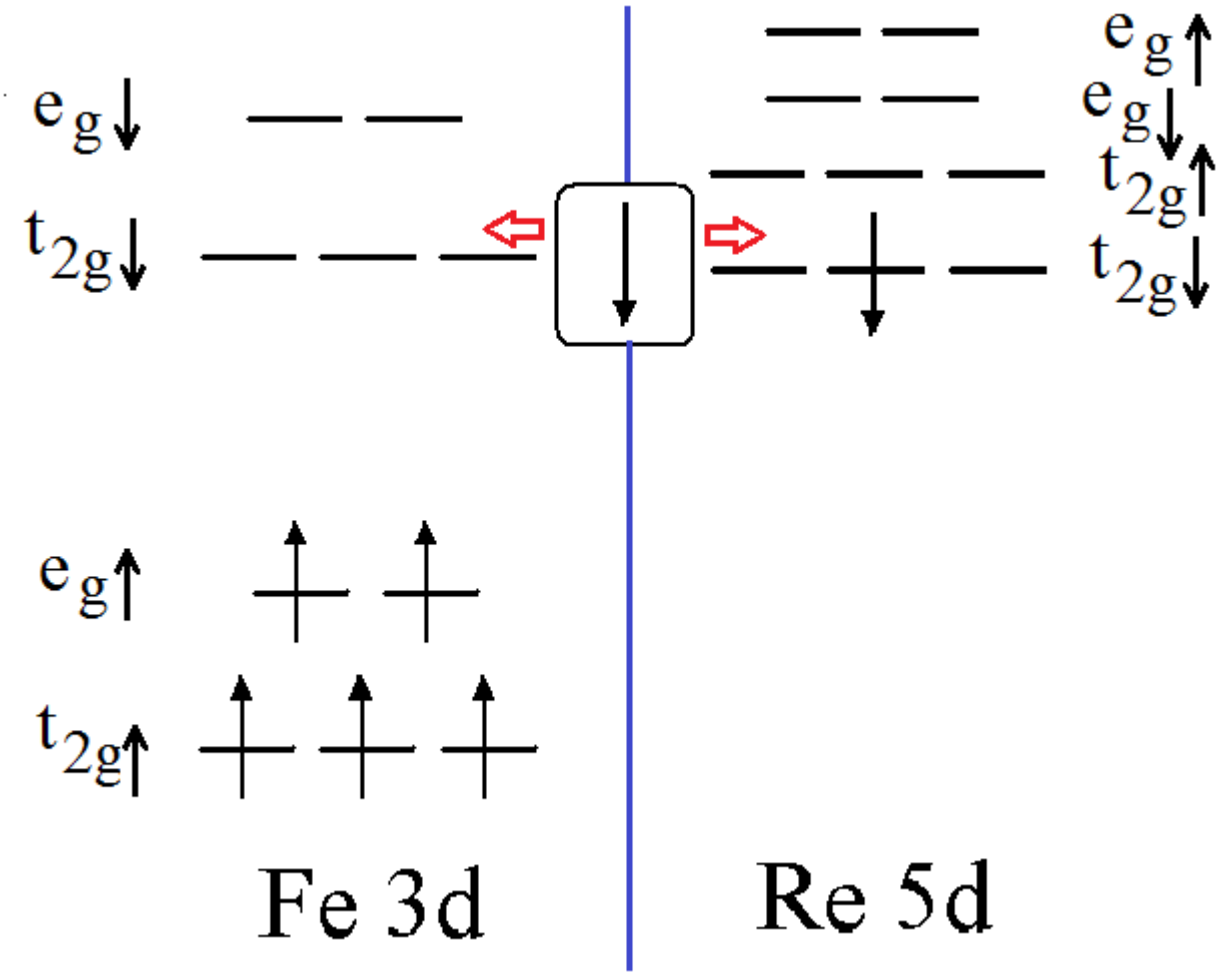
- General formula: $A_2BB'O_6$
  - *A:* "large" cation (typically rare-earths and/or alkaline-earths)
  - *B, B' :* "small" cations (typically transition-metals)



Stability condition:

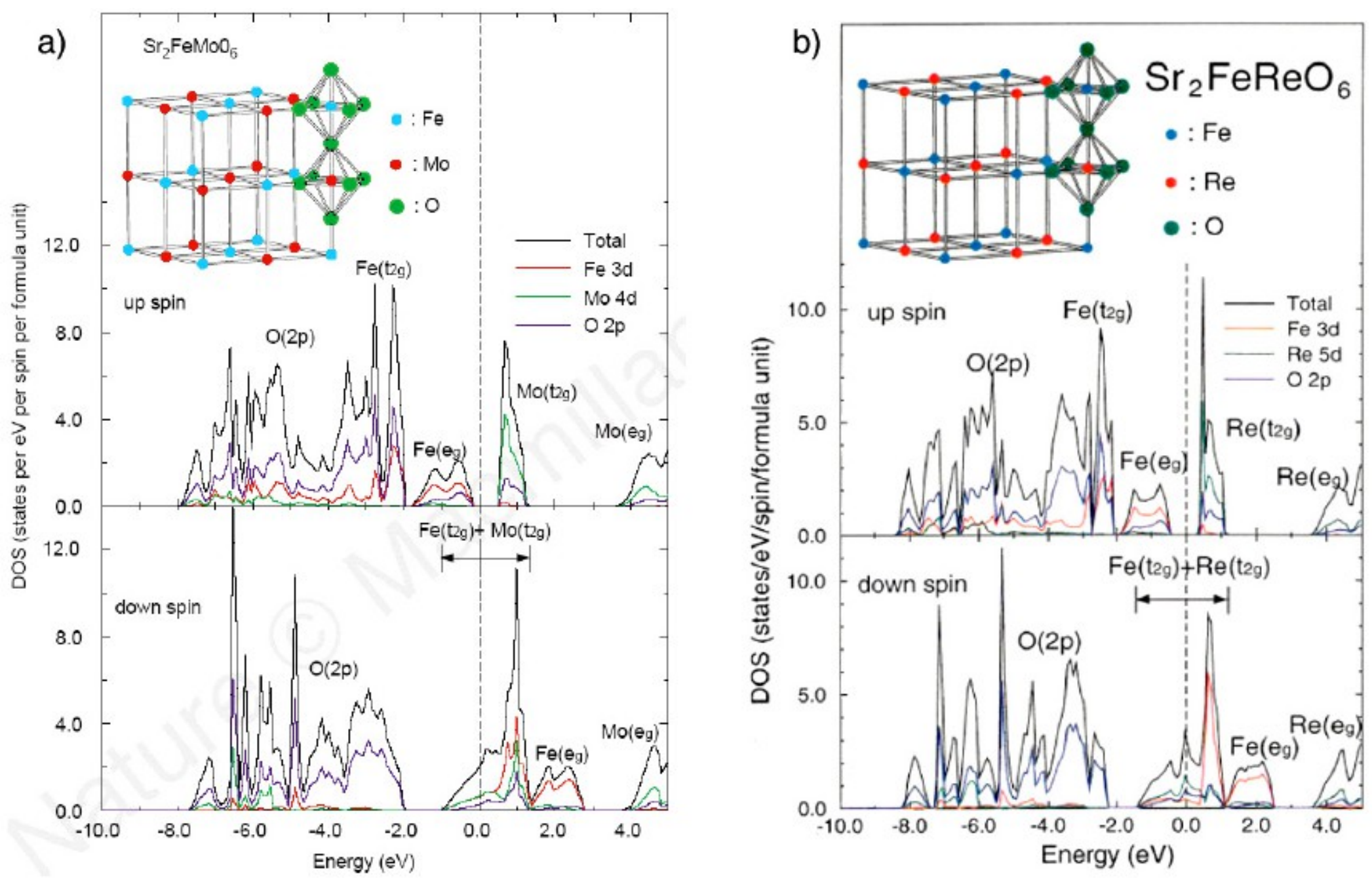
$$\langle d_{A,A'\text{-}O} \rangle \sim \sqrt{2}\, \langle d_{B,B'\text{-}O} \rangle$$

A_2FeReO_6 (A=Ba,Sr,Ca) double perovskites : Energy level scheme



Double exchange stabilizes the half-metallic ferrimagnetic state

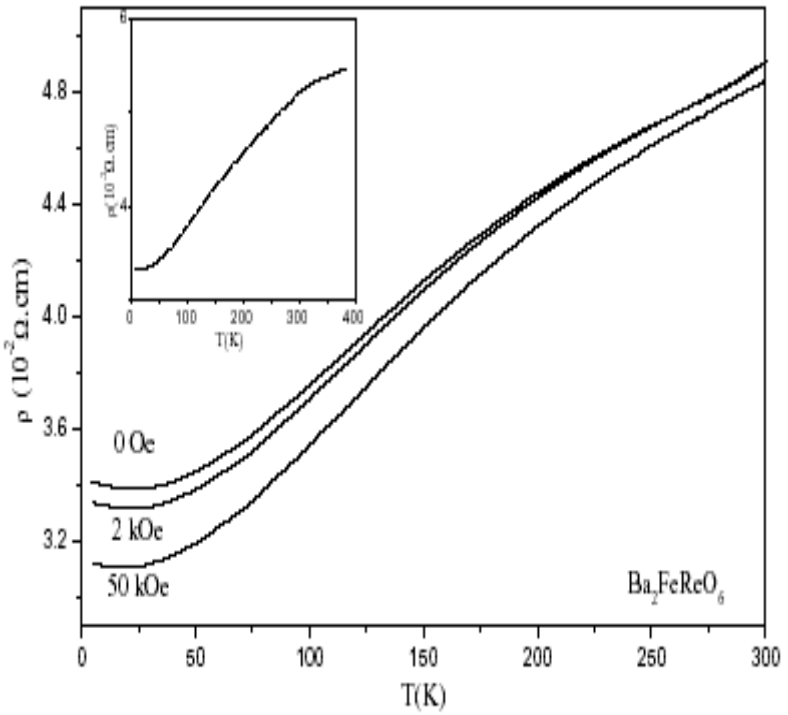
A.W. Sleight and J.F. Weiher, J. Phys. Chem. Solids **33**, 679 (1972).



K.-I. Kobayashi *et al.*, Phys. Rev. B **59**, 11159 (1999).

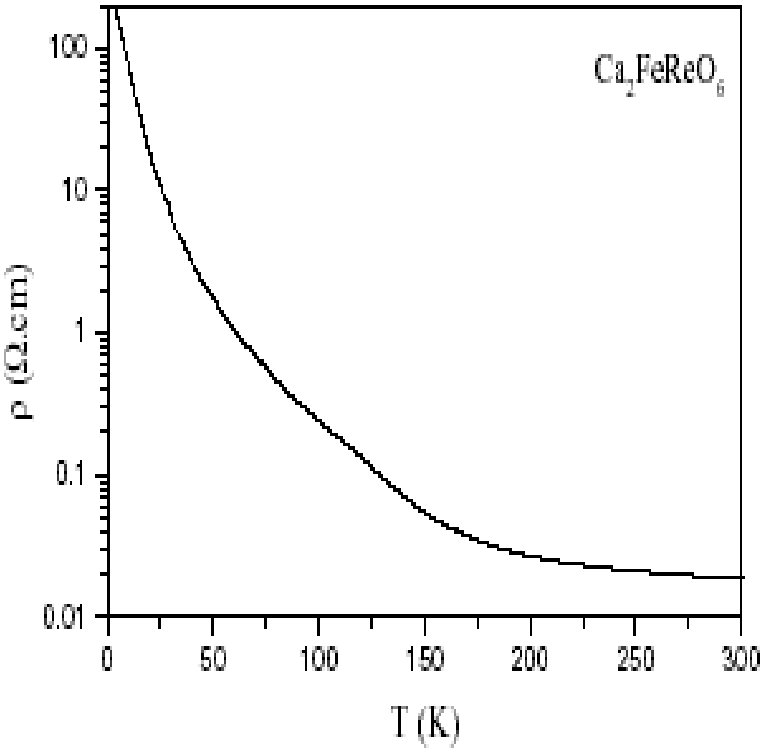
Macroscopic Properties (experimental)

Ba_2FeReO_6



- Half-Metallic
- Ferrimagnetic
- Tc = 305 K

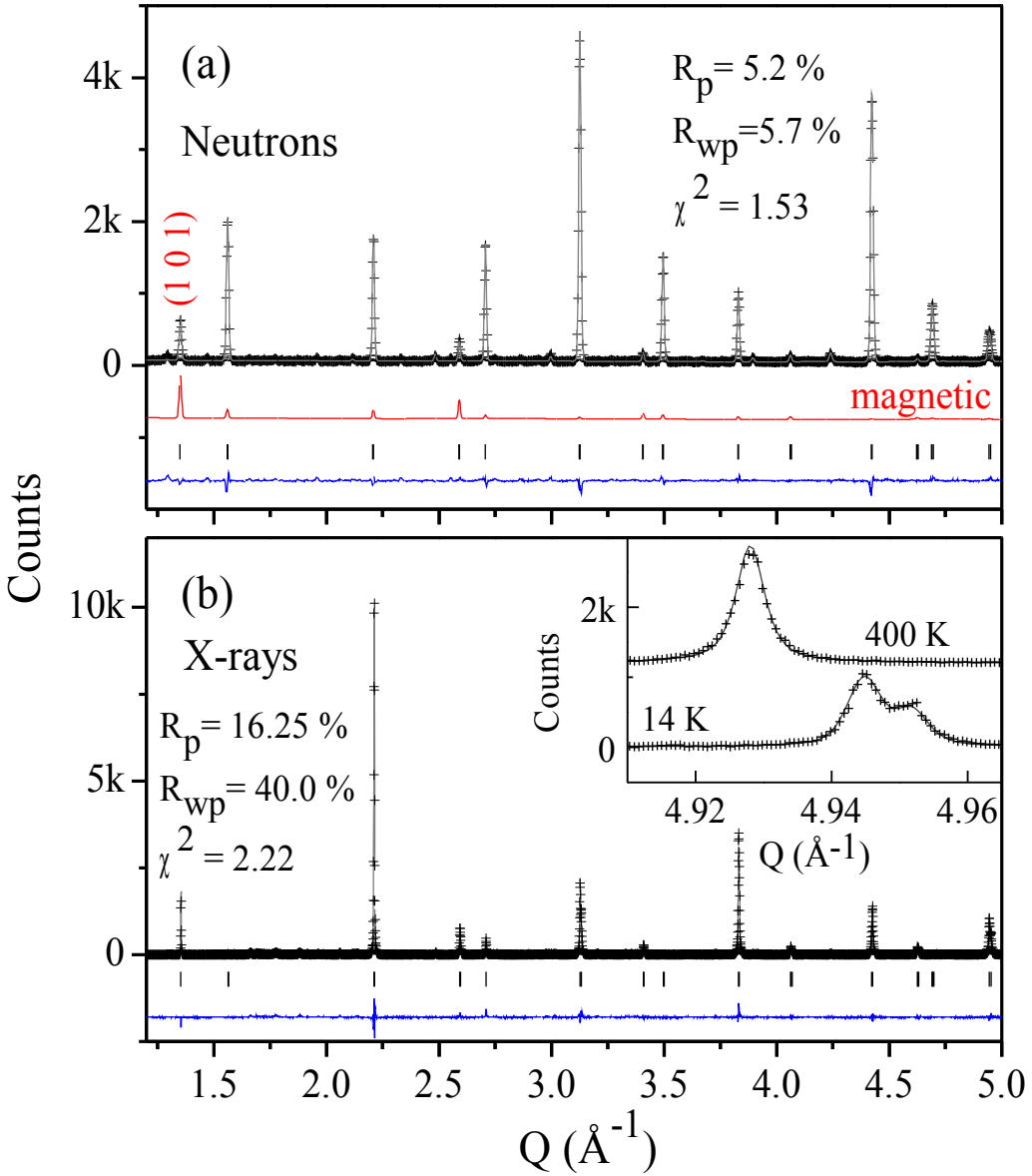
Ca_2FeReO_6



- Semiconducting
- Ferrimagnetic
- Tc = 520 K

W. Prellier et al., *J. Phys.: Condens. Matter* ***12***, *965 (2000).*

Crystal and magnetic structure of Ba_2FeReO_6: Neutrons and Synchrotron X-Ray Powder Diffraction



Neutron powder diffraction:

- ferrimagnetic ordering of Fe and Re spins
- M(Fe) = 3.2(1) μ_B

M(Re) = -1.1(1) μ_B

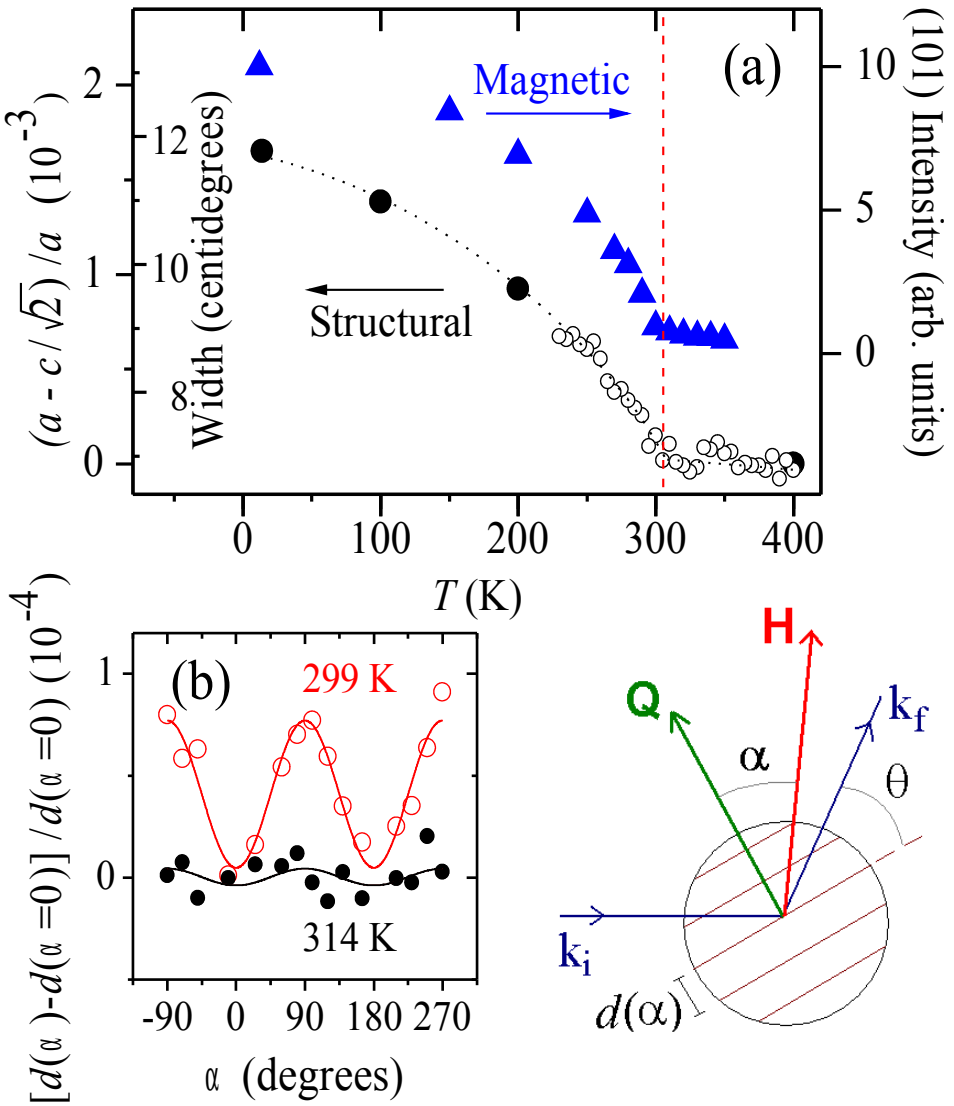
- Fe/Re anti-site disorder: ~4 %
- d_Fe-O = 2.077(1) Å.

d_Re-O = 1.950(1) Å.

- Estimated Fe valence: +2.45

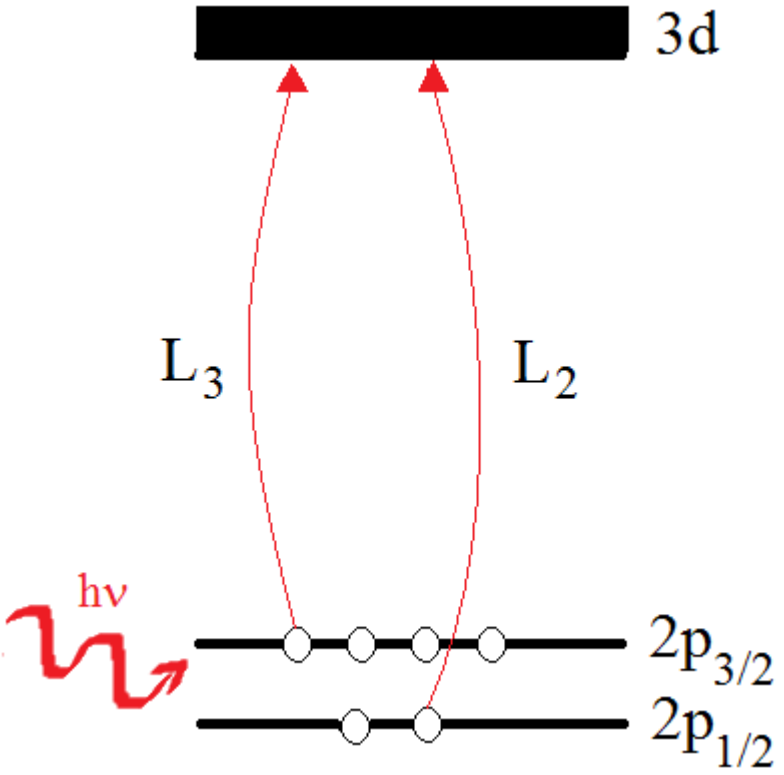
Synchrotron x-ray powder diffraction:

- High angular resolution (sharper Bragg peaks).
- Crystal symmetry lowering at low temperatures.

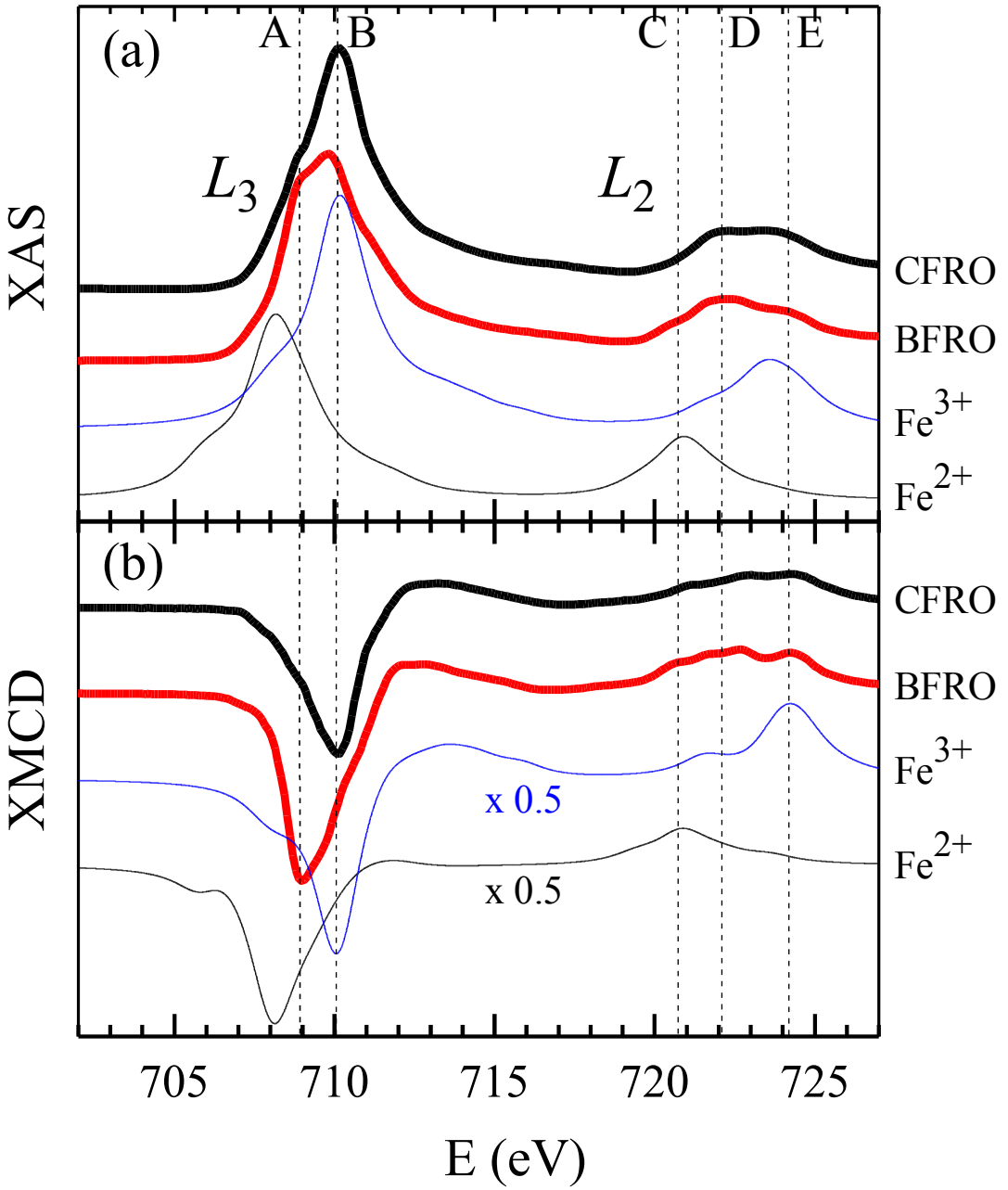


- Magnetic ordering transition at Tc= 309 K.
- Simultaneous structural transition at Tc.
- Interplanar distance modulated by angle α between magnetic field **H** and plane normal **Q**.

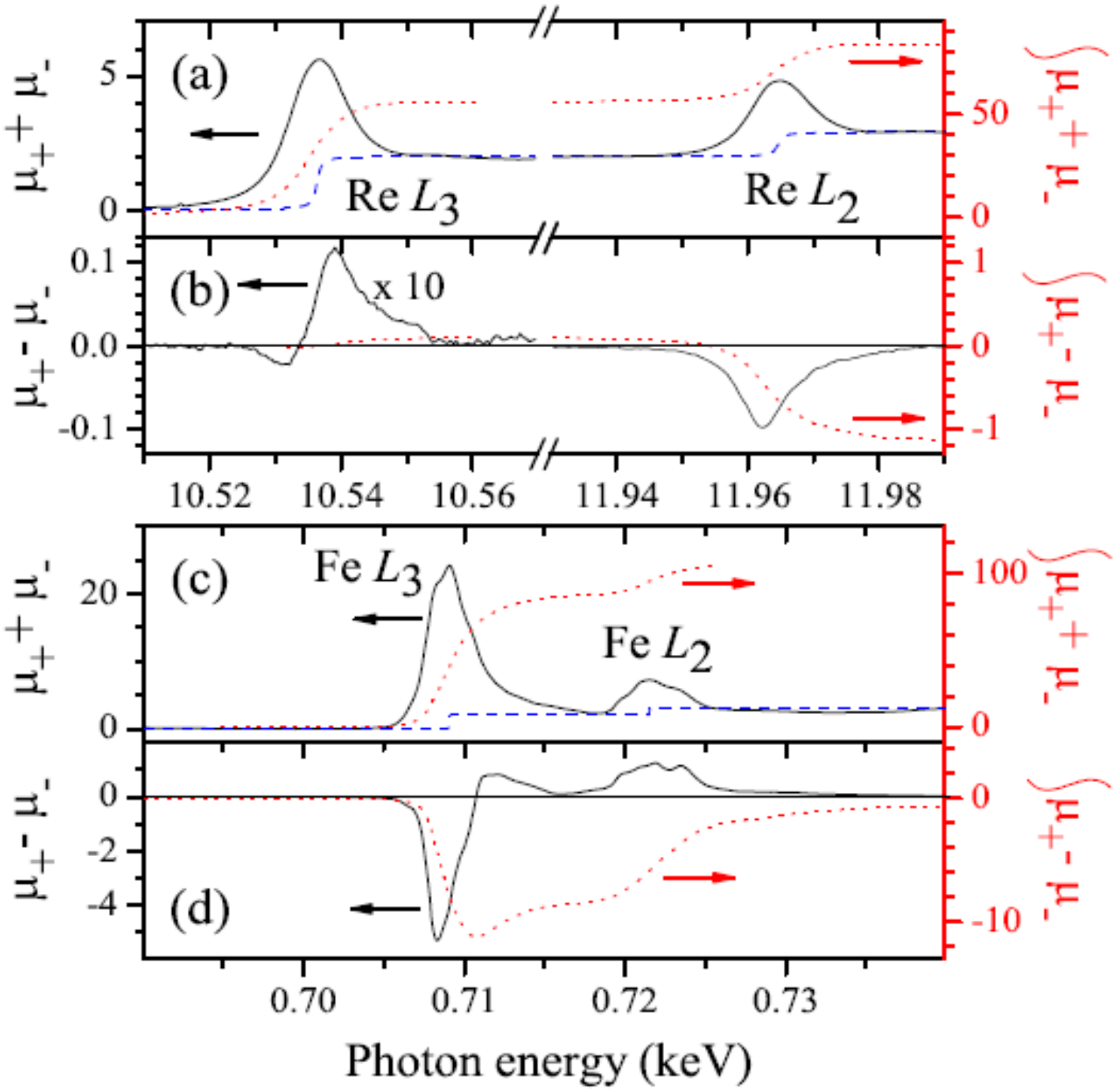
X-Ray Absorption Spectroscopy



- Ratio between A and B spectral weights for Ba_2FeReO_6 indicate mixed Fe^{2+} - Fe^{3+} valence, consistent with Fe-O distances obtained by Neutron PD.



X-Ray Magnetic Circular Dichroism on Ba_2FeReO_6



XMCD Sum Rules:

•Re:

M_{orb} = 0.19(1) μ_B

M_{spin} = -0.64(4) μB

Morb/ Mspin = -0.294

Fe:

Morb = =0.04(2) μB

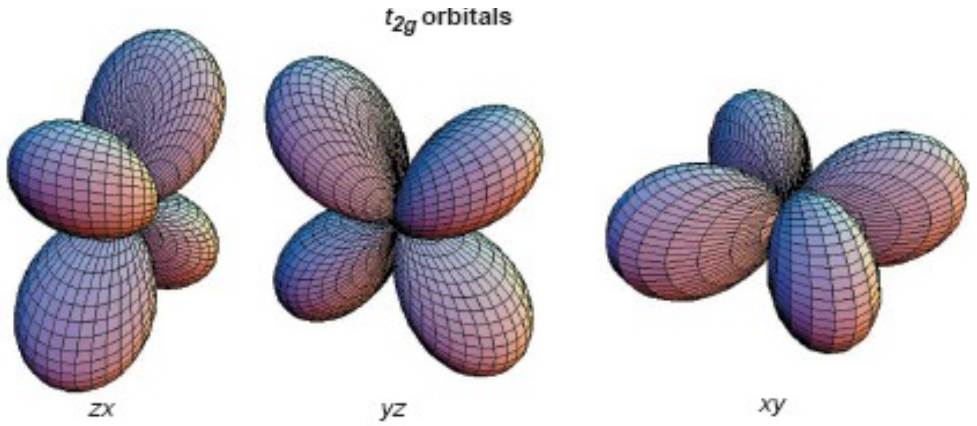
Mspin = 2.8(2) μB

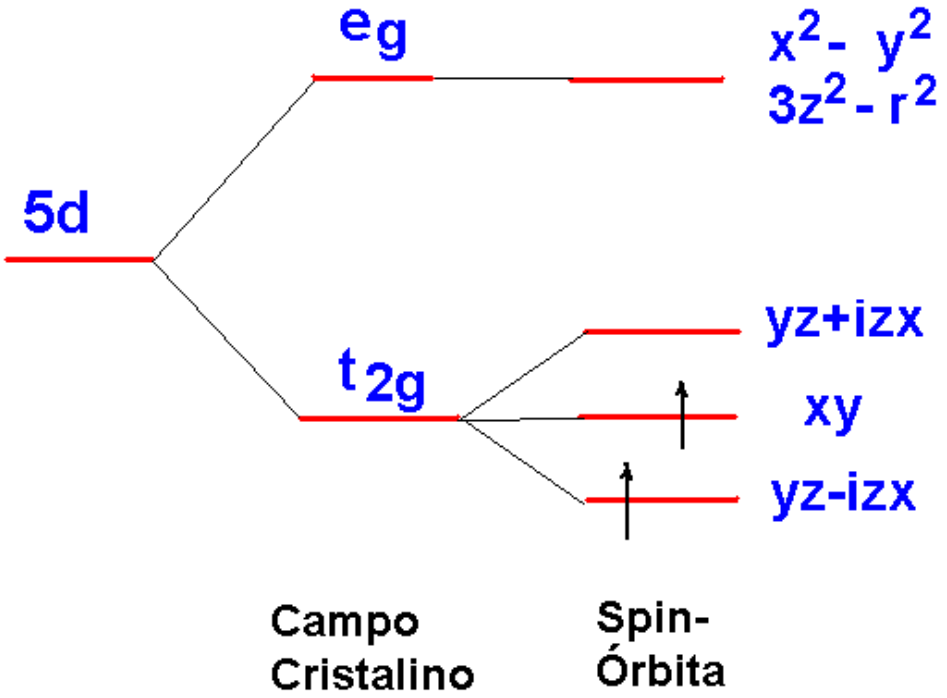
Morb/ Mspin = 0.013

• Giant orbital magnetic moment (unquenched) for Re. Ratio Morb/ Mspin = -0.294 comparable to atomistic values.

• Reason: For 5d ions, the spin-orbit coupling is a stronger interaction than for the 3d ions, and can be of the order of electron-volts.

• Unquenched orbital moments for Re 5d electrons

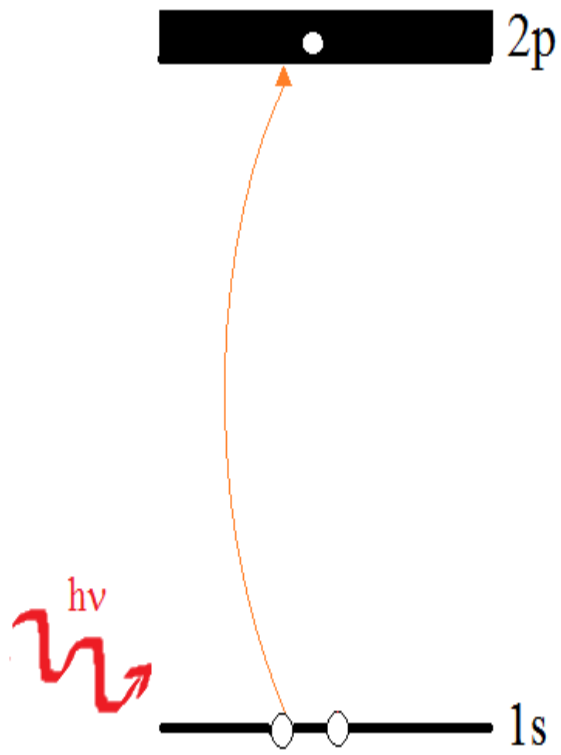


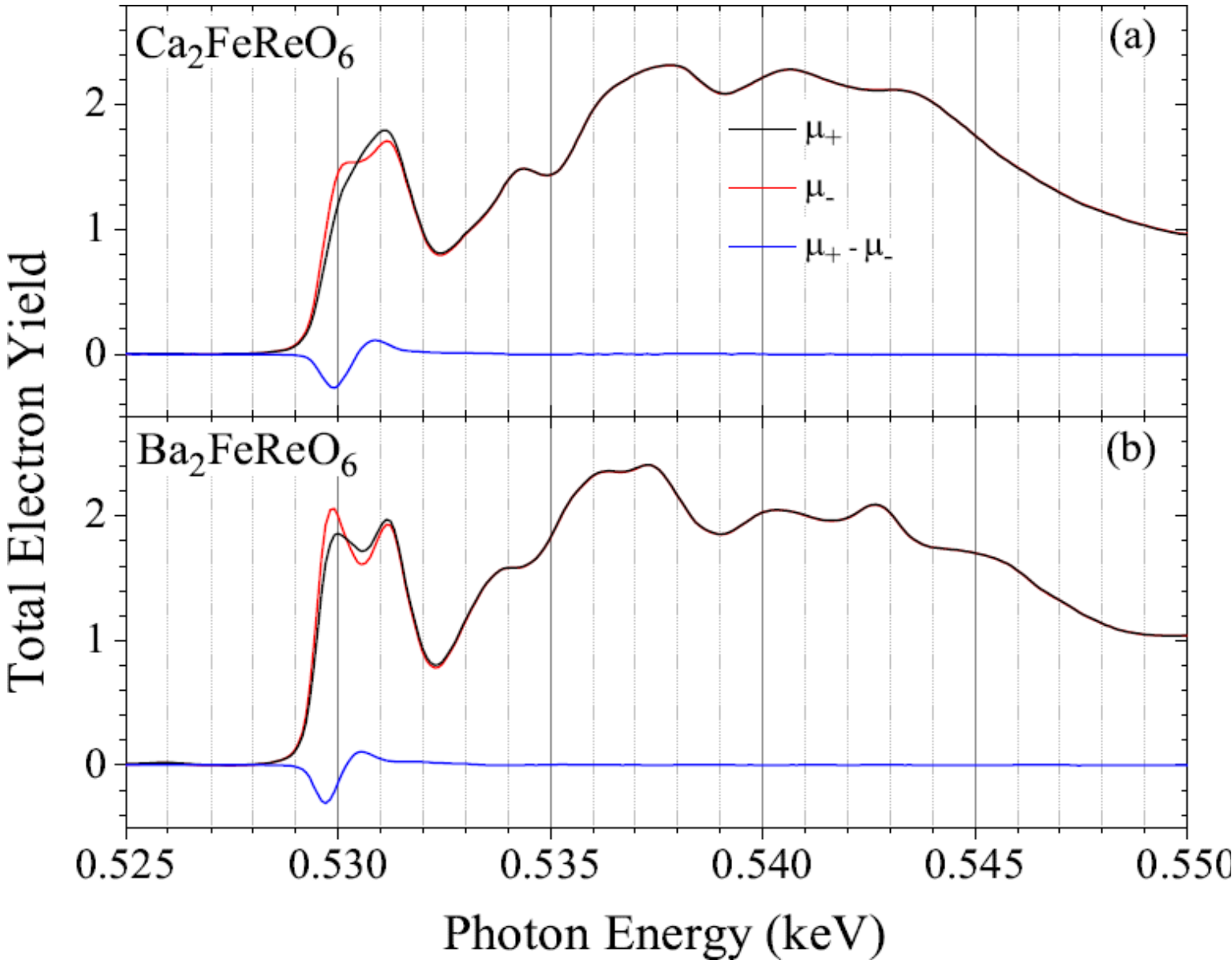


Not a normal metal: orbitally polarized metal through spin-orbit coupling !

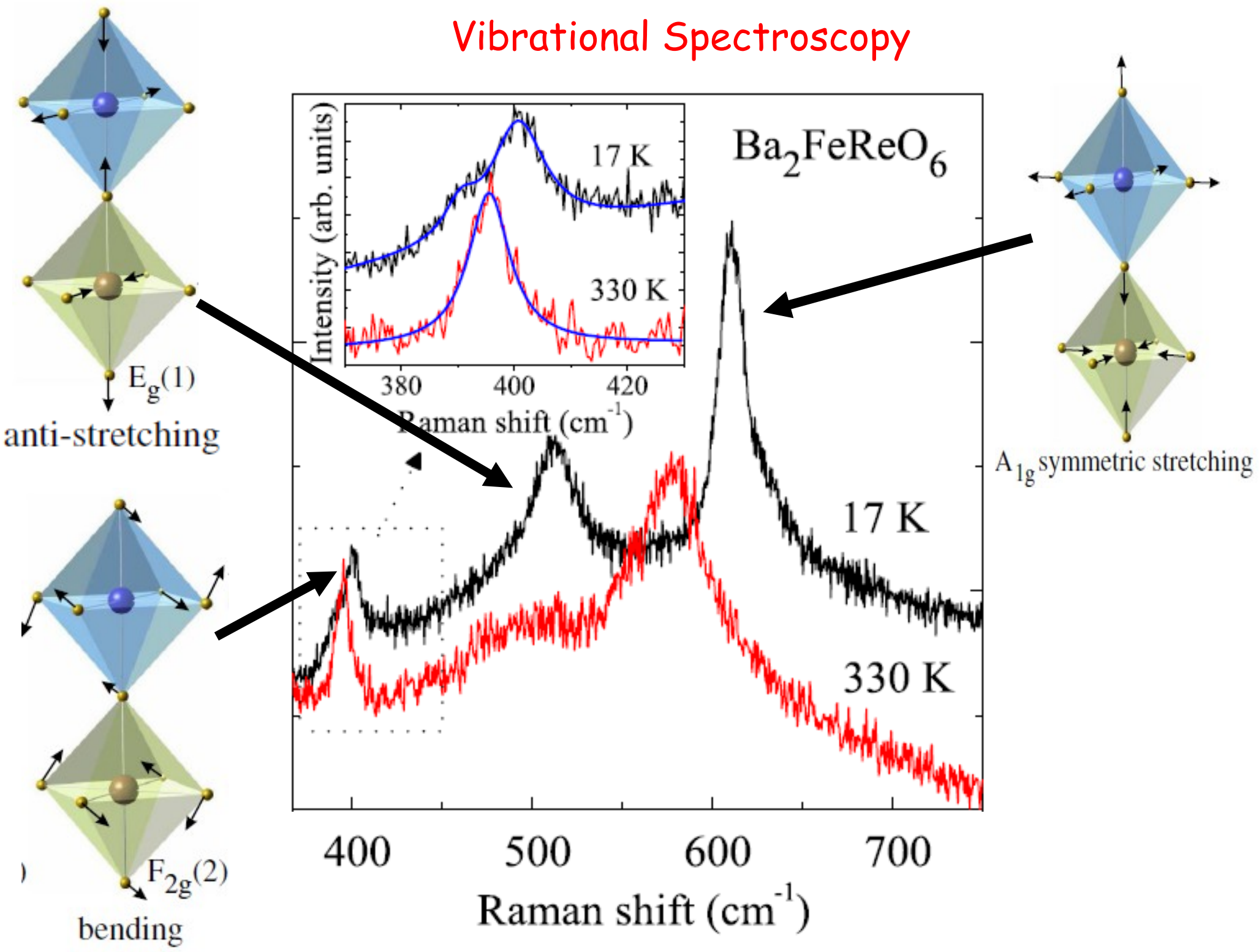
Large Re orbital moment + Large Re-O hybridization = Magnetic Oxygen ?

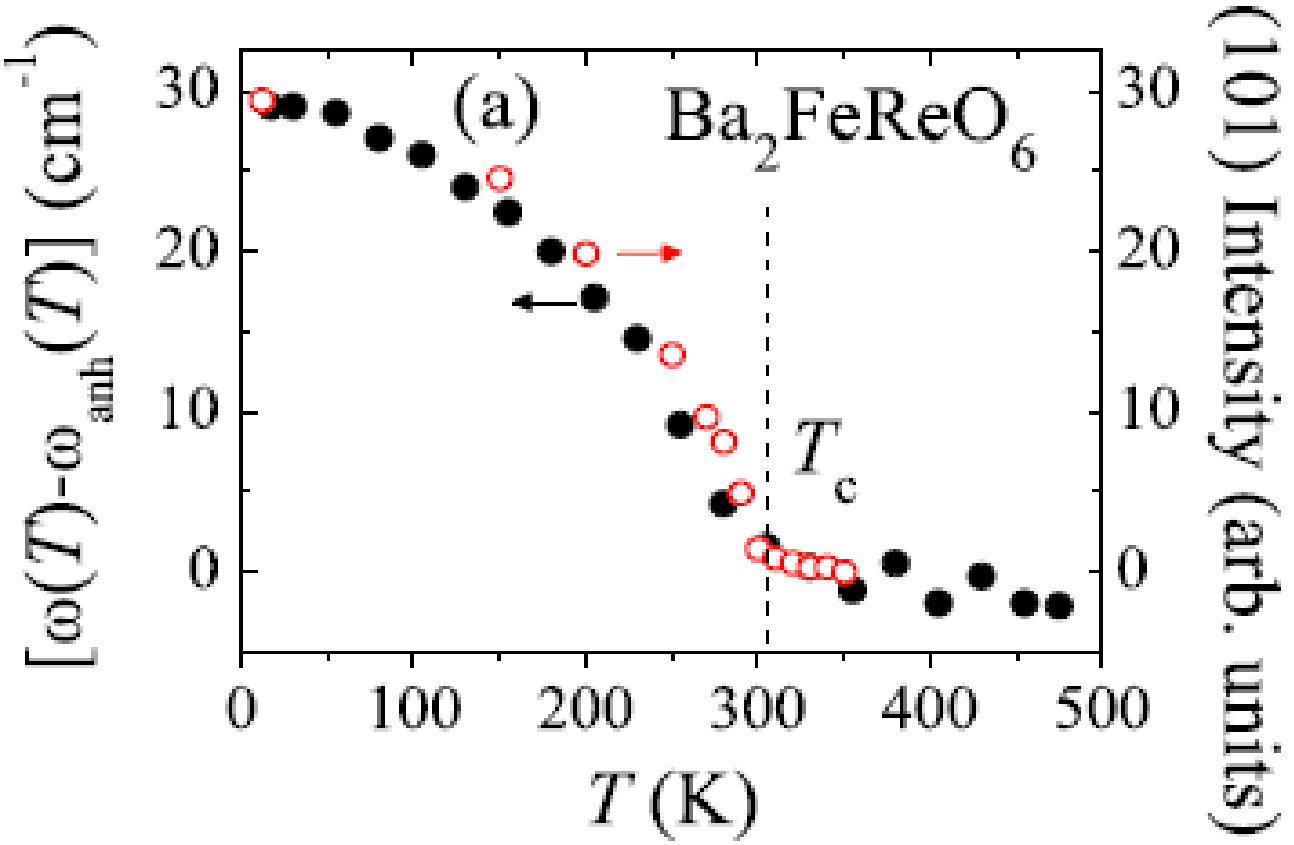
XAS, XMCD @ Oxygen K-edge





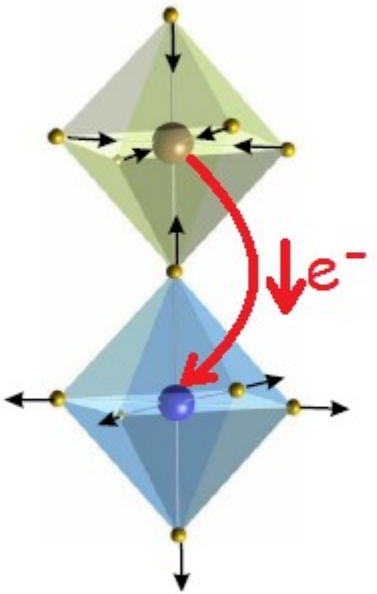
Vibrational Spectroscopy





- Signature of spin-phonon coupling → Modulation of magnetic energy by phonons.
- Conventional spin-phonon coupling mechanism (modulation of exchange integrals by phonons) does not explain why only the symmetric breathing mode couples with magnetism.

Proposed Picture



Fe^{3+}

Electronic density decreases
spin increases

Re^{5+}

Electronic density increases
spin increases

Modulation of the magnetic energy due to a fluctuation of the local atomic spin magnitude

Novel type of excitation: the **Spin-Electron-Phonon**

Conclusions

- Ba_2FeReO_6 is far from a boring metal.
- Fe valence: intermediate between Fe^{2+} and Fe^{3+}
- Orbitally active – large orbital magnetic moment, structural distortion, indicating proximity to a metal-insulator transition (as actually observed for Ca_2FeReO_6).
- Hybridizes very strongly with O 2p orbitals – leading to magnetic oxygen ions
- Magnetic energy is strongly modulated by oxygen breathing phonon mode
- Novel composite excitation – the "Spin-Electron-Phonon"

To be published:

Element-specific electronic structure and magnetism of A_2FeReO_6 (A = Ca, Ba) double perovskites: an x-ray absorption spectroscopy study

E. Granado,[1,*] J. C. Cezar,[2,3] C. Azimonte,[1] A. Rogalev,[3] F. Wilhelm,[3] J. Gopalakrishnan,[4] and K. Ramesha[4]

Already published:

PRL **108,** 177202 (2012) PHYSICAL REVIEW LETTERS week ending 27 APRIL 2012

Spin-Electron-Phonon Excitation in Re-based Half-Metallic Double Perovskites

A. F. García-Flores,[1] A. F. L. Moreira,[1] U. F. Kaneko,[1] F. M. Ardito,[1] H. Terashita,[1] M. T. D. Orlando,[2] J. Gopalakrishnan,[3] K. Ramesha,[3] and E. Granado[1]

PRL **98,** 017204 (2007) PHYSICAL REVIEW LETTERS week ending 5 JANUARY 2007

Incipient Orbital Order in Half-Metallic Ba_2FeReO_6

C. Azimonte,[1,2] J. C. Cezar,[3] E. Granado,[1,2,*] Q. Huang,[4] J. W. Lynn,[4,5] J. C. P. Campoy,[1] J. Gopalakrishnan,[5,6] and K. Ramesha[6]