



Exotic magnetism in 3d/5d ordered double perovskites

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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)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																			
1	1 H Hydrogen 1.00794	Atomic # Symbol Name Atomic Mass																	2 He Helium 4.002602																																		
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182	<table border="1"> <tr> <td>C Solid</td> <td colspan="4">Metals</td> <td colspan="3">Nonmetals</td> </tr> <tr> <td>Hg Liquid</td> <td>Alkali metals</td> <td>Alkaline earth metals</td> <td>Lanthanoids</td> <td>Actinoids</td> <td>Transition metals</td> <td>Poor metals</td> <td>Other nonmetals</td> <td>Noble gases</td> </tr> <tr> <td>H Gas</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Rf Unknown</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> </table>										C Solid	Metals				Nonmetals			Hg Liquid	Alkali metals	Alkaline earth metals	Lanthanoids	Actinoids	Transition metals	Poor metals	Other nonmetals	Noble gases	H Gas									Rf Unknown									5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
C Solid	Metals				Nonmetals																																																
Hg Liquid	Alkali metals	Alkaline earth metals	Lanthanoids	Actinoids	Transition metals	Poor metals	Other nonmetals	Noble gases																																													
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3	11 Na Sodium 22.98976928	12 Mg Magnesium 24.304											13 Al Aluminum 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948																																			
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798																																			
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.90625	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.90545	54 Xe Xenon 131.29																																			
6	55 Cs Cesium 132.90545196	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.9804	84 Po Polonium 209	85 At Astatine 209	86 Rn Radon 222																																			
7	87 Fr Francium 223	88 Ra Radium 226	89-103	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 264	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Ds Darmstadtium 271	111 Rg Roentgenium 272	112 Uub Ununbium 285	113 Uut Ununtrium 284	114 Uuq Ununquadium 284	115 Uup Ununpentium 284	116 Uuh Ununhexium 284	117 Uus Ununseptium 284	118 Uuo Ununoctium 284																																			

3d transition metals:

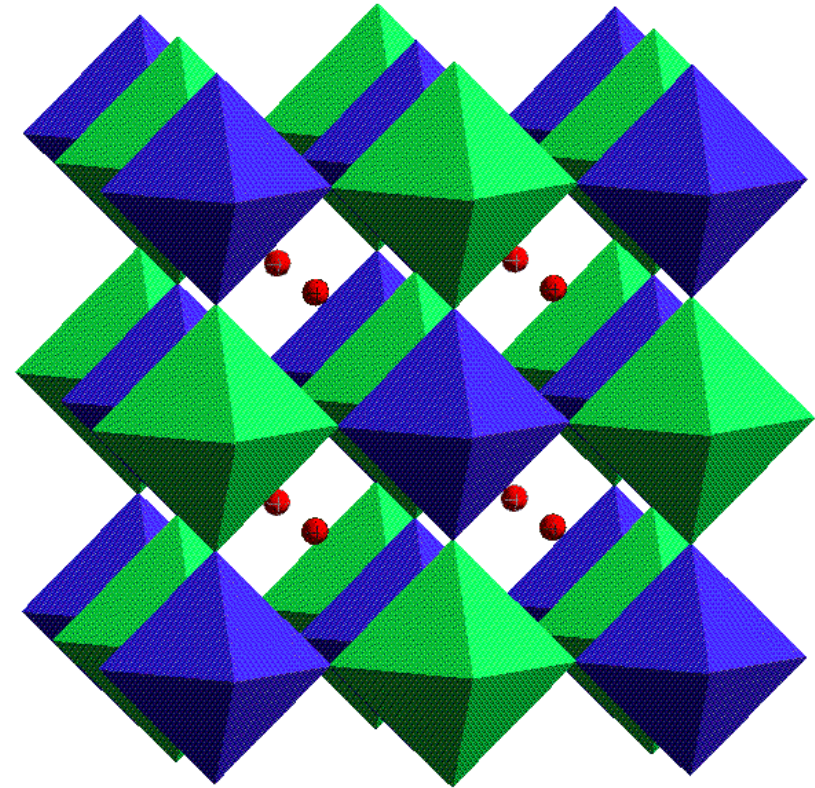
5d transition metals:

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

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

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

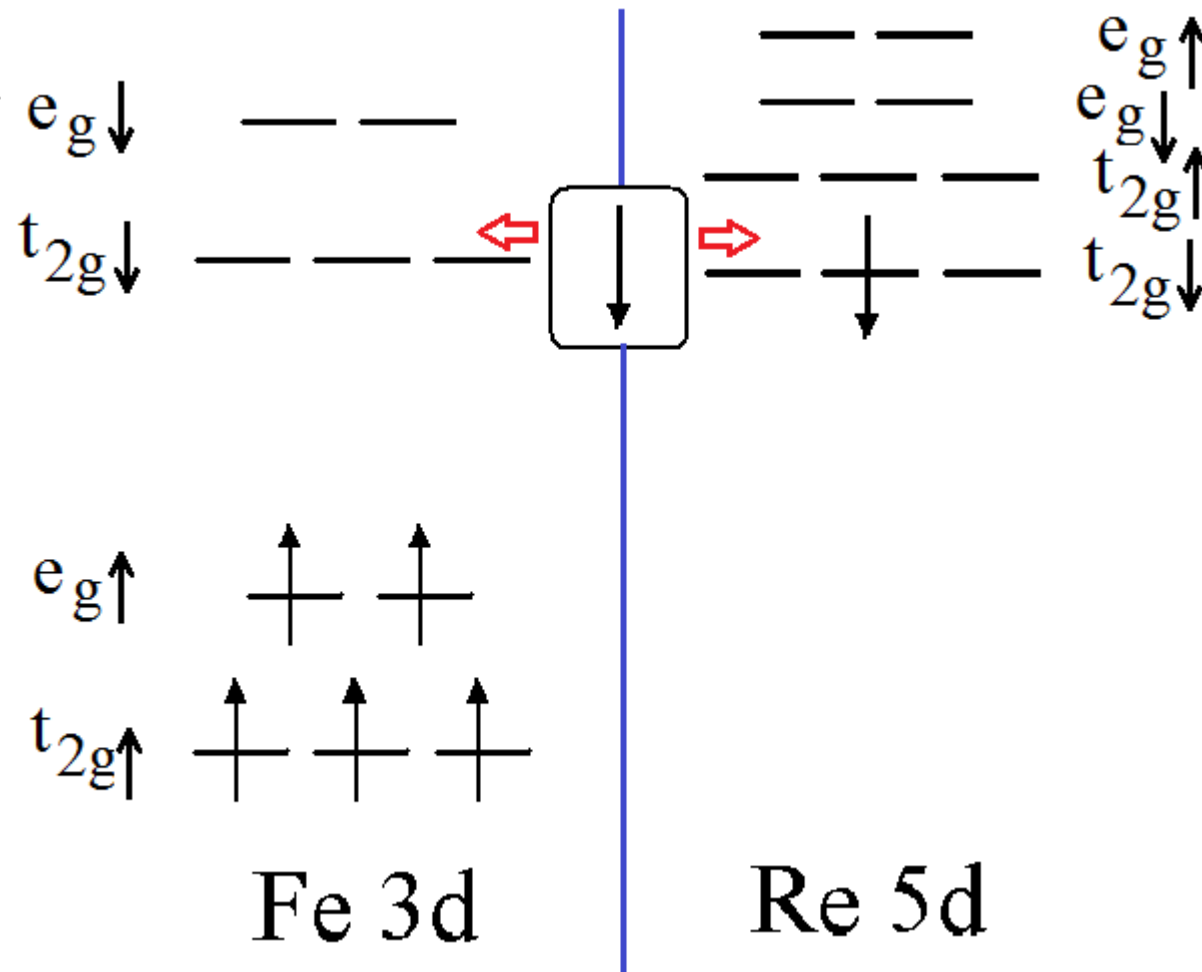
- General formula:
 $A_2BB'O_6$
 - A : "large" cation (typically rare-earths and/or alkaline-earths)
 - B, B' : "small" cations (typically transition-metals)



Stability condition:

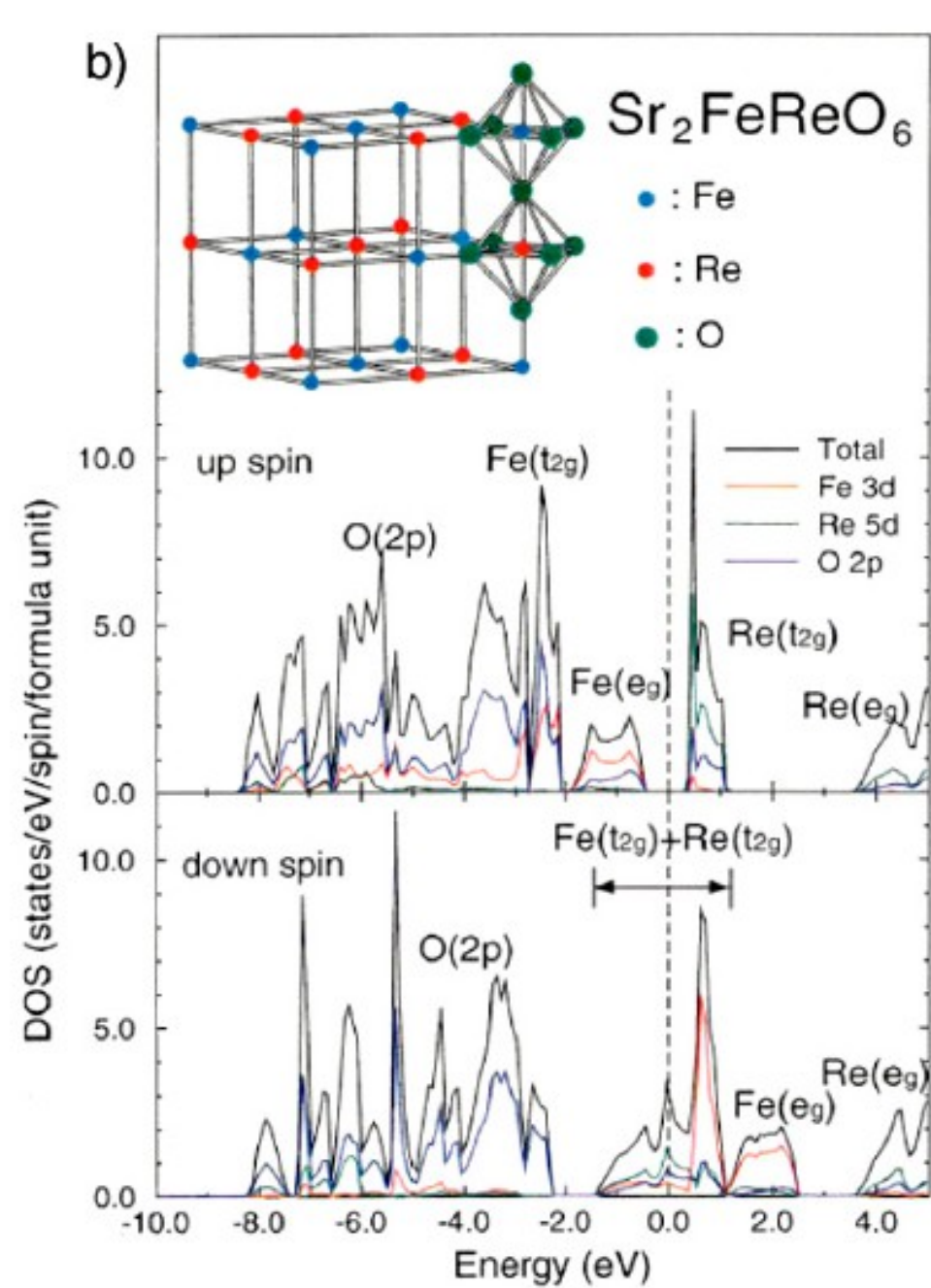
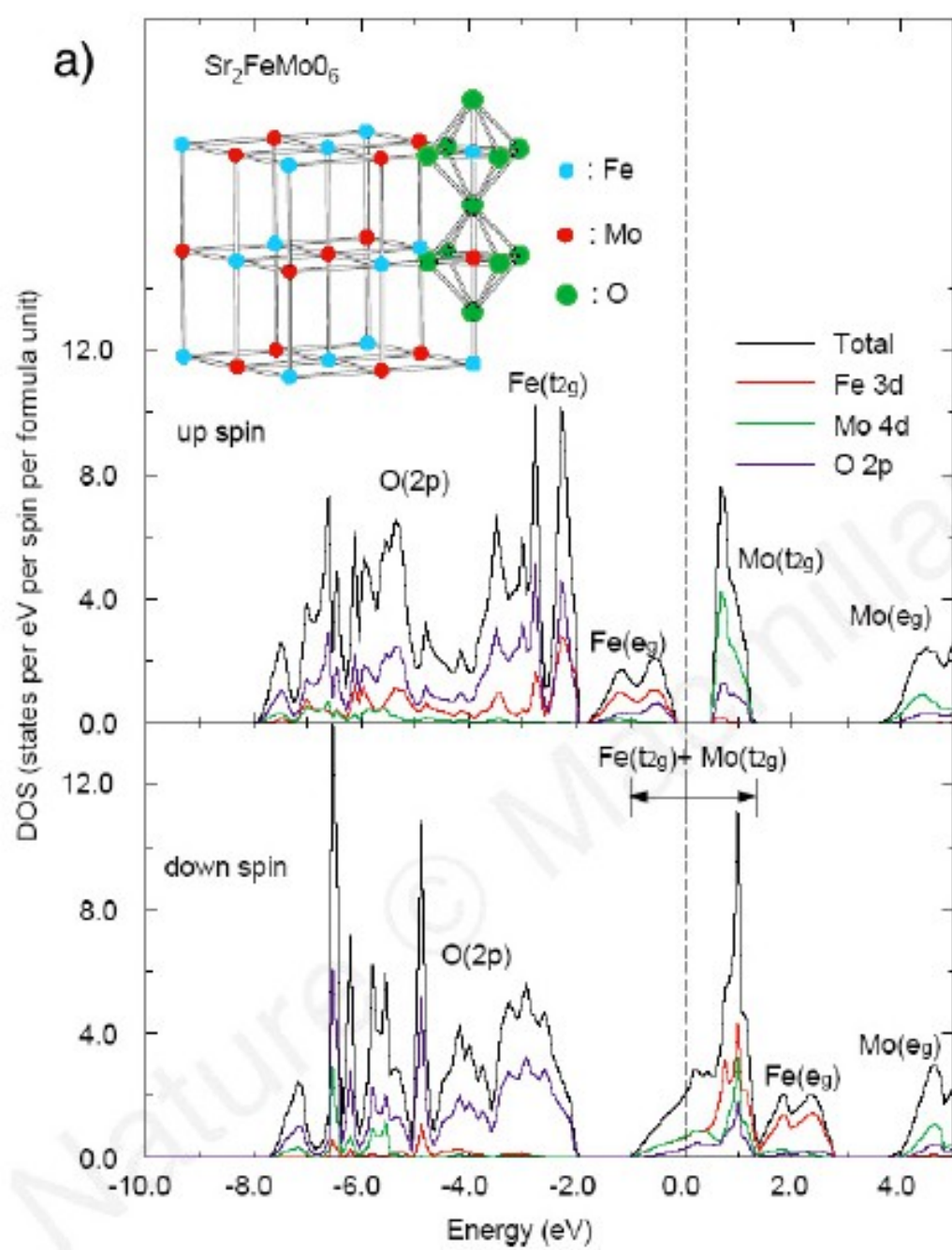
$$\langle d_{A,A'-O} \rangle \sim \sqrt{2} \langle d_{B,B'-O} \rangle$$

$A_2\text{FeReO}_6$ ($A=\text{Ba},\text{Sr},\text{Ca}$) double perovskites : Energy level scheme



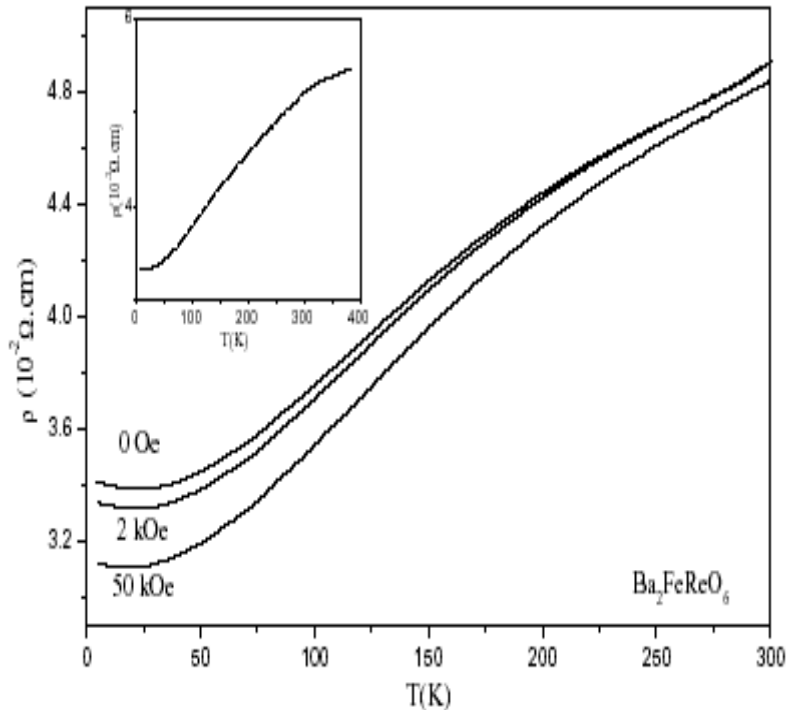
Double exchange stabilizes the half-metallic ferrimagnetic state

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

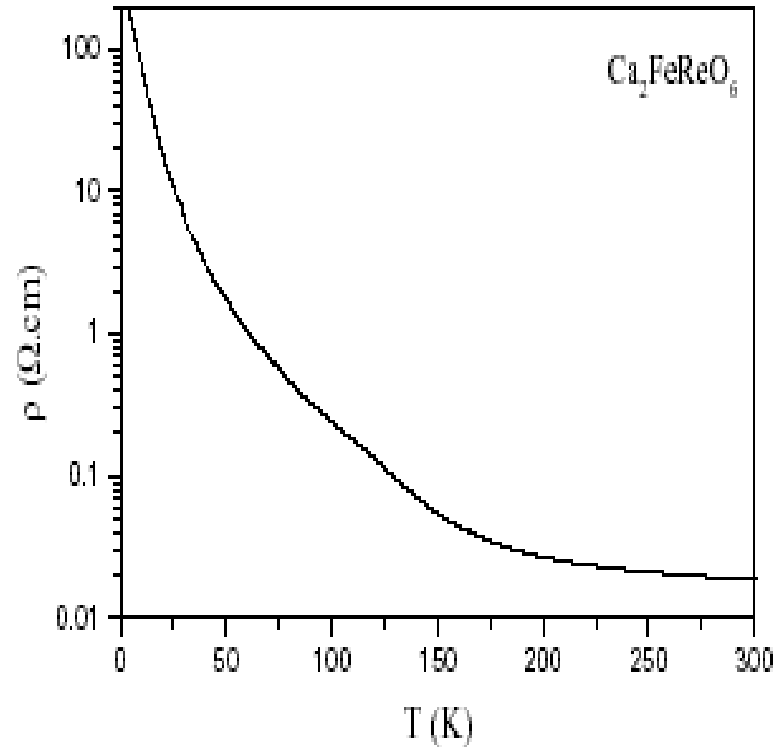


K.-I. Kobayashi *et al.*, Phys. Rev. B **59**, 11159 (1999).

Macroscopic Properties (experimental)



- Half-Metallic
- Ferrimagnetic
- $T_c = 305 \text{ K}$

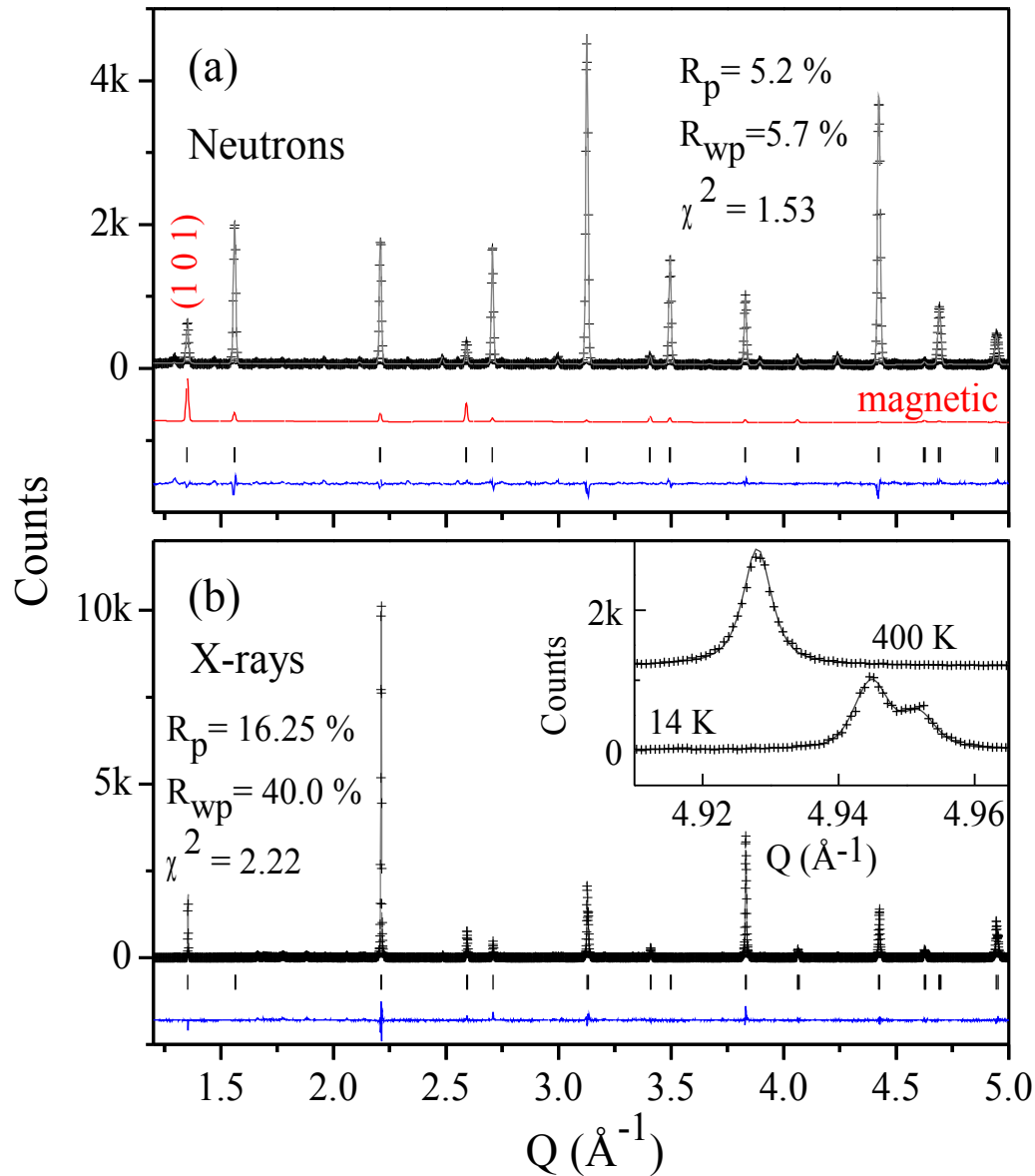


- Semiconducting
- Ferrimagnetic
- $T_c = 520 \text{ K}$

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

Crystal and magnetic structure of $\text{Ba}_2\text{FeReO}_6$:

Neutrons and Synchrotron X-Ray Powder Diffraction

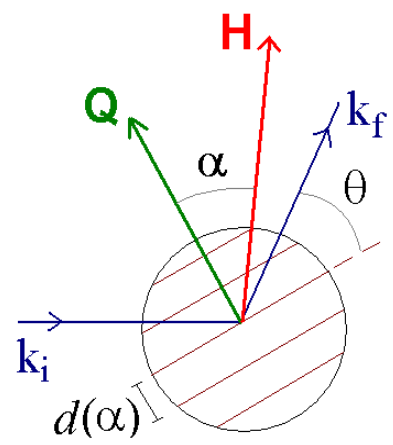
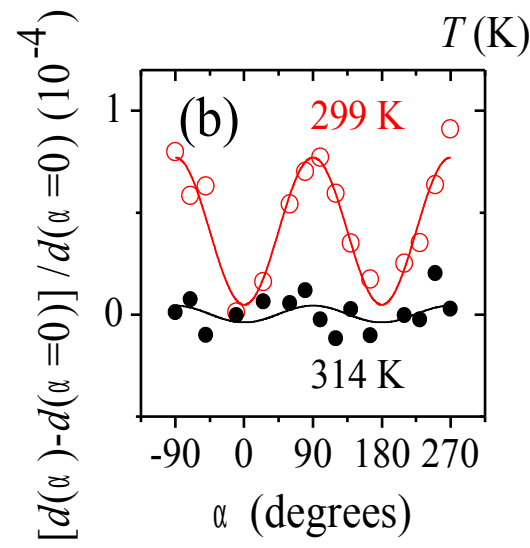
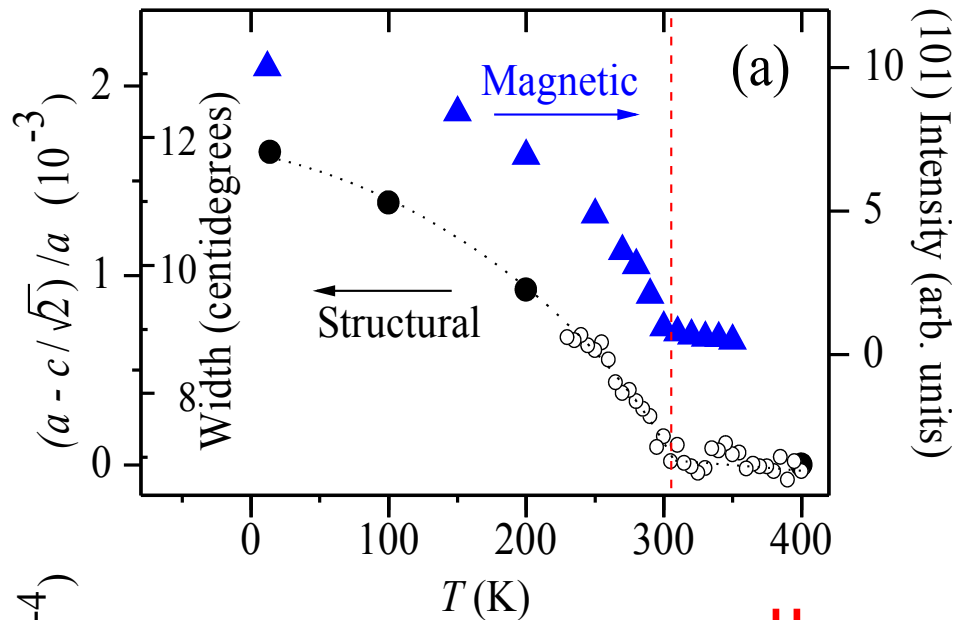


Neutron powder diffraction:

- ferrimagnetic ordering of Fe and Re spins
- $M(\text{Fe}) = 3.2(1) \mu_B$
- $M(\text{Re}) = -1.1(1) \mu_B$
- Fe/Re anti-site disorder: $\sim 4\%$
- $d_{\text{Fe-O}} = 2.077(1) \text{\AA}$
- $d_{\text{Re-O}} = 1.950(1) \text{\AA}$
- Estimated Fe valence: +2.45

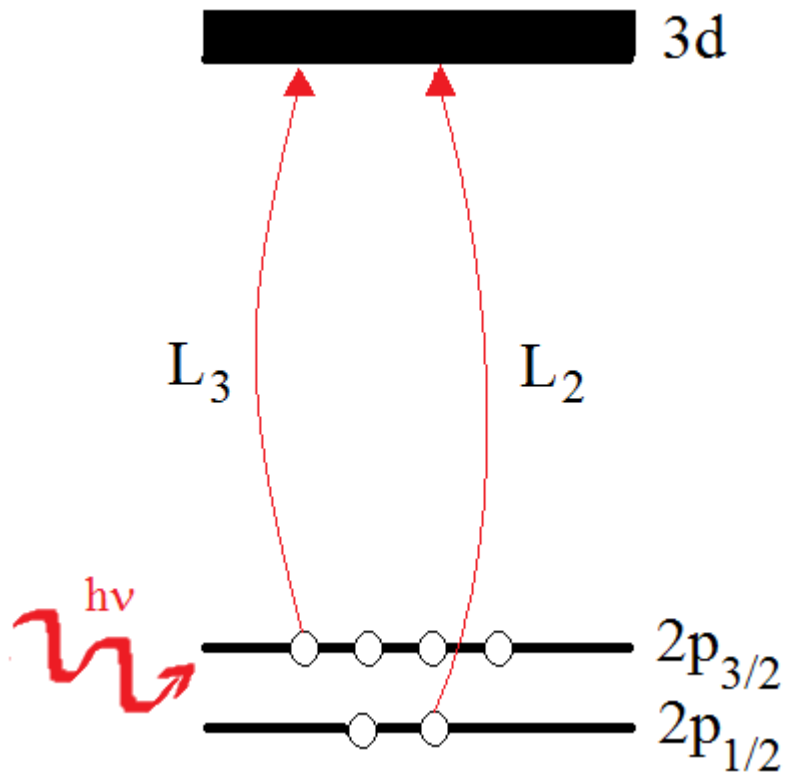
Synchrotron x-ray powder diffraction:

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

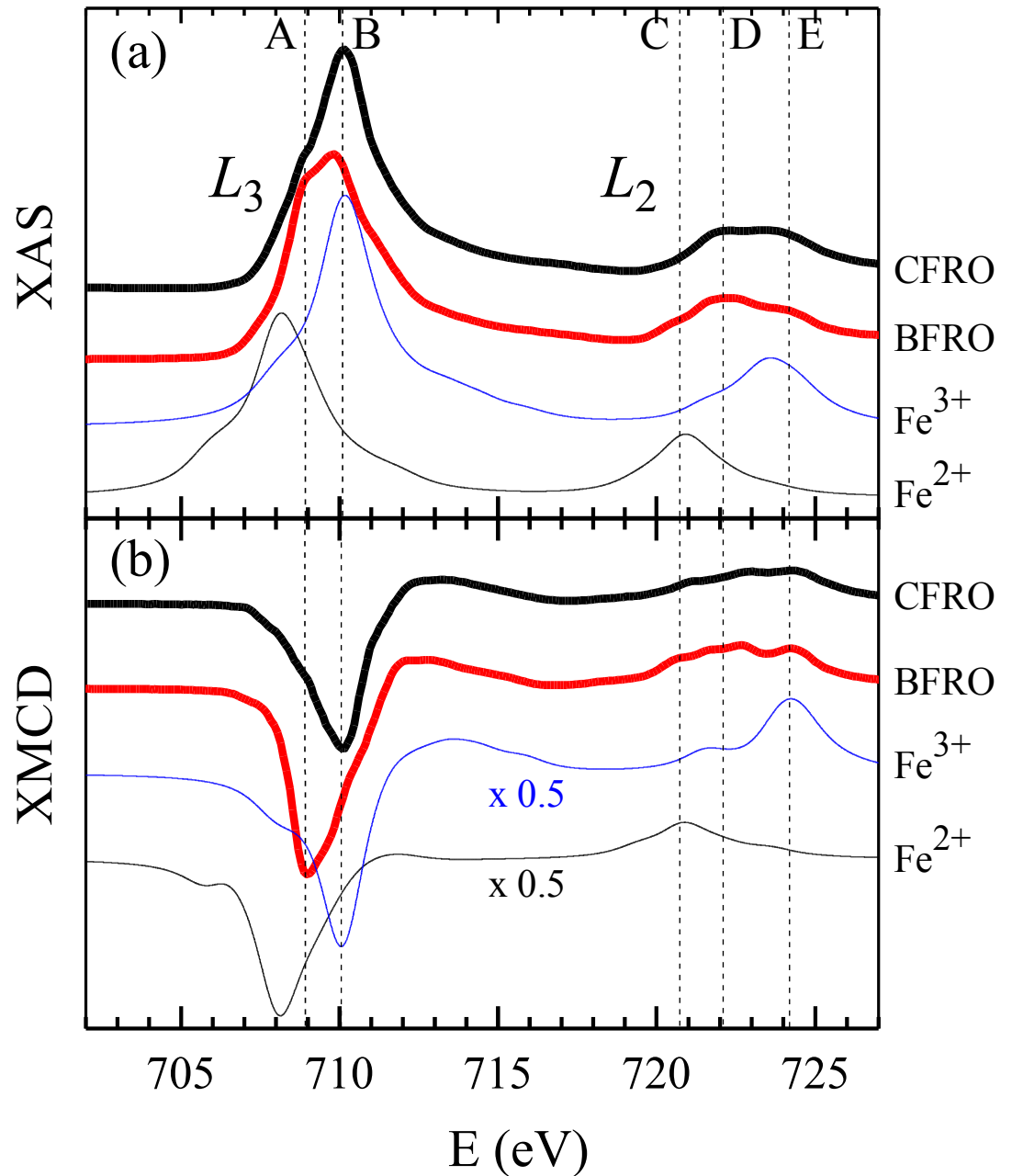


- Magnetic ordering transition at $T_c = 309$ K.
- Simultaneous structural transition at T_c .
- Interplanar distance modulated by angle α between magnetic field H and plane normal Q .

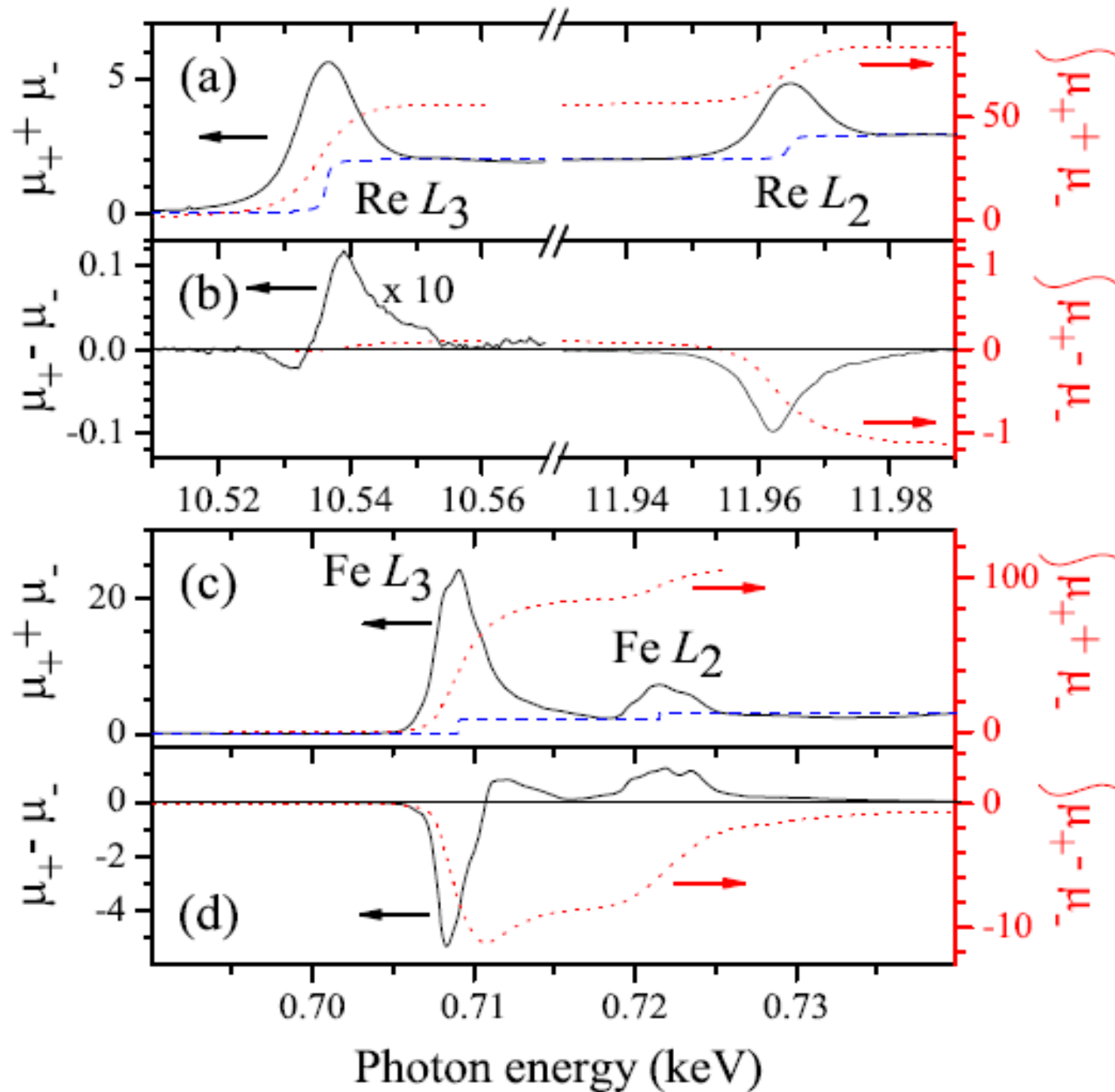
X-Ray Absorption Spectroscopy



- Ratio between A and B spectral weights for $\text{Ba}_2\text{FeReO}_6$ indicate mixed Fe^{2+} - Fe^{3+} valence, consistent with Fe-O distances obtained by Neutron PD.



X-Ray Magnetic Circular Dichroism on $\text{Ba}_2\text{FeReO}_6$



XMCD Sum Rules:

•Re:

$$M_{\text{orb}} = 0.19(1) \mu_B$$

$$M_{\text{spin}} = -0.64(4) \mu_B$$

$$M_{\text{orb}} / M_{\text{spin}} = -0.294$$

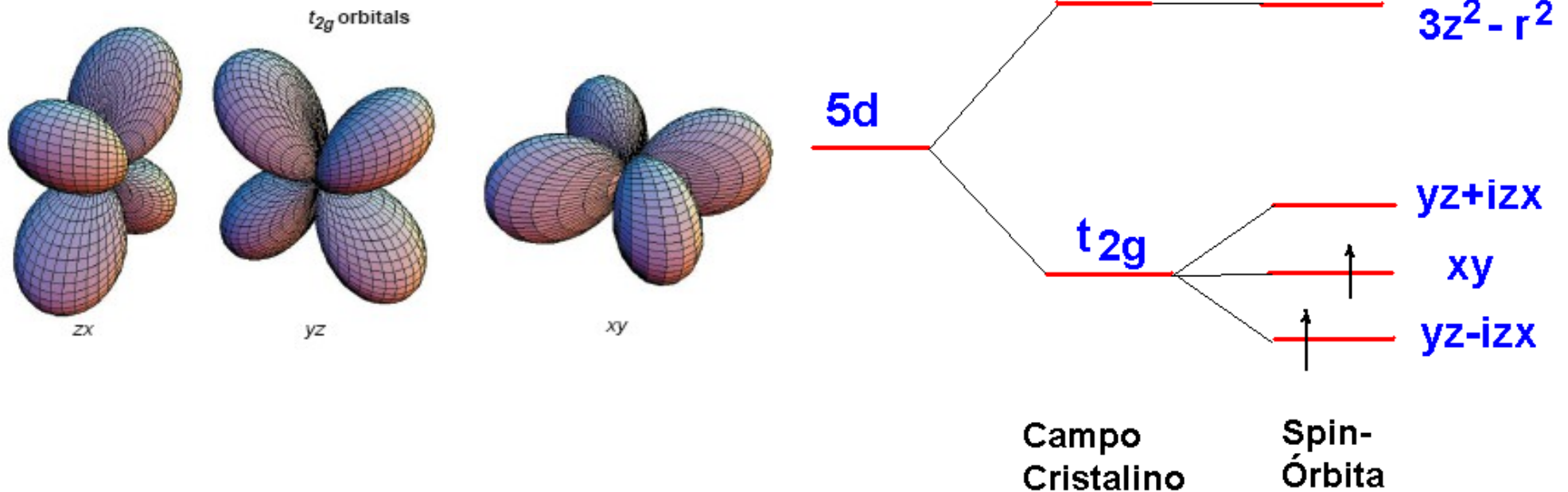
Fe:

$$M_{\text{orb}} = 0.04(2) \mu_B$$

$$M_{\text{spin}} = 2.8(2) \mu_B$$

$$M_{\text{orb}} / M_{\text{spin}} = 0.013$$

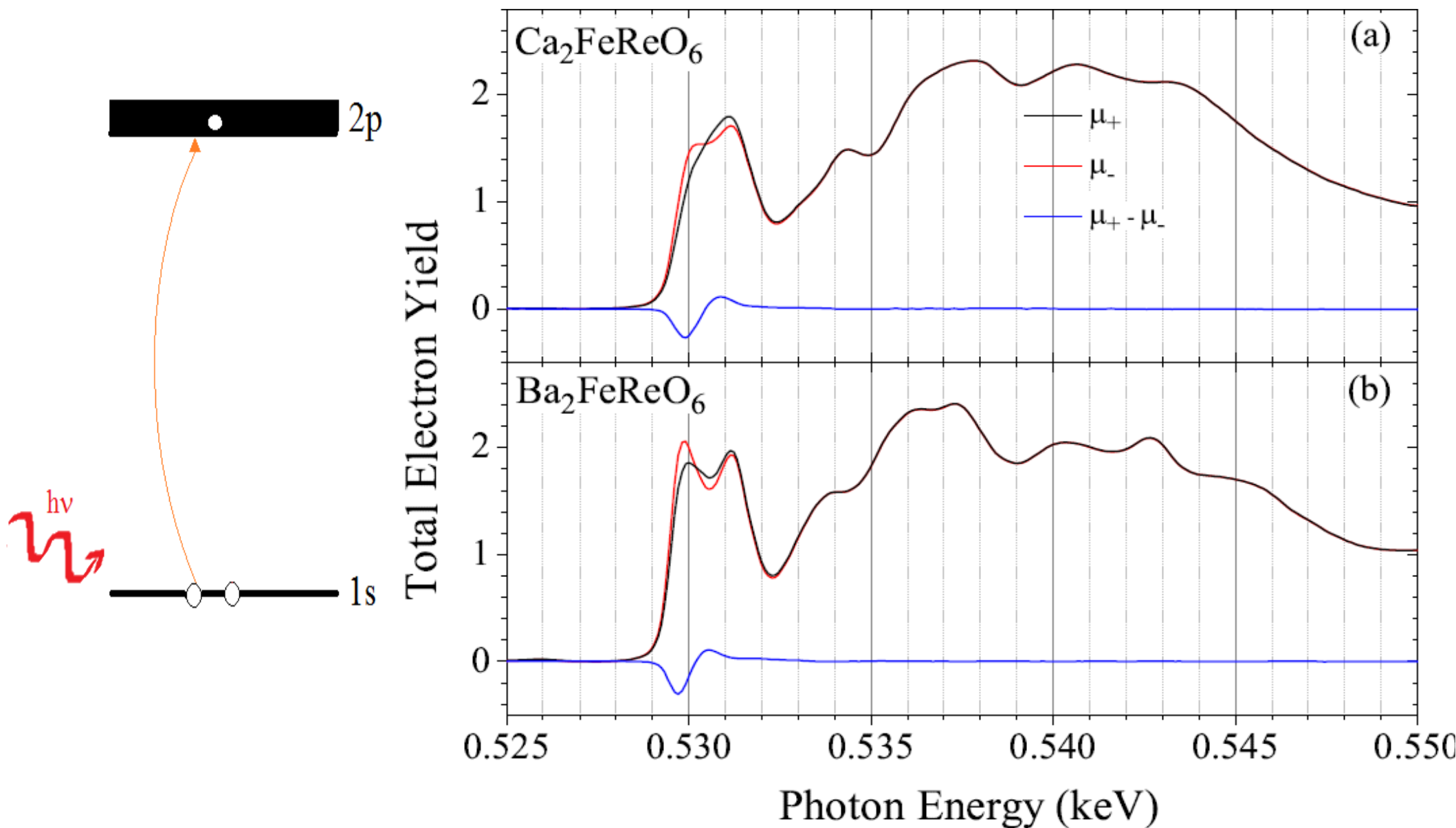
- Giant orbital magnetic moment (unquenched) for Re. **Ratio $M_{orb}/M_{spin} = -0.294$ comparable to atomistic values.**
- Reason: For 5d ions, the spin-orbit coupling is a stronger interaction than for the 3d ions, and can be of the order of electron-volts.
- Unquenched orbital moments for Re 5d electrons



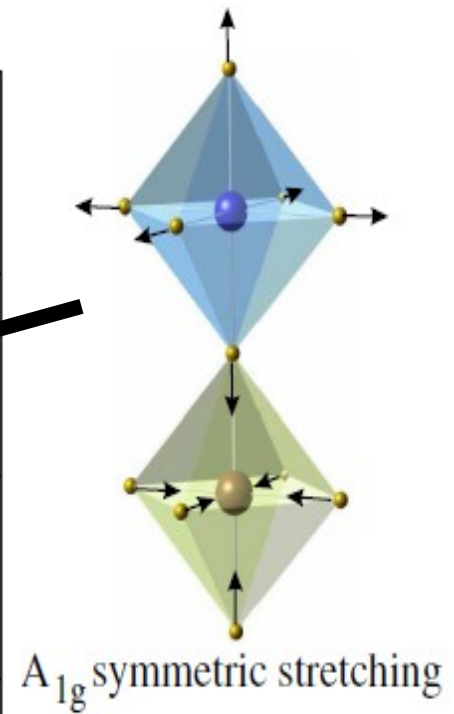
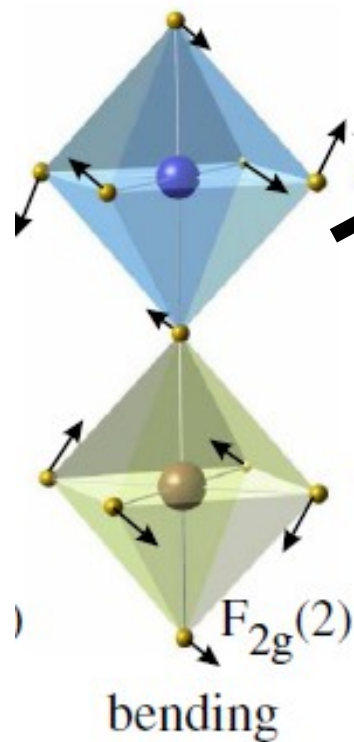
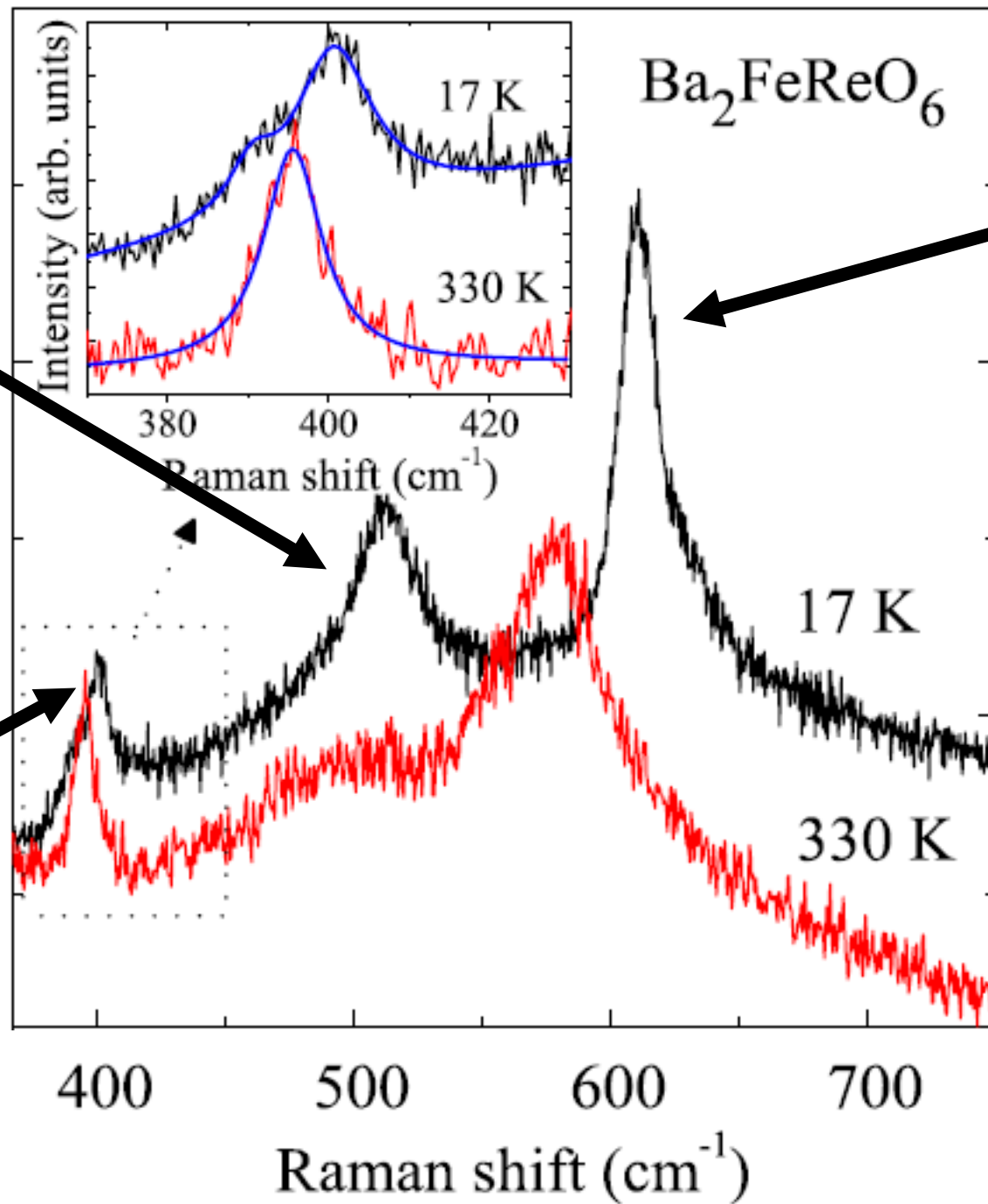
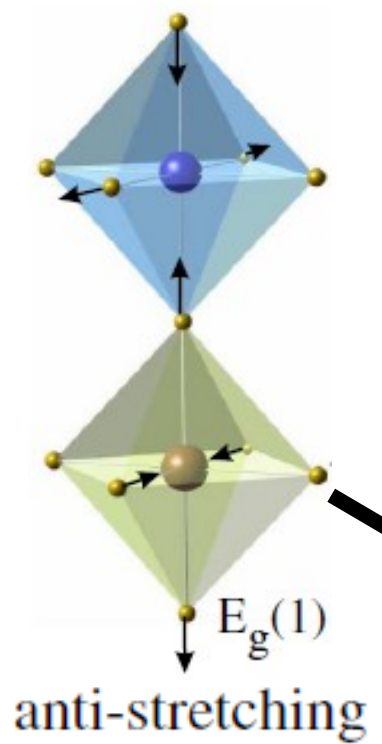
Not a normal metal: **orbitally polarized metal through spin-orbit coupling!**

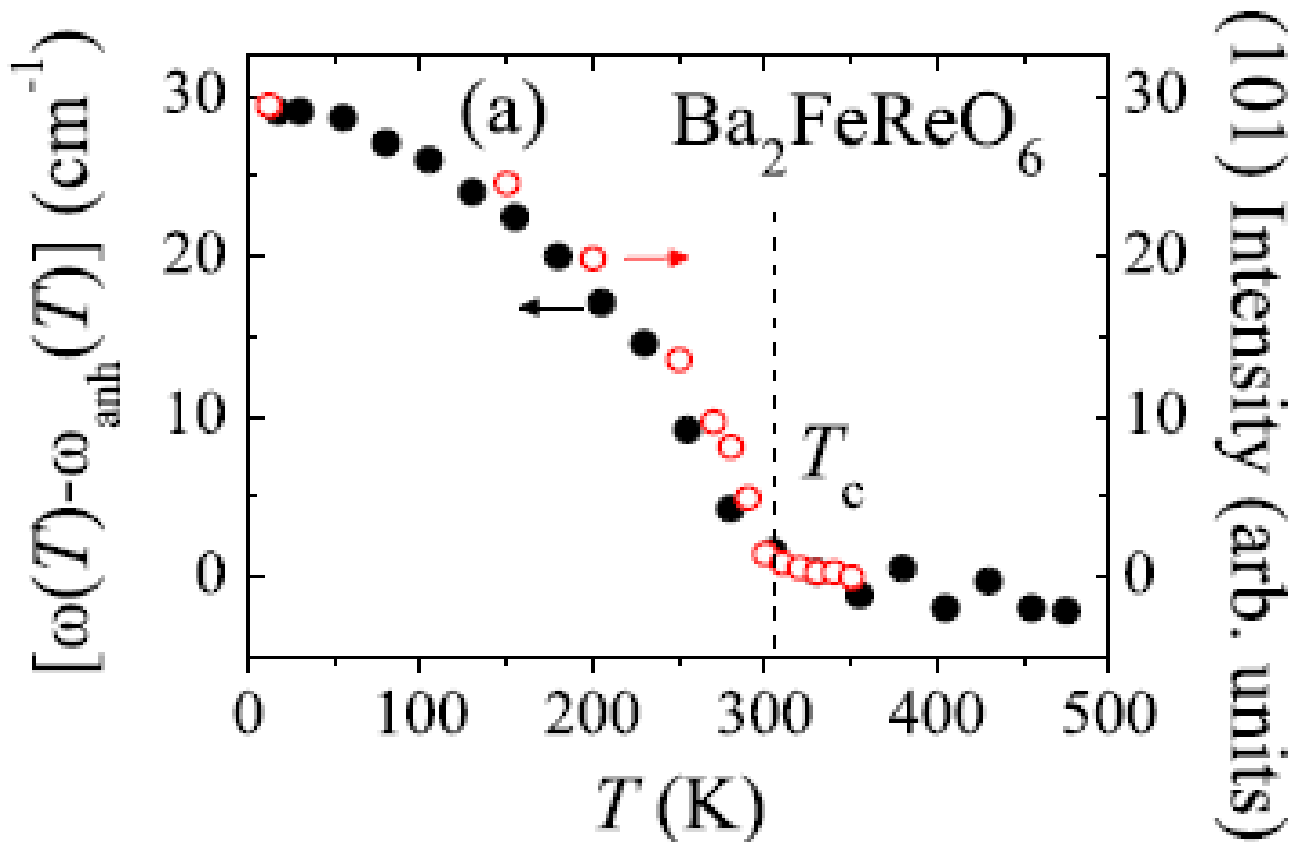
Large Re orbital moment + Large Re-O hybridization = Magnetic Oxygen ?

XAS, XMCD @ Oxygen K-edge



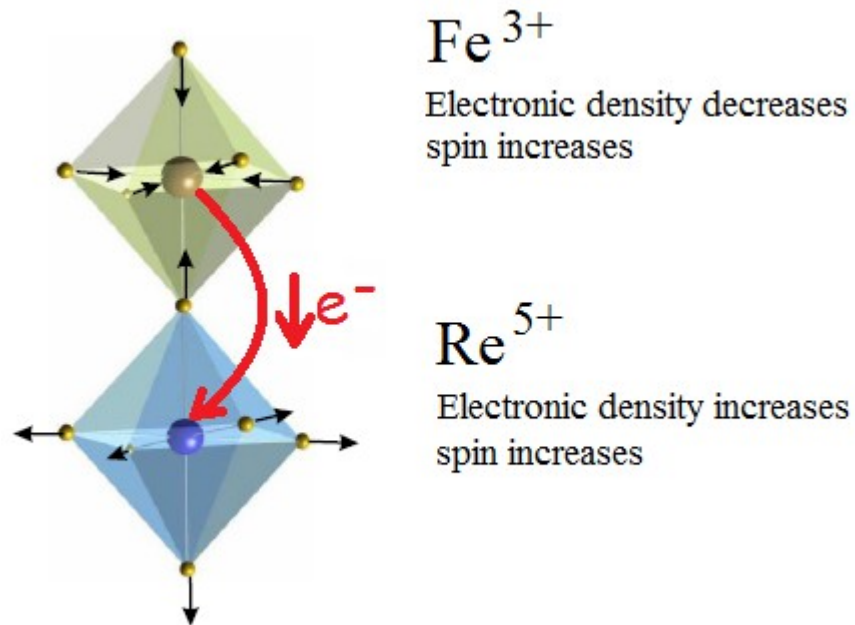
Vibrational Spectroscopy





- 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



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

Novel type of excitation: the Spin-Electron-Phonon

Conclusions

- $\text{Ba}_2\text{FeReO}_6$ 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 $\text{Ca}_2\text{FeReO}_6$).
- 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 $A_2\text{FeReO}_6$ ($A = \text{Ca}, \text{Ba}$)
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. Ramesha⁴

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. Granado¹

PRL **98**, 017204 (2007)

PHYSICAL REVIEW LETTERS

week ending
5 JANUARY 2007

Incipient Orbital Order in Half-Metallic $\text{Ba}_2\text{FeReO}_6$

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. Ramesha⁶