Orbitally Driven Spin-Singlet Dimerization in S=1 $La_4Ru_2O_{10}$

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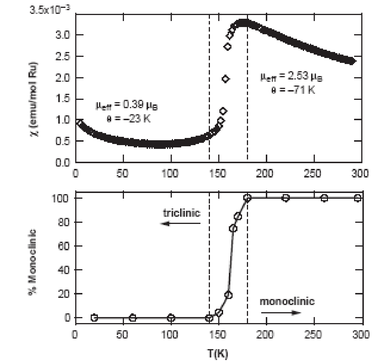
Abstract

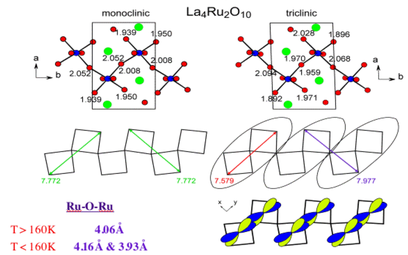
Using x-ray absorption spectroscopy at the Ru-$L_{2,3}$ edge, we reveal that across the rare 4*d*-orbital ordering transition and spin-gap formation in $La_4Ru_2O_{10}$ [1] the Ru^{4+} ions remain in the S=1 spin state [2]. We find using local-spin-density approximation + Hubbard U band structure calculations that the crystal fields in the low-temperature phase are not strong enough to stabilize the S=0 state. Instead, we identify a distinct orbital ordering with a significant anisotropy of the antiferromagnetic exchange couplings. We conclude that $La_4Ru_2O_{10}$ appears to be a novel material in which the orbital physics drives the formation of spin-singlet dimers in a quasi-two-dimensional S=1 system [2].

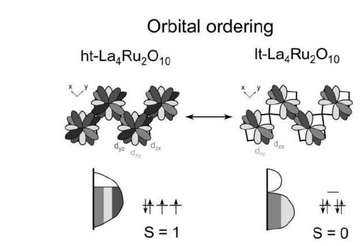
[1] P. Khalifah *et al.*, Science **297**, 2237 (2002).
[2] Hua Wu *et al.*, Phys. Rev. Lett. **96**, 256402 (2006).

Motivation

$La_4Ru_2O_{10}$: a rare example of orbital odering in 4d transition-metal oxides (P. Khalifah, *et al.*, Science 2002)



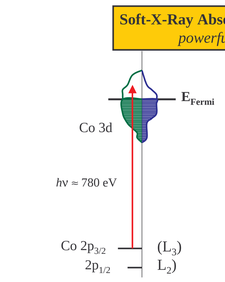




The observable consequence of full orbital-ordering transition: Loss of the Ru local moment, structural distortion etc.

x-ray absorption spectroscopy (XAS)

Soft-X-Ray Absorption: *powerful in combination with theory*



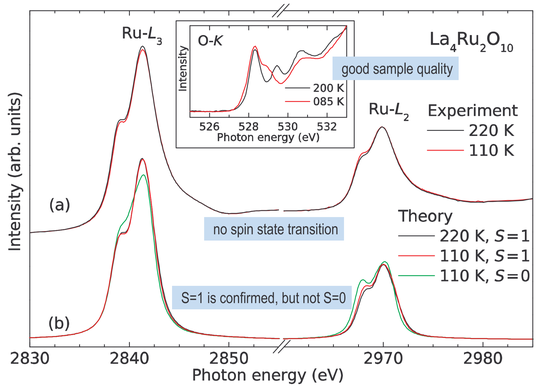
- use of core levels → local transitions → element and site specific
- involves most relevant orbitals: TM *2p-3d(4d)* According to dipole selection rule
- Multiplet structure is extremely sensitive to initial state: charge, spin and orbital

Spectrum $(h\nu) = \Sigma_f |\langle i|e.r|f\rangle|^2 \delta(h\nu - E_f + E_i)$

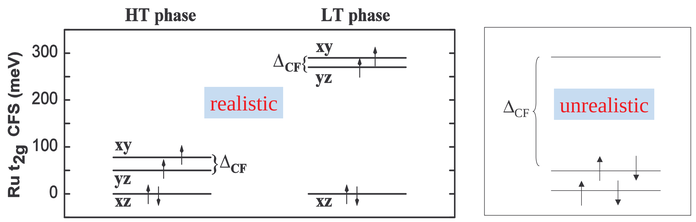
$|i\rangle$ = initial state, $|f\rangle$ = final state
e.r = dipole transition

Theory:
TM 2p-3d(4d): Cluster calculations with full atomic multiplet theory including TM-O covalency

Example: cobaltates
- determination of spin state
- XAS more reliable than neutrons, or magnetic susceptibility experiments



Ru^{4+} t_{2g} crystal-field splitting: LDA

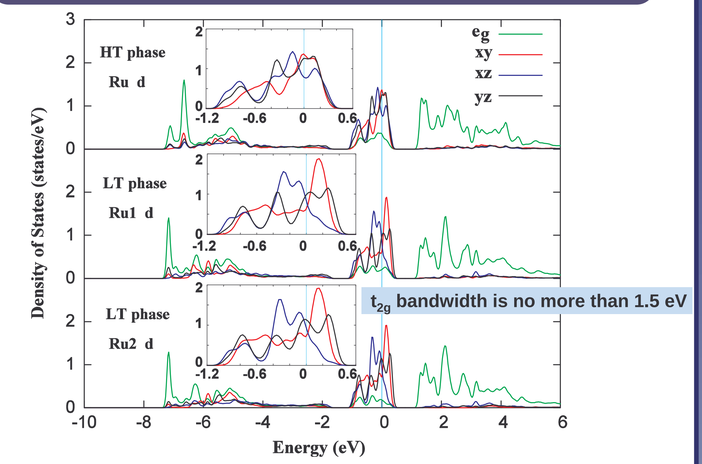


S=1: $E_{gain} = -3J_H$

S=0: $-2J_H - \Delta_{CF}$

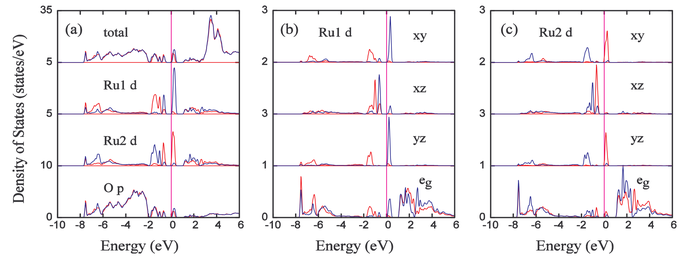
Actually, $\Delta_{CF} < 0.05$ eV, $J_H \sim 0.5$ eV. **S=1 is stable !**

LDA density of states in the nonmagnetic state



t_{2g} bandwidth is no more than 1.5 eV

LDA+U density of states in the AF-magnetic state



Small-gap insulator

Ru1: $xz^{\uparrow\downarrow}$ $yz^{\uparrow}$ $xy^{\uparrow}$

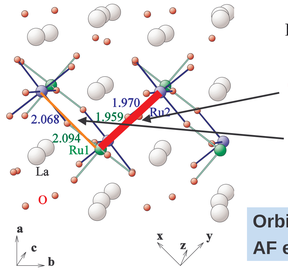
Ru2: $xz^{\downarrow\uparrow}$ $yz^{\downarrow}$ $xy^{\downarrow}$

Anti-ferro along x/y/z/

Ru1 xz / Ru2 xz orbital ordering

S=0: unstable by 390 meV/Ru

Orbitally driven spin-singlet dimerization



Ru^{4+} S=1, $xz^{\uparrow\downarrow}$ $yz^{\uparrow}$ $xy^{\uparrow}$

J_y= 65 meV

J_x=2 meV

J_z=5 meV

Orbital Ordering yields significantly anisotropic AF exchange couplings.

Conclusion: **$La_4Ru_2O_{10}$ is a novel two-dimensional S=1 system due to the occurrence of the spin-singlet dimerization, which is largely driven by the unusual orbital ordering of the 4d transition-metal ions.**