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Metal-insulator transition in A-site ordered perovskite oxides $ACu_3Fe_4O_{12}$

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We study metal-insulator transition (MIT) in $ACu_3Fe_4O_{12}$ (A=Ca, La, Pr-Nd, Sm-Lu) using local density approximation (LDA) + *U* and dynamical mean-field theory (DMFT). We find that $ACu_3Fe_4O_{12}$ systems possess two instabilities towards MIT: Peierls-type instability (A=Ca) and antiferromagnetic instability (A=La, Pr-Nd). The dominant instability can be controlled by electron doping, i.e. substitution of A-site element with different valence ions. The spin correlation function calculated by LDA+DMFT finds characteristic spin dynamics: in $CaCu_3Fe_4O_{12}$, a dynamical screening of the Fe eg-spins occurs in an antiferromagnetic coupling to ligand (O) holes. In $LaCu_3Fe_4O_{12}$, on the other hand, the ligand hole couples to the Cu S=1/2 spin exclusively, forming the Zhang-Rice singlet bound state on the CuO_4 unit. We also discuss the different magnetic ordering in $LaCu_3Fe_4O_{12}$ (antiferro) and $LuCu_3Fe_4O_{12}$ (ferro) in terms of the internal pressure and electronic structure.

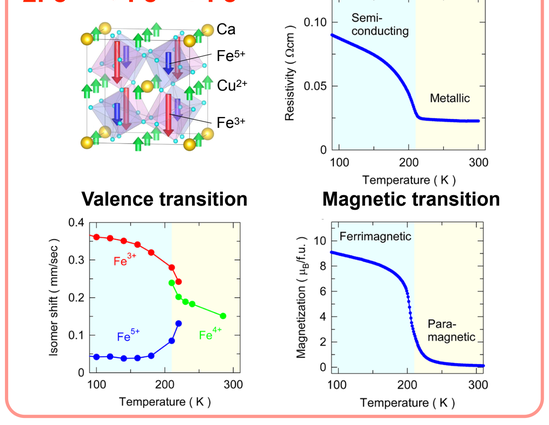
Introduction: $ACu_3Fe_4O_{12}$

Y. Shimakawa J. Phys. D: Appl. Phys. **49** 119601 (2016)
I. Yamada et al., Inorg. Chem. **52** 13751 (2013)

Charge disproportionation (CD) vs Charge transfer (CT) MIT

$CaCu_3Fe_4O_{12}$: CD-type

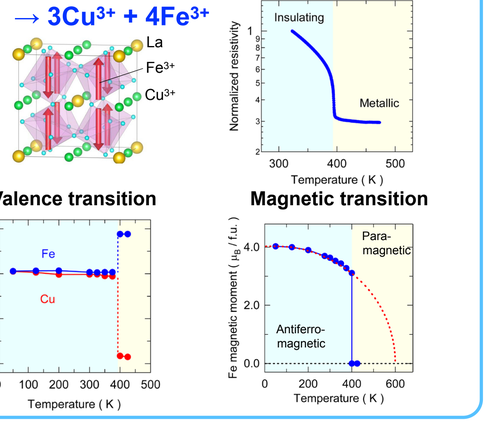
$2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$



VS

$LaCu_3Fe_4O_{12}$: CT-type

$3Cu^{2+} + 4Fe^{3.75+} \rightarrow 3Cu^{3+} + 4Fe^{3+}$



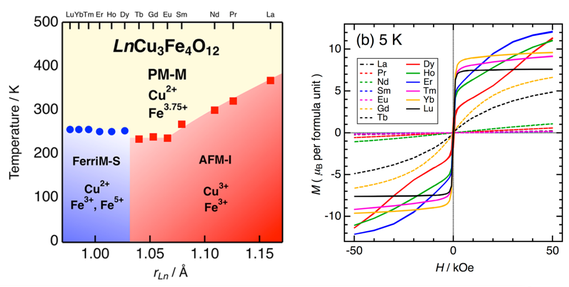
Magnetic order in $Ln^{3+}Cu_3Fe_4O_{12}$

Dy-Lu: Ferrimagnetic (FM)

$8Fe^{3.75+} \rightarrow 5Fe^{3+} + 3Fe^{5+}$

La, Pr-Nd, Sm-Tb: Antiferromagnetic (AF)

$3Cu^{2+} + 4Fe^{3.75+} \rightarrow 3Cu^{3+} + 4Fe^{3+}$



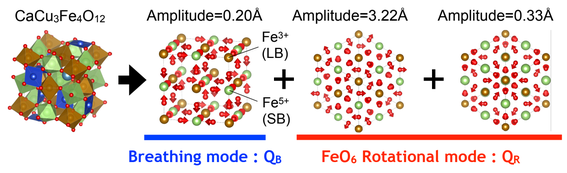
Questions

- The origin of MIT in $CaCu_3Fe_4O_{12}$ with CD / $LaCu_3Fe_4O_{12}$ with CT
- Different magnetic order in $LaCu_3Fe_4O_{12}$ (AF) and $LuCu_3Fe_4O_{12}$ (FM)

Method: LDA + *U*, LDA + DMFT

Mode decomposition

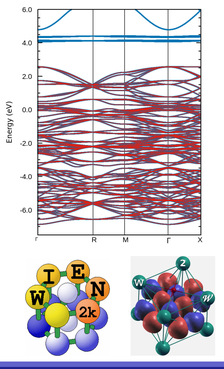
bilbao crystallographic server



Local density approximation (LDA) + *U*

- Band/energy calculation, structure optimization
- Include Coulomb interaction as static mean-field
- Using WIEN2k implementation

LDA + Dynamical mean-field theory (DMFT)

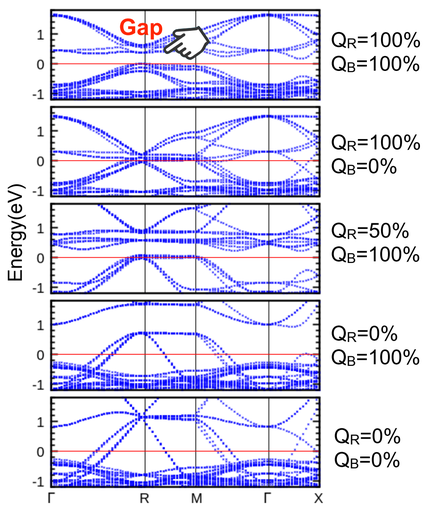


- Cu 3*d*, Fe 3*d* and O 2*p* bands included (71 bands)
- Calculate physical quantities
  - Density of states (DOS)
  - Spin correlation function

$$\chi_{\mathrm{Spin}}(\tau) = < S_z(\tau) S_z(0) >$$

Result: $CaCu_3Fe_4O_{12}$

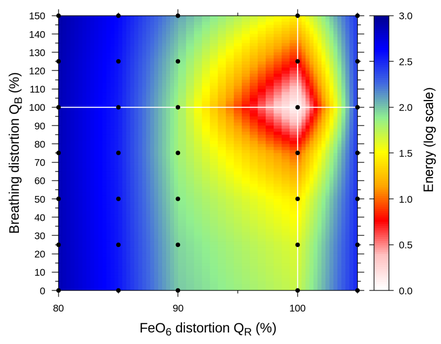
LDA + *U* bands



Peierls-type instability to MIT

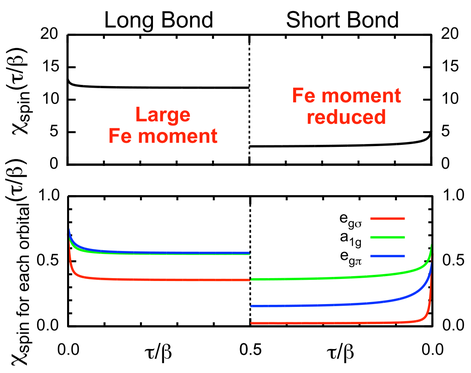
Structural distortion (FeO_6 rotation Q_R) softens the Fe-O bond breathing distortion Q_B

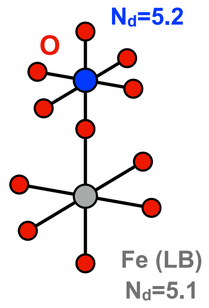
LDA+*U* energy: Q_R vs Q_B distortion



- Energy minimum at $Q_R = Q_B = 100\%$ (experimental structure)
- Q_B opens the charge gap
- Q_R reduces the band width, locating the band crossing @ R point to Fermi level E_F

LDA+DMFT spin correlation function @ Fe site

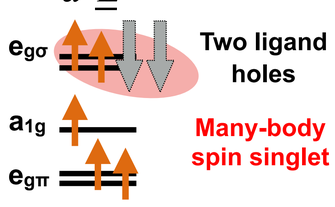




Fe-site and -orbital selective spin screening

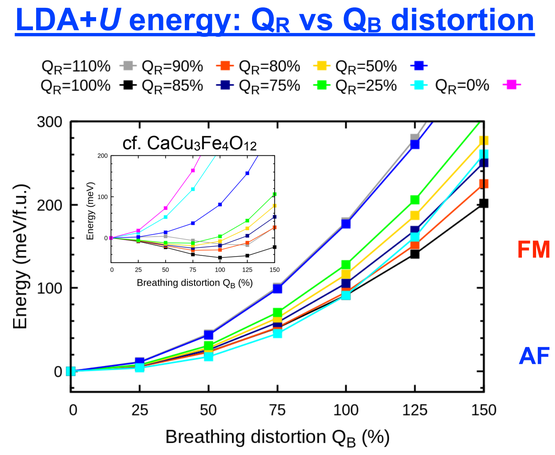
Fe e_g electrons form a spin singlet with two ligand holes

$d^5\underline{L}^2$



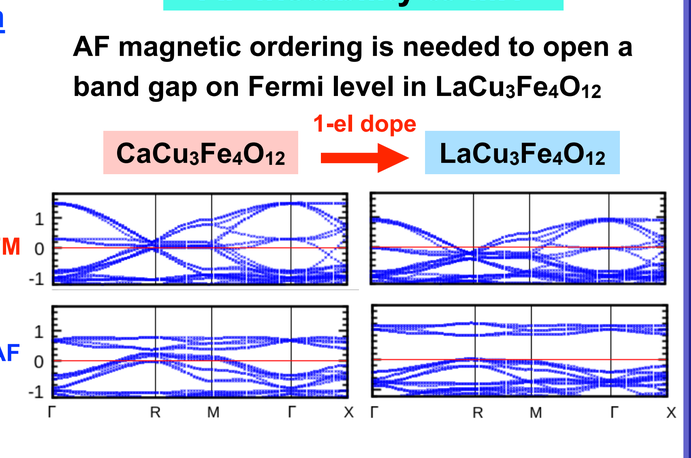
Result: $LaCu_3Fe_4O_{12}$

LDA+*U* energy: Q_R vs Q_B distortion



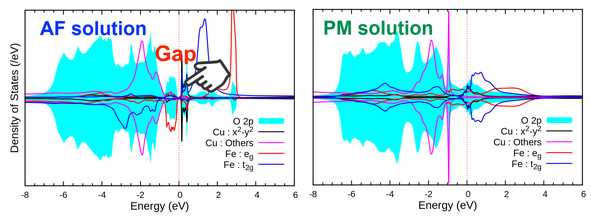
AF instability to MIT

AF magnetic ordering is needed to open a band gap on Fermi level in $LaCu_3Fe_4O_{12}$



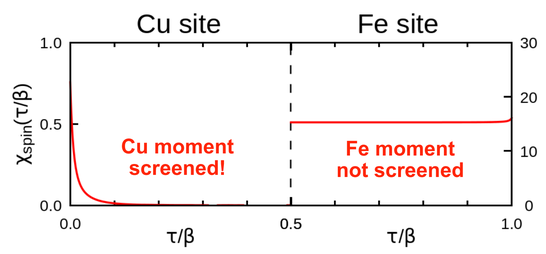
LDA + DMFT DOS

(U,J)=(7.5eV,0.98eV) for Cu 3d and (6.80eV, 0.80eV) for Fe 3d electrons

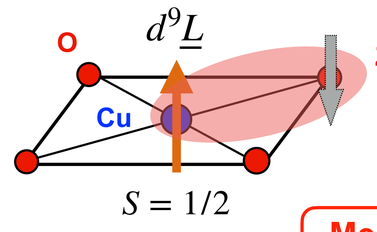


- Breathing distortion is always unstable
  - Band cross @ R-point in FM is below E_F
  - ⇒ No energy gain by the Peierls mechanism
- AF solution shows a gap @ R-point

LDA+DMFT spin correlation function



Cu-O Zhang-Rice singlet state on CuO_4 unit

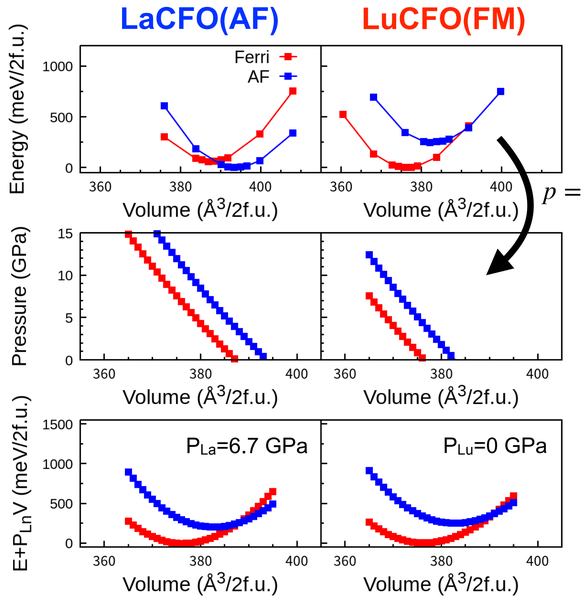


Messages

- **The origins of MIT:**
  $CaCu_3Fe_4O_{12}$: Peierls-type instability / $LaCu_3Fe_4O_{12}$: AF-ordering instability
  Important !! : two instabilities switched by 1 electron doping (i.e. $Ca^{2+} \rightarrow La^{3+}$)
- **The spin properties:**
  $CaCu_3Fe_4O_{12}$: Fe e_g-O spin singlet / $LaCu_3Fe_4O_{12}$: Cu-O Zhang-Rice singlet

Result: $LnCu_3Fe_4O_{12}$ (Ln^{3+}=La, Lu)

LDA + *U*: Volume optimization



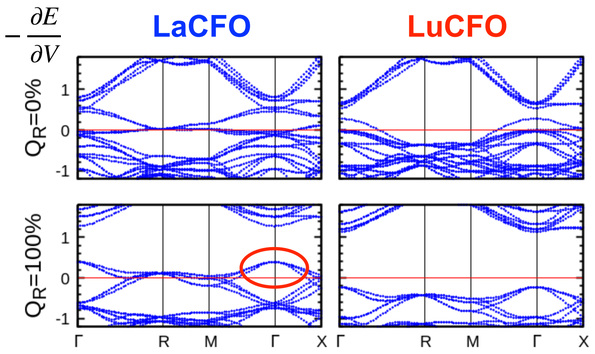
$$p = -\frac{\partial E}{\partial V}$$

- Optimized energy reproduces correct magnetic ordering for two materials
- The difference of internal pressure is 6.7GPa
- LaCFO's E-V curve mapped to LuCFO's one by adding $P_{La}V$ term

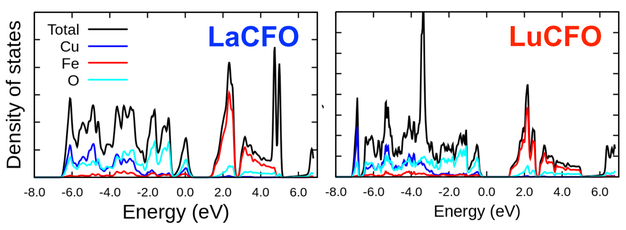
Band gap on E_F at Γ-point

LDA+*U* shows difference in electronic structure between two compounds

LDA + *U* bands: FM solution



LDA + *U* DOS: FM solution (Q_R=100%)



Messages

- **$LaCu_3Fe_4O_{12}$ can be seen as $LuCu_3Fe_4O_{12}$ under the specific pressure (6.7GPa)**
- **Closing gap in FM solution may be responsible for the transition**

Acknowledgement

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