Role of the Octahedra Rotation on the Electronic Structures of 4*d* Transition Metal Oxides

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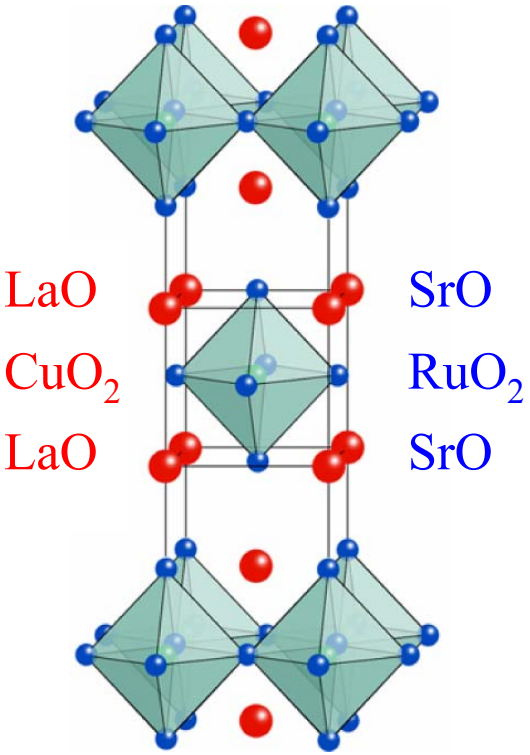
Outline

- Background - $(Sr,Ca)_2RuO_4$
- ARPES data from Sr_2RhO_4 – Missing d_{xy} Fermi Surface
- Comparison with Band Calculation
- Implication to $(Sr,Ca)_2RuO_4$
- $(Sr,Ba)_2RhO_4$ - Band Structure Manipulation
- Summary

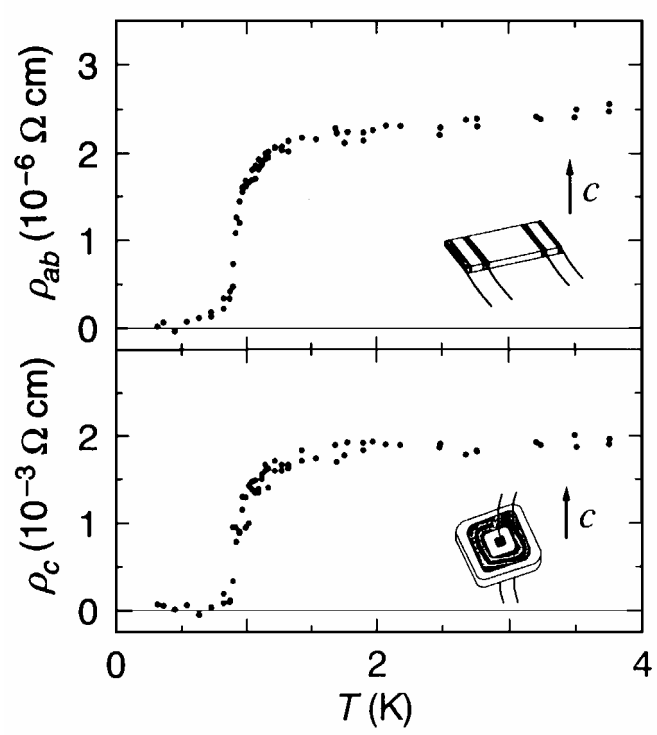
Sr_2RuO_4: spin-triplet superconductor

- Layered perovskite superconductor like La_2CuO_4

  CuO_2-plane ⟶ RuO_2-plane

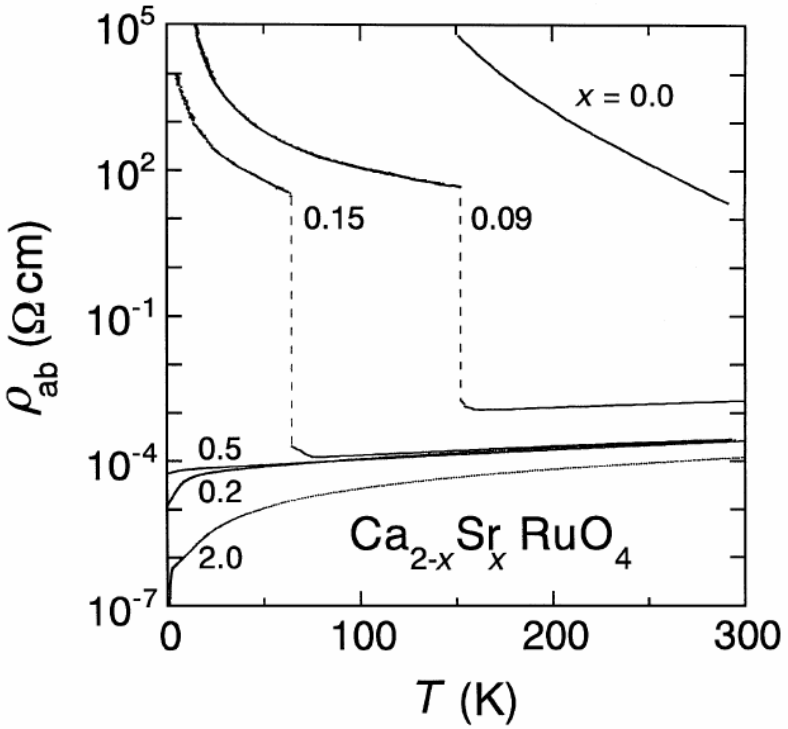


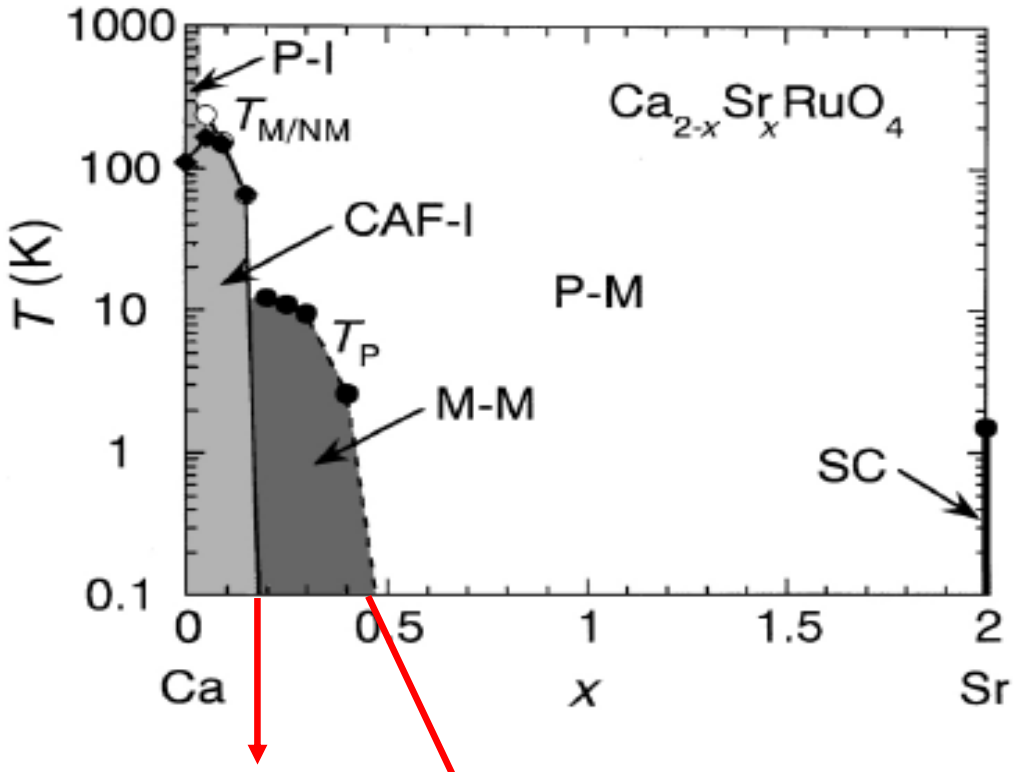
Y. Maeno *et al.*, Nature **372**, 532 (1994)



Phase diagram of $Ca_{2-x}Sr_xRuO_4$

S. Nakatsuji et al, Phys. Rev. Lett. 84, 2666 (2000).

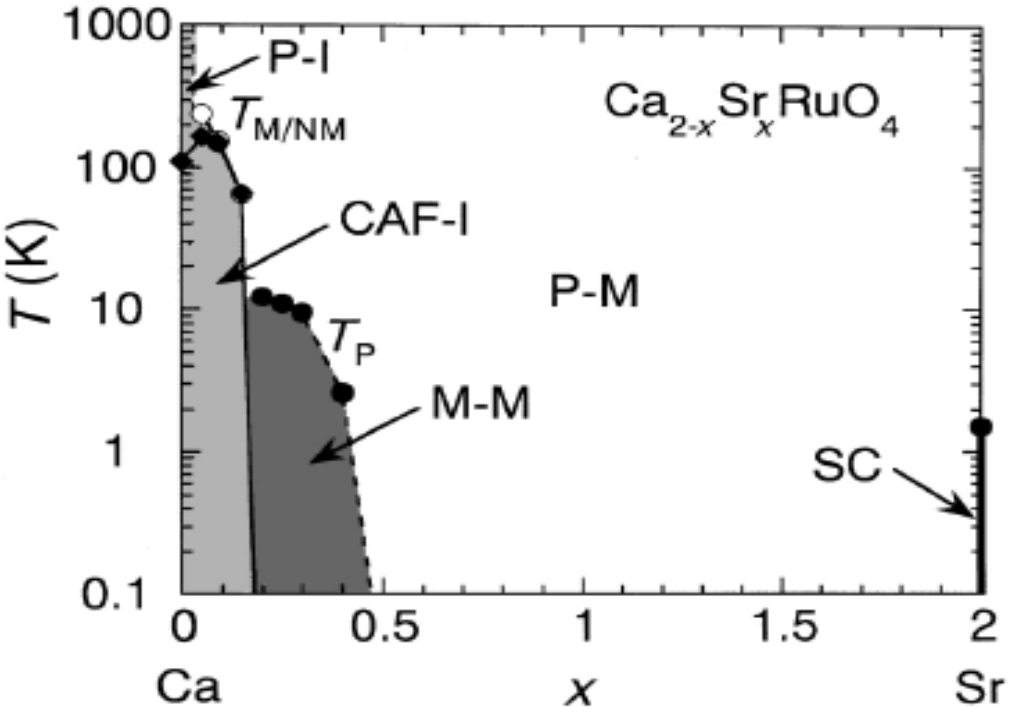


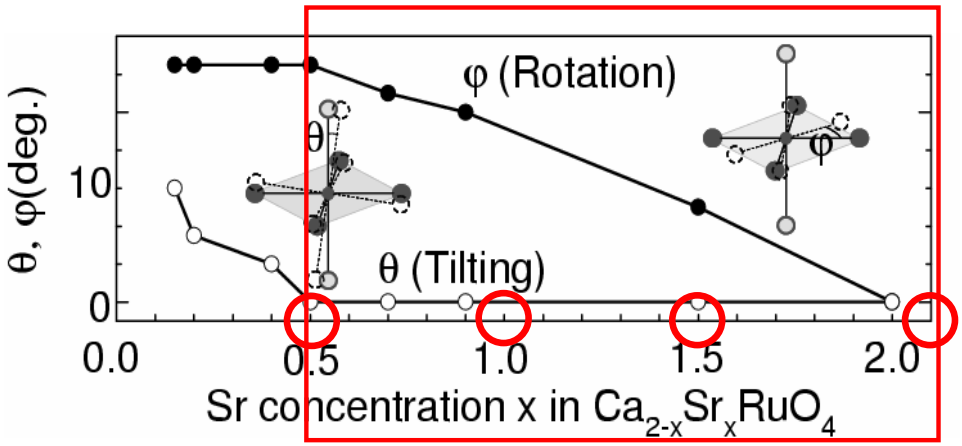


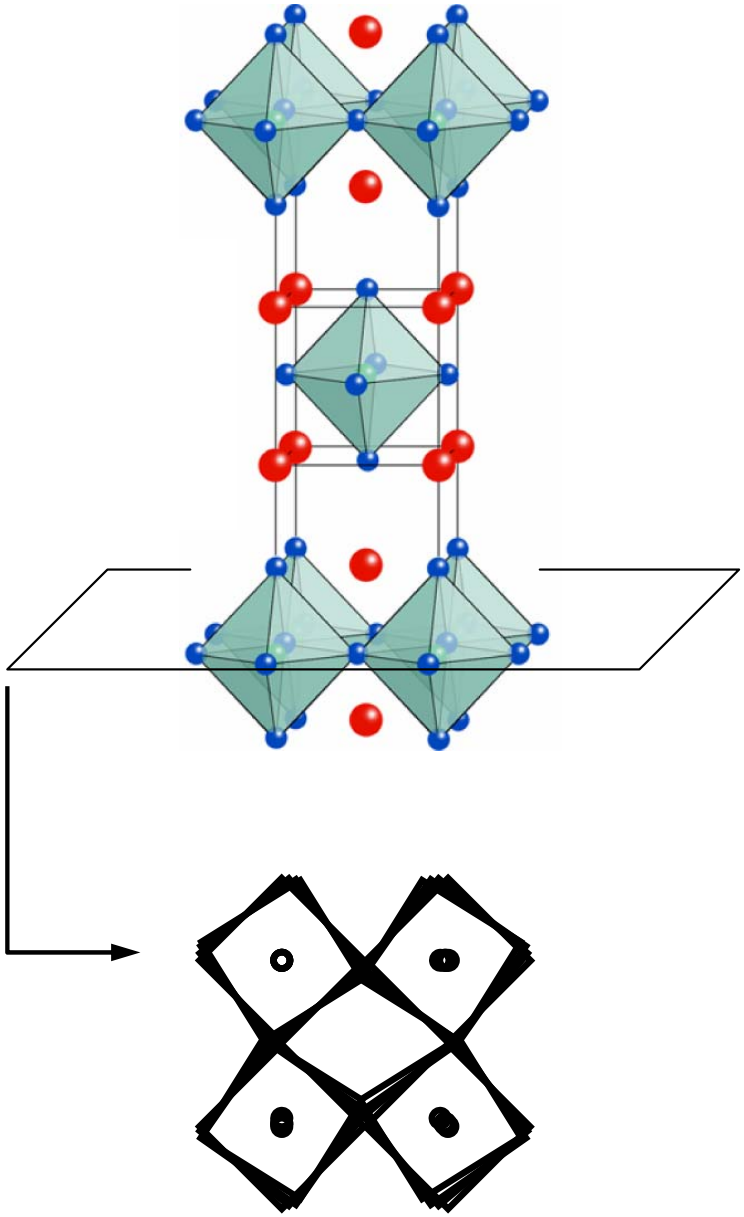
Mott transition

Orbital Selective Mott Transition (OSMT)?

Structural distortion of $Ca_{2-x}Sr_xRuO_4$







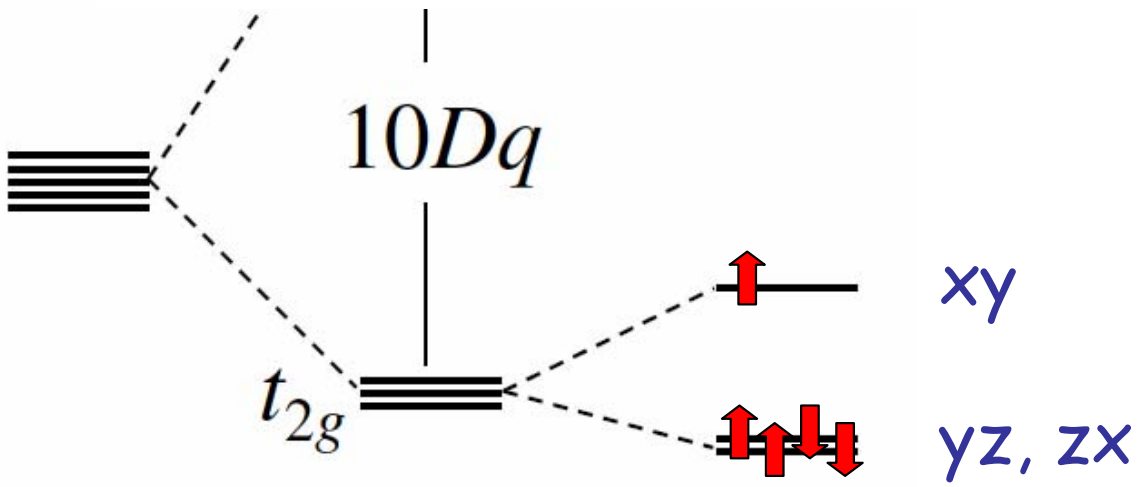
Various ground states are realized by structural distortions.

4*d* transition-metal oxide

- Large spatial extent of 4*d* orbitals
  - →large bandwidth, large 10*Dq*.
  - →tends to be weakly-correlated.
- Low-spin configuration is expected.

$Ca_{2-x}Sr_xRuO_4$

Sr_2RhO_4



Rotation of Octahedra

Rotation brings about:

- Doubling of the unit cell
- Decrease of M-O-M bond angle

which cause:

- Band folding
- Bandwidth narrowing

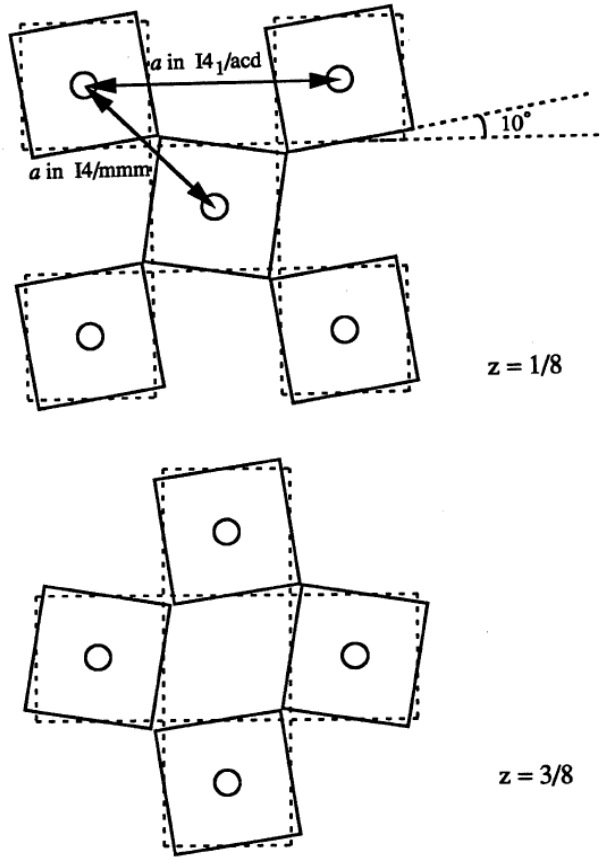
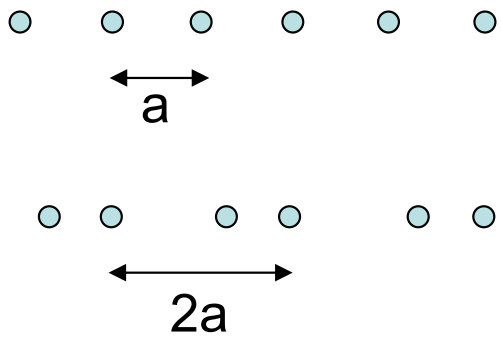
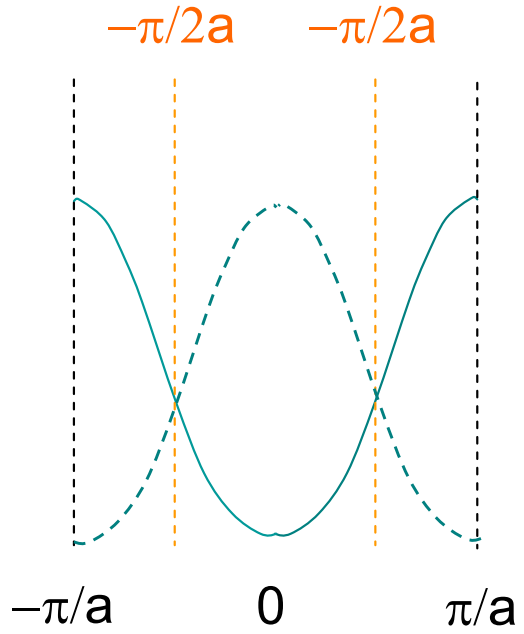


Fig. 1. Structure diagram of the Sr_2RhO_4 with $I4_1/acd$ spa group showing the RhO_6 octahedra rotation at $z = 1/8$ and z 3/8 in ref. 4. The dotted lines shows the structure of Sr_2Ru with I4/mmm space group.

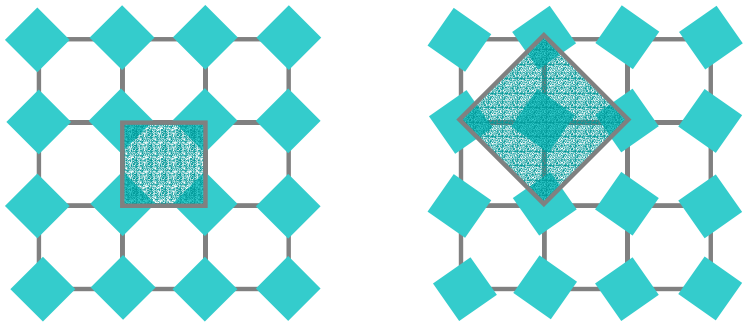
Unit cell doubling and band folding

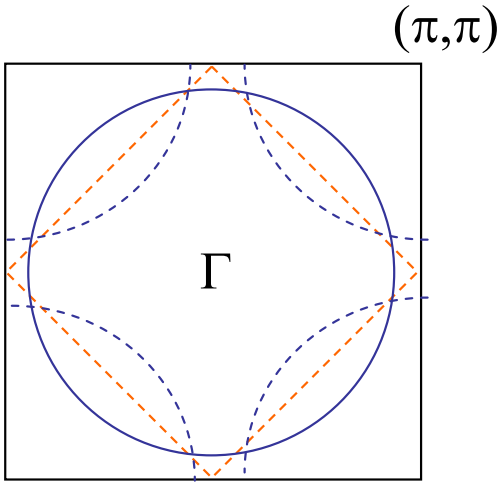
1D





2D





Band width narrowing

Octahedra rotation

⇩

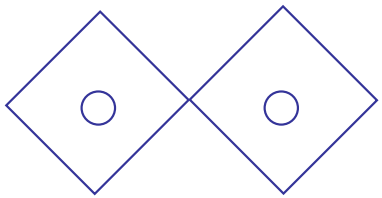
Decrease of M-O-M bond angle

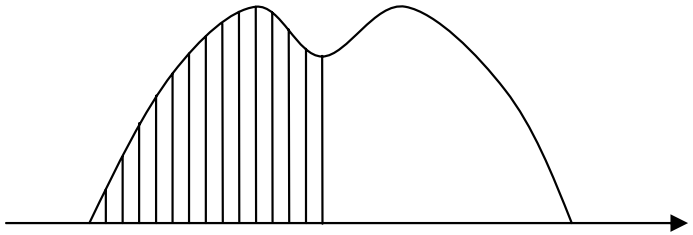
⇩

Decrease in hopping energy *t*

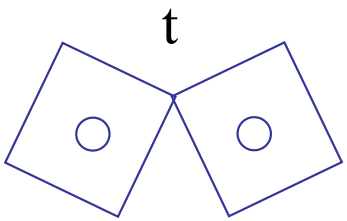
⇩

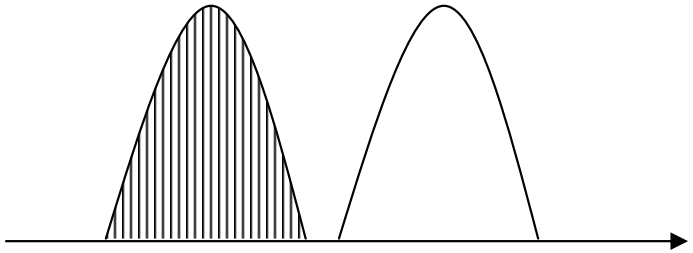
Increase in *U/t*





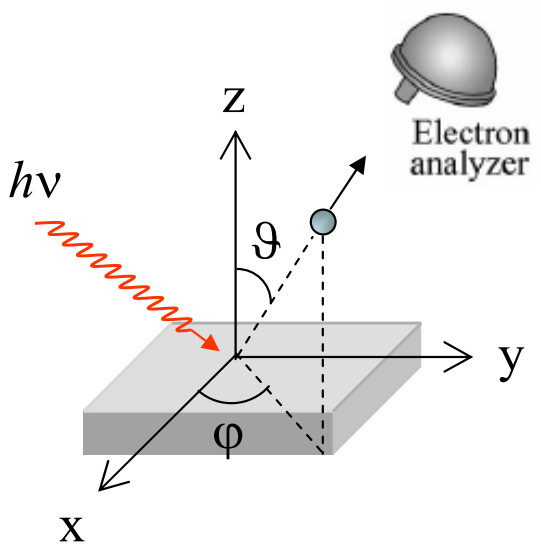
Metal, small *U/W*

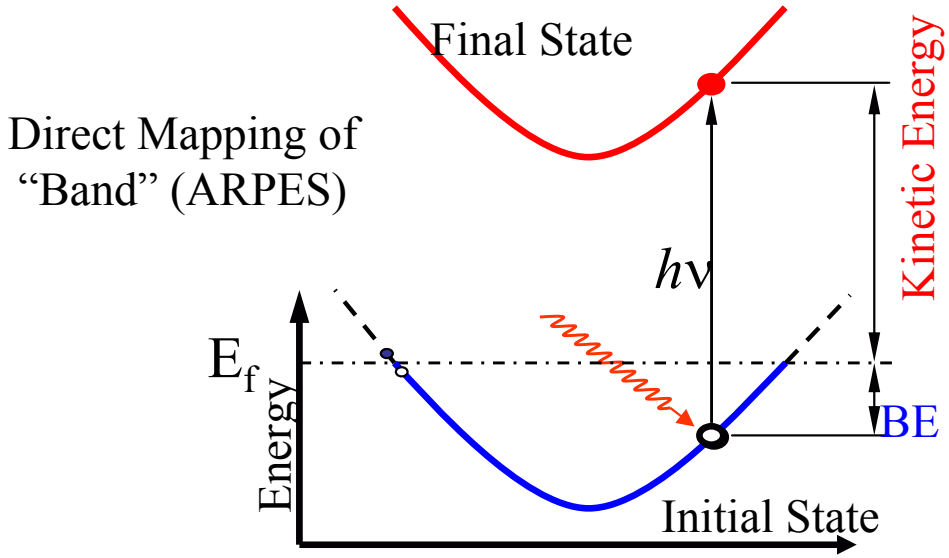




Insulator, large *U/W*

Angle-resolved photoemission spectroscopy (ARPES)

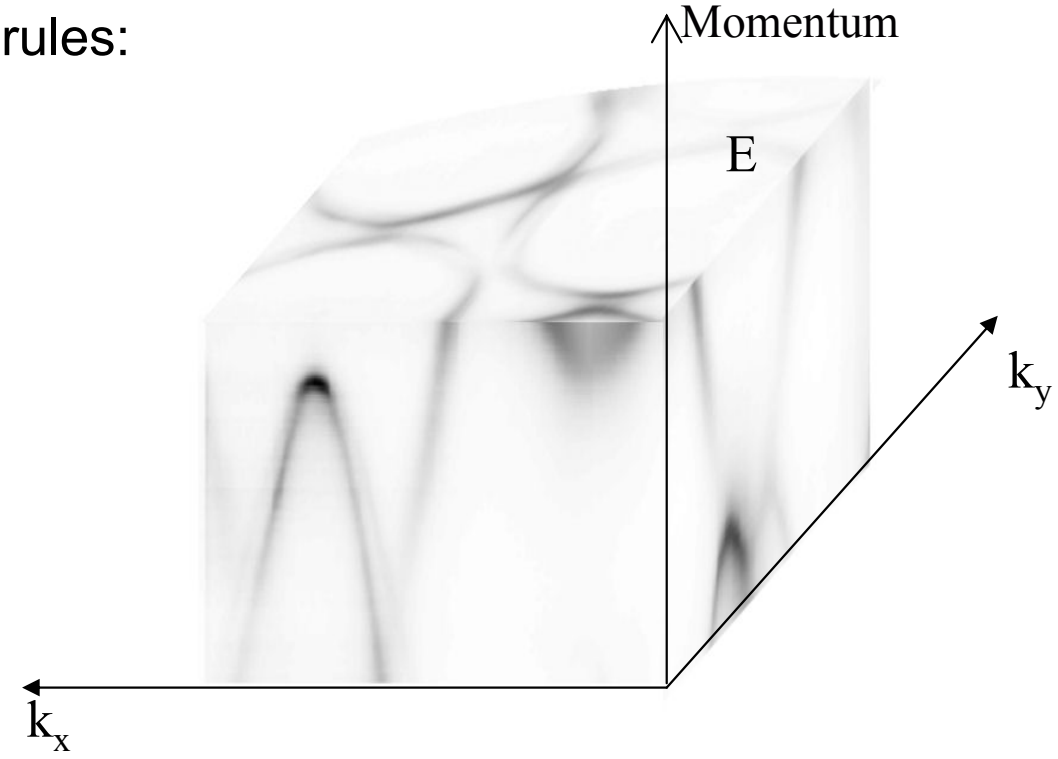




From momentum/energy conservation rules:

$$k_{pe} = -k_{N-1}$$

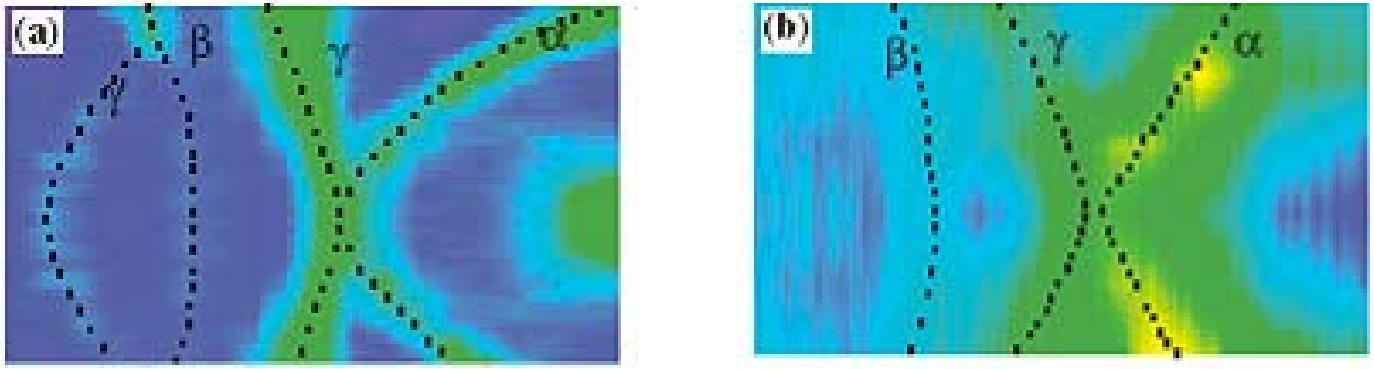
$$h\nu - E_{pe} = E_{N-1} - E_N$$



ARPES data on Ca-doped SRO

ARPES is a powerful tool to study the electronic structure.

S.-C. Wang et al. PRL 93,177007 (2004)



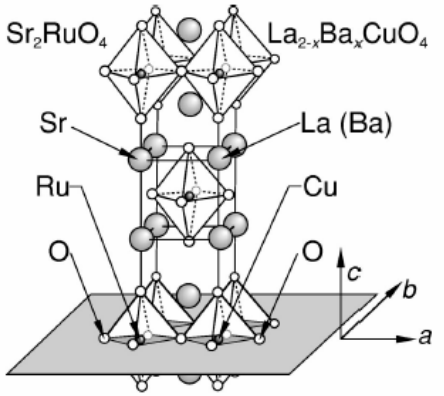
Sr_2RuO_4 $Ca_{1.5}Sr_{0.5}RuO_4$

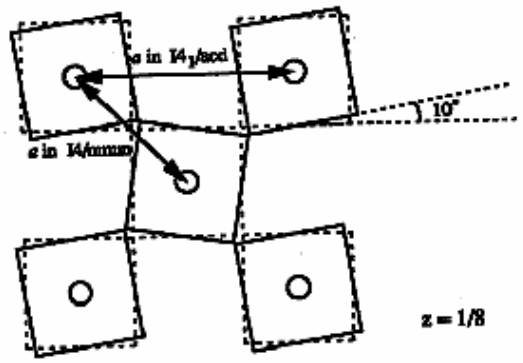
However, the disorder effects introduced by doping have discomforting effects in ARPES: the signals are generally broad and weak.

Sr_2RhO_4

39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd

- Share same crystal structure with Sr_2RuO_4.
- 5 electrons in 4*d* orbitals.
- Rotation angle ~ 10º.
- No supeconductivity.

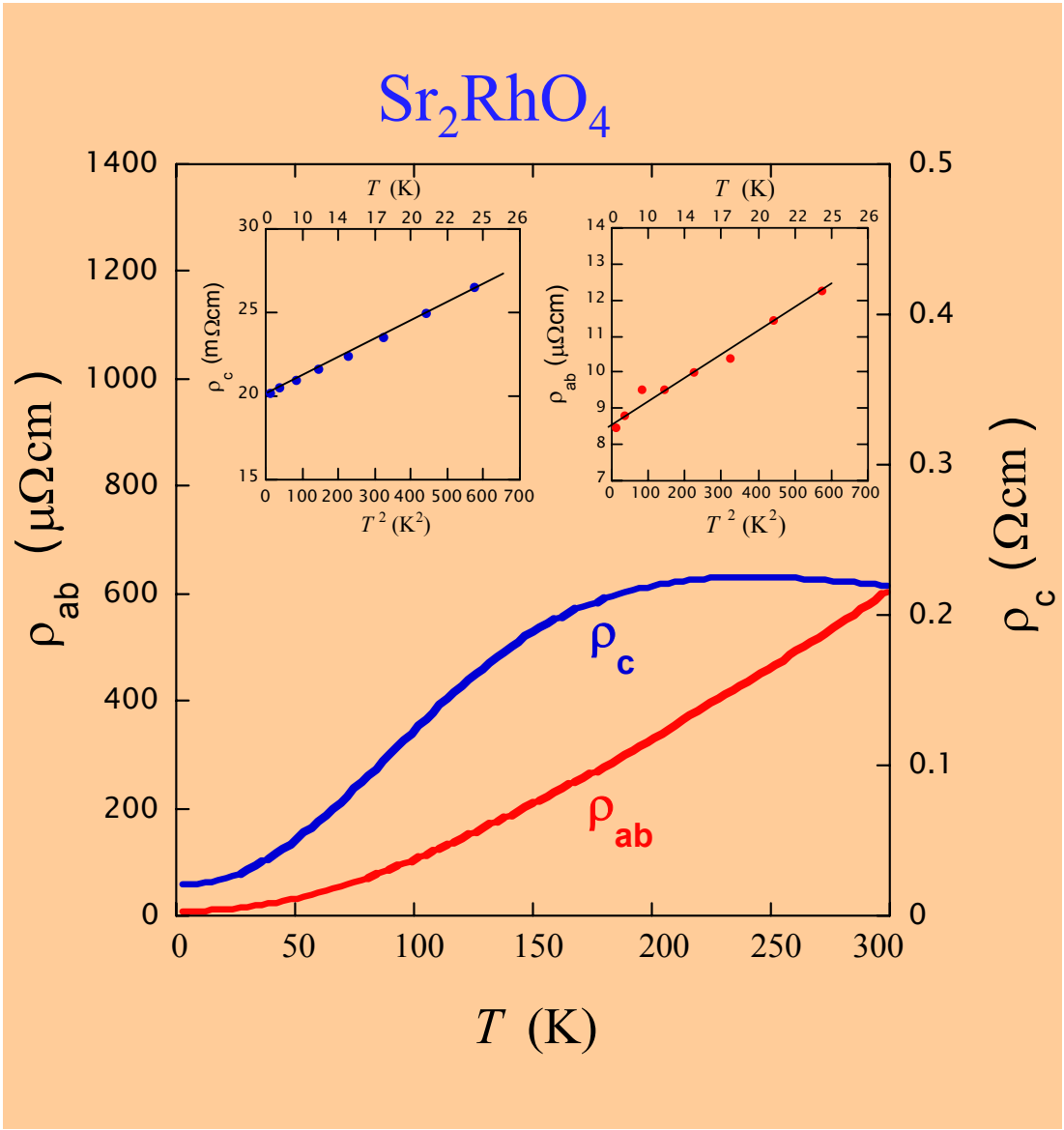




Sr_2RhO_4 presents an opportunity to study the effect of rotation without disorder.

Electrical resistivity

Similar to $\rho(T)$ in Sr_2RuO_4



- Large anisotropy

  $\rho_c / \rho_{ab}(3K) = 2400$

- T^2- dependence

  Fitting with $\rho = \rho_0 + AT^2$

  $\rho_{ab}(T)$ $\rho_0 = 8.6\ \mu\Omega cm$, $A_{ab} = 6.26\times10^{-3}\ \mu\Omega cm/K^2$

  $\rho_c(T)$ $\rho_0 = 20.1\ m\Omega cm$, $A_c = 10.55\ m\Omega cm/K^2$

- Below ~250 K, ρ_c decreases with lowering temperature.

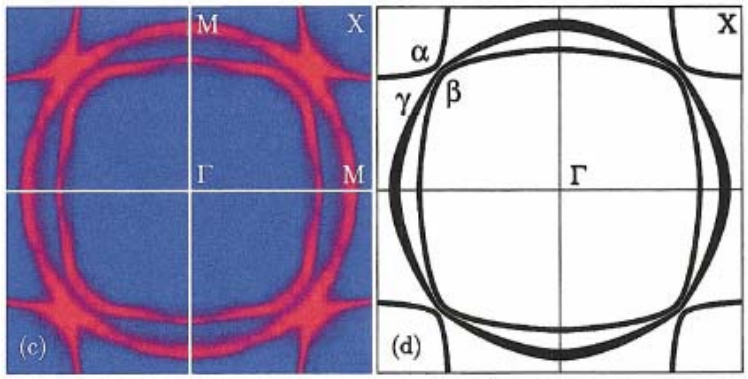
  because of suppression of thermal scattering between quasiparticles and phonon ?

- No superconducting transition was observed down to 36 mK.

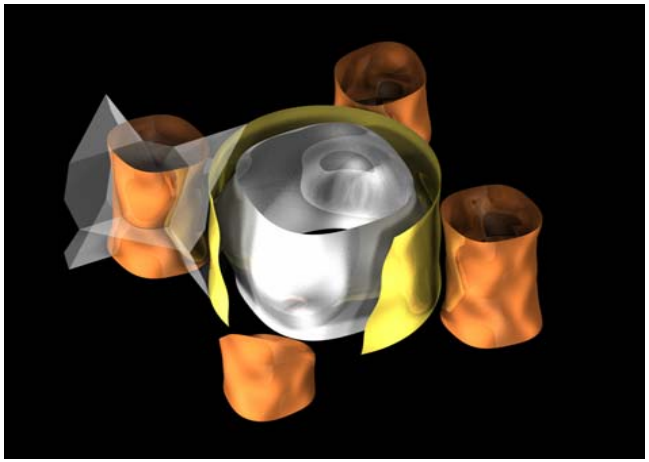
Sr_2RhO_4 is a two-dimensional Fermi liquid.

Expected FS of Sr2RhO4

FS of Sr_2RuO_4

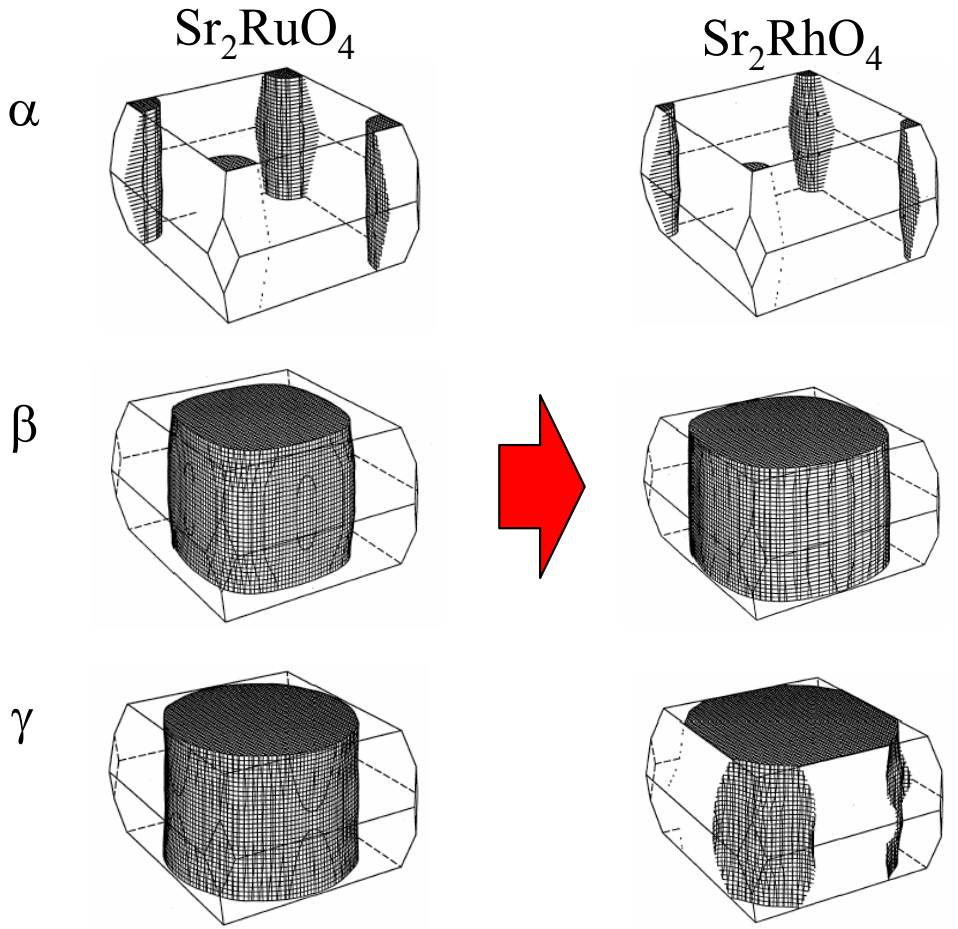


A. Damascelli *et al.* Phys. Rev. Lett. **85**, 5194-5197 (2000)



C Bergemann *et al*, PRL **84**, 2662 (2000)

By doping one electron: (rigid-band model)



Hase *et al*. J. of solid state chemistry **123**,186 (1996)

We expect basically similar FS topology in Sr_2RhO_4

ARPES measurements

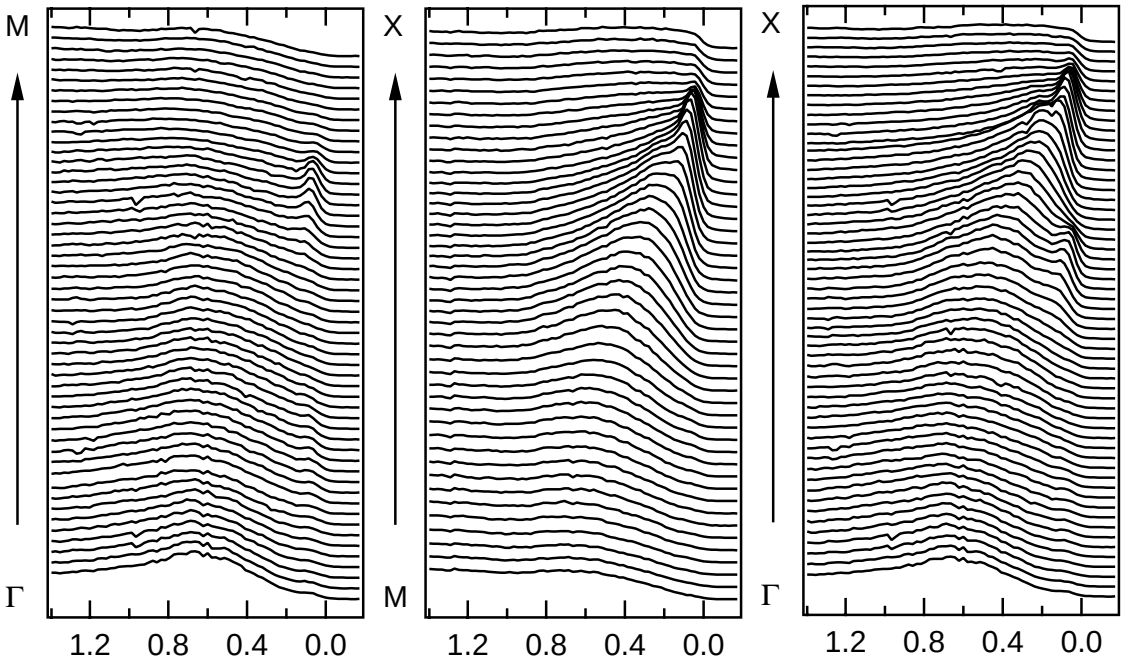
High energy ARPES

- ALS BL 7
- Analyzer : Scienta 100
- Temperature : 40K
- Total Energy Resolution : 40 meV
- Angular Resolution : 0.25º
- Photon energy : 85 eV
- Sample cleaved *in situ*

low energy ARPES

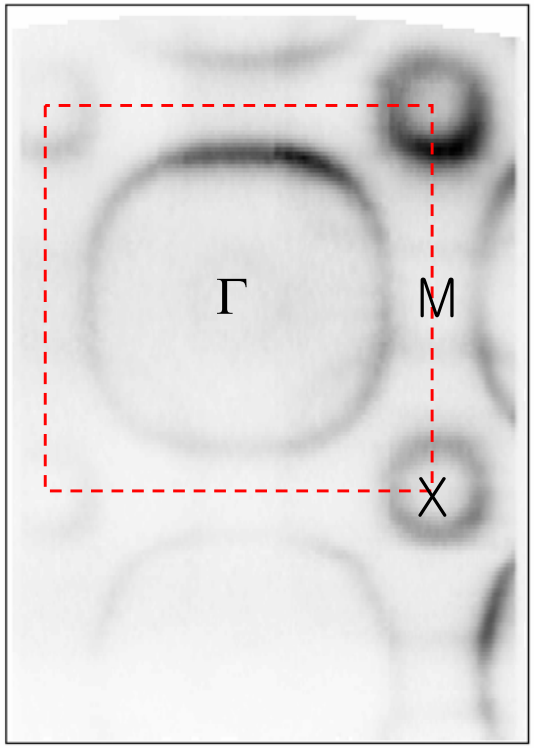
- SSRL BL
- Analyzer : Scienta 2002
- Temperature : 20K
- Total Energy Resolution : 40 meV
- Angular Resolution : 0.25º
- Photon energy : 20 eV
- Sample cleaved *in situ*

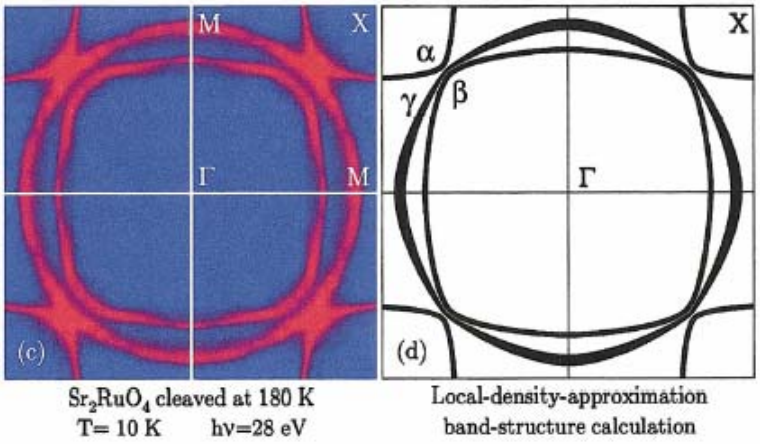
FS of Sr_2RhO_4 (ALS ARPES)



Binding Energy (eV)

Fermi Surface Mapping





Sr_2RuO_4 cleaved at 180 K
T= 10 K hν=28 eV

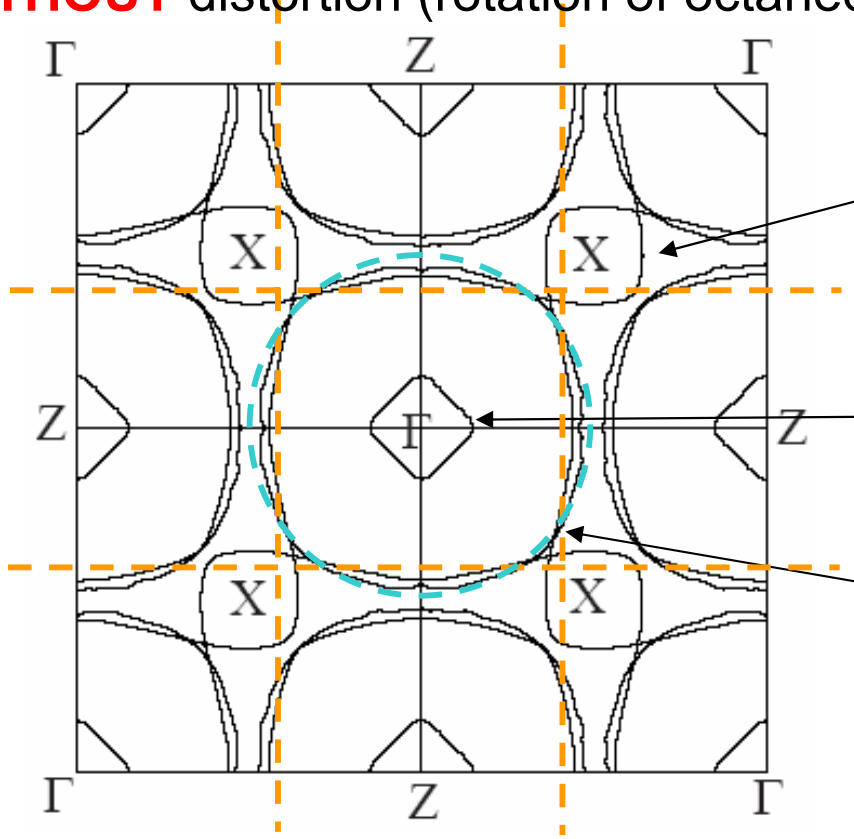
Local-density-approximation
band-structure calculation

Missing *xy*-band(γ)
FS in Sr_2RhO_4!

B.J. Kim et al., to be published in PRL

LDA calculation (I4/mmm)

WITHOUT distortion (rotation of octahedra)



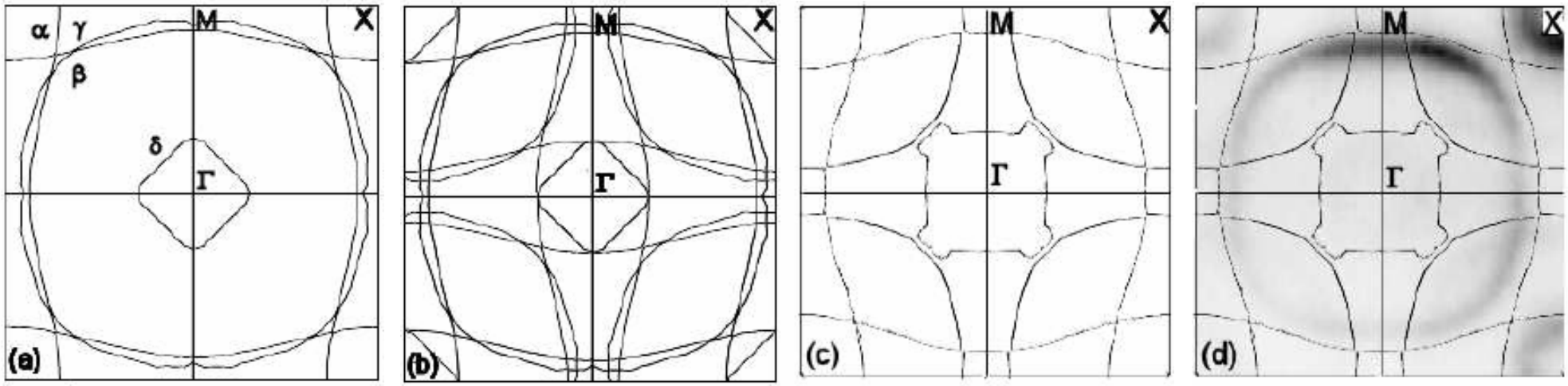
a hole pocket formed by *xz/yz* orbital band. (α)

an electron pocket formed by x^2-y^2 orbital band. (δ)

two electron pockets formed by *xy* (γ) and *yz,zx* band (β)

Occupation :		
	α	94.8%
	β	66.8%
	γ	72.5%
	δ	7.1%

Effects of the rotational distortion



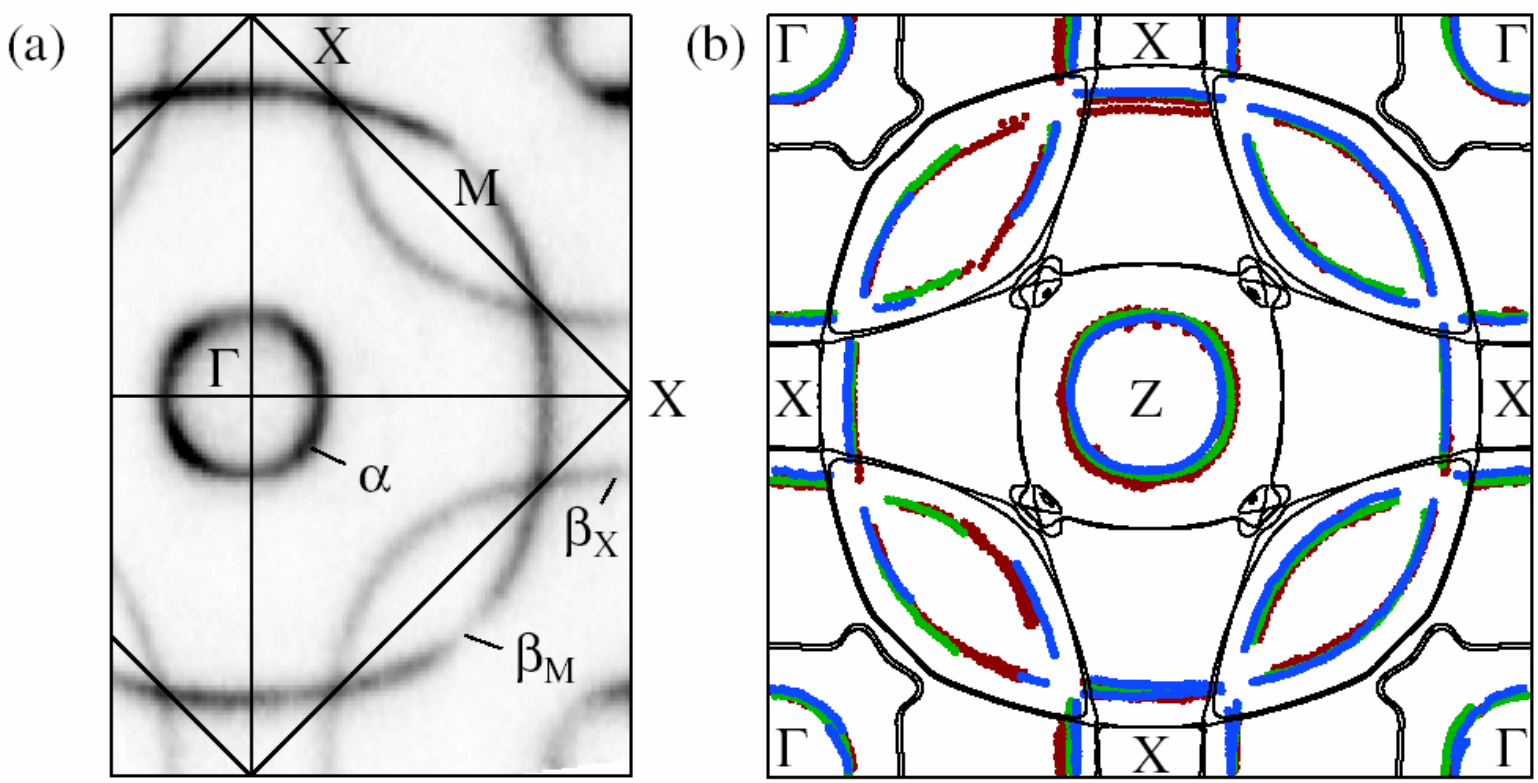
undistorted

undistorted
+band folding

distorted

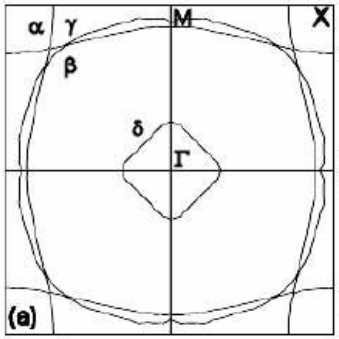
exp and calc.

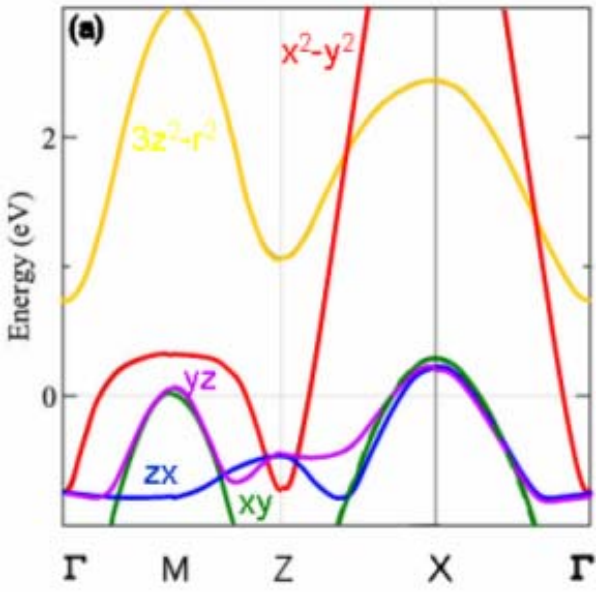
LDA calculation shows disappearance of *xy*-band (γ) FS.

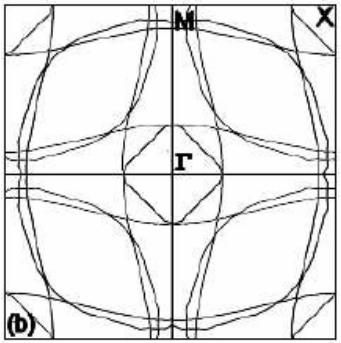


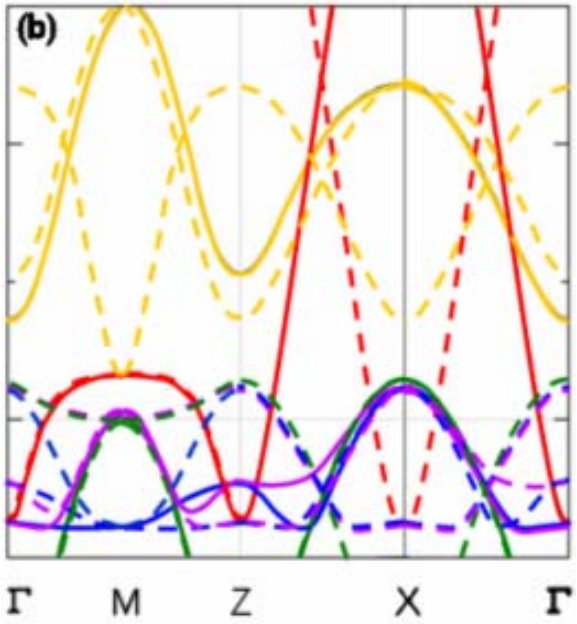
F. Baumberger et al., PRL **96, 246402** (2006)

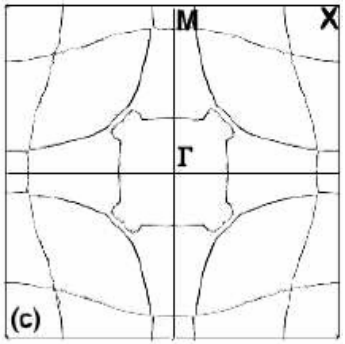
Effects of the rotational distortion

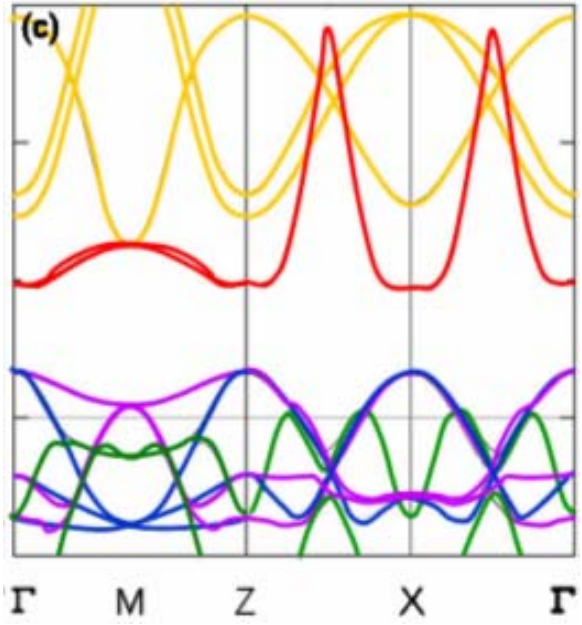




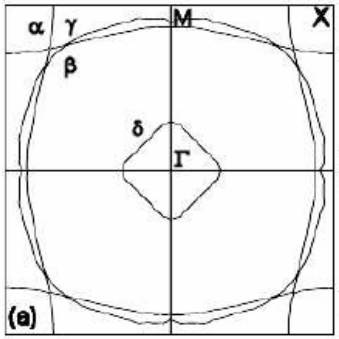


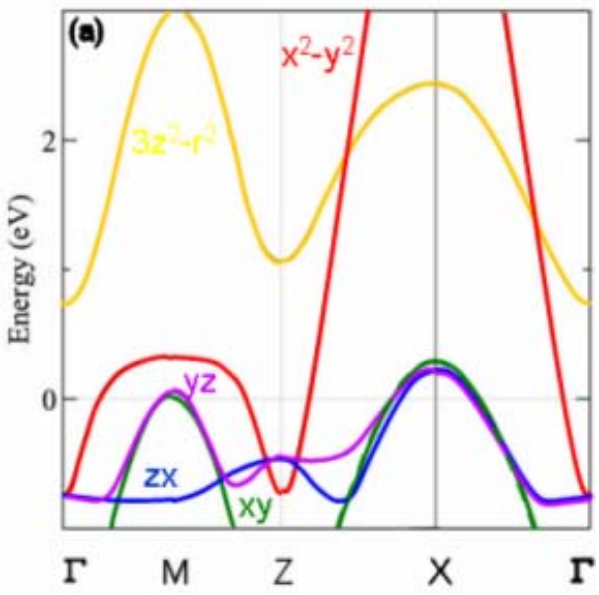


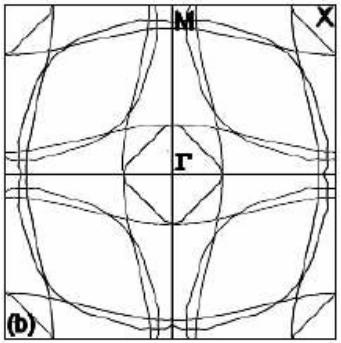


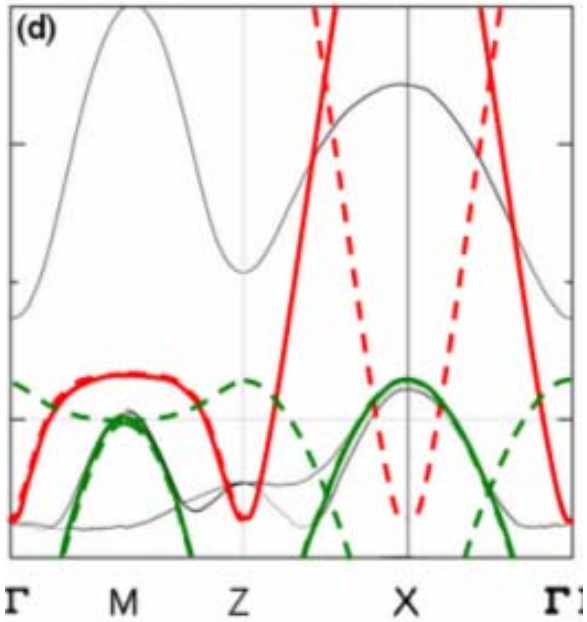


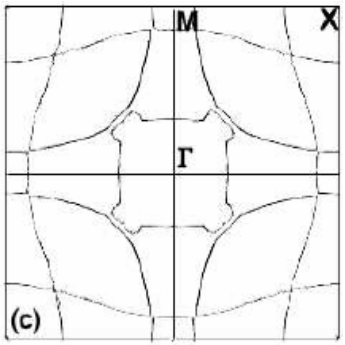
Effects of the rotational distortion

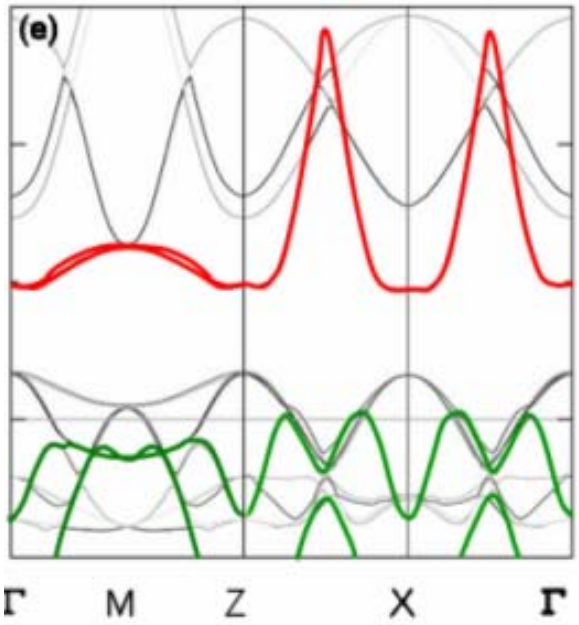




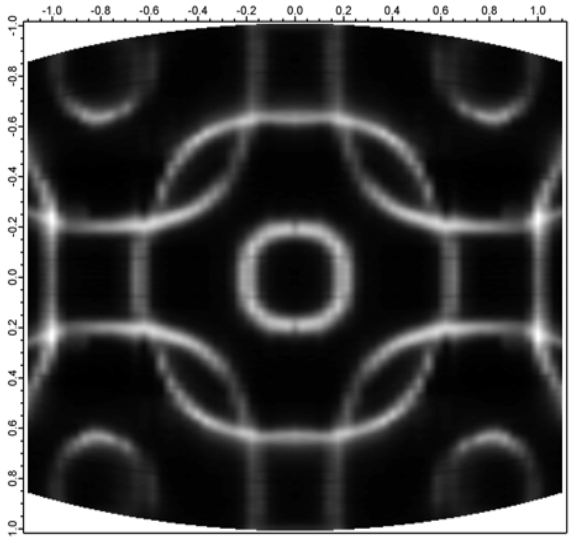


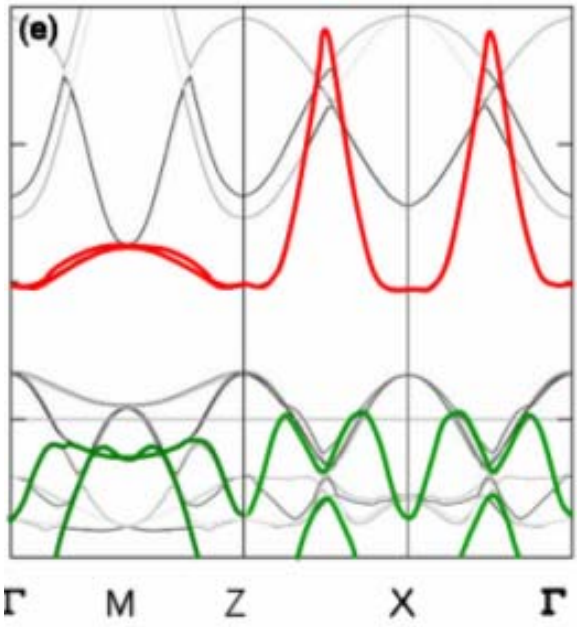


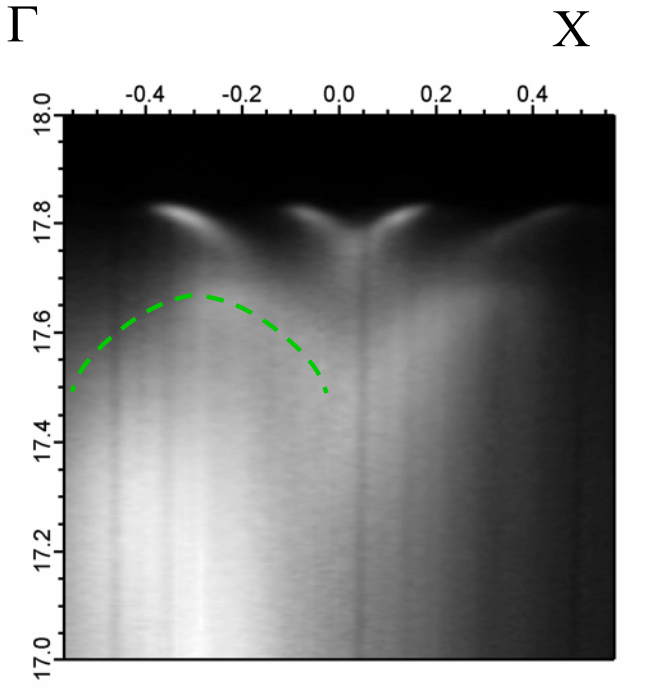


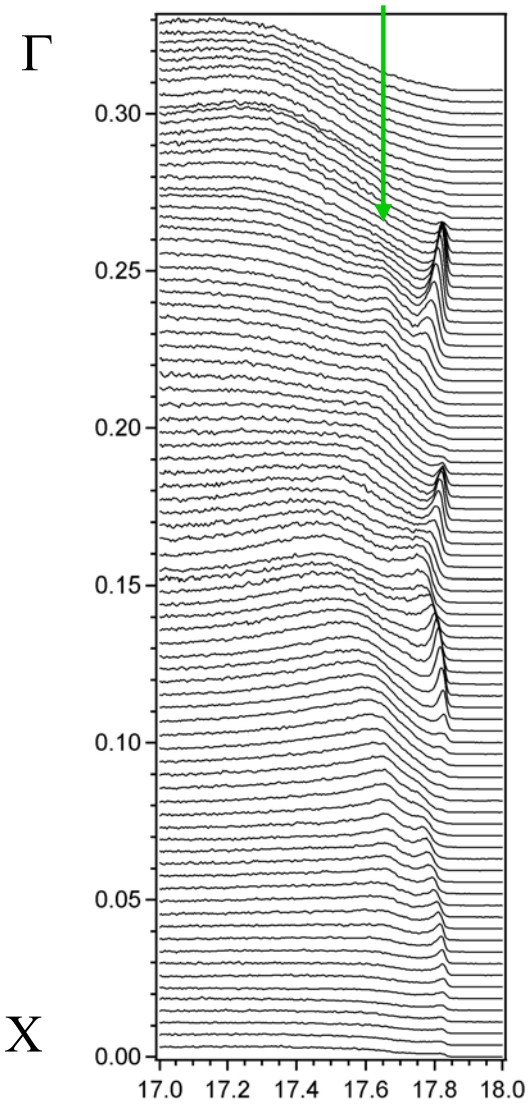


FS of Sr_2RhO_4 (ARPES)









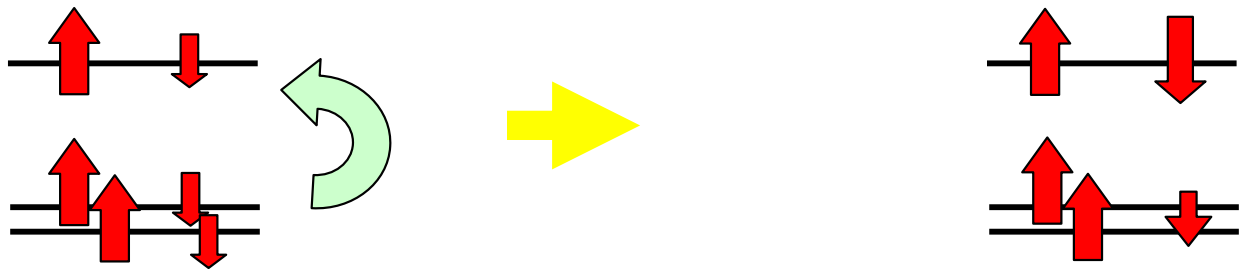
Observation of *xy*-band sunken under E_f

Effects of the rotational distortion

Complete filling of the *xy*-band
→ transfer of electrons from the *yz/zx* band to *xy* band

xy

yz, zx

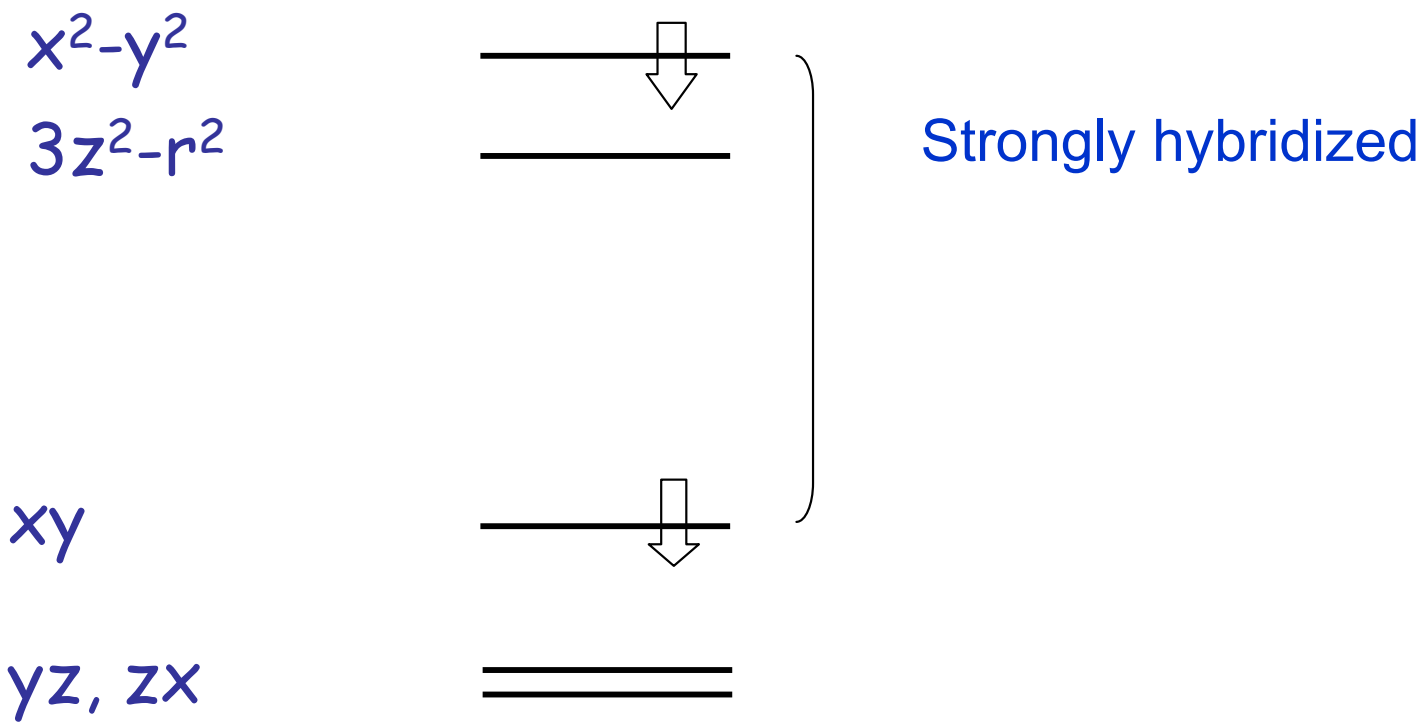


Electron occupation

α	94.8%	α	96.2%
β	66.8%	β	51.5%
γ	72.5%	γ	100%
δ	7.1%	δ	0%

Effects of the rotational distortion

Hybridization between the *xy* and x^2-y^2 band
→ Increase in the orbital occupation of the x^2-y^2 state



Destabilizes the elongation of the octahedra along *c*-axis

Structural instability

As temperature is lowered:

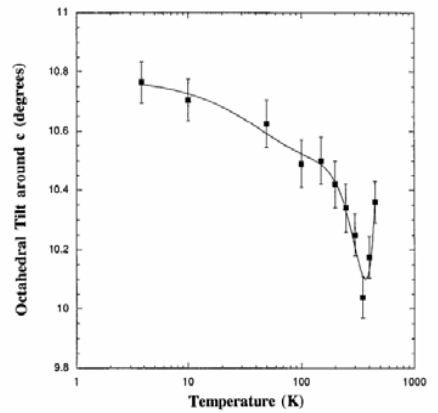


FIG. 2. Temperature dependence of tilt angles for the RhO_6 octahedra about the c-axis in degrees.

a-axis contracts by 0.35%

JOURNAL OF SOLID STATE CHEMISTRY **123,** 186–189 (1996)

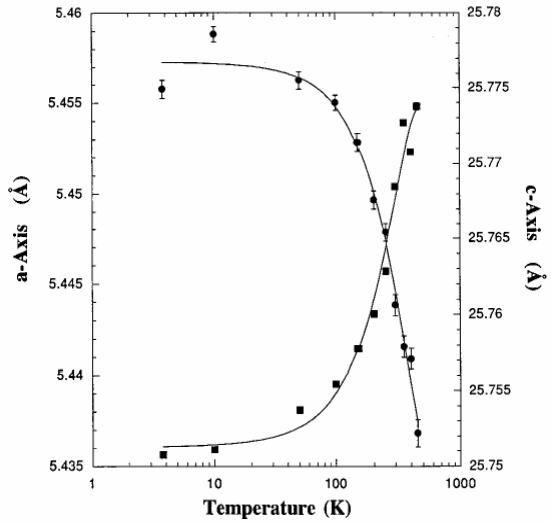


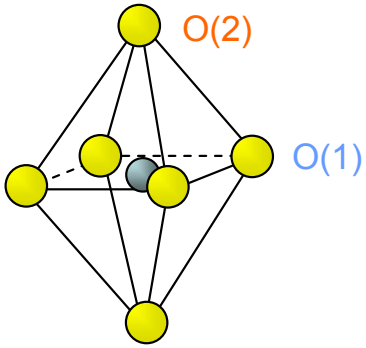
FIG. 1. Lattice constants of Sr_2RhO_4 as a function of temperature.

c-axis expands by 0.08%

rotation angle increases

HOWEVER,

Rh-O(1) contracts only by 0.2%



Rh-O(2) *contracts* by 0.26%

Summary – Sr_2RhO_4

- Rotation of the octahedra leads to hybridization of *xy* and x^2-y^2 bands.

- Hybridization of *xy* and x^2-y^2 bands results in:
  (1) transfer of electrons from *yz/zx* to *xy* band and
  (2) disappearance of the *xy* Fermi surface.

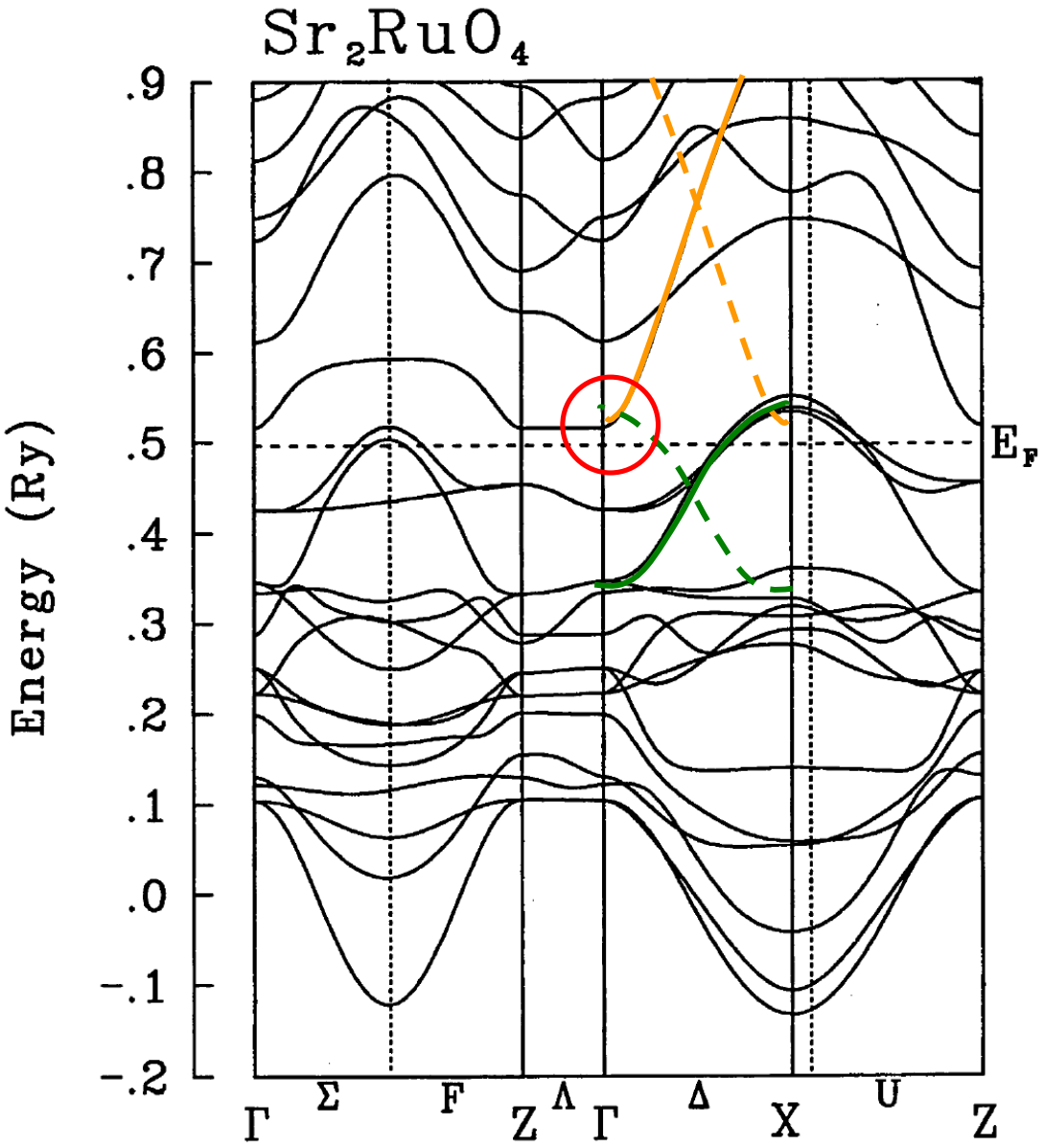
- e_g states play vital role in determining electronic structures near E_f, and therefore should be included in the theoretical models that deals with 4*d* TMOs.

Implications to CSRO system

- Orbital-selective Mott-transition at x=0.5?
- Magnetic ground state and origin of localized spin.

→depends critically on n_{xy},$n_{yz/zx}$,and the crystal structure.

Band structure (Sr end)



Same physics apply here!

Experimental evidences

S.-C. Wang et al. PRL 93,177007 (2004)

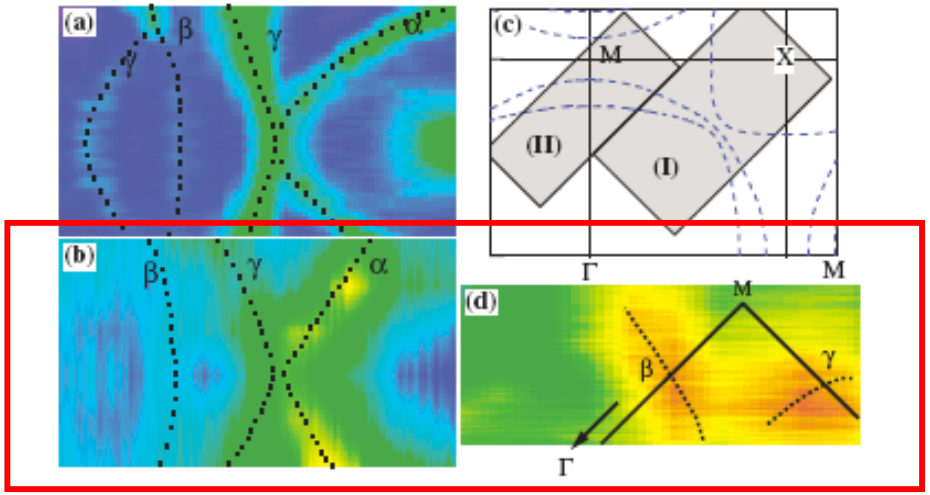


FIG. 2 (color). 2D plots of intensity integrated over a small energy region of E_F (±20 meV) for (a) Sr_2RuO_4 in the rectangular box (I) shown in (c); (b) $Ca_{1.5}Sr_{0.5}RuO_4$ in the same box (I); (d) $Ca_{1.5}Sr_{0.5}RuO_4$ in the box (II). (c) Locations of measurement in the BZ.

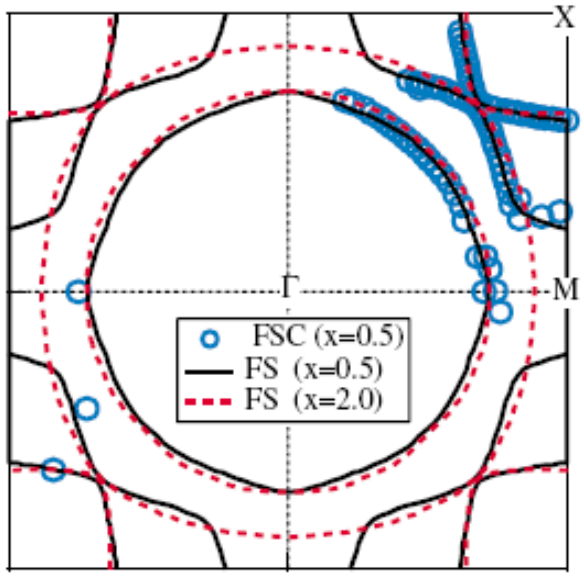
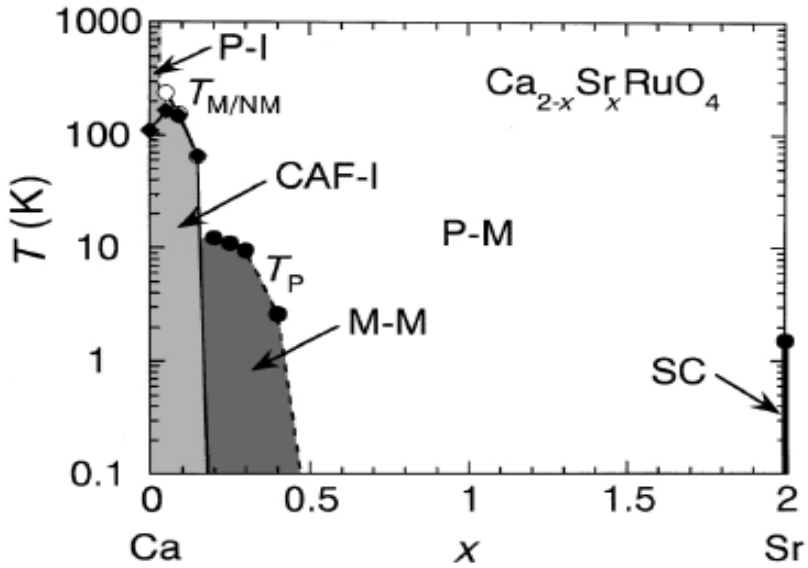


FIG. 3 (color). Measured FS crossing points (blue circles) and derived Fermi surfaces (solid black lines) in $Ca_{1.5}Sr_{0.5}RuO_4$. For comparison, extracted FSs (red dashed lines) in Sr_2RuO_4 are also plotted . Note the folded image FSs are not plotted for clarity.

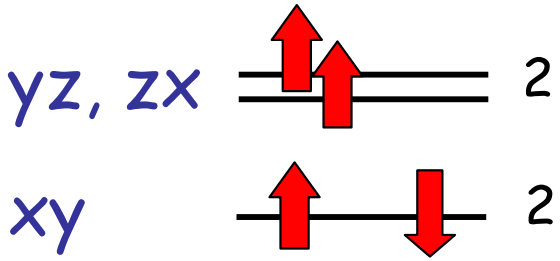
γ Sheet changes from electron-like to hole-like

Orbital-selective Mott transition?

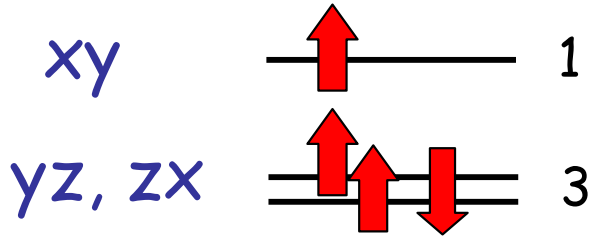
Anisimov *et al.* Eur. Phys. J. B 25,191 (2002)



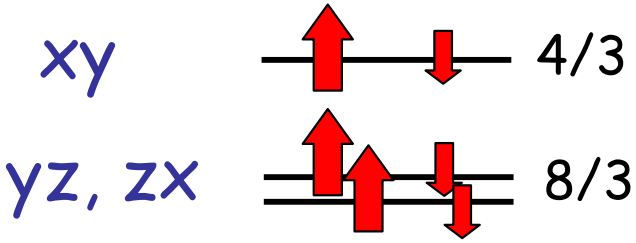
Region I (0.2>x>0)



Region II (0.5>x>0.2)



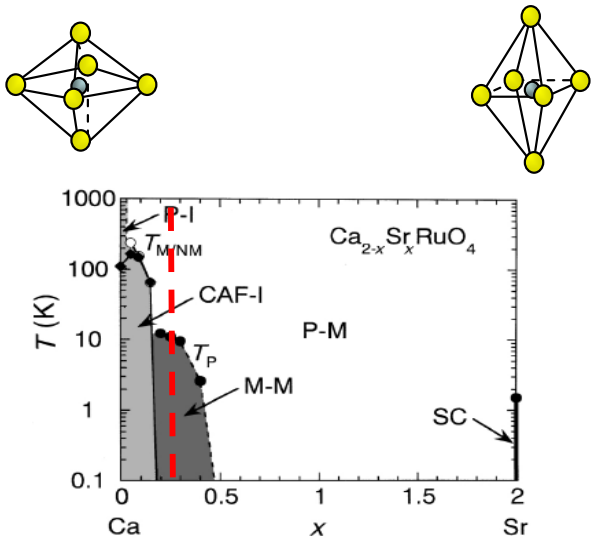
Region III (2>x>0.5)

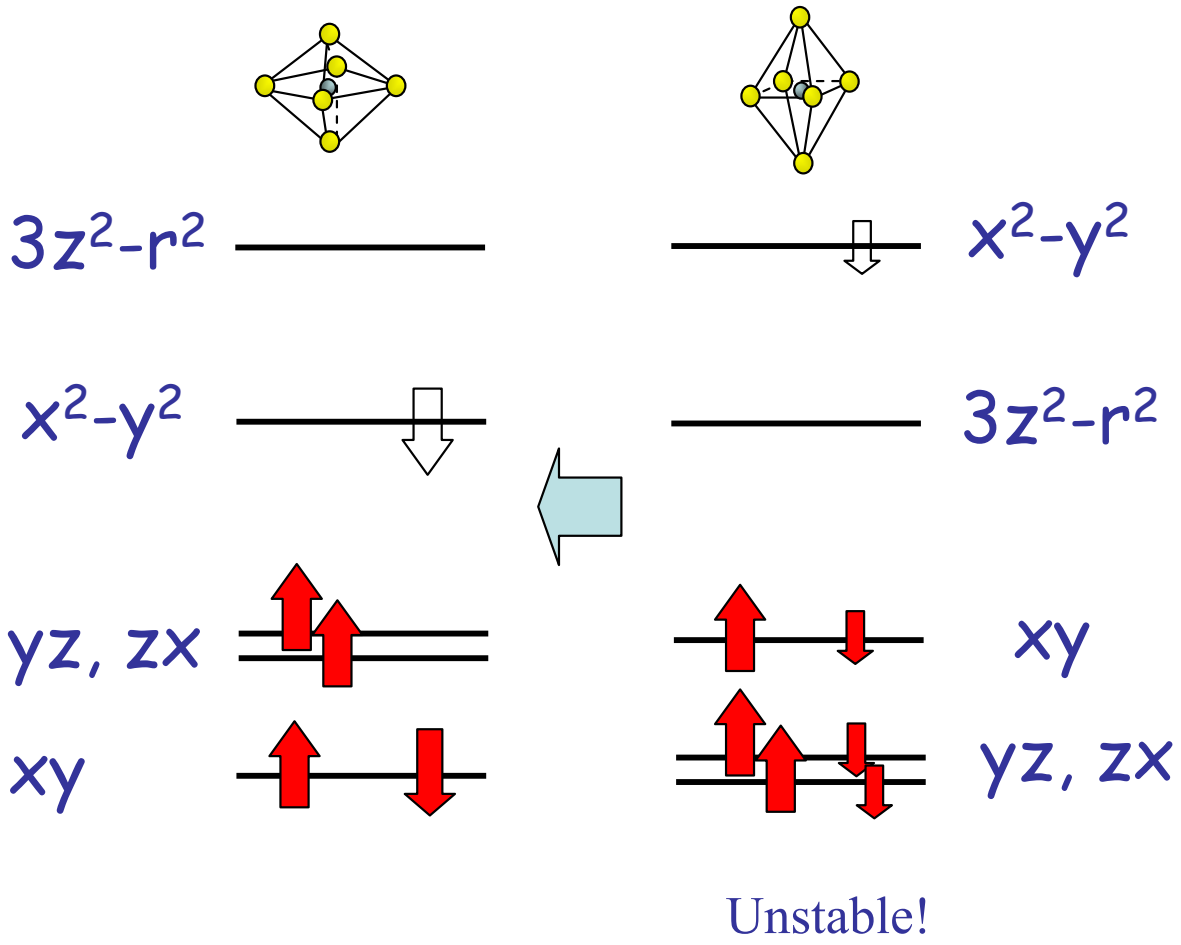


Contradicts with our finding!

Structural phase transition (x=0.2)

Flattening of octahedra at x=0.2





Unstable!

Strong hybridization with e_g states drives the structural phase transition and thus the Mott transition.

Summary

- Rotation of the octahedra leads to hybridization of xy and x^2-y^2 bands also in CSRO.
- Hybridization of xy and x^2-y^2 bands results in dramatic change in the Fermi surface topology.
- e_g states play vital role in determining electronic structures near E_f, and therefore should be included in the theoretical models that deals with 4*d* TMOs.