Part 1

Anisotropic High Conductivity of Delafossite $PdCoO_2$ Investigated by ARPES and Polarization-dependent XAS

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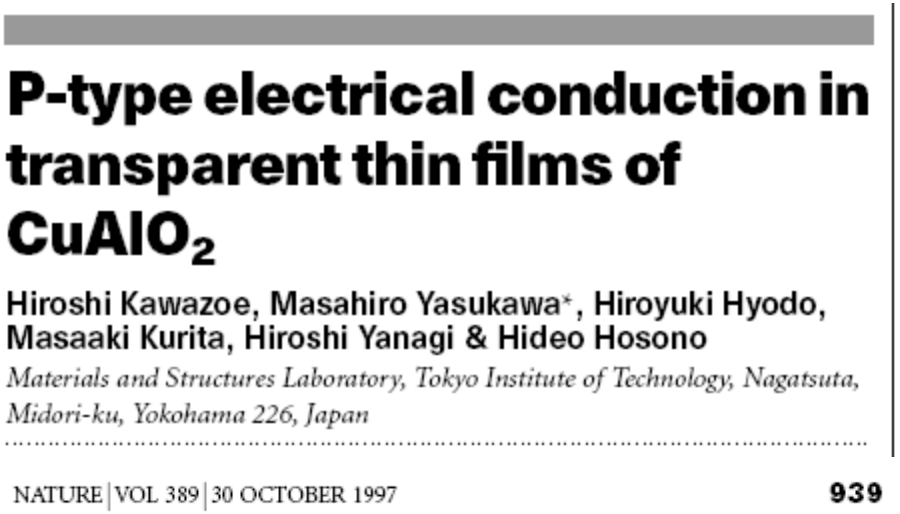
Motivation

Delafossite?

- Transparent conducting p-type and n-type materials: $CuAlO_2$, $AgInO_2$
- Magnetic frustration: $CuFeO_2$
- Highly conducting compounds: $PdCoO_2$, $PtCoO_2$, $PdCrO_2$, $PdRhO_2$
- Why are they so good conductors? [Shannon *et al*., Inorg. Chem. **10** 713 (1971)]
  ρ=4.7 $\mu\Omega$cm (cf:ρ_{Pd}=11 $\mu\Omega$cm) at RT.



P-type electrical conduction in transparent thin films of $CuAlO_2$

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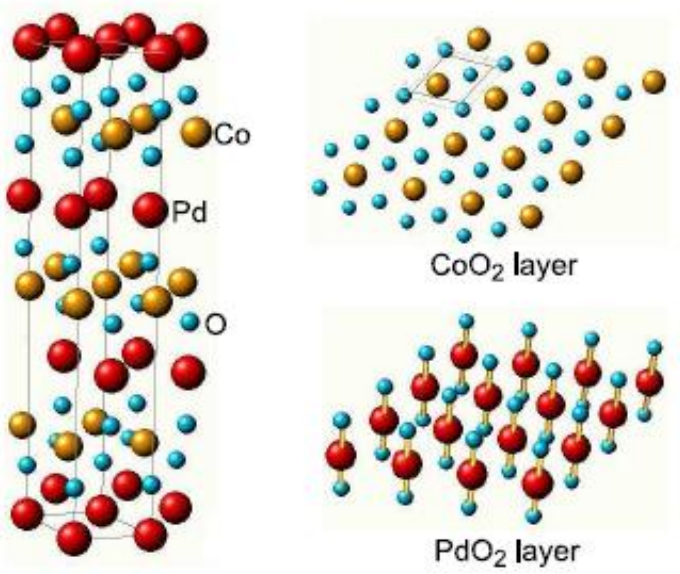
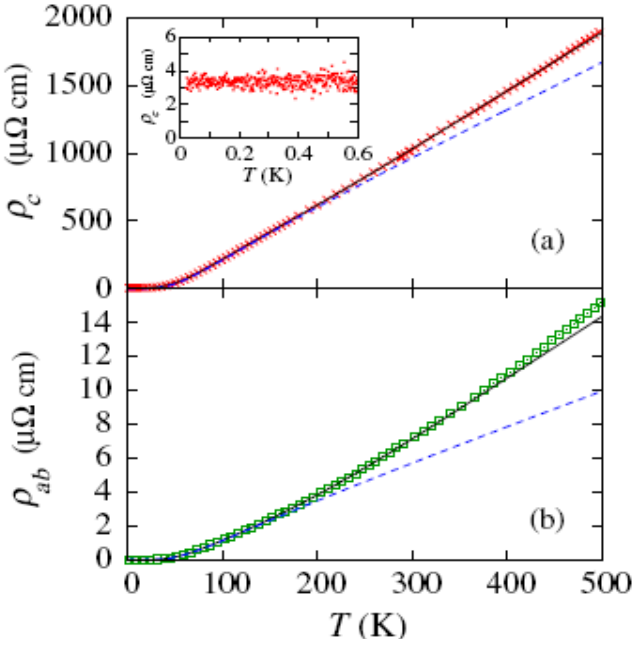
NATURE | VOL 389 | 30 OCTOBER 1997 939

Basic Properties of $PdCoO_2$

- Rhomboheral structure ($R_{\underline{3}m}$)
- Valence states: $A^{+}B^{3+}O^{2-}{}_2$
- Very good in-plane conductivity: better than that of Pd metal at RT
- High anisotropy in electric conductivity: $\sigma_{ab}/\sigma_c > 140$
- Curie-Weiss law (Θ=10.6 K) in magnetic susceptibility, but cannot exclude impurity effect: spin state of Co^{3+}?





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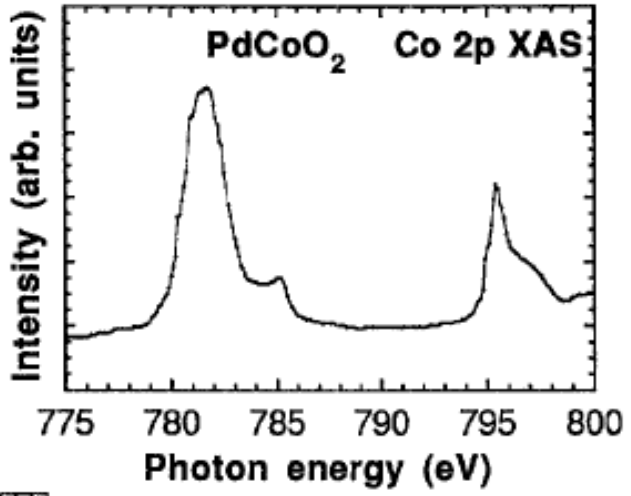
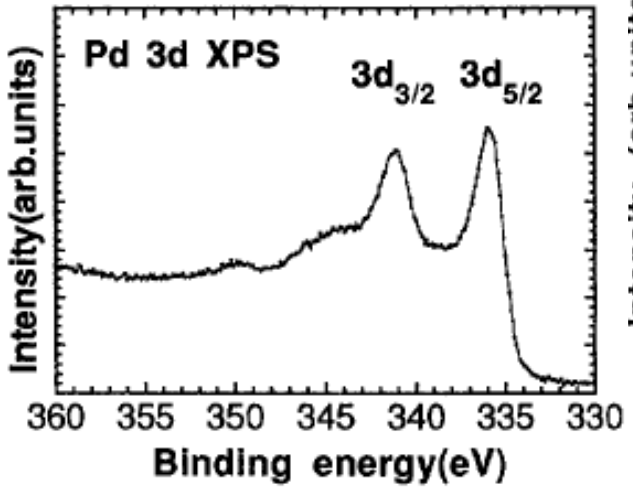
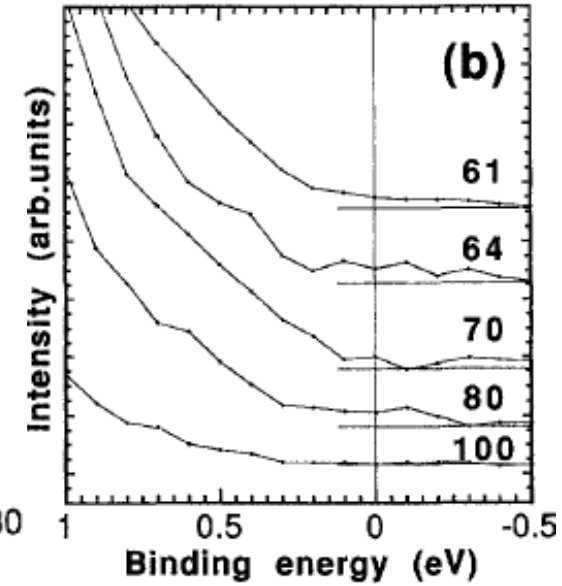
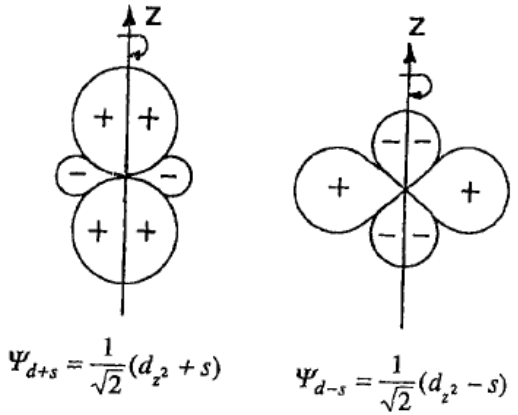
Previous spectroscopic studies

- The measurements were performed on the polycrystalline samples.
- Co^{2+} impurity phase.
- Co^{3+} $3d^6$ low spin state?
- Pd 4*d* character at the Fermi level.
- Origin of the in-plane good conductivity: s-d hybridization.





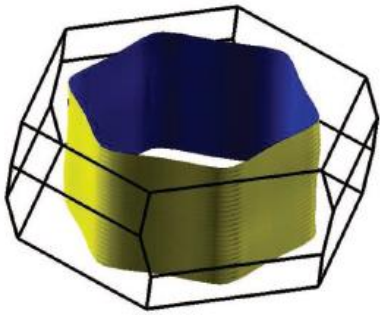


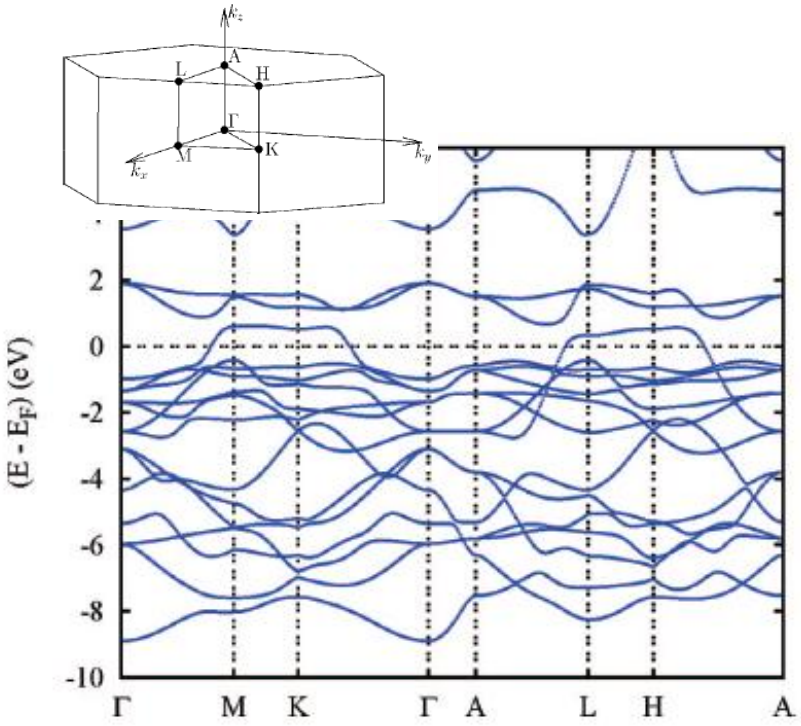


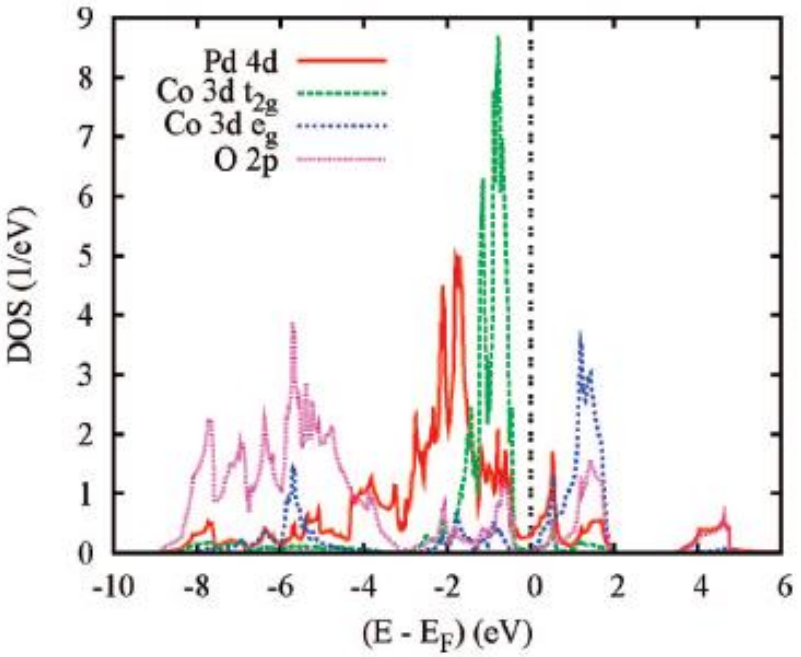
M. Tanaka et al. / Physica B 245 (1998) 157

Recent Electronic Structure Calculation

- Detailed electronic structure has been recently reported.
  [V. Eyert *et al*., Chem Mater. 20, 2370 (2008)]
- The conduction band has exclusively Pd 4*d* characters.
- Nearly two dimensional Fermi surface.
- Insulating CoO_2 layers.





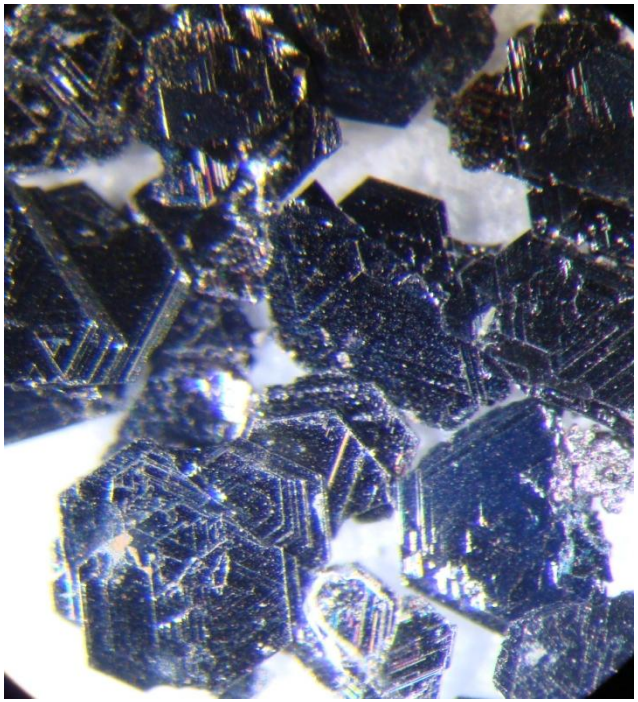


Crystal Growth and Experiments

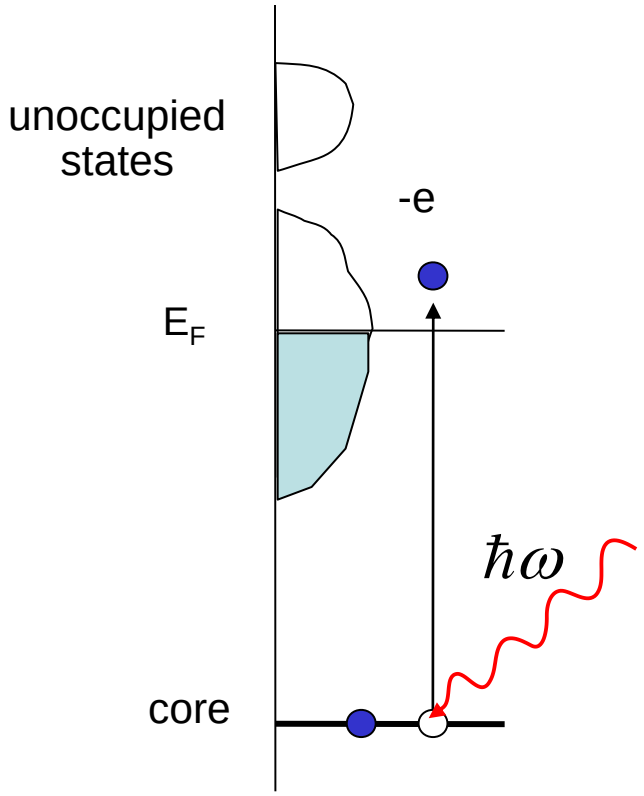
- First reported by Shannon et al.. [Inorg. Chem. **10**, 719 (1971)]
- Xtals were grown at PLS *lab*PEM by the metathetical reaction method

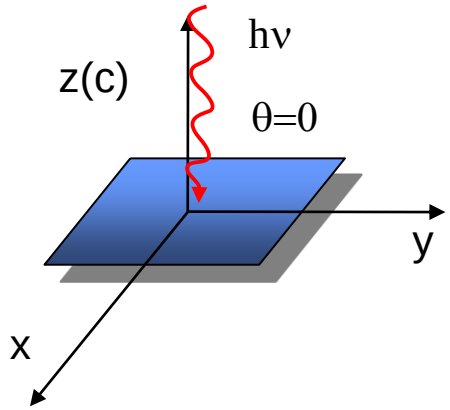
$$PdCl_2 + 2CoO \rightarrow PdCoO_2 + CoCl_2$$

- The mixture was heated at 700 °C for 40 hrs in an evacuated quartz tube.
- The phase was checked by XRD
- ARPES was performed at PLS 3A1 (U10) beamline under the pressure of 5×10^{-11} Torr.
- XAS was performed at PLS 2A (EPU6) beamline under the pressure of 2×10^{-9} Torr.

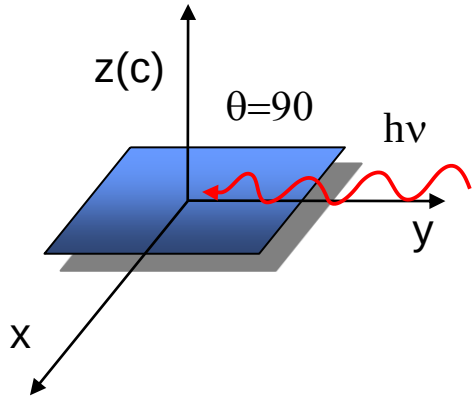


Polarization-Dependent X-ray Absorption Spectroscopy (XAS)





E//ab mode

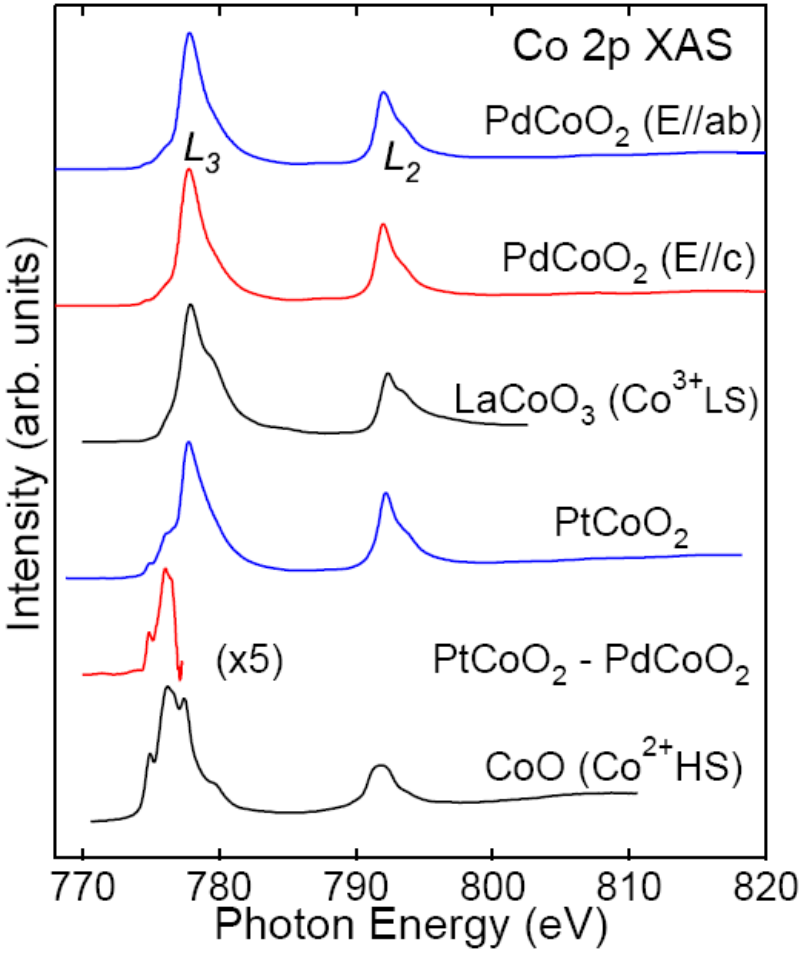


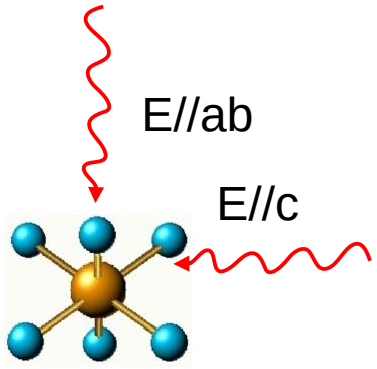
E//c mode

- Absorption coefficient:

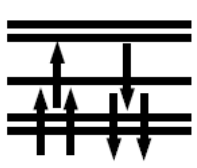
$$\sigma(\hbar\omega) \sim \sum_f \left| c_{if}\, \vec{\varepsilon} \cdot \left\langle \phi_i \left| \vec{r} \right| \phi_f \right\rangle \right|^2 \delta(E_i + \hbar\omega - E_f)$$

Valence States of the Co Cations in $PdCoO_2$



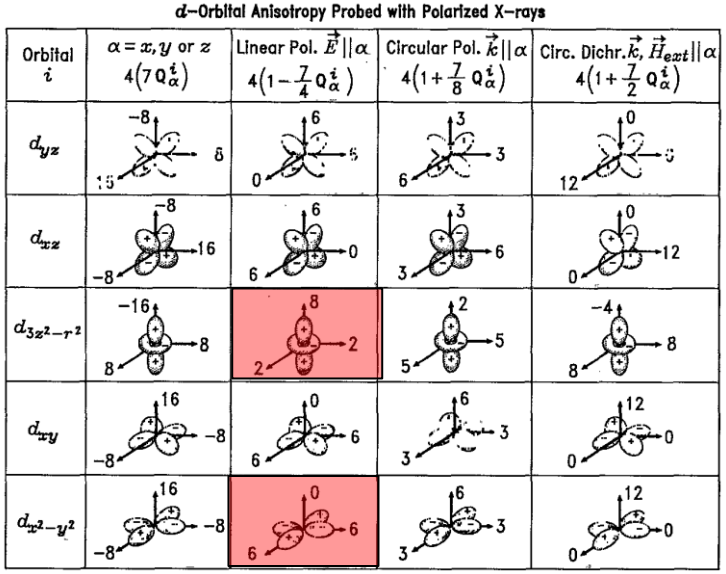


D_{3d} symmetry



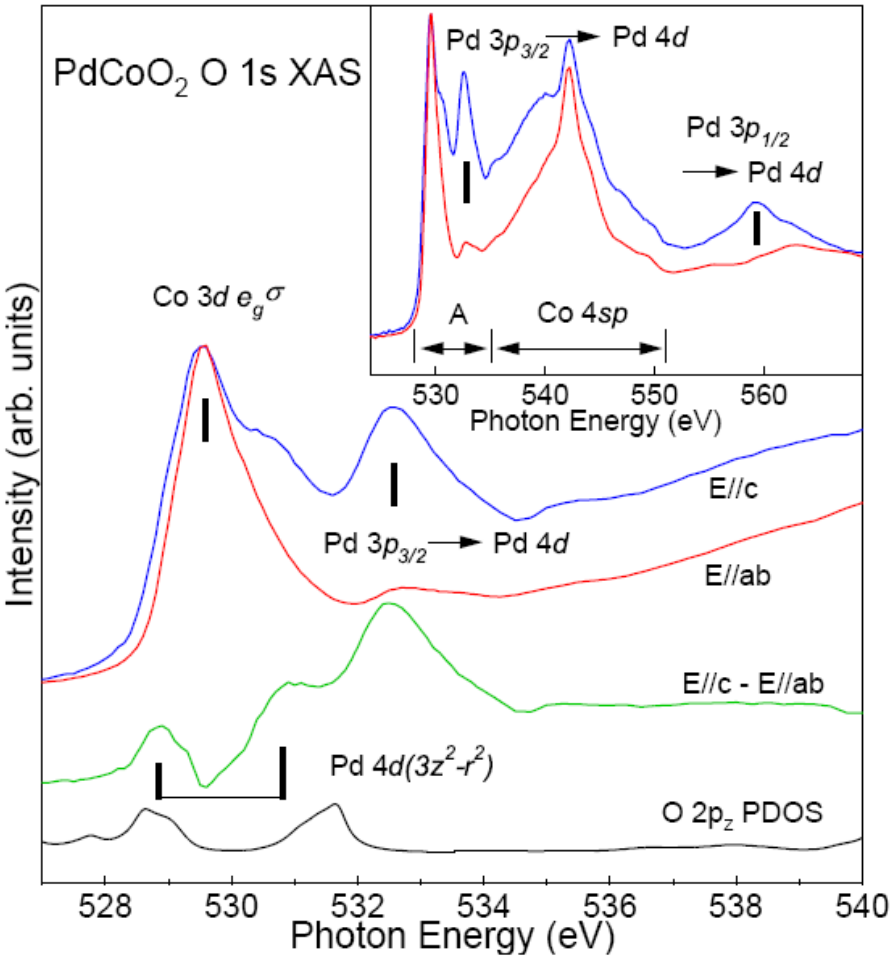
$$\left|e_g^\sigma\right\rangle = \frac{1}{\sqrt{2}}\left(\left|d_{x^2-y^2}\right\rangle \pm i\left|d_{3z^2-r^2}\right\rangle\right)$$

- Trivalent Co^{3+} ($3d^6$)
- No photon polarization dependence: empty e_g^σ states, low spin config. (S=0)



Stöhr and König, PRL **75** 3478 (1995)

Orbital Character of the Conduction Band



[Noh *et al*., PRB **80** 073104 (2009)]

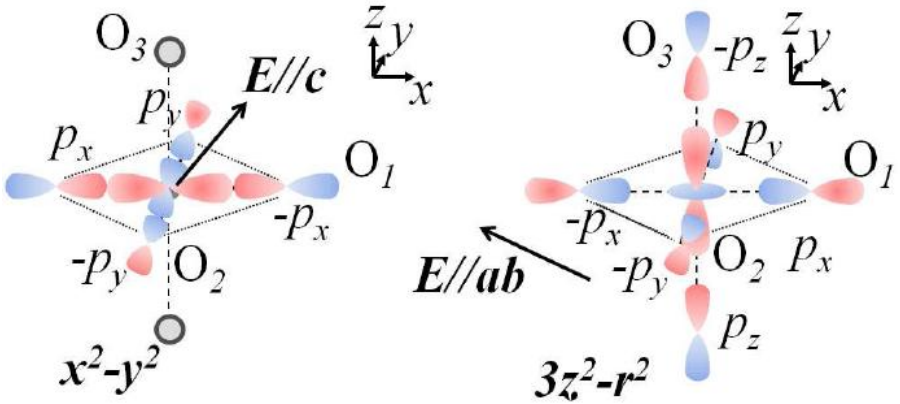
O 1s XAS ≈ O 2p-projected UDOS

$$I_{XAS} \propto \Sigma V^2_{pd}$$

- No photon polarization dependence of Co 3*d* e_g^{σ}.
- Prominent polarization dependence of Pd 4*d*($3z^2$-r^2).
- The difference spectrum contains only the character of Pd 4*d*($3z^2$-r^2).
- Good agreement with the LDA calculated O $2p_z$ partial DOS.

Contrasting pol. dependence in O 1s XAS

Co $3d^6$ (S=0) states in O K-edge XAS



$$I(E \parallel ab) \propto \left|\left\langle p_x^1 \middle| H \middle| d_{x^2-y^2} \right\rangle\right|^2 + \left|\left\langle p_x^1 \middle| H \middle| d_{3z^2-r^2} \right\rangle\right|^2$$

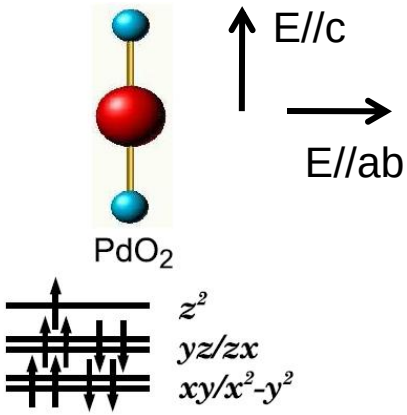
$$I(E \parallel c) \propto \frac{2}{3}\left|\left\langle p_x^1 \middle| H \middle| d_{x^2-y^2} \right\rangle\right|^2 + \frac{1}{3}\left|\left\langle p_z^3 \middle| H \middle| d_{3z^2-r^2} \right\rangle\right|^2 + \frac{2}{3}\left|\left\langle p_x^1 \middle| H \middle| d_{3z^2-r^2} \right\rangle\right|^2$$

(cf)

$$\left|\left\langle p_z^3 \middle| H \middle| d_{3z^2-r^2} \right\rangle\right|^2 = \left|\left\langle p_x^1 \middle| H \middle| d_{x^2-y^2} \right\rangle\right|^2 + \left|\left\langle p_x^1 \middle| H \middle| d_{3z^2-r^2} \right\rangle\right|^2$$

$\therefore$ *I(E//ab) = I(E//c)*

Vs. Pd $4d^9$ (S=1/2) states

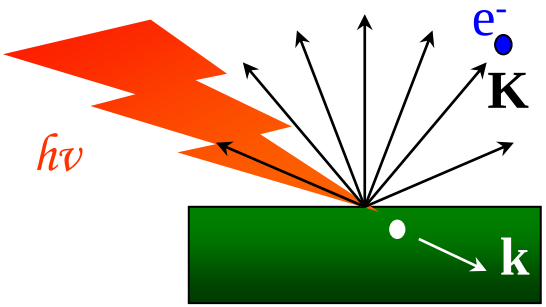


$$I(E \parallel ab) = 0 \qquad \because \overline{PdO}_{inplane} = \infty$$

$$I(E \parallel c) \propto \left|\left\langle p_z^3 \middle| H \middle| d_{3z^2-r^2} \right\rangle\right|^2$$

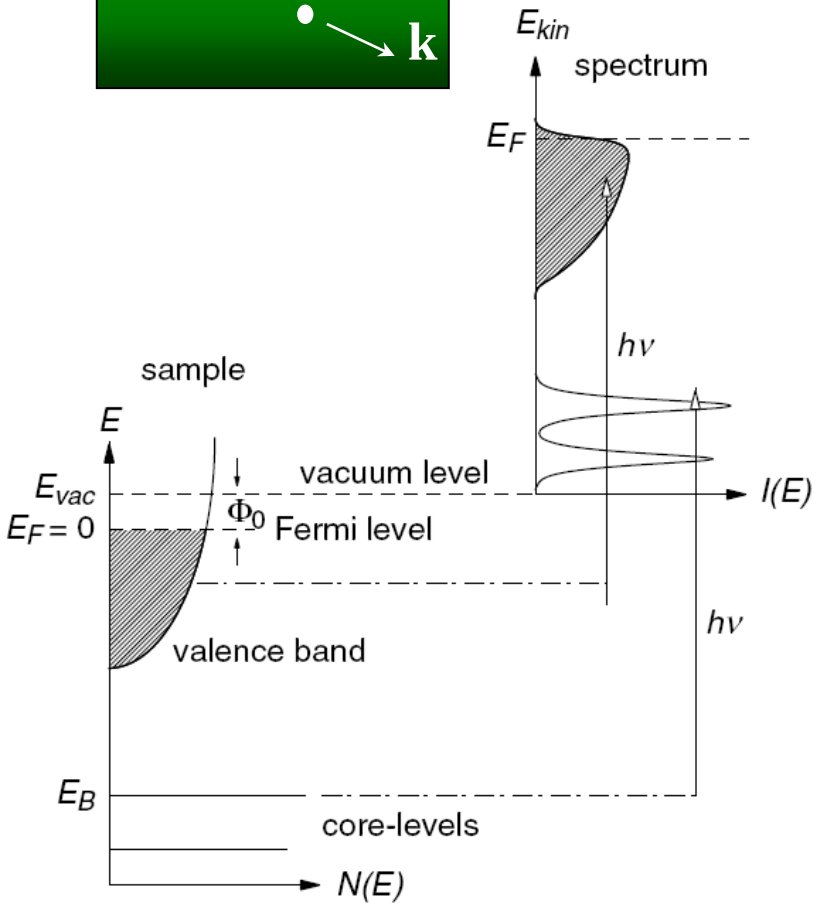
$\therefore$ *I(E//ab) << I(E//c)*

Angle-Resolved Photoemission Spectroscopy (ARPES)

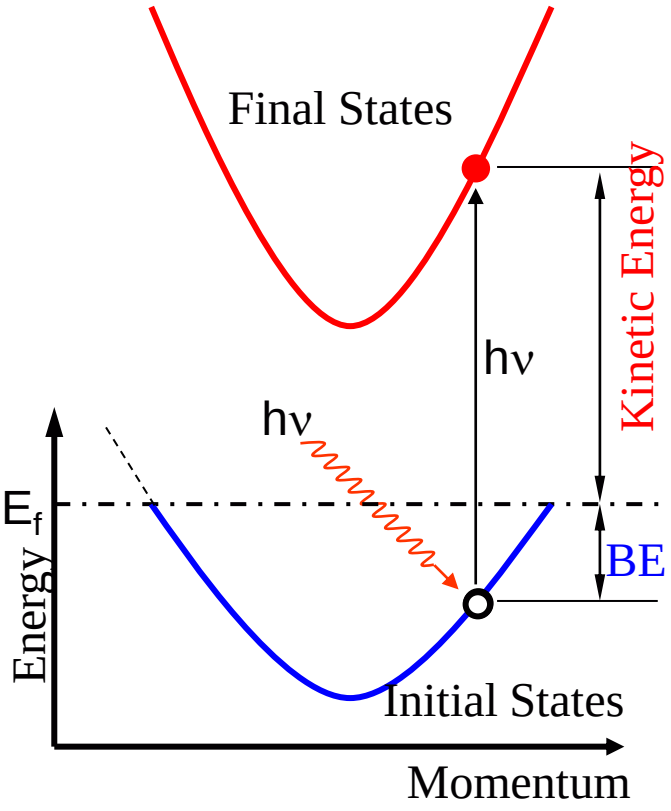


Energy conservation: $E_B = h\nu - E_{kin} - \Phi$

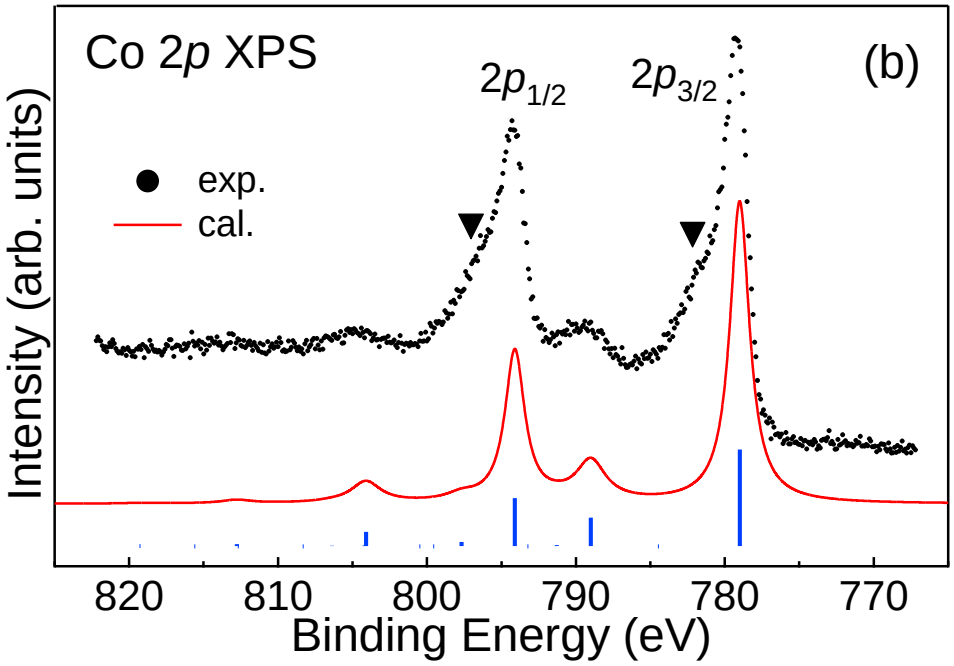
Momentum conservation: $K_{\parallel} = k_{\parallel} + G_{\parallel}$



Direct mapping of a band



Core Level PES Study of $PdCoO_2$

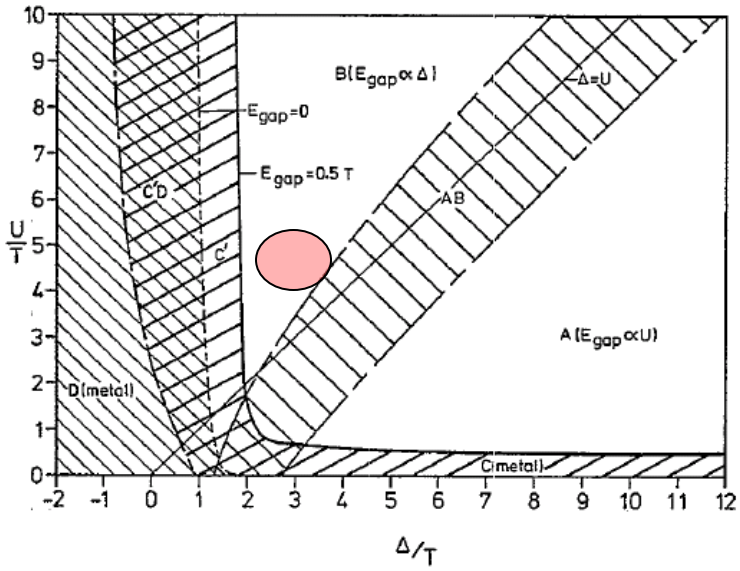


- Prominent charge-transferred satellite structures in configuration interaction model.
- Trivalent low spin Co^{3+} ($3d^6$, S=0)
- Insulating CoO_2 layers in ZSA phase diagram:
  U=5.5, Δ=3.5, W=3 eV (T= 1.0 eV)

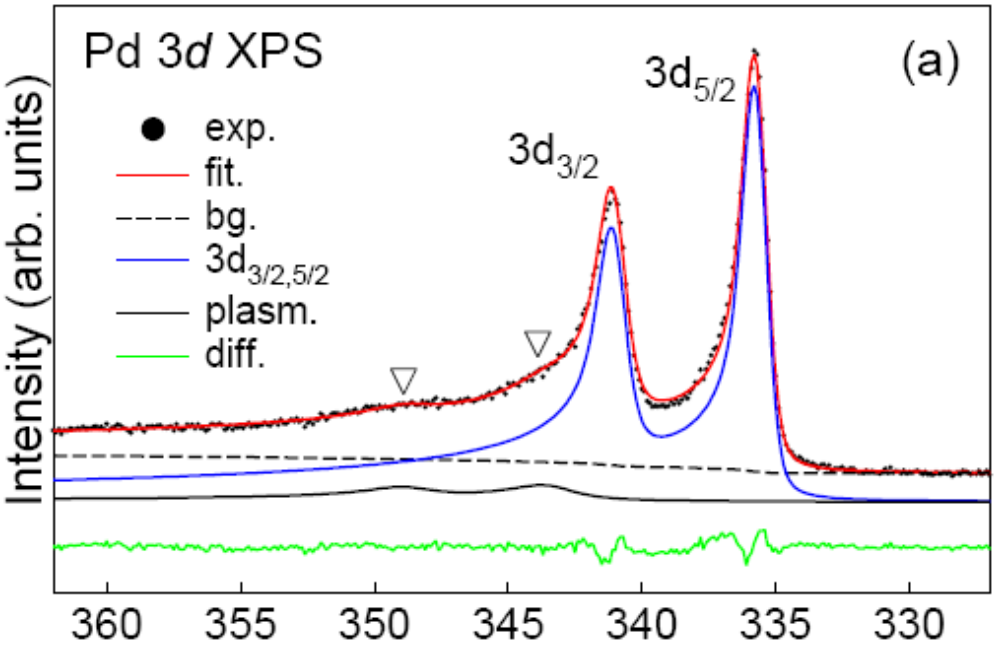
$$H_i = \begin{bmatrix} 0 & \sqrt{10-n}T & 0 \\ & \Delta & \sqrt{2(9-n)}T \\ & & 2\Delta+U \end{bmatrix} \qquad H_f = \begin{bmatrix} E_C & \sqrt{10-n}T & 0 \\ & E_C+\Delta-Q & \sqrt{2(9-n)}T \\ & & E_C+2(\Delta-Q)+U \end{bmatrix}$$

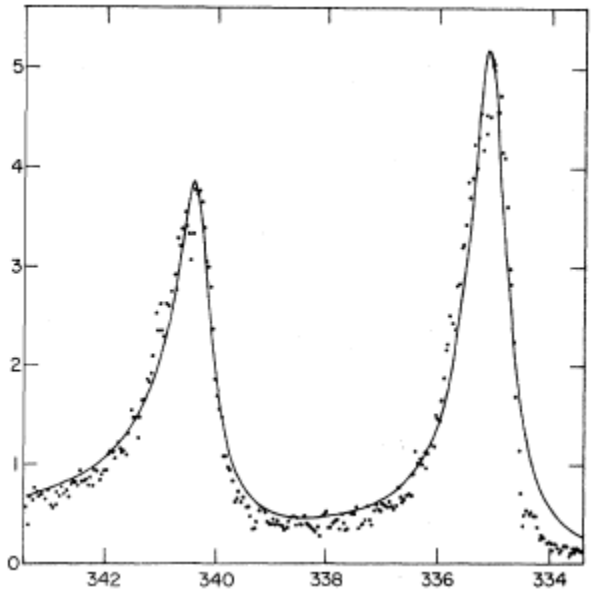
$$\Psi_i = a_0\left|d^6(t_{2g}^6)\right\rangle + a_1\left|d^7\underline{L}\right\rangle + a_2\left|d^8\underline{L}^2\right\rangle$$

$$\Psi_f = a_0\left|d^5\right\rangle + a_1\left|d^6\underline{L}\right\rangle + a_2\left|d^7\underline{L}^2\right\rangle$$



Core Level PES Study of $PdCoO_2$





$$I(\epsilon) = \frac{cos[\pi\alpha/2 + (1-\alpha)arctan(\epsilon/\gamma)]}{(\epsilon^2+\gamma^2)^{(1-\alpha)/2}},$$

- Prominent asymmetric Doniach-Sunjic line shape: asymmetric parameter α=0.26 (cf) α_{Pd}=0.25/0.11
- Plasmon structure
- Metallic PdO_2 layers

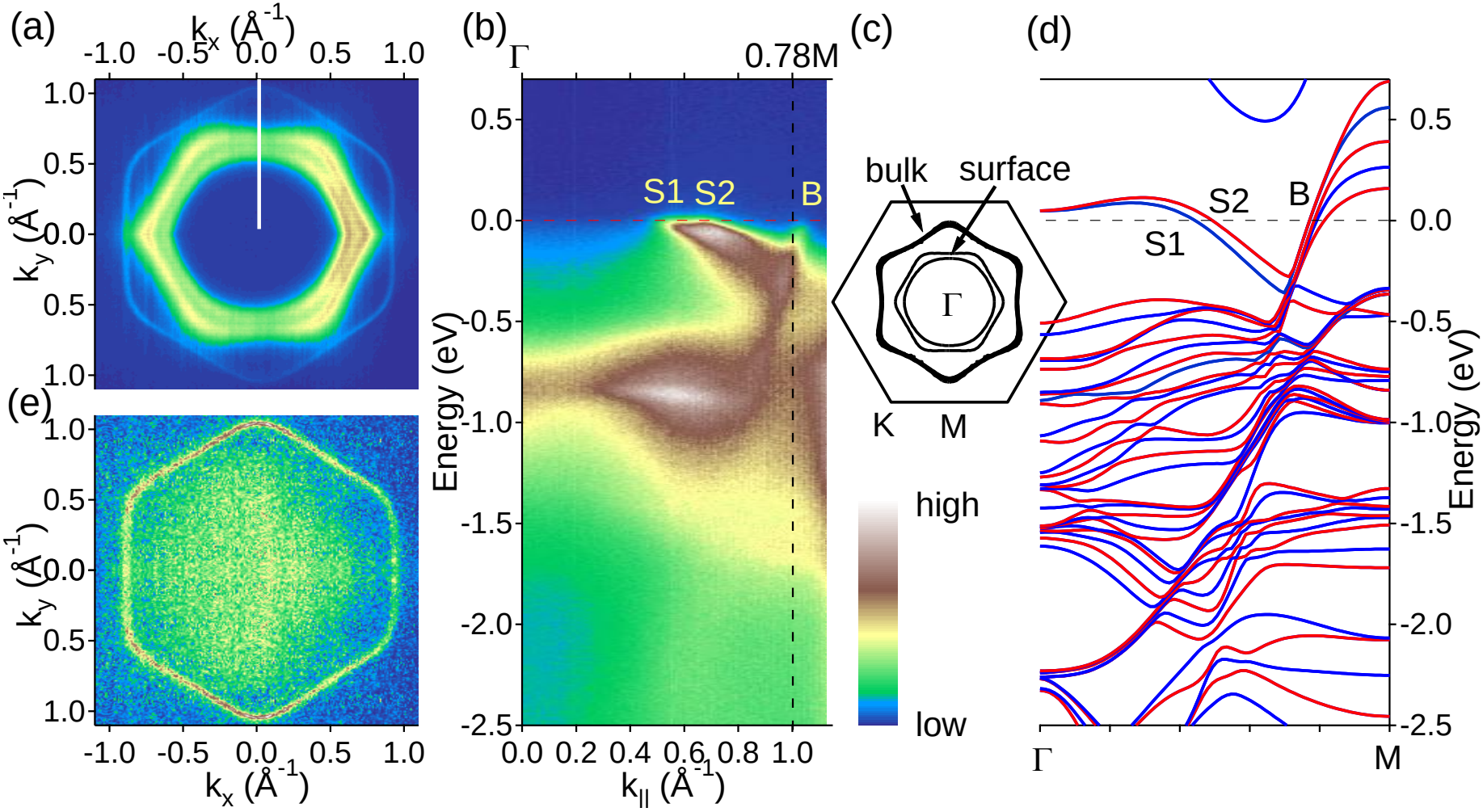
$$\alpha = 2\sum_{l=0}^{l_{max}} (2l+1)(\delta_l/\pi)^2$$

PHYSICAL REVIEW B 11 678

S. Hüfner* and G. K. Wertheim

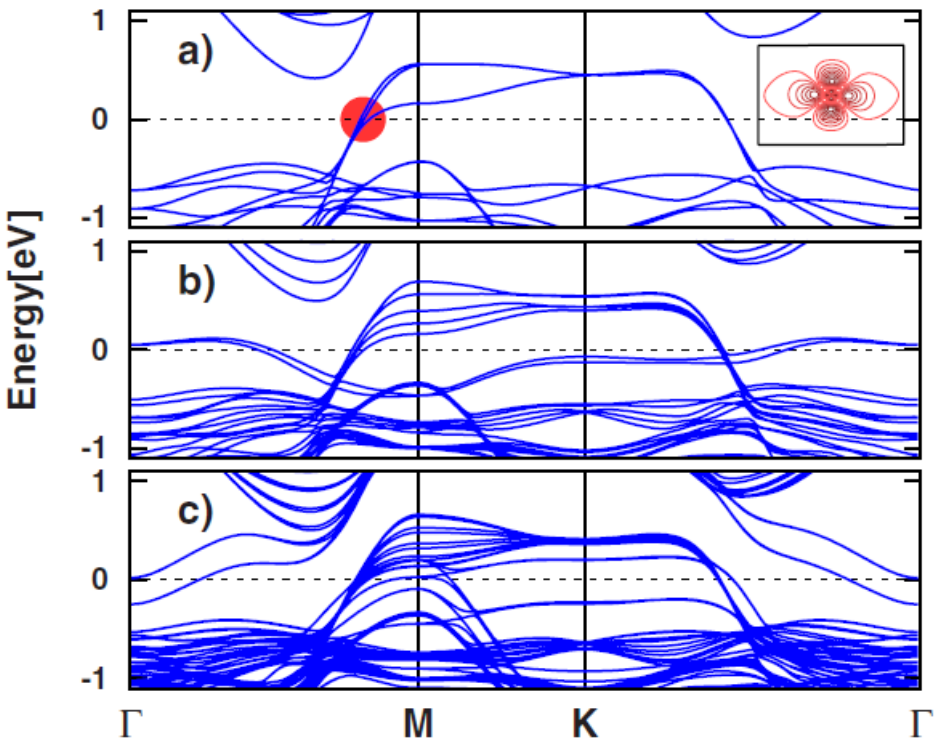
Stack structure of metallic Pd and insulating CoO_2 layers!

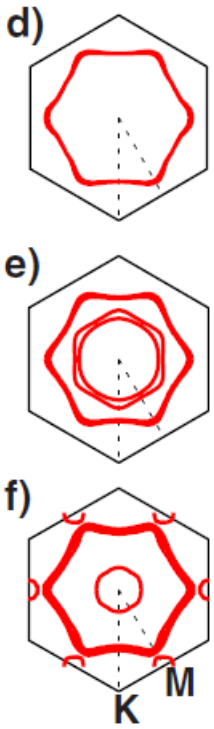
ARPES data of $PdCoO_2$



[Noh *et al.*, PRL **102** 256404 (2009)]

Surface States of $PdCoO_2$



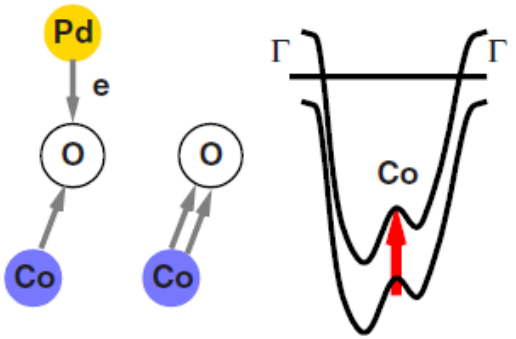


Bulk FS

FS for CoO_2-terminated surface

FS for Pd-terminated surface

a) CoO_2 terminated $PdCoO_2$



[Kim *et al*., PRB **80** 035116 (2009)]

Conductivity of $PdCoO_2$ from ARPES

Under the relaxation time approximation, conductivity tensor is

$$\sigma_{ij} = e^2 \sum_{\vec{k}}^{BZ} (-\frac{\partial f_0}{\partial \varepsilon}) \tau_{\vec{k}} v_{\vec{k}_i} v_{\vec{k}_j}, \quad v_{\vec{k}} = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial \vec{k}}$$

f_0 Fermi-Dirac distribution
$\tau_{\vec{k}}$ relaxation time
$v_{\vec{k}}$ electron velocity in band

Seebeck coefficient:

$$S_{ij} = e k_B \sigma^{-1} \sum_{\vec{k}}^{BZ} (-\frac{\partial f_0}{\partial \varepsilon}) \tau_{\vec{k}} v_{\vec{k}_i} v_{\vec{k}_j} \frac{\varepsilon_{\vec{k}} - \mu}{k_B T}$$

Electronic thermal conductivity:

$$\kappa_{ij} = k_B^2 T \sum_{\vec{k}}^{BZ} (-\frac{\partial f_0}{\partial \varepsilon}) \tau_{\vec{k}} v_{\vec{k}_i} v_{\vec{k}_j} \left[\frac{\varepsilon_{\vec{k}} - \mu}{k_B T} \right]^2 - T \sigma S S$$

T. Thonhauser *et al.*, PRB **68** 085201 (2003)

Estimation of relaxation time from ARPES

Spectral function:

$$A(\vec{k},\omega) = \frac{1}{\pi} \frac{\Sigma''(\vec{k},\omega)}{[\omega - \varepsilon_{\vec{k}} - \Sigma'(\vec{k},\omega)]^2 + [\Sigma''(\vec{k},\omega)]^2}$$

where $\Sigma'(\vec{k},\omega)$ real part of electron self energy

$\Sigma''(\vec{k},\omega)$ imaginary part of electron self energy

From energy distribution curve (EDC)

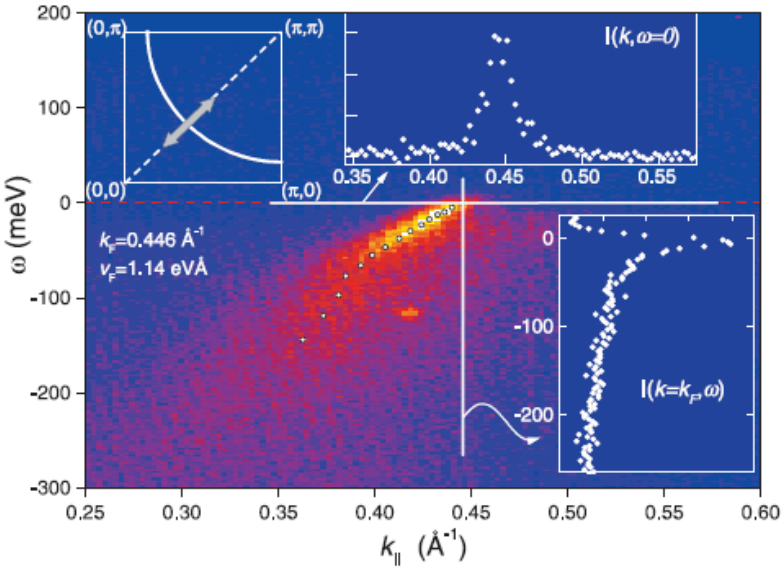
$$\tau_{\vec{k}} = \hbar / \left| 2\Sigma''(\vec{k},\omega) \right|$$

From momentum distribution curve (MDC)

$$\tau_{\vec{k}} = 1 / v_{\vec{k}} \Delta k$$

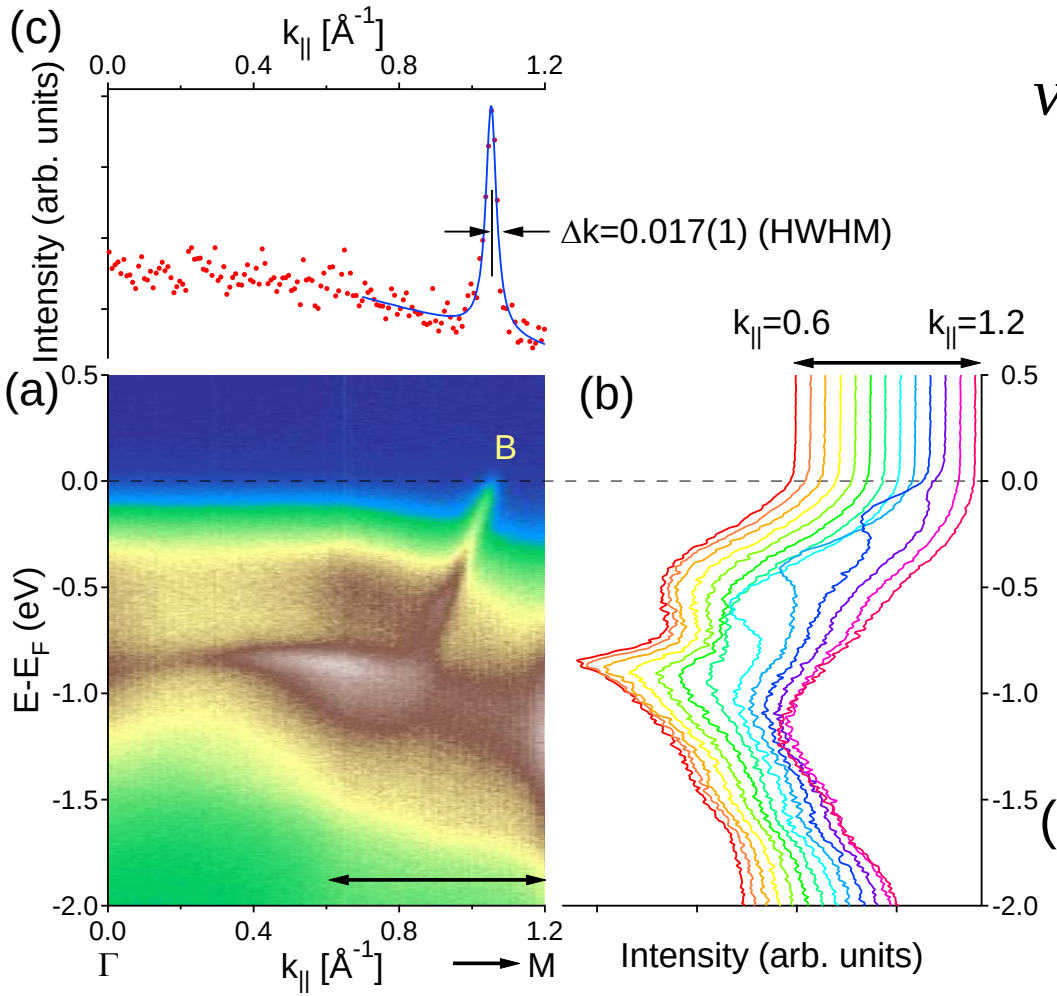
where $v_{\vec{k}} = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial \vec{k}}$

Δk : peak width in MDC



T. Valla,[1]

Estimation of relaxation time from ARPES



$$v_{k_x} = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k_x} \cong 4.96/\hbar \quad [\text{eVÅ}]$$

$$\Delta k \cong 0.017 \quad [\text{Å}^{-1}]$$

$$\tau_{k_x} = 1/v_{k_x}\Delta k \cong 7.6\times10^{-15} \text{ [sec]}$$

$$\rho_{xx} \cong 13\,\mu\Omega cm$$

(cf) transport measurement value:

$$\rho_{ab,tr} = 4.7\,\mu\Omega cm$$

Summary

- $PdCoO_2$ can be regarded as a natural two-dimensional metal-insulator superlattice structure.
  - The Co ions are in low spin trivalent state ($3d^6$, S=0).
  - The CoO_2 layers are insulating.
  - PdO_2 layers are metallic.
- The Fermi surface is in very good agreement with the LDA calculation result.
  - The electronic structure is nearly two-dimensional.
  - The conduction band has Pd $4d(3z^2\text{-}r^2)$ character.
- ρ_{ARPES} is very consistent with $\rho_{transport}$.
  - High carrier velocity, large two-dimensional Fermi surface, and long life time of the carriers.
- The surface states are well explained by the CoO_2 terminated surface with relaxation of Co and O position at the surface.

Part 2

Electronic Origin of Giant Magnetic Anisotropy in Multiferroic $LuFe_2O_4$

Han-Jin Noh*, Kyung Tae Ko[1], B.-G. Park[1], J.-H. Park[1],
Jae-Young Kim[2], A. Tanaka[3], S. B. Kim[1],
C. L. Zhang[4], S.-W. Cheong[4]

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4 Rutgers Center for Emergent Materials, Rutgers University.

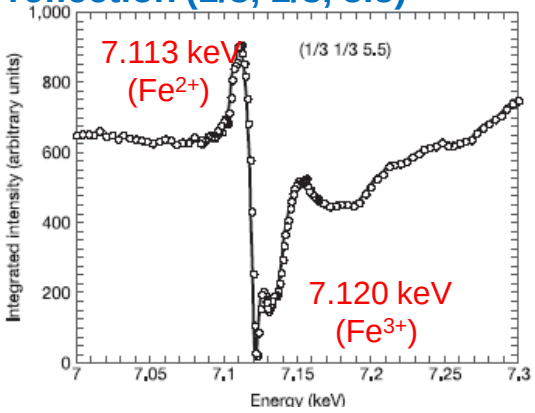
$LuFe_2O_4$, New type of ferroelectric material

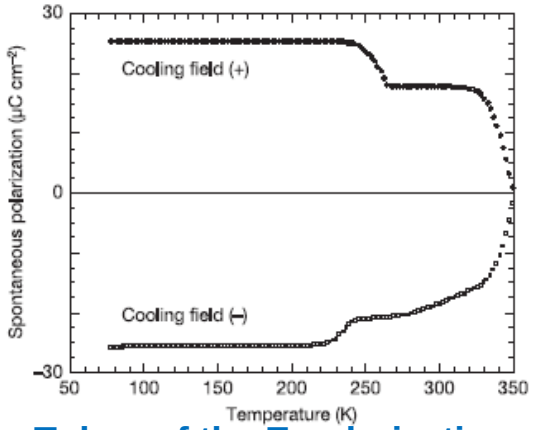
- Electronic ferroelectricity:

  inversion symmetry breaking by charge ordering.

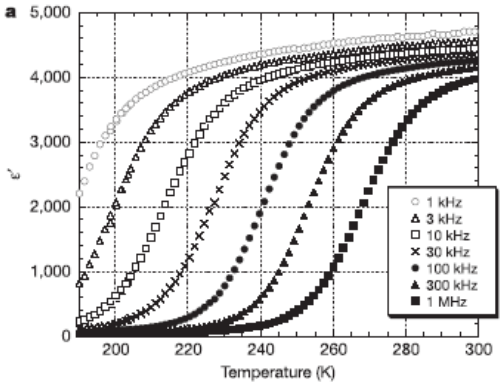
  [N. Ikeda *et al*., *Nature* **436** 1136 (2005)]

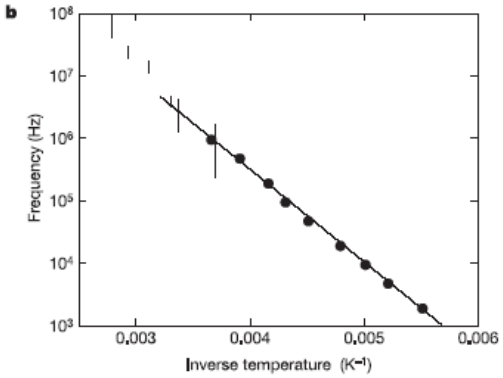
X-ray energy dep. of the superlattice reflection (1/3, 1/3, 5.5)





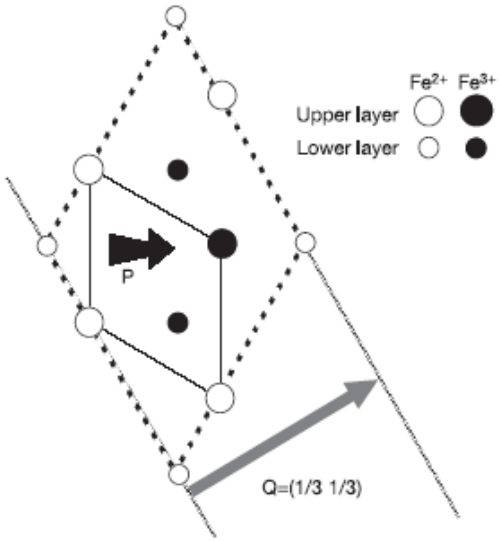
T dep. of the E polarization



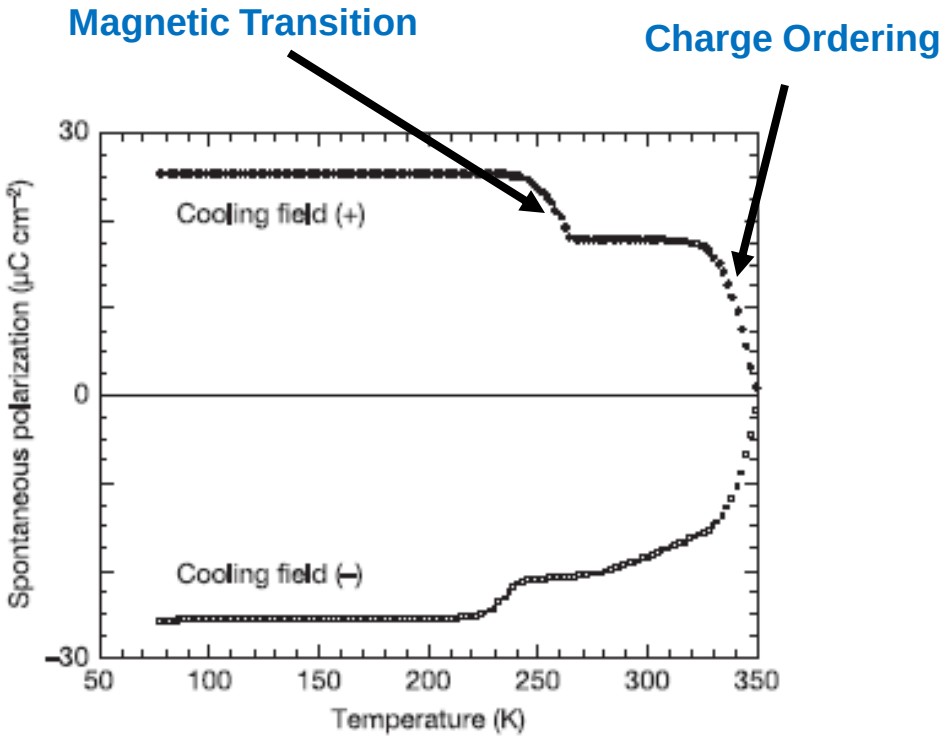


Dielectric constant dispersion: Electron fluctuation of Fe ions

Proposed CO Model

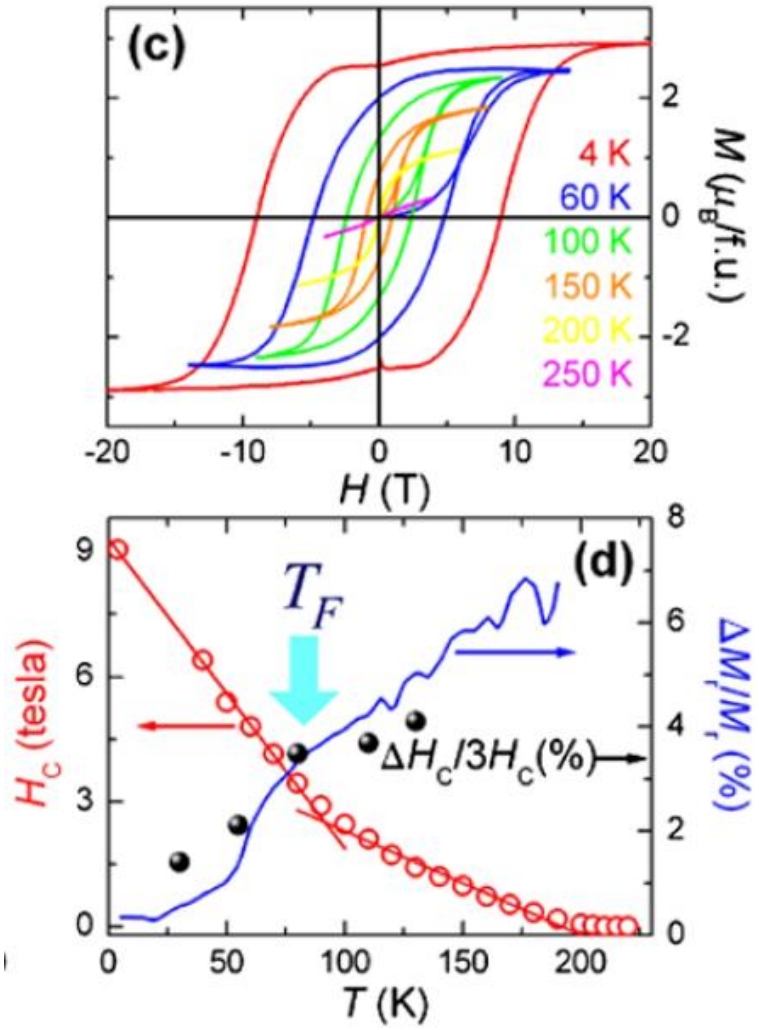


Electronic and local magnetic structure?

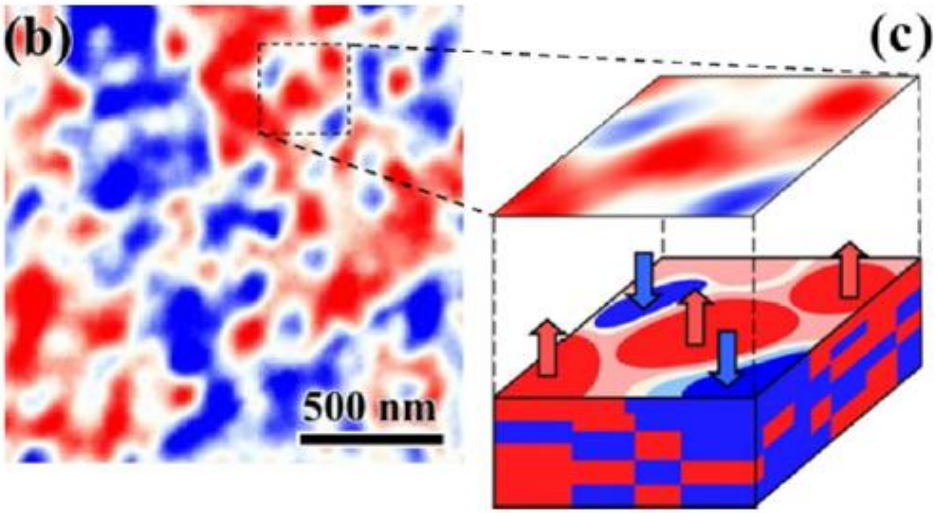


- Coupling between charge, spin, and possibly orbitals degrees of freedoms.

Giant Magnetic Coercivity

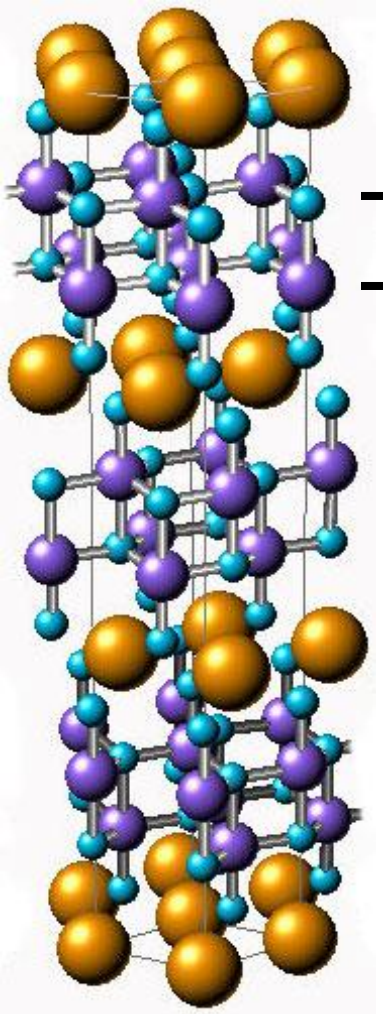


- Giant magnetic coercivity: ~10 T at 4.2 K.
- Ising domains: collective magnetic freezing
- Microscopic origin?

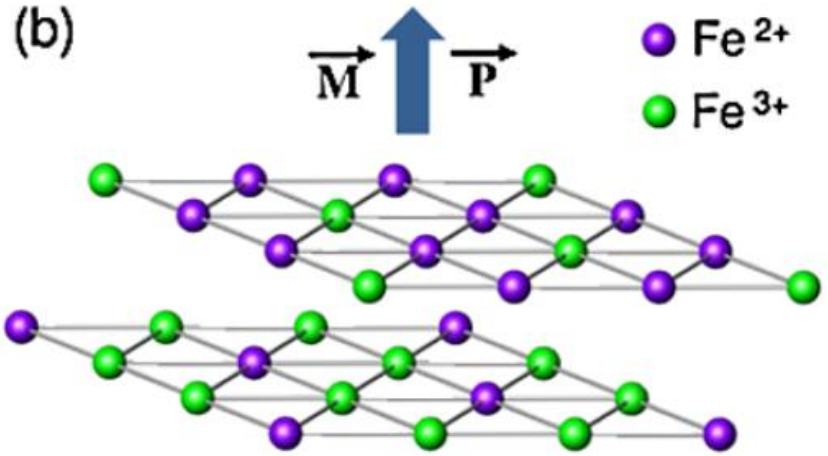


[PRL **101**, 137203 (2008), Wu *et al*.]

$LuFe_2O_4$

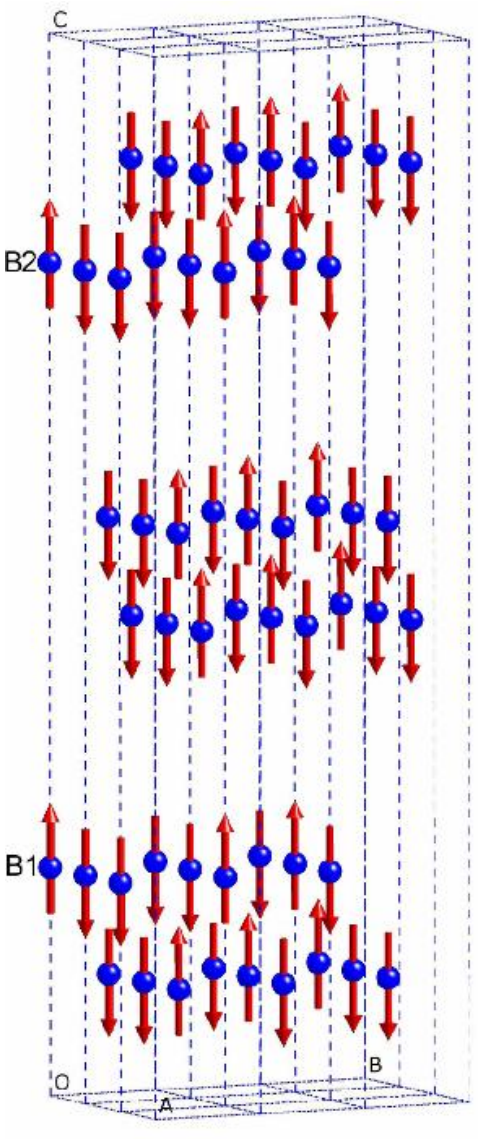


Fe-O double layer



- Rhombohedral (*R*$\underline{3}$*m*)
- Mixed valence and mixed spins of Fe ions:
  Fe^{3+} S_1=5/2, Fe^{2+} S_2=2
- Spin structure?

Neutron Scattering Study on $LuFe_2O_4$



Q=(1/3 1/3 0)
D1

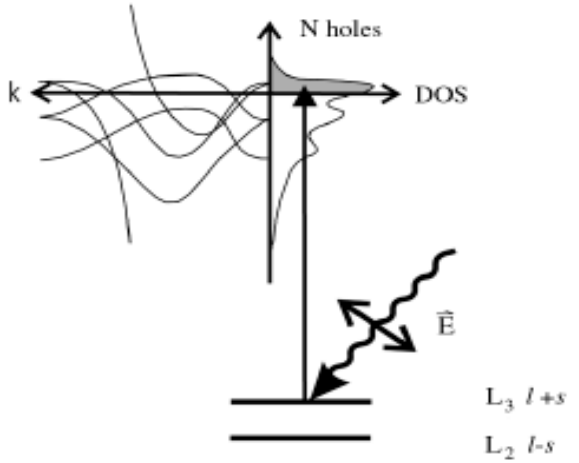
[PRL **100**, 107601 (2008), Christianson *et al*.]

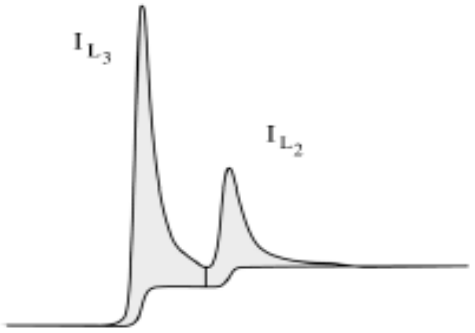
- Ferrimagnetic structure: an excess of 1/3 of the spins points along the c axis.
- Averaged spin model ($Fe^{2.5+}$ ions)
- The saturation moment:

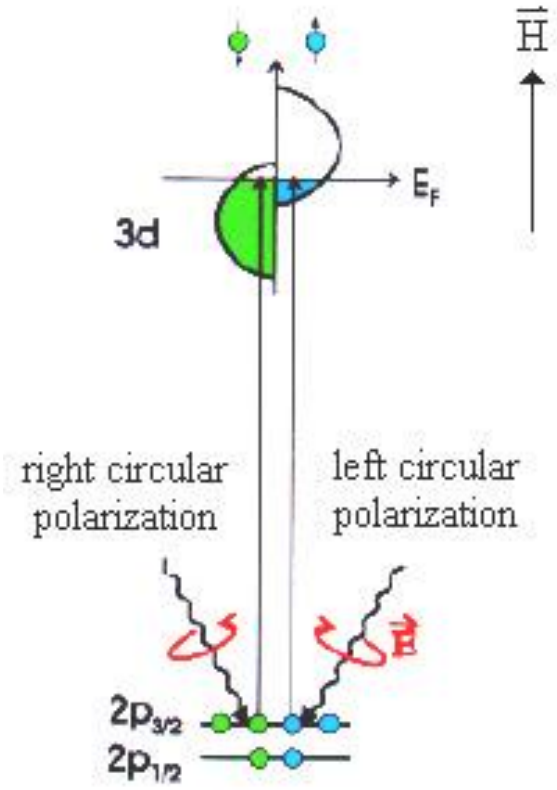
$$1/3 \times 4.5\mu_B \times 2\mathrm{Fe}/\ f.u. = 3\mu_B / f.u.$$

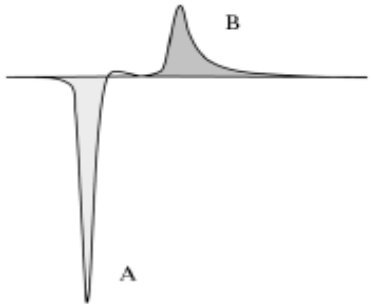
(cf) measured value: $2.9\mu_B / f.u.$

L_{23} XAS and X-ray Magnetic Circular Dichroism





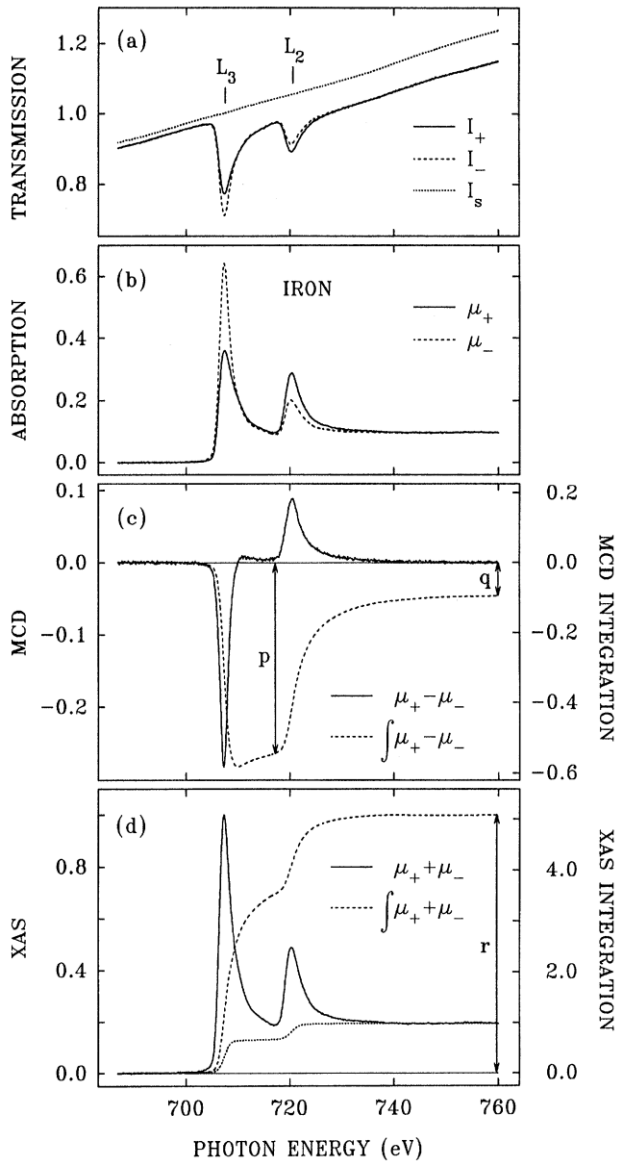




Configuration Interaction Cluster Model
with Full Ionic Multiplet Structure

F.M.F de Groot *et al*., PRB **42** 5459 (1990)
K. Cho *et al*., PRB **63** 155203 (2001)

Sum rule analysis



$$m_{orb} = -\frac{4}{3}(10 - n_d)\frac{q}{I_0}$$

$$\frac{m_{orb}}{m_{spin}} \cong \frac{2q}{9p - 6q}$$

$$p = \int_{L_3} (\mu_+ - \mu_-) d\omega$$

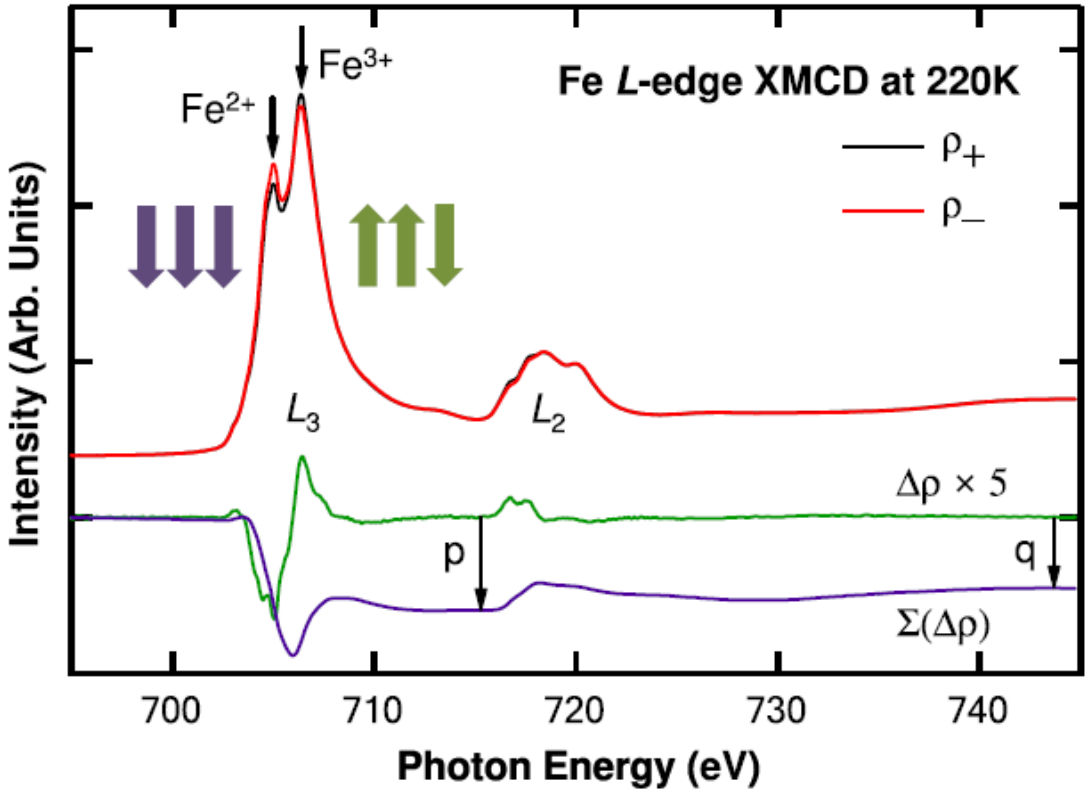
$$q = \int_{L_3 + L_2} (\mu_+ - \mu_-) d\omega$$

$$I_0 = \int_{L_3 + L_2} (\mu_+ + \mu_-) d\omega$$

B. T. Thole *et al.*, PRL **68** 1943 (1992)

C. T. Chen *et al.*, PRL **75** 152 (1995)

Fe 2p XMCD of $LuFe_2O_4$



[PRL **103**, 207202 (2009), Ko, Noh *et al*.]

- Net S_1 from Fe^{2+} is parallel to the external field B, net S_2 from Fe^{3+} is antiparallel to B; the total spin is parallel to B.
- The orbital moment is parallel to the net spin moment.
- Net S_1 is larger than net S_2.
- Sum rule analysis: $M_o/M_s = 0.34 \pm 0.05$

Saturation magnetic moment

Per 3 formula units,

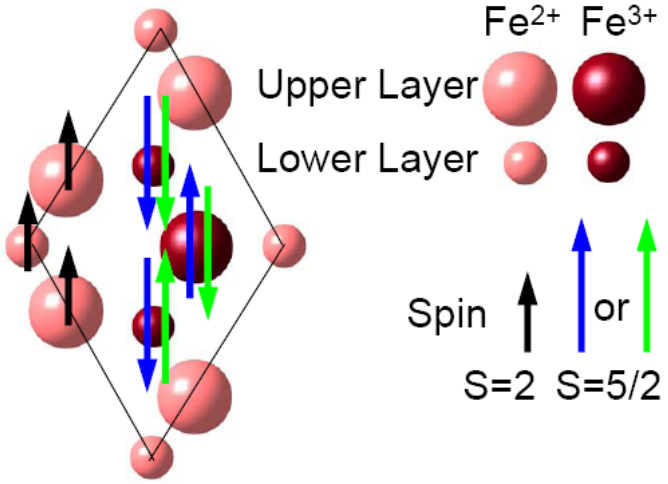
$$m_{s1,net} = 4\mu_B \times 3 = 12\mu_B$$

$$m_{s2,net} = 2 \times \frac{5}{2}\mu_B (2-1) = 5\mu_B$$

$$m_s = m_{s1,net} - m_{s1,net} = 7\mu_B$$

$$m_{orb} = m_s \times (\sim 0.34) = 2.4\mu_B$$

$$m_{tot} = m_s + m_{orb} = 9.4\mu_B$$

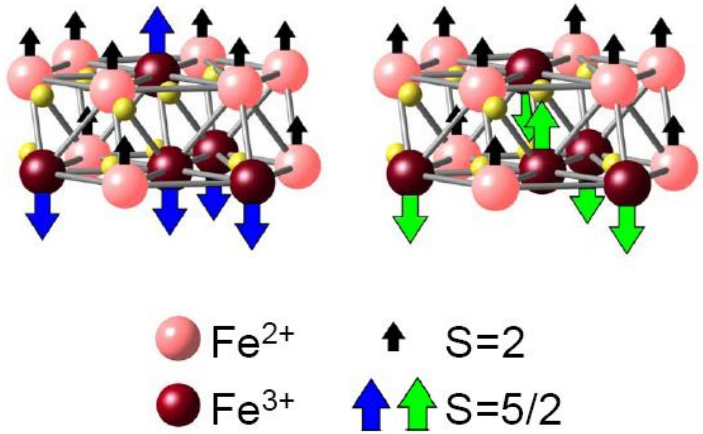


Per 1 formula unit,

$$m_{spin} = 7.0\mu_B / 3 = 2.3\mu_B$$

$$m_{orb} = 2.3\mu_B / 3 = 0.8\mu_B$$

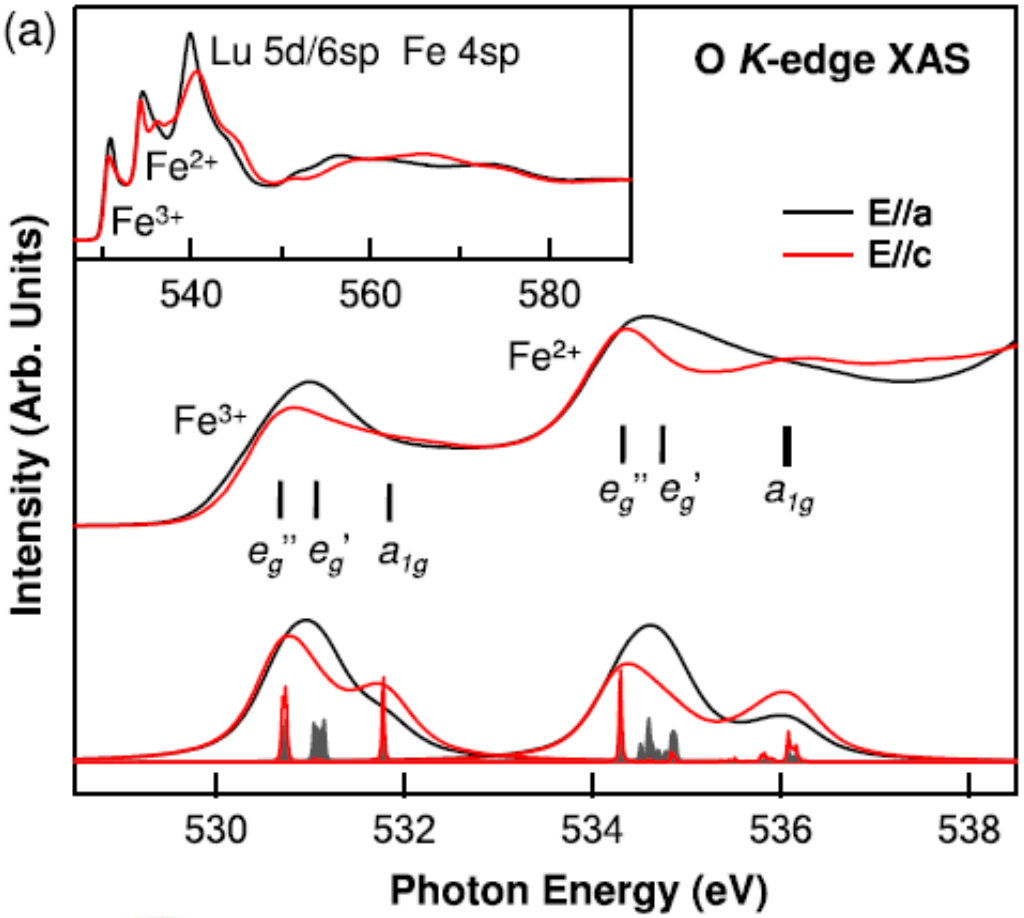
$$m_{tot} = 9.4\mu_B / 3 = 3.1\mu_B$$



(cf) measured moment:

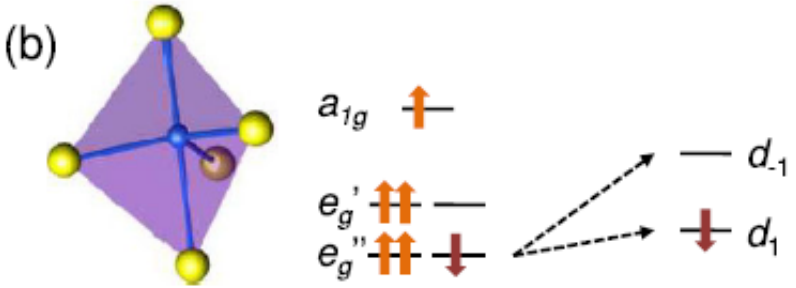
$$m_{sat} = 2.9\mu_B$$

Origin of the large orbital moment



[PRL **103**, 207202 (2009), Ko, Noh *et al*.]

- Fe^{3+} ions have perfect orbital quenching.
- Spin-orbit coupling splits the degenerate e_g" states into m=1 and m=-1 states in the Fe^{2+} (d^6) ions.



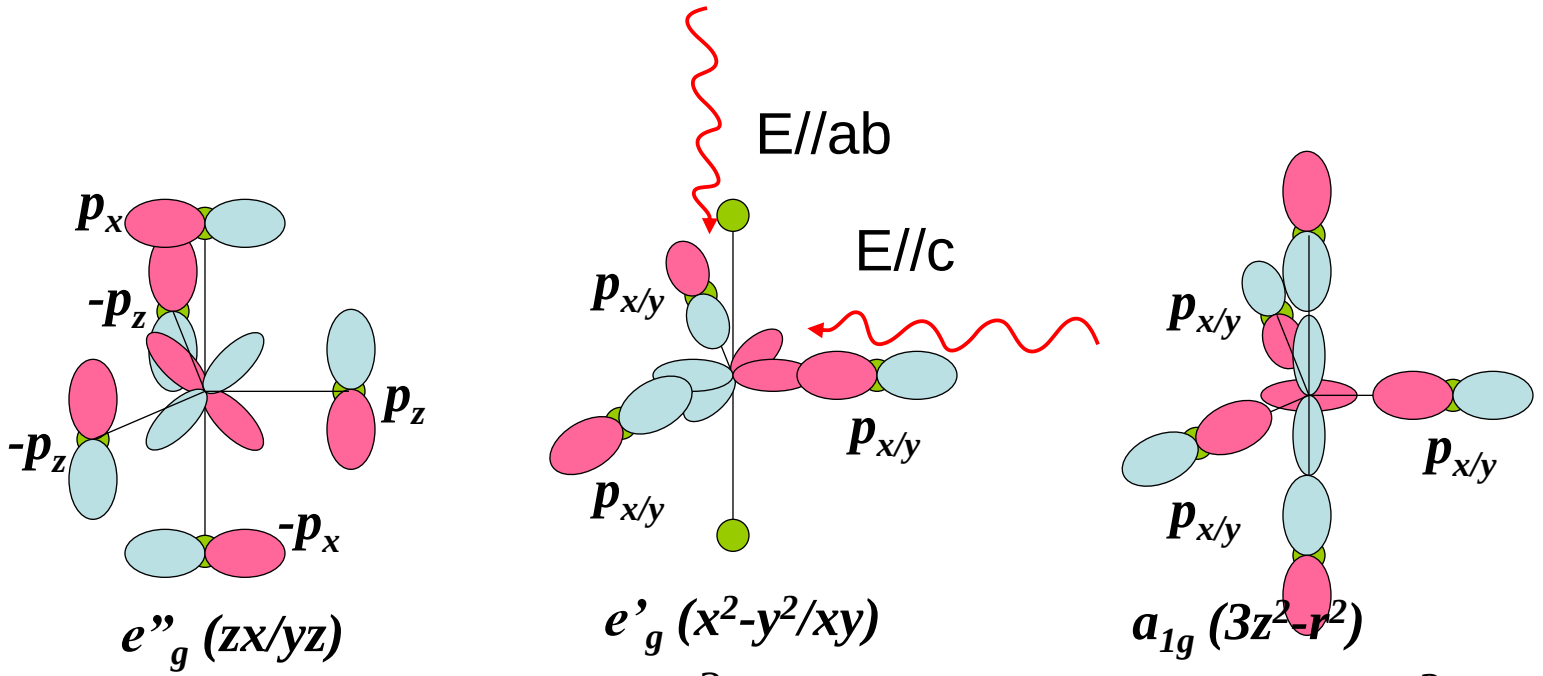
$$\left|d_{yz}\right\rangle = \frac{i}{\sqrt{2}}\left(\left|l=2,m=1\right\rangle + \left|2,-1\right\rangle\right)$$

$$\left|d_{zx}\right\rangle = \frac{-1}{\sqrt{2}}\left(\left|l=2,m=1\right\rangle - \left|2,-1\right\rangle\right)$$

O *K*-edge XAS and Orbital Selectivity

- Absorption coefficient: $\sigma(\hbar\omega) \sim \left|\vec{\varepsilon} \cdot \langle \vec{r} \rangle\right|^2$

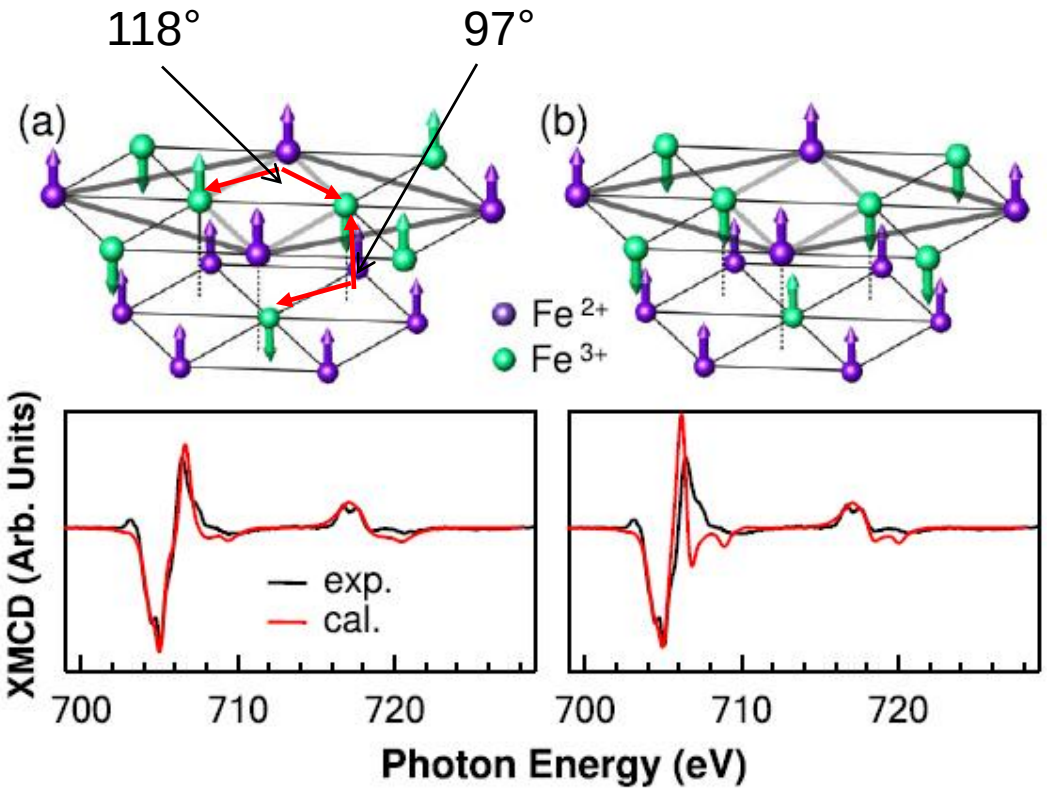
- Photon polarization dependence



$$V^2_{yz/zx} = 2V^2_{pd\pi} + \frac{3}{2}V^2_{pd\pi}\kappa^7 \qquad V^2_{xy/x^2-y^2} = \frac{3}{8}(3V^2_{pd\sigma} + 4V^2_{pd\pi})\kappa^7 \qquad V^2_{3z^2-r^2} = 2V^2_{pd\sigma} + \frac{3}{4}V^2_{pd\sigma}\kappa^7$$

Spin alignment

- Cluster model calculation + Madelung potential difference for Fe^{2+}-rich plane and Fe^{3+}-rich plane shows that the anti-parallel Fe^{3+} spin alignment in Fe^{3+}-rich plane is more plausible.



- The spin of Fe^{2+} is pinned by the spin-orbit coupling.
- The spin of Fe^{3+} is dominated by the super-exchange interaction via interlayer Fe^{3+}-O-Fe^{3+}.

[PRL **103**, 207202 (2009), Ko, Noh *et al*.]

Conclusion

- The XMCD shows that the system has the large unquenched orbital magnetic moment, which originates the giant magnetic anisotropy and coercivity.

- The combined analysis by the XMCD sum-rule and cluster model calculation definitely determines the ferrimagnetic spin alignment of $LuFe_2O_4$.

- Polarization dependent O 1*s* XAS reveals that the e_g" (d_{zx}, d_{yz}) states are the lowest, which are split by the spin-orbit coupling and results in the large orbital moment at the Fe^{2+} sites.