Valence band studies on transition metal oxides by soft x-ray photoemission

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experiments

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T. Muro (JASRI, SPring-8)

high-energy photoemission (BL25SU, SPring-8)

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Y. Maeno (U Kyoto)

Fe_3O_4

$Sr_2Ru_{1-x}Ti_xO_4$

single crystals

Outline

Fe_3O_4:

- Magnetite: A mixed-valent transition metal oxide
  (crystal structure, magnetism, electronic properties - Verwey transition)
- Photoemission and surface effects
- Verwey transition and polaron physics investigated by high-energy photoemission

$Sr_2Ru_{1-x}Ti_xO_4$:

- $Sr_2Ru_{1-x}Ti_xO_4$: Doping a non-cuprate layered-perovskite superconductor close to magnetic instabilities
- Photoemission, surface reconstruction and FS topology
- Electronic structure as derived from high-energy ARPES

Fe_3O_4: a mixed-valent transition metal oxide

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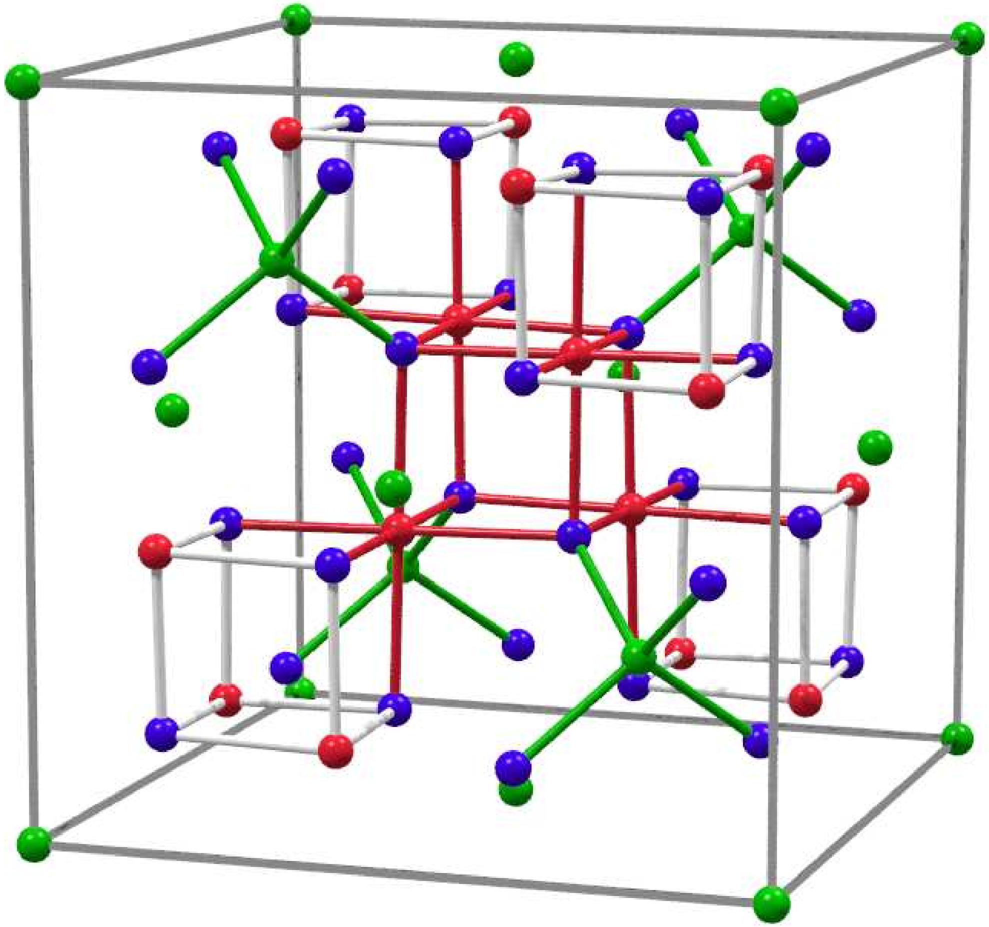
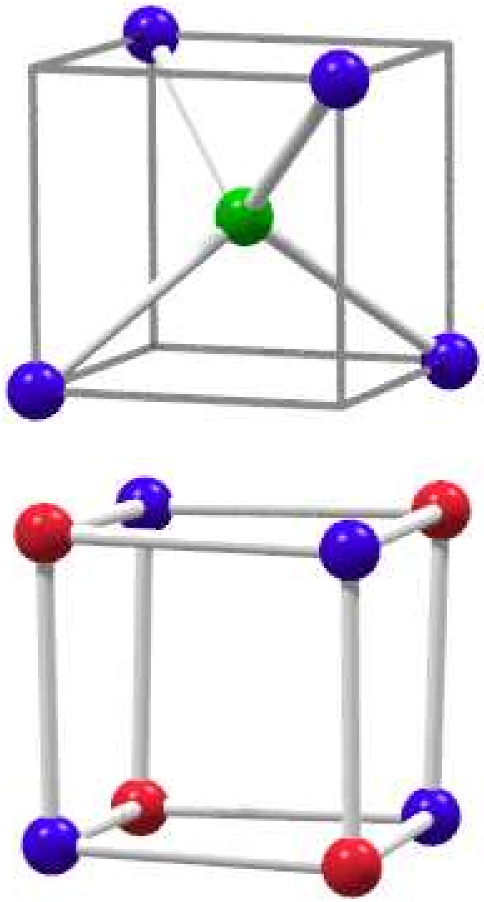
Fe_3O_4: $(Fe^{3+})(Fe^{2+}Fe^{3+})O_4$

A B$_2$ O$_4$

inverse spinel structure





Fe_3O_4: a mixed-valent transition metal oxide

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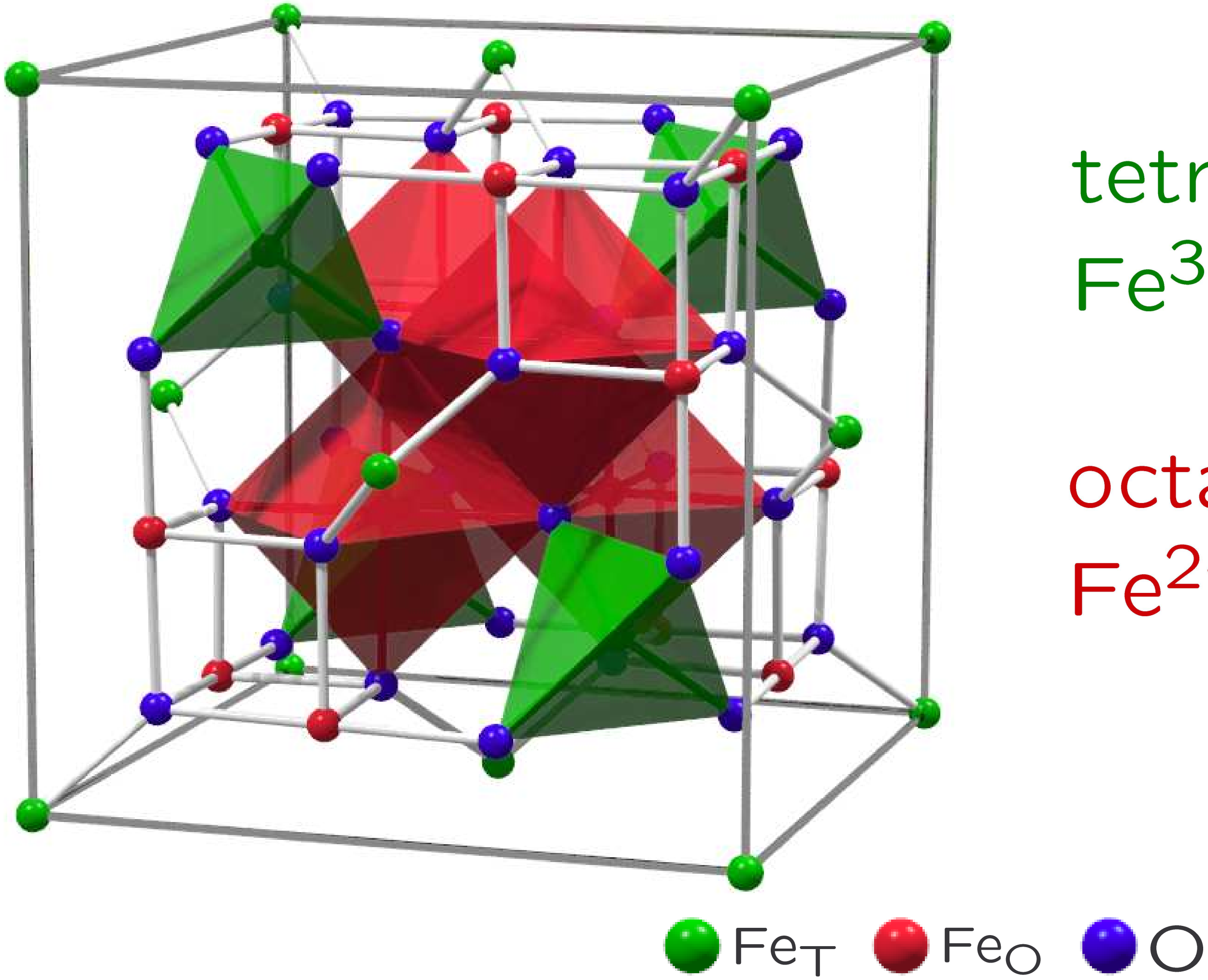


tetrahedral A sites: Fe^{3+}

octahedral B sites: $Fe^{2+} : Fe^{3+} = 1 : 1$

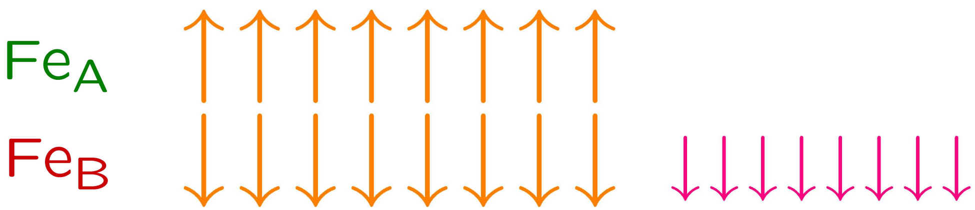
Fe_3O_4: magnetism

Local moments:

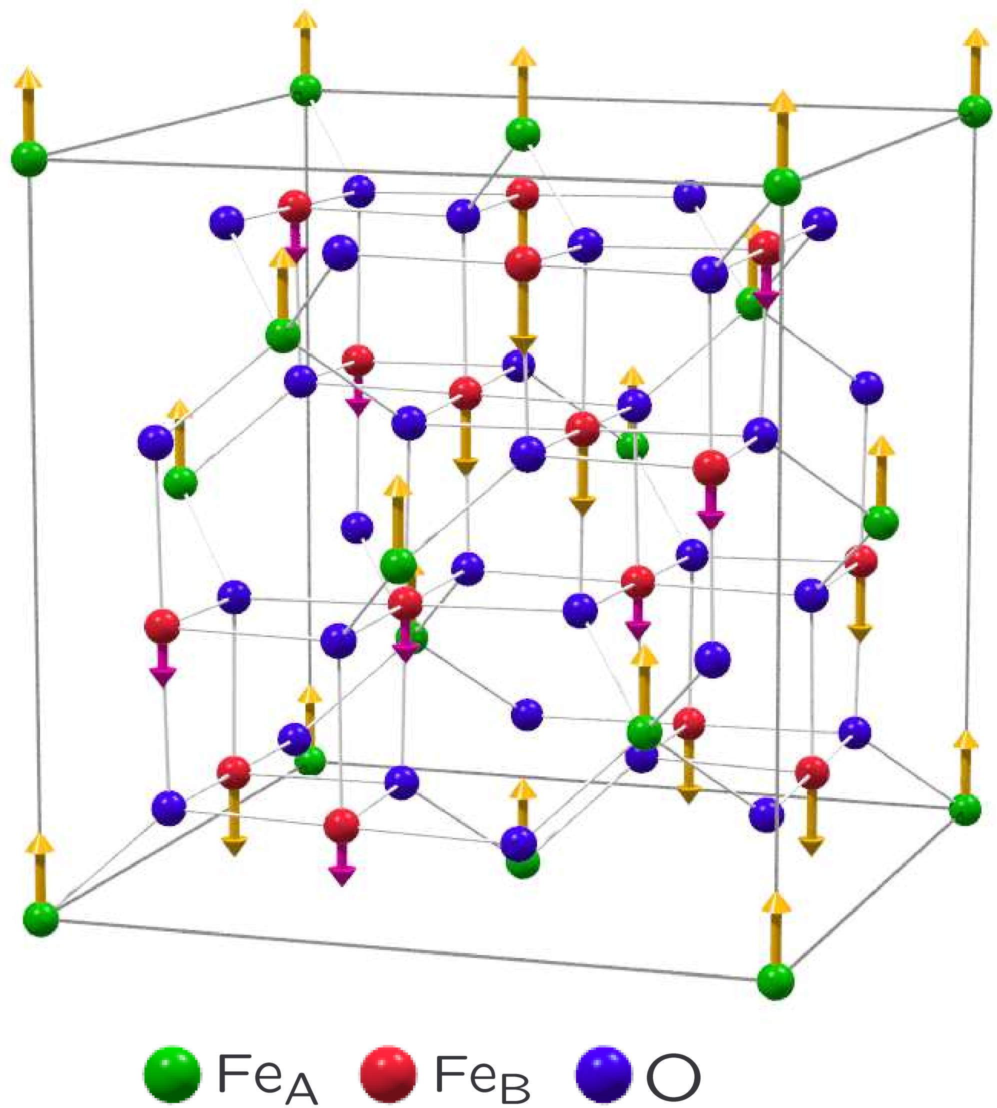
$Fe^{2+}(d^6) \rightarrow S = 2, \mu = 4.9\mu_B$

$Fe^{3+}(d^5) \rightarrow S = 5/2, \mu = 5.9\mu_B$

Antiferromagnetic coupling between A- and B-site moments:



$\Rightarrow$ **Ferrimagnetic order below T_C = 858 K**



Fe_3O_4: Verwey transition

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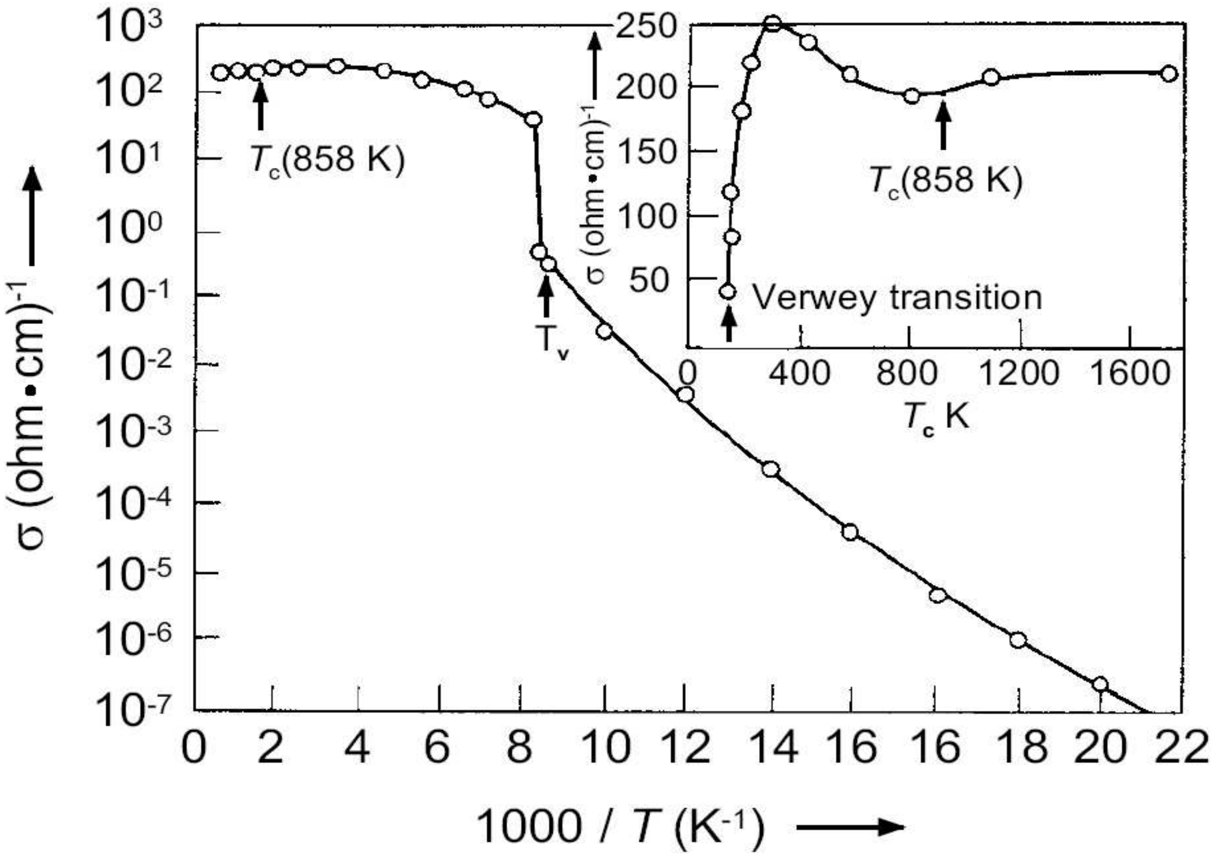
Verwey (1939)



- **huge resistivity jump at $T_V \approx 123$ K (hysteresis!)**
- **below T_V: activated behavior**
- **above T_V: initially activated, at higher T metallic**
- **poor metal at RT ($\sigma \approx 4 (m\Omega cm)^{-1}$)**

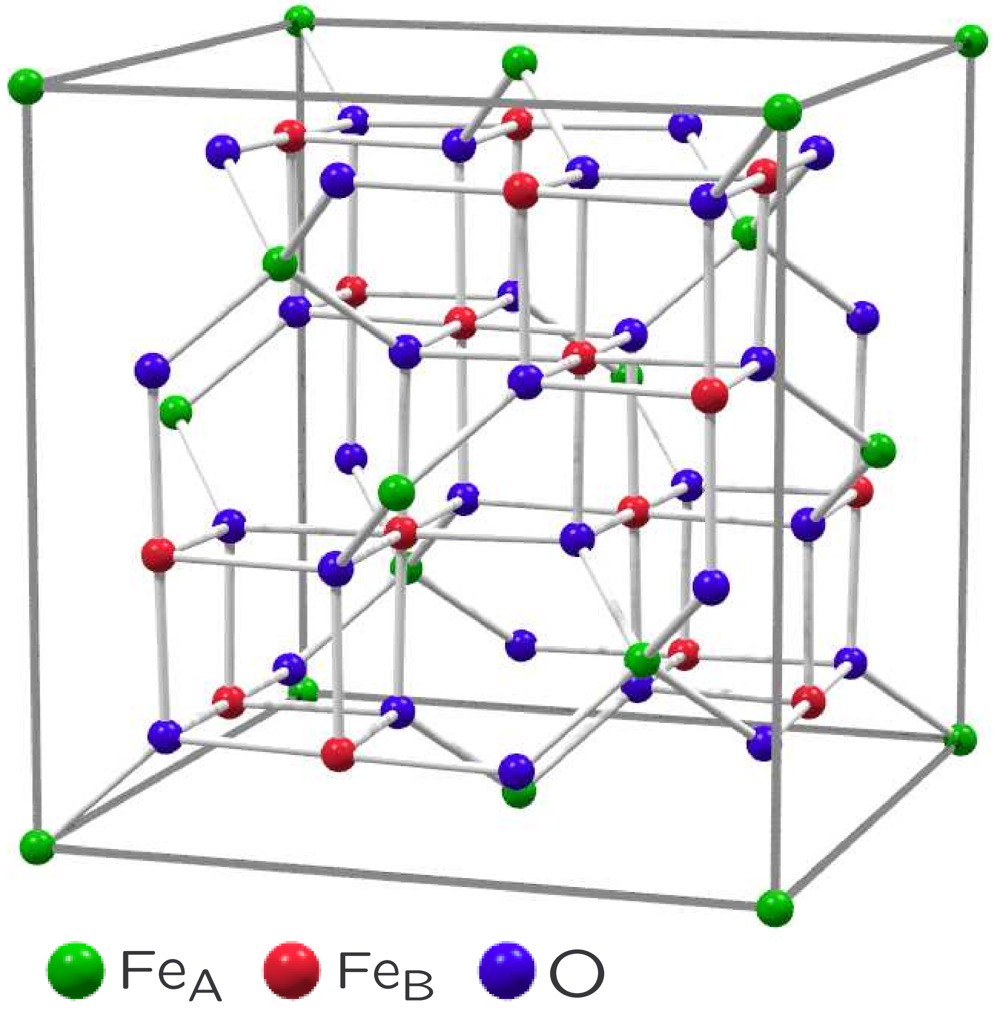
⇒ **Nature and microscopic origin of the transition?**

metal-insulator?
insulator-insulator?
…?

Fe_3O_4: Verwey transition

Verwey´s original suggestion:

electronic disorder-order transition of Fe^{2+}/Fe^{3+} ions on B-sites of spinel structure



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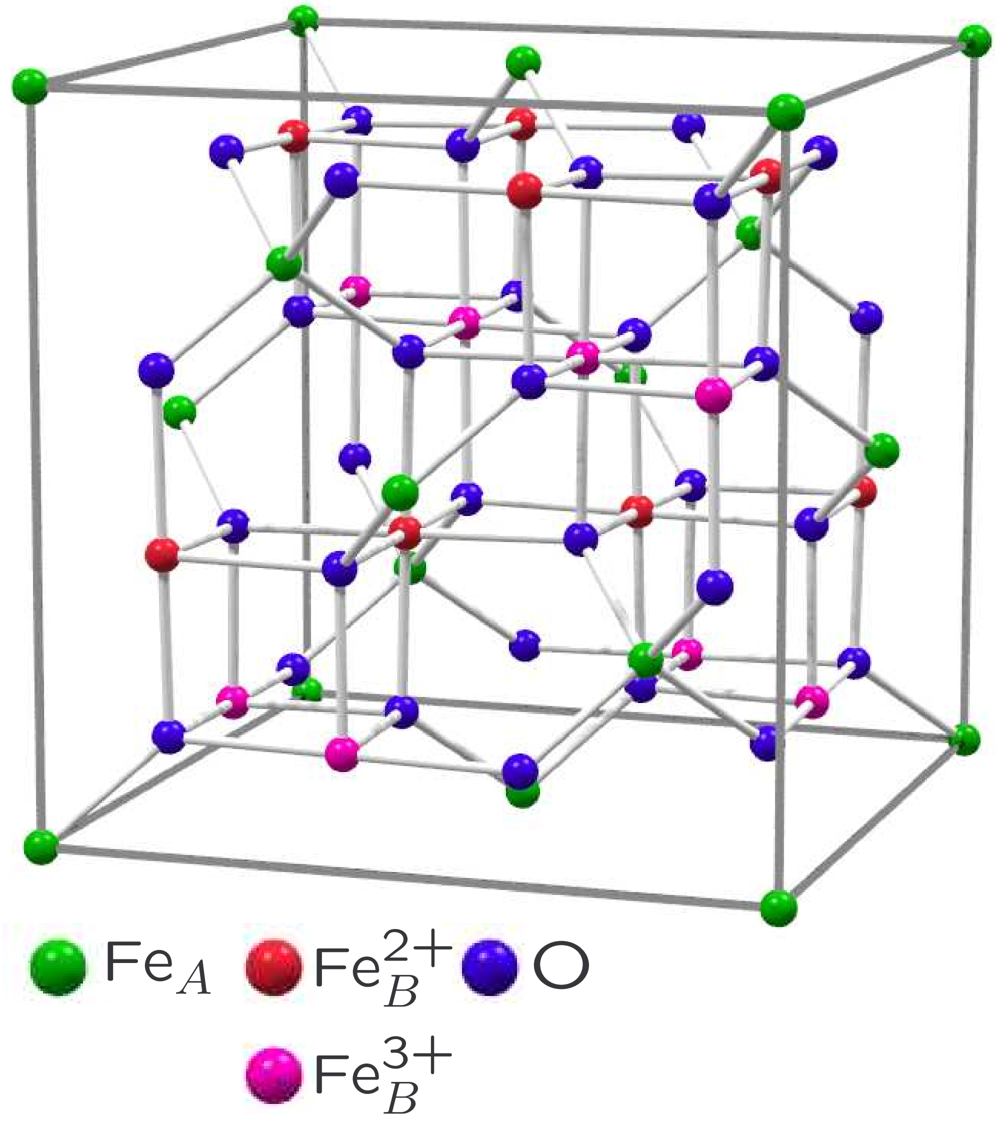

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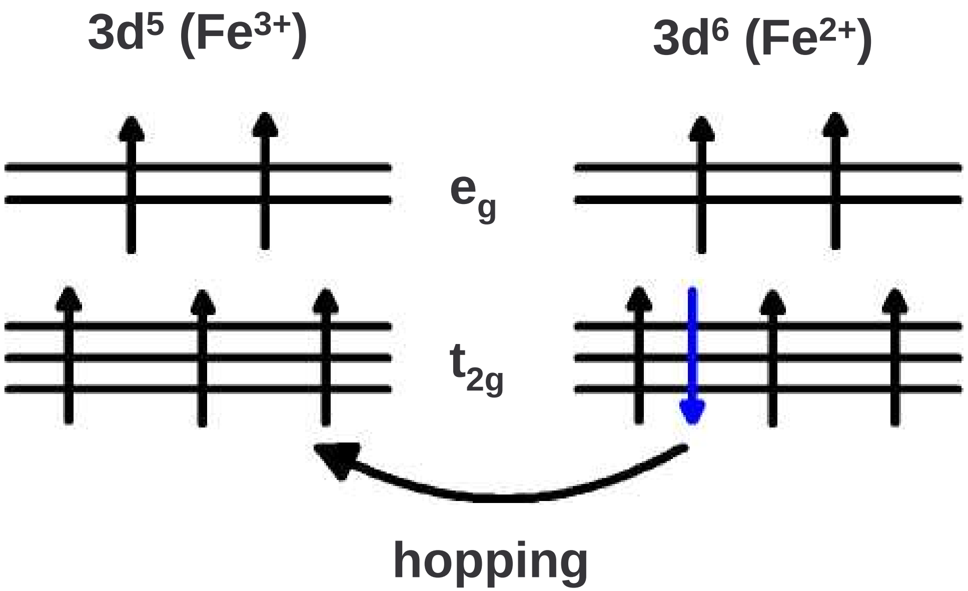

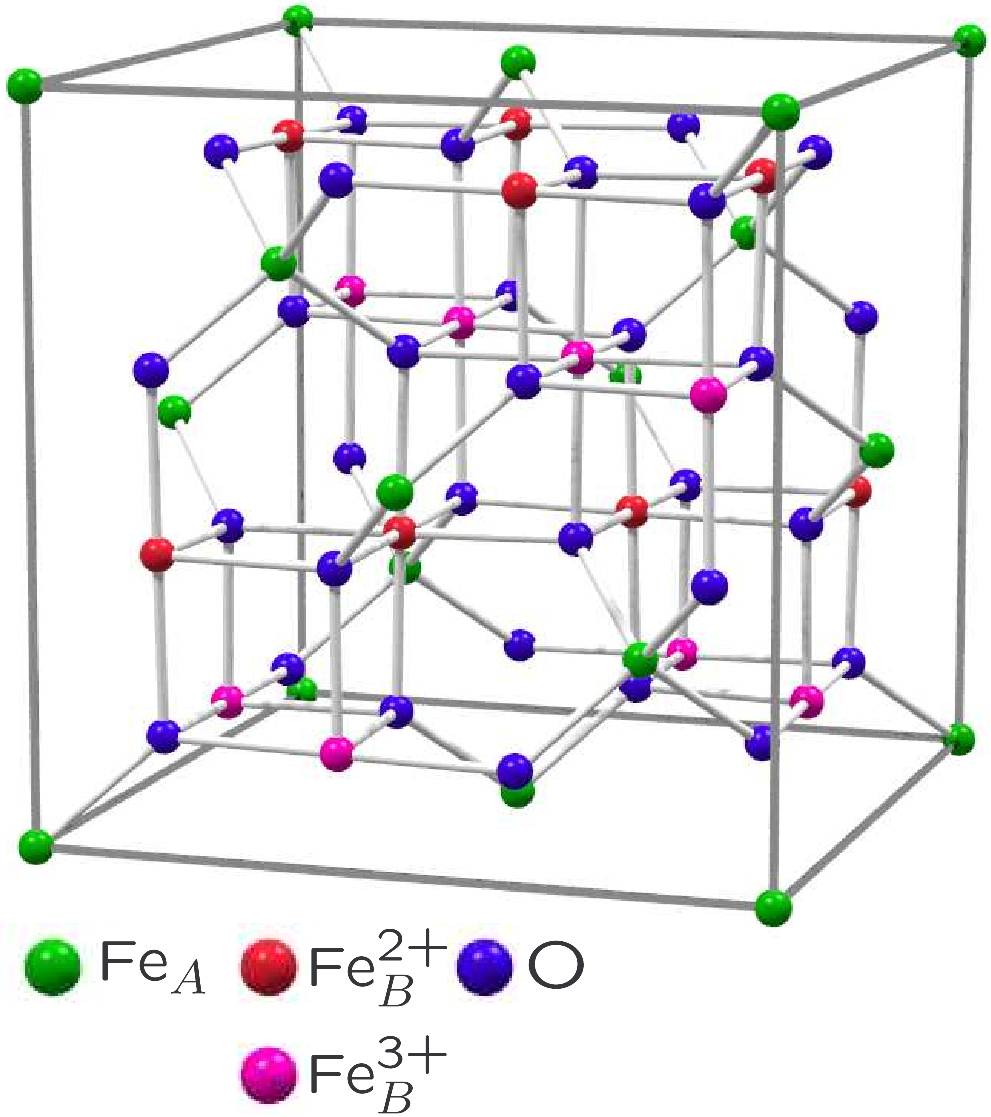

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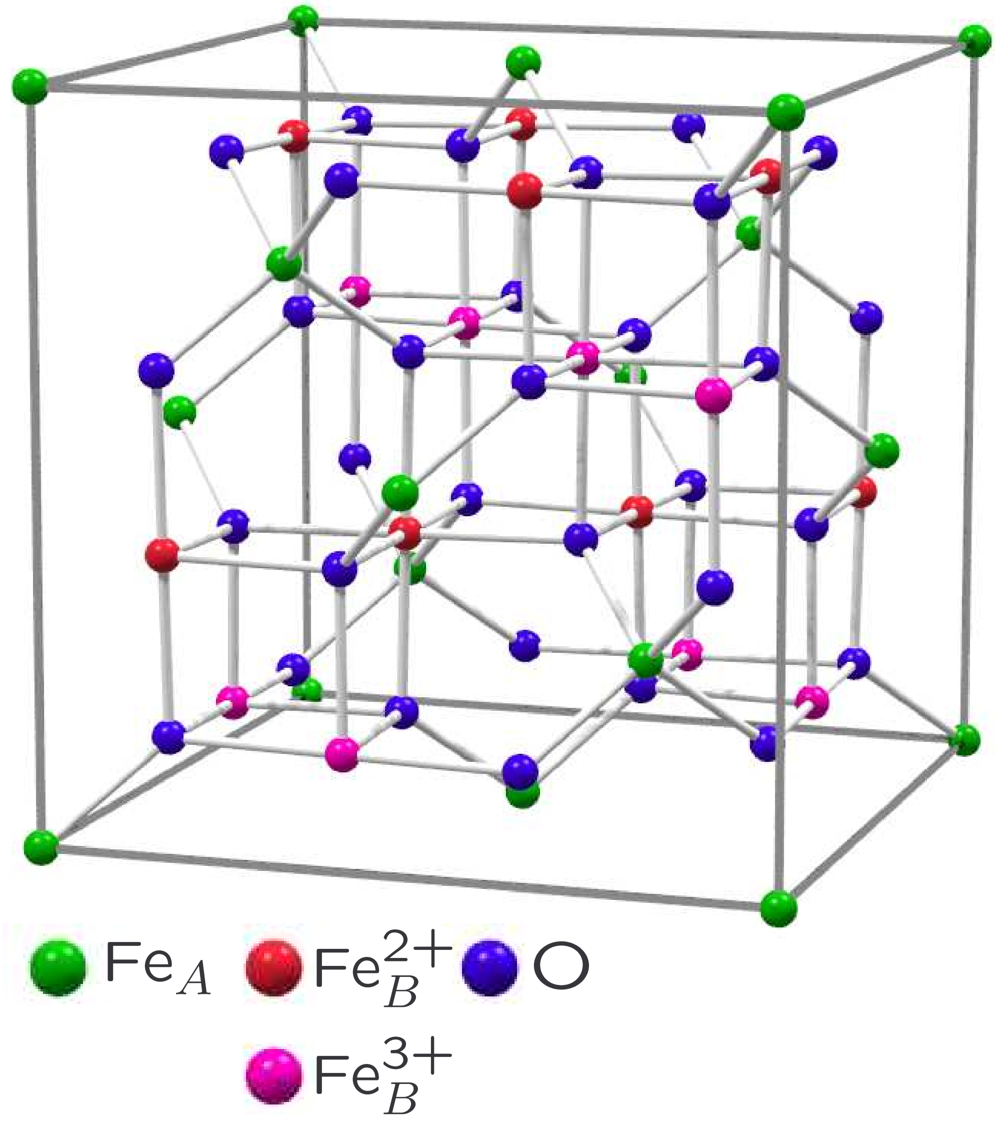


X-ray/electron/neutron diffraction:

accompanied by structural transition from cubic to monoclinic symmetry (small atomic displacements!)

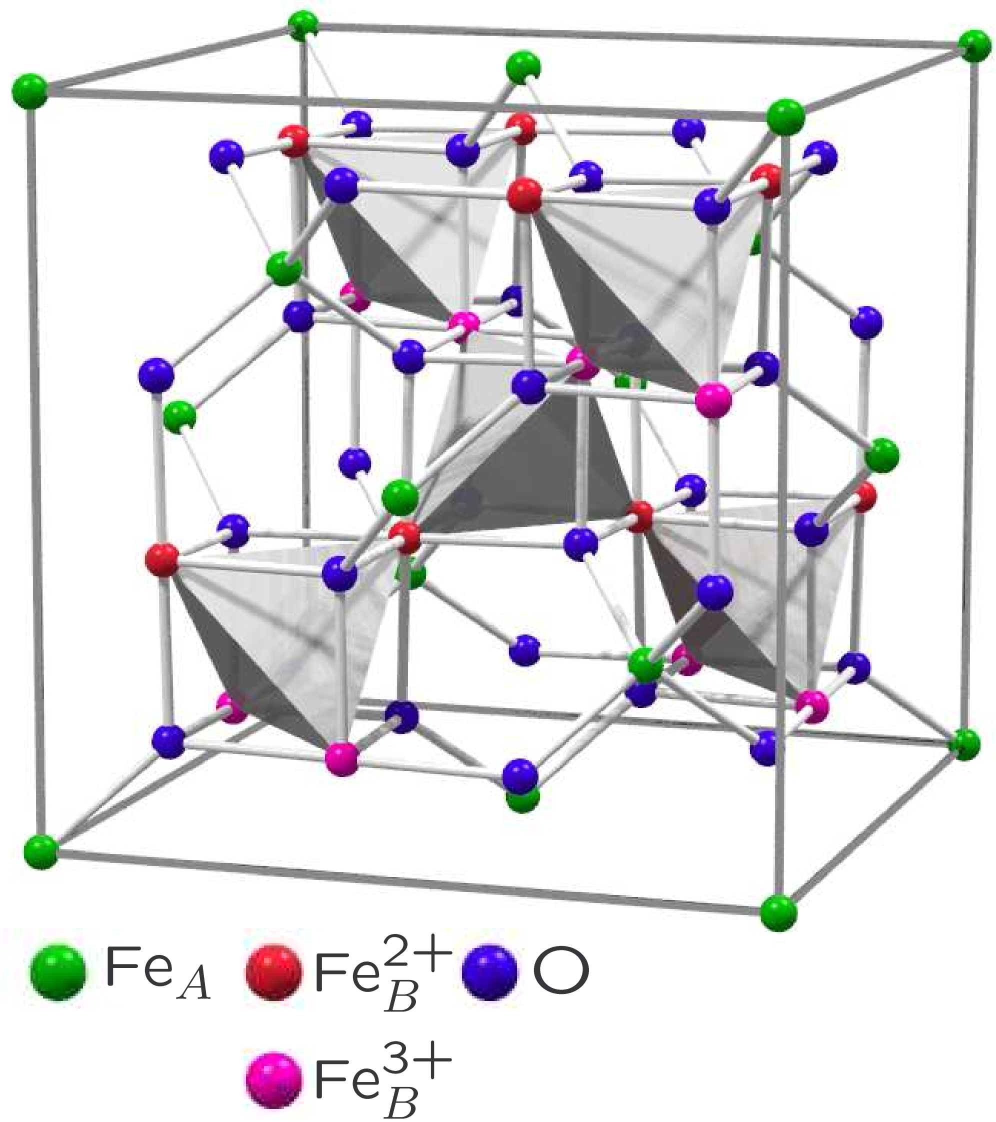
Fe_3O_4: Anderson criterion

Verwey´s original suggestion:

electronic disorder-order transition of Fe^{2+}/Fe^{3+} ions on B-sites of spinel structure

Anderson criterion (1956):

Minimizing Coulomb energy $\rightarrow$ only CO patterns with 2 Fe^{2+} and 2 Fe^{3+} per tetrahedron of Fe_B pyrochlore lattice



Fe_3O_4: electronic structure and magnetism

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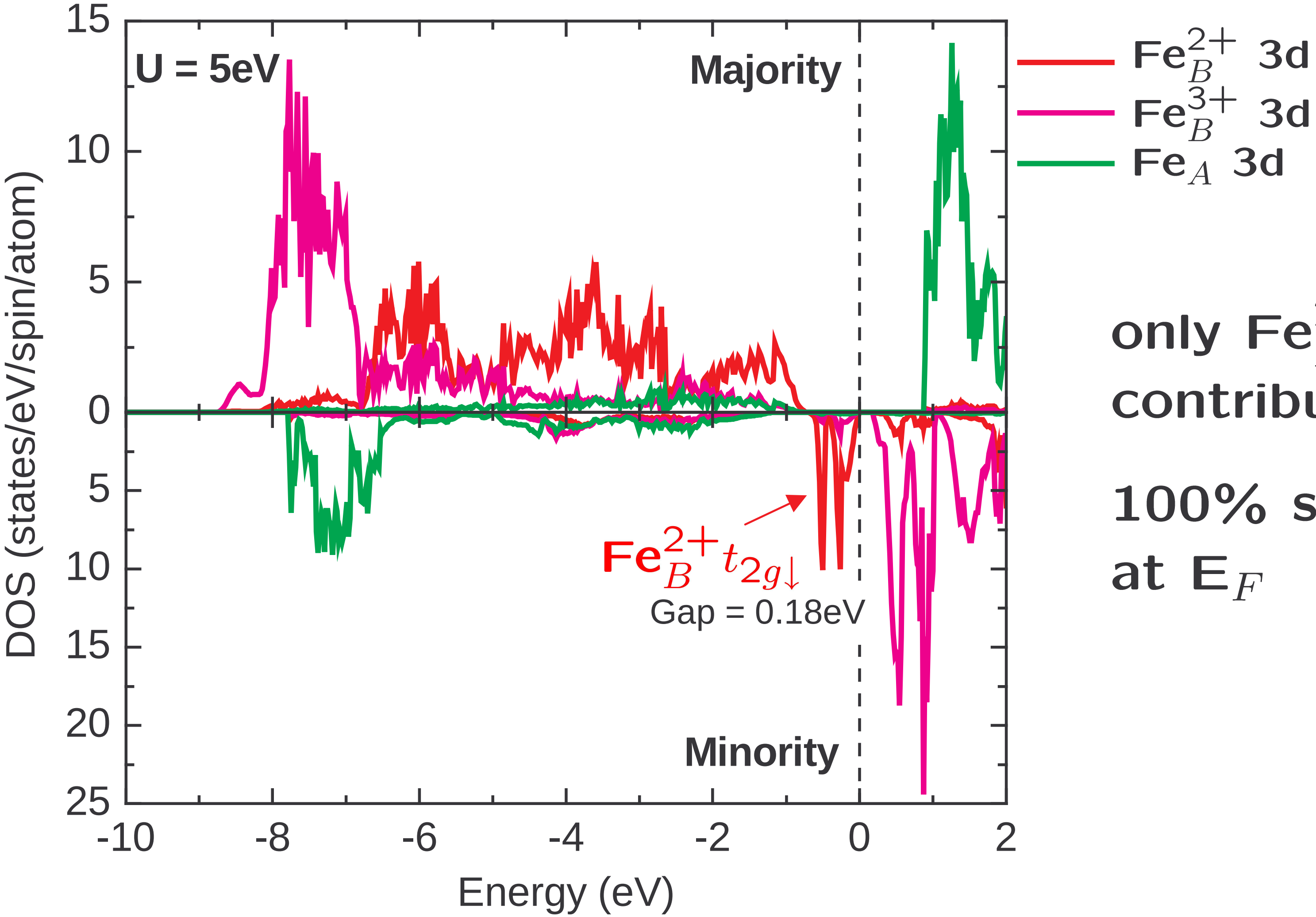
LSDA + U band structure calculation for P2/c symmetry
(I. Leonov, V. Anisimov *et al.*)



only $Fe_B^{2+} t_{2g\downarrow}$ states contribute at E_F!

100% spin polarization at E_F

Fe_3O_4: previous PES studies

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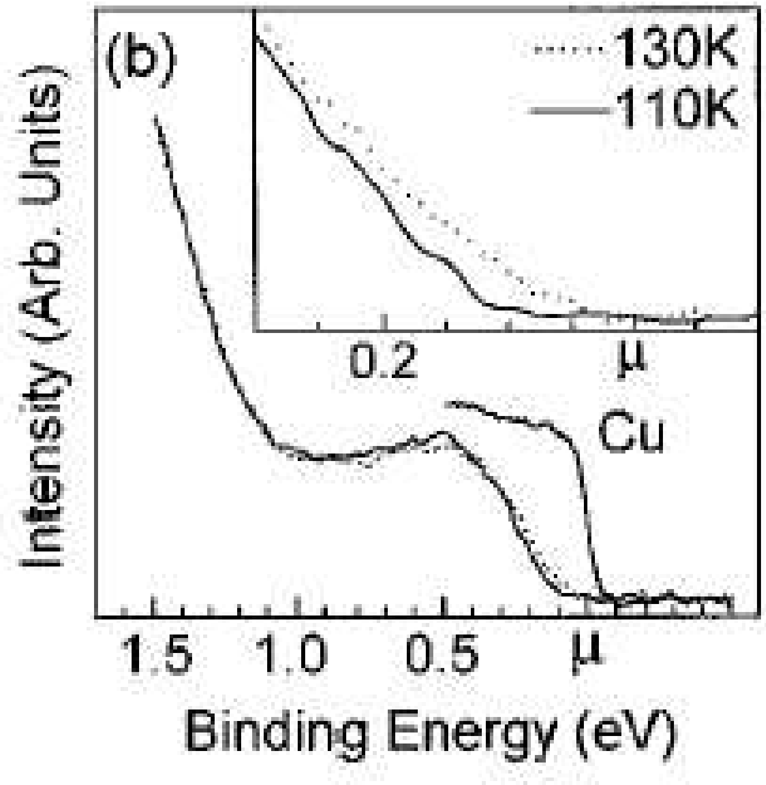
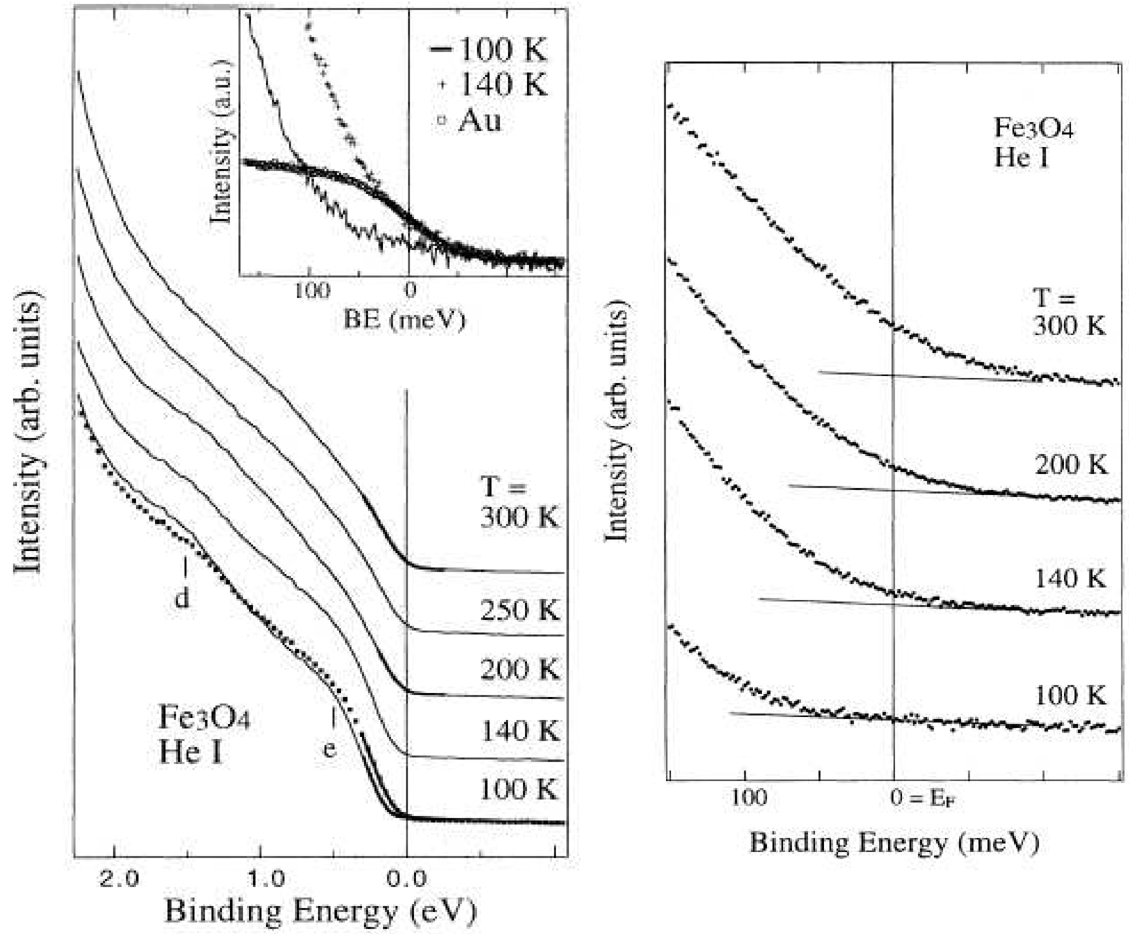
hν = 110 eV, fractured crystals



Park *et al.*, PRB **55,** 12813 (1997):

insulator – insulator transition

hν = 21.2 eV, fractured crystals

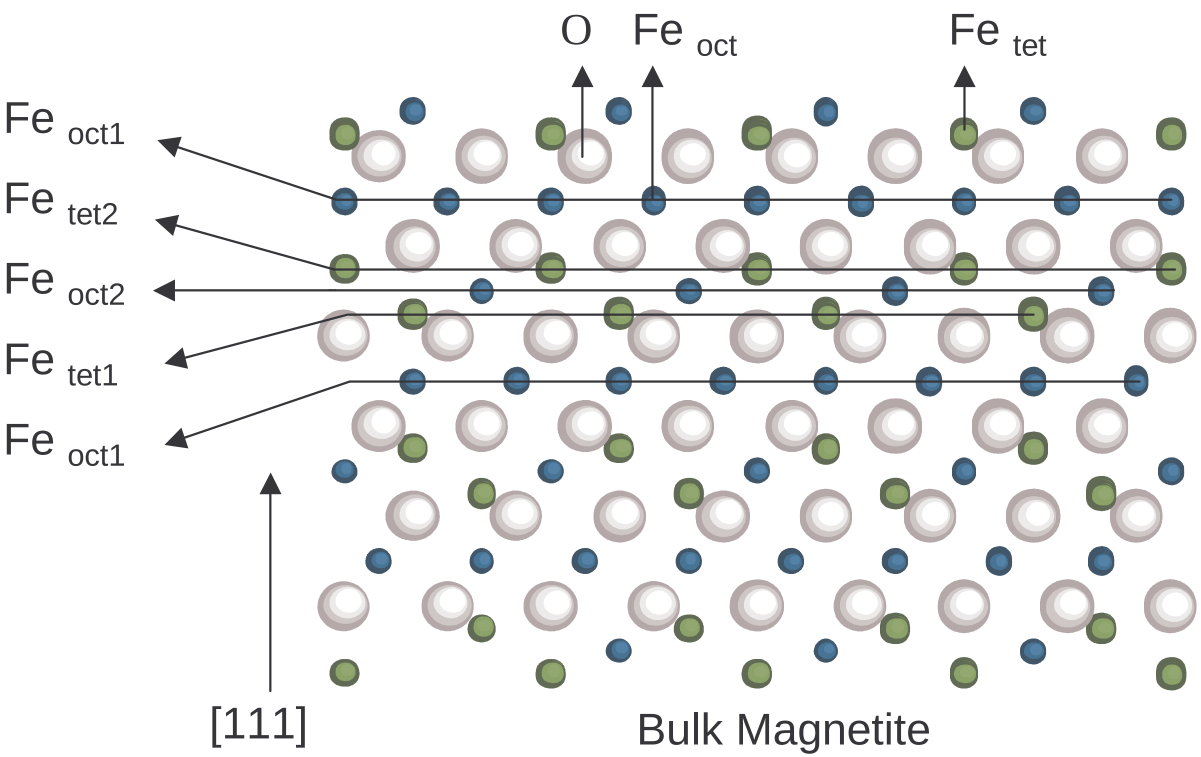


Chainani *et al.*, PRB **51,** 17976 (1995):

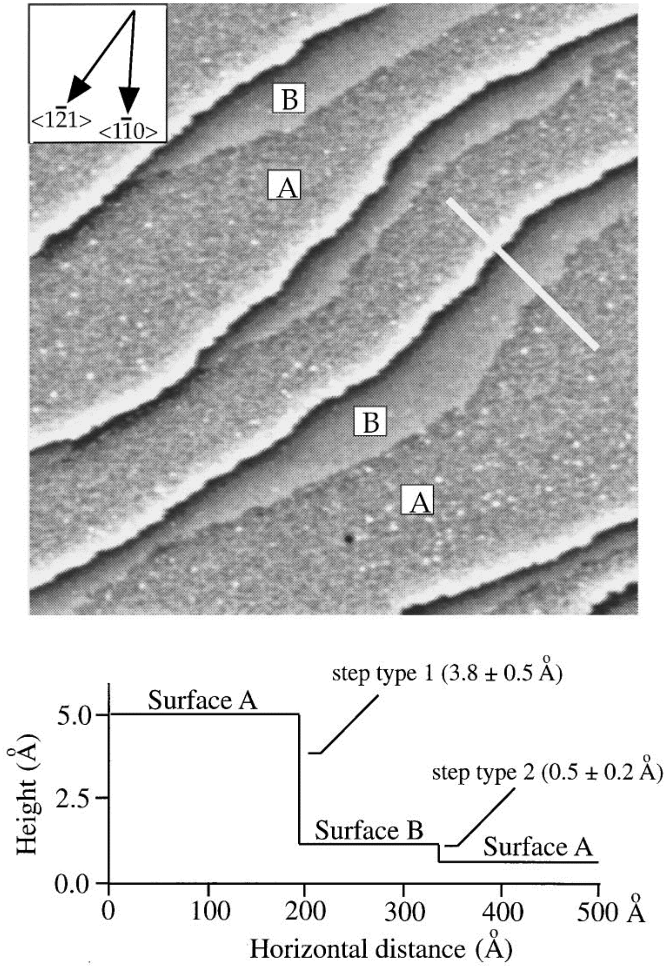
metal – insulator transition

Fe_3O_4: polar surface terminations

Various terminations of the (111)-surface:



STM



termination B: Fe $_{tet2}$Fe $_{oct2}$Fe $_{tet1}$ (1 x 1 unit cell)

termination A: $Fe_{oct2}Fe_{tet2}$ (plus O layer)

Lennie *et al.*, PRB **53**, 10244 (1996)

Fe_3O_4: preparation of ordered surfaces

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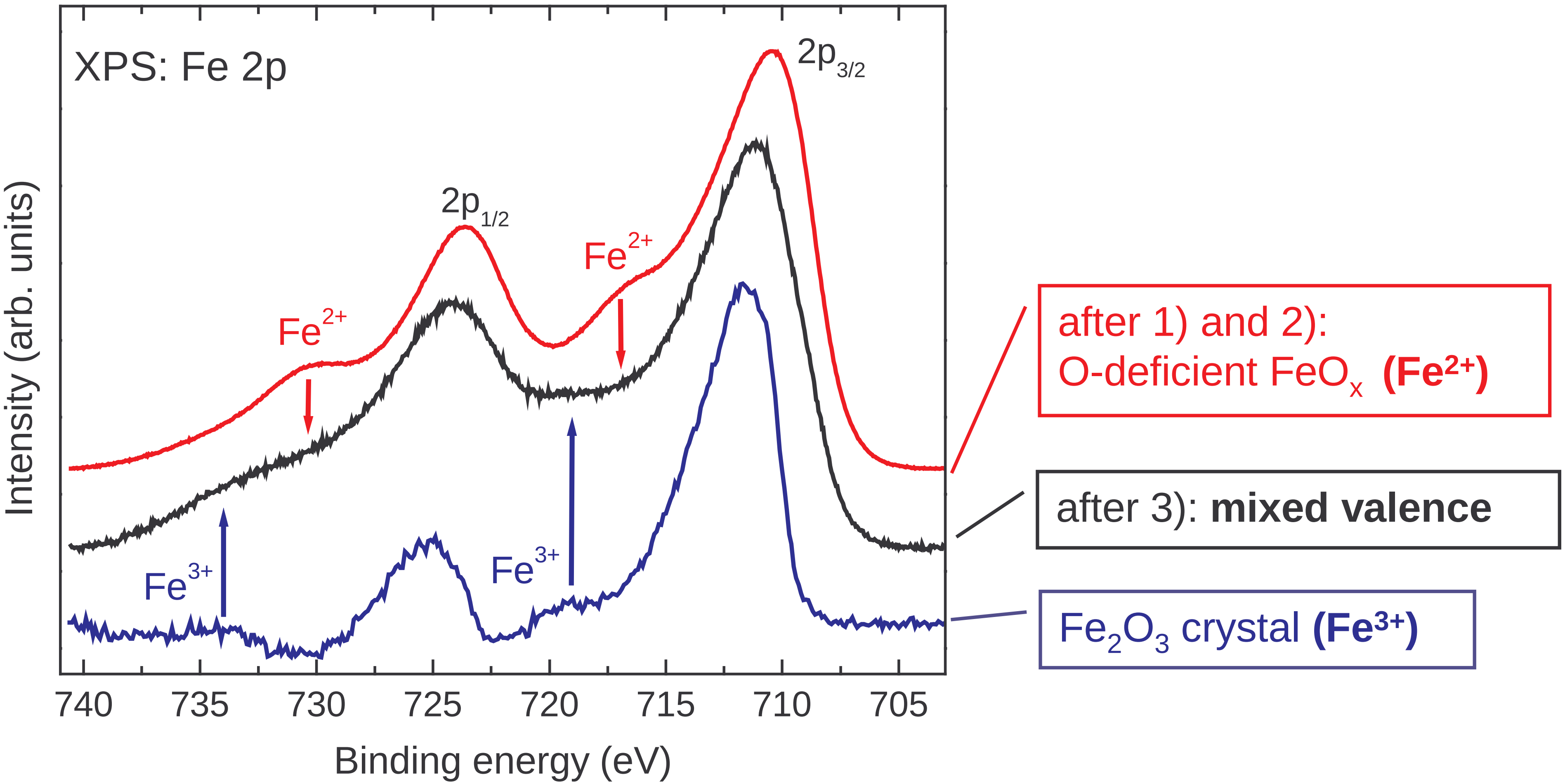
Procedure for (111) surface:

1) Ar ion bombardment
2) annealing at 800°C
3) post-oxidation (10^{-6} mbar O_2 @ 750°C)



Fe_3O_4: surface characterization

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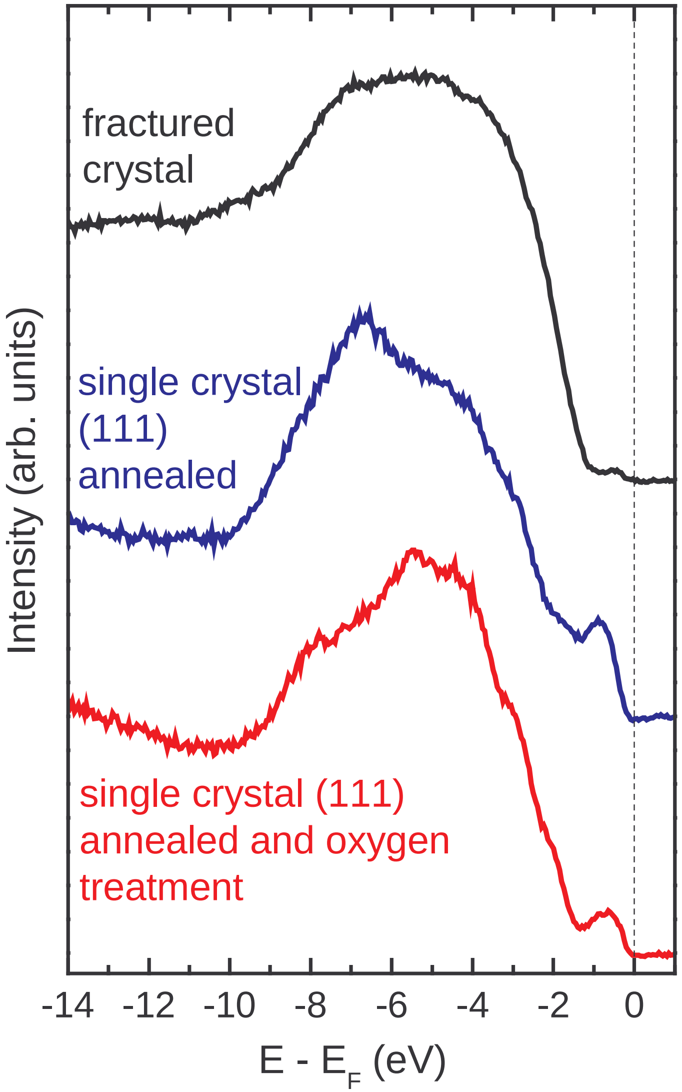
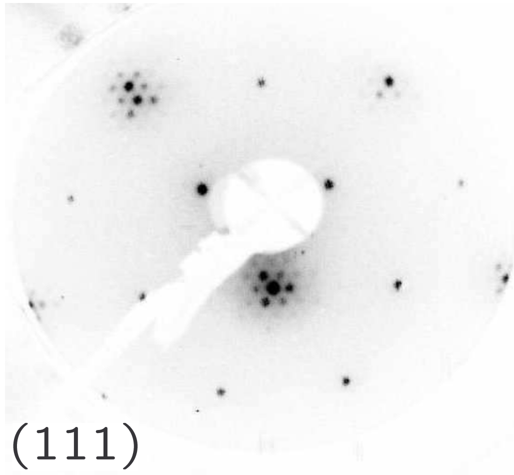
PES (HeI)

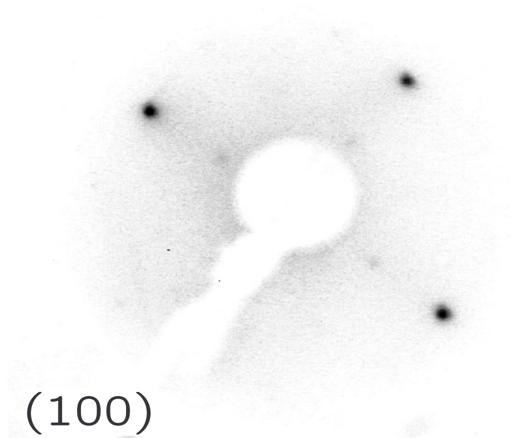


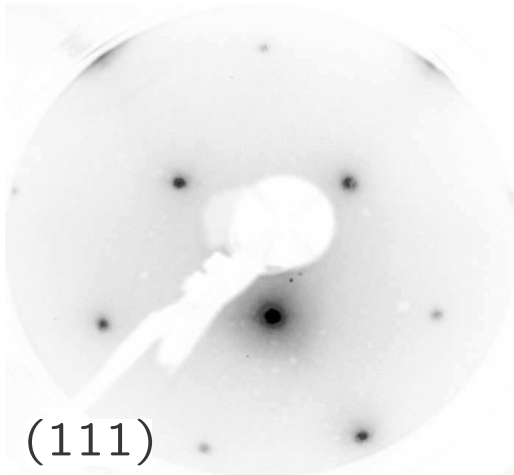
LEED



sputtered

annealed

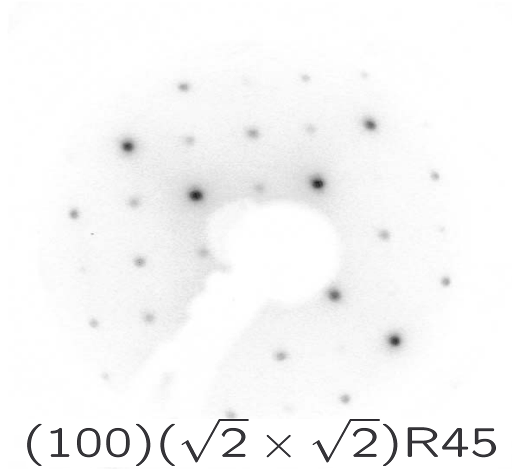




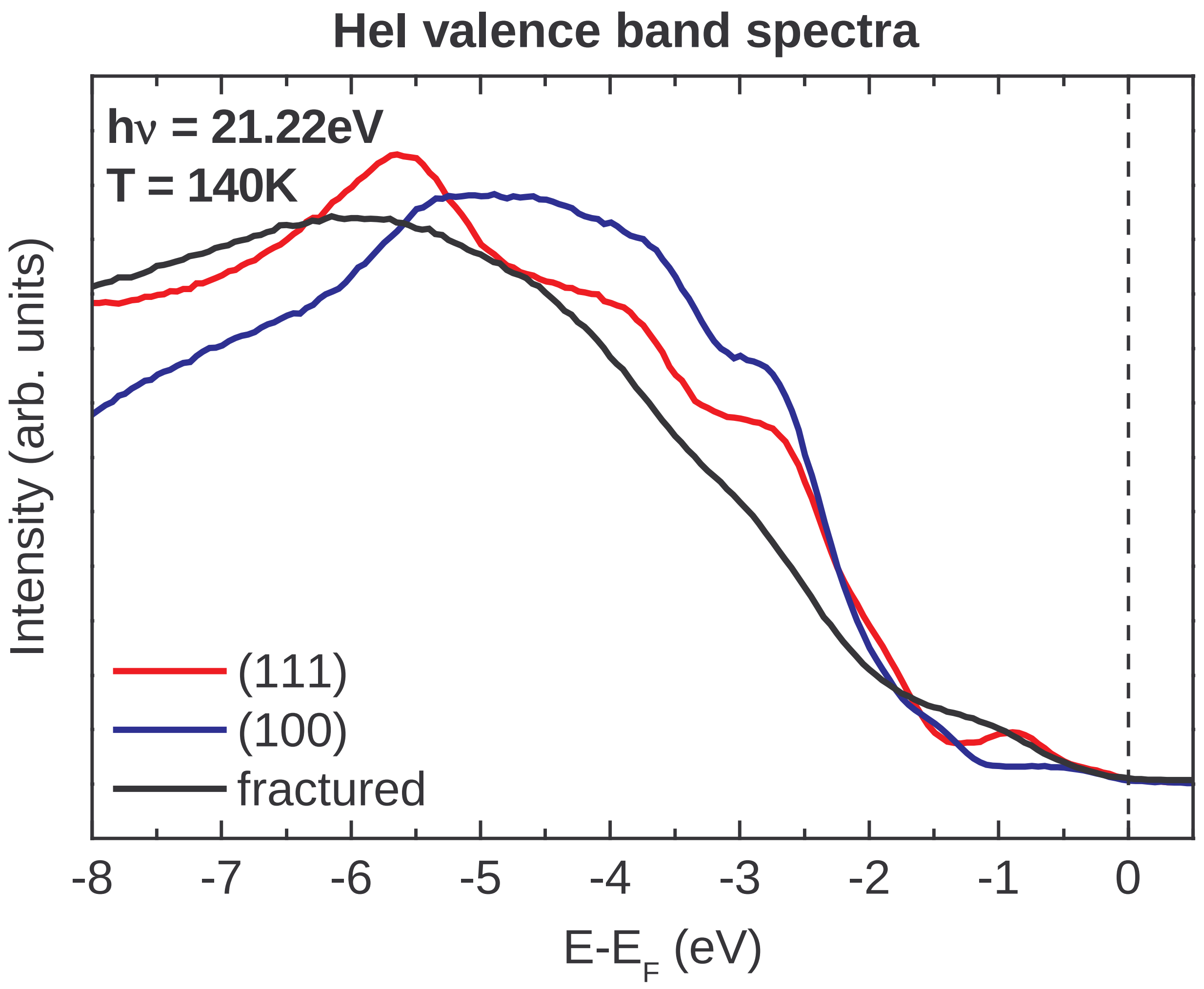
sputtered

annealed

oxidized



Fe_3O_4: electronic surface effects



pronounced differences

⇒ more bulk sensitivity needed!!

Fe_3O_4: valence band spectrum

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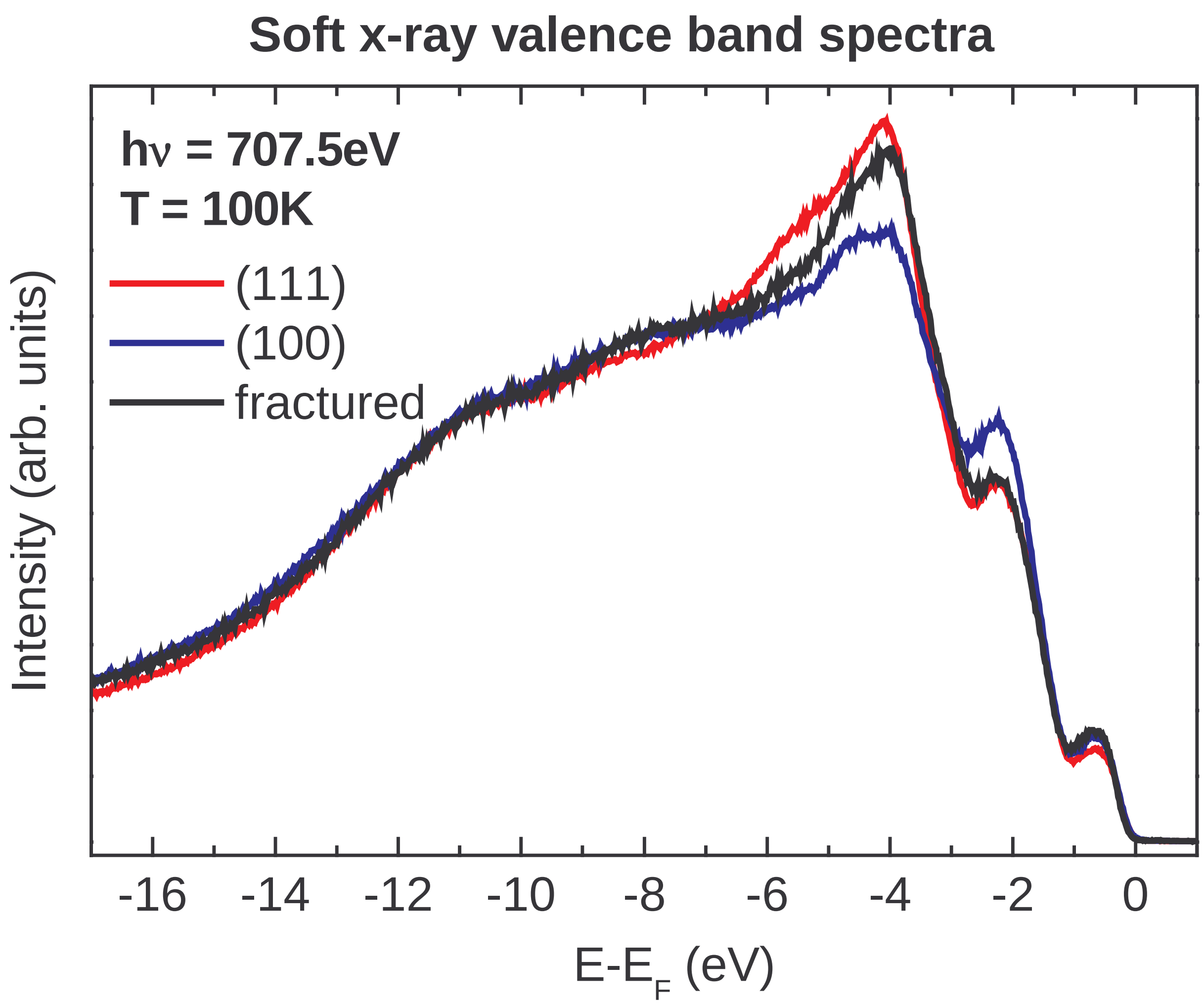

overall similarity

due to enhanced bulk sensitivity

Fe_3O_4: temperature dependence

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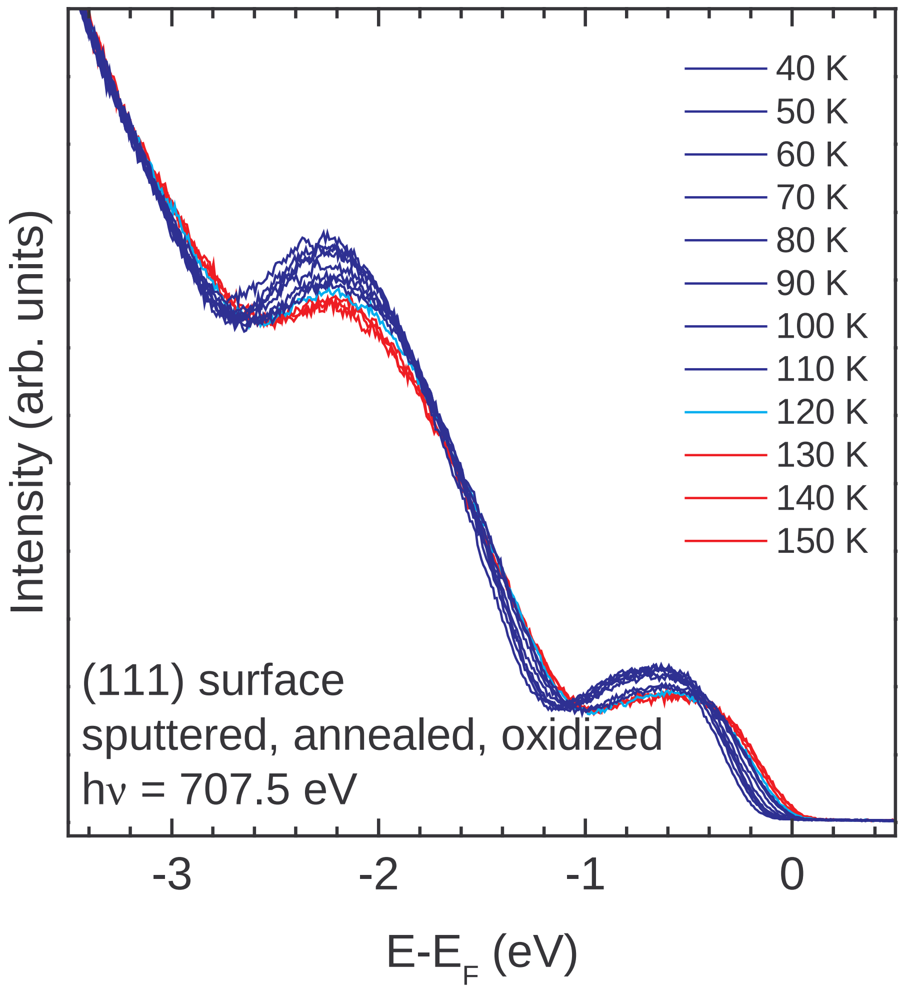
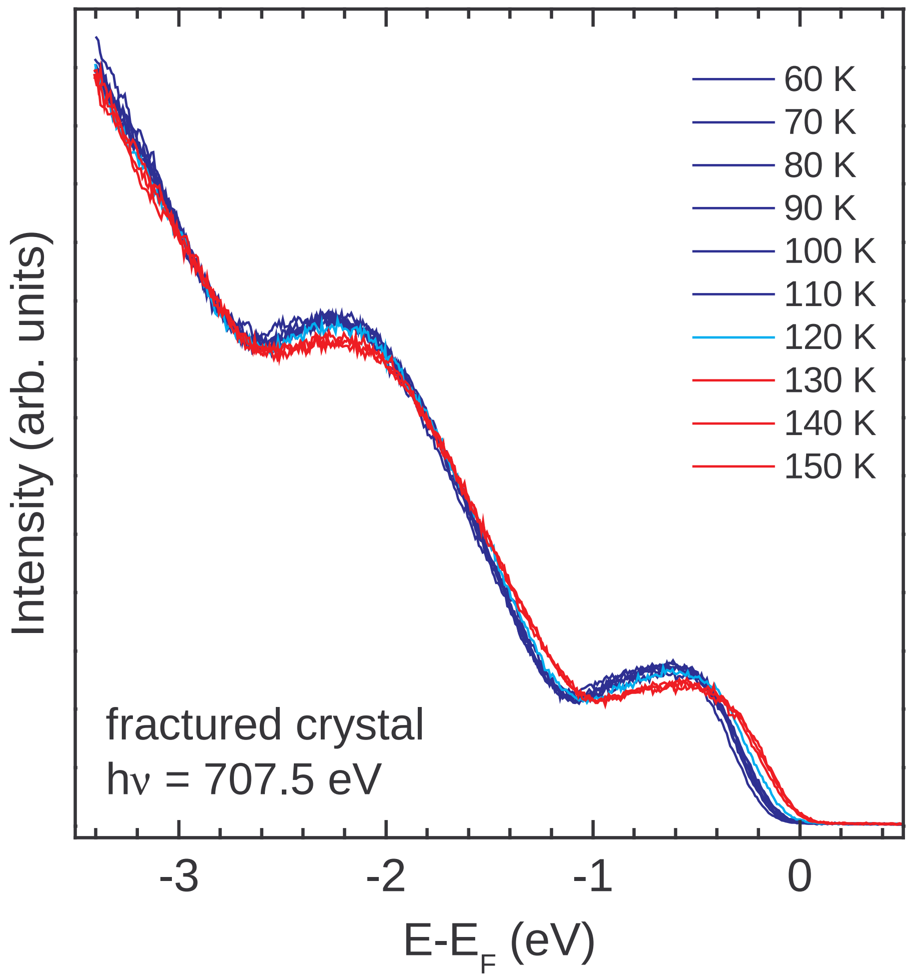
Fe_3O_4 (111)



fractured Fe_3O_4 crystal



Fe_3O_4: temperature dependence

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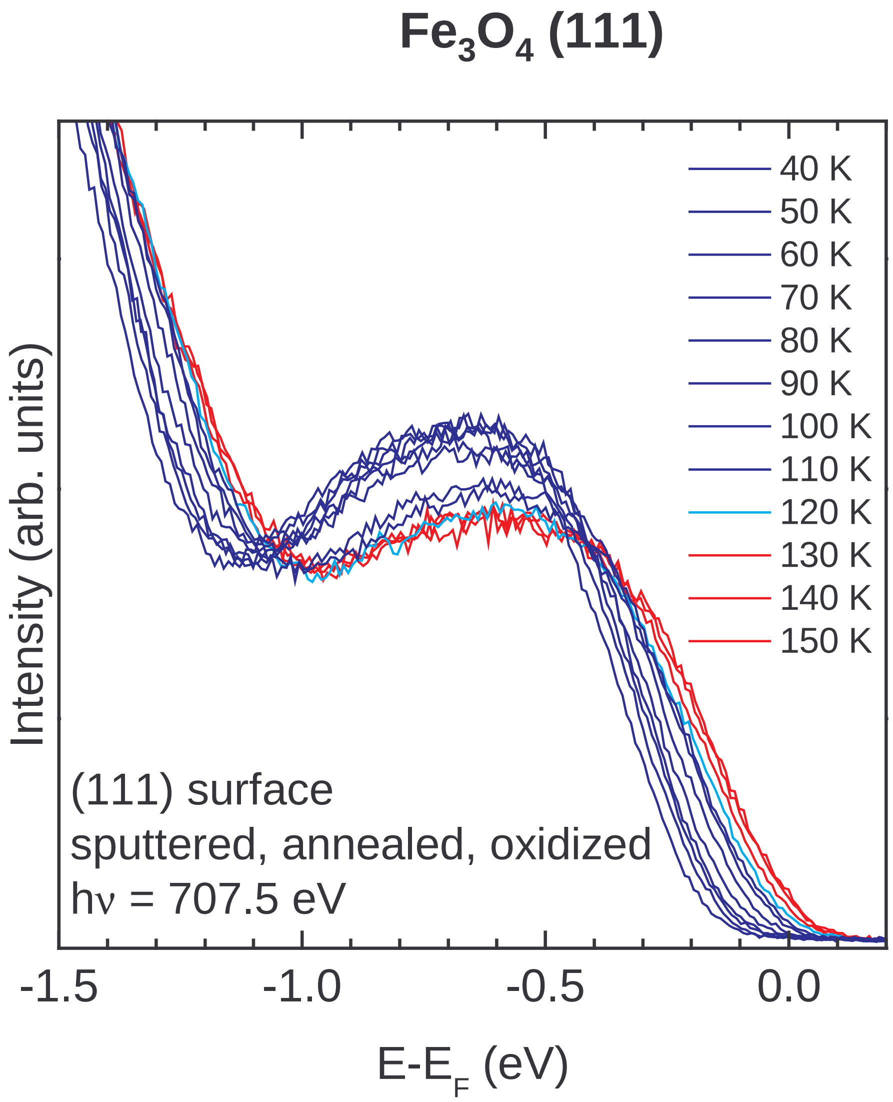
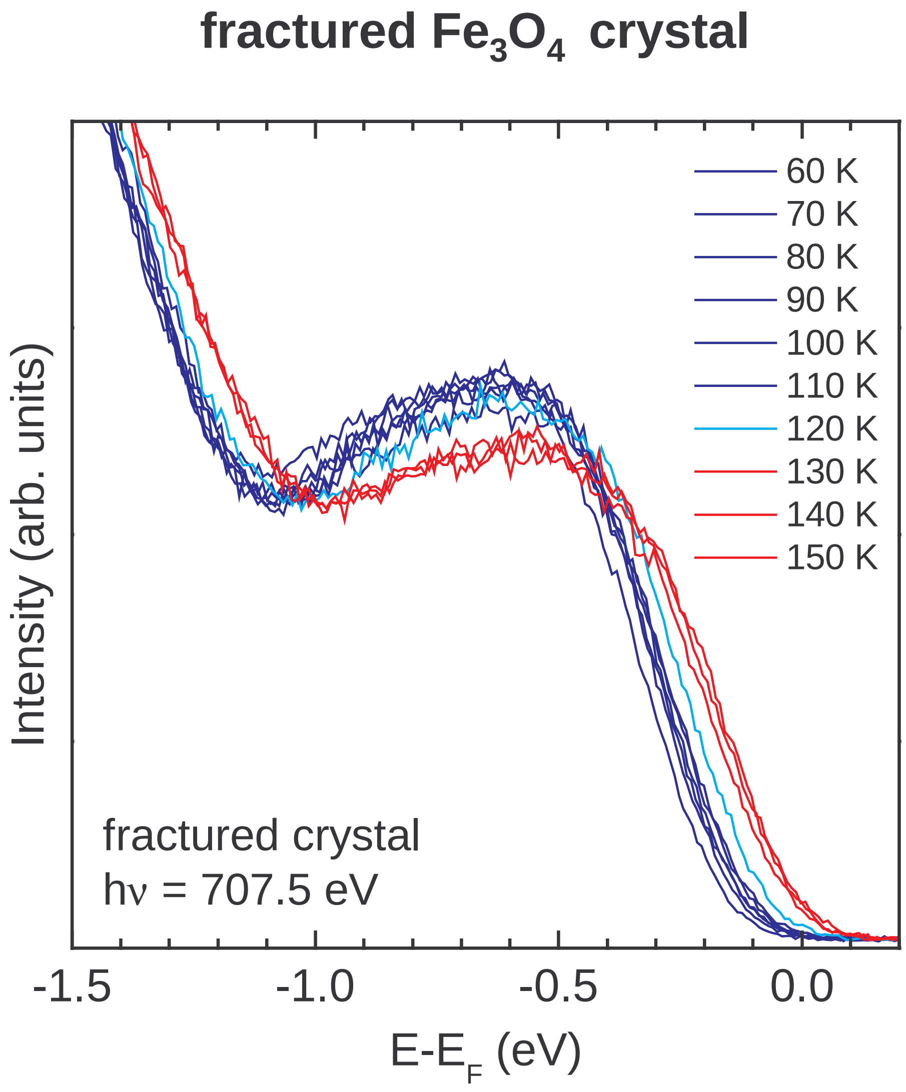
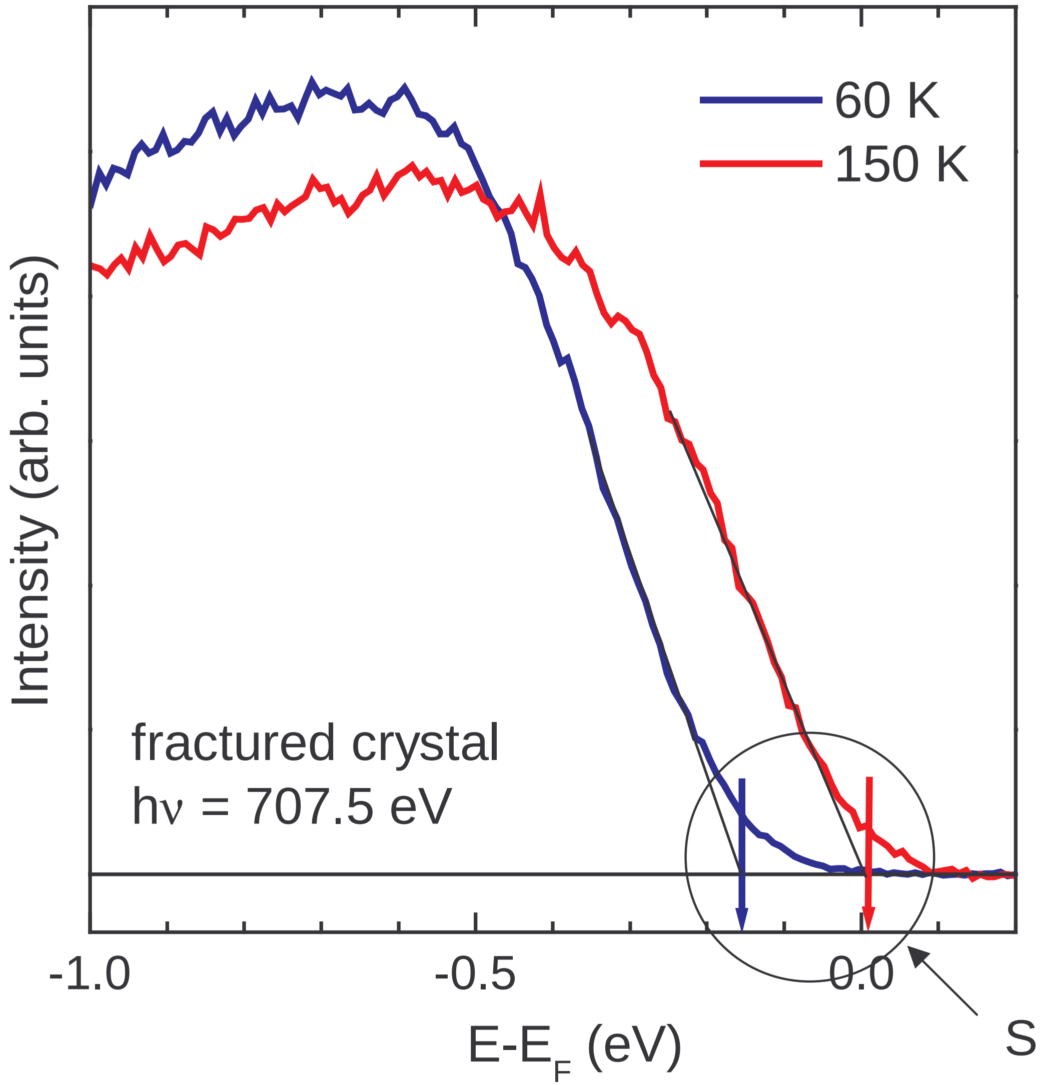
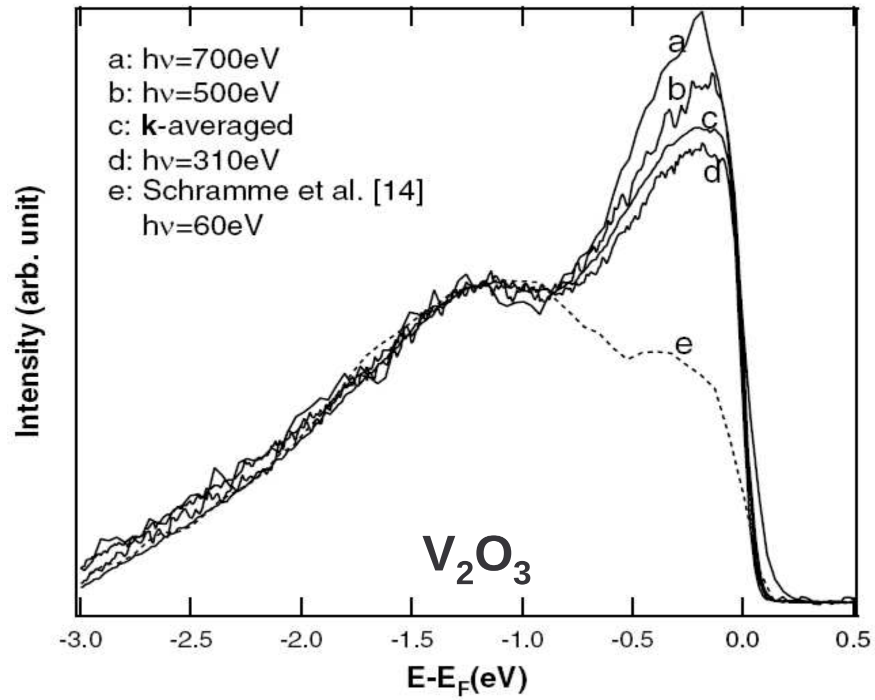




Fe_3O_4: Verwey transition



Spectral onset energy E_{on}



S.-K. Mo et al., PRL **90**, 186403 (2003)

Fe_3O_4: T-dependence of spectral onset

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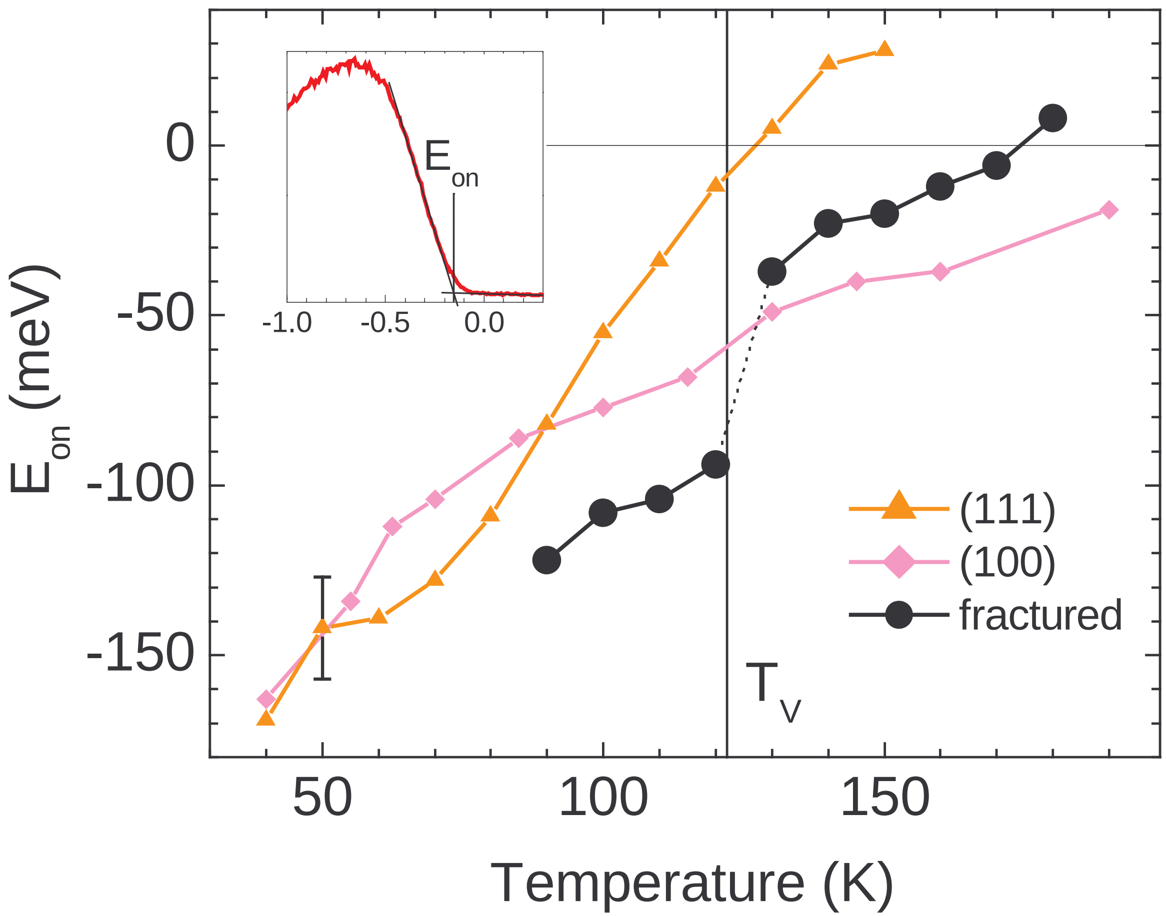

tempered surfaces:

- **continuous T-dependence**
- **no Verwey transition**

surface fractured at 40 K:

- **discontinuity at bulk T_V → Verwey transition**
- **non-equilibrium bulk-like surface configuration**
- **insulator-insulator transition**

Fe_3O_4: nature of electronic excitations above T_V

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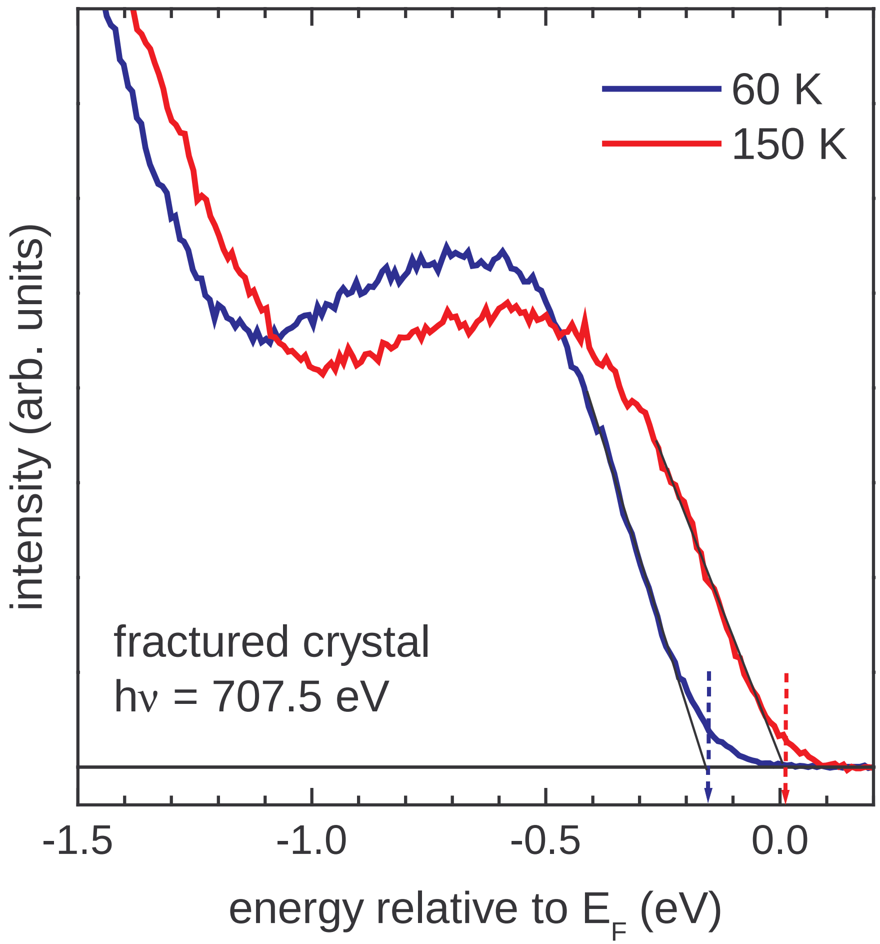
photoemission:

absence of q. p. peak



Fe_3O_4: nature of electronic excitations above T_V

photoemission:

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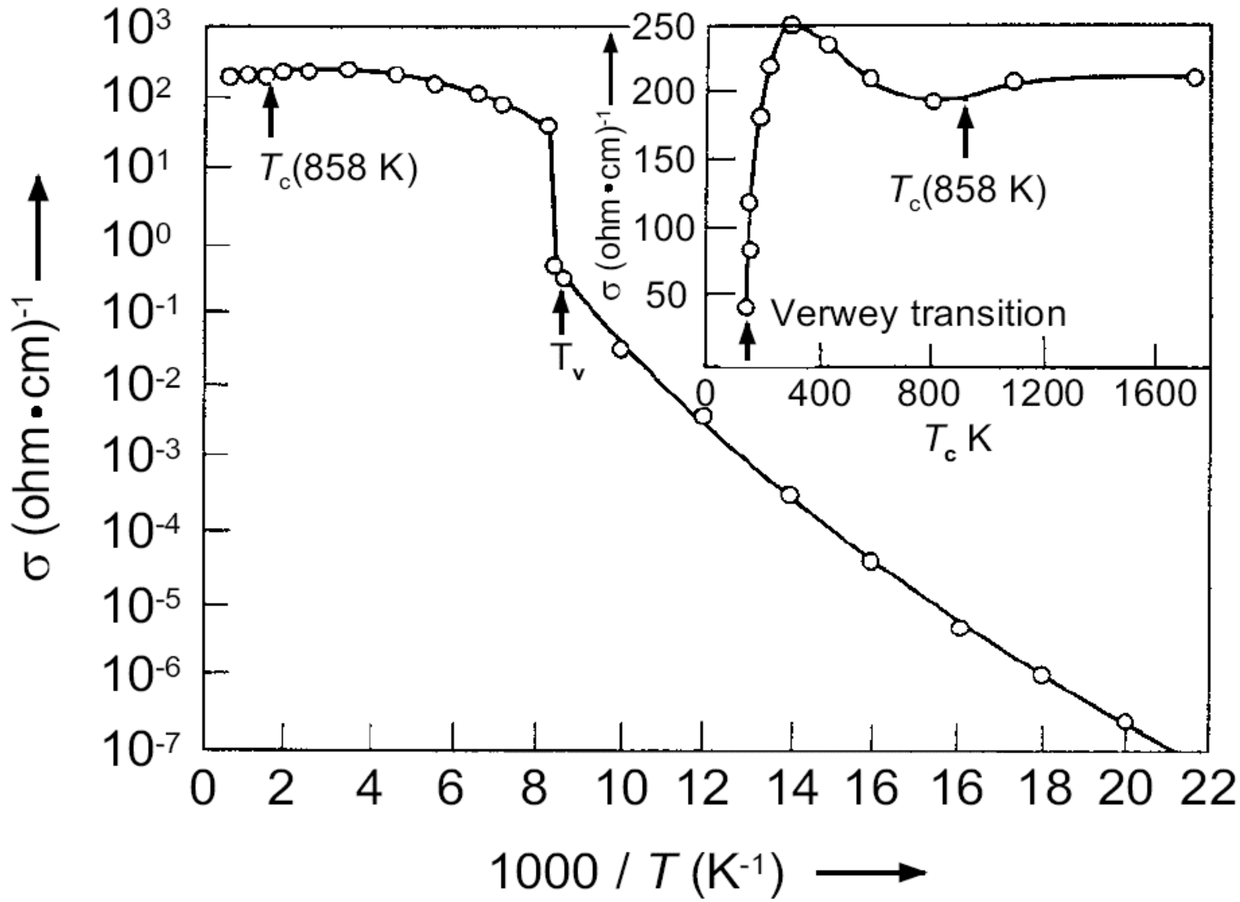
resistivity:

non-metallic T-coefficient



Fe_3O_4: nature of electronic excitations above T_V

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photoemission:

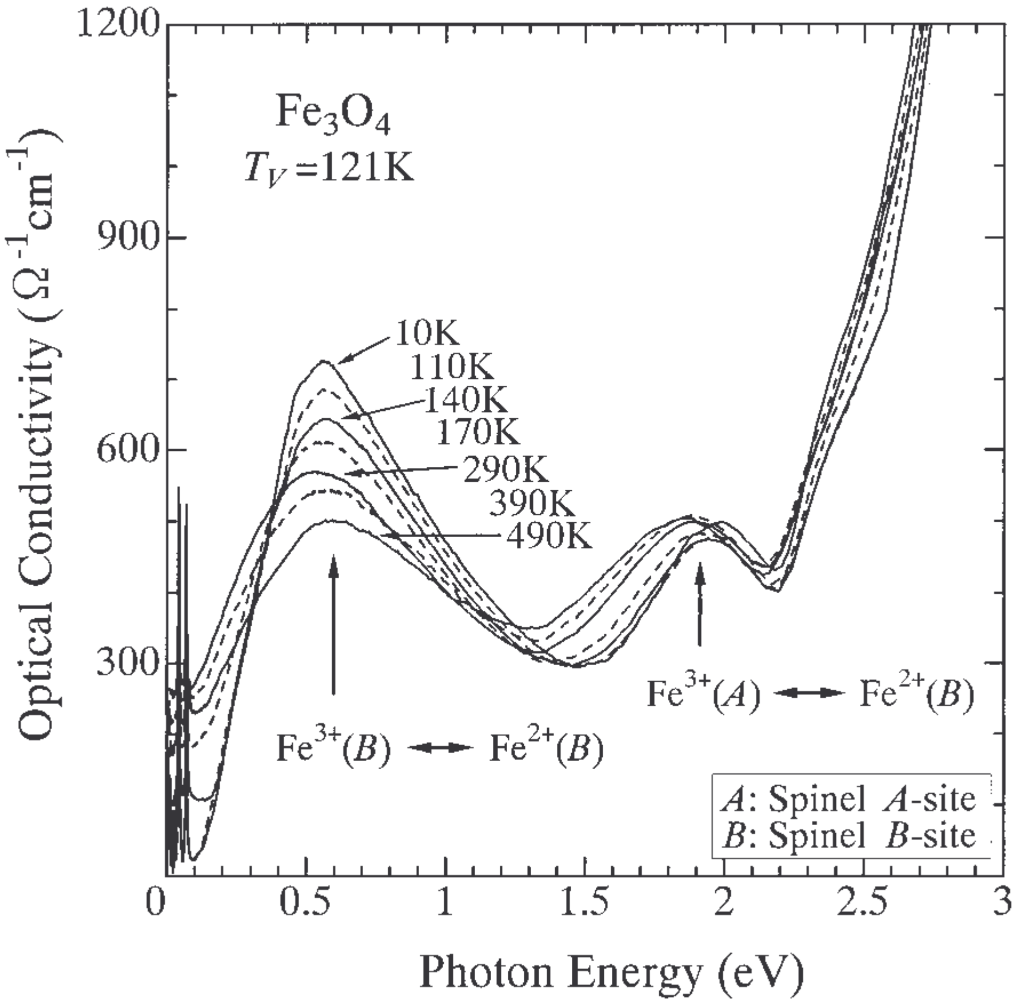
absence of q. p. peak

resistivity:

non-metallic T-coefficient

optical spectroscopy:

absence of Drude peak
broad peak at 0.6eV



Park et al., PRB **58**, 3717 (1998)

Fe_3O_4: nature of electronic excitations above T_V

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photoemission:

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resistivity:

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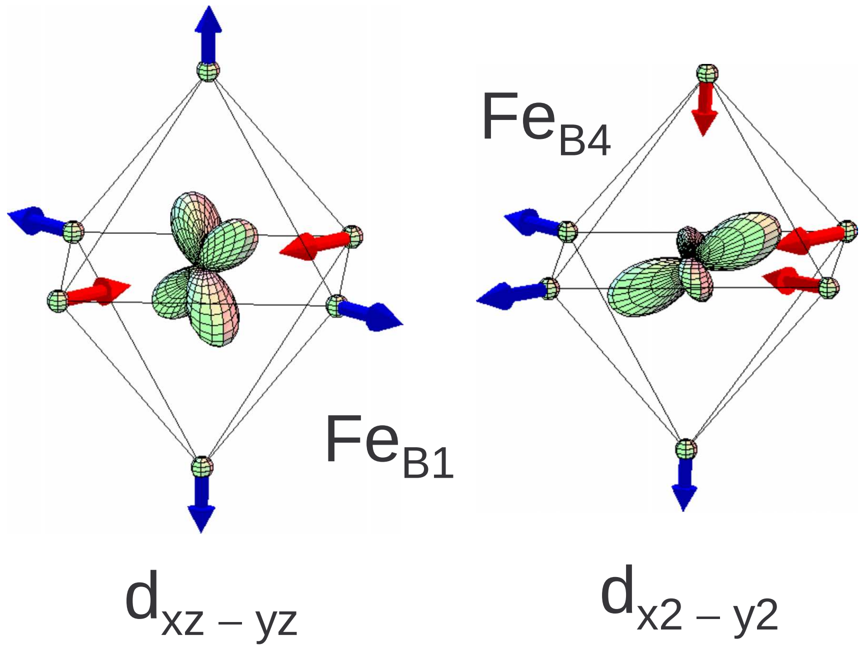
x-ray diffraction/LSDA+U:

Jahn-Teller
distortions/orbital order



Leonov et al. (2004)

Fe_3O_4: nature of electronic excitations above T_V

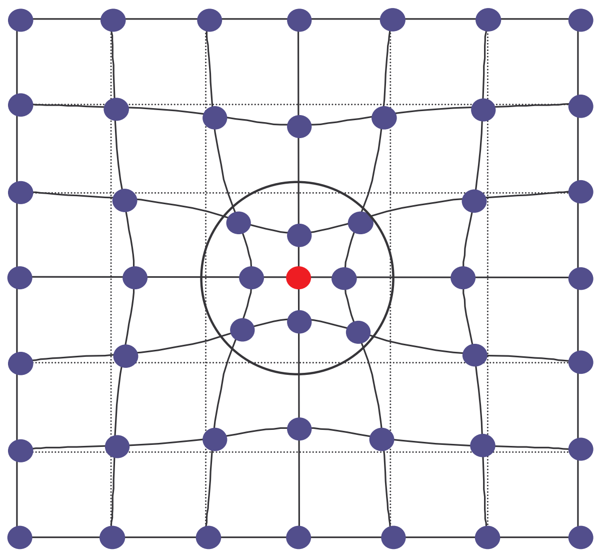
photoemission:
absence of q. p. peak

resistivity:
non-metallic T-coefficient

optical spectroscopy:
absence of Drude peak
broad peak at 0.6eV

x-ray diffraction/LSDA+U:
Jahn-Teller
distortions/orbital order

⇒ (small) polarons



Vibronic excitations and PES

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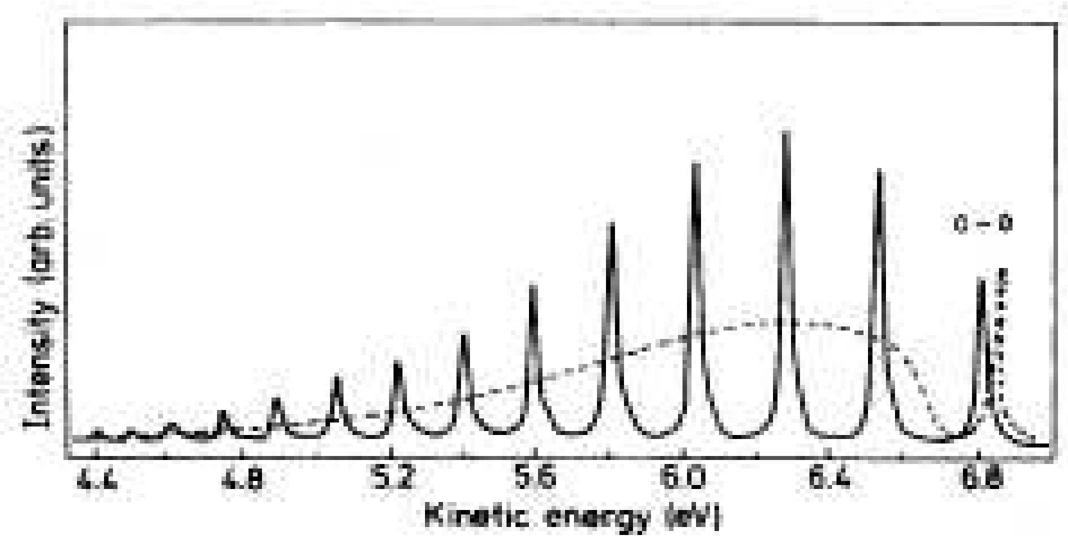
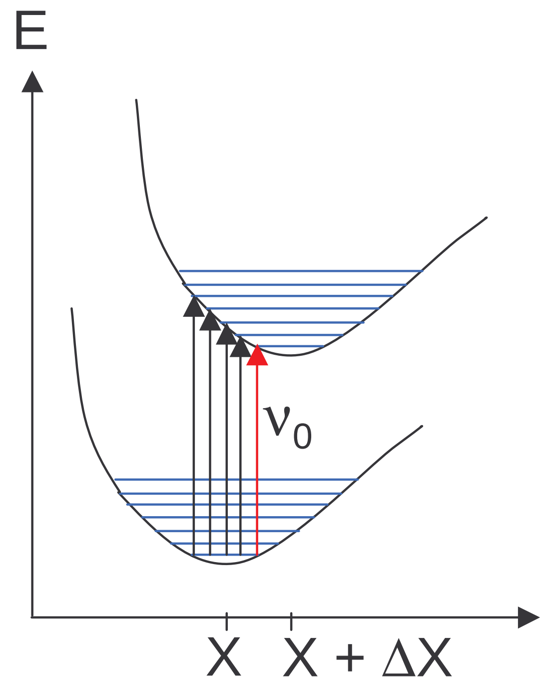
Schematic PES spectrum of H_2



Franck-Condon principle



Small polarons in Fe_3O_4

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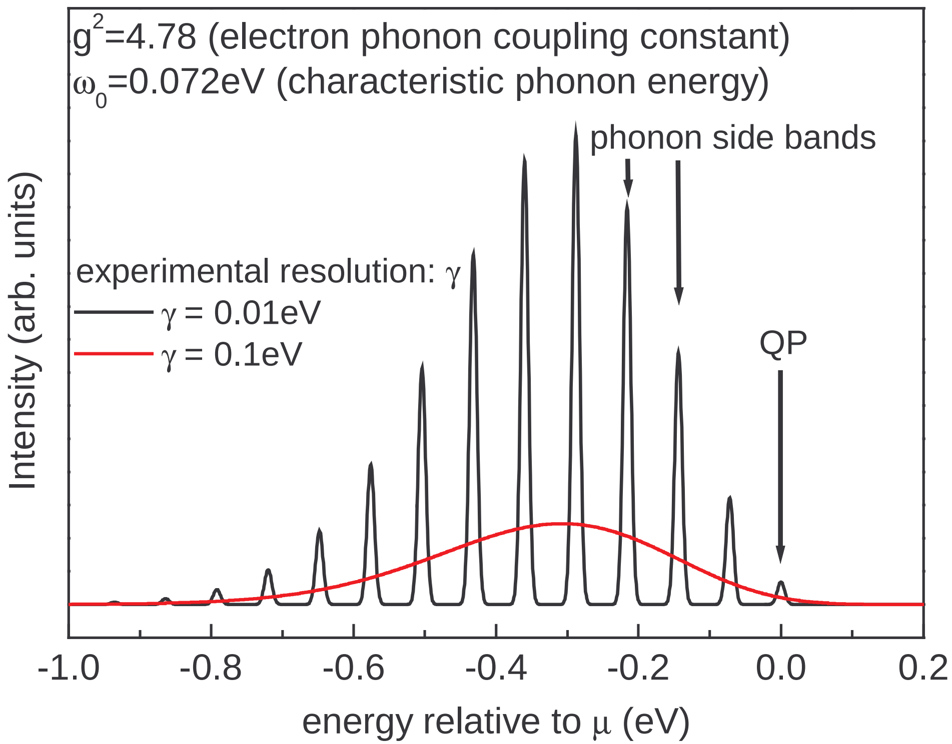
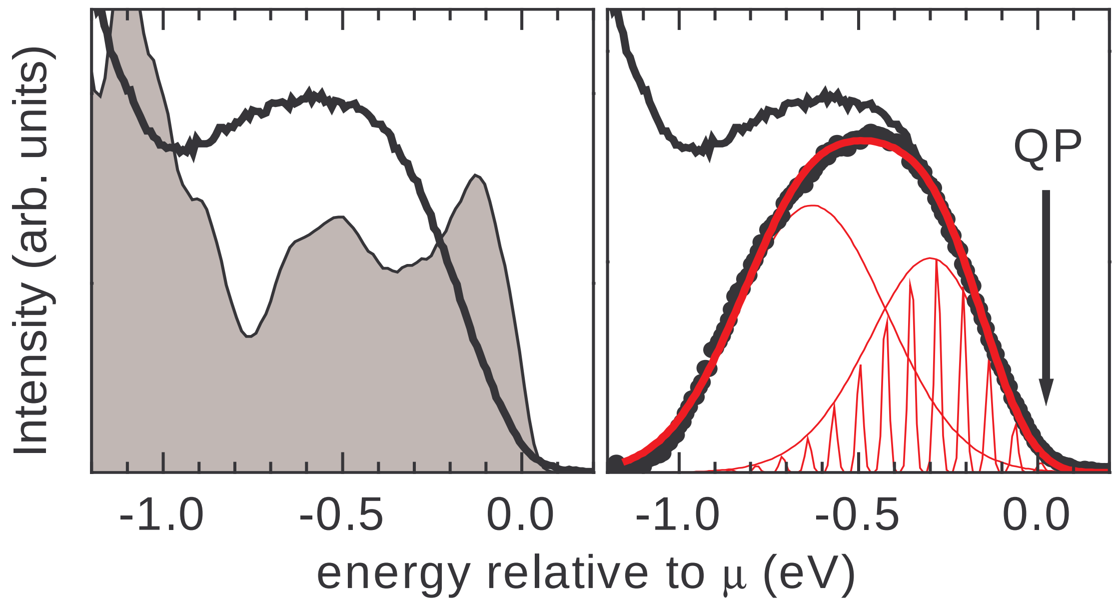
Alexandrov and Ranninger (PRB **45**, 13109 (1992)):

$$I(\epsilon) \propto e^{-g^2} N_P(\epsilon) + \sum_{n=1}^{\infty} e^{-g^2} \frac{g^{2n}}{n!} N_P(\epsilon + n\omega_0)$$

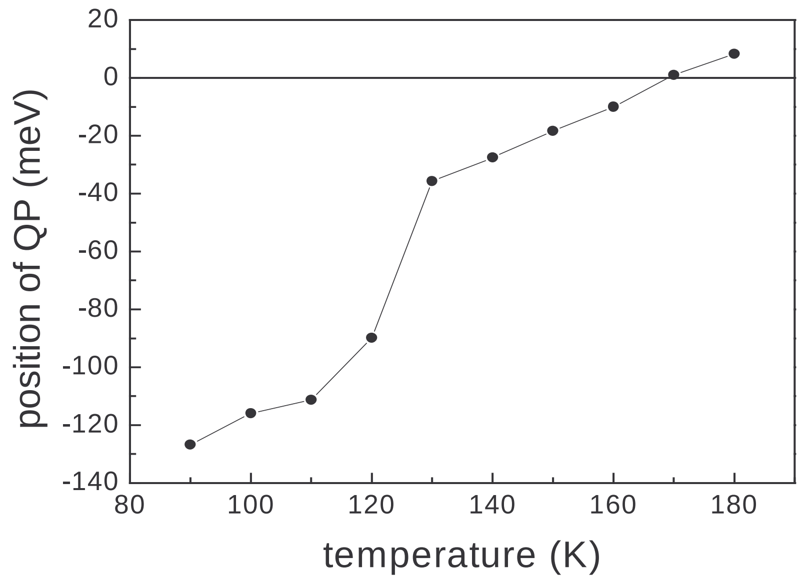
Polaronic quasiparticle intensity exponentially suppressed
Intensity of phononic sidebands in analogy to Franck-Condon factors
(*g:* electron-phonon coupling constant)

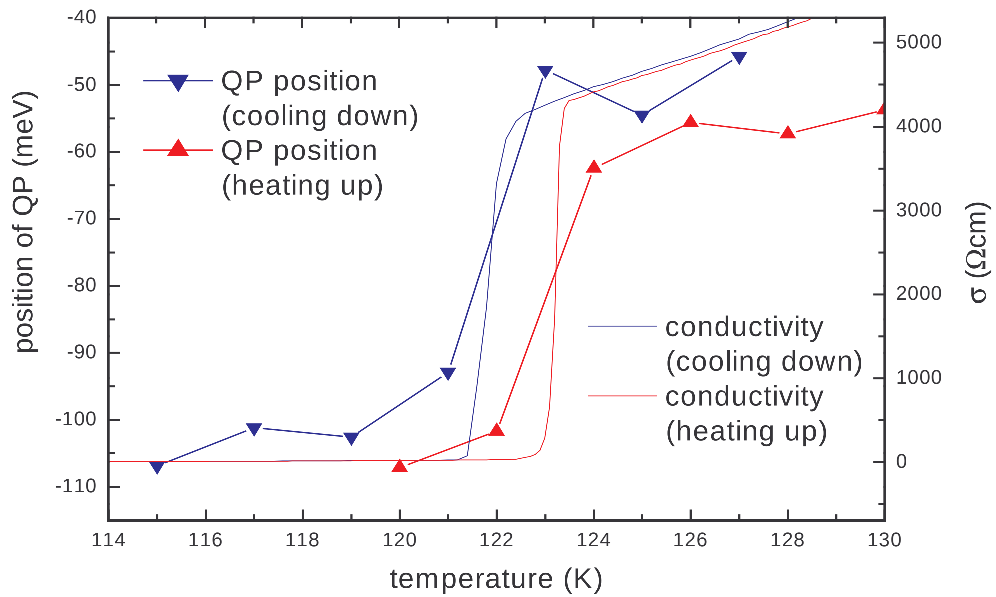




Polarons and Fe_3O_4

position of quasiparticle by using Alexandrov model





gap maintained on cooling through Verwey transition

→ insulator-insulator transition

comparison of PES and resistivity measurements

→ good agreement with temperature and hysteresis of resistivity

Fe_3O_4: soft x-ray ARPES

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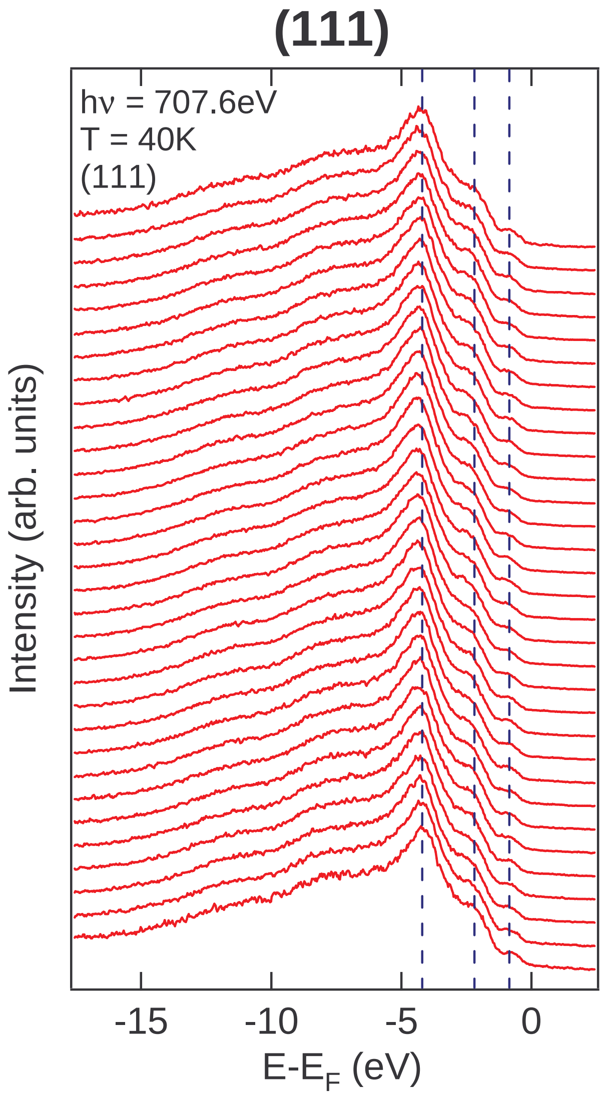

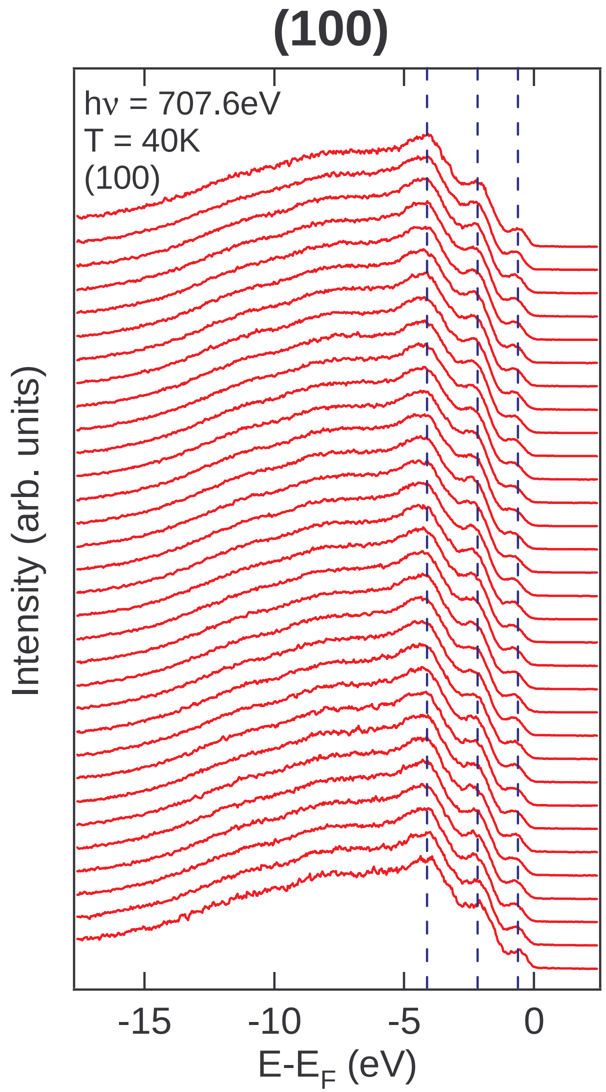

intrinsically no dispersion due to polarons

$Sr_2Ru_{1-x}Ti_xO_4$: properties

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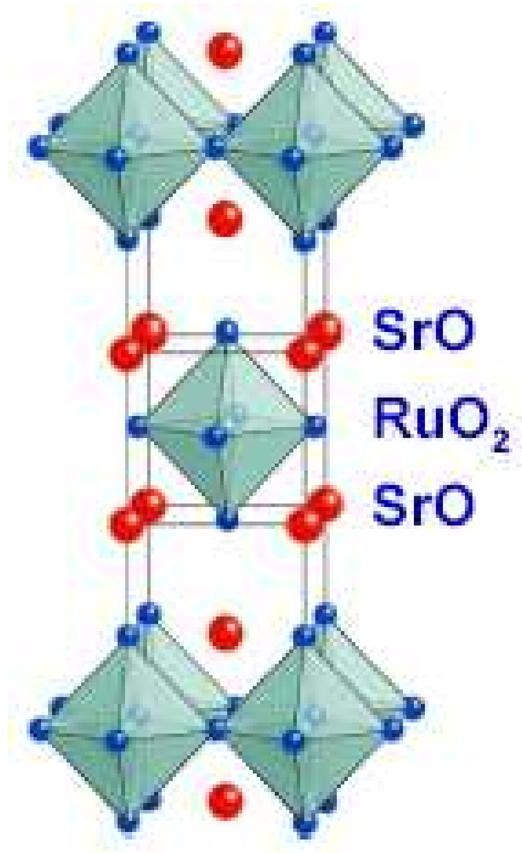
Sr_2RuO_4:

- first non-cuprate layered perovskite to display superconductivity ($T \approx 1K$)
- unusual Cooper pairing: spin triplet with p-wave symmetry
- close to magnetic instabilities (ferromagnetism *and* antiferromagnetism)
- role of spin fluctuations in pairing mechanism??



$Sr_2Ru_{1-x}Ti_xO_4$:

- static antiferromagnetic order induced upon Ti ($4d^0$) substitution $\rightarrow$ spin-density wave for $x \geq 0.03$
- maximum T_{SDW} = 25K for x = 0.09
- nesting??

$\Rightarrow$ effect of doping (Ru $4d^4 \rightarrow$ Ti $3d^0$)?
$\Rightarrow$ effect of disorder (Ti substituted in RuO_2 layers)?
$\Rightarrow$ driving mechanism for SDW? nesting?
$\Rightarrow$ effect of SDW on electronic structure (band backfolding, energy gap)?

Sr_2RuO_4: electronic structure

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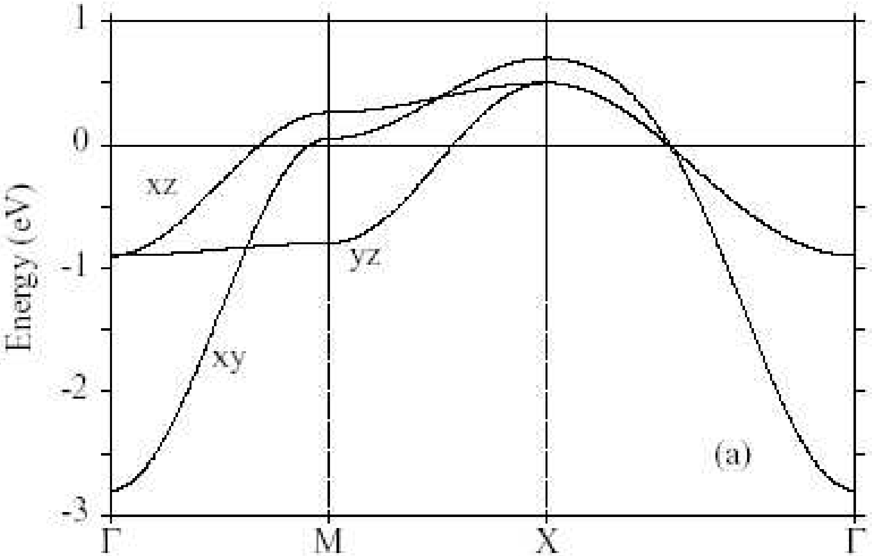
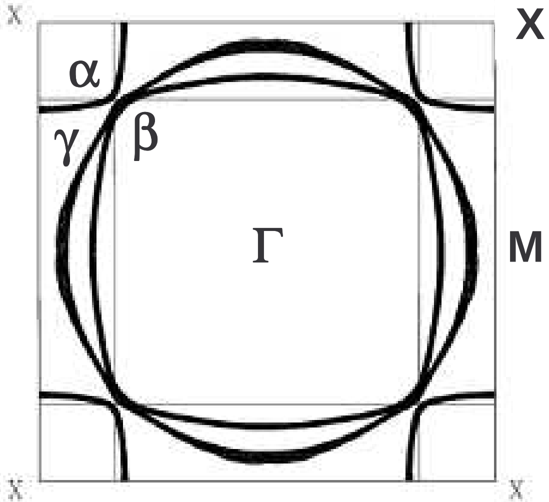
LDA band structure



A. Liebsch and A. Lichtenstein, PRL (2000)

3 Ru 4d t_{2g} bands crossing E_F → 3 FS sheets

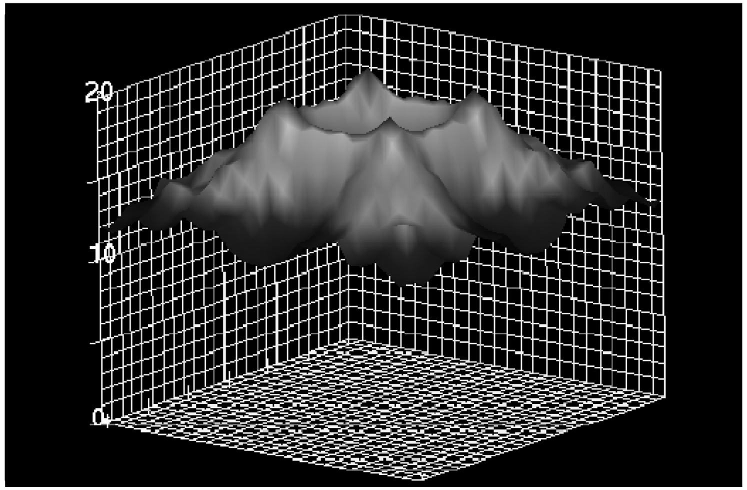
LDA Fermi surface



α (hole-like): 1D
β (electron-like): 1D } nesting
γ (electron-like): 2D

I.I. Mazin and D.J.Singh, PRL (1997)

electronic susceptibility



I.I. Mazin and D.J.Singh, PRL (1999)

$Sr_2Ru_{1-x}Ti_xO_4$: DOS and Ti „doping“

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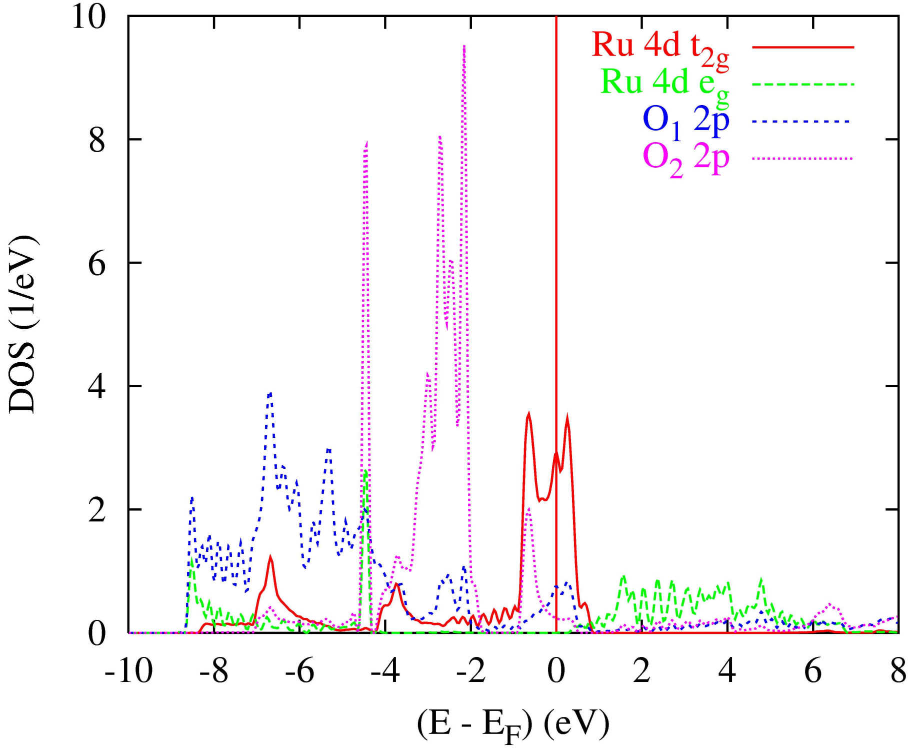
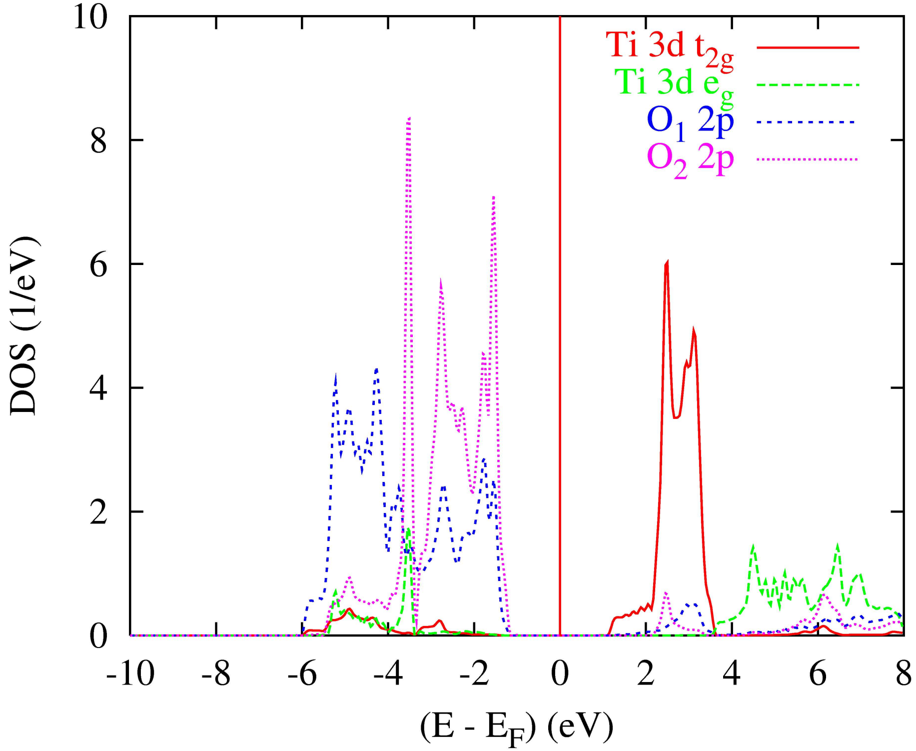
Sr_2RuO_4



Sr_2TiO_4



V. Eyert (2001)

LDA partial DOS: Ti 3d t_{2g} states shifted far above E_F → no participation in conduction band formation → no hole doping of conduction bands, no change of FS volume expected

$Sr_2Ru_{1-x}Ti_xO_4$: surface reconstruction

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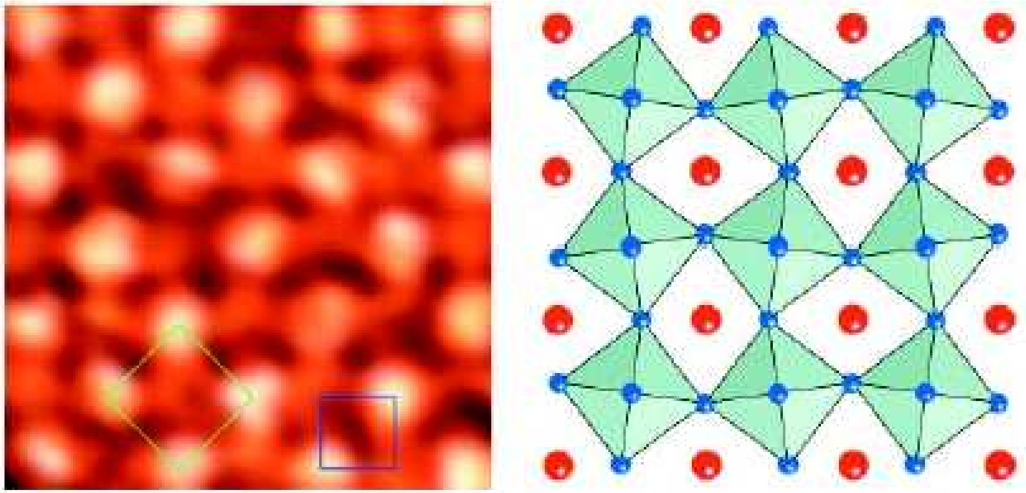
Sr_2RuO_4

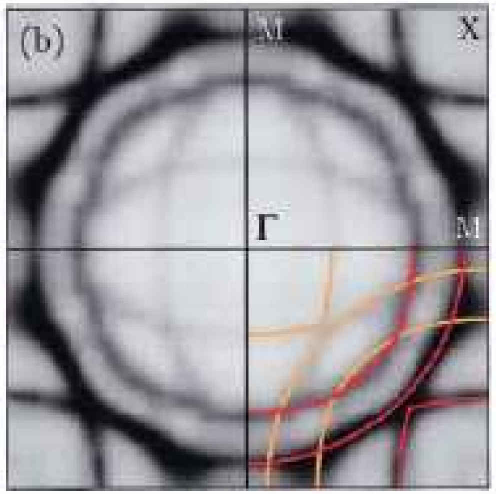


R. Matzdorf et al., Science (2000)

cleaved at

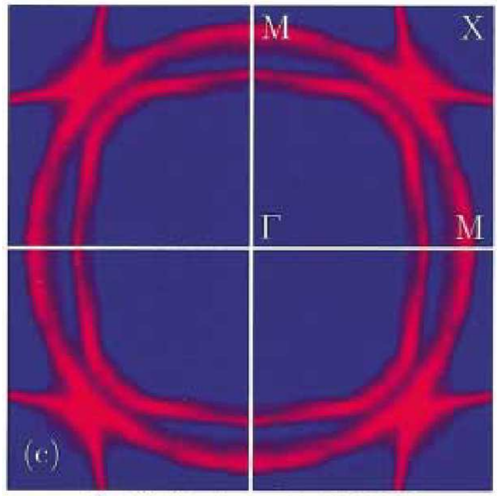
10K

Sr_2RuO_4



$\sqrt{2} \times \sqrt{2}$ **surface reconstruction in doped <u>and</u> undoped compounds**

cleaved at 180K → surface related features suppressed



Damascelli et al., PRL (2000)

High-energy ARPES: FS crossings

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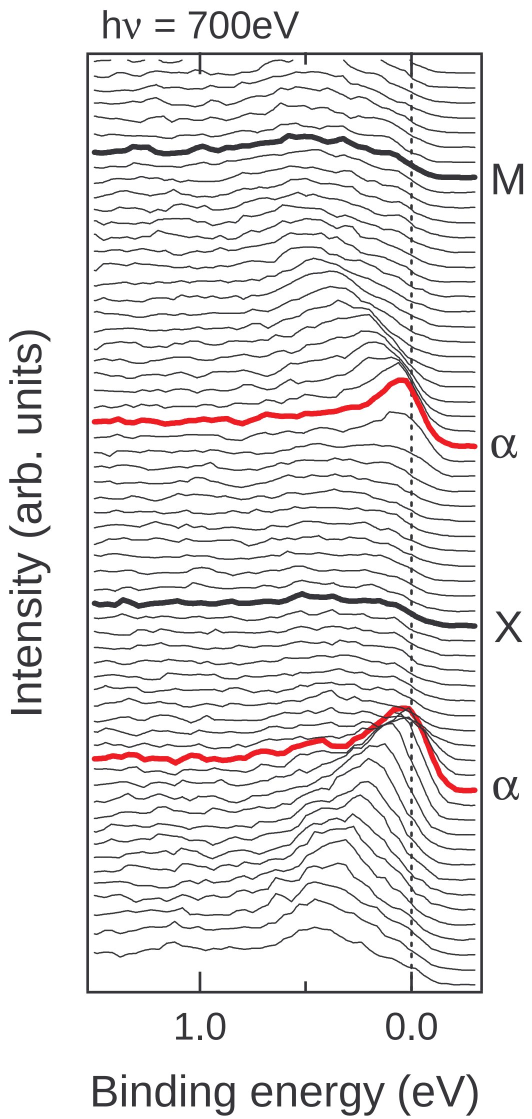
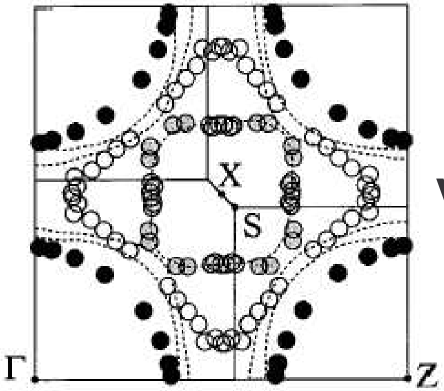
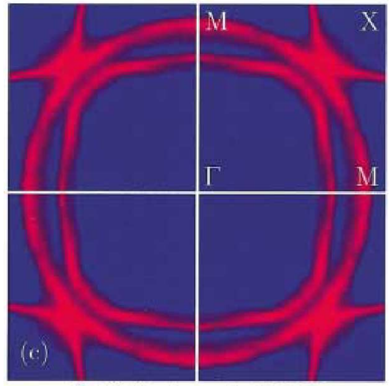
Sr_2RuO_4 - Fermi surface



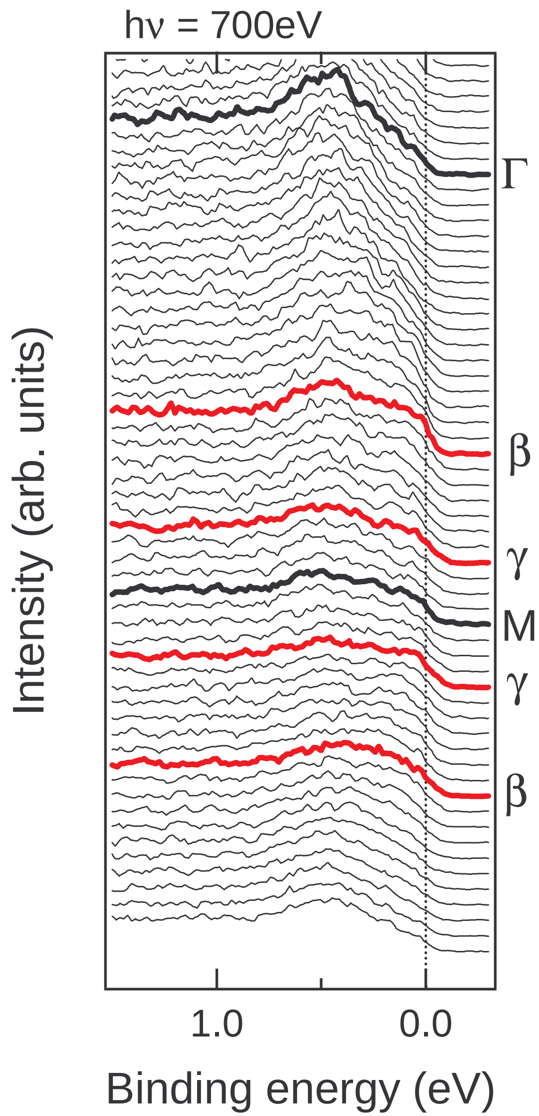


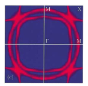
Yokoya et al., PRB (1996)

vs.

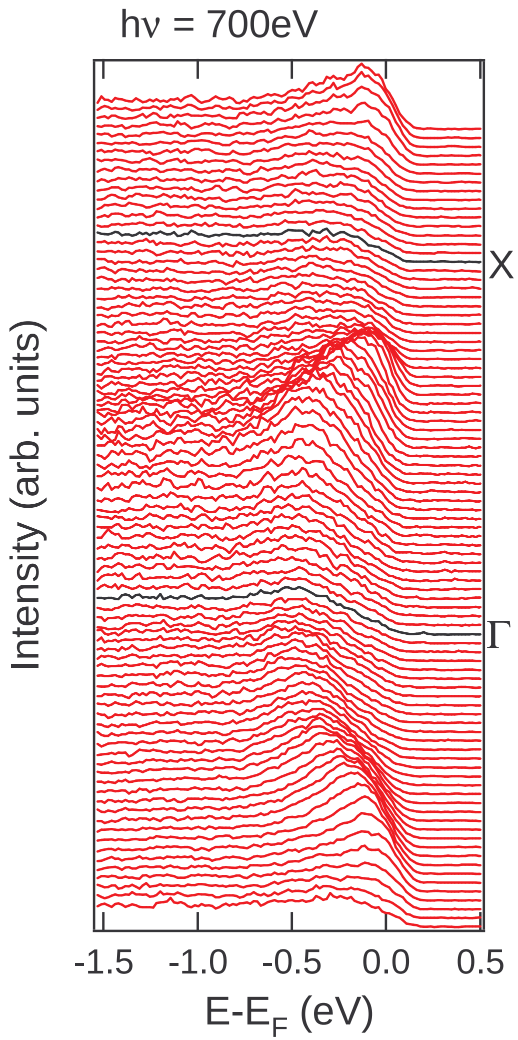


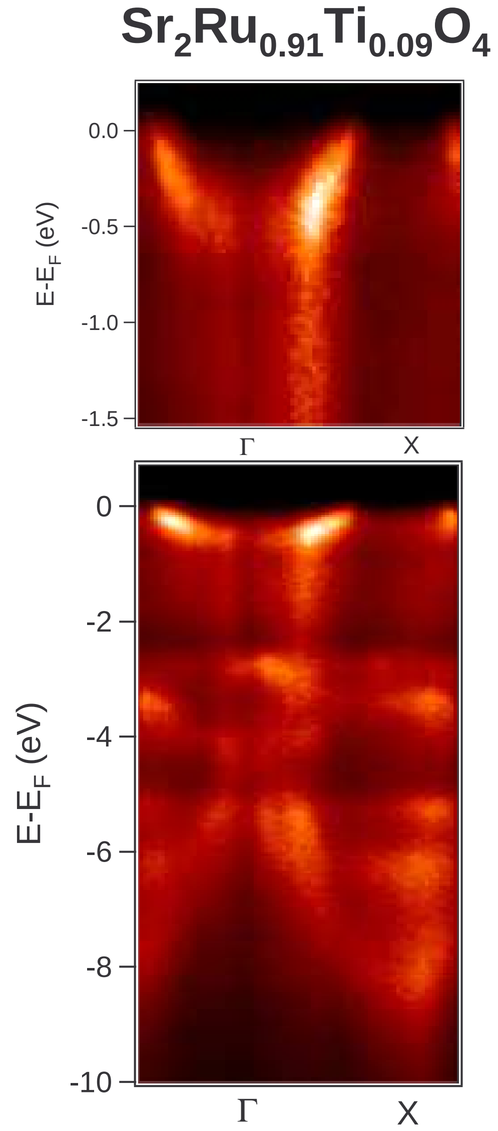
Damascelli et al., PRL (2000)

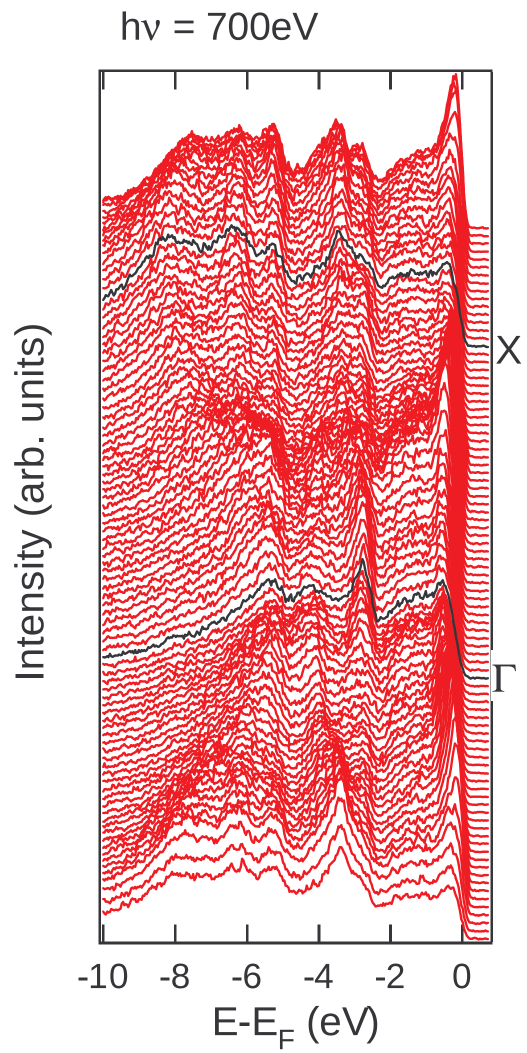


soft x-ray ARPES clearly identifies FS crossings in support of 

High-energy ARPES: band maps







- **sharp dispersing features (despite Ti 3d ions induced disorder)**
- **near E_F structure slightly broadened → disorder**

High-energy ARPES: FS and nesting

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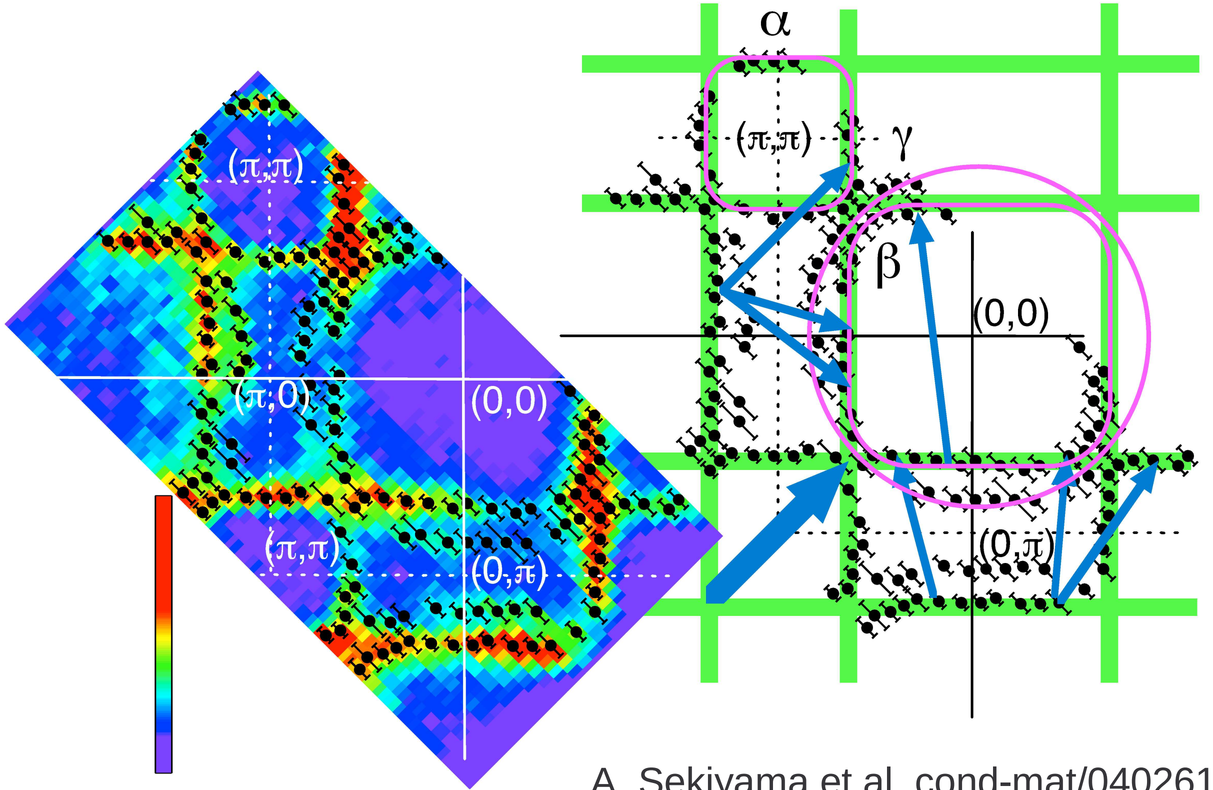
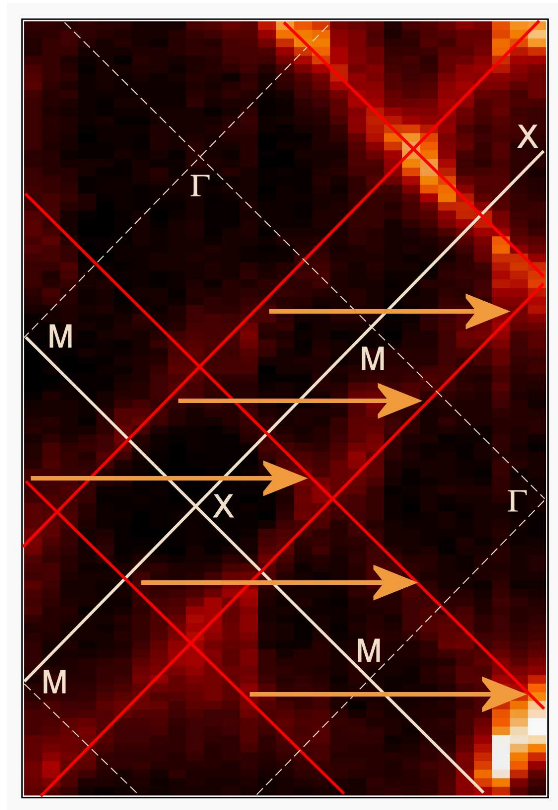
Sr_2RuO_4



A. Sekiyama et al, cond-mat/0402614

$Sr_2Ru_{0.91}Ti_{0.09}O_4$



- Fermi surfaces of x = 0 and x = 0.09 samples in agreement with bulk electronic structure (de Haas – van Alphen, LDA calculations)
- FS volume unchanged within experimental accuracy
- nesting between quasi-1D FS sheets identified as driving mechanism for SDW

Low-energy ARPES: doping, disorder, bands

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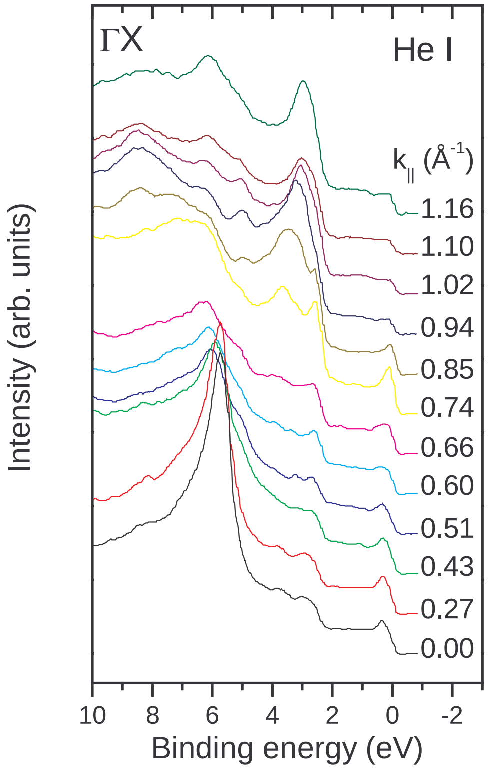
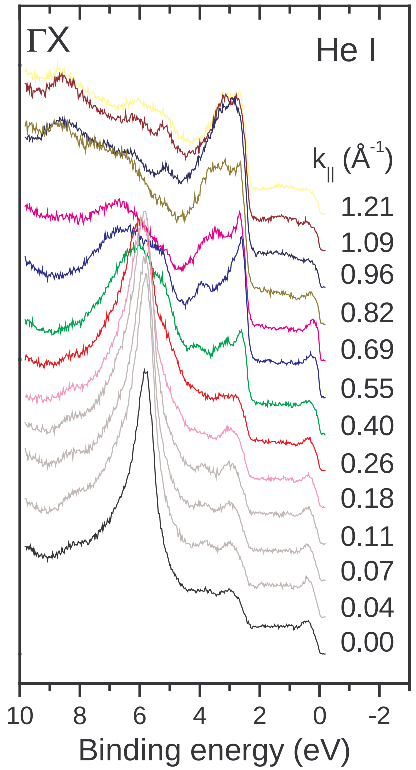
Sr_2RuO_4

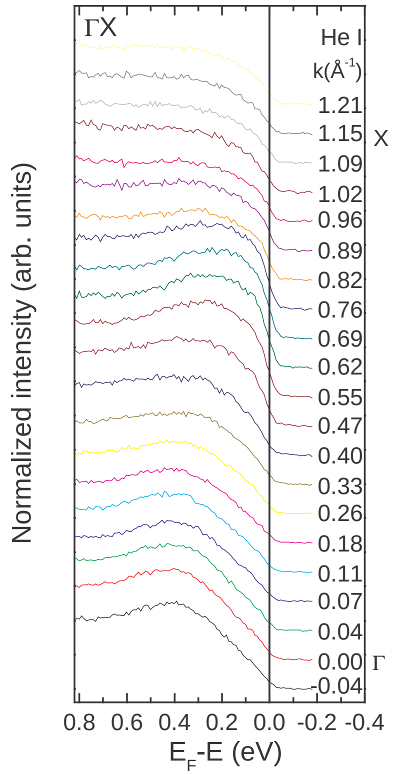


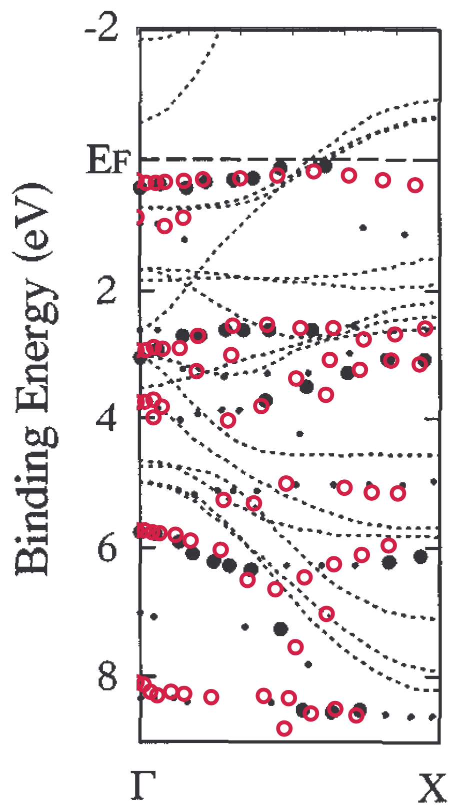
$Sr_2Ru_{0.9}Ti_{0.1}O_4$



T. Yokoya et al., PRB (1996)

$Sr_2Ru_{0.9}Ti_{0.1}O_4$





T. Yokoya et al., PRB (1996)
Red circles: x = 0.10

- good overall agreement of VB photoemission with x = 0 sample
- sharp dispersing features (despite Ti 3d ions induced disorder)
- near E_F structure slightly broadened $\rightarrow$ disorder
- good agreement of band dispersions with undoped sample
- k_F essentially unchanged $\rightarrow$ no change in band filling

Summary

- extrinsic vs. intrinisic surface effects in photoemission spectroscopy
- higher volume sensitivity by soft x-ray photoemission
- Verwey transition in magnetite (Fe_3O_4):
  - above T_V: pseudogap behavior, no quasiparticle peak, insulator, charge carriers: small JT polarons
  - below T_V: insulator, combined charge and orbital ordered phase
  - not purely electronic, electron-phonon coupling important (if not even dominant!)
- Electronic structure of $Sr_2Ru_{1-x}Ti_xO_4$:
  - x = 0: confirmation of bulk FS topology
  - x = 0.09: no effect of Ti substitution except for slight disorder potential, FS volume unchanged