Prominent Metal Phase Quasi-particle Peak and High Temperature Correlation Gap Filling in Photoemission Spectra of $(V_{1-x}Cr_x)_2O_3$: Comparison to LDA + DMFT (QMC) Theory

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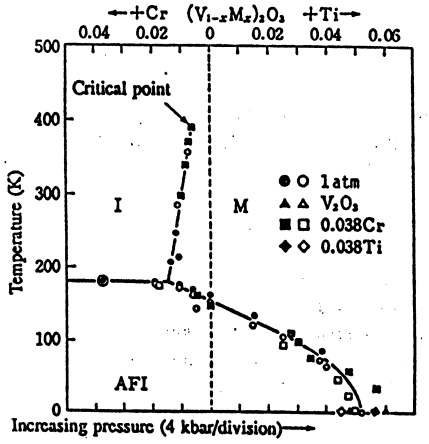
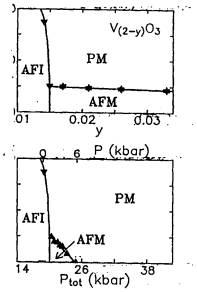
Work at UM Supported by the U.S. NSF and the U.S. DoE.

V_2O_3 phase diagram



McWhan et al. PRL '69, PRB '73



S.A. Carter et al. PRL '91
New phase boundary

Interpreted as Mott transition
Brinkman-Rice for 1-band Hubbard

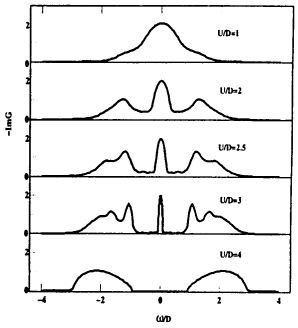
Some standard history for V_2O_3

- McWhan, Rice *et al.* (PRL, PRB 1969 – 1973)
  Vertical pair of V ions stabilize a_{1g} singlet → $a_{1g}e_g$, S = ½
  Ignore orbital degeneracy, use 1-band Hubbard
- Castellani *et al*. (PRB 1978).
  Inclusion of orbital ordering for the AFI phase
  Keep a_{1g} singlet & $a_{1g}e_g$ & S = ½
- Kotliar, George, and co-workers (e.g. Rev. Mod. Phys 1996)
  DMFT for 1-band Hubbard
  Analysis of optical spectroscopy
  UV photoemission

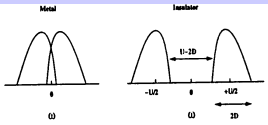
DMFT for metal-insulator transition

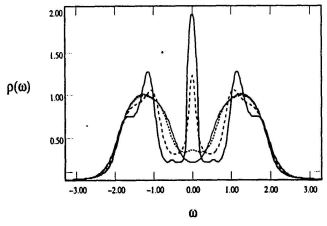
1-band Hubbard, d →infinity
k-independent self energy
A. George, G. Kotliar, W. Krauth, M. Rozenberg Rev. Mod. Phys '96

Spectral function for varying U
"Kondo-like" picture



Old gap collapse picture





Increase T in metallic phase
- lose quasi-particle peak

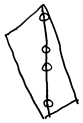
Issues of realism

Arguments from the beginning over Mott transition picture and "realism" of simple 1-band Hubbard model

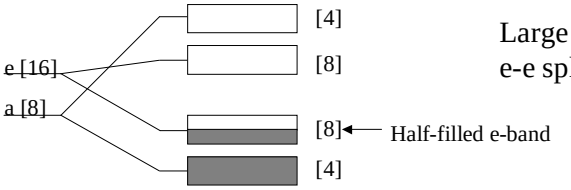
3 orbitals/ion
4 ions/cell
$2e^-/V^{3+}$ ion

→

24 states/cell
$8e^-$/cell

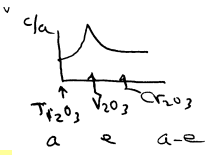


Common idea: bonding-antibonding splitting



Large a-a splitting OK
e-e splitting small

Various clever models based on various clever arguments: Goodenough, Zeiger – changing a-e splitting; Castellani et al, orbital ordering.



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Newer work--multiband models needed for V_2O_3

•LDA+U: Ezhov *et al*. (PRL 1999).
only e occupation, S=1 on site and no e site-ordering
• Paolasini *et al*. (PRL 1999).
resonant x-ray scattering claims to see e-site ordering
• Park *et al*. (PRB 2000).
Polarization-dependent x-ray absorption
S=1 and ee:ea = 2:1 in AFI phase
• Mila *et al*. (PRL 2000) and Di Matteo et al (cond-mat/2001)
2 different correlated models of c-axis pair states for AFI phase
dynamic mix of ee and ea with S=1 on sites
• Held *et al*. (PRL 2001) LDA+DMFT
multiband many body realism for PM and PI phases and single particle spectra—for PM phase, agrees with 60 eV PES

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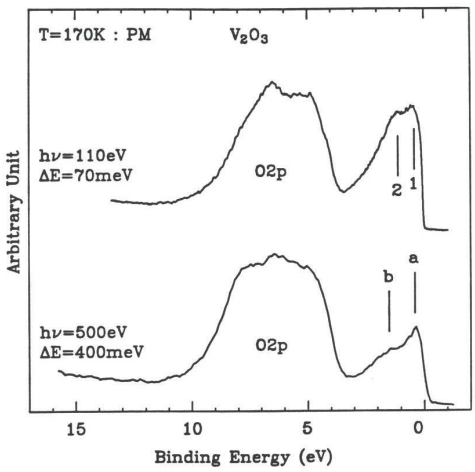
Early evidence of bulk/surface difference



J.-H. Park thesis
Univ. of Michigan, 1994

Reduction of near E_F peak in metallic phase for low photon energy relative to high photon energy implies surface effect but resolution not good at high photon energy at that time.

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High photon energy high resolution bulk sensitive resonant photoemission at SPring8

- **Samples from Purdue University: single crystals of $(V_{1-x}R_x)_2O_3$ x=0; R=Cr (x=1.2%, 1.8%, 2.8%); R=Ti (x=1.0%)**
- **Spectrometer: beamline BL25SU, SPring-8, Japan with SCIENTA SES200**
- **Base pressure: low 10^{-10} Torr.**
- **Sample cleaning: cleaved to expose a (10-12) plane.**
- **Energy resolution: ~ 90 meV.**
- **Fermi level position: Fermi edge of Pd metal electrically connected with a sample.**

SPring-8

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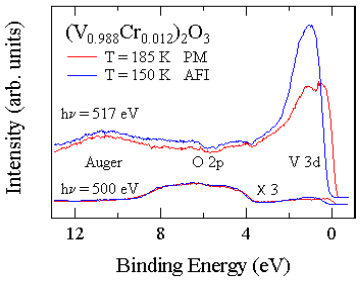
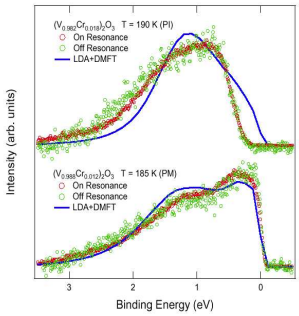
Initial results: RESPES of $(V_{0.988}Cr_{0.012})_2O_3$ at V 2p→3d edge (near 500 eV)

• On- and off-resonance spectra





• V 3*d* spectra

• Strong enhancement of V 3d signal at 2p → 3d edge.
• Within signal to noise of off-resonance spectrum, on- and off-resonance spectra of V 3d essentially identical
⇒ 2p → 3d RESPES provides V 3d spectral function.
• For metal, better agreement with LDA+DMFT (QMC) than for 60 eV spectrum used in comparison made in Held et al PRL

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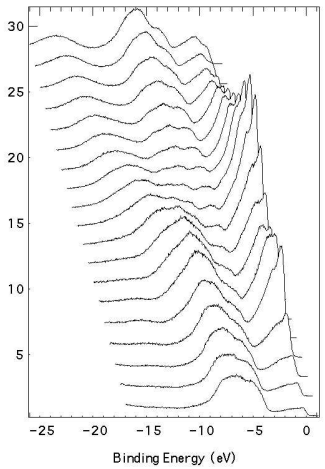
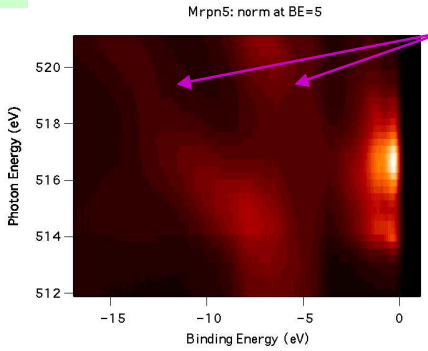
New data from ALS (Dec, Jan ' 01) --shock #1!

ALS spectromicroscopy beamline
J.D. Denlinger, JWA

PM phase RESPES done in steps of 0.5 eV





See incoherent Auger emission, can overlap RESPES spectra and give lineshape artifacts —bad!

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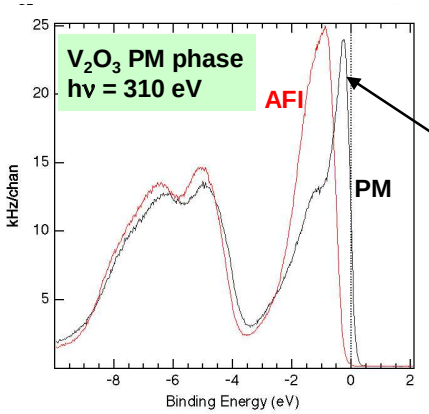
Really really big shock #2!!



ALS Spectromicroscopy Beamline—J.D. Denlinger

General overall enhancement of 3d interesting, but OK.

Large E_F peak—WOW!

What could be different from SPring8?

Special photon energy?
k_z dependence?

Spot Size? 100 microns (and position important) vs. 1 mm at SPring8 in initial experiments

Back to SPring8, April ' 02 ---Pray we can sort it out!

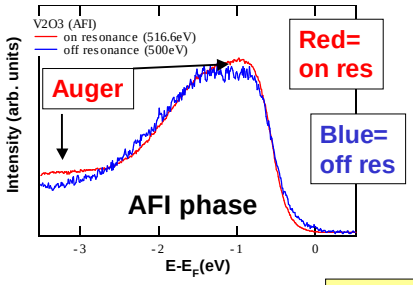
Planned to focus on large hν ARPES-- did more PES instead

Good fortune—

Beam line modified to decrease photon spot size from 1 mm to100 μmeters same as ALS

Spot size decrease also increased photon intensity so could measure off resonance with good S/N and full high resolution capability that makes this beamline unique.

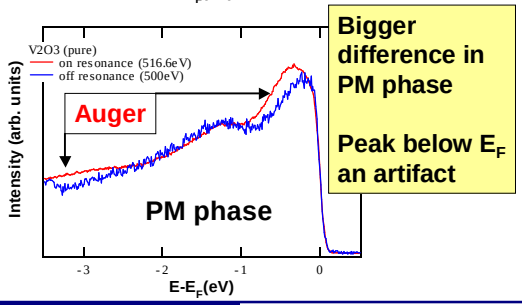
Yes, Auger in V_2O_3 RESPES lineshape



Red= on res

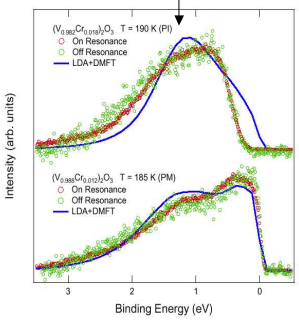
Blue= off res

With good resolution and good S/N can see on-res/off-res difference previously hidden in poor statistics of initial data for off-resonance spectra.



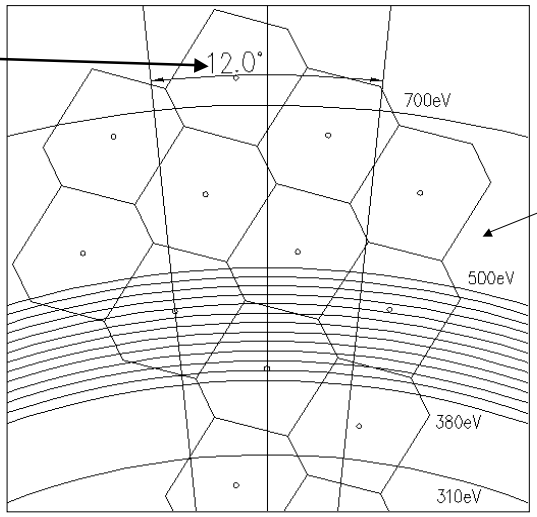
Bigger difference in PM phase

Peak below E_F an artifact



Brillouin zone sampling—(10-12) surface

analyzer angle range in angle-integrated mode covers more than 1 BZ.



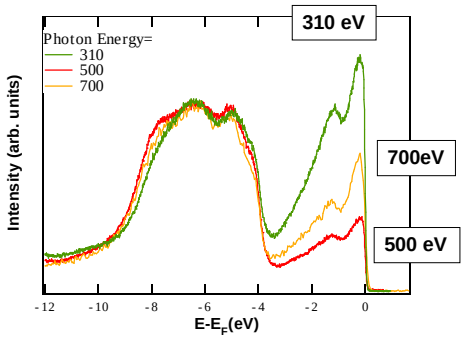
Avoid RESPES range 510eV to 560 eV

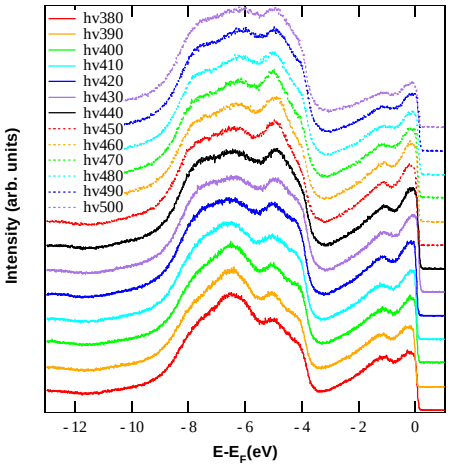
Photon energy range covers full Brillouin zone—use for kz integration

Spectra vs photon energy, PM phase 175K

Verify ALS result for E_F peak.
310 eV enhances overall 3d emission
but not special for E_F peak

hν=380~500eV, 10eV steps normalized to –6.5eV





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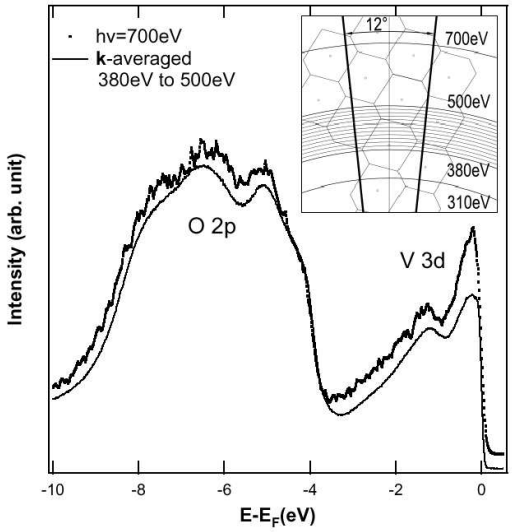
k-averaged spectrum less peaky than 700 eV



k-averaged spectrum less peaky than for 700 eV

but due to probe depth difference and not special k_z value of single photon energy

see next slide.

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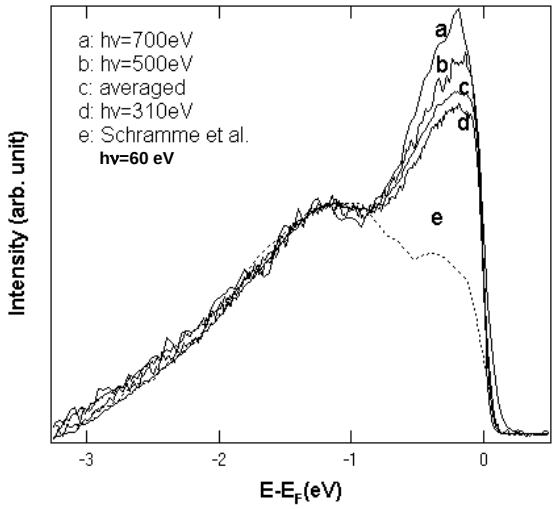
Photon energy dependence of E_F peak



Monotonic increase with hν ⇒ Probe depth outweighs k_z dependence, so compare 700 eV spectrum to theory

Much different from 60 eV spectrum compared favorably to 1160K theory in PRL (2001)

But note: some non-monotonic variation in hν range for k-averaging and below 300 eV, may show kz dependence

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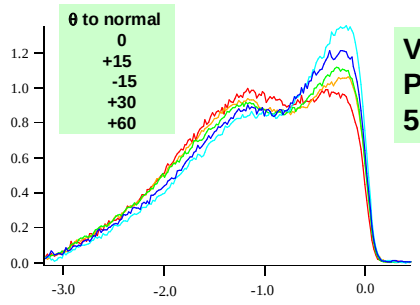
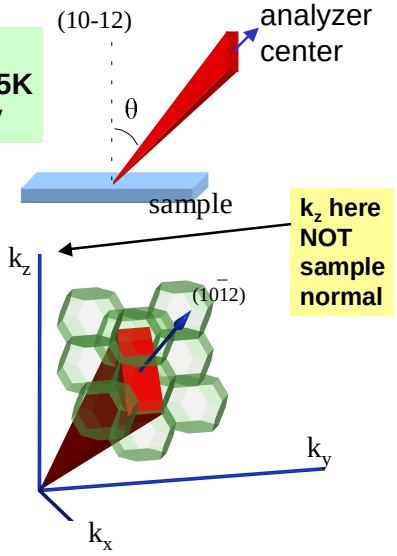
Increase surface sensitivity with emission angle-- E_F peak decreases nearly to height for 60 eV



V_2O_3 PM-175K 500 eV



hν=500eV, ΔE=85meV
θ= -15°, 0°, 15°, 30°, 60°

Each spectrum is angle integrated with acceptance angles Δθ=12°& 5.7° covering the whole Brillouin zone on spherical surface probed at 500 eV.

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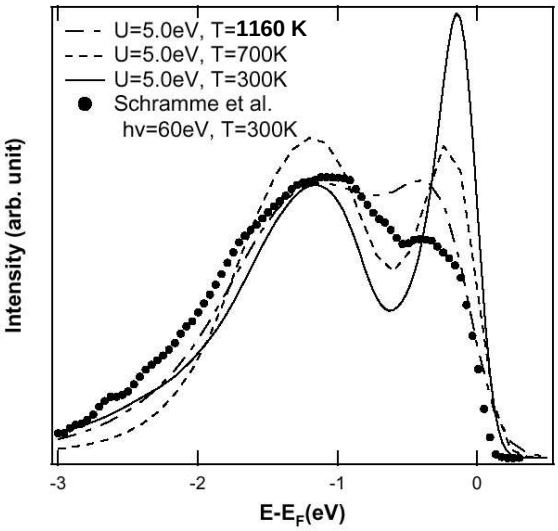
New LDA +DMFT(QMC) theory for lower T get E_F PEAK—like 1 band Hubbard



Peak sharpens up with decreasing T

Small increase of spectral weight (estimate < 10%)

LDA/DMFT (QMC) at 1160K compared favorably to 300K 60 eV data in first theory PRL (Held et al) but now shows large disagreement when compared for same T.

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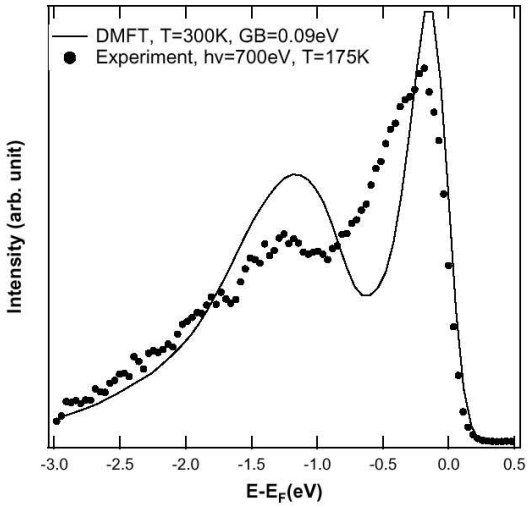
New data and new theory (U=5.0 eV, 300K)



Qualitative agreement on presence of prominent E_F peak in spectrum

Experimental peak <u>width</u> larger than theory width, roughly by factor of 2
⇒k-dependent Σ?
⇒cluster of c-axis pair?

Experimental peak <u>weight</u> larger than theory weight—
⇒ smaller U in DMFT scheme
BUT then too small to give MIT with Cr doping in current theory.
⇒U increases with Cr doping or through the MIT due to screening mechanisms.

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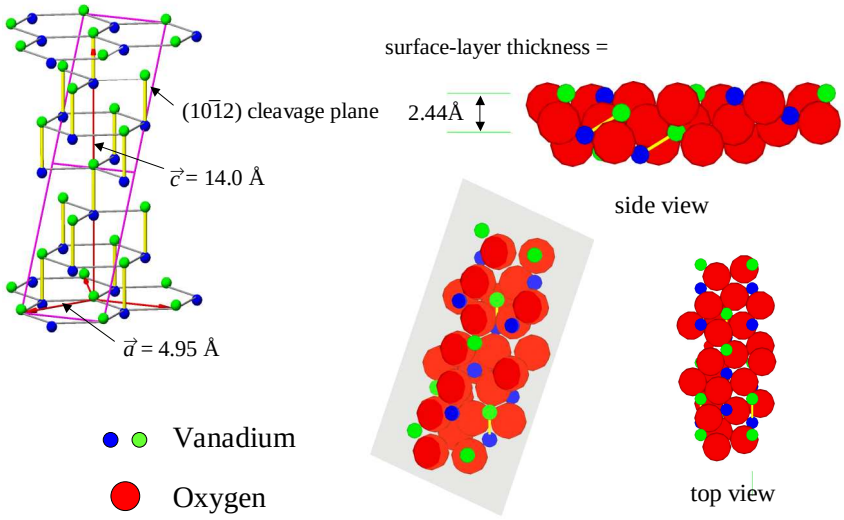
Crystal structure and surface layer



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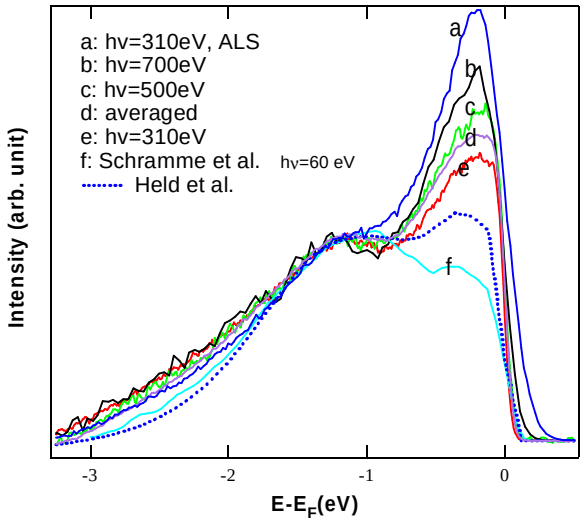
"superpeak" at ALS with photon energy 310 eV



One time observation

lucky cleave and a small photon spot

Could study smooth surface at lower photon energy?

Hope for future ARPES

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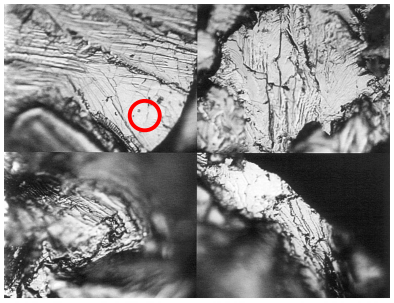
Optical micrographs of cleaved surface

Can see that optimizing with small spot finds regions with few steps, terraces.
Steps and edges may be the largest effect!



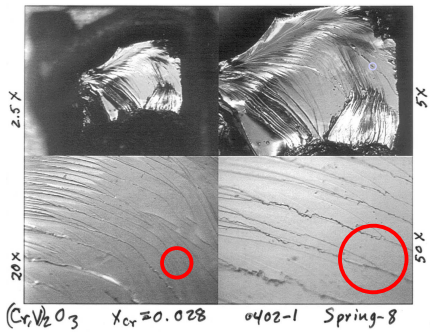
FOV: 2.6 x 2.0 mm

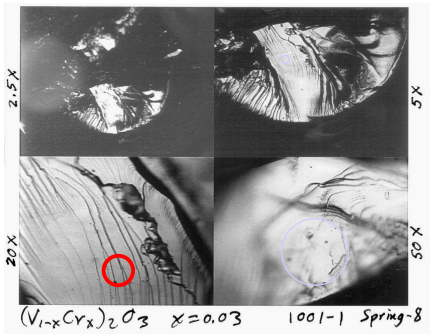
FOV: 650 x 500 μm

~100 micron spot size

Optical micrographs of cleaved surfaces

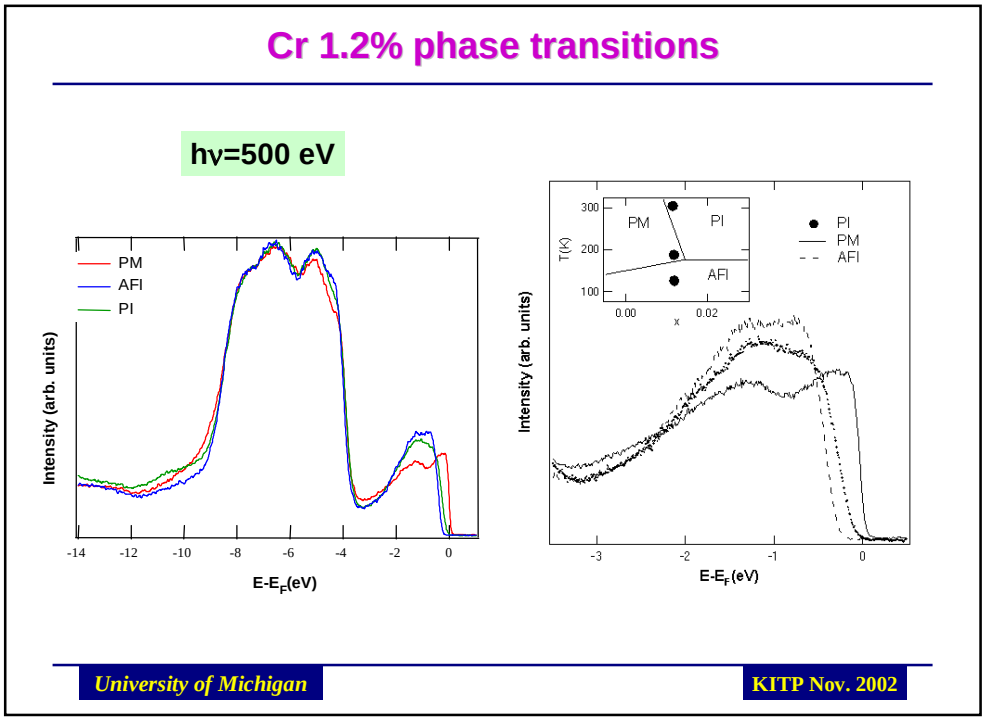
Cr doped samples seem to give nicer cleaves, smoother, fewer terraces.





Field of View: 2.5X (5.2 x 4.0 mm) 5X (2.6 x 2.0 mm)
20X (650 x 500 μm) 50X (260 x 200 μm)

~100 micron spot size


Cr 1.2% phase transitions
hν=500 eV
PM
AFI
PI
Intensity (arb. units)
E-E_F(eV)
T(K)
x
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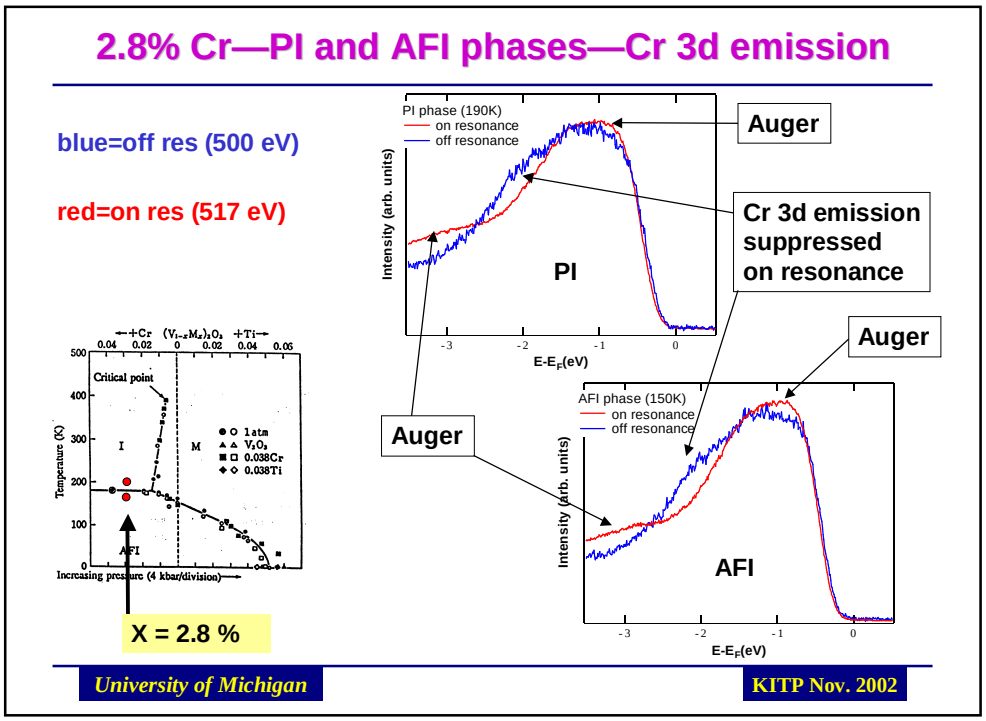
2.8% Cr—PI and AFI phases—Cr 3d emission
blue=off res (500 eV)
red=on res (517 eV)
PI phase (190K)
on resonance
off resonance
Auger
Cr 3d emission suppressed on resonance
PI
Auger
Auger
AFI phase (150K)
on resonance
off resonance
AFI
Intensity (arb. units)
E-E_F(eV)
Critical point
Temperature (K)
Increasing pressure (4 kbar/division)
X = 2.8 %
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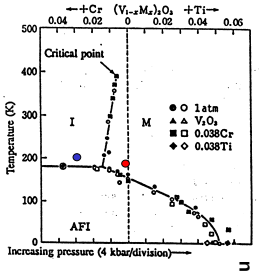
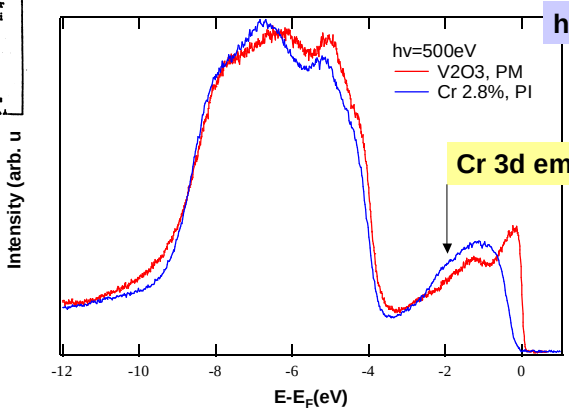
PM to PI transition



Cr 2.8% PI phase (190K, blue)

V_2O_3 PM phase (175K, red)

hν = 500 eV



Cr 3d emission here

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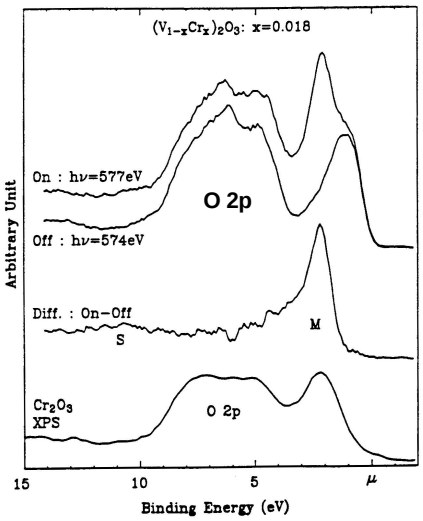
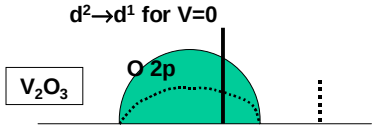
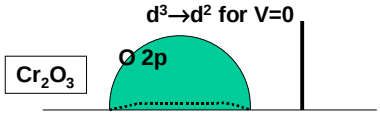
Cr 1.8% RESPES and Cr_2O_3 XPS



Hybridization V strong
$d^2 \rightarrow d^1$ for V=0



Hybridization V weak
$d^3 \rightarrow d^2$ for V=0



Anderson model idea for why Cr 3d easily seen relative to V 3d for Cr so dilute

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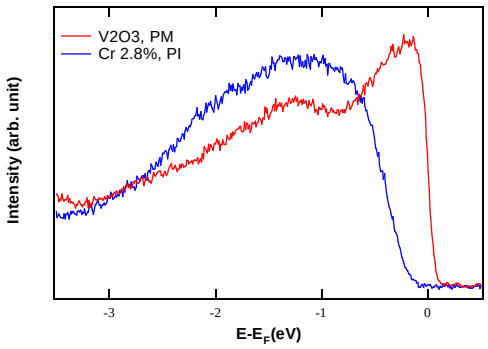
PM to PI transition, V_2O_3 and Cr 2.8%

500 eV spectra



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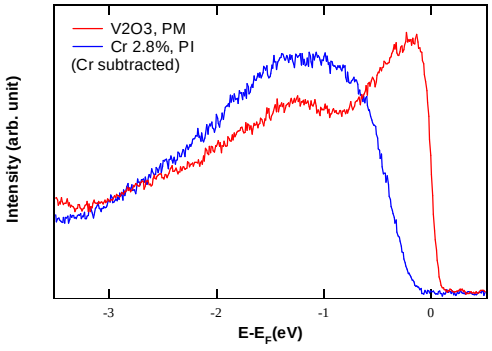
MIT, with V 3d spectrum (Cr subtracted)

500 eV spectra



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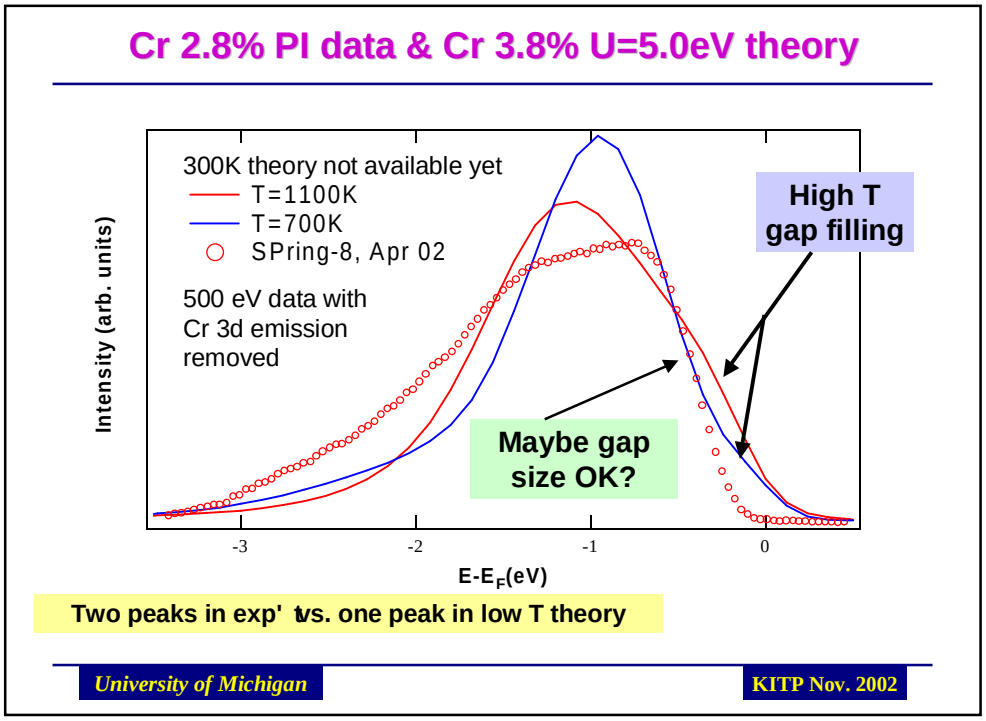
Cr 2.8% PI data & Cr 3.8% U=5.0eV theory
300K theory not available yet
T=1100K
T=700K
SPring-8, Apr 02
500 eV data with
Cr 3d emission
removed
High T
gap filling
Maybe gap
size OK?
Intensity (arb. units)
-3
-2
-1
0
E-E_F(eV)
Two peaks in exp' t vs. one peak in low T theory
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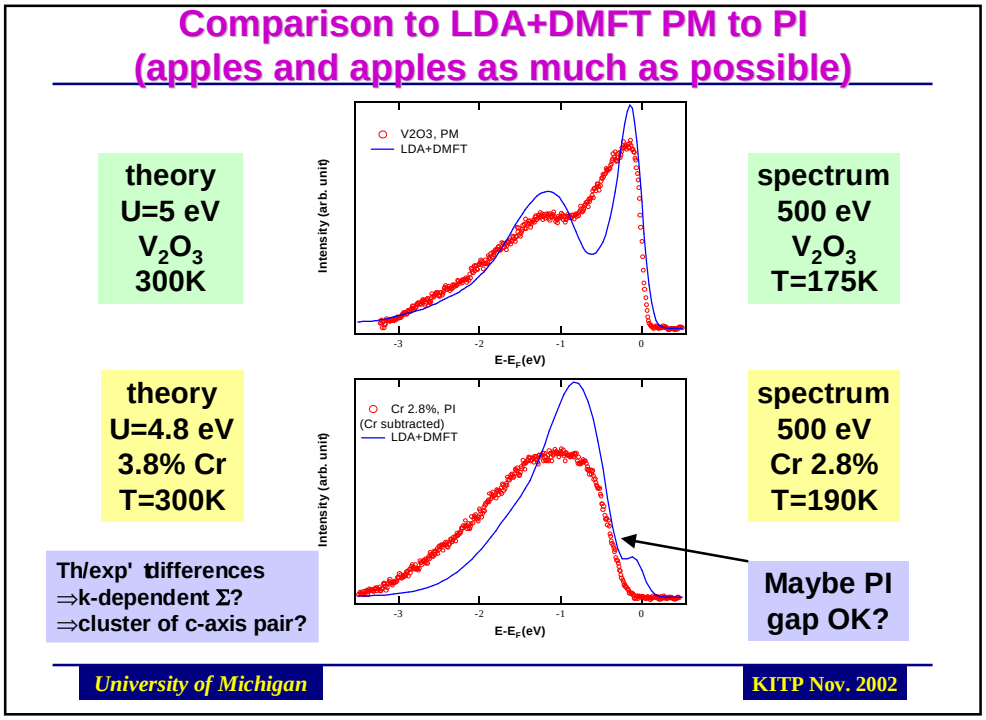
Comparison to LDA+DMFT PM to PI
(apples and apples as much as possible)
theory
U=5 eV
V2O3
300K
V2O3, PM
LDA+DMFT
Intensity (arb. unit)
E-E_F(eV)
spectrum
500 eV
V2O3
T=175K
theory
U=4.8 eV
3.8% Cr
T=300K
Cr 2.8%, PI
(Cr subtracted)
LDA+DMFT
spectrum
500 eV
Cr 2.8%
T=190K
Th/exp' t differences
⇒k-dependent Σ?
⇒cluster of c-axis pair?
Maybe PI
gap OK?
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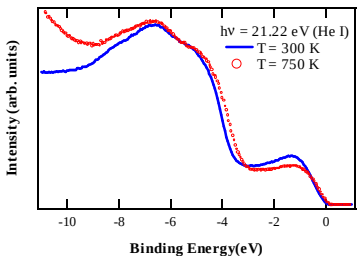
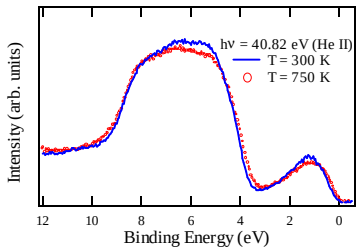
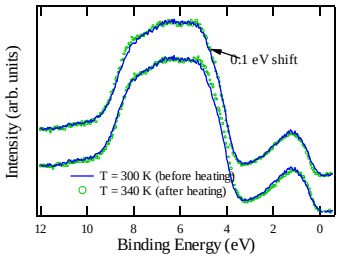
750K PI phase photoemission spectra to see high T gap filling





Home lab, helium lamp
x= 2.8%, scraped surface



Data before and after heating same except for overall 0.1 eV shift.

⇒Spectrum T-dependence OK. Just a change in surface E_F pinning.

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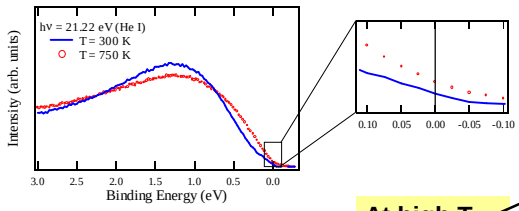
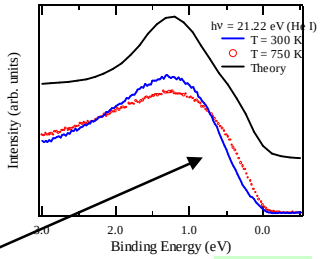
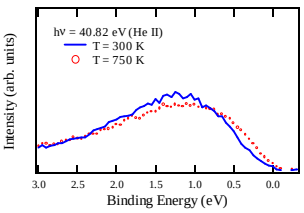
750 K PI phase photoemission – near E_F

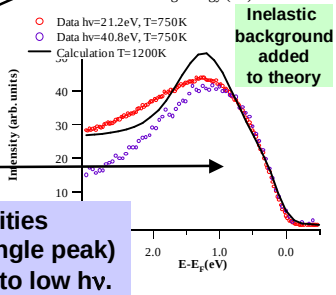
High T gap filling and E_F DOS increase







At high T near E_F curvature reverses to be like high T theory



Inelastic background added to theory

But other similarities to theory (e.g. single peak) misleading. Due to low hv.

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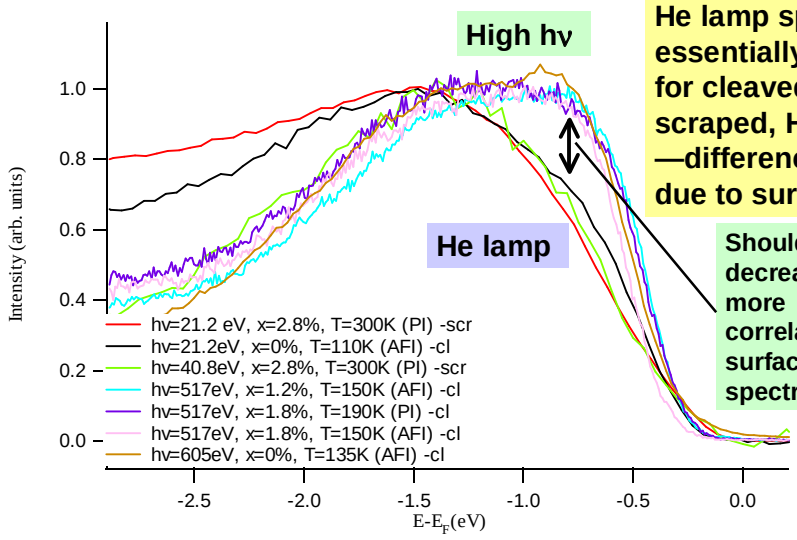
I/AFI spectra for various hν and surface prep



He lamp spectra essentially same for cleaved and scraped, He I,II —difference due to surf. sens.

Shoulder decrease in more correlated surface spectrum.

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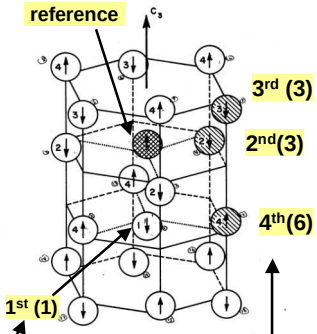
Early optical studies and coupling between neighbors connected by oxygens

NiO, Cr_2O_3 optical spectrum like Ni^{2+}, Cr^{3+} impurity
e.g. ruby $(Al_{1-x}Cr_x)_2O_3$

V_2O_3 AFI, PI optical spectra NOT like V^{3+} impurity
⇒ V^{3+} ion identity LOST in V_2O_3

$(Al_{1-x}V_x)_2O_3$ optical spectrum LIKE V^{3+} impurity for
x < .08, below miscibility gap extends to x ≈ 0.8
⇒ V^{3+} ion identity RETAINED for 2nd, 3rd, 4th nn in dilute limit
⇒ (a) V^{3+} identity lost in 1st nn pairs OR
(b) lost from multiple numbers (3,3,6) of further neighbor pairs in concentrated limit.
J. W. Allen PRL 36, 1249 (1976)



[J(1st) / J(other)]
[t(1st) / t(other)]^2
≈ 30

a-a 1st nn hopping ≈ 0.55 eV

hoppings to 2nd, 3rd, 4th neighbors ≈ 0.1 eV
from downfolding (Anisimov, Lichtenstein)

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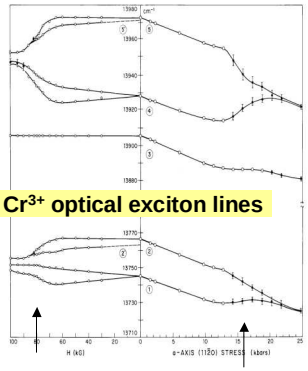
Uniaxial stress induced spin flop in Cr_2O_3-- strain dependence of a-e splitting

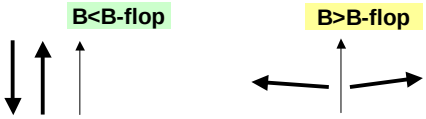
Maybe relevant to idea of:
Changing trigonal distortion through MIT in V_2O_3
Laad et al, cond-mat/0211210



Cr^{3+} optical exciton lines

B-flop T-flop

Spin flop when c-axis magnetic field overcomes magnetic anisotropy K



spins AF along c-axis

spins flopped and canted

B-flop ∝ K = K-dipolar + K-ion

K-ion ∝ trigonal crystal field v ∝ a-e splitting

Basal plane stress drives K to zero---spins flop
PRL 27, 1526 (1971)

a-e splitting very strain dependent in corundum structure

Summary

- High hν, high resolution, small photon spot PES to get bulk 3d spectrum; see prominent E_F peak in PM phase
- LDA+DMFT PM phase E_F peak weight too small for U large enough to give MIT under Cr doping.
  ⇒ U changes with Cr doping or through MIT due to various possible effective screening mechanisms
- PI phase: one peak in LDA+DMFT at low T vs two peaks in experiment
- High T gap filling of PI phase theory seen in 750K PES data
- Early optical absorption spectra $(V,Al)_2O_3$, Cr_2O_3
  --show loss of V^{3+} identity in I, AFI phases
  --due to nearest neighbor c-axis pair hopping or multiple further neighbor hopping in concentrated crystal
  --trigonal crystal field splittings very strain sensitive