Prominent Metal Phase Quasi-particle and High Temperature Correlation Gap Filling in Photoemission Spectra of (V_1-xCr_x)_2O_3: Comparison to LDA+DMFT Theory

# High Resolution High Photon Energy Small Photon Spot Bulk Sensitive Photoemission Study of the Metal-Insulator Transition in $(V_{1-x}Cr_x)_2O_3$: Comparison to LDA + DMFT Theory


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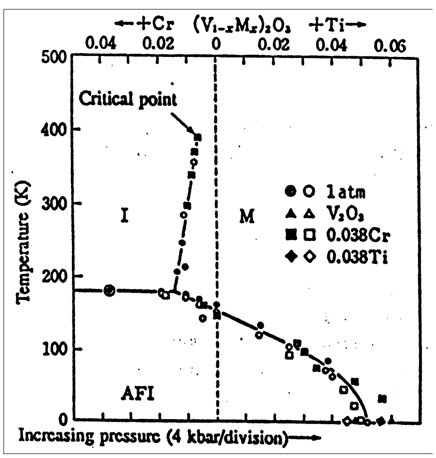
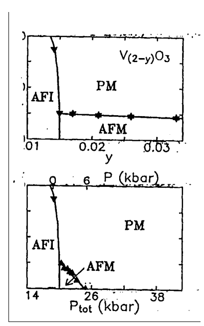
## $V_2O_3$ phase diagram

**McWhan et al. PRL '69, PRB '73**




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




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

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## 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**

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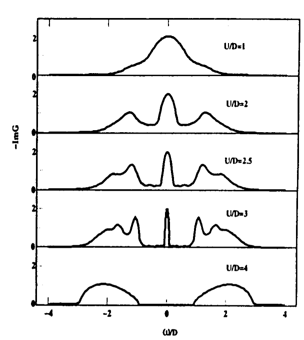
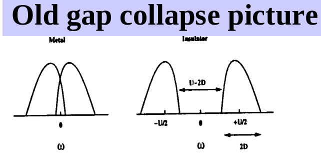
## DMFT for metal-insulator transition

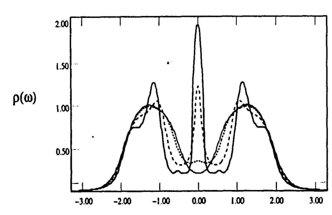
**1-band Hubbard, d →infinity**
**k-independent self energy**
**A. George, G. Kotliar, W. Krauth, M. Rozenberg Rev. Mod. Phys '96**

**Spectral function for varying U**
**"Kondo-like" picture**




**Old gap collapse picture**




**Increase T in metallic phase**
**- lose quasi-particle peak**

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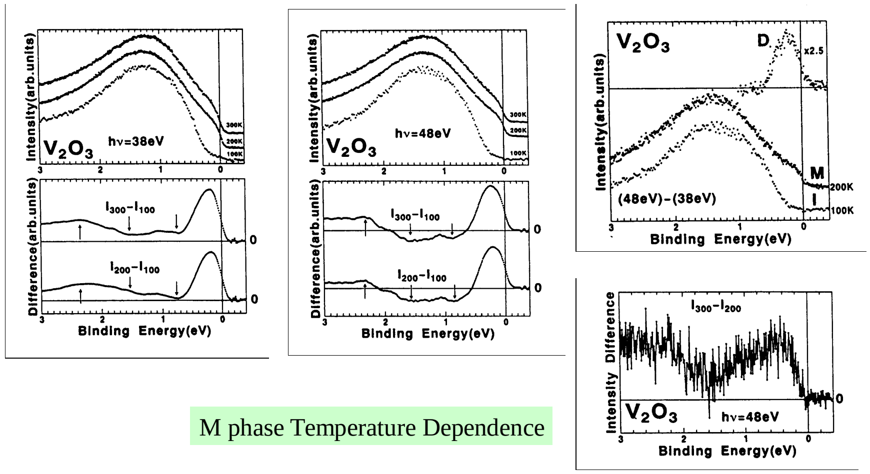
## Photoemission & 1-band Hubbard

S. Shin et al. J. Phys. Soc. Jpn. 64, 1230 (1995)



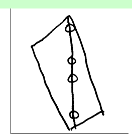

M phase Temperature Dependence



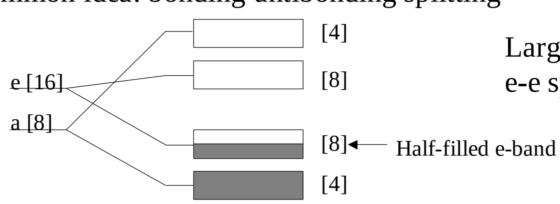
## Issues of realism

**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**

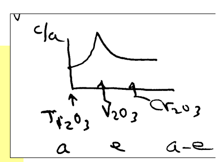


Common idea: bonding-antibonding splitting




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.**



## 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—COMPARE TO PHOTOEMISSION**

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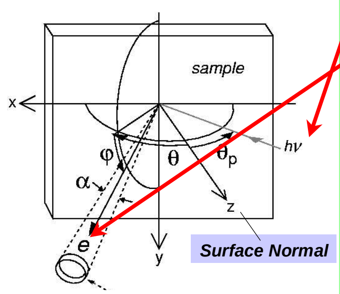
## Angle resolved photoemission spectroscopy (ARPES) to measure ρ (k,ω)




- Photon In
- (Photo-)Electron Out
- Electron KE, hν, ⇒ bind. en. ω
- Angles θ, φ → k-par, cons. at surf.
- k-perp -- not conserved, must model surface potential
- Electron Energy Distribution (ω) = ρ (k,ω) x Fermi function x (ARPES cross-section)

MDC (fix ω, scan k) EDC (fix k, scan ω) "FS" map (ω=$E_F$, scan k region)

Cross-section resonances specific to atom and ang. mom. for hν at core level level absorption edges------- "RESPES"

Varying angles, move on spherical k-space surface, radius fixed by hν → k-perp changes with hν

Larger KE, larger escape depth → Higher hν, more bulk

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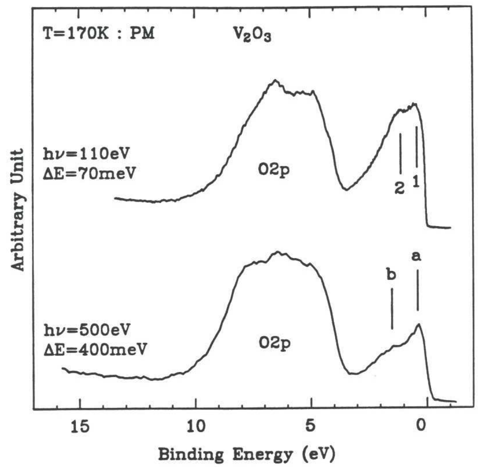
## Early evidence of bulk/surface difference




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

**Systematic 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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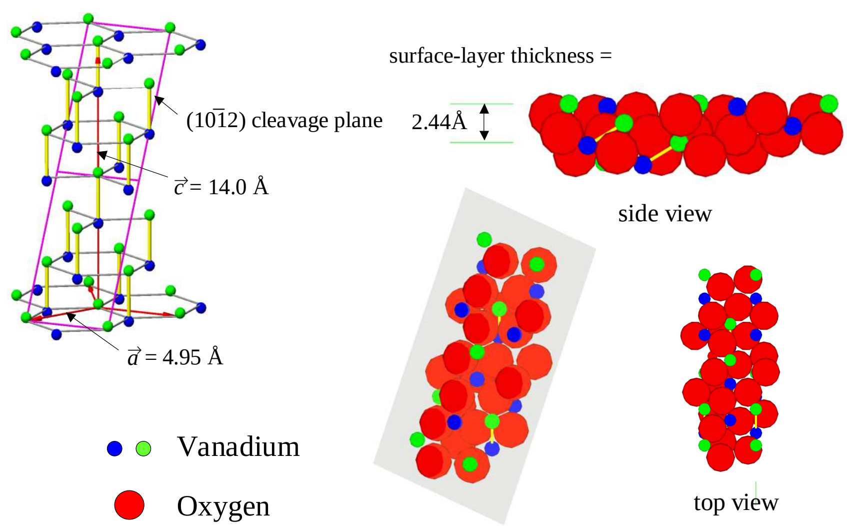
## Crystal structure and surface layer

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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.**

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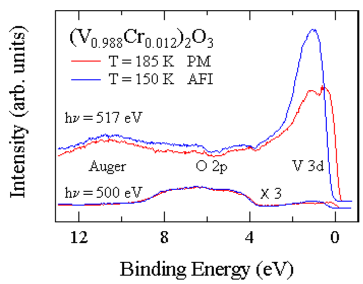
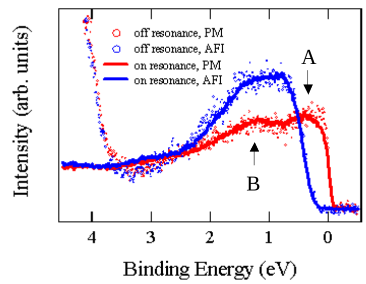
## Initial results, slide 1: RESPES of $(V_{0.988}Cr_{0.012})_2O_3$ at V $2p \rightarrow 3d$ edge

- On- and off-resonance spectra




- V 3*d* spectra




- **Strong enhancement of V 3*d* signal at $2p \rightarrow 3d$ edge.**
- **Within signal to noise of off-resonance spectrum,**
  **on- and off-resonance spectra of V 3*d* essentially identical**
  **$\Rightarrow 2p \rightarrow 3d$ RESPES provides V 3*d* spectral function.**

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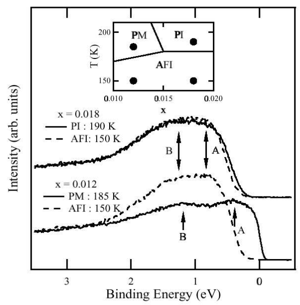
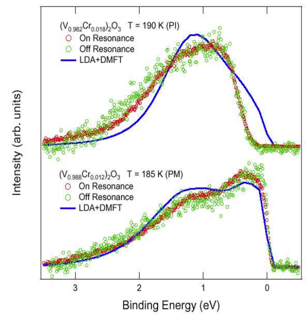
## Initial results, slide 2




**Compare to LDA+DMFT(QMC) 1100K from Held et al, PRL 86, 5345 (2001).**

**Fair agreement for PM phase—$E_F$ feature not strong, with maximum ≈0.3 eV below $E_F$. Prominent central peak smeared out due to multiband realism?**

**Less good agreement for PI phase—theory shows gap filling at high T of calculation, and other spectral differences.**

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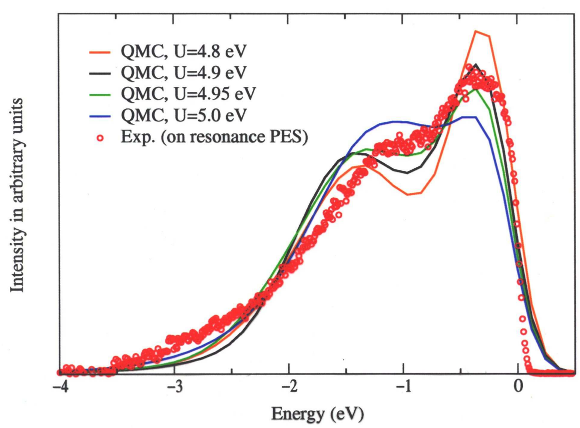
## Initial results, slide 3: LDA+DMFT (1100K) – for various U values & initial data

**Relative magnitudes of coherent/incoherent peaks change rapidly with U in 1100K theory—U 4.95 eV OK**




**Peak below $E_F$ in spectrum agrees with theory**

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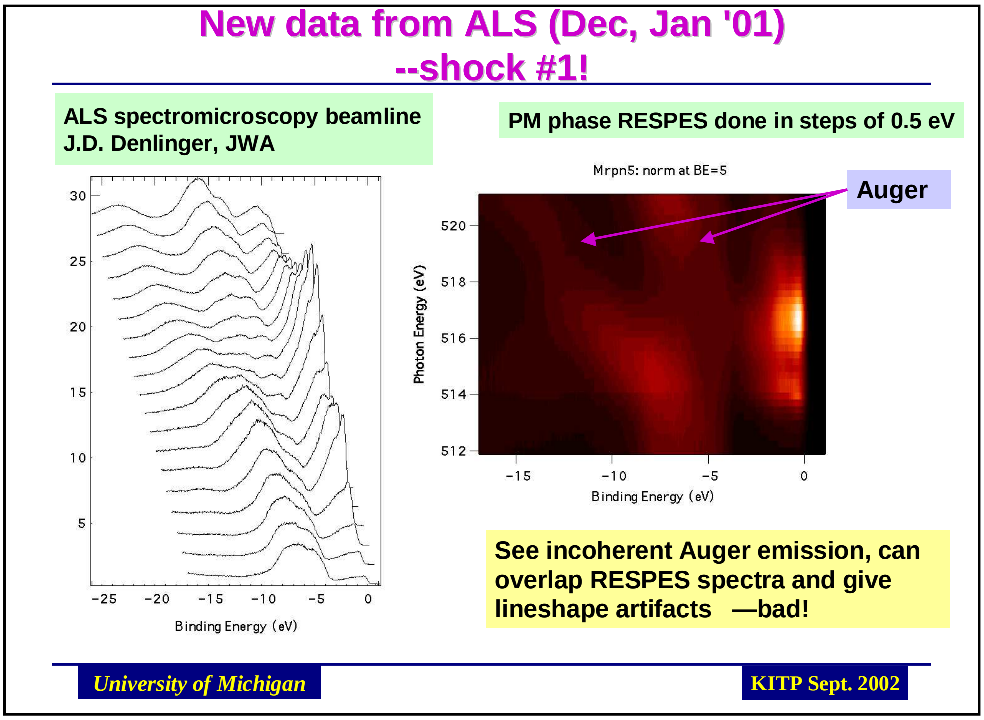
New data from ALS (Dec, Jan '01)
--shock #1!
ALS spectromicroscopy beamline
J.D. Denlinger, JWA
PM phase RESPES done in steps of 0.5 eV
Mrpn5: norm at BE=5
Auger
Photon Energy (eV)
Binding Energy (eV)
Binding Energy (eV)
See incoherent Auger emission, can overlap RESPES spectra and give lineshape artifacts —bad!
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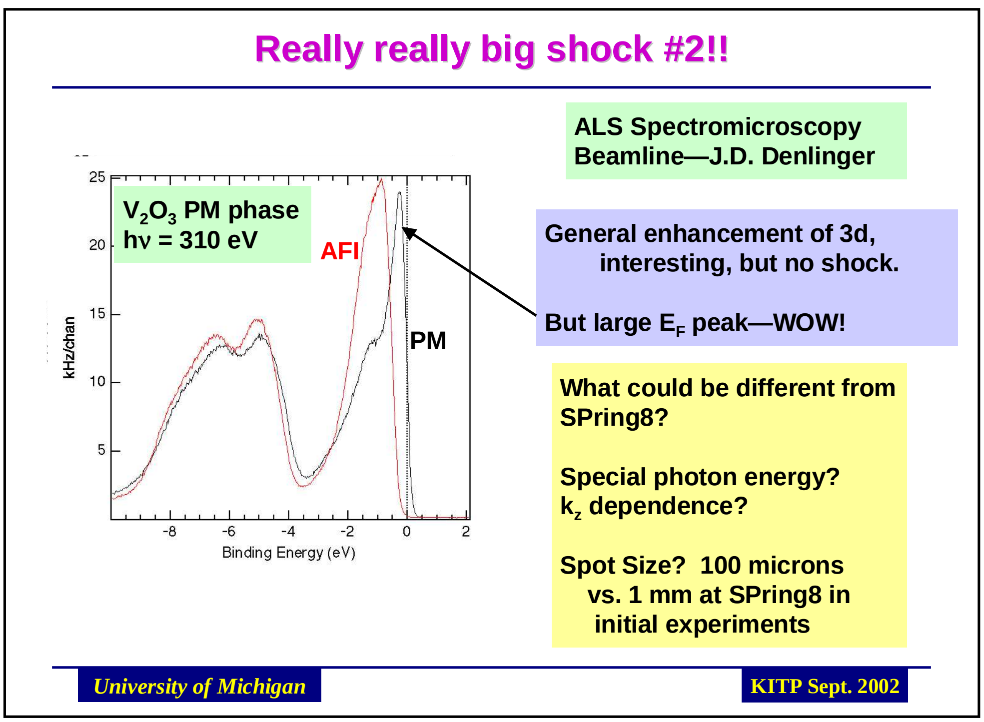
Really really big shock #2!!
ALS Spectromicroscopy Beamline—J.D. Denlinger
V2O3 PM phase
hν = 310 eV
AFI
PM
kHz/chan
Binding Energy (eV)
General enhancement of 3d, interesting, but no shock.
But large EF peak—WOW!
What could be different from SPring8?
Special photon energy?
kz dependence?
Spot Size? 100 microns vs. 1 mm at SPring8 in initial experiments
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## 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 had been modified to decrease photon spot size from 1 mm to100 μm, same as ALS**

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

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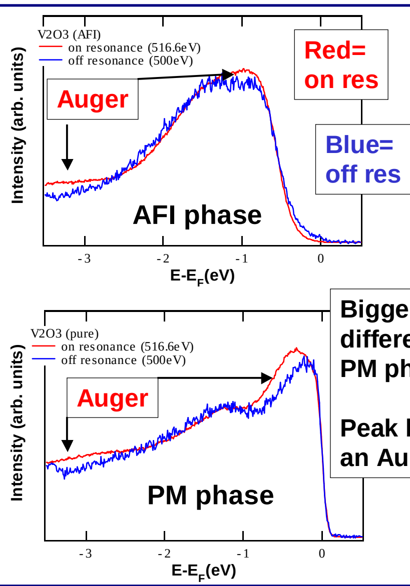
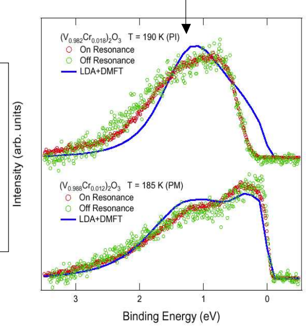
## Yes, find Auger in RESPES lineshape




**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 Auger artifact**

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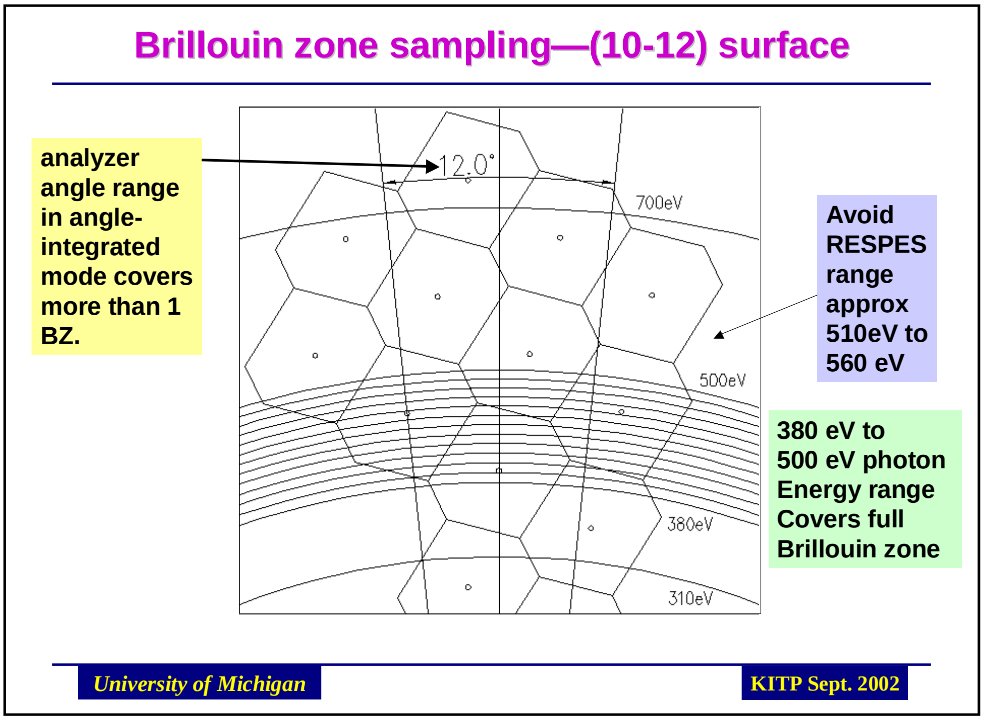
Brillouin zone sampling—(10-12) surface
analyzer angle range in angle-integrated mode covers more than 1 BZ.
12.0°
700eV
500eV
380eV
310eV
Avoid RESPES range approx 510eV to 560 eV
380 eV to 500 eV photon Energy range Covers full Brillouin zone
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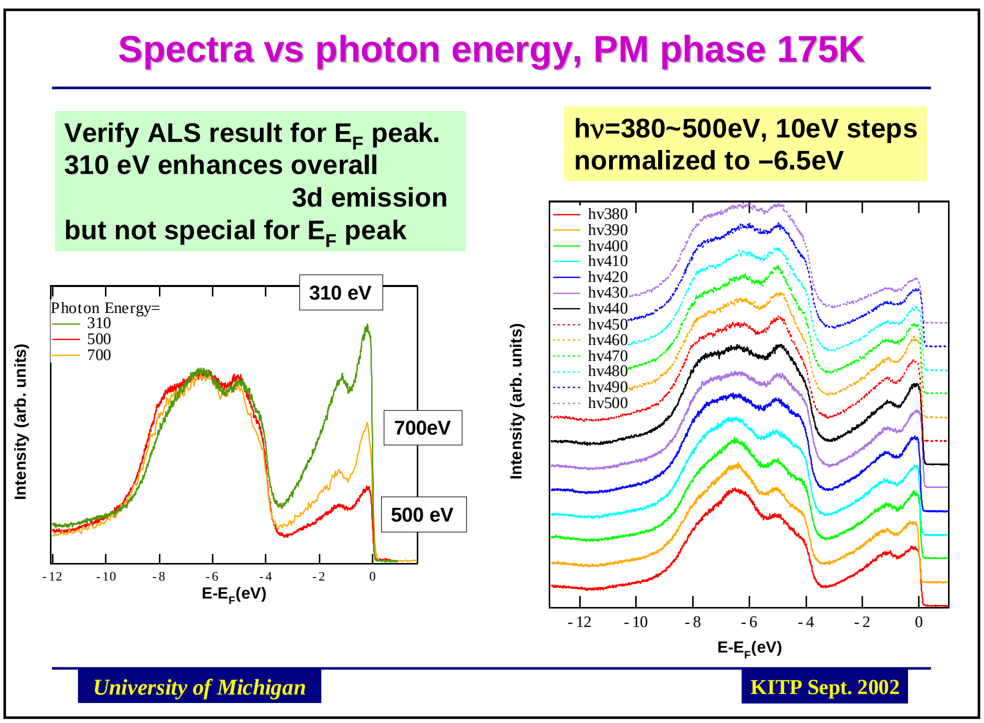
Spectra vs photon energy, PM phase 175K
Verify ALS result for E_F peak. 310 eV enhances overall 3d emission but not special for E_F peak
hν=380~500eV, 10eV steps normalized to –6.5eV
Photon Energy=
310
500
700
310 eV
700eV
500 eV
Intensity (arb. units)
E-E_F(eV)
hv380
hv390
hv400
hv410
hv420
hv430
hv440
hv450
hv460
hv470
hv480
hv490
hv500
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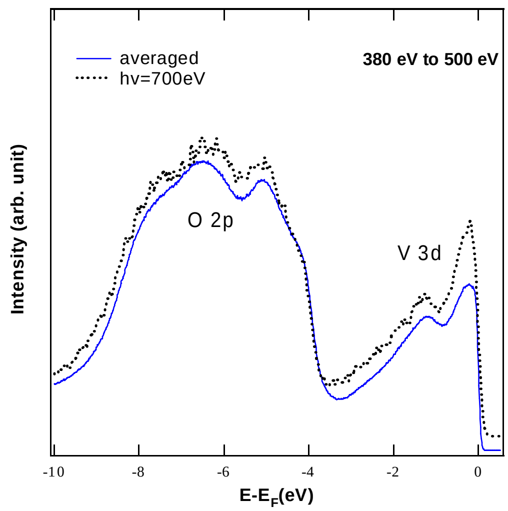
## k-averaged spectrum less peaky than 700 eV due to probe depth effect, not $k_z$




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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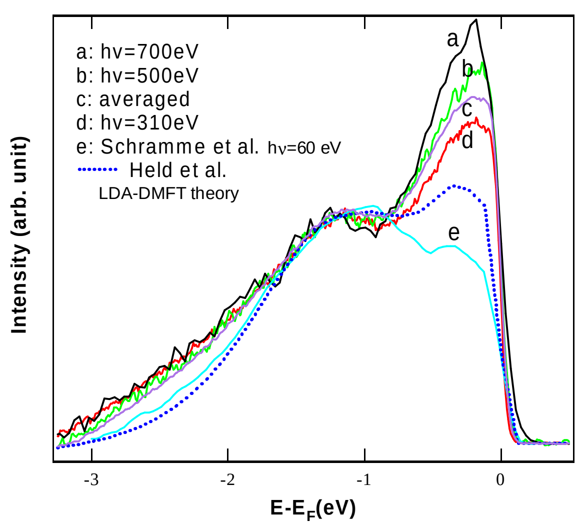
## Figure with two main messages




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

**Previous ≈agreement between 1100K LDA/DMFT and 60 eV data fortuitous**

**Now would need U too small to give MIT if use 1100 K theory**

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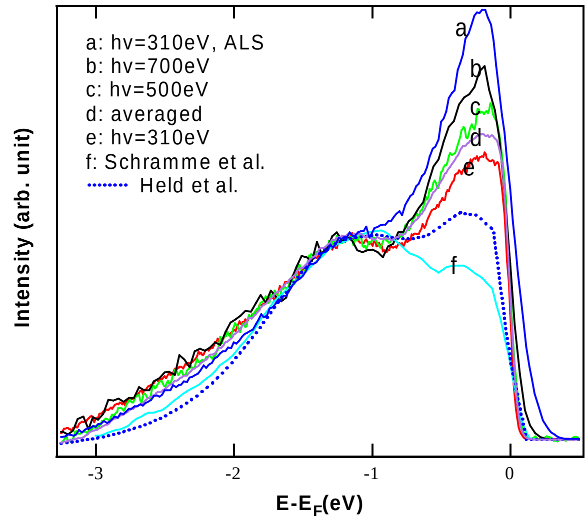
## Preceding figure, including "ALS superpeak"

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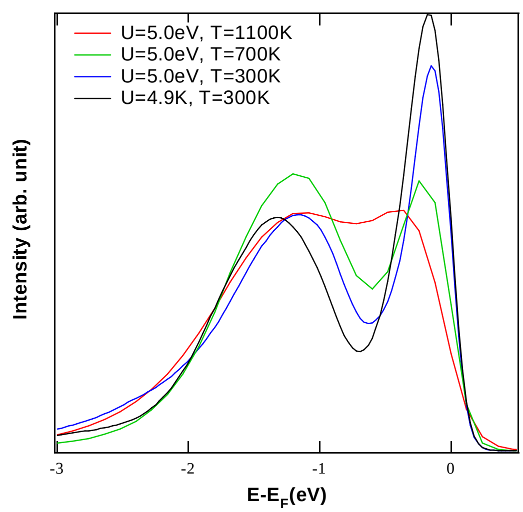
## New LDA +DMFT(QMC) Theory for lower T get $E_F$ PEAK—like 1 band Hubbard




**D. Vollhardt et al**

**Peak sharpens up with decreasing T**

**No longer peaks below $E_F$**

**Some increase of spectral weight in $E_F$ peak.**

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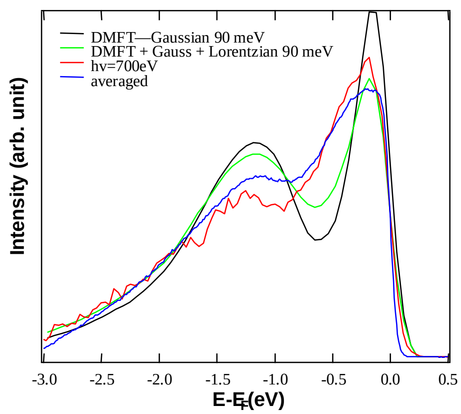
## New data and new theory (U=5.0 eV, 300K)




Qualitative agreement on presence of true $E_F$ peak in spectrum

Experimental peak width larger than theory width, roughly by factor of 2

Experimental peak weight larger than theory weight.

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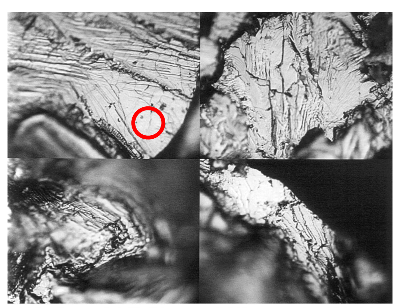
## Optical micrographs of cleaved surface

Can see that optimizing with small spot finds regions with fewer steps, terraces.

V2O3 (7-SES) 5X 12/22/01

FOV: 2.6 x 2.0 mm



V2O3 (7-SES) 20X 12/22/01

FOV: 650 x 500 µm

○ ~100 micron spot size

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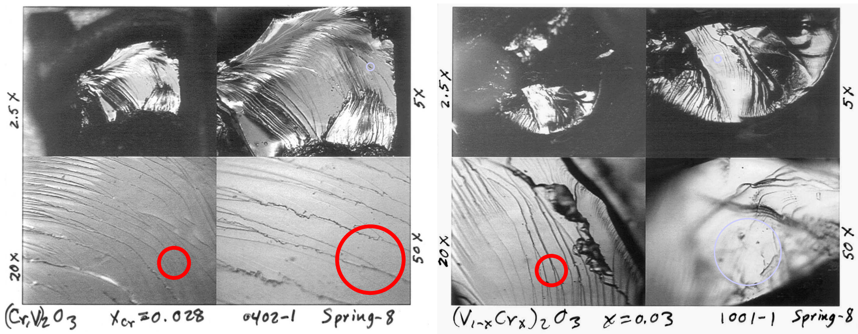
## Optical micrographs of cleaved surfaces

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




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

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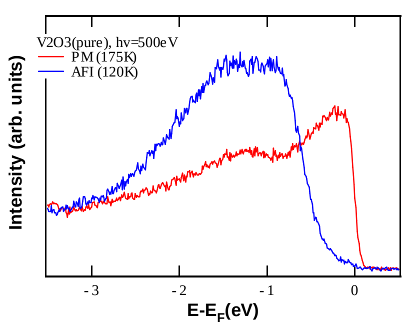
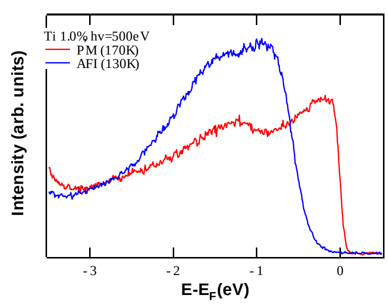
## PM/AFI transition – pure $V_2O_3$ and Ti 1.0%




**Pure $V_2O_3$ PM (175K) red and AFI (120K) blue**

**Ti 1.0% PM(170K, red) and AFI (130K, blue)**

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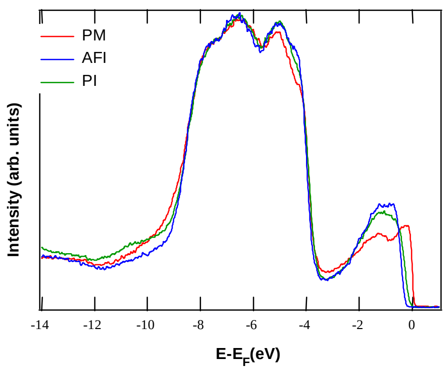
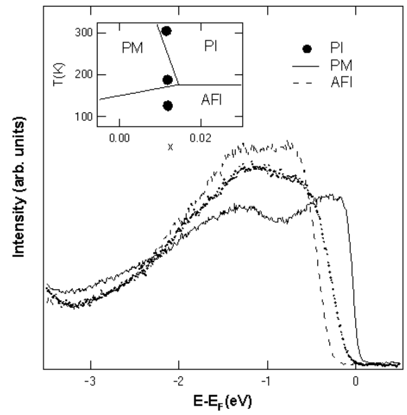
## Cr 1.2% phase transitions

hν=500 eV

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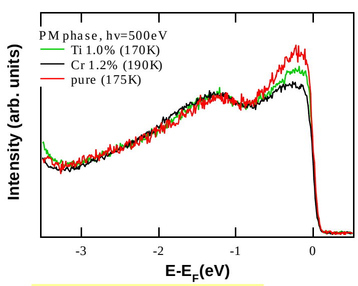
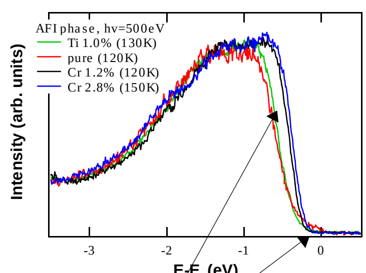
## PM and AFI phases with different x's




**PM phase:**
**Ti 1.0% (170K, green)**
**Cr 1.2% (190K, black)**
**Pure (175K, red)**

**AFI phase:**
**Ti 1.0% (130K, green)**
**Pure (120K, red)**
**Cr 1.2% (120K, black)**
**Cr 2.8% (150K, blue)**

**Coherent/incoherent ratio: Pure>Ti 1.0%>Cr 1.2% ; Ti maybe surprising, but surface differences hard to control.**

**Onsets of spectra are almost same, but shoulders much different**

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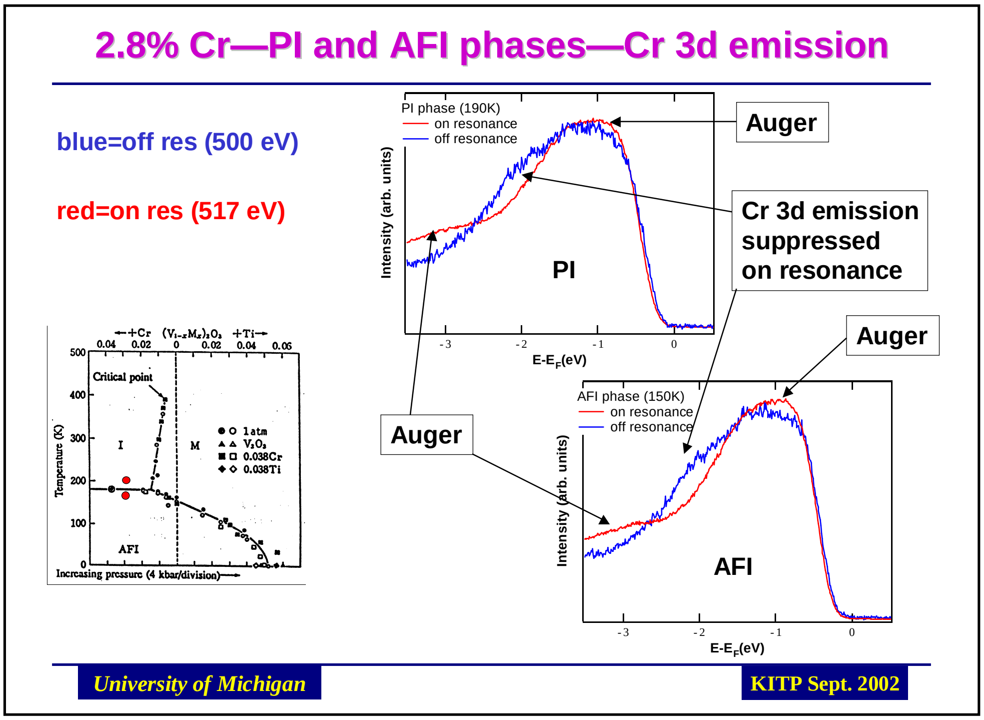
2.8% Cr—PI and AFI phases—Cr 3d emission
blue=off res (500 eV)
red=on res (517 eV)
PI phase (190K)
on resonance
off resonance
Intensity (arb. units)
PI
E-E_F(eV)
Auger
Cr 3d emission suppressed on resonance
Auger
Auger
AFI phase (150K)
on resonance
off resonance
AFI
Critical point
Temperature (K)
Increasing pressure (4 kbar/division)
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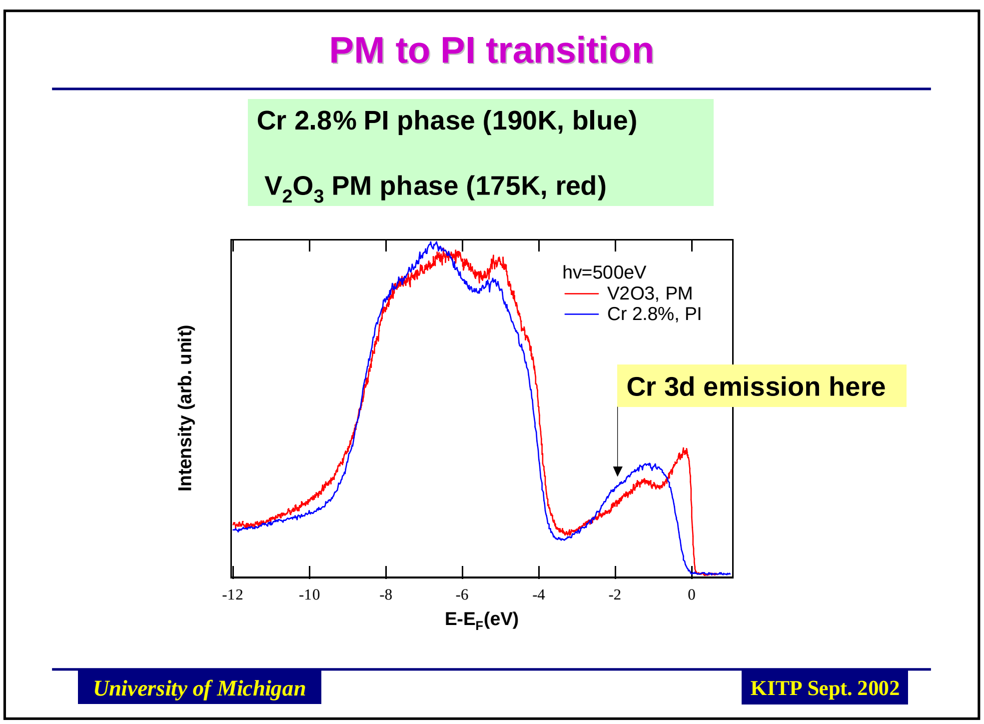
PM to PI transition
Cr 2.8% PI phase (190K, blue)
$V_2O_3$ PM phase (175K, red)
hv=500eV
V2O3, PM
Cr 2.8%, PI
Cr 3d emission here
Intensity (arb. unit)
E-E_F(eV)
-12
-10
-8
-6
-4
-2
0
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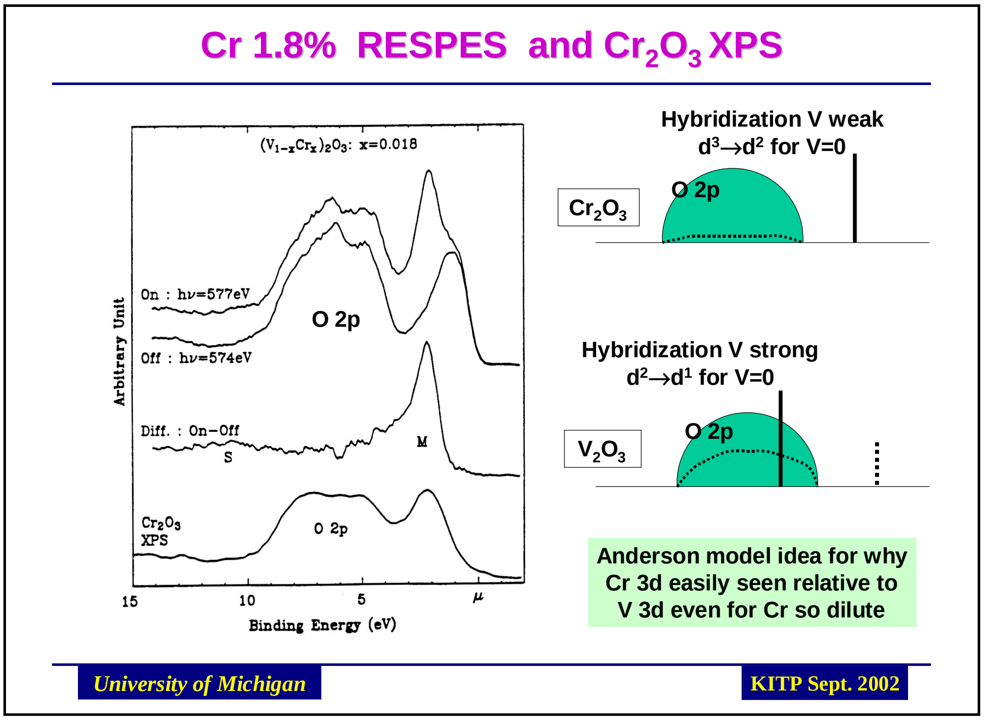
Cr 1.8% RESPES and Cr2O3 XPS
(V1-xCrx)2O3: x=0.018
On : hν=577eV
Off : hν=574eV
O 2p
Diff. : On−Off
S
M
Cr2O3
XPS
O 2p
Arbitrary Unit
15
10
5
μ
Binding Energy (eV)
Hybridization V weak
d3→d2 for V=0
Cr2O3
O 2p
Hybridization V strong
d2→d1 for V=0
V2O3
O 2p
Anderson model idea for why
Cr 3d easily seen relative to
V 3d even for Cr so dilute
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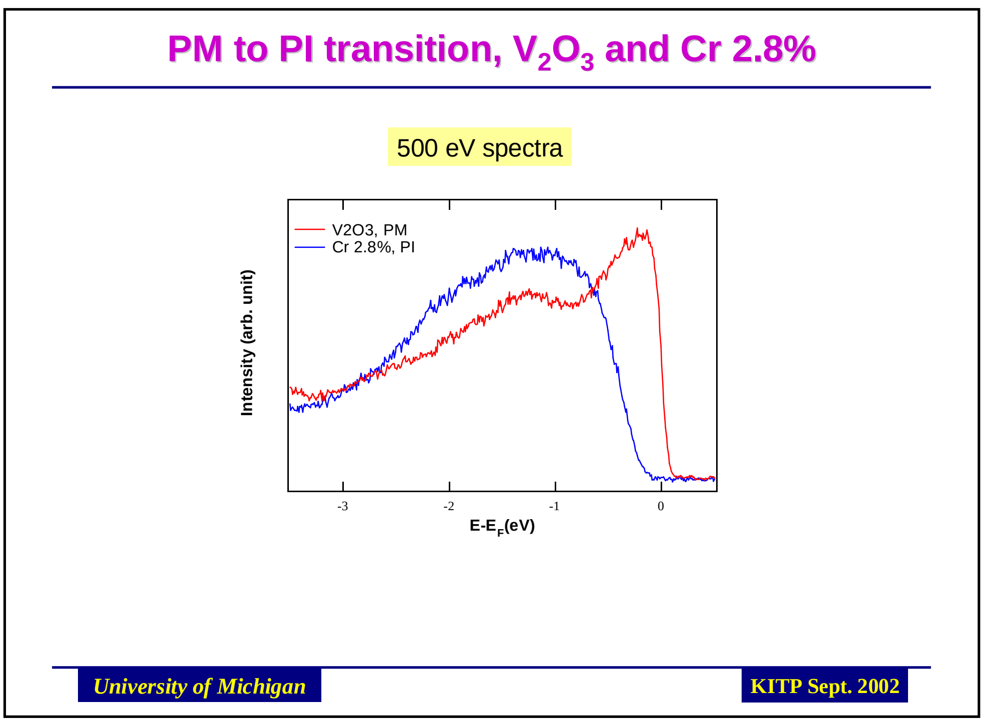
PM to PI transition, V2O3 and Cr 2.8%
500 eV spectra
V2O3, PM
Cr 2.8%, PI
Intensity (arb. unit)
-3
-2
-1
0
E-EF(eV)
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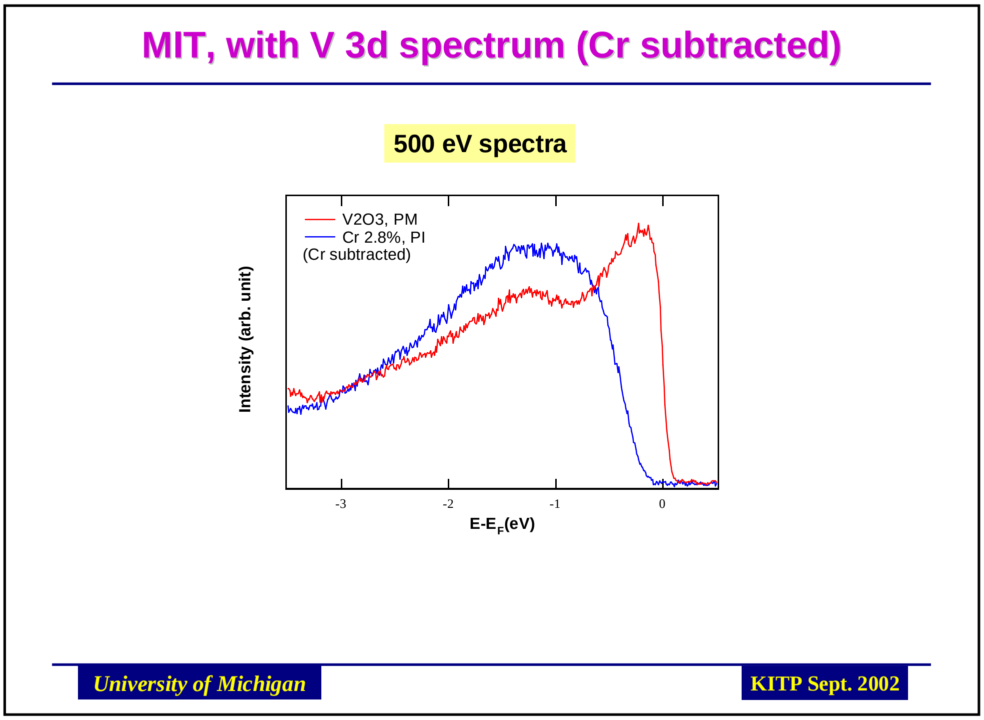
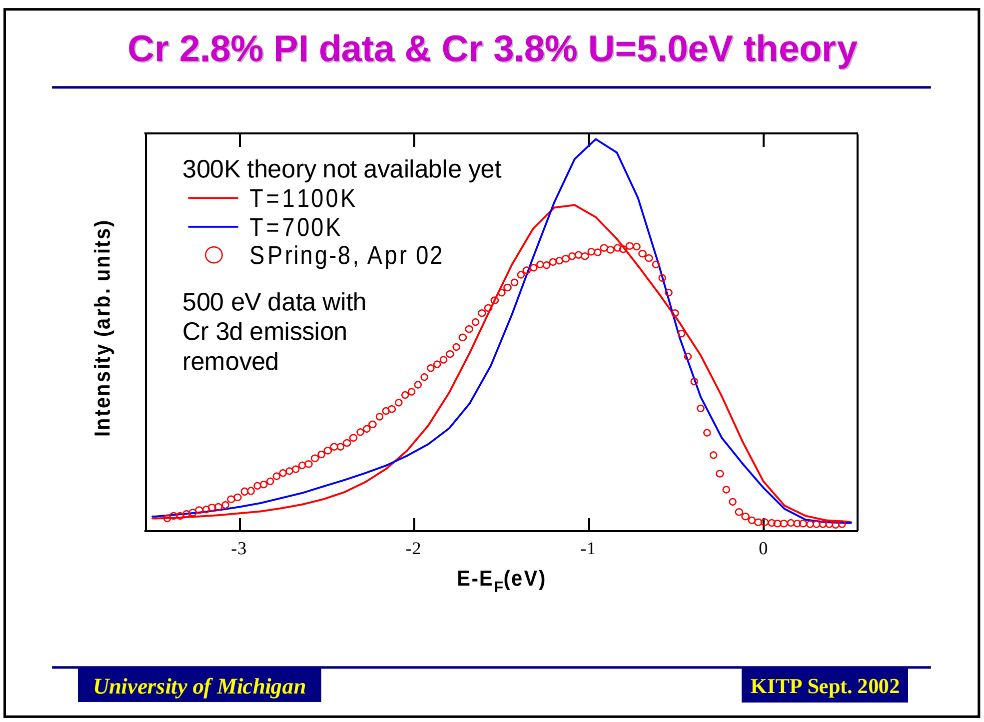
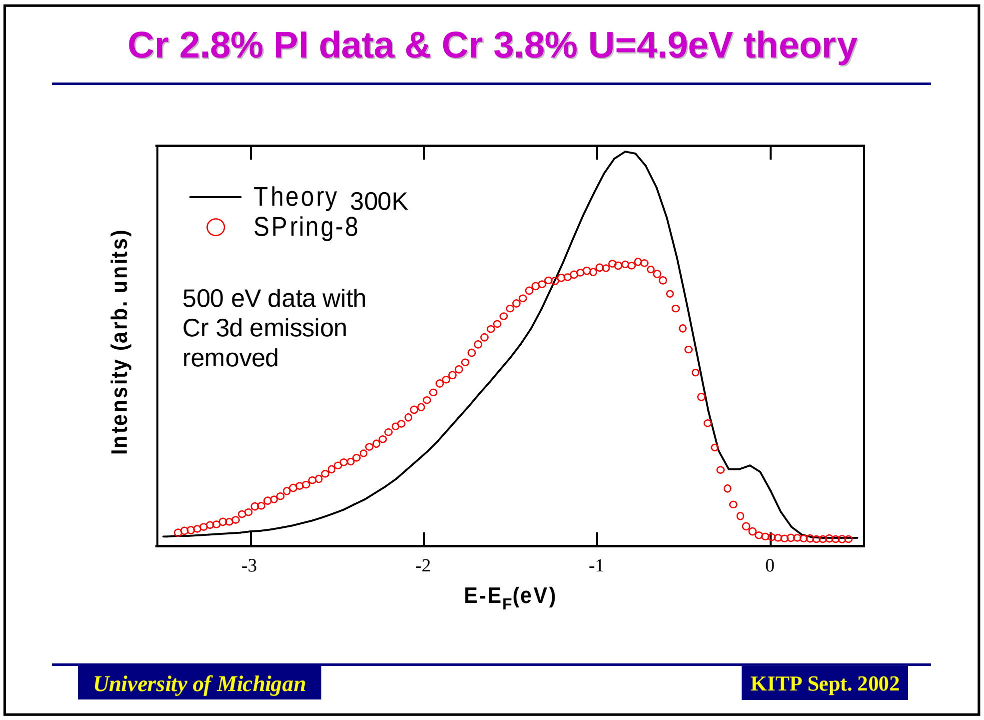
Prominent Metal Phase Quasi-particle and High Temperature Correlation Gap Filling in Photoemission Spectra of (V_1-xCr_x)_2O_3: Comparison to LDA+DMFT Theory




Cr 2.8% PI data & Cr 3.8% U=4.9eV theory
Theory 300K
SPring-8
500 eV data with
Cr 3d emission
removed
Intensity (arb. units)
-3
-2
-1
0
E-E_F(eV)
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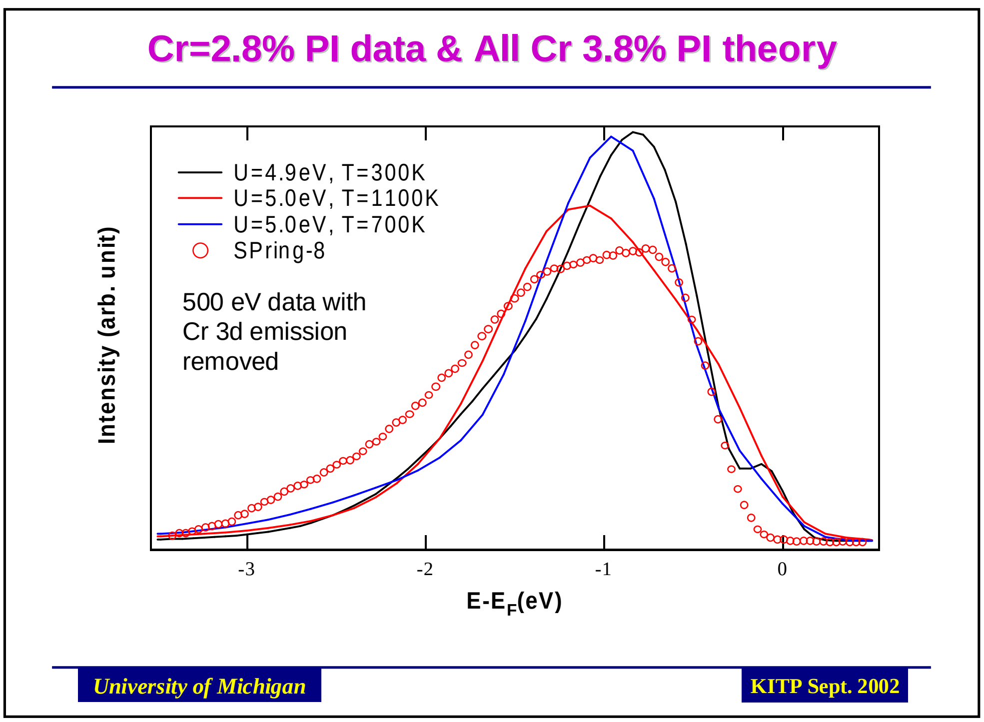
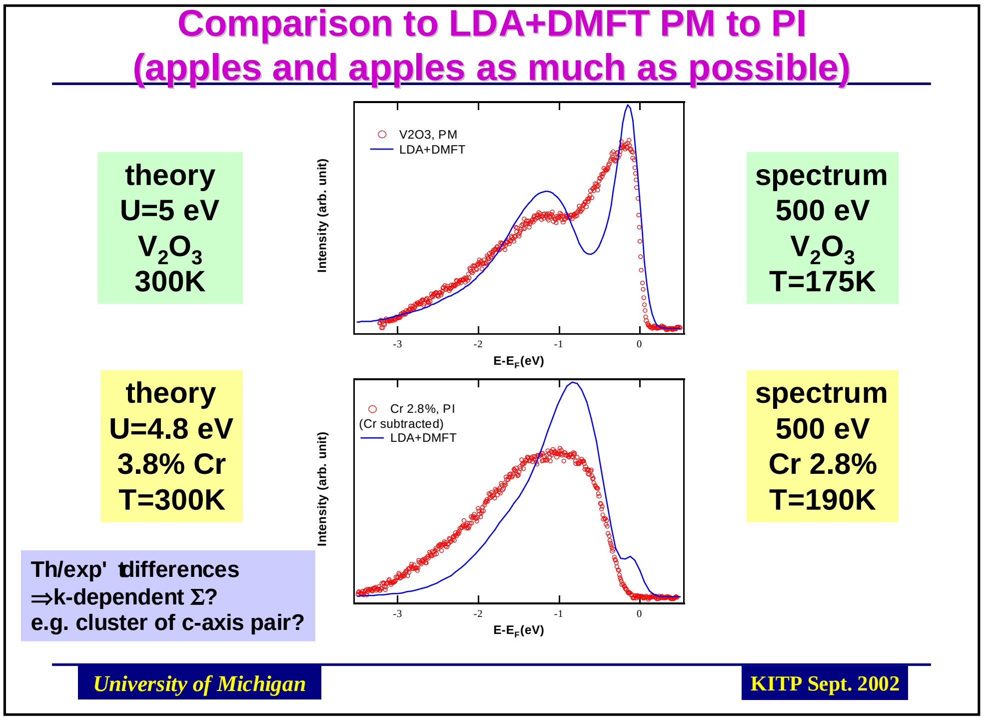
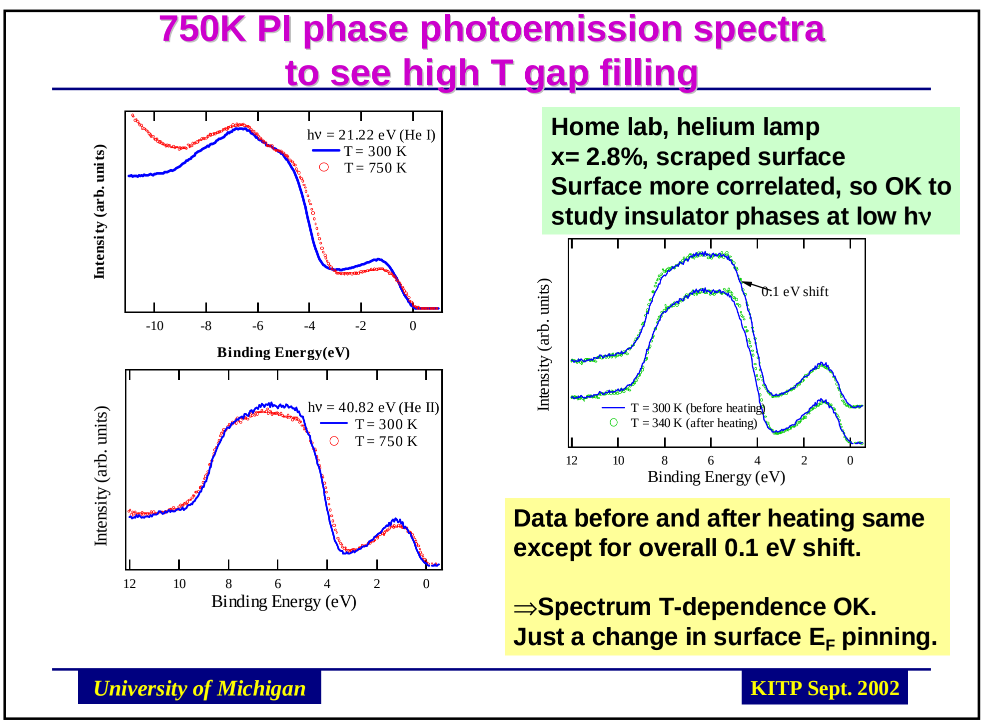
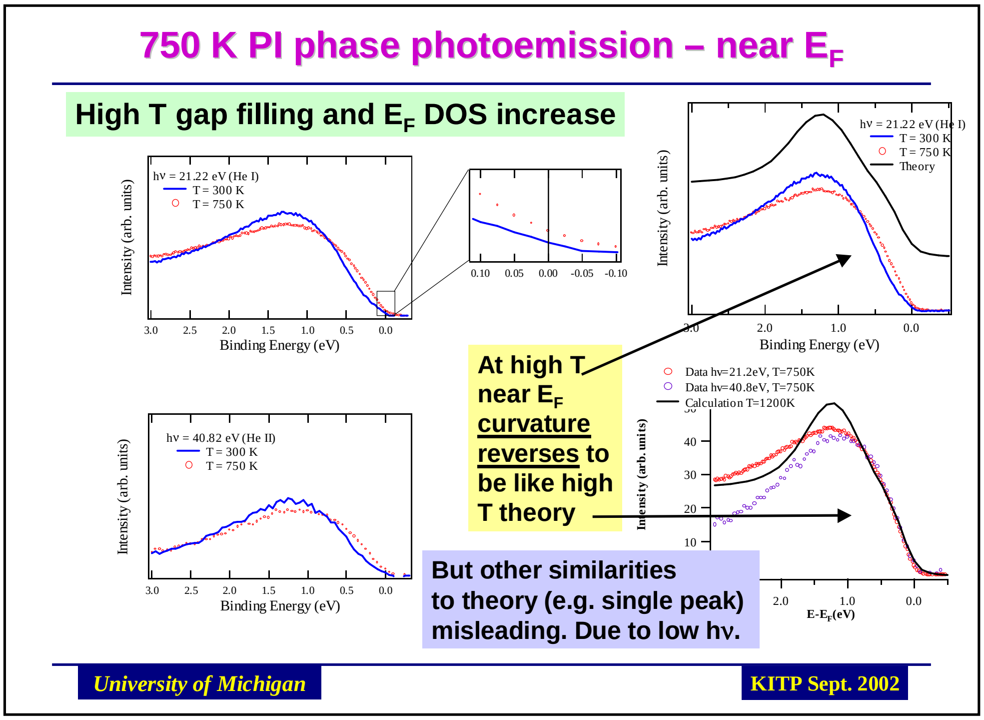

Cr=2.8% PI data & All Cr 3.8% PI theory
U=4.9eV, T=300K
U=5.0eV, T=1100K
U=5.0eV, T=700K
SPring-8
500 eV data with
Cr 3d emission
removed
Intensity (arb. unit)
-3
-2
-1
0
E-E_F(eV)
University of Michigan
KITP Sept. 2002

Prominent Metal Phase Quasi-particle and High Temperature Correlation Gap Filling in Photoemission Spectra of (V_1-xCr_x)_2O_3: Comparison to LDA+DMFT Theory




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
But other similarities to theory (e.g. single peak) misleading. Due to low hν.
hν = 21.22 eV (He I)
T = 300 K
T = 750 K
Theory
hν = 40.82 eV (He II)
Intensity (arb. units)
Binding Energy (eV)
Data hν=21.2eV, T=750K
Data hν=40.8eV, T=750K
Calculation T=1200K
E-E_F(eV)
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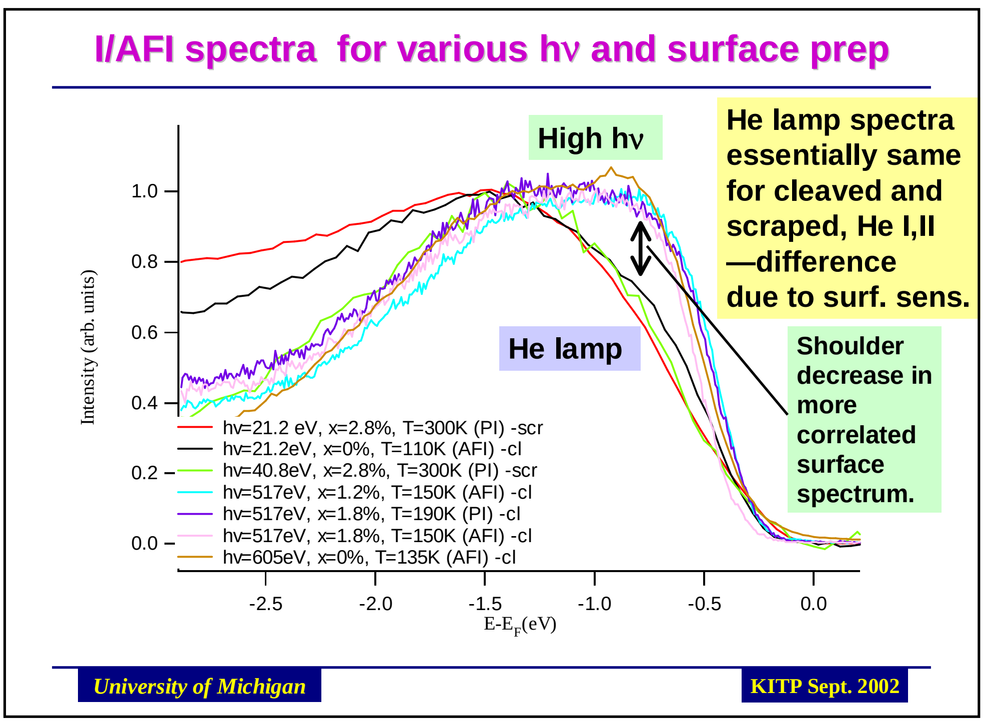
I/AFI spectra for various hν and surface prep
High hν
He lamp
He lamp spectra essentially same for cleaved and scraped, He I,II —difference due to surf. sens.
Shoulder decrease in more correlated surface spectrum.
hν=21.2 eV, x=2.8%, T=300K (PI) -scr
hν=21.2eV, x=0%, T=110K (AFI) -cl
hν=40.8eV, x=2.8%, T=300K (PI) -scr
hν=517eV, x=1.2%, T=150K (AFI) -cl
hν=517eV, x=1.8%, T=190K (PI) -cl
hν=517eV, x=1.8%, T=150K (AFI) -cl
hν=605eV, x=0%, T=135K (AFI) -cl
Intensity (arb. units)
E-E_F(eV)
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## Some early optical studies

End by brief summary of evidence from optical spectra for important role of c-axis pairs in forming electronic structure of PI and AFI phases.

(The idea does not mean
that other V-V couplings are unimportant, just that couplings for c-axis pairs are the largest.)

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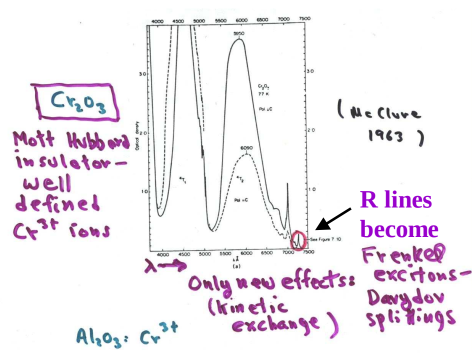
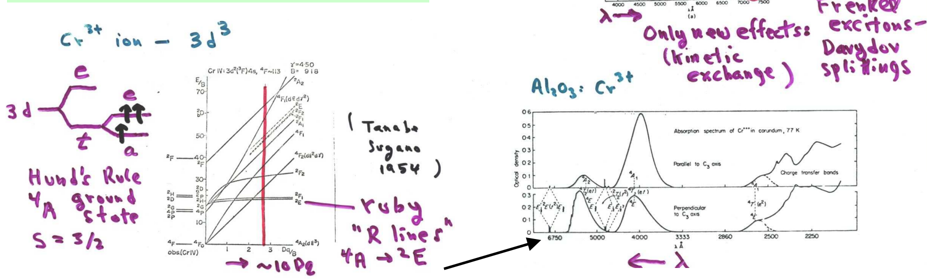
## $Cr^{3+}$ optical spectrum in ruby and $Cr_2O_3$

**$Cr^{3+}$ optical absorption spectrum of ruby persists in concentrated crystal—just weakly coupled $Cr^{3+}$ ions**

**$Cr_2O_3$ a "real" Mott -Hubbard insulator. Same for NiO, etc.**

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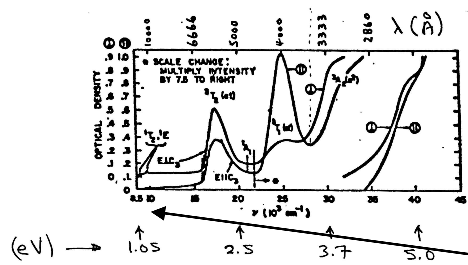
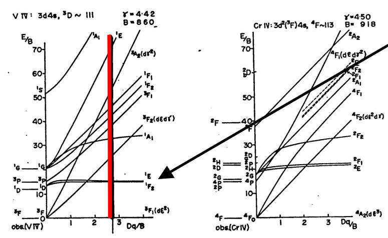
## $V^{3+}$ ion energy levels and $Al_2O_3{:}V^{3+}$




$Al_2O_3$ $V^{3+}$ optical absorption McClure 1962

R line analog



Sugano-Tanabe 1954

2 d-electrons ($V^{3+}$)

3 d-electrons ($Cr^{3+}$)

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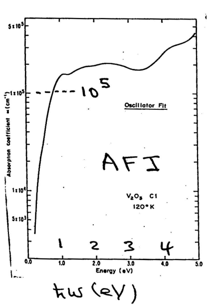
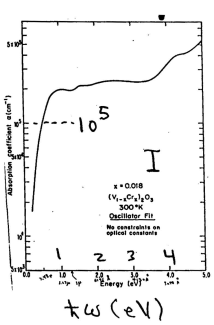
## $V^{3+}$ spectrum lost in I and AFI $V_2O_3$ phases

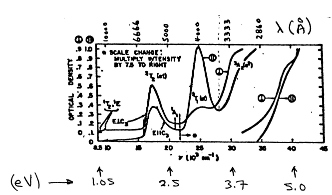
$V_2O_3$




$(V_{1-x}Cr_x)_2O_3$

$V_2O_3$ α's from John Fan thesis (Harvard 1970)




I and AFI phase α's **really different** from $Al_2O_3{:}V^{3+}$ ⇒ $V^{3+}$ ion identity lost

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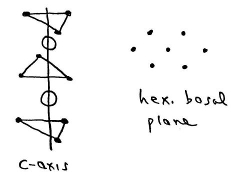
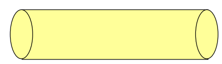
## $(V_2O_3)_x(Al_2O_3)_{1-x}$ – early optical study

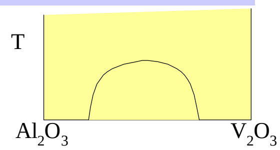
**A. x~0.1% crystal field spectrum**
**x~100% no $V^{3+}$ spectrum**
1. **Evolution of optical properties with x**
2. **Do coupled pairs of $V^{3+}$ ions retain basic ionic identity?**




**B. Samples (T. B. Reed)**
1. **Concentration gradient**




2. **V rich 2nd phase, x > .08**




| **Neighbors Sharing oxygens** | **#** |
|---|---|
| **1st** | **1** |
| **2nd** | **3** |
| **3rd** | **3** |
| **4th** | **6** |

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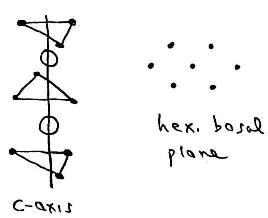
## $(V_2O_3)_x(Al_2O_3)_{1-x}$ – doping statistics

C. Corundum crystal structure




| Neighbors Sharing oxygens | # |
|---|---|
| 1st | 1 |
| 2nd | 3 |
| 3rd | 3 |
| 4th | 6 |

D. Statistics (assuming random distribution)

P(no neighbor) = $(1-x)^{13}$
P(neighbor) = $1-(1-x)^{13}$
P(1st neighbor) = $x = 1-(1-x)^1$
P(2nd neighbor) = $1-(1-x)^3$
P(3rd neighbor) = $1-(1-x)^3$
P(4th neighbor) = $1-(1-x)^6$

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