PY482 Lecture. February 28th, 2013

Studying Metal to Insulator Transitions in Solids using Synchrotron Radiation-based Spectroscopies.

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Department of Physics

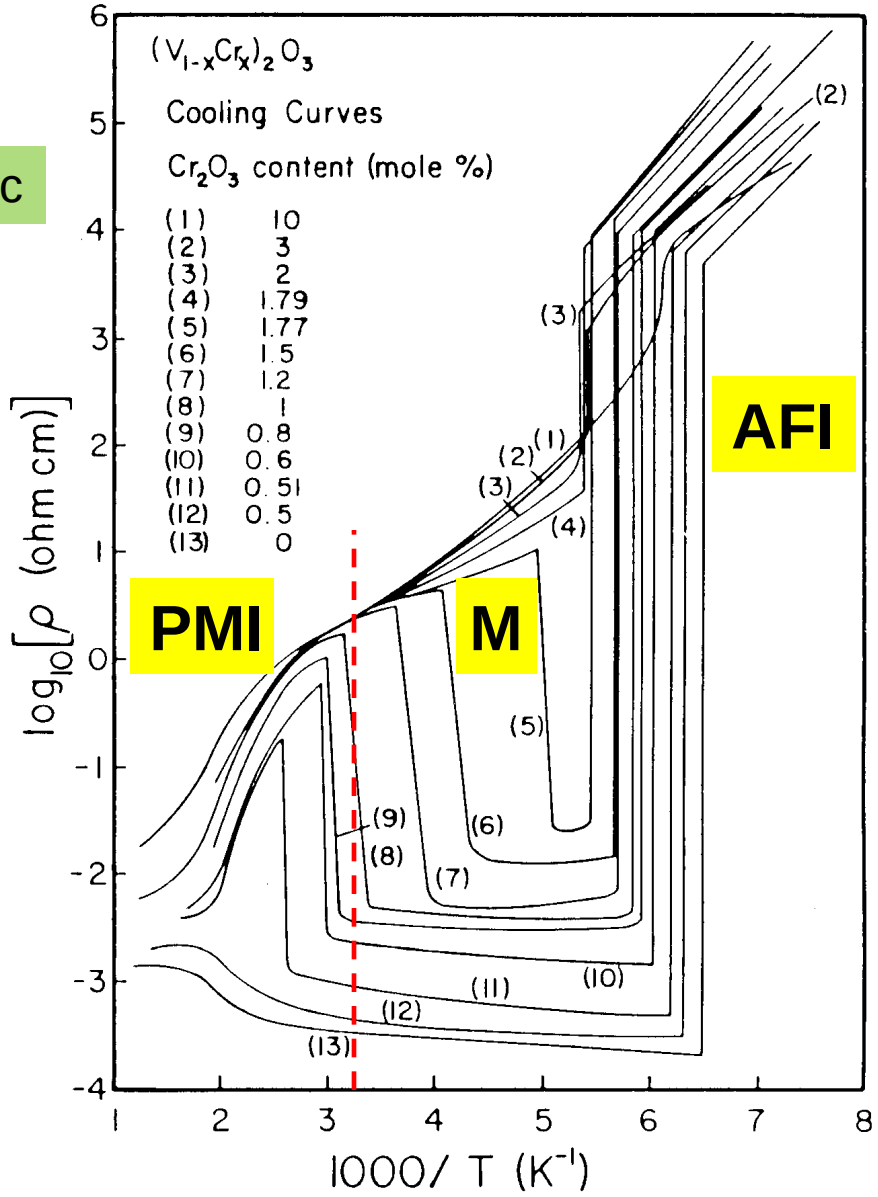
Outline

- Introduction
- Electric Conductivity Transitions in Solids
- Measuring Electronic Structure in Solids
  - *Photoemission Spectroscopy*
  - *X-Ray Absorption Spectroscopy*
  - *X-Ray Emission Spectroscopy*
  - *Synchrotron Radiation*
- Strained Thin Films of VO_2
- Controlling transition temperatures with moderate strain.
- Suppressing structural transitions with large strain.

Example: Conductivity Transitions in Cr-doped V_2O_3

Monoclinic

Trigonal



PMI = Paramagnetic insulator

M = Metal

AFI = Antiferromagnetic insulator

H. Kuwamoto, J.M. Honig and J. Appel, Phys. Rev. B **22**, 2626 (1980).

Example: Metal - Insulator Transitions in VO_2

- **BULK** VO_2 displays an abrupt insulator to metal transition at ~340K accompanied by a **monoclinic** to **rutile** structural phase transition.
- The transition is driven by the formation and tilting of V-V pairs along the *c*-axis going from metallic rutile to insulating monoclinic phase.
- The mechanism driving this dimerization is far from fully understood, and involves the interplay of lattice and electron correlation effects.

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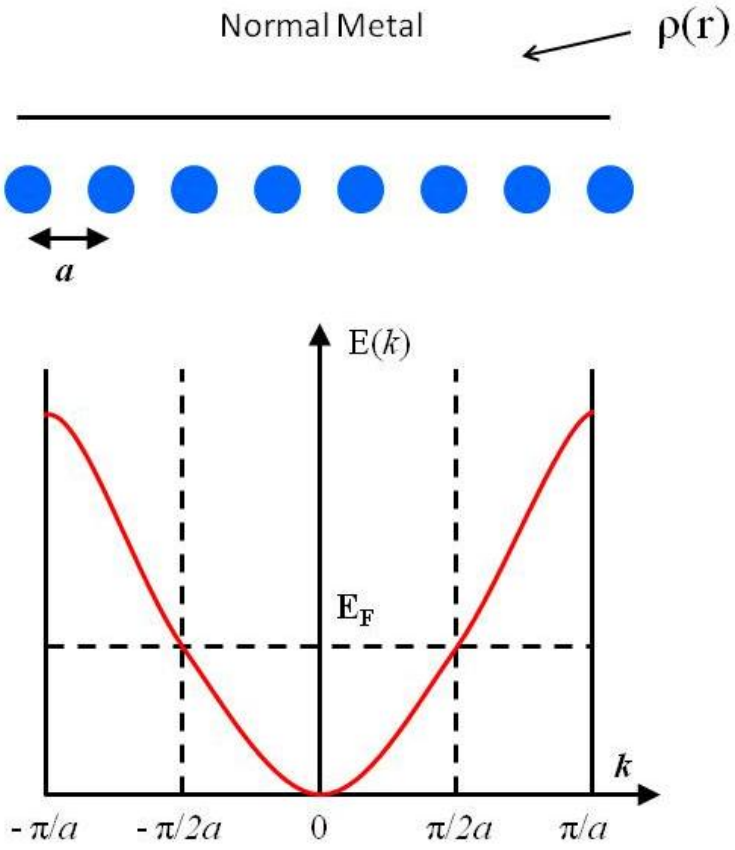

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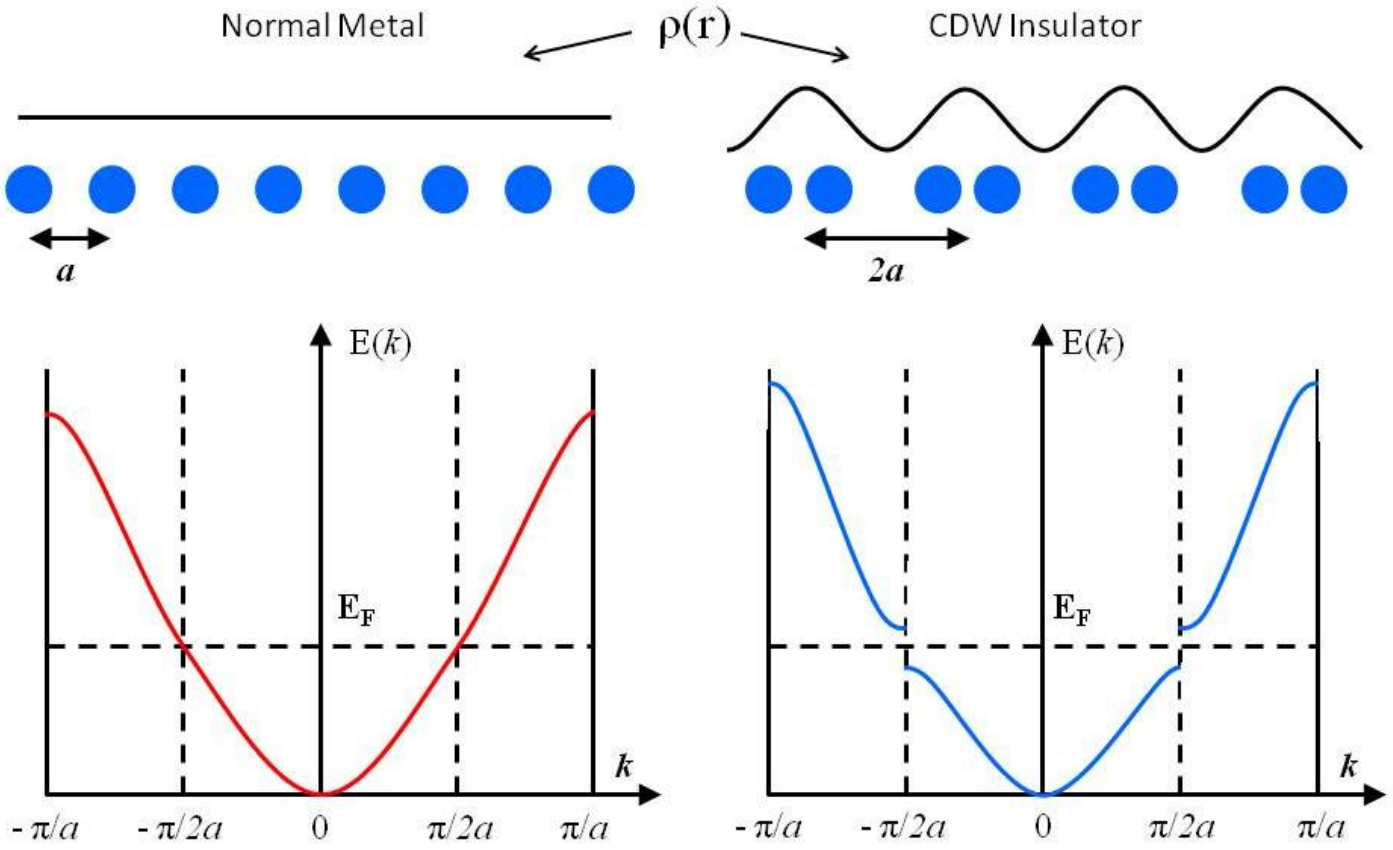
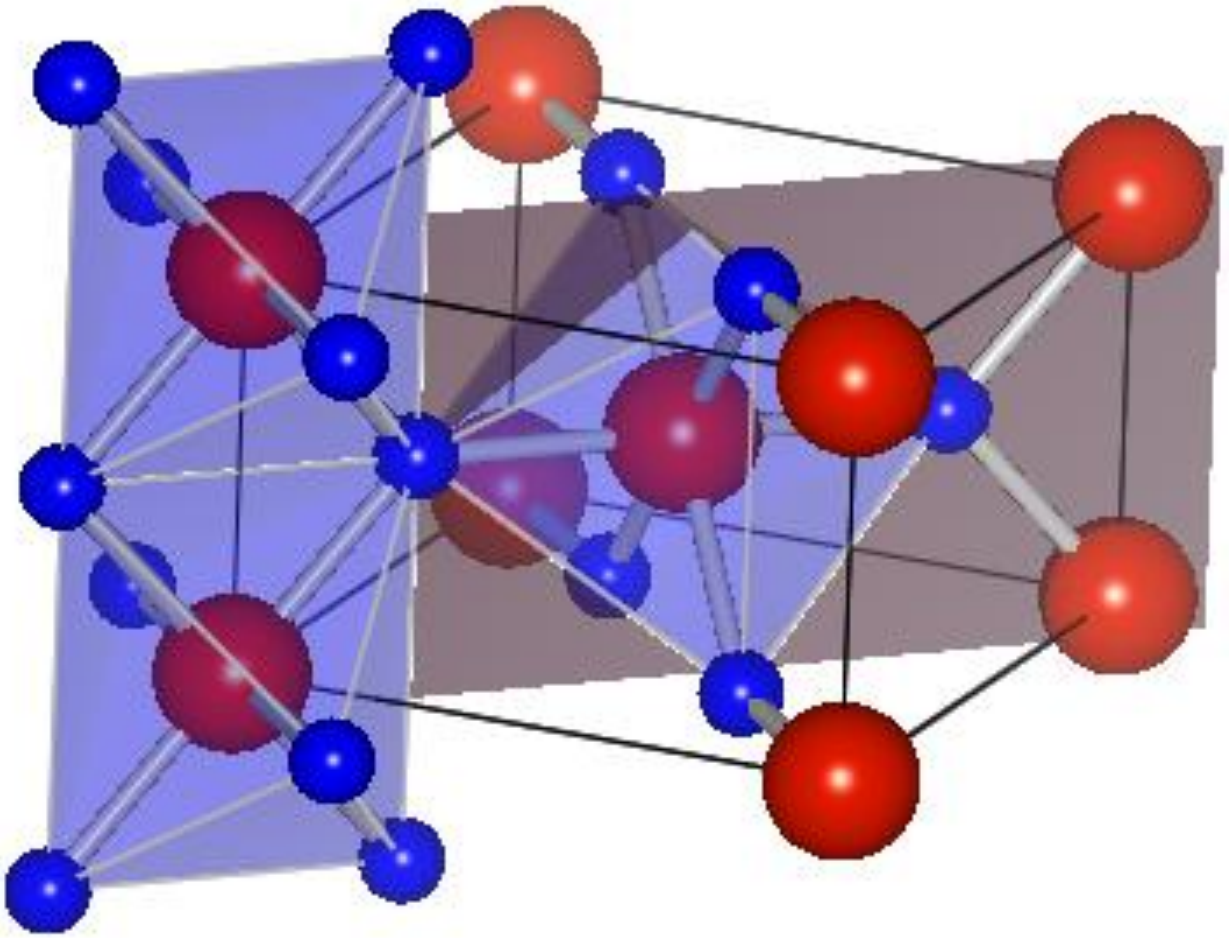
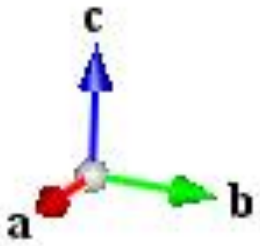


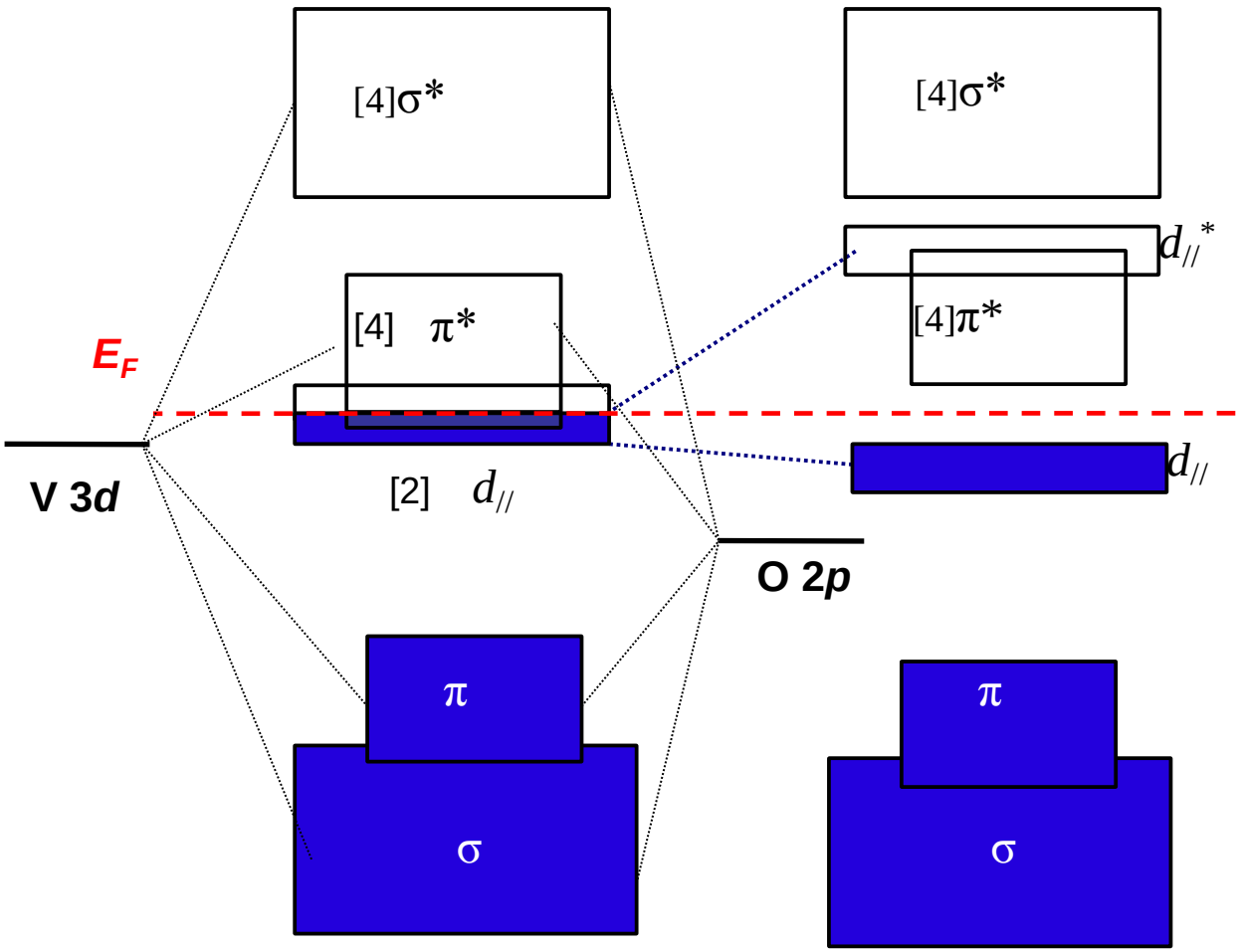
Schematic Crystal Structure for Rutile VO_2



(110)



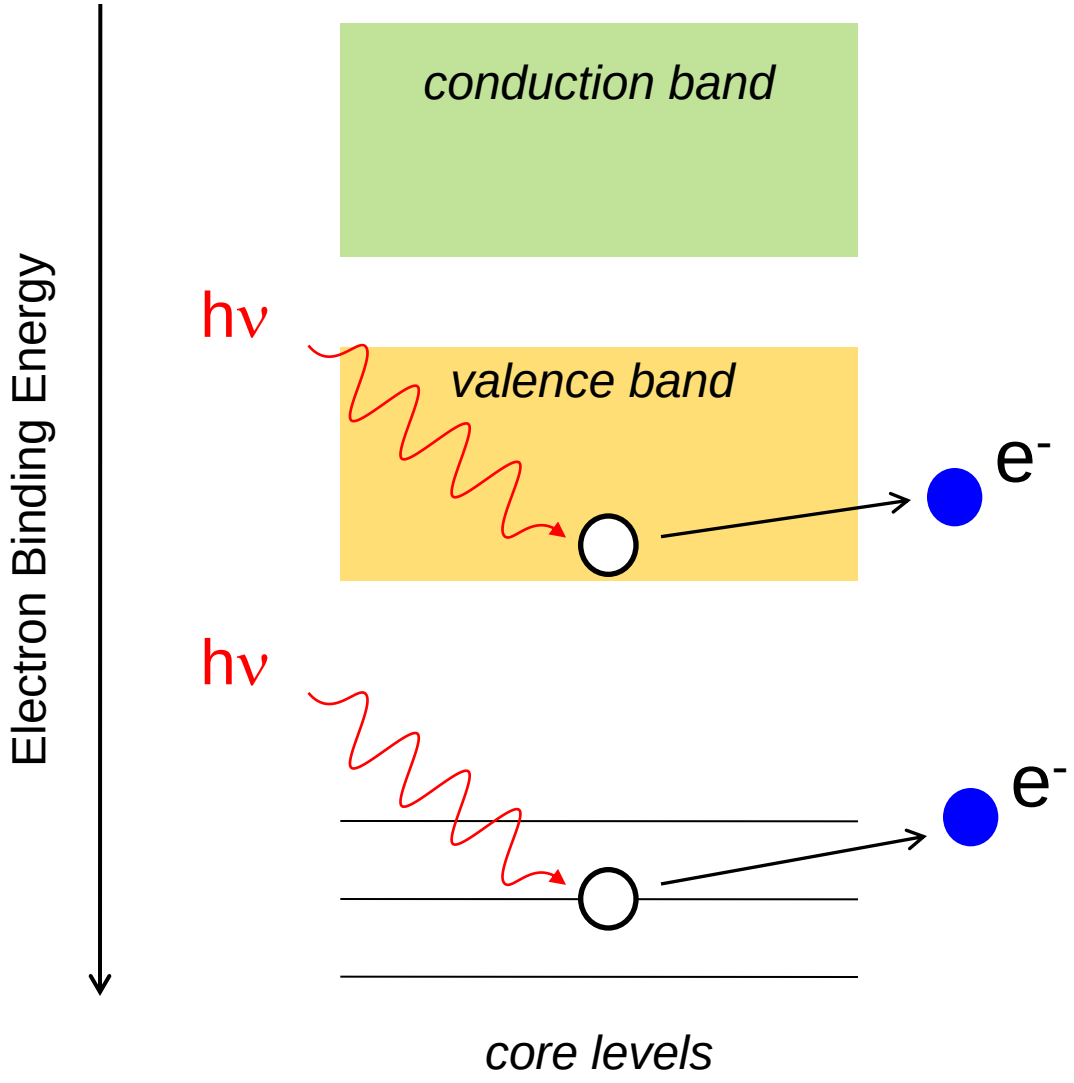
Electronic Structure of VO_2



high-temperature rutile (***R***) **metallic** Phase of VO_2

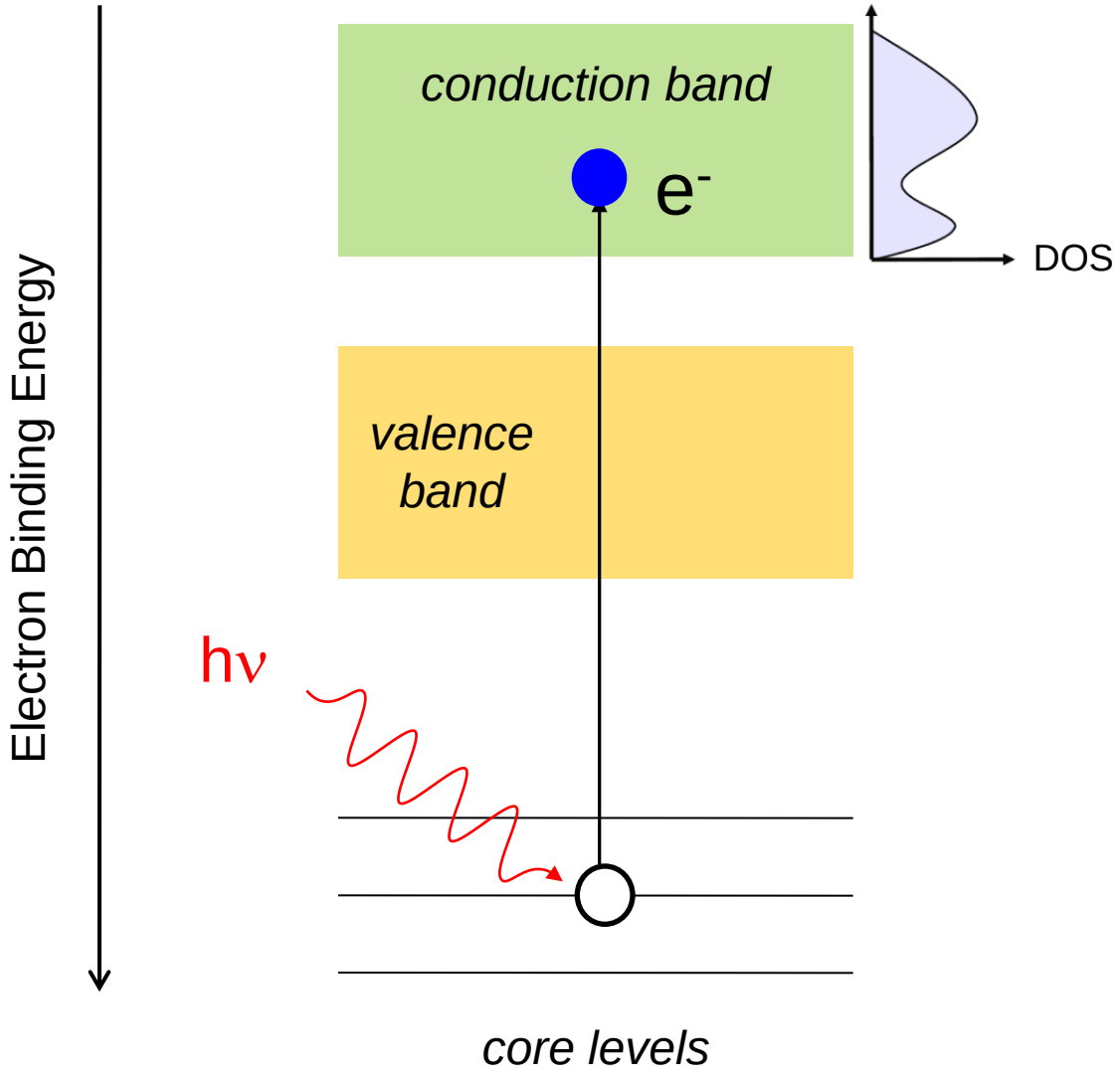
low-temperature monoclinic (***M₁***) **insulating** phase of VO_2

Photoemission Spectroscopy



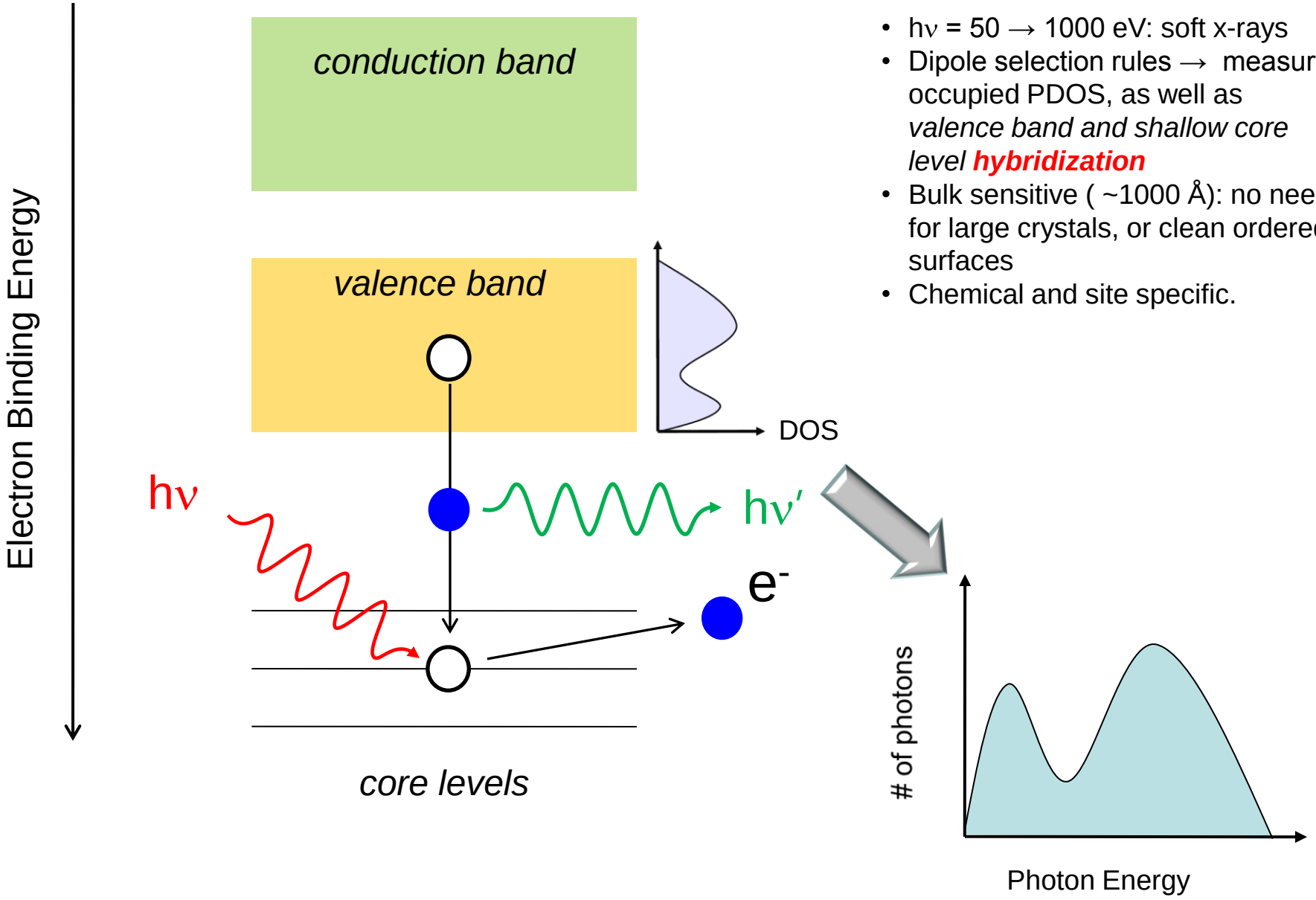
- Measuring the **kinetic energy** of emitted electrons gives electron **binding energy**
- Angle resolved photoemission spectroscopy (ARPES) measures the **momentum** of emitted electrons and gives **band dispersion and Fermi surfaces**
- Angle integrated photoemission integrates momentum of emitted electrons and gives the valence band **density of states**
- X-ray photoemission spectroscopy gives **core level binding energies**
- **Surface sensitive (~5-10 Å)**
  - generally need single crystals
  - always need atomically clean surfaces
- **UHV required**
- **Inapplicable to good insulators**
- **Inapplicable in electric or magnetic fields**

Soft X-Ray Absorption Spectroscopy (XAS)



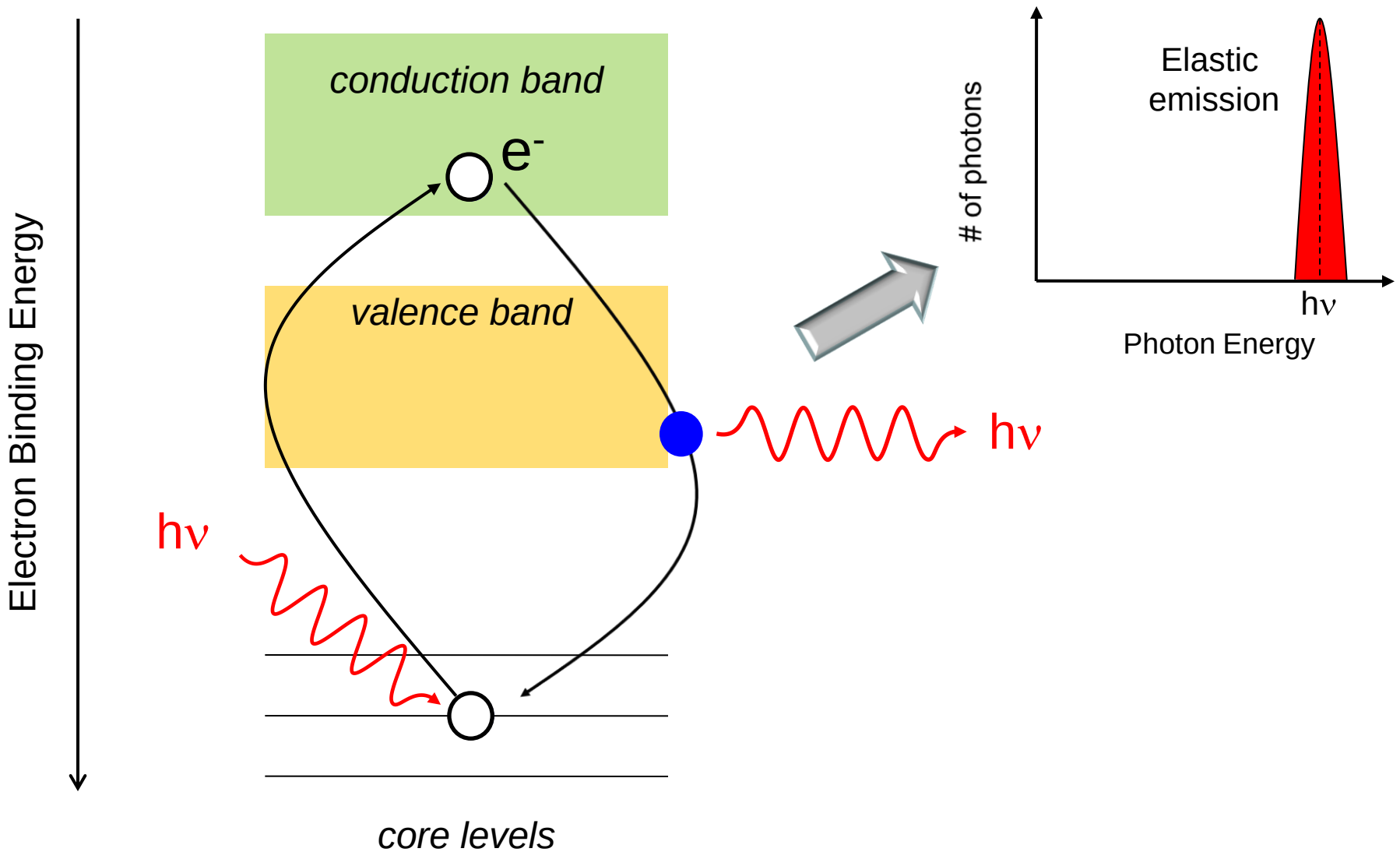
- Incoming photon energies hν = 50 → 1000 eV
- Sweep the incident photon energy through an absorption edge, and measure current through sample or total fluorescence
- Bulk sensitive (~1000 Å) no need for large crystals, clean ordered surfaces (TFY)
- Atomic, site, and chemically specific
- Dipole selection rules → measure unoccupied conduction band PDOS for *K*-edge absorption

Soft X-Ray Emission Spectroscopy (XES)



- hν = 50 → 1000 eV: soft x-rays
- Dipole selection rules → measure occupied PDOS, as well as *valence band and shallow core level* ***hybridization***
- Bulk sensitive (~1000 Å): no need for large crystals, or clean ordered surfaces
- Chemical and site specific.

Resonant Inelastic X-Ray Scattering (RIXS)



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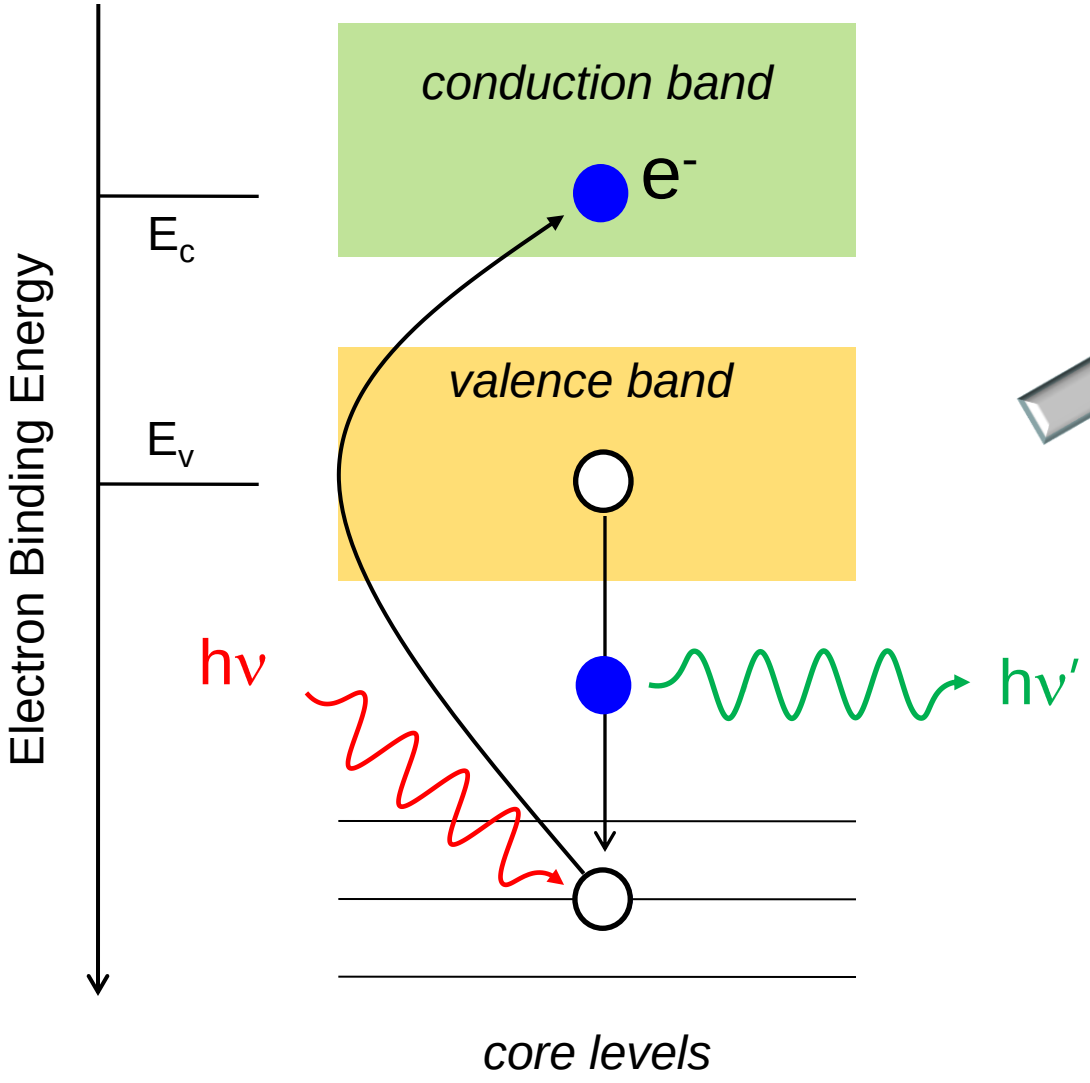
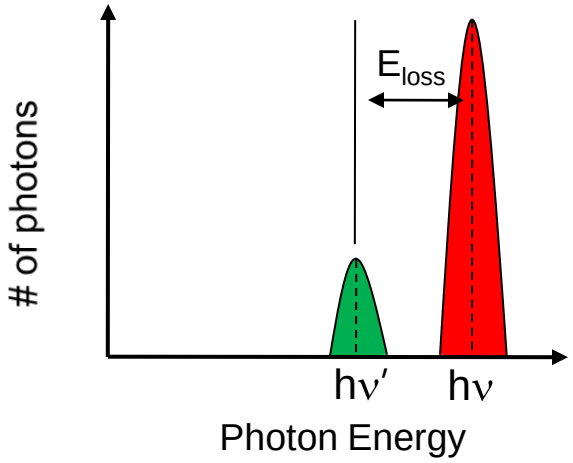
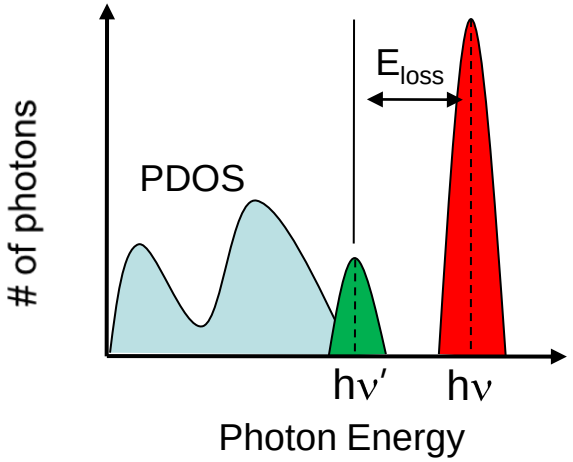


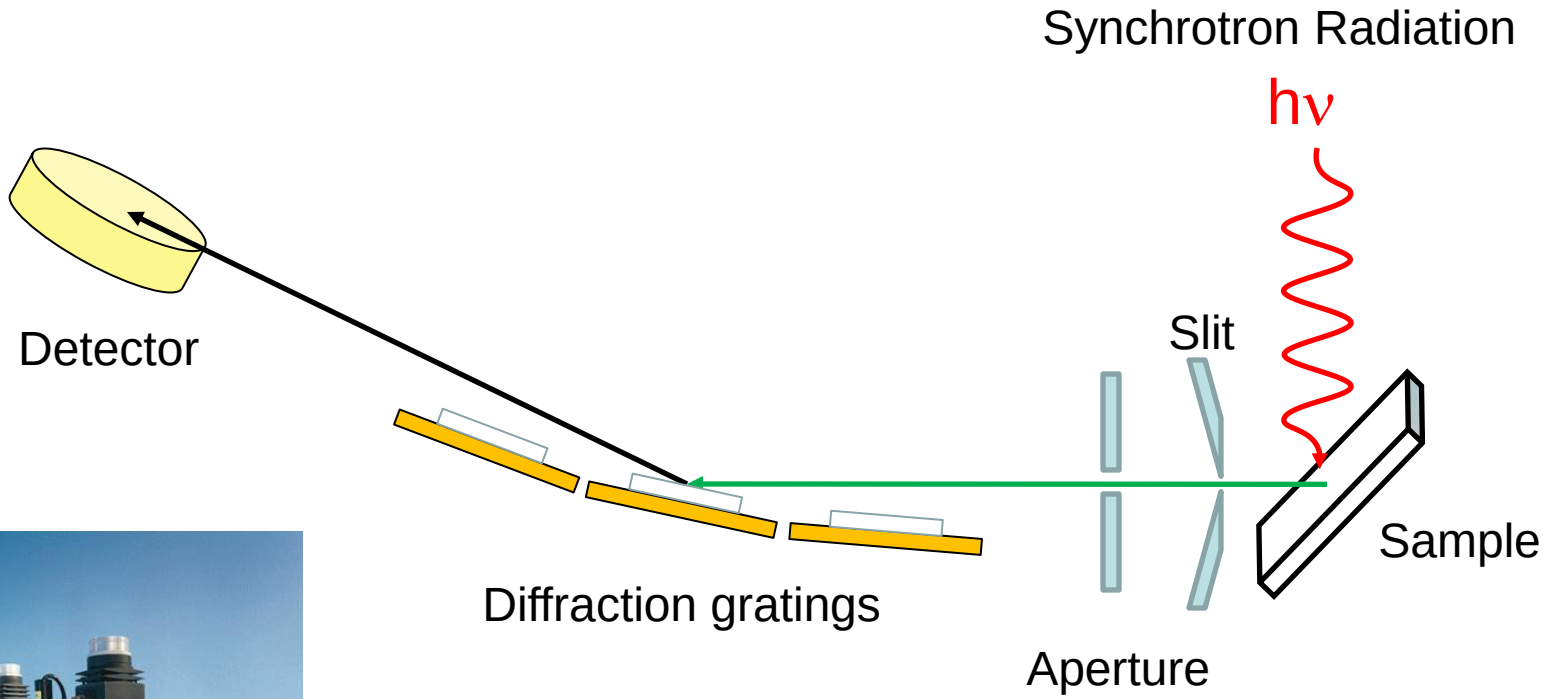


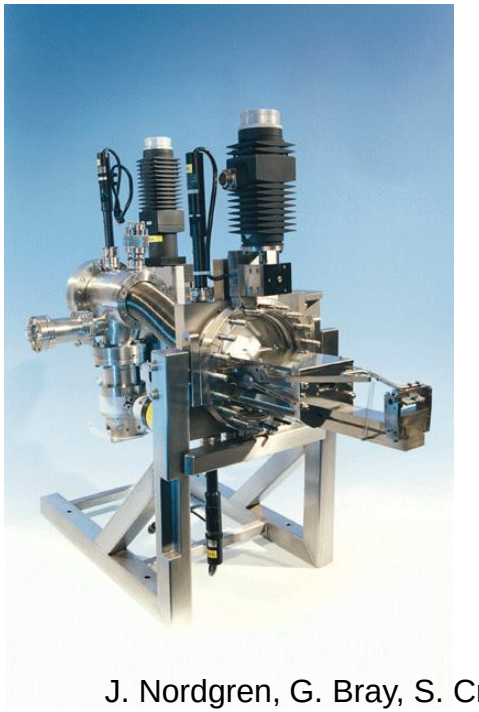
- $E_{loss} = E_c - E_v$
- RIXS features overlap RXES PDOS features, since they are competing processes



The core hole acts as an intermediate state, and the energy resolution of RIXS features is not limited by the core hole lifetime

XES Spectrometer





- The “standard” instrument
- Undulator radiation required
- Operational conditions: 100 cps, with 0.5 eV energy resolution at ~500 eV (O *K*-edge)
- New instruments are being developed…

J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.E. Rubensson, and N. Wassdahl, Rev. Sci. Instrum. 60, 1690 (1989).

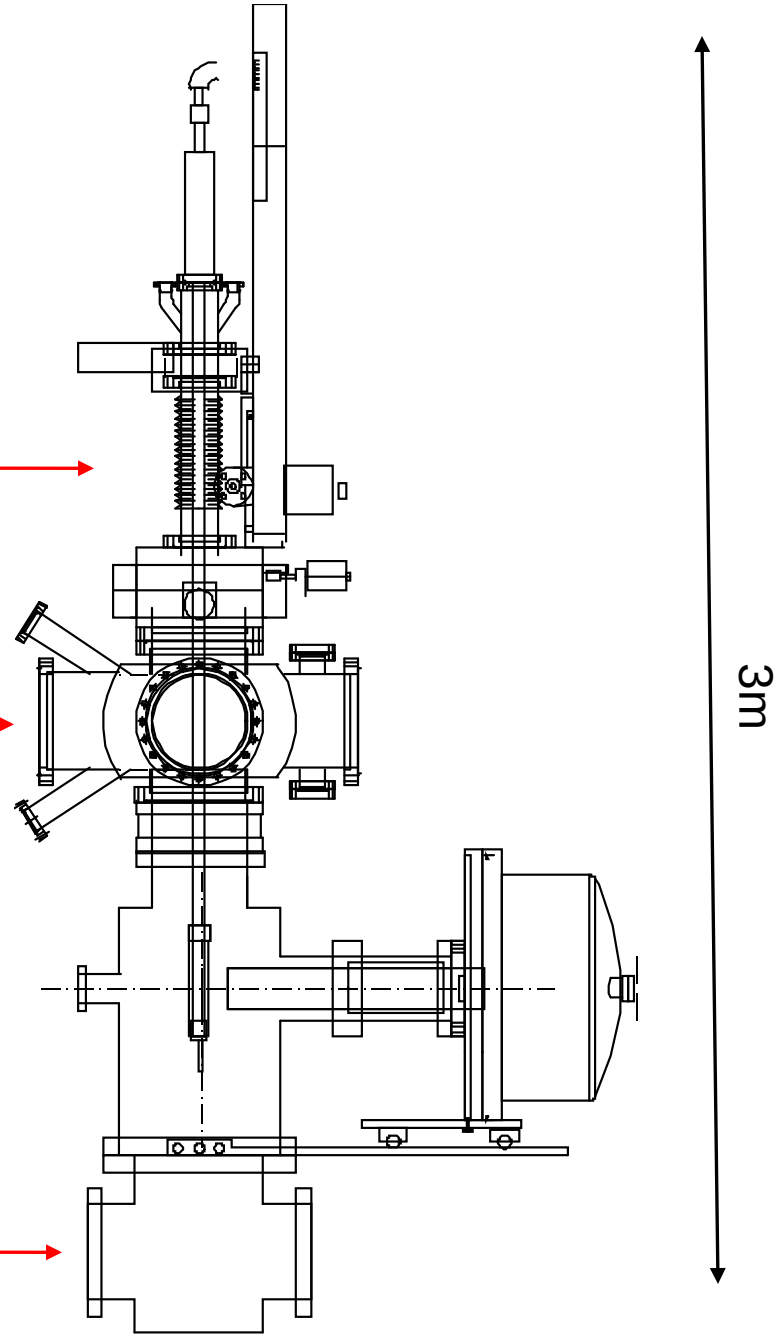
The Boston University High Resolution Photoemission and X-Ray Emission Spectrometer System

Sample manipulator, with liquid helium cooling, electron beam heating, 5 degrees of freedom for sample motion, sample transfer and load lock.

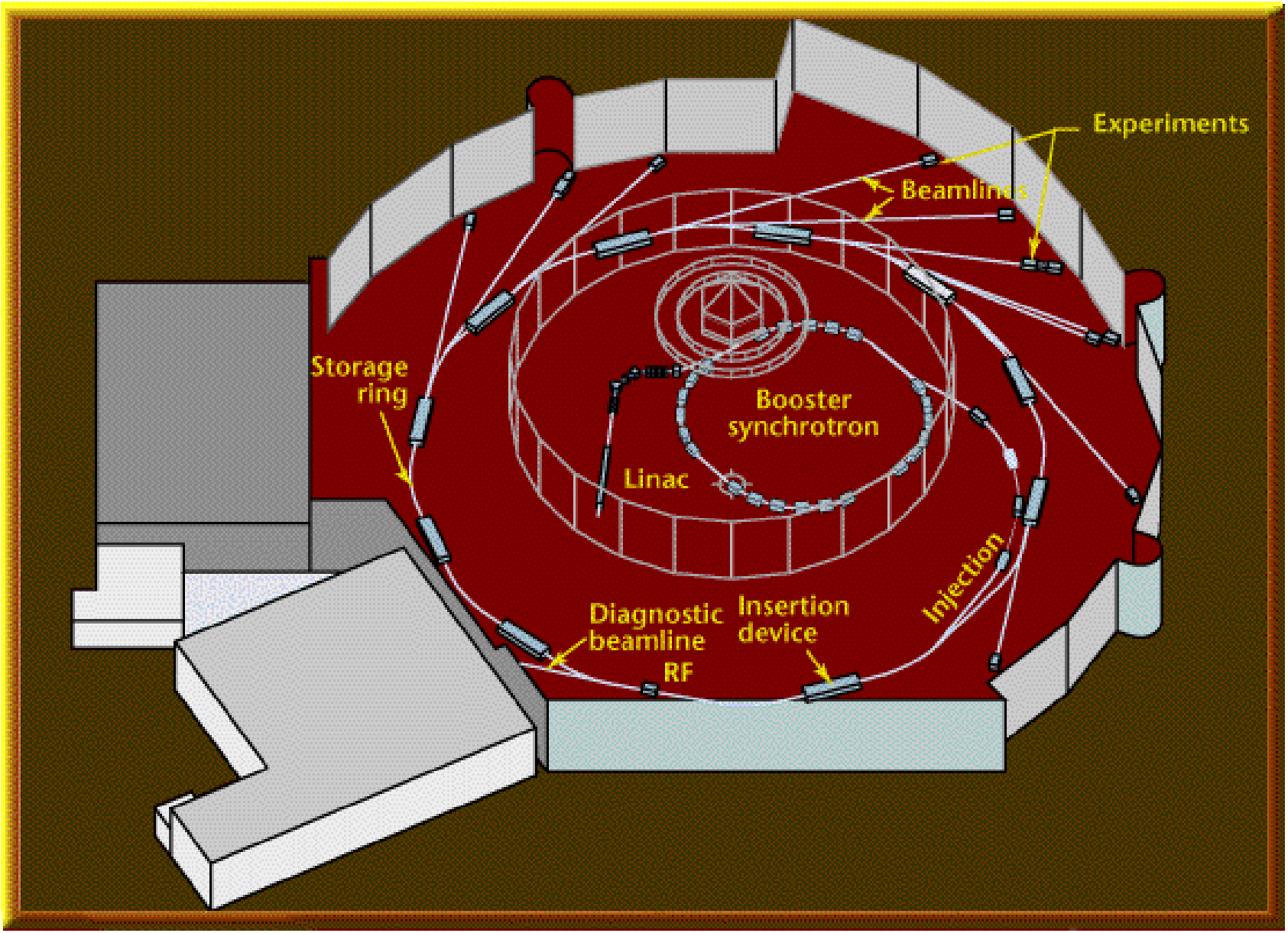
Sample preparation chamber: pumped with a 360 l/s turbo pump, titanium sublimation pump, and cryoshield. Features a LEED optics, CMA Auger spectrometer, multiple metal evaporators and gas dosing system.

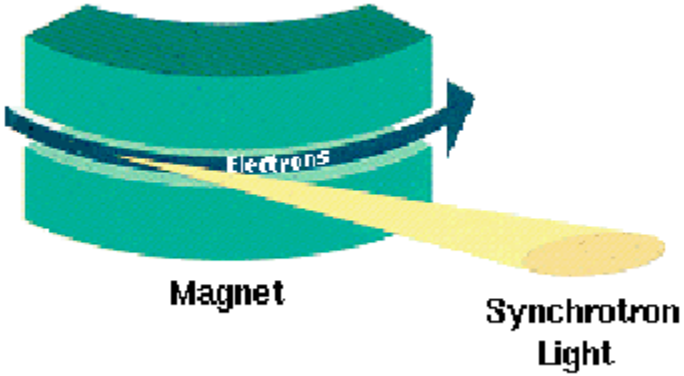
Spectrometer Level: double μ metal lined chamber, housing 100 mm Scienta electron analyzer, and soft x-ray emission spectrometer

Pumping level for Spectrometer Chamber: 400 l/s ion pump, titanium sublimation pump, cryoshield

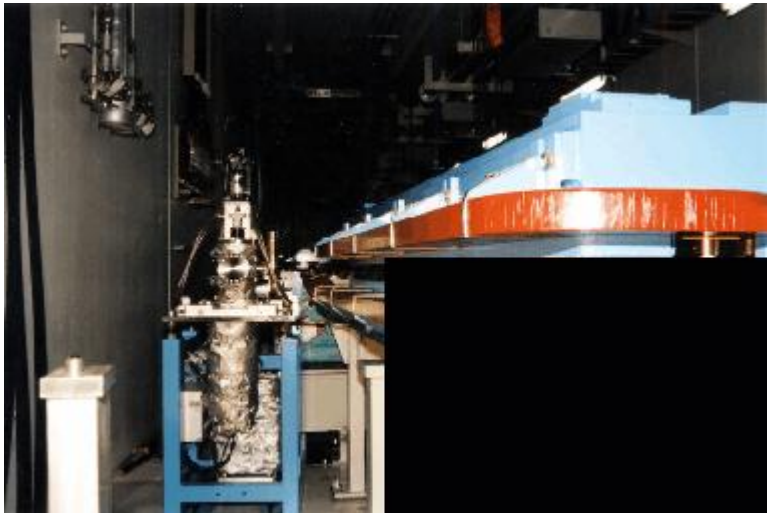


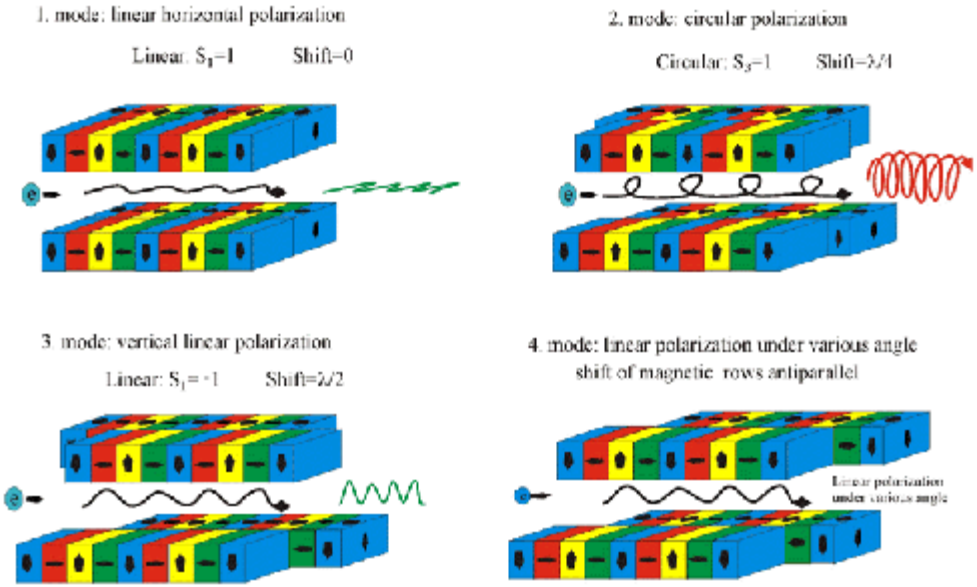
Synchrotron Radiation Light Sources





Bending Magnet Sources



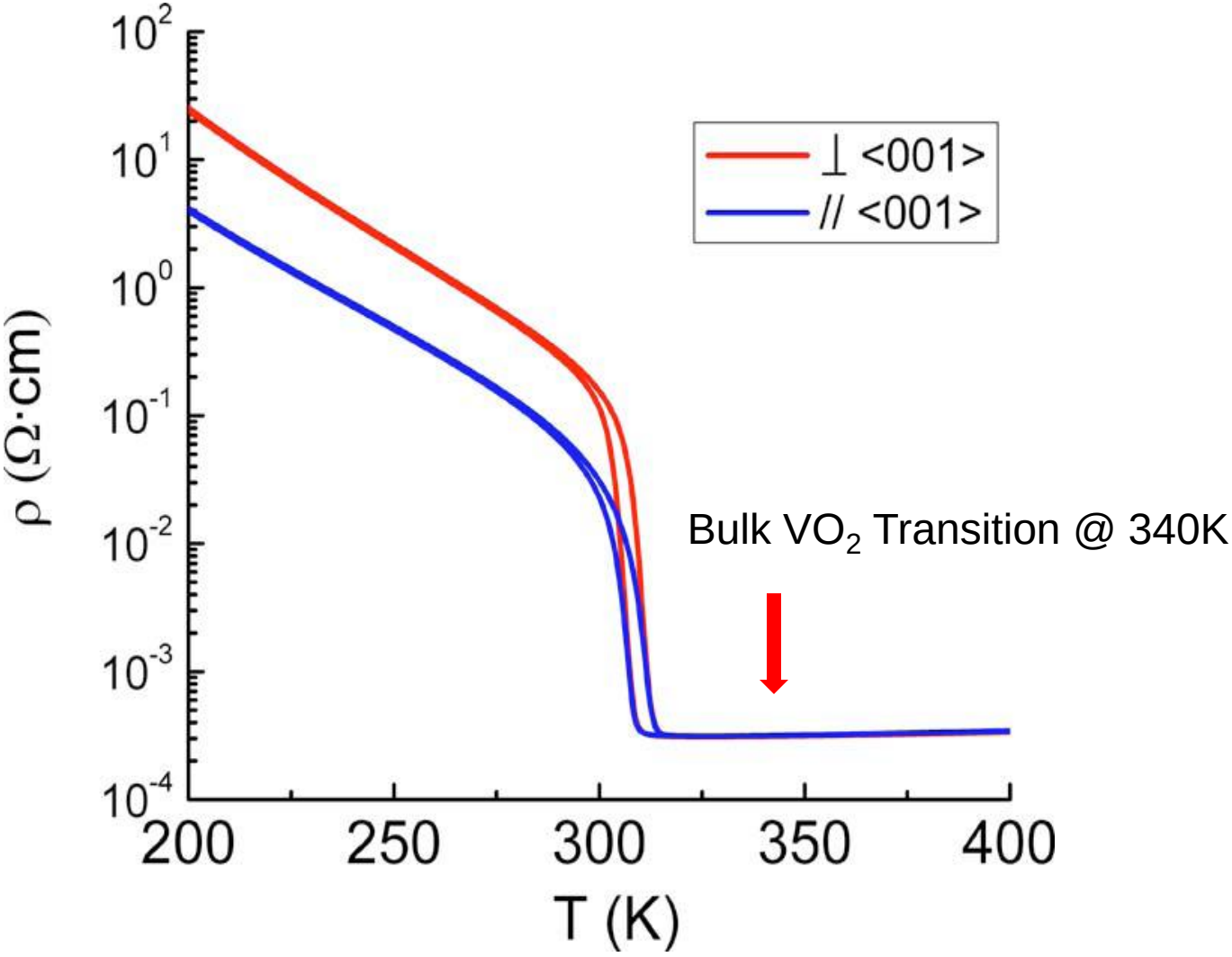


Undulator Sources

Controlling the Metal - Insulator Transition in VO_2 Thin Films using Strain

- 40 nm thick VO_2 films were grown epitaxially on TiO_2 using reactive bias target ion beam deposition, with the b_{Rutile} axis normal to the surface plane (i.e. c_{Rutile} axis in the surface plane).
- Strained VO_2 films display a large anisotropy in the dc conductivity
- There is also a shift of the metal-insulator transition temperature that depends on the magnitude and type of strain …..

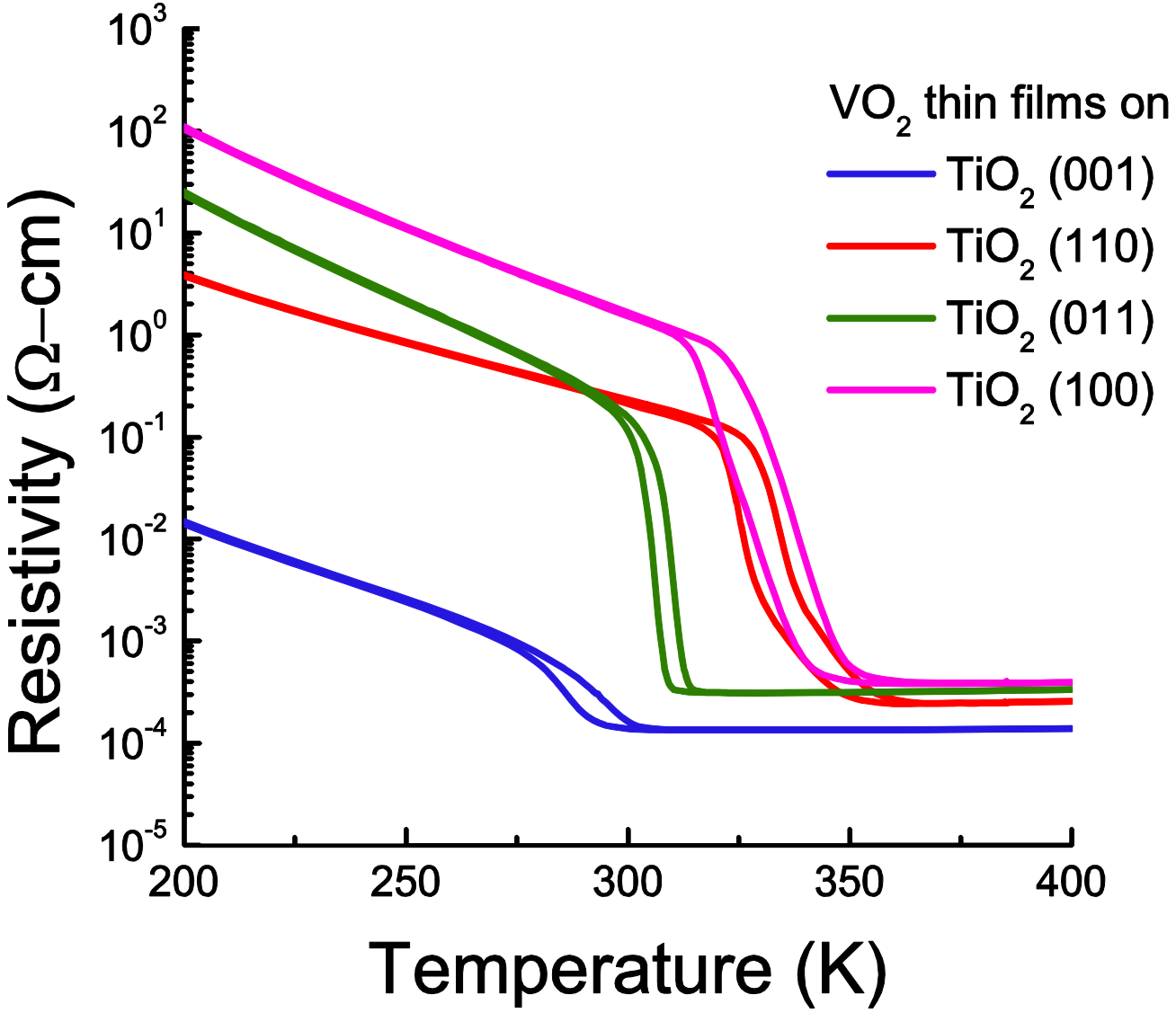
DC Resistivity in Compressively Strained VO_2



Resistivity as function of temperature for VO_2 grown on TiO_2(001), measured parallel and perpendicular to the c-axis of rutile VO_2.

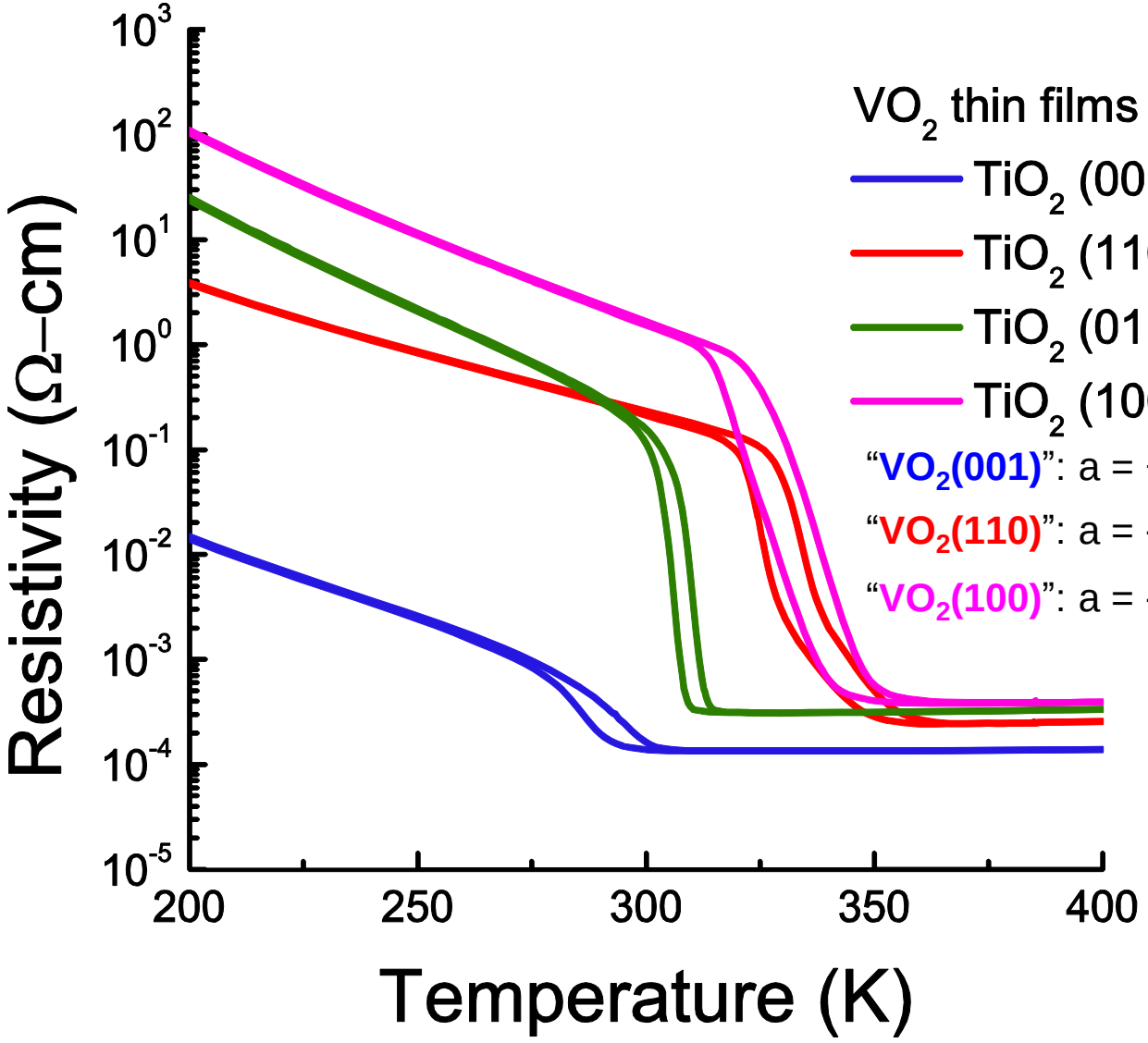
J. Lu, K.G. West, and S.A. Wolf, Appl. Phys. Lett. **93**, 262107 (2008).

DC Resistivity in Strained VO_2



Resistivity as function of temperature for VO_2 grown on various TiO_2 substrates.

DC Resistivity in Strained VO_2



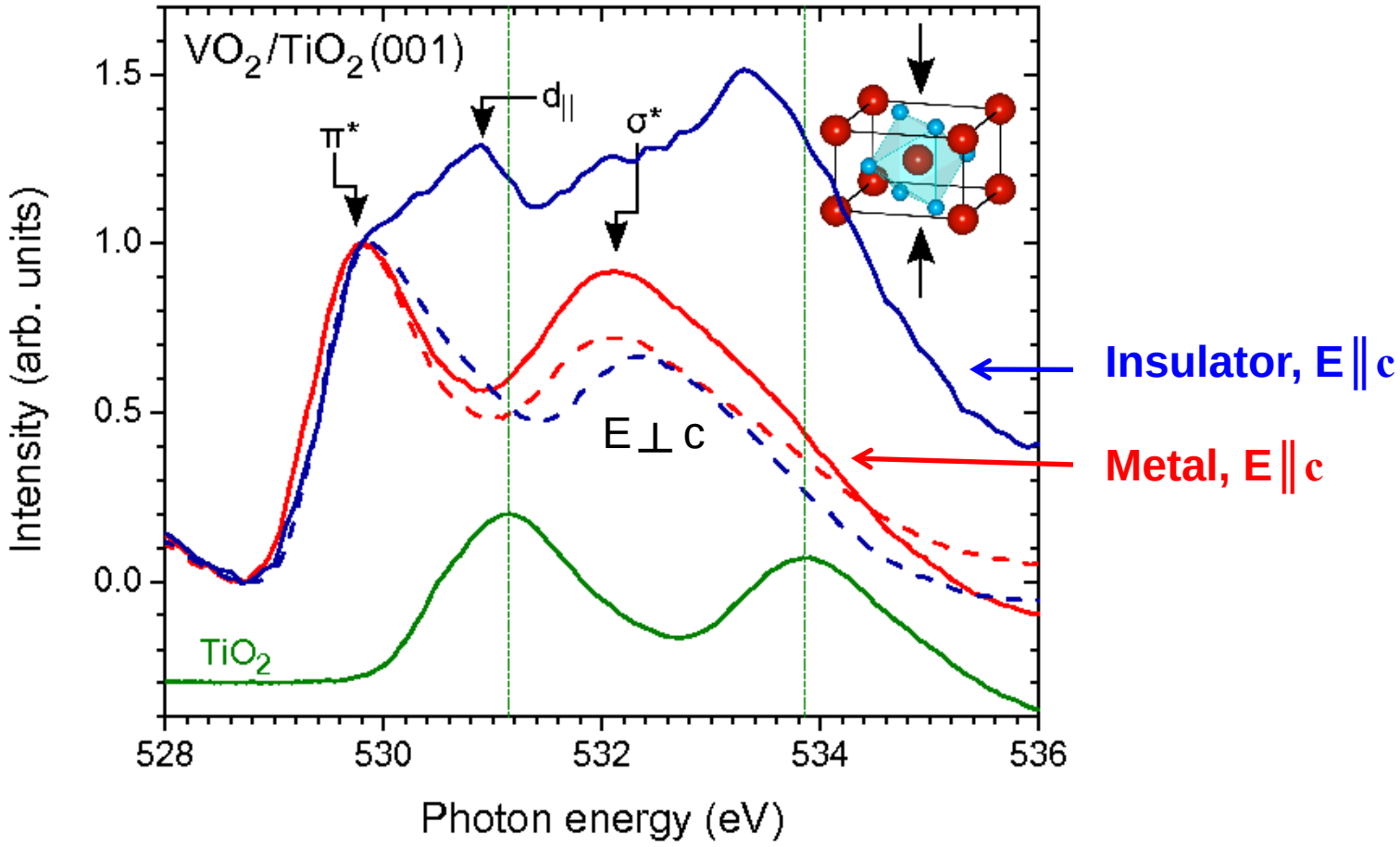
"**VO_2(001)**": a = +1.3%; b = +1.3%; c = -2.5%

"**VO_2(110)**": a = - 0.4%; b = - 1.3%; c = +1.7%

"**VO_2(100)**": a = - 0.5%; b = - 1.4%; c = +3.7%

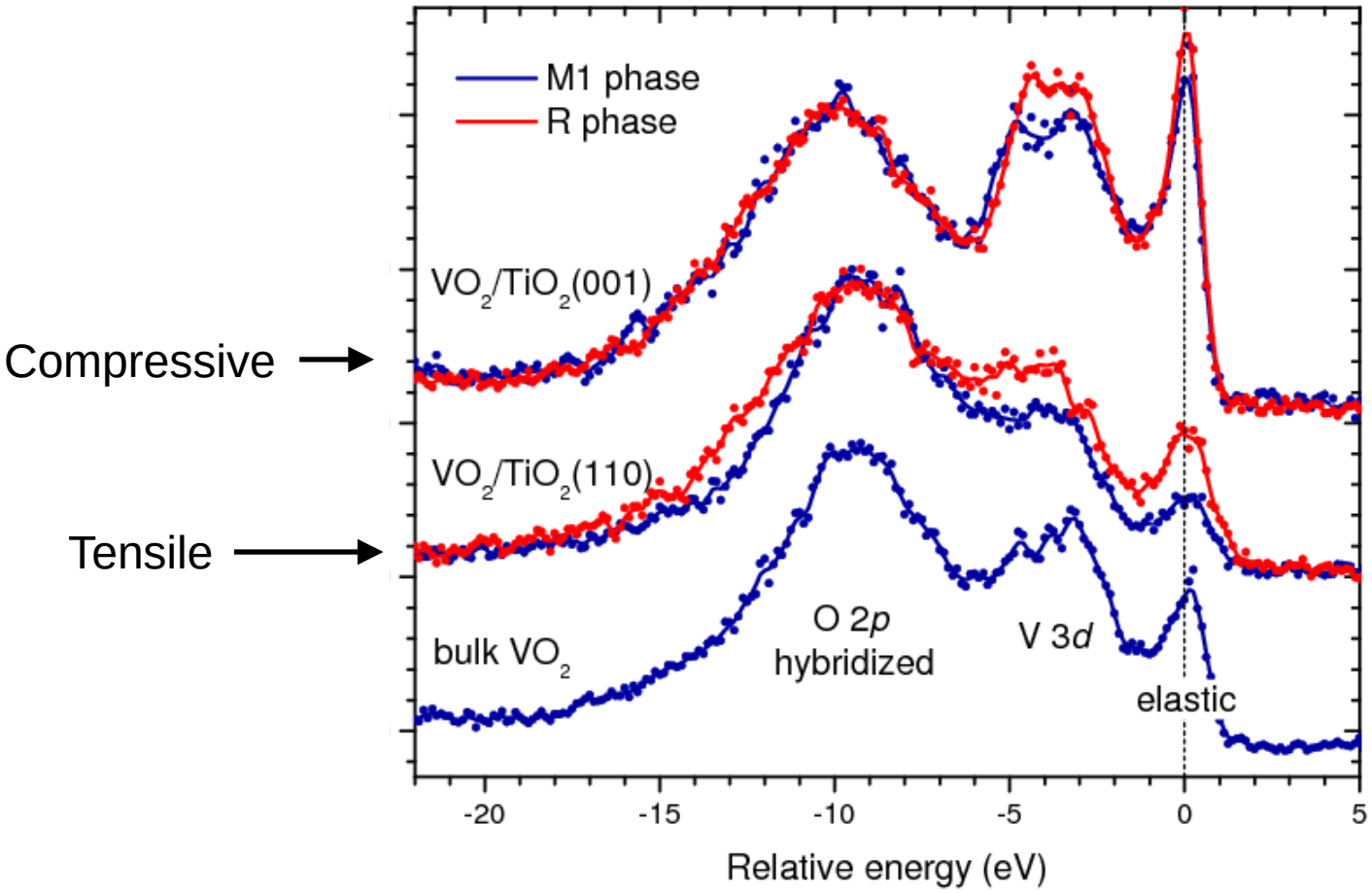
Resistivity as function of temperature for VO_2 grown on various TiO_2 substrates.

O *K*-edge XAS: $VO_2/TiO_2(001)$: Compressive, -2.5% c_R



- $VO_2/TiO_2(001)$ is **compressively** strained – *c*-axis is reduced compared with bulk VO_2 and the *a*-axis is increased. T_{MIT} = **300 K**
- Observe π* and σ* unoccupied states at ~ 529 eV and ~ 532 eV
- For E ‖ *c*, a peak develops at ~ 531 eV in the monoclinic phase, but not in the rutile phase – this is the $d_{\|}$ state.

V $2p_{3/2}$ XES: VO_2(001) & (110) – Valence Band PDOS



For tensile strained VO_2, the O 2*p*/V 3*d* hybridization is stronger than in the bulk.

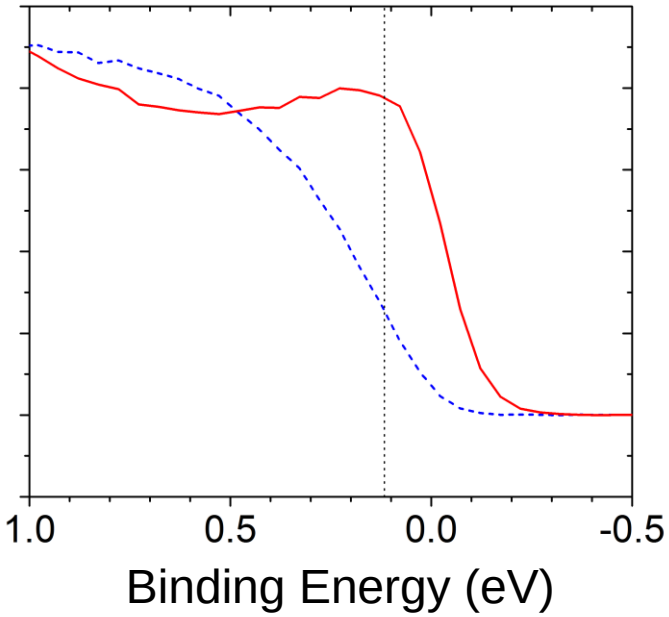
For compressive strained VO_2, it is weaker than in the bulk.

- Elastic scattering intensity varies with strain. This intensity is related to the degree of localization of the states involved, implying **more localized** V 3*d* states for compressive strain.
- V 3*d* signal at 4 eV **decreases** relative to O 2*p* hybrid states for both types of film when going metal to insulator. V 3*d* band occupancy is constant, therefore this change is due to **increased** hybridization in the insulating phase. R phase V-O = 1.92 Å. M_1 phase V-O = 1.76 Å

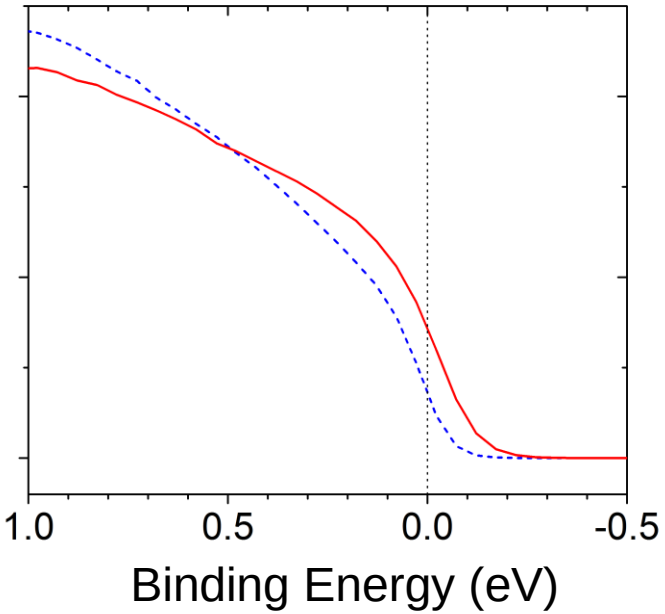
VO_2(110) vs. VO_2(100)

VO_2(110)

+1.7% Strain



+3.7% Strain

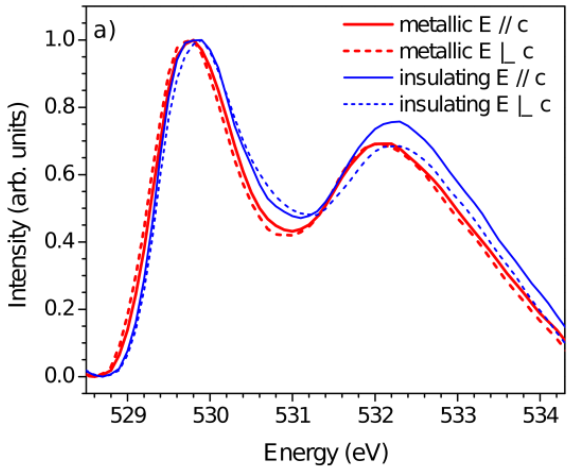


VO_2(100)

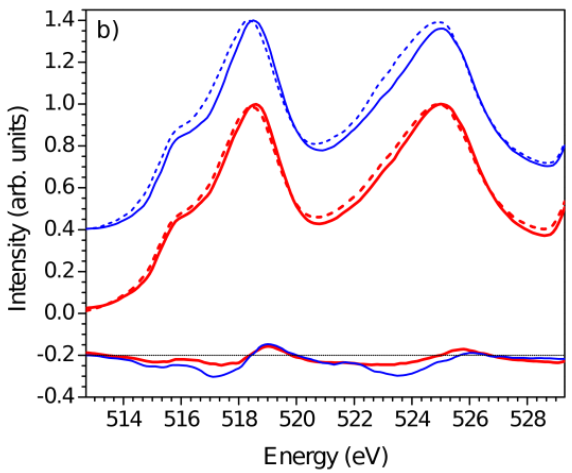
- The magnitude of the insulating gap is **~ 300 meV** (leading edge). for **moderately-strained** VO_2(110).
- For **larger strain** of VO_2(100), gap is **< 50 meV**.
- In both systems, a small shift in the leading edge of the O 2*p* manifold observed.
- Clearly, the behavior of the two systems is different...

XAS and XES from V(100)

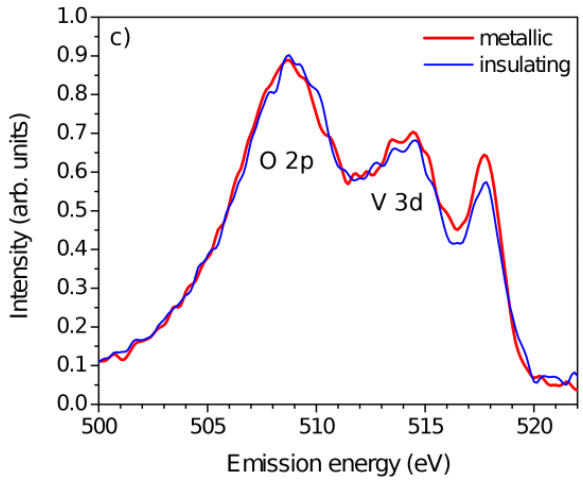
O *K*-edge XAS



V *L*-edge XAS



V L_3 RXES



- XAS and XES measurements from VO_2(100) reveal no changes across the MIT
- Absence of $d_{\|}$ peak in O *K*-edge XAS implies there is **no V-V dimerization**.
- Absence of anisotropy in V *L*-edge XAS implies there is no orbital switching (associated with structural distortion).
- No change in ratio of V 3*d* : O 2*p* ratio in RXES, implying bonding is unchanged across MIT.
- **Together, these results indicate there is no structural rearrangement for highly-strained VO_2, i.e. it keeps a rutile-like structure in both metallic and insulating phases**.

Summary

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