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

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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 VO₂
- Controlling transition temperatures with moderate strain.
- Suppressing structural transitions with large strain.
Example: Conductivity Transitions in Cr-doped V$_2$O$_3$

PMI = Paramagnetic insulator

M = Metal

AFI = Antiferromagnetic insulator

**Example**: Metal - Insulator Transitions in VO$_2$

- **BULK** VO$_2$ displays an abrupt insulator to metal transition at $\sim$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.
Metal - Insulator Transitions in VO$_2$

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![Diagram showing the transition between normal metal and another phase](attachment:image.png)
Metal - Insulator Transitions in VO\textsubscript{2}

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![Diagram of metal to insulator transition](image-url)
Schematic Crystal Structure for Rutile VO$_2$
Electronic Structure of VO\textsubscript{2}

- High-temperature rutile (**R**) metallic Phase of VO\textsubscript{2}
- Low-temperature monoclinic (**M\textsubscript{l}**) insulating phase of VO\textsubscript{2}

\[ [4] \sigma^* \]
\[ [4] \pi^* \]
\[ [2] \ d_{//} \]
\[ \sigma \]
\[ \pi \]

\[ E_F \]
\[ V \ 3d \]
\[ O \ 2p \]
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 $h\nu = 50 \rightarrow 1000$ 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

Diagram:
- $h\nu$ represents incoming photon energy
- $e^-$ represents an electron
- Conduction band
- Valence band
- Core levels
- DOS (Density of States)
Soft X-Ray Emission Spectroscopy (XES)

- $h\nu = 50 \rightarrow 1000$ 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)

- Electron Binding Energy
- Photon Energy
- conduction band
- valence band
- core levels
- Elastic emission
- h\textsubscript{\nu}
Resonant Inelastic X-Ray Scattering (RIXS)

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

- \( E_{\text{loss}} = E_c - E_v \)
- RIXS features overlap RXES PDOS features, since they are competing processes.
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…

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 $b_{\text{Rutile}}$ axis normal to the surface plane (i.e. $c_{\text{Rutile}}$ 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$_2$.

Resistivity as function of temperature for VO$_2$ grown on various TiO$_2$ substrates.
DC Resistivity in Strained VO$_2$

Resistivity as function of temperature for VO$_2$ grown on various TiO$_2$ substrates.

VO$_2$ thin films on
- TiO$_2$ (001)
- TiO$_2$ (110)
- TiO$_2$ (011)
- TiO$_2$ (100)

- "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%
**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. $T_{\text{MIT}} = 300$ K
- Observe $\pi^*$ and $\sigma^*$ unoccupied states at $\sim 529$ eV and $\sim 532$ eV
- For $E \parallel c$, a peak develops at $\sim 531$ eV in the monoclinic phase, but not in the rutile phase – this is the $d_{\parallel}$ state.
Elastic scattering intensity varies with strain. This intensity is related to the degree of localization of the states involved, implying more localized V 3d states for compressive strain.

V 3d signal at 4 eV decreases relative to O 2p hybrid states for both types of film when going metal to insulator. V 3d 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
- The magnitude of the insulating gap is $\sim 300$ 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 measurements from VO\textsubscript{2}(100) reveal no changes across the MIT

- Absence of $d_{\parallel}$ 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 $3d$ : O $2p$ ratio in RXES, implying bonding is unchanged across MIT.
- Together, these results indicate there is no structural rearrangement for highly-strained VO\textsubscript{2}, i.e. it keeps a rutile-like structure in both metallic and insulating phases.
Summary

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