Magnetic Order and Muon Diffusion in VO$_2$

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Texas Tech

Support:
Provided by the Welch Foundation (D-1321)

Experimental Facility:
ISIS: EMU
TRIUMF:
M15 - HiTime
M20 - Helios

MuSR (2/Jun/2014)
Basic Properties of VO$_2$

Transitions

- Reversible, Metal-Semiconducting at $T_{MST} = 340$ K
- Structural: Rutile ($T>T_{MST}$) $\rightarrow$ Monoclinic (M1, $T<T_{MST}$)

<table>
<thead>
<tr>
<th></th>
<th>Metallic</th>
<th>Semiconducting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Gap</td>
<td>$\sim 0$ eV</td>
<td>$\sim 1$ eV</td>
</tr>
<tr>
<td>Optical Property</td>
<td>Reflective (Near IR)</td>
<td>Translucent</td>
</tr>
<tr>
<td>Conductivity</td>
<td>$\sim 10^3$-$10^4$ (Ωcm)$^{-1}$</td>
<td>$\sim 10^{-1}$-$10^{-3}$ (Ωcm)$^{-1}$</td>
</tr>
</tbody>
</table>

Triggered by:

- Temperature, E-field, Optical Excitation, Pressure

Potential Applications

- Microwave wave guides, smart-windows, reconfigurable and switchable antennae, ultra-fast optical filters
Structure: Metallic \((T>T_{\text{MST}})\)

- Tetragonal body-centered unit cell
- \(V\) surrounded by octahedron of \(O\) atoms
- \(V^{4+}\) has single \(e^-\) near Fermi level, occupies lowest 3\(d\) level
- Asymmetry in crystal field splits 3\(d\) states with lowest orbital aligned along \(c\)-axis \((\rightarrow \text{higher conductivity})\)

Images from: M. Nazarri, PhD Dissertation, Texas Tech, 2013;
Structure: Semiconducting \((T < T_{\text{MST}})\)

• V–V dimerization → doubled unit cell

• V atoms pair along \(c\)-axis

• One V per pair:
  • Shift in \(a-b\) plane
  • Closer to partner along \(c\)

• Dimerization pairs \(e^-\) into singlet state, lead to
  • High resistivity
  • Non-zero bandgap

Images from: M. Nazarri, PhD Dissertation, Texas Tech, 2013;

Semiconducting (Monoclinic)
Pink V1 paired with twisting
Orange V2 paired without twisting
Background

**H investigated as a dopant (~0 to 3.8% H)**
- Nominal resistivity change; remains metallic down to 200 K (at 3.8% H)
- Effect has been observed but role H *actually* plays needs investigation  

**Dopants introduced, modify transition temperature**
- W, Ti, Au: Lower transition temperature
- Cr, Al: Raise transition temperature
- **Minimal effects** on properties other than $T_{MST}$
- *Actual* role dopants play needs additional thorough investigation  

**Applications require exposure to H**
- Long-term effects of H has not been studied
- Intentional H incorporation into VO$_2$ has major effect on transition  
  → Important to understand:
  - *How H may propagate into & Behavior in bulk VO$_2$*
Project Focus: VO$_2$ Compounds

- General study of Mu in VO$_2$
  - ie: Unique contribution to H defect studies (early time)
  - Stability, Charge & Site dynamics, Energy Barriers, Diffusion Parameters, etc

- Local environment of VO$_2$ [vs VO$_2$:X]
  - Role dopants play in modifying various phases and transition
  - Sensitive magnetic probe:
    - Dimer $S_{net} = 0$
    - Magnetic moments introduced by disruption of V-V dimerization

- Local probe of yet to be understood transition
  - Mechanism (Mott-Hubbard vs Peierls)
  - Role Dopants play (c.f. Modification of environment, etc)
**Experiment Details**

**ZF-MuSR**
EMU (ISIS), HiTime and Helios (TRIUMF)
- Mu diffusion 8 K to 560 K
- Dynamics (field fluctuations or mu motion)
- Local magnetic environment

**wTF-MuSR**
EMU, $B_{TF} = 100\text{G}$
- ZF $\alpha$ calibration
- Basic character info

**HTF-MuSR**
HiTime, $B_{ext}$ up to 6.5 T
- Identify & characterize sites
- Investigate $\mu^0/\mu^0$-like states & formation
- Characterize magnetism
Results and Discussion

1) Static between 100 K and ~300 K
   \[ \Delta = 0.171 \pm 0.004 \text{ MHz} \]

2) Detect change in mu site around MST
   \[ \Delta(T > T_{MST}) = 0.165 \pm 0.005 \text{ MHz} \]
3) Dynamic at higher T, fit down to ~340 K
4) T < 35 K, trade off in Asy; $B_{\text{loc, max}} = 0.62 \pm 0.08 \text{ kG}$
5) Small fraction fits to same $B_{\text{loc}}$ between 35 K & 100 K suggesting small fraction of high local order starting ~100 K
6) TF show relaxation features at 340 and near 450 K

7) Fit field – critical power law
   $B_{\text{loc}, \text{max}} = 0.62 \pm 0.08$ kG
ZF-MuSR: VO$_2$:W (97.6:2.4 at%)
Summary

• Mu is sensitive to a feature near the MST and low temperature magnetism

• $T < 35 \text{ K}$ Magnetic phase $B_{\text{loc}}=0.62 \pm 0.08 \text{ kG}$ in $\text{VO}_2$

• $35 \text{ K}$ to $\sim 100 \text{ K}$ localized magnetic features

• Static between $100 \text{ K} – 300 \text{ K}$

• Significant dynamics above 450K; possibly starting near 340K -- just above MST

• 5 at% Ti & 2.4 at % W show $T_c \sim 175 \text{ K}$ with $B_{\text{loc}} \sim 1.1 \text{ kG}$
Thank You!
Thank you
Transition Mechanism Question

- Basic properties of stoichiometric VO$_2$ well into each phase are well understood
- Driving mechanism of transition highly debated
  - (1) instability in Fermi surface caused by periodic lattice deformations (V-V pairing) which causes an energy gap to open (Peiels Mechanism)
  - OR
  - (2) is it related to strong e$^-$ -- e$^-$ correlations that introduce an energy gap from the mutual repulsion (Mott-Hubbard mechanism)
- Understanding of this transition is required for better control and optimization of the properties for any application
Goals with MuSR

Use $\mu^+$ as experimentally accessible analog to hydrogen

- Probe $\mu^0$/H like states
- $\mu$/H diffusion

Mu as sensitive local probe to investigate local magnetic environment

- Through transition
- Well into each phase
### Experimentally Accessible Analog to Hydrogen

<table>
<thead>
<tr>
<th></th>
<th>Muon</th>
<th>Proton</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mass</strong> ($m_p$)</td>
<td>0.1126 $\approx$ 1/9</td>
<td>1</td>
</tr>
<tr>
<td><strong>Spin</strong></td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td><strong>Gyro. Ratio, $\gamma$ (s$^{-1}$ T$^{-1}$)</strong></td>
<td>8.51607 x $10^8$ $\approx$ 3.2 x $\gamma_p$</td>
<td>2.67520 x $10^8$</td>
</tr>
<tr>
<td><strong>Lifetime, $\tau$ ((\mu)s)</strong></td>
<td>2.19709</td>
<td>Stable</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Muonium</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Red. e$^-$ mass ($m_e$)</strong></td>
<td>0.995187</td>
<td>0.999456</td>
</tr>
<tr>
<td><strong>G. S. Radius (Å)</strong></td>
<td>0.531736</td>
<td>0.529465</td>
</tr>
<tr>
<td><strong>G. S. Energy (eV)</strong></td>
<td>-13.5403</td>
<td>-13.5984</td>
</tr>
</tbody>
</table>

**FIG. 1.** The hyperfine energy-level (Breit-Rabi) diagram for isotropic 1$\sigma$-Mu as a function of the dimensionless magnetic field $x = B (g_\mu \mu_\mu - g_\mu \mu_\mu) / (h \lambda)$. A fictitious value for the quantity $\omega_- / \omega_+$ has been used for clarity; its true value is 0.9904. The dashed lines are the high-field asymptotes for levels 2 and 4.


Brewer, http://musr.ca →

Field applied perpendicular to initial spin polarization
→ $\mu^+$ spin precession about applied field at:

$$\nu_{\mu^+} = \gamma_\mu \times |B| \ \ \ |\gamma_\mu = 135.54\text{MHz/T}$$

$\text{Mu}^0 = \mu^+ + \text{e}^-$
→ spin-orbit coupling
→ affects local field of $\mu^+$
→ different precession frequencies for:

$$|\uparrow_\mu> + |\uparrow_\text{e}> \ \ & \ |\uparrow_\mu> + |\downarrow_\text{e}>$$

Brewer, http://musr.ca

B.D. Patterson, Rev. Mod. Phys., 60, (1988) 1
TF-µSR: Sample signal from relaxing $\mu^+$

$$P(t) = G(t) \cos \left( \gamma_{\mu^+} \left| B_{\mu^+} \right| + \delta \right)$$
B applied || to μ⁺ spin pol. See time evolution of P(t) along original direction

=> Change in Spin P(t) from:
1) local environment (nearby nuclear moments)
2) muonium motion (e⁻ spin-flip w/ each site change, transferring back to μ⁺ contributing to Δ P(t) )


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ZF-$\mu$SR

No net B applied
See time evolution of $P(t)$ in natural environment

$\Rightarrow$ Change in Spin $P(t)$ from:
1) local environment (nearby nuclear moments)
2) $\mu^+$ motion


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