Characterization of the Magnetic Phase in Ti-Doped Vanadium Dioxide

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Project Purpose:

Use μ^+ as experimentally accessible analog to H and probe of the local magnetic environment in Vanadium Dioxide (VO_2) to:

- Identify transition mechanism (*Peierls* vs *Mott-Hubbard*)
- Understand *role* dopants play in changing material properties such as transitions, conductivity, bandgap, magnetism, *etc*
- Explore magnetism caused by disruption of V-V dimer
- Study H behavior (stability/dynamics, energy barriers, *etc*)

VO_2 Properties [1-4]:

- Reversible, Metal-Semiconductor Transition (T_{MST} =340K) triggered thermally, optically, electrically, barometrically
- Metallic ($T > T_{MST}$, E_G ~0eV):
  Rutile (*Fig 1*), reflective, $\sigma \sim 10^3$–10^4 $(\Omega\cdot cm)^{-1}$
- Semiconducting ($T < T_{MST}$, E_G ~1eV):
  Monoclinic (*Fig 2*), translucent, $\sigma \sim 10^{-1}$–10^{-3} $(\Omega\cdot cm)^{-1}$
- Dopants modify transition temperature and properties
  - Ti, W, Au (etc.): lowers T_{MST} ; F, Cr, Al (etc.): raises T_{MST} [3] minimal effects on properties other than T_{MST}
  - Adding H reduces T_{MST} while increasing σ in monoclinic phase with 3.8 at% H, T_{MST} ~ 200K with nominal σ difference between phases. *Effect* is known but *role* H plays is unknown. [4]

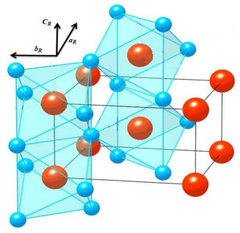


Fig. 1: *Rutile structure [2] where V^{4+} has loosely bound e^- → high σ*

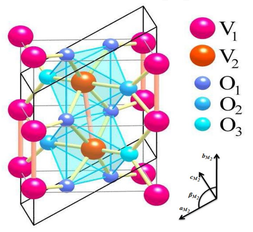


Fig. 2: *Monoclinic structure [2] V pair with and without twisting. Pairs e^- into singlet state → low σ*

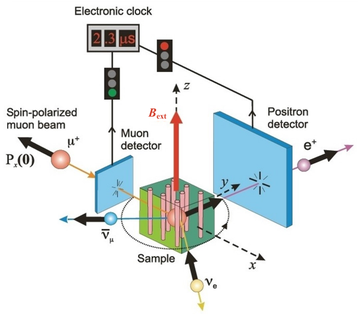
Project Significance:

This work directly contributes to understanding the role and behavior of H in bulk VO_2 compounds; it provides the initial discovery and characterization of the magnetic phases and provides insight into the debated mechanism responsible for the MST.

VO_2 has many potential applications such as in smart windows, smart radiators, microwave wave guides, optical fiber, ultrafast tunable antenna [7]. Applications require exposure to H, which has a major effect on the transitions and electrical properties [4]. The *effect* of H is known but the *role* H plays in modifying the host has yet to be understood.

For applications, it is essential to understand aspects such as how
(1) H may propagate into and behave within VO_2
(2) magnetic and electrical properties behave in the compounds

Muon Spin Relaxation (MuSR) [5]:



- Implant μ^+ into sample
- μ^+ starts clock
- μ^+ precesses in $\boldsymbol{B}_{eff} = \boldsymbol{B}_{ext} + \boldsymbol{B}_{int}$
- μ^+ decays, emits e^+ preferentially along direction of spin
- e^+ hits detector, stops clock
- Time evolution of μ^+ spin tracked via $A(t)$ of e^+ emission

Fig. 3: *Experimental setup for a typical MuSR experiment with an externally applied field [5]. Only one of four positron detectors shown.*

The Experiment:

- ZF (B_{ext}=0T) MuSR Measurements
- *HiTime* and *Helios* spectrometers, M15 & M20C surface muon channels at TRIUMF (Vancouver, Canada)
- Bulk sintered 7×7×1 mm^3 samples, VO_2:Ti (1, 3, 5 at%)
- Temperature range: ~2K to ~285K

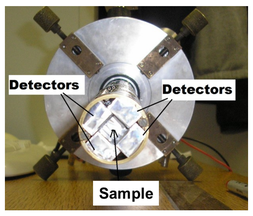
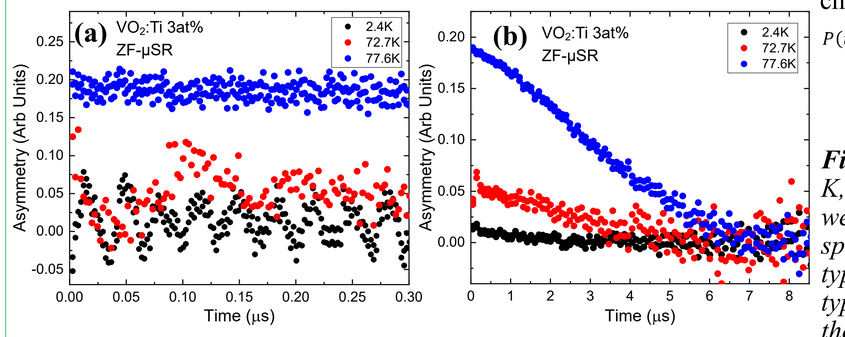


Fig. 4: *Sample mounted for use in HiTime surrounded by 4 detectors (scintillator cubes). The sample is covered by a thin piece of foil tape to hold it in position directly on top of another scintillator (veto cube) that is used to detect any μ^+ that miss the sample so that only events from muon decay inside the sample are recorded.*

Results and Analysis:



Time domain asymmetry spectra evolve with temperature (Fig 4) and are characterized here by the model:

$$P(t) = \sum_i A_i e^{-\lambda_i t}\cos(\gamma_\mu B_{eff,i} t + \phi_i) + \sum_j A_j \left(\frac{1}{3} + \frac{2}{3}(1-\Delta_j^2 t^2) e^{-\frac{\Delta_j^2 t^2}{2}}\right)$$

A_i, A_j = Asymmetry for oscillating & sKT components
$\{\lambda_i, \phi_i\}$ = Relaxation rate and phase of oscillating component
← Static Kubo-Toyabe (sKT) component
Δ_j = Second moment of measured field distribution for sKT

Fig 4 [left]: *Example of time domain spectra from VO_2:Ti 3 at%, at 2.4 K, 72.7 K, and 77.6 K.* ***(a)*** *The early time shows a fast relaxing oscillation, indicating a well-defined magnetic phase which is present only below Tc.* ***(b)*** *Full time spectra showing major differences in initial asymmetry above and below T_C, typical for a magnetic transition. The highest temperature spectra shown is typical for a state where only nuclear moments contribute to the field sensed by the μ^+ and is characterized by a Kubo-Toyabe function [6].*

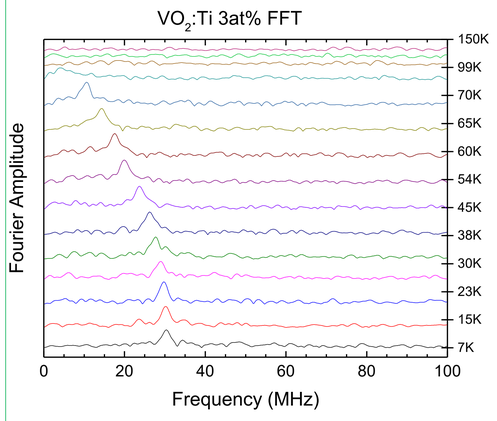


Fig. 5: *Fast Fourier Transforms of several time-domain ZF spectra showing at least one precessing component developing with decreasing temperature (top to bottom). The peak frequency is proportional to the measured field ($f = \gamma_\mu \boldsymbol{B}_{eff}$).*

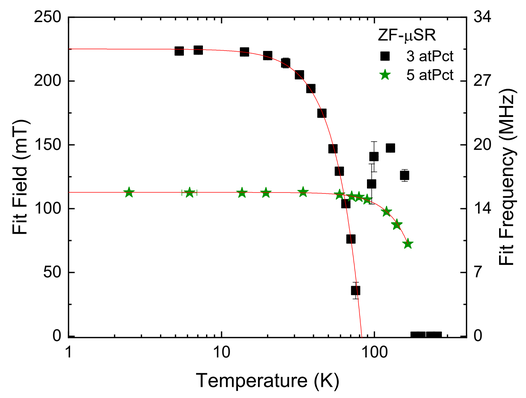


Fig. 6: *Fits to primary frequency in the time-domain ZF-MuSR data on VO_2:Ti 3at% (■) and 5 at% (★). All samples show additional fields in the magnetic region. Here we have only plotted the most prevalent.*

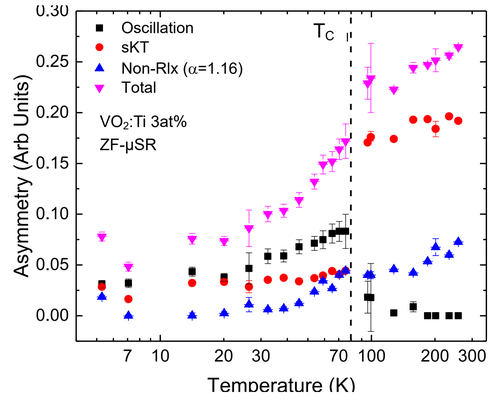


Fig 7: *Temperature dependence of component asymmetry for VO_2:Ti 3 at%. Asymmetry is proportional to the fraction of the material in that state. As T approaches T_C, the oscillating component (magnetic phase, ■) is replaced by a non-relaxing component (▲) likely from the increasingly fast fluctuations associated with the break-up of the low T long range order. At T_C, the oscillation is completely replaced by the static Kubo-Toyabe (sKT,●) indicating only nuclear fields are present.*

Fits to predominant frequency in ZF time domain spectra directly measure magnetic field at μ^+ site, yield

- 5 at%: B_{loc} = 111.8 ± 0.5 mT as T → 0 ; T_C= 175 ± 2 K
- 3 at%: B_{loc} = 224.7 ± 0.5 mT as T → 0 ; T_C= 80.0 ± 1 K
- 1 at%: T_C= ~37 ± 2K [not shown above]. B_{loc} is clearly present and develops with decreasing T, however, below 20K significant changes in the time domain signal indicate multiple fields present with very broad distribution.

References:

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Conclusion:

Here we present an initial characterization of a substantial magnetic phase in three Ti-doped samples of VO_2 by way of Zero Field Muon Spin Rotation and Relaxation measurements. Our results are commensurate with our related work on a W-doped VO_2 compound, where we see similar shifts in the onset of the magnetic phase suggesting that the spatial distortion in the structure due to the presence of the impurities stabilizes the magnetic phase to higher temperatures. The magnetism itself is introduced by a disruption of the V-V dimerization and is observed to occur in stoichiometric VO_2 around 35K.

Project Status, Future Work:

- A refined model is needed to characterize other fields present (not presented here) in the spectra. These additional fields suggest AFM order or other magnetic phases.
- Analyze Mu (H-like) behavior in the non-magnetic regime to provide insight into how H behaves and what role H impurities play in modifying the properties of VO_2 .
- Combine these results with data from stoichiometric VO_2 and VO_2:W (1 and 2.4 weight %) to establish trends with impurity content to begin to develop a robust model for the transitions (magnetic, structural, optical, electric ...) in these compounds.