Magnetism and Muon Dynamics in Vanadium Oxide Compounds

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Project Focus

•Characterize μ^+ behavior in Vanadium Dioxide (VO_2) compounds where μ^+ serves as local magnetic probe and experimentally accessible Hydrogen analog for insight into:

-H behavior (e.g. stability, dynamics, energy barriers *etc*)

-Mechanism responsible for transitions

-Role dopants play in modifying local system, transitions, properties (T_c, MST, ρ *etc*)

-Magnetic moments introduced by disruption of V-V dimerization

Material Properties, VO_2 [1-3]

•Reversible, Metal-Semiconducting transition (T_{MST} = 340 K)

•MST triggered via Temperature, **E**-Field, optically or pressure

•T > T_{MST}: Metallic,
Rutile, reflective (Near IR), σ~10^3–10^4 $(\Omega cm)^{-1}$

•T < T_{MST}: Semiconducting,
Monoclinic, translucent, σ~10^{-1}–10^{-3} $(\Omega cm)^{-1}$

•Dopants modify transition temperature and properties

-H (~0 to 3.8 % H) [2]

-Nominal resistivity change; remains metallic down to ~200 K (at 3.8% H)

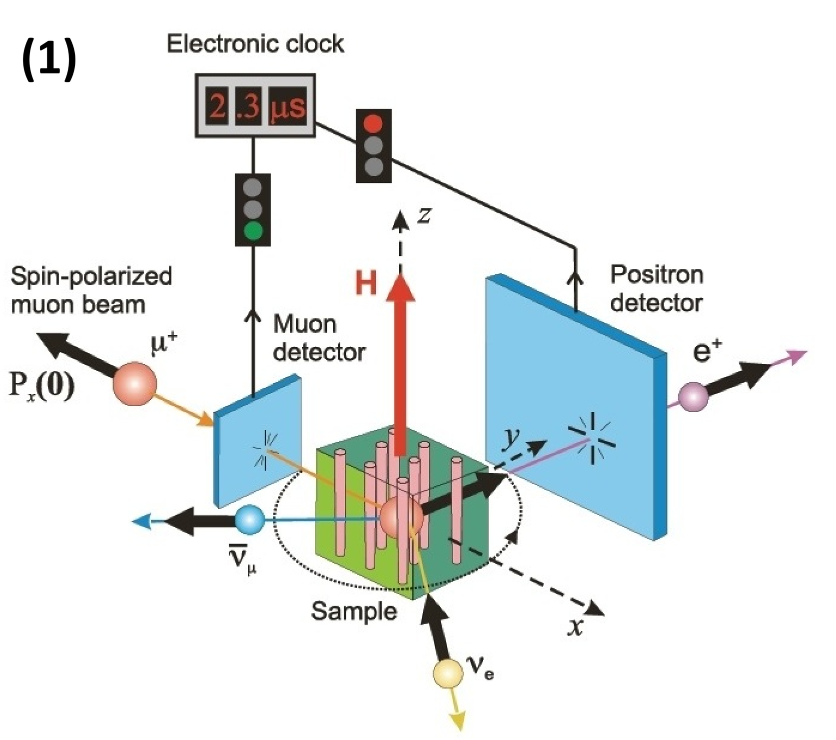
-W, Ti, Au,…(i.e.): Reduce T_{MST} with minimal effects on other properties [3]

-Cr, Al,… (i.e.): Raise T_{MST} with minimal effects on other properties [3]

Muon Spin Rotation and Relaxation (MuSR) [4]

•MuSR utilizes the unique sensitivity of 100% spin polarized and positively charged muons (μ^+) to probe the local magnetic and electronic environment

(1)



• μ^+ implanted

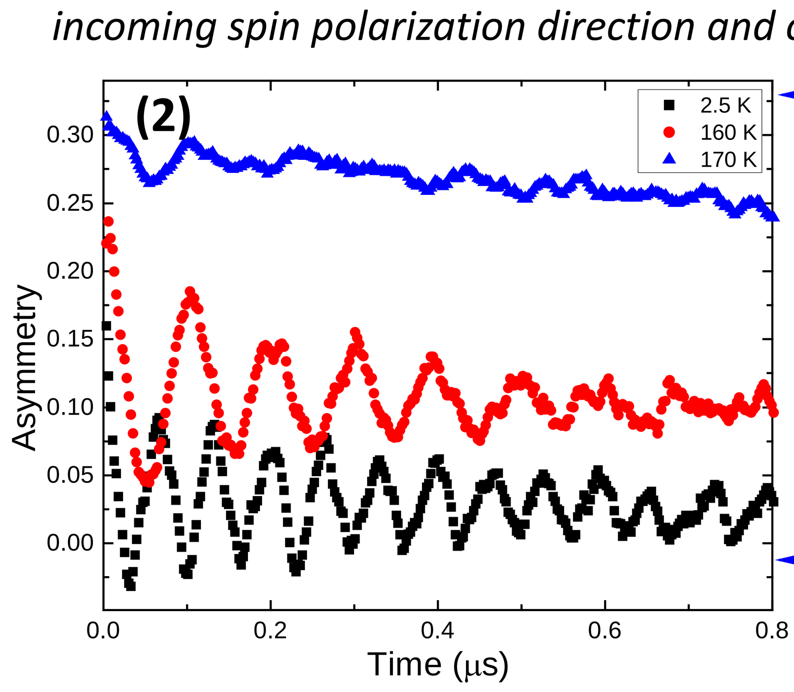
• S_μ precesses about B_{eff} (γ_μ=135.54 MHz/T)

• μ^+ decay with e^+ emitted preferentially along S_μ

• Time evolution of S_μ tracked via asymmetry, $A(t)$, of e^+ emission **(3)**

$$A(t) = \frac{N_1 - \alpha N_3}{N_1 + \alpha N_3}$$

*Fig 1 [above]: Schematic for typical MuSR measurements with **B** applied ⊥ to incoming spin polarization direction and only showing 1 of 4 detectors.*



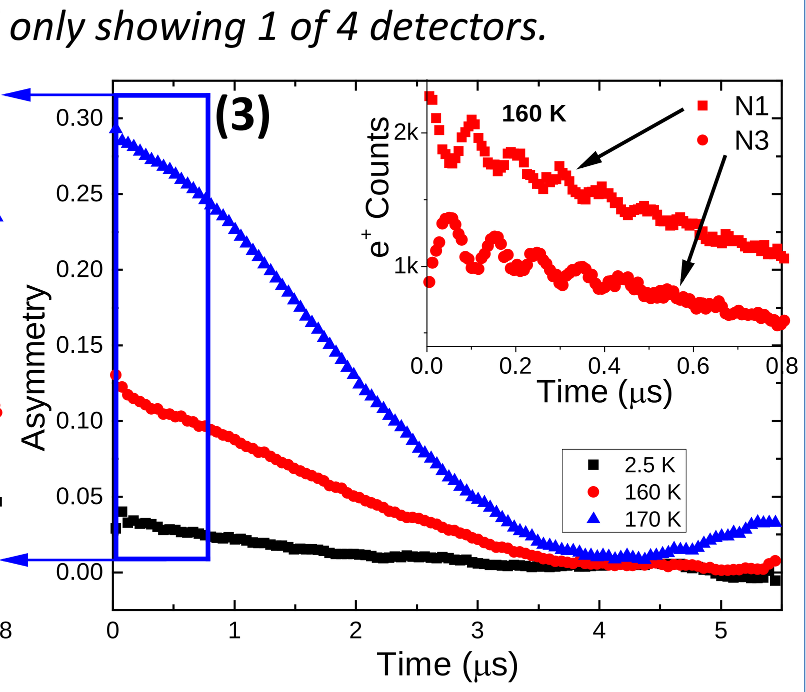


*Fig 2 [left]: First 0.8 μs of asymmetry of ZF muon spin polarization in VO_2:W 2.4% plotted at 2.5 K, 160 K and 170 K. There are at least 2 frequencies present with rather large relaxation rates that are nearly undetectable above 170 K. The large relaxation rate reflects rapid dynamics or a broad distribution of field values at the muon stopping site. A component's amplitude is proportional to the muon fraction in a particular state. **Fig 3** [right]: First 5.5 μs of asymmetry at 2.5 K, 160 K and 170 K showing a typical, for ZF, Kubo-Toyabe [5] relaxation at higher temperature, characteristic of relaxation due to nuclear dipolar interactions. **[Inset]**: Raw counts from opposing positron counters for the T=160K data; used to calculate the time dependent asymmetry, A(t).*

The Experiment

•TF (B_{ext} ⊥ S_μ) and ZF (B_{ext}=0) MuSR measurements

- EMU spectrometer, surface muon channel, ISIS (Didcot, UK)
- HiTime & Helios spectrometers, M15 & M20C surface muon channels, TRIUMF (Vancouver, Canada)

•Bulk sintered 7x7x1 mm^3 samples
VO_2, VO_2:W (1 & 2.4 at%) and VO_2:Ti (1, 3 & 5 at%)

•Temperature range: ~2 K to 700 K

•Magnetic field range: Zero applied to 6.5 T

Analysis

$$P(t) = \sum_i A_i e^{-\lambda_i t}\cos\left(\gamma_\mu B_{eff,i} t + \phi_i\right) + \sum_j A_j P_{D,j}^{KT}\left(t, \Delta_j, \nu_j\right)$$

$$P_D^{KT}(t) = P_S^{KT}(t)e^{-\nu t} + \nu \int_0^t P_S^{KT}(\tau) e^{-\nu\tau} P_D^{KT}(t-\tau)\,d\tau$$

$$P_S^{KT}(t) = \frac{1}{3} + \frac{2}{3}\left(1 - \Delta^2 t^2\right)e^{-\frac{1}{2}\Delta^2 t^2}$$

Spin polarization function, ***P(t)***, fit with the following parameters:

•A_i, A_j = Amplitude for oscillating & KT components, respectively

•{λ_i , ϕ_i} = Relaxation rate and phase of oscillating component

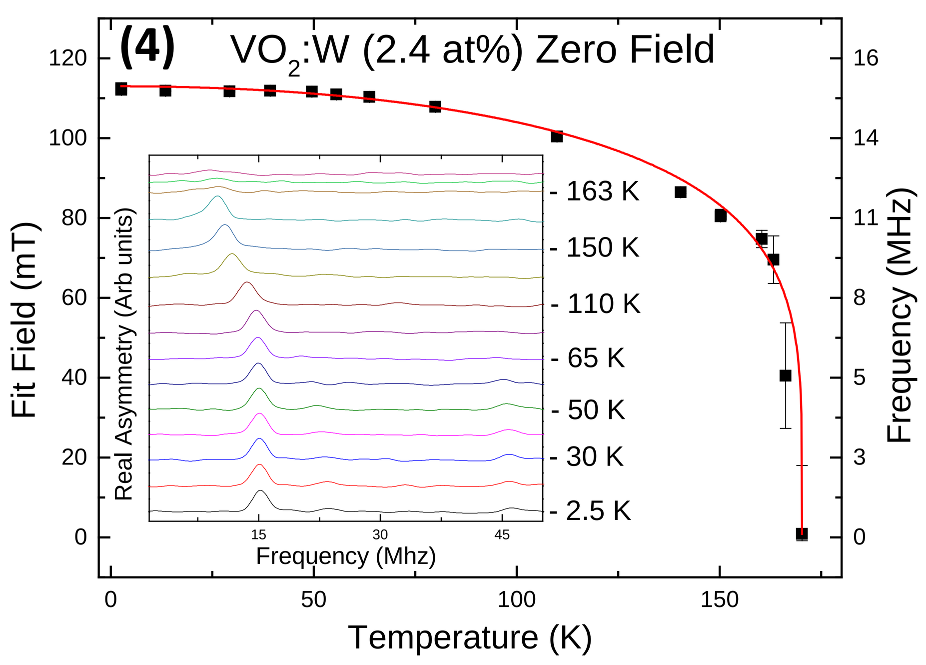
•B_{eff} = B_{ext} + B_{loc} = effective field at the muon site; determined directly by fitting to the component's oscillation frequency, ***f***, where $f = \gamma_\mu B_{eff}$

•Δ = second moment of measured field distribution

•υ = field fluctuation rate [i.e. muon motion (hop rate) or field dynamics]

Evolution of the muon spin polarization from interactions with pure nuclear dipolar fields is modeled by the Kubo-Toyabe[5] function (P_S^{KT},P_D^{KT}). These KT functions assume a Gaussian distribution of fields that may vary with time, as detected by the muon.

Results & Discussion



•$B_{loc}(T\rightarrow 0)$ = 113 ± 1 mT; T_c = 170.3 ± 0.1 K

• At least 2 distinct frequencies present below 170 K (Fig 2 & 4)

•ZF verified via concurrent non-magnetic reference material data

•Similar features in VO_2:Ti 5 at% (B_{loc} = 111.8±0.2 mT;T_c~175 K)

***Fig 4**: Fit to the prominent frequency (field) for ZF data on VO_2:W 2.4 at%. The developing field follows a critical power law. **[Inset]**: FFT of several time domain data (Fig 2) clearly showing at least one precessing component that develops with decreasing temperature. The line width and peak amplitude are related to the variation (in time or space) of field at the muon stopping site.*

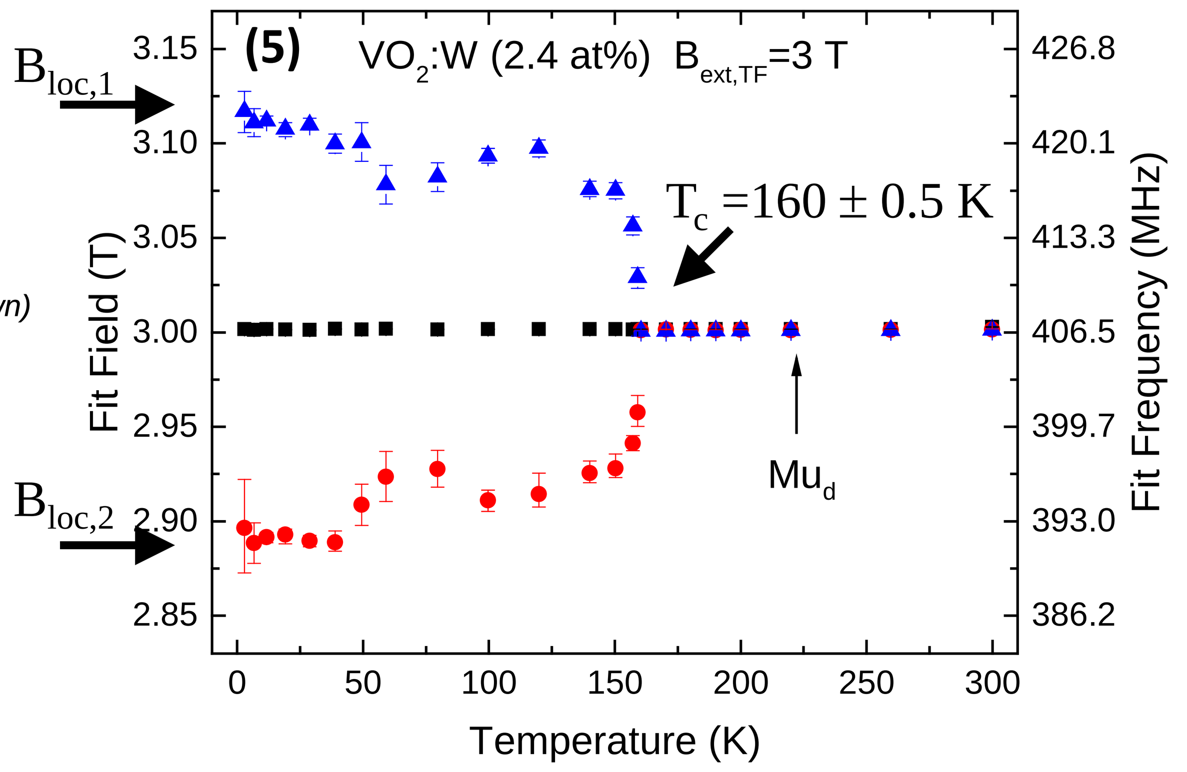
• B_{loc}=B_{eff} – B_{ext} | B_{ext}= 3T ; B_{eff} directly measured by muon

• $B_{loc,1}(T\rightarrow 0)$ = 111 ± 2 mT ; $B_{loc,2}(T\rightarrow 0)$ = –111 ± 3 mT

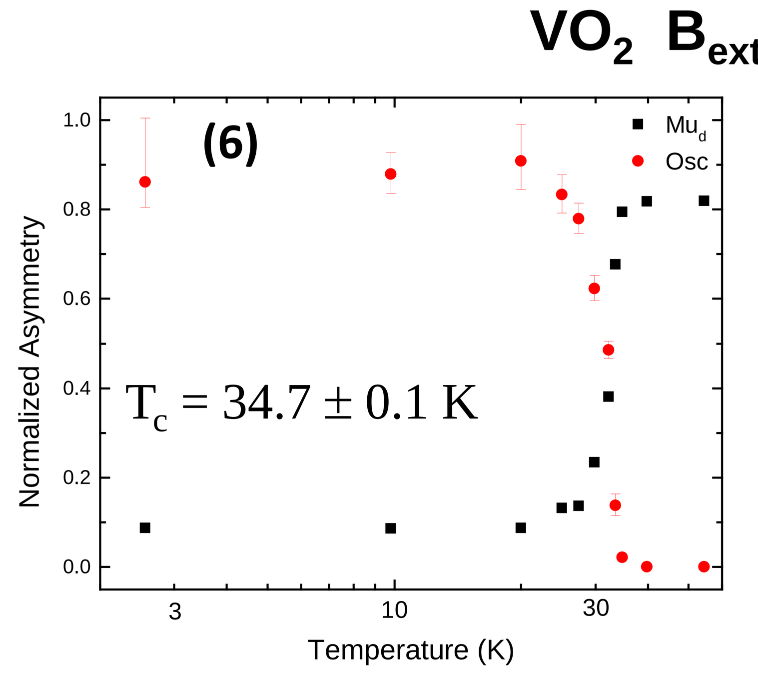
• Symmetric field development below T_c ⇒ AFM

• Long-range order confirmed via neutron diffraction *(not shown)*

***Fig 5**: Fits to the three most prominent frequencies (field) in time domain spectra utilizing a RRF of 406.4 MHz from TF (3 T ⊥ S_μ) data on VO2:W (2.4 at%). The field detected by the muon is a combination of the externally applied field (B_{ext}) and contributions from within the material itself. Here, it is clear that one field ($B_{loc,1}$) 1 is aligned with the B_{ext} and the second ($B_{loc,2}$) is anti-aligned with B_{ext}; a distinction that is impossible to determine from ZF measurements (Fig 4).*



VO_2 $B_{ext,TF}$= 100 mT



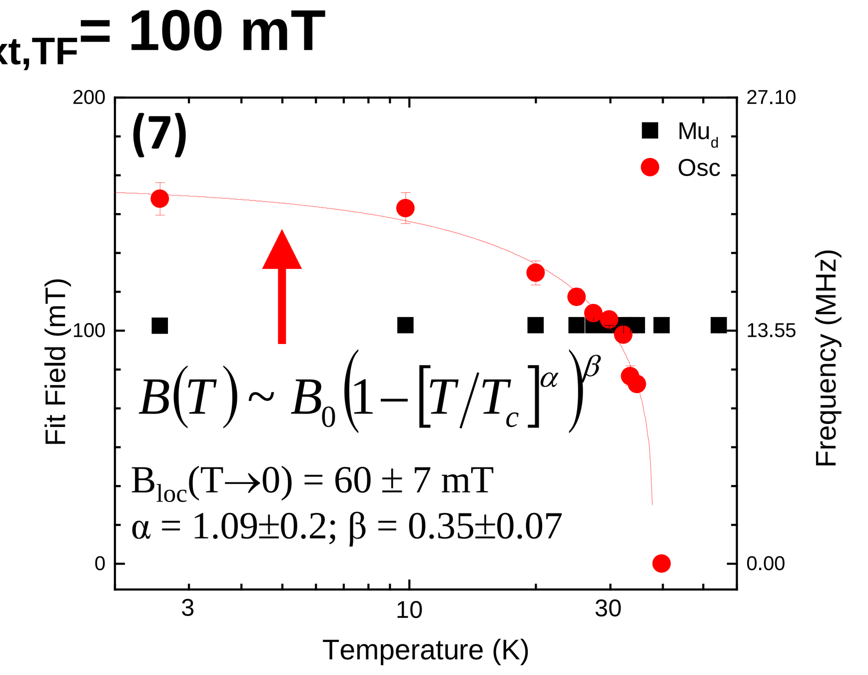
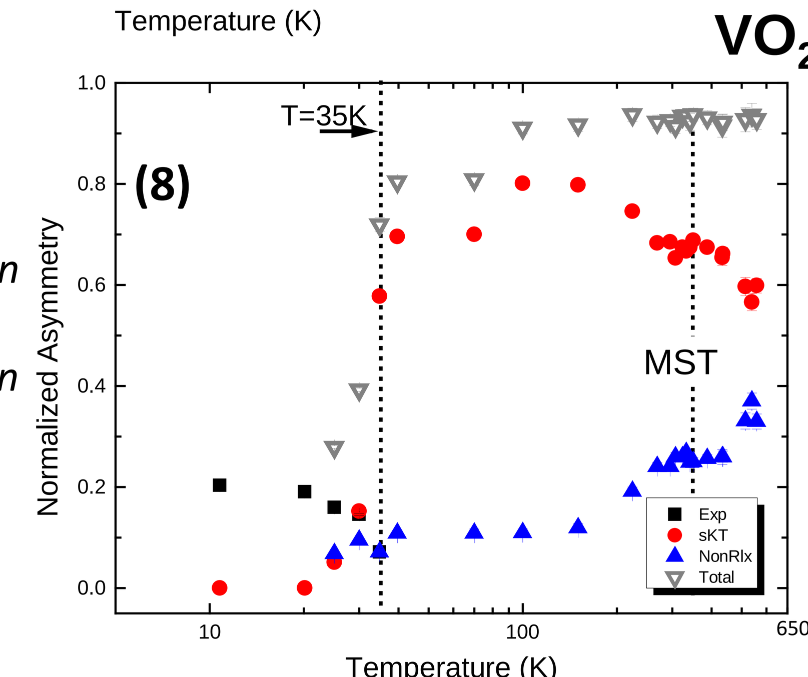


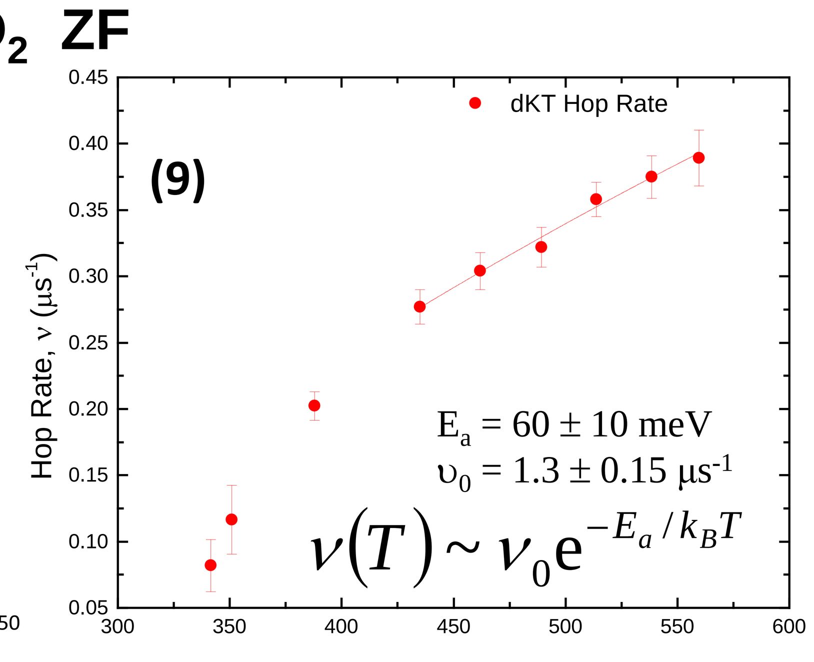
***Fig 6** and **7**: Fits to TF (100 mT ⊥ S_μ) data on stoichiometric VO_2 reveal magnetic order below T_c as shown by the sharp increase in the fit amplitude and field (frequency) of the oscillating component (●). The trade-off in asymmetry between the oscillating and diamagnetic component (■) reflect respective fraction of the material in each phase.*

VO_2 ZF

***Fig 8**: Fits to ZF data on stoichiometric VO_2 reveal differences in local field distribution, Δ_{KT}, in each phase and significant dynamics above 400 K. Dynamic Kubo-Toyabe [5] hop rates **(9)**, fit with an Arrhenius function, produce an activation energy, E_a, and low prefactor, υ_0, characteristic of motion triggered by a wag mode or phonon assisted tunneling. The reduced asymmetry **(8)** between 35 K and 100 K is associated with short range magnetic correlations (fit frequency not shown). Below the MST, the muon (probe) is static.*

$\Delta(T<T_{MST})$ = 0.171 ± 0.004 μs^{-1} ; $\Delta(T>T_{MST})$ = 0.165 ± 0.005 μs^{-1}





Summary

We report findings from MuSR measurements conducted on VO_2 compounds where we find low temperature antiferromagnetism with a substantial local field. We see Mu_d dynamics begin above 400 K. We find that the introduction of W or Ti stabilize the magnetic phase to a much higher temperature and develop a larger field as compared to what we measure in stoichiometric VO_2. The muon is sensitive to the MST and structural transition [6].

Project Status, Future Work

This is part of an active project where we have data from several more samples and experimental configurations, including neutron diffractometry. Additional MuSR experiments have been approved to further characterize the magnetic fluctuations within this system. We also plan on collecting bulk magnetization data. We are trying to find a source for single crystal samples to better characterize and understand many of these observed features.

References

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