

Magnetic order and muon motion in VO₂

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Abstract. We report the first transverse, longitudinal and zero field measurements performed on Vanadium Dioxide (VO₂) where we find a significant local magnetic field below $T = 34.7 \pm 0.16$ K at the muon site and Mud motion above 340 K. Distinct shifts in the muon relaxation rates and Kubo-Toyabe delta parameters, near the metal to semiconductor and structural transition ($T_{MST} \approx 340$ K), show that μ^+ SR measurements may provide additional means to further characterize the mechanisms contributing to these transitions that are yet to be understood.

1. Introduction

Vanadium dioxide (VO₂) has an ultra-fast, reversible metal-semiconductor phase transition (MST) at $T_{MST} \approx 340$ K that coincides with a structural phase transition (rutile $T > T_{MST}$; monoclinic $T < T_{MST}$) below which the bandgap changes from nominally 0 eV to about 1 eV and the conductivity decreases by several orders of magnitude [1, 2, 3]. This transition can be triggered thermally, optically, electrically or with application of pressure. Incorporating just a few percent of H reduces T_{MST} to near 200 K while tremendously reducing the change in properties, such as conductivity and bandgap [4]. Dopants such as titanium, tungsten, niobium or gold only reduce T_{MST} to between 280 K and 320 K whilst having minimal effect on the electronic or optical properties of the host material [5]. T_{MST} increases upwards of 400 K when elements such as fluorine, aluminum or chromium are introduced to the system. Many studies have looked specifically at the effects that some dopants and impurities have on material characteristics when crossing the MST [5] as there are a plethora of potential technological applications, but there is still no consensus as to whether the fundamental mechanism responsible for the transition is related to electron-phonon interactions or strong electron-electron interactions (i.e. Peierls mechanism or Mott-Hubbard transition) [6]. Furthermore, the role impurities play has yet to be determined. An understanding of the mechanism governing the transitions is required for device application as control and optimization of the material properties is critical.

In the metallic phase ($T > T_{MST}$), VO₂ is described as rutile with a tetragonal body-centered unit cell where each V is surrounded by an octahedral arrangement of oxygen atoms. Below T_{MST} , in the semiconducting phase, the system has a doubled unit cell in which V atoms pair along the c -axis where one V atom (of each pair) shifts in the a - b plane as well as closer to its partner (parallel to the c -axis). The net result is a zig-zag chain of vanadium atoms. Whilst in the rutile structure, each V⁴⁺ cation has an electron near the Fermi level occupying the lowest $3d$ level. Asymmetry in the crystal field causes the $3d$ states to be split so that the lowest orbital is predominantly aligned along the c -axis ($3d_{||}$). In the semiconducting phase, dimerization of



the V^{4+} ions result in pairs of these $3d$ electrons being forced into a singlet state ($S_{pair} = 0$) and hence contributes to the high resistivity and non-zero bandgap. Impurities (dopants, structural defects, vacancies etc) in the VO_2 system do affect resulting properties of the transitions such as the temperature at which it occurs, change in conductivity, transition rate, variation in optical absorption, transmission and reflectivity. If impurities modify VO_2 properties by disrupting the dimerization process, an outcome of this partial dimerization may be the development of a non-zero net spin.

Here we present some of our initial findings from the first investigation of VO_2 compounds via the muon spin research technique where the muon (μ^+) is used both as an experimentally accessible analog to the hydrogen impurity as well as a sensitive local magnetic probe to reveal properties not previously reported. For oxides in general, an implanted μ^+ typically bonds with oxygen, forming the $[OMu]^-$ complex (c.f. $[OH]^-$), which we specifically refer to as Mu_d throughout this paper since the bound complex is diamagnetic.

2. Experimental Details

A bulk sintered $7 \times 7 \times 1$ mm³ sample of VO_2 , acquired from a commercial source, was used in these experiments. XRD measurements were completed at the materials characterization lab at the STFC ISIS facility (Didcot, UK) and show no obvious chemical phases beyond what is expected for VO_2 . Transverse field muon spin rotation (TF- μ^+ SR) measurements were conducted using the HiTime spectrometer on the M15 surface muon channel at TRIUMF (Vancouver, Canada) in temperatures from 2.5 K to 300 K and magnetic fields up to 6.5 T applied perpendicular to the initial muon spin polarization direction. Low TF measurements ($B_{TF} = 100$ G) were completed on the EMU instrument at the STFC ISIS facility (Didcot, UK). Both of these measurements are aimed at characterizing the μ^+ stopping site, investigating the possibility of Mu^0 (μ^+e^-) formation and explore the possibility of local magnetism through the MST and well into each phase. Zero field muon spin relaxation measurements (ZF- μ^+ SR) were primarily conducted on EMU (ISIS) in a temperature range of 8 K to 560 K. The main goal of these measurements were to characterize motional dynamics of Mu_d and any variations in the local field throughout each phase. Supplemental ZF measurements were completed with the HiTime and Helios spectrometers on the M15 and M20C surface muon channels (respectively) at TRIUMF, below 300 K, where the higher frequency resolution capabilities (c.f. properties of the continuous wave source and instrument design) allow for additional characterization of the local magnetic environment. Longitudinal field muon spin relaxation measurements (LF- μ^+ SR) were conducted with EMU (ISIS) and Helios (M20C, TRIUMF) with magnetic fields up to 4.5 T applied parallel to the initial muon spin polarization direction and the goal of characterizing any dynamics associated with the observed magnetic features.

3. Results and Discussion

μ^+ SR data reveal three distinct regimes of Mu_d behavior in VO_2 . For ZF data analysis, the baseline is determined at each temperature by applying a low transverse field ($B_{TF} = 100$ G) and adjusting the alpha parameter so that the precession signal is centered about zero asymmetry. This corrects for detector efficiency and any anisotropy in the experimental geometry. The ZF data between 100 K and 300 K fit well to a static Kubo-Toyabe function [7] (sKT) with $\Delta = 0.171 \pm 0.004 \mu s^{-1}$ and a non-relaxing component (Figure 1a).

Above 300 K there is some slight variation in Δ between 320 K and 350 K where there is a small but definite decrease which leads to $\Delta = 0.165 \pm 0.005 \mu s^{-1}$ above 350 K. Above 450 K the signal character in the time domain changes dramatically (Figure 1b), as a drop in Δ when initially characterized with a static Kubo-Toyabe function. The signal above 340 K is appropriately fit using a dynamic Kubo-Toyabe function [7] (dKT) where the Δ is fixed at the stable value determined between 350 K and 450 K and the hop rate (ν) is then allowed to

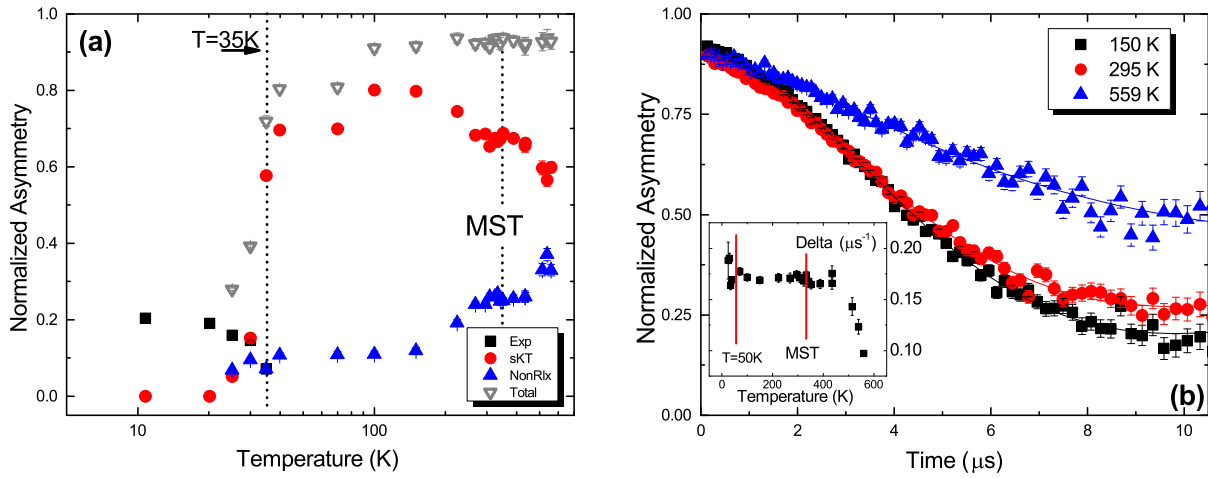


Figure 1. (a): ZF Asymmetry from 8 K to 600 K where the sharp decrease in asymmetry near 35 K is due to the abrupt ($\delta T < 5$ K) development of a magnetic phase. The slight decrease in static Kubo-Toyabe (sKT) asymmetry near 100 K is attributed to the development of highly localized magnetic environment or magnetic fluctuations as a precursor to the significant local field development below 35 K. Features around 340 K relate to the MST. **(b):** ZF time-domain signal data from EMU at ISIS. *Inset:* Temperature dependence of sKT Δ . The sharp drop above 450 K suggests the onset of motion.

vary. These dynamics can be traced down to, at least, 340 K (T_{MST}) and possibly to 300 K. Considerable uncertainty in ν arises below 340 K since the change in local field distribution at the Mu_d site is a result of the structural transition which contributes to a real variation in Δ . Additionally, the high correlation between Δ and ν , in the function itself, mandates that one determine Δ in a region where dynamics are sufficiently slow so that a static function is appropriate before applying a dynamic function to extract ν . Therefore, any variation in Δ between 300 K and 340 K directly contributes to the uncertainty of ν , in this region. Assuming the structural transition provides a real change in Δ and that the stability of Δ between 350 K and 450 K accurately reflects the second moment of the field distribution at the Mu_d site in the rutile state ($T > T_{MST}$), we can assign Δ ($0.165 \pm 0.005 \mu s^{-1}$) to the Mu_d site in this phase. With Δ fixed, analysis reveal dynamics begin slightly above 340 K and continue to above 560 K (Figure 2) which we assign to the onset of Mu_d motion. A simple Arrhenius fit [$\nu(T) \sim \nu_0 \exp(-E_a/KT)$] to the hop rates above 400 K (where fits are more reliable) result in an activation energy of $E_A \approx 60 \pm 10$ meV and prefactor of $\nu_0 = 1.3 \pm 0.15 \mu s^{-1}$. The hop rate leveling off at higher temperatures and hence the extremely low prefactor is consistent with local motion triggered by a wag mode or a phonon assisted tunneling process. Below 100 K there is a slight drop in the ZF sKT component's asymmetry accompanied by a comparable rise in the asymmetry of the non-relaxing component. Near 35 K the overall character of the time domain signal changes significantly as the sKT quickly vanishes as an exponentially relaxing signal (as observed at ISIS) then dominates the spectra implying either a fast depolarization or frequencies beyond the detection limit.

Weak ($B_{TF} = 100$ G) transverse field measurements from 8 K to 560 K, conducted at ISIS, were fit to a single relaxing oscillation and a non-oscillating component ($P(t) = A_1 \exp(-\lambda_1 t) \cos(\omega_L t + \phi) + A_2$) and reveal significant features at 35 K, 100 K and 340 K. Crossing over 340 K (MST) from below, we observe a decrease in A_2 and a sharp minimum in λ_1 followed by a peak in λ_1 near 450 K (Figure 3). When traversing 100 K from above, we observe an increase in A_2 and correlated decrease in A_1 . At the lowest temperature, A_2 is nearly

1/3 of the total maximum asymmetry (measured at $T = 560$ K).

Higher TF measurements ($B_{TF} = \{0.03, 0.1, 3.0\}T$) between 2.6 K and 300 K, at TRIUMF, show qualitatively comparable behavior to what is observed at ISIS in low field (Figure 3). Accounting for the difference in measurement limits of the instruments at ISIS and TRIUMF, one can understand why below 100 K at TRIUMF we resolve two different regimes of Mu_d behavior that were only hinted at in the data from ISIS. Specifically, a high frequency oscillation with a small amplitude develops between 35 K and 100 K (4), and below 35 K a significant local field develops (5). Above 120 K, these high TF data show a single, well defined oscillation with a frequency that matched the signal found in the non-magnetic CaCO_3 reference material mounted behind the VO_2 sample suggesting that between 120 K and 300 K, the effective field at the muon site (B_{eff}) is simply equal the externally applied field (B_{ext}). Peaks in the relaxation rate of this diamagnetic component are centered around 100 K and 35 K, with a minimum near 70 K (not shown) and corresponds with the onset of the change in signal character. Below 35 K a minimum of two oscillating components are required, as a second frequency with growing asymmetry and

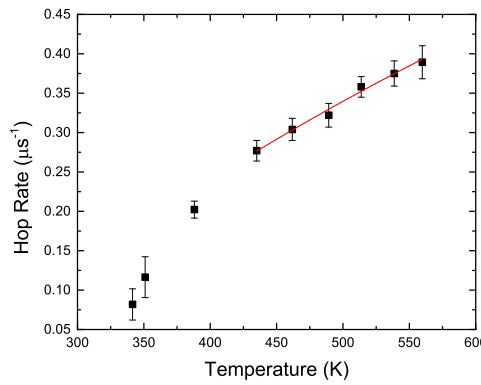


Figure 2. Hop rates extracted from fits to time domain data with a dynamic Kubo-Toyabe function (dKT). An Arrhenius fit to the higher temperature hop rates yields $E_A = 60 \pm 10 \text{ meV}$ and $\nu_0 = 1.3 \pm 0.15 \mu\text{s}^{-1}$. The very low hop rates, ν_0 and E_A are characteristic of local motion.

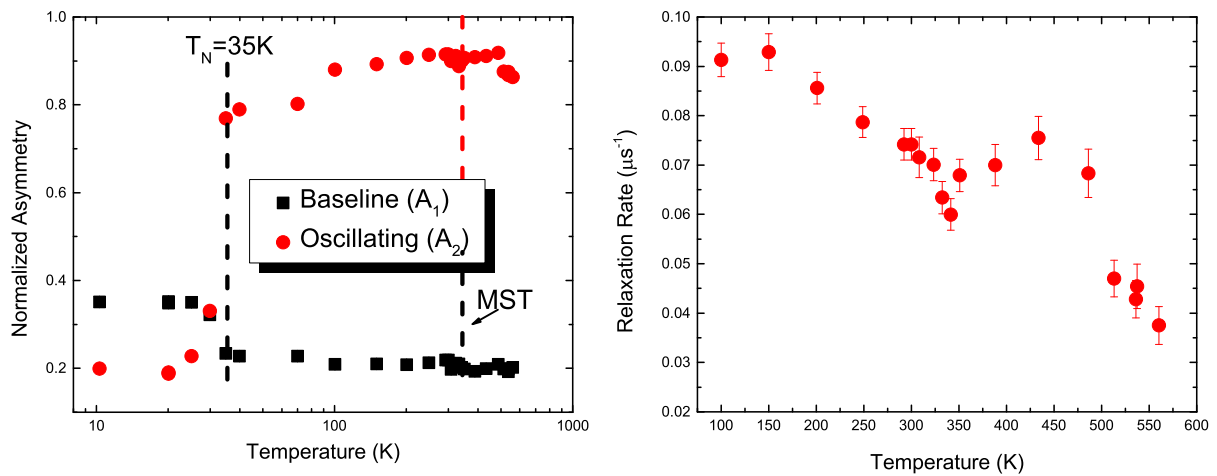


Figure 3. $B_{TF} = 100 \text{ G}$ fit asymmetry for oscillating (A_1) and baseline (A_2) components (left) and the relaxation rate (λ_1) associated with the oscillating component (right).

relaxation rate develops rapidly below 35 K (Figure 5). A third higher frequency component to account for the frequency present between 35 K and 100 K (Figure 4) should be included but has not yet been folded into this preliminary analysis of the spectra, below 35 K. The growth in asymmetry of this shifted signal is complemented by the reduction in diamagnetic asymmetry. The fit frequency and relaxation rate of the shifted signal (below 35 K) follow a critical power law ($f(T) \sim f_0(1 - [T/T_c]^\alpha)^\beta$) with $\alpha = 1.09 \pm 0.2$, $\beta = 0.35 \pm 0.07$ and $f_0 \approx 22 \pm 1$ MHz (Figure 4). Since $B_{ext} = 102.05 \pm 0.04$ mT (determined via fits to diamagnetic component) and $f_0 \rightarrow B_{0,eff} = 162 \pm 7$ mT, there is clearly a non-zero local field ($B_{loc} = 60 \pm 7$ mT) contribution. The source of B_{loc} has not yet been determined. Similar results are found at the other measured fields. Note that this low temperature behavior is not consistent with Mu^0 formation but instead developing magnetic order and alignment with the externally applied field.

These measurements on VO₂ are the first part of a large scale project geared towards understanding the Mu_d behavior, local electronic and magnetic field structure and an attempt to probe the fundamental mechanisms responsible for the various transitions occurring in VO₂ compounds. Part of this project includes investigating VO₂ compounds doped with a variety of elements that alter the MST by either raising or lowering T_{MST} as well as stabilizing the low temperature magnetic phase by significantly disrupting the dimerization. Additional measurements and some modeling are required to better determine the source of the magnetism and driving mechanisms for each transition.

As of now, we suggest that a disruption in the V–V dimers introduce a non-zero net spin and hence lead to the observed magnetic features. Additional μ^+ SR measurements coupled with other techniques, such as neutron scattering and bulk magnetization measurements, are required to determine properties such as moment direction, size and further characterize the low temperature magnetic phase. We are furthering this effort by continuing to investigate VO₂ compounds with different impurities and varying concentrations with the goal of also mapping

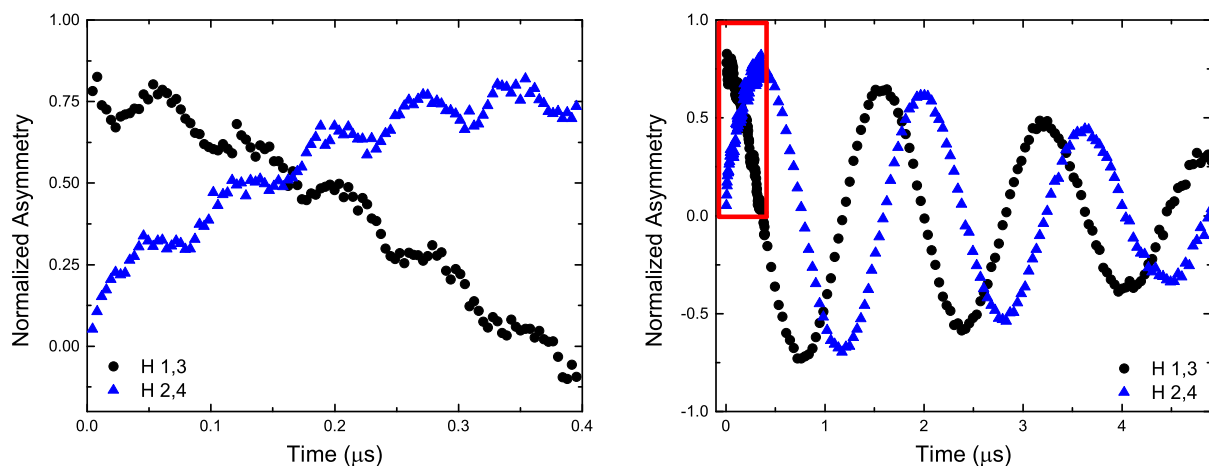


Figure 4. TF- μ^+ SR spectra with $B_{TF} = 100$ mT where both pair of opposing counters (labeled H 1,3 and H 2,4) are shown in the time domain with a rotating reference frame frequency set at $f_{RRF} = 13.25$ MHz. These plots show a region where the non-magnetic phase and a small fraction of the magnetism is observed. *Left:* Highlighting the small amplitude oscillation that fits to a field that roughly matches the 162 mT field observed at 5 K. At 5 K, this component dominates the spectra. *Right:* Precession at a frequency that matches the μ^+ signal in non-magnetic reference material and what one expects for the 100 mT externally applied field. The red rectangle highlights the region enlarged in the left frame.

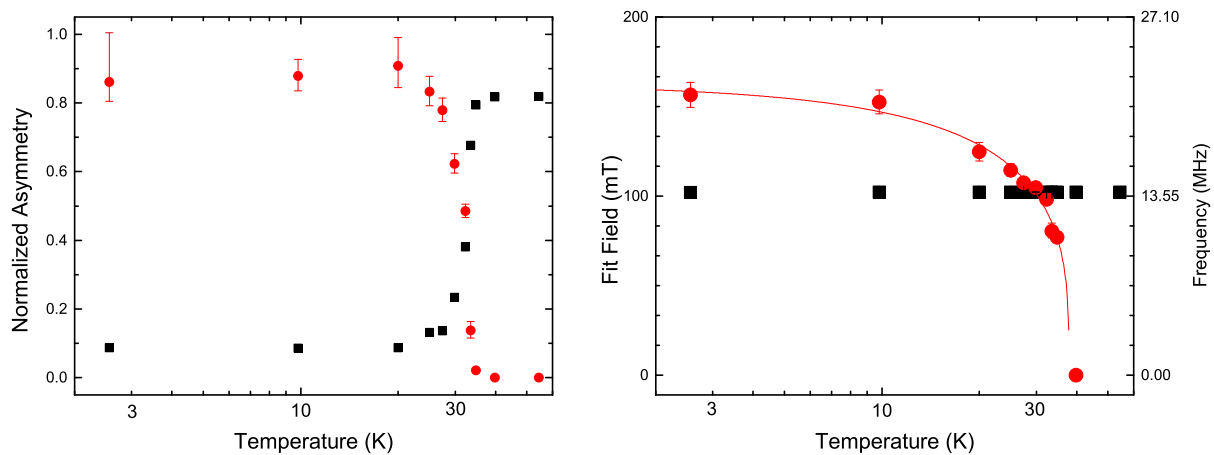


Figure 5. Normalized asymmetry (*left*) associated fit frequencies [fields] (*right*) from two component analysis on TF- μ^+ SR data in an applied field of 100 mT utilizing a rotating reference frame. The developing internal field ($T_c = 34.7 \pm 0.12$ K) follows a critical power law (fit shown, discussed in text) and at its maximum, $B_{loc} = 60 \pm 7$ mT.

out the role that the impurities play in modifying the local environment.

4. Summary

From this first analysis, we report the detection of a significant local magnetic field that develops in stoichiometric VO₂ below $T_c \approx 35$ K with a maximum value of $B_{loc} = 60 \pm 7$ mT and that the muon detects features that are consistent with short range magnetic correlations that begin below 100 K and persist down to T_c . Between 100 K and 300 K, we find no significant dynamics in either Mu_d motion or variations in local fields. We find that the muon is, in fact, sensitive to the MST and structural transition around 340 K. In the metallic phase ($T > T_{MST}$), we find that $\Delta = 0.165 \pm 0.005 \mu s^{-1}$ is slightly different from the $\Delta = 0.171 \pm 0.004 \mu s^{-1}$ measured in the semiconducting phase ($T < T_{MST}$). We find that Mu_d dynamics, either local motion triggered by a wag mode or phonon assisted tunneling, are significant above 450 K ($E_A \approx 60 \pm 10$ meV, $\nu_0 = 1.3 \pm 0.15 \mu s^{-1}$) but can be traced down to 340 K.

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