

Local Magnetism in the Spin-singlet State of VO₂

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(Received July 30, 2022)

Local magnetic field studies of vanadium dioxide (VO₂), which has a spin-singlet phase under the metal-insulator transition at 340 K, were performed using μ SR method. By comparing the results of two samples with different qualities, it was discovered that a nonmagnetic state and microscopic magnetic ordered states coexist in the spin-singlet phase. This may be attributed to crystal lattice imperfections inherent in VO₂.

KEYWORDS: spin singlet, metal-insulator transition, μ SR

1. Introduction

Vanadium dioxide (VO₂) has several crystal polymorphs and exhibits a wide range of physical properties. The metal-insulator transition (MIT) between tetragonal rutile VO₂(R) and monoclinic VO₂(M1) has drawn the interest of numerous researchers since its discovery [1]. It has been actively investigated for applications in electronic devices such as memory, sensors, optical switches, and thermochromic dimming materials [2,3] because of the MIT occurring at around room temperature (340 K). Also in basic research, the transition mechanism has been the subject of much controversy (i.e. Mott-Hubbard [4], spin-Peierls [5], or molecular orbital crystals [6]).

Recently, Mengyan and coworkers reported the magnetism of VO₂ via the muon spin research method [7]. Muon spin rotation/relaxation/resonance (μ SR) method uses elementary muons as magnetic probes to detect small local magnetic fields in materials, such as nuclear magnetism, with high sensitivity. According to their research, some magnetic order is found even in the nonmagnetic singlet phase of VO₂ below the MIT temperature. The origin of this order has been attributed to residual impurities and lattice defects. However there are no other reports of such magnetic order, and it is vital to re-examine this issue, including sample quality.

To this end, we prepared two types of VO₂ samples of different quality (high purity powder and deteriorated powder samples) and performed a comparative μ SR study of local magnetic states in the presumed nonmagnetic singlet phase. Our goals are to verify whether the aforementioned magnetic order is intrinsic and to gain insight into the MIT mechanism of VO₂.

2. Experiments

In this study, a commercially available powder of VO₂ (99.9% purity, Kojundo Chemical Lab. Co., Ltd.) was used as a “pristine” sample (in the as-received condition without sintering or other heat treatment), and compared with another sample which was seemingly deteriorated as had been kept in air for more than 10 years. The sample qualities were checked using the powder X-ray diffractometer (SmartLab, Rigaku Co.) under ambient conditions. The magnetic susceptibility was measured using the SQUID magnetometer (MPMS, Quantum Design, Inc.) from 5 to 400 K. μ SR experiments were performed using the ARTEMIS spectrometer installed in the S1 area at Muon Science Establishment (MUSE), Japan Proton Accelerator Research Complex (J-PARC).

3. Results and Discussion

Figure 1 shows the powder X-ray diffraction patterns of pristine and deteriorated samples. The insets are photographs of each sample; the colors and textures are very different. While all diffraction peaks in the pristine sample can be indexed to monoclinic VO₂ (M1) [8], there are several peaks that appear to be impurities in the deteriorated sample. Although the peaks of these impurities are too broad to be accurately identified, they are assumed to be VO₂ (B) [9], a polymorph of VO₂ (M1), and a hydrated VO₂·xH₂O (JCPDS data card 00-018-1445) [10], based on their approximate peak positions.

Figure 2 shows the temperature dependence of the magnetic susceptibility χ in these samples. A magnetic transition with hysteresis (MIT) was observed around 340 K in both samples. Below the MIT temperature, the pristine sample shows almost constant small values of χ , while the deteriorated sample shows large Curie paramagnetic behavior, which may be due to the impurities. As a reference, when pristine samples were annealed at 1373 K in Ar atmosphere, the magnitude of Curie component increased about twice as much as before treatment (data not shown).

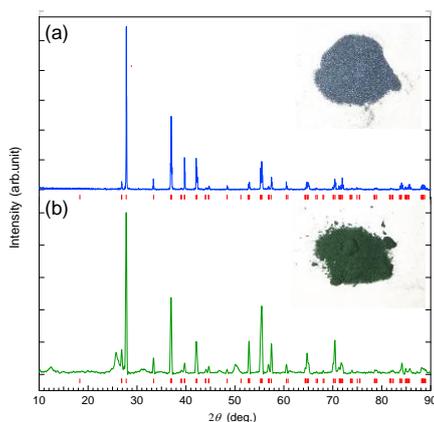


Fig. 1. Powder X-ray diffraction patterns of (a) pristine and (b) deteriorated VO₂ samples. The vertical bars indicate the positions of the Bragg reflections of VO₂ (M1). The insets are photographs of each sample.

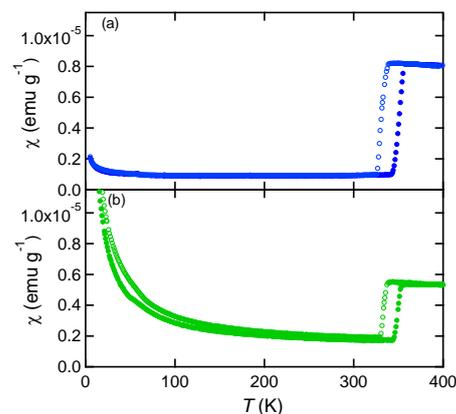
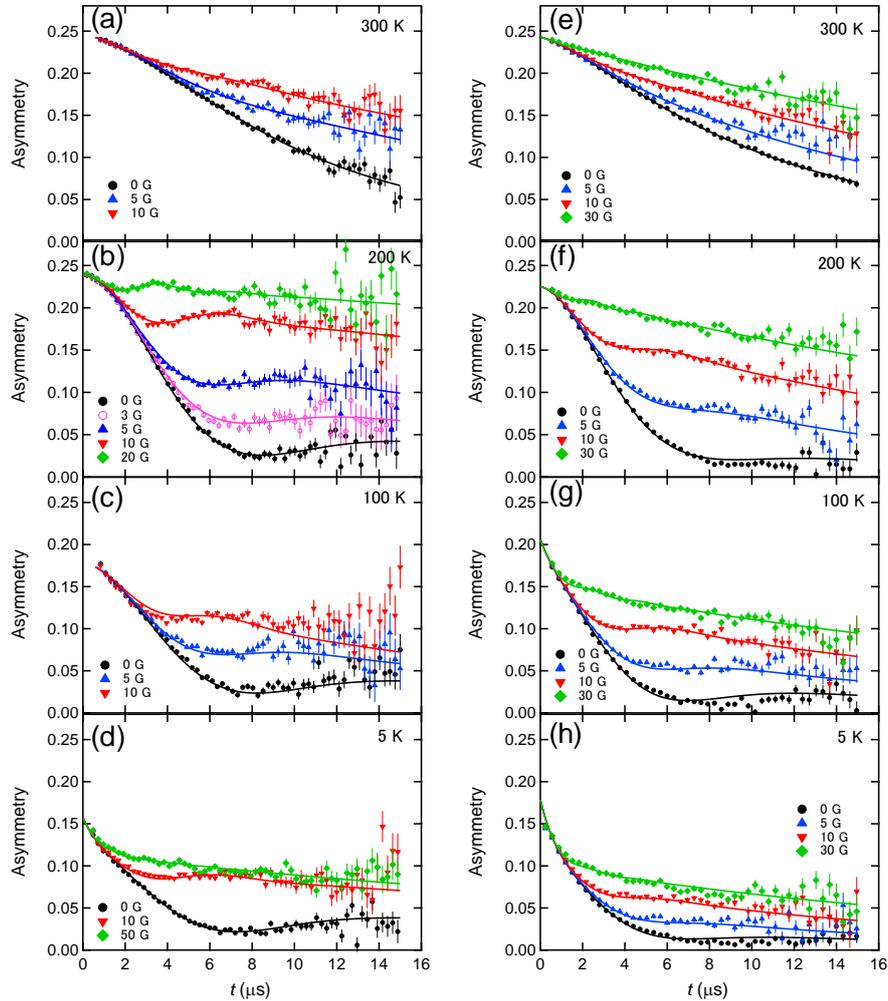


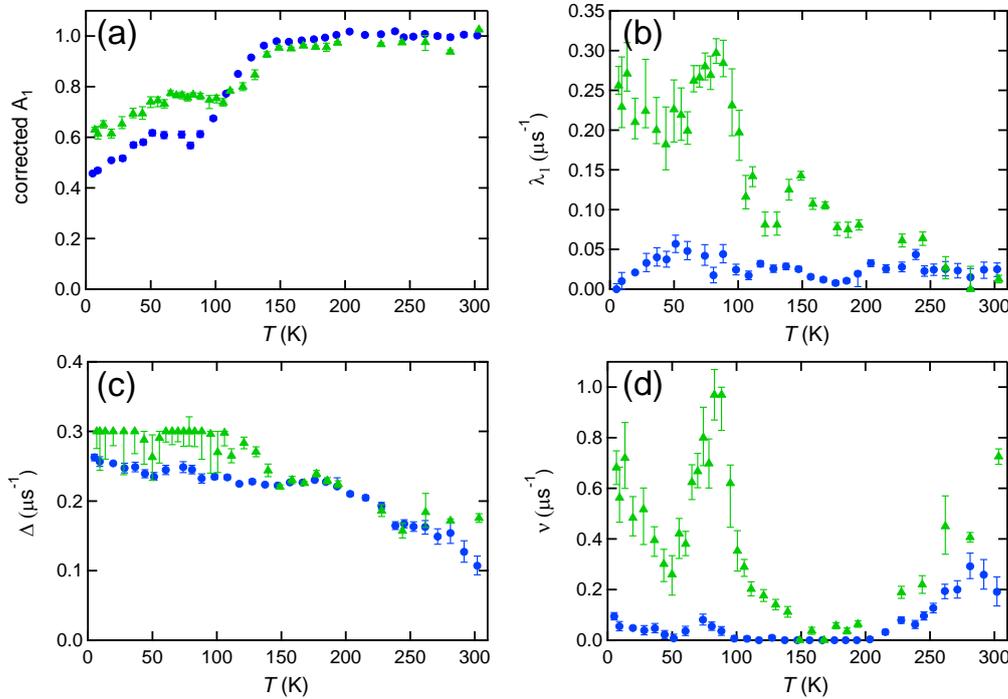
Fig. 2. Temperature dependence of magnetic susceptibility χ of (a) pristine and (b) deteriorated VO₂ samples. Filled (Open) circles are data acquired during temperature rising (falling).



Figs. 3. Zero field and longitudinal field μ SR time spectra of (a)~(d) pristine and (e)~(h) deteriorated VO_2 samples measured at selected temperatures (5, 100, 200, and 300 K).

Figures 3 show the μ SR time spectra in respective VO_2 samples measured at 5, 100, 200, and 300 K. These spectra were measured under zero magnetic field (ZF) or a weak longitudinal magnetic field (LF) of 3~50 G. By comparing data from different LFs, μ SR can estimate the magnitude of the local magnetic field generated inside a material and its fluctuations. Since these spectra show decoupling (recovery of muon spin polarization) under LFs of a few tens of gauss, relaxation is mainly due to the nuclear magnetic fields of V. However, in some of these spectra, there is a contribution of an exponential component suggesting relaxation due to electron spins. A disappearance of the initial signal intensity at $t = 0$ (a missing asymmetry) is a manifestation of a large local field resulting from a magnetic ordering. We analyzed these spectra using the following equation,

$$AP_z(t) = A_1 G_{\text{KT}}(\Delta, \nu) \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + A_{\text{const.}}$$



Figs. 4. Temperature dependence of μSR fitting parameters under zero magnetic field for pristine (blue circle) and deteriorated (green triangle) VO_2 samples. (a) corrected asymmetry A_1 , (b) relaxation rate λ_1 , (c) nuclear magnetic distribution width Δ , and (d) muon hopping rate ν . Note that Δ is restricted to the parameter ($\Delta < 0.3$) based on the fitting results in Figure 3 (not shown).

A is the signal amplitude, called asymmetry, which is proportional to the volume fraction of each component ($A_1, A_2, A_{\text{const}}$). The first term on the right-hand side, G_{KT} , is the Kubo-Toyabe function that represents a muon-spin relaxation due to randomly oriented nuclear spins [11]. Δ is the nuclear magnetic distribution width, ν is the muon hopping rate, and $\lambda_{1,2}$ are the relaxation rates caused by the electron spins of V. The second term on the right-hand side represents the rapid-relaxation component that corresponds to a missing asymmetry. Unfortunately, the second term cannot be fitted correctly due to the time resolution of the instrument. A_{const} is the constant term which mainly represents the background component such as the sample holder. The solid lines in Figure 3 show the fitting curves obtained by using the above equation. In the following sections, we will discuss the fitting parameters only obtained from ZF spectra, considering the fitting results of these LF spectra (not shown here).

Figures 4 show the temperature dependence of the corrected asymmetry A_1 [$A_1/(A - A_{\text{const}})$], λ_1 , Δ , and ν of each sample. As the temperature decreased, A_1 tends to decrease stepwise for both samples. The decreases in A_1 suggest the emergence of magnetic orders. However, the decreases in A_1 are not steep enough to determine the magnetic transition temperatures. The similar behaviors are observed in the earlier μSR results [7]. However, it does not necessarily correspond to the magnetic order they observed. The value of A_1 at the lowest temperature is larger for the deteriorated sample (~ 0.6) than for the pristine sample (~ 0.4), indicating that more missing asymmetry ($1 - A_1$) exists in the pristine sample. This contradicts the prediction that more impurities induce the increase in the volume fraction of the microscopic magnetic order in VO_2 by

destroying more V-V dimers. However, this is presumably due to the excessive sample deterioration, which has further transformed the microscopic magnetic order into paramagnetic, where the spin fluctuation rate is out of the μ SR time range ($>10^{11}$ Hz). This is consistent with the behavior of χ that the impurity effect almost appears exclusively as an increase of Curie paramagnetic component; the clear MIT is still observed in the deteriorated sample (see Fig. 2). In other words, the effect of deterioration (increased impurity content due to moisture, etc.) on the magnetic state of VO_2 is localized, and it is not reasonable to assume that the microscopic magnetic orders with large volume fractions are due solely to impurities.

The longitudinal relaxation rates λ_1 gradually increase as A_1 begin to decrease [Fig.4(b)]. The increase of λ_1 is more pronounced in the deteriorated sample, suggesting the enhancement of muon spin relaxation from the V electron spins. In particular, the peak structures below 200 K is reminiscent of magnetic transitions. Because of the correlation of λ_1 with Δ and ν , it is not possible to clearly distinguish whether these peaks are phase transitions or not. However, considering the stepwise decrease of A_1 , several different microscopic magnetic orders (clusters?) appear to coexist in the singlet phase. A significant number of V spins do not form dimers regardless of the amount of impurities, because the both samples follow the similar trend. Therefore, it seems unlikely that the microscopic magnetic order was only caused by external factors, such as the type and amount of impurities.

Similar to titanium oxides, vanadium oxides have a number of compounds with slight different oxygen ratios, such as the Magnéli and Wadsley phases [12]. In these phases, the stacking patterns of the transition metal octahedra are different, and MIT and magnetic transitions occur at various temperatures. There should be slight compositional deviations with partially deviated octahedral stacking patterns in VO_2 , because VO_2 is also one of the Magnéli-phase compounds. The aforementioned behaviors of A_1 and λ_1 can be explained by the existence of multiple local structures in the VO_2 singlet phase that exhibit different magnetic transition temperatures. Such a mixed state can be regarded as a type of lattice imperfection identical to a disordered dimer crystal structure.

Another possibility for the emergence of local magnetic fields in the singlet phase is muon-induced effects; positive muon (μ^+) behaves similarly to hydrogen ions in matter. If implanted μ^+ binds to the oxygen formed VO_6 octahedron, the V-V dimer can be destroyed by changing the valence state of the adjacent V ions. However, single μ^+ in VO_2 cannot develop a magnetic order resulting in the missing asymmetry. It is also unlikely that μ^+ forms polaronic state (Mu^0) with an excess electron in such a narrow-gap (~ 0.6 eV) semiconductor [13]. Furthermore, the concentration of injected muons at a time is extremely small, so that muons cannot work together to develop a magnetic order.

From the above reasons, we conclude that the singlet state and microscopic magnetic orders coexist in VO_2 at low temperatures. This also suggests that the range within which the magnetic state of VO_2 is affected by a single impurity or defect is narrow; probably a certain amount of V-V dimers could survive even if heavily doped. This tendency is also consistent with the local character of V-V dimers reported in TiO_2 - VO_2 mixed crystal system that exhibit a spinodal decomposition [14]. In any case, μ SR and other local probes would be useful to elucidate the MIT mechanism of VO_2 .

4. Summary

The local magnetic field in the singlet phase VO₂ was investigated using the μ SR method for two samples with different impurity contents. In both samples, the coexistence of a singlet state and microscopic magnetic orders was observed. The coexisting state may be originated from structural imperfections inherent in VO₂ rather than external impurity effects.

Acknowledgment

This work was supported by the MEXT Elements Strategy Initiative to Form Core Research Centers, from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (MEXT) under Grant No. JPMXP0112101001 and partially supported by JSPS KAKENHI (Grant No. 20K05312). The μ SR experiments were performed under user programs (Proposal No. 2019MS02) at the Materials and Life Science Experimental Facility of the J-PARC. We also acknowledge the Neutron Science and Technology Center, CROSS for the use of PPMS in their user laboratories.

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