μSR Investigation of the Hollandite Vanadate K$_2$V$_8$O$_{16}$

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Abstract

The quasi-one-dimensional hollandite vanadate K$_2$V$_8$O$_{16}$ is believed to have a spin-singlet-like transition at ≈ 170 K. We investigated a polycrystalline sample of K$_2$V$_8$O$_{16}$ using zero-field μSR. Paramagnetic electronic fluctuations, manifested as a relaxation of the muon polarization function, exist at all temperatures. There are only smooth and slight changes in the relaxation rate as the temperature of the sample is decreased from 200 K. Below about 10 K, there is a significant increase in the relaxation rate, implying a slow-down of the paramagnetic fluctuations.

Keywords: vanadate, low dimensional system, K$_2$V$_8$O$_{16}$, magnetism, muon

1. Introduction

Many of the mixed valent vanadium oxides are strongly correlated quasi-one-dimensional electronic systems that have rich transport and magnetic properties. A significant fraction of these compounds are characterized by a metal-insulator transition that is accompanied by the existence of charge-order phase transitions and spin singlet formation[1, 2]. Recently, the Hollandite vanadium oxide compound K$_2$V$_8$O$_{16}$ and members of its family have been obtained via high pressure synthesis[3]. There is a transition in K$_2$V$_8$O$_{16}$ from a metallic (high temperature) to an insulating (low temperature) state at ≈ 170 K. This is accompanied, as determined by X-ray diffraction, by a tetragonal to monoclinic transition with a characteristic supercell of $\sqrt{2}a \times \sqrt{2}a \times 2c$ [3]. Also, at ≈ 170 K, as shown in Fig. 1, the DC magnetic susceptibility shows a significant step-like reduction. At low temperatures, a Curie-like tail is observed that has been attributed to a small volume of impurities in the material. $^{51}$V NMR measurements of the Knight shift and lattice spin relaxation rates $1/T_1$ have recently been carried out on K$_2$V$_8$O$_{16}$ at both ambient and high pressures [4, 5]. These studies concluded that at ambient pressure, ferromagnetic spin fluctuations exist in the (high temperature) metallic phase while the ground state of the (low temperature) insulating phase is non-magnetic down to 2.6 K.

It is believed that K$_2$V$_8$O$_{16}$ (and related compounds such as Rb$_2$V$_8$O$_{16}$ and and KRbV$_8$O$_{16}$ [6, 7]) forms a charge-ordered (CO) phase below the ≈ 170 K transition temperature. Initially this was assigned microscopically as being, by...
analogy with certain other vanadium oxide compounds, due to the formation of $V^{3+} - V^{3+}$ and $V^{4+} - V^{4+}$ spin singlets along the double strings of edge-shared VO$_6$ octahedra that are located within the tubular V$_8$O$_{16}$ framework. The charge ordering pattern could not be determined in detail in the NMR investigation discussed above [4, 5], but the authors pointed out that the observation of the nonmagnetic NMR spectrum below the metal-insulator transition temperature is consistent with the formation of spin singlets. Recent theoretical calculations postulate more non-uniform charge ordered patterns of $V^{3+}$ and $V^{4+}$ within a double chain [8, 9].

The primary motivation behind our present preliminary $\mu$SR study of the local magnetic properties of K$_2$V$_8$O$_{16}$ are as follows: (i) determine if there is a signature in the $\mu$SR data for the spin-singlet formation at $\approx 170$ K, and (ii) to investigate the low temperature behavior with a local magnetic probe, i.e. in the temperature regime where the DC magnetization is believed to be dominated by impurity contributions.

2. Experiment

Powder samples of K$_2$V$_8$O$_{16}$ were prepared via solid-state reaction of suitable amounts of KVO$_3$, V$_2$O$_3$, and V$_2$O$_5$ under high pressure and temperatures, as described in more detail elsewhere [3, 6, 7, 10]. The $\mu$SR measurements reported here were carried out at the M15 and M20B surface muon beamlines at TRIUMF where nearly 100% spin-polarized positive muons with a nominal momentum of 28 MeV/c were implanted into the samples. The polycrystalline sample was placed in a thin packet and mounted in a He gas exchange cryostat with low-background capabilities [11, 12]. The majority of the measurements were done using the conventional zero-field (ZF) $\mu$SR technique [13, 14], carried out above $\approx 1.7$ K. Some longitudinal field (LF) $\mu$SR data were also collected.

3. Results and Discussion

Examples of the zero-field muon spin polarization $G_z(t)$ at various temperatures are shown in Fig. 2, demonstrating that the muon polarization relaxes, and furthermore, that the effective relaxation rate changes with temperature. Moreover, the amplitude of the muon asymmetry is large at all temperatures, indicating that essentially all the sample is responsible for the relaxation. Measurements at several temperatures confirm that relaxation is still present in a longitudinal field of up to several tens of Gauss, as shown in Fig. 2(b) and (c).

All the ZF-$\mu$SR data are well-described by the following function:

$$G_z(t) = A_0 \times \left[ \frac{1}{3} + \frac{2}{3} (1 - \Delta^2 \tau^2) \exp\left(-\frac{1}{2} \Delta^2 \tau^2\right) \right] \times \exp[-(\lambda \tau)^\beta] + A_{bgd}. \quad (1)$$

The first term in Eq. (1) models the following two physical mechanisms which we believe are responsible for the relaxation of the muon polarization in our samples: (1) neighboring nuclear moments, such as from $^{51}$V, $^{39}$K, etc.
which are quasi-static on the muon lifetime and (2) fluctuating electronic moments. The nuclear contribution is modeled by the static ZF Kubo-Toyabe function with distribution width $\Delta$ while the effect of electronic fluctuations is modeled by a phenomenological stretched exponential function with electronic relaxation parameter $\lambda$ and exponent $\beta$. It is assumed that these two depolarization mechanisms are uncorrelated, and therefore the terms describing them appear as a product in Eq. (1). The second term ($A_{\text{bkgd}}$) in Eq. (1) is a (small) constant background that takes into the account the possible existence of a slight volume of impurity phase in the sample. The data are fitted by assuming that $\lambda$ can be different at each temperature, but $\beta$, $\Delta$, $A_0$ and $A_{\text{bkgd}}$ are all temperature independent. The fitted values of $\beta$, $\Delta$, and $A_0$, are $0.661(3)$, $0.1715(4) \times 10^6$ s$^{-1}$ and $0.2034(2)$ respectively. The fitted value of $\beta$ is between $0.5$ and $1$, suggesting that the observed relaxation is due to fluctuating dilute moments. The temperature dependence of $\lambda$ is summarized in Fig. 3.

Also shown in Fig. 3 are fits to the few LF-\(\mu\)SR data that we have measured. Here, the static Kubo-Toyabe function in Eq. (1) is replaced by the dynamic Kubo-Toyabe function in a longitudinal field. In this case, the field distribution width ($\Delta$) is estimated as $(0.171 \pm 0.02) \times 10^6$ s$^{-1}$ at 30 K and $(0.169 \pm 0.02) \times 10^6$ s$^{-1}$ at 1.8 K, while the field fluctuation rate ($\nu$) was almost zero at both temperatures. These are consistent with our ZF analysis.

The muon polarization in the vicinity of the spin-singlet transition temperature at $\approx 170$ K (see Fig. 1), character-
ized by the temperature dependence of $\lambda$ for example, shows at most only slight changes across this region (see Fig.3). This behavior was not initially anticipated – naively, one may expect that since such a transition is accompanied by the opening of a gap in the excitation spectrum of the electronic moments, their fluctuation rates and hence $\lambda$ would be significantly modified. Also interesting is the behavior of $\lambda$ as one cools below 170 K. There is at first a slight increase in $\lambda$ as one decreases the temperature. Then, between $\approx 10$ K and $\approx 1.8$ K, a much more dramatic rise in $\lambda$ is observed. In Fig. 3b, we compare $\lambda/T$ with the bulk DC susceptibility $\chi$ (measured in field-cooling mode with $H = 1$ kG) below 10 K. The data are suggestive of a linear relationship between the two parameters below $\approx 3$ K. The behavior of $\lambda$ and $\lambda/T$ hints that critical behavior may occur below $\approx 3$ K. Furthermore, this implies that the increase of $\chi$ at low-$T$ is not caused by a small amount of impurity phase, as commonly believed in the literature, but rather is an intrinsic feature of $K_2V_8O_{16}$ (since $\mu^*$SR should not be sensitive to a small amount of impurities).

Our present $\mu$SR results imply the following: in $K_2V_8O_{16}$, there are paramagnetic electronic fluctuations at high temperatures which are not strongly affected by the “spin-singlet” transition at $\approx 170$ K. As the sample is cooled to $\approx 1.8$ K, these paramagnetic fluctuations slow down significantly, hence producing the increase in $\lambda$. However, the behavior of the relaxation at lower temperatures must be investigated before one can conclude whether there is magnetic ordering or spin freezing upon further cooling. Nevertheless, our measurements thus far do indicate that in $K_2V_8O_{16}$, the transition at $\approx 170$ K is not into a “truly” singlet state. In other words, some non-zero V spins are most likely to still survive even below 170 K, although it is difficult to estimate the content of these spins based solely on the $\mu^*$SR result. In fact, the model proposed by Huriuchi et. al. [8, 9] of a “strong but imperfect” spin singlet formation may be representative of the spin arrangement in this system. Very recent structural analyses of $K_2V_8O_{16}$ at low temperatures indicate the absence of dimerization of V-spins in one of the four zigzag chains [16]. This would be consistent with the present $\mu^*$SR result.

Possible experimental extensions of the current work include carrying out both DC magnetization and $\mu$SR studies in $K_2V_8O_{16}$ at temperatures below 1.8 K. Furthermore, it will be interesting to probe the situation in analogous systems such as $Rb_2V_8O_{16}$ and $KRbV_8O_{16}$ where similar qualitative behavior of the DC magnetization (as shown in Fig. 1 for $K_2V_8O_{16}$) has been observed [6, 7]. These efforts are either underway or being planned.

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