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Microscopic magnetic nature of K_2NiF_4-type $3d$ transition metal oxides

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Abstract. In order to elucidate the magnetic nature of K_2NiF_4-type $3d$ transition metal oxides, we have measured μ^+SR spectra for Sr_2VO_4, $LaSrVO_4$, and Sr_2CrO_4 using powder samples. ZF- and wTF-μ^+SR measurements propose that Sr_2VO_4 enters into the static antiferromagnetic (AF) order phase below 8 K. In addition, TF-μ^+SR measurements evidence that the transition at 105 K is not magnetic but structural and/or electronic in origin. For $LaSrVO_4$, static long-range order has not been observed down to 20 K, while, as T decreases from 145 K, wTF asymmetry starts to decrease below 60 K, suggesting the appearance and evolution of localized magnetic moments below 60 K. For Sr_2CrO_4, by contrast, both ZF- and wTF-μ^+SR have confirmed the presence of antiferromagnetic order below 117 K, as predicted in the $\chi(T)$ curve.

1. Introduction

The discovery of high-T_c superconductivity in Ba-doped La_2CuO_4 [1] led to extensive studies of the structural, electrical and magnetic properties of layered perovskites A_2MO_4 with a K_2NiF_4-type structure, particularly for the compounds with M = Co, Ni, and Cu. However, due to the difficulty of preparing high-quality A_2MO_4 samples with M = V, Cr, and Mn, the electronic and magnetic properties of these compounds are still not fully clarified. Very recently, the following high-quality and/or novel A_2MO_4 compounds were successfully synthesized under high pressures [2, 3];

- $3d^1$ system: Sr_2VO_4
- $3d^2$ system: $LaSrVO_4$, Sr_2CrO_4, and Ca_2CrO_4

- $3d^3$ system: $LaSrCrO_4$, $YSrCrO_4$, $YCaCrO_4$, Ca_2MnO_4 and Sr_2MnO_4

Based on resistivity (ρ) and susceptibility (χ) measurements, all these compounds were found to be insulators showing magnetic transitions below ambient temperature [2]. This opens the opportunity for a systematic study on the relationship between the number of d electrons and magnetic order and/or magnetic nature in the K_2NiF_4-type lattice, particularly with μ^+SR. This is important because it is very difficult (though not impossible) to synthesize large enough samples for neutron scattering measurements using the high-pressure technique.

We have therefore initiated μ^+SR experiments on these materials and a preliminary result on Sr_2VO_4 was already published elsewhere [4]. Here we report the μ^+SR results on the $3d^1$ and $3d^2$ system compounds, namely, Sr_2VO_4, $LaSrVO_4$ and Sr_2CrO_4.

2. Experimental

Powder samples of Sr_2VO_4, $LaSrVO_4$, and Sr_2CrO_4 were prepared by a solid-state reaction technique at high pressures [2, 3]. The μ^+SR spectra were measured at the surface muon beam lines using the **LAMPF** and **HiTime** spectrometer of TRIUMF in Canada.

3. Results and discussion

3.1. $3d^1$ system: Sr_2VO_4

Figure 1 shows the temperature variation of the ZF-μ^+SR spectrum for Sr_2VO_4. The ZF-spectrum obtained at the lowest T measured (1.8 K) looks to be fitted by a static Kubo-Toyabe function. However, for such fit, we need two additional exponential relaxing signals in order to reproduce a rapid decay in an early time domain (below 0.1 μs) and the behavior that $A_0 P_{\rm ZF}(t) \sim 0$ at $t \geq 5$ μs, meaning three different muon sites in the lattice This also indicates that the muon-spin responsible for the KT signal is static, while those for the exponential relaxing signals are dynamic. This is an inconsistent situation, even though the three muon sites are crystallographically equivalent, but magnetically nonequivalent. We therefore fitted the data by a combination of an exponentially relaxing cosine signal for a static internal field and an exponentially relaxing non-oscillatory signal for the 1/3 tail signal;

$$A_0\, P_{\rm ZF}(t) = A_{\rm AF} \exp(-\lambda_{\rm AF} t) \cos(\omega^{\mu}_{\rm AF} t) + A_{\rm tail} \exp(-\lambda_{\rm tail} t). \quad (1)$$

Figure 2 shows the temperature dependences of the μ^+SR parameters in Eq. (1). Combining with wTF-μ^+SR measurements, it is proposed that Sr_2VO_4 enters into an antiferromagnetic ordered phase below $T_{\rm N} = 8$ K. However, even at the lowest temperature measured (1.8 K), the distribution of the internal magnetic field ($H_{\rm int}$) is very broad, and the exponential relaxation rate ($\lambda_{\rm AF}$) of the oscillatory signal is eventually comparable to the muon-spin precession frequency [$f_{\rm AF} \equiv \omega^{\mu}_{\rm AF}/(2\pi)$] [Fig. 2(b)]. This supports orbital-stripe order and collinear AF spin order [5, 6] for the ground state of Sr_2VO_4 rather than alternating spin-orbital order [7]. This is because, even for the single muon site in the lattice, dipole field calculations showed that there are several $H_{\rm int}$s in the former case, while only one well defined $H_{\rm int}$ would be expected in the latter case (see Fig. 3).

Concerning the 1/3 tail signal, although $A_{\rm tail}$ is only $\sim$ 22% of A_0, the magnitude and temperature dependence of $\lambda_{\rm tail}$ are reasonable for the 1/3 tail signal (Fig. 2). The smaller $A_{\rm tail}$ is probably due to the coexistence of a spin-glass like phase, which provides no 1/3 tail signal.

Then, we have measured muonic Knight shift measurements above $T_{\rm N}$ with $H_{\rm TF} = 50$ kOe for further studying the nature of the transition around $T_{\rm c} \sim 105$ K, which is observed by χ measurements but was not clearly detected by wTF and ZF-μ^+SR. Figure 4 shows the variation of the Fourier transform spectrum of the TF-μ^+SR time spectrum with T. The Fourier transform spectrum exhibits a Gauss distribution at 300 K, while it changes to a Lorentz distribution at

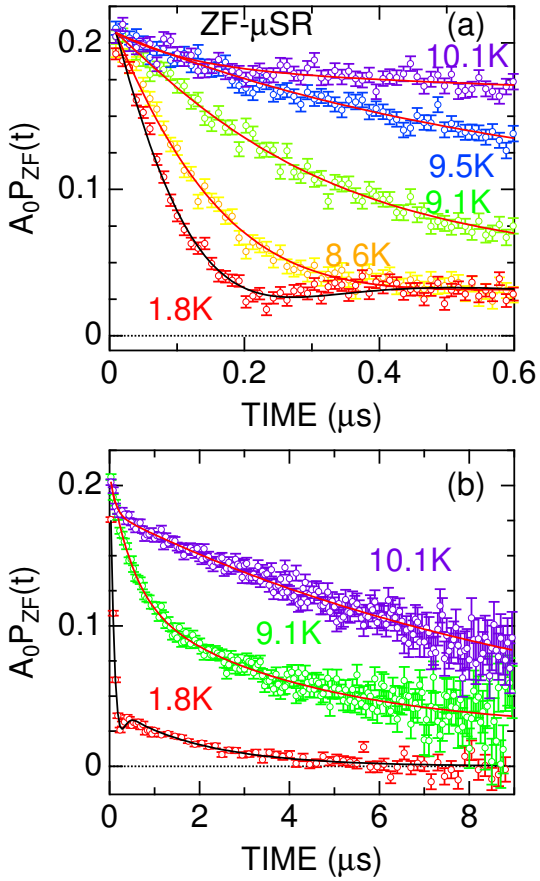

Figure 1. T dependence of the ZF-μ^+SR spectrum for Sr_2VO_4 below 10 K (a) in an early time domain, $t \leq 0.6$ μs and (b) in a full time domain measured. Solid lines represent the fit result using Eq. (1).

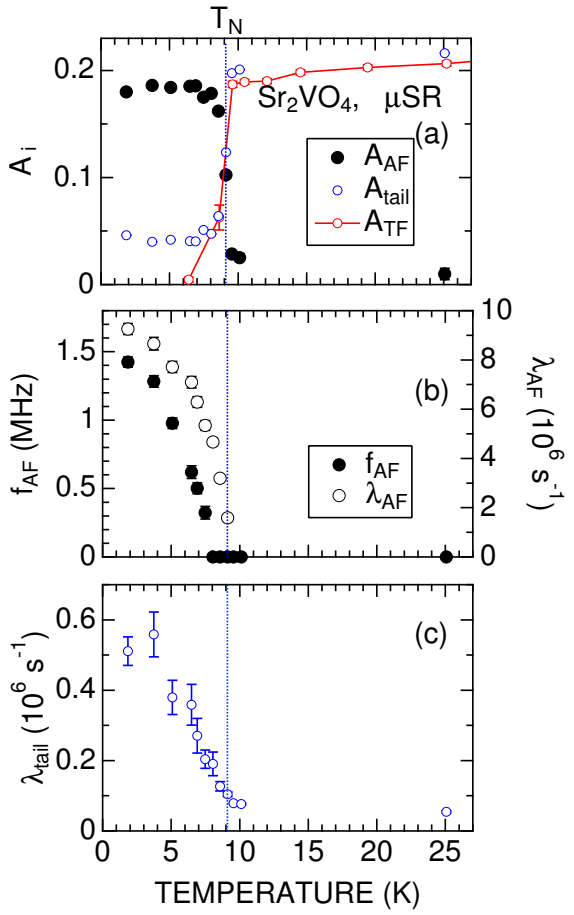

Figure 2. T dependences of (a) the asymmetries ($A_{\rm AF}$, $A_{\rm tail}$, and $A_{\rm TF}$), (b) the muon spin precession frequency for the $A_{\rm AF}$ signal ($f_{\rm AF} \equiv \omega_{\rm AF}/2\pi$) and its exponential relaxation rate $\lambda_{\rm AF}$, and (c) the exponential relaxation rate of the tail signal ($\lambda_{\rm tail}$).

10 K. In fact, the TF-μ^+SR spectrum was well fitted with a power exponential relaxed cosine oscillation (using a rotating frame analysis [8]) in the whole T range measured;

$$A_0\, P_{\rm TF}(t) \quad = \quad A \exp[-(\lambda t)^{\beta}] \cos(\omega^{\mu} t + \phi). \tag{2}$$

Figure 5 shows the temperature dependences of the TF-μ^+SR parameters together with χ and $1/\chi$. As T decreases from 300 K, β is almost T-independent (=2) down to $T_{\rm c}$, then decreases gradually with decreasing T and reaches around 1 at $\sim$ 80 K, and then, β is T-independent again until 30 K, and finally, decreases slightly with further decreasing T. Roughly speaking, $\beta = 2$ above $T_{\rm c}$, whereas $\beta = 1$ below $T_{\rm c}$. This means that the phase above $T_{\rm c}$ is paramagnetic and the implanted muons *see* only the nuclear magnetic moments, since the V moments are fluctuating very rapidly. However, below $T_{\rm c}$, thermal fluctuations of V moments become so slow that the muons sense the fluctuating V moments. Such picture is consistent with the T dependences of λ and χ.

On the other hand, above $T_{\rm c}$, λ increases slightly with decreasing T, but below $T_{\rm c}$, λ

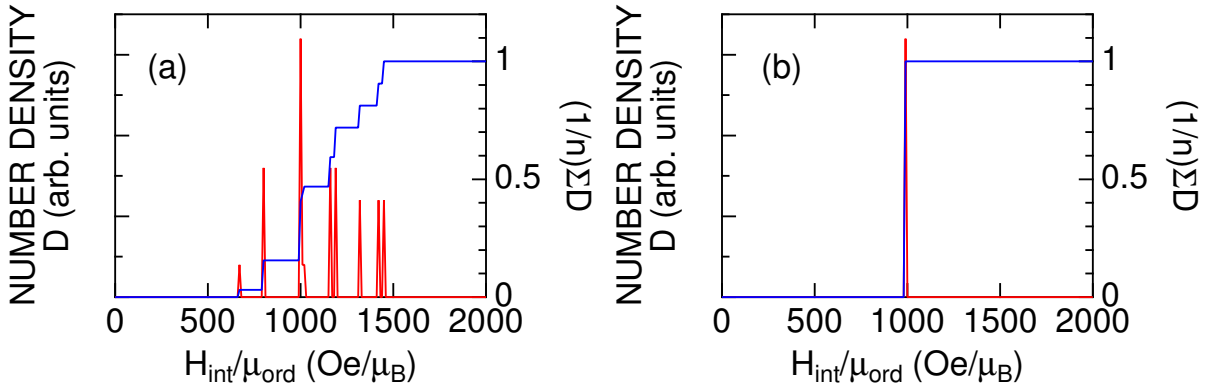

Figure 3. Predicted distribution of the internal magnetic field for (a) the orbital-stripe order and collinear AF spin order [5, 6] and (b) alternating spin-orbital order [7] obtained by dipole field calculations. Here, we assumed that the implanted muons locate at the vicinity of the apical oxygen anion 1 Å away; namely, crystallographically one muon site in the lattice.

increases rapidly with increasing a slope ($d\chi/dT$). The muonic Knight shift (K) is defined as $K \equiv (\omega^{\mu}_{\rm sample} - \omega^{\mu}_{\rm ref.})/\omega^{\mu}_{\rm ref.}$, where $\omega^{\mu}_{\rm ref.}$ is the angular frequency of a reference ($CaCO_3$). K is found to be negative below 300 K, and decreases with decreasing T down to T_c, then, below T_c K increases with further lowering T. From the $K - \chi$ plot, the hyperfine coupling constant ($A_{\rm hf} \equiv K/\chi$) above T_c is estimated as -480 Oe/μ_B. However, below T_c, $A_{\rm hf}$ increases with decreasing T and approaches 0, when $T \to 0$.

From the $1/\chi(T)$ curve [Fig. 5(c)], the effective magnetic moment ($\mu_{\rm eff}$) of V ions below T_c is found to be smaller by 33% than that above T_c. This implies either the formation of a spin-singlet like state below T_c or a ferrimagnetic coupling between the nearest neighboring V ions. In addition, since the $\lambda(T)$ curve rapidly increases with decreasing T below 50 K and the $\beta(T)$ curve starts to decrease from 1 also below 50 K, short-range order would be formed below 50 K. Therefore, it is highly desirable to perform careful inelastic neutron scattering studies in this T range.

3.2. $3d^2$ system: $LaSrVO_4$ and Sr_2CrO_4

For $LaSrVO_4$, the $\chi(T)$ curve shows a sharp maximum around $T_N = 10$ K, implying the presence of an AF transition. However, since the past work on $LaSrVO_4$ reported the absence of such maximum [9], it is very important to confirm whether the AF transition exists at low T by μ^+SR. The weak transverse field asymmetry ($A_{\rm TF}$) starts to decrease below $\sim$ 70 K, and decreases linearly with lowering T and reaches 0 at around T_N. This means the appearance of localized moments below 70 K and the evolution of them with decreasing T, and finally the whole volume of the sample enters into a magnetic ordered or disordered state. Moreover, below around T_N, ZF-μ^+SR detected a damped oscillatory signal, which demonstrates the appearance of static magnetic order below T_N.

For Sr_2CrO_4, the $\chi(T)$ curve shows a broad maximum around $T_N \sim 117$ K, indicating the presence of an AF transition. The $A_{\rm TF}(T)$ curve also shows a step-like change from a full value ($\sim$ 0.23) to zero at T_N. This means that the whole volume of the sample enters into an AF ordered state at T_N. Below T_N, ZF-μ^+SR spectrum includes only one oscillatory signal down to 45 K, but two oscillatory signals below 45 K. This also shows the appearance of static magnetic order below T_N and a slight change in the magnetic structure at 45 K. Although χ rapidly

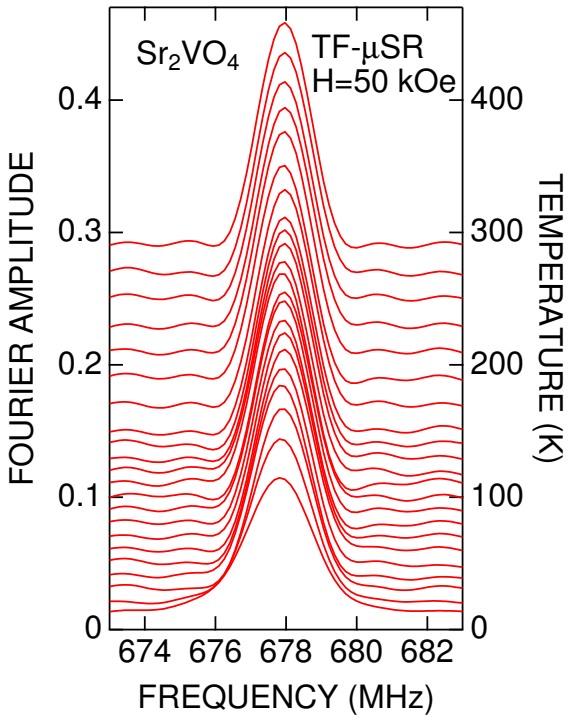

Figure 4. T dependence of the Fourier transform spectrum of the TF-μ^+SR time spectrum for Sr_2VO_4. The TF spectrum was obtained with $H_{TF} = 50$ kOe.

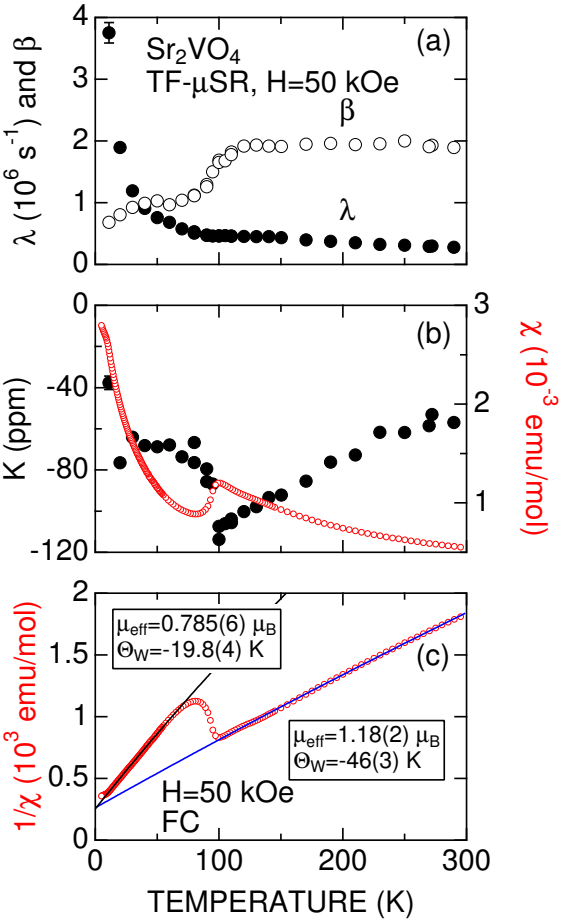

Figure 5. T dependences of (a) the power (β) and relaxation rate (λ) and (b) the Knight shift (K) and χ, and (c) $1/\chi$. The data were obtained by fitting the TF-μ^+SR spectrum with eq. (2). χ was measured with H = 50 kOe in a field cooling mode. In (c), the Curie-Weiss fit [$\chi = \chi_0 + C/(T - \Theta_W)$] in the temperature range between 110 and 320 K provides that $\chi_0 = 4.1(9) \times 10^{-5}$ emu/mol, $\mu_{eff} = 1.18(2)\ \mu_B$, and $\Theta_W = -46(3)$ K, while the fit in the temperature range between 10 and 70 K provides hat $\chi_0 = 6(1) \times 10^{-5}$ emu/mol, $\mu_{eff} = 0.785(6)\ \mu_B$, and $\Theta_W = -19.8(4)$ K.

increases with decreasing T below 15 K, there is no critical change in the $f_{AF}(T)$ curve at this T range. Therefore, the reason of the increase in χ at low T is most likely due to magnetic impurities.

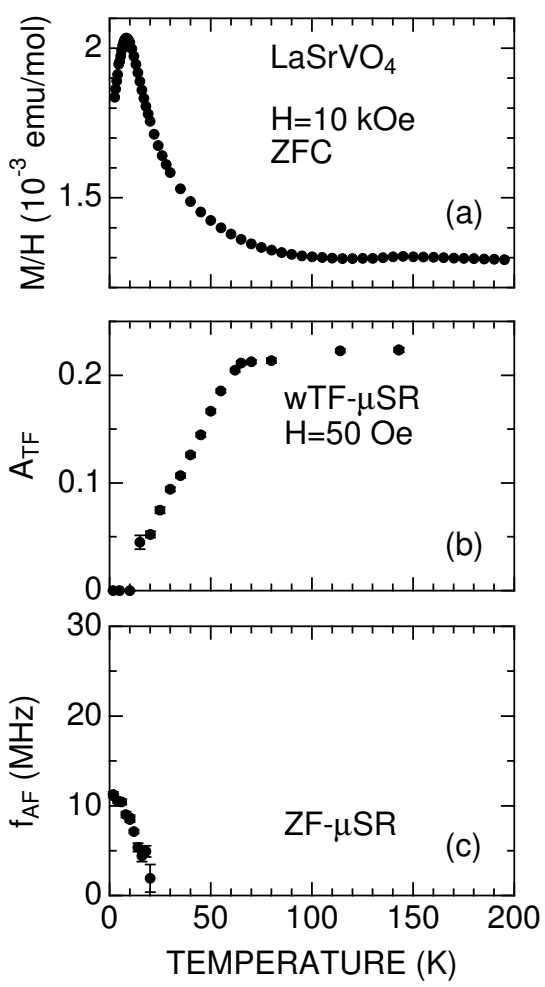

Figure 6. T dependences of (a) susceptibility (χ), (b) the weak transverse field asymmetry ($A_{\rm TF}$), and (c) the muon-spin precession frequency ($f_{\rm AF}$) below $T_{\rm N}$ for $LaSrVO_4$.

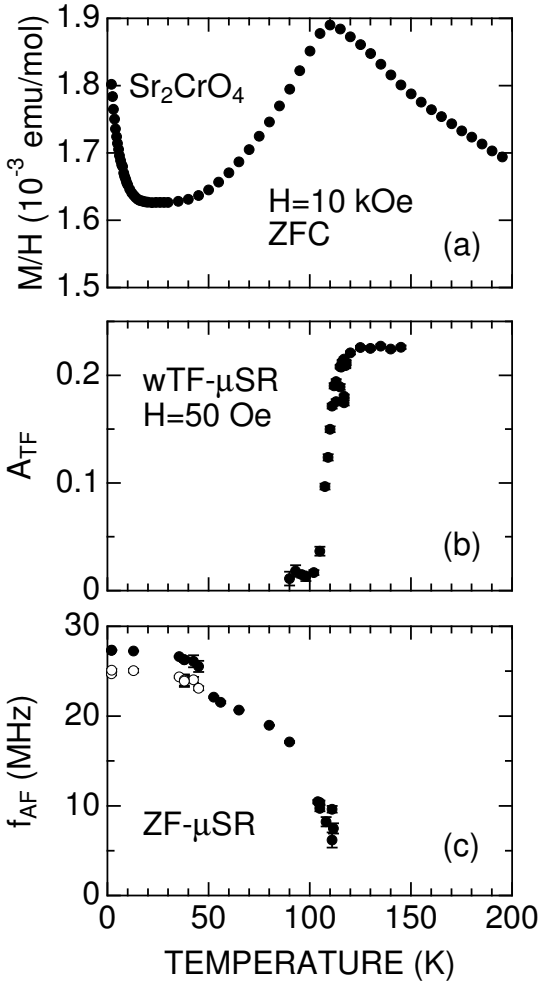

Figure 7. T dependences of (a) susceptibility (χ), (b) the weak transverse field asymmetry ($A_{\rm TF}$), and (c) the muon-spin precession frequencies ($f_{\rm AF}$s) below $T_{\rm N}$ for Sr_2CrO_4.

4. Summary

We have measured μ^+SR spectra for Sr_2VO_4, $LaSrVO_4$, and Sr_2CrO_4 using powder samples. For the two complex vanadium oxides, the microscopic magnetic nature detected with μ^+SR is very different from that obtained by susceptibility (χ) measurements. Such discrepancy is probably due to the difference of time-windows between μ^+SR and χ measurements, together with the different spatial resolution. That is, μ^+SR is a local probe, while χ provides average information. For Sr_2CrO_4, on the other hand, static magnetic order is found to appear below $T_{\rm N} = 107$ K, at which the $\chi(T)$ curve exhibits a broad maximum.

Acknowledgments

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