Muon-spin relaxation measurements on the dimerized spin-1/2 chains $NaTiSi_2O_6$ and TiOCl

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We report muon spin relaxation (μSR) and magnetic susceptibility investigations of two Ti^{3+} ($S=1/2$) chain compounds, $NaTiSi_2O_6$ and TiOCl, each of which exhibits a spin gap at low temperature. From these we conclude that the spin gap in $NaTiSi_2O_6$, which arises from orbital ordering at $T_{OO}=210$ K, is temperature independent below T_{OO}, with a value of $2\Delta=700(100)$ K. In TiOCl, we find thermally activated spin fluctuations corresponding to a spin gap $2\Delta=440(60)$ K below $T_{c1}=67$ K. We can describe both the μSR and susceptibility data in terms of a model based on the dimerization of the Ti^{3+} chains. We also compare the methods used to extract the spin gap and the concentration of free spins within the samples from μSR and magnetic susceptibility data.

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The interplay between spin, charge, and orbital degrees of freedom is particularly subtle in strongly correlated oxides containing octahedrally coordinated Ti^{3+} ions (t_{2g}^1). Such compounds are typically insulators because the $S=1/2$ spins are localized in the t_{2g} orbitals. In oxides containing chains of Ti^{3+} ions, superexchange via oxygen gives rise to antiferromagnetic coupling. A well-known instability that can affect half-integer spin chains is the spin-Peierls (SP) transition,[1] in which magnetoelastic coupling dimerizes the chain and allows a spin gap 2Δ to open below a characteristic temperature T_{SP} resulting in a spin-singlet ground state [e.g., $T_{SP}=14$ K for $CuGeO_3$ (Ref. 2) and $T_{SP}=18$ K for $MEM(TCNQ)_2$ (Ref. 3)]. In contrast, for integer spins a Haldane gap will be present, precluding any low-temperature instability.[4]

Recently, two oxides, $NaTiSi_2O_6$ (NTSO) and TiOCl, have been intensively studied because they undergo dimerization transitions at unusually high temperatures. NTSO has the pyroxene structure with chains of TiO_6 octahedra that are only weakly coupled to one another.[5] TiOCl has TiO bilayers within the *ab* plane, well separated by Cl^- ions. At low temperature, dimerized chains of Ti^{3+} ions form along the *b* axis, with their spins coupled by direct exchange.[6] The magnetic susceptibility, χ drops sharply at 210 K for NTSO (Ref. 5) and 67 K for TiOCl (Ref. 7) due to the opening of a spin gap. Previous measurements of the spin gap (which we quote in kelvins) in these compounds, $\Delta\sim500$ K for NTSO (Ref. 5) and $\Delta=430(60)$ K for TiOCl,[8] suggest that the ratio of the spin gap to the dimerization temperature is larger than for the canonical SP case (for which $2\Delta/T_{SP}=3.53$).[1] This has been taken to be evidence that the dimerization transitions are more complex than the canonical SP case, and points to the possible role of orbital physics.

X-ray diffraction studies of NTSO show that the Ti^{3+} chains dimerize below 210 K.[9] Phonon anomalies measured using Raman scattering[10] are consistent with the dimerization being driven by an orbital ordering at $T_{OO}=210$ K, below which the system is condensed in one of two possible orbitally ordered spin-singlet states, breaking translational symmetry. This model is supported by a number of theoretical studies,[11–13] although a composite $S=1$ Haldane chain ground state, with spin-triplet dimers of ferromagnetically coupled Ti^{3+} spins, has also been proposed[14] (see also Refs. 12 and 15).

Unusually, the dimerization of TiOCl occurs in two stages. There is a second-order phase transition at $T_{c2}=91$ K into an incommensurate dimerized phase, and a first-order transition at $T_{c1}=67$ K into a commensurate SP phase.[6–8,16,17] Although early work suggested that orbital fluctuations may play a dominant role in driving the transition,[16,18–20] recent experiments have ruled this out.[17,21,22] In particular, optical measurements, in combination with a cluster calculation, revealed that the crystal-field splitting is large enough to quench the orbital degree of freedom.[17] It appears that frustration between the two staggered chains in the bilayer crystal structure of TiOCl leads to an incommensurate SP state between T_{c1} and T_{c2}.[8,17,23,24] The magnitude of the spin gap has previously been measured using optical techniques[20,25] and NMR (Refs. 8 and 26) to be $2\Delta\approx430$ K, which is large compared to the observed transition temperatures.

Muon spin relaxation (μSR) experiments[27] probe magnetic ordering and dynamics from a microscopic viewpoint. The applicability of this technique to spin-gapped systems has been demonstrated by studies of the canonical SP compounds $CuGeO_3$ (Refs. 28 and 29) and $MEM(TCNQ)_2$,[30,31] the two-leg spin-ladder compound NaV_2O_5,[32] and the Haldane chain compound Y_2BaNiO_5.[33] In this paper, we present the results of μSR experiments on NTSO and TiOCl. We also made magnetic susceptibility measurements using a superconducting quantum interference device (SQUID) magnetometer that allows us to compare our results with previous data[5,7,17] and to provide an independent measurement of the defect concentration of our samples. Using both tech-

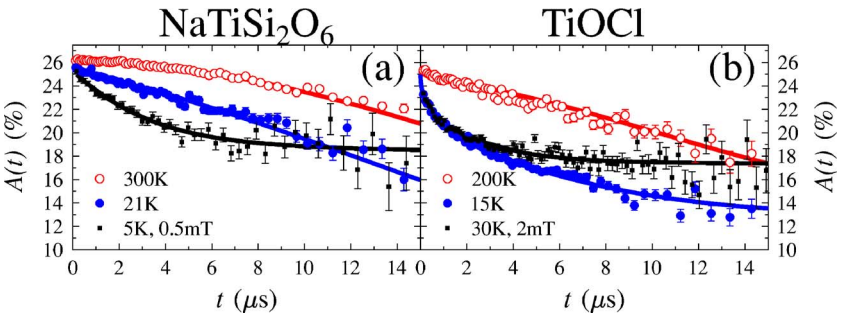

FIG. 1. (Color online) Examples of muon decay asymmetry data in (a) $NaTiSi_2O_6$ and (b) TiOCl, with fits to Eqs. (1) and (2), respectively. Longitudinal field data are fitted as described in the text.

niques, we have measured the magnitude of the spin gap and found the concentration of unpaired spins in the dimerized state.

Our polycrystalline sample of NTSO was prepared by a solid-state reaction[5] of $Na_2TiSi_4O_{11}$, Ti, and TiO_2. The sample of TiOCl was composed of small single crystals synthesized using standard vapor-transport techniques[34] from TiO_2 and $TiCl_3$. Our μSR experiments were carried out using the MuSR and ARGUS spectrometers at the ISIS Facility, United Kingdom. These were done in zero-applied magnetic field (ZF) and in small magnetic fields along the axis of the initial muon spin polarization. Spin-polarized positive muons (μ^+, mean lifetime of 2.2 μs, momentum of 28 MeV/c, and $\gamma_\mu = 2\pi \times 135.5$ MHz T^{-1}) were implanted into the polycrystalline samples where they stop within $\sim$1 ns. The decay positron asymmetry function[27] $A(t)$ is proportional to the average spin polarization of the muons stopped within the sample. Examples of the measured asymmetry spectra are presented in Fig. 1.

The absence of coherent muon precession, which would be indicative of a spontaneous magnetic field, together with the observation that both high- and low-temperature spectra relax to the same value with negligible missing asymmetry (Fig. 1), excludes the presence of long-range magnetic order in either material. The form of the muon spin relaxation is dependent on the distribution and time dependence of the local magnetic fields around the site where the muon is implanted. In spin-gapped materials, we write $A(t)$ as a product of relaxation functions.[28,30,31] We approximate a Gaussian Kubo-Toyabe function[27] (which models the Gaussian distribution of randomly orientated nuclear spins) using $\exp[-(\sigma t)^2]$. If the electronic spin fluctuations are fast compared to the width of the magnetic-field distribution, $\sqrt{\langle B_\mu^2 \rangle}/\gamma_\mu$, as we find to be the case in NTSO, we can use a simple exponential $\exp(-\lambda t)$ to describe the depolarization due to fluctuating electronic spins [Eq. (1)]. Preliminary data analysis for TiOCl showed that this did not describe the low-temperature data correctly and that using a square root exponential $\exp(-\sqrt{\Lambda t})$ better described the electronic depolarization [Eq. (2)], as would be expected for a dilute distribution of defect spins.[35] We add a constant background A_{BG} to describe those muons landing outside the sample, giving our two fitting functions,

$$A(t) = A(0)\exp[-(\sigma t)^2]\exp(-\lambda t) + A_{BG}, \quad (1)$$

$$A(t) = A(0)\exp[-(\sigma t)^2]\exp(-\sqrt{\Lambda t}) + A_{BG}. \quad (2)$$

At high temperature, the relaxation due to the nuclear spins dominates. Because the observed value of σ is small, we do not see a recovery in the muon asymmetry at longer times; this is also due, in part, to the presence of the electronic fluctuations. Fitting the data with σ as a free parameter over the whole temperature range, 15–340 K, showed that in NTSO it was, within the experimental error, temperature independent and it was subsequently fixed at $\sigma = 0.06$ MHz. In TiOCl, the same process gave $\sigma = 0.08$ MHz.

For both compounds, we must consider the temperature variation of the spin gap. X-ray measurements[9] show that the degree of dimerization in NTSO is essentially constant below T_{OO}, so we take Δ to be independent of temperature there. In TiOCl, however, the superstructure reflection (0, 1.5, 0) varies strongly with temperature.[23] This indicates that the dimerization changes significantly at temperatures below T_{c2}. The structural dimerization gives alternating exchange constants along the chain $J_{1,2} = J(1 \pm \delta)$ and we take δ to vary linearly with the structural dimerization.[36] For small dimerizations, as is the case in TiOCl, the intensity of this reflection is proportional to δ^2. The spin gap is proportional[36] to $\delta^{2/3}$, or if the logarithmic corrections are included and a power law is deduced,[37] $\delta^{0.65}$; we use the former value for our calculations and found that the parameters obtained were insensitive to small changes in this power law. Thus, from the published peak intensities,[23] we obtain an estimate of the temperature dependence of the spin gap (Fig. 3, inset) that we can use to fit to both the μSR and magnetic susceptibility data.

The temperature variation of λ is shown in Fig. 2(a) (NTSO) and of Λ in Fig. 3(a) (TiOCl). At low temperature, one possible relaxation mechanism for the muon spin is via thermally activated electronic spins fluctuating across the spin gap.[38] The data for both materials show that an additional temperature-independent relaxation mechanism causes saturation of the relaxation rate at low temperature, so we parametrize the temperature dependence of λ using

$$\lambda(T) = \lambda_0/[1 + A\exp(-2\Delta/T)], \quad (3)$$

where A is a constant, and similarly for Λ.

For NTSO, Eq. (3) fits the data quite well at temperatures up to T_{OO}. There is no sharp change in λ at T_{OO}, perhaps due to the effects of short-range correlations enhancing spin-singlet fluctuations at temperatures near the transition.[11] Fitting the λ values up to T_{OO} gives $2\Delta = 700 \pm 100$ K.

In contrast, for TiOCl, the behavior is more complex. We see no significant changes in Λ either at T_{c2} or at $T^* \simeq 120$ K, the temperature at which a pseudogap has been proposed.[8,20,25] However, Λ rises sharply below T_{c1} and we are able to fit the Λ values below T_{c1} to Eq. (3), yielding

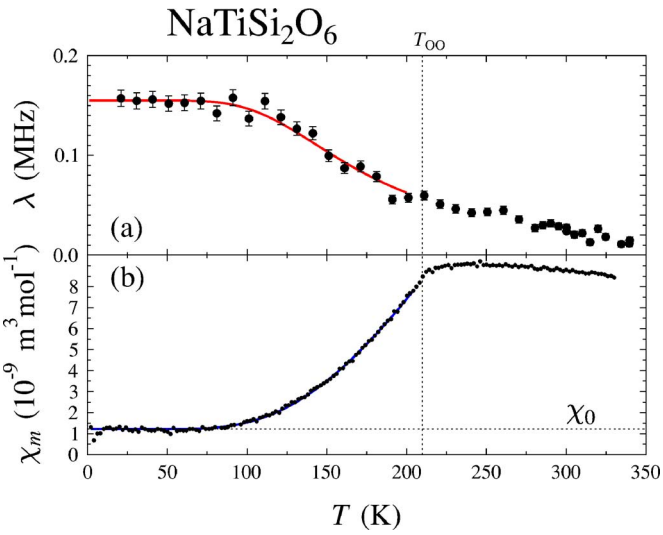

FIG. 2. (Color online) Fitted data for NTSO. (a) Electronic relaxation rate λ. The red solid line is a fit to Eq. (3). (b) Magnetic susceptibility χ_m after subtraction of the low-temperature Curie tail, with the temperature-independent response marked χ_0. The blue line is a fit to Eq. (4).

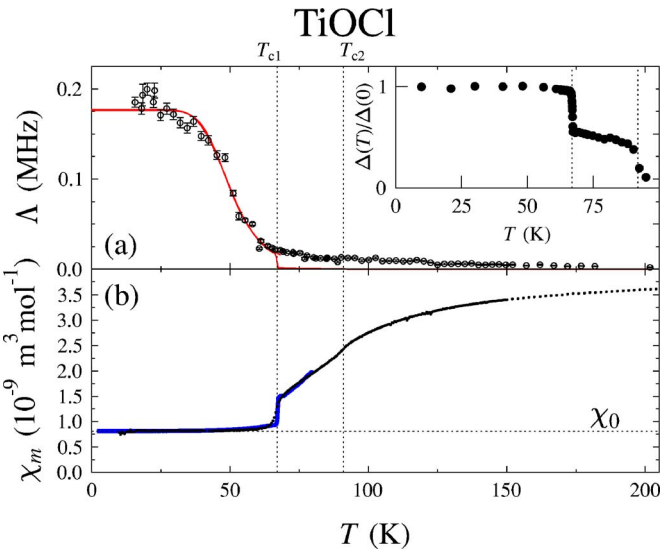

FIG. 3. (Color online) Fitted data for TiOCl. (a) Electronic relaxation rate Λ. The red solid line is a fit to Eq. (3) below T_{c1}. (Inset) Temperature dependence of the effective spin gap derived from x-ray diffraction data, (Ref. 23) as described in the text. (b) Magnetic susceptibility χ_m after subtraction of the low-temperature Curie tail. The solid blue line is the fit, described in the text, using Eq. (4) with the spin gap values shown in the inset, fitting up to 80 K. The temperature-independent response is marked χ_0.

$2\Delta = 440 \pm 60$ K. Figure 3 shows that our model for the spin gap only succeeds in describing the data up to T_{c1}, suggesting that other relaxation processes become significant above this temperature. Using the square root exponential $\exp(-\sqrt{\Lambda t})$ allows us to parametrize the data consistently to low temperature and shows that the activation of the fluctuations continues outside the fast fluctuation regime. Our value for the spin gap also agrees with the values previously measured using other techniques.[8,20,25,26]

To gain a rough estimate of n, the concentration of unpaired spins within the samples, from the μSR data, we followed the method used in Ref. 31. We assume the unpaired spins to have $S=1/2$, given the spin of the Ti^{3+} ions, although a defect in a chain would produce two free spins and any impurity creating the defect may itself have a spin, so our value will be larger than the concentration of defects and impurities. Measurements were made in small magnetic fields, $\leqslant 5$ mT for NTSO and 2 and 10 mT for TiOCl, applied along the direction of the initial muon spin polarization at low temperature. The asymmetry spectra were fitted using the product of a longitudinal field Kubo-Toyabe function[27] and an exponential relaxation to model the weak dynamics.[31] Fitting the data to this function, we can extract the width of the distribution of local fields at the muon site. From this we estimate the concentration of unpaired spins surrounding the muon using the expression given in Ref. 39 and adapted to the muon case in Ref. 31. For NTSO, this gives an impurity concentration $n=1.7(3)\%$, and for TiOCl we find $n=1.1(2)\%$.

Magnetic susceptibility χ measurements [Figs. 2(b) and 3(b)] showed that our samples were comparable with those used in previous studies. From the low-temperature Curie tail in χ, we estimate the concentration of unpaired spins to be $n=2.10(4)\%$ for NTSO and $0.6(1)\%$ for TiOCl. The approximate agreement between these values and those obtained from μSR supports our model describing the muon depolarization. The Curie tail was subtracted from χ and the remainder, χ_m, fitted to a sum of a term due to the thermal activation of spins across the spin gap of magnitude 2Δ and a temperature-independent term χ_0, i.e.,

$$\chi_m = C \exp(-2\Delta/k_B T) + \chi_0. \quad (4)$$

The result of fitting Eq. (4) to the data for NTSO is shown in Fig. 2(b). Using a constant value for the spin gap in NTSO, this gives an excellent parametrization of the data from low temperature to 200 K and leads to a value of the spin gap of $2\Delta = 595(7)$ K, somewhat smaller than what the μSR measurements suggest. For TiOCl, the temperature-dependent spin gap described above was used for 2Δ in Eq. (4), and the fit is plotted in Fig. 3(b). Given that this model should only work in the limit $\Delta \gg T$,[36] it can be seen to be remarkably successful in describing the form of the data below 80 K, showing that the susceptibility is indeed varying with the structural dimerization. Fitting to the data at temperatures below 80 K leads to a value for the spin gap of $2\Delta = 270(10)$ K. The temperature-independent contribution to the susceptibility was $\chi_0 = 1.21(1) \times 10^{-9}$ m^3 mol^{-1} for NTSO, consistent with previous data.[6] For TiOCl, we found $\chi_0 = 0.82(1) \times 10^{-9}$ m^3 mol^{-1}.

Using both μSR and magnetic susceptibility measurements, we have obtained values for the spin gaps in both NTSO and TiOCl, as well as determined the concentration of unpaired spins in each material. Our results are summarized in Table I. We see that both techniques give consistent results for the concentration of unpaired spins, supporting our model for the muon depolarization. The values of the spin gaps are

TABLE I. Parameters derived from μSR and magnetic susceptibility data χ. The spin gap 2Δ, the concentration of unpaired spins n, and $T_{mf}=2\Delta/3.53$, the temperature at which mean-field theory estimates that the SP transition should occur, given the value of 2Δ measured by μSR.

Sample	NTSO	TiOCl
2Δ (K) μSR	700(100)	440(60)
2Δ (K) χ	595(7)	270(10)
n (%) μSR	1.7(3)	1.1(2)
n (%) χ	2.10(4)	0.6(1)
T_{mf} (K)	200(25)	125(10)

not in such good agreement, with the μSR values being a little larger than those from the susceptibility measurements, perhaps because the muon data may include the effect of some other relaxation processes not accounted for in Eq. (3).

For NTSO, we are able to parametrize the data from both techniques using the assumption of constant dimerization. The two techniques agree reasonably well in the value of the spin gap, $2\Delta=700(100)$ K, and we can compare this to the transition temperature of $T_{OO}=210$ K using the mean-field result.[1] We find that the value of the gap fits the mean-field relation very well, consistent with the dimerization being driven by a spin-Peierls mechanism. However, the predicted gap value for an orbital-Peierls transition ($\Delta \sim J$) (Ref. 12) is also in excellent agreement with our value, as are the predictions of Hikara and Motome.[11] From the magnitude of the spin gap, we cannot distinguish between the two possible mechanisms for the transition in this material. Measurements of the orbital occupation will be necessary to make a decisive conclusion as to the mechanism.

For TiOCl, our model based on the measured dimerization gives a consistent description of the form of both data sets. The μSR measurements show a sharp, thermally activated increase in the muon relaxation rate below $T_{c1}=67$ K. Fitting the data below T_{c1} leads to a value of the spin gap of $2\Delta=440(60)$ K. We also attempted a different parametrization for the data, which assumes that the spin fluctuations are fast compared with the distribution of magnetic fields, as is the case in NTSO. Fitting Eq. (1) to the asymmetry data, and the λ values to a simple activation, $\lambda \propto \exp(2\Delta/T)$, leads to $2\Delta=420(40)$ K. However, Eq. (1) fails to describe the raw data at temperatures lower than 10 K below T_{c1}, so this method is less satisfactory for measuring the spin gap. The method only works over such a limited range because of the large gap relative to T_{c1} and the width of the magnetic-field distribution. Above T_{c1} other spin fluctuation processes come into play on the μSR time scale, and since there is negligible variation in the μSR relaxation rate, we can no longer compare it to the model. Fitting the magnetic susceptibility data is much more successful just above T_{c1}; we can describe the jump in the susceptibility at the transition and also the behavior up to 80 K, where the magnitude of the spin gap becomes comparable to the temperature. The gap 2Δ measured by μSR agrees with those measured using other techniques[8,20,25,26] and, via naive application of the mean-field theory of the SP transition, corresponds to $T_{SP}=2\Delta/3.53=125(10)$K. Intriguingly, this estimate of T_{SP} is close to the temperature where pseudogap formation has been proposed.[8,20,25] A similar application of the mean-field theory to our value of 2Δ obtained from susceptibility yields $T_{SP}\approx 75$ K, which lies between T_{c1} and T_{c2}. These results may suggest different energy scales associated with the pseudogap and the dimerization, illustrating the complex nature of TiOCl. Further investigation of this system, using other techniques, may illuminate this issue.

In conclusion, we have estimated the magnitude of the spin gap in the two Ti^{3+} chain compounds $NaTiSi_2O_6$ and TiOCl using both μSR and magnetic susceptibility measurements. These values are in reasonable agreement in the former compound, but in the latter, the disparity hints at two separate energy scales. Both techniques give values for the concentration of unpaired spins in agreement with one another. Our measurements also demonstrate the complementary information that can be discovered about spin-gapped materials by investigating both their microscopic and bulk properties.

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