Novel Spin-Gap Behavior in Layered $S = \frac{1}{2}$ Quantum Spin System TiOCl

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We have investigated the spin fluctuations and their interplay with lattice instabilities in a layered $S = \frac{1}{2}$ quantum spin system TiOCl. Our $^{47,49}$Ti and $^{35}$Cl NMR data demonstrate a pseudo spin-gap behavior below $T^* = 135K$, followed by successive phase transitions at $T_{c1} = 94K$ and $T_{c2} = 66K$ into the singlet ground state with an unusually large energy gap $E_g = 430K$. The broad distribution of the local electric field gradient in the intermediate phase between $T_{c1}$ and $T_{c2}$ suggests unconventional spin and lattice (probably orbital) states with an emerging spin-gap.

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The provocative proposal that the mechanism of high temperature superconductivity in layered cuprates may be related to the exotic properties of low dimensional quantum spin systems, such as the RVB (Resonanting Valence Bond) state [1], has been a major driving force behind the rapid advance of quantum magnetism. Naturally, the initial emphasis was placed on understanding materials involving Cu$^{2+}$ ions with the 3d$^9$ configuration ($S = \frac{1}{2}$) [2,3]. More recently, $S = \frac{1}{2}$ quantum magnets involving V$^{4+}$ [4-6] and Ti$^{3+}$ [7-12] ions with 3d$^1$ configurations have been attracting strong attention. Potential interests include the realization of doped metallic states in 3d$^1$ Mott insulators, and ultimately, superconductivity [6]. In addition, the near degeneracy of the $t_{2g}$-orbitals often gives rise to the orbital and/or charge ordering [13]. In the orbital ordered state, the configuration of the occupied 3d$_{xy,yz,zx}$-orbitals exhibits a long range order. On the other hand, the valence of ions differs site by site in charge ordered states. The additional orbital and charge degrees of freedom make the underlying physics of 3d$^1$ quantum spin systems more intriguing, yet more complicated. A fascinating example is a mixed valence system NaV$_2$O$_5$ [5,14] (the average valence of V-ions is +4.5). NaV$_2$O$_5$ undergoes orbital and charge ordering at $T_c = 34K$, where a large energy gap $E_g = 98K$ opens [14-17]. The ratio $2E_g/k_BT_c = 6$ is much larger than the BCS value 3.5 expected for conventional spin-Peierls transitions with lattice-dimerization. Intensive theoretical and experimental efforts have been underway to understand the exotic phase transition.

An equally exciting new avenue to investigate $S = \frac{1}{2}$ quantum spin systems with 3d$^1$ electrons is the titanates involving Ti$^{3+}$ ions. Starting from the metal-insulator transition in Sr$_{1-x}$La$_x$TiO$_3$ [7], growing efforts are under way in search for a new form of quantum magnetism in titanates: strong orbital fluctuations in LaTiO$_3$ [8]; a quasi 1D $S = \frac{1}{2}$ chain system (Na$_x$Lia$_x$)$_2$Ti$_2$O$_7$ [9]; 3D Pyrochlore system MgTi$_2$O$_4$ [10]; and a quasi-2D layered system TiOCl [11,12].

Among these titanates, the TiOCl system has particularly unique characteristics. First, Ti$^{3+}$O$_2^-$ form bilayers separated by Cl$^-$ bi-layers. The quasi-2D layered structure may be considered a close analogue to those realized in high $T_c$ cuprates. In fact, Beynon and Wilson [11] reported the very little temperature dependence in uniform susceptibility $\chi(T)$, and discussed the possible realization of a RVB ground state in the Mott-insulator. They also noted that $\chi(T)$ is very sensitive to impurities, and demonstrated that a Sc$^{3+}$ ion ($S = 0$) substituted into a Ti$^{3+}$ site ($S = \frac{1}{2}$) gives rise to a localized spin $S = \frac{1}{2}$, in analogy with creation of a free spin by Zn$^{2+}$ ($S = 0$) substituted into Cu$^{2+}$ ($S = \frac{1}{2}$) sites in cuprates. Second, in a very recent report, Seidel et al. observed a sharp, nearly isotropic drop of $\chi(T)$ below ~100K in defect-free samples, signaling the emergence of an energy gap [12]. The drop in $\chi(T)$ is even more pronounced in high quality single crystals. Since $\chi(T)$ above ~200K can be fitted with a $S = \frac{1}{2}$ Heisenberg chain model with the nearest neighbor exchange interaction $J = 660K$, Seidel et al. proposed, based on LDA+U calculations, that the effective dimension of the TiO layers are reduced from 2D to 1D by an orbital order at Ti$^{3+}$ sites along the a- or b-axis. The gapped behavior of $\chi(T)$ was attributed to a spin-Peierls transition [12]. Third, but related to the second point, the near degeneracy of the energy levels of different 3d$^1$ orbital configurations without mixed-valence nature might make TiOCl an ideal model system to investigate spin-Peierls-like transitions with additional orbital degrees of freedom but probably without charge order.

In this Letter, we report the first NMR investigation of TiOCl. While the spin-Peierls transition in CuGeO$_3$ (without orbital and charge degrees of freedom) and the exotic order in NaV$_2$O$_5$ (with orbital and charge degrees of freedom) have seen many detailed microscopic investigations, to the best of our knowledge this is the first successful microscopic experiments reported for TiOCl. We demonstrate that TiOCl reveals a unique spin-gap behavior accompanied by lattice instabilities, and undergoes successive phase transitions at $T_{c1} = 94 \pm 2K$ and $T_{c2} = 66 \pm 2K$. Unlike CuGeO$_3$ and NaV$_2$O$_5$,.....
the fluctuation effects in TiOCl are so strong above $T_c$ that a pseudo spin-gap manifests itself as high as $T^* = 135 \pm 10K$. Moreover, our observation of a broad continuum in the NMR lineshape data indicates that the intermediate phase between $T_{c1}$ and $T_{c2}$ is not a simple, dimerized state in 1D. Below $T_{c2}$, TiOCl undergoes a first order phase transition to a fully gapped state (rather than to the gapless RVB state) with an extraordinarily large energy gap $E_g = 430 \pm 60K$. The unusually large energy gap $(2E_g/k_B T_{c1,c2} = 10 \sim 15)$ as well as the presence of the intermediate state between $T_{c1}$ and $T_{c2}$ suggest that the observed phase transitions are not conventional spin-Peierls transitions, and point towards the significance of the roles played by the additional orbital degrees of freedom over the entire temperature range.

Our TiOCl single crystals were synthesized by standard vapor-transport techniques from TiO$_2$ and TiCl$_3$ [12]. A large number of very thin, flaky single crystals with typical dimensions of 2mm$\times$2mm were assembled on a Macor sample holder. NMR measurements were conducted by applying an external magnetic field in parallel with the aligned crystal c-axis. Random alignment within the TiO-plane prevented us from conducting measurements along the a- and b-directions. We emphasize that, unlike $^{63,65}$Cu and $^{51}$V NMR, the sensitivity of $^{47,49}$Ti NMR is notoriously low [18]. Very short transverse relaxation times $T_2$ at Ti sites and the small volume of the available crystals made the NMR measurements even more difficult. We needed to average spin-echo signals up to $\sim 10^6$ scans to obtain a reasonable signal to noise ratio. In general, NMR signal intensities increase as $1/T$ in proportion to the Boltzmann factor. However, the exponentially growing spin-lattice relaxation time $T_1$ below $T_{c1}$ slows down the NMR pulse-sequence, hence the measurements at lower temperatures were equally difficult and time consuming. Despite our intensive efforts, we have been able to find $^{47,49}$Ti NMR signals only for the central transition from the $I_z = +\frac{3}{2}$ to $-\frac{3}{2}$ state. The detection of $^{35}$Cl NMR signal was somewhat easier, and we did manage to find the $I_z = \pm \frac{3}{2}$ to $\pm \frac{1}{2}$ transitions above $T_{c1}$ [19]. All the nuclear spin-lattice relaxation data were deduced by fitting the nuclear spin recovery after an inversion $\pi$-pulse to the standard rate equations. We confirmed that $^{47}$Ti (nuclear spin $I = 5/2$) and $^{49}$Ti (nuclear spin $I = 7/2$) NMR gives identical $1/T_1$. Given that the magnetic recovery process of nuclear magnetization $M(t)$ is dominated by different terms for $^{47}$Ti ($M(t) \sim \exp[-15t/T_1]$) and $^{49}$Ti ($M(t) \sim \exp[-28t/T_1]$), we conclude that $1/T_1$ is dominated entirely by magnetic fluctuations at all temperatures. The difference in the recovery characteristic of $M(t)$ also helped us identify the pairs of $^{47}$Ti and $^{49}$Ti lines below $T_{c2}$, where the NMR lines split into doublets.

The experimental information on the spin degrees of freedom is summarized in Fig. 1. Quite generally, the $^{47,49}$Ti nuclear spin-lattice relaxation rate, caused by low frequency magnetic fluctuations may be expressed as [20],

$$\frac{1}{T_1} = T \sum_\mathbf{q} |F(\mathbf{q})|^2 \frac{1}{\omega_n},$$

where $F(\mathbf{q})$ is the form factor of the electron-nucleus hyperfine couplings, and $\chi''(\mathbf{q}, \omega_n)$ is the imaginary part of the dynamical susceptibility at the observed NMR frequency $\omega_n$. $1/T_1$ appears to asymptote to a constant value near 300K, $1/T_1 \sim 1400 \text{ sec}^{-1}$. This implies that $\chi''(\mathbf{q}, \omega_n)$ asymptotes to a Curie law at higher temperatures. This is consistent with the behavior expected for typical $S = \frac{1}{2}$ 1D Heisenberg chains such as Sr$_2$CuO$_3$ [21]. However, we caution that $1/T_1 \sim \text{const.}$ may also be expected for $S = \frac{1}{2}$ 2D Heisenberg model [22].

In general, the growth of short-range order enhances low frequency spin fluctuations (hence $1/T_1(T)$) with decreasing temperature in the absence of a gap in the spin excitation spectrum. The most striking feature in Fig.1 is that $1/T_1T$ begins to decrease below $T^* \sim 135K$. This implies that low frequency spin fluctuations are suppressed below $T^*$, by almost two orders of magnitude between $135K$ and $65K$. Interestingly, the observed behavior of $1/T_1T$ is qualitatively similar to the pseudo-gap phase in underdoped high $T_c$ cuprates. Needless to say, it does not necessarily imply that the underlying mechanism is identical.

We can also probe the lattice degrees of freedom by observing the EFG (Electric Field Gradient) reflected on NMR lineshapes. In Fig.2, we present the $^{47,49}$Ti and $^{35}$Cl NMR lineshapes for the central transition. We observed a single NMR line for both Ti and Cl down to $T_{c1} = 94 \pm 2K$. For $^{35}$Cl, we also managed to detect $I_z = \pm \frac{3}{2}$ to $I_z = \pm \frac{1}{2}$ satellite transitions, but again there was only one kind of signal [19]. These results indicate that there is only one kind of Ti and Cl site in TiOCl within our experimental resolution, and rule out any potential orbital order configurations above $T_{c1}$ that would lead to more than one inequivalent sites. Below $T_{c1}$, both $^{47,49}$Ti and $^{35}$Cl NMR central lines begin to broaden, signaling a second order phase transition. We confirmed that the magnitude of the $^{35}$Cl NMR line splitting is inversely proportional to the external magnetic field. Therefore the line splitting is caused by the second-order nuclear quadrupole interaction with the EFG. We also found that the drop of $1/T_1T$ is accelerated below $T_{c1}$. In addition, close inspection of the $\chi(T)$ data reported in [12] reveals a kink at $T_{c1}$, followed by a rapid decrease with temperature with positive curvatures. These results suggest that a clear gap structure emerges in the spin excitation spectrum at $T_{c1}$, accompanied by a static
distortion of the lattice. The NMR lineshape exhibits a broad continuum below $T_{c1}$ down to $T_{c2}$ as summarized in Fig.3(b). The broad continuous distribution of the local EFG environment implies the presence of numerous inequivalent Ti and Cl sites in the TiOCl lattice. The most plausible scenario is that the emergence of the spin-gap at $T_{c1}$ is accompanied by an orbital-order (possibly incommensurate). That is, the phase transition at $T_{c1}$ is not a simple spin-Peierls transition due to lattice dimerization, even though the well-developed short-rage spin order below 400K and the gapped behavior of $\chi(T)$ below ~100K [12] suggest the contrary.

We found additional evidence for the involvement of the lattice in the phase transition at $T_{c1}$ by $^{35}$Cl nuclear relaxation data $351/T_1$ as shown in Fig.3(a). $351/T_1$ is two orders of magnitude slower than $1/T_1$ at 47,49Ti-sites. This implies that the magnetic hyperfine coupling of $^{35}$Cl nuclear spins with Ti 3d electron spins is at least by an order of magnitude smaller. The qualitatively different temperature dependence between $351/T_1$ [see Fig.3(a)] and $1/T_1$ [see Fig.1(a)] suggests that slowing of EFG fluctuations below $T^*$ toward the phase transition at $T_{c1}$ causes the cusp of $351/T_1$ at $T_{c1}$ [24]. Even more straightforward evidence is that the $^{35}$Cl spin-echo decay (transverse $T_2$ relaxation) in Fig.3(c) and (d) shows typical motional narrowing effects below $T^*$ towards $T_{c1}$ due to lattice softening. The slow lattice dynamics at or below the $^{35}$Cl NMR frequency (37.6 MHz) transforms the spin echo-decay to Lorentzian-like as $T_{c1}$ is approached. Taken together with the precursive suppression observed for $1/T_1T$ below $T^*$ in Fig.1(a), we conclude that the drastic softening of the lattice below $T^*$ drives the observed pseudo spin-gap behavior prior to the actual second-order phase transition at $T_{c1} = 94K$. The high onset temperature ~200K of the gradual decrease of $1/T_1$ suggests that phonon softening at higher frequency scales begins at much higher temperature. At $T_{c2}$, the continuum of the $^{35}$Cl and $^{47,49}$Ti NMR lineshape suddenly collapses into doublets, whose line positions correspond to the two extrema observed above $T_{c2}$. This strongly suggests that the unit cell of TiOCl has two and only two inequivalent Ti and Cl sites below $T_{c2}$ [25]. The low-frequency Ti 3d spin fluctuations exhibit an activation behavior below $T_{c2}$, as shown in Fig.1(b). From the fit to an exponential form, $1/T_1T \sim \exp(-E_g/k_B T)$, we deduce the energy gap $E_g = 430 \pm 60K$. These results are consistent with the formation of a singlet ground state at $T_{c2}$ by lattice dimerization. Our results are also consistent with the recent observation of doubling of the unit cell along the b-axis at 66 ± 1K by Y.S. Lee et al. based on x-ray scattering measurements [26]. On the other hand, there are many experimental signatures which are at odds with conventional second order spin-Peierls transitions. $1/T_1$ [Fig.1], the NMR lineshapes [Fig.2], and $351/T_1$ [Fig.3(a)] change discontinuously at $T_{c2}$. $^{35}$Cl spin-echo decay curve also changes suddenly to a slow Gaussian type at $T_{c2}$ [Fig.3(d)]. This indicates that the soft vibration of the lattice disappears suddenly below $T_{c2}$. All these NMR results as well as the discontinuous change in $\chi(T)$ [12] and the x-ray data [26] at $T_{c2}$ indicate that the phase transition at $T_{c2}$ is first order. Furthermore, the observed energy gap is unusually large, $2E_g/k_B T_{c1,c2} = 10 \sim 15$. In the case of conventional, mean-field spin-Peierls gap, one would expect the ratio to be close to the BCS value, $2E_g/k_BT_c = 3.5$, as observed for CuGeO$_3$ ($2E_g/k_BT_c = 3.3$ [27,28]). The observed ratio in TiOCl is even larger than that for NaV$_2$O$_5$, $2E_g/k_BT_c \sim 6$ [14,17]. It is important to realize that $E_g$ is comparable to the apparent exchange energy $J = 660K$ estimated by the 1D fit of $\chi(T)$ [12]. Such a large magnitude of the energy gap $E_g$ strongly suggests that the spin excitations from the singlet ground state is dressed by other electronic degrees of freedom, most likely of the orbital origin.

To summarize, TiOCl is a rather unique layered $S = \frac{1}{2}$ quantum-material with a pre-existing pseudo spin-gap above $T_{c1}$, the unconventional intermediate spin and lattice (probably orbital) states between $T_{c1}$ and $T_{c2}$, and a first order phase transition into a singlet ground state with an unusually large energy gap. At first sight, the strong fluctuation effects evidenced in the pseudo-spin-gap behavior suggest a genuinely 1D nature of the TiOCl along the a- or b-axis, achieved by an orbital order well above $T_{c1}$. We recall that the pre-existing orbital order above $T_{c1}$ may reduce the effective dimensions of the TiO layer from 2D to 1D, as suggested by Seidel et al. based on LDA+U calculations [12]. On the other hand, the additional orbital degrees of freedom along the two orthogonal directions within the 2D TiO-layers may cause strong orbital fluctuations, which could effectively suppress the tendency towards a spin-Peierls transition at finite temperature. In such a scenario, the manifestation of the pseudo spin-gap above $T_{c1}$ may be the consequence of the suppression of the spin-Peierls transition, and the successive phase transitions at $T_{c1}$ and $T_{c2}$ may arise from a competition between different orbital orders. In addition, if the second nearest-neighbor exchange interaction $J'_{a}$ in the zig-zag chain structure along the a-axis (see Fig.1(c) in [12]) exceeds 0.241$J_{a}$ (where $J_{a}$ being the nearest-neighbor exchange interaction along the a-axis), a spontaneous spin dimerization along the a-axis may be favoured [29] over the unit-cell doubling along the b-axis observed below $T_{c2}$, introducing frustration. In any case, the unprecedented behavior of TiOCl points towards the crucial roles played by the orbital degrees of freedom and their fluctuations below ~200K. Recalling that TiOCl is not a mixed-valence system such as NaV$_2$O$_5$, TiOCl may be an ideal model spin-Peierls system with additional orbital degrees of freedom, and we call for further microscopic studies.

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FIG. 1. (a) $1/T_1$ (○) and $1/T_1T$ (●) at $^{47,49}$Ti sites. $1/T_1$ was measured at the center peak for $T \lesssim T_{c1}$. Solid and dashed curves are guides for eyes. (b) The same $1/T_1T$ data plotted in a semi-log scale. Solid line is the best exponential fit. $1/T_1T$ was identical for the doublets below $T_{c2}$.

FIG. 2. NMR lineshapes of the $I_z = \pm \frac{1}{2}$ to $-\frac{1}{2}$ central transition for $^{35}$Cl (left panels) and $^{47,49}$Ti (right panels). The FFT envelope was obtained at 9 Tesla by repeating spin-echo measurements at several frequencies.

FIG. 3. (a) $35/1/T_1$. (b) $^{35}$Cl NMR frequencies observed at 9 Tesla. Dashed lines represent continuum. Solid error bars represent the frequency range corresponding to the half-intensity. (c) $^{35}$Cl NMR spin-echo decay observed at the main peak, as a function of the pulse separation time $2\tau$ between 90-180 degree R.F. pulses above $T_{c1}$, and (d) below $T_{c1}$. Solid curves are guides for eyes.
Figure (a) shows the plot of $1/T_1 T$ versus $T$ [K] with $T_c1$ and $T_c2$ marked. The line is marked with $T^*$.

Figure (b) is a semi-logarithmic plot of $1/T_1 T$ versus $1/T$ [K$^{-1}$] with $T_c1$, $T_c2$, and $Eg=430K$ marked. The line is marked with $T^*$. 

Both plots are with units $[sec^{-1}K^{-1}]$ and $[msec^{-1}]$. 

(a) (b)
Figure (a) shows the variation of $T_1/T_2$ with temperature $T$ for different spin-echo intensities. Figure (b) displays the frequency $f$ as a function of temperature $T$. Figure (c) illustrates the spin-echo intensity for various temperatures $T$. Figure (d) presents the relationship between the spin-echo intensity and the time delay $2\tau$. The critical temperatures $T_c1$ and $T_c2$ are indicated in each graph.