Detection of magnetic order in the $S=1$ chain compound $LiVGe_2O_6$ using implanted spin-polarized muons

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(Received 29 January 2003; published 12 June 2003)

The temperature dependence of the internal field in the one-dimensional $S=1$ chain compound $LiVGe_2O_6$ has been measured using muon-spin rotation. Two muon-spin-precession frequencies are observed, corresponding to two distinct stopping sites. The results demonstrate that $LiVGe_2O_6$ undergoes a second-order phase transition to long-range magnetic order at $T_N=24.5$ K. In the paramagnetic regime, we find exponential muon-spin relaxation which is dominated by fluctuations of the ^{51}V nuclear moments.

DOI: 10.1103/PhysRevB.67.224411 PACS number(s): 76.75.+i, 75.10.Pq

The study of one-dimensional quantum spin chains has been of strong theoretical and experimental interest in recent years. On the basis of field-theoretic models Haldane conjectured that antiferromagnetic (AF), integer-spin chains possess a spectrum in which there is a nonzero energy gap (the Haldane gap) between the ground state and the lowest-lying excited states.[1] This prediction has been verified experimentally in a number of $S=1$ chains, including $CsNiCl_3$,[2] $AgVP_2S_6$,[3] and $YBaNiO_5$.[4,5] In the half-integer spin case, the excitation spectrum is gapless, unless a magnetoelastic coupling causes a spin-Peierls transition[6,7] and opens a gap by dimerizing the chain. Spin-Peierls ground states have been observed in a number of $S=\frac{1}{2}$ spin-chains, including $CuGeO_3$[8] and $MEM(TCNQ)_2$.[9]

The discovery of a new $S=1$ quasi-one-dimensional Heisenberg spin system, $LiVGe_2O_6$, was recently reported.[10] This compound showed unexpected behavior which is substantially different from that of previously investigated $S=1$ model systems. The nature of the ground state has been a matter of some controversy. A discontinuous change in gradient of the temperature dependence of the susceptibility was interpreted as a spin-Peierls phase transition.[10] A preexisting Haldane gap would normally preclude such a spin-Peierls transition in integer spin chain systems, but it was suggested that the Haldane gap was closed by the presence of a significant biquadratic exchange.[11] This interpretation has stimulated much theoretical interest.[12,13] However, ^7Li nuclear-magnetic-resonance (NMR) measurements on $LiVGe_2O_6$ appear to be more consistent with a first-order phase transition to a magnetic phase which could be either AF or modulated.[14] There is also a peak in the specific heat which is indicative of a clear phase transition.[15] X-ray and neutron-diffraction experiments[15] showed that no distortion takes place, but indicated a second-order phase transition to an AF state, a result which is in agreement with a recent high-field NMR study.[16] In this paper, we demonstrate, using muon-spin rotation experiments, that $LiVGe_2O_6$ undergoes a second-order phase transition to an AF state. We observe that the local magnetic field at the muon sites is quasistatic on the muon time scale. Using this technique, we measure the temperature dependence of the internal field and extract a critical exponent consistent with the three-dimensional ordering. Our results also shed light on the possible rôle of orbital fluctuations.

$LiVGe_2O_6$ has a monoclinic structure with space group $P2_1/c$[10] and consists of isolated chains of VO_6 octahedra, joined at the edges and lying along the c direction. The chains are separated by nonmagnetic GeO_4 tetrahedra, so that the interchain coupling is much smaller than the intrachain coupling. The Vanadium ions exist in the V^{3+} oxidation state ($3d^2$) with an effective $S=1$ moment.[10,14] Polycrystalline samples were prepared by heating stochiometric quantities of GeO_2, Li_2O, and V_2O_3 in a sealed, evacuated Pt tube, with thermal treatment similar to that described elsewhere.[14] The muon-spin rotation (μSR) experiments were carried out using the πM3 beamline at the Paul Scherrer Institute (PSI) in Switzerland and the EMU beamline at the ISIS Pulsed muon facility in UK. In our μSR[17] experiment, spin polarized positive muons (μ^+, momentum 28 MeV/c) were implanted into polycrystalline $LiVGe_2O_6$. The muons stop quickly (in $<10^{-9}$ s), without significant loss of spin polarization. The observed quantity is then the time evolution of the muon spin polarization, which can be detected by counting emitted decay positrons forward f and backward b of the initial muon-spin direction; this is possible due to the asymmetric nature of the muon decay,[17] which takes place in a mean time of 2.2 μs. In our experiments, positrons are detected by using scintillation counters placed in front of and behind the sample. We record the number of positrons detected by forward (N_f) and backward (N_b) counters as a function of time and calculate the asymmetry function $G_z(t)$ using

$$G_z(t)=\frac{N_f(t)-\alpha_{exp}N_b(t)}{N_f(t)+\alpha_{exp}N_b(t)}, \quad (1)$$

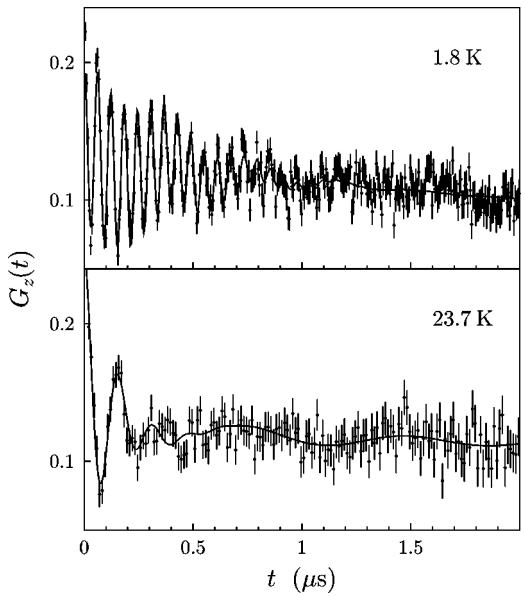

FIG. 1. Zero-field μSR data (PSI) for $LiVGe_2O_6$ at 1.8 K. Two precession frequencies are clearly visible.

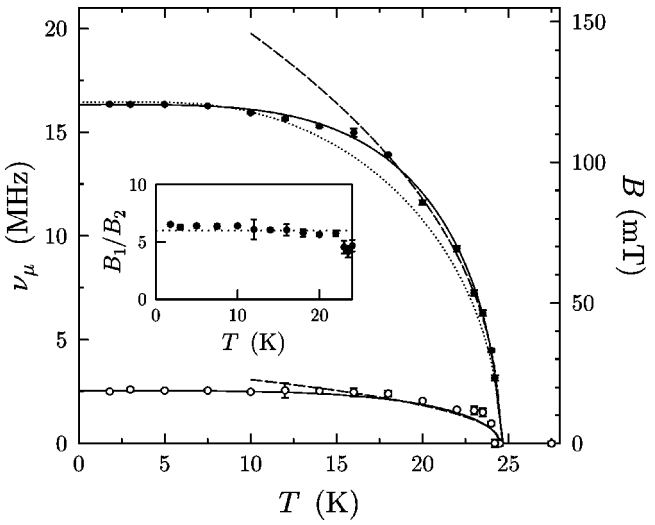

FIG. 2. Temperature dependence of the muon-spin precession frequency $\nu_\mu = \gamma_\mu |B|/2\pi$ for each of the two muon sites in $LiVGe_2O_6$. The corresponding value of the internal field is also shown. The lines are fits to the data (see text). The inset shows the ratio of the fields at the two sites as a function of temperature (this is approximately constant except close to T_N where the frequencies become difficult to determine precisely).

where α_{exp} is an experimental calibration constant and differs from unity due to nonuniform detector efficiency. The quantity $G_z(t)$ is then proportional to the average spin polarization $P_z(t)$ of muons stopping within the sample. The former quantity has a maximum value less than one since the positron decay is only preferentially, not wholly, in the direction of the muon spin. $P_z(t)$ has a maximum value of one. The muon-spin precesses around a local magnetic field B (with an angular frequency $\gamma_\mu |B|$, where $\gamma_\mu = 2\pi \times 135.5$ MHz T^{-1}).

A polycrystalline sample of $LiVGe_2O_6$ was packed in a silver foil and mounted on a He^4 cryostat situated in the πM3 beamline. The measured asymmetry function may then be fitted using

$$G_z(t) = A_S P_z(t) + A_{Ag}, \tag{2}$$

where A_S and A_{Ag} represent the asymmetry contributions from muons stopping within the sample and silver backing plate, respectively. In a magnetically ordered state, $P_z(t)$ may be written as

$$P_z(t) = \sum_{i=1}^{N} f_i \left[\frac{1}{3} e^{-t/T_1^{(i)}} + \frac{2}{3} e^{-t/T_2^{(i)}} \cos(\gamma_\mu |B_i| t) \right], \tag{3}$$

where the sum is taken over the N possible muon sites, f_i is the fraction of muons stopping at the ith site, and $1/T_1^{(i)}$ and $1/T_2^{(i)}$ are, respectively, the longitudinal and transverse relaxation rates for the muon at the ith site.

Figure 1 shows raw μSR data for $LiVGe_2O_6$ at 1.8 K and at 23.7 K. A precession signal is observed in both traces demonstrating unambiguously that the local field at the muon sites is quasistatic on the microsecond time scale. Two frequencies are clearly visible at both temperatures. Hence, the data can be fitted using Eq. (3) with $N=2$ since the two signals correspond to two separate muon sites. The precession signal corresponds to the entire volume fraction of the sample throughout the ordered temperature region. At 1.8 K, the higher frequency is found to be $\sim$16 MHz and corresponds to 85%–90% of the signal, while the lower frequency is $\sim$2.5 MHz.

The frequency $\nu_\mu = \gamma_\mu |B|/2\pi$ of the two precession signals as a function of temperature is shown in Fig. 2. The frequency of both components follows a similar temperature dependence, and both frequencies fall to zero at 24.5 $\pm$0.1 K which we identify as the Néel temperature T_N. The similar temperature dependences show that the order parameter itself has a unique temperature dependence but the position of the muon sites differently scales the magnitude of the observed frequency in each case. The order parameter varies continuously and falls smoothly to zero at T_N, behavior which is consistent with a second-order phase transition, in agreement with Refs. 15 and 16 but in disagreement with Ref. 14. The solid lines in Fig. 2 are fits using the phenomenological form[18] $\nu_\mu(T) = \nu_\mu(0)[1-(T/T_N)^\alpha]^\beta$, with $T_N = 24.5 \pm 0.1$ K, $\alpha = 4.1 \pm 0.2$, and $\beta = 0.52 \pm 0.02$. For comparison, a mean-field fit is shown as a dotted line. The critical regime can be fitted using $\nu_\mu(T) \propto [1-(T/T_N)]^\beta$ (shown as dashed lines, plotted between 10 K and T_N, although the fits were made to the data only between 20 K and T_N). This yields $\beta = 0.40 \pm 0.05$, in agreement with the behavior of the frequency shift in ^{7}Li NMR on polycrystalline $LiVGe_2O_6$, though a value closer to 0.3 was obtained for a single-crystal specimen.[16] These values are consistent with bulk three-dimensional ordering (the higher β values obtained for the polycrystalline samples in both NMR and μSR experiments may reflect a distribution of T_N[16]).

In many oxides it is found that μ^+ stops about 1 Å from an oxygen anion. We have performed dipole-field calcula-

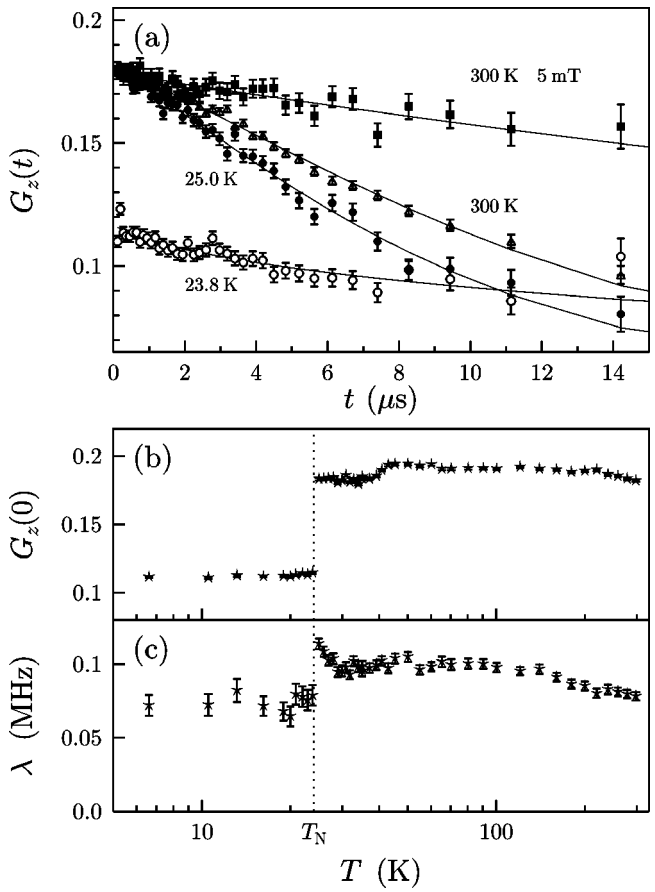

FIG. 3. (a) μSR data (ISIS) for $LiVGe_2O_6$ just below and just above the transition in zero applied magnetic field and at room temperature in zero field and with a longitudinal field of 5 mT. (b) Temperature dependence of the initial asymmetry. (c) Temperature dependence of the muon-spin relaxation rate.

tions using the AF structure proposed by neutron measurements[15] but in which the moments are aligned along the c axis.[16] We find several candidate sites 1 Å from oxygen anions for the higher frequency 16 MHz precession frequency, located within 2–3 Å of the V^{3+} ions. In this structure the V^{3+} ions lie in the planes $z/c=0.25$ and $z/c=0.75$. Candidate sites corresponding to the 2.5 MHz precession frequency are found near the planes $z/c=0$ and $z/c=0.5$, roughly equidistant between nearest V^{3+} ions, and hence experiencing a much smaller dipolar field.

μSR experiments were also carried out at the pulsed muon facility at ISIS and raw data are shown in Fig. 3(a). The small size of the sample necessitated the use of "fly-past" mode, in which muons missing the sample are forced to stop at a large distance away from the main part of the spectrometer, leading to little or no background contribution to the signal. The pulsed nature of the source means that the fast spin precession signals in the ordered state are unobservable due to temporal broadening by the 80 ns pulse width. Thus, the presence of the sharp magnetic transition at 24.5 K is observable as a loss of initial polarization $G_z(0)$ [as seen in Fig. 3(a) by comparing the data for 23.8 K and 25 K]. This loss of polarization can be followed as a function of temperature, as shown in Fig. 3(b).

The observed relaxation can be fitted with a single T_1 for both muon sites so that a fitting function of the form $G_z(t)=G_z(0)e^{-\lambda t}$ is appropriate. Below the transition temperature, the observed relaxation [shown in Fig. 3(c)] is only due to the first term on the right-hand side of Eq. (3). Close to the transition, there is a small peak in relaxation rate corresponding to slowing down of fluctuations. At temperatures well above the transition, there is a little change in spin relaxation rate between 25 K and 300 K [see also Fig. 3(a)]. In the presence of fluctuations at rate ν and in a longitudinal field B_L, the relaxation rate is given by $\lambda=2\Delta^2\nu/(\nu^2+(\gamma_\mu B_L)^2)$ (see, e.g., Ref. 19), where Δ/γ_μ is the width of the local field distribution. We find that the application of a longitudinal field $B_L=5$ mT at 300 K largely quenches the relaxation, demonstrating that ν in this regime is of the order of $\gamma_\mu B_L$, i.e., a few megahertz. The high-temperature relaxation rate in zero field is ~ 0.1 MHz, so that Δ can be estimated, yielding a width of ≈ 0.4 mT. Hence, we conclude that this relaxation is most likely the result of very small, slowly fluctuating moments. These moments cannot be electronic in origin since (i) they are too small and (ii) we expect that the electronic moments will be fluctuating extremely rapidly in the paramagnetic state, probably at the exchange frequency which would be well above the maximum resolvable fluctuation rate resolvable using μSR. The fluctuations of the electronic moments are thus expected to be "motionally narrowed" for $T>T_N$ and hence cannot be responsible for the observed relaxation. The significant nuclear moments in $LiVGe_2O_6$ are ^{7}Li and ^{51}V. It is known that the ^{7}Li nuclear moments would be effectively static on the muon time scale since they have $T_1>0.01$ s for all temperatures studied.[16] A static nuclear moment distribution would, however, yield Gaussian muon-spin relaxation, while the measured relaxation is exponential. Recent experiments[16] have searched for a ^{51}V NMR signal which should be easily observable since the nuclear moment of ^{51}V is large. The absence of such a signal has been attributed to a very short $T_1<2$ μs. The width of the field distribution at the muon site is also in good agreement with what might be expected for ^{51}V moments by scaling the low-temperature value of the internal field due to the electronic V moments by the ratio of the ^{51}V nuclear moment ($5.15\mu_N$) to the known electronic moment ($1.14\mu_B$). We, therefore, conclude that the $T>T_N$ relaxation is dominated by fluctuating ^{51}V moments.

One possible interpretation for the observed susceptibility in $LiVGe_2O_6$ involves midgap states and removes the need to invoke a magnetic phase transition.[13] Our results are in clear contradiction to this view since the phase transition to long-range magnetic order is demonstrated, supporting previous NMR[14,16] and neutron-diffraction[15] experiments. In a gapless chain system, a transition to long-range AF order could be induced by a very small interchain coupling. However, the interchain coupling needs to be much larger in a Haldane system to induce AF order, larger than expected to be the case for $LiVGe_2O_6$.[10] However, the absence of a spin-flop transition in experiments up to 44.5 T[16] is evidence for a

large uniaxial anisotropy (suggesting a rather small splitting Δ_{CF} of the t_{2g} orbitals into a (d_{xy},d_{yz}) doublet and (d_{xz}) singlet, since the anisotropy arising from the spin-orbit coupling $\lambda_{SO}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ is $\sim\lambda_{SO}^2/\Delta_{CF}$[10]). This uniaxial anisotropy could be responsible for closing the Haldane gap[20] or significantly weakening the effective intrachain interactions so that the one dimensionality of the system is reduced,[11,14] pushing the system beyond the critical ratio of interchain to intrachain exchange necessary to promote AF order.[21,22] The small orbital splitting, consequently, ensures that a description of the system purely in terms of a spin Hamiltonian must be modified by the inclusion of orbital degrees of freedom. In particular, the μSR results provide evidence for fast fluctuations of the ^{51}V nuclear moments that may be very relevant in this context.

In conclusion, our μSR measurements yield clear evidence showing that $LiVGe_2O_6$ undergoes a second-order phase transition to long-range AF magnetic order. In view of the importance of orbital fluctuations, further investigations of the orbital occupancy and possible orbital ordering would be highly desirable.

The authors would like to thank the staff of the PSI and ISIS muon facilities for their assistance, in particular, A. Amato and S. P. Cottrell. This work was supported by EPSRC (UK).

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