Very low-frequency excitations in frustrated two-dimensional $S = 1/2$ Heisenberg antiferromagnets

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Abstract

$\mu$SR and $^7$Li NMR relaxation measurements in frustrated two-dimensional $S = 1/2$ Heisenberg antiferromagnets on a square lattice are presented. It is found that both in $\text{Li}_2\text{VOSiO}_4$ and $\text{Li}_2\text{VOGeO}_4$, spin dynamics at frequencies well below the Heisenberg exchange frequency are present. These dynamics are associated with the motions of walls separating coexisting collinear domains with a magnetic wave vector rotated by 90°.
Two-dimensional $S = 1/2$ Heisenberg antiferromagnets (2DQHAF) have attracted a lot of interest in the last decade mainly due to their interplay with high $T_c$ superconductors. These systems are characterized by strong quantum fluctuations in view of the reduced dimensionality and low spin value, with long range order taking place, in principle, only at zero temperature ($T$). Still it is possible to further enhance quantum fluctuations without introducing defects, static or itinerant, by frustrating the antiferromagnetic exchange interaction. This situation is encountered in the $J_1$-$J_2$ model on a square lattice, where the next nearest neighbour interaction $J_2$, along the diagonal of the square, competes with the nearest neighbour interaction $J_1$, along the side of the square. On increasing $J_2$ one expects first a quantum phase transition from a Néel ordered phase to a non-magnetic ground state, whose precise nature is still subject of debate, and then another transition to a collinear ground state. The collinear phase can be considered as formed by two interpenetrating sublattices with a reciprocal orientation of the Néel vectors which classically can assume any orientation. However, this degeneracy is lifted by quantum fluctuations and, as a consequence of an order from disorder process, just two collinear ground-states are realized: collinear I, with magnetic wave-vector $\mathbf{Q} = (q_x = \pi/a, q_y = 0)$, and collinear II, with $\mathbf{Q} = (0, \pi/a)$. These two ground states are degenerate and it is not possible a priori to tell which of one of them will be realized, unless other interactions are considered.

Recently two prototypes of frustrated 2DQHAF with $J_2/J_1 \simeq 1$, Li$_2$VOSiO$_4$ ($J_2/J_1 = 1.1$ and $J_1 + J_2 \simeq 8.2$ K) and Li$_2$VOGeO$_4$ ($J_2/J_1 = 0.9$ and $J_1 + J_2 \simeq 6$ K), have been discovered. Li$_2$VOSiO$_4$, which is the most studied of the two compounds, shows a collinear ground state always of type I, with the spins pointing along the $x$ direction. The degeneracy among the two collinear phases is relieved by a structural distortion occurring just above the transition to the collinear phase at $T_N$. For $J_1 + J_2 \geq T > T_N$ the system is characterized by a correlated spin dynamics with domains of type I and II extending over a length of the order of $\xi$, the in-plane correlation length.

In this manuscript we will provide evidence, based on µSR and $^7$Li NMR measurements, that for $J_1 + J_2 \geq T > T_N$ very slow spin dynamics are developed in the two systems, with characteristic frequencies $\omega_c \ll (J_1 + J_2)k_B/\hbar$. These dynamics are associated with the motions of domain walls separating the collinear I and II phases which dynamically coexist above $T_N$. New µSR data showing that both in Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ the transition to the collinear I ground state is possibly triggered by the in-plane XY anisotropy are also
presented.

The measurements were performed on powder samples prepared by solid state reaction, as described in ref. 9. Longitudinal field (LF) and zero field (ZF) $\mu$SR measurements were performed at ISIS pulsed source using 29 MeV/c spin-polarized muons. The background signal was estimated below $T_N$, equal to 2.86 K for Li$_2$VOSiO$_4$ and 2.1 K for Li$_2$VOGeO$_4$, from the amplitude of the slowly decaying oscillation in a transverse field of 100 Gauss. For $T < T_N$, the frequency of the oscillating ZF $\mu$SR signal directly yields the amplitude of the local field at the muon site $B_{\mu}$, which is proportional to the sublattice magnetization (see Fig. 1). The $T$-dependence of $B_{\mu}$ in Li$_2$VOGeO$_4$ is very close to the one observed in Li$_2$VOSiO$_4$. In particular, one finds a critical exponent for the sublattice magnetization very close to $\beta = 0.235$, the one predicted for a 2D XY system on a finite size. The absolute value of $B_{\mu}$, similar for both compounds, allows to estimate where the $\mu^+$ is probably localized. By assuming a simple dipolar coupling with V$^{4+}$ magnetic moments, whose absolute value should range between 0.6 and 0.25 $\mu_B$, two possible $\mu^+$ sites have been identified. One around (Si,Ge)O$_4$ tetrahedral oxygens, the other close to VO$_5$ apical oxygen.

Above $T_N$, for $T \lesssim J_1 + J_2$, the decay of the muon polarization was observed to be rapidly quenched by a LF and to become field-independent above 200 Gauss (see Fig.2). The remanent decay, driven by high frequency spin fluctuations, is weakly $T$-dependent and should be compared to NMR spin-lattice relaxation rate $1/T_1$. These observations point out that the dominant contribution to the decay of $\mu^+$ polarization in ZF is not a spin-lattice relaxation process induced by field fluctuations at frequencies $\omega_c \sim (J_1 + J_2)k_B/h$, as we have erroneously put forward on the basis of ZF measurements only, but it is driven by very low-frequency fluctuations with $\omega_c \ll (J_1 + J_2)k_B/h$. In this case the decay of the polarization is not described by $P_\mu(t) \propto \exp(-\lambda t)$, as for LF above 200 Gauss, but one has to resort to the complete Kubo-Toyabe function. In the presence of a LF, if the system is not in the purely static or very fast fluctuations regime $\omega_c \gg \gamma \sqrt{\langle \Delta h^2 \rangle}$, with $\gamma = 2\pi \times 13.55$ kHz/Gauss the muon gyromagnetic ratio and $\sqrt{\langle \Delta h^2 \rangle}$ the mean square amplitude of field fluctuations, the fit of $P_\mu(t)$ data with the complete Kubo-Toyabe function is rather cumbersome. Nevertheless, if $\omega_c \gtrsim \gamma \sqrt{\langle \Delta h^2 \rangle}$, one can resort to the analytical expression for $P_\mu(t)$ derived by Keren, which provides a powerful method to fit the decay of muon polarization in LF.

For $T \gg J_1 + J_2$ a non-negligible $T$-independent decay, due to nuclear dipolar coupling,
is still present. Although this contribution might be disregarded for $T \to T_N$, in order to correctly estimate the frequency of these low-energy dynamics also for $T \to J_1 + J_2$, the raw $\mu$SR data of $P_\mu(t)$ have been first divided by $P_\mu(t)$ for $T \gg J_1 + J_2$. Then the data have been fitted according to

$$P_\mu(t) = \exp(-\lambda t)P_\mu(t)^K(B, \omega_c, <\Delta h^2>)$$

where the first term describes the spin-lattice relaxation driven by the fast fluctuations, while the second one is Keren analytical approximation of Kubo-Toya be function (see Eqs. 3 and 4 of Ref. 14), which depends on the intensity of the longitudinal field $B$, as well as on $\omega_c$ and $<\Delta h^2>$. By fixing $\lambda \approx 0.015 \mu s^{-1}$ from the high LF measurements above 200 Gauss and fitting $\mu$SR data at different magnetic fields, it was possible to estimate $<\Delta h^2>$ and the T-dependence of $\tau_c \equiv 1/\omega_c$ (see Fig. 3). We have found that $\omega_c$ is always at least 6 times larger than $\gamma \sqrt{<\Delta h^2>}$, supporting the applicability of Keren analytical expression. $\tau_c(T)$ is observed to diverge exponentially on decreasing T, with an effective activation barrier around 3 K for Li$_2$VOGeO$_4$ and close to 8 K for Li$_2$VOSiO$_4$. These low frequency fluctuations can originate, in principle, either from $\mu^+$ diffusion or from a slow spin dynamics. The first possibility seems quite unlikely if one considers that in perovskites the activation energies are usually at least two orders of magnitude larger. In particular, in Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ the muon is located either close to the apical oxygen of the VO$_5$ pyramids or close to an oxygen of SiO$_4$ tetrahedra where it experiences a strong attractive coulomb potential which hinders its diffusion. On the other hand, the second situation is more likely once one realizes that the more rapid increase on cooling of $\tau_c$ in Li$_2$VOSiO$_4$ seems related to the larger exchange coupling.

These very slow fluctuations should cause also an enhancement of $^7$Li NMR transverse relaxation rate $1/T_2$, which was derived from the decay of the echo amplitude after a $\pi/2 - \tau - \pi$ sequence. Two main contributions to $1/T_2$ are present. The first is temperature independent and is due to nuclear dipole-dipole interaction among $^7$Li nuclei. Its value can be estimated from the lattice sums to be $(1/T_2)_{\text{dip}} \approx 5 \text{ ms}^{-1}$. The second one is a temperature dependent contribution proportional to the amplitude of the spectral density at $\omega = 0$, which could be very sensitive to these low-frequency fluctuations. So one can write that $1/T_2 = (1/T_2)_{\text{dip}} + (1/T_2)'$, with

$$\frac{1}{T_2}' = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} <h_z(t)h_z(0)> dt = \frac{\gamma^2}{2} <\Delta h^2_z> \tau_c.$$
Here \( h_z(t) \) is the fluctuating component of the local field at \( ^7\text{Li} \) nuclei along the external magnetic field. Now, by assuming \( \omega_c \simeq (J_1 + J_2)k_B/\hbar \), one would derive a contribution to \( 1/T_2 \) of at least one order of magnitude smaller than the experimental one. Moreover, if \( \omega_c \) was well above the nuclear Larmor frequency \( (\omega_L) \), \( 1/T_2 \) and \( 1/T_1 \) should show the same \( T \)-dependence, while it is evident from Fig. 4 that \( 1/T_2 \) starts diverging in a \( T \) range where \( 1/T_1 \) is still constant. Only a very low-frequency dynamics at \( \omega_c \ll (J_1 + J_2)k_B/\hbar \) can explain the experimental data for \( ^7\text{Li} \) NMR transverse relaxation rate. Therefore, the temperature dependence of \( (1/T_2)'/\propto \tau_c \) should be characterized by an exponential divergence, with an effective activation barrier equal to the one estimated from \( \mu \text{SR} \) relaxation measurements.

In fact, the barrier derived from \( 1/T_2 \) and \( \mu \text{SR} \) decay rate was found to be the same within \( \pm 15\% \), pointing out that both techniques are probing the same dynamics and definitelly ruling out the possibility of \( \mu^+ \) diffusion. This implies that there are two main dynamics contributing to the spectral density: one with characteristic frequencies of the order of \( (J_1 + J_2)k_B/\hbar \), probed by NMR \( 1/T_1 \) and \( \mu \text{SR} \) decay rate for \( B > 100 \) Gauss, the other with \( \omega_c \ll (J_1 + J_2)k_B/\hbar \), which is evident in low field \( \mu \text{SR} \) decay rates and NMR \( 1/T_2 \).

Since nuclear spin-lattice relaxation rate probes the amplitude of the spectral density at \( \omega_L \), one would expect to observe an enhancement in \( ^7\text{Li} \) \( 1/T_1 \) on decreasing the Larmor frequency towards \( \omega_c \). For this reason \( ^7\text{Li} \) NMR \( 1/T_1 \) was measured at \( B = 3.5 \) kGauss and compared with the one measured at 16 kGauss. One finds that upon cooling, approaching \( T_N \), an enhancement of \( 1/T_1 \) with decreasing field is evident (see Fig. 4), suggesting the presence of very low-frequency dynamics. These dynamics are not due to spin diffusion, which in 2D systems gives rise to a logarithmic divergence of \( 1/T_1 \). First, because if spin diffusion was present one should observe a frequency dependence also for \( T > 3 \) K, while it is absent (see Fig. 4b). Second, the low-frequency divergence induced by spin-diffusion should be cut at frequencies corresponding to energies of the order of the spin anisotropy, which are usually more than three orders of magnitude larger than \( \hbar \omega_c \).

Now, which is the possible origin of the spin dynamics at frequencies \( \omega_c \ll (J_1+J_2)k_B/\hbar \)? In frustrated 2DQHAF with \( J_1 \simeq J_2 \) the degeneracy of the two collinear ground states leads to the coexistence of domains of type I and II above \( T \simeq E(T) \), the energy barrier separating the two collinear phases. In these vanadates the degeneracy is lifted by a structural distortion occurring just above \( T_N \), so that the double potential well describing the energy levels becomes asymmetric and the system collapses always in the collinear I phase. On the other
hand, for $J \geq T > T_N$, above the structural distortion, the double potential well is symmetric and the spectral density is characterized both by a fast dynamic, at $\omega_c \sim (J_1 + J_2)k_B/\hbar$, and a slow thermally activated dynamic with $\omega_c = \omega_o \exp(-E(T)/T)$, $\omega_o$ being a characteristic attempt frequency. These low-frequency fluctuations can originate from the motions of domain walls separating the two collinear phases, or, in other terms, from the phase modes of soliton strings separating domains with a pitch vector $Q$ rotated by 90°. Such a low-frequency dynamic is present in one-dimensional QHAF as CuGeO$_3$, where the slowing down of soliton phase modes manifests itself as an increase of the NMR linewidth. $\omega_c$ can be much smaller than $(J_1 + J_2)k_B/\hbar$ first because of the activated type of dynamics, second because $1/\omega_o$ corresponds to the time required for a domain wall to visit all lattice sites within a domain, which increases with the in-plane correlation length $\xi(T) \propto \exp(2\pi \rho_s/T)$, $\rho_s$ being an effective spin-stiffness.

In order to verify if the temperature dependence of $\tau_c$ reported in Fig. 3 for Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ is compatible with such a picture, the data were fitted using for $E(T)$ the expression derived by Chandra et al.:

$$E(T) = \left(\frac{J_1^2 S^2}{2J_2}\right) \left[0.26\left(\frac{1}{S}\right) + 0.318\left(\frac{T}{J_2 S^2}\right)\right] \xi^2(T)$$  \hspace{1cm} (3)$$

One observes (Fig. 3) that on approaching $T_N$ the increase of $\tau_c$ can be well approximated by an activated $T$-dependence, with $E(T)$ given by Eq. 3, with values for $2\pi \rho_s$ slightly below $(J_1 + J_2)$, as expected for a frustrated system. In particular, one finds $2\pi \rho_s \approx 7.6$ K for Li$_2$VOSiO$_4$ and $2\pi \rho_s \approx 4.9$ K for Li$_2$VOGeO$_4$. A departure from this trend is evident for $T \rightarrow J_1 + J_2$ and can be associated with the inadequacy of the simple exponential expression used for $\xi(T)$ at $T \simeq J_1 + J_2$. The consistency of the $\tau_c(T)$ behaviour with the $T$-dependence of $E(T)$ predicted for the energy barrier separating the two collinear phases, reinforces our conclusion in favour of a slow dynamics driven by the motions of domain walls.

In conclusion, from the analysis of $\mu$SR and $^7$Li NMR relaxation rates in Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ it has been shown, for the first time, that in frustrated 2DQHAF, with $J_1 \simeq J_2$, low frequency spin dynamics are present at frequencies well below the Heisenberg exchange frequency. These dynamics are associated with the motions of domain walls separating the collinear I and II phases which coexist above $T_N$ and are characterized by a pitch vector rotated by 90°.

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ments at ISIS.

1 see for example E. Dagotto and T. M. Rice, Science 271, 619 (1995) and E. Dagotto, Rep. Prog. Phys. 62, 1525 (1999) and references therein
2 P. Chandra and B. Doucot, Phys. Rev. B 38, 9335 (1988)
3 H. J. Schulz and T. A. L. Ziman, Europhys. lett. 18, 355 (1992); S. Sorella, Phys. Rev. Lett. 80, 4558 (1998); L. Capriotti and S. Sorella, Phys. Rev. Lett. 84, 3173 (2000)
5 P. Chandra, P. Coleman and A. I. Larkin, Phys. Rev. Lett. 64, 88 (1990)
6 V. N. Kotov, M. E. Zhitomirsky and O. P. Sushkov, Phys. Rev. B 63, 064412 (2001); V. N. Kotov, J. Oitmaa, O. P. Sushkov and Z. Weihong; Phys. Rev. B 60, 14613 (1999)
7 R. Melzi et al., Phys. Rev. Lett. 85, 1318 (2000)
8 R. Melzi et al., Phys. Rev. B 64, 024409 (2001)
9 P. Millet and C. Satto, Mat. Res. Bull. 33, 1339 (1998)
10 S. T. Bramwell and P. C. W. Holdsworth, Phys. Rev. B 49, 8811 (1994); S. T. Bramwell and P. C. W. Holdsworth, J. Phys.: Condens. Matter 5, L53 (1993)
11 R. Kubo, Hyperfine Interactions 8, 731 (1981)
12 see R. De Renzi and S. Fanesi, Physica B 289-290, 209 (2000) and references therein
13 Y. J. Uemura et al., Phys. Rev. B 31, 546 (1985)
14 A. Keren, Phys. Rev. B 50, 10039 (1994)
15 A. Schenck in Muon Spin Rotation: Principles and Applications in Solid State Physics (Hilger, Bristol 1986)
16 C. P. Slichter, in Principles of Nuclear Magnetism, (Springer-Verlag, Berlin 1980)
17 H. Benner and J. P. Boucher, in Magnetic Properties of Layered Transition Metal Compounds, edited by L. J. De Jongh (Kluwer Academic, Norwell, MA, 1990), p.323
18 H. J. Schulz, T. A. L. Ziman and D. Poilblanc, J. Phys. I France 6, 675 (1996)
19 see H. J. M. de Groot and L. J. de Jongh in Magnetic Properties of Layered Transition Metal Compounds, Ed. L. J. de Jongh (Dodrecht, Kluwer), p. 379 (1990)
20 G. S. Uhrig et al., Phys. Rev. B 60, 9468 (1999)
FIG. 1: Temperature dependence of the local field at the muon site in Li$_2$VOSiO$_4$ (circles) and Li$_2$VOGeO$_4$ (squares), normalized by $B_\mu(0) = 313$ Gauss and $B_\mu(0) = 339$ Gauss, respectively. The temperature is normalized by $T_N = 2.86$ K for Li$_2$VOSiO$_4$ and by $T_N = 2.1$ K for Li$_2$VOGeO$_4$. The dotted line shows the critical behaviour expected for a critical exponent $\beta = 0.235$.

FIG. 2: a) Time evolution of the muon polarization in Li$_2$VOSiO$_4$ in a LF of (from the bottom to the top) 5, 10, 20, 50, 900 Gauss, for $T = 2.95$ K (just above $T_N$). In b) $P_\mu(t)$ for a LF of 5 Gauss is reported for clarity. The solid lines correspond to the best fits obtained from Eq. 1 with $\gamma\sqrt{\langle \Delta h^2 \rangle} = 0.65\mu s^{-1}$ and $\tau_c = 0.265\mu s$.

FIG. 4: a) Temperature dependence of $^7$Li NMR $1/T_2$ in Li$_2$VOGeO$_4$ above $T_N$, for $H = 3.7$ kGauss. The dotted line shows the best fit according to an activated $T-$ dependence of $1/T_2$ with an effective barrier of 3.5 K. b) Temperature dependence of $^7$Li NMR $1/T_1$ in Li$_2$VOGeO$_4$ above $T_N$, for $H = 3.7$ kGauss (closed circles) and $H = 16$ kGauss (empty circles).

FIG. 3: Temperature dependence of the correlation time for the low-frequency fluctuations in Li$_2$VOSiO$_4$ (circles) and in Li$_2$VOGeO$_4$ (squares). These data have been derived from the fit of $P_\mu(t)$ in a LF of 5 gauss according to Eq. 1, after dividing the raw $\mu$SR data by $P_\mu(t)$ for $T \gg J_1 + J_2$ (see text). The dotted lines show the best fits according to $\tau_c = (1/\omega_0)exp(E(T)/T)$, with $E(T)$ given by Eq. 3. The increase in the error bars at high $T$ originates from the increase in the weight of the dipolar contribution to $P_\mu(t)$ at higher $T$. 
Fig. 1 (P. Carretta et al.)

\[ \frac{B_\mu(T)}{B_\mu(0)} \]

\[ \frac{T}{T_N} \]

- \( \text{Li}_2\text{VOGeO}_4 \)
- \( \text{Li}_2\text{VOSiO}_4 \)
Fig. 2 (P. Carretta et al.)

(a) $P_\mu (t)$ vs $t$ (µs)

(b) $P_\mu (t)$ vs $t$ (µs)
Fig. 3 (P. Carretta et al.)
2.0 2.5 3.0 3.5 4.0 4.5

$1/T_2$ (ms$^{-1}$)

$T$ (K)

Fig. 4 (P. Carretta et al.)

$H = 16$ kGauss
$H = 3.7$ kGauss

$1/T_1$ (ms$^{-1}$)

$T_N$

$T$ (K)