Two-Spinon and Four-Spinon Continuum in a Frustrated Ferromagnetic Spin-1/2 Chain

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Inelastic neutron scattering measurements show the existence of a strong two-spinon continuum in the frustrated ferromagnetic spin-1/2 chain compound $LiCuVO_4$. The dynamic magnetic susceptibility is well described by a mean-field model of two coupled interpenetrating antiferromagnetic Heisenberg chains. The extracted values of the exchange integrals are in good agreement with the static magnetic susceptibility data and an earlier spin-wave description of the bound state near the lower boundary of the two-spinon continuum. In addition, there is clear evidence for a four-spinon continuum at high energies.

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Fractional excitations have in recent years been identified as one of the most fascinating and important aspects in the dynamics of strongly correlated materials and models. This is highlighted by numerous theoretical and experimental investigations in low-dimensional materials, such as in the spin-1/2 quantum Heisenberg antiferromagnetic (1D HAF) chain [1–3], the fractional quantum Hall effect [4], conducting polymers [5], and also in three dimensions by the indirect observation of magnetic monopoles in spin ice [6]. Among these, the 1D HAF chain provides the clearest picture of fractional excitations: as obtained from the exact solution of this model system [1], its elementary excitations are spin-1/2 particles called spinons which are created in pairs, such that continua of even numbers of spinons are responsible for the experimentally observed dynamics. In this Letter, we address the question of whether the predictions of this theoretical model apply also to the more generic case of a 1D Heisenberg magnet dominated by strong frustration.

So far neutron scattering experiments have demonstrated the existence of a continuum of two spinons in materials realizing the 1D HAF chain: from its qualitative identification in $CuCl_2\,2N(C_5D_5)$ [7] to the high-precision data on $KCuF_3$ [2] and $SrCuO_2$ [3] enabling a quantitative analysis, much progress has been made. In spite of these experiments providing us with beautiful pictures of the excitation continua it is an important open point to establish that spinons as fractional excitations are a generic property of a class of low-dimensional magnets beyond those modeling the exactly solvable and possibly isolated case of the 1D HAF chain.

We address this question with inelastic neutron scattering experiments on a generic 1D magnet, the strongly frustrated ferromagnetic (FFM) chain $LiCuVO_4$, and report two important results going beyond previous ones for the ideal HAF chain model: (i) a two-spinon excitation continuum is observed in the presence of strong frustration and substantial ferromagnetic exchange and (ii) an additional four-spinon continuum is clearly identified.

The FFM chain belongs to the more general class of $J_1 - J_2$ chains [J_1 is the nearest-neighbor (NN), J_2 the next-nearest neighbor (NNN) exchange] with Hamiltonian

$$\mathcal{H} = J_1 \sum_j \mathbf{S}_j \cdot \mathbf{S}_{j+1} + J_2 \sum_j \mathbf{S}_j \cdot \mathbf{S}_{j+2}. \qquad (1)$$

Equation (1) represents a particular rich class of models that has been widely studied for the case J_1, $J_2 > 0$, the frustrated antiferromagnetic (AFM) chain [8]. AFM materials showing a spinon continuum are the spin-Peierls compound $CuGeO_3$ with a gap related to dimerization [9], and Cs_2CuCl_4, where the coupling of AFM chains is due to two-dimensional AFM exchange on a triangular lattice [10–12].

The FFM chain with $J_1 < 0$, $J_2 > 0$ is of more recent and general interest. Related systems cover a broad range of phenomena, extending from superconductivity [13] and entanglement [14] to novel multipolar spin-nematic phases in external magnetic field [15]. For $-4J_2 < J_1 < 0$, the classical ground state of the FFM model is a spiral and the $S = 1/2$ quantum ground state is a singlet, which is now widely accepted to be dimerized [16]. The accompanying excitation gap, however, is difficult to identify and may actually be exceedingly small [17]. On the other hand, the structure of the ground state and the characteristics of the excitation spectrum are not known. Recently, the quasi-1D material $LiCuVO_4$ has been established as a representative of the quantum FFM chain model with $S = 1/2$ [18]. It offers the possibility to search for the existence of fractional excitations in a 1D system substantially different from the HAF model.

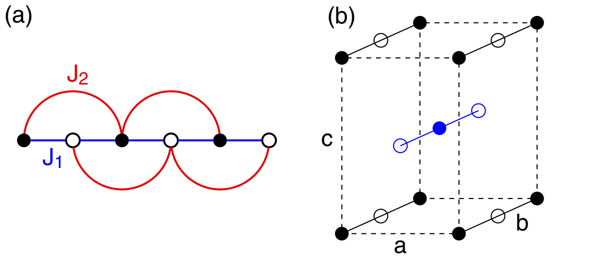

FIG. 1 (color online). (a) Sketch of the $J_1 - J_2$ chain. (b) Simplified unit cell of $LiCuVO_4$ with only Cu atoms shown.

The Cu^{2+} ions in $LiCuVO_4$ form spin-1/2 chains along the orthorhombic b axis, see Fig. 1(b) [19,20]. Nearest-neighbor spins are coupled ferromagnetically ($J_1 < 0$) and next-nearest neighbors antiferromagnetically ($J_2 > 0$), with $|J_1| < J_2$ [18]. Small interchain interactions lead to 3D order below $T_N \approx 2.4$ K, where the reduced ordered moments ($m_0 \approx 0.3\mu_B$) form a nearly circular cycloid in the ab plane with incommensurate propagation vector $\boldsymbol{\kappa}_{\mathrm{IC}} = (0, 0.532, 0)$ [20], which corresponds to $k_{\mathrm{IC}} = 0.468$ for a 1D chain due to the centering translation of the *Imma* space group. $LiCuVO_4$ is an excellent realization of the Hamiltonian Eq. (1), since an inversion center on the main bond J_2 excludes the Dzyaloshinski-Moriya interaction and the small ratio of the spin-flop ($H_{\mathrm{SF}} = 2.5$ T [21]) to the saturation field ($H_{\mathrm{sat}} = 49$ T [18]) limits anisotropic exchange to less than 0.5% of the main interaction. No spin gap (to the precision of <0.1 meV) has been observed in $LiCuVO_4$ [18].

Inelastic neutron scattering measurements were performed on the thermal triple-axis spectrometer IN20 at Institut Laue-Langevin using a horizontally and vertically focusing Si(111) monochromator and a PG(002) analyzer. The final wave vector was $k_f = 2.662$ Å^{-1} and a PG(002) filter was installed in the scattered beam. Energy scans were performed at constant wave vector $\mathbf{Q} = (1, k, 0)$ on the focusing side in W configuration. Data were corrected for absorption, higher-order contamination in the monitor, and vertical focal length of the monochromator (all wavelength dependent). Background due to incoherent elastic and small-angle scattering was subtracted. The same single crystal as used in Ref. [18] was mounted with the c axis vertical in an orange-type cryostat.

The measurements were performed at low temperatures, $T = 1.42$ K $< T_N \approx 2.4$ K, i.e., in the 3D ordered phase, to obtain the $T = 0$ dynamics with the best possible resolution. Since the data are taken at energies well above the crossover from 3D to 1D behavior they nevertheless describe the underlying 1D system [22]. Experimentally, we observe no difference in the two-spinon continua for temperatures below and just above T_N.

Figure 2(a) shows the intensity of the inelastic scattering as a function of the wave vector along the chain (k) and energy. A continuum with two prominent features is clearly observed: First, there is a striking asymmetry between wave vectors to the left and to the right of $k \approx 0.5$,

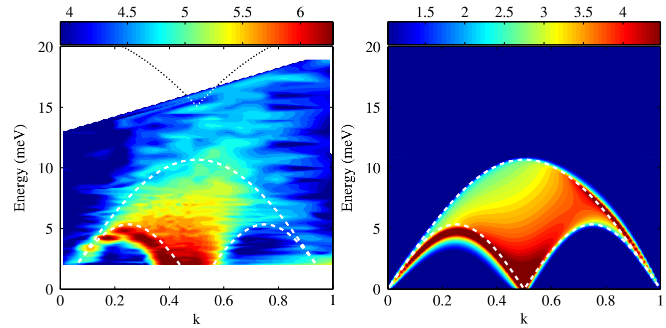

FIG. 2 (color online). Measured (left) and calculated (right) dynamic structure factor of $LiCuVO_4$ as a function of in-chain wave vector k and energy. The dashed (white) lines show the boundaries of the two-spinon continuum of a HAF chain and the dotted line the upper boundary of the four-spinon continuum.

with a strong weight transfer towards lower energy for $k < 0.5$. This is also seen in Fig. 3(a), where the intensity is shown as a function of energy for two wave vectors located to the left and right of k_{IC} at approximately the same distance from k_{IC}. The intensity for $k < k_{\mathrm{IC}}$ shows a strong peak slightly below the lower boundary of the continuum while for $k > k_{\mathrm{IC}}$ a broad maximum is observed. Second, the intensity in Fig. 2(a) extends to energies well beyond the two-spinon boundary, which strongly suggests the existence of four-spinon excitations.

The main features of the data, and in particular, the asymmetry with respect to k_{IC}, are captured semiquantitatively by a simple model of the FFM chain, which we will now describe. We start from the limit where the dominating NNN exchange J_2 is the only nonvanishing exchange. A single chain in $LiCuVO_4$ then separates into two noninteracting subsystems: spins 1/2 on even sites and spins 1/2 on odd sites [closed resp., open circles in Fig. 1(a)]. The dynamics of one of these subsystems (spins on odd or even sites) is that of the excitation continuum of a standard $S = 1/2$ Heisenberg chain with exchange J_2 [1], given by the dynamic susceptibility $\chi_{\mathrm{HAF}}(k, \omega)$. In our model the coupling between the two subsystems is accounted for in a

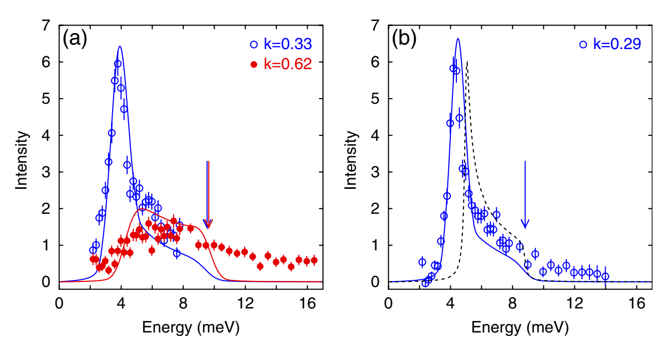

FIG. 3 (color online). Dynamic structure factor of $LiCuVO_4$ as a function of energy at selected wave vectors: symbols are experimental data and lines are results from the fit. The dashed line in (b) is a calculation for $J_1 = 0$. The arrows indicate the upper limit of the two-spinon continuum.

mean-field (or RPA) approximation. This amounts to treating the NN exchange J_1 from the spins on one subsystem as an effective field for the spins on the other subsystem, and leads to

$$\chi(k,\omega) = \frac{\chi_{\mathrm{HAF}}(k,\omega)}{1 + V(k)\chi_{\mathrm{HAF}}(k,\omega)} \tag{2}$$

with $V(k) = 2J_1\cos(\pi k)$, where $k \in [0, 1]$ is the in-chain wave vector in units of $2\pi/b$. Here b is the NNN distance and also the lattice constant of $LiCuVO_4$. We note that this approach preserves the gapless behavior of the HAF chain but this low-energy deficiency of the RPA approximation will be irrelevant for the description of experimentally observed continua, where the energy scales are much larger. This applies, in particular, to $J_1 < 0$ where a possible gap is exceedingly small [17].

For the evaluation of the dynamic structure factor

$$S(k,\omega) = \frac{1}{\pi}\frac{1}{1 - \exp(-\omega/k_B T)}\chi''(k,\omega), \tag{3}$$

contributions to $\chi_{\mathrm{HAF}}(k,\omega)$ will come from the two-spinon continuum (the most important contribution) as well as from continua from four and more spinons according to bosonization [23] and Bethe ansatz analysis [24,25]. In the following we will first evaluate and discuss the two-spinon contribution and then turn to the four-spinon contribution. For practical purposes, we do not use the exact expressions [24,25], but instead the Müller ansatz [26], a phenomenological expression for the two-spinon contribution to $\chi''_{\mathrm{HAF}}(k,\omega)$ at $T = 0$,

$$\chi''(k,\omega) = \frac{A}{\sqrt{\omega^2 - \omega_L^2(k)}}\Theta(\omega - \omega_L(k))\Theta(\omega_U(k) - \omega) \tag{4}$$

where $\omega_L(k) = (\pi/2)J_2|\sin(2\pi k)|$ is the lower and $\omega_U(k) = \pi J_2 \sin(\pi k)$ the upper boundary of the two-spinon continuum, respectively. This ansatz has proved useful and of sufficient accuracy for the interpretation of experimental spectra in the past [2,3]. Its square root divergence at $\omega_L(k)$ and the cutoff at $\omega_U(k)$ agree with what has been found from the Bethe ansatz analysis [23,24]. Use of the Müller ansatz for $\chi''_{\mathrm{HAF}}(k,\omega)$ allows us to explicitly calculate the real part of $\chi_{\mathrm{HAF}}(k,\omega)$ via the Kramers-Kronig relations. At $T = 0$, the two-spinon contribution exhausts only 73% of the first moment [24]. The remaining part comes essentially from four-spinon contributions [25], whereas higher continua can be neglected quantitatively. Moreover, the energy dependence of the four-spinon contribution is close to that of two spinons for $\omega < \omega_U(k)$. It is therefore justified to use Eq. (4) with $A = 1$ at $T = 0$. Results from the bosonization approach [11] allow us to conclude that this remains true at the finite but low temperatures of the experiment. The remaining manifestation of the four-spinon continuum is its higher upper boundary, $\omega_U^{(4\text{-spinon})} = \pi\sqrt{2(1 + |\cos(\pi k)|)}$.

In order to compare the model with the experimental data, we calculated the dynamic structure factor Eq. (3) using the full $\chi(k,\omega)$ in Eq. (2). The resulting $S(k,\omega)$ was multiplied by the square of the magnetic form factor of the Cu^{2+} ion and convoluted with the instrumental resolution. The model was fitted to all wave vectors and energies below the upper boundary of the two-spinon continuum simultaneously with only three free parameters: an overall intensity factor and the two exchange interactions $\tilde{J}_1 = J_1 A$ and J_2. Since our RPA model does not capture chiral fluctuations [27], responsible for the small incommensurability observed in $LiCuVO_4$ [18], we rescaled the experimental k values linearly, shifting the experimental $k = 0.468$ to 0.5 while keeping $k = 0$ and 1 fixed.

The best fit to the data gives $\tilde{J}_1 = -2.4$ meV and $J_2 = 3.4$ meV. Results are shown as solid lines in Fig. 3 for a few selected wave vectors. A 2D plot of the calculated $S(k,\omega)$ is shown in Fig. 2(b). The model captures qualitatively the characteristic features of our neutron scattering data for energies $\omega \leq \omega_U(k)$: the existence of a continuum with a large asymmetry of the line shape between wave vectors below and above $k \approx 0.5$, the sharp excitation near the lower boundary of the two-spinon continuum for $k < 0.5$, and a shift of weight towards the upper two-spinon boundary for $k > 0.5$. These drastic modifications of the two-spinon continuum are related to the fact that the interaction $V(k)$ changes sign at $k = 0.5$. For $k < 0.5$, there appears a bound state that is split off from the pure HAF continuum, the shape of which is also modified by the interaction. Because of instrumental resolution effects, the bound state and the lower edge of the continuum are merged into a single relatively sharp peak at or just below the HAF continuum. For $k > 0.5$, the opposite sign of the interaction gives rise to an antibound state near the upper edge of the HAF continuum, resulting in a single peak near $\omega_U(k)$. When $k \to 0.5$ from above, the interaction strength $V(k)$ decreases and no resonances occur.

We now consider the quantitative predictions from our model. The type of approximation of Eq. (2) was introduced by Schulz [28] in a different context, namely, to deal with interchain interactions J_i that couple spins in different parallel chains separated by $\mathbf{R}_i$, leading to $V(\mathbf{Q}) = \sum_i 2J_i\cos(\mathbf{Q}\cdot\mathbf{R}_i)$. Following this approach for $LiCuVO_4$, we treat the 1D NN coupling J_1 in Eq. (2) and the 3D residual interactions on the same level. With the only non-negligible interchain interaction J_5 [18], we obtain $V(k) = 2(J_1 + 2J_5)\cos(\pi k)$. This allows us to connect the present results, based on a purely quasi-1D model, to those of a 3D spin-wave model (SWM) [18]. In the SWM, the AFM exchange J_2 (after taking into account the quantum renormalization factor of $\pi/2$) was 3.56 meV, in excellent agreement with the present result of $J_2 = 3.4$ meV. The ferromagnetic exchange in the SWM, $J_1 + 2J_5 = -2.34$ meV, is also in excellent agreement with the present result of $\tilde{J}_1 = -2.4$ meV.

Finally, the experimental data in Figs. 2(a) and 3(a) clearly reveal finite intensity at energies well beyond the

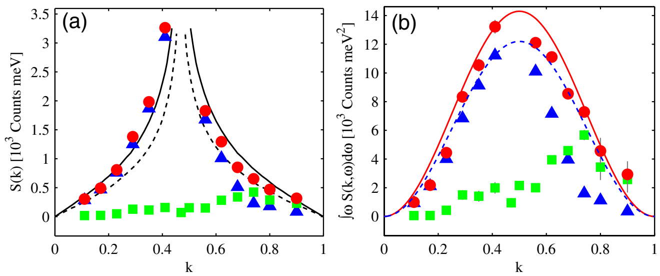

FIG. 4 (color online). Contribution of states above the upper two-spinon boundary $\omega_U(k)$ to the integrated dynamic structure factor $S(k)$ (a) and to the first moment (b): (red) circles: integration over the full measured energy range, (blue) triangles: integration up to $\omega_U(k) + \Delta$, (green) squares: integration from $\omega_U(k) + \Delta$ to upper end of data, where $\Delta = 1$ meV (2 meV) for $k < 0.47$ ($k \geq 0.47$) accounts for resolution broadening (and antibound state). The solid line in (a) is the calculated $S_{\mathrm{HAF}}(k)$ [24], shifted and scaled, the dashed line the two-spinon contribution to $S_{\mathrm{HAF}}(k)$ [24]. The lines in (b) are cosine-shaped guides to the eye.

upper two-spinon boundary $\omega > \omega_U(k)$. For an isolated HAF chain, the energy-integrated dynamic response $S(k) = \int S(k, \omega) d\omega$ coming from four-spinon states above $\omega_U(k)$ corresponds only to about 1% for $k = 0.25$ [25]. From our experimental data, the energy-integrated $S(k)$ for energies beyond $\omega_U(k)$ takes up 6% at $k = 0.23$ and 40% at $k = 0.68$, see Fig. 4(a). The experimental total first moment from the whole measured energy range, $\int S(k, \omega)\omega d\omega$, is still approximately cosine shaped as for the 1D HAF chain [cf. circles and solid line in Fig. 4(b)], whereas integration up to the upper two-spinon boundary yields a much more asymmetric curve [cf. triangles and dashed line in Fig. 4(b)]. Evidently, the first moment is not exhausted within the range of the two-spinon continuum, including bound and antibound states. We interpret these findings as direct evidence of a remarkable enhancement of the four-spinon continuum in the FFM chain compared to that of an isolated HAF chain. The significant spectral weight coming from above $\omega_U(k)$ for $k > 0.5$ may indicate that two- and four-spinon states cannot be distinguished in the presence of a sizable ferromagnetic coupling.

In conclusion, our neutron scattering experiment on the quasi-1D highly frustrated ferromagnetic spin-1/2 chain $LiCuVO_4$ demonstrates clearly the existence of both two- and four-spinon continua. The observed shift of intensity to lower (higher) energies in the first (second) half of the Brillouin zone are in qualitative agreement with an RPA model of two interpenetrating quantum chains.

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