Longitudinal and transverse Zeeman ladders in the Ising-like chain antiferromagnet BaCo$_2$V$_2$O$_8$

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We explore the spin dynamics emerging from the Néel phase of the chain compound antiferromagnet BaCo$_2$V$_2$O$_8$. Our inelastic neutron scattering study reveals unconventional discrete spin excitations, so called Zeeman ladders, understood in terms of spinon confinement, due to the interchain attractive linear potential. These excitations consist in two interlaced series of modes, respectively with transverse and longitudinal polarization. The latter have no classical counterpart and are related to the zero-point fluctuations that weaken the ordered moment in weakly coupled quantum chains. Our analysis reveals that BaCo$_2$V$_2$O$_8$, with moderate Ising anisotropy and sizable interchain interactions, remarkably fulfills the conditions necessary for the observation of these longitudinal excitations.

PACS numbers: 75.10.Pq,75.30.Ds,75.50.Ee,78.70.Nx

The nature of the excitations in spin half antiferromagnets is a topic of considerable current interest in the field of quantum magnetism. In three dimensions (3D), the Néel state is a very good approximation of the ground state. It is characterized by staggered long-range magnetic order and its excitation spectrum is dominated by single-particle states, so called spin waves or magnons, that correspond to a precession of the ordered moment around its equilibrium direction. These quasi-particles carry a total spin of unity and correspond to transverse excitations. Quantum fluctuations, usually resulting in minor corrections in two and three dimensions, become especially relevant in the one-dimensional (1D) case, destroying the long-range order as well as the precession modes, even at $T = 0$. The spin excitation spectrum is instead a continuum composed of pairs of $S = 1/2$ excitations called spinons that are created or destroyed only in pairs, like domain walls in an Ising magnet.

Physical realizations of 1D systems, however, eventually order at very low temperature, owing to small coupling between chains. This dimensional cross-over, from the continuum of spinons towards the classical picture of a 3D Néel state dressed with spin waves, is an appealing issue [1]. More precisely, in the ordered state of quasi-1D systems, each chain experiences an effective staggered molecular field. As a first consequence, a linear attractive potential between the spinons appears, which competes with their propagating character, and finally leads to their confinement in bound states. A spectacular manifestation of this effect in the case of Ising spins, initially described by Shiba [2], is the quantization of the excitation continuum in a series of discrete lines below the Néel temperature. This effect, called Zeeman ladder, was proposed to explain the discretization of the excitations observed in the ordered phase of CsCoCl$_3$ and CsCoBr$_3$ with Raman spectroscopy [2, 3]. Recently, a similar series of modes was also observed in the Ising ferromagnetic chain compound CoNb$_2$O$_6$ [4, 6]. It should be pointed out, however, that since there are three possible spin states for a pair of spinons, three types of bound states are expected. Besides the two transverse modes, a third bound state type, corresponding to fluctuations parallel to the direction of the ordered moment, hence a longitudinal mode, is also expected to accompany the crossover from 1D to 3D physics. Its observation has however been established up to now only in the quasi-1D Heisenberg spin 1/2 antiferromagnet KCuF$_3$ [6].

In this article, we introduce a new focus on this physics. We examine the excitations of BaCo$_2$V$_2$O$_8$, which realizes a quasi-1D spin half antiferromagnet, intermediate between the Ising and Heisenberg cases. By means of inelastic neutron scattering, we especially describe below the ordering temperature the emergence of transverse and longitudinal excitations, in the form of two well defined Zeeman ladders. This remarkable material thus displays, through the dimensional cross-over, both signatures of the quantum fluctuations mentioned above.

BaCo$_2$V$_2$O$_8$ consists of screw chains of Co$^{2+}$ running along the fourfold $c$-axis of the body-centered tetragonal structure [1]. These chains are weakly coupled yielding an antiferromagnetic (AF) ordering (propagation vector $\mathbf{k}_{AF} = (1, 0, 0)$ [8–10]) in zero field below $T_N \simeq 5.5$ K [10–
The magnetic moment in the distorted octahedral environment is described by a highly anisotropic effective spin $S = 1/2$ [13] with $g_{xx} = 2.95$ and $g_z = 6.2$ [14], thus allowing quantum fluctuations [15]. The validity of this description is sustained by the observation of the first crystal field level at 30 meV [10]. This physics is described by the XXZ Hamiltonian:

$$
\mathcal{H} = J \sum_i [\epsilon (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y) + S_i^z S_{i+1}^z] \quad (1)
$$

where, according to the analysis of the magnetization curve [15], the intrachain AF interaction is $J = 5.6$ meV and the anisotropy parameter is $\epsilon = 0.46$.

The neutron experiment was performed on the JCNS/CEA–CRG cold neutron three-axis spectrometer IN12 at the Institut Laue-Langevin high-flux reactor, Grenoble, France. A series of energy scans at constant scattering vector $Q$ was measured in the Néel phase to obtain the spin dispersion perpendicular (along $a$) and parallel (along $c$) to the chains.

Direct evidence for the emergence in the ordered phase of unconventional dispersive excitations is shown in Fig. 1. At the zone center $Q = (2, 0, 0)$ and at $T = 1.6$ K, a series of sharp modes ranging between about 1.5 and 6 meV, with decreasing intensities as the energy increases, is observed [see Fig. 1(b)]. These sharp modes show a sizable dispersion along the chain direction, as can be seen in Fig. 1(a). The presence of an intense peak dispersing between 6 and 7 meV with an out-of-plane weaker dispersion along the $c$–axis can also be noticed. As expected for magnetic excitations, all these modes disappear above $T_N$ [see Fig. 1(b)]. The relative $Q$ dependence of their intensities suggests that the peak around 7 meV can be interpreted as an optical mode, whereas the series of low energy excitations is acoustic-like. The existence of both types of excitations is indeed expected considering the 16 Co$^{2+}$ ions per unit cell in a classical picture. Yet, other interpretations for this intense mode could be considered such as kinetic bound state of spinons or bound state of pairs of spinons [4, 6].

In the remaining, however, we shall focus on the low energy series, and first investigate their polarization relative to the direction of the staggered moment. A neutron scattering experiment is indeed only sensitive to the spin components perpendicular to $Q$. Since the ordered moment is along the $c$–axis, measurements with $Q \parallel c$ reveal transverse excitations ($|| a$ and $|| b$) while measurements with $Q \parallel a$ disclose the superposition of transverse ($|| b$) and longitudinal ($|| c$) excitations. Energy-scans were thus measured at $T = 1.6$ K at various $Q$ positions (Fig. 2). For $Q = (0, 0, 0)$, a single series is observed with the lowest energy mode around 1.8 meV. As the scattering vector rotates towards the $a$ direction, a twin series of modes, shifted at slightly higher energies, rises progressively with an intensity that increases with respect to the first series. The lowest mode of this second series is gapped with a minimum at about 2 meV. These results evidence unambiguously the transverse ($T$) nature of the first series of discrete modes and the longitudinal ($L$) nature of the second one.

An important characteristic of this quasi-1D chain system is the strength of the interchain interactions. It can be evidenced from the dispersion of the excitations in the direction perpendicular to the chain axis. Figure 3(c) presents the energy dependence of the lowest energy mode of the $T$ and $L$ series along $a^*$ obtained from the energy-scans shown in Figs. 3(a,b). Although not visible for $l = 1$, a sizable dispersion, of the order of 0.1 meV, is observed for $l = 2$ with an expected minimum of the gapped mode at the AF points. Because of the complexity of the unit cell, there are likely several relevant and competing interchain interactions in BaCo$_2$V$_2$O$_8$. They may add or compensate each other, resulting in this peculiar $l$ dependence of the dispersion [16].

Last, we extracted the position of the modes in order to
investigate the bounding mechanism of the spinons. The modes in the energy range 1.5–6 meV at \( Q = (0, 0, 2) \) and at \( Q = (3, 0, 1) \) were fitted by a series of Gaussian functions (see Fig. 4). Their full width at half maximum was obtained from a fit of the lowest energy \( T \) and \( L \) modes and held constant to the same value (0.2 meV) for the subsequent modes of the series. It was necessary to add to the model an increasing background as the energy increases, very probably due to a continuum of excitations. For \( Q = (0, 0, 2) \), eight sharp \( T \) modes could be extracted. For \( Q = (3, 0, 1) \), five \( T \) modes and five \( L \) modes could be separated. The sixth and seventh modes of the series were fitted by a unique Gaussian function including the \( T \) and \( L \) modes too close in energy to be separated. This analysis shows that the spacing between the modes appears in a very nontrivial sequencing.

In order to interpret these results, a good starting point is the pure 1D quasi-Ising limit (\( \epsilon \ll 1 \) in Eq. (1)). A state containing two spinons is created by reversing one spin from one of the 2 degenerate Néel states. Two AF bonds are broken, leading to a state with energy \( J \), degenerate with all states resulting from reversing an arbitrary number of subsequent spins. These states carry a spin \( S_z = \pm 1 \) for an odd number of reversed spins and \( S_z = 0 \) for an even number. As soon as \( \epsilon \neq 0 \), the excitation spectrum becomes a continuum composed of such two domain walls which propagate independently. It is worth noting that in this picture, the \( S_z = \pm 1 \) states form transverse excitations, while the \( S_z = 0 \) states form longitudinal ones. This 1D domain wall picture, as well as the existence of a continuum with an energy gap, were first described by Villain [17]. Shiba then showed that the introduction of interchain couplings \( J' \), acting as a molecular field, gives to the two domain wall states an additional potential energy proportional to the distance comprised between them. This causes the above mentioned quantization of the excitation continuum, leading to a series of discrete dispersing lines below the 3D ordering temperature [2–4].

Following [4, 18–20], we propose first to analyze, at the bound state dispersion minima, the sequence of their energies with:

\[
E_j^{T,L} = 2E_0^{T,L} + \alpha z_j \quad \text{with } j = 1, 2, 3, \ldots
\]  

(2)

The prefactors \( z_j \) are the negative zeros of the Airy function \( Ai(-z_j) = 0 \), \( z_j = 2.34, 4.09, 5.52, 6.79, 7.94, \ldots \) etc. and \( \alpha \approx (h^2 c J)^{1/3} \) where \( h \) is the interchain molecular field [4]. As shown in the insets of Fig. 4, the energies of the \( T \) and \( L \) modes were satisfactorily fitted to Eq. (2) for various \( Q \), yielding \( \alpha \approx 0.42 \pm 0.03 \) meV, \( 2E_0^{T} \approx 0.85 \pm 0.15 \) meV, and \( 2E_0^{L} \approx 1.08 \pm 0.05 \) meV [10]. In absence of a model taking into account both arbitrary \( \epsilon \) and interchain interaction, we then assume that the dispersion along \( c^* \) of the first bound state \( E_1^T \) is roughly similar to the dispersion of the lower boundary
of the two-spinon continuum in the pure 1D case, namely $2E_{\text{o}}^T$. For any $J$ and $\epsilon$, this boundary is given by [21]:

$$2E_{\text{o}}^T(l) = \begin{cases} 
\frac{J}{1+K} \sqrt{1+k^2 - 2k \cos \pi l} & \text{for } l \leq \ell_{K}, \\
\frac{J}{1+K} \sin \pi l & \text{for } \ell_{K} \leq l \leq 1 - \ell_{K}, \\
\frac{J}{1+K} \sqrt{1+k'^2 + 2k' \cos \pi l} & \text{for } l \geq 1 - \ell_{K}
\end{cases}$$

with $\cos(\pi \ell_{K}) = \kappa$, $k' = \frac{1-\kappa}{1+\kappa}$, $k = \sqrt{1-k^2}$, $1/\epsilon = \cosh(\pi K'/K)$, and $J = I\pi/[K \sinh(\pi K'/K)]$ ($K$ and $K'$ are respectively the elliptic integrals of argument $k$ and $k'$).

Fitting the dispersion along $c^*$ of $E_{\text{o}}^T - \alpha z_1 = 2E_{\text{o}}^T$ with this model in several Brillouin zones gives $J \approx 2.8 \pm 0.4$ meV and $\epsilon \approx 0.41 \pm 0.02$ (see for instance Fig. 1). This analysis locates $\text{BaCo}_2\text{V}_2\text{O}_8$ in the intermediate anisotropic regime, in agreement with previous estimations of $\epsilon$ [15, 22]. Note that $J$ is twice smaller than the estimation given in Refs. [14, 15]. Last, assuming $h \sim J'$ (each Co having only one Co neighbor in the ‘diagonal’ direction of the $(a, b)$ plane [10]), a quite strong interchain interaction $J' \sim 0.3$ meV can be inferred from the determination of $\alpha$, consistent with the dispersion along $a^*$ at $l = 2$ (Fig. 3). $\text{BaCo}_2\text{V}_2\text{O}_8$ is then rather far from the perfect 1D regime with a $J'/J \sim 0.1$ ratio comparable to the one used to explain ESR measurements [15], but at variance with the small $J'$ value obtained from phase diagram calculations [22].

Coming back to the mass difference between the $T$ and $L$ modes, it is worth noting that in the $\epsilon \ll 1$ limit, the distinguishing feature of longitudinal excitations, compared to the case of transverse excitations, is the existence of a specific coupling with the Néel states. As the $\epsilon$ term exchanges two neighboring spins, the Néel state is directly coupled to $S_z = 0$ excited states containing 2 reversed spins. This makes the longitudinal modes more massive (at higher energy) than their transverse counterpart, as we observe in $\text{BaCo}_2\text{V}_2\text{O}_8$. The ground state is then an admixture of $S_z = 0$ two domain wall states added to the Néel state, producing a weakening of the ordered moment. Note that in the $\epsilon \ll 1$ limit, the intensity of longitudinal modes should scale with $\epsilon^2$. Indeed longitudinal excitations were hardly observed in systems close to the Ising limit such as CsCoCl$_3$ and CsCoBr$_3$ [2, 23]. The somehow more isotropic character of $\text{BaCo}_2\text{V}_2\text{O}_8$ (larger $\epsilon$ value) however is expected to enhance the longitudinal modes.

In the limit of purely isotropic Heisenberg spins ($\epsilon = 1$), a longitudinal mode is also expected. This situation has been illustrated in a neutron study carried out in $\text{KCuF}_3$ [6]. The spectrum near the AF zone center consists of a doubly degenerate, well-defined, gapless transverse spin-wave mode, plus a damped longitudinal mode characterized by a finite energy gap. This longitudinal mode could however not be resolved in another 1D material, namely $\text{BaCu}_2\text{Si}_2\text{O}_7$, which has a much weaker interchain coupling [24]. It was suggested that a sufficiently strong dispersion perpendicular to the chains is probably necessary in order to stabilize a longitudinal mode, which otherwise could decay into a pair of gapless transverse spin waves. In $\text{BaCo}_2\text{V}_2\text{O}_8$, we have determined sizable interchain couplings. Moreover, in contrast to the experimental observation in $\text{KCuF}_3$, the $\text{BaCo}_2\text{V}_2\text{O}_8$ longitudinal modes are remarkably intense and resolution limited. The reason is probably that these longitudinal modes cannot decay into transverse modes since the latter have a large gap due to the spin anisotropy.

It is finally very instructive to recall that $\text{BaCo}_2\text{V}_2\text{O}_8$ has also raised recently much interest for its field-induced behavior, that is describable in terms of Tomonaga-Luttinger physics [8, 9, 25]. An exotic magnetic ordered phase, unknown in classical systems, is induced by a magnetic field applied parallel to the chain axis. A longitudinal incommensurate spin density wave (amplitude of the moments modulated along the field direction) is actually stabilized thanks to the particular values of $J'$ and $\epsilon$ [22]. Those ingredients, i.e., sizable interchain interactions and intermediate anisotropic character, are the same as the ones we have invoked to account for the quantized transverse and longitudinal magnetic excitations, observed in the diagram.
BaCo$_2$V$_2$O$_8$. This material is thus a rare example of spin 1/2 system displaying spin longitudinal modes, of pure quantum origin, in both the dynamical and the field-induced static regimes.

We would like to thank R. Ballou and J. Robert for fruitful discussions and B. Vettard for his technical support. This work was partly supported by the French ANR project NEMSICOM.

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SUPPLEMENTAL MATERIAL

1. Crystalline and magnetic structures of BaCo$_2$V$_2$O$_8$

BaCo$_2$V$_2$O$_8$ crystallizes in the centrosymmetric tetragonal body-centered $I4_1/acd$ (No. 142) space group, with $a = 12.444$ Å, $c = 8.415$ Å, and eight chemical formulas per unit cell [1]. The 16 magnetic Co$^{2+}$ ions of the unit cell are equivalent (Wyckoff site $16f$). The spin-3/2 Co$^{2+}$ ions (effective spin-1/2) are arranged in edge-sharing CoO$_6$ octahedra forming screw chains, running along the $c-$axis, and separated by non-magnetic V$^{5+}$ and Ba$^{2+}$ ions (see Fig. 1 in Ref. [2]). Figure 5 shows one of the two domains of the antiferromagnetic (AF) structure determined in a previous single-crystal neutron diffraction experiment at $H = 0$ and $T = 1.8$ K [2].

The dominant interaction is the intrachain nearest neighbor AF exchange coupling (occurring between two Co$^{2+}$ ions of the same chain located at $z = n/8$ and $z = n/8 + 1/4$, with $n$ integer). This interaction imposes an AF ordering along the chains with the spins parallel to the chain $c-$axis. Looking at the crystalline and AF structures, the dominant interchain interaction is very probably AF along the ‘diagonal’ direction $a \pm b$, that is between two Co atoms of the same type of chain (blue or red chains) located at the same $z$. This explains the stabilization of the observed two magnetic domains. The various exchange interactions occurring between the two types of chains have been described in details in Ref. [3] and were shown to yield an effective ‘parallel’ (i.e., along the $a$ and $b$ directions) interchain coupling of negligible weight as compared to that of the ‘diagonal’ interaction.

2. Sample and additional neutron scattering data

The BaCo$_2$V$_2$O$_8$ single-crystal used in the inelastic neutron scattering (INS) experiments was grown at Institut Néel (Grenoble, France) by the floating zone method [4]. A 5 cm long cylindrical crystal rod, of about 3 mm diameter, was obtained, with the growth axis at about 60° from the $c-$axis. An about 1 cm thick slice was cut perpendicular to the $c-$axis.

For the neutron experiment performed on the IN12 spectrometer and described in the article, the sample was mounted in a standard cryostat with the $b-$axis vertical. The final wave vector $k_f$ was fixed at 1.5 Å$^{-1}$ and the higher order contamination was removed using a velocity selector placed before the monochromator.

Additional INS data are presented in Fig. 6. This figure reports measurements obtained on the CEACRG thermal neutron three-axis spectrometer IN22 at the Institut Laue-Langevin high-flux reactor, Grenoble, France. The sample was mounted in a standard cryostat with the $b-$axis vertical and the final wave vector $k_f$ was fixed at 3.84 Å$^{-1}$. Pyrolytic graphite (002) monochromator and analyzer were used, while the $\gamma/2$ contamination was suppressed by using a graphite filter on the incident neutron beam. These measurements show a non-dispersive mode at 30 meV whose intensity decreases with $|Q|$ and which dramatically broadens at high temperature. It is ascribable to the first crystal field level of the Co$^{2+}$ atoms. Note that an alternative explanation of the intense longitudinal modes observed in BaCo$_2$V$_2$O$_8$ could be associated to the true $S = 3/2$ nature of the Co$^{2+}$ spin with large anisotropy as described in Ref. [5]. This explanation is however rather unlikely in view of the high energy value of the first crystal field level.

3. Additional details about the data analysis

The magnetic Bragg peaks corresponding to the antiferromagnetic structure of BaCo$_2$V$_2$O$_8$ with $k = (0,0,1)$ appear at $Q = (h + 1, k, l)$ with $h + k + l$ even (condition due to the $I$ type of the lattice). Table I summarizes, for the scattering vectors shown in Fig. 2, the values of $\alpha$,
FIG. 6: (Color online) $\mathbf{Q} = (4, 0, l)$ constant energy scans (open symbols) measured at various scattering vectors $\mathbf{Q} = (4, 0, l)$ at $T = 1.6$ K and $k_f = 3.84$ Å$^{-1}$ on IN22, and fitted by a Gaussian function (solid lines). The absence of dispersion for this 30 meV excitation, together with its huge broadening at high temperature (solid black circles), evidence its crystal field nature.

TABLE I: Threshold energies $2E^T_o$ and $2E^L_o$, coefficient $\alpha$, and agreement factor $r^2$ for the transverse ($T$) and longitudinal ($L$) modes at four different Bragg positions. As the result of the fit slightly depends on the number of modes considered, this number $n_{\text{modes}}$ is specified.

| $\mathbf{Q}$ | $i$ | $2E^T_o$ (meV) | $\alpha$ (meV) | $r^2$ | $n_{\text{modes}}$ |
|--------------|-----|----------------|---------------|------|----------------|
| $(0, 0, 2)$  | $T$ | 1.00(8)        | 0.386(11)     | 0.9946 | 8               |
|              |     | 0.85(8)        | 0.419(13)     | 0.9962 | 5               |
|              |     | 0.79(6)        | 0.435(12)     | 0.9978 | 4               |
| $(2, 0, 2)$  | $T$ | 0.79(9)        | 0.427(18)     | 0.9948 | 4               |
| $(2, 0, 1)$  | $T$ | 0.77(9)        | 0.430(15)     | 0.9956 | 5               |
|              |     | 0.72(9)        | 0.418(13)     | 0.9972 | 4               |
| $(3, 0, 1)$  | $T$ | 0.71(9)        | 0.435(16)     | 0.9946 | 5               |
|              |     | 0.66(11)       | 0.448(22)     | 0.9939 | 4               |
| $(2, 0, 2)$  | $L$ | 1.10(8)        | 0.407(16)     | 0.9955 | 4               |
| $(2, 0, 1)$  | $L$ | 1.08(7)        | 0.404(12)     | 0.9966 | 5               |
|              |     | 1.03(7)        | 0.444(18)     | 0.9954 | 4               |
| $(3, 0, 1)$  | $L$ | 1.13(9)        | 0.392(15)     | 0.9941 | 5               |
|              |     | 1.06(6)        | 0.413(11)     | 0.9978 | 4               |

$2E^T_o$ and $2E^L_o$ obtained by fitting to Eq. (2) the positions in energy of the transverse ($T$) and longitudinal ($L$) discrete modes [see the insets of Figs. 4(a,b) for instance]. The number of modes included in the fits (4 to 8 starting from the lowest energy ones) was varied in order to estimate the error bars. The small dispersion of the results comes from the fact that, as in CoNb$_2$O$_6$ [see Fig. 3(b) in Ref. [6]], the energies of the modes do not vary perfectly linearly with the negative zeros of the Airy functions. Note that the threshold energies $2E^T_o$ and $2E^L_o$, as well as the coefficient $\alpha$, do not depend on the Bragg position. The fitted values, averaged on the various fits, are: $2E^T_o = 0.85 \pm 0.15$ meV, $2E^L_o = 1.08 \pm 0.05$ meV, and $\alpha = 0.42 \pm 0.03$ meV.

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