

Disorder instability of the magnon condensate in a frustrated spin ladder

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(Received 4 October 2011; revised manuscript received 31 October 2011; published 14 November 2011)

The effect of disorder is studied on the field-induced quantum phase transition in the frustrated spin-ladder compound $\text{H}_8\text{C}_4\text{SO}_2\cdot\text{Cu}_2(\text{Cl}_{1-x}\text{Br}_x)_4$ using bulk magnetic and thermodynamic measurements. The parent material ($x = 0$) is a quantum spin liquid, which in applied fields is known to form a magnon condensate with long-range helimagnetic order. We show that bond randomness introduced by a chemical substitution on the nonmagnetic halogen site destroys this phase transition at very low concentrations, already for $x = 0.01$. The extreme fragility of the magnon condensate is attributed to *random frustration* in the incommensurate state.

DOI: [10.1103/PhysRevB.84.174414](https://doi.org/10.1103/PhysRevB.84.174414)

PACS number(s): 75.10.Jm, 75.10.Pq, 75.40.Cx, 75.50.Lk

I. INTRODUCTION

Three-dimensional (3D) long-range order is robust and usually highly resistant to weak spatially random perturbations. In particular, this applies to field-induced magnetic order in gapped quantum spin systems. This type of quantum phase transition has recently attracted a great deal of attention due to its interpretation in terms of a Bose-Einstein condensation (BEC) of magnons.^{1,2} In magnetic materials, disorder can be introduced by randomizing the strength of magnetic bonds. In simple models, its primary effect is to produce a random potential for the condensing magnons. The result is a qualitatively new phase with nonzero magnetization and susceptibility, but only short-range correlations, the so-called magnetic Bose glass.^{3,4} However, unless the disorder is very strong, the ordered BEC phase is expected to reemerge at higher fields.⁴⁻⁷ An intriguing question is whether *weak* randomness in quantum magnets can go beyond creating a random magnon potential, in a way that disrupts the formation of the condensate altogether.

In the present work we investigate the effect of bond strength disorder on the *geometrically frustrated* gapped quantum magnet $\text{H}_8\text{C}_4\text{SO}_2\cdot\text{Cu}_2\text{Cl}_4$ (SCC for short).⁸ Bond disorder is introduced by a chemical substitution on the nonmagnetic site in the isostructural $\text{H}_8\text{C}_4\text{SO}_2\cdot\text{Cu}_2(\text{Cl}_{1-x}\text{Br}_x)_4$ (hereafter abbreviated as SCX). We find that extremely low Br concentrations have a catastrophic effect on the phase transition and magnetic properties. This behavior is attributed to *frustration disorder*, enhanced by the incommensurate and quasi-one-dimensional spin correlations in the parent compound.

To our knowledge, the parent compound SCC is quite unique being a strongly quasi-one-dimensional gapped Heisenberg spin system where geometric frustration is strong enough to cause dynamic spin correlations to be incommensurate. From the point of view of structural chemistry, it belongs to a large and diverse family of organic complexes involving transition metal halogenides (see, for example, Refs. 9–11). Antiferromagnetic (AF) interactions between the $S = 1/2$ Cu^{2+} ions are carried by Cu-X-X-Cu superexchange pathways (X = halogen ion). The resulting spin network can be described as four-leg “spin tubes” with a high degree of geometric frustration^{8,12} and weak intertube coupling. The ground state is a spin liquid, with a gap $\Delta \approx 0.5$ meV in the magnetic excitation spectrum. The exact spin Hamiltonian is presently unknown. However, due to the strong one-dimensionality, all relevant low-energy low-temperature properties are gov-

erned by the lowest-energy triplet of magnons.¹³ In SCC, the latter have a very large spin velocity v along the c axis, $\hbar v c \approx 14$ meV. A key observation is that, due to the geometric frustration, the minimum of dispersion is at an *incommensurate* wave vector $q_0 c / (2\pi) = 0.48$. In magnetic fields exceeding $H_c = 3.75$ T a condensation of magnons¹⁴ produces an incommensurate phase with spontaneous 3D long-range helimagnetic order of spin components transverse to the applied fields and a propagation vector $(0.78, 0, 0.48)$.^{12,15} This pitch of the spin spiral corresponds to the incommensurate dynamic spin correlations in zero field.

II. EXPERIMENTAL PROCEDURES AND RESULTS

To investigate the effect of disorder on this field-induced phase transition, we focused on the chemically modified material SCX, with the Br concentration x ranging 0–5%. The idea is that substituting Cl^- by the larger radius Br^- will affect the Cu-Cu superexchange coupling locally.¹⁶ Since the relevant Cu-X-X-Cu bond angles are far from 90° , Kanamori-Goodenough rules¹⁷ suggest that the AF nature of the interaction will be preserved, although its magnitude may be significantly affected. A random distribution of Br substitution sites will thus result in a randomization of AF bond strengths.

A series of well-faceted single crystal samples of typical mass 100 mg were grown by temperature gradient method from ethanol solution with varying relative Cl/Br content. For each nominal Br concentration x , the samples were characterized by x-ray diffraction using a Bruker Apex-II single crystal diffractometer and by microelemental chemical analysis (Schöniger method). We found all crystals to be isostructural to the parent compound. Atomic positions were refined together with the actual Br concentration, assuming a uniform distribution of substitution sites. The fitted Br content is in good agreement with chemical data and the nominal Br concentration in solution. As far as the lattice parameters are concerned, the strongest effect of Br substitution is on the c (ladder-leg) axis, which shows a linear increase from 10.035 Å to 10.050 Å, as x varies from 0 to 5%.

A. Characterization of the disorder-free material

The clearest signature of the field-induced ordering transition in disorder-free SCC is the lambda anomaly in the temperature dependence of specific heat.¹⁴ Figure 1(a) shows

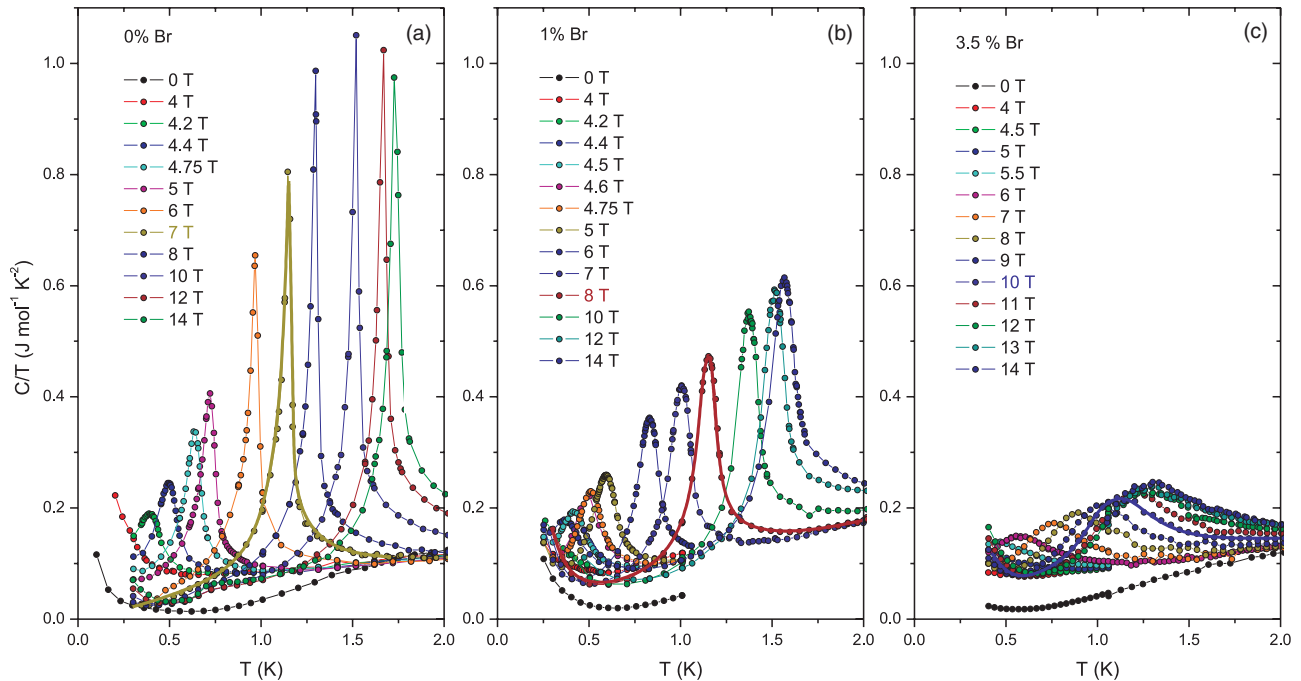


FIG. 1. (Color online) Connected symbols: specific heat measured as a function of temperature at various applied fields in SCX with $x = 0$ (a), $x = 0.01$ (b), and $x = 0.035$ (c). The heavy solid curves are guides to the eye emphasizing curves peaked at $T \sim 1$ K for easy visual comparison.

the heat capacity measured in a 3.5 mg $x = 0$ sample as a function of temperature in several fields applied along the crystallographic c axis, using a Quantum Design PPMS with a dilution refrigerator insert. The sharp lambda anomaly is quite prominent and allows us to trace the phase boundary on the H - T phase diagram, as shown in solid symbols in Fig. 2. The phase transition is also manifest in the field dependence of magnetic susceptibility $\chi = dM/dH$ (Fig. 3, solid symbols), measured for $H \parallel c$ on a 25 mg crystal using a Quantum Design SQUID magnetometer with an IQuantum ^3He refrigerator.²⁴ The transition appears as a sharp peak, separating the gapped phase at low fields and the ordered, susceptible high-field state. For a BEC of magnons, magnetization M is mapped onto boson density, and susceptibility χ , on the compressibility of the Bose gas.² In these terms, the transition is that between an incompressible “Mott-insulator” magnon phase below H_c , to a compressible Bose condensate of magnons at high fields. Note that at an elevated temperature of 800 mK, the step in the $\chi(H)$ curve is broadened, but a sharp peak marking the phase transition persists. The third manifestation of the 3D ordering transition is found in $M(T)$ curves measured at fixed fields applied along the c axis (Fig. 3, inset). Upon cooling through the ordering temperature, the magnetization (boson density) shows an almost discontinuous jump following a well-defined minimum, which is a known characteristic signature of BEC.¹⁸

B. Effect of disorder

The central result of this work is that Br substitution at very low concentrations *destroys* the thermodynamic field-induced transition described above. Already for $x = 1\%$ the lambda

anomalies in the $C(T)$ curves at all fields are replaced by visibly broadened peaks [Fig. 1(b)]. For $x = 3.5\%$ the peak widths increase further [Fig. 1(c)]. This behavior indicates that the sharp transition for $x = 0$ gives way to a crossover in disordered samples, presumably to a state with short-range order. Indeed, preliminary neutron diffraction experiments on deuterated samples, performed at the TASP 3-axis spectrometer

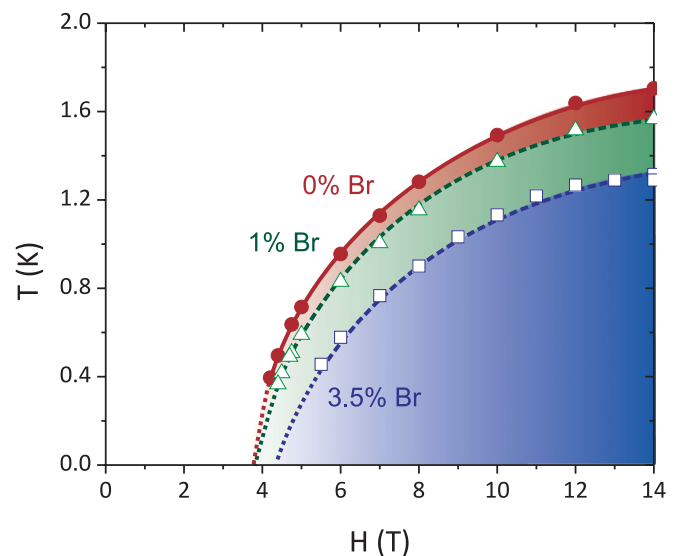


FIG. 2. (Color online) Solid symbols: H - T phase boundary of SCC deduced from specific heat data. Open symbols: field dependence of crossover temperatures in SCX for $x = 0.01$ and $x = 0.035$. The latter are defined as positions of broad specific heat maxima in constant-field scans. Lines are guides for the eye.

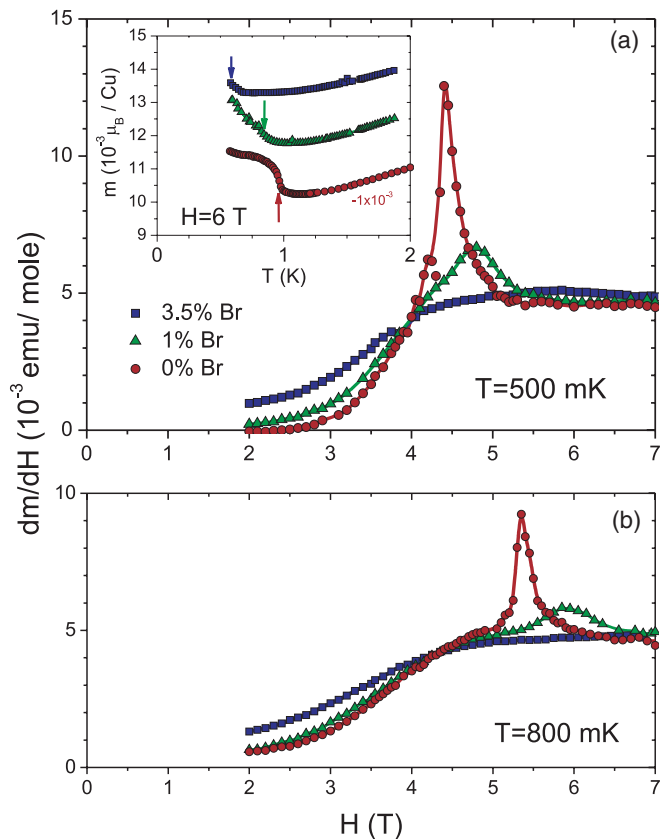


FIG. 3. (Color online) Field dependence of DC magnetic susceptibility measured in SCX with $x = 0$, $x = 0.01$, and $x = 0.035$, at $T = 500$ mK (a) and $T = 800$ mK (b). Lines are guides for the eye. Inset: magnetization as a function of temperature measured at a constant field $H = 6$ T $> H_c$. The $x = 0$ data set (circles) has been shifted down by $1 \times 10^{-3} \mu_B/\text{Cu}$ for visualization purposes. The arrows indicate the positions of C/T maxima for the respective Br concentrations.

at Paul Scherrer Institut and at the D23 diffractometer at ILL, failed to observe any magnetic diffraction peaks associated with helimagnetic order. A thorough search for such reflections was performed in the $(h, 0, l)$ reciprocal-space plane for $0.45 < l < 0.55$, at $T = 50$ mK and $H = 6$ T.²⁵ While it cannot be fully excluded that the peak absence is not due to disorder, but to a drastic change of the propagation vector along the chain axis, due to the large spin wave velocity this scenario appears unlikely.

If the high-field phase is indeed short-range ordered, one can expect diffuse magnetic scattering in the form of anisotropically broadened peaks at Bragg positions. In SCX no such scattering could be found, but this result cannot be considered conclusive. Unfortunately, experimental limitation would have made it unobservable even if it were present. In the disorder-free material where the peaks are sharp, they are extremely weak and correspond to only $0.04 \mu_B$ ordered moment.⁸ Even a small broadening due to short-range order in SCX would render them invisible above the rather high intrinsic background.

Returning to the specific heat data in Fig. 1, we note that even as the peaks broaden upon Br substitution, their positions are not subject to a substantial shift. The corresponding

crossover temperatures at each field were identified with the maxima in $C(T)$, obtained in empirical narrow-range Lorentzian fits. The thus determined crossover lines, for $x = 1\%$ and $x = 3.5\%$, are shown in open symbols in Fig. 2.

The effect of chemically introduced randomness on the magnetic properties is no less dramatic. The field dependence of magnetic susceptibility for the disordered samples is shown in Fig. 3. At all temperatures, the sharp peak seen for $x = 0$ is replaced by a broad feature at $x = 1\%$, and altogether absent for $x = 3.5\%$. This behavior is accompanied by an overall broadening of the step in the $\chi(H)$ curve with increasing x . The jump in the temperature dependence of the magnetization is also smeared out by disorder (inset in Fig. 3). Thus, magnetometric measurements confirm that the BEC transition in the parent compound is replaced by a broad crossover in the disordered systems.

III. DISCUSSION

The effect of bond disorder on the field-induced BEC of magnons has been previously studied experimentally in a number of prototype materials, including IPA-Cu(Cl_{1-x}Br_x)₃,¹⁹ Tl_{1-x}K_xCuCl₃ (Ref. 20), and most recently Ni(Cl_{1-x}Br_x)₂·4SC(NH₂)₂.¹¹ It was found that disorder may considerably affect the phase boundary, modify the critical behavior, and give rise to a compressible disordered state just below the 3D ordering transition. However, in *all* of these materials, the transition itself is preserved, even for a large concentration of disorder sites that significantly alters the critical field and temperature. The strength and sharpness of anomalies in thermodynamic properties remains practically unaffected by disorder. The behavior of SCX is clearly different. Here the condensate appears to be extraordinarily fragile with respect to randomness, resulting in qualitative contrast between thermodynamic anomalies in the pure and disordered samples. It is this contrast that we emphasize as the main experimental finding, since weak or broadened anomalies *per se* do not necessarily signify the absence of a phase transition (see, for example, Refs. 21 and 22). Below we propose a qualitative model that attributes this behavior to a geometric frustration of magnetic interactions and the incommensurate nature of spin correlations.

Consider a single geometrically frustrated spin tube in SCC. In a magnetic field that exceeds H_c , it is a gapless Luttinger spin liquid²³ with a correlation length that diverges at $T \rightarrow 0$. These increasingly long-range correlations will be incommensurate and helimagnetic. Their pitch $\phi_0 = q_0 c$ will be defined by the magnitude of geometric frustration of interactions in the spin tube. A random distribution of Br sites in SCX will result in a random distribution of the frustration ratios along the spin tube, and, in turn, a randomized phase of the spiral spin correlations. For site j , we can write $\phi(j) = \phi_0 j + \sum_{i < j} \delta\phi_i$, where $\delta\phi_i$ are defect-induced phase slips. Now consider the interaction of two adjacent spin tubes, assuming no correlations between their substitution sites. Due to the random phase slips in the spin spirals in each spin tube, intertube exchange interactions will average to zero at the mean-field level. Thus, 3D interactions that are critical for establishing long-range magnetic order at a finite temperature will be entirely wiped out by the *random frustration* introduced

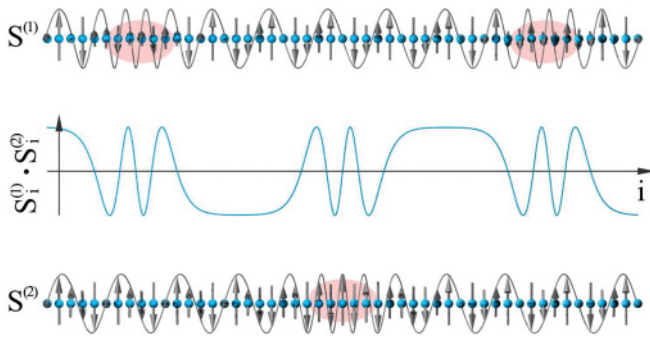


FIG. 4. (Color online) A cartoon representation of the random frustration mechanism. The plot in the center shows the exchange energy (scalar product) of interacting spins from two adjacent one-dimensional helimagnets. Defects (shaded ellipses) induce randomly positioned phase slips, which ensures that interchain interactions average to zero.

by bond disorder. This scenario is schematically illustrated in Fig. 4. While it is not directly supported by the experimental data, it appears very plausible in the particular case of SCX. Indeed, in our material, the interchain interactions are known to be weak.⁸ At the same time, due to the very large spin velocity (temperature equivalent of about 150 K), one-dimensional correlations are already very well developed at the experimental temperatures of a few kelvins. In other words, upon cooling in a field, individual spin tubes are practically ordered, and it is the the intertube ordering that occurs at the transition point in the disorder-free material.

It is important to emphasize that in the proposed scenario even *weak* and sparse defects will suppress 3D order. Indeed, even small phase slips induced by each impurity will, over large distances, lead to an accumulation of phase difference between adjacent spin tubes. This is a specific consequence of the incommensurate and quasi-1D nature of the disorder-free system.

Incommensurability and frustration being the key ingredients of our model makes it *distinct* from the basic mechanism of Bose glasses. The latter emerges from the mapping the magnetic system onto a lattice gas of magnons with a spatially random chemical potential. Neither incommensurability or frustration are explicitly present in the resulting bosonic Hamiltonian, and are therefore overlooked by the approach. For our newly proposed mechanism, there are numerous theoretical questions to be further addressed. Is there a critical strength of frustration disorder that is required to disrupt the magnon condensate? What are the critical properties of the order/disorder transition induced by random frustration? How does the random frustration physics interplay with that of the “conventional” Bose glass?

ACKNOWLEDGMENTS

This work is partially supported by the Swiss National Fund under Project No. 2-77060-11 and through Project 6 of MANEP. We thank V. Glazkov (Kapitza Institute, Russian Academy of Science) for his involvement at the early stages of this project.

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