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Evidence of a magnetic Bose glass in $(CH_3)_2CHNH_3Cu(Cl_{\{0.95\}}Br_{\{0.05\}})_3$ from neutron diffraction

Tao Hong,[1] A. Zheludev,[2,3,*] H. Manaka,[4] and L.-P. Regnault[5]
[1]*Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[2]*Laboratorium für Festkörperphysik, ETH Zürich, Zürich CH-8093, Switzerland*
[3]*Laboratory for Neutron Scattering, ETH Zürich and Paul Scherrer Institute, Villigen PSI CH-5232, Switzerland*
[4]*Graduate School of Science and Engineering, Kagoshima University, Korimoto, Kagoshima 890-0065, Japan*
[5]*INAC-SPSMS-MDN, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
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We report the single-crystal study of the bulk magnetization and neutron-scattering measurements on a quantum $S=1/2$ spin ladders system IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ with quenched disorder. In zero field, the disordered spin liquid phase is preserved as in pure IPA-$CuCl_3$. Due to the bond randomness, a different Bose glass phase was directly observed in $H_c<H<H'$, which separates the spin liquid phase from the unconventional Bose-Einstein condensation phase. The observed finite value of boson compressibility (dM/dH) and lack of field-induced three-dimensional long-range order are consistent with the theoretical prediction.

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A "Bose glass" (BG) is an exotic state of matter that emerges in systems of interacting bosons in the presence of quenched disorder. At sufficiently low temperatures, *disorder-free* bosons are subject to so-called Bose-Einstein condensation (BEC). BEC can involve atoms in liquid ^{4}He,[1] laser-cooled ions in magnetic traps,[2] Cooper pairs in superconductors,[3] or magnons in magnetic systems.[4] Due to peculiarities of Bose statistics, particles lose their individuality and occupy a unique quantum-mechanical state. The wave function of this condensate establishes long-range quantum phase coherence across a macroscopic sample. For repulsive bosons, quenched disorder disrupts the condensate and interferes with phase coherence. The result is a peculiar glassy state with only short-range phase correlations.[5,6] While some experimental evidence of this was found in ultracold atoms,[7] high-temperature superconductors,[8] and quantum magnets,[9,10] none of the studies were direct. The key characteristic, namely the wave function of the condensate disrupted by disorder on the microscopic scale, remained inaccessible. In this Rapid Communication, we report a direct neutron-diffraction observation of short-range correlations of the BEC order parameter in a magnetic BG. This phase is realized in the quantum spin ladder compound IPA-$Cu(Cl_{0.95}Br_{0.05})_3$, where disorder is induced by random chemical substitution.[11]

The disorder-free parent compound IPA-$CuCl_3$ is a prototypical $S=1/2$ antiferromagnetic (AF) spin ladder material with the ladders running along the a axis of the crystal.[12,13] Nearest-neighbor spin interactions along the legs of each ladder are AF. Nearest-neighbor interleg correlations are ferromagnetic (FM). However, interleg coupling is dominated by next-nearest-neighbor interactions. These are formed by Cu-Cl-Cl-Cu superexchange pathways, and are robustly AF. As discussed in Ref. 13, magnetic anisotropy in this material is negligible. Zero-point quantum spin fluctuations in such Heisenberg ladder structures destroy conventional magnetic order. The result is a nonmagnetic "spin liquid" state. The lowest-energy excitations are a triplet of long-lived $S=1$ quasiparticles with a minimum excitation energy Δ. For IPA-$CuCl_3$, this energy gap is $\Delta=1.17$ meV.[12] The quasiparticles obey Bose statistics, and are mutually repulsive at short distances. Since the energy cost of creating each quasiparticle is at least Δ, the ground state is a vacuum of bosons. The vacuum persists in modest applied magnetic fields. However, due to Zeeman effect, the gap in the $S_z=+1$ magnon decreases linearly with increasing field H, and reaches zero at $H_c=\Delta/(g\mu_B)$. For IPA-$CuCl_3$, $H_c=9.7$ T.[14] Once $H>H_c$, the quasiparticle energy becomes negative, and macroscopic number of them are incorporated in the ground state. Since each carries a spin projection $S_z=+1$, their density is equal to the uniform magnetization: $\langle\rho\rangle=m\equiv\langle S_z\rangle$. *Simultaneously*, the emerging bosons undergo magnon BEC.[4,15] The signature of this quantum phase transition is the appearance of spontaneous long-range *staggered* (AF) magnetic order of spin components *perpendicular* to the direction of applied field. This transverse magnetization, written in complex form $\Psi=\langle S_x\rangle+i\langle S_y\rangle$, is the effective wave function of the Bose condensate. In IPA-$CuCl_3$ it was previously *directly* probed by means of magnetic neutron diffraction, where the measured scattering intensity is proportional to the Fourier transform of the spin-correlation function.[13,16] The BEC phase is characterized by a new set of magnetic Bragg peaks with half-integer Miller indexes. Their intensity is proportional to the square of the BEC order parameter. Note that in other experimental realizations of BEC of magnons, such as that in thin films[17] or ^{3}He,[18] the condensate wave function remains experimentally inaccessible.

The best way to introduce quenched disorder in a magnetic system is by chemical substitution. Most previous studies targeted the magnetic ions, randomly substituting them by nonmagnetic or different spin impurities. The problem with this approach is that it qualitatively alters the nature of the spin liquid state. Upon substitution, local $S=1/2$ degrees of freedom are liberated in direct proportion to the impurity concentration.[19] These free spins are the dominant contribution to bulk magnetization, give rise to a divergent magnetic susceptibility, and enable conventional long-range ordering at low temperatures.[20] In addition, each impurity becomes a potent scattering center. This causes a collision damping of magnons,[21] making the very quasipar-

ticles that are supposed to condense poorly defined. Thus, any physics related to the BEC transition is wiped out. With this in mind, in the present study we adopted a radically different "softer" method. Quenched disorder was introduced in IPA-$CuCl_3$ by a partial substitution of nonmagnetic Br^- for the likewise nonmagnetic Cl^-.[10] This modification does not directly involve the spin-carrying Cu^{2+} ions and does not add additional anisotropy term. Instead it affects the bond angles in the Cu-halogen-halogen-Cu superexchange pathways. The strength of magnetic interactions on the affected bonds is thereby modified, but their AF character is preserved.

IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ single crystals were grown in solution as described in Ref. 11. The microscopic homogeniety of Br distribution was confirmed by single-crystal x-ray diffraction studies, that also confirmed the Br content to be within 10% of nominal. Bulk magnetization data were taken at $T=500$ mK. The magnetic field was applied along the c axis of the crystal.[10] Neutron experiments were carried out in the $(h,k,0)$ scattering plane on an assembly of five fully deuterated crystals with a total mass of 0.8 g and a mosaic spread of 0.7°. Inelastic measurements were performed on IN22 three-axis spectrometer at ILL using a standard He-flow cryostat with a Be neutron filter after the sample and fixed final neutron energy $E_f=5$ meV. High-field diffraction data were collected using a vertical field cryomagnet and a dilution refrigerator insert on the IN22, with a pyrolytic graphite (PG) filter after the sample and $E_f=14.7$ meV. The experimental resolution was calculated in the Popovici approximation.

Previous bulk studies have shown that in IPA-$Cu(Cl_{1-x}Br_x)_3$ the spin liquid ground state *remains intact* up to about $x=13\%$ Br content.[11] In the present work we shall focus on the $x=0.05$ material. While magnetic-susceptibility experiments revealed some residual free spins in this system, their concentration is negligibly small.[11] From the bulk magnetization, where the paramagnetic contribution at $T=500$ mK remains smaller than $0.003\mu_B$ per formula up to $H=8$ T, we estimate that there are fewer than one free $S=1/2$ spin for every 10 Br substitutions.[10] These are likely due to crystallographic defects: IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ crystals grown from solution are systematically smaller and of inferior quality compared to those of the pure compound. The singlet ground state in IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ was confirmed in recent mu-SR studies, where no long-range magnetic order was observed down to at least $T=330$ mK.[22] However, the clearest evidence of that this material is an immaculate spin liquid is provided by our recent inelastic neutron-scattering experiments. The excitation spectrum shown in Fig. 1 was measured at $T=1.5$ K and reveals well-defined bosonic quasiparticles with a spin gap $\Delta=1.24(1)$ meV. Just like in the pure IPA-$CuCl_3$ (Ref. 12) and PHCC,[23] the quasiparticle spectrum terminates at a critical wave vector $h_c\sim-0.2$. Apart from the slightly larger gap energy, these excitations are almost indistinguishable from those in pure IPA-$CuCl_3$. They are also at least as long lived: knowing our energy resolution, we can estimate the intrinsic quasiparticle energy width to be $\Gamma<0.03$ meV. Thus, despite the structural disorder, IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ indeed *remains a true quantum spin liquid*.

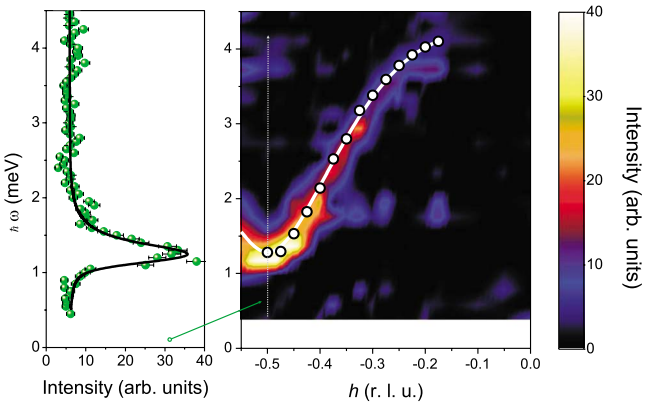

FIG. 1. (Color online) The excitation spectrum (false color plot) measured in IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ at $T=1.5$ K in zero applied field reveals sharp dispersive quasiparticles with an energy gap $\Delta=1.24(1)$ meV. A typical energy scan (left panel, symbols) shows a well-defined peak with an energy width entirely due to experimental resolution (solid line, calculation).

In external magnetic fields exceeding $H_c\sim10$ T, IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ becomes magnetized [Fig. 2(a), circles].[10] The magnetization derivative does not jump abruptly, as in IPA-$CuCl_3$ under similar conditions [Fig. 2(a), solid curves]. Instead, it gradually increases between H_c and

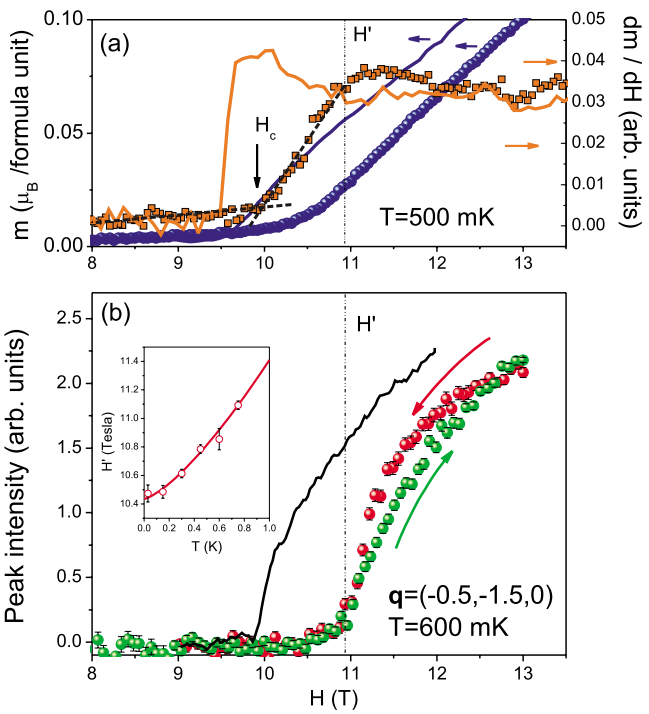

FIG. 2. (Color online) Signatures of various quantum phases in IPA-$Cu(Cl_{0.95}Br_{0.05})_3$. The uniform magnetization (a, circles, from Ref. 10) represents the density of bosons in the ground state. The rate of increase in uniform magnetization is the boson compressibility (a, squares). The thin solid lines correspond to the disorder-free parent compound IPA-$CuCl_3$. (b) The magnetic Bragg intensity measured at the maximum represents the effective BEC order parameter. The measured temperature dependence of H' is shown in the inset. The solid curve is a guide for the eyes.

$H' \sim 11$ T [Fig. 2(a), squares] and is roughly constant at higher fields. H_c was determined by linear interpolations of the dM/dH curve, as shown in Fig. 2. H' was determined in power-law fits to the temperature dependence of the (0.5, 1.5, 0) magnetic Bragg peak measured upon cooling. The net magnetization and its derivative are to be interpreted as the density and compressibility of $S_z=+1$ quasiparticles now present in the ground state. Our key result is that, unlike in the parent compound, in the doped material these quasiparticles initially *fail to form a condensate*, the latter only setting in at higher fields. In the pure system, sharp Bragg reflections corresponding to magnetic long-range order appear simultaneously with bulk magnetization [Fig. 2(b), solid curve].[13,16] In contrast, in IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ only broad peaks are observed around the propagation vector (1/2,1/2,0). At $T=600$ mK they are totally absent below H_c, appear somewhere between H_c and H' but remain barely detectable, and grow rapidly beyond H' [Fig. 2(b), circles]. They persist to the maximum attainable experimental field of 13 T. Similar behavior is observed at other temperatures. The measured T dependence of H' is plotted in the inset of Fig. 2.

The main panel of Fig. 3 shows scans across one representative reflection. Here the dashed lines are the experimental resolution. The finite intrinsic peak widths unambiguously indicate that ordering is short range. The corresponding correlation lengths are history dependent. This is because in order to enter the BEC phase the system has to cross through the disordered BG state. The resulting pinning of magnetic domain walls or vortexes by the random potential makes true long-range order kinetically inaccessible. In a sample zero-field-cooled (ZFC) to 30 mK, at $H=13$ T, the correlation lengths are $\zeta_a=70(6)$ lattice units along the ladder direction (a axis of the crystal) and only $\zeta_b=11.7(0.1)$ lattice units perpendicular to it (b axis). If a sample is cooled in a 13 T field, the peaks are much sharper, though still broader than resolution, with $\zeta_a=143(8)$ and $\zeta_b=52(2)$. The peak intensity is correspondingly higher in the field-cooled (FC) sample, and shows hysteresis when the field is repeatedly decreased below H_c, then again increased [Fig. 2(b)]. Similar hysteresis was observed in IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ at all temperatures between 30 and 750 mK but never in pure IPA-$CuCl_3$.[13,16] History-dependent behavior and a difference between FC and ZFC samples are a signature of a magnetic glass.

Based on bulk magnetization data, it was previously suggested that a BG emerges in IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ in magnetic fields exceeding $H_{c3} \sim 40$ T, while for $H_c < H < H_{c3}$ the system is in a BEC phase.[10] The present direct measurement of the effective BEC wave-function correlations unambiguously show that the glass forms already at H_c, as soon as the bosons precipitate in the ground state. This behavior can be qualitatively understood in the framework of recent theories.[24,25] The ground state of weakly interacting spin ladders are a linear combination of valence-bond states composed of local singlet spin pairs. Due to the spatially randomized interaction strength, certain singlets may have a reduced gap energy. When the magnetic field is increased past H_c, these are the first to become magnetized. Each such broken singlet corresponds to a $S_z=+1$ boson localized by the quenched disorder. The phenomenon is similar to Anderson localization of fermions in a random potential. The role of

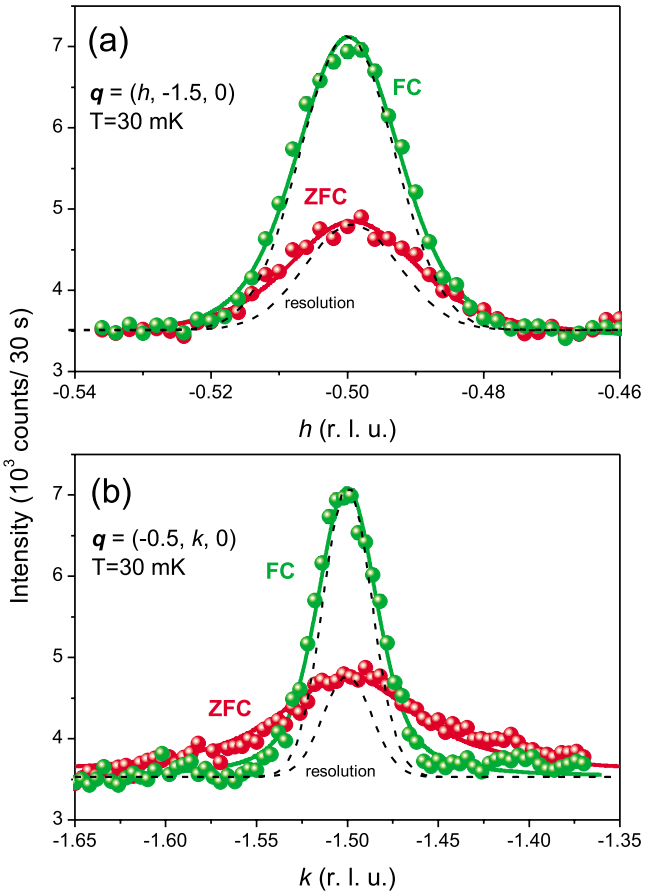

FIG. 3. (Color online) Neutron scans across the $(-0.5,-1.5,0)$ point measured in ZFC and FC IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ samples at $T=30$ mK in $H=13$ T applied field (symbols), in the BEC phase. The magnetic peaks are broader than experimental resolution (dashed lines), indicating that only short-range correlations of the BEC order parameter are present. The solid lines are Voigt function fits to the data.

the Pauli exclusion principle that enables the latter is played by the strong short-range repulsion between spin ladder excitations. The result is the magnetic BG with a finite boson density, but only short-range frozen transverse spin (effective wave-function) correlations.[5,6] A lack of long-range magnetic order and a nonzero yet finite compressibility (dM/dH) are the two key feature of a BG. The latter distinguish it from other disordered phases of quantum spin systems: the incompressible Mott glass[26] and the random single phase that has divergent compressibility.[27] The quasi-one-dimensional character of IPA-$Cu(Cl_{0.95}Br_{0.05})_3$ undoubtedly favors boson localization and helps stabilize the BG state. Indeed, only in one dimension does the BG phase appear for arbitrary weak disorder.[5] In higher dimensions the magnitude of disorder needs to exceed some threshold value to disrupt the condensate.[6]

At a certain higher field, that we identify with H', the gaps associated with even the strongest bonds in the system are overcome by Zeeman energy. Beyond this point one expects to recover the coherent BEC phase[24] in which the compressibility is constant and AF spin correlations are long range.[4] Qualitatively, the field range $H'-H$ corresponds to

the energy difference between the strongest and weakest AF bonds. The same energy scale determines the doping-induced shift of the gap at $H=0$. For IPA-Cu$(Cl_{0.95}Br_{0.05})_3$ the latter is of the order of 0.1 meV, and corresponds to a field range of 1 T, consistent with the measured $H'-H_c$.

In our experiments, beyond H', the compressibility indeed levels off and AF correlations rapidly build up. However, the latter remain short range. In this system, there is not necessarily a contradiction. We suggest that while at higher fields the BEC phase may be the true ground state, at low temperatures it remains kinematically inaccessible. As the external field is increased beyond H_c, local correlated regions grow in size around each broken singlet that act as nucleation centers. By the time H' is reached, the macroscopic sample is a mosaic of uncorrelated finite-size AF domains or a textured pattern of magnetic vortexes. At low temperatures the domain walls and/or vortexes are pinned by the random potential. The system is frozen in this short-range correlated state. In a field-cooled sample, the BG-BEC boundary is crossed at a higher temperature, where the domain walls and vortexes are more mobile. The result is fewer pinned defects, longer-range correlations and sharper diffraction peaks. This interpretation allows us to reconcile the conclusions of previous bulk measurements[10] with the present neutron-scattering study. For $0<H<H_c$, IPA-Cu$(Cl_{0.95}Br_{0.05})_3$ is a true spin liquid. For $H_c<H<H'$ the system becomes a magnetic BG. Long-range order in the form of BEC may be the ground state for $H'<H<H_{c3}$, but the system stays frozen in a metastable glassy state. Between H_{c3} and the saturation field $H_{c2}\sim 60$ T a second BG phase is realized, as discussed in Ref. 10. It is related to the saturation transition, which can also mapped on BEC.[28]

In summary, the unique ability of neutron scattering to probe the effective condensate wave-function correlations and of magnetization measurements to probe boson density and compressibility in magnetized quantum spin liquids, allowed us to directly observe the exotic magnon BG phase.

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*andrey.zheludev@psi.ch

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