Specific Heat of the $S = 1/2$ Two-Dimensional Shastry-Sutherland Antiferromagnet
SrCu$_2$(BO$_3$)$_2$ in High Magnetic Fields

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We characterize the field-induced magnetic phases of SrCu$_2$(BO$_3$)$_2$, a frustrated spin-1/2 Heisenberg antiferromagnet in the two-dimensional Shastry-Sutherland lattice, using specific heat in magnetic fields up to 33 T. We find that the spin gap persists above the expected critical field $H_c = \Delta/J_{	ext{ant}}$ of 21 T despite the appearance of magnetic moment in the ground state. At the magnetization plateau at 1/8 of the saturation, the $S_z = +1$ triplets that carry the magnetization of the ground state are observed to form a two-dimensional spin gas of massive bosons. A spin gas consisting of a large number of massive particles continues to completely dominate the specific heat in the field region above the plateau, although the magnetization increases with increasing field. Ordering is observed at a temperature immediately below the spin-gas regime.

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Geometrical frustration is one of the important subjects in strongly correlated systems [1]. In particular, the fascinating interplay of geometrical frustration and quantum fluctuation in two dimensions provides a fertile ground for new physics, as has been theoretically demonstrated for Heisenberg antiferromagnets in the triangular lattice and the kagomé lattice. For the $S = 1/2$ triangular antiferromagnet, there now appears to be a consensus that Néel order must exist despite the strong frustration [2]. The $S = 1/2$ kagomé antiferromagnet has been predicted to possess a gap separating the ground state from upper triplet levels and a band of low-lying singlet excitations within the triplet gap, although the exact nature of the ground state is still under debate [3]. These predictions are yet to be borne out by experiment, because no isotropic $S = 1/2$ model system has been identified in the laboratory for these lattices.

In the last few years, there has been a rapid progress in the understanding of the $S = 1/2$ Heisenberg antiferromagnet in the Shastry-Sutherland lattice [4], another two-dimensional frustrated geometry, for which the exact ground state is known at zero and low magnetic fields despite geometrical frustration. The progress owes largely to the discovery of the spin gap and other novel magnetic properties in SrCu$_2$(BO$_3$)$_2$ [5], the only known laboratory model for the geometrically frustrated $S = 1/2$ two-dimensional Heisenberg antiferromagnet.

The low-field ground state of the Shastry-Sutherland antiferromagnet is simply a product of spin-dimer singlet wave functions, and the dimerization by the diagonal bond $J$ causes a gap to form [4]. The gapped triplet excitations, which are also spin dimers at least to a good approximation, have a large mass as a result of the unique lattice topology involving orthogonal arrangement of dimers [5]. In SrCu$_2$(BO$_3$)$_2$, the coupling strengths extracted from experiments are $J = 85$ K for the intra-dimer exchange and $J' = 54$ K for the inter-dimer exchange [5] or $J = 70$ K and $J' = 42$ K [14]. The large $J'$ makes the energy gap $\Delta$ substantially smaller than $J/5$ [12]. In fact, the ratio $J'/J$ is very close to the critical value $0.70$ [6] for the quantum phase transition to a square-lattice Néel state. In other words, $J$ and $J'$ are extremely frustrated.

The striking feature of SrCu$_2$(BO$_3$)$_2$ is the existence of magnetization plateaus at 1/8, 1/4, and 1/3 of the saturation magnetization [2] [14]. Although there is a substantial spin-phonon coupling in this compound [15], the plateaus are an intrinsic property of Heisenberg spins in the Shastry-Sutherland lattice and due to geometrical frustration [6] [16]. The spin state at any magnetization plateau is obviously gapped [17], and a possible connection between magnetization plateaus and quantized Hall-conductance plateaus has been pointed out [16]. In contrast, the states between $H_c$ and the first plateau, between two adjacent plateaus, and between the highest plateau and the saturation field have been believed to be all gapless by a prevalent view on magnetization plateaus.

In this paper, we examine three field-induced magnetic phases of SrCu$_2$(BO$_3$)$_2$: the one between $H_c$ and the first plateau with 1/8 of the saturation magnetization, the plateau phase, and much of the phase between the 1/8 and 1/4 plateaus. The results refute the conventional view on the nature of the first phase and uncover the presence of a two-dimensional spin gas in the other phases, as well as ordering in the third phase.

Prior to our work, two-dimensional Bose gas has been realized in spin-polarized atomic hydrogen adsorbed on the surface of superfluid $^4$He [18]. However, the spin gas in SrCu$_2$(BO$_3$)$_2$ is the first example that is amenable to thermodynamic studies.

The calorimeter for this investigation employed the relaxation method [19]. In order to optimize the relaxation time at different temperature and magnetic-field regions, three samples of different sizes were used, all taken from a high-purity single crystal whose growth procedure has been described in Ref. [20]. The sample sizes were roughly $3 \times 3 \times 0.07$ mm$^3$, $4 \times 3 \times 0.3$ mm$^3$, and...
The spin gap decreasing linearly with magnetic field and the dependence observed in the earlier experiment, with the reproducibility. The 14 T data precisely follow the field the earlier result, indicating a high sample quality and was excellent agreement between the present data and at magnetic fields up to 12 T [12]. At zero field, there and 14 T for comparison with earlier specific-heat results 0.53 K and 15 K. Additional data were taken at zero field 3 × 3 × 1.3 mm³, and the magnetic field was applied parallel to the crystalline c axis, perpendicular to the two-dimensional layers of the $S = 1/2$ Cu²⁺ spins. In this field orientation, the spin gap for the $S_z = +1$ triplets is split into two branches that are 4.1 K apart by the Dzyaloshinskii-Moriya interaction [21, 22]. According to the $g$ factor measured by ESR [21], the lower gap is expected to close at $H_c = \Delta / g \mu_B$ of 21 T.

The measurements were done primarily in magnetic fields between 22 T and 33 T at temperatures between 0.53 K and 15 K. Additional data were taken at zero field and 14 T for comparison with earlier specific-heat results at magnetic fields up to 12 T [12]. At zero field, there was excellent agreement between the present data and the earlier result, indicating a high sample quality and reproducibility. The 14 T data precisely follow the field dependence observed in the earlier experiment, with the spin gap decreasing linearly with magnetic field and the position of the broad maximum remaining at 8 K.

Figure 1 shows the specific heat at 22 T and 24 T, where the spin gap is expected to be absent and the ground state is magnetic [3, 14], together with the 14 T result for comparison. The $T^3$ phonon contribution to the specific heat has been subtracted from all the data presented in this paper, as determined by Kageyama et al. [12] Instead of a broad maximum at 8 K, a new hump appears at 22 T and 24 T at temperatures below 1.4 K. The position of this low-temperature maximum decreases with increasing magnetic field. At 22 T, the low-temperature tail of the hump clearly shows a gapped behavior, whereas the 24 T data do not extend to a sufficiently low temperature.

The overall behavior of the specific heat can be explained in terms of the dimer-quadrumer model of Hofmann et al. [27], who incorporated the repulsion between triplet spin dimers and bound pairs of triplet dimers as a mean field. The line for 14 T in the figure is a calculation using exactly the same parameters chosen by these authors to fit the specific-heat data at fields up to 12 T. Similar to their fits, the 14 T calculation reproduces the experimental data very well at temperatures below the broad peak.

In order to fit the data at 22 T and 24 T, we have found that it is necessary to allow the gap energy $\Delta_+^0$ of the $S_z = +1$ triplets and the mean-field strength $v_0$ of the repulsion term to be fitting parameters. The best fits shown in the figure are obtained by choosing $\Delta_+ = 4.6$ K and 3.2 K for 22 T and 24 T, respectively, and $v_0 = 10$ K for both fields. The fit at 22 T is good primarily at temperatures below the broad low-temperature peak, whereas the fit at 24 T agrees well with the data up to 4 K. The good overall agreement leads us to conclude that the ground state is gapped at both fields.

The remarkable persistence of the gap in the field-induced magnetic phase contradicts the widely held view that the ground state above $H_c$ evolves with increasing magnetic field by simply increasing the number of $S_z = +1$ triplets within itself. We propose in contrast that mixing of at least one of the $S_z = +1$ triplet levels with the singlet ground state is responsible for the evolution of the magnetization below the 1/8 plateau and for the anticrossing that keeps the gap open even above $H_c$. The mixing is probably caused by the Dzyaloshinskii-Moriya interaction. The gap keeps the ground state in a spin-liquid phase with a non-zero magnetization. This explains why the translational symmetry is maintained in this field region even at a temperature as low as 35 mK, as has been found by NMR [27]. We conclude that the region from zero field up to the lower edge of the 1/8 magnetization plateau is a contiguous phase, with no ordering even at fields above $H_c$.

The situation resembles the behavior of the Haldane-gap antiferromagnet NENP, where the staggered $g$ tensor of two non-equivalent Ni sites causes the triplet excitation to anticross the ground state at $H_c$. [25, 24] and magnetization develops with no long-range order due to the inter-chain coupling [24]. It is interesting to note that isolated triplet spin dimers in the Shastry-Sutherland lattice have been predicted to be unstable below the 1/8 plateau and they cannot be constituents of the ground state in this field region [21].

The present result is consistent with the ESR experiments [21, 22], which have found no excitation level that reaches the ground state at $H_c = 21$ T. In fact no such level has yet been discovered up to 40 T. Instead, the behavior of the lower $S_z = +1$ branch, and possibly also the upper branch, suggests anticrossing around $H_c$ [22].

The fitting parameters are also in good agreement with the ESR data [22], which give $\Delta_+ = 4.8$ K and 6.6 K for the two branches of excitations at 22 T. The ESR values at 24 T are 5.2 K and 5.5 K. Our value for the repulsion

![Figure 1: Specific heat of SrCu$_2$(BO$_3$)$_2$ at 14 T, which is below the expected critical field $H_c$ of 21 T, and at 22 T and 24 T in the region between $H_c$ and the first magnetization plateau at 1/8 of the saturation. The solid lines are the fits discussed in the text. The broken line is the $T^3$ phonon contribution that has been subtracted from the data.](image)
FIG. 2: Specific heat of SrCu$_2$(BO$_3$)$_2$ at 27.5 T (○), which is the midpoint of the 1/8 magnetization plateau, and at higher fields in the region between the 1/8 and 1/4 plateaus: 29.6 T (□), 31 T (△), 32 T (○), and 33 T (△). The dotted line indicates $C = R/8$. The solid line through the 27.5 T data points below 5 K is a single-parameter fit for a non-interacting two-dimensional Bose gas. Other solid lines are guides to the eye. The $T^5$ phonon contribution shown by the broken line has been subtracted from the data. The inset shows the ordering temperature as a function of magnetic field.

parameter $v_0 = 10$ K at 22 T and 24 T is considerably smaller than 17 K for fields up to 12 T and at 14 T. This is expected, since the mixing of an $S_z = +1$ excited state with the ground state at fields above $H_c$ turns it into a more singlet-like object, which experiences less repulsion due to the inter-dimer exchange $J'$.

Figure 2 shows the specific heat for fields of 27.5 T and higher. 27.5 T corresponds to the midpoint of the 1/8 magnetization plateau, where Cu NMR has found evidence for a rhomboid ordered structure involving $S_z = +1$ triplets. Within our experimental accuracy, the specific heat at this field is 1/8 of the gas constant $R$ over a wide temperature range except for a gradual rise at temperatures above 5 K and a small decrease at temperatures below 1 K. This is conclusive evidence that a two-dimensional spin gas is formed by the $S_z = +1$ triplets whose number equals 1/8 of the total spin dimers. This conclusion is consistent with the $^{11}$B NMR spectra, according to which the spin superstructure disappears somewhere between 35 mK and 1.5 K. Evidently, the transition from a rhomboid spin solid to the spin gas occurs at a temperature below 0.63 K, our lowest temperature for the plateau region.

The solid line drawn in Fig. 2 through the 27.5 T data points below 5 K is the heat capacity of 1/8 mole of ideal two-dimensional Bose gas, with the particle mass being the only fitting parameter. The fit yields a bosonic mass of $(8.7 \pm 1.0) \times 10^{-28}$ kg, which is 960 times the electronic mass. It is 62% of the mass of the lowest triplet excitation, $(1.4 \pm 0.1) \times 10^{-27}$ kg, obtained from a sinusoidal fit of the dispersion measured by inelastic neutron scattering at zero field. The similarity of the two masses suggests that the triplet excitations at lower fields are somewhat extended objects similar to the ground-state triplets at the magnetization plateau. It is important to note that the thermal de Broglie wavelength of the spin gas at 0.63 K is as large as 1.7 times the average interparticle distance. Hence, the freezing of the spin gas into a rhomboid structure takes place in a highly degenerate regime.

Surprisingly, the specific heat between 29.6 T and 33 T, in the field region above the magnetization plateau, is completely different from that in the region below the plateau and is identical with the 27.5 T data except for the low-temperature anomaly that signals phase transition. In particular, it remains at $R/8$ in the mid-temperature range within our experimental accuracy, demonstrating that the same number of particles form a two-dimensional spin gas at these fields as at the plateau. It is natural to conclude that these particles at the two field regions are identical.

On the other hand, the magnetization above the plateau increases continuously with increasing field and reaches a 52% higher value at 33 T. It is very unlikely that the extra magnetization is carried by the particles of the spin gas, since $\langle S_z \rangle$ will then have to be larger than unity and this would require mixing of an $S_z = +2$ excited state. A presence of such a state should result in a low-temperature specific-heat hump whose position changes with magnetic field, very much like the behavior shown in Fig. 1 for the field region below the magnetization plateau. We propose that the extra magnetization is carried by additional $S_z = +1$ particles that are thermodynamically inert at least up to the highest temperature of this experiment.

Phenomenologically, the particle-number conservation that underlies the two-dimensional gas behavior can be explained by large energy required for excitations that do not conserve the particle number. We believe, however, that this remarkable phenomenon deserves a fundamental explanation, which is presently lacking.

Momoi and Totsuka have predicted that two species of $S_z = +1$ bosons compose the state above the 1/3 magnetization plateau, beyond the field region explored by experiments to date. They are those same particles that form the plateau phase and additional particles that condense into a magnetic superfluid, whose density increases with increasing magnetic field. A similar two-species state in the field region above the 1/8 magnetization plateau can explain why the number of particles that make up the spin gas remains the same as in the plateau phase. However, the robustness of the particle number against thermal excitations still remains a mystery.

The sharp transition marked by the low-temperature peak in the specific heat is probably due to freezing of the spin gas. The strong field dependence of the trans-
tion temperature indicates that either the particle mass or the strength of the repulsive interaction increases with the density of the thermodynamically invisible particles. Since freezing in two dimensions is generally a Kosterlitz-Thouless transition, which has no signature in specific heat, the sharp peak suggests an importance of spin-phonon coupling or inter-layer spin coupling.

In summary, we have uncovered a distinct spin behavior in each of three high magnetic-field regions of SrCu$_2$(BO$_3$)$_2$. In the region below that of the 1/8 magnetization plateau, where translational symmetry exists, the spin gap remains open, indicating hybridization of at least one of the two $S_z = \pm 1$ triplet states with the singlet ground state, which now acquires a magnetic moment. We conclude that there is no phase transition between this region and the low-field, non-magnetic region. The regions at and above the magnetization plateau constitute a second contiguous phase, where those triplets whose number equals 1/8 of the spin dimers form a two-dimensional gas of massive bosons above the field-dependent freezing temperature. In addition, the region above the plateau contains thermodynamically inert particles that carry the magnetization in excess of 1/8 of the saturation value. Further studies are called for to identify these carriers and to elucidate their role in the ordering.

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[1] P. Schiffer and A. P. Ramirez, Comm. Cond. Mat. Phys. 18, 21 (1996); A. P. Ramirez, Czech. J. Phys. 46, Suppl. 6 3247 (1996); A. P. Ramirez, Annu. Rev. Mater. Sci. 24, 453 (1994).
[2] B. Bernu et al., Phys. Rev. B 50, 10048 (1994).
[3] See for instance A. V. Syromyatnikov and S. V. Maleyev, Phys. Rev. B 66, 132408 (2002) and references therein.
[4] B. S. Shastry and B. Sutherland, Physica B 108, 1069 (1981).
[5] H. Kageyama et al., Phys. Rev. Lett. 82, 3168 (1999).
[6] S. Miyahara and K. Ueda, Phys. Rev. Lett. 82, 3701 (1999).
[7] Zheng Wei Hong et al., Phys. Rev. B 60, 6608 (1999).
[8] E. Müller-Hartmann et al., Phys. Rev. Lett. 84, 1808 (2000).
[9] S. Miyahara and K. Ueda, Phys. Rev. B 61, 3417 (2000).
[10] S. Miyahara and K. Ueda, J. Phys. Soc. Jpn. Suppl. B 69, 72 (2000).
[11] C. Knetter et al., Phys. Rev. Lett. 85, 3958 (2000).
[12] H. Kageyama et al., J. Exp. Theor. Phys. 90, 129 (2000).
[13] W. Zheng et al., Phys. Rev. B 65, 014408 (2001).
[14] K. Onizuka et al., J. Phys. Soc. Jpn. 69, 1016 (2000).
[15] S. Zherlitsyn et al., Phys. Rev. B 62, R6097 (2000); B. Wolf, et al., Phys. Rev. Lett. 86, 4847 (2001).
[16] G. Misguich et al., Phys. Rev. Lett. 87, 097203 (2001).
[17] M. Oshikawa et al., Phys. Rev. Lett. 78, 1984 (1997).
[18] A. P. Mosk et al., Phys. Rev. Lett. 81, 4440 (1998); A. I. Safonov et al., Phys. Rev. Lett. 81, 4545 (1998).
[19] R. Bachmann et al., Rev. Sci. Instrum. 43, 205 (1972).
[20] H. Kageyama et al., J. Crystal Growth 206, 65 (1999).
[21] H. Nojiri et al., J. Phys. Soc. Jpn. 68, 2906 (1999); H. Nojiri et al., J. Magn. Magn. Mater. 226, 1101 (2001).
[22] H. Nojiri et al., cond-mat/0212479