NMR Evidence for the Persistence of a Spin Superlattice Beyond the 1/8 Magnetization Plateau in $SrCu_2(BO_3)_2$

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(Received 29 October 2007; revised manuscript received 13 April 2008; published 15 July 2008)

We present ^{11}B NMR studies of the 2D frustrated dimer spin system $SrCu_2(BO_3)_2$ in the field range 27–31 T covering the upper phase boundary of the 1/8 magnetization plateau, identified at 28.4 T. Our data provide a clear evidence that above 28.4 T the spin superlattice of the 1/8 plateau is modified but does not melt even though the magnetization increases. Although this is precisely what is expected for a supersolid phase, the microscopic nature of this new phase is much more complex. We discuss the field-temperature phase diagram on the basis of our NMR data.

DOI: 10.1103/PhysRevLett.101.037202 PACS numbers: 75.10.Jm, 75.25.+z, 75.30.Kz

A variety of novel quantum phenomena has been discovered by applying a magnetic field to interacting systems of $S = 1/2$ spin dimers, which have a singlet ground state and an energy gap Δ to the triplet excitations at zero field [1–6]. A magnetic field splits the triplets and closes the gap at the critical field $H_c = \Delta/g\mu_B$. Above H_c, a finite density of triplets (magnetization) generally undergoes Bose condensation, resulting in an antiferromagnetic order perpendicular to the field [2,7–9]. Another remarkable phenomenon that may occur at higher fields is the magnetization plateau, where the magnetization stays constant at a fractional value of the saturation over a finite range of magnetic field [3,10,11]. In particular, a plateau with non-integer density of triplets per unit cell generally implies localization of the triplets into a spin superlattice breaking the translational symmetry of the crystal [12]. Such a state is stabilized when the kinetic energy of the triplets is reduced, e.g., by frustration, so that the repulsive interaction becomes dominant.

The nature of phases between the plateaus is particularly interesting, since they are the bosonic analog of doped Mott insulators. A simple scenario for an incommensurate density of triplets is the melting of the superlattice and the appearance of Bose condensation. A more exotic possibility predicted for certain dimer spin models [13–16] is the formation of a supersolid phase, where the interstitial triplets undergo Bose condensation in the background of the commensurate superlattice. This means that the longitudinal spin density modulation coexists with a new transverse staggered order.

To date only a few spin systems are known to show symmetry-breaking magnetization plateaus. The best example is $SrCu_2(BO_3)_2$ [3], an orthogonal dimer system of Cu^{2+} ions ($S = 1/2$) with the primary interactions described by the two-dimensional Shastry-Sutherland model [17,18]. This material shows a gap $\Delta = 35$ K to the triplet excitations, which have a very small dispersion width (kinetic energy) [19,20], and plateaus at 1/8, 1/4, and 1/3 of the saturated magnetization (see Fig. 1) [10]. A symmetry-breaking spin superlattice in the 1/8 plateau has been confirmed by NMR experiments [4,21]. Furthermore, a supersolid phase has been proposed for the Shastry-Sutherland model above the 1/3 plateau [22]. However, $SrCu_2(BO_3)_2$ also contains an intradimer Dzyaloshinski-Moriya (DM) interaction and a staggered g tensor, which break the spin-rotation symmetry and prevent true Bose condensation [23–25]. This explains the gradual increase of magnetization starting far below the expected critical field $\Delta/g\mu_B = 23$ T and the absence of phase transitions up to the boundary of the 1/8 plateau (26.5 T). Since anisotropic interactions are often present in real materials,

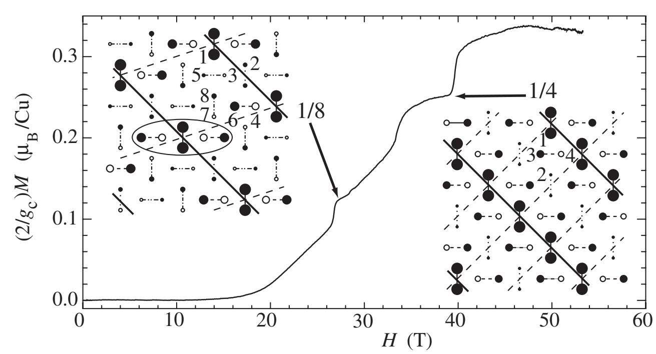

FIG. 1. The magnetization divided by $g_c/2$ ($g_c = 2.28$ [33]) is plotted against the pulsed magnetic field along the c axis (taken from Ref. [10]). The measurement was performed at $T = 1.4$ K. However, since the 1/8 plateau is not observed above 0.6 K in steady fields [21,29], we believe that the sample was adiabatically cooled during application of the pulse field. Also shown are the calculated spin density profiles for the 1/8 and 1/4 plateaus [27]. The solid (open) circles indicate magnetization of Cu ions parallel (antiparallel) to the external field with the magnitude represented by the circle size. The ellipsoid indicates a triplet unit extending over three dimers.

understanding their influence on the potential supersolid phase is an important issue. For $SrCu_2(BO_3)_2$, steady fields above the $1/3$ plateau are yet unavailable, and the magnetization shows a direct jump from $1/4$ to $1/3$ plateaus (Fig. 1). Therefore, the vicinity of the $1/8$ plateau provides a unique opportunity to look for such novel phenomena.

In this Letter, we report results of NMR experiments on boron sites in $SrCu_2(BO_3)_2$ in the field range 27–31 T. We identified the upper boundary of the $1/8$ plateau phase at 28.4 T from a clear splitting of NMR lines. The range of the internal field distribution, however, is nearly unchanged across the boundary. This provides direct evidence that spatial order of highly polarized triplet dimers persists above the $1/8$ plateau even though the magnetization changes continuously, pointing to an analog of the supersolid phase. In this study we used the same single crystal as was employed in our previous high field NMR experiments [4,21,23]. The NMR measurements were performed using a dilution refrigerator installed in a 20 MW resistive magnet at the Grenoble High Magnetic Field Laboratory. The c axis of the crystal was aligned along the field direction *in situ* within 1° by observing the angular variation of the NMR spectra at 18 T.

Figure 2 shows the ^{11}B NMR spectra at $T = 0.19$ K obtained at three different field values, $H_{\rm ext} = 27.5$, 28.7, and 29.9 T. The upper blue lines represent the distribution of the frequency shift divided by the nuclear gyromagnetic ratio, $\delta f/\gamma_N$, where $\delta f = f - \gamma_N H_{\rm ext}$, $\gamma_N = 13.66$ MHz/T, and f is the resonance frequency. The spectrum taken at 27.5 T is representative for the entire $1/8$ plateau as its shape does not change in the whole field range 26.8–28.2 T [4] (data not shown). The distinct spectral shapes at 28.7 and 29.9 T indicate that these fields are outside the plateau. Note that the ^{11}B NMR spectrum is determined by the distribution of the internal magnetic field $H_{\rm int}$ at nuclear sites, produced by the field-induced spin density, as well as by the quadrupole splitting ν_Q for the spin $3/2$ nuclei

$$\delta f_i/\gamma_N = H_{\rm int} + i\nu_Q/\gamma_N; \qquad i = -1, 0, 1. \tag{1}$$

The spectrum thus represents convolution of the distribution function of $H_{\rm int}$ with the sum of three δ functions separated by ν_Q/γ_N. One can recognize the threefold periodic structure for all the spectra shown in Fig. 2 (an example is indicated by the arrows in the lowest panel) with $\nu_Q = 1.25$ MHz. This value is the same as obtained in low fields [26], indicating that magnetic field does not induce strong lattice distortion. The distribution of $H_{\rm int}$ can then be obtained by deconvoluting the spectra using the inverse Fourier transform (the lower red lines in Fig. 2).

The distribution of $H_{\rm int}$ at 27.5 T agrees with the previous results obtained in a more primitive way [21]. It was shown in Ref. [21] that the many sharp peaks distributed over a wide range of $H_{\rm int}$ are well reproduced by the spin density distribution of the Shastry-Sutherland model calculated by exact diagonalization [4,27], which predicted a superlattice of highly polarized triplets surrounded by oscillating spin density shown in Fig. 1. In particular, the leftmost peak with the largest absolute value of the internal field, $H_{\rm int} = -0.2$ T, is assigned to the B site nearest to the Cu site bearing the largest magnetization (site 1 in Fig. 1) [21]. Such distribution of $H_{\rm int}$ disappears completely when the field is decreased below 26.5 T, which is the lower boundary of the $1/8$ plateau [4]. In particular, there is no other ordered phase corresponding to a smaller fraction of magnetization such as $1/9$, in contradiction to Ref. [28]. The situation is very different when the field is increased *above* the plateau. The overall width of the distribution of $H_{\rm int}$ in Fig. 2 remains nearly unchanged. This is the direct evidence that *highly polarized triplets are still present in the high field phase* even though the magnetization deviates from a commensurate fraction. However, unlike in the $1/8$ plateau, the spectral shape changes in the high field phase, indicating some evolution of the spin structure.

We now examine how the spectrum changes in more detail. Figure 3 shows the low-frequency part of the spectrum corresponding to $H_{\rm int} \leq -0.13$ T with changing field or temperature: (a) With increasing field at $T = 0.31$ K, the two most negative peaks get split above $H_{\rm ext} = 28.4$ T, marking the upper boundary of the $1/8$ plateau. The presence of the split and unsplit peaks at 28.3 T indicates coexistence of the two phases, pointing to a first-order transition. The transition field remains the same at $T = 0.12$ K (data not shown). (b) With decreasing temperature at $H_{\rm ext} = 28.7$ T, i.e., slightly above the plateau boundary, one of the split peaks disappears suddenly between 0.19 and 0.16 K, suggesting another phase boundary. (c) With

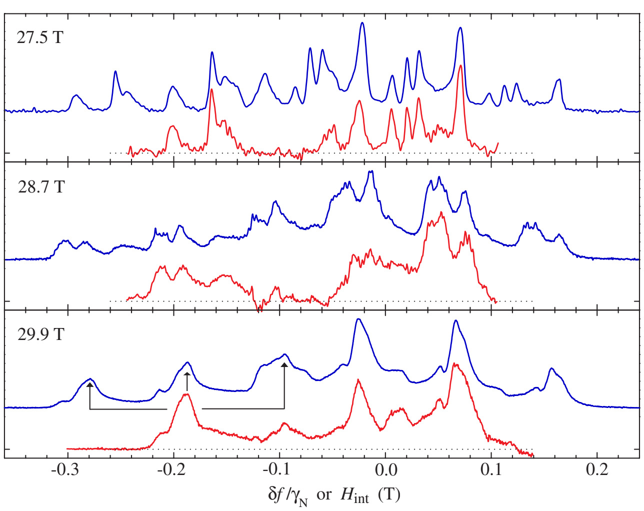

FIG. 2 (color online). The upper blue lines show the ^{11}B NMR spectra at 27.5 T (inside the $1/8$ plateau) and at 28.7 and 29.9 T (outside the plateau) obtained at $T = 0.19$ K. The lower red lines show the distribution of the internal field $H_{\rm int}$ (see the text). The arrows in the lowest panel show an example of the quadrupole split three peaks deconvoluted into a single peak. The global similarity of all three spectra confirms the presence of spin superlattice above the $1/8$ plateau.

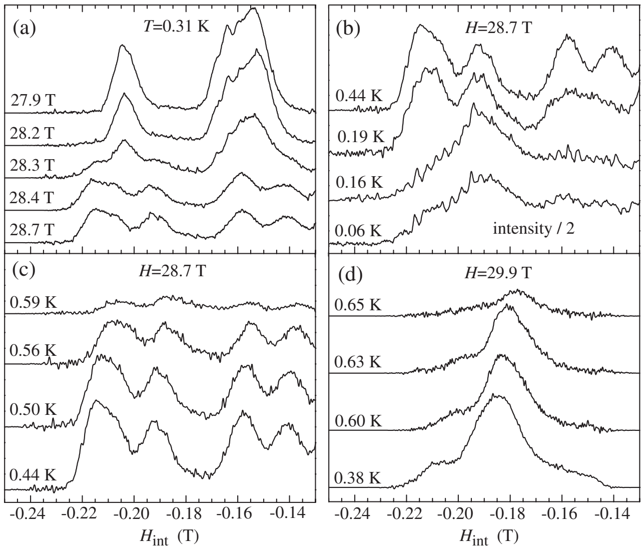

FIG. 3. Variation of the low-frequency part of the [11]B NMR spectra across the phase boundaries. See the text for details.

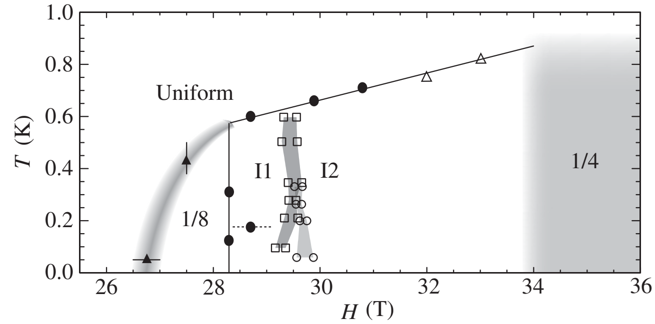

FIG. 4. The phase diagram constructed from the present (solid circles) and the previous (solid triangles [21]) NMR results and the specific heat data (open triangles [30]). The bars indicate the width of the transition. The transitions near 29.5 T detected by the torque measurements [29] are shown by open circles (increasing field) and open squares (decreasing field). The two data points at the same temperature represent the width of the transition. The lines and the shades are guides to the eye.

increasing temperature at $H_{ext} = 28.7$ T, the intensity rapidly decreases and the peaks completely disappear at $T_c = 0.60$ K (zero intensity data are not shown), marking the transition to the paramagnetic uniform phase. Indeed, at higher temperatures only three quadrupole split NMR lines are observed corresponding to a small *uniform* internal field of -0.03 T. (d) With increasing field, T_c becomes higher: $T_c = 0.66$ K at $H_{ext} = 29.9$ T and $T_c = 0.71$ K at $H_{ext} = 30.9$ T (data not shown). We notice that while the intensity of the peaks is reduced near T_c, their positions do not change significantly. This means that the amplitude of the spin density modulation is only slightly reduced but the volume fraction of the ordered phase vanishes towards T_c, indicating again a first-order transition.

The phase boundaries thus determined are plotted in Fig. 4, together with the previous NMR data on the transition between the 1/8 plateau and the uniform phase [21]. Our H-T phase diagram is in good agreement with the recent magnetization and torque measurements in steady magnetic fields [29], which revealed an abrupt change without hysteresis upon entering into the 1/8 plateau and a jump with hysteresis upon leaving the 1/8 plateau. In addition, another first-order transition with hysteresis near 29.5 T was observed as shown in Fig. 4, which was only weakly detected by NMR (data not shown). [Implicitly, this is clear from the difference between the spectra of Figs. 3(c) and 3(d)]. Thus there are at least two distinct intermediate phases (I1 and I2 in Fig. 4) between the 1/8 and the 1/4 plateaus. Our T_c data extrapolate smoothly to the peak temperatures of the specific heat at higher fields [30] also shown in Fig. 4. From our NMR results it is now clear that the primary order parameter is the superlattice modulation of the longitudinal magnetization $\langle S_z \rangle$. In the intermediate phases, T_c increases linearly with field. Such behavior is distinct from the *domelike* variation in a typical field-induced Bose condensed phase [6]. The transition at T_c occurs in a narrow temperature window (≤ 20 mK) in contrast to the broad width (more than 100 mK) observed for the transition between the 1/8 plateau and the uniform phase [21].

What is the nature of the intermediate phases ? Our main conclusion is that in both I1 and I2 phases triplet dimers with large static magnetization are still present; i.e., a spin superlattice persists. The similarity of the internal field distribution for different fields in Fig. 2 suggests that the spin structure is locally similar to the one in the 1/8 plateau. In particular, the *triple-dimer* structure of the triplet unit consisting of the central dimer with parallel moments and the two neighboring orthogonal dimers with staggered moments (the ellipsoid in Fig. 1) should be preserved.

The clear line splitting at the transition from the 1/8 plateau to the I1 phase [Fig. 3(a)] suggests additional symmetry breaking, as expect for a supersolid phase. Indeed, the kinetic energy of triplets at high fields is enhanced due to the correlated hopping process in the Shastry-Sutherland model [22], and this should promote the formation of a supersolid phase [16]. However, as mentioned earlier, the DM interaction and the staggered g tensor in $SrCu_2(BO_3)_2$ break the continuous spin-rotation symmetry in the ab plane, which is a prerequisite for a true supersolid transition. Nevertheless, it is possible that the transition causes breaking of some remaining discrete symmetries. The anisotropic interactions and the resultant transverse staggered magnetization [23] obey all the discrete symmetries of the crystal including the C_2 rotation around the c axis. We note that the spin superstructure of the 1/8 plateau shown in Fig. 1 is also invariant under the C_2 rotation at the center of the triplet dimer, giving the same value of H_{int} for the two B nuclei nearest to the Cu at site 1. However, if a new long-range order of the transverse magnetization breaking the C_2 symmetry occurs in the I1 phase, the NMR line from these B sites should split as observed in Fig. 3(a) [31]. This would be analogous to a supersolid phase since the diagonal long-range order (superlattice of $\langle S_z \rangle$) coexists with some kind of off-diagonal long-range order (transverse staggered magnetization).

In the I2 phase, the spectrum gets broadened and somewhat featureless, suggesting increased disorder or an incommensurate structure. We note that the stripe structure predicted for the 1/4 plateau can be obtained by doping triple-dimer triplet units into the vacant sites in the rhomboid cell of the 1/8 plateau (Fig. 1). This will maintain similar local spin structure but introduce certain disorder if the doped triplets localize randomly. The same process is possible by starting from the square cell of the 1/8 plateau, which is obtained by shifting one of the two stripes of the rhomboid cell by half of its period. Since both supercells are energetically nearly degenerate [27], they may alternate in the I1 phase, doubling the unit cell. This could be another explanation for the line splitting at the upper boundary of the 1/8 plateau and may lead to an incommensurate structure at higher doping.

Finally, we mention possible relevance of the theory describing effects of the DM interaction on the frustrated spin ladders exhibiting the half-magnetization plateau [32]. It was found that the DM interaction, if it competes with the interdimer exchange, stabilizes the superlattice modulation of $\langle S_z \rangle$ far beyond the original plateau region in the phase diagram, similar to what occurs in $SrCu_2(BO_3)_2$. In this model, however, the DM interaction also transforms the phase transitions separating the plateau and the neighboring phases into a crossover, in contrast to our observation in $SrCu_2(BO_3)_2$. This is because the DM interaction mixes the singlet and the triplet states; hence, $\langle S_z \rangle$ no longer represents the conserved boson density. To clarify the effects of the DM interaction in the more complicated Shastry-Sutherland model would be a future theoretical challenge.

In conclusion, our NMR results in $SrCu_2(BO_3)_2$ demonstrate that a superlattice of highly magnetized triplet dimers persists above the 1/8 magnetization plateau, where the magnetization is no longer constant. Although the presence of the DM interaction prevents the formation of a genuine supersolid phase, the NMR line splitting at the upper boundary of the 1/8 plateau suggests a new ordered phase of different symmetry. The magnetic phase diagram between the 1/8 and the 1/4 plateau is much more complex than expected and requires further experimental and theoretical work.

We are grateful for stimulating discussions with F. Mila, S. Miyahara, O. Tchernyshyov, and C. D. Batista on theoretical aspects and with F. Lévy and I. Sheikin on the magnetization and torque data. The work was supported by Grant-in-Aids for Scientific Research on Priority Areas No. 16076204 and No. 19052004 from the MEXT Japan and by the French ANR Grant No. 06-BLAN-0111.

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