A Novel Ordered Phase in SrCu$_2$(BO$_3$)$_2$ under High Pressure

Takeshi WAKI$^{1,*}$, Koichi ARAI$^{1,**}$, Masashi TAKIGAWA$^{1,**}$, Yuta SAIGA$^{1,2}$, Yoshiya UWATOKO$^{1}$, Hiroshi KAGEYAMA$^{3}$ and Yutaka UEDA$^{1}$

$^{1}$Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581
$^{2}$Department of Physics, Satatama University, Satatama 338-8570
$^{3}$Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502

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We report results of $^{11}$B NMR and susceptibility measurements on the quasi 2D frustrated dimer spin system SrCu$_2$(BO$_3$)$_2$ under high pressure. At 2.4 GPa and in a magnetic field of 7 T, NMR lines split with decreasing temperature in two steps. A gradual splitting below $T=30$ K breaking the four-fold symmetry of magnetic response is followed by a further sudden splitting below 3.6 K. The latter indicates a magnetic phase transition, which is also marked by a kink in the susceptibility at 1.44 GPa. From the magnetic hyperfine shift data, we conclude that the low-$T$ phase has a doubled unit cell containing two types of dimers, one in a nearly singlet state and the other with a finite magnetization down to $T=0$.

KEYWORDS: SrCu$_2$(BO$_3$)$_2$, Shastry-Sutherland model, high pressure, NMR, phase transition

A variety of exotic phenomena has been discovered in the quasi two dimensional dimer spin system SrCu$_2$(BO$_3$)$_2$.$^{1,2}$ It has an alternating stack of the magnetic CuBO$_3$ layers (Figs. 1(a) and 1(b)) and the non-magnetic Sr layers.$^{3,4}$ The magnetic layer containing orthogonal arrays of spin-1/2 Cu$^{2+}$ dimers is a realization of the 2D Shastry-Sutherland model,$^{5}$

$$H = J \sum_{n.n.} S_i \cdot S_j + J' \sum_{n.n.n.} S_i \cdot S_j,$$

where $J$ ($J'$) is the intradimer (interdimer) Heisenberg exchange interaction. The ground state of this model is obvious in two limiting cases: the dimer singlet phase for $J'/J << 1$ and the Néel ordered phase for $J'/J > 1$. The dimer singlet phase is known to be stable up to $J'/J = 0.68$.$^{6,9}$ Various experiments have established that SrCu$_2$(BO$_3$)$_2$ has a dimer singlet ground state at ambient pressure and zero magnetic field.$^{1,9,10}$ with the energy gap of 33 K$^{11-13}$ and $J'/J = 0.60-0.64$. The X-ray study shows a tetragonal to monoclinic structural transition at 4.7 GPa.$^{25}$ In this letter, we report results of the nuclear magnetic resonance (NMR) experiments on $^{11}$B nuclei at $P=2.4$ GPa and the susceptibility measurements up to $P=1.44$ GPa. Our data provide evidence for a magnetic phase transition below 4 K into an ordered phase with two distinct types of dimers.

A single crystal of SrCu$_2$(BO$_3$)$_2$ prepared by the traveling-solvent-floating-zone method$^{29}$ was cut into a thin plate ($2.0 \times 2.8 \times 0.3 \text{mm}^3$) for NMR measurements to reduce distribution of demagnetizing field. It was placed in a piston-cylinder-type pressure cell made of NiCrAl and BeCu alloys filled with 1:1 mixture of N-pentane and isoamyl-alcohol. The pressure was calibrated against the load applied at room temperature by separate measure-

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$^*$E-mail address: twac@issp.u-tokyo.ac.jp
$^{**}$Present address: Hitachi Medical Corporation, Kashiwa, Chiba
$^{***}$E-mail address: masashi@issp.u-tokyo.ac.jp

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Fig. 1. (Color online) The magnetic layer of SrCu$_2$(BO$_3$)$_2$ viewed along (a) the c-direction and (b) the [T10]-direction. (c) A possible ordered structure in the low-$T$ phase. Shaded circles represent the magnetic dimers.
ments of the superconducting transition temperature of Sn metal. The pressure cell was mounted on the NMR probe with a double-axis-goniometer to enable arbitrary alignment of the crystal in magnetic fields. The $^{11}$B NMR spectra were obtained by Fourier transforming the spin-echo signal. The demagnetizing field was corrected by comparing the NMR frequencies at ambient pressure to those published data obtained on a nearly spherical crystal in magnetic fields. The $^{11}$B nuclei have spin $3/2$, frequencies of $\nu_B = 13.66 \text{ MHz/T}$ is the nuclear gyromagnetic ratio and $K$ is the magnetic hyperfine shift caused by the coupling between nuclei and magnetization on neighboring Cu sites. The second term is the first order quadrupole shift with $\nu_Q$ proportional to the electric field gradient (EFG) along the magnetic field direction. This term vanishes for the central line ($m=1/2$). The third term, the second order quadrupole shift, is identical for the two satellite lines ($m=3/2$ and $-1/2$).

$\nu_{m,m-1} = (1 + K) \gamma H + (m - 1/2) \nu_Q + \delta \nu^{(2)}_m$, (2)

$m=3/2, 1/2, -1/2$. Here $\gamma = 13.66 \text{ MHz/T}$ is the nuclear gyromagnetic ratio and $K$ is the magnetic hyperfine shift caused by the coupling between nuclei and magnetization on neighboring Cu sites. The second term is the first order quadrupole shift with $\nu_Q$ proportional to the electric field gradient (EFG) along the magnetic field direction. This term vanishes for the central line ($m=1/2$). The third term, the second order quadrupole shift, is identical for the two satellite lines ($m=3/2$ and $-1/2$).

SrCu$_2$(BO$_3$)$_2$ has tetragonal structure with the space group $I4_2d$ at ambient pressure and temperatures below 395K. The Cu and B atoms both occupy a unique $8i$ site located on the $(110)$ or $(\overline{1}0\overline{1})$ mirror plane (Fig. 1(a)). A unit cell contains two magnetic CuBO$_3$ layers related by the translation $t(1/2, 1/2, 1/2)$. The four B atoms in a unit cell per layer, B1 - B4 in Fig. 1(a), give distinct NMR frequencies for general field directions. The number of NMR lines is reduced for symmetric directions. When the field $\mathbf{H}$ is in the $(10\overline{1})$ mirror plane containing the $c$- and the $[110]$-directions, B3 and B4 sites are equivalent but B1 and B2 are not due to buckling of CuBO$_3$ layers (Fig. 1(b)). Then B1, B2 and (B3, B4) give three sets of quadrupole split three lines. For $\mathbf{H} \parallel [110]$, B1 and B2 also become equivalent resulting in two sets of lines. For $\mathbf{H} \parallel c$, all four sites are equivalent. The NMR spectra at ambient pressure are indeed consistent with these predictions at all temperatures.

At $P=2.4 \text{ GPa}$, only one set of NMR lines is observed at high temperatures for $\mathbf{H} \parallel c$ (Fig. 2(a)), consistent with the crystal symmetry at ambient pressure. Upon cooling below 30 K, however, each line begins to split gradually and gets broadened. All three quadrupole split lines show clear double peak structure at 10 K and 4 K (Fig. 2(a)). In order to make site assignment for the split peaks, we examined variation of the spectra with the field direction. The value of $\nu_Q$ determined from the spacing between the two satellite lines is plotted against the angle $\theta$ between $\mathbf{H}$ and the $c$-direction in Fig. 3(c) for $\mathbf{H} \parallel (\overline{1}0\overline{1})$ and in Fig. 3(d) for $\mathbf{H} \parallel (110)$. The $\theta$-dependence of $K$ is
then determined from the average frequency of the two satellite lines after subtracting $\delta \nu_m^{(2)}$ calculated from the $\nu_Q(\theta)$ data as shown in Figs. 3(a) and 3(b).

The distinction between (B1, B2) and (B3, B4) revealed by the line splitting for $H \parallel c$ must be ascribed to the loss of four-fold symmetry (4) around the c-direction. This symmetry requires that $\nu_Q(\theta)$ and $K(\theta)$ at B1 and B2 (B3 and B4) for $H \parallel (\bar{1}10)$ be identical to those at B3 and B4 (B1 and B2) for $H \parallel (110)$. The data in Fig. 3 show that this condition is grossly violated for the magnetic shift $K$ but not for the quadrupole coupling $\nu_Q$. This strongly suggests that the symmetry change is primarily due to magnetic origin since any structural change should be better sensed by $\nu_Q$. Thus we conclude that the two sublattices of orthogonal Cu dimers are clearly visible. The solid and dashed lines in Fig. 1(a) become inequivalent with different magnetizations. We expect though this may accompany a slight structural change. Detailed structural analysis is left for future studies.

The $K(\theta)$ and $\nu_Q(\theta)$ data can be fitted to the standard formula for anisotropic shifts, $u + v \cos^2(\theta - \alpha)$ with $u$, $v$, and $\alpha$ being the fitting parameters as shown by the lines in Figs. 3(a) - 3(d). We found that $K(\theta)$ and $\nu_Q(\theta)$ at B1 for $H \parallel (\bar{1}10)$ (at B3 for $H \parallel (110)$) are identical to $K(-\theta)$ and $\nu_Q(-\theta)$ at B2 (at B4). Thus the mirror symmetries are preserved. The loss of 4 changes the space group from $I\bar{4}2m$ to orthorhombic $Fmm2$. Our data indicate that the entire crystal forms a single domain.

We now discuss the NMR spectra in Fig. 2 at lower temperatures. For $H \parallel [110]$, (B1, B2) and (B3, B4) give distinct lines at all temperatures. No line splitting is observed down to 3.6 K. At 3.5 K, however, all lines develop clear two peak structure. With further decreasing temperature, these two peaks change into one sharp and one broad lines with nearly equal intensity denoted as $Bns$ and $Brnb$ ($n=1$ - 4) in Fig. 2(b). Figure 3(e) shows the variation of the low frequency satellite lines ($m=1/2$) when the field is rotated from [110] toward the c-direction at 2.1 K. Both the sharp and the broad lines from (B1, B2) split in a similar manner as observed at higher temperatures. Therefore, each of B1 and B2 must be divided into two sites below 3.6 K, (B1s, B1b) and (B2s, B2b), yielding eight inequivalent B sites for general field directions. A similar spectrum with sharp and broad lines is observed also for $H \parallel c$ at 2.1 K (Fig. 2(a)), although there is only one set of broad lines. We found that this belongs to (B3, B4), while the broad lines from (B1, B2) overlap with the sharp lines, by extending the measurements shown in Fig. 3(e) to smaller values of $\theta$.

Figure 4 shows the $T$-dependence of the shifts at various sites for (a) $H \parallel c$ and (b) $H \parallel [110]$ compared with the data at ambient pressure. Above 40 K, the results at 2.4 GPa are nearly unchanged from ambient pressure. Line splitting appears for $H \parallel c$ below 30 K as mentioned above. In spite of a clear change of symmetry, the splitting develops gradually without sign of a phase transition. In contrast, the second splitting at 3.6 K occurs suddenly and clearly marks a phase transition. The shifts for the sharp lines approach zero as $T \rightarrow 0$, pointing to a singlet ground state. We can indeed fit the data to an activation law, $\alpha + \beta \exp(-\Delta/T)$, yielding $\Delta=11-15$ K. These values are much smaller than the gap at ambient pressure (24 K) at the same field of 7 T. The shifts for the broad lines, on the other hand, maintain large values down to the lowest temperature, pointing to a magnetic state without an excitation gap.

These results indicate coexistence of g-magnetic and gnon-magnetic Cu dimers in the low-$T$ phase. The sharp (broad) lines should come from those B sites which couple dominantly to the non-magnetic (magnetic) Cu dimers. Preliminary results at different fields show that both the hyperfine field ($K$ multiplied by $H$) and the line width for the broad lines are approximately proportional to the field, indicating no spontaneous moment at zero-field. The increased number of NMR lines indicates doubling of the primitive unit cell in the low-$T$ phase. It is most likely that each of the Cu dimer sublattices develop spatial order of magnetic and non-magnetic dimers, forming either a superstructure in the $ab$-plane (see Fig. 1(c) for an example) or alternating magnetic...
A gradual loss of four-fold symmetry near 30 K is followed by a correlation date would be the staggered component of the two-spin probability than the non-magnetic dimers, a natural candidate as a result of Bose condensation of two-magnon proposal for frustrated spin systems on a square lattice parameter. Recently, a bond-nematic order has been under time-reversal and considered a bond-nematic order parameter. Recently, a bond-nematic order has been proposed for frustrated spin systems on a square lattice as a result of Bose condensation of two-magnon bound states. Whether such a scenario is relevant for SrCu$_2$(BO$_3$)$_2$ is an interesting issue.

What is the order parameter describing the low-$T$ phase? While no anomaly is observed at ambient pressure and at 0.91 GPa, the data at 1.44 GPa show a clear kink at 4 K, providing further evidence for bulk nature of the phase transition. The slightly different transition temperature is presumably due to the difference in magnetic field. Note that the susceptibility approaches a finite value as $T \to 0$ consistent with the coexistence of two types of Cu sites.

To conclude, we have demonstrated that SrCu$_2$(BO$_3$)$_2$ under pressure exhibits symmetry lowering in two steps. A gradual loss of four-fold symmetry near 30 K is followed by a clear phase transition below 4 K. We propose that the low-$T$ phase has spatial order of two types of dimers: one is nearly in a singlet state while the other has a finite susceptibility down to $T=0$.

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