LETTER TO THE EDITOR

Cu nuclear spin-spin coupling in the dimer singlet state in SrCu$_2$(BO$_3$)$_2$

K. Kodama, J. Yamazaki, M. Takigawa, H. Kageyama, K. Onizuka and Y. Ueda
Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan

Abstract. We report results of nuclear magnetic resonance (NMR) experiments in SrCu$_2$(BO$_3$)$_2$, a quasi two-dimensional spin system with a singlet ground state. When magnetic field is applied along the c-axis, each of the quadrupole split Cu resonance lines splits further into four lines. The spin-echo intensity for some of the split lines oscillates against the separation time between $\pi/2$ and $\pi$ rf-pulses. These phenomena are due to strong nuclear spin-spin coupling mediated by the electronic spin system, which exists only within a pair of nuclei. Thus the results provides direct evidence for the dimer singlet ground state in this material.

The discovery of excitation gap and quantized magnetization plateaus in the quasi-two-dimensional spin system SrCu$_2$(BO$_3$)$_2$ by Kageyama et al. have since stimulated vast amount of experimental and theoretical work. As shown in figure 1, the Cu$^{2+}$ spins ($s=1/2$) in this compound form a planar network of dimers, which is identical to the Shastry-Sutherland (SS) model when only the nearest neighbor intra-dimer exchange ($J$) and the second nearest inter-dimer exchange ($J'$) interactions are retained. Extensive studies on the SS-model have revealed interesting novel aspects. First, the simple direct-product of dimer singlet is an exact eigenstate for any value of $J'/J$ and is the ground state when $J'/J$ is smaller than a certain critical value. In the opposite limits, $J'/J \gg 1$, the model reduces to the nearest neighbor Heisenberg model on a square-lattice with the obvious Neel order. It was proposed that the two phases are separated by a first order transition at $T = 0$ near $J'/J = 0.7$. For SrCu$_2$(BO$_3$)$_2$, the exponential decrease of susceptibility and Cu nuclear spin-lattice relaxation rate at low temperatures indicate that the ground state is singlet with a finite energy gap for excited states. The magnitude of the excitation gap $\Delta$ is determined to be 35K from the inelastic neutron scattering and the electron spin resonance experiments.

Secondly, excitations from the dimer singlet ground state in the SS-model have extremely localized character. Using perturbation expansion in $J'/J$, Miyahara et al. found that hopping of an excited triplet from one dimer to another is allowed only from sixth order. A very small dispersion width of 0.2 meV for the magnetic excitations

‡ To whom correspondence should be addressed (masashi@issp.u-tokyo.ac.jp)
was indeed observed by the neutron inelastic scattering experiments in SrCu$_2$(BO$_3$)$_2$ [12]. The most striking feature of SrCu$_2$(BO$_3$)$_2$ is the plateaus in the magnetization curve under high magnetic field at fractional values (1/8, 1/4, and 1/3) of the fully saturated magnetization [4, 5]. It is proposed that small kinetic energy of the triplets and weak repulsive interaction between them are responsible for the formation of superstructure of triplet dimers at these plateaus [5, 6], although no direct experimental evidence has been obtained yet.

The nature of quantum phase transition in the SS-model, however, is not well understood yet. Possibilities have been discussed for intermediate phases between the dimer singlet and the Neel state for a certain range of $J'/J$ such as a plaquette-type singlet state [14] or a helical spin order [3]. The exchange parameters appropriate for SrCu$_2$(BO$_3$)$_2$ were estimated as $J = 85$ K and $J' = 54$ K ($J'/J = 0.64$) by fitting the magnetic susceptibility data to numerical simulation of the SS-model [8]. Analysis of the energy of various excitation modes has lead to slightly different values, $J = 72$ K and $J' = 43$ K ($J'/J = 0.60$) [11]. For such parameter values, theories appear to agree that the ground state is the dimer singlet. Various properties of SrCu$_2$(BO$_3$)$_2$ known so far are indeed compatible with the dimer singlet ground state, although it may be at close proximity to a quantum critical transition.

In this letter, we report the results of nuclear magnetic resonance (NMR) experiments at $^{63}$Cu and $^{11}$B nuclei (both with nuclear spin 3/2) in SrCu$_2$(BO$_3$)$_2$. We observed four-fold splitting of Cu NMR lines and sinusoidal oscillation of Cu spin echo intensity against the separation time between the $\pi/2$ and $\pi$ rf-pulse. These phenomena are naturally explained by strong nuclear spin-spin coupling acting only within a pair, therefore, provide direct evidence for the dimer singlet ground state.

The NMR measurements were performed on a single crystal prepared by the traveling-solvent-floating-zone method and cut into an approximately cubic shape (2.1x2.3x1.9 mm). The applied magnetic field $H$ did not exceed 8 T, therefore, the Zeeman energy was much smaller than the excitation gap. The NMR spectra were
obtained from the Fourier transform of the spin-echo signal. SrCu$_2$(BO$_3$)$_2$ has tetragonal structure with $I42m$ space group, in which Cu(BO$_3$) and Sr layers stack alternately. The atoms in the magnetic Cu(BO$_3$) layer depicted in Fig. 1 are not strictly coplanar and the only symmetry operation at either Cu or B sites is the mirror reflection normal to $\langle 110 \rangle$. Then the direction normal to the mirror plane coincides with one of the principal axes of the electric field gradient (EFG) and the magnetic hyperfine shift ($K$) tensors, however, both do not possess axial symmetry. When the magnetic field $H$ is along the $c$-axis, the quadrupolar and the magnetic shifts are identical for all Cu (B) sites but the $c$-axis is not a principal axis of the EFG or $K$ tensors. For other field directions, there are more than two inequivalent sites. For example, there are two Cu (B) sites for $H \parallel [110]$. At one of these sites, $H$ is normal to the mirror plane and thus along one of the principal axes of EFG and $K$ tensors.

Figure 2 shows the $^{11}$B NMR spectrum at $T = 3$ K for $H = 8$ T along the $c$-axis. The spectrum consists of three lines split by electric quadrupole interaction, yielding the quadrupole splitting $^{11}\nu_{cc} =^{11}V_{cc}e^{11}Q/2h = 1.25$ MHz, where $^{11}V_{cc}$ is the $cc$-component of the EFG tensor and $^{11}Q$ is nuclear quadrupole moment. Other components of quadrupole splitting are obtained from the spectrum for $H \parallel [110]$ as $^{11}\nu_{\alpha\alpha} = 0.694$ MHz, and $^{11}\nu_{\beta\beta} = 0.555$ MHz, where $\alpha$ is a principal axis and $\beta$ is perpendicular to it.

The magnetic hyperfine shift $^{11}K$ at B sites along three directions $c$, $\alpha$ and $\beta$ are determined from the position of the central line for the transition $I_z = 1/2 \leftrightarrow -1/2$ at $H = 8$ T. There are good linear relations between the shifts and the magnetic susceptibility $\chi$ as shown in figure 3. From the slope of the $K$ vs $\chi$ plot, three components of the hyperfine coupling tensor defined as $^{11}A_{ii} =^{11}K_{ii}/(\mu_B N_A \chi_{ii})$ are determined as $^{11}A_{cc} = -0.259$, $^{11}A_{\alpha\alpha} = -0.202$, and $^{11}A_{\beta\beta} = 0.115$ in unit of $T/\mu_B$. The coupling constant $^{11}A_{ii}$ represents the $i$-component of the hyperfine field at B nuclei provided that each Cu had a uniform moment of $1 \mu_B$ along the $i$-direction. We found that the dipolar field from Cu spins alone does not account for the anisotropy of $^{11}A_{ii}$, indicating
sizable anisotropy of the transferred hyperfine interaction. The temperature dependence of $\chi_{cc}$ is shown in the inset of figure 3. Since the susceptibility was measured at 1 T and the magnetization is not linear in field when the temperature is much lower than the gap, only the data above the peak temperature of $\chi$ are used in the $K$ vs. $\chi$ plot.

We now turn to the results at Cu sites. Figure 4 shows the $^{63}$Cu NMR spectrum for the central transition at $H = 8$ T along the $c$-axis at $T = 3.0$ K. The spectrum consists of equally spaced four lines in spite of the fact that all Cu sites are equivalent for $H \parallel c$. Similar four-peaks structure was observed for the quadrupole-split satellite spectra. The quadrupolar splitting for $^{63}$Cu nuclei was obtained as $^{63}\nu_{cc} = 22.13$ MHz. As will be explained shortly, the four-fold splitting is due to the coupling of two Cu nuclear spins on the same dimer. The magnetic shift is then determined from the average frequency of the four peaks. The observation of Cu NMR signal is limited to $T \leq 4.2$ K because of the short spin-spin relaxation time at higher temperatures. The hyperfine coupling constant at Cu nuclei $^{63}A_{cc}$ was determined by plotting the shift for $^{63}$Cu against the shift for $^{11}$B, both taken at the same field and several temperatures below 4.2 K as shown in figure 5. From the slope of this plot and the value of $^{11}A_{cc}$ determined above, we obtain $^{63}A_{cc} = -23.76 \pm 0.15$ T/$\mu_B$. Complete determination of the EFG and $K$ tensors at B and Cu sites will be presented in a separate paper.

We found remarkable oscillation of the spin-echo intensity of the $^{63}$Cu resonance as shown in figure 6. Here the spin-echo intensity of the peak B of the central line is plotted against twice the separation time $\tau$ between $\pi/2$ and $\pi$ rf-pulses. Such oscillation is observed only for the peaks B and C. Similar oscillation was observed for the satellite spectra, although at different peaks. For the high frequency satellite, only the peaks C and D show the echo-oscillation, while for the low frequency satellite, oscillation was observed for the peaks A and B.

The line splitting and the echo-oscillation are both explained easily by Rudermann-
Kittel-Kasuya-Yosida type indirect interaction between Cu nuclear spins mediated by the electron spin system. The indirect coupling between two nuclear spins $I_1$ and $I_2$ are generally expressed as \[16\]

\[H_{\text{ind}} = -a_z I_1^z I_2^z, \tag{1}\]

\[a_z = \frac{\hbar^2}{2} \gamma_{N1} \gamma_{N2} (g_z A_z)^2 \chi_{12} \tag{2}\]

where $\gamma_{Ni}$ is the nuclear gyromagnetic ratio for $I_i$ and only the on-site hyperfine coupling constant along the field direction $A_z$ is considered. The non-local electron spin susceptibility $\chi_{12}$ describes the spin polarization at site 1 when a fictitious magnetic field were applied only to the spin at site 2. At $T=0$ it is expressed as

\[\chi_{12} = \sum_n \frac{\langle 0 | S_{2z} | n \rangle \langle n | S_{1z} | 0 \rangle}{E_n} + c.c., \tag{3}\]

where $|0\rangle$ is the ground state and $|n\rangle$ is an excited state with the energy $E_n$. In case of an isolated dimer with the exchange $J$,

\[\chi_{12} = -\frac{1}{2J}. \tag{4}\]

Equation (1) implies that local magnetic field acting on $I_1$ is produced by $I_2Z$, which can take four different values $\pm 1/2$ or $\pm 3/2$. This results in the four-fold splitting of the NMR line for $I_1$. Since $I_2$ can be either of the two isotopes $^{63}\text{Cu}$ or $^{65}\text{Cu}$, there should be strictly speaking eight-fold splitting. However, both isotope have spin $3/2$ and the difference in $\gamma$ is only 7%. Thus they are not experimentally resolved. Assuming that the spectrum in figure 4 represent the isotopic average for $I_2$, the value of $a_z$ for the case when $I_2$ is a $^{63}\text{Cu}$ nucleus is deduced as $a_z/\hbar = 119$ kHz.

It is well known that such a nuclear spin coupling gives rise to spin-echo oscillation \[17\]

\[I(2\tau) = \cos(a_z \tau/\hbar) \tag{5}\]
when the two spins are identical (like spins). Because of the quarupole splitting, only those $^{63}$Cu nuclei with $I_z = \pm 1/2$ behave as like spins when the central line for the transition $I_z = 1/2 \leftrightarrow -1/2$ is being observed. This is why only the peaks B and C show oscillation. The selection rules for the satellite lines is explained in a similar manner. The data in figure 3 is fit to a sum of oscillatory and non-oscillatory parts both decaying exponentially with different time constant. The oscillation frequency is obtained as $a_z/h = 119$ kHz in agreement with the value deduced from the splitting of the spectrum.

The four-fold splitting of the spectrum and the coherent spin-echo oscillation indicate that nuclear spins are strongly coupled in pairs and the couplings between pairs are very weak. The results thus provide direct evidence for the dimer-singlet ground state in SrCu$_2$(BO$_3$)$_2$. If one nucleus were coupled to many neighbors, for example as one would expect for the plaquette type singlet state, the spectrum should consist of many lines, which with random isotopic configuration would result in a single broad peak. Likewise, random superposition of echo-oscillation containing many frequency components would show rapid damping. The long-lived coherent echo-oscillation implies that the inter-dimer coupling if any is orders of magnitude smaller than the intra-dimer coupling. Similar phenomena have been observed also for the chain Cu sites in the ladder-chain composite material Sr$_{14}$Cu$_{24}$O$_{41}$, where dimer singlet state is formed due to charge order in the one-dimensional chain subsystem [18].

For the case of an isolated dimer, the coupling constant $a_z/h = 119$ kHz corresponds to the exchange constant $J = 75$ K. Here we have used equations (1), (2) and (4) with the values $A_c = -23.76$ T/$\mu_B$ and $g_c = 2.28$, the latter being obtained from the ESR measurements [18]. This value of $J$ is remarkably close to the intradimer exchange estimated for SrCu$_2$(BO$_3$)$_2$. Although $J'/J$ is not a small number for SrCu$_2$(BO$_3$)$_2$, the spin correlation within a dimer must remain almost unchanged from an isolated dimer.

In conclusion, $^{63}$Cu and B NMR measurement has been performed on a single crystal of SrCu$_2$(BO$_3$)$_2$. The values of the hyperfine coupling constant and the quadrupole splitting were determined. The spectrum of Cu splits into four lines and the spin-echo intensity oscillates against $2\tau$ with the oscillation frequency equal to the line splitting. They are caused by the nuclear spin-spin coupling mediated by the strong intradimer coupling of the electron spins. These results provide firm evidence that the ground state is indeed the dimer singlet state.

Acknowledgments

The work was supported by the Grant-in Aid for Scientific Research No. 10304027 for the Japan Society of the Promotion of Science and the Priority Area (A) on "Novel quantum phenomena in transition metal oxides" and the Priority Area (B) on "Field-induced new quantum phenomena in magnetic systems" from the Ministry of Education, Culture, Sports Science and Technology of Japan.
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