Quantum Properties of Low-Dimensional Antiferromagnets

Proceedings of French-Japanese Symposium

Held in Fukuoka, Japan
November 20-22, 2001

Under the Auspices of Japan Society for the Promotion of Science (JSPS),
Centre National de la Recherche Scientifique, France (CNRS),
and Kyushu University

Edited by
Yoshitami Ajiro
Jean-Paul Boucher

Kyushu University Press

Cu NMR Observation of the Dimer Singlet State in the Quasi-Two-Dimensional Spin System $SrCu_2(BO_3)_2$

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

February 8, 2002

Abstract

The nuclear magnetic resonance (NMR) experiments have been performed on the quasi-two-dimensional spin-gap system $SrCu_2(BO_3)_2$. When the magnetic field is applied along the *c*-axis, each of the quadrupole-split Cu resonance spectrum splits further into four lines. We also found that the spin-echo intensity for some of the split lines oscillates against the separation time between the $\pi/2$ and π rf-pulses. These results can be exlained by indirect coupling between Cu nuclear spins on the same dimer mediated by the exchange interaction among electron spins.

PACS number: 75.40.Gb, 42.50.Md, 76.30-v

1 Introduction

$SrCu_2(BO_3)_2$ is a spin-gap system with a quasi two-dimensional (2D) spin network.[1] The Cu spins (s=1/2) of the compound form a 2D-network of dimers. It is topologically equivalent to the Shastry-Sutherland model [2] when only the nearest neighbor intra-dimer exchange (J) and the second neighbor inter-dimer exchange (J') interactions are considered. The value of the excitation gap is 35K as determined by inelastic neutron scattering [3] and various other measurements. Comparison between observed magnetic susceptibility, specific heat and the spin-gap value with calculation on the Shastry-Sutherland model [4] yielded the values of the exchange parameters as $J = 85$ K and $J' = 54$ K. The most striking feature of this material is the plateaues in the magnetization under high magnetic field at fractional values (1/8, 1/4, and 1/3) of the fully saturated magnetization.[5]

Extensive theoretical studies on the Shastry-Sutherland model have revealed several interesting aspects. First, the simple direct-product of dimer singlet is an exact eigenstate and also the ground state for certain range of J'/J.[2, 6] Koga and Kawakami proposed a phase diagram of the Shastry-Sutherland lattice by using the series expansion method.[7] The ground state is the dimer singlet state for $J'/J < 0.677$, and it is an antiferromagnetic ordered state for $J'/J > 0.86$. It is proposed that a spin-gap state characterized as a plaquatte singlet state exists between the dimer singlet phase and the antiferromagnetic phase, although this is still under debate. If this is correct, the present system with the ratio $J'/J \sim 0.635$ is in the dimer singlet phase near the phase boundary between the two spin-gap phases.

Secondly, the excited triplet in this system has a localized nature. In the perturbation expansion in J'/J, the hopping process of the excited triplet is possible only from the sixth order perturbation.[6] The bandwidth estimated by the neutron inelastic scattering is about 0.2 meV[3], which is consistent with the one calculated by the perturbation expansion.[8] The quantized plateux observed in the magnetization curve can also be explained by the this characteristic.[5]

One of the recent problem of this compound is the characteristics of the excited state. In ESR measurement, the resonance line of the first excited state splits into four branches in the applied magnetic field.[9] In the recent neutron scattering, the fine peak structure is also observed in the energy spectrum of the first excited state.[10] These results indicate that the excited state is not simple triplet state. Recently, Cepas et al. suggested that Dzyaloshinski-Moriya interaction affects the excited state.[10] In this compound, Dzyaloshinski-Moriya interaction exists between the spins of the nearest neighbor dimers since there is no center of inversion at the middle point of the interdimer bond. They indicated that the first excited state consist of five states, which is consistent with the results of ESR and neutron scattering.

In this proceeding, we report the characteristics of NMR spectra of Cu nucleus. The line-shape of the spectra and the spin echo oscillation against the separation time between the $\pi/2$ and π rf pulse, can be explained in terms of the strong nuclear spin-spin coupling mediated by the strong intradimer coupling between electron spins of Cu.

2 Experimental Results

The NMR measurement was performed on the single crystal prepared by the traveling-solvent-floating-zone method. In the present measurement, the applied magnetic field H is no more than 8 T, which is much smaller than the excitation gap. The spin-echo NMR spectra of ^{11}B obtained at 3.0 K is shown in Fig. 1. The magnetic field is 8 T and it is parallel to the c-axis. In this configuration, four B atoms in the Cu(BO$_3$) plane are equivalent. The spectrum splits into three lines, which is due to the electric field gradient. The quadrupole splitting $^{11}\nu_c$ at $H//c$, is about 1.25 MHz. In the case of $H//(110)$, there are two kinds of B sites in the Cu(BO$_3$) plane. The quadrupole splitting $^{11}\nu_a$=0.694 MHz, and $^{11}\nu_b$=0.555 MHz. $^{11}\nu_c$ and $^{11}\nu_b$ are not principle values because the principle axis of the electric field gradient slightly tilts from c-axis to (110)-axis.

Figure 2 shows the $K-\chi$ plot. $^{11}K_c$ is the shift of ^{11}B-nuclei for $H//c$, and $^{11}K_a$ and $^{11}K_b$ are the shifts for $H//(110)$. χ is the uniform magnetic susceptibility. In this analysis, we used the date of the shifts and χ obtained at T >30 K because the magnetization is not proportional to the external field at $T << \Delta$. The hyperfine coupling constants at B sites are determined as A_c=-2.947 kOe/μ_B, A_a=-2.069 kOe/μ_B, and A_b=1.176 kOe/μ_B. Because the principle axis of the hyperfine field also deviates from c-axis toward (110),

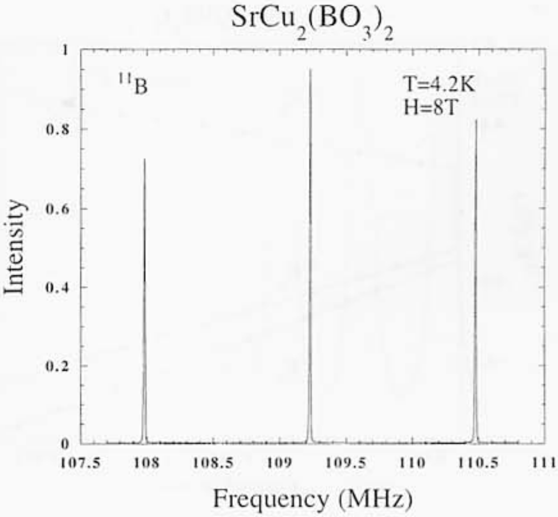

Figure 1: The spin-echo NMR spectra of ^{11}B obtained at T =3.5K. The magnetic field is 8 T and it is parallel to c-axis.

A_c and A_b are not the principle values.

The NMR spectrum of the ^{63}Cu central line obtained at T =3.0K and H =8 T, is shown in Fig. 3. The magnetic field is parallel to the c-axis. Because, in this configuration, four Cu atoms in the $Cu(BO_3)$ plane are equivalent, the central and the satellite transitions are expected to show a single line. However, the observed central and satellite lines consist of four lines, respectively (The satellite line is not shown here). As mentioned in the next section, it can be explained by considering the coupling between two Cu nuclear spins on the same dimer. The quadrupole splitting is determined as $^{63}\nu_c$=22.1 MHz. Because the Cu signal could not be observed at T >4.2 K, in order to determine the hyperfine coupling constant of Cu-nuclei, the ratio of the shifts of Cu and ^{11}B were measured. In Fig. 4, the shift of ^{63}Cu at $H//c$ is plotted against that of ^{11}B. Both date were taken at the same temperature and the same magnetic field. A_c can be estimated as -259 kOe/μ_B.

In Fig. 5, the spin echo intensity of the second peak (the peak with the second heighest frequecny) of the central line is plotted as a function of 2τ, where τ is the separation time between the $\pi/2$ and π rf pulses. The intensity oscillates against 2τ. This oscillation is observed only for the second and the third peaks. This behavior can also be explained in term of the nuclear spin-spin coupling.

3 Discussion

As shown in Fig. 3, the center and the satellite lines of Cu-spectrum split into four lines. The spin-echo intensity oscillates against τ as shown in Fig. 5. In this section, we analyze these results by considering the indirect nuclear spin-spin coupling via exchange interaction between electron spins. [11]

Generally, the indirect coupling between two nuclear spins I_1 and I_2 mediated by

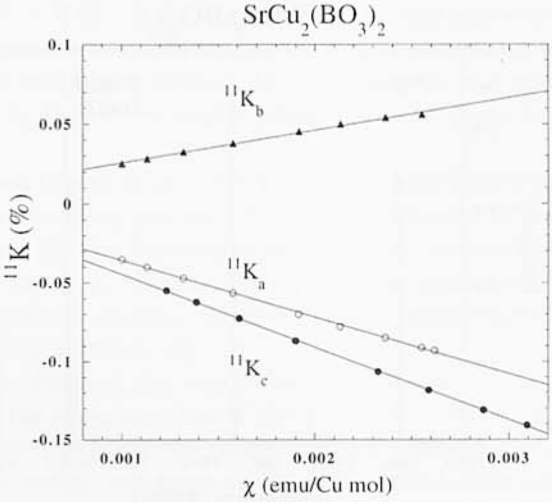

Figure 2: The $K - \chi$ plot of ^{11}B. The solid lines are fitting results by considering that the shift is linear to the magnetic susceptibility.

electron spin interaction can be written as

$$H_{ind} = a_z I_1^z I_2^z, \tag{1}$$

$$a_z = \hbar^2 \gamma_{N1} \gamma_{N2} (g A_z)^2 \frac{\chi_{12}}{(g\mu_B)^2} \tag{2}$$

where A_z is a hyperfine coupling constant, γ_N is the nuclear gyromagnetic ratio. The non-local susceptibiliry of electron spin χ_{12} represent how much spin polarization is induced on the Cu spin 1 when magnetic field is applied to the spin 2 on the same dimer. In case of an isolated dimer with the exchange interaction J, χ_{12} can be written as

$$\chi_{12} = \frac{(g\mu_B)^2}{2J} \tag{3}$$

The local magnetic field at I_1 induced by I_2 is $a_z I_2^z / \hbar\gamma_{N1}$. It splits the Cu-spectrum into four lines because there are four possible values of I_2^z ($\pm 3/2$, $\pm 1/2$). Strictly speaking, the spectrum consists of eight lines because I_2 can be either ^{63}Cu or ^{65}Cu. In the latter case, the field induced by I_2 is larger by a factor $^{65}\gamma/^{63}\gamma$=1.071. However, the difference is too small to be resolved experimentally.

Considering that the spectrum in Fig, 3 represent the isotopic average for the second spin being either ^{63}Cu or ^{65}Cu, the coupling strength in the case that second spin is ^{63}Cu $a_z/\hbar\gamma_{N1}$ is estimated to be 119.4kHz. For an isolated dimer, from eqs. (2) and (3), this value corresponds to the intra-dimer exchange J =89 K. Here we use the hyperfine coupling constant A_c=-259 kOe/μ_B, and the g-facor g_c=2.28 which was estimated by ESR measurement.[9] This value is in good agreement with the estimation in ref. [4].

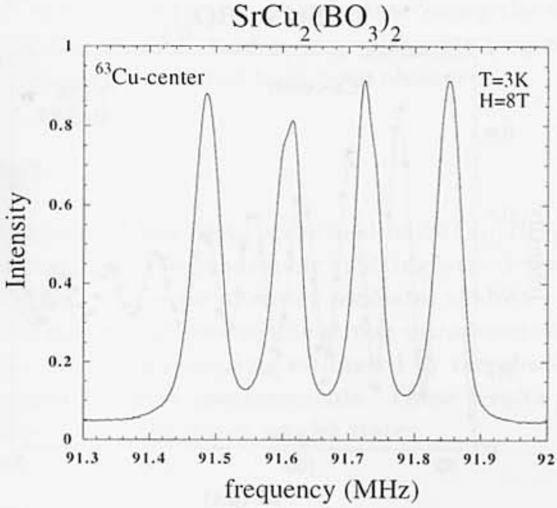

Figure 3: The spin-echo NMR spectrum of central line at ^{63}Cu at T =3K. The magnetic field is 8 T and parallel to the c-axis.

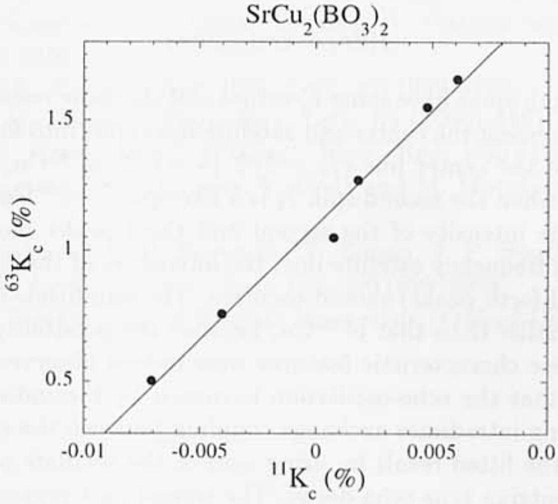

Figure 4: $^{63}K_c$ is plotted against $^{11}K_c$. $^{63}K_c$ and $^{11}K_c$ are the shifts of ^{63}Cu and ^{11}B obtained at $H//c$, respectively.

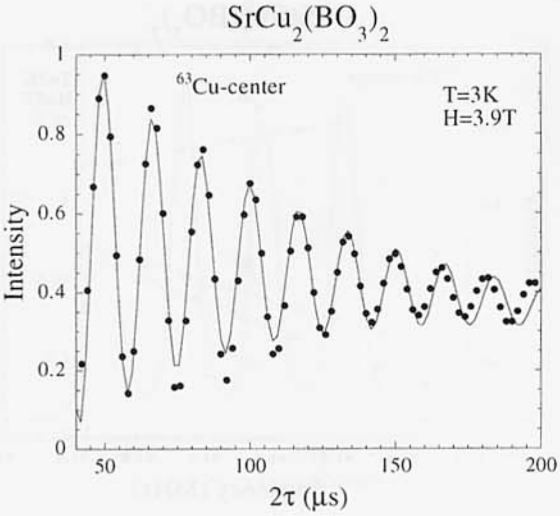

Figure 5: The spin-echo intensity of center line of ^{63}Cu is plotted as function of 2τ. The data is taken at T =3 K. The magnetic field is 3.9T and it is paralell to the c-axis.

The spin echo intensity ocsillates against the separation time τ as shown in Fig. 5. It can be expained by considering the isolated dimer. Considering the two nuclear spin system with the coupling a_z, the echo intesity is given as

$$I(2\tau) = \cos(a_z/\hbar\tau) \tag{4}$$

in the case that the both spins have same I_z-values and the same resonance frequencies.[11] In the present measurement the center and satellite lines split into four lines as mentioned above. In the case of the center line ($I_z = 1/2 \leftrightarrow -1/2$) of ^{63}Cu, the echo intensity is expected to oscillate when the second spin I_2 is a like-spin, i.e., ^{63}Cu nucleus in the states $I_z = \pm 1/2$. Then the intensity of the second and third peaks should oscillate. In the case of the low (high) frequency satellite line, the intensities of the lines with the first and the second (third and forth peaks) should oscillate. The amplitude of the echo oscillation of ^{65}Cu should be smaller than that of ^{63}Cu, because the possibility that I_2 is also ^{65}Cu is smaller. All of these characteristic features were indeed observed in the experiments, strongly supporting that the echo-oscillation is caused by the indirect nuclear spin-spin coupling via the strong intradimer exchange coupling between the electron spins.

The solid line is the fitted result by using sum of the oscillate part and non-oscillate one, which have Lorentzian type echo decay. The second part represent the contributtion from those nuclear spins with unlike second spin. ¿From the fitting, the period of the echo oscillation $4\pi/a_z$ is 16.7 μs. From eqs. (3) and (4), the intradimer coupling J is determined as 88K, in good agreement with the value obtained from the separation of the line splitting.

The line splitting and the echo-oscillation provide evidence that the indirect nuclear coupling is significantly strong only within a dimer. The estimated value of J based on the model of an isolated dimer is in good agreement with those obtained from other measurements. It is consistent with the ground state being the direct products of the dimer singlet state. If the ground state were a plaquette singlet state, the apparent pairwise nuclear spin coupling would not have been observed.

4 Conclusion

Cu- and B-NMR measurement has been performed on $SrCu_2(BO_3)_2$. The values of the hyperfine coupling constant and the quadrupole splitting were determined. The spectrum of Cu splits into four lines. The echo intensity oscillates against τ. They are caused by the nuclear spin-spin coupling mediated by the strong intradimer coupling of the electron spins. The value of the intradimer coupling estimated by the above consideration agrees well with those estimated by other measurements. These results provide firm evidence that the ground state is indeed the dimer singlet state.

5 References

[1] H. Kageyama, K. Yoshimura, R. Stern, N. V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C.P. Slichter, T. Goto and Y. Ueda : Phys. Rev. Lett. 82 (1999)3168.
[2] B. S. Shastry and B. Sutherland : Physica B108(1981)1069.
[3] H. Kageyama, M. Nishi, N. Aso, K. Onizuka, T. Yoshihama, K. Nukui, K. Kodama, K. Kakurai and Y. Ueda : Phys. Rev. Lett. 84 (2000) 5876.
[4] S. Miyahara and K. Ueda : J. Phys. Soc. Jpn. 69 (2000) 72 Suppl. B.
[5] K. Onizuka, H. Kageyama, Y. Ueda, T. Goto, Y. Narumi and K. Kindo : J. Phys. Soc. Jpn. 69 (2000) 1016.
[6] S. Miyahara and K. Ueda : Phys. Rev. Lett. 82(1999)3701.
[7] A. Koga and N. Kawakami : Phys. Rev. Lett. 84 (2000) 4461.
[8] Z. Weihong, C. J. Hamer and J. Oitmaa : Phys. Rev. B60 (1999) 6608.
[9] H. Nojiri, H. Kageyama, K. Onizuka, Y. Ueda and M. Motokawa : J. Phys. Soc. Jpn. 68(1999)2906.
[10] O. Cepas, K. Kakurai, L. P. Regnault, T. Ziman, J. P. Boucher, N. Aso, M. Nishi, H. Kageyama and Y. Ueda: J. Phys. Soc. Jpn. 68(1999)2906.
[11] A. Abragham : The Princiles of Nuclear Magnetism (Oxford University Press, Oxford, 1961).