Exact Dimer Ground State and Quantized Magnetization Plateaus in the Two-Dimensional Spin System $SrCu_2(BO_3)_2$

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Magnetic susceptibility, Cu NQR, and high-filed magnetization have been measured in polycrystalline $SrCu_2(BO_3)_2$ having a two-dimensional (2D) orthogonal network of Cu dimers. This cuprate provides a new class of 2D spin-gap system ($\Delta = 30$ K) in which the ground state can be solved "exactly." Furthermore, in the magnetization, two plateaus corresponding to $\frac{1}{4}$ and $\frac{1}{8}$ of the full Cu moment were first observed for 2D quantum spin systems. [S0031-9007(99)08878-X]

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Since the so-called pseudo spin gap has been suggested to have intimate relevance to the appearance of high-T_c superconductivity, a considerable number of studies have been made on low-dimensional quantum spin systems with a spin-singlet ground state over the past decade [1]. Experimentally, however, they are limited to quasi-one-dimensional (quasi-1D) cases such as $SrCu_2O_3$ ($S = \frac{1}{2}$ ladder system) [2], Y_2BaNiO_5 ($S = 1$ Haldane system) [3], and $Cu(NO_3)_2 2.5H_2O$ ($S = \frac{1}{2}$ alternating chain) [4], except for a quasi-two-dimensional (quasi-2D) system CaV_4O_9 [5], for which a model based on the plaquette singlets is considered to explain the origin of the spin gap [6]. For this reason, it is important to discover other examples of 2D spin systems having a finite spin gap to an excited state.

In this Letter, we investigated a 2D quantum spin system $SrCu_2(BO_3)_2$ by means of magnetic susceptibility, nuclear quadrupole resonance (NQR), and high-field magnetization, and have found that $SrCu_2(BO_3)_2$ is a new spin-gap system with an exact ground state. Moreover, in the magnetization curves at 1.7 and 0.5 K, we have succeeded in observing $\frac{1}{4}$ and $\frac{1}{8}$ plateaus of the saturation magnetization, which is the first observation of the quantized magnetizations in 2D spin systems.

$SrCu_2(BO_3)_2$ has a tetragonal unit cell with the cell constants of $a = 8.995$ Å and $c = 6.649$ Å at room temperatures [7]. All Cu^{2+} ions with a localized spin $S = \frac{1}{2}$ are located at crystallographically equivalent sites. The structure is characterized by the layers of interconnected rectangular planar CuO_4 and triangular planar BO_3 groups as shown in Fig. 1(a). These layers extend parallel to the c axis, and are structurally separated from each other by planes composed of Sr^{2+} ions. A unique 2D magnetic linkage of the Cu^{2+} spins is formed as illustrated in Fig. 1(b): The first-nearest-neighbor (1 NN) Cu pairs (the distance of 2.905 Å) share an edge to form dimeric units, which are connected orthogonally with each other through B^{3+} ions, providing pathways for weak interdimer interaction. Each Cu^{2+} ion has four second-nearest-neighbor (2NN) Cu^{2+} ions (5.132 Å). In other words, each Cu dimer is surrounded by six 2NN Cu^{2+} ions.

The $SrCu_2(BO_3)_2$ sample was prepared by a solid state reaction method from $Sr(NO_3)_2$, CuO, and B_2O_3 with 99.99% purities. Powders were ground, followed by the heat treatment at 850 °C for 2 weeks with intermediate gridings. The powder x-ray diffracting pattern indicated a single-phase product with no impurity. The magnetic susceptibility was measured using a superconducting quantum interference device magnetometer in the temperature T range from 1.7 to 400 K in an applied magnetic field H of 1.0 T. The Cu NQR spectra were measured with a homemade phase-incoherent-type spectrometer. The frequency was scanned from 16.0 to 27.0 MHz with approximate intervals of about 0.1 MHz. The spin-lattice relaxation rate $1/T_1$ at $^{63}Cu/^{65}Cu$ nuclear was measured

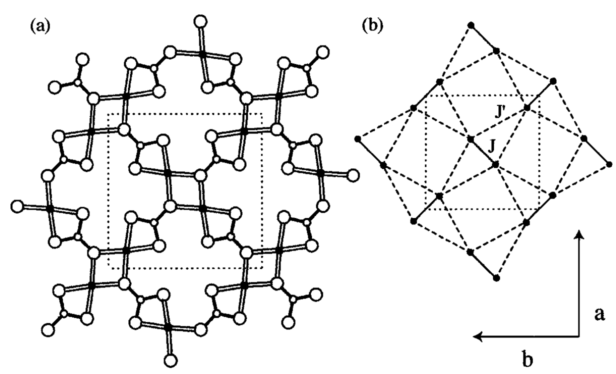

FIG. 1. (a) Schematic view of the crystal structure of $SrCu_2(BO_3)_2$ along [001]. The closed circles, small open circles, and large open circles denote, respectively, the Cu^{2+}, B^{3+}, and O^{2-} ions. The unit cell is represented by dotted lines. (b) 2D coordinates of the Cu^{2+} spins. The 1NN and the 2NN Cu pairs are denoted by the solid and broken lines, respectively.

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by the saturation recovery and inversion recovery methods on the center line of the quadrupole spectrum. The magnetization measurement was carried out up to 45 T at 4.2, 1.7, and 0.5 K using an induction method with a wire-wound pulse magnet whose duration time is about 20 ms.

We show in Fig. 2 the T dependence of the magnetic susceptibility χ_{raw} measured at 1.0 T. A prominent characteristic is that χ_{raw} shows a maximum at around 20 K and it rapidly drops toward zero with reducing temperature, suggesting the existence of an energy gap in the spin excitation spectrum. χ_{raw} was fitted well to the Curie-Weiss law over the T range of 160 to 400 K with the Weiss temperature of $\theta = -92.5$ K and the effective g factor, $g = 2.14$, accompanied with a constant susceptibility $\chi_0 = -2.01 \times 10^{-5}$ emu/mol Cu. As seen in the inset of Fig. 2, a small Curie-Weiss-like upturn is seen in the χ_{raw} curve below 4 K, which would appear due to magnetic impurities and/or defects of Cu^{2+} ions in $SrCu_2(BO_3)_2$. In order to estimate the Curie-Weiss term at low temperatures, the data below 3.5 K were fitted to $C'/(T - \theta')$. This gave $\theta' = -2.5$ K and $C' = 2.7 \times 10^{-3}$ emu K/mol Cu, corresponding to 0.72% of nearly free $S = \frac{1}{2}$ impurities. Spin susceptibility χ_{spin} was finally evaluated after subtracting $C'/(T - \theta') + \chi_0$ from χ_{raw}. By fitting χ_{spin} at a low temperature range with $\chi_{\text{spin}} \propto \exp(-\Delta_s/T)$, we roughly evaluated the gap Δ_s to be 19 ± 1 K. The fitting curve is drawn in the inset of Fig. 2.

A microscopic investigation by means of Cu NQR has confirmed the existence of the spin-singlet ground state with the finite energy gap in $SrCu_2(BO_3)_2$. Typical spin-echo spectra of $^{63}Cu/^{65}Cu$ NQR lines measured at constant τ (τ being the time separation between the exciting and refocusing rf pulses) of 80 μs are shown in the inset of Fig. 3 obtained at $T = 4.3$ and 3.1 K. The solid curves are the best calculated profile with the Gaussian distribution of the electric field gradient with a FWHM of 400 kHz (4.3 K) and 250 kMz (3.1 K). The ratio of two resonance frequencies measured at 4.3 K is found to be exactly the same as that of the nuclear quadrupole moment of Cu ($^{63}Q/^{65}Q = 1.081$). Accordingly, we can conclude that these lines are classified to $^{63}Cu/^{65}Cu$ NQR lines. The quadrupole frequency υ_Q for 4.3 K can be obtained to be 23.01 MHz for ^{63}Cu (higher resonance branch). On the contrary, when the temperature is lowered (see the spectrum at 3.1 K), the NQR line signal splits into two components with $\upsilon_Q = 22.85$ and 23.25 MHz for ^{63}Cu. This split is attributable to the nuclear spin-spin coupling in the dimer, which was also observed for the dimer chain site in $Sr_{14}Cu_{24}O_{41}$ [8]. This will be treated in full detail elsewhere as well as spin-echo oscillating behavior observed also in this compound.

The T dependence of $1/T_1$ is presented in Fig. 3. The recovery curves were fitted to the single exponential terms, and comparison of the recovery curves for ^{63}Cu and ^{65}Cu revealed that the relaxation process is dominantly magnetic

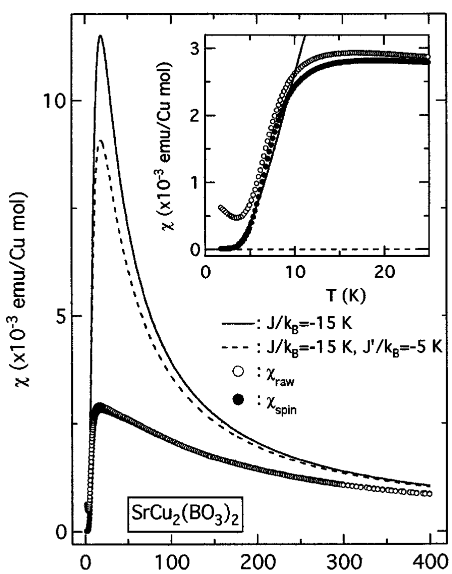

FIG. 2. Temperature dependence of the magnetic susceptibility in $SrCu_2(BO_3)_2$ powder. The open and closed circles represent, respectively, the measured susceptibility χ_{raw}, and spin susceptibility χ_{spin} after subtracting the Curie-Weiss and constant terms from χ_{raw}. The solid and broken lines show the theoretical curves based on a dimer model. The enlarged plot is shown in the inset, where the solid curve indicates the fit to $\chi_{\text{spin}} \propto \exp(-\Delta_S/T)$.

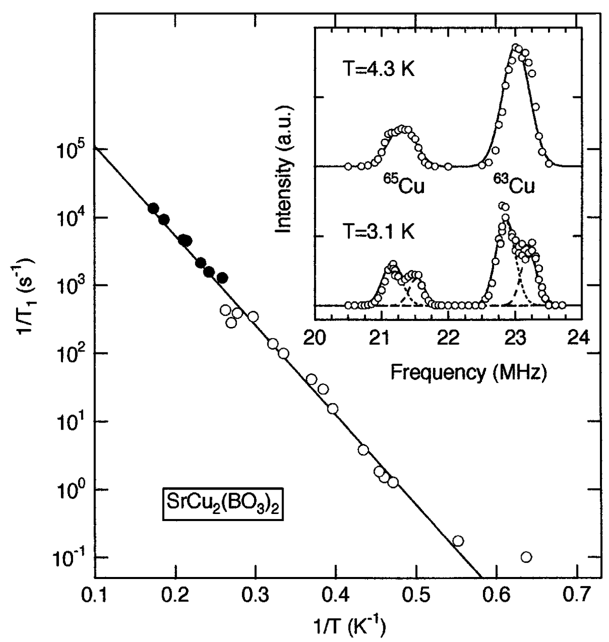

FIG. 3. Temperature dependence of $1/T_1$ measured by saturation recovery method at Kyoto University (open) and by inversion recovery method at University of Illinois at Urbana-Champaign (closed). The solid line shows the activated T dependence with $\Delta_R \sim 30$ K. In the inset is shown the Cu NQR spectra measured at 4.3 and 3.1 K.

[$^{63}T_1/^{65}T_1 = 1.112$ for 3.1 K is close to $(^{65}\gamma/^{63}\gamma)^2 = 1.1475$]. Then, we fitted the data to the activated T dependence, $1/T_1 \propto \exp(-\Delta_R/T)$ (Δ_R: the dynamical spin gap), and obtained $\Delta_R = 30$ K a little larger than $\Delta_S = 19$ K estimated from the magnetic susceptibility.

Now that we are sure that $SrCu_2(BO_3)_2$ has the finite energy gap between the ground and exited states, the next step is to clarify the origin of the spin gap. From the viewpoint of the crystal structure, or rather the arrangement of magnetic Cu^{2+} ions, one may intuitively expect that the magnetic properties of the present material would be just those of the 1NN Cu dimers. An $S = \frac{1}{2}$ dimer model [9] is simplest among spin-gap systems and widely known to be applicable to many materials: CsV_2O_5 [10], $BaCuSi_2O_6$ [11], and various Cu complexes [12]. Considering the dimer bridging angle (∠Cu-O-Cu) of 102.42°, it is reasonable to suppose that the intradimer exchange interaction (symbolized by J) is antiferromagnetic; $J < 0$. (In general, there is an inverse correlation between the value of J and the angle at the bridging oxygen atom, and J changes its sign near 97.6° [13].)

Our χ_{spin} data were first analyzed using an $S = \frac{1}{2}$ isolated antiferromagnetic (AF) dimer model [9], where the spin susceptibility χ_d is expressed as

$$\chi_d = \frac{Ng^2\mu_B^2}{3k_BT}\left[1 + \frac{1}{3}\exp(-2J/k_BT)\right]^{-1}. \quad (1)$$

Here, N, μ_B, and k_B are Avogadro number, the Bohr magneton, and Boltzmann constant, respectively. Note that J is a unique fitting parameter. Although we attempted to fit the χ_{spin} data in such a manner that the temperature at maximum χ_d coincides with that of χ_{spin} (= 18.5 K), Fig. 2 clearly shows that the result was far from satisfaction: Compared with the theoretical curve with $J/k_B = -15.0$ K (solid line), the peak of χ_{spin} is significantly suppressed. In order to resolve the great discrepancy between χ_{spin} and χ_d, an AF 2NN interaction J' (<0) was introduced. We calculated susceptibility by a mean-field approximation given in Ref. [14]. Nevertheless, it hardly improved the fit as seen in the curve assuming $J'/k_B = -5$ K (broken line). To obtain the best fit, one has to assume an unreasonably large negative value of $J'/k_B = -50$ K apparently beyond the validity of a mean-field approximation ($|J'| \ll |J|$). It should be pointed out that, if the 1NN interaction is antiferromagnetic ($J < 0$), the 2NN Cu spins feel a spin frustration highly relevant to a resonating-valence-bond state [15]. The effect of the spin frustration is actually seen in the fairly small spin gap in contrast with the large Weiss temperature.

Magnetization measurement is a useful tool to clarify the nature of a spin-singlet ground state since it can provide crucial information on a magnetic excited state. Figure 4 shows the magnetization M of $SrCu_2(BO_3)_2$ as a function of H, where no hysteresis was observed between the field increasing and decreasing processes. As expected, the continuous transition from the singlet ground state to the gapless magnetic state occurs at around 20 T corresponding to the gap of 30 K in agreement with the T_1^{-1} result. With decreasing temperature, this transition becomes more distinct. For comparison, we show the theoretical magnetization at zero temperature based on the isolated dimer model with a critical field of 20 T [4,14], again in disagreement with the experimental data.

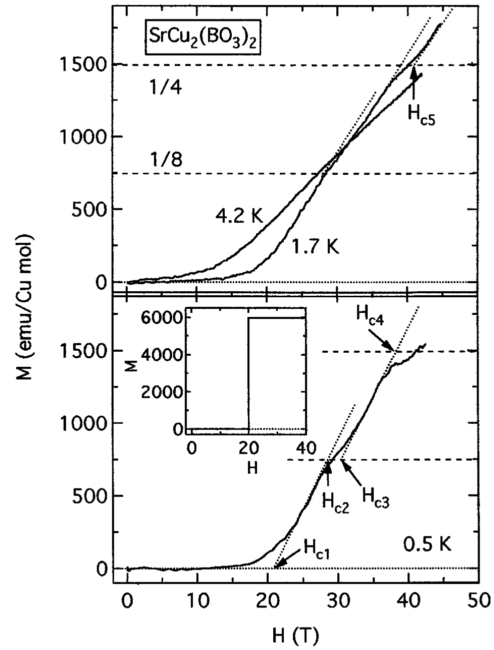

FIG. 4. Magnetization curves of $SrCu_2(BO_3)_2$ obtained at 4.2 and 1.7 K (top); and 0.5 K (bottom). The broken lines correspond to $\frac{1}{4}$ and $\frac{1}{8}$ of the full magnetization ($= 1/2Ng\mu_B$ emu/mol Cu with $g = 2.14$). Inset: Zero-temperature magnetization curve for the isolated dimer model with a critical field of 20 T.

Our experimental study has triggered a theoretical search for this 2D spin system. Recently, Miyahara and Ueda showed that $SrCu_2(BO_3)_2$ is close to the critical point between the spin-singlet state and the Néel ordered state [16]. The unusual behavior of the susceptibility is a consequence of the closeness to the criticality, and their theoretical calculations reproduced the χ-T curve quite satisfactorily. Furthermore, $SrCu_2(BO_3)_2$ having the 2D orthogonal dimer network [17] has been found to be a clean system with the "exact" dimer ground state. $SrCu_2(BO_3)_2$ is the first example where this exact ground state is achieved.

The most important finding in the present high-field study is that the two plateaus corresponding to $\frac{1}{4}$ and $\frac{1}{8}$ of the saturation moment appear in the magnetizations at 1.7 and 0.5 K. The critical fields are evaluated by extrapolating the M vs H curves in the slope regions to the zero, $\frac{1}{8}$ and $\frac{1}{4}$ plateau lines in Fig. 4. As a result, $H_{c1} = 20.9$ T, $H_{c2} = 27.9$ T, $H_{c3} = 29.8$ T, $H_{c4} = 37.0$ T, and $H_{c5} = 41.0$ T are obtained. With increasing H, we have the gapped and gapless ground states by turns: In the gapped regions $H < H_{c1}$, $H_{c2} < H < H_{c3}$, and $H_{c4} < H < H_{c5}$, $SrCu_2(BO_3)_2$ has the finite energy gap between the ground and the lowest exited states, and, in the gapless regions $H_{c1} < H < H_{c2}$, $H_{c3} < H < H_{c4}$, and $H_{c5} < H$, the system has no excitation gap and the magnetization increases continuously. The observed plateaus are not flat although the data at 0.5 K have clearer plateaus than in the case of 1.7 K. This is partly because of thermal fluctuation and also because of the fact that the measurement using powder sample averages the field-direction-dependent critical fields due to the anisotropy of the g factor.

Theoretically, several 1D quantum spin models have been shown to have magnetization plateaus [18–20]. For example, the $\frac{1}{2}$ and the $\frac{1}{3}$ plateaus appear, respectively, in an $S = 1$ alternating AF Heisenberg chain and in an $S = \frac{1}{2}$ AF Heisenberg chain with period-3 exchange coupling. Recently, these quantization conditions have been generalized by Oshikawa, Yamanaka, and Affleck [21]. They investigated the general Heisenberg spin chains at zero temperature in the presence of H and showed that the magnetization per site m is topologically quantized as $n(S - m) =$ integer, where n is the period of the ground state, and S is the magnitude of spin. From the experimental point of view, the quantized plateaus have been indeed found in the magnetization curves of 1D compounds $[Ni_2(medpt)_2(\mu\text{-ox})(\mu\text{-}N_3)]ClO_4 \cdot 0.5H_2O$ ($\frac{1}{2}$ plateau) [22] and NH_4CuCl_3 ($\frac{1}{4}$ and $\frac{3}{4}$ plateaus) [23], both of which are considered to satisfy the quantization conditions.

In contrast to the 1D spin systems mentioned above, the problem of the quantized magnetization plateaus in 2D spin systems has not been addressed yet. It should be stressed that $SrCu_2(BO_3)_2$ is the first example having quantized magnetization plateaus in the 2D spin systems. The recent theory by Miyahara and Ueda suggests that triplet excitations from the ground state are almost localized, which accounts for the $\frac{1}{4}$ and $\frac{1}{8}$ plateaus in the 2D orthogonal dimer lattice [16]. Moreover, other plateaus at $\frac{1}{2}, \frac{1}{10}, \frac{1}{16}, \ldots$ have been predicted.

In summary, we have investigated both the static and the dynamical magnetic properties of $SrCu_2(BO_3)_2$ by means of magnetic susceptibility, Cu NQR, and high-field magnetization measurements, and have found the existence of the spin-singlet ground state with the energy gap of 30 K. It is concluded that $SrCu_2(BO_3)_2$ is a new spin-gap system with the exact dimer ground state [17]. Furthermore, the quantized magnetization plateaus have been observed at $\frac{1}{4}$ and $\frac{1}{8}$ of the full magnetization, which is the first case in the 2D quantum spin systems. The recent theoretical investigation has succeeded to explain these interesting magnetic behaviors of $SrCu_2(BO_3)_2$ [16]. Investigations using a single crystal are necessary in order to understand fully the nature of the spin-singlet ground state and to observe the predicted magnetization plateaus. It is also interesting to examine the effect of hole/electron doping, which may induce superconductivity.

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