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Anomalous Magnetizations in Single Crystalline $SrCu_2(BO_3)_2$

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The magnetic properties of a two-dimensional spin-gap compound $SrCu_2(BO_3)_2$, realizing the Shastry-Sutherland model, were investigated using high-quality single crystals. The analysis of the temperature-dependent magnetic susceptibility revealed a spin gap of 34 K. The magnetization curve at 0.4 K possibly has, in addition to the already established one-quarter and one-eighth plateaux, another quantized plateau at one-tenth of the full Cu-moment, which is one of the plateaux predicted by Miyahara and Ueda.

KEYWORDS: $SrCu_2(BO_3)_2$, Shastry-Sutherland model, quantized magnetization plateaux, exact dimer ground state

Low-dimensional materials have been the focus in the area of condensed matter physics because the dimensionality of the structures leads to unusual and exotic magnetic/electronic phenomena such as high-T_c superconductivity.[1)] $SrCu_2(BO_3)_2$ has a two-dimensional structure, which consists of alternately stacked $CuBO_3$- and Sr-layers.[2)] The peculiar magnetic network of the magnetic Cu^{2+} ions (d^9, thus $S = 1/2$), in which neighboring Cu^{2+}–Cu^{2+} dimers are orthogonally connected in the layer, has given rise to amazing aspects with respect to the ground state:[3-5)] $SrCu_2(BO_3)_2$ is a highly frustrated two-dimensional spin-gap system with a gap Δ of about 30 K. Irrespective of the interdimer interaction, the direct product of the dimer singlets is the exact ground state, realizing the Shastry-Sutherland model[6)] proposed almost 20 years ago. Moreover, a recent theory[7)] revealed that this compound resides in the vicinity of the critical point between the gapped exact dimer state and the gapless Néel-ordered state.

The excited states of $SrCu_2(BO_3)_2$ are also of great interest as seen in the magnetizations: we observed quantized magnetization plateaux at 1/4 and 1/8 of the saturation of the Cu moment M_s.[3-5)] The superstructures for the 1/4 and 1/8 plateaux are illustrated in Figs. 1(a) and 1(b), respectively. The origin of the observed plateaux was discussed by Miyahara and Ueda.[7)] They argued that, because of the extremely localized character of the excited triplets and also because of their repulsive interaction, the triplets would favor ordered rather than liquid states. Considering the tetragonal symmetry of the original lattice, the necessary condition for the triplets to assure ordered structures is that corresponding magnetic unit cells are square, which is fulfilled when $M/M_s = 1/4$, 1/8 (see Figs. 1(a) and 1(b)). Based on this condition, other plateaux at 1/2, 1/10, 1/16, $1/32 \cdots$ were predicted. Therefore, observation of the remaining plateaux may be verifying their theory.

In order to elucidate the intrinsic magnetic properties of $SrCu_2(BO_3)_2$ in sufficient depth, in particular to solve the plateau problem, high-quality bulk single crystals are indispensable. Recently, we have succeeded, after extensive trial-and-error, in growing large single crystals by means of a vertical traveling solvent floating zone (TSFZ) technique.[8)] In this letter, we will show the results of magnetic susceptibility and high-field magnetization measurements for the single crystals, and elaborate on both the ground and the excited states.

Single crystals of $SrCu_2(BO_3)_2$ of high purity were grown by the TSFZ method with an image furnace using an appropriate amount of a polycrystal $SrCu_2(BO_3)_2$ and a solvent $LiBO_2$ under flowing O_2 gas (P_{O_2} = 1 atm).[8)] The temperature variation of the magnetic susceptibility was measured in the magnetic field H of 1.0 T in the temperature range between 2 K and 350 K using a superconducting quantum interference device (SQUID) magnetometer. A piece of the obtained single crystals (0.14 g) was set on a sample holder in such a way that the c axis was oriented parallel ($/\!/$) or perpendicular ($\perp$) to the applied magnetic field. The high-field magnetization measurement was performed using an induction method with a wire-wound pulse magnet which produces magnetic fields up to 42 T. The duration time was about 20 ms. Two pieces of the crystals (0.19 g) were aligned in the direction, $H \perp c$ and cooled to 0.4 K using a conventional ^{3}He-pumping device.

We first show in Fig. 2 the temperature dependence of the parallel and perpendicular magnetic susceptibilities of $SrCu_2(BO_3)_2$, $\chi_{raw/\!/}$ and $\chi_{raw\perp}$, respectively. For comparison, the previous data for the powdered sample

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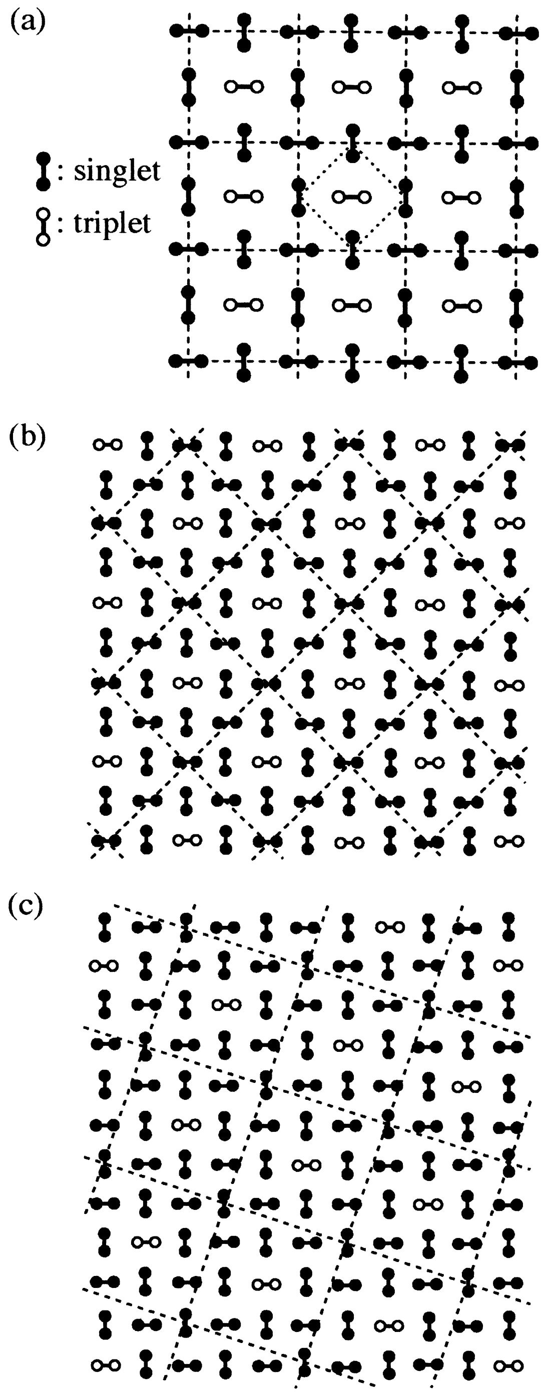

Fig. 1. Ordered structures between the excited triplets (open) and the remaining singlets (solid) corresponding to 1/4 (a), 1/8 (b), and 1/10 (c) plateaux. The magnetic unit cells are denoted by broken lines, and the chemical unit cell by dotted lines in (a).

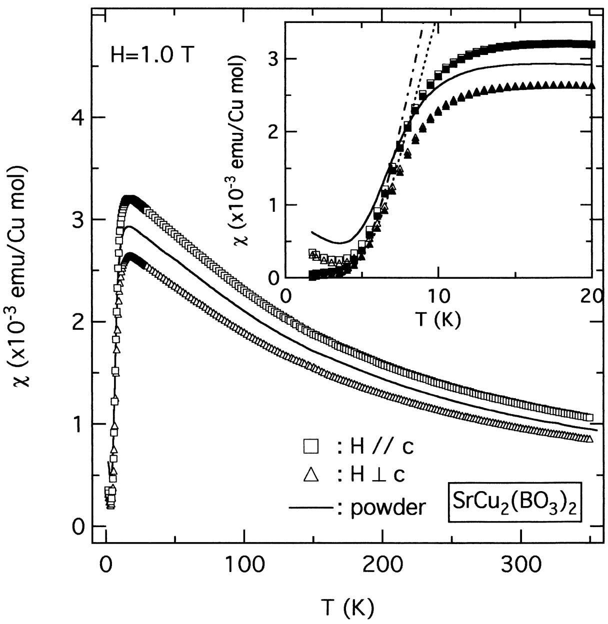

Fig. 2. Temperature variation of the magnetic susceptibilities for $SrCu_2(BO_3)_2$, $\chi_{raw/\!/}$ (square) and $\chi_{raw\perp}$ (triangle), parallel and perpendicular to the tetragonal c axis, respectively. The previous data for the powdered sample is also shown by the solid line.[3)] The inset is the enlarged plot in the low-temperature region. The spin susceptibilities, $\chi_{spin/\!/}$ and $\chi_{spin\perp}$, are marked by the solid symbols. The broken lines ($\cdot-\cdot-\cdot$, $---$) represent the fitted curves of $\chi_{spin/\!/}$ and $\chi_{spin\perp}$, respectively, to the isolated dimer model (see text), where $g_{/\!/} = 2.28$ and $g_\perp = 2.07$, determined by ESR, are used.

are also shown by the solid line.[3)] At high temperatures well above the spin gap, both $\chi_{raw/\!/}$ and $\chi_{raw\perp}$ obey the Curie-Weiss law $\chi = Ng^2\mu_B^2 S(S+1)/[3k_B(T-\theta)]$, where N denotes Avogadro number, μ_B, the Bohr magneton, k_B, Boltzmann constant, g, the g-factor, and θ, the Weiss constant. Using $S = 1/2$ for the Cu^{2+} ion and $g_{/\!/} = 2.28$ and $g_\perp = 2.07$ determined by the electron spin resonance (ESR) measurements,[9)] we fitted the data in the temperature range between 250 K and 350 K to the above formula, and obtained $\theta = -102.5$ K together with a constant susceptibility $\chi_0 = -2.603 \times 10^{-5}$ emu/Cu mol. The obtained Weiss constant is slightly larger in magnitude than the previous results for the polycrystal (-92.5 K)[3)] and for the field-oriented polycrystal along the c axis (-97.8 K).[4)]

When the temperature is decreased, the susceptibilities reach a maximum at about 15 K, decrease abruptly and then tend to approach zero at 0 K, achieving the exact dimer ground state. There is a Curie-like upturn below 4 K, presumably due to a defect in the crystal. It is noteworthy that the contribution of this extrinsic term is significantly reduced compared with that for the polycrystalline samples,[3,4)] ensuring high crystal quality. Indeed, the fit to the Curie law C'/T in the low-temperature region gave $C' = 1.5 \times 10^{-3}$ emu K/Cu mol, corresponding to only 0.14% of free spin-1/2. Spin susceptibilities of $SrCu_2(BO_3)_2$, $\chi_{spin/\!/}$ and $\chi_{spin\perp}$ were finally evaluated by subtracting $C'/T + \chi_0$ from $\chi_{raw/\!/}$ and $\chi_{raw\perp}$, respectively.

The value of Δ was re-estimated in several ways as follows: based on the fit of the spin susceptibilities below 6 K to the isolated dimer model $\chi = Ng^2\mu_B^2/k_BT[3 + \exp(\Delta/T)]$ (see the inset of Fig. 2), where Δ is the uniquely fitted parameter, we obtain $\Delta = 34 \pm 1$ K, which is in good agreement with the recent nuclear magnetic resonance (NMR) result (34 ± 1 K),[10)] and is very close to the value of 30 K evaluated from the nuclear quadrupole resonance (NQR) and the magnetization measurements.[3)] On the other hand, if one fits $\chi_{spin/\!/}$ and $\chi_{spin\perp}$ to $\chi_s \propto \exp(-\Delta/T)$ as we did previously for the polycrystal,[3)] a much smaller value of $\Delta = 19$ K is obtained again. Thus, the former model seems to give a

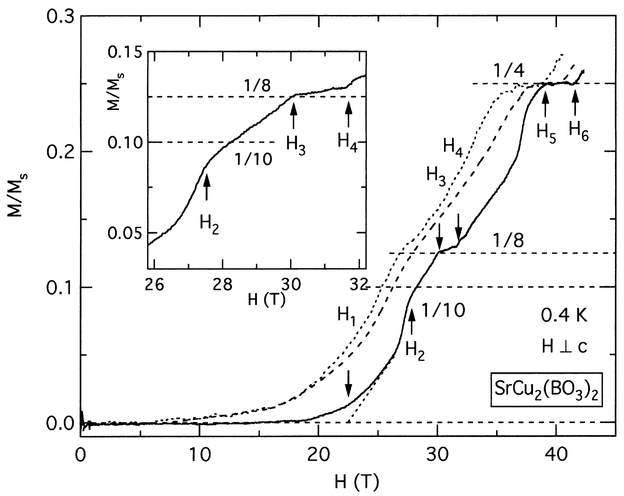

Fig. 3. Magnetization curve of $SrCu_2(BO_3)_2$ perpendicular to the c direction (the solid line) measured at 0.4 K. For comparison, the parallel and perpendicular magnetizations at 0.5 K for the field-oriented sample are shown by the dotted and the broken lines, respectively.[4)]

more appropriate description of the χ-T, at least in this temperature region.

Let us now move onto the result of the magnetization measurements. The solid line in Fig. 3 denotes the perpendicular magnetization $M_\perp$ at 0.4 K as a function of H, which is a major improvement over previous data (also shown in Fig. 3 by the broken lines),[4)] possibly adding a new plateau as described in the next paragraph. We see from Fig. 3 that the gap closes at about $H_1 = 22.5\,\mathrm{T}$, corresponding to $\Delta = 31.3\,\mathrm{K}$ (where we assumed $g_\perp = 2.07$[9)]). As observed previously, there are two quantized plateaux at $M/M_s = 1/4$, 1/8, which evidently become more distinct. The field-induced gapped state[11)] for the 1/4 plateau exists between $H_5 = 39.1\,\mathrm{T}$ and $H_6 = 41.6\,\mathrm{T}$, and that for the 1/8 plateau between $H_3 = 30.1\,\mathrm{T}$ and $H_4 = 31.7\,\mathrm{T}$. The fact that the 1/4 plateau is wider than the 1/8 plateau, i.e., $(H_6 - H_5)/(H_4 - H_3) \sim 1.5$, suggests that the former state has a bigger field-induced gap than the latter, in contrast to the case of NH_4CuCl_3,[12)] in which the observed plateaux at 1/4 and 3/4 have almost the same width. The estimated critical fields $H_3 \sim H_6$ are somewhat higher than those for the oriented polycrystal ($H \perp c$).[4)] This means that the orientation of the polycrystal was poor as checked by NMR measurement[9)] and, as a consequence, the $M_\perp$ vs H curve for the oriented polycrystal must involve the contribution of the parallel component $M_{/\!/}$.

Of greater significance here is that the magnetization curve has an inflection at $H_2 = 27.5\,\mathrm{T}$, which, broadly speaking, appears at 1/10 of the saturation moment. This anomaly is possibly attributed to the 1/10 plateau, which is, as mentioned earlier, one of the plateaux predicted by Miyahara and Ueda.[7)] The superstructure corresponding to the 1/10 plateau is illustrated in Fig. 1(c), where the magnetic unit cell is square and is five times as large as the chemical unit cell. According to their theory, with descending plateaux as 1/2, 1/4, 1/8, 1/10, 1/16, $1/32\cdots$, the field-induced gap decreases, resulting in narrower plateau width. This is the reason for the rather obscure 1/10 plateau in contrast to the clear 1/4 and 1/8 plateaux and for the unsuccessful observation of other predicted plateaux such as 1/16 and 1/32 plateaux. Therefore, lower temperature measurement is probably necessary in order to ensure the existence of the 1/10 plateau and to detect the remaining plateaux.

Let us now look at the detailed curvature of the magnetization in the gapless regions. As is well known for one-dimensional spin systems, the magnetization near the plateau edge is proportional to $\sqrt{|H - H_c|}$ (H_c: the critical field).[13)] Similar behavior is seen for the edges at H_3, H_4 and H_6, while those at H_1 and H_5 are somewhat round. Another point to note is the tendency of the magnetization curve to shoot up at 27 T or 37 T toward the next plateau edge. Presently, there exists no theory to describe such characteristics of $SrCu_2(BO_3)_2$ or more generally of two-dimensional spin systems.

In summary, we have measured the temperature-dependent magnetic susceptibilities and the high-field magnetization using single crystals of $SrCu_2(BO_3)_2$. From the analysis of the susceptibility data, we evaluated the spin gap to be 34 K, in good accordance with the results of NMR and the magnetization measurements. In the magnetization, in addition to the previously observed 1/4 and 1/8 plateaux of the saturation Cu moment, another plateau at 1/10 is probably present, which strongly supports the theory by Miyahara and Ueda.

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