Journal of Alloys and Compounds 317–318 (2001) 177–182

Journal of ALLOYS AND COMPOUNDS

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Quantized magnetization plateaux in the orthogonal dimer system $SrCu_2(BO_3)_2$

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Abstract

We carried out high-field magnetization measurements up to 57 T and down to 0.08 K on a single crystal of a two-dimensional spin-gap material $SrCu_2(BO_3)_2$. We successfully observed the predicted plateau at 1/3 of the total magnetization around 50 T, in which the magnetic superstructure is characterized by a novel stripe order of excited triplets. The 1/3 plateau is stable over much wider field region than the previously observed 1/4 and 1/8 plateaux. A sharp jump in the magnetization between 1/3 and 1/4 plateaux may be associated with a first-order transition. Furthermore, several anomalous behaviors were observed in a lower-field region including field-direction dependent magnetizations around 30 T. The obtained magnetizations are compared with theoretical calculations based on a hard-core boson model and on a perturbation expansion method. The magnetization measurements were also performed on 1% zinc-doped single crystal.

Keywords: Magnetization; $SrCu_2(BO_3)_2$; Stripe; Shastry–Sutherland model

1. Introduction

There has been a resurgent interest in the phenomena of quantized magnetization plateaux because the plateaux of recent interest are caused principally by quantum many-body effects [1], in contrast to classical-spin systems previously investigated such as $CoCl_2 2H_2O$ [2] and $Ca_3Co_2O_6$ [3]. Experimentally, several quantum-spin systems were reported to have magnetization plateaux. A 1/2 plateau of the total magnetization was observed in $[Ni_2(Medpt)_2(\mu\text{-ox})(\mu\text{-}N_3)]Cl_4\ 0.5H_2O$ [4], and 1/4 and 3/4 plateaux in NH_4CuCl_3 [5]. The observed plateaux for the former and latter materials have been nicely explained by the theoretical investigations on an $S=1$ chain system with bond alternation [6] and on an $S=1/2$ three-dimensionally coupled dimer system [7], respectively. It was, furthermore, shown that the necessary condition that plateaux appear in general one-dimensional (1D) systems is $n(S-m)$=integer, where n is the period of the spin state, S the magnitude of spin and m the magnetization per site in the unit cell [8]. Recently, this condition was found to be valid for any dimension [9].

The present paper will deal with $SrCu_2(BO_3)_2$ for which quantized plateaux were recently observed in the magnetization curves [10]. $SrCu_2(BO_3)_2$ is a layered material with a tetragonal symmetry, composed of alternating stacks of $2CuBO_3$ and Sr planes along the c-axis. In the $CuBO_3$ plane, nearest-neighbor Cu^{2+} ions constitute an $S=1/2$ dimeric unit, and each dimer connects orthogonally with four nearest-neighbor dimers, as shown in Fig. 1. The intradimer and interdimer interactions, symbolized by J and J', respectively, lead to an exact ground state with spin gap Δ, thus realizing the 2D Shastry–Sutherland model [11,12]. The values of J, J' and Δ were estimated to be 100, 68 [10,12] and 34 K [13–15], respectively.

The 1/4 and 1/8 plateaux in $SrCu_2(BO_3)_2$ were first detected by magnetization measurements on a polycrystalline sample performed up to a magnetic field $H=43$ T and down to a temperature $T=1.5$ K with a pulse magnet at ISSP, the University of Tokyo [10], followed by those using field-oriented samples for $H \parallel c$ and $H \perp c$ [14] and a single crystal for $H \perp c$ [15]. Miyahara and Ueda explained theoretically that the origin of the plateaux lies in the almost localized nature of the triplet excitations [12].

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0925-8388/01/$ – see front matter
PII: S0925-8388(00)01316-5

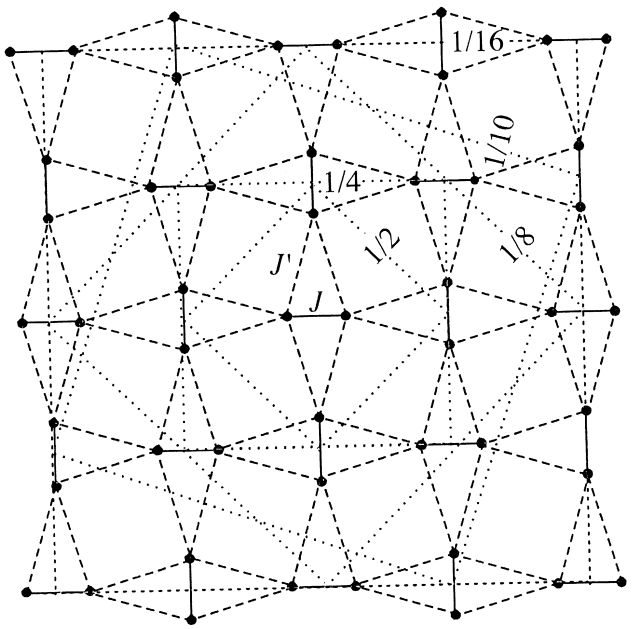

Fig. 1. $S=1/2$ orthogonal dimer lattice realized in $SrCu_2(BO_3)_2$, indicating in-plane interactions which act within the dimers J and between the dimers J'. Square unit cells containing 4, 8, 16, 20, 32 spins are represented by dotted lines.

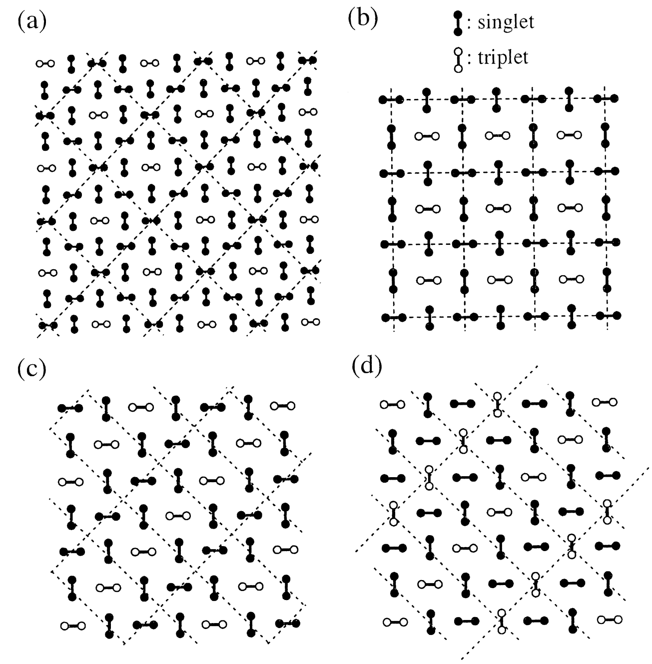

Fig. 2. Possible ordered structures between the excited triplets (open) and the remaining singlets (solid) for the 1/8 plateau (a) the 1/4 plateau (b) and (c), and the 1/3 plateau (d). The magnetic unit cells are represented by broken lines.

Moreover, in the light of the tetragonal symmetry of the crystal structure, they initially argued the following necessary condition for the triplets to ensure ordered rather than disordered structures: corresponding magnetic superstructures should also be of tetragonal symmetry. In fact, this condition satisfies the superstructures shown in Fig. 2a and b for the 1/8 and 1/4 plateaux, respectively. Following this simple geometrical argument, one expects other plateaux at 1/2, 1/10, 1/16, 1/32 . . . , which also have square unit cells as illustrated in Fig. 1.

However, recent detailed analyses carried out independently by Momoi and Totsuka [16] and by Miyahara and Ueda [17] have revealed the possibility that the superstructure for the 1/4 plateau is of the stripe type with a rectangular unit cell, as shown in Fig. 2c. According to Ref. [17], the triplet–triplet interaction between the nth nearest-neighbor pair of dimers V_n does not exhibit a monotonous decrease with increasing n. Especially important is that V_2 is smaller than V_3 for any J'/J. Thus, the superstructure in Fig. 2c, where excited triplets are arranged linearly avoiding V_3, should be more stable than that in Fig. 2b. Moreover, a prediction has been made that a 1/3 plateau with a superstructure of stripe order (see Fig. 2d) will be observable if a magnetic field higher than that ever studied is applied.

Unfortunately, in spite of intensive experimental activities [10,13–15,18–21], the existence of the stripe order even for the 1/4 plateau has not yet been confirmed. This is partly because the required magnetic field is beyond the capability of the facilities currently used for microscopic techniques such as neutron diffraction. In this paper, we measured the magnetization curves for single-crystalline $SrCu_2(BO_3)_2$ up to 57 T to successfully observe the 1/3 plateau. It should be emphasized that, unlike the case of the 1/4 plateau, the stripe superstructure (Fig. 2d) is the unique candidate for the 1/3 plateau. It is also interesting to investigate doping effect on the magnetization plateaux. Since the observed plateaux in $SrCu_2(BO_3)_2$ is closely related to the localized character of the excited triplets, we expect that a slight substitution of Zn for Cu, i.e. introduction of spin vacancy may significantly affect the field-dependent magnetization, possibly destroying the already-observed plateaux or/and creating new plateaux.

2. Experimental

The high-field magnetization measurements were conducted using an induction method with a multilayer pulse magnet at the High Magnetic Field Laboratory, KYOKUGEN in Osaka University. The pulse width was about 8 ms, and the use of a plastic dilution refrigerator allowed to measure down to 50 mK. Measurement accuracy of magnetization is less than 5% in magnitude. High-quality single crystals of $SrCu_2(BO_3)_2$ were obtained by a travelling solvent floating-zone (TSFZ) technique using $LiBO_2$ as a solvent, as described in detail in Ref. [22]. We used one of the grown single crystals of high quality with approximate dimensions of 2×2×2 mm. Magnetization data for $H \perp c$ were collected at 0.08 and 1.5 K in magnetic fields up to 57 T, and those for $H \parallel c$ were collected at 1.4 and 4.2 K up to 53 T. To investigate the impurity effect on the plateaux, we performed the magnetization measurements at 1.3 K on 1% zinc doped crystals $Sr(Cu_{0.99}Zn_{0.01})_2(BO_3)_2$ grown by the TSFZ method as well. The analysis of inductively coupled plasma–atomic emission (ICP–AE) spectroscopy and scanning electron microscope (SEM) for the obtained doped single crystal ensured the successful Zn-substitution as well as homogeneity of the crystal. Single crystals growth with a zinc ratio more than 1% has not been succeeded yet.

3. Results and discussion

Fig. 3a shows the obtained magnetization curves of $SrCu_2(BO_3)_2$ for $H \parallel c$ and for $H \perp c$, where within the experimental accuracy, no hysteresis was observed upon increasing or decreasing H. We also show the differential magnetization curves $\Delta M/\Delta H$ in Fig. 3b. It appears that the difference between the two curves arises only from the g-factor. As demonstrated in Fig. 4, the parallel and perpendicular magnetizations can be normalized using $g_{\parallel}=2.28$ and $g_{\perp}=2.05$ determined by electron spin resonance (ESR) [13]. Strictly speaking, there is a slight difference around 30 T, which will be discussed later. Note that this is the first measurement of parallel magnetization using the single crystal. The obtained magnetization curve for $H \parallel c$ has more distinct 1/4 and 1/8 plateaux compared with that obtained using the field-oriented polycrystal [14] with poor orientation, as evaluated by nuclear magnetic resonance. On the other hand, the result for $H \perp c$ below 42 T is almost identical to that previously reported using the single crystal [15]. As shown in Fig. 3a, the critical fields are determined to be $H_1=29.6$ T, $H_2=31.2$ T, $H_3=36.7$ T and $H_4=43.6$ T for $H \perp c$, and $H_1=26.9$ T, $H_2=28.2$ T, $H_3=34.1$ T and $H_4=39.1$ T for $H \parallel c$, which is almost consistent with the previous results [14,15].

A glance at Fig. 3a reveals a wide plateau at 1/3 of the full magnetization. As mentioned earlier, the 1/3 plateau cannot accommodate any magnetic superstructure with a square unit cell. Therefore, this observation confirms for the first time the existence of the novel stripe order, where the magnetic unit cell is composed of four singlets and two triplets. The onset field H_5 of the 1/3 plateau is estimated to be 43.6 T for $H \perp c$ and 40.2 T for $H \parallel c$. As evident in Fig. 3a and b, the 1/3-plateau phase is stable over a much wider field range than the 1/8 and 1/4 plateaux.

The common feature of the observed three plateau phases is the gradual increase of the magnetization with H, indicating nonstoichiometry of the ordered triplets. It is noted that this effect does not originate from thermal fluctuation because, as will discussed later, the contribution

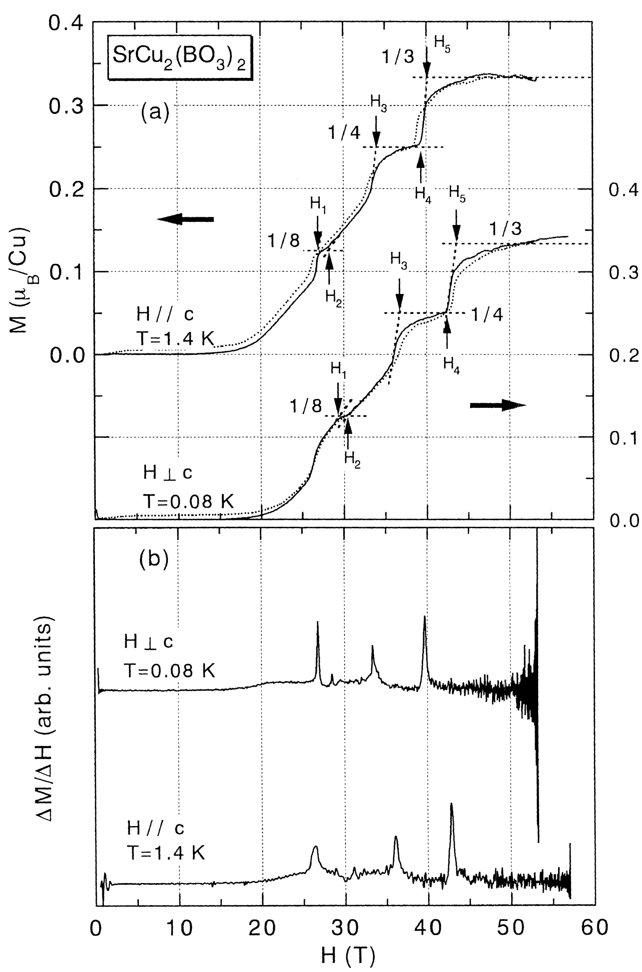

Fig. 3. (a) Magnetization curves for $SrCu_2(BO_3)_2$ measured at 0.08 K for $H \perp c$ and at 1.4 K for $H \parallel c$ (solid), and for 1% Zn doped single crystal measured at 1.3 K (dotted). The broken lines correspond to 1/3, 1/4 and 1/8 of the total magnetization. (b) Differential magnetization curves $\Delta M/\Delta H$ for $SrCu_2(BO_3)_2$.

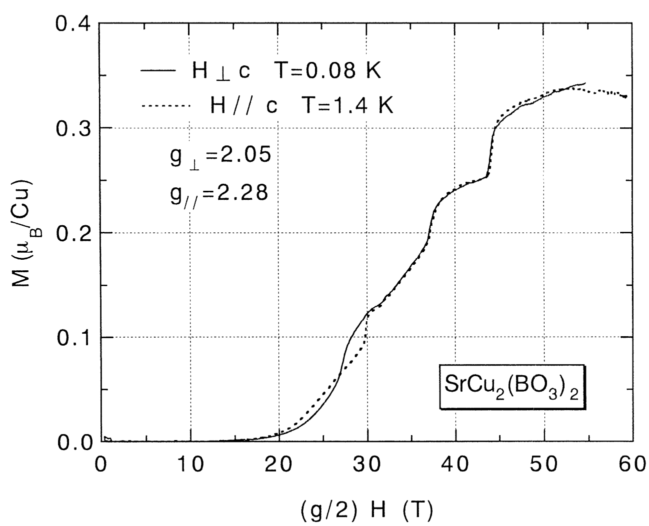

Fig. 4. Normalized parallel and perpendicular magnetizations for $H \perp c$ (solid) and for $H \parallel c$ (broken), where $g_{\parallel}=2.28$ and $g_{\perp}=2.05$ are used.

of thermal fluctuation to the magnetizations can be neglected at least below 1.5 K. This nonstoichiometric nature in $SrCu_2(BO_3)_2$ is strikingly in contrast to the cases of $[Ni_2(Medpt)_2(\mu\text{-ox})(\mu\text{-}N_3)Cl_4$ $0.5H_2O$, [4] and NH_4CuCl_3 [5], where the nearly flat plateaux were observed.

It is interesting to note the nature of the transitions between the plateaux. A sudden jump was observed between the 1/4 and 1/3 plateaux. This may indicate a first-order phase transition between the two states, although there is no hysteresis between the field increase and decrease processes. The first-order phase transition between the plateaux would be a consequence of the extremely localized triplet excitations, as discussed theoretically [12,16]. On the contrary, a complex behavior is seen between the 1/8 and 1/4 plateaux. The magnetization grows gradually above H_2 until H approaches to H_3 when the magnetization suddenly rises to the 1/4 plateau. A possible explanation is that the system is in a liquid (disordered) state for $H_2<H<H_3$ and its transition to the 1/8-plateau phase at H_2 is of a second order, while that to the 1/4-plateau phase at H_3 is of a first order.

In Ref. [15], we pointed out the existence of the 1/10 plateau, judging from the perpendicular magnetization that displays a bump at about 1/10 of the total magnetization, as observed in this experiment as well. The behavior of the parallel magnetization, however, is not indicative of the 1/10 plateau, as seen in Fig. 4. It is possible that the appearance of the 1/10 plateau depends on the field direction, i.e. the orientation of the excited triplets. Alternatively, this phenomenon could be a quantum effect of some kind.

Let us focus our attention on the temperature dependence of the magnetization curves. Shown in Fig. 5 are the normalized magnetizations at 4.2, 1.5 and 0.08 K. Compared with the 1.5 K curve, the 4.2 K curve is considerably obscured due to the effect of thermal fluctuation. However, the 0.08 K curve is very similar to the 1.5 K curve (apart from the anisotropy around 30 T as mentioned earlier), indicating that thermal fluctuation is negligible at least below 1.5 K and thus these two curves are almost equivalent to those for zero-temperature limit. Nevertheless, the magnetizations for both 1.5 and 0.08 K begin to have a finite value at about 16 T. This value is considerably lower than the expected critical field of $H_c=24.5$ T determined from $k_B\Delta=g_\perp \mu_B H_c$. Here, k_B and μ_B denote the Boltzmann constant and the Bohr magneton, respectively, and $\Delta=34$ K and $g_\perp=2.05$ are used. The ESR measurement [13] has also revealed anomalous behaviors in this field region, which include multiple magnetic excitations and the deviation of field-dependent spin gap Δ_H from the relation $\Delta_H=g\mu_B H/k_B$. We infer from these facts that the mixing occurs between the initial spin-singlet ground state and the excited triplet states mediated by, e.g. the Dzyaloshinsly–Moriya interaction and as a result the ground state becomes partially magnetic below H_c.

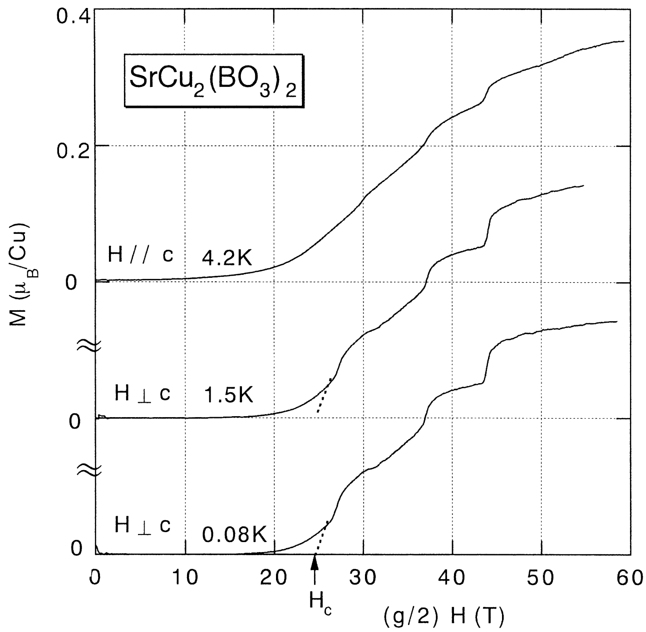

Fig. 5. Temperature dependence of magnetization curves. H_c denotes the critical field expected from the relation described in the text. Dotted lines are the guides to the eye.

There are several theoretical calculations of the magnetizations on the Shastry–Sutherland model with varying J'/J ([16,17,23,24] and G. Misguich, private communication). In Fig. 6a and b, we compare the experimental data with the calculations in terms of a hard-core boson model by Momoi and Totsuka [16] (theory I) and Miyahara and Ueda [17] (theory II), where $J=100$ K and $J'=68$ K are used. Shown in Fig. 6c is the result of Fukumoto and Oguchi [23] based on the perturbation expansion method up to the third order, where $J=85$ K and $J'=55$ K are assumed. It is noteworthy that these three models quantitatively reproduce the experimental data particularly around the 1/3 plateau. The main difference between theories I and II, in short, is that the former considers correlated hopping terms and neglects long-range interactions, whereas the case is reversed in the latter. In connection with this difference, the 1/3 plateau ends at 80 T according to theory I, while theory II predicts that it ends at 110 T. Moreover, theory II (and theory III) concluded that a 1/2 plateau exists, but theory I did not. Thus, the future direction of this area of study will be one that requires even higher magnetic fields.

Finally, we shortly discuss the impurity effect on the magnetizations. It is naively expected that the substitution of a Zn ion for the Cu site should break a spin-singlet pair creating a localized $S=1/2$. Thus created localized moment might affect the already observed plateaux and/or induce new plateaux. Unlike such an expectation, no appreciable change was observed in the magnetizations

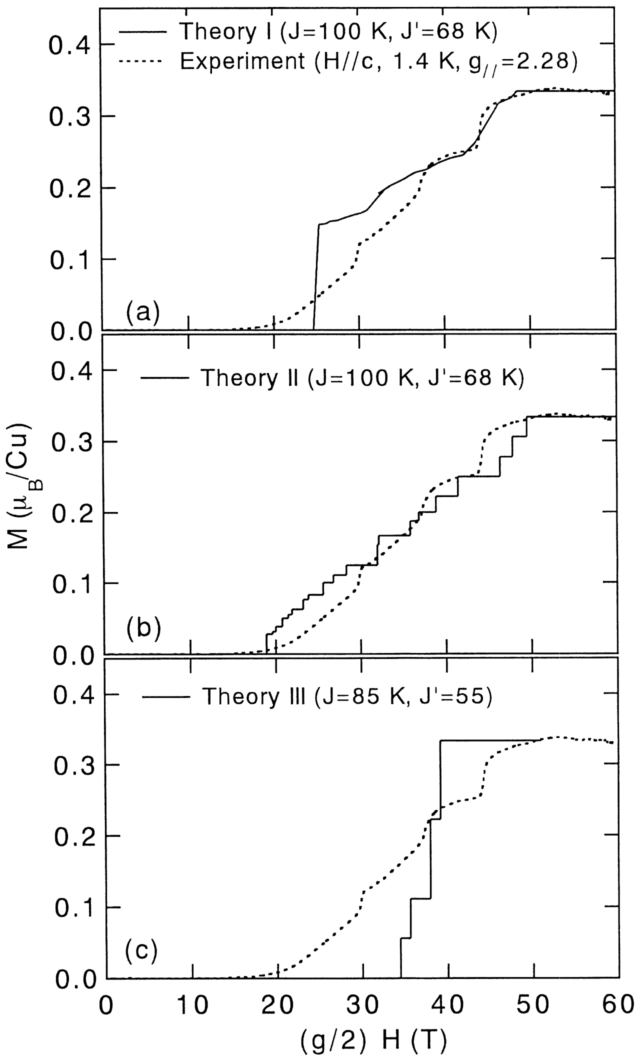

Fig. 6. Theoretical magnetizations (solid curves) calculated by (a) Momoi and Totsuka [16], (b) Miyahara and Ueda [17], and (c) Fukumoto and Oguchi [23]. The dotted curve is the experimental result for $H \parallel c$ normalized by $g_{\parallel}$=2.28.

between 1% zinc-doped and the pure samples as seen in Fig. 3.

4. Conclusions

In conclusion, our high-field magnetization measurement for $SrCu_2(BO_3)_2$ allowed the first experimental verification of the stripe order in the orthogonal dimer lattice through the observation of the 1/3 plateau that appears around 50 T. The transition between the 1/3 and 1/4 plateaux seems to be of the first order. The calculated magnetizations satisfactorily reproduce the experimental magnetization result around the 1/3 plateau region. The gradual increases in the magnetization from 16 T far below the expected critical field may indicate that the ground state is no longer the perfect dimer singlet state. The 1% zinc substitution for the Cu site does not affect the observed plateaux nor spin-singlet ground state. We consider the number of spin vacancies created by the Zn substitution may be too small to induce some dramatic changes. To further understand the role of spin vacancies on the Shastry–Sutherland system, preparation as well as magnetization measurements of samples with higher Zn concentration is desirable and is in progress.

Acknowledgements

It is our great pleasure to thank S. Miyahara, K. Ueda, T. Momoi, K. Totsuka, Y. Fukumoto, A. Oguchi for kindly providing us with their theoretical results and also for motivating us to carry out this experiment. H.K. wishes to thank Ritsuko Ezumi for her continuous encouragement. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References

[1] W. Chen, K. Hida, H. Nakano, J. Phys. Soc. Jpn. 68 (1999) 625.
[2] H. Kobayashi, T. Haseda, J. Phys. Soc. Jpn. 19 (1964) 765.
[3] H. Kageyama, K. Yoshimura, K. Kosuge, M. Azuma, M. Takano, H. Mitamura, T. Goto, J. Phys. Soc. Jpn. 66 (1997) 3996.
[4] Y. Narumi, M. Hagiwara, R. Sato, K. Kindo, H. Nakano, M. Takahashi, Physica B 246 (1998) 509.
[5] W. Shiramura, K. Takatsu, B. Kurniawan, H. Tanaka, H. Uekusa, Y. Ohashi, K. Takizawa, H. Mitamura, T. Goto, J. Phys. Soc. Jpn. 67 (1998) 1548.
[6] K. Totsuka, Phys. Lett. A 228 (1997) 103.
[7] A.K. Kolezhuk, Phys. Rev. B 59 (1999) 4181.
[8] M. Oshikawa, M. Yamanaka, I. Affleck, Phys. Rev. Lett. 78 (1997) 1984.
[9] M. Oshikawa, Phys. Rev. Lett. 84 (2000) 1535.
[10] H. Kageyama, K. Yoshimura, R. Stern, N.V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C.P. Slichter, T. Goto, Y. Ueda, Phys. Rev. Lett. 82 (1999) 3168.
[11] B.S. Shastry, B. Sutherland, Physica 108B (1981) 1308.
[12] S. Miyahara, K. Ueda, Phys. Rev. Lett. 82 (1999) 3701.
[13] H. Nojiri, H. Kageyama, K. Onizuka, Y. Ueda, M. Motokawa, J. Phys. Soc. Jpn. 68 (1999) 2906.
[14] H. Kageyama, K. Onizuka, Y. Ueda, N.V. Mushnikov, T. Goto, K. Yoshimura, K. Kosuge, J. Phys. Soc. Jpn. 67 (1998) 4304.
[15] H. Kageyama, K. Onizuka, T. Yamauchi, Y. Ueda, S. Hane, H. Mitamura, T. Goto, K. Yoshimura, K. Kosuge, J. Phys. Soc. Jpn. 68 (1999) 1821.
[16] T. Momoi, K. Totsuka, Phys. Rev. B 61 (2000) 3231.
[17] S. Miyahara, K. Ueda, Phys. Rev. B 61 (2000) 3417.
[18] P. Lemmens, M. Grove, M. Fisher, G. Güntherodt, V.N. Kotov, H. Kageyama, K. Onizuka, Y. Ueda, Phys. Rev. Lett. 85 (2000) 2605.
[19] H. Kageyama, K. Onizuka, Y. Ueda, M. Nohara, H. Suzuki, H. Takagi, J. Exp. Theor. Phys. 90 (2000) 129.

[20] T. Rõõm, U. Nagel, E. Lippmaa, H. Kageyama, K. Onizuka, Y. Ueda, Phys. Rev. B 61 (2000) 14342.
[21] H. Kageyama, M. Nishi, N. Aso, K. Onizuka, T. Yosihama, K. Nukui, K. Kodama, K. Kakurai, Y. Ueda, Phys. Rev. Lett. 84 (2000) 5876.
[22] H. Kageyama, K. Onizuka, T. Yamauchi, Y. Ueda, J. Crystal Growth 206 (1999) 65.
[23] Y. Fukumoto, A. Oguchi, J. Phys. Soc. Jpn. 69 (2000) 1286.
[24] E. Müller-Hartmann, R.R.P. Singh, C. Knetter, G.S. Uhrig, Phys. Rev. Lett. 84 (2000) 1808.