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SOLIDS

Low-Temperature Specific Heat Study of $SrCu_2(BO_3)_2$ with an Exactly Solvable Ground State¶

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Abstract—The specific heat of a two-dimensional spin gap system $SrCu_2(BO_3)_2$ realizing the Shastry–Sutherland model was measured between 1.3 and 25 K under various magnetic fields up to 12 T. The analysis based on an isolated dimer model in a low temperature region revealed that the value of the spin gap at zero field is $\Delta = 34.4$ K. It turned out that Δ decreases in proportion to H due to the Zeeman splitting of the excited triplet levels. This simplest model, however, fails to reproduce the result in a high-temperature region, suggesting rather strong spin–spin correlation of the system. © *2000 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Exactly solvable models have been extensively studied in the area of strongly correlated electron systems for the purpose of elucidating various exotic physical phenomena because some rigorous results can be derived from them, sometimes providing us a crucial key to solve underlying problems of the phenomena. Such models, even if being far from realistic, can remain tantalizing theoretical subjects owing to the beauty of the solutions. For example, Majumdar and Ghosh first proved that an exact dimer ground state for *z* one-dimensional spin chain imposed a stringent condition on the first and second nearest neighbor interactions [1]. Stimulated by this discovery, a number of systems with the identical exact wave function have been explored from the theoretical point of view for one-, two,- and three-dimensions (see, for example [2] and references therein). However, in spite of extensive efforts by chemists to tailor experimental examples, no material had been discovered for a long time.

Recently, we reported the magnetic properties of an inorganic compound $SrCu_2(BO_3)_2$, which consists of a two-dimensional orthogonal dimer lattice, concluding that this material verifies the Shastry–Sutherland model, which has the exact dimer ground state [3–5]. Although an imaginary lattice Shastry and Sutherland considered—i.e., a two-dimensional square lattice with some additional diagonal bonds—differs from the real one of $SrCu_2(BO_3)_2$, these two are equivalent from a topological point view. The value of the spin gap was estimated from various measurements like measurements of the temperature variation of the magnetic susceptibility (34 K) [6] and electron spin resonance (ESR; 34.7 K) [7]. It was also found that the spin system for $SrCu_2(BO_3)_2$ is fairly frustrated, located very close to the critical point $(J'/J)_c = 0.70$ between the exact dimer state and the Néel-ordered state [3, 5]: the ratio of intradimer and interdimer interactions, respectively, $J = 100$ K and $J' = 68$ K, is 0.68. Furthermore, several quantized plateaux were observed in the magnetization [3, 6, 8], which originates from the extremely localized triplet excitations [5].

In the present paper, we performed the specific heat measurement of $SrCu_2(BO_3)_2$ under magnetic fields H in order to obtain more information on the exchange interactions as well as the effect of the spin-gapped behavior upon H. The data were analyzed in terms of an isolated dimer model, and the spin gap in the absence of the field was evaluated to be 34.4 K. Furthermore, it was found that application of magnetic fields causes the Zeeman splitting of the excited triplet states, leading to a H-linear decrease in the value of the spin gap.

2. EXPERIMENT

The specific heat measurement was performed by a heat-relaxation method [9] in a temperature range between 1.3 and 25 K under magnetic fields between 0 and 12 T. A bulk single crystal of $SrCu_2(BO_3)_2$ was used, which was grown by the traveling solvent floating zone (TSFZ) method with an image furnace using a solvent, $LiBO_2$ under flowing O_2 gas ($P_{O_2} = 1$ atm, 99.99%). For a detailed procedure of the crystal growth, see [10]. A piece of the crystal with the dimensions of $2 \times 2 \times 1$ mm was attached to a sapphire

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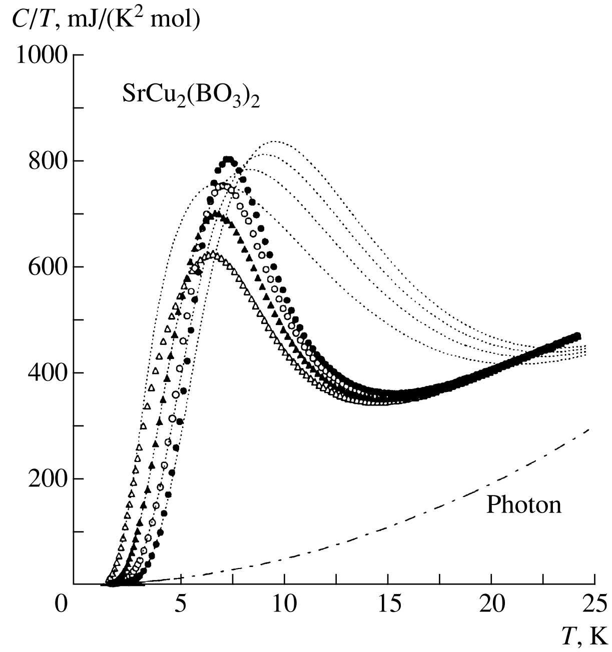

Fig. 1. C/T versus T measured at $H = 0$ (●), 6 (○), 9 (▲), and 12 T (△). Dotted curves are the calculations based on the isolated dimer model for $\Delta(0) = 34.4$ K. Dot-dashed curve represents the phonon term, βT^3 ($\beta = 0.460$ mJ/K^4 mol).

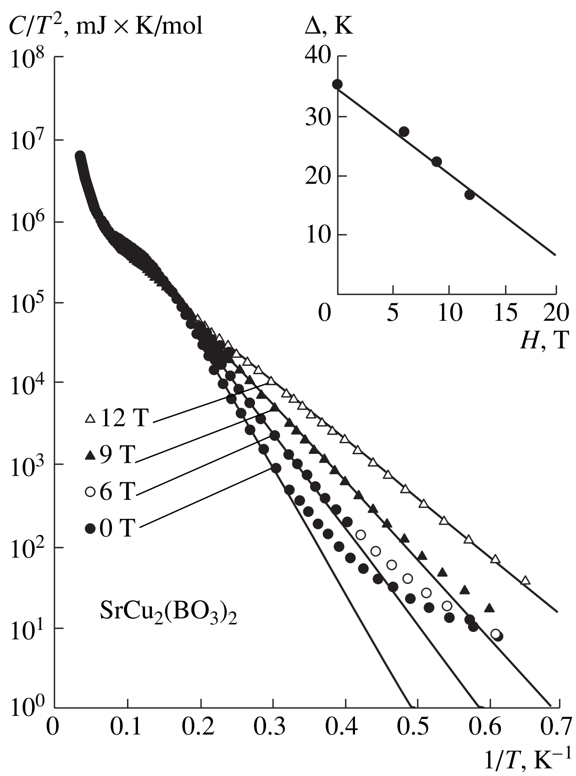

Fig. 2. Logarithmic plot of CT^2 as a function of $1/T$. Solid lines denote the fit to equation (2). Inset shows the magnetic field variation of $\Delta(H)$.

substrate by a small amount of Apiezon N grease. The magnetic fields were applied perpendicular to the ab plane, i.e., the Shastry–Sutherland lattice. The substrate was weakly coupled by tungsten wires to a copper heat sink. A bare chip of Cernox resistance sensor (Lake Shore) was used as a thermometer to minimize the addenda heat capacity. The magnetic field dependence of the thermometer was calibrated using a capacitance thermometer. The heat capacity of the sample was obtained by subtracting the addenda heat capacity, which was determined in a separate run without the sample. No appreciable magnetic field dependence was observed for the addenda heat capacity. The resolution of the measurement was about 0.5%, and the absolute accuracy determined from the measurement of a Cu standard was better than 5%. The measurements were performed with increasing temperature.

3. RESULTS AND DISCUSSION

A total specific heat divided by T, C/T, measured in the absence of a magnetic field is plotted as a function of T by closed circles in Fig. 1. With decreasing T from 15 K, C/T rises, reaches a round maximum at 7.5 K, and then falls rapidly, approaching naught. These behaviors, that is to say, the so-called Schottky anomalies are typical of spin–singlet system with a finite spin gap to a lowest exited state. A gradual increase in C/T with T above 15 K comes from the phonon term, with is in general known to vary as $C \propto \beta T^3$. As also shown in Fig. 1, qualitatively similar features described above appear even when magnetic fields are applied, indicating that the system still has a spin–gapped ground state at least for $H < 12$ T. A prominent difference is that a peak of C/T shifts to lower temperature with rising H: the temperature at which C/T–T curve reaches a maximum ($=T_{max}$) for $H = 6.9$ and 12 T is, respectively, 7.3, 6.9 and 6.8 K, implying a reduction in the actual size of the spin gap $\Delta(H)$ with H. This is quantitatively discussed below.

Because of a lack of an appropriate theory for the specific heat from the standpoint of the Shastry–Sutherland model, we will analyze the experimental data utilizing the isolated dimer model, where J' is neglected and only J is taken into consideration. Let us define the magnetic specific heat under a certain magnetic field H as $C(H)$. Take the example of $H = 0$, $C(0)$ is given by the following formula,

$$C(0) = \frac{3R(\Delta(0)/T)^2\exp(\Delta(0)/T)}{[1+3\exp(\Delta(0)/T)]^2}, \qquad (1)$$

where R is 8.30 J/(K mol) (see, for example, [11]). Likewise, $C(H)$ for a finite magnetic fields is easily calculated. In the low temperature limit, the magnetic specific heat the isolated dimer model can be reduced to the following expression as long as the system is in a gapful state:

$$C(H) \propto T^{-2}\exp(-\Delta(H)/T). \quad (2)$$

Thus CT^2 is plotted against $1/T$ in a logarithmic scale as shown in Fig. 2. One can see all data roughly follows a linear reversal-temperature dependency. Using the reduced expression of equation (2), we obtained $\Delta(0)$ = 35.9 K, $\Delta(6\text{ T})$ = 27.5 K, $\Delta(9\text{ T})$ = 22.5 K, and $\Delta(12\text{ T})$ = 16.8 K. The deviation from the calculations (the solid lines in Fig. 2) in lower temperature region, more prominent in case of lower field, is for a most part due to the phonon contribution which is neglected here and will be included later. The obtained values of $\Delta(H)$ are plotted in the inset of Fig. 2 as a function of H. It is clear that $\Delta(H)$ decreases nearly in proportion to H. The origin of the decrease should be the Zeeman splitting of the excited states. Namely, a three-fold degeneracy of the lowest excited triplet states (S = 1) in the absence of the magnetic field is lifted up by applied magnetic field. $\Delta(0)$ was estimated to be 35.0 K using the following relation: $\Delta(H) = \Delta(0) - g\mu_B H$, where g is the g-factor of the Cu^{2+} electron spin and μ_B is the Bohr magneton. An isotropic g-value, i.e., g = 2.0 was assumed. The obtained value of $\Delta(0)$ is consistent with that obtained in other measurements using a single crystalline $SrCu_2(BO_3)_2$ such as the magnetic susceptibility (34 K) [6], ESR (34.7 K) [7] and Boron nuclear magnetic resonance (B-NMR; 36 K) [12], Cu-NMR (35 K) [12], and neutron scattering (34 K) [13].

Next, let us take a phonon term into consideration. Then, the total specific heat is given by the sum of the magnetic and phonon terms, $C = C(H) + \beta T^3$. Dotted curves in Fig. 1 denote the results of the global least-square fit in the T range well below the spin-gap size, namely, 2.6 K < T < 4.8 K for 0 T, 2.4 K < T < 4.1 K for 6 T, 2.1 K < T < 3.5 K for 9 T, and 1.5 K < T < 2.8 K for 12 T, from which we obtained once again a reasonable value of $\Delta(0)$ = 34.4 K together with β = 0.460 mJ/(K^4 mol) and g =2.03. The phonon contribution is independently shown by the dot-dashed curve in Fig. 1, which also seems to reproduce the temperature dependence of the experiment above 15 K.

As demonstrated above, it seems that the isolated dimer model nicely reproduces the experimental data, providing a consistent value of $\Delta(0)$. In a higher temperature region, however, the deviation between the experiment and the theory is appreciable. One can notice from Fig. 1 that experimental T_{max} is lower as compared with the theoretical one in any magnetic field, and above T_{max} the value of experimental C/T is much suppressed. In Fig. 3, we show the T variation of the magnetic entrope of the system for H = 0, which should reach $2R\ln 2$ ideally in the high-T limit. For comparison, a theoretical curve for the isolated dimer model for $\Delta(0)$ = 34.4 K is shown by the solid line. The experimental entropy starts to deviate largely from the theoretical one at around 10 K. For example, the magnetic entrope at 25 K is still about and 74% of that for the isolated dimer model and 62% of the full entropy. This indicated that the spin system of $SrCu_2(BO_3)_2$ is effectively correlated over much higher temperatures, and thus consistent with the estimation of exchange constants by Miyahara and Ueda; J = 100 K and J' = 68 K [5]. It is noteworthy that the value of J is identical with that of $\Delta(0)$ for the isolated dimer model, and J = 35 K (=$\Delta(0)$) derived from the isolated dimer model is too much smaller.

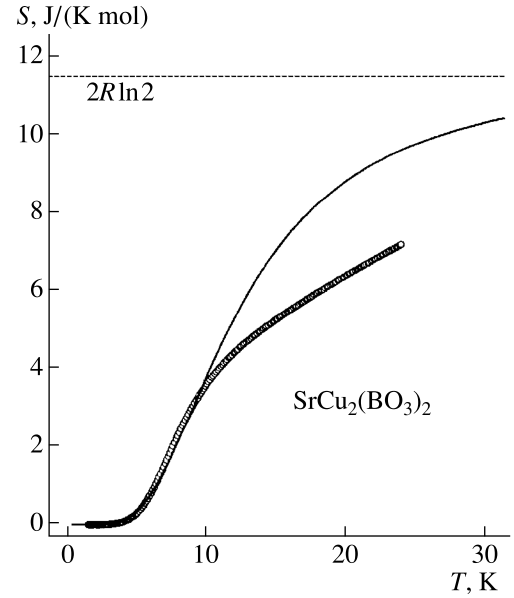

Fig. 3. Magnetic entropy of $SrCu_2(BO_3)_2$ at H = 0 (circles). Solid curve represents the magnetic entrope for the isolated dimer model for $\Delta(0)$ = 34.4 K.

To summarize, we have measured the specific heat of $SrCu_2(BO_3)_2$ under various magnetic fields. From the fitting based on the isolated dimer model, the gap was estimated to be 34.4 K, which is in good agreement with the values determined from other physical measurements. With increasing H, the gap decreases in proportion with H. The simple dimer model, however, can not explain the data at all in higher-temperature, region, suggesting rather stronger correlation of the spin system. We are looking forward to a theory based on the Shastry–Sutherland model with J and J' to reproduce our specific heat data over the whole T range.

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