

Ba- and Ca-Substitution Effect on the Spin Gap in $\text{SrCu}_2(\text{BO}_3)_2$ with the Exact Dimer Ground State

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We prepared Ba- and Ca-substituted samples, $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$ (A=Ba, Ca; $0 < x \leq 0.3$), aiming to change systematically a spin gap as well as magnetization plateaux. It was found, however, that the magnitude of the spin gap is almost independent of the composition, suggesting that the chemical pressure hardly changes the intralayer exchange couplings. Moreover, the substitution may be the cause of a lattice distortion, only making the plateaux fade out.

Key words: $\text{SrCu}_2(\text{BO}_3)_2$, Quantized plateaux, Exact dimer state, Chemical pressure

Introduction

Investigations of solvable models may be an essential theoretical approach to the comprehension of novel and unique physical phenomena in strongly-correlated electron systems, such as high- T_c superconductivity, Mott-transitions, and non-Fermi-liquid behaviors [1]. This is because such models are able to offer some rigorous results, describing the true nature of the phenomena, although some of them are too idealized in some aspects and consequently far from realistic. For example, the exact dimer (ED) models, in which an eigenstate is expressed exactly by the direct product of the singlet pairs, have been extensively studied [2]. Among them, the Majumdar-Ghosh model [3] made up of a zigzag chain with the nearest neighbor (NN) and the next-nearest-neighbor (NNN) interactions, J and J' , respectively, is most famous, but may be improbable in reality in the sense that the strict condition of $J'/J=0.5$ is required to satisfy the exactness.

Recently, we have found that an $S=1/2$ magnet $\text{SrCu}_2(\text{BO}_3)_2$ with a peculiar layer of orthogonally connected copper dimers as shown in Fig. 1 is a new two-dimensional (2D) spin-gap system with a gap (Δ) of 30 K and is, surprisingly enough, a beautiful realization of ED ground state [4, 5]. The lattice is topologically equivalent to the Shastry-Sutherland lattice, in which ED ground state was proven in 1981 [6]. A schematic phase diagram as a function of J'/J is presented in Fig. 2 according to Miyahara and Ueda [7]. The exchange

constants were determined to be $J=100$ K and $J'=68$ K and the ratio $J'/J=0.68$ is very close to the critical point $(J'/J)_c=0.70$ between ED state and an antiferromagnetic (AF) state. Of equal importance are the quantized plateaux at 1/4 and 1/8 of the full Cu moment in the magnetization, which was first observed for 2D spin-gap systems [4]. As discussed by Miyahara and Ueda [7], the extremely localized character of the excited triplets is responsible for the plateaux.

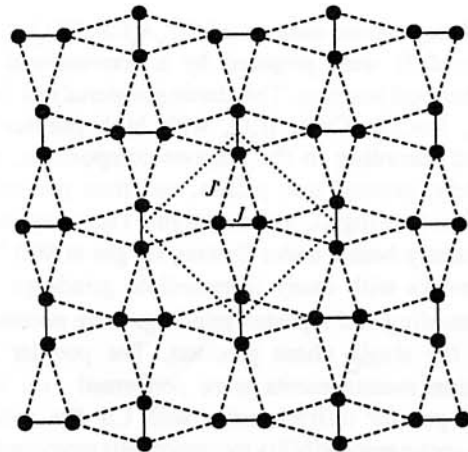


Fig. 1 The 2D orthogonal dimer lattice in $\text{SrCu}_2(\text{BO}_3)_2$. Circles denote the Cu^{2+} ions.

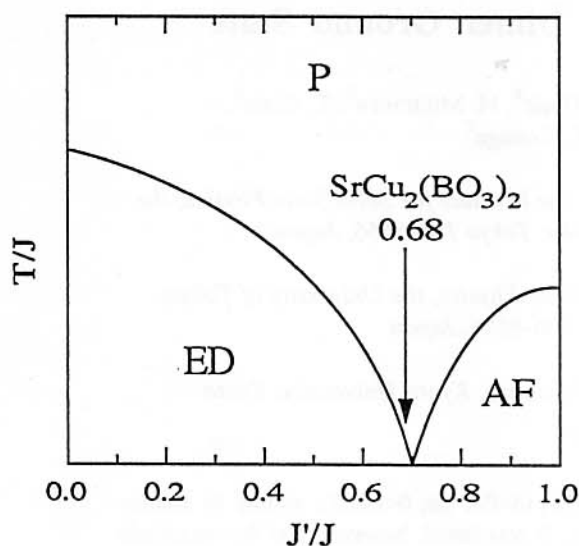


Fig. 2 Schematic phase diagram of the present spin system as a function of J'/J .

Figure 2 demonstrates that, in ED region, the value of Δ can be controlled by varying J'/J . It would be even more interesting if J'/J exceeds the critical boundary $(J'/J)_c$, above which the system should exhibit AF order. In this study, we prepared Ba- and Ca-substituted samples for Sr, aiming to vary J'/J systematically in terms of a chemical pressure effect, and measured magnetic susceptibilities and magnetization curves, investigating how the substitution affects Δ as well as the quantized plateaux.

Experimental

Polycrystalline samples of $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$ ($\text{A}=\text{Ba}$, Ca ; $0 < x < 0.3$) were prepared by a conventional solid state chemical reaction. The starting materials of SrCO_3 , CaCO_3 , BaCO_3 , CuO , B_2O_3 with high purities were weighed according to the purpose composition, mixed intimately, pressed into pellets, and then preheated at 850°C in flowing O_2 gas overnight. The samples were subsequently heated under flowing O_2 gas at 900°C for 2~4 weeks with many intermediate grindings. Long time annealing and repeated grindings were necessary to ensure the single phase products. The powder X-ray diffraction measurements were performed on a Mac Science powder diffractometer with $\text{Cu K}\alpha$ radiation. The magnetic susceptibility measurements were conducted in a temperature range between 1.7 and 400 K in an applied magnetic field of 1.0 T using a Quantum Design MPMS SQUID magnetometer. The high-field magnetization measurements were performed at 0.5 K using a pulsed field magnet with an approximate duration time of 20 ms. The field was swept up to 42 T.

Results and Discussion

The powder X-ray diffraction studies revealed the successful preparation of the single phase products of the solid solution $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$ at least up to $x=0.3$. The lattice parameters determined by fitting the positions of six high-angle lines in the X-ray diffraction patterns are presented in Fig. 3. For $\text{A}=\text{Ba}$, both the a and c axes expand with increasing x , while in the case of $\text{A}=\text{Ca}$ the unit cell parameters shrink. This inclination can be explained reasonably in terms of the difference in the ionic radii ($\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$). Our data are roughly consistent with those for the single crystals of $\text{Sr}_{0.735}\text{Ba}_{0.265}\text{Cu}_2(\text{BO}_3)_2$ and $\text{Sr}_{0.661}\text{Ca}_{0.339}\text{Cu}_2(\text{BO}_3)_2$ given by the closed symbols in Fig. 3 [8]. It is noted that the change in the c axis by the substitution is more prominent than the case of the a axis, which clearly reflects the characteristic of the layered structure.

Figure 4 shows the temperature variation of the magnetic susceptibilities χ for $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$. In general, all the susceptibility data show nearly the same behavior as follows: χ obeys the Curie-Weiss law at high-temperature region above 150 K with a Weiss constant of 90~130 K. When the temperature is lowered, χ starts to deviate from the Curie-Weiss law, takes a maximum at around 18~20 K ($=T_{\text{Max}}$), then decreases abruptly reaching zero at 0 K. A Curie-like upturn is seen at low temperatures below 4 K, which would be due to the extrinsic effect coming from a small amount of impurities or defect of the crystal. Judging from the precipitous drop of χ below T_{Max} , all substituted samples should have the spin-singlet ground state as the end material $\text{SrCu}_2(\text{BO}_3)_2$ has, which will be confirmed in the next paragraph (by the magnetization measurements). The similar behavior of χ naively implies that J'/J is independent of the composition. As mentioned earlier,

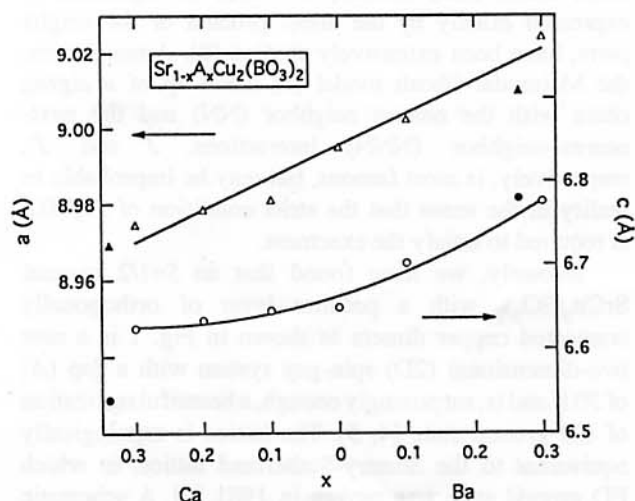


Fig. 3 Variation of the crystallographic unit-cell parameters as a function of composition in $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$. Solid symbols represent the results of Norrestam *et al.* Solid curves are guided to the eyes.

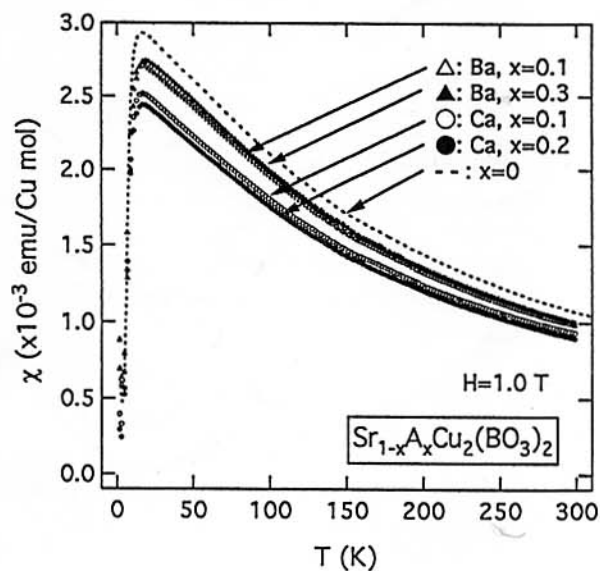


Fig. 4 Temperature-dependent magnetic susceptibilities for $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$ system.

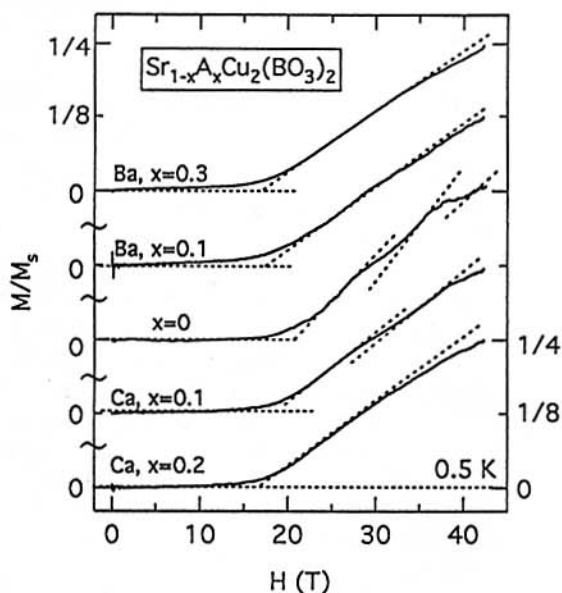


Fig. 5 Magnetization curves of $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$ system.

the chemical pressure effect by Ba- and Ca-substitution is more dominant for the interlayer direction [001] than for the intralayer direction, and therefore the slight change of the NN and the NNN distances would not be enough to vary the intralayer coupling constants.

Magnetization curves up to 42 T measured at 0.5 K are shown in Fig. 5, where the saturation magnetization M_s is calculated by assuming that a g factor of 2.14 obtained for $\text{SrCu}_2(\text{BO}_3)_2$ is available for the substituted compounds. It is obvious that all the substituted samples have a finite energy gap between the gapful ground state and the gapless excited state. By extrapolating the magnetization curves in the slope region to the abscissa, the critical fields were roughly evaluated to be 19.0 T for the sample of $A=\text{Ca}$, $x=0.1$ ([Ca, 0.1]), 17.5 T for

[Ba, 0.1], 17.0 T for [Ba, 0.3] and [Ca, 0.2]. Roughly speaking, these values are nearly the same as 20.9 T for the end material $\text{SrCu}_2(\text{BO}_3)_2$. This fact again suggests that the chemical pressure hardly changes J and J' and thus Δ . Furthermore, the 1/4 and 1/8 plateaux tend to fade off (or disappear) with x . The plateaux were observed only for [Ca, 0.1]. For the other substituted samples, any plateaux were not observed though the change of slope is seen in the M vs. H curves at 30~35 T. Presumably, the lattice distortion caused by the substitution may easily disturb the plateau formation. The unit cells corresponding to 1/4- and 1/8-plateau structures contain, respectively, eight and sixteen Sr/A atoms, which means that $\text{Sr}_{0.9}\text{A}_{0.1}\text{Cu}_2(\text{BO}_3)_2$, for example, has about one A atom in the former magnetic unit cell. Compared with $\text{SrCu}_2(\text{BO}_3)_2$, the observed plateaux for [Ca, 0.1] are considerably obscured. The positions of the plateaux for [Ca, 0.1] and $\text{SrCu}_2(\text{BO}_3)_2$ are nearly the same, which once again suggests the almost invariable J and J' .

To conclude, we prepared Ba- and Ca-substituted samples, $\text{Sr}_{1-x}\text{A}_x\text{Cu}_2(\text{BO}_3)_2$ ($A=\text{Ba}, \text{Ca}$; $0 < x \leq 0.3$), and investigated the magnetic properties. Unfortunately, the magnitude of the spin-gap is nearly independent of the composition, suggesting that the substitution for Sr shows little influence upon the intralayer exchange couplings, J and J' . Moreover, the substitution seems to cause a lattice distortion, only making the plateaux fade out.

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