Doping Effects on the two-dimensional Spin Dimer Compound SrCu$_2$(BO$_3$)$_2$

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(Dated: March 22, 2022)

A series of compounds M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ with Sr substituted by M=Al, La, Na and Y were prepared by solid state reaction. XRD analysis showed that these doping compounds are isostructural to SrCu$_2$(BO$_3$)$_2$. The magnetic susceptibility from 1.9K to 300K in an applied magnetic field of 1.0T and the specific heat from 1.9K to 25K in applied fields up to 14T were measured. The spin gap is deduced from the low temperature susceptibility as well as the specific heat. It is found that the spin gap is strongly suppressed by magnetic fields. No superconductivity is observed in all four samples.

PACS numbers: Valid PACS appear here

I. INTRODUCTION

During the past few years, a number of novel quantum spin systems have been discovered experimentally. Among them, the spin ladder compounds, such as SrCuO$_3$ and CuV$_2$O$_5$, and the dimerised spin gap compound SrCu$_2$(BO$_3$)$_2$ found by Kageyama et al. in two dimensions have attracted great attention recently. SrCu$_2$(BO$_3$)$_2$ was first synthesized by Smith et al. It has a tetragonal unit cell with lattice parameters $a = b = 8.995\,\text{Å}$ and $c = 6.649\,\text{Å}$ at room temperature. In this compound, Sr and CuBO$_3$ planes are stacked along the c axis alternatively. In the CuBO$_3$ plane, a neighboring pair of rectangular planar CuO$_4$ forms a spin dimer and the dimers are interconnected by triangular planar BO$_3$. The two-dimensional coordinates of the Cu$^{2+}$ spins were shown in Fig. 1.

Miyahara et al. found that the in-plane coupling of spins in this system is topologically equivalent to that in the Shastry-Sutherland model and the magnetic properties of SrCu$_2$(BO$_3$)$_2$ can be well described by this model. The Shastry-Sutherland model is a special case of the frustrated Heisenberg model defined by the Hamiltonian

$$ H = J \sum_{n} S_i S_j + J' \sum_{n m} S_i S_j $$

where $nn$ ($nnn$) stands for the nearest (next-nearest) neighbor spins, and $J$ ($J'$) stands for the next-nearest inter-dimer (intra-dimer) coupling. The Shastry-Sutherland model corresponds the case $J/J' < 0.68$, whose ground state is a dimerised spin singlet. In the limit $J/J' \rightarrow 0$ or $J/J' \rightarrow \infty$, the ground state of the frustrated Heisenberg model is antiferromagnetically long range ordered and low-lying spin excitations are critical.

In the intermediate $J/J'$ regime, the ground state becomes non-critical and the spin excitations are gapped. With decreasing $J/J'$, a phase transition from a gapless to a gapped spin singlet state is shown to take place at a critical value $(J/J')_c \sim 0.7$. The ratio of $J/J'$ in SrCu$_2$(BO$_3$)$_2$ is about 0.68, a little bit smaller than the critical value. This suggests that the ground state of SrCu$_2$(BO$_3$)$_2$ is in a spin-gapped state.

Recently, Shastry and Kumar studied the doped Shastry-Sutherland system from the RVB theory of the t-J-like model. They found that the Mott-Hubbard gap will collapse upon doping, and the pre-existing spin pairs will propagate freely, leading to superconductivity. Similar conclusion was reached by Kimura and coworkers. However, they found that superconductivity is more favored around the quarter filling rather than the half filling.

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In this paper, we report the magnetic susceptibility and specific heat measurements on the dimer compounds SrCu$_2$(BO$_3$)$_2$ and M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ (M=Al, La, Na and Y). The spin excitation gaps of M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ are deduced from the low temperature data and found to be close to that of SrCu$_2$(BO$_3$)$_2$. The gap is strongly suppressed by the applied fields. However, no superconductivity is observed in these systems.

II. SYNTHESIS AND EXPERIMENTAL DETAILS

The polycrystalline materials SrCu$_2$(BO$_3$)$_2$ and M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ with M=Al, La, Na and Y were synthesized by solid state reaction. Stoichiometric amounts of high-purity SrCO$_3$, CuO, B$_2$O$_3$, Y$_2$O$_3$, La$_2$O$_3$, NaO and Al$_2$O$_3$ powders were ground and mixed, then pressed with a pressure of 10MPa into pellets and heated in air at 830 °C for 4 hours. The resulting pellets were then reground, repelletized and sintered at 870 °C in oxygen atmosphere for one week.

X-ray diffraction measurements (XRD) were carried out on powder samples of SrCu$_2$(BO$_3$)$_2$ and M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$. Fig. 2 shows the XRD patterns for all samples. The patterns indicate that they are all single-phase products. From the precise position of 2θ, the lattice parameters were obtained and shown in Table 1. The in-plane parameters $a$ and $b$ of all the four samples M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ and $c$ of La and Na substituted samples are almost unchanged in comparison with SrCu$_2$(BO$_3$)$_2$. However, the $c$-axis lattice parameters $c$ of Al and Y substituted samples are changed notably. This is because the ionic radius of La$^{3+}$ (1.06Å) and Na$^+$ (0.97Å) are very close to that of Sr$^{2+}$ (1.12Å), while Al$^{3+}$ (0.51Å) and Y$^{3+}$ (0.89Å) are considerably smaller than it. These results indicate that the doped elements are located between CuBO$_3$ layers. It leads to the variation of interlayer spacing and leaves the CuBO$_3$ plane almost unchanged.

The magnetic susceptibility and the specific heat measurements were performed in commercial Quantum Design PPMS. The susceptibility was measured using a vibrating sample magnetometer. The specific heat was measured using the relaxation method. The field dependence of thermometer and addenda was carefully calibrated before the specific heat was measured.

All doped materials M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ are insulators. Their resistances are all above 200MΩ at room temperature.

III. RESULTS AND DISCUSSIONS

Fig. 3 shows the magnetic susceptibility $\chi$=$M/H$ as a function of temperature $T$ for SrCu$_2$(BO$_3$)$_2$ and M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ in an applied field of 1.0T from 1.9K to 300K. For all samples, $\chi$ follows well the Curie-Weiss law in high temperatures. A broad peak appears around 15K. In low temperatures, a spin gap opens and $\chi$ drops sharply below 10K (Fig. 4). Below 4K, a small Curie-Weiss-like upturn is observed. This upturn is the contribution of magnetic impurities or defects.

The excitation gap $\Delta$ can be determined from the temperature dependence of $\chi$ in low temperatures. In general, the low-lying spin excitation spectrum around the gap minima has approximately the form $\varepsilon(\mathbf{k}) \sim \Delta + \alpha (\mathbf{k} - \mathbf{Q}_0)^2$, (2)

where $\mathbf{Q}_0$ is the vector where the minimum gap is located. In the limit $T \ll \Delta$, it can be readily shown that the spin susceptibility and the specific heat are respectively given by

$$\chi \sim \exp(-\Delta/T),$$

$$C \sim \frac{1}{T} \exp(-\Delta/T).$$  

FIG. 2: XRD patterns for M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ (M=Al, La, Na and Y) and SrCu$_2$(BO$_3$)$_2$ polycrystalline compounds.

FIG. 3: Temperature dependence of the magnetic susceptibility in M$_0$$_1$Sr$_{0.9}$Cu$_2$(BO$_3$)$_2$ (M=Al, La, Na, Y) and SrCu$_2$(BO$_3$)$_2$ polycrystalline compounds in a field of 1.0T.
Adding the contribution from magnetic impurities or defects and the contribution from ion cores, the total susceptibility in low temperatures can be expressed as

\[ \chi = \frac{C'}{T - \theta'} + a \exp(-\Delta/T) + \chi_0. \]  

(5)

The first term on the right hand side is the contribution of magnetic impurities and \( \theta' \) is the Curie temperature. The last term is the diamagnetic contribution from ion cores.

The low temperature susceptibility data can indeed be described by Eq. (5). Our fitting curves are shown by solid lines in Fig. 4. The values of \( \chi_0, C' \) and \( \Delta \) are listed in Table 1. The spin gap is 21.5K for \( \text{SrCu}_2\text{(BO}_3\text{)}_2 \), consistent with the result of Kageyama [3]. By comparison with \( \text{SrCu}_2\text{(BO}_3\text{)}_2 \), we find that the spin gap is suppressed by doping. The suppression of the energy gap is most apparent for \( M = Y \) and La samples. The spin gap in the La doped material is only 14.1K.

The Curie-tail in the magnetic susceptibility is more pronounced in the Al doped compound than in \( \text{SrCu}_2\text{(BO}_3\text{)}_2 \) and other doping systems. A probable cause for this is that part of \( \text{Cu}^{2+} \) within the CuBO\(_3\) plane was replaced by Al\(^{3+}\) and the dimerized Cu spin structure was distorted, leading to the large susceptibility upturn in the low temperature regime.

In order to further understand both the ground states and low-lying excited states, we measured the specific heat of \( M_{0.1}\text{Sr}_{0.9}\text{Cu}_2\text{(BO}_3\text{)}_2 \) with \( M = Y, \text{La and Al} \) from 1.9K to 25K in applied fields up to 14T. The specific heat \( C \) divided by temperature \( T \), \( C/T \), is shown in Fig. 5. For all three samples, a peak in \( C/T \) at around 7.5K is observed clearly in zero field, and the peak is suppressed to lower temperatures in applied fields. For an example, for \( \text{Y}_{0.1}\text{Sr}_{0.9}\text{Cu}_2\text{(BO}_3\text{)}_2 \), the peak positions for \( H=0 \text{T}, 7 \text{T}, 11 \text{T}, 14 \text{T} \) are, 7.4K, 6.8K, 6.2K, 6.1K, respectively. They are very close to the values for \( \text{SrCu}_2\text{(BO}_3\text{)}_2 \) reported previously [12, 13, 14]. Above 13K, \( C/T \) gradually increases with increasing \( T \) since the phonon contribution becomes the dominant part of total specific heat. Comparing the magnetic susceptibility \( \chi \) and the \( C/T \) at zero field, we find that the peak position of \( \chi \) is about twice the peak temperature of \( C/T \). This is due to the fact that \( \chi \) is a measure of two-particle excitations, while \( C/T \) is only a measure of one-particle density of states [11].

In low temperature regime, the specific heat is a sum of the contribution from low-lying magnetic excitations and the contribution from phonons. The latter is proportional to \( T^3 \). Thus the low temperature specific heat can be expressed as:

\[ C = \frac{A}{T} \exp(-\Delta/T) + \beta T^3. \]  

(6)

By fitting the experimental data with the above equation below 7K, we obtained the gap value \( \Delta \) in different \( H \) (Table 1). As shown in Fig. 6, \( \Delta \) drops linearly with \( H \). This linear field dependence of \( \Delta \) can be explained by the Zeeman splitting of excited triplet levels (\( S=1 \)). From the gap value determined from the specific heat data, we find that \( \Delta \) is suppressed most markedly in the La-doped sample, in agreement with the susceptibility data. For the Al-doped sample, the peak value of the specific heat is much less than those of other samples. It suggests that the Al doping can suppress most strongly low lying spin excitations in the CuBO\(_3\) planes in comparison with other samples.

![FIG. 4: Susceptibility \( \chi \) versus temperature \( T \) below 20K for \( M_{0.1}\text{Sr}_{0.9}\text{Cu}_2\text{(BO}_3\text{)}_2 \) (\( M = \text{Al, La, Na, Y} \)) and \( \text{SrCu}_2\text{(BO}_3\text{)}_2 \) compounds. The solid lines are fitting curves with Eq. (5).](image)

![FIG. 5: \( C/T \) for \( M_{0.1}\text{Sr}_{0.9}\text{Cu}_2\text{(BO}_3\text{)}_2 \) (\( M = \text{Y, La and Al} \)) polycrystalline compounds measured at \( H=0, 7, 11 \text{ and 14T} \).](image)
TABLE I: Values of lattice parameters \((a, b, c)\), the diamagnetic susceptibility of ion cores \(\chi_0\), \(C'\) and \(\Delta\) for \(\text{SrCu}_2(\text{BO}_3)_2\) and \(\text{M}_{0.1}\text{Sr}_{0.9}\text{Cu}_2(\text{BO}_3)_2\). \(\Delta^1\) and \(\Delta^2\) represent the spin gap deduced from the susceptibility and specific heat data, respectively.

| sample | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(\chi_0\) (×10\(^{-3}\)) | \(C'\) (×10\(^{-3}\)) | \(\Delta^1(1T)\) (K) | \(\Delta^2(0T)\) (K) | \(\Delta^2(7T)\) (K) | \(\Delta^2(11T)\) (K) | \(\Delta^2(14T)\) (K) |
|--------|----------|----------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Al     | 8.993    | 6.640    | -1.18    | 18.21           | 17.9            | 22.1            | 14.4            | 10.8            | 10.0            |
| La     | 8.993    | 6.649    | -1.59    | 14.88           | 14.1            | 19.6            | 15.6            | 11.7            | 8.9             |
| Na     | 8.992    | 6.648    | -1.08    | 15.42           | 19.8            | –               | –               | –               | –               |
| Y      | 8.992    | 6.642    | -1.30    | 12.45           | 16.4            | 26.5            | 20.5            | 14.9            | 11.0            |
| Sr     | 8.995    | 6.649    | -0.74    | 10.57           | 21.5            | –               | –               | –               | –               |

FIG. 6: Spin gap \(\Delta(H)\) versus field \(H\) for \(\text{M}_{0.1}\text{Sr}_{0.9}\text{Cu}_2(\text{BO}_3)_2\) with \(M=\text{Y}, \text{La}\) and \(\text{Al}\). The solid lines are linear fits to the data points.

Kageyama and co-workers \cite{3, 12} measured the magnetic susceptibility, Cu NQR, and inelastic neutron scattering spectra of \(\text{SrCu}_2(\text{BO}_3)_2\). From the susceptibility data, it was found that the spin gap is \(\sim 19\text{K}\), in agreement with our value of the spin gap, \(\sim 21\text{K}\), obtained by the same kind of measurement. However, the spin gap estimated from the other measurements is larger than that from the susceptibility. \(\Delta\) estimated from the Cu NQR and the inelastic neutron scattering measurements are about 30K and 34K, respectively. The spin gap estimated from specific heat \cite{15}, ESR \cite{16} and Raman scattering \cite{17} measurements agrees with that from inelastic neutron scattering measurements. Our specific heat results show that the spin gaps for \(\text{M}_{0.1}\text{Sr}_{0.9}\text{Cu}_2(\text{BO}_3)_2\) with \(M=\text{Y}, \text{Al}\) and \(\text{La}\) are about 27K, 22K and 20K, less than that for \(\text{SrCu}_2(\text{BO}_3)_2\), consistent with our susceptibility measurements. However, the spin gap estimated from the susceptibility measurements is about 10K less than that from the specific heat measurements.

Recently, electron or hole doping effects on \(\text{SrCu}_2(\text{BO}_3)_2\) were investigated by a number of authors. Zorko et al. \cite{18} investigated the doping effect by immersing \(\text{SrCu}_2(\text{BO}_3)_2\) into \(^{Li}\text{NH}_3\) solution. They found that the doping did not change much the magnetic susceptibility behavior, in agreement with our observation. The substitution of Sr by \(\text{La}\) or \(\text{Ba}\) was tried by Zorko and Arčon \cite{19} and by Choi et al. \cite{20}, respectively. Zorko et al. \cite{19} also tried to substitute Cu by Mg. However, no superconductivity was observed in these doped systems.

IV. CONCLUSIONS

In conclusion, \(\text{SrCu}_2(\text{BO}_3)_2\) and \(\text{M}_{0.1}\text{Sr}_{0.9}\text{Cu}_2(\text{BO}_3)_2\) with \(M=\text{Al}, \text{La}, \text{Na}\) and \(\text{Y}\) polycrystalline samples were successfully prepared by solid state reaction. XRD analysis showed that these doping compounds are single-phased with similar structure as for \(\text{SrCu}_2(\text{BO}_3)_2\). The spin gap is suppressed by doping. However, there is no superconductivity observed in the four doped samples. The doping effects on \(\text{SrCu}_2(\text{BO}_3)_2\) need to be further investigated.

Acknowledgments

We would like to thank Z. J. Chen and L. Lu for useful discussions. This work is supported by the National Natural Science Foundation of China.

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