# Crossbreeding between Experiment and Theory on Orthogonal Dimer Spin System

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We have investigated two-dimensional spin systems $SrCu_2(BO_3)_2$ and $Nd_2BaZnO_5$, both of which have a unique topology that is equivalent to the Shastry-Sutherland lattice. The magnetization curve of $SrCu_2(BO_3)_2$ reveals that, unlike 1/8 and 1/4 plateaux, a 1/3 plateau is very stable, surviving at least up to 69 T. The pressure dependence of susceptibility up to 10 kbar indicates that the pressure causes the system to approach the critical point to some other states. On the other hand, $Nd_2BaZnO_5$ with rather classical spins exhibits an antiferromagnetic long range ordering at 2.4 K. Finally, other experimental candidates of extended Shastry-Sutherland system will be briefly presented.

## §1. Introduction

Exactly 20 years ago, B. S. Shastry and B. Sutherland (S-S) considered the model composed of a two-dimensional square lattice with some additional diagonal bonds (Fig. 1(c)), in which the direct product of the dimer singlets is an exact ground state when the intradimer coupling $J$ is larger than the interdimer coupling $J'$ .[1)] The next important event occurred in 1991 when R. W. Smith and D. A. Keszler succeeded to synthesize $SrCu_2(BO_3)_2$ containing the arrangement of the $Cu^{2+}$ ions as shown in Fig. 1(a).[2)] In 1998, crossbreeding between theory and experiment eventually started, then involving a number of theoreticians and experimentalists, to reveal some interesting phenomena such as magnetization plateaux and almost dispersionless triplet excitations.[3)-13)]

This paper will deal with several orthogonal dimer systems. Although the first

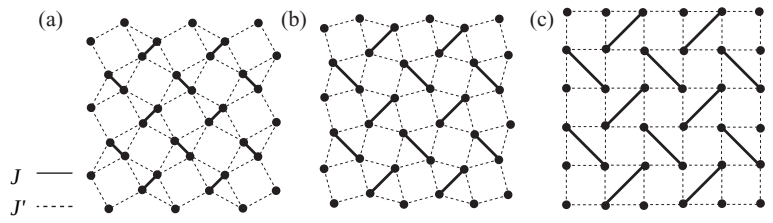


Fig. 1. Topologically identical structures realized by (a) $SrCu_2(BO_3)_2$, (b) $Nd_2BaZnO_5$ and (c) Shastry-Sutherland.

compound $SrCu_2(BO_3)_2$ now looks well understood, there still remain some open questions. The magnetization curve for $H//c$ up to 53 T, for example, is far from the saturation. [14] We will thus demonstrate new magnetization data obtained using a recently developed magnet available up to 69 T. Another interesting and challenging issue is tuning exchange interactions because $SrCu_2(BO_3)_2$ is theoretically shown to be in the vicinity of the critical point to an antiferromagnetic or a plaquette singlet state. [9),11] To achieve this goal, we studied pressure dependence of the magnetic susceptibility up to 10 kbar. The next material is a new oxide $Nd_2BaZnO_5$, [15] the magnetic network (Fig. 1(b)) of which is again topologically equivalent to the S-S lattice. The magnetic properties of this material will be discussed based on the magnetic susceptibility and the magnetization measurements. In the final part of the paper, we would like to briefly mention the future direction of the study on the orthogonal dimer system, namely, the extended S-S systems such as $KIrO_3$.

## §2. Experimental

Poly- and single- crystals of $SrCu_2(BO_3)_2$ were prepared using a conventional solid state reaction and a travelling solvent floating zone method, respectively, as described elsewhere. [2),16] The high field magnetization measurement up to 69 T at $T = 1.4$ K was conducted using pulsed field magnets at the High Magnetic Field Laboratory, KYOKUGEN in Osaka University. We used one piece of the grown crystals of high quality with an approximate dimension of 2mm × 2mm × 2mm. The magnetic susceptibility measurement of polycrystalline samples under pressure was performed at $H = 0.1$ T in a SQUID magnetometer (MPMS, Quantum Design) at Saitama University, in which we installed a high pressure cell with the Cu-Be clamping-type using a pressure-transmitting fluid (Fluorinert FC70:FC7751:1). [17]

To synthesize $Nd_2BaZnO_5$, [15] the stoichiometric starting materials $Nd_2O_3$, ZnO and $BaCO_3$ were mixed intimately in an agate mortar, pressed into a pellet, preheated at 1173 K in air overnight to decompose the carbonate. The sample was then heated at 1273 K for 1 week with several intermediate grindings. The powder X-ray diffraction study by M21X (Mac Science) using $CuK_\alpha$ allowed us to conclude that the sample obtained is $Nd_2BaZnO_5$ without any trace of impurity phases. The magnetic susceptibility of $Nd_2BaZnO_5$ was curried out using a SQUID magnetometer at University of Tokyo in the temperature range between 1.8 K and 300 K. The magnetization measurement up to 7 T at 1.8 K was performed using a PPMS magnetometer (Quantum Design).

## §3. $SrCu_2(BO_3)_2$: Dimer phase

The magnetization curve up to 69 T at 1.4 K is presented in Fig. 2(a), where the magnetic field was applied perpendicular to the S-S lattice, i.e., the *ab* plane. There is little difference between field increasing and decreasing processes, and the obtained curve below 53 T is almost identical to that reported in Ref. 14). The point we would like to emphasize here is the fact that the 1/3 plateau is considerably stabler than the 1/4 and 1/8 plateaux; It survives from about 40 T to at least 69 T

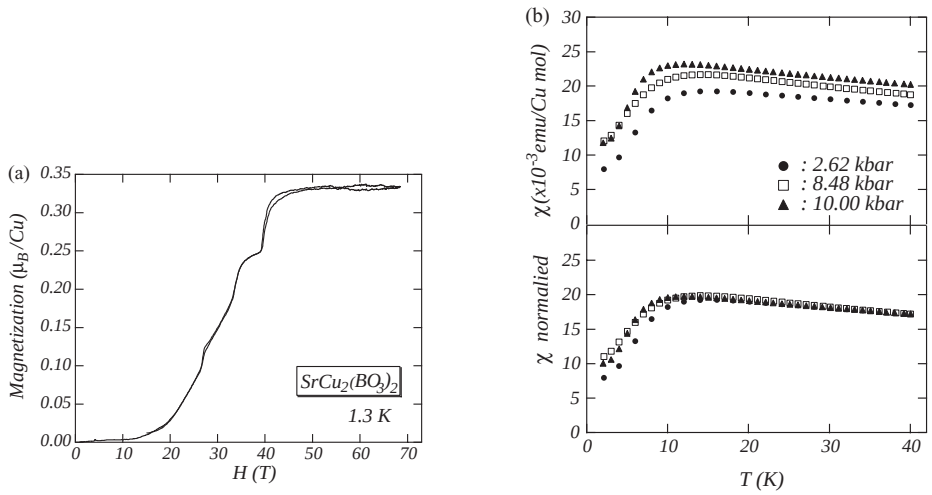


Fig. 2. (a) The magnetization curve of $SrCu_2(BO_3)_2$ measured at 1.3 K with the single crystal being aligned as $H$ // $c$. (b) (upper) The temperature dependence of the magnetic susceptibility of $SrCu_2(BO_3)_2$ at 2.62 kbar (circles), 8.48 kbar (squares) and 10.00 kbar (triangles). (lower) the susceptibilities normalized at 40 K.

(the maximum field studied here), and is at least 6 times as wide as the 1/4 plateau.

To date, there are several theoretical calculations to fit our experimental magnetization. Among them, the Chern-Simons theory by Misguich et al. [12] assuming $J = 74$ K and $J' = 29.5$ K reproduces most nicely our previous data (below 53 T), especially with respect to the critical fields of the 1/3 and 1/4 plateaux as well as the rounding feature of these plateaux. Their theory, however, claims that the 1/3 plateau ends at about 53 T, in disagreement with the present experiment. On the contrary, Miyahara and Ueda, [18] Totsuka and Momoi [19] predict that the 1/3-magnetization phase will persist until 110 T, 80 T, respectively, although the agreement with the experiment in the low field region looks poorer. Apparently, higher field experiments to cover whole magnetization as well as more elaborated theoretical treatment are needed to advance our understanding of triplet excitations in the presence of $H$.

Before moving onto the pressure effect, let us discuss the phase diagram as a function of $J'/J$ and $J''/J$ proposed by Koga and Kawakami, [20] where $J''$ denotes the out-of-plane interdimer interaction. It is shown that with increasing $J'/J$ the dimer phase undergoes a phase transition to the RVB plaquette-singlet phase, whereas raising $J''/J$ results in the antiferromagnetic transition. Since the present material is a layered material with the $Sr^{+2}$ ions being intercalated between the Cu-B-O layers, the pressure should mainly affect the interlayer distance, thus changing $J''$ substantially but leaving $J$ and $J'$ almost unchanged. The upper panel of Fig. 2(b) demonstrates raw data of the magnetic susceptibility vs $T$ at various pressures. As pressure is elevated as 2.62 kbar, 8.48 kbar and 10.00 kbar, the temperature at which the susceptibility takes maximum tends to be lowered slightly: 16.1 K, 14.0 K and 12.0 K. The contrast becomes clearer when we normalize the raw data at 40 K as seen

in the lower panel of Fig. 2(b). (If the difference of the susceptibility upon pressure in the high-$T$ region originates only from the pressure cell used, then the normalized susceptibility should represent the intrinsic one.) Although it is difficult from this result to estimate a set of exchange constants precisely, the decrease of temperature at maximum susceptibility possibly indicates that $J''$ is effectively varied by pressure, making the system closer to the critical point between the dimer phase and some other phases. In order to obtain the other phase whatever, it is necessary to execute experiments in higher pressure.

## §4. $Nd_2BaZnO_5$: Antiferromangnetic phase

$Nd_2BaZnO_5$ with a space group $I4/mcm$ (tetragonal) can be also regarded as a layered compound.[15] As shown in Fig. 3(a), the Nd-O and the Ba-Zn-O layers alternatively stack along the $c$ direction. The magnetic ions, i.e., the $Nd^{3+}$ ions occupying a crystallographically equivalent site ($8h$), form the two-dimensional network as shown in Fig. 1(b), where the nearest neighbor and the next nearest neighbor $Nd^{3+}$-$Nd^{3+}$ distances are very close: $d_{NN} = 3.324$ Å and $d_{NNN} = 3.525$ Å, respectively. The $Nd^{3+}$ ion is 8-fold oxygen coordinated with three kinds of Nd-O distance (2.299 Å ×2, 2.493 Å ×2, 2.636 Å ×4) to provide superexchange interactions, $J$ and $J'$. The temperature dependence of the magnetic susceptibility as well as the inverse susceptibility for the polycrystal of $Nd_2BaZnO_5$ is shown in Fig. 4(a). The susceptibility at high-$T$ regime obeys the Curie-Weiss law, and the fitting yields the Weiss constant $\theta_W = -44.5$ K, where $J = 9/2$ and $g = 8/11$ are used, which are expected for the ground state of the tripositive neodymium ion with the $4f^3$ configuration. The negative sign of $\theta_W$ is an indication of antiferromagnetic interaction. On cooling, the deviation from Curie-Weiss behavior is observed from 70 K maybe due to development of short range ordering, and further decreasing $T$ finally results in the antiferromagnetic transition at 2.4 K as seen in the inset of Fig. 4(a). We can confirm the antiferromagnetic state by plotting the magnetizations against $H$, where spin-flop like behavior is observed for the 1.8 K curve (Fig. 4(b)). The gradual increase with $H$ after the spin-flop transition should come from the strong exchange

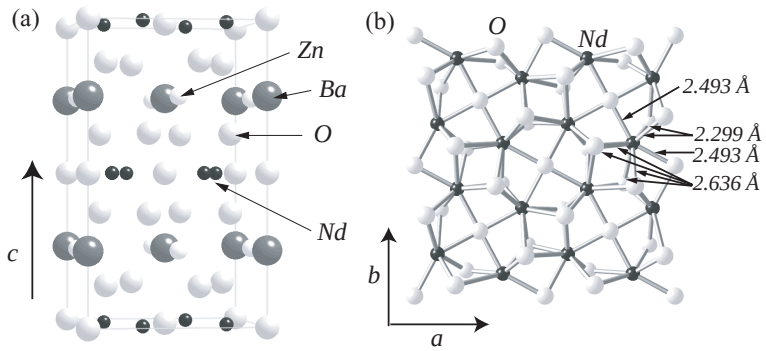


Fig. 3. Crystal structure of $Nd_2BaZnO_5$.

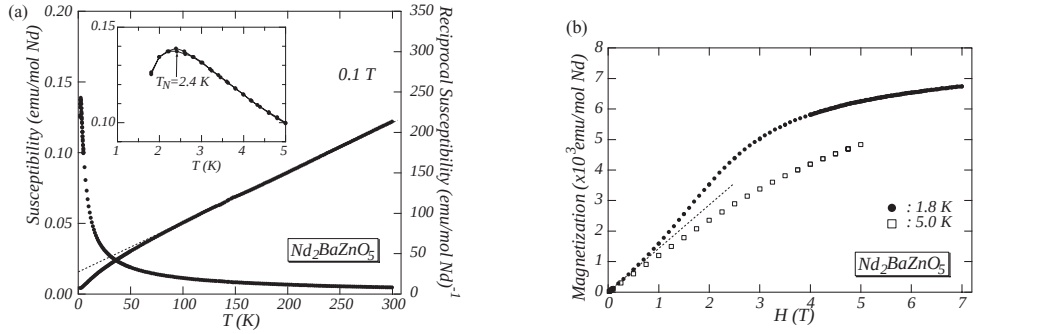


Fig. 4. (a) Magnetic susceptibility and reciprocal susceptibility for $Nd_2BaZnO_5$. The inset represents the enlarged plot for the low temperature region. (b) Magnetization curves for the polycrystalline sample of $Nd_2BaZnO_5$ measured at 1.8 K (closed) and 5.0 K (open).

anisotropy of the $Nd^{3+}$ ion which is typical for $f$ electron systems. Considering the closer values between $d_{\mathrm{NN}}$ and $d_{\mathrm{NNN}}$ as mentioned above, we can intuitively expect that $J'$ and $J$ are close to each other as well. If so, there should be strong spin frustration, and this can explain why the obtained $\theta_{\mathrm{W}}$ is much smaller than $T_{\mathrm{N}}$ ($\theta_{\mathrm{W}}/\mathrm{T_N} = -19$). In Fig. 5, we redraw the phase diagram as a function of $1/S$ and $J/J'$ in the isotropic limit, which was established by Shastry and Sutherland.[1] $SrCu_2(BO_3)_2$ ($J'/J = 0.64$) and $Nd_2BaZnO_5$ ($J'/J = 1$) are successfully mapped onto this phase diagram, though the neodymium oxide is magnetically anisotropic.

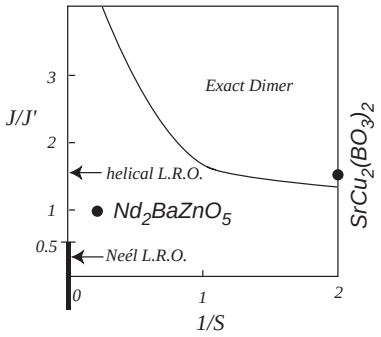


Fig. 5. The phase diagram proposed by Shastry and Sutherland,[1] on which $SrCu_2(BO_3)_2$ and $Nd_2BaZnO_5$ are mapped.

## §5. Extended S-S models

As described in Ref. 21), one can theoretically invent various analogues of the S-S lattice. Chemists must accomplish a mission to explore model materials. $KIrO_3$ is a possible candidate of the three-dimensional version of the S-S model. Its structure, shown in Fig. 6, has a cubic symmetry with a space group of $Pn\text{-}3Z$ (No. 203).[22] Each $IrO_6$ octahedron is coupled to edge-share with the neighboring $IrO_6$

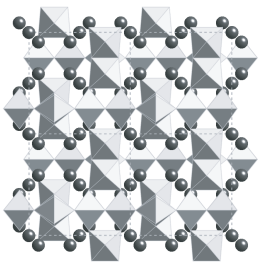

Fig. 6. Crystal structure of $KIrO_3$, where the $IrO_6$ octahedra and the K ions are represented.

octahedron, and the dimers are connected in a three dimensional way by corner sharing. Since $5d$ electron systems tend to take low spin state due to relatively large crystal field stabilization energy, it is natural to assume that the $Ir^{5+}$ ions ($5d^4$), located at a crystallographically equivalent site ($12g$), carry $S = 1$. Interestingly, there exist several $4d$ and $5d$ transition metal oxides such as $La_4Os_6O_{19}$, $La_4Ru_6O_{19}$ containing the identical magnetic network with $KIrO_3$.[23),24)] $KIrO_3$ differs from the others in that the former has one kind of valence (5+), while the latter has a mixed valence (4.333+). Investigation of the magnetic and electric properties of this series of compounds is currently underway.

## Acknowledgements

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