Exact Dimer Ground State of the Two Dimensional Heisenberg Spin System SrCu$_2$(BO$_3$)$_2$

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The two dimensional Heisenberg model for SrCu$_2$(BO$_3$)$_2$ has an exact dimer ground state which was proven by Shastry and Sutherland almost twenty years ago. The critical value of the quantum phase transition from the dimer state to the Néel ordered state is determined. Analysis of the experimental data shows that SrCu$_2$(BO$_3$)$_2$ has the dimer ground state but its coupling constants are close to the transition point, which leads to an unusual temperature dependence of the susceptibility. The almost localized nature of the triplet excitations explains the plateaus observed in the magnetization curve. [S0031-9007(99)09090-0]

The pseudospin gap behaviors observed in high T_c cuprates have stimulated intensive investigations on magnetic systems with spin gaps. As products of this type of activity, several new spin gap systems have been found experimentally. Among them, some of the examples which have two dimensional character include the coupled spin ladder systems, SrCu$_2$O$_3$ [1], CaV$_2$O$_5$ [2], and the plaquette resonanting-valence-bond (RVB) system, CaV$_4$O$_9$ [3].

Recently Kageyama *et al.* found a new two dimensional spin gap system SrCu$_2$(BO$_3$)$_2$ [4]. The crystal structure of SrCu$_2$(BO$_3$)$_2$ is tetragonal and all Cu^{2+} ions with a localized spin $S = 1/2$ are located at crystallographically equivalent sites. The two dimensional layers containing the Cu^{2+} ions are separated by planes of Sr^{2+} ions.

The susceptibility drops sharply below the maximum at around $T = 20$ K. The peak of the measured susceptibility is much suppressed compared with that of the theoretical value expected for a dimer model. The spin gap estimated by the nuclear magnetic relaxation rate is $\Delta = 30$ K. Another novel feature appears in the magnetization under high magnetic fields. The authors report that the two magnetization plateaus corresponding to $1/4$ and $1/8$ of the full Cu^{2+} moment are observed for the first time for the two dimensional quantum spin systems.

The magnetic properties of SrCu$_2$(BO$_3$)$_2$ may be described by the two dimensional Heisenberg model with the nearest-neighbor (nn) and next-nearest-neighbor (nnn) couplings,

$$\mathcal{H} = J \sum_{\text{nn}} \mathbf{s}_i \cdot \mathbf{s}_j + J' \sum_{\text{nnn}} \mathbf{s}_i \cdot \mathbf{s}_j. \qquad (1)$$

The system is illustrated in Fig. 1(a) and topologically equivalent to the model considered by Shastry and Sutherland [5]. We note that the nearest-neighbor bonds define a unique covering of all spins. On the other hand, the system with only next-nearest-neighbor couplings is equivalent to the square lattice Heisenberg model. We assume that both coupling constants are antiferromagnetic, J and $J' > 0$, and then the present Heisenberg model is frustrated.

Shastry and Sutherland have shown that the singlet dimer state is an exact eigenstate of the Hamiltonian. In this paper we determine the critical value for the transition from the gapful dimer ground state to the antiferromagnetically ordered gapless state. Analysis of experimental data shows that SrCu$_2$(BO$_3$)$_2$ is a spin gap system with the dimer ground state but is close
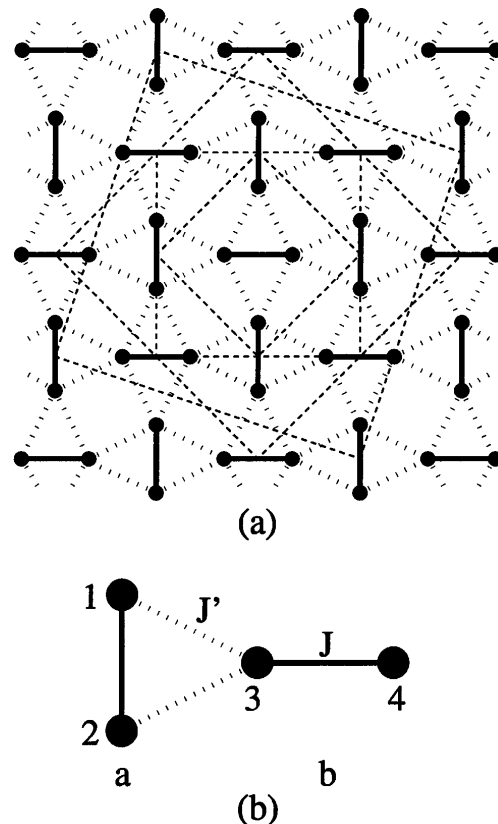

FIG. 1. (a) Lattice structure of the Cu^{2+} spins of SrCu$_2$(BO$_3$)$_2$. The nearest-neighbor bonds are expressed by solid lines and the next-nearest-neighbor bonds by broken lines. Square unit cells containing 4, 8, 16, and 20 spins are shown by dashed lines. (b) Elementary unit for the interaction between a pair of nearest-neighbor bonds.

to this quantum transition point. The unusual magnetic properties of $SrCu_2(BO_3)_2$ are explained consistently from this point of view.

In the following analysis we use the dimer bases defined for each nearest-neighbor bond:

$$|s\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \qquad (2)$$

$$|t_1\rangle = |\uparrow\uparrow\rangle, \qquad (3)$$

$$|t_0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \qquad (4)$$

$$|t_{-1}\rangle = |\downarrow\downarrow\rangle. \qquad (5)$$

As Shastry and Sutherland [5] have shown, the direct product of the singlet states

$$|\Psi\rangle = \prod_a |s\rangle_a, \qquad (6)$$

where a represents the nearest-neighbor bonds, is always an eigenstate of the Hamiltonian (1).

The proof for the exact eigenstate is simple. Since the wave function is an eigenstate, actually the ground state, of the first term of the Hamiltonian, let us consider the effect of the second term. It is easy to show by elementary calculations that for any neighboring pair of the nearest-neighbor bonds the matrix element of the second term of Eq. (1) vanishes,

$$\mathcal{H}'_{ab}|s\rangle_a|s\rangle_b = 0. \qquad (7)$$

To be explicit, $\mathcal{H}'_{ab} = J'(\mathbf{s}_1 \cdot \mathbf{s}_3 + \mathbf{s}_2 \cdot \mathbf{s}_3)$ where the site indices are shown in Fig. 1(b). Note that the vanishing of the matrix element is due to the odd parity of the singlet with respect to the reflection which exchanges the two spins $\mathbf{s}_1 \leftrightarrow \mathbf{s}_2$.

The energy of the dimer state is given by $E_{\text{dimer}} = -(3/8)NJ$ where N is the total number of spins which is assumed to be even. It is clear that the dimer state is the ground state for small $J' \ll J$.

Now we consider the other limit, $J' \gg J$. In this limit the model is topologically equivalent to the two dimensional square lattice Heisenberg model as mentioned before. According to the recent quantum Monte Carlo simulations the ground state energy per site is $-0.669J'$ [6]. The first order correction due to the dimer coupling J is obtained from the spin-spin correlation of the next-nearest-neighbor pair of the square lattice model, which is calculated as 0.204 [7]. By using these results the ground state energy of the ordered phase is estimated as $E_{\text{AF}} = -N(0.669J' - 0.102J)$. The transition point between the two phases may be obtained by equating the two energies, which leads to $(J'/J)_c = 0.71$. Since the ground state energy for the antiferromagnetic phase is estimated by a variational calculation, the transition point thus obtained gives an upper bound.

Figure 2 shows the energy obtained by the exact diagonalization for finite systems, $N = 8$, $N = 16$, and
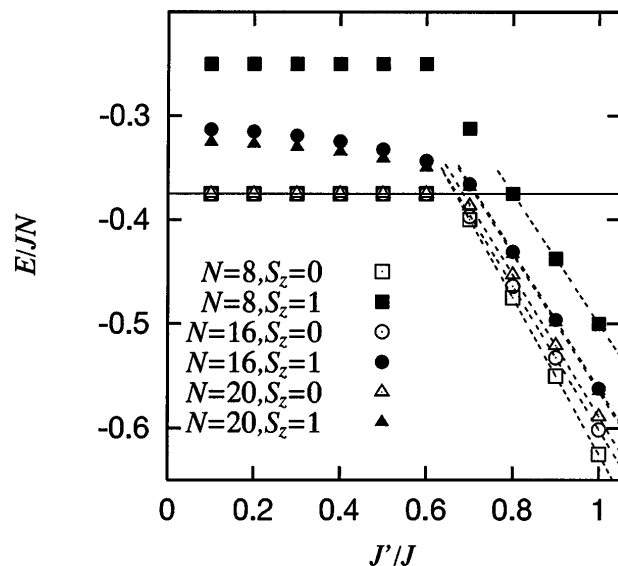

FIG. 2.　Ground state energy per site for finite lattices: $N = 8$, 16, and 20. The lowest energies of triplet excitations are also shown by filled symbols.

$N = 20$. Periodic boundary conditions are used for the calculations. By considering the finite size effects, we obtain an estimation, $(J'/J)_c > 0.69$. Therefore we conclude that the transition point is $(J'/J)_c = 0.7 \pm 0.01$.

One can estimate the excitation gap in the dimer phase by the perturbation theory. After some calculations the spin gap up to the fourth order correction is given by

$$\Delta = J\left[1 - \left(\frac{J'}{J}\right)^2 - \frac{1}{2}\left(\frac{J'}{J}\right)^3 - \frac{1}{8}\left(\frac{J'}{J}\right)^4\right]. \qquad (8)$$

Up to this order the triplet excitations are completely localized. This unusual behavior is understood by considering the matrix elements for the triplet excitations. To be explicit we start from the state with a triplet with the spin quantum number $s_z = 1$ at the bond a in Fig. 1(b). The states connected with this state by the Hamiltonian are

$$\mathcal{H}'_{ab}|t_1\rangle_a|s\rangle_b = \frac{J'}{2} |t_1\rangle_a|t_0\rangle_b - \frac{J'}{2} |t_0\rangle_a|t_1\rangle_b. \qquad (9)$$

It is important to note that when a triplet moves to neighboring bonds it leaves another triplet behind. The next crucial observation is that the following matrix elements vanish also by symmetry reasoning: parity with respect to the reflection,

$$\mathcal{H}'_{ab}|s\rangle_a|t_m\rangle_b = 0 \qquad (m = 0, \pm 1). \qquad (10)$$

The above two facts, Eqs. (9) and (10), set a stringent constraint for the motion of a triplet. Hopping of a triplet is possible through a closed path of dimer bonds and thus the hopping processes start from the sixth order in the perturbation. On the other hand, in a similar system in one dimension, the triplet excitations are completely localized [8]. In the present system, the triplet excitations are nearly localized with extremely small dispersion.

The spin gap for finite systems is shown in Fig. 3. For the dimer region, $J'/J < 0.7$, the finite size effects are small, which is a consequence of the almost localized wave functions of the triplet excitations. The perturbation result given by Eq. (8) is very accurate for $J'/J \leq 0.5$. On the other hand, for the antiferromagnetic region the finite size effects are significant, indicating usual dispersive magnon excitations. Since the dimer ground state is always an eigenstate it makes a level crossing with the Néel ordered state at the transition point. For such a case there are two possibilities concerning the nature of the transition [9]. From the results shown in Fig. 3 it is difficult to determine uniquely whether it is weakly first order or continuous.

Susceptibility at high temperatures is obtained by the high temperature series expansion as

$$\chi = \frac{(g\mu_B)^2}{4T}\left(1 - \frac{J + 4J'}{4T} + \frac{-J^2 + 8JJ' + 8J'^2}{16T^2}\right).$$

(11)

From the expansion, the paramagnetic Weiss constant is given by $\theta = (J + 4J')/4$.

Kageyama et al. determined the excitation gap $\Delta = 30$ K from the NMR relaxation rate. It should be noted that from the low temperature increase of the susceptibility it is estimated as $\Delta = 19$ K. In the following analysis of the experimental data we use the former value which is identified as the spin gap by the authors of [4]. The susceptibility data at high temperatures are fitted by a Curie-Weiss law with the Weiss constant $\theta = 92.5$ K and the effective g factor $g = 2.14$. The spin gap and the Weiss constant are sufficient to determine the coupling constants uniquely. By using the fit up to the sixth order shown in
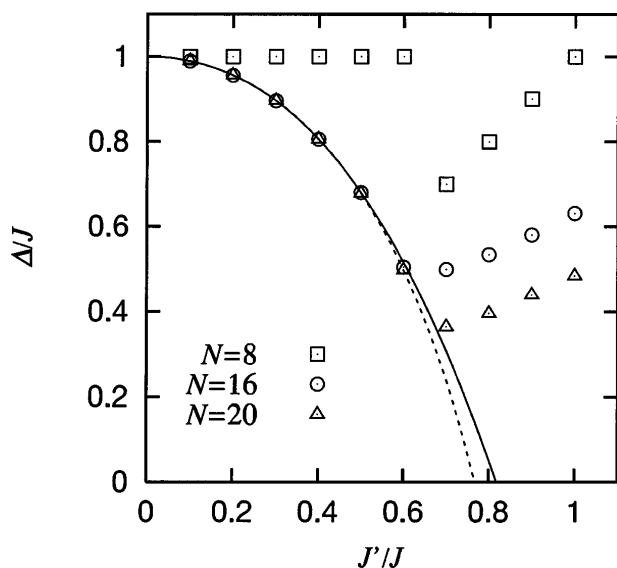
Fig. 3, $J = 100$ and $J' = 68$ K are obtained. Temperature dependence of susceptibility is shown in Fig. 4. In the figure a comparison is made between the theoretical calculations for finite clusters $N = 8$ and $N = 16$ and the experiments. The theoretical values are calculated by the quantum transfer matrix method for the systems with periodic boundary conditions [10]. Considering the ambiguity for the estimation of the gap from the experiments on one side, and the smallness of clusters used for theoretical calculations on the other side, the agreement between the experiment and the theory is satisfactory. A better fit may be obtained when slightly smaller values are used for the Weiss constant and the spin gap.

The characteristic feature of the susceptibility of this compound, the usual Curie-Weiss-type behavior at higher temperatures above the peak and the steep drop below the peak, is well reproduced. The estimated coupling constants $J'/J = 0.68$ are close to the critical value $(J'/J)_c = 0.7$. Figure 4 also shows the theoretical results for smaller values of the ratio $J'/J = 0$, 0.2, and 0.4 with the Weiss constant fixed, $\theta = 92.5$ K. We can conclude that the closeness to the transition point is the origin of the unusual temperature dependence of the susceptibility.

Next we discuss the magnetization curve. Figure 5 shows magnetization as a function of the applied magnetic field. The results are obtained by the numerical exact diagonalization for the system with $N = 20$ spins. One can clearly identify plateaus corresponding to $1/4$ and $1/2$ of the full moment. Experimentally, plateaus are observed for $1/4$ and $1/8$ of the full moment. Since the calculations were done for a small cluster, it is not possible to find a plateau at $1/8$. The critical value for the plateau at $1/4$
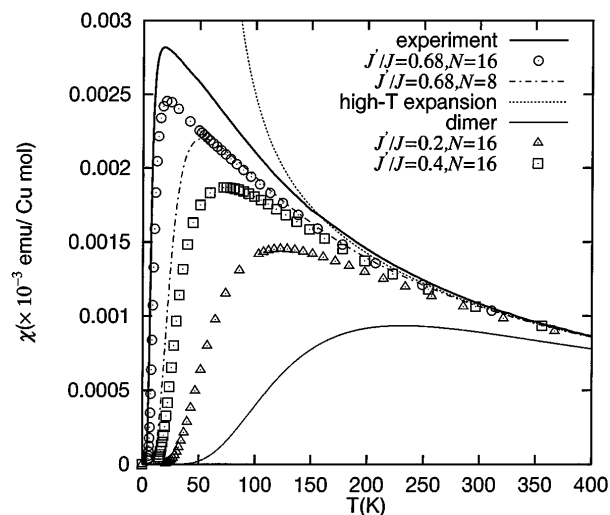

FIG. 3. Spin gap for finite lattices: $N = 8$, 16, and 20. The solid line is the perturbation result up to the fourth order. The dashed line is a fit obtained by adding fifth and sixth order terms to the perturbation result.

FIG. 4. Temperature dependence of susceptibility for finite clusters, $N = 8$ and 16. $J = 100$ K and $J' = 68$ K are used. The experimental data are shown by the thick solid line. Also shown are the theoretical results for smaller values of the ratio $J'/J = 0$ (dimer), 0.2, 0.4 with the Weiss constant fixed $\theta = 92.5$ K.
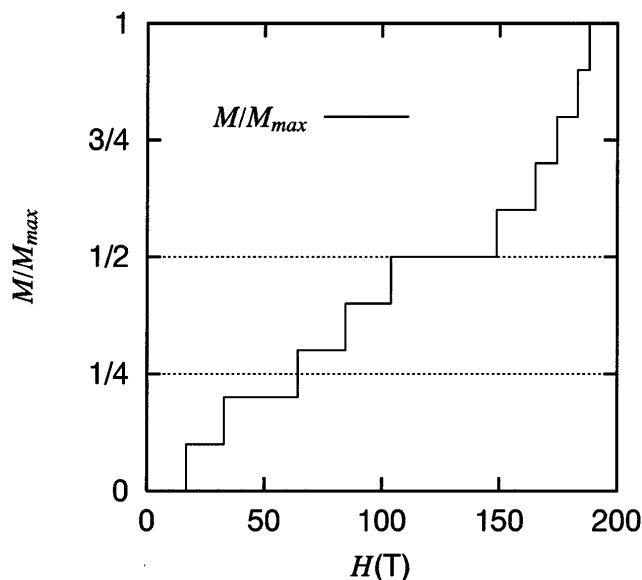
FIG. 5. Magnetization process for the finite cluster of 20 spins. $J = 100$ and $J' = 68$ K are used.

estimated for the present set of parameters $J = 100$ K, $J' = 68$ K is about 40 T which is comparable with the experimentally observed critical field $H_{c4} = 37$ T [4].

Formation of the plateaus is related with the almost localized wave functions of the triplet excitations. At special values of magnetization, where the triplet excitations can take a regular lattice structure, energy cost would be locally minimum. It is natural to assume that the commensurability energy is more favorable when a unit cell is a simple square since the original structure has the tetragonal symmetry. The square unit cells are possible for $N = 4, 8, 16, 20, 32, \ldots$, which corresponds to plateaus at $1/2, 1/4, 1/8, 1/10, 1/16, \ldots$; see Fig. 1(a). The plateaus observed experimentally, $1/4$ and $1/8$, are just two of them. Our theory predicts that there will be a clear plateau for $1/2$ of the full moment at around 100 T and also for $1/10$ at a smaller magnetic field than $H_{c2} = 28$ T. Since the plateau of the latter is expected to be small, a lower temperature and a clean sample will be required. The experiments on these plateaus are a crucial test for the present theory. Another prediction of the theory is the superstructure at each plateau which should be observable, for example, by NMR.

In conclusion we have identified that $SrCu_2(BO_3)_2$ has the exact dimer ground state found by Shastry and Sutherland [5]. In the model the quantum phase transition occurs at $J'/J \sim 0.7$ from the dimer state to the antiferromagnetically ordered state. This transition is either weakly first order or continuous and $SrCu_2(BO_3)_2$ is a unique spin gap system which is close to the quantum transition point. Unusual temperature dependence of the susceptibility is a consequence of the closeness to the transition point. Another interesting feature appears in the excitations. The low lying triplet excitations are almost localized and easily form regular lattices under certain magnetic fields. The commensurability energy associated with the superstructures leads to the plateaus in the magnetization curve at $1/2, 1/4, 1/8, 1/10, 1/16, \ldots$, of the full moment.

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