

# Theoretical analysis of the experiments on the double-spin-chain compound $\text{KCuCl}_3$

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We have analyzed the experimental susceptibility data of  $\text{KCuCl}_3$  and found that the data are well explained by the double-spin-chain models with strong antiferromagnetic dimerization. Large quantum Monte Carlo calculations were performed in the spin systems with frustration. This was made possible by removing the negative-sign problem with the use of the dimer basis that has spin-reversal symmetry. The numerical data agree with the experimental data within 1% relative errors in the whole temperature region. We also present a theoretical estimate for the dispersion relation and compare it with recent neutron-scattering experiments. Finally, the magnitude of each interaction bond is predicted. [S0163-1829(98)04730-4]

The low-dimensional quantum systems with an excitation energy gap are now attracting much interest both experimentally and theoretically.<sup>1</sup> The possibility of high- $T_c$  superconductivity upon doping carriers to the gapped insulator lies as the background. The spin-ladder model and its realization in a real compound  $\text{SrCu}_2\text{O}_3$  may be the most well-known substance for this scenario.<sup>2</sup> Of course, various other compounds are also synthesized, which can be explained by the low-dimensional quantum spin Hamiltonian.<sup>3-8</sup> These experimental achievements now offer much data for theoretical investigations.

Tanaka *et al.*<sup>4</sup> have measured the magnetic susceptibility of the  $\text{KCuCl}_3$ , and proposed that it can be explained by the double-spin-chain Hamiltonian. The susceptibility data show the spin-gap behavior. They estimated the amount of the excitation gap  $\Delta$  by fitting the low-temperature data with its theoretical expression,  $\chi(T) \propto T^{-1/2} \exp(-\Delta/T)$ , given by Troyer *et al.*<sup>9</sup> The estimated gap,  $\Delta/k_B \sim 35$  K, is consistent with their recent measurements of the magnetization process at low temperature, which gives  $\Delta/k_B \sim 31.1$  K.<sup>10</sup>

For a thorough understanding of the system, it is necessary to determine the strength of each interaction bond of the model Hamiltonian that best describes the subject material. For frustrated systems, one usually calculates all the eigenvalues of a given model Hamiltonian on a finite lattice by the numerical diagonalization, and then compares the obtained physical quantities at finite temperatures with the experimental data. Since the numerical diagonalization technique is restricted to very small sizes with 18  $S=1/2$  spins or less, the results suffer a severe finite-size effect. The quantum Monte Carlo (QMC) method can handle much larger systems, but has not been applied to the frustrated systems because of the negative-sign problem. Recently, one of the authors has solved this problem in the double-spin-chain system.<sup>11</sup> It makes it possible to treat large system sizes even at very low temperatures, and thus we are able to compare directly the numerical results to the experimental data without suffering the size effect.

In this paper, we calculate the susceptibility of the double-spin-chain model with 162 spins, and aim at the determina-

tion of the interaction bonds that explain  $\text{KCuCl}_3$ . For this purpose, it is necessary to calculate the dispersion relation of the excited state in comparison with the neutron-scattering experimental results. The susceptibility alone is not sufficient to discuss the details of the system, since it is the integrated quantity. We use our analytic expression for the dispersion relation obtained recently for general double-spin-chain models.<sup>12</sup> Our analysis partly disagrees with the experiments, which may be understood by possible two-dimensional couplings.

We consider the following spin Hamiltonian under the open boundary conditions:

$$\mathcal{H} = \sum_{n=1}^{N-1} \{J_1(\boldsymbol{\sigma}_n \cdot \boldsymbol{\sigma}_{n+1} + \boldsymbol{\tau}_n \cdot \boldsymbol{\tau}_{n+1}) + J_2 \boldsymbol{\sigma}_n \cdot \boldsymbol{\tau}_n + J_3 \boldsymbol{\tau}_n \cdot \boldsymbol{\sigma}_{n+1}\} + J_2 \boldsymbol{\sigma}_N \cdot \boldsymbol{\tau}_N. \quad (1)$$

Here,  $N$  is the linear size of the system, and  $|\boldsymbol{\sigma}| = |\boldsymbol{\tau}| = 1/2$ . Figure 1 shows the shape of the lattice.

Three cases of the above Hamiltonian, (i)  $J_1 = J_3$ , (ii)  $J_3 = 0$ , and (iii)  $J_1 = 0$ , are especially investigated. In each case,  $J_2$  is a set variable ranging from  $J_2 = -8$  to  $J_2 = 8$ . The first one,  $J_1 = J_3$ , is what we call here the ‘zig-zag’ or, more commonly, the railroad-trestle model. This model has frustration for  $J_2 > 0$ , and thus have not been analyzed on its thermodynamic properties yet. The second one is the ordinary two-leg ‘ladder’ model, and the third one is the ‘bond-alternation’ model. By changing the sign of the  $J_2$  bond, the Hamiltonian can describe both the dimer-gap system and the Haldane-gap system. The difference in the origin of the gap affects the structure of the excited states and thus

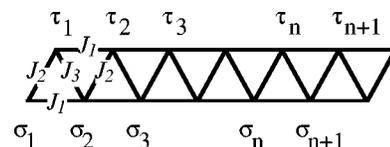


FIG. 1. Shape of the general double-spin-chain model.

the finite temperature behavior of various physical quantities. We also comment on this point at the end of this paper.

Before demonstration of the numerical evidence, we briefly summarize the simulational technique. We have done the ordinary world-line QMC simulations, but the choice of the representation basis is considered different from the conventional  $s^z$  one. Two spins,  $\sigma_n$  and  $\tau_n$ , are coupled and considered as a unit of an update. This dimer unit takes four states associated with the  $s^z$  eigenvalues of each spin,  $|\sigma^z, \tau^z\rangle$ . We rearrange these four states so that they have the spin-reversal symmetry

$$v_1 = (|\uparrow, \uparrow\rangle + |\downarrow, \downarrow\rangle) / \sqrt{2}, \quad (2)$$

$$v_2 = (|\uparrow, \uparrow\rangle - |\downarrow, \downarrow\rangle) / \sqrt{2}, \quad (3)$$

$$v_3 = (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) / \sqrt{2}, \quad (4)$$

$$v_4 = (|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle) / \sqrt{2}. \quad (5)$$

Here,  $\uparrow$  and  $\downarrow$  denote the  $s^z$  eigenstates. Now, two  $J_1$  bonds and one  $J_3$  bond become a single effective bond connecting the neighboring dimer units, and the  $J_2$  bond contributes only to the inner energy of a dimer unit. We can remove the negative-sign problem by using this representation basis. The Trotter number  $m$  is chosen so that  $\beta(2J_1 + J_3)/m$  varies from 0.35 to 0.15 at each temperature, and the extrapolations to the infinite  $m$  are done. A typical number of Monte Carlo steps is 500 000, divided into ten parts, to see the statistical deviation. The first 50 000 steps are discarded for the equilibrium. The autocorrelation time of the susceptibility is less than an order of unity.

We have performed simulations for several values of  $J_2$  in each choice of the  $J_1$  and  $J_3$  bonds. First, we have set  $J_1 = J_3$  and done simulations thoroughly by changing a value of  $J_2$  from  $-8$  to  $8$  in a step of  $2$ . A rough estimate for the value of  $J_2$  is made at this stage. Then, we proceeded to the other cases,  $J_1 = 0$  and  $J_3 = 0$ .

Figure 2(a) shows the QMC results of the susceptibility compared with the experimental data, and Fig. 2(b) is its low-temperature plot. The experimental data are the minimum susceptibility when the magnetic field is applied in the cleavage plane. The absolute value of the susceptibility depends upon the direction of the field, which can be understood by considering the anisotropy of the  $g$  value.<sup>4</sup> Here, the  $g$  value is determined by comparison at high temperatures,  $T > 100$  K. Error bars of the QMC data are almost negligible. The magnitude of each interaction bond is determined in order that the low-temperature data agree quantitatively with the experiment.

Triangles are the best fit to the experiment in the case of  $J_1 = J_3$ , and the values of the interaction bonds are  $J_1 = J_3 = 8.35$  K,  $J_2 = 6J_1$ , i.e., all the interaction bonds are antiferromagnetic. The  $g$  value  $g = 2.05$ . Circles are those of the ordinary ladder case, and the values are  $J_1 = 12.3$  K,  $J_3 = 0$ ,  $J_2 = 4J_1$ , and  $g = 2.05$ . Crosses are the case of the bond-alternation model:  $J_1 = 0$ ,  $J_3 = 12.9$  K,  $J_2 = 4J_1$ , and  $g = 2.03$ . All three data quantitatively agree with the experiment at all the temperatures. Our estimate for the  $g$  value is also consistent with the electron-spin resonance (ESR) measurement, giving  $g = 2.05$ .<sup>10</sup> Relative errors from the experi-

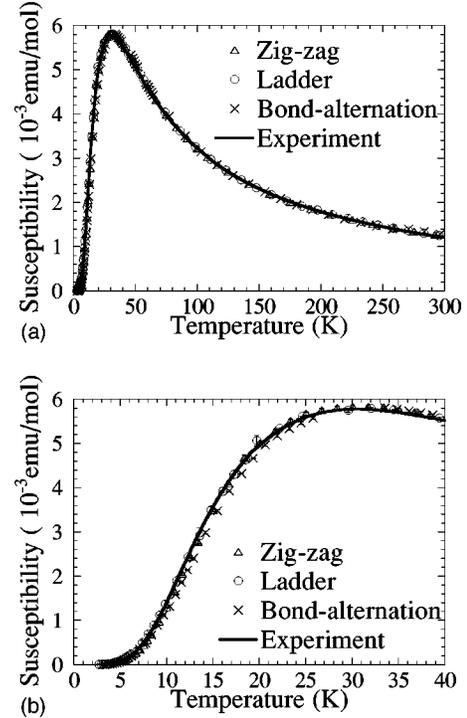


FIG. 2. (a) The QMC results of the susceptibility (symbols) compared with the experimental data (line); (b) its low-temperature plot. The number of the spins is 162 and the open boundary conditions are used. The strength of each interaction bond is ( $\Delta$ ) Zig-zag:  $J_1 = J_3 = 8.35$  K,  $J_2 = 6J_1$ ,  $g = 2.05$ , ( $\circ$ ) Ladder:  $J_1 = 12.3$  K,  $J_3 = 0$ ,  $J_2 = 4J_1$ ,  $g = 2.05$ , and ( $\times$ ) Bond alternation:  $J_3 = 12.9$  K,  $J_1 = 0$ ,  $J_2 = 4J_3$ ,  $g = 2.03$ , respectively.

ment are within 1% in every case, and are smallest in the ‘‘ladder’’ case. However, it is not clear if the small deviations among the three cases are relevant or not, because we have used a very simplified model spin Hamiltonian for a real compound. Systematic errors from an adoption of this model may be the most important ones. Therefore, we cannot determine the strength of each interaction bond from the fitting of the susceptibility data alone. The only common feature known from this plot is that the  $J_2$  bond is strongly dimerized antiferromagnetically, and thus the origin of the gap is the dimer gap.

This conclusion contradicts the prediction by Tanaka *et al.*<sup>4</sup> that  $\text{KCuCl}_3$  is the Haldane chain. Thus, we clarify in the following the difference of the susceptibility in the dimer-gap system and that in the Haldane-gap system. In Fig. 3, we plot a product of the susceptibility and the temperature  $\chi T$  against the temperature. This value is independent from the scale of the interaction bond. We use the logarithmic scale for the temperature axis so that the rescaling of the temperature by changing the values of interaction bonds just causes a parallel shift along the temperature axis. Circles are the data of the dimer-gap system:  $J_1 = J_3 = 8.35$  K,  $J_2 = 6J_1$ ,  $g = 2.05$ , and crosses are those of the Haldane-gap system:  $J_1 = J_3 = 45$  K,  $J_2 = -4J_1$ ,  $g = 2.00$ . These interactions are determined by fitting the low-temperature data, while the  $g$  value is estimated at high temperatures. As seen from this figure, the functional form of  $\chi T$  in the Haldane-gap system cannot be fit to the experiment by any parallel shift.

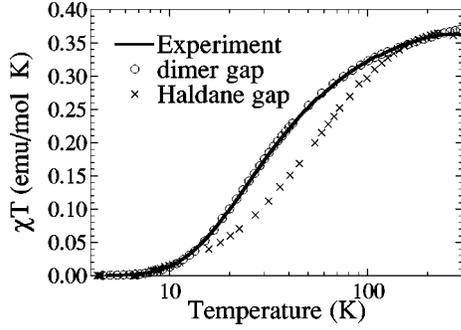


FIG. 3. Product of the susceptibility and the temperature  $\chi T$  is plotted against the temperature. The QMC results of the dimer-gap system ( $\circ$ ) and the Haldane-gap system ( $\times$ ) are compared with the experimental data (line). The strength of each interaction bond is ( $\circ$ ):  $J_1=J_3=8.35$  K,  $J_2=6J_1$ ,  $g=2.05$ , and ( $\times$ ):  $J_1=J_3=45$  K,  $J_2=-4J_1$ ,  $g=2.00$ , respectively.

For an explanation of this difference, let us consider the dimer limit  $J_1=J_3=0$ ,  $J_2>0$ , where the ground state is an array of independent singlet dimers and thus is nondegenerate. When the interactions between singlet dimers ( $J_1$  and  $J_3$ ) are introduced, the ground state is somewhat modified, but still has the nature of the singlet dimer. On the other hand, the ground state in the Haldane limit,  $J_1=J_3=0$ ,  $J_2<0$ , is an array of independent triplet dimers and is highly degenerate. When  $J_1$  and  $J_3$  are switched on, the degeneracy is lifted up, resulting in the unique ground state. The density of states of low-lying excited states are larger than the singlet dimer case, reflecting this high degeneracy of the ground state at  $J_1=J_3=0$ . Therefore, the susceptibility peak in the Haldane system becomes lower and broader than in the dimer system. We may determine the origin of the gap from the full width at half maximum of the susceptibility, or the functional form of  $\chi T$ .

We determine the interaction bonds by the dispersion relation of the excitation energy. This value is sensible to the details of the model. Recently, Kato *et al.*<sup>13</sup> applied the neutron-scattering analysis on this compound, and presented the dispersion relation. We compare our analytic dispersion relation with this experiment.

In our previous paper,<sup>12</sup> we have deduced an expression giving the dispersion of the general double-spin-chain systems as a function of the interaction bonds. There, we employed a single domain-wall variation after the nonlocal unitary transformation<sup>14,15</sup> is applied. This approximation is quite excellent near  $k=\pi$ , checked with the numerical diagonalization results of finite systems, and with exactly known results. On the other hand, it becomes overestimated as the wave number  $k$  approaches zero.

By using the values of the interaction bonds obtained from the susceptibility fitting, we give the dispersion of the excitation energy in Fig. 4. The first excitation is at  $k=\pi$  in the ‘‘zig-zag’’ and ‘‘ladder’’ models, and is at  $k=0$  in the ‘‘bond-alternation’’ model. Within our analysis, the first excitation is always at  $k=\pi$  for  $J_1>\min(J_2,J_3)/2$ , and is otherwise at  $k=0$ , where  $\min(J_2,J_3)$  stands for the minimum value of  $J_2$  and  $J_3$ .

The dispersion of the ‘‘ladder’’ case is consistent with the experimental dispersion parallel to the double chain when the constant wave number perpendicular to the chain  $k_\perp$  is

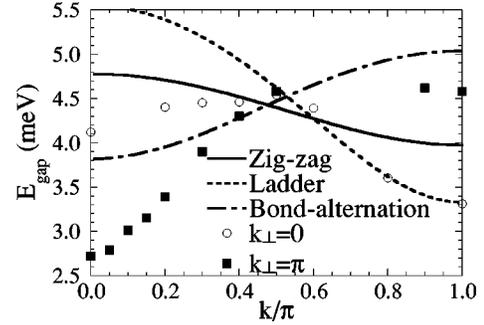


FIG. 4. The dispersion relation of the excited states of the system. Zig-zag:  $J_1=J_3=8.35$  K and  $J_2=6J_1$ , Ladder:  $J_1=12.3$  K,  $J_3=0$ , and  $J_2=4J_1$ , and Bond alternation:  $J_3=12.9$  K,  $J_1=0$ , and  $J_2=4J_3$ , respectively. The neutron-scattering experimental data are plotted by circles for the constant wave number perpendicular to the chain  $k_\perp=0$ , and by solid squares for  $k_\perp=\pi$ .

equal to zero. Our estimate of the gap is  $\Delta/k_B\sim 38$  K, which is a little larger than the results of the magnetization process experiment.<sup>10</sup> So, the ‘‘ladder’’ model may be the most favorable candidate for explaining the  $\text{KCuCl}_3$  at the present stage. However, it should be noticed that the experimental dispersion is dependent upon  $k_\perp$ . If a double-chain is isolated from each other, there should not be the  $k_\perp$  dependences. Therefore, it might be evidence of two-dimensional interaction couplings. This point is left for future study.

One usually fits the susceptibility data to the theoretical expression  $\chi(T)=(1/2\sqrt{\pi aT})\exp(-\Delta/T)$ , given by Troyer *et al.*<sup>9</sup> supposing the form  $\epsilon_k=\Delta+a|k-\pi|^2$  for the magnon dispersion. This expression is valid when  $T\ll\Delta,D$ , where  $D$  is the bandwidth of the magnon dispersion. If we take the effect of the bandwidth into account, we obtain

$$\chi(T)=\frac{e^{-\Delta/T}}{2\pi\sqrt{aT}}\gamma\left(\frac{1}{2},\frac{D}{T}\right), \quad (6)$$

where  $\gamma(x,p)$  is the incomplete  $\gamma$  function defined by

$$\gamma(x,p)\equiv\int_0^p t^{x-1}e^{-t}dt. \quad (7)$$

Since  $D\ll\Delta$  from Fig. 4,  $\chi(T)$  behaves as

$$\chi(T)\sim\begin{cases} \frac{e^{-\Delta/T}}{2\sqrt{\pi aT}}\left(1-\sqrt{\frac{T}{\pi D}}e^{-D/T}\right) & (T\ll D\ll\Delta), \\ \frac{1}{\pi}\sqrt{\frac{D}{a}}\frac{e^{-\Delta/T}}{T}\left(1-\frac{3D}{T}\right) & (D\ll T\ll\Delta). \end{cases} \quad (8)$$

Thus, the expression of Troyer overestimates the susceptibility. In the fitting for  $\text{KCuCl}_3$  by Tanaka *et al.*,<sup>4</sup> the theoretical curve of Troyer severely deviates from the experimental curve for  $T>20$  K, which is well explained by  $D=2.2$  meV=25 K of the ‘‘ladder’’ model in our estimate.

In summary, we have analyzed the susceptibility and the neutron-scattering measurements on the  $\text{KCuCl}_3$  from the theoretical point of view. Large-scale quantum Monte Carlo simulations clarified that this compound is well explained by the double-spin-chain Hamiltonian with strong *antiferromag-*

*netic* dimerization. Since the susceptibility alone is not sufficient to determine all the interaction-bond strengths, we also calculated the dispersion relation of the excited state in comparison with recent neutron-scattering experiments. As long as we restrict our theoretical analysis to the isolated double-spin-chain Hamiltonian, the best one to explain both measurements is the ladder model, which is defined by  $J_1 = 12.3$  K,  $J_2 = 4J_1$ ,  $J_3 = 0$ , and  $g = 2.05$ . This  $g$  value agrees with the ESR measurement.<sup>10</sup> However, the experimental dispersion relation has a strong dependence on the constant wave number perpendicular to the chain,  $k_\perp$ , which cannot be explained by our theoretical analysis on the isolated double-spin-chain model. Thus, the system may have two-dimensional interactions that are not relevant at low temperatures.

The quantum Monte Carlo simulation has become the most realistic method to investigate the various quasi-one-

dimensional compounds that can be expressed by the general double-spin-chain Hamiltonian, even if the system has frustration. Present calculations can be extended to analyze other experiments easily. For example, we comment on that of  $\text{Cu}_2(1,4\text{-Diazacycloheptane})_2\text{Cl}_4$ , recently done by Hammar *et al.*<sup>7</sup> Their susceptibility data are consistent with our calculations down to the lowest temperature that could not be obtained by numerical diagonalization. The choice of the interactions is  $J_1 = J_3 = 2.26$  K,  $J_2 = 6J_1$ , and  $g = 2.04$ .

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