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Susceptibility behavior of $CuGeO_3$: Comparison between experiment and the quantum transfer-matrix approach

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Thermodynamical properties of the one-dimensional $S=1/2$ Heisenberg model with dimerized nearest and uniform next-nearest neighbor interactions are studied by the numerically exact quantum transfer-matrix method and the results are applied to $CuGeO_3$. The Suzuki-Trotter formula is used to obtain a classical system with spin $\sigma=3/2$ and effective interactions between nearest neighbors only. The magnetic susceptibility curve is calculated and compared with experimental results in a wide temperature range, revealing the presence of frustration in the model proposed for $CuGeO_3$. Temperature dependence of the dimerization parameter below the spin-Peierls transition point is also estimated. [S0163-1829(99)12941-2]

INTRODUCTION

Both experimental and theoretical interest in quasi one-dimensional frustrated quantum spin systems has been strongly forced since 1993, when it was shown[1] that the magnetic susceptibility of $CuGeO_3$ measured in all crystal directions drastically drops below $T_{SP}=14.3$ K. It was attributed to the spin-Peierls (SP) phase transition, which manifests itself when a system of quasi-one-dimensional quantum spin chains undergoes dimerization due to lattice distortion. Below the SP transition point T_{SP}, a finite energy gap Δ opens between the nonmagnetic singlet ground state and the first excited triplet state and reaches the maximum value $\Delta \simeq 2.1$ meV at $T=0$ K. Since then, a wide range of experimental measurements have been performed to investigate the nature of the SP transition in the $CuGeO_3$ compound. Among them, as an example, we mention neutron[2,3] and x-ray[4] scattering studies together with nuclear magnetic resonance (NMR) (Ref. 5) and electron spin resonance[6] works. Thermodynamical properties of pure and doped $CuGeO_3$ have been examined in many experiments including specific heat[7,8] and magnetic susceptibility[9–11] measurements.

To describe these properties, a $S=1/2$ one-dimensional antiferromagnetic Heisenberg model of $CuGeO_3$ with nearest neighbor (NN) and next-nearest neighbor (NNN) interactions was proposed,[12,13] with the Hamiltonian in the form

$$H=-J\sum_{i=1}^{N}(S_iS_{i+1}+\alpha S_iS_{i+2})+\sum_{i=1}^{N}(-1)^i\delta S_iS_{i+1}, \tag{1}$$

where N denotes the size of the chain, $J(<0)$ and $\alpha(>0)$ are the NN exchange integral and the ratio of the NNN exchange integral to the NN one, respectively. The parameter δ describes dimerization. Below T_{SP}, the value of δ is nonzero and the alternation of J has to be taken into account.

So far, in order to estimate theoretically the J and α values, full diagonalization has been applied[12–14] to rings with $N\leqslant 18$ (i.e., 9 spin pairs at most). The finite-size data have been extrapolated to the thermodynamic limit and compared to the susceptibility measurement results above the SP transition point. Also, a newly developed density matrix renormalization group (DMRG) technique has been used to estimate the temperature dependence of the dimerization parameter δ in the region below T_{SP}.[15] In addition, the exact diagonalization technique combined with the recursion method[16] was recently applied to chains with $N\leqslant 26$ to investigate the dynamical structure factor $S(\omega,q)$ and to compare the results with the complete spectrum of the inelastic neutron scattering. Some estimates based on *ab initio* calculations of the electronic structure[17,18] have been also reported.

Generally, from the direct calculations and the fitting to the experimental data, the estimates of the coupling spread over the interval $-180\ \mathrm{K}\leqslant J\leqslant -135$ K, whereas the inelastic neutron scattering measurement[2] gives $J\simeq -120$ K. The value of α varies from 0.24 up to 0.45.

In this paper we report new experimental susceptibility measurements and the application of the quantum transfer-matrix (QTM) technique to calculate the thermodynamical properties of $CuGeO_3$ and to evaluate the best-fit values of J and α. This technique is not subject to statistical errors and yields the estimates of the thermodynamical functions in the macroscopic limit, if the transfer matrix is defined in the strip geometry.

QTM TECHNIQUE

In order to perform calculations for the macroscopic chain (infinite N value), we need to reverse the transfer from the chain to the Trotter direction. Although the standard QTM algorithm based on the Trotter formula fails for $\alpha\neq 0$, we can accomplish this in the following way.

First, we divide the Hamiltonian (1) into two parts $H=H_A+H_B$,

$$H_A=H_{1,4}+H_{5,8}+H_{9,12}+\cdots,$$

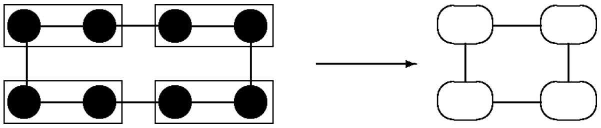

FIG. 1. The replacement of the $S=1/2$ spin pair by the effective $\sigma=3/2$ spin.

$$H_B=H_{3,6}+H_{7,10}+H_{11,14}+\cdots, \tag{2}$$

in which $H_{i,i+3}$ describes the interactions inside the four-spin block beginning at the ith site of the quantum chain. Then we use the Trotter expansion to obtain the mth classical approximation Z_m of the partition function Z,

$$Z_m=\sum_{\{S_{r,i}\}}\prod_{r=1}^{m}\prod_{i=1}^{N/4}L_{2r-1,4i-3}(S)L_{2r,4i-1}(S), \tag{3}$$

where

$$L_{r,i}(S)=\langle S_{r,i}\ldots{}_{r,i+3}|e^{-\beta/mH_{i,i+3}}|S_{r+1,i}\ldots S_{r+1,i+3}\rangle. \tag{4}$$

Z_m is now the partition function of the classical system of $2m\times N$ spins, with effective interactions grouped into eight-spin blocks. For this system, we define a global transfer matrix between the rth and $(r+1)$th rows and expand it into the product of four-spin local transfer matrices $L_{r,i}(S)$.

Second, we introduce an effective classical spin $\sigma=3/2$ and, as shown in Fig. 1, we replace each pair of $S=1/2$ spins, distributed along a given row r, by the spin σ

$$(S_{r,i},S_{r,i+1})\rightarrow\sigma_{r,j}, \quad \text{where } j=1\ldots N/2. \tag{5}$$

At the same time, the local transfer matrix $L_{r,i}(S)$ can be expressed as $L_{r,j}(\sigma)$, i.e., can be rewritten in the basis of σ. Now, we can reverse the transfer direction by defining the new local transfer matrix $V_{r,r+1}$

$$\begin{aligned}\langle\sigma_{r,j}\sigma_{r+1,j}|V_{r,r+1}|\sigma_{r,j+1}\sigma_{r+1,j+1}\rangle\\ =\langle\sigma_{r,j}\sigma_{r,j+1}|e^{-\beta/mH_{j,j+1}}|\sigma_{r+1,j}\sigma_{r+1,j+1}\rangle.\end{aligned}$$

The global transfer matrices W_1 and W_2 (for odd and even columns of spins, respectively) can be expressed by the corresponding products of $V_{r,r+1}$[19]. Finally, the mth classical approximant to the partition function of Eq. (1) can be written in the form

$$Z_m=\mathrm{Tr}[W_1W_2]^{N/4}. \tag{6}$$

For an infinite system (i.e., when $N\rightarrow\infty$) the free energy per spin f_m is simply given by the maximum eigenvalue $\lambda_{max}(m)$ of the transfer matrix W_1W_2. For this reason, we have calculated $\lambda_{max}(m)$ using the iteration method.

Thermodynamical values of the initial quantum system were found by numerical differentiation of each approximant f_m and extrapolations of the results to infinite Trotter number m. The asymptotic behavior of a given thermodynamical value A_m as $m\rightarrow\infty$ can be written in the form

$$A_m=\sum_{n=1}^{\infty}\frac{a_n}{m^{2n}}+A_\infty. \tag{7}$$

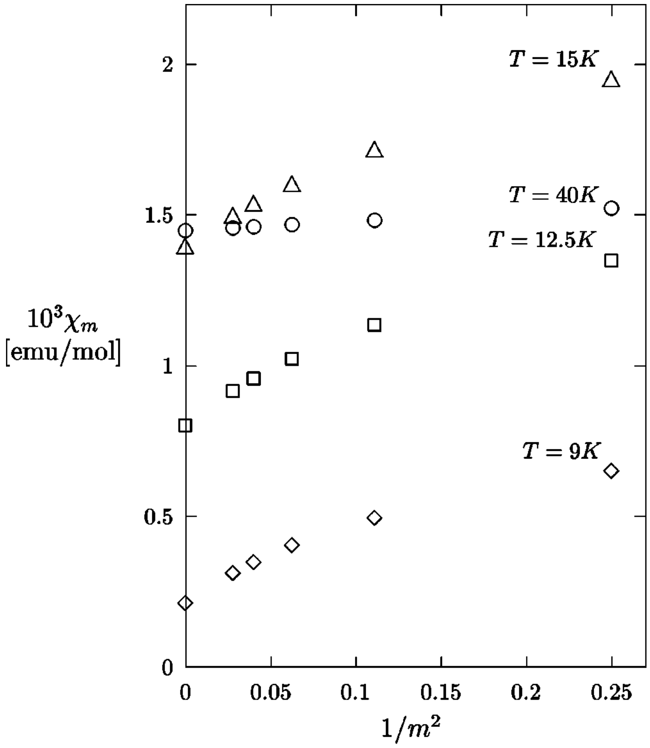

FIG. 2. The convergence of our numerical data at different temperatures. The Trotter number is in the range from $m=2$ to $m=6$. Our best estimates for $m=\infty$ are also plotted.

When m values are large enough, the linear behavior of A_m with respect to $1/m^2$ is often revealed.[20,21]

The examples of our numerical susceptibility data convergence at different temperatures are presented in Fig. 2. Above T_{SP}, the linear extrapolations in $1/m^2$ can be performed so that we reach an accuracy higher than 2%. In the region below the critical point, the convergence is deteriorated due to the nonlinear behavior of the approximants and the uncertainties in the extrapolations increase to about 10% at $T=9$ K.

RESULTS

In order to estimate the J and α values we calculated the magnetic susceptibility approximants χ_m along the c crystal direction for $m\leqslant 6$ and compared the extrapolated (the limit $m\rightarrow\infty$) values to the very well calibrated experimental results performed on a single crystal of pure $\mathrm{CuGeO_3}$, similar to those of Grenier *et al.*[10] We chose the g_c factor equal to 2.07, i.e., the value found from the NMR experiment.[5] The experimental values for a and b crystal directions can be revealed from our results by the simple rescaling according to the law $\chi_x/\chi_c=(g_x/g_c)^2$, where $x=a,b$.

To estimate the J and α values, we performed the calculation in the nondimerized phase. The best fit was obtained for the following set of parameters:

$$J=-166\text{ K}\pm 2\text{ K} \quad \text{and} \quad \alpha=0.36\pm 0.01. \tag{8}$$

The extrapolated data are given in Fig. 3 by full circles. Our results for the parameters (8) fit very well the experimental

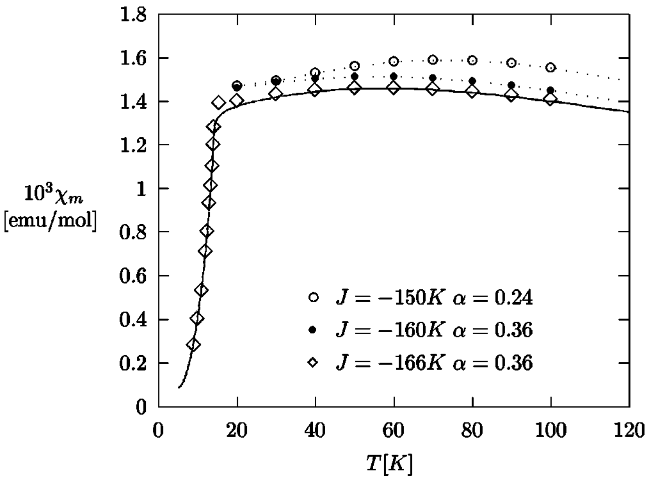

FIG. 3. Temperature behavior of the experimental and theoretical magnetic susceptibility for $CuGeO_3$. Solid and open circles mark the QTM estimates for the previous parameters. Our best fit is plotted with diamonds. Solid line corresponds to present experimental measurements along the c direction.

data, drawn by the full line, down to the low-temperature region. The QTM data calculated for the parameters given in the legend are also plotted.

Our estimate of α proposed for $CuGeO_3$ is significantly greater than the critical value $\alpha_c = 0.2411$ (Ref. 13) and confirms the existence of frustration in the spin model proposed for $CuGeO_3$.

Parameters (8) are fully consistent with those coming from other numerical approaches. Especially, we would like to refer to the exact diagonalization performed above 20 K by Fabricius *et al.*[14] and the latest DMRG results of Klümper *et al.*[15] Results of both mentioned approaches were compared to experimental data similar to our measurements.[22] The results obtained for different crystal axes and with a slightly smaller Landé factor are in excellent agreement. Our values are also consistent with the parameters of Riera and Dobry[12] obtained on a basis of a comparision with the first experimental results of Hase *et al.*[1]

Subsequently, using the parameters (8), we have fitted the experimental susceptibility curve below T_{SP} (see Fig. 3) imposing the temperature dependence of the dimerization parameter δ. The estimates of δ are presented in Fig. 4 together with the error bars. They show a sharp increase in the region close to T_{SP} and saturation as T tends to zero. This behavior is in good agreement with the power law for the gap $\Delta \sim \delta^{2/3}$[4]. In the zero-temperature limit we received $\delta(0) = 0.022 \pm 0.002$ (in units of J). The values of δ obtained earlier from the exact diagonalization technique for chains with a fixed size up to $N=16$ (Refs. 12 and 13) are slightly different: 0.014 ($J=-160$ K) and 0.030 ($J=-150$ K), respectively. However, we would like to emphasize that our fitting was performed for a much wider temperature range including the SP phase and no errors occurred due to the finite-size effect. In fact, our estimate of the displacement $\delta(0)$ compares well with the DMRG result of Klümper *et al.* $\delta(0) = 0.026$. The latter was found assuming an extra elastic term in the Hamiltonian (1).

According to the mean-field theory $\delta(T) = \Delta(T)/pJ$, where $p = 1.637$.[23] Substituting $\delta(0) = 0.022$, we obtained $\Delta(0) \simeq 0.5$ meV, the value four times smaller in comparison to those coming from experimental measurements. A similar discrepancy is common for the results based on calculations of thermodynamical properties, but may be treated as an independent suggestion that the spin frustration plays an important role in formation of Δ.

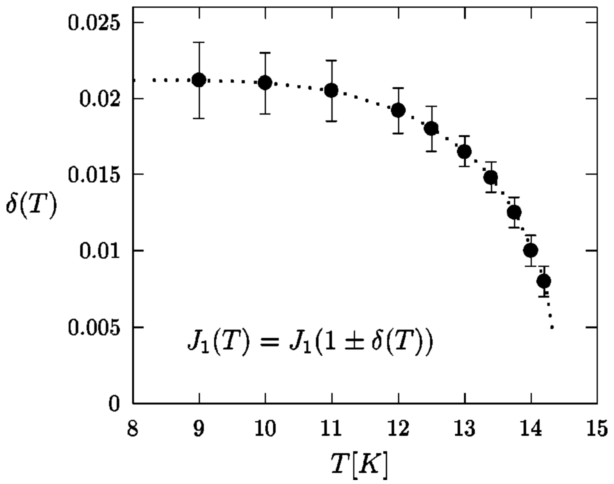

FIG. 4. The temperature dependence of the dimerization parameter δ in units of J.

Quantitatively, our result does not follow the estimates of Yokoyama and Saija[16] ($J=-180$ K, $\alpha=0.45$, $\delta(0) = 0.001$) based on a spin dynamics investigation. This discrepancy may stem from the fact that both evaluations are made at different temperatures and the results describe different physical properties. Also, it is understandable that the unexpectedly strong frustration value obtained by Yokoyama has to reduce the dimerization parameter δ in order to keep a reasonable value of the spin gap Δ.

CONCLUSIONS

We have performed the single-crystal susceptibility measurements for pure $CuGeO_3$ and have shown that the modified QTM technique can be successfully used for characterization of frustrated $S=1/2$ antiferromagnetic quantum chains. The application to the SP compound $CuGeO_3$ gives numerical results fully consistent with the experimental susceptibility data within 2% in the nondimerized phase and the best-fit values of the exchange integrals very close to those of Klümper *et al.*

Finally, we would like to point out the important advantage of the QTM technique that is that it can be adopted for the doped systems.

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[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[2] M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B **50**, 6508 (1994).

[3] L. P. Regnault, M. Äin, B. Hennion, G. Dahlenne, and A. Revcolevschi, Physica B **213&214**, 278 (1995).

[4] Q. J. Harris, Q. Feng, R. J. Birgenau, K. Hirota, K. Kakurai, J. E. Lorenzo, G. Shirane, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, Phys. Rev. B **50**, 12 606 (1994).

[5] K. Le Dang, G. Dahlenne, J.-P. Renard, A. Revcolevschi, and P. Veillet, Solid State Commun. **91**, 927 (1994).

[6] M. Honda, T. Shibata, K. Kindo, S. Sugai, T. Takeuchi, and H. Hori, J. Phys. Soc. Jpn. **65**, 691 (1996).

[7] J. C. Lasjaunias, P. Monceau, G. Remenyi, S. Sahling, G. Dahlenne, and A. Revcolevschi, Solid State Commun. **101**, 677 (1997).

[8] H. Kuroe, J. Sasaki, T. Sekine, N. Koide, Y. Sasago, K. Uchinokura, and M. Hase, Phys. Rev. B **55**, 409 (1997).

[9] J. P. Pouget, L.-P. Regnault, M. Aïn, B. Hennion, J.-P. Renard, P. Veillet, G. Dahlenne, and A. Revcolevschi, Phys. Rev. Lett. **72**, 4037 (1994).

[10] B. Grenier, J.-P. Renard, P. Veillet, C. Paulsen, R. Calemczuk, G. Dahlenne, and A. Revcolevschi, Phys. Rev. B **57**, 3444 (1998).

[11] P. E. Anderson, J. Z. Liu, and R. N. Shelton, Phys. Rev. B **56**, 11 014 (1997).

[12] J. Riera and A. Dobry, Phys. Rev. B **51**, 16 098 (1995).

[13] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).

[14] K. Fabricius, A. Klümper, U. Löw, B. Büchner, T. Lorenz, G. Dahlenne, and A. Revcolevschi, Phys. Rev. B **57**, 1102 (1998).

[15] A. Klümper, R. Raupach, and F. Schönfeld, Phys. Rev. B **59**, 3612 (1999).

[16] H. Yokoyama and Y. Saiga, J. Phys. Soc. Jpn. **66**, 3617 (1997).

[17] L. F. Mattheiss, Phys. Rev. B **49**, 14 050 (1994).

[18] S. Zagoulaev and I. I. Tupitsyn, Phys. Rev. B **55**, 13 528 (1997).

[19] F. Esposito and G. Kamieniarz, Phys. Rev. B **57**, 7431 (1998).

[20] G. Kamieniarz, R. Matysiak, A. Caramico D'Auria, F. Esposito, and U. Esposito, Phys. Rev. B **56**, 645 (1997).

[21] G. Kamieniarz, Phase Transit. **57**, 105 (1996).

[22] A. Revcoleschi and G. Dahlenne, Adv. Mater. **5**, 9657 (1993).

[23] J. W. Bray, H. R. Hart, L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, and J. C. Bonner, Phys. Rev. Lett. **35**, 744 (1975).