## Magnetic susceptibility in the spin-Peierls system CuGeO<sub>3</sub>

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We study numerically, using a one-dimensional Heisenberg model coupled to the lattice in the adiabatic approximation, the spin-Peierls transition in the linear  $\operatorname{Cu}^{2+}$  spin- $\frac{1}{2}$  chains in the inorganic compound CuGeO<sub>3</sub>, which has been recently observed experimentally. We suggest that the magnetic susceptibility, the temperature dependence of the spin gap, and the spin-Peierls transition temperature of this material can be reasonably described by including nearest- and next-nearest-neighbor antiferromagnetic interactions along the chain. We estimate that the nearest-neighbor exchange parameter J is approximately 160 K, and that the next-nearest-neighbor exchange parameter is approximately 0.36J.

The purpose of the present study is to describe the spin-Peierls transition in the linear  $\operatorname{Cu}^{2+}$  spin- $\frac{1}{2}$  chains in the inorganic compound  $\operatorname{Cu}\operatorname{GeO}_3$  which has been recently observed.<sup>1-4</sup> The transition temperature  $T_c \approx 14$  K has been inferred from the rapid drop of the magnetic susceptibility towards zero, indicating the opening of an energy gap for singlet-triplet spin excitations.<sup>5,6</sup> The existence of this transition was also confirmed by measurements of the heat capacity,<sup>7</sup> which exhibits a sharp anomaly at  $T_c$  corresponding to a second-order phase transition. The effect of a magnetic field on the transition temperature has also been measured,<sup>4</sup> and the experimental results were compared with the theoretical predictions obtained by Cross and Fisher,<sup>8</sup> confirming the spin-Peierls nature of the observed transition.

We adopt a simple model Hamiltonian consisting of antiferromagnetic Heisenberg interactions along a chain. Since a one-dimensional (1D) spin system has no phase transition at finite temperature because of fluctuations, it is necessary to take into account interchain couplings in order to describe the spin-Peierls transition. These interchain couplings are usually taken to be the coupling to the three-dimensional phonons, in a mean-field sense. The effect of interchain interactions was studied by Inagaki and Fukuyama.<sup>9</sup> We consider the spin-lattice coupling in the adiabatic approximation. The study was performed by exact diagonalization on finite chains. We suggest that in order to obtain a reasonable fit of the magnetic susceptibility a next-nearest-neighbor antiferromagnetic interaction along a chain should be included in the model. If the predictions resulting from our model are confirmed by additional experimental work, the  $CuO_2$ chains in this compound would be one of the few experimental realizations of a 1D spin-1/2 Heisenberg antiferromagnet with competing interactions.<sup>10</sup> The present study should also be considered as part of a current theoretical effort to understand magnetic properties, in particular the singlet-triplet spin gap, in low-dimensional spin systems such as  $Sr_2Cu_4O_6$  and  $(VO)_2P_2O_7$ .<sup>11</sup>

Analytical studies of spin-Peierls transitions in spin-1/2 antiferromagnetic chains, based on the transforma-

tion of Pauli spin operators to spinless fermion operators, have shown that the homogeneous magnetic chain is unstable with respect to dimerization as the temperature decreases and a spin gap appears as a result of such dimerization.<sup>12–14</sup> There has been also an intensive work, both analytical and numerical, on the half-filled one-dimensional Hubbard-Peierls model, which reduces to the antiferromagnetic Heisenberg model in the large-Ulimit.<sup>15</sup> The Hubbard-Peierls model has been widely used to model conducting polymers and other 1D electronphonon systems.

The 1D microscopic Hamiltonian for the spin degrees of freedom that we consider is

$$H_{s} = J_{1} \sum_{i} \mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i} + J_{2} \sum_{i} \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1} , \qquad (1)$$

where the index *i* runs over the lattice cells (i = 1, ..., N/2, N: number of sites) with periodic boundary conditions. We assume linear dependence of the exchange integrals on the atomic displacements u, so that

$$J_1 = J (1 + \gamma u), \quad J_2 = J (1 - \gamma u) ,$$
 (2)

where  $\gamma$  is a constant. It is convenient to introduce the dimensionless quantity  $\delta = \gamma u$ .

The spin-lattice interaction enters in this model only through  $J_1$  and  $J_2$ . The underlying physical picture is the following. The spin chains in  $CuGeO_3$  are oriented along the c direction (see, for example, Fig. 1 in Ref. 3). According to experimental results<sup>2</sup> the relevant lattice distortions are observed along the b axis, perpendicular to the chain direction. In this situation, the variables uin Eq. (2) correspond to oxygen displacements below the spin-Peierls transition temperature.<sup>4</sup> It has been recently reported<sup>3</sup> that there is a comparable shift of the Cu ions along the c direction. The exchange constants  $J_1$  and  $J_2$ , calculated following the path Cu-O-Cu, have in principle a complicated dependence on the displacement u. Then, the expressions for  $J_1$  and  $J_2$  given above should be considered as a first-order approximation in u (or  $\delta$ ) of this complicated function. Besides, the application of Hamiltonian (1) to this material implies that we are

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neglecting the two-dimensional (2D) interchain exchange interactions which have a magnitude of approximately 10% of the intrachain coupling.<sup>5</sup>

The main difference between the Hamiltonian given by Eqs. (1) and (2), and the one corresponding to the dimerized or alternating bond chain,<sup>16</sup> is that in the former both  $J_1$  and  $J_2$  are temperature dependent because  $\delta = \delta(T)$ . We calculate the temperature dependence of these couplings by minimizing at each temperature the free energy  $\mathcal{F}$  of the total Hamiltonian  $H = H_s + H_{\rm ph}$  with respect to  $\delta$  (adiabatic approximation). Then  $\mathcal{F}_{\rm min}(T) = \mathcal{F}(\delta_{\rm eq}(T))$ . The elastic term of the Hamiltonian is

$$H_{\rm ph} = \frac{1}{2}NKu^2 = \frac{1}{2}\frac{NK}{\gamma^2}\delta^2$$
, (3)

where K is the elastic constant. It is also customary to introduce the dimensionless spin-lattice coupling constant  $\lambda = J\gamma^2 K^{-1}$ . This method of calculation was devised by Beni and Pincus<sup>17</sup> for their study of the spin-Peierls transition in a spin chain with XY interactions. For a finite chain, and for a given set of parameters J and  $\lambda$ , once we have determined the equilibrium displacement  $\delta_{eq}$  at each temperature, any thermodynamical quantity can be computed in the dimerized region.

The first stage of our study consisted in estimating the parameters J and g by fitting the experimental data for the susceptibility<sup>1</sup> with the theoretical curve in the uniform or nondimerized  $(J_1 = J_2 = J)$ , region. We computed the susceptibility by generating all energy levels  $E_i$  and their multiplicities  $d_i$  in each sector of fixed total  $S_z$ , using a Householder algorithm. The susceptibility was then obtained through its relation to the expected squared magnetization, summed over energy levels and total  $S_z$  sectors;

$$\chi(T) = g^2 \mu_B^2 \beta \frac{\sum_{S_z} S_z^2 \sum_i d_i e^{-\beta E_i}}{\sum_{S_z} \sum_i d_i e^{-\beta E_i}} .$$
(4)

This approach has the advantage that explicit eigenvectors are not required.

The observed average g factor is approximately 2.14 with a slight anisotropy along the a, b, and c axis. The experimental data have a broad maximum near 56 K (see Fig. 1). A fitting of these data using the uniform Heisenberg model reproduces the position of this maximum of the susceptibility if the exchange constant J is chosen to be 88 K.<sup>1</sup> However, as it can be seen in this reference the overall fitting is quite poor. A somewhat better fitting can be achieved by choosing  $J = 170 \text{ K.}^{18}$  However, for  $T \leq 150~{
m K}$  the fitting is still quite poor. We have seen numerically that there is no satisfactory fitting of the experimental data in the region  $T > T_{max} = 56$  K using a nearest-neighbor Heisenberg model. One of the simplest extensions of this model is to include in the spin part of the Hamiltonian a next-nearest-neighbor interactions term:

$$H_{2n} = J' \sum_{j} \mathbf{S}_{j} \cdot \mathbf{S}_{j+2} , \qquad (5)$$

where the index j runs over the lattice sites (j = 1, ..., N). The possibility of an antiferromagnetic (J' > 0) secondneighbor coupling through the Cu-O-O-Cu exchange path was suggested in Ref. 2. Another possibility is to consider the interchain coupling which would lead to a 2D model. Taking into account the underlying physical picture discussed above, it is reasonable to assume that J' is independent of u at least in first-order approximation.

We determined J by imposing that the maximum in the susceptibility is at 56 K as indicated in Ref. 1. Then, we determined the ratio  $\alpha_2 = J'/J$  in order to fit the maximum of the susceptibility  $\chi_{\text{max}} = \chi(T_{\text{max}})$ . For this fitting we chose the susceptibility measured in a polycrystal sample<sup>18</sup> shown in Fig. 1. In this figure we also reproduce the magnetic susceptibility measured on a single crystal<sup>1</sup> along the a, b, and c axis. Taking into account this dispersion of the data, we conclude that a reasonable fit is obtained with the following set of parameters:



FIG. 1. The magnetic susceptibility of CuGeO<sub>3</sub>. Experimental curves labeled a, b, and c, obtained on a single crystal, are from Ref. 1. The experimental curve with a dashed line corresponds to measurements on a polycrystal (Ref. 18). The solid curve is a theoretical one corresponding to the Heisenberg model with nearest- and next-nearest-neighbor interactions, with  $\alpha_2 = 0.36$ , obtained numerically on a chain with 16 sites. In the inset, the theoretical susceptibility obtained for lattices with even and odd number of spins for T < 30 K are shown.

$$J = 160 \, {
m K}, \ \ lpha_2 = 0.36 \ .$$

To simplify the calculations, we have taken g equal to 2.00. This value of g, which is somewhat smaller than the experimental value, should be considered as an effective value since we are neglecting the interchain couplings. Notice that the temperature region where we are fitting the available experimental data is still far from the asymptotic regime described by the Curie law. The effect of the neglected interchain coupling on the fitting parameters has been discussed in the literature (see, e.g., Refs. 16 and 9). The results for the calculated susceptibility and the experimental data are shown in Fig. 1. In both theoretical and experimental data a contribution from the orbital part of the susceptibility,  $\chi^{\rm orb} = 1.5 \, 10^{-4} \, {\rm emu/mole}$  has been added. In this temperature region,  $T > T_{max}$ , the finite size effects are negligible and already for N = 12 the results do not vary by taking larger clusters. For temperatures smaller than  $T_{max}$  but in the uniform region, i.e., above the spin-Peierls transition temperature, there are strong finite size effects. The magnitude of these finite size effects can be seen in the inset of Fig. 1 where we show the susceptibility below 30 K for N = 8, 10, 12, 14, and 16, andN = 9, 11, 13, and 15.

A possible unwanted feature of the Heisenberg model with nearest- and next-nearest-neighbor interactions is the presence of a temperature-independent spin gap, i.e., in the absence of dimerization. This spin gap can be inferred from an exact solution at zero temperature found by Majumdar and Ghosh<sup>19</sup> and was confirmed by subsequent numerical work. Recent studies on this problem indicate that for  $\alpha_2 \geq 0.25$  there is a finite singlet-triplet gap.<sup>20</sup> For  $\alpha_2 = 0.36$ , we have calculated the spin gap at zero temperature on finite lattices with  $N \leq 24$  spins. To extrapolate to the bulk limit we adopted the form predicted by spin-wave theory,<sup>21</sup> or alternatively, the essentially equivalent law,

$$\Delta(N) = \Delta_{\infty} + \frac{c}{N^2} . \tag{6}$$

The resulting extrapolated value of the spin gap is approximately equal to  $0.015 \pm 0.005$  in units of J, or  $2.4 \pm 0.8$  K, much smaller than the smallest measured value for the CuGeO<sub>3</sub>.<sup>4</sup>

The second stage in the calculation was the estimation of the coupling constant  $\lambda$ . In order to do this estimation, we chose another piece of experimental data, the singlet-triplet spin gap at zero temperature. The fitting of these data is very convenient from the numerical point of view since at T = 0 we can diagonalize larger lattices using the Lanczos algorithm. Using the spin part of the Hamiltonian given by Eqs. (1) and (5), we first determined the value of  $\delta$  that reproduces the experimental singlet-triplet spin gap, which is  $\approx 2.15 \text{ meV}$  (from Ref. 4) or 0.153 in units of J = 160 K. Results for the spin gap for several values of  $\delta$  and for several sizes are shown in Fig. 2(a). The extrapolation of the spin gap to the bulk limit for each value of  $\delta$  was also done using Eq. (6). The extrapolated spin gaps as a function of  $\delta$  are shown in Fig. 2(b). A quadratic interpolation gives the final result:  $\delta_{eq}(T=0) = 0.014 \pm 0.001$ .

Then, for each lattice size N = 8, 10, ..., 22 and for  $\delta = 0.014$ , we computed the inverse of the coupling constant  $\lambda(N)^{-1}$  that minimizes the ground-state energy of the total Hamiltonian,  $H_s + H_{2n} + H_{\rm ph}$ . The results are shown in Fig. 2(c). Finally, by extrapolating  $\lambda(N)^{-1}$  to the bulk limit we obtain  $\lambda^{-1} = 21.3 \pm 0.5$  or  $\lambda \approx 0.05$ .

Now, all the parameters of the Hamiltonian have been determined and we like to check the validity of this model by reproducing other experimental results or predicting the value of properties still not experimentally measured. Alternatively, the values of J = 160 K and  $\lambda \approx 0.05$  could



FIG. 2. (a) Spin gap (in units of J), at T = 0, for the dimerized Heisenberg model with nearest- and next-nearestneighbor interactions as a function of the inverse of the lattice size and for several values of  $\delta$ . (b) Spin gap in units of J, at T = 0, as a function of  $\delta$  in the bulk limit. The diamond indicates the point corresponding to the experimental value of the spin gap. (c) Inverse of the adimensional spin-lattice coupling constant  $\lambda$  as a function of the inverse of the lattice size. The dashed line corresponds to a quadratic extrapolation which leads to  $\lambda^{-1} \approx 21.3$  in the bulk limit.





FIG. 3. (a)  $\delta_{eq}$  (see text) as a function of the temperature for N=12, 14, and 16. (b) Spin gap as a function of the temperature for N=12, 16, and 20. Experimental data from Ref. 4 are indicated with solid circles.

be determined independently by other experiments.

The first and most obvious check of the consistency of this model is the calculation of the spin-Peierls transition temperature  $T_c$ . Experimentally,  $T_c \approx 14$  K. To estimate  $T_c$  we computed the free energies for each lattice size N, and then, we minimized the free energy to determine  $\delta_{eq}(T, N)$  as explained above.  $T_c(N)$  is the value of the temperature at which the dimerization begins. For each lattice size, we used  $\lambda(N)^{-1}$  calculated previously. Results for the calculation of  $\delta_{eq}(T, N)$  for N = 12, 14, and 16 are shown in Fig. 3(a). These curves have some resemblance with the experimental data for the lattice contraction  $\Delta_b$  as shown in Fig. 4 of Ref. 4. In fact,  $\Delta_b$  is related to the atomic displacements u of Eq. (2) and hence to  $\delta_{\rm eq}$ . The spin-Peierls transition temperature, calculated for N = 16, is approximately 10.5 K, which is reasonably close to the experimental value of 14 K. We have not yet attempted an extrapolation of  $\delta_{\rm eq}(T,N)$  and  $T_c(N)$  to the bulk limit.<sup>22</sup>

As stated above, once  $\delta_{eq}(T, N)$  has been computed, any thermodynamical quantity can be calculated in the dimerized region. In the first place, we estimated the



FIG. 4. (a) Magnetic susceptibility, in arbitrary units, near the spin-Peierls transition for N=12, 14, and 16 as a function of the temperature. The solid (dashed) curves correspond to the nondimerized (dimerized) Heisenberg chains. (b) Comparison of the theoretical susceptibility obtained for the 16-site chain with experimental data from Ref. 1 obtained with a magnetic field parallel to the c axis.

spin gap as a function of T for N = 12, 16, and 20. To simplify this calculation we adopted for the three lattices  $\delta_{eq}(T, N)$  corresponding to N = 16. At each temperature, we computed the spin gap as the zero-temperature singlet-triplet gap of the model with  $\delta = \delta_{eq}(T, N)$ . The results are shown in Fig. 3(b) together with the experimental data from Ref. 4. Although there are strong finite size effects there is a reasonable tendency of the theoretical data towards the experimental ones.

Finally, we have computed the magnetic susceptibility near the spin-Peierls transition, for N=12, 14, and 16. The results are shown in Fig. 4(a,b). In Fig. 4(a), it can be seen that the susceptibility for each lattice size decays as T goes to zero more rapidly for the dimerized Heisenberg model than for the uniform one, which is consistent with a larger spin gap in the dimerized case. Notice that for a *finite* chain there is always a finite gap even in the absence of dimerization and for J' = 0. As the lattice size is increased, the spin gap in the dimerized model remains finite while the spin gap of the uniform model drops to a small value (due to the presence of J'). This behavior explains the fact that the difference between the dimerized and the uniform curves is larger as the lattice size is increased, as can be seen in this figure.

In Fig. 4(b), we compare the theoretical susceptibility obtained for the 16-site chain with experimental data from Ref. 1 obtained with a small magnetic field parallel to the c axis. The spin-Peierls transition temperature calculated previously, is shown with an arrow. The agreement between theoretical and experimental results is quite good taking into account the approximations involved and the strong finite size effects expected in this low-temperature region.

In summary, we described the magnetic susceptibility, the temperature dependence of the spin gap, and the spin-Peierls transition temperature of the CuGeO<sub>3</sub> using a one-dimensional antiferromagnetic Heisenberg model with nearest- and next-nearest-neighbor interactions coupled to the lattice in the adiabatic approximation. We obtained a quite satisfactory overall agreement with experimental results with only three free parameters. This agreement gives in turn support to the interpretation of the observed features as a spin-Peierls transition. The nearest-neighbor exchange is approximately equal to 160 K, and the ratio of next-nearest- to nearestneighbor exchange constants is approximately 0.36. This value of the parameter  $\alpha_2$  would imply a spin gap of the order of 2.4 K, even in the absence of dimerization. If this spin gap is not detected experimentally, it is quite apparent that one should necessarily adopt a two-dimensional model. In fact, some small discrepancies between our model and experiment should be attributable to weak interchain coupling as well to a slight spin anisotropy. In particular, the calculated transition temperature could be even lower if fluctuation effects are included in our treatment of the lattice distortion. However, we do not think that it is relevant to include these effects before confirmation of the main consequences derived from the present model. Details of the calculations and a systematic study of finite size effects are discussed in an enlarged version of this paper.<sup>22</sup>

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- <sup>1</sup>M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993). See also M. Hase *et al.*, Phys. Rev. B **48**, 9616 (1993).
- <sup>2</sup>J. E. Lorenzo et al., Phys. Rev. B 50, 1278 (1994).
- <sup>3</sup>K. Hirota et al., Phys. Rev. Lett. **73**, 736 (1994).
- <sup>4</sup>Q. J. Harris et al., Phys. Rev. B 50, 12606 (1994).
- <sup>5</sup>M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B **50**, 6508 (1994).
- <sup>6</sup>T. M. Brill et al., Phys. Rev. Lett. 73, 1545 (1994).
- <sup>7</sup>H. Kuroe *et al.*, J. Phys. Soc. Jpn. **63**, 365 (1994); S. Sahling *et al.*, Solid State Commun. **92**, 423 (1994).
- <sup>8</sup>M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979); M. C. Cross, *ibid.* **20**, 4606 (1979). The theory of Cross and Fisher has been also applied to organic spin-Peierls compounds. See, e.g., J. C. Bonner *et al.*, Phys. Rev. B **35**, 1791 (1987).
- <sup>9</sup>S. Inagaki and H. Fukuyama, J. Phys. Soc. Jpn. **52**, 877 (1983).
- <sup>10</sup>J. C. Bonner, in Magneto-structural Correlations in Exchange Coupled Systems, edited by R. D. Willet et al., NATO ASI Series (Reidel, Dordrecht, 1985), p. 157.

- <sup>11</sup>See, e.g., T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).
- <sup>12</sup>E. Pytte, Phys. Rev. B 10, 4637 (1974).
- <sup>13</sup>L. N. Bulaevskii, A. I. Buzdin, and D. I. Khomski, Solid State Commun. 27, 5 (1978).
- <sup>14</sup>J. W. Bray et al., in Extended Linear Chain Compounds, edited by J. S. Miller (Plenum, New York, 1983), Vol. 3, pp. 353-415.
- <sup>15</sup>See, e.g., D. K. Campbell, J. Tinka Gammel, and E. Y. Loh, Jr., Phys. Rev. B **42**, 475 (1990), and references therein.
- <sup>16</sup>J. C. Bonner *et al.*, Phys. Rev. B **27**, 248 (1983).
- <sup>17</sup>G. Beni and P. Pincus, J. Chem. Phys. 57, 3531 (1972).
- <sup>18</sup>H. Hori et al., J. Phys. Soc. Jpn. 63, 18 (1994).
- <sup>19</sup>C. K. Majumdar and D. K. Ghosh, J. Math. Phys. **10**, 1388 (1969). An extension of the exact solution found by these authors is discussed by B. S. Shastry and B. Sutherland, Phys. Rev. Lett. **47**, 964 (1981).
- <sup>20</sup>K. Okamoto and K. Nomura, Phys. Lett. A **169**, 433 (1992).
- <sup>21</sup>K. Sano and K. Takano, J. Phys. Soc. Jpn. **62**, 3809 (1994).
- <sup>22</sup>A. Dobry, A. Greco, S. Koval, and J. Riera (unpublished).