# Reexamination of the microscopic couplings of the quasi-one-dimensional antiferromagnet $CuGeO_3$

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Experimental data for the magnetic susceptibility and magnetostriction of $CuGeO_3$ are analyzed within a one-dimensional antiferromagnetic model with nearest-($J_1$) and next-nearest-neighbor interactions ($J_2$). We show that the ratio of the exchange constants in the antiferromagnetic chains of $CuGeO_3$ amounts to $J_2/J_1 = 0.354(0.01)$, i.e., it is significantly larger than the critical value for the formation of a spontaneous gap in the magnetic excitation spectrum without lattice dimerization. The susceptibility data are reproduced by our numerical results over the temperature range from 20 to 950 K to a high degree of accuracy for $J_1 = 80.2(3.0)$ and $J_2 = 28.4(1.8)$. The pressure dependence of the exchange constants is estimated from magnetostriction data. Furthermore, the specific-heat data are checked for consistency against the calculated entropy of the above model. [S0163-1829(98)06002-0]

## I. INTRODUCTION

The investigation of low-dimensional quantum spin systems has attracted widespread and general interest in active research on a large class of magnetic materials, experimentally as well as theoretically, since the properties are strongly affected by quantum fluctuations. In particular, there is strong theoretical and experimental effort to understand the origin of singlet-triplet spin gaps in low-dimensional spin systems such as $Sr\,Cu_2O_3$ and $VO_2P_2O_7$, which occur in the presence of competing spin interactions, e.g., due to a spin-ladder geometry.

Evidence for frustrated spin interactions has also been reported for the quasi-one-dimensional antiferromagnet $CuGeO_3$.[1–3] Initially this compound has received much interest, since it is an example of an inorganic compound undergoing a spin-Peierls transition.[4] Subsequent extensive experimental studies have revealed that many properties of the ordered phase are well described by the well known spin-Peierls scenario,[5–8] such as the presence of a lattice dimerization[9] and a singlet triplet spin-gap scaling with the lattice distortion.[10] However, recently it was found that the formation of the nonmagnetic low-temperature phase in $CuGeO_3$ sensitively depends on details of the magnetic exchange.[3]

The traditional spin-Peierls theory[7,6] is based on one-dimensional antiferromagnetic chains with nearest-neighbor couplings only. Such magnetic systems do not show any long-range antiferromagnetic order in the ground state, however they possess critical quantum fluctuations which drive the lattice dimerization, i.e., the spin-Peierls transition. Substances with frustrated spin interactions are not strictly governed by the traditional spin-Peierls theory[7,6] as the magnetic system in these cases may show spontaneous long-range magnetic dimerization in the ground state even without any lattice dimerization. The additional spin-phonon coupling merely stabilizes this magnetic dimerization upon developing the lattice distortion. Whether this or the former scenario is realized depends on the strength of the frustration parameter $\alpha = J_2/J_1$.

Frustration of the spin interactions in $CuGeO_3$ has been inferred previously from the investigation of the magnetic susceptibility ($\chi$) in the nondimerized phase,[1,2] which is in disagreement with a nearest-neighbor Heisenberg model.[4,2,1] A much better agreement has been found in theoretical studies of the spin susceptibility $\chi(T)$ invoking a Heisenberg chain with competing nearest- and next-nearest neighbor exchange couplings $J_1$ and $J_2$.[2,1]

However, two markedly different choices of exchange couplings, i.e., $(J_1,\alpha) = (75\ \mathrm{K}, 0.24)$ (Ref. 2) and $(J_1,\alpha) = (80\ \mathrm{K}, 0.36)$,[1] were derived within model calculations and the *same* experimental data for the magnetic susceptibility as well as inelastic neutron scattering. For these quantities an increase of $\alpha$ on one hand, and a decrease of $J_1$ on the other, have similar consequences leading apparently to a large uncertainty of the exchange parameters.

Thus these previous studies of the quantum magnetism in $CuGeO_3$ reveal some evidence for the relevance of magnetic frustration in $CuGeO_3$, whereas it is obviously difficult to extract precise values of the exchange parameters. A precise knowledge of the ratio $\alpha$ is of course very important, since the theory predicts a critical ratio $\alpha_c$ for a spin gap to develop in the magnetic excitation spectrum. This gap opens

 

irrespective of a lattice distortion. The existence of this gap is established exactly at the Majumdar-Ghosh point $\alpha=1/2$ (Ref. 11) and by several numerical studies[12,2,1] which strongly suggest $\alpha_c \approx 0.2411$.

In order to decide whether the spin gap in $CuGeO_3$ is at least partially a manifestation of frustrated spin interactions in a low-dimensional magnet we have performed a comparative study of theoretical results and experimental data for thermodynamic properties. Using our numerical results for the Heisenberg chain with nearest- and next-nearest neighbor interaction we show that a comparison of the magnetic susceptibility alone allows for the unique determination of the exchange constants in the frustrated one-dimensional magnet $CuGeO_3$ with result $\alpha=0.354\pm0.01$, i.e., a frustration significantly larger than the critical value $\alpha_c$.

In the course of our investigations we also determine the pressure dependence of the coupling parameters from magnetostriction data. We also analyze the experimental specific-heat data for consistency with the theoretical entropy results.

## II. THEORY AND NUMERICS

The dominant magnetic interactions in $CuGeO_3$ are due to a Heisenberg spin exchange between $Cu^{2+}$ ions along the $c$ axis of the crystal. The Hamiltonian for the spin chain in the nondimerized phase reads

$$H=2\sum_i \left(J_1\mathbf{S}_i\mathbf{S}_{i+1}+J_2\mathbf{S}_i\mathbf{S}_{i+2}\right), \tag{2.1}$$

where we have adopted the normalization factor of Ref. 13. The nearest-neighbor coupling $J_1$ is induced by the exchange path Cu-O-Cu, and the next-nearest-neighbor coupling $J_2$ is caused by the path Cu-O-O-Cu. A microscopic calculation of $J_{1,2}$ is difficult[14] and independent derivations are important.

In order to obtain quantitative results we calculate various physical properties in dependence on the couplings $J_1$ and $J_2$, notably the magnetic susceptibility, and perform a two-parameter fit of the experimental data. The aim is to achieve a best fit above the transition temperature $T_{SP}=14.3$ K within the model of a magnetic system with interactions described above and an adiabatic decoupling of the spin-phonon interactions. In this sense $J_1$ and $J_2$ are treated as effective coefficients explicitly dependent on the lattice geometry, i.e., microscopic bond angles and lattice constants. Unfortunately, analytic results for the thermodynamics of the model are available only for $\alpha=0$ (nearest-neighbor Heisenberg chain). We therefore resort to complete numerical diagonalizations of finite systems with chain lengths up to $L=18$. In general, the numerical treatment of strongly correlated quantum spin chains is plagued by finite-size effects at *low* temperatures. Here, however, we are interested in relatively high temperatures with $k_BT>0.5J_1$. A comparison of numerical data for successive chain lengths $L=16,17,18$ shows that finite-size corrections are essentially negligible for our purposes (see, e.g., the inset in Fig. 6 where the entropy for $N=17,18$ is displayed for low $T$). In Figs. 1 and 2 numerical results for the magnetic susceptibility and specific heat per lattice site are depicted. Note the characteristic dependence of the extremal values $\chi_{max}$ and the corresponding $T_{max}$ on the frustration parameter $\alpha$. $T_{max}$ is decreasing

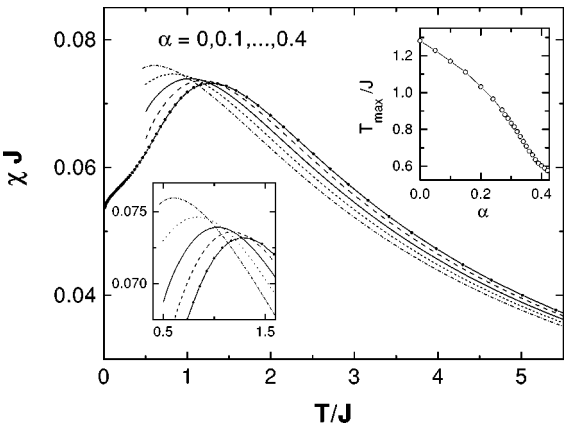


FIG. 1. Plot of numerical results for the susceptibility per site (in units of $J_1$) versus the reduced temperature $T/J_1$ for $\alpha=$ 0.1, . . . , 0.4, and analytical results for $\alpha=0$ following (Ref. 31) down to zero temperature. Shown in insets: behavior of the susceptibility in the neighborhood of the maximal values $\chi_{max}$ and plot of the corresponding temperature $T_{max}$ as a function of $\alpha$.

with increasing $\alpha$, whereas $\chi_{max}$ is increasing. The behavior of the specific heat is similar, however its maximal value $C_{max}$ is a decreasing function of $\alpha$. Consequently, at low temperatures the entropy strongly increases with increasing $\alpha$.

From the numerical data we first observe that the experimental susceptibility data $\chi$ allow for an unambiguous determination of $J_1$ *and* $J_2$ if we use the position $T_{max}=56$ K and absolute value $\chi(T_{max})$ of the maximum of $\chi$. In practice, we determine for a sequence of frustration parameters $\alpha=J_2/J_1$ the value of $J_1$ leading to $T_{max}=56$ K. For this set of coupling parameters the value of $\chi_{max}$ is calculated, see Fig. 3. The experimental value for $\chi_{max}$ (see below) is reproduced in this plot for $\alpha=0.354$ within an error of 0.01. Note that $\alpha=0.24$ as used in Ref. 2 would yield a value of $\chi_{max}$ far too large in comparison with the actually measured value. The nearest-neighbor coupling corresponding to $\alpha=0.354$ is $J_1=80.2$ K$\pm3.0$. In Fig. 4 the susceptibility $\chi$ for the values $\alpha=$ 0.354 and 0.24 is compared with the experimental data.

The experimental magnetic susceptibility shown in Fig. 4 has been measured on a large ($\sim$170 mg) single crystal which was grown from the melt by a floating-zone method

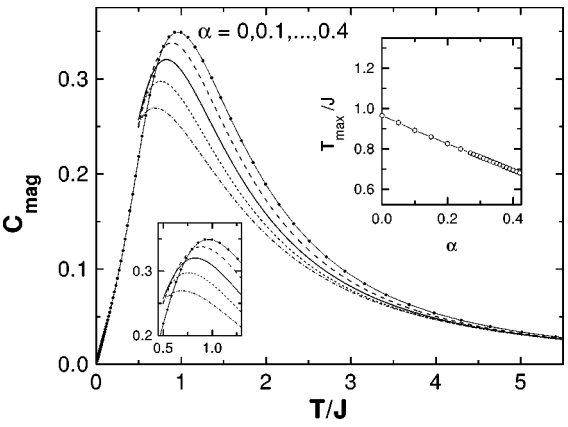


FIG. 2. Plot of numerical and analytical results for the specific heat per site similar to Fig. 1.

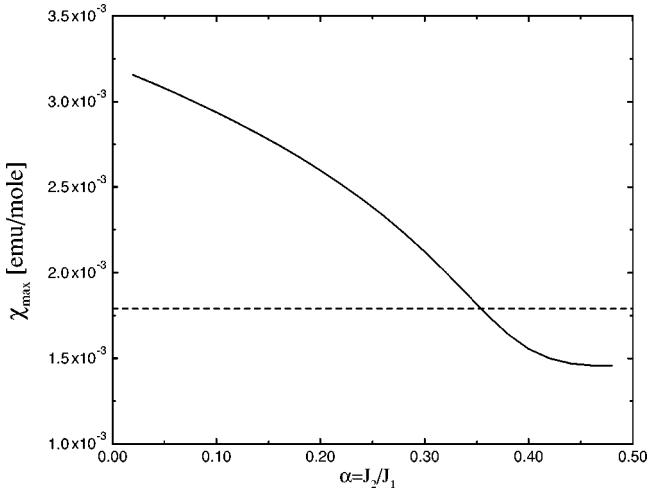


FIG. 3. Plot of the maximal value of the magnetic susceptibility $\chi_{\max}$ as a function of $\alpha = J_2/J_1$ (solid line) in the two parameter model. The experimental value (dashed line) is crossed at $\alpha = 0.354$. (The corresponding value of $T_{\max}$ is 56 K.)

associated with an image furnace.[15] The measurements have been performed up to a temperature of 950 K using a Faraday balance. Two sets of data have been recorded by applying external fields of $H = 1$ T parallel to the $a$ and $b$ axes of the crystal, respectively. As shown in the inset of Fig. 4 the susceptibilities found for the two field directions are identical besides a scaling factor, i.e., $\chi(H\|a) = 0.917\chi(H\|b)$. Taking into account the ratio of the Landé factors of $(g_a/g_b)^2 = 0.91(1)$ as derived from ESR measurements[16] this simple scaling is expected for the Cu spin susceptibility from the Hamiltonian given in Eq. (2.1).

We mention that the temperature dependence of the measured susceptibility is in agreement with the data reported by Hase *et al.*[4] However, the absolute values of our measurements are slightly ($\sim 5\%$) larger. These small differences between our and the data in Ref. 4 might originate from the much larger size of our crystal leading to a better signal to background ratio and/or from slightly different orientations of the magnetic fields with respect to the crystal axes. Note that our data agree perfectly with those reported in Ref. 17, which have been also measured on a large single crystal.

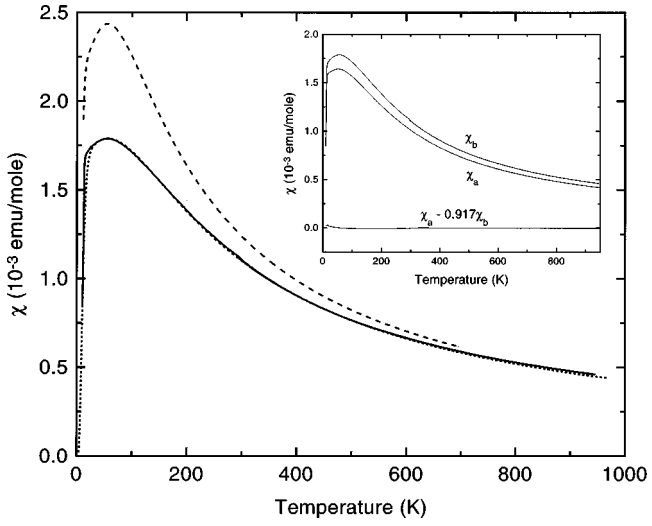


FIG. 4. Depiction of the experimental results for the magnetic susceptibility measured in a field of $H = 1$ T parallel to the $b$ axis of $CuGeO_3$ in dependence on temperature (solid line). Also shown are the theoretical results for $\alpha = 0.354$ (dotted line) and $\alpha = 0.24$ (dashed line). Inset: Experimental susceptibilities measured for $H = 1$ T parallel to the $b$ and the $a$ axes, respectively, and the (weighted) difference of the susceptibilities (see text).

For the comparison of the theoretical and experimental susceptibilities in the main part of Fig. 4 as well as for the determination of the exchange constants in Fig. 3 (see above) we consider the experimental susceptibility for $H\|b$ showing the largest values (and thus the smallest influence of impurities). Note that all findings are also in agreement with the data for $H\|a$ due to the scaling behavior of the susceptibilities. In the theoretical calculations of $\chi_b$ the Landé factor of $g_b = 2.256$ is used as derived from ESR measurements.[16] Furthermore we assume a cancellation of van Vleck paramagnetism ($\chi_{VV}$) and core diamagnetism ($\chi_{\text{core}}$), i.e., $\chi_{VV} + \chi_{\text{core}} \simeq 0$. On the one hand, this assumption about the magnetic background is based on the findings for $\chi_{VV}$ in other cuprates.[18] On the other hand, it is supported by the observations in $CuGeO_3$, e.g., the scaling of the susceptibilities for the different field directions (see above) and the small (negative) slope of the magnetization curves in the dimerized phase.[19]

As visible in Fig. 4 the measured $\chi(T)$ is reproduced very well by the theoretical calculations for $\alpha = 0.354$ in the entire temperature range. In contrast to this there is a strong deviation of the theoretical curve for $\alpha = 0.24$ from the measured one, especially at $T \sim T_{\max}$. This deviation is much larger than the error of our theoretical and experimental data. The effect of finite-size corrections on the numerical results has been reduced by a scaling analysis based on a transfer-matrix approach.[20] The theoretical results are reliable down to temperatures of $\approx 35$ K and thus the uncertainties of our determination of the exchange constants are only due to uncertainty of the extraction of the Cu spin susceptibility from the experiment. We have therefore repeated our analysis with several other assumptions. If we subtract a background of $\chi_{VV} + \chi_{\text{core}} = 5 \times 10^{-5}$ emu/mole the result would read $\alpha = 0.362 \pm 0.01$. For the quoted error bars of $J_1$, $\alpha$ a large relative error of 3% in the measurements (of $g_b^2$ and/or $\chi$) has already been taken into account. A comparable analysis of the data in Ref. 4 leads to $\alpha = 0.371 \pm 0.01$ ($\alpha = 0.38 \pm 0.01$ if a background of $5 \times 10^{-5}$ emu/mole is subtracted), a value which overlaps with the above result. We are thus lead to the conclusion that it is only possible to describe the observed susceptibility of $CuGeO_3$ by the calculations assuming the Hamiltonian in Eq. (2.1), if a very large frustration ratio is assumed.

In addition to the strength of the microscopic couplings we can determine their pressure dependence. We obtain this from magnetostriction data[3] which are related to the pressure dependence of the magnetic susceptibility[21,3,22] which is rather directly accessible in numerical studies

$$\frac{1}{L_i}\left(\frac{\partial L_i}{\partial H}\right)_{p_i} = \frac{H}{V}\left(\frac{\partial \chi}{\partial p_i}\right)_H = \frac{H}{V}\left[\partial_1 \chi \left(\frac{\partial J_1}{\partial p_i}\right)_T + \partial_2 \chi \left(\frac{\partial \alpha}{\partial p_i}\right)_T\right], \tag{2.2}$$

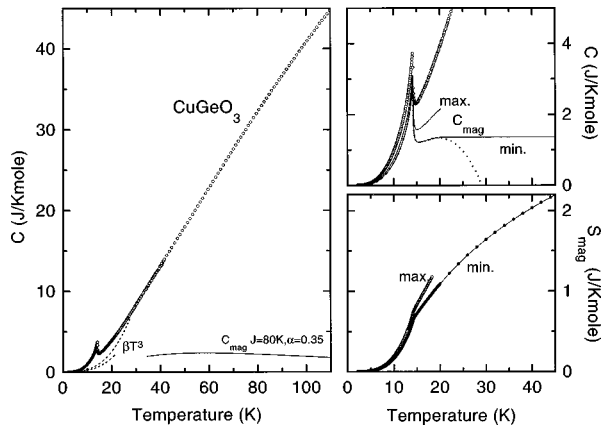


FIG. 5. Left panel: Experimentally observed specific heat of $CuGeO_3$ ($\bigcirc$) taken from Ref. 24. The extrapolated low-temperature phonon backgrounds $C_{ph}=\beta T^3$ with $\beta=0.32$ mJ/K$^4$ mole and $\beta=0.22$ mJ/K$^4$ mole are indicated by the dashed lines. The solid line shows the calculated magnetic specific heat for the exchange constants revealing the best fit to the magnetic susceptibility. Right upper panel: Experimentally observed specific heat of $CuGeO_3$ ($\bigcirc$) and the estimated minimum and maximum magnetic specific heats (solid lines, see text). Right lower panel: Minimum and maximum magnetic entropy as revealed from the specific-heat data in the upper panel.

where $\partial_{1,2}$ denotes the derivative of $\chi$ with respect to $J_1$ and $\alpha$. Based on this relation and the data for temperatures 40 and 60 K we find $\partial J_1/\partial p_i = 3.3(3), -7.5(5), -1.4(2)$ K GPa$^{-1}$, and $\partial\alpha/\partial p_i = -0.03(3), 0.01(4), 0.04(2)$ GPa$^{-1}$ for the three lattice axes $i=a$, $b$, and $c$. Note that the values for the pressure dependence of $\alpha$ obtained along this way are consistent with the hydrostatic pressure dependence obtained in Ref. 23. However, in our analysis the hydrostatic pressure dependence of $J_1$ is much stronger than that of $J_2$ which is essentially zero.

## III. ENTROPY ANALYSIS

Unfortunately it is impossible to measure the temperature dependence of the magnetic specific heat in $CuGeO_3$ directly. As displayed in the left part of Fig. 5 at temperatures close to the predicted maximum of $C_{mag}$ the total specific heat[24] is dominated by the phonon contribution $C_{ph}$, i.e., it is about one order of magnitude larger than the calculated magnetic contribution. Therefore it is impossible to extract $C_{mag}$ with sufficient accuracy to resolve the small differences predicted for different exchange constants in a $J_1-J_2$ model, see Fig. 2. Note that this would require a knowledge of the phonon contribution with an unrealistic accuracy of the order of $10^{-3}$ or higher. Nevertheless, one can use the measurements of $C$ to check different exchange parameters suggested in the literature[4,10,25–27] for consistency. In the following we will demonstrate that indeed most of these values for $J_1$, $J_2$ can be excluded by comparing the theoretical magnetic entropy to that extracted from the specific-heat measurements.

It is well known that a reliable separation of magnetic and phonon contributions of $C$ is possible at low temperatures[28,29,24] and we will use this separation to estimate the magnetic entropy at higher temperatures. Note that the spin-Peierls phase transition does not modify $C_{ph}$ significantly, i.e., the anomaly of $C$ is due to the magnetic contribution. This is inferred on one hand, from the extremely small structural changes at the phase transition and on the other hand, is consistent with the findings in measurements as functions of magnetic fields and doping.[24,30]

Analyses of the specific heat at low temperatures have been reported several times.[28,29,24] Well below $T_{SP}$ the magnetic part of the specific heat $C_{mag}$ shows activated behavior due to the large spin gap. At low temperatures the phonon contribution follows the usual $T^3$ law, i.e., $C_{ph}=\beta T^3$ with $\beta\simeq 0.3$ mJ/K$^4$ mole. Taking this temperature dependence and assuming a maximal value of $\beta\simeq 0.32$ mJ/K$^4$ mole we obtain an upper boundary for the phonon specific heat below about 20 K. Note that larger values of $\beta$ are impossible, since the phonon specific heat at very low temperatures (e.g., at $T\simeq 2$ K) has to be smaller than the total specific heat. At higher temperatures $C_{ph}$ deviates from this $T^3$ behavior as illustrated in Fig. 5. The extrapolation of the low-temperature behavior exceeds the measured specific heat already at moderate temperatures of about 30 K, i.e., the $T^3$ law with a large $\beta=0.32$ mJ/K$^4$ may serve as an upper limit $C_{ph}^{max}$ for $C_{ph}$ in this temperature range, too. In order to derive a lower limit $C_{mag}^{min}$ for the magnetic contribution from this $C_{ph}^{max}$ and the measured data we thus take the difference $C-C_{ph}^{max}$. The difference function shows a maximum well above $T_{SP}$ at about 18 K (see the right part of Fig. 5) and a further extrapolation of this function to higher temperatures leads to a decrease which is unreasonable for an estimate of $C_{mag}$. We therefore take the value of $C-C_{ph}^{max}$ at 18 K as a lower limit of $C_{mag}$ at higher temperatures (see Fig. 5). Of course this treatment yields only a very small lower limit for $C_{mag}$, which is indeed much smaller than the predicted $C_{mag}$ (see Fig. 5).

To extract an upper limit for $C_{mag}$ from the experimental data in $CuGeO_3$ is more difficult, since the total specific heat does not give strict lower limits of $C_{ph}$. For a rough orientation we show in Fig. 5 a very conservative estimate of $C_{mag}^{max}$ which is obtained by subtracting $C_{ph}=\beta T^3$ with $\beta=0.22$ mJ/K$^4$ from the raw data, i.e., by assuming a phonon background which is about 25% smaller than that obtained by fitting the low-temperature specific heat.[24]

As shown in the upper right part of Fig. 5 our estimates yield a very large error bar for the magnetic specific heat above $T_{SP}$. Note that we do not aspire a more realistic extraction of $C_{mag}$ here, since our very conservative estimate of $C_{mag}^{min}$ already suffices to rule out most of the exchange constants reported for $CuGeO_3$ in the literature.

For the following comparison between theory and experiment we consider the magnetic entropy $S_{mag}$ which is derived from $C_{mag}$ by integration. On the one hand, the relative error of the experimental $S_{mag}$ is much smaller as shown in Fig. 5. On the other hand, the theoretical calculations of $S_{mag}$ for finite chains are reliable down to much lower temperatures than those of $C_{mag}$ (see below).

The comparison between the experimental magnetic entropy and the calculations for several choices of $J_1$ and $J_2$ is displayed in Fig. 6. The two curves for unfrustrated chains ($\alpha=0$) are based on the exact solution of the one-dimensional Heisenberg antiferromagnet, i.e., the theoretical

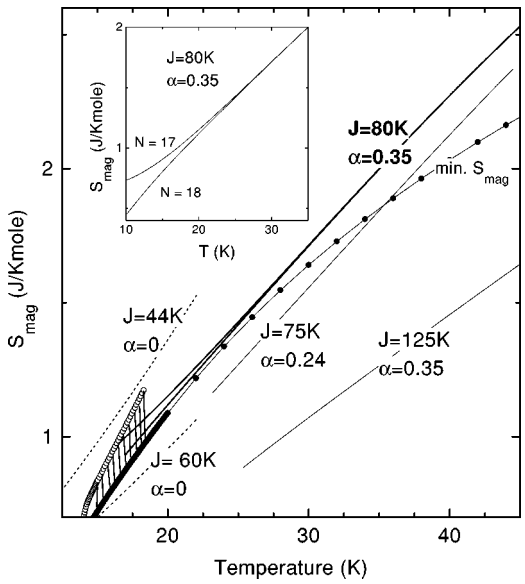


FIG. 6. Comparison between the minimum (●) and maximum (○) magnetic entropy as revealed from the specific-heat data and calculations of $S_{\mathrm{mag}}$ assuming different exchange constants given in the figure. The dashed lines correspond to results of exact thermodynamic calculations for $\alpha=0$ and the solid lines are obtained from numerical diagonalizations. For the parameters $J=80$ K, $\alpha=0.35$ the numerical data for both $N=17$ and $N=18$ are shown in order to take into account the finite-size effects. The inset shows this latter numerical data on an extended scale.

results are valid in the entire temperature range. As described in the initial paper on the spin-Peierls transition in $CuGeO_3$ (Ref. 4) assuming $\alpha=0$ and determining $J$ from the temperature at the maximum of $\chi$ yields $J=44$ K. The corresponding magnetic entropy is much larger than the upper limit we have extracted from the data. At temperatures slightly above $T_{\mathrm{SP}}$ it amounts to about 95% of the total entropy in $CuGeO_3$ and thus assuming the parameters $J_1=44$ K, $J_2=0$ clearly contradicts the magnetic entropy in $CuGeO_3$.

Another value suggested for the intrachain exchange constant in a model with $\alpha=0$ is $J=60$ K. This value has been reported in Ref. 10 based on their inelastic neutron-scattering data. More recently, in Ref. 25 a similar value and in addition a large (frustrated) intrachain exchange was found from the analysis of the dispersion curves in the dimerized phase, i.e., below $T_{\mathrm{SP}}$. It is apparent from Fig. 6 that above $T_{\mathrm{SP}}$ the magnetic entropy calculated for $J_1=60$ K, $J_2=0$ in a one-dimensional model is significantly smaller than the lower limit $S_{\mathrm{mag}}^{\mathrm{min}}$ extracted from the data. We emphasize that including an interchain exchange $J_b$ does not remove this discrepancy. At present it is—to our knowledge—not possible to calculate the influence of $J_b$ on the magnetic entropy quantitatively. However, the qualitative behavior is apparent. If there is a significant influence at all, $S_{\mathrm{mag}}$ would be reduced by an additional magnetic interaction between the chains, i.e., the deviation between experiment and theory would even increase. Thus, the specific heat does clearly not support the parameters suggested in Ref. 25.

The three solid lines in the right part of Fig. 6 correspond to calculations of $S_{\mathrm{mag}}$ for different exchange constants and finite $\alpha$. Since these entropies have been calculated for finite chains, finite-size effects have to be considered at low temperatures. Upper and lower bounds of the magnetic entropy in the thermodynamic limit can be obtained by considering the results for odd and even numbers of atoms in the finite chains, respectively. In the inset of Fig. 6 a corresponding analysis for $N=17$ and $N=18$ is shown for $S_{\mathrm{mag}}$ with $J_1=80$ K and $\alpha=0.35$. It is apparent that the slope of the curves, i.e., $C_{\mathrm{mag}}/T$, differ already significantly at temperatures above 30 K and therefore a meaningful comparison of calculated and measured specific heats is impossible at lower temperatures. However, the difference of the magnetic entropies for $N=17$ and $N=18$ remains small. Even at $T/J\simeq 0.2$, i.e., at $T\simeq 16$ K in the above example, the maximum error of the calculated $S_{\mathrm{mag}}$ due to finite-size effects is smaller than 10%. This enables a comparison of the numerical data to the experimental data for $S_{\mathrm{mag}}$ extracted from the specific heat as described above.

It is apparent from Fig. 6 that there is a strong discrepancy between the numerical and experimental data for the set of parameters $J_1=125$ K, $\alpha=0.35$. These parameters have been suggested recently in Ref. 26 to give the best description of the magnetic specific heat in $CuGeO_3$. In this latter work $C_{\mathrm{mag}}$ has been extracted from Raman-scattering data and it was concluded that it is impossible to fit both the susceptibility and the magnetic specific heat with a single choice of $J_1$ and $J_2$. However, it is apparent from Fig. 6 that the parameters suggested in Ref. 26 and consequently the ''magnetic specific heat'' extracted from Raman scattering is in striking discrepancy to the measurement of the specific heat at low temperatures. Thus our data do not support the reported inconsistency in the determination of exchange parameters from $\chi$ and $C_{\mathrm{mag}}$.[26] Further investigations seem necessary to explain the striking discrepancy between $C_{\mathrm{mag}}$ as revealed in Ref. 26 from quasielastic scattering and the true magnetic specific heat.

The deviation between the data and the calculations for the exchange constants $J_1=75$ K, $\alpha=0.24$, which have been extracted by Castilla *et al.* from their analysis of the magnetic susceptibility and the dispersion curves, is less pronounced but still significant. At temperatures below about 35 K the calculated magnetic entropy is smaller than the conservative lower bound we have estimated from the data. In agreement to our findings from $\chi$ the magnetic entropy shows that it is impossible to describe the magnetic properties of $CuGeO_3$ with Hamiltonian (2.1) and the exchange constants $J_1=75$ K, $\alpha=0.24$. Note that this discrepancy is now obtained from data at low temperatures, i.e., from the specific heat below 20 K. Moreover, it is impossible to explain the deviation between theory and experiment including an interchain coupling (see the above discussion for $J=60$ K, $\alpha=0$).

A very nice convergence of theory and experiment appears upon further increasing $\alpha$ to 0.35 (and $J=80$ K). As shown in Fig. 6 the magnetic entropy calculated for the parameters which yield the best fit to the susceptibility is always larger than the lower bound extracted from the data. Moreover, it is apparent from Fig. 6 that the difference between the theoretical $S_{\mathrm{mag}}(J_1=80$ K, $\alpha=0.35)$ and the lower bound systematically decreases with decreasing temperature, i.e., with increasing accuracy of $S_{\mathrm{mag}}^{\mathrm{min}}$. At temperatures below 20 K the error bars of the theoretical calculations ($N=17,18$) which increase with decreasing temperature

merge with those of the experimental $S_{\mathrm{mag}}$ which increase with increasing temperature. We conclude that within the error bars of theory and experiment both the value of $S_{\mathrm{mag}}$ at $T \gtrsim T_{\mathrm{SP}}$, which is determined from data at very low temperatures, as well as the temperature dependence of $S_{\mathrm{mag}}$, i.e., the magnetic specific heat, are well described for $J=80$ K, $\alpha=0.35$. In contrast to that, for all other choices of exchange parameters in Fig. 6 significant discrepancies between the model calculations and the experimental data are apparent. Though the accuracy for the determination of $C_{\mathrm{mag}}$ is not sufficient to unambiguously determine the exchange constants from these data alone, the specific heat strongly confirms our analysis of the susceptibility. In particular, in contrast to the conclusions of Ref. 26 there is no evidence that it is necessary to invoke markedly different exchange constants to explain $\chi$ and $C_{\mathrm{mag}}$.

## IV. CONCLUSION

We have presented numerical results for thermodynamical properties of a quantum spin-1/2 chain with nearest and next-nearest-neighbor interactions which is believed to be at the heart of the magnetic system of $CuGeO_3$. The microscopic interaction parameters have been determined as well as their uniaxial pressure dependence. We have shown that the frustration parameter is $\alpha=0.354$. This is much larger than the value used for the explanation of Raman-scattering data.[27,23] We expect our result to be reliable as we have based our reasoning on established thermodynamical relations. Furthermore, we have demonstrated that the experimental magnetic susceptibility data are accounted for in even quantitative details by the quasi-one-dimensional model and $\alpha=0.354$.

Within the present accuracy the magnetic specific heat calculated for the exchange constants derived from our analysis of $\chi$ is consistent with the analysis of the experimental data. On the other hand, for several other choices of exchange parameters which have been suggested for $CuGeO_3$ we find not only a worse description of the susceptibility but simultaneously discrepancies to the specific-heat data.

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