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$CuSiO_3$: A quasi-one-dimensional $S=\frac{1}{2}$ antiferromagnetic chain system

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$CuSiO_3$, isotypic to the spin-Peierls compound $CuGeO_3$, was discovered recently as a metastable decomposition product of the silicate mineral dioptase, $Cu_6Si_6O_{18}\cdot 6H_2O$. We investigated the physical properties of $CuSiO_3$ using susceptibility, magnetization, and specific heat measurements on powder samples. The magnetic susceptibility $\chi(T)$ is reproduced very well above $T=8$ K by theoretical calculations for an $S=\frac{1}{2}$ antiferromagnetic Heisenberg linear chain without frustration $(\alpha=0)$ and a nearest-neighbor exchange coupling constant of $J/k_B=21$ K, much weaker than in $CuGeO_3$. Below 8 K the susceptibility exhibits a substantial drop. This feature is identified as a second-order phase transition at $T_0=7.9$ K by specific heat measurements. The influence of magnetic fields on T_0 is weak, and ac-magnetization measurements give strong evidence for a spin-flop phase at $\mu_0 H_{SF}\simeq 3$ T. The origin of the magnetic phase transition at $T_0=7.9$ K is discussed in the context of long-range antiferromagnetic order (AF) versus spin-Peierls (SP) order. Susceptibility and specific heat results support the AF ordered ground state. Additional temperature dependent ^{63,65}Cu nuclear quadrupole resonance experiments have been carried out to probe the Cu^{2+} electronic state and the spin dynamics in $CuSiO_3$.

I. INTRODUCTION

The one-dimensional spin system $CuGeO_3$ has attracted considerable attention in past years, since it was the first (and up to now the only) inorganic compound that exhibits a spin-Peierls transition (SP).[1,2] The simplicity of crystal growth and the large variety of possible substitutions on the Cu and Ge sites promoted a huge amount of experimental and theoretical studies. Completely new phenomena like the coexistence of the SP state with a long-range antiferromagnetically ordered state in slightly doped $CuGeO_3$ (Si on the Ge site or Zn on the Cu site),[3–9] and the strong influence of the frustration due to the next-nearest-neighbor exchange on the magnetic and thermodynamic properties[10] were reported. Partial substitution of Ge by Si in $CuGe_{1-x}Si_xO_3$ has been an important subject in this field, but despite considerable efforts, it was not possible to substitute more than 50% Ge by Si without changing the structure ($x\leqslant 0.1$ for single crystals,[4–7] $x\leqslant 0.5$ for polycrystals[8]). Pure $CuSiO_3$ was considered to be nonexistent. However, recently Otto *et al.*[11] succeeded in the synthesis of reasonable amounts of pure isostructural $CuSiO_3$ by using the silicate mineral dioptase $Cu_6Si_6O_{18}\cdot 6H_2O$ as a starting material. Compared to the Ge homologue the lattice parameters *a* and *c* are reduced by about -3.5% and -3.7%, respectively, whereas *b* increases by about $+3.5\%$. The unit cell volume of $CuSiO_3$ is reduced $(\approx -3.8\%)$ in accordance with the smaller size of Si. This naturally leads to a modification of bond angles and lengths,[11] which should have a strong influence on the strength of the magnetic interaction governed by the superexchange between neighboring Cu^{2+} ions via the O^{2-} ions. The most crucial structural modification is the reduction of the Cu-O(2)-Cu bond angle from 99° in $CuGeO_3$ to 94° in $CuSiO_3$ which is accompanied by a shrinking of the in-chain Cu-Cu distance. The obvious question is how these structural changes do affect the ground state properties of this system. Here we present an investigation of the physical properties of $CuSiO_3$, based on susceptibility, specific heat, and Cu-nuclear quadrupole resonance experiments.

II. EXPERIMENTAL DETAILS

High quality crystals of dioptase from the type locality Altyn Tyube (Kazakhstan) were heated up to 873 K and held at this temperature for six hours in order to obtain dehydrated dioptase (black dioptase). The black dioptase was decomposed by a subsequent heat treatment at higher temperatures (1050 K) and for 20 hours under nitrogen atmosphere. The finely ground samples of darkish brown color were characterized by x-ray powder diffraction using the Guinier method. The diffraction pattern reveals a mixture of three different phases. A quantitative phase analysis reveals that about 76 wt. % of the mixture consist of the new phase $CuSiO_3$. The other phases are CuO (tenorite, 13.7 wt. %) and SiO_2 (amorphous, 10.3 wt %). The orthorhombic unit cell of the new phase $CuSiO_3$ was refined from Guinier data giving $a=4.6357(6)$ Å, $b=8.7735(11)$ Å, and $c=2.8334(4)$ Å. The lattice constants of $CuSiO_3$ are in good agreement with an extrapolation of the results from the diluted system $CuGe_{1-x}Si_xO_3$ (Ref. 8) to $x=1$. The crystal structure was determined to be isostructural to $CuGeO_3$. Details of the

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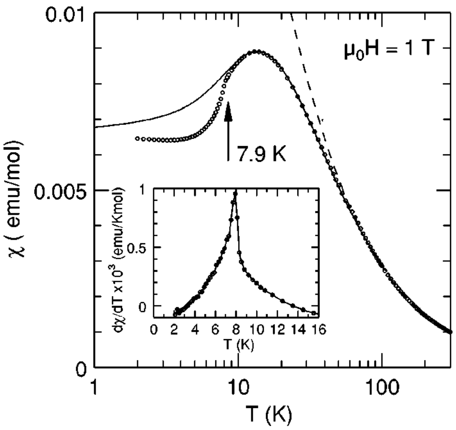

FIG. 1. Raw data of the magnetic susceptibility of a $CuSiO_3$ sample measured under a field of $\mu_0\ H=1$ T in a log-T scale. The solid curve corresponds to the numerical calculations of Klümper *et al.* (Ref. 13) for $S=1/2$ 1D Heisenberg chains with nearest-neighbor coupling and without next-nearest-neighbor coupling $(J'=0)$. The fitting of the numerical results to the experimental $\chi(T)$ data requires a coupling constant $J/k_B=21$ K and an effective moment of $\mu_{\mathrm{eff}}=1.60\ \mu_B$ $(g=1.85)$. At high temperatures $T\geqslant 200$ K, $\chi(T)$ is fitted with a Curie-Weiss law (dashed line) with $\mu_{\mathrm{eff}}=1.56\ \mu_B$ $(g=1.80)$ and $\theta=-7.2$ K. The inset shows $d\chi/dT$ as a function of temperature.

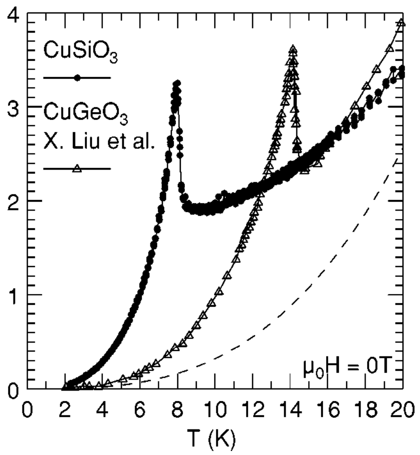

FIG. 2. Heat capacity of a $CuSiO_3$ sample and of $CuGeO_3$ (data taken from Ref. 15). The dashed line represents the phonon contribution $C_{\mathrm{ph}}=\beta T^3$ $(\beta=0.32\ \mathrm{mJ/mol\,K^4})$ for $CuGeO_3$.

synthesis and structure characterization are given in Ref. 11. Magnetization, specific heat, and NQR measurements were performed on samples taken from the same batch. The dc-magnetization measurements at low fields $\mu_0\ H\leqslant 1$ T were carried out using a commercial SQUID magnetometer (MPMS, Quantum Design). The ac- and dc-magnetization measurements in higher fields ($1\ \mathrm{T}\leqslant\mu_0\ \mathrm{H}\leqslant 14$ T) and the specific heat measurements were performed in a commercial multipurpose device (PPMS, Quantum Design). Ac and dc magnetization are extracted from the induction signal of a mutual inductance coil arrangement. The specific heat was determined by standard relaxation technique and an advanced two-tau model was applied to analyze the thermal response. The data obtained were corrected by subtracting the specific heat contributions of the sample holder, thermometers, heaters, and glue. The NQR measurements were performed on a conventional pulsed spectrometer using the point-by-point method. The masses of the samples are $m=91.40$ mg, 8.72 mg, and 180.20 mg for susceptibility, specific heat, and NQR measurements, respectively.

III. RESULTS

The temperature dependence of the magnetic susceptibility χ(T) of the $CuSiO_3$ powder sample in a magnetic field of 1 T is shown in Fig. 1. Below room temperature, $\chi(T)$ increases with decreasing temperature, confirming localized Cu^{2+} moments. Between 200 K and 300 K the susceptibility data follow nicely a Curie-Weiss law with a Weiss temperature of $\theta=-7.2$ K, indicating rather weak antiferromagnetic coupling. An effective moment of $\mu_{\mathrm{eff}}=1.56\mu_B$ per Cu^{+2} ion is determined which corresponds to a g factor of 1.80. Both impurity phases CuO and SiO_2 exhibit a small susceptibility which could be neglected in a first analysis. Scaling the measured susceptibility with the estimated amount of pure $CuSiO_3$ in the sample results in an μ_{eff} value of $1.79\mu_B$ and a g factor of 2.06. These values are very close to those found for $CuGeO_3$ and expected theoretically for free $S=1/2$ spins with $g=2$ and $\mu=g\mu_B\sqrt{S(S+1)}=1.73\mu_B$.

At lower temperatures the susceptibility exhibits a broad maximum at $T_{m,\chi}=13.5$ K, which is a hallmark for low-dimensional spin systems.[12] Above 8 K, $\chi(T)$ could be fitted very well with the numerical results of Klümper[13] for $S=1/2$ Heisenberg chains. The best fit is obtained with a nearest-neighbor coupling of $J/k_B=2T_{m,\chi}/1.282^{12}=21$ K and a slightly enhanced μ_{eff} value of 1.60 μ_B (note that we used the unscaled susceptibility for the fit and that we define J by the exchange Hamiltonian: $H=J\Sigma\mathbf{s}_i\mathbf{s}_{i+1}+\alpha\mathbf{s}_i\mathbf{s}_{i+2}$). The quality of the fit suggests that frustration effects, i.e., an antiferromagnetic interaction J' between next-nearest neighbors, are negligible in $CuSiO_3$ $(\alpha=J'/J=0)$. This is in contrast to $CuGeO_3$ where α values between 0.24 and 0.35 are proposed.[10,14] Furthermore, it is evident that the Cu-O(2)-Cu exchange in $CuSiO_3$ is much weaker $(J/k_B=21\ \mathrm{K})$ than in $CuGeO_3$ $(J/k_B\approx 160\ \mathrm{K})$. Below 8 K, $\chi(T)$ decreases very rapidly and saturates at the lowest temperatures. The derivation of the susceptibility $d\chi/dT$ shows a peak at $T_0=7.9$ K which gives clear evidence for a cooperative phase transition at this temperature (see inset of Fig. 1). The signature of the transition in the susceptibility looks more like a long-range antiferromagnetic order in a polycrystaline sample than a spin-Peierls transition. For the latter scenario, one expects a vanishing susceptibility at lowest temperatures $\chi(T\rightarrow 0)=0$, which is not observed. The absence of a Curie-like tail in the susceptibility at the lowest temperatures indicates the absence of defects and thus points to a high crystalline perfection of the $CuSiO_3$ phase.

The presence of a phase transition at T_0 is clearly confirmed by the specific heat results. The temperature dependence of the total specific heat of three $CuSiO_3$ crystals (total mass of 8.72 mg, 1 mol = 139.6 g) below 20 K is shown in Fig. 2. For a comparison, the data of Liu *et al.*[15] for $CuGeO_3$ are plotted in the same figure. The specific heat of $CuSiO_3$ shows a very clear λ-shaped, asymmetric anomaly at $T_0=7.9$ K with a specific heat jump of $\Delta C\approx 1.50\pm 0.05$ J/mol K. This is comparable to the ΔC value of approximately 1.8 J/mol K found for CuGeO$_3$.[15] The total specific heat obtained is the sum of the lattice term $C_{\mathrm{ph}}(T)$ from the phonons and the magnetic term $C_m(T)$ from the spin system. The separation of the two contributions is not trivial. At low temperatures, the phonon contribution should follow a T^3 law, i.e., $C_{\mathrm{ph}}=\beta T^3$. Because of the smaller mass of the Si ions compared to the Ge ions ($m_{\mathrm{Si}}/m_{\mathrm{Ge}}\approx 0.39$) one can expect a harder phonon spectra in CuSiO$_3$ and thus a reduced phonon contribution [$\beta_{\mathrm{CuSiO_3}}<\beta_{\mathrm{CuGeO_3}}\approx 0.32$ mJ/mol K^4 (Refs. 15, 10 and 16)]. Thus, the estimate of the phonon contribution for CuGeO$_3$ (see Fig. 2, dashed line) yields therefore an upper limit for the phonon contribution in CuSiO$_3$. This clearly demonstrates, that below 20 K, the specific heat of CuSiO$_3$ is dominated by the magnetic contribution. Well below T_0, $C(T)$ follows a T^3 power law with a coefficient β_m (≈ 4.5 mJ/mol K^4), more than one order of magnitude larger than that expected for the phonon contribution, indicating that it has to be related to the magnetic interactions. Such a power law is expected for long-range ordered 3D antiferromagnets with weak or absent anisotropy. The T^3 power law at low temperatures is in contrast to the experimental findings on the spin-Peierls compound CuGeO$_3$ where the opening of a gap in the magnetic excitation spectra leads to an exponential decrease of the specific heat. Therefore our specific heat measurements, too, support long-range antiferromagnetic order rather than a spin-Peierls dimerization at T_0.

At higher temperatures $T>T_0$, the specific heat $C_m(T)$ of a Heisenberg chain without frustration exhibits a maximum at $T_{m,c}=0.75\ T_{m,\chi}$ (Ref. 12) $=10.1$ K with a value of $C_m(T_{m,c})\approx 0.35R\approx 2.9$ J/mol K, which is independent of J.[12,13,10,17] Scaling this value with the amount of pure CuSiO$_3$ in the sample results in an expected magnetic contribution of 2.2 J/mol K. The experimental value of the specific heat at 10 K is only slightly lower. Further measurements and analysis are currently under progress to improve the estimation of the magnetic specific heat contribution. At even higher temperatures ($T>J/k_B$) $C_m(T)$ becomes very small and $C(T)$ originates mainly from the phonon contribution. Therefore the germanate exhibits a larger total specific heat than the silicate as evidenced from Fig. 2.

The influence of magnetic fields up to 14 T on the magnetic susceptibility and the specific heat is shown in Fig. 3. In the susceptibility $\chi(T,H)$ the signature of the transition at $T_0=7.9$ K is smeared out, the drop in the susceptibility is reduced and the susceptibility maximum at $T_{m,\chi}$ is shifted significantly to lower temperatures with field. This shift of $T_{m,\chi}$, which indicates the suppression of the antiferromagnetic in-chain correlations with increasing field, is in good agreement with the theoretical calculations of Klümper[13] (see inset in Fig. 3) for the $S=1/2$ Heisenberg chain. In the specific heat $C(T)$ the transition at $T_0=7.9$ K is clearly observable in fields up to 14 T and the T^3 power law at low temperatures is preserved. The antiferromagnetic order temperature T_0 shows only a weak field dependence as indicated in the magnetic phase diagram plotted in Fig. 4(a). No other transitions are visible in our $C(T,H)$ measurements. The temperature dependent $\chi(T)$ measurements at fixed fields (Fig. 3) and additionally field dependent ac-susceptibilty measurements at fixed temperatures [Fig. 4(b)] evidences a broadened (due to the random orientation of the powder particles) transition at $\mu_0 H_{\mathrm{SF}}\approx 3T$, which looks very similar to a spin-flop transition. The phase diagram corresponds to that observed for the AF phase in doped CuGeO$_3$, but it is quite different from that expected and confirmed for a spin-Peierls transition. The almost field independent transition temperature and the presence of a spin-flop-like transition are strong evidences for an antiferromagnetically ordered ground state in CuSiO$_3$.

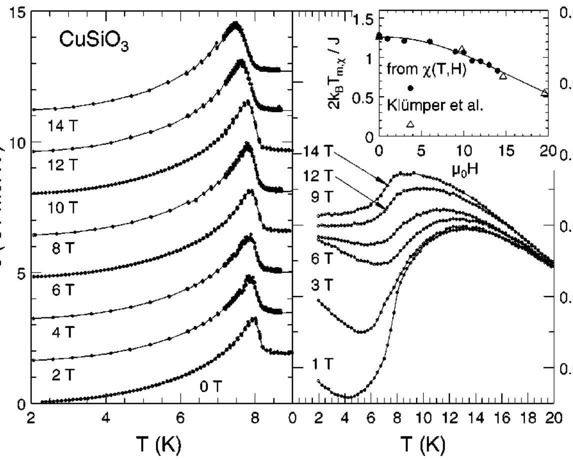

FIG. 3. Temperature dependence of the specific heat (left side; note that the origin of the vertical axis is shifted by 1.6 J/mol K for the curves with $\mu_0 H\geqslant 0T$) and the magnetic susceptibility (right) for different magnetic fields. The inset shows the shift of the temperature $T_{m,\chi}$ defined by the maximum susceptibility $\chi(T_{m,\chi})=\chi_{\max}$ in reduced units as a function of applied field and in comparison with the theoretical prediction of Klümper *et al.* (Ref. 13)

We have investigated the nuclear quadrupole resonance (NQR) of Cu in CuSiO$_3$ to deduce microscopic informations at nuclear sites. A spectrum at 4.2 K is shown in Fig. 5. The lines are fitted well by a Gaussian function and the central frequencies $^{63,65}\nu_{\mathrm{NQR}}$ and the line widths $^{63,65}\Delta\nu_{\mathrm{NQR}}$ were determined at different temperatures (see inset of Fig. 5). The NQR signals at 4.2 K have been found at 26.88 ± 0.02 MHz for ^{63}Cu and 24.88$\pm$0.02 MHz for ^{65}Cu. The

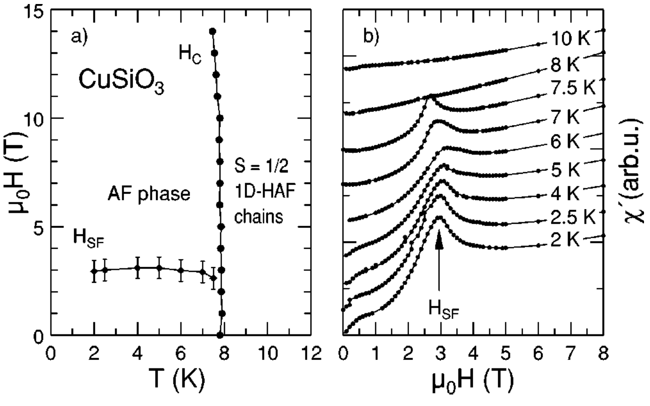

FIG. 4. Magnetic phase diagram of CuSiO$_3$ probed by specific heat and susceptibility measurements (left). H_c denotes the AF transition whereas H_{SF} indicates the spin flop transition as evidenced from ac-susceptibility measurements (left side; note that the origin of the vertical axis is shifted by a constant value for curves at different temperatures).

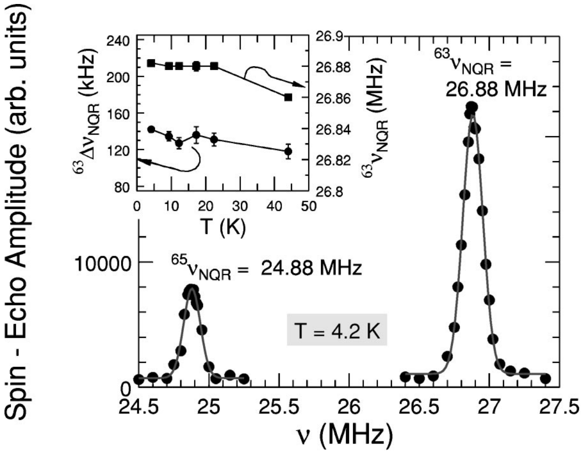

FIG. 5. ^{63}Cu and ^{65}Cu NQR spectra in $CuSiO_3$ at 4.2 K. The solid curves correspond to the fitting of a Gaussian function to the experimental data. The inset shows the temperature dependence of the ^{63}Cu NQR frequency (right axis) and of the ^{63}Cu NQR linewidths (left axis).

ratio of the frequencies of the NQR signals are in good agreement with that expected from the nuclear quadrupole moments of Cu ($^{63}Q/^{65}Q = 1.081$). Also the ratio of the signal intensities $^{63}I/^{65}I = 2.8$ corresponds to that of the natural abundance of the isotopes ^{63}Cu and ^{65}Cu with $^{63}I/^{65}I = 2.20$. Furthermore the presence of the impurity phase CuO is confirmed nicely by L measurements. At room temperature the ^{63}Cu NQR frequency of CuO is found at $^{63}\nu_{NQR} = 20.6$ MHz, which is in good agreement with the literature.[18] Due to the AF order in CuO at $T_N = 230$ K (Ref. 19) the $^{63}\nu_{NQR}$ is shifted to much higher frequencies below T_N ($^{63}\nu_{NQR} \approx 137$ MHz for the central line at 4.2 K).[20] Therefore the observed resonance signals presented in Fig. 5 could be clearly assigned to the Cu NQR lines of the $CuSiO_3$ phase. No other resonance lines are observed in the frequency range of 20–90 MHz indicating the crystallographically equivalence of the Cu site. Compared to $CuGeO_3$ with 34.23 ± 0.02 MHz for ^{63}Cu and 31.66 ± 0.02 MHz for ^{65}Cu at 4.2 K,[21,22] the NQR lines in $CuSiO_3$ are shifted to lower frequencies. One possible explanation is the effect of the modified bond lengths and angles on the electric field gradient EFG which affects strongly $^{63,65}\nu_{NQR}$.[18] The EFG at the Cu site originates mainly from the ionic charge distribution of the surrounding ions (so called lattice contribution) and the $3d$ Cu charge distribution (valence) itself.[18] Compared to $CuGeO_3$ the Cu-O bond lengths are enlarged. In a simple point charge model for the lattice contribution this could reduce the EFG and therefore lower the NQR frequencies. Details of the NQR results and a complex analysis of the data will be presented elsewhere. Surprisingly $^{63,65}\nu_{NQR}$ and the line widths $^{63,65}\Delta\nu_{NQR}$ exhibit only a weak temperature dependence between 4.2 and 40 K and especially around the transition at $T_0 = 7.9$ K, no anomaly is observed (see inset Fig. 5). Usually an antiferromagnetic phase transition is associated with the appearance of strong internal magnetic fields on the Cu site. This should result in a remarkable transformation of the pure NQR spectrum at $T > T_N$ to a high frequency AFMR spectrum for $T < T_N$ which is perturbed by quadrupole interaction. The origin of this absence of any signature of the transition is presently not clear.

IV. DISCUSSION

$CuSiO_3$, isotypic to the spin-Peierls compound $CuGeO_3$ was synthesized from the mineral dioptase and the physical properties of this new compound were determined by means of susceptibility, specific heat, and Cu nuclear quadrupole resonance measurements. The susceptibility of $CuSiO_3$ is in good agreement with the theoretical results for a quasi-one-dimensional $S = 1/2$ Heisenberg antiferromagnet with a nearest-neighbor exchange constant of $J/k_B = 21$ K and without a significant next-nearest neighbor exchange interaction ($J' = 0$). This is in contrast to the findings for $CuGeO_3$ where frustration effects due to next-nearest-neighbor interactions play a crucial role ($\alpha = J'/J \approx 0.35$) and where a much higher exchange coupling constant of $J/k_B \simeq 160$ K was found. According to the so-called Goodenough-Kanamori-Anderson[23] (GKA) rules a change from an antiferromagnetic exchange to a ferromagnetic exchange is expected when the bond angle is near 90°. Therefore the much smaller J value in $CuSiO_3$ could easily be attributed to the reduction of the Cu-O(2)-Cu bond angle from 99° in $CuGeO_3$ to 94° in $CuSiO_3$. In contrast, the disappearance of the frustration is surprising, since the corresponding bond angles are fare away from 90°. One possible explanation is, that the smaller Cu-O(2)-Cu bond angle of 94° leads to a cancellation of the antiferromagnetic and ferromagnetic exchange contributions and a vanishing nearest-neighbor exchange J. The remaining next-nearest-neighbor exchange J' would then transform one atomic chain into two independent spin chains. Since the susceptibility (and the specific heat) is the same as that of a single spin chain, the present experimental results do not allow to distinguish between both cases. General calculations for the edge-sharing cuprates leads to a ferromagnetic exchange coupling constant J for an bond angle of 94°, wheras J' is always antiferromagnetic with only a weak dependence on the angle.[24] The ferromagnetic nearest-neighbor exchange for the 94° configuration has been experimentally found in Li_2CuO_2.[25] However the arrangement of the chains (parallel chains in Li_2CuO_2 versus tilted chains in $CuSiO_3$) and the nature of the side groups (Li versus Si), which are also expected to influence J, are different to $CuSiO_3$. Thus an estimate of the J value for $CuSiO_3$ based on an LDA calculation performed by using the real lattice structure of $CuSiO_3$ does not support a ferromagnetic nearest-neighbor exchange.[26]

The large residual susceptibility below T_N, the T^3 power law in the magnetic specific heat at low temperatures, the spin-flop-like transition in a magnetic field as well as the H-T magnetic phase diagram are very strong evidence for the antiferromagnetic nature of the transition. The comparatively large ratio between the ordering temperature T_N and the temperature of the maximum in the susceptibility $T_{m,\chi}$ indicate that the ratio between interchain-and intrachain exchange ($J_\perp/J$) is significantly larger in $CuSiO_3$ than in $CuGeO_3$. This is a natural consequence of the weakness of the intrachain exchange. An estimate of the interchain coupling constant for quasi-one-dimensional chains is given by the following expression:[27] $J_\perp = T_N/1.28\sqrt{\ln(5.8J/T_N)} = 3.7$ K. From this we obtain a ratio of $J_\perp/J \approx 0.18$. LDA band structure calculations also reveal a much weaker intrachain coupling J and a larger $J_\perp/J$ ratio[26] (≈ 0.14) compared to

CuGeO$_3$, which is in agreement with our experimental results. However, they also suggests that the frustration should still be significant in CuSiO$_3$. The weaker intrachain coupling J and the much larger $J_\perp/J$ ratio obviously favor the occurrence of an AF transition instead of a SP transition. The presented investigations do not give any information about the strength of the magnetoelastic coupling in CuSiO$_3$. This coupling is a prerequisite for a spin-Peierls transition.

In conclusion, it is shown that CuSiO$_3$ is a quasi-one-dimensional $S=1/2$ Heisenberg chain system which undergoes a transition to long range antiferromagnetic order at $T_N=7.9$ K. There is no direct evidence for spin-Peierls transition in this new compound. Field dependent susceptibility measurements reveal a spin-flop phase at $\mu_0 H_{\rm SF}\approx 3$ T. Among all inorganic low-dimensional Cu based spin systems the edge-sharing compound CuSiO$_3$ exhibits the smallest intrachain exchange AF-coupling constant of $J/k_B=21$ K. The existence of the two homologeus compounds CuGeO$_3$ and CuSiO$_3$ with different ground state properties provides an excellent basis for the application of theoretical models and methods of low-dimensional physics.

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

[2] J.P. Boucher and L.P. Regnault, J. Phys. I **6**, 1939 (1996).

[3] M. Hase, I. Terasaki, Y. Sasago, K. Uchinokura, and H. Obara, Phys. Rev. Lett. **71**, 4059 (1993).

[4] S.B. Oseroff, S.W. Cheong, B. Aktas, M.F. Hundley, Z. Fisk, and L.W. Pupp, Jr., Phys. Rev. Lett. **74**, 1450 (1995).

[5] M. Poirier, R. Beaudry, M. Castonguay, M.L. Plumer, G. Quirion, F.S. Razavi, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **52**, 6971 (1995).

[6] J.P. Renard, K.Le. Dang, P. Veillet, G. Dhalenne, A. Revcolevschi, and L.P. Regnault, Europhys. Lett. **30**, 475 (1995).

[7] L.P. Regnault, J.P. Renard, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. **32**, 579 (1995).

[8] M. Weiden, R. Hauptmann, W. Richter, C. Geibel, P. Hellmann, M. Köppen, F. Steglich, M. Fischer, P. Lemmens, G. Güntherodt, A. Grimmel, and G. Nieva, Phys. Rev. B **55**, 15 067 (1997).

[9] T. Masuda, I. Tsukada, K. Uchinokura, Y.J. Wang, V. Kiryukhin, and R.J. Birgeneau, Phys. Rev. B **61**, 4103 (2000).

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

[11] H.H. Otto and M. Meibohm, Z. Kristallogr. **214**, 558 (1999).

[12] J.C. Bonner and M.E. Fischer, Phys. Rev. **135**, B640 (1964).

[13] A. Klümper, Eur. Phys. J. B **5**, 677 (1998).

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

[15] X. Liu, J. Wosnitza, and H.v. Löhneysen, Z. Phys. B: Condens. Matter **98**, 163 (1995).

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

[17] D.C. Johnston, R.K. Kremer, M. Toyer, X. Wang, A. Klümper, S.L. Budko, A.F. Panchula, and P.C. Canfield, Phys. Rev. B **61**, 9558 (2000).

[18] T. Shimizu, J. Phys. Soc. Jpn. **62**, 772 (1993).

[19] S.B. Ota and E. Gmelin, Phys. Rev. B **46**, 11 632 (1992).

[20] T. Tsuda, J. Phys. Soc. Jpn. **57**, 2908 (1988).

[21] J. Kikuchi, H. Yasuoka, M. Hase, Y. Sasago, and K. Uchinokura, J. Phys. Soc. Jpn. **63**, 872 (1994).

[22] M. Itoh, S. Hirashima, and K. Motoya, Phys. Rev. B **52**, 3410 (1995).

[23] J.B. Goodenough, Phys. Rev. **100**, 564 (1955); J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959); P.W. Anderson, Solid State Phys. **14**, 99 (1963).

[24] Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **57**, 5326 (1998).

[25] F. Sapina, J. Rodriguez-Carvajal, M.J. Sanchis, A. Beltran, and D. Beltran, Solid State Commun. **74**, 779 (1990).

[26] H. Rosner, S.-L. Drechsler, K. Koepernik, R. Hayn, and H. Eschrig, cond-mat/0004239 (unpublished).

[27] H.J. Schulz, Phys. Rev. Lett. **77**, 2790 (1996).