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Specific heat, thermal expansion, and pressure dependencies of the transition temperatures of doped $CuGeO_3$

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We present high-resolution measurements of the specific heat and the thermal expansion of the inorganic spin-Peierls cuprate $CuGeO_3$ doped with 1.4% Zn and 0.5% Si, respectively. Both compounds exhibit rather well-defined spin-Peierls transitions at about 11 K, which cause anomalies in both the specific-heat and the thermal-expansion coefficients. By comparing these anomalies we derive very large pressure dependencies of the transition temperatures. In particular, the pressure dependencies of the doped compounds are significantly larger than those in pure $CuGeO_3$. From this difference we conclude that the suppression of the spin-Peierls transition in $CuGeO_3$ by doping with Zn or Si is significantly reduced under pressure. [S0163-1829(97)50726-0]

The discovery of a spin-Peierls transition in the inorganic compound $CuGeO_3$ by Hase *et al.*[1] has renewed the interest in low-dimensional antiferromagnets. The spin-Peierls transition is a magnetoelastic phase transition occurring in quasi-one-dimensional, antiferromagnetic insulators. Below the transition temperature the antiferromagnetic spin-$\frac{1}{2}$ chains dimerize, i.e., the former uniform distances between neighboring spins now alternate. Due to the magnetoelastic coupling the exchange constant between neighboring spins also alternates $[J_{1,2}=J_0\ (1\pm\delta)]$ and the singlet ground state is separated from the band of excited triplet states by an energy gap. During the last years $CuGeO_3$ has been intensively studied and most of the characteristic features of the spin-Peierls transition were observed,[2] e.g., the opening of a gap in the magnetic excitation spectrum below T_{SP} (Refs. 3 and 4) and the dimerization of the one-dimensional spin-$\frac{1}{2}$-Heisenberg chains.[5–7]

Nevertheless, there are several features of $CuGeO_3$ which are difficult to explain within existing theories. First of all the magnetic susceptibility of the high-temperature uniform phase (U) strongly deviates from that which is calculated for a one-dimensional Heisenberg chain with nearest-neighbor exchange. A much better agreement between theory and experiment is obtained if an additional antiferromagnetic next-nearest-neighbor exchange, i.e., a magnetic frustration along the chains, is assumed.[8,9] Furthermore, the spin-Peierls transition temperature of $CuGeO_3$ is strongly pressure dependent [$\simeq$5 K/GPa (Refs. 10 and 11)]. Within the Cross-Fisher theory,[12] the only source for this pressure dependence is a pressure-dependent phonon frequency. However, the anisotropy of the uniaxial pressure dependencies of T_{SP} clearly correlates with that of the uniaxial pressure dependencies of the magnetic susceptibility indicating that the pressure dependence of T_{SP} is not of phononic but of magnetic origin.[13]

$CuGeO_3$ allows for substitutions of Zn and Si on the Cu and Ge sites, respectively. For both dopants a drastic suppression of the spin-Peierls transition and the occurrence of an antiferromagnetic ordering with a maximum T_N of about 5 K is found. For certain concentrations of Si and Zn there is even a sequence of both transitions and a coexistence of dimerization and antiferromagnetic ordering is observed.[14–16]

In this Rapid Communication we present measurements of the thermal expansion coefficients and the specific heat on single crystalline $CuGe_{0.995}Si_{0.005}O_3$ ($1.9\times2.3\times8.4$ mm^3) and $Cu_{0.986}Zn_{0.014}GeO_3$ ($8.1\times2.8\times5$ mm^3). Both samples were cut from larger single crystals grown by a floating zone technique. The specific heat (C_p) has been measured by a quasiadiabatic heat-pulse method and the longitudinal thermal expansion coefficients $\alpha_i=(1/L_i)\partial L_i/\partial T$ (L_i denotes the length of the sample along the axis i) with a capacitance dilatometer.

Figure 1 displays the specific heat data of $Cu_{0.986}Zn_{0.014}GeO_3$ in the temperature range below 20 K. For comparison, we also show C_p of pure $CuGeO_3$. Whereas the pure compound exhibits a T_{SP} of $\simeq$14.3 K, the doped sample has a T_{SP} of 11.5 K derived by a usual entropy conserving construction. Besides this strong suppression of T_{SP} we find a drastic reduction of the size and a significant change of the shape of the specific heat anomaly. The anomaly of the undoped sample is very sharp and has a λ-like shape indicating that the transition is strongly affected by fluctuations. The anomaly of the doped sample is significantly broadened and thus best described by a broadened mean-field step. Due to the strong dependence of T_{SP} on the Zn content this broadening may be caused by slight inhomogeneities of the Zn distribution.

In $CuGeO_3$ the low-temperature ($T\lesssim6$ K) specific heat is well described by a sum of a phononic ($C_{ph}=\beta T^3$, $\beta=0.3$ mJ/mole K^4) and a magnetic contribution showing activated behavior $[(C_{mag}=\delta\exp(-\Delta E/T,\ \Delta E=23\ \text{K})]$.[17,18] Since in the temperature range above $\simeq$17 K we do not find any differences between the specific heats of both samples,

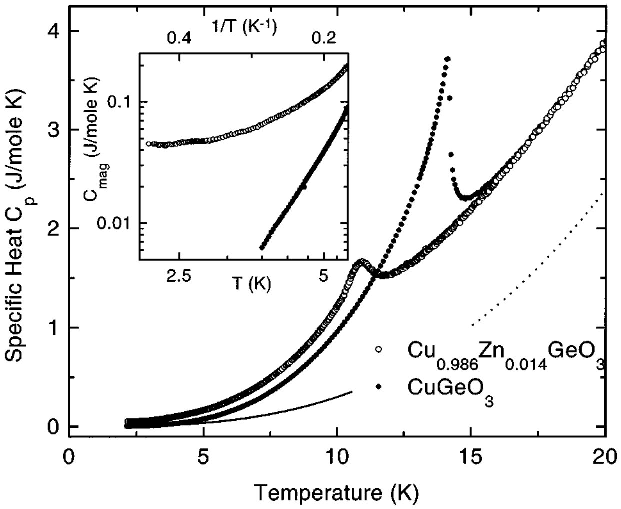

FIG. 1. Specific heat of $Cu_{0.986}Zn_{0.014}GeO_3$ (○) and $CuGeO_3$ (●). The solid line represents the phononic contribution $C_{ph} = \beta T^3$ for $T \rightarrow 0$. Inset: Expanded view of the low-temperature range in a plot of $\log C_{mag}$ vs $1/T$ (see text).

we conclude that the phonon contribution of C_p is not significantly influenced by doping. In order to analyze C_{mag} of the doped sample we therefore subtract C_{ph}, which is obtained on pure $CuGeO_3$ (solid line in Fig. 1), from the data. The inset of Fig. 1 displays C_{mag} of the doped and the pure compound in a plot of $\log C_{mag}$ vs $1/T$. Apparently, C_{mag} of the doped sample is completely different from that of the pure compound. First, it is significantly larger than that of $CuGeO_3$ and second, C_{mag} is not linear in this representation. Thus, we cannot extract a gap in the magnetic excitation spectrum from the specific heat. The different low-temperature behavior between C_{mag} of Zn-doped and pure $CuGeO_3$ can be compared to susceptibility measurements.[19] Already at very low Zn concentrations the drop of χ due to the spin-Peierls transition is drastically reduced compared to that of pure $CuGeO_3$. Moreover, in doped $CuGeO_3$ there is a strong increase of $\chi(T)$ for $T \rightarrow 0$ that has been attributed to spins which do not become singlet because of the existence of Zn ions.[19] The excitations of these unpaired spins might be the reason for the large low-temperature specific heat of the Zn-doped sample.

In Fig. 2 we show the specific heat of $CuGe_{0.995}Si_{0.005}O_3$ together with C_p of the Zn-doped sample. The suppression of the spin-Peierls transition is even stronger than in the Zn-doped sample. In $CuGe_{0.995}Si_{0.005}O_3$ we find a T_{SP} of 11.1 K, which is slightly smaller than in the Zn-doped sample. However, the size of the specific heat anomaly is significantly smaller and the broadening is more pronounced than in $Cu_{0.986}Zn_{0.014}GeO_3$. The main difference between the C_p's of both samples occurs at low temperatures. In $CuGe_{0.995}Si_{0.005}O_3$ there is a second anomaly at $T \simeq 2.9$ K (see inset of Fig. 2). As has been shown by neutron scattering and susceptibility measurements, this anomaly arises from an antiferromagnetic ordering, which coexists with the dimerization.[14,15] Similar observations have been reported for 0.9% and 2% Zn-doped samples.[20] Thus, the rather large low-temperature specific heat of our 1.4% Zn-doped sample is most probably related to an antiferromagnetic ordering at $T_N \lesssim 2$ K.

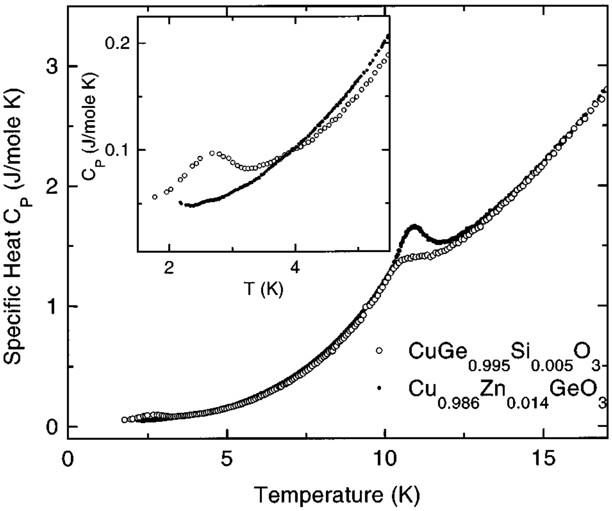

FIG. 2. Specific heat of $CuGe_{0.995}Si_{0.005}O_3$ (○) and $Cu_{0.986}Zn_{0.014}GeO_3$ (●). Inset: Expanded view of the anomaly of C_p of $CuGe_{0.995}Si_{0.005}O_3$ due to the antiferromagnetic order.

Now we turn to the measurements of the thermal expansion coefficients. Figure 3 displays α_i along the a, b, and c axes of the Zn-doped and the pure compound. As in the pure compound, the α_i of $Cu_{0.986}Zn_{0.014}GeO_3$ show pronounced anomalies of different signs and sizes at the spin-Peierls transition. (Please note the different scales in the left part of Fig. 3.) It is apparent from Fig. 3 that the structural anisotropy at the transition is not changed in the doped compound. Again, the largest anomaly occurs along the b and the smallest one along the c axis. The anomaly size of α_a is intermediate and is of opposite sign. Qualitatively, the influence of Zn doping on the α_i is similar to that on the specific heat, i.e., we find a reduction of the sizes and a broadening of the anomalies. However, the reduction of the anomaly sizes quantitatively differs. Compared to the pure compound, the anomaly of C_p is reduced by about a factor of 4, whereas those of the α_i are reduced by a factor of less than 2. Concerning the low-temperature range we also find an unusual behavior, since at about 4 K all three α_i of the doped compound reveal sign changes.

The anomalies of the α_i are a consequence of the development of spontaneous strains (ϵ_i) in the dimerized (D) phase arising from a strain order-parameter coupling.[10,17,21] The right part of Fig. 3 shows the spontaneous strains of $Cu_{0.986}Zn_{0.014}GeO_3$, which are obtained by $\epsilon_i = \int(\alpha_i - \alpha_{i,extr})dT$. The $\alpha_{i,extr}$ are smooth background polynomials representing the extrapolated behavior of the α_i of the U phase to $\alpha_{i,extr}(T=0)=0$ (solid lines in Fig. 3). It has been shown previously that in the D phase of pure $CuGeO_3$ the spontaneous strains are proportional to the square of the structural order parameter.[7,21] It is justified to assume that the strain order-parameter coupling is not changed by doping. Thus, the ϵ_i allow for a study of the (squared) order parameter of the doped sample. It can be inferred from Fig. 3 that the ϵ_i have a nonmonotonic temperature dependence. With decreasing temperature the $|\epsilon_i|$ continuously increase for $12 \text{ K} \gtrsim T \gtrsim 4$ K, but for $T \lesssim 4$ K a slight decrease arising from the sign changes of the α_i is found. That means that for $T \lesssim 4$ K the spin-Peierls order parameter slightly *decreases* with decreasing temperature.

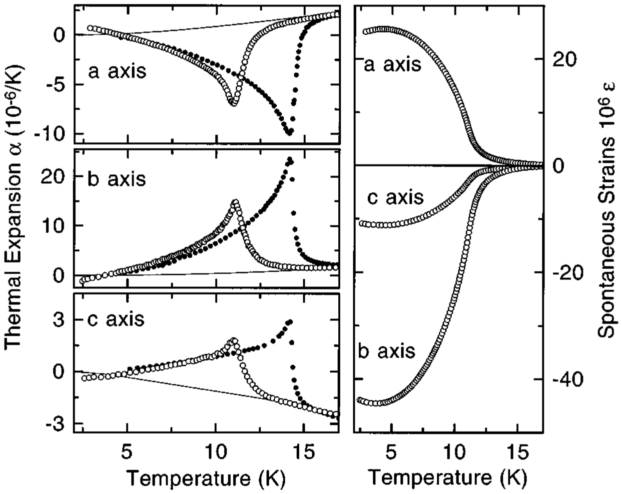

FIG. 3. Left panel: Thermal expansion coefficients of $Cu_{0.986}Zn_{0.014}GeO_3$ (○) and $CuGeO_3$ (●). The solid lines represent the extrapolated behavior of α_i of the U phase to $\alpha_i(T=0)=0$. Right panel: Spontaneous strains of $Cu_{0.986}Zn_{0.014}GeO_3$ representing the squared spin-Peierls order parameter (see text).

Neutron-scattering data of a 0.9% Zn-doped sample reveal a very similar temperature dependence for the intensities of superstructure reflections, which ‘‘directly’’ measure the squared order parameter.[20]

In Fig. 4 the thermal expansion coefficients along the a and c axis of $CuGe_{0.995}Si_{0.005}O_3$ are shown. Both the spin-Peierls and the antiferromagnetic transition give rise to large anomalies of α_a and α_c. Compared to the Zn-doped sample, the enhanced transition width at T_{SP} is again visible, but in contrast to the specific heat, the anomaly sizes of the α_i are nearly equal for the Si- and Zn-doped sample. Along both axes the anomalies at T_N and at T_{SP} are of different signs and at both transitions the sizes of the anomalies along the a axis are about twice as large as those along the c axes, i.e., the anisotropy between the a and the c axis is the same at both transitions. Due to experimental reasons it was not possible to measure α_b of this sample.

Since in the purely dimerized phase, i.e., for $T_N<T<T_{SP}$, the α_i of the Si-doped sample are almost identical to those of the Zn-doped one, the spontaneous strains of both samples are nearly equal (see Figs. 3 and 4). In particular, both α_i also reveal sign changes already at $T>T_N$, i.e., the ϵ_i and thus the order parameter have a nonmonotonic temperature dependence. Again, similar results are obtained from neutron-scattering measurements on Si-doped $CuGeO_3$.[14] The strong decrease of the $|\epsilon_i|$ for $T<T_N$ is more difficult to explain. A comparison with neutron-scattering data indicates that the ϵ_i are not determined by the order parameter of the D phase alone. Instead, there is an additional effect due to the antiferromagnetic ordering. Exactly speaking, there is an additional coupling between the ϵ and the Néel order parameter. A quantitative separation of both contributions is, however, not possible.

From the similarity of the order parameters in the D phases we conclude that the source of the suppression of the spin-Peierls transition in $CuGeO_3$ by Si and Zn doping is similar. However, the reason for this strong suppression by such small amounts of both Si and Zn is still an open question. In the following we will show that, surprisingly, this strong influence of Si and Zn is significantly reduced under pressure.

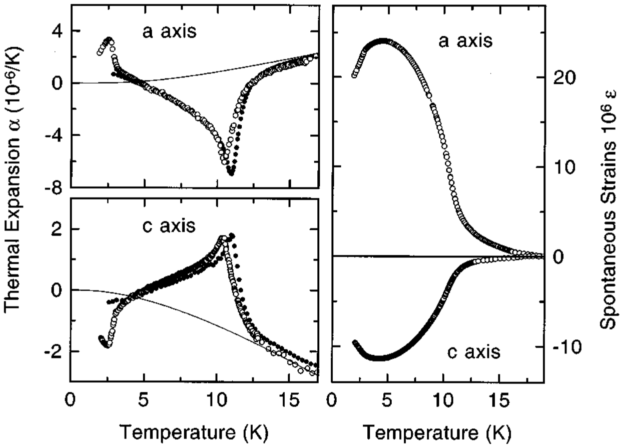

FIG. 4. Left panel: Thermal expansion coefficients of $CuGe_{0.995}Si_{0.005}O_3$ (○) and $Cu_{0.986}Zn_{0.014}GeO_3$ (●). The solid lines represent the extrapolated behavior of α_i of the U phase to $\alpha_i(T=0)=0$. Right panel: Spontaneous strains of $CuGe_{0.995}Si_{0.005}O_3$ (see text).

The measurements of α_i and C_p allow us to derive the uniaxial pressure dependencies of the transition temperatures via the Ehrenfest relation,

$$\partial T_c/\partial p_i|_{p_i\to 0}=V_m T_c \Delta\alpha_i/\Delta C_p . \qquad (1)$$

T_c is the transition temperature T_N or T_{SP}, respectively, and V_m the volume per mole. $\Delta\alpha_i$ and ΔC_p are the ‘‘jumps’’ of the thermal expansion coefficient along the i axes and the specific heat, respectively.[22]

In Table I we summarize the uniaxial pressure dependencies of T_{SP} and T_N of the different samples. In addition, the hydrostatic pressure dependencies $\partial T_c/\partial p_{hydr}=\Sigma\partial T_c/\partial p_i$ are also given. For $Cu_{0.986}Zn_{0.014}GeO_3$ we find very large and strongly anisotropic uniaxial $\partial T_{SP}/\partial p_i$'s. Uniaxial pressure along the b and c axis leads to an increase of T_{SP} by 12.1 and 2.8 K/GPa, respectively, whereas pressure along the a axis suppresses T_{SP} by -6.8 K/GPa. Although the $\partial T_{SP}/\partial p_i$'s partially cancel under hydrostatic pressure, the hydrostatic pressure dependence of 8.1 K/GPa is also very large. Apparently, the anisotropy of the uniaxial pressure dependencies of T_{SP} in $Cu_{0.986}Zn_{0.014}GeO_3$ is almost identical to that in the pure sample (see Table I). However, in the doped compound the absolute values are significantly larger. This increase of the $\partial T_{SP}/\partial p_i$'s is a consequence of the fact that ΔC_p is much more strongly suppressed by Zn doping than $\Delta\alpha_i$ (see Figs. 1 and 3).

For the Si-doped sample this different suppression of $\Delta\alpha_i$ and ΔC_p is even more pronounced (see Figs. 2 and 4) and, accordingly, the $\partial T_{SP}/\partial p_i$'s are even larger. We find -11 and $+4.9$ K/GPa for p_a and p_c, respectively. The pressure dependencies of T_N show a clear anticorrelation to those of T_{SP}. They have the same anisotropy but opposite signs ($+7.1$ and -3.3 K/GPa for p_a and p_c, respectively). As mentioned above, we could only measure α_a and α_c. Since the anisotropy between $\partial T_c/\partial p_a$ and $\partial T_c/\partial p_c$ for both T_N and T_{SP} is nearly the same as in the other two samples, we assume a corresponding anisotropy relative to $\partial T_c/\partial p_b$.

TABLE I. Uniaxial and hydrostatic pressure dependences of T_{SP} and T_N of $\mathrm{CuGeO_3}$, $\mathrm{Cu_{0.986}Zn_{0.014}GeO_3}$, and $\mathrm{CuGe_{0.995}Si_{0.005}O_3}$ for $p_i \rightarrow 0$. In $\mathrm{CuGe_{0.995}Si_{0.005}O_3}$ α_b could not be measured, therefore the values for p_b and p_{hydr} are only estimates assuming the usual anisotropy (see text).

	$\mathrm{CuGeO_3}$ $T_{\mathrm{SP}}=14.3$ K $\partial T_{\mathrm{SP}}/\partial p_i$ (K/GPa)	1.4% Zn $T_{\mathrm{SP}}=11.5$ K $\partial T_{\mathrm{SP}}/\partial p_i$ (K/GPa)	0.5% Si $T_{\mathrm{SP}}=11.1$ K $\partial T_{\mathrm{SP}}/\partial p_i$ (K/GPa)	 $T_N=2.9$ K $\partial T_N/\partial p_i$ (K/GPa)
p_a	$-3.7(5)$	$-6.8(10)$	$-11.1(10)$	7.1(8)
p_b	7.2(5)	12.1(10)	(21)	(-14)
p_c	1.6(5)	2.8(10)	4.9(10)	$-3.3(8)$
p_{hydr}	5.1(5)	8.1(10)	(15)	(-10)

Based on this assumption, we also give estimates for the values of $\partial T_c/\partial p_b$ and $\partial T_c/\partial\, p_{\mathrm{hydr}}$.

The pressure dependences derived from the Ehrenfest relation are valid in the limit of vanishing pressure. But it is known that in pure $\mathrm{CuGeO_3}$ an almost linear increase of T_{SP} is present under hydrostatic pressure up to about 2 GPa.[11,23] If we assume a linear pressure dependence of T_{SP} in the doped compounds too, we obtain the very surprising result that for $p_{\mathrm{hydr}} \gtrsim 1$ GPa the extrapolated T_{SP}'s of the doped compounds exceed that of the pure sample. In other words, under pressure T_{SP} of $\mathrm{CuGeO_3}$ would be enhanced by doping. Since such an enhancement seems very unlikely, we expect that in the doped compound $T_{\mathrm{SP}}(p)$ is strongly nonlinear. Measurements of doped $\mathrm{CuGeO_3}$ under finite pressure are in progress to clarify this question. Nevertheless, our measurements indicate that the strong suppression of T_{SP} by doping, which is present at zero pressure, seems to vanish under already moderate hydrostatic pressure. Moreover, the occurrence of the antiferromagnetic ordering in $\mathrm{CuGe_{0.995}Si_{0.005}O_3}$ disappears. Uniaxial pressures along the b and c axis cause similar changes as hydrostatic pressure at, however, smaller and larger values of p_b and p_c, respectively. Uniaxial pressure along the a axis causes the opposite effects, i.e., T_{SP} is strongly suppressed and in $\mathrm{CuGe_{0.995}Si_{0.005}O_3}$ a drastic increase of T_N occurs. Apparently, the kind of (magnetic) order in doped $\mathrm{CuGeO_3}$ is extremely sensitive to pressure. In particular, the different signs of the pressure dependences of T_N and T_{SP} in $\mathrm{CuGe_{0.995}Si_{0.005}O_3}$ indicate a competition between the spin-Peierls and the Néel state. Moreover, we mention that the anisotropy, which is present for both the $\partial T_{\mathrm{SP}}/\partial p_i$'s and the $\partial T_N/\partial p_i$'s, is also found for another quantity of $\mathrm{CuGeO_3}$, namely for the uniaxial pressure dependences of the magnetic susceptibility χ in the uniform phase.[13,24] This ''universal'' anisotropy points to a common origin of the pressure-dependent changes of T_{SP}, T_N, and χ.

Summarizing our study of the influence of Si and Zn doping on the specific heat and thermal expansion of $\mathrm{CuGeO_3}$: We find a quantitatively very different suppression of the anomalies occurring in C_p and the α_i at T_{SP}. Due to this difference a drastic increase of the pressure dependences of T_{SP} is found for the doped compounds, which indicates that the influence of Si and Zn is significantly reduced under pressure. Moreover, we have shown, using the Ehrenfest relation, that the uniaxial pressure dependences of T_N are clearly anticorrelated to those of T_{SP}.

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[22] There are different possibilities to get a measure for the values of $\Delta\alpha_i$ and ΔC_p. For example, one is to use the maximum deviations of α_i and C_p of their extrapolated backgrounds. Another possibility is to construct length and entropy conserving idealizations of the anomalies of α_i and C_p, respectively. The different ways cause different values of $\Delta\alpha_i$ and $\Delta\mathrm{C}_p$, but—as long as the same procedure is used for both quantities—the resulting pressure dependences are rather insensitive to this uncertainty, since they depend on $\Delta\alpha_i/\Delta C_p$ [see Eq. (1)].

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