Thermodynamic properties of the incommensurate phase of $CuGeO_3$

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We present high-resolution measurements of the specific heat and the thermal expansion of the inorganic spin-Peierls cuprate $CuGeO_3$ in a magnetic field of 16 T. At the transition from the incommensurate to the uniform phase both quantities show pronounced anomalies, which allow us to derive the uniaxial pressure dependences of the transition temperature. In high magnetic fields the specific heat is dominated by magnetic excitations and follows a T^3 law at low temperatures. The thermal expansion measurements show the occurrence of spontaneous strains along all three lattice constants and yield high-resolution measurements of the temperature dependence of the incommensurate structural distortion. The sizes of the spontaneous strains in the incommensurate phase are significantly reduced, but both their anisotropy as well as their temperature dependences are very similar to those in zero field. [S0163-1829(96)52046-1]

During the last three years $CuGeO_3$ has been the subject of intensive investigations and the occurrence of a spin-Peierls transition ($T_{SP} \simeq 14$ K) in this inorganic compound is well established now. Most of the characteristic features of this transition are observed, e.g., the opening of a gap in the magnetic excitation spectrum below T_{SP} (Refs. 1–3) and the dimerization of the one-dimensional spin-$\frac{1}{2}$-Heisenberg chains.[4–6] In addition to the dimerization, very pronounced spontaneous strains (ϵ) of all three lattice constants are found, which are proportional to the square of the structural order parameter Q.[6,7] This proportionality ($\epsilon = kQ^2$) is expected from a Ginzburg-Landau expansion of the free energy when a usual linear quadratic coupling between Q and ϵ is assumed (see, e.g., Refs. 6 and 7). The temperature magnetic-field phase diagram[8,9] is also found to be in fair agreement with the theoretical expectations.[10,11] For low fields a reduction of T_{SP} occurs which is proportional to H^2. For higher fields ($H \gtrsim 12$ T) a transition to an incommensurate phase takes place. In this I phase the lattice distortion is expected to be incommensurate with respect to the underlying lattice. There are, however, different models for the spatial character of the incommensurate modulation; domain walls[12] or a sinusoidal modulation.[11] An incommensurate lattice modulation is indeed observed in $CuGeO_3$ for $H \gtrsim 12$ T by x-ray scattering.[13,14] Although these measurements favor the domain-wall picture, significant discrepancies between theory and experiment are still present.[14]

In order to study the magnetic and structural properties of the I phase we have performed high-resolution measurements of such thermodynamic properties as specific heat and thermal expansion. Both quantities were measured on the same single crystal of $CuGeO_3$ with a size of about $6 \times 5 \times 8.3$ mm^3. The specific heat (C_P) was determined by a quasiadiabatic step-by-step method. 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) were measured with a capacitance dilatometer.

Figure 1 displays the specific heat data of $CuGeO_3$ in a magnetic field of 16 T, which was oriented along the b axis. For comparison, we also show the data relative to zero magnetic field (see also Refs. 15 and 16). It is obvious that the main influence of the field is a strong decrease of both the transition temperature and the size of the anomaly. Nevertheless, a sharp and rather large anomaly of C_P is found at the transition between the I and the high-temperature uniform (U) phases. The λ-like shapes of the anomalies indicate that in $CuGeO_3$ the transitions are strongly affected by fluctuations, whereas the specific heat anomalies of the organic spin-Peierls compounds seem to show ''mean-field'' behavior,[17–19] i.e., the ''upturns'' of C_P close to T_{SP} are not observed. There are two possibilities to discuss this difference of the anomaly shapes. Either the better sample homogeneity of $CuGeO_3$ allows us to observe the fluctuations at the spin-Peierls transition or fluctuations are more pronounced in $CuGeO_3$. For example, one may speculate that the good agreement with mean-field behavior in the organic compounds is related to the preexisting soft phonon which

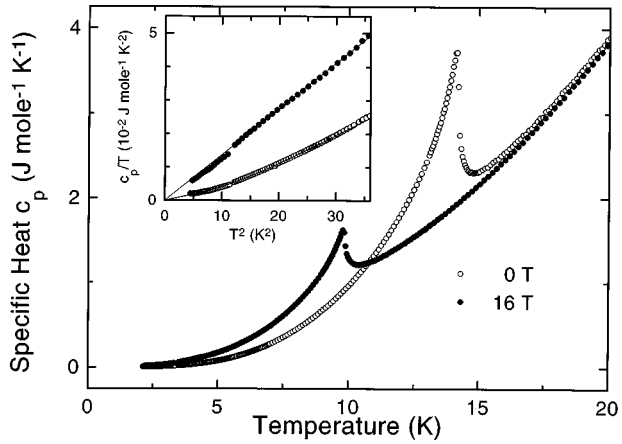

FIG. 1. Specific heat of $CuGeO_3$ in $H = 0$ (○) and 16 T (•). Inset: C_P/T vs T^2; the solid lines are fits assuming activated behavior (○: $H = 0$) and a T^3 law (•: $H = 16$ T, see text), respectively.

has not been found in $CuGeO_3$ so far.

Although the broadening of the transitions associated with sample inhomogeneities is rather small in $CuGeO_3$, there is a significant asymmetry with regard to the maximum of $C_P(T)$. Due to this asymmetry a description of the anomaly shape by a ''purely'' critical behavior of C_P is questionable. As shown by the authors of Ref. 16 for their zero-field data, which—although obtained on a different crystal—are in very good agreement with our data, it is not possible to unambiguously assign a universality class to the transition via the critical exponent of C_P. We note that—apart from their different sizes—the shapes of the anomalies close to T_{SP} do not differ significantly in $H=0$ and 16 T. Thus, we do not analyze the critical behavior of C_P in this communication.

In the low-temperature range, however, we find distinct differences between the zero- and high-field data. The inset of Fig. 1 shows C_P/T versus T^2 for $H=0$ and 16 T, respectively. As expected the data in zero field exhibit a clear curvature down to the lowest temperatures in this representation. This is due to the activated behavior of the magnetic contribution of C_P. The solid line represents a fit in terms of $C_P=\beta_{\rm ph}T^3+\delta\exp(-\Delta E/T)$. Restricting the fit to $T<6$ K we obtain a value $\beta_{\rm ph}=0.3$ mJ mole^{-1} K^{-4} for the lattice contribution. The magnetic contribution is given by $\delta=3.6$ J mole^{-1} K^{-1} and the energy gap amounts to $\Delta E=23$ K, in fair agreement with the results reported in Ref. 16.

The high-field data show a completely different low-temperature behavior. The entire specific heat follows a pure T^3 law. There is no indication for a gap in the magnetic excitation spectrum of the I phase. Assuming that $\beta_{\rm ph}$ does not depend on H, the specific heat is described by $C_P=(\beta_{\rm ph}+\beta_{\rm mag})T^3$. For $\beta_{\rm mag}$ we determine a value of 1.4 mJ mole^{-1} K^{-4}, which is significantly larger than $\beta_{\rm ph}$. Thus, in the low-temperature range the specific heat of the I phase is dominated by the magnetic excitations, which are strongly suppressed in zero field due to the opening of the gap.

The T^3 dependence of the magnetic specific heat is present in a rather large temperature range of the I phase, i.e., up to 5.5 K$\gtrsim T_{SP}/2$. Moreover, we also find the T^3 law with the *same* coefficient $\beta_{\rm mag}$ for smaller magnetic fields down to 12.5 T. Apparently, neither the temperature dependence nor the absolute value of C_P strongly changes as a function of the magnetic field in the I phase. A very strong field dependence of both the temperature dependence and the absolute value of C_P at low temperatures is, however, present in the D phase as can be extracted already from a comparison of the data in 0 T and 6 T shown in Ref. 16.

Let us shortly discuss the implications of the T^3 law we observe for the magnetic specific heat of the I phase. To our knowledge, the only existing theoretical calculation of C_P, which uses the soliton lattice solution for the I phase based on a mean-field Hamiltonian,[20] cannot explain our experimental finding. Fujita and Machida find in their calculations a BCS behavior of C_P for both zero field as well as in the I phase; i.e., they obtain a finite but reduced gap in the I phase as well. Even if we assume a very small value of this gap, it is impossible to fit our data with the theoretically expected BCS temperature dependence.

From the experimentally observed specific heat, one can in principle extract the dispersion relations of the magnetic excitations. Assuming a Bose statistics suggested by the T^3 law and a dispersion relation of the form $\omega\propto k^n$ the specific heat at low temperatures is proportional to $T^{D/n}$ where D denotes the dimension of the system. For three-dimensional excitations our finding implies linear dispersion relations in the I phase of $CuGeO_3$ as in usual antiferromagnets. For $D=1$ (or 2), rather strange dispersion relations are obtained, which makes the assumption of low-dimensional magnetic excitations in the I phase rather unlikely. Further theoretical and experimental work is necessary to decide whether there are really three-dimensional excitations with $\omega\propto k$ in the I phase or whether the T^3 law of C_P we observe in a large temperature and field range is due to an accidental superposition of different contributions.

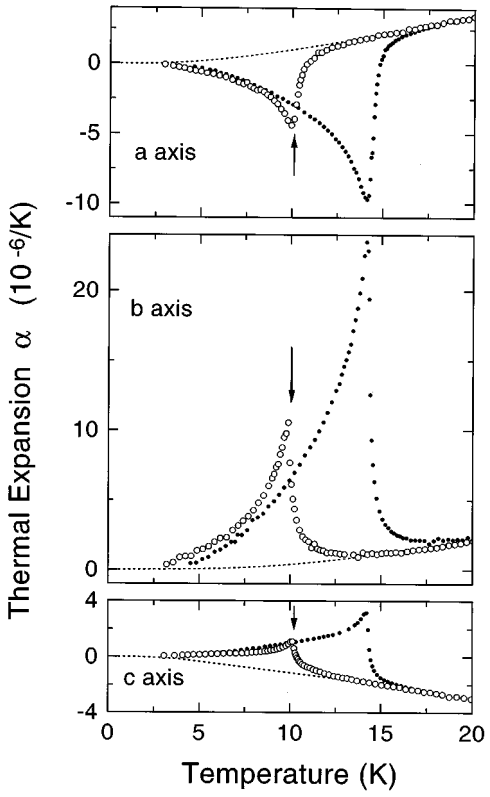

FIG. 2. Thermal expansion coefficients of $CuGeO_3$ in $H=0$ (•) and 16 T (◦). The dashed lines represent the extrapolated behavior of α_i of the U phase to $\alpha_i(T=0)=0$. The arrows mark the transition temperatures derived at the maximum slopes of $\alpha_i(T)$.

Our findings for the thermal expansion in the incommensurate phase markedly differ from those of the specific heat. In Fig. 2 we show the thermal expansion coefficients along the a, b, and c axes. Concerning the thermal expansion one has to distinguish between the structural and magnetic anisotropy. The magnetic anisotropy arises from the different values of the gyromagnetic ratios[21] along the different crystal axes. In our experimental setup the magnetic field is always parallel to the crystal axis whose thermal expansion coefficient is measured. Therefore, the transition temperatures slightly differ in the measurements carried out along the different crystal axes (see Fig. 2 and Table I).

The thermal expansion data in $H=0$ are also shown in Fig. 2. For each lattice constant the zero- and high-field data were obtained during the same run, i.e., for exactly the same orientation of the crystal. The anomalies occurring at the I/U

TABLE I. Uniaxial pressure dependences of T_{SP} along the different crystal axes in $H=0$ and $H=16$ T as calculated from the thermal expansion and specific heat anomalies. The different T_{SP}'s in $H=16$ T are due to the slightly different g factors of $CuGeO_3$.

axis	$H=0$ $T_{SP}=14.35(10)$ K		$H=16$ T	
	$\left.\frac{\partial T_{SP}}{\partial p_i}\right\|_{p_i=0}$ (K/GPa)	T_{SP} (K)	$\left.\frac{\partial T_{SP}}{\partial p_i}\right\|_{p_i=0}$ (K/GPa)
a	−3.7(5)	10.13(10)	−2.8(5)
b	7.2(5)	10.02(10)	5.3(5)
c	1.6(5)	10.23(10)	1.1(5)

transition are strongly reduced in size (by about a factor of 2) compared to those found in zero field. Despite this strong decrease, the anomalies are still rather large and indicate that the U/I transition strongly depends on pressure (see below). Furthermore, the anomalies reveal the occurrence of spontaneous strains within the I phase, which are also seen in the temperature dependences of the lattice constants (Fig. 3). The spontaneous strains are obtained by integration of the anomalous contribution $\delta\alpha_i \equiv \alpha_i - \alpha_{i,\mathrm{extr.}}$ below T_{SP}. The $\alpha_{i,\mathrm{extr.}}$ are smooth polynomials (given by the dashed lines in Fig. 2) representing the extrapolation of the α_i in the U phase to 0 at $T=0$ K.[7]

In zero field the ϵ_i are proportional to the square of the order parameter.[6,7,22] The characteristic temperature dependence of an order parameter is also visible in $H=16$ T (right part of Fig. 3). The temperature dependence of the structural order parameter in the I phase, i.e., the incommensurate lattice deformation, has not been measured by diffraction techniques so far. Thus, we cannot unambiguously prove $\epsilon_i \propto Q^2$ in the I phase. However, this leading order of the strain order parameter coupling is usually observed at structural transitions and, moreover, there is no indication that higher order terms are important at the U/I transition in $CuGeO_3$. In the following we will assume $\epsilon \propto Q^2$ for both phases and a comparison of the ϵ_i in $H=16$ T and $H=0$ allows for a comparison of the structural order parameters in the I and D phases, respectively.

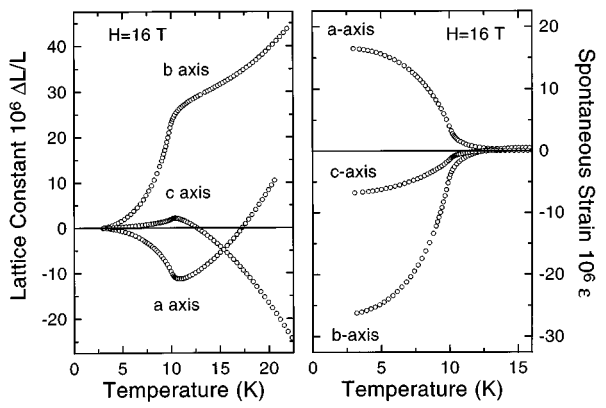

FIG. 3. Left panel: Temperature dependence of the lattice constants of $CuGeO_3$ in $H=16$ T. Right panel: Spontaneous strains $\epsilon_i = \int \alpha_i - \delta\alpha_{i,\mathrm{extr.}}$ in the I phase.

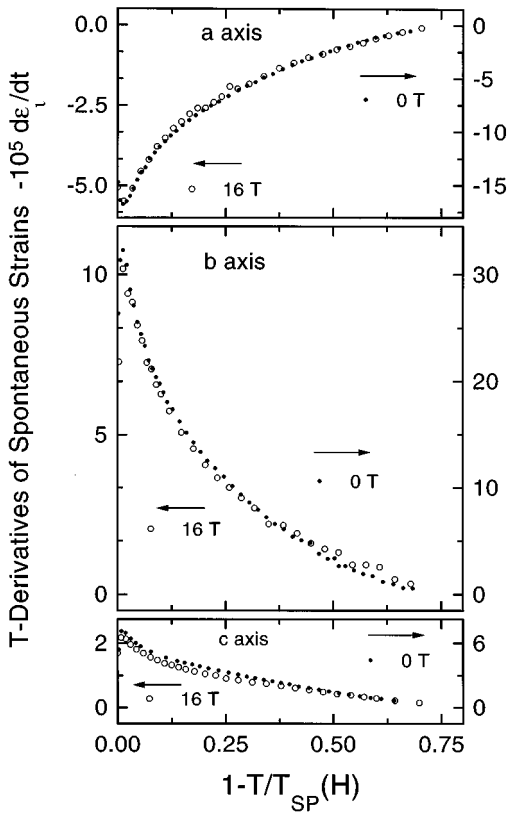

FIG. 4. Temperature derivatives of the spontaneous strains $-\partial\epsilon_i/\partial t \propto \partial Q^2/\partial t$ vs reduced temperature t in $H=16$ T (∘: left scale) and $H=0$ (•: right scale).

Besides differences in the critical behavior of the order parameter close to T_{SP}, which will be discussed elsewhere,[22] the ϵ_i occurring at the I phase compare well to those in zero field. In Fig. 4 we show $T_{SP}(H)\,\delta\alpha_i = -\partial\epsilon_i/\partial t$ versus reduced temperature $t=1-T/T_{SP}(H)$. That means, we compare the derivatives $\partial\epsilon_i/\partial t = k_i^{D/I}(\partial Q^2/\partial t)$ of the spontaneous strains occurring in the D and I phases, respectively. ($k_i^{D/I}$ denote the strain order parameter coupling constants.) Please note that by comparing the temperature derivatives of the $\epsilon_i(t)$ possible differences of their temperature dependences in $H=0$ and $H=16$ T will show up more clearly than by comparing the $\epsilon_i(t)$ themselves. It is apparent from Fig. 4 that, apart from the absolute values (see the different scales in Fig. 4), the temperature derivatives of the ϵ_i in the I phase are very similar to those in $H=0$. This holds for all three crystal axes. Moreover, the ratio between $\partial\epsilon_i/\partial t$ in $H=0$ and in $H=16$ T is independent on the crystal axis and amounts to a value of 3, i.e., the structural anisotropy does not change in a magnetic field. We emphasize that for the specific heat in $H=0$ and $H=16$ T such a similarity is not present at all (see Fig. 1). The magnetic and the structural degrees of freedom show completely different magnetic-field dependences.

The reduced ϵ_i in the I phase may arise either from three wave-vector-dependent strain order parameter coupling constants $[k_i^I = k_i^I(q)]$ or a reduced average amplitude A of the distortion. The identical anisotropy in $H=0$ and $H=16$ T strongly indicates that the reduction for all three lattice constants is determined by a common parameter, e.g., by A.

There is a straightforward qualitative explanation of such a reduction within the domain-wall picture. A is expected to reduce when approaching the domain walls.[12] The reduced ϵ_i in the I phase is then a consequence of the reduced average value of the dimerization within a single domain. Moreover, the ϵ_i should show a further decrease with increasing field due to the increasing number of domains. However, a sinusoidal modulation of the lattice distortion $[A(x) = A_0 \sin(qx)]$ also causes a reduction of the average value of the dimerization. Thus, from our present data it is impossible to discriminate between these two models of the structural distortion. Measurements up to still higher fields are planned to study the field dependence of $\epsilon_i(T,H)$ in the I phase to clarify this question.

Finally we derive the uniaxial pressure dependences of the U/I transition by comparing the anomaly sizes of the α_i and C_P as described in Refs. 7 and 22. Similar as for $H = 0$ T the uniaxial pressure dependences of T_{SP} in $H = 16$ T are very large and strongly anisotropic (see Table I). For pressure along the a axis T_{SP} decreases, whereas it increases for pressure along the two other axes. The hydrostatic pressure dependence given by the sum of the $\partial T_{SP}/\partial p_i$ amounts to $+3.6$ K/GPa. All the pressure dependences in $H = 16$ T are significantly smaller than those in $H = 0$ (Table I). There are, however, pronounced similarities to the zero-field data. The anisotropies of the $\partial T_{SP}/\partial p_i$ at the U/I transition and at $H = 0$ are nearly identical. Moreover, the pressure-induced relative changes of T_{SP} in $H = 0$ and $H = 16$ T are very similar. For instance, along the b axis an increase of about 50%/GPa is found for both $T_{SP}(H = 0)$ and $T_{SP}(H = 16$ T) indicating a pressure-independent H/T phase diagram in reduced scales, which is in agreement with theoretical predictions. However, as we have recently shown[23] the $\partial T_{SP}/\partial p_i$ unexpectedly correlate with the magnetoelastic coupling.

To summarize, we have reported measurements of the specific heat and the thermal expansion of $CuGeO_3$ in $H = 16$ T. For both quantities we find pronounced anomalies at the U/I transition. The specific heat at low temperatures is dominated by the magnetic excitations. In contrast to the findings in zero field our data in $H = 16$ T yield no indication for a gap in the magnetic excitations. Instead the magnetic specific heat follows a pure T^3 law. The thermal expansion below T_{SP} is dominated by the incommensurate lattice distortion leading to spontaneous strains of all three lattice constants which scale with the structural order parameter. Remarkably, the temperature dependences of the commensurate and incommensurate lattice distortion at $H = 0$ and 16 T, respectively, are very similar, whereas the magnetic specific heats markedly differ.

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