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Giant anomalies of the thermal expansion at the spin-Peierls transition in $CuGeO_3$

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The thermal-expansion coefficients α of the spin-Peierls cuprate $CuGeO_3$ have been measured along the three orthorhombic directions using a high-resolution capacitance dilatometer. We observe giant, strongly anisotropic anomalies at the spin-Peierls transition temperature (T_{SP}) and spontaneous strains along all three crystal axes below T_{SP}. From the jumps of α and the specific heat we estimate large uniaxial pressure dependencies of T_{SP}, in particular for pressure applied perpendicular to the one-dimensional Cu^{2+} chains. In addition, we observe an anomalous temperature dependence of the thermal expansion above the transition showing a striking similarity to that of the magnetic susceptibility.

The magnetic and structural properties of $CuGeO_3$ have attracted widespread attention, since Hase *et al.*[1] reported this compound to be the first example of an inorganic spin-Peierls system. $CuGeO_3$ has an orthorhombic structure with a strong one-dimensional character: The structure consists of chains of edge sharing CuO_6 octahedra and chains of corner sharing GeO_4 tetrahedra.[2] Both types of chains are oriented parallel to the c direction.

Hase *et al.* reported that the magnetic susceptibility of $CuGeO_3$ disappears below $T_{SP} \simeq 14$ K, which was interpreted as the formation of magnetic singlets due to a dimerization of the Cu chains, i.e., a spin-Peierls phase transition (SPT). The existence of a gap in the magnetic excitation spectrum anticipated by the results of Hase *et al.* was later directly confirmed by inelastic neutron scattering.[3] Lorenzo *et al.* reported the appearance of a spontaneous strain along the b axis at the phase transition,[4] which gave an indication for a coupling of the magnetic transition to lattice degrees of freedom. This anomalous behavior of the lattice constant b has been confirmed later in a high-resolution x-ray-diffraction study by Harris *et al.*,[5] which shows in addition a small anomaly of the lattice constant a at T_{SP}. Direct evidence for a change in the crystal structure at T_{SP} was found by Pouget *et al.* using x-ray and neutron diffraction.[6] They have observed superstructure reflections below T_{SP}, which could be indexed in a $2a \times b \times 2c$ lattice. Pouget *et al.* concluded that $CuGeO_3$ undergoes a second-order structural phase transition concomitantly to the disappearance of the magnetic susceptibility. The structure in the spin-Peierls phase was studied in more detail by Hirota *et al.* using neutron diffraction,[7] who developed a model for the structural distortion.

In order to investigate the relationship between the dimerization of the Cu ions below T_{SP} and spontaneous strains we have performed high-resolution measurements of the thermal expansion coefficient α of a $CuGeO_3$ single crystal. Pronounced anomalies of α are observed at T_{SP} along all three crystal axes reflecting a strongly anisotropic coupling between the order parameter of the SPT and lattice strains.

A single crystal of $CuGeO_3$ of about $6.0 \times 5.1 \times 8.5$ mm^3 was cut from a large cylindrical crystal (80 mm long) grown by a floating zone technique.[8] The structural and magnetic properties of single crystals prepared in this way are described in detail in Ref. 6. The coefficients of the thermal expansion $\alpha \equiv (1/L)\Delta L/\Delta T$ (L: length of the sample) along the three crystal axes were measured with a capacitance dilatometer with a resolution better than $\Delta L/L = 10^{-8}$.[9] The lengths changes were recorded while continuously heating the sample with a rate of 60 mK/min between 4 and 200 K. In addition we used a step by step method between 4 and 20 K. In this steady-state method the capacitance is measured in temperature intervals of about 0.1 K in thermal equilibrium. The results obtained with the two methods agree with each other within the experimental resolution.

In Fig. 1 we show α as a function of temperature between 4 and 200 K. Apparently, at T_{SP} pronounced anomalies of the thermal expansion of all three lattice parameters occur. These anomalies are shown on a smaller temperature scale in Fig. 2. The transition temperature as well as the shape of the anomalies are similar along the three directions, whereas signs and sizes of the anomalies strongly differ (see Table I). The largest anomaly is found along the b axis. A jump of α with comparable absolute value but opposite sign is present along the a axis whereas the smallest anomaly is observed along the c axis, i.e., parallel to the Cu^{2+} chains.

The changes of α occur in a relatively narrow temperature range of about $\Delta T \simeq 0.4$ K around $T_{SP} = 14.3$ K and the width of the transition correlates well with the jumps in the derivative of the magnetic susceptibility at T_{SP} reported by Pouget *et al.* for a similar single crystal.[6] We emphasize that the rather sharp anomalies of the thermal expansion, i.e., of the lattice parameters, at T_{SP} show that precursor effects com-

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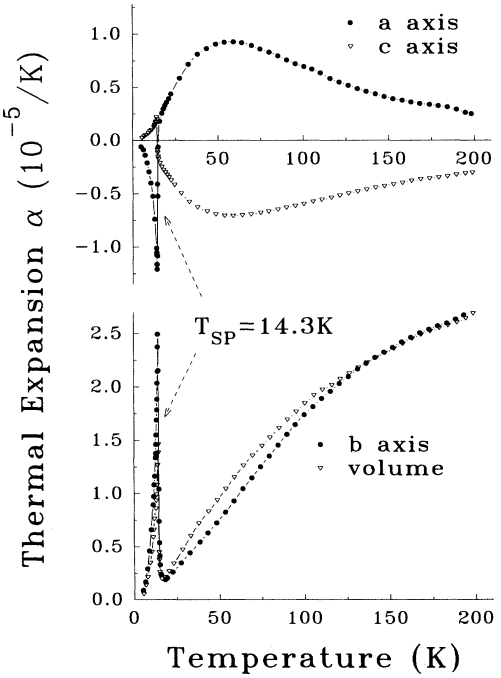

FIG. 1. Coefficients of the linear thermal expansion along the three crystal axes and of the volume expansion $(\alpha_a+\alpha_b+\alpha_c)$ of $CuGeO_3$ as a function of temperature.

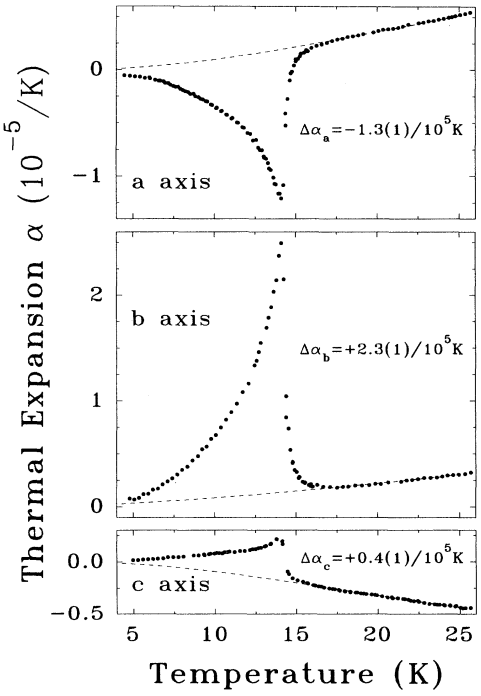

FIG. 2. Anomalies of the thermal expansion of $CuGeO_3$ at the spin-Peierls transition. The values of $\Delta\alpha_i$ given in the figure are determined from the data by an usual area conserving construction. The broken lines are extrapolations of the high-temperature behavior to $\alpha_i(T=0)=0$.

TABLE I. Measured jumps of the thermal expansion coefficients at T_{SP} and derived spontaneous strains, critical exponents (see text and Fig. 4), and uniaxial pressure dependencies of T_{SP} (at $p=0$) estimated according to Eq. (1) with $\Delta C_p=1.62(5)$ J/mole K, $V_m=3.61\times10^{-5}$ m^3/mole, and $T_{SP}=14.3$ K.

Crystal axes	$\Delta\alpha$ (10^{-5}/K)	$\epsilon(T=4$ K) (10^{-5})	2β	$dT_c/dp\|_{p=0}$ (K/GPa)
a	−1.3(1)	5.0(2)	0.61(2)	−4.2(5)
b	2.3(1)	−7.3(2)	0.61(2)	7.4(3)
c	0.4(1)	−1.7(2)	0.69(8)	1.3(3)
Volume	1.4(1)	−4.0(2)	0.63(2)	4.5(4)

monly observed at structural phase transitions are not very important at the SPT in $CuGeO_3$.

The (anisotropic) jumps of the thermal expansion at a phase transition are related to the (anisotropic) pressure dependencies of the transition temperature via the Ehrenfest relation:

$$\left.\frac{dT_{SP}}{dp_i}\right|_{p=0} = V_m T_{SP}\frac{\Delta\alpha_i}{\Delta C_p}, \qquad (1)$$

where p_i denotes external pressure along the lattice direction i, V_m the volume per mole, and ΔC_p the jump of the specific heat at the phase transition. In order to extract the uniaxial pressure dependencies we have also measured the specific heat of our single crystal.[10] The width and shape of the anomaly in the specific heat is comparable to those of the thermal expansion coefficient displayed in Fig. 2 and the jump at T_{SP} amounts to $\Delta C_p=1.62(5)$ J/mole K. The uniaxial pressure dependencies estimated from these measurements of $\Delta\alpha$ and ΔC_p are listed in Table I. Along the *b* axis one obtains a large increase of T_{SP} of $dT_{SP}/dp_b\simeq7.4$ K/GPa. Smaller increases of T_{SP} are also present for an uniaxial pressure parallel to the *c* axis and for hydrostatic pressure. On the other hand, uniaxial pressure along the *a* axis strongly suppresses the SPT.

A dimerization of the Cu ions at the SPT does not directly imply an anomaly in the thermal expansion in any direction. The increase of T_{SP} by applying uniaxial pressure parallel to the *c* axis, i.e., with decreasing distance between the Cu ions, qualitatively supports the idea that the phase transition is a magnetically triggered transition. However, the much larger dependencies of T_{SP} on uniaxial pressures along the *a* and *b* axes indicate that the positions of the atoms surrounding the one-dimensional Cu chains in $CuGeO_3$ are strongly involved in the formation of the nonmagnetic ground state below T_{SP}.

The coefficients of thermal expansion can be transformed into relative changes of the lattice parameters by integration. As demonstrated in Fig. 3 we find anomalies and spontaneous strains below T_{SP} for all three lattice constants. The findings for the lattice parameters *b* and *a*, where the anomalies at T_{SP} are extremely large, confirm the observations of Lorenzo *et al.* and Harris *et al.* based on neutron and x-ray diffraction, respectively.[4,5] The smaller effects along the *c* direction remained undetected up to now due to an insufficient resolution of the diffraction experiments.

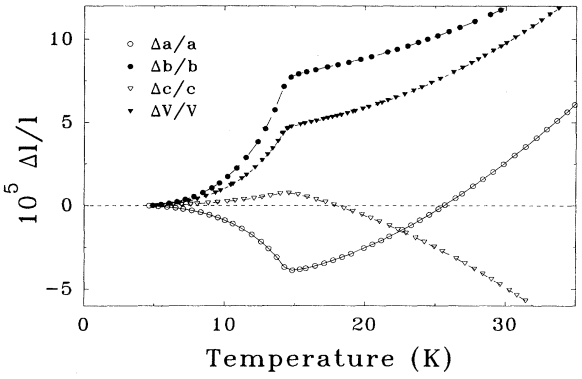

FIG. 3. Temperature dependence of the relative lattice constants in $CuGeO_3$ close to the spin-Peierls transition.

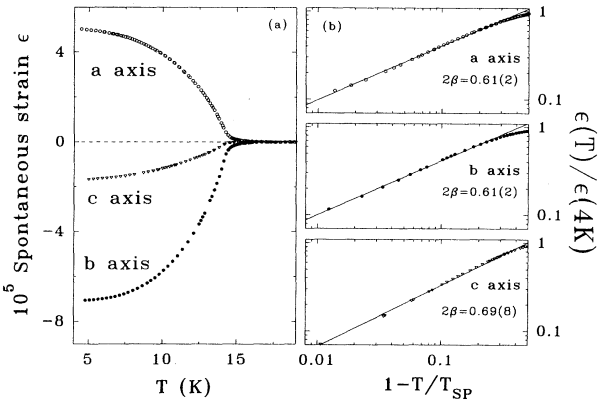

FIG. 4. (a) Temperature dependence of the spontaneous strains ϵ_i below T_{SP} as determined from the data in Fig. 3 after subtraction of the smooth background shown in Fig. 2. (b) Reduced spontaneous strains as function of the reduced temperature ($T_{SP}=14.3$ K) in a double logarithmic scale. The lines represent the fits with power laws of the form $\epsilon_i \propto (1-T/T_{SP})^{2\beta_i}$. The errors of β were determined by fitting the data for different temperature ranges, with slightly modified T_{SP}, and background polynoms.

In a first approach within the phenomenological Landau theory the spontaneous strains can be treated by coupling terms between elastic strains (ϵ_i) and the order parameter of the phase transition (Q), i.e., the lattice distortion connected with the dimerization of the Cu ions (see also Ref. 5). Usually one adds a linear quadratic strain order parameter coupling $\mu_i \epsilon_i Q^2$ to the free energy, where the μ_i denote the coupling constants. Considering in addition the elastic energy of the lattice, $C\epsilon_i^2$ (C: elastic constant), and the condition of a stress free system, $\partial F/\partial \epsilon_i = 0$, one yields spontaneous strains proportional to the square of the order parameter, i.e., $\epsilon_i(T) \propto Q^2(T)$.

For a quantitative analysis of the spontaneous strains we have extrapolated the α_i in the undistorted lattice to $\alpha_i(T=0)=0$ as indicated by the broken lines in Fig. 2. The $\epsilon_i \equiv [L(T)-L_{ext}(T)]/L_{ext}(T)$ (L,L_{ext} the measured and extrapolated length of the crystal) obtained after subtraction of this background are displayed in Fig. 4(a) (see also Table I). Apparently they show the typical temperature dependencies of an order parameter.

As expected for a renormalized temperature dependence the spontaneous strains follow a power law $\epsilon_i \propto (T_{SP}-T)^{2\beta_i}$ close to the phase transition. This is shown in Fig. 4(b), where we plot the reduced spontaneous strains $\epsilon(T)/\epsilon(4K)$ as a function of the reduced temperature $t=(T_{SP}-T)/T_{SP}$ in a double logarithmic scale. The power law is fulfilled for $0<t\leq 0.3$, i.e., in a temperature range of about 4 K below the phase transition. From the nearly identical temperature dependencies of the reduced spontaneous strains along the a and the b axis $2\beta_{a,b}=0.61(2)$ is derived, whereas the exponent determined from the strain along the c axis is somewhat larger [$2\beta_c=0.69(8)$], most probably due to the larger error of this latter value.[11] The data in Fig. 4 are thus consistent with the most simple assumption that the three spontaneous strains appearing below T_{SP} can be described by an usual strain order-parameter coupling with different coupling constants for the three orthorhombic crystal axes. This is confirmed by a comparison between $\Delta b/b$ and the intensity of superstructure reflections below T_{SP}.[5] The presence of this pronounced anisotropic coupling between lattice strains and the order parameter of the SPT is the main conclusion from our measurements.

We mention that significantly smaller values of the critical exponent β can be inferred from the temperature dependence of the energy gap for the spin-singlet to -triplet excitation.[3,12,13] However, the experimental uncertainty of the energy gap is much larger than that of the spontaneous strains in Fig. 4 and, moreover, the exponents have been determined at temperatures well below the phase transition, where strong deviations from a simple power law are present.

Finally we comment on the very strange temperature dependencies of α at temperatures above the SPT. Whereas the absolute value as well as the temperature dependence of the coefficient of the volume thermal expansion ($\alpha_a+\alpha_b+\alpha_c$) shown in the lower part of Fig. 1 appears at first sight comparable to that of other cuprates, the anisotropy and the temperature dependence of each single α_i is extremely anomalous in the entire temperature range up to 200 K (Fig. 1). The very large thermal expansion of the lattice parameter b is related to a soft longitudinal acoustic phonon branch along this direction as pointed out previously by Lorenzo *et al.*[5] Along the lattice parameter a the thermal expansion increases on cooling down to about 60 K where a broad maximum is observed. The coefficient α_c is even negative between T_{SP} and 200 K. Again an extremum appears at $T \simeq 60$ K. As apparent from Fig. 1 the unusual temperature dependencies of α_a and α_c are essentially identical besides a negative scaling factor. Note that a negative scaling factor is also obtained when comparing the jumps of the coefficients of the thermal expansion at T_{SP} (see Fig. 2) or the spontaneous strains below T_{SP} (see Fig. 4) along these two crystal axes.

The very strange anisotropic thermal expansion reflects to our opinion the interplay between rather rigid bonds within the GeO_4 tetrahedra and the CuO_6 octahedra on one hand and much weaker bonds between these two important building blocks of the structure on the other hand. It is most probably mainly determined by sterical properties of the crystal structure of $CuGeO_3$. Nevertheless, it seems worthwhile to note that there is a striking similarity between the

anomalous temperature dependencies of the thermal expansion and the magnetic susceptibility (χ). The susceptibility of $CuGeO_3$ shows a broad maximum at $T \simeq 60$ K, i.e., at the temperature where we find extrema of α_a and α_c. It seems natural to assume that a coupling between lattice strains and the antiferromagnetism of the Cu chains, which is apparent at the SPT, is also important for the interpretation of the anomalous behavior of α and/or χ well above T_{SP}. Moreover, the signs of the anomalies at 60 K and at T_{SP} are correlated. Both anomalies of α_a show the same signs as those of χ, i.e., a broad maximum at 60 K and a sharp decrease at T_{SP}, whereas the anomalies of α_c show a different sign, again in both cases. Note that this correlation may also hold for α_b (or the volume expansion), where no extremum is present at 60 K. A closer inspection of the data in Fig. 1 yields that an anomalous contribution to α_b with a flat minimum around 60 K might be masked by the much higher absolute value.

A significant change of the effective antiferromagnetic coupling of the Cu ions (J) as a function of the atomic positions in the structure is a precondition for the SPT. Thus the "magnetic contribution" to the free energy connected with the antiferromagnetic coupling of the Cu spins in $CuGeO_3$ depends on strains. This coupling also has consequences for the thermal expansion above T_{SP}, since the α_i measure second derivatives of the (total) free energy versus temperature and lattice strains.[14] In the simplest description the magnetic contributions to the α_i follow a similar temperature dependence as the magnetic contribution to the specific heat (C_{mag}), which has been calculated for one-dimensional antiferromagnetic chains.[15] These calculations yield broad maxima at $T \simeq J/k_B$ for both, C_{mag} as well as χ. Therefore similarities we find in the temperature dependencies of χ and the α_i, respectively, can qualitatively be explained in the framework of these calculations, if we consider in addition large strain dependencies of J with different signs for the different crystal axes. Furthermore, the strong discrepancy between the measured susceptibility of $CuGeO_3$ and the calculations for one-dimensional antiferromagnetic chains[1,15] might partially also be related to strong strain dependencies of J. The anisotropic changes of the lattice constants as a function of temperature apparent from Fig. 1 will lead to a change of the antiferromagnetic coupling, i.e., J becomes a function of temperature. Further investigations of the crystal structure as a function of temperature and magnetic field seem necessary in order to understand the unusual coupling between structure and magnetism in $CuGeO_3$.

In conclusion we have reported giant anomalies of the thermal expansion coefficient along the three orthorhombic directions at the spin-Peierls transition in $CuGeO_3$. The dimerization of the Cu ions is accompanied by pronounced structural changes perpendicular to the linear antiferromagnetic chains. The coupling between lattice strains and the order parameter of the spin-Peierls transition leads to large anisotropic pressure dependencies of T_{SP}, i.e., the phase transition depends sensitively on interatomic distances and/or bond angles within the unit cell. In addition we observe similarities between the magnetic susceptibility and the thermal expansion well above the spin-Peierls transition indicating an unusually strong magnetoelastic coupling in $CuGeO_3$, which might be directly related to the stabilization of the nonmagnetic dimerized state below T_{SP}.

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