Magnetic Frustration Induced Formation of the Spin-Peierls Phase in $CuGeO_3$: Experimental Evidence

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(Received 10 April 1996)

Measurements of the magnetostriction of single crystalline $CuGeO_3$ at temperatures between 2 and 60 K and for magnetic fields up to 14 T are presented. At low temperatures the magnetostriction is dominated by changes of the spontaneous strains at the phase transitions characteristic for spin-Peierls systems. At higher temperatures a magnetoelastic coupling is found which is unexpectedly large and strongly anisotropic. A comparison of the magnetostriction well above the spin-Peierls transition temperature T_{SP} and the thermal expansion anomalies at T_{SP} yields a striking correlation between the uniaxial pressure dependencies of the spin-susceptibility and T_{SP}. It is argued that this strongly supports electronic models of the spin-Peierls transition in $CuGeO_3$ which are based on competing antiferromagnetic intrachain interactions. [S0031-9007(96)00828-9]

PACS numbers: 75.80.+q, 75.10.Jm, 75.50.Ee

During the past three years extensive experimental studies have revealed that many properties of $CuGeO_3$ are well described by a model of spin-$1/2$ Heisenberg chains which exhibit a spin-Peierls (SP) transition at a temperature $T_{SP} \simeq 14$ K [1–5]. Specifically this applies to the experimental evidence at temperatures below T_{SP} which establish the existence of a dimerized (D) phase. In particular, lattice dimerization [2], a spin-gap scaling with the lattice distortion [3], and a magnetic field versus temperature phase diagram [1,4] have been observed which are consistent with an SP scenario. Although it turns out that analogous to the well known organic SP compounds the properties of the ordered phase are well described by a theory of Cross and Fisher (CF) [6], serious discrepancies arise for the remaining phases. According to CF's theory T_{SP} is determined by the ratio of the spin lattice coupling constant λ and the frequency ω_0 of the phonon, which softens at the phase transition, i.e., $T_{SP} \simeq 1.02(\lambda/\omega_0)^2$. Qualitatively consistent with this, soft phonons above T_{SP} have been observed in those organic chain compounds, where the predicted transition temperature is experimentally accessible [7,8]. In contrast to this, a preexisting soft phonon has not been detected in $CuGeO_3$ so far. Moreover, CF's theory is based on the one-dimensional spin-$1/2$ Heisenberg model (J model). Yet there is a striking disagreement between the experimentally observed magnetic susceptibility χ in the uniform (U) phase of $CuGeO_3$, i.e., for $T > T_{SP}$, and theoretical analysis of the J model [1,9,10]. Intimately related to this, a consistent interpretation of the magnetic properties of $CuGeO_3$ in terms of the J model alone seems impossible leading to markedly different values of the exchange coupling constant J [1,3,11].

In principle the deviation between CF's theory and experiment may originate from various sources such as, e.g., the finite interchain interactions [3] or a nonlinear coupling between magnetic and lattice degrees of freedom. At present, and to the best of our knowledge, calculations which incorporate one or both of these effects and lead to an improved agreement with the magnetic properties of $CuGeO_3$ have not been reported. Fortunately, however, such agreement has been found in recent theoretical studies of the dynamic spin susceptibility $\chi(\mathbf{q}, \omega)$ using a model of competing intrachain magnetic interactions [9,10]. Qualitatively, sizable frustration of the magnetic exchange in $CuGeO_3$ can be inferred from a linear combination of atomic orbital description of the atomic orbitals in the one-dimensional CuO_2 chains of $CuGeO_3$ [9]. To model these competing interactions a J-J' model has been invoked [9,10]. Here J (J') refers to nearest (next-nearest)-neighbor Cu-spin exchange coupling. In fact, assuming $J \simeq 150 - 170$ K and $J'/J \simeq 0.24 - 0.36$ convincing agreement is obtained between the model calculations [9,10] and measured NMR as well as inelastic neutron scattering data. Most important, theory for the J-J' model predicts a critical ratio $\gamma_c = J'_c/J$ for a spin gap to develop in the magnetic excitation spectrum. This gap opens irrespective of lattice distortions or spin-lattice interactions. Existence of this gap is established exactly at the Marjumdar-Gosh point $J'/J = 1/2$ [12] and by additional studies [9,10,13] which strongly suggest $\gamma_c \approx 0.25$.

Consequently, both the SP mechanism as well as the frustration of the antiferromagnetic exchange are of similar significance: they both can lead to a dimerization of the spin system. Thus it is tempting to suggest that the SP phase in $CuGeO_3$ is stabilized not only by spin-lattice coupling, as in CF's theory, but also by the frustration of magnetic exchange. As pointed out in Ref. [9] this additional stabilization may be of special importance, if J'/J is close to the critical value γ_c.

In this Letter we report a comparative study of the magnetostriction and the thermal expansion of $CuGeO_3$. Our data reveal a striking correlation between the pressure

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dependence of the magnetic susceptibility in the U phase and the SP transition temperature. We argue that this correlation allows for a natural interpretation in terms of a *single* parameter dependence of T_{SP} on the magnetic frustration and moreover suggest that T_{SP} is rather insensitive to the lattice dynamics. This strongly supports the concept of an SP transition in $CuGeO_3$ which is driven by competing magnetic interactions.

First we focus on the magnetostriction, which is the length change $[L(H,T) - L(0,T)]/L(0,T) = \Delta L/L$ of a sample as function of the magnetic field H at fixed temperature T. All experiments were performed on a $CuGeO_3$ single crystal grown by a floating zone technique [14]. Data were recorded at temperatures between 2 and 60 K in magnetic fields up to 14 T using a high resolution capacitance dilatometer. According to the measured (H,T) phase diagram of the SP compounds [4], which we report in the insets of Fig. 1 (left panel), at high fields an incommensurate magnetic phase (I) is expected for $T \lesssim 11$ K, whereas for higher temperatures the U phase will occur. At the corresponding critical fields $H_C^{I(U)}(T)$ a first (second) order phase transition into the I (U) phase occurs. As shown for two selected (H,T) paths in Fig. 1 (left panel) this leads to huge anomalies in the magnetostriction at $T < T_{\mathrm{SP}}(H=0)$. A detailed discussion of the magnetostriction in the ordered phases will be given elsewhere.

The right panel of Fig. 1 shows the magnetic field dependence of the normalized lattice constant b for $T > T_{\mathrm{SP}}$. It displays a finite magnetostriction for $CuGeO_3$ even in the U phase. Interestingly, the magnetostriction changes sign at $T_{\mathrm{SP}}(H=0)$ and moreover remains finite at temperatures even far above the SP transition. Thus the negative slope $\partial b(H,T)/\partial H$ for $T > T_{\mathrm{SP}}(H=0)$ is not due to fluctuations of the SP order parameter. As obvious from the inset in the right panel of Fig. 1 we observe a decrease of the lattice constant b proportional to H^2 over

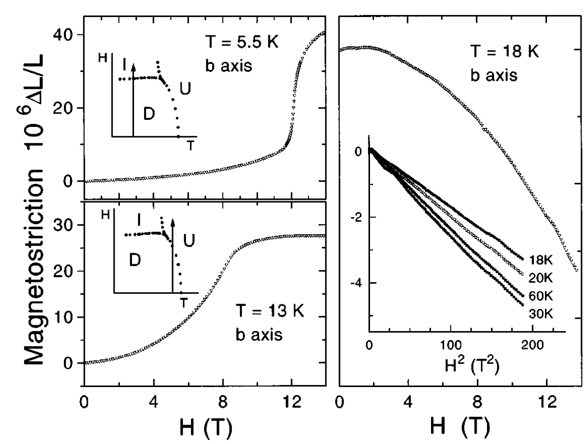

FIG. 1. Magnetostriction of the lattice constant b in $CuGeO_3$. Left: $T < T_{\mathrm{SP}}(0)$. The arrows in the insets indicate the paths in the H-T phase diagram. Right: Magnetostriction in the U phase. The inset shows the normalized lattice constant b versus H^2 for various temperatures.

the entire temperature range studied above T_{SP}. This temperature dependence is rather weak and features a broad maximum at approximately 30 K. Finally, the magnetostriction is of similar absolute magnitude and temperature dependence also along the a and c directions. For $T = 60$ K this is depicted in the lower left panel of Fig. 3. This figure demonstrates a pronounced anisotropy of the magnetostriction with the lattice constant a (c) increasing (decreasing) as a function of increasing magnetic field.

The magnetostriction allows for a direct interpretation in terms of the pressure dependence of the magnetic susceptibility. This can be understood by expanding the free energy F of the U phase in terms of the magnetic field H and the stress tensor σ

$$F(H,\sigma) = F_0 + \frac{1}{2}\sum_{ab}\chi^0_{ab}H_aH_b + \sum_{ij}\epsilon^0_{ij}\sigma_{ij} + \frac{1}{2}\sum_{abij} m^{ab}_{ij}H_aH_b\sigma_{ij} + \frac{1}{4}\sum_{abijkl} m^{ab}_{ijkl}H_aH_b\sigma_{ij}\sigma_{kl} + \cdots, \qquad (1)$$

where roman subscripts label lattice directions. χ^0_{ab} and ϵ^0_{ij} refer to the susceptibility and strain tensor at zero field and stress, respectively. The expansion (1) which yields a field independent susceptibility and a magnetostriction proportional to H^2 is sufficient to describe the U phase up to 14 T [4]. Using (1) the longitudinal magnetostriction, i.e., ϵ_{jj} for a fixed j, divided by the $H_i^2/2$ is identical to the uniaxial pressure derivative of the susceptibility for vanishing pressure

$$\frac{2\epsilon_{jj}}{H_i^2} = \frac{\partial^3 F}{\partial H_i^2 \partial\sigma_{jj}}\bigg|_{\sigma=0} = \frac{\partial\chi_{ii}}{\partial\sigma_{jj}}\bigg|_{\sigma=0} = -\frac{\partial\chi_{ii}}{\partial p_j}\bigg|_{p=0}, \qquad (2)$$

where $p_j = -\sigma_{jj}$ are the uniaxial pressure components. In Fig. 2 we show the diagonal pressure derivatives

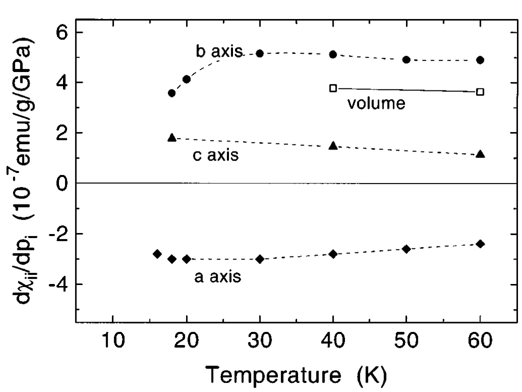

FIG. 2. Uniaxial pressure dependencies $\partial\chi_{ii}/\partial p_i|_{p\to 0}$ in $CuGeO_3$ versus temperature. The hydrostatic pressure dependence of the averaged susceptibility (□) has been calculated by adding the $\partial\chi_{ii}/\partial p_i$ weighted by the g values [15].

$\partial\chi_{ii}/\partial p_i$ in the U phase between 16 and 60 K as obtained from (2). From the absolute values of $\partial\chi_{ii}/\partial p_i$ we estimate a rather large magnetoelastic coupling for $CuGeO_3$. In particular, for pressures parallel to the b axis the average susceptibility $\bar{\chi} = (\chi_{aa} + \chi_{bb} + \chi_{cc})/3$ (see Fig. 2 caption) at 60 K increases by more than 5% per GPa. For a comparison with measurements as a function of hydrostatic pressures we have also calculated the hydrostatic pressure derivative of $\bar{\chi}$. We obtain an initial slope $\partial\bar{\chi}(60\text{ K})/\partial p|_{p=0} = 3.6(6) \times 10^{-7}$ emu/g/GPa in fair agreement to measurements at finite pressure up to 1.2 GPa yielding $\partial\bar{\chi}(60\text{ K})/\partial p \simeq 5 \times 10^{-7}$ emu/g/GPa [16].

Per se, our measurement of a nonzero magnetostriction in the uniform phase does not imply any new physics, leaving aside the fact that—to our knowledge—we have performed the first measurement of this quantity for any of the known SP systems. In fact, CF's theory requires the exchange coupling constant to depend on the strains, i.e., $J = J(\epsilon_{ij})$, and therefore it implies a finite magnetoelastic coupling above T_{SP}. Next, however, we combine these results with the pressure sensitivity of the SP transition temperature and reveal a remarkable correlation of both quantities. Because of Ehrenfest's relations the uniaxial pressure derivatives $\partial T_{SP}/\partial p_i$ are proportional to the anomalies $\Delta\alpha_i$ of the thermal expansion coefficients α_i at T_{SP} [5]. These anomalies are huge and strongly anisotropic. To allow for a precise and quantitative comparison of $\partial T_{SP}/\partial p_i$ and the uniaxial pressure dependencies of $\bar{\chi}$, we have determined both the thermal expansion and the magnetostriction during a single measuring run, i.e., on the same single crystal with exactly the same orientation. The thermal expansion anomalies are shown in the right panel of Fig. 3. We stress that the relative variations $|[\partial T_{SP}/\partial p_i]/T_{SP}|$ are extremely large

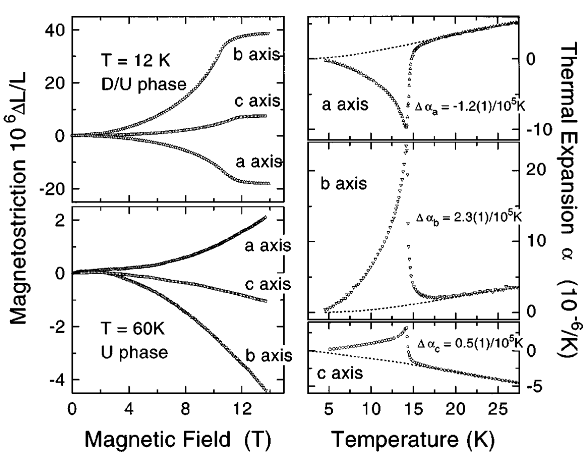

FIG. 3. Left: Anisotropy of the magnetostriction in $CuGeO_3$ at 12 and 60 K. Right: Thermal expansion of $CuGeO_3$. The $\Delta\alpha_i$ denote the largest deviation from the background (broken lines). The uniaxial pressure dependencies obtained from the $\Delta\alpha_i$ amount to $-3.8(5)$, 7.2(4), and 1.6(4) K/GPa for $p \parallel a$, $p \parallel b$, and $p \parallel c$, respectively (see Ref. [5]).

and amount up to 50% per GPa. Most important, however, the anisotropy of the anomalies is very similar to that of the magnetostriction in the U phase. In fact, comparing all three ratios of the uniaxial pressure dependencies $[\partial T_{SP}/\partial p_i]/[\partial\bar{\chi}(T)/\partial p_i]$ for a fixed temperature, e.g., $T = 60$ K, far above T_{SP} we find 1.6(3), 1.6(3), and 1.3(5) 10^7 K g/emu for i into the a, b, and c directions, respectively. As is evident from Fig. 3 $\partial\chi_{ii}/\partial p_i$ displays only a weak temperature variation which implies that the latter ratios are nearly temperature independent for all $T > 25$ K. Therefore, though both χ as well as T_{SP} exhibit strongly anisotropic uniaxial pressure derivatives, involving different signs and magnitudes, their respective ratio at fixed T is (within experimental error) a single number. This strongly suggests that the pressure dependence of χ and T_{SP} is based on a common variable.

It is this striking correlation between an increase (decrease) of T_{SP} and a corresponding increase (decrease) of the susceptibility well above T_{SP} which is the main experimental result of this Letter. It strongly suggests that the transition temperature is connected to the value of the magnetic susceptibility. We emphasize that this scaling behavior between $\chi(T \gg T_{SP})$ and T_{SP} as function of pressure is obtained from the experimental data without the use of any model or theory.

The pressure induced scaling of the susceptibility χ in the U phase with the SP transition temperature implies a similar correlation between $\partial\chi_{ii}(T \gg T_{SP})/\partial p_j$ and the spontaneous strains of the D phase. This is related to the fact that while $\partial T_{SP}/\partial p_i$ is directly proportional to $\Delta\alpha_i$ the spontaneous strains are determined by integrating α_i with respect to the temperature (for details see [5]). Stated differently, one expects the magnetostriction above T_{SP} to scale with the order parameter of the SP state. This is consistent with a comparison of our data in the upper and lower left panel of Fig. 3 where the magnitude of the strain changes at the field driven D/U transition displays an anisotropy which is very similar to that of the magnetostriction in the U phase. Moreover, this seems to pertain not only to the spontaneous strains of the D phase but also to the magnetostriction below T_{SP}. Interestingly, the latter is of opposite sign in the D as compared to the U phase.

In the following we contrast our results against two possible scenarios for the SP transition in $CuGeO_3$. First we consider CF's theory in which two sources exist which can lead to a finite pressure derivative $\partial T_{SP}/\partial p_i$. On the one hand, the spin-lattice coupling constant λ can be nonlinear, i.e., $\partial\lambda/\partial p_i \neq 0$, and on the other hand the soft-phonon frequency ω_0 may depend on pressure, i.e., $\omega_0 = \omega_0(p)$. Since measurements at finite hydrostatic pressure up to $p = 1.2$ GPa [16] show a *linear* increase of T_{SP}, we exclude a significant nonlinear spin-lattice coupling as a source of the pressure dependence of T_{SP}. Furthermore, at present, experimental evidence of a substantial, pressure induced phonon shift in $CuGeO_3$ does not exist. Although this does not rule out future interpretation of a finite $\partial T_{SP}/\partial p_i$ based on CF's theory in terms of a pressure dependent soft phonon, we stress that within this scenario the correlation between the uniaxial pressure dependencies of χ and T_{SP} which we observe would be completely *accidental* [17].

Second, we turn to electronic scenarios of the SP transition, based on the J-J' model. In this model the ratio $\partial\chi/\partial(J'/J)$ is found to be *positive* for $T > T_{SP}$ while $\partial T_{SP}/\partial(J'/J)$ is *negative*. This effect has been observed in numerical studies [9]. Therefore, a natural interpretation of the correlation between the magnetoelastic coupling in the U phase and the uniaxial pressure dependencies of T_{SP} is obtained by assuming that for $CuGeO_3$ the frustration J'/J increases under hydrostatic pressure. This is consistent with neutron scattering data [18]. Moreover, upon opening of the spin gap, i.e., at $T \leq T_{SP}$, the J-J' model predicts a *sign change* of $\partial\chi/\partial(J'/J)$. In this respect it is intriguing to note that, even though (2) has been derived only for the U phase, it conforms with the measured sign change of the magnetostriction at T_{SP}. Therefore our experimental data strongly support a theoretical description of the SP transition in $CuGeO_3$, in which competing magnetic interactions play an important role.

Taking the preceding discussion serious we are forced to conclude that all possibly remaining parameters which may influence T_{SP} display only a relatively weak pressure variation. Yet, $|\partial T_{SP}/\partial p_i|$ is extremely large. In fact, measuring the transition temperature up to $p = 1$ GPa [19], one may span an enormous interval of values of T_{SP} ranging from 10 to 21 K for $p \parallel a$ and $p \parallel b$, respectively. Thus we are tempted to claim stabilization of the SP phase in $CuGeO_3$ based on magnetic frustration only. This strongly differs from the usual CF scenario.

Further detailed theoretical investigations of the J-J' model including a finite spin-lattice coupling are highly desirable in order to check whether properties of $CuGeO_3$ can be obtained which are in better agreement with CF's theory. Such calculations should also focus on the issues raised in this Letter. For example, can variations of the ratio J'/J which lead to changes in $\chi(60\text{ K})$ on the order of only 5% lead to an increase of T_{SP} by up to $\simeq$50%. Moreover, clarification of these questions based on alternative approaches which describe either the susceptibility in the U phase or the transition temperature T_{SP} of $CuGeO_3$ remains an open problem. This pertains, e.g., to theories incorporating finite interchain coupling.

In conclusion, we have presented measurements of the magnetostriction and the thermal expansion of $CuGeO_3$. We find a pronounced, strongly anisotropic magnetoelastic coupling in the uniform phase which, surprisingly, correlates with the pressure sensitivity of T_{SP} and the spontaneous strains of the dimerized phase. We have shown that this correlation provides strong experimental evidence for an SP transition in $CuGeO_3$ which is strongly enhanced by competing antiferromagnetic interactions.

We thank E. Müller-Hartmann, A. Klümper, D. Khomskii, and M. Braden for stimulating discussions. This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungsbereich 341. A. R. and G. D. acknowledge support by NEDO.

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