

## Incommensurate Phase of $\text{CuGeO}_3$ : From Solitons to Sinusoidal Modulation

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An experimental and theoretical study of the field dependence of the structural modulation in the incommensurate high field phase of the spin-Peierls cuprate  $\text{CuGeO}_3$  is presented. The averaged structural order parameter is determined from magnetostriction and thermal expansion experiments in magnetic fields up to 28 T. The results are compared to density matrix renormalization group calculations using a self-consistent one-dimensional approach. The experimental and numerical data agree very well with each other and clearly show a continuous change from a solitonlike lattice close to the dimerized incommensurate transition to a sinusoidal distortion at higher fields. [S0031-9007(98)06507-7]

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The discovery of a spin-Peierls (SP) transition in the inorganic compound  $\text{CuGeO}_3$  [1] has renewed the interest in this instability of one-dimensional spin-half antiferromagnetic compounds [2,3]. With decreasing temperature SP systems undergo a continuous structural transition at  $T_{\text{SP}}^0$  from an undistorted uniform (U) phase with a gapless spin excitation spectrum to a collective nonmagnetic singlet state with a dimerized (D) lattice. This phase transition occurs, since the magnetic energy gain due to dimerization of the antiferromagnetic exchange overcompensates the elastic energy loss resulting from the deformation of the lattice. A characteristic feature of SP compounds is a magnetic field induced structural phase transition from the D phase to a magnetic high field phase with an incommensurate (I) lattice modulation stabilized by the Zeeman energy [2]. Similar commensurate-incommensurate transitions are observed in a wide variety of compounds [4]. Often they are described by a formation of a regular array of domain walls (soliton lattice). In the case of SP compounds each soliton carries a spin 1/2, leading to a finite magnetization [5]. It is apparent that SP systems allow for a detailed study of a soliton lattice, since the period of the incommensurate lattice modulation, i.e., the number of solitons, can easily be tuned by the external magnetic field [5–8].

Intensive studies of  $\text{CuGeO}_3$  during the last few years have led to a quite comprehensive understanding of this first inorganic SP compound [3]. Results from investigations as a function of a magnetic field have generally been in fair agreement with the theoretical predictions of Cross and Fisher [9]. The character of the spatial modulation in the I phase is, however, still to be clarified. Various models exist, ranging from a purely sinusoidal modulation to the above mentioned soliton lattice [5,9]. The latter is experimentally found in  $\text{CuGeO}_3$  from x-ray measurements for fields slightly

above the D/I phase transition at  $H_{\text{D/I}} \approx 12.3$  T [7]. Similar results are obtained for the local spin density distribution measured by NMR up to 17 T [10]. In both cases, however, quantitative discrepancies between theory and experiment are present. The presence of a soliton lattice close to the D/I transition has also been inferred from ultrasound measurements [11].

In this Letter we report on a determination of the structural modulation over a wide field range in the I phase of  $\text{CuGeO}_3$  by a comparative experimental and theoretical study. Both our measurements of the spontaneous strain up to 28 T, as well as our density matrix renormalization group (DMRG) calculations reveal a continuous change from a soliton lattice close to the D/I transition to a sinusoidal distortion at higher fields.

The experiments have been performed in the hybrid magnet of the High Magnetic Field Laboratory in Grenoble (GHMFL) on the same single crystal of  $\text{CuGeO}_3$  as in our previous studies up to 16 T [12–14]. Using a capacitance dilatometer, the length changes  $\Delta L(T, H)$  of the crystal along the  $a$  and  $b$  directions have been measured as a function of temperature ( $6.5 \leq T \leq 30$  K) and magnetic field ( $0 \leq H \leq 28$  T). The anomalies of the lattice constants at both field and temperature driven phase transitions are different in signs and sizes. However, their field and temperature dependencies are essentially the same and, in particular, they do not differ for directions parallel and perpendicular to the chain direction  $c$  [12,14,15]. Thus, in the following we restrict the discussion on the lattice constant  $a$ .

In Fig. 1(a) we show the relative change of the lattice constant  $\Delta a/a$  as a function of temperature for some representative fields. The large anomalies at 0 and 8 T represent U/D transitions, whereas the smaller anomalies at 16 and 28 T signal U/I transitions (see also Refs. [12,13]). In order to analyze these changes in more detail we

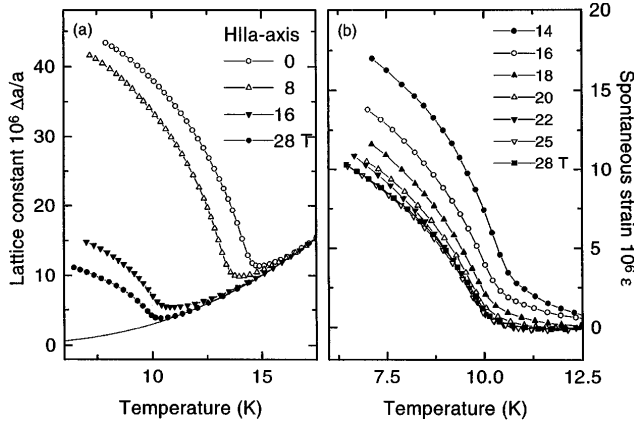


FIG. 1. Temperature dependence of (a) the lattice constant  $\Delta a/a$  and (b) the spontaneous strain  $\epsilon$  of  $\text{CuGeO}_3$  for different magnetic fields.

consider the spontaneous strains  $\epsilon$ , i.e., the deviations from the behavior in the U phase [12,13,15]. Figure 1(b) shows  $\epsilon$  for various fields, which are obtained by subtracting the (field independent) background shown in Fig. 1(a) (solid line) from the measured  $\Delta a/a$ . For fields below 18 T the spontaneous strains are already finite above the transition temperature, indicating strong fluctuations when approaching the Lifshitz point at  $\sim 12.3$  T.

At low temperatures  $\epsilon$  strongly decreases with increasing field for  $H_{D/I} \leq H \leq 20$  T [Fig. 1(b)]. However, with further increasing  $H$  this field dependence weakens and a nearly field independent finite  $\epsilon$  occurs. This saturation is most clearly seen by the almost identical  $\epsilon$  (and raw data) for fields of 25 and 28 T. We mention that  $\epsilon(H)/\epsilon(H=0)$  does not explicitly depend on temperature as long as  $T$  is not very close to  $T_{SP}$ , due to a scaling behavior of  $\epsilon$  [12,13]. Thus, it is possible to extract a temperature independent scaling factor from the data, which measures the field dependent reduction of  $\epsilon$ .

An alternative possibility to derive  $\epsilon(H)$  is to measure the magnetostriction  $\Delta a(H)/a$  displayed in Fig. 2. In agreement with our earlier investigations up to 14 T [14], the  $a$  axis shows a continuous increase in the U phase ( $T = 20$  K), which is proportional to  $H^2$ , and a nonmonotonous behavior at  $T = 12.5$  K due to the field induced D/U transition. The third curve in Fig. 2 is taken at  $T = 7$  K, i.e., with  $\text{CuGeO}_3$  in the I phase for  $H \geq 12.5$  T. The D/I transition at  $H \approx 12.5$  T causes an almost jumplike decrease of  $\Delta a/a$ , followed by a rather strong continuous decrease. However, this decrease of  $\Delta a/a$  very rapidly weakens and at fields above  $\approx 20$  T the magnetostriction changes its slope, i.e.,  $\Delta a/a$  again increases with field, similar to the findings in the U phase. Indeed, comparing the high field magnetostriction at 7, 12.5, and 20 K we find no significant differences, i.e.,  $\Delta a/a = cH^2$  with  $c = 1.3 \pm 0.2 \times 10^{-8} \text{ T}^{-2}$ . This similarity of the magnetostriction in the U and I phases is a consequence of the saturation

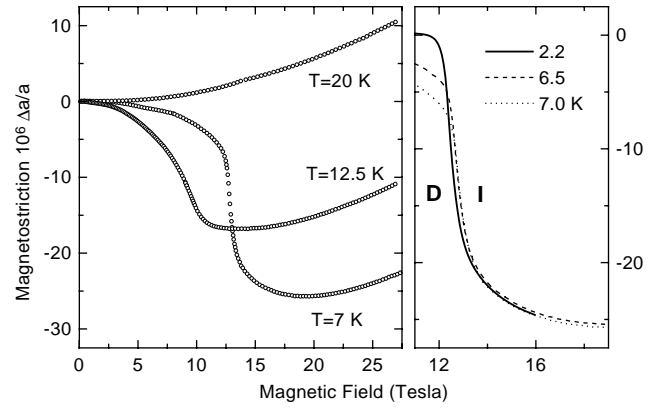


FIG. 2. Magnetostriction of the  $a$  axis of  $\text{CuGeO}_3$  at different temperatures (the data at 2.2 K have been measured in a superconducting 16 T magnet).

of  $\epsilon$  in high fields, since the magnetostriction and  $\epsilon(H)$  are directly related to each other. The field dependence of  $\epsilon$  at  $T < T_{SP}^0$  is given by the difference of the magnetostriction at  $T$  and  $T_0 > T_{SP}^0$  [13]. Figure 3 shows the  $\epsilon(H)$  derived from the difference of the magnetostriction at  $T = 7$  K and  $T_0 = 20$  K, respectively. Note that due to the weak temperature dependencies of the magnetostriction in both the I phase (right part of Fig. 2) and the U phase (see above and Ref. [14]) the extracted  $\epsilon(H)$  does not depend significantly on the choice of these temperatures.

It is apparent from Fig. 3 that the field dependencies of  $\epsilon$  as obtained from the magnetostriction and thermal expansion agree well with each other. In both cases a saturation of  $\epsilon$  at about one-fourth of its zero field value is observed for  $H \geq 23$  T. Remarkably, a similar saturation is also found for  $T_{SP}$  as shown in the inset in Fig. 3. For  $H \geq 23$  T our measurements yield a field independent

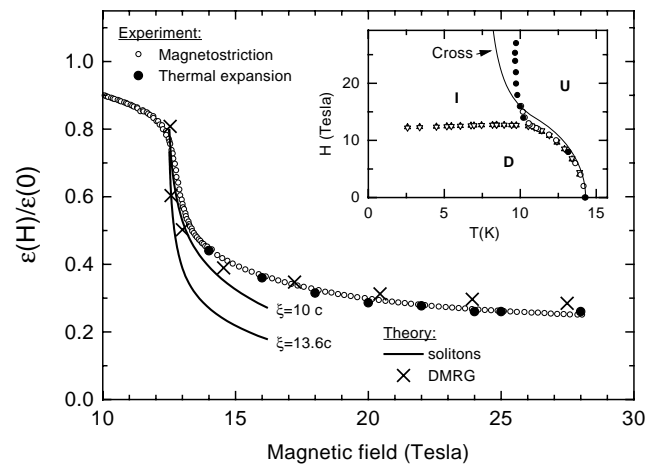


FIG. 3. Spontaneous strain  $\epsilon(H)/\epsilon(0)$  in the I phase as derived from thermal expansion ( $\bullet$ ) and magnetostriction ( $\circ$ ) and  $\langle A^2(H) \rangle$  calculated for a soliton lattice (solid lines) and by DMRG ( $\times$ ) (see text). The inset compares the experimental phase diagram to the calculation of Cross [9].

$T_{\text{SP}}$ , which amounts to  $\sim 10 \text{ K} = 0.7T_{\text{SP}}^0$ , in agreement with other experimental investigations of  $\text{CuGeO}_3$  [16]. Here we focus on the saturation of  $\epsilon(H)$ , which is related to the field dependent structural modulation in the I phase. For the D phase, both a Landau expansion of the free energy as well as a comparison of  $\epsilon(T, H)$  to the intensities of superstructure reflections (see, e.g., [13]) reveal that  $\epsilon$  is proportional to the square of the structural order parameter, i.e., the dimerization amplitude  $A$ . In the I phase the situation is more complicated due to the spatial modulation of  $A$ , whose periodicity depends on the magnetic field. Following the arguments in Ref. [17],  $\epsilon$  is now proportional to the average value of the squared order parameter  $\langle A^2 \rangle$ .

For a sinusoidal modulation  $A$  is given by

$$A(l, H) = (-1)^l A_0(H) \sin[q(H)lc], \quad (1)$$

where  $c$  denotes the lattice constant along the chain direction,  $l$  is the site index,  $q(H)$  is the field dependent modulation wave vector, and  $A_0(H)$  allows for an additional field dependence of the dimerization amplitude. It is apparent that from the sinusoidal modulation alone, i.e., for a field independent  $A_0$ , one expects a constant  $\langle A^2(H) \rangle = 0.5A^2(0)$ . Assuming in addition that the  $A_0(H)$  scales with  $T_{\text{SP}}(H)$  the observed simultaneous saturation of  $\epsilon(H)$  and  $T_{\text{SP}}(H)$  in high fields, as well as the absolute value of the spontaneous strain ( $\epsilon(H) \sim 0.5[T_{\text{SP}}(H)/T_{\text{SP}}^0]^2 \epsilon(0)$ ) might be consistent with Eq. (1). However, a sinusoidal modulation apparently yields no reason for the strong continuous field dependence of  $\epsilon$  in a rather wide field range below  $H \sim 20 \text{ T}$ .

Within the soliton picture  $A$  is given by

$$A(l, H) = (-1)^l A_0 k \text{sn}\left(\frac{lc}{k\xi}, k\right), \quad (2)$$

where  $\text{sn}(x, k)$  is a Jacobi elliptic function of modulus  $k$ , which is determined by the field dependent intersoliton distance  $L(H) = \pi/q(H)$ , and  $\xi$  is the soliton width [5]. From x-ray scattering  $\xi = 13.6c$  is derived close to  $H_{\text{D/I}}$  [7], and the modulation period  $q(H)$  can be extracted from the magnetization, which we have measured up to 16 T. We emphasize that following Eq. (2) the field dependence of the distortion amplitude is unambiguously determined from these two parameters, i.e., there is no unknown prefactor as is the case for a sinusoidal modulation. The solid lines in Fig. 3 are the resulting  $\langle A^2(H) \rangle$  when the experimental  $q(H)$  and  $\xi = 13.6c$  or  $\xi = 10c$  are used. Apparently, the calculations reproduce well the strong decrease of  $\epsilon$  very close to  $H_{\text{D/I}}$  where  $\xi$  has been measured [7]. However, there is a striking discrepancy between the experimental finding and the calculations assuming Eq. (2) at higher fields. The observed saturation of  $\langle A^2 \rangle$  is in qualitative disagreement to a soliton lattice with constant  $\xi$ . This model strictly implies a decreasing  $\epsilon(H)$ , since the intersoliton distance decreases with increasing field.

Summarizing the discussion so far, our experimental data for  $\langle A^2(H) \rangle$  suggest a crossover from a soliton lat-

tice at low fields to a sinusoidal modulation at high fields. This qualitative conclusion from the measurements is quantitatively confirmed by numerical DMRG calculations. These calculations consider one-dimensional magnetic exchanges and an adiabatic approximation for the phonons, leading to the following general effective Hamiltonian (see also, e.g., Refs. [18,19])

$$H = \sum_{i=1}^L \{J(1 + A_i) \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J\alpha \mathbf{S}_i \cdot \mathbf{S}_{i+2}\} + g\mu_B H S_z + \frac{K}{2} \sum_i A_i^2. \quad (3)$$

Here  $J(J\alpha)$  and  $A_i$  are the (next) nearest neighbor exchange coupling and the dimerization, respectively.  $\mathbf{S}_i$  denote  $S = 1/2$  spin operators at site  $i$  and  $S_z$  is the  $z$  component of the total spin of the  $L$ -site chain. The last two terms are the Zeeman energy and the elastic energy associated with the lattice modulation. In the D phase the local dimerization equals  $A_i = (-1)^i A_0$ . For the I phase we follow the self-consistent approach of Feiguin *et al.* [19], and determine the modulations  $A_i$  by minimizing  $\langle H \rangle$  with respect to all the  $A_i$ . Starting from a sinusoidal modulation the conditions  $\partial \langle H \rangle / \partial A_i = 0$  are used to iteratively improve the  $A_i$ , where the above expectation value is taken with respect to the ground state of the previous iteration which is determined by means of the DMRG (with 128 states kept). For details of this procedure, the calculation of the magnetization, and the DMRG technique itself, see [19–21].

The parameters in the Hamiltonian Eq. (3) are determined from properties of  $\text{CuGeO}_3$  at  $H = 0$ . A fit of the magnetic susceptibility and entropy in the U phase yields  $J = 160 \text{ K}$  and  $\alpha = 0.35$  [18,22]. The remaining parameter  $K \simeq 18J$ , which determines  $A_i = \pm 0.014$ , then follows from the experimentally observed singlet-triplet gap at  $H = 0$ . A similar set of parameters is frequently used in numerical studies of  $\text{CuGeO}_3$  (see, e.g., Ref. [18]).

In order to investigate the field dependence we determine the lattice modulation in the various  $S_z$  subsectors and the magnetizations for rings of 100 and 200 sites. Figure 4 shows two representative modulations for  $S_z = 1$  and  $S_z = 5$  corresponding to magnetic fields close to the D/I boundary and a higher field ( $\simeq 17 \text{ T}$ ), respectively. The calculations yield an obvious solitonlike modulation for the small fields. Fitting  $\text{sn}(x, k)$  to the modulation pattern calculated for  $S_z = 1$  (Fig. 4) yields  $\xi \simeq 11c$ , in fair agreement with the experimental result  $\xi = 13.6c$  [7]. However, the DMRG calculations clearly show the failure of the soliton picture at higher fields. Already at moderate fields, i.e., for  $S_z = 5$  (Fig. 4), the modulation looks almost like a simple sinusoidal distortion. Moreover, from the saturation of the maximum modulation  $A_{\text{max}}$  shown in the inset in Fig. 4 a solitonic picture with constant  $\xi$  can be excluded. This constant  $A_{\text{max}}$  is observed when the distance between the nodes of the order parameter becomes smaller than  $\simeq 28c \simeq 2\xi$ .

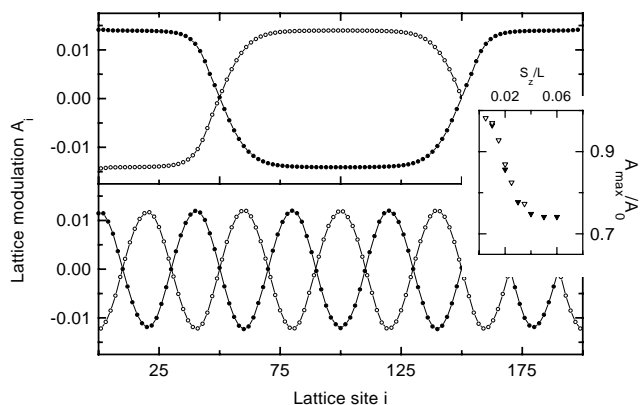


FIG. 4. Local lattice modulation for a 200 site chain in the  $S_z = 1$  (upper curve) and the  $S_z = 5$  (lower curve) subsectors. The open (filled) symbols represent odd (even) sites. Inset: maximum dimerization amplitude as a function of the magnetization  $m = S_z/L$  calculated for 100 (filled symbols) and 200 (open symbols) site chains.

It is now straightforward to compare these results from the DMRG studies with our measurements of  $\epsilon(H)$ . As shown in Fig. 3 there is indeed a very good quantitative agreement between theoretical and experimental  $\langle A^2(H) \rangle / A^2(0)$ . We stress that this agreement is obtained without any additional fit parameter. From the Hamiltonian in Eq. (3) and properties of the U and D phases at  $H = 0$ , which fix the parameters, we derive quantitatively the observed critical field  $H_{D/I}$  as well as the field dependence and the saturation value of  $\epsilon(H)$ .

We mention that we have also calculated the properties of the I phase assuming the experimental spin gap and other magnetic exchange constants in Eq. (3), such as  $J = 150$  K,  $\alpha = 0.24$  and  $J = 120$  K,  $\alpha = 0$ . Again, a crossover from a solitonlike to a sinusoidal distortion is found. However, the calculated saturation values of  $\epsilon(H)$  are larger than the experimental value of about 0.27. They amount to  $\approx 0.45$  and  $\approx 0.36$  for  $\alpha = 0$  and  $\alpha = 0.24$ , respectively. Thus, the good agreement between our experimental and numerical data shown in Fig. 3 suggests that the structural modulation of the I phase significantly depends on the frustration of the magnetic exchange. A detailed discussion of this latter point will be presented in a forthcoming publication [21].

In summary, we have experimentally and theoretically investigated the structural modulation of the incommensurate phase of the spin-Peierls cuprate  $\text{CuGeO}_3$  by measuring the spontaneous strain, and by numerical DMRG calculations, respectively. The field dependence of the averaged structural order parameter extracted from the data is in very good agreement with the results of the calculations. A description of the spatial modulation in terms

of a soliton lattice is possible only very close to the field driven commensurate-incommensurate phase transition at  $H_{D/I} \approx 12.5$  T. With increasing field both our experimental, as well as the numerical data reveal a continuous change towards a sinusoidal modulation, which provides a good description of the distortion for fields above about  $\sim 20$  T.

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