Soliton Lattice in Pure and Diluted $CuGeO_3$

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We report a synchrotron x-ray scattering study of the magnetic-field-induced incommensurate phase of the spin-Peierls compound $CuGeO_3$, in magnetic fields up to 13 T. By measuring first and third harmonics of the incommensurate Bragg reflections as a function of field we show that the lattice modulation has the form of a soliton lattice. The soliton half-width, 13.6 lattice spacings, is surprisingly large. Dilution of the CuO_2 spin-$\frac{1}{2}$ chains with spin-0 (Zn) and spin-1 (Ni) impurities results in a short-range-ordered incommensurate state with an anisotropic correlation length comparable to the average impurity separation. [S0031-9007(96)00422-X]

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Commensurate-incommensurate (C-IC) transitions have been observed in a wide variety of condensed matter systems [1]. In 1949 Frank and van der Merwe (FvdM) [2] proposed a continuum model of a C-IC transition in a classical one-dimensional (1D) system and showed that the transition proceeds by a continuous proliferation of domain walls (solitons). The IC phase corresponds to a regular array of these solitons (a soliton lattice). We have recently discovered a new type of C-IC transition in a quasi-1D quantum many body system, realized in the spin-Peierls compounds TTF-CuBDT [3] and $CuGeO_3$ [4]. Our observation opens a new experimental window on quantum effects in C-IC transitions, and on 1D quantum magnetism in general.

The zero-field ground state of the spin-Peierls Hamiltonian, a 1D spin-$\frac{1}{2}$ Heisenberg Hamiltonian on a deformable lattice, is a collective nonmagnetic singlet state with a dimerized lattice [5]. A high magnetic field induces a transition from the dimerized state into a phase with a nonzero magnetic moment accommodated by an incommensurate lattice modulation. Here we show that the lattice modulation in the IC phase of $CuGeO_3$ can be described as a soliton lattice, as predicted by theories which map the spin-Peierls Hamiltonian onto continuum field theories akin to the FvdM model [6–9]. According to these theories, each soliton carries a spin $\frac{1}{2}$, which gives rise to the bulk magnetic moment in the IC phase. However, the soliton width extracted from our data is much larger than predicted by calculations based on the nearest-neighbor Heisenberg model previously thought to describe spin-Peierls systems [5–9]. We also report a microscopic characterization of the effects of magnetic and nonmagnetic impurities on the IC state.

$CuGeO_3$ has an orthorhombic structure and contains Cu-O_2-Cu spin chains extending in the c direction, with the bridging oxygen ions equidistant from the spin-$\frac{1}{2}$ copper ions. The Cu-O-Cu bond angle is $\sim 100°$ [10]. The nearest-neighbor Heisenberg superexchange obtained by fitting inelastic neutron scattering data [11] to a des Cloiseaux-Pearson dispersion is $J_c = 10.4$ meV. The exchange constants perpendicular to the spin chains are much smaller ($J_a = 0.1J_c, J_b = -0.01J_c$). Hase, Terasaki, and Uchinokura [12] recently showed that $CuGeO_3$ undergoes a spin-Peierls transition at 14.3 K, a discovery that has rekindled significant interest in the spin-Peierls problem. Dilution of the spin chains by Zn (spin-0) and Ni (spin-1) impurities depresses the spin-Peierls transition temperature, and at a critical concentration of $\sim 3\%$ Zn or Ni impurities the spin-Peierls state is replaced by a Néel state [13]. This observation is surprising and has not yet been explained.

Single crystals of pure and diluted $CuGeO_3$ were grown by a CuO flux method. Their elemental compositions were determined by electron probe microanalysis, and three crystals of compositions $CuGeO_3$, $Cu_{0.985}Zn_{0.015}GeO_3$, and $Cu_{0.98}Ni_{0.02}GeO_3$ were selected for the x-ray experiments. The crystals had typical dimensions $2 \times 2 \times 0.1$ mm^3 and showed sharp zero-field spin-Peierls transitions at 14.3, 12.3, and 12.0 K, respectively. They were oriented and loaded into a 13 T split-coil, vertical field superconducting magnet mounted on a two-circle goniometer. A sample rotator inside the magnet was used for *in situ* adjustments of the sample orientation. The experiment was carried out at beam line X22B of the National Synchrotron Light Source with 8 keV x rays. Momentum resolutions of ~ 0.01 Å^{-1} (full width at half maximum) both parallel and perpendicular to the scattering plane were determined by slits before and after the sample in conjunction with the sample mosaicity.

The data were collected in a two-circle mode near the (3.5, 1, 2.5) superlattice reflection, with momentum transfers of the form $\mathbf{q} = (3.5K, K, L)$ in the (horizontal) scattering plane. [Momentum transfers are quoted in reciprocal lattice units (r.l.u.), that is, in units of the reciprocal lattice vectors $a^* = 1.31$ Å^{-1}, $b^* = 0.74$ Å^{-1}, and $c^* = 2.14$ Å^{-1}.] Note that the (3.5, 1, 0) direction

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deviates by only 9° from the *a* axis. This scattering geometry has several advantages. First, (3.5, 1, 2.5) is one of the most intense accessible superlattice reflections. Second, in contrast to our previous work [4] the absolute magnitude of the incommensurability could be determined by scanning in the *c* direction along the spin chains (reciprocal space coordinate *L*). Third, the critical magnetic field H_c is slightly anisotropic because of a small *g*-factor anisotropy [14]. In our experiment the field was applied almost along the *b* axis, where the critical field is minimum. The value determined from our data at low temperatures, $H_c = 12.1$ T, agrees well with susceptibility measurements in this direction [14].

Figure 1 shows, on a logarithmic scale, scans through the (3.5, 1, 2.5) reflection of $CuGeO_3$ in the spin chain direction. The data were taken above H_c, and the temperature was 4 K. No significant changes were observed in any of our samples below this temperature. As previously reported [4], the peak position is incommensurate with the lattice, and the incommensurability increases with increasing field. Further, a weak third harmonic reflection whose amplitude decreases with increasing field is clearly visible. In order to achieve good counting statistics, the counting time for the scan through one of the third harmonic satellites was much longer than for the scan through the primary reflection. The peak intensities and positions were extracted from these data by fits with Gaussians of width equal to the instrumental resolution. The incommensurability of the third harmonic was constrained to be three times that of the first harmonic. C and IC phases coexist over a narrow field range [4], and for fields close to H_c a C reflection of small amplitude was added. As evidenced by the excellent quality of the fits, no other fitting parameters were necessary.

The field dependence of the incommensurability, ΔL, is shown in Fig. 2, together with the data for the diluted samples to be discussed below. No lock-in to higher order commensurate wave vectors is observed for any of the samples, as expected on general grounds for 1D quantum systems [15]. The intensity ratio of third and first harmonics, I_3/I_1, is plotted in Fig. 3(a) as a function of magnetic field. The latter quantity parametrizes the *shape* of the lattice modulation: While a sine-wave distortion is characterized by a single wave vector in reciprocal space [16], the Fourier transform of the soliton lattice also contains harmonics of the fundamental wave vector. Because of the bond alternation only odd harmonics are relevant for the IC lattice modulation in spin-Peierls systems [6–9]. The theoretical scenario for the C-IC transition is as follows: Close to the transition the solitons are well separated, and the lattice modulation resembles a square wave with a large harmonic content. Far from the transition the solitons overlap more strongly, and the harmonic content decreases. Qualitatively, all of these features of the soliton lattice model are observed in our experiment, although the divergence of the intersoliton distance does not come to completion as a first order transition intervenes [4].

Quantitatively, the displacement of the magnetic atom at lattice site *l* in the soliton lattice phase is predicted to follow [7–9]

$$u(l) = (-1)^l \,\mathrm{sn}(l/\Gamma k, k)\,, \qquad (1)$$

where $\mathrm{sn}(x, k)$ is a Jacobi elliptic function of modulus *k*, and Γ is the soliton half-width. The intersoliton

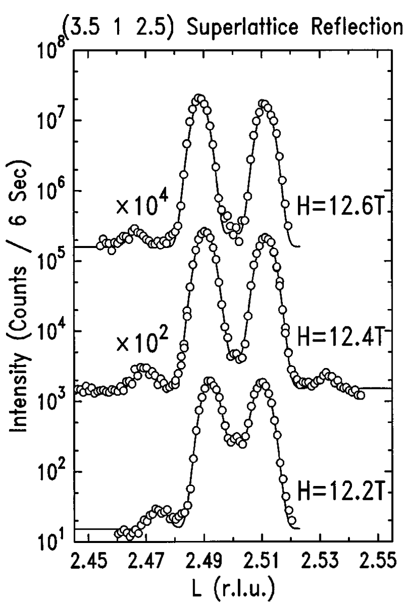

FIG. 1. Scans through the (3.5, 1, 2.5) superlattice reflection of $CuGeO_3$ at $T = 4$ K. Successive scans were multiplied by 100 in order to achieve a constant offset on the logarithmic scale. The lines are the results of fits to resolution-limited Gaussians, as discussed in the text.

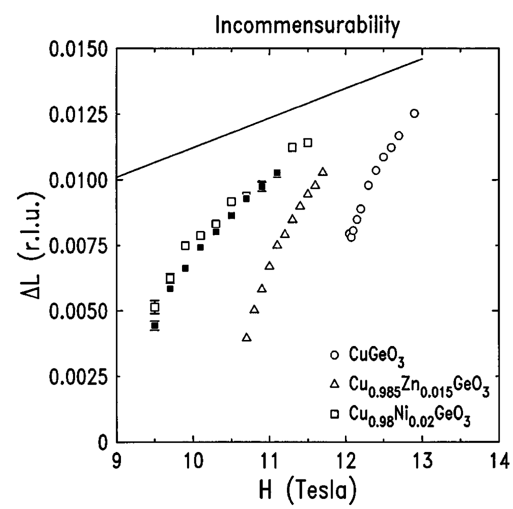

FIG. 2. Incommensurability vs magnetic field in the IC phases of pure and diluted $CuGeO_3$. The closed and open symbols represent data taken at 1.6 and 4 K, respectively. The solid line is the result of a one parameter fit by Eq. (2) in the text. The dashed line is the prediction of Cross [20] for the asymptotic incommensurability in high magnetic fields.

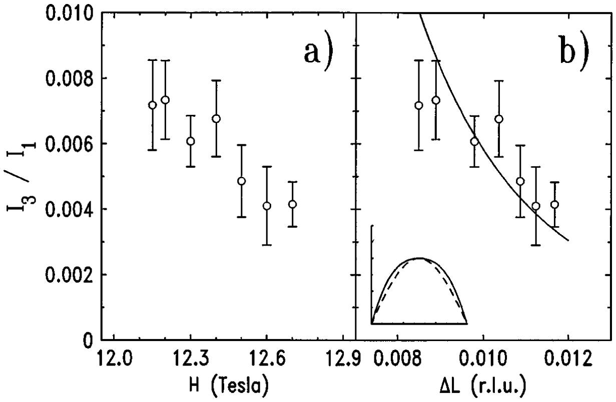

FIG. 3. Intensity ratio of third and first harmonic reflections as a function of (a) magnetic field and (b) the incommensurability of Fig. 2, for pure $CuGeO_3$ at $T = 4$ K. The line in (b) is a result of a one-parameter fit by Eq. (2) in the text. The shape of the lattice modulation specified by Eq. (1) and the measured ΔL and $I_3.I_1$ for $H = 12.2$ T is indicated in the inset (solid line) and compared to a sine wave (broken line).

distance (half the wavelength of the lattice modulation) is $\pi/\Delta L = 2kK(k)\Gamma$, where K is the complete elliptic integral of the first kind. Equation (1) is a generic function which has been applied to a variety of 1D systems [17,18], and we are aware of no other explicit prediction for the shape of the IC lattice modulation in spin-Peierls systems. The Fourier transform of Eq. (1) can be calculated analytically [19], and the intensity ratio of third and first harmonic reflections is

$$I_3/I_1 = [Q/(Q^2 + Q + 1)]^2, \qquad (2)$$

where $Q = \exp[-\pi K(\sqrt{1 - k^2})/K(k)]$. We can thus implicitly express I_3/I_1 as a function of Γ and the measured incommensurability ΔL. The result of a fit of this expression to our data is shown in the solid line of Fig. 3(b). We obtain $\Gamma = (13.6 \pm 0.3)c$, where $c = 2.94$ Å is the lattice constant in the spin chain direction. This should be compared to intersoliton distances of $\sim(40-70)c$ in the field range we investigated. The solitons therefore overlap appreciably, and the soliton lattice is close to (but distinctly different from) a sine wave [inset in Fig. 3(b)].

We are aware of only one explicit theoretical prediction for the zero-temperature critical behavior of the incommensurability, but the expression given by Buzdin, Kulic, and Tugushev [8] is for the *XY* model and is thus not directly applicable to our data. In high magnetic fields (that is, far from criticality) the incommensurability for the Heisenberg model is expected [20] to approach $\Delta L = 4\mu_B H/\pi J_c c$ (dashed line in Fig. 2). The data for both pure and diluted samples are consistent with an asymptotic approach to this line.

Our measurement of the soliton half-width provides a more specific test of extant theoretical predictions. For the (nearest-neighbor) Heisenberg model $\Gamma = \pi J_c c/2\Delta_0$, where Δ_0 is the zero-field spin excitation gap, was predicted in Ref. [6]. Using the measured [11] $J_c = 10.4$ meV and $\Delta_0 = 2.1$ meV, we obtain $\Gamma = 8.0c$, which would correspond to an I_3/I_1 ratio more than a factor of 5 larger than observed (at $H = 12.7$ T).

In principle, the intensities of higher harmonic satellites could be affected by a "static Debye-Waller factor" resulting from phason disorder due to pinning of the solitons to impurities. In order to assess whether such an effect could account for the significant discrepancy between the theoretical prediction and the measured value of the soliton width, we have numerically calculated the structure factors of systems with the predicted $\Gamma = 8c$ in the presence of randomly placed strong pinning centers, each of which pins the position of the soliton adjacent to it. We find that the concentration of such pinning centers would have to be higher than $\sim 2.5\%$ of the magnetic atoms in order to reduce I_3/I_1 by a factor of 5. At this level of concentration, impurities are known [13] to substantially depress the zero-field spin-Peierls transition temperature. Moreover, in samples that actually contain (1–2)% of impurities the IC satellites are severely broadened (see below). The optimal transition temperature (14.3 K) of our pure sample and the complete absence of any broadening of the IC satellites therefore rule out pinning effects as the origin of the lower-than-predicted value of I_3/I_1.

More elaborate microscopic theories of the spin-Peierls state in $CuGeO_3$ are thus needed to explain the large soliton width and should address the possible influence of long-range competing exchange interactions, [21], interchain exchange interactions and zero-point motion of the solitons on the shape of the lattice modulation. It is also interesting that the shape of the experimentally observed lattice modulation interpolates between a soliton lattice with the predicted soliton width and the purely sinusoidal modulation advocated by Bonner *et al.* [22].

The diluted samples show zero-field spin-Peierls transitions very similar to the pure system, albeit with depressed transition temperatures. However, the effects of both Zn and Ni impurities on the IC state are dramatic. Figure 4 shows scans parallel and perpendicular to the spin chains in $Cu_{0.985}Zn_{0.015}GeO_3$ below and above the critical field of 10.6 T. A substantial broadening of the scans in the IC phase is apparent. The peak widths are independent of the magnetic field, but an additional broadening is observed at higher temperatures [23]. By contrast, both longitudinal and transverse scans in the IC phase of pure $CuGeO_3$ remain resolution limited at all fields and temperatures. We did not take transverse scans for $Cu_{0.98}Ni_{0.02}GeO_3$, but the longitudinal width shows behavior very similar to the Zn-substituted sample.

The data were fitted by Lorentzians convoluted with the Gaussian resolution function, and typical results of these fits are shown in Fig. 4. The incommensurability thus extracted from our data is depicted in Fig. 2 as a function of field. The correlation length in the IC state in the spin chain direction is $\xi_c = 230 \pm 20$ Å $\sim 80c$ for both diluted samples, and in the a direction perpendicular

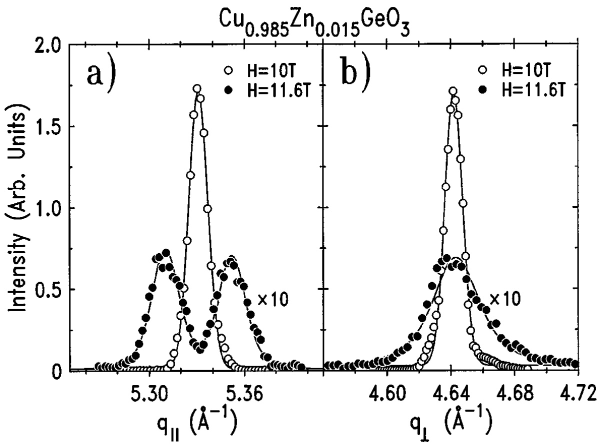

FIG. 4. Scans through the (3.5, 1, 2.5) reflection of $Cu_{0.985}Zn_{0.015}GeO_3$ (a) parallel and (b) perpendicular to the spin chains. The scan in (b) is along (3.5, 1, 0), only 9° away from the *a* axis. The lines are the results of fits, as discussed in the text. The temperature is 4 K, and the 10 and 11.6 T data are below and above the C-IC transition, respectively. The data for 11.6 T were multiplied by 10.

to the spin chains we obtain $\xi_a = 70 \pm 10$ Å $\sim 15a$ for $Cu_{0.985}Zn_{0.015}GeO_3$. Scans in the *b* direction are substantially less accurate because of the limited stepping accuracy of our sample rotator. We do, however, find that $\xi_a \lesssim \xi_b < \xi_c$, which qualitatively mirrors the anisotropy of the zero-field critical fluctuations in $CuGeO_3$ [24].

In the diluted systems the signal-to-background ratio is too small to detect the third harmonic satellites. However, the integrated intensity summed over both IC reflections is the same as the integrated intensity of the C reflection to within ~30%, which means that the average displacement of the atoms from their positions in the uniform phase remains comparable to the atomic displacement in the C phase. Even in the spin chain direction the correlation length is comparable to the average distance between impurities for both diluted samples. The most likely origin of the severe disruption of both intrachain and interchain correlations is a strong pinning of the magnetic solitons to the impurities, with an associated phase pinning of the lattice modulation. The analog of this effect in the C phase, 180° phase slips in the dimerization pattern at impurity sites, does not result in a significant broadening of the superlattice reflections outside of the experimental resolution.

In summary, we have reported two unanticipated observations: First, the incommensurate high field phase of $CuGeO_3$ can be described as a soliton lattice with a soliton width significantly larger than predicted. Spin-0 and spin-1 impurities in the spin-$\frac{1}{2}$ chains disrupt the soliton lattice severely, resulting in an anisotropic, short-range-ordered incommensurate state at high fields. An explanation of these observations is a challenge for the theory of 1D quantum magnetism.

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