NMR Evidence for a Magnetic Soliton Lattice in the High-Field Phase of $CuGeO_3$

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We present copper NMR spectra obtained in the high magnetic field phase of the inorganic spin-Peierls compound $CuGeO_3$. In the whole range 13–17 T, the observed line shapes bring clear evidence for the existence of a static incommensurate distribution of the local spin density $S_z(i)$ corresponding to a magnetic soliton lattice. The absolute value of S_z at the top of a soliton is found equal to 0.065 at 1.4 K and 16.3 T. The temperature dependence of the amplitude of the local spin distribution is proportional to $(1 - T/T_c)^{0.32}$. [S0031-9007(96)00926-X]

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The spin-Peierls (SP) state is a collective ground state which can occur for an array of spin-$\frac{1}{2}$ Heisenberg antiferromagnetic (AF) chains on a deformable lattice [1]. On decreasing temperature (T), the SP systems undergo at $T_{\rm SP}$ a second-order phase transition from an undistorted (U) to a dimerized (D) phase. While the spin excitation spectrum of the U chains is gapless, the lattice dimerization opens a singlet-triplet gap, allowing a magnetic energy gain which outweighs the loss in elastic energy. However, the application of an external magnetic field $H > H_c$ induces another phase transition to a new ground state with a finite magnetization at $T = 0$. Most of the theoretical models predict in this state an incommensurate (IC) modulation of both the dimerization amplitude and the spin polarization. It turns out that the SP Hamiltonian can be mapped onto that of 1D strongly interacting spinless fermions coupled to the phonons, where the magnetic field plays the role of the fermion chemical potential. SP systems thus provide the unique possibility to study the response of quasi-1D interacting fermion systems under a continuous change of the chemical potential. It has also been argued that the field induced commensurate-IC phase transition should have a strong "solitonic" character close to H_c, with dimerized domains separated by walls ("solitons") bearing a spin $\frac{1}{2}$ [2–5]. However, due to the high magnetic fields involved, an experimental characterization of the IC phase at a microscopic level has not been possible until recently. The IC character of the modulation of the atomic position is now confirmed by x-ray experiments [6]. This Letter presents the first detailed experimental insight into the local distribution of the spin polarization, as previous attempts were able to detect only an inhomogeneous distribution of magnetization [4,7,8].

The present study has been carried out on the first inorganic SP compound, $CuGeO_3$ [9], in which $T_{\rm SP} =$ 14 K at zero field and $H_c \simeq 12.5$ T at 4.2 K. We studied the NMR line shape of copper nuclei, which probe directly the local magnetization at the position of the $\frac{1}{2}$ spins of the SP system. Our results obtained in the IC phase, in the range 13–17 T, give for the first time a direct access to the spatial distribution along a chain of the static (time-averaged) magnetization $g\mu_B\overline{S_z(i)}$. This magnetization clearly corresponds to a soliton lattice, i.e., to dimerized domains where $\overline{S_z(i)} = S_z^{\rm min} \simeq 0$, separated by walls where $\overline{S_z(i)}$ varies rapidly and takes a maximum value $S_z^{\rm max}$ much larger than the spatial average value $\langle S_z \rangle$. We were able to determine the absolute value of $S_z^{\rm max}$, as well as its T dependence in the IC phase.

Experiments were carried out on a single crystal of $CuGeO_3$ of $\simeq$100 mg, cleaved along the b-c plane from a larger crystal grown from the melt by a floating zone technique, in an image furnace [10]. H was set parallel to the chain (c) axis so that, from the NMR point of view, both crystallographic Cu sites were equivalent [11]. NMR spectra were recorded at fixed Larmor frequencies by sweeping the magnetic field step by step and recording the integral over the spin echo. The full spectrum recorded in the U phase at $T = 20$ K, shown in Fig. 1(a), reveals remarkably narrow lines (FWMH $\sim$ 120 G), indicating a high crystalline quality [11]. Figure 1(b) shows the same spectrum recorded in the high-field phase. In spite of the fact that the central line of each isotope overlaps with a satellite of the other isotope, one can see that all the lines exhibit nearly the same pattern, that is a wide, continuous distribution with a peak at the low field side, a shoulder at higher field, and sharp edges on both sides. Such a spectrum is the signature of an infinite number of nonequivalent copper sites corresponding to an *incommensurate static modulation of the local magnetic field* [12,13]. There is no significant modification or modulation of the electric field gradient (EFG) tensor (defining the separation between the NMR lines), as expected from the absence of any measurable change in the EFG at the transition from the U to the SP phase [11,14]. Note that from the NMR spectra in the U phase [Fig. 1(a)], and

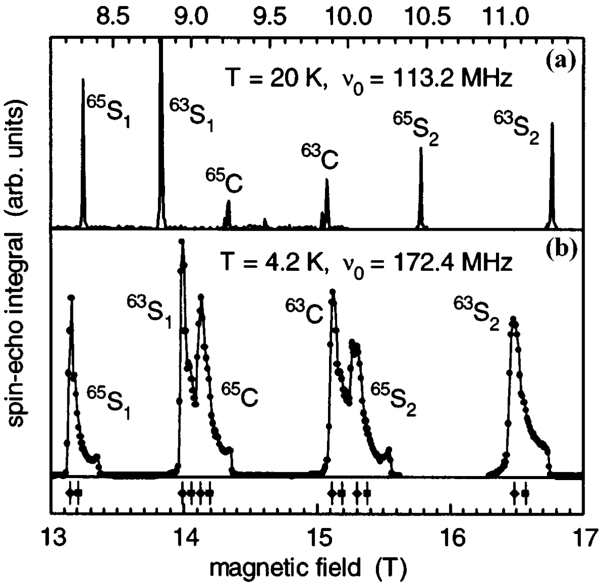

FIG. 1. The field sweep Cu NMR spectra of the (a) U and (b) incommensurate phase, with magnetic field $\parallel$ c axis. For each of the two isotopes ^{63}Cu and ^{65}Cu, the symbols C, S_1, S_2 denote the central line [transition $(-1/2 \leftrightarrow 1/2)$] and two satellites [transitions $(\pm 3/2 \leftrightarrow \pm 1/2)$]. Below lower spectrum, the expected (calculated) line position is given for the SP phase at 4.2 K ($\simeq$ zero magnetization) by diamonds, and for the U phase at 20 K ($\simeq$ average magnetization) by squares.

in the SP phase, in which the macroscopic and the local spin susceptibility vanishes at low temperature, we know the precise correspondence between the spin susceptibility and the position of NMR lines (for any chosen Larmor frequency). This provides the key information in the interpretation of the line shape in the IC phase; for all the lines in Fig. 1(b), the position of the low field peak corresponds to $\overline{S_z} = 0$, while that of the high-field shoulder corresponds to $S_z^{\max}$ values approximately four times larger than the average $\langle S_z \rangle$ deduced from the macroscopic susceptibility. This is precisely what is expected in the soliton lattice picture, with dimerized domains with zero spin polarization and $S_z^{\max}$ value corresponding to the center of the soliton. An interpretation in terms of a canted IC spin density wave can be excluded, since it would give rise to a similar line shape but reversed, i.e., with a peak and a step corresponding to $S_z^{\max}$ and $\overline{S_z} = 0$, respectively. The static character of the observed spin distribution also implies that the lattice is 3D ordered, the transverse coherence being ensured by the associated lattice distortion.

In order to proceed with more quantitative analysis of the line shape [15], we recall that the local additional magnetic field $h(i)$ experienced by a nucleus at site i on a chain is related to the local spin polarization and the local spin susceptibility $\chi(i)$ through the relation

$$h(i) = -A\overline{S_z(i)} = \frac{A}{g\mu_B}\chi(i)H\,, \tag{1}$$

where the value of A, the hyperfine coupling constant along the c direction, is equal to -46 kG [11,14]. The NMR line shape corresponds to the density of the local field distribution $g(h)$:

$$g(h) \propto |dh(i)/di|^{-1}. \tag{2}$$

If we reasonably assume $h(i)$ to be a periodic function of period l/c, symmetric with respect to its maximum, and monotonic over $l/(2c)$, the integral over the line shape

$$i(h) \propto \int^h g(\tilde{h})\,d\tilde{h}\,, \tag{3}$$

provides a direct determination of $h(i)$ or $\overline{S_z(i)}$ as a function of i given in arbitrary units. Equation (3) provides, then, a simple and direct reconstitution of the local spin-polarization profile in real space, which is presented in Fig. 2 for the low temperature NMR line shape. In addition to the raw data and the numerical integral of these data, the full line represents a convenient fitting function through the integral data points, enabling us to visualize the i dependence over the full period. In order to account for the effects of experimental resolution due to the "intrinsic" linewidth, the derivative of this function has been convoluted by a Gaussian with variance $\sigma = 0.01$ T, providing a fit to the experimental line shape (dotted line). One can see that the effects of the convolution, which are neglected in Eqs. (2) and (3), are significant only very near the edges of the line shape, i.e., the information on $h(i)$ is somewhat blurred only in the vicinity of its extrema.

As already mentioned, the x-axis scale of raw NMR spectra can be directly converted from magnetic field into

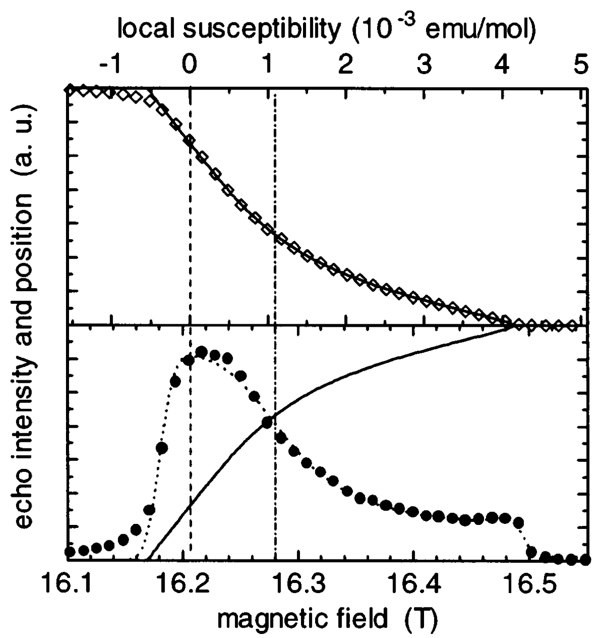

FIG. 2. The ^{63}Cu $(3/2 \leftrightarrow 1/2)$ line shape (circles) taken at 1.4 K and 169.5 MHz, and the numerical integral of these data (diamonds). The lines are explained in the text.

local spin susceptibility. In order to minimize the experimental error, the scale in Fig. 2 is defined as follows: (i) The position of the first moment of the line shape (16.28 T), indicated by the dash-dotted line, is adjusted to the value of the average macroscopic susceptibility, $\chi_M(16.3\text{ T},\ T \simeq 0) = 1.1 \times 10^{-3}$ emu/mol [16]. (ii) From Eq. (1) $\Delta\chi/[\text{emu/mol}] = 0.015\Delta h/[\text{T}]$.

We find the origin of the spin susceptibility scale (zero value denoted by dashed line) close to the position of $S_z^{\min}$, as expected in the solitonic picture. Note that using Eq. (1), the χ scale of Fig. 2 (in 10^{-3} emu/mol) can be converted into the absolute value of $\overline{S_z(i)}$ by applying a factor 1/71, leading to a value of $|S_z^{\max} - S_z^{\min}| \cong 0.065$.

In the solitonic picture [2,4], each soliton carries a spin $\frac{1}{2}$ and there are two solitons per period l. The period is thus simply related to the magnetization M by $l/c = g\mu_B/M$, leading to $l/c \simeq 65$ for the data of Fig. 2. Treating the spinless fermions Hamiltonian within a mean field approximation (MFA), the envelope of the spatial dependence of the spin-lattice distortion has the snoidal form $u(i) \propto \text{sn}(4K(k_1)ic/l, k_1)$, where $\text{sn}(y,k)$ and $K(k)$ are the Jacobi elliptic function of modulus k and the complete elliptic integral of the first kind, respectively. Within the same approximation, Fujita and Machida [5] have shown that the time averaged spin polarization can be expressed as

$$\overline{S_z(i)} = a_0 - a_1\text{sn}^2\left(2K(k)\left[\frac{i}{l/c} + \frac{1-(-1)^i}{4}\right], k\right), \tag{4}$$

where $k_1 = [1 - (1-k^2)^{1/2}]/[1 + (1-k^2)^{1/2}]$. The envelope of $\overline{S_z(i)}$ is the same for even and odd spin sites, but shifted by half of the period. This shift accounts for the staggered component of $\overline{S_z(i)}$, which reflects the AF character of the system. The real NMR line shape is best approximated from the sn^2 function for $k \simeq 0.95$, as shown in Fig. 3. More quantitatively, the discrete Fourier transform of the experimental $h(i)$ dependence shown in Fig. 2 leads to an amplitude ratio of 0.27 for the first harmonic over the fundamental $\cos(2\pi ic/l)$. The same ratio is obtained for the pure sn^2 function, for $k = 0.90$. Regarding the low temperature limit of the amplitude of the modulation a_1 in Eq. (4),

$$a_1 = \frac{4}{\pi}k^2K(k)K\left(\sqrt{1-k^2}\right)\frac{c}{l}, \tag{5}$$

the experimental value ($a_1 \cong 0.065$) corresponds to $k = 0.86$. We also remark that $k_1(k = 0.90) = 0.393$, meaning that the spin-lattice distortion $u(i)$ is much more sinusoidal than $\overline{S_z(i)}$; the third harmonic (the second one being zero) of $u(i)$ is then expected to be only 3% of the fundamental $\sin(2\pi ic/l)$.

While on the qualitative and semiquantitative level we thus find a general agreement between NMR results and the theoretical predictions, there are important differences in the experimental shape of $\overline{S_z(i)}$. The soliton peak is found to be sharper and the dimerized domains less flat than theoretically predicted, which should be related to the approximations used to obtain Eqs. (4) and (5) [5]. After the Jordan-Wigner transformation of the Hamiltonian, the electron-electron interaction term is treated within the Hartree approximation, which in fact corresponds to the *XY* instead of the Heisenberg model. The resulting Hamiltonian is then treated within the MFA, which is likely to be justified if the 3D character of the electron-phonon coupling suppressed the 1D fluctuations. Finally, the equations are solved in the continuum limit, which may be questionable at the center of the soliton, where the i dependence is strong.

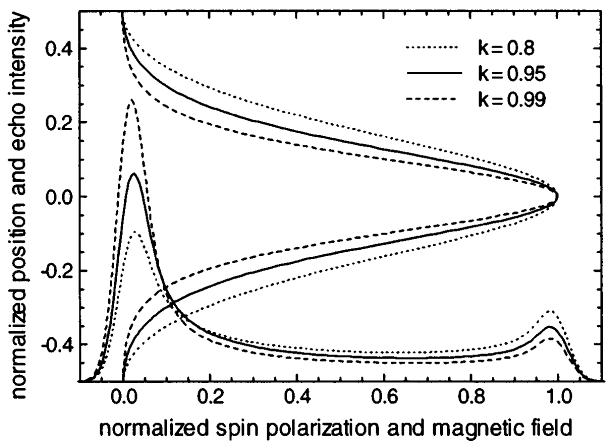

FIG. 3. The predicted position dependence of the spin polarization (sn^2 function of modulus k), plotted with reversed ($x \leftrightarrow y$) coordinate axes, and the corresponding NMR line shape [from Eq. (2), convoluted by the Gaussian with $\sigma = 0.03$] in the same representation as in Fig. 2.

Equation (5) predicts that the amplitude of modulation a_1 is proportional to magnetization $M \propto l^{-1}$, and it increases with k, as solitons became "sharper." Experimentally, from Fig. 1(b) we learn that a_1 is roughly proportional to the magnetic field, i.e., $\chi^{\max}$ is approximately H independent. This is consistent with the prediction if we admit that the H dependence of the magnetization, which decreases faster than linearly at low field, and of the soliton shape, being somewhat sharper at low field, compensate to give approximately constant $\chi^{\max}$. This assumption has to be confirmed by a more consistent study of the H dependence of the NMR line shape.

There is also another theoretical description of solitons, which consists in transforming the 1D spinless fermions Hamiltonian into its phase form and applying the self-consistent harmonic approximation [2,4]. Within this formalism, the amplitude of the staggered magnetization at the top of the soliton at $T = 0$ is independent of H and given by $S_z^{\max} = (\Delta/\pi^2 J)^{1/2}$, where Δ is the gap in the excitation spectrum of the SP phase. According to the values of Δ (24 K) and J (120 K) [17], this leads to H independent values of $S_z^{\max} \simeq 0.14$, which is incompatible with our experimental results.

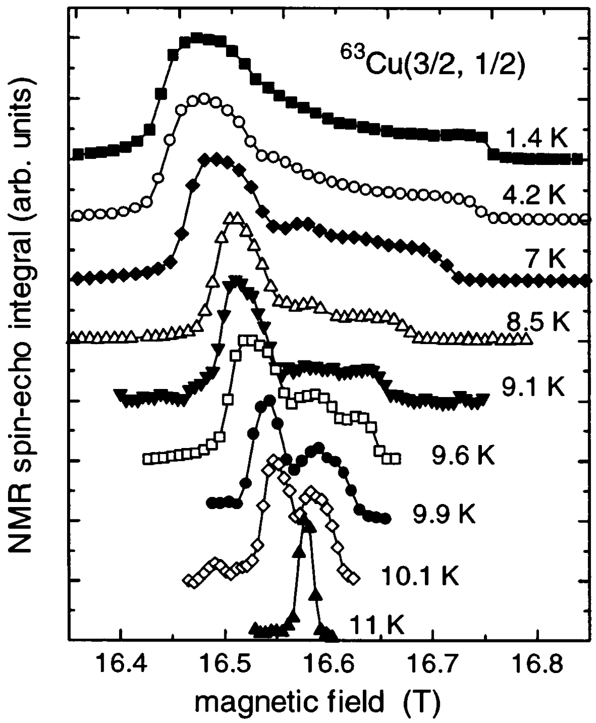

FIG. 4. Temperature dependence of the NMR line shape taken at 172.4 MHz.

The T dependence of the full width of NMR line shape (Fig. 4), i.e., of the amplitude of spin-density modulations, is expected to be proportional to the order parameter. It can be very well described by a power law $\propto (1 - T/T_c)^\alpha$, with $T_c = 10.0 \pm 0.05$ K and the "critical" coefficient $\alpha = 0.32 \pm 0.03$. Although the data shown in Fig. 4 do not allow for the real determination of critical behavior, and the power-law fit covers all the measured temperatures, it is interesting to remark that as in other IC systems [13,18], α is close to the value expected for a 3D phase transition with a two-component order parameter. This, in addition to the static character of the spin distribution, is consistent with a pinned 3D soliton lattice.

As regards the line shape, note that on approaching T_c, a peak appears in the center of the line. We tentatively attribute this peak to a partial motional narrowing of the line, corresponding to nuclei belonging to parts of the crystal in which the soliton lattice becomes depinned, and where at the time scale of NMR, $\overline{S_z(i)}$ is averaged to the mean value over even and odd positions, $\frac{1}{2}\langle S_z(i) + S_z(i+1)\rangle$, or down to the full spatial average $\langle S_z \rangle$. Such an effect, sometimes called "floating phase," has been observed in IC dielectrics [19].

In conclusion, our Cu NMR measurements in a $CuGeO_3$ single crystal bring the first clear evidence that the ground state in the magnetic field range 13–17 T is a field-induced magnetic 3D soliton lattice. The observed line shape corresponds to a spatial distribution of spin polarization, with domains where $\overline{S_z(i)}$ is close to zero. The static character of this distribution implies that the soliton lattice is pinned by defects. As far as the microscopic distribution of $\overline{S_z(i)}$ is concerned, we found a qualitative agreement with theories involving a staggered component of $\overline{S_z(i)}$ parallel to the magnetic field.

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