Double Gap and Solitonic Excitations in the Spin-Peierls Chain $CuGeO_3$

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We have studied magnetic excitations in the spin-Peierls phase of $CuGeO_3$ by inelastic neutron scattering. There is a dispersive mode which is gapped throughout the Brillouin zone. This mode is separated by an unexpected second gap of ≈2 meV, from a continuum of magnetic excitations. The first gap (or "triplet gap") and its associated dispersive mode are due to the breaking of a singlet dimer into a delocalized triplet. We propose that the second gap (or "solitonic gap") and the continuum correspond to dissociation of that triplet into two unbound spin-$\frac{1}{2}$ solitons that are separated by a dimerized region of arbitrary length. [S0031-9007(97)02400-9]

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The recent observation by Hase [1] of a characteristic magnetic susceptibility in $CuGeO_3$, dropping abruptly to zero below $T_{SP} = 14.3$ K, clearly suggested that it was a new one-dimensional spin-Peierls compound. This was confirmed by x-ray photographs [2,3] that revealed, below T_{SP}, superlattice peaks indexing according to the propagation vector $\mathbf{k}_{SP} = (0.5, 0, 0.5)$. These two experimental evidences indicate that: (1) A gap has opened over a nonmagnetic singlet ground state as demonstrated by neutron studies [4,5], and (2) that the crystal was undergoing a magnetoelastic distortion where copper ions dimerize with their left or right nearest neighbor along the chains. As a result, the initially uniform exchange coupling becomes staggered.

In this Letter we present experimental evidence that there are in fact two gaps in this system and not only one as predicted by the classical approach [6,7]. Although this observation could fit in the framework of Cross-Fisher theory [7], we shall use a solitonic approach to elaborate an explanation which accounts for two gaps. A dimerized system has an obvious excitation which consists of breaking a dimer bond into a triplet at a cost of a certain magnetoelastic energy. The triplet will be delocalized along the chain generating eigenstates of definite momentum. However, there is another possible excitation in this system because the triplet can absorb a second amount of energy corresponding to a second gap and thus dissociate into two $S = \frac{1}{2}$ traveling solitons that generate the continuum. This has some analogies to the well known two-spinon continuum of the uniform (undimerized) Heisenberg $S = \frac{1}{2}$ AF chain (HAFC) that has been investigated extensively in $KCuF_3$ (see Fig. 6 of Ref. [8]). Above T_{SP} the analogy is even more complete as we shall see in Fig. 3. On the other hand, it has been suggested that competing next-nearest-neighbor exchange (NNNE) was the driving mechanism in the dimerization process of $CuGeO_3$ instead of magnetoelastic coupling as generally admitted. In support of this idea were satisfactory fits [9–11] of the magnetic susceptibility of $CuGeO_3$ above T_{SP}. Since this susceptibility was not well reproduced by the Bonner-Fisher curve [12], which is appropriate to the isolated $S = \frac{1}{2}$ AF NNE chain, incorporation of NNNE gave better results. Yet in the final part of section II of our discussion we express some reservation with respect to this interpretation based on competing NNNE.

Single crystals of $CuGeO_3$ belong to the orthorhombic space group *Pbmm*. Magnetic chains of Cu^{++}, $S = \frac{1}{2}$ ions are parallel to the c axis. The spin-Peierls gap is observable at $\mathbf{k}_{AF} = (0, 0, 0.5)$ or equivalent points, but there are no magnetic Bragg peaks. Dispersion curves of magnetic excitations along the three principal directions a, b, and c are of simple sinusoidal shape [4,5]; estimates for intrachain nearest-neighbors exchange (NNE) along c gave $J_1 \approx 120$ K, as derived from fits to classical magnon theory in Ref. [4] or to Bonner-Blöte relation in Ref. [5]. Fits to classical magnon theory [4,5] indicate that NNE between chains are only 1 and 2 orders of magnitude smaller along the b and a directions, respectively.

Inelastic neutron scattering measurements have been performed on two triple-axis spectrometers: (1) 4F1 (Orphée reactor, LLB Saclay), which was operated at constant $k_f = 1.55$ Å^{-1} (5.01 meV) with a horizontally focusing graphite analyzer and a beryllium filter to cut out higher-order components of the diffracted beam, (2) IN14 (HFR, ILL Grenoble) with a similar set up as on 4F1. Resolution on both apparatus was of the order of 0.2 meV (FWHM) as deduced from the incoherent peak at zero energy transfer. In both experiments the same single crystal (nearly 1 cm^3) was oriented with the b and c crystallographic axes in the scattering plane. Two series of inelastic scans were recorded for neutron energy transfers ranging from −0.3 meV to 11.5 meV. All scans are corrected for $\lambda/2$ contamination in the incident beam [13].

Figure 1 shows three energy scans at $T = 2.6$ K. They correspond to excitations near the zone boundary along c^*, the direction of the chains. Five elements are visible on the scan at $\mathbf{Q} = (0, 1, 0.5)$: (1) the zero-energy incoherent peak showing the spectrometer resolution; (2) a first gap, called hereafter the "triplet gap" with a value of $\Delta = 2$ meV at $\mathbf{Q} = (0, 1, 0.5)$; (3) a well-defined magnonlike mode first observed by Nishi *et al.* [4]. This mode is in fact a spin-triplet mode as shown by measurements in a magnetic field [5]. Its asymmetric shape is due to convolution of instrumental resolution and steep curvature of the dispersion curve in the vicinity of $\mathbf{Q} = (0, 1, 0.5)$. (4) The intensity between the middle peak (or triplet mode) and the plateau, falls to the background level. This is clearly a new gap in energy that we call hereafter the "solitonic gap." At $\mathbf{Q} = (0, 1, 0.5)$, this solitonic gap is close to 2 meV. Defining the background in this experiment is an issue that will be addressed when presenting Fig. 3. (5) Finally, brought out by the solitonic gap, we find some intensity (low but clearly present) which constitutes the expected continuum that extends at least up to the maximum energy transfer of our study, i.e., 11.5 meV. Scans for $\mathbf{Q} = (0, 1, 0.48)$ and $\mathbf{Q} = (0, 1, 0.46)$ display the same structure as that for $\mathbf{Q} = (0, 1, 0.5)$ except that the incoherent peak is not shown. We recall that neutron [5,15] and Raman [14] scattering have already given clear evidence for the existence of such a continuum.

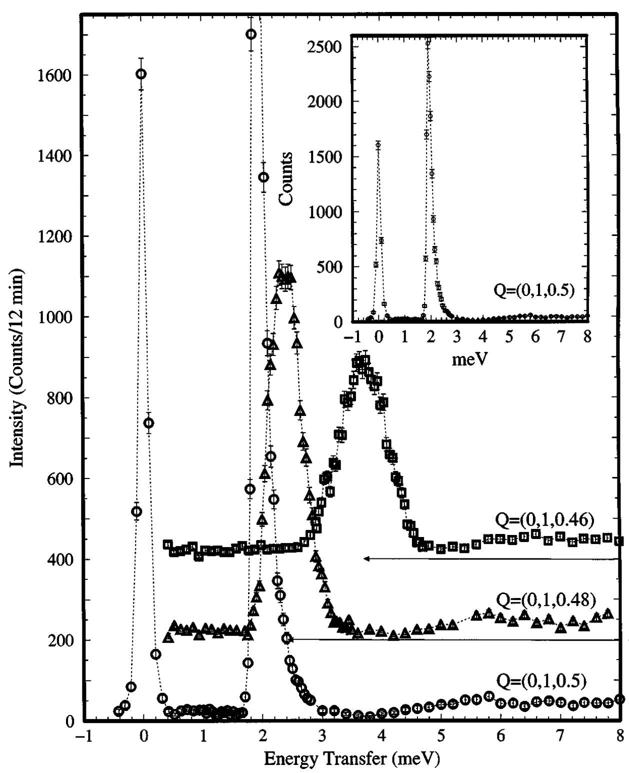

FIG. 1. (IN14–ILL) Three energy scans for $\mathbf{Q} = (0, 1, Q_c)$ with $Q_c \in \{0.5, 0.48, 0.46\}$, at $T = 2.6$ K. They are vertically shifted apart for clarity. The horizontal graduation is common to all scans; the left vertical axis is for the $\mathbf{Q} = (0, 1, 0.5)$ scan only. Each horizontal arrow indicates the zero intensity level for the scan above it. In the inset is a general view of the first scan displaying the five elements described in the text. Now labeling a dimer in its singlet state by $\bullet\!-\!\bullet$, the triplet state by $\Uparrow$, and a spin $\frac{1}{2}$ on a copper site by $\uparrow$, we can represent the peak of the magnonlike mode as a traveling triplet $\bullet\!-\!\bullet \quad \bullet\!-\!\bullet \Uparrow \bullet\!-\!\bullet \quad \bullet\!-\!\bullet$, then after the solitonic gap the continuum would correspond to delocalized spins $\frac{1}{2}$ such as $\bullet\!-\!\bullet \uparrow \bullet\!-\!\bullet \quad \bullet\!-\!\bullet \uparrow \bullet\!-\!\bullet$.

Figure 2 shows a series of six energy scans regularly spaced along b^* between $\mathbf{Q} = (0, 1, 0.5)$ and $\mathbf{Q} = (0, 2, 0.5)$ at $T = 1.7$ K. No incoherent peak here, only the peak of the dispersive mode followed again by the solitonic gap and the continuum are visible in this series of scans. Note that owing to coupling between chains, as already mentioned, there is dispersion along $\mathbf{Q}_b$ and therefore the positions of the peaks are not constant in energy as they would be for a pure one-dimensional system.

Figure 3 provides a more detailed picture of the energy scans at $\mathbf{Q} = (0, 1, 0.5)$. It shows that when the temperature is raised to $T = 29$ K the peak of the dispersive mode drops and widens, filling in the double gap region and merging with the continuum. We have recovered, then,

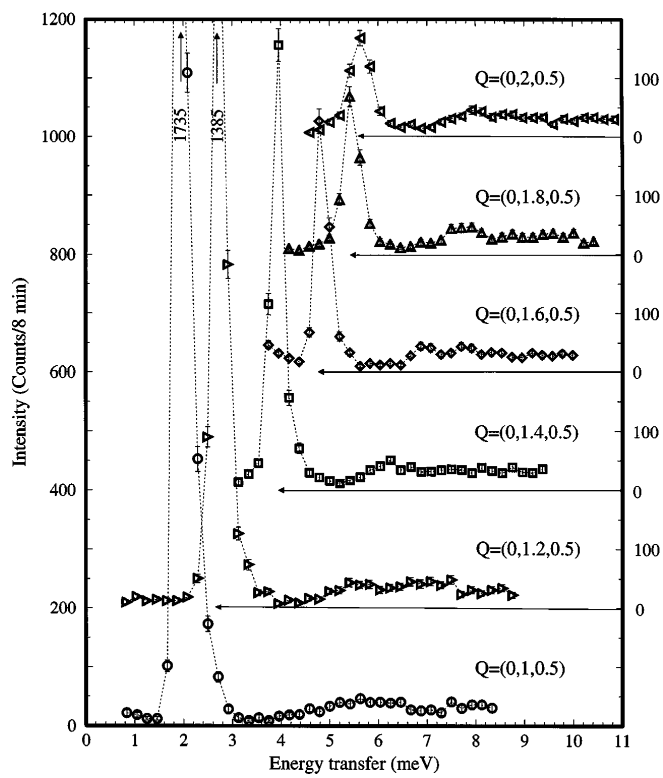

FIG. 2. (4F1–LLB) Six energy scans for $\mathbf{Q} = (0, Q_b, 0.5)$ with $Q_b \in \{1, 1.2, 1.4, 1.6, 1.8, 2\}$, at $T = 1.7$ K. Same convention for axes as in Fig. 1. Maximum peak position is indicated by a vertical arrow, the intensity reached is written below. The sharp peak of the magnonlike mode, the solitonic gap, and the continuum are clearly visible in all scans.

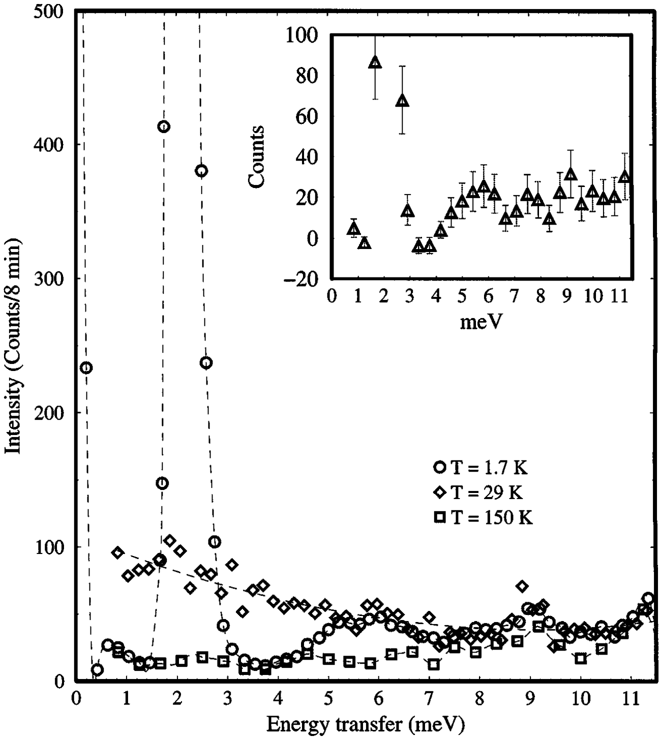

FIG. 3. (4F1–LLB) Three energy scans at $\mathbf{Q} = (0, 1, 0.5)$. (1) At 1.7 K (circles) we have, successively, the incoherent peak, the triplet gap, the magnonlike mode that reaches 1983 counts at 2 meV, the solitonic gap, and the continuum. (2) At 29 K (diamonds) the continuum, similar to that of the $S = \frac{1}{2}$ HAFC. (3) At 150 K (squares) the purely paramagnetic region. In the inset, subtraction of the scan at 1.7 K from the one at 150 K showing the magnonlike mode and the continuum.

the continuum of the uniform HAFC. When we reach $T = 150$ K, the magnonlike mode and the continuum have totally disappeared, we are then in the truly paramagnetic region; note that the intensity falls to the level of what was measured at $T = 1.7$ K in either gap; this level is considered as the background of our experiment. In the inset we subtracted the scan at 150 K from the scan at 1.7 K. Both were corrected for Bose factor after subtraction of a background of 15 counts on each. What remains is the dispersive mode, the solitonic gap, and the continuum. A phonon is distinguishable near 11 meV in the 150 K data.

The fact that the double gap has been overlooked in previous experiments [4,5,15] is due to poorer resolution of the instruments used before. In these former experiments, the high energy tail of the incompletely resolved dispersive mode precluded observation of the solitonic gap by causing a smooth crossover to the higher energy continuum. In the present experiment high resolution was obtained through the use of a small $k_f = 1.55$ Å^{-1}.

It has been impossible to detect acoustic phonon branches around $\mathbf{k}_{SP}$, and moreover, preliminary polarized neutron measurements at $\mathbf{Q} = (0, 1, 0.5)$ and $\mathbf{Q} = (0.5, 5, 0.5)$ indicate that all of the intensity in the peak of the dispersive mode is magnetic, as is the major part, if not all, of the intensity in the continuum. The absence of an inelastic nuclear contribution is consistent with the fact that in the dimerized phase of $CuGeO_3$, intensities of nuclear superlattice peaks at $\{\mathbf{k}_{SP}\}$ are very weak and displacements of atoms extremely tiny. Nonetheless, superlattice nuclear peaks are sensitive to a magnetic field as proved by the commensurate-incommensurate transition that occurs at 12.5 T [16]. All this suggests that there could exist a magnetoelastic coupling through spin-charge hybridization [17].

Haldane [18] analyzed three models that are related to $CuGeO_3$: (I) the AF chain with NNE J_1 and NNNE J_2, (II) the AF chain with NNE only but with imposed staggering of the exchange, (III) the AF chain coupled to a phonon field $u(x)$ [7]. Although all three models predict a gap, only model III predicts a double gap which is consistent with our experimental results on the excitation spectrum of $CuGeO_3$.

Model I.—In the case of NNE J_1 and NNNE J_2, the Hamiltonian of the chain has full translational invariance. If J_2 is smaller than a critical coupling $[J_2/J_1 < 0.2412(1)]$, the ground state is a spin liquid but if J_2 is larger, the ground state is dimerized and twice degenerate. We will refer to this situation as "spontaneous dimers." The effective long-wavelength, low-energy theory is described by a sine-Gordon model [19]:

$$H = \int dx \, \tfrac{1}{2}[\Pi^2 + (\nabla\phi)^2] + \alpha \cos(\beta\phi). \qquad (1)$$

In this equation, Π is the momentum conjugate to ϕ which is related to the z component of the spin at position x by $S^z(x) = -\nabla\phi(x)/\sqrt{2\pi} + \mathrm{C}(-)^x \cos[\sqrt{2\pi}\,\phi(x)]$. When $J_2 \neq 0$, the value of the sine-Gordon coupling is $\beta = 2\sqrt{2\pi}$. If J_2 is larger than the critical value, one is in the massive (or gapped) phase of the theory of Eq. (1). The $\beta = 2\sqrt{2\pi}$ sine-Gordon theory has no bound states [20], and the elementary excitations are kinks that correspond to a $\pm 2\pi$ variation of the argument of the cosine term in Eq. (1) over a localized region of space. These solitons therefore have spin $S = \frac{1}{2}$. The picture is simple: An excitation means that a singlet in the dimerized ground state is broken into a triplet that immediately disintegrates into two free solitons. As a consequence, the magnetic excitations form a continuum above some threshold and there is no well-defined mode below. This is not what we observe in our experiments.

Model II.—The externally dimerized chain has an explicit doubling of the unit cell by the additional term $\delta \sum_n (-)^n \vec{S}_n \cdot \vec{S}_{n+1}$. This also leads to a sine-Gordon model Eq. (1) but now with a coupling $\beta = \sqrt{2\pi}$. The kinks that still correspond to a $\pm 2\pi$ variation of the argument of the cosine in Eq. (1) have now spin $S^z = \pm 1$. The sine-Gordon theory with $\beta = \sqrt{2\pi}$ has two breather bound states [20], one of which is degenerate with the kink states. This state completes the $S = 1$ triplet which is expected due to the full rotational invariance of the theory. The other bound state is a singlet and thus plays no role in the magnetic excitation spectrum. Here the picture is quite different from that of model I. The singlet bonds are pinned to the lattice by the dimerizing potential. The elementary excitation corresponds to breaking a singlet bond in a triplet and then this triplet will move along the chain. This triplet state is not a domain wall and cannot disintegrate as has been seen in numerical simulations [9,10,21]. There are continua above this well-defined mode that are due to excitations of several triplets. Haas and Dagotto have recently performed a study [21] of the dynamical properties of an externally dimerized chain including a NNNE J_2. They have shown that there is a continuum starting immediately above the spin triplet mode contrary to our finding of a solitonic gap in $CuGeO_3$.

To the extent that NNNE should be visible on the shape of the dispersion curve it becomes informative to calculate the dynamics of a colinear $S = \frac{1}{2}$ Heisenberg AF model with $J_1 < 0$ and J_2, and lattice spacing c. It yields the following dispersion relation:

$$h\nu(q) = 2|\sin qc|\sqrt{J_1(J_1 - 4J_2) + 4{J_2}^2 \sin^2 qc}\,, \quad (2)$$

which is valid only for $J_2/J_1 < 0.25$ (Villain's criterion. If $J_2 > 0$ and $J_2/J_1 > 0.25$ the calculation ought to be conducted differently as appropriate for helimagnetic AF). We see that the curve $\nu(q)$ is narrowed by the last term with the J_2 factor, which makes it depart markedly from a sinusoidal shape in contrast to our observations on $CuGeO_3$. The relevance to $CuGeO_3$ is enforced by noting that the underlying AF system in $CuGeO_3$ would have AF Bragg peaks at $\mathbf{k}_{AF} = (0, 0, 0.5)$ as verified in $CuGe_{0.993}Si_{0.007}O_3$ [22] where AF and dimerization coexist.

Model III.—A more realistic model [7,23] would incorporate an additional coupling of the sine-Gordon field with an elastic field of the form $u(x)\cos[\sqrt{2\pi}\,\phi(x)]$. The Hamiltonian Eq. (1) again has full translational invariance. This invariance is spontaneously broken and there are thus domain walls: The displacement $u(x)$ in a domain wall goes from $+u_0$ on one side of the chain to $-u_0$ on the other side, or vice versa. The spin soliton involves only a variation of π of the argument of the cosine and thus has spin $S = \frac{1}{2}$, as in the case of the spontaneously dimerized chain. This elementary soliton can be visualized as an isolated $S = \frac{1}{2}$ copper spin that separates two regions of the chain that are dimerized. These solitons have been studied in the past [23]. No detailed information is available on the sine-Gordon theory coupled to an additional scalar field; however, since the coupling is well in the massive regime, it is clear that we expect bound states of these solitons. The most likely candidate is a triplet of the same nature as in the externally dimerized chain. If enough energy is available to overcome the binding energy, this triplet state can then disintegrate into two solitons. We expect then a triplet mode that is well-defined below the solitonic continuum. This is consistent with what we observe.

To summarize, we have shown by high resolution inelastic neutron measurements that there is a mid-gap dispersive mode and confirmed the existence of a continuum of excitations. We have proposed that this continuum is made of unbound $S = \frac{1}{2}$ domain walls.

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