Double gap and solitonic excitations in the spin-Peierls chain CuGeO$_3$

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We have studied magnetic excitations in the dimerized spin-Peierls phase of CuGeO$_3$, by high resolution inelastic neutron scattering. We measured the well-defined spin triplet dispersive mode which is gapped throughout the whole Brillouin zone. We also observed that this mode is separated by an unexpected second gap of $\approx 2$ meV from a continuum of magnetic excitations extending to higher energy. The first gap (or 'triplet gap') and its associated dispersive mode is 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-1/2 solitons that are separated by a dimerized region of arbitrary length.

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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-Rays photographs [2,3] that revealed, below $T_{SP}$, superlattice peaks indexing according to the propagation vector $k_{SP}=(0.5,0,0.5)$. These two experimental evidences indicate: 1- That a gap has opened over a non magnetic 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.

Single crystals of CuGeO$_3$ are grown in an image furnace by the traveling floating zone method. They belong to the orthorhombic space group Pbmm. Magnetic chains of Cu$^{++}$, $S=1/2$ ions are parallel to the c axis. The spin-Peierls gap is observable at $k_{AF}=(0,0,0.5)$ 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 one and two orders of magnitude smaller along the b and a directions respectively.

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 [6,8]. Although this observation could fit in the framework of Cross-Fisher theory [8], 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 $S=1/2$ traveling solitons that generate the continuum. This has some analogies to the well known two-spinon continuum of the uniform (undimerized) Heisenberg $S=1/2$ AF chain (HAFC) that has been investigated extensively in KCuF$_3$ (see figure 6 of ref [9]). Above $T_{SP}$ the analogy is even more complete as we shall see on figure 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 [10,12] of the magnetic susceptibility of CuGeO$_3$ above $T_{SP}$. Since this susceptibility was not well reproduced by the Bonner-Fisher curve [13], which is appropriate to the isolated $S=1/2$ 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.

Inelastic neutron scattering measurements have been performed on two triple-axis spectrometers: 1- 4F1 (Orphée reactor, LLB Saclay) has an incident beam, fixed in direction, extracted by a pair of graphite monochromators (the second one being vertically focussing). It was operated at constant $k_f=1.55$ Å$^{-1}$ (5.01 meV) with a horizontally focussing graphite analyser and a beryllium filter to cut out higher-order components of the diffracted beam. 2- IN14 (HFR, ILL Grenoble) has one vertically focussing graphite monochromator and a horizontally focussing graphite analyzer, the rest of the set up was similar on both spectrometers.
The resolution on both apparatus was very close to 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 [14].

Figure (1) shows three energy scans at $T=2.6$ K. They correspond to excitations near the zone boundary along the $c^*$ direction parallel to the chains. Five elements are visible on the scan at $Q=(0,1,0.5)$: 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 $Q = (0,1,0.5)$. 3- A well-defined magnon-like 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 $Q=(0,1,0.5)$. 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 $Q=(0,1,0.5)$, this ‘solitonic gap’ is close to 2 meV. Defining the background in this experiment, is an issue that will be addressed when presenting figure (3). 5- Finally, brought out by the ‘solitonic gap’ we find some intensity (low but clearly present) which constitute the expected continuum that extends at least up to the maximum energy transfer of our study, i.e. 11.5 meV. Scans for $Q=(0,1,0.48)$ and $Q=(0,1,0.46)$ display the same structure as that for $Q=(0,1,0.5)$ with the exception of the incoherent peak which is not shown. We recall that neutron [4,5] and Raman [15] scattering have already given clear evidence for the existence of such a continuum.

Figure (2) shows a series of six energy scans regularly spaced along $b^*$ between $Q=(0,1,0.5)$ and $Q=(0,2,0.5)$ 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 $Q_b$ and 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 $Q=(0,1,0.5)$. 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 indicating that the two gaps have collapsed and that we have recovered the continuum of the uniform HAFC. When we reach $T=150$ K, the magnon-like 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 insert 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 [4–6] 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 high energy continuum. In the present experiment high resolution was obtained through the use of a small $k_f=1.55$ Å.

It has been impossible to detect acoustic phonon branches around $k_{SP}$, and moreover,
preliminary polarized neutron measurements at Q=(0, 1, 0.5) and 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 $\{k_{SP}\}$ 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 \[\text{\cite{17}}\]. All this suggests that there could exist a magnetoelastic coupling through spin-charge hybridization \[\text{\cite{16}}\].

There are three models that are related to our observations in 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 $u(x)$ \[\text{\cite{8}}\]. 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$_3$. An analysis of these models has been given by Haldane \[\text{\cite{18}}\].

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. Translation invariance by one lattice spacing is spontaneously broken. We will refer to this situation as ”spontaneous dimers”. The effective long-wavelength, low-energy theory is described by a sine-Gordon model \[\text{\cite{19}}\]:

$$H = \int dx \frac{1}{2} (\Pi^2 + (\nabla \phi)^2) + \alpha \cos(\beta \phi). \quad (1)$$

In this equation, $\Pi$ is the momentum conjugate to $\phi$ which is related to the $z$-component of the spin at position $x$ by: $S_z(x) = -\nabla \phi(x)/\sqrt{2\pi} + C(-)^x \cos(\sqrt{2\pi} \phi(x))$. 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 \[\text{\cite{20}}\] 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 $S=1/2$. The physical 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.

II - We turn now to the externally dimerized chain: there is an additional modulated exchange $\delta \sum_n (-)^n \vec{S}_n \cdot \vec{S}_{n+1}$. There we have explicit doubling of the unit cell. 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 \[\text{\cite{20}}\]: one 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 physical 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 \[\text{\cite{10,11,21}}\]. 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=1/2 Heisenberg AF model with $J_1 < 0$ and $J_2$, and lattice spacing $c$. It yields the following dispersion relation:

$$h\nu(q) = 2|\sin qc|\sqrt{(J_1(J_1 - 4J_2) + 4J_2^2\sin^2 qc)}$$  \hspace{1cm} (2)

which is only valid for $J_2/J_1 < 0.25$ (Villain’s criterion). 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 analogy with CuGeO$_3$ is enforced by noting that the underlying AF system in CuGeO$_3$ would have AF Bragg peaks at $k_{AF}=(0,0,0.5)$ as verified in CuGe$_{0.993}$Si$_{0.007}$O$_3$ [22] where AF and dimerization coexist. (If $J_2 > 0$ and $J_2/J_1 > 0.25$ the calculation ought to be conducted differently as appropriate for helimagnetic incommensurate AF).

III - Finally we turn to the more realistic model having an elastic displacement field [8,23]. It involves 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 $\pi$ of the argument of the cosine and thus has spin S=1/2, as in the case of the spontaneously dimerized chain. This elementary soliton can be visualized as an isolated S=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 inelastic neutron measurement 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=1/2 domain walls.

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FIGURES

FIG. 1. (IN14-ILL) Three energy scans for $Q=(0,1,Q_c)$ with $Q_c=\{0.5, 0.48, 0.46\}$, 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 $Q=(0,1,0.5)$ scan only. Each horizontal arrow indicate the zero intensity level for the scan above it. In the insert a general view of the first scan displaying the five elements described in the text. Now labelling a dimer in its singlet state by $\bullet – \bullet$, the triplet state by $\uparrow$ and a spin 1/2 on a copper site by $\uparrow$, we can represent the peak of the magnon-like mode as a traveling triplet $\bullet – \bullet \bullet – \bullet \uparrow \bullet – \bullet \bullet – \bullet$, then after the 'solitonic gap' the continuum would correspond to delocalized spins 1/2 such as $\bullet – \bullet \uparrow \bullet – \bullet \bullet – \bullet \uparrow \bullet – \bullet$.

FIG. 2. (4F1-LLB) Six energy scans for $Q=(0,Q_b,0.5)$ with $Q_b=\{1, 1.2, 1.4, 1.6, 1.8, 2\}$ at $T=1.7$ K. Same convention for axes as on Fig (1). Maximum peak position is indicated by a vertical arrow, the intensity reached is written below. The sharp peak of the magnon-like mode, the 'solitonic gap' and the continuum are clearly visible in all scans.

FIG. 3. (4F1-LLB) Three energy scans at $Q=(0,1,0.5)$. 1- At 1.7 K (circles) we have successively, the incoherent peak, the 'triplet gap', the magnon-like 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 $S=1/2$ HAFC. 3- At 150 K (squares) the purely paramagnetic region. In the insert, subtraction of the scan at 1.7 K from the one at 150 K showing the magnon-like mode and the continuum.
