Quantum Spin Excitations in the Spin-Peierls System $CuGeO_3$

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The complete spectrum of the double spinon excitation in the spin-Peierls system $CuGeO_3$ is mapped as a function of temperature for the first time. The spin dynamics of the lower boundary and the excitation continuum evolve quite differently. Moreover, the dimerization of the lattice produces a sharp excitation in the lower energy boundary at the edge of the Brillouin zone, as well as the well known spin-gap opening at the zone center. [S0031-9007(96)01457-3]

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Intense research activity by several research groups [1] in recent years has proved that the magnetic phase transition, which is characterized by an abrupt decrease in the susceptibility along each of the crystallographic axes [2], can be explained by a spin-Peierls transition at $t_{\mathrm{sP}} = 14$ K. However, the broad feature that is also observed in the susceptibility cannot be explained by the theory for one-dimensional antiferromagnets proposed by Bonner and Fisher [3]. It is necessary to include a competing interaction between the nearest and second nearest neighbors [4]. Kamimura *et al.* [1] reported superlattice Bragg scattering at $(h/2, k, l/2)$ with h, k, l equal to odd integers, caused by the lattice dimerization and the formation of the spin-singlet pairs. $CuGeO_3$ is then the first inorganic material found to possess a spin-Peierls transition.

The spin wave excitation has been studied by Nishi *et al.* [5]. They reported the spin-gap energy to be about 2.1 meV at $(0, 2\pi, \pi)$ at 0 K. They also estimated the exchange interaction from the zone boundary energy of 16.3 meV to be $J_c = 10.4$ meV in the c direction and $J_b = 0.1 J_c$ and $J_a = -0.01 J_c$ in the b and a directions, respectively. Hence the system cannot be thought of as entirely one dimensional.

The existence of the anomalous spin dynamics in one-dimensional Heisenberg antiferromagnets (1D-HB-AF) was first reported experimentally by Endoh *et al.* in 1974 using a triple-axis spectrometer [6]. However, the more recent development of pulsed neutron techniques has made it much easier to observe spin excitations in these low-dimensional antiferromagnets, as has been demonstrated in experiments on various systems such as $KFeS_2$ [7], $KCuF_3$ [8,9], $CsVCl_3$ [10], and $La_{2-x}Sr_xCuO_4$ [11]. The quantum spin excitations of 1D-HB-AF systems are characterized by a spin excitation continuum, the lower boundary of which is formed by the des Cloizeaux and Pearson result [12] and the upper, by a boundary with twice the energy and periodicity (in Q space). This spin continuum (or double spinon continuum) can be explained by several different theories and is either the excitation of pairs of interacting spinons [9], a pair of solitons [13], or a pair of kinks [14]. In the spinon explanation, the lower boundary corresponds to a spinon pair excitation, but with one of the pair having zero momentum, and upper boundary from two spinons each with a momentum of $q/2$, where q is the total momentum. In the continuum region a pair of interacting spinons can propagate freely along the one-dimensional chain with a total momentum of q.

The spin-Peierls transition is a characteristic feature of a one-dimensional antiferromagnet that couples strongly with the lattice. It is likely that the quantum spin fluctuations in such systems are different from those where the coupling is weak [15]. Therefore the inelastic neutron scattering measurements described in this Letter provide a realistic test of the recent theoretical studies [16,17] that have been made of the spin excitations in spin-Peierls systems.

The sample was synthesized using a standard traveling floating zone method. We prepared five single crystals with a total mass of 15.0 g (about 3 cm^3). The crystals were aligned using x-ray Laue measurements to give an effective mosaic spread of about 3 deg full width at half maximum. The neutron scattering experiment was performed on the MARI spectrometer at the ISIS pulsed neutron facility of the Rutherford Appleton Laboratory [18]. MARI is a direct geometry spectrometer that uses a Fermi chopper to monochromate the incident beam, and has a vertical scattering geometry. In this experiment a low resolution high flux chopper was used with an incident energy of 45 meV. This gives an energy resolution of about 3 meV for elastically scattered neutrons and 1 meV at an energy transfer of 45 meV. The crystal was aligned so that the c axis was in the scattering plane and perpendicular to the incident beam (k_i), i.e., the c axis was in the vertical direction, while the b axis was parallel to k_i.

Figure 1(a) shows the dynamical structure factor of the spin excitation below T_{sP} at a temperature of 10 K. For

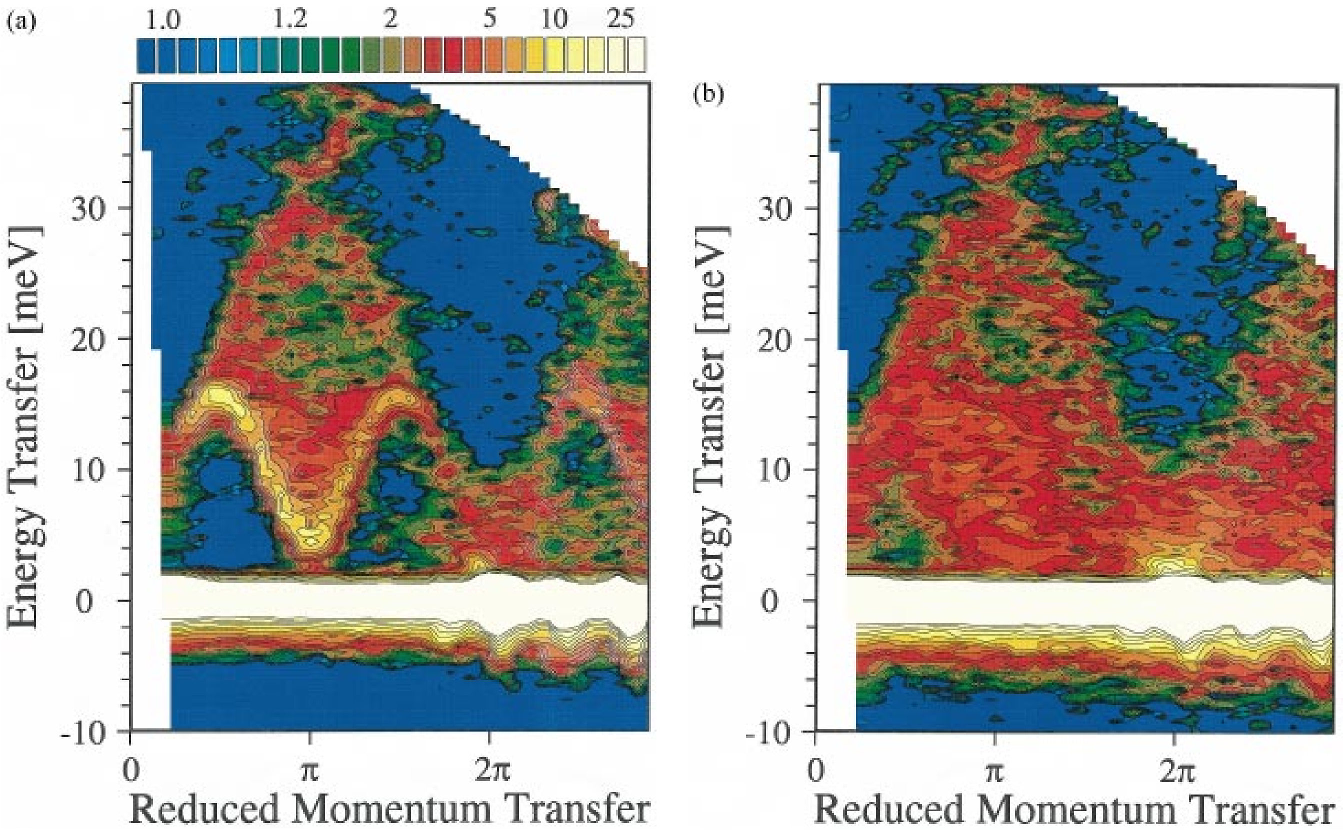

FIG. 1(color). A color contour map of the dynamical structure factor at 10 K (a) and 50 K (b).

the first time it is possible to see the image of the whole quantum spin excitation spectrum of a one-dimensional antiferromagnet. The data are plotted as a function of the c component of the momentum transfer (Q_c) in reduced lattice units [10]. This makes the assumption that the magnetic correlations are one dimensional and along the c axis. Hence 1.06 Å^{-1} corresponds to the zone center of the antiferromagnetic correlation, i.e., at $(0, 0, \pi)$. The spin-wave dispersion proposed by des Cloizeaux and Pearson [12] can be clearly seen at the lower boundary of the continuum. The maximum energy at the zone boundaries $(0, 0, \pi/2)$ and $(0, 0, 3\pi/2)$ is about 16 meV. The intense band at the elastic position is due to incoherent elastic scattering from the sample as well as the background from the cryostat. The spin gap can also be seen to be 5.0 meV, which is consistent with the results published by Nishi *et al.* [5] at the same reciprocal point. There is a nuclear Bragg peak at $(0, 0, 2\pi)$ and obvious phonon scattering around it. It is also possible to see the spin excitations in the second zone above $(0, 0, 2\pi)$, although it is too contaminated by the phonon scattering to be useful. The double spinon scattering can also be clearly seen extending up to the upper boundary at 32.0 meV at $(0, 0, \pi)$. The origin of the intensity above 32 meV is not clear in this experiment. It may come from phonon scattering or a spin excitation of higher order. Further measurements are necessary to investigate this.

There should also be a contribution from phonon scattering in the first zone. However, the phonons are fully three dimensional which will produce asymmetric scattering that will be suppressed by the summation used when plotting the data as a function of Q_c. We can safely assume that the scattering from the phonons is negligible in the first zone, particularly at low temperatures.

Figure 1(a) shows two significant differences from the theoretical results. First, there exists a peak in intensity on the lower boundary of the continuum at the zone boundaries $(0, 0, \pi/2)$ and $(0, 0, 3\pi/2)$ and, second, there is a "rampart" or ridge of scattering surrounding a valley in the spin continuum.

It has been suggested that the intense peak at the zone boundary at 16 meV is caused by a resolution effect due to the spectroscopic technique. If this is the case, the intensity should change dramatically as the geometric configuration of the measurement changes. In a separate experiment the peak could also be seen despite the fact that the crystal was rotated by 90°.

The dispersion of the lower boundary can be fitted by employing the exact solution of the *XY* model, but with coefficients multiplied by $\pi/2$ for the 1D-HB-AF model [19]. The exchange energy $J = (J_1 + J_2)/2$ is estimated to be about 9.8 meV with $J_2/J_1 = 0.51$, which is very similar to the Nishi *et al.* results [5] of 10.4 meV. However, it conflicts with Castilla's estimation of 13.0 meV (at 150 K), used to explain

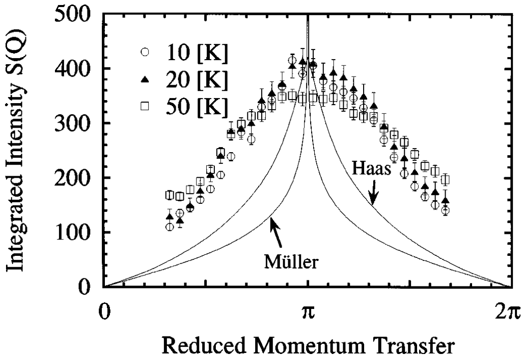

FIG. 2. The static structure factor $S(Q)$ of the spin dynamics found by integrating in energy from 3 to 32 meV in the first Brillouin zone. There is very little change with temperature. The theoretical results show a sharp rise in the intensity at the zone center that does not correspond to observed $S(Q)$.

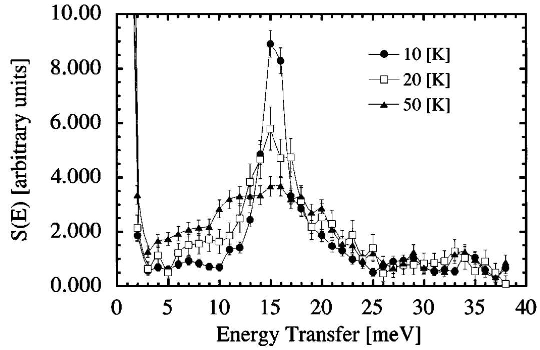

FIG. 3. A constant-Q scan of the dynamical structure factor at the zone boundary $(0, 0, \pi/2)$. A large increase in the peak intensity below T_{sP} can be seen at the lower boundary of the continuum.

the broad susceptibility [4]. Here J_1 is the interaction between the spins in a singlet pair and J_2 is the interaction between neighboring spins in different pairs.

Figure 1(b) shows the same spectrum at 50 K. The phonon scattering originating from $(0, 0, 2\pi)$ becomes significantly more intense. Surprisingly the spin continuum does not change very much and maintains its outline. However, the lower boundary broadens dramatically. This implies a large change in the dynamical spin correlation with temperature.

The static structure factor $S(Q)$ is depicted in Fig. 2. This is obtained by integrating the spectrum in energy from 3.0 to 32.0 meV within $(0, 0, 0)$ and $(0, 0, 2\pi)$. $S(Q)$ seems to conserve its shape independent of temperature and the formation of the spin singlet pairs below T_{sP}. The only observable change is in the intensity around $(0, 0, \pi)$, which is caused by the merging of the excitation spectra with the elastic line scattering as the spin gap closes. Figure 2 also shows the analytical result from the Néel states, and from a 1D-HB-AF system [19], and from the recent numerical results on spin-Peierls systems [17]. All the calculations show a sharp rise or singular pole at the zone center $(0, 0, \pi)$. However, this is not observed in these measurements.

Figure 3 shows the spectrum at the zone boundary, $(0, 0, \pi/2)$, obtained by integrating $S(Q, E)$ in the range $Q = (0, 0, \pi/2 \pm \Delta)$ with $\Delta = 0.05\pi$; i.e., it is a constant-Q scan of $S(Q, E)$. There is a large change in the intensity at the lower boundary below T_{sP} but very little in the high energy region. The sharp rise in the intensity at the zone boundary cannot be explained by quantum field theory with the bosonization method used for the 1D-HB-AF [9]. A recent Raman scattering measurement has also confirmed the presence of the sharp peak below T_{sP} in a double magnon scattering process [20]. However, it could arise from the three-dimensional effect in the spin correlation. Interestingly, this peak is reminiscent of the sharp feature in the spectral function reported by Haas and Dagotto [17], which is due to the halving of the Brillouin zone.

Figures 2 and 3 clearly show that although the dynamical spin correlation changes dramatically with temperature, the static arrangement of the spins remains the same. Moreover, most of the changes in the dynamical spin correlation occur below T_{sP} where the lattice dimerizes and the spin-singlet pairs are created.

Figure 4 shows the $S(Q, E)$ map at 300 K. Although it is clearly contaminated by the populated phonons, surprisingly the spin continuum seems to persist even

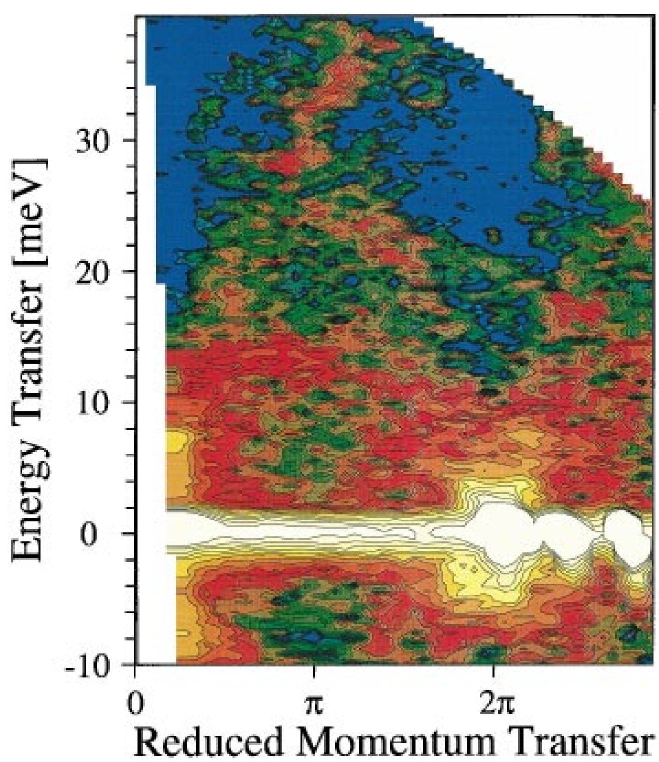

FIG. 4(color). The dynamical structure factor at 300 K. The spin continuum persists, but with the maximum reduced from 32 to 30 meV. The lower boundary has changed completely with no evidence for antiferromagnetic coupling.

though the temperature is now much greater than the coupling energy of $J = 9.8$ meV (110 K). However, its form is slightly different; it is broader and its maximum is shifted down to 30 meV. At these temperatures there is no evidence of the antiferromagnetic spin correlations at the lower boundary, although a new dispersive feature appears which bridges $(0, 0, 0)$ and $(0, 0, 2\pi)$. This could be the dispersion relation of an acoustic phonon [21]. Interestingly the shape of the spectrum of the phonon dispersion is about a half in energy of that of the broadened spin continuum.

In summary, for the first time it has been possible to observe the complete spectrum of the spin excitations in a one-dimensional Heisenberg antiferromagnet with a spin-Peierls transition. The evolution of these excitations has been studied as a function of temperature. A sharp peak is seen at the zone boundary below the spin-Peierls transition that is at variance with the current theoretical models for these systems. The spin-Peierls transition involves a strong lattice instability that results in the formation of singlet pairs. An understanding of these data may also supply important information about the spin dynamics in strongly correlated electron systems [22] as well as the high-T_c superconductors. Recently we have been made aware that a magnetic continuum has also been observed by Martin *et al.* on triple-axis spectrometers [23].

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[1] O. Kamimura *et al.*, J. Phys. Soc. Jpn. **63**, 2467 (1994); J. P. Pouget *et al.*, Phys. Rev. Lett. **72**, 4037 (1994); K. Hirota *et al.*, Phys. Rev. Lett. **73**, 736 (1994).
[2] M. Hase *et al.*, Phys. Rev. Lett. **70**, 3651 (1993).
[3] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).
[4] G. Castilla *et al.*, Phys. Rev. Lett. **75**, 1823 (1995).
[5] M. Nishi *et al.*, Phys. Rev. B **50**, 6508 (1994).
[6] Y. Endoh *et al.*, Phys. Rev. Lett. **32**, 170 (1974).
[7] D. Welz *et al.*, Phys. Rev. B **45**, 12 319 (1992).
[8] S. E. Nagler *et al.*, Phys. Rev. B **44**, 12 361 (1991).
[9] D. A. Tennant *et al.*, Phys. Rev. Lett. **70**, 4003 (1993); R. A. Cowley *et al.*, Physica (Amsterdam) **194A**, 280 (1993).
[10] S. Itoh *et al.*, Phys. Rev. Lett. **74**, 2375 (1995).
[11] K. Yamada *et al.*, J. Phys. Soc. Jpn. **64**, 2742 (1995).
[12] J. des Cloizeaux and J. J. Pearson, Phys. Rev. **128**, 2131 (1962).
[13] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
[14] L. D. Faddeev and L. A. Takhtajan, Phys. Lett. **85A**, 375 (1981).
[15] G. Müller *et al.*, Phys. Rev. B **24**, 1429 (1981).
[16] A. M. Tsvelik, Phys. Rev. B **45**, 486 (1992); J. C. Bonner and H. W. J. Blöte, Phys. Rev. B **25**, 6959 (1982).
[17] S. Haas and E. Dagotto (private communication).
[18] A. D. Taylor *et al.*, in *Proceedings of the International Collaboration on Advanced Neutron Source (ICANS-XI), 1990* (KEK Report 90-25, 1991), Vol. 2, pp. 705–710.
[19] J. C. Boner and H. W. J. Blöte, Phys. Rev. B **25**, 6959 (1982).
[20] N. Ogita *et al.* (private communication).
[21] K. Hirota *et al.*, Phys. Rev. B **52**, 15 412 (1995).
[22] G. Appeli *et al.*, Springer Ser. Solid-State Sci. **119**, 205 (1995).
[23] M. C. Martin *et al.* (private communication).