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# Neutron-scattering study on the spin-Peierls transition in a quasi-one-dimensional magnet $CuGeO_3$

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We experimentally show that in the inorganic spin-Peierls compound $CuGeO_3$ the inelastic-neutron-scattering intensity with $\Delta E=1$ meV at (0,1,0.5) exponentially decreases below $T_{SP}(=14$ K) due to the formation of the spin-Peierls gap. We also found that the magnetic excitation spectrum exhibits a pronounced energy dispersion, the intrachain and interchain exchange parameters $J_c\approx 10.4$ meV, $J_b\approx 0.1J_c$, and $J_a\approx -0.01J_c$, and the gap energy at $T=0$ K is 2.1 meV, suggesting that $J_b/J_c\approx 0.1$ is rather large compared to the organic spin-Peierls system.

Low-dimensional magnetic systems have received much research attention during recent years, both theoretically and experimentally, especially quantum spin systems. The spin-Peierls (SP) transition is one of the most attractive phenomena among them, being first discovered in the organic compound TTF-CuBDT,[1] and afterwards in several other organic compounds.[2,3]

Very recently, however, Hase, Terasaki, and Uchinokura[4] reported the existence of the SP transition in inorganic $CuGeO_3$. Their single-crystal measurements clearly indicate that the magnetic susceptibilities in $CuGeO_3$ rapidly drop to zero along all axes below the SP transition temperature $T_{SP}(=14$ K). In addition, they observed the magnetic field dependence of $T_{SP}(H)$, as well as showing $CuGeO_3$'s magnetic phase diagram to be in qualitative agreement with that of a typical organic SP system.[5] As evidence of this transition, lattice dimerization should occur, and in fact, one of the authors recently reported an observation of satellite peaks at $(0,1,\frac{1}{2})$ and $(0,1,\frac{3}{2})$ caused by dimerization of the Cu atoms.[6] However, this SP transition temperature $T_{SP}=3.8$ K is too low in comparison to other published data, and is probably due to the nonstoichiometry of oxygen. We reexamined the existence of the satellite peaks using a single crystal of $CuGeO_3$ in which $T_{SP}$ is 14 K. However, we could not find the superlattice peak at $(0,k,l+\frac{1}{2})$ in the $b$-$c$ scattering plane of $CuGeO_3$.

Very recently, however, electron diffraction,[7] x-ray and neutron scattering,[8] and subsequent neutron diffraction[9] observed the superlattice reflection at $(h+\frac{1}{2},k,l+\frac{1}{2})$ below $T_{SP}$. This fact suggests that $CuGeO_3$ is a first-discovered inorganic SP system, thereby motivating the present study in which inelastic-neutron-scattering experiments were performed on a single crystal of $CuGeO_3$ in order to further elucidate the SP transition mechanism from a magnetic point of view.

$CuGeO_3$'s crystal structure is believed to be orthorhombic $(D_{2h}^5-P_{bmm})$ at room temperature,[10] being built up by $[CuO_2]^{2-}$ linear chains in which a Cu atom is located at the center of the square of four O atoms. The single crystal ($45\times 7\times 3$ mm$^3$) was grown via the floating zone method, and inelastic-neutron-scattering experiments were performed using the Polarized Neutron Triple Axis (PONTA) and High Q Resolution (HQR) spectrometers installed at the Japan Research Reactor 3M (JRR-3M), Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. The (0,0,2) reflection of pyrolytic graphite (PG) was used for both the monochromator and analyzer, and a PG filter was placed in front or behind the sample to eliminate higher-order contamination.

For the quasi-one-dimensional SP system, the excitation dispersion spectrum is generally known to have an energy gap at $q=0$. In addition, this alternating-spin singlet state changes to a uniform state above $T_{SP}$ and the finite energy gap vanishes at the center of Brillouin zone. To observe such phenomena, we measured the temperature dependence of the neutron-scattering intensity at an energy transfer $\Delta E=1$ meV at the lower energy of the SP gap ($q=0$) using the triple axis mode with $E_i=13.7$ meV at $(0,1,\frac{1}{2})$. As shown in Fig. 1, as the temperature decreases the neutron-scattering intensity increases, reaching a maximum at about $T_{SP}=14$ K, then exponentially decreasing below $T_{SP}$ due to the formation of the SP gap. An overdamped mode occurs in the intensity profile above $T_{SP}$, and therefore, the intensity gradu-

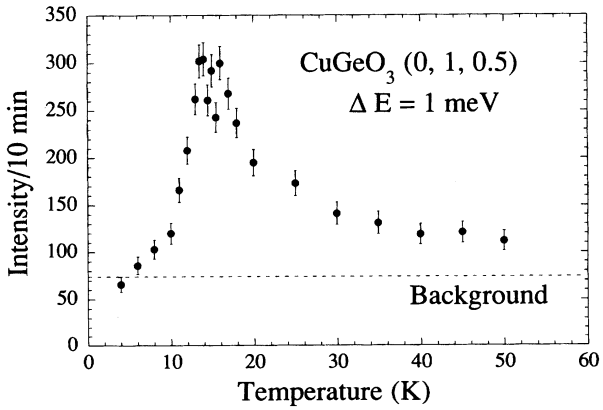


FIG. 1. The temperature dependence of the neutron-scattering intensity at $\Delta E=1$ meV at $q=0$.

 

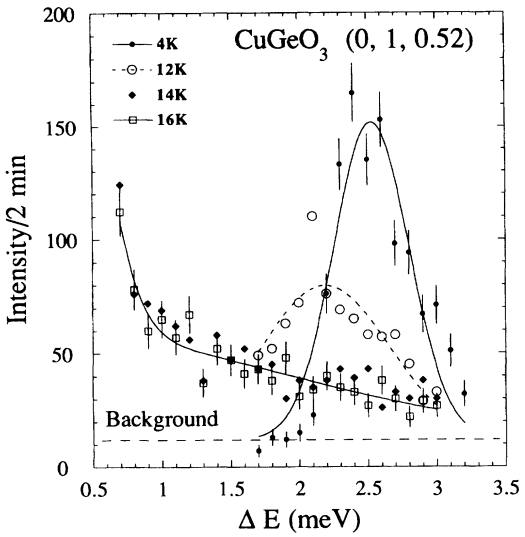


FIG. 2. Energy scan profiles of the magnetic exciton at (0,1,0.52) for various temperatures with $E_i = 13.7$ meV.

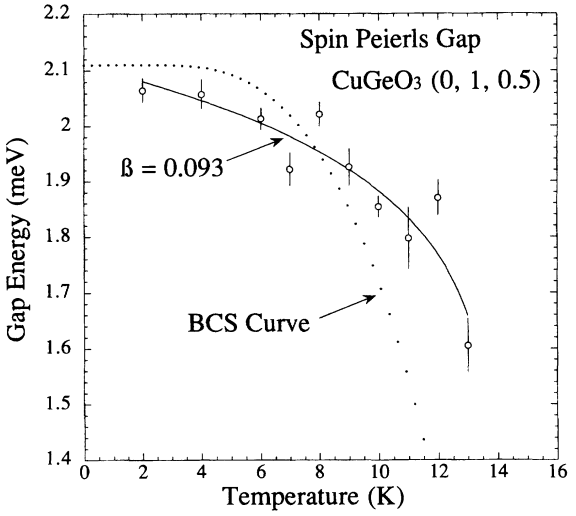


FIG. 4. The temperature dependence of the spin-Peierls gap at the zone center (0,1,0.5). Calculated results using Eq. (2) are also shown, as are those based on BCS theory.

ally decreases as temperature is increased. It should be noted that the excitation spectrum from the singlet ground state to the excited triplet state should occur below $T_{SP}$, although the resultant excitation peaks around $T = 14$ K are not spin waves in a strict sense, since no long-range magnetic order exists as that shown in the antiferromagnetic state. Thus, these propagating quasiparticles in the excited triplet state should be called "magnetic excitons" instead of magnons. The temperature dependence of the magnetic exciton profiles of $CuGeO_3$ at (0,1,0.52) is shown in Fig. 2 for $E_i = 13.7$ meV and collimator setting; open $-40'-40'-80'$, where a very sharp peak appears at 4 K. The magnetic exciton at $q = 0.02c^*$ has a wavelength 50 times that of the $c$ lattice

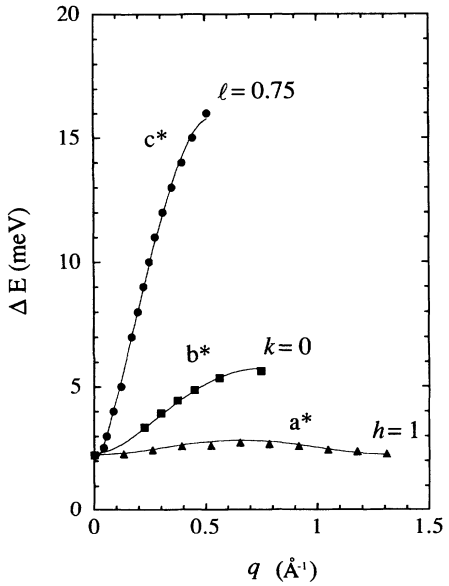


FIG. 3. The dispersion relations of the magnetic excitons in $CuGeO_3$ along each principal axis at $T = 4$ K. The solid lines indicate resultant curve fittings using the Heisenberg antiferromagnetic spin-wave formula. (0,1,0.5) is the zone center; $q = 0$.

constant. Note a broad weak peak is present at 12 K on the lower-energy side, while at 14 K the SP energy gap vanishes and the magnetic exciton energy is simultaneously overdamped. The neutron-scattering profiles between 14 and 16 K were very similar and had about a 4-meV FWHM around $\Delta E = 0$ meV.

Figure 3 shows the dispersion relations of the magnetic excitons along each principal axis ($a$, $b$, and $c$), where it is obvious from these results that (0,1,0.5) is the zone center. Since the strongest correlation energy occurs along the $c^*$ axis parallel to the direction of the $CuO_2$ chain, this confirms that $CuGeO_3$ has a one-dimensional magnetic character along this axis. Using the des Cloizeaux and Pearson formula,[11] the characteristic energy for a one-dimensional excitation is $\pi J_c/2 = 16.3$ meV. However, the intrachain exchange parameter $J_c = 10.4$ meV (120.4 K) is larger than the expected value $J_c = 7.58$ meV (88 K) obtained from magnetic susceptibility data.[4] To estimate the interchain exchange constants, we analyzed our data in terms of the Heisenberg antiferromagnetic Hamiltonian $H = \Sigma_{ij} J_{ij} \hat{S}_i \hat{S}_j$. The dispersion relation can be obtained from the Heisenberg antiferromagnetic spin-wave formula, i.e.,

$$\{E(q)\}^2 = \{(\pi/2)J_c + J_b + E_A - J_a(1-\cos 2\pi h)\}^2 - \{(\pi/2)J_c \cos 2\pi l + J_b \cos \pi k\}^2, \quad (1)$$

where $J_a$, $J_b$, and $J_c$ are, respectively, the exchange parameters along each principal axis and the uniaxial anisotropic magnetic energy $E_A$ is used to replace the SP energy gap. Consequently, the exchange energies along the $b$ ($J_b$) and $a$ axes ($J_a$) were, respectively, estimated as $J_b \approx 0.1 J_c$ and $J_a \approx -0.01 J_c$. The one-dimensionality of $CuGeO_3$ is not so pronounced as $KCuF_3$, which has a quasi-one-dimensional quantum antiferromagnetic system.[12]

The temperature variation of the SP energy gap at $(0,1,\frac{1}{2})$ is shown in Fig. 4, where the gap energy is 2.1 meV when extrapolated to 0 K. Using this energy a value of $\beta \approx 0.093$ was determined by

$$\Delta(T)=\Delta(0)(1-T/T_{SP})^{\beta}, \quad (2)$$

where $T_{SP}=14$ K. In the SP system, one-dimensional spins couple to three-dimensional lattice distortions[13]; phenomena resembling BCS theory in which conduction electrons make a singlet pair through the phonons. Therefore, to compare the SP energy gap to a superconducting one, we also show the calculated values from the BCS equation, where the energy at 0 K is normalized to 2.1 meV. The temperature dependence of $CuGeO_3$'s SP energy gap does not agree with the BCS equation and a much smaller critical exponent exists. These phenomena are caused by a one-dimensional quantum spin fluctuation in $CuGeO_3$. The equation $2\Delta(0)=3.50T_{SP}$ is very close to the BCS formula $2\Delta(0)=3.53T_{SP}$. The 2.1-meV (24.5 K) SP gap energy is consistent with the value obtained by the magnetic susceptibility experiments.[4] When the lattice dimerizes, two unequal and alternating $J$'s are produced:

$$J_{1,2}=J_c\{1\pm\delta(T)\}. \quad (3)$$

The mean-field theory gives

$$\delta(T)=\Delta(T)/pJ_c, \quad (4)$$

where $p$ is 1.637.[1] Substituting $\Delta(0)=24.5$ K and $J_c=120$ K, we got $\delta(0)=0.12$ and $J_2(0)/J_1(0)=0.78$.

Now, proof of a strong spin-phonon coupling was obtained via phonon measurements using inelastic-neutron-scattering experiments.[14] These experiments showed that the phonon mode of $CuGeO_3$ becomes very broad at energies from 5 to 30 meV, hence indicating that the phonon couples to the magnetic excitation mode. This occurs because the energy width of the phonon mode broadens, when the phonon couples to other elementary excitations.[15,16] Quite recent polarized Raman spectra experiments carried out on a single crystal of $CuGeO_3$ (Refs. 17–19) found broad vibronic bands at energies greater than 2000 $cm^{-1}$. When the incident and scattered light are polarized along the $c$ axis, newly observed peak energies below 14 K were represented to be the summation or difference between the phonon and magnetic exciton energies: 28.3(=23+5.3), 45.9(=41.2+4.7), and 101.6(=106.6−5.0) meV, where the magnetic exciton energy was 5.6 meV for $(0,0,\frac{1}{2})$ at 5 K via our inelastic-neutron-scattering measurements. Therefore, it is likely that the longitudinal acoustic phonon caused by the dimerizing motion of the Cu-Cu atoms couples to the magnetic exciton.

As was shown in Refs. 7 and 8, the superlattice reflections due to the lattice distortions appear at $(h+\frac{1}{2},k,l+\frac{1}{2})$ not at $(h,k,l+\frac{1}{2})$ for the phase difference among chains. However, we observed the divergent nature of the neutron intensity and it exponentially drops at $(0,1,\frac{1}{2})$ in this system, clearly indicating that this point is a magnetic critical wave vector. In addition, we observed the magnetic field dependence between the singlet ground state and triplet excited state in the SP phase of $CuGeO_3$,[20] showing that $(0,k,l+\frac{1}{2})$ is actually the energy minimum point of the singlet state. Therefore, we concluded that the magnetic condensation wave vector to spin singlet state was not the same as the lattice softening wave vector in $CuGeO_3$.

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