Evidence for a Singlet-Triplet Transition in Spin-Peierls System $CuGeO_3$

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The magnetic field dependence of the spin-Peierls gap in $CuGeO_3$ has been studied by means of neutron inelastic scattering. The splitting of the single gap state into three distinct excitation branches under a magnetic field can be regarded as direct evidence for the singlet-triplet transition in a spin-Peierls system.

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As one of the interesting phenomena in low-dimensional magnetic systems, the spin-Peierls (SP) transition has been attracting much attention both theoretically and experimentally. Theoretically, the nature of the ground state and the existence and properties of the SP gap in low-lying excitations have been subjects of interest [1]. Experimentally, the SP transitions have been studied so far in organic compounds such as TTF-CuBDT [2] and (MEM)-$(TCNQ)_2$ [3] as model SP systems. More recently, a new quasi-one-dimensional compound $CuGeO_3$ was discovered and has proved to be a novel inorganic SP system in several respects. Hase, Terasaki, and Uchinokura [4] discovered that the magnetic susceptibilities in the three principal directions dropped to zero below a transition temperature T_{SP} of 14 K. The crystal structure of this substance is orthorhombic (P_{bmm}) with $a = 4.81$ Å, $b = 8.47$ Å, and $c = 2.94$ Å at room temperature [5]. The superexchange interactions between the Cu^{2+} spins at $z = 0$ and $\frac{1}{2}$ are mediated by two short-bonded (1.94 Å) oxygen atoms at $z = \frac{1}{4}$ and $\frac{3}{4}$. Hence it is expected that these Cu-O_2-Cu bonds form quasi-one-dimensional antiferromagnetic (AF) chains along the c axis.

According to the basic concept of the SP transition, magnetically the spin system acquires a singlet ground state with an energy gap, and simultaneously lattice dimerization should occur. In the early stage of our study, the lattice distortion could not be detected in the b^*-c^* reciprocal lattice plane [6]; instead a spontaneous strain was observed along the b^* direction below T_{SP} [7,8]. Very recently, however, two groups [9,10] independently observed the superlattice reflection at $(h + \frac{1}{2}, k, \ell + \frac{1}{2})$ with h, k, ℓ integers originating from the lattice dimerization, confirming that $CuGeO_3$ is a typical SP system. More recently, an elastic neutron scattering study clarified the nature of this dimerization [11]. According to this study the dimerization of Cu-Cu pairs occurs along the c axis with an interatomic distance of 2.930 Å, and the separation between dimers is 2.955 Å.

The magnetic excitations in this quasi-one-dimensional system have been studied by Nishi, Fujita, and Akimitsu [6]. A gap formation in the magnetic excitations at the SP transition was clearly observed at $\mathbf{Q} = (0, 1, 0.5)$. The dispersion relations on the three principal axes were also determined. The correlation is strongest along the c axis, giving a J_c of 10.4 meV. The ratios of $J_b/J_c \approx 0.1$ and $J_a/J_c \approx -0.01$ for the two interchain exchanges were also obtained. These results indicate that the material may not be as good a one-dimensional system as was thought earlier. In fact the magnetic susceptibility above T_{SP} cannot be fitted well by the Bonner-Fisher curve for a spin-$\frac{1}{2}$ antiferromganetic chain in contrast to the known organic SP systems [2,3].

The effect of a magnetic field on the SP transition has also been a subject for theoretical interest [12]. Experimentally, the phase diagrams in T and H space were determined in the organic SP systems and compared with the theoretical predictions [13]. However, no direct observation of the SP gap as a function of magnetic field by inelastic neutron scattering was possible because large single crystals of such organic substances were not available.

In this Letter we report the results of an inelastic neutron scattering study of the magnetic excitation state in $CuGeO_3$ as a function of magnetic field up to 6 T. Performing the experiments in two different field configurations (see Fig. 1), the polarizations of the triplet modes observed under applied field are determined. This is the first direct evidence for the theoretical result that the gap in a SP system corresponds to a singlet-triplet transition.

The single crystal of $CuGeO_3$ was grown by the traveling-solvent floating-zone method with flowing O_2 gas. We used two pieces of single crystals with the sizes of 5 mm∅ × 9 mm. An inelastic neutron scattering experiment was performed using the Institute for Solid State Physics (ISSP) polarized neutron triple axis (PONTA) spectrometer installed at the JRR-3M research reactor of the Japan Atomic Energy Research Institute (JAERI) in Tokai, Japan. The incident energy of the unpolarized neutrons was fixed to be 14.7 meV from the (0,0,2) reflection of a pyrolytic graphite (PG) monochromator. In order

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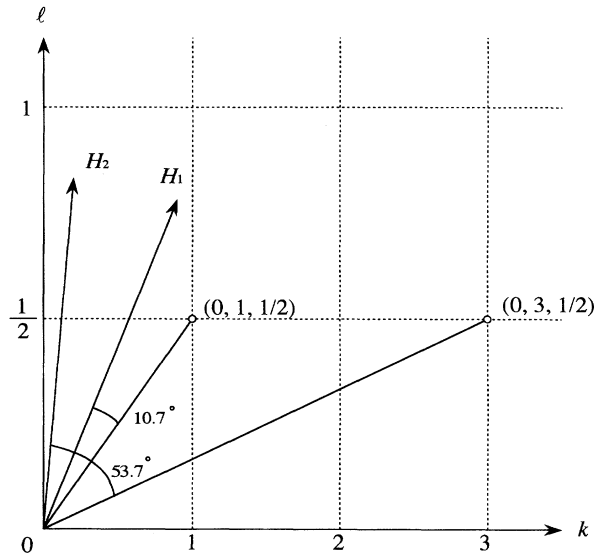

FIG. 1. The relationships between the scattering vectors and applied fields. The spectra at $(0, 1, \frac{1}{2})$ and $(0, 3, \frac{1}{2})$ were obtained at 5 K with field directions designated as H_1 and H_2, respectively.

to eliminate higher-order contaminations, a PG filter was placed in front of the monochromator. The PG (0,0,2) reflection was also used as the analyzer in the triple-axis mode with the collimations of open(40′)-20′-20′-40′. A horizontal-field superconducting magnet capable of generating fields up to 6 T was used. The sample was mounted inside an aluminum can oriented so as to give crystallographic $(0, k, \ell)$ zones in the scattering plane. Because of the limited accessible scattering angles of the horizontal field superconducting magnet, only the excitations at reciprocal points $(0, 1, \frac{1}{2})$ and $(0, 3, \frac{1}{2})$ were measured. Note that the superlattice reflections due to the lattice dimerization were observed at $(\frac{1}{2}, 1, \frac{1}{2})$ and $(\frac{1}{2}, 1, \frac{3}{2})$, etc., not at $(0, 1, \frac{1}{2})$. However, we should emphasize here that the smallest gap is obtained at $(0, 1, \frac{1}{2})$, not at $(\frac{1}{2}, 1, \frac{1}{2})$, from the dispersion curve along the a^* axis [6].

The relationships between the scattering vectors and the directions of the applied fields for these two configurations designated as H_1 and H_2, respectively, are depicted in Fig. 1. These two configurations were chosen such that in H_1 the magnetic field direction is as parallel as possible to the scattering vector and in H_2 as perpendicular as possible to the scattering vector, at the same time allowing the energy scan up to ~3.7 meV energy transfer at these reciprocal points within the limited windows of the magnet. The angles between the magnetic field directions and the scattering vectors are $\alpha = 10.7°$ ($\sin^2 10.7° = 0.034$) and 53.7° ($\sin^2 53.7° = 0.650$) for H_1 and H_2 configurations, respectively. Because of the selection rule for magnetic neutron scattering, the cross section of the components of magnetic fluctuations can be seen in these configurations as

$$(1 + \cos^2\alpha)\langle M_\perp M_\perp\rangle + (\sin^2\alpha)\langle M_\parallel M_\parallel\rangle, \quad (1)$$

where $\langle M_\perp M_\perp\rangle$ and $\langle M_\parallel M_\parallel\rangle$ denote magnetic fluctuations perpendicular and parallel to the applied magnetic field, respectively. Inserting the above values for the angles α, we obtained

$$(1 + 0.966)\langle M_\perp M_\perp\rangle + 0.034\langle M_\parallel M_\parallel\rangle \quad (2)$$

for the H_1 configuration and

$$(1 + 0.350)\langle M_\perp M_\perp\rangle + 0.650\langle M_\parallel M_\parallel\rangle \quad (3)$$

for the H_2 configuration. The spectra in the H_1 configuration at $(0, 1, \frac{1}{2})$ under applied fields of 0, 1.5, 3.2, 4.5, and 6 T at 5 K are shown in Fig. 2. The value of the energy gap at zero field is 2.0 ± 0.1 meV, in agreement with previous data [6]. The splitting of this single gap into upper and lower energies in the applied field can be clearly observed.

Figure 3 shows the spectra in the H_2 configuration at $(0, 3, \frac{1}{2})$ under applied fields of 0 and 6 T at 5 K. In contrast to the H_1 configuration the development of a three-peak structure under applied field of 6 T is obvious.

In the H_1 configuration (Fig. 2), the scattering vector is almost parallel to the magnetic field ($\sin^2 10.7° = 0.034$); thus only $\langle M_\perp M_\perp\rangle$ components are observed and the $\langle M_\parallel M_\parallel\rangle$ component associated with the longitudinal spin fluctuation is not observed. On the other hand, in H_2 configuration (Fig. 3) we can see both the $\langle M_\parallel M_\parallel\rangle$ and $\langle M_\perp M_\perp\rangle$ components of the magnetic excitations at $(0, 3, \frac{1}{2})$. The appearance of a triplet-peak structure under a magnetic field clearly demonstrates the spin excitation mode in a threefold degenerate state.

Figure 4 depicts the field dependence of the energy positions of the observed gap energies as obtained from the Gaussian fits. It can be inferred that the field dependence of the energies is linear with a slope of ±0.12 meV/T and that the energy splittings at $(0, 1, \frac{1}{2})$ and $(0, 3, \frac{1}{2})$ are identical. This linear dependence can be well fitted by the equation $\Delta E = \Delta E(0) \pm g\mu_B H$,

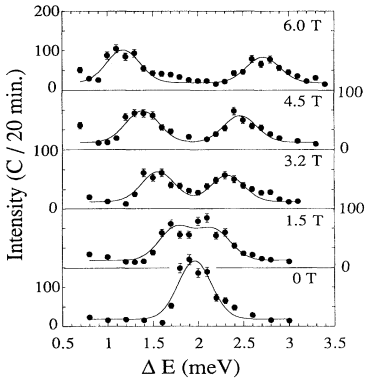

FIG. 2. Constant-Q spectra at $(0, 1, \frac{1}{2})$ at 5 K under the magnetic fields 0, 1.5, 3.2, 4.5, and 6.0 T, respectively (H_1 configuration).

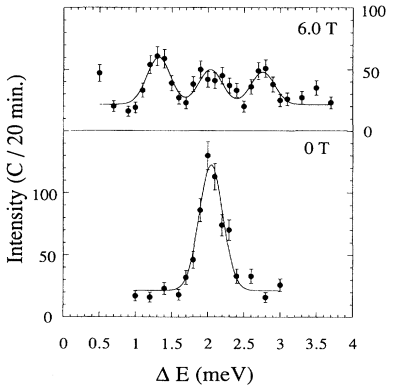

FIG. 3. Constant-Q spectra at $(0, 3, \frac{1}{2})$ at 5 K under magnetic fields of 0 and 6 T, respectively (H_2 configuration).

where the g value is 2.1. From the magnetization measurements [14], the critical field H_c at which the SP phase disappears and the magnetic triplet phase appears is about 13 T. However, if the data for the lower energy peak are extrapolated, as in the inset of Fig. 4, the field for which $\Delta E = 0$ is 15 T. This discrepancy may be explained by the theoretical prediction that the transition from the SP state to a magnetic state may be of the first order [15]. This should be confirmed by an experiment under higher magnetic field.

The fit results for the intensities of upper and lower energy peaks in Fig. 3 compared with those of Fig. 2 indicate that the intensities of these peaks in both configurations are equal, if one considers the known magnetic form factor for Cu^{2+} and the factor due to the magnetic selection rule as described above. This means that the intensities of $\langle M_\perp M_\perp \rangle$ observed in both configurations are the same.

Comparing the intensities of $\langle M_\parallel M_\parallel \rangle$ and $\langle M_\perp M_\perp \rangle$ at $(0, 3, \frac{1}{2})$ and 6 T, where both components are visible at the same time, it can be inferred from Eq. (3) that the intensity associated with $\langle M_\parallel M_\parallel \rangle$ is identical with the intensity associated with $\langle M_\perp M_\perp \rangle$.

All these results underline the isotropic character of the gap mode. This is consistent with the susceptibility measurements under applied fields by Hase, Terasaki, and Uchinokura [4], i.e., the Hamiltonian describing the magnetic system is very isotropic. Considering this isotropic nature, the splitting of the energy gap into three distinct levels under an applied field suggests that this is an excitonlike transition from a nonmagnetic singlet ground state to the magnetic triplet states in a SP system.

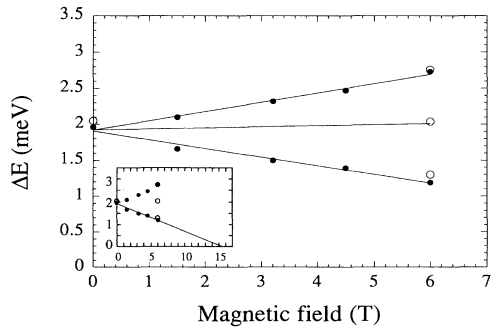

FIG. 4. Energy gap vs magnetic field at $(0, 1, \frac{1}{2})$ (closed circles) and $(0, 3, \frac{1}{2})$ (open circles). Inset: Linear extrapolation of the lowest energy branch to $\Delta E = 0$.

We note here that the field dependence of a gap due to a single-site anisotropy term of the Hamiltonian in a classically ordered AF system would look different. On the other hand, there is a class of AF systems which show nearly the same field dependence of the gap mode, namely, Haldane systems with $S = 1$. In the two typical Haldane systems NENP [16] and $CsNiCl_3$ [17], $\langle M_\perp M_\perp \rangle$ fluctuations show Zeeman splitting with a slope of $\sim$ 0.12 meV/T, while the $\langle M_\parallel M_\parallel \rangle$ mode remains unchanged. This similarity may be understood from the following physical picture. In a SP system we have a static singlet formation of the neighboring $S = \frac{1}{2}$ as a result of a static dimerization of the lattice, indicated by the appearance of superlattice peaks. According to one theoretical picture of a Haldane $S = 1$ system, namely, the valence bond solid (VBS) proposed by Affleck *et al.* [18], the individual $S = 1$ spins are subdivided into two fictitious $S = \frac{1}{2}$ spins, and the two neighboring $S = \frac{1}{2}$ spins then form a singlet pair (valence bond). Since there is no static dimerization involved in this picture, one might think of a dynamical singlet formation in this case. The above observation of the field dependence of the gap mode in SP and Haldane systems, therefore, strongly supports the static singlet formation in SP systems on one hand and the dynamical singlet formation in the $S = 1$ Haldane system on the other.

While preparing this manuscript, we learned that the recent ESR result under applied magnetic fields up to 14 T by Brill *et al.* [19] could be explained by a magnetic transition from a Zeeman splitting of the $S = 1$ magnetic triplet state, in qualitative agreement with the result presented here.

To summarize, we report direct evidence for the singlet-triplet transition in a SP system $CuGeO_3$ by inelastic neutron scattering under an applied field. The isotropic nature of these excitations is clearly demonstrated, supporting the excitonic description of the transitions from the singlet ground state to an excited triplet state.

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