Evidence of a spin-Peierls distortion in the quasi-one-dimensional magnetic compound CuGeO$_3$

LETTER TO THE EDITOR

Evidence of a spin–Peierls distortion in the quasi-one-dimensional magnetic compound CuGeO₃

Masakazu Nishi

The Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

Abstract. Neutron diffraction experiments were carried out on an inorganic quasi-one-dimensional magnet with spin $\frac{1}{2}$, CuGeO₃, and showed satellite peaks arising due to the dimerization of Cu atoms. Displaying a spin–Peierls transition, Cu ions with spin $\frac{1}{2}$ were found to reach a singlet ground state having alternating displacements between Cu atoms. Taking the shift of a Cu atom as an order parameter, the critical exponent β becomes 0.5 and the shift resulting from dimerization along the c axis is about 1% of the lattice constant c at 2.7 K.

The spin–Peierls transition is a kind of magneto-elastic transition occurring in a few quasi-one-dimensional (Q1D) insulating systems, initially discovered in the organic compound TTF-CuBDT (Bray *et al* 1975). Since the discovery, several other organic compounds undergoing such a transition have been observed (Huizinga *et al* 1979, Schwerdtfeger *et al* 1982), whereas recently Hase *et al* (1993) reported on the magnetic susceptibility of the inorganic material CuGeO₃ which, surprisingly, clearly exhibits the characteristic properties of the spin–Peierls transition at $T_{SP} = 14$ K. They also measured the magnetic field dependence of the phase transition temperature $T_{SP}(H)$ of polycrystalline CuGeO₃.

This particular transition does not occur in the majority of Q1D antiferromagnets, with the necessary conditions to produce it being as follows (Jacobs *et al* 1976): (i) a one-dimensional material is most suitable; (ii) the material must be an insulator, not a metal; (iii) a spin quantum number of $\frac{1}{2}$ is required; (iv) an antiferromagnetic intra-chain exchange constant is necessary; and (v) the intra-chain exchange interaction must be of the isotropic Heisenberg type. As a result of the spin–Peierls transition, the dimerization of Cu atoms must occur and a pair of Cu atoms spins form the single ground state.

In this letter, neutron diffraction is employed to measure the lattice distortion in single-crystalline CuGeO₃, where satellite reflections corresponding to twice the period were observed along the c axis.

Briefly, powders of CuO (99.99% pure, Rare Metallic Co. Ltd, Tokyo) and GeO₂ (99.999% pure, Furuuchi Chemical Co. Ltd, Tokyo) were stoichiometrically mixed and the resultant water removed in a vacuum for about 12 h at 250 °C. Samples were mounted in a quartz vacuum chamber and placed in a furnace that was heated up to 1100 °C then held for 48 h, followed by gradual cooling to room temperature. Numerous needle-like single crystals were grown in the turquoise-blue powder, which did not contain any impurities as confirmed by powder x-ray diffraction. The largest single crystal was $2 \times 3 \times 8$ mm³, and it was used for the neutron diffraction experiment, carried out with the polarized neutron triple-axis (PONTA) spectrometer and high-Q-resolution (HQR) spectrometer installed at the Japan

Research Reactor-3M (JRR-3M) at the Japan Atomic Energy Research Institute (JAERI) (Tokai, Japan). Experimental conditions at the PONTA spectrometer were as follows: an incident neutron energy of E_i = 14.77 meV, a wavelength λ = 2.353 Å and collimation set at 40'–40'–40'–40'. The sample was mounted in a pumped He cryostat. To decrease the half-λ contamination, pyrolitic graphite (PG) filters were placed in front of the monochromator and also between the sample and the analyser, decreasing the half-λ intensity to 10^{-6}. The HQR spectrometer was used in the double-axis mode with E_i = 13.84 meV, λ = 2.431 Å, and collimation set at open–open–40'. A PG filter was placed between the monochromator and the sample to reduce the half-λ contamination to less than 10^{-3}. The same cryostat was employed.

The crystal structure of $CuGeO_3$ is orthorhombic (D_{2h}^5—*Pbmm*) (Völlenkle *et al* 1967) built up of $[GeO_3]$ and $[CuO_2]$ chains in which a Cu atom is located at the centre of a square of four O atoms. If dimerization occurs, the unit cell doubles along the chain direction and a new satellite peak should appear at l = 0.5. However, in the neutron diffraction experiment carried out with the PONTA spectrometer in the $(0, k, l)$ scattering plane, a satellite peak was observed at the superlattice position $(0, 1, 0.5)$ as shown in figure 1, instead of $(0, 0, 0.5)$. This resultant discrepancy indicates that the dimerization phase is out of phase by π between the two $[CuO_2]$ chains along the b axis. It should be noted that the background intensities at T = 2.7 and 7.3 K are markedly different, a behaviour indicating the long-range order is imperfect even at T = 2.7 K $(1 - T/T_{SP} \simeq 0.3)$.
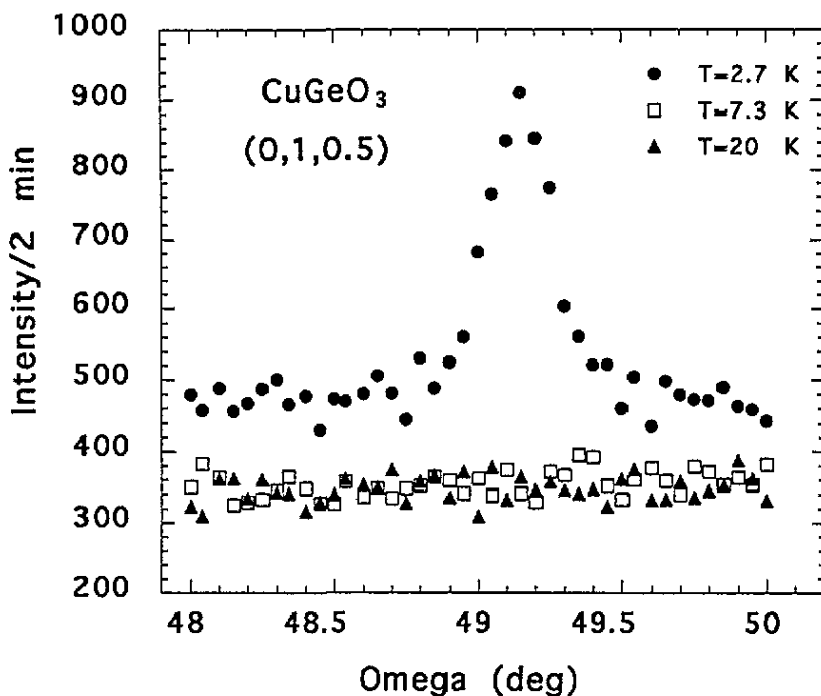

Figure 1. Satellite peak at the superlattice position $(0, 1, 0.5)$ in single-crystal $CuGeO_3$ as observed with the PONTA spectrometer.

Figure 2 shows the temperature dependence of the $(0, 1, 0.5)$ peak intensity measured with the HQR spectrometer, where a linear relation is indicated by the straight-line fit to

the observed data from 2.7 to 3.7 K. The intensity of the satellite peak is proportional to the square of the shift of the Cu atom when it is taken as an order parameter; hence the critical exponent β becomes 0.5. Since no hysteresis was evident at the spin–Peierls transition temperature $T_{SP} = 3.8$ K (data not shown), when this fact is taken together with the presence of strong diffuse scattering at 2.7 K, a second-order transition is concluded to have occurred.
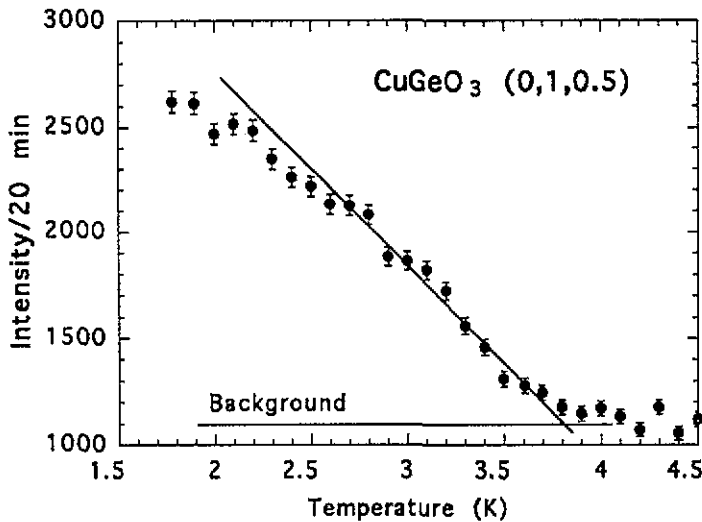

Figure 2. Temperature dependence of the peak intensity at the superlattice position (0, 1, 0.5) in single-crystal CuGeO$_3$ as observed with the HQR spectrometer.

Although the neutron polarization analysis method is generally considered as the best way to determine whether Bragg peaks have a magnetic or nuclear origin, the PONTA spectrometer is not equipped to perform polarization analysis on a sample below 4 K. Consequently, attention is focused on the (0, 1, 0.5) and (0, 1, 1.5) satellite peaks as observed by unpolarized neutron scattering, and their corresponding integrated intensity ratio $R = 0.856$ is given in table 1. In the case of antiferromagnetic–nuclear peaks, when the spin of the Cu atom is pointed in an arbitrary direction that is not along a principal axis, then four domains exist in the orthorhombic crystal symmetry of CuGeO$_3$. If we postulate a simple model in which the four domains are equally distributed, then the calculated R value would sinusoidally vary with changes in the angle between the b and c axes, and have a maximum value when the spin of the Cu atom is along the b axis and a minimum value along the c axis. However, because the maximum calculated R value is less than half that observed, given in table 1, such an antiferromagnetic model does not correspond with the experimental results.

Furthermore, the temperature dependence of the (0, 1, 0.5) peak intensity (figure 2) is remarkably different from the square of the Brillouin function that is often observed in three-dimensional antiferromagnetic ordering. The combination of these results strongly suggests that the two satellite peaks are actually nuclear peaks coming from the dimerization of the Cu atoms. In the dimerized state, their calculated intensity ratio is 1.28—a value calculated by considering only the displacement of the Cu atoms, although the position of the other O and Ge atoms will be influenced by the dimerization such that the structure factors are

Table 1. Observed integrated intensities of the (0, 1, 0.5) and (0, 1, 1.5) satellite peaks of $CuGeO_3$ and their corresponding ratio, and calculated data assuming an antiferromagnetic structure in which the Cu atom spins are aligned along each axis.

	Integrated intensity		
	(0, 1, 1.5)	(0, 1, 0.5)	Ratio
Observed	2216±144	2588±139	0.856±0.102
a	0.5076	2.1245	0.2389
b	0.4817	1.4316	0.3365
c	0.0259	0.6929	0.0374

altered below T_{SP}. When we correspondingly compare the (0, 1, 0.5) and (0, 2, 1) integral intensities, the displacement of the Cu atom in the orthorhombic structure is calculated to be about 1% of the lattice constant c (2.941 Å) at $T = 2.7$ K.

Meanwhile, a problem remains in that the spin–Peierls transition temperature of $T_{SP} = 3.8$ K is different from that of $T_{SP} = 14$ K obtained by Hase *et al* (1993). Nevertheless, the value of $T_{SP} = 3.8$ K was confirmed here since the magnetic susceptibility suddenly decreased when the temperature was lowered below 3.8 K, thereby indicating an inherent difference in the nature of the T_{SP} value of $CuGeO_3$, which may be due to the preparation method, i.e. use of a quartz vacuum chamber instead of an air atmosphere. It is hypothesized that a single crystal growing in a powder compound may acquire a vacancy, or that a disorganization possibly occurred in the O atoms. To elucidate this question, we are currently investigating the dynamics of the phonon and magnetic exciton of a bulk $CuGeO_3$ sample via neutron inelastic scattering experiments.

In conclusion, in a single crystal of the QID magnetic compound $CuGeO_3$, neutron diffraction experiments showed new satellite peaks along the c axis having reflections corresponding to twice the period. These peaks cannot be explained as those produced by an antiferromagnetic structure, and instead are suggested to come from the dimerization of the Cu atoms. Subsequent crystal structural analysis of the $CuGeO_3$ sample proved this phase transition to be a spin–Peierls transition that Hase *et al* (1993) speculated to exist on the basis of magnetic susceptibility measurements.

References

Bray J W, Hart H R, Interrante L V Jr, Jacobs I S, Kasper J S, Watkins G D, Wee S H and Bonner J C 1975 *Phys. Rev. Lett.* **35** 744–7
Hase M, Terasaki I and Uchinokura K 1993 *Phys. Rev. Lett.* **70** 3651–4
Huizinga S, Kommandeur J, Sawatzky G A, Thole B T, Kopinga K, de Jonge W J M and Roos J 1979 *Phys. Rev.* B **19** 4723–32
Jacobs I S, Bray J W, Hart H R, Interrante L V Jr, Kasper J S, Watkins G D, Prober D E and Bonner J C 1976 *Phys. Rev.* B **14** 3036–51
Schwerdtfeger C F, Oostra S and Sawatzky G A 1982 *Phys. Rev.* B **25** 1786–90
Völlenkle H, Wittman A and Nowotny H 1967 *Monatsh. Chem.* **98** 1352–7