Dimerization of $\mathrm{CuGeO_3}$ in the Spin-Peierls State

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The dimerization of the Cu ions in the spin-Peierls state of $\mathrm{CuGeO_3}$ below 14 K has been determined by neutron-diffraction measurements. In addition to superlattice reflections with indices $h/2\,k\,l/2$ (h,k,l, all odd) recently observed in electron and x-ray diffraction studies, we also found peaks for which k = even. Oxygen displacements in the a-b plane of about 0.01 Å, accompanied by comparable shifts of the Cu ions along the chain direction c, can be related to the dimerized spin state in a natural fashion.

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Since Hase, Terasaki, and Uchinokura [1] reported the first example of spin-Peierls transition in an inorganic linear $\mathrm{Cu^{2+}}$ ($S = \frac{1}{2}$) chain compound, $\mathrm{CuGeO_3}$, a large number of experiments of various types have been performed [2–8]. The existence of a finite energy gap for the spin-singlet to -triplet excitation, inferred from the disappearance of the magnetic susceptibilities below $T_c = 14\,\mathrm{K}$, has been directly confirmed by Nishi, Fujita, and Akimitsu [9] using inelastic neutron scattering. During a search for the mechanism for the transition into this spin-singlet state, Lorenzo *et al.* [10] discovered a remarkably soft longitudinal acoustic phonon branch along the b axis, perpendicular to the magnetic chains, which run parallel to the c axis. This branch is so low in energy that it actually lies below the transverse acoustic branch in the same direction. In addition, their neutron-diffraction measurements showed a spontaneous strain Δb appearing along the b axis below T_c. However, lattice dimerization, which is one of the most prominent features of the spin-Peierls state, has not been observed in spite of extensive surveys. Very recently, Kamimura *et al.* [11] found superlattice reflections with indices $h/2\,k\,l/2$ (h,k,l all odd) below T_c by electron diffraction. Superlattice reflections have also been detected in an x-ray diffraction study by Pouget and co-workers [12]. These results imply a doubling of the unit cell in the a and c directions, which may result from lattice dimerization.

In order to study the nature of the atomic displacements below T_c, we surveyed and measured superlattice reflections by neutron diffraction, for which the scattering power of oxygen is comparable to that of copper and germanium. Measurements were performed on the triple-axis spectrometer H8 located in the High Flux Beam Reactor at Brookhaven National Laboratory. The single crystals used for the present study were made from a batch grown by the floating zone method. They have dimensions about $2 \times 4 \times 3$ and $5 \times 2 \times 4\ \mathrm{mm^3}$, and are of exceptionally high quality with a mosaic width of less than 3 min of arc. The lattice parameters at room temperature are a = 4.81 Å, b = 8.47 Å, and c = 2.941 Å, and the space group *Pbmm (Pmma* in standard orientation) [13]. Each sample was mounted inside an aluminum can oriented so as to give crystallographic (hkh) or $(h2kk)$ zones, respectively. The sample can was filled with helium gas to improve heat transfer and attached to the cold finger of a closed-cycle He cryostat. The incident energy was selected to be 14.7 meV from the (0 0 2) reflection of a pyrolytic graphite (PG) monochromator. In order to eliminate higher order harmonics, PG filters were placed in front of the sample and the analyzer, which was also PG (0 0 2). Typical collimations consisted of 40′-40′-S-80′-80′, in sequence from reactor to analyzer. In order to measure the temperature dependence of the lattice constant, we remounted one of the crystals in a crystallographic ($0\ k\ l$) zone. The resolution was improved by tightening the collimation and using a PG (0 0 4) or Ge (2 2 0) analyzer.

A highly significant result of the present experiment was the observation of superlattice reflections ($h/2\,k\,l/2$) with *k even*, comparable in intensity to those with k odd previously observed in the electron and x-ray diffraction studies. Figure 1 shows the temperature dependence of the intensities of the superlattice reflections ($\frac{1}{2}5\frac{1}{2}$) and ($\frac{1}{2}\,6\,\frac{1}{2}$). With increasing temperature, these intensities drop continuously and vanish at $T_c = 14.2\,\mathrm{K}$. In spite of careful searches, we found no diffuse scattering above T_c, as shown in the inset of Fig. 1. The observed values of the structure factor, F_{obs}^2, for 14 superlattice reflections are shown in Table I, together with values for several fundamental peaks; they are scaled in such a way that the largest F_{obs}^2 at (0 4 0) is equal to 1000. It is unlikely that the superlattice reflections are strongly affected by multiple scattering, since this would involve at

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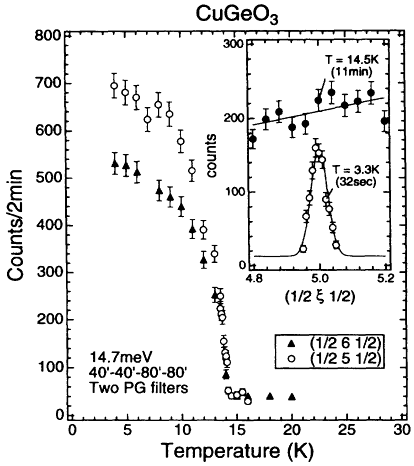

FIG. 1. Temperature dependence of the superlattice reflections at $(\frac{1}{2}\,5\,\frac{1}{2})$ and $(\frac{1}{2}\,6\,\frac{1}{2})$ on heating. Peak profiles of the $(\frac{1}{2}\,5\,\frac{1}{2})$ reflection at 3.3 and 14.5 K ($T_c = 14.2$ K) are shown in the inset.

TABLE I. Observed and calculated structure factors for the low temperature structure of $CuGeO_3$. Reflections are indexed in terms of the unit cell of the high-temperature structure. Structure factors are scaled so that the largest value at (0 4 0) is equal to 1000. The Debye-Waller thermal parameters were assumed to be zero. Scattering lengths for Cu, Ge, and O were taken as 0.7718×10^{-12}, 0.8193×10^{-12}, and 0.5805×10^{-12} cm, respectively.

$(h\,k\,l)$	$F^2_{\rm obs} \pm \sigma$	$F^2_{\rm calc}$	
		Neutron	X ray
$(h\,k\,h)$ zone			
(0 4 0)	1000 ± 3.3	1000	1000
(1 0 1)	294 ± 2.5	310	731
$(\frac{1}{2}\,0\,\frac{1}{2})$	0.01 ± 0.01	0.000	0.000
$(\frac{1}{2}\,1\,\frac{1}{2})$	0.03 ± 0.01	0.015	0.024
$(\frac{1}{2}\,2\,\frac{1}{2})$	0.01 ± 0.02	0.000	0.000
$(\frac{1}{2}\,3\,\frac{1}{2})$	0.29 ± 0.03	0.314	0.085
$(\frac{1}{2}\,4\,\frac{1}{2})$	0.13 ± 0.04	0.114	0.010
$(\frac{1}{2}\,5\,\frac{1}{2})$	0.42 ± 0.07	0.318	0.048
$(\frac{1}{2}\,6\,\frac{1}{2})$	0.47 ± 0.08	0.482	0.020
$(\frac{3}{2}\,0\,\frac{3}{2})$	0.02 ± 0.03	0.000	0.000
$(\frac{3}{2}\,1\,\frac{3}{2})$	0.67 ± 0.07	0.635	0.197
$(\frac{3}{2}\,2\,\frac{3}{2})$	0.03 ± 0.05	0.120	0.007
$(\frac{3}{2}\,4\,\frac{3}{2})$	0.03 ± 0.05	0.021	0.001
$(h\,2k\,k)$ zone			
(1 0 0)	7.45 ± 0.07	6.81	3.10
(3 0 0)	70.2 ± 0.40	75.7	84.8
(1 2 1)	36.7 ± 0.25	42.4	2.38
$(\frac{1}{2}\,3\,\frac{3}{2})$	0.01 ± 0.01	0.000	0.053
$(\frac{3}{2}\,1\,\frac{1}{2})$	0.07 ± 0.01	0.066	0.000
$(\frac{5}{2}\,1\,\frac{1}{2})$	0.05 ± 0.01	0.057	0.023

least one other $(h/2\,k\,l/2)$ reflection, which is already very weak. Thus, it is reasonable to assume that the error in the measured intensities of the superlattice reflections due to multiple scattering is less than 10%. In fact, the small size of the single crystal is actually a definite advantage in reducing such efforts.

As noted above, the room temperature structure of $CuGeO_3$ has *Pbmm* symmetry, with atoms in the following positions: Cu in 2(c) at $\frac{1}{2},0,0$; Ge in 2(f) at $x,\frac{1}{4},\frac{1}{2}$ ($x = 0.0743$); O(1) in 2(e) at $x,\frac{1}{4},0$ ($x = 0.8700$); and O(2) in 4(j) at $x,y,\frac{1}{2}$ ($x = 0.2813, y = 0.0838$) [13]. From the trend in $F^2_{\rm obs}$ for $(\frac{1}{2}\,k\,\frac{1}{2})$ reflections in Table I, it is clear that there must be a significant displacement Δy in the y parameter of O(2), since the y parameters of the other atoms are constrained to special positions. There are then four plausible models for the signs of the relative shifts Δy of the O(2) atoms in the original unit cell as listed in Table II. The shifts of atoms in the low-temperature cell which are related by a translation of a or c in the original unit cell are assumed to be opposite in sense to those in Table II. Structure factor calculations for $(\frac{1}{2}\,k\,\frac{1}{2})$ reflections for the four models in Table II reveal that only model II is qualitatively consistent with the trends in $F^2_{\rm obs}$ in Table I. In this case, the mirror symmetry perpendicular to b is destroyed, and the highest symmetry space group possible for the doubled cell is *Bbcm* (*Cmca* in standard orientation), which permits shifts of Δz for Cu, Δx and Δy for Ge and O(2), and Δx for O(1). The last shift makes no contribution to the superlattice reflections. A weighted least-squares fit of the calculated structure factors $F^2_{\rm calc}$ to the 14 values of $F^2_{\rm obs}$ in Table I based on this model with weights assigned as $1/\sigma^2$ yielded significant values for only three of these displacements; Cu: $\Delta z = -0.00139(10)$, O(2): $\Delta x = 0.00104(5)$ and O(2): $\Delta y = 0.00125(6)$, where the numbers in parentheses are estimated standard deviations. The corresponding χ^2 goodness-of-fit index was 1.1. The results are summarized in Table III. The observed and calculated values of F^2 are listed in Table I and the displacements are illustrated schematically in Fig. . Because of the loss of mirror symmetry, the O(2) atoms actually divide into two inequivalent sets in the *Bbcm* cell, but attempts to refine independent shifts by relaxing the translational constraints imposed above were unsuccessful.

The most striking feature of this structure is the dimerization of Cu-Cu pairs along the c axis with an interatomic separation of 2.926 Å, compared to 2.942 Å in the high-temperature structure. The Cu displacements in neighboring chains are out of phase and the separation between dimers is 2.959 Å. This dimerization is accom-

TABLE II. Possible models for the signs of the relative shifts Δy of the O(2) atoms in the low-temperature structure of $CuGeO_3$. The atomic coordinates in a and c directions are halved with respect to those in the fundamental cell to allow for doubling of these axes.

O(2) atoms			Δy I	II	III	IV
x	y	$\frac{1}{4}$	+	+	+	+
x	$\frac{1}{2} - y$	$\frac{1}{4}$	+	+	−	−
$\frac{1}{2} - x$	$\frac{1}{2} + y$	$\frac{1}{4}$	+	−	−	+
$\frac{1}{2} - x$	$-y$	$\frac{1}{4}$	+	−	+	−

panied by a shift in the position of the O(2) atoms in the a-b plane, with out-of-phase motions along each of three principal directions. Since the magnetic interaction between two Cu ions in the c direction is mainly due to a superexchange interaction through O(2), it is expected to be very sensitive to the configuration of Cu-O(2)-Cu bonds. Therefore, we can plausibly relate the dimerized spin state to our structural model of $CuGeO_3$ below T_c, as depicted in Fig. .

Based on the atomic displacements in Table III, we have calculated the intensities of reflections in the case of x-ray diffraction, which involves atomic form factors which are essentially proportional to the square of the number of electrons. The results shown in Table I are consistent with the electron-diffraction observation [11]; the intensities are weak at $h/2\,k\,l/2$ (h, l odd, k even). This is because x-ray and electron diffraction see mainly the Cu displacements which make no contribution to reflections with k even.

TABLE III. Atomic displacements in the low-temperature structure of $CuGeO_3$ derived from a least-squares fit of $F^2_{\rm obs}$ and $F^2_{\rm calc}$ for 14 superlattice reflections of type $\frac{1}{2}\,k\,\frac{1}{2}$ based on model II in Table II. Values are given as fractions of the edges of the doubled unit cell ($a' = 2a, c' = 2c$). Numerals in parentheses are estimated standard deviations. The χ^2 goodness-of-fit index was 1.1. The displacements are subject to a small scaling error estimated to be less than 5% due to uncertainty in the factor used to scale the superlattice and fundamental intensities.

Atomic displacement		Value
Cu	Δz	−0.00139(10)
O(2)	Δx	0.00104(5)
O(2)	Δy	0.00125(6)

The present diffraction study has provided a simple dimerization picture for $CuGeO_3$, accomplished by a straightforward structure refinement without any *a priori* physical assumption. It is gratifying to see that the structure determined is close to the simplest dimerization model one can imagine for this compound. Several important questions remain to be resolved for this fascinating compound. First of all, the magnetic excitations reported by Nishi *et al.* [2] have a minimum energy

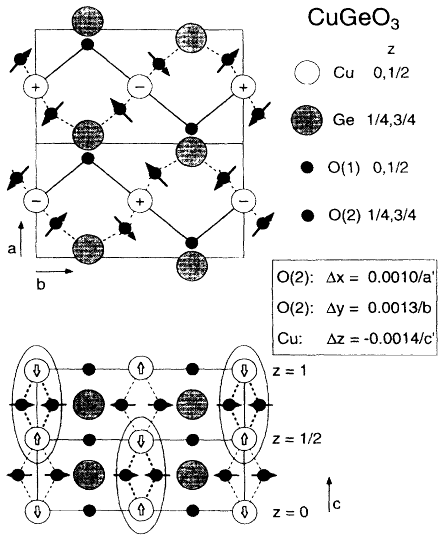

FIG. 2. Schematic representation of the low-temperature structure for $CuGeO_3$ in the spin-Peierls state. The rectangles show the unit cell for the high-temperature structure. The cell becomes doubled in a and c directions below T_c. Arrows and signs indicate the directions of displacements. For clarity, atomic displacements are drawn 10 times larger than in reality.

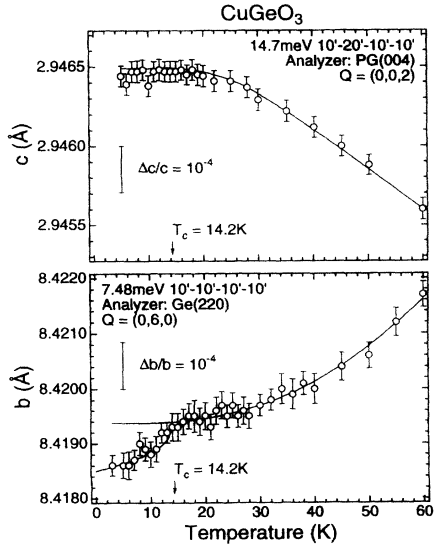

FIG. 3. Temperature dependence of the b and c lattice constants. The lattice undergoes a contraction along the b axis at T_c = 14.2 K. The solid line is a model calculation and the dotted line is a fit to the spontaneous strain Δb.

at $(0\ 1\ \frac{1}{2})$ and not at $(\frac{1}{2}\ 1\ \frac{1}{2})$, corresponding to a superlattice reflection. We expect this point will be clarified soon in theoretical studies, since the basic atomic shifts are now established. A second important question is the relation between the dimerization, characterized by $(\frac{1}{2}\ k\ \frac{1}{2})$ type superlattice peaks, and the soft longitudinal mode along the b axis discovered by Lorenzo *et al.* [10]. Yet another issue is how the spontaneous strain Δb below T_c is related to the atomic shift. This is currently being addressed in a high-resolution x-ray study by Harris *et al.* [14] intended to determine whether Δb is simply an induced strain resulting from the atomic shift. In this respect, it is interesting to note that the c axis parameter shows no anomaly at T_c, as shown in Fig. 3, in spite of the Cu dimerization along the c direction. This is in contrast to the sharp change in the b axis parameter, which corresponds to the spontaneous strain Δb. This may be a key question for a complete understanding of the magnetism in $CuGeO_3$.

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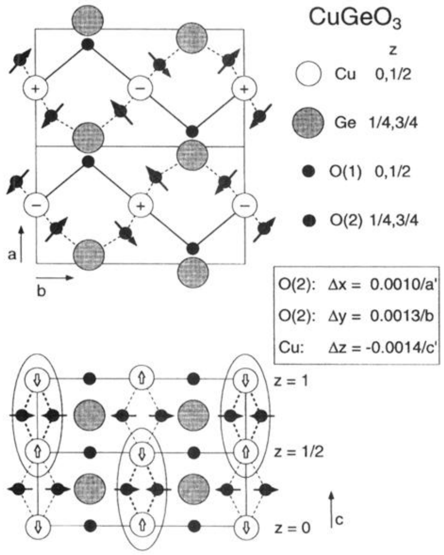
[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[2] M. Hase *et al.*, Phys. Rev. B **48**, 9616 (1993).
[3] M. Hase, I. Terasaki, Y. Sasago, K. Uchinokura, and H. Obara, Phys. Rev. Lett **71**, 4059 (1993).
[4] S. Sugai, J. Phys. Soc. Jpn. **62**, 3829 (1993).
[5] H. Hori *et al.*, J. Phys. Soc. Jpn. **63**, 18 (1994).
[6] H. Kuroe *et al.*, J. Phys. Soc. Jpn. **63**, 365 (1994).
[7] J. Kikuchi, H. Yasuoka, M. Hase, Y. Sasago, and K. Uchinokura, J. Phys. Soc. Jpn. **63**, 872 (1994).
[8] T. Hamamoto, N. Adachi, G. Kido, M. Hase, Y. Sasago, and K. Uchinokura, J. Phys. Soc. Jpn. **63**, 1218 (1994).
[9] M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B (to be published).
[10] J. E. Lorenzo *et al.*, Phys. Rev. B **50**, 1278 (1994).
[11] O. Kamimura, M. Terauchi, M. Tanaka, O. Fujita, and J. Akimitsu, J. Phys. Soc. Jpn. (to be published).
[12] L. P. Regnault (private communication); J. P. Pouget *et al.*, Phys. Rev. Lett **72**, 4037 (1994).
[13] H. Völlenkle, A. Wittmann, and H. Nowotny, Monatsh Chem. **98**, 1352 (1967).
[14] Q. J. Harris *et al.* (unpublished).



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