

## The Crystal Structure and Magnetic Properties of $\text{CuGeO}_3$

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The crystal structure of  $\text{CuGeO}_3$ , which has been reported to undergo a spin-Peierls transition at 14 K, is determined by neutron powder diffraction at 300, 20 and 4.2 K and the structure refined in the space group  $Pm\bar{m}a$  at all three temperatures, *i.e.* without displacement of the Cu atoms from a uniform one-dimensional chain; anisotropic broadening of  $(h0l)$  reflections, observed in all three data sets, is successfully modelled by an orthorhombic micro-strain along  $a$  and  $c$ , *i.e.* perpendicular to Cu–Cu chains. Below 10 K the magnetic susceptibility fits very well to the Bulaevskii model, indicating a ratio of 0.69 between the Cu–Cu exchange constants in the dimerised chain and a mean exchange constant of 88 K.

In chain compounds which behave as one-dimensional metals, there is often a metal–insulator transition due to the so-called ‘Peierls instability’.<sup>1</sup> In one-dimensional arrays of spins, the corresponding phenomenon is called the spin-Peierls transition.<sup>2</sup> The two phenomena share the common characteristic that below a transition temperature  $T_p$  or  $T_{sp}$  the chain, uniform at high temperature, takes on a distorted form, with a modulation of spacing between the units. Given the importance of fluctuations in one-dimensional systems, it is important to ask whether signs of incipient distortion are detectable at temperatures well above  $T_p$  or  $T_{sp}$ . Until the last few months, the only examples known of this spin-Peierls transition were all molecular solids.<sup>3–5</sup> However, it has been reported that  $\text{CuGeO}_3$  shows such a transition at 14 K.<sup>6</sup> Hence, we have examined the structure of  $\text{CuGeO}_3$  by neutron powder diffraction at ambient temperature, as well as temperatures just above and below the reported transition temperature. We find that the structure of  $\text{CuGeO}_3$  is best described in the  $Pm\bar{m}a$  space group but that clear indications exist of orthorhombic strain at all three temperatures. A fit to low temperature magnetic susceptibility is consistent with spin-Peierls behaviour and provides an estimate of the extent to which the Cu chains are dimerised at low temperature.

Polycrystalline samples of  $\text{CuGeO}_3$  were prepared by melting together CuO and  $\text{GeO}_2$  in stoichiometric proportions in a Pt crucible in  $\text{O}_2$  at 950 °C followed by slow cooling. Neutron powder diffraction profiles were recorded on the BT1 diffractometer at the National Institute for Standards and Technology, Gaithersburg, USA. The profiles at 300 and 20 K used Cu(220) ( $\lambda$ , 1.5573 Å) with collimation of 14' and 7' respectively, while that at 4.2 K used Cu(311) ( $\lambda$ , 1.539 Å) with 14' collimation. Scattered intensity from 32 detectors was merged to give profiles that were refined by the Rietveld method for constant wavelength data using the programme FULLPROF.<sup>7</sup> In addition to positional and isotropic thermal parameters, site occupancies and preferred orientation were refined. There was no indication of deficiencies in occupation of any of the sites. At all three temperatures clear differences of peak width were observed for  $(h0l)$  reflections, which were modelled by introducing an orthorhombic micro-strain along  $a$  and  $c$ ,<sup>8</sup> *i.e.* perpendicular to the Cu–Cu chain axis. The temperature dependence of the magnetic moment of the same polycrystalline sample was measured in applied fields from 1 to 7 T between 300 and 2 K, using a Quantum Design MPMS SQUID magnetometer.

Fig. 1 shows the observed and calculated diffraction profiles of  $\text{CuGeO}_3$  at room temperature and 4.2 K and Table 1 contains the most important refinement parameters.† The structure refined differs from the one derived from earlier single crystal X-ray diffraction,<sup>9</sup> where a  $Pb2_1M$  space group was used, but is in general agreement with powder diffraction studies.<sup>10</sup> It consists of chains of corner-sharing  $\text{GeO}_4$  tetrahedra surrounding the chains of edge-sharing  $\text{CuO}_6$ . The latter are tetragonally elongated in a ferro-distortive fashion perpendicular to the Cu chain axis. Attempts were made to refine the structure at all three temperatures in a doubled unit

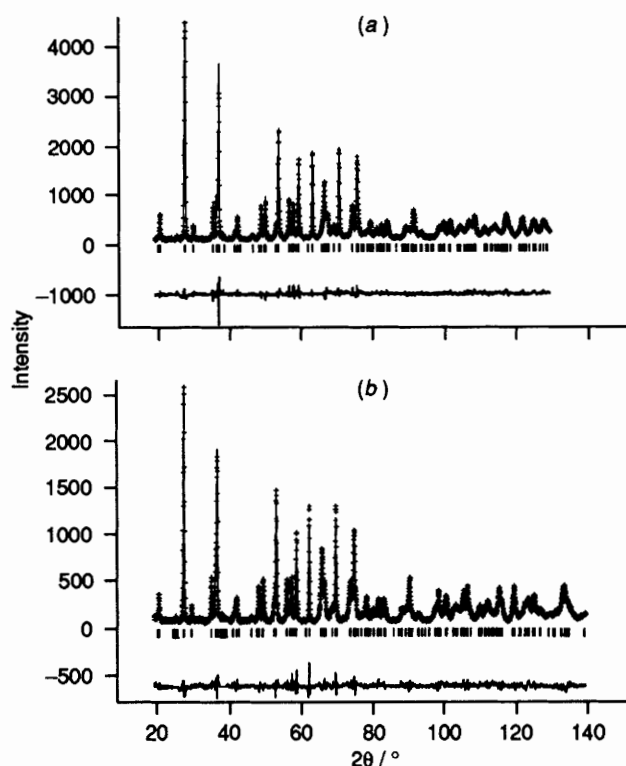


Fig. 1 Observed and calculated neutron powder diffraction profiles of  $\text{CuGeO}_3$  at (a) 300 and (b) 4 K. The bottom trace is the difference between observed and calculated profiles and the vertical bars the calculated peak positions. In the 4 K profile the hatched regions contain scattering from the cryostat and are excluded from the refinement.

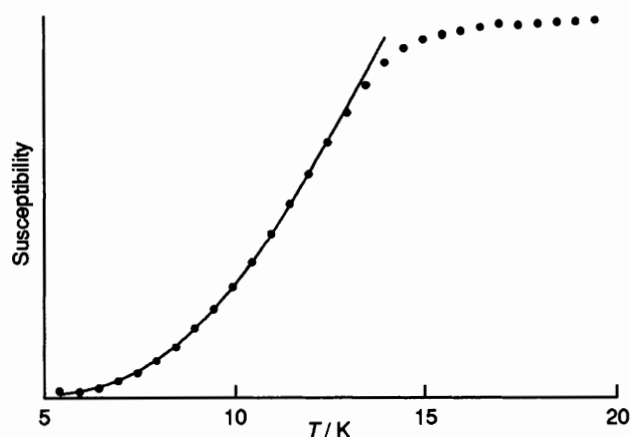


Fig. 2 The magnetic susceptibility of  $\text{CuGeO}_3$  measured in an applied field of 500 G. The full line is a fit to the Bulaevskii model.<sup>11</sup>

**Table 1** Lattice and refinement parameters of CuGeO<sub>3</sub> at room temperature, 20 and 4 K

	Room temp.	20 K	4 K	
Lattice parameters				
<i>a</i> /Å	8.5124(5)	8.4668(3)	8.4526(3)	
<i>b</i> /Å	2.94389(9)	2.94683(5)	2.94330(4)	
<i>c</i> /Å	4.7981(3)	4.7877(2)	4.7816(1)	
Preferred Orientation	0.971(3)	0.985(3)	0.987(3)	
Strain Along <i>a</i>	0.000140(1)	0.000143(1)	0.000138(5)	
Strain Along <i>c</i>	0.000235(7)	0.000289(5)	0.000256(5)	
<i>R</i> <sub>wp</sub>	8.57	8.72	9.99	
<i>R</i> <sub>exp</sub>	5.66	4.98	7.06	
<i>R</i> <sub>bragg</sub>	4.53	3.85	5.23	
χ <sup>2</sup>	2.29	3.06	2.00	

Room temp.	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> /Å
	Cu	0.0000	0.0000	0.5000	0.82(5)
	Ge	0.2500	0.5000	0.0766(4)	0.61(4)
	O(1)	0.2500	0.0000	0.8659(6)	0.69(6)
	O(2)	0.0836(3)	0.5000	0.2848(4)	0.92(5)

20 K	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> /Å
	Cu	0.0000	0.0000	0.5000	0.49(5)
	Ge	0.2500	0.5000	0.07310(4)	0.28(5)
	O(1)	0.2500	0.0000	0.8641(6)	0.53(6)
	O(2)	0.0831(3)	0.5000	0.2808(4)	0.34(5)

4 K	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> /Å
	Cu	0.0000	0.0000	0.5000	0.48(4)
	Ge	0.2500	0.5000	0.0741(4)	0.39(4)
	O(1)	0.2500	0.0000	0.8620(6)	0.65(5)
	O(2)	0.0827(2)	0.5000	0.2808(4)	0.45(4)

cell and space groups allowing variation in Cu–Cu separation, but no improvement was found. Difference Fourier maps do not indicate any displacement of the Cu from their mean positions or unusually large fluctuations along the Cu–Cu chain. On the other hand, the *R*-factors are considerably reduced (*e.g.* *R*<sub>wp</sub> from 13 to 8.67 in the 300 K data set) by inclusion of orthorhombic strain in the two directions perpendicular to the Cu chain axis, which may simulate a small departure from orthorhombic symmetry not resolvable by the powder data. It is noteworthy, however, that on cooling from room temperature to 20 K the equatorial Cu–O bond lengths increase (from 1.934 to 1.941 Å) and the Cu–Cu distance within the chains (equal to the *b* lattice parameter) likewise increases. This is associated with an increase in the orthorhombic strain along both *a* and *c*-axis (see Table 1). On further cooling to 4.2 K, the orthorhombic strain decreases again, indicating the possibility that a structural phase transition has taken place.

Fig. 2 shows the moment of a polycrystalline sample of CuGeO<sub>3</sub> measured in a field of 500 G. The decrease below 14 K signals the onset of the magnetic transition. Measurements in fields up to 7 T show no significant renormalisation of the transition temperature as indicated by a maximum in *dy/dT*. The continuous line in Fig. 2 is a fit to the Bulaevskii model of an antiferromagnetic chain with alternating exchange constants, in which the parameters fitted are the *g* value, the mean Cu–Cu exchange constant and the ratio between the two values of the exchange constant in the alternating chain.<sup>11</sup> The fit, between 2 and 14 K, after correction for a Curie tail, yields a *g* value of 2.16, an exchange constant of 88 K and a ratio,  $\gamma$ ,

of 0.69. However, it is conceivable that the alternating chain antiferromagnetic model might simulate other magneto-elastic coupling phenomena than a spin-Peierls transition.

In sum, we have shown that, unlike the few other well-authenticated examples of the spin-Peierls phenomena, the structure of CuGeO<sub>3</sub> shows no significant deviation from its high temperature structure on passing through the transition, although there is some diminution in orthorhombic strain along *a* and *c*. Greater detail about the atomic displacements and the lattice phonon inducing the transition must await experiments on single crystals. A recent  $\mu$ SR study of CuGeO<sub>3</sub><sup>12</sup> shows only a slight slowing down of spin dynamics in the region of 14K.<sup>12</sup>

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### Footnote

† A list of atomic coordinates and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

*Note added at proof:* Recently, in a single crystal study, superlattice peaks have been identified due to a dimerised state below T<sub>sp</sub>.<sup>13</sup> Furthermore, a neutron scattering experiment found anomalies in phonon and diffraction data well above T<sub>sp</sub>.<sup>14</sup> In both cases, emphasis is put on the interaction perpendicular to the Cu–Cu chain. The origin of the strain in this paper should prove to be important in understanding the CuGeO<sub>3</sub> spin-Peierls system.

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