

LETTER TO THE EDITOR

Observation of the Néel state in doped CuGeO_3

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Abstract. The effect of doping on the spin–Peierls (SP) transition in single crystals of CuGeO_3 has been investigated using neutron scattering techniques and susceptibility measurements. When the Cu^{2+} site is partly substituted by either Zn^{2+} (4%) or Ni^{2+} (1.5%) the SP is suppressed, and a long-range Néel state develops below $T_N = 2.8$ K (Zn) and $T_N = 2.2$ K (Ni) with a wave vector of $(0, 1, \frac{1}{2})$. This observation contrasts with earlier reports of a spin glass transition in the doped compounds in the same temperature range. Our results also indicate that the reported Néel state in the nominally pure compound results from impurities. Preliminary measurements of the Zn-doped sample show that the gap that opens in the magnetic excitations below T_{SP} collapses in the doped compound.

The discovery by Hase *et al* [1] of a spin–Peierls (SP) transition in CuGeO_3 has received considerable attention recently due to the fact that CuGeO_3 is inorganic and has a comparatively simple structure, unlike the other well known SP systems (see, for example, [2]). One of the most important consequences of this discovery is that for the first time the effect of doping on this transition can be studied in detail.

Experimental evidence that CuGeO_3 undergoes a SP transition was shown by the isotropic decrease of the magnetic susceptibility below $T_{SP} = 14$ K [1, 3]. In SP systems, the coupling of the 1D antiferromagnetic order to the 3D phonons of the crystal lattice induces a dimerization of the magnetic ions, leading to the formation of a non-magnetic singlet ground state separated by an energy gap from the triplet. For CuGeO_3 it is believed that the one-dimensional correlations develop along the c axis where the $\text{Cu–O}_2\text{–Cu}$ chains correspond to the shortest Cu–Cu distance. The observation of additional structural superlattice reflections below T_{SP} at $(h + \frac{1}{2}, k, l + \frac{1}{2})$ [4] corroborates the occurrence of the dimerization process of the Cu ions, but indicates that the dimerization is not simply along the chain direction and is induced by slight displacements of the O(2) atoms [5]. The formation of the energy gap below T_{SP} in CuGeO_3 , and the splitting of the triplet state in an applied field, have been observed using neutron scattering [6]. However, the energy gap is not minimal at the dimerization wave vector $(h + \frac{1}{2}, k, l + \frac{1}{2})$ but reaches its minimum at $(0, 1, \frac{1}{2})$ [7]. These properties differ from those expected for a simple dimerization along the c axis and still lack a full explanation.

The substitution of Cu by Zn, Ni or Mn in CuGeO_3 generally suppresses the SP phase [3, 8]. For concentrations larger than approximately 1.5% of Zn or Ni, a second transition near 3.5 K is clearly visible in susceptibility measurements. Initial reports attributed this transition to the creation of a glassy state after a large hysteresis was found in the susceptibility [3]. Several theoretical studies have addressed the problem of doping in the general context of $S = \frac{1}{2}$ antiferromagnetic Heisenberg spin chains, and analogies with

the Kondo problem have been drawn [9, 10]. In a recent paper, the problem of doping is treated for the special case of the SP instability and theoretical arguments are given for a possible re-entrant spin glass phase depending on the concentration of the impurity [11]. In such a mean-field approach, the doping breaks the chains and produces unpaired Cu^{2+} spins which are then expected to freeze at low temperature. Experimentally, however, the fact that a second transition is also seen near 3.5 K in specific heat measurements on Zn-doped CuGeO_3 [8] makes it unlikely that this transition is connected to a spin glass state [12]. In this letter we present the effects of partial substitution of the Cu^{2+} ($S = \frac{1}{2}$) by either non-magnetic Zn or magnetic Ni ($S = 1$). From neutron scattering experiments on single crystals we show that the low-temperature transition is into a long-range Néel state.

The single crystals were grown using the floating zone method in an infrared image furnace at the University of Warwick. All the crystals were grown from a seed under 1 atm of oxygen such that the c axis was along the growth direction. A slow growth rate of 2 mm hr^{-1} ensured good crystal quality, as indicated by well defined cleavage planes perpendicular to the a axis. The compositions of the single crystal studied were $\text{Cu}_{0.96}\text{Zn}_{0.04}\text{GeO}_3$ ($2 \times 2.5 \times 40 \text{ mm}^3$), $\text{Cu}_{0.985}\text{Ni}_{0.015}\text{GeO}_3$ ($2 \times 3 \times 40 \text{ mm}^3$) and pure CuGeO_3 ($2 \times 4 \times 40 \text{ mm}^3$), where the dimensions are given along the a , b and c directions respectively.

The neutron scattering measurements were performed using the TASVII spectrometer situated at the cold source of the DR3 reactor at Risø National Laboratory, Denmark. The reactor to detector collimation was 28 min–open–60 min–120 min, and the $(0, 0, 2)$ reflection from pyrolytic graphite was used to define the energies of the incident and scattered beams. Elastic and inelastic scans were performed with an incident energy of 4.5 meV with a Be filter in the incident beam which offers excellent higher-order rejection. The samples were mounted in the $(0, k, l)$ scattering plane in a helium flow cryostat which had a base temperature of 1.5 K, and could be controlled within approximately 0.1 K.

Preliminary characterization of the samples was carried out by susceptibility measurements using a SQUID magnetometer (figure 1). In the pure compound, the SP transition occurs at $T_{SP} \approx 14 \text{ K}$ which agrees with previous reports. In the 1.5% Ni sample, the SP transition is shifted to lower temperatures, while in the 4% Zn sample the SP transition is almost completely suppressed and a second transition is clearly visible around 4 K. These results are in broad agreement with an earlier study on polycrystalline samples [3].

In the initial phase of the neutron scattering experiments the instrument was set to the elastic position, and a careful survey was made of the scattering at high-symmetry positions in the $(0, k, l)$ plane at high temperature (30 K). The samples were then cooled to base temperature and the survey repeated. For the Zn-doped sample an additional peak was located at $(0, 1, \frac{1}{2})$, while at all other zone boundaries ($(0, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, $(0, \frac{3}{2}, 0)$) no peaks were found. As shown in figure 2, the scattering at $(0, 1, \frac{1}{2})$ disappears above 4.2(1) K. This transition temperature corresponds approximately to the cusp observed in the susceptibility measurements (Zn doped) and indicates that the magnetic origin of the transition. We thus identify the low-temperature transition in Zn-doped CuGeO_3 with an antiferromagnetic ordering of the Cu^{2+} moments. Similar results were also obtained from the Ni-doped sample, as shown in figure 2, except that the scattering at $(0, 1, \frac{1}{2})$ was approximately an order of magnitude weaker than in the Zn-doped sample, and indicate a lower $T_N = 2.5(1) \text{ K}$. The reason for the absence of a second transition in the susceptibility measurement of the Ni-doped sample (figure 1) is unclear. The nearly linear shape of the order parameter in the Zn compound indicates mean-field behaviour below T_N , a tendency not clearly established in the Ni compound. We emphasize that the low-temperature phase

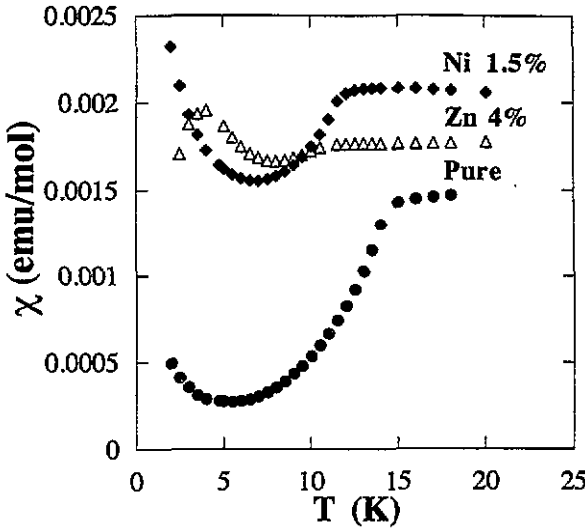


Figure 1. The normalized magnetic susceptibility along the *c* axis from single crystals of pure and doped CuGeO₃: ●, pure; ◆, 1.5% Ni, and △, 4% Zn.

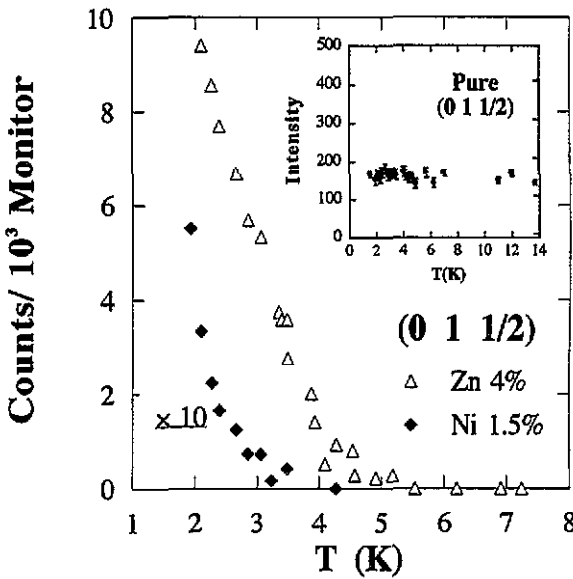


Figure 2. The temperature dependence of integrated intensity at the $(0, 1, \frac{1}{2})$ reflection in 4% Zn (Δ) and 1.5% Ni samples (\blacklozenge). The Ni intensity has been multiplied by a factor of ten. The inset shows the temperature dependence of integrated intensity at the same wave vector in the pure sample.

transition is into a state with long-range order, as can be seen in figure 3, where we compare the rocking curve widths of the magnetic peaks below T_N with the width of a nuclear peak. These findings indicate that the doping limits the extent of the 1D correlations along the chains and allows 3D correlatons to drive a transition at lower temperatures into a Néel

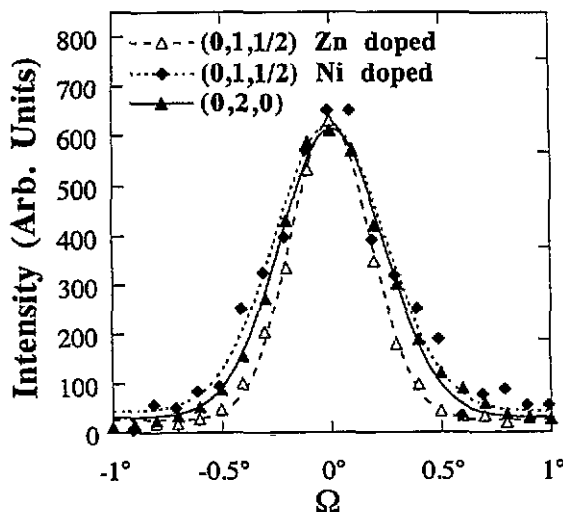


Figure 3. Comparison of the angular widths of the magnetic reflection $(0, 1, \frac{1}{2})$ as measured in the 4% Zn (Δ) and in the 1.5% Ni (\blacklozenge) samples and the nuclear reflection $(0, 2, 0)$ (\blacktriangle).

state.

We note that we also observed the presence of a weak, temperature-independent peak at $(0, 1, 0)$ in the doped compounds. This reflection is normally extinct in the pure compound due to the glide plane symmetry along the a -axis. Lorenzo *et al* [13] did not observe this reflection, while Arai *et al* [14] reported a peak at $(0, 1, 0)$ as well as other forbidden reflections in the nominally pure compound. We presume that these reflections appear when there is disorder in the lattice.

In the pure compound we did not observe a peak at $(0, 1, \frac{1}{2})$ down to 1.5 K. The inset to figure 2 shows the temperature dependence of the background in the pure compound. Our results give a straightforward explanation for the peak observed by Nishi [15] at the same wavevector in the nominally pure compound. In that experiment, a peak was observed at $(0, 1, \frac{1}{2})$ below $T_N = 3.8$ K in an undoped sample. Our study suggests that this peak is not an intrinsic effect but arises from impurities or other defects along the chains in CuGeO_3 .

A series of inelastic scans was also performed at $(0, 1, \frac{1}{2})$ on the pure and on the Zn-doped samples. Results taken at 1.5 K with the spectrometer operated in constant- Q mode are shown in figure 4. In the pure sample, a magnetic excitation is clearly visible with a gap of 1.9 meV. This value is broadly in agreement with the data of Nishi *et al* [7]. For the doped sample, the magnetic response appears to be very different with a suppression of the scattering around the energy of excitation from the pure compound. Instead of a well defined peak, the response is broadened into a diffusive excitation around 1.7 meV, which disappears at higher temperatures. At the present time we do not know whether or not this mode is intrinsic to the doped material, or is due to a gradient of concentration along the growth direction, and further experiments on the doped material are planned in the near future to elucidate this point.

In summary, we have performed neutron scattering experiments that have helped to clarify the nature of the low-temperature phase transition in Zn- or Ni-doped CuGeO_3 for concentrations at and above 1.5%. The transition observed in both compounds at 2.8(1) K (Zn) and 2.2(1) K (Ni) corresponds to the onset of an antiferromagnetic order at $(0, 1, \frac{1}{2})$. Our results show that the ordering in the Néel state is long range, in contrast with previous

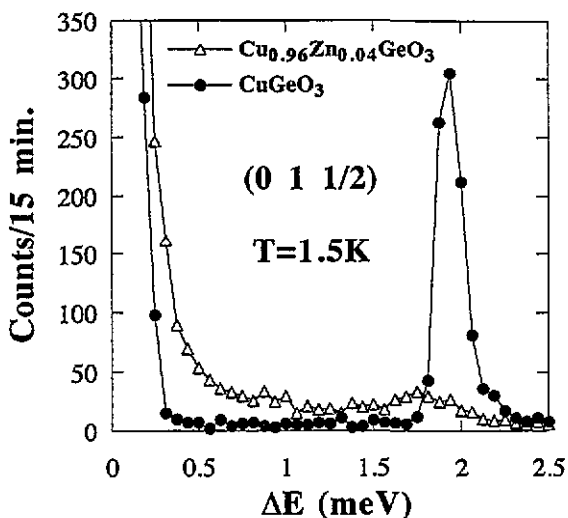


Figure 4. The scattered neutron intensity observed in a constant- Q scan at $(0, 1, \frac{1}{2})$ in the pure (\bullet) and in the 4% Zn-doped (Δ) samples at 1.5 K. The curves have been normalized using the Bragg peak intensity to account for differences in sample size.

reports of a spin glass transition in the same temperature range. Finally, an earlier report of a peak at $(0, 1, \frac{1}{2})$ in the pure compound probably results from impurities or defects along the chains, and is not intrinsic to CuGeO_3 .

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