# New phase diagram of Zn-doped $CuGeO_3$

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A series of high-quality single crystals of $Cu_{1-x}Zn_xGeO_3$ have been examined by neutron-scattering techniques. An antiferromagnetic (AF) ordering is confirmed for four samples in the range $0.009 \leq x \leq 0.047$, in complete agreement with previous reports. We show that the spin-Peierls (SP) phase transition persists to 4.7% Zn, whereas previous magnetic-susceptibility measurements reported a deterioration of the SP transition above 2% Zn. We present some details of the successive transitions upon lowering temperature into the spin-Peierls phase which is followed by a transition into an antiferromagnetically ordered phase. Below the Néel temperature we observe the coexistence of the SP lattice dimerization and AF states. [S0163-1829(96)51734-0]

## I. INTRODUCTION

Shortly after the discovery of the inorganic spin-Peierls cuprate $CuGeO_3$,[1] a series of extensive studies were begun on systems where Cu atoms were replaced with Zn (Refs. 2–6) or Ge was replaced with Si (Refs. 7–9). It is now well established that a new antiferromagnetically (AF) ordered phase appears as shown in the phase diagram of Fig. 1 obtained on powder samples.[2] The spin-Peierls (SP) transition temperature is near 14 K for the undoped material, decreases in temperature with increased Zn concentration, and seemed to disappear around 2% Zn;[2,6] at 4% Zn the magnetic susceptibility no longer shows a SP transition but only shows an AF transition with a Néel temperature of $T_N \sim 4$ K (Ref. 3) (inset of Fig. 1).

Two recent neutron-scattering reports have shown the existence of the AF ordering with its associated superlattice peak at $(0\ 1\ \frac{1}{2})$ for 3.4% Zn-doped[5,6] and 0.7% Si-doped[9] $CuGeO_3$. In the latter study, Regnault *et al.* showed the successive SP and AF transitions with two separate branches of magnetic excitations below $T_N$.[9] The coexistence of the SP and AF states was first demonstrated in their work.

The AF state in Zn-doped $CuGeO_3$ is certainly unusual. Undoped, the low-dimensional chains in $CuGeO_3$ form a SP ground state with an accompanying lattice dimerization below about 14 K. The AF order is induced when impurities are doped into this SP spin-singlet ground state. The present paper presents preliminary neutron-scattering results on 0.9% to 4.7% Zn-doped $CuGeO_3$ showing the SP and AF transitions and the interplay between these two states.

## II. EXPERIMENTAL DETAILS

A series of four relatively large ($\sim 0.4$ cm$^3$) $Cu_{1-x}Zn_xGeO_3$ single crystals were grown using the floating-zone method. The Zn concentrations $x$ for the crystals were analyzed using electron-probe microanalysis resulting in $x=$ 0.009, 0.021, 0.032, and 0.047. These values are somewhat lower than the nominal concentrations, as expected. The space group of $CuGeO_3$ is *Pbmm* (*Pmma* in standard orientation), with lattice constants at room temperature of $a=4.81$ Å, $b=8.47$ Å, and $c=2.941$ Å. The mosaic spread of these crystals was less than 0.3 degrees. Neutron-scattering measurements were carried out on the H7 and H8 beamlines of the High Flux Beam Reactor at Brookhaven National Laboratory. The crystals were mounted in aluminum cans which were subsequently attached to the cold finger of a cryostat. The samples were aligned so as to place $(0\ k\ l)$ or $(h\ k\ h)$ zones in the experimental scattering plane. Incident neutrons with energies of 14.7 meV were selected by a pyrolytic graphite (PG) monochromator and PG filters where used to eliminate higher-order harmonics. The beam was horizontally collimated typically with

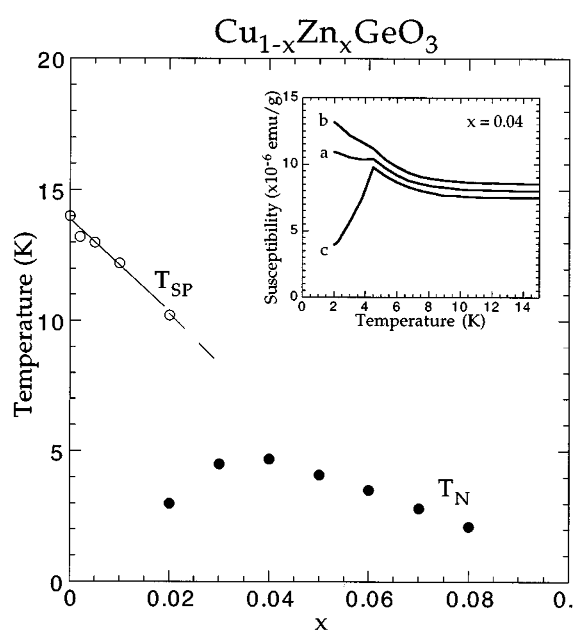


FIG. 1. The previously reported phase diagram for $Cu_{1-x}Zn_xGeO_3$ as deduced from magnetic susceptibility measurements of powders (Ref. 2). The inset shows the susceptibility measurement of an $x=0.04$ single crystal (Ref. 3) in the $a$, $b$, and $c$ crystalographic directions as labeled.

 

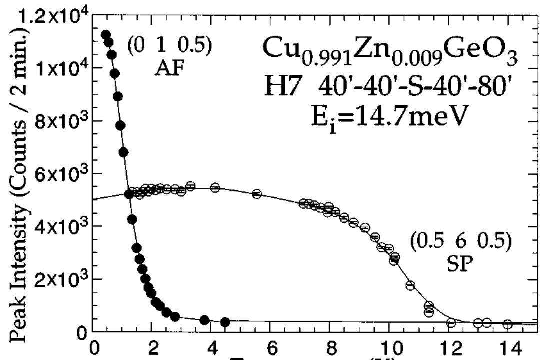


FIG. 2. Intensities of the (0.5 6 0.5) SP superlattice peak and the (0 1 0.5) AF superlattice peak as a function of temperature for a 0.9% Zn-doped sample showing the onset of the SP state followed by the onset of the AF state. The SP lattice dimerization superlattice peak was followed down to 1.3 K and shows a small decrease below 2 K.

40′-40′-Sample-40′-80′ in sequence from the reactor core to the detector.

## III. PHASE TRANSITIONS

We show the temperature dependence of the intensities of the two superlattice peaks at ($\frac{1}{2}$ 6 $\frac{1}{2}$) due to the lattice dimerization which occurs below the SP transition and at (0 1 $\frac{1}{2}$) from the AF ordering for $Cu_{0.991}Zn_{0.009}GeO_3$ in Fig. 2. The SP transition temperature is reduced by about 3° compared to the undoped material, and the transition is broader indicating a possible range of $T_{SP}$'s. Below about 2 K the AF superlattice peak is observed. These two transition temperatures are in agreement with the previous powder study by Hase *et al.*[2] The SP dimerization superlattice peak intensity persists in the AF state with a very slight decrease in intensity below the Néel temperature ($T_N$), showing the coexistence of these two states.

Figure 3 again shows the ($\frac{1}{2}$ 6 $\frac{1}{2}$) SP dimerization peak and the (0 1 $\frac{1}{2}$) AF peak intensities as functions of temperature now for a 3.2% Zn-doped crystal. A broadened and reduced $T_{SP}$ is again observed in this sample. However, the ($\frac{1}{2}$ 6 $\frac{1}{2}$) peak has become noticeably weaker (note the right-hand scale). The AF peak intensity shows an onset giving a Néel temperature near 4 K. In this sample we can clearly observe a decrease in the SP superlattice peak intensity below $T_N$ (indicated in Fig. 3 by a dashed line). This indicates that while the two states are coexisting, the magnitude of the SP lattice dimerization is affected by the onset of antiferromagnetism.

Similar measurements of $T_{SP}$ and $T_N$ were performed on the 2.1% and 4.7% Zn-doped $CuGeO_3$ crystals. The results for all Zn-doped compounds investigated are presented in the inset to Fig. 3. In contrast to the initial phase diagram determined by susceptibility measurements (Fig. 1), we have shown that the SP transition does not go away upon doping with Zn, but instead remains at approximately 10 K as the dopant level is increased. Furthermore the SP dimerization and AF ordered states are observed to coexist in all Zn-doped samples studied. All Bragg peaks for the 0.9% and 3.2% Zn-doped crystals are resolution limited meaning that the SP and AF orderings are long range in nature.

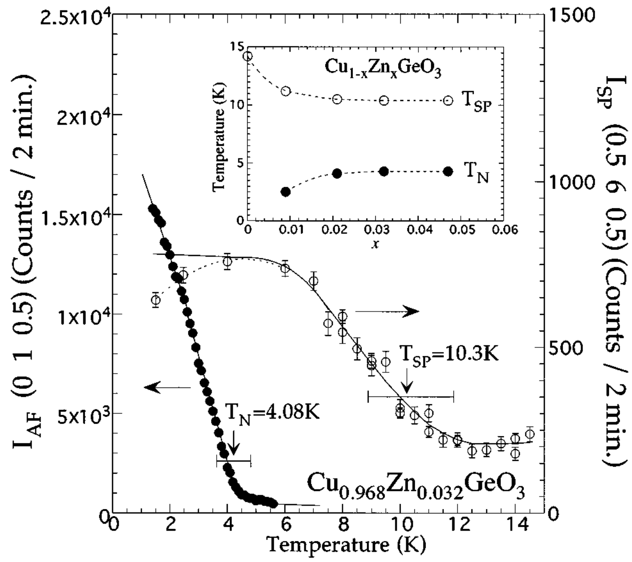


FIG. 3. Intensities of the SP and AF superlattice peaks as functions of temperature for a 3.2% Zn-doped crystal. The intensity of the SP lattice dimerization peak is seen to decrease below $T_N$, however, the states are clearly coexisting. The inset shows $T_{SP}$ and $T_N$ measured on samples of 0, 0.9, 2.1, 3.2, and 4.7 percent Zn-doped crystals. These points fall near the powder measurements of Fig. 1, but clearly show $T_{SP}$ persisting to higher Zn concentrations.

Figures 2 and 3 also show how the AF state becomes more dominant as the Zn doping increases. The relative intensity of the AF peak to the SP peak increases significantly with increasing Zn doping. Comparing the scattering intensities for the two crystals presented we can see that for the 3.2% Zn sample the AF scattering has increased by approximately twofold over the 0.9% Zn sample (indicating an increase in the magnetic moment of the AF state), while the SP dimerization scattering intensity has decreased. In the 3.2% Zn sample we estimate the zero temperature magnetic moment to be $\mu \approx 0.2\mu_B$; this is quite close to the value ($\mu \approx 0.22\mu_B$) reported by Hase *et al.*[6] for their 3.4% Zn crystal. The decrease in the intensity of the SP superlattice peak can be used to estimate the decrease in the atomic displacement $\delta$ from the SP dimerization in pure $CuGeO_3$. Using the observed form factor of the (0 2 1) Bragg peak as a reference and comparing the previously measured pure $CuGeO_3$ results (here we will denote the atomic displacement of a sample with $x$ Zn dopant as $\delta_x$) we find that $\delta_{0.032} \approx \frac{1}{2}\delta_0$.

## IV. DISCUSSION

The most interesting result from the study of doped $CuGeO_3$ is the coexistence of the SP lattice dimerization and the Néel state at low temperatures. This was first reported for a 0.7% Si-doped sample by Regnault *et al.*[9] and is reported in the present paper for a wide range of Zn doping. Usually two ordered phases of these types are mutually exclusive. Recently Fukuyama *et al.*[10] proposed a theoretical model of disorder-induced antiferromagnetic long-range order in a spin-Peierls system. Some key features of the theory appear to be realized in the current neutron data of the Zn-doped system. More quantitative data are needed for a concrete comparison with this theory; accurate and reliable determinations of the two order parameters with increasing $x$ and eventual line broadening of the SP and AF superlattice peaks at higher dopant concentrations are required.

The spectral shapes of magnetic excitations are also of vital interest. This phase of our investigations is just being undertaken, and some examples of interesting results are shown in Fig. 4. The magnetic excitations of the dimer mode of $Cu_{0.991}Zn_{0.009}GeO_3$ and $Cu_{0.968}Zn_{0.032}GeO_3$ are broadened yet still well defined in good agreement with Regnault *et al.*[9] Hase *et al.*[6] reported measurements on an $x=0.34$ Zn-doped sample which displays overdamped magnetic excitations; that crystal is the only one in which this overdamped behavior has so far been observed and it is unknown as to why Hase's crystal yields different results. Regnault *et al.*[9] reported differences in the magnetic excitations of the two phases including a new AF branch at low energies (or low $q$) and the shift of spectral weight. We do observe some significant shifts as demonstrated in the lower panel of Fig. 4, however, we have had considerable difficulties in observing the AF excitation as reported by Regnault *et al.* Very recently we have found an experimental window in which to study the AF excitations for a wide range of $q$ (Ref. 11) and our preliminary results are consistent with those of Regnault *et al.* for small $q$. Further detailed investigations on the dimer and AF magnetic excitations are currently in progress.[11]

The results presented here, together with the Si-doped data of Regnault *et al.*[9] clearly demonstrate the coexistence of antiferromagnetic ordering and spin-Peierls lattice dimerization. Research is continuing to further clarify any changes that occur as the SP phase develops an AF ordering.

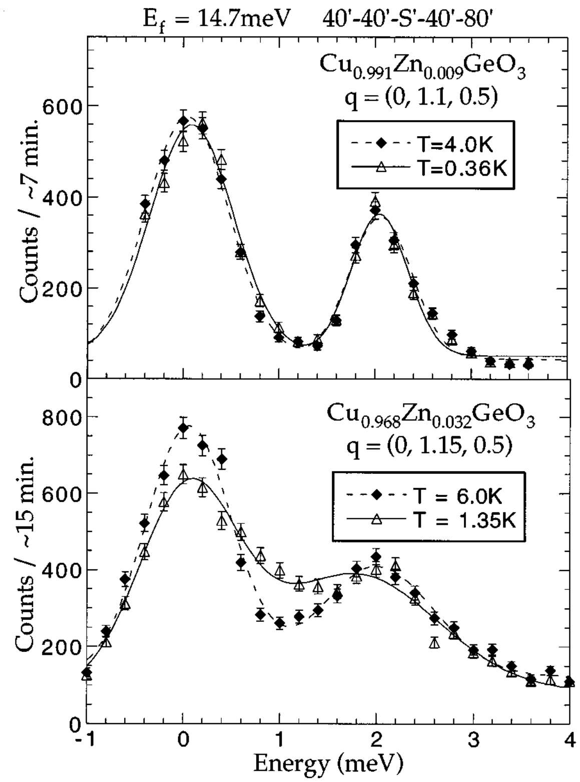


FIG. 4. Magnetic excitation spectra for a 0.9% (top panel) and 3.2% (bottom) Zn-doped $CuGeO_3$ crystals. The symbols are the data and the lines are fits to two Gaussians. The open triangles and solid line fit correspond to data taken at $T<T_N$ and the solid diamonds with a dashed line fit are for $T_N<T<T_{SP}$.

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