New phase diagram of Zn-doped CuGeO$_3$

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Abstract

A series of high-quality single crystals of Cu$_{1-x}$Zn$_x$GeO$_3$ have been examined by neutron scattering techniques. An antiferromagnetic (AF) ordering is confirmed for samples with $x \geq 0.02$, in complete agreement with previous reports. We show that the spin-Peierls (SP) phase transition persists to 6% 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.

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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 [2,3,4,5,6] or Ge was replaced with Si [7,8,9]. It is now well established that a new antiferromagnetically (AF) ordered phase appears as shown in the phase diagram of Figure 1 obtained on powder samples [2]. The spin-Peierls (SP) transition temperature is near 14K 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 $T_N \sim 4K$ [3] (inset of Figure 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 2% and 4% Zn-doped CuGeO$_3$ showing the SP and AF transitions and the interplay between these two states.

II. EXPERIMENTAL DETAILS

A series of relatively large ($\sim 0.4cm^3$) Cu$_{1-x}$Zn$_x$GeO$_3$ single crystals were grown using the floating-zone method. The nominal values of $x$ for the crystals used in the present study are 0.02, 0.04, and 0.06 [10]. The space group of CuGeO$_3$ is Pbmm (Pmma in standard
orientation), with lattice constants at room temperature of \(a = 4.81\AA, b = 8.47\AA,\) and \(c = 2.941\AA.\) The mosaic spread of these crystals were 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 14.7meV 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 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 \(\text{Cu}_{0.98}\text{Zn}_{0.02}\text{GeO}_3\) in Figure 2. The SP transition temperature is reduced by about 3 degrees compared to the undoped material, and the transition is broader indicating a possible range of \(T_{SP}\)’s. Below about 2K 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 4% 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 4K. 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 $T_{\text{SP}}$ and $T_{\text{N}}$ were performed on a 6% Zn-doped CuGeO$_3$ crystal. The results for all Zn-doped compounds investigated are presented in the inset to Figure 3. In contrast to the initial phase diagram determined by susceptibility measurements (Figure 1), we have shown that the SP transition does not go away upon doping with Zn, but instead remains at approximately 10K 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 2% and 4% Zn-doped crystals are resolution limited meaning that the SP and AF orderings are long-range in nature.

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 4% Zn sample the AF scattering has increased by approximately two-fold over the 2% Zn sample (indicating an increase in the magnetic moment of the AF state), while the SP dimerization scattering intensity has decreased. In the 4% 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]. 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 $\delta_{0.04} \approx \frac{2}{3}\delta_0$.

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. [4] 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. [11] 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 Figure 4. The magnetic excitations of Cu$_{0.98}$Zn$_{0.02}$GeO$_3$ and Cu$_{0.96}$Zn$_{0.04}$GeO$_3$ are essentially unchanged from the undoped crystals, remaining sharp and well defined. This result is in sharp contrast to the overdamped magnetic excitations for an $x = 0.04$ sample reported recently by Hase et al. [12]. This difference is presumably due to the improved quality of the present crystals though we lack microscopic probes to demonstrate the nature of the improvement.

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 in contrast to the report of Regnault et al. we have not observed sharp AF excitations.

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.

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[12] The 3.4% Zn-doped sample reported by Hase et al. in Ref. [6] shows underdamped profiles in excitations only for energies above 8meV. Reexamination of this crystal has revealed
an SP transition in agreement with the present results.
FIGURES

FIG. 1. The previously reported phase diagram for Cu$_{1-x}$Zn$_x$GeO$_3$ as deduced from magnetic susceptibility measurements of powders [2]. The inset shows the susceptibility measurement of an $x = 0.04$ single crystal [3].

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 2% 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 1.3K and shows a small decrease below 2K.

FIG. 3. Intensities of the SP and AF superlattice peaks as functions of temperature for a 4% 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, 2, 4, and 6 percent Zn-doped crystals. The two solid lines reproduce the phase diagram of Hase et al. (Fig 1) for comparison.

FIG. 4. Magnetic excitation spectra for a 2% (top panel) and 4% (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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$\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$

![Graph showing temperature vs. $x$ for $\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$. The graph includes two sets of data, one for $\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$ and another for $\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$. The data points are marked with 'a' and 'b' and are plotted as a function of $x$. The inset shows the susceptibility as a function of temperature for $x=0.04$. The susceptibility values are given in $\times 10^{-6}$ emu/g. The graph also includes a line indicating the temperature $T_{SP}$ and another line indicating the temperature $T_N$. The x-axis represents the concentration $x$, ranging from 0 to 0.1, and the y-axis represents the temperature in Kelvin (K), ranging from 0 to 20 K.](image)
$\text{Cu}_{0.98}\text{Zn}_{0.02}\text{GeO}_3$

H7 40'-40'-S-40'-80'

$E_i=14.7\text{meV}$
Cu$_{0.96}$Zn$_{0.04}$GeO$_3$

Cu$_{1-x}$Zn$_x$GeO$_3$

$T_N$ = 4.08 K

$T_{SP}$ = 10.3 K
Counts / ~15 min.

$E_f = 14.7\text{meV}$ 40'-40'-S'-40'-80'

$\text{Cu}_{0.98}\text{Zn}_{0.02}\text{GeO}_3$

$q = (0, 1.1, 0.5)$

- $T = 4.0\text{K}$
- $T = 0.36\text{K}$

Counts / ~7 min.

$\text{Cu}_{0.96}\text{Zn}_{0.04}\text{GeO}_3$

$q = (0, 1.15, 0.5)$

- $T = 6.0\text{K}$
- $T = 1.35\text{K}$

Energy (meV)