Reentrant Spin-Peierls Transition in Mg-Doped CuGeO$_3$

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We report a synchrotron x-ray scattering study of the diluted spin-Peierls (SP) material Cu$_{1-x}$Mg$_x$GeO$_3$. In a recent paper we have shown that the SP dimerization attains long-range order only for $x < x_c \sim 0.022 \pm 0.001$. Here we report that the SP transition is reentrant in the vicinity of the critical concentration $x_c$. This is manifested by broadening of the SP dimerization superlattice peaks below the reentrance temperature, $T_r$, which may mean either the complete loss of the long-range SP order or the development of a short-range ordered component within the long-range ordered SP state. Marked hysteresis and very large relaxation times are found in the samples with Mg concentrations in the vicinity of $x_c$. The reentrant SP transition is likely related to the competing Néel transition which occurs at a temperature similar to $T_r$. We argue that impurity-induced competing interchain interactions play an essential role in these phenomena.

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Low-dimensional quantum spin systems exhibit a variety of intriguing and often counter-intuitive properties. A prominent example of such a material is the spin-Peierls (SP) system which consists of an array of one-dimensional (1D) antiferromagnetic spin-chains with $S=\frac{1}{2}$ on a deformable 3D lattice. Below the spin-Peierls transition temperature, $T_{SP}$, the spin-chains dimerize and a gap opens in the magnetic excitation spectrum. The discovery of an inorganic SP compound CuGeO$_3$ (Ref. [3]) made possible a systematic study of impurity effects on SP systems [3]. In CuGeO$_3$, Zn$^{2+}$, Mg$^{2+}$ ($S=0$), and Ni$^{2+}$ ($S=1$) can be readily substituted for Cu$^{2+}$ ($S=\frac{1}{2}$) thus directly affecting the spin-chains [3]. Generally, it is found that with increasing impurity concentration, the SP transition temperature rapidly decreases and a Néel state appears at low temperatures [3].

While a large amount of work has been devoted to the doped CuGeO$_3$ system since its discovery, the temperature-doping (T-x) phase diagram of this system has recently been substantially revised [3]. In particular, Masuda et al. [3] have shown that in the Mg-doped compound, the SP transition abruptly disappears at a critical Mg concentration $x_c \sim 0.023$, and the Néel temperature $T_N$ exhibits a conspicuous jump at the same Mg concentration. The staggered magnetic moment in the Néel phase and the magnitude of the SP lattice displacement were also found to change substantially in the vicinity of $x_c$ [3]. Moreover, in the vicinity of $x_c$, two peaks in the temperature dependence of the magnetic susceptibility were found [3]; these peaks were attributed to two separate Néel transitions, and coexistence of two different phases (phase separation) for $x \sim x_c$ was proposed. Zn-doped CuGeO$_3$ exhibits very similar properties, and therefore this behavior appears to be universal for diluted CuGeO$_3$ in which the Cu$^{2+}$ is replaced by a non-magnetic ion.

We have recently reported high resolution synchrotron x-ray diffraction measurements on high-quality single crystals of Mg-doped CuGeO$_3$ [4]. We found that while measurable SP lattice dimerization persists for $x$ larger than $x_c$, the SP dimerized state attains long range order (LRO) only for $x < x_c$. Moreover, for $x$ in the vicinity of $x_c$, SP LRO is achieved at a temperature which is significantly lower than the SP transition temperature determined in magnetic susceptibility or heat capacity measurements [4]. We have proposed that these unusual phenomena result from competing interactions that are inevitably present in any diluted SP material. These results clearly demonstrate that synchrotron x-ray diffraction is an extremely valuable experimental method to study doped SP materials. However, the important low-temperature region of the T-x phase diagram which contains the Néel phase has thus far not been thoroughly investigated with this experimental technique.

In this paper, we report a synchrotron x-ray scattering study of the T-x phase diagram of Cu$_{1-x}$Mg$_x$GeO$_3$ with emphasis on the low-temperature regime. We find that for the Mg concentration $x$ in the vicinity of $x_c$ the SP transition is reentrant. This is manifested by broadening of the SP dimerization superlattice peaks below the reentrance temperature, $T_r$. This broadening most likely results from the loss of SP long-range order below $T_r$, for samples with $x \lesssim x_c$. However, we cannot exclude another possible scenario in which a short-range ordered (SRO) component with significant volume fraction develops within the long-range ordered SP state below $T_r$. 

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In this case, a two-phase state is realized. Marked hysteresis and very large relaxation times are found in the samples with Mg concentrations in the vicinity of \( x_c \). The reentrant SP transition may be related to the competing Néel transition which occurs at the temperature similar to \( T_r \). As we argued in Ref. [7], we believe that the structural and related magnetic properties of doped CuGeO\(_3\) are strongly influenced by impurity-induced competing interchain interactions and, possibly, random fields, and therefore are similar to the properties of other systems with competing interactions and/or fields, such as Spin Glasses (SG) and Random Field Ising Model (RFIM) compounds. Here we propose that the reentrant SP state can be naturally explained by the effects of the competing interactions since such a reentrant transition is commonly found in SG compounds.

The experiment was carried out at MIT-IBM beamline X20A at the National Synchrotron Light Source at Brookhaven National Laboratory. The 8.5 keV x-ray beam was focused by a mirror, monochromatized by a pair of Ge (111) crystals, scattered from the sample, and analyzed by a Si (111) analyzer. High quality \( \text{Cu}_{1-x}\text{Mg}_x\text{GeO}_3 \) single crystals with \( x = 0.017, 0.0209, \) and \( 0.0229 \) from the same batches as those studied in Ref. [5] were used. Carefully cleaved samples were loaded into a helium flow cryostat; the lowest temperature achievable in this setup was 1.4 K. The experiment was carried out in the vicinity of the (1.5, 1, 1.5) SP dimerization peak position with the \((H\ K\ H)\) zone in the horizontal scattering plane. Longitudinal (parallel to the scattering vector) and transverse scans in the \((H\ K\ H)\) zone were collected. In the direction perpendicular to the scattering plane, the intensity was automatically integrated due to our experimental setup. Since the beamline was optimized for the vertical scattering geometry rather than the horizontal scattering geometry required by the helium cryostat, the spatial resolution of this experimental setup was worse than that achieved in our previous work, Ref. [3]. To determine the resolution, we used our previous result that at temperatures of order 5–6 K the \( x = 0.017 \) and \( 0.0209 \) samples attain long range order, which was defined as a state with a correlation length \( \xi \) of at least five thousand Ångströms; significantly larger correlation lengths are essentially macroscopic. To extract the intrinsic correlation length, the data for all samples were fitted to a convolution of the measured resolution function with the intrinsic cross section. Several different intrinsic line-shapes produced fits of similar quality. To be consistent with the data analysis of Ref. [3], we use 3D Lorentzian-squared line-shapes in this paper.

![FIG. 1. Temperature dependencies of the (1.5, 1, 1.5) SP peak intensity (top panel) and the corresponding longitudinal inverse correlation length (bottom panel) taken on heating and on cooling in the \( x = 0.0209 \) sample. The inset shows the low-temperature inverse correlation length.](image-url)
arising, for example, from an anomaly in the background. The solid lines are the results of fits to the convolution of the measured experimental resolution function with the intrinsic 3D Lorentzian-squared line shape, which in our case reduces to a Lorentzian to the 1.5 power scattering profile for the in-plane scans due to the out-of-plane integration. The inverse correlation length $\xi$ at $T=1.4$ K determined in such a way from both the longitudinal and transverse scan is $2.5 \times 10^{-4} \, \AA^{-1}$. The exact value of the low-temperature correlation length should be taken with caution since fits to different intrinsic line shapes produced fits of similar quality with correlation length values deviating from the above result by as much as a factor of 2. Due to this ambiguity in the line-shape analysis, we also cannot exclude the possibility that the peak broadening is due to the development of a large volume short-range ordered component in the otherwise LRO system. This does not affect, however, the important qualitative result that the SP transition is reentrant at low temperature in this sample.

The data of Fig. 1 show marked hysteresis. The hysteresis results from anomalously slow dynamics in the samples with $x$ in the vicinity of $x_c$. The inset in Fig. 2 illustrates this phenomenon. In the inset we show the time dependence of the SP peak intensity after the sample was cooled from $T=2$ K to $T=1.4$ K.

FIG. 2. Transverse scans at the (1.5, 1, 1.5) SP peak position in the $x=0.0209$ sample at $T=5$ K and $T=1.4$ K taken on cooling. The peak intensities were scaled to be the same. The solid lines are the results of fits as discussed in the text. The inset shows the time dependence of the SP peak intensity after the sample was cooled from $T=2$ K to $T=1.4$ K.

Samples with $x$ much lower than $x_c$ show different behavior. Fig. 4 shows the temperature dependencies of the SP peak intensity and width for the $x=0.017$ sample. The Néel temperature in this sample is $T_N \approx 2.1 \pm 0.1$ K (Ref. 8). The decrease of the SP peak intensity below $T_N$ is very small, and the hysteresis is much less pronounced than in the case of $x \sim x_c$. The hysteresis and the accompanying slow dynamics are also virtually absent for samples of Cu$_{1-x}$Mg$_x$GeO$_3$ with Mg concentrations much larger than $x_c$.

As we noted in Ref. 7, we cannot rigorously exclude
the scenario in which for \( x < x_c \) the low-temperature SP correlation length saturates at some finite value that is larger than our resolution limit. Therefore, it is possible that true LRO is never achieved in the \( x=0.0209 \) sample. However, if a true phase boundary between the LRO and the SRO SP regions does exist in the T-\( x \) phase diagram of Cu\(_{1-x}\)Mg\(_x\)GeO\(_3\), the impurity concentration \( x=0.0209 \) is very close to the true critical concentration \( x_c \) because of the large lower limit that Ref. \([7]\) puts on the SP correlation length at T=4 K. The decrease of the correlation length at low temperature in this sample, therefore, is almost certainly associated with the reentrant character of the true phase boundary. Another possible scenario is that a first order transition as a function of \( x \) occurs at \( x=x_c \). In this case, two-phase coexistence (phase separation) takes place in a non-zero region around \( x_c \), and the impurity concentration \( x \) at which SP LRO is established in the entire sample might not be precisely defined. In this scenario, \( x=0.0209 \) is smaller than \( x_c \), and the low-temperature decrease of the correlation length is again associated with the reentrant phase boundary of the SP phase.

The rich and complex properties of diluted CuGeO\(_3\) described here and also in Refs. \([8,9]\) clearly cannot be explained by simple dilution effects alone. We believe, however, that these properties can be consistently explained by taking into account the close intrinsic analogy between doped SP compounds and other disordered systems with competing fields or interactions, such as the RFIM compounds \([1]\) and spin glasses \([10]\). In Ref. \([1]\), we have argued that in-chain dilution of a SP compound induces competing interactions and, concomitantly, frustration in the dimerized system. Briefly, it is energetically favorable to change the phase of the dimerization across the impurity in an isolated chain, because otherwise an unpaired spin is created. The (mean field) interaction with the neighboring chains is, on the other hand, minimized when the dimerization phase is constant, thus creating competing interactions and frustration. Since the system can be mapped onto an effective 3D Ising model in which the two dimer configurations possible in a given chain are associated with the up and down states of the Ising spins, this is analogous to the situation in 3D Ising systems with mixed ferromagnetic and antiferromagnetic bonds \([1]\). Therefore, it is natural to expect that doped SP materials share many common properties with spin glass systems. There also are higher order random field effects. The properties of the latter systems are extensively discussed in the literature \([3,10]\), so that the above analogy can significantly improve our understanding of doped SP materials.

![FIG. 4. Temperature dependencies of the (1.5, 1, 1.5) SP peak intensity and the corresponding inverse correlation length in the x=0.017 sample on heating and on cooling.](image)

The mapping into Ising magnet with random ferromagnetic and antiferromagnetic bonds is especially useful for understanding of the reentrant behavior and the slow dynamics found in Cu\(_{1-x}\)Mg\(_x\)GeO\(_3\) because these phenomena are commonly found in SG compounds \([10,11]\). In the heuristic model proposed by Aeppli et al. \([11]\), the destruction of the LRO at the reentrant transition in SG materials is attributed to the effects of random fields imposed on the LRO network by randomly frozen finite spin clusters that form in these materials at low temperatures. Expressed in the Ising pseudospin language, a similar scenario is likely valid for doped SP compounds. Additional evidence for the important role of the induced random-field effects in Cu\(_{1-x}\)Mg\(_x\)GeO\(_3\) comes from the anomalous behavior exhibited by this compound in the vicinity of the high-temperature SP transition \([12]\).

Evidently, the Néel and the SP order parameters in doped CuGeO\(_3\) are coupled to each other. At low dilution levels, both the SP dimerization and the Néel order coexist in a complex macroscopically uniform state in which both the SP and the AF correlations retain LRO \([12]\). This picture is consistent with our data for the \( x=0.017 \) sample. However, for higher impurity concentrations, the SP peak intensity is dramatically suppressed at temperatures near \( T_N \), indicating the competing character of the SP and the Néel states. In addition, the structural reentrance temperature \( T_r \) and the magnetic ordering temperature \( T_N \) in the \( x=0.0209 \) sample are
similar. Taking into account the competition between these two states and the analogy to the SG reentrant behavior described above, we propose that the main features of the T-x phase diagram of Cu$_{1-x}$Mg$_x$GeO$_3$ can be explained as follows. Competing interactions and/or fields play an essential role in this material. This accounts for the spin-glass-like behavior at the structural SP transition \[7\], and for the destruction of the SP LRO at low temperatures for \(x \sim x_c\). The self destruction of the SP state results in the jump of the Néel temperature for concentrations around \(x = x_c\). It is also plausible that the reentrant character of the SP SRO state is one of the factors that define the Néel temperature for \(x > x_c\), and that the double-peak structure of the magnetic susceptibility in the vicinity of \(x_c\) is also related to this phenomenon. We should, however, note that other descriptions of the phase behavior of Cu$_{1-x}$Mg$_x$GeO$_3$, notably the existence of a tricritical point and the corresponding first order transition line with its associated two-phase coexistence (phase separation) \[5,8\], are possible.

In conclusion, we have carried out a synchrotron x-ray scattering study of the diluted SP material Cu$_{1-x}$Mg$_x$GeO$_3$ with emphasis on the behavior at low temperatures. We have found that in the vicinity of \(x_c\), the SP transition is reentrant and that the system exhibits anomalously slow dynamics and marked hysteresis in the reentrant temperature regime. We believe that these phenomena can be consistently described by a model that incorporates the close analogy between the doped SP system and other disordered systems with competing interactions/fields such as SG and RFIM compounds. Clearly, further theoretical work along these lines is called for.

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