Antiferromagnetic long-range order in Cu$_{1-x}$Zn$_x$GeO$_3$ with extremely low Zn concentration

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We have measured the magnetic susceptibilities of single crystals of Cu$_{1-x}$Zn$_x$GeO$_3$ with extremely low Zn concentration ($x$) lower than $x = 5 \times 10^{-3}$ at very low temperatures to investigate the spin-Peierls and antiferromagnetic transitions. The results show that the undoped CuGeO$_3$ has no antiferromagnetic phase down to 12 mK and there exists an antiferromagnetic long-range order with the easy axis along the $c$ axis for $x$ down to $1.12(2) \times 10^{-3}$. The minimum observed Néel temperature was $0.0285$ K for $x = 1.12(2) \times 10^{-3}$ sample. From the concentration dependence of the Néel temperature it is concluded that there is no critical concentration for the occurrence of the antiferromagnetic long-range order. This indicates that the dimerization sustains the coherence of the antiferromagnetic phase of the spin polarization in impurity-doped systems and is consistent with the theory of the impurity-doped spin-Peierls system. The temperature dependence of the susceptibilities at $T > T_N$ of all samples indicates that the magnetic correlations between localized spins are enhanced by a relatively large interchain interaction of CuGeO$_3$.

Low-dimensional antiferromagnetic (AF) systems are very attractive because they exhibit various interesting phenomena such as spin-Peierls (SP) transition and high-temperature superconductivity. Among them, the SP transition occurs in one-dimensional AF spin systems with spin half ($S = 1/2$), whose ground state has a spin gap as a result of a dimerization of the chain. This transition drew much attention by a recent discovery of the first inorganic SP system CuGeO$_3$ by Hase, Terasaki and Uchinokura. The compound has an orthorhombic crystal structure which consists of linear chains of Cu$^{2+}$ ions ($S = 1/2$) along the $c$ axis, well separated from one another by Ge-O chains but still weakly coupled antiferromagnetically along the $b$ axis and ferromagnetically along the $a$ axis. This cuprate has a great advantage for the study of the SP transition over the organic SP materials, because we can easily study the effect of substitution on the SP transition. Up to now, the substitutions by Zn$^{2+}$ ($S = 0$) and Ni$^{2+}$ ($S = 1$) for Cu$^{2+}$ and by Si$^{4+}$ for Ge$^{4+}$ (Refs. 10 and 11) were performed in detail, resulting into the suppression of the SP transition and the occurrence of the antiferromagnetic long-range order (AF-LRO). Especially, in Cu$_{1-x}$Zn$_x$GeO$_3$, a neutron scattering experiment showed a clear evidence for the coexistence of AF-LRO and lattice dimerization. The coexistence is very interesting because these two types of LRO’s were generally believed to be mutually exclusive. However Fukuyama et al. proposed a theoretical model of impurity-induced AF-LRO in a SP system (in particular for CuGe$_{1-x}$Si$_x$O$_3$).

At present the AF-LRO is believed to be induced by the substitution for Cu$^{2+}$, which has $S = 1/2$ spin on it, by other ions: Zn$^{2+}$ ($S = 0$) or Ni$^{2+}$ ($S = 1$) etc. (or Ge$^{4+}$ ($S = 0$) by Si$^{4+}$ ($S = 0$) in the case of CuGe$_{1-x}$Si$_x$O$_3$). In this case we may speculate that there exists a critical concentration $x_c$ below which AF-LRO does not occur even at $T = 0$ K. An alternative possibility is that AF-LRO persists to zero impurity concentration (no critical concentration). Anyway it is very interesting to see how extremely dilute substitution causes or affects the AF-LRO. Very recently Grenier et al. have performed the measurements on the susceptibility of the single crystals of CuGe$_{1-x}$Si$_x$O$_3$ with small Si concentration ($x \geq 2 \times 10^{-3}$) down to 70 mK and observed the occurrence of the AF-LRO. But they failed to confirm whether critical concentration exists or not because of the uncertainty of Si concentration in low Si-doping level (according to them $x_{Si}$ corresponds to $x_{Zn}/3$, see the discussion section).

In the present work, we extended the measurements on the magnetic susceptibility of Cu$_{1-x}$Zn$_x$GeO$_3$ single crystals down to extremely low Zn concentration of $x = 1.12 \times 10^{-3}$ to determine the behavior of the Néel temperature in that region. For that purpose we have also extended the temperature region down to 5 mK.

A series of Cu$_{1-x}$Zn$_x$GeO$_3$ single crystals were grown using a floating-zone method. No traces of other impurity phases were detected in x-ray diffraction patterns. The Zn concentration $x$ was determined with Inductively-Coupled-Plasma Atomic Emission Spectroscopy (ICP-AES) and Electron Probe Micro Analyzer (EPMA) for $x < 5 \times 10^{-3}$ and $x > 5 \times 10^{-3}$, respectively. The samples for the ultra-low temperature measurements were grown, doped with $x = 1.12(2), 1.18(2), 2.13(4), 3.08(6), 3.81(8), 4.91(10), 7(2), 13(2), 17(3), 18(3), 21(2), 22(2), 24(3), 26(2) \times 10^{-3}$ Zn, where the values in the parentheses are experimental errors, or undoped.
For the measurements below 2 K each sample was stuck on a quartz glass with a small amount of N-grease to reduce a background signal. It was immersed in nonmagnetic liquid $^3$He which was cooled by way of a sintered powder heat exchanger with a combination of $^3$He-$^4$He dilution refrigerator and PrNi$_5$ adiabatic demagnetization refrigerator. The temperature was determined with the germanium and carbon resistor thermometers above 20 mK and with a platinum NMR thermometer below 20 mK, both calibrated against the $^3$He melting curve. Thermal contact between the sample and the coolant was found good enough since the susceptibility of the sample quickly followed the temperature change of the refrigerator and showed no hysteresis on cooling and warming processes above 12 mK. AC susceptibility was measured with a SQUID (Superconducting QUantum Interference Device) magnetometer where the amplitude and the frequency of the applied AC field were $5 \times 10^{-3}$ mT and 16 Hz, respectively. To determine SP transition temperatures for all samples, DC susceptibility measurements were also performed at $H = 0.1$ T above 2 K in a separate cryostat.

The temperature dependence of the susceptibilities along the $b$ ($\chi_b(T)$) and $c$ ($\chi_c(T)$) axes for Cu$_{1-x}$Zn$_x$GeO$_3$ with $x = 1.18(2) \times 10^{-3}$ is shown in Fig. 1. Two phase transitions are clearly seen in $\chi_c(T)$. One is characterized by a rapid drop at around 14.3 K, corresponding to the suppressed SP transition by the Zn substitution, which was first reported in Ref. 8. The other shows a cusp in $\chi_c(T)$ at around 0.04 K, below which $\chi_c(T)$ decreases toward zero whereas $\chi_b(T)$ increases slightly. The anisotropic behavior clearly indicates that the transition at 0.04 K is the AF (Néel) transition with the easy axis parallel to the $c$ axis as was observed in more heavily Zn-doped samples. A similar behavior was observed in the sample with $x = 4.91(10) \times 10^{-3}$, so only $\chi_c(T)$ was measured for the other samples. The results for $\chi_c(T)$ in the low concentration region are summarized in Fig. 1. All the samples exhibit the SP and the AF transitions around 14 K and below 1 K, respectively.

In the same figure, the result is also given for the undoped sample which was prepared in the same way as the doped ones. Although the concentration of impurities is extremely low in the undoped sample, it may contain defects which play the same role as Zn$^{2+}$ ions. Both the impurities and defects cut the dimerized chains of Cu$^{2+}$ and produce nearly isolated $S = 1/2$ states on the broken edges in the case of large distance between defects. Thus such defects (or Zn$^{2+}$) cause the increasing susceptibility in the spin-Peierls state and we can estimate their concentration by the Curie-Weiss fitting. In Fig. 1 we show the relation between Zn concentration estimated by ICP-AES and those estimated by Curie-Weiss fitting in low Zn concentration region ($x < 5 \times 10^{-3}$). In spite of extremely low Zn concentration, the latter agrees with the former within an accuracy of 20%. This shows the validity of the determination of Zn concentration. The fitting for the undoped sample gives us the effective value of $x = 2.3(2) \times 10^{-4}$. Its susceptibility seems to saturate below 0.012 K. There are two possible reasons for the occurrence of this saturation. One is that the undoped sample was not cooled below 0.012 K. The other is that the susceptibility is indeed constant below 0.012 K, which indicates that the AF transition may occur below 0.012 K. We cannot determine which is the case. But we can say that above 0.012 K AF transition does not occur in the undoped sample.

The Néel temperature $T_N$ and SP transition temperature $T_{SP}$ are summarized in Fig. 1 for all samples. The behavior of $T_N$ in very low concentration region and the appearance of the AF transition at 0.0285 K for such low Zn concentration as $x = 1.12(2) \times 10^{-3}$ imply that there is no critical concentration for the occurrence of the AF-LRO. This may come from the fact that the dimerization sustains the phase coherence of the spin polarization although it suppresses the magnitude of the spin polarization.
The spin-singlet background, according to Ref. 17, it is these localized spins that are generated by the polarization of the soliton width, respectively. When we use the lattice constant along the chain, $c$, the critical concentration becomes weaker. The best fitted value is $A = 2.3$ K and $B = 5.7 \times 10^{-3}$. For the undoped sample (effectively $x = 2.3(2) \times 10^{-4}$) $T_N$ is estimated to be 1 mK or lower, which is consistent with our failure to observe an AF transition for the undoped sample.

Now let us discuss the temperature dependence of the susceptibilities above $T_N$. As shown in Fig. 3, all $\chi_c(T)$ at $T > T_N$ exhibit a weaker temperature dependence than $1/T$, which indicates that there exists magnetic correlation between nearly isolated $S = 1/2$ states on the broken edges. According to a theoretical calculation for a 1D-AF-Heisenberg-alternating chain with distributed AF interaction $J$, the susceptibility $\chi_c(T)$ at low temperatures is given as

$$\chi = C T^{-\alpha}, \quad (0 < \alpha < 1)$$

where $C$ and $\alpha$ are the constants which depend on the distribution of $J$. The value of $\alpha$ approaches to 1 as the magnetic correlation becomes weaker. The best fitted value of $\alpha$ is given in Fig. 3 as a function of Zn concentration $x$. We can see a general trend that $\alpha$ increases with the reduction of $x$. For $x = 1.12(2) \times 10^{-3}$ where the average distance between impurities is about 900c (c is the lattice constant along the chain, $c = 2.94$ Å), $\alpha$ is still smaller than 1 ($\alpha = 0.978$). If a coupling between these localized spins is generated by the polarization of the spin-singlet background, according to Ref. 17, it is supposed to appear at

$$T^* = T_{SP} \exp(-L/\xi)$$

where $L$ and $\xi$ are the average distance between Zn ions and the soliton width, respectively. When we use the calculated soliton width ($\xi = 11.8c$) for the Si-doped CuGeO$_3$, $T^*$ for $x = 1.12(2) \times 10^{-3}$ is estimated to be $1.1 \times 10^{-32}$ K. This temperature is clearly much lower than the temperature range where the magnetic correlations between localized spins are observed. This fact implies that the magnetic correlations between localized spins are enhanced by the relatively large interchain interaction of CuGeO$_3$ ($J_0 = 0.1J_c$).

Recently Masuda et al$^{18}$ reported that there are two AF phases in Cu$_{1-x}$Mg$_x$GeO$_3$. One has the dimerization and AF-LRO at the same time at $x < x_c$ and the other has only AF-LRO at $x > x_c$. They called the former dimerized antiferromagnetic (D-AF) phase and the latter uniform antiferromagnetic (U-AF) phase. They found a first-order phase transition between the two phases as the Mg concentration $x$ changes. The critical concentration $x_c$ is about 0.023, where the SP transition vanishes. This fact shows that CuGeO$_3$ would be a conventional (classical) antiferromagnet, if there were no SP transition. Apparently the dimerization suppresses the growth of the AF-LRO by reducing the magnitude of the spin polarization. On the other hand the dimerization enhances the coherence of the (AF) phase of the spin polarization, because of the existence of the three-dimensional LRO of the lattice (dimerization). These competing effects of the dimerization seems to determine the nature of the impurity-induced AF phase in low concentration region. The introduction of impurities reduces the dimerization and at the same time induces the spin polarization. Growth of the polarization and the reduc-
tion of the dimerization induce the AF-LRO at very low temperatures, which is the main reason why we can observe the AF-LRO in such a low concentration region of Cu$_{1-x}$Zn$_x$GeO$_3$.

Until now it has not been so clearly determined whether the same phenomenon occurs in Zn-doped CuGeO$_3$. However it has been suggested that this phenomenon is universal in the impurity-doped CuGeO$_3$ at least when the substitution is done for Cu$^{2+}$, whether the impurities are nonmagnetic or magnetic (see the discussion in Ref. 13). Apparently the samples studied in this paper belongs to D-AF phase if there exist two AF phases in Zn-doped CuGeO$_3$.

Figure 5. The constant $\alpha$ in Eq. (4) as a function of Zn concentration $x$. The definition of $\alpha$ is given in the text.

Here we compare our work with the very recent one by Grenier et al. on CuGe$_{1-x}$Si$_x$O$_3$.[2] First we note that the systems are different: one is the substitution for Cu$^{2+}$, which has $S = 1/2$ spin on it, by Zn$^{2+}$ ($S = 0$) and the other is the substitution for Ge$^{4+}$ ($S = 0$) outside the spin chain by Si$^{2+}$ ($S = 0$). However the reduction of the SP transition and occurrence of AF-LRO have been observed to behave similarly and may be compared. As already stated, they measured the susceptibilities of their samples with $x_{Si} \geq 0.002$ and $x = 0$ down to 70 mK. Their conclusion that the pure CuGeO$_3$ does not undergo Néel transition and there is no critical concentration for the occurrence of the AF phase is consistent with our conclusion. However if we take their scaling relation $x_{Si} \simeq x_{Zn}/3$, our minimum concentration sample $x_{Zn} = 1.12(2) \times 10^{-3}$ corresponds to $x_{Si} \simeq 4 \times 10^{-4}$, which is about 5 times less than that of Ref. [2] and in fact this sample shows Néel transition at $T_N = 0.0285$ K, which is one order of magnitude lower than that of theirs ($T_N = 0.25$ K). Moreover their values of the concentration in the very low concentration region are uncertain and they drew their conclusion (absence of critical concentration) by modifying the concentration values by fitting to the suppression of SP transition (see Ref. [13]). This suggests (and also they themselves stated) that Zn-doped CuGeO$_3$ is more suitable for this kind of study. On the pure CuGeO$_3$ sample we measured the susceptibility down to 5 mK compared to their 70 mK. Therefore we may say that our study is extensive on the study of AF-LRO in the very low concentration region and that our experimental results and conclusion are more firmly established than theirs. Another important point is, as already stated, Zn-doped and Si-doped CuGeO$_3$ may belong to different systems. The phase diagram obtained in Fig. 8 of Ref. [13] seems to indicate that there is no first-order phase transition between D-AF and U-AF phases in Si-doped CuGeO$_3$ in contrast to the observation of the one in Mg-doped CuGeO$_3$ by Masuda et al.[14] This casts a grave doubt on the belief that the AF phase(s) in the both substitution systems for Cu$^{2+}$ and for Ge$^{4+}$ is similar. Therefore it is highly desirable to do the detailed experiments in both systems and compare them.

In conclusion we have revealed how the AF-LRO behaves when the Zn concentration is extremely low. The undoped CuGeO$_3$ does not have AF-LRO down to 12 mK. On the other hand, all the Zn-doped samples showed AF-LRO. The lowest observed $T_N$ was 0.0285 K in the sample with $x = 1.12(2) \times 10^{-3}$. From the concentration dependence of $T_N$ we concluded the absence of a critical concentration for the occurrence of AF-LRO. This may come from the fact that the dimerization sustains the phase coherence of the spin polarization and is also consistent with the theory of the impurity-doped SP system.[1] The temperature dependence of the susceptibilities at $T > T_N$ indicates that the magnetic correlations between localized spins are enhanced by a relatively large interchain interaction of CuGeO$_3$.

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