Antiferromagnetic Order with Spatially Inhomogeneous Ordered Moment Size of Zn- and Si-Doped $CuGeO_3$

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(Received 10 January 1997)

We report muon spin relaxation measurements of the doped spin-Peierls system $(Cu_{1-x}Zn_x)$-$(Ge_{1-y}Si_y)O_3$. Spontaneous muon spin precession in zero applied field was observed, confirming the presence of antiferromagnetic order in this series of compounds. In contrast to usual antiferromagnets, muon spin precession is accompanied by a relaxation signal indicating a large spatial inhomogeneity of the ordered moment size. Assuming an exponential decay of the moment size away from the doping centers, we estimated a decay length of $\xi \sim 10$ lattice units along the chain. We suggest that both Zn and Si doping induces the same maximum moment size around the doping center. [S0031-9007(97)03590-4]

PACS numbers: 75.40.Cx, 75.50.Ee, 76.75.+i

One-dimensional quantum spin systems have received considerable attention recently because of the quantum mechanical nature of their ground states. One particularly interesting phenomenon is the spin-Peierls transition: a structural transition coupled with singlet pairing of neighboring spins along an $S = 1/2$ antiferromagnetic spin chain. This type of transition was first observed in several organic compounds in the 1970's [1–3]. The discovery of a new spin-Peierls material $CuGeO_3$ [4], however, changed the course of experimental investigations of spin-Peierls phenomena, because this material allows doping at the spin site (Zn → Cu [5]) and at the side chain (Si → Ge [6]). From several previous measurements, antiferromagnetic order of Cu moments has been identified in both the Zn-doped systems [7–12] and the Si-doped systems [6,13,14].

To understand the ordering mechanism, recent theoretical investigations of the Si-doped system suggested that perturbations to the lattice may be important [15]. A silicon ion has a significantly smaller ionic radius than germanium and may cause local strain which prevents the spin-Peierls dimerization. The authors of Ref. [15] solved the spin-lattice Hamiltonian and showed that staggered moments are induced around the doping center, which leads to antiferromagnetic order. In the framework of this theory, both the lattice order parameter and the spin order parameter (ordered moment size) have a large spatial inhomogeneity; the size of the ordered moments will be maximum around the doping center, and decay exponentially along the chain (see Fig. 1). For the Zn-doped system, the mechanism responsible for the antiferromagnetic order is not yet clear; still, it has been proposed that a semi-infinite $S = 1/2$ spin chain will have staggered moments near the chain end [16,17]. If the lattice dimerization is somehow suppressed by Zn doping, the induced staggered moments may lead to an antiferromagnetic order. In this case as well, a large spatial inhomogeneity of the ordered moment size is expected [16].

Experimentally, spatial inhomogeneity of the moment size has been suggested from neutron diffraction measurements of the Zn-doped system [10]; as indirect evidence, the absence of low-temperature saturation of the antiferromagnetic Bragg peak intensity has been pointed out. However, direct evidence, such as diffuse scattering due to spatial inhomogeneity of moment size and/or lattice dimerization, has not been reported.

Muon spin relaxation (μSR) is a powerful method to investigate spatial inhomogeneity of ordered moments [18,19]. In a usual antiferromagnet, which has homogeneous and commensurate ordered moments, the coherent precession of muon spin is observed [20], because the local field at the muon site takes the same magnitude at every unit cell. With increasing inhomogeneity in the moment size, the muon spin precession becomes damped; in the limit of spatially uncorrelated magnetic order, the muon

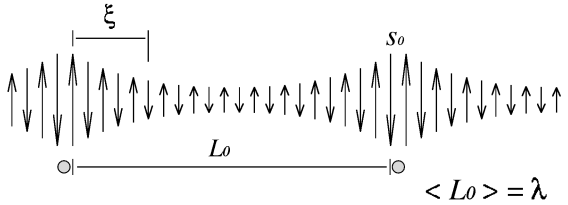

FIG. 1. Schematic view of an antiferromagnetic order with a spatial inhomogeneity. The moment size takes a maximum (s_0) around the doping center, and exponentially decays with a correlation length ξ.

spin relaxation is given by the so-called Kubo-Toyabe function, which is commonly observed in spin-glass systems [18] and from nuclear dipolar fields [19]. In this paper, we report zero-field muon spin relaxation in Si- and Zn-doped $CuGeO_3$, and compare the observed spectra with a model involving spatial inhomogeneity in the ordered moments.

Single crystalline samples of Si- and Zn-doped $CuGeO_3$ were grown using the floating-zone method as described in Refs. [6,8], and references therein. The crystals were cleaved and tiled on an Ag plate or sandwiched between thin mylar films. Muon spin relaxation measurements were performed at the TRIUMF continuous-beam muon facility. Spin polarized muons were implanted in the crystal with their spin polarized parallel to the a axis. The muon spin polarization was reconstructed from the forward-backward asymmetry of the decay positrons, using the zero-field/longitudinal field ZF/LF$-\mu$SR technique [19]. We used a conventional μSR spectrometer combined with a dilution refrigerator and/or a "low-background" apparatus [21] equipped with a ^{4}He flow cryostat.

In Fig. 2(a), we show typical muon spin relaxation spectra of the nominally pure and Si/Zn-doped compounds. In the undoped $CuGeO_3$, there was no antiferromagnetic order down to 0.05 K, supporting the nonmagnetic nature of the spin-Peierls ground state. In the doped systems, muon spin precession was observed, confirming the antiferromagnetic order of these compounds. In contrast to typical precession in well-ordered ferromagnets and/or antiferromagnets [20], the muon spin exhibited a relaxation signal together with the precession. We confirmed with longitudinal-field decoupling measurements [18,19] that the relaxation is due to a distribution of static fields, rather than dynamical T_1 relaxation. In Fig. 2(b), we show the Fourier transform of a spectrum for a Si-doped ($y = 0.02$) sample. There is spectral weight centered around zero frequency, and a continuum up to around 7 MHz (= 500 G).

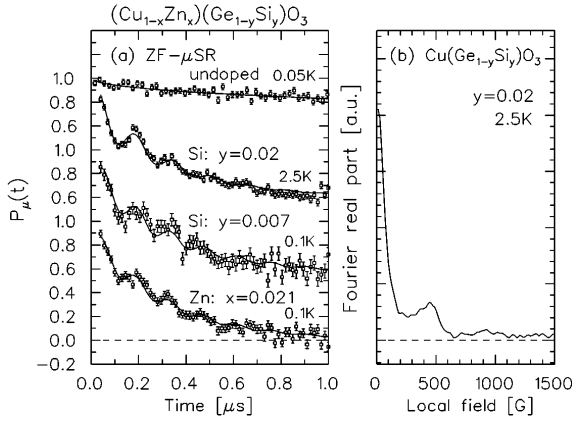

FIG. 2. (a) Zero-field μSR spectra of $(Cu_{1-x}Zn_x)(Ge_{1-y}Si_y)O_3$, the undoped system ($x = y = 0$), Si-doped systems ($y = 0.02$ and 0.007), and Zn-doped system [$x = 0.021(3)$]. The solid line is a phenomenological fit with Eq. (1). (b) Fourier transformed μSR spectrum of a Si doped system ($y = 0.02$).

The continuum suggests a broad field distribution in the sample with a maximum field of ~500 G. For analysis, we phenomenologically fit the μSR spectra in the time domain with a damped precession plus an exponential function

$$P_\mu(t) = A_{\rm rlx}\exp(-\Delta t) + A_{\rm osc}e^{-\Gamma t}\cos(2\pi f t + \phi). \quad (1)$$

In Fig. 3, the precession frequency (f) and the relaxation rate (Δ) are shown as a function of temperature. One interesting feature is that the frequency in the $T \to 0$ limit agrees within ~15% between the samples studied here. This suggests that the maximum local field observed (~500 G) does not depend on the doping type (Si or Zn), nor the Si concentration.

Since the precession and relaxation signals appear at the same temperature, and the ratio f/Δ is mostly temperature independent, it is probable that there is no macroscopic phase separation in the doped crystals. A natural explanation for the coexistence of the precession and the relaxation is a spatial inhomogeneity of ordered moments. This picture has been presented in a theory of Si-doped $CuGeO_3$ [15], which predicts a largest ordered moment size around the doping center, accompanied by a decay of moment sizes away from the center. As a simplified model, we assume the ordered moment size to have an exponential decay with a correlation length ξ:

$$S(x) \propto \exp(-x/\xi) + \exp[-(L_0 - x)/\xi] = s_0\cosh\left(\frac{x - L_0/2}{\xi}\right) \Big/ \cosh\left(\frac{L_0/2}{\xi}\right), \quad (2)$$

where L_0 is the length of the perturbed chain, x is the distance along the chain from one of the doping centers, and s_0 is the maximum moment size around the doping center.

Although the muon local field is a vector sum of the dipolar fields from every ordered moment, we approximate the local field is proportional to the size of moments

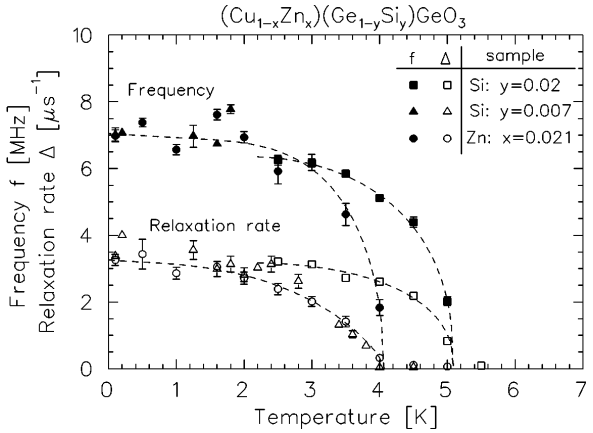

FIG. 3. Precession frequency (f) and the relaxation rate (Δ) of doped $CuGeO_3$. The dashed lines are guides to the eye. The T_N of the Si-doped $y = 0.007$ sample and the Zn-doped $x = 0.021(3)$ sample happened to be close to each other.

nearby: $H(x) \propto S(x)$. Since the dipolar fields quickly decay as r^{-3}, contributions from moments located further than 10 Å are generally negligible. This approximation does not change the general features of the local field distribution, especially when the correlation length ξ is significantly larger than the lattice spacing. The corresponding distribution of the local field is

$$\rho(H; L_0) = \frac{1}{L_0}\frac{dx}{dH} = \frac{2\xi}{L_0}\frac{1}{\sqrt{H^2 - H_{\min}^2}}, \qquad (3)$$

with the minimum and the maximum fields

$$H_{\min} = H_0/\cosh\left(\frac{L_0/2}{\xi}\right), \qquad (4)$$

$$H_{\max} = H_0\,. \qquad (5)$$

Here H_0 is a scaling factor which depends on the maximum moment s_0 and the muon site in the unit cell. The maximum and minimum local fields correspond, respectively, to the muon local field at the doping center [$H_{\max} = H(0)$] and at the middle of the perturbed chain [$H_{\min} = H(L_0/2)$].

In the doped systems, the chain length takes a Poisson distribution, with an average chain length $\lambda \equiv \langle L_0 \rangle$. We average Eq. (3) over the chain-length distribution, and show the resulting field distribution $\rho(H)$ and the corresponding muon spin relaxation $P_\mu(t)$ in Fig. 4.

The general behavior of the muon spin relaxation $P_\mu(t)$ is characterized by the ratio of the average chain length and the correlation length λ/ξ; when the ratio $\lambda/\xi < 2$, the muon spin exhibits damped oscillations around zero. In this regime, the chain length L_0 is comparable to the correlation length ξ, so that the local field becomes well defined. In the regime of $\lambda/\xi > 2$, the spectrum shows relaxation accompanied by a small-amplitude oscillation. The oscillation signal originates from muons which land near the doping center, and its amplitude decreases with larger λ/ξ ratios. The frequency of this small-amplitude precession is determined by the maximum field H_0, so that the frequency is independent of the λ/ξ ratio.

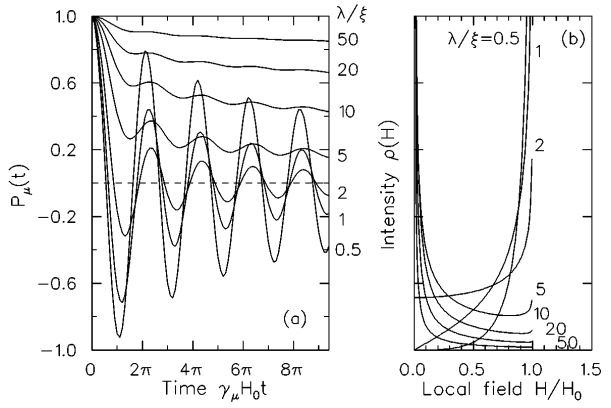

FIG. 4. (a) Muon spin relaxation and (b) local field distribution of spatially inhomogeneous antiferromagnetic order (Fig. 1), characterized by a correlation length ξ and the average chain length λ.

In order to compare the model relaxation [Fig. 4(a)] to the μSR data, we fit the model relaxation with Eq. (1), namely, the phenomenological function which we used for the μSR data analysis. From the fit, we obtained the precession amplitude $A_{\rm osc}$ and the phase shift ϕ as a function of the effective doping concentration $(\lambda/a)^{-1}$, and show them in Fig. 5 (solid lines). In the same figure, we plot our experimental results as well. In order to extract the correlation length ξ from the μSR data, one needs to know the average chain length λ, because muon is a local probe and its relaxation is characterized by the ratio λ/ξ. Here, we assumed that one Si ion perturbs *two* neighboring chains [$(\lambda/a)^{-1} = 2y$], whereas one Zn ion cuts one chain [$(\lambda/a)^{-1} = x$]. This assumption is based on the location of the doping sites (Zn → Cu and Si → Ge). Also, the enhancement factor of ~2 for the Si doping has been suggested by the doping concentration dependence of the spin-Peierls transition temperature compared to that of the Zn-doped systems [5,6,22]. With these assumptions of the effective doping concentrations, the precession amplitudes $A_{\rm osc}$ of both Si and Zn doping fall on the same correlation length, which is $\xi \sim 10$ lattice units. This is in agreement with the theoretical estimate of $\xi/a = 11.8$, which was obtained by the ratio of the spin-Peierls energy gap and the in-chain antiferromagnetic coupling of the undoped $CuGeO_3$ [15].

In the μSR measurements, the phase shift (ϕ) of the small amplitude precession generally took a large negative value [see Fig. 5(b)]. This is consistent with the behavior

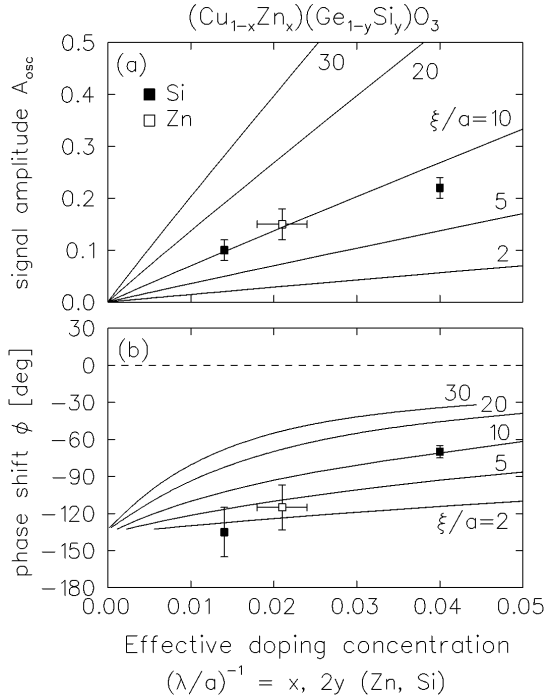

FIG. 5. (a) Muon spin oscillation amplitude $A_{\rm osc}$ and (b) the phase shift ϕ as a function of effective doping concentration $[(\lambda/a)^{-1}]$. The points are from our μSR data, with an assumption that a Si ion perturbs two neighboring chains, and a Zn ion affects one chain.

of our model relaxation [solid lines in Fig. 5(b)]. If the small-amplitude precession were caused by a small region of the usual antiferromagnetic order, the phase shift would be zero. Hence, the large negative shift supports the existence of spatial inhomogeneity of the ordered moment size [23].

As shown in Figs. 2(a) and 3, the muon precession frequency in the $T \to 0$ limit agrees within $\sim 15\%$ in the crystals we have measured. In our model relaxation, the frequency corresponds to the maximum field H_0, namely, the local field at the muon site closest to the maximum induced moment s_0. Indifference of the precession frequency to the samples suggests that the size of the maximum moment s_0 is independent of the doping type and the concentration. Since we do not know the muon site in $CuGeO_3$, it is not possible to determine s_0 from the observed field $H_0^{\rm obs} \sim 500$ G. Our dipolar field calculations for muon site candidates suggest that $s_0 = 0.2 \sim 0.5\ \mu_{\rm B}$ (see Table I [24]). This is in the same order of magnitude with the average ordered moment size ($\langle s \rangle \sim 0.2\ \mu_{\rm B}$), which has been obtained from a neutron scattering measurements of a Zn-doped $x = 0.034$ crystal [10].

In summary, we have observed spatially inhomogeneous antiferromagnetic order of Si- and Zn-doped $CuGeO_3$. A correlation length of the ordered moment $\xi/a \sim 10$ has been estimated, with the assumptions that one Si affects two neighboring chains, whereas one Zn ion cuts one chain. We have found that the maximum moment size (s_0) around the doping center seems to be independent of the doping type and concentration. The existence of large spatial inhomogeneity in the ordered moment size is a signature of true coexistence of Néel order and the spin-Peierls state in doped $CuGeO_3$ compounds; the moments appear in the vicinity of the doping center, where the disturbance to the spin-Peierls state is the maximum. Doped $CuGeO_3$ seems to be a first example which exhibits a competition between the two ground states, namely, a quantum mechanical ground state (spin-Peierls state) and the classical ground state (Néel state).

TABLE I. Maximum moment size s_0 for O($4j$)-μ bond length assumed.

Length $r_{0\mu}$ (Å)	Direction[a] θ (deg)	Dipolar field[b] H_0/s_0 (kG/μ_B)	Estimated s_0 (μ_B) for $H_0^{\rm obs} = 500$ G
0.9	−115(3)	2.8(2)	0.18(2)
1.0	−118(3)	2.5(2)	0.20(2)
1.1	−128(3)	1.8(2)	0.28(3)
1.2	−138(3)	1.2(2)	0.43(7)
1.3	−143(3)	0.8(2)	0.6(2)

[a]The angle between the a axis and the O-μ bond. The bond was found to be within the $a \times b$ plane. The O($4j$) ion is located at $x, y, 1/2$ ($x = 0.2813$, $y = 0.0838$) [25].
[b]The error shown is the systematic error due to an uncertainty of the local spin structure around the doping site.

The authors would like to thank Professor H. Fukuyama and Dr. G. Shirane for very helpful discussions. One of the authors (K. M. K.) acknowledges financial support from JSPS. This research has been supported by NEDO (Japan) and NSF (DMR-95-10454). Laboratoire de Chimie des Solides and Institut d'Electronique Fondamentale are Unités Associées au Centre National de la Recherche Scientifique.

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[23] It is generally shown that the phase shift (ϕ) of a precession signal originates from an asymmetry of the spectral weight around the peak frequency (f). The large negative phase shift in the doped $CuGeO_3$ is a direct consequence of the continuum below $H_0 \sim 500$ G.
[24] For the muon site estimate, we assumed (1) O-μ bond formation with a bond length ($r_{O\mu}$) and (2) point charges at the neighboring atomic positions. We find the bond direction which minimizes the electrostatic potential. For dipolar field calculations, we assumed the spin orientation ($\| c$ axis) and the periodicity (F/AF/AF in the $a/b/c$ axis direction) determined by neutron scattering measurements [10].
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