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Cu nuclear quadrupole resonance study of the spin-Peierls compound $Cu_{1-x}Mg_xGeO_3$: A possibility of precursory dimerization

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We report on a zero-field ^{63}Cu nuclear quadrupole resonance (NQR) study of nonmagnetic Mg impurity substituted $Cu_{1-x}Mg_xGeO_3$ (single crystals; the spin-Peierls transition temperature $T_{sp}\sim 14$, 13.5, and 11 K for $x=0$, 0.0043, and 0.020) in a temperature range from 4.2 to 250 K. We found that below $T^*\sim 77$ K, Cu NQR spectra are broadened and nonexponential Cu nuclear spin-lattice relaxation increases for undoped and more remarkably for Mg-doped samples. The results indicate that random lattice distortion and impurity-induced spins appear below T^*, which we associate with a precursor of the spin-Peierls transition. Conventional magnetic critical slowing down does not appear down to 4.2 K below T_{sp}.

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The discovery of the first inorganic spin-Peierls compound $CuGeO_3$ (the transition temperature $T_{sp}\sim 14$ K) (Ref. 1) and subsequent reports on unprecedented impurity effects[2–7] have renewed the interests of a quasi-one-dimensional spin $S=1/2$ Heisenberg antiferromagnet coupled to phonons. No soft mode of phonon at T_{sp} is one of the characteristics of $CuGeO_3$. An appreciable interchain exchange interaction,[8] lattice, and phonon anomaly perpendicular to the chain[9,10] are different from an ordinary spin-Peierls system or conventional theoretical result.[11] A pseudogap in the magnetic excitation spectrum below 20 K observed by inelastic neutron scattering[12] and a local dimerization until at least 40 K observed by diffusive X-ray scattering[13] resemble a pseudogap of the electronic Peierls materials.[14] In contrast to conventional competition between Néel ordering and lattice dimerization, the impurity substitution (Zn, Mg, Ni, or Si) for Cu or Ge induces a dimerized antiferromagntic ordering state,[3–6] where a spin-wave mode coexists in the spin-Peierls gap.[7] The coexistence at $T=0$ K is understood within the framework of the phase Hamiltoninan.[15]

Nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) are unique and powerful techniques to study low-frequency dynamics and local spin fluctuations in space. The intensive studies using Cu NQR and NMR techniques have revealed many aspects of $CuGeO_3$.[16–19] The spin-gap opening at T_{sp} was evidenced by an abrupt decrease of the Cu nuclear spin-lattice relaxation rate $1/T_1$ without any appreciable change of Cu NQR spectrum,[16] although a singlet-triplet excitation, a spin gap, and ion displacement were directly confirmed by neutron scattering.[20,21] The above T_{sp} spin dynamics, the Cu $1/T_1$, is understood by a quasi-one-dimensional $S=1/2$ antiferromagnetic correlation without spin-phonon coupling.[16,22,23] To our knowledge, however, there are no reports of Cu NQR spectrum far above T_{sp} for $CuGeO_3$ nor of impurity effects on the low-frequency spin dynamics, after the work on Zn doping.[24]

In this Communication, we report the high-temperature measurement of Cu NQR spectrum for undoped $CuGeO_3$ and the Cu NQR study of nonmagnetic Mg impurity substitution effect on $Cu_{1-x}Mg_xGeO_3$ (single crystals; $T_{sp}\sim 14$, 13.5, and 11 K for $x=0$, 0.0043, and 0.020) in a wide temperature range of $T=4.2$–250 K. We found that the broadening of Cu NQR spectra and the increase of nonexponential Cu nuclear spin-lattice relaxation occur below about 77 K much higher than T_{sp}, which suggest a precursor of the spin-Peierls transition. We did not observe critical divergence of $1/T_1$ for $x=0.020$ down to 4.2 K, although the magnetic ordering occurs at about 2.5 K.[4]

The single crystals grown by a floating-zone method are well characterized in Ref. 4. Zero-field ^{63}Cu NQR spin-echo measurements were carried out with a coherent-type pulsed spectrometer. NQR frequency spectra with quadrature detection were measured by integration of the ^{63}Cu nuclear-spin echoes as the frequency was changed point by point. Nuclear spin-lattice relaxation was measured by an inversion recovery spin-echo technique, where the ^{63}Cu nuclear spin-echo amplitude $M(t)$ was recorded as a function of time interval t, between an inversion π pulse and a $\pi/2$ pulse ($\pi-t-\pi/2-\pi$-echo).

Figure 1 shows ^{63}Cu NQR spectra for undoped $x=0$ (a) and for Mg doping of $x=0.020$ (b) in the temperature range of $T=4.2$–250 K. The observed Cu NQR spectra for Mg doping are nearly symmetrically broadened, not of Gaussian nor of Lorentzian type but rather have a triangle-shaped line profile for $x=0.020$ at 4.2 K. Implication of the characteristic line shape is not clear. In general, the Cu NQR frequency ν is given by $\nu=(e^2qQ/2h)\sqrt{1+\eta^2/3}$, where eq is the maximum component of the electric-field gradient tensor at the nuclear site, Q is the nuclear quadrupole moment, and η $(0\leqslant\eta\leqslant 1)$ is an asymmetry factor.[25] The muon spin-relaxation measurements have not detected any static internal magnetic field for Zn-doped samples above about 4 K.[6] Thus it is likely that the random distribution of the electric-field gradient (eq and η) is the origin of broadening.

Figure 1(c) shows the temperature dependence of the peak frequency $^{63}\nu$ for $x=0$, 0.0043, and 0.020. The observed

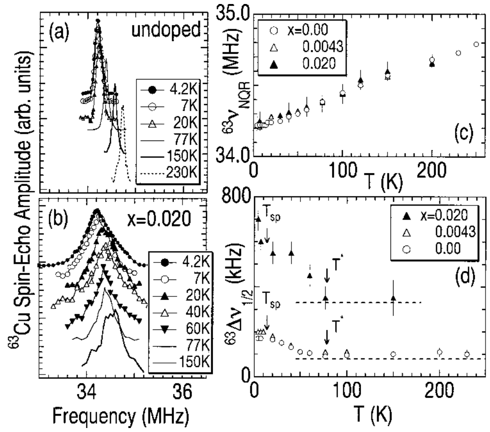

FIG. 1. The temperature dependence of ^{63}Cu NQR frequency spectrum for $x=0$ (a) and for $x=0.020$ (b). The temperature dependence of the peak frequency $^{63}\nu$ (c) and of the linewidth (full width at half maximum) $^{63}\Delta\nu_{1/2}$ (d) for $x=0$, 0.0043, and 0.020. The dashed lines in (d) are guides to the eye.

linear temperature dependence of $^{63}\nu$, nearly independent of Mg content, is similar to that of the cuprate mono-oxide CuO.[26] Figure 1(d) shows the temperature dependence of the linewidth defined as full width at half maximum $^{63}\Delta\nu_{1/2}$. The linewidth as well as the peak frequency does not show any appreciable change at T_{sp}, in agreement with the previous reports on $CuGeO_3$.[16,22,27] The linewidth of the $x=0.020$ sample is about three times larger than that of $x=0$ at $T>T^*$. In Fig. 1(d), we obtain a significant result that $^{63}\Delta\nu_{1/2}$ increases rapidly below about 77 K$\gg T_{sp}$ (denoted as T^*) for all samples including $CuGeO_3$. For each x, $^{63}\Delta\nu_{1/2}$ at 4.2 K is about two times larger than that above T^*.

NQR is a measure of deviation of charge distribution from cubic symmetry around the nuclear site, being quite sensitive to crystal imperfections. The observed nearly symmetric line shape implies a random distribution of local charge.[25] If the origin of $^{63}\Delta\nu_{1/2}$ is a static distribution of lattice distortion around crystal imperfection, $^{63}\Delta\nu_{1/2}$ would decrease as the temperature is decreased so as to scale with the temperature dependence of $^{63}\nu$. However, the actual $^{63}\Delta\nu_{1/2}$ increases below T^*. Thus the inhomogeneity of lattice distortion must depend on temperature and must increase rapidly below T^*. Without dimerization, a freezing of some lattice motion below T^* and the active motion above T^* would lead to the observed temperature dependence of $^{63}\Delta\nu_{1/2}$. However, no softening of phonon at T^* has been observed in these materials, i.e., no slowing down of lattice motion. The appearance of nonexponential nuclear spin-lattice relaxation at T^* (shown below) could not be accounted for by a uniform freezing of the lattice motion. Some inhomogeneous electron spin-lattice formation must be caused at T^*. The pretransitional lattice fluctuations above T_{sp} observed by the diffraction experiment,[13] which are explained by the random-phase approximation calculation,[28] may be closely related with the increase of $^{63}\Delta\nu_{1/2}$. According to the recent quantum Monte Carlo simulation,[29] a precursory dimerization takes place near the edges far above T_{sp}. T^* corresponds to the onset of preformed dimer bonds. In the soliton picture,[30] T_{sp} is an order-to-disorder transition temperature of locally dimerized segments. T^* may correspond to the onset of development of the interchain correlation between the soliton and antisoliton.

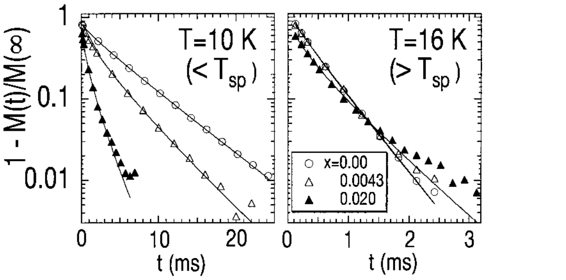

FIG. 2. Mg-doping dependence of ^{63}Cu recovery curves 1-$M(t)/M(\infty)$ at 10 K (a) and at 16 K (b) for $x=0$, 0.0043, and 0.020. The solid curves are the least-squares fitting results using Eq. (1).

Figure 2 shows Mg-doping effect on ^{63}Cu recovery curve $p(t)\equiv 1-M(t)/M(\infty)$ of the ^{63}Cu nuclear magnetization $M(t)$ at 10 K ($<T_{sp}$) (a) and at 16 K ($>T_{sp}$) (b). The recovery curve changes from a single exponential function to nonexponential one as Mg is substituted and as the temperature is decreased. To account for the nonexponential function, we assume a minimal model, which consists of a host homogeneous relaxation process and of a single inhomogeneous relaxation one. The solid curves are the least-squares fitting results using the following equation:[31]

$$p(t)=p(0)\exp[-(t/T_1)_{NQR}-\sqrt{t/\tau_1}]. \tag{1}$$

The fit parameters are $p(0)$, $(T_1)_{NQR}$,[32] and τ_1. $p(0)$ is a fraction of an initially inverted magnetization, and $(T_1)_{NQR}$ is the nuclear-spin-lattice relaxation time due to the host Cu spin fluctuations. τ_1 is an impurity-induced nuclear-spin-lattice relaxation time, which is originally termed a longitudinal direct dipole relaxation time, because the second term of Eq. (1) is derived from a random T_1 process of $1/T_1(r)=C/r^6$ (C is a constant, and r is a distance between an impurity-induced spin S and a Cu nuclear spin I) through a direct dipole coupling $\propto I_\pm S_z/r^3$ (S_z is the z component of S, and $I_\pm$ is a raising or lowering operator of I). The randomly distributed impurity-induced spins yield the stretched exponential function of Eq. (1). The original Mg ion does not carry spin 1/2. Atomic defects or Mg ions cut chains into segments. The existence of spatially extended staggered moment induced by an edge or an impurity has been pointed out for a finite or a semi-infinite chain.[29,30,33] The assumption of impurity-induced spins could be only a working hypothesis to introduce τ_1. Since the essence of the stretched exponential function is randomness in the T_1 process, one may speculate that $T_1(r)$ with a local-spin density induced by Mg is approximated by a power law, leading to the stretched exponential function. In the soliton picture,[30] the soliton which stays in the middle of a segment or near the edges due to an interchain coupling, carries spin 1/2, so that it can act as an impurity spin.

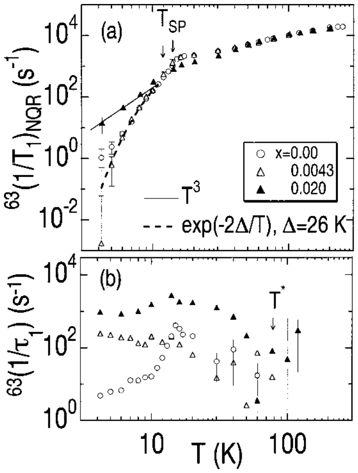

FIG. 3. Log-log plots of $^{63}(1/T_1)_{NQR}$ (a) and $^{63}(1/\tau_1)$ (b) as functions of temperature for undoped $x=0$ and for Mg-doped samples of $x=0.0043$ and 0.020. In (a), the solid line is a T^3 function, and the dashed curve is the least-squares fitting result using a function of $1/T_1=R_1\exp(-2\Delta/T)$.

Figure 3 shows log-log plots of $^{63}(1/T_1)_{NQR}$ (a) and $^{63}(1/\tau_1)$ (b) as functions of temperature for $x=0$, 0.0043, and 0.020. Far above T^*, $^{63}(1/T_1)_{NQR}$ for Mg-doped samples is nearly the same as that for an undoped one. For undoped and $x=0.0043$, the activation-type temperature dependence of $^{63}(1/T_1)_{NQR}$ is observed below T_{sp}. The spin gap Δ is estimated to be $\sim$26 K by fits of $1/T_1=R_1\exp(-2\Delta/T)$ (R_1 and Δ are fitting parameters),[34] which agrees with the value estimated from the static susceptibility.[1] For $x=0.020$, however, the temperature dependence of $^{63}(1/T_1)_{NQR}$ is changed into a power-law type ($\sim T^3$), probably because of an inhomogeneous distribution of $\Delta(r)$. Conventional critical divergence toward the magnetic ordering does not appear.

Below around T^*, $^{63}(1/\tau_1)$ immediately increases as the temperature is decreased down to T_{sp} even for $x=0$, which indicates the increase of the impurity-induced spin correlation. Far below T_{sp}, $^{63}(1/\tau_1)$ is systematically enhanced by Mg doping, which is due to an increase of the number of impurity relaxation centers. It is likely that the origin of $^{63}(1/\tau_1)$ for $x=0$ is due to nonintentionally introduced imperfections (defects, dislocations, . . .). The actual sample is not a perfect crystal, because the observed linewidths of ^{63}Cu NQR spectra of our $x=0$ ($\sim$180 kHz at 4.2 K, $\sim$100 kHz above 100 K) are broader than those expected from T_1 or T_2 broadening (a few kHz), i.e., inhomogeneous broadening. The estimated $^{63}\Delta\nu_{1/2}$ for $x=0$ is nearly the same as or somewhat sharper than the reported values below 40 K.[16,17,22,27] In Fig. 3(b), $^{63}\tau_1$ for each x makes a kink at around T_{sp}. In terms of an impurity spin picture, $^{63}(1/\tau_1)$ is nearly proportional to the lifetime of the impurity spin scattered by the host magnetic excitations. Then, the kink of $^{63}(1/\tau_1)$ reflects a change in the host magnetic excitation spectrum at the true transition temperature T_{sp}, which is evident in $^{63}(1/T_1)_{NQR}$.

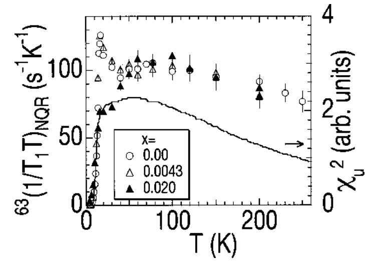

FIG. 4. The temperature and Mg-doping dependence of $^{63}(1/T_1T)_{NQR}$. The solid curve is the squared static uniform susceptibility χ_u^2 of undoped $CuGeO_3$ reproduced from Ref. 1.

Figure 4 shows the Mg-doping effect on $^{63}(1/T_1T)_{NQR}$. For comparison, the squared static susceptibility χ_u^2 of undoped $CuGeO_3$ (solid curve) is also reproduced from Ref. 1. In general, $1/T_1T$ is the low-frequency dynamical spin susceptibility at an NQR frequency summed over a momentum space via a nuclear-electron coupling.[35] For $x=0$ above T_{sp}, $^{63}(1/T_1T)_{NQR}$ is understood by the sum of the staggered spin susceptibility $\chi(q=\pi)\sim 1/T$ and the Bonner-Fisher-type uniform spin susceptibility χ_u (to be exact, χ_u^2).[22,23] The upturn of $^{63}(1/T_1T)_{NQR}$ just above T_{sp}, which is ascribed to the staggered $\chi(q=\pi)\sim 1/T$, is suppressed by Mg doping of $x=0.020$. Then, the contribution from the uniform mode $q=0$ is uncovered, being similar to the temperature dependence of χ_u^2. The $q=\pi$ mode is easily affected by imperfection, comparatively more than the $q=0$ mode, as can be seen for $La_2Cu_{1-x}Zn_xO_4$.[36] However, one should note that $^{63}(1/T_1T)_{NQR}$ for $x=0.020$ and χ_u^2 for $x=0$ above T_{sp} are similar but do not completely agree with each other. The suppression of $^{63}(1/T_1T)_{NQR}$ for $x=0.020$ begins from below 60–120 K more steeply than that of χ_u^2 below about 50 K. Thus the further mechanism of the suppression is needed. The precursory dimerization enhanced by Mg below around T^* is a possible candidate. Our observations of the suppressed $\chi(q=\pi)$ and of the deviation between $^{63}(1/T_1T)_{NQR}$ and χ_u^2 for Mg-doped samples will be constraints on dynamical theory toward the low-temperature dimerized antiferromagnetic transition.

To conclude, below $T^*\sim 77$ K, the inhomogeneous broadening of Cu NQR spectra and the impurity-induced Cu nuclear spin-lattice relaxation occur for undoped and more remarkably for Mg-doped $CuGeO_3$. Precursory dimerization, inhomogeneous in real space, is suggested. The host antiferromagnetic correlation above T_{sp} is suppressed by Mg doping of $x=0.020$. No magnetic critical divergence down to 4.2 K is a puzzle.

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