Cu Nuclear Quadrupole Resonance Study of the Spin-Peierls Compound 
Cu$_{1-x}$Mg$_x$GeO$_3$: A Possibility of Precursory Dimerization

Y. Itoh$^{1,2}$, T. Machi$^1$, N. Koshizuka$^1$, T. Masuda$^3$, and K. Uchinokura$^3$

$^1$Superconductivity Research Laboratory, International Superconductivity Technology Center, 1-10-13 Shinonome, Koto-ku Tokyo 135-0062, Japan
$^2$Japan Science and Technology Corporation, Japan
$^3$Department of Advanced Materials Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

We report on a zero-field $^{63}$Cu nuclear quadrupole resonance (NQR) study of nonmagnetic Mg impurity substituted Cu$_{1-x}$Mg$_x$GeO$_3$ (single crystals; the spin-Peierls transition temperature $T_{sp} \sim 14, 13.5$, and $11$ K for $x=0.0043$, and $0.020$) in a temperature range from 4.2 K 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 $T_{sp}$.

The discovery of the first inorganic spin-Peierls compound CuGeO$_3$ (the transition temperature $T_{sp} \sim 14$ K) [1, 2] and subsequent reports on unprecedented impurity effects [3, 4] 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 inter-chain exchange interaction [5], lattice and phonon anomaly perpendicular to the chain [6, 7, 8] are different from an ordinary spin-Peierls system or conventional theoretical result [1, 9]. A pseudogap in the magnetic excitation spectrum below 20 K observed by inelastic neutron scattering [10] and a local dimerization until at least 40 K observed by diffusive X-ray scattering [11, 12] resemble a pseudogap of the electronic Peierls materials [11]. 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 antiferromagnetic ordering state [11, 12], where a spin-wave mode coexists in the spin-Peierls gap [13]. The coexistence at $T=0$ K is understood within the framework of the phase Hamiltonian [13].

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$_3$ [14, 15]. 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 [12].

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 [22].

In this Letter, 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$_x$GeO$_3$ (single crystals; $T_{sp} \sim 14, 13.5$, and $11$ K for $x=0.0043$, 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 [13].

The single crystals grown by a floating-zone method are well characterized in Ref. [13]. 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 $\pi$-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
is about 3 times larger than that of Mg content, is similar to that of the peak frequency does not show any appreciable inhomogeneity of lattice distortion must depend on temperature and must increase rapidly below \( T^* \). 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 \( \Delta \nu_{1/2} \). 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.

Figure 2 shows Mg-doping effect on \( ^{63}\text{Cu} \) recovery curve \( p(t) \equiv 1 - M(t)/M(\infty) \) of the \( ^{63}\text{Cu} \) nuclear magnetization \( M(t) \) at 10 K (\( \leq T_{sp} \)) (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],

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

The fit parameters are \( p(0), (T_1)_{NQR} \) [32] and \( \tau_1 \). \( p(0) \) 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. \( \tau_1 \) 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 \( J \)) through a direct dipole coupling.
\(\alpha I_{\pm} S_z/\nu^3\) (\(S_z\) 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, so that it can act as an impurity spin picture \([30]\), the soliton which stays in the middle of a segment or near the edges due to an interchain coupling. The assumption of impurity-induced spins could be only a working hypothesis to introduce \(\tau_1\). 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 \([31]\), 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.

Figure 3 shows 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. 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 \(\Delta\) is estimated to be \(\sim 26\) K by fits of \(1/T_1= R_1\exp(-2\Delta/T)\) (\(R_1\) and \(\Delta\) are fitting parameters) \([32]\), 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 \(T_{sp}\) for even \(x=0\), 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 non-intentionally introduced imperfections (defects, dislocations, . . . ). The actual sample is not a perfect crystal, because the observed linewidths of \(63\text{Cu NQR} \) 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 \(63_{\Delta \nu}/2\) 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 life time 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 \(63(1/T_1)_{NQR}\).

Figure 4 shows the Mg-doping effect on \(63(1/T_1 T)_{NQR}\). For comparison, the squared static susceptibility \(\chi^2\) of undoped CuGeO\(_3\) is also reproduced from Ref. [1]. In general, \(1/T_1 T\) 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 \(T_{sp}\), \(63(1/T_1 T)_{NQR}\) is understood by the sum of the staggered spin susceptibility \(\chi(q=0)\)
π)\sim 1/T and the Bonner-Fisher-type uniform spin susceptibility \chi_u (to be exact, \chi^2_u) [23]. The upturn of \(\chi_{QNR}\) 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 \(\chi^2_u\). The \(q = \pi\) mode is easily affected by imperfection, comparatively more than the \(q=0\) mode, as can be seen for La2Cu1-xZnxO4 [36]. However, one should note that \(\chi_{QNR}\) for \(x=0.020\) and \(\chi^2_u\) for \(x=0\) above \(T_{sp}\) are similar but do not completely agree with each other. The suppression of \(\chi_{QNR}\) for \(x=0.020\) begins from below 60-120 K more steeply than that of \(\chi^2_u\) 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 \(\chi_{QNR}\) and \(\chi^2_u\) 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 CuGeO3. 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.

We thank Dr. J. Kikuchi, and Prof. M. Ogata for stimulating discussions. This work was supported by New Energy and Industrial Technology Development Organization (NEDO) as Collaborative Research and Development of Fundamental Technologies for Superconductivity Applications.

---

[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. 70, 3651 (1993).
[2] M. Hase et al., Phys. Rev. Lett. 71, 4059 (1993); Physica B 215, 164 (1995); S. B. Oseroff et al., Phys. Rev. Lett. 74, 1450 (1995).
[3] L. P. Regnault et al., Europhys. Lett. 32, 579 (1995).
[4] T. Masuda et al., Phys. Rev. Lett. 80, 4566 (1998); Phys. Rev. B 61, 4103 (2000); Y. J. Wang et al., Phys. Rev. Lett. 83, 1676 (1999); H. Nakano et al., J. Phys. Soc. Jpn. 68, 3662 (1999).
[5] N. Koide et al., Czech. J. Phys. 46, 1981 (1996); S. Coad, J-G. Lussier, and D. F. McK. Paul, J. Phys. Mater 8, 6251 (1996).
[6] K. M. Kojima et al., Phys. Rev. Lett. 79, 503 (1997).
[7] M. C. Martin et al., Phys. Rev. B 56, 3173 (1997).
[8] M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B 50, 6508 (1994).
[9] M. Braden et al., Phys. Rev. Lett. 80, 3634 (1998); ibid. 83, 1858 (1999).
[10] J. E. Lorenzo et al., Phys. Rev. B 50, 1278 (1994).
[11] M. C. Cross, and D. S. Fisher, Phys. Rev. B 19, 402 (1979).
[12] L. P. Regnault et al., Phys. Rev. B 53, 5579 (1996).
[13] J. P. Pouget et al., Phys. Rev. Lett. 72, 4037 (1994); J. P. Schoeffel et al., Phys. Rev. B 53, 14971 (1996).
[14] P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).
[15] H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Jpn. 65, 1182 (1996); M. Saito and H. Fukuyama, ibid. 66, 3259 (1997).
[16] J. Kikuchi et al., J. Phys. Soc. Jpn. 63, 872 (1994).
[17] M. Itoh et al., Phys. Rev. B 54, R9631 (1996); ibid. 53, 11606 (1996); Physica C 263, 486 (1996).
[18] Y. Fagot-Revurat et al., Phys. Rev. Lett. 77, 1861 (1996); M. Horvatic et al., ibid. 83, 420 (1999).
[19] Y. Fagot-Revurat et al., Phys. Rev. B 55, 2964 (1997).
[20] O. Fujita et al., Phys. Rev. Lett. 74, 1677 (1995); M. Arai et al., Phys. Rev. Lett. 77, 3649 (1996).
[21] K. Hirota et al., Phys. Rev. Lett. 73, 736 (1994).
[22] M. Itoh, S. Hirashima, and K. Motoya, Phys. Rev. B 52, 3410 (1995).
[23] A. Yu. Zavidonov, I. A. Larionov, and M. Itoh, Phys. Rev. B 61, 11625 (2000).
[24] M. Itoh et al., Physica B 281&282, 671 (2000).
[25] M. H. Cohen and F. Reif, Solid State Phys. 5, 321 (1964).
[26] Y. Itoh et al., J. Phys. Soc. Jpn. 59, 1143 (1990).
[27] A. A. Gippius et al., J. Phys. Condens. Matter 12, L71 (2000). In contrast to this report, we did not observe any split of the Cu NQR spectrum with quadrature detection for undoped CuGeO3, being in agreement with the other reports [16, 17, 22].
[28] C. Gros and R. Werner, Phys. Rev. B 58, R14677 (1998); M. Holicki, H. Fehske, and R. Werner, Phys. Rev. B 63, 174417 (2001).
[29] H. Onishi and S. Miyashita, J. Phys. Soc. Jpn. 69, 2634 (2000).
[30] D. Khomskii, W. Geertsema, and M. Mostovoy, Czech. J. Phys. 46, 3239 (1996); M. Mostovoy, and D. Khomskii, Z. Phys. B 103, 209 (1997).
[31] M. R. McHenry, B. G. Silbermagel, and J. H. Wernick, Phys. Rev. Lett. 27, 426 (1971); Phys. Rev. B 5, 2958 (1972).
[32] In Refs. [16, 17, 22], \(1/T_1\) is estimated by \(p(t) = p(0)\exp(-3t/T_1)\). But, under an asymmetric electric field gradient (an asymmetry factor \(\eta \sim 0.16 [16, 17]\)), all the \(x-, y-,\) and \(z\)-components of the local field fluctuations contribute to zero-field Cu \(T_{QNR}\). Then, a numerical factor 3 is not needed.
[33] S. Eggert and I. Affleck, Phys. Rev. Lett. 75, 934 (1995); M. Takigawa et al., Phys. Rev. B 55, 14129 (1997).
[34] E. Ehrenfreund and L. S. Smith, Phys. Rev. B 16, 1870 (1977).
[35] T. Moriya, J. Phys. Soc. Jpn. 18, 516 (1963); Prog. Theor. Phys. 16, 641 (1956).
[36] K. Uchinokura et al., Physica B 205, 234 (1995); P. Carretta, A. Rigamonti, and R. Sala, Phys. Rev. B 55, 3734 (1997).