Raman-scattering study of the anomalous spin-Peierls state in heavily Mg-doped $CuGeO_3$ under pressure

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By means of Raman scattering we have observed the appearance of the folded phonon modes and the two-magnetic-excitation bound state under high pressures in 3.5% Mg-doped $CuGeO_3$ crystals. The spin-Peierls (SP) gap mode is also observed. These facts indicate clear evidence that the SP phase transition extinguished by Mg doping is revived by the application of high pressure. The revived SP state has a large spin gap and a very weak lattice dimerization when compared with pure sample, which is interpreted in terms of the strongly frustrated spin chain with a spontaneous spin gap. Moreover, a new phonon peak is observed above 2.8 GPa in the SP phase and even far above the SP transition temperature, indicating a pressure-induced structural phase transition. We propose a P-T phase diagram for this sample.

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I. INTRODUCTION

One-dimensional quantum spin systems have attracted much attention mainly due to the intriguing phase transitions driven by strong quantum fluctuations. When the spins of $S=1/2$ are interacting with the underlying lattice, the spin-Peierls (SP) state is formed at low temperatures. In the SP phase the chain becomes dimerized and the spins form a singlet state, producing a gap in the magnetic excitation spectrum.

An inorganic $CuGeO_3$ crystal has one-dimensional spin-1/2 Cu^{2+} chains along the c axis and Hase *et al.*[1] found by the magnetic-susceptibility measurement that the SP transition occurred at $T_{SP}\cong 14$ K. Since this discovery in $CuGeO_3$, many interesting physical properties in the SP state have been revealed. One of them is the impurity effect in SP system.[2] The ability to introduce both in-chain and interchain dopants in $CuGeO_3$ allows us to change the spin-spin and the interchain magnetic interactions. The impurity doping suppresses the occurrence of the SP transition and activates an underlying antiferromagnetic (AF) phase transition, which compete with each other.[2–7] When the dopant concentration was low, the coexistence of both the SP and AF phases was confirmed by neutron scattering,[8–11] i.e., the dimerized AF phase is formed at low temperatures. At high dopant concentrations, the long-rang SP order disappears and the uniform AF phase without the lattice dimerization is stabilized. From the magnetic-susceptibility study in high-quality $Cu_{1-x}Mg_xGeO_3$ crystals, Masuda *et al.*[12] stated that a compositional first-order phase transition between the dimerized and uniform AF phases occurred at a critical concentration x_c and, consequently, the Néel temperature exhibits a conspicuous jump. With increasing impurity concentration above x_c the SP correlation length quickly decreases.[13,14] Detailed studies revealed that a separation of the dimerized and uniform AF phases existed around x_c.[14–16] The critical concentration x_c for Mg is approximately 2.3% at ambient pressure.[12] A similar temperature-impurity concentration phase diagram was obtained also for Zn-doped $CuGeO_3$.[15]

The temperature dependence of the magnetic susceptibility above T_{SP} deviates largely from the Bonner-Fisher theoretical curve.[1] The nearest-neighbor (nn) AF exchange interaction J_{nn} competes with the next-nearest-neighbor (nnn) AF exchange interaction J_{nnn} in $CuGeO_3$. The temperature dependence of the magnetic susceptibility experimentally observed was well described in terms of the *frustrated* quantum spin chain with a frustration parameter $\alpha=J_{nnn}/J_{nn}=0.24$–$0.36$.[17,18] Kuroe *et al.*[19] studied the quasielastic light scattering from the spin fluctuations due to the energy density in $CuGeO_3$ and obtained the magnetic specific heat above T_{SP}. The temperature dependence of the specific heat was also described with $\alpha=0.3$–0.4.

The existence of the strong frustration of the spin interactions in $CuGeO_3$ was pointed out, while it is well known that the theory[20,21] predicts a critical value $\alpha_c=0.2411$ for a finite spontaneous spin gap to develop in the magnetic excitation spectrum of the one-dimensional spin system without a lattice distortion.

The SP transition temperature T_{SP} of pure $CuGeO_3$ increases on applying hydrostatic pressure.[22,23] Neutron-inelastic-scattering[24,25] and Raman-scattering[26] studies showed that the SP-gap energy $\hbar\Delta$ also increased with increasing pressure. These facts indicate that the application of pressure stabilizes the SP state. On applying pressure, the length of the b axis strongly decreases[27] and the interchain exchange interaction J_b along the b axis is expected to increase, while the c axis and the Cu-O(2)-Cu bond angle and bond length change only slightly. Here the bond angle and length strongly reflect the magnitude of J_{nn}.[28] This leads to a prediction that the SP state becomes unstable, while the AF state is stabilized by the enhancement of the three dimensionality, but in fact the SP state becomes stable under pressure. Nishi *et al.*[24,25] obtained the dispersion curves of the magnetic excitation by inelastic neutron scattering at high

pressure. They observed a decrease of the energy of the Brillouin-zone-boundary magnetic excitation along the *c* axis at high pressure. The energy of the zone-boundary magnetic excitation reflects the magnitude of the nearest-neighbor exchange interaction J_{nn}. They estimated J_{nn} and the next nearest-neighbor one J_{nnn} in the frame of the spin-wave theory, resulting in a decrease in J_{nn} and an increase in the frustration parameter α. van Loosdrecht *et al.*[26] obtained a similar result from the Raman-scattering experiment on the pressure dependence of the frequency of the zone-boundary two-magnetic-excitation peak coming from the magnetic-excitation density of states.

Their analyses treated the SP-gap energy $\hbar\Delta$ phenomenologically as a uniaxial anisotropic magnetic energy in the spin-wave theory. According to the mean-field theory in the *unfrustrated* spin chain, the SP-gap energy at 0 K is given as $\hbar\Delta_0 = 1.76k_BT_{SP} = 2.4J_{nn}\exp(-0.48\omega_0^2 J_{nn}/g^2)$, where g is the spin-phonon coupling parameter and ω_0 is the frequency of the characteristic phonon at Brillouin-zone boundary.[29] Since g and ω_0 are almost independent of pressure, the observed increase in Δ_0 and T_{SP} upon applying pressure would be due to an increase in J_{nn} in the *unfrastrated* spin chain, which is contrary to the above-mentioned facts. The increase of the frustration parameter α, therefore, undertakes an important role in stabilizing the SP phase in $CuGeO_3$ under high pressures. However, a more sophisticated analysis is needed to reveal the mechanism of the SP transition at high pressures.

As mentioned above, the impurity doping suppresses the SP transition. On the other hand, the pressure dependence of T_{SP} of doped sample was reported to be strongly enhanced over that of pure sample,[30,31] i.e., the pressure effects on doped sample are expected to be stronger than those of pure one. Recently Masuda *et al.*[32,33] reported from magnetic-susceptibility measurement that the extinguished SP transition was revived by the application of pressure in heavily Mg-doped $CuGeO_3$ crystals. The pressure-revived SP state is expected to be different from pure sample at ambient pressure, because the frustration parameter α is probably large and there is a possibility that it crosses the critical value α_c in the process of increasing pressure. Moreover, Mg is the most adequate nonmagnetic impurity to synthesize high-quality single crystals and study the impurity effects on the SP transition.[12]

In this paper we study Raman scattering in heavily Mg-doped $CuGeO_3$ at low temperatures under high pressures, and, in particular, we focus on the revival of the SP transition by the application of pressure in 3.5% Mg-doped sample, which does not undergo the SP phase transition at ambient pressure. The results clearly show the revival of the SP phase under pressure, but it has a larger spin gap and a weaker lattice distortion than pure $CuGeO_3$ at ambient pressure. This fact cannot be explained within Cross-Fisher theory[34] in the *unfrustrated* AF spin chain. We also observed a pressure-induced structural phase transition at low temperatures, similar to that in pure $CuGeO_3$,[26,35] and propose a *T-P* phase diagram for 3.5% Mg-doped $CuGeO_3$.

II. EXPERIMENT

Single crystals of Mg-doped samples were grown by the floating-zone method. The Mg concentration in the Mg-doped $CuGeO_3$ was determined and the homogeneity was checked by inductively coupled plasma atomic emission spectroscopy (ICP-AES). High pressures were applied by using a clamp-type diamond anvil cell together with IIa-type artificial diamond crystals in order to avoid luminescence.[36] We used 4:1 methanol-ethanol (ME) mixture as a pressure medium. The hydrostaticity is probably worse than when helium is used as a pressure medium at low temperatures.[26,35] Samples were cleaved along the (100) plane, and several pieces of thin plates were piled in the gasket hole with a diameter of about 300 μm in order to get strong Raman-scattering intensity. The *b* and *c* crystallographic axes of all the plates were aligned within a few degrees. The cell was mounted in a helium-gas-flow-type cryostat with a temperature regulation better than ± 0.3 K. Pressure was measured *in situ* using the ruby luminescence method.[37] Raman spectra in quasibackscattering geometry were excited using the Ar^+-ion laser lines. The $a(c,b+c)\bar{a}$ spectra were dispersed by a Jobin-Yvon T64000 triple-grating monochromator equipped with a microscope and detected by a liquid-N_2-cooled charge-coupled-device (CCD) detector.

III. RESULTS

In the SP state of $CuGeO_3$, the folded phonon modes and the two-magnetic-excitation bound (resonant) state were observed by means of Raman scattering.[38–41] The former are folded from the Brillouin-zone boundary onto the zone center and become Raman active owing to the formation of the lattice dimerization by the SP transition. The latter is created near twice the SP-gap energy by a strong attractive interaction between the magnetic excitations. Moreover, the SP-gap mode was observed in lightly doped $CuGeO_3$ by Raman scattering.[39,40] The observation of the two-magnetic-excitation bound state and the SP-gap mode is a strong piece of evidence for the opening of the SP gap in the magnetic excitation spectrum.

First let us show the temperature dependence of Raman spectrum at about 3.9 GPa in 1.65% Mg-doped $CuGeO_3$ in Fig. 1. This sample undergoes the SP transition at about 12 K at ambient pressure. One can see the two-magnetic-excitation bound state at 67 cm^{-1} and the folded phonon peak at 825 cm^{-1} in the SP phase. Moreover, we can see the two-magnetic-excitation peak at Brillouin-zone boundary at about 215 cm^{-1} and a new phonon at 471 cm^{-1}, which is activated by the pressure-induced structural phase transition. Unfortunately another folded phonon peak at 369 cm^{-1} is not seen because the strong A_g^2-phonon peak is superimposed on it.

Next let us report on these characteristic Raman peaks in 3.5% Mg-doped $CuGeO_3$ in order to discuss the revival of the SP transition and the pressure-induced structural phase transition in detail.

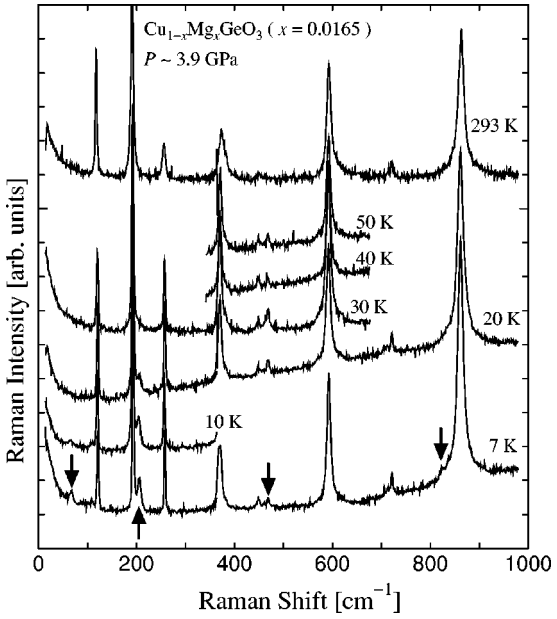

FIG. 1. Pressure dependence of Raman spectrum at about 3.9 GPa in 1.65% Mg-doped $CuGeO_3$. The arrows denote the two-magnetic-excitation bound state, the two-magnetic-excitation peak at Brillouin-zone boundary, a new phonon that is activated by the pressure-induced structural phase transition, and the folded phonon peak.

A. Folded phonon modes

Figure 2 shows the pressure dependence of Raman spectrum between 300 and 400 cm^{-1} at 6 K in 3.5% Mg-doped $CuGeO_3$. A new small peak at 369 cm^{-1} denoted by an arrow appears above 0.45 GPa. It is assigned to a folded phonon mode, which is induced by pressure, and was observed in the SP states of pure and doped $CuGeO_3$ crystals at ambient pressure, too.[38,41] The frequency of the folded phonon mode does not change with increasing pressure, while a strong A_g^2-phonon peak shifts to higher frequency and is superimposed on the 369-cm^{-1} folded phonon peak above 2.81 GPa.

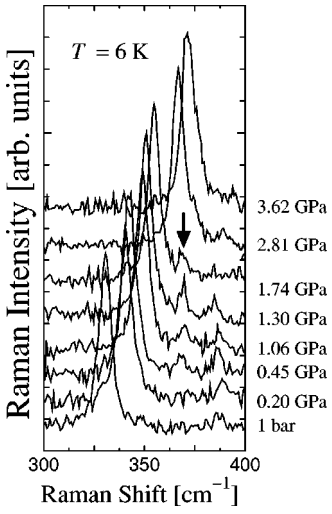

FIG. 2. Pressure dependence of Raman spectrum between 300 and 400 cm^{-1} at 6 K in 3.5% Mg-doped $CuGeO_3$. The arrow denotes the folded phonon peak.

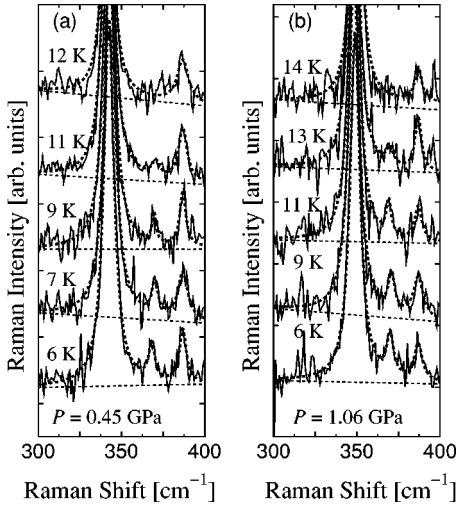

FIG. 3. Temperature dependence of Raman spectra between 300 and 400 cm^{-1} in 3.5% Mg-doped $CuGeO_3$ at 0.45 GPa (a) and 1.06 GPa (b). The dotted lines denote the fitted curves calculated by Eq. (1) and the backgrounds.

Figure 3 shows the temperature dependence of Raman spectra between 300 and 400 cm^{-1} at 0.45 and 1.06 GPa. These spectra are fitted by the following spectrum function:

$$I(\omega)=\{n(\omega)+1\}\sum_{i=1}^{3}\frac{k_i^2\omega\Gamma_i}{(\omega^2-\omega_i^2)^2+(\omega\Gamma_i)^2}+\text{background}, \tag{1}$$

where k_i, Γ_i, and ω_i are the coupling coefficient between the incident light and the ith phonon, the damping of the ith phonon, and its frequency, respectively. Here $n(\omega)$ is the Bose factor and the suffixes $i=1$, 2, and 3 denote the A_g^2 phonon, the folded phonon, and the B_{3g} phonon at 385 cm^{-1}, respectively. The fitted curves are denoted by the dotted lines in Fig. 3. The 369-cm^{-1} folded phonon peak decreases in intensity with increasing temperature and disappears above 12 K at 0.45 GPa and above 14 K at 1.06 GPa.

Figure 4(a) shows the pressure dependence of Raman spectrum between 790 and 860 cm^{-1} at 6 K. Another folded phonon mode, which was also not observed at ambient pressure, appears near 818 cm^{-1} at high pressures. It is noteworthy that the frequency of the folded phonon jumps abruptly to the high-frequency side between 1.74 and 2.81 GPa; on the other hand, above this pressure the 369-cm^{-1} folded phonon peak hides behind the A_g^2-phonon peak. We observed the same frequency jump in pure and 1.65% Mg-doped $CuGeO_3$, too. This fact implies that a structural change occurs in these crystals under high pressure at low temperature, as will be discussed later in detail. Figure 4(b) shows the temperature dependence of the folded phonon peak, which jumped from 818 to 825 cm^{-1}, when $P=3.59$ GPa. It disappears above 20 K.

The 369-cm^{-1} folded phonon is about a factor of 10^{-1} weaker in intensity than that of pure sample, but it is very

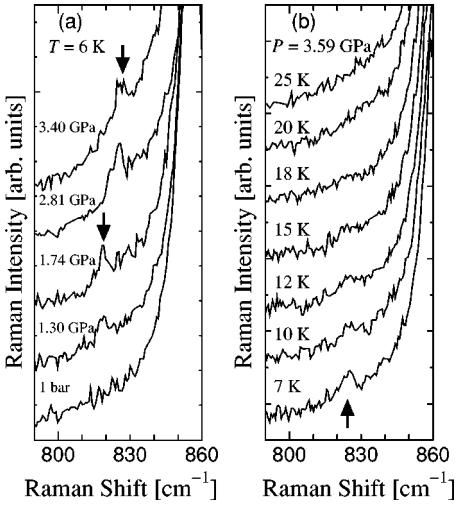

FIG. 4. Pressure dependence (a) and temperature one (b) of Raman spectrum between 790 and 860 cm^{-1} in 3.5% Mg-doped $CuGeO_3$. The arrows denote the folded phonon peak.

sharp. On the other hand, a very broad structure coming from the folded phonon was observed at low temperatures in heavily Zn- and Si-doped samples, which do not show the SP transition in our previous study.[41] This is due to the strong short-range-order lattice dimerization. The appearance of the sharp folded phonon peaks under high pressures at low temperatures indicates the formation of the long-rang-order lattice dimerization. The integrated intensity of the 369-cm^{-1} folded phonon peak normalized by that of the A_g^2-phonon peak $(k_2/k_1)^2$ is plotted as a function of temperature in Fig. 5(a).

Figure 5(b) also shows the temperature dependence of the integrated intensity of the 825-cm^{-1} folded phonon peak at 3.59 GPa, normalized by that of A_g^4-phonon peak at 857 cm^{-1}. The integrated intensity of the folded phonon is proportional to the square of the order parameter,[41,42] i.e., the squared lattice distortion δ^2. These are fitted with the temperature dependence of the squared lattice distortion δ^2 calculated by Riera and Dobry[18] and denoted by the dotted curves in Figs. 5(a) and 5(b). Although it was obtained when $\alpha=0.36$, it fits well the present result. Kuroe and Sekine[43] too calculated $(\delta/\delta_0)^2$ as a function of T/T_{SP} when α

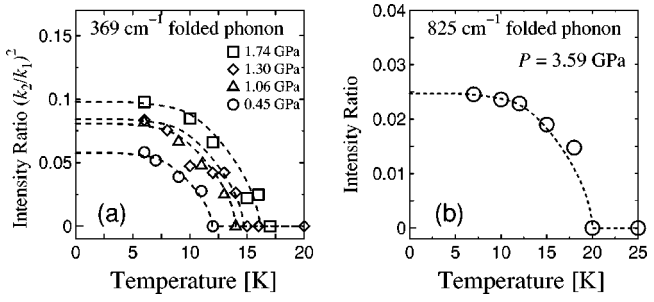

FIG. 5. Temperature dependence of the intensities of the folded phonons at 369 cm^{-1} (a) and 825 cm^{-1} (b) in 3.5% Mg-doped $CuGeO_3$, which are, respectively, normalized by the A_g^2 and A_g^4 phonons. The dotted curves denote the theoretical ones (Ref. 18).

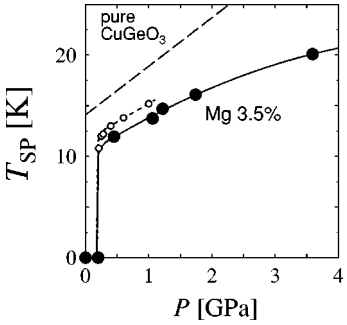

FIG. 6. T_{SP} as a function of pressure in 3.5% Mg-doped $CuGeO_3$. The small circles and dotted line denote the result of the magnetic susceptibility in 3.5% Mg-doped sample (Ref. 33) and the dashed line denotes that of pure sample (Ref. 22). Since the SP transition is not observed at 1 bar and 0.20 GPa, the values of T_{SP} are regarded as 0 K. The solid curve is only guide for the eye.

$=0.40$ and confirmed that it hardly changes in both the cases of $\alpha=0.36$ and 0.40. Here δ_0 is the lattice distortion at 0 K. Then we estimated T_{SP} and plot it as a function of pressure in Fig. 6. It is obvious from Fig. 2 that the SP phase is revived between 0.20 and 0.45 GPa, as shown in Fig. 6. The small circles and dotted line below 1 GPa show the T_{SP} obtained from the magnetic-susceptibility measurement by Masuda *et al.*[33] Their result shows that the SP transition revives above 0.21 GPa. It is in good agreement with the present result. The dashed line represents the result of pure $CuGeO_3$ by Takahashi *et al.*[22] The T_{SP} of 3.5% Mg-doped $CuGeO_3$ is lower than that of pure crystal and increases more slowly with increasing pressure.

B. Magnetic excitations

In pure $CuGeO_3$ the SP-gap mode is not observable for Raman scattering due to the selection rule. On the other hand, our previous studies at ambient pressure showed that the two-magnetic-excitation bound (resonant) state was created near twice the SP-gap energy by a strong attractive interaction between them.[38,39] Moreover, the selection rule is broken in lightly impurity-doped crystals, so that the SP-gap mode was observed.[39,40] In this section we report the observation of the two-magnetic-excitation bound state, the SP-gap mode, and the zone-boundary two-magnetic-excitation peak for 3.5% Mg-doped $CuGeO_3$ by Raman scattering under high pressures at low temperatures.

Figure 7 shows the low-frequency Raman spectra of 3.5% Mg-doped $CuGeO_3$ at 6–7 K as a function of pressure. Above 1.99 GPa we observed the two-magnetic-excitation bound state, which is created near twice the SP-gap energy and increases in frequency with increasing pressure. Moreover, the SP-gap mode was observed at 41 cm^{-1} when $P=4.26$ GPa. The two-magnetic-excitation bound state was not observed above T_{SP}.

When $P=4.26$ GPa we estimate the binding energy of the two-magnetic-excitation bound state as 12 cm^{-1} at about 7 K. It is very large compared with the result ($\sim$1 cm^{-1}) for pure $CuGeO_3$ at ambient pressure.[38,39] van Loosdrecht *et al.*[26] reported that the binding energy for pure sample

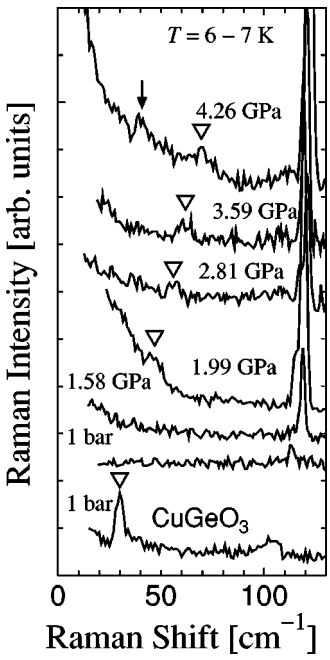

FIG. 7. Pressure dependence of the low-frequency Raman spectrum at 6–7 K in 3.5% Mg-doped $CuGeO_3$. The triangles and the arrow denote the two-magnetic-excitation bound state and the gap mode, respectively. The result of pure sample at ambient pressure is also shown.

reached about 15 cm^{-1} at 4.4 GPa. These facts show that the binding energy strongly depends on pressure.

Figure 8 shows the low-frequency Raman spectra of 3.5% and 1.65% Mg-doped samples and pure one at 7 K when $P = 3.40 \sim 3.89$ GPa. The peak frequency of the two-magnetic-excitation bound state and its intensity decreases with increasing Mg concentration. Figure 9 shows the pressure dependence of the peak frequency of the two-magnetic-excitation bound state of 3.5% Mg-doped $CuGeO_3$ at 6–7 K together with that of pure sample. The peak frequency of the doped sample is lower and its gradient against pressure is smaller than that of pure one. The SP-gap energy increases with increasing pressure and decreases with increasing Mg concentration. In other words, the SP state is suppressed by the doping of impurity and is stabilized by the application of pressure.

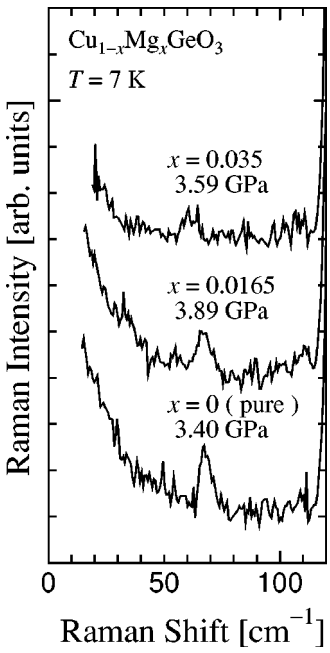

FIG. 8. Low-frequency Raman spectrum of $Cu_{1-x}Mg_xGeO_3$ crystals with $x=0$, 0.0165, and 0.035 at 7 K under high pressure.

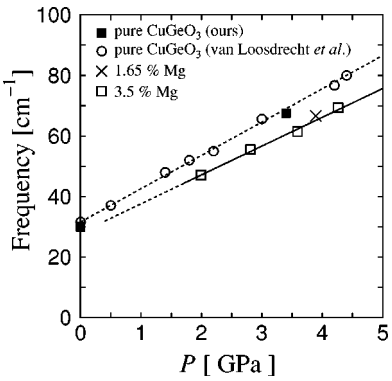

FIG. 9. Pressure dependence of the peak frequency of the two-magnetic-excitation bound state of 3.5% Mg-doped $CuGeO_3$ at 6–7 K together with results of pure [ours and van Loosdrecht's (Ref. 26)] and 1.65% Mg-doped samples. The solid and dotted lines are only guide for the eye.

Figure 10 shows the pressure dependence of Raman spectrum between 180 and 250 cm^{-1} at 6 K in 3.5% Mg-doped $CuGeO_3$. The broad peak near 215 cm^{-1} denoted by an arrow is identified as the two-magnetic-excitation peak at Brillouin-zone boundary along the c axis, reflecting the density of states of the magnetic excitation. Figure 11 shows the

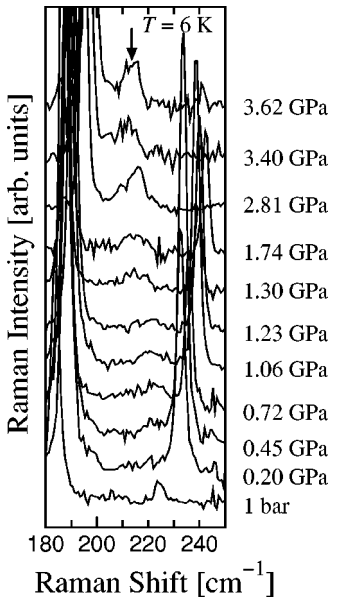

FIG. 10. Pressure dependence of Raman spectrum between 180 and 250 cm^{-1} at 6 K in 3.5% Mg-doped $CuGeO_3$. The arrow denotes the zone-boundary two-magnetic-excitation peak.

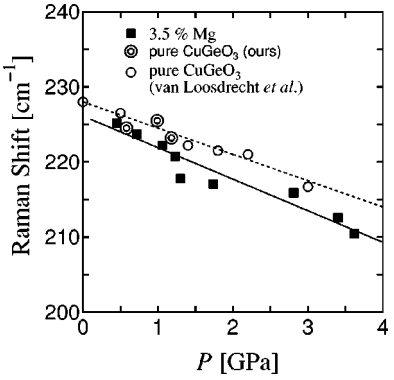

FIG. 11. Pressure dependence of the frequency of the zone-boundary two-magnetic-excitation peak at 6 K in 3.5% Mg-doped $CuGeO_3$ and pure one [ours and van Loosdrecht's (Ref. 26)]. The solid and dotted lines are only guide for the eye.

peak position as a function of pressure. The result of pure sample is also shown in this figure together with that by van Loosdrecht *et al.*[26] The pressure dependences of pure and 3.5% Mg-doped samples show the same behavior except for the low pressure region, i.e., they decrease with increasing pressure. However, the frequency change of the 3.5% Mg-doped sample against pressure is stronger than that of pure one, indicating that the pressure effects on the Mg-doped sample are stronger than those on pure one. Moreover, the frequency of 3.5% Mg-doped sample is lower than that of pure one, suggesting that the nearest-neighbor exchange interaction J_{nn} is reduced by the Mg doping.

For pure $CuGeO_3$, Nishi *et al.*[24,25] showed by inelastic neutron scattering measurement that the SP-gap energy increases upon applying pressure, but at zone boundary along the *c* axis it decreases with increasing pressure, which agrees with the present result. It is noteworthy that this peak appeared above 0.45 GPa, i.e., in the SP phase and sharpened with increasing pressure, although primarily it is not related to the SP transition. The growth of the long-range SP correlations strongly suppresses the one-dimensional quantum spin fluctuations,[19] which probably sharpens the zone-boundary two-magnetic-excitation peak. It is noted that the 222-cm^{-1} small sharp peak at ambient pressure is identified to the B_{1g}^2 mode. It becomes very strong in intensity and shifts to higher frequency at high pressures. The intensity increase is due to the tilt from the normal incidence in the optical alignments under high pressures, because this phonon is forbidden when the incident light is completely normal to the *a* plane.[38]

C. Phase diagram for 3.5% Mg-doped $CuGeO_3$

Raman-scattering studies of van Loosdrecht *et al.*[26] and Goñi *et al.*[35] showed that a structural phase transition occurs at low temperatures under high pressures in pure $CuGeO_3$, but their Raman spectra obtained in the new phase are different from each other. van Loosdrecht *et al.*[26] used ME or Ar as a pressure medium and they observed three new peaks at 247, 393, and 471 cm^{-1} below $\sim$215 K for $1.6 < P < 6$ GPa. This new phase retains the characteristic peaks of

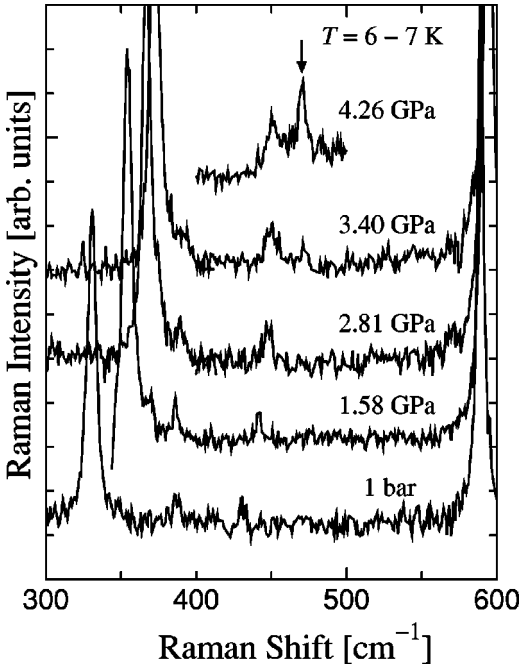

FIG. 12. Pressure dependence of Raman spectrum between 300 and 600 cm^{-1} at 6–7 K in 3.5% Mg-doped $CuGeO_3$. The arrow denotes the new phonon peak which is activated by the pressure-induced structural phase transition.

the SP phase at low temperatures. On the other hand, Goñi *et al.*[35] used helium as a pressure medium and observed new peaks at 150 and 300 cm^{-1} below 180 K for $3 < P < 6$ GPa, but the SP phase transition did not occur down to 3 K. We studied the new phase by Raman scattering for pure, 1.65% and 3.5% Mg-doped $CuGeO_3$ using ME as a pressure medium. Figure 12 shows Raman spectra of 3.5% Mg-doped sample at $T = 6-7$ K between 300 and 600 cm^{-1} at various pressures. We observed a new peak at 471 cm^{-1} denoted by an arrow above 3.40 GPa. Figures 13(a) and 13(b) show the

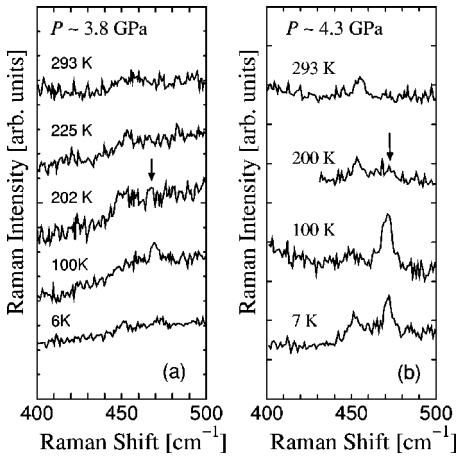

FIG. 13. Temperature dependence of Raman spectrum between 400 and 500 cm^{-1} at about 3.8 GPa (a) and 4.3 GPa (b) in 3.5% Mg-doped $CuGeO_3$. The arrows denote the new phonon peak which is activated by the pressure-induced structural phase transition.

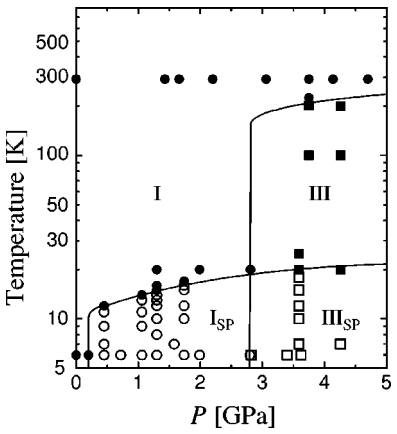

FIG. 14. *P-T* phase diagram of 3.5% Mg-doped $CuGeO_3$.

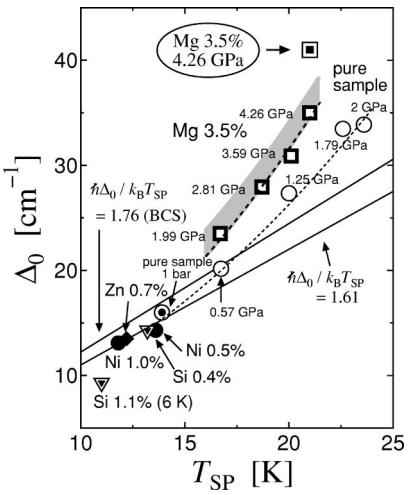

FIG. 15. The SP-gap frequency at 0 K (Δ_0) as a function of T_{SP}. The present datum at 4.26 GPa is denoted by a square with dot. The data of Si, Zn, and Ni-doped samples (Refs. 39 and 44) and those of pure sample (Ref. 45) (circle with dot) at ambient pressure and at high pressures (Refs. 24 and 25) (open circles) are plotted. The half frequency of the two-magnetic-excitation bound state (open squares) is also plotted. The thick and thin dotted lines are only guide for the eye.

temperature dependence of the new peak at about 3.8 and 4.3 GPa, respectively. It remains observable up to about 200 K, but disappears above it. It indicates a pressure-induced structural phase transition. Figure 1 also shows the appearance of this peak at low temperature under high pressure in 1.65% Mg-doped sample. As stated in the previous sections, the SP phase transition occurs at low temperatures, i.e., the SP state exists even in the new phase at low temperatures. This fact is in agreement with the result by van Loosdrecht *et al.*,[26] although two other peaks at 247 and 393 cm^{-1} were not observed probably owing to their weak intensities.

Considering all the facts we obtained, we propose a *P-T* phase diagram in Fig. 14. We observed four remarkable phases by means of Raman scattering. Phase I has almost the same Raman spectrum as that at room temperature and ambient pressure. In phase I_{SP}, we observed new peaks, which are characteristic of the SP phase, i.e., two folded phonons at 369 cm^{-1} and 818 cm^{-1}, and the two-magnetic-excitation bound state. In phase III above 2.8 GPa, the new peak appears at 471 cm^{-1}, which remains observable up to around 200 K. In phase III_{SP} the folded phonon at 825 cm^{-1}, the two-magnetic-excitation bound state, and the SP-gap mode are observed together with the new peak characteristic of phase III, indicating the SP state possessing a different lattice structure from phase I_{SP}. Moreover, the frequency of the folded phonon peak was observed to jump from 818 to 825 cm^{-1} at 2.81 GPa. We believe that the phase transition from I_{SP} to III_{SP} undergoes a slight structural change, retaining the SP state.

Goñi *et al.*[35] and van Loosdrecht *et al.*[26] have also proposed phase diagrams for pure sample from their results of Raman scattering. The former result is different from ours, but the latter resembles ours except for the revival of the SP transition. The difference comes from the different pressure media, i.e., the degree of their hydrostaticity. Helium is soft even in the solid state and supposed to have better hydrostaticity than ME mixture at low temperature and high pressure.

IV. DISCUSSION

In our previous paper[39] we observed the SP-gap mode in lightly Si- and Zn-doped $CuGeO_3$ at ambient pressure and reported that the following result holds for the SP-gap energy $\hbar\Delta_0$ at 0 K:

$$\frac{\hbar\Delta_0}{k_B T_{SP}} = C_1, \tag{2}$$

with $C_1 = 1.61$, which is slightly smaller than $C_1 = 1.76$ of BCS theory. In Fig. 15, we plot the SP-gap frequency of 3.5% Mg-doped sample at 4.26 GPa in addition to our results of Si, Zn, and Ni-doped samples[39,44] and the results of pure sample at ambient and high pressures by inelastic neutron scattering.[24,25,45] We also plot the half frequency of the two-magnetic-excitation bound state (denoted by open squares). The SP-gap frequency should be higher than this value because of the binding energy. The present datum at 4.26 GPa was obtained at about 7 K but regarded as Δ_0 (Δ at 0 K) since the temperature is much lower than T_{SP}. The SP-gap frequencies of pure and 3.5% Mg-doped samples under high pressures do not fit to Eq. (2), in particular that of 3.5% Mg-doped sample is very large when compared with Δ_0 expected from Eq. (2).

Figure 16 shows the intensity of the 369-cm^{-1} folded phonon peak normalized by that of the A_g^2-phonon peak at 0 K, $(k_2/k_1)_0^2$, in phase I_{SP} as a function of T_{SP} in logarithmic scales. Here $(k_2/k_1)_0^2$ is proportional to the square of the lattice order parameter, i.e., the squared lattice distortion δ_0^2.[41,42] In this figure we add our results[41,44] of pure sample and Si-, Zn-, and Ni-doped samples at ambient pressure and the results of pure one under high pressures. In 3.5% Mg-doped sample, it is obvious that the lattice distortion is 0 up to 0.2 GPa and increases with increasing pressure above 0.45 GPa. However, it is about a factor of 0.1–0.2 smaller than that of pure crystal at ambient pressure. Recently Masuda *et al.*[33] observed by the synchrotron x-ray diffraction that the

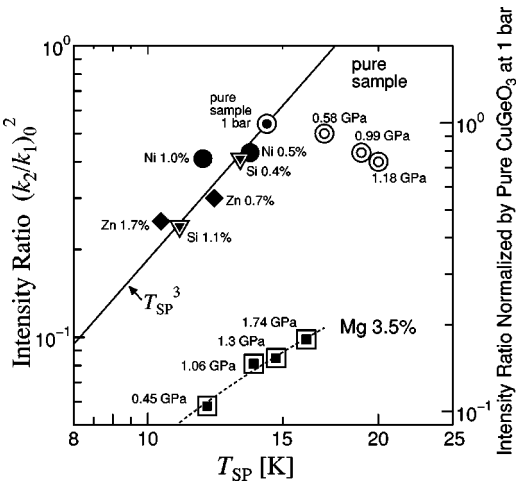

FIG. 16. The intensity of the 369-cm^{-1} folded phonon peak normalized by that of the A_g^2-phonon peak at 0 K, $(k_2/k_1)_0^2$, as a function of T_{SP} in logarithmic scales. The data of pure, Si, Zn, and Ni-doped samples (Refs. 41 and 44) at ambient pressure and those of pure sample at high pressures (double circles) are also plotted. The dotted line is only guide for the eye.

superlattice peak intensity corresponding to the SP dimerization of 3.5% Mg-doped sample at 1 GPa is about a factor of 0.15 weaker than that of pure one at ambient pressure, which is in good agreement with our result. It indicates that the lattice dimerization in this crystal is induced by pressure, but it is not so strong as pure crystal.

Cross and Fisher[34] obtained that the relation between the lattice distortion parameter (δ_0) and the SP-gap frequency (Δ_0) at 0 K is given as

$$\delta_0 \propto \Delta_0^{3/2}. \tag{3}$$

In pure $CuGeO_3$ and lightly impurity-doped crystals Eq. (2) with $C_1 = 1.61$ holds at ambient pressure and then we obtain

$$\delta_0^2 \propto (k_2/k_1)_0^2 = C_2 T_{SP}^3, \tag{4}$$

where C_2 is a constant. The normalized intensities of the folded phonon $(k_2/k_1)_0^2$ obtained in pure and doped samples at ambient pressure fit well with a line of Eq. (4). But $(k_2/k_1)_0^2$ of pure sample at high pressures deviates from this relation. It decreases with increasing pressure, i.e., the lattice dimerization is suppressed with increasing pressure, in agreement with the result of the neutron diffraction measurement.[23] On the other hand, the present result of the revived SP phase under high pressures in 3.5% Mg-doped $CuGeO_3$ deviates entirely from this relation.

We summarize that the SP gap and the lattice distortion in the SP state of pure and lightly doped $CuGeO_3$ at ambient pressure fit to Eqs. (3) and (4), but those of pure sample gradually deviate from these equations with increasing pressure. And the SP state of 3.5% Mg-doped sample revived by pressure is anomalous, i.e., this sample has a larger SP gap but a much smaller lattice distortion than pure sample does, which cannot be explained in the framework of Cross-Fisher theory. One of the possible explanations is the increase of the frustration parameter $\alpha(=J_{nnn}/J_{nn})$ by the application of pressure. When α is lager than the critical value α_c, a spontaneous spin gap is formed without lattice dimerizations. We think that α of 3.5% Mg-doped sample is increased with increasing pressure and exceeds α_c at high pressures. Then we observe a large spin gap and a small lattice distortion in the pressure-revived SP state of 3.5% Mg-doped $CuGeO_3$. However, α_c probably has a larger value than 0.2411 of the ideal one-dimensional spin chain, because the interchain exchange interaction ($J_b \cong 0.1 J_{nn}$)[46] is strong in $CuGeO_3$.

The energy of the magnetic excitation at Brillouin-zone boundary reflects the magnitude of the exchange interaction J_{nn}. As shown in Figs. 10 and 11, the frequency of the two-magnetic-excitation peak at Brillouin-zone boundary decreases with increasing pressure, which suggests that the nearest-neighbor exchange interaction J_{nn} decreases with increasing pressure. Assuming that J_{nnn} is constant, the decrease of J_{nn} leads that α increases with increasing pressure. Masuda *et al.*[33] recently estimated from the temperature dependence of the magnetic susceptibility for 3.2% Mg-doped sample that the frustration parameter α increases from 0.36 to 0.40 under high pressure.

Raupach *et al.*[47] studied the pressure dependence of the SP temperature T_{SP} and analyzed the spin gap and the lattice distortion as a function of T_{SP} in the *frustrated* AF spin chain by using the density-matrix-renormalization-group technique. Considering their result, Eqs. (2) and (4) may be replaced by

$$\hbar\Delta_0 \cong \hbar\Delta_s + C_1 k_B T_{SP} \exp\left(-\frac{\hbar\Delta_s}{3k_B T_{SP}}\right) \tag{5}$$

and

$$(k_2/k_1)_0^2 \cong C_2 T_{SP}^3 \exp\left(-\frac{\hbar\Delta_s}{k_B T_{SP}}\right). \tag{6}$$

Here Δ_s is the frequency of the spontaneous spin gap without the SP lattice distortion and becomes 0 when $\alpha \leqslant \alpha_c$. On the assumption that the frustration parameter of 3.5% Mg-doped $CuGeO_3$ is larger than α_c, the large SP gap and the weak lattice dimerization in the pressure-revived SP state of 3.5% Mg-doped $CuGeO_3$ can be roughly explained by Eqs. (5) and (6). For example, let us consider the case of $P \cong 2$ GPa in 3.5% Mg-doped $CuGeO_3$. In this case T_{SP} is about 16.5 K, as shown in Fig. 6. Assuming $\Delta_s \cong 1.7 k_B T_{SP}/\hbar = 19.5$ cm^{-1}, we estimate that $\Delta_0 \cong 30.0$ cm^{-1} and $(k_2/k_1)_0^2$ is a factor of 0.28 smaller than that of pure sample at ambient pressure. The present experimental datum at 1.74 GPa gives that $(k_2/k_1)_0^2$ is a factor of ~ 0.18 smaller than that of pure sample at ambient pressure, which roughly agrees with the estimated one at 2 GPa. Furthermore, we observed the two-magnetic-excitation bound state at about 47 cm^{-1} when $P = 1.99$ GPa. Taking the binding energy into account, we obtain $\Delta_0 > 23.5$ cm^{-1}, which is close to the estimated value. Probably the frustration parameter α of pure $CuGeO_3$ is close to α_c at ambient pressure and it exceeds α_c at high pressures.[47]

However, we could not observe the spontaneous spin gap (Δ_s) above T_{SP}. As seen in Fig. 10, the zone-boundary two-

magnetic-excitation peak appeared above 0.45 GPa, i.e., in the SP phase and it sharpened with increasing pressure. The growth of the long-range SP correlation strongly suppresses the one-dimensional quantum spin fluctuations and then we were able to observe the two-magnetic-excitation bound state and the SP-gap mode at high pressures. Thus, the strong quantum spin fluctuations probably broadens the bound state and the SP-gap mode, and obstructed their observations at low pressures. Moreover, Fig. 1 shows that the zone-boundary two-magnetic-excitation peak disappears above 30 K, indicating that the quantum spin fluctuations are also very strong at high temperatures. Then it is difficult to observe the spontaneous spin gap above T_{SP} and at low pressures because of the strong one-dimensional quantum spin fluctuations.

V. CONCLUSION

We studied Raman scattering in heavily Mg-doped $CuGeO_3$ crystals under high pressures at low temperatures. The 3.5% Mg-doped sample does not undertake the spin-Peierls transition at ambient pressure. However, the folded phonon modes and the two-magnetic-excitation bound state appeared under high pressures. The SP gap mode was also observed. These facts give clear evidence for the revival of the SP transition by the application of high pressure. The revived SP state, however, has a large spin gap and a weak lattice dimerization. This anomalous SP state was interpreted in terms of the strongly frustrated spin chain with a frustration parameter $\alpha = J_{nnn}/J_{nn}$ larger than the critical value α_c. Although this sample possesses the spontaneous spin gap (Δ_s) even above T_{SP}, it is difficult to observe it because of the strong one-dimensional quantum spin fluctuations.

A new phonon peak was observed at 471 cm^{-1} above 2.8 GPa, indicating a pressure-induced structural phase transition. It remains observable far above the SP transition temperature. We proposed a *P-T* phase diagram for this sample.

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[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[2] M. Hase, I. Terasaki, Y. Sasago, K. Uchinokura, and H. Obara, Phys. Rev. Lett. **71**, 4059 (1993).

[3] S.B. Oseroff, S-W. Cheong, B. Aktas, M.F. Hundley, Z. Fisk, and L.W. Rupp, Jr., Phys. Rev. Lett. **74**, 1450 (1995).

[4] M. Hase, N. Koide, K. Manabe, Y. Sasago, K. Uchinokura, and A. Sawa, Physica B **215**, 164 (1995).

[5] J.-G. Lussier, S.M. Coad, D.F. McMorrow, and D.McK. Paul, J. Phys.: Condens. Matter **7**, L325 (1995).

[6] J.P. Renard, K.Le. Dang, P. Veillet, G. Dhalenne, A. Revcolevschi, and L.P. Regnault, Europhys. Lett. **30**, 475 (1995).

[7] M. Poirier, T. Beaudry, M. Castonguay, M.L. Plumer, G. Quirion, F.S. Razavi, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **52**, R6971 (1995).

[8] L.P. Regnault, J.-P. Renard, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. **32**, 579 (1995).

[9] M. Hase, K. Uchinokura, R.J. Birgeneau, K. Hirota, and G. Shirane, J. Phys. Soc. Jpn. **65**, 1392 (1996).

[10] Y. Sasago, N. Koide, K. Uchinokura, M.C. Martin, M. Hase, and G. Shirane, Phys. Rev. B **54**, R6835 (1996).

[11] M.C. Martin, M. Hase, K. Hirota, G. Shirane, Y. Sasago, N. Koide, and K. Uchinokura, Phys. Rev. B **56**, 3173 (1997).

[12] T. Masuda, A. Fujioka, Y. Uchiyama, I. Tsukada, and K. Uchinokura, Phys. Rev. Lett. **80**, 4566 (1998).

[13] Y.J. Wang, V. Kiryukhin, R.J. Birgeneau, T. Masuda, I. Tsukada, and K. Uchinokura, Phys. Rev. Lett. **83**, 1676 (1999).

[14] H. Nakao, M. Nishi, Y. Fujii, T. Masuda, I. Tsukada, K. Uchinokura, K. Hirota, and G. Shirane, J. Phys. Soc. Jpn. **68**, 3662 (1999).

[15] T. Masuda, I. Tsukada, K. Uchinokura, Y.J. Wang, V. Kiryukhin, and R.J. Birgeneau, Phys. Rev. B **61**, 4103 (2000).

[16] M. Nishi, H. Nakao, Y. Fujii, T. Masuda, K. Uchinokura, and G. Shirane, J. Phys. Soc. Jpn. **69**, 3186 (2000).

[17] G. Castilla, S. Chakravarty, and V.J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).

[18] J. Riera and A. Dobry, Phys. Rev. B **51**, 16 098 (1995).

[19] H. Kuroe, J. Sasaki, T. Sekine, N. Koide, Y. Sasago, K. Uchinokura, and M. Hase, Phys. Rev. B **55**, 409 (1997).

[20] T. Tonegawa and I. Harada, J. Phys. Soc. Jpn. **56**, 2153 (1987).

[21] K. Okamoto and K. Nomura, Phys. Lett. A **169**, 433 (1992).

[22] H. Takahashi, N. Môri, O. Fujita, J. Akimitsu, and T. Matsumoto, Solid State Commun. **95**, 817 (1995).

[23] S. Katano, O. Fujita, J. Akimitsu, and M. Nishi, Phys. Rev. B **52**, 15 364 (1995).

[24] M. Nishi, O. Fujita, J. Akimitsu, K. Kakurai, and Y. Fujii, Phys. Rev. B **52**, R6959 (1995).

[25] M. Nishi, K. Kakurai, Y. Fujii, M. Yethiraj, D.A. Tennant, S.E. Nagler, J.A. Fernandez-Baca, O. Fujita, and J. Akimitsu, Physica B **241-243**, 537 (1998).

[26] P.H.M. van Loosdrecht, J. Zeman, G. Martinez, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. **78**, 487 (1997).

[27] S. Bräuninger, U. Schwarz, M. Hanfland, T. Zhou, R.K. Kremer, and K. Syassen, Phys. Rev. B **56**, R11 357 (1997).

[28] M. Braden, G. Wilkendorf, J. Lorenzana, M. Ain, G.J. McIntyre, M. Behruzi, G. Heger, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **54**, 1105 (1996).

[29] J.W. Bray, L.V. Interrante, I.S. Jacobs, and J.C. Bonner, in *Extended Linear Chain Compounds*, edited by J.S. Miller (Plenum Press, New York, 1983), Vol. III, p. 353.

[30] T. Lorenz, H. Kierspel, S. Kleefisch, B. Bühner, E. Gamper, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **56**, R501 (1997).

[31] M. Fischer, P.H.M. van Loosdrecht, P. Lemmens, G. Güntherrodt, B. Büchner, T. Lorenz, M. Breuer, J. Zeman, G. Martinez, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **57**, 7749 (1997).

[32] T. Masuda, R. Kuroda, and K. Uchinokura, J. Magn. Magn. Mater. **226-230**, 425 (2001).
[33] T. Masuda, D. Yano, R. Kuroda, K. Uchinokura, H. Kuroe, T. Sekine, Y. Katsuki, K. Ohwada, Y. Fujii, H. Nakao, and Y. Murakami, Phys. Rev. B **67**, 024423 (2003).
[34] M.C. Cross and D.S. Fisher, Phys. Rev. B **19**, 402 (1979).
[35] A.R. Goñi, T. Zhou, U. Schwarz, R.K. Kremer, and K. Syassen, Phys. Rev. Lett. **77**, 1079 (1996).
[36] T. Sekine, A. Uji, Y. Oono, Y. Tanokura, T. Masuda, and K. Uchinokura, J. Phys. Soc. Jpn. **70**, 290 (2001).
[37] S. Buchsbaum, R.L. Mills, and D. Schiferl, J. Phys. Chem. **88**, 2522 (1984).
[38] H. Kuroe, T. Sekine, M. Hase, Y. Sasago, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, Phys. Rev. B **50**, 16 468 (1994).
[39] T. Sekine, H. Kuroe, J. Sasaki, Y. Sasago, N. Koide, K. Uchinokura, and M. Hase, J. Phys. Soc. Jpn. **67**, 1440 (1998).
[40] G. Els, G.S. Uhrig, P. Lemmens, H. Vonbreg, P.H.M. van Loosdrecht, G. Güntherodt, O. Fujita, J. Akimitsu, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. **43**, 463 (1998).
[41] H. Kuroe, J. Sasaki, T. Sekine, T. Masuda, N. Koide, I. Tsukada, and K. Uchinokura, J. Phys. Soc. Jpn. **68**, 2046 (1999).
[42] F.A. Fleury, Comments Solid State Phys. **4**, 167 (1972).
[43] H. Kuroe and T. Sekine (unpublished).
[44] T. Sekine, T. Kaneko, and H. Kuroe (unpublished).
[45] J.G. Lussier, S.M. Coad, D.F. McMorrow, and D.McK. Paul, J. Phys.: Condens. Matter **8**, L56 (1996).
[46] M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B **50**, 6508 (1994).
[47] R. Raupach, A. Klümper, and F. Schönfeld, Eur. Phys. J. B **17**, 51 (2000).