Raman-scattering study on the revival of the spin-Peierls transition in heavily Mg-doped $CuGeO_3$ under high pressures

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Abstract

Raman-scattering study has been carried out in 3.5% Mg-doped $CuGeO_3$ crystals under high pressures at low temperatures. This sample does not undertake the spin-Peierls (SP) transition at ambient pressure. The folded phonon modes and the two-magnetic-excitation bound state appear under high pressures. The SP gap mode is also observed. These facts give a clear evidence that the SP phase transition is revived by the application of high pressure. A new phonon peak is observed above 2.8 GPa, indicating a pressure-induced structural phase transition. It remains observable far above the SP transition temperature. We propose a P-T phase diagram for this sample.

Key words: Raman scattering; spin-Peierls transition; pressure effect; $CuGeO_3$

An inorganic $CuGeO_3$ crystal has one-dimensional Cu^{2+} chains along the c axis. Since Hase *et al*. [1] reported the spin-Peierls (SP) transition in $CuGeO_3$ by magnetic susceptibility measurement, many interesting physical properties have been revealed. In the SP phase the chain becomes dimerized and the spins form a singlet state, producing a gap in the magnetic excitation spectrum. With increasing pressure, the crystal strongly contracts in the b direction, and the one dimensionality of the Cu^{2+} chains is reduced. It implies that the SP state becomes unstable, but in fact the SP transition temperature ($T_{\rm sp}$) increases with increasing pressure, indicating the SP phase becomes stable. By the doping of impurity, the SP transition is strongly suppressed. Above a critical concentration, 2.3% in the case of Mg impurity, the SP phase disappears [2]. Recently Masuda *et al*. [3] reported the revival of the SP transition by applying pressure in magnetic susceptibility measurement for 3.2% Mg-doped sample. On the other hand, the Raman scattering is one of the useful experimental methods to study the SP transition [4-6]. In the SP phase, some characteristic Raman peaks, i.e. the folded-phonon modes [5], the two-magnetic-excitation bound (resonant) state and the SP gap mode were observed [6]. In this report, we show that all these characteristic peaks appear for 3.5% Mg-doped sample at low temperatures when high pressure is applied using a diamond anvil cell with 4:1 methanol/ethanol mixture as a pressure medium [7].

Figure 1 shows the Raman spectrum between 300 and 400 cm^{-1} at 6 K. 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 folded from the Brillouin-zone boundary onto the zone center by the lattice dimerization and becomes Raman-active in the SP phase. On the other hand, a strong A_g^2-phonon peak shifts to the higher frequency side with increasing pressure, and is superimposed on the folded phonon peak at high pressures. Another folded phonon mode was observed at 818 cm^{-1} under high pressures. The frequency of this folded phonon jumps abruptly to the higher frequency side at about 2.8 GPa. The appearance of the folded phonons at high pressures obviously indicates the formation of the lattice dimerization. We measured the temperature dependence of the two folded phonons and estimated $T_{\rm sp}$ as a func-

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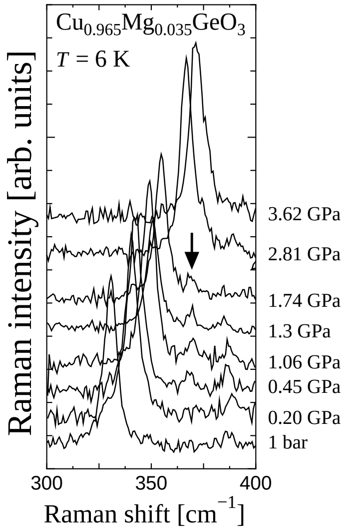

Fig. 1. Pressure dependence of the 369-cm^{-1} folded phonon mode (denoted by an arrow) at 6 K.

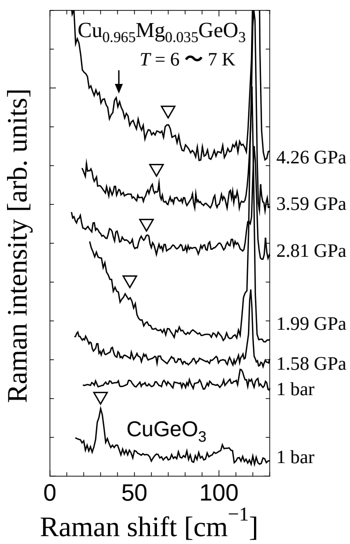

Fig. 2. Pressure dependence of the low-frequency Raman spectrum at low temperatures. The result of pure sample is also shown.

tion of pressure. It is in good agreement with the result of the magnetic susceptibility measurement below 1 GPa for 3.2% Mg-doped sample by Masuda *et al*. [3]. Figure 2 shows the low-frequency Raman spectrum as a function of pressure. Above 1.99 GPa we observed the two-magnetic-excitation bound state denoted by triangles, which is created near twice the SP gap energy by a strong attractive interaction between them. Its frequency increases with increasing pressure and the SP gap mode (an arrow) is observed at 40 cm^{-1} at 4.26 GPa, which becomes allowed by the doping of impurity.

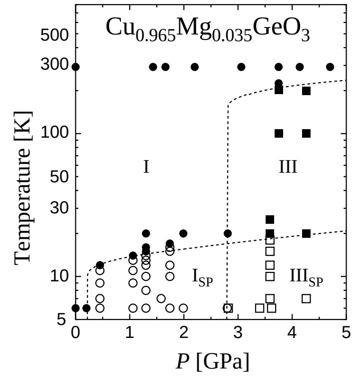

Fig. 3. P-T phase diagram.

We observed another new phonon peak at 471 cm^{-1} above 2.8 GPa together with the SP gap and the folded phonon modes at low temperatures. It indicates a pressure-induced structural phase transition. Considering all the facts we obtained, we propose a P-T phase diagram (Fig. 3). Phase I has almost the same Raman spectrum as that at room temperature and ambient pressure. In phase I$_{\rm sp}$, we observed new peaks which are characteristic of the SP phase. 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$_{\rm sp}$ the folded phonon, 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 with a different lattice structure from phase I$_{\rm sp}$. Goñi *et al*. [8] and van Loosdrecht *et al*. [9] have also proposed phase diagrams for pure sample from their results of Raman scattering. The former result is different from ours, probably owing to the difference of pressure medium, but the latter resembles ours except for the revival of the SP transition.

In conclusion, we obtained a clear evidence of the revival of the SP transition in 3.5% Mg-doped CuGeO$_3$ under high pressures by Raman scattering.

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