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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	42
number	2
page range	289-293
year	1996-07-15
URL	http://hdl.handle.net/10097/28620

Sci. Rep. RITU A42 (1996) pp. 289-293
No. 2, May 1996

High-Field Magnetization of Doped Spin-Peierls System $Cu_{1-x}Zn_xGeO_3^*$

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(Received January 31, 1996)

We measured magnetizations of doped spin-Peierls $Cu_{1-x}Zn_xGeO_3$ with $x = 0$, 0.005, 0.010 and 0.020 in order to study effects of impurities on a magnetic phase. A rapid change of the magnetization associated with a phase transition from dimerized to other phases is seen. The magnetization above 16 T shows weak x and temperature dependence. A critical field associated with the phase transition decreases with increasing x. Effects of impurities on the magnetic phase are weaker than on the dimerized phase. The soliton model is applicable to the magnetic phase.

KEYWORDS: spin-Peierls system, $CuGeO_3$, magnetic phase, impurity effect, magnetization

1. Introduction

Quantum spin systems exhibit various interesting phenomena which classical systems do not have. The most siginificant difference between the two systems is a spin-singlet ground state due to exchange interactions between spins in low-dimensional quantum spin systems. A spin-Peierls (SP) system is one example and has a spin-singlet ground state with an energy gap between ground and excited states. Experimentally Bray *et al.* have observed an SP transition in an organic material TTF-CuBDT in 1975.[1] After this observation, experimental and theoretical researches on the SP system have been done extensively.[2] However, we think that studies of the SP system finished before perfect understnding. In 1993, about two decades after the observation of the SP transition in TTF-CuBDT, Hase, Terasaki and Uchinokura discovered the SP transition in an inorganic compound $CuGeO_3$,[3] and then the SP transition has attracted much attention again. Investigations of the SP system have been advanced further because of several properties in $CuGeO_3$ such as easy synthesis and a simple crystal structure.[4]

We summarize the SP transition. The SP transition can appear in an $S = 1/2$ one-dimensional (1D) Heisenberg-XY antiferromagnetic (AF) quantum spin system coupled with three-dimensional phonon fields. Above a transition temperature T_{SP}, a separation between neighboring ions (or molecules in organic SP systems) including one unpaired spin in each ion is constant in a chain (a uniform chain). On the contrary, below T_{SP}, a lattice dimerization occurs in the chain (a dimerized chain), and an exchange interaction between neighboring spins alternates. As a result, the spin-singlet ground state with the energy gap is realized. The SP transition appears in a condition that a decrease of energy in the spin system overcomes an increase of elastic energy in the lattice. It is emphasized that the SP transition is a rare phenomenon in real materials. Generally, interchain exchange interactions exist in real materials and lead to a three-dimensional AF order (a Nèel order).

One of unsolved problems in the SP system is magnetic and structural properties in high magnetic fields. Figure 1 shows a magnetic-phase diagram. In addition to phases with dimerized and uniform chains (D and U phases), a magnetic (M) phase appears in high magnetic fields at low temperatures. It is noted that there is a universal behavior in the magnetic-phase diagram expressed by $gH/2T_{SP}(0)$ and $T/T_{SP}(0)$, where $T_{SP}(0)$ and g are T_{SP} in the absence of H and a g value.[5,6] In the M phase, the crystal structure changes and accordingly finite magnetizations appear. The appearance of the M phase with finite magnetizations seems to be quite natural, because there is no gain of Zeeman energy in the D phase. A discommensurate phase with magnetic solitons[7-12] or an incommensurate phase with a sinusoidal modulation[13,14] is a candidate for the M phase. Recently, Kiryukhin *et al.* have observed incommensurate superlattice peaks in the M phase for TTF-CuBDT[15] and $CuGeO_3$[16] using a high-resolution x-ray diffraction technique. However, higher harmonics of incommensurate peaks which determine a correct model has not been confirmed perfectly. Therefore, it is necessary to study the M phase further.

We have studied effects of impurities on the M phase. Investigations on effects of impurities provide various important results, *e.g.*, confirmation of a valence-bond solid in a Haldane system by ESR measurements in Cu-doped NENP.[20] Effects of impurities have been already studied in the low-field phases of $CuGeO_3$.[21] In $Cu_xZn_{1-x}GeO_3$, T_{SP} decreases rapidly with increasing x, and a novel AF order appears at low temperatures for $0.02 \leq x \leq 0.08$.[22,23] Thus, it is also expected that an

*IMR, Report No. 2037

observation of effects of impurities gives information on the M phase.

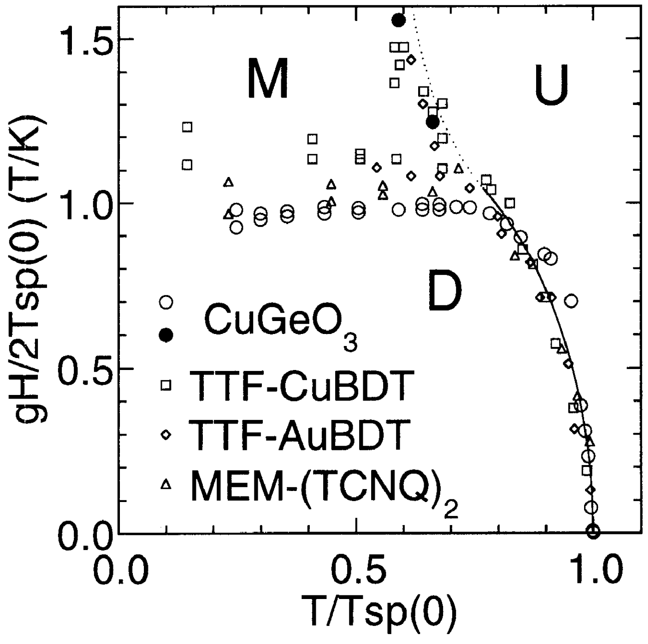

Figure 1. The magnetic-phase diagram represented by $gH/2T_{SP}(0)$ and $T/T_{SP}(0)$ of the spin-Peierls system. D, U and M denote the dimerized, uniform and magnetic phases. This figure includes experimental results of $CuGeO_3$ (open and closed circles from refs. 6 and 17), of TTF-CuBDT from ref. 18, of TTF-AuBDT from ref. 5 and of MEM-$(TCNQ)_2$ from ref. 19. Solid and dotted curves are theoretical phase boundaries of Cross (ref. 14)

2. Experiment

We made powder samples of $Cu_{1-x}Zn_xGeO_3$ with x=0, 0.005, 0.010 and 0.020 by a solid-state-reaction method. Starting materials are CuO (purity of 99.999 %), GeO_2 (99.9999 %) and ZnO (99.9 %). Stoichiometric mixture was sintered in a ZrO_2 crucible at 1000 °C for 50 hours in air. The values of $T_{SP}(0)$ are 14.0, 13.0, 12.1 and 10.2 K for x=0, 0.005, 0.010 and 0.020.[21] Magnetic-field dependence of magnetization $[M(H,T,x)]$ was measured by a vibrating sample magnetometer in H up to 15 T generated by a water-cooled magnet and by an extraction-type magnetometer in H up to 23 T generated by a hybrid magnet at High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University. The measurements were performed at various temperatures between 2.2 and 15.0 K.

3. Results

Figure 2 shows $M(H,T,x)$ for $x = 0.005$ measured in increasing H.[24,25] At 2.4 K, we observe a rapid change of $M(H,T,x)$ with an inflection point around 12 T, which indicates a phase transition between the D and M phases.[6] Besides, $M(H,T,x)$ below 8 T exhibits a concave behavior. As the temperature is raised, low-field $M(H,T,x)$ alters strongly, The rapid change around 12 T and the concave behavior below 8 T become less clear and finally disappear above 12.9 K. On the other hand, high-field $M(H,T,x)$ is insensitive to the temperature. $M(H,T,x)$ for $x = 0.010$ and 0.020 shows similar properties.[24,25]

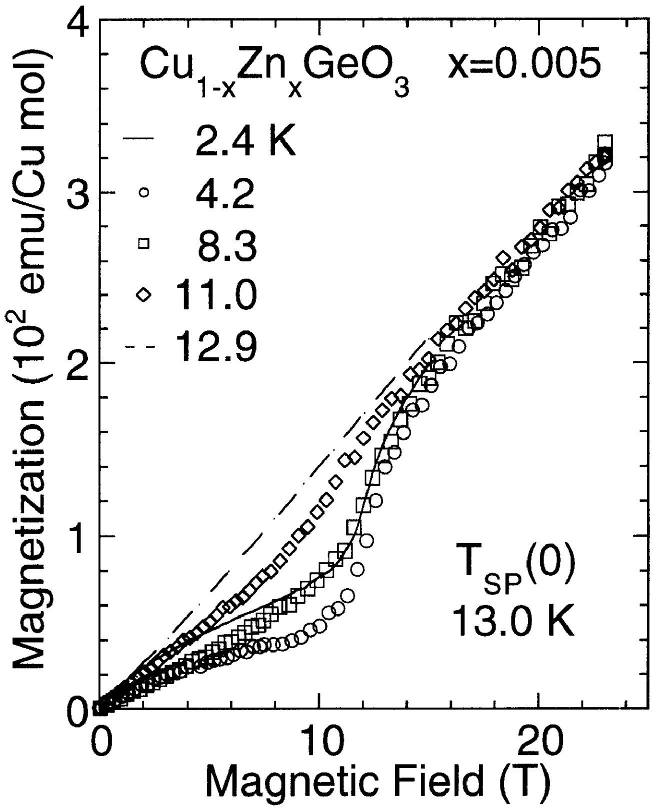

Figure 2. $M(H,T,x)$ of $Cu_{1-x}Zn_xGeO_3$ with $x = 0.005$ in increasing magnetic fields.

Figure 3 shows $M(H,T,x)$ for $x = 0.005$ in both increasing and decreasing H at 2.4 and 8.3 K. We can see hysteresis of $M(H,T,x)$ between increasing and decreasing fields at 2.4 K, while we cannot see it at 8.3 K. Therefore, the phase transition is of first and second order at low and high temperatures, respectively. The hysteresis is observed below 7.0 K for $x = 0.005$. Similarly, hysteresis is detected below 9.5, 7.0 and 2.4 K for x=0, 0.010 and 0.020.

Figure 4 shows $M(H,T,x)$ in increasing H at 4.2 K. As x increases, magnitude of $M(H,T,x)$ increases and the change of $M(H,T,x)$ associated with the phase transition becomes less evident. It should be emphasized that $M(H,T,x)$ depends on x weaklier in high H (the M phase) than in low H (the D phase), i.e., impurities influence $M(H,T,x)$ in high H less than in low H. In particular, $\partial M(H,T,x)/\partial H$ above 16 T is almost independent of x.

Figure 5 shows the magnetic-phase diagram expressed by H and T. The data above 5.5 T denote a critical field (H_c) related to the phase transition. The critical field is defined as a field of the inflection point in $M(H,T,x)$ *vs.* H. On the contrary, the data below 5.5 T indicate the H dependence of T_{SP} obtained from the T dependence of magnetic susceptibility in various H. At low temperatures, H_c is nearly independent of the temperature and decreases with Zn-doping. H_c in increasing

H (open symbols) is slightly larger than H_c in decreasing H (closed symbols) at low temperatures because of hysteresis in $M(H,T,x)$.

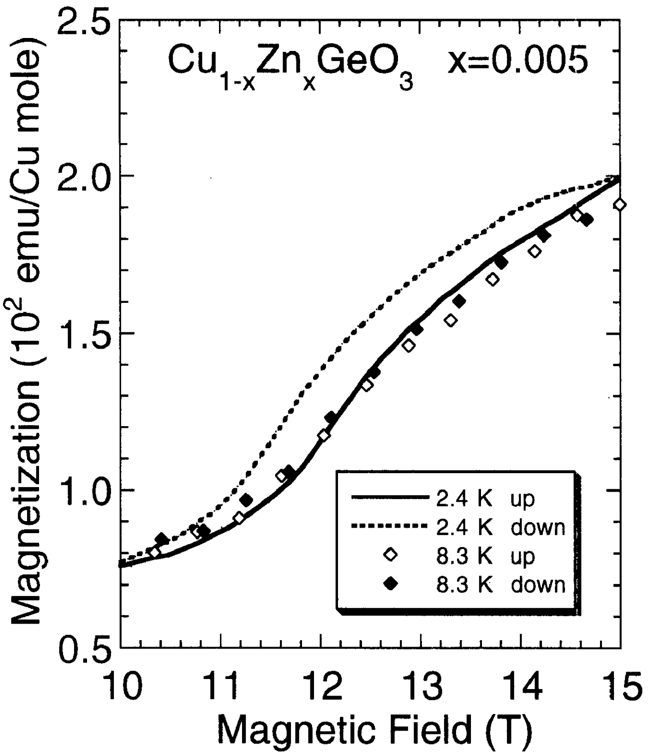

Figure 3. $M(H,T,x)$ of $Cu_{1-x}Zn_xGeO_3$ with $x = 0.005$ in both increasing and decreasing magnetic fields (up and down).

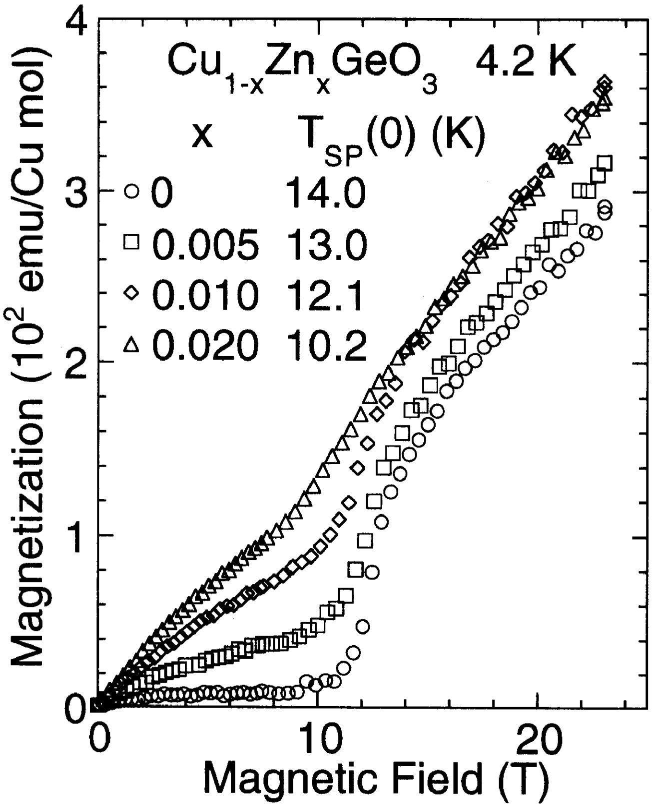

Figure 4. $M(H,T,x)$ of $Cu_{1-x}Zn_xGeO_3$ at 4.2 K in increasing magnetic fields.

The reduction of H_c upon doping is caused by a decrease of the energy gap (Δ). According to the theory of Lu *et al.*, Δ decreases with increasing x.[26] In the pure SP system, H_c is linealy proportional to Δ.[7] H_c possibly decreases with decreasing Δ in the impure SP system.

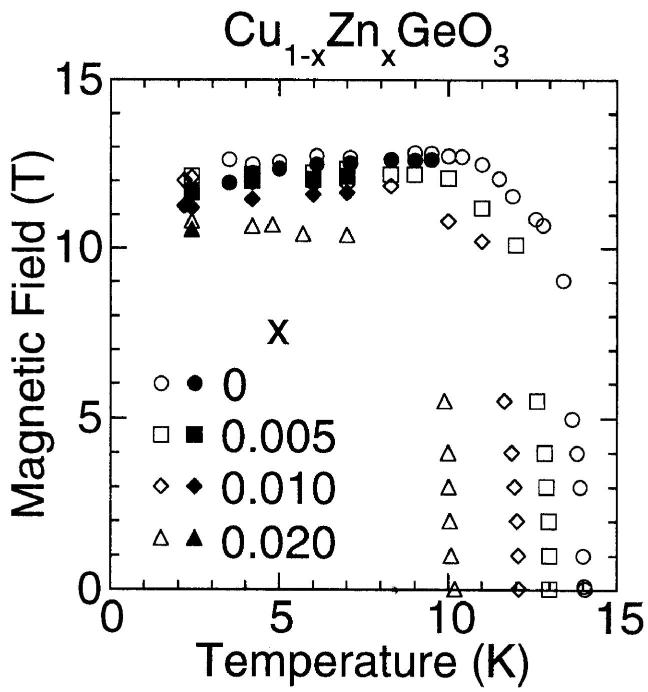

Figure 5. The magnetic-phase diagram of $Cu_{1-x}Zn_xGeO_3$. Open and closed symbols represent the critical fields in increasing and decreasing fields.

4. Discussions

Let us now discuss the weak x dependence of $M(H,T,x)$ in the M phase. Here we consider the origin of the magnetism in both the D and M phases. In the D phase, $M(H,T,x)$ at finite T is generated by four contributions; spins which cannot become singlet due to impurities (we call these spins "residual spins"), spins in triplet states, magnetic solitons which might exist at low T in the D phase[7] and an orbital part. In pure $CuGeO_3$, main component of $M(H,T,x)$ at sufficiently low temperatures below $T_{SP}(0)$ is the orbital part, and contributions of the triplet-state spins and the solitons are negligible.[3] On the other hand, $M(H,T,x)$ in Zn-doped $CuGeO_3$ at low temperatures is caused mainly by the residual spins. The orbital part is independent of x and is small.[3,21] Contributions of the triplet-state spins and the solitons probably depend weakly on x and are also negligible. Magnetizations caused by the triplet-state spins and the solitons are characterized by Δ and a soliton-formation energy [E_S ($= 0.287\Delta$)],repectively.[7] Δ and E_S are associated with H_c. As is seen in Fig. 5, H_c at low temperatures exists between 10 and 13 T in all the samples, *i.e.*, the x dependence of H_c is weak. Thus, Δ and E_S depend weakly on x. On the contrary, in the M phase at low temperatures, the magnetic solitons contribute to $M(H,T,x)$ besides the residual spins.

We estimate the number of spins contributing to $M(H,T,x)$ at low temperatures in both the D and M phases. The solitons are isolated net $S = 1/2$ spins when density of the solitons is low. The residual spins are also probably isolated net $S = 1/2$ spins. Finite spin density exists near the residual spin as spin density of an edge state in the Haldane system.[27-29] However, a net spin of the edge state is 1/2. Therefore, the net spin of the residual spin is also possibly 1/2. In addition, 1D AF correlation in each chain in the D phase does not develop enough for small x.[21] Thus, the residual spin is an isolated spin.

We define $n(H,T,x)$ which indicates a ratio of the number of the isolated $S = 1/2$ spins to that of total Cu^{2+} ions (density of the isolated S=1/2 spins).

$$n(H,T,x) \equiv \frac{M(H,T,x)}{N_A g \mu_B \frac{1}{2} \tanh(\frac{g\mu_B H}{2k_B T})},$$

where N_A, μ_B and k_B are the Avogadro number, the Bohr magneton and the Boltzmann constant. Figure 6 shows $n(H,T,x)$ at 4.2 K. $n(H,T,x)$ for $x = 0.005$ and 0.010 is nearly independent of H and close to x below 8 T. On the other hand, $n(H,T,x)$ for $x = 0.020$ shows weak H dependence and is smaller than x in the D phase.

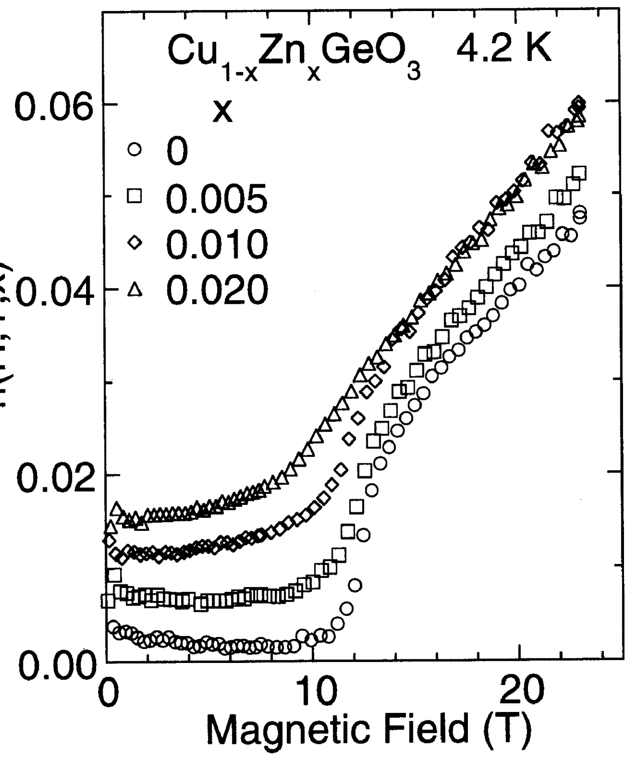

Figure 6. $n(H,T,x)$ of $Cu_{1-x}Zn_xGeO_3$ at 4.2 K.

It is considered that $\Delta n(H,T,x)$ [$\equiv n(H,T,x) - n(H \sim 0,T,x)$] reflects the density of the solitons originating in the M phase. Figure 7 shows $\Delta n(H,T,x)$ at 4.2 K. $n(H \sim 0,T,x)$ are 1.5×10^{-3}, 6.5×10^{-3}, 11.3×10^{-3} and 16.0×10^{-3} for x=0, 0.005, 0.010 and 0.020. It is noted that $\Delta n(H,T,x)$ is nearly independent of x in the M phase. The small influence of impurities upon the M phase can be qualitatively explained by the soliton model. The density of the solitons is determined by a lattice distortion of the whole system.[10,12] A local disorder due to substitution does not affect the lattice distortion in the M phase so much because of the small x. As is seen in Fig. 7, both the densities of the residual spins and the solitons are small in comparison with 1. Besides, a width of the soliton (ξ) is shorter than an average distance between two neighboring solitons. According to the theory of Nakano and Fukuyama,[7] $\xi = 1.57Ja/\Delta$, where J and a are the exchange interaction [30] and a distance between two neighboring spins in a chain. Using $\Delta = 24.5$ K evaluated from magnetic excitations[31] and $J = 140$ K obtained below, we estimate $\xi/a \sim 9$. The small ξ supports the idea that the soliton is isolated.

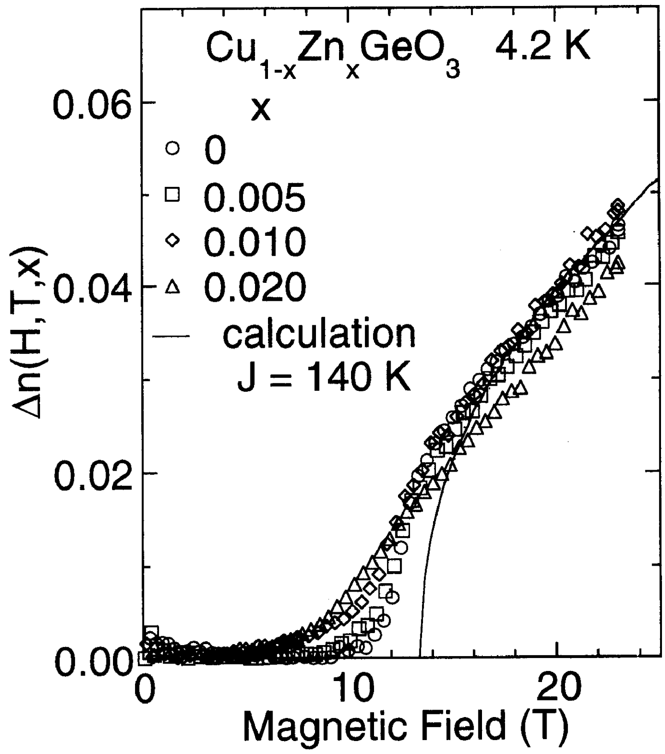

Figure 7. $\Delta n(H,T,x)$ of $Cu_{1-x}Zn_xGeO_3$ at 4.2 K. The solid curve is the theoretical magnetization.

Finally, we calculate the density of the solitons in the M phase. This density is expressed as aQ/π,[10] where a wave vector $\pi/a + Q$ gives a lattice distortion in the M phase. In the theory of Cross,[14] JaQ was calculated as a function of H. Therefore, we can evaluate the density of the solitons. A theoretical density with $J = 140$ K is denoted as a solid curve in Fig. 7, and is consistent with the experimental data above 16 T. The eatimated J in this work is close to values obtained from a magnetic-dispersion curve (121 K)[31] and a saturation field in high-field magnetization (183 K).[32]

5. Summary

We measure the magnetic-field dependence of the magnetization of the doped spin-Peierls cuprate $Cu_{1-x}Zn_xGeO_3$ with x=0, 0.005, 0.010 and 0.020 up to 23 T from 2.2 to 15.0 K in order to investigate influence of substitution on the magnetic phase. The rapid change of the magnetization related to the phase transition between the dimerized and other phases is observed. The magnetization above 16 T shows weak x and temperature dependence. The critical field is independent of temperature at low temperatures and decreases slightly with doping. Effects of doping on the magnetic phase are weak, although impurities affect significantly the dimerized phase. The results in this work suggest that the magnetic phase can be explained by the soliton model.

Acknowledgment

We would like to appreciate H. Obara of Electrotechnical Laboratory for collaboration, and H. Fukuyama, N. Nagaosa, A. Tanaka and Y. Katoh of the University of Tokyo, and K. Machida of Okayama University for invaluable discussions.

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