Magnetic properties of Cu$_6$Ge$_6$O$_{18}$-xH$_2$O ($x=0-6$): A compound of $S=1/2$ Heisenberg competing antiferromagnetic chains coupled by interchain interaction

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We studied magnetic properties of powder samples of Cu$_6$Ge$_6$O$_{18}$-xH$_2$O ($x=0-6$). Susceptibility above the antiferromagnetic (AF) transition temperature (T_N) agrees with susceptibility obtained from the one-dimensional Heisenberg $S=1/2$ model with competing AF interactions. Since the estimated ratio (0.27–0.31) between nearest-neighbor and next-nearest-neighbor AF exchange interactions is close to a critical value (0.24–0.30) which determines whether a spin gap exists or not, the spin system in Cu$_6$Ge$_6$O$_{18}$-xH$_2$O is probably located near a boundary between spin systems with gapless and gapped magnetic excitation. The value of T_N/T_{max}, where T_{max} is the temperature at which the susceptibility is maximum, shows a unique dependence on x. We speculate that a spin gap due to competing AF interactions exists at $x<1.54$ and that magnetic excitation is gapless at $x>1.54$, explaining qualitatively the dependence of T_N/T_{max} on x.

I. INTRODUCTION

Magnetic properties of low-dimensional quantum spin systems depend on strongly a value of spin (S), the number of exchange interactions per spin, and relative magnitude among exchange interactions, and interesting phenomena such as the spin-Peierls (SP) transition,[1] the Haldane gap,[2] and a spin gap in the $S=1/2$ two-leg-ladder system[3] appear in some conditions. Discovery of a model compound including an interesting spin system expands experimental studies on the spin system, which stimulates further theoretical interest. For example, after the observation of the SP transition in CuGeO$_3$,[4] many works on this cuprate and the SP transition have been carried out.[5–17] This leads to further understanding of the SP system and quantum spin systems.

The one-dimensional Heisenberg $S=1/2$ model with competing antiferromagnetic (AF) interactions (competing model) is one of intriguing spin systems. The Hamiltonian of this model is expressed as

$$\mathbf{H}=J\sum_{i=1}^{N}(\mathbf{S}_i\cdot\mathbf{S}_{i+1}+\alpha\mathbf{S}_i\cdot\mathbf{S}_{i+2}). \qquad (1)$$

A spin gap opens between spin singlet ground and excited states when α exceeds a critical value of $\alpha_c=0.24-0.30$.[9,18–20] Therefore, a quantum phase transition occurs at α_c. Considering the above-mentioned spin systems, we can expect that a model compound in which a spin gap is formed by competing AF interactions advances studies of the competing model. Such a compound, however, has not been found yet and therefore is desired. It is known that there exist nearest-neighbor and next-nearest-neighbor AF interactions in spin chains in the SP CuGeO$_3$,[9,10] and there are reports that the value of α in CuGeO$_3$ is larger than α_c.[10,15,17] However, since the SP transition occurs at low temperatures, the spin gap in CuGeO$_3$ is not caused solely by the competing AF interactions.

In order to find a model compound possessing a spin gap due to competing AF interactions, we have investigated sev-eral cuprates having spiral or zigzag chains of Cu^{2+} ions. In this paper, we will report magnetic properties of Cu$_6$Ge$_6$O$_{18}$-xH$_2$O ($x=0-6$). This cuprate has spiral chains of Cu^{2+} ions and the chains are coupled to one another by interchain exchange interaction. In fact, we knew that magnetic properties of isostructural Cu$_6$Si$_6$O$_{18}$-xH$_2$O had already been investigated when we started to study Cu$_6$Ge$_6$O$_{18}$-xH$_2$O. An antiferromagnetic long-range order (AFLRO) instead of a spin-singlet ground state appears below an AF transition temperature of $T_N=15.5-15.9$ K in Cu$_6$Si$_6$O$_{18}$-6H$_2$O.[21,22] There is a broad maximum around $T_{max}\sim45$ and 110 K in magnetic susceptibility of Cu$_6$Si$_6$O$_{18}$-xH$_2$O with $x=6$ and 0, respectively.[22,23] However, we determined to study Cu$_6$Ge$_6$O$_{18}$-xH$_2$O, because compounds having the same crystal structures do not show necessarily the same magnetic properties. For example, CuGeO$_3$ with the space group *Pmma* (No. 51) exhibits the SP transition, while CuSiO$_3$ with the same structure[24] exhibits an AF transition instead of the SP transition.[25] As a result, we found that susceptibility of Cu$_6$Ge$_6$O$_{18}$-xH$_2$O above T_N was consistent with susceptibility obtained from the competing model, although an AF transition occurred at low temperatures. Beside, we obtained an experimental result suggesting existence of a spin gap, although we could not prove existence of a spin gap due to an AF transition.

II. CRYSTAL STRUCTURE AND SPIN SYSTEM OF Cu$_6$Ge$_6$O$_{18}$-xH$_2$O

Cu$_6$Ge$_6$O$_{18}$-xH$_2$O was first synthesized by Brandt and Otto[26] and was shown to have the same structure as that of Cu$_6$Si$_6$O$_{18}$-6H$_2$O, a natural mineral called dioptase.[27] The space group of these cuprates is $R\bar{3}$ (No. 148). The value of x can be changed in the range of 6 to 0 without change in the crystal structure by choosing conditions of thermal treatment below 823 K.[26,28,29] On the other hand, these cuprates are transformed into SP CuGeO$_3$ or CuSiO$_3$ with the space group of *Pmma* (No. 51) at high temperatures.[24,26]

Localized spins exist only on Cu^{2+} ions ($S=1/2$) and

(a)

(b)
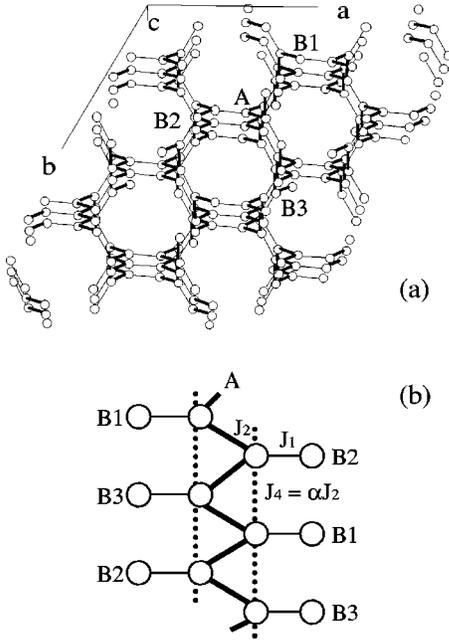
FIG. 1. (a) Schematic drawing of Cu^{2+}-ion positions ($\bigcirc$) in $Cu_6M_6O_{18}$-xH_2O (M=Ge or Si; x=0–6). Thin and bold bars indicate the 1NN and 2NN Cu-Cu bonds. Each spiral chain (e.g., chain A) formed by 2NN bonds has three nearest-neighbor chains (e.g., chains B1, B2, and B3). (b) An illustration of the spin system in $Cu_6Ge_6O_{18}$-xH_2O. The one-dimensional Heisenberg $S=1/2$ model with competing AF interactions can be formed in the spiral chain by the 2NN and 4NN bonds indicated by bold solid and dotted bars whose exchange interactions are expressed as J_2 and J_4, respectively. Each Cu^{2+} ion has one 1NN bond, and a Cu^{2+} ion represented by Bi (i=1–3), which is connected to every third Cu^{2+} ion in the spiral chain A by the exchange interaction in the 1NN bond (J_1), belongs to one spiral chain Bi.

their positions are shown schematically in Fig. 1(a). In the case of x=6, an octahedron surrounding a Cu atom is formed by two O(2), two O(3), and two O(4) atoms, where the O(4) atoms are apical oxygen and correspond to oxygen of water molecules. From Cu-O distances which will be shown in Table II later, we know that localized spins exist in $d_{x^2-y^2}$ orbits extending towards O(2) and O(3).

Next, we consider exchange interactions between spins on Cu^{2+} ions that determine magnetic properties of $Cu_6Ge_6O_{18}$-xH_2O. In the case of x=6, the distances between two Cu^{2+} ions are 2.96 and 3.27 Å for the first-nearest-neighbor [1NN; thin solid bars in Figs. 1(a) and 1(b)] and second-nearest-neighbor (2NN; bold solid bars) Cu-Cu bonds, respectively, while the distance is 4.93 Å for the third-nearest-neighbor bond and is greater than the above two distances. Therefore, exchange interactions in the 1NN and 2NN Cu-Cu bonds (J_1 and J_2) should be taken into account. From the Cu-O-Cu angles shown in Table II later, J_2 is positive (AF) and the magnitude of J_2 is larger than that of J_1. It has been shown that J_2 is AF and J_1 is negative (ferromagnetic; F) by measurements of magnetic Bragg peaks below T_N in $Cu_6Si_6O_{18}$-xH_2O with x=6 and 0.[21,23] Each Cu has two 2NN bonds and spiral chains are formed by the 2NN bonds. Because of the spiral chains, we may not be
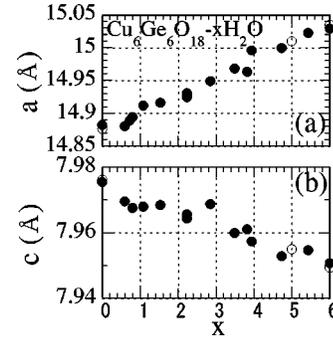
FIG. 2. Dependence of lattice parameters of $Cu_6Ge_6O_{18}$-xH_2O on x. Closed and open circles indicate the data obtained in this work and from Ref. 26, respectively.

able to ignore exchange interaction (J_4) in the next-nearest-neighbor Cu-Cu bond in the chain [dotted bars in Fig. 1(b)] through a Cu-O(2)-O(2)-Cu path. The next-nearest-neighbor Cu-Cu bond in the chain corresponds to the fourth-nearest-neighbor (4NN) Cu-Cu bond in the whole crystal.

The spin system is shown schematically in Fig. 1(b). The spin system in the spiral chains can be expressed by the competing model if J_4 is AF. Each Cu^{2+} ion has one 1NN bond and a spiral chain (e.g., chain A) is connected to three nearest-neighbor chains (chains B1, B2, and B3) by the 1NN bonds. A circle indicated by Bi means a Cu^{2+} ion in a chain Bi. A Cu^{2+} ion connected to every third Cu^{2+} ion in chain A belongs to one chain Bi.

III. EXPERIMENTS

Crystalline powder of $Cu_6Ge_6O_{18}$-$6H_2O$ was synthesized by reaction of copper(II) acetate $[Cu(CH_3COO)_2]$ and GeO_2 in an aqueous solution.[26] Samples with x<6 were obtained by thermal treatment at 423 to 823 K in air. Values of x were estimated by measuring the weights of samples before and after thermal treatment. Water is not removed when the temperature of the thermal treatment is lower than 373 K. Besides, once water has been removed, rehydration is impossible under ambient conditions.[26] Therefore, the water content was unchanged during our x-ray diffraction and magnetic susceptibility measurements. We obtained x-ray diffraction patterns at room temperature. As shown in Fig. 2, a increases and c decreases monotonically with increase in x. Structure parameters were refined by the Rietveld method from the x-ray diffraction data using the RIETAN program[30] and are summarized in Tables I and II. X-ray diffraction patterns of samples with x=0 and 6 at 8.5 K were also obtained and were identical with those at room temperature. Magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (quantum design MPMSXL). Electron spin resonance (ESR) measurements were performed by an x-band spectrometer (JEOL-JES-RE3X) at room temperature with a typical resonance frequency of 9.46 GHz. The gyromagnetic ratio of Cu^{2+} (g) is 2.08 or 2.07 for the powder sample with x=6 or 0. Besides, we confirmed that $Cu_6Ge_6O_{18}$-xH_2O is an insulator.

TABLE I. Atomic coordinates and isotropic displacement parameters B_{iso} ($\mathring{A}^2$) for $Cu_6Ge_6O_{18}$-xH_2O. Estimated standard deviations are shown in parentheses. All the atoms have fully occupied 18(f) sites of the space group $R\bar{3}$ (No. 148). Lattice parameters a and c, and agreement factors are also shown in this table. Some B_{iso}'s became negative when they were treated as free parameters. In this case, the B_{iso}'s were fixed to 1 ($B_{iso}=1$ without a standard deviation in this table).

Atom	x	y	z	B_{iso} ($\mathring{A}^2$)
$x=0$		$a=14.8821(5)$ Å		$c=7.9754(2)$ Å
Cu	0.4108(5)	0.4010(4)	0.0532(8)	0.8(2)
Ge	0.1795(3)	0.2186(3)	0.0377(7)	0.6(1)
O(1)	0.078(2)	0.183(2)	0.905(2)	0.9(6)
O(2)	0.288(2)	0.298(2)	0.930(3)	0.7(6)
O(3)	0.162(2)	0.280(1)	0.209(2)	1
$x=1.54$		$a=14.9159(7)$ Å		$c=7.9684(3)$ Å
Cu	0.4108(5)	0.4020(4)	0.0547(7)	0.9(1)
Ge	0.1795(3)	0.2193(3)	0.0378(6)	0.9(1)
O(1)	0.074(2)	0.181(2)	0.905(2)	0.8(5)
O(2)	0.290(2)	0.299(2)	0.926(3)	1
O(3)	0.161(2)	0.280(1)	0.208(2)	0.9(5)
O(4) water	0.151(9)	0.186(8)	0.54(1)	8(4)
$x=2.24$		$a=14.9305(7)$ Å		$c=7.9656(3)$ Å
Cu	0.4108(5)	0.4023(4)	0.0540(7)	1.0(1)
Ge	0.1798(3)	0.2200(3)	0.0379(6)	1.0(1)
O(1)	0.075(2)	0.181(2)	0.901(2)	0.9(5)
O(2)	0.291(2)	0.300(2)	0.928(3)	1
O(3)	0.163(2)	0.282(1)	0.208(2)	0.7(5)
O(4) water	0.155(6)	0.179(5)	0.565(7)	6(2)
$x=6$		$a=15.0290(6)$ Å		$c=7.9507(2)$ Å
Cu	0.4089(4)	0.4041(3)	0.0578(7)	0.8(1)
Ge	0.1793(3)	0.2201(3)	0.0390(6)	1.0(1)
O(1)	0.073(2)	0.179(2)	0.897(2)	1
O(2)	0.288(2)	0.300(2)	0.930(2)	1.0(5)
O(3)	0.162(2)	0.279(1)	0.207(2)	1
O(4) water	0.148(2)	0.178(2)	0.571(2)	3.5(6)

x	R_{WP}	R_P	R_E	R_I	R_F
0	0.0450	0.0334	0.0266	0.0227	0.0156
1.54	0.0393	0.0308	0.0299	0.0239	0.0163
2.24	0.0405	0.0321	0.0299	0.0218	0.0149
6	0.0402	0.0319	0.0274	0.0210	0.0130

IV. RESULTS AND DISCUSSION

Figure 3 shows temperature (T) dependence of magnetic susceptibility $\chi(T)$ of $Cu_6Ge_6O_{18}$-xH_2O measured in magnetic fields of $H=0.1$ T. In $\chi(T)$ of the sample with $x=6$, we can see a broad maximum around $T_{max}=100$ K. The value of T_{max} increases with a decrease in x. The broad maximum indicates that $Cu_6M_6O_{18}$-xH_2O ($M=$ Ge or Si) can be classified as low-dimensional antiferromagnets. This is consistent with the above-mentioned notion that the spin system consists of spiral chains coupled by the interchain exchange interaction. A Curie-Weiss term is seen in $\chi(T)$ at low tem-

peratures. We fitted $C/(T+\theta)+\chi_0$ to susceptibility below 6 K. Since the T range used in this fitting was very narrow, susceptibility of $Cu_6Ge_6O_{18}$-xH_2O was assumed to be T independent and was contained in the T-independent term, χ_0. In the sample with $x=6$, for example, we estimated θ to be 2.41 K and estimated the ratio (p) of spins contributing to the Curie-Weiss term to be 2.07×10^{-3} from the Curie constant C. Similar values of θ and p were obtained in other samples. In Fig. 3, $(1/1-p)[\chi(T)-C/(T+\theta)]$ of the sample with $x=6$ is also shown by a dotted curve. It should be noted that the Curie-Weiss term hardly affects the determination of

TABLE II. Interatomic distances and angles in $Cu_6Ge_6O_{18}$-xH_2O. The spin system having the exchange interactions between spins in the 2NN and 4NN bonds corresponds to the competing model.

	$x=0$	1.54	2.24	6
Cu–O(2) (Å)	1.95, 1.96	1.91, 1.97	1.93, 1.95	1.97, 1.99
Cu–O(3) (Å)	1.90, 1.96	1.88, 1.97	1.91, 1.94	1.94, 1.97
Cu–O(4) (Å)		2.41, 2.68	2.53, 2.57	2.58, 2.65
Cu–Cu (1NN) (Å)	2.94	2.93	2.93	2.96
Cu–Cu (2NN) (Å)	3.26	3.26	3.27	3.27
Cu–Cu (4NN) (Å)	5.64	5.64	5.64	5.64
O(2)–O(2) (4NN) (Å)	2.86	2.85	2.84	2.86
Cu-O(3)–Cu (1NN)	99.33°	99.18°	99.02°	98.45°
Cu-O(2)–Cu (2NN)	112.45°	114.36°	114.53°	111.49°

T_{max} and T_N, and comparison between experimental and theoretical susceptibilities in Fig. 4. The inset of Fig. 3 shows derivative curves $[d\chi(T)/dT]$. In $d\chi(T)/dT$ of the sample with $x=6$ or 0, there is one clear peak at 38.5 or 73.5 K, which indicates phase transition to the AF long-range order. There is one transition in samples except for $x\sim1.54$, as shown below. In the sample with $x=1.54$, the peak is widely broadened and therefore it is considered that two transitions overlap each other between 35 and 60 K.[31]

We assumed that the orbital part of susceptibility was 1×10^{-4} emu/Cu mol and subtracted that part from the experimental susceptibility. The remaining susceptibility is defined as $\chi_{spin}(T)$ and $\chi_{spin}(T)T_{max}$ is plotted as a function of T/T_{max} in Fig. 4(a). Taking experimental errors into account,

we can say that these curves are similar to one another and show no systematic change as a function of x. Here, we compare these curves with theoretical ones obtained from the competing model whose Hamiltonian in the notation of this paper is
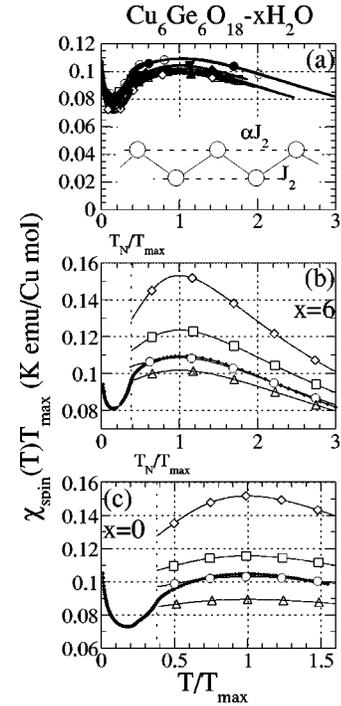
FIG. 4. (a) $\chi_{spin}(T)T_{max}$ versus T/T_{max}, where $\chi_{spin}(T)$ is defined as $\chi(T)-1\times10^{-4}$ (emu/Cu mol). Each curve in this figure corresponds to the curve with the same symbols as in Fig. 3. The inset shows the competing model. (b) The experimental $\chi_{spin}(T)T_{max}$ curve in the sample with $x=6$ (●) and theoretical ones obtained from the competing model. The parameters are $\alpha=0$ (◇; the Bonner-Fisher curve), $\alpha=0.20$ (□), $\alpha=0.27$ (○), and $\alpha=0.30$ (△). The g value determined by EPR measurements is 2.08. The vertical dashed line indicates the position of T_N/T_{max}. (c) The experimental $\chi_{spin}(T)T_{max}$ curve in the sample with $x=0$ (●) and theoretical ones obtained from the competing model. The parameters are $\alpha=0$ (◇; the Bonner-Fisher curve), $\alpha=0.24$ (□), $\alpha=0.29$ (○), and $\alpha=0.34$ (△). The g value determined by EPR measurements is 2.07. The vertical dashed line indicates the position of T_N/T_{max}.

FIG. 3. Temperature dependence of magnetic susceptibility $\chi(T)$ of $Cu_6Ge_6O_{18}$-xH_2O. The values of x are 6 (●), 5.43 (○), 3.95 (■), 2.90 (□), 2.24 (▲), 1.54 (△), 1.08 (◆), 0.80 (◇), and 0 (▼) from the upper to lower solid curves. The dotted curve represents $(1/1-p)[\chi(T)-C/(T+\theta)]$ of the sample with $x=6$. The inset shows $d\chi(T)/dT$ curves of the samples with $x=6$, 1.54, and 0. One division of the vertical scale means 5×10^{-6} emu/Cu mol K. The two arrows indicate AF transition temperatures in the sample with $x=1.54$.

$$\mathbf{H} = \sum_{i=1}^{N} (J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J_4 \mathbf{S}_i \cdot \mathbf{S}_{i+2}). \qquad (2)$$

Theoretical curves with various values of α ($=J_4/J_2$) (Ref. 32) and an experimental one of the sample with $x=6$ or 0 are shown in Fig. 4(b) or 4(c). The experimental curve of the sample of $x=6$ or 0 agrees with the theoretical curve of $\alpha = 0.27$ or $\alpha = 0.29$, while it does not agree with the theoretical curves of the other values of α in these figures. It is noted that the Bonner-Fisher curve cannot reproduce the experimental curves. Similarly, a theoretical curve of $\alpha = 0.31$ is consistent with the experimental curve of the sample with $x=0.80$, which is the smallest in Fig. 4(a) (not shown). These evaluated α are close to α_c. These results indicate two important facts. First, the competing model can explain the magnetic property of $Cu_6Ge_6O_{18}$-xH_2O above T_N at least as the first approximation, although the interchain exchange interaction (J_1) cannot be ignored actually. However, there is no theoretical curve taking J_2, J_4, and J_1 into account. Second, the spin system in $Cu_6Ge_6O_{18}$-xH_2O is located near a boundary between spin systems with gapless and gapped magnetic excitation, although α depends weakly and nonsystematically on x shown in Fig. 5(a). The same conclusion was obtained even when the value of the orbital part of susceptibility was changed from 1 to 1.5×10^{-4} emu/Cu mol. Of course, there is a clear difference between the competing model and $Cu_6Ge_6O_{18}$-xH_2O. The ground state is a spin singlet in the model, while it is AFLRO in $Cu_6Ge_6O_{18}$-xH_2O due to interchain interaction (J_1).

The dependence of T_{max} or T_N/T_{max} on x is shown in Fig. 5(b) or 5(c). As x decreases, T_{max} and therefore magnitude of exchange interactions increase monotonically. The value of T_N/T_{max} decreases with decrease in x from $x=6$, while it is nearly constant below $x=1.54$. At $x=1.54$, T_N/T_{max} jumps abruptly from 0.23 to 0.39, and two AF transitions are seen. The jump indicates that AFLRO's at $x>1.54$ and $x<1.54$ belong to essentially different phases. The two AF transitions at $x=1.54$ are probably due to a phase separation into high and low x phases. A phase separation always appears in the case of a first-order phase transition. The jump is reminiscent of Mg concentration dependence of T_N in $Cu_{1-y}Mg_yGeO_3$.[16] The value of T_N changes abruptly at a critical concentration $y_c=0.023$. Lattice dimerization exists and affects AFLRO at $y<y_c$, while AFLRO appears in a uniform lattice at $y>y_c$. Since the AFLRO's belong to essentially different phases, T_N jumps at y_c.

Let us now discuss the dependence of T_{max} on x. The change in T_{max} cannot be attributed to only Cu-Cu distances and Cu-O-Cu angles because these values are almost independent of x (Table II). In a Cu octahedron, π bonds are formed between Cu and O(4) of a water molecule.[33] Thus, electron distribution in the Cu octahedron is probably changed by extraction of water. Therefore, it is considered that exchange of spins in the Cu-O(2) and Cu-O(3) bonds increases with decrease in x, resulting in an increase in exchange interactions and therefore T_{max}.

Next, let us discuss the dependence of T_N/T_{max} on x. Based on the results indicating that the spin system in
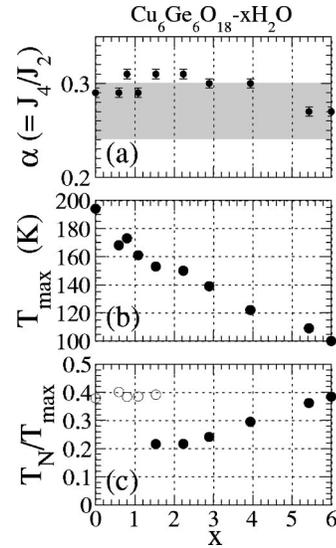
FIG. 5. (a) Dependence of α on x in $Cu_6Ge_6O_{18}$-xH_2O. The value of the vertical axis of the hatched area indicates the critical value α_c (0.24–0.30) obtained in Refs. 9, and 18–20 when interchain exchange interaction does not exist. (b) Dependence of T_{max} on x. (c) Dependence of T_N/T_{max} on x.

$Cu_6Ge_6O_{18}$-xH_2O is probably located near a boundary between spin systems with gapless and gapped magnetic excitation, we assume that a spin gap due to competing AF interactions exists at $x<1.54$ and that magnetic excitation is gapless at $x>1.54$. Of course, the existence of a spin gap has not been confirmed in the susceptibility. However, it should be emphasized that powder-averaged susceptibility of $CuWO_4$ does not clearly show existence of a spin gap due to appearance of AFLRO at 24 K,[34] although this cuprate has a gap of 1.4 meV (16 K) at the magnetic zone center originating in alternation of AF exchange interactions in $S=1/2$ chains.[35] It should also be emphasized that a spin gap and AFLRO can coexist. Examples are doped $CuGeO_3$,[13,14] $CuWO_4$,[34,35] $CsNiCl_3$ ($S=1$),[36] and $SrNi_2V_2O_8$ ($S=1$).[37]

Disorder is introduced by inhomogeneity of water in samples with $0<x<6$ and has a destructive effect on AFLRO. Thus, T_N/T_{max} decreases with a decrease in x at $x>1.54$. Disorder also has a destructive effect on a spin gap. The destruction of a spin gap leads to development of AF correlation and therefore leads to an increase in T_N/T_{max}. Thus, as x increases at $x<1.54$, a decrease in T_N/T_{max} due to the destructive effect on AFLRO compensates an increase in T_N/T_{max} due to the destructive effect on a spin gap. As a result, T_N/T_{max} is almost independent of x at $x<1.54$. Note that T_N increases with an increase in dopant concentration at a low concentration in spin systems that have a singlet ground state and a spin gap between singlet and excited states, such as $CuGeO_3$,[5,16] $S=1/2$ two-leg-ladder $SrCu_2O_3$,[38] and $S=1$ Haldane-material $PbNi_2V_2O_8$.[39,40] In these cases, it is considered that development of AF correlation due to destruction of a spin gap is more dominant than the destructive effect of disorder on AFLRO and T_N increases with an increase in dopant concentration.

We also considered other models, but they could not explain our results. One example is a random mixture with competing spin anisotropies whose T-x phase diagram may be similar to that in Fig. 5(c).[41] However, the two transition lines do not intersect in $Cu_6Ge_6O_{18}$-xH_2O, while two transition lines intersect in a random mixture with competing spin anisotropies. Thus, competing spin anisotropies cannot explain Fig. 5(c). In addition, there is no result indicating that the samples with $x = 0$ and 6 have different spin directions below T_N.

V. SUMMARY

We measured the magnetic susceptibilities of powder samples of $Cu_6Ge_6O_{18}$-xH_2O ($x = 0-6$). Susceptibility above T_N is consistent with susceptibility obtained from the one-dimensional Heisenberg $S = 1/2$ model with competing AF interactions. It is considered that the spin system is located near a boundary between spin systems with gapless and gapped magnetic excitation because the estimated ratio (0.27–0.31) between nearest-neighbor and next-nearest-neighbor AF exchange interactions is close to the critical value (0.24–0.30), which determines whether a spin gap exists or not. The value of T_N/T_{max} exhibits a unique dependence on x. From the results, we speculate that a spin gap due to competing AF interactions exists at $x < 1.54$ and that magnetic excitation is gapless at $x > 1.54$. In order to prove that the speculation is correct, we have to confirm the existence of a spin gap. Therefore, it is necessary to make single crystals of $Cu_6Ge_6O_{18}$-xD_2O, which we have not yet succeeded in, and to measure neutron scattering. Besides, in order to determine α more accurately, we will use theoretical susceptibility obtained from the competing model taking J_1 into account, which has not been reported so far.

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