Magnetic properties of $Rb_2Cu_2Mo_3O_{12}$ including a one-dimensional spin-1/2 Heisenberg system with ferromagnetic first-nearest-neighbor and antiferromagnetic second-nearest-neighbor exchange interactions

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We have investigated magnetic properties of $Rb_2Cu_2Mo_3O_{12}$ powder. Temperature dependence of magnetic susceptibility and magnetic-field dependence of magnetization have shown that this cuprate can be considered as a compound of a one-dimensional spin-1/2 Heisenberg system with ferromagnetic first-nearest-neighbor (1NN) and antiferromagnetic second-nearest-neighbor (2NN) competing interactions (competing system). Values of the 1NN and 2NN exchange interactions are estimated as $J_1=-138$ K and $J_2=51$ K ($\alpha\equiv J_2/J_1=-0.37$). This value of α suggests that the ground state is a spin-singlet incommensurate state. In spite of relatively large J_1 and J_2, no magnetic phase transition appears down to 2 K, while an antiferromagnetic transition occurs in other model compounds of the competing system with ferromagnetic 1NN interaction. For that reason, $Rb_2Cu_2Mo_3O_{12}$ is a suitable compound to study properties of the incommensurate ground state that are unconfirmed experimentally.

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I. INTRODUCTION

Quantum spin systems exhibit various interesting properties. They have been studied extensively. One example of interesting spin systems is a one-dimensional spin-1/2 Heisenberg system with first- and second-nearest-neighbor (1NN and 2NN) exchange interactions. When the 2NN interaction is antiferromagnetic (AF), competition between the two interactions occurs irrespective of the sign of the 1NN interaction. Therefore, intriguing phenomena are expected to appear. We label the spin system with antiferromagnetic 2NN interaction as a competing system in this article.

The competing system has been investigated theoretically over many years. Here we define Hamiltonian of the competing system as follows:

$$\mathcal{H}=\sum_{i=1}^{N}(J_1S_i\cdot S_{i+1}+J_2S_i\cdot S_{i+2}), \tag{1}$$

where S_i is a spin-1/2 operator at the ith site, and J_1 or J_2 is a 1NN or 2NN exchange interaction constant. When both J_1 and J_2 are AF, the ground state is a spin-liquid state. A spin gap opens between the spin-singlet ground and excited states when $\alpha\equiv J_2/J_1$ exceeds a critical value α_c.[1] At present, α_c is evaluated as 0.24–0.30.[2–5] The exact ground state is obtained when $\alpha=0.5$.[6,7] The ground state is expressed by products of singlet pairs formed between nearest-neighbor spins. It has twofold degeneracy. When J_1 is ferromagnetic (F) and J_2 is AF, the ground state is the ferromagnetic state for $-0.25<\alpha\leqslant 0$ and an incommensurate state with $S_{tot}=S^z_{tot}=0$ for $\alpha<-0.25$.[8] Here S_{tot} and S^z_{tot} are the total spin and its z-component. When $\alpha<-0.25$, it has been suggested that the gap is strongly reduced to the extent that the gap is too small for observation by any numerical method.[9] The exact ground state is obtained when $\alpha=-0.25$, according to Hamada *et al.*[10] A state with $S_{tot}=S^z_{tot}=0$ and $N+1$ states with $S_{tot}=N/2$ and $S^z_{tot}=0,\pm1,\pm2,\ldots\pm N/2$ (ferromagnetic states) are degenerate in energy and become the ground state. The state with $S_{tot}=S^z_{tot}=0$ is expressed by a linear combination of states of products of all singlet pairs which are distributed uniformly on all lattice sites. Hamada *et al.* called this state the uniformly distributed resonating valence bond (UDRVB) state. The spin-singlet ground state at $\alpha<-0.25$ approaches the UDRVB state in the limit of $\alpha\rightarrow-0.25$.[8] Sun *et al.* have conjectured the existence of a new phase in the region of $-(\pi-1)/2(\pi+1)<\alpha<-0.25$ where the ground state is incommensurate and has a nonzero total spin magnitude (partially ferromagnetic polarized state).[11]

The first realization of the competing system is the spin-Peierls cuprate $CuGeO_3$. The first paper reporting the appearance of the spin-Peierls transition,[12] indicated that magnetic susceptibility of $CuGeO_3$ does not agree with the calculated susceptibility of a one-dimensional spin-1/2 Heisenberg antiferromagnetic system. At first, this discrepancy had not been solved by experimental work on magnetic properties of pure and doped $CuGeO_3$.[13–16] Afterward, the possibility of existence of antiferromagnetic J_2 in addition to antiferromagnetic J_1 was suggested.[5,17] The calculated susceptibility of the competing system with antiferromagnetic J_1 and J_2 was sufficient to explain the experimental one.[5,18] Until now, several model compounds of the competing system have been found.[19–25] They are summarized in Table I. Nevertheless, in compounds with antiferromagnetic J_1, the spin gap expected in the case that $\alpha>\alpha_c$ has not been confirmed experimentally.[29] In compounds with ferromagnetic J_1 already reported, values of α imply that the ground state is incommensurate. These compounds are not suitable for study of the incommensurate ground state because antiferromagnetic long-range order appears at low temperature. Therefore, discovery of further model compounds is desired be-

TABLE I. Model compounds including the competing system. J_1 or J_2 is a first- or second-nearest neighbor interaction constant; α is defined as J_2/J_1. T_N indicates the AF transition temperature.

	J_1 (K)	J_2 (K)	α	T_N (K)
$CuGeO_3$[a]	150–160	36–57.6	0.24–0.36	SP
$Cu(ampy)Br_2$[b]	17	3.4	0.2	
$(N_2H_5)CuCl_3$[c]	4.1	16.3	4	1.55
$Cu_6Ge_6O_{18}-6H_2O$[d]	222	60	0.27	38.5
$Cu_6Ge_6O_{18}-0H_2O$[d]	451	131	0.29	73.5
$Li_{1.16}Cu_{1.84}O_{2.01}$[e]	67	19	0.29	22.3
$Pb[Cu(SO_4)(OH_2)]$[f]	−30	15	−0.5	2
$La_6Ca_8Cu_{24}O_{41}$[g]	−215	78	−0.36	12.2[h]
Li_2CuO_2[g]	−100	62	−0.62	8.3[i]
$Ca_2Y_2Cu_5O_{10}$[g]	−25	55	−2.2	29.5[j]
$Rb_2Cu_2Mo_3O_{12}$[k]	−138	51	−0.37	
$SrCuO_2$[l]	1–100	1800	18–1800	2

[a]References 5 and 18. SP indicates occurrence of the spin-Peierls transition.
[b]Reference 19. Cu[2-(2-aminomethyl)pyridine]Br_2 is abbreviated to $Cu(ampy)Br_2$. No magnetic phase transition is seen down to 1.6 K.
[c]Reference 20.
[d]Reference 21.
[e]Reference 22. The magnetic structure at low temperature is helimagnetic.
[f]Reference 23.
[g]Reference 24.
[h]Reference 26.
[i]Reference 27.
[j]Reference 28.
[k]This work. No magnetic phase transition is seen down to 2 K.
[l]Reference 25. The value of J_1 is roughly estimated absolute value and the sign of J_1 is not determined. Thus, the value of α is also the roughly estimated absolute value.

cause it expands experimental studies on the competing system and stimulates further theoretical interest. A typical example is development of understanding of quantum spin systems after the observation of the spin-Peierls transition in $CuGeO_3$.[12]

We have investigated several cuprates having spiral or zig-zag chains of Cu^{2+} ions ($S=1/2$) in order to find model compounds including the competing system. Recently, we reported $Cu_6Ge_6O_{18}$-xH_2O ($x=0-6$) as a one model compound.[21] This cuprate has spiral chains of Cu^{2+} ions. The chains are coupled to one another by an interchain exchange interaction. Magnetic susceptibility of $Cu_6Ge_6O_{18}$-xH_2O above AF transition temperature (T_N) was consistent with susceptibility obtained from the competing system with antiferromagnetic J_1, but an AF transition occurred at low temperature. In addition, we obtained an experimental result suggesting the existence of a spin gap, but we were unable to prove it because of an AF transition. In this article, we will show that $Rb_2Cu_2Mo_3O_{12}$, which has zig-zag chains of Cu^{2+} ions, is a compound including the competing system with ferromagnetic J_1.

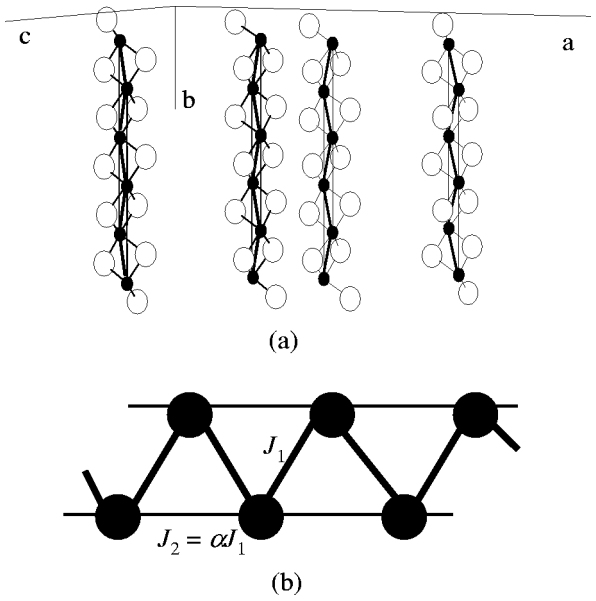

FIG. 1. (a) Schematic drawing of Cu^{2+}-ion positions (closed circles) and O^{2-}-ion positions (open circles) in $Rb_2Cu_2Mo_3O_{12}$. There are two crystallographic Cu sites and twelve O sites. Among them Cu(1), Cu(2), O(3), O(4), O(8), and O(12) are drawn in this figure. Oxygen connected to copper by a bar means neighboring oxygen of the copper. As a result, identical CuO_2 chains are formed. Exchange interactions are expected in 1NN and 2NN Cu-Cu bonds in chains indicated by bold and thin bars between Cu^{2+} ions through Cu-O-Cu and Cu-O-O-Cu paths, respectively. To show clearly CuO_2 chains, parts of Cu^{2+} and O^{2-} ions are omitted. The minimum distance between Cu^{2+} ion in a chain and that in neighboring chain is 4.90 Å and is larger than the distance of the 1NN Cu-Cu bond (3.08 and 3.09 Å). (b) An illustration of the spin system in $Rb_2Cu_2Mo_3O_{12}$. Closed circles indicate Cu^{2+} ions, and J_1 and J_2 are exchange interaction constants in the 1NN and 2NN Cu-Cu bonds.

II. CRYSTAL STRUCTURE AND SPIN SYSTEM OF $Rb_2Cu_2Mo_3O_{12}$

Solodovnikov and Solodovnikova first synthesized $Rb_2Cu_2Mo_3O_{12}$ and determined its crystal structure.[30] The space group is monoclinic $C2/c$ (No. 15). Lattice parameters are $a=27.698$ Å, $b=5.1018$ Å, $c=19.292$ Å, and $\beta=107.256^\circ$ with $Z=8$ $Rb_2Cu_2Mo_3O_{12}$ formula units per unit cell at room temperature. Localized spins exist only on Cu^{2+} ions ($S=1/2$). Their positions are shown schematically in Fig. 1(a). There are two crystallographic Cu sites. Slightly distorted chains formed by edge-shared CuO_6 octahedra parallel to the b axis correspond to $S=1/2$ zig-zag chains. The 1NN Cu-Cu bond in the chains (bold bars in Fig. 1) has a slight alternation: a Cu-Cu distance is 3.08 Å and Cu-O-Cu angles are 90.1° and 102.0° in one bond; and the distance is 3.09 Å and the angles are 92.0° and 101.2° in the other bond. We assume that the exchange interactions in these bonds J_1 are the same because the difference in the distances and angles between the two bonds is small. As shown later, experimental results and calculated ones based on this assumption are not mutually contradictory. The sign of J_1 cannot be determined from the crystal structure because both cases are allowed in such Cu-O-Cu angles. Because the Cu-O-Cu

angle is in the vicinity of 90°, the exchange interaction in the 2NN Cu-Cu bonds J_2 (thin bars in Fig. 1; 5.10 Å) in the chains is expected to exist through Cu-O-O-Cu paths like the spin-Peierls compound $CuGeO_3$. According to theoretical results of Mizuno *et al.*[24] the sign of J_2 is presumed to be AF. On the other hand, Cu-Cu distances in the other bonds except for the 1NN bond are larger than 4.90 Å. The Cu-O-Cu or Cu-O-O-Cu paths bringing magnetic interactions with magnitude comparable to J_1 or J_2 are not expected in the other bonds, although the other interactions cannot be ignored perfectly. Consequently, $Rb_2Cu_2Mo_3O_{12}$ is probably as the first approximation a compound including the competing system that is represented schematically in Fig. 1(b).

III. METHODS OF EXPERIMENTS AND CALCULATION

Crystalline powder of $Rb_2Cu_2Mo_3O_{12}$ was synthesized by solid-state reaction method. A stoichiometric mixture of Rb_2CO_3 (2N purity), CuO (4N purity), and MoO_3 (5N purity) was sintered at 733 K for 260 h in air with intermittent regrinding. We measured x-ray diffraction patterns at room temperature. The main phase is $Rb_2Cu_2Mo_3O_{12}$, but a small amount of $Rb_2Mo_3O_{10}$ (nonmagnetic) was detected. Therefore, a small amount of CuO (antiferromagnet) probably exists, but peaks of CuO are not observed as independent peaks. Notwithstanding, effects of the impurities are negligible because the magnetic susceptibility of $Rb_2Cu_2Mo_3O_{12}$ is much larger than those of the impurities.

Dependence of magnetic susceptibility $[\chi(T)]$ on temperature (T) was measured using a superconducting quantum interference device magnetometer (MPMSX L; Quantum Design). Dependence of magnetization $[M(H)]$ on the magnetic field (H) was measured using an extraction-type magnetometer in H up to 30 T induced by a hybrid magnet at the High Magnetic Field Center, NIMS. Electron spin resonance (ESR) measurements were performed using an X-band spectrometer (JES-RE3X; JEOL) at room temperature with a typical resonance frequency of 9.46 GHz. The powder-averaged gyromagnetic ratio of Cu^{2+} (g) was 2.03.

We calculated all energy levels in the competing system with $10 \leqslant N \leqslant 16$ under the periodic boundary condition by means of exact diagonalization. We then calculated dependence of magnetic susceptibility on temperature and dependence of magnetization on the magnetic field. Details of the calculation method are described in Ref. 31.

IV. RESULTS AND DISCUSSION

The solid curve in Fig. 2 represents magnetic susceptibility $\chi(T)$ of $Rb_2Cu_2Mo_3O_{12}$ powder measured in $H=0.1$ T. The susceptibility is defined as $M(H)/H$. As will be shown later in Fig. 4, $M(H)$ is linearly proportional to H below 1 T. We can see a broad maximum around $T_{max}=14.3$ K in the experimental $\chi(T)$. The susceptibility decreases with a decrease in T at low temperature, but the susceptibility does not appear to reach 0 at 0 K. No magnetic phase transition is detected to 2 K. The broad maximum does not mean occurrence of an AF transition because $\chi(T)$ at 2 K is smaller than half of $\chi(T)$ at T_{max} (χ_{max}). In an AF transition, on the other hand, $\chi(T)$ at sufficiently small T is about two thirds of $\chi(T)$ at AF transition temperature T_N in powder samples. Therefore, the broad maximum suggests existence of a low-dimensional AF spin system. The three dashed curves show calculated $\chi(T)$ of the competing system. Parameters are $J_1=22.3$ K and $\alpha=0$ for curve 1 (the Bonner-Fisher curve), and $J_1=29.5$ K and $\alpha=0.24$ for curve 2. For curves 1 and 2, the values of J_1 are determined such that T_{max} of the experimental $\chi(T)$ agrees with that of the calculated $\chi(T)$. Curve 3 is explained later. In all three calculated curves, the g value is 2.03, and the value of the other parts (χ_{const}) of susceptibility, except for spin susceptibility, is assumed to be 1.5×10^{-4}(emu/Cu mol). Curves 1 and 2 do not agree with the experimental $\chi(T)$. Because temperature dependence of calculated $\chi(T)$ becomes weak with an increase in α for $\alpha<1$, the competing system with $\alpha<1$ cannot explain the experimental $\chi(T)$. Similarly, the competing system with $\alpha>1$ does not reproduce $\chi(T)$ of $Rb_2Cu_2Mo_3O_{12}$ because calculated $\chi(T)$ decreases by the introduction of J_1 to two decoupled AF chains formed by J_2.[20] The fact that the calculated $\chi(T)$ of the competing system with antiferromagnetic J_1 are smaller than the experimental $\chi(T)$ suggests the existence of ferromagnetic interaction. In addition, as mentioned above, J_2 is considered to be AF. Consequently, a remaining possibility is the case that J_1 is F and J_2 is AF.

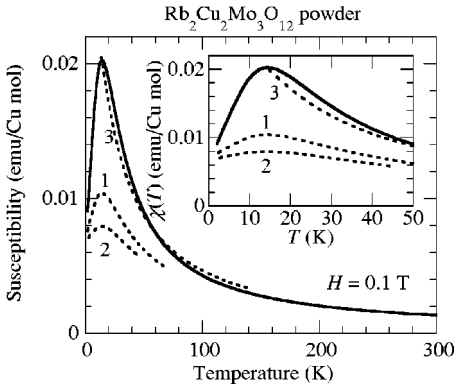

FIG. 2. Temperature dependence of susceptibility of $Rb_2Cu_2Mo_3O_{12}$ powder (solid curve) and calculated values obtained from the competing system (dashed curves). The parameters are $J_1=22.3$ K and $\alpha=0$ (Bonner-Fisher curve), $J_1=29.5$ K and $\alpha=0.24$, and $J_1=-138$ K and $\alpha=-0.37$ in curves 1, 2, and 3, respectively. The powder-averaged g value determined by ESR measurements is 2.03 at room temperature. In calculated curves, the value of the other parts (χ_{const}) of susceptibility aside from spin susceptibility is assumed to be 1.5×10^{-4} (emu/Cu mol). The inset shows susceptibility below 50 K.

In order to confirm whether the experimental $\chi(T)$ can be explained by the competing system with ferromagnetic J_1 and antiferromagnetic J_2, we calculated susceptibility. Figure 3 shows examples where $\alpha=-0.37$ and $N=12-16$. As described later, the calculated $\chi(T)$ with $\alpha=-0.37$ is consistent with the experimental $\chi(T)$. When $T/|J_1| \geqslant 0.1$, susceptibilities of $N=12-16$ agree with one another, indicating the susceptibility of $N\rightarrow\infty$. On the other hand, susceptibility at $T/|J_1|<0.1$ does not converge. We performed finite-size scaling to estimate the susceptibility of $N\rightarrow\infty$, but failed to

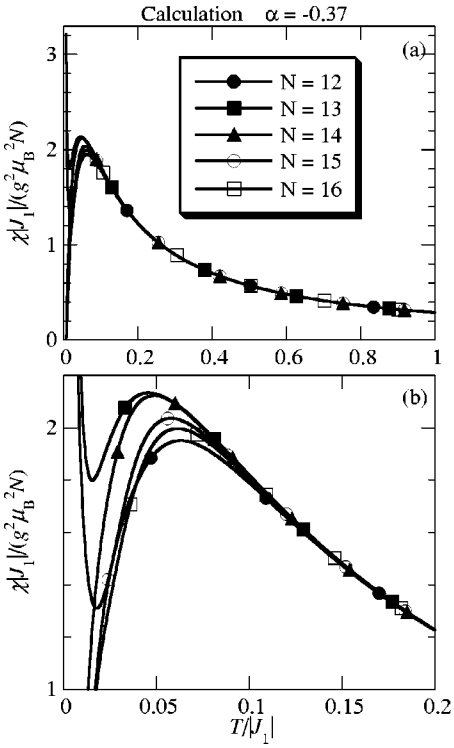

FIG. 3. Calculated susceptibilities of the competing system with $\alpha=-0.37$ at $T/|J_1| \leqslant 1$ or $\leqslant 0.2$ in (a) or (b).

estimate it. Tonegawa and Harada estimated the ground-state energy and the ground-state two-spin correlation function in the infinite-size limit by extrapolating the exact results for finite-size systems of up to 20 spins.[8] Cabra *et al.* commented that strong non-monotonic finite-size effects could be observed in particular at the smaller system sizes and that a reasonable approximation to the limit $N\rightarrow\infty$ seemed to be obtained from results for $N=20$ and 24.[32] The ground state of the competing system at $\alpha<-0.25$ is incommensurate, while wave numbers are limited to n/N with integer n in calculation for finite N. For those reasons, we infer that $N=16$ is insufficient to obtain susceptibility at low temperature and that exact results in the spin system with $20\leqslant N$ are necessary to obtain susceptibility of $N\rightarrow\infty$ at lower temperatures. As a result, we compared the experimental susceptibility with the calculated one at $T/|J_1|\geqslant 0.1$. We could not determine the value of $T_{\max}$ in our calculation. However, a broad maximum in susceptibility of the competing system exists, as indicated by a broad maximum that is visible in the susceptibility that was calculated by another group.[33] Therefore, existence of the broad maximum in $\chi(T)$ of $Rb_2Cu_2Mo_3O_{12}$ is consistent with the calculated result in the competing system.

We compared the experimental $\chi(T)$ with the calculated $\chi(T)$, but we were unable to determine values of J_1 and α uniquely in susceptibility. For that reason, we estimated those values through comparison between experimental and calculated magnetization. Figure 4 shows magnetization at 2.6 K. The experimental $M(H)$ indicated by the dashed curve starts to be saturated around 14 T, but is not saturated perfectly until 30 T. Since the slope of the experimental $M(H)$

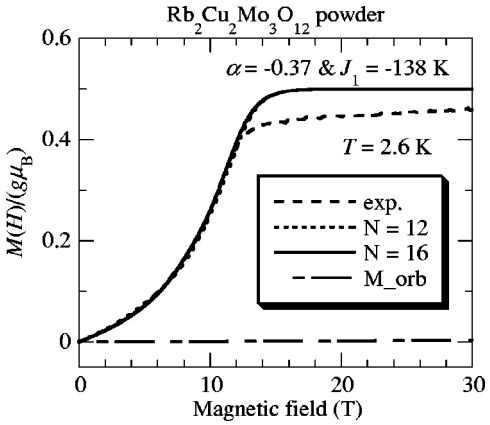

FIG. 4. Magnetic-field dependence of magnetization of $Rb_2Cu_2Mo_3O_{12}$ powder (dashed curve) and calculated ones obtained from the competing system with $N=12$ or $N=16$ (dotted or solid curve) at 2.6 K. The parameters are $J_1=-138$ K and $\alpha=-0.37$ in the calculated curves. The powder-averaged g value determined by ESR measurements is 2.03 at room temperature. The dash-dotted curve corresponds to $M_{\text{const}}\equiv\chi_{\text{const}}H$ with $\chi_{\text{const}}=1.5\times10^{-4}$(emu/Cu mol).

above 14 T in the unit of emu/Cu mol is ten times larger than $\chi_{\text{const}}\sim 1.5\times10^{-4}$(emu/Cu mol) indicated by the dashed-dotted curve in Fig. 4, the gradual increase above 14 T cannot be explained by a constant part of susceptibility. We calculated $M(H)$ with various values of J_1 and α, but we could not determine optimum values to reproduce well the experimental $M(H)$ in the whole region of H. Therefore, we consider that extra interactions aside from J_1 and J_2 exist, although extra interactions are not obvious from the crystal structure. At present, however, there is no theoretical result of a spin system including J_1, J_2, and extra interactions. Thus, we used our calculated results of the competing system. Since the experimental $M(H)$ can be reproduced in some extent by the competing system as is shown later, we consider that extra interactions are not so large in comparison to J_1 and J_2. Probably calculated $M(H)$ of the competing system should be slightly larger than the experimental $M(H)$ in the whole region of H, because it is expected that introduction of extra interactions reduces $M(H)$ in the whole region of H and improves discrepancy between experimental and calculated $M(H)$. However, it is impossible to determine uniquely a calculated $M(H)$ which is slightly larger than the experimental $M(H)$, because we do not have clear standard to do so. Accordingly, we determined calculated $M(H)$ which could reproduce experimental $M(H)$ at low H and the onset field of saturation. A dotted or solid curve represents calculated $M(H)$ of $N=12$ or 16 when $J_1=-138$ K and $\alpha=-0.37$. In contrast to susceptibility at low temperature, convergence of the calculated magnetization is sufficient at $N\geqslant 12$. Therefore, we infer that a calculated curve with $N=16$ is similar to magnetization of the infinite chain. The saturation field in our calculated $M(H)$ is almost the same as that in calculated $M(H)$ for $\alpha=-0.33$ by Cabra *et al.*[32] Consistency between the experimental and calculated $M(H)$ is well below 12 T. Since calculated $M(H)$ is shifted to lower fields with a de-

crease in absolute value of J_1 (not shown), we infer that our value of $|J_1|$ (138 K) is an upper limit of $|J_1|$. We also calculated magnetization with $J_1=22.3$ K and $\alpha=0$ or $J_1=29.5$ K and $\alpha=0.24$ (not shown). Calculated susceptibility with these values was shown in Fig. 2 and did not agree with the experimental susceptibility. The calculated magnetization is not saturated even at 30 T and is much different from the experimental magnetization.

We investigated whether the competing system with $J_1=-138$ K and $\alpha=-0.37$ could also explain the experimental $\chi(T)$. Calculated $\chi(T)$ with these values is shown in Fig. 2 by the dashed curve 3. It agrees with the experimental $\chi(T)$ in the compared region. As a result, susceptibility and magnetization suggest that $Rb_2Cu_2Mo_3O_{12}$ is a compound of the competing system with ferromagnetic 1NN and antiferromagnetic 2NN interactions at least as the first approximation. From the value of α, the ground state of the spin system in $Rb_2Cu_2Mo_3O_{12}$ is an incommensurate state with $S_{\mathrm{tot}}=S^z_{\mathrm{tot}}=0$. There is a strongly reduced spin gap that is too small to be observed using any numerical method. The small susceptibility at low temperature in comparison with χ_{max} may reflect the ground state and very small spin gap. Discrepancy between the experimental and calculated $\chi(T)$ may appear at lower temperature, which is probably attributable to other interactions aside from J_1 and J_2.

V. SUMMARY

We measured temperature dependence of magnetic susceptibility and magnetic-field dependence of magnetization of $Rb_2Cu_2Mo_3O_{12}$ powder. Comparison of experimental and calculated results revealed that this cuprate can be considered as a compound of a one-dimensional spin-1/2 Heisenberg system with ferromagnetic first-nearest-neighbor and antiferromagnetic second-nearest-neighbor competing exchange interactions (competing system). The values of the exchange interactions were estimated as $J_1=-138$ K and $J_2=51$ K ($\alpha\equiv J_2/J_1=-0.37$). The value of α indicates that the ground state is a spin-singlet incommensurate state. No magnetically ordered phase was observed down to 2 K, which is much smaller than the values of J_1 and J_2. In contrast, other model compounds of the competing system with ferromagnetic J_1 exhibit an AF transition. Therefore, $Rb_2Cu_2Mo_3O_{12}$ is a suitable material to investigate the incommensurate ground state that is expected theoretically, but unconfirmed experimentally in the competing system. Future studies must address internal magnetic fields at low temperature by NMR or μSR measurements and low-lying excited states by neutron-scattering measurements. In this paper, we could not reproduce well the experimental susceptibility and magnetization by our calculation technique. Accordingly, it is necessary to calculate susceptibility and magnetization of the competing system with J_1, J_2, and extra interactions in the case that $20\leqslant N$ and to evaluate susceptibility and magnetization of the infinite chains.

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