Static and Dynamic Magnetic Properties of spin-$\frac{1}{2}$ Inequilateral Diamond-Chain Compounds $A_3Cu_3AlO_2(SO_4)_4$ ($A=\text{K, Rb, and Cs}$)

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Spin-$\frac{1}{2}$ compounds $A_3Cu_3AlO_2(SO_4)_4$ ($A=\text{K, Rb, and Cs}$) have one-dimensional (1D) inequilateral diamond-chains. We analyze the temperature dependence of the magnetic susceptibility and determine the magnetic exchange interactions. In contrast to azurite, a dimer is formed on one of the sides of the diamond. From numerical analyses of the proposed model, we find that the dimer together with a nearly isolated 1D Heisenberg chain characterize magnetic properties including magnetization curve and magnetic excitations. This implies that a dimer-monomer composite chain without frustration is a good starting point for describing these compounds.

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I. INTRODUCTION

Highly frustrated quantum magnets provide various exotic ground states such as gapless spin-liquid and gapped singlet dimer phases. In a magnetic field, the magnets exhibit magnetization plateaus because of the competition of frustration and quantum fluctuations. The typical constituent of frustrated magnets is a triangular unit of spin with antiferromagnetic (AFM) interaction for each bond. The spin-$\frac{1}{2}$ diamond-chain where the triangular unit is connected linearly is thus regarded as a typical highly frustrated system in one dimension. Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ has originally been suggested to be a spin-$\frac{1}{2}$ distorted diamond-chain with AFM interactions for three bonds of a triangular unit. A recent theoretical approach based on density functional theory together with numerical many-body calculations has proposed a microscopic model of azurite with less frustrated interactions. Two of three $\text{Cu}^{2+}$ spins are coupled strongly by AFM interaction $J_2$ [see Fig. 1(b)] to form a dimer singlet, whereas another spin consists of a monomer spin that is weakly connected to neighboring monomer spins by AFM interaction $J_m$, which has been indicated in the early stage of research in azurite. This model, including the two energy scales of $J_2$ and $J_m$, has nicely reproduced the double-peak structures observed in the magnetic susceptibility (a peak at 5 K and a broad peak at 23 K) and the specific heat. In a magnetic field, the 1/3 magnetization plateau is interpreted as a result of almost fully polarized monomer spins and bounded dimer spins. The model predicts a gapless low-energy spin excitation originating from a spin-liquid behavior due to an effective spin-$\frac{1}{2}$ Heisenberg chain. However, three-dimensional magnetic interactions in azurite cause a magnetic order below 1.85 K.

Recently, a new highly one-dimensional (1D) diamond-chain compound $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ has been reported. In this compound, the magnetic susceptibility exhibits a double-peak structure similar to azurite, but the temperatures of the peaks (50 and 200 K) are one order of magnitude higher than those in azurite. Despite such high characteristic temperatures, there is no magnetic order down to 0.5 K, indicating a possible spin-liquid ground state. It is, thus, important to clarify common features characterizing the distorted diamond-chain compounds in both azurite and the new compound.

In this paper, we analyze the temperature dependence of the magnetic susceptibility in $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ as well as newly synthesized compounds where Rb and Cs are substituted for K by using the finite-temperature Lanczos (FTL) method and the exact diagonalization (ED) method. The estimated magnetic exchange interactions are found to form strong dimer bonds and monomer-monomer chains. This is similar to azurite, although the dimer-bond positions as well as their energy scales are different. The frustration is less effective in $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ than in azurite, and the spin-liquid behavior at low temperatures is attributed to an effective spin-$\frac{1}{2}$ Heisenberg chain. Therefore, it is reasonable to conclude that diamond-chain compounds consisting of $\text{Cu}^{2+}$ are less frustrated materials and thus a good starting point for the compounds is a dimer-monomer composite structure. Based on the estimated exchange interactions in $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$, we predict the magnetization curve with the 1/3 plateau and inelastic neutron-scattering spectrum by density matrix renormalization group (DMRG) calculations.

This paper is organized as follows. We describe the crystal structure of $\text{A}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ ($A=\text{K, Rb, and Cs}$) and discuss this effective model in Sec. II. In Sec. III, we analyze the temperature dependence of the magnetic susceptibility of $\text{A}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ and determine the magnetic exchange interactions. The magnetization curve and dynamical spin structure factor in $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ are shown in Sec. IV. Finally, a summary is given in Sec. V.
is the Bohr magneton, and $g$ is the gyromagnetic ratio.

Before fitting calculated magnetic susceptibilities to experimental ones, we need to roughly evaluate the value of exchange interactions. From the crystal structure analysis of $K_3Cu_3AlO_2(SO_4)_4$, the average Cu-O-Cu angle is estimated to be 104.7°, 95.2°, 102.5°, 105.8°, and 132.0° for the $J_1$, $J_2$, $J_3$, $J_4$, and $J_5$ bond, respectively. Since the Cu-O-Cu angle significantly influences on the value of the exchange interactions, the variation of the angles can give strong bond-dependent exchange interactions. According to the angle-dependent exchange interaction of cuprate, $J_5$ with the largest angle is expected to be an AFM interaction with very roughly $\sim 500$ K, whereas $J_2$ with the smallest angle is to be ferromagnetic (FM) ($\sim -100$ K). The values of the exchange interactions for other bonds are expected to be in between $J_2$ and $J_5$. For simplicity, we take $J_1 = J_3 = J_4$ because of similar Cu-O-Cu angles. We emphasize that the side of the $J_1$ bond and the side of the $J_5$ bond, which are opposite sides of a diamond, are inequivalent. This means that the diamond is distorted making opposite sides inequivalent, i.e., an inequilateral diamond. We thus call $A_3Cu_3AlO_2(SO_4)_4$ the inequilateral diamond-chain compound.

III. MAGNETIC SUSCEPTIBILITIES

Taking into account this initial guess for the exchange interactions, we first investigate the temperature dependence of the spin susceptibility for $K_3Cu_3AlO_2(SO_4)_4$ by performing the FTL calculations for a 24-site diamond periodic chain [eight triangular units (the total number of site $N = 8 \times 3$)] together with the ED calculations for an 18-site diamond periodic chain. The calculated spin susceptibility $\chi$ is compared to the experimental data obtained by subtracting the diamagnetic susceptibility $\chi_{dia}$, the impurity-spin paramagnetic susceptibility $\chi_{imp}$, and the Van Vleck paramagnetic susceptibility $\chi_{VV}$ from the experimentally observed magnetic susceptibility. Figure 2(a) shows the experimental result (red solid line) and fitted results (black dashed line for $N = 24$ and brown dot-dashed line for $N = 18$) of $\chi$ for $K_3Cu_3AlO_2(SO_4)_4$. The parameter values are listed in Table III. With increasing system size from $N = 18$ to 24, the fitted results systematically approach the experimental one, indicating that the deviation from the experiment at $T < 70$ K is due to the finite size effect. We find that the double-peak structure is reproduced clearly: A broad peak at 200 K comes from large $J_5$ forming a dimer on the corresponding bond, whereas the low-temperature peak at 50 K is attributed to a 1D Heisenberg interaction with positive $J_4$ being similar to the case of azurite. The other parameters only affect the heights of the two peaks. Since low-temperature $\chi$ for $N = 24$ below 30 K agrees with $\chi$ for an eight-site Heisenberg chain with the exchange interaction $J_4$, it is naturally expected that the low-temperature $\chi$ in experiment is reproduced by the exact $\chi$ for the 1D Heisenberg model. In fact, the Bethe-
susceptibility in FIG. 2. (Color online) Temperature dependence of spin solution for the infinite Heisenberg chain is plotted by the denoted by the brown dot-dashed line, and the Bethe-ansatz width of the line. In (a), an ED result for an 18-spin chain is data obtained by the FTL method for a 24-spin inequilateral mental data. The black dashed lines represent the fitted = Rb and Cs. The red solid lines show the experi-
mental data, although some deviations probably due to the dotted line in Fig. 2(a) well reproduces the experimen-
tal uncertainty of the FTL is within the maximum interaction in azurite (\(\sim J\)). Similarly \(J_4 = J'_4 = J_m\) in A = K is 16 times larger than \(J_m\) in azurite (\(\sim 4.62 \) K). Another important difference appears on the \(J_2\) bond: \(J_2\) is FM in K\(_3\)Cu\(_3\)AlO\(_2\)(SO\(_4\))\(_4\), whereas the dimer is located on the bond in azurite. It is also remarkable that there is only weak frustration in the diamond of K\(_3\)Cu\(_3\)AlO\(_2\)(SO\(_4\))\(_4\) since the magnitude of the FM \(J_4\) interaction inducing frustration in a triangle is very small as compared with two other interactions \(J_2\) and \(J_5\).

To confirm the magnetic interactions on \(A\)-site substi-
tuted compounds, we synthesized a single phase crystal with \(A = \text{Rb and Cs}\) by a solid-state reaction in which high-purity \(A_2\)SO\(_4\), CuO, CuSO\(_4\) and AlK(SO\(_4\))\(_2\) powder were mixed with a molar ratio of 1 : 2 : 1 : 1. The mixture was heated at 600°C for three days and then slowly cooled in air.

We fit calculated \(\chi\) to the experimental ones for \(A = \text{Rb and Cs}\) in Fig. 2(b). The two-peak structure is less pronounced but visible for \(A = \text{Cs}\). From the estimated parameter values of the exchange interactions listed in Table I we find that \(J_5\) for \(A = \text{Rb and Cs}\) is 10% smaller than that for \(A = \text{K}\). Actually the broad peak position shifts to a lower temperature by nearly the same amount. In contrast, \(J_4 = J'_4 = J_m\) increases from \(A = \text{K and Rb to Cs}\), inducing a slight shift of the low-
temperature peak to a high-temperature peak. Other parameters with FM interactions reduce their magnitude from \(A = \text{K to Rb and Cs}\). These material-dependent changes in the interactions indicate a small change in Cu-
O-Cu bond angles between K and Rb (Cs). A detailed crystal structure analysis will be necessary to confirm this and remains a future problem.

### TABLE I. The exchange interactions and the gyromagnetic ratio obtained by fitting calculated \(\chi\) to experimental ones.

| \(A\) | \(J_1\) | \(J_3\) | \(J_4\) | \(J_5\) | \(J_m\) | \(M\) | \(g\) |
|---|---|---|---|---|---|---|---|
| K | -30 | -300 | 510 | 75 | 2.14 |
| Rb | -17 | -252 | 462 | 84 | 2.12 |
| Cs | -19 | -238 | 456 | 95 | 2.17 |

IV. MAGNETIZATION CURVE AND DYNAMICAL SPIN STRUCTURE FACTOR

To confirm the validity of the estimated exchange interactions, we calculate the magnetization curve for K\(_3\)Cu\(_3\)AlO\(_2\)(SO\(_4\))\(_4\) and compare it with available experimental data. The magnetization curve is calculated by DMRG for a [\(N = 120(\sim 40 \times 3)\)]-site periodic chain at zero temperature. The number of states kept in the DMRG calculation is \(m = 300\), and the resulting truncation error is less than \(2 \times 10^{-6}\). Figure 3 shows the calculated magnetization curve (red solid curve) as well as the experimental data (blue solid line) for a low magnetic field up to \(H = 72\) T. The agreement with the experimental data is quite good. The magnetization near zero field is proportional to \(H\), which is characteristic behavior in the 1D Heisenberg model and consistent with the fact that the low-energy scale is controlled by 1D interaction \(J_4\) as evidenced by good agreement with the exact magnetization curve (green dashed line) for the 1D Heisenberg model. The calculated curve exhibits a magnetization plateau at the magnetization \(M = 1/3\) as expected. The 1/3 plateau starts from 108 T, which can be accessible by a pulse magnet experiment. Such an experiment is desired to confirm our proposed model. The

FIG. 2. (Color online) Temperature dependence of spin susceptibility in \(A_2\)Cu\(_3\)AlO\(_2\)(SO\(_4\))\(_4\) for (a) \(A = \text{K}\) and (b) \(A = \text{Rb and Cs}\). The red solid lines show the experimental datum. The black dashed lines represent the fitted data obtained by the FTL method for a 24-spin inequilateral diamond-chain. Note that the error of the FTL is within the width of the line. In (a), an ED result for an 18-spin chain is denoted by the brown dot-dashed line, and the Bethe-ansatz solution for the infinite Heisenberg chain is plotted by the green dotted line. The parameters are listed in Table I. The obtained value of \(J_5\) is the largest and 15 times larger than the maximum interaction in azurite (\(\sim 33 \) K). Similarly \(J_4 = J'_4 = J_m\) in \(A = \text{K}\) is 16 times larger than \(J_m\) in azurite (\(\sim 4.62 \) K). Another important difference appears on the \(J_2\) bond: \(J_2\) is FM in K\(_3\)Cu\(_3\)AlO\(_2\)(SO\(_4\))\(_4\), whereas the dimer is located on the bond in azurite. It is also remarkable that there is only weak frustration in the diamond of K\(_3\)Cu\(_3\)AlO\(_2\)(SO\(_4\))\(_4\) since the magnitude of the FM \(J_4\) interaction inducing frustration in a triangle is very small as compared with two other interactions \(J_2\) and \(J_5\).
calculated onset field of the 1/3 magnetization plateau is 119 and 130 T for \( A = \text{Rb} \) and \( \text{Cs} \), respectively (not shown here). The slight increase in the onset field as compared with the \( A = \text{K} \) case is attributed to the increase in \( J_d \).

We also examine the dynamical spin structure factor for \( \text{K}_3\text{Cu}_2\text{AlO}_2(\text{SO}_4)_4 \), defined by

\[
S(q, \omega) = -\frac{1}{\pi N} \text{Im} \langle 0 | S_{q, \omega}^z - \mathcal{H} + E_0 + i\eta S_{q, \omega}^z | 0 \rangle, \tag{2}
\]

where \( q \) is the momentum for the triangular unit cell, \(|0\rangle\) is the ground state with energy \( E_0 \), \( \eta \) is a broadening factor, and \( S_q^z = N^{-1/2} \sum_i \epsilon_q R_i S_i^z \) with \( R_i \) being the position of spin \( i \) and \( S_i^z \) being the \( z \) component of \( S_i \). \( S(q, \omega) \) is calculated by using the dynamical DMRG\(^{18} \) for a \((N=240)\)-site periodic chain (80 triangular cells). The truncation number is \( m = 400 \), and the truncation error is less than \( 7 \times 10^{-3} \). The value of \( \eta \) is taken to be 0.65 meV.

Figure 4 shows the contour plot of \( S(q, \omega) \). At the low-energy region below 10 meV, we find a clear dispersive behavior fitted quite well by \((\pi/2)J|\sin q|\) with \( J = J_d \) (the red dashed line). This indicates that the lowest-energy branch comes from the 1D Heisenberg chain connected by the \( J_d \) bond. At the high-energy region around 40 meV, there is a dispersive structure having a minimum at \( q = \pi \). This is nothing but the dispersion of a dimer predominantly formed on the \( J_b \) bond. The dispersion relation is well reproduced by the second-order perturbation theory in terms of \( J_m(= J_d' \) giving a dispersion of \( \omega_q = J_5 + J_m \cos q + \frac{1}{4}J_m^2/J_5(3 - \cos 2q) \) (the green dashed line)\(^{19,20} \), although there is a small deviation. Both the low-energy and high-energy structures should appear in inelastic neutron-scattering experiments. In fact, a preliminary experiment for the powder sample of \( \text{K}_3\text{Cu}_2\text{AlO}_2(\text{SO}_4)_4 \) has shown the corresponding structures\(^{13} \).

V. SUMMARY

We have examined the temperature dependence of the magnetic susceptibility for the inequilateral diamond-chain compound \( A_3\text{Cu}_2\text{AlO}_2(\text{SO}_4)_4 \) \((A = \text{K}, \text{Rb}, \text{and Cs}) \) both experimentally and theoretically. The systematic analyses for \( A = \text{K}, \text{Rb}, \) and \( \text{Cs} \) clearly demonstrate that one of the bonds of the diamond has a strong AFM exchange interaction, producing a dimer. On the other hand, the bond shared by two triangles in the diamond is FM, in contrast to azurite where a dimer is formed on this bond. These behaviors are in accord with the angle dependence of the Cu-O-Cu bond. The dimer controls a high-temperature peak of the magnetic susceptibility as well as a high-energy dispersive structure in the dynamical spin structure factor. On the other hand, a low-energy peak in the magnetic susceptibility and low-energy excitations are controlled by monomers forming a 1D Heisenberg chain. Therefore, the dimer-monomer composite structure is a good starting point of diamond-type quantum spin compounds including azurites, in contrast to the original idea that the diamond-chain compounds are highly frustrated. Spin-liquid behaviors observed in the diamond-chain compounds thus are attributed to the presence of a 1D Heisenberg chain.
formed by the monomers. In $A_3Cu_3AlO_2(SO_4)_4$, the magnetization curve with the $1/3$ plateau and inelastic neutron-scattering spectra separated by the two energy scales are expected as theoretically demonstrated. Experiments to confirm these predictions are in progress.

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1. L. Balents, Nature 464, 199 (2010).
2. Introduction to Frustrated Magnetism, edited by C. Lacroix, P. Mendels, and F. Mila, Springer Series in Solid-State Sciences (Springer, Berlin, 2011), Vol. 164.
3. T. Imai and Y. S. Lee, Phys. Today 69(8), 30 (2016).
4. K. Takano, K. Kubo, and H. Sakamoto, J. Phys.: Condens. Matter 8, 6405 (1996).
5. K. Okamoto, T. Tonegawa, Y. Takahashi, and M. Kaburagi, J. Phys.: Condens. Matter 11, 10485 (1999).
6. K. Okamoto, T. Tonegawa, and M. Kaburagi, J. Phys.: Condens. Matter 15, 5979 (2003).
7. H. Kikuchi, Y. Fujii, M. Chiba, S. Mitsudo, T. Idehara, T. Tonegawa, K. Okamoto, T. Sakai, T. Kuwai, and H. Ohta, Phys. Rev. Lett. 94, 227201 (2005).
8. H. Jeschke, I. Opahle, H. Kandpal, R. Valentí, H. Das, T. Saha-Dasgupta, O. Janson, H. Rosner, A. Brühl, B. Wolf, M. Lang, J. Richter, S. Hu, X. Wang, R. Peters, T. Pruschke, and A. Honecker, Phys. Rev. Lett. 106, 217201 (2011).
9. K. C. Rule, A. U. B. Wolter, S. Sülloß, D. A. Tennant, A. Brühl, S. Köhler, B. Wolf, M. Lang, and J. Schreuer, Phys. Rev. Lett. 100, 117202 (2008).
10. A. Honecker, S. Hu, R. Peters, and J. Richter, J. Phys.: Condens. Matter 23, 164211 (2011).
11. M. Fujihala, H. Koorikawa, S. Mitsuda, M. Hagihala, H. Morodomi, T. Kawae, A. Matsuo, and K. Kindo, J. Phys. Soc. Jpn. 84, 073702 (2015).
12. J. Jaklič and P. Prelovšek, Adv. Phys. 49, 1 (2000).
13. M. Fujihala, H. Koorikawa, S. Mitsuda, K. Morita, T. Tohyama, K. Tomiyasu, A. Koda, H. Okabe, S. Itoh, T. Yokoo, S. Ibuka, M. Tadokoro, M. Itoh, H. Sagayama, R. Kumai, Y. Murakami, D. Nakamura, and S. Takeyama, arXiv:1705.01158.
14. Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B 57, 5326 (1998).
15. $\chi_{\text{dia}}$ is estimated from $\chi_{\text{imp}}$, $\chi_{\text{imp}}$ is assumed to be Curie-Weiss-type, i.e., $\chi_{\text{imp}} = n_{\text{imp}}C/(T)$, where $C$ is the Curie constant for $S = 1/2$ and we set $n_{\text{imp}} = 0.017$. The Van Vleck paramagnetic susceptibility was estimated using

$$
\chi_{\text{VV}} = \left(\frac{N\mu_B^2}{\lambda}\right)\Delta g = 9.42 \times 10^{-4} \Delta g \text{ emu/mol},
$$

where $N$ is the number of Cu$^{2+}$ ions, $\Delta g = g - g_e$ is the anisotropy of the gyromagnetic ratio, and $\lambda = 829 \text{ cm}^{-1}$ is the spin-orbit coupling coefficient of Cu$^{2+}$.
16. G. A. Bain and J. F. Berry, J. Chem. Educ. 85, 532 (2008).
17. R.B. Griffiths, Phys. Rev. 133, A768 (1964).
18. S. Sota and T. Tohyama, Phys. Rev. B 82, 195130 (2010).
19. M. Reigrotzki, H. Tsunetsugu, and T. M. Rice, J. Phys.: Condens. Matter 6, 9235 (1994).
20. O. P. Sushkov and V. N. Kotov, Phys. Rev. Lett. 81, 1941 (1998).