Two magnetization plateaus in the kagome fluoride Cs$_2$LiTi$_3$F$_{12}$

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We synthesized a kagome fluoride Cs$_2$LiTi$_3$F$_{12}$ with $S = 1/2$ spins, and studied magnetic properties of the compound. The temperature dependence of the magnetic susceptibility indicates that it has dominant antiferromagnetic interactions and that it has no magnetic order down to 2 K. We found two magnetization plateaus in its magnetization process approximately at 1/3 and 0.8 $\mu_B$ per Ti. The monoclinic crystal structure gives four inequivalent nearest-neighbor exchange interactions. Our density functional theory calculations suggest that three of them are antiferromagnetic and one of them is weakly ferromagnetic, resulting in a magnetic system composed of antiferromagnetically coupled linear chains and $\Delta$ chains. This explains the observed suppression of magnetic order. Numerical diagonalization gives a magnetization curve in good agreement with the experimental results.

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I. INTRODUCTION

Quantum Heisenberg spin systems on a kagome lattice have attracted much attention from both theoretical and experimental viewpoints. In the last decade and a half, a number of kagome antiferromagnets with $S = 1/2$ have been extensively studied [1]. Much of this research is driven by the desire to realize highly frustrated Hamiltonians where strong quantum effects lead to an exotic state of matter, the quantum spin liquid [2]. Most $S = 1/2$ kagome antiferromagnets are Cu$^{2+}$ based materials, which include Cu containing minerals, such as herbertsmithite [3], vesignieite [4,5], kapellasite [6], centennialite [7], and Cu based fluorides Cs$_2$T$_2$Cu$_3$F$_{12}$ ($T = \text{T}i$, Zr, Hf, Sn) [8]. However, the Cu$^{2+}$ ion has relatively large spin-orbit coupling, and thus a large Dzyaloshinsky-Moriya interaction [9]. In the context of the search for spin liquids, this is undesirable as it may induce magnetic ordering.

Recently, we found a new series of kagome fluorides $A_2B$M$_3$F$_{12}$ ($A, B = \text{alkali metal ion}$, $M = \text{T}i$, V, and Cr) [10–12]. Among them, the Ti compounds have spin $S = 1/2$. Compared to the $S = 1/2$ magnetic ion Cu$^{2+}$, Ti$^{3+}$ has much smaller spin-orbit coupling. We have already reported the crystal structure and magnetic properties of the three Ti$^{3+}$ kagome compounds Rb$_2$NaTi$_3$F$_{12}$, Cs$_2$NaTi$_3$F$_{12}$, and Cs$_2$KTi$_3$F$_{12}$ [10]. Owing to lattice distortion from rhombohedral to monoclinic, they have a slightly distorted kagome lattice. We revealed that the magnetic states of kagome antiferromagnets strongly depend on lattice distortion. Indeed, our theoretical study clarified that the lattice distortions make the kagome lattice magnetically anisotropic [13].

In this paper we report the crystal structure and magnetic properties of the new kagome magnet Cs$_2$LiTi$_3$F$_{12}$ which is a member of the above-mentioned $A_2B$Ti$_3$F$_{12}$ family. This compound has a slightly distorted kagome lattice of Ti$^{3+}$. Since the crystal structure of Cs$_2$LiTi$_3$F$_{12}$ is qualitatively the same as another $A_2B$Ti$_3$F$_{12}$, we can use the new material to systematically study the effect of lattice distortion on the magnetism of $S = 1/2$ kagome antiferromagnets. The measured magnetic properties of Cs$_2$LiTi$_3$F$_{12}$ are similar to those of Cs$_2$KTi$_3$F$_{12}$; therefore, it comes as a surprise that the magnetic models are different between these two. Moreover, Cs$_2$LiTi$_3$F$_{12}$ has smaller antiferromagnetic interactions than the previously studied $A_2B$Ti$_3$F$_{12}$, allowing us to study high field magnetism. In high fields, Cs$_2$LiTi$_3$F$_{12}$ shows not only the 1/3 magnetic plateau but also a magnetic plateau with a larger magnetization. We discuss details of the magnetic properties of Cs$_2$LiTi$_3$F$_{12}$.

II. METHODS

Polycrystalline samples of Cs$_2$LiTi$_3$F$_{12}$ were synthesized with a solution method under N$_2$ atmosphere. Single crystals of Cs$_2$LiTi$_3$F$_{12}$ were grown with a flux method using alkali metal chlorides in a Ni crucible under Ar atmosphere. A polycrystalline sample of a nonmagnetic isosstructural compound Cs$_2$KGa$_3$F$_{12}$ was prepared with a solid state reaction in a Cu tube under Ar atmosphere.

Powder x-ray diffraction measurements were performed at room temperature using Miniflex600 (Rigaku) with a Cu $K\alpha$ source. X-ray diffraction data of a single crystal with a typical size of $90 \times 80 \times 30$ $\mu$m$^3$ were obtained using a Rigaku R-AXIS RAPID-S diffractometer with Mo $K\alpha$ radiation. The sample was cooled down to approximately 150 K using a nitrogen-gas-flow-type refrigerator. The structural parameters

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including anisotropic displacement parameters were refined using a full matrix least-squares method with the SHELXL-97 software [14].

Polycrystalline samples were used for magnetic susceptibility and magnetization measurements, and one single crystal was used for heat capacity measurements. DC magnetization was measured in a temperature range of 2–300 K using a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL) in the Research Center for Low Temperature and Materials Sciences, Kyoto University. Magnetization processes up to 75 T were measured using an induction method with a multilayer pulsed magnet at the International MegaGauss Science Laboratory of the Institute for Solid State Physics, the University of Tokyo. Heat capacity measurements were performed using a commercial relaxation calorimeter (Quantum Design PPMS-14LHS).

To understand our experimental observations, we carried out a two-step calculation. The first step is the determination of the electronic structure and magnetic interaction parameters of Cs$_2$LiTi$_3$F$_{12}$ using density functional theory (DFT) calculations with the all electron full potential local orbital (FPLO) [15] basis and the generalized gradient approximation (GGA) [16] exchange correlation functional. We account for strong electronic correlations on the Ti$^3^+$ ions using the GGA+$\Gamma$ correction. The Hunds rule coupling for Ti$3d$ was fixed at $J_H = 0.64$ eV [18]. We used an energy mapping technique to determine the most important exchange interactions in Cs$_2$LiTi$_3$F$_{12}$ [19–21]. By lowering the symmetry of Cs$_2$LiTi$_3$F$_{12}$ to P1, all six Ti$^3^+$ ions in one unit cell become inequivalent, and 15 collinear spin configurations with different total energies can be created. We fit these energies against the Heisenberg Hamiltonian written as $H = \sum_{i<j} J_{ij} S_i \cdot S_j$ without double counting of bonds. This calculation allows us to resolve all “nearest-neighbor” exchange couplings in the kagome plane.

The second step of our calculation is numerical diagonalization of finite-size clusters with Heisenberg interactions determined from the DFT calculations. Our numerical diagonalizations are carried out based on the Lanczos and/or Householder algorithms in the subspace characterized by $\sum_j S_j^z = M_z$, where the $z$ axis is taken as the quantized axis of each $S = 1/2$ spin operator $S_j$ at site $j$. Our numerical diagonalizations provide us with the lowest energy of the Heisenberg Hamiltonian with the number of sites $N$ in the subspace belonging to $M_z$. The energy is denoted by $E(N, M_z)$. To obtain the steplike magnetization process when the Zeeman term $-\mu B H$ is added to $H$, we use the relation $2 \mu_B H = E(N, M_z + 1) - E(N, M_z)$ which determines the magnetic field $H$ for the occurrence of the magnetization increase from $M_z$ to $M_z + 1$. Note here that the isotropy of the system is assumed and that the saturation magnetization is given by $N S$. Therefore, the normalized magnetization per magnetic site is given by $M = M_z/(N S)$, which corresponds to the magnetization per Ti site in units of $\mu_B$. Some of the Lanczos diagonalizations were carried out using an MPI-parallelized code that was originally developed in the study of Haldane gaps [22]. The usefulness of our program was confirmed in various large-scale parallelized calculations [23–35]. We carried out our diagonalizations of the systems with $N = 24, 30, \text{and} 36$. The shapes of the finite-size clusters are taken to be the same ones as were used in the previous study [13].

### III. RESULTS AND DISCUSSION

By using a solution method, we succeeded in synthesizing polycrystalline samples of Cs$_2$LiTi$_3$F$_{12}$. Powder x-ray diffraction measurements revealed that Cs$_2$LiTi$_3$F$_{12}$ has a monoclinic structure. In addition, we obtained brown crystals of Cs$_2$LiTi$_3$F$_{12}$ with a typical size of $2 \times 2 \times 2$ mm$^3$. However, we found that large crystals are composed of several domains, which is likely due to monoclinic deformation with decreasing temperature. Single crystal x-ray diffraction measurement revealed details of the crystal structure, as summarized in Table I. No disorder of the constituent ions is observed. This structure is qualitatively the same as that previously reported for $A_2B$Ti$_3$F$_{12}$ compounds [10], and it can be regarded as an ordered structure of the cubic modified pyrochlore $AM_2$F$_6$ [36]. Ordering of Li$^+$ and Ti$^{3+}$ in the pyrochlore lattice of $M$ results in formation of a kagome lattice of Ti$^{3+}$. Thus, this structure consists of kagome layers which are made up of corner-sharing TiF$_6$ octahedra, separated by nonmagnetic Cs$^+$ ions and Li$^-$ ions. Moreover, TiF$_6$ octahedra are compressed along axes which point out of the kagome plane, and this distortion leads to a small lifting of the degeneracy between the three $t_{2g}$ orbitals. Therefore, the single $3d$ electron of Ti$^{3+}$ occupies the $3d_{xy}$ orbitals which are almost parallel to the kagome plane.

Reflecting the monoclinic distortion, Cs$_2$LiTi$_3$F$_{12}$ has three crystallographically different Ti sites. Both Ti1 and Ti2 form one-dimensional (1D) chains along the $b$ axis and the chains are bridged by Ti3. Therefore, there are four inequivalent exchange interactions. The Ti-Ti distances and the Ti-F-Ti bond angles are within the range of 3.734–3.797 Å and 134.2°–142.7°, respectively. These ranges are slightly larger than those of other $A_2B$Ti$_3$F$_{12}$ compounds. The large distances between two Ti ions of approximately 3.7 Å indicate that

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U$ (Å$^2$)</th>
</tr>
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<tbody>
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<td>0.75</td>
<td>0.61986(6)</td>
<td>0.02070(14)</td>
</tr>
<tr>
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<td>0.25</td>
<td>0.62174(6)</td>
<td>0.01798(14)</td>
</tr>
<tr>
<td>Li1</td>
<td>0.7311(11)</td>
<td>0.25</td>
<td>0.5117(19)</td>
<td>0.0262(6)</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0113(2)</td>
</tr>
<tr>
<td>Ti2</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.0101(2)</td>
</tr>
<tr>
<td>Ti3</td>
<td>0.76963(9)</td>
<td>0.25</td>
<td>0.05607(18)</td>
<td>0.0106(2)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0222(5)</td>
<td>0.25</td>
<td>0.9397(8)</td>
<td>0.0310(10)</td>
</tr>
<tr>
<td>F2</td>
<td>0.5909(2)</td>
<td>0.4344(3)</td>
<td>0.3107(4)</td>
<td>0.0170(5)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0881(2)</td>
<td>0.9336(3)</td>
<td>0.8669(4)</td>
<td>0.0164(5)</td>
</tr>
<tr>
<td>F4</td>
<td>0.1525(3)</td>
<td>0.0164(4)</td>
<td>0.2946(5)</td>
<td>0.0291(6)</td>
</tr>
<tr>
<td>F5</td>
<td>0.5631(3)</td>
<td>0.75</td>
<td>0.1001(6)</td>
<td>0.0170(7)</td>
</tr>
<tr>
<td>F6</td>
<td>0.3477(2)</td>
<td>0.5467(3)</td>
<td>0.0046(4)</td>
<td>0.0173(5)</td>
</tr>
<tr>
<td>F7</td>
<td>0.1755(3)</td>
<td>0.75</td>
<td>0.6323(6)</td>
<td>0.0187(7)</td>
</tr>
<tr>
<td>F8</td>
<td>0.3002(4)</td>
<td>0.75</td>
<td>0.2573(6)</td>
<td>0.0194(7)</td>
</tr>
</tbody>
</table>
direct exchange interactions between two Ti are negligibly small. Thus, the dominant interactions are superexchange interactions. The obtained Ti-F-Ti bond angles are much larger than 90° which leads to the expectation that the magnetic exchanges between nearest neighbor Ti ions are antiferromagnetic.

The temperature dependence of the magnetic susceptibility $\chi$ and of the inverse of the magnetic susceptibility $\chi^{-1}$ (right scale). The black dashed line indicates the result of the Curie-Weiss fit. The inset shows the magnetic field dependence at low temperatures.

FIG. 1. Temperature dependence of the magnetic susceptibility $\chi$ and of the inverse susceptibility $\chi^{-1}$. The black dashed line indicates the result of the Curie-Weiss fit. The inset shows the magnetic field dependence at low temperatures.

The magnetic entropy at 80 K is slightly larger than the theoretical value $2 k_B S/T$, and then saturates above 80 K. Moreover, each $C/T$ curve shows a broad peak at $J = 29.8$ K. The value of $J$ for Cs$_2$LiTi$_3$F$_{12}$ is the smallest among four $A_2B$Ti$_3$F$_{12}$ compounds. Those of Rb$_2$NaTi$_3$F$_{12}$, Cs$_2$NaTi$_3$F$_{12}$, and Cs$_2$KTi$_3$F$_{12}$ are 43, 44, and 47 K, respectively [10].

In the low temperature region, $\chi-T$ shows a broad maximum approximately at 12 K $\simeq J/3$, which implies short range order effects [37]. This behavior is expected in low dimensional (both one- and two-dimensional) systems where magnetic order is absent. In our previous study, $\chi-T$ curves of $A_2B$Ti$_3$F$_{12}$ strongly depend on the distastion of the kagome lattice. Among them, a broad maximum at $T \simeq J/3$ was observed also in $\chi$ of Cs$_2$KTi$_3$F$_{12}$, which has the smallest distortion and arguably the most frustrated Hamiltonian of the three compounds [10,13]. A theoretical study proposed that the susceptibility of the $S = 1/2$ kagome antiferromagnet exhibits a broad maximum at $T \sim J/6$ [38]. The difference between the theory and experiment is considered to arise from the distortion of the kagome lattice, which is similar to Rb$_2$SnCu$_3$F$_{12}$ [39]. The small upturn of the susceptibility measured under 0.1 T below 4 K is due to magnetic impurities, because it is suppressed under 5 T. The amount of magnetic impurity that causes an upturn at low temperatures is evaluated to be approximately 1% from the Curie constant obtained by fitting the $\chi-T$ curve in this region.

To investigate the details of the magnetic states of $S = 1/2$ Cs$_2$LiTi$_3$F$_{12}$, we measured the temperature dependence of the heat capacity $C$ under several magnetic fields using a relatively large crystal grown with the flux method. We applied the magnetic field along the [111] direction of the crystal in the cubic indices. The heat capacity divided by temperature $C/T$ is plotted in the inset of Fig. 2. Under zero field, the absence of $\lambda$-like anomalies indicates no long range magnetic ordering down to 0.5 K. The $C/T - T$ curves show the magnetic field $H$ dependence below 12 K. The temperature of 12 K corresponds to the temperature where the $\chi-T$ curve shows a broad maximum indicating short range magnetic ordering. Moreover, each $C/T$ curve shows a broad peak at $T_{\text{max}}$, and $T_{\text{max}}$ decreases with increasing $H$. This behavior is likely due to formation of short range magnetic order which is restrained by the magnetic field. This behavior is very similar to that of Cs$_2$KTi$_3$F$_{12}$.

By subtracting the lattice contribution and integrating $C/T$, we evaluated the magnetic entropy $S_M$. The calculated $S_M$ gradually increases with increasing temperature, and reaches 5 J/K approximately at $-\theta_{\text{CW}}$, and then saturates above 80 K. The magnetic entropy at 80 K is slightly larger than the theoretical value $R \ln 2 = 5.76$ J/K for $S = 1/2$. This discrepancy is likely due to errors of specific heat and lattice contribution.

FIG. 2. Magnetic entropy of Cs$_2$LiTi$_3$F$_{12}$ up to 80 K. The inset shows the heat capacity divided by temperature under various magnetic fields. The data for nonmagnetic Cs$_2$KGa$_3$F$_{12}$ are also plotted to show the lattice contribution.
TABLE II. Nearest-neighbor intersite Ti-Ti distances and labels for exchange couplings in Cs$_2$LiTi$_3$F$_{12}$. Two couplings $J_a$ and $J_b$ correspond to the same distance but connect two symmetry inequivalent Ti sites. Note that $J_5$ and $J_{10}$ correspond to interlayer couplings.

<table>
<thead>
<tr>
<th>$d$ (Å)</th>
<th>Ti1</th>
<th>Ti2</th>
<th>Ti3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1</td>
<td>3.7970</td>
<td>$J_{1b}$</td>
<td>6.2814</td>
</tr>
<tr>
<td>Ti2</td>
<td>6.2814</td>
<td>$J_5$</td>
<td>3.7970</td>
</tr>
<tr>
<td>Ti3</td>
<td>3.7339</td>
<td>$J_1$</td>
<td>3.7695</td>
</tr>
</tbody>
</table>

Using the experimentally obtained crystal structure and $\theta_{CW}$, we determined the exchange couplings. As mentioned before, the distorted kagome lattice has three Ti sites; the 1D Ti1 chain and Ti2 chain are bridged by Ti3. And hence, it has four “nearest-neighbor” exchange couplings. Here we use two kinds of labels for the exchange couplings, which are summarized in Table II. One kind of labels $J_a$ are couplings labeled according to the physical structure, ordered by increasing Ti-Ti distance as shown in Table II. As there are two identical distances Ti1-Ti1 and Ti2-Ti2 along the 1D chains, which however are symmetry inequivalent and do not have the same exchange, they are called $J_{1a}$, $J_{1b}$. The other kind of labels $J_B$ and $J_D$ are related to the model for the distorted kagome lattice; $J_A$ and $J_B$ are couplings along the one-dimensional chains, and $J_C$ and $J_D$ are those in the zigzag chains bridging $J_A$ and $J_B$ chains, respectively. Note that $J_A$ is always assigned to be the largest 1D chain coupling. The exchanges are visualized in Fig. 3. We can determine the relevant value of the interaction strength $U$ by demanding that the Curie-Weiss temperature calculated as $\theta_{CW} = -\frac{4}{3}S(S+1)[\frac{1}{2}J_1 + \frac{1}{2}J_2 + \frac{1}{3}J_{3a} + \frac{1}{3}J_{3b} + \frac{2}{3}J_5 + \frac{1}{3}J_{10}]$ match the experimentally determined value. The Heisenberg Hamiltonian parameters of Cs$_2$LiTi$_3$F$_{12}$ obtained by energy mapping are shown in Fig. 3 and in Table III for seven values of the interaction strength $U$. The value $U = 2.4$ eV required to match the experimental value of $\theta_{CW}$ is reasonable for Ti$^{3+}$ and agrees well with the values that describe the magnetic exchange of the sister compounds RbNaTi$_3$F$_{12}$, CsNaTi$_3$F$_{12}$, and CsKTi$_3$F$_{12}$ [13]. The selected interlayer couplings $J_5$ and $J_{10}$ are very small and will be neglected in the further discussion. The obtained parameters are shown in Table IV.

Interestingly, the model we obtain for Cs$_2$LiTi$_3$F$_{12}$ is quite different from those for the other known compounds. It is characterized by strong antiferromagnetic spin chains $J_A$. This is coupled to the kagome lattice environment by ferromagnetic couplings $J_C$ with a strength $|J_C/J_A| = 0.104$. Two thirds of the Ti$^{3+}$ ions in the plane form anisotropic $\Delta$ chains, with a ratio $J_D/J_B = 2.46$. Our previous study clarified exchange couplings for other $A_2BTi_3F_{12}$ fluorides [13]: Rb$_2$NaTi$_3$F$_{12}$ has very small $J_D$ and it consists of antiferromagnetic spin chains with $J_B$ and anisotropic $\Delta$ chains with $J_C/J_A = 0.292$; Cs$_2$NaTi$_3$F$_{12}$ has relatively small $J_C$ and it is considered

TABLE III. Exchange couplings of Cs$_2$LiTi$_3$F$_{12}$ calculated within GGA+$U$ at $J_H = 0.64$ eV and $8 \times 8 \times 8$ k points. The line in bold is obtained by requiring that the set of couplings yield the experimental Curie-Weiss temperature $\theta_{CW} = -29.8$ K.

<table>
<thead>
<tr>
<th>$U$ (eV)</th>
<th>$J_1 = J_0$ (K)</th>
<th>$J_2 = J_C$ (K)</th>
<th>$J_{10} = J_A$ (K)</th>
<th>$J_5 = J_B$ (K)</th>
<th>$J_9$ (K)</th>
<th>$J_{10}$ (K)</th>
<th>$\theta_{CW}$ (K)</th>
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<tr>
<td>2.0</td>
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<td>20.7(2)</td>
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<tr>
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<td><strong>-9.3(1)</strong></td>
<td><strong>89.1(2)</strong></td>
<td><strong>18.2(2)</strong></td>
<td><strong>-0.1(1)</strong></td>
<td><strong>0.7(1)</strong></td>
<td><strong>-29.8</strong></td>
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<tr>
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<td>78.7(1)</td>
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<tr>
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<td>51.4(1)</td>
<td>7.3(1)</td>
<td>0.1(1)</td>
<td>0.0(2)</td>
<td>-17.5</td>
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</table>
TABLE IV. Exchange couplings for Cs$_2$LiTi$_3$F$_12$ determined by energy mapping, using the GGA+$U$ exchange correlation functional with $U$ values that reproduce the experimental Curie-Weiss temperatures $\theta_{CW} = -29.8$ K. See Fig. 3 for the assignment of $J_A$, $J_B$, $J_C$, and $J_D$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$J_A$ (K)</th>
<th>$J_B/J_A$</th>
<th>$J_C/J_A$</th>
<th>$J_D/J_A$</th>
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<tr>
<td>Cs$_2$LiTi$_3$F$_12$</td>
<td>89.1</td>
<td>0.204</td>
<td>-0.104</td>
<td>0.503</td>
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to consist of antiferromagnetic spin chains with $J_A$ and nearly isotropic $\Delta$ chains with $J_D/J_B = 0.967$; Cs$_2$KTi$_3$F$_12$ has almost the same $J_B$, $J_C$, $J_D$. Although the temperature dependence of $\chi$ for Cs$_2$LiTi$_3$F$_12$ is very similar to that of Cs$_2$KTi$_3$F$_12$, the models are completely different.

Based on the model Hamiltonian, we can develop an approximate expectation for the magnetization process. As the overall strength of $J_D$ and $J_B$ couplings is 0.503 and 0.204 of $J_A$, respectively, the saturation of the $\Delta$ chain is expected to be reached while the $J_A$ spin chain shows a slow linear increase of magnetization [40]. At these low fields, the $\Delta$ chain will exhibit a 1/2 magnetization plateau [41] which results in a 1/3 magnetization plateau of the full system as it affects only two thirds of the Ti$^{3+}$ ions. The 1/3 magnetization plateau should be offset by a small, slightly increasing contribution from the $J_A$ antiferromagnetic spin chain. Due to the large anisotropy, the $\Delta$ chain should show a jump to full saturation [41].

Now, let us investigate the behavior of the magnetization process of Cs$_2$LiTi$_3$F$_12$ through both experiment and calculation, results of which are shown in Fig. 4. We experimentally measured the magnetization process up to 75 T at 1.3 and 4.2 K. First, let us observe the characteristic behavior of our experiment based on the lower-temperature measurement. By increasing $H$ from 0 T, $M$ starts to increase with a finite slope. Around $H \sim 7$ T, there appears an inflection point of $M \sim 0.04 \mu_B$ per Ti. The inflection point will be discussed in comparison with our numerical-diagonalization result. At about 15 T, $M$ increases with a considerable gradient. This corresponds to the fact that the broad peak in $C/T$ moves to almost 0 K at 14 T. At around $H \sim 36$ T, another inflection point appears at $M \sim 0.37 \mu_B$. There is a possibility that the inflection point is related to the 1/3 magnetization plateau behavior that was mentioned in the discussion of the $\Delta$ chain in the previous paragraph. By further applying $H$, $M$ increases again at 50 T until approximately 70 T. Above 70 T, $M$ exhibits a behavior of smaller gradients, which suggests a plateau behavior. The magnetic moment at this magnetization plateau is approximately 0.8 $\mu_B$.

To analyze the behavior of the experimental $M$, we carried out numerical-diagonalization calculations, results of which are shown by steplike magnetization processes in Fig. 4. In the following, the comparison between the experimental result and the numerical result will be discussed. The experimental inflection point of $M \sim 0.37 \mu_B$ is close to $M = (1/3) \mu_B$, but seems slightly larger than $M = (1/3) \mu_B$; in theoretical results, on the other hand, the plateau just at $M = (1/3) \mu_B$ is unclear because the results of $N = 30$ and 36 show small widths at $M = (1/3) \mu_B$, although the result of $N = 24$ shows a large width at $M = (1/3) \mu_B$. Instead, magnetizations $M = (4/9) \mu_B$ for $N = 36$ and $M = (2/5) \mu_B$ for $N = 30$ show large widths. These theoretical behaviors are possibly related to the experimental $M \sim 0.37 \mu_B$ that is larger than $M = (1/3) \mu_B$. However, the field $H \sim 36$ T of this inflection point is smaller than the field range of $M = (4/9) \mu_B$ for $N = 36$ and $M = (2/5) \mu_B$ for $N = 30$. The reason is unclear at present. The present experimental measurement certainly detects the lower-field inflection point of $M \sim 0.04 \mu_B$ at $H \sim 7$ T. A similar inflection point was also observed in the case of Cs$_2$KTi$_3$F$_12$ [10]. Our result for $N = 36$ reveals a large width of $M = (1/3) \mu_B$ for $N = 36$. There is a possibility that our theoretical large width is related to the experimental inflection point. For further investigation of whether or not the experimental inflection point suggests the plateau behavior, theoretical studies by numerical diagonalizations for larger clusters giving higher resolution results will be required.

The most marked point is the behavior around $M \sim 0.8 \mu_B$. Our theoretical results reveal a plateau behavior approximately between 60 and 125 T. On the other hand, the low-temperature experimental result clearly reveals small gradients of $M$ above 70 T. The small gradients suggest that our experimental measurement matches the behavior of the low-field side edge of the plateau in the theoretical results. In the magnetization process of the $\Delta$ chain, we expect a significant jump of the magnetization just before saturation [41]. This would corresponds to the maximum of $dM/dH$ at 55 T in Cs$_2$LiTi$_3$F$_12$. Since 2/3 of Ti atoms form the $\Delta$ chain, saturation of the $\Delta$ chain gives $(2/3) \mu_B$. We think...
that saturation of the $\Delta$ chain plus a small magnetization of the 1D chain could lead to a 0.8 $\mu_B$ magnetization plateau in Cs$_2$LiTi$_3$F$_{12}$.

Note also that a behavior of a plateau with a large $M$ near the saturation was not observed in Cs$_2$KTi$_3$F$_{12}$ owing to the limitation of the magnetic field in Ref. [10], although the existence of a plateau with the same height for Cs$_2$KTi$_3$F$_{12}$ was theoretically predicted [13]. Reference [13] also suggested the existence of a plateau with a large $M$ near the saturation for Cs$_2$NaTi$_3$F$_{12}$ and Rb$_2$NaTi$_3$F$_{12}$. The agreement of the plateau around $M \sim 0.8$ $\mu_B$ for Cs$_2$LiTi$_3$F$_{12}$ between the experiment and theory suggests that higher-field measurements for Cs$_2$KTi$_3$F$_{12}$, Cs$_2$NaTi$_3$F$_{12}$, and Rb$_2$NaTi$_3$F$_{12}$ will be interesting future studies. The above explanation of 0.8 $\mu_B$ magnetization plateau for Cs$_2$LiTi$_3$F$_{12}$ is different from those for the other Ti kagome fluorides, which all have differently distorted kagome lattices. We believe that it is this diversity that gives new insights into the magnetic properties of (distorted) kagome antiferromagnets.

IV. CONCLUSIONS

We have studied crystal structure and magnetic properties of Cs$_2$LiTi$_3$F$_{12}$, which has an $S = 1/2$ distorted kagome lattice. The distortion of the kagome lattice is the largest among the four $A_2$TiF$_{12}$ compounds. The temperature dependence of $\chi$ and the magnetization curve of Cs$_2$LiTi$_3$F$_{12}$ are very similar to those of Cs$_2$KTi$_3$F$_{12}$, which has the smallest distortion of the kagome lattice. However, density functional theory predicts different magnetic models for Cs$_2$LiTi$_3$F$_{12}$ and Cs$_2$KTi$_3$F$_{12}$. This is an indication that the electronic and magnetic anisotropy of the compounds cannot be read off in a simple way from the structural distortion. The magnetic model of Cs$_2$LiTi$_3$F$_{12}$ consists of antiferromagnetically coupled spin chains and anisotropic $\Delta$ chains. Both our experiment and numerical diagonalization studies reveal that this system exhibits 1/3 and 0.8 magnetization plateaus. It is an interesting open question if the new material Cs$_2$LiTi$_3$F$_{12}$ has a spin gap.

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