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Defect-induced short-range-order from a spin-ice related state in deformed pyrochlore $Co_2(OH)_3Cl$

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Recently, we observed a kagome-ice-like partial ferromagnetic order with coexisting fluctuation in a deformed pyrochlore structure $Co_2(OH)_3Cl$. Here, we show that when lattice defects are present, the remaining fluctuating spins in this material further freeze at lower temperatures below $T<T_g=4$ K after it initially freezes into the partial ferromagnetic order near $T_C=10$ K. This low-temperature transition is glasslike requiring an extremely slow relaxation process in $Co_2(OH)_3Cl$. Enhanced disorder in $(Co_{1-x}Al_x)_2(OH)_3Cl$ leads to a short-range order for the fluctuating spins. This result can be considered as an interesting analogy to the low-temperature anomaly in defect-containing pure and doped water ice, especially in the light of its relevance to the problem of residual entropy in ice-water or spin-ice transition.

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I. INTRODUCTION

Geometrically frustrated magnetic materials, in which the lattice geometry leads to frustration of the spin-spin interactions, display a variety of interesting magnetic behaviors.[1] Of particular recent interest are the rare-earth pyrochlore compounds $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$, and $Ho_2Sn_2O_7$, termed as "spin ice."[2–4] In these materials, the spin alignment and the macroscopic quantum degeneracy are shown to be a magnetic equivalence of the ice rule in water ice.[5,6] The spin ice has received intense attention because of the dynamics associated with the macroscopic degeneracy are experimentally accessible by many magnetic probes, and because the geometrical frustration of competing interactions is an essential element of important problems in fields extending to protein folding and neural networks.[7,8] The experimentally observed degeneracy and zero-point residual entropy for water ice and spin ice apparently contradict a fundamental principle of thermodynamics (the third law), which demands a single ordered ground state and hence zero entropy. As to the spin ice, a first-order phase transition to a true ground state is theoretically predicted,[9] but has not been observed to date, despite rigorous efforts down to the experimentally attainable temperature of 10 mK. Whether the spin ice keeps the macroscopic quantum degeneracy down to 0 K remains an open and controversial issue.

We recently found a new geometrically frustrated material series $M_2(OH)_3X$ ($M=$Cu, Co, Ni, Mn, Fe, etc., $X=$Cl, Br) on deformed pyrochlore lattice for d-electron systems.[10–12] In special, clinoatacamite $Cu_2(OH)_3Cl$ and another compound $Co_2(OH)_3Cl$ showed interesting behaviors. $Cu_2(OH)_3Cl$ is the first example approaching a $S=1/2$ (Cu^{2+}) Heisenberg pyrochlore lattice, showing an intriguing transition from long range order into a coexisting state of long-range order and fluctuation down to $T=0$.[10] While much of the spin dynamics in clinoatacamite is still unclear, $Co_2(OH)_3Cl$ has been shown to be a material closely related to the spin ice.[12] A partial ferromagnetic order similar to that in "kagome ice," which originally refers to the field-induced partial order for the original spin ice,[13,14] develops around $T_C=10.5$ K at zero field.[12] The deformed tetrahedron with a 10% shorter bond along the c-axis direction seems to induce the partial magnetic order by playing a similar role to the magnetic field in the regular tetrahedral pyrochlore spin ice. Because the magnetic interaction in $Co_2(OH)_3Cl$ is much stronger than that in the original spin-ice compounds, we expect $Co_2(OH)_3Cl$ to be an easy material for experimentally exploring possible low-temperature phase transition due to impurity doping. Meanwhile, it is also interesting to compare its spin dynamics in this system, in which the degeneracy is partially lifted, to the ideal spin ice.

The present work, however, was initiated directly by experimental observation of a prolonged time relaxation of magnetization at low temperatures in polycrystalline $Co_2(OH)_3Cl$. The M-H magnetization curves at 2 K showed a small loop which was absent at 5 K [Fig. 1(a)]. The remanent magnetization after removing an applied field showed prolonged time relaxation with a rapidly increasing time constant below 4 K [Fig. 1(b)]. The anomaly also appeared in ac susceptibility as will be shown later and intriguingly it varied for differently heat-treated samples despite the absence of an impurity phase. Then, we succeeded in growing single crystal $Co_2(OH)_3Cl$ and Al-doped polycrystalline samples. A comparison study as reported here reveals an interesting defect-induced low-temperature transition in the present system.

II. EXPERIMENT

In this work, we studied the spin dynamics in various $Co_2(OH)_3Cl$ samples using susceptibility, specific heat, and neutron diffraction measurements. For our study, polycrystalline samples of $Co_2(OH)_3Cl$ and $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$ (H replaced with D for neutron diffraction) were prepared via hydrothermal solution reactions from $CoCl_2$ ($AlCl_3$) and NaOH (NaOD), respectively. The solutions of 2M $CoCl_2$ $6H_2O$ (3N) (as well as $AlCl_3$ in the case of Al doping) and 2M

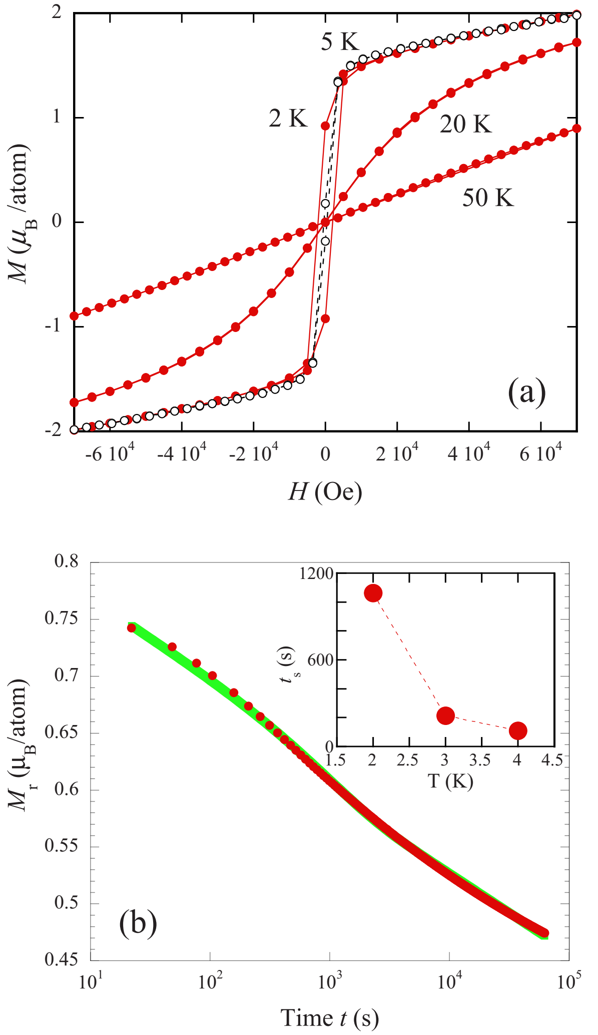

FIG. 1. (Color online) (a) M-H hysteresis loop appeared at 2 K for a polycrystalline $Co_2(OH)_3Cl$ sample. (b) Remanent magnetization at 2 K after removing a 5 T field. M_r showed a slow decay following the equation $M_r = 0.035e^{-(t/\tau)} - 0.03 \ln t + 0.80$ with a large time constant $\tau = 1020$ s. The inset plot depicts the quick increase of τ below 4 K.

NaOH (3N) were first heated respectively to their boiling temperature near 99 °C and mixed with a molar ratio of 1:0.6 and heated for several hours to form solid $Co_2(OH)_3Cl$. The preliminarily reacted powder was then washed thoroughly with purified water to remove solvable NaCl and $CoCl_2$. A high-temperature heating at 200 °C in pure water in Teflon vessel greatly improved the crystalline nature of the samples. Great effort has been made to grow single crystal and we managed to grow a small amount of single crystals ($\sim$0.1 mm on each length) of pure $Co_2(OH)_3Cl$ by heating the preliminarily grown powder at temperatures as high as 300 °C in $CoCl_2$ solution for 1 week with slow cooling. All the samples were inspected by high-resolution synchrotron powder x-ray diffraction performed at BL02B2, Spring-8, Japan, as well as electron microscopy. Special attention was paid to characterization of the polycrystalline and single crystalline samples of $Co_2(OH)_3Cl$. dc and ac susceptibility measurements were performed on a Quantum Design MPMS superconducting quantum interference device magnetometer. The heat capacity was measured by an adiabatic heat pulse method with a ^{3}He cryostat using 0.7 g of the polycrystals. A neutron powder diffraction experiment was performed using a wavelength of 1.826 46 Å on the Kinken powder diffractometer, HERMES, of the Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor at the Japan Atomic Energy Research Institute (JAERI), Tokai.[15]

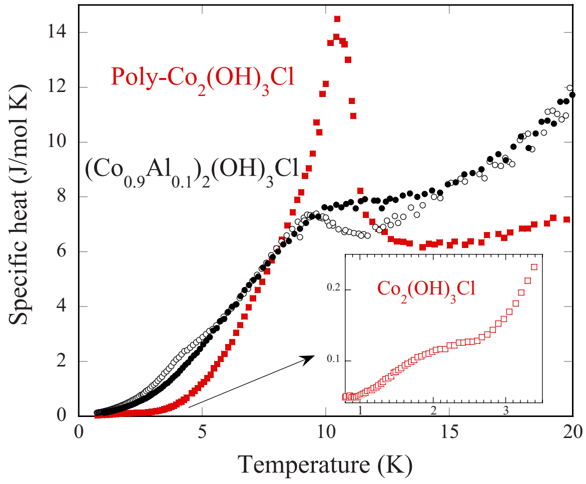

FIG. 2. (Color online) Temperature dependence of specific heat $C_p(T)$. The squares and open circles represent data for polycrystalline $Co_2(OH)_3Cl$ and $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$, respectively, at zero field; the filled circles are data for $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$ under a magnetic field of 0.5 T. The inset plot is an enlarged view of the low-temperature section for $Co_2(OH)_3Cl$.

III. RESULTS AND DISCUSSION

No significant difference between the polycrystalline and single crystalline samples of $Co_2(OH)_3Cl$ was detected except sharper x-ray diffraction peak for the single crystals. The kagome ice transition at $T < T_C = 10.5$ K in polycrystals of $Co_2(OH)_3Cl$ is accompanied by a sharp peak in the specific heat, $C_p(T)$.[12] We further observed a very small broad anomaly at lower temperatures below 3 K (inset plot in Fig. 2), which falls in the same temperature range as the magnetization anomaly shown in Fig. 1(b). The low-temperature anomaly grows in $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$, where its smearing by a magnetic field clearly indicates that the anomaly is associated with the spin system.

In order to reveal the nature of the low-temperature anomaly, we studied the magnetization (M) and the resultant dc susceptibility ($\chi_{dc} \equiv M/H$, where H is the applied magnetic field) as well as the real and imaginary parts (χ' and χ'') of the ac susceptibility (χ_{ac}) for single crystalline and polycrystalline $Co_2(OH)_3Cl$, as well as polycrystalline $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$. Spin freezing into the kagome ice state at approximately $T_C = 10$, 10.5, and 9.5 K, respectively, for single crystalline and polycrystalline $Co_2(OH)_3Cl$ and $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$ is evident both from the diversion of the dc magnetization under zero-field cooled (ZFC) and

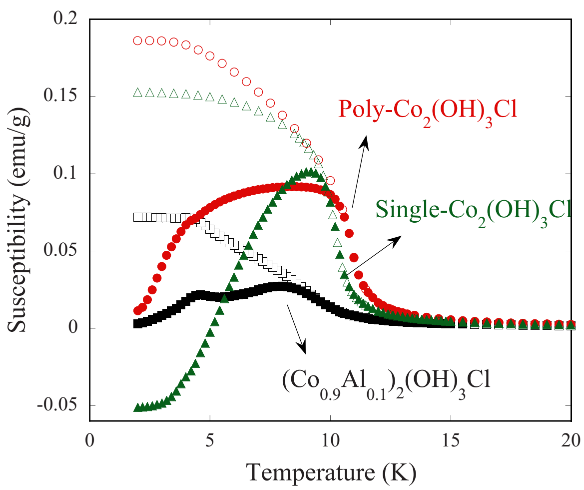

FIG. 3. (Color online) Temperature dependences of dc susceptibilities measured at 50 Oe under field-cooling (open symbols) and zero-field-cooling (filled symbols) conditions, respectively.

field-cooled (FC) conditions (Fig. 3), as well as from the frequency-dependent ac susceptibilities (Fig. 4). Meanwhile, a striking difference between the single crystal and polycrystalline samples is seen. While the single crystal $Co_2(OH)_3Cl$ showed a single peak on the ZFC dc magnetization curve, a further freezing appears for the polycrystalline sample at lower temperatures below approximately 3–4 K, where the specific heat anomaly appeared. Below this low freezing temperature, the dc magnetization under FC saturates and that under ZFC quickly drops. This feature becomes more evident in the diluted sample of $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$.

This difference in the low-temperature anomaly appears distinctly in the ac susceptibilities. The new low-temperature freezing below around 4 K occurs in the polycrystalline samples, but it is nearly invisible in the single crystal (Fig. 4). The freezing temperature T_g shifted to higher temperatures with increasing frequency, which is similar to a spin glass, but the T_g exhibited a larger frequency dependence quantified as $p=\Delta T_g/T_g\,\Delta(\log f_0)\approx 0.08$. The low-temperature freezing involves an extremely slow relaxation process as we observed in the long relaxation time for remanent magnetization in Fig. 1(b). This anomaly was enhanced in impurity-doped $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$ [Fig. 4(c)]. The polycrystalline sample did not contain any detectable impurity. We have also noticed that post heat treatment remarkably influenced this anomaly. Longer heating at 200 °C increased the anomaly. On the other hand, heating in $CoCl_2$ solution instead of pure water decreased the anomaly. Therefore, it is reasonable to assume a micro quantity of defects (deficient Co) is responsible for the low-temperature anomaly in the polycrystalline samples. All of the above-described data demonstrate consistently that a very small amount of structural disorder induces a further glasslike freezing for the spins in the kagome ice state.

We further investigated the dependence of the ac susceptibility on the frequency of the ac field at varied temperatures for polycrystalline $Co_2(OH)_3Cl$ and $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$ that showed the low-temperature anomalies. As shown in Fig. 5, the imaginary part of the ac susceptibilities for these two samples shows maximum peaks which varies with the temperature. It is known that in a spin-ice compound, there are multiple dynamic relaxation processes.[16] The freezing into the spin-ice state shows a single relaxation time constant in the χ''-frequency plot, reflecting a quantum relaxation that originates from the slowly fluctuating dipolar magnetic field.[16] Therefore, we conclude that the low-temperature freezing in the present system is not due to this kind of

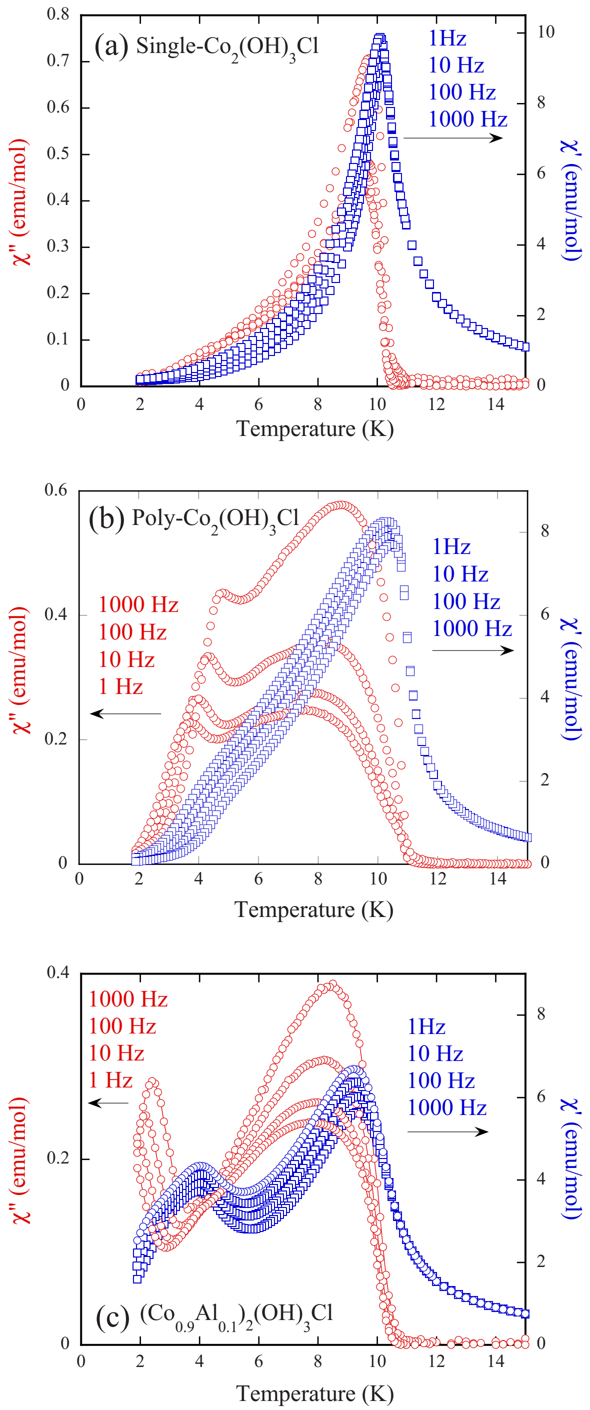

FIG. 4. (Color online) Temperature dependences of ac susceptibilities at various frequencies for [(a) and (b), respectively] single crystal and polycrystalline $Co_2(OH)_3Cl$ and (c) polycrystalline $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$).

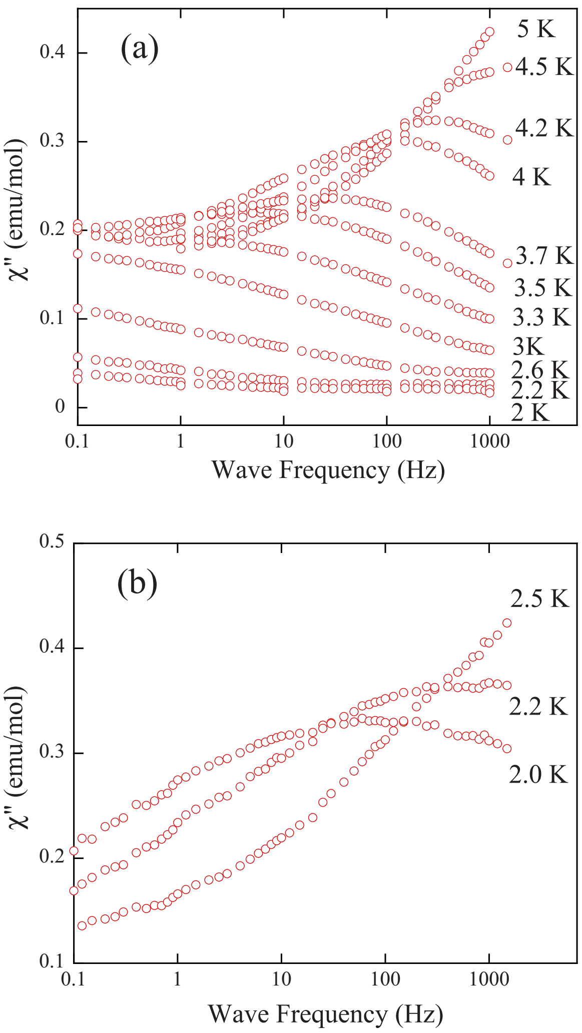

FIG. 5. (Color online) Frequency dependence of the imaginary part of ac susceptibility at various temperatures for (a) polycrystalline $Co_2(OH)_3Cl$ and (b) $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$, respectively.

quantum relaxation. Instead, it rather resembles the freezing of a conventional spin glass.

Neutron diffraction for $(Co_{0.9}Al_{0.1})_2(OD)_3Cl$ showed the origin for the low-temperature anomaly. Similar to the result we reported for $Co_2(OD)_3Cl$,[12] the magnetic Bragg reflection peaks [(101), (012), (110), etc.] appeared below around 10 K where the partial ferromagnetic order of the kagome ice state develops for the spin on the triangular lattice plane. However, a small angle diffused peak around 6° began to grow below around 3.5 K in $(Co_{0.9}Al_{0.1})_2(OD)_3Cl$. At the lowest obtained temperature of 1.45 K, it is clearly recognized (Fig. 6). This anomaly was not notable in the pure compound of polycrystalline $Co_2(OD)_3Cl$ within the measuring time. Obviously, the diffused peak corresponds to the low-temperature anomaly described above and suggests a short-range spin correlation. We attribute it to spin correlation for the three remaining disordered spins on the kagome lattice plane. From the quickly prolonged relaxation time from the magnetization data, we can safely suppose a static spin disorder.

Such a new spin correlation developing from spin-ice state has not been reported for the original spin-ice compounds. Impurity doping studies have been presented by Snyder *et al.* for $Dy_{2-x}M_xTi_2O_7$ $(M=Y,Lu)$[17] and by Ehlers *et al.* for the $Ho_{2-x}Y_xTi_2O_7$ system.[18] The geometrical frustration is not relieved by impurity doping, and the spin dynamics is nearly unaltered. The present result also differs with the well-known spin glass pyrochlore compound $Y_2Mo_2O_7$ and $Y_2(Mo_xTi_{1-x})_2O_7$, in which disorder induces a spin glass transition.[19,20]

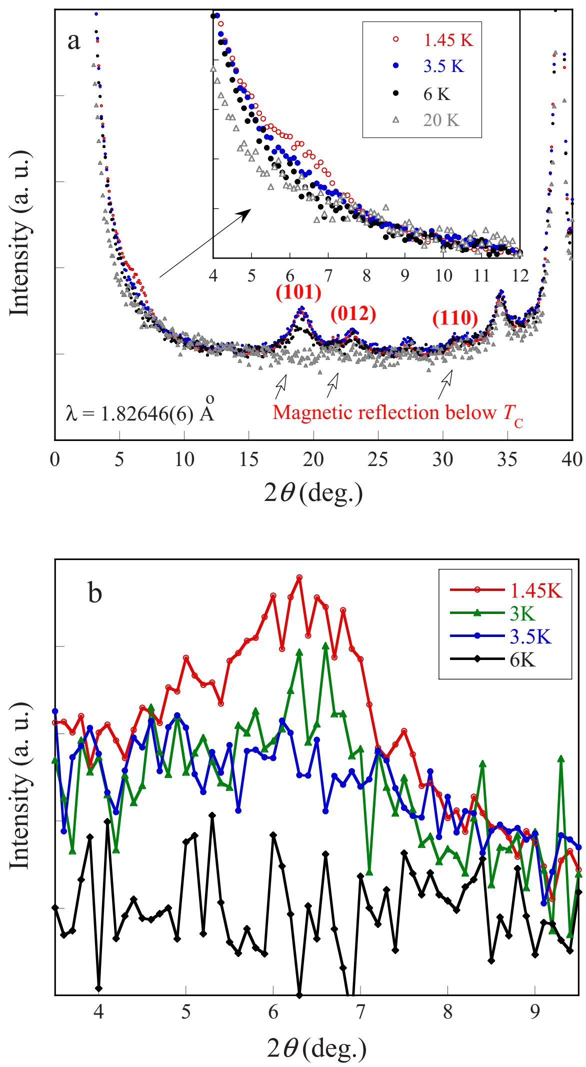

FIG. 6. (Color online) (a) Neutron diffraction intensity patterns for $(Co_{0.9}Al_{0.1})_2(OD)_3Cl$ at low temperatures. Besides the magnetic reflection peaks developing below T_C, a diffused scattering at low angles as indicated by the arrow emerged below $T<4$ K. (b) The difference between the diffraction intensities and a fitted base line of the intensities of 6 K is plotted, respectively.

The defect-induced glasslike transition in $Co_2(OH)_3Cl$ and the development of short-range spin correlation in doped $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$ can be interestingly compared with the water ice. For water ice, a glassy transition for proton position near 100 K, which was enhanced by defects, was observed by thermodynamic measurement, where thermal equilibrium was lost with an extremely slow relaxation process.[21] Further, the removal of protons by doping KOH leads to a long range ordered state.[22] The authors suggested that the glass transition in pure water ice occurs due to a phase transition toward a true ground state of ordered hydrogen positioning which requires a geological time scale to observe and the proton dynamics are strongly restored in the doped samples allowing the system to locate its "true" ground state. In $Co_2(OH)_3Cl$, defects induces a glasslike transition. Nevertheless, the impurity doping only bring out a short-range order. Unlike the water ice, the geometrical frustration is not completely relieved by impurity doping.

IV. CONCLUSION

In summary, a microamount of defects induce a low-temperature glasslike transition for the remaining dynamic spins in kagome ice $Co_2(OH)_3Cl$. A short range spin correlation develops in impurity-doped $(Co_{0.9}Al_{0.1})_2(OH)_3Cl$. This low-temperature transition resembles the low-temperature freezing of proton in water ice, where thermal equilibrium is lost with a superlong relaxation time beyond the limit of a practically observable time scale.[21] The glass transition in water ice is suggested to occur due to a phase transition toward a true ground state of ordered hydrogen positioning but the realignment of the hydrogen atoms would require a geological time scale. The spin reorientation in $Co_2(OH)_3Cl$ similarly would require a geological time scale. When the spins are diluted, a short-range order begins to emerge. $Co_2(OH)_3Cl$ represents an interesting system for studying the geometric frustration on pyrochlore lattice. It is noteworthy that this low temperature transition occurs in a readily accessible range of temperatures, which should facilitate future studies of spin correlation: we hope that such studies will contribute to a complete understanding of the true ground state of geometrically frustrated systems.

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