Coexisting Ferromagnetic Order and Disorder in a Uniform System of Hydroxyhalide $Co_2(OH)_3Cl$

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Order or disorder often exists in a uniform spin system consisting of one kind of magnetic ion. Nevertheless, they rarely coexist in normal conditions. Our thermodynamic and microscopic magnetic studies of $Co_2(OH)_3Cl$, a distorted tetrahedral lattice compound with uniform Co^{2+} spin, demonstrate that the spins located on one corner of the tetrahedron are periodically ordered, but those on the other three are disordered below a ferromagnetic transition at $T_C = 10.5$ K. The partial order resembles that of the field-induced ''kagomé-ice'' state in spin ice pyrochlore compounds. Evidence suggests that a distortion in the tetrahedron is responsible for this partial ferromagnetic order in a zero field.

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Water ice with a tetrahedral geometry is a rare case for crystals, where the oxygen is regularly ordered; meanwhile the proton is disordered following Pauling's ice rule of ''two protons near the oxygen and two protons far from the oxygen'' [1]. Geometric frustration has also been found for magnetic spins on tetrahedral lattice. Antiferromagnetic Heisenberg spins on a lattice have been suggested to form spin liquids down to $T = 0$ [2–4]; a striking recent finding is that even ferromagnetic systems on tetrahedral lattice are disordered, which is apparent for pyrochlore compounds $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$, and $Ho_2Sn_2O_7$. The rare-earth spins with giant moments of $\mu \approx 10\mu_B$ behave as classical Ising spins oriented parallel to the center of the tetrahedron. Furthermore, the spins are disordered, obeying a ''spin ice'' rule: ''two spins pointing inward, two spins outward'' analogously to the macroscopic quantum degeneracy of the proton position in crystal ice [5–7]. Such magnetic materials exemplify many generic aspects of disordered condensed matter, which renders them important as theoretical testing materials, especially because the spin state can be probed and manipulated.

We present experimental results of magnetization, muon spin rotation and relaxation (μSR), neutron diffraction, and specific heat measurements on hydroxyhalide $Co_2(OH)_3Cl$. The results demonstrate that magnetic order and disorder can coexist in this uniform system. We also show that the partial ferromagnetic order is a spin-ice-related state. In addition to being the first example of ice-related disorder in a transition metal magnet, results show that spin ice type behavior can be achieved with potentially nonclassical spins because this $S = 3/2$ system of Co^{2+} ($3d^7$) is close to the quantum limit of $S = 1/2$.

Polycrystalline $Co_2(OH)_3Cl$ [$Co_2(OD)_3Cl$ in the case of neutron diffraction] was prepared from a hydrothermal solution reaction from $CoCl_2$ and NaOH (NaOD) at 200 °C. Powder synchrotron x-ray diffraction performed at BL02B2, Spring-8, as well as electron microscopy, confirmed existence of a pure phase of the reported hexagonal structure [8] with $a = 6.84195(9)$ Å, $c = 14.5042(1)$ Å [space group: $R\bar{3}m$ (no. 166)] with good crystalline properties. Magnetization was measured with a SQUID magnetometer. The heat capacity was measured using an adiabatic heat pulse method with a ^{3}He cryostat using an amount of 0.7 g of the polycrystals. Muon spin rotation/relaxation (μSR) experiments were carried out preliminarily on a mu port at KEK-MSL (Japan) and in detail on m20 at TRIUMF (Canada) using a positive surface muon beam in basically the same manner as reported for $Cu_2(OH)_3Cl$ [9]. A neutron powder diffraction experiment was performed using a wavelength of 1.8143 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 [10]. The synchrotron x-ray diffraction data were refined along with the neutron diffraction data using Rietveld method with a computer-assisted program Rietan 2000 [11].

The magnetic ions of Co^{2+} in $Co_2(OH)_3Cl$ form a three-dimensional network of linked tetrahedra that can be viewed as alternative stacking layers of kagomé and triangular lattice planes in the (001) direction (Fig. 1). A prominent structural feature is a notable distortion in the tetrahedron. The Co-Co distance on one side of the tetrahedron that has Cl nearby is 3.42 Å, whereas those on the other three sides bonded by O are 3.12 Å, indicating a 10% longer Co-Co distance on the kagomé lattice plane.

Figure 2(a) depicts the temperature dependence of magnetic susceptibility, $\chi(T) \equiv M(T)/H$, and its inverse,

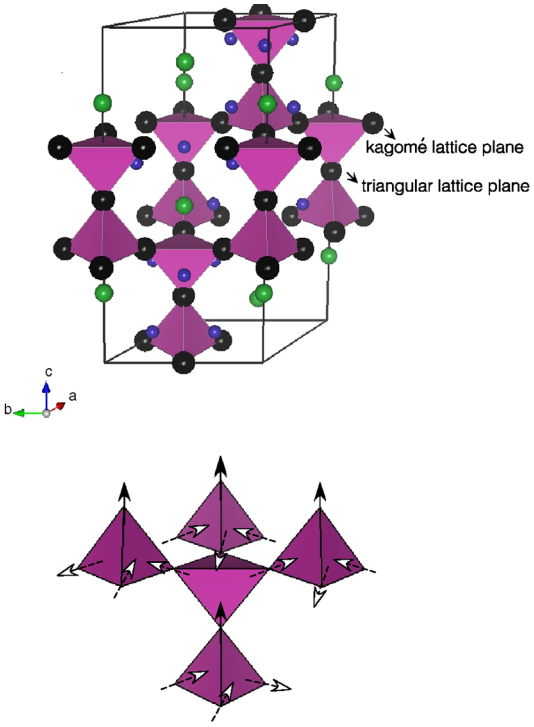

FIG. 1 (color online). Upper panel: crystal structure of $Co_2(OH)_3Cl$ that can be viewed as alternated stacked layers of kagomé and triangular lattice planes in the c-axis direction. Co ions (black) form tetrahedra with three O (blue or dark gray) and one Cl (green or gray) near the four sides. Lower panel: the suggested magnetic structure—the spins on the triangular lattice plane are ferromagnetically ordered and those on the kagomé lattice plane are disordered, with "1-in 2-out" and "2-in 1-out" spin degrees of freedom.

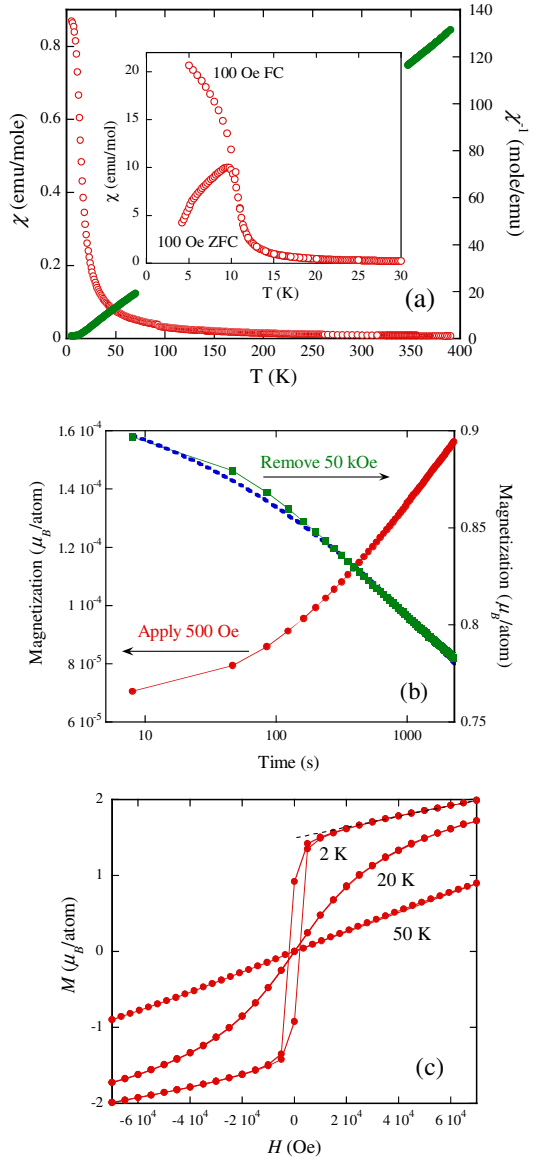

FIG. 2 (color online). Magnetization results for polycrystalline $Co_2(OH)_3Cl$. (a) Temperature dependence of the susceptibility χ (open circles, left axis) and its inverse (solid circles, right axis) per mole formula, measured at 10 kOe. The inset shows the temperature dependence of the susceptibility under field-cooling (FC) and zero-field-cooling (ZFC) conditions at 100 Oe. (b) Time relaxation of the magnetization per Co spin at 2 K upon applying and removing fields. The dashed line shows fitting to $M_r(t)$ as described in the text. (c) Field dependence of the magnetization $M(H)$ per Co spin at typical temperatures.

$\chi^{-1}(T)$, where T is the temperature. Susceptibility followed the Curie-Weiss law, $\chi^{-1}(T) = (T - \theta_W)/C$, with a Weiss temperature of $\theta_W = 7.8$ K, indicating ferromagnetic interactions. The Curie constant C corresponds to an effective moment of 4.8 bohr magnetons (μ_B), consistent with spin $S = 3/2$ Co^{2+}. Meanwhile, the susceptibility under zero-field-cooled (ZF) and field-cooled (FC) conditions diverts below the T_C around 10 K, indicating coexisting glassiness [inset plot in Fig. 2(a)]. A slow relaxation process is apparent below T_C in the time evolution of the remanent magnetization per atom Co, as expressed by $M_r(t) = 0.29\mu_B[e^{-[t(s)/4886]^{0.3}} + 2.28]$, suggesting the coexistence of glassiness with a constant ferromagnetic component [Fig. 2(b)]. An extrapolated remanent magnetization of $1.5\mu_B$ per Co spin [Fig. 2(c)] was observed, which is only around $1/3$ of the full spin moment of Co^{2+} estimated from the susceptibility.

Positive muon μ^+ is a unique local probe that is used to investigate spin fluctuations directly, in addition to being an effective probe to detect magnetic order. Because of its large gyromagnetic ratio $\gamma_\mu = 2\pi \times 135.5$ MHz/T and a weak coupling to its magnetic surroundings, it is a very sensitive probe of magnetism. Dynamic coupling was apparent at temperatures higher than 400 K producing an exponential function for the zero-field (ZF, less than 1 mOe) relaxation as $a(t) = a_0 e^{-\lambda t}$, where a_0 is the full asymmetry of the incident muon spins at time zero and λ is the depolarization rate, which is related to the electronic spin fluctuations rate υ by $\lambda \propto 1/\upsilon$. The dynamic coupling found at high temperatures and its low Curie temperature T_C suggest the existence of frustration in this material. Longitudinal field (LF) μSR at high temperatures suggests

that roughly 1/4 of the depolarization was decoupled by a weak external field of less than 100 G; for $T \leq 50$ K, the partial decoupling vanished [Fig. 3(a)]. Four candidate sites are visible for the positive muons: one site near Cl and three identical sites near three O ions (Fig. 1). Because the Cl site is distant from the magnetic ions, it should feel a weaker local field, which accounts for the 1/4 decoupled asymmetry. We conjecture that, together with the critical slowing toward the transition, the local field at Cl site is enhanced and all muon spins are depolarized by dynamic fields. Below 50 K, the muon spin relaxation appears as the sum of two exponential functions [Fig. 3(c)], which supports the two-site relaxation described above.

The slower depolarization part evolved into a function known for magnetic order below T_C, with visible oscillations of the asymmetry spectra, which directly demonstrates uniform static local fields, i.e., long range order [Fig. 3(c) and the inset plot]. Meanwhile, the quick dynamic depolarization part persisted down to the lowest temperature. Therefore, the time relaxation of muon spin asymmetry is expressed in the form of

$$a(t) = a_0\left\{P_{\mathrm{lro}} * \left[\frac{1}{3}e^{-\Lambda t} + \frac{2}{3}e^{-\alpha t}\cos(2\pi f t + \phi)\right] + (1 - P_{\mathrm{lro}}) * e^{-\lambda t}\right\}, \quad (1)$$

where P_{lro} is the proportion attributable to the long range order. In a magnetically ordered polycrystalline sample, $\frac{1}{3}$ of the muon spins retain the initial direction parallel to the internal field; $\frac{2}{3}$ that are vertical to the field rotate and are damped. The Λ in Eq. (1) expresses longitudinal field relaxation arising from the (spin) field fluctuation of the long range order and the 2/3 damping reflects its transverse field relaxation. Therefore, $\Lambda = T_1^{-1}$, and α includes additional spin-spin relaxation T_2^{-1}. As shown by the baseline in the inset plot in Fig. 3(c) as well as the ZF spectrum in Fig. 3(b), the long range order accounts for only roughly 60% of the total depolarization. The decoupling behaviors of LF-μSR in Fig. 3(b) are consistent with this argument by showing an unrecoverable dynamic relaxation part [12]. Taking reference of the high temperature behaviors and a view of the structure, it is reasonable to conclude that muons at the O sites are affected by an ordered field, whereas those at the Cl sites are affected by a disordered field.

The partial ferromagnetic order was further verified by neutron diffraction. Strong magnetic Bragg peaks appeared at the (101), (012), (110), (211), and (131) positions at $T < T_C$ (Fig. 4). The neutron diffraction result conforms to the magnetic structure, as suggested by the μSR experiment, that the spins on the triangular lattice plane (i.e., $z = c/6$, $c/2$, $5c/6$ positions in Fig. 1) are ordered and that those on the kagomé lattice plane ($z = 0$, $c/3$, $2c/3$) are disordered. The direction of the spins on the triangular lattice plane was determined to be along the c axis and its magnetic moment was determined as $4.61\mu_B$, which is close to the moment estimated from magnetization.

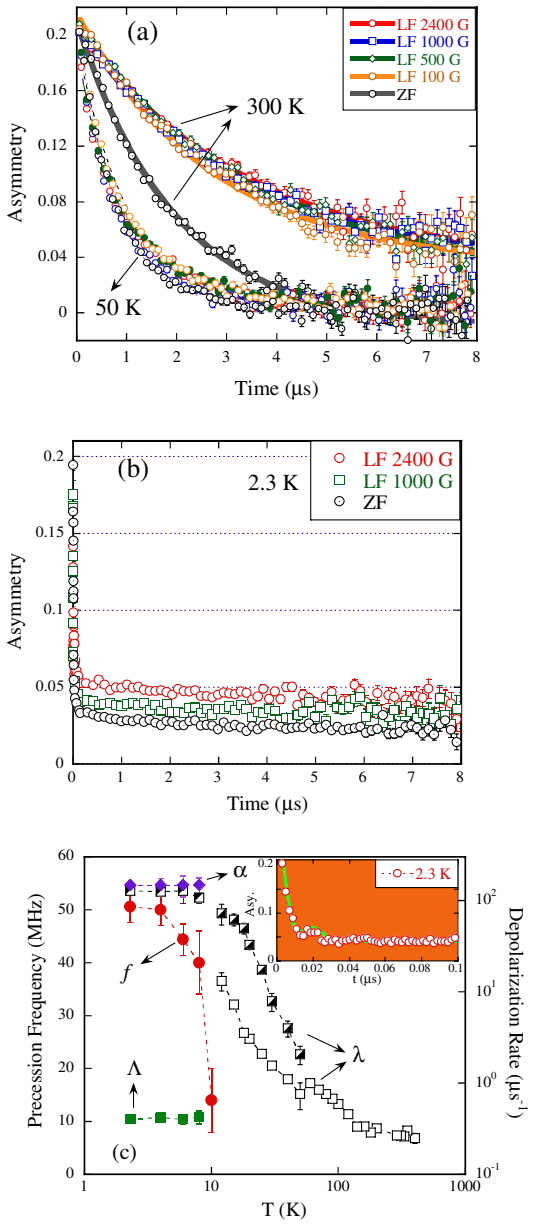

FIG. 3 (color online). μSR Results for polycrystalline $Co_2(OH)_3Cl$. (a) LF spectra showing 1/4 decoupling at 300 K and no decoupling at 50 K. (b) LF decoupling of the ordered part at 2.3 K. (c) Phase diagram of $Co_2(OH)_3Cl$. Squares represent the individual depolarization rates, as denoted by the arrows in the plot; circles represent the muon spin precession frequency. The inset plot shows oscillations of the asymmetry at 2.3 K.

Specific heat data, $C_p(T)$, imply an estimation of the magnetic entropy across the ferromagnetic transition at $T_C = 10.5$ K (Fig. 5). Assuming an Ising spin behavior with full entropy at temperatures higher than T_C, the whole entropy across the magnetic transition is estimated as approximately $0.90(1)R\ln 2$ per spin. Therefore, residual entropy around $0.1R\ln 2$ exists, which is consistent with the

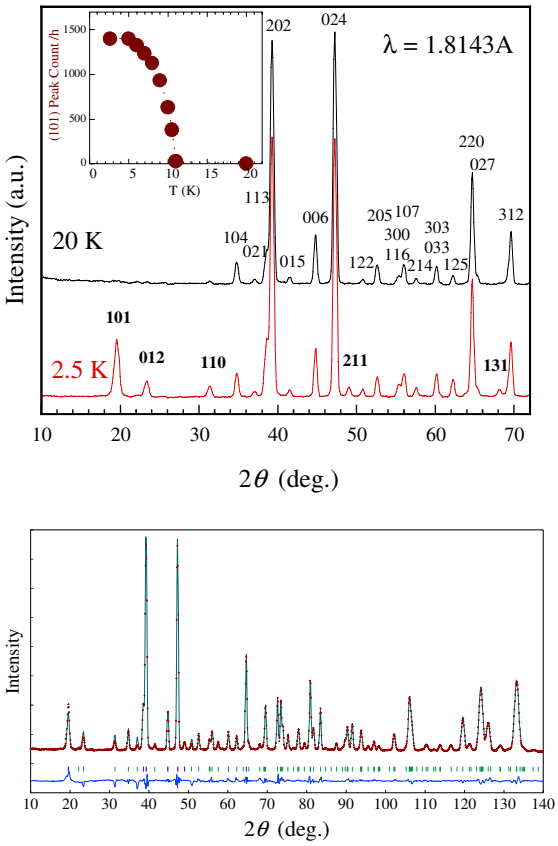

FIG. 4 (color online). Neutron diffraction for $Co_2(OD)_3Cl$ at 20 and 2.5 K, respectively. The inset plot shows the appearance of a magnetic Bragg peak (101) below T_C. The lower plot shows the fit to the proposed magnetic structure ($R = 5.18$).

proposed partial order. The agreement of the entropy to $R\ln 2$ for this $S = 3/2$ Co^{2+} system suggests that the magnetic moments are constrained to point along easy axes with the Ising anisotropy.

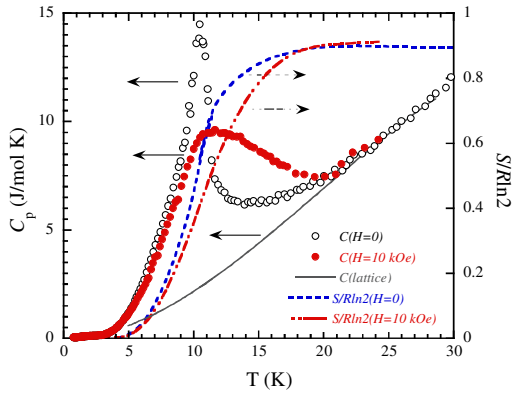

FIG. 5 (color online). Temperature dependence of specific heat $C_p(T)$ per mole of $Co_2(OH)_3Cl$ at zero field (open circles) and 10 kOe (solid circles), and magnetic entropy S per Co^{2+} spin (dashed lines, right axis), respectively. For calculation of magnetic entropy, the lattice contribution (indicated by the solid line), which did not change in the magnetic field, was estimated through extrapolation from high temperatures.

Therefore, the magnetic structure can be illustrated as in the lower panel of Fig. 1. It resembles that of the field-induced partial ferromagnetic order in the rare-earth pyrochlores. In those spin ice compounds, an applied magnetic field can fix the spins on the triangular lattice plane, reducing the spin freedom from "2-in 2-out" for all spins to "1-in 2-out" for spins on the kagomé lattice plane [5,7]. Such a "kagomé ice" state has residual entropy of $0.11R\ln 2$ [7], which is similar to the residual entropy of $0.10R\ln 2$ that we found for $Co_2(OH)_3Cl$. As shown in the spin ice compounds, the "1-in 2-out" configuration would have a saturated magnetization of $1/3$ of the full magnetic moment [13]. In $Co_2(OH)_3Cl$, the $0.10R\ln 2$ residual entropy, the $1/3$ remanent magnetization, the time relaxation of magnetization, the μSR and neutron diffraction consistently indicate a "kagomé ice"-like partial ferromagnetic order in a zero field. The distortion of the tetrahedron in $Co_2(OH)_3Cl$ is considered to be responsible for the partial order by partially lifting the degeneracy as done by an external field in the pyrochlore spin ices.

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[12] At 2.3 K the precession frequency is roughly 50 MHz, corresponding to an average local field around 3700 G [$\omega = \gamma_\mu B_{\rm local}$ with $\gamma_\mu = 2\pi \times 135.54$ MHz/T]. An external longitudinal field of $B_L = 2400$ G would lift the asymmetry baseline of the long range order part from $\frac{1}{3}a_0 p_{\rm lro}$ to $0.39a_0 P_{\rm lro}$ following equation $P_Z(x) = \frac{3}{4} - \frac{1}{4x^2} + \frac{(x^2-1)^2}{16x^3}\log\frac{(x+1)^2}{(x-1)^2}$ where $x = B_L/B_{\rm local}$. The P_Z for LF = 2400 G in Fig. 4(b) is 0.05/0.21, producing $P_{\rm lro} = 0.61$, which is in good consistency with the ZF spectrum.
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