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$\text{RbCl}_{\text{Cu}}^{5/10}$
 $P_{\text{O}}^{2/10}$

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Structural and double magnetic transitions in the frustrated spin- $\frac{1}{2}$ capped-kagome antiferromagnet $(\text{RbCl})\text{Cu}_5\text{P}_2\text{O}_{10}$

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The structural and magnetic properties of the geometrically frustrated spin- $\frac{1}{2}$ capped-kagome antiferromagnet $(\text{RbCl})\text{Cu}_5\text{P}_2\text{O}_{10}$ are investigated via temperature dependent x-ray diffraction, magnetization, heat capacity, and ^{31}P NMR experiments on a polycrystalline sample. It undergoes a structural transition at around $T_t \simeq 310$ K from high temperature trigonal ($P\bar{3}m1$) to a low temperature monoclinic ($C2/c$) unit cell, where the low temperature structure features the capped-kagome geometry of Cu^{2+} ions. Interestingly, it shows the onset of two successive magnetic transitions at $T_{N1} \simeq 20$ K and $T_{N2} \simeq 7$ K. The shape of ^{31}P NMR spectra unfold the possible nature of the transitions below T_{N1} and T_{N2} to be incommensurate and commensurate antiferromagnetic type, respectively. A large value of Curie-Weiss temperature as compared to T_{N1} sets the frustration parameter $f \simeq 8$, ensuring strong magnetic frustration in the compound. From the ^{31}P NMR spin-lattice relaxation rate, the leading antiferromagnetic exchange coupling is estimated to be $J/k_B \simeq 117$ K. This unusual double magnetic transitions make this compound beguiling for further investigations.

I. INTRODUCTION

Geometrically frustrated magnets have received enormous attention in recent days because of their potential to host rich variety of magnetic and structural phases under different conditions [1, 2]. One of the most engrossing ground states is quantum spin liquid (QSL), a highly entangled and dynamically disordered state, lacking magnetic long-range-order (LRO) [3]. Among different frustrated magnets, triangular lattice is the simplest example of geometrically frustrated magnet where the spins are arranged at the vertices of a triangle, defy the antiparallel arrangements, and lead to magnetic frustration. In a triangular lattice, the triangles are edged shared to form a two-dimensional (2D) layer. While in a kagome lattice, the triangles are corner shared in a 2D layer which amplify the degree of frustration compared to an edge shared triangular lattice. In the perfect low spin ($S = 1/2$) kagome lattice antiferromagnets (KLAF), quantum fluctuations along with strong magnetic frustration impede the conventional magnetic LRO and gives rise to a strongly correlated QSL or other non-trivial ground states [4]. A celebrated example is herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, which is the first realization of perfect $S = 1/2$ kagome compound with no magnetic LRO down to 50 mK, confirming QSL [5–7].

Several phase diagrams have been reported theoretically for KLAF, predicting a large variety of ground states as a function of the ratio of exchange couplings and also applied magnetic field [8–10]. Experimentally, many compounds have been discovered and investigated which either show subtle deviation from ideal 2D kagome geometry or are having strong anisotropy, leading to mag-

netic LRO and/or other exotic phases at finite temperatures [11]. Apart from perfect kagome lattice, many special derivatives of kagome lattice are also discovered that include square-kagome [12], octa-kagome [13], staircase-kagome [14, 15], sphere-kagome [16], strip-kagome [17, 18], tripod-kagome [19, 20], hyper-kagome [21, 22] etc. Because of the more intricate lattice geometry, these derivatives harbor an array of intriguing magnetic ground states. To name a few, QSL is realized in the square-kagome compound $\text{KCu}_6\text{AlBiO}_4(\text{SO}_4)_5\text{Cl}$ [12] and hyperkagome compound $\text{Na}_4\text{Ir}_3\text{O}_8$ [21], spin-singlet and antiferromagnetic ordering are observed in octa-kagome lattices $\text{BiOCu}_2(\text{Te,Se})\text{O}_3(\text{SO}_4)(\text{OH})\cdot\text{H}_2\text{O}$, respectively [13], spin-ice type ground state is reported in tripod kagome lattice $\text{Mg}_2\text{Dy}_3\text{Sb}_3\text{O}_{14}$ [19] etc.

Recently, a new kagome variant, capped-kagome lattice compound with general formula $(MX)\text{Cu}_5\text{O}_2(T^{5+}\text{O}_4)_2$ [$M = \text{K, Rb, Cs, Cu}$; $X = \text{Cl, Br}$; $T^{5+} = \text{P, V}$] is being pursued rigorously. This series belongs to the Averievite family, an oxide mineral found as a product of post-eruption volcanic activity. Most of these compounds show a structural transition from high symmetric trigonal at high temperatures to low symmetric monoclinic phase at low temperatures. In this series, the magnetic properties of the only compound $(\text{CsCl})\text{Cu}_5\text{V}_2\text{O}_{10}$ (CC-CVO) are elaborately studied which undergoes the structural transition at 310 K [23, 24]. Magnetic susceptibility reveals a large Curie-Weiss (CW) temperature $\theta_{\text{CW}} \simeq -185$ K and the compound encounters a magnetic LRO at around $T_N \simeq 24$ K. Zn^{2+} substitution at the capped Cu^{2+} site [i.e. $(\text{CsCl})\text{Cu}_{5-x}\text{Zn}_x\text{V}_2\text{O}_{10}$] suppresses the magnetic as well as the structural transitions and is expected to yield QSL for $x = 2$ [25, 26]. Some preliminary magnetic data are also reported for the phosphate analogue compounds $(\text{CsCl, CsBr, CsI})\text{Cu}_5\text{P}_2\text{O}_{10}$ [27]. Recently, two more new capped-kagome compounds (Molybdate-Tellurites) based on Ni^{2+} and Cu^{2+} are also

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reported [28]. Thus, the interesting structural aspects and highly frustrated geometry contemplate these compounds very special in the context of new quantum phase transitions.

In this work, we carried out a comprehensive study of the structural and magnetic properties of a phosphate averievite $(\text{RbCl})\text{Cu}_5\text{P}_2\text{O}_{10}$, abbreviated as RCCPO. RCCPO is reported to crystallize in a monoclinic structure with space group $C2/c$ (No. 15) at room temperature [29]. The crystal structure illustrated in Fig. 1 consists of capped-kagome layers, made up of corner sharing anion-centered OCu_4 tetrahedral units, arranged in an up-down-up-down fashion [see Fig. 1(b)]. There are three inequivalent Cu sites in the formula unit. Two Cu sites (Cu2 and Cu3) possess distorted CuO_4 square planer geometry while Cu1 site forms a distorted CuO_5 square pyramid. The CuO_4 squares share corners in order to make the kagome plane and the CuO_5 square pyramids share the edges with the adjacent CuO_4 squares that form the OCu_4 tetrahedra units and hence the capped-kagome network. Here, O5 is the common oxygen that provides the interaction path among two Cu2 and one Cu3 ions at the triangular base and the apical Cu1 ion in an anion-centered OCu_4 tetrahedron. The Cl^- ions are located at the center of the hexagonal rings while the Rb^+ ions are located in the inter-layer spacing. The non-magnetic PO_4 tetrahedra are placed between the capped-kagome layers and connect the capped Cu^{2+} of one layer with Cu^{2+} ions of the neighbouring layers. This provides three dimensional (3D) coupling along the c -direction [see Fig. 1(a)]. Further, owing to low symmetry crystal structure, the Cu^{2+} - Cu^{2+} distances within each OCu_4 tetrahedral unit are unequal that induces distortion in the capped-kagome layer [see Fig. 1(c - e)]. All these effects render the spin-lattice more complex, opening up the possibility of observing non-trivial ground states. Our magnetic measurements reveal that RCCPO is a highly frustrated magnet and it undergoes two consecutive magnetic transitions at low temperatures.

II. EXPERIMENTAL DETAILS

Polycrystalline sample of RCCPO was synthesized by the conventional solid-state reaction technique. The synthesis involves two steps. In the first step, the precursor $\text{Cu}_2\text{P}_2\text{O}_7$ was prepared by heating the stoichiometric mixture of CuO (Aldrich, 99.999%) and $\text{NH}_2\text{H}_2\text{PO}_4$ (Aldrich, 99.999%). These reagents were finely ground, pressed into pellets, and prereacted in air at 350 °C for 12 h in order to remove ammonia and water. The obtained soft pellets were ground again, sealed in evacuated quartz tube, and heated at 800 °C for 24 h. In the second step, the obtained $\text{Cu}_2\text{P}_2\text{O}_7$ powder was mixed in a stoichiometric ratio with CuO (Aldrich, 99.999%) and RbCl (Aldrich, 99.999%), ground, pelletized, sealed in evacuated quartz tube, and annealed at 550 - 570 °C with multiple intermediate re-grindings. The phase pu-

urity of the product was confirmed by powder x-ray diffraction (XRD) recorded at room temperature using a PANalytical x-ray diffractometer (CuK_α radiation, $\lambda_{\text{avg}} \simeq 1.5418 \text{ \AA}$). To check if any structural transition is present, temperature-dependent powder XRD was performed over a broad temperature range ($13 \text{ K} \leq T \leq 400 \text{ K}$). For low-temperature measurements, a low- T attachment (Oxford Phenix) while for high-temperature measurements, a high- T oven attachment (Anton-Paar HTK 1200N) to the x-ray diffractometer was used. Rietveld refinement of the powder XRD was performed using the FULLPROF software package [30], taking the initial structural parameters from the previous report [29].

The dc magnetization (M) was measured as a function of temperature ($1.9 \text{ K} \leq T \leq 380 \text{ K}$) in different magnetic fields, using the vibrating sample magnetometer (VSM) attachment to the Physical Property Measurement System [PPMS, Quantum Design]. Similarly, ac susceptibility was measured as a function of temperature ($1.9 \text{ K} \leq T \leq 100 \text{ K}$) and frequency ($200 \text{ Hz} \leq \nu \leq 10 \text{ kHz}$) in an ac field of 10 Oe using ACMS option of the PPMS. Heat capacity (C_p) as a function of T and H was measured on a small piece of sintered pellet using thermal relaxation technique in PPMS.

The nuclear magnetic resonance (NMR) measurements were carried out using a laboratory-built phase-coherent spin-echo pulse spectrometer on the ^{31}P nuclei (nuclear spin $I = 1/2$ and gyromagnetic ratio $\gamma_N/2\pi = 17.237 \text{ MHz/T}$). We perform the experiments at two radio frequencies ($f = 49.6$ and 120.6 MHz) and over a wide temperature range ($1.8 \text{ K} \leq T \leq 300 \text{ K}$). The ^{31}P NMR spectra were obtained by sweeping the magnetic field, keeping the frequency fixed. The temperature-dependent NMR shift, $K(T) = [H_{\text{ref}} - H(T)]/H(T)$ was calculated by taking the resonance field of the sample (H) with respect to the resonance field of a nonmagnetic reference (H_{ref}) H_3PO_4 . ^{31}P spin-lattice relaxation rate ($1/T_1$) was measured by the standard saturation recovery method. ^{31}P spin-spin relaxation rate ($1/T_2$) was obtained by measuring the decay of the echo integral with variable spacing between the $\pi/2$ and π pulses.

III. RESULTS

A. X-ray Diffraction

In order to detect the structural transition or lattice distortion, if any, powder XRD was measured at different intermediate temperatures from 13 K to 400 K. Figure 2 displays the powder XRD patterns of RCCPO at 400 K, 200 K, and 13 K along with the Rietveld fit. At room-temperature (300 K), all the diffraction peaks can be well indexed to the monoclinic unit cell with $C2/c$ symmetry. The obtained lattice parameters at room temperature are $a = 10.868(4) \text{ \AA}$, $b = 6.207(5) \text{ \AA}$, $c = 16.181(5) \text{ \AA}$, $\beta = 93.391(3)^\circ$, and the unit cell volume $V_{\text{cell}} \simeq 1089.621 \text{ \AA}^3$, which are in close agreement with

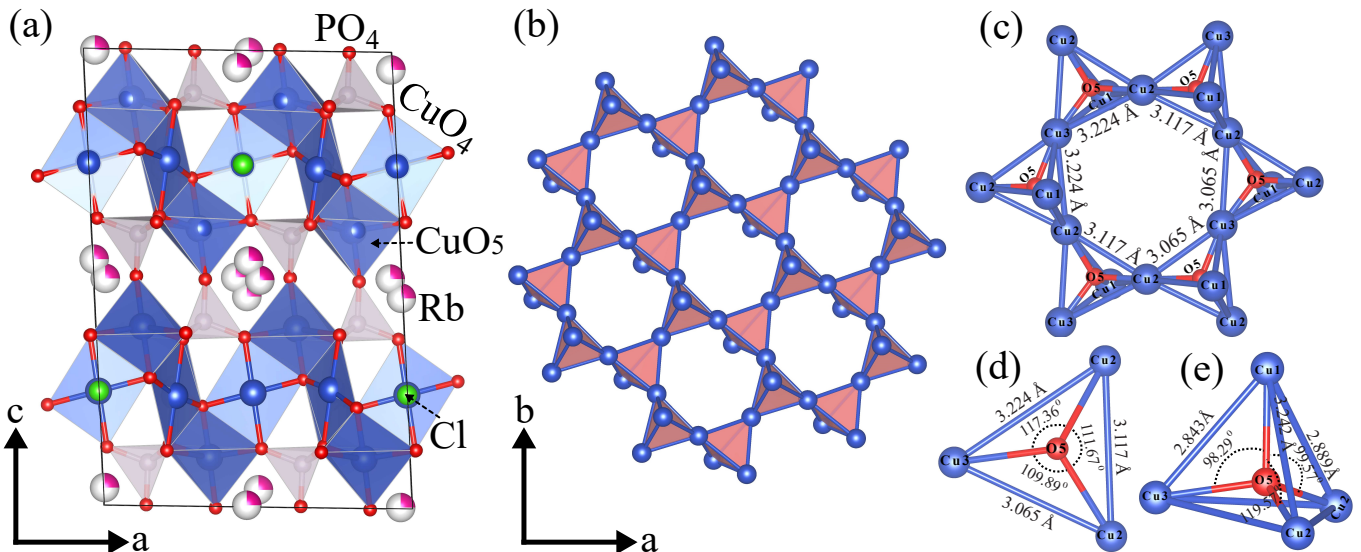


FIG. 1. (a) Crystal structure of $(\text{RbCl})\text{Cu}_5\text{P}_2\text{O}_{10}$ projected in the ac -plane. The connection of $\text{Cu}(2,3)\text{O}_4$ square planes (plaquettes) and $\text{Cu}(1)\text{O}_5$ square pyramids form the capped-kagome layers. PO_4 tetrahedra are connecting these layers along the c -direction. (b) A section of the capped-kagome layer in the ab -plane. (c) Hexagonal ring showing the bond lengths. (d) Triangular base of the OCu_4 tetrahedron with the bond lengths and bond angles. (e) The bond lengths and bond angles of the apical Cu atom with basal Cu atoms of the OCu_4 tetrahedron.

the previous report [29]. Absence of any visible change in the XRD pattern down to 13 K indicates no structural distortion from 300 K down to 13 K. However, a change in the diffraction pattern was observed above $T_t \sim 310$ K with splitting of certain Bragg peaks and the appearance of new peaks. Above ~ 340 K, the XRD pattern completely stabilize in a more symmetric crystal structure with less number of Bragg peaks compare to the room-temperature crystal structure. The analysis of XRD pattern at 400 K confirmed a trigonal structure with space group $P\bar{3}m1$ (No. 164). The refined lattice parameters are $a = 6.185(4)$ Å, $c = 8.241(5)$ Å, and $V_{\text{cell}} \simeq 273.1$ Å³. Thus, a structural transition occurs at around 310 K from high temperature trigonal to low temperature monoclinic structure, similar to the analog compound CCCVO. In an intermediate temperature regime around 300 K both the phases co-exist and the data could be fitted using two phases. The obtained atomic parameters at 400 K (Trigonal) and 200 K (Monoclinic) are listed in Table I and II, respectively.

The temperature evolution of lattice parameters from 13 K to 400 K are presented in Fig. 3. As shown in Fig. 3(a), associated with the symmetry lowering, the in-plane and out-of-plane lattice constants transform into $a_m \simeq \sqrt{3}a_t$, $b_m \simeq b_t$, and $c_m \simeq 2c_t$, respectively [31, 32]. Here, the subscripts m and t denoting the monoclinic and trigonal structures, respectively. Figure 3(b) presents the temperature variation of angle (β) and V_{cell} from 13 K to 300 K in the monoclinic phase. β increases with decreasing temperature but V_{cell} is found to decrease systematically upon cooling. The variation of V_{cell} with temperature can be expressed in terms of the internal energy

TABLE I. Structural parameters of RCCPO obtained from the Rietveld refinement of the powder-XRD data at 400 K [Trigonal, Space group: $P\bar{3}m1$ (No. 164)]. Our fit yields $a = 6.185(4)$ Å, $c = 8.241(5)$ Å, $V_{\text{cell}} \simeq 273.1$ Å³, $R_p \simeq 14.5$, and $\chi^2 = \left(\frac{R_{\text{wp}}}{R_{\text{exp}}}\right)^2 \simeq 7.2$. Listed are the Wyckoff positions and the refined atomic coordinates for each atom.

Atom	Wyckoff	x	y	z	Occ.
Rb1	1a	1.000	1.000	1.000	0.60
Rb2	2c	1.000	1.000	0.877(3)	0.20
Cl1	1b	1.000	1.000	0.500	1.00
Cu1	2d	0.333	0.666	0.210(1)	1.00
Cu2	3f	0.000	0.500	0.500	1.00
P1	2d	0.333	0.666	0.800(2)	1.00
O1	2d	0.333	0.666	1.014(1)	1.00
O2	6i	0.061(3)	0.530(1)	0.752(4)	1.00
O3	2d	0.333	0.666	0.452(1)	1.00

$[U(T)]$ of the system [33]

$$V_{\text{cell}}(T) = \frac{\gamma U(T)}{K_0} + V_0, \quad (1)$$

where V_0 is the cell volume at $T = 0$ K, K_0 is the bulk modulus of the system, and γ is the Grüneisen parameter. $U(T)$ is the internal energy which can be expressed in terms of the Debye approximation [34] as

$$U(T) = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3}{(e^x - 1)} dx. \quad (2)$$

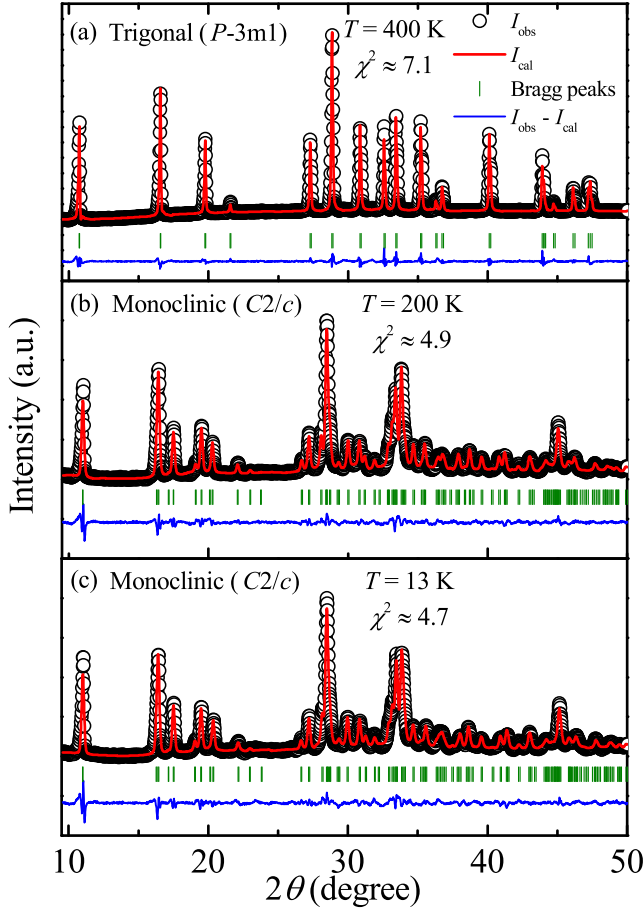


FIG. 2. Powder XRD patterns (open circles) at (a) 400 K, (b) 200 K, and (c) 13 K. The solid lines denote the Rietveld refinement of the data. The Bragg peak positions are indicated by green vertical bars and the bottom solid line indicates the difference between the experimental and calculated intensities. The crystal structure and the corresponding space group at different temperatures are also indicated.

Here, N is the number of atoms in the unit cell, k_B is the Boltzmann constant, and θ_D is the Debye temperature. The variable x inside the integration stands for the quantity $\frac{\hbar\omega}{k_B T}$ with phonon frequency ω and Planck constant \hbar . Here, $\theta_D = \frac{\hbar\omega_D}{k_B}$ and ω_D is the upper limit of ω . The best fit of the $V_{\text{cell}}(T)$ data using Eq. (1) [solid line in Fig. 3(b)] yields the parameters: $\theta_D \simeq 225$ K, $V_0 \simeq 1084.25 \text{ \AA}^3$, and $\frac{\gamma}{K_0} \simeq 8.08 \times 10^{-12} \text{ Pa}^{-1}$.

B. Magnetization

The temperature dependent dc susceptibility $\chi(T)$ ($\equiv M/H$) of the polycrystalline RCCPO sample measured in the applied field of $\mu_0 H = 0.5$ T is shown in the Fig. 4(a). At high temperatures, $\chi(T)$ increases with decreasing temperature in a Curie-Weiss (CW) manner as expected in the paramagnetic regime. No clear indi-

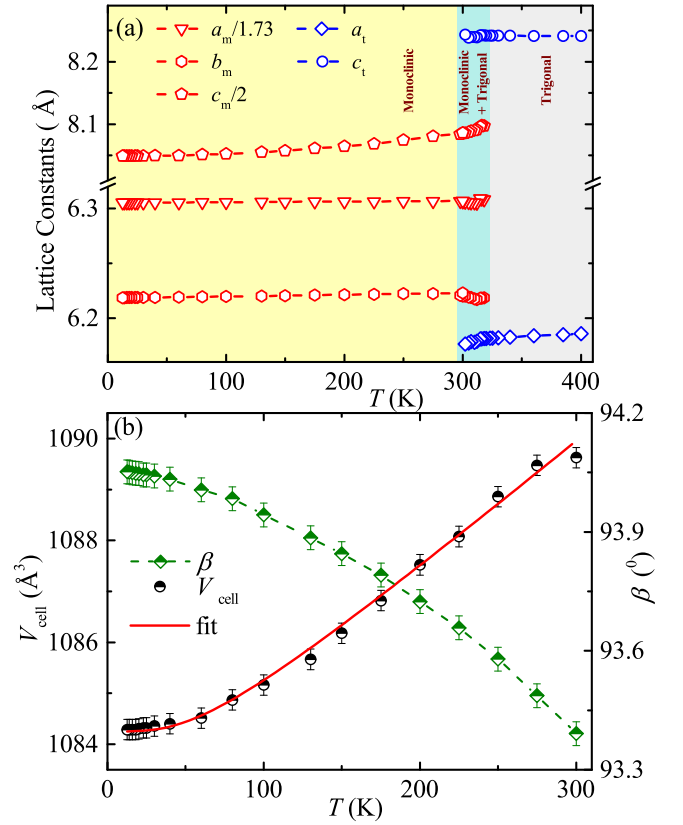


FIG. 3. (a) Lattice constants (a , b , and c) as a function of temperature from 13 K to 400 K. The lattice constants in the monoclinic phase are scaled with respect to the high symmetry trigonal structure. The areas shaded in yellow, gray, and cyan colors represent the regimes for pure monoclinic, trigonal, and coexistence of both the phases, respectively. (b) Monoclinic angle (β) and the unit cell volume (V_{cell}) as a function of temperature from 13 K to 300 K. The solid line represents the fit of $V_{\text{cell}}(T)$ using Eq. (1).

cation of any magnetic LRO is detected down to 2 K. $\chi(T)$ measured under field-cooled-warming (FCW) and field-cooled-cooling (FCC) conditions show a clear thermal hysteresis [inset of Fig. 4(a)] confirming the structural phase transition.

Figure 4(b) shows the inverse magnetic susceptibility $1/\chi(T)$ for $\mu_0 H = 0.5$ T. In the paramagnetic regime $1/\chi(T)$ typically shows a linear behavior with temperature, due to uncorrelated moments. To extract the magnetic parameters, $1/\chi(T)$ was fitted in the temperature range $200 \text{ K} \leq T \leq 300 \text{ K}$ below the structural transition by the CW law

$$\chi(T) = \chi_0 + \frac{C}{T - \theta_{\text{CW}}}, \quad (3)$$

where, χ_0 is the temperature-independent susceptibility, which includes Van-Vleck paramagnetism and core diamagnetism. The second term is the CW law where C is the Curie constant and θ_{CW} is the CW temperature. The fit yields $\chi_0 \simeq 2.19 \times 10^{-4} \text{ cm}^3/\text{mol-Cu}^{2+}$,

TABLE II. Structural parameters of RCCPO obtained from the Rietveld refinement of the powder-XRD data at 200 K [Monoclinic, Space group: $C2/c$ (No. 15)]. Our fit yields $a = 10.860(4)$ Å, $b = 6.221(5)$ Å, $c = 16.130(5)$ Å, $\beta = 93.724(3)^\circ$, $V_{\text{cell}} \simeq 1087.44$ Å³, $R_p \simeq 14.8$, and $\chi^2 = \left(\frac{R_{\text{wp}}}{R_{\text{exp}}}\right)^2 \simeq 4.9$. Listed are the Wyckoff positions and the refined atomic coordinates for each atom.

Atom	Wyckoff	x	y	z	Occ.
Rb1	8f	0.506(2)	0.028(2)	0.546(2)	0.25
Rb2	8f	0.471(2)	0.033(2)	0.506(2)	0.25
Cl1	4e	0.500	1.065(1)	0.750	1.00
Cu1	8f	0.346(2)	0.472(3)	0.606(1)	1.00
Cu2	8f	0.242(2)	0.807(2)	0.741(2)	1.00
Cu3	4e	0.500	0.606(2)	0.750	1.00
P1	8f	0.350(2)	0.436(1)	0.403(2)	1.00
O1	8f	0.488(2)	0.421(2)	0.379(1)	1.00
O2	8f	0.281(1)	0.226(1)	0.382(1)	1.00
O3	8f	0.283(2)	0.642(2)	0.381(2)	1.00
O4	8f	0.358(2)	0.384(2)	0.497(2)	1.00
O5	8f	0.327(2)	0.544(2)	0.720(2)	1.00

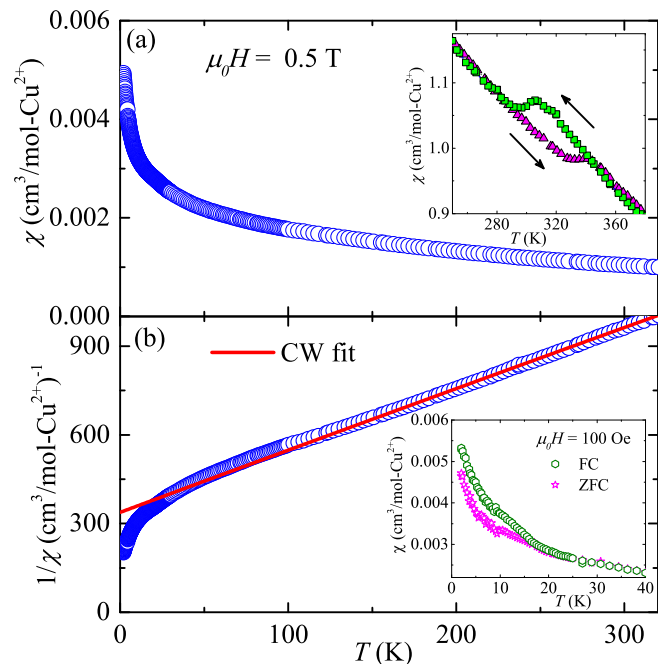


FIG. 4. (a) Temperature dependent dc susceptibility $\chi(T)$ measured at an applied field of $\mu_0 H = 0.5$ T. Inset: Thermal hysteresis around the structural transition measured under FCW and FCC conditions. (b) Inverse susceptibility ($1/\chi$) vs T at $\mu_0 H = 0.5$ T and the solid line is the CW fit for $200 \text{ K} \leq T \leq 300 \text{ K}$ below the structural transition. Inset: $\chi(T)$ measured at $H = 100$ Oe in ZFC and FC protocols.

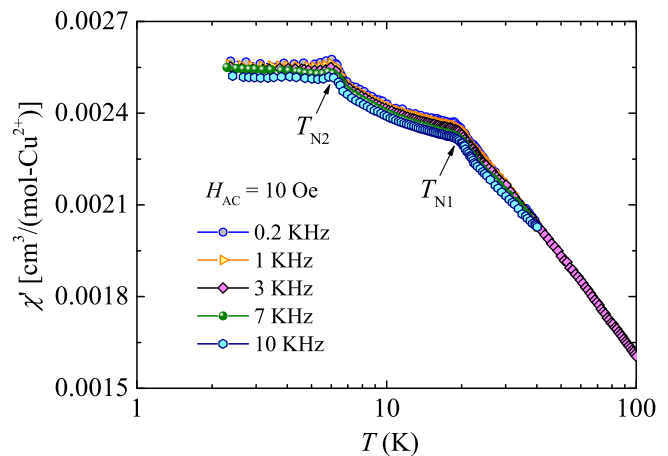


FIG. 5. Real part of ac susceptibility $\chi'(T)$ vs T at different frequencies. The arrows point to the magnetic anomalies.

$C \simeq 0.46 \text{ cm}^3 \text{ K/mol-Cu}^{2+}$, and $\theta_{\text{CW}} \simeq -160 \text{ K}$. The large negative value of θ_{CW} suggests that the dominant exchange interactions between Cu^{2+} ions are AFM in nature. From the value of C , the effective moment is calculated to be $\mu_{\text{eff}} \simeq 1.93 \mu_{\text{B}}/\text{Cu}^{2+}$ using the relation $\mu_{\text{eff}} = \sqrt{3k_{\text{B}}C/N_{\text{A}}\mu_{\text{B}}^2}$, where N_{A} is the Avogadro's number and μ_{B} is the Bohr magneton. For a spin-1/2 system, the spin-only effective moment is expected to be $\mu_{\text{eff}} = g\sqrt{S(S+1)}\mu_{\text{B}} \simeq 1.73\mu_{\text{B}}$, assuming Landé g -factor $g \simeq 2$. However, our experimental value of $\mu_{\text{eff}} \simeq 1.93\mu_{\text{B}}/\text{Cu}^{2+}$ is slightly higher than the spin-only value and corresponds to $g \simeq 2.22$. Such a large value of g is typically observed for powder samples containing magnetic Cu^{2+} ion [35]. The core diamagnetic susceptibility χ_{core} of RCCPO is calculated to be $-2.22 \times 10^{-4} \text{ cm}^3/\text{mol}$ by adding the core diamagnetic susceptibilities of individual ions Rb^+ , Cl^- , Cu^{2+} , P^{5+} , and O^{2-} [36]. The Van-Vleck paramagnetic susceptibility (χ_{VV}) is estimated by subtracting χ_{dia} from χ_0 to be $\sim 4.41 \times 10^{-4} \text{ cm}^3/\text{mol}$. This value of χ_{VV} is close to the values reported for other cuprates [37, 38].

As depicted in the inset of Fig. 4(b), the zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities in $H = 100$ Oe show a weak splitting at $T_{\text{N1}} \simeq 20 \text{ K}$, indicating either the onset of a magnetic LRO or a spin-glass type transition. The extent of frustration in a spin system can be quantified by the frustration ratio $f = \frac{|\theta_{\text{CW}}|}{T_{\text{N1}}}$. According to the mean field theory, θ_{CW} is the sum of all exchange interactions present in the system. Typically, for a non-frustrated AFM system, f is close to 1. However, for a highly frustrated AFM, f value is much larger than 1. For RCCPO, the frustration ratio is calculated to be $f \simeq 160/20 \simeq 8$ which corroborate strong frustration in the system.

Figure 5 presents the temperature dependent ac susceptibility measured in different frequencies and at a fixed ac field of $H_{\text{AC}} \simeq 10$ Oe. In contrast to dc $\chi(T)$, real part of the ac susceptibility $\chi'(T)$ shows two anomalies at

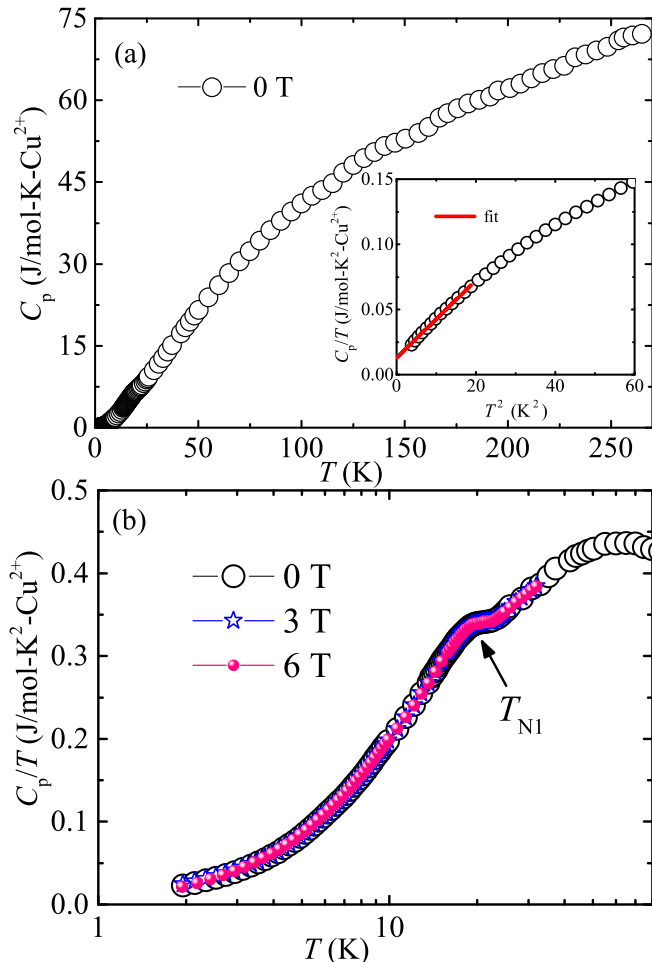


FIG. 6. (a) $C_p(T)$ of RCCPO measured in zero-field. Inset: C_p/T vs T^2 in zero-field, showing the linear regime below T_{N2} . Solid line is the linear fit. (b) C_p/T vs T measured in different applied fields in the low-temperature region, around T_{N1} .

$T_{N1} \simeq 20$ K and $T_{N2} \simeq 7$ K, reflecting two magnetic transitions. The peak at $T_{N1} \simeq 20$ K is found to be weakly frequency dependent, which shifts towards higher temperatures with increasing frequency. This is a possible indication of canted antiferromagnetism or spin-glass-type transition. On the other hand, the peak at $T_{N2} \simeq 7$ K is found to be frequency independent, suggesting the onset of a robust AFM LRO.

C. Heat Capacity

Temperature dependent heat capacity $C_p(T)$ measured in zero-field is presented in Fig. 6(a). At high temperatures, C_p is dominated by the phonon excitations while at low temperatures, it is dominated by the magnetic contribution. As the temperature is lowered, C_p shows a weak cusp at $T_{N1} \simeq 20$ K [see Fig. 6(b)]. The position of this cusp is unaffected by the external magnetic

field up to 6 T. However, no obvious feature is evident at $T_{N2} \simeq 7$ K, likely due to weak entropy change across T_{N2} . Below 4 K, the spin-wave dispersion gives rise to a T^3 behaviour, as expected in a 3D AFM ordered state [38]. The plot of C_p/T vs T^2 in the inset of Fig. 6(a) highlights the linear behavior below 4 K. Moreover, in case of a SG transition, $C_p(T)$ at low temperatures deviates from the T^3 behaviour and is usually described by $C_p(T) = \beta T^3 + \delta T^{3/2}$ [39]. Thus, only T^3 dependence of $C_p(T)$ also rules out a SG transition at T_{N2} and establishes canted-AFM nature of the transition. Due to the unavailability of a suitable non-magnetic analogue, we are unable to separate the magnetic part of the heat capacity from the total $C_p(T)$.

D. ^{31}P NMR

NMR is an immensely powerful local tool to study the static and dynamic properties of a spin system. The crystal structure of RCCPO have a unique ^{31}P site. Two adjacent capped-kagome layers in the ac -plane are connected through the PO_4 tetrahedra. Since ^{31}P is coupled with the Cu^{2+} ions, through ^{31}P NMR, one can probe the static and dynamic properties of Cu^{2+} spins.

1. ^{31}P NMR Spectra

The field-sweep ^{31}P NMR spectra measured at different temperatures ($2.4 \text{ K} \leq T \leq 280 \text{ K}$) in a radio frequency of 49.6 MHz are shown in Fig. 7. Each NMR spectrum is normalized by its maximum amplitude and offset vertically by adding a constant. The spectral line consists of a single spectral line, typical for $I = 1/2$ nuclei [40]. The spectral line is symmetric at high temperatures and becomes asymmetric as we go down in temperature. Since our measurements are done on randomly oriented polycrystalline sample, asymmetric shape of the spectra can be attributed to a powder pattern due to an asymmetric hyperfine coupling constant and/or an anisotropic susceptibility [41]. With decreasing temperature, the line broadens and the peak position shifts with temperature.

The NMR shift $K(T)$ is the direct measure of intrinsic spin susceptibility $\chi_{\text{spin}}(T)$ and is free from extrinsic contributions. Therefore, one can write $K(T)$ in terms of $\chi_{\text{spin}}(T)$ as

$$K(T) = K_0 + \frac{A_{\text{hf}}}{N_A} \chi_{\text{spin}}(T), \quad (4)$$

where, K_0 is the temperature-independent chemical shift and A_{hf} is the hyperfine coupling constant between the ^{31}P nuclei and Cu^{2+} electronic spins. The isotropic NMR shift K_{iso} obtained by fitting the NMR spectra is plotted as a function of T in Fig. 8. The upper inset of Fig. 8 shows K_{iso} vs χ plot with T as an implicit parameter.

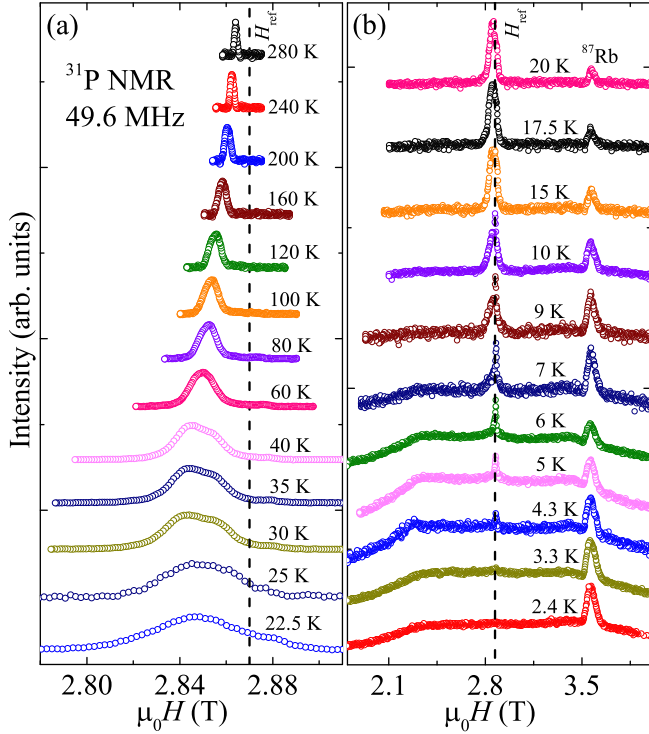


FIG. 7. (a) Temperature evolution of ^{31}P NMR spectra measured in a radio frequency $f = 49.6$ MHz, above T_{N1} . The vertical dashed line corresponds to the ^{31}P non-magnetic reference field position. (b) ^{31}P NMR spectra below T_{N1} . The peak at the right side corresponds to signal of ^{87}Rb present in the sample.

A straight line fit over a temperature range $60\text{ K} \leq T \leq 280\text{ K}$ yields the isotropic part of the hyperfine coupling $A_{\text{iso}} \simeq 2.93\text{ T}/\mu_{\text{B}}$. The small deviation from linearity below 60 K can be attributed to a small amount of paramagnetic impurities to which K_{iso} is insensitive. The full width at half maximum (FWHM) obtained from the spectral fit is plotted against T in the lower inset of Fig. 8. It increases with lowering temperature and then shoots up below about 30 K which suggests the growth of internal field as we approach the magnetic ordering at T_{N1} .

Figure 7(b) presents ^{31}P NMR spectra below T_{N1} . Below about 22 K, the NMR line broadens drastically implying that ^{31}P senses the internal field in the ordered state. The spectrum seems to form a triangular line shape, typically expected for a powder sample in an incommensurate spin-density-wave (SDW) state [42–45]. Below the second transition $T_{N2} \simeq 9.5\text{ K}$, a huge internal field pops up leading to a drastic line broadening, and the line attains a nearly rectangular shape superimposed with a sharp line at the center of gravity $H \simeq 2.87\text{ T}$, which is the zero-shift resonance position of ^{31}P nuclei. With decreasing temperature, this line broadening increases and the intensity of the central narrow line decreases. This rectangular line shape is reminiscent of a commensurate AFM ordering [44–47]. An additional sig-

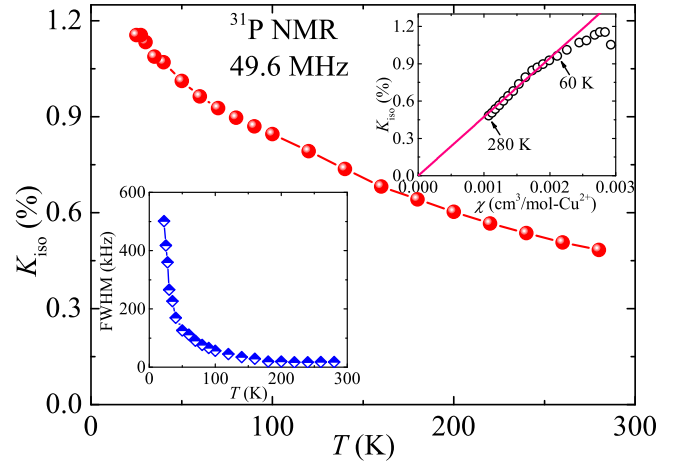


FIG. 8. Temperature dependent ^{31}P NMR iso-shift K_{iso} measured at 49.6 MHz. Upper inset: K_{iso} vs χ (measured at 3 T). The solid line is the straight line fit. Lower inset: Full width at half maximum (FWHM) vs T .

nal appears at low temperatures which overlaps with the right shoulder of the rectangular pattern. This peak position is almost temperature independent and corresponds to the signal of ^{87}Rb present in the sample.

2. Spin-lattice relaxation rate $1/T_1$

To understand the local spin-spin correlation, ^{31}P spin-lattice relaxation rate $1/T_1$ was measured as a function of temperature down to 2.4 K at the central peak position and in two different frequencies, 49.6 MHz and 120.6 MHz. For an $I = 1/2$ nucleus, the recovery of the longitudinal magnetization is expected to follow a single exponential behavior. Indeed, our recovery curves were fitted well by the stretched exponential function

$$1 - \frac{M(t)}{M(\infty)} = Ae^{-(t/T_1)^\beta}, \quad (5)$$

where, $M(t)$ is the nuclear magnetization at a time t after the saturation pulse, $M(\infty)$ is the equilibrium nuclear magnetization, and β is the stretch exponent. Recovery curves for 120.6 MHz in four different temperatures along with the fits are shown in Fig. 9(a).

The temperature dependence of $1/T_1$ extracted following the above fitting procedure are presented in Fig. 9(b) for both the frequencies. The exponent β as a function of T for both the frequencies is also plotted in the inset of Fig. 9(b). At high temperatures ($T > 30\text{ K}$), the value of β is found to be close to 1 and is almost temperature independent, suggesting a uniform relaxation process in this temperature range. However, a drastic drop in β value below about 25 K indicates the distribution of relaxation time in the ordered state which is possibly due to some kind of disorder at the magnetic sites [48]. Similarly, $1/T_1$ in the high temperature regime

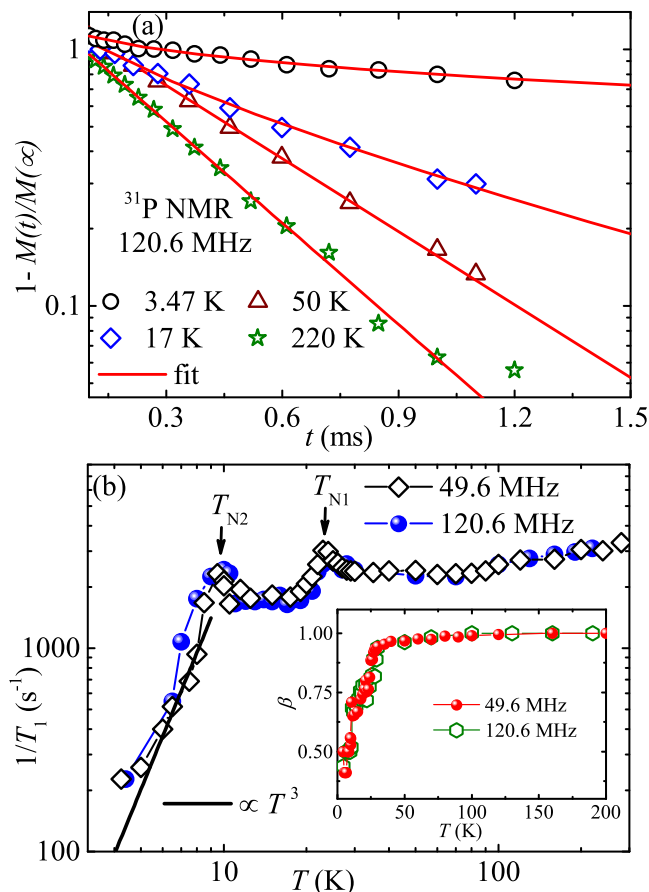


FIG. 9. (a) Longitudinal magnetization recovery curves for 120.6 MHz at four selective temperatures measured on the ^{31}P nuclei and the solid lines are fits using Eq. (5). (b) ^{31}P NMR spin-lattice relaxation rate ($1/T_1$) vs T measured in 49.6 MHz and 120.6 MHz. The downward arrows point to $T_{N1} \simeq 23.5$ K and $T_{N2} \simeq 9.5$ K. The solid line represents T^3 behaviour below T_{N2} . Inset: Exponent β as a function of T for both the frequencies.

($T > 75$ K) is almost temperature independent due to localized moments in the paramagnetic state [49]. At low-temperatures, $1/T_1$ exhibits two sharp peaks at around $T_{N1} \simeq 23.5$ K and $T_{N2} \simeq 9.5$ K, indicating the slowing down of fluctuating moments as we approach the magnetic transitions. These findings corroborate the double transitions observed from the ac susceptibility measurements. Note that the transition anomalies in $1/T_1$ appear at slightly higher temperatures compared to that observed in ac susceptibility data, which is due to different thermocouples with different calibrations used in the NMR and PPMS cryostats. Below T_{N2} , $1/T_1$ drops swiftly toward zero because of the release of critical fluctuations and the scattering of magnons by the nuclear spins [50–52]. For $T \gg \Delta/k_B$, $1/T_1$ follows either a T^3 behavior or a T^5 behavior due to a two-magnon Raman process or a three-magnon process, respectively, where Δ/k_B is the energy gap in the spin-wave excitation spec-

trum [50]. On the other hand, for $T \ll \Delta/k_B$, it follows an activated behavior $1/T_1 \propto T^2 e^{-\Delta/k_B T}$. As shown in Fig. 9(b), $1/T_1$ below T_{N2} follows a nearly T^3 behaviour, ascertaining that the relaxation is mainly governed by a two magnon process similar to that reported for other frustrated magnets [52].

From the constant value of $1/T_1$ at high-temperatures, one can estimate the leading exchange coupling between Cu^{2+} ions, using the hyperfine coupling between P and Cu atoms. At high temperatures, $1/T_1$ can be expressed as [49, 52]

$$\left(\frac{1}{T_1}\right)_{T \rightarrow \infty} = \frac{(\gamma_N g \mu_B)^2 \sqrt{2\pi} z' S(S+1)}{3 \omega_{ex}} \left(\frac{A_z}{z'}\right)^2, \quad (6)$$

where $\omega_{ex} = (|J^{\max}| k_B / \hbar) \sqrt{2zS(S+1)/3}$ is the Heisenberg exchange frequency, z is the number of nearest-neighbor spins of each Cu^{2+} ion, and z' is the number of nearest-neighbor Cu^{2+} spins attached to a given P site. In RCCPO, each Cu^{2+} ion in the kagome plane has six nearest-neighbours while each capped Cu^{2+} ion can see only three neighbouring ions. Therefore, on an average each Cu^{2+} spin sees 4.5 neighbouring spins. Similarly, each P site is strongly connected to five nearest-neighbour Cu^{2+} spins. Thus, using the parameters $A_z \simeq 2.93$ T/ μ_B , $\gamma_N = 108.303 \times 10^2$ rad sec $^{-1}$ Oe $^{-1}$, $z = 4.5$, $z' = 5$, $g = 2.22$, $S = \frac{1}{2}$, and the relaxation rate at 160 K $\left(\frac{1}{T_1}\right)_{T \rightarrow \infty} \simeq 2714.7$ sec $^{-1}$, the magnitude of the leading antiferromagnetic exchange coupling is calculated to be $J^{\max}/k_B \simeq 117$ K.

3. Spin-spin relaxation rate $1/T_2$

In order to measure the spin-spin relaxation rate $1/T_2$, the decay of the transverse magnetization (M_{xy}) was monitored after a $\pi/2 - \tau - \pi$ pulse sequence as a function of the pulse separation time τ . The recovery curves are then fitted by the following equation

$$M_{xy} = M_0 e^{-(2\tau/T_2)}. \quad (7)$$

Recovery curves at few selected temperatures along with the fits are depicted in Fig. 10(a). The extracted $1/T_2$ is plotted as a function of temperature in Fig. 10(b). Similar to $1/T_1$, $1/T_2$ also exhibits two sharp peaks further establishing double transitions at $T_{N1} \simeq 23.5$ K and $T_{N2} \simeq 9.5$ K.

IV. DISCUSSION AND SUMMARY

This averievite family of compounds are an interesting class of compounds where replacement of any ion in the structure affects the geometry of OCu_4 tetrahedron and alters the magnetic properties significantly. For instance, in the phosphates ($\text{CsCl}, \text{CsBr}, \text{CsI}$) $\text{Cu}_5\text{P}_2\text{O}_{10}$, the value of θ_{CW} which represents the overall energy scale of the

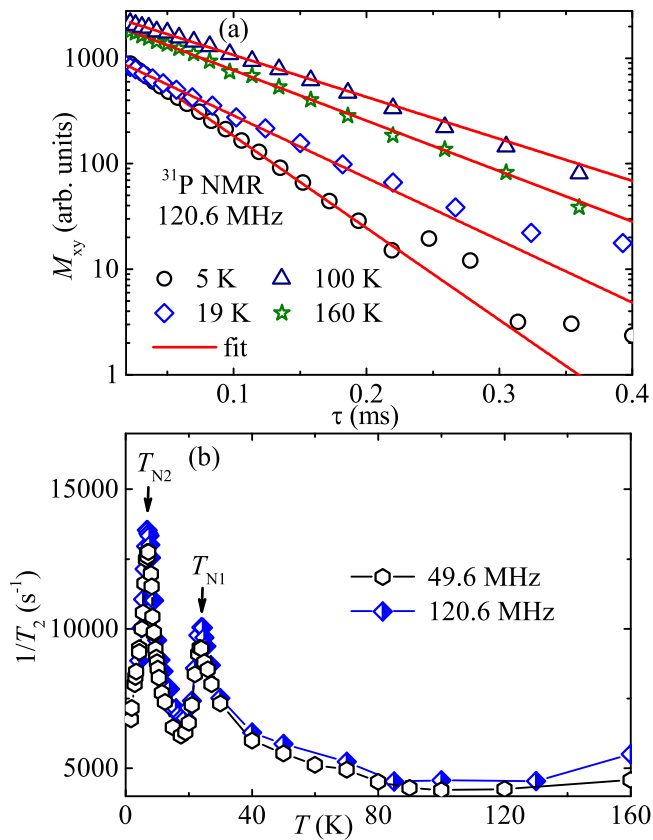


FIG. 10. (a) Transverse magnetization recovery curves as a function of τ at four different temperatures. The solid lines show the fit using Eq. (7). (b) ^{31}P NMR spin-spin relaxation rate ($1/T_2$) vs T measured in 49.6 MHz and 120.6 MHz. The downward arrows mark the transition temperatures at $T_{N1} \simeq 23.5$ K and $T_{N2} \simeq 9.5$ K.

exchange couplings as well as the value of T_N increase systematically as the halide ion is changed from Cl to I in the order of increasing ionic radius [27]. The obtained values of θ_{CW} and T_N for RCCPO are comparable to that of the analogue compound CCCVO, resulting almost identical frustration parameter ($f \simeq 8$ for RCCPO, $f \simeq 7.7$ for CCCVO). A recent theoretical work has shown that the replacement of V^{5+} by P^{5+} in CCCVO where the ionic radius of P^{5+} is two times smaller than that of V^{5+} , the coupling within the kagome layer remains almost same whereas the coupling between kagome layer and capped Cu atom becomes five times larger, increasing the degree of frustration within OCu_4 tetrahedra [24]. In this analogy, RCCPO should have a larger θ_{CW} value than CCCVO because of the replacement of V^{5+} by P^{5+} . Here, another difference is that RCCPO contains Rb^+ that has smaller ionic radius than Cs^+ in CCCVO, which possibly plays a crucial role due to which the overall energy scale of the exchange couplings is comparable.

In contrast to a single magnetic transition in all phosphate compounds [$(\text{CsCl}, \text{CsBr}, \text{CsI})\text{Cu}_5\text{P}_2\text{O}_{10}$], there appears two magnetic transitions ($T_{N1} \simeq 20$ K and $T_{N2} \simeq$

7 K) in RCCPO at low temperatures which makes this compound an exception in this series. It is to be noted that, despite same crystal structure (monoclinic), their space group symmetry is found to be different ($C2/c$ for RCCPO and $P2_1/c$ for the other phosphates). The OCu_4 tetrahedra in RCCPO is highly distorted compared to the other phosphates. In RCCPO, each tetrahedron consists of three in-equivalent Cu sites in contrast to two Cu sites in other phosphates. A diligent scrutiny of the crystal structure [see Fig. 1(c), (d), and (e)] reveals that Cu-Cu bond distances and $\angle \text{Cu} - \text{O} - \text{Cu}$ bond angles in the triangular base of the tetrahedron are inequivalent for RCCPO in contrast to the equilateral triangular base in other phosphates. Similarly, the Cu-Cu bond distances and $\angle \text{Cu} - \text{O} - \text{Cu}$ bond angles of the apical (or capped) Cu with respect to the Cu atoms at the base are all in-equivalent for RCCPO in contrast to other phosphates. Moreover, the six Cu-Cu bond distances in the hexagonal ring [Fig. 1(c)] are also found to be unequal and varies from 3.065 to 3.225 Å for RCCPO while this hexagon is isotropic with same bond distance for all other phosphates. Thus, the strong distortion in the crystal structure could be the reason for having different ground state properties in RCCPO.

Double magnetic transitions are predicted to occur in anisotropic triangular lattice antiferromagnets (TLAFs) when the magnetic anisotropy is of easy-axis type [44, 53–55]. On lowering the temperature, the collinear up-up-down state appears before 120° state and the temperature range of the intermediate phase $(T_{N1} - T_{N2})/T_{N1}$ reflects the relative strength of easy-axis anisotropy with respect to the isotropic intralayer coupling. Experimentally, double transitions are reported in several TLAFs [56–59]. Double magnetic transitions in zero-field are also observed in staircase-kagome magnets $(\text{Mn}, \text{Ni}, \text{Co})_3\text{V}_2\text{O}_8$ and $\text{PbCu}_3\text{TeO}_7$ [14, 15, 60, 61]. In $(\text{Mn}, \text{Ni}, \text{Co})_3\text{V}_2\text{O}_8$, both the phases are reported to be incommensurate in nature, originating from two decoupled sub-lattices in the kagome staircase structure [62]. However, in RCCPO, the two transitions are different. Our ^{31}P NMR spectral measurements elucidate probably an incommensurate-type phase below T_{N1} and a commensurate phase below T_{N2} . Since the capped-kagome structure is a corner sharing of triangular motifs, the observed two successive transitions can possibly be attributed to anisotropy in the compound. However, a more precise knowledge about nature and origin of the transitions can only be obtained from neutron scattering experiments and complementary theoretical calculations.

In summary, we present the structural and magnetic properties of a geometrically frustrated quantum magnet $(\text{RbCl})\text{Cu}_5\text{P}_2\text{O}_{10}$. Below $T_t \simeq 310$ K, the monoclinic structure portrays a capped kagome lattice of Cu^{2+} ions. Sizable magnetic frustration is gauged from a large value of frustration parameter. The dual magnetic transitions at low temperatures where a commensurate AFM ordering preceded by an incommensurate ordering in a capped kagome lattice is unusual and can possibly be ascribed to

strong distortion and/or magnetic anisotropy in the spin-lattice. Nevertheless, these ambiguous features call for further experimental investigations on this compound.

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