Realising square and diamond lattice $S = 1/2$ Heisenberg antiferromagnet models in the $\alpha$ and $\beta$ phases of the coordination framework, KTi($C_2O_4)_2\cdot xH_2O$

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We report the crystal structures and magnetic properties of two pseudo-polymorphs of the $S = 1/2$ Ti$^{3+}$ coordination framework, KTi($C_2O_4)_2\cdot xH_2O$. Single-crystal X-ray and powder neutron diffraction measurements on $\alpha$-KTi($C_2O_4)_2\cdot xH_2O$ confirm its structure in the tetragonal $I4/mcm$ space group with a square planar arrangement of Ti$^{3+}$ ions. Magnetometry and specific heat measurements reveal weak antiferromagnetic interactions, with $J_1 \approx 7$ K and $J_2/J_1 = 0.11$ indicating a slight frustration of nearest- and next-nearest-neighbor interactions. Below 1.8 K, $\alpha$-KTi($C_2O_4)_2\cdot xH_2O$ undergoes a transition to G-type antiferromagnetic order with magnetic moments aligned along the c axis of the tetragonal structure. The estimated ordered moment of Ti$^{3+}$ in $\alpha$-KTi($C_2O_4)_2\cdot xH_2O$ is suppressed from its spin-only value to 0.62(3) $\mu_B$, thus verifying the two-dimensional nature of the magnetic interactions within the system. $\beta$-KTi($C_2O_4)_2\cdot 2H_2O$, on the other hand, realises a three-dimensional diamond-like magnetic network of Ti$^{3+}$ moments within a hexagonal $P6_22$ structure. An antiferromagnetic exchange coupling of $J \approx 54$ K—an order of magnitude larger than in $\alpha$-KTi($C_2O_4)_2\cdot xH_2O$—is extracted from magnetometry and specific heat data. $\beta$-KTi($C_2O_4)_2\cdot 2H_2O$ undergoes Néel ordering at $T_N = 28$ K, with the magnetic moments aligned within the ab plane and a slightly reduced ordered moment of 0.79 $\mu_B$ per Ti$^{3+}$. Through density-functional theory calculations, we address the origin of the large difference in the exchange parameters between the $\alpha$ and $\beta$ pseudo-polymorphs. Given their observed magnetic behaviors, we propose $\alpha$-KTi($C_2O_4)_2\cdot xH_2O$ and $\beta$-KTi($C_2O_4)_2\cdot 2H_2O$ as close to ideal model $S = 1/2$ Heisenberg square and diamond lattice antiferromagnets, respectively.

I. INTRODUCTION

The discovery of new magnetic materials allows for the realization of theoretical ground state predictions as well as the identification of novel emergent phenomena. Both rely on a fine balance between several material “ingredients” that determine the magnetic properties, including exchange frustration[1], low-dimensionality[2], and spin-orbit coupling[3]. Systems based on the $S = 1/2$ Heisenberg frustrated square lattice (FSL) model, for example, are extensively studied as they provide a rich magnetic phase diagram depending on the degree of frustration between exchange interactions along the sides, $J_1$, and across the diagonal, $J_2$, of the square net. For the antiferromagnetic phase diagram[4], theoretical predictions for the development of Néel and columnar antiferromagnetic orders within the respective dominant $J_1$ or $J_2$ regimes have been experimentally established in several materials[5][13]. Intriguingly, at the border of these two regimes, materials in which the degree of frustration is maximized—i.e. $0.4 < J_2/J_1 < 0.6$—are predicted to map a region of the phase diagram within which a quantum spin liquid (QSL) ground state is realized[14][16]. Indeed, in a recent theoretical and experimental investigation of the solid-solution, Sr$_2$Cu(Te$_{1-x}$W$_x$)$_2$O$_6$ where $x = 0$ and $x = 1$ represent Néel and columnar ordered systems, respectively, QSL signatures have been observed for the $x = 0.5$ compound[17]. Interestingly, the behavior exhibited by complex materials derived from the FSL, such as BaCdVO(PO$_4$)$_2$[16], where signatures of a spin-nematic ground state have been observed in an applied field[18][19], has further enriched the phase diagram of FSL materials, leading to new theoretical predictions[20]. By extending the $J_1 - J_2$ model to incorporate the effects of interplanar coupling, $J_3$, magnetic ground states inaccessible to the pure FSL model can also be realised[21].

While often sought within manifestations of low-dimensional models, the three-dimensional diamond lattice offers an alternative route towards unconventional magnetic ground states. Recent investigations of $A$-site spinels have revived interest in the Heisenberg frustrated diamond lattice (FDL) model following the experimental
observation of spin-spiral structures\textsuperscript{22} and spin-liquid regimes\textsuperscript{23, 24}. As such structures indicate exchange competition, this behavior can be ascribed to the presence of a frustrated further-neighbor coupling, $J_2$, beyond the nearest-neighbor interaction, $J_1$. Beyond the theoretically predicted critical point at $J_2/J_1 > 0.125$, a set of degenerate spin-spiral states were found to describe a novel spin-liquid regime\textsuperscript{25}. Signatures of this dynamic behavior have been observed in material realizations of the $J_1$-$J_2$ FDL model, such as in MnSe\textsubscript{2}S\textsubscript{4}\textsuperscript{24} and CoAl\textsubscript{2}O\textsubscript{4}\textsuperscript{26}, where theory combined with experimental diffuse neutron scattering studies conclude the presence of a continuous spin-spiral surface in momentum space\textsuperscript{23, 24}. Perturbations further enrich the magnetism of such FDL systems, and spin-orbit coupling\textsuperscript{27, 29}, further-neighbor couplings, and structural distortions\textsuperscript{22} can play a significant role in determining the magnetic ground state.

In this vein, alternative chemical realizations of highly sought magnetic models can be achieved through the synthesis of coordination framework materials. When compared to their inorganic counterparts, the versatility of possible organic linkers in coordination frameworks offers a wider command over the dimensionality and magnetic properties of the magnetic sublattice\textsuperscript{30, 31}. Indeed, a range of architectures, ranging from the star lattice\textsuperscript{32}, to square\textsuperscript{33} and diamond networks\textsuperscript{34} have been prepared in coordination frameworks.

Motivated by the richness of intriguing behavior exhibited within the FDL and FSL models, we here explore a Ti\textsuperscript{3+}-based coordination framework realization of a diamond lattice, $\beta$-KTi(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}2H\textsubscript{2}O ($\beta$), in addition to identifying its previously predicted\textsuperscript{35} square planar network pseudo-polymorph, $\alpha$-KTi(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}xH\textsubscript{2}O ($\alpha$). We report the crystal structures, thermodynamic properties, and magnetic structures of both pseudo-polymorphs using a combination of single-crystal X-ray diffraction, powder neutron diffraction, magnetic susceptibility, specific heat measurements, and \textit{ab initio} calculations. Beginning with Section II, we present our synthetic route for micro- and polycrystalline samples and summarize our experimental methods. In Sec. III, we identify the crystal structure of $\alpha$ and provide evidence for the quasi-two-dimensional behavior of this non-stoichiometric hydrate. This is followed by a discussion of our structural and magnetic investigation of $\beta$ in Sec. IV. A discussion of the electronic structure calculations, single-ion properties, and exchange pathways of both compounds ensues in Sec. V. Finally, we conclude in Sec. VI and provide an outlook for future experiments.

II. EXPERIMENTAL METHODS

Polycrystalline samples of $\alpha$ and $\beta$ were synthesized hydrothermally according to modified versions of previously published methods\textsuperscript{36, 37}. In a typical synthesis of either sample, an aqueous solution of K\textsubscript{2}CO\textsubscript{3} (Sigma Aldrich 99.99\%) and H\textsubscript{2}CO\textsubscript{3}·2H\textsubscript{2}O (Sigma Aldrich > 99.5\%) was prepared in a round bottom flask and heated to 343 K ($\alpha$) or 363 K ($\beta$) under constant stirring. After 1 hour of sparging with N\textsubscript{2} gas, TiCl\textsubscript{3} (Sigma Aldrich ≥ 12\% TiCl\textsubscript{3} basis) was introduced to the solution, and either an orange or a maroon colored precipitate immediately formed for $\alpha$ and $\beta$, respectively. The reaction proceeded for 30 minutes, after which the round bottom flask was quenched in an ice bath. The resulting product was collected by filtration and washed with acetone. The molar ratios of K\textsubscript{2}CO\textsubscript{3}, H\textsubscript{2}CO\textsubscript{3}·2H\textsubscript{2}O, TiCl\textsubscript{3}, and H\textsubscript{2}O used were 1 : 3 : 5 : 277 and 2 : 6 : 1 : 1000 for $\alpha$ and $\beta$, respectively. It should be noted that the $\beta$ phase appears to be more thermodynamically stable as if not immediately collected from solution, samples of $\alpha$ slowly recrystallize into $\beta$. Deuterated samples of $\alpha$-KTi(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·xD\textsubscript{2}O were synthesized using D\textsubscript{2}O. Deuteration of $\beta$ was not achieved. While products are air-stable for short periods (≈ 1 day), handling in an inert environment is necessary to avoid H-D exchange.

Single-crystal X-ray diffraction (SC-XRD) measure-
ments were performed at 150 K using a Bruker D8 VEN- TURE diffractometer equipped with a PHOTON-II de-
tector and a Mo Kα source with λ = 0.71073 Å using ω scans. The reduction and integration of the collected
data were performed using the APEX III software pack-
age. Structure solutions were obtained using direct meth-
ods by utilizing SHELXT-2013 [38] followed by refinements
ting use SHELXL-2013 [39] on the OLEX2 software with multi-
scan absorption correction. Non-hydrogen atoms were
modeled with anisotropic displacement parameters.

Powder neutron diffraction (PND) data [40] were col-
clected on the time-of-flight High-Resolution Powder
Diffractometer (HRPD) [41] at the ISIS Neutron and
Muon Source. Vanadium-windowed flat plate sample
containers were used, and measurements were carried out
on 2 g samples of each compound at 1.8 K and 300 K. All
three fixed angle detector banks (centered around 165°,
90°, and 30°) were used for the nuclear structural re-
finement. To probe the magnetic structures of α and β,
PND data [42] were collected for the same 2 g samples
using the long wavelength WISH diffractometer [43]
at the ISIS Neutron and Muon Source. Cylindrical va-
dium containers were used, and measurements were car-
rried out at 1.2 K, 2 K, 3 K, 4 K, 6 K, and 15 K for α
and at 1.2 K and 35 K for β. Rietveld refinements of
the nuclear and magnetic structures were conducted on
the GSAS [44, 45] and FULLPROF [46] software packages, re-
spectively. Instrumental impurity phases (i.e. steel and
vanadium) were modeled using the Le Bail method.

Temperature-dependent DC magnetic susceptibility
data were measured on 13.21 mg (α) and 38.09 mg (β)
samples using both field cooled and zero-field cooled pro-
tocols in a 0.1 T applied field between 1.8 K and 300 K
using a Quantum Design MPMS 3 SQUID magnetome-
ter. Specific heat data were recorded in a temperature
range of 1.8 K to 300 K in zero-field on a Quantum De-
sign PPMS DynaCool using 9.11 mg and 6.71 mg pressed
powder samples of α and β, respectively.

Quantum Monte Carlo (QMC) simulations were per-
formed using the directed loop (loop) [47, 48] algorithm
of the ALPS [49, 50] simulation package. The tempera-
ture dependence of the magnetic susceptibility and spe-
cific heat were calculated for a 60 × 60 square lattice
model (2 × 60² spins) with 10⁵ thermalization and sweep
steps. The high-temperature-series expansion (HTE) of
the S = 1/2 FSL and FDL models were calculated using
the [4,6] Pade approximants derived from the HTE10 [51]
code.

Fully relativistic density-functional theory (DFT)
band-structure calculations were performed in the FPLO
code [52] using Perdew-Wang approximation for the
exchange-correlation potential [53]. States near the Fermi
level were used to construct Wannier functions, ana-
lyze their composition, and calculate hopping param-
eters tᵢ that determine the antiferromagnetic superex-
change Jᵢ = 4tᵢ²/U, where U is the on-site Coulomb re-
pulsion parameter. A well-converged k-mesh with 242
irreducible k-points for the α and 168 k-points for the

FIG. 2. (a) The crystal structure of α-KTi(C₂O₄)₂·xH₂O
as viewed along the [111] direction where the (b) oxalate-
bridged square antiprismatic Ti³⁺ ions form square planar
sheets within the ab plane separated by a disordered layer
of orange K⁺ ions and water molecules which are omitted for
clarity. (c) G-type antiferromagnetic ordering of the magnetic
moments obtained from the analysis of PND data at 1.2 K,
where the orange Ti³⁺ magnetic moments lie along the crys-
tallographic c axis with nearest-neighbor (J₁), next-nearest-
neighbour (J₂), and interplanar (J₃) exchange interactions
highlighted in black, blue, and gray, respectively. Both struc-
tures were generated using the VESTA [55] visualization soft-
ware.
III. RESULTS FOR $\alpha$-KTi(C$_2$O$_4$)$_2$$ \cdot $xH$_2$O

A. Crystal Structure

Analysis of SC-XRD data collected at 150 K reveals that diffraction patterns of $\alpha$ can be indexed by the tetragonal space group $I4/mcm$. The refined parameters within this model are presented in Table I. Through a multibank Rietveld analysis of PND data collected for a deuterated sample of $\alpha$ on HRPD, the $I4/mcm$ model was verified at both 1.8 K and 300 K. A single deuterium site was located on a Fourier difference map, at a location similar to that obtained from SC-XRD, and refined according to an O-D bond distance restraint (0.97(3) Å). The refinement was initially carried out with the occupancy of the water site fixed to 0.5, as obtained from SC-XRD, to represent a dihydrate, yielding $\chi^2 = 7.23$ and $R_p = 3.45\%$. A significant improvement to the fit [Fig. 2(a)] is obtained, however, when the occupancy of the water site is varied resulting in $\chi^2 = 4.80$ and $R_p = 2.83\%$. The refinement converges to a non-stoichiometric hydrate occupancy of $x = 5.57(1)$, as obtained from SC-XRD, to represent $\alpha$-KTi(C$_2$O$_4$)$_2$$ \cdot $1.48(4)D$_2$O, with the rest of the refinement parameters presented in Table II.

The resulting crystal structure is consistent with that predicted by Drew et al. and is illustrated in Fig. 2(a). It is composed of two-dimensional layers of oxalate-bridged square antiprismatic Ti$^{3+}$ ions separated by a disordered layer of K$^+$ ions and water molecules along the $c$ axis with an interplanar Ti-Ti distance of 7.36(1) Å. Each square antiprism is coordinated by four oxalate molecules in the $ab$ plane [Fig. 2(b)] which results in a square planar arrangement with nearest-neighbor Ti-Ti superexchange, $J_1$ [Fig. 2(c)] mediated via the Ti-O-C-O-Ti pathway at a distance of 5.69(1) Å. The next-nearest-neighbor coupling, $J_2$ [Fig. 2(c)], runs along the (010) directions at a Ti-Ti distance of 8.05(1) Å.

B. Magnetic Susceptibility and Specific Heat

The temperature dependencies of the molar magnetic susceptibility, $\chi_m$, the inverse molar susceptibility, $\chi_m^{-1}$, and the zero-field specific heat, $C_p$, of $\alpha$ are shown in Fig. 3. At 280 K, a broad feature is observed in the derivatives of both $\chi_m$ and $C_p$ [Fig. S2]. Given its small amplitude and the porosity of the square network of $\alpha$, we ascribe this feature to the freezing of the lattice water position. A similar feature has been observed in the specific heat data of (CH$_3$NH$_3$)$_2$NaTi$_2$F$_{12}$ which has been attributed to the ordering of the methyammonium groups. Above 50 K, $\chi_m$ is well described by a modified Curie-Weiss (CW) law, $\chi_m(T) = C/(T - \theta_{CW}) + \chi_0$, where $C = N_s \mu^2/3k_B$ and $\theta_{CW}$ are the Curie and Weiss constants, respectively, and $\chi_0$ is a temperature independent background term. Relatively weak antiferromagnetic interactions are suggested as $\chi_m$ is consistently best described by $\theta_{CW} = -7.86(1)$ K. We also find a positive $\chi_0 = 1.19(2) \times 10^{-4}$ emu mol$^{-1}$, as seen in other Ti$^{3+}$-containing compounds which may be ascribed to a van Vleck contribution to the susceptibility. The fitted Curie constant, $C = 0.233(1)$ emu K mol$^{-1}$, reveals a reduced effective magnetic moment, $\mu_{eff} = 1.36(1) \mu_B$ ($g = 1.57(1)$), in comparison to the $S = 1/2$ spin-only moment, $\mu_{eff} = 1.73 \mu_B$. As discussed in Sec. V, although a reduction of the effective moment in Ti$^{3+}$-containing compounds is usually a consequence of an orbital contribution, this picture is probably not applicable for $\alpha$. Instead, considering the instability of Ti$^{3+}$ in air, it may reflect the presence of a minor impurity phase, for example an oxidized surface layer of the polycrystalline sample, or a data normalization problem arising from the non-stoichiometry of $\alpha$. Indeed, this is not uncommon for Ti$^{3+}$-containing compounds, where a similar reduction in $g$, unassociated with an orbital contribution, is observed for both KTi(SO$_4$)$_2$ and KTi(SO$_4$)$_2$$ \cdot $H$_2$O. Finally, it should be noted that the possible pres-
en of a magnetic ion deficiency was examined by allowing a free occupancy refinement of the Ti$^{3+}$ and K$^+$ sites in the models considered using both the PND and SC-XRD data. While it cannot be conclusively disregarded, it is highly unlikely that a deficiency exists as the resulting goodness-of-fit parameters worsen ($\chi^2 = 7.13$ and $R_p = 3.23\%$), and only models with instead an insignificant Ti$^{3+}$ excess of 1.4(1.3)% were extracted.

Upon cooling, the build up of short-range antiferromagnetic correlations is evidenced by a broad maximum in $\chi_m$ centered around 6.1 K. This signature is also observed in the specific heat at a slightly lower temperature, as is typical for low-dimensional square lattice systems[8]. No features indicative of long-range magnetic order can be observed in either data-set down to 1.8 K. Because of the non-stoichiometric nature of $\alpha$, the values of the molar susceptibility and specific heat should be treated as approximate, and have been calculated with respect to the hydration of the deuterated sample obtained from the HRPD refinement.

To estimate the magnitude of the leading magnetic exchange parameter in $\alpha$, $J_1$, a QMC simulation was performed for the Heisenberg $S = 1/2$ square lattice model using the ALPS[49, 60] simulation package. By approximating the phonon contribution to the specific heat using $C_p = \alpha T^3 + \beta T^5 + \gamma T^7$, as done with other coordination frameworks[63, 65], a simultaneous fit to $\chi_m$ and $C_p$ above 5 K yields $J_1 = 6.42(1)$ K ($g = 1.53(1)$) when $\chi_0$ is fixed to its CW fit value. Given that the QMC method is not generally applicable to frustrated systems, the HTE10 code[51] was used to calculate the [4,6] Padé approximant of the high-temperature-series expansion of a $S = 1/2$ FSL model, with two in-plane exchange interactions, $J_1$ and $J_2$, and an interplanar coupling, $J_3$ [Fig. 2(c)]. Using a similar simultaneous fitting procedure above 7 K, the magnetic susceptibility and specific heat data were best described by a slightly frustrated system ($J_2/J_1 = 0.11$) with $J_1 = 6.80(1)$ K ($g = 1.61$) and no interplanar coupling. The fitting parameters were $J_1$ and the coefficients of the phonon contribution, while $J_2$ and $J_3$ were varied in 0.01 K steps between $-0.2 J_1$ and 0.3$J_1$, and $\chi_0$ was fixed to its CW fit value. The absence of significant interplanar coupling, $J_3/J_1 < 1.9 \times 10^{-3}$, is further implied by applying the empirical formula $T_N = (4\pi p_s)/(b - \ln(J_3/J_1))$[66] for $T_N < 1.8$ K (see Sec. IV C). Finally, as discussed in the methodology of the DFT calculations (Sec. III) where a similar magnetic behavior is observed regardless of the model used to describe structural disorder, the extent of hydration and disorder in the potassium and water containing layers separating the [Ti(C$_2$O$_4$)$_2$]$^-$ planes indeed appear to be consequential to the magnetism of the ti-

| Compound          | $\alpha$-KTi(C$_2$O$_4$)$_2$·xH$_2$O | $\beta$-KTi(C$_2$O$_4$)$_2$·2H$_2$O |
|-------------------|--------------------------------------|-----------------------------------|
| Formula weight/g mol$^{-1}$ | 299.03                               | 299.03                            |
| Temperature / K    | 150                                  | 150                               |
| Crystal system     | Tetragonal                           | Hexagonal                         |
| Space group        | I4/mcm                               | P6$_3$22 (or P6$_4$22)            |
| $\alpha$ / Å       | 8.040(4)                             | 8.7926(4)                        |
| $\beta$ / Å        | 8.040(4)                             | 8.7926(4)                        |
| $c$ / Å            | 14.8504(13)                          | 11.1247(5)                       |
| $\alpha$ / °       | 90                                   | 90                                |
| $\beta$ / °        | 90                                   | 90                                |
| $\gamma$ / °       | 90                                   | 120                               |
| $V$ / Å$^3$         | 959.98(13)                           | 744.82(8)                        |
| $Z$                | 8                                    | 3                                 |
| Crystal size / mm$^3$ | 0.07 × 0.07 × 0.03                    | 0.12 × 0.06 × 0.05               |
| Color              | Orange                               | Maroon                           |
| $\rho$ / g cm$^{-3}$ | 2.069                                | 2.000                             |
| $F(000)$           | 596.0                                | 447.0                            |
| Reflections collected | 3279                             | 5932                             |
| Independent reflections | 287 [R$_{int} = 0.0614, R_p = 0.0252] | 512 [R$_{int} = 0.0432, R_p = 0.0186] |
| Goodness-of-fit on $F^2$ | 1.091                                    | 1.087                             |
| Final R indexes [I>=2$\sigma$(I)] | $R_1 = 0.0453, wR_2 = 0.1112$ | $R_1 = 0.0214, wR_2 = 0.0509$ |
tanium oxalate containing layers, as similar CW, QMC, and HTE parameters were extracted when fitting $\chi_m$ of another $\alpha$ sample [Fig. S2].

At first glance, the solution extracted from the HTE fit is more consistent with the expected $\theta_{CW} = (J_1 + J_2)/k_B = 7.55(2)$ K for a FSL system than the QMC fit. This is further corroborated when considering the residual plots of both fits, as the HTE model better describes the experimental data over the whole fitting range [Fig. S4]. Our DFT calculations furthermore estimate that Ti-Ti exchanges beyond the nearest-neighbor positions of the $I4/mcm$ space group [Fig. 4(b)] and were thus indexed by the commensurate propagation vector $k = (0, 0, 0)$. To determine the magnetic structure, four irreducible representations—$m \Gamma_{3-}$, $m \Gamma_{3+}$, $m \Gamma_{5+}$, and $m \Gamma_{5-}$ in Miller-Love notation [67]—were found to be compatible with the paramagnetic space group and propagation vector using the BasIreps[60] and MAXMAG[68] software packages. Of these, $m \Gamma_{3+}$ and $m \Gamma_{5+}$ correspond to ferromagnetic structures, and are therefore incompatible with the magnetic susceptibility of $\alpha$. Indeed, by refining the nuclear structural model to data collected at 15 K ($R_p = 5.24\%$, $\text{Occ}_{\text{D}_2\text{O}} = 0.40(2)$) and fixing the resulting structural and instrumental parameters for the magnetic model refinement, only the magnetic space group $I4/mcm$ (in Belov-Neronova-Smirnova notation [69]) belonging to $m \Gamma_{3-}$, correctly describes the data ($\chi^2 = 1.82$, $R_{mag} = 3.16\%$) [Fig. 4(b)]. Comparative Rietveld plots for the other possible models are presented in Fig. S5.

The resulting magnetic structure is shown in Fig. 2(c) and can be described as a G-type antiferromagnet with the magnetic moments aligned along the $c$ axis. The two-dimensional character of $\alpha$-KTi$(\text{C}_2\text{O}_4)_2\cdot2\text{D}_2\text{O}$ is corroborated by the observed ordered moment $\mu = 0.62(3) \mu_B$ per Ti$^{3+}$ extracted from the Rietveld fit, similar to other square network systems [5, 70, 71], and to the expected ordered moment of $0.6 \mu_B$ for a $S = 1/2$ square lattice antiferromagnet [72]. The discrepancy between the value extracted from the fit to PND data and the expected $gS\mu_B = 0.81 \mu_B$ extracted from the HTE fit is most likely associated with data renormalization issues as discussed in Sec. IV B. Also, given that the exact Néel temperature is unknown, thermal effects, resulting in the reduction of the ordered moment, cannot be excluded as the origin of the moment reduction.

IV. RESULTS FOR $\beta$-KTi$(\text{C}_2\text{O}_4)_2\cdot2\text{H}_2\text{O}$

A. Crystal Structure

A chiral hexagonal $P6_222$ crystal structure of $\beta$ was determined through the analysis of SC-XRD data collected at 150 K, as summarised in Table. I. This is consistent with the reported structure of the related $\beta$-NH$_4$Ti$(\text{C}_2\text{O}_4)_2\cdot2\text{H}_2\text{O}$, whereby the chirality of the crystal structure is such that both enantiomers, $P6_222$ [67] and $P6_122$ [75], are reported depending on the particular single crystal studied. A multi-band refinement of this model to PND data collected on HRPD further confirms this structure at all measured temperatures [Fig. 4(a)] and gives an overall $\chi^2 = 3.06$ and $R_p = 1.81\%$ at 1.8 K with the model shown in Table. III. Because of the chirality of the crystal structure of $\beta$, standard powder diffraction measurements cannot distinguish between the enantiomers as polycrystalline samples are most likely comprised of a racemic mixture of the enantiomorph space group pair [76]. As illustrated in Fig. S5(a), the crystal structure of $\beta$ forms a three-dimensional diamond-like network of Ti$^{3+}$ ions in a distorted square antiprismatic configuration linked by oxalate groups [Fig. 3(b)]. The distortion arises from the presence of two oxalate oxygen sites, giving rise to four Ti-O1 and two Ti-O2 bonds with distances of 2.11(3) Å and 2.27(2) Å, respectively. Each oxalate group coordinates two Ti$^{3+}$ ions, thus providing a pathway for nearest-neighbour superexchange, $J_1$, with a Ti-O distance of 5.75(2) Å. Next-nearest-neighbour exchanges $J_2$, $J_3$, and $J_4$ run along the (111), (100), and (010) directions with similar Ti-Ti distances of 8.46(2) Å, 8.63(1) Å, and 8.78(3) Å, respectively [Fig. 3(c)]. Along the $c$ axis, K$^+$ ions and water molecules are packed in a column-like manner within the cavities surrounding the diamond-like sublattice [Fig. S6]. Water molecules are present on the O3 site and form hydrogen bonds with the O2 site of the oxalate groups at a distance of 1.92(2) Å.

B. Magnetic Susceptibility and Specific Heat

The temperature-dependent molar magnetic susceptibility, $\chi_m$, effective magnetic moment, $\mu_{eff}$, and specific heat, $C_p$, of $\beta$ are shown in Fig. 6. Fitting $\chi_m$ over the
temperature range 230 K to 300 K with the same modified CW model as applied to α yields θ_{CW} = −109.6(1) K and C = 0.329(1) emu K mol^{−1} (γ = 1.87). The resulting negative θ_{CW} indicates dominant antiferromagnetic interactions an order of magnitude larger than those of α. A reduced μ_{eff} = 1.62(1) μ_B is calculated from C, which is consistent with a previous report [77], and its deviation from the spin-only moment—combined with the observed temperature dependence of the magnetic moment and relatively large negative θ_{CW}—likely reflects the presence of antiferromagnetic correlations above 200 K. We also find a small and negative χ_0 = −4.88(3) × 10^{−5} emu mol^{−1}, indicating the contribution of the sample holder and core diamagnetism of β to the total magnetic susceptibility. The presence of short-range correlations is evidenced by a broad maximum in χ_m centered about 43 K, followed by an inflection point at 28 K that can be attributed to long-range antiferromagnetic ordering. This ordering transition is also present as an anomaly in C_p at the same temperature [Fig. 6(c)].

To estimate the nearest-neighbor exchange interaction

\[ J_1 = 0.5000 \quad J_2 = 0.0000 \quad J_3 = 0.0000 \]

TABLE III. Crystallographic data for β-KTi(C_2O_4)_2·2H_2O as obtained by fitting the P6_22 model to data collected on HRPD at 1.8 K. The unit cell parameters are \( a = b = 8.784(1) \) Å and \( c = 11.148(2) \) Å and the goodness-of-fit parameters are \( \chi^2 = 3.06 \) and \( R_p = 1.81\% \).

| Atom | Site | x   | y   | z   | U_{iso} (Å^2) |
|------|------|-----|-----|-----|--------------|
| Ti   | 3d   | 0.5000 | 0.0000 | 0.5000 | 0.0012(6)   |
| K    | 3b   | 0.0000 | 0.0000 | 0.5000 | 0.0019(2)   |
| O1   | 12k  | 0.2656(2) | 0.9210(2) | 0.4001(1) | 0.0068(2)   |
| O2   | 12k  | 0.4494(2) | 0.7615(2) | 0.3923(1) | 0.0063(2)   |
| O3   | 6g   | 0.7662(3) | 0.7662(3) | 0.3333 | 0.0093(5)   |
| C1   | 6i   | 0.2094(1) | 0.7906(1) | 0.3333 | 0.0055(5)   |
| C2   | 6i   | 0.3083(1) | 0.6917(1) | 0.3333 | 0.0050(5)   |
| H    | 12k  | 0.7493(5) | 0.6574(4) | 0.3152(3) | 0.0330(8)   |
FIG. 6. (a) Zero-field cooled magnetic susceptibility of β-KTi(C₂O₄)₂·2H₂O, χₘ (blue), of measured between 1.8 K and 300 K in a 0.1 T applied magnetic field and corresponding calculated effective magnetic moment (grey). A Curie-Weiss fit to χₘ (brown) yields θₜ = −109.6(1) K, C = 0.329(2) emu K mol⁻¹, and χ₀ = −4.88(3) × 10⁻⁵ emu mol⁻¹. (b) and (c) Simultaneous fit to χₘ and the zero-field specific heat CₚT⁻¹ using the diamond lattice model with a nearest-neighbor coupling J₁ calculated by a tenth-order high-temperature series expansion. The model yields J = 54.4(1) K and χ₀ = −4.11(8) × 10⁻⁵ emu mol⁻¹.

in β, J₁, the diamond lattice model was used to simultaneously fit χₘ and Cₚ using the same HTE fitting procedure applied for α. Above 60 K, the data were consistently best described by a leading exchange J₁ = 54.4(1) K (g = 1.74) and a temperature independent background term χ₀ = −4.11(8) × 10⁻⁵ emu mol⁻¹, similar to that extracted from the CW fit. Interestingly, the resulting Tₓ/T₁ = 0.51 ratio is similar to the theoretically predicted ratio, Tₓ/T₁ = 0.531(1) [78], expected for a S = 1/2 Heisenberg diamond lattice model system. A frustrated diamond lattice model extended to account for further near-neighbor couplings was also used to simultaneously fit χₘ and Cₚ [Fig. S5]. While the resulting parameters (J₂/J₁ = 0.04, J₃/J₁ = 0.03, J₄/J₁ = 0.04, and g = 1.78) better describe χₘ [Fig. S7], this model should be taken at best as suggestive of frustration given the number of exchange parameters involved. Together with Tₓ, the fitted parameters are broadly consistent with minimal frustration and place β within the Šiěl ordered region of the FDL phase diagram [79].

C. Magnetic Structure

Indeed, the onset of three-dimensional magnetic order in β is verified by the presence of additional intensity in the subtracted PND data (1.2 K − 35 K) [Fig. 4(b)]. The observed magnetic reflections can be indexed by a unit cell doubled along the c axis with the propagation vector k = (0, 0, 1/2). Symmetry analysis using ISODISTORT [80] and SARAH [81] reveal five irreducible representations, mA₁, mA₃, mA₄, mA₅, and mA₆, compatible with k and the nuclear space group, P6₃22 (or P6₃22). However, all magnetic models given by these irreducible representations, except for mA₆, conflict with the presence of (00l)-type reflections in the PND data.

Accordingly, the best description of the data (Rmag = 1.93%, χ² = 3.91), shown in Fig. 4(b), is obtained with the P₆₃2₁ magnetic space group of the mA₆ irreducible representation. The resulting ordered moment, µ = 0.79(2) µₕ, is similar to the theoretically expected value, µ = 0.76 µₕ [78], for the S = 1/2 Heisenberg diamond lattice model, and is slightly suppressed from the expected gSµB = 0.87 µₕ from the susceptibility fits. Interestingly, and in contrast to previous studies on S = 1/2 diamond lattice systems [82, 83], β is the first system in which the ordered moment of the S = 1/2 diamond lattice model can be extracted without any ambiguity related to possible orbital contributions and/or covalency effects. The reasons for this are further discussed in Sec. V. Comparative fits with other possible models are presented in Fig. S8. It should be noted that the magnetic moment direction of the P₆₃2₁ structure in the ab plane cannot be uniquely determined from the present data alone, because the structure factor of the strongest (101) peak at d ~ 7.2 Å is insensitive to the in-plane moment direction. A representative illustration of the magnetic structure, in which nearest-neighbor (J) magnetic moments are antiferromagnetic and align along the ab plane, is therefore shown in Figs. 4(c) and (d). The full determination of the magnetic ground state of β would be challenging even with a deuterated single crystal due to the 12 domains created by the lowering of symmetry from P6₃22₁’ (or P6₃22₁’) to P₆₃2₁. Given that the structure of β is chiral, it should also be noted that the analysis of polycrystalline PND data is insensitive to the enantiomorphic space group pair, and an enantiopure single crystal would be necessary for further analysis.

V. DISCUSSION

One of the most striking observations made in comparing the magnetic properties of α and β is the substantial difference between the magnitudes of their nearest-neighbor exchange interactions. Indeed, the nearest-neighbor exchange parameter, J₁, in the diamond network of Ti³⁺ ions in β is an order of magnitude larger than the corresponding leading exchange for α. To understand the
origin of this behavior, one has to consider the nature of the orbitals involved in the respective superexchange pathways of α and β and how they overlap. For a transition metal ion in the square antiprismatic coordination environment exhibited in α and β, the crystal field symmetry splits the degenerate d-orbitals into a low-lying $A_1$ ($d_{x^2-y^2}$) ground state term and two higher energy levels corresponding to the doubly degenerate $E_g$ and $E_g$ terms\[84\]. In the case of a Ti$^{3+}$ ion in such an environment, the lone 3$d^1$ electron is thus expected to populate the $d_{x^2-y^2}$ orbital within the $A_1$ ground state. Indeed, through our DFT band-structure calculations, we identify $d_{x^2-y^2}$ as the active magnetic orbital for both α and β, even in the presence of the distorted square antiprismatic coordination environment found in the latter, as also observed for β-NH$_4$Ti(C$_2$O$_4$)$_2$·2H$_2$O\[75\].

As described in the context of several other oxalate-based coordination frameworks, the interplay between the architecture of the oxalate-metal bridge and the active magnetic orbital plays a crucial role in determining the sign and strength of the resulting exchange\[85, 86\]. In the case of α, these oxalate bridges lie within the plane of the Ti$^{3+}$ ions, whereas the oxalate bridging in β spans different planes. As illustrated through the calculated Wannier functions in Fig. 7, this leads to a significant superexchange in β, where the $d_{x^2-y^2}$ orbital overlaps directly with the oxalate π-bonding orbital. This results in a contribution to the exchange pathway at the C atoms within the oxalate bridge where the magnetic orbitals of the neighboring Ti$^{3+}$ ions overlap. Conversely, when the active orbital is parallel to the oxalate group—as is more often discussed in the context of a $d_{x^2-y^2}$ active orbital in Cu$^{2+}$-containing compounds—a significantly reduced exchange interaction is expected\[85, 86\]. This appears to be the case for α, in which the Ti$^{3+}$ $d_{x^2-y^2}$ orbital overlaps with a different molecular orbital with minimal contribution at the C atoms, resulting in a reduced overlap with the neighboring Ti$^{3+}$ ion, and thus a weaker superexchange interaction.

While the effect of spin-orbit coupling is expected to be pronounced for octahedrally coordinated Ti$^{3+}$-containing compounds\[87\], our DFT results also reveal a negligible contribution from orbitally excited states for the square antiprismatic coordination of Ti$^{3+}$ in α and β. This is unsurprising given the $d_{x^2}$ ($m_l=0$) ground state. The combination of this result and our experimental observations indicate that α and β should be considered close to ideal model $S=1/2$ Heisenberg square and diamond lattice antiferromagnets, respectively.

Compared with other coordination frameworks, the magnetic response of α resembles that seen in the square lattice antiferromagnet, Cu(pz)$_2$(ClO$_4$)$_2$ (pz = pyrazine), where $J_2/J_1 \approx 0.02$\[87\]. Given the relatively large distances between the magnetic ion centers in such systems, the weak frustration present in both α and Cu(pz)$_2$(ClO$_4$)$_2$ is to be expected. As a consequence, while some advantages are associated with coordination frameworks, especially related to tuning the energy scales present in the system through different bridging molecules, designing frustration into them is more difficult in comparison to their oxide counterparts. This is a result of the complex exchange pathways, which require several sets of orbitals to align favorably to generate an appreciable exchange. As for β, to the best of our knowledge, this is the first comprehensive study of the magnetic properties of a diamond lattice coordination framework, especially one in which the magnetic ion resides in an 8-coordinate environment. However, the extracted nearest-neighbour exchange parameter, $J_1$, is of the same order of magnitude as that of Ti$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_5$ ($J = 86$ K)\[89\], and the magnetic response of β bears resemblance to that of the A-site diamond lattice spinel, CoRh$_2$O$_4$\[22\].

VI. CONCLUSIONS

In summary, we have presented a detailed investigation of the crystallographic and magnetic properties of the Ti$^{3+}$-containing coordination frameworks, α-KTi(C$_2$O$_4$)$_2$·xH$_2$O and β-KTi(C$_2$O$_4$)$_2$·2H$_2$O. Through analysis of SC-XRD and PND data, a quasi-two-dimensional square planar network of Ti$^{3+}$ ions was found within the crystal structure of α, β, on the other hand, realises a three-dimensional diamond-like array of
Ti$^{3+}$ moments. Bulk characterization indicates slight frustration of the antiferromagnetic interactions present in both systems, and simultaneous fits to the magnetic susceptibility and specific heat data demonstrate the two-dimensional character of the magnetic correlations in $\alpha$. Concomitantly, the order of magnitude difference in the extracted exchange parameters manifests the stark differences in the orbital interactions at play in each of the pseudo-polymorphs. Through supporting DFT calculations, these differences can be understood as arising from the different bridging geometries between neighboring Ti$^{3+}$ ions, which result in different orbital overlaps between the $d_{z^2}$-orbitals and the oxalate $\pi$ bonding orbitals. At low temperatures, the onset of long-range antiferromagnetic order was verified for both systems in PND data, with the resulting magnetic structures and ordered ferromagnetic order was verified for both systems in PND at low temperatures, the onset of long-range antiferromagnetic order was verified for both systems in PND.

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