I. INTRODUCTION

Magnetism on diamond-like lattices has been widely studied in both coordination frameworks [1] and ceramic systems, including materials with the scheelite crystal structure such as KRUO₃ [2] and KO₄ [3] as well as cubic spinels AB₂O₄ with a magnetic ion on the A-site [4]. The perfect diamond lattice is bipartite and frustrated, expected to order into a collinear antiferromagnetic ground state. In this study, polycrystalline samples of the fergusonite orthotantalates M-LnTaO₄ (Ln = Nd, Sm, Eu, Tb, Dy, Ho, Er) are synthesized and then characterized using powder diffraction and bulk magnetometry and heat capacity. TbTaO₄ orders antiferromagnetically at 2.25 K into a commensurate magnetic cell with \( \bar{K} = 0 \), magnetic space group 14.77 (P2₁/c) and Tb moments parallel to the a-axis. No magnetic order was observed in the other materials studied, leaving open the possibility of exotic magnetic states at \( T < 2 \) K.

The magnetic Ln³⁺ ions in the fergusonite and scheelite crystal structures form a truncated hyperhoneycomb net that can be labelled as \( \mathcal{H}(−1) \) by analogy with the harmonic honeycomb series \( \mathcal{H}(N) \) [Modic et al., Nat. Commun. 5, 4203 (2014)]. This \( \mathcal{H}(−1) \) magnetic lattice is an elongated form of the diamond lattice and is therefore predicted to host exotic magnetic ground states. In this study, polycrystalline samples of the fergusonite orthotantalates M-LnTaO₄ (\( \mathcal{H}(−1) \)) phases depending on the synthesis conditions. The tantalates have also been proposed as thermal barrier coatings for gas turbines [23]. The niobates and tantalates share two common crystallographic polymorphs: fergusonite (I2/a, monoclinic, M) and scheelite (tetragonal, T) polymorphs of the oxides LnTaO₄ and LnNbO₄, of which the former is the subject of this experimental study.

Rare-earth orthoniobates LnNbO₄ and orthotantalates LnTaO₄ (\( \mathcal{H}(−1) \)) are of wide interest as a result of their luminescent [18, 19], proton-conducting [20], oxide-ion-conducting [21] and dielectric properties [22]. The tantalates have also been proposed as thermal barrier coatings for gas turbines [23]. The niobates and tantalates share two common crystallographic polymorphs: fergusonite (I2/a, monoclinic, M) and scheelite (I4₁/a, tetragonal, T) [24-31]. Additionally, the tantalates may crystallize in different monoclinic and tetragonal (\( M' \), \( T' \)) phases depending on the synthesis conditions. The \( T \) phase has been observed using in situ diffraction experiments, but it rapidly converts to the \( M \) phase upon cooling and cannot be isolated at room temperature. The \( M-T \) transformation temperature occurs at 1325–1410 °C for the tantalates and 500–800 °C for the niobates; within each series this transition temperature increases with decreasing Ln³⁺ radius [32]. The two monoclinic polymorphs of LnTaO₄ are closely related: to change from \( M \) to \( M' \) only involves halving the b-axis and removing the body-centering [27, 33]. The metal-oxygen coordination polyhedra (distorted square antiprisms for Ln³⁺ and distorted octahedra for Ta⁴⁺) are approximately the same in both phases [28]. However, the change of centering means that the \( M \) and \( M' \) structures have significantly different arrangements of the polyhedral building blocks: distinct layers perpendicular to a in the \( M' \) phase, but a different, non-layered arrangement in the \( M \) phase [29] as shown in Fig. 2. The arrangement of lanthanide ions in the \( M \) phase is equivalent to the stretched diamond or \( \mathcal{H}(−1) \) network as discussed earlier.
Numerous diffraction studies have been carried out on the lanthanide niobates and tantalates with both powder and single-crystal samples but found magnetic transitions only below 2 K (i.e. no feature at 25 K in NdNbO₄), again with negative Curie-Weiss temperatures indicating antiferromagnetic interactions. At around the same time Starovoitov et al. independently measured isothermal magnetisation on M-LnNbO₄ with Ln = Nd, Eu, Sm, Gd, Dy, Ho and Yb, finding evidence for single-ion anisotropy in all samples except GdNbO₄, as expected for a f⁷ system with L = 0. Tsunekawa et al. measured the susceptibility of single crystals of selected M-LnNbO₄ (Ln = Nd, Gd, Dy, Ho) and M-LnTaO₄ (Ln = Nd, Ho, Er) in the range 4.2 to 300 K; again θ_{CW} < 0 for all compounds, with no magnetic ordering observed. Deviations from the Curie-Weiss law at low temperatures and a marked anisotropy in the susceptibility were observed in all cases except GdNbO₄; this behaviour was attributed to a crystal field with its principal direction along the c-axis, with the greatest effect occurring for Ln = Nd.

This article reports the bulk magnetic characterisation of eight powder samples in the series M-LnTaO₄, Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er. The compounds with the larger lanthanides Ln = La, Ce and Pr do not form the M structure and were therefore excluded from this study. We confirm the absence of long-range ordering in NdTaO₄, HoTaO₄ and ErTaO₄ above 2 K, extending the range investigated in a previous study. TbTaO₄ was also studied using high-resolution powder neutron diffraction. It exhibits a transition at T = 2.25 K to a commensurate antiferromagnetic structure with k = 0. No magnetic transitions occurred above 2 K for the remaining samples with Ln = Sm, Eu, Gd, Dy. These measurements indicate the presence of magnetic frustration in M-LnTaO₄ and lay the foundations for future investigations, as possible hosts for novel magnetic states as predicted for the H(-1) lattice.
Polycrystalline samples of $M$-$Ln$TaO$_4$ were synthesized according to a ceramic procedure, starting from $Ta_2O_5$ (Alfa Aesar, 99.993 %) and $Ln_2O_3$ ($Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Y$) or $Ta_2O_7$ (Alfa Aesar; all lanthanide oxides ≥ 99.99 %). Lanthanide oxides were dried in air at 800 °C overnight before weighing. For each compound, 1:1 molar amounts of the reagents were ground with an agate pestle and mortar, pressed into a 13 mm pellet and placed in an alumina crucible. Pellets were fired for 3 x 24 h at 1500 °C in air with intermediate regrinding. The exception was ErTaO$_4$, which first formed the $M'$ phase (P2/c) at 1500 °C and required an additional 2 x 24 h at an elevated temperature, 1600 °C, to form solely the desired $M$ phase. Heating and cooling rates were 3 °C per minute.

Powder X-ray diffraction (PXRD) was carried out at room temperature on a Bruker D8 diffractometer (Cu Ka, $\lambda = 1.541$ Å) in the range $10 \leq 2\theta (^\circ) \leq 70$ with a step size of 0.02°, 0.6 seconds per step. Rietveld refinements [13] were carried out using TOPAS [14] with a Chebyshev polynomial background and a modified Thompson-Cox-Hastings pseudo-Voigt peak shape [15]. VESTA [16] was used for crystal structure visualisation and production of figures.

Powder neutron diffraction (PND) was carried out on a 3 g sample of TbTaO$_4$ on the D1B and D2B diffractometers (high intensity and high resolution respectively), ILL, Grenoble, using an Orange cryostat (1.5 ≤ $T(K)$ ≤ 300). Wavelengths were refined to 2.52461(6) Å for D1B and 1.594882(10) Å for D2B. Determination of the magnetic structure was carried out using FULLPROF [17] and TOPAS [14]. The background was modelled with a Chebyshev polynomial and the peak shape modelled with a modified Thompson-Cox-Hastings pseudo-Voigt function with axial divergence asymmetry [15].

DC magnetisation was measured on warming on a Quantum Design MPMS 3 at a field of 500 Oe in the temperature range 2 ≤ $T(K)$ ≤ 300, after cooling from 300 K in zero applied field (ZFC) or 500 Oe applied field (FC). Isothermal magnetisation was measured on a Quantum Design PPMS DynaCool using the ACMS-II option in the field range $\mu_0 H = 0$–9 T. In a low field, up to 500 Oe, the $M(H)$ curve was linear and the susceptibility could therefore be approximated by $\chi(T) = M/H$.

Zero-field heat capacity of TbTaO$_4$ was measured on the PPMS in the range 1.8 ≤ $T(K)$ ≤ 30. The sample was mixed with an equal mass of Ag powder (Alfa Aesar, 99.99 %, –635 mesh) to improve thermal conductivity, then pressed into a 1 mm thick pellet for measurement. Apiezon N grease was used to provide thermal contact between the sample platform and the pellet. Fitting of the relaxation curves was done using the two-tau model. The contribution of Ag to the total heat capacity was subtracted using scaled values from the literature [18]. The TbTaO$_4$ lattice contribution was estimated and subtracted using a Debye model with $\theta_D = 370$ K [19].

### III. RESULTS

#### A. Crystal structure

For $Ln = Nd–Ho & Y$, a small amount, < 5 wt %, of the metastable $M'$-phase (space group P2/c; Fig. 2(b)) was formed in the first heating step but disappeared on further heating. ErTaO$_4$ formed only the $M'$ phase at 1500 °C but formed the desired $M$ phase after heating at 1600 °C. Attempts to produce $M$-YbTaO$_4$ by the same methods were unsuccessful, in agreement with previous authors who found that making this phase requires quenching from high temperature and/or pressure [23, 30]. Synthesis of YbTaO$_4$ by spark plasma sintering (SPS) was attempted as reported in the literature (various experiments with $T \leq 1600$ °C, $p \leq 500$ bar, fast or slow cooling [51]) but was unsuccessful, producing only the $M'$ phase with unreacted Yb$_2$O$_3$ and Ta$_2$O$_5$. It thus appears that the relative stability of $M'$ over $M$ increases across the lanthanide series with decreasing ionic radius, since LuTaO$_4$ also favours the $M'$ phase [23] and the solid solution Y$_{1-\frac{2}{3}}$Yb$_{\frac{2}{3}}$TaO$_4$ favours $M'$ when $x \geq 0.5$ [52].

PXRD and Rietveld refinement indicated that each sample eventually formed a single phase with the monoclinic $M$-$Ln$TaO$_4$ crystal structure, space group $I2/a$, shown in Fig. 2(a). Unit cell dimensions and the $Ln^{3+}$ and Ta$^{5+}$ atomic positions were refined, but the positions of O$^{2-}$ ions were fixed at values taken from neutron diffraction of NdTaO$_4$ [34] because of the low X-ray scattering power of oxygen compared with the heavier metal ions. Refinement of fractional site occupancies with fixed overall stoichiometry indicated that there was no disorder between the $Ln^{3+}$ and Ta$^{5+}$ cations. This result is as expected because 6-coordinate Ta$^{5+}$ is much smaller than any of the 8-coordinate lanthanide ions [53]. Refined unit cell parameters (Supplemental Material) are in good agreement with literature results [23, 25, 31, 34]. A representative Rietveld fit is shown in Fig. 3; fits for the remaining compounds are in the Supplemental Material. The unit cell volume decreased linearly with decreasing lanthanide ionic radius (Fig. 3).

We obtained high-resolution powder neutron diffraction (PND) data for the paramagnetic phase of TbTaO$_4$ at 30 K using the D2B beamline at the ILL [54]. The measurements confirmed that the nuclear structure of TbTaO$_4$ is consistent with previous reports for LnTaO$_4$ compounds [23, 31, 34]. Fig. 5(a) shows a Rietveld refinement of PND data collected at $T = 30$ K with $\lambda \approx 1.59$ Å. Interatomic distances were also obtained. The Ta$^{5+}$ ions are surrounded by four shorter and two longer Ta-O bonds, forming octahedra distorted by a second-order Jahn-Teller effect [31], while the Tb$^{3+}$ ions are 8-coordinate. The refined bond lengths are listed in Table 1.

In addition, we were able to resolve and follow the evolution of the nuclear structure with temperature using PND data collected on the D1B beamline. No phase transitions were observed in the temperature range 3–300 K.
FIG. 3. Room temperature PXRD pattern for NdTaO$_4$: red dots – experimental data; black line – calculated intensities; green line – difference pattern; blue tick marks – Bragg reflection positions.

FIG. 4. Unit cell volumes of $M$-LnTaO$_4$ compounds after PXRD and Rietveld refinement with dashed line of best fit to guide the eye. Error bars are smaller than the datapoints. Ionic radius is for an 8-coordinate ion [53].

TABLE I. Refined interatomic distances for TbTaO$_4$ from PND data collected at 1.59 Å (D2B, ILL).

| Atoms  | Distance /Å | $T = 1.5$ K | $T = 30$ K |
|--------|-------------|-------------|-------------|
| Ta–O(2) | × 2         | 1.877(4)    | 1.871(4)    |
| Ta–O(1) | × 2         | 1.938(4)    | 1.945(3)    |
| Tb–O(2) | × 2         | 2.301(4)    | 2.297(4)    |
| Tb–O(1) | × 2         | 2.314(3)    | 2.311(2)    |

FIG. 5. PND data for TbTaO$_4$ collected at $\lambda = 1.59$ Å on the D2B diffractometer: (a) 30 K, (b) 1.5 K. Red dots – experimental data; black line – calculated intensities; green line – difference pattern; tick marks – nuclear (blue) and magnetic (pink) Bragg reflection positions.

The lattice parameters were constant between 3 and 50 K and then varied smoothly between 50 and 300 K. Small decreases in $a$ and $\beta$ on warming were offset by increases in $b$ and $c$, Fig. S1. There were similar subtle changes to the atomic fractional coordinates between 50 and 300 K (Figs S2 and S3).

B. Bulk magnetic properties

1. Magnetic susceptibility

The zero-field-cooled (ZFC) magnetic susceptibility at 500 Oe for each LnTaO$_4$ compound (Fig. 6) was fitted to the Curie-Weiss law, $\chi = C/(T - \theta_{CW})$. The effective magnetic moment was calculated from the experimental data using $\mu_{eff}/\mu_B = \sqrt{8C}$ and compared to the theoretical paramagnetic moment $g_J \sqrt{J(J + 1)}$. Linear fitting was carried out in both high-temperature and low-temperature regimes to account for different thermal population of excited states at higher temperatures. The results from the two fitting regimes (Table II) are significantly different, indicating that crystal field effects at high temperatures may influence the magnetic correlations and thus the susceptibility. The low-temperature fits are therefore more likely to represent the true properties of these materials [55, 56]. The magnetic moments derived from Curie-Weiss fitting agree well with the expected free-ion moments as well as those obtained by Tsunekawa et al. [41].
No sharp peaks in the susceptibility were observed for any of the eight compounds except TbTaO$_4$ ($T_N = 2.9$ K). Field-cooled (FC) susceptibility at 500 Oe was also measured on TbTaO$_4$ and found to be identical to the ZFC data, suggesting three-dimensional antiferromagnetic ordering without glassiness.

The shape of the EuTaO$_4$ susceptibility curve resembles that of other Eu-containing ceramics and is believed to result from van Vleck paramagnetism, i.e. non-zero occupation of low-lying magnetic excited states $^7$F$_j$ to $^7$F$_{5/2}$ [57–59]. The inverse susceptibility plot is linear at 200–300 K, but applying the Curie-Weiss law produced unrealistically large values of the magnetic moment and Curie-Weiss temperature ($5 \mu_B$ and $-340$ K respectively) as a result of the population of excited states. No fitting was carried out at low temperature as the plot of $\chi^{-1}(T)$ was not linear.

The susceptibility of SmTaO$_4$ at high temperatures shows a large contribution from temperature-independent paramagnetism: both $\chi(T)$ and $\chi^{-1}(T)$ tend to a constant value, without becoming linear. Curie-Weiss fitting was therefore carried out in the low-temperature range only. The calculated effective magnetic moment is $0.72 \mu_B$, slightly lower than the expected free ion value of $0.85 \mu_B$, likely owing to the large crystal field splitting in the $J = 5/2$ ground state multiplet of Sm$^{3+}$ [60, 61]. The negative Curie-Weiss temperature indicates antiferromagnetic interactions between adjacent Sm$^{3+}$ ions, as indeed is the case for all the remaining LnTaO$_4$ samples.

### 2. Isothermal magnetisation

Fig. 7 shows the isothermal magnetisation at 2 K for the LnTaO$_4$ compounds. For the samarium and europium compounds, the magnetisation plots initially curve upwards then become linear above 3 T without saturating. In all other samples the magnetisation, plotted in units of Bohr magnetons per formula unit ($\mu_B$/f.u.), tends towards a saturation value $M_{\text{sat}}$ at high field. The expected value of $M_{\text{sat}}$ depends on both the identity of the lanthanide ion and the extent of single-ion anisotropy – the tendency for a spin to align along a particular local axis or local plane. For example, compounds containing Gd$^{3+}$ typically display Heisenberg-type behaviour with saturation at the maximum value of $g_J J = 7 \mu_B$/f.u., while systems with Ising (easy-axis) or XY (easy-plane) behaviour are expected to saturate around $g_J J/2$ or $2g_J J/3$ respectively. However, individual systems may vary from these values depending on the local symmetry of the lanthanide ion coordination environment [60, 61]. The experimental values of $M_{\text{2K,ST}}$ for each compound and the calculated $g_J J$ for each lanthanide ion are given in Table [11].

The experimental data indicate that the compounds with Ln = Nd, Tb, Dy, Ho and Er all show some degree of local anisotropy; further experiments such as neutron diffraction would be needed to investigate this further. However, neutron absorption would make it difficult to measure the anisotropy in DyTaO$_4$ without an isotopically enriched sample. A previous study on large single crystals of LnTaO$_4$ (Ln = Nd, Ho, Er) also found substantial anisotropy in the magnetic susceptibility measured along the different crystal axes [11]. In that study, the plots of inverse susceptibility along each crystal axis have the same gradient but different $x$-intercepts, i.e. Curie-Weiss temperatures: for example, NdTaO$_4$, which showed the greatest anisotropy, had $\theta_{\text{CW}} = -7$, $-56$ and $-52$ K along the $a$, $b$ and $c$ axes respectively.

### 3. Specific heat

The magnetic heat capacity for TbTaO$_4$ shows a sharp $\lambda$-type transition at $T = 2.25$ K, where there is a corresponding feature in the plot of $d(\chi T)/dT$ [62]. Fig. 8 This provides further evidence for three-dimensional antiferromagnetic ordering as deduced from the susceptibility data. The magnetic entropy associated with the transition was obtained by integration of the heat capacity curve over the full temperature range (1.8–30 K) and found to approach 2 J mol$^{-1}$ K$^{-1}$ (Fig. 8 inset). Since the expected maximum entropy is $R \ln 2 = 5.76$ J mol$^{-1}$ K$^{-1}$ for Ising spins with effective spin of $1/2$, the remaining entropy change is assumed to occur below the lowest temperature measured (1.8 K) which has non-zero $C_{\text{mag}}/T$ and is close to $T_N$.

### C. Magnetic structure of TbTaO$_4$

We obtained high-resolution PND data for the magnetic phase of TbTaO$_4$ at 1.5 K using the D2B beamline at the ILL [54]. Variable-temperature PND was also carried out on the D1B beamline in order to track the evolution of the magnetic structure with temperature. On cooling below $T = 2.3$ K, magnetic Bragg peaks were observed to appear and increase in intensity as the temperature was lowered. No discernible diffuse scattering was observed above this temperature. The magnetic peaks could be indexed to a commensurate magnetic cell with $\bar{k} = 0$ in the magnetic space group 14.77 (P2$_1$/c). Refinement of the magnetic structure using TOPAS (Fig. 7(b)) shows Tb moments parallel to the $a$-axis in $A$-type antiferromagnetic order: the moments coalign within the $ac$ plane, forming ferromagnetic slabs coupled antiferromagnetically along $b$, Fig. 9(a). The structure is similar to that of NaCeO$_2$ which has the same $A$-type order but Ce$^{3+}$ moments aligned along the tetragonal $c$-axis [17]. Further details of the magnetic structure may be found in the Supplemental Material (Table S3).

The refined ordered moment is plotted as a function of temperature in Fig. 10 showing good agreement with the transition temperature found by heat capacity and magnetic susceptibility. At 1.5 K the moment of
TABLE II. Bulk magnetic properties of $M$-$Ln$TaO$_4$, $Ln =$ Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er.

| $Ln$ | $g_J \sqrt{J(J+1)}$ | High $T$ fit (K) | $\mu_{\text{eff}}$ ($\mu_B$) | $\theta_{\text{CW}}$ (K) | Low $T$ fit (K) | $\mu_{\text{eff}}$ ($\mu_B$) | $\theta_{\text{CW}}$ (K) | $g_J$ | $M_{\text{2K,ST}}$ ($\mu_B$/f.u.) |
|------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------|-----------------|
| Nd   | 3.62                | 150–300         | 4.08(8)         | $-71.3(14)$     | 30–50           | 3.27(7)         | $-19.7(4)$      | 3.29 | 1.312(26)       |
| Sm   | 0.85                | N/A             | N/A             | N/A             | 2–8             | 0.724(29)       | $-2.33(19)$     | 0.71  | 0.0749(15)       |
| Eu   | 0                   | N/A             | N/A             | N/A             | N/A             | N/A             | N/A             | N/A  | 0.1037(21)       |
| Gd   | 7.94                | 150–300         | 8.20(16)        | $-6.42(13)$     | 10–50           | 8.09(16)        | $-2.82(6)$      | 7    | 6.88(14)         |
| Tb   | 9.72                | 150–300         | 10.33(21)       | $-12.75(25)$    | 10–50           | 9.92(20)        | $-6.50(13)$     | 9    | 5.48(11)         |
| Dy   | 10.65               | 150–300         | 10.70(21)       | $-6.44(13)$     | 10–50           | 10.57(21)       | $-6.09(12)$     | 10   | 6.00(12)         |
| Ho   | 10.61               | 150–300         | 10.90(22)       | $-14.50(29)$    | 10–50           | 10.70(21)       | $-8.20(16)$     | 10   | 6.72(13)         |
| Er   | 9.58                | 150–300         | 9.95(20)        | $-19.1(4)$      | 10–50           | 9.50(19)        | $-7.03(14)$     | 9    | 5.98(12)         |

FIG. 6. (a) ZFC susceptibility, (b) reciprocal susceptibility $\chi^{-1}$ as a function of temperature for the $Ln$TaO$_4$ samples with $Ln =$ Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er.

$7.5(4) \mu_B$/Tb$^{3+}$ is slightly below the expected value of $9 \mu_B$.

The nearest-neighbor superexchange in TbTaO$_4$ follows Tb–O–Tb pathways. These pathways may be divided into $J_{1a}$ and $J_{1b}$ according to the different Tb–O bond lengths. Figs 9(b) and 9(c) highlight these two interactions: $J_{1a}$ vectors (shorter) in the $ab$ plane and $J_{1b}$ vectors (longer) in the $bc$ plane. In the mean-field approximation, the average exchange interaction $\bar{J}_1$ may be calculated as $\bar{J}_1 = [3k_B\theta_{\text{CW}}]/[2nJ(J+1)]$, where $J$ is the spin quantum number and $n$ the number of nearest-neighbor spins [63]. Using an effective spin of $1/2$ for the Tb$^{3+}$ ion [64] we estimate $\bar{J}_1 \approx 3.3$ K, of the same order as the Néel temperature. However, the mean-field approximation may not be completely valid given the significant single-ion anisotropy observed in $M(H)$ data.
IV. DISCUSSION

We report the magnetic behaviour of a new family of \( \text{Ln}^{3+} \) oxides containing a stretched diamond lattice. Other such materials include the alkali metal-lanthanide oxides \( \text{NaLnO}_2 \) (\( \text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd} \)) and \( \text{LiLnO}_2 \) (\( \text{Ln} = \text{Er}, \text{Yb} \)), which crystallize in the tetragonal space group \( I4_{1}/amd \) [16, 17, 65]. The observation of the stretched diamond lattice in monoclinic \( \text{LnTaO}_4 \) materials provides a new opportunity to study the interplay of the crystal electric field with competing \( J_1 \) and \( J_2 \) magnetic interactions. In particular, while \( \text{TbTaO}_4 \) exhibits long-range \( A \)-type antiferromagnetic order similar to that of \( \text{NaCeO}_2 \) [17], the other materials with \( \text{Ln} = \text{Nd–Er} \) do not order at \( T \geq 2 \) K. The absence of ordering above 2 K, in contrast to e.g. \( \text{NaLnO}_2 \) (Ce, Gd antiferromagnetic; Nd ferromagnetic [65]) suggests the potential for novel magnetic states at low temperature.

We link the stretched diamond lattice to the wider harmonic honeycomb family of magnetic networks [14] by extending the series to \( \mathcal{H}(-1) \). Like the materials in the wider series \( \mathcal{H}(N) \), which include \( \text{YbCl}_3 \) [66] and the \( \beta \) and \( \gamma \) polymorphs of \( \text{Li}_2\text{IrO}_3 \) [15], magnetism on the \( \mathcal{H}(-1) \) lattice is governed by the interplay of nearest-neighbor and next-nearest-neighbor interactions. Describing the stretched diamond lattice as \( \mathcal{H}(-1) \) provides a useful framework to draw parallels between different materials within the harmonic honeycomb series.

There are two parameters which are useful for comparing the level of stretching in different \( \mathcal{H}(-1) \) lattices.
The first is the angle or angles around each lattice vertex. In an ideal cubic diamond lattice, all these angles are equal at 109.5°. When the diamond lattice is distorted, the number of different angles increases: there are two in tetragonal, three in hexagonal, and four in monoclinic symmetry. We compare the average deviation from ideal tetrahedral geometry by defining a parameter $d_a$, the angle distortion index, as follows:

$$d_a = \frac{\phi_{\text{max}} - \phi_{\text{min}}}{\phi}$$  \hspace{1cm} (1)

where $\phi_{\text{max}}$ and $\phi_{\text{min}}$ are the largest and smallest angles respectively, and $\phi$ is the mean angle. Secondly, we define a bond distortion index $d_b$, in a similar way:

$$d_b = \frac{r_2 - r_1}{\frac{1}{2}(r_1 + r_2)}$$  \hspace{1cm} (2)

where $r_1$ and $r_2$ are the two ‘nearest-neighbor’ interaction distances (red and blue in Fig. [1]). These distances are equal in the case of the undistorted (cubic) or the tetragonal or hexagonal stretched diamond lattices, but not in monoclinic materials such as the tantalates. Table III lists the distortion indices for several magnetic materials containing the $\mathcal{H}(-1)$ lattice. Values were calculated using the program VESTA [46] to examine the published crystal structures.

The presence or absence of bond or angular distortion in the $\mathcal{H}(-1)$ lattice thus appears to have no clear impact on the magnetic properties, with ordering of Tb-TaO$_4$ occurring at a similar temperature to NaNdO$_2$ and NaGdO$_2$ despite the higher symmetry of NaLnO$_2$. The absence of long-range order for the other LnTaO$_4$ compounds further demonstrates the non-trivial role of distortion in the low-temperature magnetic properties of the $\mathcal{H}(-1)$ harmonic honeycombs.

Finally, we note that LaTaO$_4$, while not forming the fergusonite structure type, nonetheless displays rich structural phase behaviour including an incommensurate–commensurate phase transition at 483 K coinciding with a dielectric anomaly [71, 72]. Dias et al. have made comparative dielectric measurements on LaTaO$_4$ ($P2_1/c$), NdTaO$_4$ ($I2/a$), and DyTaO$_4$ and LuTaO$_4$ ($P2_1/a$). Despite the differences in structure, the dielectric constants of the Nd, Dy and Lu tantalates are $\leq 25$% smaller than that of LaTaO$_4$ and still within the range of useful microwave materials [73]. Considering that Nd$^{3+}$ and Dy$^{3+}$ have non-zero magnetic moments, there is a possibility of coupling between magnetic and electric properties which should be investigated in these and the other magnetic tantalates.

**V. CONCLUSIONS**

Polycrystalline samples of LnTaO$_4$ ($Ln = $ Nd, Sm–Er, Y) in the monoclinic $M$, or fergusonite, structure type have been synthesized using a ceramic procedure. The trivalent lanthanide ions in the crystal structure form a three-dimensional net equivalent to an elongated or ‘stretched’ diamond lattice. This lattice can also be considered a truncated form of the hyperhoneycomb lattice $\mathcal{H}(0)$, part of the harmonic honeycomb series, and is therefore denoted $\mathcal{H}(-1)$. Bulk magnetic characterisation of the tantalate samples confirms a previous literature result for $Ln =$ Nd, Ho, Er, and reveals that the remaining compounds do not order above 2 K with the exception of TbTaO$_4$, which has $T_N = 2.25$ K. High-resolution PND was used to examine the paramagnetic and magnetic phases of TbTaO$_4$, revealing that it forms a commensurate $k=0$ magnetic unit cell. The Tb moments lie parallel to the $a$-axis in $A$-type antiferromagnetic order. Future work will include specific heat measurements at $T < 2$ K in order to search for further magnetic transitions and investigate the magnetic ground states of the remaining tantalates.

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TABLE III. Distortion indices and magnetic behaviour of materials with the stretched diamond lattice.

| Crystal symmetry | Formula | Space group | $d_a$ (%) | $d_b$ (%) | $T_N$ (K) | Magnetic structure         |
|------------------|---------|-------------|-----------|-----------|-----------|---------------------------|
| Cubic            | CoRh$_2$O$_4$ [7] | Fd$ar{3}$m | 0         | 0         | 25        | Néel AFM $\parallel$ (100) |
|                  | MnAl$_2$O$_4$ [4]   | Fd$ar{3}$m | 0         | 0         | 40        | Canted AFM                |
|                  | FeAl$_2$O$_4$ [4]   | Fd$ar{3}$m | 0         | 0         | 12        | Spin glass                |
|                  | CoAl$_2$O$_4$ [4]   | Fd$ar{3}$m | 0         | 0         | 4.8       | Spin glass                |
|                  | CuAl$_2$O$_4$ [67]  | Fd$ar{3}$m | 0         | 0         | <0.4      | No long range order        |
|                  | FeSc$_2$S$_4$ [68]  | Fd$ar{3}$m | 0         | 0         | <0.05     | Spin-orbital liquid        |
|                  | MnSc$_2$S$_4$ [69]  | Fd$ar{3}$m | 0         | 0         | 2.3, 1.9  | Long-range spiral order    |
| Tetragonal        | CuRh$_2$O$_4$ [7]   | I$_4$/amd   | 7         | 0         | 24        | Incommensurate helical order |
|                  | NiRh$_2$O$_4$ [63]  | I$_4$/amd   | 3         | 0         | <0.1      | No long range order        |
|                  | NaCeO$_3$ [70]      | I$_4$/amd   | 42        | 0         | 3.18      | Néel AFM $\parallel$ c    |
|                  | NaNdO$_3$ [65]       | I$_4$/amd   | 41        | 0         | 2.4       | FM                        |
|                  | NaGdO$_3$ [63]       | I$_4$/amd   | 40        | 0         | 2.4       | AFM                       |
|                  | LiYbO$_3$ [61]       | I$_4$/amd   | 41        | 0         | 0.45      | Incommensurate helical order |
|                  | KRuO$_4$ [72]        | I$_4$/a     | 42        | 0         | 22.4      | Néel AFM $\parallel$ c    |
|                  | KOsO$_4$ [61]        | I$_4$/a     | 39        | 0         | 35        | Néel AFM $\parallel$ c    |
| Hexagonal         | $\beta$-KTi(C$_2$O$_4$)$_2$·2H$_2$O [1] | P6$_2$22   | 34        | 0         | 28        | Coplanar AFM              |
| Monoclinic        | NdTaO$_4$           | I$_2$/a     | 42        | 2.9       | <2        | No long range order        |
|                  | GdTaO$_4$           | I$_2$/a     | 41        | 2.6       | <2        | No long range order        |
|                  | TbTaO$_4$           | I$_2$/a     | 41        | 2.2       | 2.25      | Néel AFM $\parallel$ a    |
|                  | DyTaO$_4$           | I$_2$/a     | 41        | 4.1       | <2        | No long range order        |
|                  | HoTaO$_4$           | I$_2$/a     | 41        | 4.1       | <2        | No long range order        |
|                  | ErTaO$_4$           | I$_2$/a     | 41        | 3.9       | <2        | No long range order        |
|                  | NdNbO$_4$ [65, 68]   | I$_2$/a     | 40        | 1.1       | <1        | No long range order        |
|                  | GdNbO$_4$ [68, 69]   | I$_2$/a     | 39        | 0.7       | 1.67      | AFM                       |
|                  | TbNbO$_4$ [68, 68]   | I$_2$/a     | 39        | 1.0       | 1.82      | AFM                       |
|                  | DyNbO$_4$ [68, 68]   | I$_2$/a     | 39        | 0.3       | 1.6       | AFM                       |
|                  | HoNbO$_4$ [65, 68]   | I$_2$/a     | 39        | 1.1       | <1        | No long range order        |
|                  | ErNbO$_4$ [68, 68]   | I$_2$/a     | 38        | 0.6       | <1.3      | No long range order        |
|                  | YbNbO$_4$ [65, 68]   | I$_2$/a     | 38        | 1.2       | <1.3      | No long range order        |
|                  | Pr(BO$_2$)$_3$ [70]  | C2/c        | 61        | 12.1      | –         | Singlet ground state      |
|                  | Nd(BO$_2$)$_3$ [70]  | C2/c        | 61        | 12.0      | <0.4      | No long range order        |
|                  | Gd(BO$_2$)$_3$ [70]  | C2/c        | 64        | 12.6      | 1.1       | AFM                       |
|                  | Tb(BO$_2$)$_3$ [70]  | C2/c        | 66        | 13.1      | 1.95, 1.05| Undetermined              |

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[1] A. H. Abdeldaim, T. Li, L. Farrar, A. A. Tsirlin, W. Yao, A. S. Gibbs, P. Manuel, P. Lightfoot, G. J. Nilsen, and L. Clark, Realising square and diamond lattice $S = 1/2$ Heisenberg antiferromagnet models in the $\alpha$ and $\beta$ phases of the coordination framework, KTi(C$_2$O$_4$)$_2$·2H$_2$O, Phys. Rev. Mater. 4, 104414 (2020).

[2] C. A. Marjerrison, C. Mauws, A. Z. Sharma, C. R. Wiebe, S. Derakhshan, C. Boyer, B. D. Gaulin, and J. E. Greedan, Structure and Magnetic Properties of KRuO$_4$, Inorg. Chem. 55, 12897 (2016).

[3] S. Injac, A. K. L. Yuen, B. J. Kennedy, M. Avdeev, and F. Orlandi, Structural and magnetic studies of KO$_x$O$_4$, a 5$d^1$ quantum magnet oxide, Phys. Chem. Chem. Phys. 21, 7261 (2019).

[4] N. Tristan, J. Hemberger, A. Krimmel, H. A. Krug Von Nidda, V. Tsurkan, and A. Loidl, Geometric frustration in the cubic spinels MAl$_2$O$_4$ ($M$=Co, Fe, and Mn), Phys. Rev. B 72, 174404 (2005).

[5] G. Chen, L. Balents, and A. P. Schnyder, Spin-Orbital Singlet and Quantum Critical Point on the Diamond Lattice: FeSc$_2$S$_4$, Phys. Rev. Lett. 102, 096406 (2009).
[37] P. F. Y. Wang and R. L. Gravel, Magnetic and Electrical Properties of NdNbO₄ and GdNbO₄, Phys. Status Solidi 12, 609 (1965).

[38] J. D. Cashion, A. H. Cooke, M. J. M. Leask, T. L. Thorp, and M. R. Wells, Crystal growth and magnetic susceptibility of some rare-earth compounds - Part 2 Magnetic Susceptibility Measurements on a Number of Rare-Earth Compounds, J. Mater. Sci. 3, 402 (1968).

[39] A. T. Starovoitov, V. I. Ozhogin, and V. A. Bokov, The Study of the Magnetic Properties of Several Rare-Earth Niobates in Strong Pulsed Fields, Phys. Status Solidi 32, 151 (1969).

[40] S. Tsuchikawa, H. Yamauchi, Y. Yamaguchi, and T. Fukuda, Paramagnetic properties of ferroelastic rare earth orthoniobates, J. Alloys Compd. 192, 108 (1993).

[41] S. Tsuchikawa, H. Yamauchi, K. Sasaki, Y. Yamaguchi, and T. Fukuda, Paramagnetic anisotropies in RTaO₄ (R = Nd, Ho and Er) crystals, J. Alloys Compd. 245, 89 (1996).

[42] R. J. Cava and R. S. Roth, The structure of LaTaO₄ at 300°C by neutron powder profile analysis, J. Solid State Chem. 36, 139 (1981).

[43] H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2, 65 (1969).

[44] A. A. Coelho, TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++, J. Appl. Crystallogr. 51, 210 (2018).

[45] R. A. Young, ed., The Rietveld Method (Oxford University Press, 1993).

[46] K. Momma and F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44, 1272 (2011).

[47] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Phys. B 192, 55 (1993).

[48] D. Smith and F. Fickett, Low-Temperature Properties of Silver, J. Res. Natl. Inst. Stand. Technol. 100, 119 (1995).

[49] E. S. R. Gopal, Specif. Heats Low Temp. (Springer US, Boston, MA, 1966).

[50] V. Y. Markiv, N. M. Belyavina, M. V. Markiv, Y. Titov, A. M. Sych, A. N. Sokolov, A. A. Kapshuk, and M. S. Sobolyanuk, Peculiarities of polymorphic transformations in YbTaO₄ and crystal structure of its modifications, J. Alloys Compd. 346, 263 (2002).

[51] P. Wu, Y. Zhou, F. Wu, M. Hu, X. Chong, and J. Feng, Theoretical and experimental investigations of mechanical properties for polymorphous YTaO₄ ceramics, J. Am. Ceram. Soc. 102, 7656 (2019).

[52] P. Wu, X. Chong, F. Wu, M. Hu, H. Guo, and J. Feng, Investigation of the thermophysical properties of (Y₁₋ₓYbₓ)TaO₄ ceramics, J. Eur. Ceram. Soc. 40, 3111 (2020).

[53] R. D. Shannon, Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides, Acta Crystallogr. A32, 751 (1976).

[54] N. D. Kelly, C. V. Colin, S. E. Dutton, V. Nassif, I. Puente Orench, and E. Suard, Nuclear and magnetic diffraction study of monoclinic TbTaO₄, Inst. Laue-Langevin 10.5291/ILL-DATA.5-31-2854 (2021).

[55] M. B. Sanders, F. A. Cevallos, and R. J. Cava, Magnetism in the KBaRE(BO₄)₂ (RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) series: Materials with a triangular rare earth lattice, Mater. Res. Express 4, 036102 (2017).

[56] S. Guo, T. Kong, W. Xie, L. Nguyen, K. Stolze, F. A. Cevallos, and R. J. Cava, Triangular Rare-Earth Lattice Materials RbBaR(BO₄)₂ (R = Y, Gd–Yb) and Comparison to the KBaR(BO₄)₂ Analogs, Inorg. Chem. 58, 3308 (2019).

[57] H. Nishimine, M. Wakeshima, and Y. Hinatsu, Structures, magnetic, and thermal properties of LnₓMoO₄ (Ln=La, Pr, Nd, Sm, and Eu), J. Solid State Chem. 178, 1221 (2005).

[58] B. Vijaya Kumar, R. Velchuri, V. Rama Devi, B. Sreedhar, G. Prasad, D. Jaya Prakash, M. Kanagaraj, S. Arumugam, and M. Vithal, Preparation, characterization, magnetic susceptibility (Eu, Gd and Sm) and XPS studies of LnₓZrTiO₄ (Ln=La, Eu, Dy and Gd), J. Solid State Chem. 184, 264 (2011).

[59] M. B. Sanders, J. W. Krizan, and R. J. Cava, RₓE₂BₓZn₂O₁₄ (RE = La, Pr, Nd, Sm, and Eu): A new family of pyrochlore derivatives with rare earth ions on a 2D Kagome lattice, J. Mater. Chem. C 4, 541 (2016).

[60] S. T. Bramwell, M. N. Field, M. J. Harris, and T. P. Parkin, Bulk magnetization of the heavy rare earth titanates pyrochlores - A series of model frustrated magnets, J. Phys. Condens. Matter 12, 483 (2000).

[61] R. J. C. Dixey and P. J. Saines, Optimization of the Magnetoelastic Effect in Low Applied Magnetic Fields in LnOOCO₃ Frameworks, Inorg. Chem. 57, 12543 (2018).

[62] M. E. Fisher, Relation between the specific heat and susceptibility of an antiferromagnet, Philos. Mag. 7, 1731 (1962).

[63] A. P. Ramirez, Strongly geometrically frustrated magnets, Annu. Rev. Mater. Sci. 24, 453 (1994).

[64] P. Mukherjee, A. C. Sackville Hamilton, H. F. J. Glass, and S. E. Dutton, Sensitivity of magnetic properties to chemical pressure in lanthanide garnets LnₓA₁₋ₓX₁₋ₓO₁₂, Ln = Gd, Tb, Dy, Ho, A = Ga, Sc, In, Te, X = Ga, Al, Li, J. Phys. Condens. Matter 29, 405808 (2017).

[65] Y. Hashimoto, M. Wakeshima, and Y. Hinatsu, Magnetic properties of ternary sodium oxides NaLnO₂ (Ln=rare earths), J. Solid State Chem. 176, 266 (2003).

[66] G. Sala, M. B. Stone, B. K. Rai, A. F. May, D. S. Parker, G. B. Halázs, Y. Q. Cheng, G. Ehlers, V. O. Garlea, Q. Zhang, M. D. Lumsden, and A. D. Christianson, Crystal field splitting, local anisotropy, and low-energy excitations in the quantum magnet YbCl₃, Phys. Rev. B 100, 180406(R) (2019).

[67] H. Cho, R. Nirmala, J. Jeong, P. J. Baker, H. Takeda, N. Mera, S. J. Blundell, M. Takigawa, D. T. Adroja, and J.-G. Park, Dynamic spin fluctuations in the frustrated A-site spinel Cu₃Al₂O₆, Phys. Rev. B 102, 014439 (2020).

[68] V. Fritsch, J. Hemberger, N. Böttgen, E. W. Scheidt, H. A. Krug Von Nidda, A. Loidl, and V. Tsurkan, Spin and Orbital Frustration in MnSc₂₋ₓSₓ (0 ≤ x ≤ 1), Phys. Rev. Lett. 92, 116401 (2004).

[69] V. K. Trunov and L. N. Kinzhibalo, Change of LnNbO₄ (Ln=Nd, Ho and Er, Tm, Yb, Lu) series: Materials with a triangular rare earth lattice, Mater. Res. Express 4, 036102 (2017).

[70] P. Mukherjee, E. Suard, and S. E. Dutton, Magnetic properties of monoclinic lanthanide metabolates, Ln(BO₄)₂, Ln = Pr, Nd, Gd, Tb, J. Phys. Condens. Matter 29, 405807 (2017).
[71] G. W. Howieson, S. Wu, A. S. Gibbs, W. Zhou, J. F. Scott, and F. D. Morrison, Incommensurate–Commensurate Transition in the Geometric Ferroelectric LaTaO$_4$, [Adv. Funct. Mater. 30, 1 (2020)]

[72] G. W. Howieson, K. K. Mishra, A. S. Gibbs, R. S. Katiyar, J. F. Scott, F. D. Morrison, and M. Carpenter, Structural phase transitions in the geometric ferroelectric LaTaO$_4$, [Phys. Rev. B 103, 014119 (2021)]

[73] A. Dias, K. P. F. Siqueira, and R. L. Moreira, Micro far-infrared dielectric response of lanthanide orthotantalates for applications in microwave circuitry, [J. Alloys Compd. 693, 1243 (2017)]