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Magnetic properties of monoclinic lanthanide metaborates, $Ln(BO_2)_3$, $Ln = Pr, Nd, Gd, Tb$

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Abstract

The bulk magnetic properties of the lanthanide metaborates, $Ln(BO_2)_3$, $Ln = Pr, Nd, Gd, Tb$ are studied using magnetic susceptibility, heat capacity and isothermal magnetisation measurements. They are found to crystallise in a monoclinic structure containing chains of magnetic Ln^{3+} and could therefore exhibit features of low-dimensional magnetism and frustration. $Pr(BO_2)_3$ is found to have a non-magnetic singlet ground state. No magnetic ordering is observed down to 0.4 K for $Nd(BO_2)_3$. $Gd(BO_2)_3$ exhibits a sharp magnetic transition at 1.1 K, corresponding to 3D magnetic ordering. $Tb(BO_2)_3$ shows two magnetic ordering features at 1.05 K and 1.95 K. A magnetisation plateau at a third of the saturation magnetisation is seen at 2 K for both $Nd(BO_2)_3$ and $Tb(BO_2)_3$, which persists in an applied field of 14 T. This is proposed to be a signature of quasi 1D behaviour in $Nd(BO_2)_3$ and $Tb(BO_2)_3$.

Keywords: lanthanide metaborate, monoclinic, quasi-1D, magnetic properties

Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic materials exhibiting geometrical frustration or low-dimensional behaviour have attracted widespread interest due to the unique magnetic properties observed such as the spin ice state in $Ln_2Ti_2O_7$ ($Ln = Dy, Ho$) [1], dispersionless spin wave excitations in $Gd_3Ga_5O_{12}$ [2], order–order transition in $Ca_3Co_2O_6$ [3] and quantum critical points (QCPs) in $CoNb_2O_6$ [4] and $LiCuSbO_4$ [5]. The lattice geometry prevents all the magnetic interactions from being satisfied simultaneously in frustrated systems which suppresses, or in the ideal case, completely inhibits magnetic long-range ordering. Ideal 1D magnetic systems also have no long-range order but in bulk materials, inter-chain coupling often leads to complete 3D magnetic ordering. However, such quasi 1D systems still exhibit properties characteristic of 1D magnetism such as magnetisation plateaux and metamagnetism. If the quasi 1D

materials are in turn frustrated, exotic magnetic behaviour has been predicted [6–10].

1D materials containing magnetic lanthanide (Ln^{3+}) ions are uncommon; one family of compounds which have recently garnered interest are the lanthanide formates, $Ln(HCOO)_3$. In these compounds, the magnetic Ln^{3+} form 1D chains which are arranged on a triangular lattice. Powder neutron diffraction (PND) experiments on $Tb(HCOO)_3$ indicate development of magnetic order at 1.6 K. This has been ascribed to 1D ferromagnetic order along the chains, analogous to the triangular Ising antiferromagnet state. The direction of chain magnetisation is reported to alternate between neighbouring chains, however the variation is frustrated, inhibiting 3D magnetic ordering [11, 12].

Lanthanide metaborates, $Ln(BO_2)_3$, have been well-studied for their applications in phosphors [13–15], however their bulk magnetic properties have not been investigated. They



Table 1. Room temperature (RT) crystal structure parameters for monoclinic $Ln(BO_2)_3$ —space group $C2/c$.

Ln		Pr	Nd	Gd ^a	Tb
a (Å)		6.412 49 (3)	6.370 43 (6)	6.251 59 (5)	6.217 81 (5)
b (Å)		8.098 27 (6)	8.079 75 (9)	8.026 02 (9)	8.025 64 (6)
c (Å)		7.907 30 (5)	7.886 32 (9)	7.826 49 (8)	7.806 59 (4)
β (Å)		93.7129 (5)	93.6935 (7)	93.6292 (8)	93.3723 (4)
Volume (Å ³)		409.765 (5)	405.078 (7)	391.909 (7)	388.889 (6)
χ^2		5.71	5.00	4.05	3.51
R_{wp}		3.58	3.32	5.72	2.66
Ln : $4e$ (0, y , $\frac{1}{4}$)	y	0.0501 (2)	0.0499 (2)	0.0464 (2)	0.04500 (13)
	B_{iso} (Å ²)	0.61 (5)	1.55 (3)	0.5 ^b	0.76 (5)
$B1$: $4e$ (0, y , $\frac{1}{4}$)	y	0.4714 (4)	0.4699 (5)	0.4590 ^b	0.4728 (4)
	B_{iso} (Å ²)	0.41 (4)	0.53 (8)	0.5 ^b	1.37 (8)
$B2$: $8f$ (x , y , z)	x	0.1074 (2)	0.1066 (5)	0.09800 ^b	0.1095 (2)
	y	0.3166 (2)	0.3164 (3)	0.32600 ^b	0.3137 (2)
	z	0.5249 (2)	0.5256 (4)	0.52100 ^b	0.5248 (2)
	B_{iso} (Å ²)	0.18 (2)	0.23 (5)	0.5 ^b	0.14 (2)
$O1$: $8f$ (x , y , z)	x	0.1414 (2)	0.1430 (5)	0.15045 ^b	0.1493 (3)
	y	0.3629 (2)	0.3605 (4)	0.36671 ^b	0.3621 (2)
	z	0.3578 (2)	0.3571 (4)	0.35116 ^b	0.3553 (2)
	B_{iso} (Å ²)	0.52 (3)	0.58 (5)	0.5 ^b	0.97 (3)
$O2$: $8f$ (x , y , z)	x	0.1395 (3)	0.1407 (5)	0.14316 ^b	0.1455 (2)
	y	0.4368 (2)	0.4362 (4)	0.43845 ^b	0.4351 (3)
	z	0.6479 (3)	0.6480 (4)	0.64816 ^b	0.6508 (3)
	B_{iso} (Å ²)	0.70 (3)	0.47 (5)	0.5 ^b	0.75 (5)
$O3$: $8f$ (x , y , z)	x	0.0479 (3)	0.0491 (5)	0.05526 ^b	0.0522 (4)
	y	0.1617 (3)	0.1601 (5)	0.17006 ^b	0.1582 (4)
	z	0.5472 (3)	0.5476 (5)	0.55122 ^b	0.5434 (4)
	B_{iso} (Å ²)	0.18 (2)	0.93 (7)	0.5 ^b	1.30 (7)
$LnBO_3$ wt%		1.3 (4)	1.8 (4)	0.4 (5)	1.8 (3)
H_3BO_3 wt%		0.56 (14)	1.82 (17)	— ^c	0.90 (14)
$Ln-O1$ (Å)		2.602 (3) $\times$ 2	2.580 (4) $\times$ 2	2.472 (9) $\times$ 2	2.489 (4) $\times$ 2
		2.801 (3) $\times$ 2	2.781 (4) $\times$ 2	2.832 (9) $\times$ 2	2.815 (4) $\times$ 2
$Ln-O2$ (Å)		2.568 (3) $\times$ 2	2.548 (4) $\times$ 2	2.477 (9) $\times$ 2	2.457 (6) $\times$ 2
$Ln-O3$ (Å)		2.383 (4) $\times$ 2	2.364 (5) $\times$ 2	2.373 (10) $\times$ 2	2.330 (4) $\times$ 2
		2.520 (4) $\times$ 2	2.510 (4) $\times$ 2	2.561 (10) $\times$ 2	2.467 (4) $\times$ 2
$\langle Ln-O \rangle$ (Å)		2.575	2.557	2.543	2.512

^aParameters determined from PXRD only.^bNot refined, positions taken from previous structural report [24].^cCould not be obtained from PXRD.

crystallise in two structures depending on the radius of the Ln^{3+} ion—an ambient pressure monoclinic structure for $Ln = La-Tb$ and an orthorhombic structure for $Ln = Tb-Er$ which are synthesised at high pressures [16–19]. Inspection of the reported crystal structure reveals that the magnetic Ln^{3+} form chains in the monoclinic structure. Lanthanide metaborates, $Ln(BO_2)_3$, could therefore be a new example of a Ln^{3+} quasi-1D magnetic system.

Here we report on the synthesis, characterisation and bulk magnetic properties of monoclinic $Ln(BO_2)_3$ ($Ln = Pr, Nd, Gd, Tb$). To our knowledge, this is the first report on the bulk magnetic properties of these materials. A broad feature at 5 K is observed in the magnetic susceptibility and heat capacity (HC) for $Pr(BO_2)_3$, and no magnetic scattering is observed in low temperature neutron diffraction, indicative of a nonmagnetic singlet ground state. Within the limits of our experiments ($T \geq 0.4$ K), no ordering is observed for $Nd(BO_2)_3$, whereas a

sharp magnetic transition is observed for $Gd(BO_2)_3$ at 1.1 K and $Tb(BO_2)_3$ shows two sharp ordering features at 1.05 K and 1.95 K. Both $Nd(BO_2)_3$ and $Tb(BO_2)_3$ show magnetisation plateaus at a third of the saturation magnetisation at 2 K which persist in a field of 14 T. The magnetic properties are discussed in the context of 1D magnetism and frustration.

2. Experimental section

Samples of $Ln(BO_2)_3$ ($Ln = Pr, Nd, Gd, Tb$) have been prepared by solid state synthesis. Samples were prepared by mixing stoichiometric amounts of Ln_2O_3 ($Ln = Nd, Gd$) (99.999% Alfa Aesar), Pr_6O_{11} (99.999% Alfa Aesar), or Tb_4O_7 (99.999% Alfa Aesar) with H_3BO_3 (99.99% Alfa Aesar). A 50% excess of H_3BO_3 was added to compensate for the loss of B due to volatilisation during heating. Ln_2O_3 ($Ln = Nd, Gd$) and Pr_6O_{11} were pre-dried at 800 °C prior to being weighed

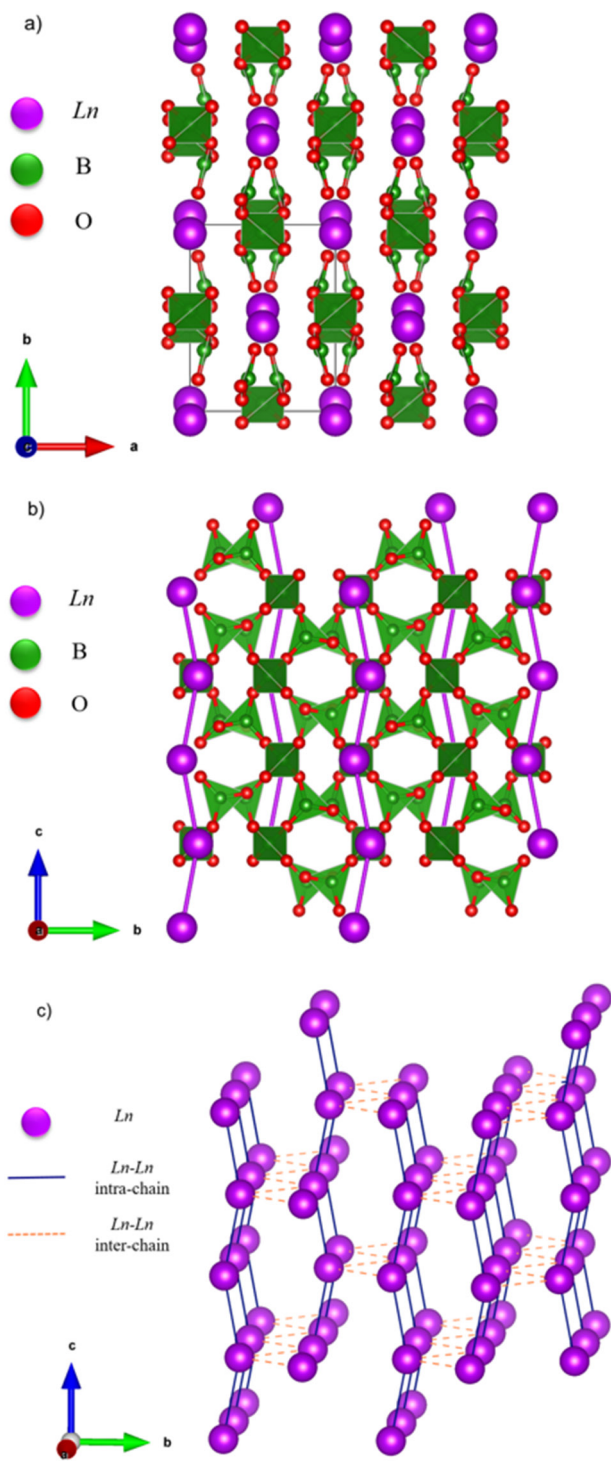


Figure 1. General crystal structure for monoclinic $\text{Ln}(\text{BO}_2)_3$ —(a) ribbons of borate groups consisting of $(\text{BO}_4)^{5-}$ tetrahedra and $(\text{BO}_3)^{3-}$ triangles propagate along the c axis (b) magnetic Ln^{3+} form 1D chains between the ribbons (c) if inter-chain dipolar interactions are considered along with intra-chain interactions, the magnetic Ln^{3+} form a distorted honeycomb lattice in three dimensions

out to ensure the correct stoichiometry. A pre-reaction was carried out at 350 °C for 2 h to allow for decomposition of H_3BO_3 . After regrinding, samples were heated between 800 °C

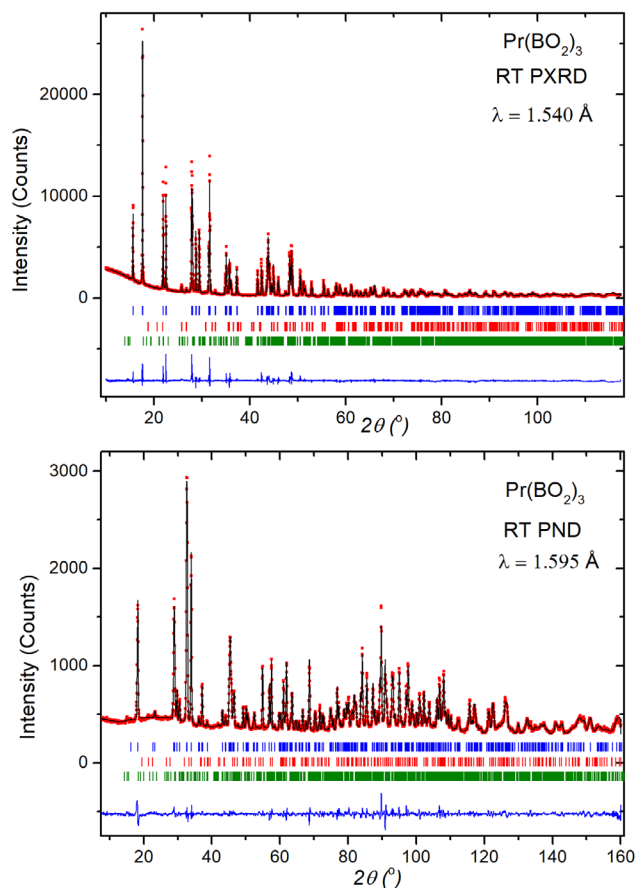


Figure 2. RT PXRD (upper) and PND (lower) patterns for $\text{Pr}(\text{BO}_2)_3$: experimental data (red dots), modelled data (black line), difference pattern (blue line), Bragg positions: (blue ticks)— $\text{Pr}(\text{BO}_2)_3$, (red ticks)— PrBO_3 , (green ticks)— H_3BO_3 .

and 900 °C for a period of 48–192 h with intermediate regrindings to obtain the final product.

Powder x-ray diffraction (PXRD) was used to confirm formation of the desired products. Short scans were collected over $10^\circ \leq 2\theta \leq 60^\circ$ ($\Delta 2\theta = 0.015^\circ$) using a Bruker D8 x-ray diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.540 \text{ \AA}$). For more quantitative analysis, longer scans for 2 h over a wide angular range $10^\circ \leq 2\theta \leq 90^\circ$ ($\Delta 2\theta = 0.01^\circ$) were collected. Low temperature PXRD data over the same angular range was collected for $\text{Pr}(\text{BO}_2)_3$ at 12 K using an Oxford Cryosystems Phenix stage.

For $\text{Ln}(\text{BO}_2)_3$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Tb}$), room temperature (RT) PND experiments for structural characterisation were carried out on the D2B diffractometer at ILL, Grenoble ($\lambda = 1.595 \text{ \AA}$). Samples for the PND experiments were synthesised by the same method as described above but enriched boric acid (^{11}B) (99% purity, Sigma Aldrich) was used to reduce the absorption from ^{10}B . Additional PND measurements were carried out for $\text{Pr}(\text{BO}_2)_3$ at 3.5 K and 12 K on D2B to investigate any structural transition. Low temperature PND measurements, $T \geq 1.5 \text{ K}$, were carried out on $\text{Pr}(\text{BO}_2)_3$ on the D1B diffractometer at ILL, Grenoble ($\lambda = 2.525 \text{ \AA}$) to investigate the existence of any magnetic ordering. PXRD and PND Rietveld refinements were carried out using the Fullprof suite of programs [20]. The background was modelled using linear

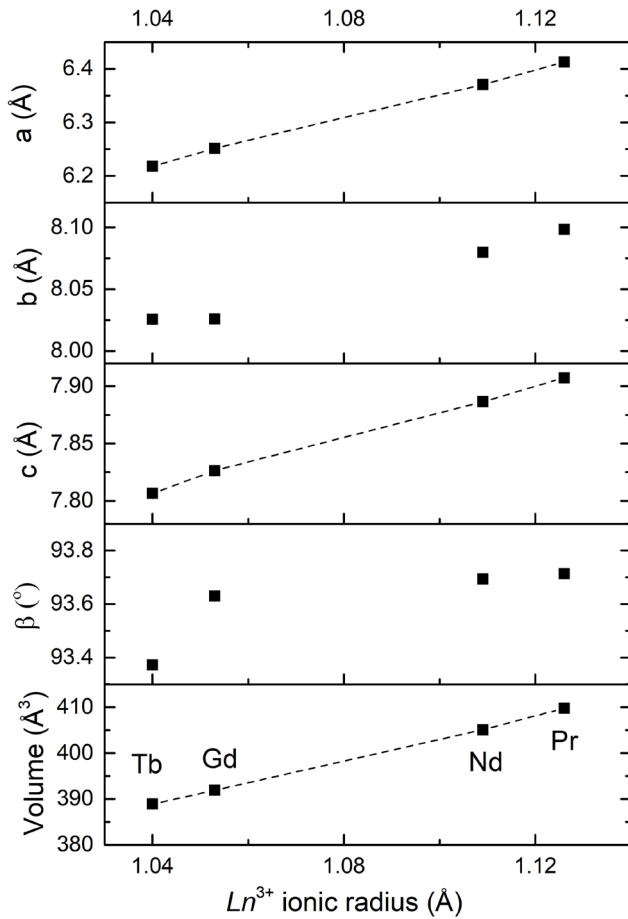


Figure 3. Plot of lattice parameters for $\text{Ln}(\text{BO}_2)_3$ as a function of Ln^{3+} ionic radii: lines are a guide to the eye.

interpolation, and peak shape using a pseudo-Voigt function. The appropriate scattering length for enriched boron was used in the PND Rietveld refinement.

Magnetic measurements were made on a Quantum Design Magnetic Properties Measurement System (MPMS) with a superconducting quantum interference device (SQUID) magnetometer. The zero field cooled (ZFC) susceptibility $\chi(T)$ was measured in a field of 100 Oe in the temperature range 2–300 K for all $\text{Ln}(\text{BO}_2)_3$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$). In a low field of 100 Oe, the isothermal magnetisation $M(H)$ curve is linear at all T and so the linear approximation for $\chi(T)$ is valid, that is, $\chi(T) \sim M/H$. $M(H)$ measurements in the field range, $\mu_0 H = 0\text{--}9$ T were carried out on all samples at selected temperatures using the ACMS (AC measurement system) option on a Quantum Design Physical Properties Measurement System (PPMS).

Zero field HC measurements for $\text{Ln}(\text{BO}_2)_3$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$) were performed using a Quantum Design PPMS in the temperature range 0.4–20 K using the Helium-3 option. To improve thermal conductivity at low temperatures, samples were mixed with approximately equal mass of silver powder (99.99%, Alfa Aesar). The contribution of the silver to the HC was then deducted [21] to obtain the HC of the sample. The lattice contribution was subtracted using a Debye model [22] with $\theta_D = 325$ K for $\text{Pr}(\text{BO}_2)_3$, $\theta_D = 315$ K for $\text{Nd}(\text{BO}_2)_3$, $\theta_D = 275$ K for $\text{Gd}(\text{BO}_2)_3$ and $\theta_D = 250$ K for $\text{Tb}(\text{BO}_2)_3$ to obtain the magnetic contribution to the HC, $C_{\text{mag}}(T)$.

Table 2. Comparison of structural information for $\text{Pr}(\text{BO}_2)_3$ from combined PXRD + PND refinements at 12 K and 300 K (RT).

		12 K	300 K
a (Å)		6.40092 (6)	6.41249 (3)
b (Å)		8.08400 (4)	8.09827 (6)
c (Å)		7.90419 (7)	7.90730 (5)
β (°)		93.9367 (7)	93.7129 (5)
Volume (Å ³)		408.038 (6)	409.765 (5)
χ^2		5.90	5.71
R_{wp}		3.61	3.58
$\text{Ln}: 4e(0, y, 1/4)$	y	0.0509 (5)	0.05007 (2)
	B_{iso} (Å ²)	0.38 (6)	0.61 (5)
$\text{B1}: 4e(0, y, 1/4)$	y	0.4712 (3)	0.4714 (4)
	B_{iso} (Å ²)	0.21 (5)	0.41 (4)
$\text{B2}: 8f(x, y, z)$	x	0.1072 (3)	0.1074 (2)
	y	0.3163 (2)	0.3166 (2)
	z	0.5248 (2)	0.5249 (2)
	B_{iso} (Å ²)	0.16 (3)	0.18 (2)
$\text{O1}: 8f(x, y, z)$	x	0.1423 (3)	0.1414 (2)
	y	0.3628 (3)	0.3629 (2)
	z	0.3560 (3)	0.3578 (2)
	B_{iso} (Å ²)	0.27 (4)	0.52 (3)
$\text{O2}: 8f(x, y, z)$	x	0.1397 (3)	0.1395 (3)
	y	0.4364 (3)	0.4367 (2)
	z	0.6481 (3)	0.6480 (3)
	B_{iso} (Å ²)	0.36 (4)	0.70 (3)
$\text{O3}: 8f(x, y, z)$	x	0.0467 (3)	0.0479 (3)
	y	0.1609 (3)	0.1617 (3)
	z	0.5477 (3)	0.5472 (3)
	B_{iso} (Å ²)	0.41 (4)	0.18 (2)

3. Results

3.1. Crystal structure

PXRD indicated formation of $\text{Ln}(\text{BO}_2)_3$, $\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$, with minor impurities of LnBO_3 (<2% by weight) and unreacted H_3BO_3 (<2% by weight) detected (table 1). Attempts to synthesise $\text{Ln}(\text{BO}_2)_3$ ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}$) were unsuccessful. A mixture of $\text{Ln}(\text{BO}_2)_3$ and LnBO_3 was obtained for Dy while only the LnBO_3 phase was obtained for Ho and Er. We conclude that the monoclinic phase cannot be obtained for $\text{Ln}(\text{BO}_2)_3$ ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}$) by this synthesis method. This is consistent with earlier reports where a high pressure synthesis was required for $\text{Ln}(\text{BO}_2)_3$, $\text{Ln} = \text{Dy--Er}$, and only the orthorhombic phase could be obtained [19].

Lanthanide metaborates, $\text{Ln}(\text{BO}_2)_3$, $\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}$, crystallise in a monoclinic unit cell with space group $C2/c$. Ribbons of borate units comprising alternating corner sharing BO_3^{3-} triangles and BO_4^{5-} tetrahedra propagate along the c axis (figure 1(a)). The Ln^{3+} ions occupy sites between the ribbons forming 1D chains (figure 1(b)). The interactions between chains are complex, with the Ln^{3+} ions forming a distorted 3D honeycomb lattice (figure 1(c)).

The crystal structure for $\text{Ln}(\text{BO}_2)_3$ was refined using a structural model from previous reports [17, 23, 24] by Rietveld refinement of the RT PND and PXRD patterns for $\text{Ln} = \text{Pr}, \text{Nd}, \text{Tb}$ and from the PXRD alone for $\text{Ln} = \text{Gd}$.

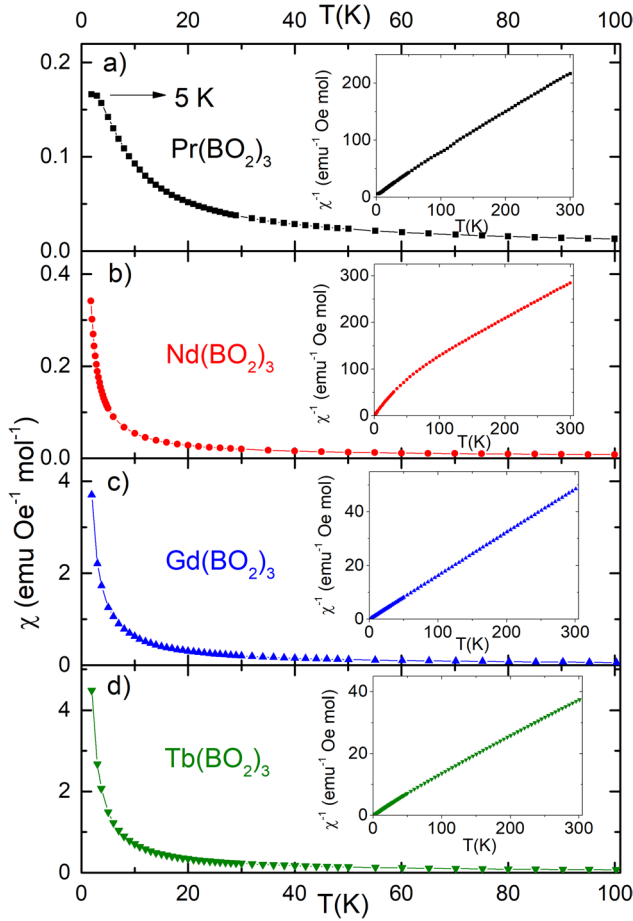


Figure 4. ZFC magnetic susceptibility $\chi(T)$ measured in a field of 100 Oe for $\text{Ln}(\text{BO}_2)_3$; the inverse susceptibility $\chi^{-1}(T)$ is inset.

PND is sensitive to the B and O positions and so a combined refinement gives accurate information about the crystal structure. The boron content in the structure was refined and found to be stoichiometric within error, the B occupancy was therefore fixed to be consistent with the $\text{Ln}(\text{BO}_2)_3$ stoichiometry. The combined PXRD + PND refinements for $\text{Pr}(\text{BO}_2)_3$ are shown in figure 2 and the refined parameters are compiled in table 1. The lattice parameters a and c are found to change linearly with the Ln^{3+} ionic radius [25] while b and β deviate slightly from the linear trend (figure 3). However they compensate each other and overall the lattice volume varies linearly with the Ln^{3+} ionic radius.

The low-temperature crystal structure for $\text{Pr}(\text{BO}_2)_3$ was refined from a combined PXRD and PND refinement at 12 K. There is a decrease in the lattice parameters and slight shifts in the atomic positions on cooling (table 2); however the monoclinic crystal structure is retained. No further structural changes are detected between 3.5 K and 12 K from the PND data. We conclude that there is no structural transition at low temperatures, $T \geq 3.5$ K, in $\text{Pr}(\text{BO}_2)_3$.

3.2. Bulk magnetic properties

Magnetic susceptibility, $\chi(T)$, zero field magnetic HC, $C_{\text{mag}}(T)$ and isothermal magnetisation $M(H)$ measurements are shown in figures 4–6 respectively. For all samples, the

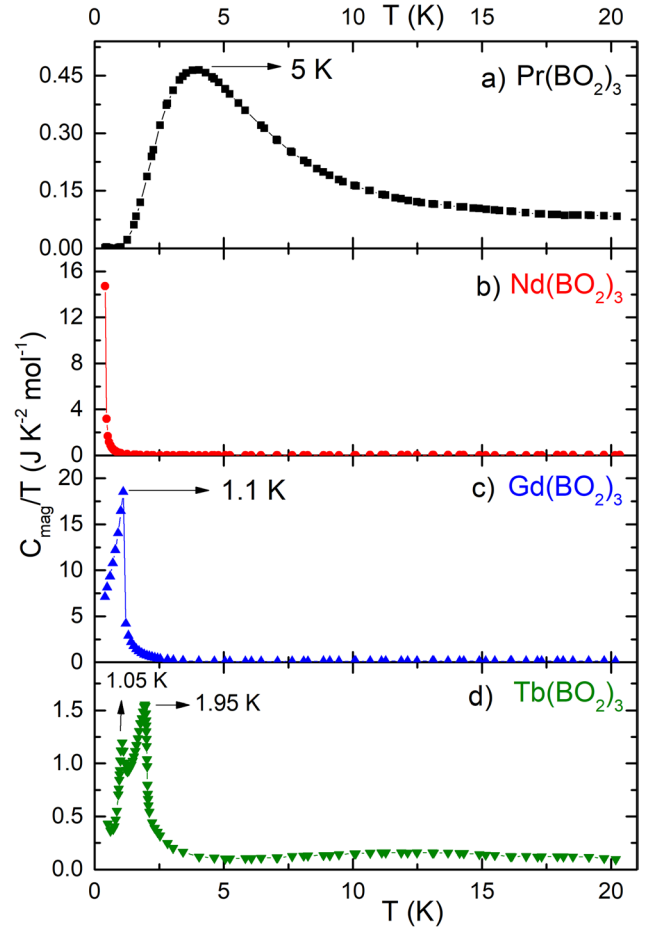


Figure 5. Zero field magnetic HC $C_{\text{mag}}(T)$ for $\text{Ln}(\text{BO}_2)_3$.

reciprocal susceptibility χ^{-1} is linear above 100 K and was used to fit to the Curie–Weiss law, $\chi = \frac{C}{T - \theta_{\text{CW}}}$ where C is the Curie constant and θ_{CW} is the Curie–Weiss temperature. Parameters for the Curie–Weiss fits are summarised in table 3. The Curie–Weiss temperatures are negative for all samples indicating antiferromagnetic interactions. Significant temperature-independent paramagnetism (TIP) is observed in $\text{Nd}(\text{BO}_2)_3$ and so the high T fit to the Curie–Weiss law gives an unrealistically large value for θ_{CW} , and hence is not reported. Instead, as has been reported for other frustrated Nd^{3+} systems [26–30], we consider the low T regime, 2–30 K. A fit in this temperature range gives $\mu_{\text{eff}} = 2.14 \mu_{\text{B}}$ and $\theta_{\text{CW}} = -0.20$ K. The experimentally determined magnetic moments generally agree well with the theoretical values.

With the exception of $\text{Pr}(\text{BO}_2)_3$ no features in the magnetic susceptibility or HC are observed above 2 K. $\text{Pr}(\text{BO}_2)_3$ shows a broad feature at 5 K in the magnetic susceptibility (figure 4(a)) and HC (figure 5(a)). No additional ordering transitions are observed below 2 K in the specific heat. The isothermal magnetisation shows no signs of saturation in a field of 9 T (figure 6(a)). Low temperature PND of $\text{Pr}(\text{BO}_2)_3$ shows no magnetic Bragg peaks or diffuse scattering down to 1.5 K (figure 7). We conclude that it has a non-magnetic singlet ground state as has been reported for other Pr^{3+} containing samples [30, 31]. The low symmetry crystal structure is consistent with this hypothesis. The broad feature at 5 K

Table 3. Magnetic properties of monoclinic $Ln(\text{BO}_2)_3$.

Ln	T_N (K)	θ_{CW} (K)	Theoretical		Experimental	
			$\mu_{\text{eff}} (\mu_B)$	$M_{\text{sat}} = g_J J (\mu_B/\text{f.u.})$	$\mu_{\text{eff}} (\mu_B)$	$M_{\text{max}2\text{K},9\text{T}} (\mu_B/\text{f.u.})$
Pr	—	−14 (3)	3.58	3.2	3.38 (3)	1.3
Nd	<0.4	TIP ^a	3.62	3.3	3.15 (7)	1.0
Gd	1.1	−0.4 (2)	7.94	7.0	7.032 (5)	6.0
Tb	1.05, 1.95	−13 (3)	9.72	9.0	8.11 (7)	2.9

^aLow temperature fit from 2 to 30 K gives $\mu_{\text{eff}} = 2.14 \mu_B$ and $\theta_{CW} = -0.20$ K. This value of θ_{CW} has been used for calculating J_1 in table 4.

in the bulk magnetic measurements is attributed to van Vleck paramagnetism, as has been reported elsewhere [31].

Zero field HC measurements below 2 K indicate magnetic transitions for all the other lanthanide metaborates studied, with the exception of $\text{Nd}(\text{BO}_2)_3$ where the onset of a sharp transition can be seen beyond the temperature limit of our measurements (0.4 K). Two sharp magnetic transitions at 1.05 K and 1.95 K are seen in $\text{Tb}(\text{BO}_2)_3$ whereas a single sharp λ type transition at 1.1 K is observed for $\text{Gd}(\text{BO}_2)_3$.

Isothermal magnetisation measurements for all three paramagnetic metaborates saturate at high fields at lower temperatures, $T \leq 4$ K. $\text{Gd}(\text{BO}_2)_3$ saturates at $6 \mu_B/\text{f.u.}$ in a field of 9 T, close to the saturation value, M_{sat} , expected for Heisenberg spins ($M_{\text{sat}} = g_J J = 7 \mu_B/\text{f.u.}$ for Gd^{3+}). Both $\text{Nd}(\text{BO}_2)_3$ and $\text{Tb}(\text{BO}_2)_3$ saturate at values close to $\sim M_{\text{sat}}/3$. Measurements to higher fields show the persistence of the plateau at $M_{\text{sat}}/3$ in the limiting field of $\mu_0 H = 14$ T (figure S1 (stacks.iop.org/JPhysCM/29/405807/mmedia)).

3.3. Discussion

We now consider the bulk magnetic properties of the monoclinic lanthanide metaborates in the context of 1D magnetism and frustration. $\text{Pr}(\text{BO}_2)_3$ has a non-magnetic singlet ground state, this is likely due to crystal electric field (CEF) effects that lead to the ground state being a well-isolated singlet as reported for other Pr^{3+} systems [30, 31]. We thus exclude $\text{Pr}(\text{BO}_2)_3$ from this discussion and focus on $Ln = \text{Nd}, \text{Gd}, \text{Tb}$.

The magnetic behaviour is determined by the connectivity of the magnetic Ln^{3+} and the competition among the different magnetic interactions. In addition to the superexchange, the dipolar interaction also needs to be considered at low temperatures as the trivalent rare-earth ions have large magnetic moments [32–34]. CEF effects will also have a significant impact on the single-ion anisotropy and the magnetic properties for Ln^{3+} with non-zero values of orbital angular momentum [35, 36]. For $\text{Nd}(\text{BO}_2)_3$ and $\text{Tb}(\text{BO}_2)_3$, such effects could lead to the ground state doublet being well isolated at low temperatures with $S = 1/2$ and Ising behaviour as reported for other systems [29, 37, 38]. Accurate modelling of all the relevant interactions require further inelastic neutron scattering experiments, however an order of magnitude approximation can be obtained from the bulk magnetic data as follows: The scale for the dipolar interaction can be estimated as $D \cong \frac{\mu_0 g_L^2 \mu_B^2}{4\pi R_{nn}^3}$, where R_{nn} is the distance between neighbouring Ln^{3+} and g_L is the Landé factor [33–35, 39]. The Curie–Weiss constant θ_{CW} contains contributions from the nearest -neighbour exchange

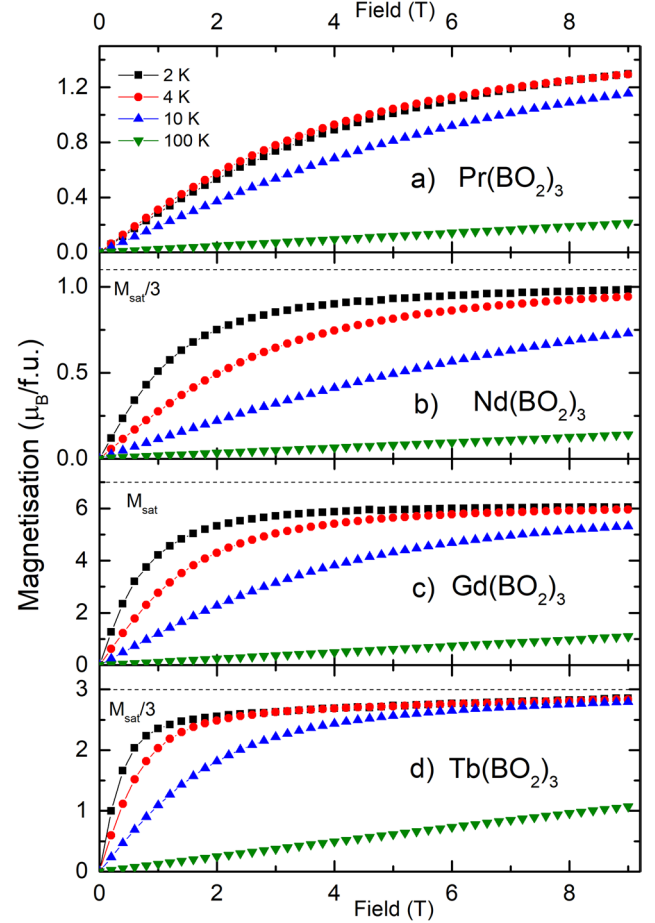


Figure 6. Isothermal magnetisation $M(H)$ curves at selected temperatures for $Ln(\text{BO}_2)_3$.

as well as other terms [32, 40, 41]. However, one can obtain an approximate value for the nearest-neighbour isotropic exchange using the mean-field result [40–42] as $J_1 \cong \frac{3k_B \theta_{CW}}{2nS(S+1)}$ where n is the number of nearest-neighbour $Ln^{3+} = 2$ and S is the spin quantum number. Approximations for D and J_1 are given in table 4.

We propose that the relative magnitude of the J_1 and D interactions determine whether these materials exhibit quasi 1D behaviour. The inter ($D_{\text{inter-chain}}$) and intra-chain ($D_{\text{intra-chain}}$) dipolar interactions are of comparable magnitude ($D_{\text{inter-chain}}/D_{\text{intra-chain}} \sim 0.7$, table 4) and so, considering predominantly dipolar interactions, the magnetic Ln^{3+} form a distorted hyper honeycomb lattice (figure 1(c)) and are expected to show 3D magnetic ordering. If the J_1 interactions dominate, quasi 1D magnetic behaviour may still be observed.

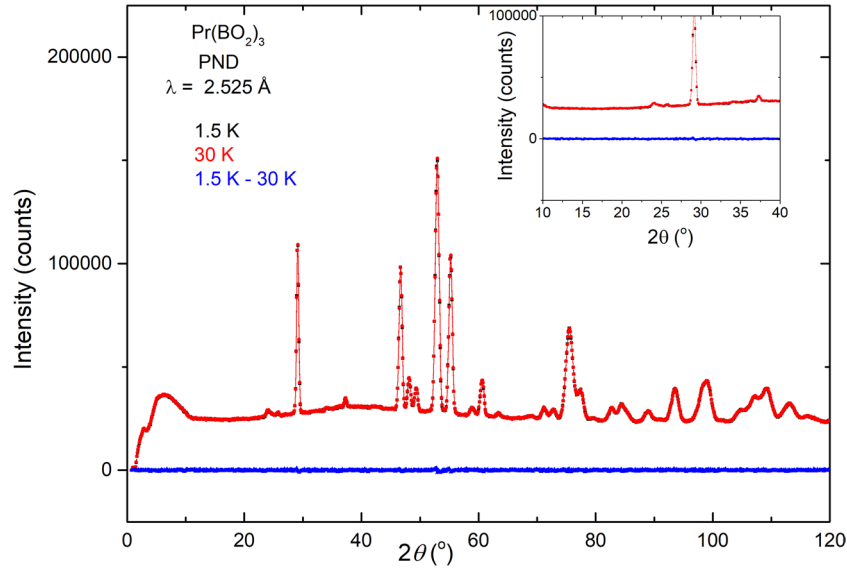


Figure 7. PND pattern for $\text{Pr}(\text{BO}_2)_3$ on D1B, ILL at 1.5 K and 30 K and the difference plot; inset: a zoom-in of the same plot at low 2θ ; note the absence of any magnetic Bragg or diffuse scattering.

Frustration in quasi 1D systems can arise due to competition between nearest neighbour (J_1) and next nearest neighbour exchange interactions (J_2). In general, it is highly dependent on the single-ion anisotropy of the magnetic Ln^{3+} ion and the relative magnitude of competing interactions; this has been observed in the case of other series of lanthanide containing geometrically frustrated magnets like the pyrochlores [32]. However a quantitative estimate can be obtained by considering the criterion proposed by Ramirez which states that a material is strongly frustrated if the frustration index, $f = \left| \frac{\theta_{\text{CW}}}{T_0} \right|$, is > 10 , where T_0 is the ordering temperature [42]. Using this, we obtain $f = 0.4$ for $\text{Gd}(\text{BO}_2)_3$ and $f = 11.9$ and 6.4 corresponding to the two transitions for $\text{Tb}(\text{BO}_2)_3$.

For $\text{Gd}(\text{BO}_2)_3$ the dipolar interactions are marginally greater than the J_1 exchange interactions. The ordering transition ($T_N = 1.1$ K) is very close to the Curie–Weiss temperature, as expected for an antiferromagnet with no geometric frustration. The isothermal magnetisation is consistent with the Heisenberg nature of the Gd^{3+} spins. Thus we postulate that the sharp λ type transition in the zero field HC at 1.1 K corresponds to 3D ordering of a Heisenberg antiferromagnet.

For $\text{Ln} = \text{Nd}$ and Tb , the J_1 interactions, calculated for both the usual spin quantum number, and considering them as effective $S = 1/2$ systems, are much greater than both $D_{\text{intra-chain}}$ and $D_{\text{inter-chain}}$; hence the magnetic behaviour would be quasi 1D in nature. This is consistent with the bulk magnetic measurements; specifically the observation of a plateau at 1/3 of the saturation magnetisation at 2 K, for both $\text{Nd}(\text{BO}_2)_3$ and $\text{Tb}(\text{BO}_2)_3$. We propose that this corresponds to a field-induced transition similar to that in other quasi 1D Ising compounds like CoV_2O_6 and CoNb_2O_6 [43, 44]. However unlike those systems, the plateau persists in a field of 14 T. Also unusually, the magnetisation plateaux are observed above the magnetic ordering for both $\text{Ln} = \text{Nd}$ and Tb . We postulate that this is due to existence of short-range magnetic correlations above the long-range ordering transitions. $\text{Tb}(\text{BO}_2)_3$ has two sharp

Table 4. Dipolar (D) and nearest-neighbour exchange (J_1) interactions for monoclinic $\text{Ln}(\text{BO}_2)_3$, $\text{Ln} = \text{Nd, Gd, Tb}$; Ln-Ln distances are obtained from structural PXRD and PND analysis.

Ln	Nd	Gd	Tb
Ln-Ln intra-chain (Å)	4.0241 (5)	3.9838 (5)	3.9696 (4)
$D_{\text{intra-chain}}$ (K)	0.005	0.04	0.022
Ln-Ln inter-chain (Å)	4.5374 (17)	4.5212 (17)	4.5269 (15)
$D_{\text{inter-chain}}$ (K)	0.003	0.03	0.015
J_1 (K)	$S = 3/2: -0.04$ $S = 1/2: -0.2$	$S = 7/2: -0.02$	$S = 3: -0.8$ $S = 1/2: -12.5$

transitions at 1.05 K and 1.95 K in zero field. This is reminiscent of the behaviour observed in quasi 1D CoNb_2O_6 which has two transitions at 1.97 K and 2.97 K, corresponding to a superposition of two commensurate phases and an incommensurate magnetic structure respectively [45]. The ordering transitions lie well below the Curie–Weiss temperature, implying possible frustration in $\text{Tb}(\text{BO}_2)_3$.

For $\text{Nd}(\text{BO}_2)_3$ no magnetic ordering is seen down to 0.4 K although the sharp increase in C_{mag}/T at 0.4 K can be attributed to the onset of an ordering transition. The weaker D and J_1 interactions are postulated to lead to magnetic ordering at lower temperatures as compared to $\text{Tb}(\text{BO}_2)_3$. The low temperature Curie–Weiss fit at lower temperatures for $\text{Nd}(\text{BO}_2)_3$ gives $\theta_{\text{CW}} = -0.2$ K and no conclusions can be drawn regarding the frustration as the ordering transition is beyond the temperature limit of our measurements.

Further work such as zero field PND measurements at $T < T_0$, inelastic neutron scattering experiments and PND measurements in field are required to determine the magnetic ground state and precisely model the magnetic interactions, single-ion anisotropy and field-induced transitions in $\text{Ln}(\text{BO}_2)_3$. This would provide a more complete understanding of the origin of the quasi 1D magnetic behaviour and frustration in these materials. Further,

the lanthanide metaborates could also find practical applications as low temperature magnetocaloric materials, $T \geq 2$ K, as has been reported for the lanthanide formates [11].

4. Conclusion

We have synthesised polycrystalline samples of $\text{Ln}(\text{BO}_2)_3$, $\text{Ln} = \text{Pr, Nd, Gd, Tb}$, characterised the structure using RT PXRD and PND and studied their bulk magnetic properties. The RT Rietveld refinements show that they crystallise in a monoclinic structure, consistent with previous reports. It is found that $\text{Pr}(\text{BO}_2)_3$ has a non-magnetic singlet ground state. $\text{Gd}(\text{BO}_2)_3$ undergoes antiferromagnetic ordering at 1.1 K and the magnetisation saturates at $6 \mu_B/\text{f.u.}$, consistent with isotropic Gd^{3+} spins. The onset of magnetic ordering is seen in $\text{Nd}(\text{BO}_2)_3$ at 0.4 K while $\text{Tb}(\text{BO}_2)_3$ shows two sharp magnetic ordering features at 1.05 K and 1.95 K. Both $\text{Nd}(\text{BO}_2)_3$ and $\text{Tb}(\text{BO}_2)_3$ show a $M_{\text{sat}}/3$ magnetisation plateau in fields up to 14 T at $T = 2$ K, consistent with quasi 1D behaviour seen in other Ising compounds like CoV_2O_6 and CoNb_2O_6 .

The monoclinic $\text{Ln}(\text{BO}_2)_3$, $\text{Ln} = \text{Pr, Nd, Gd, Tb}$ exhibit a wide range of interesting magnetic behaviour. We hope that this work will motivate further investigations into the magnetic properties of these hitherto unexplored materials.

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