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

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$_3$Ga$_5$O$_{12}$ [2], order-order transition in Ca$_2$Co$_3$O$_8$ [3] and quantum critical points (QCPs) in CoNb$_2$O$_6$ [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
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 metalates, 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.

| Ln   | Pr  | Nd  | Gd$^a$ | Tb  |
|------|-----|-----|--------|-----|
| \(a\) (Å) | 6.41249 (3) | 6.37043 (6) | 6.25159 (5) | 6.21781 (5) |
| \(b\) (Å) | 8.09827 (6) | 8.07975 (9) | 8.02602 (9) | 8.02564 (6) |
| \(c\) (Å) | 7.90730 (5) | 7.88632 (9) | 7.82649 (8) | 7.80659 (4) |
| \(\beta\) | 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) |
| \(\chi^2\) | 5.71 | 5.00 | 4.05 | 3.51 |
| \(R_{wp}\) | 3.58 | 3.32 | 5.72 | 2.66 |

*Parameters determined from PXRD only.

$^a$Not refined, positions taken from previous structural report [24].

$^b$Could not be obtained from PXRD.

Table 1. Room temperature (RT) crystal structure parameters for monoclinic Ln(BO$_2$)$_3$—space group C2/c.

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$_2$O$_3$ (Ln = Nd, Gd) (99.999% Alfa Aesar), Pr$_6$O$_{11}$ (99.999% Alfa Aesar), or Tb$_4$O$_7$ (99.999% Alfa Aesar) with H$_3$BO$_3$ (99.99% Alfa Aesar). A 50% excess of H$_3$BO$_3$ was added to compensate for the loss of B due to volatilisation during heating. Ln$_2$O$_3$ (Ln = Nd, Gd) and Pr$_6$O$_{11}$ were pre-dried at 800 °C prior to being weighed.
out to ensure the correct stoichiometry. A pre-reaction was carried out at 350 °C for 2 h to allow for decomposition of H3BO3. After regrinding, samples were heated between 800 °C 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° ⩽ 2θ ⩽ 60° (Δ2θ = 0.015°) using a Bruker D8 x-ray diffractometer (Cu Kα radiation, λ = 1.540 Å). For more quantitative analysis, longer scans for 2 h over a wide angular range 10° ⩽ 2θ ⩽ 90° (Δ2θ = 0.01°) were collected. Low temperature PXRD data over the same angular range was collected for Pr(BO2)3 at 12 K using an Oxford Cryosystems PheniX stage.

For Ln(BO2)3 (Ln = Pr, Nd, Tb), room temperature (RT) PND experiments for structural characterisation were carried out on the D2B diffractometer at ILL, Grenoble (λ = 1.595 Å). Samples for the PND experiments were synthesised by the same method as described above but enriched boric acid (11B) (99% purity, Sigma Aldrich) was used to reduce the absorption from 10B. Additional PND measurements were carried out for Pr(BO2)3 at 3.5 K and 12 K on D2B to investigate any structural transition. Low temperature PND measurements, T ⩾ 1.5 K, were carried out on Pr(BO2)3 on the D1B diffractometer at ILL, Grenoble (λ = 2.525 Å) 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...
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, $\mu_0H = 0–9$ 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 Pr(BO$_2$)$_3$, $\theta_D = 315$ K for Nd(BO$_2$)$_3$, $\theta_D = 275$ K for Gd(BO$_2$)$_3$ and $\theta_D = 250$ K for Tb(BO$_2$)$_3$ to obtain the magnetic contribution to the HC, $C_{\text{mag}}(T)$.

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

|          | 12 K          | 300 K         |
|----------|---------------|---------------|
| $a$ (Å)  | 6.40992 (6)   | 6.41249 (3)   |
| $b$ (Å)  | 8.08400 (4)   | 8.09827 (6)   |
| $c$ (Å)  | 7.90149 (7)   | 7.90730 (5)   |
| $\beta (\degree)$ | 93.9367 (7) | 93.7129 (5)  |
| Volume (Å$^3$) | 408.038 (6) | 409.765 (5)   |
| $\chi^2$ | 5.90          | 5.71          |
| $R_{\text{wp}}$ | 3.61       | 3.58          |
| $Ln: 4e$ (0, y, $\frac{1}{4}$) | y $0.0509$ (5) | $0.05007$ (2) |
| $B_{\text{iso}}$ (Å$^2$) | 0.38 (6) | 0.61 (5)  |
| $B1: 4e$ (0, y, $\frac{1}{4}$) | y $0.4712$ (3) | 0.4714 (4) |
| $B_{\text{iso}}$ (Å$^2$) | 0.21 (5) | 0.41 (4)  |
| $B2: 8f$ (x, y, z) | x $0.1072$ (3) | 0.1074 (2) |
| $B_{\text{iso}}$ (Å$^2$) | 0.21 (5) | 0.41 (4)  |
| $O1: 8f$ (x, y, z) | x $0.1423$ (3) | 0.1414 (2) |
| $B_{\text{iso}}$ (Å$^2$) | 0.16 (3) | 0.18 (2)  |
| $O2: 8f$ (x, y, z) | x $0.1397$ (3) | 0.1395 (3) |
| $B_{\text{iso}}$ (Å$^2$) | 0.27 (4) | 0.52 (3)  |
| $O3: 8f$ (x, y, z) | x $0.0467$ (3) | 0.0479 (3) |
| $B_{\text{iso}}$ (Å$^2$) | 0.36 (4) | 0.70 (3)  |

### 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 $\text{LnBO}_3$ (<2% by weight) and unreacted $\text{H}_3\text{BO}_3$ (<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 $\text{LnBO}_3$ was obtained for Dy while only the $\text{LnBO}_3$ 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 $\text{BO}_3^-$ triangles and $\text{BO}_4^-$ tetrahedra propagate along the $c$ axis (figure 1(a)). The $\text{Ln}^{3+}$ ions occupy sites between the ribbons forming 1D chains (figure 1(b)). The interactions between chains are complex, with the $\text{Ln}^{3+}$ 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 $\text{Ln} = \text{Gd}$. The lattice contribution was subtracted using a Debye model [22] with $\theta_D = 325$ K for Pr(BO$_2$)$_3$, $\theta_D = 315$ K for Nd(BO$_2$)$_3$, $\theta_D = 275$ K for Gd(BO$_2$)$_3$ and $\theta_D = 250$ K for Tb(BO$_2$)$_3$ to obtain the magnetic contribution to the HC, $C_{\text{mag}}(T)$.
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 Pr(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 $\text{Ln}^{3+}$ ionic radius [25] while $b$ and $\beta$ deviate slightly from the linear trend (figure 3). However they compensate each other and overall the lattice volume varies linearly with the $\text{Ln}^{3+}$ ionic radius.

The low-temperature crystal structure for Pr(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 Pr(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 reciprocal susceptibility $\chi^{-1}$ 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 $\theta_{\text{CW}}$ 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 Nd(BO$_2$)$_3$ and so the high T fit to the Curie–Weiss law gives an unrealistically large value for $\theta_{\text{CW}}$, 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 $\mu_{\text{eff}} = 2.14 \mu_B$ and $\theta_{\text{CW}} = -0.20$ K. The experimentally determined magnetic moments generally agree well with the theoretical values.

With the exception of Pr(BO$_2$)$_3$ no features in the magnetic susceptibility or HC are observed above 2 K. Pr(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 Pr(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
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 Nd(BO2)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 Tb(BO2)3 whereas a single sharp λ type transition at 1.1 K is observed for Gd(BO2)3.

Isothermal magnetisation measurements for all three paramagnetic metaborates saturate at high fields at lower temperatures, $T \leq 4$ K. Gd(BO2)3 saturates at 6 $\mu_B$/f.u. in a field of 9 T, close to the saturation value, $M_{sat}$, expected for Heisenberg spins ($M_{sat} = gJ/7 \mu_B$ for Gd3+). Both Nd(BO2)3 and Tb(BO2)3 saturate at values close to $\sim M_{sat}/3$. Measurements to higher fields show the persistence of the plateau at $M_{sat}/3$ in the limiting field of $\mu_BH = 14$ T (figure S1 (stacks.iop.org/JPhysCM/29/405807/mmedia)).

### 3.3. Discussion

We now consider the bulk magnetic properties of the monoclinic Ln(BO2)3. 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 Nd(BO2)3 and Tb(BO2)3, such effects could lead to the ground state doublet being well isolated at low temperatures with $S = \frac{1}{2}$ and Ising behaviour as reported for other $Pr^{3+}$ systems [30, 31]. We thus exclude Pr(BO2)3 from this discussion and focus on $Ln = Nd, Gd, Tb$.

The magnetic behaviour is determined by the connectivity of the magnetic $Ln^{3+}$ and the competition among the different magnetic interactions. 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 $J_1 \approx \frac{\lambda g \mu_B^2}{2\hbar n(S+1)}$ where $n$ is the number of nearest-neighbour $Ln^{3+}$ 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.

#### Table 3. Magnetic properties of monoclinic $Ln$(BO2)3.

| $Ln$ | $T_N$ (K) | $\theta_{CW}$ (K) | $\mu_{eff}$ ($\mu_B$) | $M_{sat}$ = $gJ/\mu_B$ (f.u.) | $\mu_{eff}$ ($\mu_B$) | $M_{max3K,9T}$ (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                     |

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

$$f = \left| \frac{\theta_{CW}}{T_0} \right|$$

is > 10, where $T_0$ is the ordering temperature [42]. Using this, we obtain $f = 0.4$ for Gd(BO$_2$)$_3$ and $f = 11.9$ and 6.4 corresponding to the two transitions for Tb(BO$_2$)$_3$.

For Gd(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 $\lambda$ type transition in the zero field HC at 1.1 K corresponds to 3D ordering of a Heisenberg antiferromagnet.

For $Ln$ = 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 Nd(BO$_2$)$_3$ and Tb(BO$_2$)$_3$. We propose that this corresponds to a field-induced transition similar to that in other quasi 1D Ising compounds like CoV$_2$O$_6$ and CoNb$_2$O$_6$ [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 $Ln$ = Nd and Tb. We postulate that this is due to existence of short-range magnetic correlations above the long-range ordering transitions. Tb(BO$_2$)$_3$ has two sharp transitions at 1.05 K and 1.95 K in zero field. This is reminiscent of the behaviour observed in quasi 1D CoNb$_2$O$_6$ 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 Tb(BO$_2$)$_3$.

For Nd(BO$_2$)$_3$ no magnetic ordering is seen down to 0.4 K although the sharp increase in $C_{\text{mag}}/T$ 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 Tb(BO$_2$)$_3$. The low temperature Curie–Weiss fit at lower temperatures for Nd(BO$_2$)$_3$ gives $\theta_{CW} = -0.2$ 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 $Ln$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 \( \text{Ln} \)(BO\(_2\))\(_3\), \( \text{Ln} = \) 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 Pr(BO\(_2\))\(_3\) has a non-magnetic singlet ground state. Gd(BO\(_2\))\(_3\) undergoes antiferromagnetic ordering at 1.1 K and the magnetisation saturates at \( 6 \) \( \mu \)Gf.u, consistent with isotropic Gd\(^{3+}\) spins. The onset of magnetic ordering is seen in Nd(BO\(_2\))\(_3\) at 0.4 K while Tb(BO\(_2\))\(_3\) shows two sharp magnetic ordering features at 1.05 K and 1.95 K. Both Nd(BO\(_2\))\(_3\) and Tb(BO\(_2\))\(_3\) show a \( M_{sat}/3 \) magnetisation plateau in fields up to 14 T at \( T = 2 \) K, consistent with quasi 1D behaviour seen in other Ising compounds like Co\(_2\)V\(_2\)O\(_8\) and Co\(_2\)Nb\(_2\)O\(_6\).

The monoclinic \( \text{Ln} \)(BO\(_2\))\(_3\), \( \text{Ln} = \) 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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References

[1] Bramwell S T and Gingras M J P 2001 Science 294 1495–501
[2] d’Ambrumenil N, Petrenko O A, Mutka H and Deen O P 2015 Phys. Rev. Lett. 114 227203
[3] Agrestini S, Fleck C L, Chapon L C, Mazzoli C, Bombardi A, Lees M R and Petrenko O A 2011 Phys. Rev. Lett. 106 197204
[4] Cotlea R, Tennant D A, Wheeler E M, Wawrzynska E, Prabhakaran D, Telling M, Habicht K, Smeibidl P and Kiefer K 2010 Science 327 177–80
[5] Dutton S E et al 2012 Phys. Rev. Lett. 108 187206
[6] Moessner R and Ramirez A P 2006 Phys. Today 59 24–9
[7] Balelos T 2010 Nature 464 199–208
[8] Mikeska H J and Kolezhuk A K 2004 One-dimensional magnetism Quantum Magnetism (Lecture Notes in Physics vol 645) ed U Schollwöck et al (Berlin: Springer) (https://doi.org/10.1007/BFb0195919)
[9] Collins M F and Petrenko O A 1997 Can. J. Phys. 75 605–55
[10] Kobayashi S, Mitsuda S, Ishikawa M, Miyatani K and Kohn K 1999 Phys. Rev. B 60 3331–45
[11] Saines P J, Paddison J A M, Thygesen P M M and Tucker M G 2015 Mater. Horiz. 2 528–35
[12] Harcombe D R, Welch P G, Manuel P, Saines P J and Goodwin A L 2016 Phys. Rev. B 94 174429
[13] Mayolet A, Zhang W, Martin P, Chassigneux B and Krupa J C 1996 J. Electrochem. Soc. 143 330
[14] Meng F, Zhang X, Li W, Xie T and Seo H J 2012 J. Phys. Chem. Solids 73 564–7
[15] Zhang X, Meng F, Li W, Kim S II, Yu Y M and Seo H J 2013 J. Alloys Compd. 578 72–6
[16] Weidelt J 1970 Z. Anorg. Allg. Chem. 374 26–34
[17] Gorioounova A, Held P, Becker P and Bohary L 2003 Acta Crystallogr. E 59 183–5
[18] Gorioounova A 2003 PhD Thesis University of Cologne (http://kups.uni-koeln.de/id/eprint/956)
[19] Emme H, Nikelski T, Schleid T, Pöttgen R, Möller M H and Huppertz H 2004 Z. Naturforsch. Teil B 59 202–15
[20] Rodríguez-Carvajal J 1993 Physica B 192 55–69
[21] Smith D R and Fickett F R 1995 J. Res. Natl. Inst. Stand. Technol. 100 119
[22] Gopal E S R 1966 Lattice Heat Capacity at Low Temperatures (The International Cryogenics Monograph Series) (Boston, MA: Springer) (https://doi.org/10.1007/978-1-4684-9081-7_3)
[23] Pakhomonov V I, Siltiäskäy G B, Medvedev A V and Dzhurinskii B F 1972 Inorg. Mater. 8 1107
[24] Abdullaev G K, Mamedov K S and Dzhafarov G G 1975 Sov. Phys. Crystallogr. 20 161
[25] Shannon R D 1976 Acta Crystallogr. A 32 751–67
[26] Hallas A M, Arvailo-Lopez A M, Sharma A Z, Munsie T, Attfield J P, Wiebe C R and Luke G M 2015 Phys. Rev. B 91 104417
[27] Hatnean M C, Lees M R, Petrenko O A, Kebbe D S, Balakrishnan G, Gutmann M J, Klekovkina V V and Malkin B Z 2015 Phys. Rev. B 91 174416
[28] Anand V K, Bera A K, Xu J, Herrmannsdörfer T, Ritter C and Luke B 2015 Phys. Rev. B 92 184418
[29] Scheie A, Sanders M, Krizan J, Qiu Y, Cava R J and Broholm C 2016 Phys. Rev. B 93 180407
[30] Dun Z L, Trinh J, Lee M, Choi E S, Li K, Hu Y F, Wang Y X, Blanc N, Ramirez A P and Zhou H D 2017 Phys. Rev. B 95 104439
[31] Zorko A, Bell F, Mendels P, Marty K and Bordet P 2010 Phys. Rev. Lett. 104 057202
[32] Gardner J S, Gingras M J P and Greedan J E 2010 Rev. Mod. Phys. 82 53–107
[33] Raju N P, Dion M, Gingras M J P, Mason T E and Greedan J E 1999 Phys. Rev. B 59 14489–98
[34] Palmer S E and Chalker J T 2000 Phys. Rev. B 62 488–92
[35] Gingras M J P 2011 Spin Ice Introduction to Frustrated Magnetism (Springer Series in Solid-State Sciences vol 164) eds C Lacroix, P Mendels, F Mila (Berlin: Springer) (https:// doi.org/10.1007/978-3-642-10589-0_12)
[36] Capel H W 1965 Physica 31 1152–76
[37] Lhotel E, Petit S, Guttiñey S, Florea O, Cimoglia Hatnean M, Colin C, Ressouche E, Lees M R and Balakrishnan G 2015 Phys. Rev. Lett. 115 197202
[38] Sible R et al 2016 arXiv:1610.08714
[39] Petrenko O A and Paul D M 2000 Phys. Rev. B 63 024409
[40] Greedan J E 2001 J. Mater. Chem. 11 37–53
[41] Applegate R P, Zong Y and Corruccini L R 2007 J. Phys. Chem. Solids 68 1756–61
[42] Ramírez A P 1994 Annu. Rev. Mater. Sci. 24 453–80
[43] Maartense I, Yaeger I and Wanklyn B M 1977 Solid State Commun. 24 93–9
[44] Kimberly S A J, Mutka H, Chatterji T, Hofmann T, Henry P F, Bordallo H N, Argyriou D N and Attfield J P 2011 Phys. Rev. B 84 104425
[45] Sarvezuk P W C, Kinst E J, Colin C Y, Gusmão M A, da Cunha J B M and Isnard O 2011 J. Appl. Phys. 109 07E160