# Experimental report

19/01/2017

**Proposal:** 5-31-2456 **Council:** 4/2016

**Title:** Magnetic properties of lanthanide metaborates

**Research area:** Physics

**This proposal is a new proposal**


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**Local contacts:** Emmanuelle SUARD


**Samples:** Pr(BO2)3
Nd(BO2)3
Tb(BO2)3

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 3 | 2 | 05/09/2016 | 07/09/2016 |


## Abstract:

Lanthanide metaborates Ln(BO2)3 contain one-dimensional chains of magnetic Ln3+ and may exhibit geometrical frustration, low dimensional ordering and other interesting magnetic features. However their magnetic properties have not been studied before.
We have synthesised powder samples of lanthanide metaborates (Ln = Pr, Nd, Gd, Tb) and studied their magnetic properties as a function of temperature and magnetic field.
Rietveld refinement shows that previous reports for the crystal structure are not fully accurate. We propose to correctly analyse the crystal structure for Ln = Pr, Nd, Tb using powder neutron diffraction on D2B.
Magnetic measurements reveal an ordering transition for Pr(BO2)3 at T = 5 K. We aim to solve the magnetic structure and analyse the nature of the ordering transition through powder neutron diffraction experiments on D2B. This would also provide insight into the magnetic structure and magnetic properties of the other Ln(BO2)3.

# Experimental Report

**Background:**

Lanthanide metaborates, $Ln(BO_2)_3$ have been well-studied for their applications in phosphors but their magnetic properties have not been explored in any detail. The magnetic $Ln^{3+}$ in $Ln(BO_2)_3$ ($Ln$ = Pr – Tb) form one-dimensional chains[1,2]. They may be geometrically frustrated, exhibit short range correlations or low-dimensional ordering due to the one-dimensional nature of the magnetic $Ln^{3+}$ chains.

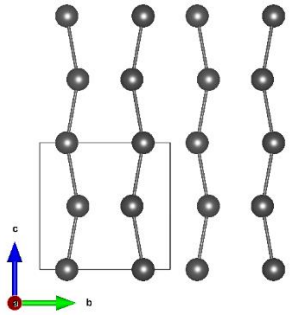

Fig. 1 – One-dimensional chains in $Ln(BO_2)_3$ ($Ln$ = Pr – Tb)

Here we focus on $Ln(BO_2)_3$ ($Ln$ = Pr, Nd, Tb). We prepared powder samples using enriched ($^{11}B$) boric acid (99% purity). Sample characterisation was carried out using powder X-Ray Diffraction (PXRD) and Rietveld Refinement. The magnetic susceptibility was measured from 2-300 K for all samples. No ordering is observed for $Ln$ = Nd and Tb while a feature is seen at 5 K for $Ln$= Pr.

**Experimental aims and measurements:**

As our experiments on $LnBO_3$ (D1B) and $Ln(BO_2)_3$ (D2B) were scheduled together, all measurements to determine the crystal structure were carried out on D2B. Low temperature (LT) measurements to investigate magnetic ordering were carried out on D1B. We now discuss the results for $Ln(BO_2)_3$:

1. Room temperature (RT) powder neutron diffraction (PND) experiments on D2B were carried out on all $Ln(BO_2)_3$ ($Ln$ = Pr, Nd, Tb) for precise determination of the crystal structure, especially the B and O positions which cannot be determined from PXRD. Also low temperature (LT) scans for $Pr(BO_2)_3$ were collected at 3.5 K and 12 K to investigate any structural transition prior to measuring it on D1B to study the magnetic ordering.
2. Long scans at 1.5 K and 30 K were collected for $Pr(BO_2)_3$ and $Tb(BO_2)_3$ on D1B. Shorter scans were collected for $Tb(BO_2)_3$ at intermediate temperatures.

**Results:**

**1. Crystal structure determination (D2B):**

Combined RT PXRD+ PND refinements were carried out for $Ln(BO_2)_3$ ($Ln$ = Pr, Nd, Tb) using Fullprof. All the metaborates crystallise in a monoclinic structure (space group C2/c). The one-dimensional $Ln^{3+}$ chains are linked to $[BO_4]^{5-}$ tetrahedra which are connected via $[BO_3]^{3-}$ triangles on either side. Fig. 2 shows the RT PND Rietveld refinement for $Pr(BO_2)_3$, very small amounts of $PrBO_3$ and $H_3BO_3$ (~1% by weight) are also present. Lattice parameters from the combined RT refinements are compiled in Table 1. No structural transition is

| *Ln* | a (Å) | b (Å) | c (Å) | β (°) |
|---|---|---|---|---|
| Pr | 6.41206(3) | 8.09777(6) | 7.90642(5) | 93.7123(5) |
| Nd | 6.37020(7) | 8.07910(9) | 7.88524(9) | 93.6888(7) |
| Tb | 6.21781(4) | 8.02565(6) | 7.80659(4) | 93.3723(4) |

Table 1: Lattice parameters from RT combined structural refinements – PXRD + PND data (from D2B) for $Ln(BO_2)_3$: Space group C2/c

observed for $Pr(BO_2)_3$ down to 3.5 K; only changes in intensities of the nuclear peaks are observed due to significant changes in the B and O atomic positions on cooling.

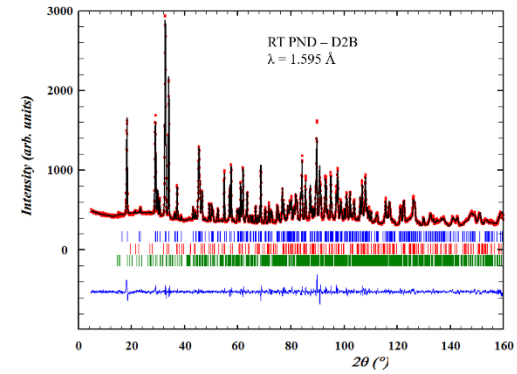


Fig 2: RT PND Rietveld refinement on D2B for $Pr(BO_2)_3$

**2. Magnetic ordering (D1B):**

No magnetic Bragg peaks or diffuse scattering was observed for $Pr(BO_2)_3$ down to 1.5 K. The bulk measurements and PND data lead us to conclude that $Pr(BO_2)_3$ has a non-magnetic ground state, as reported in the literature for other Pr samples[3]. For $Tb(BO_2)_3$, we observe increased magnetic intensity of the nuclear Bragg peaks at 1.5 K which disappears at 2.5 K. The magnetic peaks were indexed by the vector **k** = 0 using the program ksearch in the Fullprof Suite. Different irreducible representations were generated using Basireps, and the final magnetic Rietveld refinement was carried out in Fullprof. The magnetic Rietveld refinement and magnetic structure for $Tb(BO_2)_3$ at 1.5 K are shown in Fig. 3.

**Conclusions:**

We were able to accurately determine the crystal structure for the monoclinic $Ln(BO_2)_3$ (*Ln* = Pr, Nd, Tb) using the RT PND data on D2B. The absence of any structural transition down to 3.5 K for $Pr(BO_2)_3$ was confirmed. The LT PND data on D1B for $Pr(BO_2)_3$ showed that it has a non-magnetic ground state. We observed magnetic Bragg peaks for $Tb(BO_2)_3$ at 1.5 K on D1B and solved the magnetic structure. Zero field heat capacity measurements down to 0.4 K on $Tb(BO_2)_3$ were carried out after this experiment and showed two sharp transitions at 1 K and 1.75 K; the magnetic ordering observed for $Tb(BO_2)_3$ on D1B corresponds to the latter transition. Ultra LT PND experiments are being planned on $Tb(BO_2)_3$ to obtain a more complete understanding of the magnetic properties.

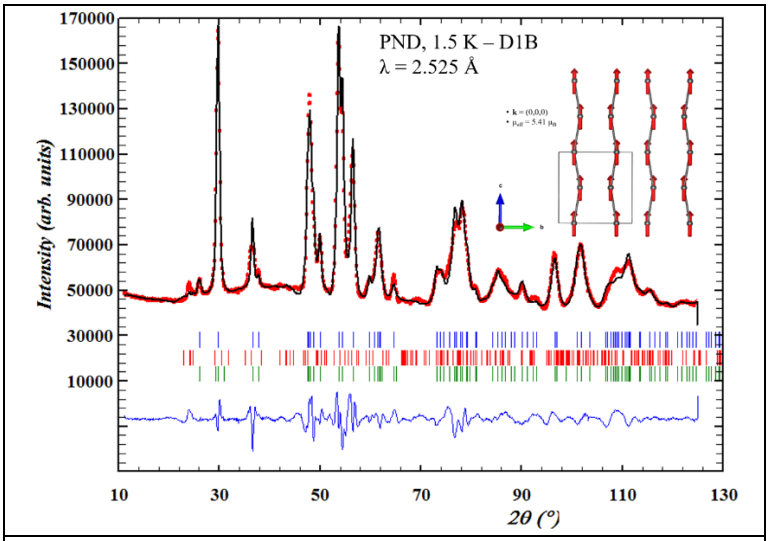


Fig. 3 – Magnetic Rietveld refinement for $Tb(BO_2)_3$ at 1.5 K on D1B; inset: Corresponding magnetic structure.

The data collected will form a key component of the PhD thesis of Paromita Mukherjee (main proposer). The results will be prepared for publication in a peer reviewed journal.

**References:**


1. G. K. Abdullaev, *et. al*, Kristallografiya **20**, 265 (1975)
2. A. Goriounova, *et.al*, Acta Cryst. E **59**, I83 (2003)
3. Zorko, *et.al*, PRL 104, 057202 (2010)