Experimental report

19/01/2017

Proposal: 5-31-2418 **Council:** 4/2015

Title: Crystal Structure and Magnetic Properties of Lanthanide Borates

Research area: Physics

This proposal is a new proposal

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Paromita MUKHERJEE

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Samples: ErBO3
TbBO3
HoBO3
YbBO3

Instrument	Requested days	Allocated days	From	To
D2B	2	0		
D1B	0	2	07/09/2016	09/09/2016

Abstract:

The crystal structure of lanthanide borates remains under debate. We have synthesised powder samples of monoclinic lanthanide borates and wish to analyse the crystal structure more accurately through neutron scattering measurements.
We are also investigating the magnetic properties of lanthanide borates and their viability for low temperature magnetic cooling. Magnetic measurements show an ordering transition for HoBO3 at around 6 K. We wish to study changes in the magnetic structure and features of two-dimensional magnetic ordering in HoBO3 as a function of temperature.

Experimental Report

Background:

There has been much debate about the crystal structure of the 'vaterite' type or π orthoborates $Ln BO_3$ [*Ln* = Eu-Yb][1-4]; some of the main structural models are summarised in Fig.1. The nature and exact arrangement of the B-O units present in π-$Ln BO_3$ remain unresolved. Previous studies have mainly focused on the optical properties of $Ln BO_3$. However they may be geometrically frustrated due to the layered triangular arrangement of the magnetic Ln^{3+} ions (Fig. 2), present in both the proposed hexagonal and monoclinic structures. Measurement of the magnetic properties of these materials forms the basis of our project. However in order to understand the magnetic properties, we also need to have a precise understanding of the crystal structure.

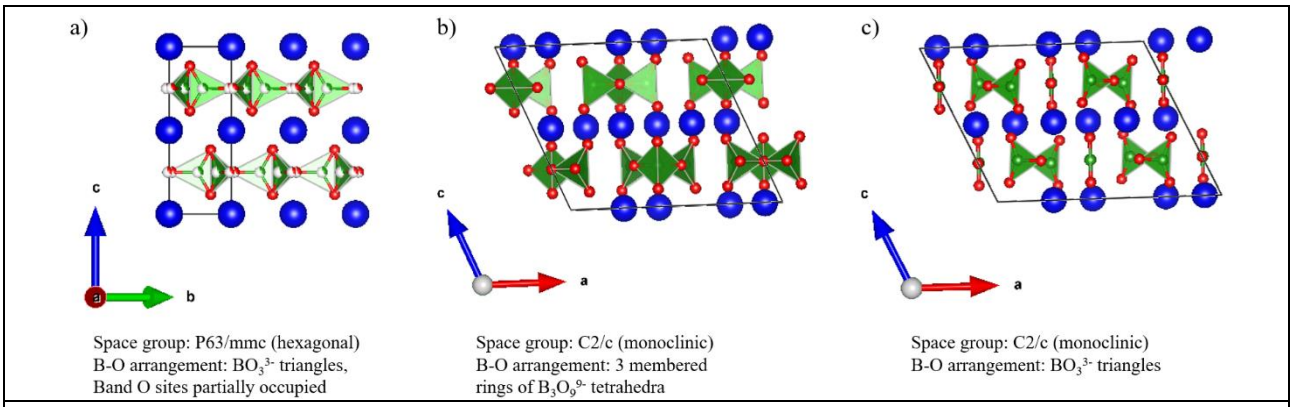

Fig 1: Some of the main structural models proposed for π $Ln BO_3$; a) shows the distorted hexagonal structure with BO_3^{3-} triangles while b) and c) show the monoclinic structure with $B_3O_9^{9-}$ tetrahedra and BO_3^{3-} triangles respectively

Here we focus on $Ln BO_3$ [*Ln* = Tb, Ho, Er, Yb]. 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 which indicated a monoclinic unit cell consistent with Fig. 1b. The magnetic susceptibility was measured from 2-300 K for all samples. A feature is seen at 6 K for *Ln* = Ho, no ordering is observed down to 2 K for the other samples.

Experimental aims and measurements:

As our experiments on $Ln BO_3$ (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 $Ln BO_3$:

1. Room temperature (RT) powder neutron diffraction (PND) experiments on D2B were carried out on $Ln BO_3$ [*Ln* = Tb, Ho, Er, Yb] to determine the B-O environment accurately as this cannot be determined from PXRD. Low temperature (LT) scans for $HoBO_3$ were collected at 3.5 K and 12 K to investigate any structural transition prior to measuring it on D1B to study magnetic ordering.

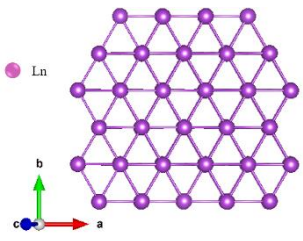

Fig. 2 – Layered triangular arrangement of magnetic Ln^{3+} in π-$Ln BO_3$ (*Ln* = Eu - Yb)

2. Long scans at 1.5 K and 30 K were collected for $HoBO_3$ on D1B.

Results:

1. Crystal structure determination (D2B):

Our attempt at a PND Rietveld refinement for $ErBO_3$ is shown in Fig. 3. It is consistent with the monoclinic structure; however in all the RT PND patterns, we observe significant peak broadening (Fig. 3 inset) which cannot be captured by standard size/strain models. The peak broadening is increased as the Ln^{3+} ionic radius decreases from Tb to Yb. As this is a layered structure, the peak broadening may be caused by defects or stacking faults. Significant peak broadening in PND combined with the absence of the same in the PXRD implies that such defects/faults are possibly present in the B-O layers in the material. There is no structural transition in $HoBO_3$ down to 3.5 K.

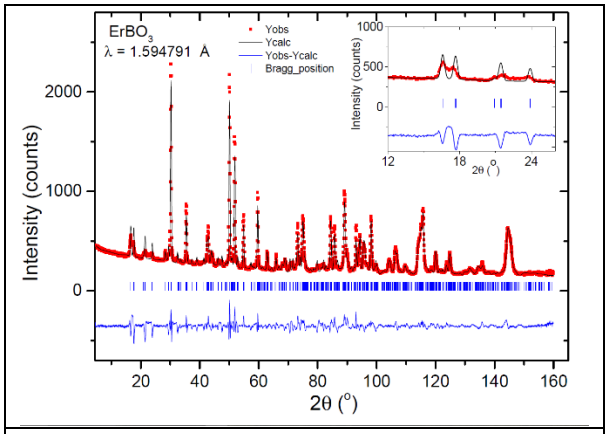

Fig 3: RT PND Rietveld refinement on D2B for $ErBO_3$; inset: peak broadening which cannot be accounted for by the current structural model

2. Magnetic ordering (D1B):

No magnetic Bragg peaks or diffuse scattering was observed for $HoBO_3$ down to 1.5 K. Therefore the feature at 6 K is not due to magnetic ordering. Similar features have been observed for the double perovskite Ba_2HoSbO_6[5] which is a van Vleck paramagnet with a non-magnetic ground state. We conclude that $HoBO_3$ also has a non-magnetic ground state.

Conclusions:

We observed significant peak broadening in the RT PND data for π-$LnBO_3$ on D2B. More analysis is required to quantify the extent of disorder in the B-O layers in these materials. Further experiments such as neutron PDF and B-11 NMR are being planned to obtain more information about the composition and arrangement of defects/stacking faults in the B-O layers.

The LT PND data for $HoBO_3$ on D1B shows that it has a non-magnetic ground state, crystal electric field (CEF) calculations are required to confirm this. Bulk measurements are being carried out on other members of the π $LnBO_3$ family to investigate ordering transitions below 2 K.

The data collected will be included in the PhD thesis of Paromita Mukherjee (main proposer).

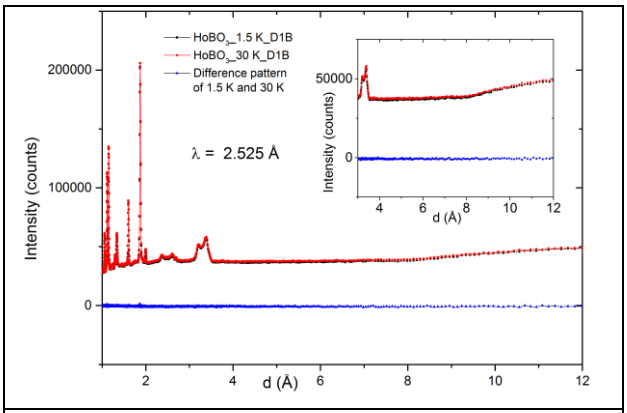

Fig. 4 – PND pattern for $HoBO_3$ on D1B at 1.5 K and 30 K and the difference plot

References:

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