Experimental report

29/09/2023

Proposal: 5-23-798 **Council:** 4/2023

Title: Understanding the Interplay between Magnetic and Anion Order in Diaspores

Research area: Chemistry

This proposal is a new proposal

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Samples: Ni(OH)F

Instrument	Requested days	Allocated days	From	To
D20	1	1	14/09/2023	15/09/2023
D2B	1	1	13/09/2023	14/09/2023

Abstract:

Diaspores crystallise forming chains of edge-sharing octahedral dimers that are interconnected at the corners, providing an opportunity for strong magnetic exchange anisotropy and competition between ferromagnetic and antiferromagnetic interactions. We have synthesised the currently unreported Ni(OH)F Diaspore, and observe a variation in the magnetic behaviour compared to the Co, Fe analogues. Ni(OH)F shows weak ferromagnetism (wFM), which may result from a change in the magnetic exchange interactions and hence magnetic structure allowing spin canting. However, both disorder and ordering of OH and F have been reported for various materials in the M(OH)F materials. The coupling of order parameters associated with structural distortions such as anion order with order parameters arising from the magnetic spin may further lead to the generation of additional ferromagnetic components. This will open the investigation as to why this magnetic behaviour is not yet seen in the Co or Fe analogues and further our understanding in the possibility of tuning magnetic properties through the distortion of the nuclear structure and non-magnetic atoms.

Understanding the Interplay between Magnetic and Anion Order in Ni(OH)F Diaspore – Preliminary report

Context

We have synthesised the previously unreported Ni(OH)F diaspore using hydrothermal synthesis methods, negating the requirement of hazardous HF in sample preparation. The hydroxyfluoride diaspores *M*(OH)F, where *M*=Fe, Mg and Zn consist of edge-sharing MX_6 octahedral dimer chains that are interconnected to each other at the corners (space group *Pnma*)[1][2]. The OH and F anions alternate along *a*, with OH being located between two edge-sharing octahedral units, and O at the interconnecting corner-sharing octahedra (Fig. 1 insert). However, the *M*=Co analogue has a degree of disorder over the anion site and has protons located at both edge-sharing and corner-sharing octahedra, indicating disorder of (OH) and F[3].

Ni(OH)F is an antiferromagnet with a weak ferromagnetic component from spin canting. This is different to the previously reported Co and Fe analogues which are antiferromagnetic with no spin canting allowed by symmetry in their magnetic structures. We aim to understand how the differences in these magnetic properties arise, whether that be from changes to the anion ordering of (OH) and F, or by differences in the electronic configurations leading to changes to the magnetic structure.

Experiment details

We prepared a sample of Ni(OD)F which was measured on both D2B and D20. We initially took measurements on D2B (λ = 1.594644 Å) to collect high resolution data at T = 10K, 60K and room temperature. This is currently being used in combined refinements on ID22 (ESRF) at the same temperatures to identify any subtle peak splitting that may arise with anion ordering. Variable temperature data was collected on D20 (λ = 1.54300 Å) with a 1hr measurement at 1.6K (base temperature) and 70K (~15K above the magnetic transition temperature, T_N). 10-minute scans were taken every 1K between 2K and 70K, and every 5K between 70K and 300K. This data will be used to confirm the magnetic structure and track any temperature dependence of structural order parameters.

Results

Using combined refinements on D2B neutron data and ID22 PXRD, we have identified the presence of peak splitting at low temperatures on peaks *h*01 and *h*11. These may be attributed to a pseudo-orthorhombic unit cell with a slight opening of the β angle or from some anion ordering. We intend to explore this using a symmetry-based approach to identify possible anion ordering models to see if there is any improvement to the fit.

Using D20, we were able to confirm the magnetic structure of *Pnm'a'* (BNS: 62.447) which is defined by the $m\Gamma^{2+}$ representation. This magnetic structure consists of ferromagnetic (FM) interactions within the dimers that are coupled antiferromagnetically (AFM) to the corner-shared neighbouring dimer, with the magnetic moments aligned along *c*. This magnetic structure allows for a weak FM component from spin canting along *a*. This magnetic structure differs to the reported magnetic structures for the *M* = Co, Fe analogues ($m\Gamma^{2-}$), which defined by only AFM superexchange along *a* between both edge and corner-sharing octahedra, and FM interactions along the edge-sharing chains (*b*) with the magnetic moments aligned along *b* (Fig. 3). By performing sequential Rietveld refinements, we can extract the changes in lattice parameters and volume on heating (Fig. 2). We see that below the T_N, there is a contraction along the short unit cell axis, *b*, which is likely correlated to the magnetostriction with the onset of magnetic ordering[4]. Interestingly, there is a negative thermal expansion along *c* below T_N which may be related to some degree of magnetic frustration, steric effects from the

presence of OH groups within the channels, or an ordering of OH/F, however this is still to be investigated and fully understood.

We intend to use a symmetry-based approach to determine whether the extent of interplay between anion order/disorder and the magnetic structure. We will identify suitable anion ordered models (that account for different OH/F occupancies on the different anion sites) that may account for the subtle peak splitting observed and by looking at the quality of the fit vs the mode amplitudes we can identify the most suitable model. We will use this to determine whether there is a more appropriate structural description of the anion ordering resulting from the interplay with the magnetic structure in e_g-natured transition metal diaspores compared to those containing t_{2g} natured transition metals.

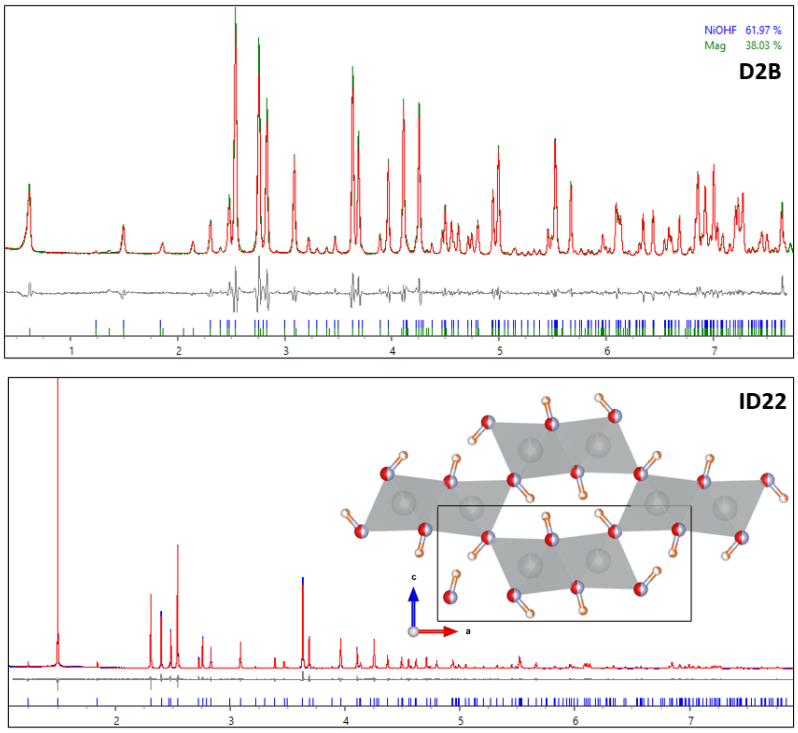

Figure 1: Combined Rietveld refinement at 10K on data collected on D2B (top) and ID22 (bottom). The x-axis is shown in Q ($Å^{-1}$). The structure of Ni(OH)F was refined and shown. Due to the similarity in both x-ray and neutron scattering lengths for O and F, their occupancies were fixed to 0.5 on each anion site and will later be correlated to the H occupancies which were allowed to refine freely.

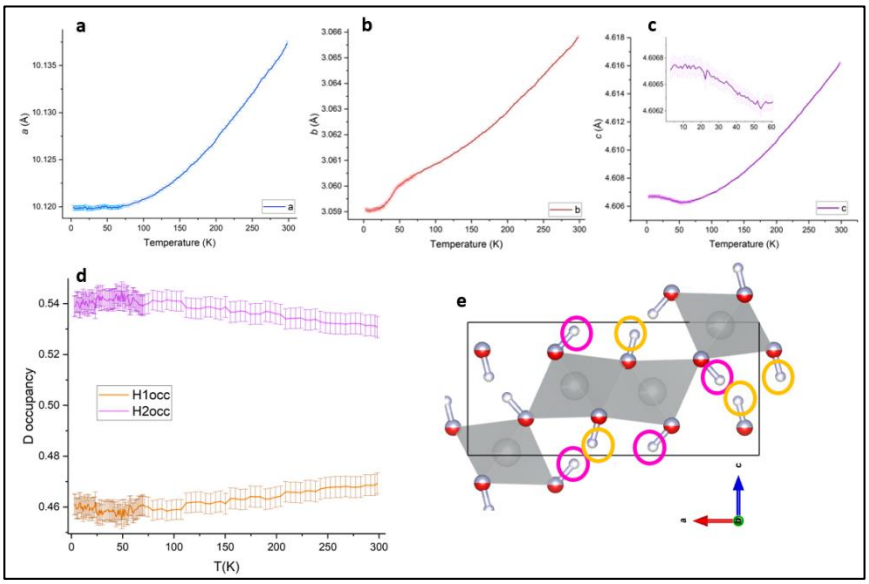

Figure 2: Extraction of lattice parameters (*2a, 2b, 2c*) and H occupancies (*2d*) from variable temperature data collected on D20. Deuterium was used in the refinement due to the changed in neutron scattering length between H and D. *2e* highlights the two different H positions.

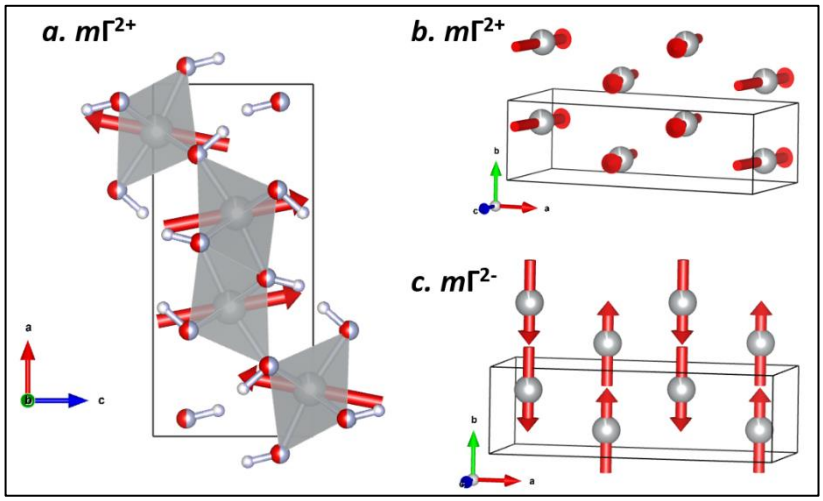

Figure 3: The determined magnetic structure of Ni(OH)F (*a, b*) compared to the known magnetic structure (*c*) for FeOOH, Co(OH)F and Fe(OH)F.

References

[1] W. A. Crichton, J. B. Parise, H. Muller, J. Breger, W. G. Marshall and M. D. Welch, Mineral. Mag, vol. 76, no. 1, pp. 25-36, 2012. [2] H. Serier, M. Gaudon, A. Demourgues and A. Tressaud, J. Solid State Chem., vol. 180, no. 12, pp. 3485-3492, 2007 [3] H. B. Yahia, M. Shikano, M. Tabuchi, H. Kobayashi, M. Avdeev, T. T. Tan, S. Liu and C. D. Ling, Inorg. Chem., vol. 53, no. 1, p. 365–374, 2014. [4] Tapan Chatterji et al 2010 J. Phys.: Condens. Matter 22 316001