Experimental report

19/10/2022

Proposal: 5-31-2841 **Council:** 10/2020

Title: Determining the magnetic structures of the Cr-based antiperovskites Cr3BN (B = Ge and As)

Research area: Physics

This proposal is a new proposal

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Samples: Cr3AsN
Cr3GeN

Instrument	Requested days	Allocated days	From	To
D20	2	2	17/05/2021	19/05/2021

Abstract:

Antiperovskites, A3BX, have received only a small fraction of interest compared to conventional perovskites, ABX3, however it is now being realised that they also display similarly diverse properties whilst maintaining the chemical flexibility of their better-known counterparts. One of the most studied antiperovskite families are those with Mn on the A-site. These materials have attracted a resurgence of interest due to the functional properties they display, such as caloric effects and anomalous thermal expansion, as a result of strong coupling between the magnetic and crystal structures. Materials with Cr on the A-site are far less studied and are largely expected to remain Pauli paramagnetic at all temperatures. However, recent experiments on Cr3BN (B = Ge and As) have suggested the emergence of long-range magnetic order and unusual structural distortions. We propose to use D20 to determine the magnetic structure in Cr3GeN and Cr3AsN across the structural transitions. By exploring novel phase transitions in antiperovskites we hope to expand the library of their structural and magnetic flexibilities in order to guide the synthetic design of functional materials.

Determining the magnetic structures of the chromium antiperovskites Cr_3BN (B = Ge and As)

Summary

The largest family of crystalline materials, ABX_3 perovskites, have attracted a huge amount of research interest due to their varied functional properties and intriguing underlying physics, chemistry and crystallography. Antiperovskites, A_3BX, have received only a small fraction of this interest, however it is now being realised that they also display similarly diverse properties whilst maintaining the chemical flexibility of their better-known counterparts [1]. One of the most studied antiperovskite families are those with Mn on the A-site [2]. These materials have attracted a resurgence of interest due to the functional properties they display as a result of strong coupling between the magnetic and crystal structures. Materials with Cr on the A-site are far less studied and are expected to remain Pauli paramagnetic at all temperatures. However, recent experiments on Cr_3BN (B = Ge and As) have suggested the emergence of long-range magnetic order and unusual structural distortions not found in the Mn-based materials. We propose to use D20 to determine the magnetic structure in $C_{r3}GeN$ and Cr_3AsN as a function of temperature across the structural transitions. By studying novel symmetry lowering phase transitions in antiperovskites we hope to expand the library of their structural and magnetic flexibilities. In turn, this will guide further exploration of this promising material family for designing functional materials.

The experiment

The aim of the experiment was to determine the magnetic order of 2 chromium based antiperovskites; Cr3GeN and Cr3AsN. Unfortunately, the sample of Cr3AsN was unavailable due to degradation of sample. The Cr3GeN sample was loaded into a standard can for the furnace. The material undergoes 3 transitions at T1 = 320K, T2 = 770K and T3 = 930K. Thermodiffractograms were collected in two regions (i) around the two transitions at higher temperature and (ii) around the transition at room temperature. No magnetic peaks were observed at low temperature. No magnetic peaks were observed below any of the transition temperatures. Rietveld refinements were carried out using the ISODISTORT package to model the structural transitions. Excellent fits were achieved using this method at all temperatures; a typical refinement is shown in Figure 1.

Interestingly, a number of additional peaks (non-magnetic) were observed at low angle below several of the transitions. As of yet, we have been unable to identify these peaks. We will shortly be performing T-dependent synchrotron diffraction experiments in order to understand these additional peaks. Once we have performed this experiment, we plan to publish this data to shed further light on the unusual structural transitions possible in these antiperovskite materials.

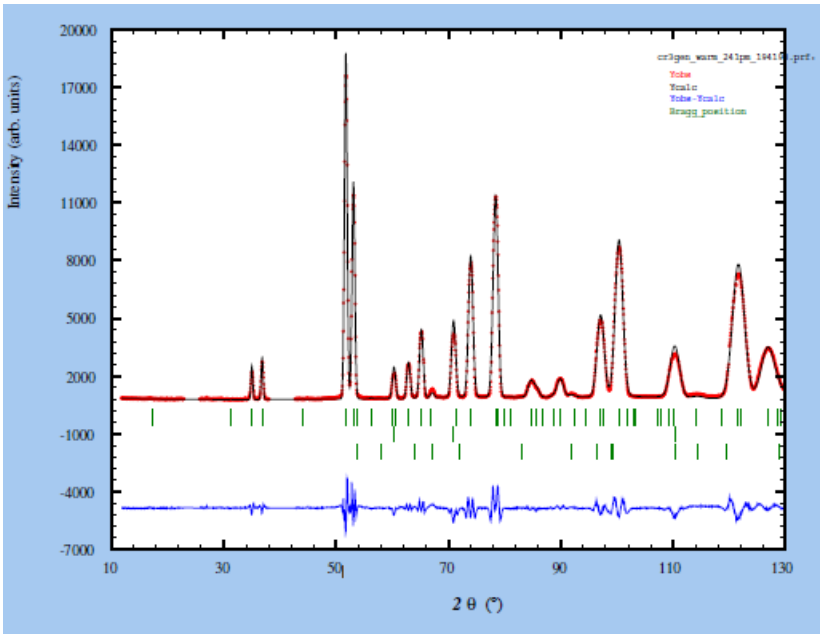

Figure 1: Rietveld refinement of Cr3GeN data collected on D20 at 450K. The data are fitted excellently using the I4/mcm model proposed in the literature.

References:

[1] Wang, Y. et al. (2020). Advanced Materials, 32(7), 1–17.
[2] (a) Chi, E. O., Kim, W. S. & Hur, N. H. Solid State Commun. 120, 307–310 (2001). (b) Takenaka, K. et al. Sci. Technol. Adv. Mater. 15, 15009–11 (2014). (c) S. Deng et al, *Chemistry of Materials* **27** 2495 (2015). (d) Boldrin, D., et al. (2018). Physical Review X, 8(4), 041035. [1e] Zemen, J., Gercsi, Z. & Sandeman, K. G., Phys. Rev. B 96, 1–8 (2017).