Experimental report

09/02/2017

Proposal: 5-31-2457 **Council:** 4/2016

Title: Impact of doping on the magnetic properties of holmium gallium garnet

Research area: Physics

This proposal is a new proposal

Main proposer: Paromita MUKHERJEE

Experimental team: Hugh GLASS
Sian DUTTON
Paromita MUKHERJEE

Local contacts: Emmanuelle SUARD

Samples: Ho3Sc2Ga3O12
Ho3Sc2Al3O12
Ho3CrGa4O12
Ho3MnGa4O12

Instrument	Requested days	Allocated days	From	To
D2B	2	2	04/06/2016	06/06/2016
D20	2	2	03/06/2016	05/06/2016
			05/06/2016	06/06/2016
D1B	2	0		

Abstract:

Lanthanide garnets Ln3A2X3O12 (usually Ln = Gd, Tb, Dy, Ho and A,X= Ga, Al, Fe) show a high degree of geometrical frustration and have been studied as potential magnetocalorics for cooling below 20 K. However the impact of chemical doping on the magnetic properties and magnetocaloric effect has not been investigated in much detail.
The proposed experiment focuses on Ln = Ho as Ho is suitable for powder neutron diffraction and we can synthesise powder samples of Ho garnets with a wide range of dopants-non-magnetic (Sc) and magnetic (Cr, Mn)on the A/X sites.
The exact distribution of the dopant ion (Cr or Mn) cannot be determined from powder X-Ray diffraction but this is important for understanding the impact of doping on the magnetic properties.Room temperature neutron diffraction experiments on D2B would give this information.
Magnetic measurements reveal ordering transitions for Ho3Sc2Al3O12 at T = 4.5 K and for Ho3MnGa4O12 at T = 5 K. We propose to study the nature of these transitions and solve the magnetic structure using powder neutron diffraction on D20 or D1B. The magnetic structure will also be compared with the parent compound, Ho3Ga5O12 to analyse the impact of dopin

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Background:

Lanthanide garnets have the general formula $Ln_3A_2X_3O_{12}$ (*Ln* = lanthanide ion and A, X usually = Ga, Al, Fe). They have three distinct cation sites depending on the coordination number with oxygen – dodecahedral occupied by Ln^{3+}, octahedral occupied by A^{3+} and tetrahedral occupied by X^{3+}. The Ln^{3+} ions form a highly frustrated three-dimensional network of corner-sharing triangles as shown in Fig. 1[1].

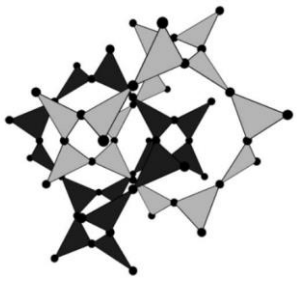


Fig. 1 – Connectivity of corner-sharing triangles of magnetic Ln^{3+} in lanthanide garnets

Chemical doping can radically alter the magnetic properties of the lanthanide garnets because the magnetic ground state is extremely sensitive to slightest perturbations in the crystal structure. Here we focus on the impact of doping in garnets with *Ln* = Ho. We prepared powder samples of: a) $Ho_3Sc_2X_3O_{12}$ (X = Ga, Al) where Sc is the non-magnetic dopant b) $Ho_3AGa_4O_{12}$ (A = Cr, Mn) where Cr and Mn are magnetic dopants. Samples were characterised by powder X-Ray diffraction (PXRD) and Rietveld Refinement. The magnetic susceptibility of all samples was measured down to 2 K – $Ho_3MnGa_4O_{12}$ exhibited a sharp magnetic ordering transition at 5.5 K while the other samples did not show any magnetic ordering down to 2 K.

Experimental aims and measurements:

1. Room temperature (RT) powder neutron diffraction (PND) experiments on D2B were carried out on all 4 samples for precise determination of the crystal structure, especially the exact distribution of cations on the octahedral and tetrahedral sites.
2. Low temperature (LT) PND measurements down to 2 K were carried out on D20 to determine the long-range ordered magnetic structure for $Ho_3MnGa_4O_{12}$ (corresponding to the ordering transition at 5.5 K). This would then be compared to $Ho_3Ga_5O_{12}$[2] to understand the effect of Mn doping. The other samples were also measured on D20 down to 2 K to check for any short-range ordering present (which may not be apparent in susceptibility measurements).

Nominal composition	Lattice parameter (Å)	Dopant	Fraction of dopant on octahedral site
$Ho_3Sc_2Ga_3O_{12}$	12.475167 (27)	Sc	0.72(2)
$Ho_3Sc_2Al_3O_{12}$	12.329722 (27)	Sc	0.84(1)
$Ho_3CrGa_4O_{12}$	12.28390 (6)	Cr	0.50(2)
$Ho_3MnGa_4O_{12}$	12.30409(3)	Mn	0.56(2)

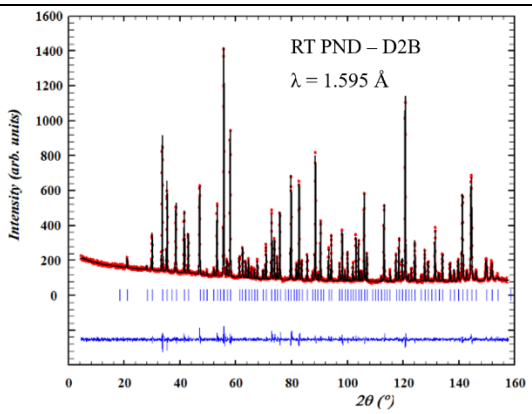
Table 1: Selected parameters from RT combined crystal structure refinements – PXRD + PND data on D2B

Results:

1. Crystal structure determination for all 4 samples (D2B):

Combined RT PXRD+ PND refinements were carried out for all 4 samples using Fullprof. All the Ho garnets are found to crystallise in the cubic *Ia-3d* space group. The non-magnetic dopant, Sc^{3+}, in $Ho_3Sc_2X_3O_{12}$ (X = Ga, Al) as well as the magnetic dopants, Cr^{3+} and Mn^{3+} in $Ho_3AGa_4O_{12}$ (A = Cr, Mn) are found to exclusively occupy the octahedral sites. Table 1 gives selected parameters from the

crystal structure refinement for all 4 samples and Fig. 2a shows the RT PND refinement for $Ho_3MnGa_4O_{12}$.



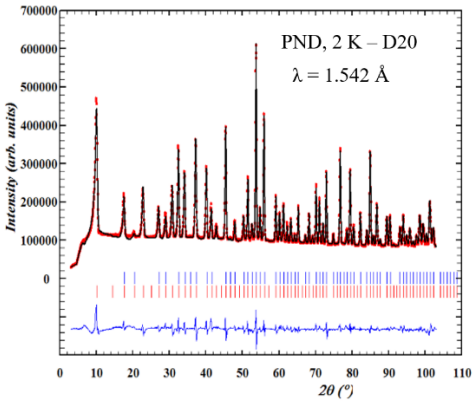


Fig 2: a) RT PND Rietveld refinement on D2B b) Magnetic Rietveld refinement at 2 K on D20 for $Ho_3MnGa_4O_{12}$

2. Magnetic structure determination (D20):

No magnetic Bragg peaks were observed for $Ho_3Sc_2X_3O_{12}$ (X = Ga, Al) and $Ho_3CrGa_4O_{12}$ down to 2 K. For $Ho_3MnGa_4O_{12}$, strong magnetic Bragg peaks are observed at 2 K; the intensity of these peaks decreases with temperature until they completely disappear at 6 K (> T_N = 5.5 K). No diffuse scattering is observed for $Ho_3MnGa_4O_{12}$ at 2 K. The magnetic structure has been indexed by the vector **k** = 0 using the program ksearch in the Fullprof Suite. Different combinations of irreducible representations for Ho^{3+} and Mn^{3+} were tried using the program SARAH. These irreducible representations were combined in SARAH to generate a single magnetic phase; the final magnetic Rietveld refinement was carried out in Fullprof. Fig. 2b shows the magnetic Rietveld refinement for $Ho_3MnGa_4O_{12}$ at 2 K; the magnetic structure is shown in Fig. 3.

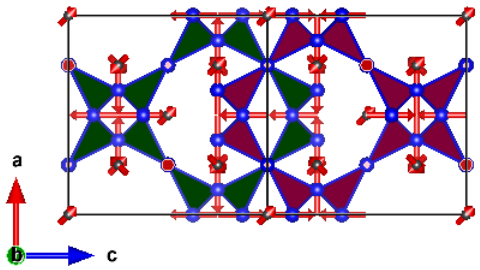


Fig. 3 – Magnetic structure for $Ho_3MnGa_4O_{12}$

Conclusions:

Combined PXRD + PND refinements at RT using the RT PND data on D2B helped in determining the precise crystal structure for $Ho_3Sc_2X_3O_{12}$ (X = Ga, Al) and $Ho_3AGa_4O_{12}$ (A = Cr, Mn). The LT data for $Ho_3MnGa_4O_{12}$ on D20 enabled us to solve the long-range ordered magnetic structure for $Ho_3MnGa_4O_{12}$, clearly showing the drastic effect Mn doping has on $Ho_3Ga_5O_{12}$. The LT data for the other three samples has motivated us to investigate the existence of ordering at T<2 K through bulk measurements.

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

References:

1. C. P. Reshmi, *et. al*, J. Magn. Mat. **324**, 1962 (2012)
2. H. D. Zhou, *et. al*, PRB **78** (2008)