Experimental report

04/04/2017

Proposal:	**5-31-2516**	**Council:**	10/2016
Title:	Determining the magnetic configurations of GdCrO3 using high energy neutrons		
Research area:	Physics		

This proposal is a new proposal

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Experimental team:	Tapan CHATTERJI Henry FISCHER
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Samples: GdCrO3 polycrysallites

Instrument	Requested days	Allocated days	From	To
D4	5	4	01/02/2017	05/02/2017

Abstract:

As a functional material, GdCrO3 is of fundamental scientific interest due to number of significant properties like spin reorientation , magnetoelectric or multiferroic properties and magnetic anisotropy. GdCrO3 is suggested to be ordered in a canted antiferromagnetic structure Γ4 (Gx, Ay, Fz, ; FzR) below Néel temperature (TN) at 170K due to Dzyaloshinsky-Moriya (D-M) exchange coupling between the Cr atoms. There is no report available in literature discussing the neutron diffraction of GdCrO3 due to high absorption of natural Gd atom. Thus, the evolution of magnetic configuration across antiferromagnetic and ferroelectric transitions is still questioned. The proposed experiment aims to study the evolution of magnetic structure of polycrystalline GdCrO3 across TN and ferroelectric temperature. Considering the high energy neutrons as a possible way to determine magnetic structure of highly absorbing materials, we have recently measured the neutron diffraction of SmCrO3 with natural Sm atoms successfully. The present proposal also requires the wavelength λ= 0.5Å neutron at Disordered Materials diffractometer D4 in order to reduce absorption.

Evolution of magnetic structure in highly neutron absorbing $GdCrO_3$ polycrystallites

Introduction

Being a member of functional material family of rare earth orthochromites, $GdCrO_3$ is emerging compounds due to novel magnetic and dielectric anomalies, anomalous magnetization reversal, multiferroic properties and controversial spin reorientation phase transition [1,3], making them potential candidate for ultrafast spin switching to modify recording media, thermomagnetic power generation and magnetic refrigeration.

Fig.1 shows the M(T) curves in zero field cooled warming(ZFC), field cooled cooling (FCC), field cooled warming(FCW) curves with applied magnetic field μ_0H= 0.01T. Before the measurement the remnant field trapped inside superconducting windings of magnet was minimized to minimum value~4 Oe by following de-Gauss method. Clearly, we have observed huge magnetization reversal in FCC mode below T_{comp}. Qualitatively, this phenomena is assumed to be originated because of opposite alignment of the Gd^{3+}moments to that of the canted Cr^{3+} moments causing a resultant magnetic moment which is opposite to applied field held by the anisotropy energy [4]. This energetically unfavorable configuration should be a non-equilibrium metastable state. But as observed, the moment value in this configuration changes negligibly (only by~0.4%) during 2 days of measurements (t~10^6 s). This stability of the system in magnetically reversed state raise doubts on the proclaimed mechanism of negative magnetization in this system. To understand and confirm the origin of this phenomenon, we need to determine the magnetic ordering of Gd and Cr spins below T_N and their evolution as the temperature is lowered. Neutrons scattering is a useful technique to probe the spin configuration and magnetism on microscopic level. But because of high absorption of neutrons, Gd-containing materials have been always disregarded for neutron diffraction experiment. Using the idea that neutron absorption cross section decreases with

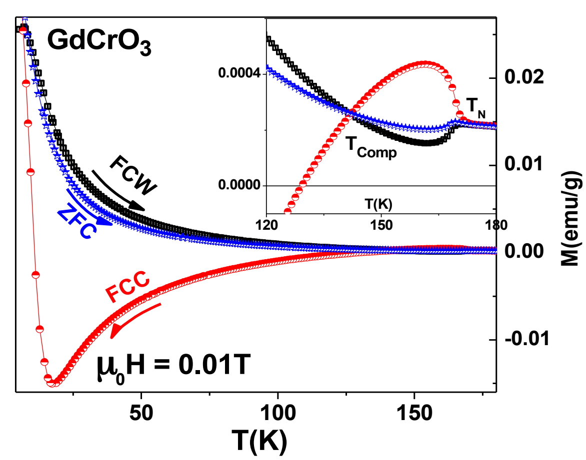
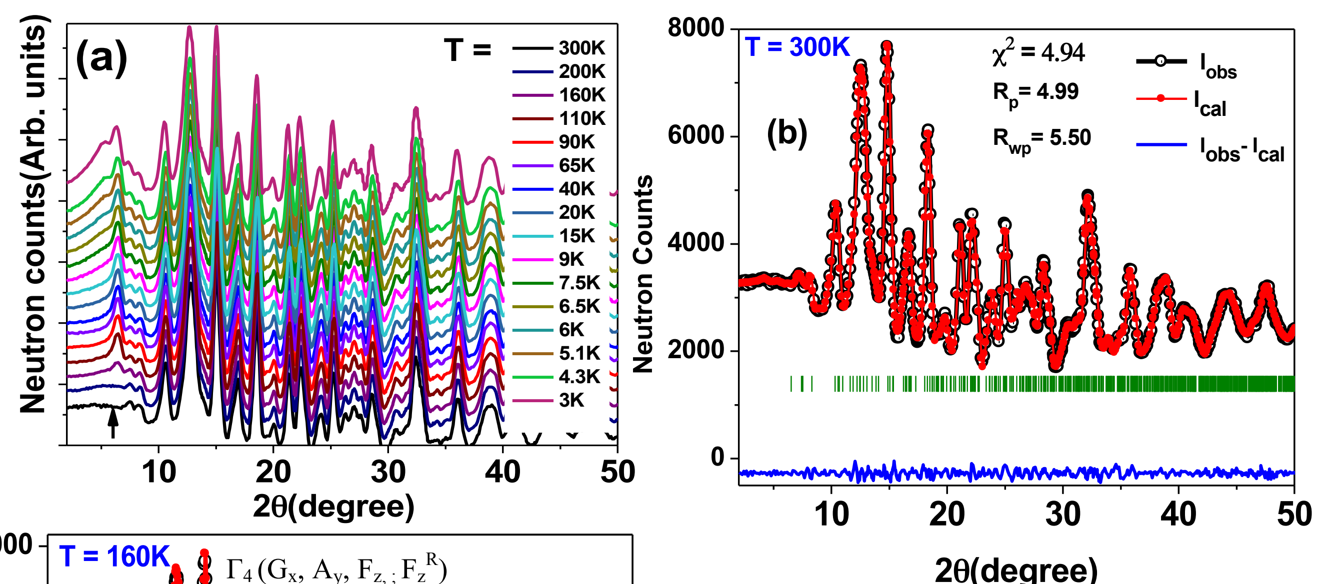


Fig. 1 The M(T) curves following ZFC, FCW and Field FCC protocol at 0.01T applied magnetic field.

increase in energy of neutrons, we performed an experiment at D4, ILL using short wavelength "hot neutrons". As shown in Fig. 2(a), we were able to observe distinct magnetic peaks below the Néel temperature.

Experiment

We used hot neutrons with λ= 0.4998.Å reflecting from Cu (220) monochromator at liquid and amorphous Diffractometer D4. After calibration of the neutron wavelength using a nickel powder sample, the neutron diffraction intensity was normalized using standard vanadium sample and corrected for background attenuation, multiple-scattering, and inelasticity (Placzek) effects. We measured the spectra at various temperatures ranging from 3-300K in warming mode without applying magnetic field.



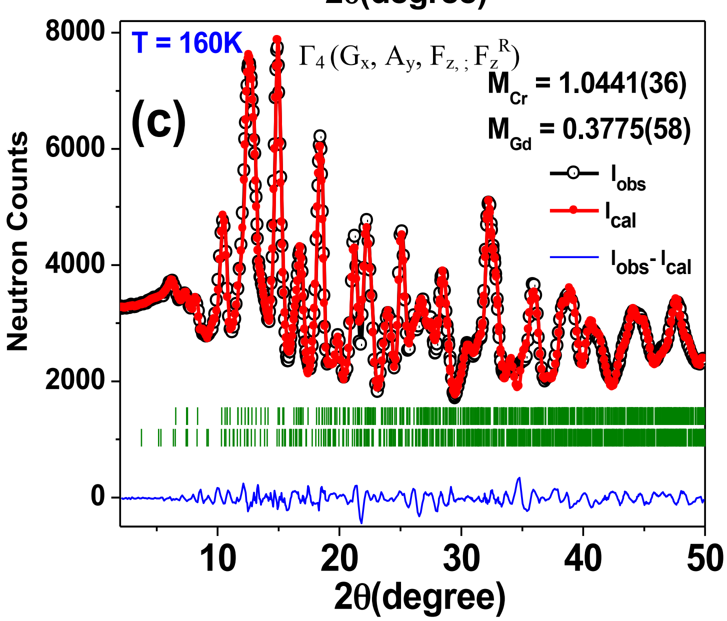


Fig. 2(a): Thermal evolution of neutron diffraction pattern **(b)** and **(c)** shows the structural and magnetic refinements of neutron diffraction patterns at 300K and 160K.

	Atom	Fractional coordinates			Thermal Parameter (A^2)	Lattice Parameter	Statistical
		X	y	z			
300K							
	Gd(4c)	-0.0136 (77)	0.05767(25)	0.25000	0.110(13)	a=5.3680(11) b=5.5609(13) c=7.6317(15)	R_p= 4.99 R_{wp}=5.50 X^2= 4. 94 R_{exp}= 3.12
	Cr (4b)	0.5	00	0.0	0.358(5)		
	O1(4c)	0.0661(15)	0.4612(81)	0.25			
	O2(8d)	-0.3092(24)	0.3107(86)	0.0477(9)			
160K							
	Gd(4c)	0.0158 (3)	0.0597(13)	0.2500	0.785(50)	a = 5.3249(8) b= 5.5441(11) c= 7.6204(12)	R_p=5.79 R_{wp}=6.72 R_{exp}= 3.56 X^2= 5.48
	Cr(4b)	0.5000	0.0000	0.0000	0.125(31)		
	O1(4c)	0.0763(84)	0.4688(15)	0.2500			
	O2(8d)	-0.304(9)	0.3083(13)	0.0503(19)			

The lower angle part of neutron diffraction data along with the Rietveld refined patterns is shown in Fig. 2(b) and 2(c). Below T_N, a peak of magnetic origin appears at (010) and (101) Bragg positions and below 7K magnetic peak (001) begin to appear. The calculated pattern is generated with distorted orthorhombic structure (Pbnm space group) and **k** = (0,0,0) propagation vector. The representation analysis using program *BasIrpes* leads to four allowed spin configurations for Cr atoms at 4b Wyckoff positions and 8 possible spin configurations for Gd at 4c Wyckoff positions. For the simultaneous ordering of both Cr and Gd atoms only four irreducible representations $\Gamma_{2,}$ $\Gamma_{4,}$ Γ_6 and Γ_8 are possible. Using the Fullproof for Rietveld refinement of the crystal and magnetic structure we found that Γ_4 representation provides unambiguously agreeable matching with experimental and calculated patterns for T=160K (<T_N). All of the structural parameters obtained from the refinement process are listed in Table.1. The determination and analysis of the magnetic structure below T_{comp} is still in progress.

References:

[1] Shuijin Lei, Lei Liu, Chunying Wang, Chuanning Wang, Donghai Guo, Suyuan Zeng, Baochang Cheng, Yanhe Xiao and Lang Zhou, J. Ma, J. Mater. Chem. A, **1**, 11982 (2013)

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[4] K. Yoshii Journal of Solid State Chemistry, **159**, 1, 2001, 204.