Experimental report

09/02/2016

Proposal: **5-41-801** **Council:** 10/2014

Title: Possible mechanism of emergence ofsignificant spontaneous electric polarization in orthoferrite HoFeO3.

Research area: Physics

This proposal is a new proposal

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Samples: HoFeO3

Instrument	Requested days	Allocated days	From	To
D10	10	6	24/04/2015	30/04/2015

Abstract:

We propose to investigate occurrence of polar order in HoFeO3 single. High quality of HoFeO3 single crystal is cut along three crystallographic directions. Our careful pyroelectric measurement reveals an evident signature of a peak in the pyroelectric current below the spin reorientation transitions along [101] and [001] directions. Thermal variations of spontaneous electric polarization along [010 and [001] shows that polar ferroelectric order appears below the spin reorientation transition. We could not convincingly detect polar order along [100] direction. We note that the magnitude of electric polarization is 9.2 and 12.4 µC/cm2 along [010] and [001] directions, respectively which is significantly higher than the previous reports in RFeO3 (R=Sm, Gd, and Dy). To understand the microscopic origin of the ferroelectric polarization in HoFeO3 we propose to perform single crystal neutron diffraction studies as a function of temperature from 100 K down to 2 K (well below spin reorientation transition temperature) at zero and applied magnetic field and also as a function of magnetic field up to 5 T. We request 10 days of neutron beam time on D10 for the proposed experiment.

Temperature evolution of magnetic structure of $HoFeO_3$

The magnetic structure of $HoFeO_3$ has been studied by neutron powder diffraction a long time ago. The distorted perovskite crystal structure of $HoFeO_3$ [1] is described using space group Pbmn , its magnetic structures were determined in early neutron diffraction measurements on powder samples [2,3] . It was found that the Fe sub-lattices order antiferromagnetically in the G-type configuration [4] with a Neel temperature of 647 K. At room temperature the Fe moments are approximately parallel to [100] and at 43 K lie in a (110) plane. Below a Neel temperature of 6.5 K the Ho sub-lattices order with their moments in the ab-plane at 27 deg. to y leading to a ferromagnetic component of moment parallel to x . The recent observation of a ferroelectric transition at 225 K [5] means that the true point symmetry of $HoFeO_3$ at 65 K cannot be higher than mm2, making the likely space group $Pbn2_1$.

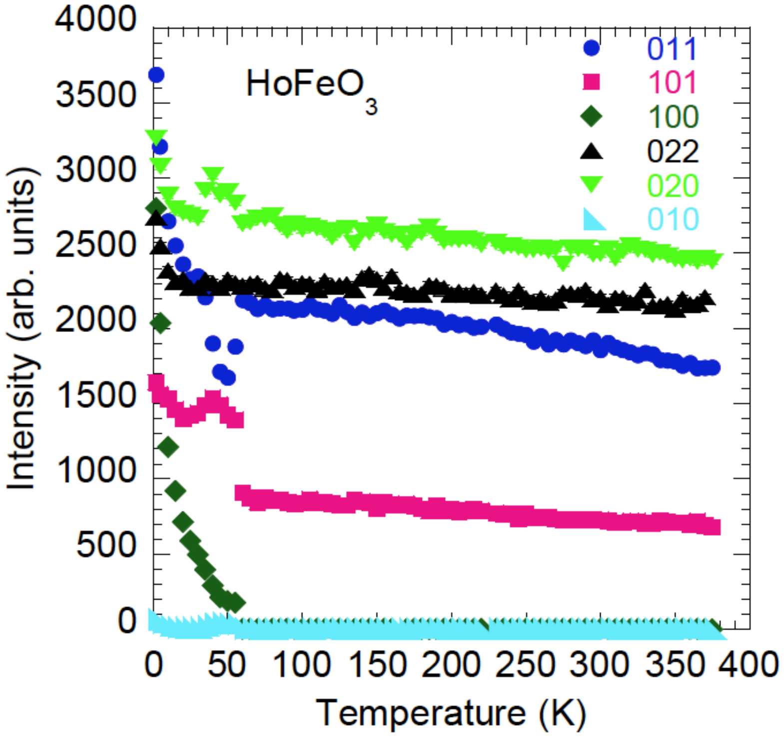

Fig. 1 – Temperature variation of a few (nuclear+magnetic) reflections.

We have done neutron diffraction on a small single crystal of $HoFeO_3$ on the diffractometer D10. The crystal was mounted on the cold tip of the D10 cryostat with its [100] crystallographic axis approximately parallel to the ω-axis of the diffractometer. At first we measured the temperature variation of a few reflections shown in Fig. 1. From these temperature variation of the reflections that have magnetic contribution we can observe two magnetic transition around T in the range of 35 to 55 K. We then measured intensity data at T = 5, 40, 55, 175 and 245 K. With the limited range of data available it was not possible to refine both the positional and magnetic parameters together. The 240 K data was therefore used in a refinement of the scale factor, the positional parameters and a single extinction parameter (mosaic spread) using each of the two symmetries with the Fe moment fixed to 4 μ_B. Both refinements gave a reasonable, although not very good (R=12), fit to the data but yielded unphysical, negative, values for the temperature factors and a very large value for the mosaic spread parameter suggesting that the data suffers from strong extinction. The extinction parameter and the scale factor were strongly correlated.

We measured diffraction intensities from $HoFeO_3$ crystal in a much larger Q range on the Heidi diffractometer at FRM II, Garching. By combining the D10 and Heidi data set we could refine the magnetic structures much better. The three different magnetic structures found as a function of temperature for $HoFeO_3$ are illustrated schematically in Fig. 2. They are described by the magnetic groups $Pb'n'2_1$, $Pbn2_1$ and Pbn'2'1 and are stable in the temperature ranges 600 -55 K, 55-37 K and

35-2 K respectively. In all three structures the fundamental coupling between the Fe sub-lattices remains the same and only their orientation and the degree of canting away from the ideal axial direction varies. The magnetic polarization of the Ho sub-lattices in these two higher temperature regions, in which the major components of the Fe moment lie along x and y, is very small. The origins and type of the reorientation transitions, which can occur in the rare earth orthoferrites have been discussed by Yamaguchi [6]. He shows that an abrupt transition from Γ_4 (Pb'n'2_1) to Γ_1 (Pbn2_1), such as that at 55 K in HoFeO3 , can occur when, with falling temperature, the energy due to anisotropic exchange between Ho and Fe ions outweighs that due to Fe anisotropy alone which favors the Γ_4 configuration. He does not include criteria for the non-abrupt Γ_2 to Γ_1 transition which takes place in HoFeO3 between 37 and 30 K.

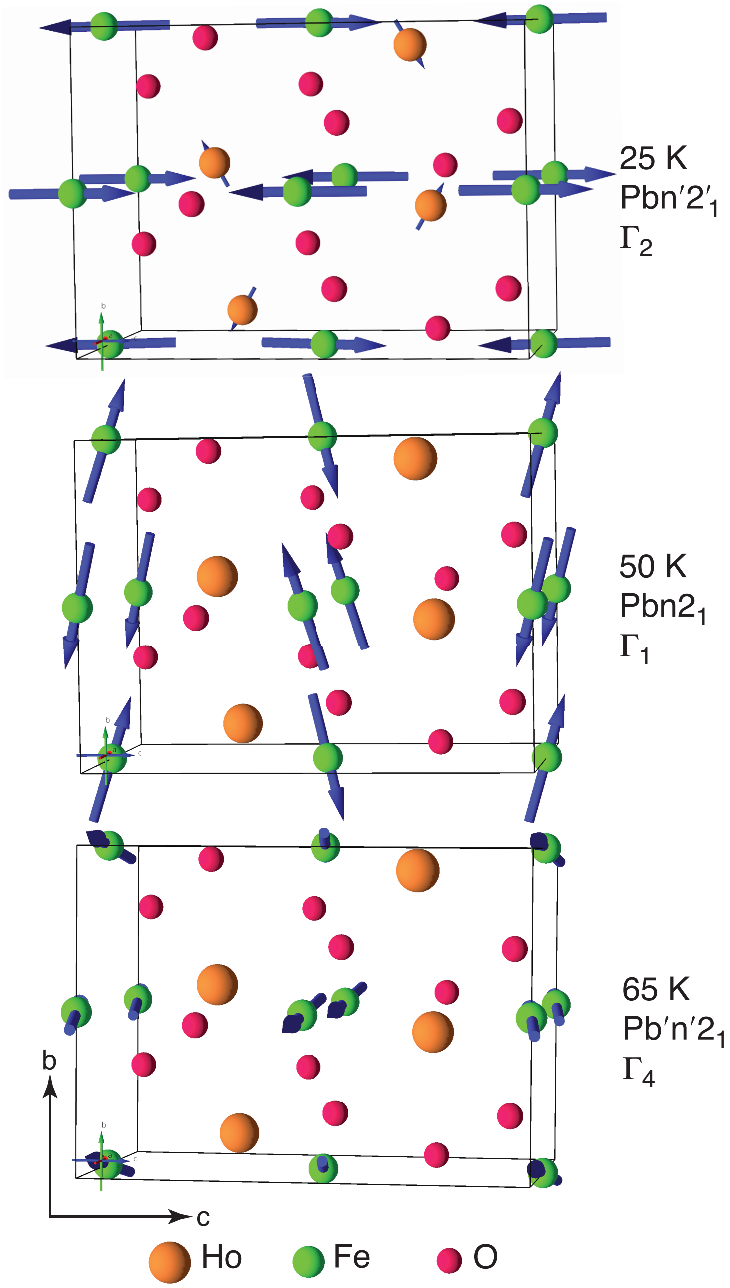

Fig. 2 – Schematic representation of the three modulation modes found for the ordered magnetic structures of $HoFeO_3$.

Figure 3 illustrates the evolution of the structure as the Ho sub-lattices order. The major component of the Ho moment is always parallel to y and the anisotropic exchange interaction forces the Fe moments to reorient along z. In Pbn'$2'_1$ components of moment in the x direction are ferromagnetically aligned and it is the direction of this ferromagnetic moment relative to MHo x MFe, which changes sign twice as on cooling from 30 - 2.5 K. Weak ferromagnetism in the orthoferrites has been attributed to to the antisymmetric exchange interaction between magnetic ions [7] . In $HoFeO_3$ below 30 K it is the sum of contributions from both Fe and Ho and will have the form

$$\begin{aligned} E_{\text{antisymmetric}} = &\sum_{i=1,4}^{j=i+1,4} \mathbf{D}_{\text{FeFe},i,j} \cdot (\mathbf{M}_{\text{Fe}}(i) \times \mathbf{M}_{\text{Fe}}(j)) + \mathbf{D}_{\text{HoHo},i,j} \cdot (\mathbf{M}_{\text{Ho}}(i) \times \mathbf{M}_{\text{Ho}}(j)) \\ &+ \sum_{i=1,4}^{j=1,4} (\mathbf{D}_{\text{FeHo},i,j} \cdot \mathbf{M}(_{\text{Fe}}(i) \times \mathbf{M}_{\text{Ho}}(j)) \end{aligned} \quad (1)$$

The Dzyaloshinski vectors [8] may include contributions from single ion anisotropy as well as anti-symmetric exchange. This antisymmetric exchange energy varies rapidly in the temperature range in which the Ho sub-lattices are ordering; whilst the ordered Ho moments are small it is dominated by the terms containing D_{FeFe} and the sense of the ferromagnetic moment is determined by the first summation in eqn.1. As the degree of Ho order increases the terms in the third summation, that containing products of the Fe and Ho moments, begin to exceed those dependent on Fe moments only and the sense of the ferromagnetic moment may change. Finally at the lowest temperatures when the Ho moments approach saturation the Ho-Ho interactions dominate. The behavior observed in this experiment shows that for $HoFeO_3$ the sums of the Fe-Fe and Ho-Ho interactions have the same sign, but that of the Ho-Fe terms is opposite.

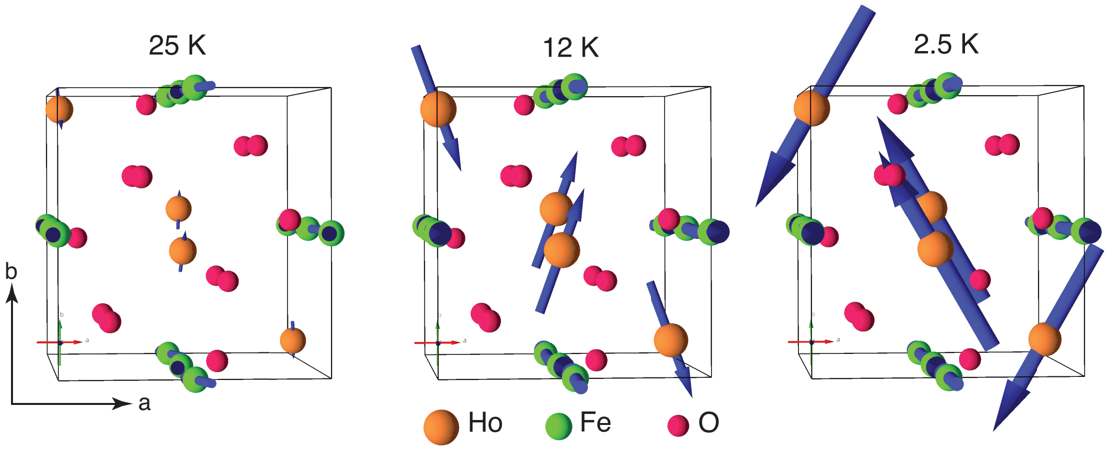

Fig. 3 - Variation of the relative orientations of the Fe and Ho moments in $HoFeO_3$ *with increasing order in the Ho sub-lattice.*

References:

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