Temperature evolution of magnetic structure of $HoFeO_3$ by single crystal neutron diffraction

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We have investigated the temperature evolution of the magnetic structures of $HoFeO_3$ by single crystal neutron diffraction. The three different magnetic structures found as a function of temperature for $HoFeO_3$ are described by the magnetic groups $Pb'n'2_1$, $Pbn2_1$ and $Pbn'2_1'$ and are stable in the temperature ranges $\approx$ 600-55 K, 55-37 K and $35> T > 2$ K respectively. In all three 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 polarisation 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 canting of the moments from the axial directions is attributed to the antisymmetric interactions allowed by the crystal symmetry. They include contributions from single ion anisotropy as well as the Dzyaloshinski antisymmetric exchange. In the low temperature phase two further structural transitions are apparent in which the spontaneous magnetisation changes sign with respect to the underlying antiferromagnetic configuration. In this temperature range the antisymmetric exchange energy varies rapidly as the the Ho sub-lattices begin to order. So long as the ordered Ho moments are small the antisymmetric exchange is due only to Fe-Fe interactions, but as the degree of Ho order increases the Fe-Ho interactions take over whilst at the lowest temperatures, when the Ho moments approach saturation the Ho-Ho interactions dominate. The reversals of the spontaneous magnetisation found in this study suggest that in $HoFeO_3$ the sums of the Fe-Fe and Ho-Ho antisymmetric interactions have the same sign as one another, but that of the Ho-Fe terms is opposite.
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I. INTRODUCTION

Rare-earth orthoferrites $RFeO_3$ where R is a rare-earth element constitute an important family of magnetic compounds intensively studied over several decades starting from the early forties of the last century. The presence of two distinct magnetic species and the consequent co-existence of magnetic interactions: Fe-Fe, Fe-R, R-R of decreasing strengths make these compounds liable to undergo several magnetic transitions as a function of temperature. Due to the strong Fe-Fe exchange interaction the Fe subsystem usually orders with a Néel temperature $T_N \sim 620 - 740$ K as a slightly canted antiferromagnetic structure with weak ferromagnetism. Although the interactions leading to the weak ferromagnetism are small they still play an important role in determining the magnetic properties and spin reorientation transitions at lower temperatures. The R-R interaction is relatively weak which means that the rare-earth sub-lattices only order below $T_{NR} \sim 5 - 10$ K . Above T_{NR} the R ions are paramagnetic but experience the molecular field of the ordered Fe sub-lattice which magnetize them partially[1–8]. The interactions within the Fe and R sub-systems are distinct from one another, and change with temperature, field and elastic stress; the competition of these with interactions between the two sub-systems lead to several possibilities for spin reorientation transitions which have been studied in both bulk materials and thin films[1–3,9–12]. Recently interest in the rare-earth orthoferrites has been revived by reports of multiferroic properties (co-existence of magnetic and ferroelectric ordering) in some members of the series[13–16]. Multiferroicity, by which a magnetic field may influence ferroelectric polarisation and electric fields magnetisation, has been reported, although contested, in the three compounds: $DyFeO_3$, $GdFeO_3$ and $SmFeO_3$[13–16]. In some materials ferroelectricity appears only on application of magnetic field. $HoFeO_3$ is very similar in both structure and magnetic properties to the aforementioned three compounds, so one may conjecture that it will also show similar multiferroic behaviour. It is for this reason that we have undertaken a more detailed study of the temperature variation of its magnetic structure.

The distorted perovskite crystal structure of $HoFeO_3$[17] is described using space group Pbmn, its magnetic structures were determined in early neutron diffraction measurements on powder samples[18,19]. It was found that the Fe sub-lattices order anti-ferromagnetically in the G-type configuration[20] with a Néel temperature of 647 K. It was reported that at room temperature the Fe moments are approximately parallel to [100] and at 43 K lie in a $(1\bar{1}0)$ plane. Below a Néel temperature of 6.5 K the Ho sub-lattices order with their moments in the ab plane at 27° to y leading to a ferromagnetic component of moment parallel to x.

So far all investigation on the temperature dependence of the magnetic structure of $HoFeO_3$ were done on powder samples. In this study we have investigated the temperature evolution of the magnetic structure of $HoFeO_3$ using single crystal samples. In the following sections we describe the results of single crystal neutron diffraction experiments and the several magnetic structures and transitions which they imply. Finally we discuss the evolution of the magnetic structure by evoking the antisymmetric Dzyaloshinski interaction.

The recent observation of a ferroelectric transition at $\approx$225 K[21] means that the true point symmetry of $HoFeO_3$ below this transition cannot be higher than mm2, making the likely space group $Pbn2_1$. In the rest of this paper the space group $Pbn2_1$ is assumed in all the structure refinements and each magnetic structure proposed conforms to one of its magnetic sub-groups.

II. EXPERIMENTAL

Neutron diffraction measurements have been made on two small single crystals using the hot neutron diffractometer Heidi of the FRM II reactor in Garching, Germany. The crystals were grown by flux method by S.N. Barilo and D.I. Zhigunov in Minsk, Belarus. This diffractometer provides a beam of monochromatic neutrons with wavelength in the range 0.55 to 1.2 Å . In the present experiment a wavelength of 0.7925 Å was used which allowed measurement of the intensities of Bragg reflections with $\sin\theta/\lambda$ up to 1.25 Å^{-1}. The sample was contained in a closed cycle cryostat with which the temperature could be controlled in the range 2 - 300 K.

III. MAGNETIC SYMMETRY AND STRUCTURE FACTORS FOR HOFEO$_3$

When described using the space group Pbnm both the Fe and Ho atoms occupy special positions. The symmetry of the Fe sites is $\bar{1}$ and that of the Ho sites m. In space group $Pbn2_1$ the Ho and Fe atoms each occupy a set of 4-fold general positions. The symmetry operations generating the 4 sites are listed in table I and, assuming the atomic shifts associated with the ferroelectric transition are small, the relative phases and signs of the contributions which each Fe sub-lattice makes to the structure factor are those listed in table II. The relative phases of contributions from the Ho sub-lattices are similar except that, because x_{Ho} and y_{Ho} are non-zero, cancellation between the positive and negative contributions is not exact and ordered Ho moments can contribute to all general reflections. The relative directions of

TABLE I. Symmetry operations in space group $Pbn2_1$ and atomic positions in the structure of $HoFeO_3$.

sub-lattice		Operator				Fe Sites			Ho sites[a]		
1	E	x	y	z	0	$\frac{1}{2}$	0	x_{Ho}	$-y_{Ho}$	$\frac{1}{4}$
2	b	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z	$\frac{1}{2}$	0	0	$\frac{1}{2}-x_{Ho}$	$\frac{1}{2}-y_{Ho}$	$\frac{1}{4}$
3	n	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1/2+z$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}+x_{Ho}$	$\frac{1}{2}+y_{Ho}$	$\frac{3}{4}$
4	2_1	$-x$	$-y$	$1/2+z$	0	$\frac{1}{2}$	$\frac{1}{2}$	$-x_{Ho}$	y_{Ho}	$\frac{3}{4}$

[a] x_{Ho}=0.98141 and y_{Ho}=0.06857

TABLE II. Relative phases and signs of the contributions of Fe atoms to the structure factors of reflections from $HoFeO_3$.

sub-lattice	Position	Phase/π	$h+k$ even l even	$h+k$ even l odd	$h+k$ odd l even	$h+k$ odd l odd
1	0 $\frac{1}{2}$ 0	0	+	+	+	+
2	$\frac{1}{2}$ 0 0	$h+k$	+	+	-	-
3	$\frac{1}{2}$ 0 $\frac{1}{2}$	$h+k+l$	+	-	-	+
4	0 $\frac{1}{2}$ $\frac{1}{2}$	l	+	-	+	-
		Reflection Type [a]	F	A	C	G

[a] The reflection types have been assigned to match those used by[19]

the components of moments of magnetic ions in the 4 sub-lattices of space group $Pbn2_1$ for the 4 compatible magnetic symmetry groups are listed in table III.

IV.   TEMPERATURE DEPENDENCE OF MAGNETIC SCATTERING FROM HOFEO$_3$

The integrated intensities of 8 low angle reflections, two from each of the groups F,C,A and G, were measured from a single crystal of $HoFeO_3$ as a function of temperature in the range 2.5 to 65 K using a neutron wavelength of 0.7925 Å. The results are presented in figure 1. Above about 40 K significant intensity is only observed in the 020 and 022 nuclear reflections (type F) and in 101 and 011 (type G) reflections. The latter are systematic absences for nuclear scattering in $Pbn2_1$ and must be due to magnetic scattering from Fe. Inspection of table III shows that G type reflections can occur for three out of the 4 magnetic groups. For the magnetic group $Pbn2_1$ there must be components of moment parallel to y, for $Pbn'2_1'$ to z and for $Pb'n'2_1$ to x. The observation that 011 is significantly more intense than 101 supports the conclusion[18] that in this temperature range the Fe moments are nearly parallel to x, the magnetic group is therefore $Pb'n'2_1$. At $\approx$ 55 K figure 1 there is a sharp transition in which the relative intensities of 011 and 101 change over. Between 55 and 45 K 011 is significantly weaker than 101 although there is no notable change in any of the other reflection intensities. This behaviour confirms that there is a reorientation transition at $\approx$ 55 K in which the magnetic space group changes to $Pbn2_1$ and the Fe moments switch to the y direction. Between 40 and 30 K the intensity of the 011 reflection gradually recovers, whilst that of 101 drops very slightly. This suggests a further change in magnetic space group to $Pbn'2_1'$ with the major component of the Fe moments reorienting parallel to z. In this temperature range also intensity starts to appear in the 100 and 102 C type reflections and the intensity of these reflections increases rapidly at lower temperatures in a way which suggests that it is due to ordering of the Ho sub-lattices. In the magnetic group $Pbn'2_1'$ the C type reflections are due to y components of moment so it can be concluded that when the Ho sub-lattices order their major moment component

TABLE III. Relative directions of components of moments on magnetic ions on the different sub-lattices of the $HoFeO_3$ structure.

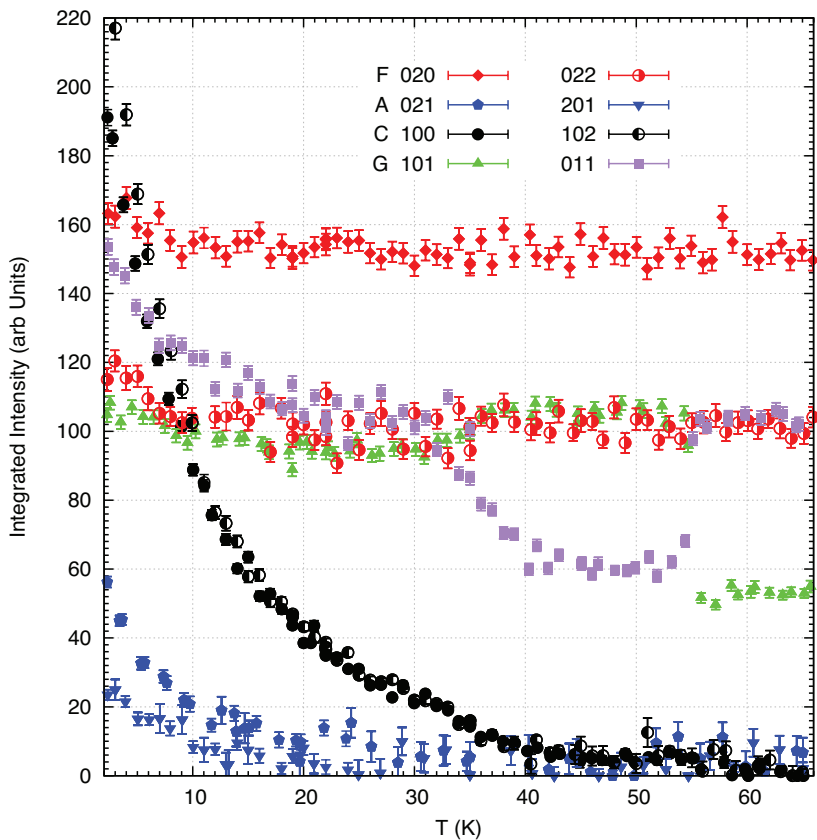| sub-lattice & Operator	$Pbn2_1$ (Γ_1) M_x	M_y	M_z	$Pbn'2_1'$ (Γ_2) M_x	M_y	M_z	$Pb'n2_1'$ (Γ_3) M_x	M_y	M_z	$Pb'n'2_1$ (Γ_4) M_x	M_y	M_z
1 E	+	+	+	+	+	+	+	+	+	+	+	+
2 b_x	+	-	-	+	-	-	-	+	+	-	+	+
3 n_y	-	+	-	+	-	+	-	+	-	+	-	+
4 2_{1z}	-	-	+	+	+	-	+	+	-	-	-	+
Type	A	G	C	F	C	G	C	F	A	G	A	F

FIG. 1. Temperature dependence of the integrated intensities of selected reflections from an HoFeO$_3$ single crystal

is in the y direction.

V. DETERMINATION OF THE MAGNETIC STRUCTURE PARAMETERS

A. The 65 K structure: absolute scale and extinction

With the polar space group Pbn2$_1$ both the Fe and Ho occupy general positions so that, although the magnetic space group dictates the relative directions of the components of moment on the different sub-lattices, there are no symmetry constraints on the magnitude and direction of the moments at the sites defined by the identity operator E. To determine these parameters the integrated intensities of a large number of reflections (911) with $\sin\theta/\lambda < 1.25$ Å^{-1} have been measured at 65 K, 35 K and 2.5 K. The 65 K data were used to confirm the positional parameters, obtain a model for extinction in the crystal and determine the absolute scale of the measured intensities. Previous analysis of more limited data measured at a longer wavelength (2.36 Å) had shown that extinction was severe and that the the extinction and scale parameters were highly correlated. The early work on HoFeO$_3$[18] and our measurements at 2.36 Å at temperatures up to 300 K, show that at 65 K the Fe sub-lattices are almost fully ordered and that the magnetic scattering is confined to the type G reflections (those with $h+k$ and l both odd). Based on this and on the conclusions of section IV it was assumed that the magnetic scattering at 65 K could be modelled using the magnetic space group Pb′n′2$_1$ with Fe moments of 4.6 $\mu_{\rm B}$ oriented parallel to x. Least squares refinements of the nuclear positional parameters, the scale factor and a single extinction parameter were carried out using this magnetic model. For refinement of the positional and temperature parameters the centrosymmetric space group Pbnm was used, the refined parameters are listed in table IV. Again there was a high (90%) correlation between the scale factor and the extinction parameter, but reasonable agreement between observed and calculated structure factors was obtained with an R factor of 8.3 on structure factors and a goodness of fit $\chi^2 = 3.8$. The relatively high value of the residual R factor is probably due to imperfect modelling of the extinction. The model predicted that extinction reduces the intensities of the strongest (nuclear) reflections by a factor of nearly 3 and the strongest magnetic ones by factors of up to 2. It may be noted that the only really significant anisotropic temperature coefficients in table IV are the B(11) of iron

and both oxygens which suggests that the principal atomic shifts in the ferroelectric transition are in the x direction.

TABLE IV. Crystal structure parameters for $HoFeO_3$ obtained from least squares refinement of integrated intensity measurements at 65 K

Atom	x	y	z	$B(11)^a$ $B(23)$	$B(22)$ $B(13)$	$B(33)$ $B(12)$
Ho	0.9813(2)	0.0686(2)	0.2500	0.03(3)	-0.03(3)	-0.06(3) -0.00(3)
Fe	0	0.5000	0	0.11(2) 0.04(2)	-0.02(3) -0.00(2)	-0.04(2) -0.02(2)
O1	0.1098(3)	0.4601(3)	0.2500	0.13(5)	0.06(4)	-0.10(4) -0.02(4)
O2	0.6920(2)	0.3048(2)	0.0564(2)	0.12(3) -0.04(3)	-0.04(3) 0.01(3)	0.02(3) -0.04(3)

^{a} The anisotropic temperature parameters B(ij) are given in units of Å^{-2}.

B. Magnetic structure at 35 K and 2.5 K

The arguments presented in section IV make it likely that at 35 K the magnetic structure is transforming between configurations with different magnetic space groups: $Pbn2_1$ and $Pbn'2_1'$. Least squares refinements of the magnetic parameters were carried out for both groups using the crystal structure parameters, extinction and scale determined from the 65 K data and assuming the same saturated Fe moment of 4.6 μ_B. The results are presented in table V. A marginally better agreement was obtained with $Pbn'2_1'$ although it is probable that at this temperature some intermediate or mixed phase state is present.

TABLE V. Components of the magnetic moments of Fe and Ho $HoFeO_3$ obtained from least squares refinements using data collected at 35 K and 2.5 K

T (K)	Magnetic Group	Fe (μ_B) M_x	M_y	M_z	Ho (μ_B) M_x	M_y	M_z	$^a R_{cryst}$	χ^2
35	$Pbn2_1$	1.0(2)	-4.45(5)	-0.54(6)	-1.1(2)	0.7(2)	1.64(15)	9.47	4.5
	$Pbn'2'$	0.6(3)	-0.08(6)	-4.55(4)	1.1(2)	1.2(2)	-0.9(2)	9.37	3.8
2.5	$Pbn'2'$	0.47(14)	-0.24(12)	-4.57(2)	3.53(7)	7.90(6)	0.1(7)	7.4	4.2

^{a} $R_{cryst} = \sum_i |F_{obs} - F_{calc}| / \sum_i |F_{obs}|$

C. Temperature variation of the magnetic parameters

In order to trace how the details of the magnetic structure change with temperature the measurements of the 8 reflections followed over the whole temperature range 2 - 65 K were analysed further. The data were separated into groups for which measurements of all 8 reflections were present at temperatures within a temperature range of 2.5 K. For each group the values of 5 parameters were refined, these were the magnitude and orientation of the Ho moment and just the orientation of the Fe moment its magnitude being fixed at $4.6\mu_B$. The magnetic space groups used in different temperature ranges were: 66 - 55K $Pb'n2_1'$, 55 - 37 K $Pbn2_1$ and 34 - 2.5 K $Pbn'2_1'$. The temperature dependence of the x,y,and z components of moment on the representative (E) sub-lattice for Fe and Ho ions obtained is shown in figure 2. Besides the anomalies round 55 K and 35 K associated with the reorientation transitions there appears to be a significant break in the variation of the x components at 20 K and again at 10 K. In this temperature range the x-components of moments are aligned ferromagnetically and the breaks are associated with abrupt changes in the direction in which the Ho moment is canted away from the y-axis.
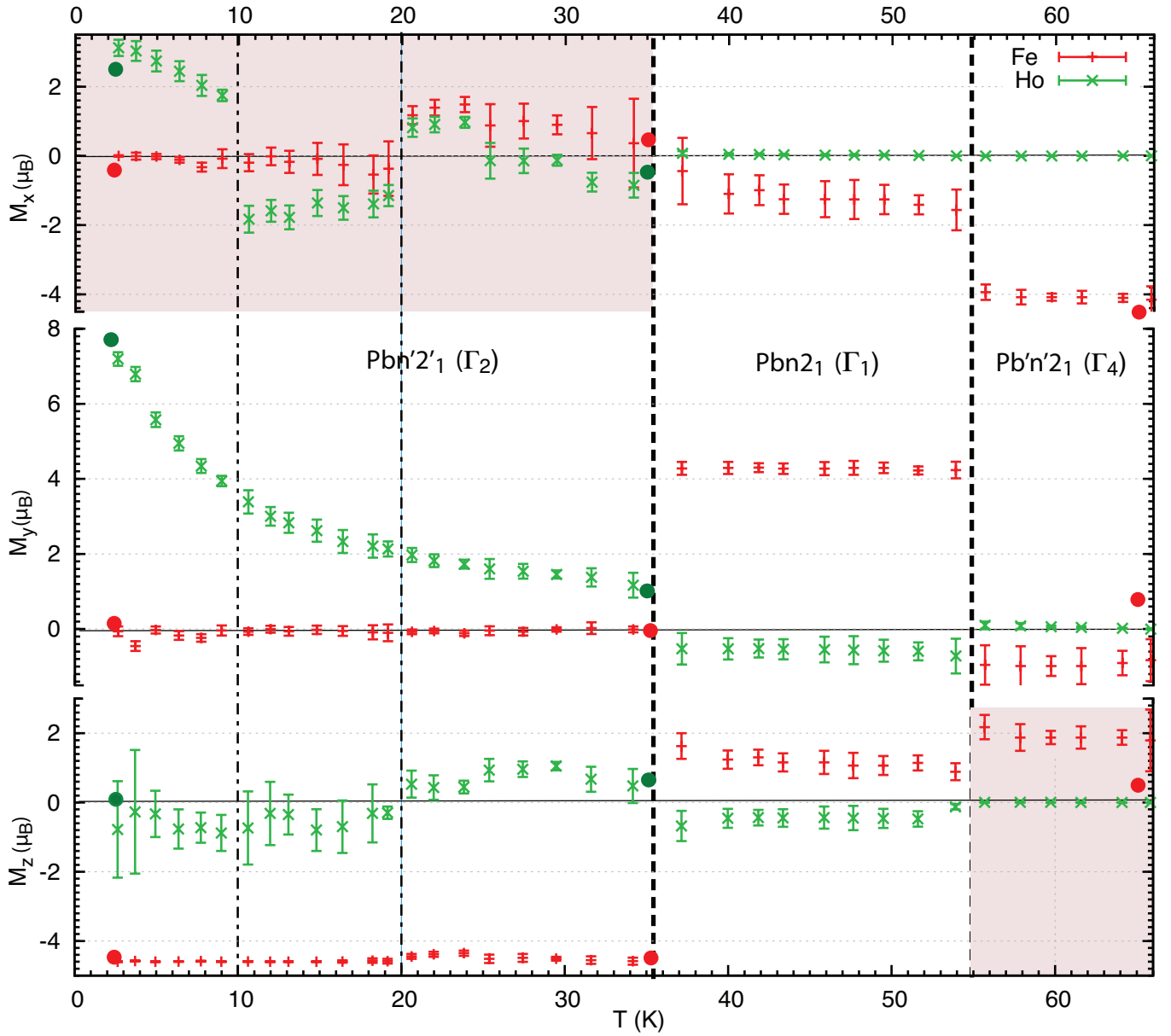
FIG. 2. Temperature variation of the x,y, and z components of moment on Fe and Ho ions in $HoFeO_3$ in the temperature range 2.5 to 66 K determined from 8 low angle reflections. Values obtained from the three large data sets are shown as filled circles. The shaded areas mark the regions where the components on the 4 sub-lattices are ferromagnetically aligned

VI.   DISCUSSION

The three different magnetic structures found as a function of temperature for $HoFeO_3$ are illustrated schematically in figure 3. They are described by the magnetic groups $Pb'n'2_1$, $Pbn2_1$ and $Pbn'2'_1$ and are stable in the temperature ranges $\approx$ 600-55 K, 55-37 K and 35> T > 2 K respectively. In all three the fundamental coupling between the Fe moments remains the same and only their orientation and the degree of canting away from the ideal axial direction varies. The magnetic polarisation 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[8]. 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 $HoFeO_3$, 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 favours the Γ_4 configuration. He does not include criteria for the non-abrupt Γ_2 to Γ_1 transition which takes place in $HoFeO_3$
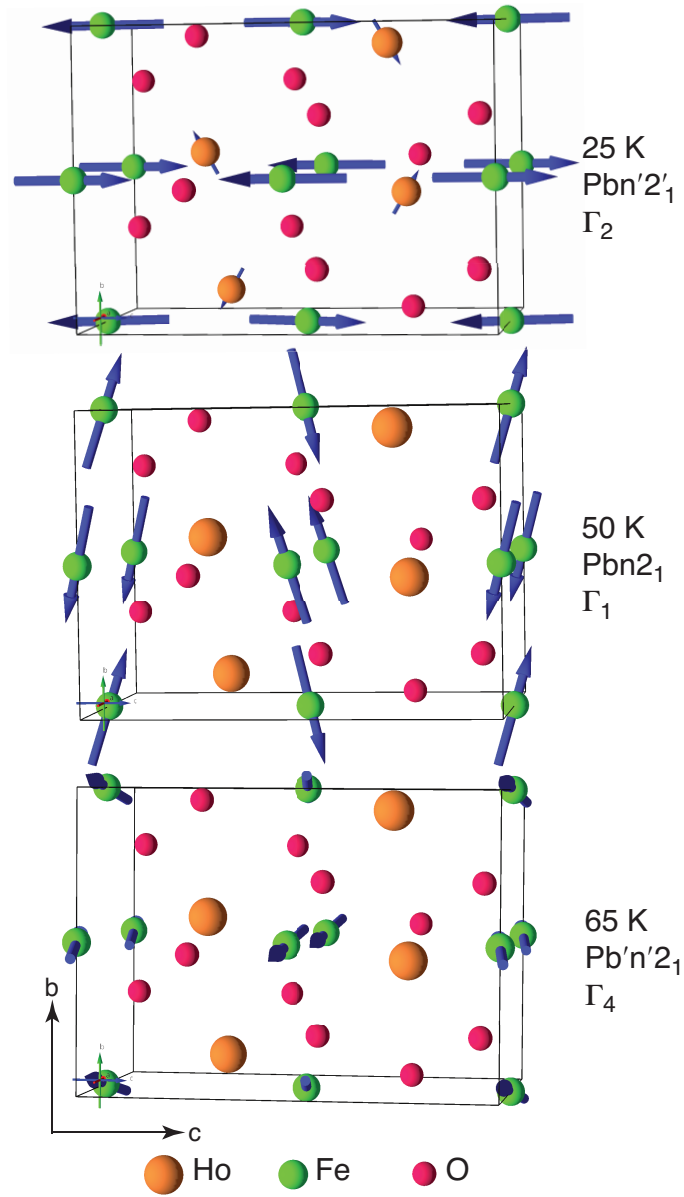
FIG. 3. Schematic representation of the three modulation modes found for the ordered magnetic structures of $HoFeO_3$.

between 37 and 30 K.

Figure 4 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 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 $\mathbf{M}_{Ho} \times \mathbf{M}_{Fe}$ which changes sign twice on cooling from 30 - 2.5 K. A similar reversal of the spontaneous ferromagnetic moment with respect to the underlying antiferromagnetic structure has been observed in $SmFeO_3$[15] although in that case only a single reversal at 5 K, rather than the double reversal indicated here, was found.

Weak ferromagnetism in the orthoferrites has been attributed to to the antisymmetric exchange interaction between
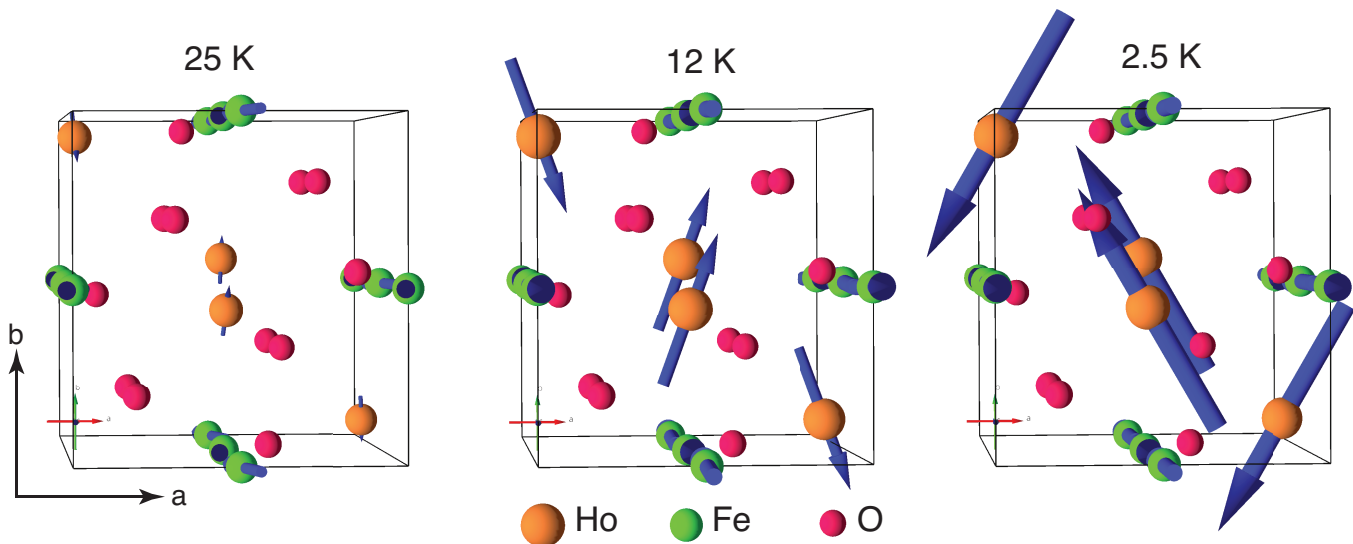
FIG. 4. Variation of the relative orientations of the Fe and Ho moments in HoFeO$_3$ with increasing order in the Ho sub-lattices.

magnetic ions[22]. In HoFeO$_3$ below 30 K it is the sum of contributions from both Fe and Ho and will have the form

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

The $\mathbf{D}_{n,i,j}$ are Dzyaloshinski vectors[23] which 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 $\mathbf{D}_{\text{FeFe}}$ 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 behaviour observed in this experiment shows that for HoFeO$_3$ the sums of the Fe-Fe and Ho-Ho interactions have the same sign as one another, but that of the Ho-Fe terms is opposite.

VII. POSSIBLE FERROELECTRICITY IN HOFEO$_3$

We mentioned already that there is an unpublished report of ferroelectricity[21] on HoFeO$_3$ that motivated us to reinvestigate the temperature evolution of magnetic structure of HoFeO$_3$ carefully by single crystal neutron diffraction. The report of ferroelectricity is based on pyrocurrent measurements on a single crystal sample and is also supported by synchrotron single-crystal X-ray diffraction experiments. The ferroelectric transition temperature was determined to be around $T_C \approx 225$ K. But recently some doubt has arisen also as to the reproducibility of the ferro-electric transition reported to occur[15] at the Néel temperature in SmFeO$_3$ and it is argued[16] that the inverse Dzyaloshinski interaction cannot drive a ferroelectric transition in a $k = 0$ antiferromagnet. The ferroelectric transition observed in HoFeO$_3$ is reported[21] to occur at 225 K well below the Néel temperature for Fe order and in a $k = 0$ structure so the ferroelectric transition must be driven by some mechanism other than the inverse DM effect. However the loss of centrosymmetry associated with such a transition removes the symmetry constraint which compels the Ho moment to be either parallel or perpendicular to the a-b plane, and allows Ho to participate in weak z-axis ferromagnetism at low temperature. This ferromagnetism would be expected to couple strongly to the ferro-electric polarity.

VIII. ACKNOWLEDGEMENT

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