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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 were found as a function of temperature for HoFeO_3 . In all three phases 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. 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 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. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4979710>]

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 magnetise 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 between these interactions involving the two sub-systems leads to several possibilities for

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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: DyFeO₃, GdFeO₃ and SmFeO₃.¹³⁻¹⁶ In some materials ferroelectricity appears only on application of magnetic field. HoFeO₃ 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 HoFeO₃¹⁷ is described using space group Pbnm, 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 configuration²⁰ 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 (110) 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 almost all investigations of the temperature dependence of the magnetic structure of HoFeO₃ have been done using powder samples. An experiment²¹ has shown that antiferromagnetic ordering can be induced in the Ho sublattices of a single crystal of HoFeO₃ at 79-123 K by a pulsed magnetic field of 77 koe applied along [010]. In the present investigation we have studied the temperature evolution of the magnetic structure of HoFeO₃ using single crystals in zero field. 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.

A ferroelectric transition at ≈ 225 K²² has recently been observed in HoFeO₃. If this is confirmed it means that the true point symmetry of HoFeO₃ below this transition cannot be higher than mm2, making the likely space group Pbn2₁. In the rest of this paper the possibility that the symmetry is lower than Pbnm is taken into account and the constraints that the higher symmetry imposes on the orientation of any Ho moments have been relaxed by using magnetic symmetry groups derived from Pbn2₁.

II. EXPERIMENTAL

The crystals of HoFeO₃ used in this study were grown using the flux method by S.N. Barilo and D.I. Zhigunov in Minsk, Belarus. They were of good quality giving sharp diffraction profiles. Heat capacity measurements as a function of temperature on a 122 mg single crystal of HoFeO₃ cut out of the larger single crystal are shown in Fig 1. The inset of the same figure shows a blow up in the low temperature region indicating spin reorientation transition at about 55 K. At lower temperature there is a further anomaly in specific heat that can be associated with Schottky anomaly due to the Ho ordering. The bulk magnetisation of the same crystal along each of the three principal axes was measured as a function of temperature at several field strengths. The results for the *b*-axis magnetisation shown in Fig. 2 indicate a spectacular drop at the spin-reorientation transition temperature $T \approx 55$ K. The present specific heat and magnetization data accord with previous data²³ for HoFeO₃ and show the expected anomalies associated with the reorientation transition at ≈ 55 K, but give no evidence of any transition at 225 K.

Neutron diffraction measurements have been made on two small single crystals first on the D10 diffractometer at ILL, then using the hot neutron diffractometer Heidi of the FRM II reactor in Garching, Germany. The Heidi 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.

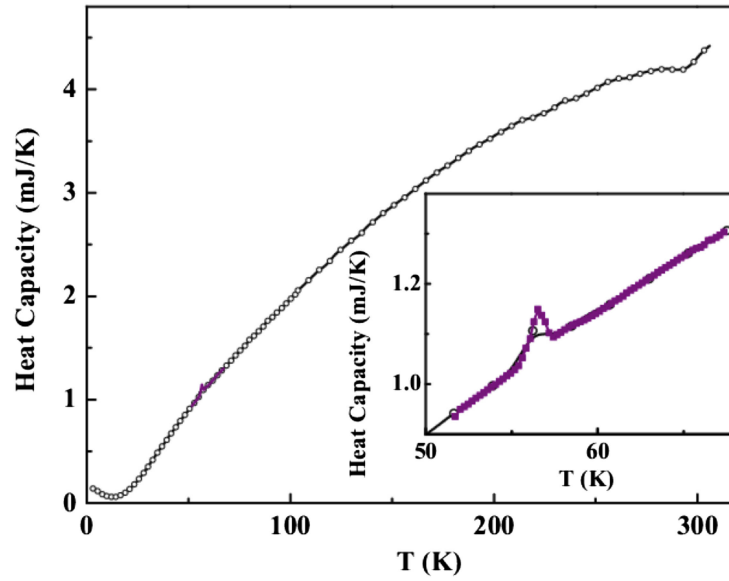


FIG. 1. Temperature dependence of the specific of the HoFeO_3 single crystal. Inset shows a blow up in the low temperature region indicating spin reorientation transition at about 55 K. At lower temperature there is a further anomaly in specific heat that can be associated with Schottky anomaly due to the Ho ordering.

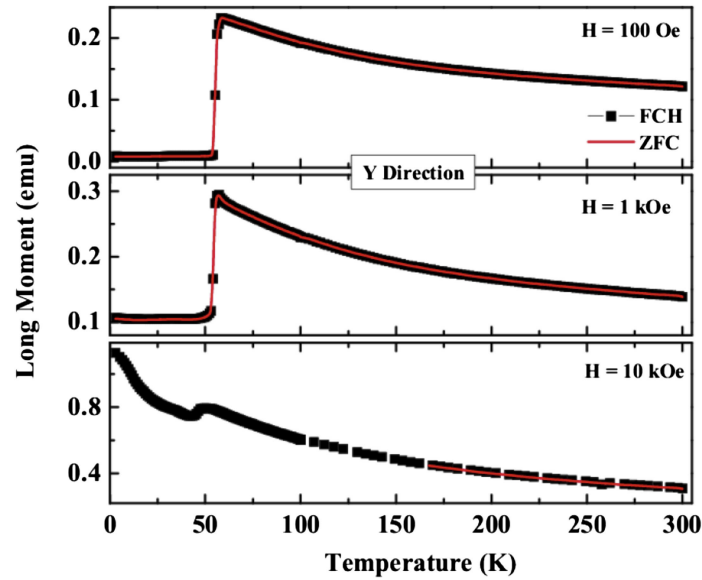


FIG. 2. Temperature dependence of the magnetization of the HoFeO_3 single crystal with magnetic field parallel to the b-axis of the crystal. The magnetization along this direction shows a spectacular drop as one goes to the spin reoriented phase below about 55 K.

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 the lower symmetry group $\text{Pbn}2_1$ the Ho and Fe atoms each occupy a set of 4-fold general positions. To maintain the m symmetry of the Ho sites in Pbnm any ordered Ho moments must be oriented either parallel or perpendicular to the mirror plane perpendicular to z on which they lie. The symmetry operations generating the 4 sites in either space group are listed in Table I and the relative phases and signs of the contributions which

TABLE I. Symmetry operations generating the atomic positions in the structure of HoFeO_3 in space groups Pbnm and $\text{Pbn}2_1$. In Pbnm 4 further centro-symmetrically related operators generate the same positions.

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

^a $x_{\text{Ho}}=0.98141$ and $y_{\text{Ho}}=0.06857$.

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	+	+	+	+
2	$\frac{1}{2}$	0	$h + k$	+	+	-	-
3	$\frac{1}{2}$	0	$h + k + l$	+	-	-	+
4	0	$\frac{1}{2}$	l	+	-	+	-
Reflection Type ^a				F	A	C	G

^aThe reflection types have been assigned to match those used by Ref. 19.

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

sub-lattice & Operator	$\text{Pbn}2_1 (\Gamma_1)$			$\text{Pbn}'2_1' (\Gamma_2)$			$\text{Pb}'n2_1' (\Gamma_3)$			$\text{Pb}'n'2_1 (\Gamma_4)$		
	M_x	M_y	M_z	M_x	M_y	M_z	M_x	M_y	M_z	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

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 the components of moments of magnetic ions in the 4 sub-lattices of space group $\text{Pbn}2_1$ for the 4 compatible magnetic symmetry groups are listed in Table III.

IV. TEMPERATURE DEPENDENCE OF MAGNETIC SCATTERING FROM HOFeO_3

In an exploratory experiment the integrated intensities of six low angles reflections from a HoFeO_3 ($\approx 200 \text{ mm}^3$) crystal were measured on the D10 diffractometer at ILL Grenoble, using a neutron wavelength $2.36 \text{ \AA}$ at temperature intervals of 5° from 375 K to 2 K. Between 375 and 60 K all the reflection intensities increased gradually, but below 60 K large fluctuations were observed. In our subsequent measurements we therefore concentrated on temperatures from 65 to 2 K. Eight low angle reflections were selected, two from each of the groups F,C,A and G, and their integrated intensities measured in steps of 1° in the range 2.5 to 65 K on the Heidi instrument at FRM Garching using a neutron wavelength of $0.7925 \text{ \AA}$. The results are presented in figure 3. 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)

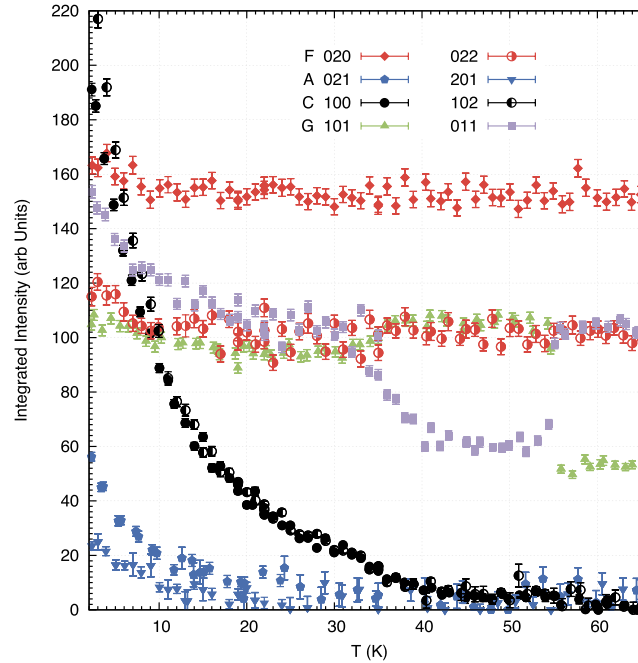


FIG. 3. Temperature dependence of the integrated intensities of selected reflections from an HoFeO_3 single crystal.

reflections. The latter are systematic absences for nuclear scattering in Pbnm 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 $\text{Pbn}2_1$ there must be components of moment parallel to y , for $\text{Pbn}'2_1'$ to z and for $\text{Pb}'n'2_1$ to x . The observation that 011 is significantly more intense than 101 supports the conclusion¹⁸ that in this temperature range the Fe moments are nearly parallel to x , the magnetic group is therefore $\text{Pb}'n'2_1$, or equally $\text{Pb}'n'm$, since there are no significant ordered Ho moments. At ≈ 55 K figure 3 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 spin reorientation transition at ≈ 55 K.²³ The magnetic space group changes to $\text{Pbn}2_1$ (or Pbnm) 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 $\text{Pbn}'2_1'$ 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 $\text{Pbn}'2_1'$ 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 is in the y direction.

V. DETERMINATION OF THE MAGNETIC STRUCTURE PARAMETERS

A. The 65 K structure: Absolute scale and extinction

In the magnetic groups based on $\text{Pbn}2_1$ in which neither Fe or Ho lie on symmetry elements the magnetic space group dictates the relative directions of the components of moment on the different sub-lattices, but 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 $\sin \theta/\lambda < 1.25 \text{ \AA}^{-1}$ have been measured at 65 K, 35 K and 2.5 K using both the original crystal and a smaller one ($\approx 50 \text{ mm}^3$). The 65 K data were used to confirm the positional parameters, obtain a model for extinction in the crystals and determine the absolute scale of the measured intensities. Analysis of the limited data set measured in the preliminary experiment

TABLE IV. Crystal structure parameters for HoFeO₃, in space group Pbnm, obtained from least squares refinement of integrated intensity measurements at 65 K.

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

^aThe anisotropic temperature parameters B(ij) are given in units of Å⁻². Unweighted R-factor R1 = 8.34, weighted R-factor R3 = 3.34, $\chi^2 = 3.8$, Number of observed reflections $N_{obs} = 677$, No of refined parameters $p = 27$.

at 2.36 Å had shown that extinction in the larger crystal was severe and that the the extinction, scale and magnetic moment parameters were so highly correlated that a satisfactory refinement could not be obtained with such long wavelength data. The early work on HoFeO₃¹⁸ 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'm with Fe moments of 4.6 μ_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. and the centro-symmetric space group Pbnm. The refined parameters are listed in Table VII. The anisotropy of the temperature coefficients B(ij) is very small with only the B(11) of iron and both oxygen being at all significant; they show that any atomic displacements consequent on a loss of centro-symmetry are also small. 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 (weighted R=4.5) on structure factors. 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.

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. Since in this temperature region the onset of some Ho order is expected the groups Pbn2₁ and Pbn'2'₁, which do not constrain the Ho moment directions, were used. 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 . Refinements in which the extinction parameter was varied gave essentially the same results and no significant change in its value. The magnetic parameters obtained are presented in Table V. For the 35 K data a marginally better agreement was obtained with Pbn'2'₁ than Pbn2₁ although it is probable that at this temperature some intermediate or mixed phase state is present. For the 2.5 K data only Pbn'2'₁ gave a good fit.

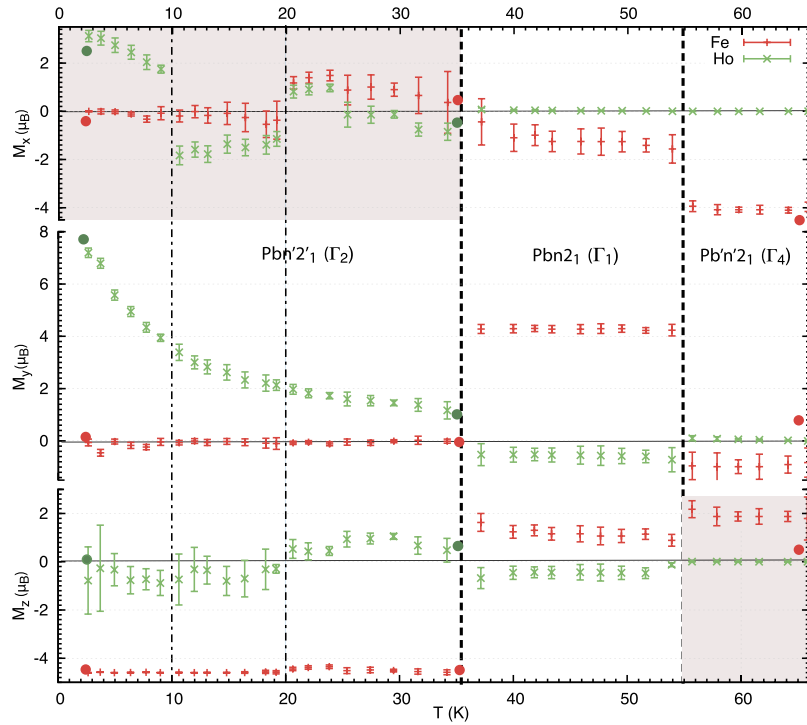
C. Temperature variation of the magnetic parameters

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

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

T (K)	Magnetic Group	Fe (μ_B)			Ho (μ_B)			^a R_{cryst}	χ^2
		M_x	M_y	M_z	M_x	M_y	M_z		
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

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

FIG. 4. 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.

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 $\text{Pbn}'2_1$, 55 - 37 K $\text{Pbn}2_1$ and 34 - 2.5 K $\text{Pbn}'2'_1$. 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 4. 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. Below 35 K 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.

VI. DISCUSSION

Figure 5 gives schematic representation of the three modulation modes found for the ordered magnetic structures of HoFeO_3 and Figure 6 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

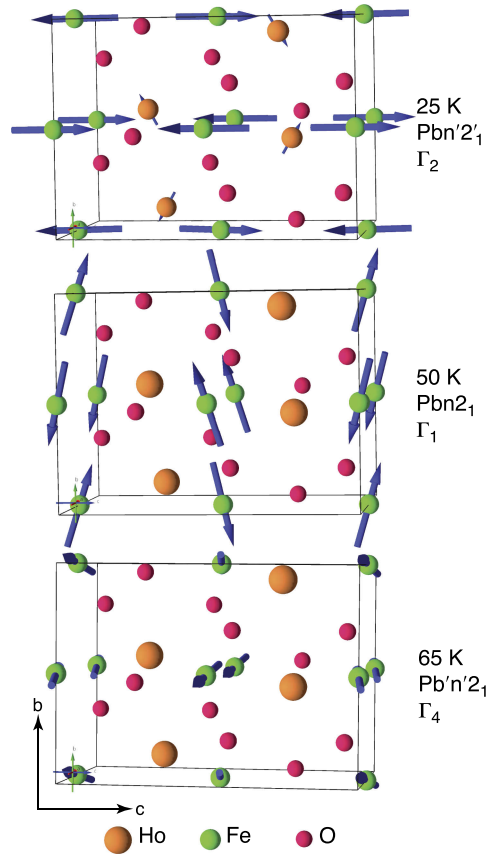


FIG. 5. Schematic representation of the three modulation modes found for the ordered magnetic structures of HoFeO_3 .

anisotropic exchange interaction forces the Fe moments to reorient along z . In $\text{Pbn}'2'_1$ components of moment in the x direction are ferromagnetically aligned and it is the direction of this ferromagnetic moment relative to $\mathbf{M}_{\text{Ho}} \times \mathbf{M}_{\text{Fe}}$ 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 reported for SmFeO_3 from bulk magnetisation measurements,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 the antisymmetric exchange interaction between magnetic ions.²⁴ In HoFeO_3 below 30 K it is the sum of contributions from both

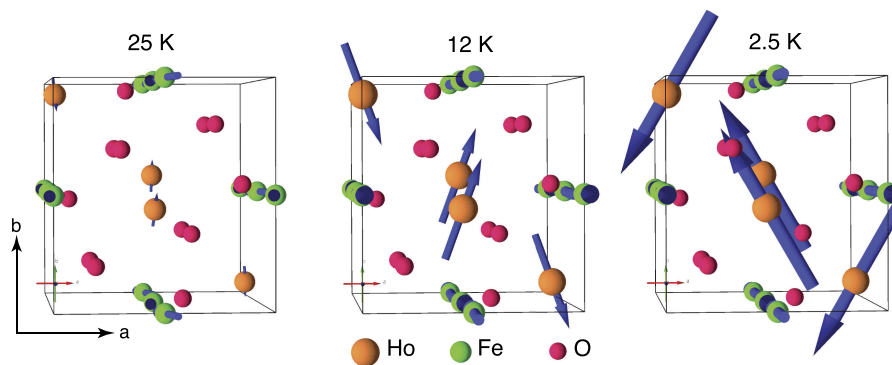


FIG. 6. Variation of the relative orientations of the Fe and Ho moments in HoFeO_3 with increasing order in the Ho sub-lattices.

Fe and Ho and will have the form

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

The $\mathbf{D}_{n,i,j}$ are Dzyaloshinski vectors²⁵ which may include contributions from single ion anisotropy as well as antisymmetric 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 eq. (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.

It has been mentioned already that there is an unpublished report of ferroelectricity in HoFeO_3 ²² that motivated us to reinvestigate the temperature evolution of its magnetic structure using single crystal neutron diffraction. The temperature dependence of the low angle (magnetic structure sensitive) reflections (Section IV) did not show any indication that a change in magnetic structure could be associated with the reported transition $T_C \approx 225$. However these data, restricted to low angles, would not be expected to reveal small displacements of atoms from their special positions associated with a loss of centro-symmetry. Recently moreover some doubt has arisen as to the reproducibility of the ferro-electric transition reported to occur¹⁵ at the Néel temperature in SmFeO_3 and it has been argued¹⁶ that the inverse Dzyaloshinski interaction cannot drive a ferro-electric transition in a $k = 0$ antiferromagnet. A ferro-electric transition at 225 K in HoFeO_3 well below the Néel temperature for Fe order and in a $k = 0$ structure would have to be driven by some mechanism other than the inverse DM effect. It was noted earlier that the HoFeO_3 Γ_4 structure stable between the Fe Néel temperature and 55K is fully compliant with the centro-symmetric magnetic group $\text{Pb}'n'm$ in the absence of Ho ordering. However, at temperatures below the Fe Néel temperature, the Ho are subject to an internal field due to the ordered array of Fe moments. The contributions to this polarising field from the x-components of the Fe moments sum to zero because of the mirror symmetry of Ho. The resultant polarising field is therefore due only to the weak ferromagnetic components ($\parallel z$). Ho however has strong single-ion anisotropy and the structures found at lower temperature show that the easy axis is $\parallel y$. Any moment induced on Ho would therefore be expected to have both y and z components, a configuration which breaks $\text{Pb}'n'm$ symmetry and allows the oxygen octahedra coordinating the Fe to become polar. The sense of such polarity would depend directly on the sense of the weak ferromagnetic moment and so would couple directly to an applied magnetic field. Ferro-electricity has been induced in DyFeO_3 by a similar, symmetry breaking, but external magnetic field by Ref. 13 who suggested that the polarisation was due to exchange striction between adjacent Fe^{3+} and Ho^{3+} layers.

VII. CONCLUSIONS

The present study of the temperature dependence of the magnetic structure of HoFeO_3 conforms the structures designated Γ_4 and Γ_2 which have been previously reported.^{18–20} The first is stable from the Fe Néel temperature down to 55K and the second at low temperature. The present results show that in the abrupt reorientation transition at 55K the Fe spins reorient in the x-y plane, from being nearly parallel to x to being nearly parallel to y. In this transition the magnetic space group changes from $\text{Pb}'n'm$ to Pbnm and the weak ferromagnetism is lost. At around 35 K a previously unreported and non-abrupt reorientation transition occurs. The Fe moments reorient parallel to z and the Ho moments begin to order with moments parallel to y. The low temperature Γ_2 structure is again weakly ferromagnetic with the weak ferromagnetic moment in the x direction. The Γ_2 structure undergoes

two further changes as the degree of Ho order increases on cooling below 35 K. At ≈ 20 K and again at ≈ 10 K the direction of the ferromagnetic component of Ho changes sign relative to $\mathbf{M}_{\text{Ho}}(y) \times \mathbf{M}_{\text{Fe}}(z)$. This can be understood if the the sums of the Fe-Fe and Ho-Ho antisymmetric couplings have the same sign but that of the Fe-Ho ones differ. Finally we have found no direct evidence to confirm the reported ferroelectric transition at 225 K. However it should be noted that in the Γ_4 phase any polarisation of the Ho sub-lattices would result in the loss of centro-symmetry.

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APPENDIX : RESULTS OF DIFFERENT REFINEMENTS

We have refined the structure of HoFeO_3 at $T = 65$ K by using different crystal structure models. The magnetic structure was taken to be Γ_4 with Fe moment fixed to $4.6\mu_B$ along the a axis. Three different models of crystal structure have been assumed. The first is with the space group $Pbnm$ with anisotropic temperature factor. The refined results are given in the main text in Table IV. Here we give the results of refinement using centrosymmetric space group $Pbnm$ with isotropic temperature factor (Table VI) and also the results of refinement in the non-centrosymmetric polar space group $Pbn2_1$ with Fe position fixed as $(0, 1/2, 0)$ to define the origin (Table VII). R_1 is unweighted R-factor on F and R_3 is the weighted R-factor on F . In all these refinements we have checked carefully the correlation matrices whether there existed any excessive correlations.

Finally we have calculated bond lengths from both $Pbnm$ and $Pbn2_1$ models. There are significant differences in these distances from 5 to 10 times the estimated standard deviations. Fig 7 shows the

TABLE VI. Crystal structure parameters for HoFeO_3 , in the centrosymmetric space group $Pbnm$ with isotropic temperature factor, obtained from least squares refinement of integrated intensity measurements at 65 K.

Atom	x	y	z	ITF ^a
Ho	0.9813(2)	0.0686(2)	0.2500	0.018(12)
Fe	0	0.5000	0	0.13(1)
O1	0.1096(3)	0.4603(3)		0.23(2)
O2	0.6921(2)	0.3048(2)	0.0564(2)	0.26(1)

^aThe isotropic temperature parameters ITF are given in units of $\text{\AA}^{-2}$. $R_1 = 8.60$, $R_3 = 3.52$, $\chi^2 = 4.0$, Number of observed reflections $N_{\text{obs}} = 677$, No of refined parameters $p = 11$.

TABLE VII. Crystal structure parameters for HoFeO_3 , in the non-centrosymmetric polar space group $Pbn2_1$ with Fe position fixed as $(0, 1/2, 0)$ to define the origin., obtained from least squares refinement of integrated intensity measurements at 65 K.

Atom	x	y	z	ITF ^a
Ho	0.9814(2)	0.0687(2)	0.2524(5)	0.011(12)
Fe	0	0.5000	0	0.13(1)
O11	0.1097(3)	0.4603(3)	0.2504(8)	0.25(2)
O21	0.6878(8)	0.3017(8)	0.0603(4)	0.19(5)
O22	0.3034(8)	0.6918(8)	0.9475(5)	0.24(5)

^aThe isotropic temperature parameters ITF are given in units of $\text{\AA}^{-2}$. $R_1 = 7.33$, $R_3 = 3.38$, $\chi^2 = 3.5$, Number of observed reflections $N_{\text{obs}} = 677$, No of refined parameters $p = 17$.

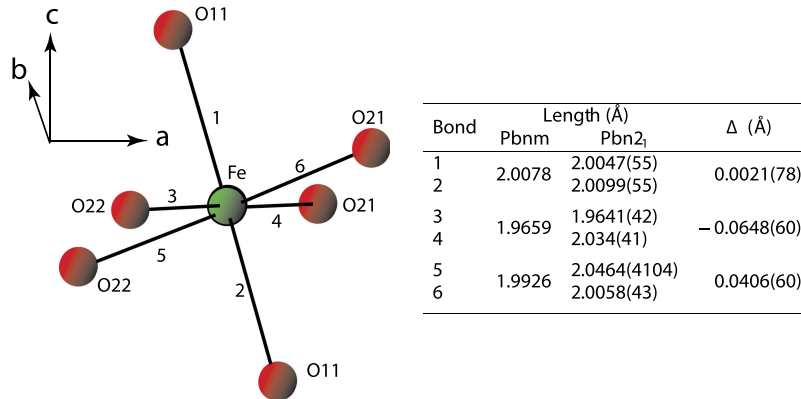


FIG. 7. The picture with table showing the asymmetry in the FeO_6 octahedron. The symmetry would suggest polarization approximately along the Y axis.

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