Single crystal polarized neutron diffraction study of the magnetic structure of HoFeO$_3$

T Chatterji$^{1}$, A Stunault and P J Brown

Institut Laue-Langevin, 6 rue Joules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

E-mail: chatterji@ill.fr

Received 12 June 2017, revised 3 July 2017
Accepted for publication 5 July 2017
Published 17 August 2017

Abstract
Polarised neutron diffraction measurements have been made on HoFeO$_3$ single crystals magnetised in both the [0 0 1] and [1 0 0] directions (Pbnm setting). The polarisation dependencies of Bragg reflection intensities were measured both with a high field of $H = 9$ T parallel to [0 0 1] at $T = 70$ K and with the lower field $H = 0.5$ T parallel to [1 0 0] at $T = 5, 15, 25$ K. A Fourier projection of magnetization induced parallel to [0 0 1], made using the $hk0$ reflections measured in 9 T, indicates that almost all of it is due to alignment of Ho moments. Further analysis of the asymmetries of general reflections in these data showed that although, at 70 K, 9 T applied parallel to [0 0 1] hardly perturbs the antiferromagnetic order of the Fe sublattices, it induces significant antiferromagnetic order of the Ho sublattices in the $x - y$ plane, with the antiferromagnetic components of moment having the same order of magnitude as the induced ferromagnetic ones. Strong intensity asymmetries measured in the low temperature $\Gamma_2$ structure with a lower field, 0.5 T parallel to [1 0 0] allowed the variation of the ordered components of the Ho and Fe moments to be followed. Their absolute orientations, in the 180° domain stabilised by the field were determined relative to the distorted perovskite structure. This relationship fixes the sign of the Dzyalshinski–Moriya (D-M) interaction which leads to the weak ferromagnetism. Our results indicate that the combination of strong $y$-axis anisotropy of the Ho moments and Ho-Fe exchange interactions breaks the centrosymmetry of the structure and could lead to ferroelectric polarization.

Keywords: polarized neutrons, weak ferromagnetism, Holmium orthoferrite

(Some figures may appear in colour only in the online journal)

1. Introduction

The family of rare-earth orthoferrites RFeO$_3$ (R = rare-earth element) contains a large number of compounds with interesting magnetic and other physical properties [1–8]. These compounds have unusually high Néel temperatures, 600–700 K, below which the Fe moments order with basically antiferromagnetic structures which also often exhibit weak ferromagnetism. Recently interest has focussed on the possibility of multiferroic properties arising from the complex interactions between 3D and 4f moments [9–12]. If such interactions lead to the development of a second ferroic order, such as ferroelectricity, at relatively high temperature, the compounds could have useful device applications. Previous studies of the rare earth orthoferrites have shown that they undergo interesting spin reorientation transitions at temperatures below about 50 K. On further cooling the magnetic rare earth ions, which at higher temperature are paramagnetic, or weakly polarized by the molecular field of the ordered Fe ions, may also become magnetically ordered. Complicated magnetic properties arise from the multiplicity of different exchange interactions. The three principal exchange interactions have strengths decreasing in the order Fe-Fe, R-Fe and R-R. At high temperature the structure is determined by Fe-Fe interactions but as the temperature is lowered magnetic transitions may be triggered by the increasing importance of the Fe-R interaction. Finally at very low temperatures the R-R interaction dominates the fully ordered magnetic structure.

In a recent paper [13] we reported the results of a single-crystal unpolarized neutron diffraction study of the temperature
evolution of the magnetic structure of HoFeO₃. This detailed study confirmed that HoFeO₃ orders at a very high temperature \((T_N \approx 700 \text{ K})\) with a \(\Gamma_4\) structure described using the Pbnm setting of the orthorhombic space group of HoFeO₃ [6]. This Pbnm setting is used throughout the present paper. The high temperature magnetically ordered phase is weakly ferromagnetic in the [100] direction and is stable in the temperature range from \(T_N \approx 700 - 55 \text{ K}\). This high temperature phase is weakly ferromagnetic in the [100] direction and is stable in the temperature range from \(T_N \approx 700 - 55 \text{ K}\). At 55 K there is an abrupt spin re-orientation transition to a \(\Gamma_1\) structure and the weak ferromagnetism is lost. Below about 35 K a previously unreported and non-abrupt reorientation transition to the \(\Gamma_2\) structure begins. The \(\Gamma_2\) structure is again weakly ferromagnetic but with \(x\) as the ferromagnetic axis. This \(\Gamma_2\) structure undergoes two further changes as the degree of Ho order increases on cooling below 35 K. At \(T \approx 20 \text{ K}\) and again at \(T \approx 10 \text{ K}\) the relative directions of the ferromagnetic component of Fe and Ho change sign.

Since the magnetic structures of both the high and low temperature structures of HoFeO₃ exhibit weak ferromagnetism it is of some interest to study their response to applied magnetic fields. Polarisated neutron Bragg scattering is the tool of choice for such a study as it exploits the coupling between the neutron polarization and that induced in the sample and, when the sample is a single crystal, can yield directional information not easily obtainable by other methods. The present paper reports the results we have obtained for HoFeO₃ using this technique.

2. Polarised neutron Bragg scattering in weak ferromagnets

The magnetic polarization induced in a crystal by an applied field gives rise to a magnetic structure factor whose phase, relative to that of the nuclear structure factor, depends on the magnetization direction, and is reversed if the magnetization is reversed. The intensity of Bragg scattering of polarised neutrons likewise depends on the relative orientations of the neutron polarization and the magnetic structure factor. The resulting polarization dependence of intensity (polarised neutron intensity asymmetry) is used in classical polarised neutron experiments to measure magnetization distributions. In cases such as that of HoFeO₃ in which some of the magnetic species have significant anisotropy there may be components of magnetic moments perpendicular to the applied field and ordered either ferromagnetically or antiferromagnetically. These also contribute to the polarised neutron asymmetries and their magnitudes can be determined from polarised neutron experiments [14, 15].

The polarised neutron asymmetries may also be used to determine the sign of the D-M interaction. To exhibit (D-M) weak ferromagnetism a material must have a magnetic structure with zero propagation vector and the magnetic symmetry group must contain an element combining rotation and translation which relates atoms with nearly antiparallel spins. Applying a magnetic field to such a structure breaks the degeneracy of the two \(180^\circ\) domains (those in which all the antiferromagnetic components are reversed), favouring the one with the ferromagnetic component parallel to the field. The magnetic structure factors of the two \(180^\circ\) domains differ in phase by \(180^\circ\) whereas their nuclear structure factors are the same. Unbalancing the domain populations therefore leads to a polarised neutron intensity asymmetry whose sign depends on that of the D-M interaction (the absolute direction in which the magnetic moments are canted with respect to their atomic environment) [16, 17].

3. Experimental methods

3.1. Crystal growth and characterization

The HoFeO₃ single crystals used in the present experiment were grown using flux method by Barilo and Zhigunov in Minsk, Belarus. The crystals were of very good quality giving sharp diffraction peaks. Magnetization and specific heat measurements on a small 122 mg single crystal of HoFeO₃ cut out of the larger single crystal have been reported by us [13] and these results are in agreement with the results reported by other authors [18]. We have also previously reported [13] the temperature evolution of the magnetic structure of these same HoFeO₃ crystals using unpolarized neutron diffraction.

3.2. The polarized neutron diffraction

Polarized neutron diffraction measurements were made on these HoFeO₃ single crystals using the spin polarized diffractometer D3 of the Institut Laue–Langvin in Grenoble. The crystals were magnetised and cooled using a cryomagnet delivering a maximum vertical field of 9 T. The polarised neutron intensity asymmetries of accessible Bragg reflections were measured both in 9 T and in the lowest field retaining good polarization viz. 0.5 T. The high field measurements were made at 70 K with the crystal magnetised parallel to the weak ferromagnetic axis [001] and the low field measurements at selected temperatures in the range 5–60 K with the HoFeO₃ crystal magnetised parallel to [100], the direction of weak ferromagnetism in the \(\Gamma_1\) phase.

The magnetic structure models, the nuclear structure parameters and the extinction model used in analysing the data were those determined from the unpolarised single crystal measurements [13] made at the FRM II reactor, Garching. The space groups used are Pbnm, and its subgroup Pbm2₁. The labels given to the different magnetic sublattices and the relative orientations of the components of their magnetic moments in the \(\Gamma_4\) and \(\Gamma_2\) structures are summarised in table 1.

4. [001]Orientation, 9T applied field at 70K

At 70 K the crystal has the \(\Gamma_4\) structure in which only the Fe moments are ordered. Applying magnetic field parallel to [001], which is the axis of weak ferromagnetism, should initially sweep out \(180^\circ\) domain walls so that the weak
The quantity measured in the polarised neutron experiment is the intensity asymmetry $A = (I^+ - I^-)/(I^+ + I^-)$. In this equation $I^+$ and $I^-$ are the intensities of neutrons scattered with the incident polarization parallel (+) and antiparallel (−) to the field direction. With the normal beam conjugacy of D3, in which the field is parallel to the crystal rotation axis and perpendicular to the incident beam, the cross-sections for Bragg scattering are

$$I^\pm \propto |N|^2 + |M_\perp|^2 \pm 2 \Re(N M_\perp^* \cdot \hat{P})$$  

$$\text{giving } A = \frac{2 \Re(N M_\perp^* \cdot \hat{P})}{|N|^2 + |M_\perp|^2}$$  

where $N$ is the nuclear structure factor, $M_\perp$ the magnetic interaction vector of the reflection and $\hat{P}$ a unit vector parallel to both the polarization and the magnetic field. In centrosymmetric HoFeO$_3$ the structure factors are real and the aligned magnetization can be separated into components $M_h$ and $M_\perp$ parallel and perpendicular to the field. The relative orientations of these vectors for a reflection whose scattering vector $\mathbf{k}$ is inclined at angles $\rho$ to $\mathbf{P}$ and $\phi$ to $\mathbf{M}_h$ in the plane perpendicular to $\mathbf{P}$ are shown in figure 1. The magnetic interaction vectors, obtained by projecting the magnetic structure factors $\mathbf{M}$ onto the plane perpendicular to $\mathbf{k}$, have the form

$$M_{\perp h} = M_h \sin \rho$$

$$M_{\perp p} = M_p \cos \rho \sin \phi.$$  

(3)

With an [0 0 1] crystal orientation $\rho = \pi/2$ for all reflections $h00$, so the asymmetries measured for these reflections depend directly on the magnetic moment $M_h$ aligned by the field. However these data cannot be used to determine its distribution between the Fe and Ho atoms directly, using Fourier techniques, when the contributions to $|M_\perp|^2$ of any antiferromagnetically aligned moments are not known. Furthermore, any inaccuracy in aligning the chosen crystallographic axis parallel to the field direction allows antiferromagnetic components to contribute to the $hk0$ asymmetries. Nevertheless a preliminary analysis of the $hk0$ reflection asymmetries was made assuming that these antiferromagnetic contributions could be neglected. This yielded the Fourier projection figure 2 which strongly suggests that almost all the magnetization is due to alignment of Ho moments. In further analysis the measured asymmetries were compared to those predicted by several different models for the magnetized structure. In the centrosymmetric space group Pbnm the Ho atoms lie on the mirror planes perpendicular to [0 0 1], which constrains their moments to lie either parallel or perpendicular to that direction. It was not found to be possible to obtain a reasonable fit to the asymmetries with models retaining this constraint. The best agreement was found with models in which $\Gamma_4$ coupling scheme as the Fe atoms and that they have significant ordered components of magnetization parallel to both [0 1 0] and [0 0 1]. These models imply the lower space group symmetry, Pbn21. Least squares fits of the components of
magnetization of Fe and Ho to the asymmetries calculated for this coupling scheme and space group gave the results shown in table 2. Initially the the \( \langle j_0 \rangle \) (spin only) form factor for Ho\(^{3+}\) was used to model the Ho magnetic scattering, however the fit was significantly improved by including a \( \langle j_2 \rangle \) (orbital) term. In the dipole approximation form factor for magnetic scattering is given by:

\[
f(K) = (M_x + M_y) \langle j_0(k) \rangle + M_z \langle j_2(k) \rangle
\]

where \( M_x \) and \( M_y \) are the spin and orbital moments and \( \langle j_0(k) \rangle \) and \( \langle j_2(k) \rangle \) the radial integrals of order 0 and 2 for the scattering ion [19].

The results in table 2 suggest the magneto-crystalline anisotropy of Ho favours the \( y \) orientation and that even with 9 T applied parallel to [001] almost half of the aligned Ho moments are antiferromagnetically arranged in the \( x - y \) plane.

### 5. Polarization dependent intensities in the \( \Gamma' \) phase with \( H = 0.5 \text{T} \parallel [100] \)

At temperatures below 35 K the \( \Gamma' \) structure is stable with the principal components of the Fe and Ho moments parallel to [001] and [010] respectively. It exhibits weak ferromagnetism parallel to [100] [13]. In the temperature range 35-2 K the ordered Ho moment increases from less than 1 \( \mu_B \) to almost 8 \( \mu_B \) at 2 K. Measurements of polarised neutron intensity asymmetries of a set of 276 reflections were made at 20, 15, and 5 K to investigate how the changing strengths of the Fe–Fe, Fe–Ho and Ho–Ho interactions influence details of the structure. For these measurements the \( x \) axis of the crystal was nearly parallel to the direction of the 0.5 T magnetic field. With the 9 T cryomagnet a minimum field of 0.5 T is required to maintain the neutron polarization; it also ensured that the weak ferromagnetic moment was fully aligned.

The magnetic parameters of the \( \Gamma' \) structure were fitted by a least squares procedure to the measured asymmetries at each of the measurement temperatures. The magnetic structure \( Pbnm 2'1' \) was used and both \( \langle j_0 \rangle \) and \( \langle j_2 \rangle \) contributions were included in the Ho form factor.

The results obtained from refinements, using the measured polarised neutron asymmetries as data, are given in table 3. These results confirm that the easy direction of the Ho moment is parallel to \( y \). The apparent change in sign of the orbital component of the Ho moment between 15 and 5 K is hardly significant. The larger residual \( R(\text{cryst}) \) at 5 K may indicate increasing inadequacy of the dipole approximation to the Ho form factor.

### 6. Discussion

#### 6.1. The sign of the antisymmetric coupling in HoFeO\(_3\)

The sign of the antisymmetric coupling which leads to weak ferromagnetism in HoFeO\(_3\) can be inferred from the magnetic moments given in table 3 since the listed components are those on the representative atoms (Fe at \( 0 \frac{1}{2} 0 \) and Ho at \( 0,0, \frac{1}{2} \)). It can also be determined directly from the signs of the asymmetries. In relatively low fields the antiferromagnetic components of moment are much larger than the weak ferromagnetic ones and so dominate the interaction vectors. These larger antiferromagnetic components are oppositely oriented in the two 180° domains and their phases relative to those of the nuclear structure factors determine the signs of the asymmetries of the corresponding reflections. In the present experiment the axis parallel to the magnetic field and polarization direction was not exactly [100] but \([-0.9782, -0.1907, 0.0823]\) allowing both the \( y \) and \( z \) anti-ferromagnetic components to contribute to the asymmetries in reflections with \( h \neq 0 \). For example the asymmetry measured in the 121 reflection at 25 K was \(-0.263(8)\); its nuclear structure factor calculated with the atomic positions given in table 1 is \(-2.1971 (10^{-12} \text{cm}) \) and the real part of the magnetic interaction vector for the 25 K \( \Gamma' \) structure (table 3) has components \( x = -0.8730, y = -0.4709, z = 2.5561 (10^{-12} \text{cm}) \). For the other 180° domain in which the \( y \) and \( z \) components of moments are reversed the components of the interaction vector are \( x = 0.7981, y = 0.5059, z = -2.5433 \). The product \( R(\text{P} \cdot M_{\text{Ho}}) \) which leads to the asymmetry is negative for the first configuration and positive for the second. The weak ferromagnetic moment which has the same sign for both 180° domains is responsible for the small differences between the absolute values of the components.

In the perovskite structure the transition metal atoms are coordinated by octahedra of O atoms which share vertices. In the ideal structure the axes of the octahedra are parallel to the crystal axes but in the distorted perovskite structure of HoFeO\(_3\) they are tilted and twisted so that their axes lie in directions: \( x = [0.84, 0.53, 0.15], y = [0.53, -0.84, 0.15], z = [-0.40, 0.14, -0.91] \), and these directions do not change significantly with temperature [13].

| Table 2. Components of magnetization on Ho and Fe in HoFeO\(_3\) at 70 K aligned by 9 T applied parallel to \( z \). |
| --- |
| **Magnetization (\( \mu_B \))** | **Model** | **M\(_x\)** | **M\(_y\)** | **M\(_z\)** | **R(\text{cryst})** |
| Fe | Spin | 4.5994(8) | -0.04(9) | 0.060(14) | 20.2 |
| Ho | Spin | 0.05(5) | 1.58(10) | 1.70(9) |
| Fe | Spin | 4.597(2) | -0.12(8) | 0.114(10) | 8.7 |
| Ho | Spin | 0.6(2) | 0.75(14) | 0.97(9) |
| Ho | Orbital | 0.20(9) | 0.41(6) | 0.53(6) |

| Table 3. Components of magnetic moment on Ho and Fe atoms in the antiferromagnetic \( \Gamma' \) structure of HoFeO\(_3\) measured with 0.5 T \( \parallel [100] \) at 25, 15 and 5 K. |
| --- |
| **Magnetic moment (\( \mu_B \))** | **Model** | **M\(_x\)** | **M\(_y\)** | **M\(_z\)** | **R(\text{cryst})** |
| Fe | Spin | -0.91(5) | -2.13(10) | 0.57(3) | 11 |
| Ho | Spin | -0.19(4) | -0.45(10) | 0.12(3) |
| Fe | Spin | -0.01(6) | 0.12(4) | 4.60(1) |
| Ho | Spin | -1.36(9) | -3.2(2) | 0.58(5) | 11 |
| Ho | Spin | -0.27(8) | -0.62(6) | 0.11(3) |
| Fe | Spin | 0.01(1) | 0.20(6) | 4.60(1) |
| Ho | Spin | -2.1(3) | -5.4(6) | 0.80(11) | 14 |
| Ho | Spin | 0.2(2) | 0.6(6) | -0.08(9) |
| Fe | Spin | 0.11(6) | 0.8(2) | 4.54(4) |
Figure 3. Schematic drawing showing the orientation of the moment on the Fe atom at (0, ½, 0) in HoFeO$_3$ relative to its coordinating octahedron of O atoms. (a) In the $\Gamma_4$ structure at 70 K and (b) in the $\Gamma_2$ structure at 25 K. For clarity the direction of rotation of the Fe moment giving rise to weak ferromagnetism is indicated by the dashed lines and is exaggerated.

Figure 3 shows schematically the orientation of the moment on the Fe atom at (0, ½, 0) relative to its coordinating octahedron (a) at 70 K in a field of 9 T parallel to [0 0 1] and (b) at 25 K in a field of 0.5 T nearly parallel to [1 0 0]. In both cases the tilt of the Fe moment towards the field direction is in the same direction as the tilt of its coordinating octahedron. At 25 K the ferromagnetic component of the Fe moment is very small and the preferred domain must be determined by the Fe-Ho interactions. In the low temperature data the contribution of Fe to the weak ferromagnetism is very small relative to that of Ho and and the precision with which it can be determined is limited both by this and by interference from antiferromagnetic components due to imperfect crystal alignment. Nevertheless the variation of the ferromagnetic (x) component of Fe moment between 25 and 5 K, although hardly significant, is in accord with the changes in reflection intensities in this temperature range found in zero field measurements [13]. From these it was deduced that the relative directions of the antiferromagnetic Ho and Fe moments change sign at around 15 K. The resultant direction of magnetization is determined by the larger Ho contribution so that when the relative directions of the moments change sign the weaker ferromagnetic moments of the Fe atoms align in the opposite direction to the magnetising field leading to reversal of the Fe x component.

6.2. Symmetry

The foregoing analysis has been carried out assuming the atomic positions of the nuclear space group Pbnm. However, maintaining this space group for the magnetic structure, constrains the Ho moments to lie either parallel or perpendicular to [0 0 1]. The magnetic fields applied in the present experiments can break the mirror symmetry of the planes on which the Ho atoms lie. The consequent loss of centrosymmetry permits the oxygen octahedra to acquire a polar character allowing ferroelectricity. The results of the measurements in the $\Gamma_4$ phase at 60 K show that the Ho moments have very high magneto-crystalline anisotropy so that a field applied parallel to [0 0 1] induces antiferromagnetic ordering parallel to [0 1 0], in addition to ferromagnetic alignment along [0 0 1]; a configuration not consistent with centrosymmetry. In the low temperature $\Gamma_2$ phase there is a small but significant component of Ho moment parallel to [0 0 1], again indicating a loss of centrosymmetry presumably due to exchange interaction with the Fe moments which are aligned parallel to z in this phase.

7. Conclusion

Polarized neutron diffraction measurements of the intensity asymmetries induced by applying magnetic fields can in principle give important information (1) about the magnetic anisotropy of some of the magnetic species and (2) can be used to determine the sign of the D-M interaction. The present measurements of intensity asymmetries from HoFeO$_3$ with the $k = (0 0 0)$ magnetic structures $\Gamma_4$, and $\Gamma_2$ type have enabled us to extract both types of information. The results of our experiment shows that strong magnetocrystalline anisotropy of Ho favours the y orientation and that with even $H = 9$ T applied field parallel to [0 0 1] almost half of the ordered Ho moment is not aligned parallel to the field but antiferromagnetically arranged in the $x - y$ plane. In addition the sign of the asymmetric coupling can be inferred from the magnetic moment components given in Table 3 since the listed moments are those on the representative atom (Fe at 0, 1/2, 0 and Ho at 0.9186, 0.0685, 3/4). It can also be determined more directly from the signs of the intensity asymmetries. Another important conclusion (3) from the present investigation is that, due to the Ho anisotropy the centrosymmetry of the structure is broken: in the $\Gamma_4$ phase by a magnetic field parallel to [0 0 1] and in the low temperature $\Gamma_2$ phase by its interaction with ordered Fe moments. The loss of centrosymmetry of the Fe site, which this implies, would allow its coordinating octahedron of oxygen to become polarised, and consequently allow ferroelectricity. At temperatures below the Fe ordering temperature, even with no applied field, the Ho are subject to the internal field due to the ordered Fe moments. It is conceivable that, due to the Ho anisotropy, the internal field could induce moments on Ho which will break the centrosymmetry. So there is a possibility that HoFeO$_3$ develop ferroelectricity at low temperatures.

References

[1] White R 1969 J. Appl. Phys. 40 1061
[2] Belov K P 1976 Sov. Phys.—Usp. 19 574
[3] Belov K P, Zvezdin A K, Katomtseva A M and Levitin R Z 1979 Orientation Phase Transitions in Rare Earth Magnetic Materials (Moscow: Nauka)
[4] Treves D 1965 J. Appl. Phys. 36 1033
[5] Gyorgy E M, Remeika J P and Hagedorn F B 1968 J. Appl. Phys. 39 1309
[6] Sirivardie J 1969 J. Solid State Commun. 7 1555
[7] Hornreich R M and Yaeger I 1973 Int. J. Magn. 4 71
[8] Yamaguchi T 1974 J. Phys. Chem. Solids 35 479
[9] Tokunaga Y, Iguchi S, Arima T and Tokura Y 2008 Phys. Rev. Lett. 101 097205
[10] Tokunaga Y, Furukawa N, Sakai H, Taguchi Y, Arima T and Tokura Y 2009 Nat. Mater. 8 558
[11] Lee J-H, Jeong Y K, Park J H, Oak M, Jang H M, Son J Y and Scott J F 2011 Phys. Rev. Lett. 107 117201
[12] Kuo C-Y et al 2014 Phys. Rev. Lett. 113 217203
[13] Chatterji T, Meven M and Brown P J 2017 AIP Adv. 7 045106
[14] Gukasov A and Brown P J 2002 J. Phys.: Condens. Matter 14 8831
[15] Brown P J 2005 Physica B 356 239
[16] Brown P J and Forsyth J B 1981 J. Phys. C: Solid State Phys. 14 5171
[17] Brown P J and Chatterji T 2011 Phys. Rev. B 84 054426
[18] Shao M et al 2011 J. Cryst. Growth 318 947
[19] Marshall W and Lovesey S W 1971 Theory of thermal neutron Scattering (Oxford: Oxford University Press) ch 5 p 109