A Single-Crystal Mössbauer Study of Spin Reorientations in the Multi-Ferroic $HoFeO_3$

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^{57}Fe Mössbauer spectroscopy on single crystal slices has been used to study the spin reorientation transition that occurs in $HoFeO_3$ for 35 K $\leq T \leq$ 60 K. We also prepared a powder sample for comparison and confirmed that the results were consistent between the two data sets. By using thin polished slices cut perpendicular to the three orthorhombic axes we have been able to follow a-axis → c-axis reorientation in detail and confirm that moments also tip toward the $b-$axis by $\sim 20°$ before returning closer to the $ac-$plane. We also show that the moments are never fully parallel or perpendicular to any of the three orthorhombic axes; a consequence of the mixed ferro-/antiferro-magnetic structure adopted by $HoFeO_3$.

Index Terms—**Mössbauer spectroscopy, multiferroics, orthoferrites, spin reorientation.**

I. INTRODUCTION

THE observation of weak electrical polarisation in several $RFeO_3$ compounds (Sm [1], [2], Gd [3], and Dy [4]) has revived interest in this system as a potential source of multiferroic materials. While the spontaneous effects are modest, it is possible that strain or doping may be exploited to enhance the ferroelectric response [5] and a complete understanding of the unperturbed systems will be essential in developing strategies to improve these materials. The original interest in the rare-earth orthoferrite system dates from the 1960s and 1970s, where they were studied using neutron powder diffraction [6], Mössbauer spectroscopy [7], and X-ray diffraction on flux-grown single crystals [8]. The iron sublattice orders antiferromagnetically (AF) with T_N = 620–740 K, depending on the rare earth [7], while the rare-earth sublattice tends to order below 15 K (~6.5 K for $HoFeO_3$ [6]). The AF structure of the iron sublattice is frequently canted, with a small ferromagnetic (FM) component, and in many of these orthoferrites, the iron sublattice also undergoes one or more spin-reorientation transitions below T_N, before the rare-earth orders [9]. These transitions appear to be driven by $R \leftrightarrow$ Fe interactions as they do not occur in the Y-, La- and Lu- based members of the series, where the rare earth is magnetically inactive [9].

The $RFeO_3$ orthoferrites crystalise in an orthorhombic structure with approximate cell parameters: $a = 5.28$ Å, $b = 5.59$ Å, and $c = 7.61$ Å (see Section II for more details). White [9] showed the high-temperature order in $HoFeO_3$ to be AF along a with a weak FM component along c, while at low ($T < 60$ K) it is AF along c with weak FM along a. It is the path between these two states that is disputed, as the rotation of the AF axis from a to c is complex. White [9] showed a 40 K wide "unknown" region from 100 to 60 K, perhaps where the two forms co-existed, while Vorob′ev *et al.* [10] and Balbashov *et al.* [11] proposed a more complex three-stage process: starting at 60 K the AF axis rotates toward the $c-$axis within the $ac-$plane but near 50 K it tips out of the $ac-$plane toward the $b-$axis as it continues its rotation toward the $c-$axis, the process being complete by 40 K. A Mössbauer study of a single crystal slice cut perpendicular to the $b-$axis confirmed the tip away from the $ac-$plane by 37(5)°, however, they also observed a two-phased region during the reorientation [12]. Finally, a recent single crystal neutron diffraction study [13] has claimed three distinct regions, with the primary AF axis along a ($T > 55$ K), along b (55 K < T < 35 K), and finally along c ($T < 35$ K), with abrupt steps at each transition.

Given the conflicting descriptions of the spin-reorientation event in $HoFeO_3$ we decided to revisit the problem using a variety of techniques to develop a self-consistent picture. Here we use ^{57}Fe Mössbauer spectroscopy on single crystal slices cut perpendicular to the three orthorhombic axes in order to elucidate the details of the zero-field magnetic structures as a function of temperature. In this report we focus on the ordering behavior of $HoFeO_3$ for 100 K $< T <$ 9 K using single-crystal Mössbauer spectroscopy to follow the spin-reorientations. This temperature range covers the a-axis → c-axis reorientation but avoids the ordering of the holmium.

II. EXPERIMENTAL METHODS

The powder samples were prepared by firing in air at 1400 °C following the method in [7]. The starting reagents (Fe_2O_3 and Ho_2O_3, each 99.9% pure) were dried at 200 °C to remove absorbed water, then a stoichiometric mixture was heated in air at 900 °C for 2 h in an alumina crucible. The sample was then ground and fired at 1400 °C

Manuscript received March 3, 2017; accepted July 2, 2017. Date of publication July 11, 2017; date of current version October 24, 2017. Corresponding author: S. Cao (e-mail: sxcao@shu.edu.cn).

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Digital Object Identifier 10.1109/TMAG.2017.2725640

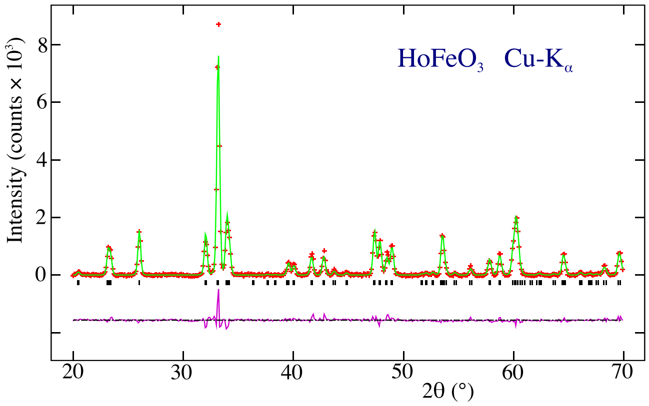

Fig. 1. Room temperature Cu K$_\alpha$ X-ray diffraction pattern for powder sample of HoFeO$_3$. Bragg markers for the orthorhombic Pnma structure are shown below the fit data, with residuals (bottom).

for 14 h. The process was repeated until no trace of the initial reagents was seen in the X-ray powder diffraction pattern (Fig. 1). Detection limits were ~0.3 wt.% for the starting materials.

Fitting the Cu K$_\alpha$ X-ray diffraction pattern of the powder sample using the general structure analysis system/EXPGUI package [14], [15] confirmed that HoFeO$_3$ adopts the orthorhombic Pnma structure (#62) with $a = 5.5925(4)$ Å, $b = 7.6093(5)$ Å, and $c = 5.2846(4)$ Å at RT. Unfortunately most of the older (and some current) literature uses the Pbnm space group in a setting that requires both a shift in the origin and a transformation of axes: $a' = c$, $b' = a$, and $c' = b$ so that the cell parameters become $a = 5.28$ Å, $b = 5.59$ Å, and c = 7.61Å. We will use this older Pbnm setting here to facilitate comparison with earlier work.

Basic magnetic characterization of the powder sample was carried out using a Quantum Design Physical Properties Measurement System. Susceptibility (1 kHz, 1 mT field) and magnetization (0.1 T applied field) are shown versus temperature in Fig. 2. The onset of the spin re-orientation at ~60 K is clearly visible in both measurements, although it is not possible to determine either the width of the transition or where the reorientation is complete from magnetization or susceptibility data. A small (~0.06 μ_B/f.u.) FM component is apparent above the transition and this increases markedly as the transition proceeds (to about 0.25 μ_B/f.u. by 45 K). The continuing increase below 40 K cannot be due to an increasing FM component of the iron ordering as this would require a substantial net rotation of the iron moments and this can be ruled out by the Mössbauer results presented below. The susceptibility of the Ho^{3+} ions in HoFeO$_3$ is highly anisotropic, being much larger in the $ab-$plane than along the $c-$axis [16], so the holmium moments couple strongly to the small $ab-$plane FM component of the iron ordering that develops as the a-axis → c-axis reorientation proceeds. Indeed, it is likely that this coupling drives the reorientation [16]. Finally, there is a marked peak in the susceptibility as the Ho^{3+} moments order near 10 K.

The single crystal of HoFeO$_3$ was grown by the optical floating zone technique [17]. Slices 5 × 5 × 1 mm were cut perpendicular to the three orthorhombic axes. The slices were hand polished down to about 200 μm, mounted on 0.25 mm thick beryllium discs and further polished down to about 50 μm for the Mössbauer work. Neutron diffraction analysis on the plates after the Mössbauer work revealed a consistent 9(1)° misalignment between the surface normals and the intended crystallographic axes. 50 μm is still too thick for a thin absorber approximation to apply, but the plates were too fragile to permit further thinning. To ensure that only γs that had passed through the HoFeO$_3$ plates were detected, the area around the polished slices was covered with lead foil and the smaller gaps were filled with tungsten-loaded GE-varnish. A closed-cycle fridge was used to cool the assembly and the spectra were fit using a conventional least-squares minimization routine to a sum of Lorentzian lines. Line positions for the combined hyperfine field ($B_{\rm hf}$) and quadrupole splitting (QS) were derived using a first-order pertubation approach as QS $\ll B_{\rm hf}$. A transmission integral was used to correct for the significant saturation effects present in the spectra.

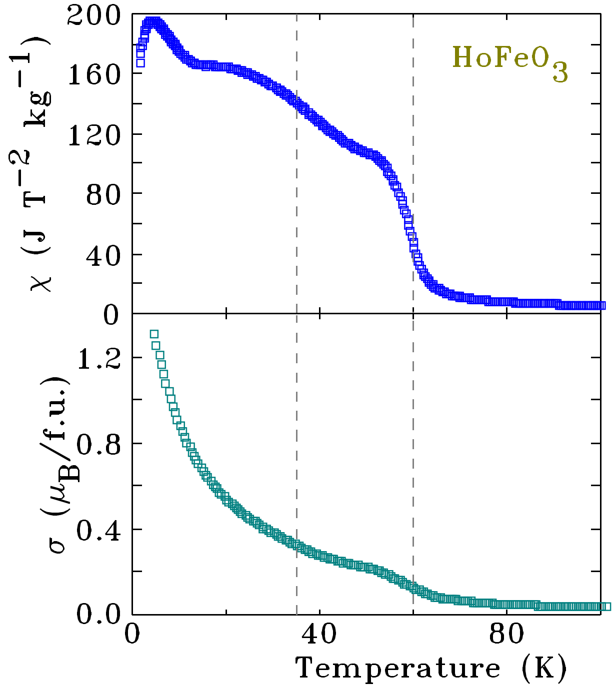

Fig. 2. ac susceptibility measured on heating following zero-field cooling to 2 K at 1 kHz in a 1 mT driving field (top) and magnetization measured on cooling in a dc field of 100 mT for a powder sample of HoFeO$_3$ (bottom). The dashed vertical lines mark the start and end of the spin reorientation as determined by Mössbauer spectroscopy. There is a small FM contribution apparent above the reorientation but it is much larger below the a-axis→c-axis rotation near 60 K. The rapid growth below 40 K reflects increasing polarisation of the holmium moments by the iron.

III. MÖSSBAUER RESULTS

Mössbauer spectroscopy can be used to follow the spin reorientation in two distinct ways: 1) using the projection of $B_{\rm hf}$ onto V$_{ZZ}$, the principal axis of the electric field gradient (efg) tensor and 2) using the angular dependence of the $\Delta m_I = 0$ transitions (lines 2 and 5 in the magnetically

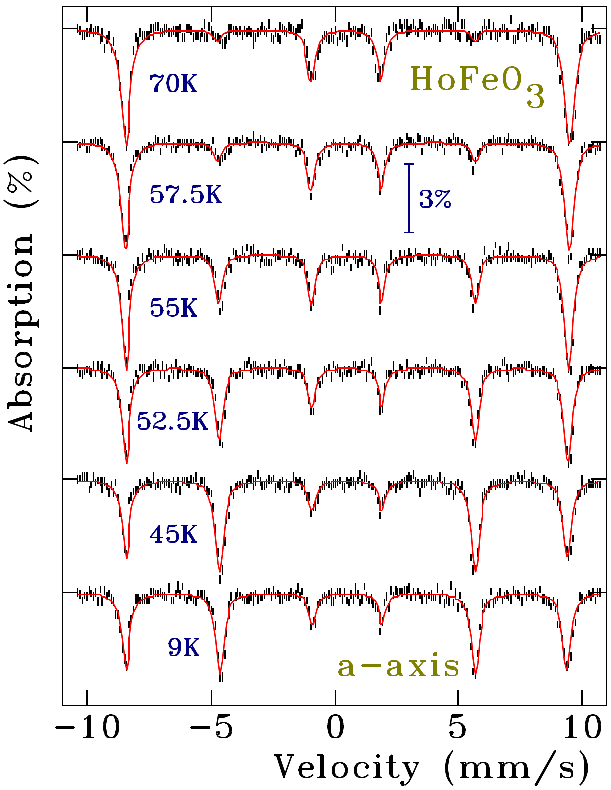

Fig. 3. Typical ^{57}Fe Mössbauer spectra for the $HoFeO_3$ single crystal plate cut perpendicular to the $a-$axis. The growth of the $\Delta m_I = 0$ transitions (lines 2 and 5) on cooling is clearly visible and reflects the rotation of the iron moments away from the $a-$axis.

split Mössbauer spectrum) to establish the angle between the $\gamma-$beam and B_{hf} in an oriented single crystal. The former exploits an internal (to the crystal) frame of reference defined by the efg, while the latter relies on an external reference frame defined by the orientation of the single crystal sample. Typical Mössbauer spectra for the slice of the $HoFeO_3$ crystal cut perpendicular to the $a-$axis are shown in Fig. 3, and the change in intensity of the $\Delta m_I = 0$ transitions at −5 and +5 mm/s (lines 2 and 5 of the 6-line magnetically split spectra) is clearly visible as we cool through the spin reorientation transition.

The low point symmetry ($\bar{1}$) of the $4a$ site occupied by the iron atoms in $HoFeO_3$ imposes no constraints on the form of the efg tensor: the tensor axes are not tied to the crystallographic axes, nor is the asymmetry parameter (η) forced to be zero. However, the observed QS is small, and the hyperfine field is clearly dominant, so neglecting the asymmetry contribution leads to an observed QS of the form

$$\mathrm{QS} = \frac{eQV_{zz}}{4}(3\cos^2\theta - 1) \tag{1}$$

where e is the elementary charge, Q is the quadrupole moment of the ^{57}Fe nucleus in its first excited state, and θ is the angle between V_{zz} and B_{hf}. For $\theta = 90°$, $\mathrm{QS} = -\frac{1}{4}eQV_{zz}$ and for $\theta = 0°$, $\mathrm{QS} = \frac{1}{2}eQV_{zz}$, so a change in QS by a factor of −2 corresponds to a change in moment direction by 90°. Fig. 4 shows the temperature dependence of QS for the three single crystal plates. Since the behavior of QS(T) reflects the change in moment direction with respect to an *internal* reference frame, the evolution is the same for all three plates. The average value changes from +0.068(4) mm/s above 60 K to −0.031(3) mm/s below 35 K, for a ratio of −2.2(2), fully consistent with a 90° rotation of the spins. Furthermore, the observation of a QS ratio close to −2 supports our simplifying assumption of $\eta \sim 0$, as a large η would suppress the effective QS below the rotation and so lead to a much larger QS ratio.

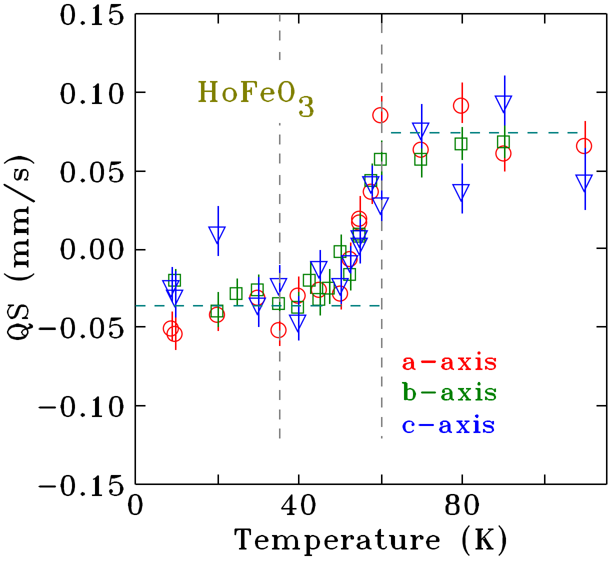

Fig. 4. Fit QSs for all three single crystal samples of $HoFeO_3$ plotted as a function of temperature. Dashed horizontal lines show the average high and low temperature values. The behavior between 35 and 60 K reflects the rotation of the iron moments within the local reference frame defined by the efg tensor, and the factor of −2 change in average value is consistent with the roughly 90° rotation of the iron moments. Dashed vertical lines mark the start and end of the spin-reorientation process determined from the line intensity data shown in Fig. 5.

The rather small QS and the low point symmetry of the iron site limits the information that can be extracted from QS(T) to a consistency check. It is clear that the iron moments undergo a 90° rotation, but little can be said about the processes involved. We therefore turn to a more sensitive measurement.

The intensity of the $\Delta m_I = 0$ transitions (lines 2 and 5 in the magnetic patterns shown in Fig. 3) depends on the orientation of B_{hf} with respect to the γ-beam (ϑ). Writing the intensity ratio as $3{:}R{:}1{:}1{:}R{:}3$ for a six line Mössbauer pattern, ϑ can be determined

$$R = \frac{4\sin^2\vartheta}{1+\cos^2\vartheta}. \tag{2}$$

The intensity is zero when the γ-beam is parallel to B_{hf}, and is maximized ($R = 4$) when the two are perpendicular. For each of the $HoFeO_3$ single crystal plates studied here, the γ-direction corresponds to a specific crystal axis and so we can determine the angle (ϑ) between each of the three axes and B_{hf} as a function of temperature. This can be seen in Fig. 3 as lines 2 and 5 clearly grow in intensity on cooling.

Fitting the spectra for the three $HoFeO_3$ single crystal plates yields the results presented in Fig. 5. Several conclusions can be drawn from a simple visual inspection of Fig. 5 as

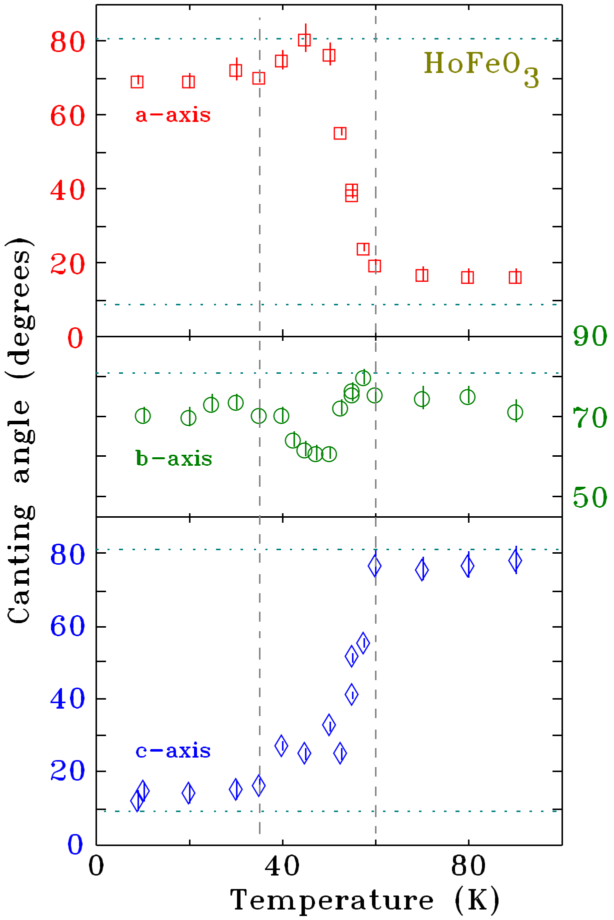

Fig. 5. Fit canting angles for the three single-crystal plates of HoFeO$_3$ cut perpendicular to the *a*−axis (top), *b*−axis (middle) and *c*−axis (bottom). The reorientation from approximately parallel to the *a*−axis above 60 K, to approximately parallel to the *c*−axis below 35 K is clearly visible, however, it is clear that the moments are never fully parallel (or perpendicular) to any of the three crystallographic axes. Dashed vertical lines mark the start and end of the spin-reorientation process. There is indeed a slight (and brief) tilt toward the *b*−axis, and that this rotation occurs *after* the moments start to tilt away from the *a*−axis (middle). The dotted horizontal lines on the figures mark the 9° misalignment of the crystals and thus define 0° and 90° for the crystallographic axis system.

follows: 1) The reorientation starts at about 60 K and is complete by about 35 K, these temperatures are marked on most of the figures presented here by two dashed vertical lines to facilitate comparison between measurements; 2) The basic reorientation involves the moments rotating from roughly parallel to the *a*−axis for T> 60 K to roughly parallel to the *c*−axis for T< 35 K, but the detailed behavior is more complex; 3) The moments are never truly parallel to any of the three crystallographic axes; and 4) The moments definitely tip toward the *b*−axis during the rotation, but the tilt is relatively modest (∼20° at most).

The first and second part of the above results are fully consistent with previous reports and so will not be discussed further. The failure of the moments to orient fully parallel to any of the three crystallographic axes (observation 3) points to the complex mixed FM+AF magnetic structure adopted by this material and is consistent with the small FM components apparent in our magnetization data (Fig. 2). The moments start out canted by 8(1)° from the *a*−axis, and remain canted by 5(1)° from the *c*−axis once the reorientation is complete. While one might argue that a failure to fit a canting angle of 90° in the high and low temperature regions could be due to an incomplete correction for saturation effects (lines 2 and 5 are significantly stronger than the outer lines for $\vartheta = 90^\circ$ and therefore more likely to be affected by saturation effects), this argument cannot be used to explain the failure to observe $\vartheta = 0^\circ$ where zero intensity would be expected in lines 2 and 5 – they are clearly present in the 70 K spectrum shown in Fig. 3, and the intensity is much larger than could be accounted for by the measured misalignment of the crystal plates. Furthermore, the temperature dependence of ϑ for the *a*−axis plate in Fig. 5 clearly shows that ϑ passes through a maximum at 45 K as the moments rotate almost perpendicular to the *a*−axis for perhaps 10 K, and then tilt slightly toward it again. The departures from $\vartheta = 0^\circ$ and $\vartheta = 90^\circ$ are clearly real for the *a*−axis plate. For the *b*−axis the primary concern is not whether the moments are perpendicular to the *b*−axis (the average canting appears to be about 10° at temperatures well away from the reorientation transition) but if they cant toward the *b*−axis, and by how much. The canting clearly occurs, but is relatively modest at ∼20°. Finally, the behavior of the *c*−axis component appears to be the simplest. Above the spin reorientation transition the moments are almost perpendicular to the *c*−axis, and once the reorientation is complete, the moments are very close to parallel to the *c*−axis.

The rotation toward the *b*−axis during the *a*-axis → *c*-axis spin reorientation was first observed in [10] and [11] using magnetostriction and FM resonance (FMR), respectively. The behavior of ϑ for the *b*−axis plate shown in Fig. 5 provides direct and independent confirmation of their result. Indeed, our observed canting toward the *b*−axis of ∼ 20° is fully consistent with the ∼ 10°−20° estimated from FMR data [11]. Furthermore, it is clear in Fig. 5 that the tilt toward the *b*−axis starts *after* the rotation away from the *a*−axis is underway, as reported in [10] and [11].

Ultimately, the complete temperature dependent magnetic structure of HoFeO$_3$ will be established using neutron diffraction. However, while neutron diffraction is an exceptional tool for establishing the *symmetry* of a magnetic structure, it is often difficult to determine the magnitudes of small components, especially FM contributions. Independent and complementary methods such as Mössbauer spectroscopy can provide invaluable constraints on some parameters, like the angles between the moments and the three orthorhombic axes, and so both guide and validate the diffraction analysis.

IV. CONCLUSION

The spin reorientation in HoFeO$_3$ proceeds through a series of smooth events. There are no abrupt transitions. At 60 K the iron moments in HoFeO$_3$ start to rotate away from the *a*−axis toward the *c*−axis, the process being complete by 35 K. The rotation also includes a brief tilt of ∼20° out of the *ac*−plane. At no temperature are the iron moments fully parallel to any of the three orthorhombic axes. The moments are never truly perpendicular to any of the crystallographic axes except near 45 K where they are briefly perpendicular to the $a-$axis

ACKNOWLEDGMENT

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada, in part by the Fonds Québécois de la Recherche sur la Nature et les Technologies, and in part by the National Natural Science Foundation of China under Grant 51372149.

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