

This is the accepted manuscript made available via CHORUS. The article has been published as:

## Electronic structure and direct observation of ferrimagnetism in multiferroic hexagonal $\text{YbFeO}_3$

Shi Cao, Kishan Sinha, Xin Zhang, Xiaozhe Zhang, Xiao Wang, Yuewei Yin, Alpha T. N'Diaye, Jian Wang, David J. Keavney, Tula R. Paudel, Yaohua Liu, Xuemei Cheng, Evgeny Y. Tsymbal, Peter A. Dowben, and Xiaoshan Xu

Phys. Rev. B **95**, 224428 — Published 26 June 2017

DOI: [10.1103/PhysRevB.95.224428](https://doi.org/10.1103/PhysRevB.95.224428)

# Electronic structure and direct observation of ferrimagnetism in multiferroic hexagonal YbFeO<sub>3</sub>

Shi Cao,<sup>1</sup> Kishan Sinha,<sup>1</sup> Xin Zhang,<sup>1</sup> Xiaozhe Zhang,<sup>2,1</sup> Xiao Wang,<sup>3</sup> Yuewei Yin,<sup>1</sup> Alpha T N'Diaye,<sup>4</sup> Jian Wang,<sup>5</sup> David J Keavney,<sup>6</sup> Tula R Paudel,<sup>1</sup> Yaohua Liu,<sup>7</sup> Xuemei Cheng,<sup>3</sup> Evgeny Y Tsybal,<sup>1,8</sup> Peter A Dowben,<sup>1,8</sup> and Xiaoshan Xu<sup>1,8</sup>

<sup>1</sup>*Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588, USA*

<sup>2</sup>*Department of Physics, Xi'an Jiaotong University, Xi'an 710049, Peoples Republic of China*

<sup>3</sup>*Department of Physics, Bryn Mawr College, Bryn Mawr, PA 19010, USA*

<sup>4</sup>*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

<sup>5</sup>*Canadian Light Source, Saskatoon, SK S7N 2V3, Canada*

<sup>6</sup>*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

<sup>7</sup>*Quantum Condensed Matter Division, Oak Ridge National Lab, Oak Ridge, TN 37831, USA*

<sup>8</sup>*Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588, USA*

(Dated: May 22, 2017)

The magnetic interaction between rare-earth and Fe ions in hexagonal rare-earth ferrites ( $h$ -REFeO<sub>3</sub>), may amplify the weak ferromagnetic moment on Fe, making these materials more appealing as multiferroics. To elucidate the interaction strength between the rare-earth and Fe ions as well as the magnetic moment of the rare-earth ions, element specific magnetic characterization is needed. Using X-ray magnetic circular dichroism, we have studied the ferrimagnetism in  $h$ -YbFeO<sub>3</sub> by measuring the magnetization of Fe and Yb separately. The results directly show anti-alignment of magnetization of Yb and Fe ions in  $h$ -YbFeO<sub>3</sub> at low temperature, with an exchange field on Yb of about 17 kOe. The magnetic moment of Yb is about  $1.6 \mu_B$  at low-temperature, significantly reduced compared with the  $4.5 \mu_B$  moment of a free Yb<sup>3+</sup>. In addition, the saturation magnetization of Fe in  $h$ -YbFeO<sub>3</sub> has a sizable enhancement compared with that in  $h$ -LuFeO<sub>3</sub>. These findings directly demonstrate that ferrimagnetic order exists in  $h$ -YbFeO<sub>3</sub>; they also account for the enhancement of magnetization and the reduction of coercivity in  $h$ -YbFeO<sub>3</sub> compared with those in  $h$ -LuFeO<sub>3</sub> at low temperature, suggesting an important role for the rare-earth ions in tuning the multiferroic properties of  $h$ -REFeO<sub>3</sub>.

## I. INTRODUCTION

The diverse magnetic properties of rare-earth (RE) transition-metal (TM) oxides owe to the interplay between the distinct magnetism of rare-earth and transition-metal ions. For the transition-metal ions, the magnetic moments come from d electrons which are well exposed to the local environment. In contrast, for rare-earth ions, the magnetic moments come from 4f electrons which are close to the inner core and have significant contributions from both spin and orbital angular momentum.<sup>1</sup> While the stronger interaction between the transition-metal ions determines the framework of the magnetic order in the RE-TM oxides<sup>2–4</sup>, the weaker interaction between the rare-earth and transition-metal ions, on the other hand, generates interesting phenomena such as spin reorientations and moment compensation.<sup>5–11</sup> Despite the importance of the RE-TM interaction, a comprehensive understanding of its underpinnings and implications is still lacking for many material systems.

In this work, we study the magnetic interaction between the rare-earth and transition-metal ions by measuring the magnetization of the rare-earth and transition-metal ions separately using an element-specific method. In particular, we study hexagonal YbFeO<sub>3</sub>, a member of hexagonal rare-earth ferrites ( $h$ -YbFeO<sub>3</sub>, RE=Ho-Lu, Y, and Sc). Hexagonal  $h$ -YbFeO<sub>3</sub> have a layered crys-

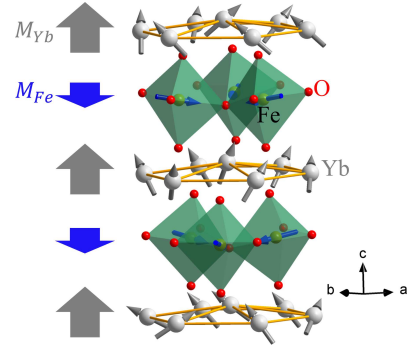


FIG. 1. (Color online) The crystal structure of  $h$ -YbFeO<sub>3</sub> and schematic of the magnetic structure. The arrows on the atoms indicate the atomic magnetic moments.  $M_{Fe}$  and  $M_{Yb}$  are the magnetization of Fe and Yb along the  $c$  axis respectively, which are anti-aligned at low temperature. The Fe moments form a 120-degree antiferromagnetic order in the basal plane, with only a very small component along the  $c$  axis. The Yb moments are partially aligned by the Yb-Fe exchange field.

tal structure in which both RE and Fe atoms adopt a two-dimensional triangular lattice, as shown in Fig. 1.<sup>12</sup> Below about 1000 K,  $h$ -YbFeO<sub>3</sub> crystal structure undergoes a distortion corresponding to a rotation of the FeO<sub>5</sub> local structure and a buckling of the rare-earth layer, which induces an improper ferroelectricity.<sup>13–17</sup> The ro-

tation of the  $\text{FeO}_5$  also cants the moment on Fe, via the Dzyaloshinskii-Moriya interaction, generating weak ferromagnetism on top of a 120-degree antiferromagnetic order below about 120 K, as illustrated in Fig. 1.<sup>18–20</sup> The spontaneous magnetization is along the  $c$  axis. Recent work demonstrated that a super-lattice structure of hexagonal Lu-Fe-O materials are promising for realizing room temperature multiferroic materials with co-existing ferroelectricity and ferromagnetism,<sup>21</sup> a property that has potential application in energy-efficient information processing and storage<sup>22</sup>.

In  $\text{h-YbFeO}_3$ , the Fe-Fe interaction is expected to dominate the framework of the magnetic ordering, as corroborated by the fact that the ordering temperature of  $\text{h-YbFeO}_3$  is almost the same as that of  $\text{h-LuFeO}_3$  (noting that  $\text{Lu}^{3+}$  is non-magnetic)<sup>16,17,23,24</sup>. The Yb-Fe interaction is weaker but enough to partially align the moment on Yb and contribute to the total magnetization. Indeed, an enhancement of magnetization of  $\text{h-YbFeO}_3$ , compared with that in  $\text{h-LuFeO}_3$ , has been observed previously<sup>23,24</sup>, to be up to about  $3 \mu_B/\text{f.u.}$  at 3 K, in contrast to  $0.018 \mu_B/\text{f.u.}$  in  $\text{h-LuFeO}_3$ .<sup>13,16</sup> The Yb-Fe interaction could, in principle, align or anti-align the moments of Fe and Yb. At the compensation temperature<sup>3,5</sup>, the magnetization of Fe and Yb cancels, and an indication of this was observed previously at about 80 K<sup>24</sup>. On the other hand, direct observation of anti-alignment between the Fe and Yb magnetization is still lacking. In addition, the previously reported large magnetization (about  $3 \mu_B/\text{f.u.}$ )<sup>24</sup> at low temperature is more consistent with a free  $\text{Yb}^{3+}$ , but unexpected when considering the effect of the crystal field generated by the local environment,<sup>25–29</sup> which could significantly change the effective magnetic moment and the magnetic anisotropy at low temperature.<sup>28,30</sup>

To elucidate the Yb-Fe interaction and the magnetic moment of Yb, we have studied the electronic structure of  $\text{h-YbFeO}_3$  using X-ray absorption spectroscopy (XAS) and the X-ray photoemission spectroscopy (XPS) and measured the magnetization of Fe and Yb separately using X-ray magnetic circular dichroism (XMCD). We have found a large exchange field (17 kOe) on Yb, while the magnetic moment of Yb is significantly reduced from the value of a free ion. Mixed valence of Yb was investigated and found only at the surface of samples grown in reducing environment, suggesting minimal effect on the magnetism of  $\text{h-YbFeO}_3$ .

## II. METHODS

Hexagonal  $\text{YbFeO}_3$  (001) films (20–50 nm) were deposited on yttrium stabilized zirconia (YSZ) (111) substrates and on  $\text{Fe}_3\text{O}_4$  (111)/ $\text{Al}_2\text{O}_3$  (001) substrates using pulsed laser (248 nm) deposition in 5 mtorr oxygen and argon environment, at 750 °C with a laser fluence of about  $1 \text{ Jcm}^2$  and a repetition rate of 2 Hz.<sup>13,14,31</sup> The film growth was monitored using reflection high energy

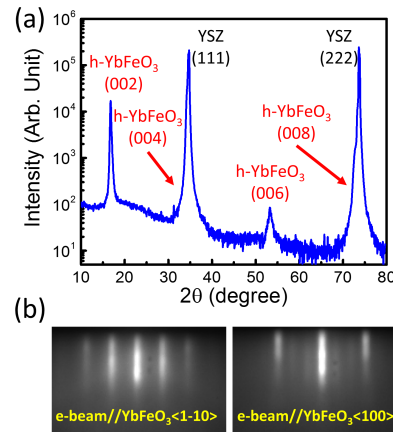


FIG. 2. (Color online) (a)  $\theta$ - $2\theta$  X-ray diffraction measurement of an  $\text{h-YbFeO}_3$  film grown on yttrium stabilized zirconia (YSZ). (b) RHEED patterns of an  $\text{h-YbFeO}_3$  film with electron beam along the  $\langle 1-10 \rangle$  and  $\langle 100 \rangle$  directions.

electron diffraction (RHEED). All the films studied with X-ray absorption spectroscopy and X-ray magnetic circular dichroism were grown in oxygen environment. The crystal structures of the  $\text{h-YbFeO}_3$  films were characterized by X-ray diffraction (XRD) using a Rigaku D/Max-B diffractometer, with the  $\text{Co K}\alpha$  radiation (1.7903 Å). The linear X-ray absorption spectroscopy on the Fe L edge and O K edge was studied using X-ray photoemission electron microscope (X-PEEM) at the SM beamline of the Canadian Light Source with linearly polarized X-ray. The circular X-ray absorption (fluorescence) spectroscopy of Yb M edge and Fe L edge measurements were performed at the bend magnet beamline 6.3.1 in the Advanced Light Source at Lawrence Berkeley National Laboratory and at the beamline 4IDC in the Advanced Photon Source at Argonne National Laboratory respectively. The angle-resolved X-ray photoemission spectra (ARXPS) were obtained using SPECS PHOIBOS 150 energy analyzer. A non-monochromatized  $\text{Al K}\alpha$  X-ray source, with photon energy 1486.6 eV, was used with various emission angles, as previously reported.<sup>32</sup>

## III. RESULTS AND ANALYSIS

### A. Crystal structure and local environment of Fe

To verify the structure and phases of the epitaxial films, we carried out X-ray diffraction, electron diffraction, and X-ray spectroscopy measurements. Figure 2 (a) shows the X-ray diffraction ( $\theta$ - $2\theta$  scan) of  $\text{h-YbFeO}_3$ /YSZ films. No additional peak other than those expected for  $\text{h-YbFeO}_3$  and the substrate is visible in this large-range scan, indicating no impurity phases. As shown in Fig. 2(b), RHEED images show diffraction streaks consistent with a flat surface and the structure of  $\text{h-YbFeO}_3$ .<sup>13,31</sup>

The X-ray absorption spectra provided further confir-

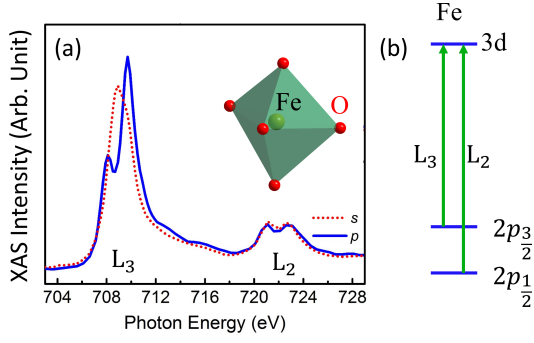


FIG. 3. (Color online) (a) X-ray absorption spectra at the Fe L edge measured using linearly polarized X-ray. Inset: the  $\text{FeO}_5$  local environment. (b) Schematic illustration of the  $L_2$  and  $L_3$  excitation.

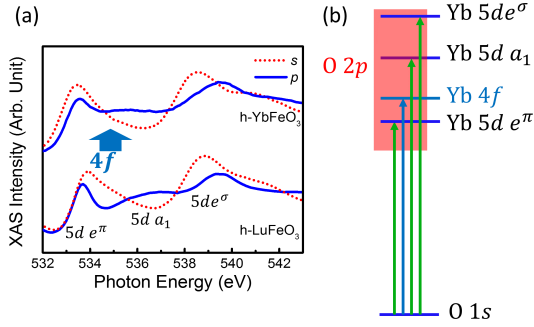


FIG. 4. (Color online) (a) X-ray absorption spectra at the O K edge of  $\text{h-LuFeO}_3$  and  $\text{h-YbFeO}_3$  measured using linearly polarized X-ray. The arrow indicates the  $4f$  state. (b) Schematic illustration of the O K edge excitation and the hybridization between the O and Yb states.

mation of the local structure of Fe, from the Fe L edge spectra taken with linearly polarized X-ray. The local environment of Fe in  $\text{h-YbFeO}_3$  is a trigonal bipyramid, with two apex O atoms (top and bottom) and three equator O atoms (in the Fe layer) as shown in Fig. 1 as well as in Fig. 3(a) inset. This structure makes the out-of-plane direction (along the  $c$  axis) and the in-plane direction (in the  $a$ - $b$  plane) two distinct crystalline directions. Using linearly polarized X-ray, we measured the absorption spectra at the Fe L edge, as illustrated in Fig. 3(b). As shown in Fig. 3(a), the spectrum with  $s$ -polarized X-ray ( $E$  vector in the  $a$ - $b$  plane) and that with  $p$ -polarized X-ray ( $E$  vector along the  $c$  axis) show obvious contrast, consistent with the large structural anisotropy. The spectra and linear dichroism in Fig. 3(a) match those observed previously for  $\text{h-LuFeO}_3$ ,<sup>20,21,33,34</sup> confirming that the local environment of the  $\text{FeO}_5$  moiety in the two materials are almost identical.

## B. The Electronic structure of Yb

While the electronic structure of Fe in  $\text{h-LuFeO}_3$  and  $\text{h-YbFeO}_3$  are superficially similar, the electronic struc-

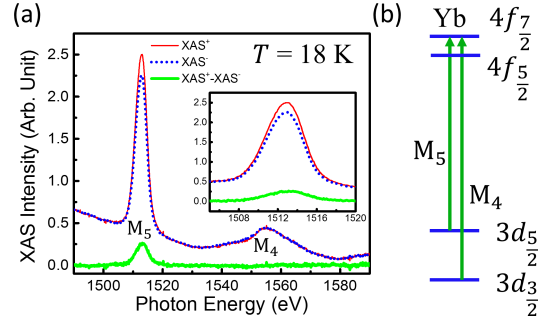


FIG. 5. (Color online) (a) X-ray absorption spectra at the Yb M edge measured using X-ray polarized counterclockwise.  $\text{XAS}^+$  ( $\text{XAS}^-$ ) is the spectrum measured in magnetic field along the  $+z$  ( $-z$ ) direction. (b) Schematic illustration of the Yb M edge excitation. The crystalline  $c$  axis of  $\text{h-YbFeO}_3$  is along the  $z$  direction.

ture of  $\text{Yb}^{3+}$  is expected to be different from that of  $\text{Lu}^{3+}$  by one less  $4f$  electron. To probe the unoccupied states of Yb, we measured the excitation of electrons from O  $1s$  states to O  $2p$  states (O K edge) using X-ray. Nominally, O  $2p$  states are fully occupied; the O  $1s$  to O  $2p$  excitation is forbidden by the Pauli exclusion principle. If, on the other hand, the O  $2p$  states are hybridized with the Yb states, the O  $2p$  states will be slightly unoccupied and give rise to observable O  $1s$  to O  $2p$  excitation; one can infer the energy of the unoccupied Yb states using the excitation energies.<sup>20</sup> As shown in Fig. 4(a), with linearly polarized X-rays, several features can be observed in the absorption spectra. Previously, we carried out symmetry analysis of the absorption spectra measured on  $\text{h-LuFeO}_3$  and identified the origin of these features mainly as the  $5d$  orbitals split in the crystal field:  $e^\pi$ ,  $a_1$  and  $e^\sigma$  [see Fig. 4(b)]<sup>20</sup>. Compared with the X-ray absorption spectra of  $\text{h-LuFeO}_3$ , the spectra of  $\text{h-YbFeO}_3$  show additional density of states, as indicated in Fig. 4(a), which is expected to be the unoccupied  $4f$  state that is hybridized with the O  $2p$  states.

The  $4f^{13}$  configuration of Yb can also be probed by measuring the excitation directly to the unoccupied  $4f$  states (in the absence  $s$ - $f$  hybridization, none exist with  $\text{Lu}^{3+}$ ). As shown in Fig. 5(a), X-ray absorption spectra at the Yb M edge were measured at 18 K. Two peaks are observed in the absorption spectra at approximately 1513 and 1555 eV, which can be assigned to  $M_5$  (initial state  $3d_{5/2}$ ) and  $M_4$  (initial state  $3d_{3/2}$ ) excitations respectively according to the photon energy<sup>35</sup> [see Fig. 5(b)]. The  $M_5$  transition in Yb, which is allowed by the angular-momentum selection rule, can be described using the one-electron (hole) picture, without many-body interactions, due to the simple initial (full  $3d_{5/2}$ , one hole in  $4f_{7/2}$ ) and final (one hole in  $3d_{5/2}$ , full  $4f_{7/2}$ ) states, consistent with the observed sharp, structureless peak in Fig. 5(a). The  $M_4$  excitation ( $3d_{3/2}$  to  $4f_{7/2}$ ), on the other hand, is not allowed by the angular-momentum selection rule. The non-zero intensity of the  $M_4$  peak

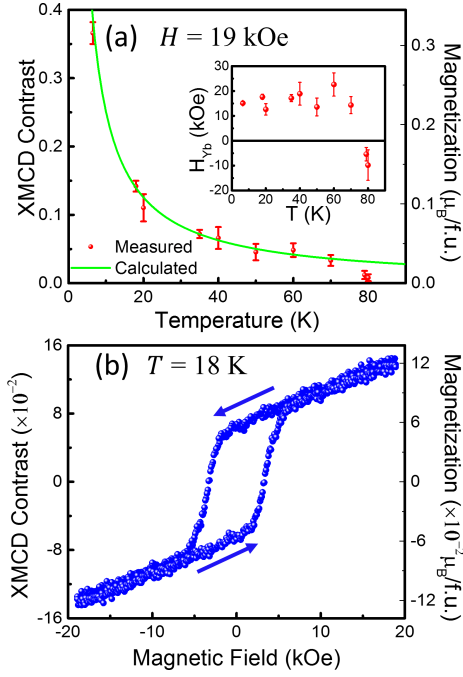


FIG. 6. (Color online) XMCD contrast of Yb  $M_5$  edge and the corresponding magnetization. (a) Temperature dependence measured in a 19 kOe magnetic field; the line is calculated using the parameters analyzed from (b). Inset:  $H_{Yb}$  extracted from the mean-field theory (see text in Section IV B). (b) Magnetic field dependence measured at 18 K. The magnetic field is along the  $c$  axis.

suggests that the crystal-field splitting and the Yb 4f-O 2p hybridization reduces the symmetry of the electronic states considerably, which is in line with the observed contribution to the O K edge excitation by the Yb 4f state shown in Fig. 4(a).

### C. The Ferrimagnetism of h-YbFeO<sub>3</sub>

#### 1. Magnetization of Yb and Fe

To study the magnetization of Yb, we carried out X-ray magnetic circular dichroism measurements, by comparing the absorption spectra using circularly polarized X-ray in opposite magnetic fields. As shown in Fig. 5(a), the X-ray absorption spectra measured in 19 kOe and -19 kOe magnetic fields along the  $z$  direction show a clear contrast. We define the XMCD contrast as  $\frac{2(I^+ - I^-)}{I^+ + I^-}$ , where  $I^+$  and  $I^-$  are the  $M_5$  peak areas of the absorption spectra in positive and negative magnetic fields respectively.

The XMCD contrast measured at  $H = 19$  kOe, for various temperatures between 6.5 and 80 K, is displayed in Fig. 6(a). The value of the XMCD signal decreases rapidly at low temperature, inconsistent with typical ferromagnetic dependence, which typically follows the

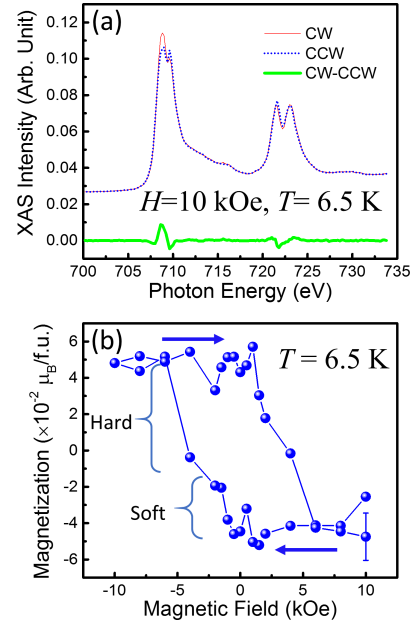


FIG. 7. (Color online) (a) Absorption spectra of Fe L edge measured with circularly polarized X-ray in a 10 kOe field at 6.5 K. CW and CCW stand for clockwise and counterclockwise polarization of the X-ray respectively. (b) Magnetic-field dependence of the magnetization of Fe at 6.5 K, which contains a soft and a hard component (see discussion in Section IV D). The magnetic field is along the  $c$  axis.

Bloch's law (decrease slowly at low temperature but much faster close to the magnetic ordering temperature)<sup>36</sup>. Figure 6(b) shows the field dependence of the XMCD contrast of Yb at 18 K. A clear hysteresis is observed with a coercive field of approximately 3.5 kOe. The magnetization converted from the XMCD contrast (See Appendix A) is also displayed in Fig. 6.

Figure 7(a) shows the spectra of X-ray absorption of Fe L edge measured in circularly polarized X-ray in a 10 kOe magnetic field at 6.5 K. A clear difference is observed between the spectra measured using X-rays of different polarizations, which can be used to estimate the magnetization of Fe.<sup>37</sup> Figure 7(b) shows the magnetic-field dependence of the Fe magnetization calculated from the XMCD contrast using the sum rule<sup>37–39</sup>. A hysteretic behavior is observed, with a coercive field of approximately 4 kOe, consistent with the value found in previous bulk magnetometry measurements.<sup>23,24</sup> This coercive field is also similar to that of Yb in Fig. 6(b), indicative of the exchange field on Yb generated by Fe. The saturation magnetization of Fe is  $0.05 \pm 0.01 \mu_B/\text{f.u.}$ , which corresponds to a small projection of the Fe moment along the  $c$  axis. From Fig. 6 and 7, we find that the magnetization of Fe is anti-parallel to the magnetic field and to that of the Yb magnetization at low temperature, as also illustrated in Fig. 1. This provides a direct observation of ferrimagnetic order in h-YbFeO<sub>3</sub>.



### 2. The Low temperature magnetic moment of Yb

As shown in Fig. 6(b), the magnetization of Yb does not saturate in the measurement condition; instead, it shows a linear relation with magnetic field when the field is much larger than the coercive field, which is consistent with a susceptibility behavior and somewhat akin to paramagnetism for Yb. We can, nonetheless, further analyze the magnetic moment on Yb using the mean-field theory,<sup>36</sup> which has been extensively discussed historically in orthoferrites and garnets<sup>10,11,40–43</sup>.

In the mean-field theory, the exchange interactions are modeled using the molecular fields. Assuming that the saturation magnetization of Fe is  $M_{Fe,S}$  (in  $\mu_B/\text{f.u.}$ ), the magnetization of Fe is given by:

$$M_{Fe} = M_{Fe,S} L(x_{Fe}), \quad (1)$$

where  $L(x) = \coth(x) - \frac{1}{x}$  is the Langevin function,  $x_{Fe} = \frac{(\Gamma_{YbFe} M_{Yb} + \Gamma_{Fe} M_{Fe} + \mu_0 H) M_{Fe,S}}{k_B T}$ ,  $M_{Yb}$  is the magnetization of Yb,  $\Gamma_{YbFe}$  and  $\Gamma_{Fe}$  are the molecular field parameters for the Yb-Fe and Fe-Fe interactions respectively,  $\mu_0$  is the vacuum permittivity,  $k_B$  is the Boltzmann constant,  $H$  is external magnetic field, and  $T$  is temperature. The magnetization of Yb is given by:

$$M_{Yb} = \mu_{Yb} L(x_{Yb}) \quad (2)$$

where  $x_{Yb} = \frac{(\Gamma_{YbFe} M_{Fe} + \mu_0 H) \mu_{Yb}}{k_B T}$  and  $\mu_{Yb}$  is the magnetic moment of Yb. No Yb-Yb exchange interaction is included since such exchange interactions are too weak to play a role in the temperature range investigated in this work.<sup>3,5</sup>

When the magnetic field is much larger than the coercive field and the temperature is much lower than the magnetic ordering temperature for the Fe ( $\approx 120$  K for h-YbFeO<sub>3</sub>)<sup>24</sup>, one may treat  $|M_{Fe}| \approx M_{Fe,S}$  as a constant. As shown in Fig. 6(b), at  $T = 18$  K, when  $H$  is between 6 and 19 kOe, the XMCD contrast shows a linear dependence with magnetic field, suggesting that  $x_{Yb}$  is small enough that the Langevin function takes a linear form with respect to the magnetic field  $H$ :

$$M_{Yb} = \mu_{Yb}^2 \frac{\Gamma_{YbFe} M_{Fe} + \mu_0 H}{3k_B T}. \quad (3)$$

According to Eq. (3), the slope of the field dependence of  $M_{Yb}$  (susceptibility) is  $\chi_{Yb} = \frac{dM_{Yb}}{dH} = \frac{\mu_{Yb}^2 \mu_0}{3k_B T}$ , which leads to  $\mu_{Yb} = 1.6 \pm 0.1 \mu_B$ , a value much smaller than the magnetic moment of a free Yb ( $4.5 \mu_B/\text{f.u.}$ )<sup>44</sup>.

### 3. Exchange field on Yb

According to Eq. (3), the remanent magnetization (magnetization in zero  $H$ ) is expected to be

$$M_{Yb,R} = \frac{\mu_{Yb}^2 \Gamma_{YbFe} M_{Fe}}{3k_B T}. \quad (4)$$

Because  $M_{Fe}$  and  $M_{Yb}$  have different sign in zero  $H$  [see Fig. 6(b) and Fig. 7(b)], one finds  $\Gamma_{YbFe} < 0$  from Eq. (4).

Using the value  $M_{Yb,R} = 0.057 \mu_B/\text{f.u.}$  at 18 K from Fig. 6(b), one can calculate the exchange field on Yb:  $H_{Yb} = (\Gamma_{YbFe} M_{Fe})/\mu_0 = 17$  kOe. We also note that the exchange field on Yb generated by Fe in h-YbFeO<sub>3</sub> is about an order of magnitude larger than the value 1.6 kOe in orthorhombic YbFeO<sub>3</sub> and that in rare-earth orthoferrites in general<sup>3</sup>. This large difference may come from the dramatic differences between the bond lengths and bond angles in the hexagonal and orthorhombic YbFeO<sub>3</sub> structures.

### D. The Possible mixed valence of Yb

Mixed valence ( $\text{Yb}^{3+}$  and  $\text{Yb}^{2+}$ ) may play a role in the magnetism of h-YbFeO<sub>3</sub> as well as the determination of the magnetization on the  $\text{Yb}^{3+}$ . In principle, there is a tendency to form  $\text{Yb}^{2+}$  due to the stability of the  $4f^{14}$  configuration. Although it will not affect the XMCD method discussed above since  $\text{Yb}^{2+}$  does not contribute to the Yb M<sub>5</sub> X-ray absorption in the first place (the excitations to the fully occupied 4f states are forbidden in  $\text{Yb}^{2+}$ ), it will be important for bulk magnetometry. We investigated the possibility of mixed valence in h-YbFeO<sub>3</sub> using ARXPS, by probing the core level electronic structure.

Figure 8(a) shows the Fe 2p X-ray photoemission spectra for both h-LuFeO<sub>3</sub> and h-YbFeO<sub>3</sub>. The good match between the Fe 2p<sub>3/2</sub> peaks of h-LuFeO<sub>3</sub> and h-YbFeO<sub>3</sub> in Fig. 8(a) indicates that Fe core level electronic structure are similar in these two ferrites. Previously, we have studied the X-ray photoemission spectra of Fe 2p using the Gupta and Sen (GS) multiplet fitting<sup>45,46</sup> of Fe 2p<sub>3/2</sub> in h-LuFeO<sub>3</sub> and concluded the Fe 2p and its satellite peaks are characteristic of a nominal  $\text{Fe}^{3+}$  valance<sup>32</sup>. The same analysis applies here in h-YbFeO<sub>3</sub> as well. These features also do not vary with emission angle (data not shown). As a result, both the surface and the bulk part of the h-YbFeO<sub>3</sub> are in the nominal  $\text{Fe}^{3+}$  valance state.

We also did not find indication of  $\text{Yb}^{2+}$  in the film samples grown in oxygen environment (used for X-ray absorption spectroscopy and X-ray magnetic circular dichroism in Fig. 2 to Fig. 7). To investigate the possible appearance of  $\text{Yb}^{2+}$ , we studied ARXPS on the h-YbFeO<sub>3</sub> films prepared in argon environment. A comparison with two samples grown in oxygen and argon environments is displayed in Fig. 8(b). At the zero-degree take-off angle (perpendicular to surface), the XPS spectra of Yb are identical for both h-YbFeO<sub>3</sub> samples. At the 70-degree take-off angle, which probes mostly the surface<sup>47,48</sup>, the XPS spectra of the sample grown in oxygen environment (lower panel) do not show clear difference from that at zero degree, also the surface appears to be slightly Yb rich. In contrast, for the sample grown in the argon environment, the XPS spectra at the 70-

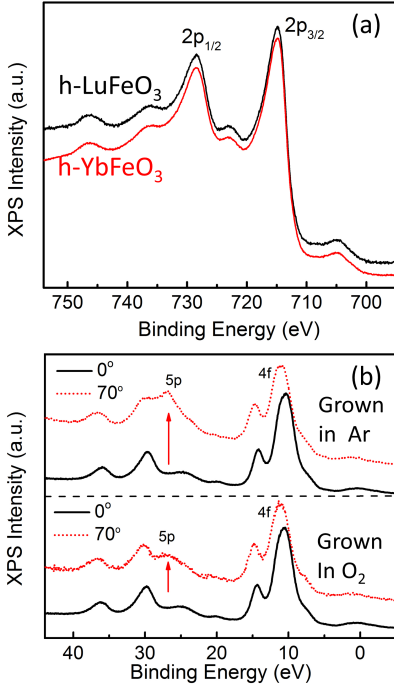


FIG. 8. (Color online) (a) The X-ray photoelectron spectra around Fe 2p edge of h-YbFeO<sub>3</sub> and h-LuFeO<sub>3</sub>. (b) The X-ray photoelectron spectra around Yb 5p edge of h-YbFeO<sub>3</sub> film samples grown in Ar and O<sub>2</sub> environment measured at 0-degree and 70-degree take-off angle, corresponding to 2 nm and 0.7 nm probing depth respectively<sup>47,48</sup>.

degree take-off angle exhibit additional intensity at the 5p peak, indicating a Yb<sup>2+</sup> valence<sup>49</sup>. The correlation between the growth conditions indicates that the presence of oxygen vacancy promotes the reduction of Yb<sup>3+</sup> at the surface. Although slightly YbO rich, the mixed surface termination (both iron oxide and YbO appear present at the surface) differs from the FeO termination seen for LuFeO<sub>3</sub>.<sup>32</sup>

## IV. DISCUSSION

### A. Origin of reduced moment of Yb

The low-temperature magnetic moment of Yb is found to be  $1.6 \mu_B$ , a value significantly smaller than  $4.5 \mu_B$  for a free Yb<sup>44</sup>. In h-YbFeO<sub>3</sub>, Yb is surrounded by 7 oxygen atoms, approximately corresponding to a C<sub>3v</sub> symmetry. Analysis using double groups indicates that the 4f<sub>7/2</sub> states are split by the crystal field into 4 levels:  $3E_{1/2} + E_{3/2}$  (see Appendix B), where  $E_{1/2}$  and  $E_{3/2}$  are both two dimensional<sup>44</sup>. The energy scale of the crystal-field splitting is typically a few meV to a few tens meV,<sup>26–28</sup> which cannot be resolved in the XAS spectra. This crystal field splitting means that, at low temperature, only the low-lying level (ground state) is populated and contributes to the magnetization. The

occupation of the low-lying level, in turn, leads to the reduced value of  $\mu_{Yb}$ , and is the reason for the temperature-dependent magnetic moments and magnetic anisotropy observed previously in rare-earth-containing oxides<sup>28,30</sup>.

### B. Possible spin reorientation and magnetization compensation

One can calculate the temperature dependence of Yb magnetization using Eq.(2). As shown in Fig. 6(a), the result (with  $\mu_{Yb}=1.6 \mu_B$ ,  $H=19$  kOe, and  $H_{Yb}=17$  kOe) is compared with the measured values. The measured and the calculated magnetization match well below 70 K, suggesting that the mean-field theory can describe the temperature dependence of  $M_{Yb}$  too. The fact that the mean-field theory can describe both the magnetic-field (Section III C 2) and temperature dependence of  $M_{Yb}$ , indicates its validity in analyzing the magnetic properties of h-YbFeO<sub>3</sub>.

On the other hand, at about 80 K, the calculated value is much larger than the measured value, suggesting a reduction of  $H_{Yb}$  at higher temperature. To reveal the temperature dependence of  $H_{Yb}$ , we calculated  $H_{Yb}$  from the measured magnetization value using Eq.(3) (with  $\mu_{Yb}=1.6 \mu_B$ ,  $H=19$  kOe); the result is displayed in Fig. 6(a) inset. Clearly, a sign change of  $H_{Yb}$  occurs at about 80 K, indicating a possible realignment between the magnetization  $M_{Yb}$  and  $M_{Fe}$ , which is discussed below.

In principle, the alignment between  $M_{Yb}$  and  $M_{Fe}$  is determined by the minimization of total energy

$$E_{total} = -\frac{1}{2}\chi_{Yb}(H + \Gamma_{YbFe}M_{Fe})^2 - M_{Fe}H,$$

or the maximization of the total magnetization

$$M_{total} = M_{Fe}(1 + \chi_{Yb}\Gamma_{YbFe}) + \chi_{Yb}H.$$

Here the external field  $H$  is along the  $c$  axis and  $M_{Fe}$  may point either along or opposite to  $H$ , corresponding to the positive and negative signs respectively.

Because  $\Gamma_{YbFe} < 0$  and  $\chi_{Yb} = \frac{\mu_{Yb}^2 \mu_0}{3k_B T}$  (see Section III C 3), the sign of  $1 + \chi_{Yb}\Gamma_{YbFe}$  is expected to change with temperature, possibly causing the reversal of the direction of the magnetization  $M_{Fe}$ :

1) At low temperature,  $1 + \chi_{Yb}\Gamma_{YbFe} < 0$ . In this case,  $M_{Fe} < 0$  ( $M_{Fe}$  anti-parallel to  $H$ ) is more favorable for maximizing  $M_{total}$ ; this means the exchange field  $H_{Yb} = \frac{\Gamma_{YbFe}M_{Fe}}{\mu_0} > 0$  (parallel to the external field).

2) When temperature is increased and  $1 + \chi_{Yb}\Gamma_{YbFe} > 0$  is satisfied,  $M_{Fe} > 0$  ( $M_{Fe}$  parallel to  $H$ ) is more favorable. In this case, one has the exchange field  $H_{Yb} = \frac{\Gamma_{YbFe}M_{Fe}}{\mu_0} < 0$  (antiparallel to the external field); this could be the reason that at about 80 K the  $H_{Yb}$  becomes negative [Fig. 6(a) inset].

3) At the compensation temperature,  $1 + \chi_{Yb}\Gamma_{YbFe} = 0$ . Therefore,  $M_{total} = \chi_{Yb}H$ , as if  $M_{Fe}$  is screened by

the part of Yb moment induced by the exchange field  $H_{Yb}$ . The magnetization compensation can be understood as the cancellation of  $M_{Fe}$  and  $M_{Yb}$  at zero field. According to Fig. 6(a) inset, the compensation temperature appears to be between 70 and 80 K, in fair agreement with the previous estimation<sup>24</sup>.

Nonetheless, the magnetization of the Yb is largely a spectator to that of the Fe. The coercivity is the same as that observed for iron, with the essential observation [Fig. 6(b)] that the magnetization does not easily saturate indicating that much of the magnetization depends on the magnetic susceptibility and possible alignment of the moments with external magnetic field  $H$  and with the magnetization of Fe (Fig. 7).

### C. Exchange field on Fe

The exchange field may also have an effect on the Fe, which can be understood by combining Eq. (1) and Eq. (2) to reach

$$x_{Fe} = \frac{[\Gamma_{YbFe}\mu_{Yb}L(\frac{\Gamma_{YbFe}M_{Fe}\mu_{Yb}}{k_B T}) + \Gamma_{Fe}M_{Fe}]M_{Fe,S}}{k_B T},$$

assuming  $H = 0$ . Since Fe moments in h-YbFeO<sub>3</sub> form a ferromagnetic order,  $\Gamma_{Fe}$  must be positive. Because of the properties of the Langevin function  $L(x)$ ,  $\Gamma_{YbFe}\mu_{Yb}L(\frac{\Gamma_{YbFe}M_{Fe}\mu_{Yb}}{k_B T})$  is always positive regardless of the sign of  $\Gamma_{YbFe}$ . Therefore, the Yb always enhances the molecular field on the Fe. That said, because in general  $\Gamma_{Fe} \ll |\Gamma_{YbFe}|$ , the effect may not be significant.

### D. Comparison between magnetic properties of h-YbFeO<sub>3</sub> and h-LuFeO<sub>3</sub>

Hexagonal LuFeO<sub>3</sub> (h-LuFeO<sub>3</sub>) is the most studied hexagonal rare-earth ferrites. Because Lu<sup>3+</sup> is non-magnetic, the magnetic properties of h-LuFeO<sub>3</sub> is less complex. By comparing h-LuFeO<sub>3</sub> and h-YbFeO<sub>3</sub>, one may gain insight on the effect of the rare earth on the magnetism.

One dramatic difference between h-YbFeO<sub>3</sub> and h-LuFeO<sub>3</sub> is in the coercive field of magnetization. For h-YbFeO<sub>3</sub> at 18 K, the coercive field is about 4 kOe, which is much smaller than the value 25 kOe for h-LuFeO<sub>3</sub>.<sup>16</sup> For both h-LuFeO<sub>3</sub> and h-YbFeO<sub>3</sub>, the magnetization-field loops of Fe have a squared shape, suggesting that the magnetic coercive field is determined by the competition between the magnetic anisotropy energy and the Zeeman energy. Compared with h-LuFeO<sub>3</sub>, h-YbFeO<sub>3</sub> has enhanced magnetization due to the contribution of Yb. Therefore, a much smaller magnetic field is needed in h-YbFeO<sub>3</sub> to overcome the magnetic anisotropy, corresponding to a much smaller coercive field.

Another difference between h-YbFeO<sub>3</sub> and h-LuFeO<sub>3</sub> is in the saturation magnetization of Fe. According to

Fig. 7, in h-YbFeO<sub>3</sub>,  $M_{Fe,S} = 0.05 \pm 0.01 \mu_B/\text{f.u.}$ , larger than that in h-LuFeO<sub>3</sub> ( $\approx 0.03 \mu_B/\text{f.u.}$ )<sup>16</sup>. We note that previously it was observed in h-LuFeO<sub>3</sub> that the magnetization contains a soft component and a hard component, in which only the hard component ( $0.018 \mu_B/\text{f.u.}$ ) is believed to be intrinsic to the weak ferromagnetic ordering, because it disappears above the magnetic ordering temperature.<sup>16</sup> In Fig. 7, there is also one soft (coercive field  $\approx 1$  kOe) and one hard component (coercive field  $\approx 4$  kOe). If we only treat the hard component to be intrinsic to the canting of the Fe moment, the weak ferromagnetic moment of Fe in h-YbFeO<sub>3</sub> is  $= 0.03 \pm 0.01 \mu_B/\text{Fe}$  [Fig. 7(b)], to still larger compared with the value  $0.018 \mu_B/\text{f.u.}$  in h-LuFeO<sub>3</sub>.<sup>16</sup> Due to the size difference of Lu<sup>3+</sup> and Yb<sup>3+</sup>,<sup>14</sup> the lattice constant of the basal plane of h-LuFeO<sub>3</sub> are smaller than that of h-YbFeO<sub>3</sub>:  $a = 5.963 \text{ \AA}$  for h-LuFeO<sub>3</sub> and  $a = 6.021 \text{ \AA}$  for h-YbFeO<sub>3</sub>.<sup>31</sup> Our recent work suggests that a compressive biaxial strain may reduce the canting of the Fe moments in h-YbFeO<sub>3</sub>,<sup>50</sup> which is in line with the correlation between the lattice constant and weak ferromagnetic moment on Fe observed here.

## V. CONCLUSION

We have studied the electronic structure and magnetic ordering of h-YbFeO<sub>3</sub> (001) thin films on YSZ (111) and on Fe<sub>3</sub>O<sub>4</sub>(111)/Al<sub>2</sub>O<sub>3</sub>(001) substrates. The magnetism of Yb in h-YbFeO<sub>3</sub> was studied using the element-specific method X-ray magnetic circular dichroism based on X-ray absorption spectroscopy. From the temperature and magnetic-field dependence of the Yb magnetization, we found that the low temperature Yb magnetic moment is significantly reduced compared with the value of free Yb<sup>3+</sup> ions, indicating the effect of crystal field. The exchange field on Yb, generated by the Fe moments, tends to anti-align the magnetization of Fe and Yb at low temperature. We also investigated possible valence mixing of Yb and only found indication of Yb<sup>2+</sup> at the surface of samples grown in an Ar environment, suggesting an insignificant effect to the magnetism of h-YbFeO<sub>3</sub>. We expect that future work, such as optical spectroscopy on probing Yb crystal field levels and theoretical calculations on Yb-Fe interaction strength, may provide more insight on the ferrimagnetism of h-YbFeO<sub>3</sub>.

## ACKNOWLEDGMENTS

This project was primarily supported by the National Science Foundation through the Nebraska Materials Research Science and Engineering Center (Grant No. DMR-1420645). Additional support was provided by the Semiconductor Research Corporation through the Center for Nanoferric Devices and the SRC-NRI Center under Task ID 2398.001. Work of Bryn Mawr College is supported by National Science Foundation Career Award (Grant



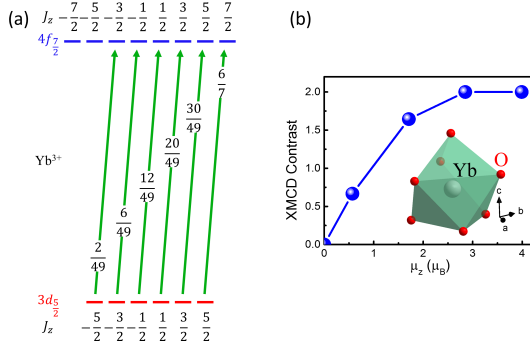


FIG. 9. (Color online) (a) Transition probability between individual  $3d_{5/2}$  and  $4f_{7/2}$  states excited by a clockwise polarized X-ray. (b) XMCD contrast as a function of  $\mu_z$  (see text) calculated assuming a free  $Yb^{3+}$  ion. The inset shows the local environment of Yb with a  $C_{3v}$  symmetry.

No. NSF DMR-1053854). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Use of the Advanced Light Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract no. DE-AC02-05CH11231. The Canadian Light Source is funded by the Canada Foundation for Innovation, the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Government of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan. The research was performed in part in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated Infrastructure and the Nebraska Center for Materials and Nanoscience, which are supported by the National Science Foundation under Award ECCS: 1542182, and the Nebraska Research Initiative.

#### Appendix A: Converting XMCD contrast to magnetization of Yb

The calculation of the magnetization of Yb from the XMCD contrast at the M edge is significantly different from that of 3d metals at the L edge (e.g. Fe, Co, Ni), due to the strong spin-orbit coupling in both initial and final states. We hereby present a method based on the XMCD contrast of the excitations from the  $3d_{5/2}$  to the individual  $4f_{7/2}$  eigenstates  $J_z = -7/2$  to  $7/2$ , where  $J_z$  is the projection of total angular momentum  $J$  on the  $z$  axis;

all possible  $4f_{7/2}$  states are superposition of these states.

Excited by an X-ray polarized clockwise, the transition from one  $3d_{5/2}$  state to one  $4f_{7/2}$  state needs to satisfy  $\Delta J_z = 1$ . One can calculate the transition probabilities  $P$  between individual states; the non-zero results are displayed in Fig. 9(a). The projection of the magnetic moment of a  $J_z$  state on the  $z$  direction is  $\mu_z = g_B J_z$ , where  $g = 1.14$  is the Lande  $g$ -factor and  $\mu_B$  is the Bohr magneton. Therefore, one can calculate the XMCD contrast, defined as  $\frac{2(P_{J_z} - P_{-J_z})}{P_{J_z} + P_{-J_z}}$ , with respect to  $\mu_z$ , where  $P_{J_z}$  ( $P_{-J_z}$ ) is the transition probability for the final state represented by  $J_z$  ( $-J_z$ ); the result is shown in Fig. 9(b). Although for large  $\mu_z$ , the XMCD contrast does not distinguish the  $|J_z|=7/2$  and the  $|J_z|=5/2$  states, for small  $\mu_z$ , the relation between XMCD contrast and  $\mu_z$  is approximately linear. The measured XMCD contrast in this work falls in the small  $\mu_z$  region (all values are less than 0.4). Therefore, we can use the relation in Fig. 9(b) to convert XMCD contrast to magnetization as a fair approximation.

#### Appendix B: Group theory analysis of the crystal field splitting of Yb states

TABLE I. Character table of the double group  $C_{3v}$ .

$C_{3v}$	E	$2C_3$	$3\sigma_v$	RE	$2RC_3$	$3R\sigma_v$
$A_1$	1	1	1	1	1	1
$A_2$	1	1	-1	1	1	-1
$E$	2	-1	0	2	-1	0
$E_{1/2}$	2	1	0	-2	-1	0
$E_{3/2+}$	1	-1	i	-1	1	-i
$E_{3/2-}$	1	-1	-i	-1	1	i
$J = 7/2$	8	1	0	-8	-1	0
$J = 5/2$	6	0	0	-6	0	0

In h- $YbFeO_3$ , the local environment of Yb has a symmetry that can be described using point group  $C_{3v}$  [see Fig. 9(b) inset]. The degenerate electronic states in general are split according to the symmetry of the local environment. Because of the strong spin-orbit coupling, the angular momentum of the 4f states takes half-integer  $J = \frac{5}{2}$  or  $J = \frac{7}{2}$ , the analysis of which requires the double group. TABLE I shows the character table for  $C_{3v}$  double group, including irreducible representations  $A_1$ ,  $A_2$ ,  $E$ ,  $E_{\frac{1}{2}}$ ,  $E_{\frac{3}{2}}$  ( $E_{\frac{3}{2}+}$  and  $E_{\frac{3}{2}-}$ ). The character of the representation with angular momentum  $J = \frac{5}{2}$  and  $J = \frac{7}{2}$  are also listed. Using these characters, one can reduce the  $J = \frac{5}{2}$  and  $J = \frac{7}{2}$  representations. The results are:  $J = \frac{5}{2} \rightarrow 2E_{\frac{1}{2}} + E_{3/2\frac{3}{2}}$  and  $J = \frac{7}{2} \rightarrow 3E_{\frac{1}{2}} + E_{\frac{3}{2}}$ .

<sup>1</sup> R.C. OHandley, Modern Magnetic Materials: Principles and Applications (Wiley, New York, 2000).

<sup>2</sup> R.M. Bozorth, Phys. Rev. Lett. 1, 362 (1958).

<sup>3</sup> D. Treves, J. Appl. Phys. 36, 1033 (1965).

- <sup>4</sup> D. Treves, Phys. Rev. 125, 1843 (1962).
- <sup>5</sup> R.L. White, J. Appl. Phys. 40, 1061 (1969).
- <sup>6</sup> X. Fabreges, S. Petit, I. Mirebeau, S. Pailhes, L. Pinsard, A. Forget, M.T. Fernandez-Diaz, and F. Porcher, Phys. Rev. Lett. 103, 067204 (2009).
- <sup>7</sup> M. Fiebig, D. Frohlich, K. Kohn, S. Leute, T. Lottermoser, V. V Pavlov, and R. V Pisarev, Phys. Rev. Lett. 84, 5620 (2000).
- <sup>8</sup> O.P. Vajk, M. Kenzelmann, J.W. Lynn, S.B. Kim, and S.-W. Cheong, Phys. Rev. Lett. 94, 087601 (2005).
- <sup>9</sup> W.A. Crossley, R.W. Cooper, J.L. Page, and R.P. Van Staple, Phys. Rev. 181, 896 (1969).
- <sup>10</sup> A.K. Zvezdin and V.M. Matveev, Sov. Phys. JETP 3, 140 (1972).
- <sup>11</sup> V.N. Derkachenko, A.M. Kodomtseva, V.A. Timofeeva, and V.A. Khokhlov, JEPT Lett. 20, 104 (1974).
- <sup>12</sup> E. Magome, C. Moriyoshi, Y. Kuroiwa, A. Masuno, and H. Inoue, Jpn. J. Appl. Phys. 49, 09ME06 (2010).
- <sup>13</sup> W. Wang, J. Zhao, W. Wang, Z. Gai, N. Balke, M. Chi, H.N. Lee, W. Tian, L. Zhu, X. Cheng, D.J. Keavney, J. Yi, T.Z. Ward, P.C. Snijders, H.M. Christen, W. Wu, J. Shen, and X. Xu, Phys. Rev. Lett. 110, 237601 (2013).
- <sup>14</sup> X. Xu and W. Wang, Mod. Phys. Lett. B 28, 1430008 (2014).
- <sup>15</sup> C.J. Fennie and K.M. Rabe, Phys. Rev. B 72, 100103 (2005).
- <sup>16</sup> J.A. Moyer, R. Misra, J.A. Mundy, C.M. Brooks, J.T. Heron, D.A. Muller, D.G. Schlom, and P. Schiffer, APL Mater. 2, 12106 (2014).
- <sup>17</sup> S.M. Disseler, J.A. Borchers, C.M. Brooks, J.A. Mundy, J.A. Moyer, D.A. Hillsberry, E.L. Thies, D.A. Tenne, J. Heron, M.E. Holtz, J.D. Clarkson, G.M. Stiehl, P. Schiffer, D.A. Muller, D.G. Schlom, and W.D. Ratcliff, Phys. Rev. Lett. 114, 217602 (2015).
- <sup>18</sup> H. Das, A.L. Wysocki, Y. Geng, W. Wu, and C.J. Fennie, Nat Commun 5, 2998 (2014).
- <sup>19</sup> H. Wang, I. V. Solovyev, W. Wang, X. Wang, P.J. Ryan, D.J. Keavney, J.-W. Kim, T.Z. Ward, L. Zhu, J. Shen, X.M. Cheng, L. He, X. Xu, and X. Wu, Phys. Rev. B 90, 014436 (2014).
- <sup>20</sup> S. Cao, X. Zhang, T.R. Paudel, K. Sinha, X. Wang, X. Jiang, W. Wang, S. Brutsche, J. Wang, P.J. Ryan, J.-W. Kim, X. Cheng, E.Y. Tsymbal, P.A. Dowben, and X. Xu, J. Phys. Condens. Matter 28, 156001 (2016).
- <sup>21</sup> J.A. Mundy, C.M. Brooks, M.E. Holtz, J.A. Moyer, H. Das, A.F. Rbola, J.T. Heron, J.D. Clarkson, S.M. Disseler, Z. Liu, A. Farhan, R. Held, R. Hovden, E. Padgett, Q. Mao, H. Paik, R. Misra, L.F. Kourkoutis, E. Arenholz, A. Scholl, J.A. Borchers, W.D. Ratcliff, R. Ramesh, C.J. Fennie, P. Schiffer, D.A. Muller, and D.G. Schlom, Nature 537, 523 (2016).
- <sup>22</sup> N.A. Spaldin, S.W. Cheong, and R. Ramesh, Phys. Today 63, 38 (2010).
- <sup>23</sup> H. Iida, T. Koizumi, Y. Uesu, K. Kohn, N. Ikeda, S. Mori, R. Haumont, P.-E. Janolin, J.-M. Kiat, M. Fukunaga, and Y. Noda, J. Phys. Soc. Japan 81, 24719 (2012).
- <sup>24</sup> Y.K. Jeong, J. Lee, S. Ahn, S.-W. Song, H.M. Jang, H. Choi, and J.F. Scott, J. Am. Chem. Soc. 134, 1450 (2012).
- <sup>25</sup> G. Huber, ECS Trans. 25, 287 (2009).
- <sup>26</sup> R.K. Tamrakar, D.P. Bisen, and N. Brahme, Infrared Phys. Technol. 68, 92 (2015).
- <sup>27</sup> P. Haumesser, E. Antic-fidancev, P. Porcher, B. Viana, and R. Gaume, J. Alloys Compd. 341, 160 (2002).
- <sup>28</sup> X.S. Xu, T. V. Brinzari, S. McGill, H.D. Zhou, C.R. Wiebe, and J.L. Musfeldt, Phys. Rev. Lett. 103, 267402 (2009).
- <sup>29</sup> D.L. Wood, L.M. Holmes, and J.P. Remeika, Phys. Rev. 185, 689 (1969).
- <sup>30</sup> I. Mikami, J. Phys. Soc. Japan 34, 338 (1973).
- <sup>31</sup> X. Zhang, Y. Yin, S. Yang, Z. Yang, and X. Xu, J. Phys. Condens. Matter 29, 164001 (2017).
- <sup>32</sup> S. Cao, T.R. Paudel, K. Sinha, X. Jiang, W. Wang, E.Y. Tsymbal, X. Xu, and P.A. Dowben, J. Phys. Condens. Matter 27, 175004 (2015).
- <sup>33</sup> W. Wang, H. Wang, X. Xu, L. Zhu, L. He, E. Wills, X. Cheng, D.J. Keavney, J. Shen, X. Wu, and X. Xu, Appl. Phys. Lett. 101, 241907 (2012).
- <sup>34</sup> S. Cao, X. Zhang, K. Sinha, W. Wang, J. Wang, P.A. Dowben, and X. Xu, Appl. Phys. Lett. 108, 202903 (2016).
- <sup>35</sup> J.A. Bearden, Rev. Mod. Phys. 39, 78 (1967).
- <sup>36</sup> N.W. Ashcroft and N.D. Mermin, Solid State Physics (Holt, Rinehart and Winston, New York, 1976).
- <sup>37</sup> J. Stohr and H.C. Siegmann, Magnetism from Fundamentals to Nanoscale Dynamics (Springer, Berlin, 2006).
- <sup>38</sup> J. Stohr and H. Konig, Phys. Rev. Lett. 75, 3748 (1995).
- <sup>39</sup> P. Carra, B.T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. 70, 694 (1993).
- <sup>40</sup> K.P. Belov, A.M. Kadomtseva, and R.Z. Levitin, Sov. Phys. JETP-USSR 20, 291 (1965).
- <sup>41</sup> K.P. Belov and S.A. Nikitin, Izv. Akad. Nauk SSSR, Ser. Fiz. 34, 957 (1970).
- <sup>42</sup> K.P. Belov and S.A. Nikitin, Sov. Phys. JETP 31, 505 (1970).
- <sup>43</sup> K.P. Belov, A.M. Kadomtseva, N.M. Kovtun, V.N. Derkachenko, V.N. Melov, and V.A. Khokhlov, Phys. Status Solidi 36, 415 (1976).
- <sup>44</sup> M.S. Dresselhaus, G. Dresselhaus, and A. Jorio, Group Theory Application to the Physics of Condensed Matter (Springer-Verlag, Berlin, 2007).
- <sup>45</sup> R.P. Gupta and S.K. Sen, Phys. Rev. B 12, 15 (1975).
- <sup>46</sup> R.P. Gupta and S.K. Sen, Phys. Rev. B 10, 71 (1974).
- <sup>47</sup> S. Tanuma, T. Shiratori, T. Kimura, K. Goto, S. Ichimura, and C.J. Powell, Surf. Interface Anal. 37, 833 (2005).
- <sup>48</sup> M.P. Seah and W.A. Dench, Surf. Interface Anal. 1, 2 (1979).
- <sup>49</sup> Y. Ohno, J. Electron Spectros. Relat. Phenomena 165, 1 (2008).
- <sup>50</sup> K. Sinha, Y. Zhang, X. Jiang, H. Wang, X. Wang, X. Zhang, P.J. Ryan, J.-W. Kim, J. Bownan, D.A. Yarotski, Y. Li, A.D. DiChiara, X. Cheng, X. Wu, and X. Xu, Phys. Rev. B 95, 094110 (2017).