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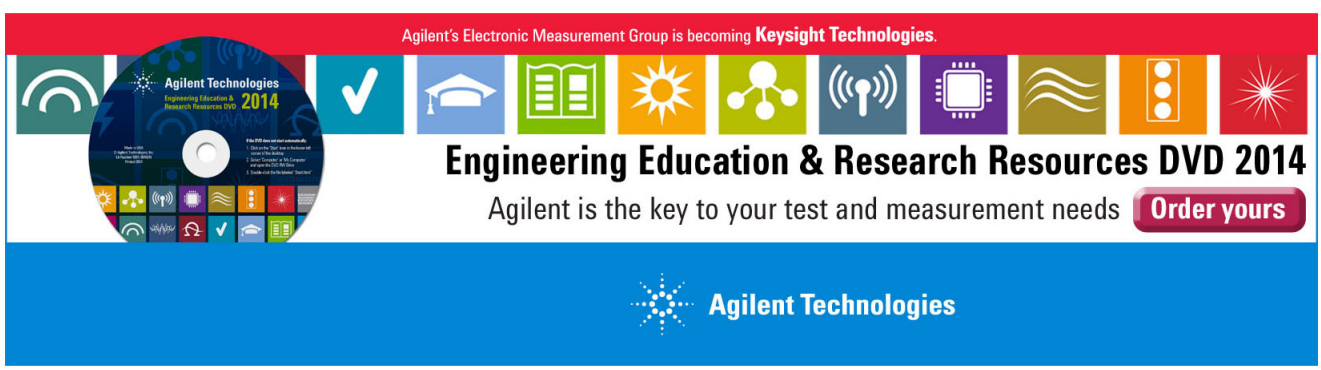

# Crystal field splitting and optical bandgap of hexagonal $LuFeO_3$ films

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Hexagonal $LuFeO_3$ films have been studied using x-ray absorption and optical spectroscopy. The crystal splitting of $Fe^{3+}$ is extracted as $E_{e'} - E_{e''} = 0.7$ eV and $E_{a_1'} - E_{e'} = 0.9$ eV, and a 2.0 eV optical bandgap is determined assuming a direct gap. First-principles calculations confirm the experiments that the relative energies of crystal field splitting states do follow $E_{a_1'} > E_{e'} > E_{e''}$ with slightly underestimated values and a bandgap of 1.35 eV. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4771601]

Multiferroic materials which simultaneously exhibit more than one type of ferroic order have many advantages over other existing materials in terms of applications in sensor, actuator, and information storage and processing.[1,2] Hexagonal ferrites (h-$RFeO_3$, R = Sc, Y, Ho-Lu) were recently found to be a class of multiferroic materials.[3–10] In particular, it is suggested by experiments that h-$LuFeO_3$ may be both ferroelectric and antiferromagnetic at room temperature, indicating important application potential.[10] It is fascinating that h-$RFeO_3$ exhibit distinct properties such as ferrimagnetism, abnormal magneto-dielectric couplings, and structural instability compare with $RMnO_3$.[3,4,6,7] These unexpected properties are supposed to have electronic origins because h-$RFeO_3$ and $RMnO_3$ are isomorphic, and the radius of $Fe^{3+}$ and $Mn^{3+}$ are almost identical.[3,4] Therefore, the information on the electronic structures is crucial in understanding the intriguing multiferroicity of h-$RFeO_3$.

Hexagonal $RFeO_3$ are not stable in free standing bulk form. They can be stabilized by quenching a levitated melt in an aerodynamic levitation furnace or in solvothermal reactions.[4,11–13] In addition, h-$RFeO_3$ has also been stabilized in films using pulsed laser deposition (PLD) and metal-organic chemical vapor deposition on yttrium stabilized zirconium oxides (YSZ) and $Al_2O_3$ substrates.[3,5–7,9,10] The crystallographic structures of h-$RFeO_3$ is isomorphic to $RMnO_3$ with space group $P6_3cm$ (185),[3,4] suggesting that h-$RFeO_3$ are also ferroelectric, which is recently demonstrated.[3,4,6,14] The larger spin on $Fe^{3+}$ compared with $Mn^{3+}$ corresponds to stronger magnetic interactions, allowing for higher magnetic ordering temperature, which has been indicated by recent experiments.[5,6,10] In stark contrast to the large amount of work devoted to $RMnO_3$, detailed studies on the h-$RFeO_3$, and especially of the electronic structures that are crucial for understanding the structural, ferroelectric, and magnetic properties are still lacking.[9,15–17]

In this paper, we investigate the electronic properties of h-$LuFeO_3$ films using x-ray absorption and optical spectroscopy. The analysis of the x-ray absorption spectra (XAS) using crystal field theory reveal a splitting of the Fe 3*d* levels significantly higher than that of $Fe^{3+}$ in $LuFe_2O_4$, indicating stronger Fe-O interactions. The extracted optical bandgap from optical absorption spectra (assuming a direct gap) is $2.0 \pm 0.1$ eV, somewhat smaller than that of perovskite ferrites.[18] The experimental findings have been confirmed by our electronic structure calculations.

The XAS was studied on 50 nm h-$LuFeO_3$ films grown on $Al_2O_3$ substrates using PLD with 30 nm Pt buffer layer (Fig. 1(a)) to avoid charging effect.[19] The XAS was taken at beam line 4-ID-C at the Advanced Photon Source using polarized synchrotron x-rays. A 20 nm thick h-$LuFeO_3$ film was grown on a YSZ substrate using PLD (Fig. 1(b)) for optical spectroscopy measurements. Part of the substrate was covered by a mask at growth, so it can be used as a reference in the optical transmittance measurements. Optical spectra were collected in transmittance mode using a Varian Cary 5000 spectrometer.

Figure 2(a) shows the XAS corresponding to transitions from a Fe $2p^63d^5$ to a Fe $2p^53d^6$ multiplet. In the spectra, two groups of peaks separated by approximately 12 eV can be distinguished. Two well-separated peaks (709.1 and 710.7 eV) are observed for the *s* polarization, while additional intensities are observed for *p* polarization as a peak at 709.8 eV, indicating a strong dichroism much more prominent than that of $YMnO_3$.[20]

These spectra details are determined by dipole and spin selection rules and a combination of effects from crystal-field, spin-orbit coupling, *d-p* and *d-d* interactions and Fe 3*d*

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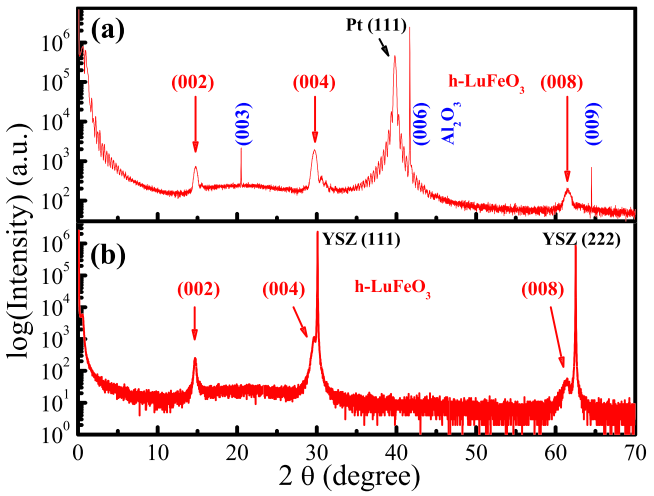


FIG. 1. The x-ray diffraction spectra of h-$LuFeO_3$ films grown on (a) $Al_2O_3$ substrates with Pt buffer layer and (b) YSZ substrates.

O $2p$ hybridization.[21,22] In terms of one-electron energy, the Fe $2p$ states are split into $2p_{1/2}$ and $2p_{3/2}$ by the spin-orbit coupling, which has the energy scale of 15 eV, resulting in the two groups of excitations $L_2\,(2p_{1/2} \rightarrow 3d)$ and $L_3\,(2p_{3/2} \rightarrow 3d)$ in Fig. 2(a).[21,23] For the Fe $3d$ states, the one-electron states are mainly split by crystal fields, which is on the order of one eV.[21,23] Here, the trigonal-bipyramid local environment of Fe gives rise to a symmetry that can be represented by the $D_{3h}$ point group as a good approximation, as shown in Fig. 2(c). In this case, Fe $3d$ states split into irreducible representations (IR) $e''(xz, yz)$, $e'(xx - yy, xy)$ and $a_1'(zz)$ while Fe $2p$ orbitals can be reduced to states corresponding to IR $e'(x, y)$ and $a_2''(z)$.[24] A recent work on $LuFe_2O_4$ in which $Fe^{3+}$ sites also sit in a trigonal-bipyramid local environment has shown that the energies of these crystal field states follow $E_{a_1'} > E_{e'} > E_{e''}$.[25] Similar results are also found for $Mn^{3+}$ in a $D_{3h}$ symmetry.[20]

The transition probability in the XAS depends on the matrix elements $|\langle\psi_i|\hat{E}\cdot\vec{r}|\psi_f\rangle|^2$, where the $\psi_i$ and $\psi_f$ are the initial and final one-electron states, $\hat{E}$ is the direction vector of the electric field, and $\vec{r}$ is the position vector. According to Hund's rule, the ground states of $Fe^{3+}$ are a multiplet ${}^6A_1'$ for a $2p_{3/2}^4 2p_{1/2}^2 3d_{e''}^2 3d_{e'}^2 3d_{a_1'}^1$ electronic configuration. In the ionic model that ignores hybridization between Fe $3d$ and O $2p$ state, the spin-allowed excited state multiplets and the corresponding one-electron state populations can be listed as shown in Table I.[22,26] Since the ground state multiplet has a symmetry of $A_1'$, the dipole-allowed excited states need to contain $E'$ or $A_2''$ to satisfy the dipole selection rules for a $D_{3h}$ symmetry.[24] The resulting dipole-allowed transitions are listed in Table I. It is clear that the photon with $z$ polarization cannot excite an electron from Fe $2p$ to Fe $3d_{e'}$ state. These selection rules are verified in the $L_3$ part of the XAS: for $s$ polarization, the intensity in the middle is much weaker, which suggests that the three peaks at 709.1, 709.8, and 710.7 eV are coming from the effect of crystal field. As shown in Fig. 2(a) as symbols, the calculated matrix elements qualitatively agree with the dichroism for $L_3$ excitation. The less obvious agreement for $L_2$ excitations is presumably due to a mixed energy splitting from crystal field and $p$-$d$ interactions.[21] The peak positions allow for a rough determination of the crystal field splitting assuming similar $d$-$d$ interactions for different Fe $3d$ states: $E_{e'} - E_{e''} = 0.7$ eV and $E_{a_1'} - E_{e'} = 0.9$ eV, as also shown in Fig. 2(d). The splitting is significantly larger than that in $LuFe_2O_4$ ($E_{e'} - E_{e''} = 0.4$ eV and $E_{a_1'} - E_{e'} = 0.8$ eV for $Fe^{3+}$ sites).[25] The differences indicate stronger Fe-O interactions, as also suggested by the different Fe-O bond length in h-$LuFeO_3$ and in $LuFe_2O_4$.[4,27]

In order to further elucidate the electronic structure of the h-$LuFeO_3$, we measured optical absorption spectra of the h-$LuFeO_3$ films. The observed spectra (Fig. 3) shows three peak-like features at approximately 2.3, 2.9, and 3.9 eV, consistent with the recently reported optical properties of h-$RFeO_3$ films.[9] Based upon the overall intensity $\sim 10^7$ m$^{-1}$, these peaks correlate to dipole-allowed excitations. Since the $Fe^{3+}$ has a $3d^5$ configuration, all the on-site excitations are spin forbidden. Therefore, the peak at 2.3 eV is coming from charge transfer excitations.[18] A $2.0 \pm 0.1$ eV optical bandgap was extracted using plots of $\alpha^2$ versus energy (Fig. 3 inset), assuming a direct gap.[28]

First-principles electronic structure calculations can provide insightful picture of crystal field splitting. We determined our projected density of states (PDOS) by the density functional theory (DFT) implemented in the Vienna ab initio simulations package (VASP).[29,30] We adopted the Perdew-Burke-Ernzerhof functional revised for solids (PBEsol)[31] in which the spin-polarized generalized gradient approximation

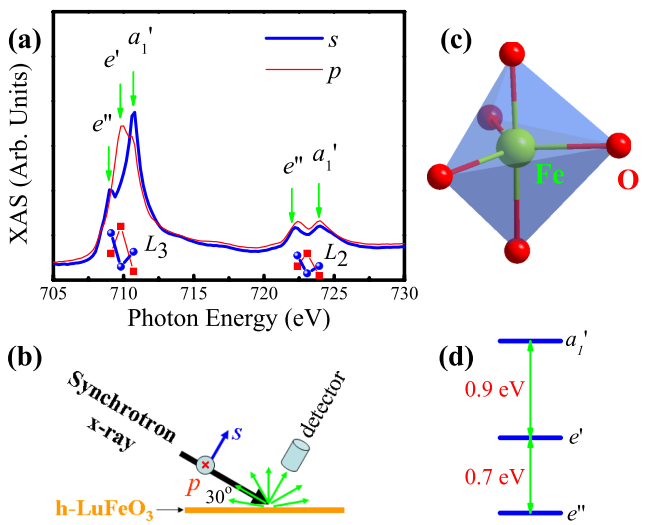


FIG. 2. Crystal field splitting of Fe sites (300 K). (a) The x-ray absorption spectra corresponding to Fe $2p$ to Fe $3d$ excitations. The symbols are the calculated matrix elements from the initial to the final one-electron states. (b) Schematics of the experimental setup. (c) Schematics of the local environment of Fe sites. (d) The crystal splitting extracted from the XAS spectra.

TABLE I. The spin-allowed excited states and the dipole selection rules from the ${}^6A_1'(2p_{3/2}^4 2p_{1/2}^2 3d_{e''}^2 3d_{e'}^2 3d_{a_1'}^1)$ ground state with a linearly polarized photon. Note that both $2p_{3/2}^4 2p_{1/2}^1$ and $2p_{3/2}^3 2p_{1/2}^2$ multiplets contain IR $E'$ and $A_2''$.

| $3d$ Configuration | IR | Allowed Polarization |
|---|---|---|
| $3d_{e''}^3 3d_{e'}^2 3d_{a_1'}^1$ | $A_1'' + A_2'' + E' + E''$ | $x, y, z$ |
| $3d_{e''}^2 3d_{e'}^3 3d_{a_1'}^1$ | $A_1'' + A_2' + E' + E''$ | $x, y$ |
| $3d_{e''}^2 3d_{e'}^2 3d_{a_1'}^2$ | $E' + A_2''$ | $x, y, z$ |

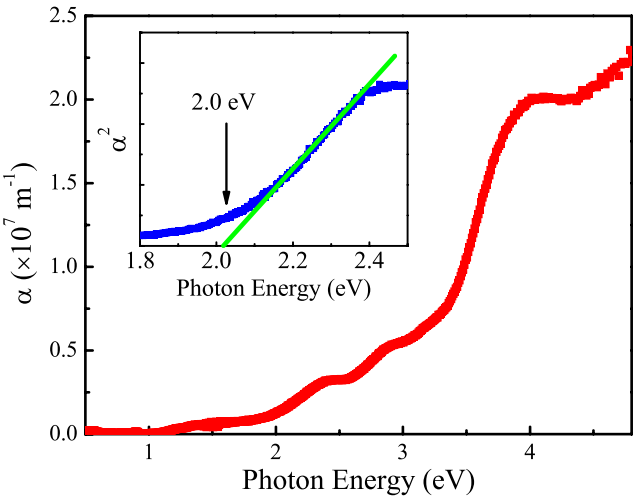


FIG. 3. Optical absorption coefficient α as a function of photon energy. Inset: $\alpha^2$ as a function of photon energy, which indicates an optical bandgap of 2.0 eV.

(GGA) is made in treating the exchange correlation effect of electrons. The resulting PDOS is presented in Fig. 4. One can clearly see that our theoretical results are consistent with the experimental data in which the crystal field states follow $E_{a_1'} > E_{e'} > E_{e''}$. An unambiguous assignment of the crystal field states and energies can be further obtained by generating maximally localized Wannier functions (MLWFs)[32] based on the ground state electronic structure in the selected energy window spanning all the crystal field states under consideration. The resulting MLWFs for each crystal field state are shown in Fig. 4 and the resulting energies are $E_{e'} - E_{e''} = 0.41$ eV and $E_{a_1'} - E_{e'} = 0.81$ eV, which are close to the experimental values of 0.7 and 0.9 eV, respectively. This qualitative agreement between experiment and theory is expected within the frame work of DFT. However, we should be aware that a more proper treatment of electron-hole excitations by GW based Bethe-Salpeter method[33,34] can further improve the theoretical prediction.

To overcome the severely underestimated bandgap due to the delocalization error arising from the incomplete cancellation of the spurious self-interaction, we used the GGA + U with the effective U value ($U_{eff}$ = U-J) of 4.61 eV.[37] This gives a bandgap of $E_g = 1.35$ eV, which still underestimates our experimental value.[28] Again, a more proper treatment of self-energy by GW method will further bring the theoretical predictions closer to the experimental value.

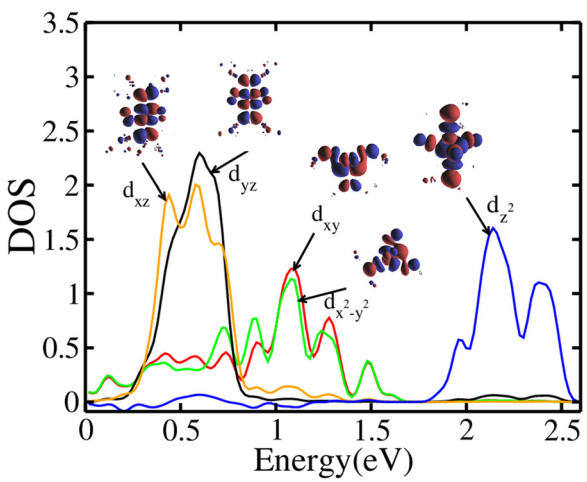


FIG. 4. Projected density of states for conduction band of h-$LuFeO_3$ with theoretical ground state structure (space group $P6_3cm$) and MLWFs (by WIEN2K software package (Refs. 35 and 36)) with crystal field splitting states characters.

In conclusion, we have studied h-$LuFeO_3$ films using x-ray and optical spectroscopy. The strong dichroism in XAS and large crystal field energy splitting of $Fe^{3+}$ may be related to the stability of hexagonal phase of $LuFeO_3$. A 2.0 eV optical bandgap originated from charge transfer excitations is determined from the optical spectra. This important information of electron structure, confirmed by DFT calculations will definitely benefit further studies of h-$LuFeO_3$.

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