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# Lattice dynamical probe of charge order and antipolar bilayer stacking in LuFe<sub>2</sub>O<sub>4</sub>

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**Lattice dynamical probe of charge order and antipolar bilayer stacking in LuFe<sub>2</sub>O<sub>4</sub>**X. S. Xu,<sup>1,\*</sup> J. de Groot,<sup>2</sup> Q.-C. Sun,<sup>1</sup> B. C. Sales,<sup>3</sup> D. Mandrus,<sup>3,4</sup> M. Angst,<sup>2</sup> A. P. Litvinchuk,<sup>5</sup> and J. L. Musfeldt<sup>1</sup><sup>1</sup>*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*<sup>2</sup>*Institut für Festkörperforschung, JCN S and JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*<sup>3</sup>*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*<sup>4</sup>*Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA*<sup>5</sup>*Texas Center for Superconductivity and Department of Physics, University of Houston, Houston, Texas 77204, USA*

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We investigated the infrared response of LuFe<sub>2</sub>O<sub>4</sub> through the series of charge, magnetic, and structural transitions. All vibrational modes couple strongly to the charge order, whereas the LuO zone-folding modes are also sensitive to magnetic order and structural distortion. The dramatic splitting of the LuO<sub>2</sub> layer mode is attributed to charge-rich/poor proximity effects and its temperature dependence reveals the antipolar nature of the W layer pattern.

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**I. INTRODUCTION**

Multiferroics are materials that carry more than one ferroic order (e.g., magnetic and electric order), a relatively rare coincidence of functionalities that gives rise to rich physics, interesting tunability, and promising applications. LuFe<sub>2</sub>O<sub>4</sub> is often cited as the prototypical electronically driven multiferroic.<sup>1</sup> Notable aspects include high ordering temperatures, large order parameters, orbitally induced magnetic anisotropy, and facile dielectric tunability in magnetic and electric fields.<sup>2–6</sup> On the other hand, many critical properties are controversial, for instance, ferroelectric vs antipolar bilayer ordering and the role of the lattice through the cascade of temperature-driven transitions.<sup>3,7–10</sup>

LuFe<sub>2</sub>O<sub>4</sub> crystallizes in a rhombohedral ( $R\bar{3}m$ ) structure with alternating Fe-containing double layers (often called Fe<sub>2</sub>O<sub>2</sub> or W layers) and LuO<sub>2</sub> layers, each with triangular connectivity. Above 500 K, the Fe site charge is 2.5+, characteristic of a disordered phase with ferroelectric fluctuations. Two-dimensional Fe<sup>2+</sup>/Fe<sup>3+</sup> charge ordering (CO) appears below 500 K, three-dimensional (3D) charge order sets in at 320 K ( $T_{CO}$ ) although fluctuations persist to much lower temperature, long-range magnetic order occurs below 240 K ( $T_N$ ), and a magnetostructural transition is observed at 175 K ( $T_{LT}$ ).<sup>3,7,8,11–14</sup> Local polarization emanates from the charge-order-induced charge imbalance in the W layer.<sup>3</sup> Order-by-fluctuation and electron-phonon coupling models have both been put forward as mechanisms for the development of the charge-ordered superstructure.<sup>15,16</sup> Since both charge order and magnetism originate from Fe site ordering, magnetoelectric coupling is strong.

To elucidate charge and bonding in a model charge ordered multiferroic, we investigated the lattice dynamics of LuFe<sub>2</sub>O<sub>4</sub>. What differentiates LuFe<sub>2</sub>O<sub>4</sub> from other coupled materials such as  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub>, CuFeO<sub>4</sub>, TmSe, and many manganites and organic molecular solids is the combined presence of fluctuation, charge order/disorder, and frustration.<sup>17,18</sup> Our chosen technique, infrared vibrational spectroscopy, is a sensitive, microscopic probe of charge, structure, and bonding, and its fast time scale ( $\sim 10^{12}$ – $10^{13}$  Hz) is well suited for the study of a fluctuating

disordered system over a wide temperature range. We find that the lattice is very sensitive to charge order and magnetism in LuFe<sub>2</sub>O<sub>4</sub>. This interaction is best exemplified by LuO<sub>2</sub> mode splitting below  $T_{CO}$  which confirms antipolar bilayer stacking<sup>19</sup> (and rules out the previously supposed ferroelectric alignment). Moreover, charge order couples strongly to and competes with magnetism between  $T_N$  and  $T_{LT}$ , as illustrated by the behavior of the LuO<sub>2</sub> zone-folding modes. Finally, our measurements reveal an additional regime below 50 K that may be related to glassy state formation.

**II. METHODS**

Large LuFe<sub>2</sub>O<sub>4</sub> single crystals were grown by floating-zone techniques.<sup>7,8</sup> Near-normal reflectance<sup>20</sup> was measured on the (001)<sub>h</sub> plane employing a Bruker 113v Fourier transform infrared spectrometer, covering the frequency range from 30–5000 cm<sup>-1</sup> (3.7–0.62 eV) at 41 different temperatures between 10 and 500 K. Room-temperature reflectance was also collected up to 6 eV using a Perkin Elmer  $\lambda$ -900 grating spectrometer. The imaginary part of the dielectric function,  $\epsilon_2(\omega)$ , was calculated from the measured reflectance by a Kramers-Kronig analysis.<sup>21,22</sup> Complementary transmittance experiments (77–300 K) on powder samples embedded in a paraffin matrix allowed us to calculate absorption,  $\alpha(\omega)$ , directly.<sup>21</sup> Standard peak-fitting techniques were employed as appropriate.<sup>23</sup> Lattice dynamical calculations were performed within the shell model approximation using the GULP package which includes long-range Coulomb interactions along with short-range ionic potentials.<sup>24</sup> The model is proven to adequately describe the lattice dynamics of ionic materials, metal oxides, in particular.<sup>25,26</sup> Ionic valence was varied to provide a reasonable match with the experimental spectra.

**III. RESULTS AND DISCUSSION****A. Structure and symmetry**

The rhombohedral ( $R\bar{3}m$ ) high-temperature structure of LuFe<sub>2</sub>O<sub>4</sub> is usually described in a hexagonal setting with the

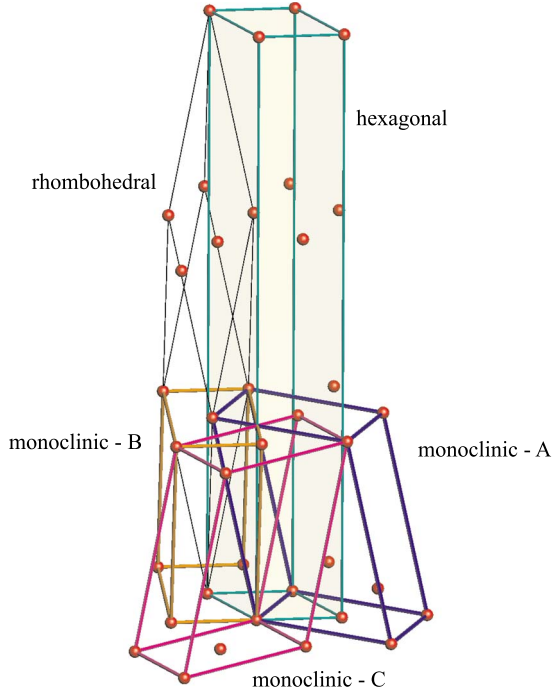


FIG. 1. (Color online) Different cells describing the high temperature  $\text{LuFe}_2\text{O}_4$ . Apart from the primitive rhombohedral and the  $R$ -centered hexagonal (standard setting) cells the lattice can also be described by one of three  $C$ -centered monoclinic cells, which are rotated by  $120^\circ$  with respect to each other. Cells describing the charge order in the three domains are obtained from the latter by tripling the monoclinic  $b$  and doubling the monoclinic  $c$  axes (omitted for clarity).

$R$ -centered cell containing three Fe/O double layers. Alternative cells describing the same structure are possible, including  $C$ -centered monoclinic cells containing only one Fe/O double layer (see Fig. 1). Charge ordering breaks the threefold rotational symmetry, lowering the symmetry to monoclinic as mentioned in Ref. 8. One consequence of the loss of threefold rotation symmetry is the occurrence of three symmetry-equivalent structures, described with cells rotated by  $120^\circ$  relative to each other. Each of the latter corresponds to a CO domain associated with one of the symmetry-equivalent propagation vectors and the occurrence of multiple CO domains implies a correspondingly twinned sample.

For each domain, the CO superstructure can be described by a multiple of one of the three  $C$ -centered monoclinic cells shown in Fig. 1. The CO propagation vector of, e.g.,  $(\frac{1}{3}\frac{1}{3}\frac{3}{2})_h$  becomes in the appropriate monoclinic cell  $(0\frac{1}{3}\frac{1}{2})_m$ , i.e., the CO triples the monoclinic cell along  $b$  and doubles it along  $c$ .<sup>27</sup> This sixfold enlarged CO cell is again  $C$  centered and the CO has space group  $C2/m$ . Bragg reflections collected by single-crystal x-ray diffraction are indeed well described by three twins of  $C$ -centered cells ( $a=5.95 \text{ \AA}$ ,  $b=10.32 \text{ \AA}$ ,  $c=17.31 \text{ \AA}$ ,  $\beta=103.2^\circ$ ) with  $C2/m$  symmetry.<sup>28</sup> The structural twinning places strong restrictions on the lattice parameters of these cells. For example, an increase in the monoclinic angle  $\beta$  for all three twins is not possible short of cleaving the crystal because the lattices would no longer match. Nevertheless, the observation of

TABLE I. Vibrational modes predicted from a group theoretical analysis according to the symmetry and lattice structure of  $\text{LuFe}_2\text{O}_4$  (Ref. 8). The  $z$  direction is chosen as  $(001)_h$ , and  $x$  is chosen to be the intersection between the mirror plane of the low-temperature  $C2/m$  cell and the hexagonal basal plane.

	High temperature $R\bar{3}m$ , No. 166	Low temperature $C2/m$ , No. 12
Predicted activity		
Infrared active	$3E_u(x,y)$ , $3A_{2u}(z)$	$27A_u(x)$ , $36B_u(y,z)$
Raman active	$3A_{1g}(zz)$ , $3E_g(xx-yy,xy)$	$32A_g(xx)$ , $28B_g(xy,xz)$

Bragg peak splitting below  $T_{LT} \approx 175 \text{ K}$  (Ref. 12) implies that a distortion eventually takes place. Its nature likely depends on the shape of in-plane domain boundaries and relative domain population, which has yet to be fully elucidated.

Associated with cell enlargement and symmetry lowering is a splitting of atomic sites (for Wyckoff positions, see Table III, Appendix). For example, in the high-temperature structure, iron has a single position, with  $3m$  (threefold rotation and mirror) site symmetry, becoming just  $m$  after removal of the rotation axis. Tripling  $b$  splits the Fe site into two different positions, one with and one without mirror symmetry, and doubling  $c$  further doubles the positions without changing their symmetry. The four sites correspond to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  minorities, with mirror symmetry, and  $\text{Fe}^{2+/3+}$  majorities at general positions. For the ferroelectric CO, suggested<sup>8</sup> to describe short-range correlations at higher temperature, there are also four sites, with the cell doubling along  $c$  replaced by removal of the twofold rotation axis.

The vibrational modes predicted by group theoretical analysis are listed in Table I.<sup>29</sup> Assuming every Fe has static charge, the high-temperature phase has 12 modes.<sup>16</sup> This includes three in-plane ( $E_u$ ) doubly degenerate modes and three out-of-plane ( $A_{2u}$ ) modes that are infrared active. These results are in agreement with the findings of Harris and Yildirim<sup>16</sup> but different from those of Vitucci *et al.*<sup>10</sup> The displacement patterns of the in-plane ( $E_u$ ) symmetry infrared-active modes are shown in Fig. 2(a). Because the  $\text{LuO}_2$  and  $\text{Fe}_2\text{O}_2$  (W) layers are connected in a perpendicular fashion, the in-plane  $\text{LuO}_2$  and  $\text{Fe}_2\text{O}_2$  modes are nearly decoupled. The other mode corresponds to relative motion between  $\text{LuO}_2$  and  $\text{Fe}_2\text{O}_2$  layers.<sup>16</sup> The low frequency and modest intensity derive from the small charge/mass ratio. For the low-temperature phase with charge order, the primitive cell is six times larger than that of the high-temperature phase. The  $C2/m$  symmetry lifts all degeneracies.<sup>30</sup> Clearly, many modes are expected, different from the results of Vitucci *et al.*<sup>10</sup>

## B. Vibrational properties of $\text{LuFe}_2\text{O}_4$

### 1. Vibrational spectra and high symmetry mode assignment

Figure 3 displays the measured reflectance and imaginary part of the dielectric function of  $\text{LuFe}_2\text{O}_4$ ,  $\mathcal{R}(\omega)$  and  $\epsilon_2(\omega)$ , at three characteristic temperatures.<sup>22</sup> Because our measurements were carried out on the  $(001)_h$  crystal face, only in-plane mode contributions are probed. As discussed above,

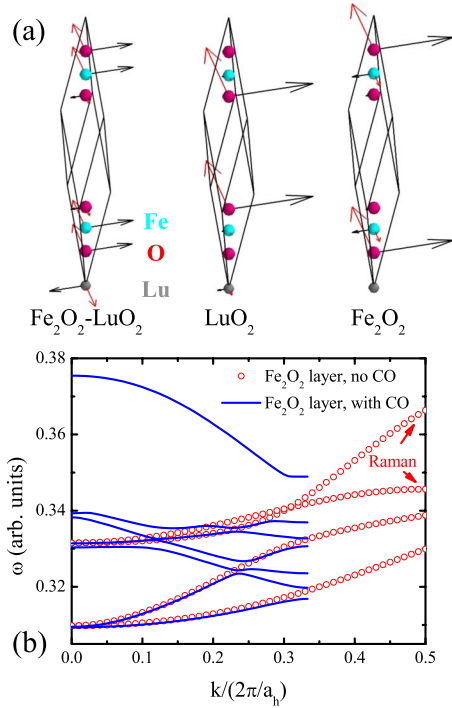


FIG. 2. (Color online) (a) Schematic view of the in-plane ( $E_u$ ) vibrational modes of  $R\bar{3}m$  symmetry. The displacement patterns shown correspond to the  $\Gamma$  (zone-center) point. Here, dark (black) and light (red) arrows correspond to two independent modes with different polarizations. The high-temperature phase primitive cell is superimposed for clarity. (b) Calculated phonon dispersion of isolated  $\text{Fe}_2\text{O}_2$  with and without charge order along  $(100)_h$  direction. The infrared-active modes are shown for the (low-temperature) charge-ordered structure whereas both the infrared- and Raman-active modes are shown for the (high-temperature) charge-disordered case.

group theory predicts three well-defined spectral features with  $E_u$  symmetry corresponding to (i) relative in-plane shearing motion between the  $\text{LuO}_2$  and  $\text{Fe}_2\text{O}_2$  layers, (ii) in-plane motion within the  $\text{LuO}_2$  layer, and (iii) in-plane motion within the  $\text{Fe}_2\text{O}_2$  layer [Table I, Fig. 2(a)]. At 500 K, the experimental  $\epsilon_2(\omega)$  spectrum does indeed contain three features. These include a weak low-frequency peak at  $\sim 70 \text{ cm}^{-1}$ , a sharp peak near  $320 \text{ cm}^{-1}$ , and a broad shoulder at higher frequency. Based upon position and intensity, one can easily assign the weak low-frequency peak as inter- $\text{LuO}_2/\text{Fe}_2\text{O}_2$  layer motion. Assignment of the anticipated intra- $\text{LuO}_2$  and intra- $\text{Fe}_2\text{O}_2$  layer modes is more challenging because the observed line shapes are rather unusual. The problem can be resolved by reconsidering the assumption of static charge. Nominally 2.5+ in the high temperature phase, the Fe site charge has an average rather than static valency due to fluctuations. Because a typical vibrational frequency ( $10^{12}$ – $10^{13}$  Hz) (Ref. 31) is much faster than the charge fluctuation in  $\text{LuFe}_2\text{O}_4$  ( $10^6$ – $10^7$  Hz),<sup>12</sup> spectral features related to the  $\text{Fe}_2\text{O}_2$  layers should reflect charge fluctuations. The  $\text{LuO}_2$ -related feature, by contrast, should be much less sensitive to fluctuations. Thus, one expects a well-defined  $\text{LuO}_2$  layer mode and a broad feature emanating

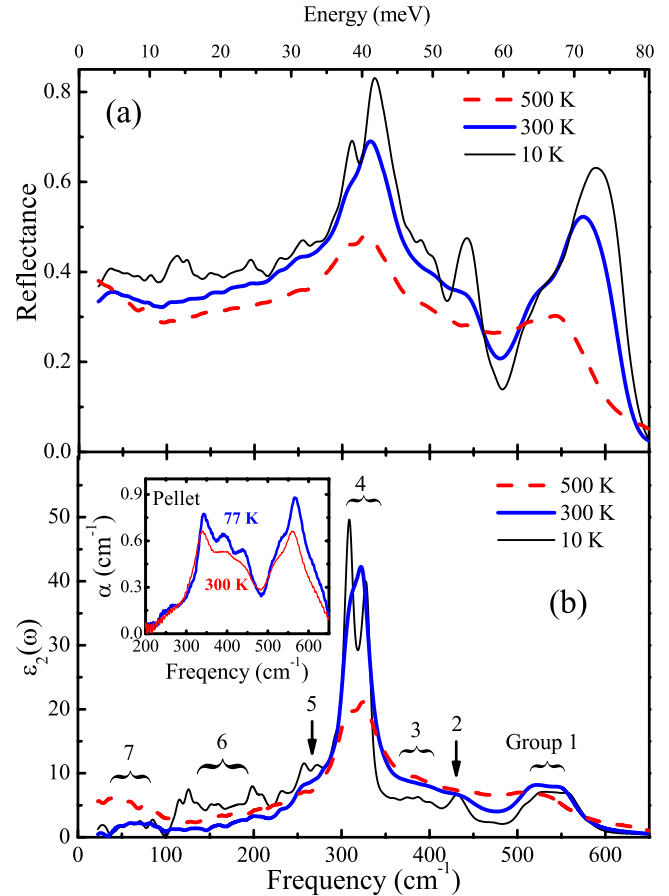


FIG. 3. (Color online) (a) Near-normal reflectance of  $\text{LuFe}_2\text{O}_4$ ,  $\mathcal{R}(\omega)$ , measured on the  $(001)_h$  crystal face. (b) Imaginary part of the complex dielectric function,  $\epsilon_2(\omega)$ , at various temperatures, calculated from the measured reflectance by a Kramers-Kronig analysis. The vibrational features are grouped according to their frequency and temperature dependence. Inset: absorption spectrum of  $\text{LuFe}_2\text{O}_4$  powder embedded in a paraffin matrix.

from  $\text{FeO}$  layer motion. We therefore assign the  $320 \text{ cm}^{-1}$  peak to in-plane motion of the  $\text{LuO}_2$  layer. Assignment of intra- $\text{Fe}_2\text{O}_2$  motion is less obvious because it is hidden in the broad shoulder at 500 K. Our shell model calculations provide numerical support for these assignments.  $\text{Lu-Fe}$ ,  $\text{LuO}_2$ , and  $\text{Fe}_2\text{O}_2$  blocks are predicted at 68, 320, and  $520 \text{ cm}^{-1}$  in reasonable agreement with the values obtained by Harris and Yildirim<sup>16</sup> (92, 332, and  $474 \text{ cm}^{-1}$ ). This relative ordering of the intra- $\text{LuO}_2$  vs intra- $\text{Fe}_2\text{O}_2$  layer modes is in line with mass arguments.

In order to precisely locate the intra- $\text{Fe}_2\text{O}_2$  modes, one has to examine the low-temperature phase response and consider the relation between the mode distribution and the primitive cell. Low-temperature charge order expands (shrinks) the primitive cell (Brillouin zone) by a factor of 6 compared to the high-temperature phase. The folded modes thus display a finite polarization due to charge-order-induced symmetry breaking. The latter also activates some Raman features that emanate from the high-temperature symmetric phase. Figure 2(b) displays the calculated phonon dispersion of an isolated  $\text{Fe}_2\text{O}_2$  layer.<sup>32</sup> Both infrared- and Raman-

TABLE II. Summary of spectral features observed in  $\varepsilon_2(\omega)$  for  $\text{LuFe}_2\text{O}_4$ .

Group	7	6	5	4	3	2	1
Frequency ( $\text{cm}^{-1}$ )	broad $\sim 70$	144–257	270, 292	308, 326	360, 374, 388, 400	430	530, 560
Assignment	LuO <sub>2</sub> -Fe <sub>2</sub> O <sub>2</sub> layer shear			LuO <sub>2</sub> in-plane	LuO <sub>2</sub> zone folding	Fe <sub>2</sub> O <sub>2</sub> in-plane	Fe <sub>2</sub> O <sub>2</sub> zone folding

active modes are plotted for the noncharge ordered structure. In the charge-ordered phase, we plot only the infrared-active modes. Due to the upward curvature of the  $\text{Fe}_2\text{O}_2$  layer phonon dispersion, infrared-active zone-folded modes (thin solid lines in Fig. 2) appear at higher frequencies than the fundamentals. This observation suggests that groups 1, 2, and 3 (Fig. 3) should be assigned as  $\text{Fe}_2\text{O}_2$  zone-folding modes,  $\text{Fe}_2\text{O}_2$  in-plane modes, and  $\text{LuO}_2$  zone-folding modes, respectively. The directional characteristics are in line with these assignments.<sup>33</sup> Table II summarizes our results.

## 2. LuO<sub>2</sub> in-plane fundamental modes and antipolar bilayer stacking in $\text{LuFe}_2\text{O}_4$

Figure 4(a) displays a closeup view of the group 4 doublet in  $\varepsilon_2(\omega)$ . These features are assigned as  $\text{LuO}_2$  layer modes. At 500 K, both components of the doublet are broad and low due to fluctuations. Their temperature dependence is, however, quite different [Fig. 4(b)]. The intensity of 308  $\text{cm}^{-1}$  component is small above  $T_{\text{CO}}$ , increases with decreasing temperature below  $T_{\text{CO}}$ , reaches a maximum at  $T_{\text{LT}}$ , and saturates at low temperature. In contrast, the intensity of the 326  $\text{cm}^{-1}$  component reaches a maximum at  $T_{\text{CO}}$  and drops with decreasing temperature before saturating at low temperature.<sup>23</sup>

Three different scenarios immediately arise that can account for the observed doublet structure. They include: (i) in-plane anisotropy effects on the  $\text{LuO}_2$  layer modes due to ferroelectric charge order (essentially the difference between parallel and perpendicular polarizations with respect to the mirror plane), (ii) long-range intralayer charge disproportionation in which both layers of a bilayer are 2+ rich and both layers of the next bilayer are 3+ rich, and (iii) the presence of two distinct  $\text{LuO}_2$  layer environments corresponding to an antipolar arrangement of W layers. Lattice dynamics calculations reveal that the effect from mechanism (i) is too small to generate the observed 18  $\text{cm}^{-1}$  splitting. Moreover, relative changes in doublet intensities with temperature would be expected to be similar, an expectation that is clearly inconsistent with observation [Fig. 4(b)]. On the other hand, mechanism (ii) could generate a sizable splitting, but it would imply interdouble-layer charge transfer, a scenario therefore excluded in previous structural analysis.<sup>8</sup> Mechanism (iii) also supports sizable mode splitting. Dynamics calculations provide a way forward with respect to the temperature-dependent peak intensities by suggesting that the two independent  $\text{LuO}_2$  layers in the antipolar cell generate two kinds of modes by superposition. In the high-temperature phase, the  $\text{Fe}_2\text{O}_2$  layers do not have electric dipoles, so the two  $\text{LuO}_2$  layers are equivalent. Therefore, the superposition generates one Raman-active and one infrared-active mode as depicted in Fig. 4(c). When temperature is

decreased, symmetry is reduced due to charge ordering, and the Raman mode becomes infrared active. Thus, a new peak emerges below  $T_{\text{CO}}$  that steals oscillator strength from the original infrared-active band. At low temperature, the two  $\text{LuO}_2$  layers are inequivalent. One type of  $\text{LuO}_2$  layer is sandwiched between charge-rich  $\text{FeO}$  slabs, whereas the other type is sandwiched between charge-poor  $\text{FeO}$  layers. When charge order is strong enough, the two types of modes correspond to intra- $\text{LuO}_2$  motion of the two distinct  $\text{LuO}_2$  layers, as depicted in Fig. 4(d). As we discuss below, this scenario clearly excludes standard ferroelectric stacking of the W layers. The intensities of  $\text{LuO}_2$  layer modes in prox-

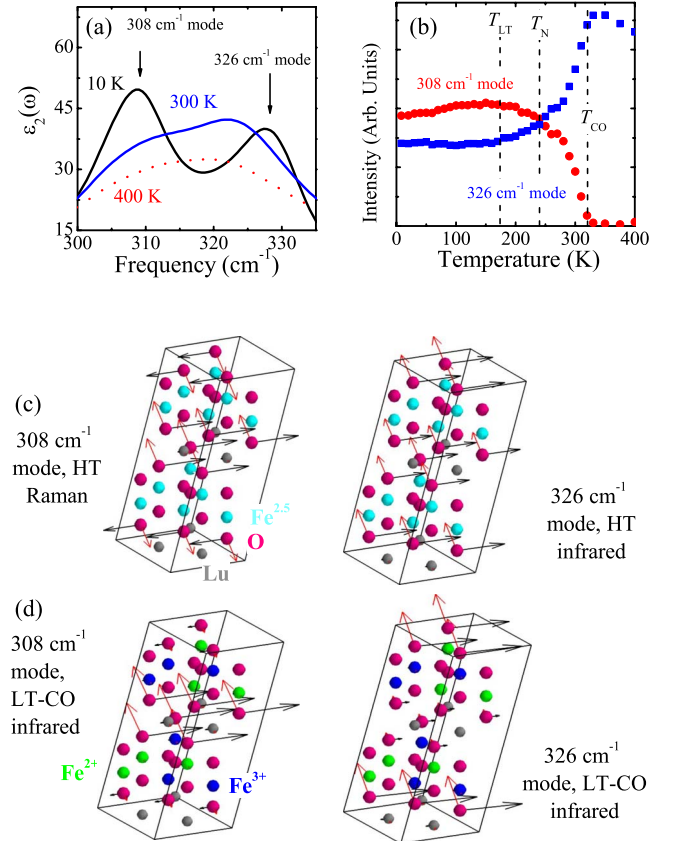


FIG. 4. (Color online) (a) Closeup view of  $\varepsilon_2(\omega)$  showing the in-plane  $\text{LuO}_2$  modes. (b) Temperature dependence of peak intensity. These data were determined from oscillator fits (Ref. 23). Relative error bars are on the order of the symbol size. (c) and (d) show calculated displacement patterns for the (high-temperature) charge-disordered phase and (low-temperature) charge-ordered phase, respectively. In (c), the left- (right-) hand pattern corresponds to a Raman (infrared) active mode. In (d), both are infrared active due to symmetry breaking. Here, dark (black) and light (red) arrows indicate two independent modes with different polarizations.

imity to charge-rich/poor iron oxide layers should be similar at low temperature.

Comparing the temperature dependence of the 308 and 326  $\text{cm}^{-1}$  components with the above predictions, we can assign the microscopic nature of each peak. The intensity of the 308  $\text{cm}^{-1}$  component increases with decreasing temperature below  $T_{\text{CO}}$ , in line with predictions for a feature originating from a high symmetry Raman-active mode, mainly from  $\text{LuO}_2$  sandwiched between charge-poor  $\text{FeO}$  layers at low temperature. The 326  $\text{cm}^{-1}$  component, on the other hand, behaves in the opposite way, perfectly consistent with the other mode, deriving mainly from  $\text{LuO}_2$  sandwiched between charge-rich  $\text{FeO}$  layers at low temperature. The proximity effect observed here, with the charge-rich (poor) layer resonating at higher (lower) frequency, is consistent with observations in other model materials.<sup>34</sup> The strong coupling between the charge order and the  $\text{LuO}_2$  vibrational modes makes the latter a unique probe of charge order.

Importantly, the doublet character of the  $\text{LuO}_2$  layer mode, its temperature dependence, and our assignment in terms of proximity to charge-rich and charge-poor  $\text{FeO}$  layers is in line with expectations for an antipolar ground state in  $\text{LuFe}_2\text{O}_4$ .<sup>8</sup> It is inconsistent with ferroelectric ordering of the W layers.<sup>35</sup> The mode behavior also rules out any other similar kind of interlayer charge ordering. For instance, the ferroelectric arrangement proposed by Xiang *et al.*<sup>11</sup> would produce three unique components to the  $\text{LuO}_2$  intralayer vibrational pattern rather than the two found in experiment. In addition, the  $\text{LuO}_2$  features are in-plane polarized, as shown by a comparison between single crystal and powder sample spectra (inset, Fig. 3).<sup>33</sup> Taken together, these findings suggest that antipolar ordering of the  $\text{Fe}_2\text{O}_2$  bilayers is the most likely arrangement, consistent with the observed temperature-dependent vibrational spectra.<sup>36</sup>

### 3. $\text{LuO}_2$ zone-folding modes couple strongly to the charge order, magnetism, and structural distortion

Figure 5(a) displays a closeup view of  $\epsilon_2(\omega)$  in the regime corresponding to  $\text{LuO}_2$  zone-folding modes of  $\text{LuFe}_2\text{O}_4$  (group 3). The spectrum is relatively flat at high temperature due to disorder and the high symmetry created by fluctuation. At least three peaks emerge at low temperature. The calculated peak area is shown in Fig. 5(b).<sup>37</sup> Besides a cusp at 320 K and a minimum just above  $T_{\text{CO}}$ , the peak area is very sensitive to magnetic order at  $T_N$  and the structural distortion at  $T_{LT}$ .

Figure 5 also shows the displacement patterns of two example  $\text{LuO}_2$  zone-folding modes suggested from calculation. Panel (c) shows a  $\text{LuO}_2$  layer twisting mode and panel (d) shows a combined  $\text{LuO}_2 + \text{Fe}_2\text{O}_2$  layer twisting mode. In the high-temperature (high symmetry) phase, these modes are infrared inactive. The reduced symmetry of the low-temperature charge-ordered phase gives rise to mode polarization. Zone-folding modes are thus anticipated to be very sensitive to structural symmetry.

These predictions are consistent with our experimental observations. Above  $T_{\text{CO}}$ , high symmetry and strong fluctuation obscures individual components of the  $\text{LuO}_2$  zone-folding modes. Below  $T_{\text{CO}}$ , charge-order-induced symmetry

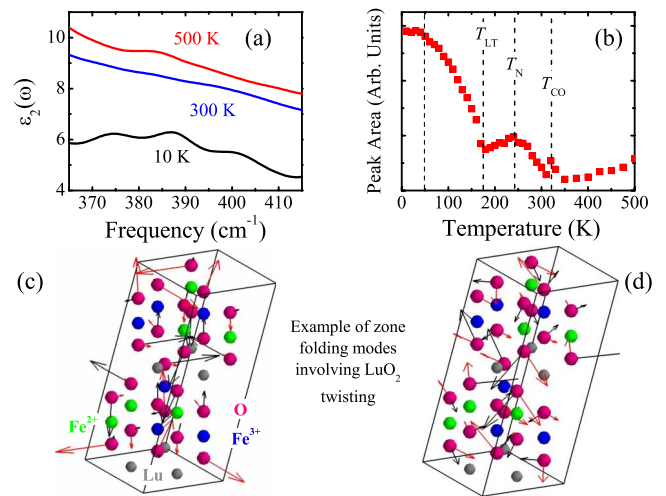


FIG. 5. (Color online) (a) Closeup view of  $\epsilon_2(\omega)$  showing features that we assign as  $\text{LuO}_2$  zone-folding modes. (b) Temperature dependence of the peak area. These data were determined from oscillator fits (Ref. 23). Relative error bars are on the order of the symbol size. (c) and (d) show typical calculated displacement patterns of  $\text{LuO}_2$  zone-center modes in the (low-temperature) charge-ordered phase.

lowering results in distinct peaks. Interestingly, when temperature is reduced below  $T_N$ , the peak area vs temperature trend is reversed. This is because charge order is damped by the development of magnetic order. The competition between charge and magnetic order is also seen in x-ray diffraction experiments and terahertz time-domain spectroscopy.<sup>8,9</sup> Further, like the 1 THz soft mode observed by Li *et al.*,<sup>9</sup>  $\text{LuO}_2$  zone-folding modes are of correct symmetry to contribute to the small polarization and dielectric changes at 240 and 175 K.<sup>2,5</sup> Below  $T_{LT}$ , peak area increases on cooling, consistent with enhanced charge order and structural distortion.<sup>8,9,12</sup>

### 4. Probing intralayer charge order: The $\text{Fe}_2\text{O}_2$ fundamental and zone-folding modes

Figure 6(a) displays a closeup view of  $\epsilon_2(\omega)$  in the group 2 spectral regime. This structure is assigned as  $\text{Fe}_2\text{O}_2$  in-plane motion. We find that the area of this feature is sensitive to charge ordering at 320 K [Fig. 6(b)] but only weakly coupled to  $T_N$  and  $T_{LT}$ . This is because charge-order-induced symmetry breaking transfers a small portion of the  $\text{Fe}_2\text{O}_2$  in-plane mode oscillator strength to the zone-folding modes, an effect that gives extra sensitivity to symmetry modifications. Figure 6(e) shows the calculated displacement pattern of the  $\text{Fe}_2\text{O}_2$  layer mode in the low-temperature charge-ordered phase. Our calculations predict a significant out-of-plane component to the displacement, indicative of lower symmetry. The Born effective charge calculated from the observed mode intensity<sup>38</sup> is  $q_{\text{eff}} = 1.5e^-$  at 10 K, less than the nominal Fe center valence in this material. This result implies that  $\text{LuFe}_2\text{O}_4$  is less ionic than simple valence counting schemes might predict, different than the conclusion of Mulders *et al.*<sup>14</sup> where a 4 eV chemical shift of the Fe  $K$  edge indicates fully ionic valence states.

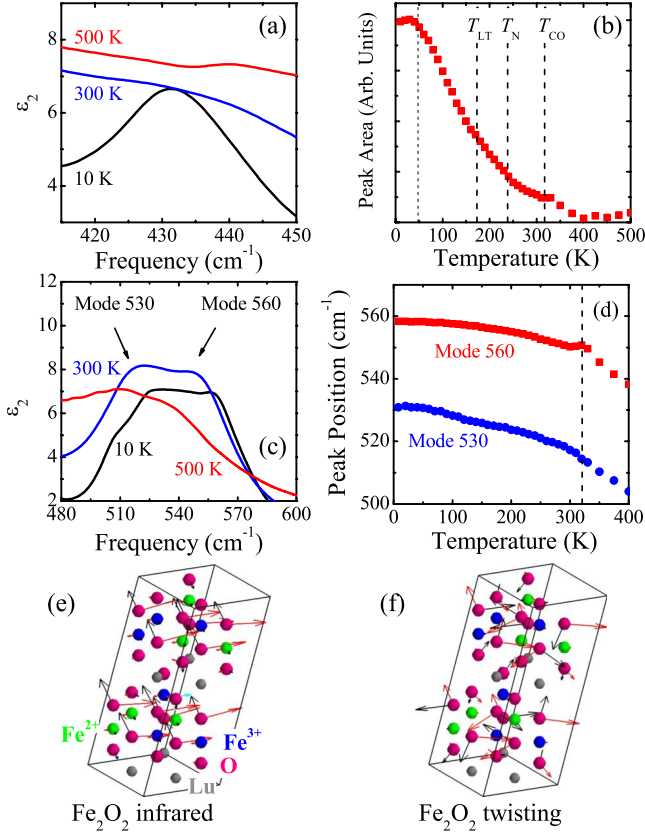


FIG. 6. (Color online) (a) Closeup view of  $\epsilon_2(\omega)$  showing the  $\text{Fe}_2\text{O}_2$  in-plane modes. (b) Peak area vs temperature for the  $\text{Fe}_2\text{O}_2$  in-plane modes. These data were determined from oscillator fits (Ref. 23). Relative error bars are on the order of the symbol size. (c) Closeup view of  $\epsilon_2(\omega)$  showing the  $\text{Fe}_2\text{O}_2$  zone-folding modes. (d) Frequency vs temperature of two  $\text{Fe}_2\text{O}_2$  zone-folding modes. As before, these data were determined from oscillator fits (Ref. 23). (e) Calculated displacement patterns of  $\text{Fe}_2\text{O}_2$  in-plane modes in the (low-temperature) charge-ordered phase. (f) Example displacement patterns for  $\text{Fe}_2\text{O}_2$  zone-folding modes in the (low-temperature) charge-ordered phase.

Figure 6(c) displays a closeup view of the  $\text{Fe}_2\text{O}_2$  zone-folded modes of  $\text{LuFe}_2\text{O}_4$  (group 1). As anticipated from our dispersion calculations, this structure is a superposition of more than one oscillator. The  $\text{Fe}_2\text{O}_2$  twisting pattern shown in Fig. 6(f) is an example of the type of motion involved. The behavior of these  $\text{Fe}_2\text{O}_2$  zone-folding modes is unique in that there is a significant temperature-induced frequency shift. We quantified this effect by fitting the spectral features with two oscillators up to 400 K. The results are shown in Fig. 6(d). Both components redshift strongly on warming, a trend that is not as obvious in other modes. At  $T_{\text{CO}}$ , the mode frequencies drop more quickly, an indication of mode instability and a sign of a structural or bonding transition driven by elevated temperature.<sup>39</sup> Intensity changes are observed as well [Fig. 6(b)]. A similar group of modes is observed in the spectra of Vitucci *et al.* The splitting is more pronounced but they do not offer a mode assignment.<sup>10</sup> We attribute this difference to sample quality issues.<sup>40</sup> Recently, Harris and Yildirim<sup>16</sup> predicted that a low-frequency Raman-active mode of  $E_g$  symmetry (in the rhombohedral unit cell, Table I)

should couple most effectively to the charge ordering. Due to charge fluctuations, however, one actually has to consider more than the modes in rhombohedral cell because the low symmetry modes already exist even at high temperature. For example, the features shown in Fig. 6(c) may also couple strongly to the 3D charge ordering.

### 5. Frozen lattice response below 50 K

As discussed above, the lattice vibrations of  $\text{LuFe}_2\text{O}_4$  are very sensitive to the series of temperature-driven transitions: 320 K ( $T_{\text{CO}}$ ), 240 K ( $T_N$ ), and 175 K ( $T_{\text{LT}}$ ). In addition, the entire spectrum freezes at  $T \sim 50$  K. The lack of change in the dynamical response is shown most clearly in the  $\text{Fe}_2\text{O}_2$  fundamental and the  $\text{LuO}_2$  zone-folding modes [Figs. 6(b) and 5(b), respectively]. This indicates that the structural distortion, charge order, and the fluctuation of the charge order remain constant below 50 K, a finding that may be related to the emergence of a glassy state, a state with unusual domain structure, or perhaps an interesting antiferromagnetic state.<sup>2,9,41–43</sup> In the former two scenarios, the freezing of the spectrum is likely tied to the kinetic arrest of the magneto-structural transition discussed in Ref. 12. By way of comparison, the perovskite  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  displays relaxorlike dynamical slowing down of the dipolar fluctuations on approach to a frozen, glasslike state.<sup>44</sup> Clearly, more investigation is needed to understand the nature of this regime in  $\text{LuFe}_2\text{O}_4$ .

## IV. SUMMARY

We investigated the vibrational response of  $\text{LuFe}_2\text{O}_4$  through the series of temperature driven transitions using infrared spectroscopy and compared our results with complementary group theoretical predictions and lattice dynamics calculations. The  $\text{LuO}_2$  layer mode is particularly sensitive to charge proximity effects with temperature-driven changes in the oscillator strength of the doublet structure that reveal antipolar ordering of the  $\text{Fe}_2\text{O}_2$  bilayers rather than the previously supposed ferroelectric alignment. Analysis of  $\text{LuO}_2$  zone-folding and  $\text{Fe}_2\text{O}_2$  layer mode trends indicate that charge order couples strongly to and competes with magnetism. We discuss our findings in comparison to other model materials.

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## APPENDIX: WYCKOFF SITES

For Wyckoff positions, see Table III.



TABLE III. Splitting of Wyckoff positions due to charge order. For domain A with propagation vector  $(\frac{1}{3}\frac{1}{3}\frac{3}{2})_h$ , the lattice parameters transform as  $\mathbf{a}_A = \mathbf{a}_h - \mathbf{b}_h$ ,  $\mathbf{b}_A = 3(\mathbf{a}_h + \mathbf{b}_h)$ , and  $\mathbf{c}_A = \frac{2}{3}(-\mathbf{a}_h + \mathbf{b}_h + \mathbf{c}_h)$ . For the atom sites shown, we give Wyckoff labels (site symmetry) and coordinates of a representative in fractions of the respective cell. Greek symbols and decimal point numbers are freely adjustable parameters.

Site	Wyckoff High- $T$ structure ( $R\bar{3}m$ )	Representative
Lu	$3a$ ( $-3m$ )	(0,0,0)
Fe	$6c$ ( $3m$ )	(0,0, $\zeta$ )
O1	$6c$ ( $3m$ )	(0,0, $\zeta$ )
O2	$6c$ ( $3m$ )	(0,0, $\zeta$ )
CO structure, domain A ( $C2/m$ )		
Lu	$2a$ ( $2/m$ )	(0,0,0)
	$4g$ (2)	(0,0.333,0)
	$2c$ ( $2/m$ )	(0,0, $\frac{1}{2}$ )
	$4h$ (2)	(0,0.333, $\frac{1}{2}$ )
Fe	$4i_1$ ( $m$ )	( $\zeta$ ,0, $\frac{3}{2}\zeta + \eta$ )
	$8j_1$ (1)	( $\zeta$ ,0.333, $\frac{3}{2}\zeta + \eta$ )
	$4i_2$ ( $m$ )	( $\zeta$ ,0, $\frac{3}{2}\zeta + \eta + \frac{1}{2}$ )
	$8j_2$ (1)	( $\zeta$ ,0.333, $\frac{3}{2}\zeta + \eta + \frac{1}{2}$ )
O1	$4i_1$ ( $m$ )	( $\zeta$ ,0, $\frac{3}{2}\zeta + \eta$ )
	$8j_1$ (1)	( $\zeta$ ,0.333, $\frac{3}{2}\zeta + \eta$ )
	$4i_2$ ( $m$ )	( $\zeta$ ,0, $\frac{3}{2}\zeta + \eta + \frac{1}{2}$ )
	$8j_2$ (1)	( $\zeta$ ,0.333, $\frac{3}{2}\zeta + \eta + \frac{1}{2}$ )
O2	$4i_1$ ( $m$ )	( $\zeta$ ,0, $\frac{3}{2}\zeta + \eta$ )
	$8j_1$ (1)	( $\zeta$ ,0.333, $\frac{3}{2}\zeta + \eta$ )
	$4i_2$ ( $m$ )	( $\zeta$ ,0, $\frac{3}{2}\zeta + \eta + \frac{1}{2}$ )
	$8j_2$ (1)	( $\zeta$ ,0.333, $\frac{3}{2}\zeta + \eta + \frac{1}{2}$ )

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- <sup>37</sup>The peak area is calculated by fitting the peak in a certain range with a straight baseline. In this way, the background contribution can be excluded, only the sharpness of the peak is retained.
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