Lattice dynamical probe of charge order and antipolar bilayer stacking in LuFe$_2$O$_4$

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We investigated the infrared response of LuFe$_2$O$_4$ 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$_2$ 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$_2$O$_4$ is often cited as the prototypical electronically driven multiferroic. Notable aspects include high ordering temperatures, large order parameters, orbital induced magnetic anisotropy, and facile dielectric tunability in magnetic and electric fields. 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.

LuFe$_2$O$_4$ crystallizes in a rhombohedral ($R\bar{3}m$) structure with alternating Fe-containing double layers (often called Fe$_2$O$_2$ or W layers) and LuO$_2$ 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$^{2+}$/Fe$^{3+}$ charge ordering (CO) appears below 300 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 ($T_{LT}$). Local polarization emanates from the charge-order-induced charge imbalance in the W layer. Order-by-fluctuation and electron-phonon coupling models have both been put forward as mechanisms for the development of the charge-ordered superstructure. Since both charge order and magnetism originate from Fe site ordering, magnetoelastic coupling is strong.

To elucidate charge and bonding in a model charge-ordered multiferroic, we investigated the lattice dynamics of LuFe$_2$O$_4$. What differentiates LuFe$_2$O$_4$ from other coupled materials such as $\alpha'$-NaV$_2$O$_5$, CuFeO$_4$, TmSe, and many manganites and organic molecular solids is the combined presence of fluctuation, charge order/disorder, and frustration. 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$_2$O$_4$. This interaction is best exemplified by Lu$_2$O$_2$ mode splitting below $T_{CO}$ which confirms antipolar bilayer stacking (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$_2$ 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$_2$O$_4$ single crystals were grown by floating-zone techniques. Near-normal reflectance was measured on the (001)$_h$ plane employing a Bruker 113v Fourier transform infrared spectrometer, covering the frequency range from 30–5000 cm$^{-1}$ (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. Complementary transmittance experiments (77–300 K) on powder samples embedded in a paraffin matrix allowed us to calculate absorption, $\alpha(\omega)$, directly. Standard peak-fitting techniques were employed as appropriate. 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. The model is proven to adequately describe the lattice dynamics of ionic materials, metal oxides, in particular. 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$_2$O$_4$ is usually described in a hexagonal setting with the...
three twins of single-crystal x-ray diffraction are indeed well described by CO triples the monoclinic cell along would no longer match. Nevertheless, the observation of possible short of cleaving the crystal because the lattices CO has space group C\(_3\)-centered monoclinic cells containing only one 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° 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., (11\(\frac{1}{2}\))\(_h\) becomes in the appropriate monoclinic cell (0\(\frac{1}{2}\)\(_m\)), i.e., the CO triples the monoclinic cell along b and doubles it along c. 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 Å, b =10.32 Å, c=17.31 Å, \(\beta=103.2^\circ\)) with C2\(/m\) symmetry. 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

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 (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° 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.

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\[ R^3m, \text{No. 166} \]

\[ C2/m, \text{No. 12} \]

Bragg peak splitting below \(T_{LT}=175\) 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 3\(/m\) (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 Fe\(^{2+}\) and Fe\(^{3+}\) minorities, with mirror symmetry, and Fe\(^{2+}\)/Fe\(^{3+}\) majorities at general positions. For the ferroelectric CO, suggested 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. Assuming every Fe has static charge, the high-temperature phase has 12 modes. 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\(^{16}\) but different from those of Vitucci et al.\(^{10}\) The displacement patterns of the in-plane (\(E_u\)) symmetry-infrared-active modes are shown in Fig. 2(a). Because the LuO\(_2\) and FeO\(_2\) (W) layers are connected in a perpendicular fashion, the in-plane LuO\(_2\) and FeO\(_2\) modes are nearly decoupled. The other mode corresponds to relative motion between LuO\(_2\) and FeO\(_2\) layers.\(^{16}\) 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.\(^{30}\) Clearly, many modes are expected, different from the results of Vitucci et al.\(^{10}\)

B. Vibrational properties of LuFe\(_2\)O\(_4\)

1. Vibrational spectra and high symmetry mode assignment

Figure 3 displays the measured reflectance and imaginary part of the dielectric function of LuFe\(_2\)O\(_4\), \(\varepsilon(\omega)\) and \(\varepsilon'(\omega)\), at three characteristic temperatures.\(^{22}\) Because our measurements were carried out on the (001)\(_h\) crystal face, only in-plane mode contributions are probed. As discussed above,
group theory predicts three well-defined spectral features with $E_u$ symmetry corresponding to (i) relative in-plane shearing motion between the LuO$_2$ and Fe$_2$O$_2$ layers, (ii) in-plane motion within the LuO$_2$ layer, and (iii) in-plane motion within the Fe$_2$O$_2$ layer [Table I, Fig. 2(a)]. At 500 K, the experimental $e_2(\omega)$ spectrum does indeed contain three features. These include a weak low-frequency peak at $\sim 70$ cm$^{-1}$, a sharp peak near 320 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-LuO$_2$/Fe$_2$O$_2$ layer motion. Assignment of the anticipated intra-LuO$_2$ and intra-Fe$_2$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 LuFe$_2$O$_4$ ($10^6$–$10^7$ Hz), spectral features related to the Fe$_2$O$_2$ layers should reflect charge fluctuations. The LuO$_2$-related feature, by contrast, should be much less sensitive to fluctuations. Thus, one expects a well-defined LuO$_2$ layer mode and a broad feature emanating from FeO layer motion. We therefore assign the 320 cm$^{-1}$ peak to in-plane motion of the LuO$_2$ layer. Assignment of intra-Fe$_2$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. Lu-Fe, LuO$_2$, and Fe$_2$O$_2$ blocks are predicted at 68, 320, and 520 cm$^{-1}$ in reasonable agreement with the values obtained by Harris and Yildirim (92, 332, and 474 cm$^{-1}$). This relative ordering of the intra-LuO$_2$ vs intra-Fe$_2$O$_2$ layer modes is in line with mass arguments.

In order to precisely locate the intra-Fe$_2$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 Fe$_2$O$_2$ layer. Both infrared- and Raman-
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 FeO₂ 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 Fe₂O₂ zone-folding modes, FeO₂ in-plane modes, and LuO₂ zone-folding modes, respectively. The directional characteristics are in line with these assignments. Table II summarizes our results.

2. LuO₂ in-plane fundamental modes and antipolar bilayer stacking in LuFe₂O₄

Figure 4(a) displays a closeup view of the group 4 doublet in ε₂(ω). These features are assigned as LuO₂ 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 cm⁻¹ component is small above T_{CO}, increases with decreasing temperature below T_{CO}, reaches a maximum at T_{LT}, and saturates at low temperature. In contrast, the intensity of the 326 cm⁻¹ component reaches a maximum at T_{CO} and drops with decreasing temperature before saturating at low temperature.

Three different scenarios immediately arise that can account for the observed doublet structure. They include: (i) in-plane anisotropy effects on the LuO₂ 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 LuO₂ 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 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. 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 LuO₂ layers in the antipolar cell generate two kinds of modes by superposition. In the high-temperature phase, the Fe₂O₂ layers do not have electric dipoles, so the two LuO₂ 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_{CO} that steals oscillator strength from the original infrared-active band. At low temperature, the two LuO₂ layers are inequivalent. One type of LuO₂ layer is sandwiched between charge-rich FeO slabs, whereas the other type is sandwiched between charge-poor FeO layers. When charge order is strong enough, the two types of modes correspond to intra-LuO₂ motion of the two distinct LuO₂ 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 LuO₂ layer modes in prox-

![FIG. 4. (Color online) (a) Closeup view of ε₂(ω) showing the in-plane LuO₂ 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.](Image 349x184 to 424x270)
sensitivity to charge-rich/poor iron oxide layers should be similar at low temperature.

Comparing the temperature dependence of the 308 and 326 cm\(^{-1}\) components with the above predictions, we can assign the microscopic nature of each peak. The intensity of the 308 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 LuO\(_2\) sandwiched between charge-poor FeO layers at low temperature. The 326 cm\(^{-1}\) component, on the other hand, behaves in the opposite way, perfectly consistent with the other mode, deriving mainly from LuO\(_2\) sandwiched between charge-rich 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.\(^{34}\) The strong coupling between the charge order and the LuO\(_2\) vibrational modes makes the latter a unique probe of charge order.

Importantly, the doublet character of the LuO\(_2\) layer mode, its temperature dependence, and our assignment in terms of proximity to charge-rich and charge-poor FeO layers is in line with expectations for an antipolar ground state in LuFe\(_2\)O\(_4\).\(^{8}\) It is inconsistent with ferroelectric ordering of the W layers.\(^{35}\) The mode behavior also rules out any other similar kind of interlayer charge ordering. For instance, the ferrielectric arrangement proposed by Xiang et al.\(^{31}\) would produce three unique components to the LuO\(_2\) intralayer vibrational pattern rather than the two found in experiment. In addition, the LuO\(_2\) features are in-plane polarized, as shown by a comparison between single crystal and powder sample spectra (inset, Fig. 3).\(^{33}\) Taken together, these findings suggest that antipolar ordering of the Fe\(_2\)O\(_2\) bilayers is the most likely arrangement, consistent with the observed temperature-dependent vibrational spectra.\(^{36}\)

3. LuO\(_2\) zone-folding modes couple strongly to the charge order, magnetism, and structural distortion

Figure 5(a) displays a closeup view of \(v_{z2}(\omega)\) in the regime corresponding to LuO\(_2\) zone-folding modes of LuFe\(_2\)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).\(^{37}\) 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 LuO\(_2\) zone-folding modes suggested from calculation. Panel (c) shows a LuO\(_2\) layer twisting mode and panel (d) shows a combined LuO\(_2\)+FeO\(_2\) 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 LuO\(_2\) zone-folding modes. Below \(T_{\text{CO}}\), charge-order-induced symmetry 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.\(^{8,9}\) Further, like the 1 THz soft mode observed by Li et al.,\(^{9}\) LuO\(_2\) zone-folding modes are of correct symmetry to contribute to the small polarization and dielectric changes at 240 and 175 K.\(^{25}\) Below \(T_{LT}\), peak area increases on cooling, consistent with enhanced charge order and structural distortion.\(^{8,9,12}\)

4. Probing intralayer charge order: The Fe\(_2\)O\(_2\) fundamental and zone-folding modes

Figure 6(a) displays a closeup view of \(v_{z2}(\omega)\) in the group 2 spectral regime. This structure is assigned as Fe\(_2\)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 Fe\(_2\)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 Fe\(_2\)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\(^{38}\) is \(q_{\text{eff}}=1.5e^-\) at 10 K, less than the nominal Fe center valence in this material. This result implies that LuFe\(_2\)O\(_4\) is less ionic than simple valence counting schemes might predict, different than the conclusion of Mulders et al.,\(^{14}\) where a 4 eV chemical shift of the Fe \(K\) edge indicates fully ionic valence states.
Yildirim predicted that a low-frequency Raman-active folded modes of LuFe$_2$O$_4$ before, these data were determined from oscillator fits. Calculated displacement patterns of Fe$_2$O$_2$ in-plane modes in the frequencies drop more quickly, an indication of mode instability to sample quality issues. Recently, Harris and XU et al. quantified this effect by fitting the spectral features with more than one oscillator. The Fe$_2$O$_2$ twisting pattern shown in Fig. 6 is an example of the type of motion involved. The Fe$_2$O$_2$ zone-folding modes is unique in that is not as obvious in other modes. At low-temperature the spectrum freezes at $T \approx 50$ K. The lack of change in the dynamical response is shown most clearly in the Fe$_2$O$_2$ fundamental and the 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. As discussed above, the lattice vibrations of LuFe$_2$O$_4$ are very sensitive to the series of temperature-driven transitions: 320 K ($T_{CO}$), 240 K ($T_N$), and 175 K ($T_{1/2}$). 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 Fe$_2$O$_2$ fundamental and the 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. Clearly, more investigation is needed to understand the nature of this regime in LuFe$_2$O$_4$.

**IV. SUMMARY**

We investigated the vibrational response of LuFe$_2$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 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 Fe$_2$O$_2$ bilayers rather than the previously supposed ferroelectric alignment. Analysis of LuO$_2$ zone-folding and Fe$_2$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.

**ACKNOWLEDGMENTS**

This work was supported by the Division of Materials Science and Engineering, Basic Energy Sciences, U.S. Department of Energy (UT and ORNL), the State of Texas through the Texas Center for Superconductivity (UH), and the Initiative and Networking Fund of the Helmholtz Association of German Research Centers through the Helmholtz-University Young Investigator Group Complex Ordering Phenomena in Multifunctional Oxides (Jülich).

**APPENDIX: WYCKOFF SITES**

For Wyckoff positions, see Table III.
LATTICE DYNAMICAL PROBE OF CHARGE ORDER AND...

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TABLE III. Splitting of Wyckoff positions due to charge order. For domain A with propagation vector \((\frac{1^{1^{1}}}{3^{1^{1}}})_b\), the lattice parameters transform as \(a_i = a_0 + b_i\), \(b_i = 3(a_0 + b_i)\), and \(c_i = \frac{1}{2}(-a_0 + b_i + c_i)\). 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.

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CO structure, domain A \((C2/m)\)

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\*Present address: Oak Ridge National Laboratory, Oak Ridge, TN.


19We describe the magnetic arrangement as “antipolar” rather than “antiferroelectric” (which is sometimes used in the literature and may be more widely known) in order to clearly indicate the lack of electric field switchability in LuFe2O4.
Our measurements were carried out at a 6° angle of incidence with respect to an aluminum mirror. The resulting reflectance was corrected for the finite reflectance of aluminum.

This function is related to optical conductivity as $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)=\varepsilon_1(\omega)+\frac{\omega}{\sigma_0}$.

See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.82.014304 for several example fits as shown in the electronic auxiliary material.

We use the commensurate approximation as in Ref. 8.

All the following discussion will be in the context of antipolar CO.

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.

Our crystals were grown in CO/CO$_2$ flow rather than Ar, a procedure that gives us excellent control over oxygen stoichiometry. Considering the different synthetic procedures, it is very likely that our samples and Vitucci et al.’s are not equivalent. Moreover, our crystals display typical quality indicators such as magnetic ordering at $T_N=240$ K (rather than 230 K) and a clear $T_LT$ transition that can be deduced even in the infrared spectra. The low-frequency reflectance is also relatively flat, another indication of nonleaky samples.

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