Charge order, dynamics, and magneto-structural transition in multiferroic LuFe$_2$O$_4$

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We investigated the series of temperature and field-driven transitions in LuFe$_2$O$_4$ by optical and Mössbauer spectroscopies, magnetization, and x-ray scattering in order to understand the interplay between charge, structure, and magnetism in this multiferroic material. We demonstrate that charge fluctuation has an onset well below the charge ordering transition, supporting the “order by fluctuation” mechanism for the development of charge order superstructure. Bragg splitting and large magneto optical contrast suggest a low temperature monoclinic distortion that can be driven by both temperature and magnetic field.

Complex oxides take advantage of the unique and flexible properties of transition metal centers to govern bonding and local structure. Further, the delicate interplay between charge, structure, and magnetism yields important consequences for functionality and cross-coupling. Iron-based materials such as multiferroic BiFeO$_3$ and LuFe$_2$O$_4$ [2, 3], bistable photomagnetic systems such as Prussian blues and related derivatives [3], dilute magnetic semiconductors [8], and the new family LaFeAsO$_1-x$F$_x$ of superconductors [3] have attracted recent attention. In this Letter, we focus on LuFe$_2$O$_4$, a frustrated system with a series of phase transitions that give rise to electronically-driven multiferroicity [2].

LuFe$_2$O$_4$ has a layered structure with Fe-containing double layers of triangular connectivity. Three-dimensional Fe$^{2+}$/Fe$^{3+}$ charge order (CO) occurs below 320 K ($T_N$). This is followed by ferrimagnetic order below 240 K ($T_N$). An additional low temperature magnetic phase transition has recently been reported at 175 K ($T_{LT}$). The CO has a so-called $\sqrt{3}\times\sqrt{3}$ superstructure [2, 8]. Because of the mixed valent iron centers and frustrated triangular lattice, the Fe$^{2+}$ and Fe$^{3+}$ populations are different within the double layer, an effect that renders an intrinsic polarization [2, 8]. The charge ordering mechanism is thus central to understanding the unusual physical properties of this multiferroic.

To elucidate the charge excitations and understand how they correlate with structure and magnetism, we measured the optical and Mössbauer spectra, magnetization, and x-ray scattering of LuFe$_2$O$_4$. We compare our comprehensive results to recent electronic structure calculations [8] and to spectral data on classical magnetite [10]. We demonstrate that strong Fe$^{2+}$→Fe$^{3+}$ charge fluctuation persists even in charge ordered states characterized by superstructure reflections, and it persists down to $T_{LT}$ below which Bragg splitting indicates that strong monoclinic distortions occur. These observations are consistent with the “order by fluctuation” mechanism [11], in which case $\sqrt{3}\times\sqrt{3}$ CO is preferable for entropy reasons and stabilized by the charge fluctuation in this geometrically frustrated system. As in magnetite, we analyze the results in terms of a polaron picture, extracting a large effective mass for the charge carriers. On the other hand, Fe$^{2+}$ on-site excitations are sensitive to the magnetic transition at $T_{LT}$ and display a sizable magneto-optical effect. Combining our spectral, magnetic, and structural data, we generate an H-T phase diagram and show that the transition at $T_{LT}$ can also be driven by a magnetic field. These results demonstrate the important interplay between charge, structure, and magnetism.

All experiments were conducted on floating-zone-grown LuFe$_2$O$_4$ single crystals from the same batch as those used in Refs. [3, 4]. Near-normal reflectance measurements were carried out on $ab$ plane samples employing a series of spectrometers covering a wide range of energy (30 meV - 6.5 eV), temperature (4 - 540 K) and magnetic field (0 - 33 T, $H \parallel c$) [12]. Optical conductivity $\sigma_1(E)$ was calculated by a Kramers-Kronig analysis [13]. Variable temperature transmittance was done on a 25 μm $ab$ plane crystal, allowing direct calculation of absorption $\alpha(E)$. The Fe-57 Mössbauer spectra of 35 mg/cm$^2$ of crushed crystals were recorded between 260 and 400 K on a constant acceleration spectrometer with a Rh matrix Co-57 source and calibrated at 295 K with α-Fe powder. The reported isomer shifts are relative to α-Fe at 295 K. X-ray scattering was performed at undulator beamline 4-ID-D at the Advanced Photon Source with 36 keV photons employing a cryostat with a split coil vertical field magnet up to 4 T. The sample was mounted with an angle of 45° between c and the field as a compromise.
between cryomagnet angular restrictions and accessibility of important regions of reciprocal space. Previous magnetization work shows that LuFe₂O₄ is rather insensitive to fields parallel to their binding. Consequently the dominate effect of the field is due to the component c.

The Mössbauer spectra, (Fig. 1(a)) were fit with a Blume-Tjon model for Fe²⁺ and Fe³⁺ relaxation, similar to [14]. Individual fits of the spectra reveal (i) two Arrhenius processes as indicated by the temperature dependence of the hopping frequency and break at T_CO (Fig. 1(b)), (ii) the difference between Fe²⁺ and Fe³⁺ isomer shifts, δ, is constant below T_CO and cannot be resolved above, and (iii) a constant linewidth and a gradual ∼ √T_CO − T broadening above and below T_CO, respectively. In order to overcome correlation effects (see below) and to reduce the large number of fit parameters, a simultaneous parametric fit of all spectra was then carried out with the constraints (i), (ii) constant δ for all T, and (iii). The fits in Fig. 1(a) are the result of this simultaneous fit. The obtained spectral parameters and relaxation frequencies (Fig. 1(b,c)) are in agreement with [14], with the exception of the sharper T dependence of these parameters around T_CO, which we attribute to the preparation of the sample as single crystal. Above T_CO, we obtained an activation energy of 0.16(2) eV. This is somewhat smaller than the 0.26 eV energy obtained by electrical conductivity measurements [14]. Below T_CO, we find the activation energy to be 0.36(9) eV. The large error bar is due to (i) small hopping frequencies, close to the detection limit, and (ii) correlations between the hopping frequency and linewidth. The Fe²⁺ line around 1.4 mm/s is increasingly broadened below T_CO due to microscropic lattice distortions in the charge ordered state (Fig. 1(a)). The fit at the bottom of Fig. 1(a) is the best fit with a constraint of 33% of Fe²⁺ transfer excitations. At slightly higher energy follow Fe³⁺ → Fe³⁺ charge transfers. Inset: √σ vs E with linear fit (dotted line). (c) n_{p,0}(T) calculated by sum rules for Fe²⁺ → Fe³⁺ charge transfer and overlapping majority channel O → Fe charge transfer and overlapping majority channel O → Lu s state excitations are observed at higher energy (≥ 3 eV). It is difficult to resolve all the excitations because they are broad and overlap significantly. Nevertheless, the 1.1 eV peak in the near infrared range (Fig. 2(a)) can be associated with Fe²⁺ → Fe³⁺ charge transfer. The optical

![FIG. 1: (Color online) Mössbauer spectra of LuFe₂O₄ and fits, see text; bottom: alternative best fit with a constraint of 33% of hopping electrons (b) Arrhenius plot of the hopping frequency. Open symbols correspond to the spectra in (a), bars to hopping frequencies in [14]. (c) Mössbauer spectral parameters, from top to bottom: hopping frequency, quadrupole splitting, isomer shift, and full linewidth at half maximum.](image1)

![FIG. 2: (Color online) Optical properties of LuFe₂O₄. (a) σ₁ vs energy E at 540 and 60 K calculated from reflectance, showing the charge transfer edge starting from ∼ 0.5 eV. Inset: √αE with linear fit (dotted line). (c) n_{p,0}(T) calculated by sum rules for Fe²⁺ → Fe³⁺ charge transfer (c) and Fe²⁺ on-site (d) excitations. (e) E_{p}(T) calculated from an absorption edge fit assuming an indirect gap.](image2)
gap $E_g$ is determined by the absorption edge of this band. A close-up view of the tail is shown in Fig. 2(b). The linear fit of $\sqrt{\alpha E}$ vs. $E$ above 0.5 eV indicates that the gap is indirect [13], in agreement with Ref. [17]. Due to the 0.3 eV feature (possibly a spin-forbidden Fe$^{2+}$ on-site excitation [18]), the typical “double slope character” is not observed and the associated coupling phonon energy for the indirect gap excitation process cannot be determined. The optical gap is sensitive to $T_{CO}$ (Fig. 2(c)), although LuFe$_2$O$_4$ is a semiconductor (non-metallic) over the full temperature range of our investigation.

To quantify the strength of the various excitations, we calculated the effective number of electrons $n_{eff}$ from the optical conductivity $\sigma_1(\omega)$ using the partial sum rule:

$$n_{eff} = \frac{m^*}{m} N \approx \int_{\omega_1}^{\omega_2} \sigma_1(\omega)/\epsilon_0 \, d\omega \times \frac{\hbar^2}{m \epsilon_0 \omega^2},$$

where $\omega_p = \sqrt{\frac{e^2}{\epsilon_0 m \epsilon_0}}$ is the plasma frequency, $e$ and $m$ are the charge and mass of an electron, $\epsilon_0$ is the vacuum dielectric constant, $V_0$ is the unit cell volume, and $\omega_1$ and $\omega_2$ are the frequency limits of integration. The absolute level of $n_{eff}$ depends on the integration range, but the temperature trends are not sensitive to this choice. For instance, to investigate changes in the Fe charge transfer band, we evaluated the partial sum rule from 0.6 - 1 eV, as indicated in Fig. 2(a). In this case, $n_{eff}$ represents effective number of electrons that are able to overcome the energy barrier to hop from Fe$^{2+}$ to Fe$^{3+}$ sites. This number increases over a broad temperature range through $T_{CO}$, as shown in Fig. 2(c).

In optical processes, electrons hopping from Fe$^{2+}$ to Fe$^{3+}$ are better described as small polarons, which correspond to combined electronic and vibrational excitations that arise when the lattice is too slow to relax [19]. Important signatures include (i) a large effective mass and (ii) optical excitation energies that are much larger than the low frequency activation energy. The effective mass of the charge carriers can be estimated using $n_{eff} = \frac{m^*}{m} N$, where $m^*$ is the effective mass and $N = 3$ (the number of Fe$^{2+}$ sites per unit cell). Considering that the 0.6 - 1 eV integration is only over half of the excitation, we get $\frac{m^*}{m} \approx 40$, which is large, but typical for polarons (e.g. $\frac{m^*}{m} \approx 100$ in Fe$_5$O$_4$ [10]). With the polaron picture and the simple model of an electron jumping between two sites [20], we can estimate the 60 K activation energy from the optical activation $h\omega_0$ as $E_a = h\omega_0/4 = 1.1(1) eV/4 = 0.28(3) eV$, in excellent agreement with value reported in the study of low frequency dielectric dispersion and DC electric conductivity ranging from 0.25 - 0.29 eV [2, 14] and compatible with that for spontaneous electron hopping obtained between 260 and 320 K from Mössbauer spectroscopy.

The $T$ dependence of $n_{eff}$ corresponding to Fe$^{2+}$ to Fe$^{3+}$ charge transfer confirms change fluctuation below $T_{CO}$ (Fig. 2(c)). Here, $n_{eff}$ begins to increase well below $T_{CO}$ (evident also in electron hopping trends via Mössbauer spectroscopy) and continues to change above this temperature. This result is consistent with the presence of 3D anti-phase domain boundary modes [21]. We attribute the experimental observation of significant charge fluctuations through $T_{CO}$ (even where diffraction shows that it is ordered) to relevance of the “order by fluctuation” mechanism in which fluctuations are needed to stabilize the $\sqrt{3} \times \sqrt{3}$ CO in the frustrated system [11]. Interestingly, the charge fluctuation onset is at $T_{LT}$ (Fig. 2(c), (e)), suggesting that the low temperature phase transition quenches the charge fluctuation. Similar to the Verwey transition in Fe$_3$O$_4$ [22], the $T$ dependence of $n_{eff}$ shows an anomaly near $T_{CO}$ consistent with the lowering of the activation energy above $T_{CO}$ [14]. However, the jump occurs above $T_{CO}$.

The strength of the Fe$^{2+}$ on-site crystal field excitation is quantified by the partial sum rule in energy range 2 - 3 eV, in accord with first principle calculations [7]. Although the data are more scattered than that discussed above because of the background from nearby excitations, two finding are immediately clear. First, the Fe$^{2+}$ on-site excitation is rather insensitive to charge and spin ordering transitions. Second, it displays a clear anomaly at $T_{LT}$ (Fig. 2(c)), which recent magnetization and neutron diffraction studies [3] identified as an additional first-order transition. Further magnetization measurements in $H||c$ up to 7 T indicate that the transition temperature is
strongly suppressed by $H$ (Fig. 3). Hysteresis of $H_{LT}(T)$ widens upon cooling, and below 50 K the high-$H$, high-$T$ phase remains frozen in even after decreasing $H$ to 0, reminiscent of kinetic arrest of first-order transitions as studied, e.g., in doped CeFe$_2$ [23].

To check for possible structural components of the transition, we closely examined structural Bragg reflections, such as (336). CO below 320 K [8] lowers the crystal symmetry to monoclinic, which could lead to a monoclinic distortion ($\beta \neq 90^\circ$), with a splitting in 2$\theta$ values of such reflections, with domain formation clearly observable also in single crystals [23]. Such a splitting could not be resolved in between 200 and 300 K (in any magnetic field), indicating that any monoclinic distortion is small. Splitting becomes evident upon cooling below $T_{LT}$ (lower right inset in Fig. 3), consistent with a significant ($\beta \approx 90.5^\circ$) monoclinic distortion [23]. Application of a magnetic field removes the splitting (upper right inset) as soon as the field component $\parallel c$ reaches $H_{LT}$ as determined by magnetization, and subsequent reduction causes a reappearance of the splitting at a field value again consistent with magnetization. These diffraction data thus suggest that $T_{LT}$ and $H_{LT}(T)$ corresponds to a strongly hysteretic magneto-structural transition. We propose that the monoclinic distortion removes geometric frustration rendering charge fluctuation unnecessary. This scenario is in line with the observed fluctuation onset at $T_{LT}$ and the “order by fluctuation” mechanism.

The anomaly at $T_{LT}$ in the Fe$^{2+}$ on-site excitations can also be explained within a structural distortion scenario. Consider an Fe center coordinated by five O ligands in a trigonal bipyramidal geometry ($D_{3d}$ symmetry). A crystal field splits the Fe 3$d$ levels into three groups [11]. The monoclinic distortion in the low $T$ phase splits these levels further, shifting the on-site excitation energies and causing the discontinuity in $n_{eff}$ (Fig. 3(d)).

The upper-left inset in Fig. 3 displays the 4.2 K reflectance of LuFe$_2$O$_4$ at 550 nm as a function of magnetic field ($H \parallel c$). At this energy, the spectral response is probing field-induced changes in Fe$^{2+}$ on-site excitations. Strikingly, the reflectance increases by $\sim 40\%$ for $H \geq 14$ T. This is consistent with a straight-forward extrapolation of $H_{LT}$ from the magnetization data (dashed line in Fig. 3). That the reflectance maintains this high value even after subsequent complete removal of $H$ is again consistent with the magnetization data (see above). Thus, at low $T$ a rather large field is required to switch the crystal structure. Since the structural distortion is most likely induced by the CO, which lowers the crystal symmetry [8], the strong $H$-dependence of this transition is a further example of the strong coupling between spin, structural, and charge degrees of freedom in LuFe$_2$O$_4$.

In summary, optical and Mössbauer spectroscopies demonstrate that charge fluctuation in LuFe$_2$O$_4$ has an onset at $T_{LT}$, well below $T_{CO}$, supporting the “order by fluctuation” mechanism for the $\sqrt{3} \times \sqrt{3}$ CO superstructure. Fe$^{2+}$ on-site crystal field excitations are sensitive to the magneto-structural transition at $T_{LT}$, which can be driven by both temperature and magnetic field (requiring 14 T at 4 K). Combining spectral, magnetic, and structural data, we generate a comprehensive $H$-$T$ phase diagram. The large temperature range of the observed dynamical effects is a consequence of the strong coupling between charge, structure, and magnetism.

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