PHYSICAL REVIEW B **81**, 144121 (2010)

Robust charge and magnetic orders under electric field and current in multiferroic $LuFe_2O_4$

Jinsheng Wen,[1,2] Guangyong Xu,[1] Genda Gu,[1] and S. M. Shapiro[1]
[1]*Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA*
[2]*Department of Materials Science and Engineering, Stony Brook University, Stony Brook, New York 11794, USA*

(Received 20 January 2010; revised manuscript received 1 April 2010; published 20 April 2010)

We performed elastic neutron-scattering measurements on the charge and magnetically ordered multiferroic material $LuFe_2O_4$. An external electric field along the [001] direction with strength up to 20 kV/cm applied at low temperature (~100 K) does not affect either the charge or magnetic structure. At higher temperatures (~360 K), before the transition to three-dimensional charge-ordered state, the resistivity of the sample is low, and an electric current was applied instead. A reduction in the charge and magnetic peak intensities occurs when the sample is cooled under a constant electric current. However, after calibrating the real sample temperature using its own resistance-temperature curve, we show that the actual sample temperature is higher than the thermometer readings, and the "intensity reduction" is entirely due to internal sample heating by the applied current. Our results suggest that the charge and magnetic orders in $LuFe_2O_4$ are unaffected by the application of external electric field and current, and previously observed electric-field and current effects can be naturally explained by internal sample heating.

DOI: 10.1103/PhysRevB.81.144121 PACS number(s): 77.84.−s, 75.80.+q, 61.05.F−

$LuFe_2O_4$ is a new multiferroic material. Here the bulk ferroelectric polarization is not due to cation displacements as in conventional ferroelectrics but instead arises from the three-dimensional (3D) charge-valence order of Fe^{2+} and Fe^{3+} ions occurring at ~340 K.[1] The magnetic order starts at lower temperature (~240 K) in the charge-ordered ferroelectric phase.[2] Recent reports of strong couplings between the two orders,[1,3] as well as large room-temperature magnetoelectric response in this material,[2,4] make $LuFe_2O_4$ a promising candidate for practical applications.

In addition to the magnetoelectric response, tremendous interest has been focused on studying the electric-field response of the magnetic structures in multiferroic systems. Nevertheless, there have been only a few observations of such effects[5–10] in known multiferroic systems, and all of them can be attributed to electric field realigning ferroelectric domains and therefore causing a macroscopic magnetic response. In $LuFe_2O_4$, the ferroelectric polarization is charge-valence driven, and the charge-valence order also couples strongly to the magnetic order. If the charge order can be affected or broken, it is then possible to affect the microscopic magnetic structures by an external electric field or current. Indeed, there have been previous reports on nonlinear current-voltage behaviors, and eventually an electric-field "breakdown" of the charge order in $LuFe_2O_4$.[11,12] There have also been claims of electrical control of the magnetic response in the same material.[13] These observations, if confirmed and fully understood, would be extremely interesting and important for achieving mutual control of electric and magnetic degrees of freedoms in multiferroic systems.

We thus performed elastic neutron-scattering measurements on single crystals of $LuFe_2O_4$, studying the response of the charge- and magnetic-order Bragg peaks under external electric field and current. No electric-field effect has been observed at low temperature ~100 K for a field strength up to 20 kV/cm. Near room temperature, an electric current effect on the ordering is observed, and we show that it is due to internal heating of the sample by the current flowing through the sample. We conclude that the charge and magnetic orders are robust and not affected by the electric field and current.

Single crystals $LuFe_2O_4$ were grown using floating-zone technique.[14] Typical crystal sizes are $\sim 10 \times 5 \times 2$ mm^3. Our neutron-scattering measurements were performed on BT9 triple-axis spectrometer at the NIST Center for Neutron Research. An incident neutron energy of 14.7 meV was selected by a pyrographic (PG002) monochromator, with beam collimations of 40′-40′-40′-80′, and another PG002 crystal was used as the analyzer. PG filters were used before the sample to reduce background from higher-order neutrons. A sample of 0.9 g was loaded in a closed-cycle refrigerator, where the thermometer is attached to the mounting base, about 3 cm away from the sample. $LuFe_2O_4$ has a hexagonal structure with three iron double layers in each unit cell. The ferroelectric polarization is directly due to the imbalance of iron valences in each double layer, and the net (induced) polarization appears along the [001] direction, perpendicular to the hexagonal plane and the double layers. The two 10×5 mm^2 (001) surfaces were painted with silver paint so that electric field and current can be applied along the [001] direction (2 mm thick) for our measurements. The single-crystal sample was oriented so that the horizontal diffraction plane is the (*HHL*) plane, defined by the vectors [110] and [001]. (See Fig. 1.) The resistance-temperature (*R*-*T*) curve has been measured using Keitheley 2000 multimeter, and the *in situ* resistance during the neutron-scattering measurements was obtained by reading the voltage across the sample while keeping the current constant.

The magnetic Bragg peaks in this compound occur at reciprocal-space positions (1/3, 1/3, *L*) and (2/3, 2/3, *L*) for both half-integer and integer *L* values[15,16] below the magnetic ordering temperature $T_N \sim 240$ K while the charge peaks only appear at half-integer *L* values.[2,3,16–18] (see Fig. 1).

We choose to monitor (2/3, 2/3, 3.5) for the charge order and (1/3, 1/3, 0) for the magnetic order. Representative scans through these two peaks are plotted in Figs. 2(a) and 2(b), respectively. These peak intensities indicate the charge/magnetic order and are plotted vs temperature in Figs. 3(a)

©2010 The American Physical Society

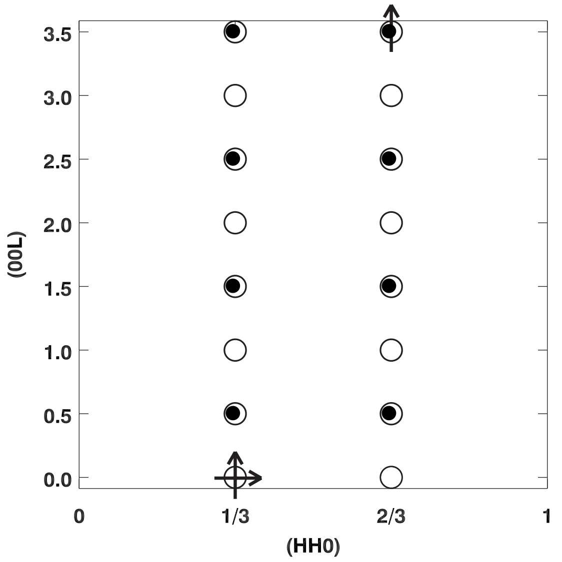

FIG. 1. Schematic of the magnetic- (open circles) and charge-order (filled circles) peaks in reciprocal space. The arrows indicate the scan directions along [110] and [001].

and 3(b). For zero field, the charge order starts as two-dimensional (2D) at around 500 K[17] and becomes 3D around $T_{CO}\sim 340$ K.[2,16] At $T_N\sim 240$ K, the magnetic order occurs, as indicated by the rise of (1/3,1/3,0) intensity shown in Fig. 3(b). Also, a boost to the intensity at (2/3,2/3, 3.5) is observed [see Fig. 3(a)], which is due to the additional scattering intensity at this wave vector coming from magnetic ordering. The intensity at (2/3,2/3,3.5) now (for $T<T_N$) has contributions from both the charge and magnetic orders. With further cooling, the intensity increases until reaching another temperature $T_L\sim 180$ K. Here another phase transition occurs, similar to that observed in Ref. 16. Note that this second phase transition is strongly sample dependent and has been shown to be missing for some samples.[2,17,19] As demonstrated by previous studies, the magnetic properties of $LuFeO_{4+\delta}$ are sensitive to oxygen stoichiometry,[20] and different temperature dependence of intensity below $T_L\sim 180$ K is likely due to different oxygen content in different samples.

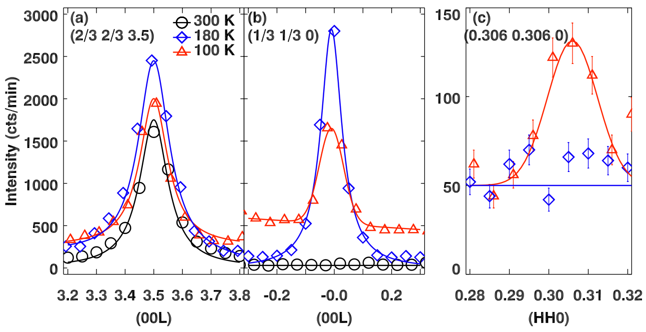

FIG. 2. (Color online) Scans through (a) charge-order peak (2/3, 2/3, 3.5) along [001] direction at different temperatures; (b) magnetic peak (1/3, 1/3, 0) along [001] direction; (c) satellite peak (0.306, 0.306, 0) along [110] direction. Error bars represent square root of the total counts, and those in (a) and (b) are smaller than the symbols. Lines through data are guide to the eyes.

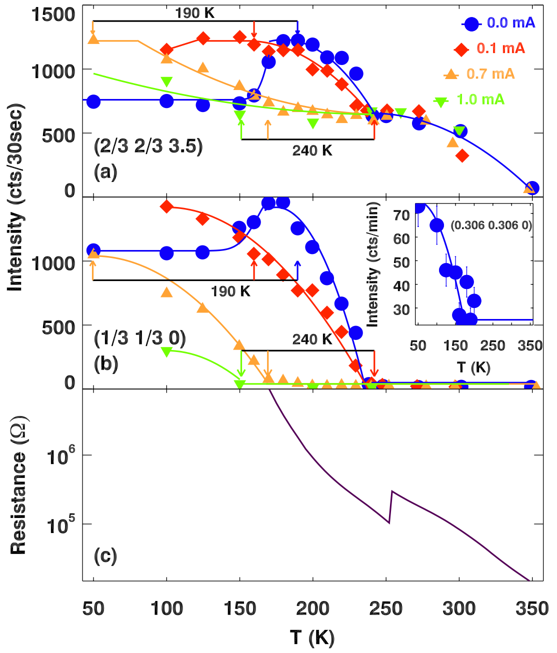

FIG. 3. (Color online) (a) Charge and (b) magnetic peak intensity as a function of thermometer temperature, obtained under cooling with different currents. Inset in (b) shows temperature dependence of the satellite peak (0.306, 0.306, 0) intensity. Error bars represent square root of the total counts and those smaller than the symbols are not shown. Lines through data are guide to the eyes. Arrows indicate the actual temperatures determined by measuring the resistance. (c) *R*-*T* curve measured with nearly zero (~1 μA) current. The resistance below 170 K exceeds the maximum of the multimeter.

The intensities for both peaks drop at T_L but become almost flat below ~150 K [Figs. 3(a) and 3(b)]. This is also demonstrated in Fig. 2, where at 100 K, both the charge and magnetic peak intensities are lower than those at 180 K. Additionally, at 100 K, there is a strong 2D diffuse-type magnetic scattering[16] which shows up as higher "background" in the *L* scans [Fig. 2(b)]. In addition, intensity starts to appear at satellite positions below T_L and in Fig. 2(c), we plot scans through a satellite peak around (0.306, 0.306, 0), whose intensity dependence on the temperature is plotted in the inset of Fig. 3(b).

These results suggest that the low-temperature (magnetic/charge) structures of $LuFe_2O_4$ are quite complicated and sometimes sample dependent. Nevertheless, our goal is to search for possible electric-field effect on the magnetic and charger orders. As suggested by Angst *et al.*, the energy difference between antiferroelectric and ferroelectric charge-order configuration is only ~3%, and it is possible to stabilize the ferroelectric configuration when the system is cooled in an electric field.[3] The low resistivity (~10^3 Ω m at room temperature) makes it very difficult to apply a static electric field and do the field-cooling measurements. Instead, we applied an electric field of 20 kV/cm along the [001] direction at 100 K, and performed scans through (2/3, 2/3, 3.5), (1/3, 1/3, 0), and (0.306, 0.306, 0) peaks. The scan profiles are identical to those shown in Fig. 2, which indicates that there is no observable electric-field effect with fields applied be-

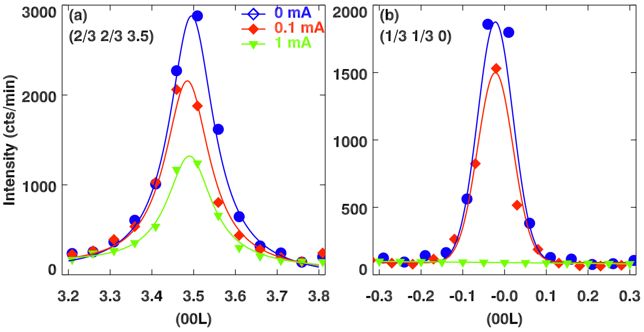

FIG. 4. (Color online) (a) Charge (2/3, 2/3, 3.5) and (b) magnetic (1/3, 1/3, 0) peak measured at 200 K, after cooled with different currents applied at 360 K. Error bars are smaller than the symbols. Lines through data are guide to the eyes.

low T_{CO}. At 100 K, the current is estimated to be on the order of microampere.

To investigate the response of the system to electric currents, we applied different currents at 360 K, cooled the system with the current maintained as constant, and performed scans at different temperatures. Results of the scans through the charge and magnetic peaks at 200 K with different currents applied are shown in Fig. 4. It is clear that for both charge and magnetic peaks, the peak intensities are reduced when cooled under electric current, and the intensity reduction increases with increasing current. The magnetic peak at 200 K is fully suppressed by a 1 mA current. To further examine the current effect, we plotted the charge- and magnetic-order peak intensity as a function of thermometer temperature with different currents in Figs. 3(a) and 3(b).

When the sample was cooled with current, both charge and magnetic peak intensities were reduced. The current effects on the intensity clearly become more pronounced as the current increases. These results correlate with earlier studies on the electric-field and current effects on transport and magnetic properties of $LuFe_2O_4$,[11–13,21] and the current reducing the peak intensity here can be attributed to the current inducing breakdown of the charge order, as suggested in Refs. 11 and 12. However, there are also indications that this may not be as simple. One indication is that with 1 mA current cooling, the temperature reading never went below 100 K. This suggests that there is a significant heating power applied to the sample (by the current applied). Another observation is that if we remove the current at 100 K, the peak intensity does not return to the zero-field-cooling value immediately. Instead, there is a 30–60 s lag for the (charge peak) intensity to fully recover with a current of 1 mA while at the same time, the temperature reading is constant. This time scale is too long for any real charge diffuse process to occur in these materials, and is a strong evidence that internal sample heating is playing a role. Because the thermometer is attached to the base of the sample mounting post, which is about 3 cm away from the sample position, it is plausible that there could be a large temperature gradient between the sample position and the thermometer location.

In order to calibrate the sample temperature, we use the temperature dependence of resistance of the sample along *c* direction as an independent measure as shown in Fig. 3(c). The current used to measure the resistance is small, on the order of 1 μA so that the condition under which the resistance was measured can be taken as zero-current cooling. Under cooling, the resistance increases continuously through T_{CO}, which is consistent with the observation that below T_{CO}, charge order is still short ranged along *c* axis, and disorder is playing an important role in the material's properties.[2] Around 250 K, the resistance drops, which is related to the magnetic phase transition, also suggesting a strong coupling between the magnetic and electrical properties in this material. Below 250 K, the resistance increases monotonically again.

The *R-T* curve provides us a good measure of the instantaneous sample temperature. During the neutron-diffraction measurements, we measured the sample's resistance by reading out the voltage across the sample while maintaining a constant current when cooling. Comparing the measured resistance with the *R-T* curve, we found that the actual sample temperatures under current cooling are higher than those read by the thermometer. The horizontal lines indicate the "real" sample temperature (240 or 190 K) determined by the *R-T* curve, and the arrows indicate the temperatures read by the thermometer. For a sample temperature of 240 K, the thermometer reads 240 K, 170 K, or 150 K with a current of 0.1 mA, 0.7 mA, or 1 mA, respectively. If we correct the temperature scales of the various cooling curves using the real sample temperatures based on resistance readings, there is no field effect on the ordering. This is demonstrated in Figs. 3(a) and 3(b). On each cooling curve (with different current applied), the data points where the real sample temperatures are 240 K (or 190 K) are marked by arrows of different colors, and they indeed have the same magnetic/charge peak intensities independent of cooling conditions. In Fig. 5, we plot the charge and magnetic peak intensity as a function of calibrated temperature for cooling with a 0.7 mA current, and compare them with those under zero-current cooling. It is clear that there is no real effect if we take out the internal heating effect. The current-heating effect is not entirely unexpected since the specific heat of $LuFe_2O_4$ is relatively low, ~ 0.5 J/(Kg) at 300 K.[20] With a small sample (<1 g), the heater with a power on the order of 0.1 W, which corresponds to a current of 1 mA through the sample at 300 K, or 0.4 mA at 200 K, is high enough to effectively heat the sample.

This naturally explains the unusual behaviors in $LuFe_2O_4$ observed by other groups.[11–13] The resistivity is low ($\sim 10^3$ Ω m) in the temperature range where most measurements are carried out so a small voltage is able to drive a large current through the sample and heat the sample significantly. The actual sample temperature in these cases will be higher than the readings from the thermometer. The material's magnetization[13] and transition temperature[11,12] will then appear to be affected by the field. The internal current heating can also explain the observed nonlinear current-voltage behavior.[11,12] In addition, because the resistance decreases with heating—if a constant voltage is applied to the sample, the sample is heated and the resistance lowers, which in turn increases the current further, and puts more thermal power on the sample, which again raises the sample temperature and lowers its resistance. Eventually an avalanche occurs,

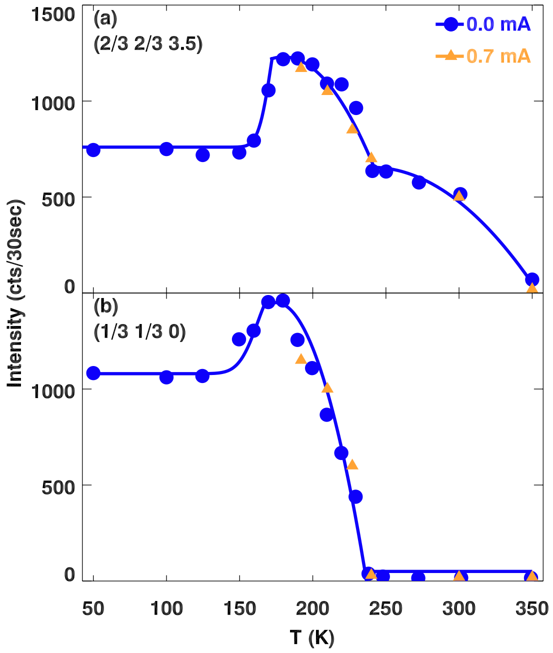

FIG. 5. (Color online) (a) Charge and (b) magnetic peak intensity as a function of calibrated temperature, obtained under cooling with a 0 and 0.7 mA current. Error bars are smaller than the symbols. Lines through data are guide to the eyes.

which was interpreted as the breakdown of the charge order.[11,12]

Here we observed that the charge order in $LuFe_2O_4$ remains intact with electrical inputs—neither high electric fields applied at low temperature nor electric currents applied at high temperature can affect it. However, the charge order seems to be rather sensitive to magnetic field, even when no magnetic order is present.[2] The fact that a charge-ordered system is magnetically sensitive instead of electrically sensitive makes $LuFe_2O_4$ very unusual. In other charge-ordered systems, electric field is able to slide or cause breakdown of the charge order.[22–24] Apparently, from our data, it is not the case for $LuFe_2O_4$. It is likely that in $LuFe_2O_4$, the pinning of the charge order, e.g., by impurities, is stronger than that in other charge-ordered systems, which makes it less electrically sensitive.

In summary, we report that the charge and magnetic orders in $LuFe_2O_4$ are not affected by electric field (up to 20 kV/cm) or current. The observed reduction in charge- and magnetic-order peak intensity is due to resistive heating. Our results also suggest that electric-field and current effects on $LuFe_2O_4$, as well as the nonlinear current-voltage behavior reported elsewhere are results of internal current heating of the sample. This case is very similar to those observed in charge-stripe-ordered cuprates and nickelates,[25–27] where an electric-field effect was observed on the charge order but later entirely attributed to resistive heating effects.[28]

We thank W. Ratcliff and M. Hücker for helpful discussions. Work at Brookhaven National Laboratory is supported by U.S. Department of Energy under Contract No. DE-AC02-98CH20886.

---

[1] N. Ikeda *et al.*, Nature (London) **436**, 1136 (2005).
[2] J. Wen, G. Xu, G. Gu, and S. M. Shapiro, Phys. Rev. B **80**, 020403(R) (2009).
[3] M. Angst *et al.*, Phys. Rev. Lett. **101**, 227601 (2008).
[4] M. A. Subramanian, T. He, J. Chen, N. S. Rogado, T. G. Calvarese, and A. W. Sleight, Adv. Mater. **18**, 1737 (2006).
[5] T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, and M. F. Jörg Ihringer, Nature (London) **430**, 541 (2004).
[6] Y.-H. Chu *et al.*, Nature Mater. **7**, 478 (2008).
[7] T. Zhao *et al.*, Nature Mater. **5**, 823 (2006).
[8] Y. Yamasaki, H. Sagayama, T. Goto, M. Matsuura, K. Hirota, T. Arima, and Y. Tokura, Phys. Rev. Lett. **98**, 147204 (2007).
[9] T. Finger, D. Senff, K. Schmalzl, W. Schmidt, L. P. Regnault, P. Becker, L. Bohat, and M. Braden, J. Phys.: Conf. Ser. **211**, 012001 (2010).
[10] I. Cabrera *et al.*, Phys. Rev. Lett. **103**, 087201 (2009).
[11] C.-H. Li, X.-Q. Zhang, Z.-H. Cheng, and Y. Sun, Appl. Phys. Lett. **93**, 152103 (2008).
[12] L. J. Zeng, H. X. Yang, Y. Zhang, H. F. Tian, C. Ma, Y. B. Qin, Y. G. Zhao, and J. Q. Li, EPL **84**, 57011 (2008).
[13] C.-H. Li, F. Wang, Y. Liu, X.-Q. Zhang, Z.-H. Cheng, and Y. Sun, Phys. Rev. B **79**, 172412 (2009).
[14] J. Iida, S. Takekawa, and N. Kimuzuka, J. Cryst. Growth **102**, 398 (1990).
[15] S. Funahashi, J. Akimitsu, K. Siratori, N. Kimizuka, M. Tanaka, and H. Fujishita, J. Phys. Soc. Jpn. **53**, 2688 (1984).
[16] A. D. Christianson, M. D. Lumsden, M. Angst, Z. Yamani, W. Tian, R. Jin, E. A. Payzant, S. E. Nagler, B. C. Sales, and D. Mandrus, Phys. Rev. Lett. **100**, 107601 (2008).
[17] Y. Yamada, K. Kitsuda, S. Nohdo, and N. Ikeda, Phys. Rev. B **62**, 12167 (2000).
[18] Y. Zhang, H. X. Yang, C. Ma, H. F. Tian, and J. Q. Li, Phys. Rev. Lett. **98**, 247602 (2007).
[19] W. Wu *et al.*, Phys. Rev. Lett. **101**, 137203 (2008).
[20] F. Wang, J. Kim, Y.-J. Kim, and G. D. Gu, Phys. Rev. B **80**, 024419 (2009).
[21] C.-H. Li, X.-Q. Zhang, Z.-H. Cheng, and Y. Sun, Appl. Phys. Lett. **92**, 182903 (2008).
[22] H. Requardt, F. Y. Nad, P. Monceau, R. Currat, J. E. Lorenzo, S. Brazovskii, N. Kirova, G. Grübel, and C. Vettier, Phys. Rev. Lett. **80**, 5631 (1998).
[23] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature (London) **388**, 50 (1997).
[24] G. Blumberg, P. Littlewood, A. Gozar, B. S. Dennis, N. Motoyama, H. Eisaki, and S. Uchida, Science **297**, 584 (2002).
[25] S. Yamanouchi, Y. Taguchi, and Y. Tokura, Phys. Rev. Lett. **83**, 5555 (1999).
[26] Y. Taguchi, T. Matsumoto, and Y. Tokura, Phys. Rev. B **62**, 7015 (2000).
[27] A. N. Lavrov, I. Tsukada, and Y. Ando, Phys. Rev. B **68**, 094506 (2003).
[28] M. Hücker, M. v. Zimmermann, and G. D. Gu, Phys. Rev. B **75**, 041103(R) (2007).