PHYSICAL REVIEW B **80**, 020403(R) (2009)

Magnetic-field control of charge structures in the magnetically disordered phase of multiferroic $LuFe_2O_4$

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(Received 1 July 2009; published 22 July 2009)

Using neutron diffraction, we have studied the magnetic-field effect on charge structures in the charge-ordered multiferroic material $LuFe_2O_4$. An external magnetic field is able to change the magnitude and correlation lengths of the charge valence order even before the magnetic order sets in. This affects the dielectric and ferroelectric properties of the material and induces a giant magnetoelectric effect. Our results suggest that the magnetoelectric coupling in $LuFe_2O_4$ is likely due to magnetic-field effect on local spins, in clear contrast to the case in most other known multiferroic systems where the bulk magnetic order is important.

DOI: 10.1103/PhysRevB.80.020403 PACS number(s): 77.84.−s, 75.80.+q, 61.05.F−

Multiferroics are materials where magnetism and ferroelectricity, which are in many cases mutually exclusive, can coexist. In certain multiferroic systems, the situation becomes more appealing when ferroelectric polarizations appear to be connected with the magnetic order and can be manipulated using an external magnetic field.[1] This aspect of these materials has inspired tremendous interest because of the great potential for device applications.[2–4] While the majority of these materials have spiral magnetic orders,[1,5–8] normally resulting from geometric frustration, there are some exceptions with systems having collinear spin structures.[9–12] However, they all share one common feature: electric-dipole moments are always induced by the formation of inversion-symmetry-breaking magnetic order, where an external magnetic field can affect the magnetic structure and therefore change the ferroelectric properties. There is another type of multiferroic where ferroelectricity and magnetism develop more independently, such as $BiFeO_3$ and $BiMnO_3$. In these systems the ferroelectricity mainly comes from the shifts of the Bi ions while magnetism is a result of Fe/Mn moments. At low temperature the two orders coexist with reasonably large electric polarization and magnetization, but the magnetoelectric response is very weak.

$LuFe_2O_4$ is a new multiferroic material where the ferroelectric polarization originates from valence order of Fe^{2+} and Fe^{3+} ions instead of cation displacements as in conventional ferroelectrics. The ferroelectricity starts to appear slightly above room temperature where no magnetic order is present in the system.[13] As far as the multiferrocity is concerned, $LuFe_2O_4$ belongs to neither of the above two categories. Here Fe^{2+} and Fe^{3+} ions form double layers [Fig. 1(a)], and the nonuniform charge structure contributes to local electrical polarizations. The bulk ferroelectric polarization **P** appears first when the system enters a three-dimensional (3D) charge-ordered phase[13] at the charge-ordering temperature T_{CO} around 340 K [Fig. 1(b)]. Although the polarization is not induced by magnetic order, a significant change in **P** is still observed when the system enters a long-range ferrimagnetic ordered phase[13] at the magnetic ordering temperature T_N at around 240 K, suggesting a large coupling between the ferroelectric polarization and the ordering of Fe spins. From the perspective of making practical devices, $LuFe_2O_4$ is ideal since it has large dielectric response and magnetoelectric coupling[14] at room temperature. In this Rapid Communication, we present neutron-scattering work on the charge order in the system. Our findings show that the static charge structure in $LuFe_2O_4$ can be affected by the application of an external magnetic field in the non-magnetic phase, which is extremely unusual. Our results naturally explain the unprecedented giant magnetoelectric response at room temperature. Furthermore, the fact that the magnetic field can directly affect the charge structure without any intermediate (magnetic) order suggests that a different magnetoelectric coupling mechanism has to be considered for this charge-ordered multiferroic system.

Single crystals of $LuFe_2O_4$ are grown using the floating

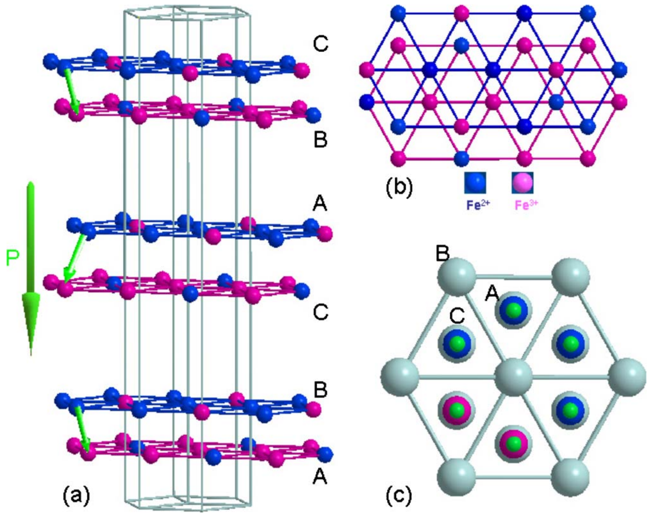

FIG. 1. (Color online) Structure of the multiferroic $LuFe_2O_4$, showing the Fe atoms only. (a) The three double layers. Here Fe atoms can occupy different "A," "B," or "C" positions in the hexagonal plane. In the charge-ordered phase, because of the charge imbalance (e.g., here the top and bottom layers each has $Fe^{2+}:Fe^{3+}$ ratios of 2:1 and 1:2), each double layer gives rise to local electric-dipole moments. With an external electric field, a bulk ferroelectric polarization **P** can be induced. (b) A top view of the charge order in Fe-O double layer. This arrangement has a periodicity of 3 along the [110] direction and gives rise to the (H/3,H/3,L/2)-type superlattice charge peaks. (c) "A," "B," and "C" positions in the hexagonal plane for which the Fe atoms occupy.

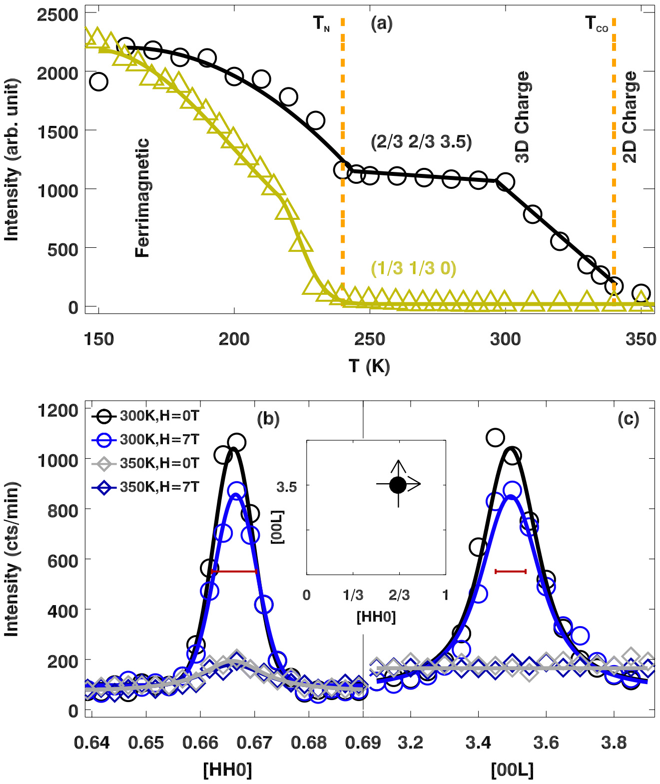

FIG. 2. (Color online) Magnetic and charge order in $LuFe_2O_4$. (a) The magnetic and charge Bragg-peak intensities as order parameters vs temperature. The lines are guides to the eyes. (b) and (c) Linear intensity profiles of the charge superlattice peak (2/3,2/3,3.5) along the [110] and [001] directions, respectively. The horizontal bars indicate the instrument resolution along the measured directions. Here the lines are fits to the data using a Lorentzian function. The inset denotes the direction of the scans performed.

zone technique.[15] The typical crystal sizes are $\sim 10\times 5\times 3$ mm^3. Our neutron-scattering measurements are performed on BT9 triple-axis spectrometer at the NIST Center for Neutron Research (NCNR). 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 used as the analyzer. PG filters are also used before the sample to reduce background from higher order neutrons. $LuFe_2O_4$ has a hexagonal structure, and the sample has been oriented so that the horizontal diffraction plane is the (HHL) plane, which is defined by vectors [110] and [001]. A magnetic field can be applied along the vertical $[1\bar{1}0]$ direction.

The magnetic Bragg peaks in this compound can be measured at reciprocal space positions such as (1/3,1/3,L) and (2/3,2/3,L) for both half-integer L and integer L values,[16,17] while the charge peaks only appear at half-integer L values. In Fig. 2(a), we plot the magnetic order parameter [intensity measured at (1/3,1/3,0)], together with the charge order parameter [intensity measured at (2/3,2/3,3.5)]. Here we show that with cooling, the intensity of the magnetic Bragg peak (1/3, 1/3, 0) only starts to rise around $T_N\sim 240$ K. Note that the magnetic order parameter in this sample is similar to those measured in Refs. 18 and 19 but does not have a second magnetic phase transition at 175 K as suggested in Ref. 17. This is likely a result of slightly different oxygen stoichiometry and appears to only affect the magnetic properties at low temperature.

Charge order in this system starts to appear at much higher temperature, when Fe^{2+} and Fe^{3+} are believed to form the structure shown in Fig. 1(b).[18,20,21] Previous work has shown that the order starts as two dimensional (2D) at around 500 K (Ref. 18) and becomes 3D around 320 K. Superlattice peaks arising from modulations of local atomic distortion due to the charge order can be detected near half-integer L values, as shown by both x-ray and electron-diffraction measurements,[18,20,21] which are only sensitive to lattice structures and not affected by magnetic moments.

We choose to monitor the superlattice peak (2/3,2/3,3.5) for the charge valence order. At temperatures above T_N the situation is relatively simple since there is no magnetic contribution to the intensity. The intensity profile for the charge superlattice peak around (2/3,2/3,3.5) at 350 K is shown in Figs. 2(b) and 2(c), with a peak along the [HH0] direction in the hexagonal plane. The scattering intensity remains constant when we scan along the out-of-plane direction $[00L]$ near $L=3.5$, suggesting a 2D nature of the ordering at this temperature. Upon cooling below 340 K, the system enters a 3D charge-ordered phase, evidenced by the peak in the L scan across the charge superlattice peak. When these local electric dipoles arising from charge imbalance of Fe-O double layers order, spontaneous polarization starts to form and bulk ferroelectricity can be induced.[13] The charge peak intensity appears to become saturated below 300 K. The sudden intensity increase at T_N corresponds to superimposed magnetic scattering intensity at this wave vector due to the magnetic order.

To investigate the response of the system to an external magnetic field, we have repeated the measurements under a magnetic-field-cooling (FC) condition. A magnetic field of $H=7$ T has been applied at 350 K, along the $[1\bar{1}0]$ direction, perpendicular to the scattering plane. Here in the 2D charge-ordered phase, no impact of the field has been observed [see Figs. 2(b) and 2(c)] compared to the measurements under zero-field cooling (ZFC). With further cooling under field, a partial reduction in the charge peak intensity is clearly evident. At 300 K, the charge peak intensity is reduced by about 25% with FC ($H=7$ T), as shown in Figs. 2(b) and 2(c). The temperature dependence of the magnetic-field effect is given in Figs. 3(a) and 3(b), where the intensity differences between the ZFC and FC ($H=7$ T) measurements have been plotted as a function of temperature. The field effect starts to be visible around 340 K when the system enters the 3D charge-ordered phase and continues to grow with further cooling. These results suggest a direct magnetic-field effect on the charge valence order since there is no evidence of field-induced magnetic order above T_N. No magnetic peak intensity is present at (1/3,1/3,0) with FC of $H=7$ T in this 3D charge-ordered phase. We have also performed magnetization measurements on the sample. Temperature dependence of the magnetic susceptibility looks similar to Fig. 1 of Ref. 22 and shows that under FC of 7 T there is no anomaly in the susceptibility at T above $T_N\sim 240$ K and the magnetic

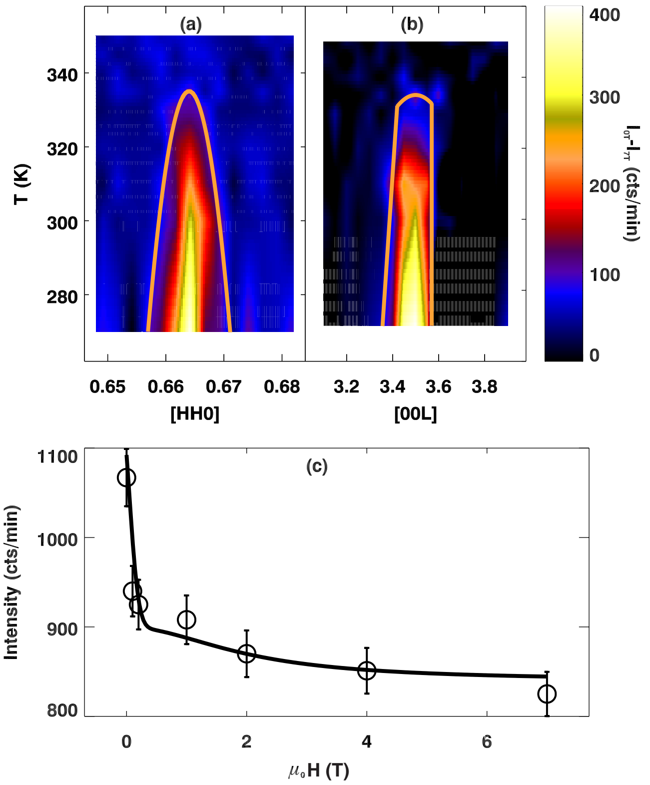

FIG. 3. (Color online) Magnetic-field response on the charge superlattice peak (2/3,2/3,3.5). (a) and (b) Temperature dependence of the intensity difference between measured linear intensity profiles across the charge peak, performed with ZFC and FC with $H=7$ T. (c) Charge peak intensity measured at 300 K with FC from 350 K at different magnetic-field strengths. The lines are guides to the eyes.

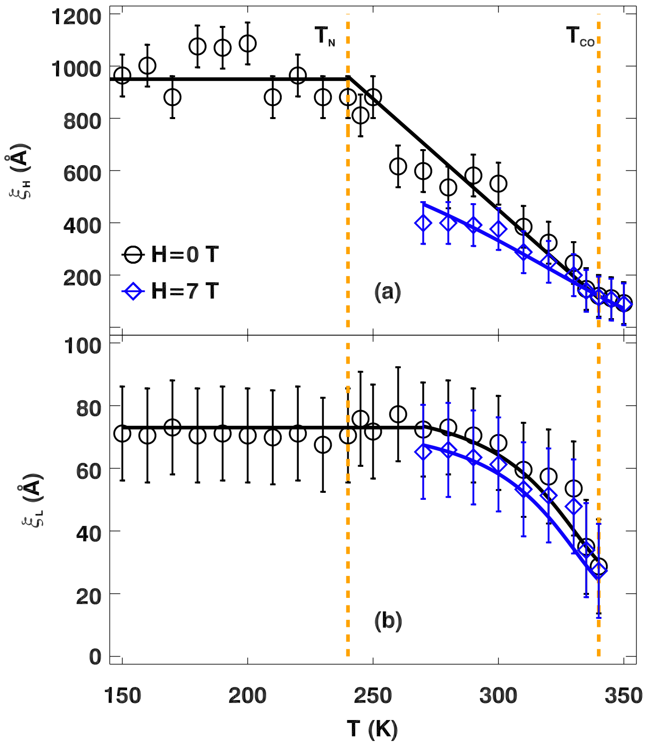

FIG. 4. (Color online) Charge order correlation lengths derived from the charge peak (2/3,2/3,3.5). (a) The correlation length in the hexagonal plane along the [110] direction. (b) The out-of-plane correlation length along the [001] direction. The correlation length is obtained as $\xi=1/\Gamma$, where Γ is the half width at half maximum of the Lorentzian function, which was used to (after convolution with the instrument resolution function) fit the linear intensity profiles of the charge superlattice peak. Note that magnetic intensity starts to appear at this wave vector when the system orders at T_N around 240 K, and therefore the numbers below the magnetic ordering temperature are only given as a reference and should not be taken as having the same physical origin (the correlation length for the charge order) as those in the 3D charge-ordered phase above T_N. The lines are guides to the eyes.

phase-transition temperature remains the same.[22,23] Magnetization measurements at room temperature also suggest an ideal paramagnetic behavior without any hysteresis up to a field of 7 T.

The magnetic-field effect on the charge order is strongly history dependent. Applying a field of $H=7$ T directly at 300 K after a ZFC process does not have any measurable effect on the charge peak intensity; neither does removing the field at 300 K after a FC process with $H=7$ T restore the charge peak intensity (back to the ZFC value). The external field can only affect the charge structure when applied above the 3D charge-ordering temperature before a FC process. In Fig. 3(c), the charge peak intensity at 300 K is plotted for FC processes with different magnetic-field strengths (field applied at 350 K). For magnetic field as small as $H=0.1$ T, a significant ($\sim 15\%$) reduction in the charge peak intensity is already present. In addition to the intensity reduction, a change in the range over which the charge order can be maintained is also observed in the FC process. In Figs. 4(a) and 4(b), we show the instrumental resolution corrected in-plane and out-of-plane correlation lengths ξ_H and ξ_L of the charge order vs temperature. In the 3D charge-ordered phase, the in-plane order appears to be long range with ξ_H approaching 800 Å, while the order remains short range along the out-of-plane direction L, with ξ_L around 70 Å. When cooling in a 7 T magnetic field, both ξ_H and ξ_L are affected. The magnetic-field reduction of the charge order correlation lengths starts at $T_{CO} \sim 340$ K and becomes more prominent with cooling.

What we have observed in this non-magnetic charge-ordered phase of $LuFe_2O_4$ is extremely unusual. As (static) charges do not respond directly to an external magnetic field, one generally does not expect charge order to be affected by a magnetic field. Of course, there are some exceptions. For instance, charge order can coexist with ferromagnetic order in manganites with colossal magnetoresistance (CMR).[24–26] An external magnetic field can affect the charge order indirectly by modifying the magnetic order in the system.[25] Another example involves charge/spin stripe order in cuprate high-temperature superconductors. Magnetic-field dependence of charge stripe order in $La_{2-x}Ba_xCuO_4$ (LBCO, $x \approx 1/8$) has been reported[27] at $T=2$ K but was attributed to the magnetic-field suppression of superconductivity. In other words, in the few rare cases where charge orders can be affected by an external magnetic field, the effect is always mediated by another order (magnetic/superconducting) being modified by the (magnetic) field. In $LuFe_2O_4$, no such intermediate order is present between T_N and T_{CO}, and the magnetic field appears to directly affect the charge structure.

This has deep implications for magnetic-field control of ferroelectric properties in multiferroic materials. The reported giant magnetocapacitance effect, where the dielectric response can be reduced by as much as 25% by external magnetic field at room temperature[14] for $LuFe_2O_4$, had been originally attributed to the field affecting charge fluctuations. Our results suggest that the room-temperature magnetoelectric effect in this multiferroic system is a direct result of the field affecting the static charge order. When charge order is reduced, the magnitude of the resulting local electric-dipole moments becomes smaller, and therefore the dielectric response is smaller. In addition, the reduction in charge-ordering correlation lengths suggests that under FC the ferroelectric domain sizes are reduced. This is completely consistent with results from macroscopic measurements (dielectric response). It would be ideal if polarization measurements can be performed under FC and ZFC conditions. Nevertheless, the low resistivity ($\sim 10^3\ \Omega \cdot m$ at room temperature) makes it very hard to apply a static electric field and obtain polarization measurements in this temperature range. In fact, there are only very few polarization measurements on this material available in the literature,[13,28] probably due to the same reason. The fact that this giant coupling occurs at room temperature, in a non-magnetic phase, in clear contrast to most other magnetoelectric coupling effects in known multiferroic systems where a magnetic order needs to be present to mediate the coupling, makes it extremely appealing and important.

Although there has been some theoretical consideration[29–32] for the magnetic-field effect on charge structure in $LuFe_2O_4$, most of these efforts are focused on the low-temperature structure where the system orders magnetically. One possibility has been raised in these works that the Zeeman splitting of different spin states caused by an external magnetic field could affect the stability of various charge structures and therefore the dielectric response. In fact, the charge order always being short ranged along the c axis is an indication that disorder (possibly stacking disorder or disorder coming from different types of charge-ordering structures coexisting) plays important roles. In the low-temperature magnetically ordered phase, a clear coupling between the charge and magnetic order has been observed[21] in $LuFe_2O_4$. At room temperature there is no long-range magnetic order, yet it is possible that Fe ions could form local spin clusters, which favor different charge order states depending on the spin structure of these clusters. We speculate that charge structures near (charge) domain boundaries are likely to be more unstable and can be affected by the change in local spin structures induced by an external magnetic field. This also explains the small reduction in correlation lengths by the external field. The results reported here provide a grand challenge for theories to explain this mechanism of magnetoelectric interaction, which can have significant impact on both the understanding of electronic structures in a magnetically disordered environment as well as development of new valence-driven functional multiferroic materials.

We thank W. Ratcliff, C. L. Broholm, and J. M. Tranquada for discussions. Work at Brookhaven National Laboratory is supported by U.S. Department of Energy (Contract No. DE-AC02-98CH20886).

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[23] The situation becomes more complicated when the system orders magnetically at T_N; the scattering intensity at (2/3,2/3,3.5) now has contributions from both magnetic order and lattice modulation due to the charge order. Our preliminary work shows that below T_N, the magnetic structure is also affected by the external field, with partial suppression of magnetic intensities at integer L values and enhancement of magnetic intensities at half-integer Ls. Detailed study is clearly required in the future to understand the complicated low-temperature magnetic and charge structure under field, and we will only focus on the field effect in the 3D charge-ordered phase above T_N in this Rapid Communication.

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