

## Pressure effects on multiferroic LuFe<sub>2</sub>O<sub>4</sub>

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(Received 10 September 2009; accepted 8 February 2010; published online 12 March 2010)

This letter reports that both ac susceptibility and electronic transport measurements of the multiferroic compound LuFe<sub>2</sub>O<sub>4</sub> under pressure show that the transition temperature from the paramagnetic state to the ferrimagnetic state decreases with increasing pressure, indicating that the pressure favors the paramagnetic state and suppresses the ferrimagnetic state. Moreover, the minimum of resistivity changes under pressure, which decreases with increasing pressure, appears at the magnetic phase transition temperature. © 2010 American Institute of Physics.

[doi:10.1063/1.3360211]

Since Zhang *et al.*<sup>1</sup> confirmed the existence of charge-stripe order through low-temperature transmission electron microscopy studies, huge variety of dielectric permittivity in the frustrated state LuFe<sub>2</sub>O<sub>4</sub> (LFO) has been explained faultlessly by the conventional charge ordering (CO) effect at low temperature. Some ferromagnetic and ferroelectric features may be attributed to the unique charge-spin frustrated mechanism<sup>2</sup> where the charge correlation represents charge order for ferroelectricity and the spin frustration exhibits magnetic order for ferromagnetic phenomenon.<sup>3</sup> Simultaneously, the single crystal LFO with the ordering of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions is believed to be a leading candidate and has been practically achievable for the room-temperature microelectronic devices.<sup>1</sup>

The LFO has a rhombohedral space group ( $R\bar{3}m$ ) (Refs. 2 and 4) with layered stacking of triangular lattices consisting of rare-earth element Lu, iron, and oxygen ions.<sup>5-8</sup> In accordance with the opinion of Ikeda *et al.*,<sup>7</sup> Park *et al.*<sup>9</sup> figured that though an average Fe valence of LFO preserves the level of +2.5, the centers of electric charge of Fe<sup>3+</sup> ions and Fe<sup>2+</sup> ions (an ideal ratio is 1:1) are not coincident practically in the charge-frustrated and mixed-valence system. Consequently, the imbalance of cations in the triangular lattice leads to electronic ferroelectrics which exhibits a three-dimensional ferroelectric ordered state<sup>3,5</sup> without originating from the orthodox covalent pairs between *p* orbital anions and *d* orbital cations. Moreover, just as a result of the coexistence of positioned iron cations occupying the same site of alike hexagonal lattice, quasi-two-dimensional (2D) ferromagnetic ordering associated with short-ranged spin-clusters takes place near the Neel temperature  $T_N$ .<sup>5,9</sup> Generally, the valence state of the iron ions in LFO is mixed on account of the coexistence of Fe<sup>3+</sup> and Fe<sup>2+</sup>.

Up to now, because of the formal similarity of spin and charge frustration,<sup>2</sup> present works are focused on the correlation<sup>6</sup> between the electric polarization and the magnetic moment, which is still less investigated. Furthermore, the basic properties of frustrated multiferroic systems are still

not completely understood. According to the previous literatures,<sup>1,4</sup> LFO compounds likely suffer from consecutive and remarkable phase transition with decreasing temperature, the particular charge-stripe phase corresponding to the charge ordered state manifests at low temperature, which is correlated with electronic ferroelectric behavior. Being different from the traditional ferroelectric material BaTiO<sub>3</sub> whose ferroelectricity is driven by the displacement of Ti<sup>4+</sup> and O<sup>2-</sup> ion pairs, the electronic ferroelectric LFO shows abnormal dielectric behavior at low temperature accompanying the phase transition,<sup>4</sup> and the involved CO-phase can also be tuned similarly by pressure.<sup>5</sup> As a tunable thermodynamic parameter, the external pressure plays an important role in material sciences. It can affect not only the crystal structure but also the magnetic structure, CO, and orbital ordering.

The polycrystalline LFO samples were synthesized by utilizing a traditional solid state reaction method. The Lu<sub>2</sub>O<sub>3</sub> (analytic purity) and Fe<sub>2</sub>O<sub>3</sub> (analytic purity) powders were mixed and milled thoroughly in stoichiometric ratios in an agate mortar and MgO was added as mineralizer. Then raw materials were sintered at 1200 °C by using a steady flow commixed CO<sub>2</sub> and H<sub>2</sub> to control oxygen content. The detailed description of the experimental conditions and procedure of sample preparation was given elsewhere.<sup>4</sup> A clamp-type piston cylinder cell was used to survey temperature dependence of resistivity at different hydrostatic pressures. Resistivity was measured with the standard four-probe technique and electrical contacts were established by using silver paint on a bar shaped sample ( $\sim 1.45 \times 2.25 \times 3.85$  mm<sup>3</sup>). The sample temperature was monitored with aluminonickel and chromel thermocouple placed near the sample and a mixture of silicone oil and kerosene (cubage 1:1) was used as a pressure transmitting medium. In our experiments, the sample was separated from the pressure transmitting medium by an insulator layer painted on the sample. All the values of pressure quoted in this letter were measured at room temperature. The ac magnetic susceptibility versus temperature was carried out by using the same system from ambient temperature to the temperature of liquid nitrogen.

The temperature-dependent relative ac magnetic susceptibility of polycrystalline LFO at different pressures is presented in Fig. 1(a). A frequency of 333.3 Hz and 0.73 K/min quasi-isothermal heating rate were used for the ac suscepti-

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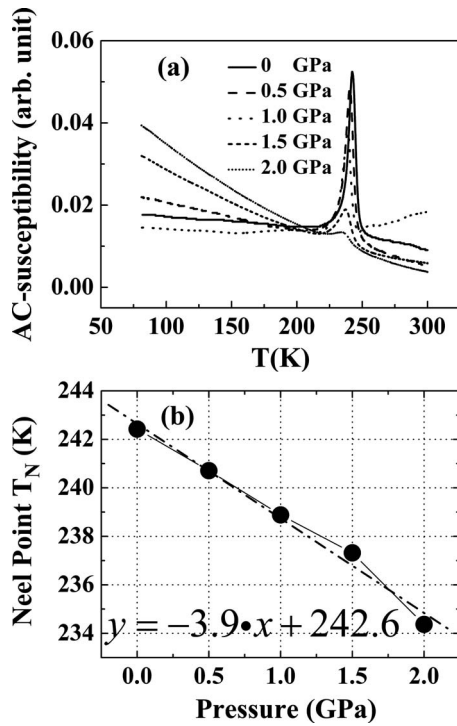


FIG. 1. (a) The temperature dependence of the ac magnetic susceptibility obtained at an ac frequency of 333.3 Hz for different pressures. (b) The Neel temperature  $T_N$  vs pressure, which is determined from the ac magnetic susceptibility measurements.

bility measurements. In all experiments, the excitation loops ( $\sim 500$  circles) generate steadily an ac field of about several oersted. Except for the curvilinear raise with decreasing temperature, the ac susceptibility data reveal a sharp characteristic peak corresponding to the transition from the paramagnetic state to the ferrimagnetic state, i.e.,  $T_N$ . For 0 GPa,  $T_N = 242.4$  K, this value is significantly lower than the reported experimental value 250 K,<sup>9,10</sup> which is likely frequency-dependent. However, the peak transfer direction is different from common multiferroic materials, e.g., the peak of  $\text{LuFeCoO}_4$  (Ref. 10) monotonically moves to higher temperatures with increasing frequency. The abnormal features of frequency dependence of ac susceptibility not only do not obey the Arrhenius behavior, suggesting that the coupling of charge and spin order affects strongly phase-transition around  $T_N$ , but also exhibit more obvious peak displacement than isomorphous  $\text{YbFe}_2\text{O}_4$ ,<sup>10</sup> indicating the forceful ordered state in LFO. It is also well known that an ac susceptibility peak corresponding to long-range order has no temperature-shift. Thus the couple of ordering may be correlated primarily with short-range ordered phase. According to the reports by Zhang *et al.*,<sup>4</sup> the diversity of crystal growth may result in the excursion of  $T_N$  at ambient pressure for our measured samples. Figure 1(a) also shows the influence of pressure on phase transition. The susceptibility peak varies with increasing pressure toward lower temperature and the relative peak value descends markedly. In order to show the variation in  $T_N$  with pressure, the  $T_N$  versus pressure is plotted in Fig. 1(b) and the pressure ( $P$ )- $T_N$  dependence can be written as an appropriate linear equation

$$T_N = v_P \times P + T_N^0, \quad (1)$$

where  $T_N$  and  $P$  are the Neel temperature and pressure, respectively,  $v_P$  is the change velocity of pressure-induced  $T_N$ ,

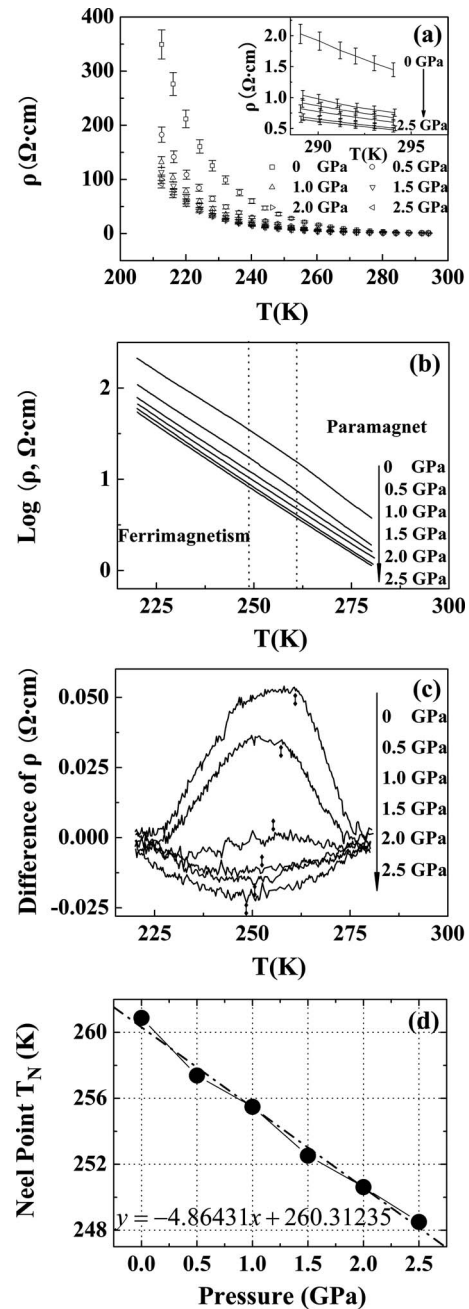


FIG. 2. (a) The resistivity  $\rho$  vs temperature. The inset shows the enlarged curves around ambient temperature. (b) The log plot of resistivity  $\rho$  vs temperature at different pressures. (c) The deviation values between real  $\text{log}(\rho)$  curves and referential straight lines of each pressure point, respectively. Symbol ( $\downarrow$ ) presents the temperature from the paramagnetic state to the ferrimagnetic state. (d) The Neel temperature ( $T_N$ ) as a function of pressure, which is determined from the electrical property measurements.

and  $T_N^0$  is the Neel temperature at ambient pressure. Through fitting the data, we obtain  $v_P = -3.9$  K/GPa, this result elucidates that the pressure favors the paramagnetic state and suppresses the weak ferromagnetic state strongly.

As well known, the origin of weak ferromagnetic state in LFO is considered as 2D ferromagnetic ordering of spin moment below  $T_N$ . The transition temperature reflected from susceptibility curves decreases remarkably with increasing pressure, indicating that the pressure suppresses the weak ferromagnetic state. According to the report by Yamada *et al.*,<sup>2</sup> the spin frustration occurs on the 2D  $\text{Fe}_2\text{O}_4$  hexagonal lattice and leads to the weak ferromagnetic state. Since the

crystal structure is affected by pressure, the Fe double layers might change. On one hand, this may be not conducive to the existence of the spin frustration configuration, causing the decrease in  $T_N$ , on the other hand, this gives rise to the slight deflection of the direction of the spin frustration formally, leading to the descent of the relative peak value (as shown in Fig. 1). In a word, the pressure suppresses the weak ferromagnetic state of LFO.

The electrical transport properties under pressure are also investigated and the temperature dependences of resistivity at different pressures are shown in Fig. 2(a). Obviously, the sample exhibits typical semiconducting behavior, whose  $\rho$  rises very gradually with decreasing temperature over nearly entire paramagnetic and ferrimagnetic temperature range for all applied pressures. As expected, the resistivity decreases with the applied pressures from 0 to 2.5 GPa in the whole measured temperature range. As far as we observe, there are no distinct changes in the resistivity versus temperature curves at the magnetic phase transition temperature  $T_N$ , indicating that ac magnetic susceptibility and dielectric permittivity<sup>10</sup> are more sensitive in reflecting the transition of ferrimagnetism than electrical transport properties. The inset of Fig. 2(a) shows enlarged details of the  $\rho$  curves at different pressures around room temperature.

In order to make out the reflection in the resistance behavior of LFO at the magnetic phase transition, the  $\log(\rho)$ -temperature dependence is plotted in Fig. 2(b) from 220 to 280 K. A definite radian can be distinguishable clearly along every curve from the paramagnetic state to the ferrimagnetic state. The pressure effects not only restrain observably the numerical value of resistivity [see Fig. 2(a)] but also weaken distinctly the radian of each data curve of  $\log(\rho)$ . Being consistent with the phenomenon of the melt of CO state in many systems under external pressure, the CO state in LFO is also unfavorable under pressure. In order to magnify the radian of  $\log(\rho)$  curves in Fig. 2(b), we choose two special points in each curve corresponding to 220 and 280 K data sites and interlink them as a fitted beeline. From 220 to 280 K, the data of the referential straight lines are used to be subtracted from the corresponding experimental data, respectively, and the deviation value curves are plotted in Fig. 2(c). The magnetic transition temperature  $T_N$  is marked accordingly. Being similar to the result of magnetic measurements, the temperature corresponding to the transition from the paramagnetic state to the ferrimagnetic state decreases with

increasing pressure. It also manifests that the CO is affected by pressure because of the coupling between magnetization and electric polarization in the multiferroic system.

The  $T_N$  values versus pressure from ambient pressure up to 2.5 GPa are presented in Fig. 2(d), which are obtained from the above measurements of electrical transport property. The data are again fitted by using Eq. (1) with a linear curve and  $v_p = -4.9$  K/GPa is obtained, indicating in like manner that the pressure favors the paramagnetic state. Comparing with the result of Fig. 1(b), we find that the absolute value of  $v_p$  acquired from the electrical measurements is larger than that ( $v_p = -3.9$  K/GPa) acquired from the magnetic measurements. Though the electrical and magnetic measurements show somehow different  $v_p$ , the changing trend of the magnetic transition temperature under pressure is the same.

The magnetic and electrical transport properties measurements of the polycrystalline LFO under pressure were carried out by using a clamp-type piston cylinder cell. We find that the pressure favors the paramagnetic state and suppresses the ferrimagnetic state.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 10774168 and 50621061) and the State Key Development Project on Fundamental Research of China (Grant No. 2005CB623602).

<sup>1</sup>Y. Zhang, H. X. Yang, C. Ma, H. F. Tian, and J. Q. Li, *Phys. Rev. Lett.* **98**, 247602 (2007).

<sup>2</sup>Y. Yamada, K. Kitsuda, S. Nohdo, and N. Ikeda, *Phys. Rev. B* **62**, 12167 (2000).

<sup>3</sup>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).

<sup>4</sup>Y. Zhang, H. X. Yang, Y. Q. Guo, C. Ma, H. F. Tian, J. L. Luo, and J. Q. Li, *Phys. Rev. B* **76**, 184105 (2007).

<sup>5</sup>C.-H. Li, X.-Q. Zhang, Z.-H. Cheng, and Y. Sun, *Appl. Phys. Lett.* **93**, 152103 (2008).

<sup>6</sup>N. Ikeda, *J. Phys.: Condens. Matter* **20**, 434218 (2008).

<sup>7</sup>N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kitô, *Nature (London)* **436**, 1136 (2005).

<sup>8</sup>C.-H. Li, X.-Q. Zhang, Z.-H. Cheng, and Y. Sun, *Appl. Phys. Lett.* **92**, 182903 (2008).

<sup>9</sup>J. Y. Park, J. H. Park, Y. K. Jeong, and H. M. Jang, *Appl. Phys. Lett.* **91**, 152903 (2007).

<sup>10</sup>K. Yoshii and N. Ikeda, *Phys. Rev. B* **76**, 024423 (2007).