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# An ultrasonic study on complex charge ordering phenomena for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$

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## Abstract

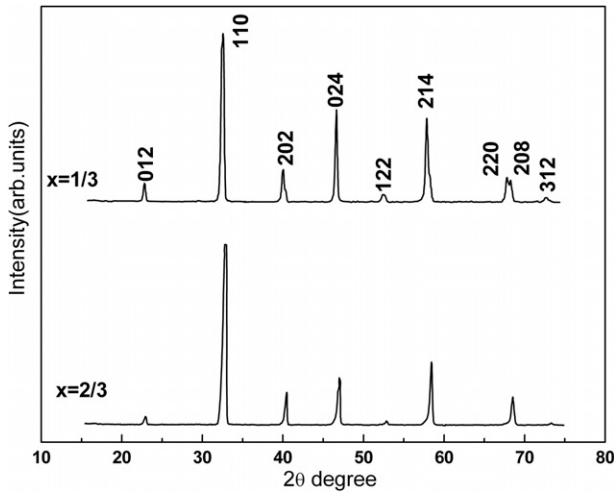
The complex charge ordering phenomena for polycrystalline  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $1/3 \leq x \leq 2/3$ ) have been studied by measuring the low temperature magnetization, resistivity and the longitudinal ultrasonic velocity ( $V_1$ ). At low doping levels ( $1/3 \leq x \leq 0.5$ ), a dramatic velocity increase is observed below 210 K, and the relative stiffening of  $V_1$  is proportional to the Sr concentration. The analysis suggests that this feature may correspond to the short-range charge ordering state of  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$ . At high doping levels ( $0.5 < x \leq 2/3$ ), the resistivity shows a sharp increase around 200 K, and the relative stiffening of  $V_1$  decreases with increasing  $x$ . This implies that the charge disproportionation transition  $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$  occurs. In particular, the  $V_1$  of  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  undergoes another softening transition below 181 K, which is attributed to the breathing-type distortion of Fe–O octahedron in the sequence  $\dots \text{Fe}^{3+}\text{Fe}^{5+}\text{Fe}^{3+} \dots$ . The detailed form of the sound velocity anomalies in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 1/3, 2/3$ ) is different, revealing the presence of complex charge ordering phenomena. To complete the ultrasonic characterization in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ , sound measurements were performed on  $\text{La}_{0.1}\text{Sr}_{0.9}\text{FeO}_3$ , whose ground state is a typical antiferromagnetic order, and the anomaly is small.

## 1. Introduction

The perovskite-type transition-metal oxide compounds (TMOs) have attracted considerable attention due to their special structural, magnetic, and electronic properties [1, 2]. Among them, the  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  system has been investigated particularly extensively due to their interesting features originating from the interplay among different valence states of iron. One finds complex charge ordering (CO) phenomena through transmission electron microscopy study [3]. For high Sr doping ( $x \sim 2/3$ ), the CO accompanies both antiferromagnetic (AFM) ordering and charge disproportionation (CD) of  $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$  [4, 5]. In this ordering state, a sequence of  $\dots \text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{5+}\text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{5+} \dots$  exists along the [111] direction of the pseudocubic perovskite unit cell. In the low doping range, superlattice structure has been observed at low temperature, which is explained on the basis of the local CO state of  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  according to the charge segregation model [3]. But direct evidence for this local CO state has not been obtained yet.

From previous works, it has been widely recognized that the CO state is a consequence of the coupling or the competition among the degrees of freedom of the charge, spin, lattice and orbit. And theoretical and experimental results for manganites have shown that the electron–phonon coupling, which is caused by the Jahn–Teller distortion of  $\text{Mn}^{3+}(\text{d}^4)$ , plays an important role for the CO state [6, 7]. Since  $\text{Fe}^{4+}(\text{d}^4)$  is isoelectronic with  $\text{Mn}^{3+}$ , similar electron–phonon coupling is expected in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ . But until now, this coupling in  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  is still under discussion. Different conclusions have been drawn using different experimental and theoretical tools [3–5, 8–10].

As a sensitive tool, the ultrasonic technique has been proven to be particularly successful in studying systems with electron–phonon coupling, spin–phonon coupling, and phase transition [7, 11]. In fact, it was observed experimentally that the formation of the CO state in  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  is accompanied by dramatic stiffening in the sound velocity below  $T_{\text{CO}}$ , which was attributed to a strong electron–lattice interaction [12]. However, a systematic ultrasonic study



**Figure 1.** XRD patterns of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 1/3, 2/3$ ) at room temperature.

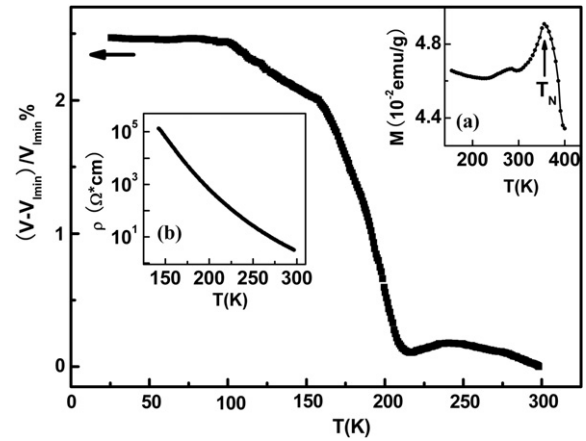
on the evolution of complex charge ordering phenomena in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  is still incomplete. In this paper, we present a systematic study of the longitudinal ultrasonic velocity ( $V_l$ ) as a function of temperature for polycrystalline  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $1/3 \leq x \leq 2/3$ ). The temperature dependence of the  $V_l$  for  $\text{La}_{0.1}\text{Sr}_{0.9}\text{FeO}_3$  is also examined for comparison. The objective of the present work is to give new experimental evidence for the short-range CO state at low doping levels and reveal the evolution of complex CO phenomena in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ .

## 2. Experimental details

The polycrystalline samples of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $1/3 \leq x \leq 2/3$ ) were prepared by a solid-state reaction method. Stoichiometric amounts of high purity  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$  and  $\text{Fe}_2\text{O}_3$  powders were well mixed, and calcinated at 1100, 1150, 1200 °C in air for 15 h. The powder finally obtained was pressed into pellets at 300 MPa and sintered at 1300 °C ( $x = 1/3$ ) and ~1200 °C ( $x = 2/3$ ) in air for 20 h, and cooled to room temperature at a rate of 1.5 K  $\text{min}^{-1}$ .

The crystal structure was characterized using a Japan Rigaku MAX-RD powder x-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The x-ray diffraction patterns of the typical samples are shown in figure 1. Both samples are single phase with no detectable secondary phases. The diffraction peaks are sharp and can be indexed with the space group  $R\bar{3}c$  in the hexagonal setting. And with more Sr doping, the structure of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  approaches cubic symmetry [13]. Thus for  $x = 2/3$  sample, the (220) and (208) peaks locate at the same position. This result is consistent with the earlier report [14] and the XRD pattern of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_3$  (No. 82-1964, PCPDFWIN Database of JCPDS, version 1.1.1.0, 2002)

The resistivity was measured as a function of temperature by the standard four-probe technique. The zero-field-cooled (ZFC) magnetization was measured in an external magnetic field of 100 Oe using a commercial quantum device (SQUID; Quantum Design MPMSXL). The longitudinal ultrasonic velocity measurement was performed on the Matec-7700 series by means of a conventional pulsed echo technique.



**Figure 2.** The temperature dependence of the longitudinal ultrasonic velocity for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ . The inset (a) shows the temperature dependence of the magnetization for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ . The inset (b) shows the temperature dependence of the resistivity for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ .

## 3. Results and discussion

The temperature dependence of  $V_l$  for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  is displayed in figure 2. A dramatic velocity increase is observed below 210 K, and there is substantial softening as the transition is approached from higher temperatures.

To investigate the origin of this ultrasonic anomaly, we have explored several possibilities. The first consideration is the magnetic transition. However, from the magnetization measurement results (shown in the inset of figure 2(a)), it can be seen that its AFM transition temperature ( $T_N$ ) is about 350 K, which is much higher than the temperature of the ultrasonic anomaly. Moreover, we recall that the typical relative change in sound velocity caused by AFM spin fluctuations is of the order of 0.1% [15], while the velocity increase for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  is about 2%. Thus it seems impossible to correlate this ultrasonic anomaly with magnetic transition. Therefore, we considered other alternative mechanisms which could cause the ultrasonic anomaly.

According to the acoustics theory, the softening in sound velocity is usually observed near the temperature of structural distortion or the formation of a glassy state where, due to the weakening of certain force constants, a particular phonon mode softens [16]. Until now, no experimental evidence has indicated that a spin-glass state exists in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ . In fact, structural distortion was observed at low temperature in this system. In 1997, superstructural spots correlated with the CO state were found at around 200 K for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$  from transmission electron microscopy [3]. Moreover, a similar ultrasonic feature is observed for  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  around its charge ordering transition [12], which is attributed to the lattice distortion arising from the Jahn–Teller effect of  $\text{Fe}^{4+}$ . Thus it is probable that this ultrasonic anomaly of  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  is caused by a similar structural distortion correlated with the charge ordering state.

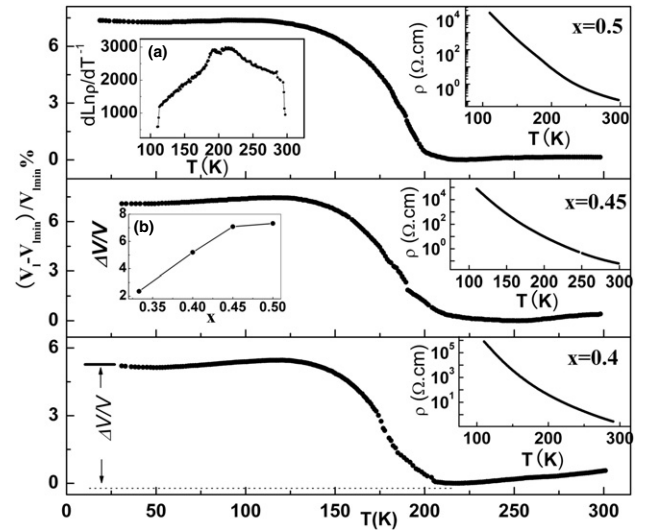
To elucidate the relationship between the ultrasonic anomaly and the structural distortion, we apply the Jahn–Teller theory to  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ . According to this theory,

the coupling of the electronic states of the ions to the long-wavelength acoustic phonons will cause one or more elastic constants to undergo an anomalous decrease as the phase transition is approached [17]. And on the basis of the Hamiltonian of small Jahn–Teller polarons with strong electron–phonon coupling, Min *et al* also found that for manganites, the CO interaction induces softening of the sound velocity above  $T_{CO}$  and hardening below  $T_{CO}$  [6]. Their calculation result has been experimentally proven using ultrasonic measurements on charge ordered  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [7] and  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  [12], and is qualitatively similar to our observation. Therefore the ultrasonic anomaly in  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  around 210 K possibly originates from the Jahn–Teller effect during the formation of the charge ordering state.

However, from the resistivity and magnetization measurements, no obvious change is observed around the temperature of the ultrasonic anomaly in  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ , which is different from the normal CO transition. For example, the charge ordering transition in manganites always accompanies a sharp increase in resistivity. This anomalous behavior of  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  is probably due to the following two features. On the one hand, the charge ordering state in  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  is of short-range type [3]. In charge rich areas, there are as many  $\text{Fe}^{4+}$  ions as  $\text{Fe}^{3+}$  ions to form the perfect charge ordering state, and in the other areas, the Fe ions are almost all  $\text{Fe}^{3+}$ . And the coherence length of the ordered state is found to be 5–10 nm along the  $a$ -axis direction in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$  from the high resolution images taken at 110 K. On the other hand, transmission electron microscopy shows that the precursor CO reflections in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$  become visible below  $\sim 250$  K and show up as superstructural spots below  $\sim 150$  K [3]. This probably means that this short-range CO transition is gradually developed over a large temperature range; thus it could not induce the obvious change in resistivity.

If the Jahn–Teller effect during the CO transition does indeed occur in the low Sr doped  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ , Sr concentration increase would lead to two results. First, more  $\text{Fe}^{4+}$  may induce a stronger Jahn–Teller effect. In manganites, the relative stiffening of the ultrasonic velocity ( $\Delta V/V$ ) can be viewed as a scale of the development of the Jahn–Teller effect [18]. Thus, more  $\text{Fe}^{4+}$  may induce more sound velocity increase. Second, with the  $\text{Fe}^{4+}$  concentration increasing, the charge ordered areas increase, which would affect the resistivity property eventually. This can be observed from the logarithmic derivative  $d(\ln \rho)/d(T^{-1})-T$  curve [7].

To verify these predictions, we measured the  $V_1$  and resistivity of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 0.4, 0.45, 0.5$ ) (shown in the figure 3). Due to the oxygen deficiency, the  $\text{Fe}^{4+}$  concentration is still less than that of  $\text{Fe}^{3+}$  in the  $x = 0.5$  sample. Similar ultrasonic features are observed for all samples. And  $\Delta V/V$  is proportional to the Sr concentration (shown in the inset of figure 3(b)). This relationship reflects that the anomaly of the  $V_1$  is closely related to the  $\text{Fe}^{4+}$  and indicates that the Jahn–Teller effect does indeed exist in the low Sr doped  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ . No significant anomalies are evident in the  $\rho(T)$  curves. However, for  $x = 0.5$ ,  $d(\ln \rho)/d(T^{-1})$  exhibits a maximum (shown in the inset of figure 3(a)), a behavior similar



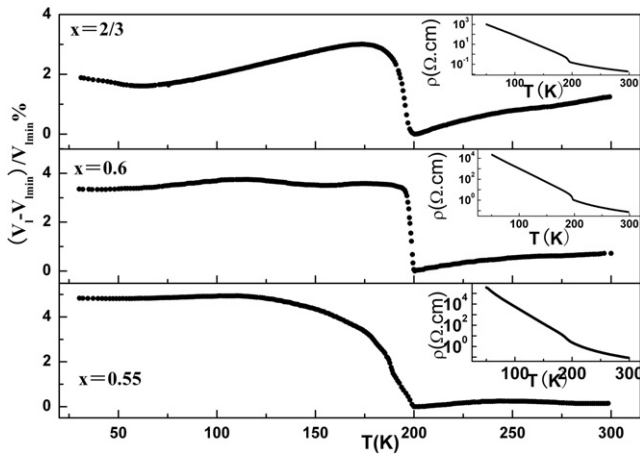
**Figure 3.** The temperature dependences of the longitudinal ultrasonic velocity and resistivity for  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 0.4, 0.45, 0.5$ ). The inset (a) shows the logarithmic derivative,  $d(\ln \rho)/d(T^{-1})$ , of the resistivity with temperature for  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ . The inset (b) shows the variation of the relative change of the ultrasonic velocity ( $\Delta V/V$ ) as a function of the Sr concentration  $x$ .

to that of manganites at their charge ordering transition [7]. This abnormal peak is very wide, implying that the charge ordering transition develops over a large temperature range. This is consistent with the transmission electron microscopy result [3].

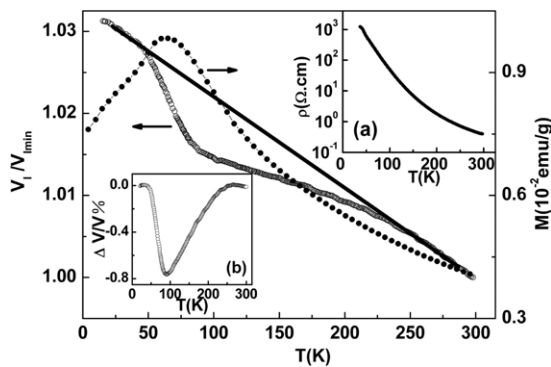
When  $x > 0.5$ , the  $\text{Fe}^{4+}$  concentration is larger than that of  $\text{Fe}^{3+}$  and the charge ordered sequence of  $\dots \text{Fe}^{3+}\text{Fe}^{4+}\text{Fe}^{3+}\text{Fe}^{4+} \dots$  will become unstable since there are two localized  $\text{Fe}^{4+}$  neighbors. This weakens the hybridization of the middle O 2p bands and the two localized  $\text{Fe}^{4+}$ , which would make the  $\text{Fe}^{4+}$  unstable. To avoid this situation, the charge disproportionation of  $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$  occurs and a different charge ordered sequence of  $\dots \text{Fe}^{3+}\text{Fe}^{5+}\text{Fe}^{3+} \dots$  was found [3].

To investigate the evolution of the complex charge ordering phenomena in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ , samples for  $0.5 < x \leq 2/3$  were prepared. The temperature dependences of the  $V_1$  and resistivities for them are displayed in figure 4. For all samples, an obvious increase in resistivity was observed at about 200 K, which corresponds to the CO transition and is different from the local charge ordering state in the low doping range. Their ultrasonic feature at around 200 K is similar in character to that of  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ , which exhibits a valley around  $T_{CO}$ . It is worth mentioning that  $\Delta V/V$  decreases when the Sr concentration  $x$  increases further from  $x = 0.5$ . This implies that the Jahn–Teller effect weakens and can be explained by the charge disproportionation phenomena.

For  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ , the representative samples showing the different CO states are the  $x = 1/3$  and  $2/3$  ones. So we focus on the attenuation on their ultrasonic features. The difference is observed when the temperature decreases below  $T_{CO}$ . After reaching its maximum value at 181 K, the  $V_1$  of  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  softens gradually until about 70 K, while only increase is observed in  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  below  $T_{CO}$ .



**Figure 4.** The temperature dependences of the longitudinal ultrasonic velocity and resistivity for  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 0.55, 0.6, 2/3$ ).



**Figure 5.** Temperature dependences of the longitudinal ultrasonic velocity and magnetization for  $\text{La}_{0.1}\text{Sr}_{0.9}\text{FeO}_3$ . The inset (a) shows the temperature dependence of resistivity. The inset (b) shows the critical contribution to the sound velocity anomaly near  $T_N$ . (The difference between the actual sound velocity and the ‘background’ was taken as the critical contribution.)

Until now, no experimental evidence has indicated that the spin-glass state exists in  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ . In fact, lattice distortion below  $T_{\text{CO}}$  in the  $x = 2/3$  sample was observed by transmission electron microscopy [3]. It is related to the breathing-type distortion of Fe–O octahedra because  $\text{Fe}^{5+}$  cations will occupy smaller octahedral sites than  $\text{Fe}^{3+}$  cations. Ishikawa also confirmed this distortion in  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  by means of optical spectroscopy measurements [5]. Thus it is highly probable that this softening in sound velocity is related to the structural distortion, while for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$ , the experimental results showed that the valence states of Fe ions are 3+ and 4+ over the whole temperature range, and the size difference between them is very small. So the  $V_l$  shows a normal increase below  $T_{\text{CO}}$ . The diversity of the CO states leads to the different behaviors in  $V_l$  below  $T_{\text{CO}}$ .

To complete the ultrasonic characterization of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ , we performed sound measurements for the  $x = 0.9$  sample, whose ground state is a typical AFM order. The sound velocity versus temperature and the critical contribution to the sound velocity near the AFM phase transition for  $\text{La}_{0.1}\text{Sr}_{0.9}\text{FeO}_3$  are shown in figure 5. It can be seen that its

$T_N$  is about 70 K. It is indubitable that the critical contribution,  $\Delta V/V \approx 0.8\%$ , to the sound velocity near  $T_N$  is due to the antiferromagnetic spin fluctuation alone and its ultrasonic character is different from that of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $1/3 \leq x \leq 2/3$ ). This result confirmed that the complex CO states play an important role for the ultrasonic anomalies for  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $1/3 \leq x \leq 2/3$ ).

#### 4. Conclusion

In summary, we have systemically studied the ultrasonic properties of polycrystalline  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $1/3 \leq x \leq 2/3$ ). And dramatic anomalies in ultrasonic velocity are observed, which are attributed to the different kinds of CO states at the low and high Sr doping levels, respectively. The transformation of the charge ordering states may be related to the stability of the  $\text{Fe}^{4+}$ . These results give new experimental evidence for the short-range CO state at low doping levels and reveal the evolution of complex CO phenomena for  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ .

#### Acknowledgment

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#### References

- [1] von Helmolt R, Wecker J, Holzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331
- [2] Rao C N R and Raveau B 1998 *Colossal Magnetoresistance, Charge ordering and Related Properties of Manganese Oxides* (Singapore: World Scientific)
- [3] Li J Q, Matsui Y, Park S K and Tokura Y 1997 *Phys. Rev. Lett.* **79** 297
- [4] Yang J B, Zhou X D, Chu Z, Hikal W M, Cai Q, Ho J C, Kundaliya D C, Yelon W B, James W J, Anderson H U, Hamdeh H H and Malik S K 2003 *J. Phys.: Condens. Matter* **15** 5093
- [5] Park S K, Ishikawa T, Tokura Y, Li J Q and Matsui Y 1999 *Phys. Rev. B* **60** 10788
- [6] Min B I, Lee J D and Youn S J 1998 *J. Magn. Magn. Mater.* **171** 881
- [7] Ramirez A P, Schiffer P, Cheong S-W, Chen C H, Bao W, Palstra T T M, Gammel P L, Bishop D J and Zegarski B 1996 *Phys. Rev. Lett.* **76** 3188
- [8] Battle P D, Gibb T C and Lightfoot P 1990 *J. Solid State Chem.* **84** 271
- [9] Matsuno J, Mizokawa T, Fujimori A, Mamiya K, Takeda Y, Kawasaki S and Takano M 1999 *Phys. Rev. B* **60** 4605
- [10] Ghosh S, Kamaraju N, Seto M, Fujimori A, Takeda Y, Ishiwata S, Kawasaki S, Azuma M, Takano M and Sood A K 2005 *Phys. Rev. B* **71** 245110
- [11] Zhu C and Zheng R 1999 *Phys. Rev. B* **59** 11169
- [12] Kong H and Zhu C 2006 *Appl. Phys. Lett.* **88** 041920
- [13] Shimony Jens U and Knudsen M 1966 *Phys. Rev.* **144** 361
- [14] Gao F, Li P L, Weng Y Y, Dong S, Wang L F, Lv L Y, Wang K F, Liu J-M and Ren Z F 2007 *Appl. Phys. Lett.* **91** 072504
- [15] Berlincourt D and Jaffe H 1958 *Phys. Rev.* **111** 143
- [16] Garland C W 1970 *Physical Acoustics* vol 7, ed W P Maston and R N Thurston (New York: Academic) p 52
- [17] Melcher R L 1970 *Physical Acoustics* vol 12, ed W P Maston and R N Thurston (New York: Academic) pp 1–21
- [18] Zheng R K, Li G, Yang Y, Tang A N, Wang W, Qian T and Li X G 2004 *Phys. Rev. B* **70** 014408