

05.2;05.3

## Increasing the temperature of the magnetic ordering in $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$ by heat treatment

© A.I. Dmitriev<sup>1</sup>, S.V. Zaitsev<sup>2</sup>, M.S. Dmitrieva<sup>1</sup>

<sup>1</sup>Federal Research Center for Problems of Chemical Physics and Medical Chemistry, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia

<sup>2</sup>Osipyan Institute of Solid State Physics RAS, Chernogolovka, Russia

E-mail: aid@icp.ac.ru

Received February 15, 2024

Revised March 21, 2024

Accepted March 23, 2024

The dependences of the magnetic moment on the temperature  $M(T)$  and the magnetic field strength  $M(H)$  of the  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  samples before and after vacuum annealing were studied. At room temperature, the initial sample is a paramagnetic. Its  $M(T)$  curve clearly shows the Néel temperature of  $T_N = 196$  K, which increases significantly as a result of annealing. After annealing, the compound  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  is in a magnetically ordered state at room temperature.

**Keywords:** lanthanum orthoferrites, canted antiferromagnetism, vacuum annealing.

DOI: 10.61011/TPL.2024.07.58720.19894

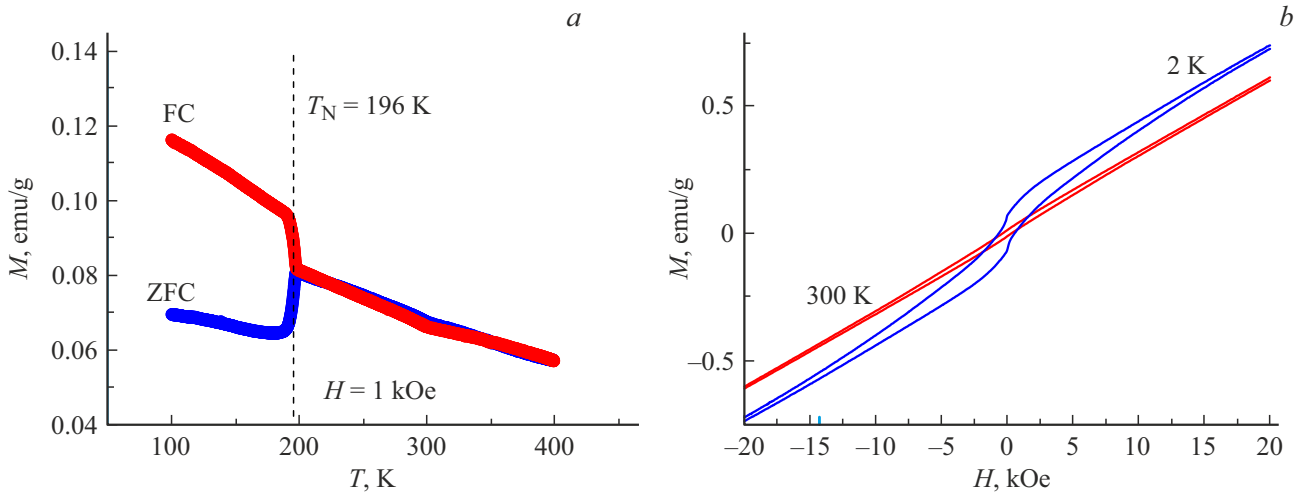
Lanthanum orthoferrite ( $\text{LaFeO}_3$ ) is a multiferroic, which makes it a candidate component material for various sensors and data storage devices [1].  $\text{LaFeO}_3$  is a canted antiferromagnet with the highest Néel temperature ( $T_N = 740$  K) [2] in the orthoferrite family. The properties of  $\text{LaFeO}_3$  may be altered by doping, which opens up new opportunities for its application in engineering. Specifically, such exotic physical phenomena as metal–insulator transitions and charge and orbital ordering have been observed in it [3]. A common alloying element is  $\text{Sr}^{2+}$ . When  $\text{La}^{3+}$  is substituted with  $\text{Sr}^{2+}$ , the charge of iron ions in  $\text{LaFeO}_3$  changes from  $3+$  to  $4+$ . The introduction of  $\text{Sr}^{2+}$  enhances ionic conductivity, but reduces  $T_N$  by a substantial margin (at certain concentrations, it goes below room temperature [2,3]). This is a hindrance to possible magnetic applications of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ . The magnetic properties of discussed compounds are induced by the superexchange mechanism involving  $3d$  electrons of transition metals and  $p$  orbitals of oxygen. Thus, oxygen plays a pivotal role in magnetic ordering of these compounds. In view of the importance of oxygen and its contribution to the formation of a magnetically ordered state, the examination of properties of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  as functions of the concentration of oxygen vacancies, which is highly sensitive to heat treatment, is of academic and practical interest. The variation of concentration of oxygen vacancies in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  during vacuum annealing has been established earlier in [4]. The aim of the present study is to develop methods for increasing  $T_N$  of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  via heat treatment.

$\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  was produced using the sol-gel method from Sr, Fe, and La nitrates. A part of the sample was then subjected to annealing in vacuum at  $650^\circ\text{C}$ . The process of synthesis was discussed in detail in [4].

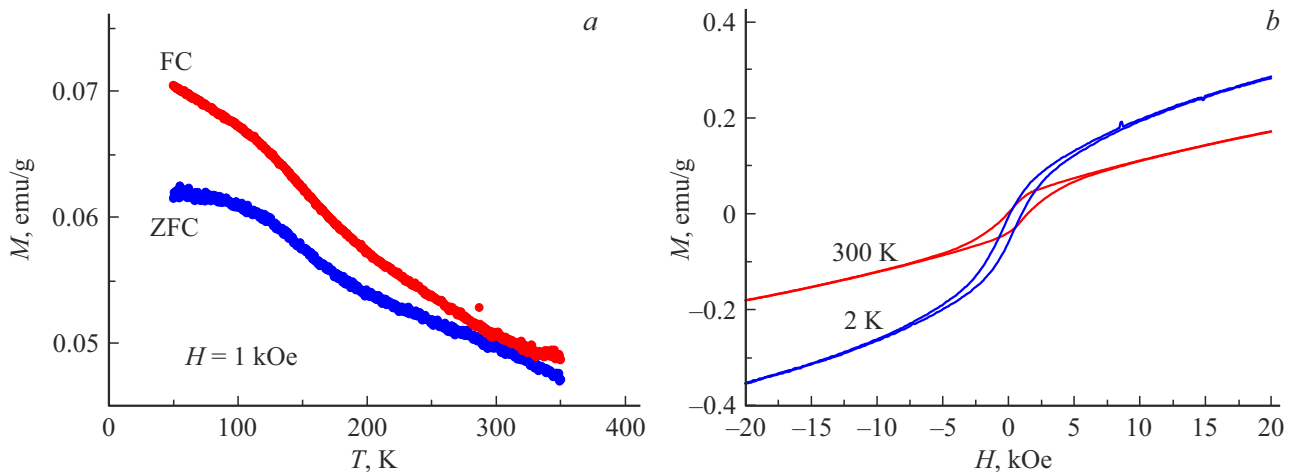
Initial  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  has a rhombohedral structure, and vacuum annealing induces the transition to a rhombic structure [4]. Dependencies of the magnetic moment on temperature  $M(T)$  and magnetic field strength  $M(H)$  were measured with a CFMS vibration magnetometer (Cryogenic Ltd, UK). Raman spectra were recorded at room temperature in backscattering geometry. A laser with a wavelength of 532 nm was used for excitation. The spectral resolution was no worse than  $1\text{ cm}^{-1}$  at an absolute accuracy of  $\pm 1\text{ cm}^{-1}$  [4].

Figure 1 shows the  $M(T)$  dependences of the sample measured prior to vacuum annealing in the ZFC (zero-field cooling) and FC (field cooling) modes in a magnetic field with strength  $H = 1\text{ kOe}$ . The  $M(T)$  curves clearly reveal Néel temperature  $T_N = 196$  K at which the FC–ZFC curves have a kink and begin to diverge. It is known that all compounds of the  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  family are antiferromagnets [1–5]. Spins are aligned in an antiparallel manner in them. However, owing to a slight deviation of spins from the strict antiparallel orientation resulting from the zigzag arrangement of oxygen octahedra containing Fe ions, the samples exhibit non-collinear antiferromagnetism (weak ferromagnetism), which is verified by the hysteretic nature of the  $M(H)$  curves (Fig. 1, *b*). At room temperature, the as-prepared sample is a paramagnet, which is evidenced by the linearity of dependencies  $M(H)$  (Fig. 1, *b*).

Figure 2, *a* presents the  $M(T)$  dependences of the annealed sample measured in the ZFC and FC modes in a magnetic field with strength  $H = 1\text{ kOe}$ . The temperature corresponding to the kink and divergence of the FC–ZFC curves exceeds room temperature. This implies that annealing induces a noticeable  $T_N$  rise in  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$ , which remains in a magnetically ordered state at room



**Figure 1.** *a* — Temperature dependences of magnetization  $M(T)$  of the non-annealed sample measured in a magnetic field with strength  $H = 1$  kOe. The dashed line denotes Néel temperature  $T_N$ . *b* — Magnetic hysteresis loops at temperatures  $T = 2$  and 300 K for the non-annealed sample.



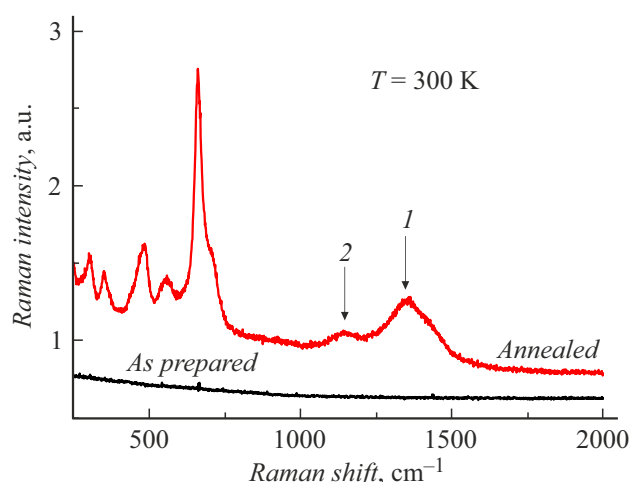
**Figure 2.** *a* — Temperature dependences of magnetization  $M(T)$  of the sample after annealing measured in a magnetic field with strength  $H = 1$  kOe. *b* — Magnetic hysteresis loops at temperatures  $T = 2$  and 300 K for the sample after annealing.

temperature. This fact is confirmed by the presence of a magnetic hysteresis loop at room temperature (Fig. 2, *b*).

Antiferromagnetic ordering at room temperature in the annealed  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  sample is evidenced by the presence of an intense Raman peak of two-magnon scattering at  $\sim 1360\text{ cm}^{-1}$  in the Raman spectra (peak 1 in Fig. 3). A similar strong line was observed at room temperature in the spectra of  $\text{LaFeO}_3$  [6]. At frequencies below  $1000\text{ cm}^{-1}$ , the Raman lines of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  are induced by phonon vibrations [7,8]. The strongest phonon mode at a frequency of  $\sim 660\text{ cm}^{-1}$  characterizes in-phase vibrations of Fe–O bonds in a  $\text{FeO}_6$  octahedron [8]. In addition, an intense line of two-phonon scattering (peak 2 in Fig. 3), which forms due to strong coupling of the phonon and spin systems in these compounds [9], is seen in the spectrum at  $\sim 1140\text{ cm}^{-1}$ . Figure 3 shows also the Raman spectrum of the as-prepared  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  sample that

has no magnon and phonon Raman peaks. The lack of a two-magnon scattering line indicates that antiferromagnetic ordering is not established at room temperature. At the same time, the suppression of phonon modes suggests that the non-annealed sample features a significant fraction of  $\text{Fe}^{4+}$  ions [6].

The  $T_N$  rise is due to the intensification of superexchange antiferromagnetic interaction between Fe ions as a result of annealing. These changes in the intensity of antiferromagnetic exchange and  $T_N$  may be attributed to the following four factors: variation of (1) the Fe–O bond length; (2) the number of nearest neighbors; (3) the Fe–O–Fe bond angle; and (4) the valence state of Fe ions. Structural and Mössbauer data suggest that the first two factors are insignificant [4]. Therefore, we take only the third and fourth factors into account. According to the Goodenough's superexchange theory, the exchange interaction between



**Figure 3.** Raman spectra at  $T = 300$  K of the sample before (*As prepared*) and after (*Annealed*) annealing. Numbers 1 and 2 denote the lines of two-magnon and two-phonon scattering, respectively.

$\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$  ions is antiferromagnetic and stronger than the one between  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  ions or  $\text{Fe}^{4+}$  and  $\text{Fe}^{4+}$ . Therefore, the introduction of  $\text{Sr}^{2+}$  ions into lanthanum orthoferrite, which contributes to the production of  $\text{Fe}^{4+}$  ions, weakens the exchange interaction and reduces  $T_N$  accordingly. Subsequent vacuum heat treatment leads to the removal of oxygen ions with the formation of a vacancy. This is accompanied by a change in valence state of iron ions (from  $4+$  to  $3+$ ) [4]. In contrast, this process enhances the exchange interaction and raises  $T_N$  accordingly. According to the aforementioned Goodenough's superexchange theory, the antiferromagnetic exchange interaction between  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$  ions is at its maximum intensity when the  $\text{Fe}-\text{O}-\text{Fe}$  bond angle is  $180^\circ$ . It has been demonstrated earlier that this angle in substituted lanthanum ferrites is significantly smaller ( $\sim 166^\circ$ ) and gets close to  $175^\circ$  in the process of annealing [10]. In other words, vacuum annealing induces a redistribution of the contributions of ferromagnetic and antiferromagnetic channels to the resultant exchange and shifts the equilibrium toward antiferromagnetism enhancement. This, in turn, leads to a significant growth of  $T_N$ , which exceeds room temperature.

Thus, the dependence of exchange interaction on the concentration of oxygen vacancies and the structure of  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$ , which have been determined earlier in [4], was established. Dependences of the magnetic moment on temperature  $M(T)$  and magnetic field strength  $M(H)$   $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  measured before and after vacuum annealing revealed that the as-prepared sample is paramagnetic at room temperature. Noncollinear antiferromagnetism (weak ferromagnetism) is established in this sample at Néel temperature  $T_N = 196$  K. Vacuum annealing induces a noticeable growth of Néel temperature  $T_N$  of the  $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_{3-\delta}$  compound, which remains in a magnetically ordered state at room temperature. The

capacity to modify the chemical composition and alter the concentration of oxygen vacancies by heat treatment opens up new ways to tailor the crystal structure and magnetic properties of substituted lanthanum orthoferrites.

### Acknowledgments

The authors wish to thank V.D. Sedykh and O.G. Rybchenko for providing samples and for stimulating discussions.

### Funding

This study was carried out under state assignments of the Federal Research Center for Problems of Chemical Physics and Medical Chemistry (124013100858-3) and the Osipyan Institute of Solid State Physics.

### Conflict of interest

The authors declare that they have no conflict of interest.

### References

- [1] S. Acharya, J. Mondal, S. Ghosh, S. Roy, P. Chakrabarti, *Mater. Lett.*, **64** (3), 415 (2010). DOI: 10.1016/j.matlet.2009.11.037
- [2] J. Blasco, B. Aznar, J. García, G. Subias, J. Herrero-Martín, J. Stankiewicz, *Phys. Rev. B*, **77** (5), 054107 (2008). DOI: 10.1103/PhysRevB.77.054107
- [3] J.Q. Li, Y. Matsui, S.K. Park, Y. Tokura, *Phys. Rev. Lett.*, **79** (2), 297 (1997). DOI: 10.1103/PhysRevLett.79.297
- [4] V.D. Sedykh, O.G. Rybchenko, N.V. Barkovskii, A.I. Ivanov, V.I. Kulakov, *Phys. Solid State*, **63**, 1775 (2021). DOI: 10.1134/S1063783421100322
- [5] C.C. Chen, X.N. Ying, *Europhys. Lett.*, **125** (5), 56001 (2019). DOI: 10.1209/0295-5075/125/56001
- [6] V. Sedykh, V. Rusakov, O. Rybchenko, A. Gapochka, K. Gavrilicheva, O. Barkalov, S. Zaitsev, V. Kulakov, *Ceram. Int.*, **49** (15), 25640 (2023). DOI: 10.1016/j.ceramint.2023.05.105
- [7] O.I. Barkalov, S.V. Zaitsev, V.D. Sedykh, *Solid State Commun.*, **354** (1), 114912 (2022). DOI: 10.1016/j.ssc.2022.114912
- [8] M.C. Weber, M. Guennou, H.J. Zhao, J. Iniguez, R. Vilarinho, A. Almeida, J.A. Moreira, J. Kreisel, *Phys. Rev. B*, **94** (21), 214103 (2016). DOI: 10.1103/PhysRevB.94.214103
- [9] M.O. Ramirez, M. Krishnamurthi, S. Denev, A. Kumar, S.-Y. Yang, Y.-H. Chu, E. Saiz, J. Seidel, A.P. Pyatakov, A. Bush, D. Viehland, J. Orenstein, R. Ramesh, V. Gopalan, *Appl. Phys. Lett.*, **92** (2), 022511 (2008). DOI: 10.1063/1.2829681
- [10] J.B. Yang, W.B. Yelon, W.J. James, Z. Chu, M. Kornecki, Y.X. Xie, X.D. Zhou, H.U. Anderson, A.G. Joshi, S.K. Malik, *Phys. Rev. B*, **66** (18), 184415 (2002). DOI: 10.1103/PhysRevB.66.184415

Translated by D.Safin