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Electron spin resonance and magnetic phase transitions in manganite perovskite $La_{0.78}Sr_{0.22}MnO_3$ synthesized by the solid-phase reaction method

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Magnetic properties of nanopowder of perovskite manganite doped with strontium $La_{0.78}Sr_{0.22}MnO_3$ are studied using electron paramagnetic resonance method. Analysis of the experiments in the temperature range $T = 77–290$ K shows that this structure is a typical nanostructure only at $T < 100$ K. In the remaining temperature region, the structure is in the superparamagnetic and noncollinear superparamagnetic magnetic state.
Keywords: electron spin resonance, magnetic nanopowder, superparamagnetic state.

Методом электронного парамагнитного резонанса исследованы магнитные свойства нанопорошка манганита перовскита, допированного стронцием $La_{0,78}Sr_{0,22}MnO_3$. Анализ экспериментов в области температур $T = 77–290$ К показал, что данная структура является типичной наноструктурой лишь при $T < 100$ К. В остальной области температур структура находится в суперпарамагнитном и неколлинеарном суперпарамагнитном магнитном состоянии.

Електронний спіновий резонанс і магнітні фазові переходи у манганіті перовськиті $La_{0,78}Sr_{0.22}MnO_3$, синтезованим методом твердофазних реакцій. *Т.В.Калмикова, А.С.Вакула, С.В.Недух, С.І.Тарапов, А.Г.Білоус, В.Н.Криворучко, Р.В.Сухов.*

Методом електронного парамагнітного резонансу досліджено магнітні властивості нанопорошку манганіту перовськиту, допованого стронцієм $La_{0,78}Sr_{0,22}MnO_3$. Аналіз експериментів в області температур $T = 77–290$ К показав, що дана структура є типовою наноструктурою лише при $T < 100$ К. У решті областей температур структура знаходиться у суперпарамагнітному і неколінеарному суперпарамагнітному магнітному стані.

1. Introduction

Manganites perovskites, which doped with various impurities, are perspective materials for different fundamental and applied problems of physics. As it is known, the main mechanism for formation of magnetic ordering in such structures is the mechanism of "double exchange interaction" [1]. In the manganites perovskites, the phase diagram turns out to be very complicated and moreover, in magnetic field the situation becomes even more complicated. However, namely that determines the merits of these structures, which manifest themselves in the possibility of relatively simple control their electromagnetic properties by using the temperature changing [2–5].

It was shown in [3–5] particularly, that doped perovskite manganites in the microwave range of wavelengths can demonstrate left-handed properties, (i.e., the structure exhibits negative refraction in a certain frequency range). These properties are very promising for the use of perovskite manganites in nanotechnologies, in development of the electronic and magnetically controlled instruments, which operates in gigahertz and terahertz ranges. Specification of the discovered properties was carried out in [2], where samples $La_{1-x}Sr_xMnO_3$ with strontium concentrations (x = 0.15, 0.225, 0.3, 0.45, 0.6) were studied using the electron paramagnetic resonance in 4 and 8 millimeter wavelength ranges. Homogeneities in the magnetic states of the samples were detected and analyzed. In addition, in [6], the magnetic states of the left-handed structures $La_{1-x}Sr_xMnO_3$ (x = 0.225–0.3) were also studied. In particular, in the sample $La_{1-x}Sr_xMnO_3$ with $x = 0.3$ at $4.2 < T <$ 290 K, the two-phase magnetic state is detected in which paramagnetic and a ferromagnetic phase are simultaneously present.

The results, which indicated above initiated further questions. The question remains unclear as for role the boundaries of the structural clusters (nanoparticles) that form the structure in the formation of the magnetic phase. This question can be explained by studying the temperature dependence of the magnetic resonance absorption (the shape and width of the peaks of the Electronic Paramagnetic Resonance-EPR), most clearly associated with the magnetic phase transitions.

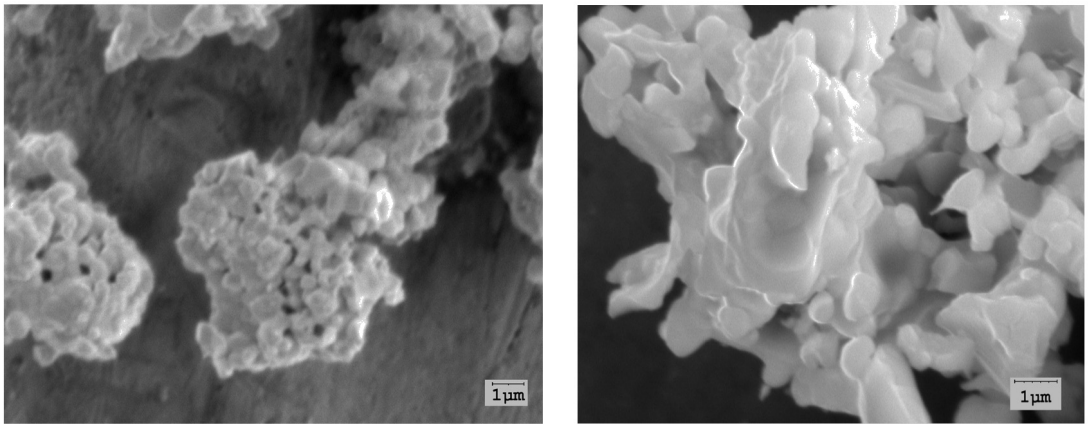
Therefore, the aim of this paper is analysis of the experimentally recorded EPR peaks of perovskite manganite doped with Sr, $La_{0.78}Sr_{0.22}MnO_3$, in the range of temperatures, where the main phase transitions (77–290 K) are observed. The concentration of Sr (x = 0.22) is chosen from those considerations that in this region (x) the competition between the types of interaction and the magnetic centers is very high [2, 3]. Despite the fact that the investigated object demonstrates the presence of not only paramagnetic, but also other magnetic phases, for simplicity we use the term "Electron Paramagnetic Resonance" to describe the absorption peaks in its electron spin system.

2. Experimental

Nanosized ferromagnetic particles of perovskite manganite $La_{0.78}Sr_{0.22}MnO_3$ were synthesized by the method of solid-phase reaction. The synthesis temperature was T = 1650°C, and the solid-phase reaction method itself was described in details in [7,8].

Using a scanning electron microscope (SEI — Secondary Electron Image — a picture obtained on the secondary electrons), images of the investigated nanoparticles of perovskite manganite $La_{0.78}Sr_{0.22}MnO_3$ in Fig. 1 were obtained. It is presented in Fig. 1a that size of the conglomerate consisting of stuck together nanoparticles is about 8–10 μm increased by 7000 times. Figure 1b shows the 10,000-fold increasing in the photo of one of these conglomerates. It can be seen that the simplest geometric objects can hardly approximate the shape of the nanoparticles. A sample of $La_{0.78}Sr_{0.22}MnO_3$ is a nanopowder. During the experimental EPR study at T = 290 K, the $La_{0.78}Sr_{0.22}MnO_3$ sample was placed in a measuring cuvette with size of 3.4×1.4×0.5 mm^3. The sample was formed as a parallelepiped with dimensions of 3.4×1.4×0.5 mm^3. The cuvette, in turn, placed on a micro-strip line, which was located between the poles of the electromagnet [9]. In this case, vector $\mathbf{h}\}$ components of the microwave field of the $\mathbf{H}\}_0$ — constant field were directed mutually orthogonally, which ensured the realization of the EPR conditions. The experiment was carried out by using the VNA-ESR spectrometer, built on base of the Network Analyzer N5230A [10].

To conduct the studying the temperature dependence of the EPR at 80 K $< T <$ 300 K, the sample was placed in a rectangular waveguide of 3.2×7.4 mm^3 section, which, like microstrips, was located between



a) b)

Fig. 1. Photo of $La_{0.78}Sr_{0.22}MnO_3$, obtained by SEI a) increase in 7000 times b) photograph of the conglomerate, enlarged in ×10,000 times.

the poles of the electromagnet (Fig.2). The waveguide was placed in a thermally insulated container with liquid nitrogen.The appearance of the cryogenic module for EPR investigation is shown in Fig. 2.

3. Results and discussion

Experimental studies were carried out at temperature of 77–290 K and in the frequency range of 7–35 GHz, under conditions of both scanning the constant magnetic field, and scanning the frequency.

Fig. 3a shows the resonant EPR peaks, which was recorded at the fixed magnetic field values in $I = I(f)$ format. As it is shown in Fig. 2b the dependence of frequency f_{res} on H_0^{res} determines the value of the anisotropy field $Ha = 450$ Oe according to the traditional technique, described in detail in, for example, [11].

In addition, the unexpectedly large value of the Ha field is connected with the presence not only exchange, but also dipole-dipole interaction between the nanoparticles [12–14]. At the big values of the magnetic field, the slope of dependence $f_{res}(H_0^{res})$ practically coincides with the calculated reference analogous dependence for an ideal paramagnet. However, for the small values of the magnetic field, the slope of the experimental curve becomes smaller and differs from the calculated dependence for the ideal paramagnet more and more with decreasing the H_0 value. This means that in the small magnetic fields $H_0^{res} \leq 4$–5 kOe the sample is in noncollinear magnetic phase and in unsaturated state.

The low-temperature measurements were carried out as follows. The sample was

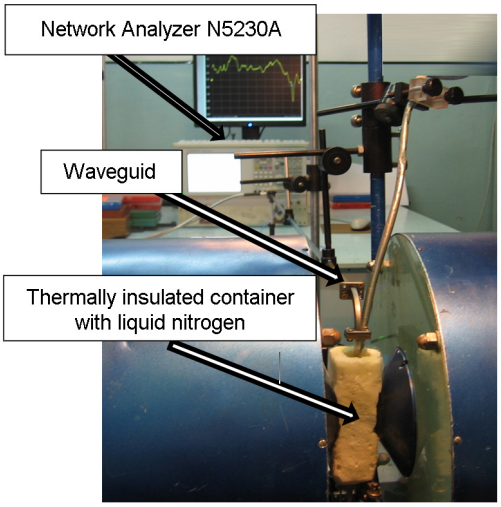


Fig. 2. Cryomodule in combination with VNA-ESR spectrometer.

cooled to the nitrogen temperature in the absence of field ($H_0 = 0$). Then the field was increased to $H_0 \approx 10.3$ kOe (so that the resonant peak was observed in the frequency range of 25–40 GHz), where the matter is certainly in the superparamagnetic phase. The line (peak) of the EPR was registered in the format $I = I(f)$ at $H_0^{res} =$ const. As the temperature increased, both $f_{res}(T)$ and the width of the EPR peak $\delta H(T)$ were recorded. These dependencies are shown in Fig. 4.

We note the unusual behavior of the resonant frequency and the line width with decreasing temperature (Fig. 3). As is known from [15], for typical nanostructures (the structures with an element size of the nanometers order) with the temperature decreasing, an increase in the value of fres

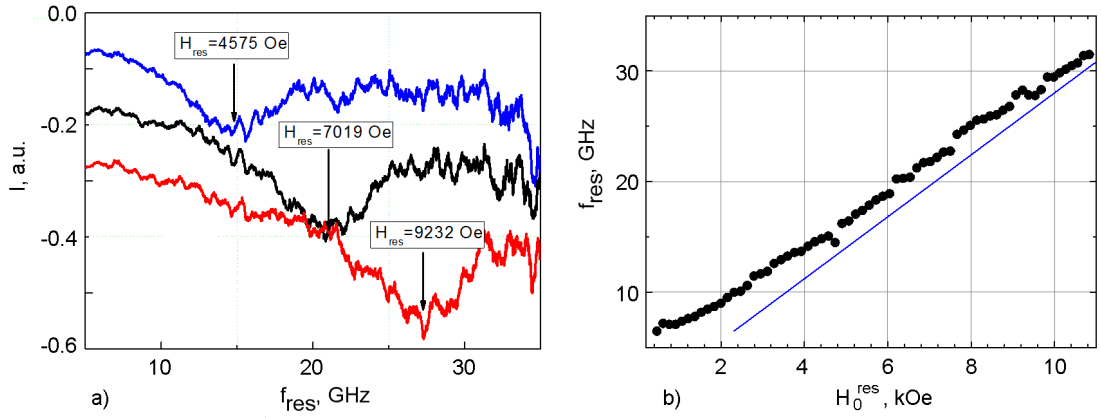


Fig. 3. Typical EPR peaks (a) and dependence of resonant frequencies f_{res} on external magnetic field H_0 (b) at T = 290 K (solid line is a benchmark EPR curve for an ideal paramagnet).

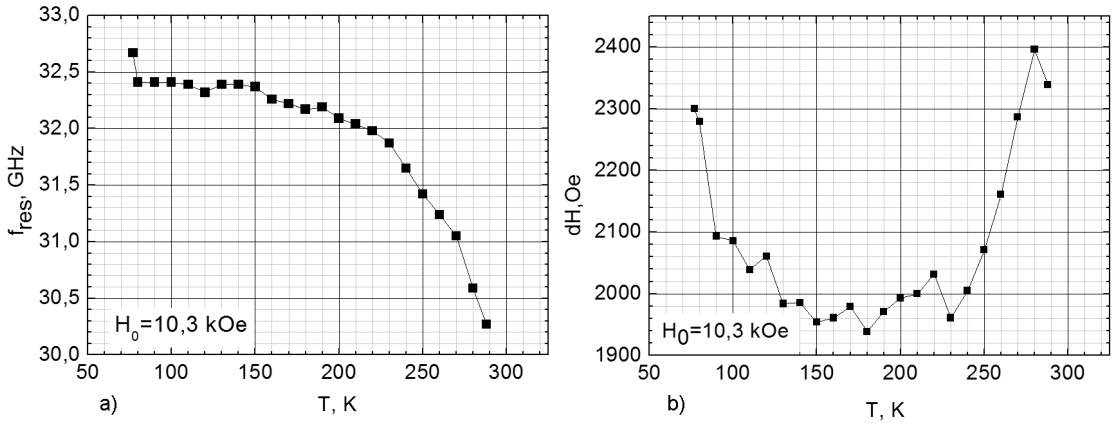


Fig. 4. Dependences of resonant frequency (a) and width of the EPR peak (b) on temperature, for fixed field H = 10.3 kOe.

should be observed. At the same time, the increasing in the width of the EPR line should be observed too. This phenomenon is because of significant width of the resonance line [16, 17] which is one of the characteristic features of the magnetic dynamics ferromagnetic nanostructured sample. The considerable width of the resonance line is also characteristic of the resonant response of an ensemble of the single-domain magnetic nanoparticles (see, for example, [18]). In this case, the local axes of the magnetization of individual nanoparticles can be randomly oriented, and the standard approximation of the "narrow resonance line" is not fulfilled. The analysis shows (see [15, 18] and the references cited there) that in these cases the resonance (Larmor) and antiresonant (Antilarmor) components of the tensor should be retained in the high-frequency susceptibility tensor $\hat{\chi}(\mathbf{r}\},$.

In our case, we actually observe the increasing in the resonant frequency with a drop in temperature. However, the width of the line does not increase, but falls. In addition, it increases only at $T \leq 100$ K. This indicates that in the studying object the properties inherent in nanostructures appear only in the region of $T \leq 100$ K. In the region of 100 K $\leq T \leq$250 K the structure behaves like a typical polycrystalline (powder), demonstrating the superparamagnetic behavior in the above-mentioned temperature range. This is evidenced by a significant decrease in the line width, recorded during the experiment in this same temperature range. The other authors [19] also observed analogous temperature dependences of the line width for the similar objects, that again confirms the reliability of our experiments.

In order to obtain additional information on the role of the boundaries, which forming the elements the sample, we analyzed the shape of the EPR line recorded in the standard format $I = I(H_0)$ at a fixed frequency and T = 290 K (Fig. 5).

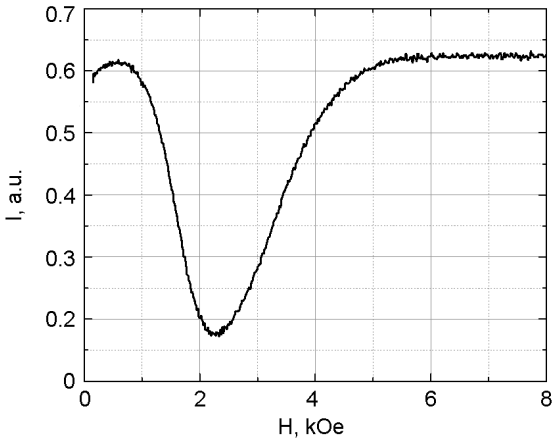


Fig. 5. Shape of the EPR peak in $La_{0.78}Sr_{0.22}MnO_3$ at $f = 10.05$ GHz, $T = 290$ K.

It can be seen that the line shape is asymmetric. This indicates that in the test sample the distribution of the magnetic moments of the particles, as well as the distribution of the particles in form, must be very heterogeneous. Indeed, the comparison with a the photograph in (Fig. 1) confirms this assumption. That is, despite the fact that the shape of the elements making up the sample is very different from the simplest forms (ellipse), the magnetic structure of the object under study has a strong dispersion, both in the form of the primordial particles, and in magnitude and in the direction of the magnetic moments of the nanoparticles.

4. Conclusions

Thus, as a result of the analysis of the ESR absorption in $La_{0.78}Sr_{0.22}MnO_3$ in the range of $f = 7–35$ GHz; $T = 77–290$ K it is shown that:

The investigated object can be considered as the nanostructure, at temperatures $T <$ 100 K. Namely, at this and lower temperatures it behaves as a single nanostructured system, with non-collinear ordering of the magnetic moments of the nanoparticles. In the region of 100 K $\leq T \leq$ 250 K, temperature fluctuations "break" the magnetic bonds and the system is in the intermediate state of the transition from the low-temperature non-collinear state to the superparamagnetic state. At $T \geq 250$ K the structure goes into the superparamagnetic state.

The geometric shape and magnetic moment of the elements forming the sample demonstrates the large dispersion, which leads to strong anisotropy of the spatial and its magnetic properties.

References

1. L.P.Gorkov, Uspehi Fiz. Nauk, **168**, 665 (1998).
2. T.V.Kalmykova, S.V.Nedukh, S.Yu.Polevoy et al., *Low Temper. Phys.*, **41**, 273 (2015).
3. D.P.Belozorov, A.A.Girich, S.I.Tarapov et al., *AIP Advances*, **4**, 037116 (2014).
4. M.K.Khodzitsky, T.V.Kalmykova, S.I.Tarapov et al., *Appl. Phys. Lett.*, **95**, 082903 (2009).
5. S.I.Tarapov, D.P.Belozorov, *Low Temper. Phys.*, **38**, 766 (2012).
6. D.P.Belozorov, S.I.Tarapov, A.M.Pogorily et al., *Appl. Phys. Lett.*, **100**, 171104 (2012).
7. A.I.Tovstolytkin, A.M.Pogorily, D.I.Podyalovskii et al., *J. Appl. Phys.*, **102**, 063902 (2007).
8. A.G.Belous, O.I.V'yunov, E.V.Pashkova et al., *Neorg. Mater.*, **39**, 212 (2003).
9. A.A.Girich, M.A.Miliaiev, S.V.Nedukh et al., *Telecommun. Radio Engin.*, **73**, 749 (2014).
10. T.V.Kalmykova, S.I.Tarapov, S.V.Nedukh et al., *Functional Materials*, **19**, 14 (2012).
11. A.Moskaltsova, M.P.Proenca, S.V.Nedukh et al., *J. Magn. Magn. Mater.*, **374**, 663 (2015).
12. A.G.Anders, A.S.Vakula, S.I.Tarapov et al., *Telecommun. Radio Engin.*, **75**, 1849 (2016).
13. C.Haase, U.Nowak, *Phys. Rev. B*, **85**, 045435 (2012).
14. S.V.Vonsovskii, Magnetism, Science, Moscow 1032 (1971).
15. V.N.Krivoruchko, A.I.Marchenko, A.A.Prokhorov, *Low Temp. Phys.*, **33**, 433 (2007).
16. A.I.Marchenko, V.N.Krivoruchko, *Low Temp. Phys.*, **38**, 157 (2012).
17. V.N.Krivoruchko, A.I.Marchenko, *J. Magn. Magn. Mater.*, **324**, 3087 (2012).
18. R.Berger, J.Kliava, J.-C.Bissey et al., *J. Appl. Phys.*, **87**, 7389 (2000).
19. M.T.Causa, M.Tovar, A.Caneiro et al., *Phys. Rev. B*, **58**, 3233 (1997).