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Left-handed properties of manganite-perovskites $La_{1-x}Sr_xMnO_3$ at various dopant concentrations

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The experimental study of Double Negative (DNG) state of electromagnetic wave propagating in lanthanum manganite-perovskites doped with strontium $La_{1-x}Sr_xMnO_3$ is provided firstly below individual Curie temperatures (in ferromagnetic metal state (FM) for $La_{1-x}Sr_xMnO_3$). Various dopant concentrations are considered for ceramic specimens: $x = 0.15;\ 0.225;\ 0.3;\ 0.45;\ 0.6$. It is shown that dependence of the DNG-peak intensity on dopant concentration is sharply non-monotone with maximum at the dopant concentrations $x = 0.225 - 0.3$. This behaviour follows the change of Curie temperature with increase of dopant concentration in such substances. The obtained dependence of DNG peak intensity supports the opinion concerning the role of disorder in highly doped manganite-perovskite magnetic ceramics under study. © *2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4869310]

Manganite doped with rare earth elements and structured as perovskite (hereinafter manganite-perovskite) has attracted particular attention of researchers primarily because of inherent strong correlation between conductivity and magnetic ordering. This relationship appears as strong correlation between electric and magnetic properties of manganite-perovskite at change of dopant concentration x and is due mainly to the double-exchange mechanism between manganese ions of different valence (Mn^{+3} and Mn^{+4}). All these properties make it possible to relate the manganite-perovskites with many important practical applications, such as cathode materials for fuel cell elements, sensors, and elements with colossal magnetoresistance.[1–4] Note that metal-insulator transition and corresponding colossal magnetoresistance in these materials is considered now as a result of joint action of double exchange between related ferromagnetic Mn^{+3} and Mn^{+4} ions and Jahn-Teller effect.[5,17]

Left-handed materials or materials with negative refraction offer a wide range of interesting physical phenomena. One of the most exciting applications is a perfect lens. Usually to obtain left-handed properties a complex artificial system of thin metallic wires (negative permittivity) and arrays of split ring resonators (negative permeability) should be constructed.[6]

Some recent papers[7–11] contain information about controlled left-handed properties of doped manganite-perovskites at microwave wavelengths. The presence of these properties in natural substances, existing in our environment, with simultaneous possibility to control these left-handed properties by variations of specimen temperature and external applied magnetic field is of great theoretical and practical interest.

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We restrict ourselves below only with one type of the doped manganite-perovskites, namely strontium doped lanthanum manganites $La_{1-x}Sr_xMnO_3$. Some features of the manganite-perovskite ceramics with strontium dopant concentration $x = 0.225$ have been considered in detail in our previous papers.[8–11] There so-called DNG (Double Negative) state was detected and its evolution in the external applied magnetic field was studied.

It should be noted here that, according to the phase diagram presented in Ref. 2, (see Fig. 4 in Ref. 2) at dopant concentrations ($0.17 \leq x \leq 0.6$) the manganite-perovskites are ferromagnetic metals in wide temperature range. Since in the vicinity (above it) of the ferromagnetic resonance the magnetic permeability is known to be negative, the negative refraction appears at magnetic field close to the resonant value and the medium becomes left-handed.[9] Namely the metallicity provides a negative dielectric constant, and the proximity to the ferromagnetic resonance - a negative magnetic permeability. In,[8–11] it was shown that the manganite-perovskite $La_{1-x}Sr_xMnO_3$ (for $x = 0.225$) is really a left-handed medium at the frequency range of 20–40 GHz, at room temperature (its Curie temperature, T_C is near 350 K) and for certain values of external magnetic field.

The material parameters (its permittivity, permeability and refractive index) become negative, but close to unity by absolute value. As a result the intrinsic impedance of the left-handed structure $Z = \sqrt{\mu/\varepsilon}$ is close to the impedance of free space, and the structure shows the left-handed properties (namely – transparency and negative refraction).

It should be noted a significant difference between monocrystalline and ceramic materials. In the last the grain boundaries contribute significantly to physical properties, so the method of the sample manufacturing plays an important role. A carrier scattering at the grain boundaries is present in the case of ceramic samples, where very likely the modification of microscopic magnetic structure exists. Therefore the dynamic effects of the metal-nonmetal transitions and magnetotransport properties are significantly different in ceramic and monocrystalline samples. As about the static characteristics associated mainly with double exchange, they differ relatively little in monocrystalline and ceramic states. Therefore, as the estimation for ferromagnetic phase transition temperature, the Curie temperature, we can use values, obtained for monocrystalline samples in,[12] namely, ($x = 0.175, T_C = 283K$; $x = 0.2, T_C = 309K$; $x = 0.25, T_C = 342K$; $x = 0.3, T_C = 369$K; $x = 0.4, T_C = 371K$; $x = 0.6, T_C = 357K$). It is interesting to emphasize here the non-monotone dependence of the Curie temperature on x and the maximum of Curie temperature at the dopant concentration $x = 0.40$[12] (x = 0.31 in Ref. 17). Such behavior is connected with localization effect due to random impurity potential and the electron-lattice interactions.[12] The main reason of disorder and so of random impurity potential in doped manganite is first of all the variation of ionic radii on *La* site. Note that corresponding radius of La^{3+} is 0.136 nm and Sr^{2+} is 0.144 nm.

The purpose of the paper is to study the effect of various *Sr* dopant concentrations on propagation of electromagnetic waves (the DNG peak) through a ceramic sample. This experimental technique has been described firstly in,[8–10] the corresponding schemes are shown in Fig. 1.

Let us dwell on details of the employed experimental technique. The considered dopant concentrations are, respectively, $x = 0.15;\ 0.225;\ 0.3;\ 0.45;\ 0.6$. For details of ceramic specimens preparation see.[13,14] Specimens were formed as plates $7.2 \times 3.4 \times 0.5\,\text{mm}^3$ and placed in central part of standard one-mode waveguide shown in Fig. 1(a). The principal TE_{10} -mode propagates in such waveguide. The waveguide is located between poles of electromagnet and fitted to Network Analyzer NA 5210. The external magnetic field H_0 was directed normally to the h-vector of electromagnetic field, providing the excitation of Electron Spin Resonance in plane specimen.

Simultaneously we performed similar experiments with specimens shaped in the form of rectangular prisms with the same cross sections (Fig. 1(b)). We tended to verify the results of previous experiments carried out in the waveguide and to control the negative refraction in the left-handed state. The prism-shaped specimen was installed into the T-bridge, placed in such a way that the external magnetic field (H_0) was applied normally to the trigonal face of the prism. A sharp change in refraction took place after specimen's transition into left-handed state: the "beam" propagating initially in the "right channel" changed its direction to "left channel" (see Fig. 1(b)). (The transition took place at some definite (H_0) different for every dopant concentration).

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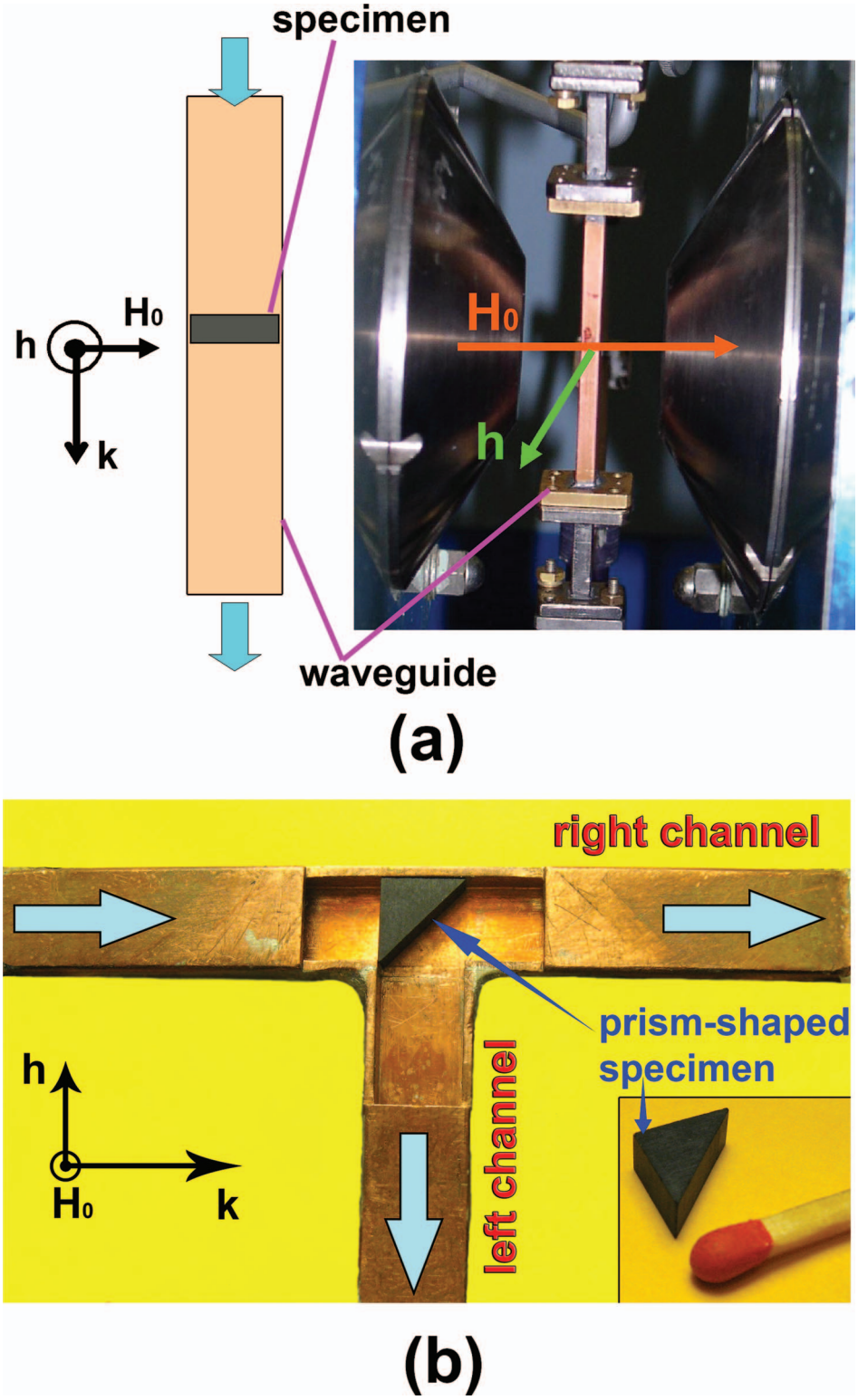

FIG. 1. Schemes of measurements the transmission for the: a) plate-shaped specimen and b) prism-shaped specimen (to check the left-handed refraction).

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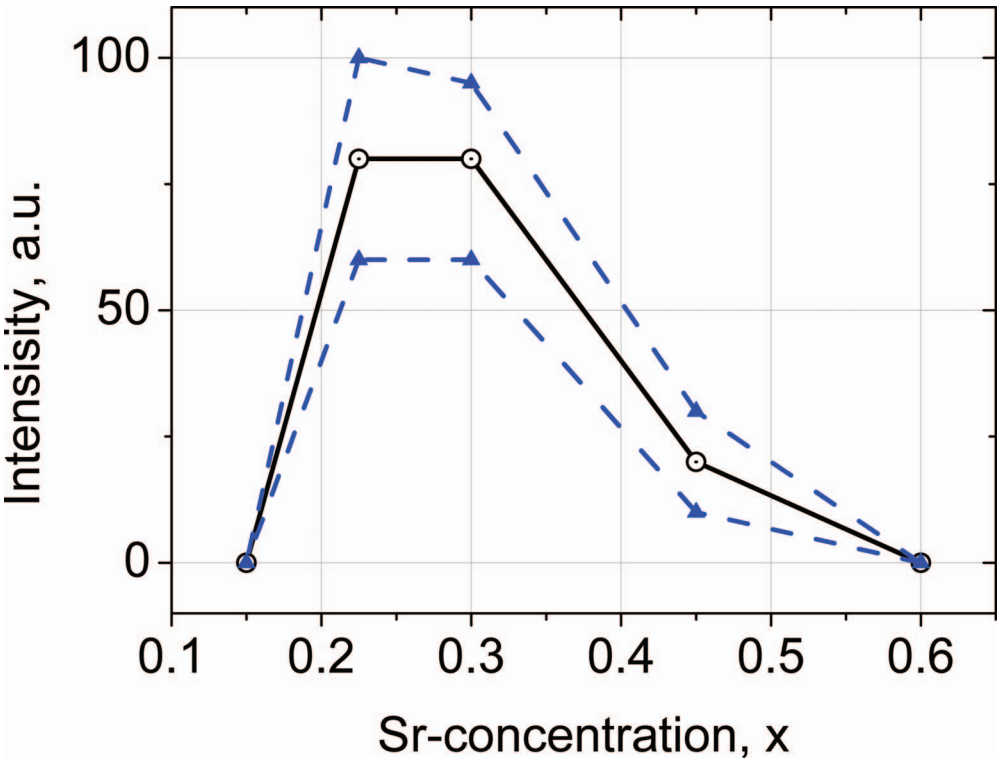

FIG. 2. Intensity of DNG peak (black solid) and its width (bounded with blue dashed lines) as a function of *Sr* concentration in ceramic samples (the temperature for all dopant concentrations should be below the corresponding Curie temperature (see above).

The experiments were performed at room temperature (in more correct way: the corresponding temperature should be far below Curie temperature of individual manganites). The spectra of the wave transmission coefficient through the sample (the DNG peak frequency positions) were measured.

We remind here that according to,[10] after transition of the material shaped as the rectangular prism to the left-handed state the microwave radiation changes its propagation direction (Fig. 1(b)) and begins to propagate not through the "right" but through the "left" channel of the device (T-junction waveguide). So the prism verifies if the DNG peak, detected in our experiments with plate samples, really corresponds to the left-handed state.

The obtained experimental DNG peak, as a function of dopant concentration is shown in Fig. 2.

At the lowest concentrations, $x = 0.15$, the DNG-peak in the spectra of the plates and prisms is absent because according to the phase diagram[2] at given concentration of the dopant (and temperature) the manganite-perovskite is a paramagnet insulator, i.e. the structure is a right-handed. With increase of dopant concentration the peak of DNG intensity (black solid line) increases too, reaches its maximum at $x = 0.225$–0.3 and then with further increasing of x the intensity of DNG peak and its width both decrease (see Fig. 2). The width of the DNG peak in Fig. 2 is bounded with two blue dashed lines. This behavior requires further study and may be due to less curved double exchange bonds $Mn^{3+} - O - Mn^{4+}$ in the system poorly doped with strontium which results in greater intensity of Zener double exchange. The ceramic structure in turn influences the width of the intensity peak.

Both the DNG peak and its width are decreasing with increase of x at high dopant concentrations due to the fact that with increase of x up to the boundary dopant concentration, $x = 0.6$, the localization of conduction electrons increases because of random impurity potential, and the structure transforms gradually into a magnetic bond-percolative ordered state.[12] (The strontium solubility values in the doped system are limited by $x \leq 0.6$). The DNG-peak (its transmittance) almost

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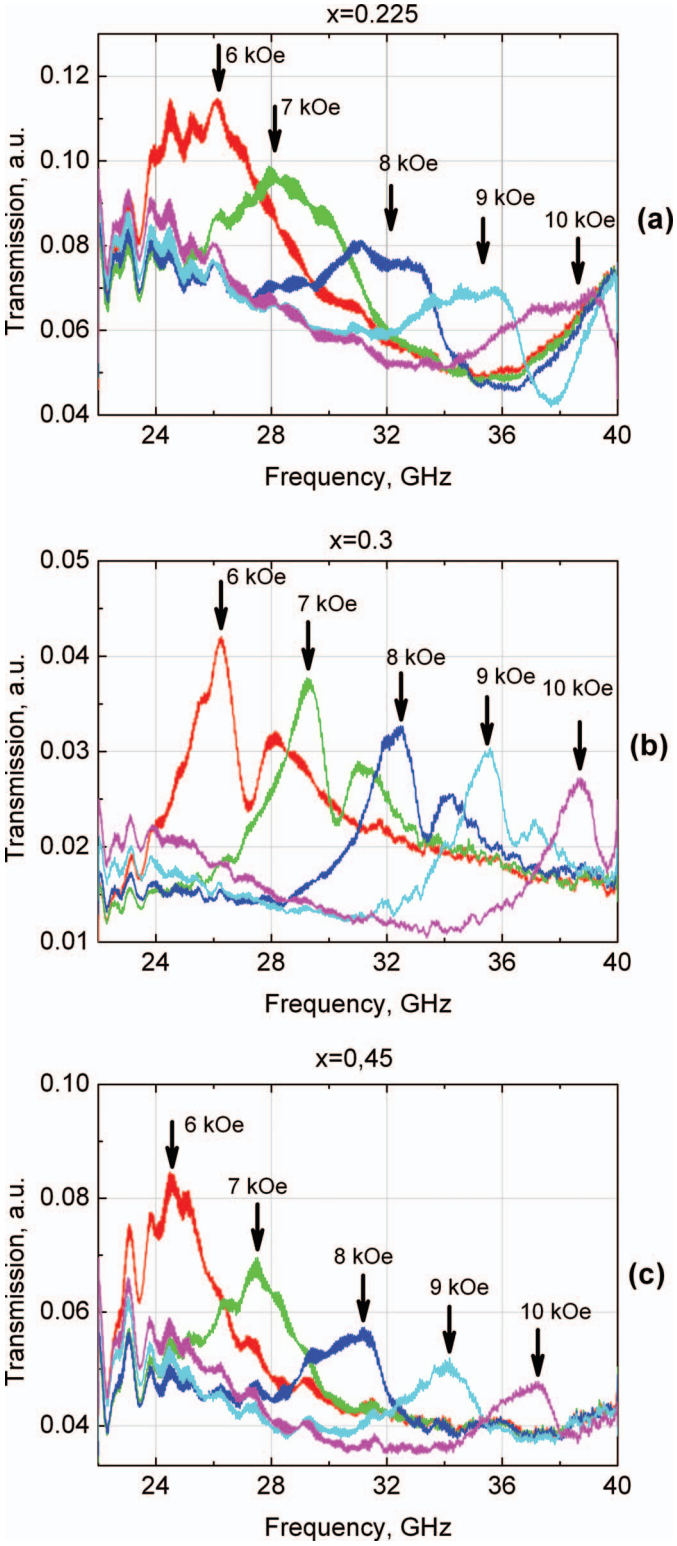

FIG. 3. DNG peaks evolution versus the frequency (corresponding dopant concentrations are (a) - $x = 0.225$; (b) - $x = 0.3$; (c) - $x = 0.45$) for different values of magnetic fields. DNG peaks are marked with arrows. The magnetic field strength is shown nearby by the arrows.

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disappears at the boundary concentration, so that only weak absorption peak remains in the spectrum. The last is easily identifiable as known peak of Electron Spin Resonance.

The same considerations can be applied to the samples in the form of a prism.

We present below some characteristic spectra (Fig. 3) showing the evolution of the DNG-peaks for ceramic manganite-perovskite samples with different dopant concentrations ($x = 0.225$,(a); $x = 0.3$(b); and $x = 0.45$(c)) in the external applied magnetic field.

The electromagnetic wave transmission coefficients are presented in Fig. 3. DNG peaks are marked with arrows. The spectral evolution (together with evolution of the DNG peak) with increase of external magnetic field is shown in Figs. 3(a)–3(c). It should be noted here that DNG peak is located near the FMR resonance line (above it) where the permeability is negative. So it shifts together with FMR line towards high frequency area when the external applied magnetic field increases. Different colors in Figs correspond to different values of applied magnetic field. We can see here that with increase of magnetic field the DNG peak really shifts towards higher frequency area.

I. SUMMARY

1. The paper studies the propagation of EHF electromagnetic waves in ferromagnetic phase of lanthanum manganite $La_{1-x}Sr_xMnO_3$ doped with strontium ($x = 0.15;\ 0.225;\ 0.3;\ 0.45;\ 0.6$) and structured as perovskite ceramics. In particular an experimental study of temperature and dopant concentration of the Double Negative (DNG) state in these substances is provided here for the first time.

A characteristic feature of the electronic system of manganites is the essential spin polarization of conduction electrons connected first of all with the double-exchange. We can speak about strongly correlated electron system governed by double-exchange interaction and Jahn-Teller electron-lattice coupling.[1,2,16,17] For lanthanum manganites doped with strontium there exists the range of dopant concentrations where the substance is a ferromagnetic metal,[2] the properties of the metal is strongly dependent on dopant concentration.

The dependence of Curie temperature T_C has non-monotone character with maximum in the range of dopant concentrations equal to 0.3–0.4 (x = 3/8 see,[15] x = 0.31 see[17]). At further increase of dopant concentration the Curie temperature decreases and above 0.6 the phase of ferromagnetic metal disappears. Such non-monotone dependence of the Curie temperature is connected with increasing disorder followed with increase of dopant concentration. The distinction in ionic radii of La^{3+} (r= 0.136 nm) and Sr^{2+} (r = 0.144 nm) plays the special role.

2. As it was pointed earlier in the papers[8–11] (dopant concentration x = 0.225), the appearance of the DNG peak with simultaneous negativity of both characteristic quantities (its permittivity ε and its permeability μ) is a special feature of EHF electromagnetic waves propagating in *Sr* doped lanthanide ceramics. The medium became left-handed with new distinctive refraction properties. These new left-handed characteristics observed in natural substances are very important for numerous potential applications.

In present paper we determined both DNG peak intensity variation depending on different dopant concentrations (Fig. 2) and the dependence of DNG peak frequency position on the magnitude of applied magnetic field (Fig. 3). It was shown that maximal intensity of DNG peak corresponds to the dopant concentration equal to $x = 0.225$-0.3. The nonmonotonic behavior of DNG peak intensity is connected with disorder caused by increasing dopant concentration.

The results obtained in the paper extend essentially the area of applicability of these very interesting materials to the EHF range.

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