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Electromagnetic Parameters Of Multicomponent Manganites Depending On Combination And Electronic Configuration Of Substituents For Manganese

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Abstract
New data on the properties ofmanganites withpaired substitution of ($Me^{2+}_{0.5}Ge^{4+}_{0.5}$) for $Mn^{3+}$and mono - substitution of Me^{2+}, Ga^{3+} ($3d^{10}$), Ge^{4+} ($3d^{10}$) are reported. Here Me^{2+}=Mg^{2+} ($2p^6$), Zn^{2+} ($3d^{10}$), Ni^{2+} ($3d^8$). ($Zn^{2+}_{0.5}Ge^{4+}_{0.5}$) - contained manganites have the highest values of magnetoresistance (MR), "metal - semiconductor" transition temperature, Curie point, and narrowest temperature interval of "ferromagnetic - paramagnetic" transition.Electromagnetic parameters of Mg^{2+} - contained compositions are considerably poorer than parameters of manganites with 3d substituents. Antiferromagnetic interaction of Ni^{2+} ion with the environment leads to the decrease of above mentioned parameters in comparison with the effect of diamagnetic Zn^{2+}. The results obtained will be meaningful for understanding ways to increase operating parameters of manganites.

Keywords: manganite, combined substitution, germanium, zinc, nickel, magnesium, gallium, electron configuration, colossal magnetoresistance, phase transitions.

1.Introduction
Manganites having colossal magnetoresistance (CMR) are currently considered as perspective functional materials for electronics [1, 2]. The required operational parameters can be achivedin manganites of complex compositions only, which are usually developed on the basis of La - Sr manganite with substitutions for Mn.
The processes of properties formation in manganites are concerning with the presence and concentration of different - valence ions, their electronic configuration, radii and localization, electron exchange [3 - 5], interaction with atmospheric oxygen [6 - 8].Magnetic and electrical parameters of manganites are mainly determined by double exchange interaction and transfer of e_g electrons between neighboring heterovalent ions Mn^{3+} and Mn^{4+}, carriers concentration, Jahn - Teller effect of Mn^{3+} ions [4 - 6].Divalent and quadrivalent ions in manganites ensures doping of different (*p* - and *n* -) types, decreases Jahn - Teller distortions, but can break or modify the double - exchange and super - exchange bonds [4, 8, 9].
In the number of works the effects of substituting divalent (Mg^{2+}, Zn^{2+}, Ni^{2+}) [9 - 11] and quadrivalent ions (Ge^{4+} [12 - 14], Ti^{4+} [14 - 16]) at Mn sites, as well as combined substitution of (Ni^{2+}+Ti^{4+}), (Mg^{2+}+Ti^{4+}) for $2Mn^{3+}$ [8, 17, 18], on phase composition, magnetic and electrical properties of La - Sr manganites have been investigated.Reported results [17, 18] showed that combined substitution can promote the formation of clusters and inhomogeneities[4, 12] enriched with the pairs of different valence cations and characterized by various crystallographic and magnetic parameters.
The purpose of this work is to establish the influence of electronic configuration of Me^{2+}ions on "semiconductor - metal" transition, magnetoresistance and Curie point in pared substituted manganites $La_{1-c}Sr_cMn^{3+}_{1-c-x-2g}Mn^{4+}_{c+2g}(Me^{2+}_{0.5}Ge^{4+}_{0.5})_xO_{3+g}$in comparison with mono - substituted manganites$La_{1-c}Sr_cMn^{3+}_{1-c-x-2g}Mn^{4+}_{c+2g}(Ga^{3+})_xO_{3+g}$, $La_{1-c+x}Sr_{c-x}Mn^{3+}_{1-c-x-2g}Mn^{4+}_{c+2g}(Me^{2+})_xO_{3+g}$, $La_{1-c-x}Sr_{c+x}Mn^{3+}_{1-c-x-2g}Mn^{4+}_{c+2g}(Ge^{4+})_xO_{3+g}$ having the same values of "x" and "c", where Me^{2+}=Mg^{2+} ($2p^6$), Zn^{2+} ($3d^{10}$), or Ni^{2+} ($3d^8$). Spin magnetic moment of Ni^{2+} is equal to $2\mu_B$, the others Me^{2+}ions are diamagnetic; Ga^{3+} and Ge^{4+} have electron shells $3d^{10}$. The values of "c" were chosen in the region of wittingly rhombohedral ferromagnetic metallic phase with high Curie point established for $La_{1-c}Sr_cMnO_3$ system ($0.175<c<0.35$) [3, 4].The work also examines the role of oxygen content.
The study and comparison of above - mentioned substituents effects would be interestingfor theunderstanding of howto control the propertiesof manganites.

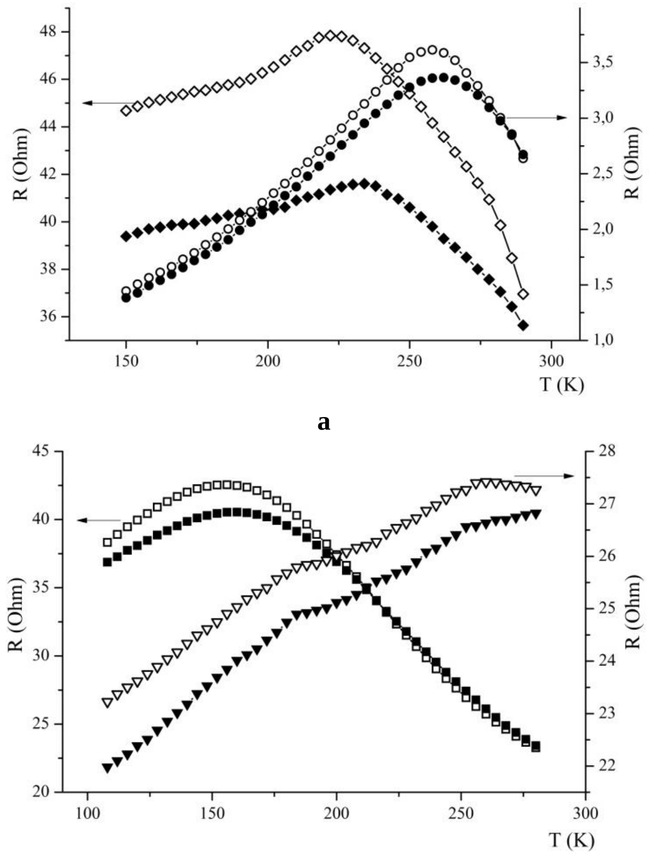
2.Experimental
The experiments were performed on polycrystalline samples synthesized by conventional ceramic processing. The initial components (dried powders of La_2O_3, $SrCO_3$, MnO_2, Ga_2O_3, GeO_2, MgO, ZnO, NiO), taken in corresponding stoichiometric proportions, were subjected to joint grinding and mixing (with the addition of ethanol) in a ball mill for 4 h. The dried and briquetted mixture was preliminarily baked at 1273 K for 4 h. This operation was followed by a second grinding for 10 h, drying, introduction of a binder (polyvinyl alcohol), granulation, pressing the samples, and the burning out the binder. Sintering was performed in air at 1473 K, and the duration of isothermal holding was 10 h. The samples were cooledalong with the furnace. From the previously obtained data [6, 11, 14] it might be inferred that sintered manganites had an excess of oxygen content (g>0).
In order to provide stoichiometric oxygen content (g=0), sintered samples were annealed in vacuum (partial oxygen pressure 10^{-1} Pa) at 1223 K for 96 h. The validity of these annealing conditions is based on the data in [6], according to which the state ofmanganites$La_{1-c}Sr_cMnO_{3+g}$close to oxygen stoichiometry was attained under the abovementioned conditions, irrespective of composition, over a broad range of the temperatures and pressure.
Measurements of dc electrical characteristics and magnetoresistance (MR= (R (H) - R (0))/R (H)) were made in the temperaturerange 100 - 290 K using copper electrodes sputter - deposited onto opposite planes of pellets (thickness

of about 4 mm). Magnetic field (H=9, 2 kOe) was parallel to the current direction. The temperature dependence of magnetic permeability (μ (T)) was measured by the induction method at a frequency of 98, 6 kHz. The Curie point (T_c) was determined as the temperature corresponding to the maximum of │dμ/dT│.

3.Results and discussion

Figure 1 illustrates temperature dependences of the resistivity of (Ni, Ge) - , (Mg, Ge) - and Ge - substituted manganites (NGM, MGMand GM, correspondingly) with c=0.19 (a) and c=0.30 (b), measured in the absence and in the presence of magnetic field.

As Figure 1 (a) displays, substitution of $Ni^{2+}$for the half amount of Ge^{4+} ions in manganite with maintained the same value of Mn^{4+} concentration (0.19 formula units, f.u.) leads to decrease of the “metal - semiconductor” transition temperature (T_{ms}). Comparison of the curves on figure 2 (b) make it possible to conclude that (Ni, Ge) - substituted manganites are characterized by essentially higher T_{ms} than analogous compositions with (Mg, Ge).



b

Fig. 1. Temperature dependencies of the resistivity of initial (sintered) manganites in the absence of magnetic field (light symbols) and at magnetic field of 9.2 kOe (black symbols): ○, ● - $La_{0,71}Sr_{0,29}Mn_{0,90}Ge_{0,10}O_3$; ◇, ◆ - $La_{0.81}Sr_{0.19}Mn_{0.90}$ $(Ni_{0.5}Ge_{0.5})_{0.10}O_3$ (a) and ▽, ▼ - $La_{0.70}Sr_{0.30}Mn_{0.90}$ $(Ni_{0.5}Ge_{0.5})_{0.10}O_3$; □, ■ - $La_{0.70}Sr_{0.30}Mn_{0.90}$ $(Mg_{0.5}Ge_{0.5})_{0.10}O_3$ (b)

It is interesting to note that manganite $La_{0,80}Sr_{0,20}Mn_{0,90}Ni_{0,10}O_3$, with the same values of substituent and Mn^{4+} concentrations (0.10 and 0.30 f.u., correspondingly), has semiconducting type of conductivity at T≥100 K. For $La_{0.70}Sr_{0.30}Mn_{0.90}$ $(Zn_{0.5}Ge_{0.5})_{0.10}O_3$ manganite (ZGM) T_{ms}≈300 K.

Magnetic field shifts the “metal - semiconductor” transition towards higher temperatures and decreases the resistance (with the exception of the sample MGM at T>210 K and GM at T>285 K).

Table 1 summarizes the data on T_{ms} and Curie point of mono - and paired substituted manganites with c=0.19 (compositions numbers 1 - 3) and c=0.30 (numbers 4 - 8).

Table 1.Comparison of the temperatures of phase transitions “metal - semiconductor” and “ferromagnetic - paramagnetic” for mono - and paired - substituted initial samples of manganites

Number of composition	Chemical composition	T_{ms}, K	T_c, K
1	$La_{0.71}Sr_{0.29}Mn_{0.90}Ge_{0.10}O_3$	258	256
2	$La_{0.81}Sr_{0.19}Mn_{0.90}$ $(Ni_{0.5}Ge_{0.5})_{0.10}O_3$	224	253
3	$La_{0.81}Sr_{0.19}Mn_{0.90}Ga_{0.10}O_3$	<100	198
4	$La_{0.80}Sr_{0.20}Mn_{0.90}Ni_{0.10}O_3$	<100	240
5	$La_{0.70}Sr_{0.30}Mn_{0.90}$ $(Mg_{0.5}Ge_{0.5})_{0.10}O_3$	155	167
6	$La_{0.70}Sr_{0.30}Mn_{0.90}Ga_{0.10}O_3$	200	259
7	$La_{0.70}Sr_{0.30}Mn_{0.90}$ $(Ni_{0.5}Ge_{0.5})_{0.10}O_3$	262	212
8	$La_{0.70}Sr_{0.30}Mn_{0.90}$ $(Zn_{0.5}Ge_{0.5})_{0.10}O_3$	300	267

As follows from the table, at low concentrations of strontium (and Mn^{4+}, respectively), especially in mono - substituted by Ga or Ni manganites, the Curie point is higher than T_{ms}, but at high content of strontium T_{ms}>$T_c$in NGM and ZGM. (Zn, Ge) - contained manganites have the highest values of T_{ms}, T_c ; germanium - substituted manganites are slightly inferior to them.

As it may be noted from the temperature dependencies of magnetic permeability (Fig. 2), temperature interval of phase transition in ZGM (initial and annealed samples) isthe most narrow as compared with that of other manganites; it’s even narrower than interval of corresponding composition with isovalent substitution of $Ga^{3+}$for Mn^{3+}. MGM has the widest transition and lowest Curie temperature.After annealing, Curie point of ZGM dropped by 5 degrees.

Characteristic temperature dependences of magnetoresistance are shown on Figure 3 for the same compositions as the curves on Fig.2.

Maximum absolute value of negative magnetoresistance reaches 42% at 194 K in initial ZGM. After annealing, the maximum value of |MR| decreases. In unitial MGM and annealed Ga - substituted manganite it is possible to receive a small positive magnetoresistance in the range of 3 %.

On the whole, |MR| exhibits a tendency to increase with decreasing temperature, that is associated with the tunneling of spin - polarized electrons across grain boundaries [4]. At the same time, as follows from comparison of the dependences shown on Fig. 2 and Fig. 3, the correlation between magnetoresistance and “ferromagnetic -

paramagnetic" transition is not observed, although it is usually assumed that the local maximum of |MR| is achieved near T_c [3, 4].

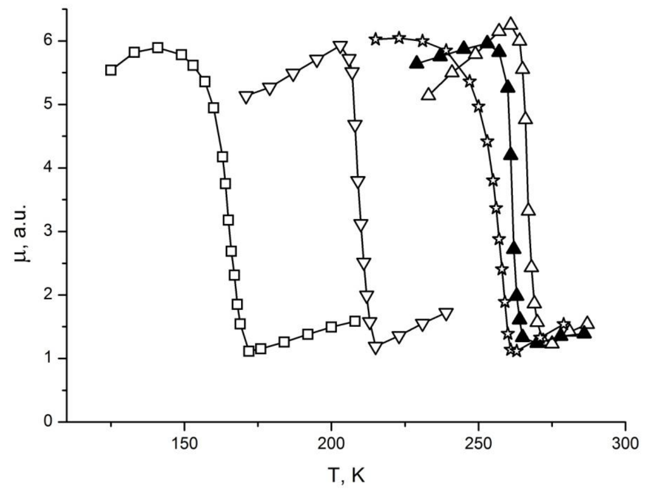


Fig.2. Temperature dependencies of the magnetic permeability of initial (light symbols) and annealed (black symbols) manganites: △, ▲ - $La_{0.70}Sr_{0.30}Mn_{0.90}(Zn_{0.5}Ge_{0.5})_{0.10}O_3$; ☆ - $La_{0.70}Sr_{0.30}Mn_{0.90}Ga_{0.10}O_3$; ▽ - $La_{0.70}Sr_{0.30}Mn_{0.90}(Ni_{0.5}Ge_{0.5})_{0.10}O_3$; □ - $La_{0.70}Sr_{0.30}Mn_{0.90}(Mg_{0.5}Ge_{0.5})_{0.1}O_3$

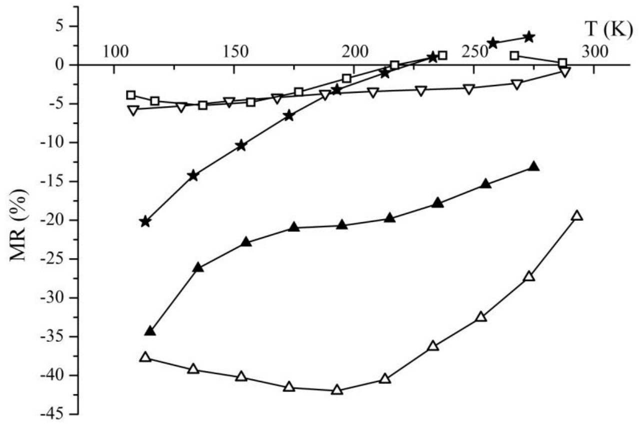


Fig.3. Temperature dependencies of the magnetoresistance of initial (light symbols) and annealed (black symbols)manganites: △, ▲ - $La_{0.70}Sr_{0.30}Mn_{0.90}(Zn_{0.5}Ge_{0.5})_{0.10}O_3$; ★ - $La_{0.70}Sr_{0.30}Mn_{0.90}Ga_{0.10}O_3$; ▽ - $La_{0.70}Sr_{0.30}Mn_{0.90}(Ni_{0.5}Ge_{0.5})_{0.10}O_3$; □ - $La_{0.70}Sr_{0.30}Mn_{0.90}(Mg_{0.5}Ge_{0.5})_{0.10}O_3$

4. Conclusion

New data concerning the influence of paired substitution of $(Zn^{2+}+Ge^{4+})$, $(Ni^{2+}+Ge^{4+})$ and $(Mg^{2+}+Ge^{4+})$ in comparison with substitution of Ca^{3+}, Ge^{4+} and Ni^{2+}on the properties of La - Sr manganites are obtained.

(Zn, Ge) - contained manganites have essentially higher values of magnetoresistance, "metal - semiconductor" transition temperature, Curie point, and narrowest temperatureinterval of "ferromagnetic - paramagnetic" transition.Their magnetic structure can be considered as most homogeneous.

Broadening of the transition interval can be associated with the formation of clusters due to the difference of charges and radii of the ions, Coulomb interaction and mechanical stresses [17, 18]. This process is most pronounced in (Mg, Ge) - substituted manganites, as in (Mg, Ti) - contained compounds [18].

From the data obtained it might be inferred that electromagnetic parameters of Mg^{2+} $(2p^6)$ - contained compositions are considerably lower than these parameters of manganites with 3d substituents, although ionic radii are correlated as follows: $R_{Ni2+}<R_{Mg2+}<R_{Zn2+}$ [19]. The presence of the spin moment of Ni^{2+} $(3d^8)$ ion entering the antiferromagnetic interaction with the environment, leads to the decrease of T_{ms}, $T_c$and |MR|in comparison with the effect of diamagnetic Zn^{2+} $(3d^{10})$.

It is interesting to note that, despite the fact that the average ionic radius of $(Zn^{2+}{}_{0.5}Ge^{4+}{}_{0.5})$ is greater than the radius of Ga^{3+}, magnetic and electrical parameters of Ga - substituted manganite are lower. This effect can be explained taking into account that the radii of Ge^{4+} and Mn^{4+} are identical [19], and at paired substitution of $(Me^{2+}{}_{0.5}Ge^{4+}{}_{0.5})$ for $Mn^{3+}$the amount of divalent ions, shielding Mn^{4+}, is lessin 2 times than the number of ions Ga^{3+}at the same level of substitution.

The data obtained are of interest from the viewpoint of designingmanganites with high magnetic and electrical parameters.

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