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Application of the heterophase structure — effective medium method for determining the electrical properties of a granular solid

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Granular compounds consisting of conductive micro or nano inclusions located in a dielectric matrix exhibit a number of unusual properties, the origin of which is directly related to the ratio of conductive and non-conductive bulk phases. In the present work, to predict the electrical properties of a granular solid based on manganite $La_{1-x}A_xMnO_3$ (where A is a divalent element), an approximation model of a heterophase structure — effective medium has been adapted, which essentially represents a synthesis of the effective medium method and the percolation theory. Analysis of transport behavior within the framework of this model showed that the effective electrical conductivity of the granular medium increases significantly with an increase in the proportion of the volume occupied by the core of the granule relative to the volume of the intergranular space and the surface layer. The results obtained in the work are in good agreement with the experimental data for ceramic samples of manganite $La_{1-x}A_xMnO_3$.

Keywords: granular solid, electrical conductivity, manganites, effective medium.

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1. Introduction

In recent years, considerable attention has been paid to the study of the properties of composite materials with inclusions of metal or semiconductor granules in a dielectric matrix [1,2]. The interest in these materials is attributable to the possibility of solving both fundamental problems of solid state physics and the prospects for practical application in modern electronic technology. The granules are electrically isolated from each other in the matrix volume in composites with a low concentration of the conductive phase. Therefore, the electrical conductivity in such materials will mainly be determined by the dielectric component. Granular components made of ferromagnetic particles in a dielectric matrix have a number of unique physical properties: giant and tunneling magnetoresistance, a wide range of changes in the magnitude of electrical resistance, etc. [2–18].

In this regard, compounds with the effect of colossal magnetoresistance are of interest, in particular, manganites with a perovskite structure of the type $La_{1-x}A_xMnO_3$, where A is a divalent element (Ca, Ba, Sr, and etc.), in which the phase separation of the initial substance forms a two-phase state with isolated metal granules in the matrix [9]. A strong interaction of the electron and spin subsystems with the crystal lattice takes place in such systems, which demonstrates the manifestation of unusual magnetic, electrical, optical and elastic properties. Concentration of element A can vary from 0 to 1, while the physical properties of manganites greatly vary. The system undergoes a chain of phase transitions with various types of ordering: magnetic, structural, electronic. Most anomalies of physical properties in these composites are observed at the concentration of the metal phase near the percolation threshold, when metal granules form a conductive cluster structure in the dielectric matrix [19]. Therefore, studies of the electrical and structural properties of composites based on ferromagnetic alloys in a dielectric matrix represent the prospect of solid state physics, physical electronics and materials science.

Well-known mathematical methods for describing the effective properties of multiphase media are currently based on the theory of homogenization [20–24]. Initially, micromechanical analysis was considered within the framework of this theory to determine static effective properties such as elastic modulus, magnetic and dielectric permittivity [25–28]. However, new multiscale approaches have been proposed for composite media in terms of elementary volume. Similar approaches include the „sphere assembly model“, in which the matrix area is filled with spheres of different sizes retaining the volume ratio between phases [29,30]. In the „self-consistency method“ model the inhomogeneities of the medium are represented by ellipsoidal or cylindrical inclusions with unknown elastic properties inside an infinite matrix space [25,31,32]. Most applications of homogenization theory are effectively adapted for porous [33], cellular [34,35] and fibrous [36]. At the same time, the use of these approximation schemes to describe the electrical conductivity of granular composites seems limited [37,38], which may suggest the absence of a more convenient method for studying similar systems with different granule materials.

The possibility of studying electrical properties and their regularities is demonstrated using the example of a typical granular manganite $La_{1-x}A_xMnO_3$ in this paper. We quantified the electrical properties using the approximation model heterophase structure- effective medium (HSEM), which is a synthesis of the effective medium method and flow theory. The previously proposed approach using the HSEM method makes it possible not only to predict the transport behavior of complex composites, but also to characterize the thermophysical and thermoelectric properties near polymorphic and superconducting junctions [39].

2. Analysis of experimental results in the framework of the HSEM model

The effective resistivity ($\rho = 1/\sigma$, where σ — specific conductivity) has the following form according to the HSEM model [39,40]:

$$\rho = \Sigma\Delta_i\rho_i f_i/\Sigma\Delta_i f_i, \tag{1}$$

where $f_i = 3\rho/(A_i\rho + (3 - A_i)\rho_i$, i — phase number, Δ_i — relative phase volume, A_i — coefficient taking into account the configuration of phase inclusions. A filamentary configuration of inclusions (parallel connection) occurs with coefficient $A_i = 0$, spherical inclusions occur with $A_i = 1$, layered configuration of inclusions (serial bonding) occurs with $A_i = 3$.

Data on the dependence of the resistivity ρ at 100 K on the diameter of the granules for ceramic samples of $La_{2/3}Sr_{1/3}MnO_3$ from Ref. [8] are used as a specific example of the application of this approximation model. The sizes of granules in this ceramic varied from 20 nm to 10 μm with a same Curie temperature $T_C \sim 352$ K for all compositions, which suggested their single-domain state.

The designations d, V_g, V_{gt}, V_3 and t in the figure (a) are given in the text. The formation of a magnetic tunnel barrier for granules of large (micron) sizes is shown in the figure (b). The vertical arrows indicate the magnetic moments for the single-domain core structure of the granules.

The manganite compounds of $La_{1-x}A_xMnO_3$ type consist of three phases: the surface layer of the granule, the core of the granule and the intergranular space [41,42]. The surface layer of the granule is a dielectric shell in contact with the intergranular space. The core of the granule is characterized by a metallic nature with preferably ferromagnetic ordering. A visual representation of a similar granular system is provided in Figure 1, *a*.

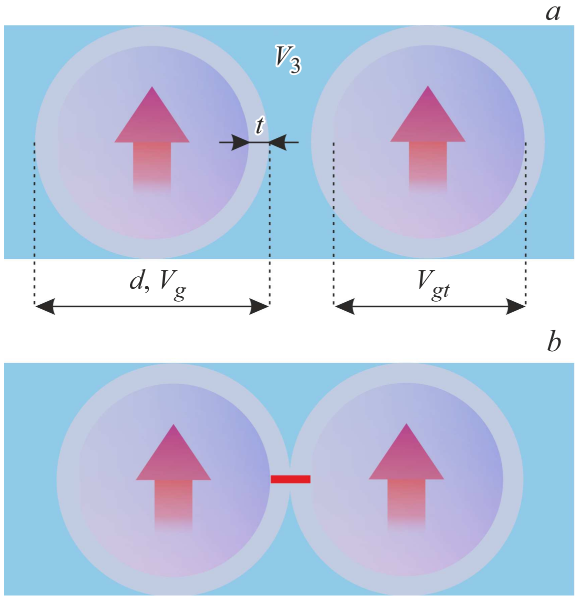

Figure 1. Schematic representation of the granular structure of manganite.

The resistivity for the granulated structure under study can be written as follows according to the expression (1):

$$\rho = (V_1\rho_1 f_1 + V_2\rho_2 f_2 + V_3\rho_3 f_3)/(V_1 f_1 + V_2 f_2 + V_3 f_3), \tag{2}$$

where are the subscripts (1, 2, 3) at V_i, ρ_i, f_i correspond to the phases: near-surface layer — 1, core of the granule — 2, intergranular space — 3. The product $\rho_3 f3 = 3/[A_3\sigma_3 + (3 - A_3)\sigma]$ for $\rho_3 \to \infty$ is equal to: $\rho_3 f_3 = 3\rho/(3 - A_3)$. The expression for the effective resistivity is written as follows:

$$\rho^{eff} = (\rho_1\Delta_1 B_2 + \rho_2\Delta_2 B_1)/(\Delta_1 B_2 + \Delta_2 B_1) + (\Delta_3 B_1 B_2)/[(3 - A_3)(\Delta_1 B_2 + \Delta_2 B_1)], \tag{3}$$

where $B_1 = A_1\rho + (3 - A_1)\rho_1$ and $B_2 = A_2\rho + (3 - A_2)\rho_2$.

The volume of the cube into which the granule is placed is defined as $V_d = d^3$ (d is the diameter of the granule). The volume of a granule with a near-surface layer V_g, the volume of a granule without a near-surface layer V_{gt} and the volume of the intergranular space V_3 are equal, respectively:

$$V_g = (4/3)\pi \cdot (d/2)^3,$$
$$V_{gt} = (4/3)\pi \cdot [(d - 2t)/2]^3,$$
$$V_3 = V_d - V_g, \tag{4}$$

where t is the thickness of the surface layer of the granule.

The relative volumes of the phases of the near-surface layer Δ_1, the core of the granule Δ_2 and the intergranular space Δ_3, respectively, have the form:

$$\Delta_1 = (V_g - V_{gt})/V_d,$$
$$\Delta_2 = V_{gt}/V_d,$$
$$\Delta_3 = (V_d - V_g)/V_d. \quad (5)$$

The thickness of the near-surface layer can be defined as follows based on equations (2)−(5):

$$t = (1/2)[1 - (\gamma/\alpha)^{1/3}]d, \quad (6)$$

where the parameters α and γ are defined as

$$\alpha = (4/3)\pi \times [B2(\rho - \rho_2) - B_1(\rho - \rho_1)]$$

and

$$\gamma = [8 - (4/3)\pi] \times [(B_1 B_2)/(3 - A_3)] - (4/3)\pi B_1(\rho - \rho_1),$$

respectively. The thickness of the surface layer of the granule is $t \approx 0.03d$ with $\rho 1 \gg \rho \gg \rho_2$. The degree of influence of the granule size of a structured solid is determined by the morphology of the granule surface and the ratio between the volumes of the core of the granules and the surface layer. The characteristic parameters of a granular solid include the ratio of the volume of the near-surface layer to the volume of the core of the granule:

$$\Delta = (V_g - V_{gt})/V_{gt} = (\alpha/\gamma) - 1 = [d/(d - 2t)]^3 - 1. \quad (7)$$

The dependences of the relative volume of the phase Δ and the thickness of the surface layer of the granule t on the diameter of the granule shown in Figure 2 are calculated based on the experimental data obtained for ceramic samples of manganite $La_{2/3}Sr_{1/3}MnO_3$ [8] and using the above ratios (6) and (7). The obtained values of the thickness of the near-surface layer in our case ranged from 2.3 to 6.3 nm with an increase of d from 20 nm to 1 μm, respectively, which satisfies the range of experimentally observed data for manganites (from 1 to 5 nm [41]), depending on their composition and synthesis conditions. The relative volume of the phase begins to decrease by 2.5 times with an increase of d from the nano-to submicron scale, suggesting that the conductivity in this case should improve. It is worth considering that the conductive properties of manganites consisting of large (micron) granules can also be determined by the impact of intergranular contact phenomena in addition to the ratio of the parameters Δ and t. In this case, the near-surface layers of granules will act as a tunnel barrier between the conductive cores, thereby forming a magnetic tunnel junction in the contact area (Figure 1, *b*). However, depending on the proximity of the tunnel contacts, that is, the degree of „indentation“ of the surface layers, there is a high probability of a transition from the tunneling to the metallic type of conductivity, whereas for nano-sized granules, semiconductor (insulating) will be more characteristic the type of conductivity.

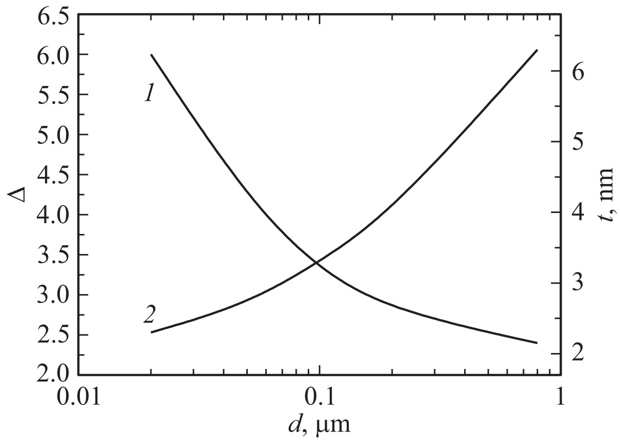

Figure 2. Calculated dependences of the relative volume of the phase Δ (1) and thickness of the surface layer of the granule t (2) on diameter of the granule d.

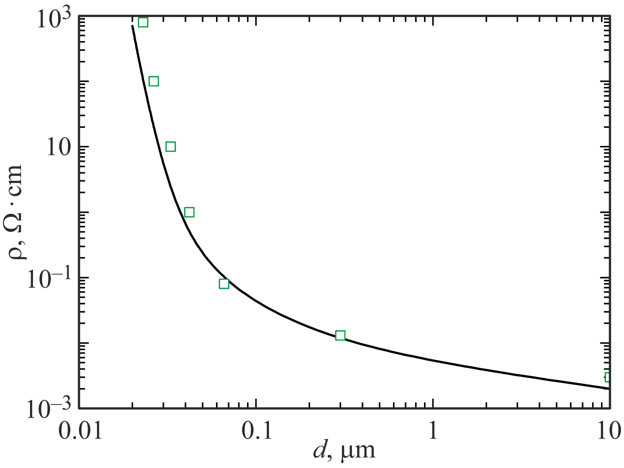

Figure 3. Calculated dependence of resistivity on granule diameter for granular composites (solid line), and experimental data of resistivity on diameter d granules (symbols) for ceramic samples $La_{2/3}Sr_{1/3}MnO_3$ [8].

Figure 3 shows the calculated dependence of the resistivity ρ of a granular composite on the diameter of granules in the range of 0.01−10 μm, as well as the data of dependence $\rho(d)$ for $La_{2/3}Sr_{1/3}MnO_3$ ceramic samples taken from Ref. [8]. The behavior of the resistivity with a change of the diameter of the granules shows an almost three orders of magnitude change of ρ as follows from this dependence. This also suggests that the effective conductivity of the system will increase for larger granules due to the formation of percolation chains. In addition, the dependence $\rho(t)$ shows similar behavior, as follows from Figure 4. Similarly, the authors consider the intergranular resistance R_g in Ref. [8], which is an increasing function depending on t, and is related as $R_g \sim t\varphi^{1/2}$ and $\varphi = 0.3$ V (φ — height of the barrier layer). However, it is impossible to compare the results of our calculations with the experimental dependence $R_g(t)$ due to the limited data

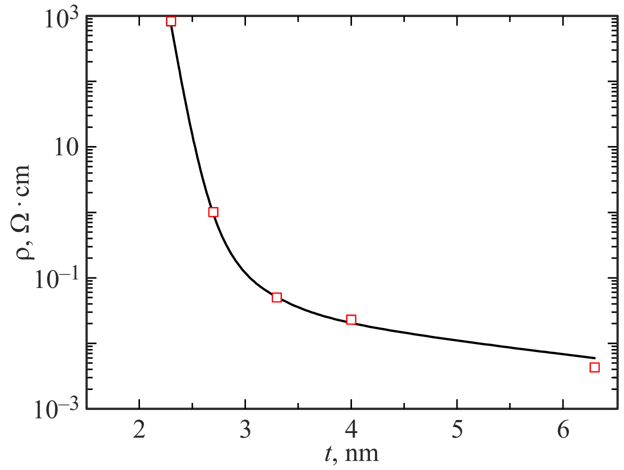

Figure 4. Calculated dependence of resistivity on surface layer thickness for granular composites (solid line), presented together with experimental data (symbols) for $La_{2/3}Sr_{1/3}MnO_3$ ceramic samples [8].

set of $t < 1.5$ nm. It should be noted that the predicted behavior of the resistivity dependence on d, within the framework of the HSEM model, is in good agreement with experimental results, which once again indicates the effectiveness of this model.

3. Conclusion

We would like to note in conclusion that the use of the approximation model of the HSEM, using the example of a granular composite $La_{2/3}Sr_{1/3}MnO_3$, showed that with an increase of the diameter of the granules and a decrease of Δ, i.e. the greater the proportion of the volume occupied by the core of the granule relative to the volume of the surface layer, the greater the effective electrical conductivity of granular composites. The obtained dependences $V_t(d)$ and $t(d)$ can be used not only for determining the electrical properties of a wide class of manganites of $La_{1-x}A_xMnO_3$ type, but also for many other granular media of „core–shell" type [43,44].

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