Strain-Dependent Resistivity of Granular Manganite Systems: A Simple Quantitative Approach

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Abstract: The effects of an applied strain tensor on the electrical resistivity of a manganite granular system are investigated using a simple approach describing the induced deformation in terms of the tilt angle between adjacent grains. The results obtained assuming the resistivity of each grain as given by a metallic part, coming from the inner grain, and a surface-related tunnel contribution, allow us to estimate appreciable resistivity variations even in the case of small deformation angles.

Keywords: thin films; granular system; transport properties; perovskites; manganites

1. Introduction

Perovskite-like compounds have been the subject of intense research in the last few decades, due to their interesting and fundamental physical properties which have suggested a large variety of possible practical applications [1,2]. This class of materials is characterized by a particularly rich phase diagram, with the coexistence of different forms of order involving several degrees of freedom such as charge, spin, orbital and crystal lattice, finally resulting in nano-scale phase separation and intrinsic inhomogeneity [3–6]. The consequent possibility of changing the physical behavior of these compounds, by playing with several factors (such as the ionic size, the chemical composition, the applied magnetic field, the external strain, etc.) has created interest in investigating their possible practical use [7]. Furthermore, the balance between competing phases could be so delicate that small changes in these factors could be related to large changes in their physical properties.

Among the most studied perovskite families are the manganites, mainly due to the observed phenomenon of colossal magneto-resistance CMR [8,9]. In manganites, the CMR effect is traced back to a paramagnetic–ferromagnetic transition which, thanks to the double-exchange mechanism, simultaneously opens a conduction channel among aligned Mn electronic spins ([3], and references therein). This is more clear evidence of the strong interplay in these compounds among different orders at a nanometre scale. Moreover, the dependence on the chemical composition of the Curie temperature below which the spin alignment appears, has opened the way to studies of their possible use as spin valves and spin filters [10,11].

The tight relation between the electrical transport behavior, the Curie temperature and the externally applied strain in manganites has also suggested the need to investigate this interplay in order to obtain a more complete theoretical picture of the complex behaviour of such compounds. Theoretical prediction of the effect of biaxial strain on the electrical and magnetic properties of crystalline manganites [12] has been confirmed experimentally [13]. The main physical effect taken into account in these studies was the crystal lattice distortion due to the externally applied biaxial strain with its effect on the double exchange mechanism and, finally, on the Curie temperature values. For these

reasons, both the theoretical and experimental works, have been related to manganite epitaxial thin films, implying stiff single crystal substrates, generally difficult to implement in many sensors of large commercial use. On the other hand, the deposition of manganite thin films on poly-crystalline substrates, typically results in granular systems. In granular thin films, the externally applied strain no longer directly influences the crystal lattice, but it is generally incorporated by changing the grain arrangement. The scientific literature about the strain effects on the electrical transport properties of manganites is largely related to studies of epitaxial thin films [14–16] while research involving the effects on manganite granular films is rather uncommon [17,18].

By proposing a simple theoretical approach, the aim of this work is to give a first quantitative hint of the sensitivity of the electrical resistivity of a manganite granular system to the external strain tensor. Manganites, similarly to many perovskite compounds, in their poly-crystalline form, present a disordered array of grains. Each grain can be described as consisting of two parts, an inner part (core, body, intragrain) where the physical properties are those of the ideal compound and an outer part (shell, intergrain, surface) with different physical properties, Figure 1a. In particular, the surface zone, due to the so-called space charge layer [19], generally shows reduced electrical transport properties. By implementing the theoretical model proposed by Zhang et al. [20], we have been able to deduce the effects of externally applied small deformations on the electrical resistivity of granular manganites. The limits and the potential developments of our work are discussed. Our theoretical results show that the resistivity changes could be appreciable even for small distortions and could stimulate future experimental investigations in the field of innovative sensors.
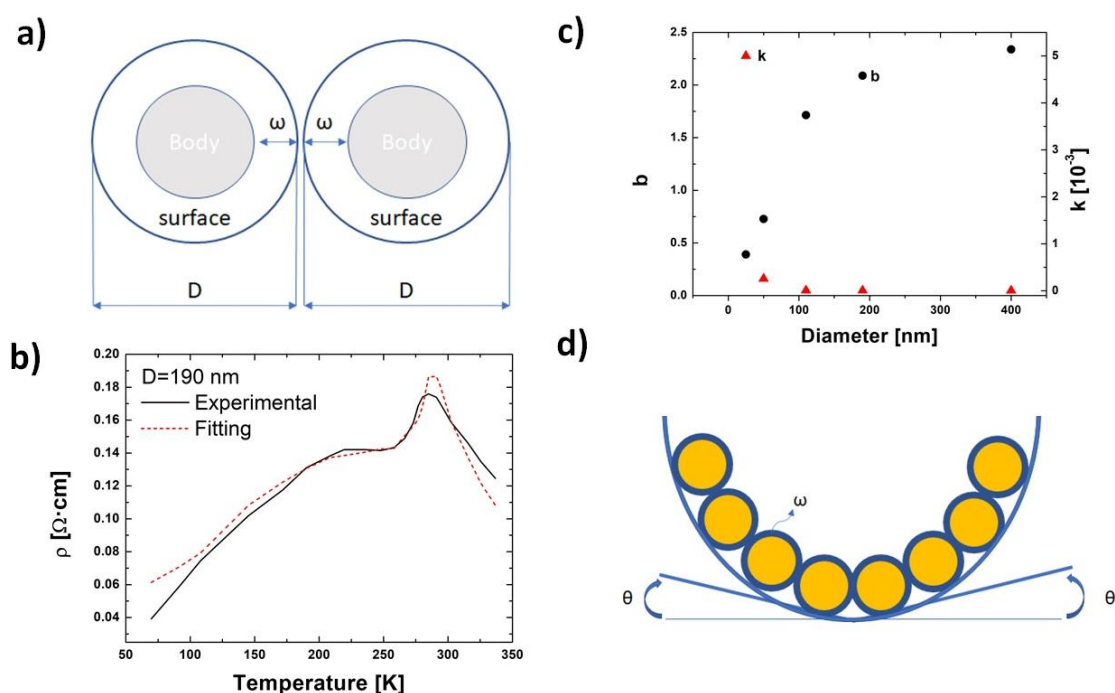

Figure 1. (**a**) schematic representation of adjacent grains; (**b**) results of the fitting procedure obtained using Equation (2) in the text, for the experimental R(T) curve corresponding to a sample with D = 190 nm in [20]; (**c**) "b" and "k" values obtained using the fitting procedure in Equation (2) for the samples characterized by different grains' size in [20]; (**d**) schematic representation of the grains' chain distortion due to the deformation applied to the sample.

2. Results and Discussion

In the case of manganites, the presence of different behaviors in the inner and outer part of grains can be traced back to differences in the double exchange energy [3]. The values of the double exchange energy indeed depend on several factors (chemical composition, spin order, dislocations,

dangling bonds) and have a strong influence on the magnetic and transport properties of the two zones. When two grains come in contact, the zone between two adjacent "cores", represented by the surface phase plus the eventual intergrain gap, acts as a potential barrier and its role on the resistivity can be described in terms of the tunnel effect. The model proposed by Zhang et al. [20] assumes the presence of both the interfacial tunneling and the intragrain metallic transport behavior [20]. The resistivity of the overall system will result from the sum of many terms associated to a suitable combination of the body phase ρ_b and surface phase ρ_s resistivity values in each single grain. Previous work performed on manganite granular systems have described the single grain resistivity in terms of a parallel connection channel model [21,22]. Our tentative attempt to fit the resistivity curves using the parallel model did not give results in good agreement with the experimental data in [20]. Therefore, following Zhang et al., we have written the resistivity of the system as the weighted sum of ρ_b and ρ_s:

$$\rho = \frac{f_b}{c}\rho_b + \frac{f_s}{c}\rho_s \tag{1}$$

where c is the material compactness, f_b is the volume fraction of the body phase and $f_s = 1 - f_b$ is that of the surface phase. In this representation, each grain is modeled as the series of two "equivalent" resistors one with metallic resistivity ρ_b (the inner part) and the other with tunnel resistivity ρ_s (the outer part). By assuming a spherical shape for the grains, see Figure 1a, and by observing that ρ_s is inversely proportional to the tunneling probability, Equation (1) can be written as a function of measurable quantities (see [20] for the details):

$$\rho = \frac{1}{c}\left[\rho_b\left(1 - \frac{3\omega}{D}\right) + \frac{3\omega K}{D^2}e^{b\left(\frac{(Dm - 3\omega m_s)^2}{(D - 3\omega)^2} - m_s^2\right)^{1/2}}\right] \tag{2}$$

where ω is the thickness of the surface zone in between two adjacent grains, D is the overall grain dimension, m and m_s are respectively the normalized magnetization of the overall grain and of the surface zone and K and b are two quantities respectively related to the surface chemistry inhomogeneity and to the transfer integral between adjacent manganese ions [20].

We have fitted the measured values for the bulk magnetization m_b in [20] assuming a temperature dependence well described in terms of the following modified Bloch's law [23]

$$m_b = \left[1 - \left(\frac{T}{T_C}\right)^{\frac{3}{2}}\right]^{\beta} \tag{3}$$

In this way, we have obtained good fitting of the experimental data in [20] using $T_C = 270$ K and $\beta = 0.1$. By assuming the same temperature dependence to describe the behavior of $m_s(T)$ in Equation (2), we have reached good agreement with the experimental resistivity data as a function of the grain dimension D in [20], fixing always, in the surface zone, the values of $T_C = 254$ K and $\beta = 2.2$ for all the different D values and using the quantities K and b as free fitting parameters. As an example, in Figure 1b, the results of our fitting procedures are shown and compared to the experimental resistivity curve for the sample with $D = 190$ nm presented in [20]. In Figure 1c, we show the behavior of the quantities K and b as a function of D. As expected, the K values are significantly large only for the case of small grain dimension (50 nm) and suddenly go to very small values with increasing D. Moreover, the b values increase with increasing D and seem to tend to saturation in the limit of very large D, where the ratio ω/D starts to be negligible.

For a granular manganite system, the described dependence of the electrical resistivity ρ upon the thickness ω and the grain size D, paves the way for further theoretical investigations of the effects on ρ due to an external strain tensor field. In the case of a continuous elastic medium, the deformation analysis involves the application of suitable loads and boundary condition as well as the knowledge of a set of independent elastic constants (e.g., Young's modulus, Poisson ratio and mass density) [24,25].

Once the deformed shape is obtained, a local approximation, which could be, in principle, piecewise linear, can be chosen in order to define through a suitable parameter the position of each grain. In this paper, for the sake of simplicity, one-dimensional deformations are considered. With the idea to show that resistivity changes due to an applied strain are to be expected also in manganite granular systems, we adopted a piecewise linear model, by considering a one-dimensional array of identical spherical grains and treat the external deformation applied to it, in terms of the tilt angle θ schematically represented in Figure 1d. In the case of a long grain chain, the θ angles are not constant but vary from an adjacent couple of grains to the next, reaching the maximum for the couple of grains in the center of Figure 1d. The electrical resistivity of the overall system will result from the series of many terms like that in Equation (2), where the quantity ω is now dependent upon θ. According to Equation (2), the ρ values exponentially depend on ω and, therefore, their observable change could be present even in the limit of small external deformations. Obviously, due to the variation in the values of θ, the changes in the electrical resistivity will not be constant, but, because of the connection in series, they will sum up along the one-dimensional granular chain. In our investigation, we have taken into account only the resistivity change due to the central adjacent grains in Figure 1d, considering, therefore, the maximum single variation in resistivity. Moreover, in our approach, the external strain acts only on the surface region of grains leaving unmodified the bulk region. From Figure 1d, it is clear that in the case of a tilt angle θ, the initial ω_0 value between the central grains is modified as:

$$\omega = \omega_0 \cdot \cos\theta \qquad (4)$$

The relative percentage change in the electrical resistivity is defined as:

$$\Delta\rho(\theta) = \frac{\rho(0) - \rho(\theta)}{\rho(0)} \cdot 100 \qquad (5)$$

In Figure 2, the results of $\Delta\rho(T)$ obtained by our model, introducing the Equation (3) in Equation (2), are presented as a function of θ and D.
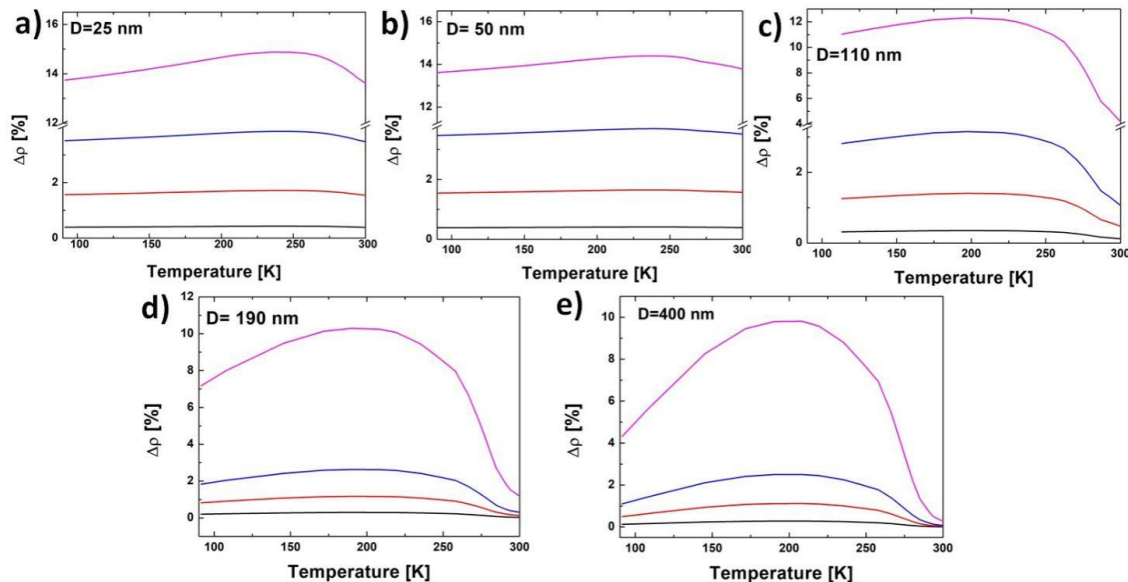

Figure 2. Percentage resistivity variations $\Delta\rho$ (Equation (5)) as a function of the temperature for different values of the tilt angle (black line is for $\theta = 5°$, red line for $\theta = 10°$, blue line for $\theta = 15°$ and the magenta line for $\theta = 30°$) and for different D values: (**a**) $D = 25$ nm, (**b**) $D = 50$ nm, (**c**) $D = 110$ nm, (**d**) $D = 190$ nm, (**e**) $D = 400$ nm.

The $\Delta\rho$ values are strongly dependent on the tilt angle θ with only slight variations of the percentage values as a function of D. The maximum $\Delta\rho$ values go from 10% to 15% for $\theta = 30°$, from 2% to 4% for $\theta = 15°$, between 1% and 2% for $\theta = 10°$ and stay below 1% (from 0.1% to 0.5%) for $\theta = 5°$. The temperature T_M at which the $\Delta\rho$ values reach their maximum ($\Delta\rho_{max}$), depends upon the grain dimensions, increasing with decreasing D values. In Figure 3b, as an example, we show the behavior upon the grain dimensions D of both T_M and $\Delta\rho_{max}$ obtained for $\theta = 5°$. With decreasing D, it is interesting to note that the T_M values approach room temperature. Moreover, at least in our simple model, the effect of the tilt angle θ on the resistivity, seems to reach a saturation value for D below 50 nm. In Figure 3a, we report the $\Delta\rho$ values as a function of D obtained at 273 K for $\theta = 5°$. As already mentioned, values in the range from 0.1% to 0.5% are observed.
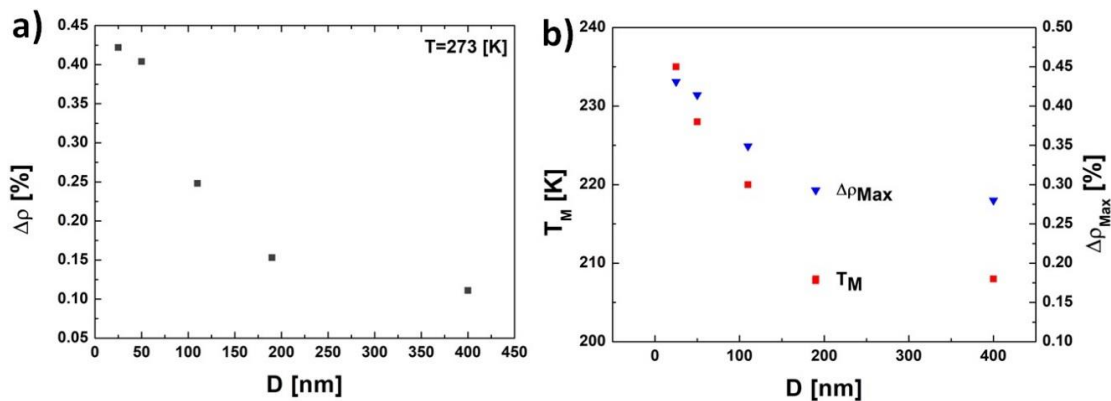

Figure 3. (**a**) percentage resistivity variation $\Delta\rho$ for different D values at $\theta = 5°$ and $T = 273$ K; (**b**) T_M temperature (red squares) corresponding to the maximum value of the percentage resistivity variation (blue triangles) for each of the considered D values.

For better clarity, the values in Figure 3a are also reported in Table 1.

Table 1. $\Delta\rho$ [%] values as a function of D for $T = 273$ K and $\theta = 5°$.

D [nm]	$\Delta\rho$ [%]
25	0.42
50	0.40
110	0.25
190	0.15
400	0.11

We remark that these values are calculated in the limit which assumes the deformation between adjacent grains along the one-dimensional chain to be described in terms of only that of the central couple in Figure 1d. As a consequence, the actual values expected in the case of a long one-dimensional chain should be reduced. On the other hand, the calculated changes are relative to the resistivity variations which, by playing with the system geometry, can correspond to important changes in terms of resistance. Although calculated using a simple approach, our quantitative results clearly show that, also in the case of granular manganites, the effects of an external strain tensor on the electrical transport properties of the system are appreciable even for small deformations. The expected $\Delta\rho$ variation at room temperature for $\theta = 5°$ is in fact, in the range 0.1–0.5% and, at least in the limit of the model, these values seem to stay constant for values of $D < 50$ nm. Finally, we point out that, by suitably modelling the tilt angle deformation along the system, the calculation can be extended to the case of two-dimensional and three-dimensional arrays of grains. Further studies in this direction are presently ongoing also to compare the model results to real experiments.

3. Conclusions

We have analyzed the effect of an external strain tensor on the resistivity of a granular manganite system. In the model proposed, a one-dimensional chain of grains is taken into consideration and the strain effect is introduced via a simple deformation of the system arrangement described in terms of the tilt angle between couples of adjacent grains. The resistivity variations calculated implementing previous theoretical analysis allow us to estimate appreciable values even in the case of small deformation angles. Future studies regarding similar analysis on two- and three-dimensional systems are presently under way, in order to describe situations closer to practical application.

Conflicts of Interest: The authors declare no conflict of interest.

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