On the role of solid solution randomness on phase coexistence in $B$-site substituted manganites.

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Abstract. We present a plausible explanation for the intriguing phase separation phenomena displayed by Pr$_{0.50}$Ca$_{0.50}$Mn$_{1-x}$M$_x$O$_3$ compounds. This explanation is based on the simulations that authors have recently published (2008 Europhys. Lett. 84 67011). The results obtained there are compared with those found for M = Ti by means of neutron and synchrotron X-ray powder diffraction. Phase separation can be explained from very local effects of M ions together with their random distribution in Mn sites.

Transition metal oxides (cuprates, manganites, cobaltites, ...) are characterized by a high number of different degrees of freedom (magnetic, lattice, electronic and even orbital) that mutually interact through a series of energy terms (Hund coupling, Jahn-Teller, kinetic energy, Coulomb repulsion, ...) that in many cases are of similar magnitude. This makes these terms to compete and provokes that the behaviour of these systems is very difficult to predict. Moreover, the different available states of the system have rather similar energies, and thus the stable state (or equilibrium state) can be easily changed by means of external stimuli (temperature, pressure, applied electric or magnetic field, stress, etc), or changing the stoichiometry by the partial substitution of one cation by another. This richness gives rise to very celebrated properties (colossal magnetoresistance, electro-resistance, giant dielectric response, superconductivity, etc.) but also, in some cases, to the apparition of coexisting phases with different macroscopic properties.

Phase coexistence or phase separation (PS) in apparently homogeneous systems is a very intriguing phenomenon giving rise to very interesting properties. It must be pointed out that we refer to cases where phase coexistence occurs only at a certain temperature range, to systems that present some type of structural transition linked to electronic, orbital and/or magnetic degrees of freedom in direct relation with the apparition of PS. In these cases, PS appears as a consequence of the delicate balance between different available states of the system and the coupling between the mentioned degrees of freedom and the lattice.

During last years, extensive research has been done on B-site substituted manganites (specially on Pr$_{0.50}$Ca$_{0.50}$Mn$_{1-x}$M$_x$O$_3$: M = Ti, Ru, Cr, Co, Ni, ...) [1-20]. These compounds display PS below the charge/orbital ordering (CO/OO) transition temperature ($T_{CO} \approx 250$K) of the parent Pr$_{0.50}$Ca$_{0.50}$MnO$_3$ compound. These investigations have shown a surprisingly high ability of these B-site impurities to produce the disappearance of long range CO/OO and to induce long range ferromagnetism and metallicity with substitution levels as low as 3%. For a long time, this has been attributed to a special ability of the substituting ions to break the long range CO/OO of the parent compound.
As an alternative general explanation for the occurrence of PS in a wide variety of transition metal oxides we have recently performed numerical simulations on the effect of randomly distributing in a system a very low (between 0.5% to 5%) amount of substituting ions [21]. Simulations consist on a geometrical analysis of the regions affected by the substituting ions, after placing them in the system at random (results are averaged over 10 realizations of this quenched disorder). These simulations show that the randomness associated to the substitution can generate the appearance of large clusters of a secondary phase that can percolate the system even at very low substituting levels (1%). The necessary ingredient for this to happen is the apparition of a (at least) very small “region of influence” (ROI) where the behaviour of the system is different from that of the matrix. The size of these regions can be as small as one or two times the Mn-Mn bond distance in the present case.

The motivation of the present work is to examine the validity of the simulations done in Ref. [21] to explain PS phenomena in Pr$_{10.5}$Ca$_{0.5}$Mn$_{1-x}$M$_x$O$_3$. For the case M = Ti we will also compare the amount of secondary phase obtained by the simulations with those obtained by neutron and synchrotron X-ray powder diffraction at low temperature [19]. These simulations are very appropriate for substituted manganites due to the fact that Mn are roughly placed in a cubic lattice and their properties are largely changed by the substitution.
As mentioned, PS in these materials coincides with the apparition of CO/OO. Above $T_{CO}$ these compounds present a single phase, even when they are examined by means of ultra-high resolution synchrotron X-ray powder diffraction [16; 17; 19; 20]. On the contrary below $T_{CO}$ two coexisting phases appear. CO/OO is characterized by the ordering of the orbitals occupied by Mn$^{3+}$ $e_g$ electrons. Above $T_{CO}$, these electrons randomly (and dynamically) occupy different orbitals at every Mn positions. Below $T_{CO}$ they confine in $a$-$c$ planes ($Pnma$ setting). Thus, a highly anisotropic charge reallocation occurs during CO/OO stabilization that drives to an anisotropic evolution of lattice parameters (expansion of $a$ and $c$ and contraction of $b$). An essential ingredient for this transition is the peculiar electronic structure of Mn$^{3+}$ and the fact that, when Jahn-Teller distortion freezes, their shape become highly anisotropic. At the places where Mn is substituted by another cation (like Ni$^{2+}$, Co$^{2+}$, Ti$^{4+}$, ...) that cannot be “squeezed” this anisotropic cell change cannot take place. Thus, a lattice deformation must appear around these sites when CO/OO takes place. This explains the apparition of huge strain fields [16; 17; 20] where Mn is substituted by another cation (like Ni$^{2+}$, Co$^{2+}$, Ti$^{4+}$, ...) and contraction of $b$

Figure 2. Fraction of the system expected to form a secondary phase from the simulations, compared with those found experimentally for $Pr_{0.50}Ca_{0.50}Mn_{1-x}Ti_xO_3$ (Ref. [19]).

To further analyze the validity of these simulations to explain the origin of the PS in $Pr_{0.50}Ca_{0.50}Mn_{1-x}M_2O_3$ we compare, in Fig. 2, the phase fraction obtained by the simulations with those reported in Ref. [19] (with $M = Ti$) at $T = 10$ K. It can be appreciated that results for this compound fairly coincide with those obtained with $R_{ROI} = \sqrt{2}a$ except for $x = 0.01$ for which the obtained value would be nearer to that predicted for $R_{ROI} = \sqrt{3}a$. In addition, $(Pr_{0.50}Ca_{0.50}Mn_{0.95}Ti_{0.01}O_3)$ presents a complex evolution of the phase fractions with temperature [20]. In fact this evolution would point towards a dependence on temperature (and thermal history) of the size of the RoI. We would like to stress that, in spite of the simplicity of these simulations, the degree of agreement with the experimental results is remarkable.

In the case of substituting ions with $d$-active electrons, their presence will induce, in addition to lattice distortions, changes in the magnetic coupling and in the transport properties within the RoI. According to the simulations, substitution levels of only 1.5% make, in most of the cases, percolating clusters of the new phase to appear. This allows to explain the rapid metalization
(and the appearance of ferromagnetism) in these compounds from just a very local effect around each substituting ion.

As an additional step forward, one could consider that the size of the regions altered magnetically by these ions can be different from that altered structurally. Another possible scenario, that can occur due to the strong coupling between lattice and magnetic degrees of freedom in manganites, is that the range (ROI) of the structural perturbation changes with the local magnetic arrangement. All these effects would not change the essential results from Ref. [21].

To conclude, we must say that we are convinced that the simulations presented in Ref. [21] are too simple to reproduce all the details characterizing PS in these systems. But, at the same time, we emphasize that they contain the two basic ingredients that drive to the apparition of PS and the rapid metalization (when it occurs) of Pr_{0.50}Ca_{0.50}Mn_{1-x}M_xO_3 compounds: the combination of very short-ranged effects of each substituting ion with the randomness of the substitution. This allows us to discard the needing of long range breaking of charge order by the substitution to explain the rich phenomena displayed by these compounds.

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