Ab initio study of the influence of nanoscale doping inhomogeneities in the phase separated state of La$_{1-x}$Ca$_x$MnO$_3$

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Abstract

The chemical influence in the phase separation phenomenon that occurs in perovskite manganites is discussed by means of ab initio calculations. Supercells have been used to simulate a phase separated state, that occurs at Ca concentrations close to the localized itinerant crossover. We have first considered a model with two types of magnetic ordering coexisting within the same compound. This is not stable. However, a non-isotropic distribution of chemical dopants is found to be the ground state. This leads to regions in the system with different effective concentrations, that would always accompany the magnetic phase separation at the same nanometric scale, with hole-rich regions being more ferromagnetic in character and hole-poor regions being in the antiferromagnetic region of the phase diagram, as long as the system is close to a phase crossover.

(Some figures may appear in colour only in the online journal)

1. Introduction

Perovskite manganites belong to a class of materials that have become increasingly important in the last few years, particularly because of the large variety of phenomena they exhibit, closely tied to the strongly correlated nature of their electronic structure. The series of manganites A$_{1-x}$B$_x$MnO$_3$ (A$^{3+}$ being a lanthanide and B$^{2+}$ an alkaline earth) is one of the most intensively studied families [1]. The interest in these materials grew significantly after the discovery of colossal magneto-resistance (CMR), a large negative magneto-resistance (CMR), a large negative magneto-resistance taking place under an applied magnetic field [2], but also considerable research has focused on their unusual properties such as phase separation [3], charge and orbital ordering [4, 5] and also on their potential applications in thin-film devices [6–8], derived from their peculiar electronic structure properties.

The case of A = La$^{3+}$ and B = Ca$^{2+}$ has become a prototypical example of manganite compounds [9, 10], showing a very rich phase diagram [11, 12]. The regions in the phase diagram with concentrations of about 18% and 50% Ca$^{2+}$ have been thoroughly studied, because samples exhibit phase separation, intrinsic to the proximity to the magnetic/electronic phase transition. In that part of the phase diagram, La$_{1-x}$Ca$_x$MnO$_3$ presents mixed Mn$^{3+}$/Mn$^{4+}$ valencies and a strong electron–phonon coupling, the magnetic coupling being a modified version of the double-exchange interaction to take into account the coupling between the electronic states and vibrational modes (vibrons). The mechanism for ferromagnetic (FM)
ordering in manganites exhibiting CMR has been recently considered [13], suggesting a breakdown of the adiabatic approximation for the itinerant electrons. These results are related with dynamic phase segregation into hole-rich itinerant-electron regions and hole-poor localized-electron regions, leading to suppression of the conventional double-exchange mechanism.

Several theoretical studies have been performed in these manganite perovskite systems using different techniques. The electronic structure of La$_{1-x}$Ca$_x$MnO$_3$ was calculated using the LAPW (linearized augmented planewave) method [14, 15]. Transport properties were studied using the virtual crystal approximation, neglecting disorder effects in the lattice [16]. The formation of a pseudogap follows from numerical calculations based on the dynamical mean field theory, indicating the existence of a charge-nonuniform ground state [17]. An extensive study of the physics of manganites, including the structure we are studying here, was carried out by Salomon et al [18]. Unfortunately, an ab initio description of the phase separation in manganites has not been given in the literature.

It is now widely accepted that some sort of electronic phase segregation is at the origin of the CMR effect in manganites. Moreo et al [19] proposed a scenario where the coexistence of two phases with different charge densities is unstable against breakup into nanometer size clusters due to the Coulomb force. Two different kinds of electronic phase segregation have been proposed to exist in manganites [20]: equal density versus different density electronic phase segregation at the micro- and nanoscale, respectively. Experimentally, magnetic phase separation has been observed in the form of nanoscale phases with different magnetic properties [21], i.e. regions in the crystal with nanometric size that present a different magnetic ordering. Imaging techniques [22] have recently shown the close relationship between nanoscale phase separated regions of an electronic/magnetic origin and CMR. According to those studies, these regions, in the several nm range, do not have chemical origin. A different view comes from an analysis of the influence of the dopant distribution on the superconductivity and phase separation that has recently appeared [23], studying the chemical inhomogeneities at the nanoscale in (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ superconducting pnictides.

The fundamental problem is that of giving a correct description of how the holes are distributed in the system. It has been known for a long time that even the simplest models [24] predict a nonuniform density distribution of dopants, which are unstable against segregation into hole-rich and hole-poor regions. To gain insight into this problem, in this paper, we have taken into account a structure with Ca$^{2+}$ doping levels close to $x \sim 0.2$ (exactly $x = 0.1875$) of La$_{1-x}$Ca$_x$MnO$_3$ from a computational point of view via ‘ab initio’ calculations. Typically, this is not done, and models are utilized instead, due to the large supercells that are required, but even the crudest supercells can help us, as we will see, to understand the electronic and chemical origins of phase separation. It is worth recalling that the above mentioned doping level is experimentally placed around the critical boundary in which the FM insulating to FM metallic transition occurs at low temperatures with respect to doping [11, 12]. We have constructed several superstructures in different magnetic configurations to explore the magnetic origin of phase separation. Since our calculations yield a homogeneous FM ground state, we will analyze the influence

![Figure 1](image-url)
of the Ca\(^{2+}\) dopant distribution in the lattice in this magnetic ground state. Varying the Ca\(^{2+}\) positions from a random distribution to a slightly correlated one, we can analyze the influence of dopant distribution in the electronic structure and the physical properties of the compound by means of ‘\textit{ab initio}’ calculations.

For the sake of completeness, we will make a similar analysis at a very different Ca\(^{2+}\) concentration \((x = 0.375)\), in which the ground state is FM metallic becoming paramagnetic insulating at high temperatures. The idea of that calculation is to study a concentration away from the phase boundaries at \(x = 0.1875\) and also away from \(x = 0.5\), where the ground state becomes an insulating antiferromagnetic (AF) and charge ordered (CO) state. At those two hole densities there is a strong tendency towards phase separation caused by intrinsic inhomogeneities \([1]\) but \(x = 0.375\) (unlike \(x = 0.1875\) and 0.5) is not close to the boundary between different ground states in the La\(_{1-x}\)Ca\(_x\)MnO\(_3\) solid solution \([11, 12]\). These analyses will help us to discuss the consequences of having chemical inhomogeneities at the nanoscale in these phase separated compounds.

2. Computational details

The electronic structure calculations were performed within the density functional theory framework \([25]\) using WIEN2k software \([26, 27]\), which utilizes an augmented plane wave plus local orbitals (APW + lo) \([28]\) method to solve the Kohn–Sham equations. This method uses an all-electron, full-potential scheme that makes no shape approximation to the potential or the electron density.

For modeling the correlated behavior of the d electrons of the system, we have included strong correlation effects by means of the LDA + \(U\) scheme \([29]\), controlled by an effective \(U\) \((U_{\text{eff}} = U - J)\), where \(U\) is the on-site Coulomb repulsion and \(J\) is the on-site exchange constant (taken as \(J = 0\), as is common practice in the literature) \([30]\). Values of \(U_{\text{eff}}\) of 2.7, 4.0 and 5.5 eV were used in the calculations. These values are in the range that has been used in the past for various Mn oxides \([31, 32]\). The structural minimization was carried out using the GGA-PBE scheme \([33]\) (generalized gradient approximation in the Perdew–Burke–Ernzerhof scheme), minimizing the forces on the atoms and the total energy of the system. The parameters of our calculations \([34]\) depend on the type of calculation but for all of them we converged with respect to the \(k\)-mesh and to \(R_{\text{mt}}K_{\text{max}}\), up to 75k points (15 in the irreducible Brillouin zone, in a \(3 \times 3 \times 3\) sampling of the full Brillouin zone for a supercell of \(N\times N\times N\) perovskite unit cells) and up to \(R_{\text{mt}}K_{\text{max}} = 6.0\). The muffin-tin radii chosen were 2.43 au for La, 2.29 au for Ca, 1.96 au for Mn and 1.73 au for O.

3. Results and discussion

3.1. Magnetic study

The goal of the first part of our work is to simulate a magnetically phase separated state by embedding an FM (AF) phase into an AF (FM) matrix. For this reason, we have set up several superstructures based on the unit cell La\(_{0.8125}\)Ca\(_{0.1875}\)MnO\(_3\) (at a concentration close to a metal–insulator transition in the phase diagram), using \(2 \times 1 \times 2\) and \(2 \times 2 \times 2\) supercells (in perovskite unit cell units), as shown in figure 1. The larger and initially more realistic cases \((2 \times 2 \times 2)\) in figure 1(c) serve as a model of the experimentally observed situation of a magnetic phase (antiferromagnetic (AFREAL) in the upper figure, ferromagnetic (FMREAL) in the lower one) completely surrounded by a magnetically different phase (FM and AF, respectively). Figure 1(b) shows the cases of an AF chain surrounded by an FM guide (AFCHAIN) and vice versa (FMCHAIN). We have also calculated the system in the simple ferromagnetic (FM) and G-type AF cases (figure 1(a)).

We have calculated all these phase separated superstructures and compared their relative stabilities (total energy calculations) with respect to an entirely FM structure and also an entirely AF structure (G-type). The results are summarized in figure 2. We can see that the purely FM structure is the most stable one in every case, the stabilization energy ranging from 130 meV/Mn compared to the FMCHAIN and AFREAL structures to 400 meV/Mn with respect to the AF structure. Calculations predict that these magnetically phase separated states are not stable. The picture is the same for all values of \(U\) we have calculated. From these calculations, we can conclude that the FM configuration at the concentration \(x_0 = 0.1875\) is the most stable, in agreement with experimental observations at that concentration \([11, 12]\). These results suggest that the coexistence of two magnetic phases in the compound requires some other changes in the crystallographic and electronic structure for it to be stable.

3.2. Chemical study

Holes in the \(e_g\) Mn levels can be introduced by the substitution of La\(^{3+}\) by Ca\(^{2+}\) over the entire compositional range...
Figure 3. Schematic representation of the Ca$^{2+}$ atom distribution in the lattice of La$_{0.8125}$Ca$_{0.1875}$MnO$_3$. $\langle r \rangle$ is the average distance between Ca$^{2+}$ atoms in the lattice. These figures show the four possible atomic orderings of the Ca$^{2+}$ atoms in the lattice (because of its symmetry) and its $\langle r \rangle$ from the most inhomogeneous case, distribution (a), to the homogeneous case, distribution (d).

Figure 4. Energies of the calculated structures for La$_{0.8125}$Ca$_{0.1875}$MnO$_3$ (y axis) in the FM configuration. The energies are normalized to the lowest value of the four possible Ca$^{2+}$ chemical distribution configurations. On the x axis we write the values of $\langle r \rangle$ for each structure (see text), from the larger one on the right (total homogeneity structure corresponds with figure 3(d)) to the smaller one on the left (total inhomogeneity structure corresponds with figure 3(a)). The inset shows an analogous study of the second magnetic stable configuration calculated in section 3.1 of this paper, which is the FMCHAIN configuration.

range in the La$_{1-x}$Ca$_x$MnO$_3$ solid solution. Additionally, hole doping can be created by means of cationic vacancies. La$_{0.8125}$Ca$_{0.1875}$MnO$_3$ is a distorted perovskite with a pseudocubic lattice parameter ($a_c$) of 3.89 Å. The tilting of the MnO$_6$ octahedra results in an orthorhombic symmetry (space group Pnma, No. 62) with lattice parameters $a_0 \approx c_0 \approx \sqrt{2}a_c$ and $b_0 \approx 2a_c$ for this composition. The ability to oxidize La$_{1-x}$Ca$_x$MnO$_3$ materials with $x \leq 0.2$ leads to important structural, electronic and magnetic variations related to the presence of cationic vacancies [10, 35, 36]. Thus, differences between non-stoichiometric and stoichiometric samples should be always considered.

Stoichiometric La$_{0.8125}$Ca$_{0.1875}$MnO$_3$ compound, i.e., with no cationic (or anionic) vacancies is considered in the present study. We initially assumed that the La$^{3+}$ and Ca$^{2+}$ atoms (the dopants) were distributed in a perfectly homogeneous manner throughout the crystal. But, experimentally, this might not be the case; nano-sized chemical inhomogeneities in the structure can occur and will not be detected below the few nanometer limit [22], but they could have a key role in the properties of a phase separated state.

The next step of the work is to study whether such dopant inhomogeneities can occur at the nanoscale. To do this, we varied the atomic positions of the Ca$^{2+}$ atoms to distribute them in various manners throughout the crystallographic unit cell. In the La$_{0.8125}$Ca$_{0.1875}$MnO$_3$ structure we can change the distribution of the Ca$^{2+}$ cations to create four possible inequivalent chemical configurations. These can be seen in figure 3. We can define the quantity ($r$) as the average distance between Ca$^{2+}$ atoms in the lattice, and use it as a measure of...
Figure 5. Majority spin (positive values) and minority spin (negative values) partial density of states (DOS) plots of the eight inequivalent Mn atoms in the ground state (both chemically and magnetically) configuration. The Fermi energy is represented by a vertical line at $E = 0$ eV.

how homogeneously these dopants are distributed:

$$\langle r \rangle = \frac{\sum_{i=1}^{N} d_i}{N}$$

where $d_i$ is the distance between nearest Ca$^{2+}$ atoms and $N$ is the number of nearest Ca$^{2+}$ atoms.

In principle, inserting chemical inhomogeneities into the lattice will generate uncompensated forces and increase the elastic energy in the structure, but we need to calculate all the energetic terms involved to obtain the most stable configuration. In our case, we will do that using ab initio calculations.

We constructed these four possible cases using an FM ordering, the most stable magnetic structure we have explored previously. We performed a full lattice relaxation for each of the cases, and then we calculated their total energies. The results are presented in figure 4. We can observe that the most stable structure corresponds to an intermediate case between the most homogeneous case (figure 3(d)) and the most inhomogeneous case (figure 3(a)), which is the one used for the calculations in the previous sections. Taking the ground state structure as the $\langle r \rangle = 6.71$ Å, we found that this one is more stable by about 19 meV/Mn with respect to the second most stable configuration, and by 219 meV/Mn with respect to the most unstable configuration (largest chemical homogeneity attainable at this concentration). This means that a non-homogeneous dopant distribution occurs in the material that would lead to a nanoscale distribution of effective concentrations. Analogous results in terms of dopant distribution energetics can be found in other magnetic configurations (hence, it is not an issue of the FM solution).

The most stable $\langle r \rangle$ value is larger than one cubic perovskite lattice parameter. Several perovskite subcells will
be involved in forming this ground state Ca$^{2+}$ distribution. Moreover, variations of the atomic position of the various Ca$^{2+}$ cations will imply different environments for each of the Mn atoms in the unit cell. Thus, the existence of areas with such a typical size suggests that the magnetic and electronic characteristics differ inside and outside the clusters leading to an electronically inhomogeneous state on a nanometric scale in La$_{0.8125}$Ca$_{0.1875}$MnO$_3$. Zones where Ca$^{2+}$ atoms are grouped lead to a local concentration displacement towards the hole-rich region (Ca$^{2+}$-rich) in the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$. In contrast, in zones where the density of Ca$^{2+}$ atoms is lower, we have La$^{3+}$-rich (electron-rich) zones, these being local concentration displacements to the AF region of the phase diagram. This scenario is consistent with the stable FM order [35] near Mn$^{3+}$, localized near Ca$^{2+}$-rich regions, in agreement with the hole distribution described by Alonso et al as the hole attractor model [36]. Our calculations show that the existing chemical inhomogeneities can be a coexisting factor that works together with the electronic/magnetic phase separation.

We calculated the electronic structure of the material in the ground state (in terms of both magnetic ordering and chemical configuration). The value obtained for the total magnetic moment in this structure is 3.8125 $\mu_B$/Mn atom, as expected. This corresponds to an average Mn valence of +3.1875. We can also analyze the magnetic moments inside the muffin-tin spheres for each of the Mn atoms. These are summarized in table 1. Their magnetic moments present differences of the order of 1% at most. Also the total $d$ charge inside the Mn muffin-tin spheres varies by only 0.015 electrons. This would all be translated into changes in effective Ca concentration $x$ of only 0.01. This can be seen in the largely homogeneous electronic structure observed in the partial density of states of the inequivalent Mn atoms in the ground state of the compound (figure 5). In a metallic solution, the way the different local concentrations correlate with an electronic phase separation in the system is not obvious, but we observe that the chemical inhomogeneities relate to a different electron count in each Mn atom.

The typical sizes of these hole/electron-rich zones that come out our calculations for the ground state chemical distribution can be seen in figure 6. We calculated the effective $x$ for each inequivalent Mn atom in the supercell according to its nearest neighbors (up to fourth neighbors), assuming the usual Ca$^{2+}$/La$^{3+}$ valencies, for this most stable chemical configuration. We observe that there is a 6.5–7.4 Å diameter zone where the effective doping of La$_{1-x}$Ca$_x$MnO$_3$ has more Ca$^{2+}$ than the real macroscopic average concentration ($x = 0.1875$) and a 4.3–6.5 Å diameter zone where the effective doping is displaced to the La$^{3+}$-rich zone in the phase diagram. These calculated cluster sizes are comparable, but somewhat lower than those reported in the literature [37] concerning the Ca-rich region in the La$_{1-x}$Ca$_x$MnO$_3$ solid solution. They show the importance of chemical ordering at the nanoscale when the system is close to a metal–insulator transition. The presence of chemical inhomogeneities on a similar nanometric scale to the experimentally observed electronic/magnetic phase separation could act as a precursor.
for the phase separated scenario to develop in the system. The largest deviation around $x = 0.1875$ in terms of Ca concentration $(x)$ is about 0.04 (slightly larger than the equivalent deviation in the magnetic moments of the Mn atoms, which was calculated to be about 0.01). The chemical variations are stronger than the electronic variations. Changes in the local doping of each Mn will vary the effective Ca concentration in the range $0.167 < x < 0.208$, which is enough to move the system to the other side of the magnetic/electronic phase transition, which occurs at about $x = 0.18$. In fact, different nanosize domains have been experimentally detected around this compositional range: FM clusters of 16 Å for $x = 0.17$ whereas an approximate size of 8 Å has been observed for $x = 0.2$ [21]. This last result confirms the existence of FM clusters confined in about two perovskite subcells, in a similar scale to the chemical inhomogeneities we find in our calculations for $x = 0.1875$. The zones with a lower Ca concentration will have an AF ground state and the zones with higher values of $x$ will be in their FM ground state, according to the phase diagram of the system.

In order to further check the reliability of these calculations, we analyzed a different Ca$^{2+}$ concentration ($x = 0.375$) which is not at the boundary between different ground states in the La$_{1-x}$Ca$_x$MnO$_3$ solid solution. For this, we constructed four different possible Ca-dopant distributions in the La$_{0.625}$Ca$_{0.375}$MnO$_3$ [38, 39]. A similar energy analysis to the one performed above shows that the chemical inhomogeneities that occur at this concentration are even larger in magnitude. The displacements in the local concentration of $(r) = 5.5$ Å structure, that can be observed in figure 7, are in the range 0.335 $< x < 0.407$. Note that $(r)$ is smaller than in the $x = 0.1875$ case (i.e. 6.71 Å). This is related to the richer calcium concentration in $x = 0.375$. The above range of Ca$^{2+}$ concentrations is always far enough from the FM insulator ground state at $x = 0.18$ as well as the AFM with CO ground state observed at $x = 0.5$. In spite of this, experimental evidence of inhomogeneities in manganites has been obtained [1]. Thus, chemical inhomogeneities are always present in these kind of samples, but a proximity to a phase boundary is required for them to act as nucleation centers of an electronic/magnetic phase separation scenario.

4. Conclusions

Our results show important evidence about an often forgotten factor (mainly due to the complications in its direct calculation and measurement) in studying the origin of electronic and magnetic phase separation close to a magnetic phase transition. By means of 	extit{ab initio} calculations, we have studied mixed magnetic phases but none of them are stable. However, chemical inhomogeneities caused by cation disorder on a scale smaller than 1 nm are stable in the system according to our total energy calculations. Close to an FM/AF phase transition, these nanoscale doping inhomogeneities are large enough to produce hole-rich/hole-poor regions in the compound at the nanometer scale. For some concentrations, like the $x \sim 0.2$ phase boundary, they are found to have a similar size to the observed phase separated regions. Thus, their effects cannot be ignored and could be substantial, whether driving electronic/magnetic phase separation or accompanying it. The cationic inhomogeneities could act as charge attractors and/or nucleation centers for the phenomenon of phase separation to develop. If the scale of the phase separation phenomenon were micrometric, or much larger than 1 nm, these chemical effects could possibly be ignored.

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