Phase separation in La$_{1-x}$Ca$_x$MnO$_3$ via nanoscale doping inhomogeneities.

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Colossal Magnetoresistance has been studied extensively for the past 20 years, and those investigations have shown it is intimately related to the phenomenon of electronic/magnetic *phase separation*. Understanding the origin of this effect is a prerequisite to the understanding of the physics of strongly correlated electron systems.

One paradigmatic system exhibiting phase separation is La$_{1-x}$Ca$_x$MnO$_3$ compound. This material has been deeply studied and there are plenty of experimental evidences of a dynamic magnetic phase separation at low temperature near x~0.2 and x~0.5. [1]

We have taken into account a structure with Ca doping levels close to x~0.2 (exactly x = 0.1875) from a computational point of view via "*ab initio*" calculations for the first time in order to study the magnetic phase separation on the nanoscale. We use density functional theory (DFT) and calculations were carried out with the WIEN2k package [2] using the LSDA+U [3] approximation, exploring tipical values of U for this compound (from 3 eV to 6 eV).

We have elaborated several large superstructures based on the unit cell La$_{0.8125}$Ca$_{0.1875}$MnO$_3$ that represent the experimentally observed situation of a magnetic phase (antiferromagnetic (AF), in this case) completely surrounded by a magnetically different phase (ferromagnetic (FM), in this case). We want to simulate a magnetically phase separated state by embedding one of these magnetic phases into the other.

We have calculated many of these phase separated superstructures introducing different magnetic configurations (one dimensional AF (FM) chains surrounded by a FM (AF) guide and two cases with an AF (FM) nanometric region completely surrounded by a FM (AF) region). For comparing their relative stability with respect to the phase-separated cases, we have calculated an entirely ferromagnetic superstructure and also an entirely antiferromagnetic superstructure. Our calculations show that the purely FM structure is the most stable one, and the AF structure is the more unstable. Magnetism alone cannot explain the observations. Initially, we have assumed that the La and Ca atoms (the dopants) are distributed in a perfectly homogeneous manner throughout the crystal. But, experimentally, we know that this might not be the case; nano-sized chemical inhomogeneities in the structure can happen and will not be detected by standard diffraction measurements.

We construct 4 different structures, depending on how these Ca atoms are distributed. We can define <r> as the average distance between Ca atoms in the lattice $< r >= \dfrac{\sum\limits_{i}^{n} r_i}{n}$, where r_i is the distance between nearest Ca atoms and n is the number of nearest Ca atoms.

We calculated the energy of these new structures and, after a structural relaxation, obtained that the most stable structure corresponds to an intermediate case between a homogeneous and a totally inhomogeneous case. These small chemical inhomogeneities will be accompanied of magnetic homogeneities, leading to a nanoscale magnetic phase separation that could be observed experimentally.

We have constructed also four different possible Ca-dopant configurations in the $La_{0.625}Ca_{0.375}MnO_3$. In this concentration the material does not show phase separation experimentally. Our calculations show that chemical inhomogeneities that occur at this concentration are smaller in magnitude, not enough to lead to a phase separated state, then the picture is consistent.

Our results show important evidences about the origin of the chemical magnetic phase separation close to a magnetic phase transition. We have calculated that magnetism alone cannot drive phase separation. Instead, dopant inhomogeneities on the nanoscale are the driving force of the phase separation phenomenon in manganites.

References:

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Figures: