Strong reduction of lattice effects in mixed-valence manganites related to crystal symmetry

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Calorimetric, thermal expansion, resistivity, and magnetization measurements in La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO₃ samples evidence the existence of a critical tolerance factor *t* that determines the relevance of lattice effects in mixed-valence manganites. Samples with x < 0.15 (i.e., with t < 0.92) exhibit a first-order magnetic transition at the Curie temperature T_C as well as anomalous volume and magnetic entropy changes, high volume sensitivity to magnetic fields and high magnetoresistance at T_C ; whereas those with t > 0.92 do not. Samples of the former group show orthorhombic structures, whereas the other are rhombohedral. Taking into account that a rhombohedral symmetry forbids a static long-range-cooperative Jahn-Teller distortion, these results are taken as a probe of the strong reduction of lattice effects beyond this critical value of the tolerance factor. A new phase boundary in the phase diagram of manganese perovskites, that separates not only crystallographic phases, but also samples in which lattice effects must be taken into account, is proposed.

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I. INTRODUCTION

 $R_{1-x}A_x$ MnO₃ materials (R = rare earth, A = divalent alkali), show, for certain doping ranges, bulk ferromagnetism below a Curie temperature T_C which for $x \approx 1/3$ achieves maximum values.¹ Such materials, that crystallize in the perovskite structure,² have been considered for decades as prototype of double-exchange (DE) ferromagnets. Around their Curie temperatures, metal insulator transitions,¹ anomalous thermal lattice expansions,³ and colossal magnetoresistance (CMR)^{4,5} are found. Although initially CMR was explained qualitatively⁶ in the framework of the double-exchange mechanism,^{7–9} Millis, Littlewood, and Shraiman realized that the order of magnitude given by the DE model alone was not correct.^{10,11} They proposed that lattice effects were responsible for the observed CMR. Lattice effects seem to act on the magnetic coupling also, as evidenced via oxygen isotope shift in the ferromagnetic ordering temperature of La_{2/3}Ca_{1/3}MnO₃.¹² De Teresa et al. found, in the same material, evidence for the existence of magnetic polarons, also linked to lattice effects, and invoked them as an explanation of CMR.¹³ Nevertheless, a scenario involving phase separation, with a percolative transition, is being considered now,¹⁴⁻¹⁶ in a similar way as it has been proposed for the phase transition of cobalt perovskites.¹⁷⁻¹⁹ Through neutron diffraction,²⁰ NMR experiments,²¹ and the observation of hysteresis in the thermal dependence of resistivity,²² it was concluded that the transition at T_C is first order. It is tempting to think that this is a general property of all the $R_{2/3}A_{1/3}$ MnO₃ perovskites, but as Mira *et al.* have demonstrated by magnetization measurements, this is not the case.²³

For example, whereas La_{2/3}Ca_{1/3}MnO₃ shows a first-order phase transition at T_C , La_{2/3}Sr_{1/3}MnO₃ does not. Such similar compounds do not only differ in the character of the transition: the magnetoresistance in $La_{2/3}Sr_{1/3}MnO_3$ is more than one order of magnitude smaller than in La_{2/3}Ca_{1/3}MnO₃.²⁴ Also, while in La_{2/3}Ca_{1/3}MnO₃ there is evidence for the existence of magnetic polarons,¹³ these could not be detected in La_{2/3}Sr_{1/3}MnO₃. All this scenario has created debate and controversy, because depending on the compound studied, different interpretations were made. So, the main issue to address is, what makes such similar compounds behave so differently? In the search for an answer, the series $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ with x=0, 0.05,0.15, 0.25, 0.50, 0.75, and 1 (whose end members exhibit different types of phase transition) has been analyzed by means of calorimetric, dilatometric, resistivity, and magnetization measurements.

II. EXPERIMENTAL DETAILS

Samples were synthesized and characterized as in Ref. 23. Complex heat capacity data were obtained from differential scanning calorimetry (DSC) carried out in a modulated TA DSC 2920 instrument, heating the samples from 183 to 623 K at 2 K/min and with a modulation of ± 0.32 K every minute. Thermal expansion measurements were performed in a three terminal capacitance dilatometer based on White's design.^{25,26} Initial magnetization isotherms curves were measured by means of a vibrating sample magnetometer in fields up to 10 kOe in order to calculate the magnetic entropy change ΔS_M .²⁷ Magnetoresistance (MR) measurements at



FIG. 1. Complex heat capacity curves of $La_{2/3}(Ca_{1-x}Sr_x)MnO_3$ with x=0, 0.05, and 1. For x=0 and 0.05 a first-order transition at T_c is followed by a second-order one at T^* , marked with arrows. For x=1 only a clear second-order one is present, at T_c .

fixed temperatures were made by the standard four probe method at a constant current in rectangular shaped samples.

III. RESULTS AND DISCUSSION

DSC curves show a very interesting evolution with x (Fig. 1). For $La_{2/3}Ca_{1/3}MnO_3$, the curve shows the presence of two phase transitions: a first-order one, at the Curie temperature, and а second-order one at about 345 Κ. La_{2/3}(Ca_{0.95}Sr_{0.05})_{1/3}MnO₃ presents a similar behavior. But, for higher x only one phase transition, of second-order, is detected. This second-order transition is present in all the samples. The change from first- to second-order character is in agreement with the results of Ref. 23. We think that the origin of this difference must be searched in an aspect not sufficiently highlighted-to our knowledge-until now: Two perovskite structures (with space groups *Pbnm* and $R\overline{3}c$) exist in the samples analyzed here, as reported in several works (as, for example, in Ref. 22). The x=0 and 0.05 samples belong to the *Pbnm* space group, with practical invariance of the structural parameters. However, for x=0.15 a transition to the $R\bar{3}c$ space group is observed. A Rietveld refinement of the x=0.15 x-ray data with both phases yields less than 3% of Pbnm. That is, the change of space group happens at a tolerance factor value, $t \approx 0.92$,²⁸ in agreement with the results of Radaelli et al.²⁹ And the key point is that, whereas cooperative-long-range Jahn-Teller (JT) distortions are possible in the Pbnm phase,^{30,31} the higher symmetry of the MnO₆ octahedra in the $R\overline{3}c$ phase (with a unique Mn-O bond length) does not allow them (the JT distortion modes are tetragonal or orthorhombic: rhombohedral symmetry does not split the e_g orbital). Accordingly, only local JT distortions have been observed in $La_{1-x}Sr_xMnO_3$ with x < 0.35.³² JT distortions may assist polaron formation,^{20,32} which causes the anomalous volume change detected by magnetostriction measurements in La_{2/3}Ca_{1/3}MnO₃ (Ref. 3) (volume change is also one of the ingredients of a first order transition³³). In this context, dilatometry experiments carried out in $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ reveal different behavior around T_C



FIG. 2. (a) Inset: Dilation vs normalized temperature of La_{2/3}Ca_{1/3}MnO₃ and La_{2/3}Sr_{1/3}MnO₃. Note the anomalous thermal expansion at T_C in the x = 0 case, and the practical absence of such anomaly in the x = 1 one. Main frame: Derivative of the dilation curves of the La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO₃ series. The anomalous thermal expansion is much sharper and symmetric for the x=0 and 0.05 samples (t < 0.92) than in the other cases. Also note the absence in the Ca-rich compounds of the long "tail" appearing below T_C in x=0.15 samples, which is characteristic of second-order transitions in 3D systems (see also Fig. 1). (b) Shift of the peak of the derivative of the dilation measurements under magnetic field. The shift is monotonically reduced with x up to x=1, for which it is negligible.

above and below the critical tolerance factor t=0.92 [Fig. 2(a)]: the spikelike anomalous volume expansion of La_{2/3}Ca_{1/3}MnO₃ does not take place in La_{2/3}Sr_{1/3}MnO₃. Also, volume sensitivity to a magnetic field (magnetovolume effect) turns out to be high in La_{2/3}Ca_{1/3}MnO₃ (t<0.92) and negligible in La_{2/3}Sr_{1/3}MnO₃ (t>0.92), as seen in Fig. 2(b). This means that, whereas La_{2/3}Ca_{1/3}MnO₃ shows strong lattice effects, La_{2/3}Sr_{1/3}MnO₃ does not.



FIG. 3. (a) ΔS_M (H=10 kOe) vs temperature of the La_{2/3}(Ca_{1-x}Sr_x)MnO₃ series. (b) Magnetoresistance vs temperature for the same samples as in (a). (c) Comparison of the evolutions of both ΔS_M , MR and maximum dilation of the whole series versus tolerance factor.

The origin of the observations is yet to be elucidated. One possibility could be that, for manganites with t < 0.92 the static, cooperative JT deformations were replaced in the ferromagnetic phase by dynamic JT distortions, that would introduce vibrational modes into the spin-spin interaction, according to Zhou and Goodenough.³⁴ A dynamic JT deformation would give isotropic ferromagnetic order between Mn ions by superexchange. Therefore, in La_{2/3}Ca_{1/3}MnO₃, a material considered historically as an example of a pure DE system, two interactions, superexchange and double exchange, would indeed play a role.³⁵ According to this interpretation, the strong interaction between coopera-



FIG. 4. T_C vs tolerance factor phase diagram for $R_{1-x}A_x$ MnO₃. Results for La_{1-x}Na_xMnO₃ samples are taken from Ref. 40. The shadowed area separates compounds showing not only different structural phases but also different types of magnetic phase transition. This frontier also delimitates the importance of lattice effects, much more relevant for compounds on the left-hand side of this phase diagram. Magnetic polarons/phase separation, isotopic effect, first-order transitions at T_C , very high MR, large magnetic entropy changes, and anomalous and magnetic field dependent thermal expansion around T_C , are also limited to the left part of this diagram.

tive, dynamic oxygen displacements and electrons can be considered on the basis of a vibronic state of Mn^{3+} -O- Mn^{4+} -O- Mn^{3+} clusters in which the hole is mobile by a JT coupling (dynamic) to oxygen vibrations between Mn.^{34,35} At T_C the JT distortion would become static and cooperative, causing the extra superexchange term to disappear abruptly. At the same time the e electrons would become localized, but the ferromagnetic interactions between Mn sites would be still active in short range zones via Zener DE (to be distinguished from the de Gennes DE). The consequence would be a superparamagnetic second phase segregated at T_C . This phase would be present up to a temperature $T^* > T_C$, which would be the Curie temperature of the system if it were a pure double-exchange ferromagnet, i.e., if the first-order transition were not present at lower temperatures. It must be noted that Moreo et al.,¹⁶ by computational studies of models of manganese oxides, showed the generation of large coexisting metallic and insulating clusters induced by disorder near first-order transitions. Also in this line, another interpretation would be to consider Zhou and Goodenough's claim of vibronic states below T_C just as a consequence of phase segregation,³⁶ without the need of invoking the superexchange interaction to explain the experimental results. For La_{2/3}Ca_{1/3}MnO₃ the transition within the ferromagnetic clusters is detected by us at $T^* \approx 345$ K in the DSC curve of Fig. 1. It is worth mentioning that it is of the order of the Curie temperature of La2/3Sr1/3MnO3, and also similar to the temperature T_p reported by Ibarra *et al.*,³ where the thermal expansion curve deviates from the Grüneisen fit. In the region of coexistence of both phases, $T_C < T < T^*$, the magnetic behavior of La_{2/3}Ca_{1/3}MnO₃ is not understandable in the context of a conventional cluster model, contrarily to what happens with La_{2/3}Sr_{1/3}MnO₃, for which the paramagnetic part can be fitted with such model. For this reason Viret *et al.*³⁷ do not find anything of special relevance in materials like La_{0.75}Sr_{0.25}MnO₃, with *t*>0.92, in contrast with *Pbnm* manganites.

The change from *Pbnm* to $R\overline{3}c$ brings about considerable variations in many physical properties. For example, the magnetic entropy change $\triangle S_M$ was measured at T_C in all the samples, and it is presented in Fig. 3(a). It is observed that x=0 and x=0.05 compounds (*Pbnm*) show large magnetic entropy changes, similar to the reported by Guo et al.,³⁸ but, for $x \ge 0.15$ it is considerably smaller. Guo *et al.* attribute the large $\triangle S_M$ in Ca-doped LaMnO₃ to the sharp volume change at T_C . Taking into account that the x=0 and x=0.05 samples both exhibit a large volume expansion and the $x \ge 0.15$ does not, our results seem to confirm their hypothesis. The magnetoresistive properties are also dramatically affected when changing from *Pbnm* to $R\bar{3}c$. Figure 3(b) shows how it is more pronounced in x=0 and x=0.05 than in the others. It is worth mentioning how closely this variation correlates with $\triangle S_M$ and the maximum dilation values [Fig. 3(c)]. Some other noticeable variations, related to crystal symmetry, such as a crossover from anisotropic to isotropic electronic transport, have also been recently reported.39

With this idea in mind, we propose that the phase diagram of Hwang *et al.*²² for $R_{0.7}A_{0.3}$ MnO₃ should be improved by taking into account a new phase boundary at *t* = 0.92. This is

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a crucial boundary for a correct and whole description of manganese perovskites, because it separates "pure" DE systems (t > 0.92) from those that are not (t < 0.92), due to lattice effects. For t < 0.92 the JT distortion is causing the disappearance of the global magnetic order below the temperature expected according to the intensity of the exchange coupling constant. Röder, Zhang, and Bishop⁴⁰ have already proposed that lattice effects decrease the T_C of the "pure" DE system. Both Guo-Meng Zhao et al.¹² and Hwang et al.²² had detected the importance of the ionic radii on the properties of these perovskites, but they did not take into account the important role of the crystal structure and its relation with the observed physical properties. Concretely, Guo-Meng Zhao et al.¹² observed a rapid increase of the oxygen isotope exponent with decreasing the average ionic radius at the $R_{1-x}A_x$ site. In the framework of our reasoning this is the consequence of activating lattice effects. In the diagram of Fig. 4 we summarize this idea representing together our data and other available from the literature. It is worth mentioning those by Radaelli *et al.*,²⁹ where a similar *t* for the structural phase change is stated, and those by Savosta et al.,⁴¹ who measured continuous second order phase transitions in Nadoped LaMnO₃. These latter results are in agreement with our phase diagram, as they all have t > 0.92.

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