Change from first- to second-order magnetic phase transition in $La_{2/3}(Ca,Sr)_{1/3}MnO_3$ perovskites

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Using a criterion given by Banerjee [Phys. Lett. **12**, 16 (1964)] to distinguish first-order magnetic transitions from second-order ones, we demonstrate that not all the title perovskites exhibit a first-order transition at their Curie temperatures T_C. We observe that, although $La_{2/3}Ca_{1/3}MnO_3$ exhibits a first-order magnetic transition at T_C, $La_{2/3}Sr_{1/3}MnO_3$ exhibits a second-order one. [S0163-1829(99)05729-X]

I. INTRODUCTION

$Ln_{2/3}A_{1/3}MnO_3$ orthomanganites (Ln = rare earth, A = alkaline earth) present a magnetic phase transition at a ferromagnetic Curie temperature T_C. Metal-insulator transitions,[1,2] anomalous thermal lattice expansions,[3] and high negative magnetoresistance[4,5] are found in the vicinity of this critical point. Such rich physics have attracted the interest of many researchers, but, despite the efforts made, the nature of this magnetic transition is still not clear.

On one hand, in the well-known $La_{2/3}Ca_{1/3}MnO_3$ it seems to be of first order, attending to large volume changes,[3] and to the small thermal hysteresis found in resistivity[2] and magnetization curves versus temperature[6] near T_C. According to Hwang *et al.*,[2] in $La_{0.7}A_{0.3}MnO_3$ (A = alkaline earth) an abrupt change of the matrix element describing the electron hopping between Mn sites b, would cause an abrupt change in the double-exchange coupling value J_{DE} and may be responsible for a first-order phase transition. Archibald, Zhou, and Goodenough[7] generalized this conclusion to the $Ln_{0.7}A_{0.3}MnO_3$ orthomanganites on the basis of the transition from polaronic to itinerant electrons, that would be reflected in a compensating discontinuous change in the mean potential energy, explaining a first-order decrease in the mean Mn-O bond length.

On the other hand, some authors have pointed to second-order behavior in some concrete cases of this family, like $La_{0.7}Sr_{0.3}MnO_3$, because of the observation of a continuous phase transition.[8,9]

In this paper our aim is to gain insight into this controversy. For this purpose we have recovered the criterion given by Banerjee in 1964,[10] that allows the determination of the first- or second-order character of a magnetic transition. He detected the essential similarity between the Landau-Lifshitz[11] and Bean-Rodbell[12] criteria and condensed them into one that provides a tool to distinguish first-order magnetic transitions from second-order ones by purely magnetic methods. It consists on the observation of the slope of isotherm plots of H/M versus M^2, M being the experimentally observed magnetization and H the magnetic field. A positive or negative slope indicates a second-order or first-order transition, respectively. We have applied this to two compounds that have been at the center of the controversy: $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$. We have also studied mixed $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ compounds in order to observe the tendency between the two end members of the series. We note that in some of the literature referred in this paper a mention to $Ln_{0.7}A_{0.3}MnO_3$ instead of $Ln_{2/3}A_{1/3}MnO_3$ is made. In any case, in the framework of the phase diagram proposed by Urushibara *et al.*[5] for $La_{1-x}Sr_xMnO_3$, it is clear that variations from $x=0.30$ to $x=0.33$ are negligible, and the conclusions we are drawing here for $x=0.30$ are valid for $x=0.33$. The same argument serves for the $x=0.30$ and $x=0.33$ Ca-doped samples.[1]

II. EXPERIMENTAL DETAILS

Samples $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$, with $x=0$, 0.05, 0.15, 0.25, and 1, were prepared by solid-state reaction of La_2O_3,

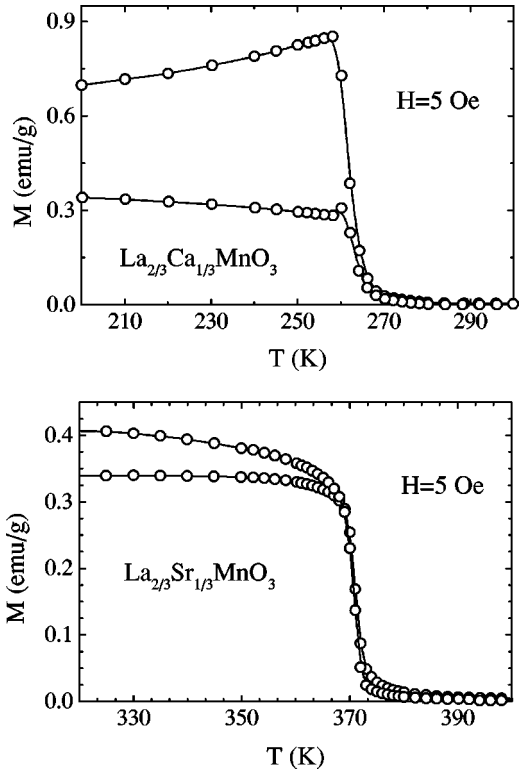

FIG. 1. Magnetization versus temperature for $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$ under an applied magnetic field of 5 Oe.

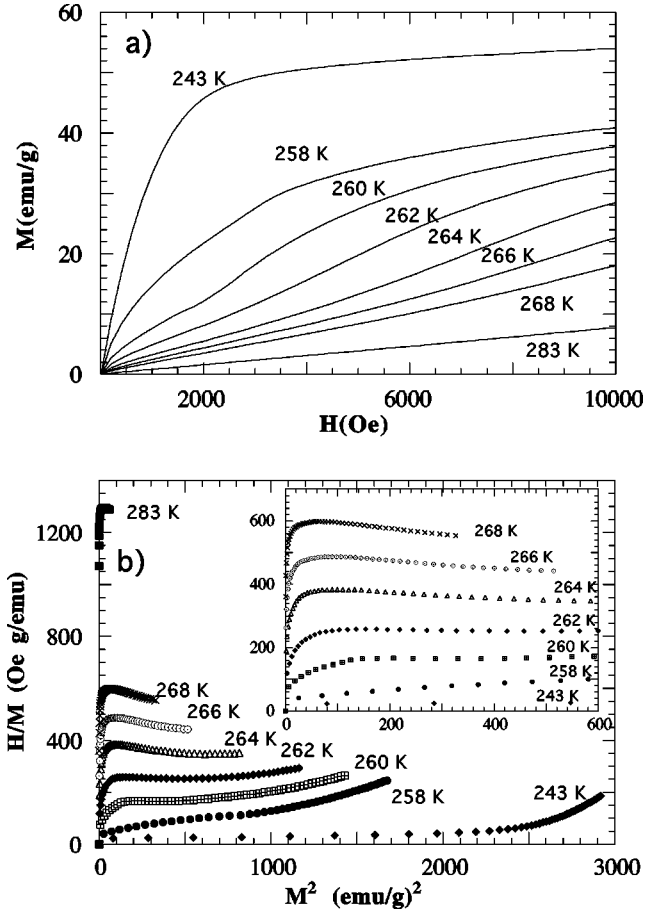

FIG. 2. (a) Magnetization versus magnetic field isotherms for $La_{2/3}Ca_{1/3}MnO_3$ in the vicinity of its T_C. Note the anomalies of slope at intermediate fields for isotherms between 258 and 268 K. (b) H/M vs M^2 plot of the above isotherms. It is clear the negative sign of the slope for some temperatures. The inset shows the detail for small values of M^2.

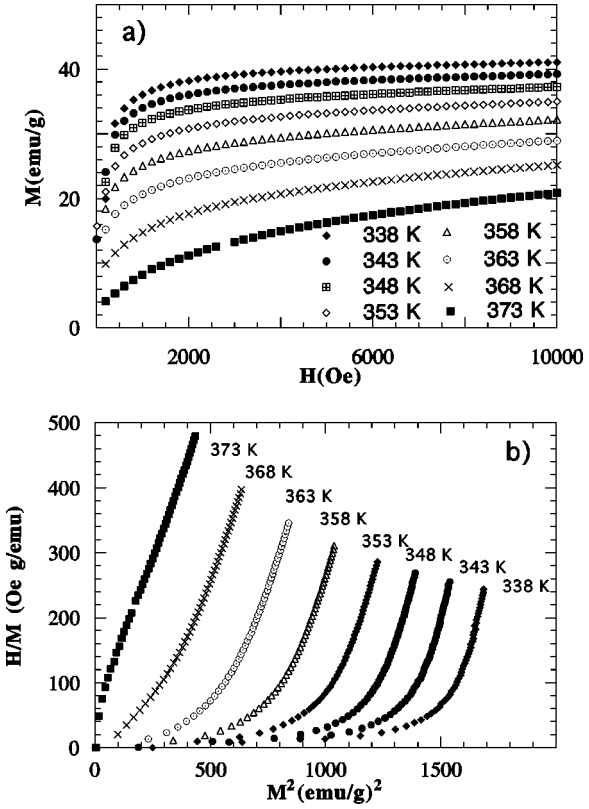

FIG. 3. (a) Magnetization versus magnetic-field isotherms for $La_{2/3}Sr_{1/3}MnO_3$ in the vicinity of its T_C. (b) H/M vs M^2 plot for such isotherms. The slope is always positive, denoting the second-order character of the phase transition.

CaO, $SrCO_3$, MnO_2, and MnO (at least 99.995% in purity), which were heated in air in two steps (1100 °C for 70 h, 1200 °C for 27 h) and pressed into disks. The temperature was slowly ramped at 5 °C/min, and cooled down to room temperature at 2 °C/min. Intermediate grindings were made. Pellets were finally annealed at 1300 °C for 100 h, with an intermediate grinding at 30 h. The nominal oxygen content was near the stoichiometric value as determined by iodometric analysis (for example, $3 \pm \delta = 2.965(3)$ and 2.98(2) for LaSrMnO and LaCaMnO, respectively). X-ray powder patterns were collected at room temperature using a Philips PW1710 diffractometer, working with CuKα radiation. The lattice parameters for the end members of the series, derived by Rietveld analysis, are in agreement with those reported in the literature. Electron spin resonance spectra of the samples were taken at 9.5 GHz (X-band) between 110 and 700 K with a Bruker ESP-300 and a Bruker EMX spectrometer. The small linewidth observed in our samples is a signature of the good quality and homogeneity of the material.[13] Magnetic measurements were performed with a Quantum Design superconducting quantum interference device and a DMS-1660 vibrating sample magnetometer.

III. RESULTS AND DISCUSSION

Low-field magnetization versus temperature was first measured for both end members of the series, in order to have an estimation of the transition temperatures. The results are presented in Fig. 1 and from them we extract Curie temperatures of the order of 260 K for $La_{2/3}Ca_{1/3}MnO_3$ and 370 K for $La_{2/3}Sr_{1/3}MnO_3$, both in agreement with data reported in previous literature.[6,9] In order to apply the Banerjee criterion we have measured initial magnetization isotherms in the vicinity of the critical points. Before each run, samples were heated above their T_C and cooled to the measuring temperature under zero field, in order to ensure a perfect demagnetization of the samples. Figure 2(a) shows the results for $La_{2/3}Ca_{1/3}MnO_3$. The first characteristic that calls our attention is the peculiar behavior of the curves at intermediate fields, where a decrease of slope followed by an increase is observed. This behavior near the critical point was observed by Bean and Rodbell in MnAs[12] (which presents a first-order transition at its Curie temperature) and used by Banerjee to test his criterion.[10] In Fig. 2(b) we apply it and obtain that H/M vs M^2 isotherms between 260 and 268 K present negative slopes in some parts, which according to the criterion used here is an indication of the first-order character of the transition. A similar change of slope in M vs H isotherms has been observed recently in the layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ (Ref. 14) at the first-order phase transition point from a ferromagnetic to a canted state[15] which exhibits colossal magnetoresistance (CMR).

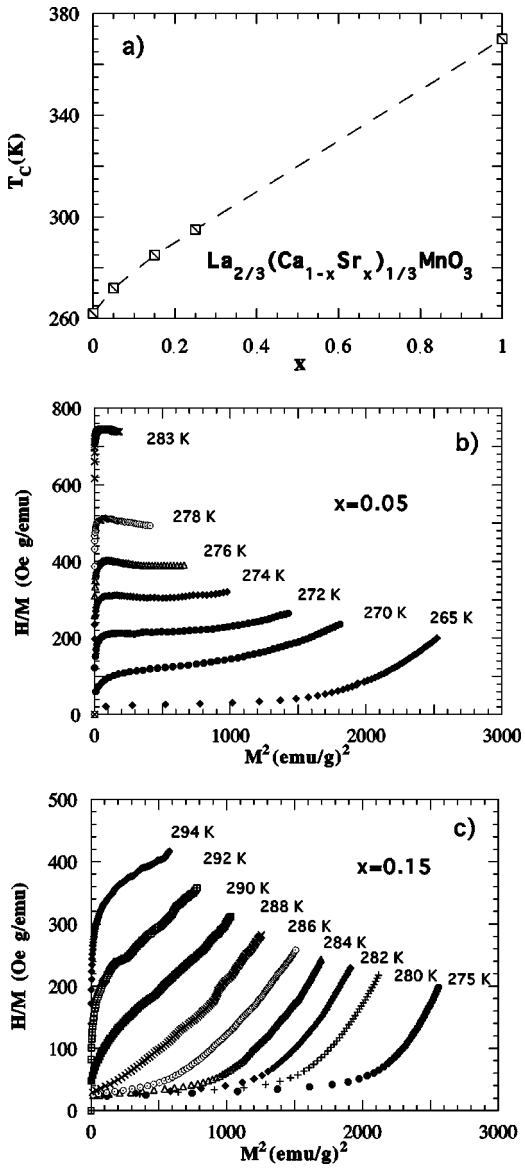

FIG. 4. (a) Dependence of the Curie temperature T_C on the Sr-doping degree x. (b) H/M vs M^2 plots of isotherms in the vicinity of the Curie point of $La_{2/3}(Ca_{0.95}Sr_{0.05})_{1/3}MnO_3$. (c) H/M vs M^2 plots of isotherms in the vicinity of the Curie point of $La_{2/3}(Ca_{0.85}Sr_{0.15})_{1/3}MnO_3$.

When the same measurements in $La_{2/3}Sr_{1/3}MnO_3$ are done it is seen that the isotherms [Fig. 3(a)] do not display the anomalous change of slope of the previous case. This difference is more clearly seen in the H/M vs M^2 plots of Fig. 3(b) where a positive slope for all the M^2 range is present.

Substitution of Ca by Sr causes an increase of T_C [Fig. 4(a)] as well as a decrease of the low-field magnetization and a reduction of the differences between zero-field-cooled and field-cooled M vs T curves. It is detected that the character of the transition is very sensitive to Sr doping. Inspecting the Banerjee plot of Fig. 4(b) it can be seen that for $x=0.05$ the material presents still a first-order phase transition at T_C, but, attending to the slopes, such character is weaker than in $La_{2/3}Ca_{1/3}MnO_3$. In the case of $La_{2/3}(Ca_{0.85}Sr_{0.15})_{1/3}MnO_3$ the phase transition is already a second-order one [Fig. 4 (c)].

When the properties of the end members of the series are compared, one of the main qualitative differences is that the transition at T_C is not accompanied by a metal-insulator transition in $La_{2/3}Sr_{1/3}MnO_3$.[5] Nevertheless, that does not seem to be a significative effect: $La_{0.8}Sr_{0.2}MnO_3$ does show a metal-insulator transition near T_C,[5] and inspecting the Arrott plots[16] given by Lofland *et al.*[17] and Mohan *et al.*[18] it is clear that the magnetic transition is also of second order for this composition.

In summary, we have determined, using a criterion given by Banerjee, that although $La_{2/3}Ca_{1/3}MnO_3$ exhibits a first-order transition at T_C, $La_{2/3}Sr_{1/3}MnO_3$ does not. Therefore the existence of a first-order transition for the $Ln_{2/3}A_{1/3}MnO_3$ orthomanganites, irrespective of the identity of Ln or A, cannot be stated. Also, taking into account that the CMR compound $La_{0.8}Sr_{0.2}MnO_3$ presents a second-order phase transition at T_C we establish that the existence of a first-order phase transition is not a universal feature of CMR materials. The nature of the ferromagnetic-paramagnetic phase transition of CMR systems has been the concern of some experiments, recently also in layered manganites,[19] but clear conclusions could not be drawn. Eventual attempts in the search for connections between colossal magnetoresistance and first-order transitions should be made with the awareness of the results presented here, for example in those trying to relate the behavior of the correlation length at T_C with the formation of magnetic polarons.[20]

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