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Ultrasonic evidence of an uncorrelated cluster formation temperature in manganites with first-order magnetic transition at the Curie temperature

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Ultrasonic attenuation and phase velocity measurements have been carried out in the ferromagnetic perovskites $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$. Data show that the transition at the Curie temperature T_C changes from first to second order as Sr replaces Ca in the perovskite. The compound with first-order transition shows also another transition at a temperature $T^* > T_C$. We interpret the temperature window $T_C < T < T^*$ as a region of coexistence of a phase-separated regime of metallic and insulating regions, in the line of recent theoretical proposals.

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I. INTRODUCTION

The advances in the comprehension of the physical properties of manganese perovskites have been given in two main boosts. The first one started in 1950, when these materials were first considered by Jonker and van Santen.[1] In that period, which spanned over more than a decade, the basic mechanisms governing their magnetic and transport properties were defined, giving rise to the description of the double-exchange interaction.[2–4] The second one took place last decade, after the discovery of colossal magnetoresistance[5,6] (CMR) (although a high MR had already been observed experimentally before, first by Searle and Wang[7] and later by Kusters *et al.*[8]). During this period, in which we are still immersed, the research activity reached a magnitude that made the topic a starring one in the community of condensed-matter physics, and the current opinion about the state of the art underwent several changes. In the first few years after the description of CMR, explanations were tried on the basis of double exchange,[9] but it was demonstrated soon that such effect alone could not explain the magnitude of CMR.[10] Later, certain evidences in favor of the existence of an inhomogeneous electronic state in these materials started to appear.[11–13] This tendence continues nowadays after the conclusions of many groups that found—and are still finding—that the homogeneous description of the magnetic and electronic states of manganites is almost ruled out.

In order to establish the basis for such behavior the idea of phase separation, i.e., the coexistence of regions of localized and itinerant carriers within the same crystallographic structure, has been proposed.[14,15] In this framework, Dagotto, Hotta, and Moreo[16] proposed in a recent review the existence of a temperature window where coexisting metallic and insulating clusters appear above the Curie temperature T_C when this transition is first order and there is a source of disorder. This temperature window would extend up to $T^* > T_C$, where these clusters dissociate to form two-Mn Zener polarons (or small polarons). The aim of the present work is to find experimental evidence of such temperature T^*. For this purpose, ultrasonic attenuation and phase velocity measurements were carried out in $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$. This technique is proved to be a very sensitive tool not only for studying defects and microscopic processes in solids, but also for probing systems undergoing magnetic and structural phase transitions.

II. EXPERIMENTAL DETAILS

Samples were prepared by solid-state reaction of La_2O_3, CaO or $SrCO_3$, MnO_2, and MnO (at least 99.995% in purity), which were heated in air in two steps (1100 °C 70 h, 1200 °C 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 pressed at 7 ton/cm^2 and annealed at 1300 °C for 100 h, with an intermediate grinding at 30 h. The nominal oxygen content was almost stoichiometric as determined by iodometric analysis. X-ray powder patterns were collected at room temperature using a Philips PW1710 diffractometer, working with Cu$K\alpha$ radiation. The lattice parameters, derived by Rietveld analysis, are in agreement with those reported in the literature.

Cylindrical pellets, with a diameter of 10.0 mm and heights 2.4 mm (LaCaMnO) and 3.1 mm (LaSrMnO), were used to perform ultrasonic measurements. The two opposite faces of each sample were polished so that the difference between two points in each surface was not more than 1 μm. The ultrasonic velocity and attenuation measurements were performed on a Matec-6600 series by means of the conventional pulse-echo technique. *Y*-cut quartz transducers of 5 MHz fundamental frequency were used for transverse ultrasonic excitation. They were coupled to the sample surface with a grease for high-temperature uses (leak point 550 K). The sample was coupled at high temperature, and then

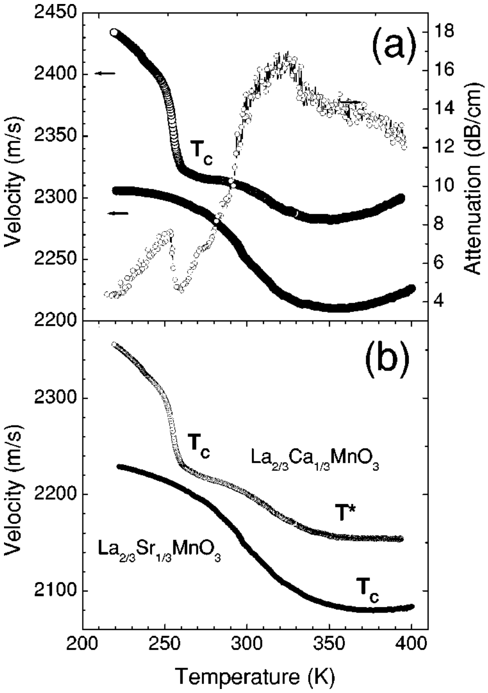

FIG. 1. (a) Transversal ultrasonic velocity vs temperature of $La_{2/3}Ca_{1/3}MnO_3$ (open symbols) and $La_{2/3}Sr_{1/3}MnO_3$ (filled symbols), and attenuation vs temperature of $La_{2/3}Ca_{1/3}MnO_3$ (attenuation not measurable in LaSrMnO), as measured. (b) Ultrasonic velocity vs temperature for the same samples after background substraction. Note the steep decrease of velocity as well as the peak in attenuation at the T_C of LaCaMnO. Note also the similar velocity anomalies in the region 350–370 K, corresponding to T^* in LaCaMnO and to T_C in LaSrMnO.

cooled until 200 K and maintained at this temperature for 15 min before measurements were carried out. The ultrasonic elapsed time for a pulse round trip (transit time) was obtained with the pulse-echo-overlap technique at the initial temperature. Then, time variation with temperature was automatically monitored with a sensitivity of 0.05 ns at 5 MHz. The experiment was taken in a closed-cycle refrigerator (Janis) and the temperature of the sample was varied at a rate of about 0.5 K/min.

III. RESULTS AND DISCUSSION

In Fig. 1(a) we show ultrasonic velocity vs temperature data for $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$, and attenuation vs temperature data for $La_{2/3}Ca_{1/3}MnO_3$, obtained with 5-MHz transversal waves between 220 and 400 K. For LaSrMnO it was impossible to measure the attenuation because its high value allowed to obtain only two echoes at room temperature (at higher temperatures the second echo became negligible). The transit time was measurable at room temperature, and then time variations were measured with our automated improved Matec system. The influence of thermal expansion has not been taken into account, because it is negligible: if $(\delta l)/l = 2\times10^{-4}$ we have that for our sample, with $l = 2.4$ mm thick (4.8-mm microwave path) and a velocity of about 2500 m/s, δt (t denotes time) is 5×10^{-4} s and therefore, at T_C, the associated variation of velocity is far smaller than the one we measured.

In our original ultrasonic velocity data, an approximately linear increment with temperature was observed at temperatures above 350 K for both samples. At this temperature range no mechanism related with magnetic phase transitions is expected, and this variation should be attributed to another mechanism, as produced by crystalline defects present in the material. This component must be substracted from original data, in order to obtain the true transition temperatures. As is well known,[17] dislocation lines present in the material can oscillate driven by an oscillatory applied stress, showing a resonant behavior. From experimental data and the kink picture for dislocation anelasticity, Moreno-Gobbi and Eiras[18] have shown, working on crystalline copper, that this resonant mechanism gives a term proportional to T for velocity and proportional to T^2 for attenuation in the temperature interval investigated in the present work. The coefficient of proportionality depends on L^2 for velocity and L^4 for attenuation, where L is the average free length of the segment of dislocation lines. In the present paper we assume a background of this kind in order to take into account the behavior of velocity observed at high temperatures. The velocity background was fitted to the high-temperature region of velocity vs temperature curves, and then substracted from original data. These fits gave a term 0.37 T for LaCaMnO and 0.46 T for LaSrMnO. The so-corrected velocity data are presented in Fig. 1(b). The differences between the numerical values of the coefficients of proportionality have their origins in the different values of L expected for different materials.[17]

The ultrasonic velocity for $La_{2/3}Ca_{1/3}MnO_3$ presents two clear anomalies: an abrupt hardening at about 250–260 K, and another lesser at about 350–360 K. The first one marks the T_C of this system[19–23] ($T_C = 260$ K). The behavior is similar to that found at MHz frequencies by other authors,[24,25] and at kHz frequencies by Cordero *et al.*[26] The abrupt decay of the curve at T_C signals the first-order character of this transition,[27] an interpretation that is in agreement with results obtained from other techniques.[19–23] The decay in velocity is accompanied by a peak in the attenuation curve at T_C. This peak is asymmetric, in agreement with the results of Cordero *et al.*,[26] who explain it invoking the presence of inhomogeneous phases below T_C in a similar way to relaxor ferroelectrics.[28,29]

The second anomaly takes place above T_C, showing a hardening process at $T^* \simeq 350$–360 K (Fig. 2). In Fig. 1 a very large attenuation peak at 320 K accompanying this velocity anomaly is also observed. This was not observed by Cordero *et al.* at kHz frequencies, but is clearly observed in our MHz measurements. The reason lies on the higher sensitivity of MHz techniques to small inhomogeneities, as magnetic clusters, due to the shortest wavelength (≈ 0.5 mm at 5 MHz for transversal waves).

In Figs. 1 and 2 it is also observed that the only noticeable anomaly in the ultrasonic velocity curve of $La_{2/3}Sr_{1/3}MnO_3$ is a hardening process beginning at about 370 K (in the order of that of LaCaMnO in the same temperature region), which is coincident with the second-order phase-transition point of this compound, clearly observed by magnetization measure-

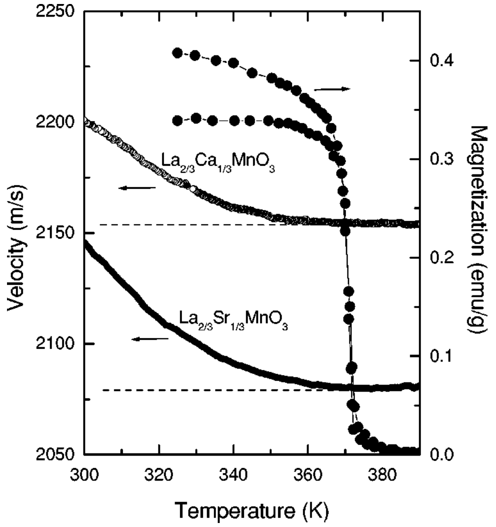

FIG. 2. Detail of the corrected transversal ultrasonic velocity vs temperature of $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$ in the T^* region. For comparison, magnetization vs temperature data (zero field cooled and field cooled) of $La_{2/3}Sr_{1/3}MnO_3$ are included.

ments ($T_C \simeq 370$ K).[22,30] In the explored temperatures, no more transitions were detected. Based on this behavior we can perfectly associate the process of hardening observed at 370 K to this second-order phase transition.

One of the open issues in the comprehension of the physics of ferromagnetic manganese perovskites at present is to determine the nature of the magnetic phase above T_C. From our ultrasonic velocity data it seems that this phase is different in the two systems considered. First of all, whereas LaCaMnO displays a first-order transition at T_C, LaSrMnO presents a second-order one. This difference, which has already been highlighted by magnetic measurements,[22] and attributed by Mira *et al.*[23] to a change in the crystal symmetry, from orthorhombic to rhombohedral, seems to have further implications. Magnetoresistance, thermal expansion, magnetovolume, and magnetocaloric effects experience a considerable change when moving from one compound to the other.[23,31,32] Also, calorimetric data showed evidence for an anomaly at a similar T^* in those manganites $La_{1-x}(Ca,Sr)_xMnO_3$ with a first-order transformation at T_C,[23] in agreement with the ultrasonic data presented here that show the existence of a transition point at $T^* > T_C$ in LaCaMnO. It is worth mentioning that our T^* is similar to the point at which both the volume thermal expansion deviates from a Gruneisen fit and the inverse magnetic susceptibility deviates from a Curie-Weiss fit, after results of de Teresa *et al.* in $La_{2/3}Ca_{1/3}MnO_3$ (Ref. 33). Supporting our results, we have to mention that neutron-diffraction studies[34] in the paramagnetic region of $La_{2/3}Sr_{1/3}MnO_3$ show differences with respect to $La_{2/3}Ca_{1/3}MnO_3$. We want also to call the attention on the similar values of the temperatures of the second-order transitions, $T^* \simeq 350-360$ K for $La_{2/3}Ca_{1/3}MnO_3$ and $T_C \simeq 370$ K for $La_{2/3}Sr_{1/3}MnO_3$. In some sense, it leads us to think that the magnetic interaction between the Mn atoms is of the same strength in both compounds and only the occurrence of the first-order change in LaCaMnO is breaking the long-range order at a temperature below T^*. After Röder, Zhang, and Bishop,[35] this might be due to lattice effects, which would decrease the T_C associated with the double-exchange coupling.

The anomaly at T^* shows that the magnetic phase transition is not from ferromagnetism to a purely paramagnetic state, but some sort of magnetic structure is present. Such idea is in accordance with the theoretical results of Moreo *et al.*,[13] who have proposed, after computer simulations, that large coexisting metallic and insulating clusters of equal electronic density are generated in manganese oxides with first-order magnetic transitions. Kimura *et al.*[36] have qualified these compounds as relaxor ferromagnets, with a relaxation from one phase to the other. The fluctuations between both phases have been seen by transmission electron Microscopy by Podzorov *et al.*[37] In such a case, after Kimura *et al.*[36] the transition would be diffuse, such as the one observed by us at T^*. Nowadays there is growing experimental work that leads one to assume the electronic phase-separated nature of such materials, and now it is well established that this phase separation is not due to chemical inhomogeneities or to the existence of phases with a different chemical composition.[38] Although this approach is quite recent in manganese perovskites, it had already been proposed by Señarís Rodríguez and Goodenough[39] to explain the magnetic and electrical properties of Sr-doped cobalt perovskites, thinking of a percolative transition at T_C.

In summary, we consider that our data confirm the existence, in $La_{2/3}Ca_{1/3}MnO_3$, of the temperature window $T_C < T < T^*$ proposed by Dagotto, Hotta and Moreo,[16] where probably the coexistence of a phase-separated regime of metallic and insulating regions could be taking place. Such window is not observed in $La_{2/3}Sr_{1/3}MnO_3$, a material with a conventional second-order ferromagnetic to paramagnetic phase transition at its Curie temperature.

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