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# Infrared study of charge delocalization induced by pressure in the $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ manganite

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We measured the pressure dependence of the room-temperature infrared absorption spectrum of the pseudocubic  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  manganite. On increasing pressure up to 10 GPa we observe the increase of a broad band associated with polaronic absorption, which partially screens the high-frequency phonon at high pressures. We also measured absorption spectra of the same sample as a function of temperature, and of the layered  $\text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_4$  manganite as a function of pressure. The comparison between different sets of spectra clearly shows that the increase of the broad-band absorption observed in the  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  manganite is due to a pressure-induced charge delocalization process. However, the metallic state is not achieved at room temperature, at least in the explored pressure range.

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## I. INTRODUCTION

It is well known that the transport properties of manganese perovskites  $A_{1-x}A'_x\text{MnO}_3$  ( $A$  is the rare earth and  $A'$  is a divalent cation)<sup>1</sup> are determined by two competing effects.<sup>2</sup> While the magnetic double exchange increases the electron kinetic energy and hence charge delocalization, the strong Jahn-Teller (JT) coupling, which is at the origin of the JT polarons, tends to localize the excess charge in the local distortion of the oxygen octahedron around the  $\text{Mn}^{+3}$  ion.<sup>3</sup> The transition from the paramagnetic insulating phase to the ferromagnetic metallic phase may then be explained in terms of magnetic double exchange promoted by polaronic carriers along the path  $\text{Mn}^{+3}-\text{O}^{2-}-\text{Mn}^{+4}$ . In the above scenario, the charge localization is directly related to the distortion of the  $\text{MnO}_6$  octahedron. Diffraction measurements as a function of the temperature<sup>4</sup> on  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  have indeed shown that the large JT distortions of the octahedron in the insulating state reduces to vanishingly small values below the insulator to metal (IM) transition temperature, when excess charges are delocalized.

In studying the IM transition, also the role of the  $A$ -site average ionic radius  $R_a = (1-x)r_A + xr_{A'}$  (where  $r_A$  and  $r_{A'}$  are the ionic radii of the  $A$  and  $A'$  atoms, respectively) has been considered. In the  $T$  vs  $R_a$  phase diagram, at constant doping  $x$ , the increase of  $R_a$  produces both a reduction of the octahedron distortion and an increase of the Curie temperature  $T_c$ .<sup>5,6</sup> The common idea is that the IM transition can occur if a sufficient reduction of the "free volume" around the  $A$  site is obtained. The octahedron is thus forced to be undistorted and the Mn-O-Mn bonding angle tends to  $180^\circ$ .<sup>7,8</sup> These structural modifications have the net result of increasing the Mn-O-Mn hopping rate, and therefore the charge delocalization. This effect can in principle be achieved either by increasing the average dimension of the atom at the  $A$  site (internal pressure) or by contracting the cage of the  $\text{MnO}_6$  octahedra (external pressure  $P$ ). Follow-

ing this idea the effect of the external pressure has been studied mainly by means of resistivity measurements in the 0–2 GPa pressure range. A small increase of the Curie temperature measured at ambient pressure  $T_c(0)$  was indeed observed by applying a pressure  $P$  in a small range on several pseudocubic manganites.<sup>7,9</sup> As a matter of fact an equivalence between internal and external pressure has been established in the 0–1.5 GPa pressure range,<sup>7</sup> although recent Raman experiments on  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  indicate that this equivalence does not hold in the high pressure regime.<sup>10</sup>

Resistivity measurements have shown that  $T_c$  linearly increases with  $P$  in the low pressure (LP) regime (0–1 GPa) and that the absolute value of  $(dT_c/dP)_{\text{LP}}$  depends on  $T_c(0)$ .<sup>9,11,12</sup> In particular, manganites with high  $T_c(0)$  are less sensitive to pressure than those with low  $T_c(0)$ . In considering the pressure dependence of  $T_c$ , we recall that<sup>9</sup>

$$\frac{d \ln T_c}{dP} = -\frac{7}{2}k(d) - 2\theta \tan(\theta)k(\theta) - 2\frac{d\alpha}{dP}. \quad (1)$$

The first two terms represent the pure steric contribution, determined by the average Mn-O bond-length ( $d$ ) compressibility  $k(d)$  and by the O-Mn-O angle ( $\theta$ ) compressibility  $k(\theta)$ . The last term in Eq. (1) is due to the pressure dependence of the phonon-carrier coupling parameter  $\alpha$ .<sup>13</sup> For the  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  manganite [ $T_c(0) = 220$  K] in the LP regime, the steric contribute is  $\sim 0.02 \text{ GPa}^{-1}$  (from x-ray diffraction data<sup>14</sup>) and  $(d \ln T_c/dP)_{\text{LP}} \sim 0.09 \text{ GPa}^{-1}$  (on the basis of the data available in literature<sup>9,11,15</sup>) Eq. (1) thus yields  $(-2d\alpha/dP)_{\text{LP}} \sim 0.07 \text{ GPa}^{-1}$ . As previously found,<sup>9</sup> the  $d\alpha/dP$  term has a dominant role in determining  $dT_c/dP$  in low  $T_c$  manganites. Under the crude approximation of keeping constant  $dT_c/dP$  over a wide pressure range, a room temperature metallization pressure  $P_{\text{IM}}$  can be predicted around 4–5 GPa for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . A similar value for  $P_{\text{IM}}$  can be estimated by assuming the above mentioned equivalence between internal and external pressure.<sup>7</sup> We want to stress that  $dT_c/dP = \text{const}$  is a drastic assumption, in

that different experimental data suggest a slight decrease of  $dT_c/dP$  even at low pressures.<sup>11,12</sup>

Infrared (IR) spectroscopy is a powerful tool to study charge delocalization processes, as proved in particular by temperature dependent measurements on different layered perovskites<sup>16</sup> and on pseudocubic  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites.<sup>17–19</sup> The absorption spectra of these compounds in the insulating phase show that the high frequency IR-active phonons are superimposed on a broad background. This latter feature is very sensitive to the extent of charge localization, being mainly related to the photoionization of the polarons originated by the excess charges self trapped in a local lattice distortion.<sup>16,17</sup> The aim of the present work is to study, by means of IR absorption spectroscopy, the effect of the applied pressure on the charge delocalization in the  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  (LCMO) manganite.

## II. MEASUREMENTS AND RESULTS

We measured the absorption of LCMO in the  $550\text{--}1300\text{ cm}^{-1}$  IR range both at ambient pressure in the temperature range  $25\text{--}296\text{ K}$ , and at room temperature as a function of pressure (up to  $10\text{ GPa}$ ). The former measurements allow us to characterize the charge delocalization effect on the absorption spectrum at the IM transition. Finally, we performed room temperature measurements as a function of pressure (up to  $10\text{ GPa}$ ) on the layered  $\text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_4$  (SLMO) manganite, which, at ambient pressure, is an insulator at any temperature and doping concentration.<sup>20</sup> In SLMO, to be regarded as a reference compound, the external pressure is expected to be much less effective than in the pseudocubic system, since the  $A$  sites are not trapped in a tridimensional cage of  $\text{MnO}_6$  octahedra as in LCMO, but they are intercalated between disconnected  $\text{MnO}_6$  single sheets.<sup>20</sup>

Infrared measurements were performed by using a Bomem DA3 interferometer equipped with KBr beam splitter and MCT detector, on polycrystalline samples of LCMO manganite prepared by a standard solid state reaction method and characterized by x-ray diffraction,<sup>21</sup> and of SLMO manganite.<sup>16</sup> Each sample was finely milled to obtain a powder with an average grain size of the order of  $1\text{ }\mu\text{m}$ . Ambient pressure measurements in the temperature range  $296\text{--}25\text{ K}$  were made on LCMO by following a standard procedure.<sup>22</sup> At each temperature we measure the signal transmitted by a pure KBr pellet  $I_0(\omega)$ , and that transmitted by the sample powder dispersed in a KBr pellet  $I(\omega)$ . The optical density  $O_d(\omega) = \ln[I_0(\omega)/I(\omega)]$  is, to a first approximation, proportional to the optical conductivity of the sample, and thus directly provides the spectral shape of the sample absorption.<sup>22</sup> The  $O_d(\omega)$  obtained at different temperatures are shown in Fig. 1, where the frequency range is empirically divided into region I, phonon contribution, and region II, broad-band contribution. On cooling the sample down to  $225\text{ K}$  (insulating phase) the broad-band decreases and thus the minimum around  $700\text{ cm}^{-1}$  deepens, owing to the increasing localization of excess charges. A dramatic change in the  $225\text{--}215\text{ K}$  range is then observed, associated with the IM transition at  $220\text{ K}$ . When entering the metallic

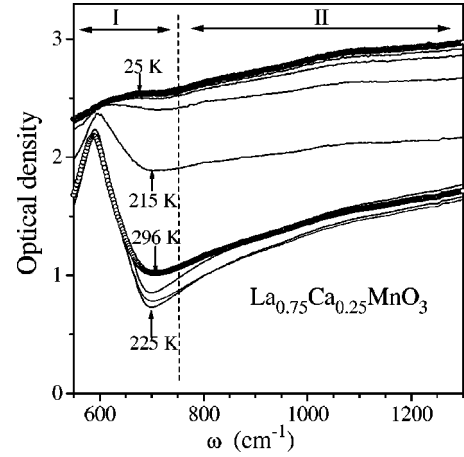


FIG. 1. Ambient pressure optical density  $O_d(\omega)$  of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  (LCMO) at  $T=296, 250, 225, 220, 215, 180, 140, 115, 60$ , and  $25\text{ K}$ . The broken line separates the spectral regions I and II (see text).

phase, the broad-band strongly increases and significantly screens the phonon peak owing to the onset of the charge delocalization at the IM transition. On further cooling, the delocalization process continues further: the broad band increases up to an asymptotic level and the phonon peak is almost completely screened. These results mark the evolution pattern from the insulating to the metallic phase of LCMO.

Room temperature spectra as a function of pressure were collected using a membrane diamond anvil cell (MDAC) with steel gaskets having a typical  $200\text{ }\mu\text{m}$  diameter hole. We measured  $I_0(\omega)$  on a KBr pellet obtained by synthesizing salt powder within the gasket hole, and  $I(\omega)$  after smearing manganite grains on the top surface of the KBr pellet. This procedure ensures hydrostatic pressure conditions for the sample, allowing a minimum working pressure of the order of  $1\text{ GPa}$ . Few ruby nanospheres were also placed in the cell to measure the pressure through the standard ruby fluorescence technique.<sup>23</sup> Further details on the experimental procedure will be reported in a forthcoming paper. In spite of the small diameter hole in the gasket, reliable  $O_d(\omega)$  spectra are obtained with the employed experimental setup in the frequency range  $550\text{--}1300\text{ cm}^{-1}$  with a resolution of  $8\text{ cm}^{-1}$ . The  $O_d(\omega)$  spectra of the LCMO and SLMO manganites measured at different pressures are shown in Figs. 2 and 3, respectively. A comparison between temperature and pressure dependence of the LCMO spectral shapes is shown in the inset of Fig. 2, where the  $O_d(\omega)$  measured at ambient pressure for  $T_{\text{max}}=296\text{ K}$  and  $T_{\text{min}}=25\text{ K}$ , and those measured at room temperature for  $P_{\text{min}}=1.6$  and  $P_{\text{max}}=10\text{ GPa}$  are reported. The ambient pressure measurements are multiplied by the same scaling factor (1.4), which normalizes the ( $296\text{ K}\text{--}0\text{ GPa}$ ) spectrum onto the ( $296\text{ K}\text{--}1.6\text{ GPa}$ ) one in the spectral region II. The slight difference between the phonon peaks can be ascribed to the different pressure at which the two measurements have been performed ( $P=0$  and  $P_{\text{min}}=1.6\text{ GPa}$ ). In any case the overall agreement between the spectra gives us confidence on the reliability of the high pressure results, excluding the occurrence of significant spu-

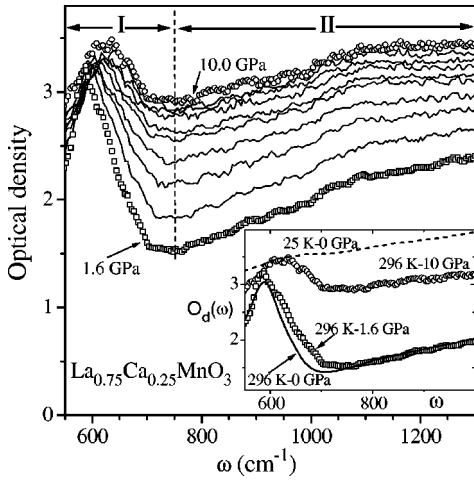


FIG. 2. Room temperature optical density  $O_d(\omega)$  of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  (LCMO) at  $P = 1.6, 2.4, 3.4, 4.3, 5.6, 6.3, 7.3, 8.2, 9.1,$  and  $10$  GPa. The broken line separates the spectral regions I and II. In the inset, the  $296$  and  $25$  K  $O_d(\omega)$  at  $P = 0$  GPa are multiplied by the same scaling factor to be conveniently compared with the pressure dependent ones (see text).

rious effects due to scattering phenomena or pellet inhomogeneities in the high pressure measurements.

The phonon contribution, well evident in region I (see Figs. 2 and 3), is assigned to the in plane Mn-O stretching mode of  $B_u$  symmetry in LCMO (Ref. 24) and of  $E_u$  symmetry in SLMO.<sup>25,16</sup> Figures 2 and 3 show a remarkable pressure-induced hardening of the phonon peak, basically due to the contraction of the interatomic distances under pressure. Although a detailed analysis of this effect is beyond the aim of the present paper, we want to stress that a similar pressure-induced hardening has been found for the high frequency Raman active modes in a recent high pressure work.<sup>10</sup> Here we mainly focus on the pressure dependence of the broad-band which, as previously discussed, can be seen as a marker of the extent of charge delocalization. In

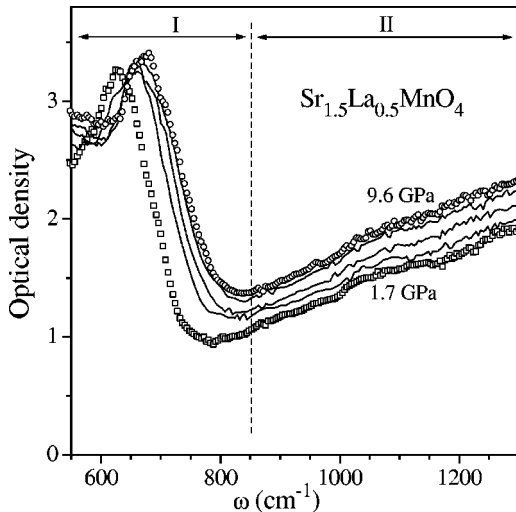


FIG. 3. Room temperature optical density  $O_d(\omega)$  of  $\text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_4$  (SLMO) at  $P = 1.7, 3.8, 5.9, 8.0,$  and  $9.6$  GPa. The broken line separates the spectral regions I and II.

Fig. 2 an increase of the absorption in region II is quite evident on increasing pressure, in parallel to a remarkable screening of the phonon peak. These pressure-induced effects on the optical density of LCMO resemble those observed for decreasing temperature in the same system (Fig. 1). The pressure as well as the temperature dependence of the broad-band can then be ascribed to the increased extent of charge delocalization. In addition, the screening of the phonon line at high pressures can be explained by the presence of delocalized charges in the  $\text{MnO}_6$  octahedra planes. On the contrary, in SLMO (see Fig. 3), the broad-band only slightly increases and the overall absorption shape remains basically unchanged over the whole pressure range implying that an almost negligible delocalization effect occurs. We stress that the weak pressure dependence shown by the SLMO optical density make us confident that the pressure behavior observed in LCMO cannot be ascribed to any spurious effect due to the DAC cell. The obtained results show the relevance of caging on delocalization processes: the external pressure pushes the system towards charge delocalization in the pseudocubic LCMO, while it is almost ineffective in the layered SLMO, at least up to  $10$  GPa.

### III. DISCUSSION AND CONCLUSIONS

The pressure-induced charge delocalization in LCMO can be qualitatively explained by considering the polaronic origin of the broadband. As noted above, the external pressure symmetrizes the octahedron structure thus increasing the Mn-O-Mn hopping rate and, consequently, the polaron delocalization. Bearing in mind that the polaronic band is directly related to the distribution of the polaron binding energies, one can conclude that the presence of less tightly bound polarons results in an enhancement of the polaronic absorption band on its low frequency side. These qualitative conclusions could be predicted on the basis of previous data in the low-pressure regime.<sup>7,9</sup> However, interesting results come out from a more detailed analysis of the high pressure data. In particular, two main features in Fig. 2 should be considered: (i) the phonon line is still well evident at  $10$  GPa even if significantly screened and (ii) the rate of increase of the polaronic absorption decreases with increasing pressure.

As far as (i) is concerned, the inset of Fig. 2 clearly shows that the metallic state, characterized by a complete screening of the phonon peak at  $25$  K, is not achieved at  $10$  GPa, i.e., well above the  $P_{IM}$  value above predicted. The pressure dependence of the polaronic absorption (ii) can be characterized by an effective number of carriers  $n^*$ ,<sup>18</sup> obtained by integrating in region II the  $O_d(\omega)$  spectrum at each pressure. The  $n^*(P)$  values are reported in Fig. 4 for both LCMO and SLMO. The  $n^*(T)$  values obtained from the LCMO temperature dependent  $O_d(\omega)$  are shown for comparison in Fig. 4(b). The  $n^*(P)$  and the  $n^*(T)$  values are normalized to the minimum pressure and to the ambient temperature values, respectively. The temperature-driven IM transition in LCMO is clearly marked by an abrupt increases of  $n^*(T)$  around  $T_c$  [Fig. 4(b)], and below  $100$  K an asymptotic value is reached. As shown in Fig. 4(a), the pressure-driven delocalization



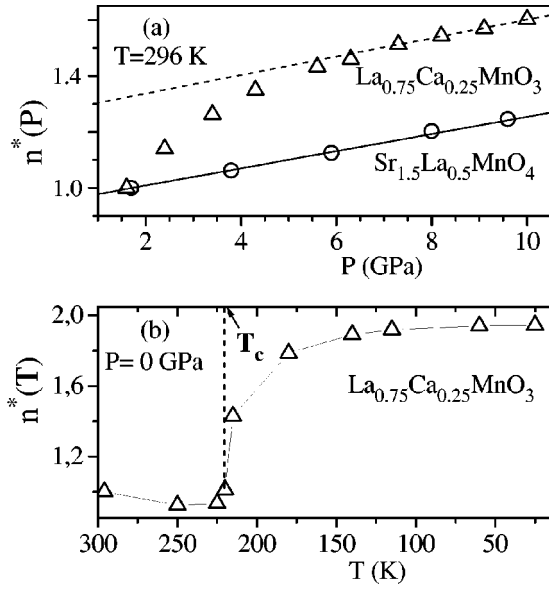


FIG. 4. Effective number of carriers  $n^*$  in regions II as a function of pressure (a) for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  and  $\text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_4$  and as a function of temperature (b) for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . In (a), the full and dashed lines are linear best fits with the same slope to the SLMO and to the high pressure LCMO data.

mechanism is remarkable for LCMO albeit much less efficient in the high pressure regime ( $P \geq 6$  GPa), where the  $n^*(P)$  values are well described by the same linear trend observed in SLMO over the whole pressure range.

In conclusion, our results, while confirming the relevance of both pseudocubic structure and pressure in charge delocalization processes, show that the pressure-induced delocalization mechanism is strongly inhibited for  $P \geq 6$  GPa and that the IM transition is not achieved when the pressure is increased up to 10 GPa in the LCMO manganite, in agreement with recent Raman results.<sup>10</sup>

A possible explanation of our result is provided by a strong decrease of  $dT_c/dP$  when  $T_c$  is increased by the applied pressure. Indeed, as noted above, the more  $T_c$  is increased, the more its pressure dependence is reduced. By integrating Eq. (1) one has

$$\frac{T_c(P)}{T_c(0)} = \left( \frac{d(P)}{d(0)} \right)^{-7/2} \left( \frac{\cos \theta(P)}{\cos \theta(0)} \right)^2 e^{-2[\alpha(P) - \alpha(0)]}. \quad (2)$$

For our LCMO sample, high pressure x-ray diffraction measurements<sup>14</sup> provide  $d(P)$  and  $\theta(P)$ , and the value

$\alpha(0)=0.6$  is reported in Ref. 26. Since our data show that  $T_c(10\text{ GPa}) \leq 300\text{ K}$  (i.e., the room temperature metallization is not achieved), Eq. (2) provides that  $\alpha(10\text{ GPa}) \geq 0.5$ . Therefore, in the 0–10 GPa pressure range, the average pressure dependence is  $|\alpha(10\text{ GPa}) - \alpha(0)|/\Delta P \leq 0.01\text{ GPa}^{-1}$ . Taking into account that this value is an upper limit for  $|d\alpha/dP|$  around 10 GPa, the comparison with the  $|(d\alpha/dP)_{\text{LP}}| \sim 0.035\text{ GPa}^{-1}$  quoted above shows that the pressure dependence of the carrier-phonon coupling  $\alpha$  is strongly reduced in the high pressure regime. In this context, it is worth noticing that  $\alpha \propto E_{\text{JT}}/\hbar\omega$ , where  $E_{\text{JT}}$  is the Jahn-Teller energy and  $\omega$  is the characteristic phonon frequency.<sup>13</sup> Since  $E_{\text{JT}}$  decreases with increasing pressure (see Ref. 12, and references therein), the above conclusion is well consistent with the pressure behavior of the JT phonon frequency  $\omega_{\text{JT}}$  observed in recent Raman measurements. As a matter of fact the Raman results show that the  $\omega_{\text{JT}}$  frequency increases for increasing pressure up to about 7 GPa, and is almost pressure independent in the high-pressure regime (up to 14 GPa).<sup>10</sup>

We remark that the above discussion is based on the idea that the octahedron is forced to be undistorted by increasing the applied pressure and an average Mn-O bondlength ( $d$ ) is thus considered. On the other hand, the results of high pressure x-ray diffraction measurements on LCMO show an abrupt onset of a huge octahedron distortion for pressures above 6–7 GPa.<sup>14</sup> This result may suggest the onset of a competitive pressure-activated localization mechanism, which at high pressure balances the effects of the pressure-induced delocalization, thus explaining why the IM transition is not achieved. As a final guess, we recall that a large variety of results on different manganites indicate that the metallic phase can coexist with the insulating phase for  $T < T_c$  and is completely established only for  $T \ll T_c$ .<sup>27</sup> In this phase separation scenario,<sup>28</sup> one may argue that charge localization in insulating domains prevents the occurrence of a pressure-induced metallic phase in the whole LCMO sample, thus explaining our high pressure results. Further experimental studies are in progress, to explain high pressure experimental findings.

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