Anomalous High Pressure Dependence of the Jahn-Teller Phonon in La$_{0.75}$Ca$_{0.25}$MnO$_3$

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Raman spectra of La$_{0.75}$Ca$_{0.25}$MnO$_3$ have been collected for the first time over a wide pressure range (0–14 GPa) using a diamond anvil cell. The frequency range explored (200–1100 cm$^{-1}$) and the very good quality of the data allowed us to carefully analyze the pressure evolution of the phonon modes of the MnO$_6$ octahedra. The results show an abrupt transition at $\sim$7.5 GPa with an evident deviation from the linear trend of the frequency of the Jahn-Teller phonon versus the applied pressure, accompanied by a strong phonon broadening. This behavior disagrees with the predicted insulator to metal transition and, on the contrary, indicates the occurrence of a new unpredicted phase in the very high pressure regime.

The A$_{1-x}$A’$_x$MnO$_3$ pseudocubic manganites (A is a rare earth and A’ is a divalent cation) have been the subject of extended investigations because of either the potential technological applications or the basic interest in solid state physics. As a matter of fact, the phase diagram of these compounds is particularly rich and many variables such as pressure, applied magnetic field, doping concentration $x$, A-site average ionic radius $r_A = x_A R_A + x_{A’} R_{A’}$ (where $R_A$ is the A-ion radius) can determine the different phases of the system [1]. At ambient pressure the $T$ vs $x$ phase diagram of La-Ca manganites shows two phases in the 0.2 < $x$ < 0.5 Ca concentration range: a paramagnetic insulating phase above $T_C$ and a ferromagnetic metallic phase below [2]. The occurrence of the insulator to metal (IM) transition is governed by the balance between two competing effects: the “double exchange” magnetic interaction [3], which increases the electron kinetic energy and hence delocalization, and the strong Jahn-Teller (JT) coupling which tends to localize the carrier in a local lattice distortion [4]. Diffraction measurements, performed as a function of temperature, have shown that the large JT distortion of the MnO$_6$ octahedra in the insulating state reduces to vanishingly small values at the IM transition [5]. The interplay between charge localization and octahedra distortion has been found also when the metallic phase is approached by varying other parameters. In the $T$ vs $r_A$ phase diagram, at constant electronic doping $x$, the increase of $r_A$ produces indeed both a reduction of the octahedra distortion and an enhancement of the metallic character. With $x = 0.3$, $T_C$ increases by about 200 K going from $r_A = 1.19$ Å to $r_A = 1.24$ Å [6,7]. In principle a reduction of the JT distortion could also be obtained by applying an external pressure. Actually an increase of $T_C$ was observed as the pressure is increased [8,9]. The comparison between the effects on $T_C$ of the “internal pressure” (determined by $r_A$) and of the external pressure yields an empirical conversion factor $r_A/P = 3.7 \times 10^{-3}$ Å/GPa in the 0–1.5 GPa range [8]. The underlying idea is that an IM transition occurs if a sufficient reduction of the “free volume” around the A site is obtained, i.e., if the octahedra are forced to be undistorted and the Mn-O-Mn angle tends to 180° [8,10]. This can be achieved either by increasing the average dimension of the atom at the A site (internal pressure) or by contracting the cage of the MnO$_6$ octahedra (external pressure). This guess has been proved in a relatively small pressure range [8,9] whereas there is no experimental indication that it holds also in the very high pressure regime. Within this scheme and taking into account the $r_A/P$ conversion factor, the room temperature metallization pressure for La$_{0.75}$Ca$_{0.25}$MnO$_3$ can be estimated as $P_{IM} = 5$ GPa. From a spectroscopic point of view, the signature of the IM transition can be identified by a significant narrowing and frequency hardening of the octahedron bending and stretching modes, as pointed out by both theoretical and experimental investigations [11–13]. These effects are direct consequences of the charge-lattice coupling reduction and of the free carrier screening in the metallic phase. Raman spectroscopy is therefore an ideal tool for studying these materials, and it is particularly suitable for high pressure studies. Several papers have been published in the last few years [13–16], but there is a complete lack of experimental data as a function of pressure. With the idea of searching for a pressure-driven IM transition, Raman spectra of a polycrystalline La$_{0.75}$Ca$_{0.25}$MnO$_3$ sample have been collected over a wide pressure range (0–14 GPa) using a membrane diamond anvil cell (MDAC).

Raman spectra were measured in back-scattering geometry, using a micro-Raman spectrometer (LABRAM by Dilor) with a charge-coupled device (CCD) detector and an adjustable notch filter. The sample was excited by the 632.8 nm line of a 16 mW He-Ne Laser. The confocal microscope was equipped with a 20× magnification.
objective which gives laser spot about 10 \( \mu m \) wide at the sample surface. The notch filter cutoff at low frequency and the very intense diamond Raman peak at high frequency (1331 \( cm^{-1} \) at zero pressure) limited the reliability of the spectra outside the 200–1100 \( cm^{-1} \) frequency range. The MDAC (by BETSA) was equipped with low fluorescence IIA diamonds with 800 \( \mu m \) culet diameter, the gaskets were made of a 250 \( \mu m \) thick steel foil (AISI 301). Under working conditions the gasket thickness was ranging from 30 to 50 \( \mu m \) with a typical 200 \( \mu m \) diameter hole. Polycrystalline samples of the orthorhombic (Pnma) \( La_{0.75}Ca_{0.25}MnO_3 \) manganite were prepared by a standard solid state reaction method and characterized by x-ray diffraction, EXAFS spectroscopy, ac susceptibility, and resistivity measurements [17,18]. In particular, the magnetoresistance curve reported in Ref. [18] shows a quite narrow and intense peak around \( T_C \). By finely milling the sample, we obtained a powder with an average grain size of the order of 1 \( \mu m \). Manganite grains were then placed in the center of the top surface of an NaCl pellet, obtained by synthesizing salt powder at high pressure directly within the gasket hole. Few ruby nanospheres were also placed around and over the manganite sample in order to measure the pressure through the standard ruby fluorescence technique [19]. We verified that pressure gradients, if any, were within the experimental uncertainty of ~0.2 GPa. The loading procedure we adopted ensures hydrostatic conditions for the sample grains and, owing to the high thermal conductivity of diamond, prevents spurious effects due to laser-induced sample heating [14,15]. A complete reproducibility of the spectra was obtained on releasing the pressure on the sample.

Raman spectra were collected from five different points of the sample. Since the laser spot impinges only a few sample grains, the relative intensities of the peaks were slightly different from point to point depending on the average orientation of the grains. Therefore the spectra were analyzed separately and the best fit parameters were averaged for each pressure. In Fig. 1 the Raman spectrum collected at 2 GPa is shown. Four broad phonon peaks are well evident in the 200–800 \( cm^{-1} \) spectral region and a weak structure, ascribed to electronic scattering, is present around 1000–1100 \( cm^{-1} \). The strong rise of the intensity on the high frequency side is due to the diamond Raman peak. Spectra were fitted in the 200–1100 \( cm^{-1} \) frequency range with the function [13]

\[
S(\nu) = \left[ 1 + n(\nu) \right] \frac{A\nu^3}{\nu^2 + \Gamma^2} + \sum_{i=1}^{5} \frac{A_i\nu^3}{(\nu^2 - \nu_i^2)^2 + \nu^2\Gamma_i^2}.
\]

FIG. 1. The Raman spectrum at 2 GPa of \( La_{0.75}Ca_{0.25}MnO_3 \) and the best fit curve from Eq. (1) (solid line) are shown. The four phonon contributions (solid lines) and the electronic contributions LFE and HFE (dashed lines) are also shown separately.

The first term represents the low frequency electronic (HFE) Raman scattering due to diffusive hopping of the carriers. The sum, in the second term, is meant to account for both the four phonon peaks and the high frequency electronic (HFE) contribution (\( \nu_i, A_i, \) and \( \Gamma_i \) are the peak frequency, amplitude, and linewidth, respectively). The quantity \( n(\nu) \) is the Bose-Einstein thermal population factor. The agreement between the experimental data and the fitting curve was quite good at all the investigated pressures. As an example the best fit curve and the different components are also shown in Fig. 1.

Raman spectra collected at different pressures from a given point of the sample are shown in Fig. 2. The pressure dependence of the LFE and HFE responses could not be thoroughly analyzed owing to the spectral range limitation discussed above. Nevertheless, as far as the HFE peak is concerned, we can at least exclude that a significant softening of its peak frequency occurs as the pressure

FIG. 2. The Raman spectra of \( La_{0.75}Ca_{0.25}MnO_3 \) at different pressures. The pressure increases from bottom to top from 2 to 14 GPa. The zero pressure frequencies of \( \nu_3 \) and \( \nu_4 \) phonons are shown as vertical dotted lines.
is increased. In Ref. [13] it was suggested that this contribu-
tion should be associated with the photoionization of
small polaron. In particular, a remarkable softening of the
peak frequency was observed with decreasing temperature
[13], when the metallic phase is approached and the polaron
binding energy is consequently decreased. On the
basis of this suggestion, our results on the HFE peak ex-
clude the occurrence of a pressure induced metalization
over the whole explored pressure range.

Comparing the present data with the assignments
reported in Ref. [15], the four observed phonon peaks
[~240 cm\(^{-1}\) (\(\nu_1\)), ~330 cm\(^{-1}\) (\(\nu_2\)), ~480 cm\(^{-1}\) (\(\nu_3\)),
~630 cm\(^{-1}\) (\(\nu_4\)) at zero pressure] can be ascribed to
the octahedron modes \(A_g(2)\) (\(b\)-axis rotation), \(B_{3g}(4)\)
(\(c\)-axis rotation), \(A_g(3)\) (apical oxygen bending), and
\(B_{2g}(1)\) (in-plane oxygen stretching), respectively. The
pressure dependence of the phonon frequencies is shown
in Fig. 3a. The frequency \(\nu_1\) is almost unaffected by
pressure as expected for a \(b\)-axis rotation, and this mode
has been demonstrated to be nearly independent of both
transport and magnetic properties [14]. On the contrary,
\(\nu_2\) shows an abrupt hardening around \(P^* \sim 7.5\) GPa
with a total frequency shift of 30 cm\(^{-1}\). The bending phonon
frequency \(\nu_3\) shows a weak, roughly linear pressure
dependence, while the stretching phonon frequency \(\nu_4\)
shows a strong linear increase up to \(P^*\) followed by a satu-
ration around 680 cm\(^{-1}\). The stretching mode \(\nu_4\) is the
most sensitive to pressure with a slope of 6.4 cm\(^{-1}\)/GPa
in the 0–\(P^*\) range (see Fig. 3a). In the same pressure
range, almost identical frequency values and slope were

found for the higher frequency mode in \(\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4\)
layered manganite for which, however, the linear trend
continues up to 14 GPa [20]. This is a JT phonon in both
layered (general formula \(A_iA_{j2-\text{c}}\text{MnO}_4\)) and pseudocubic
manganites. The saturation effect found for the latter
system must be related to some abrupt change of the JT
distortion. The different high pressure behavior of the
two manganites can be ascribed to the different extent of
\(A\) trapping [21]. Indeed, in the layered manganite the ele-
ment at the \(A\) site is inserted between disconnected planes
of MnO\(_6\) octahedra, whereas it is completely trapped
within the strongly connected 3D octahedra cage in the
pseudocubic manganite. The present phonon frequency
pressure dependence and the compressibility evaluated by
diffraction data [17] allowed us to calculate the Gruneisen
parameter values given by \(\gamma_i = -\partial \ln(\nu_i)/\partial \ln(V)\). In
the 0–\(P^*\) pressure region we found \(\gamma_1 = \gamma_2 < 1,
\gamma_3 \approx 1\), and \(\gamma_4 \approx 2\). These values support the proposed
assignment of the phonon modes. Indeed, a value \(\gamma > 1\)
is frequently encountered for internal stretching modes,
while \(\gamma \leq 1\) is characteristic of external molecular modes
such as rigid rotation modes.

As far as the phonon profile is concerned, it is worth
noticing that the presence of a strong coupling shortens
the phonon lifetime and consequently broadens the phonon
widths. Indeed the linewidths observed in the JT undis-
torted end-member CaMnO\(_3\) are almost 1 order of magni-
tude narrower [14,20] than those of doped samples [20,22].
Moreover, an abrupt 30% narrowing of the Raman peaks
was observed below \(T_C\) [13], where the JT octahedra dis-
ortion vanishes. In Fig. 3b the pressure dependence of
the phonon linewidths is shown. While the widths \(\Gamma_1\) and
\(\Gamma_3\) are almost pressure independent (apart, maybe, from
a small discontinuity of \(\Gamma_3\) around \(P^*\)), both \(\Gamma_2\) and \(\Gamma_4\) show
a strong increase with the pressure. In particular, this in-
crease appears as an abrupt broadening around \(P^*\) for the
octahedra rotation mode (\(\Gamma_2\)), while it is more gradual, al-
breit more substantial, for the stretching mode (\(\Gamma_4\)) where
it results as high as 100%.

The above results disagree with the hypothesis of the
occurrence of a pressure induced IM transition: neither the
phonon frequencies and widths nor the HFE contribution
shows the expected behavior for a metalization transition
[11,13]. On the contrary, the pressure behavior of the
stretching and rotational modes in the two pressure regions
\(P < P^*\) and \(P > P^*\) suggests a different interpretation.
Lattice compression strongly and steadily hardens the
frequency of the stretching mode \(\nu_4\) in the \(P < P^*\)
region. The Mn-O-Mn angle is expected to increase
towards the ideal 180° value of the cubic structure, so that
a consequent increase of the bandwidth and of the metallic
character of the system would occur. However, a real
metallic phase is not achieved: the observed remarkable
pressure-driven increase of the \(\Gamma_4\) width is in contrast with
a charge delocalization. At the same time pressure hardly
affects the rotation frequency of the MnO\(_6\) octahedra

![FIG. 3. Pressure dependence of frequencies (a) and linewidths (b) for the four phonon peaks: \(\nu_1\) (up triangles), \(\nu_2\) (down triangles), \(\nu_3\) (diamonds), \(\nu_4\) (circles). The dash-dotted line in the (a) upper panel is the linear fit of \(\nu_4\) frequencies in the 0–\(P^*\) pressure range. Vertical dashed lines indicate \(P^* = 7.5\) GPa, arrows \(P_{1M} = 5\) GPa. Solid lines are a guide for the eye.](image-url)
indicating that these are not being severely distorted and/or reoriented by pressure. However, this effect shows up in the abrupt variations in frequency and linewidth observed for ν2 at P* and it may correspond to a new equilibrium position for the octahedra. This is not an IM transition since it would imply a further stiffening of the stretching mode ν4 as well as a reduction of the corresponding damping whereas the opposite behavior was observed. Finally, the unusually weak pressure dependence of the phonon frequencies (particularly of the JT mode ν4) in the P > P* pressure region suggests that the structural and/or charge arrangement is in progress as also confirmed by the observed progressive redistribution of the intensities between ν3 and ν4 in favor of the high frequency one [23]. These findings, together with the continuous increase of all the phonon widths as a function of increasing pressure, suggest that the charge-lattice interaction is strengthened by the lattice compression. The presence of an anomaly in the pressure dependence of our sample’s structure and the guess of an increased role played by lattice-charge interaction are in agreement with the results of a recent high pressure experiment, where an abrupt and huge increase of the JT distortion of the octahedra has been found around P* [17].

We want to stress that our conclusions are not in contrast with the previous results where a reduction of the electron–phonon coupling as a function of increasing pressure was claimed [9]. The experimental data in Ref. [9] refer to a small pressure region (0–1.1 GPa) and the observed increase of Tc is consistent with the hardening of the ν4 stretching mode that we observe in the P < P* region. At present we are not able to give a satisfactory explanation of the experimental findings in the high pressure regime although it is evident that, besides steric effects, some other elements (such as configurational disorder [2,7], magnetic interactions) should be taken into account. We can guess indeed that the saturation effect shown by the JT phonon could originate from the onset at P* of a pressure activated mechanism which enters into competition with the hardening due to the lattice compression dominant in the P < P* pressure range. In this context can be noticed the recently observed softening of the JT mode at the onset of the antiferromagnetic order in LaMnO3 [22,24].

The Raman measurements reported in the present Letter provide the first high pressure (0–14 GPa) spectroscopic data on manganites. The very good quality of the Raman spectra allowed us to carefully determine the pressure dependence of four octahedra phonon modes. No spectroscopic evidence for the IM transition, expected on the basis of the correspondence between internal and external pressures, was found. On the contrary, the abrupt discontinuity observed in both frequency and width versus pressure at P* = 7.5 GPa can be seen as an indication of the onset of a new unpredicted phase which seems to persist up to 14 GPa.

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