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Persistence of Jahn Teller distortion up to the insulator to metal transition in $LaMnO_3$

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High pressure (P) - low temperature (T) Raman measurements performed on $LaMnO_3$ up to 34 GPa provide the first experimental evidence for the persistence of the Jahn Teller distortion over the entire stability range of the insulating phase. This result resolves the ongoing debate about the nature of the pressure driven insulator to metal transition (IMT), demonstrating that $LaMnO_3$ is not a classical Mott insulator. The formation of domains of distorted and regular octahedra, observed from 3 to 34 GPa, sheds new light on the mechanism behind the IMT suggesting that $LaMnO_3$ becomes metallic when the fraction of undistorted octahedra domains increases beyond a critical threshold.

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$LaMnO_3$ is the parent compound for many doped manganites which exhibit colossal magnetoresistance (CMR). This system displays a complex correlation between structural, orbital, magnetic, and electronic degrees of freedom. At ambient conditions $LaMnO_3$ is a paramagnetic insulator and is regarded as the archetypal cooperative Jahn Teller (JT) and orbitally ordered system [1]. It has an orthorhombic *Pmna* structure and transforms into an antiferromagnetic (A-type) insulator at T_N=140 K [2]. At T_{JT}=750 K, $LaMnO_3$ changes from a static orbital ordered state with cooperative JT distortion to an orbital disordered state with dynamic, locally JT distorted octahedra [3]. This order-disorder transition is also accompanied by an abrupt decrease in the electrical resistivity.

While there has been considerable effort to decouple these interactions, many fundamental questions on the interplay and relative significance of electron-lattice (e-l) and electron-electron (e-e) interactions in $LaMnO_3$ remain unresolved. High P resistivity and infrared measurements found the IMT at 32 GPa [4]. Extrapolating Raman and X-ray diffraction data, the complete suppression of the JT distortion was predicted at 18 GPa supporting the view of $LaMnO_3$ as a classical Mott insulator [4].

However, recent theoretical calculations and experimental findings have put into question the disappearance of the JT distortion in the very high pressure regime, reviving the debate on the character of the insulating phase and the origin of the IMT [5–10].

Theoretical investigations (LDA+U) suggest that the JT interaction plays a significant role up to much higher P than 18 GPa[5–8]. Calculations indicate the persistence of the structural distortion up to the IMT [5] and emphasize the role of both Coulomb and JT interactions for an accurate description of the IMT [6], suggesting that the IMT is not a Mott-Hubbard type [7]. The JT interaction was found to be insufficient to stabilize the orbital ordering at ambient conditions [8], pointing out the importance of Coulomb interactions in describing the insulating phase of $LaMnO_3$.

From experimental measurements, EXAFS data confirmed the persistence of the JT distortion up to 15 GPa but questioned the disappearance of distortion above 18 GPa [9]. More recent EXAFS data collected up to 37 GPa could not determine whether the JT distortion is present or not at the highest P due to the insufficient resolution of the data, but indicate the progressive formation of undistorted units of MnO_6 [10]. Formation of mixed states, whether structural or magnetic, is not a new phenomenon in manganites at high P [11], and has been recently observed in Ga and Ca doped $LaMnO_3$ compounds [12–15].

In the present work we performed Raman measurements up to 34 GPa, collecting data over several low T cycles. Formation of domains of regular octahedra is observed above 3 GPa and coexistence of JT distorted and undistorted MnO_6 units is found over the entire P-range at ambient and low T. The Raman signal from JT distorted octahedra is still observed at 32 GPa, providing the first experimental evidence of the persistence of the JT distortion up to the IMT.

The single crystal $LaMnO_3$ sample was prepared with a standard floating zone method [16]. The sample was then loaded with neon gas as a hydrostatic pressure medium in a diamond anvil cell (DAC) designed to be accommodated in a cryostat [17]. We used synthetic ultrapure anvils with 300 μm culets in order to minimize the diamond fluorescence. The pressure was measured *in-situ* using the ruby fluorescence technique [18]. Raman spectra were collected in a quasi-backscattering geometry with a custom system [17, 19]. The laser beam was

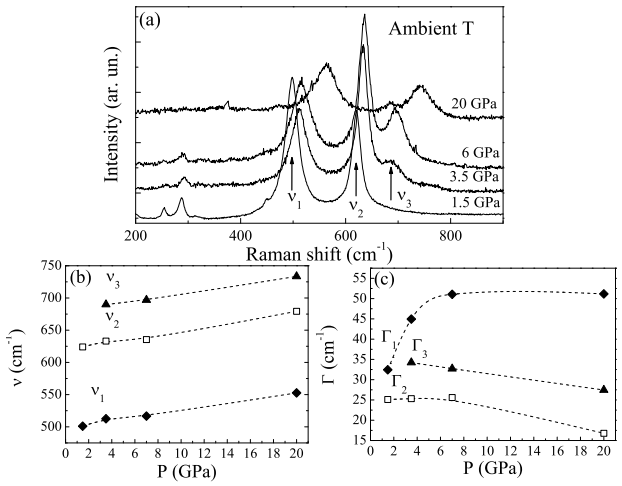

FIG. 1: (a) High P Raman spectra collected at ambient T. (b): Pressure dependence of the main phonon peak frequencies. (c): Pressure dependence of peak widths. Dashed lines are guides for the eye.

directed away from the spectrometer reducing the overall background. Use of double spatial filtering (one for the laser and one for the Raman signal) effectively suppresses laser plasma lines and unwanted Raman/fluorescence signals (e.g. from the diamond anvils). The DAC was modified in order to allow off-axis entrance of incident light. The Raman system is coupled to a helium flow cryostat specifically designed by Cryo Industries for Mao-Bell type cell. The beam spot can be focused down to 20 μm^2. The sample was cooled down to 10 K and then compressed up to 34 GPa. The pressure was released to 5 GPa after the warming cycle and the sample was subsequently cooled down again to 50 K. Raman spectra were analyzed using a linear combination of damped harmonic oscillator (DHO) functions [20] and, best fit values for peak frequencies and line widths were thus obtained.

Raman spectra collected at ambient T as a function of P are displayed in Fig.1(a). The spectrum collected at 1.5 GPa is consistent with previous results at ambient conditions [21]. The two main peaks are related to phonon modes involving oxygen ions. The one at approximately 490 cm^{-1} (ν_1) is associated with an out-of phase bending (B_{2g}) and an out of phase stretching of the octahedra (A_g, JT mode). The peak centered at 611 cm^{-1} (ν_2) corresponds to an in-phase stretching mode with B_{2g} symmetry. Above 3 GPa a new phonon peak ν_3 appears around 680 cm^{-1}. Upon further increase of P, a progressive transfer of spectral weight from ν_2 to the new P-activated peak ν_3 occurs. This phenomenon, previously observed in $LaMnO_3$ [4] and in Ga doped $LaMnO_3$ [12, 13] manganites at high P, is related to the formation of domains of undistorted octahedra resulting in a higher-energy Raman peak. The transfer of spectral weight from ν_2 to ν_3 is evidence of a P-induced conversion of distorted octahedra into regular ones. Coexistence of distorted and undistorted MnO_6 domains is observed up to the maximum P, indicating the persistence of the JT distortion. No indication of mixed structural states was observed in previous diffraction work [4], suggesting that the spatial and temporal scale of these domains is too small to be observed with a technique like X-ray diffraction. The weaker phonon peaks around 280 cm^{-1} correspond to in and out of phase rotations of the octahedra [21]. The disappearance of these peaks is consistent with the reduction of the JT distortion with P [22].

The evolution of phonon frequencies and line-widths with P is shown in Fig.1 (b) and (c) respectively. Bending and stretching modes, ν_1, ν_2, and ν_3, display the same P-dependence as was recently pointed out [23]. Two line widths, Γ_2 and Γ_3, decrease with P (Fig.1 (c)), whereas Γ_1 is found to increase up to 8 GPa and then to reach a plateau up to 20 GPa. A P-induced reduction of the JT distortion is consistent with the observed narrowing of Γ_2 and Γ_3 [24]. The differing behavior of Γ_1 with P may be associated to the formation of domains of regular octahedra, which affects the buckling of the MnO_6 units with respect to the ac plane. The bending linewidth, which is the most sensitive to octahedra buckling, becomes broader due buckling disorder. As the number of regular octahedra increases, the broadening effect is reduced and the system approaches a new equilibrium configuration with different buckling angles.

Fig.2 shows Raman spectra collected as a function of P and T. $LaMnO_3$ was cooled down to 10 K and then P was increased up to 34 GPa. A remarkable decrease in the intensity-noise ratio is observed in the Raman spectra collected above 25 GPa (Fig.3 (a)). Since no structural transition has been reported together with the IMT, this effect is a spectral signature of $LaMnO_3$ entering the metallic state between 30 and 32 GPa (grey spectra in Fig.2). Progressive transfer of spectral weight from ν_2 to ν_3 is observed with increasing P, indicating that domains of undistorted octahedra also form at low T. The behavior of the ν_2 and ν_3 peak intensities indicates that the number of domains of regular octahedra grows as the JT distortion is continuously reduced under P. The Raman peak associated with the JT distorted octahedra is well evident at 32 GPa (see black arrow in Fig.2). This is the first experimental evidence for the persistence of the JT distortion up to the IMT and demonstrates that the IMT is intrinsically related to the suppression of the JT distortion. This result indicates that $LaMnO_3$ cannot be considered a classical Mott-insulator and e-l coupling is fundamental in the description of the IMT.

Low T Raman spectra collected at two selected P are shown in Fig.3(a). The phonon peak ν_1 develops an asymmetric lineshape, as it is observed in the spectrum collected at 34 GPa. This asymmetry may be associated with a Fano resonance occurring at the onset of the metallic phase, a phenomenon which has been previously

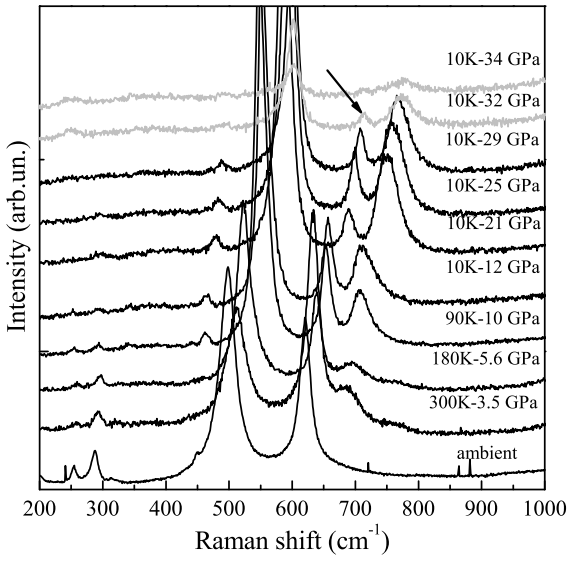

FIG. 2: Raman spectra for $LaMnO_3$ collected as a function of P and T. The grey spectra were collected when $LaMnO_3$ enters metallic state. The black arrow indicates the ν_2 peak that is still observed at 32 GPa.

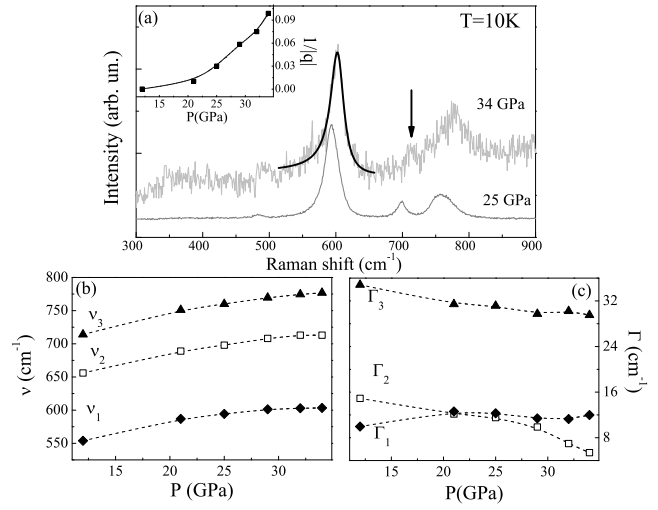

FIG. 3: (a) Raman spectra collected at 10 K at two selected pressures. Inset: Pressure dependence of the inverse of the asymmetry Fano parameter q. (b): Pressure dependence of phonon peak frequencies. (c): Pressure dependence of peak widths.

observed in several manganite compounds [25, 26]. Both a standard Fano profile ($I(\omega) = I_0(\epsilon + q)^2/(1 + \epsilon^2)$ with $\epsilon = (\omega - \omega_\nu)/\Gamma$ and q as the asymmetry parameter) [27] and a DHO function were used to fit ν_1 phonon peak lineshape. The best fit for the spectrum collected at 34 GPa was obtained with a Fano profile and is shown in Fig.3 (a). The inverse of the Fano asymmetry parameter $1/|q|$ (inset in Fig.3 (a)) is found to increase with P. Since Fano resonance is a spectral signature of coupling between a discrete mode and continuum, this result confirms that $LaMnO_3$ is definitely entering the metallic state above 32 GPa. The P-dependence of phonon frequencies, obtained with a Fano fit for ν_1 and with a DHO fit for ν_2 and ν_3, is shown in Fig.3 (b). The three phonon frequencies increase almost linearly up to 34 GPa. Linewidths for ν_2 and ν_3 are found to decrease due to the decrease of the e-l coupling [24] (Fig.3(c)) whereas the ν_1 peak width does not show any significant P-dependence above 20 GPa.

In summary, *in-situ* Raman measurements were performed up to 34 GPa at low T. The Fano-like lineshape that develops in the ν_1 peak together with the decrease of the intensity-noise ratio above 25 GPa prove that $LaMnO_3$ is entering the metallic state. The phonon mode associated with the JT distorted MnO_6 units is observed up to 32 GPa providing the first experimental evidence for the presence of the JT distortion in the entire stability range of the insulating phase. Our results indicate that $LaMnO_3$ cannot be considered as classical Mott-insulator and underscore the importance of e-l interactions in the description of this P-driven IMT.

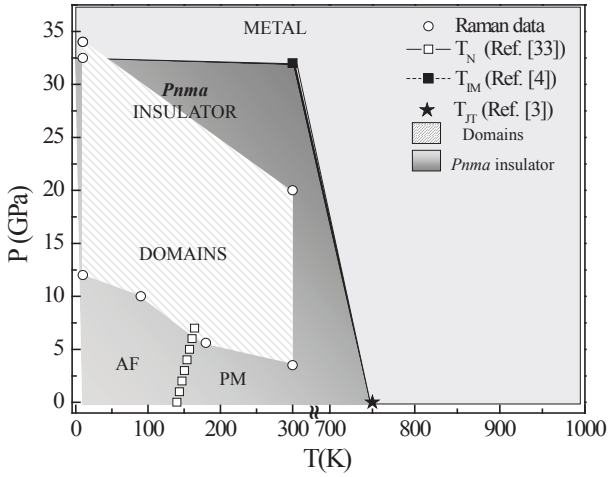

FIG. 4: P-T phase diagram. PM= paramagnetic phase. AF= antiferromagnetic phase. Gray dashed area and white circles frame the P-T region with coexistence of domains. P-T evolution of T_N (white squares) [32]. The star and the black square indicate the JT transition and the IMT temperatures respectively [3, 4]. Dark grey area indicates the insulating P-T region. The light grey color is used for the P-T region of the phase diagram which has been poorly explored.

The new P-activated peak provides evidence for the formation of MnO_6 undistorted units and appearance of domains above 3 GPa. Domains of distorted and undistorted octahedra are present up to 32 GPa and a weak signal from ν_2 is still observed at 34 GPa at 10 K (dashed grey area enclosed by white circle in Fig.4). In recent years, several theoretical and experimental

studies related the enhanced CMR effect, observed above T_C in hole doped manganites, to the existence of inhomogeneous and competing states [11, 28–31]. Our finding together with recently results [12–14], indicate that separation into domains may be a ubiquitous phenomenon at high P. The presence of domains over the entire stability range of the insulating phase sheds new light on the mechanism behind the P-induced IMT. Below 29 GPa the system is not metallic and consists of a dynamic mixture of distorted and undistorted octahedra. The IMT transition begins when the number of symmetric octahedra domains increases beyond a critical threshold. In this scenario, it is interesting to consider whether or not the CMR effect may be induced in an undoped sample as $LaMnO_3$ by applying P. The nature of this mixed state: dimensions, dynamics, and possible magnetic, electronic and orbital properties also require further theoretical and experimental investigations especially in the large region of the P-T phase diagram which is poorly explored (light grey area in Fig.4).

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