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High-pressure dependence of Raman phonons of $R\text{MnO}_3$ $(R = \text{Pr, Tb})$

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Abstract

The insulating character of undoped manganites $R\text{MnO}_3$ is related to the Jahn–Teller (JT) distortion of the MnO_6 octahedra, which can be reduced by applying hydrostatic pressure. We analyze the dependence of the Raman phonons with pressure up to 10 GPa, for PrMnO_3 and TbMnO_3. The variation of the stretching and bending modes indicates that the compressibility of Mn–O bonds is higher than R–O ones in PrMnO_3, but smaller in TbMnO_3. The variation of the tilt mode frequency, in TbMnO_3, can be explained by an increase of the octahedra tilt angle, which is consistent with a larger compressibility of the Tb–O bonds. Therefore, while PrMnO_3 evolves towards the structure of the metallic-ferromagnetic doped perovskites, TbMnO_3 does not.

Keywords: Magnetically ordered materials; Electron–phonon interactions; Phase transitions; Phonons; Inelastic light scattering

1. Introduction

Undoped manganese perovskites, $R\text{MnO}_3$ (with R = rare earth) are insulating and paramagnetic at room temperature (RT). Their insulating character is due to the splitting of the e_g level in the Mn^{3+}, caused by the Jahn–Teller (JT) distortion of MnO_6 octahedra. Doping with divalent cations induce the appearance of Mn^{4+}. Most of the doped manganite compounds $R_{1-x}A_x\text{MnO}_3$ (R = rare earth, A = Ca, Sr, Ba, etc.) are insulating at RT and become metallic at temperatures below the ferromagnetic order temperature (T_c), driven by the double-exchange mechanism (for example, see reviews [1]). The charge carrier bandwidth is related to the Mn–O–Mn angle, increasing when it approaches 180° [2]. The phonons involved in the theories for these CMR systems are even stretching modes, like symmetric stretching (breathing mode), or antisymmetric stretching mode (JT mode). The atomic displacements of both these modes are identical to the lattice distortions induced by the JT effect in order to split the Mn^{3+} e_g electronic level [3].

The application of hydrostatic pressure in manganese perovskites has significant effects on their magnetic and electrical properties through structural changes. These changes lead to a modification of the effective carrier bandwidth. Pinisard-Gaudart et al. [4] observed that the contraction of MnO_6 octahedra in LaMnO_3 is nearly isotropic, but the average tilt angle diminishes with increasing pressure, showing that this compound evolves towards a wider electronic band system. It has also been observed, for LaMnO_3, that the JT effect disappears above 18 GPa, but the insulating state remains up to 32 GPa, where it undergoes a bandwidth-driven insulator to metal transition [5]. Pressure effects on the structural parameters in $(\text{Nd}_{0.125}\text{Sm}_{0.875})_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ were also investigated [6]. This compound is a ferromagnetic metal below $T_c = 120$ K, but the application of a pressure around 0.5 GPa (and up) stabilizes the charge ordered insulating phase at low temperatures. A previous study on $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ has shown a chemical pressure induced metal–insulator transition, depending on 'y', due to the subtle competition between the double-exchange interaction and the charge ordering [7]. Nevertheless, the behavior of the Raman spectra observed for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ disagrees with the predicted insulator to metal transition. The abrupt discontinuity observed in both width and frequency versus pressure (at 7.5 GPa) indicates the occurrence of an unpredicted insulating phase, which seems to persist up to 14 GPa [8].

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RMnO$_3$ compounds with $R = $La to Dy, and in particular with Pr and Tb, crystallize in the orthorhombic *Pbnm* structure [9], are paramagnetic insulators at RT and order antiferromagnetically at Néel temperatures decreasing from 140 to 30 K, as the ionic radius of the rare earth decreases. PrMnO$_3$ and TbMnO$_3$ present the same *Pbnm* structure, but TbMnO$_3$ has a stronger JT distortion due to the smaller size of Tb ion [9].

We have studied the evolution of Raman phonons in RMnO$_3$ ($R = $Pr and Tb) with pressure (at RT and up to 10 GPa), in order to check the expected tendency to become metallic with increasing pressure, as it occurs in LaMnO$_3$. Another goal is to determine the importance of the JT distortion in the stabilization of the insulating ground state, through the evolution of JT phonons with pressure in both compounds.

2. Experimental details

Pressure measurements were carried out with a diamond anvil cell with steel gaskets having a typical 200 μm diameter hole. A NaCl pellet was formed within the gasket hole. Fine powders of RMnO$_3$ (with $R = $Pr or Tb), obtained by citrate techniques [9], were then deposited on the top surface of the NaCl pellet. This procedure ensures hydrostatic pressure conditions for the sample. Ruby microspheres were also placed in the cell to measure the pressure by the standard ruby fluorescence technique.

Raman spectra were obtained with a Jobin-Yvon HR 460 monochromator and a N$_2$ cooled CCD, exciting the samples with the 514.5 nm line of an Ar–Kr laser. The incident and scattered beams were focused using an Olympus microscope. A Kaiser Super-Notch filter was used to suppress the elastic scattered light.

3. Results and discussion

The Raman active modes of the *Pbnm* structure, taking the mirror plane '*m*' perpendicular to the *c*-axis, are: $7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$. Mn ions do not participate in any Raman mode, as they are located at inversion centers, while R and apical oxygen ions, O(1) ions, display the same kind of movements.

Figs. 1 and 2 show the evolution with pressure, at RT, of the Raman spectra of PrMnO$_3$ and TbMnO$_3$, respectively. High-temperature Raman spectra are also shown for comparison (bottom) in both cases. The peaks indicated in the graph correspond to the following modes and symmetries [3,10]: the symmetric stretching of the basal oxygens O(2) of the octahedra around 610 cm^{-1} (B_{1g}); the asymmetric stretching around 490 cm^{-1} (A_g) associated with the JT distortion, that involves basal oxygens O(2) and apical ones O(1); the

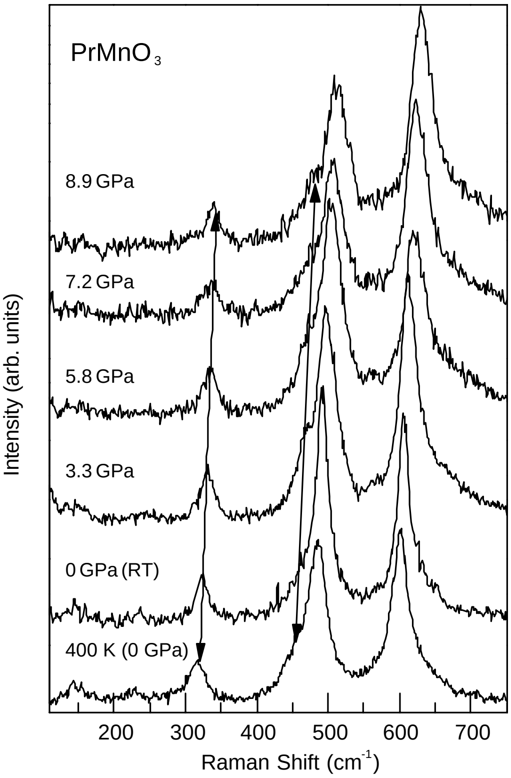

Fig. 1. Evolution of the Raman spectra of PrMnO$_3$ with pressure (only selected pressures are shown). Raman spectrum at 400 K (and 0 GPa) is shown for comparison (bottom). Arrows are a guide for the eyes and indicate the evolution with pressure of the bending and tilt modes.

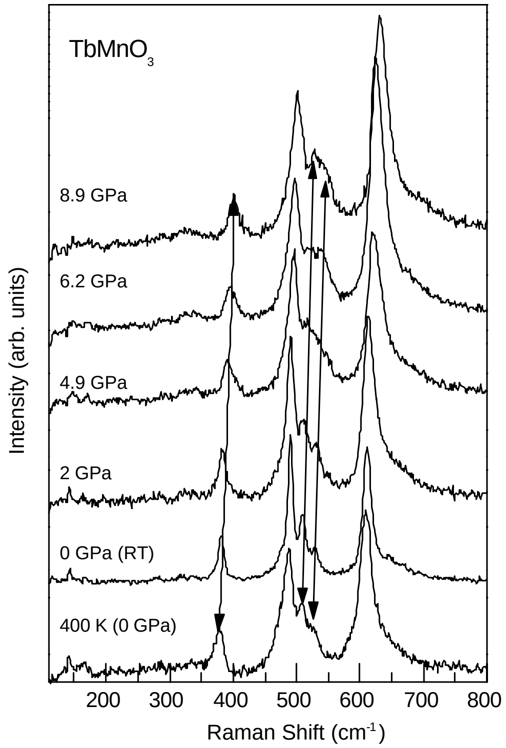

Fig. 2. Evolution of the Raman spectra of TbMnO$_3$ with pressure (only selected pressures). Raman spectrum at 400 K is shown for comparison (bottom). Arrows indicate the same as in Fig. 1.

bending modes ($A_g + B_{1g}$) at 510 and 529 cm^{-1} in TbMnO$_3$ and at 462 cm^{-1} in PrMnO$_3$; and the tilt of the octahedra at around 350 cm^{-1} (A_g). The evolution with pressure of the bending and tilt modes is indicated with arrows. These modes suffer the largest change with chemical pressure, as function of R ion, in the undoped RMnO$_3$ series [10,11]). The stretching modes remain almost constant when the R ionic radius is changed (chemical pressure), while they present an important shift to higher values as the hydrostatic pressure increases (Figs. 1 and 2).

Fig. 3 shows the dependence of the frequencies, for PrMnO$_3$, normalized to their values at RT and 0 GPa, with increasing pressure (Fig. 3b) and increasing temperature (Fig. 3a). Fig. 4 shows the behavior of different structural parameters, with pressure (right) and temperature (left), of LaMnO$_3$ from Refs. [4,12]. Notice that although the structural parameters correspond to LaMnO$_3$, their behavior is expected to be similar for PrMnO$_3$ ones, since Pr and La ionic radii are similar. Stretching modes are directly related to the force constants of Mn–O bonds, which in turn, are determined by the interatomic distances. Bending modes involve Mn–O–Mn angle bending but also R–O(1) bond stretching. We have demonstrated the correlation between the bending mode frequencies and R–O(1) bond lengths in the RMnO$_3$ series [10]. Therefore, the dependence of the bending modes on pressure is a measure of the compressibility of R–O(1) bonds. We have defined the relative change in the frequency, β, as $\beta = (\delta\omega/\delta P)1/\omega_0$, where ω_0 is the frequency value at ambient temperature and pressure . The β values for both compounds are collected in Table 1, together with some structural parameters. Comparing the relative frequency change of the different modes in Fig. 3, a smaller change in the bending mode than in the stretching modes indicates a larger compressibility of the Mn–O bonds than the Pr–O bonds. In this case, the tilt angle, which is the deviation from 180°, should decrease with pressure. This is, in fact, the observed behavior in LaMnO$_3$, studied by time of flight (TOF) neutron diffraction [4]. We might then expect a decrease of the tilt mode frequency as the tilt angle decreases as observed with temperature (Figs. 3a and 4) and with chemical pressure [10,11]. But, the tilt frequency increases with increasing pressure because the unit cell volume decreases.

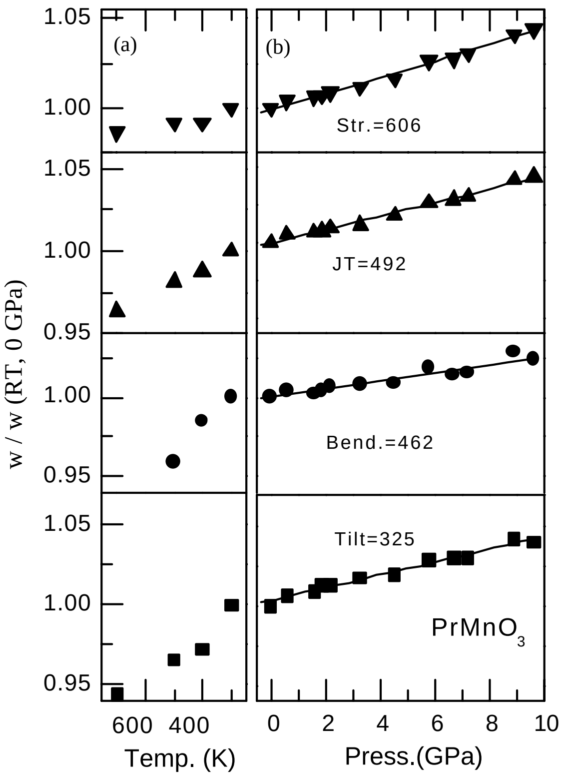

Fig. 3. Dependence of the studied Raman modes frequencies, for PrMnO$_3$, normalized to their values at RT and 0 GPa with increasing temperature (a) and increasing pressure (b). Linear fits are shown for (b).

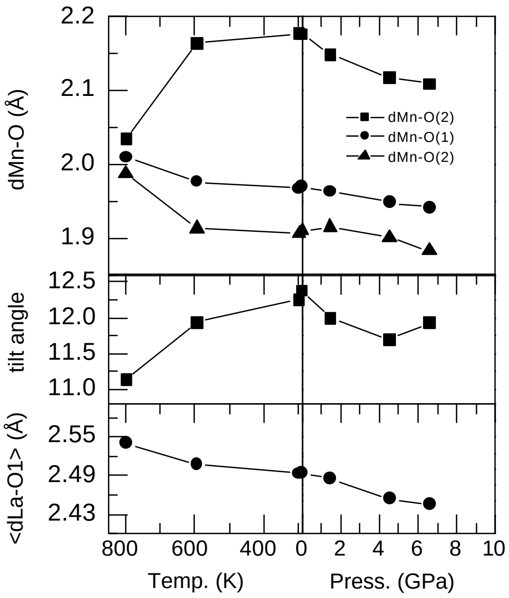

Fig. 4. Behavior of different structural parameters, with pressure (right) and temperature (left), of LaMnO$_3$ taken from Refs. [4,12].

Fig. 5 shows the behavior with temperature (Fig. 5a) and pressure (Fig. 5b) of the normalized frequencies of the different modes for TbMnO$_3$. The change in the mean value of the frequencies of the two bending modes is slightly greater than the change in the stretching ones (Table 1). This means that, in this case, the compressibility of Tb–O bonds is greater than that of Mn–O bonds. Therefore, the tilt angle is predicted to increase with pressure, distorting the structure by tilting it. This agrees with the greater change observed in the frequency of the tilt mode for the Tb compound compared to the Pr one (Table 1). Looking at the change in the structural

Table 1
Relative change of the frequencies (GPa^{-1}) $\beta = (\delta\omega/\delta P)1/\omega_0$, for $PrMnO_3$ and $TbMnO_3$, and selected structural parameters at ambient pressure and temperature

	Tilt	Bending	JT	Stretching	$r(R)$ (Å)	d(JT) (Å)	Tilt angle (deg)
$PrMnO_3$	4.0×10^{-3}	2.6×10^{-3}	4.5×10^{-3}	4.5×10^{-3}	1.16	0.19	14.44
$TbMnO_3$	7.4×10^{-3}	4.7×10^{-3}	3.1×10^{-3}	4.5×10^{-3}	1.10	0.32	17.37

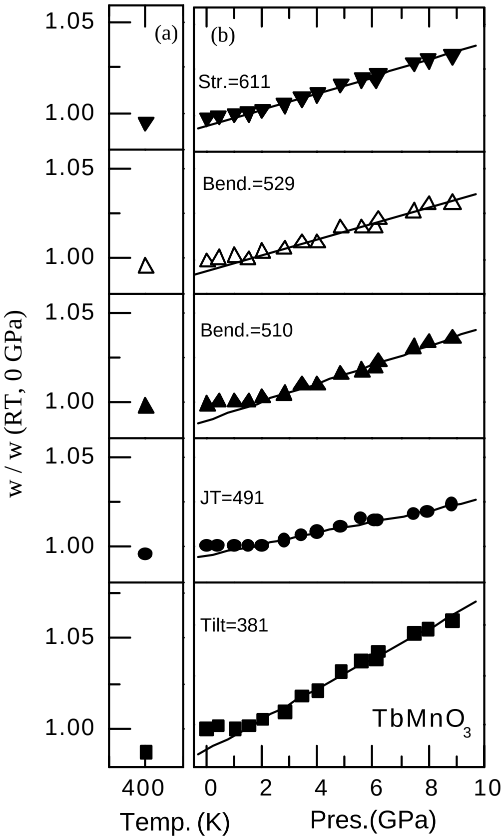

Fig. 5. Dependence of the studied Raman modes frequencies, for $TbMnO_3$, normalized to their values at RT and 0 GPa with increasing temperature (a) and increasing pressure (b). Linear fits are shown for (b).

parameters with temperature for both compounds, we can see that the sign of the change in the tilt angle is opposite for the Tb and Pr compounds (for Tb the tilt angle decreases while for Pr it increases, when lowering the temperature (Fig. 4 and Ref. [13])).

4. Conclusions

The phonons of $PrMnO_3$ and $TbMnO_3$ show different behavior with pressure although they present the same *Pbnm* structure as a result of their different JT distortions and tilt angles at ambient conditions. The compressibility of Mn–O bonds is larger than *R*–O(1) ones in the compound with the smaller JT distortion and smaller *R* ionic radius ($PrMnO_3$), but the contrary occurs in $TbMnO_3$ compound. The Raman phonons evolution with pressure indicates that the tilt angle decreases in $PrMnO_3$ while it increases in $TbMnO_3$. Therefore, while $PrMnO_3$ evolves with pressure towards the structure of the metallic-ferromagnetic doped perovskites, the orthorhombic distortion in $TbMnO_3$ increases.

Acknowledgments

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