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Raman phonons and the Jahn–Teller transition in $RMnO_3$ manganites

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Abstract

We have studied the behavior of the Raman phonons through the transition from a static to dynamic Jahn–Teller order in stoichiometric $RMnO_3$ samples, (in particular, $LaMnO_3$ single crystal and $PrMnO_3$ and $YMnO_3$ polycrystalline pellets). Thermal expansion effects on the phonon frequencies are not relevant above 300 K in La and Pr samples. The intensity of the spectrum decreases drastically as the temperature increases but is still observable in the pseudo-cubic phase. The remaining spectral weight, above the Jahn–Teller transition, can be explained by the presence of dynamic Jahn–Teller distortions that lower the symmetry of the cubic perovskite. The Raman spectra of $LaMnO_3$ and $PrMnO_3$, which presents a similar structural transition temperature, shows the same behavior while that of $YMnO_3$ is clearly different. This is explained by the fact that this compound presents a stronger cooperative Jahn–Teller distortion. Anharmonic scattering of the phonons are the origin of the phonon softening and partially that of the strong width increase as temperature reaches that of the Jahn–Teller transition.

Keywords: Magnetically ordered materials; Electron–phonon interactions; Exchange and superexchange; Phonons; Inelastic light scattering

PACS: 63.20-e; 75.30 Vn; 63.20 Kr

1. Introduction

Doped manganese perovskites $R_{1-x}A_xMnO_3$ (R = La, Nd or Pr, A = Ca, Sr, Ba . . .) have recently attracted much interest because of the high values of the magnetoresistance that many of these compounds present [1]. The strong change in the conductivity by an external magnetic field is due to the close relation between magnetic order and electronic conduction in doped materials with divalent cations or non-stoichiometric samples. Some of these compounds present a charge order transition accompanied by an insulating behavior and antiferromagnetic order. Phase segregation, stripes and many subtle spin or/and orbital orders are present in these compounds revealing the delicate equilibrium between different competing interactions. Stoichiometric $RMnO_3$ compounds with the *Pbnm* orthorhombic structure present a strong Jahn–Teller cooperative distortion of the Mn–O octahedra related to the orbital ordering of Mn e_g levels. $LaMnO_3$ compound is antiferromagnetic below 135 K and undergoes at 800 K a structural transition to the nearly cubic perovskite that has been described as rhombohedral, monoclinic or orthorhombic. A detailed study of a stoichiometric sample [2] shows that above 800 K the cooperative Jahn–Teller order disappears but dynamic Jahn–Teller fluctuations are still present. The importance of the phonons is often invoked and proved by the drastic observed isotope effects [3], but the Raman spectra of doped compounds are still not deeply understood. Raman phonons have been studied in orthorhombic $LaMnO_3$ single crystals [4,5], and, in Sr doped [5,6] and Ba doped compounds [7], as well as in Ca doped pellets [6,8] and thin films [9]. Several of these works report the effect of the oxygen content and the rhombohedral structure on the Raman features. Recently Dediu et al. [10] report the appearance of two peaks, below the charge order temperature in $Pr_{0.65}Ca_{0.35}MnO_3$, related to the unit cell doubling along the *a*-axis, and assign change in the slope of the dependence of the peak frequency and width vs. temperature to the transition from dynamical to static JT distortions. The relation between the shape of the Raman phonons and the JT distortion is often appealed to but not explained.

With the conviction that static and dynamical Jahn–Teller distortions related to Mn^{3+} ions are crucial in the understanding of Raman phonons and of the properties of doped or non-stoichiometric compounds, we have studied the Jahn–Teller transition of stoichiometric $RMnO_3$ samples where diffraction studies have described in detail the structural changes through this transition. In the present

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work the correlation between the structural changes and the phonons are clearly evidenced.

2. Experimental details

The here studied samples $LaMnO_3$, $PrMnO_3$ and $YMnO_3$ present the *Pbnm* orthorhombic structure ($D2h^{16}$, with $Z=4$), though the latter can present an hexagonal $P6_3cm$ ($C36v$ $Z=6$) one. $LaMnO_3$ is a single crystal, while Pr and Y samples are polycrystalline pellets. Raman spectra were obtained with a Renishaw Ramascope with CCD detector and excited with the 514.5 nm line of an Ar+ laser. The spectra were recorded at temperatures between 950 and 300 K in the backscattering geometry with an Olympus microscope. The sample located inside a Linkem TS-1500 furnace. All spectra have been corrected by the spectral response of the experimental set-up.

The spectra have been obtained with a $\times 10$ objective (focus diameter larger than 10 micron) and low laser power (about 1 mW) in order to avoid heating the sample locally by the laser beam. Increasing the power of the beam to 4 mW leads to a local overheating estimated to be about 100 K.

3. Results and discussion

The Raman active modes of *Pbnm* structure (mirror plane 'm' is perpendicular to the long *c*-axis) are: $7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$ and the non-zero components of the Raman tensors are: (*xx*,*yy*,*zz*), (*xy*), (*xz*) and (*yz*) for A_g, B_{1g}, B_{2g} and B_{3g} representations, respectively. Here, we have chosen the *Pbnm* axes orientation (Fig. 1).

The main features of $RMnO_3$ Raman spectra (Fig. 2) correspond to high frequency peaks around 480 and 610 cm^{-1} that consists in different Mn–O bond-stretching modes and to a region around 300 cm^{-1} which corresponds to different Mn–O octahedra tilts. In Fig. 1 we present the symmetry and atomic displacements of the main peaks. The symmetry of 480 and 610 cm^{-1} peaks have been determined to be (in the *Pbnm* setting) A_g and B_{1g}, respectively [4].

Fig. 2 shows the evolution of the $LaMnO_3$ Raman phonons from 300 to 900 K, well above the structural transition at 800 K. An important shift to lower values of the phonon frequencies is observed together with a dramatic increase of the widths and decrease of peak intensity. Figs. 3 and 4 show the evolution of Raman spectra, with temperature, for $PrMnO_3$ and $YMnO_3$ samples, respectively. $PrMnO_3$ spectra show the same behavior as for $LaMnO_3$, while for the $YMnO_3$, at high temperatures, the features of the orthorhombic spectra clearly remain.

The simplest approximations to anharmonic effects are the quasiharmonic and pseudoharmonic ones [11,12]. The first one takes into account the changes in the phonon frequencies with temperature due to the modification of the interatomic forces because of thermal expansion. The simplest approach to anharmonic decay of optical phonons is the pseudoharmonic approximation where, in fact, each phonon is considered as independent but with a renormalized energy and a finite lifetime due to anharmonic interactions [13].

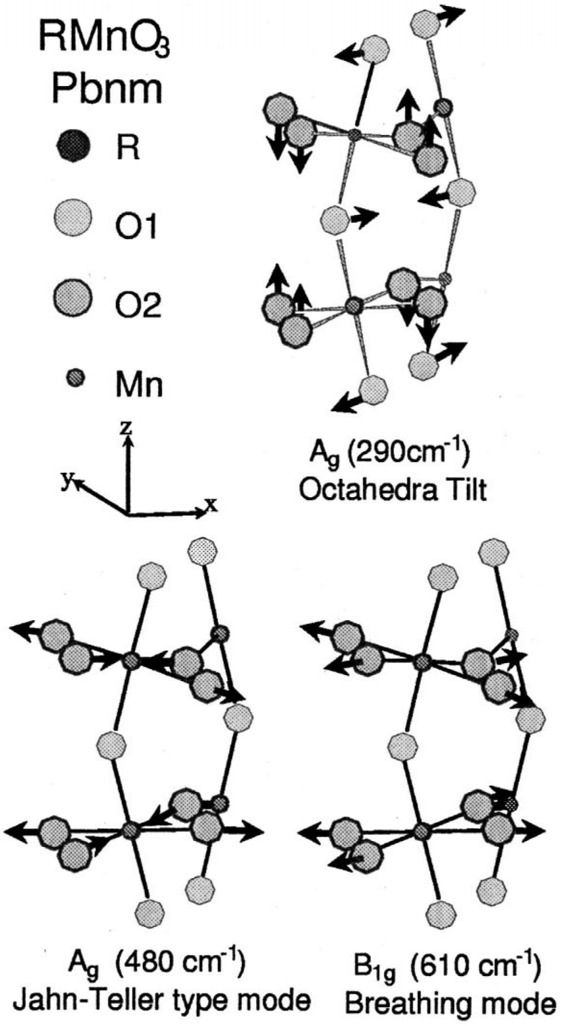

Fig. 1. Several relevant Raman normal modes of $RMnO_3$ (*Pbnm*).

In order to estimate the importance of both terms in the observed dependence with temperature of the phonon frequencies and widths (related to phonon lifetimes) we have evaluated the expected changes in the phonon frequencies caused by the variation of the interatomic distances in the crystal. Taking into account a simple model for the interatomic force constants: $K = F_{ij}/r_{ij}^3$, and $\varpi = \sqrt{(K/m)}$, where F_{ij} are constants that depend on *i* and *j* ions, and r_{ij} are, in the present case, Mn–O distances, we can estimate the changes in the stretching modes (at 610 and 480 cm^{-1}) due to the changes with temperature of these distances obtained from Ref. [2]. Structural changes

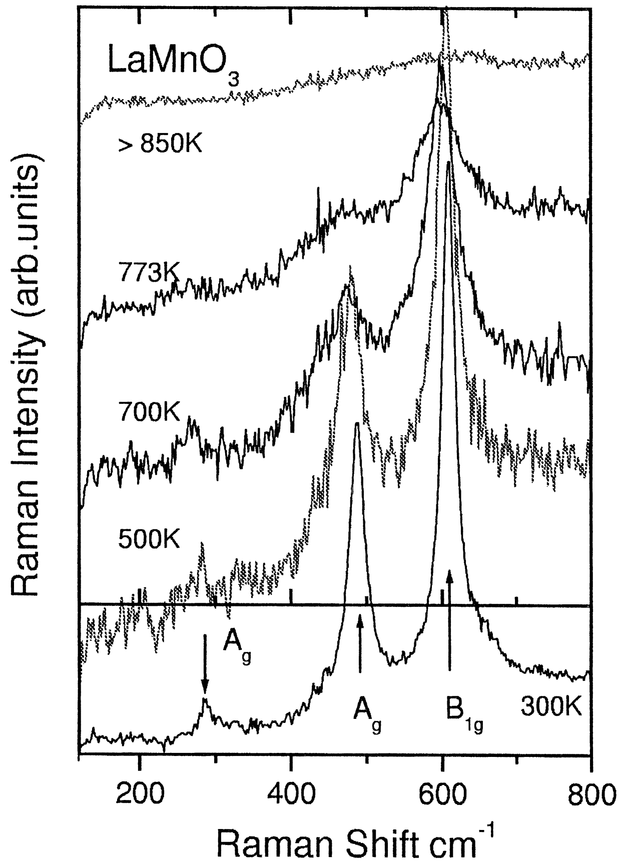

Fig. 2. Raman spectra from 300 to 900 K of a stoichiometric $LaMnO_3$ single-crystal.

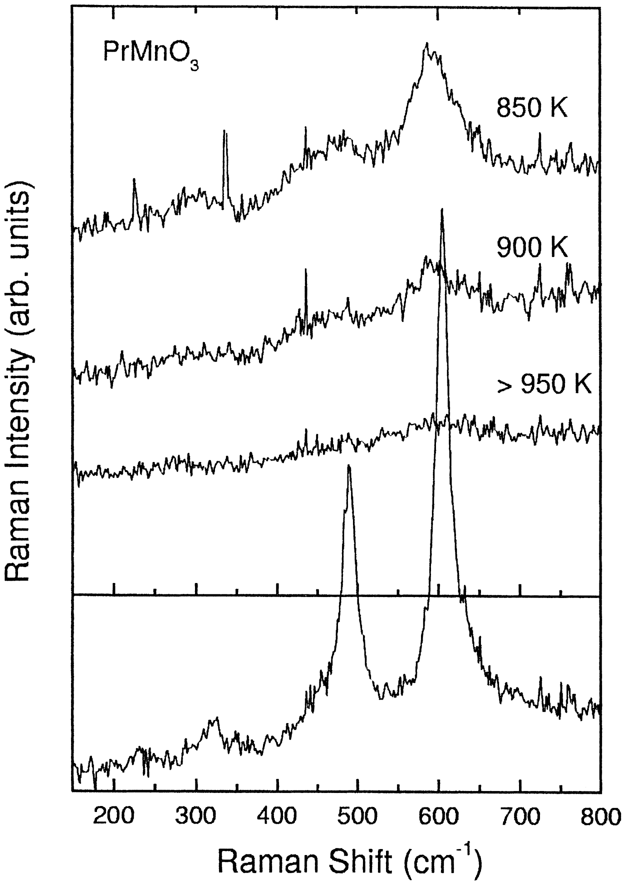

Fig. 3. Raman spectra at 300 K and high temperatures of a stoichiometric $PrMnO_3$ polycrystalline sample.

occurring as the temperature increases tend to increase the stretching mode frequencies contrary to the observed strong decrease (Figs. 2–4). Then, the dominant mechanism for the observed frequency shift is due to anharmonic scattering of phonons, which is also the expected mechanism for peak broadening. In particular, the most probable mechanism is the three phonon one where one phonon relaxes into two phonons of the same energy [12]. In Fig. 5 we present the integrated intensity of the three modes corrected by the thermal factor $(1+n(\varpi,T))$ corresponding to first order Raman Stokes phonons. We would expect a temperature independent intensity but observe a strong decrease. In the case of $LaMnO_3$ there is a structural phase transition at about 800 K to a quasi-cubic structure and, considering that a cubic perovskite has no Raman modes allowed, the Raman peaks are expected to disappear at or near the phase transition temperature. The observed intensity of the three modes start to decrease slightly above 300 K. The continuous line of Fig. 5 represents the behavior of (a–b) (lattice parameters) which is related to the static Jahn–Teller distortion due to orbital ordering. The direct measure of the static Jahn–Teller distortion is the comparison between both Mn–O(2) distances whose difference behaves in the same manner (see data of Ref. [2]) as (a–b). The correlation between the Jahn–Teller distortion and the phonon intensity is very good in a large temperature range. Nevertheless, at and above the phase transition temperature, when Mn–O octahedra are regular according to diffraction data, the peaks are still observable (Fig. 2). At this moment the cooperative static charge order has disappeared but fluctuations of Mn–O octahedra, that is dynamic Jahn–Teller distortions, are occurring. These fluctuations lower the Mn–O octahedra symmetry allowing Raman modes observation. Another effect of dynamical Jahn–Teller distortion is the broadening of the Raman peaks in a similar way of an inhomogeneous broadening due to a distribution of octahedron configurations.

We have also checked the frequency changes (from the spectra at 300 K and the one at about 900 K) for the Jahn–Teller mode and the symmetric stretching mode for the three compounds, and the changes in their widths. The frequency of both modes change almost the same amount for the La and Pr samples but, however, Y compound shows a smaller change for both frequencies and widths up to the highest measured temperature. An explanation to this different behavior can be that static Jahn–Teller effect is stronger for the $YMnO_3$ compound and, although it has not been reported, it is right to suppose that it might have a

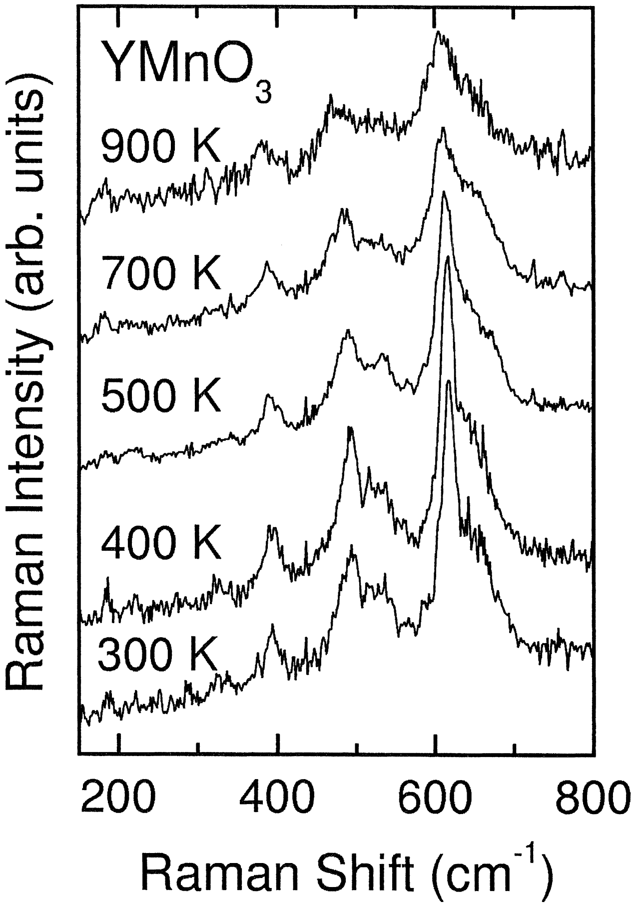

Fig. 4. Raman spectra from 300 K to 900 K of an orthorhombic $YMnO_3$ polycrystalline sample.

structural transition to a pseudo-cubic phase (where the static Jahn–Teller effect disappears) at a higher temperature.

4. Conclusions

The main Raman phonons of stoichiometric $RMnO_3$ samples have been related to Mn–O octahedra movements. All peaks show a strong shift to lower energies above 300 K that can be explained by three phonon scattering processes that renormalize their frequencies. The effect of the lattice expansion on the phonon frequencies has been estimated taking into account the variation of bond lengths and is found to be very small. The width of all peaks present a very strong increase, in particular for the Jahn–Teller mode. The integrated intensity of all peaks decreases drastically above 300 K following very well the evolution of the magnitude of the static Jahn–Teller distortion except above the structural transition where remaining spectral weight is observed up to, at least, 900 K, indicating that dynamic Jahn–Teller distortions are occurring. Same Raman behavior was observed for the La and Pr samples, where it is known that similar structural transitions occur at close temperature values (around 800 K). Nevertheless, for the Y sample, the orthorhombic features remained at high temperatures, with frequencies well defined and narrower peaks than those corresponding to the other compounds at the same temperatures. This is because the static Jahn–Teller effect is stronger for the Y compound

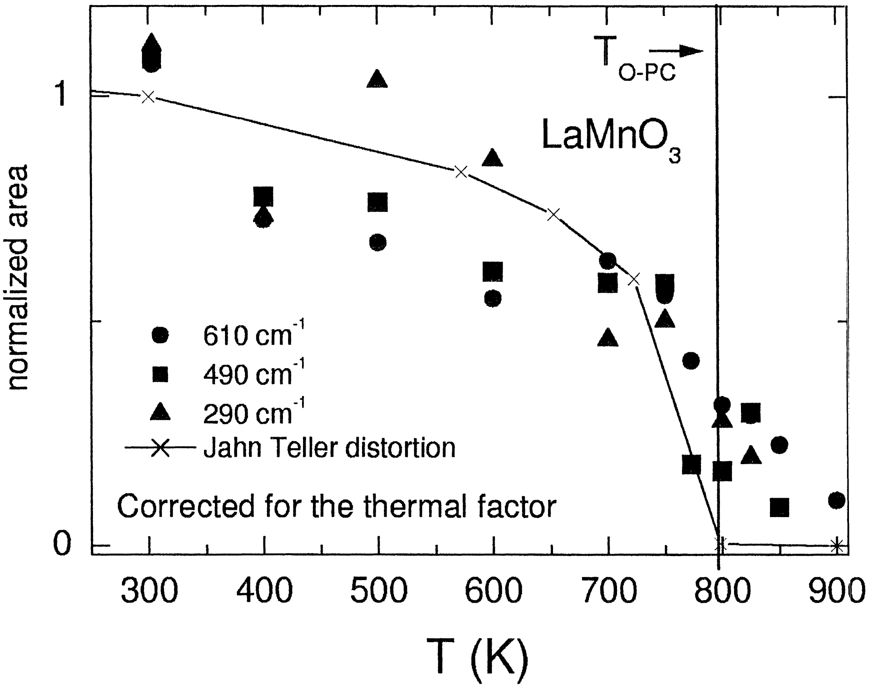

Fig. 5. Normalized intensities of the three Raman peaks of $LaMnO_3$ compound and its Jahn–Teller distortion (continuous line) obtained from structural data of Ref. [2] as a function of temperature through the Jahn–Teller transition.

and the structural transition to a pseudo-cubic phase might occur at higher temperatures.

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