First principles calculation of the phonons modes in the hexagonal YMnO$_3$ ferroelectric and paraelectric phases

Julien Varignon, Sébastien Petit, Marie-Bernadette Lepetit

To cite this version:

Julien Varignon, Sébastien Petit, Marie-Bernadette Lepetit. First principles calculation of the phonons modes in the hexagonal YMnO$_3$ ferroelectric and paraelectric phases. 2012. <hal-00677352>
First principles calculation of the phonons modes in the hexagonal YMnO₃ ferroelectric and paraelectric phases

Julien Varignon,¹ Sébastien Petit,¹ and Marie-Bernadette Lepetit¹

¹CRISMAT, ENSICAEN-CNRS UMR6508, 6 bd. Maréchal Juin, 14050 Caen, FRANCE
(Dated: February 16, 2012)

The lattice dynamics of the YMnO₃ magneto-electric compound has been investigated using density functional calculations, both in the ferroelectric and the paraelectric phases. The coherence between the computed and experimental data is very good in the low temperature phase. Using group theory, modes continuity and our calculations we were able to show that the phonons modes observed by Raman scattering at 1200K are only compatible with the ferroelectric P₆₃mc space group, thus supporting the idea of a ferroelectric to paraelectric phase transition at higher temperature. Finally we proposed a candidate for the phonon part of the observed electro-magnon. This mode, inactive both in Raman scattering and in Infra-Red, was shown to strongly couple to the Mn-Mn magnetic interactions.

I. INTRODUCTION

Materials presenting magneto-electric coupling exhibit magnetic properties coupled to the electric properties, such as polarization or dielectric constant. These materials have attracted a lot of attention over the last years since the magneto-electric coupling allows a possible control of the magnetic properties by an electric field and over electric properties using a magnetic field.

Unfortunately, the microscopic origin of the coupling between the magnetic and electric order parameters is still ill known. The knowledge of phonons spectra can however bring help on understanding this coupling. Indeed, not only the phonons modes are strongly related to the existence and amplitude of a spontaneous polarization, but in addition strong spin-phonons coupling occur in multiferroic material. This coupling can even be strong enough in order to result in hybrid excitations built from the mixing between phonons and spin-waves. The existence of such hybrid modes, called electromagnons, were recently discovered in RMnO₃ orthorhombic manganites using optical measurements. More recently such excitations were also found by inelastic neutrons scattering in the hexagonal manganite YMnO₃.

Hexagonal YMnO₃ is a layered compound where the manganese ions are located in triangle-based bipyramids. These bipyramids are arranged in planes parallel to the (a, b) direction so that the manganese ions form a distorted triangular lattice (see figure 1). They share an oxygen atom in the (a, b) planes. The yttrium atom is located in between the bipyramids layers. YMnO₃ is paraelectric at high temperature with space group P6₃mc. Under a critical temperature it is ferroelectric, with space group P6₃cm; the polarization is aligned along the c direction. The temperature of this paraelectric (PE) to ferroelectric (FE) phase transition is however still under debate. Indeed, usually assumed to be around \( T \approx 920 \text{ K} \), it was recently proposed to occur at a higher temperature, \( T \approx 1050 - 1100 \text{ K} \). A very recent neutrons diffraction investigation suggests the existence of an iso-symmetric phase transition at \( T \approx 920 \text{ K} \), resulting in a strong lowering of the polarization amplitude, while the non-centrosymmetric to centrosymmetric transition occurs at \( 1258 \pm 4 \text{ K} \). At much lower temperature (\( T_N \approx 75 \text{ K} \)) YMnO₃ undergoes a paramagnetic (PM) to antiferromagnetic (AFM) transition. The Mn³⁺ ions are in a high spin state \( S = 2 \). Neutrons diffraction experiments witness an in-plane spins orientation associated with a 120° ordering, with the spins perpendicular to the Mn–O bonds. The ferroelectric and antiferromagnetic order parameters are coupled and a giant atomic motion was revealed at the Néel temperature. The magnetic transition is however an iso-structural transition and the space group remains P6₃cm in the AFM phase. The magnetic space group is more subject to caution. Indeed, while most authors favor an identical P6₃cm magnetic and structural space group, the absence of a linear magneto-electric coupling and the existence of a ferromagnetic component recently observed are incompatible with the P6₃cm magnetic group. Group analysis shows that these experimental data can only be accounted for in the P6₃ magnetic group.

Phonons spectra are often used to help understanding both the ferroelectric/paraelectric transitions and the magneto-electric coupling. While the YMnO₃ phonons...
spectrum has been experimentally studied both by Ram-
man and Infra-Red measurements, there is still
many opened questions concerning not only modes assign-
ations but also the fact that several of the symmetry
allowed modes are not experimentally observed. First
principle calculations not only could help understanding
the experimental observation but also could yield more
light on the recently observed electromagnon\(^3\). The
present paper thus presents first principle calculations
of the YMnO\(_3\) phonons spectrum in the different space
groups associated with the FE and PE phases, that is
\(P6_{3}cm\) and \(P6_{3}/mmc\). The next section will be de-
voted to the methodological details and preliminary re-
sults (geometry optimization, Born effective charges, po-
larization, dielectric tensor, etc…) and section III will
describe and discuss phonons results.

II. METHOD AND PRELIMINARY RESULTS

We performed geometry optimization, spontaneous pol-
arization and phonons frequencies calculations within
the Density Functional Theory (DFT) as implemented in
the Crystal09 package\(^4\). Since the manganese 3d shells
are strongly correlated we used hybrid functionals in or-
der to better take into account the self-interaction cancel-
lation. Three different functionals were used in this work,
namely the classical B3LYP functional\(^5\), the recently
developed B1WC\(^6\) functional for ferroelectric systems
and a B1PW\(^7\) functional corresponding to the B1WC
one with the Perdew-Wang exchange functional \(^8\). Only
the B1PW results are presented in the paper, the re-
sults obtained with the other functionals can be found
in the supplementary data. Small core pseudo-potentials
were used for the heavy atoms (Mn and Y) associated
with semi-valence and valence 2\(\xi\) and 2\(\zeta\) plus polarization
basis sets\(^9\). The oxygen ions are represented in an
all-electrons basis set of 2\(\xi\) quality specifically optimized
for O\(^2-\) ions\(^10\). The mono-determinantal character of the
Kohn-Sham approximation does not allow the possibility
to deal with magnetic frustration as observed in YMnO\(_3\).
Indeed, only collinear magnetism is possible in the CRYS-
TAL code. A non-magnetic electronic density can be cal-
culated, however it does not account for the open-shell and
high spin character of the Mn\(^{3+}\) ions, which are re-
sponsible for a large stabilization energy (of the order of
two Hubbard 3d-shell \(U\) per Mn atom, this is of the order
of 10eV) and crucial for a reasonable electronic structure
representation. A “pseudo” antiferromagnetic configura-
tion can be proposed on a \(2 \times 2 \times 1\) cell. In this case, only
two among the three antiferromagnetic (AFM) couplings
are satisfied within each triangle. It results in a lower en-
ergy for the antiferromagnetic bonds and an associated
loss of symmetry. When the geometry optimization is
performed, the Mn-Mn distances associated with anti-
aligned spins are shorter than the bonds with aligned
spins, resulting in a structure with unphysical symme-
try and characteristics. The choice of a ferromagnetic
(FM) configuration for the Mn\(^{3+}\) S=2 spins thus seems
the best compromise. Indeed, not only this configuration
respects the system symmetry (a crucial aspect for accu-
rate phonons modes), but also the energy error that can
be associated with the loss of the inter-atomic exchange
energy (that is \(1/2J \approx 1.5\) meV per bond) is much weaker
than the error associated with the loss of the magnetic
character for the Mn\(^{3+}\) ions. For these reasons all our cal-
culations will be done within a ferromagnetic Mn spins
alignment.

Within this procedure, we computed the polarization
(using Berry phase approach) for the different experi-
mental geometries available in the literature at different
temperatures. Table I reports the computed polarization
values. One sees immediately that our computed values
are in very good agreement with the experimental ones,
despite the fact that the magnetic order used in the cal-
culation is ferromagnetic and not antiferromagnetic. The
quality of these results thus validate our choices for the
calculations. In addition it supports the idea, first pro-
posed by Lee et al\(^{11}\), that in this system the magneto-
electric coupling is mainly driven by elastic effects rather
than by a direct coupling between the polarization and the
magnetic order.

| Structures | 10 K\(^{12}\) | 180 K\(^{12}\) | 300 K\(^{12}\) |
|------------|-----------|----------|----------|
| Exp. \(P_S\) | \(\sim 1^{15}\) | 6.2\(^{16}\) | 4.5\(^{17}\) |
| This work  | 1.1       | 6.2      | 4.9      |

Table I: Spontaneous polarization \(P_S\) in \(\mu C.cm^{-2}\) for different temperatures. Experimental and computed values using the experimental geometries at the given temperatures.

In a second step we optimized the geometry. Both
the cell parameters and the atomic positions compare
very well with the experimental values in the paramag-
etic phase\(^{22}\). Indeed, the error on the lattice param-
eters is weaker than 0.5% and for the atomic positions
\(\sum_{at} |r_{at}^{exp} - r_{at}^{calc}|^2 = 0.0087\) Å\(^2\).

Finally we computed the Born effective charge tensor
\(Z\) for the optimized geometry. They are reported in
table II. Again our results compare well with the experi-
mental evaluations validating our methodological choices.

III. THE PHONONS SPECTRA

Table III displays the \(\Gamma\) point optical transverse (TO)
phonon modes, both for the paraelectric (columns 1-2)
and ferroelectric (columns 6-7) phases. Raman and Infra-
Red (IR) experimental data are given for comparison. The
\(P6_{3}/mmc\) group of the paraelectric phase decom-
poses in
\[ 1A_{1g} \oplus 3A_{2u} \oplus 3B_{1g} \oplus 2B_{2u} \oplus 1E_{1g} \oplus 3E_{1u} \oplus 3E_{2g} \oplus 2E_{2u} \]
optical modes, out of which the \(A_{1g}\), \(E_{1g}\) and \(E_{2g}\) are
Raman active while the \(A_{2u}\) and \(E_{1u}\) are IR active, leav-
ing the \(B_{1g}\), \(B_{2u}\) and \(E_{2u}\) modes inactive both in Raman
and IR. The $P6_3cm$ group of the ferroelectric phase decomposes in

$$9A_1 \oplus 5A_2 \oplus 5B_1 \oplus 10B_2 \oplus 14E_1 \oplus 15E_2$$

optical modes, out of which the $A_1$, $E_1$ are active both in Raman and IR, the $E_2$ are active in Raman only and the $A_2$, $B_1$ and $B_2$ are inactive both in Raman and IR.

For the ferroelectric phase, the optical longitudinal (LO) phonon modes have also been evaluated and are reported in the supplementary data.

### A. High temperature discussion

At high temperature only four modes were experimentally measured by Fukumura et al\(^{23}\). These modes were respectively assigned by Fukumura et al to one $A_{1g}$ mode (666 cm\(^{-1}\)), one $E_{1u}$ mode (420 cm\(^{-1}\)) and two $E_{2g}$ modes (120 and 395 cm\(^{-1}\)) of the $P6_3/mmc$ group of the high temperature PE phase. In addition figure 5 of reference 14 clearly shows that these modes are observed continuously from 300 K to 1200 K in the same energy ranges. Going back to our calculations, if we want to assign these modes by continuity from the low temperature phase ($P6_3cm$ to $P6_3/mmc$), we have to suppose that the mode at 395 cm\(^{-1}\) should be assigned as $E_{2u}$ (computed at 402 cm\(^{-1}\) in the $P6_3/mmc$ group and at 392 cm\(^{-1}\) in the $P6_3cm$ group, and measured at 483 cm\(^{-1}\) in the low temperature phase). Similarly, the mode at 420 cm\(^{-1}\) should be assigned as $E_{1u}$ and not as $E_{1g}$ and the mode at 120 cm\(^{-1}\) should be assigned as $E_{2u}$ rather than $E_{2g}$. At this point there is a clear contradiction between the continuity requirement of the phonons modes between the low and high temperature phase and the Raman symmetry requirements. Indeed the “ungerade” $E_{1u}$ and $E_{2u}$ irreducible representations (irreps) are not Raman active and no crystal disorientation or twinning could induce an inversion between a “gerade” and an “ungerade” mode. We must thus assume that the symmetry group at 1200 K cannot be the $P6_3/mmc$ group.

What type of hypotheses are left? The first possibility is the existence of an intermediate phase in the 1200 K temperature range as suggested by several authors\(^{7,25,26}\). However the $P6_3/mmc$ symmetry group suggested is no more than the $P6_3/mmc$ group, compatible with the phonon spectrum. Indeed, symmetry group analysis shows that the $P6_3/mmc$ to $P6_3/mmc$ transformation only exchange the $B_{1g}$ with the $B_{2g}$, and the $B_{1u}$ with the $B_{2u}$ irreps. A second possibility would be that the intermediate phase corresponds to the $P6_3mc$ group. In this group the inversion center is lost, and the $E_{1g}$ and $E_{1u}$ irreps of $P6_3/mmc$ are associated with the $E_1$ irrep of the $P6_3mc$ group and with the $E_1$ irrep of the low temperature phase (resp. $E_{2g}$ and $E_{2u}$ are associated with $E_2$). Both the $E_1$ and $E_2$ irreps are Raman active in the $P6_3mc$ group and the experimental Fukumura et al\(^{23}\) data can be easily associated with the computed modes (see table III, columns 3-4). The average error between the computed and measured frequencies is 18 cm\(^{-1}\), essentially supported by the higher $A$ mode (3 cm\(^{-1}\) for all the other modes). The main problem with this hypothesis is that the unit cell tripling at the $P6_3mc$ to $P6_3cm$ transition should have been seen in diffraction experiments, while it does not seem to be the case\(^{25}\). Therefore, the only possibility compatible with all data seems to be that a $P6_3/mmc$ to $P6_3cm$ phase transition occurs at a temperature higher than 1200 K, as proposed by Jeong\(^{27}\) and Gibbs\(^{8}\) from neutrons diffraction measurements ($T_c = 1258 K \pm 14 K$). In other terms, all the high temperature data from Fukumura et al\(^{23}\) should be interpreted within the ferroelectric $P6_3cm$ group.

### B. Low temperature discussion

At low temperature our computed modes fit quite well with the available experimental data, both Raman and IR (see table III, columns 6 and further). Table IV displays the average errors between our computed modes and the experimental data for each irreducible representation. The experimental phonons modes can be associated with the computed ones except for a few exceptions. i) The mode at 190 cm\(^{-1}\) seen by Iliev et al in the $A_1$ irreducible representation cannot be associated with a computed mode. This mode, not seen by the other authors,
| Irrep | This work | Raman | This work | IR | Raman |
|-------|-----------|-------|-----------|----|-------|
|       | $P6_3/mmc$ | $P6_3mc$ | $P6_3cm$ | $Zaghioui$ | $Iliev$ |
|       | $1100K$ | $10K$ | $300K$ | $15K$ | $10K$ | $300K$ |
| $E_{2u}$ | 121 | $E_2$ | 121 | 120 | $A_2$ | 33 |
| $B_{1g}$ | 187 | $B$ | 179 | 136 | $B_2$ | 147 |
| $E_{2g}$ | 159 | $E_2$ | 148 | 179 | $E_2$ | 190 |
| $A_{2u}$ | 109 | $A$ | 138 | 136 | $E_1$ | 148 |
| $E_{1u}$ | 187 | $E_1$ | 177 | 136 | $B_1$ | 147 |
| $B_{2u}$ | 211 | $B$ | 204 | 204 | $E_1$ | 148 |
| $E_{2g}$ | 257 | $E_2$ | 235 | 235 | $E_1$ | 241 |
| $E_{1u}$ | 264 | $E_1$ | 241 | 241 | $A_1$ | 241 |
| $E_{2u}$ | 402 | $E_2$ | 402 | 395 | $A_1$ | 301 |
| $E_{1u}$ | 426 | $E_1$ | 421 | 420 | $E_1$ | 301 |
| $E_{1g}$ | 483 | $E_1$ | 471 | 471 | $E_1$ | 471 |
| $E_{2g}$ | 500 | $E_2$ | 484 | 484 | $A_1$ | 409 |
| $A_{2u}$ | 518 | $A$ | 467 | 467 | $A_1$ | 467 |
| $B_{1g}$ | 495 | $B$ | 457 | 457 | $A_1$ | 457 |

Table III: Hexagonal YMnO$_3$ vibrational frequencies in cm$^{-1}$ for the paraelectric ($P6_3/mmc$) and ferroelectric ($P6_3cm$) phases. The frequencies for one of the possible intermediate phases ($P6_3mc$) was also computed. Modes with problematic assignment are in bold faces; modes that are symmetry allowed but not seen are designed by dashes.
cannot be associated with a $A_1$ mode. Indeed, the $A_1$ modes are IR active and all predicted modes are observed by Zaghrioui et al\textsuperscript{16} up to more than 450 wave numbers. If not artifactual, the 190 cm\textsuperscript{-1} mode must belong to another irreducible representation. The only possibility in this energy range is an $E_2$ mode predicted at 150 cm\textsuperscript{-1}. Indeed, all other IR or Raman active modes in this energy range are experimentally observed and easily associated with the computed phonons. ii) The 210 cm\textsuperscript{-1} $A_1$ mode seen by Fukumura et al\textsuperscript{14}. Once again a $A_1$ mode around 210 cm\textsuperscript{-1} is incompatible both with the computed values and with the other experimental results (IR or Raman). Most probably this mode has been improperly assigned as a $A_1$ mode and should rather be considered as a $E_1$ (seen at 211 cm\textsuperscript{-1} by Zaghrioui et al\textsuperscript{16}) or a $E_2$ mode (seen at 215 cm\textsuperscript{-1} by Iliev et al\textsuperscript{13}).

Another point we would like to address is the reason why all phonons modes are not observed in experimental data. As far as the IR active modes are concerned we computed an estimate of the intensities, the analysis of which gives us some insight on the reasons some modes are not observed. In the $A_1$ representation two modes are not seen in reference 16, namely the highest mode computed around 720 cm\textsuperscript{-1} and the mode computed around 460 cm\textsuperscript{-1}. The IR computed intensity of the 720 cm\textsuperscript{-1} $A_1$ mode is very weak (between 5 and 12 km/mol according to the functional used) and it is thus not surprising this mode is not seen experimentally. The IR intensity of the $A_1$ mode computed around 460 cm\textsuperscript{-1} mode is of the same order of magnitude as the next computed $A_1$ mode at 492 cm\textsuperscript{-1} which was associated to the experimental mode found at 434 cm\textsuperscript{-1}). Even if the IR intensity remains small it is non negligible and the second mode is observed. Assuming an equivalent shift in energy between experiments and calculation on these two modes, the first mode should be searched around 400 cm\textsuperscript{-1} in the IR spectrum however it is not seen. In the $E_2$ irreducible representation, five modes are not seen in IR experiments, namely the modes computed at 269 cm\textsuperscript{-1}, 386 cm\textsuperscript{-1}, 461 cm\textsuperscript{-1}, 515 cm\textsuperscript{-1} and 668 cm\textsuperscript{-1}. The calculations reveals that all these modes are associated with very low IR intensities that could explain they are not seen by Zaghrioui et al\textsuperscript{16}.

### Table IV: Average errors per irrep on the YMnO$_3$ vibrational frequencies compared to different experimental data (in cm\textsuperscript{-1}).

| Irrep | IR | Raman |
|-------|----|-------|
| $A_1$ | 14 | 20 |
| $E_1$ | 8  | 18   |
| $E_2$ | 11 | 4    |

### Table V: Displacements vector (normalized to classical amplitudes) associated with the first $A_2$ mode found around 33 cm\textsuperscript{-1}.

| Atom | Positions | Displacements |
|------|-----------|---------------|
| $Y_1$ | 0.0000 0.0000 0.0000 | 0.0000 0.0000 0.0000 |
| $Y_2$ | 1/3 -1/3 0.0000 | 0.0000 0.0000 -0.0713 |
| Mn$_1$ | $x_{Mn_1}$ 0.0000 $z_{Mn_1}$ | 0.0322 0.0558 0.0000 |
| O$_1$ | $x_{O_1}$ 0.0000 $z_{O_1}$ | 0.0206 0.0357 0.0000 |
| O$_2$ | $x_{O_2}$ 0.0000 $z_{O_2}$ | 0.0272 0.0471 0.0000 |
| O$_3$ | 0.0000 0.0000 $z_{O_3}$ | 0.0000 0.0000 0.0000 |
| O$_4$ | 1/3 2/3 0.0000 | 0.0000 0.0000 -0.0145 |

### Figure 2: (Color online) Schematic picture of the atomic displacements in the $(\vec{a}, \vec{b})$ plane for the lowest $A_2$ phonon mode. The blue, solid lines, Mn triangles remain nearly un-touched and rotate as a whole around the $\vec{c}$ axis. The red, dashed and magenta, dotted Mn triangles are alternatively enlarged/reduced, the Mn ions moving within the $(\vec{a}, \vec{b})$ plane while the central oxygens move conversely along the $\vec{c}$ direction. A jmol xyz file can be found in the supplementary data in order to visualize the displacements of one manganese plane.

This phonon mode, active neither in Infra-Red nor in Raman experiments exhibits displacements that can be expected to strongly affect the magnetic exchange coupling constants along the red, dashed and magenta, dotted bonds as picture in figure 2.

Let us notice that the effective exchange $J$ between two manganese atoms is the sum of a direct exchange contribution $J_d$ (Pauli exchange, always ferromagnetic,
Figure 3: Main super-exchange paths between two manganese atoms. Let us remember that in YMnO$_3$ the manganese is $3d^4$ and the singly occupied orbitals are $d_{xy}$, $d_{x^2-y^2}$, $d_{xz}$, $d_{yz}$ if $z$ is along the $c$ axis. We can evaluate

$$J_1 \sim \langle Mn_1 d_{xy} | O p_z \rangle^2 \langle O p_z | Mn_2 d_{xz} \rangle^2$$

$$J_2 \sim \langle Mn_1 d_{x^2-y^2} | O p_z \rangle^2 \langle O p_z | Mn_2 d_{yz} \rangle^2$$

$$J_3 \sim \langle Mn_1 d_{xz} | O p_y \rangle^2 \langle O p_y | Mn_2 d_{x^2-y^2} \rangle^2$$

$$J_4 \sim \langle Mn_1 d_{yz} | O p_x \rangle^2 \langle O p_x | Mn_2 d_{xy} \rangle^2$$

The $A_2$ phonon mode under consideration involves the following atomic displacements on the red, dashed and magenta, dotted Mn triangles (see figure 2).

- The Mn-Mn bond length elongation / contraction (in opposite phases between red and magenta triangles). This movement affects the direct part of the exchange : $J_d$, increasing its ferromagnetic character when the Mn-Mn distances are contracted and decreasing it when the Mn-Mn distances are elongated.

- The up and down movement (along the $c$ direction) of the oxygens atoms at the center of these triangles. This movement strongly affects both the Mn-O distances, reducing them when the oxygens come closer to the Mn plane, and the Mn-O-Mn angle.

One sees immediately using figure 3 that, when the oxygen comes closer to the Mn plane, the overlap between the magnetic orbitals of the Mn atoms and the $2p$ bridging orbitals of the central oxygen increases, thus increasing the antiferromagnetic character of $J_1$. At the same time the Mn-Mn bond length increases thus decreasing the ferromagnetic character of $J_d$. Both terms goes in the same direction resulting in a enlarged antiferromagnetic character for the bonds of the (alternatively red/magenta) triangles when the central oxygen comes closer to the Mn plane and a reduced antiferromagnetic character when the central oxygen goes away from the Mn plane.

The blue, solid line, Mn triangles (centered around the unit cell origin) are subject to a rotation as a whole around the $c$ axis going through their central oxygen (O$_3$). One thus does not expect the magnetic exchange within the blue Mn triangles to be affected by this $A_2$ phonon mode. However this rotation results in a strong distortion of the triangles with blue red and magenta bond inducing a magnetic interaction scheme quite far from the nearly homogeneous triangular lattice of the static structure.

The main conclusion of this analysis is that this $A_2$ phonon mode is strongly coupled to the magnetic interactions.

Let us now put these results into perspective with the characteristics of the hybrid phonon-magnon excitation, studied using inelastic polarized and non-polarized neutron scattering by Pailhès and coworkers. One notices that this $A_2$ mode seems to fulfill all the requirements for a good candidate for the phonon participating to the hybrid mode. Indeed, it is an optical mode in the adequate energy range, exhibiting atomic displacements consistent with the umbrella motion proposed in reference 4 and that can be expected from the above analysis to be strongly coupled to the spin degree of freedom.

IV. CONCLUSION

The present paper proposes Γ point phonon calculations for the YMnO$_3$ compound both in the ferroelectric phase and in the paraelectric phase. Our calculations agrees well with the Infra-Red and Raman experimental data. The experimental versus calculated modes correspondence is discussed in details for the few problematic modes. We were able to explain the fact that several modes could not be seen in IR experiments due to their very low (calculated) intensities. A careful analysis of the phonons modes correspondence, when going from the ferroelectric to the paraelectric phase, is performed and leads to the conclusion that, the phonon modes observed in Raman scattering at 1200K cannot be associated with the paraelectric phase $P6_3/mmc$ space group. The different intermediate subgroups allowed between the paraelectric $P6_3/mmc$ space group and the ferroelectric $P6_3/mcm$ group were also checked against the modes continuity and the experimental data and had to be discarded. The only possibility agreeing
with the phonon calculations and the experimental data is that the \( P6_3/mmc \) to \( P6_3cm \) phase transition occurs at a temperature higher than 1200 K, supporting the proposition of Jeong\(^27\) and Gibbs\(^8\) \((T_c = 1258 \pm 14 \text{ K})\). Finally we studied in more details the first optical mode. This mode belongs to \( A_2 \) irreducible representation and is inactive both in IR and Raman experiment. This mode however seems to have all necessary characteristics to be a good candidate for the phonon part of the electro-magnon mode observed in inelastic neutrons scattering by Petit, Paillès et al.\(^3,4\).

Acknowledgments

The authors thank V. TaPhuoc and Ph. Ghosez and collaborators for helpful discussions. This work was done with the support of the French national computer center IDRIS under project no 081842 and the regional computer center CRIHAN under project no 2007013.

1. V. G. Baryaktar and I. E. Chapius, Sov. Phys. Solid State 11, 2628 (1970); I. A. Akchiezer and L. N. Davydov, Sov. Phys. Solid State 12, 2563 (1971).
2. A. Pimenov, A. A. Mukhin, V. YU. Ivanov, V. D. Travkin, A. M. Balbashov and A. Loidl, Nature Physics 2, 97 (2006).
3. S. Petit, F. Moussa, M. Hennion, S. Paillès, L. Pinsard-Gaudart and A. Ivanov, Phys. Rev. Letters 99, 266604 (2007).
4. S. Paillès, X. Fabrèges, L. P. Régnauld, L. Pinsard-Godart, I. Mirebeau, F. Moussa, M. Hennion and S. Petit, Phys. Rev. B 79, 134409 (2009).
5. G. A. Smolenskii and I. E. Chupis, Sov. Phys. Usp. 25, 475 (1982).
6. T. Katsufuji, M. Masaki, A. Machida, M. Moritomo, K. Kato, E. Nishibori, M. Takata, M. Sakata, K. Ohoyama, K. Kitazawa and H. Takagi, Phys. Rev. B 66, 134434 (2002).
7. S. Abrahams, Acta Crys. B 65, 450 (2009).
8. A. S. Gibbs, K. S. Knight and Ph. Lightfoot, Phys. Rev. B 83, 094111 (2011).
9. E. F. Bertaut, R. Pauthenet and M. Mercier, Physics Letters 7, 110 (1963).
10. A. Muñoz, J. A. Alonso, M. J. Martínez-Lope, M. T. Casáis, and J. L. Martínez and M. T. Fernández-Díaz, Phys. Rev. B 62, 9498 (2000).
11. S. Lee, A. Pirogov, M. Kang, K.-H. Jang, M. Yonemura, T. Kuniyama, S.-W. Cheong, F. Gozzo, N. Shin, H. Kimura, Y. Noda and J.-G. Park, Nature 451, 805 (2008).
12. K. Singh, N. Bellido, Ch. Simon, J. Varignon and M.-B. Lepeitit, to be published elsewhere.
13. M. N. Iliev, H.-G. Lee, V. N. Popov, M. V. Abrušev, A. Hamed, R. L. Meng, and C. W. Chu, Phys. Rev. B 56, 2488 (1997).
14. H. Fukumura, S. Matsui, H. Harima, K. Kiso, T. Takahashi, T. Yoshimura and N. Fujimura, J. Phys.: Condens. Matter 19, 365239 (2007).
15. J. Vermette, S. Jandl, A. A. Mukhin, V. Yu Ivanov, A. Balbashov, M. M. Gospodinov and L. Pinsard-Gaudart, J. Phys.: Condens. Matter 22, 356002 (2010).
16. M. Zaghlouhi, V. Ta Phuoc, R. A. Souza, and M. Gervais, Phys. Rev. B 78, 184305 (2008).
17. R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V.R. Saunders, C.M. Zicovich-Wilson, Z. Kristallogr. 220, 571 (2005); R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, Ph. D’Arco, M. Llunell, CRYSTAL09 User’s Manual, University of Torino, Torino, (2009).
18. A. D. Becke, Phys. Rev. A, 38, 3098 (1988).
19. D. I. Bile, R. Orlando, R. Shaltaf, G. M. Rignanese, J. Jijueguez and P. Ghosez, Phys. Rev. B, 33, 8800 (1986).
20. J. P. Perdew and Y. Wang, Phys. Rev. B, 33, 8800 (1986).
21. M and Y : P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 299 (1985); Evarestov et al., Solid State Commun. 127, 367 (2003).
22. B. B. van Aken, A. Meetsma and Th. T. M. Palstra, Acta Cryst. C 57, 230 (2001).
23. B. B. van Aken, T. T. M. Palstra, A. Filippetti and N. A. Spaldin, Nature Materials 3, 164 (2004).
24. S. H. Kim, S. H. Lee, T. H. Kim, T. Zyung, Y. H. Jeong and M. S. Jung, Crys. Res. Tech. 35, 19 (2000).
25. G. Néert, Y. Ren, H. T. Stokes and T. T. M. Palstra, arXiv:cond-mat/0504546.
26. G. Néert, M. Pollet, S. Marinel, G. R. Blake, A. Meetsma and T. T. M. Palstra, J. Phys.: Condens. Matter 19, 466212 (2007).
27. Il-Kyoung Jeong, N. Hurb and Th. Proffen, J. Appl. Cryst. 40, 730 (2007).