First-principles study of the dielectric and dynamical properties of orthorhombic CaMnO$_3$

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Abstract
The structural, dielectric and dynamical properties of the low temperature antiferromagnetic orthorhombic phase of CaMnO$_3$ have been computed from first principles, using a density functional theory approach within the local spin density approximation. The theoretical structural parameters are in good agreement with experiment. The full set of zone-center phonons is reported, allowing new assignment of experimental Raman data and providing reference values for the interpretation of future infrared phonon measurements. It is shown that the static dielectric constant is very large and comparable in amplitude to that of isostructural CaTiO$_3$. In contrast to the pseudocubic structure, it is also highly anisotropic. These features are discussed in relationship to the anomalous Born effective charges and the presence of low frequency polar modes.

1. Introduction
Magnetic perovskite oxides constitute an exciting subject of study. Indeed, the interplay between their structural, magnetic and transport properties make them fascinating from both experimental and theoretical points of view. For example, the mixed valency perovskite Ca$_{1-x}$La$_x$MnO$_3$ is one of the most studied materials for its colossal magnetoresistance [1]. Also, the oxygen deficient manganites LaMnO$_{3-δ}$ and CaMnO$_{3-δ}$ are interesting for their transport and optical properties [2].

In this paper we report a first-principles study of stoichiometric CaMnO$_3$. The ground-state crystal structure of CaMnO$_3$ is orthorhombic with space group $Pnma$ [4]. The structure can be regarded as a distorted perovskite structure having four formula units [4, 5]. It is an insulator with an observed bandgap of about 3 eV [6]. The formal ionic configuration of CaMnO$_3$ is Ca$^{2+}$ Mn$^{4+}$ O$^{2-}$. In the octahedral crystal field, the 5$d$ orbitals of the Mn$^{4+}$ ion split into lower three-fold degenerated $t_{2g}$ levels and higher two-fold degenerated $e_g$ levels; the occupation being $t_{2g}^3$ and $e_g^0$ [7]. Because of the Mn$^{4+}$ configuration, there is no tendency to Jahn–Teller distortion. The magnetic structure is antiferromagnetic and the G-type order is energetically the most favorable. The magnetic interactions between the Mn ions are due to superexchange interactions. The observed Néel temperature is about 130 K [8], which estimates the exchange energy to be around 6.6 meV.

Previous first-principles calculations on CaMnO$_3$ focused mainly on the cubic phase and the electronic structure of the system. Here, we report a first-principles study of the dielectric and dynamical properties of the ground-state orthorhombic phase. This will allow us to reinvestigate the previous assignment of experimental Raman data and to provide benchmark results for the infrared active modes. It will also point out that the static dielectric constant is not only surprisingly large, and comparable to that of isostructural CaTiO$_3$, but also highly anisotropic, which is unexpected in view of the pseudocubic character of the structure.

2. Technical details
The first-principles simulations were performed according to the density functional theory scheme (DFT) within the local spin density approximation (LDA) and using the plane-wave implementation of the ABINIT package [9]. We used the Hartwigsen–Goedecker–Hutter (HGH) [10] parametrization for the pseudopotentials, where the 3$s$ and 3$p$ orbitals were treated as valence states for Mn and Ca atoms and 2$s$ and 2$p$ orbitals were considered as valence states for O atoms. The total number of valence states is therefore 15 for Mn, 10
for Ca and 6 for oxygen. Convergency was reached for an energy cutoff of 72 Hartree for the plane-wave expansion and a 6 × 4 × 6 k-point mesh for the Brillouin zone integration. The phonon frequencies, Born effective charges and dielectric tensor were computed according to the density functional perturbation theory (DFPT) [11] scheme as implemented in the ABINIT package.

3. Structural properties

At high temperature, CaMnO₃ adopts a cubic perovskite structure. At room temperature it exhibits an orthorhombic Pnma (N.62) structure [12] with 20 atoms in the primitive unit cell, which moreover exhibits a G-type antiferromagnetic antiferrodistortive (AFD) instabilities which are related to tilts by an atomic displacement [17]. It is a tensor that is formally defined as:

\[ \kappa_{\alpha\beta} = \partial \kappa / \partial x \mid_{E=0} \]

where \( \Omega_0 \) is the unit-cell volume and the derivative is evaluated under the condition of vanishing macroscopic electric field.

In our calculations, we imposed a G-type antiferromagnetic order and did the structural relaxation at fixed volume. The chosen volume is associated to a pseudocubic cell parameter of 3.73 Å which corresponds to the experimental cubic lattice constant [3] and also closely agrees with the experimental pseudocubic lattice constant of the orthorhombic phase [4]. The cell shape and atomic positions were relaxed according to this constraint and the results are reported in table 1.

The relaxed structure is in excellent agreement with the experimental data. The cell parameters \( a \) and \( b \) are only slightly overestimated while the \( c \) parameter is slightly underestimated (errors of \( \approx 0.5\% \)). The calculated atomic positions are also in good agreement with the experimental data, the distortion with respect to the ideal cubic positions being predicted with an accuracy similar to what is usually achieved in the class of \( \text{ABO}_3 \) compounds [13].

From the inspection of the density of states, we found a theoretical electronic bandgap of 0.8 eV for our relaxed antiferromagnetic orthorhombic structure. Although this strongly underestimates the experimental value (3.1 eV [14]), as usual within the LDA, our calculation properly reproduces the insulating character of the structure.

4. Dielectric properties

The Born effective charge of a given atom \( \kappa \) is a dynamical concept that is related to the change of polarization induced by an atomic displacement [17]. It is a tensor that is formally defined as:

\[ Z_{\kappa,\alpha\beta} = \partial \rho / \partial \kappa_{\alpha\beta} \mid_{E=0} \]

where \( \Omega_0 \) is the unit-cell volume and the derivative is evaluated under the condition of vanishing macroscopic electric field.

The Born effective charges have been calculated for the four atoms of table 1. The full tensors are as follows:

\[ Z^\ast(\text{Ca}) = \begin{pmatrix} 2.51 & 0.00 & 0.19 \\ 0.00 & 2.43 & 0.00 \\ 0.27 & 0.00 & 2.52 \end{pmatrix} \]

\[ Z^\ast(\text{Mn}) = \begin{pmatrix} 6.82 & -0.37 & -0.72 \\ 0.07 & 5.78 & 1.42 \\ -0.69 & -1.54 & 6.56 \end{pmatrix} \]

\[ Z^\ast(\text{O}_1) = \begin{pmatrix} -1.73 & 0.00 & 0.06 \\ 0.00 & -5.11 & 0.00 \\ -0.20 & 0.00 & -1.76 \end{pmatrix} \]

\[ Z^\ast(\text{O}_2) = \begin{pmatrix} -3.80 & -0.08 & -1.94 \\ -0.11 & -1.55 & -0.01 \\ -1.97 & 0.00 & -3.61 \end{pmatrix} \]

Below each tensor, the main values of the symmetric part of \( Z^\ast \) are also mentioned, for direct comparison with (i) the nominal atomic charges (\( Z^\ast(\text{Ca}) = +2 \), \( Z^\ast(\text{Mn}) = +4 \) and \( Z^\ast(\text{O}) = -2 \)) and (ii) the Born effective charges in the cubic phase at \( a_0 = 3.73 \) Å (\( Z_{\text{C}}^\ast(\text{Ca}) = +2.61 \), \( Z_{\text{C}}^\ast(\text{Mn}) = +7.43 \), \( Z_{\text{C}}^\ast(\text{O}_1) = -2.55 \) and \( Z_{\text{C}}^\ast(\text{O}_2) = -4.94 \)). First, we notice the anomalously large values of the Mn and O charges, which are significantly larger than the nominal atomic charges. These values are rather similar to those previously reported for the isostructural CaTiO₃ [16] and also to those in most ferroelectric and related \( \text{ABO}_3 \) compounds [13, 17]. In the latter, the anomalously large \( Z^\ast(\text{O}) \) and \( Z^\ast(\text{B}) \) were related to the partial hybridization between O 2p and B-metal d

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & Orthorhombic & Pseudocubic & \\
\hline
 & This work & Exp. [4] & Exp. [15] \\
\hline
\hline
\( a \) & 5.287 & 5.279 & 5.275 \\
\( b \) & 7.498 & 7.448 & 7.460 \\
\( c \) & 5.235 & 5.264 & 5.275 \\
\( a_0 \) & 3.730 & 3.726 & 3.730 \\
\hline
\( \text{Ca} \) (4c) & x & 0.040 & 0.033 & 0.000 \\
& y & 0.250 & 0.250 & 0.250 \\
& z & -0.008 & -0.006 & 0.000 \\
\( \text{Mn} \) (4b) & x & 0.000 & 0.000 & 0.000 \\
& y & 0.000 & 0.000 & 0.000 \\
& z & 0.500 & 0.500 & 0.500 \\
\( \text{O}_1 \) (4c) & x & 0.485 & 0.490 & 0.500 \\
& y & 0.250 & 0.250 & 0.250 \\
& z & 0.071 & 0.066 & 0.000 \\
\( \text{O}_2 \) (8d) & x & 0.287 & 0.287 & 0.250 \\
& y & 0.036 & 0.034 & 0.000 \\
& z & -0.288 & -0.288 & 0.250 \\
\hline
\end{tabular}
\caption{Theoretical and experimental unit-cell parameters (Å) and non-equivalent atomic positions (reduced coordinates) in the antiferromagnetic orthorhombic Pnma structure of CaMnO₃. The Wyckoff positions of the reported atoms are mentioned in brackets.}
\end{table}
CaMnO$_3$ at the

The dynamical changes in CaMnO$_3$ are similarly sensitive to atomic distortion as they differ from that reported for orthorhombic CaTiO$_3$ in which it is slightly larger than in the cubic phase, which is a trend structure [16].

proposed from shell-model results in [15].

We report in table 2 the calculated frequencies of the Raman active modes and a related new assignment of the experimental data.

5.1. Raman active modes

Over this decomposition, three modes are acoustic (symmetries $A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$) and the last 25 modes are infrared (IR) active (symmetries $B_{1u}$, $B_{2u}$ and $B_{3u}$). According to the structure defined in table 1, the IR $B_{3u}$ modes are polarized along the x direction, $B_{2u}$ along the y direction and $B_{1u}$ along the z direction. The eight A$_g$ silent modes, not further discussed below, are calculated at frequencies of 123, 140, 179, 220, 313, 392, 438 and 466 cm$^{-1}$.

5. Dynamical properties

The irreducible representation in the orthorhombic $Pmn_a$ phase CaMnO$_3$ at the $\Gamma$ point is:

\[
\epsilon_\infty = \begin{pmatrix}
11.3 & 0.0 & 0.0 \\
0.0 & 13.1 & 0.0 \\
0.0 & 0.0 & 10.8
\end{pmatrix}.
\]

The calculated tensor is only slightly anisotropic, coherently with the pseudocubic character of the structure. Its elements are significantly larger than in related compounds like CaTiO$_3$ ($\epsilon_\infty \approx 6$ [16]), as expected from the smaller LDA bandgap of CaMnO$_3$. The optical dielectric tensor in the orthorhombic phase does not differ significantly from that previously reported in the ideal cubic structure (\(\epsilon_\infty = 10.43\)) from our calculations and \(\epsilon_\infty = 11.25\) from [19]. We notice, however, that it is slightly larger than in the cubic phase, which is a trend different from that reported for orthorhombic CaTiO$_3$ in which \(\epsilon_\infty\) decreases when non-polar distortions are frozen into the structure [16].

## Table 2. Comparison of the calculated and experimental frequencies (cm$^{-1}$) of the Raman modes of the antiferromagnetic orthorhombic phase of CaMnO$_3$. The first column labels the symmetry of each mode. The second and third columns correspond to the present first-principles (FP) calculations and the related assignment of the experimental data of [15]. The fourth and fifth columns correspond to the shell-model (SM) calculations and related assignment in [15].

| Symmetry | Present | Reference [15] |
|----------|---------|----------------|
| $A_g$    | 152 150 | 154 160        |
| $A_g$    | 167 160 | 200 184        |
| $B_{2g}$ | 172 —   | 148 —          |
| $B_{2g}$ | 180 —   | 232 258        |
| $B_{2g}$ | 189 179 | 178 179        |
| $B_{2g}$ | 203 —   | 290 —          |
| $B_{3g}$ | 227 258 | 292 —          |
| $B_{3g}$ | 241 —   | 281 —          |
| $A_g$    | 250 243 | 242 243        |
| $A_g$    | 275 278 | 299 278        |
| $A_g$    | 314 322 | 345 322        |
| $B_{3g}$ | 320 320 | 304 320        |
| $B_{3g}$ | 330 —   | 354 —          |
| $B_{3g}$ | 372 —   | 366 —          |
| $B_{3g}$ | 425 —   | 453 465        |
| $B_{3g}$ | 434 —   | 459 —          |
| $A_g$    | 450 438 | 467 487        |
| $B_{2g}$ | 465 465 | 485 —          |
| $B_{2g}$ | 469 —   | 541 564        |
| $B_{2g}$ | 488 —   | 536 —          |
| $A_g$    | 504 487 | 555 —          |
| $B_{3g}$ | 595 564 | 743 —          |
| $B_{3g}$ | 655 —   | 749 —          |
| $B_{3g}$ | 674 —   | 754 —          |

was unambiguously assigned to impurity and the modes at 382 and 438 cm$^{-1}$ were kept aside since their frequencies differ strongly from those of the shell model. Below 200 cm$^{-1}$ the assignment was particularly ambiguous since two modes were calculated at 154 and 200 cm$^{-1}$, while three were observed in the spectra.

From our calculation, the experimental lines at 243, 278 and 322 cm$^{-1}$ can be assigned to the $A_g$ modes at 250, 275 and 314 cm$^{-1}$ respectively. For the low frequencies, the assignment can be significantly improved if we assign to the calculated modes at 152 and 167 cm$^{-1}$, the experimental modes at 150 and 160 cm$^{-1}$ rather than those at 160 and 184 cm$^{-1}$ as previously proposed (i.e. ruling out the experimental mode at 184 cm$^{-1}$ instead of the one at 150 cm$^{-1}$). For the high frequency $A_g$ modes, the overall agreement between experimental and theoretical data is best if we assign the experimental line at 438 cm$^{-1}$ (not assigned in [15]) to the calculated mode at 450 cm$^{-1}$ and the one at 487 cm$^{-1}$ to the calculated mode at 504 cm$^{-1}$.

The experimental line at 179 cm$^{-1}$, assigned to a $B_{1g}$ mode in [15], is in good agreement with our calculation (189 cm$^{-1}$). Amongst the two experimental lines at 320 and 564 cm$^{-1}$ previously assigned to $B_{3g}$ modes [15], only the first one is reproduced within our calculation with a very good accuracy (320 cm$^{-1}$) while, for the second one, we get a theoretical frequency of 469 cm$^{-1}$. Since the assignment between $B_{1g}$ and $B_{3g}$ modes is rather ambiguous, we propose that the
Table 3. Symmetry and frequency of the 25 IR modes. The mode effective charges \((\tilde{Z}_{\omega_{0,m}}, \alpha)\) defined in (11) and the oscillator strengths \((S_{\omega_{0,m}}^\alpha)\) are also provided for each mode as well as the contribution to the static dielectric constant \(\epsilon_{\omega_{0,m}}\). From our conventions, \(\alpha = xx\) for \(B_{3u}\) modes, \(\alpha = yy\) for \(B_{2u}\) modes and \(\alpha = zz\) for \(B_{1u}\) modes.

| Symmetry | \(\omega\) (cm\(^{-1}\)) | \(\tilde{Z}_{\omega_{0,m}}^\alpha\) | \(S_{\omega_{0,m}}^\alpha\) (10\(^{-4}\) a.u.) | \(\epsilon_{\omega_{0,m}}^\alpha\) |
|----------|----------------|-----------------|-----------------|----------------|
| \(B_{3u}\) | 101 | 15.95 | 57.0 | 238.40 |
| \(B_{1u}\) | 147 | 10.74 | 17.00 | 35.09 |
| \(B_{3u}\) | 150 | 13.63 | 34.00 | 65.37 |
| \(B_{3u}\) | 153 | 3.97 | 2.20 | 4.06 |
| \(B_{2u}\) | 155 | 2.03 | 0.43 | 0.70 |
| \(B_{2u}\) | 179 | 5.60 | 8.50 | 11.40 |
| \(B_{2u}\) | 208 | 14.26 | 38.00 | 37.67 |
| \(B_{1u}\) | 215 | 5.60 | 6.30 | 5.80 |
| \(B_{3u}\) | 216 | 3.10 | 1.70 | 1.50 |
| \(B_{3u}\) | 234 | 5.06 | 5.00 | 3.90 |
| \(B_{2u}\) | 251 | 4.60 | 5.60 | 3.80 |
| \(B_{3u}\) | 287 | 3.40 | 3.50 | 1.80 |
| \(B_{1u}\) | 290 | 0.59 | 0.09 | 0.04 |
| \(B_{2u}\) | 324 | 2.70 | 0.98 | 0.37 |
| \(B_{1u}\) | 326 | 2.59 | 1.90 | 0.78 |
| \(B_{3u}\) | 340 | 1.04 | 0.36 | 0.13 |
| \(B_{1u}\) | 345 | 2.36 | 1.40 | 0.51 |
| \(B_{1u}\) | 381 | 6.18 | 6.10 | 1.80 |
| \(B_{3u}\) | 414 | 0.60 | 0.06 | 0.00 |
| \(B_{2u}\) | 423 | 1.92 | 1.20 | 0.25 |
| \(B_{3u}\) | 437 | 1.89 | 1.20 | 0.26 |
| \(B_{2u}\) | 469 | 4.22 | 5.50 | 1.07 |
| \(B_{2u}\) | 488 | 4.14 | 5.70 | 1.04 |
| \(B_{3u}\) | 495 | 1.40 | 0.54 | 0.09 |
| \(B_{2u}\) | 504 | 3.40 | 3.80 | 0.65 |

experimental line at 564 cm\(^{-1}\) might in fact correspond to the \(B_{1g}\) mode calculated at 595 cm\(^{-1}\).

Finally, from [15], it seems that the \(B_{2g}\) modes are theoretically predicted with less accuracy since modes calculated with the shell model at 180 and 425 cm\(^{-1}\) are associated to the lines measured at 258 and 465 cm\(^{-1}\). From our first-principles calculation, this agreement seems significantly better and we propose to assign the experimental modes, while in figure 1 we report the calculated IR reflectivity spectra (without damping) at normal incidence, respectively on the [100], [010] and [001] surface of a CaMnO\(_3\) monocrystal. Such effects are, however, unexpected here since in this case \(e_g\) orbitals are not Jahn–Teller unstable and remain degenerated.

5.2. IR active modes

Table 3 summarizes the calculated IR frequencies of the TO modes, while in figure 1 we report the calculated IR reflectivity spectra (without damping) at normal incidence, respectively on the [100], [010] and [001] surface of a CaMnO\(_3\) monocrystal for direct comparison with experimental data. Unfortunately no IR measurement on monocrystal in the orthorhombic phase of CaMnO\(_3\) was found to compare with our results. An IR spectra was reported in [21] but on a polycrystalline sample, and no symmetry attribution was reported for the 15 observed frequencies, which makes comparison very difficult considering the high number of modes. The only remark that can be made concerns the high frequency part of the spectrum. The three highest frequencies are measured in [21] at 533, 580 and 628 cm\(^{-1}\), which deviate strongly with our results where the maximum frequency of IR modes is calculated at 504 cm\(^{-1}\). This could eventually be related to inaccuracies in our calculations but also suggests that these experimental frequencies might correspond to a combination of modes (for example, the highest measured frequency 628 cm\(^{-1}\) can be recovered as being the exact sum of the modes calculated at 305 and 323 cm\(^{-1}\)).

In addition to the frequencies, we also report in table 3 the mode effective charges [11], the oscillator strengths and the contribution of each polar mode to the static dielectric tensor. The total static dielectric tensor can be decomposed as follows:

\[
\epsilon_{\omega_{0,m}} = \epsilon_{\omega_{0,m}}^\alpha + \sum m \epsilon_{\omega_{0,m}}^\beta
\]

where \(\alpha\) and \(\beta\) are the Cartesian directions \((x, y\) or \(z))\), \(\epsilon_{\omega_{0,m}}^\alpha\) is the optical dielectric tensor and \(\epsilon_{\omega_{0,m}}^\beta\) is the contribution to the dielectric constant of each individual phonon mode \(m\). This latter contribution is computed from the following relation:

\[
\epsilon_{\omega_{0,m}}^\beta = \frac{4\pi S_{\omega_{0,m}}^\beta}{\Omega \omega_{m}^2}
\]

where \(\Omega\) is the volume of the cell, \(S_{\omega_{0,m}}^\beta\), and \(\omega_{m}\) are respectively the oscillator strength and the frequency of the mode \(m\).

The computed static dielectric tensor is reported below:

\[
\epsilon_0 = \begin{pmatrix}
262 & 0.0 & 0.0 \\
0.0 & 68.0 & 0.0 \\
0.0 & 0.0 & 120.0
\end{pmatrix}
\]

This also corresponds to an average dielectric constant, \(\epsilon_0^\alpha = \frac{1}{3} \left(\epsilon_{xx}^0 + \epsilon_{yy}^0 + \epsilon_{zz}^0\right) = 150\) which is the quantity that one would measure in an ideal ceramic sample with randomly oriented grains.
First we notice that the dielectric constant of CaMnO₃ is particularly large, especially along the x direction, and takes values comparable to those previously reported for the orthorhombic phase of CaTiO₃ [16]. In the latter case, the large dielectric constant was associated with the ‘incipient ferroelectric’ character of the compound. The present result suggests that the same type of behavior might be true in CaMnO₃. Second, the static dielectric tensor does not only take large dielectric constant (\(\epsilon_{xx} = 262\)) originates essentially in the contribution of the lowest \(B_{3u}\) mode at 101 cm\(^{-1}\) (238), which combines giant mode effective charge and oscillator strength and a low frequency. Along the z direction, there are still highly polar modes (\(B_{1u}\)) with giant mode effective charge but at higher frequencies so that the static dielectric constant is smaller. Along the y direction, the most polar mode (\(B_{2g}\)) is at a still larger frequency. So, although, the distortion from the cubic phase is small and the material remains optically rather isotropic, the small distortions are enough to produce strong anisotropy of the dynamical properties.

6. Conclusion

The structural, dielectric and dynamical properties of the antiferromagnetic orthorhombic phase of CaMnO₃ have been studied from first principles. The relaxed structure is in good agreement with experimental data. As within the cubic phase, the Born effective charges of Mn and O are highly anomalous. The whole set of zone-center phonon modes has been computed and a new assignment of experimental data has been proposed. The static dielectric tensor has also been obtained; it shows amplitudes comparable to CaTiO₃ and is also highly anisotropic. Inspections of the phonon frequencies and of the static dielectric tensor both emphasize that, although from the structural and optical points of view the orthorhombic phase can be considered as a pseudocubic structure, from the dynamical point of view, it is highly anisotropic.

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