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# First-principles study of dynamical and dielectric properties of tetragonal zirconia

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Using the variational density-functional perturbation theory, we investigate the dynamical and dielectric properties of tetragonal zirconia ($t$-ZrO$_2$). We obtain the phonon frequencies at the center of the Brillouin zone, the Born effective charge tensors, and the dielectric permittivity tensors. For all these quantities, a comparison is made with the related values in the cubic phase. The Born effective charge tensors are found to be quite anisotropic. The calculated phonon frequencies present a better agreement with the infrared and Raman experimental values than previous theoretical calculations. We propose symmetry assignments that solve the contradictions existing in the literature. The electronic and static dielectric permittivity constants are in relatively good agreement with experimental values. We perform a detailed analysis of the contribution of the various infrared-active modes to the static dielectric permittivity and explain its strong anisotropy.

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## I. INTRODUCTION

Zirconia ($ZrO_2$) is considered nowadays one of the most important ceramic materials.[1] It can be used in a wide range of industrial applications including catalysis, coatings, paint additives, and oxygen sensors.[2]

Recently, $ZrO_2$ has attracted a lot of attention in the framework of the quest for an alternative high-permittivity (high-$\epsilon$) material to conventional $SiO_2$ as the gate dielectric in metal-oxide-semiconductor (MOS) devices.[3–5] Indeed, the metal oxide $ZrO_2$ as well as its silicates in the form of amorphous films is stable in direct contact with Si up to high temperature, which is highly desirable to avoid the degradation of the interface properties by formation of a low-$\epsilon$ interfacial layer.

Zirconia undergoes polymorphic transformations with changes in external parameters. At high temperature, the compound is highly defective and its structure is fluorite type ($Fm\overline{3}m$). The decreasing temperature induces a cubic to tetragonal ($P4_2/nmc$) phase transition ($c$-$t$) at about 2350°C (Ref. 6). This transition is followed by a tetragonal to monoclinic ($P2_1/c$) martensitic phase transition ($t$-$m$) at about 1150°C (Ref. 7). The $ZrO_2$ structure may also depend on the presence of dopants (MgO, CaO, $Y_2O_3$). For instance, an addition of 3% (wt) $Y_2O_3$ stabilizes the tetragonal form at room temperature.[8] Finally, the contribution of the surface energy also influences the structural stability of nanocrystallites. A crystallite of 30 nm or less is now believed to stabilize the tetragonal form at room temperature.[9]

Recent research on the understanding of the mechanisms involved in the cubic-tetragonal-monoclinic structural transitions suggested that they result from two successive condensations of Brillouin zone (BZ) boundary phonons.[10,11] One of the triply degenerate $X_2^-$ phonons in the cubic phase transforms into a zone center $A_{1g}$ phonon in the tetragonal form. The other two $X_2^-$ phonons take up a position at the $M$ point of the tetragonal BZ. Their condensation is responsible for the tetragonal to monoclinic transition. A calculation based on a quasiharmonic lattice-dynamical model confirms the exclusively soft-mode mechanism of the lattice transformation of zirconia.[12,13] Some problems remain, however. The presence of a totally symmetric soft mode in the Raman spectra of the tetragonal phase has not been confirmed. Also, the symmetry attributions of the vibration modes of the tetragonal phase that have been given so far in the literature are in contradiction with one another.[13–15]

The main problem encountered in the experimental determination of the dynamical and dielectric properties of tetragonal zirconia is that good-quality single crystals are not available. Undoped powders stabilized by their small particle size must then be used, the results being analyzed in the framework of effective medium theory.[16] Though the latter has proved successful in determining the dielectric properties of small powder particles, some assumptions must be made. Moreover, this analysis does not make it possible to elucidate the symmetry of the resulting modes. Therefore theoretical calculations are highly desirable.

In this work, we use density-functional perturbation theory to study the dynamical and dielectric properties of tetragonal zirconia. We compute the Born effective charge tensors, the phonon frequencies at the Γ point of the Brillouin zone, and the dielectric permittivity tensors. The Born effective charge tensors are quite anisotropic and larger than the nominal ionic charges. This phenomenon, which has already been observed in various oxides (see Ref. 17 and references therein), is called the "anomalous effective charge." It indicates a mixed covalent-ionic character of the Zr-O bonding. For the phonon frequencies, we find a better agreement with experiments than in previous theoretical calculations. Our symmetry assignments clarify some important issues discussed in the literature and solve the existing contradictions. The relationship between the phonon modes of the cubic and the tetragonal phases is illustrated. The agreement with experiments is also rather good for the electronic and static dielectric permittivity constants. The static dielectric tensor is found to be highly anisotropic, while the electronic dielectric tensor is only slightly anisotropic. The former is decomposed into its electronic component and the individual contributions of the IR-active modes. Two IR-active $E_u$ modes contribute to the static dielectric constant in the plane perpendicular to the tetragonal axis, while only one IR-active $A_{2u}$ mode contributes to it along the tetragonal axis. The lowest $E_u$ modes accounts for more than 80% of the difference between the electronic and static dielectric constants in the direction perpendicular to the $c$ axis. A comparison with the cubic phase previously studied by two of us[18] using the same method and technical details is also presented. The different values assumed by the static dielectric tensor in $t$-ZrO$_2$, both for directions parallel versus perpendicular to the optical axis and in relation with the cubic phase, are discussed in terms of differences in oscillator strengths and frequencies.

This paper is organized as follows. In Sec. II, we discuss the technical details of our calculations. We compare our calculated structural parameters with the experimental ones and those from other theoretical calculations. In Sec. III, we present the calculated Born effective charge tensors. Section IV is dedicated to the phonon frequencies at the $\Gamma$ point of the Brillouin zone, while Sec. V deals with the dielectric permittivity tensors. This section also contains the above-mentioned analysis of the difference between electronic and static dielectric constants. Finally, our results are summarized in Sec. VI.

## II. TECHNICAL DETAILS

Our calculations are performed within the local density approximation (LDA) to density-functional theory,[19,20] as implemented in the ABINIT package.[21] The exchange-correlation energy is evaluated using Perdew-Wang's parametrization[22] of Ceperley-Alder electron-gas data.[23] The all-electron potentials are replaced by extended norm-conserving, highly transferable pseudopotentials,[24] with Zr($4s$,$4p$,$4d$,$5s$) and O($2s$,$2p$) levels treated as valence states. The wave functions are expanded in plane waves up to a kinetic energy cutoff of 30 Ha. The Brillouin zone is sampled by a $4\times4\times4$ Monkhorst-Pack[25] mesh of $k$ points.

Linear response properties such as the Born effective charge tensors or the phonon frequencies are obtained as second-order derivatives of the total energy with respect to an external electric field or to atomic displacements. These second-order derivatives are calculated within a variational approach to density-functional perturbation theory, implemented in the ABINIT package.[21,26–28]

The electronic and structural properties of $t$-ZrO$_2$ have already been studied in detail within a first-principles approach.[29] The tetragonal phase (space group $P4_2/nmc$) is fully characterized by two lattice constants ($a$ and $c$) and the displacement $d_z$ of the oxygen atoms along the tetragonal axis with respect to their ideal cubic positions. The unit cell contains two formula units of ZrO$_2$. In Table I, our calculated structural parameters for $t$-ZrO$_2$ are compared with those of Ref. 29 and with the experimental values.[7] The agreement between the three sets of data is very good.

TABLE I. Calculated structural parameters of $t$-ZrO$_2$ compared to experimental values (Ref. 7). The length unit is the angstrom. The displacement $d_z$ of the oxygen atoms along the $z$ axis is expressed in units of $c$ with respect to the ideal cubic positions.

| | Theory | | Experiment |
|---|---|---|---|
| | This work | From Ref. 29 | |
| $a$ | 5.02 | 5.04 | 5.05 |
| $c$ | 5.09 | 5.11 | 5.18 |
| Volume | 32.07 | 32.50 | 33.04 |
| $d_z$ | 0.0400 | 0.0423 | 0.0574 |

## III. BORN EFFECTIVE CHARGE TENSORS

We first compute the Born effective charge tensors ($Z^*_{ij,\tau}$). They are defined as the force in the direction $i$ on the atom $\tau$ due to an homogeneous unitary electric field along the direction $j$ or, equivalently, as the induced polarization of the solid along the direction $i$ by a unit displacement in the direction $j$ of the sublattice generated by atom $\tau$. The Born effective charge tensors govern, with the electronic permittivity tensor $\epsilon_\infty$, the strength of Coulomb interaction responsible of the splitting between the longitudinal (LO) and transverse (TO) optic modes.

Due to the symmetry of the $t$-ZrO$_2$ structure, the Born effective charge tensor of Zr atoms is diagonal and has only two independent components: along and perpendicular to the $c$ axis, $Z^*_\parallel=5.15$ and $Z^*_\perp=5.74$, respectively. This latter value is identical to the one calculated for cubic zirconia,[18] while $Z^*_\parallel$ is 10% smaller. We note that $Z^*$ is anomalously large for the Zr atom compared to the nominal ionic charge $Z=4$. This behavior has also been observed in the case of PbZrO$_3$ (Ref. 30), of $c$-ZrO$_2$ (Ref. 18), or of ZrSiO$_4$ (Ref. 31); it indicates a mixed covalent-ionic bonding. The Born effective charge tensor of O atoms is also diagonal, but with three independent components[32] $Z^*_{11}=-3.52$, $Z^*_{22}=-2.49$, and $Z^*_{33}=-2.57$. It is quite anisotropic: for comparison, in cubic zirconia, the charge tensor is isotropic and $Z^*=-2.87$ (Ref. 18). Such a strong anisotropy of the Born effective charge tensor for O atoms has already been observed in SiO$_2$-stishovite (Ref. 33), TiO$_2$-rutile (Ref. 34), and ZrSiO$_4$ (Ref. 31).

## IV. PHONON FREQUENCIES AT THE Γ POINT

We compute the phonon frequencies at the $\Gamma$ point of the Brillouin zone. Group theoretical analysis predicts the following irreducible representation for optical and acoustical zone center modes:

TABLE II. Fundamental frequencies of tetragonal zirconia in $\mathrm{cm}^{-1}$ with their symmetry assignments. For the Raman modes, the experimental values are taken from Ref. 14 (first column) and Ref. 15 (second column). For the infrared modes, the data come from Ref. 39 (first column) and Ref. 41. Other theoretical results (Refs. 41 and 42) are also given for comparison in the last two columns. The symmetry assignments proposed in all these are given in parentheses when they differ from the present ones.

| Mode | Theoretical results | | | Experimental results | |
|---|---|---|---|---|---|
| Raman | This work | Ref. 41 | Ref. 42 | Ref. 14 | Ref. 15 |
| $A_{1g}$ | 259.1 | 138($B_{1g}$) | 242($B_{1g}$) | 266($E_g$) | 269($E_g$) |
| $B_{1g}$ | 330.5 | 332($A_{1g}$) | 282($A_{1g}$) | 326 | 319 |
| $B_{1g}$ | 607.0 | 669 | 589 | 616($A_{1g}$) | 602($A_{1g}$) |
| $E_g$ | 146.7 | 149 | 191 | 155($B_{1g}$) | 149 |
| $E_g$ | 473.7 | 578 | 483 | 474 | 461 |
| $E_g$ | 659.2 | 703 | 659 | 645 | 648($B_{1g}$) |
| Infrared | This work | Ref. 41 | Ref. 42 | Ref. 39 | Ref. 41 |
| $A_{2u}$(TO) | 338.5 | 294 | 274 | 320 | 339 |
| $A_{2u}$(LO) | 663.8 | — | — | — | 650($E_u$) |
| $E_u$(TO1) | 152.7 | 135 | 146 | 140 | 164 |
| $E_u$(LO1) | 270.5 | — | — | — | 232 |
| $E_u$(TO2) | 449.4 | 442 | 466 | 550 | 467 |
| $E_u$(LO2) | 734.1 | — | — | — | 734($m$-$ZrO_2$) |
| Silent | | | | | |
| $B_{2u}$ | 673.4 | — | 724 | | |

$$\Gamma=\underbrace{A_{1g}\oplus 2B_{1g}\oplus 3E_g}_{\text{Raman active}}\oplus\underbrace{A_{2u}\oplus 2E_u}_{\text{IR active}}\oplus\underbrace{A_{2u}\oplus E_u}_{\text{Acoustic}}\oplus\underbrace{B_{2u}}_{\text{Silent}}$$

Because of the nonvanishing components of the Born effective charge tensors, the dipole-dipole interaction must be properly included in the calculation of the interatomic force constants.[28,35,36]. In particular, the dipole-dipole contribution is found to be responsible for the splitting between the LO and TO modes $E_u$ (perpendicular to $c$) and $A_{2u}$ (parallel to $c$) at the $\Gamma$ point.

In the Raman experimental spectra, six lines corresponding to the six Raman-active modes have been observed for pure $t$-$ZrO_2$ at high temperature[14,37] and for samples stabilized by dopants.[14,38–40] In the case of pure $t$-$ZrO_2$, the Raman spectra are found to be very similar except for a slight shift down of the frequencies, which was attributed to the increase in lattice constant with dopant concentration and to temperature effects.[14] In the absence of $t$-$ZrO_2$ single crystals of good quality, a reliable assignment of those line could not be made. However, the symmetry classification proposed by Feinberg and Perry[14] is widely used in the literature. It is reported in Table II, together with the measured phonon frequencies for their yttria-stabilized $t$-$ZrO_2$ sample. Theoretical studies have been performed using lattice-dynamical models[13,41,42] predicting phonon frequencies in relatively good agreement with the experimental values (see Table II). The symmetry assignment given in Ref. 14 was criticized by these authors, who proposed a second assignment, which is also indicated in Table II. In particular, it was argued that the $A_{1g}$ mode must be at lower frequency to account for the change in the dynamical properties of $ZrO_2$.[13,42] More recently, using crystallite size effects to stabilize the tetragonal phase, the experimental Raman spectra of pure $t$-$ZrO_2$ could be obtained at room temperature.[15] A third assignment of the vibration modes was also proposed after a theoretical calculation using a linear chain model: compared to Ref. 14, it consists in an interchange of the $B_{1g}$ mode and the highest $E_g$ mode (see Table II).

As for the IR spectra, experiments have been carried out on crystals,[43] doped powders,[14,39,44] and undoped powders stabilized by their small particle size.[41] But in the absence of $t$-$ZrO_2$ single crystals of good quality, a general agreement has not been reached so far. The two most recent studies,[39,41] which have been reported in Table II, agree to assign the $E_u$ TO modes at about 150 and 500 $\mathrm{cm}^{-1}$. These assignments where also confirmed by calculations.[13,41,42] However, the situation is more confused for the $A_{2u}$ mode. To properly fit their reflectance spectra, Pecharromán *et al.*[41] had to introduce three oscillators besides the two $E_u$ modes. They placed the $A_{2u}$ at 339 $\mathrm{cm}^{-1}$ and attributed the extra modes at 580 and 672 $\mathrm{cm}^{-1}$ to a secondary oscillator and to the presence of monoclinic zirconia, respectively. Hirata *et al.*[39] also mentioned a broadband located at 320 $\mathrm{cm}^{-1}$, but they attributed it to a $B_u$ mode associated with traces of monoclinic phase.

Our calculated phonon frequencies and symmetry assignments are reported in Table II and compared with those of various experimental works and with previous theoretical studies. For the phonon frequencies, our results are globally in better agreement with experimental data than those of previous works. Our symmetry assignments meet all the requirements discussed in the literature, solving the existing contradictions and clarifying some important issues.

For the Raman spectra, our calculation presents a rms absolute deviation of 8.4-9.6 $\mathrm{cm}^{-1}$ and a rms relative

TABLE III. Relationship of phonon modes for cubic and tetragonal phases. The calculated frequencies are given in cm$^{-1}$. For the infrared modes, only the TO frequencies are reported.

| | Cubic | | | | Tetragonal | |
|---|---|---|---|---|---|---|
| | $\Gamma$ | | $X$ | | $\Gamma$ | |
| Acoustic | $F_{1u}$ | 0.0 | | | $A_{2u}$ | 0.0 |
| | | | | | $E_u$ | 0.0 |
| | | | $X_4^-$ | 361.3 | $B_{1g}$ | 330.5 |
| | | | $X_5^-$ | 141.2 | $E_g$ | 146.7 |
| Optic | $F_{2g}$ | 587.0 | | | $B_{1g}$ | 607.0 |
| | | | | | $E_g$ | 659.2 |
| | | | $X_2^-$ | $190.5i$ | $A_{1g}$ | 259.1 |
| | | | $X_5^-$ | 567.8 | $E_g$ | 473.7 |
| | $F_{1u}$ | 269.4 | | | $A_{2u}$ | 338.5 |
| | | | | | $E_u$ | 152.7 |
| | | | $X_1^+$ | 697.1 | $B_{2u}$ | 673.4 |
| | | | $X_5^+$ | 325.4 | $E_u$ | 479.4 |

deviation of 2.7–2.6% with respect to the experimental data of Refs. 14 and 15. For comparison, the corresponding rms absolute (relative) deviations are 74.4–79.9 cm$^{-1}$ (22.1–23.1%) and 28.3–27.8 cm$^{-1}$ (11.8–13.3%) for the calculations of Refs. 41 and 42, respectively. Our symmetry assignments reconcile the arguments developed in Refs. 13,42 with those proposed in Ref. 15. On the one hand, the $A_{1g}$ mode is at lower frequency compared to the assignments by Feinberg and Perry, in agreement with Refs. 13 and 42. On the other hand, the $B_{1g}$ is found to have high frequency in accordance with Ref. 15.

For the IR-active frequencies, our calculation presents a rms absolute deviation of 18.8 and 59.5 cm$^{-1}$ and a rms relative deviation of 7.6% and 12.3% with respect to the experimental data of Refs. 41 and 39, respectively. Whereas the corresponding rms absolute (relative) deviations are 34.1 and 64.2 cm$^{-1}$ (13.1% and 12.4%) and 38.9 and 55.4 cm$^{-1}$ (12.8% and 12.4%) for the semiempirical calculations of Refs. 41 and 42, respectively. We find a LO-TO splitting for the $A_{2u}$ mode of 325 cm$^{-1}$ that is much larger than the 15 cm$^{-1}$ found in Ref. 41. Our result is consistent with the large difference between $\epsilon_\infty$ and $\epsilon_0$ as discussed in the next section. As a result, we propose that the LO peaks at 650 and 734 cm$^{-1}$ should be attributed to the $A_{2u}$ and the second $E_u$ modes.

TABLE IV. Dielectric tensors of tetragonal and cubic zirconia. For $t$-ZrO$_2$, the tensors are diagonal and have different components parallel ($\parallel$) and perpendicular ($\perp$) to the $c$ axis. The average values of the dielectric constants, calculated as in Eq. (1), are also reported. For $c$-ZrO$_2$, the tensors are diagonal with a unique component. The contributions of the different phonon modes [$\Delta\epsilon_m$ defined by Eq. (2)] to the static dielectric tensor are also indicated. For $t$-ZrO$_2$, the phonon mode contribution to $\epsilon_0^\parallel$ ($m=1$) comes from the IR-active $A_{2u}$ mode, while the contributions to $\epsilon_0^\perp(m=1,2)$ come from the two IR-active $E_u$ modes. For $c$-ZrO$_2$, the phonon mode contribution ($m=1$) comes from the IR-active $F_{1u}$ mode.

| | $\parallel$ | $\perp$ | Average | Cubic |
|---|---|---|---|---|
| $\epsilon_\infty$ | 5.28 | 5.74 | 5.59 | 5.75 |
| $\Delta\epsilon_1$ | 15.03 | 35.45 | | 29.77 |
| $\Delta\epsilon_2$ | | 6.91 | | |
| $\epsilon_0$ | 20.31 | 48.10 | 38.84 | 35.52 |

In Table III, we have reported the relationship between the phonon modes of the cubic[18] and tetragonal phases. Cubic zone-boundary ($X$ point) modes become zone-center ($\Gamma$ point) modes in the tetragonal structure. Note in particular that the unstable $X_2^-$ zone-boundary mode in the cubic phase transforms into a stable zone-center $A_{1g}$ phonon in the tetragonal form.

## V. DIELECTRIC PERMITTIVITY TENSORS

In this section, we present the electronic ($\epsilon_\infty$) and static ($\epsilon_0$) permittivity tensors. Due to the symmetry of the $t$-ZrO$_2$ crystal, these have two independent components $\epsilon_\parallel$ and $\epsilon_\perp$ along and perpendicular to the $c$ axis, respectively. In Table IV, the calculated values of $\epsilon_\infty$ and $\epsilon_0$ are compared to those in $c$-ZrO$_2$ (Ref. 18), where the permittivity tensors are isotropic. In the tetragonal phase, the $\epsilon_\infty$ tensor is only slightly anisotropic with about 10% difference between the parallel and perpendicular values. On the contrary, the $\epsilon_0$ tensor is highly anisotropic: the value of $\epsilon_0$ parallel to the $c$ axis is more than twice smaller than the perpendicular value. While the values of $\epsilon_\infty$ for the cubic and tetragonal phases are very close, there is a huge difference in the values of $\epsilon_0$.

Again, the main problem encountered in the experimental determination of the dielectric properties of tetragonal zirconia is that good-quality single crystals are not available. The results obtained for undoped powders stabilized by their small particle size must be analyzed in the framework of effective medium theory.[16] As a result, a unique value of $\epsilon$ is found without distinction between the directions parallel and perpendicular to the $c$ axis. In order to compare our results with experimental data, we average the values parallel and perpendicular to the $c$ axis:

$$\overline{\epsilon}=\frac{2\epsilon_\perp+\epsilon_\parallel}{3}. \tag{1}$$

This average does not really have any physical meaning, and therefore the comparison is rather qualitative.

The values of $\epsilon_\infty$ reported in the literature for $t$-ZrO$_2$ range from 4.2 (Ref. 41) to 4.9 (Ref. 45). They are basically the same as those found for $c$-ZrO$_2$ (Refs. 43 and 46). Our theoretical values ($\overline{\epsilon_\infty}=5.59$ and $\epsilon_\infty=5.75$ for the tetragonal and cubic phases, respectively) are larger than the experimental ones by about 10–15%, as often found in the LDA to the density-functional theory. For $\epsilon_0$, the values found in the literature vary from 34.5 (Ref. 47) to 39.8 (Ref. 48) for $t$-ZrO$_2$ and from 27.2 (Ref. 47) to 29.3 (Ref. 48) for $c$-ZrO$_2$. For the tetragonal phase, our calculated average $\overline{\epsilon_0}=38.84$ falls right in the range of the experimental data, whereas for the cubic phase our calculated value $\epsilon_0=35.52$ is much larger than experimental estimates. Actually, we find that this

TABLE V. Oscillator strength tensor $S_m$ (in $10^{-4}$ atomic units), magnitude of mode-effective charge vectors $Z_m^*$, LO frequencies $\omega_m$, frozen-eigenvector LO frequencies $\omega_m^{(1)}$, LO-TO splitting $\Delta\omega$, and frozen-eigenvector LO-TO splitting $\Delta\omega_m^{(1)}$ (in $\mathrm{cm}^{-1}$), for each of the IR-active modes in the tetragonal (upper part) and the cubic (lower part) phases. See the text for the description of vector or tensor structure corresponding to the two types of modes.

| | $S_m$ | $Z_m^*$ | $\omega_m$ | $\omega_m^{(1)}$ | $\Delta\omega_m$ | $\Delta\omega_m^{(1)}$ |
|---|---|---|---|---|---|---|
| $A_{2u}$ | 12.28 | 8.14 | 663.8 | 663.9 | 325.3 | 325.4 |
| $E_u(1)$ | 5.91 | 5.95 | 270.5 | 409.6 | 117.6 | 256.7 |
| $E_u(2)$ | 9.95 | 6.98 | 734.1 | 667.0 | 284.8 | 217.7 |
| $F_u$ | 7.63 | 6.42 | 669.5 | 670.8 | 400.1 | 401.4 |

value is comparable with the calculated average value in the tetragonal phase.

For a deeper analysis of the static dielectric tensor, we can rely not only on the frequencies of the IR-active modes, but also on the corresponding eigendisplacements and Born effective charges. Indeed, the static dielectric tensor can be decomposed in the contributions of different modes as follows (see Refs. 28 and 49):

$$\epsilon^0_{\alpha\beta}(\omega)=\epsilon^\infty_{\alpha\beta}+\sum_m \Delta\epsilon_{m,\alpha\beta}=\epsilon^\infty_{\alpha\beta}+\frac{4\pi}{\Omega_0}\sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2}, \quad (2)$$

where $\Omega_0$ is the volume of the primitive unit cell. $S_{m,\alpha\beta}$ is the mode-oscillator strength.

The contributions of the individual modes $\Delta\epsilon_m$ to the static dielectric constant are presented in Table IV. For each IR-active mode, the relevant components of the oscillator strength tensor (the parallel-parallel component for $A_{2u}$ mode and the perpendicular-perpendicular component for $E_u$ modes) are reported in Table V. We also present the magnitude of the mode-effective charge vector[28] which is parallel and perpendicular to the tetragonal axis for the $A_{2u}$ and $E_u$ modes, respectively. The atomic movement for these vibrational modes has been described in detail in Refs. 10, 11, and 41.

In Table V, the $E_u(1)$ mode has the lowest oscillator strength ($S_m$) and the lowest mode-effective charge ($Z_m^*$). However, it has the lowest frequency (see Table II) which results in the largest contribution to the static dielectric constant in Table IV. Comparatively, the $E_u(2)$ mode gives a much smaller (but not negligible) contribution despite its larger oscillator strength and mode-effective charge. In fact, the frequency factor plays a crucial role in Eq. (2). The $A_{2u}$ has the largest oscillator strength [about twice that of the $E_u(1)$ mode] and the largest mode-effective charge. However, its frequency is about twice larger than that of the $E_u(1)$ mode, its contribution to the static dielectric constant being roughly twice smaller than that of the $E_u(1)$ mode. This difference between the $A_{2u}$ and $E_u$ modes explains why the $\epsilon_0$ tensor is highly anisotropic while the $\epsilon_\infty$ tensor is only slightly anisotropic. The same argument holds to rationalize the difference in the static dielectric tensor with respect to the cubic phase. Indeed, in this latter case, the oscillator strength and the mode-effective charge of the $F_u$ mode are comparable to those of the $E_u$ modes of the tetragonal phase while the frequency of the $F_u$ mode is 1.7 times larger than that of the $E_u(1)$ mode (see Table III). As a result, the static dielectric constant is noticeably smaller in the cubic case.

From the mode-oscillator strength $S_{m,\alpha\beta}$, it is also possible to gain insight into the mixing of the eigenvectors of the dynamical matrix when going from TO to LO modes. In general, the eigenvectors of the dynamical matrix for $\mathbf{q}\rightarrow 0$ will not be identical to those for $\mathbf{q}=0$. Sometimes, symmetry constraints will be sufficient to guarantee that some of the eigendisplacements are identical, even if the eigenfrequencies are different. In this case, we have the following relationship that links LO and TO frequencies along the wave vector $q_\alpha$ [see Eq. (62) of Ref. 28]:

$$\Delta\omega_m=\left(\omega_m^2(\mathrm{TO})+\frac{4\pi}{\Omega_0}\frac{\sum_{\alpha\beta} q_\alpha S_{m,\alpha\beta}q_\beta}{\sum_{\alpha\beta} q_\alpha\epsilon^\infty_{\alpha\beta}q_\beta}\right)^{1/2}-\omega_m(\mathrm{TO}). \quad (3)$$

More generally, this equation can be seen as the first-order approximation for the LO-TO splitting $\Delta\omega_m^{(1)}$. The calculated values are presented in Table V, together with the full LO-TO splittings $\Delta\omega_m$ derived from Table II. The differences between $\Delta\omega_m^{(1)}$ and $\Delta\omega_m$ indicate the occurrence of eigenvector modifications. For the $A_{2u}$ mode, there is almost a perfect agreement, showing that there is practically no mixing of the eigenvectors when going from the TO to the LO case: the LO and TO modes overlap almost perfectly. A similar behavior is also observed for the $F_u$ mode in the cubic phase. By contrast, the two $E_u$ modes in the tetragonal phase are strongly hybridized when going from the TO to LO case.

## VI. CONCLUSION

Using density-functional perturbation theory, we have investigated the dynamical and dielectric properties of tetragonal zirconia. We have computed the linear-response functions: the Born effective charge tensors, the phonon frequencies at the $\Gamma$ point of the Brillouin zone, and the dielectric permittivity tensors. An important anisotropy was observed in the Born effective charge tensors. These effective charges are found to be larger than the nominal ionic charge, indicating a mixed covalent-ionic bonding between Zr and O. Our calculated phonon frequencies are globally in better agreement with experiments than previous theoretical calculations, although the present results are obtained without any adjustable parameter. We have proposed new symmetry assignments that meet all the arguments discussed in the literature. Our assignments solve the apparent contradictions of previous works, clarifying some important issues. We have also illustrated the relationship between the phonon modes of the cubic and the tetragonal phases. The electronic and static dielectric permittivity constants have been computed and found to be in rather good agreement with experiment. A detailed analysis of the contribution of the different vibrational modes to the static dielectric constant has been performed, including the computation of mode-effective charges and oscillator strengths. For the direction perpendicular to the tetragonal axis, we have observed that the lowest $E_u$ mode contributes to more than 80% of the ionic contribution. A detailed comparison with the cubic phase has also been proposed. Our analysis reveals that the different values of the static dielectric tensor in tetragonal and cubic zirconia can be understood in terms of the frequencies of the relevant modes.

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