First-principles prediction of oxygen octahedral rotations in perovskite-structure EuTiO$_3$

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We present a systematic first-principles study of the structural and vibrational properties of perovskite-structure EuTiO$_3$. Our calculated phonon spectrum of the high symmetry cubic structural prototype shows strong M- and R-point instabilities, indicating a tendency to symmetry-lowering structural deformations composed of rotations and tilts of the oxygen octahedra. Subsequent explicit study of 14 different octahedral tilt-patterns showed that the $I4/mcm$, $Imma$ and $R3c$ structures, all with antiferrodistortive rotations of the octahedra, have significantly lower total energy than the prototype $Pn3m$ structure. We discuss the dynamical stability of these structures, and the influence of the antiferrodistortive structural distortions on the vibrational, optical and magnetic properties of EuTiO$_3$, in the context of recent unexplained experimental observations.

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I. INTRODUCTION

Europium titanate, EuTiO$_3$, was the first ternary compound of divalent Eu$^{2+}$ to be identified. It is a G-type antiferromagnet (AFM) with the low magnetic ordering temperature of 5.3 K, consistent with the highly localized 4f electrons on the Eu$^{2+}$ ions. Until recently, its structural ground state was thought to be the ideal cubic perovskite structure, with $Pm3m$ symmetry. EuTiO$_3$ is insulating with a high dielectric constant ($\sim 400$) at low temperature, indicating quantum paraelastic behavior and proximity to ferroelectric instability. Strong interactions between the magnetic and dielectric properties have been reported including evidence for an unusual third-order coupling. It has been suggested that EuTiO$_3$ is the prototype for studying quantum paraelastic behavior in magnetic systems.

In addition to these experiments on bulk EuTiO$_3$, there has been a series of recent studies on EuTiO$_3$ thin films. Motivated in part by the subsequently verified prediction that epitaxial strain should induce ferroelectricity and multiferroicity. Likewise "chemical strain", i.e. doping at the A-site with larger divalent ions, has been shown to induce ferroelectricity, e.g. in alloys with BaTiO$_3$. The latter is particularly intriguing, as multiferroic (Eu,Ba)TiO$_3$ ceramics fulfill the requirements for a solid state search for the electric dipole moment of electron.

In this work we re-visit bulk EuTiO$_3$, with a particular focus on the possibility that the ground state is not, in fact, the high symmetry $Pm3m$ perovskite prototype, but a lower symmetry structure possessing rotations or tilts of the oxygen octahedra. Until recently, all computational studies of EuTiO$_3$ had neglected this possibility. We mentioned recently in Ref. 17 that in the course of calculating the properties of (Eu,Ba)TiO$_3$ we noticed a calculated antiferrodistorted ground state for EuTiO$_3$. Then in Ref. 17 the influence of such possible oxygen octahedra tilts on the induced polarization in strained EuTiO$_3$ was discussed. Finally, a recent study confirmed experimentally the presence of a structural phase transition in EuTiO$_3$ using specific heat measurements, and suggested, in analogy to SrTiO$_3$, that the low-temperature phase should have oxygen rotations and $I4/mcm$ symmetry.

Our present ab initio study of EuTiO$_3$ was motivated by a series of experimental papers in which infrared (IR) reflectivity and time-domain terahertz transmission spectra of EuTiO$_3$ ceramics yielded intriguing results that can be better understood if the crystalline symmetry is lower then $Pn3m$. The studies found three polar optical phonons between 6 – 600 K, typical for the perovskite structure. Analysis of the oscillator strengths (or equivalently, the mode-plasma frequencies) and comparison of their values with those of known perovskite prototypes such as PbTiO$_3$ (with ferroelectrically active A- and B-site cations) and BaTiO$_3$ (with active B-site cations) suggested that (i) The lowest-energy transverse-optical (TO) phonon TO1 corresponds predominantly to the Slater mode with opposite vibration of the Ti cations and the oxygen octahedra (Fig. 1 left); softening of this mode dominates the quantum paraelectric behavior, (ii) The second lowest-energy TO2 phonon consists of vibrations of the Eu cation against the TiO$_6$ octahedra, commonly known as the Last mode, and (iii) The highest frequency TO4 (the TO3 mode is not IR active) phonon represents oxygen octahedral bending, usually called an Axe mode (Fig. 1 right).

However, some features observed in the experiment are not understood: (i) A significant temperature dependence of the oscillator strength was found for the TO1 and TO2 modes, indicating changes in the vibrational mode eigenvectors with temperature. The changes are most apparent in the temperature range 250 – 400 K (see...
Figure 5 in Ref. [24], with the oscillator strength for the TO1 mode decreasing and for the TO2 mode increasing with increasing temperature. (ii) The width of the peak in the imaginary dielectric function $\epsilon''$ that is associated with the soft TO1 mode increases when temperature is lowered. This is unusual, because at low temperature anharmonic effects that could give rise to the widening of the peak in $\epsilon''$ usually decrease (see Figure 3(b) in Ref. [24]). (iii) The mode at around 420 cm$^{-1}$ in the IR reflectivity spectrum is temperature dependent (see Figure 2 in Ref. [23]). However the Eu$_2$Ti$_2$O$_7$ pyrochlore phase, to which this peak was tentatively assigned, does not show a structural phase transition.

In this work we present a detailed density-functional theory based study of the structural and vibrational properties of antiferromagnetic EuTiO$_3$. Our main finding is that the ground state is not in fact the high symmetry $Pm\overline{3}m$ structure (in analogy with other perovskite materials, for example KNbO$_3$[29]), but a lower symmetry phase with tilts and rotations of the oxygen octahedra. The calculated properties of the lower symmetry phase are more consistent with the measured behavior than those calculated for the high symmetry $Pm\overline{3}m$ structure. In addition, we obtain a strong magneto-phonon interaction in our new ground-state structure. The remainder of this paper is organized as follows: In Section II we describe the technical details of our calculations; Section III contains the results of our calculations of the structural and dynamical properties of EuTiO$_3$, and a new interpretation of the IR optical properties along with the influence of magnetic fields. We conclude in Section IV.

II. CALCULATION DETAILS

We carried out first-principles density-functional calculations within the spin-polarized generalized gradient approximation (GGA)[30]. For the electronic structure calculations and structural relaxations we used projector augmented-wave potentials as implemented in Vienne $Ab$ initio Simulation Package (VASP)[25, 26]. We considered the following valence-electron configuration: 5s$^2$5p$^6$4f$^7$6s$^2$ for Eu, 3s$^2$3p$^6$3d$^2$4s$^2$ for Ti, and 2s$^2$2p$^4$ for oxygen.

To account for the strong electron correlation effects on the f-shells of Eu atoms, we used the DFT+U scheme[31] in Dudarev’s approach[32] with an on-site Coulomb parameter $U=5.7$ eV and Hund’s exchange $J_H=1.0$ eV after Ref. [17]. We have checked our main conclusions (i.e. the stability of the antiferrodistorted phases relative to the cubic phase) for several values of these parameters ($U=4$ to $8\ units$) as well as without the LDA+U correction and obtained the same result. We used a kinetic energy cutoff of 500 eV and a $6 \times 6 \times 6$ $(4 \times 4 \times 4)$ Γ-centered $k$-point mesh for the unit cell (supercell) simulations. Spin-orbit interaction was not taken into account. The experimental lattice parameter of the cubic phase of EuTiO$_3$, 3.90 Å[33, 34] was used instead of the theoretical value of 3.943 Å. For structural relaxations which involved changes of the unit cell shape we performed a fixed-volume relaxation to suppress the known GGA overestimation of the lattice volume. In the structural relaxations we minimized Hellman-Feynman forces to 0.5 meV/Å. To investigate the structural stability, we utilized $2 \times 2 \times 2$ supercells containing 40 atoms. This allowed us to investigate all possible structural distortions which can originate from the zone-boundary instabilities in a systematic way and to minimize the error in total energy calculations when comparing energies of the different structures. For each symmetry investigated, the initial ideal perovskite structure was distorted according to the corresponding oxygen octahedral rotation pattern, and then the internal atomic positions and lattice parameters were relaxed until the convergence criteria were reached.

The calculations of the dynamical properties were performed using the force-constant method[34, 35] To investigate possible dynamical instabilities we used a $2 \times 2 \times 2$ supercell of the primitive 5-atom EuTiO$_3$ unit cell; this supercell size allows most common oxygen octahedra tilting and rotational patterns, as well as the likely commensurate AFM magnetic orders. The Hellman-Feynman forces were calculated for displacements of atoms of up to 0.04 Å. The dynamical matrix for each $q$-point in the Brillouin zone was constructed by Fourier transforming the force constants calculated at the Γ-point and the Brillouin zone boundaries. Phonon-mode frequencies and atomic displacement patterns for each $q$-point were obtained as eigenvalues and eigenvectors of the dynamical matrices. Born effective charges for symmetry-inequivalent ions in the simulation cell[36, 37] were calculated with the Berry-phase technique[38].

III. RESULTS AND DISCUSSION

A. Properties of the high-symmetry $Pm\overline{3}m$ structure

In the following we show that assuming $Pm\overline{3}m$ is the ground state structure leads to discrepancies with existing experiments in the nature of the long-wavelength phonon modes and in the mode-plasma frequencies. Because of the notorious uncertainty in DFT lattice constants we investigate whether these discrepancies can be removed by varying the unit cell volume. We find that a partial agreement (in the mode-plasma frequencies) can be reached, but only if the lattice parameter is increased to unphysical values at which the lattice is unstable with respect to the polar displacements. Furthermore, our analysis of the full phonon spectrum of $Pm\overline{3}m$ structure indicates strong antiferrodistortive instabilities.

First, we calculated the zone-center phonon frequencies and eigenvectors in cubic EuTiO$_3$ (see Table III) and obtained results consistent with other recent calculations[16]. As we mentioned above, in Ref. [24] it was suggested that
TO2 for two lattice parameters of cubic EuTiO
of the soft polar mode TO1 and second energy polar mode
Table I. . Slater, Last, and Axe mode decomposition (in %)
of the oxygen cage results.

![Image](https://example.com/image)

Table I. . Slater, Last, and Axe mode decomposition (in %)
of the soft polar mode TO1 and second energy polar mode
TO2 for two lattice parameters of cubic EuTiO3 perovskites.

| Mode  | ω, cm⁻¹ | Slater | Last | Axe |
|-------|---------|--------|------|-----|
| TO1   | 60      | 60     | 37   | 3   |
| TO2   | 153     | 61     | 38   | 1   |

Cell parameter a = 3.90 Å:

| Cell parameter a = 3.95 Å: |
| TO1   | 96i     | 88     | 12   |
| TO2   | 123     | 27     | 72   |

We used the Born effective charges of 2.63|e| for Eu, 7.46|e| for Ti, -2.18|e| for O_⊥ and -5.74|e| for O_∥ which we calculated at the experimental lattice constant of 3.90 Å in our calculation of the mode-plasma frequencies.

Interestingly, our calculated mode-plasma frequencies (Table II) match well with the experimental values in the high temperature (300 – 600 K) range, but are markedly different from the low temperature experimental values (see Figure 5 of Ref. 24). Since our DFT calculations do not include thermal effects, particularly the strong hardening of the soft mode found with increasing temperature in EuTiO_3, we expect them instead to match the low temperature values. As we saw earlier, the soft mode eigenvectors show significant volume dependence. Therefore, to check whether the discrepancy lies in our choice of unit cell volume, we investigated the volume dependence of the key quantities entering Eqn. 1. We found that the Born effective charges are largely insensitive to the volume: for values of the lattice constant a between 3.8 Å and 4.0 Å the Born effective charges change from 2.68 to 2.61|e| for Eu, from 7.46 to 7.49|e| for Ti, from -2.26 to -2.13|e| for O_⊥, and from -5.69 to -5.83|e| for O_∥. Therefore, the changes in mode-plasma frequencies must be caused by the changes in the mode eigenvectors.

Next, we varied the lattice parameter to see if we could obtain good agreement between the calculated and low temperature experimental values of the MPFs. In fact we found good agreement only by increasing a to 3.95 Å. From Table II we can see that at a = 3.95 Å the TO1 mode is predominantly of Slater-type, while the TO2 mode has Last character. However, the Slater mode becomes imaginary, indicating a polar structural instability not observed experimentally in EuTiO_3 under normal conditions. Moreover, increasing the lattice parameter to 3.95 Å is clearly not a physically reasonable choice – the lattice constant at low temperature (our DFT results correspond to 0 K) should be smaller than that at room or higher temperature because of thermal expansion of the lattice.

Therefore, we conclude that the observed discrepancy between the measured low-temperature MPFs and the
calculated values is not due to an inappropriate choice of the lattice parameter in our calculations. Next we explore further the low-temperature structural properties of EuTiO$_3$ in attempt to explain the discrepancy.

Our calculated phonon spectrum of EuTiO$_3$ in the $Pm\bar{3}m$ phase (Fig. 2) indeed reveals strong structural instabilities at the $R$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and $M$ ($\frac{1}{2}, \frac{1}{2}, 0$) high symmetry points, and along the M-R symmetry line. These instabilities are seen as a modes with imaginary wavenumbers and are similar to those found in calculations for $Pm\bar{3}m$ SrTiO$_3$, which is known experimentally to have the $I4/mcm$ ground state with alternating rotations of the oxygen octahedra around the c axis (Glazer notation$^{11}$ $a^0d^0c^-$. As in the case of SrTiO$_3$, our calculated eigenvectors indicate that these instabilities are non-polar, and arise from the tilting and rotation of the oxygen octahedra. The eigenvector for the M-point instability shows in-phase rotations of the oxygen octahedra around one or more pseudocubic axes, whereas at the R point, octahedra rotate with alternating out-of-phase sense.

B. Search for the structural ground state

Motivated by our finding of rotational instabilities in ideal cubic perovskite EuTiO$_3$, we next search for the structural ground state by comparing the calculated total energies of structures containing different combinations of rotations of the TiO$_6$ octahedra.

As categorized by Howard and Stokes,$^{42}$ condensation of combinations of M- and R-point octahedral rotations in the perovskite structure can yield any of 15 possible symmetry space-groups (including ideal perovskite structure), summarized in Figure 3. The following space group symmetries are allowed: $Pm\bar{3}m$, $I\bar{m}3$, $I4/mmm$, $P4/nmm$, $I4/mcm$, $Imma$, $R\bar{3}c$, $Imma$, $P4_2/mmc$, $C2/mcm$, $Pnma$, $C2/m$, $C2/c$, $P2_1/m$ and $P1$. We calculated the total energies of each of these combinations, fully relaxing the ionic positions within the constraints of the chosen symmetry, and with the unit cell volume set to the experimental value. The shape of the unit cell was allowed to change according to the symmetry constraints.

We found that many of the low symmetry tilt patterns relaxed to higher symmetry structures, as indicated by the arrows in Figure 3. Three structures remained stable – those with $R\bar{3}c$, $Imma$ and $I4/mcm$ space groups. All three are stabilized by around 25 meV per formula unit compared with the prototype $Pm\bar{3}m$ structure. The $I4/mcm$ is lowest in energy ($\sim$27 meV per formula unit lower than $Pm\bar{3}m$), $Imma$ is the second most stable structure ($\sim$26 meV per formula unit lower), then $R\bar{3}c$ at $\sim$25 meV per formula unit lower. G-type antiferromagnetic configuration was found to be of lower energy than the ferromagnetic one in all tilted phases. Importantly, the energy differences between the $I4/mcm$, $Imma$ and $R\bar{3}c$ structures are very small, within $\sim$2 meV per formula unit, which is the range of numerical errors. Therefore, we can not predict which rotation scenario is the ground state of EuTiO$_3$. All three structures have no imaginary phonons through the entire Brillouin zone (see Figure 4) and so are dynamically stable. Note that the $I4/mcm$ structure is obtained by condensing out-of-phase rotations of oxygen octahedra about only one axis (see Figure 4). $Imma$ results from the same out-of-phase rotations about two axes, and $R\bar{3}c$ from out-of-phase ro-
Table II. Experimental and theoretical values of the phonon wavenumbers and mode-plasma frequencies (both quantities in cm\(^{-1}\)) for the crystalline structures of EuTiO\(_3\) with \(Pm\bar{3}m\), \(I4/mcm\) and \(R\bar{3}c\) space groups, with ferromagnetic (FM) and G-type antiferromagnetic (AFM) magnetic ordering on the A-site cations. Mode-plasma frequency values are given in italics. TO1, TO2 and TO4 label the optically active modes in the ideal perovskite structure; these modes are split in the tilted structures.

| No. | Mode | Exp.\(^a\) | \(Pm\bar{3}m\) | \(I4/mcm\) | \(R\bar{3}c\) |
|-----|------|------------|----------------|-------------|-------------|
|     |      | 10 K 400 K | AFM FM        | AFM FM      | AFM FM      |
| 1   | TO1  | 82 1550 125 1250 | 67 1289 60 1327 | 107 1323 101 1394 | 80 1300 72 1353 |
| 2   |      | 128 1607 118 1622 | 124 1500 117 1540 |               |             |
| 3   | TO2  | 153 400 159 860 | 155 925 153 864 | 154 898 153 813 | 153 565 152 452 |
| 4   |      | 156 314 156 239 | 160 984 157 911 |             |             |
| 5   |      | 164 218 |               | 164 147 |             |
| 6   |      | 251 40 251 45 | 242 200 241 188 |             |             |
| 7   |      | 419 250 419 242 | 419 233 419 241 |             |             |
| 8   | TO4  | 539 619 540 625 | 537 824 536 820 | 523 732 522 729 | 514 737 513 732 |
| 9   |      | 531 718 530 715 | 533 733 532 728 |             |             |
| 10  |      | 802 805 | 803 804 |             |             |

\(^a\) Experimental data from Ref. \(^{24}\)

Figure 4. (Color online) Schematic representation of EuTiO\(_3\) in \(I4/mcm\) space group structure with oxygen octahedra tilting. Left – view along the \(z\) direction, where the out-of-phase tilting occurs; right – view along the \(y\) direction without any tilting. The amount of tilting corresponds to the one obtained in calculations. Drawings were produced by VESTA visualisation software\(^{26}\).

To check whether our conclusions on the phase stability are affected by volume, we next investigated the athermal equation of state for the three candidate ground-state phases, as well as for the undistorted one. We found that the \(E(V)\) dependence is adequately described by means of the first-order Murnaghan equation of state\(^{43}\).

\[
E = E_0 + \frac{B_0 V}{B_0'} \left( \frac{V_0}{V} \right)^{B_0'} - \frac{B_0 V_0}{B_0' - 1},
\]

where \(B_0\) is the bulk modulus, \(B_0'\) its pressure derivative, \(V_0\) the equilibrium volume, and \(E_0\) is the energy minimum corresponding to the equilibrium volume. Our calculated parameters for this Eqn., obtained by fitting of \(ab\ initio\) total energies, are listed in Table IV. The equilibrium values for \(V_0\), \(E_0\) and bulk modulus \(B_0\) for tetragonal, orthorhombic and rhombohedral phases are almost the same, however the pressure derivative \(B_0'\) for \(R\bar{3}c\) phase is about 1.5 times lower then for the \(I4/mcm\) phase. This indicates that the internal relaxations in the rhombohedral phase are less sensitive to the volume changes than in the tetragonal phase. Also, the \(R\bar{3}c\) structure is more rigid than the cubic and the tetragonal ones. Measurements of the bulk moduli and their pressure derivatives at different temperatures would be helpful in distinguishing between these lower-symmetry phases.

C. IR optical properties in structures with tilting

Finally, we attempt to distinguish between the three candidate ground state structures by comparing their calculated phonon and mode-plasma frequencies with the measured optical properties. We find that the calculated frequencies of the \(R\bar{3}c\) structure show best agreement with experiment, suggesting it as a likely experimental structure.

Our results are summarized in Tables III and IV as well as in Figure 6. In all cases we used the Born effective charges calculated for the \(Pm\bar{3}m\) reference structure in our evaluation of the mode plasma frequencies, and our reported values do not include the LO-TO split-
Table III. Phonon wavenumbers and mode-plasma frequencies (both quantities in cm\(^{-1}\)) for the orthorhombic \textit{Imma} phase of \(\text{EuTiO}_3\), with ferromagnetic (FM) and antiferromagnetic (AFM) ordering on the A-site cations. Mode-plasma frequency values are given in italics. The meaning of the TO1, TO2 and TO4 labels is the same as in Table II.

| No. | Mode | AFM | FM |
|-----|------|-----|----|
| 1   |      | 36  | 34 |
| 2   |      | 40  | 49 |
| 3   | TO1  | 98  | 1318 | 85 | 1414 |
| 4   |      | 104 | 104 |
| 5   |      | 106 | 105 | 1479 |
| 6   |      | 110 | 107 |
| 7   |      | 110 | 1233 | 112 |
| 8   |      | 131 | 1596 | 119 | 1609 |
| 9   | TO2  | 154 | 822 | 152 | 656 |
| 10  |      | 155 | 201 | 155 | 816 |
| 11  |      | 159 | 945 | 156 | 107 |
| 12  |      | 164 |    |    | 166 |
| 13  |      | 237 | 134 | 235 | 134 |
| 14  |      | 249 |    | 247 |    |
| 15  |      | 283 | 122 | 282 | 76 |
| 16  |      | 413 |    | 412 |    |
| 17  |      | 414 |    | 415 |    |
| 18  |      | 416 | 224 | 418 | 167 |
| 19  |      | 418 | 230 | 422 | 302 |
| 20  |      | 424 |    | 424 |    |
| 21  |      | 436 |    | 434 |    |
| 22  |      | 491 |    | 486 |    |
| 23  |      | 499 |    | 498 |    |
| 24  | TO4  | 516 | 730 | 513 | 716 |
| 25  |      | 523 | 736 | 524 | 743 |
| 26  |      | 537 | 725 | 535 | 707 |
| 27  |      | 801 |    | 802 |    |

Calculations were performed for the G-type AFM ordered phase; the coupling between phonon properties and magnetism is discussed at the end of this section.

First we look at the frequency of the soft TO1 mode (see Table II). Our calculated values are 107 cm\(^{-1}\) and 128 cm\(^{-1}\) for \(\text{I}_{4}/\text{mcm}\) (the symmetry lowering splits the TO1 mode into one doubly degenerate and one singly degenerate \(c\) polarized mode), 80 cm\(^{-1}\) and 124 cm\(^{-1}\) (\(R\bar{3}c\)) and 98 to 131 cm\(^{-1}\) (\(\text{Imma}\)). The experimental value is 82 cm\(^{-1}\), suggesting that the \(R\bar{3}c\) structure is most likely. We note, however, that the soft-mode frequency is very sensitive to the volume of the structure and small changes in choice of volume (GGA versus experimental for example) can strongly change the predicted values. Regarding the mode plasma frequencies of this mode, the experimental value is 1550 cm\(^{-1}\), and the average calculated values for the three structures are 1417 cm\(^{-1}\) (\(\text{I}_{4}/\text{mcm}\)), 1433 cm\(^{-1}\) (\(R\bar{3}c\)) and 1382 cm\(^{-1}\) (\(\text{Imma}\)) all showing comparable agreement with the experimental value. Note that the relatively large mode splittings that we obtain for TO1 modes in the lower symmetry structures could explain the experimentally observed large peak width in
Table IV. Theoretical structural parameters of EuTiO$_3$ for $d^0 d^0 e^-$ (I4/mcm), $d^0 b^- b^-$ (Imma) and $a^- a^- a^- (R3c)$ oxygen octahedral rotation patterns.

| Wyckoff | I4/mcm |   |   |   |
|---------|--------|---|---|---|
| Eu      | 2(b)   | x | y | z |
| Ti      | 2(c)   | 0 | 0.5 | 0.25 |
| O(1)    | 2(a)   | 0 | 0 | 0 |
| O(2)    | 4(h)   | 0.21578 | 0.71578 | 0 |

Cell parameters

| $a$ (Å) | 5.494 |
| $c$ (Å) | 7.861 |

Table V. Calculated Murnaghan equation of state parameters for the I4/mcm, Imma and R3c structures. $V_0$ is the theoretical volume and $a_0 = (V_0)^{1/3}$ is the theoretical pseudo-cubic lattice constant.

| Wyckoff | Pm3m | I4/mcm | Imma | R3c |
|---------|------|--------|------|-----|
| Eu      | 2(a) |   | 0    | 0.25 |
| Ti      | 2(b) |   | 0    | 0   |
| O       | 6(e) | 0.53813 | 0.25 |

Cell parameters

| $a$ (Å) | 5.528 |
| $c$ (Å) | 13.448 |

Figure 6. (Color online) Calculated and measured$^{24}$ mode-plasma frequencies, plotted as a function of the mode wavenumbers. Our calculated values for four different structural symmetries are presented. Values originating from the TO1, TO2 and TO4 modes of the ideal perovskite are grouped together; the ungrouped symbols correspond to additional modes that appear due to the symmetry lowering.

The imaginary component of the complex dielectric function (see Figure 3b in Ref. 24) when two modes with lifted degeneracy are fitted as one mode.

For completeness, we also list in Tables $^{11}$ and $^{13}$ our calculated frequencies and mode plasma frequencies of the TO2- and TO4-like modes. There are no striking differences that provide persuasive evidence for one structure over another. In the I4/mcm structure, the splitting of the TO2 mode, which is caused by the symmetry lowering, is small (see modes 3 and 4 in Table $^{11}$). However the mode-plasma frequencies of the symmetry-split TO2 modes are significantly different: Mode 3 consists mainly of out-of-phase shifts of Eu and Ti atoms, without oxygen contribution, whereas the $c$-axis-polarized mode 4 has non-zero oxygen displacements which reduce the relative shifts of the Ti atoms, resulting in a lower dipole for this mode. The average value of the mode-plasma frequencies for these three modes is 703 cm$^{-1}$, which is significantly lower than the corresponding value in the Pm3m structure (925 cm$^{-1}$) but still much higher than experimental one (400 cm$^{-1}$). The average value of the mode-plasma frequency for the TO4 mode (modes 8 and 9) is 727 cm$^{-1}$, compared with 820 cm$^{-1}$ for the reference Pm3m structure. In the R3c phase the TO2 mode also splits by a small amount (7 cm$^{-1}$) with average mode-plasma-frequency of 704 cm$^{-1}$, and the TO4 mode averaged mode-plasma frequency is 734 cm$^{-1}$; both values are similar to those of the I4/mcm structure. Like in the I4/mcm structure, mode 1 is built by Eu displacements against oxygen cage, with small in-phase contribution of Ti sublattice. The eigenvectors are also similar to those of the Pm3m and I4/mcm structures. In the Imma structure (see Table $^{11}$), the wavenumbers of the TO2-group are in the range 154-159 cm$^{-1}$, and those of the TO4-group are in the range 516-537 cm$^{-1}$. As in the R3c structure, modes in the range 237-283 cm$^{-1}$ are activated and should be observed as a doublet with a splitting of 50 cm$^{-1}$.

One interesting observation is the presence of an IR-active mode with frequency ~419 cm$^{-1}$ in all three structures (mode 7 in Table $^{11}$ and 18-19 in Table $^{13}$). This two-fold degenerate mode (it is a doublet in the low-symmetry Imma structure) has a relatively low mode-plasma frequency of 250 cm$^{-1}$ (and, correspondingly, a
low oscillator strength). The eigenvector of this mode shows that this vibration originates from the out-of-phase displacements of Ti atoms in the neighboring sublattices. However, the atomic displacements are not collinear, which leads to an uncompensated dipole in the plane, orthogonal to the c-axis. A mode with a similar frequency (≈430 cm$^{-1}$) is observed at low temperatures in the experimental IR reflectivity data (see Figure 2 in Ref. [24]). The fact that experimentally this mode is observable only at low temperatures gives an additional indication that it could be a fingerprint of the antiferrodistortive phase transition.

To make the comparison with the available experimental data easier, we show in Fig. 6 the calculated and experimental model-plasma frequencies as a function of wavenumber. Clearly the calculated values for the $Pm3n$ structure are strikingly different from the experimental values providing further evidence that this is unlikely to be the ground state structure. It remains difficult to distinguish between the $I4/mcm$, $R3c$ and $Imma$ structures which all show similarly good agreement with current experimental data. Our predicted differences in the degeneracies and ordering of the components of the TO1 and TO2 modes, could in principle be distinguished experimentally using polarized optical spectroscopy on single crystals.

D. Magneto-structural coupling

Strong magneto-structural coupling and multiferroic effects were predicted previously for $Pm3n$ EuTiO$_3$; here we investigate whether such behavior persists in our newly predicted tilted ground-state structures. Indeed, we find that constraining the spins to be aligned ferromagnetically decreases the soft-mode wavenumber by ≈7 cm$^{-1}$ for all three tilted structures; this is the same as previously calculated for the $Pm3n$ structure (7 cm$^{-1}$), and close to the value estimated from the low-temperature IR reflectivity spectra at different magnetic fields (3 cm$^{-1}$). We obtain a decrease of about 2 cm$^{-1}$ for all modes belonging to the TO2 group. The frequency of the TO4 Axe mode is almost insensitive to the magnetic ordering. The modes corresponding to tilting of the oxygen octahedra, on the other hand, show strong magneto-phonon coupling, since they cause changes in the Eu-O-Eu angles which in turn strongly modify the superexchange pathways between the magnetic ions. These modes are listed in Table II as mode 5. We find that ferromagnetic constraint on the Eu spins hardens this mode in the $I4/mcm$ structure from 164 cm$^{-1}$ to 218 cm$^{-1}$, whereas in the $R3c$ structure it is softened by 17 cm$^{-1}$. Since the tilt mode is not polar, however, the dielectric function is not affected.

Finally we mention that Shvartsman et al. recently measured an unusual off-diagonal magnetoelastic coupling in EuTiO$_3$, which they rationalized using our predictions of tilted ground states. In their experiments, the applied electric field breaks inversion symmetry, allowing a Dzyaloshinskii-Moriya interaction and subsequent magnetoelastic response analogous to that in perovskite FeTiO$_3$, which also shows magnetic A-site ions and octahedral tiltings.

IV. CONCLUSIONS

In summary, our density functional calculations for perovskite EuTiO$_3$ predict that its ground state consists of tilts and rotations of the oxygen octahedra, rather than the simple cubic perovskite structure as previously believed. By comparing the total energies of all symmetry allowed tilting patterns, we identified three candidate ground states: $a^0 b^0 c^− (I4/mcm)$, $a^0 b^- b^- (Imma)$ and $a^- a^- a^- (R3c)$. We compared the calculated phonon properties with available experimental data for the three candidate structures to identify the most likely ground state. Our calculated energy differences are two small to allow us to predict which of these phases is the ground state; indeed a phase coexistence might be possible, and additional experiments are required for further progress. In particular, a search for the infra-red-active mode in the range 220-290 cm$^{-1}$ is a signature of $R3c$ and $Imma$ structures, but is not active in $I4/mcm$ phase. Also the magnetic-field dependence of the mode at ≈164 cm$^{-1}$ would distinguish between the $I4/mcm$ and $R3c$ structures.

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1 T. R. McGuire, M. W. Shafer, R. J. Joenk, H. A. Alperin, and S. J. Pickart, Journal of Applied Physics 37, 981 (1966).
2 G. McCarthy, W. White, and R. Roy, Journal of Inorganic and Nuclear Chemistry 31, 329 (1969).
3 C.-L. Chien, S. DeBenedetti, and F. D. S. Barros, Phys. Rev. B 10, 3913 (1974).
4 S. Chae, Y. Chang, D.-W. Kim, B. Lee, I. Choi, and C. Jung, Journal of Electroceramics 22, 216 (2009).
