Ab initio calculations of phonon spectra in $ATiO_3$ perovskite crystals ($A$ = Ca, Sr, Ba, Ra, Cd, Zn, Mg, Ge, Sn, Pb)

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The phonon spectra of calcium, strontium, barium, radium, cadmium, zinc, magnesium, germanium, tin, and lead titanates with the perovskite structure are calculated from first principles within the density functional theory. By analyzing the unstable modes in the phonon spectra, the possible lattice distortions are determined and the energies of the corresponding phases are calculated. From analyzing the phonon spectra, force constants, and eigenvectors of TO phonons, a conclusion is drawn on the origin of the ferroelectricity in considered crystals. It is shown that the main factors determining the possible off-centering of atoms in the $A$ position are the geometric size and electronic configuration of these atoms.

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I. INTRODUCTION

Crystals of the perovskite family are well-known materials undergoing various structural distortions with decreasing temperature. When the character of these distortions is ferroelectric, a number of physical properties of these crystals (dielectric constant, piezoelectric coefficients, etc.) becomes anomalously large. For this reason, these materials have found wide application in modern electronics.

The problem of further optimization of the ferroelectric properties requires a deeper understanding of the microscopic mechanisms responsible for the appearance of ferroelectricity and the ferroelectric properties. In solving this problem, very useful information can be obtained from the ab initio calculations which have already made a significant contribution to the understanding of the ferroelectric phenomena in the perovskite crystals.$^{1-11}$

In discussing the properties of ferroelectrics, it is very important to understand whether these properties result from a collective displacement of atoms in a lattice (displacive phase transition) or they are due to specific features of certain constituent atoms in a crystal (order–disorder phase transition). This problem arises, in particular, in discussing the nature of the phase transitions that occur in incipient ferroelectrics doped with certain impurities.$^{13-15}$

Earlier studies of titanates with the perovskite structure have dealt mainly with four compounds (CaTiO$_3$, SrTiO$_3$, BaTiO$_3$, and PbTiO$_3$) and their solid solutions. However, a comparison of the results obtained in these studies is hampered by different calculation techniques used in these investigations and different methods used to construct atomic (pseudo)potentials.

The aim of this work is to carry out first-principles calculations of the phonon spectra of ten $ATiO_3$ crystals with the perovskite structure and determine the structure of the most stable phases. In order to test our approach, we first apply it for calculating the properties of the four above-mentioned systems. Then we predict the properties of poorly investigated or hypothetical perovskite compounds RaTiO$_3$, CdTiO$_3$, MgTiO$_3$, ZnTiO$_3$, SnTiO$_3$, and GeTiO$_3$. From comparison of the results obtained in a unified way for a large number of related materials, conclusions are made about the relation of the structural distortions in $ATiO_3$ crystals to the size and electronic structure of the $A$ atom. From the analysis of the on-site force-constant matrix and the TO-phonon eigenvectors, we draw conclusions about the origin of the ferroelectricity in these materials and find conditions under which the ferroelectric phenomena can be associated with off-center atoms.

II. CALCULATION TECHNIQUE

The calculations were performed using the ABINIT software$^{16}$ based on the density functional theory, pseudopotentials, and the plane-wave expansion of the wave functions. The exchange-correlation interaction was described in the local density approximation (LDA).$^{17}$ The used pseudopotentials were optimized separable nonlocal pseudopotentials$^{18}$ which were constructed using the OPIUM code and to which the local potential correction$^{19}$ was added in order to improve their transferability. For elements with atomic numbers $Z < 46$, the construction was performed in a non-relativistic way; for other elements, a scalar-relativistic approximation was used. Table I lists the parameters used for constructing pseudopotentials. The local potential was the $s$ potential except for the oxygen atom, for which the local $d$ potential was used. The parameters of pseudopotentials were finely adjusted by comparing the calculated and experimental values of the lattice parameters for a number of oxides and sulfides of the elements.

The lattice parameters and the equilibrium atomic positions in the unit cell were obtained by minimizing the Hellmann–Feynman forces acting on the atoms ($< 10^{-5}$ Ha/Bohr), with the total energy being calculated self-
consistently with an accuracy of better than $10^{-10}$ Ha.\textsuperscript{20}
In the calculations, particular attention was paid to the convergence of the results with respect to the kinetic energy cut-off for plane waves and the density of the $k$-point mesh used in the integration over the Brillouin zone. For all the calculated properties presented below, the convergence was attained at an energy cut-off of 30 Ha and the $8\times8\times8$ $k$-point mesh constructed according to Ref.\textsuperscript{21}.

The Born effective charges $Z^*$, optical dielectric constant $\epsilon_\infty$, elastic moduli $C_{ij}$, bulk modulus $B$, force-constant matrix $\Phi_{ij}$, and phonon spectra were calculated using the density-functional perturbation theory.\textsuperscript{22,23} The phonon frequencies were calculated exactly at five points of the Brillouin zone ($\Gamma$, $X$, $M$, $R$, and the $\Lambda$ point located halfway between the $\Gamma$ and $R$ points), and then the phonon spectrum was computed over the entire Brillouin zone using the interpolation technique.\textsuperscript{22,26}

### III. TESTING OF THE CALCULATION TECHNIQUE

The correctness of the described approach was tested by comparing the calculated lattice parameters, spontaneous polarizations, and phonon spectra with available experimental data and calculations performed by other authors for well-studied CaTiO$_3$, SrTiO$_3$, BaTiO$_3$, and PbTiO$_3$ compounds.

The lattice parameters corresponding to a minimum total energy of the crystals are given in Table\textsuperscript{II} The obtained values agree well with the experimental data\textsuperscript{27} if one takes into account that the LDA usually slightly underestimates the lattice parameter. An analysis of the relative energies (per formula unit) of low-symmetry phases (Table\textsuperscript{III}) shows that for barium titanate, the most energetically favorable phase is the rhombohedral one and for lead titanate, it is the tetragonal phase. The calculated values of the $c/a$ ratio for tetragonal BaTiO$_3$ and PbTiO$_3$ are close to the experimental values (Table\textsuperscript{II}). For CaTiO$_3$, the most energetically favorable phase is the orthorhombic $Pbnm$ phase and for SrTiO$_3$, it is the tetragonal $I4/mcm$ phase. The values of spontaneous polarization calculated by the Berry phase method\textsuperscript{28} are 0.26, 0.31, and 0.89 C/m$^2$ for tetragonal BaTiO$_3$, rhombohedral BaTiO$_3$, and tetragonal PbTiO$_3$, respectively. These values are close to the experimental data (0.26, 0.33, 0.75 C/m$^2$, Ref.\textsuperscript{24}).

The calculated optical-phonon frequencies are also in good agreement with available experimental data and calculations performed by other authors (Tables\textsuperscript{IV} and\textsuperscript{V}). The imaginary frequencies in Tables\textsuperscript{IV} and\textsuperscript{V} correspond to unstable modes, the squares of whose frequencies are negative.

The good agreement of our calculations with the experimental data and the calculations of other authors for CaTiO$_3$, SrTiO$_3$, BaTiO$_3$, and PbTiO$_3$ suggests that the proposed approach can be used to predict the properties of poorly studied and hypothetical titanates with the perovskite structure and to discuss the factors causing the appearance of ferroelectricity in them. The properties of these crystals calculated for the theoretical lattice parameter (i.e., the value corresponding to a minimum of the total energy) are given in Tables\textsuperscript{III} to\textsuperscript{VII}. Table\textsuperscript{III} presents the energies of different low-symmetry phases measured relative to the energy of the parent cubic phase. Table\textsuperscript{IV} gives the frequencies of optical phonons (three infrared-active $\Gamma_{15}$ modes and one infrared-inactive $\Gamma_{25}$ mode) in the cubic phase. Table\textsuperscript{V} gives the lowest phonon frequencies at high-symmetry points of the Brillouin zone. The values of the Born effective charges and optical dielectric constants for the cubic phase of ATiO$_3$ compounds are given in Table\textsuperscript{VI}. Finally, the elastic moduli of several crystals are presented in Table\textsuperscript{VII}.

The phonon dispersion curves along some high-symmetry directions calculated for the cubic phase of ten titanates are shown in Fig. I. The imaginary phonon frequencies associated with the structural instability of the crystals are represented in Fig. I by negative values.

### IV. RESULTS

As follows from Fig. I, unstable optical modes of different symmetry are present in the phonon spectra of all studied titanates. At first, we discuss the phonon spectra of well-studied compounds.

A specific feature of the dispersion curves of SrTiO$_3$ is that among three unstable phonons at the $\Gamma$, $R$, and $M$ points, the most unstable phonon is that at the $R$ point (the $R_{25}$ mode)\textsuperscript{22} and that the phonon frequency depends only weakly on the wave vector along the $R$–$M$ line. As shown in Ref.\textsuperscript{8} in the real space, these unstable phonons with the wave vectors near the edges of the cubic Brillouin zone correspond to the rotation of the oxygen octahedra linked together by shared vertices, with the correlation length for rotations being three to five lattice periods. Thus, the $R_{25}$ mode and the $M_3$ mode (which corresponds to the unstable phonon at the $M$ point) describe the structural distortions associated with the rotation of the octahedra. The unstable $\Gamma_{15}$ phonon mode at the $\Gamma$ point corresponds to the ferroelectric distortion of the structure.

The $R_{25}$ mode is triply degenerate, and the distortions described by the three-component order parameters $(\eta, 0, 0)$, $(\eta, \eta, 0)$, and $(\eta, \eta, \eta)$ lead to low-symmetry phases with the space groups $I4/mcm$, $Imma$, and $R3c$, respectively. The $M_3$ mode is nondegenerate, and its condensation lowers the crystal symmetry to $P4/mmb$. The triply degenerate $\Gamma_{15}$ mode results in the well-known space groups $P4mm$, $Amnm2$, and $R3m$. From comparing the energies of these phases (Table\textsuperscript{III}), it follows that the lowest-energy phase in SrTiO$_3$ is the $I4/mcm$ one, into which strontium titanate transforms with decreasing temperature. The instability of the ferroelectric mode in this compound is not sufficiently strong for ferroelectricity to occur.
FIG. 1. Phonon dispersion curves for the cubic phase of $A\text{TiO}_3$ compounds. The labels indicate the symmetry of unstable modes.
TABLE I. Electronic configurations of atoms and parameters used to construct pseudopotentials: $r_s$, $r_p$, and $r_d$ are the core radii of the pseudopotentials for the $s$, $p$, and $d$ projections; $q_s$, $q_p$, and $q_d$ are the cut-off wave vectors used to optimize pseudopotentials; and $r_{\text{min}}$, $r_{\text{max}}$, and $V_{\text{loc}}$ are the limits and the depth of the correcting local potential (parameter values are in atomic units, and energy is given in Ry).

| Atom | Configuration | $r_s$ | $r_p$ | $r_d$ | $q_s$ | $q_p$ | $q_d$ | $r_{\text{min}}$ | $r_{\text{max}}$ | $V_{\text{loc}}$ |
|------|--------------|------|------|------|------|------|------|-----------------|-----------------|---------------|
| Ca   | 3$s^2$p$^6$3$d^04s^0$ | 1.46 | 1.68 | 1.82 | 7.07 | 7.07 | 7.27 | 0.01 | 1.40 | 1.6 |
| Sr   | 4$s^2$4$p^4$4$d^05s^0$ | 1.68 | 1.74 | 1.68 | 7.07 | 7.07 | 7.07 | 0.01 | 1.52 | 1.5 |
| Ba   | 5$s^2$5$p^6$5$d^06s^0$ | 1.85 | 1.78 | 1.83 | 7.07 | 7.07 | 7.07 | 0.01 | 1.68 | 1.95 |
| Ra   | 6$s^2$6$p^6$7$s^0$6$d^07p^0$ | 1.84 | 1.73 | 1.98 | 7.8 | 7.8 | 7.8 | 0.01 | 1.68 | -1.3 |
| Mg   | 2$s^2$2$p^6$3$s^03p^0$ | 1.50 | 1.88 | —     | 6.7 | 8.1 | —     | 0.01 | 1.0 | -0.84 |
| Zn   | 3$d^{10}$4$s^0$4$p^0$ | 1.82 | 1.82 | 2.00 | 7.07 | 7.07 | 7.47 | 0.01 | 1.60 | 2.5 |
| Cd   | 4$d^{10}$5$s^0$5$p^0$ | 2.04 | 2.18 | 2.10 | 7.07 | 7.07 | 7.07 | 0    | 1.88 | -1.6 |
| Ge   | 3$d^{10}4s^0$3$p^0$ | 1.68 | 1.68 | 1.96 | 7.07 | 6.0 | 7.77 | 0.01 | 1.58 | 0.48 |
| Sn   | 4$d^{10}$5$s^0$5$p^0$ | 2.14 | 2.08 | 2.18 | 7.07 | 7.07 | 7.07 | 0.01 | 1.90 | 0.64 |
| Pb   | 5$d^{10}$6$s^0$6$p^0$ | 1.72 | 1.98 | 1.80 | 6.05 | 5.52 | 7.17 | 0.1  | 1.43 | 1.6 |
| Ti   | 3$s^2$3$p^6$3$d^04s^0$ | 1.48 | 1.72 | 1.84 | 7.07 | 7.07 | 7.07 | 0.01 | 1.41 | 2.65 |
| O    | 2$s^2$2$p^6$3$d^0$ | 1.40 | 1.55 | 1.40 | 7.07 | 7.57 | 7.07 | —   | —   | —   |

TABLE II. Comparison of calculated and experimental lattice parameters of different phases of $ATiO_3$ compounds (experimental data are obtained at 300 K, unless otherwise specified).

| Compound | Space group | Source | Lattice parameters |
|----------|-------------|--------|--------------------|
| CaTiO$_3$ | $Pbnm$ | This work | $a = 5.3108$, $b = 5.4459$, $c = 7.5718$ Å |
|          |            | Exp.$^{27}$ | $a = 5.3670$, $b = 5.4439$, $c = 7.6438$ Å |
| SrTiO$_3$ | $Pm3m$ | This work | $a = 3.8898$ Å |
|          |            | Exp.$^{27}$ | $a = 3.905$ Å |
|          |            | $I4/mcm$ | $a = b = 5.4680$, $c = 7.8338$ Å |
|          |            | Exp.$^{27}$ | $a = b = 5.510$, $c = 7.798$ Å (20 K) |
| BaTiO$_3$ | $Pm3m$ | This work | $a = 3.9721$ Å |
|          |            | Exp.$^{27}$ | $a = 3.996$ Å (393 K) |
| P4mm     | This work | $a = 3.9650$, $c/a = 1.0106$ |
|          | Exp.$^{27}$ | $a = 3.9920$, $c/a = 1.0361$ (293 K) |
| Amm2     | This work | $a = 3.9620$, $b = 5.6384$, $c = 5.6484$ Å |
|          | Exp.$^{27}$ | $a = 3.990$, $b = 5.669$, $c = 5.682$ Å (263 K) |
| R3m      | This work | $a = 3.9817$ Å, $\alpha = 89.933^\circ$ |
|          | Exp.$^{27}$ | $a = 4.001$ Å, $\alpha = 89.85^\circ$ (105 K) |
| PbTiO$_3$ | P4mm | This work | $a = 3.8858$, $c = 4.1151$ Å, $c/a = 1.0590$ |
|          | Exp.$^{27}$ | $a = 3.904$, $c = 4.152$ Å |

In CaTiO$_3$, in addition to the instabilities found above, three weak antiferroelectric-type instabilities associated with the $X_5$, $X_5'$, and $M_3^0$ modes arise and the $R-M$ segment of the phonon spectrum becomes practically dispersionless (compare mode energies in Table III). In the latter case, as shown by theoretical calculations, the simultaneous condensation of two unstable $R_0$ and $M_3$ modes results in the formation of the $Pbnm$ phase having the lowest energy among the possible distorted phases (Table III). The transition from the high-temperature $Pm3m$ phase to the low-temperature $Pbnm$ phase can occur through one of three intermediate phases ($P4/mmb, I4/mcm$, and $R3c$), whose energies are $0.11–0.17$ eV higher than the energy of the $Pbnm$ phase. The ferroelectric $P4mm$ and $R3m$ phases in CaTiO$_3$ have much higher energies and never arise. As for the weakly unstable $X_5$, $X_5'$, and $M_3^0$ modes, they are doubly degenerate and the distortions described by the order parameters ($\eta, 0$) and ($\eta, \eta$) result in the $Pnma$, $Cnmc$, and $Cnmm$ phases. The energy gain resulting from the transformation into these phases, however, does not exceed 7 meV.

The phonon spectrum of BaTiO$_3$ significantly differs from the spectra discussed above by the absence of instability at the $R$ point and the appearance of highly unstable $X_5$ and $M_3^0$ modes (at the $X$ and $M$ points,
TABLE III. Relative energies of different low-symmetry phases of ATiO₃ compounds (energies of the most stable phases are in boldface).

| Compound | Unstable mode | Space group | Energy (meV) | Unstable mode | Space group | Energy (meV) | Unstable mode | Space group | Energy (meV) |
|----------|---------------|-------------|--------------|---------------|-------------|--------------|---------------|-------------|--------------|
| MgTiO₃   | Γ₂₅           | P₄mm        | −125ᵃ        | M₂           | Cmm        | −417ᵃ        | Γ₁₅, Γ₂₅     | Amm₂        | −1380ᵃ       |
| X₃       | P₄2/mmc       | −147ᵃ       | X₃           | Pmma         | −500        | R₂₅ + M₃     | Cmcm         | −1658ᵃ       |
| R₁₃      | I₄/mmm        | −228ᵃ       | Γ₂₅          | R₃₂          | −686ᵃ       | R₂₅          | R₃c          | −1727        |
| R₁₃      | R₃m           | −289ᵃ       | Γ₁₅          | R₃m          | −695        | R₁₅, R₂₃     | Immα         | −1764ᵃ       |
| X₅       | Cmcm          | −304        | Γ₁₅          | P₄mm         | −1028       | R₂₅ + M₃     | Pmmm         | −1992        |
| M₄       | Pmma          | −344ᵃ       | M₄           | P₄/mmbm      | −1107       |               |               |              |
| M₄       | P₄/mmm        | −417ᵃ       | R₂₅          | I₁₄/mcm      | −1111       |               |               |              |
| CaTiO₃   | X₅           | Cmcm         | −0.0ᵃ        | M₂           | Cmm         | −6.7         | R₂₅          | I₁₄/mcm      | −365         |
| X₅       | Pmma          | −0.0ᵃ       | Γ₁₅          | R₃m          | −73.7       | R₂₅          | R₃c          | −385         |
| X₅       | Cmcm          | −0.6        | Γ₁₅          | Amm₂         | −85.4ᵃ      | R₂₅ + M₃     | Cmcm         | −404ᵃ       |
| X₅       | Pmma          | −0.9        | Γ₁₅          | P₄mm         | −123        | R₂₅          | I₁ma         | −412ᵃ       |
| M₄       | Pmma          | −5.0        | M₄           | P₄/mmbm      | −321        | R₂₅ + M₃     | Pmmm         | −497         |
| SrTiO₃   | Γ₁₅          | P₄mm        | −0.71        | M₄           | P₄/mmbm     | −9.45        | R₂₅          | I₁₄/mcm      | −30.9        |
| Γ₁₅      | Amm₂         | −0.75ᵃ      | R₂₅          | R₃c          | −27.5       |               |               |              |
| Γ₁₅      | R₃m          | −0.75        | R₂₅          | I₁₁ma        | −28.9       |               |               |              |
| BaTiO₃   | M₄           | P₄/mnm      | −11.1        | X₅           | Cmm         | −1.45        | Γ₁₅          | Amm₂         | −7.4         |
| X₅       | Pmma         | −1.22        | Γ₁₅          | P₃mm         | −5.6        | Γ₁₅          | R₃m          | −8.1         |
| RaTiO₃   | M₄           | P₄/mnm      | −11.1        | X₅           | Cmm         | −16.9        | Γ₁₅          | Amm₂         | −28.5        |
| X₅       | Pmma         | −14.2        | Γ₁₅          | P₄mm         | −21.8       | Γ₁₅          | R₃m          | −29.7        |
| CdTiO₃   | R₁₃          | I₄/mmm      | −24ᵃ         | X₃           | Pmma        | −160        | R₂₅          | I₁₄/mcm      | −912         |
| R₁₃      | R₃m          | −30ᵃ         | Γ₁₅          | R₃m          | −245        | M₄           | P₄/mmbm      | −920         |
| X₃       | P₄₂/mmc      | −45        | X₃           | Cmcm         | −282        | R₂₅ + M₃     | Cmcm         | −1157ᵃ       |
| X₃       | Cmcm         | −66ᵃ        | Γ₁₅          | P₄mm         | −340        | R₂₅          | R₃c          | −1197        |
| X₃       | Pmma         | −104ᵃ       | Γ₁₅, Γ₂₅     | Amm₂         | −412        | R₁₅, R₂₅     | I₁ma         | −1202ᵃ       |
| Γ₂₅      | P₄m₂         | −134        | Γ₂₅          | R₃₂          | −486        | R₂₅ + M₃     | Pmmm         | −1283        |
| ZnTiO₃   | X₃           | P₄₂/mmc     | −171ᵃ        | M₂           | Cmm         | −564ᵃ        | R₂₅          | I₁₄/mcm      | −1443        |
| Γ₂₅      | P₄m₂         | −341        | M₂           | P₄/mmbm      | −688ᵃ       | M₃           | P₄/mmbm      | −1449        |
| R₁₃      | I₄/mmm       | −375ᵃ       | X₅           | Pmma         | −752ᵃ       | Γ₁₅          | R₃₂          | −1486        |
| X₃       | Pmma         | −447        | X₅           | Cmm          | −867        | R₂₅ + M₃     | Cmcm         | −2036ᵃ       |
| X₃       | Cmcm         | −449ᵃ       | Γ₁₅          | R₃m          | −868        | R₁₅, R₂₅     | I₁ma         | −2215ᵃ       |
| R₁₃      | R₃m          | −465ᵃ       | Γ₁₅          | P₄mm         | −1104       | R₂₅          | R₃c          | −2271        |
| M₄       | Pmma         | −555ᵃ       | Γ₁₅, Γ₂₅     | Amm₂         | −1254       | R₂₅ + M₃     | Pmmm         | −2312        |
| GeTiO₃   | Γ₂₅          | P₄m₂        | −0.5ᵃ        | M₃           | P₄/mmbm     | −444        | R₂₅ + M₃     | Cmcm         | −733ᵃ        |
| Γ₂₅      | R₃₂          | −1.5ᵃ       | R₂₅          | I₁₄/mcm      | −455        | R₂₅ + M₃     | Pmmm         | −810         |
| R₁₃      | I₄/mmm       | −314ᵃ       | R₁₃          | R₃m          | −501ᵃ       | Γ₁₅          | P₄mm         | −854         |
| X₃       | Pmma         | −328        | R₂₅          | R₃c          | −589        | Γ₁₅, Γ₂₅     | Amm₂        | −881ᵃ        |
| X₃       | Cmcm         | −428        | R₁₅, R₂₅     | Ima          | −704ᵃ       | Γ₁₅          | R₃m          | −1053        |
| SnTiO₃   | R₁₃          | I₄/mmm      | −1.1ᵃ        | M₃           | P₄/mmbm     | −57         | R₁₅, R₂₅     | Imaᵇ         | −84         |
| R₁₃      | R₃m          | −1.7ᵃ       | R₂₅          | I₁₄/mcm      | −67         | Γ₁₅          | R₃m          | −240         |
| X₃       | Pmma         | −21         | R₂₅          | R₃c          | −74         | Γ₁₅          | Amm₂        | −242ᵃ        |
| X₃       | Cmcm         | −23         | R₂₅ + M₃     | Cmcm         | −78ᵃ        | Γ₁₅          | P₄mm        | −291         |
| PbTiO₃   | M₃           | P₄/mmbm     | −10.1        | R₂₅          | R₃c          | −21.6        | Γ₁₅          | Amm₂        | −70.4ᵃ       |
| R₂₅      | I₁₄/mcm      | −19.6       | R₂₅          | Imaᵇ        | −22.2       | Γ₁₅          | P₄mm        | −84.4        |
| R₂₅ + M₃ | Cmcm         | −19.7ᵃ      | Γ₁₅          | R₃m          | −66.3       |               |               |              |

ᵃResults of additional calculations.
ᵇThe P₆mm structure found in earlier calculations relaxes to the Ima one.
respective) corresponding to the antiferroelectric distortions of the structure into the \(Pmna, Cmcm\), and \(P4/nmm\) phases. Among the unstable modes, the ferroelectric \(\Gamma_{15}\) mode is the most unstable and it determines the distortions observed in the crystal (the energies of three above-mentioned antiferroelectric phases are higher than that of the polar \(P4/nmm\) phase). We note that the weaker phonon instability in our calculations as compared to the results of Ref. 13 is because our calculations were performed for the theoretical lattice parameter, whereas the calculations of Ref. 13 were performed for its experimental value. To illustrate the influence of the lattice strain on the phonon spectrum, the low-energy part of this spectrum calculated for the same lattice parameter as in Ref. 13 is shown in Fig. 1 by the dashed line.

The weak dependence of the unstable TO phonon frequency on the wave vector along the \(\Gamma–X–M–\Gamma\) path for vibrations polarized along the fourfold axes of the cubic structure was first discovered in Ref. 13. This dependence gives evidence for the dominant role of the vibrations in the \(\cdots–O–Ti–O\cdots\) linear chains oriented along these axes and for the weak interaction between adjacent chains.

A comparison of the phonon spectra of \(BaTiO_3\) and \(RaTiO_3\) shows that these spectra are very similar. In calcium titanate, the most unstable mode is the \(\Gamma_{15}\) mode whose frequency depends only weakly on the wave vector along the \(\Gamma–X–M–\Gamma\) path. The instability of phonons in

**TABLE IV.** Frequencies of optical phonons at the \(\Gamma\) point in the cubic phase of \(ATiO_3\) compounds (in \(\text{cm}^{-1}\)).

| Compound | Source | \(\text{TO}_1\) | \(\text{TO}_2\) | \(\text{TO}_3\) | \(\text{LO}_1\) | \(\text{LO}_2\) | \(\text{LO}_3\) | \(\Gamma_{25}\) |
|----------|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| MgTiO_3  | this work | 260i | 151 | 649 | 106i | 372 | 905 | 191i |
| CaTiO_3  | this work | 165i | 176 | 607 | 122 | 407 | 857 | 93 |
| SrTiO_3  | this work | 68i | 162 | 549 | 152 | 428 | 792 | 202 |
| BaTiO_3  | this work | 151i | 151 | 522 | 114 | 439 | 751 | 219 |
| CdTiO_3  | this work | 187i | 97 | 616 | 34 | 353 | 820 | 231i |
| GeTiO_3  | this work | 247i | 122 | 583 | 68i | 356 | 762 | 49i |
| SnTiO_3  | this work | 185i | 126 | 505 | 80 | 375 | 689 | 183 |
| PbTiO_3  | this work | 150i | 116 | 499 | 96 | 394 | 693 | 292 |
| **exp.** |       | 182i | 63 | 447 | 47 | 418 | 610 | — |
| **thor.** |       | 182i | 63 | 447 | 47 | 418 | 610 | — |

*Data for the tetragonal phase.*

**TABLE V.** Lowest phonon frequencies at high-symmetry points of the Brillouin zone in the cubic phase of \(ATiO_3\) compounds (in \(\text{cm}^{-1}\)).

| Compound | Source | \(\Gamma\) | \(X\) | \(M\) | \(R\) | \(\Lambda\) |
|----------|--------|------------|-------|------|------|------|
| MgTiO_3  | this work | 260i | 190i | 314i | 315i | 246i |
| CaTiO_3  | this work | 165i | 32i | 215i | 226i | 122i |
| SrTiO_3  | this work | 68i | 98 | 86i | 119i | 100 |
| BaTiO_3  | this work | 151i | 96i | 59i | 134i | 105 |
| RaTiO_3  | this work | 219i | 189i | 167i | 128 | — |
| ZnTiO_3  | this work | 353i | 319i | 437i | 424i | 337i |
| CdTiO_3  | this work | 231i | 184i | 333i | 328i | 265i |
| GeTiO_3  | this work | 247i | 148i | 254i | 251i | 201i |
| SnTiO_3  | this work | 185i | 56i | 144i | 148i | 97i |
| PbTiO_3  | this work | 150i | 30 | 96i | 113i | 15i |
| **thor.** |       | 182i | 31i | 35i | 145i | 58i |

*The \(\Gamma_{25}\) mode.*
RaTiO$_3$ is even more pronounced than in BaTiO$_3$. Taking into account the calculated energies of the distorted phases (Table III), we can suppose that RaTiO$_3$ is also a ferroelectric and that, as the temperature decreases, it undergoes three successive phase transitions as barium titanate does. The temperatures of these transitions are likely to exceed those in barium titanate. The values of the spontaneous polarization calculated by the Berry method in RaTiO$_3$ are also higher than those in BaTiO$_3$; they are 0.36 C/m$^2$ in the tetragonal phase and 0.41 C/m$^2$ in the rhombohedral phase. The calculated elastic moduli of the cubic RaTiO$_3$ phase method in RaTiO$_3$ of the spontaneous polarization calculated by the Berry likely to exceed those in barium titanate. The values a ferroelectric and that, as the temperature decreases, it undergoes three successive phase transitions as barium titanate does.

Now, we consider the phonon spectrum of CdTiO$_3$. This spectrum has a number of unstable modes at the $X$, $M$, and $R$ points ($X_3$, $X_5$, $X'_5$, $M_3$, $M'_5$, $M'_2$, $R_{25}$, $R_{15}$ modes) and two unstable modes at the $G$ point. It is surprising that the main instability at the $G$ point is due to the $G_{25}$ mode associated with the deformation of the oxygen octahedron rather than to the ferroelectric $G_{15}$ mode (see mode frequencies in Table IV). This deformation can result in the formation of the $Pma2$, $Amgm2$, and $R32$ phases, depending on the number of nonzero components of the order parameter. The energy of the most stable of these phases ($R32$, Table III) is lower than the energy of the polar phases. Because of the qualitative similarity between the phonon spectra of calcium and cadmium titanates and between the eigenvectors of their unstable modes at the $R$ and $M$ points, CdTiO$_3$ can be considered as an analog of CaTiO$_3$ characterized by an even higher instability. Therefore, at room temperature, the structure of its nonpolar phase is $Pbnm$, as in the case of CaTiO$_3$. This conclusion was also made in Ref. 36. According to our data, the energy of this phase is lower than that of the cubic phase by 1.28 eV (Table III), which is somewhat higher than the value obtained in Ref. 36 (0.8 eV) and Ref. 10 (0.91 eV).

Although the ferroelectric instability associated with the $G_{15}$ mode is not very important in the cubic CdTiO$_3$, it is known that this instability exists in the $Pbnm$ phase and results in the ferroelectric phase transition at 80 K. The first-principles calculations of the properties of the orthorhombic $Pbnm$ phase did not found a stable ferroelectric distortion in it. In contrast, our calculations of the phonon spectrum at the $G$ point of the orthorhombic CdTiO$_3$ reveal two unstable $B_{1u}$ and $B_{2u}$ modes resulting in the formation of polar $Pb2_1m$ and $Pbn2_1$ phases, respectively. These lattice distortions have been observed in X-ray studies of cadmium titanate at low temperatures. The properties of these phases will be considered in a separate paper.

The phonon spectrum of ZnTiO$_3$ is qualitatively similar to that of CdTiO$_3$, but it has an additional weak unstable $M'_3$ mode and is even less stable. The $G_{25}$ mode in it is also less stable than the ferroelectric $G_{15}$ mode (Table IV). However, as the most unstable modes in ZnTiO$_3$ are the $R_{25}$ and $M_3$ ones, the $Pbnm$ phase has the lowest energy (Table III). The calculations of the phonon spectrum at the $G$ point of the orthorhombic zinc titanate reveal two unstable $B_{1u}$ and $B_{2u}$ modes, which can cause the formation of the same polar phases as in cadmium titanate.

The phonon spectrum of MgTiO$_3$ is intermediate between those of zinc titanate and calcium titanate. It also has unstable $G_{15}$ and $G_{25}$ modes, but in magnesium titanate the ferroelectric $G_{15}$ mode is less stable (Table IV). Nevertheless, as the phonons at the $R$ and $M$ points have the lowest frequency, the $Pbnm$ phase is the most energetically favorable (Table III). The calculations of the phonon spectrum at the $G$ point in the orthorhombic magnesium titanate reveal one unstable $B_{1u}$ mode, which can cause the $Pbnm$ phase transition.

Finally, we discuss the phonon spectra of PbTiO$_3$, SnTiO$_3$, and GeTiO$_3$. The ferroelectric instability in these three compounds is associated with the $G_{15}$ mode which competes with the unstable $R_{25}$ and $M_3$ modes. From comparing the energies of different distorted phases (Table III), it follows that even in GeTiO$_3$, in which the unstable phonons at the $G$, $R$, and $M$ points are close in frequency, the ferroelectric instability is dominant. The calculated spontaneous polarization is 1.28 C/m$^2$ in the tetragonal SnTiO$_3$ and 1.37 C/m$^2$ in the rhombohedral GeTiO$_3$. Our value of the spontaneous polarization in SnTiO$_3$ is significantly higher than the value of 0.73 C/m$^2$ obtained in Ref. 40. Among the perovskite compounds studied to date, GeTiO$_3$ is likely to have the highest spontaneous polarization.

It should be noted that in PbTiO$_3$ and SnTiO$_3$, the most energetically favorable phase is the tetragonal $P4mm$ phase, whereas in GeTiO$_3$ it is the rhombohedral $R3m$ phase. At the same time, the lattice strain in the tetragonal GeTiO$_3$ (c/a = 1.821) is much higher than in lead titanate (c/a = 1.0590). This result calls into question the conclusion that the stabilization of the tetragonal phase in PbTiO$_3$ is due to a high lattice strain (large c/a ratio).

V. DISCUSSION

As follows from Fig. 1, the phonon spectra of all ATiO$_3$ perovskite crystals studied in this work are characterized by several unstable modes, one of which is always the ferroelectric $G_{15}$ mode. In the case where the $R_{25}$ and $M_3$ modes competing with it have a lower frequency, the crystal undergoes distortions—the octahedra rotations, and its symmetry is lowered to $I4/mcm$ or $Pbnm$. The tendency toward such structural phase transitions increases with decreasing the $A$ atom size.

From analyzing the characteristics of the $G_{15}$ mode, one can draw a conclusion on the nature of the ferroelectric instability in studied crystals. As mentioned above, the dispersion law of this mode in BaTiO$_3$ and RaTiO$_3$ indicates strongly correlated motion of atoms along the ...–O–Ti–O–... chains. The analysis of the $G_{15}$ phonon eigenvectors (Table VIII) shows that the $A$ atoms do not
TABLE VIII. Eigenvectors of the dynamic matrix for an unstable T01 phonon at the Γ point in the cubic phase of ATO3 compounds.

| Compound | x_A | x_Ti | x_O⊥ | x_O∥ |
|----------|-----|------|-------|-------|
| MgTiO3   | +0.6828 | +0.1831 | −0.4800 | −0.1985 |
| CaTiO3   | +0.5693 | +0.2391 | −0.5225 | −0.2696 |
| SrTiO3   | +0.3434 | +0.3852 | −0.5372 | −0.3956 |
| BaTiO3   | +0.0299 | +0.6734 | −0.3561 | −0.5404 |
| RaTiO3   | +0.0051 | +0.6750 | −0.2841 | −0.6188 |
| ZnTiO3   | +0.5167 | +0.1889 | −0.5655 | −0.2403 |
| CdTiO3   | +0.4124 | +0.2558 | −0.5919 | −0.2875 |
| SnTiO3   | +0.4177 | +0.2123 | −0.5670 | −0.3709 |
| PbTiO3   | +0.2973 | +0.2865 | −0.5675 | −0.4305 |

TABLE IX. Diagonal elements of the on-site force-constant matrix Φ_xx(0, 0) for A and Ti atoms in the cubic phase of ATO3 compounds (in Ha/Bohr²).

| Compound | A atom | Ti atom |
|----------|--------|---------|
| MgTiO3   | −0.0109 | +0.1431 |
| CaTiO3   | +0.0163 | +0.1370 |
| SrTiO3   | +0.0445 | +0.1196 |
| BaTiO3   | +0.0755 | +0.0873 |
| RaTiO3   | +0.0856 | +0.0750 |
| ZnTiO3   | −0.0229 | +0.1072 |
| CdTiO3   | −0.0008 | +0.1113 |
| SnTiO3   | −0.0150 | +0.0949 |
| PbTiO3   | +0.0912 | +0.0786 |
|         | +0.0269 | +0.0803 |

The values of the diagonal elements of the on-site force-constant matrix Φ_xx(0, 0) in Table IX show that the off-centering of the A atoms should be observed in ATO3 perovskites for A = Mg, Zn, Cd, and Ge. The Sn, Ca, and Pb atoms are fairly close to the stability limit against the transition to an off-center position. It should be recalled that in this work, the calculations were performed for the theoretical lattice parameter (corresponding to a minimum of the total energy). As the systematically underestimated lattice parameters in the LDA weaken the ferroelectric instability, many authors perform calculations for the experimental lattice parameters. In order to estimate the influence of this systematic error, we carried out a computer simulation which showed that an increase in the lattice parameter by 1% (which is a typical LDA error) decreases Φ_xx(0, 0) in PbTiO3 by 0.006 Ha/Bohr² for the A atom and by 0.016 Ha/Bohr² for the Ti atom. As a result, the atoms with Φ_xx(0, 0) close to the stability limit against the transition to an off-center position can actually be off-center. Perhaps, this occurs in lead titanate, as indicated by extended X-ray-absorption fine-structure (EXAFS) studies.²¹

The main parameter determining the tendency of the A atom in ATO3 compounds to become off-center is its atomic size. However, if one plots the dependence of Φ_xx(0, 0) on the ionic radius of the A atom (Fig. 2), it becomes clear that the curve for Zn and Cd atoms, as well as the curve for Ge, Sn, and Pb atoms, are different from that for the “main” Mg–Ca–Sr–Ba–Ra series. This difference is likely a consequence of different configuration of the outer electron shell for the atoms. This configuration is d^{10} for Zn and Cd; d^{10}s² for Ge, Sn, and Pb; and s²p⁶ for the atoms of the main series. The difference in the properties of these groups of atoms is clearly manifested in the Born effective charges of the A atoms (Table VI). Indeed, for the main series, the effective charge Z_A differs only slightly from the nominal charge of the cation (which indicates the predominantly ionic character of the
is due to off-centering of these atoms. According to the V. V. Lemanov, in 13 3
K. Parlinski, Y. Kawazoe, and Y. Waseda, 14
The properties of one more member of this family of ti-
tive or small positive values can be off-center. Therefore,
itdistance in these crystals is determined by the matrix, one
atoms can exist in solid solutions of titanates with the
atoms, whereas Cd atoms remained in the on-site posi-
succeded by Ca, Cd, and Pb impurities in SrTiO
The obtained results suggest that off-center impurity
the Pb atoms in SrTiO and BaTiO can be off-
The results of this study differ somewhat from those
obtained by Kvyatkovskii 12 according to which the mul-
twell adiabatic potential occurred only for Mg and Zn
atoms, whereas Cd atoms remained in the on-site posi-
tions. The discrepancy between our results is likely due
to the fact that in Ref. 11 the calculations were performed
previous unknown systems were predicted. The analysis of
the phonon spectra, the force constant matrix, and the
eigenvectors of unstable TO phonons enabled to establish
the relative contributions of the chain instability and off-
centering of atoms to the appearance of ferroelectricity
in these compounds. The main factors determining the possible off-centering of the A atoms are the geometric
size of these atoms and the configuration of their outer
electron shell.

VI. CONCLUSIONS

The pseudopotentials constructed in this work have
been used to calculate the phonon spectra of ATiO3 per-
ovskite crystals within the density functional theory. All
known results on the structural instability in these com-
pounds were reproduced and the properties of new, pre-
viously unknown systems were predicted. The analysis of
the phonon spectra, the force constant matrix, and the
eigenvectors of unstable TO phonons enabled to establish
the relative contributions of the chain instability and off-
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size of these atoms and the configuration of their outer
electron shell.

\[ A - O \text{ bond}; \] for the other two groups, the charge \( Z_a \) is
significantly larger, which indicates that the bonding be-
comes more covalent in character. 2

The discrepancy between our results is likely due to the
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Our calculations show that the energy of the ilmenite phase
of SnTiO3, GeTiO3, CdTiO3, ZnTiO3, and MgTiO3 at
\( T = 0 \) is lower than the energy of the most stable of the
distorted perovskite phases. However, the energy difference
between these phases is large enough (0.30–0.33 eV) only
for the two last compounds.

We use the mode notation introduced in Ref. 44.

In the case of SrTiO3, despite the presence of the unstable
\( R_{25} \) and \( M_3 \) modes in the phonon spectrum of the cubic

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phase, the $M_3$ instability disappears when switching on the $R_{25}$ rotations, and the energy of the $Pbnm$ phase (which relaxes to the $Imma$ phase) is 2 meV higher than that of the $I4/mcm$ phase.

Further calculations have revealed two additional phases, $Cmcm$ and $Imma$, which are closer in energy to the ground state (Table IV).

The fact that the lattice symmetry is lowered to the polar $Amm2$ group follows from the transformation properties of the order parameter $(\eta, \eta, 0)$. The spontaneous polarization in this phase is 0.018 C/m$^2$.

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