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Ferroelectric Phase Transition in Orthorhombic $CdTiO_3$: First-Principles Studies

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Abstract—Parameters of the crystal structure and phonon spectra for orthorhombic cadmium titanate with space group *Pbnm* and its two possible ferroelectrically distorted phases (with space groups $Pbn2_1$ and $Pb2_1m$) were calculated from first principles within the density functional theory. The obtained structural parameters and frequencies of Raman- and infrared-active modes are in good agreement with available experimental data for the *Pbnm* phase. Expansion of the total energy in a Taylor series of two order parameters showed that the ground state of the system corresponds to the $Pbn2_1$ structure into which the *Pbnm* phase transforms through a second-order phase transition without intermediate phases. A substantial discrepancy between calculated and experimentally observed lattice distortions and spontaneous polarization in the polar phase was explained by quantum fluctuations, as well as by existence of twins and competing long-period structures.

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1. INTRODUCTION

The calculations of phonon spectra of ten titanates $A\text{TiO}_3$ (A = Ca, Sr, Ba, Ra, Cd, Zn, Mg, Ge, Sn, Pb) with a perovskite structure [1] revealed that the orthorhombic phases (space group *Pbnm*) of $CdTiO_3$, $ZnTiO_3$, and $MgTiO_3$ are characterized by a ferroelectric-type instability, which manifests itself in phonon spectra of the above crystals as one or two unstable modes with symmetries B_{1u} and B_{2u} at the Γ point. In the present study, the characteristics of these modes are considered and the results of first-principles calculations of the crystal structure, phonon spectra, and spontaneous polarization of the parent orthorhombic $CdTiO_3$ phase (space group *Pbnm*) and its two ferroelectrically distorted orthorhombic modifications (space groups $Pbn2_1$, $Pb2_1m$) are compared with available experimental data.

The ferroelectric phase transition in cadmium titanate was discovered by Smolenskiĭ [2] in 1950. Since then, this phase transition was studied by dielectric [3–6] and X-ray [3, 4, 7] methods; Raman scattering [3, 8], IR reflectance, and submillimeter reflectance [9] spectroscopy; and pyroelectric current measurements [4]. The specific features of the phase transition in $CdTiO_3$ are a smallness of lattice distortions and a considerable scatter in the data on the phase transition temperature (50–82 K) and spontaneous polarization (0.002–0.009 C/m^2). Even the data on the structure of the low-symmetry phase are contradictory. In particular, the study of the dielectric properties [6] suggests that the $2_1/m$ axis is polar, whereas structural investigations with the use of synchrotron radiation indicate that the $2_1/n$ axis is polar [7]. In [5, 8, 9], the analysis of the temperature dependences of the dielectric constant and the intensity of Raman scattering lines allowed the authors to assume that, upon cooling, one more phase transition accompanied by a change in the polarization direction occurs in cadmium titanate at a temperature of about 50 K.

The paper by Fabricius and López Garcìa [10] is the only work in which $CdTiO_3$ was studied from first principles. In this work, the authors calculated the electric field gradient at cadmium atoms for different sets of atomic coordinates proposed in the literature for the *Pbnm* and $Pbn2_1$ structures and revealed that the relaxation of the latter structure transforms it into a more stable nonpolar *Pbnm* structure.

In view of the discrepancies of the experimental data available in the literature for cadmium titanate, it is expedient to perform first-principles calculations in order to elucidate the factors responsible for these contradictions and to resolve them.

2. CALCULATION TECHNIQUE

The calculations were carried out within the density functional theory with the pseudopotentials and the plane-wave expansion of wave functions as implemented in the ABINIT code [11]. The exchange–correlation interaction was described within the local-density approximation according to the procedure proposed in [12]. As pseudopotentials, we used the optimized separable nonlocal pseudopotentials [13] generated with the OPIUM code to which the local potential was added in order to improve their transferability [14]. The parameters used for constructing the pseudopotentials, the results of their testing, and other details of calculations are described in [1].

3. RESULTS OF THE CALCULATIONS

3.1. Phonon Spectrum of the Pbnm Phase

The calculated frequencies of the "softest" phonons at the Γ point that can be associated with the ferroelectric instability in orthorhombic crystals of $CaTiO_3$, $CdTiO_3$, $ZnTiO_3$, and $MgTiO_3$ with space group *Pbnm* and in tetragonal $SrTiO_3$ with space group *I*4/*mcm* are presented in Table 1. All phonons in $CaTiO_3$ and $SrTiO_3$ turn out to be stable (which corresponds to experiment), whereas one or two unstable modes (the frequencies of which are imaginary) arise in the other three titanates. The strongest instability in these crystals is determined by the phonon with symmetry B_{1u}, which can be associated with the phase transition $Pbnm \longrightarrow Pbn2_1$. In $CdTiO_3$ and $ZnTiO_3$, the phonon with symmetry B_{2u} also appears to be unstable. This phonon can be associated with the phase transition $Pbnm \longrightarrow Pb2_1m$. It should be noted that, among the three crystals under consideration, the *Pbnm* structure can be obtained only for $CdTiO_3$ ($ZnTiO_3$ and $MgTiO_3$ usually crystallize in an ilmenite structure). In this respect, hereafter, we will thoroughly consider only the properties of cadmium titanate.

Table 1. Calculated frequencies (cm^{-1}) of the softest ferroelectric modes in crystals of four titanates with the orthorhombic structure *Pbnm* and tetragonal strontium titanate

Mode	$SrTiO_3$	$CaTiO_3$	$CdTiO_3$	$ZnTiO_3$	$MgTiO_3$
A_{2u}	55	–	–	–	–
E_u	39	–	–	–	–
B_{3u}	–	82	54	73	115
B_{2u}	–	97	81*i*	54*i*	81
B_{1u}	–	82	104*i*	103*i*	133*i*
Γ_{15}	68*i*	165*i*	187*i*	240*i*	260*i*

Note: The frequencies of the unstable TO phonons at the Γ point of the Brillouin zone in the cubic praphase [1] are given in the lower row.

The calculated lattice parameters and equilibrium atomic coordinates for orthorhombic $CdTiO_3$ with space group *Pbnm* are compared with available experimental data in Table 2. It is seen that the results of the calculations are in good agreement with experimental data. It should be noted that better agreement is observed for the experimental data obtained at lower temperatures. A small systematic underestimation of the calculated lattice parameters is a characteristic feature of the local-density approximation used.

Table 2. Lattice parameters *a*, *b*, and *c* (Å) and atomic coordinates for $CdTiO_3$ with space group *Pbnm*

Parameter	This work	Experiment	
		[15]	[7]*
a	5.2427	5.3053	5.284
b	5.3815	5.4215	5.403
c	7.5744	7.6176	7.590
Cd_x	–0.01017	–0.00847	–0.00891
Cd_y	+0.04637	+0.03873	+0.03997
Cd_z	+0.25000	+0.25000	+0.25000
Ti_x	+0.00000	+0.00000	+0.00000
Ti_y	+0.50000	+0.50000	+0.50000
Ti_z	+0.00000	+0.00000	+0.00000
$O1_x$	+0.10130	+0.0902	+0.0918
$O1_y$	+0.46252	+0.4722	+0.4714
$O1_z$	+0.25000	+0.25000	+0.2500
$O2_x$	+0.69348	+0.7008	+0.70083
$O2_y$	+0.30304	+0.2969	+0.29660
$O2_z$	+0.05341	+0.0472	+0.04783

* At $T = 150$ K.

The vibrational spectrum of the crystal with space group *Pbnm* consists of 60 modes, including 24 modes (with symmetries A_g, B_{1g} B_{2g}, and B_{3g}) active in Raman scattering spectra, 25 optical modes (with symmetries B_{1u}, B_{2u}, and B_{3u}) active in IR reflectance spectra, 8 optical modes with symmetry A_u, and three acoustic modes inactive in the above spectra.

The calculated frequencies of the modes active in IR reflectance and Raman scattering spectra are compared with available experimental data [3, 8, 9] in Table 3. For the modes active in Raman scattering spectra, the results of the calculations agree well with the data of measurements performed for ceramic samples [3] and single crystals [8]. The typical relative discrepancy between frequencies is about 3%. A comparison of the frequencies of the modes determined from polarized Raman scattering spectra [8] with the results of our calculations demonstrates that the peaks observed at 303 and 392 cm^{-1} in the *yy* polarization (in the crystal setting accepted in [8]) is most likely erroneously assigned to the B_{1g} modes (in our crystal setting). The positions of these peaks are close to the positions of the peaks of the A_g modes, which should also be observed for the above polarization. The experimental peak in the *yz* polarization at 307 cm^{-1} assigned to the B_{2g} or B_{3g} mode in actual fact is most likely a "leak" of the A_g mode.

A comparison of the calculated frequencies of the modes with the results obtained from analyzing IR reflectance spectra [9] appears to be a more complex problem. A direct comparison of the experimental frequencies with the calculated frequencies for the mode symmetries given in [9] revealed their substantial dis-

Table 3. Frequencies ν_i of the optical modes active in Raman scattering and IR reflectance spectra and oscillator strengths f_i of the IR-active modes for $CdTiO_3$ with space group *Pbnm*

Mode	ν_i, cm^{-1}			Mode	$f_i \times 10^3$, arb. units	ν_i, cm^{-1}	
	this work	experiment				this work	experiment [9]
		[3]	[8]				
A_g	96	95	99	B_{3u}	3.87	54	61?
	128	123	125		1.27	104	111
	195	190	194		0.60	167	165
	295	295	299		0.38	275	284
	414	390	390		0.30	302	306
	449	461	465		0.71	379	383
	512	–	496		0.13	423	–
B_{3g}	140	135, 141	144		0.17	445	458
	211	–	–		0.96	513	525
	353	342	346	B_{2u}	5.98	81i	61**
	486	–	479*		0.62	90	111**
	683	–	–		0.86	177	177
B_{2g}	117	–	114		0.01	202	–
	280	–	307?		0.37	321	321
	445	–	459*		0.14	345	349
	488	–	509*		0.12	437	–
	764	–	–		1.04	476	483
B_{1g}	111	110	115		0.02	530	525
	142	141	141	B_{1u}	3.42	104i	44**
	205	–	–		0.89	60	96**
	356	–	–		0.78	128	143**
	448	–	–		1.24	224	225
	492	–	504		0.62	396	387
	738	–	–		0.02	428	–
					1.19	481	511

*Components of a broad weakly structured line.

**A strong deviation from the calculations is a result of anharmonicity.

crepancy. In order to identify reliably the experimentally observed modes, the oscillator strength f_i was additionally determined for each calculated mode (the oscillator strength characterizes the contribution of the mode to the complex dielectric constant) and it was assumed that the symmetries of the observed modes were incorrectly identified in [9]. This can be a result of the high twin density characteristic of $CdTiO_3$ crystals [8, 15, 16], which can undeniably manifest itself in measurements with crystals having larger areas.

The calculated frequencies and oscillator strengths for the cadmium titanate modification with space group *Pbnm* are compared with the results of investigations of the IR reflectance spectra in Fig. 1. Under the assumption that the modes identified as B_{3u} in [9] for the crystal setting *Pnma* correspond to the B_{1u} modes in our setting *Pbnm* and that the B_{1u} modes in [9] correspond to the B_{2u} and B_{3u} modes in our setting, the agreement between calculated and experimental data becomes more reasonable (Fig. 1, Table 3). A considerable shift in frequencies of three softest modes with symmetry B_{1u} and two softest modes with symmetry B_{2u} with respect to the calculated frequencies is explained by the manifestation of anharmonicity. The modes with calcu-

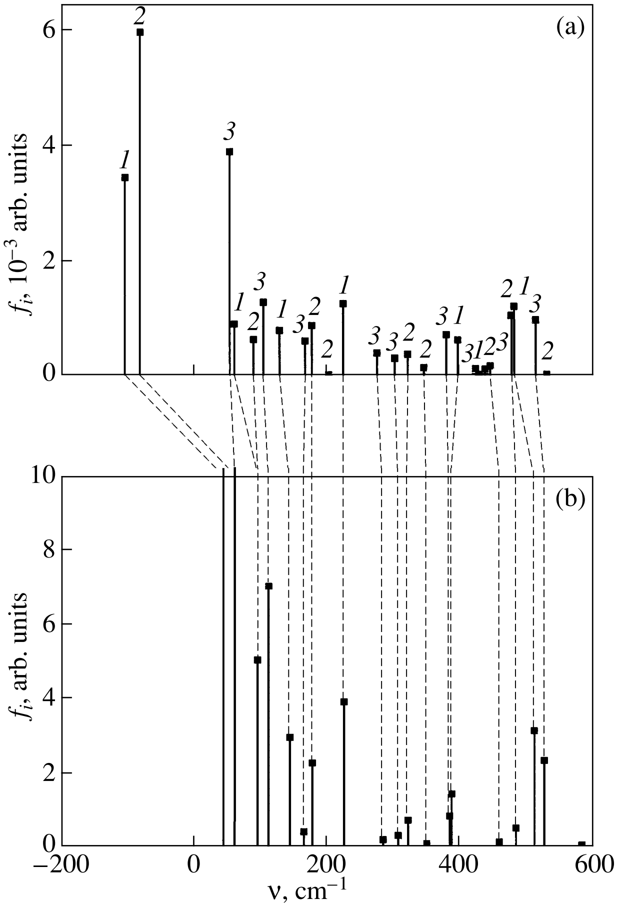

Fig. 1. Comparison of (a) the calculated frequencies and oscillator strengths of the IR-active modes for cadmium titanate with space group *Pbnm* with (b) the corresponding characteristics obtained from analysis of the IR reflectance spectra. Numerals near the points indicate the mode symmetry (B_{1u}, B_{2u}, B_{3u})

lated frequencies of 54 and 104 cm^{-1} are most likely indistinguishable in the experiment against the background of other modes, and four modes with the smallest oscillator strengths are not observed in the spectra at all.

3.2. Lattice Distortions upon Ferroelectric Phase Transitions

As was shown above, the used technique of first-principles calculations describes well the properties of orthorhombic CdTiO$_3$ with space group *Pbnm*. Now, let us consider the properties of the ferroelectrically distorted phases of cadmium titanate. The equilibrium atomic coordinates in the distorted phases were determined using the relaxation of the Hellmann–Feynman forces in the structures obtained from the parent nonpolar phase *Pbnm* by introducing a perturbation with symmetry B_{1u} (for the $Pbn2_1$ phase) or B_{2u} (for the $Pb2_1m$ phase). The structure of the nonpolar *Pbnm* phase and the character of atomic displacements in the case of its distortion upon transition to the low-symmetry phases are shown in Fig. 2. The transition of the crystal to the $Pb2_1m$ phase is accompanied by antiphase displacements of the titanium and oxygen atoms along the y axis, whereas the cadmium atoms are left almost in place. Upon distortion of the lattice associated with the transition to the $Pbn2_1$ phase, both metal atoms are slightly displaced along the z axis (by approximately identical distances). In this case, the displacements of the titanium and oxygen atoms contain a considerable y component in addition to the z component.

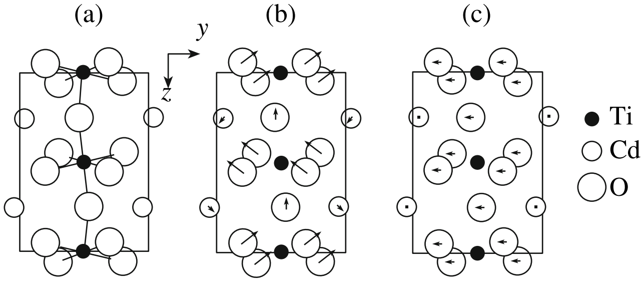

Fig. 2. (a) Projection of the structure of the orthorhombic phase of CdTiO$_3$ with space group *Pbnm* onto the *bc* plane and (b, c) character of atomic displacements in the case of ferroelectric transitions to the (b) $Pbn2_1$ and (c) $Pb2_1m$ phases.

The transition to the polar phases leads to the appearance of two nonequivalent sets of oxygen atoms O2 (designated by the letters *a* and *b* in Table 4). The disappearance of the *n* plane upon transition to the $Pb2_1m$ phase results in the appearance of two nonequivalent cadmium atoms (Cd1, Cd2). The energy gain (per formula unit) associated with the distortion is equal to 6.21 meV for the $Pbn2_1$ phase and 1.38 meV for the $Pb2_1m$ phase.

A comparison of the calculated atomic displacements and the spontaneous lattice strains with the results of low-temperature X-ray measurements [4, 7] (Table 4) demonstrates that, in the experiments, the atomic displacements and the spontaneous lattice strains are significantly smaller. Specifically, it follows from the comparison of the calculated lattice parameters in Tables 2 and 4 that a considerable increase (by 0.045 Å) in the lattice parameter along the polar c axis should be observed in the $Pbn2_1$ phase and the lattice parameter a rather than the lattice parameter b should substantially increase in the $Pb2_1m$ phase. In the experiment, the largest spontaneous deformation below the phase transition temperature was observed for the lattice parameter b [4] (elongation of the order of 0.002 Å), which is inconsistent with the predictions for both ferroelectric phases. The possible factors responsible for these discrepancies will be discussed below.

Table 4. Lattice parameters a, b, and c (Å) and atomic coordinates for ferroelectrically distorted phases $Pbn2_1$ and $Pb2_1m$ of cadmium titanate

Parameter	$Pbn2_1$		$Pb2_1m$	
	this work	experiment [4]*	this work	experiment [7]
a	5.2392	5.2946	5.2498	5.281
b	5.3777	5.4151	5.3870	5.403
c	7.6192	7.6029	7.5699	7.583
$\mathrm{Cd1}_x$	−0.01101	−0.0083	−0.01400	−0.01106
$\mathrm{Cd1}_y$	+0.04425	+0.0407	+0.04583	+0.04076
$\mathrm{Cd1}_z$	+0.25324	+0.25	+0.25000	+0.25000
$\mathrm{Cd2}_x$	+0.01101	+0.0083	+0.00509	+0.00697
$\mathrm{Cd2}_y$	−0.04425	−0.0407	−0.04696	−0.04076
$\mathrm{Cd2}_z$	+0.75324	0.75	−0.25000	−0.25000
Ti_x	+0.00080	+0.004	+0.00459	+0.00190
Ti_y	+0.49548	+0.493	+0.50699	+0.5045
Ti_z	+0.00334	+0.004	+0.00080	+0.00214
$\mathrm{O1}a_x$	+0.10277	+0.091	+0.10313	+0.0925
$\mathrm{O1}a_y$	+0.46191	+0.473	+0.45559	+0.4759
$\mathrm{O1}a_z$	+0.24044	+0.241	+0.25000	+0.25000
$\mathrm{O1}b_x$	−0.10277	−0.091	−0.09897	−0.0911
$\mathrm{O1}b_y$	−0.46191	−0.473	+0.53144	+0.5338
$\mathrm{O1}b_z$	+0.74044	+0.741	−0.25000	−0.25000
$\mathrm{O2}a_x$	+0.68779	+0.723	+0.69372	+0.6999
$\mathrm{O2}a_y$	+0.31805	+0.308	+0.29494	+0.2951
$\mathrm{O2}a_z$	+0.04267	+0.047	+0.05436	+0.0501
$\mathrm{O2}b_x$	+0.29839	+0.323	+0.30806	+0.2989
$\mathrm{O2}b_y$	+0.71471	+0.710	+0.68835	+0.7017
$\mathrm{O2}b_z$	−0.06583	−0.045	−0.05264	−0.0457

* Correct signs of atomic displacements are recovered.

3.3. Parameters of the Effective Hamiltonian

Torgashev et al. [8] and Gorshunov et al. [9] assumed that, below the ferroelectric phase transition temperature, one more phase transition accompanied by a change in the polarization direction occurs in cadmium titanate. In order to verify this hypothesis, we calculated the dependence of the total energy of the crystal on the distortion of the lattice with symmetries B_{1u} and B_{2u}.

As is known, the normal lattice vibrations form a complete orthonormal basis set in which it is possible to expand any combination of atomic displacements. We used the expansion of the lattice distortions (determined in Subsection 3.2) in the $Pbn2_1$ and $Pb2_1m$ phases in the basis set of eigenvectors of the dynamic matrix of $\mathrm{CdTiO_3}$ with space group $Pbnm$. For the $Pbn2_1$ phase, this expansion contains the contributions of seven modes with symmetry B_{1u} (the acoustic mode with symmetry B_{1u} that describes the uniform atomic displacements in the unit cell was excluded) and seven totally symmetric modes A_g (Fig. 3). For the $Pb2_1m$ phase, the expansion involves the contributions of nine modes with symmetry B_{2u} (also without acoustic mode) and seven A_g modes. In this case, the contributions of the modes with symmetries B_{1u} and B_{2u} with the lowest frequencies to the total energy of distortions amount to 92.8 and 95.4%, respectively. Therefore, when constructing the effective Hamiltonian, we can restrict ourselves to the expansion in powers of the amplitudes of these two modes.

The total energy of the crystal was expanded in a Taylor series in powers of the distortion amplitudes ξ and η described by the normalized normal modes with symmetries B_{1u} and B_{2u} with the lowest frequencies. In this case, the lattice parameters were assumed to be fixed and equal to the lattice parameters for the $Pbnm$ phase. The resulting expansion has the form

$$\begin{aligned} E_{\mathrm{tot}}(\xi, \eta) = {} & E_{\mathrm{tot}}(0, 0) + b_1\xi^2 + c_1\xi^4 + b_2\eta^2 \\ & + c_2\eta^4 + d\xi^2\eta^2 \end{aligned} \tag{1}$$

with the coefficients $b_1 = -0.4075$ Ha (Hartree), $b_2 = -0.2614$ Ha, $c_1 = 183.49$ Ha, $c_2 = 249.58$ Ha, and $d = 457.4$ Ha. It turned out that the expansion is adequately described by the fourth-degree polynomials of two orders parameters and that sixth-degree invariants can be omitted in the expansion. Therefore, the phase transition in $\mathrm{CdTiO_3}$ is far from the tricritical point (the closeness to which was noted in [5]). Then, since we have $d > 2\sqrt{c_1c_2}$, the minima of the total energy correspond to the order parameters $\pm(\xi, 0)$ and $\pm(0, \eta)$ and are separated from each other by the energy barriers. This means that the formation of the monoclinic phase with space group Pb and tilted polarization vectors is energetically unfavorable. The calculation from relationship (1) demonstrates that the energy minima are observed at the mode amplitudes ($\xi = 0.03332$, $\eta = 0$) and ($\xi = 0$, $\eta = 0.02288$) and that the energy gains associated with the lattice distortion are equal to 6.16 and 1.86 meV, respectively, which are close to the energies corresponding to the true distortions (see Subsection 3.2).

Since we included only two modes with the lowest frequencies in expansion (1), it was necessary to check that the energetically most favorable phase $Pbn2_1$ remains stable with respect to small distortions with symmetry B_{2u} with allowance made for all modes involved in the distortion. For this purpose, we calculated the phonon spectrum of the $\mathrm{CdTiO_3}$ crystal in the $Pbn2_1$ phase. In this spectrum, the ferroelectric mode polarized along the y axis has the lowest vibrational frequency equal to 83 $\mathrm{cm^{-1}}$. The positive values of all mode frequencies confirm that the ground state of the $CdTiO_3$ crystal corresponds to the polar $Pbn2_1$ phase.

Although the above analysis of the stability of the polar $Pbn2_1$ phase corresponds to the temperature $T = 0$, it is unlikely that a change in the coefficients c_1, c_2, and d in the thermodynamic potential with an increase in the temperature can lead to the violation of the condition $d > 2\sqrt{c_1c_2}$ and the transition to the monoclinic phase. Therefore, the possibility of appearing sequential ferroelectric phase transitions in $CdTiO_3$ with a variation in the temperature is most likely ruled out. Possibly, the specific features observed in the dielectric constant of $CdTiO_3$ crystals near 50 K [3, 5, 6] are associated with the existence of side minima of the total energy that are separated from the main minima by low potential barriers.

3.4. Spontaneous Polarization

The spontaneous polarization P_s in the orthorhombic phases $Pbn2_1$ and $Pb2_1m$ of cadmium titanate was calculated by the Berry's phase method [17]. The calculated spontaneous polarizations P_s corresponding to the lattice distortions determined in Subsection 3.2 for the $Pbn2_1$ and $Pb2_1m$ phases are equal to 0.29 and 0.21 C/m^2, respectively. The spontaneous polarization P_s corresponding to the minima in expansion (1) is equal to 0.21 C/m^2 for the $Pbn2_1$ phase and 0.16 C/m^2 for the $Pb2_1m$ phase. It is worth noting that both calculated values of P_s considerably exceed experimentally obtained polarizations of 0.002–0.009 C/m^2 [4, 5].

4. DISCUSSION OF THE RESULTS

As was shown in [1], the ferroelectric instability is characteristic of the cubic phase of all ten titanates with a perovskite structure studied. In crystals that undergo structural phase transitions to the $Pbnm$ and $I4/mcm$ phases, the ferroelectric instability is weakened and observed only in three crystals with the $Pbnm$ structure ($CdTiO_3$, $ZnTiO_3$, and $MgTiO_3$) among five titanates characterized by the aforementioned phase transitions (Table 1). A comparison of the frequencies of the softest ferroelectric modes at the Γ point in the cubic praphase and the $Pbnm$ and $I4/mcm$ phases shows that, upon structural phase transition, the ferroelectric instability is retained in crystals in which this instability is strongest in the cubic phase. Therefore, it is not surprising that the temperature of the ferroelectric phase transition in $CdTiO_3$ is considerably lower than that in $BaTiO_3$ or $PbTiO_3$.

Investigations of $SrTiO_3$ have long revealed that, despite the existence of the ferroelectric instability in this compound, the corresponding phase transition is not observed in the crystal with a decrease in the temperature. It is believed this is associated with quantum fluctuations, i.e., zero-point vibrations of atoms [18]. One more factor responsible for this behavior can be the structural phase transition that occurs in the crystals and, as was shown above, weakens the ferroelectric instability.

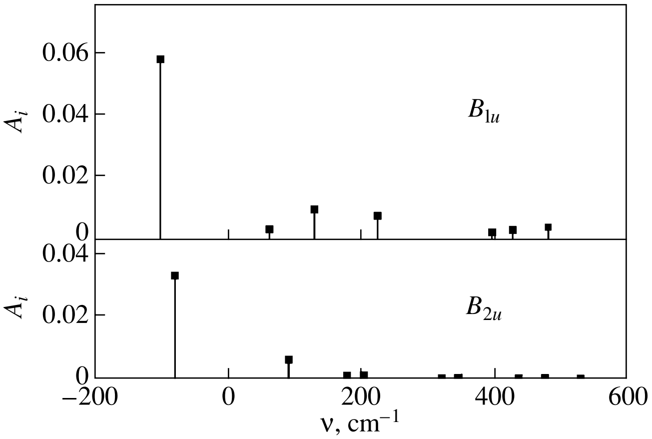

Fig. 3. Relative contributions of different modes with symmetries B_{1u} and B_{2u} to the ferroelectric distortions upon transitions to the $Pb2_1m$ and $Pbn2_1$ phases of cadmium titanate.

It seems likely that the strong influence of quantum fluctuations on the physical properties of crystals should also manifest itself for $CdTiO_3$. As was shown in [19], quantum effects most strongly affect the modes with a small "reduced mass," in particular, the ferroelectric mode to which light oxygen atoms make a significant contribution. This explains the fact that the replacement of the ^{16}O isotope by the heavier ^{18}O isotope in strontium titanate leads to the real ferroelectric phase transition [20].

In order to take into account the quantum fluctuations, expression (1) for the "potential" energy should be complemented by the kinetic energy of nuclei. When performing first-principles calculations, this energy is ignored in order to calculate correctly the forces acting on atoms (the Born–Oppenheimer approximation).

Although the approach used below requires a more detailed justification, it is possible to attempt (according to [19]) to take into account the quantum fluctuations at the level of mode motion and to add the kinetic energy of the mode in the form of the operator $(-\hbar^2/2M^*)\nabla^2$ to the potential energy (1) of the mode, where M^* is some reduced mass. With the aim of determining the quantitative criterion corresponding to the complete suppression of the phase transition by quantum fluctuations, we consider the simple one-dimensional problem in which a particle with a mass M^* moves in a double-well potential $V(x) = -ax^2 + bx^4$. We assume that the phase transition is suppressed by quantum fluctuations when the kinetic energy of zero-point vibrations of the mode exceeds the well depth of the potential under consideration. The numerical solution

Table 5. Frequencies of the unstable ferroelectric modes in the high-symmetry phases, energy gains in the case of lattice distortion [1], and ratios $h\nu/E_0$ for three ferroelectric phase transitions in the $SrTiO_3$ and $CdTiO_3$ compounds

Phase transition	ν, cm^{-1}	E_0, meV	$h\nu/E_0$
$SrTiO_3$, $Pm3m \longrightarrow R3m$	$68i$	0.75	11.2
$CdTiO_3$, $Pbnm \longrightarrow Pb2_1m$	$81i$	1.38	7.28
$CdTiO_3$, $Pbnm \longrightarrow Pbn2_1$	$104i$	6.21	2.08

to the Schrödinger equation demonstrates that this holds true under the condition $b/\sqrt{M^*a^3} > 0.428$. By eliminating the unknown mass M^* from this condition, the criterion can be rewritten in the physically clear form $h\nu/E_0 > 2.419$. Here, $\nu = \sqrt{-2a/M^*}/2\pi$ is the magnitude of the imaginary vibration frequency in the vicinity of the maximum of the potential barrier (determined within the classical approximation), and $E_0 = a^2/4b$ is the depth of the potential well for the potential under consideration. For the four-minimum potential well described by relationship (1), the quantitative value of the criterion can be slightly different.

Let us use the obtained criterion to evaluate the degree of influence of quantum fluctuations on the ferroelectric phase transitions in $CdTiO_3$. The frequencies of the unstable ferroelectric modes determined from first principles under the assumption of classical motion of nuclei, the energies E_0 of the ordered phases, and the ratios $h\nu/E_0$ for the hypothetical ferroelectric phase transition in $SrTiO_3$ and two phase transitions under consideration in $CdTiO_3$ are listed in Table 5. It can be seen from this table that the quantum fluctuations should suppress the ferroelectric phase transition in strontium titanate and the transition to the $Pb2_1m$ phase in cadmium titanate. As regards the phase transition to the $Pbn2_1$ phase in cadmium titanate, this transition is susceptible to strong quantum fluctuations but is not completely suppressed. Therefore, the only phase transition that can be associated with the experimentally observed ferroelectric phase transition in $CdTiO_3$ is the transition to the $Pbn2_1$ phase.

The quantum fluctuations can also be responsible for the significant discrepancies in the structural positions of atoms and in the values of the spontaneous polarization P_s. In quantum-mechanical calculations of the ground state for multiwell potentials, the displacement corresponding to the most probable atomic position is always smaller than the displacement corresponding to the minimum of the potential energy. Therefore, the quantum fluctuations should lead to a decrease in the distortions upon phase transition and a decrease in the spontaneous polarization P_s. One more probable factor responsible for the decrease in the experimentally determined polarization for $CdTiO_3$ can be associated with the manifestation of twinning in crystals [8, 15, 16] and the presence of long-period structures competing with the $Pbnm$ phase [16].

5. CONCLUSIONS

Thus, the first-principles calculations of the structural parameters and the phonon spectrum of orthorhombic $CdTiO_3$ enabled us to refine the identification of Raman scattering and IR reflectance spectra. The revealed dependence of the total energy of the crystal on the amplitudes of two unstable modes indicates that the ferroelectrically distorted $Pbn2_1$ phase is the ground state of the crystal at the temperature $T = 0$. This phase appears to be the most stable with respect to quantum fluctuations, which are rather strong and suppress other possible lattice distortions. The quantum fluctuations have been found to be one of the main factors responsible for the discrepancy between calculated and experimentally observed values of the spontaneous polarization and the structural distortions upon phase transition.

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