Lattice dynamics and dielectric properties of TiO₂ anatase: A first-principles study

Masayoshi Mikami* and Shinichiro Nakamura

Science and Technology Research Center, Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

Osamu Kitao[†] and Hironori Arakawa

Photoreaction Control Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5,

Higashi 1-1, Tsukuba, Ibaraki 305-8565, Japan

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Lattice vibrations and dielectric properties of the anatase phase of titanium dioxide are investigated from a theoretical perspective. A first-principles pseudopotential band calculation based on density-functional perturbation theory is performed to evaluate normal vibrations, dielectric tensors, and Born effective charges. The present theoretical predictions agree with experimental values overall. Born effective charge tensor elements appear anomalously large, as in the rutile phase, with a larger anisotropy of oxygen. Dielectric permittivity tensors are also discussed in comparison with those of rutile.

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I. INTRODUCTION

Titanium dioxide (TiO₂) has many polymorphs. Among them, rutile $(P4_2/mnm, D_{4h}^{14})$, anatase $(I4_1/amd, D_{4h}^{19})$, Fig. 1), and brookite $(Pbca, D_{2h}^{15})$ are of naturally grown phases. They are wide-bandgap semiconductors, transparent in the visible, with high refractive indecies. The potential applications of TiO₂ are in a considerably wide range: conventional catalyst support, photocatalytic substrate, and photochemical/photoelectrochemical material. Among the polymorphs, the rutile phase has been the most extensively investigated from both experimental and theoretical perspectives, because of the availability of good single crystals for characterization as well as the simplicity of the atomic structure.

Recently, however, experimental investigations have focused on the anatase phase, due to its promising efficiency for photochemical/photoelectrochemical use.^{1–4} Numerous applications have been reported for electrochemical solar cells, rocking-chair lithium batteries, photocatalysis, optical coating, and so forth. In addition, nanosized anatase phase has attracted significant interest because it is generally expected to have unusual physical/chemical properties as opposed to its bulk properties.⁵

Raman and infrared (IR) spectroscopies as useful probes of microscopic structures thus come to be of significant importance for characterization of the the nanocrystalline as well as the bulk. Specifically, the spectroscopy revealed crystallographic structure information about TiO₂ optical coatings much faster and with thinner specimens than conventional x-ray diffraction analysis.⁶ Raman monitoring of phase transformations has also been reported; gel-to-anatase phase transformation,⁷ anatase-to-columbite (TiO₂-II, orthorhombic α -PbO₂ structure) phase transformation under high pressure,⁸⁻¹² and evolution of the anatase phase into rutile phase upon annealing.¹³ The inhibiting effect of impurities such as SiO₂ on the anatase-to-rutile transformation reaction was also investigated with Raman spectroscopy.¹⁴ troscopies, wherein the blueshift of the lowest-wave-number mode has been discussed in view of phonon confinement,^{15,16} oxygen deficiency,^{15,17–20} or internal pressure.²¹ The correlation between Raman spectroscopy linewidth and nanoparticle size was also discussed in relation to defect density.²² IR experiments have been conducted to characterize molecularadsorbed anatase surfaces.²³

The full understanding of the normal vibrations of anatase bulk is thus of great importance as a standard to be compared with those of polycrystalline or the nanophase of anatase. However, such spectroscopic data for the anatase bulk have been limited so far because of poor availability of single crystalline for the spectroscopic characterization. To the best knowledge of the present authors, most reports on Raman spectroscopy of the anatase phase such as Ref. 24 have relied on two reports, by Ohsaka *et al.*²⁵ and by Beattie and Gilson.²⁶ Both papers reported similar experimental results, although two modes were assigned differently as will be seen later. Regarding the IR spectroscopy of the anatase phase, only Gonzalez *et al.*²⁷ reported the spectroscopic data on the



FIG. 1. Crystal structure of anatase phase. Left: conventional unit cell, Right: primitive unit cell. Small and big circles denote titanium and oxygen atoms, respectively.

crystalline of anatase bulk. Their experimental values appeared quite different from those of polycrystalline anatase.²⁸ Their report also showed that the experimental IR wave numbers are quite different from empirical theoretical predictions calculated by the rigid-ion model²⁹ or *GF*-matrix²⁵ method based on the Raman experimental result of Ref. 25.

The first-principles study of the normal vibrations in the anatase phase is thus expected to give a firm baseline for the properties in nanosized or compressed phases. Incidentally, the dielectric properties derived from the lattice dynamics such as static dielectric permittivity are also interesting in comparison with those of the rutile phase calculated by Lee et al.^{30,31} Density functional perturbation theory (DFTP) enables us to obtain the lattice dynamics and dielectric properties simultaneously by calculating the second-order responses to atomic displacements and homogeneous electric fields.³² The capability of DFPT has been established for many cases.^{32,33} The present work is also a natural extension of our previous first-principles work for the anatase phase.³⁴ The rest of this paper is organized as follows. In Sec. II, the computational method is described. In Sec. III, calculated results are discussed in comparison with experimental results and physical properties of rutile. Finally, Sec. IV concludes the paper.

II. COMPUTATION METHOD

The present results have been obtained using to the ABINIT code³⁵ that is based on *ab initio* pseudopotentials and a plane-wave basis set. It relies on the adaptation to a fixed potential of the band-by-band conjugate gradient method³⁶ and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential.³⁷

The calculation conditions in this work follows the Ref. 34 from which the crystal structure is taken [a=3.747 Å and c=9.334 Å in Fig. 1 (left)].

The local density approximation (LDA) (Ref. 38) is adopted for exchange-correlation energy. The Teter-type extended norm-conserving pseudopotentials³⁹ are employed for titanium and oxygen atoms.³⁴ For the titanium (oxygen) pseudopotential, 3s, 3p, 4s, and 3d (2s and 2p) electrons are taken as the valence states.^{31,40} The plane-wave basis set with the energy cutoff of 100 Ry is satisfactory for Teter-type potentials.³⁴ Brillouin-zone integration is computed with kpoints in a Monkhorst-Pack⁴¹ (4,4,4) grid for the primitive unit cell [Fig. 1 (right)].

Linear response properties such as lattice dynamics, dielectric permittivity tensors, or Born effective charges are calculated within a variational approach, DFPT, which is reviewed by Baroni *et al.*³² Technical details can be found in Refs. 42 and 43. In order to obtain the phonon dispersion, dynamical matrices are computed *ab initio* for *q* wave vectors belonging to the Monkhorst-Pack (4,4,4) grid for the primitive unit cell.⁴⁴ They are utilized to obtain real-space interatomic force constants (IFC's). Once IFC's are obtained, dynamical matrices at any wave vector, can be obtained by fast Fourier transform. Still, polar materials need special treatment of the IFC's due to the long-range dipole-dipole interTABLE I. Born effective charge tensors of anatase phase (This work) and the principal values of the Born effective charges of rutile phase (Ref. 31). For anatase phase, the direction i = 1, 2, and 3 are along a, b, and c in the conventional cell, respectively. Note that one takes a coordinate system for rutile phase, wherein axes are along the [110], [110], and [001] directions (i = 1, 2, and 3, respectively), the Born effective charge tensors are diagonalized (principal values).

	Anatase		Rutile			
i	$Z_i^*(\mathrm{Ti})$	$Z_i^*(\mathbf{O})$	$\zeta_i^*(\mathrm{Ti})$	$\zeta_i^*(\mathbf{O})$		
1	+6.678	-1.161	+7.335	-4.978		
2	+6.678	-5.517	+5.343	-1.360		
3	+5.713	-2.856	+7.541	-3.771		
3		-2.8^{a}				

^aRef. 27.

action between ionic effective charges. Technical details in the general case of polar materials with anisotropic effective charges have been described by Gonze and Lee.⁴³

III. RESULTS AND DISCUSSION

A. Born effective charge tensors

The Born effective charge tensors are summarized in Table I, wherein they are diagonalized in anatase with only two (three) independent components for the Ti atoms (O atoms). One component of the effective charge of oxygen estimated from the IR study^{45,60} is in good agreement with the present theoretical value. The result appears qualitatively similar with the case in TiO₂ rutile.^{30,31} The effective charges of Ti in anatase is larger than the nominal ionic charge of the Ti ion (Z=+4). This trend is also observed in the case of TiO₂ rutile^{30,31} and perovskite Ti compounds,⁴⁶ where the anomalous effective charges are explained in view of a mixed covalent-ionic bonding.⁴⁶ When the positive atom (Ti) is displaced towards the negative atom (O), the change in the bond hybridization causes the transfer of electrons from the negative to the positive atoms. The polarization due to the atomic displacement is thus dynamically augmented through the hybridized bonds. The presence of Ti(3d states)-O(2p states) hybridization in anatase is indeed observed in the previous works.47,48

Here we also notice that the effective charge of $Z_{xx}^*(\text{Ti}) [= Z_{yy}^*(\text{Ti})]$ is larger than $Z_{zz}^*(\text{Ti})$. From the FLAPW calculation, a noticeable feature can be found in the nonbonding states near the band gap; the nonbonding O p_{π} orbital at the top of the valence bands and the nonbonding Ti d_{xy} at the bottom of the conduction bands.⁴⁷ This may lead to the larger effective charge of $Z_{xx}^*(Z_{yy}^*)$, because electron transfer during an atomic displacement mostly relates to the highest occupied states and the lowest unoccupied states.⁴⁶

On the other hand, strong anisotropy of the Born effective charge tensor for O atoms is observed; one component smaller than the nominal ionic charge (-2) and much smaller than the others. This trend is also similar with the case of rutile,^{30,31} because both phases have the similar local geometry of titanium/oxygen site.⁴⁹

Mode	Theory ^a	Theory ^b	Theory ^c	Exp. ^b	Exp. ^d	Exp. ^e	Exp. ^f
Raman							
$E_{g}(1)$	145.6	144	152	144	144		
$E_{g}^{'}(2)$	171.1	197	307	197	197		
$B_{1g}^{'}(1)$	398.4	400	400	399	400		
$B_{1g}(2)$	518.4	519	515	519	515		
A_{1g}	535.9	507	519	513	519		
$E_g(3)$	662.1	640	640	639	640		
Infrared							
$E_{u}(1)$	248.6(TO)	169	329(TO)			262(TO)	358
	340.6(LO)		428(LO)			366(LO)	
	(0.0349)						
$A_{2u}(1)$	375.3(TO)	654	566(TO)			367(TO)	552
	743.1(LO)		844(LO)			755(LO)	
	(0.0431)						
<i>E</i> _{<i>u</i>} (2)	479.9(TO)	643	644(TO)			435(TO)	702
	892.2(LO)		855(LO)			876(LO)	
	(0.0445)						
Silent							
B_{2u}	564.6	507	435				

TABLE II. The phonon eigenmodes and the fundamental wave numbers of anatase at Γ (in cm⁻¹).

^aThis work. Oscillator strengths (in parentheses) in atomic unit. (1 a.u. = $0.342036 \text{ m}^2/\text{s}^2$).

^cRef. 29.

^dRef. 26.

^eRef. 27.

The quantitative difference in the physical properties, especially in the anisotropy of the oxygen effective charge tensor, may come from the subtle structural difference between rutile and anatase. In the both phase, each oxygen atom has three titanium neighbors, consisting of a planar shape. In the rutile phase, the OTi_3 fragment has an approximate Y shape with the Ti-O-Ti angle (" 2θ ") of around 99° (see Fig. 1 in Ref. 49). On the other hand, in the anatase phase, it has an approximate T shape with the Ti-O-Ti angle (" 2θ ") of around 156° (Fig. 2 in Ref. 49). Note that an ideal planar shape would be the trigonal structure with the oxygen atom in the center (the Ti-O-Ti angle of 120°). Thus in the anatase phase, the distortion at the oxygen away from the ideal trigonal structure is in the opposite sense to that observed in the rutile phase. This may lead to the quantitative difference in the anisotropy of the effective charge of oxygen in the TiO_2 phases.

B. Phonon analysis

We have calculated the phonon wave numbers of anatase phase at Γ point of the Brillouin zone. Since there are six atoms in the primitive unit cell, there are fifteen optical modes (Γ_{opt}) and three acoustic modes. From factor group analysis for this unit cell ($I4_1/amd$ space group, D_{4h}^{19}), the optical modes at the Γ point are classified into the following symmetry species:

$$\Gamma_{\text{opt}} = A_{1g} + A_{2u} + 2B_{1g} + B_{2u} + 3E_g + 2E_u$$

The modes A_{1g} , B_{1gx} , and E_g are Raman active, whereas the modes A_{2u} and E_u are IR active. The mode B_{2u} is a silent mode.^{50,61} The *E* modes are doubly degenerate, observed to be perpendicular to the *c* axis of the conventional unit cell. The other modes are parallel to the *c* axis.

The calculated mode wave numbers at Γ are summarized in Table II, along with the other theoretical results and the experimental data. Incidentally, the phonon dispersion over the Brillouin zone is also shown in Fig. 2. From the comparison between this work and the experimental data, we obtain rms absolute deviations of 20.5 cm⁻¹ and a rms of relative deviations of 5.8%. The magnitudes of the deviations appear acceptable in view of other DFPT works such as Ref. 31 on the rutile phase. Thus the predicted B_{2u} mode frequency may be reliable within the rms deviations in contrast to empirical theories (the *GF*-matrix method²⁵ or rigid-ion model method²⁹).

Among the Raman modes, we also notice the small difference between the calculated modes of $B_{1g}(2)$ and A_{1g} . The rms deviations in the present study imply that these two modes may be identified as one peak in practical Raman experiments. This is why the mode assignment of the two wave numbers in the experiments at ambient condition has appeared practically difficult.^{25,26}

Even though we take the rms deviations into account, the predicted wave numbers of the $E_u(2)$ and $E_g(2)$ modes appear to deviate somewhat from the experimental values. The deviations may come from the approximations employed in

^bRef. 25.

^fRef. 28.



FIG. 2. Phonon-band structure of anatase calculated by densityfunctional perturbation theory. The labels denote the high-symmetry points in the Brillouin Zone for the tetragonal body-centered system (Ref. 58).

the present calculation, such as the LDA. Still, we may point out other possible sources for the deviations from experimental perspective.

The first question is the condition of the specimens. It is generally difficult to prepare ideal crystalline samples of transition oxides for optical characterization. Since titania is famous for having many polymorphs and nonstoichiometric phases, not only impurities but also imperfections such as grain boundaries^{51,62} appear inevitable in many cases. In addition, we can refer to reports that the decrease of transmittance was caused by the charge state of Ti⁺³ in the TiO₂ films.⁵² Also, IR reflectivity data are very sensitive to surface treatment. For example, the present calculated IR wave numbers differ from those in the IR study of polycrystalline anatase.²⁸ This implies that the experimental IR result may not be related to the bulk property of anatase. In fact, the color of the samples in that study were reportedly gray or vellowish, which suggests that the samples were not of good quality. Remembering that the specimens in the Raman experiment by Ohsaka *et al.* were brownish in color,²⁵ we may suppose that the specimen might have contained imperfections.

We also note that it might still be debatable whether the mode of around 197 cm⁻¹ is the $E_g(2)$ of anatase phase. In the past Raman experiments of anatase phase, it has been known that the lowest wave number modes $[E_g(1)]$ are so strong that the second lowest wave number is not always observed, mostly in polycrystalline and nanocrystalline specimens. Even if the second lowest wave number was observed, it was mostly detected as a very weak peak (around 197 cm⁻¹) on the shoulder of the lowest wave number peak.²⁵ Thus the mode of 171 cm⁻¹ could be hidden in the tail of the lowest wave number peak. It is also interesting to note that only the mode of round 197 cm⁻¹ is extraordinary as it has a negative pressure dependence,^{8,10-12} while all the phonon modes including the $E_g(2)$ mode are unlikely to

TABLE III. Electronic (ϵ_{ij}^{∞}) and static (ϵ_{ij}^{0}) dielectric permittivity tensors of anatase phase. The theoretical prediction with the scissor correction technique are denoted in parentheses.

αα	$\epsilon^{\infty}_{\alpha\alpha}$					$\epsilon_{\alpha\alpha}^0$	
	Theory ^a	Theory ^b	Exp. ^c	Exp. ^d	Exp. ^e	Theory ^a	Exp. ^c
xx	7.07(6.00)	5.97	5.82	6.55		45.9	45.1
zz	6.21(5.39)	5.57	5.41	6.20		24.4	22.7
scalar					5.62		

^aThis work.

^bRef. 47.

^cRef. 27.

^dRef. 59.

^eRef. 55, wherein scalar parts of ϵ_{ij}^{∞} are listed for selected materials.

explain atomic motions needed for the phase transition from anatase to TiO₂-II, as pointed out by Sekiya *et al.*⁸ In addition, it is observed that the variation of the negative dependence showed discrepancies among the experiments.^{8–12} In this sense, the discrepancies in the $E_g(2)$ mode between the present calculated result and the experimental estimations may be observed.

C. Dielectric permittivity tensors

The calculated and experimental values of the electronic (ϵ_{ii}^{∞}) and static (ϵ_{ii}^{0}) dielectric permittivity tensors are given in Table III. The theoretical electronic dielectric permittivity tensors are larger than the experimental estimations by 10 % or more, as often found in the LDA to the DFT.^{31,33} The presently accepted view is that a dependence on the polarization should be present in the exchange-correlation functional. This is also related to the underestimation of band gaps in practical LDA calculations.⁴³ In order to correct the LDA band gap in calculating the dielectric permittivity tensors, we make use of the scissor correction technique with scissor parameter 1.15 eV, the difference from the experimental band gap of 3.2 eV,⁵³ and our calculated LDA band gap of 2.05 eV.³⁴ The corrected values show good agreement with the experimental and theoretical estimations. We notice that the calculated electronic dielectric tensors of the anatase phase are smaller than those of the rutile phase; 7.535 (6.366) along the a axis and 8.665 (7.290) along the c axis without (with) the scissor correction.³¹ This trend is consistent with experimental results.^{54–56} Wemple gave an account of the difference between the TiO₂ phases, in view of the smaller anion density of anatase on the basis of his empirical model.55

The static dielectric permittivity tensors are calculated using the dynamical matrix and effective charges presented above (Table I). They appear to be in good agreement with the experimental estimations from IR spectroscopy.²⁷ Incidentally, the magnitude of the static dielectric tensors is much smaller than the calculated values of TiO₂ rutile (ϵ_{xx} = 117.5, ϵ_{zz} = 165.4).³¹

The magnitude of the static dielectric permittivity can be analyzed by the mode oscillator strength as follows (see, for example, Ref. 43, and references therein):

$$\boldsymbol{\epsilon}_{ij}^{0} = \boldsymbol{\epsilon}_{ij}^{\infty} + \sum_{m} \Delta \boldsymbol{\epsilon}_{m,ij} = \boldsymbol{\epsilon}_{ij}^{\infty} + \frac{4\pi}{\Omega_{0}} \sum_{m} \frac{S_{m,ij}}{\omega_{m}^{2}}$$

where Ω_0 is the volume of the primitive unit cell and ω_m is the wave number of the mode *m*. $S_{m,ij}$ is the mode-oscillator strength of the mode *m*, related to the eigendisplacements $U_m(\tau i)$ of the atom τ in the *i* direction and Born effective charge tensors by

$$S_{m,ij} = \left(\sum_{\tau i'} Z^*_{ii',\tau} U^*_m(\tau i')\right) \left(\sum_{\tau' j'} Z^*_{jj',\tau'} U_m(\tau' j')\right)$$

Displacements are normalized in the condition

$$\sum_{\tau j} M_{\tau} [U_m^*(\tau j)] U_n(\tau j) = \delta_{mn}$$

where M_{τ} is the mass of the atom τ . The magnitudes of the mode-oscillator strengths (Table II) are comparable to the calculated values for the rutile phase.³¹

IV. CONCLUSION

We have investigated the dynamical and dielectric properties of the anatase phase of titanium dioxide using the firstprinciples calculation based on density functional perturbation theory. We have calculated the Born effective charge tensors, the phonon wave numbers at the center of the Brillouin zone, the phonon dispersion, and the electronic/static dielectric permittivity tensors. Our theoretical predictions are consistent with the experimental values. The Born effective charge tensors of the anatase phase are anomalously large and explained in terms of a mixed covalent-ionic Ti-O bonding, as was explained for the rutile phase. The anisotropic character has been explained in view of the local atomic structure of the Ti or O site. The subtle difference of the local geometry of the O site in rutile and anatase phase may lead to the quantitative difference of the anisotropy of the effective charge tensors of oxygen atoms. We have presented possible explanations for the experimental difficulties to detect the E_g (2) mode and to distinguish $B_{1g}(2)$ and A_{1g} modes

*Electronic address: mikami.masayoshi@mv..m-kagaku.co.jp

- [†]Also at Department of Chemical System Engineering, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, To-kyo 113-8656, Japan.
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from our theoretical perspective. The predicted silent mode of B_{2u} may be more reliable than the previous results calculated by empirical models. The calculated dielectric permittivity tensors agree with the other theoretical result and the latest IR experimental results. The magnitude of the dielectric permittivity tensors is rather large, although it is still smaller than those of the rutile phase. Further experimental studies are thus awaited to resolve the issues of the somewhat large difference between theoretical predictions and experimental results in several normal vibrations and the discrepancy of the experimental dielectric permittivity tensors, with anatase crystalline specimens of sufficiently good quality.

The present work in conjunction with our previous theoretical work³⁴ demonstrates that first-principles calculations based on LDA can describe both the structural and dynamical properties of the anatase phase of TiO_2 as a whole. The present results thus encourage further theoretical works. For example, a theoretical study of other polymorphs such as the brookite phase could be helpful to understand the experimental results.⁵⁷

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⁴⁵Gonzalez *et al.* assumed that the effective ionic charges is static to have the crystal neutrality condition $(Z_{zz,TI}/Z_{zz,O} = -2)$. Thus they showed their concern about the somewhat large effective charge tensor element in comparison to the nominal charge -2. However, their assumption of the *static* ionic charges is not necessary. The neutral condition about the *dynamical* charge tensors is always requested from the acoustic sum rule. See also Ref. 60.

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