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Dielectric constants and Born effective charges of TiO_2 rutile

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The high-frequency dielectric-constant tensor and the Born effective charge of TiO_2 rutile are calculated using variational density-functional perturbation theory. The calculated structural properties and high-frequency dielectric constant show agreement with experiments at the level of a few percent. The Born effective charges of TiO_2 rutile are found to be much larger than the charges corresponding to Ti^{4+} or O^{2-} ions. We compare these results with those obtained for SiO_2 stishovite, for which the value of the Born effective charges is closer to an ionic picture.

TiO_2 forms several polymorphs such as naturally occurring rutile, anatase, and brookite. Dielectric and optical properties of TiO_2 have been extensively studied because of its role as a dielectric material for electronic devices and a refractory material in glazes, enamels, and glasses. TiO_2 in the tetragonal structure, called rutile, is of special importance: more than 20 compounds crystallize in the same structure,[1] allowing for detailed comparison of different properties. Despite the structural analogy and isovalency of Ti and Si ions, rutile and stishovite, a high-pressure polymorph of SiO_2, have pronounced differences in dielectric, optical, and lattice-dynamical properties. Rutile has unusually large static dielectric constants with substantial frequency dependence and is regarded as an incipient ferroelectric due to soft long-wavelength transverse-optic mode,[2–4] whereas all of these are not observed in stishovite. These distinct behaviors can be attributed to the fact that Ti in rutile is a transition-metal element with $3d$ electrons, while SiO_2 has only s and p electrons. The large static dielectric constants and incipient ferroelectric properties can also be found in perovskites.[5]

Calculations of structural and dielectric properties of rutile from first principles complement knowledge from experiments. In this work, we perform *ab initio* calculations of the ground-state structure within density-functional theory,[6] and high-frequency dielectric constant tensors and Born effective charge of rutile using density-functional perturbation theory.[7,8] Calculated structural properties and high-frequency dielectric constants show reasonable agreement with experiments. Born effective charges of TiO_2 rutile are found to be much larger than the charges that would be transferred in a pure ionic-bonding picture (+4 for Ti, and −2 for O), while those of SiO_2 stishovite are approximately equal to these nominal ionic charges.

Density-functional theory (DFT), widely used for the study of material properties, has been already described in several review papers, to which we refer the reader.[9,10] We worked in the local-density approximation (LDA) to the exchange-correlation energy. The density-functional perturbation theory (DFPT) comes from the use of perturbation-theory tools within DFT. It allows an efficient and accurate calculation of derivatives of the total energy with respect to different perturbations. Dielectric tensor and effective charge tensor are related, respectively, to second-order derivatives of total energy with respect to electric field, and mixed second-order derivatives of total energy with respect to electric field and ionic displacement.[7] We have used a recently proposed variational approach to DFPT,[8] in which a self-consistent conjugate-gradient minimization algorithm[11] is used.

Extended norm-conserving pseudopotentials for Ti and O atoms replace the bare electron-ion interaction. We have considered $3s$, $3p$, $4s$, and $3d$ as valence states for the Ti pseudopotential, and $2s$ and $2p$ as valence states for the O pseudopotential.[12] The O pseudopotential conserves the chemical hardness.[13] Electronic wavefunctions are expanded in a plane-wave basis up to kinetic energy 90 Ryd. Brillouin-zone integration is done with **k** points in a (4,4,6) Monkhorst-Pack grid,[14] corresponding to nine points in the irreducible Brillouin zone. Further, details on our method can be found elsewhere.[12,15] These techniques were applied to systems of SiO_2 such as α quartz[8]

TABLE I. Structural parameters of rutile. Lattice constants a and c are in Å and the unit-cell volume v_0 is in Å^3.

	a	c	v_0	c/a	u
This work	4.534	2.920	60.04	0.6439	0.3037
Experiment (Ref. 18)	4.5936	2.9587	62.434	0.6441	0.3048
Theory (Ref. 19)	4.653	2.965	64.84	0.637	0.305
Theory (Ref. 20)	4.584	2.961	62.22	0.646	0.304

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and stishovite[16] and demonstrated good agreement with experiments.

First, we calculate the structural parameters of rutile. Rutile has a symmetry of D_{14}^{4h} in which Ti atoms are at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and O atoms are at $(u,u,0)$, $(1-u,1-u,0)$, $(\frac{1}{2}-u,\frac{1}{2}+u,\frac{1}{2})$, and $(\frac{1}{2}+u,\frac{1}{2}-u,\frac{1}{2})$. We obtain lattice constants a and c, the internal parameter u from the minimum-energy configuration. In Table I, we compare our results to experiments and other density-functional-theoretical values. Lattice constants agree with experiments within 2% and the internal parameter u within 0.5%. Our calculated structural parameters will be used for further calculations.

Next, we calculate electronic (high-frequency) dielectric constant tensors of rutile. The dielectric constant is 7.535 along a axis and 8.665 along c axis. The corresponding experimental values[2] are 6.843 and 8.427, respectively. Discrepancies can be attributed to well-known LDA underestimation of band gaps as well as the fact that our calculation represents 0 K, while the experiment was done at room temperature. Similar sizes of errors were found in LDA calculations on dielectric constants of Si,[17] α quartz,[8] and stishovite.[16] Here, we note that the anisotropy is only qualitatively reproduced, unlike the one of α quartz. The calculated high-frequency dielectric tensors of stishovite are 3.31 and 3.50 along a and c axis, respectively. Therefore, the ionic polarizabilities in rutile are much larger than those in stishovite.

We also calculate Born effective charge tensor Z_{ij}^* of rutile. In the rutile structure, the effective charge tensors of the constituent atoms have only three independent parameters. In Table II, we show the effective charge tensors of Ti and O atoms in rutile in comparison with those of Si and O atoms in stishovite. When we take coordinate axes along and perpendicular to the bond directions, the effective charge tensors are diagonalized. The diagonal elements are the principal values ζ_i^* of the effective charge tensors, also shown in Table II. ζ_i^*'s of rutile, ranging from 5.340 to 7.543 for Ti and from -1.365 to -4.983 for O atoms are much larger than those of stishovite. These effective charges of rutile are larger than the maximum possible valencies in a pure ionic-bond picture, which are +4 for Ti and -2 for O atoms. For Si and O atoms in stishovite, the effective charges are close to valencies in an ionic bond.

TABLE II. Born effective charge tensors Z_{ij}^* and their principal values ζ_i^* of the Ti (Si) atom at $(0,0,0)$ and the O atom at $(u,u,0)$ in rutile (stishovite). The effective charge tensors for other Si and O atoms can be found by symmetry consideration. Components not shown are zero. Results on stishovite are from Ref. 16.

	Rutile		Stishovite	
Component	Ti	O	Si	O
Z_{xx}^*, Z_{yy}^*	6.335	-3.174	3.803	-1.902
Z_{xy}^*, Z_{yx}^*	0.995	-1.809	0.343	-0.557
Z_{zz}^*	7.543	-3.767	4.055	-2.027
ζ_1^*	7.330	-4.983	4.146	-2.459
ζ_2^*	5.340	-1.365	3.460	-1.345
ζ_3^*	7.543	-3.767	4.055	-2.027

Due to the asymmetry of the rutile structure, the effective charges of atoms in both rutile and stishovite are anisotropic. Since Ti or Si atoms are in relatively symmetric environments, i.e., at centers of O octahedra, the principal values of the effective charges differ only by 29% for Ti atoms in rutile and 17% for Si atoms in stishovite with respect to the z components. However, O atoms have threefold coordinations and their effective charges are more anisotropic. The principal values differ 96% in rutile and 55% in stishovite. The anisotropy of the effective charges for Ti and O atoms in rutile is larger than that of Si and O atoms in stishovite.

In conclusion, we have calculated high-frequency dielectric constants and Born effective charges of rutile. The high-frequency dielectric constants show reasonable agreement with experiment. The Born effective charges of rutile is much larger and more anisotropic than those of stishovite in the same structure. These large effective charges of rutile exceed the maximum possible charge transfer in an ionic-bond picture.

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