Quantum Monte Carlo study of high-pressure cubic TiO_2

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We have studied the high-pressure cubic fluorite polymorph of TiO_2 (c-TiO_2) using the diffusion Monte Carlo (DMC) method. The estimated bulk modulus is within the range reported previously in density functional studies, high, but does not rival that of diamond. The calculated excitation energies within DMC are consistent with the results of GW approximation. The infrared frequency of c-TiO_2, obtained via the frozen phonon method within DMC, shows non-negligible anharmonicity. This suggests that c-TiO_2 might be stabilized if this anharmonicity is considered. Our DMC results could help to establish more accurate results for c-TiO_2 compared with the widely-scattered mean-field results. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4730608]

Titanium dioxide (TiO_2) is of great interest due to its wide range of applications in the semiconductor technology and electrochemical industries.[1] The optical and electronic properties of TiO_2 make it a dominant candidate for anti-reflection coating of solar cells or as a pigment in the polymer industry.[2] TiO_2 exhibits many crystalline polymorphs at different temperatures and pressures, including the high-pressure cubic fluorite structure.[3–7] Mattesini *et al.*[8] have demonstrated that c-TiO_2 has important optical absorption transitions in the visible light range which could enable it to efficiently absorb sunlight, so that it might be an important candidate material for solar cell materials.[8] Subsequently it was found that c-TiO_2 could be synthesized at a pressure of 48 GPa and temperatures between 1900 and 2100 K.[9] One of the important remaining questions is whether the structure of the experimentally synthesized phase is cubic fluorite (space group $Fm\bar{3}m$) or pyrite (space group $Pa\bar{3}$), which is a distortion of fluorite. Kim *et al.*[10] have reported that fluorite is stabilized under pressure, whereas pyrite showed an instability throughout the whole pressure range. However, the situation is rather unclear. The experimental bulk modulus of c-TiO_2 is lower than predicted by density functional theory (DFT) calculations. Swamy and Muddle[11] reported a large bulk modulus for c-TiO_2, claiming a hardness greater than those of known hard materials, although a study by Liang *et al.*[12] does not support this conclusion. Recently, Zhou *et al.*[13] discussed a mechanism which might account for the discrepancy between the experimental and DFT bulk modulus of c-TiO_2 phase. They showed that an abrupt change in the energy-volume curve of TiO_2 at 43 GPa arises from a phase transition from the columbite structure (*Pbcn* space group) to a modified fluorite structure (*Pca*21). The present authors[14] have also claimed that the experimental structure may not be fluorite. The wide variation in the DFT results demonstrates the need for more reliable calculations beyond mean-field approaches, for example, using quantum Monte Carlo (QMC) methods. In the present work we have studied the fluorite structure of c-TiO_2 at high-pressures using both DFT and QMC methods. Bulk properties are obtained by fitting the calculated results to a model equation of state (EOS). Excitation energies at the Γ and *X* points, as well as the IR frequency, are evaluated using QMC.

We performed DFT calculations using a plane wave basis set and pseudopotentials (PPs) as implemented in the Quantum ESPRESSO (QE) package.[15] We used both the local-density approximation (LDA) Perdew-Zunger (PZ)[16] and generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE)[17] density functionals. Ultrasoft[18] PPs (USPPs) were used for both Ti and O. The Brillouin-zone (BZ) integrations were performed using $8 \times 8 \times 8$ Monkhorst-Pack meshes.[19] A plane wave cutoff energy of 45 (1000) Ry was used for the plane wave expansions of the wave functions (charge density).

We used Dirac-Fock[20] and norm conserving O and Ti PPs (NCPPs) for the QMC calculations. The Ti NCPP was constructed using the atomic code implemented in QE, with 12 valence electrons ($3s^2\ 3p^6\ 3d^2\ 4s^2$). We have performed careful tests of our PPs by (1) comparing DFT results for rutile TiO_2 obtained with our PPs to results with the default PPs provided with QE and (2) comparing with full-potential linearised augmented-plane wave (FP-LAPW) results obtained with the WIEN2k code.[21] We also tested softer Dirac-Fock Ti PPs from the literature.[22,23] We have confirmed that larger core Dirac-Fock Ti PPs, in which the 3*s* electrons are treated as core states, overestimate the lattice constants, which demonstrates the importance of the 3*s* semi-core electrons for the binding. We therefore decided to use a small core Ti NCPP generated within DFT in which the 3*s* electrons are treated explicitly. The results for the benchmark rutile phase of TiO_2 along with other available data are presented in Tables I and II, respectively.

The PBE functional overestimates the lattice parameters and hence underestimates the phonon frequencies, as has been reported in other GGA calculations. The consistency among the DFT results supports the validity of our PPs. The muffin-tin radii for the Ti and O atoms in the all-electron calculations were chosen to be 1.95 and 1.73 a.u., respectively. We employed $R_{MT}K_{MAX} = 8$ in the FP-LAPW calculations, where R_{MT} is the minimum radius of the muffin-tin spheres and K_{MAX} gives the magnitude of the largest *k* vector in the

TABLE I. The structural properties of rutile TiO_2 at zero pressure. a and c are the lattice parameters of the crystal, u is the internal parameter, and V is the volume per cell.

Method	a (Å)	c (Å)	u	V (Å^3)
PBE-NCPP[a]	4.643	2.970	0.306	64.095
PBE[b]	4.641	2.966	0.305	63.884
Expt.[c]	4.587	2.954	0.305	62.154

[a]This work.
[b]Reference 24.
[c]Reference 25.

plane wave expansion. Our PBE-NCPP results are consistent with the all-electron FP-LAPW, again supporting the validity of our PPs, as shown in Table III.

The QMC calculations were performed using the CASINO code.[29] Trial wave functions of Slater-Jastrow type were used, with the parameterized Jastrow factor of Ref. 30 and a total of 48 variational parameters, whose values were optimized using the variance minimization scheme of Ref. 31. The single particle orbitals were generated using QE-DFT (Ref. 15) and the PBE-NCPP with a plane wave cutoff energy of 3800 eV. The plane-wave orbitals were converted to a Blip (B-spline) representation as described in Ref. 32, which greatly improves the more efficiency of the QMC calculations. After carefully examining the time step bias using the scheme explained in Ref. 33, we chose to use a time step of $dt = 0.01$ a.u., which gives a very weak dependence of the time step bias on the volume. We used a target number of walkers of 640. To investigate the finite-size errors in the QMC calculations we used the method proposed in Ref. 34, which we refer to as the CCMH method after its authors. Another common way to account for finite size effects is to replace the Ewald electron-electron interaction by the Model Periodic Coulomb (MPC) potential.[35–37] We have found that these corrections give the same results within statistical errors in this case. Another scheme known as the KZK correction[38] is available, which is evaluated by performing DFT calculations using a functional which is fitted to DMC data for homogeneous electron gases of different densities. The locality approximation used to evaluate the nonlocal part of the pseudopotential energy in DMC is another source of the bias.[39] To investigate this bias we also used the T-move scheme[39] to calculate the nonlocal energy. However, the results with the T-move and locality schemes were consistent with another, which suggests that the bias due to the approximate scheme for evaluating the nonlocal energy is small in this case.

TABLE II. The Raman modes of rutile TiO_2 at zero pressure.

Method (cm^{-1})	PBE-NCPP[a]	PBE[b]	Expt.[c]	Expt.[d]
B_{1g}	160.4	154.2	142	143
A_{2g}	422.9	423.6	···	···
E_g	431.8	429.2	445	447
A_{1g}	580.9	565.9	610	612
B_{2g}	780.0	774.3	825	827

[a]This work.
[b]Reference 24.
[c]Reference 26.
[d]Reference 27.

TABLE III. The calculated lattice parameter (a), bulk modulus (B_0), the first pressure derivative of bulk modulus (B_0'), and the equilibrium volume (V_0) of c-TiO_2 at zero pressure.

Method	a (Å)	B_0 (GPa)	B_0'	V_0 (Å^3)
LDA-USPP[a]	4.734	286	3.99	106.35
PBE-USPP[a]	4.829	225	4.45	112.58
PBE-NCPP[a]	4.836	249	4.24	113.09
PBE-WIEN2k[a]	4.840	250	4.33	113.30
DMC (Ewald + CCMH)[a]	4.778	249(6)	6.3(6)	109.1(2)
LDA[b]	4.72	···	···	105.16
BSTATE-GGA[c]	4.822	272	4.68	···
BSTATE-LDA[c]	4.729	324	4.68	···
GGA[d]	···	395(4)	1.75(5)	112.75(6)
GGA[e]	···	277	4.07	112.70
Expt.[f]	4.870	202(5)	1.3(1)	115.50(2)

[a]This work.
[b]Reference 28.
[c]Reference 12.
[d]Reference 11.
[e]Reference 13.
[f]Reference 9.

We have studied the EOS of c-TiO_2 using both the DFT and QMC methods. We used periodically repeated simulation cells containing 81 atoms ($3 \times 3 \times 3$ supercell). The orbitals were calculated at the L point in the BZ of the simulation cell to reduce the finite size errors.[40] The DMC data was accumulated over at least 6000 steps, leading to statistical errors of less than 10 meV/atom. Figure 1 shows the DMC energy data including finite size corrections from both the CCMH and KZK schemes, fitted to a 3rd order Birch-Murnaghan EOS.[41] The calculated EOS parameters along with our DFT results and other available data are presented in Table III. As the finite size corrections calculated with the various different schemes are within statistical error bars of one another, we henceforth concentrate on the Ewald + CCMH data.

The DMC results for the lattice parameter and bulk modulus are within the range obtained with the LDA and GGA and are different from the experimentally reported value.[9] It is well known that the LDA (GGA) tends to underestimate (overestimate) lattice parameters,[42] which is consistent with the fact that our DMC result is intermediate between the LDA and GGA results. This implies that there is another reason for the discrepancy between the theoretical and experimental results for c-TiO_2. This would support the suggestion of Zhou *et al.*[13] that the experimental structure may not be c-TiO_2. To obtain a more accurate comparison, we tried to estimate the thermal effects in our calculations. However, since the phonon dispersion of c-TiO_2 has negative branches at all the volumes studied,[10] the thermal effects cannot be evaluated accurately within the harmonic approximation.

In DMC calculations, the excitation energies of c-TiO_2 at the X and Γ wave vectors were evaluated by promoting an electron from the occupied valence states at X or Γ into the unoccupied conduction band states at X or Γ. This creates an exciton, and consequently the excitation energy is reduced by its binding energy, which can be approximated by the Mott-Wannier formula,[43] $E_b = 1/2\varepsilon r$, where ε is the relative permittivity and r is the localization radius. The value of ε is

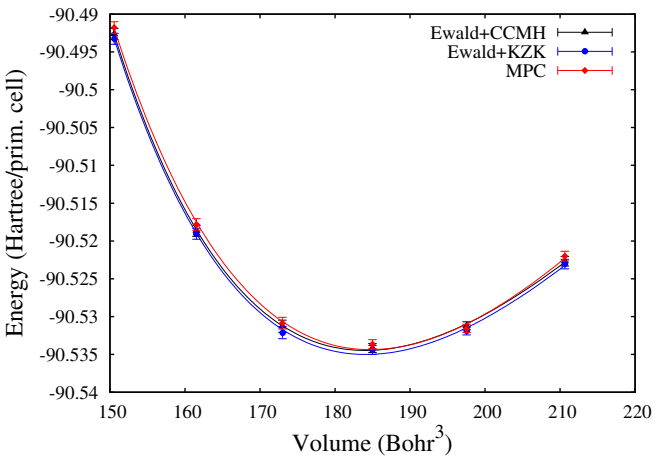

FIG. 1. MPC and Ewald DMC energies per atom in the CCMH and KZK schemes. The lines are 3rd order Birch-Murnaghan fits to the data points.

TABLE V. The frequency of the IR mode of c-TiO_2 at zero pressure calculated using the frozen phonon method and the Demo-Phonon (Ref. 45) and WIEN2k codes.

	Harmonic IR frequency (cm^{-1})	
Method	DFPT[a]	Frozen phonon
LDA-USPP[b]	109.6	119(1)
PBE-USPP[b]	i71.5[c]	i36(3)
PBE-NCPP[b]	i73.5	i84(3)
Supercell method, FP-LAPW[b]	···	117.6
DMC[b]	···	212(4)
DMC with SCH correction[b]	···	226(5)
LDA[d]	176.5	···

[a]DFPT stands for density functional perturbation theory.
[b]This work.
[c]i denotes unstable (imaginary) frequencies.
[d]Reference 28.

estimated to be large for c-TiO_2, and this correction is tiny. We used the same optimized Jastrow factor as in the ground state calculations, which promote cancellation of errors between the ground and excited state calculations. Various excitation energies were computed within DMC for a $2 \times 2 \times 2$ supercell. The DMC and DFT results are reported in Table IV, along with GW data from the literature. As expected, the QMC method improves on the DFT estimates. The DMC band gaps are generally larger than the GW ones. More reliable results could be obtained with larger simulation cells, but such calculations would be very expensive.

Rignanese *et al.*[28] have shown that c-TiO_2 could be a suitable candidate for semiconductor device applications. The high dielectric permittivity of the material is related to its IR frequency. However, there is a discrepancy between the LDA and all-electron FP-LAPW frequencies obtained within the harmonic approximation (see Table V). We therefore calculated the IR mode within the frozen phonon method by the more accurate DMC approach. In this mode the Ti atom moves outwards (u_{Ti}) whereas the O atom moves inwards (u_O) such that the center of mass within the unit cell remains unchanged, i.e., $u_{Ti}/u_O = 2M_O/M_{Ti}$, where M is the mass. We used values of u_O in the range 0.09-0.27 a.u. so that we could distinguish the changes in energy arising from the atomic displacements from the statistical error bars of 0.0001 Hartree per atom. We then extracted the quartic anharmonicity from the potential. The error bar for the harmonic frequency is less than $10\,cm^{-1}$.

The results including the finite size error corrections were well fitted by a polynomial, $\Delta E(u) = A_2u^2 + A_4u^4$, with a relatively large ratio of $A_4/A_2^2 \approx 4$. The variation of E(u) with the displacement of the O atom is plotted in Fig. 2. The harmonic IR frequency obtained from $\Delta E(u)$ is given in Table V. The CCMH and KZK finite size correction schemes are found to give consistent results for the IR frequency. Note that we used different lattice constants for the DFT and DMC calculations, each obtained as the equilibrium value from the EOS.

Having evaluated the anharmonic contribution to the IR frequency, we obtained a better estimate using the self-consistent harmonic (SCH) method[46] (see Table V). The correction increases the IR frequency by about 7%. This suggests the importance of anharmonicity in c-TiO_2. We have not investigated the effect of including anharmonicity on the whole phonon spectrum because of the computational expensive. However, the anharmonicity, as well as the phonon-phonon interaction, has an important role in stabilizing materials which may be predicted to be unstable within the conventional approaches such as density functional perturbation theory.[47,48] The case of c-TiO_2 is interesting for the investigation of anharmonicity, as the question of its stability is still controversial.

TABLE IV. The Excitation energies at the Γ and X wave vectors of c-TiO_2. The statistical error bars on the DMC energies are ±0.07 eV. $\Gamma_{25'\nu} \rightarrow \Gamma_{15\nu}$ is the width of the valance band at the Γ point calculated via indirect excitations to X_{2c}, and $X_{5\nu} \rightarrow X_{2'\nu}$ is the width of the two highest valance bands at the X-point calculated via indirect excitations to Γ_{12c}.

	(in unit of eV)					
Exciton	DMC (Ewald)[a]	LDA-USPP[a]	PBE-USPP[a]	PBE-NCPP[a]	PBE-WIEN2k[a]	GW[b]
$X_{2'\nu} \rightarrow \Gamma_{12c}$	2.90	1.05	1.11	1.22	1.13	2.369
$X_{5\nu} \rightarrow \Gamma_{12c}$	5.21	3.29	3.17	3.23	3.17	4.932
$\Gamma_{15\nu} \rightarrow X_{2c}$	4.76	2.76	2.65	2.63	2.64	3.994
$\Gamma_{25'\nu} \rightarrow X_{2c}$	10.76	8.27	7.67	7.62	7.63	9.921
$\Gamma_{15\nu} \rightarrow \Gamma_{12c}$	4.10	1.98	1.97	2.06	1.98	3.602
$\Gamma_{25'\nu} \rightarrow \Gamma_{15\nu}$	6.01	5.49	5.02	4.98	4.99	5.927
$X_{5\nu} \rightarrow X_{2'\nu}$	2.31	2.23	2.06	2.02	2.04	2.563

[a]This work.
[b]Reference 44.

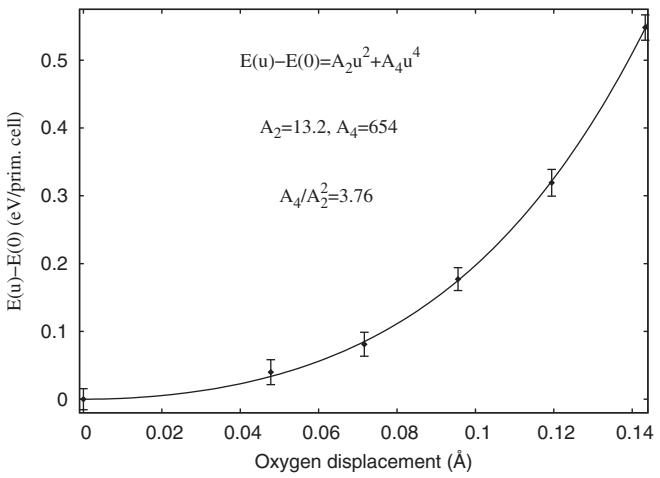

FIG. 2. The variation of E(u) with the O displacement for the IR (TO) mode of c-TiO_2, calculated within DMC. The calculations were performed at the zero-pressure volume obtained from the DMC equation of state.

In summary, we have presented results for the equation of state of c-TiO_2 obtained with the DMC method. The bulk modulus calculated for c-TiO_2 is within the range of values obtained in DFT calculations; it is large, but not comparable to that of diamond. The $X_{2'\nu} \rightarrow \Gamma_{12c}$ band gap calculated within DMC is substantially larger than the DFT values and is a little larger than the GW value. The IR frequency shows a relatively large anharmonicity, which suggests that c-TiO_2 is an interesting case for studying anharmonicity and phonon-phonon interactions. We have also suggested that the cubic phase might be stabilized at finite temperatures by anharmonic vibrational effects.

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