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Relative stability, structure, and elastic properties of several phases of pure zirconia

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(Received 28 July 1997)

The structure of ambient- and high-pressure (OrthoI and OrthoII) phases of ZrO₂ have been studied using *ab initio* local-density-functional theory. Energetics, the equation of state, and bulk modulii of these phases were determined. Such calculations have been able to clarify the various high-pressure forms of the material. Several other potential forms of the material are also investigated and their properties compared with the identified phases. [S0163-1829(98)01502-1]

I. INTRODUCTION

 ZrO_2 is an important modern ceramic used as a refractory, in oxygen sensors and, as a gem, a substitute for diamond. It is polymorphic over a wide range of temperatures and pressures; consequently the transformation toughening — particularly pressure induced — is of considerable current interest. This is notwithstanding the fact that zirconia is expected to have analogous chemical and structural properties to SiO₂ (Ref. 1) and other potentially hard² ceramics with important geophysical implications.

About ten distinct phases of zirconia have been observed to date experimentally, although it is possible that some of these may be misinterpretations of others. It is well known that zirconia assumes a monoclinic³ $(P2_1/c)$ or *baddeleyite* unit cell containing four ZrO_2 molecules (Z=4) at ambient conditions. It transforms into a tetragonal⁴ form $(P4_2/nmc, Z=2)$ at about 1440 K, a cubic fluorite (Fm3m, Z=4) form⁵ around 2640 K, and then finally a melt at about 2950 K. There is less consensus on the structure of the high-pressure phases, the main reason for this being the difficulty associated with in situ high-pressure experiments. Confusion also arises from the differing sets of conditions and histories of the various samples, but it is generally accepted that zirconia assumes an orthorhombic symmetry in at two regions in its phase diagram. Magnesiastabilized tetragonal zirconia cooled to around 30 K has been found to transform to an orthorhombic phase⁶ with space group $Pbc2_1$. A closely related structure, with space group Pbca, has been found by quenching powdered zirconia from 900 K and 6 GPa,⁷ from *in situ* experiments⁸ at room temperature, and as small grains in a ZrO₂-MgAl₂O₄ composite.9 This phase is isostructural with brookite (TiO₂, Z=8) and consists of alternate domains of $Pbc2_1$ oxygen nets resulting in the doubling of the *a* lattice parameter. Yet another related phase with space group *Pbcm* has been observed twice.^{10,11} This phase is unusual in that it is disordered with an oxygen sublattice consisting of the average of differing $Pbc2_1$ domains which occur with equal probability. This type of disorder is rare at low temperatures and a consequence of this is a large increase in entropy across the phase transition. Pbca (one domain) and $Pbc2_1$

are both maximal subgroups of Pbcm (Ref. 12) and virtually indistinguishable by x-ray distribution (XRD) techniques due to the low oxygen scattering factors. They are, however, easily distinguishable by neutron diffraction. However, veryhigh-pressure neutron diffraction experiments are not currently practical, and so it would be a useful¹² exercise to determine the preferred structure under pressure and its atomic positions. We label this, the first high-pressure phase encountered at low temperature, as OrthoI.

Another orthorhombic phase has been reported by several authors^{1,13-16} and determined to be isostructural to the ninefold coordinated cotunnite (PbCl₂) structure. This phase is readily obtained after quenching from about 1000 °C and 18 GPa. An x-ray study at ambient temperature by Block et al.¹³ reportedly produced the cotunnite phase at pressures greater than 16.6 GPa. However, Léger et al.8 also using in situ XRD at room temperature found a phase transition from OrthoI to another orthorhombic phase at around 22 GPa, but argued against it having cotunnite-type structure. Similarly Arashi et al.¹⁷ observed a phase transition at 13 GPa and 15 GPa using in situ XRD and micro Raman spectroscopy, respectively, but were not able to confirm a cotunnite structure. The cotunnite phase is promising as a new superhard material as it appears to have a high bulk modulus of about 320 GPa^{13,15} which approaches that of diamond (440 GPa). This phase appears to be quenchable^{1,15} and a cotunnite structure has also been proposed for Ca- and Y-stabilized zirconia.^{18,19} Following convention we will label the cotunnite phase as OrthoII.

Recently a hexagonal phase was found by Ohtaka *et al.*²⁰ by quenching pure ZrO_2 powders from above 1000 °C and 20 GPa. This structure is plausible as it appears to have an increased symmetry derived from that of OrthoII which itself has a pseudohexagonal packing of the O atoms to start with. In an early article Davey²¹ also found a triangular close-packed lattice, but this report should be regarded as questionable.

The nature of the post-cotunnite phase is not known, but a quenchable tetragonal phase distinct from the high-temperature tetragonal structure was reported by Arashi *et al.*¹⁷ at 35 GPa and was retained up to 60 GPa. The low number of Raman bands indicated that this phase had pos-

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sible inversion symmetry and the most likely space groups were P4/m, $P4_2/n$, P4/mmm, or P4/mbm. Ming and Manghnani¹⁶ found that post-laser-treated zirconia at 7.3 GPa had an x-ray pattern very similar to the tetragonal MnF₂,²² and this is one possibility we shall explore later in this paper. A tetragonal phase obtained at 3.3 and 4.4 GPa by Block¹³ *et al.* and the orthorhombic $P2_12_12_1$ (Refs. 23,24) we suggest are misinterpretations of the OrthoI phase. Zirconia has also been made to adopt a rhombohedral cell in stabilized zirconia²⁵ and the abraded surfaces thereof,²⁶ considered to be distortion of fluorite along the [1 1 1] direction.

It is also possible to make reasonable guesses of possible polymorphs by comparison of analogous oxides or halides. We will consider the stability of ZrO_2 isostructural to (a) *rutile*-TiO₂, also adopted by a number of oxides including SiO₂ (*stishovite*), (b) alpha-PbO₂ (*columbite*), (c) *anatase*-TiO₂, and (d) a modified fluorite-type structure with space group $Pa\overline{3}$ proposed for high-pressure SiO₂.²⁷

In most instances, for these types of materials, the coordination number of the cation increases with increasing pressure due to the larger compressibility of the anions. Recently, Léger *et al.*²⁸ found a hexagonal phase in BaF₂ with coordination of 11, which is the highest reported for ionic compounds with the AX₂ stoichiometry. This will also be tested as a potential post-cotunnite phase for zirconia.

In this paper we calculate at an *ab initio* level the geometries, total energies, and bulk moduli of virtually all known and postulated phases of zirconia. As the most important open questions on the structure and phase diagram of zirconia relate to the *in situ* form of OrthoI, the energetics of OrthoII, and the nature of even higher-pressure or highpressure and -temperature phases we hope that the present investigation may contribute to answering answer some of these questions.

II. COMPUTATIONAL APPROACH

We use the local-density approximation (LDA) functional of Ceperley and Alder,²⁹ as parametrized by Perdew and Zunger,³⁰ to obtain accurate exchange and correlation energies of the electronic wave function for a particular ionic configuration. A plane wave basis is used and sampled over reduced k points. This necessitates the use of soft pseudopotentials, of which the Troullier-Martins³¹ scheme was used here. For the Zr pseudopotential, cutoff radii of 2.64, 3.08, and 2.34 a.u. were used for the s, p, and d components, respectively. For O, radii of 1.45 a.u. were used for both the s and p channels. A criterion of at least 10^{-4} eV/Atom was placed on the self-consistent convergence of the total energy and most of the calculations reported here used a plane wave cutoff of 64 Ry. In some cases the results were tested with a larger number of plane waves and k points. Little variation was found. Throughout, the approach was implemented through the FHI94 code available from the Fritz Haber Institute. Berlin.

Just as the experimental conditions make the elucidation of the crystal structures a difficult task, so too do computational restrictions on any theoretical study of such materials. First the number of atoms in the static cell (limited here to about 30) imposes somewhat constrictive boundary conditions on the system. It also excludes a calculation of the



FIG. 1. Most common (ambient) phases of $ZrO_2:P2_1/c$ (baddeleyite), Fm3m (fluorite), and $P4_2/nmc$ (high-temperature tetragonal phase). Larger spheres represent oxygen atoms.

disordered phase of zirconia, where one could conceivably average over a large ensemble of randomly generated motifs, but many hundreds of atoms would be needed. There are methods³² for efficiently dealing with disordered solids within a periodic framework but we have not implemented any of these. Second, the calculations are performed effectively at zero temperature although the use of experimental geometry and the maintenance of point group symmetry during lattice relaxation presumably simulates some thermal effect as the atoms relax. This and the first point prevent a rather detailed study of the actual phase transition mechanisms, especially if they are phonon driven.

III. RESULTS AND DISCUSSION

A. Ambient-pressure phases

We are more concerned in this paper with the lesserknown high-pressure phases of ZrO_2 than with the nature, stabilizing, and transitions of the high-temperature structures, which is quite an involved study in itself^{33–35} and certainly not well known theoretically. Consequently the three more well-known ambient-pressure phases were primarily used as benchmarks to test for the transferability of the Zr and O pseudopotentials. These are the baddeleyite, tetragonal, and cubic phases, respectively, with unit cells shown in Fig. 1. The structural parameters were taken from experiment and are given in Table I, and these parameters are used as starting points to the energy minimization procedures. Thereafter the unit cell was scaled isotropically in each case and the resulting energy versus volume curve was fitted to the first-order Birch³⁶ equation of state

$$E = \frac{9}{16}B_0V_0(\rho - 1)^2[B_0'(\rho - 1) - 4\rho + 6] + E_0$$

TABLE I. Experimental parameters of posible structures of the ambient phases of ZrO_2 : (a) baddeleyite $(P2_1/c)$, (b) tetragonal $(P4_2/nmc)$, and (c) fluorite (Fm3m).

System	Lattice constants (Å)	Wykoff coordinates
Baddeleyite $(P2_1/c)$	a = 5.168 b = 5.232	Zr(0.276,0.041,0.208) O (0.070,0.336,0.341) O (0.442.0.755.0.479)
Tetragonal $(P4_2/nmc)$	a = 3.6570 c = 5.3037	C (0.442,0.753,0.479) Zr(0.750,0.250,0.750) O (0.750,0.750,0.942)
Fluorite (<i>Fm</i> 3 <i>m</i>)	a=5.53	Zr(0.000,0.000,0.000) O (0.250,0.250,0.250)

where $\rho = (V_0/V)^{2/3}$, B'_0 is the first derivative of the bulk modulus with respect to pressure, and E_0 , B_0 , and V_0 is the zero-pressure energy, bulk modulus, and equilibrium volume, respectively. The results are summarized in Table II.

The calculated Birch equation of state for each of the ambient structures is shown in Fig. 2; the zero-temperature state is correctly favored as the monoclinic baddeleyite $(P2_1/c)$ phase with a calculated equilibrium volume per molecule of 245.5 a.u.³ compared to 240.6 a.u.³ observed experimentally. It is known that the baddeleyite phase is highly prone to twinning and is difficult to make as good single crystals. This, and the possible dependance of elastic properties on crystallite size, is probably the cause of the wide range of measured bulk modulii published for this phase-from 95 GPa (Ref. 8) for XRD on a powdered sample, to about 189 GPa (Ref. 37) using Brillouin scattering on carefully grown single crystals. Another theoretical study using the potential-induced breathing method (which, by the way, is not as accurate to full LDA calculations) was used by Cohen, Mehl, and Boyer³⁸ who calculated a bulk modulus to be 152 GPa, i.e., within the range of the various experimental results. By rigidly scaling the unit cell we initially found the bulk modulus to be 258 GPa which prompted us to perform a further study by allowing the cell structure to relax at each compressional stage. The new results were a great improvement when compared with experiment as B_0 was calculated as 157 GPa. This shows that relaxation effects can be



FIG. 2. Calculated energy-volume Birch equation of state for the three ambient phases of ZrO_2 shown in Fig. 1.

TABLE II. Equilibrium volumes and bulk modulii of ambient phases of ZrO_2 . The experimental values are in brackets; references to the experimental values are given in the text.

System	Volume (a.u. ³)	B_0 (GPa)
Baddeleyite $(P2_1/c)$	240.6 (245.5)	157 (95–189)
Tetragonal $(P4_2/nmc)$	239.4 (239.4)	200 (176–190)
Fluorite $(Fm3m)$	229.5 (219.9)	267 (215)

very important in this type of calculation of the elastic constants of materials. Also, if the Brillouin results are to be believed, it shows that the type of atomic relaxation is purely elastic in nature. No absolute experimental determination of the elastic properties of the high-temperature phases of *pure* zirconia has been done due to the difficulties involved. However, there is a considerable amount of data available for the stabilized cubic phase and somewhat fewer for the partially—or fully—stabilized tetragonal phase. Consequently, for comparison with our calculated results, we have had to extrapolate the elastic constants down to zero impurities or to critical points.

The tetragonal phase $(P4_2/nmc)$ is a simple distortion of the cubic phase; indeed they are equivalent if the Wykoff zcoordinate of the O site is taken as zero and the ratio c/a $=\sqrt{2}$. We initially calculated the bulk modulus for the tetragonal phase to be 251 GPa with rigid scaling, i.e., not allowing for relaxation in the unit cell. The elastic constants of pure tetragonal zirconia have been taken for monoclinic data and extrapolated to the m-t critical point;³³ they are $c_{11} = 340$ GPa, $c_{12} = 33$ GPa, $c_{33} = 325$ GPa, and c_{13} = 160 GPa. The bulk modulus for tetragonal systems, B_0 $=\frac{1}{9}[2c_{11}+c_{33}+2(c_{12}+2c_{13})]$, in turn gives 190 GPa. Mirgorodsky et al.³³ performed a lattice dynamical calculation on tetragonal zirconia and obtained $c_{11}=395$ GPa, c_{12} = 26 GPa, c_{33} = 326 GPa and c_{13} = 105 GPa, giving B_0 as 176 GPa. An ultrasonic pulse method was used by Fukuhara and Yamauchi³⁹ for yittria-stabilized zirconia polycrystal, (Y)TZP, over a wide temperature range. They found that B_0 decreased steadily with increasing temperature from about 190 GPa at 300 K to 150 GPa at 1800 K. This is once again in relatively poor agreement with the nonrelaxed results. When the relaxation of the lattice was included the calculated bulk modulus was lowered to 200 GPa which is in far better agreement with experiment. Note also in Fig. 2 that the energy at the experimental equilibrium energy for both $P2_1/c$ and $P4_2/nmc$ (the lowest point on the graph) changed very little after lattice damping, indicating the close agreement between theory and experiment with regards to the optimal crystal geometry at that point. The equilibrium volume itself also fared well in our calculation, being 239.40 au³, which is in very good agreement with the experimental value of 239.41 au³.

The cubic *fluorite* phase (Fm3m) had a calculated bulk modulus of 267 GPa, which should be quite accurate as the internal atomic positions for this lattice symmetry are formally fixed here. This compares to the results for yttriastabilized cubic zirconia extrapolated to zero impurities, resulting in a bulk modulus of 215 GPa.⁴⁰ Theoretical studies include those by Cohen *et al.*,³⁸ who found a value of B_0 =288 GPa, Jansen,³⁴ who used the same density-



FIG. 3. Crystal structures of the OrthoI (brookite and $Pbc2_1$) and OrthoII (cotunnite) phases of ZrO_2 .

functional method as we did, found B_0 to be 227 GPa and Mirgorodsky *et al.*³³ determined B_0 as 194 GPa. Wilson *et al.*⁴¹ obtained $B_0 \approx 200$ GPa using several ionic models and Orlando *et al.*⁴² using full the Hartree-Fock approximation obtained 222 GPa using the Murnaghan⁴³ equation of state which tends to give somewhat lower values than the Birch equation. We also determined the zero-pressure volume of the fluorite has to be 229.536 au³ which is to within 5% of the experimental value of 219.942 au³.

The cubic fluorite phase was also used to check the convergence of the energy cutoff in the plane wave expansion and the number of special k points. We compared the total energy for a 64 Ry cutoff (which is used for subsequent calculations) to the energy using an expansion truncated at 80 Ry, and found the change was 0.027 eV/atom but this also places an *absolute* estimate of error on the energetics of the calculations. From this we can conclude that we have good convergence for our plane wave expansion to within the error of 0.027 eV/atom. Similarly we performed the same calculation using 8 and then 27 k points. Once again we found the energy remaining largely unaffected. It is therefore presumed that the same convergence will apply to the lower-symmetry systems but it is computationally far too expensive to check this directly for all the phases considered.

An estimate the average error in calculation of the geometric parameters is therefore about 3% and, equivalently, about 20% for the bulk moduli. The overall agreement with the ambient phases is therefore seen to be very good and, we feel, demonstrates the transferability of the Zr and O pseudopotentials that we have employed.

B. High-pressure phases

1. OrthoI phase

Two of the potential candidates for structures of phases of the OrthoI structure of ZrO_2 are shown in Fig. 3. As discussed earlier, calculations of the disordered phase (*Pbcm*) TABLE III. Calculated and experimental cell coordinates of two possible phases of the OrthoI structure of ZrO_2 . The experimental results were taken from Ref. 7 and 6 for the *Pbca* and *Pca2*₁, respectively. Note that the Wyckoff coordinates apply to the standard coordinate setting of **abc** with space group symbol *Pca2*₁ as opposed to the **bac** of *Pbc2*₁.

Structure	Wyckoff coordinate (experiment)	Wykoff coordinate (theory)
Pbca	Zr(0.884,0.033,0.256)	Zr(0.885,0.035,0.253)
	O(0.791,0.371,0.131)	O(0.799,0.392,0.146)
	O(0.978,0.748,0.495)	O(0.975,0.739,0.496)
$Pca2_1 (Pbc2_1)$	Zr(0.030,0.267,0.750)	Zr(0.027,0.263,0.750)
	O(0.361,0.068,0.894)	O(0.362,0.067,0.890)
	O(0.229,0.537,0.000)	O(0.227,0.532,0.997)

were not performed and so in the absence of a deeper understanding of a possible random structure of this phase identification of the OrthoI structure is tentative.

As no in situ structural parameters are available for the brookite (Pbca) phase we used data from a Rietveld analysis obtained by Ohtaka et al.⁷ on a sample quenched from 900 K and 6 GPa. For the initial lattice parameters used in the calculation we used the in situ data of Léger et al.8 performed between 8 and 11 GPa and at room temperature; they were a = 9.94 Å, b = 5.17 Å, and c = 4.94 Å. The lattice was then relaxed using a gradient method while maintaining a crystal point symmetry, in this case only inversion symmetry. The two results for the lattice coordinates are compared in Table III. The bulk modulus was calculated to be 272 GPa, which compares fairly well to 220 GPa experimental obtained by Léger et al.8 The ratio of the theoretical volumes of the monoclinic and *Pbca* phases at zero pressure is 0.915. This is acceptably close to the experimental value of Léger et al. who found the ratio to be 0.902.

The structure parameters for magnesia-partially-stabilized zirconia of Kisi *et al.*⁶ (a=5.260, b=5.068, and c=5.077 Å) were used for the closely related $Pbc2_1$ phase, and once again the atoms in the unit cell were relaxed to equilibrium; comparison between the theoretical and experimental geometry is again illustrated in Table III.

In Fig. 4 are plots of the energy vs volume for the brookite (*Pbca*) and monoclinic (*Pbc2*₁) phases. There is a region where a single domain is energetically favored (calculated to be at about 2.4 GPa), but the brookite structure in fact has the lowest equilibrium energy. This and a dynamics calculation performed with no symmetry constraints on the *Pbca* phase (which failed to produce a single O domain) leads us to suggest that brookite is in fact the preferred phase at high pressures, confirming the *in situ* work of Léger *et al.*⁸

The actual transition pressure from the monoclinic to the brookite (*Pbca*) phase we calculate to occur at 4.1 GPa. Experimental determinations of the transition pressure generally range from 3 to 11 GPa (Refs. 8,10,13,14,23,24 and 44) (including phases identified as other than *Pbca*), but Kawasaki *et al.*⁴⁵ demonstrated the strong dependance of this transition on crystallite size. For crystallite sizes >100 n.m. they found the threshold pressure to be around 3.4 GPa, which, considering the sensitivity of the calculated pressure



FIG. 4. Calculated energy-volume equation of state for possible structures of the OrthoI and OrthoII phases of ZrO_2 shown in Fig. 3. The transition from the monoclinic to *Pbca* phases is indicted by an arrow and is calculated to occur at 4.1 GPa. The transition from the brookite to cotunnite phase takes place at 19.0 GPa.

with regards to absolute energy, is in very good agreement with our calculated result.

2. OrthoII (cotunnite) phase

The cotunnite structure is also shown in Fig. 3. Experimental Wyckoff fractional coordinates for this structure were obtained from the in situ Rietveld analysis of Haines et al.¹⁵ at 24.6 GPa after recovery from laser heating. As these were not obtained from pressure alone, they are considered as only approximate parameters and from such values the cotunnite structure was optimized over both a and c unit cell dimensions and then the lattice was allowed to relax. Table IV contains details of the final stable structure. The transition pressure from the *Pbca* phase, indicated in Fig. 4, has been calculated to be 19.0 GPa. The only cotunnite-type structure to be produced at room temperature¹³ started transforming at 16.6 GPa and was completed at 22.0 GPa. Once again this is in consensus with our results. The bulk modulus was found to be 305 GPa which is slightly lower than the 332 GPa of Haines et al.¹⁵ and the 314 of Ref. 38. The unit cell was also scaled along each axis independently; the resulting linear compressibilities indicate a slight anisotropy, being -1.847 $\times 10^{-3}$, -2.093×10^{-3} , and -1.946×10^{-3} GPa⁻¹ for a, b, and c respectively.

3. Other possible phases

Table V contains the structural data of other potential phases of ZrO_2 , the crystal structures of which are shown in

TABLE IV. Calculated and experiment cell coordinates of the cotunnite (OrthoII) structure of ZrO_2 . The experimental results were take from Ref. 15.

Parameters (experiment)	Parameters (theory)
a = 5.741, b = 3.246, c = 6.341 (Å)	a = 5.598, b = 3.340, c = 6.553 (Å)
Zr(0.251,0.250,0.109)	Zr(0.247,0.250,0.118)
O(0.364,0.250,0.422)	O(0.360,0.250,0.429)
O(0.021,0.750,0.328)	O(0.028,0.750,0.333)

TABLE V. Calculated parameters of possible strutures of the other phases of ZrO_2 .

System	Lattice constants (Å)	Wykoff coordinates
Cubic (Pa3)	a=5.261	Zr(0.000,0.000,0.000)
		O (0.336,0.336,0.336)
Orthorhombic (<i>Pbcn</i>)	a=4.967	Zr(0.000,0.184,0.250)
$(\alpha - PbO_2)$	b = 5.804	O(0.275,0.402,0.425)
	c=5.324	
Tetragonal $(P\overline{4}2m)$	a=5.193	Zr(0.000,0.000,0.000)
(MnF_2)	c=5.165	Zr(0.500,0.500,0.000)
		Zr(0.500,0.000,0.500)
		O (0.288 0.288 0.246)
		O (0.212 0.212 0.726)
Tetragonal (P4 ₂ /mnm)	a=4.961	Zr(0.000,0.000,0.000)
(rutile)	c=3.283	O (0.304,0.304,0.304)
Tetragonal (I4 ₁ /amd)	a = 4.095	Zr(0.000,0.750,0.125)
(anatase)	c = 10.659	O (0.000,0.750,0.328)
Hexagonal (P6 ₃ /mmc)	a=3.616	Zr(0.333,0.666,0.250)
(BaF_2)	c = 5.478	O (0.000,0.000,0.000)
		O (0.333,0.666,0.750)

Fig. 5. These structures are now considered for possible inclusion in the overall phase diagram of zirconia. Many of theses structures have been observed in other systems to ZrO_2 and have been considered here as potential candidates for high-pressure phases of the material. All the structures were repeatedly optimized over lattice parameters and atomic positions until there was no appreciable change in energy.

The relative merits of each of the structures can be seen from examination of the Birch equation of state shown in Fig. 6. One of theses structures—namely, the anatase $(I4_1/amd)$ phase—has a somewhat lower energy than the other phases considered. This phase has a larger volume (~18%) than the adjacent monoclinic phase and consequently may be part of the mechanism involved in transformations in the neighborhood of a crack tip in monoclinic zirconia. It is known⁴⁶ that partially stabilized tetragonal zirconia can be used to retard crack growth in composites due



FIG. 5. Other possible crystal structures of phases of ZrO_2 : *Pa*³ (modified fluorite), *Pbcn*(α -PbO₂), *P*4₂/*mnm* (rutile), *P* $\overline{42}m(MnF_2)$, *I*4₁/*amd* (anatase), and *P*6₃/*mmc*(BaF₂).



FIG. 6. Calculated energy-volume equation of state for the other structures of phases of ZrO_2 shown in Fig. 5.

to the volume change associated with the tetragonal to monoclinic zirconia phase transformation, and it is possible that a subsequent change to the anatase phase may further arrest crack propagation. The pressure required for this transition we predict to occur at about -15 GPa from the baddeleyite phase.

The tetragonal phase isostructural to MnF_2 proposed some time ago by Ming and Manghnani¹⁶ appears to be quite plausible, at least as a high-temperature and -pressure phase. The density is about that of OrthoI and the total energy is below both fluorite and baddeleyite. Also, there is a good correspondence between the experimental lattice parameters¹⁶ (a=5.046 Å, c=5.129 Å) and the calculated ones (a=5.193 Å, c=5.165 Å). The very-highpressure tetragonal phase reported by Arashi *et al.*¹⁷ suggested the Zr atoms occupied the same positions as the MnF₂ phase, but these phases have differing lattice parameters and densities and therefore must be regarded as being distinct.

The hexagonal phase with 11-fold coordination has an equilibrium volume very close to that of the cotunnite structure, but the associated energy is much too high to consider this as a post-cotunnite phase of zirconia. The rutile phase which is prevalent in many metal oxides does not appear to feature in the lower-temperature portion of the phase diagram of zirconia. Cohen *et al.*³⁸ using the potential-induced breathing method found the hypothetical rutile structure to have a bulk modulus of 236 GPa, in good agreement with this work which predicts 233 GPa.

C. Relative energies

As discussed above the relative energies of the phases give some indication of the potential ordering of expected structures. In Table VI we have collected together the energies and other parameters of the various phases that we have considered in the previous sections. Most of the possible important phases have energies that are far too high to affect the status of the known zero-temperature structures, and therefore can only be potential high-temperature phases.

The energetic order of the phases we have found is now

 $E^{\text{brookite}} < E^{\text{cotunnite}} < E^{\text{monoclinic}} < E^{\text{fluorite}} < E^{\alpha-\text{PbO}_2} < E^{\text{rutile}}$

Wilson *et al.*⁴¹ have performed similar calculations with several ionic-type hard potentials. They argued that the only genuinely transferable potential model was one including compressible ions and a dipole+quadrupole polarizability. Using this model they obtained the following order in energy of the various phases:

$$E^{\text{monoclinic}} \leq E^{\text{rutile}} \leq E^{\alpha - \text{PbO}_2} \leq E^{\text{fluorite}} \leq E^{\text{cotunnite}}$$

This is quite different to our findings. However, the same authors using no polarizability obtained a ordering of energies, namely,

$$E^{\text{fluorite}} < E^{\text{cotunnite}} < E^{\text{monoclinic}} < E^{\alpha - \text{PbO}_2} < E^{\text{rutile}}$$

which seems to be in much better agreement with our results. The more accurate potential-induced breathing model predicted an ordering of^{38}

$$E^{\text{fluorite}} < E^{\text{cotunnite}} < E^{\text{rutile}} < E^{\text{monoclinic}}$$

This indicates that the task of obtaining a reliable calculation of the relative ordering of energies is quite formidable

TABLE VI. Calculated parameters of possible strutures of ZrO_2 . (A) denotes the ambient phase; (OI) and O(II) denote orthorhombic phases. Energies and volumes are expressed relative to the baddelyite ambient phase.

Sustem	Relative energy	Coordination	Palativa voluma (%)	\mathbf{P} (CPa)	מ'
System	(ev/atom)	number	Kelative volume (%)	B_o (GFa)	D ₀
Hexagonal (BaF ₂)	0.4921	11	-17.5	286	4.60
Cubic (Pa3)	0.1590	6 + 2	-3.2	257	4.66
Rutile	0.1542	6	7.4	233	4.67
α -PbO ₂	0.0609	6 + 2	3.0	241	4.63
Tetragonal (A)	0.0482	~ 8	-7.1	200	6.25
Anatase	0.0344	6	18.3	209	4.63
Fluorite (A)	0.0152	8	-9.4	267	4.42
Tetragonal (MnF ₂)	0.0114	8	-7.0	264	4.64
Baddeleyite (A)	0.0000	7	0.0	157	2.38
Orthorhombic (Pbc2 ₁)	-0.0200	7	-6.1	265	4.62
Cotunnite (OII)	-0.0254	9	-18.6	305	4.68
Brookite (OI)	-0.0332	7	-8.5	272	4.63

especially for the lower structures, which are all within 0.08 eV/atom of each other. As we can see from our values shown in Table VI the lower phases are very closely spaced in energy — in many ways like the polymorphs of SiO_2 — and we note that while semiempirical methods on the whole reproduce the elastic properties quite well, the successful prediction of the preferred low-temperature phases and transition pressures of this type of material can only be achieved with these strenuous full quantum mechanical calculations.

IV. CONCLUSION

We have seen how a plane wave *ab initio* modeling of the structures of ZrO_2 has led us to suggest structures for the various phases of this material. The low-temperature phases,

their bulk modulii, transition pressures, and crystal parameters are all correctly predicted by this method. We show that at temperatures for which the ionic kinetic contribution to the energy is small, the transition order is anatase \rightarrow monoclinic $\rightarrow Pbca \rightarrow$ cotunnite at -15, 4.1, and 19.0 GPa, respectively. By far the hardest phase is the cotunnite-type structure which we calculate has a bulk modulus of 305 GPa. Further theoretical study towards production of this phase under less extreme conditions (1000 °C and 18 GPa) or for a cation other than Zr could be quite rewarding.

ACKNOWLEDGMENTS

The F.R.D. is thanked for their support. We express our appreciation to M. Müller for computational advice.

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