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Structure and stability of ZrSiO$_4$ under hydrostatic pressure

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We present the results of a combined experimental and theoretical investigation aimed to determine structural and equation-of-state parameters and phase stability thermodynamic boundaries of ZrSiO$_4$ polymorphs. Experimental unit-cell data have been obtained for a powdered sample in a diamond-anvil cell using energy-dispersive synchrotron x-ray diffraction with emphasis on the pressure range 0–15 GPa. Static total-energy calculations have been performed within the density functional theory at local density and generalized gradient approximation levels using a plane-wave pseudopotential scheme. Our quantum-mechanical simulations explore the pressure response of the two observed tetragonal structures (zircon- and scheelite-type reidite) as well as of other potential post-scheelite polymorphs up to about 60 GPa. We find very good agreement between our experimental and calculated pressure-volume values for the low-pressure phase of ZrSiO$_4$. A microscopic analysis of the bulk compressibility of zircon and reidite in terms of polyhedral and atomic contributions is proposed to clarify some of the discrepancies found in recent theoretical and experimental studies. Our results show the relevant role played by the oxygen atoms in the description of this property. The zircon-reidite equilibrium phase transition pressure is computed around 5 GPa. No other post-scheelite phase is found stable above this pressure though a decomposition into ZrO$_2$ (cottunite) and SiO$_2$ (stishovite) is predicted at about 6 GPa. These two transition pressure values are well below the experimental ranges detected in the laboratory in concordance with the large hysteresis associated with these transformations.

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I. INTRODUCTION

Understanding the behavior of materials exposed to variable thermodynamic conditions and chemical agents rests in many instances on detailed knowledge of the correlation between their observable properties and the local geometry and interactions around their constitutive atoms. The particular structural and chemical features of the bonding network in ZrSiO$_4$ provide a paradigmatic case to investigate this correlation. This mixed oxide presents simultaneously two nominally 4+ cations, shows the lowest compressibility for a material containing SiO$_4$ tetrahedra, contains interstices appropriate for hosting and retain rare-earth elements, and exhibits an anomalous and possibly unique displacive mechanism regarding silicate solid-solid transformations.  

A straightforward strategy to study the physics and chemistry of the local environment of atoms in crystalline solids is the application of hydrostatic pressure. The equations of state (EOS) of the two observed tetragonal polymorphs of ZrSiO$_4$, zircon and reidite, have been the subject of recent experimental and theoretical investigations. Contrarily to previous data of the zero-pressure bulk modulus for zircon ($B_0 = 230$ GPa),$^2$ van Westrenen et al.$^3$ and Ono et al.$^4$ obtained values around 10% lower. In addition, Ono et al.$^4$ pointed out that the main reason for the difference between their $B_0$ value for reidite ($392 \pm 9$ GPa) and that reported by Scott et al. ($301.4 \pm 12.5$ GPa) is the nonhydrostaticity of the medium in the high-pressure experiments of these authors.$^5$ Scott et al. claimed that their results in the hydrostatic regime are completely indistinguishable from the higher-pressure results.

The compressibility of both structures has been also analyzed in terms of their elementary polyhedra which in both lattices are nonregular SiO$_4$ tetrahedra and ZrO$_8$ triangular dodecahedra (see Refs. 6 and 7, and references therein). For the zircon phase, Hazen and Finger concluded that its remarkable incompressibility is mainly due to the ZrO$_8$ polyhedra with $B_{ZrO_8} \approx 280$ GPa, whereas $B_{SiO_4}$ has a surprisingly low value around 225 GPa.$^2$ Smyth et al. recommended in this respect that “the anomalous results of Hazen and Finger” should be reexamined.$^8$ The lack of polyhedral compressibilities in the reidite structure makes it also worth performing a polyhedral analysis in this structure. Contrarily to zircon, the high $B_0$ value of reidite is achieved by the low compressibility of SiO$_4$ tetrahedra according to the experiments of Scott et al.$^5$

Zircon and reidite show strong structural anisotropy under temperature and pressure as manifested by the different values of their corresponding linear expansion coefficients and linear compressibilities.$^6$ With respect to pressure effects, the observed behavior can be summarized as follows: (i) reidite is less anisotropic than zircon, and (ii) the compressibility along the $a$ axis is greater than that along the $c$ axis in zircon whereas the opposite result is found in reidite. The structural anisotropy can be traced back as due to the orientation and linkage of the constitutive polyhedra and, ultimately, to the disposition of Si-O, Zr-O, and O-O bonds. In the explanation

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given by Smyth et al.\textsuperscript{5} (later quoted in the review of Finch and Hanchar\textsuperscript{6}), we have found that Zr-O bond strengths are not correctly correlated with the observed linear compressibilities.

The last issue that has attracted our interest in this contribution is the determination of pressure and temperature ranges of stability for zircon and reidite. Static-pressure\textsuperscript{1,3,4,9,10} and shock-wave compression\textsuperscript{11–13} experiments have identified reidite as the only high-pressure polymorph of ZrSiO$_4$. At elevated temperature and pressure, ZrSiO$_4$ is observed to decompose into SiO$_2$ (stishovite) and ZrO$_2$ (cottunite).\textsuperscript{14} Due to the high energetic barriers associated with the hysteresis of these processes, the equilibrium thermodynamic boundaries are not well constrained though positive Clapeyron $p$-$T$ slopes for both transitions are suggested.\textsuperscript{6,14}

In this study, we aim to contribute to the understanding of the structural and stability behavior of ZrSiO$_4$ under hydrostatic pressure. Diamond-anvil cell experiments using energy-dispersive synchrotron x-ray diffraction in powdered samples and static total-energy calculations based on the density functional approximation were carried out in the pressure ranges 0–15 GPa and 0–60 GPa, respectively. This combined experimental and theoretical investigation allows us to clarify some of the discrepancies found in previous works. In particular, we report and analyze in detail the EOS of zircon and reidite in terms of bond, polyhedral, and linear compressibilities with a special emphasis on a comparison with previous experimental data. Furthermore, we obtain atomic compressibilities from the topology of the crystalline electron densities. The second objective of our study is to characterize the thermodynamics of the zircon→reidite and reidite→SiO$_2$ (stishovite) + ZrO$_2$ (cottunite) transformations. Equilibrium transition properties are evaluated and the effects of the temperature on the thermodynamic boundaries are analyzed. Finally, two potential post-scheelite polymorphs (fergusonite- and wolframite-type structures) are also discussed.

The present paper is organized in three more sections. Next, a brief description of the experimental and computational procedures is given. Section III A contains the structural and EOS results of zircon and reidite, and Secs. III B and III C the polyhedral and atomic [in terms of Bader’s atoms in molecules (AIM) formalism\textsuperscript{15}] analyses of these properties. Phase transition properties and stability ranges of ZrSiO$_4$ polymorphs are presented in Sec. III D. The paper ends with the main conclusions of our work.

II. EXPERIMENTAL METHODS AND COMPUTATIONAL DETAILS

A. Experimental methods

The zircon sample used in the present work has been purchased from Strem Chemicals Inc. According to the manufacturer, the product is typically 99+% pure. The major impurities are iron oxide, aluminum oxide, and zirconium oxide. The sample comes in the form of a white powder.

High-pressure powder x-ray diffraction patterns were recorded at room temperature using the white-beam method and synchrotron radiation at Station F3 of HASYLAB-DESY in Hamburg, Germany. The diffractometer, working in the energy-dispersive mode, has been described elsewhere.\textsuperscript{16}

High pressures were obtained in a Syassen-Holzapfel type diamond-anvil cell. A finely ground powder sample and a ruby chip were placed in a 200-μm-diam hole in an inconel gasket, pre-indented to a thickness of 60 μm. A 16:3:1 methanol:ethanol:water mixture was used as the pressure-transmitting medium. The pressure in the cell was determined from the wavelength shift of the ruby R$_1$ luminescence line and applying the nonlinear pressure scale of Mao et al.\textsuperscript{17} The Bragg angle of each run was calculated from a zero-pressure spectrum of sodium chloride in the diamond-anvil cell.

Figure 1 shows an energy-dispersive x-ray diffraction spectrum of zircon. In a typical run, a series of spectra were recorded for a pressure increment of 1–2 GPa at a time. At each pressure, values for the lattice parameters and the unit-cell volume were derived and refined by a least-squares method, using the observed peak positions in the diffraction spectrum. The pressure-volume data were then described by the Birch-Murnaghan equation of state:\textsuperscript{18}

\begin{equation}
 p = \frac{3}{2}B_0(x^{-7/3} - x^{-5/3})(1 - \frac{3}{4}(4 - B'_0)(x^{-2/3} - 1)), \tag{1}
\end{equation}

where $x = V/V_0$, $V$ is the volume per formula unit at pressure $p$ and $V_0$ is the corresponding volume at zero pressure. The least-squares fitting parameters are the bulk modulus and its pressure derivative evaluated at zero pressure ($B_0$ and $B'_0$, respectively).

B. Computational details

Total-energy calculations at selected unit-cell volumes of zircon, reidite, fergusonite-type, wolframite-type, stishovite (SiO$_2$), and cottunite (ZrO$_2$) structures were performed under the framework of the density functional theory using the Vienna $ab$ initio simulation package (VASP) code\textsuperscript{19} in connection with the projector-augmented wave (PAW) method.\textsuperscript{20} The exchange and correlation energy was treated via the lo-
The total force on the atoms was less than 1 meV/Å. Geometry relaxation was considered to be completed when the energies were converged to below 0.1 meV/atom and the geometries and stresses on the unit cell. For the energy calculation of the optimized crystal structures, the tetrahedron method with Blöchl correction was applied. In special, the total energy, using the Hellmann-Feynman forces on the atoms and zero-point vibrational contributions neglected.

Thermal contributions are included by means of an nonempirical quasiharmonic Debye-like model that only requires the set of \((E, V)\) points and the calculated static bulk modulus to evaluate thermodynamic properties at different temperatures. We have found a good agreement between the results of several thermodynamic properties obtained within this model and those obtained by Fleche in zircon using a more sophisticated procedure that involves explicit evaluation of \(\Gamma\)-point vibrational frequencies. However, due to the approximate character of the Debye model, we mainly focus on the static results, the effect of temperature being only considered qualitatively in the discussion of the transformation equilibrium boundaries. The main outcome of our simulation strategy is the pressure dependence (from 0 up to 60 GPa) of all the unit-cell parameters, atomic coordinates, polyhedral volumes, and Gibbs energies of the ZrSiO\(_4\), SiO\(_2\), and ZrO\(_2\) structures.

Finally, using the AIM formalism and the CRITIC program, a microscopic analysis of the electron density of zircon and reidite has been carried out with the aim of evaluating the atomic contributions to the bulk compressibility. To this end, at the VASP equilibrium geometries we have generated all-electron wave functions from CRYSTAL calculations using the same exchange and correlation functionals as in the pseudopotential ones. We have checked that the residual strains associated with the nonoptimized electron densities in the CRYSTAL calculations do not introduce significant modifications in the final atomic decomposition of the crystal compressibility. The AIM formalism allows the chemical characterization of the topology of the electron density in terms of (i) critical points where the gradient of the electron density is zero and (ii) nonoverlapping electronic basins surrounded by surfaces with a nil flux of the electron density gradient. Integrations within these basins lead to atomic volumes of EXP.25

### III. RESULTS

#### A. Structural properties and equations of state (EOS)

Zircon and reidite belong, respectively, to the \(I4_1/amd\) and \(I4_1/a\) space groups. Their conventional unit cells are tetragonal and contain 4 Zr and 8 Si atoms at special positions [Zr at \(4a(0, \frac{1}{2}, \frac{1}{2})\) and \(4b(0, \frac{1}{2}, \frac{1}{2})\) and Si at \(4b(0, \frac{1}{2}, \frac{1}{2})\) and \(4d(0, \frac{1}{2}, \frac{1}{2}), \text{respectively}\)] and 16 O atoms at \(16f(0, y^2, z^2)\) and \(16f(x^2, y^2, z^2), \text{respectively}\). Both structures have been described in detail previously (see, for example, Refs. 6 and 7, and references therein). Our experimental and calculated lattice parameters \((a\) and \(c\) and oxygen coordinates at zero pressure are collected in Table I along with other representa-
tive experimental data. We found a good agreement between previous and present results. Notice that the expected underestimation of the structural parameters at the LDA level is only within 1%, whereas the GGA overestimates up to 4% the volume of ZrSiO$_4$ polymorphs. At the LDA level, the agreement between the theoretical and experimental values is very good for zircon and a little worse for reidite, the discrepancies probably being related to the effect of the residual strain in the shock-induced reidite sample. In this respect, we must note that our calculated oxygen positions are closer to those of other scheelite-type compounds than the values determined by Kusaba et al.$^{12}$

According to the experimental data reported in Refs. 2, 28, and 29, the room-temperature (RT) value of $B_0$ in zircon lays within a range of 225–230 GPa. Similar or higher values have been obtained using several computational techniques.$^{25,30–33}$ The evaluation of $B_0$ from the elastic constants experimentally determined by Ozkan et al.$^{34}$ gives also a value of 225.2 GPa. We refer to the data from all these works as set I. In set II, we include recent investigations of the compressibility of zircon in diamond anvil cells using x-ray diffraction techniques. In these experiments, van Westrenen et al.$^{3}$ and Ono et al.$^4$ have reported, respectively, 199±1 GPa and 205±8 GPa for $B_0$ at RT when they set $B'_0$ to 4. In addition, GGA calculations of Farnan et al.$^{31}$ yield a slightly lower value (196 GPa). It should be pointed out that the effect of fixed or variable $B'_0$ parameters does not explain the existence of these two sets of $B_0$ values around 225 GPa and 200 GPa, respectively. The origin of such discrepancies was analyzed in detail by van Westrenen et al.$^3$ who listed a number of factors affecting the experimental determination of the EOS parameters. Nevertheless, a clear conclusion could not be drawn to explain the existing discrepancies and a combination of effects was proposed.$^3$

Our pressure-volume and pressure-normalized volume diagrams plotted in Fig. 2 ($V_0$ is the corresponding zero-pressure volume per formula unit of zircon) illustrate quantitatively the observed differences in the response of the unit-cell volume of zircon to hydrostatic pressure. First, the $p$-$V$ diagram [Fig. 2(a)] shows an overall good agreement between our LDA $p$-$V$ data and the experiments (in particular, those by van Westrenen et al.$^3$ up to around 15 GPa, the GGA calculations providing volumes about 5% higher. Second, the $p$-$V/V_0$ diagram [Fig. 2(b)] classifies more clearly the curves according to their $B_0$ values. It is apparent the very good agreement between our experimental and calculated LDA ($p$, $V/V_0$) values, both yielding $B_0$ around 230 GPa and therefore supporting the data of set I. In the low-pressure range covered by the experiments of Ono et al., the deviations from our experimental results are almost negligible, indicating that the error bars of the corresponding $B_0$ values should be taken into consideration. Larger discrepancies appear at increasing pressures with respect to the experimental values of van Westrenen et al.$^3$, as expected from the two different values of $B_0$. Honestly speaking, we might remark that our GGA $p$-$V/V_0$ results are in fair agreement with the measured points of van Westrenen et al. and yield a $B_0$ value close to the data of set II. This result could reveal that it is delicate to decide for zircon the relevant experimental $B_0$ from our DFT calculations. Nevertheless, in the next subsections we will mainly make use of our LDA calculations as they provide a reasonable overall description of the structure, the compressibility, and the phase transition properties of ZrSiO$_4$. Results at the LDA level of computation have been also reported in our previous work on group-IV nitrides$^{35}$ using the same VASP methodology.

For reidite, the difference between the two experimental values of $B_0$ [392±9 (Ref. 4) and 301.4±12.5 (Ref. 5)] is as large as around 100 GPa. These two values are much higher than our computed ones. GGA results produce definitively a too compressible scheelite-type polymorph, whereas our LDA value is around 14% lower than that reported by Scott et al. The particular ($p$, $V/V_0$) data points of Ono et al. below 13 GPa do not show, however, large discrepancies with respect to our calculated values. Differences come from the rate $V/V_0$ decreases as pressure is applied. Notice that the zero-pressure volume of reidite by Ono et al. is not directly obtained in their experiments, but determined in the EOS fitting procedure. Their value is almost 2% lower than previous experimental data of Reid and Ringwood$^9$ and Kusaba et al.$^{12}$ which might be considered as a factor to overestimate

FIG. 2. (Color online) Volume (a) and normalized volume (b) versus pressure diagrams. Symbols stand for the experimental data of this work (solid squares), Ref. 3 (crosses), and Ref. 4 (stars). Standard deviations of the volume in the range 0.01–0.02 Å$^3$ (Ref. 3) and (most of the points) in the ranges 0.02–0.04 Å$^3$ (Ref. 4, zircon) and 0.03–0.08 Å$^3$ (Ref. 4, reidite). Lines correspond to our calculated data under the LDA (solid) and GGA (dashed) approximations. Arrows represent calculated volume collapses at the LDA and GGA zircon→reidite transition pressures (see Sec. III D).
B. Polyhedral analysis of the structures

For our purposes, it is interesting to recall that distorted SiO$_4$ tetrahedra and distorted ZrO$_4$ triangular dodecahedra are present in both polymorphs. As pointed out by Mursic et al.,$^{38}$ “it is useful to describe the Zr-O polyhedral environment as two interpenetrating tetrahedra” that we denote as ZrO$_4$(o) and ZrO$_4$(p), the o and p labels indicating their oblate and prolate conformations. The degree of distortion of the SiO$_4$, ZrO$_4$(o), and ZrO$_4$(p) tetrahedra can be quantified by means of the quadratic elongation ($\lambda$) and angular variance ($\sigma^2_{\theta}$) parameters proposed by Robinson et al.$^{39}$

$$\lambda_i = \frac{1}{4} \sum_{k=1}^{4} \left( \frac{d_{ki}}{d_{0i}} \right)^2 , \quad \sigma^2_{\theta_{ij}} = \frac{1}{6} \sum_{k=1}^{6} (\theta_{ki} - 109.47^\circ )^2 ,$$

where $d_{0i}$ and $\theta_{ki}$ stand for the bond lengths and angles of tetrahedron $i$, and $d_{0i}$ is the center-to-vertex distance for a regular tetrahedron whose volume is equal to that of the distorted one.

A detailed structural characterization of all the cationic polyhedra of the zircon and reidite structures is given in Table II using the equilibrium unit cells obtained in our LDA calculations at zero pressure, the corresponding volumes being shown in Table III. The RT experimental values collected in these tables are easily derived from the unit-cell geometries provided by Hazen and Finger$^2$ and by Kusaba et al.$^{12}$ for the zircon and reidite structures, respectively. For the tetrahedra considered in this work the four distances $d_i$ are equal, whereas two different angles $\theta_i$ and $\theta_i'$ with multiplicities 2 and 4, respectively, are found. Both angles are shown in Table II for each polyhedron although it is to be noted that they are related through the equation $\cos \theta_i + 2 \cos \theta_i' = -1$.

According to our calculations, the ZrO$_4$ tetrahedra are rather distorted in both phases, the degree of distortion being smaller in reidite. On the contrary, SiO$_4$ are rather regular tetrahedra in both phases. The picture emerging from the experimental results is similar, although the distortion of

\[ \kappa_z = 0.95 \times 10^{-3} \text{ GPa}^{-1} \] and \[ \kappa_c = 1.69 \times 10^{-3} \text{ GPa}^{-1} \]. In reidite, our calculated values \( (\kappa_z = 1.10 \times 10^{-3} \text{ GPa}^{-1} \text{ and } \kappa_c = 1.69 \times 10^{-3} \text{ GPa}^{-1} \) show greater discrepancies with the values reported by Scott et al.$^5$ \( (\kappa_z = 7.42 \times 10^{-4} \text{ GPa}^{-1} \text{ and } \kappa_c = 1.08 \times 10^{-3} \text{ GPa}^{-1} \), though it is to be noted that the latter do not recover the value they reported for the bulk \( (\kappa = 2\kappa_o + \kappa_c)\). As pointed out by these authors, the low compressibility along the a axis in reidite has to be related to the repulsions between oxygen atoms whose shortest interatomic distances are found in the ab plane. Finally, pressure effects on the normalized oxygen positions in zircon and reidite polyhedra are shown in Fig. 3(b). With the exception of the z coordinate in zircon, we observe a decreasing of the O positions as pressure increases, the greatest relative diminutions being found for the z coordinate in reidite and the y coordinate in zircon. As we will see below, the pressure dependence of the oxygen coordinates is closely related to the way the polyhedra of the crystal are linked to each other and, consequently, controls the relation between the bulk and polyhedral compressibilities.
SiO$_4$ tetrahedron in reidite is now a little greater than in zircon. We conclude that the more efficient ionic packing in the reidite structure can be associated with the higher regularity of its Zr$^{4+}$ polyhedra, which in turn produces an increasing in the average number of next-nearest neighbors and a decrease in the unit-cell volume. To the best of our knowledge, no other theoretical or experimental analyses of the polyhedral shapes and orientation of SiO$_4$ and ZrO$_8$ polyhedra in the cell is not modified up to 4.33 Å, angles in degree, and $\sigma^2_{0i}$ in degree$^2$. The multiplicity of $\theta_i$ ($\theta'_i$) is 2 (4).

TABLE II. Zero-pressure structure and distortion parameters of elementary polyhedra of zircon and reidite according to present LDA calculations. Second rows contain values derived from the experimental data of Refs. 2 (zircon) and 12 (reidite). $d_i$ in Å, angles in degree, and $\sigma^2_{0i}$ in degree$^2$. The multiplicity of $\theta_i$ ($\theta'_i$) is 2 (4).

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>Zircon</th>
<th>Reidite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_4$</td>
<td>LDA</td>
<td>Expt.</td>
</tr>
<tr>
<td>ZrO$_4(o)$</td>
<td>1.622</td>
<td>1.623</td>
</tr>
<tr>
<td>ZrO$_4(p)$</td>
<td>2.257</td>
<td>2.267</td>
</tr>
</tbody>
</table>

SiO$_4$ tetrahedron in reidite is now a little greater than in zircon. We conclude that the more efficient ionic packing in the reidite structure can be associated with the higher regularity of its Zr$^{4+}$ polyhedra, which in turn produces an increasing in the average number of next-nearest neighbors and a decrease in the unit-cell volume. To the best of our knowledge, no other theoretical or experimental analyses of the polyhedral shapes and orientation of SiO$_4$ and ZrO$_8$ polyhedra in the cell is not modified up to 4.33 Å, angles in degree, and $\sigma^2_{0i}$ in degree$^2$. The multiplicity of $\theta_i$ ($\theta'_i$) is 2 (4).

Overall, the qualitative image of the shape and orientation of SiO$_4$ and ZrO$_8$ polyhedra in the cell is not modified up to at least 60 GPa in each of the two polymorphs. We believe that a quantitative analysis of the pressure effects on distances and angles of these polyhedra may be also worth to be performed. According to our calculations, the Si-O distances and the degree of distortion of the SiO$_4$ tetrahedra of zircon and reidite decrease as pressure increases: $d$$=1.581$ Å, $\theta$ = 97.46°, $\lambda$ = 1.022, and $\sigma^2_{0i}$ = 89.71 deg$^2$ for zircon and $\theta$ = 1.613 Å, $\theta$ = 118.74°, $\lambda$ = 1.014, and $\sigma^2_{0i}$ = 50.40 deg$^2$ for reidite, at about 30 GPa. In zircon, the difference between the two sets of Zr-O distances becomes larger as pressure is applied (0.17 Å at $p$ around 30 GPa to be compared with 0.13 Å at $p$ = 0). This behavior of the Zr-O distances induces a more strained ZrO$_8$ dodecahedra at increasing pressure, thus reducing the stability of the zircon polymorph, an argument in line with the analysis performed by Mursic et al. in their high-temperature study of zircon. On the contrary, the calculations show that the difference between the Zr-O distances in reidite decreases as pressure increases (0.06 Å at $p$ = 30 GPa to be compared with 0.10 Å at $p$ = 0). This behavior of the Zr-O distances induces a more strained ZrO$_8$ dodecahedra at increasing pressure, thus reducing the stability of the zircon polymorph, an argument in line with the analysis performed by Mursic et al. in their high-temperature study of zircon. On the contrary, the calculations show that the difference between the Zr-O distances in reidite decreases as pressure increases (0.06 Å at $p$ = 30 GPa to be compared with 0.10 Å at $p$ = 0). The $\theta$ angles of the ZrO$_4$ tetrahedra at about 30 GPa differ less than 1% from those at $p$ = 0 shown in Table II, with the exception of $\theta_{ZrO_4}$ in reidite which is 3% higher. Concerning the O(o)-Zr-O(p) angles ($\theta_i$), we found that the values at 30 GPa differ from those at $p$ = 0 only around 1%.

C. EOS: Polyhedral interpretation and AIM picture

A microscopic analysis of the compressibility of zircon and reidite ($\kappa$) is performed now in terms of the polyhedral and atomic compressibilities ($\kappa_i$) and occupation factors ($f_i$). The compressibility of polyhedron (atom) $i$ is defined as $\kappa_i = -\delta \ln V_i / \delta p$, and the occupation factor of $i$ as the ratio between the volume occupation of that polyhedron (atom) $[n_i \times V_i$, $n_i$ being the number of $i$ polyhedra (atoms) per formula unit] and the volume per formula unit ($V$). As a consequence, the polyhedral (atomic) volumes and compressibilit-
ties, and the crystal volume and compressibility, can be written as follows (see Refs. 41–43):

\[ V_i = V_i^{-1}, \quad \kappa_i = \kappa - \frac{\partial \ln f_i}{\partial p}, \quad V = \sum_i n_i V_i, \quad \kappa = \sum_i f_i \kappa_i. \]  

(3)

The analysis of the polyhedral contributions to the crystal compressibility has to be performed in terms of the compressibilities and occupation factors of SiO\(_4\) and ZrO\(_8\) polyhedra and also noting that O\(_6\) octahedral voids complete the unit-cell volume. This compressibility decomposition is not possible using ZrO\(_8\)(p) and ZrO\(_8\)(o) tetrahedra because they (and obviously ZrO\(_8\)) share common regions of space in the cell. \( f_{SiO_4} \) and \( f_{ZrO_8} \) are functions of the oxygen coordinates \( x \), where \( x \) contains the set of coordinates of O atoms in general positions \([y^x, z^x]\) for O in zircon and \([x^x, y^x, z^x]\) for O in reidite. In the case of zircon, the expressions for \( f_{SiO_4}^x \) and \( f_{ZrO_8}^x \) are

\[ f_{SiO_4}^x = \frac{2}{3} \left( \frac{1}{2} - 2y^x \right) \left( 4y^x z^x - z^x - \frac{3}{2}y^x + \frac{3}{8} \right), \]

\[ f_{ZrO_8}^x = \frac{1}{3} (4y^x + 1)(y^x + 2z^x) + \frac{1}{24} (1 - 4y^x)(1 + 4y^x)(1 + 8z^x). \]  

(4)

We omit larger expressions for reidite.

Table III shows the zero-pressure properties of elementary polyhedra of zircon and reidite obtained from our LDA calculations as well as the values derived from available experimental information. Table III also includes the properties associated with the O\(_6\) voids. In zircon, the calculated polyhedral compressibilities \( \kappa_{SiO_4} = 2.89 \) and \( \kappa_{ZrO_8} = 4.55 \) in \( 10^{-3} \) GPa\(^{-1}\) units) confirm the criticisms of Smyth et al.,\(^8\) with respect to the anomalous results reported by Hazen and Finger \( \kappa_{SiO_4} = 4.4 \pm 1.1, \kappa_{ZrO_8} = 3.6 \pm 0.6.\)\(^2\) and support the analysis of the experimental data of Scott et al.,\(^5\) in reidite, though our \( B_{SiO_4} = 1/\kappa_{SiO_4} \) value around 450 GPa is not as high as the value (>700 GPa) quoted for this polyhedron. In both structures, the volume occupied by the dodecahedron of zircon and reidite is almost 9 times greater than that of the tetrahedron and, thus, the total contribution \( f_i \kappa_i \) of ZrO\(_8\) to the crystal compressibility is much more important than that of SiO\(_4\). We must note, however, that the contribution of the voids to the volume reduction of zircon and reidite under hydrostatic pressure is about twice that of the ZrO\(_8\) polyhedra, because both phases are relatively open structures. Then, although the average compressibility of the voids is slightly smaller than that of ZrO\(_8\) in both structures, the total contribution of the voids to the bulk compressibility becomes dominant. It is also remarkable that, according to the polyhedral picture, about 98% of the volume difference between zircon and reidite structures can be explained as due to the lower volume occupied by the O\(_6\) voids in reidite (see Table III). The small size and low compressibility of the SiO\(_4\) tetrahedra make them to play an almost negligible role in the crystal response to pressure. Finally, note that the compressibilities shown in Table III for the ZrO\(_8\) tetrahedra are in concordance with the discussion at the end of Sec. III B.

The LDA-calculated pressure effects on the oxygen coordinates depicted in Fig. 3(b) lead to \( f_{SiO_4}(p) \) and \( f_{ZrO_8}(p) \) functions with slopes of different sign and magnitude in both polymorphs, negative and small for the ZrO\(_8\) curves (average decreasing of about 1% from 0 to 60 GPa) and positive and much greater for the SiO\(_4\) curves (average increasing of about 5% in the same range of pressure). This behavior and Eqs. (3) show that \( \kappa_{SiO_4} < \kappa = \kappa_{ZrO_8} \) for all pressures studied (up to 60 GPa), (ii) the compressibilities of the bulk and the dodecahedra are similar in both structures, in concordance with the findings of Errandonea et al.,\(^36\) quoted above, and (iii) the average of the compressibilities of these two types of polyhedra is not a good estimation of the compressibility of ZrSiO\(_4\), contrary to \( AB_{2}O_{4} \) spinels.\(^44\)

The AIM analysis of the electron density of zircon and reidite provides further insight into the compressibility of these systems. The relevant properties at zero pressure appear summarized in Table IV. First, according to the calculated \( \kappa_i \) values, Zr is more difficult to compress than O and this atom is slightly less compressible than Si in both structures, \( \kappa_i \) being about 6–7% higher than the compressibility of the bulk. Besides, the three atoms are expected to be a little more difficult to compress in reidite than in zircon. \( \kappa_0 \) in these systems \( 4.65 \times 10^{-3} \) GPa\(^{-1}\) in zircon and 4.12 \( \times 10^{-3} \) GPa\(^{-1}\) in reidite) is smaller than in the \( AB_{2}O_{4} \) (A = Mg, Zn; B = Al, Ga) spinels where \( \kappa_0 \approx 5.0 \times 10^{-3} \) GPa\(^{-1}\) and, in contrast to zircon and reidite, O is the most compressible ion in the crystal.\(^45\) On the contrary, the relative compressibility of O and Si in zircon and reidite is analogous to that previously inferred for N and Si in \( \beta- \) and \( \gamma- \) SiN\(_2\).\(^35\) Second, according to our calculations, \( V_O = 1.3–1.5 \) times \( V_Zr \) and 3.7 times \( V_{Si} \), the oxygen atoms dominating the unit-cell space mainly due to the stoichiometry of the unit cell (see \( f_i \) values in Table IV). As a consequence, the bulk compressibility of zircon and reidite (\( \kappa = \Sigma f_i \kappa_i \)) becomes mainly determined by the compressibility of oxygen, as in \( AB_{2}O_{4} \) spinels,\(^45\) and in the same way as the bulk compressibility of \( \beta- \) and \( \gamma- \) SiN\(_2\) (A = C, Si, Ge) becomes determined by the compressibility of N.\(^35\) Moreover, as \( V = \Sigma f_i V_i \), we can see from Table IV that 95% of the volume difference between zircon and reidite is due, in the AIM picture, to the lower volume occupied by O in the reidite structure. This result is in agreement with that shown above in terms of the consti-
tutive polyhedra, where the O6 voids were found to be the main responsible of the volume difference between both phases.

D. Relative stability and phase transitions properties

ZrSiO4 is known to display a pressure-induced first-order phase transition from zircon to reidite. At elevated temperatures, ZrSiO4 decomposes into its simple oxides, very likely β-cristobalite SiO2 and tetragonal ZrO2 at zero pressure, or stishovite SiO2 and cottunite-type ZrO2 at high pressure. There is a good deal of experimental data concerning both thermodynamic and mechanistic aspects of these transformations and less information from the theoretical side. The experimental information collected so far clearly shows that the zircon→reidite and ZrSiO4→ZrO2 + SiO2 transformations are kinetically hindered. Thus, we should bear in mind this fact to analyze the difference between our calculated thermodynamic (equilibrium) transition pressures (p1) and the experimental ones (p1,exp). When the parent and product phases are close to equilibrium, the energetic barriers associated with these transformations can be overcome only at sufficiently high temperatures, and then observed transition pressures may be compared with the thermodynamic ones. From the high temperature data and assuming a positive Clapeyron slope for the former transformation, the experimental transition pressure is expected to be below 10 GPa at room temperature. Our LDA static value of around 5.3 GPa is in concordance with this expectation and is also in good agreement with the calculated values of Crocombette and Ghaleb and Farman et al. In addition, a decrease in the volume of ZrSiO4 of 10.3% for this transformation at p1 has been obtained (see arrow at 5.3 GPa in Fig. 2), a value very close to the calculated (LDA) and experimental ones at zero pressure [10.5% and about 10–11%, respectively (see Table I)]. Besides, a relative volume change of around 8.9% has been also obtained for the ZrSiO4(reidite)→ZrO2(cottunite-type) + SiO2(stishovite) decomposition at its computed equilibrium pressure (6.3 GPa).

Both transformations exhibit an increase of the bulk modulus at the corresponding transition pressures that can be explained as mainly due to the volume reduction.

We have also explored the effect of temperature in the equilibrium pressure boundaries of these two transformations. The addition of vibrational energy and entropy contributions to the static results was performed with the Debye model. We have found a qualitatively satisfactory picture with both Clapeyron slopes slightly positive in the temperature ranges covered by our calculations: p1 increases 1.9 GPa from 0 to 1800 K for zircon→reidite transformation, whereas in the ZrSiO4(reidite)→ZrO2(cottunite-type) + SiO2(stishovite) decomposition the increment in p1 is 1.5 GPa in the range 0–1400 K. This means that there is a small decrease of entropy associated with these transitions, supporting the exhaustive analysis of Finch and Hanchar in many ABO3 compounds including ZrSiO4.

Finally, the study of post-scheelite phases of ZrSiO4 has been performed by computing the fergusonite- and wolframite-type structures of this compound. They belong, respectively, to the I2/a and P21/c monoclinic space groups. We used two different sets of starting cell parameters and atomic positions in the geometrical optimization of the fergusonite-type structure. The first one corresponds to a slightly distorted scheelite-type phase, derived from the I41/am-I2/a group-subgroup relationships, and the second one to structures having a P21/c space group. This latter strategy allows us to explore a possible relaxation of the I2/a structure of ZrSiO4 to the P21/c symmetry, a feature noted by Sen et al. in LiYF4 from their molecular dynamics simulations. According to our first strategy, the optimal structures always correspond to the scheelite-type lattice, but according to the second one, they correspond to the scheelite-type lattice in the volume regime from about 51 to 56 Å3 and to the wolframite-type phase in the volume regime from about 47 to 50 Å3. Then, full geometrical optimizations of this latter structure have been carried out at several volumes in the range 47 Å3 ≤ V ≤ 65 Å3. The energy-volume curve obtained shows a minimum at V0 = 56.71 Å3 and around 50 kJ/mol higher in energy than that of the reidite structure at zero pressure. Furthermore, an hypothetical reidite→wolframite-type structure phase transition is predicted at a pressure about 62 GPa, well beyond the decomposition of ZrSiO4 into its simple oxides.

IV. CONCLUSIONS

We presented a combined theoretical and experimental analysis of the structure and stability of ZrSiO4 under hydrostatic pressure, with emphasis on the zircon→reidite phase transition. Our LDA calculations provide an accurate overall description of the behavior of this system. Both LDA calculations and our diamond-anvil cell experiments give a B0 value for zircon around 230 GPa, thus supporting the experimental and theoretical results included in set I discussed above. Since recent static compression data yield B0 values around 10% lower, we suggest that ultrasonic measurements on synthetic pure zircon were performed in order to determine elastic constants and bulk modulus. Our LDA value of B0 for reidite (258 GPa) is much smaller than that obtained by Ono et al. (around 400 GPa), about 14% smaller than the value reported by Scott et al., but within the range of values predicted recently by Errandonea et al. from the compressibility of ZrO8 polyhedra (220±40 GPa). LDA calculations inform that ZrO8 polyhedra compress at a similar rate as that of the bulk in both zircon and reidite. According to the AIM picture, Zr is more difficult to compress than O and this atom is slightly less compressible than Si in both zircon and reidite. Interestingly, the bulk compressibility of these structures becomes determined by the O6 voids and the oxygen atoms, according to the polyhedral and AIM analyses, respectively. In agreement with the available experimental information, the degree of structural anisotropy under pressure obtained for zircon is greater than that of reidite, the linear compressibility of the former along the a (c) axis being greater (smaller) than that along c (a). The calculated static equilibrium transition pressure for this transformation (5.3 GPa) agrees reasonably with the equilibrium experimental value inferred at room conditions from the high-
temperature experimental data. Finally, a decomposition of ZrSiO$_4$ into ZrO$_2$ (cottonite) and SiO$_2$ (stishovite) is predicted at about 6 GPa.

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