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\textit{Ab initio} lattice dynamics and phase transformations of ZrO$_2$

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Zirconia, ZrO$_2$, is one of the most important ceramic materials in modern technology. Its versatility is closely related to phase transformations. Although the transformations have been repeatedly investigated by experiments, fundamental aspects of the transformations are still under debate. In the present paper, we have made first principles calculations to study the lattice dynamics of ZrO$_2$ polymorphs and phase transformation at finite temperatures. Cubic phase shows a soft mode at the X point in the Brillouin zone, which should spontaneously induce cubic-to-tetragonal transformation. In tetragonal and monoclinic ZrO$_2$, all vibrational modes have real frequency. Calculations of Helmholtz free energies show that the tetragonal phase becomes more stable than the monoclinic phase above 1350 K, which is in quantitative agreement with experimental results. This confirms that vibrational entropy contributes to destabilize monoclinic ZrO$_2$ at elevated temperatures.

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I. INTRODUCTION

ZrO$_2$ has three polymorphs, cubic (c-ZrO$_2$), tetragonal (t-ZrO$_2$), and monoclinic (m-ZrO$_2$) phases. At elevated temperatures, ZrO$_2$ shows two kinds of solid-solid phase transformations, i.e., cubic-tetragonal (c-t) (Refs. 1 and 2) and tetragonal-monoclinic (t-m) (Refs. 3 and 4) transformations. The c-t transformation is characterized by displacement of oxygen ion and elongation of cation sublattice in the [001] and [001] directions. The t-m transformation occurs with a volume expansion and a shear distortion parallel to the basal plane of t-ZrO$_2$. ZrO$_2$-based ceramics exhibits various outstanding properties that are closely related to the phase transformations. Alloying with suitable aliovalent cations stabilizes c-ZrO$_2$ at a room temperature and originates their functional properties such as high oxide-ionic conductivity. Cubic-stabilized ZrO$_2$ has been widely used as a solid electrolyte in a solid oxide fuel cell (SOFC) and an oxygen gas sensor. In 1975, Garvie et al. found the transformation toughening in t-ZrO$_2$ solid solutions. The large volume expansion associated with the t→m transformation is known as the origin of shielding force on crack propagation and thereby leads to high fracture toughness. In order to control and to improve the properties of ZrO$_2$-based ceramics, it is necessary to fully understand the mechanism of these phase transformations. The phase transformation has been mainly analyzed through phenomenological approach. The c-t transformation of ZrO$_2$ was first observed by Smith and Cline, and was originally considered as a first-order transformation. On the other hand, Sakuma and coworkers proposed that the transformation was interpreted as a second-order type. Analyses from the Landau theory or the time-dependent Ginzburg-Landau (TDGL) equation have revealed that the c→t transformation can be explained by both of first-order and second-order models. Such phenomenological approaches have limitation to reveal the substance of phase transformation. The t-m transformation is regarded as a martensitic transformation, i.e., a large thermal hysteresis, an athermal transformation, a burst phenomenon, surface tilting, formation of twin and dislocation and an orientation relationship between the two phases.

First principles calculations have been very successful to predict structures, properties, and behaviors of materials in a quantitative manner. Although most of the calculations have been done for the ground state, i.e., at the zero temperature, recent progresses in computational technique enable us to determine the full phonon dispersion of solids. Thereby one can compute specific heats, vibrational entropy, and other thermodynamical quantities as a function of temperature and high pressures. However, such calculations are still in the early stage for applications to materials science issues, since they are still computationally demanding. The present study aims to clarify the origin of phase transformations in ZrO$_2$ by first principles lattice dynamics calculations.

II. COMPUTATIONAL METHODOLOGY

The structures of ZrO$_2$ polymorphs were preliminarily determined by ground state calculations. The total energy calculations were performed using VASP code, which is based on the density functional theory (DFT). Exchange and correlation functional was given by the generalized gradient approximation (GGA) as proposed by Perdew and Wang. Electron-ion interaction was represented by the projector augmented wave (PAW) method with plane waves up to an energy of 500 eV. The reference configurations for valence electrons were 4s$^2$ 4p$^6$ 5s$^2$ 4d$^2$ for Zr and 2s$^2$ 2p$^4$ for O. Lattice constants and internal positions in primitive cells at various volumes were fully optimized. The k-point meshes of Brillouin zone sampling in primitive cells, based on the Monkhorst-Pack scheme, were $4 \times 4 \times 4$ for cubic ($c$-ZrO$_2$, 10 irreducible points), $5 \times 5 \times 3$ for tetragonal ($t$-ZrO$_2$, 12 irreducible points) and $3 \times 3 \times 3$ for monoclinic.

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TABLE I. Calculated structural parameters of a unit cell and total energy per formula unit for c-, t-, and m-ZrO\(_2\) in comparison with a previous pseudopotential calculation and with an experiment.

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Present</th>
<th>Calc.(^a)</th>
<th>Expt.(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-ZrO(_2) (Fm(3)m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a (\text{Å}))</td>
<td>5.145</td>
<td>5.0371</td>
<td>5.108</td>
</tr>
<tr>
<td>Energy (eV/f.u.)</td>
<td>–28.413</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-ZrO(_2) (P(4_2/)nmc)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a (\text{Å}))</td>
<td>3.642</td>
<td>3.5567</td>
<td>3.591</td>
</tr>
<tr>
<td>(c (\text{Å}))</td>
<td>5.295</td>
<td>5.1044</td>
<td>5.169</td>
</tr>
<tr>
<td>(c/\sqrt{2}a)</td>
<td>1.028</td>
<td>1.0140</td>
<td>1.018</td>
</tr>
<tr>
<td>O(0, 0.5, (z))</td>
<td>0.196</td>
<td>0.2082</td>
<td>0.204</td>
</tr>
<tr>
<td>Energy (eV/f.u.)</td>
<td>–28.503</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-ZrO(_2) (P(_2_1/c))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a (\text{Å}))</td>
<td>5.211</td>
<td>5.1083</td>
<td>5.1505</td>
</tr>
<tr>
<td>(b (\text{Å}))</td>
<td>5.286</td>
<td>5.1695</td>
<td>5.2116</td>
</tr>
<tr>
<td>(c (\text{Å}))</td>
<td>5.388</td>
<td>5.2717</td>
<td>5.3173</td>
</tr>
<tr>
<td>(\beta) (deg)</td>
<td>99.590</td>
<td>99.21</td>
<td>99.230</td>
</tr>
<tr>
<td>Zr1((x), (y), (z))</td>
<td>(0.277, 0.043, 0.210)</td>
<td>(0.2769, 0.0422, 0.2097)</td>
<td>(0.2754, 0.0395, 0.2083)</td>
</tr>
<tr>
<td>O1((x), (y), (z))</td>
<td>(0.070, 0.336, 0.343)</td>
<td>(0.0689, 0.3333, 0.3445)</td>
<td>(0.0700, 0.3317, 0.3447)</td>
</tr>
<tr>
<td>O2((x), (y), (z))</td>
<td>(0.450, 0.758, 0.478)</td>
<td>(0.4495, 0.7573, 0.4798)</td>
<td>(0.4496, 0.7569, 0.4792)</td>
</tr>
<tr>
<td>Energy (eV/f.u.)</td>
<td>–28.612</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 47.  
\(^{b}\)Calculated from cubic root of the \((\sqrt{2}a)^2\times c\) of t-ZrO\(_2\) unit cell in Ref. 48.  
\(^{c}\)Reference 48.  
\(^{d}\)Reference 49.
tetragonal phase is a stable structure with regard to the lattice vibration. Dispersion curve of the phonon of $m$-ZrO$_2$ is composed of real frequency except that imaginary frequency of the transverse acoustic (TA) mode at the vicinity of $\Gamma$ point along the $\Gamma Y$ line. The direct method occasionally obtains unexpected softening of long wavelength phonon owing to the limitation of supercell size. Such problem can be resolved by sufficiently larger supercell. However, it should be noted that this error is small ($0.7\text{THz}$). Figure 1 also shows phonon-DOS of three phases in the ground state and their partial components per atom. Since a zirconium atom is heavier than an oxygen atom, partial phonon-DOS indicates that oxygen has higher frequencies than zirconium in all phases. In the cubic phase, the phonon-DOS of zirconium atoms mainly distributes below 10 THz and has a sharp peak at 3.2 THz. The spectrum of oxygen atoms exists higher than 5 THz and has large peaks at 16.5 and 19.0 THz. In the spectra of $t$-ZrO$_2$, discriminative peaks disperse and become smaller compared with those of $c$-ZrO$_2$. $m$-ZrO$_2$ has much broader phonon-DOS spectra and has no remarkably strong peaks. The frequency of phonon scatters with lowering symmetry.

Lattice vibration at $\Gamma$ point can be closely investigated by infrared (IR) and Raman spectra. To our knowledge, no experimental IR and Raman spectra of pure $c$-ZrO$_2$ is reported thus far. Therefore, discussion on the phonon at $\Gamma$ point is limited to $t$- and $m$-ZrO$_2$ here. Group theoretical analysis indicates that $t$-ZrO$_2$ has three IR-active modes ($2E_u + A_{2u}$) and six Raman-active modes ($3E_g + A_{1g} + 2B_{1g}$). In the case of $m$-ZrO$_2$, 15 IR-active modes ($8A_u + 7B_u$) and 18 Raman-
TABLE II. Frequencies (cm\(^{-1}\)) and symmetry assignment of IR-active phonon mode at \(\Gamma\) point in \(t\)- and \(m\)-ZrO\(_2\). Parentheses indicate the different symmetry assignment proposed in the literatures from the present results. “(u)” means that the assignment is unidentified.

<table>
<thead>
<tr>
<th>Present study</th>
<th>(t)-ZrO(_2)</th>
<th>(m)-ZrO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.(^a)</td>
<td>Calc.(^b)</td>
</tr>
<tr>
<td>76 (E_u)</td>
<td>154</td>
<td>152.7</td>
</tr>
<tr>
<td></td>
<td>270.5 (LO)</td>
<td>232 (LO)</td>
</tr>
<tr>
<td>325 (A_{2u})</td>
<td>334</td>
<td>338.5</td>
</tr>
<tr>
<td></td>
<td>663.8 (LO)</td>
<td>354 (LO)</td>
</tr>
<tr>
<td>435 (E_u)</td>
<td>437</td>
<td>449.4</td>
</tr>
<tr>
<td></td>
<td>734.1 (LO)</td>
<td>650 (LO)</td>
</tr>
</tbody>
</table>

\(^a\)Reference 47.  
\(^b\)Reference 51.  
\(^c\)Reference 55.  
\(^d\)Reference 56.  
\(^e\)Reference 54.  

active modes (9\(A_g\) + 9\(B_g\)) exist. The calculated frequencies of IR- and Raman-active mode at \(\Gamma\) point in \(t\)- and \(m\)-ZrO\(_2\) are tabulated in Tables II and III, respectively, in comparison with previous theoretical and experimental results. The present study cannot obtain the frequencies of IR-active LO modes, for the Born effective charges were not considered. The frequency of lower \(E_u\) mode of \(t\)-ZrO\(_2\) is underestimated half as much as the previous reports. Except these points, our calculations well reproduce the experimental IR spectra of \(t\)-ZrO\(_2\). As is the case with Ref. 47 and 54, calculated IR-active modes in \(m\)-ZrO\(_2\) show clear deference from experimental ones. Although theoretical calculations obtain phonons with frequencies of around 180, 230, and 300 cm\(^{-1}\), the peaks of equivalent modes have not been reported in experimental spectra.\(^{36,37}\) Zhao and Vanderbilt\(^{37}\) calculated the intensity of an IR spectrum for \(m\)-ZrO\(_2\). They have found that the peak intensities of these modes are very weak and have proposed that these peaks are probably obscured by strong ones existing near. As can be seen in Table III, our calculations of Raman-active modes in both \(t\)- and \(m\)-ZrO\(_2\) are in good agreement with the data of the literature. The correspondence between the present results and the previous experiments for IR and Raman spectra implies that our calculations on lattice dynamics are suitable to analyze the thermodynamical properties of ZrO\(_2\) polymorphs.

C. Thermodynamical properties and phase transformation

Based on quasiharmonic approximation, we can obtain Helmholtz free energy (\(F\)), entropy of vibration (\(S_{\text{vib}}\)), and
specific heat at constant volume \( C_v \) at finite temperature from phonon-DOS with various lattice volumes \( V \).\(^{64}\) Application of the quasiharmonic approximation to \( c\)-ZrO\(_2\) was impracticable because density of soft modes remarkably increases even with small volume expansion of about 0.7%. We will hereafter discuss only \( t\)- and \( m\)-ZrO\(_2\). Figure 2 shows a plot of the Helmholtz free energy of \( t\) and \( m\)-ZrO\(_2\) against a lattice volume at temperatures from 0 to 1000 K. A lattice volume with minimum free energy against lattice volume \( V \) is isothermal bulk modulus \( B \) and pressure, respectively. Minimum energy points are connected by a dashed line in Fig. 2. As shown in this figure, the lattice volume becomes larger with increase of temperature. Thermal volume expansion can be indirectly reproduced by the quasiharmonic approximation without taking anharmonicity into account. Figure 3 shows the temperature dependence of volume expansion \( \delta V/V \), isothermal bulk modulus \( B \), molar specific heat at constant volume \( C_v \) and that at constant pressure \( C_p \), and entropy \( S \) against temperature in \( m\)-ZrO\(_2\). Solid lines are the calculated results and blank symbols are experimental results quoted from Refs. 1 and 3.

As indicated in Fig. 3, our calculations are in good agreement with experimental data of \( \delta V/V, C_v \), and \( S \). Softening of \( B \) with temperature can be observed. Chan \textit{et al.}\(^{66}\) reported \( B \) of 201 and 192 GPa at 293 K and 1273 K for \( m\)-ZrO\(_2\), respectively, using sound velocity measurements. The present calculations underestimated the experimental \( B \). This is, however, a general trend for calculation with the GGA. These results imply that the temperature dependence of these physical parameters can be satisfactorily evaluated without taking into account the influence of Born effective charges. This is probably due to that total phonon-DOS, from which thermodynamical functions are calculated,\(^{64}\) is impervious to LO/TO splitting. Born effective charge only affects the frequencies of LO modes with long wavelength and leave the frequencies of TO modes invariant. Therefore, LO/TO splitting contributes little to the total phonon-DOS because the influence of LO modes is limited only to the small volume of a reciprocal lattice in the vicinity of the \( \Gamma \) point.\(^{57}\)

The \( t\)-\( m \) phase transformation of ZrO\(_2\) has been accepted as a typical martensitic transformation in ceramics and exhibits a thermal hysteresis. The temperatures of the \( t\)-\( m \) transformation on cooling \( M_s \) and heating \( A_s \) were reported to be about 1200 K and 1500 K, respectively.\(^{3,4}\) The transformation temperature determined from Gibbs free energies should exist between \( M_s \) and \( A_s \) because the transformation needs driving force to overcome strain energy and interface energy induced by the transformation. Comparing the temperature-dependent free energies of the \( t \) and \( m \) phases, we are able to obtain the transformation temperature. Solid-solid phase transformation can be discussed with Helmholtz free energy instead of Gibbs free energy in an ambient pressure because volume change \( \Delta V \) is very small. Given that \( P \) is 1 atm, the calculated value of \( P\Delta V \) for \( t\)- and \( m\)-ZrO\(_2\) is 6.9 \times 10^{-7} \text{ eV at 300 K. The effect of } P\Delta V \text{ is thus negligible.}\)

Figure 4(a) indicates plots of difference of Helmholtz free energy \( \Delta F_{t\rightarrow m} \), internal energy \( \Delta U_{t\rightarrow m} \), and entropy term \( \Delta S_{t\rightarrow m} \) against temperature. It can be clearly found from Fig. 4(a) that the calculated temperature of \( t\)-\( m \) phase transformation is about 1350 K. This is consistent with the pre-

![FIG. 2. Plots of Helmholtz free energy (F) per formula unit against lattice volume (V) per formula unit in (a) tetragonal and (b) monoclinic phases from 0 to 1000 K at every 100 K. Solid lines are F-V fitting curves according to the third-order Birch-Murnaghan equation of states. Dashed line connects minimum energy points at each temperature.](image)

![FIG. 3. Plots of (a) volume expansion (\( \delta V/V \)), (b) bulk modulus (\( B \)), (c) molar specific heat at constant volume (\( C_v \)) and that at constant pressure (\( C_p \)), and (d) entropy (\( S \)) against temperature in \( m\)-ZrO\(_2\). Solid lines are the calculated results and blank symbols are experimental results quoted from Refs. 1 and 3.](image)
FIG. 4. (a) Temperature dependence of difference of Helmholtz free energy ($\Delta F_{t-m}$), internal energy ($\Delta U_{t-m}$), and entropy term ($T\Delta S_{t-m}$) between $t$ and $m$ phases. Energies per formula unit are indicated. (b) Partial component of $T\Delta S_{t-m}$ for zirconium and oxygen per atom are plotted against temperature.

diction that the enegergical transformation temperature is between experimental $M_s$ and $A_s$. To our best knowledge, the $t$-$m$ transformation temperature of ZrO$_2$ can be quantitatively reproduced for the first time without any empirical parameters. $t$-ZrO$_2$ is less stable than $m$-ZrO$_2$ with the regard to the internal energy over the whole range of temperature. On the other hand, the $T\Delta S_{t-m}$ of $t$-ZrO$_2$ is always larger than that of $m$-ZrO$_2$. This is due to the fact that $S_{ vib}$ of $t$-ZrO$_2$ is always larger than that of $m$-ZrO$_2$. Contributions of zirconium and oxygen atoms to $T\Delta S_{t-m}$ are shown in Fig. 4(b). Both elements in $t$-ZrO$_2$ have larger vibrational entropy than those in $m$-ZrO$_2$. It can be concluded that inversion of free energy between $t$- and $m$-ZrO$_2$ at elevated temperatures is originated from the effect of vibration. These results suggest that ab initio calculations for lattice dynamics on the basis of the quasiharmonic approximation are powerful tools to theoretically investigate solid-solid phase transformation in a quantitative manner.

IV. CONCLUSION

Phonon vibrations and their density of states in $c$-, $t$-, and $m$-ZrO$_2$ were systematically investigated by first principles calculations using VASP code combined with the direct method. In $c$-ZrO$_2$, the frequency of $X_2$ mode was calculated to be imaginary. This unstable soft-mode should induce $c \rightarrow t$ phase transformation. On the other hand, it was found that the phonon modes have real frequencies in $t$- and $m$-ZrO$_2$ and are observed to be stable vibrations.

Based on the quasiharmonic approximation, temperature dependence of Helmholtz free energies of $t$- and $m$-ZrO$_2$ was computed. Our calculations indicated that $t$-ZrO$_2$ become more stable than $m$-ZrO$_2$ at temperatures higher than 1350 K. The calculated temperature of $t$-$m$ phase transformation is in quantitatively good agreement with experimental data. Further investigation reveals that vibrational entropy of Zr and O ions is attributed to the stabilization of $t$-ZrO$_2$ at elevated temperatures. Phonon is one of the principal factors to control $c$-$t$-$m$ phase transformation in ZrO$_2$.

ACKNOWLEDGMENTS

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AB INITIO LATTICE DYNAMICS AND PHASE...

PHYSICAL REVIEW B 71, 064301 (2005)

67. As a result of calculation with taking into account Born effective charges quoted from Ref. 51, errors of specific heat ($\Delta C_p$), entropy ($\Delta S$), and Helmholtz free energy ($\Delta F$) in $t$-ZrO$_2$ are calculated to be $0.01 \ J/K\ mol$, $0.25 \ J/K\ mol$ and $4 \ meV$ per formula unit at 1300 $K$, respectively. These errors are negligible in this study.