First Principles Phase Diagram Calculations for the Octahedral-Interstitial System ZrO$_X$, 0 ≤ X ≤ 1/2

Benjamin Paul Burton*, Axel van de Walle$^{11}$, and Harold T. Stokes$^{22}$

Metallurgy Division National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, U.S.A.
$^1$Engineering and Applied Science Division, California Institute of Technology, 1200 E. California Blvd. MC 309-81, Pasadena, CA 91125, U.S.A.
$^2$Department of Physics and Astronomy, Brigham Young University, Provo, UT 84602, U.S.A.

(Received April 21, 2011; accepted November 8, 2011; published online December 19, 2011)

First principles based phase diagram calculations were performed for the octahedral-interstitial solid solution system $\alpha$ZrO$_X$ (\(\alpha\)Zr[\(\alpha\)\_\{\[\alpha\]\_\}O\_X; \{\} = vacancy; 0 \leq X \leq 1/2\) ). The cluster expansion method was used for ground state analysis, and to calculate the phase diagram. The predicted diagram has four ordered ground-states in the range 0 ≤ X ≤ 1/2, but one of these, at X = 5/12, is predicted to disproportionate at T ≈ 20 K, well below the experimentally investigated range T ≈ 420 K. Thus, at T ≥ 420 K, the first-principles based calculation predicts three ordered phases rather than the four that have been reported by experimentalists.

**KEYWORDS:** ZrO$_X$, Zr suboxides, zircalloy, first principles, phase diagram calculation, vacancy-interstitial ordering, order–disorder, alloy theory

1. Introduction

Zircalloy is used as nuclear fuel-rod cladding in light water reactors, but it is metastable with respect to oxidation by the UO$_2$ fuel.1–4

Oxidation of zircalloy transforms it from the high-temperature (high-T), oxygen-poor, bcc solution (\(\beta\)ZrX) into the low-T, oxygen-rich, hcp-based solution (\(\alpha\)ZrO$_X$). At temperatures between about 1173 and 573 K various ordered phases have been reported.5–13

Octahedral interstitial ordering of oxygen (O), and vacancies (\{\} ) in \(\alpha\)ZrO$_X$ (\(\alpha\)Zr[\{\{\}\}O\_X; 0 \leq X \leq 1/2\) ) increases microhardness14 and brittleness1 and therefore, promotes stress corrosion cracking. Oxygen:vacancy (O:[] ) order–disorder transitions were studied via heat capacity measurements: Arai and Hirabayashi12 examined alloys with O/Zr ratios of 0.16 and 0.24 at 473–973 K; Tsuji and Amaya15 made similar measurements on alloys with O/Zr ratios of 0.0, 0.10, 0.13, and 0.24, at 325–905 K.

Arai and Hirabayashi12 achieved a high degree of long-range O[ ] order in samples that were cooled from 623 to 523 K, during a period of about one month, which indicates a high mobility of oxygen in \(\alpha\)Zr[\{\{\}\}O\_X, even at such modest temperatures; hence a system that is highly reactive even at such moderate temperatures.

A recent computational study16 reported ground-state structures and order–disorder transition temperatures for Zr$_2$O and Zr$_3$O, but did not present a calculated phase diagram, or report if the calculated order–disorder transitions in Zr$_2$O and Zr$_3$O are first-order, as experiment indicates, or continuous.

The results presented below are mostly consistent with experimental studies with respect to the comparison between computationally predicted ground-state (GS) structures and reported (experimental) low-temperature (T ≲ 500 K) ordered phases. With the exception that in the range 0.25 ≲ X ≲ 0.5 the calculations predict only two ordered phases at T > 150 K, rather than the three called \(\alpha_{Zr}^2\), \(\alpha_{Zr}^2\), and \(\alpha_{Zr}^3\) in Arai and Hirabayashi.12

Experimental values for the maximum solubility of O in Zr, X$_{\text{max}}$, range from: X$_{\text{max}}$ ≈ 29 at. %6,17 to X$_{\text{max}}$ ≈ 35 at. %18 and X$_{\text{max}}$ ≈ 40 at. %10,12,13 The first-principles results presented here support a higher value; i.e., X$_{\text{max}}$ ≥ 1/2. This may reflect an insufficiently negative calculated value for the formation energy of monoclinic ZrO$_2$.

2. Methodology

2.1 Total energy calculations

Formation energies, \(\Delta E_f\) (Fig. 1) were calculated for fully relaxed hcp \(\alpha\)Zr, hcp \(\alpha\)ZrO (hcp \(\alpha\)Zr with all octahedral interstices occupied by O), and 96 \(\alpha\)Zr[ \{\{\}\}O\_$_m$ supercells of intermediate composition (m, n integers). All calculations were performed with the density functional theory (DFT) based Vienna \textit{ab initio} simulation program (VASP, version 4.4.5) using projector-augmented plane-wave pseudo-potentials, and the generalized gradient approximation for exchange and correlation energies. Electronic degrees of freedom were optimized with a conjugate gradient algorithm, and both cell constant and ionic positions were fully relaxed. Pseudopotential valence electron configurations were: Zr: 4s4p5s4d; O: 3s²3p⁴.

Total energy calculations were converged with respect to k-point meshes by increasing the density of k-points for each \(\{\}\) supercell until convergence. A 500 eV energy cutoff was used, in the “high precision” option which guarantees that \textit{absolute} energies are converged to within a few meV/site (a few tenths of a kJ/site of exchangeable species; O, [ ] ).

Residual forces were typically 0.02 eV or less.

Calculated formation energies, \(\Delta E_f\), relative to a mechanical mixture of \(\alpha\)Zr + \(\alpha\)ZrO, for the 96 \(\alpha\)Zr[ \{\{\}\}O\_$_m$ supercells are plotted as solid circles in Fig. 1. Values of \(\Delta E_f\) are

\[
\Delta E_f = \frac{E_{\text{tot}} - mE_{\text{tot}\alpha\text{Zr}} - nE_{\text{tot}\alpha\text{ZrO}}}{(m + n)},
\]

E-mail: benjamin.burton@nist.gov
E-mail: avdw@caltech.edu
E-mail: stokesh@byu.edu
where: $E_{\text{Str}}$ is the total energy of the $aZr_{m+n}$[ $\alpha_nO_n$ supercell; $E_{aZr}$ is the energy/atom of $aZr$; $E_{aZrO}$ is the energy/atom of $aZrO$.

2.2 The cluster expansion Hamiltonian

The cluster expansion, CE,\(^{21}\) is a compact representation of the configurational total energy. In the $aZr[ 1-xO_x$ system, the solid solution configuration is described by pseudospin occupation variables $\sigma_i$, which take values $\sigma_i = -1$ when site-$i$ is occupied by $[ ]$ and $\sigma_i = +1$ when site-$i$ is occupied by $O$.

The CE parameterizes the configurational energy, per exchangeable cation, as a polynomial in pseudospin occupation variables:

$$E(\sigma) = \sum_\ell m_\ell J_\ell \left( \prod_{i \in \ell} \sigma_i \right)$$  \hspace{1cm} \text{(2)}

Cluster $\ell$ is defined as a set of lattice sites. The sum is taken over all clusters $\ell$ that are not symmetrically equivalent in the high-T structure space group, and the average is taken over all clusters $\ell'$ that are symmetrically equivalent to $\ell$. Coefficients $J_\ell$ are called effective cluster interactions, ECI, and the multiplicity of a cluster, $m_\ell$, is the number of symmetrically equivalent clusters, divided by the number of cation sites. The ECI are obtained by fitting a set of VASP FP calculated structure energies, $\{E_{\text{Str}}\}$. The resulting CE can be improved as necessary by increasing the number of clusters $\ell$ and/or the number of $E_{\text{Str}}$ used in the fit.

Fitting was performed with the Alloy Theoretic Automated Toolkit (ATAT)\(^{19,22-24}\) which automates most of the tasks associated with the construction of a CE Hamiltonian. A complete description of the algorithms underlying the code can be found in ref. 23. The zero- and point-cluster values were $-0.421118$ and $0.006221$ eV, respectively. The six pair and six 3-body ECI that comprise the complete CE Hamiltonian are plotted in Figs. 2(a) and 2(b), respectively. ECI for the isostructural TiO\(_X\) (open symbols, blue online) and HfO\(_X\) (open symbols, red online) systems are also plotted for comparison. As expected, nearest neighbor (nn) O–O pairs are highly energetic, and therefore strongly avoided; hence nn-pair ECI are strongly attractive (ECI $>0$, for O–O nn pairs); but beyond nn-pairs, the O–O pairwise ECI are close to zero. The ratio of magnitudes for nn-pair ECIs that are parallel ($J_i$) and perpendicular ($J_{i\perp}$) to $c_{\text{Hex}}$, respectively, is $J_i/J_{i\perp} \approx 2.5$. Note that the fourth nn-pair ECI is the second-nn parallel to $c_{\text{Hex}}$, ($J_i'$) and $J_i'/J_i \approx 0.09$.

The results presented here are similar to those in Ruban et al.\(^{16}\) although their effective pair interactions and ours are not identically defined.

Long-period superstructure (LPSS) phases were reported\(^{18}\) in samples with with bulk compositions close to Zr\(_2\)O (essentially the $\alpha'_1$ field in Arai and Hirabayashi,\(^{12}\) their Fig. 9). Hence, it is reasonable to speculate that the CE-Hamiltonian might be like that in an axial next nearest
neighbor Ising model (ANNHI-model),25 in which one expeks $J_\parallel$ and $J_\perp$ to be opposite in sign, and of comparable magnitudes ($0.3 \lesssim -J_\parallel/J_\perp \lesssim 0.7$); however, $J_\parallel/J_\perp \approx 0.09$ (Fig. 2).

3. Results

3.1 Ground-states

The CE was used for a ground-state (GS) analysis that included all configurations of $[ ]$ and $O$ in systems of 18 or fewer Zr-atoms (octahedral interstitial sites); a total of $2^{18} = 262,144$ structures. Five GS were identified in the range, $0 \leq X \leq 1/2$, i.e., at $X = 0, 1/6, 1/3, 5/12, \text{and } 1/2$; solid circles (black online) on the convex hull (solid line) in Fig. 1. The extension of the convex hull towards monoclinic solid circles (black online) on the convex hull (solid line) in Fig. 1. The extension of the convex hull towards monoclinic zirconia (ZrO$_2$) is also plotted in Fig. 1. The CE-results suggest that all four VASP-GS in the $\alpha$Zr$_{1-x}$O$_x$ subsystem are also GS of the Zr–O binary, and that the maximum solubility of O in $\alpha$Zr$_{63}$ is $X_{\text{max}} \approx 1/2$ (higher than the experimental value, $X \approx 0.4$). Note that, the predicted CE-GS at Zr$_{63}$ is not a GS for the VASP calculations (not a VASP-GS); hence the VASP-predicted maximum solubility of O in Zr is $X_{\text{max}} \approx 0.5$.

The larger open squares (red online) in Fig. 1 are CE-calculated values for the $\Delta E_f$ that correspond to the VASP calculations, and the smaller open squares (blue online) are $\Delta E_f$ for the remaining 262,144 $- 96 = 262,048$ structures in the GS analysis. The open diamond symbol (green online) indicates the calculated formation energy for the P6$_3$22 structure for Zr$_6$O that was originally proposed by Holmberg and Dagerhamn;27 this structure is also described in Table I. All space group determinations were performed with the FINDSYM program.19,26)

Crystal structures of the VASP- and CE-GS in Zr–ZrO are described in Table I and their idealized structures are drawn in Figs. 3(a)–3(d): Zr is represented by spheres connected with bond-sticks (yellowish-green online); O is represented by isolated spheres with bond-sticks (blue online); and $[ ]$ are represented by isolated spheres (red online).

Various low-T ordered structures have been reported6–13 with the most recent review by Sugizaki et al.,13 who used neutron diffraction to study short-range order in ZrO$_{63}$ solid solutions. Their Figs. 1(a)–1(c) presented representations of three ordering schemes that were observed within different homogeneity ranges: (a) ZrO$_3$ at $X \lesssim 1/3$ (P321); (b) ZrO$_2$ at $1/3 \lesssim X \lesssim 0.4$ (P6$_3$22); (c) ZrO$_2$ near the solubility limit $X \approx 0.4$ (P3$\overline{3}$m). Space groups for these idealized structures were not reported by Sugizaki et al.,13 they were determined in this work with the FINDSYM program.26 Comparing structures (a)–(c) above to the results of this work: (a) VASP calculations indicate that this structure is clearly not a GS; (b) is the P6$_3$22 structure shown as an open diamond (green online) in Fig. 1, its formation energy is very close, but higher than, the VASP-GS at $X = 1/3$; (c) is the same P3$\overline{3}$m structure as the VASP-GS at $X = 1/2$.

3.1.1 Zr$_6$O, $X = 1/6$, $\alpha''$

The structure of Zr$_6$O is thought to be isomorphous to that of Hf$_6$O and Ti$_6$O$_3$12,18 $a \approx \sqrt[3]{3a_0}$; $c \approx c_0$; $Z = 3$ ($a_0$ and $c_0$ are the cell constants of the disordered $P6_3/mmc$ alloy).9 This is also the VASP-GS at $X = 1/6$, Fig. 3(a) and Table I.

3.1.2 Zr$_2$O, $X = 1/3$, $\alpha''$, ..., $\alpha''$

Based on X-ray diffraction studies, Holmberg and Dagerhamn5 proposed a P6$_3$22 structure (open diamond, green online, in Fig. 1) with $a \approx \sqrt[3]{3a_0}$ and $c \approx c_0$ for a

<table>
<thead>
<tr>
<th>System</th>
<th>$X$</th>
<th>Atomic fraction</th>
<th>Space group</th>
<th>Pearson symbol</th>
<th>Calculated cell constants ($\overline{\text{Å}}$)</th>
<th>Idealized atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$_6$O</td>
<td>1/6</td>
<td>R3 (2)</td>
<td>$a \approx \sqrt[3]{3a_0}$</td>
<td>$c \approx c_0$</td>
<td>$Z = 6$ (6a)</td>
<td>$a = 6.374$, $c = 3.834$</td>
</tr>
<tr>
<td>Zr$_2$O</td>
<td>1/3</td>
<td>P6$_3$22</td>
<td>$a \approx \sqrt[3]{3a_0}$</td>
<td>$c \approx c_0$</td>
<td>$Z = 6$ (6a)</td>
<td>$a = 6.374$, $c = 3.834$</td>
</tr>
<tr>
<td>Zr$_3$O$_3$</td>
<td>5/12</td>
<td>R3 (2)</td>
<td>$a \approx \sqrt[3]{3a_0}$</td>
<td>$c \approx c_0$</td>
<td>$Z = 18$ (18a)</td>
<td>$a = 12.74$, $c = 10.07$</td>
</tr>
<tr>
<td>Zr$_2$O$_2$</td>
<td>1/2</td>
<td>P6$_3$1m</td>
<td>$a \approx \sqrt[3]{3a_0}$</td>
<td>$c \approx c_0$</td>
<td>$Z = 6$ (6a)</td>
<td>$a = 6.374$, $c = 3.834$</td>
</tr>
</tbody>
</table>

014004-3 ©2012 The Physical Society of Japan
sample with $X \geq 0.26$. Based on single crystal neutron diffraction studies Yamaguchi\(^{16}\) reported X-ray, electron and neutron diffraction data on samples in the range ZrO\(_{0.18}\)–ZrO\(_{0.30}\) (1/5 $\leq X \leq 3/7$) and listed atomic coordinates for a “P3c1” structure with $a \approx \sqrt{3}a$, $c \approx 3c$. Yamaguchi\(^{16}\) also reported confirmation of the P6\(_{122}\)2 structure in the composition range $0.33 < X < 0.4$ (1/2 $< X < 2/3$). The FP results presented here suggest that the VASP-GS at $X = 1/3$ is the R3\(_c\) structure depicted in Fig. 3(b). The calculated energy-difference between these two structures is only 0.006 eV, and this difference is probably within DFT error, but the precision of these calculations is sufficient to recognize the R3\(_c\) structure as the VASP-GS.

### 3.1.3 Zr\(_{12}\)O\(_5\), $X = 5/17$

This structure does not correspond to any reported phase, and because it is predicted to disproportionate at $T \geq 20$ K. It is not expected to be observed experimentally.

### 3.1.4 Zr\(_2\)O, $X = 1/2$, $\alpha''_4$

The only Zr\(_2\)O structure listed in Pearson\(^{27}\) is cubic, and the apparent solubility limit of $X \approx 0.4$, rather than $X = 1/2$, which suggests that the VASP calculations may underestimate the stability of monoclinic ZrO\(_2\), and therefore finds the GS tieline between the P31m GS at $X = 1/2$ and monoclinic ZrO\(_2\), rather than between the R3\(_c\) GS at $X = 1/3$ and monoclinic ZrO\(_2\). Another possibility is that the experimentally measured low-temperature equilibrium between Zr-suboxides and monoclinic ZrO\(_2\) was measured at too low a fugacity of oxygen to stabilize the P31m phase at $X = 1/2$. As one expects from the ECI (Fig. 2), there are no O–O nn pairs in the VASP-GS P31m structure, or in any of the four structures with formation energies within 0.01 eV (right panel Fig. 1).

### 3.2 The phase diagram

A first principles phase diagram (FPPD) calculation was performed with grand canonical Monte Carlo (MC) simulations using the emc2 code which is part of the ATAT package\(^{22–24}\). Input parameters for emc2 were: a simulation box with at least 1568 octahedral sites (15×15×6 supercell); 2000 equilibration passes; 2000 Monte Carlo passes. The predicted phase diagram is shown in Fig. 4. Most phase boundaries were determined by following long-range order-parameters of the various ordered phases as functions of $X$ and $T$. Here, long-range order parameters, $\eta$, are defined as the fraction of sites hosting O or [ ], relative to the corresponding fraction in the specified GS. Typically, but not always, these order parameters vary from unity in the perfectly ordered GS to zero in the disordered phase, and to different non-zero values in ordered phases other than their specified GS. Continuous or discontinuous changes in order parameters constrain and/or characterize phase boundaries. Dotted boundaries are used to acknowledge uncertainties in phase boundary determinations.

### 3.3 The intermediate temperature $\alpha'$-phase

As observed experimentally in samples with $X = 0.41$,\(^{10}\) (up-pointing triangles, green online, Fig. 4) a two-step order–disorder process is predicted for 0.25 $\leq X \lesssim 0.5$ (Fig. 5). The data reported in Hirabayashi et al.\(^{10}\) appear to indicate that both order–disorder transitions are second-order (continuous) in character, at least at $X = 0.41$, but the calculations reported here suggest that the lower-T transition is strongly first-order (at least at $X = 1/2$) while the higher-T transition is continuous.

The simulated intermediate-temperature $\alpha'$-phase crystal structure was determined by symmetry analysis, using the ISODISTORT program.\(^{19,28}\) There are two plausible transi-
Note the different results for the diagram calculated from this work (dotted phase boundaries are less transformational diagram) (symbols) and the tentative diagram (solid lines) in Arai and Hirabayashi (their Figs. 1 and 9, respectively); (b) the diagram calculated from this work (dotted phase boundaries are less precisely determined than solid boundaries). Note the different results for 0.25 ≤ X ≤ 0.42 and 420 ≤ T ≤ 725 K.

Path (1) can be ruled out because it requires a first-order 63/mmc → 63/mcm transition, with unit-cell expansion along both a_{hex} axes; which neither experiment nor computation supports.

Path (2) permits a continuous 63/mmc → 3m1 transition, as observed experimentally and supported computationally. The average α, 3m1 structure is described in Table II and depicted in Fig. 6; where partially occupied O1 sites are represented by relatively smaller and larger spheres (blue online). The precise occupations of sites O1 and O2 can be written as x and 2X − x, respectively; where x < 1/2 is the O-occupancy of site O1, and X = O/Zr; i.e., at X = 0.41 and x = 0.22 then 2X − x = 0.60. With respect to space-group determination, the only requirement is that the occupancy of site-O1 must differ from that of site-O2. The 3m1 structure is clearly consistent with the computational results shown in Figs. 7(a) and 7(b). For clarity, the O1[-]-distributions (online O = red, [ ] = gray) in these figures were simulated on reduced (6×6×3) supercells by cooling from 1000 to 900 K, and Zr-atoms were omitted. Note the strong preference for O1[-]-ordering along c_{hex}; i.e., strong O-O on avoidance along c_{hex}. In the average 3m1 structure this leads to alternating nn-layers, ⊥ c_{hex} that are relatively O-rich and O-poor ([ ]-rich). Visually, this statistical difference is obscured in the simulation.

**Table II.** Atomic positions in 3m1 (ITT 164) α’ crystal structure: a ≈ a_{0} = 3.32 Å; c ≈ c_{0} = 5.14000 Å; *X = O/Zr.*

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>2d</td>
<td>1/3</td>
<td>2/3</td>
<td>≈1/4</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>x_{O1} &lt; 1/2</td>
</tr>
<tr>
<td>O2</td>
<td>1b</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>2X − x_{O1}</td>
</tr>
</tbody>
</table>
Fig. 6. (Color online) Average $P\overline{3}m1$ structure of the $\alpha'$-phase. Small and intermediate sized spheres (blue online) represent less- and more oxygen-rich vacancy-sites ($O[\cdot]$ -sites), respectively. Larger spheres (red online) represent Zr atoms. More and less O-rich $O[\cdot]$ -sites segregate into alternating layers perpendicular to $c_{\text{hex}}$; reflecting nearest neighbor O-O avoidance.

Fig. 7. (Color online) Simulated O-, [ ]-distributions (red: gray online, respectively) at: (a) $X = 0.41$, $T = 300 \text{ K}$; and (b) $X = 0.27$, $T = 300 \text{ K}$. For clarity, Zr-atoms are omitted and a reduced ($6 \times 6 \times 3$) supercell was used. At $X = 0.41$ no O-O nn pairs are evident parallel to $c_{\text{hex}}$. At $X = 0.27$, almost all nn pairs parallel to $c_{\text{hex}}$ are $O[-]$, although two columns (first row, columns 4 and 5) have some O-O nn pairs, while perpendicular to $c_{\text{hex}}$ there are many more O-O and $[\cdot]-[\cdot]$ nn pairs.

4. Discussion

4.1 Comparison of calculated and experimental phase diagrams

The main differences between the FPPD presented here and the “tentative phase diagram” in Arai and Hirabayashi$^{12}$ [Fig. 4(a); their Fig. 9] are with respect to their representations of broad homogeneity ranges for three ordered phases in the range $0.25 \lesssim X \lesssim 0.42$ and $420 \lesssim T \lesssim 725 \text{ K}$. In this range, Arai and Hirabayashi report three low-T ordered phases, $\alpha''$, $\alpha'''$, and $\alpha''''$; whereas the FPPD has only two; note that the predicted GS at $X = 5/12$ disproportionate at $T \approx 20 \text{ K}$. Also, the FPPD-predicted $\alpha'$-phase field is significantly larger than the corresponding field in Fig. 4(a), and at $X = 0.41$ the $\alpha' \rightleftharpoons \alpha Z_{\text{hcp}}$ transition is predicted to occur $\approx500 \text{ K}$ higher than experiment suggests, Fig. 5(a). Typically, FPPD calculations overestimate order–disorder transition temperatures especially when, as here, the excess vibrational contribution to the free energy$^{29,30}$ is ignored. This trend has been observed in numerous systems,$^{30}$ although exceptions have been noted in systems where atomic size mismatch effects play a significant role,$^{29}$ so it is not surprising that agreement between experiment and theory is not close for the $\alpha' \rightleftharpoons \alpha Z_{\text{hcp}}$ order–disorder transition. Note however, that the maximum temperatures for stabilities of phases other than $\alpha'$ are roughly equal to those shown in Fig. 4(a).

4.2 Long-period superstructures at $X \approx 1/3$

Based on X-ray, neutron, and electron scattering data, Fehlmann et al.$^7$ and Yamaguchi and Hirabayashi$^{10}$ reported a variety of long-period superstructures (LPSS) in samples with bulk compositions $X \approx 1/3$ [the $\alpha''$ field, Fig. 4(a)] that were subjected to various heat treatments. The FPPD calculation presented here does not predict LPSS fields, but a similar calculation for HfO$_x$ appears to predict Devil’s Staircases of ordered phases at HfO and Hf$_2$O.$^{31}$ In an ANNNI-model like Hamiltonian, one expects, $0 \lesssim -J'_y/J_x \lesssim 0.7$, however, the 12-pair fit which includes $J'_y$ yields $J_x$ and $J'_y$ with the same sign and $J_x \approx J'_y/10$. Physically, the fitted values for $J_x$ and $J'_y$ are easy to rationalize in terms of O–O nn-repulsion, and this argues against stable LPSS phases, unless they are stabilized by competition between higher-order interactions; e.g., third and further nn-pair-ECI or multiplet interactions. In fact, FPPD calculations for the HfO$_x$ system, which has a CE Hamiltonian very similar to that for ZrO$_x$, indicate a Devil’s Staircase of LPSS phases at Hf$_2$O.$^{31}$

5. Conclusions

Ground-state ordered phases are predicted at $X = 0, 1/6, 1/3, 5/12$, and 1/2, but the one at $X = 5/12$ is predicted to disproportionate at $T \approx 20 \text{ K}$, hence it is not expected to be observed experimentally. In the range $0.25 \lesssim X \lesssim 0.5$, in which Arai and Hirabayashi$^{12}$ report three phases ($\alpha'', \alpha''', \alpha''''$ only two are predicted; i.e., the phase fields that Arai and Hirabayashi$^{12}$ draw for $\alpha''$ and $\alpha'''$ are predicted to be a single-phase solid solution. Figure 1(a) clearly indicates that a zeroth order model for octahedral interstitial O:[$\cdot$]-ordering is one in which first- and second-nn pairwise interactions ($J_j$ and $J_{jj}$, respectively) strongly favor O:[$\cdot$] nn-pairs; i.e., O–O nn-pairs are highly unfavorable, and $J_j/J_{jj} \approx 2.5$. Including $J_{jj}$ in the ECI fit does not yield an ANNNI-like$^{25}$ CE-Hamiltonian; however, recent FPPD calculations for the HfO$_x$ system,$^{31}$ (the HfO$_x$–CE is very similar to the ZrO$_x$–CE) predict Devil’s Staircases of LPSS phases at Hf$_2$O and Hf$_3$O.

©2012 The Physical Society of Japan

014004-6
The most probable transition path (on cooling) for O-rich solutions with $X \lesssim 0.4$, is $Pb_{3}/mmc \rightarrow P\bar{3}m1 \rightarrow P\bar{3}m1$; hence the average $\alpha'$-structure has $P\bar{3}m1$ symmetry with alternating O-rich and $\frac{1}{2}$-rich layers $\perp c_{\text{Hex}}$.

19) Disclaimer: the use of a specific software package should not be misinterpreted as implying a NIST endorsement of that package.
31) B. P. Burton and A. van de Walle: arXiv:1107.4318; submitted to CALPHAD J.