First Principles Phase Diagram Calculations for the Octahedral-Interstitial System ZrO\(_X\), \(0 \leq X \leq 1/2\)

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Abstract

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

I. 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 ($\beta$Zr$_X$) into the low-T, oxygen-rich, hcp-based solution ($\alpha$ZrO$_X$). At temperatures between about 1173K and 573K various ordered phases have been reported.$^{5-13}$

Octahedral interstitial ordering of oxygen (O), and vacancies ([ ] in $\alpha$ZrO$_X$ ($\alpha$Zr[$\big]{1-X}O_X$, $0 \leq X \leq 1/2$) increases microhardness$^{14}$ and brittleness$^{11}$, and therefore, promotes stress corrosion cracking. Order-disorder transitions were studied via heat capacity measurements: Arai and Hirabayashi$^{12}$ studied alloys with O/Zr ratios of 0.16 and 0.24 at 473K-973K; Tsuji and Amaya$^{15}$ made similar measurements on alloys with O/Zr ratios of 0.0, 0.10, 0.13, and 0.24, at 325K-905K.

Arai and Hirabayashi$^{12}$ achieved a high degree of long-range ordering in samples that were cooled from 623K to 523K, during a period of about one month, which indicates a high mobility of oxygen in $\alpha$Zr[$\big]{1-X}O_X$, even at such modest temperatures; hence a system that is highly reactive even at such moderate temperatures.

A recent computational study$^{16}$ reported ground-state structures and order-disorder transition temperatures for Zr$_6$O and Zr$_3$O, but did not present a calculated phase diagram, or report if the calculated order-disorder transitions in Zr$_6$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 ($T \lesssim 500K$) ordered phases. With the exception that in the range $0.25 \lesssim X \lesssim 0.5$ the calculations predict only two ordered phases at $T150K$,
rather than the three called $\alpha''_2$, $\alpha''_3$ and $\alpha''_4$ in Arai and Hirabayashi (1976).\cite{12}

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

II. METHODOLOGY

A. 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[$\text{ }]_{1-n}O_n$ supercells of intermediate composition. All calculations were performed with the density functional theory (DFT) based Vienna \textit{ab initio} simulation program (VASP, version 445\cite{19,20}) using projector-augmented plane-wave pseudopotentials, 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$_{sv}$: 4s4p5s4d; O$_s$: 3s$^2$3p$^4$.

Total energy calculations were converged with respect to k-point meshes by increasing the density of k-points for each structure 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[$\text{ }]_{1-n}O_n$ supercells are plotted as solid circles in Fig. 1. Values of $\Delta E_f$ are,

$$\Delta E_f = (E_{Str} - E_{\alpha Zr} - E_{\alpha ZrO})/2$$ (1)

where: $E_{Str}$ is the total energy of the $\alpha$Zr[$\text{ }]_{1-n}O_n$ supercell; $E_{\alpha Zr}$ is the energy/atom of $\alpha$Zr; $E_{\alpha ZrO}$ is the energy/atom of $\alpha$ZrO.
FIG. 1: Comparison of VASP (solid circles) and CE (larger open squares, red online) formation energies, ΔE_f, and a ground-state analysis on structures with 18 or fewer octahedral-interstitial sites (smaller open squares, blue online). Extension of the convex hull towards the formation energy of monoclinic zirconia, ZrO₂, indicates that the four ordered GS at X=1/6, 1/3, 5/12 and 1/2 are also predicted to be GS of the Zr-O binary.

B. The Cluster Expansion Hamiltonian

The cluster expansion, CE_{\text{31}}^{\text{P6}}_{\text{32}}, is a compact representation of the configurational total energy. In the αZr[ ]_{1−X}O system, the solid solution configuration is described by pseudospin occupation variables σ_i, which take values σ_i = −1 when site-i is occupied by [ ] and σ_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:
\[
E(\sigma) = \sum_{\ell} m_\ell J_\ell \left\langle \prod_{i \in \ell'} \sigma_i \right\rangle
\]  

(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)\textsuperscript{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\textsuperscript{23}. The zero- and point-cluster values were -0.421118 eV and 0.006221 eV, respectively. The six pair and six 3-body ECI that comprise the complete CE Hamiltonian are plotted in Figs. 2a and 2b, 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-[ ] nn pairs); but beyond nn-pairs, the O-[ ] pairwise ECI are close to zero. The ratio of magnitudes for nn-pair ECIs that are parallel- \((J_\parallel)\) and perpendicular \((J_\perp)\) to \(c_{\text{Hex}}\), respectively, is \(J_\parallel/J_\perp \approx 2.5\). Note that the 4’th nn-pair ECI is the second-NN parallel to \(c_{\text{Hex}}\), \((J'_\parallel)\) and \(J'_\parallel/J_\parallel \approx 0.09\).

These results are similar to those presented in Ruban et al\textsuperscript{16} although their effective pair interactions and ours are not identically defined.

Long-period superstructure (LPSS) phases were reported\textsuperscript{17,18} in samples with with bulk compositions close to Zr\(_3\)O (essentially the \(\alpha'\) field in Arai and Hirabayashi\textsuperscript{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 (ANNNI-model),\textsuperscript{25} in which one expects \(J_\parallel\) and \(J'_\parallel\) to be opposite in sign, and of comparable magnitudes \((0.3 \lesssim -J'_\parallel/J_\parallel \lesssim 0.7\textsuperscript{25})\); however, \(J'_\parallel/J_\parallel \approx 0.09\) (Figs. 2).
FIG. 2: Effective Cluster Interactions (ECI) for pair and 3-body interactions. Solid black symbols indicate the ZrO₅ₓ-fit which was used in the phase diagram calculation reported here. Open squares and down-pointing triangles (blue online) indicate the results of a fit for the TiO₅ₓ system. Open circles and open up-pointing triangles (red online) are from a fit for the HfO₅ₓ system. (a) The first two pair-ECI are for nearest-neighbor O-[ ] pairs that are parallel- (J∥) and perpendicular (J⊥), respectively, to cHex, and the 4’th nn pair-ECI is the second-nn parallel to cHex (J′∥). Pairwise-ECI are plotted as functions of inter-site separation. (b) 3-body interactions are plotted as functions of the index nᵢ₋j₋k which increases, nonlinearly, as the area of triangle i-j-k increases. Positive pairwise ECI imply a strong nn-pairwise O-[ ] attraction, i.e. a strong nn-pairwise O-O repulsion.

III. RESULTS

A. 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 2¹⁸ = 262,144 structures (reduced by symmetry). Five GS were identified in the range, 0 ≤ X ≤ 1/2, i.e. at X = 0, 1/6, 1/3, 5/12 and 1/2; solid circles (black online) on the
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$_{hcp}$ is $X_{max} \approx 1/2$ (higher than the experimental value, $X \approx 0.4$). Note that, the predicted CE-GS at Zr$_3$O$_2$ is not a GS for the VASP calculations (not a VASP-GS); hence the VASP-predicted maximum solubility of O in Zr is $X_{max} \approx 0.5$.

The larger open squares (red online) in Figure 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=262048 structures in the GS analysis. The open diamond symbol (green online) indicates the calculated formation energy for the P6$_3$22 structure for Zr$_3$O that was originally proposed by Holmberg and Dagerhamn$^{5}$; this structure is also described in Table I. All space group determinations were performed with the FINDSYM program.$^{19,26}$
TABLE I: Crystal structure parameters for predicted ground-state phases in the $\alpha Zr^{[1-X]}O_X$ system. Cell constants are given in Å.

| System | X atomic fraction O | Space Group | Calculated cell constants (Å) | Idealized Atomic Coordinates |
|--------|---------------------|-------------|-------------------------------|-----------------------------|
| Zr$_6$O | 1/6                 | R$\bar{3}$  | $a \approx \sqrt{3}a_0$ 5.5333 | O: 1/6, 1/6, 1/6 Zr: 3/4, 1/12, 5/12 |
|         | 1/7                 | hP7         | $c \approx 3c_0 = 15.33$    | Zr: 11/12, 7/12, 1/4 Zr: 1/12, 5/12, 3/4 Zr: 7/12, 1/4, 11/12 |
| Zr$_3$O | 1/3                 | R$\bar{3}$c | $a \approx \sqrt{3}a_0$ 5.5671 | O: 1/6, 1/6, 1/6 Zr: 3/4, 1/12, 5/12 |
|         | 1/4                 | hP8         | $c \approx 3c_0 = 15.381$   | Zr: 11/12, 7/12, 1/4 Zr: 1/12, 5/12, 3/4 Zr: 7/12, 1/4, 11/12 |
| Zr$_3$O | 1/3                 | P6$_3$22    | $a \approx \sqrt{3}a_0$ 5.5585 | O: 1/3, 2/3, 0 Zr: 1/3, 0, 0 |
|         | 1/4                 | hP8         | $c \approx c_0 = 5.1327$    | Zr: 0, 1/3, 0 Zr: 2/3, 2/3, 0 Zr: 0, 2/3, 1/2 |

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|    | 5/12 | R₃ |  \( a \approx \sqrt{3}a_0 \) | O: 1/12, 1/12, 1/12 |
|----|------|-----|-------------------------------|---------------------|
|    | 5/17 | hP17 |  \( c \approx 3c_0 = 30.861 \) | O: 1/2, 1/2, 1/2 |

| Zr₁₂O₅ | 5/12 | R₃ |  \( a \approx \sqrt{3}a_0 \) | O: 1/4, 1/4, 1/4 |
|        | 148  |     |  \( c \approx 3c_0 = 30.861 \) | O: 2/3, 2/3, 2/3 |

| Zr₂O  | 1/2  | P₃1m |  \( a \approx \sqrt{3}a_0 \) | O: 1/3, 2/3, 1/2 |
|       | 162  |      |  \( c \approx c_0 = 5.1572 \) | O: 2/3, 1/3, 1/2 |

|        | 1/3  | hP9  |  \( c \approx c_0 = 5.1572 \) | Zr: 0, 1/3, 3/4 |

|        |      |      |                               | Zr: 1/3, 1/3, 1/4 |
|        |      |      |                               | Zr: 1/3, 0, 3/4 |
|        |      |      |                               | Zr: 2/3, 0, 1/4 |
|        |      |      |                               | Zr: 2/3, 2/3, 3/4 |
|        |      |      |                               | Zr: 0, 2/3, 1/4 |
FIG. 3: Idealized crystal structures of the four cluster-expansion-predicted suboxide ground-states: (a) Zr$_6$O; (b) Zr$_3$O; (c) Zr$_{12}$O$_5$; (d) Zr$_2$O. Spheres connected by bond-sticks (yellowish-green online) represent Zr. Isolated spheres with bond-sticks (blue online) represent oxygen. Isolated spheres (red online) represent vacant octahedral sites.
Crystal structures of the VASP- and CE-GS in Zr-ZrO are described in Table I and their idealized structures are drawn in Figures 3 a-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 reported with the most recent review by Sugizaki et al., who used neutron diffraction to study short-range order in ZrO$_{0.3}$ solid solutions. Their Figs. 1a-c presented representations of three ordering schemes that were observed within different homogeneity ranges: (a) ZrO$_x$ at $X \approx 1/3$ (P321); (b) ZrO$_y$ at $1/3 \approx X \approx 0.4$ (P6$_3$22); (c) ZrO$_z$ near the solubility limit $X \approx 0.4$ (P31m). Space groups for these idealized structures were not reported by Sugizaki et al.; they were determined in this work with the FINDSYM program. 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 P31m structure as the VASP-GS at $X=1/2$.

1. Zr$_6$O, $X=1/6$, $\alpha''_1$

The structure of Zr$_6$O is thought to be isomorphic to that of Hf$_6$O and Ti$_6$O: $a \approx \sqrt{3}a_0$; $c \approx c_0$; $Z=3$ ($a_0$ and $c_0$ are the cell constants of the disordered P6$_3$mmc alloy). This is also the VASP-GS at $X=1/6$, Fig. 3(a) and Table 1.

2. Zr$_3$O, $X=1/3$, $\alpha''_2$...

Based on X-ray diffraction studies, Holmberg and Dagerhamn proposed a P6$_3$22 structure (open diamond, green online, in Fig. 1) with $a \approx \sqrt{3}a_0$ and $c \approx c_0$ for a sample with $X \geq 0.26$. Based on single crystal neutron diffraction studies Yamaguchi 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 $a \approx \sqrt{3}a_0$, $c \approx 3c_0$. Yamaguchi also reported confirmation of the P6$_3$22 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 R3c structure depicted in Figure 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 R\textsuperscript{3}c structure as the VASP-GS.

3. \( \text{Zr}_1\text{O}_5, X=5/17 \)

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

4. \( \text{Zr}_2\text{O}, X=1/2, \alpha''_4 \)

The only \( \text{Zr}_2\text{O} \) structure listed in Pearson\textsuperscript{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 \( \text{ZrO}_2 \), and therefore finds the GS tieline between the \( \text{P}\text{\bar{3}}1\text{m} \) GS at \( X=1/2 \) and monoclinic \( \text{ZrO}_2 \), rather than between the R\textsuperscript{3}c GS at \( X=1/3 \) and monoclinic \( \text{ZrO}_2 \). Another possibility is that the experimentally measured low-temperature equilibrium between Zr-suboxides and monoclinic \( \text{ZrO}_2 \) was measured at too low a fugacity of oxygen to stabilize the \( \text{P}\text{\bar{3}}1\text{m} \) phase at \( X=1/2 \). As one expects from the ECI (Fig. 2), there are no O-O nn pairs in the VASP-GS \( \text{P}\text{\bar{3}}1\text{m} \) structure, or in any of the four structures with formation energies within 0.01 eV (right panel Fig. 1).

B. 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\textsuperscript{22,23}. Input parameters for emc2 were: a simulation box with at least 1568 octahedral sites (15x15x6 supercell); 2000 equilibration passes; 2000 Monte Carlo passes. The predicted phase diagram is shown in Figure 4. Most phase boundaries were determined by following order-parameters of the various ordered phases as functions of \( X \) and \( T \); here order parameters are defined such that they are unity in a specified GS-phase, zero in the disordered phase, and typically some non-zero value in ordered phases other than their specified GS. Dotted boundaries are used to acknowledge uncertainties in phase boundary determinations.
FIG. 4: Comparison of experimental and calculated phase diagrams for the system \( \alpha Zr \)[1\( -X \)O\( X \)]:
(a) a combination of the "transformational diagram" (symbols) and the "tentative diagram" (solid lines) in Arai and Hirabayashi\(^\text{12}\) (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 \( \lesssim X \lesssim 0.42 \) and 420\( K \lesssim T \lesssim 725K \).

C. The Intermeadiate Temperature \( \alpha' \)-Phase

As observed experimentally in samples with \( X = 0.41 \)\(^\text{11}\) (up-pointing triangles, green online, Fig. 4) a two-step order-disorder process is predicted for 0.25 \( \lesssim X \lesssim 0.5 \) Figures 5. The data reported in Hirabayashi et al.\(^\text{13}\) 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.
\( \alpha' \)-phase

FIG. 5: Calculated order-parameter vs temperature curves for: a) \( X=0.41 \); b) \( X=1/2 \). Heating simulations are indicated by right-pointing triangles (red online) and cooling simulations are represented by left-pointing triangles (blue online). As observed experimentally, there is a two-step disordering process on heating.

The simulated intermediate-temperature \( \alpha' \)-phase crystal structure was determined by symmetry analysis, using the ISODISTORT program\textsuperscript{19,28}. There are two plausible transition paths from the \( P6_3/mmc \) high-T disordered phase to the \( P\overline{3}1m \) GS:

- (1) \( P6_3/mmc \to P6_3/mcm \to P\overline{3}1m \), \( K_1 \) irreducible representation, \((-1,-2,0),(2,1,0),(0,0,1)\) basis;
- (2) \( P6_3/mmc \to P\overline{3}m1 \to P\overline{3}1m \), \( \Gamma^+_3 \) irreducible representation, \((0,-1,0),(1,1,0),(0,0,1)\) basis.

Path (1) can be ruled out because it requires a first-order \( P6_3/mmc \to P6_3/mcm \) transition, with unit-cell expansion along both \( a_{Hex} \) axes, which neither experiment nor computation supports.

Path (2) permits a continuous \( P6_3/mmc \to P\overline{3}m1 \) transition, as observed experimentally.
TABLE II: Atomic positions in P\(\text{\textbar}3\text{m}1\) (IT 164) \(\alpha'\) crystal structure: \(a \approx a_0 \approx 3.32\text{\AA}; c \approx c_0 \approx 5.14000\text{\AA}; * X=O/Zr.

| Atom | Wyckoff site | \(x\) | \(y\) | \(z\) | occupancy |
|------|-------------|------|------|-----|-----------|
| Zr   | 2d          | 1/3  | 2/3  | \(\approx 1/4\) | 1          |
| O\(_1\) | 1a      | 0    | 0    | 0   | \(x_{O1}<1/2\) |
| O\(_2\) | 1b      | 0    | 0    | 1/2 | 2\(X^* - x_{O1}\) |

and supported computationally. The average \(\alpha'\), P\(\text{\textbar}3\text{m}1\) structure is described in Table II and depicted in Fig. 6, where partially occupied O:\([\ ])\)-sites are represented by relatively smaller and larger spheres (blue online). The precise occupations of sites O\(_1\) and O\(_2\) can be written as \(\chi\) and 2\(X - \chi\), respectively; where \(\chi < 1/2\) is the O-occupancy of site O\(_1\), and X=O/Zr; i.e. at X=0.41 and \(\chi = 0.22\) then 2\(X - \chi = 0.60\). With respect to space-group determination, the only requirement is that the occupancy of O\(_1\) must be different from that of O\(_2\). The P\(\text{\textbar}3\text{m}1\) structure is clearly consistent with the computational results shown in Figures 7a and 7b. The O:\([\ ])\]-distributions (online O=red, [\ ])=gray) in these figures were simulated on reduced (6x6x3) supercells by cooling from 1000K to 900K. For clarity Zr-atoms are omitted to highlight the strong preference for O:\([\ ])\]-ordering along \(c_{\text{Hex}}\); i.e. strong O-O nn avoidance along \(c_{\text{Hex}}\). In the average P\(\text{\textbar}3\text{m}1\) structure this leads to alternating nn-layers, \(\perp c_{\text{Hex}}\) that are relatively O-rich and O-poor ([\ ]-rich). Visually, this statistical difference is obscured in the simulation snapshots (Figures 7a and 7b) because one has: discrete O and [\ ]; O:\([\ ])\]-disorder; and antiphase boundaries.

IV. DISCUSSION

A. 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. 4b; 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\(K \lesssim T \lesssim 725\(K\). 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 disproportionates at T\(\approx 20\(K\). Also, the FPPD-predicted \(\alpha'\)-phase field is signifi-
FIG. 6: Average $P\bar{3}m1$ structure of the $\alpha'$-phase. Small and intermediate sized spheres (blue online) represent less- and more oxygen-rich oxygen:vacancy-sites (O: [ ]-sites), respectively. Larger spheres (red online) represent Zr atoms. More- and less O-rich O:[ ]-sites segregate into alternating layers perpendicular to $c_{Hex}$; reflecting nearest neighbor O-O avoidance.

Significantly larger than the corresponding field in Fig. 4a, and at X=0.41 the $\alpha'-\alpha Zr_{hcp}$ transition is predicted to occur $\approx 500K$ higher than experiment suggests, Fig. 5a. Typically, FPPD calculations overestimate order-disorder transition temperatures especially when, as here, the excess vibrational contribution to the free energy is ignored; so it is not surprising that agreement between experiment and theory is not close for the $\alpha' \rightleftharpoons \alpha Zr_{hcp}$ order-disorder transition. Note however, that the maximum temperatures for stabilities of phases other than $\alpha'$ are roughly equal to those shown in Fig. 4a.

B. Long-Period Superstructures at X$\approx1/3$

Based on X-ray, neutron, and electron scattering data, Fehlmann et al. and Yamaguchi and Hirabayashi reported a variety of long-period superstructures (LPSS) in samples with bulk compositions X$\approx1/3$ (the $\alpha''$ field, Fig. 4a) 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 Hf$_3$O and Hf$_2$O. In an ANNI-model like Hamiltonian, one expects, $0.3 \lesssim -\frac{J'_\parallel}{J_\parallel} \lesssim 0.7$, however, the 12-pair fit which includes $J'_\parallel$ yields $\parallel$ and $J'_\parallel$ with the same sign and $J'_\parallel \approx J_\parallel/10$. Physically,
FIG. 7: Simulated O:[ ]-sites (red:gray online, respectively) distributions at: (a) X=0.41, T=900K; and (b) X=1/2, T=900K. For clarity, Zr-atoms are omitted and a reduced (6x6x3) supercell were used. At X=0.41 no O-O nn pairs are evident parallel to \( c_{Hex} \). At X=1/2, almost all nn pairs parallel to \( c_{Hex} \) are O-[ ], although two columns (first row, columns 4 and 5) have some O-O nn pairs), while perpendicular to \( c_{Hex} \) there are many more O-O and [ ]-[ ] nn pairs.

the fitted values for \( J_\parallel \) and \( J_\perp \) 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. 3’rd 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 Devis’s Staircase of LPSS phases at Hf\(_3\)O\(_{30}\).

V. 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\(\approx\) 20K, 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 (\(\alpha''_2\), \(\alpha''_3\) and \(\alpha''_4\)) only two are predicted; i.e. the phase fields that Arai
and Hirabayashi\textsuperscript{12} draw for $\alpha''_2$ and $\alpha''_3$ are predicted to be a single-phase solid solution. Figure 1a clearly indicates that a zeroth order model for octahedral interstitial O:]-ordering is one in which first- and second-nn pairwise interactions ($J_\parallel$ and $J_\perp$, respectively) strongly favor O-[ nn-pairs; i.e. O-O nn-pairs are highly unfavorable, and $J_\parallel/J_\perp \approx 2.5$. Including $J'_\parallel$ in the ECI fit does not yield an ANNNI-like\textsuperscript{29} CE-Hamiltonian; however, recent FPPD calculations for the HfO\textsubscript{X} system\textsuperscript{30} (the HfO\textsubscript{X}-CE is very similar to the ZrO\textsubscript{X}-CE) predict Devis’s Staircases of LPSS phases at Hf\textsubscript{3}O and Hf\textsubscript{2}O.

The most probable transition path (on cooling) for O-rich solutions, $X \gtrsim 0.4$ is P6\textsubscript{3}/mmc $\rightarrow$ P\textsubscript{3}m1 $\rightarrow$ P\textsubscript{3}1m; hence the average $\alpha'$-structure has P\textsubscript{3}m1 symmetry with alternating O-rich and [ -]-rich layers $\perp c_{Hex}$.

\begin{footnotesize}
\begin{itemize}
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