

First-principles study of dynamic instability and phase transformation in the WRe and WOs sigma phase

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The formation of the intermetallic σ phase (space group $P4_2/mnm$) has a detrimental effect on the ductility of transition-metal alloys. This theoretical study uses first-principles calculations to investigate the stability and thermodynamic properties of the WRe and WOs σ phases. Our study indicates that the σ phase becomes thermodynamically stable at its ideal composition for temperatures above 1050 K and 130 K for the WRe and WOs phases, respectively. We find that models that neglect the phonon contribution to the free energy may underestimate the amount of disorder in the σ phase at elevated temperatures. Furthermore, the σ phase becomes dynamically unstable for Re concentrations above 73 at.% Re and 53 at.% Os. For the WOs phase, the dynamic stability is sensitive to the lattice site occupation, and vibrations of the Os atoms are linked to the transformation into a dynamically stable orthorhombic phase.

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I. INTRODUCTION

Refractory metals are a group of transition metals that possess several attractive properties that differentiate them from other metals. This includes unusually high melting temperatures and high values of strength and hardness [1]. They have attracted considerable interest in various research fields as their properties make them suitable for harsh environments of high thermal loads. Tungsten (W) is a refractory metal that has gained attention in recent years as it is regarded as a prime material for plasma-facing components in fusion reactors [2–4] due to its relatively high thermal conductivity (approximately 150 W/mK at room temperature), the high melting point (3680 K), and good erosion resistance to sputtering [5,6]. However, experiments show that under neutron irradiation, intermetallic phases, known as σ ($P4_2/mnm$) and χ ($I\bar{4}3m$), form between W and its two main transmutation products: rhenium (Re) and osmium (Os) [7–12]. The σ phase is a topologically close-packed (TCP) phase consisting of two or more transition metals [13]. The precipitation of this phase is particularly undesirable as it is known to affect the mechanical properties of the host matrix negatively, primarily by causing embrittlement [13,14].

For this reason, considerable effort has been devoted to characterizing and studying the σ phase in transition metals. To accomplish this, atomic-scale simulation methods such as molecular dynamics (MD) and first-principle methods based on density functional theory (DFT) have been employed. In particular, DFT calculations are proven useful in describing the lattice site occupation of the σ phases in multiple transition-metal systems [15–18]. For the WRe and WOs σ phases, DFT has been used to estimate the thermodynamic, elastic, and fracture-related properties [19–22] and to explore the formation enthalpy and preferential site occupation [15,17,23]. Atomistic simulations have also shown that WRe precipitates impede dislocation motion in W samples, which reduces the ductility [24,25].

Vibrations in the crystal lattice, known as phonon modes, influence the free energy and thereby also affect the relative thermodynamic stability of different phases and other physical properties, such as thermal expansion and thermal and electrical conductivity [26]. Evaluation of the phonon band structure and density of states (PDOS) is important for assessing the dynamic stability of crystal phases. Structures that are dynamically unstable exhibit imaginary modes and tend to undergo spontaneous atomic displacements and/or lattice transformations [27]. Despite its importance, the dynamic stability of the WRe and WOs phases have, to the best of our knowledge, not been widely investigated so far.

In this work, we explore the dynamic stability through *ab initio* modeling, while investigating the impact of stoichiometry and site occupancy on the stability of the WRe and WOs σ phases. To this end, the phonon band structure is evaluated for 32 sublattice configurations of WOs and WRe. Using supervised machine learning, boundaries between

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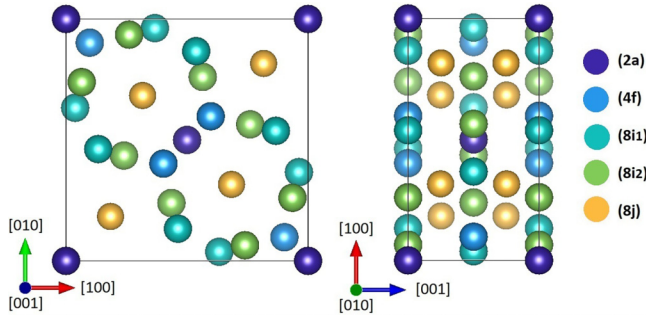


FIG. 1. Unit cell of the σ phase with the five Wyckoff sites marked with different colors. (Created using VESTA [28]).

dynamically stable and unstable configurations are established, revealing that both the concentration of transmutation products and the occupancy of lattice sites influence the stability. Notably, the dynamic stability of the WOs phase is more sensitive to these parameters than the WRe phase. To further investigate the underlying mechanisms, the electron density of states (EDOS) is analyzed and compared for stable and unstable configurations. For the WOs phase, a particular imaginary phonon mode is shown to transform the σ phase to a dynamically stable orthorhombic phase. In addition to the dynamic stability study, we calculate the phonon contribution to the free energy of the σ phases to estimate the thermodynamic stability of the phases at finite temperature. The results of this study give insight into the thermodynamic and dynamic stability of the WRe and WOs σ phases that form in W-based plasma-facing components under the nonequilibrium conditions of fusion reactors.

II. METHOD

A. The σ phase and the sublattice model

The σ phase has a tetragonal unit cell that belongs to the space group $P4_2/mnm$ and contains 30 atoms located on the five Wyckoff sites 2a, 4f, 8i₁, 8i₂, and 8j [29], as shown in Fig. 1. The sites have the coordination numbers 12, 15, 14, 12, and 14, respectively. Although the σ phase is known to be nonstoichiometric, complete atomic disorder is usually not observed [30]. An often used way of treating the disorder in the σ phase is to utilize a sublattice model [21,31–34]. The principle behind the model is to treat each Wyckoff site as a sublattice that a single atomic species can occupy, resulting in $2^5 = 32$ unique sublattice configurations.

The formation enthalpy at 0 K of the sublattice configurations, ΔH_f , is calculated by subtracting the energies of body-centered-cubic (bcc) W and hexagonal-close-packed (hcp) Re/Os in their reference states from the total energy,

$$\Delta H_f = E_{klmno}^\sigma - x_W E_W^{\text{bcc}} - x_{\text{Re/Os}} E_{\text{Re/Os}}^{\text{hcp}}, \quad (1)$$

where the superscript $klmno$ refers to the occupation of the five Wyckoff sites in the order 2a, 4f, 8i₁, 8i₂, and 8j. The parameter x_c is the concentration of element c in the $klmno$ configuration and the reference state energies were calculated as $E_W^{\text{bcc}} = -12.95$ eV/at, $E_{\text{Re}}^{\text{hcp}} = -12.43$ eV/at, and $E_{\text{Os}}^{\text{hcp}} = -11.23$ eV/at.

B. Free-energy calculations

The sublattice model is usually applied without including any vibrational contribution to the free energy. However, a previous study on the Cr–Re σ phase found that including free vibrational energy in the model significantly alters the relative stability of the configurations [35]. Therefore, it is of relevance to compute the vibrational properties of the WRe and WOs σ configurations and compare how the relative stability at elevated temperature differs from the formation enthalpy at zero absolute temperature.

Within the harmonic approximation (HA), the Helmholtz free energy is calculated as

$$F^{\text{HA}}(T) = E(V_0) + F_{\text{vib}}(T, V_0) + F_{\text{el}}(T, V_0), \quad (2)$$

where $E(V_0)$ and V_0 are the ground-state energy and volume at 0 K, respectively, F_{vib} is the vibrational free energy, calculated as

$$F_{\text{vib}}(T, V_0) = \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu, V_0) + k_B T \sum_{\vec{q}, \nu} \ln \left[1 - \exp \left(-\frac{\hbar \omega(\vec{q}, \nu, V_0)}{k_B T} \right) \right], \quad (3)$$

where k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, and $\omega(\vec{q}, \nu, V_0)$ is the frequency of mode ν with wave vector $\vec{q}$. The phonon frequencies are volume dependent as indicated in the notation. The first term in Eq. (3) is the zero-point energy (ZPE), while the second term is the free-energy contribution of the phonons at finite temperatures.

The term $F_{\text{el}}(T, V)$ is the free-energy contribution of electron excitations, which comprises two parts: $F_{\text{el}} = E_{\text{el}} - TS_{\text{el}}$, where

$$E_{\text{el}}(T, V) = \int_{-\infty}^{\infty} n(\varepsilon, V) f(\varepsilon, T) \varepsilon d\varepsilon - \int_{-\infty}^{E_F} n(\varepsilon, V) \varepsilon d\varepsilon \quad (4)$$

and

$$S_{\text{el}}(T, V) = -k_B \int_{-\infty}^{\infty} n(\varepsilon, V) \{ f(\varepsilon, T) \ln f(\varepsilon, T) + [1 - f(\varepsilon, T)] \ln [1 - f(\varepsilon, T)] \} d\varepsilon, \quad (5)$$

where ε is the energy level, E_F is the Fermi energy, $n(\varepsilon, V)$ is the EDOS, and $f(\varepsilon, T)$ is the Fermi-Dirac distribution; see, e.g., [36].

The relative stability ΔF^{HA} , which is the finite-temperature analog of Eq. (1), is the difference in F^{HA} between the σ configuration and its reference structures,

$$\Delta F^{\text{HA}}(T) = F_{klmno}^{\text{HA}, \sigma} - x_W F_W^{\text{HA}, \text{bcc}} - x_{\text{Re/Os}} F_{\text{Re/Os}}^{\text{HA}, \text{hcp}}. \quad (6)$$

It was evaluated for temperatures between 0 and 1500 K, with a step size of 10 K. When ΔF^{HA} becomes negative, it indicates the thermodynamic stability of the σ phase.

Within the HA, the constant volume heat capacity is calculated as

$$C_V(T) = \sum_{\vec{q}v} k_B \left(\frac{\hbar\omega(\vec{q}, v)}{k_B T} \right)^2 \frac{\exp\left(\frac{\hbar\omega(\vec{q}, v, V_0)}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega(\vec{q}, v, V_0)}{k_B T}\right) - 1\right]^2}. \quad (7)$$

According to the Debye model, the heat capacity can be described by the following expression:

$$C_V^{\text{Debye}}(T) = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{t^4 \exp(t)}{[\exp(t) - 1]^2} dt \quad (8)$$

where R is the gas constant, Θ_D is the Debye temperature, and $t = \frac{\hbar\omega}{k_B T}$. By fitting this equation to the harmonic C_V in Eq. (7) in the temperature range 0 to 1500 K, the Θ_D was estimated.

The HA disregards any anharmonic effects, such as thermal expansion. To assess the anharmonicity of the σ phase, we compare the results for several dynamically stable configurations on the convex hull with those from the quasiharmonic approximation (QHA). According to the QHA, Helmholtz free energy can be described as

$$F^{\text{QHA}}(T) = E(V) + F_{\text{vib}}(T, V) + F_{\text{el}}(T, V). \quad (9)$$

The main difference from the HA [Eq. (2)] is that the volume $V(T)$ is temperature dependent, such that the thermal expansion is accounted for. Thus, a crude estimate of the anharmonic contribution to Helmholtz free energy can be formulated as

$$F^{\text{anh}}(T) = F^{\text{QHA}}(T) - F^{\text{HA}}(T). \quad (10)$$

The F^{QHA} for a set of WRe configurations on the convex hull was obtained from our previous work [20], while that for one WOs configuration was computed herein using the same setup and modeling strategy as outlined in [20]. The relative stability predicted by QHA, $\Delta F^{\text{QHA}}(T, V)$, can be computed as in Eq. (6) by replacing F^{HA} with F^{QHA} .

Finally, we emphasize here that neither the HA nor the QHA includes phonon-phonon interactions. However, as the study is limited to moderate temperatures compared to the melting temperature ($T < 0.5T_m$) [37], such interactions are expected to have a small impact on the free energy.

C. Phonon calculations and dynamic instability

To evaluate the temperature-dependent free energy and probe the dynamic stability, the phonon dispersion and PDOS were calculated for the sublattice configurations. The phonon calculations were carried out using phonopy [38,39], in which a variant of the Parlinski-Li-Kawazoe method [40,41] is used to calculate the force constants via the finite-displacement supercell approach [39]. Convergence tests of the supercell size were conducted to ensure that all the relevant contributions to the force constants were included. The lengths of the tetragonal unit cell in the [100] and [010] directions are 9.47–9.80 Å (depending on the Re/Os concentration) and were assumed to be enough for convergence. For the height in the [001] direction, supercells of 2, 3, and 4 multiplicity of the unit cell were tested. It was determined that the $(1 \times 1 \times 2)$ supercell gave well enough converged results with the difference in free energy compared with $(1 \times 1 \times 3)$ being less than 5.50 meV/atom at 1000 K. Furthermore, a supercell of

an even multiple of the unit cell in the [001] direction has the advantage that the Z (0, 0, 1/2) point on the first Brillouin zone boundary is explicitly sampled, which better captures the phonon behavior, as discussed in [42]. The PDOS was obtained by integrating over the first Brillouin zone with a Γ -centered q -point mesh of size $21 \times 21 \times 40$.

For the reference structures, bcc W and hcp Re and Os, we utilized supercells of $(4 \times 4 \times 4)$, $(5 \times 5 \times 3)$, and $(4 \times 4 \times 3)$ unit cell multiplicity, respectively, which gave converged results. The integration of the Brillouin zone was carried on Γ -centered q -point meshes of sizes $89 \times 89 \times 89$, $83 \times 83 \times 45$, and $84 \times 84 \times 46$, respectively. Any dynamical instabilities of the studied configurations were identified based on the observation of imaginary phonon modes [27]. For several of the unstable configurations, we traced the displacements along the potential energy surfaces of the imaginary modes to ensure that they led to double-well potentials, which is characteristic of lattice instability [26].

D. Numerical details

The Vienna *Ab initio* Simulation Package (VASP 5.4) [43,44] was used for all DFT calculations in this work. We used the built-in projector augmented wave potentials [45,46] with extended valence configurations of $5s^2 5p^6 6s^1 5d^5$ for W, $5p^6 6s^1 5d^7$ for Os, and the recommended valence configuration of $6s 5d^6$ for Re. The generalized gradient approximation based on the Perdew-Burke-Ernzerhof exchange-correlation was applied [47]. The Methfessel-Paxton method [48] for smearing with a broadening of 0.1 eV was applied and the Monkhorst-Pack scheme [49] was used to generate a Γ -centered k -point grid. An energy cutoff of 650 eV and a k -point grid of $7 \times 7 \times 13$ for the unit cell were sufficient for convergence. When treating supercells, the k -point grid was adjusted to maintain consistent density and for the EDOS calculations, it was doubled in each reciprocal lattice direction. A quasi-Newton algorithm [50] was used for ionic relaxation of the unit cells with a force convergence criterion of 0.1 meV/Å. A stopping criterion of 10^{-5} meV was applied for the self-consistency loop.

III. RESULTS

A. Mechanical and thermodynamic stability

In Table I, ΔH_f of the 32 possible sublattice configurations of WRe and WOs are listed along with ΔF^{HA} , ZPE, and Θ_D for the dynamically stable ones. The ZPE values are found to range from 23.95 to 25.71 meV/atom for the WRe configurations and from 23.94 to 25.60 meV/atom for WOs. The difference between ZPE values is much less than that of ΔH_f , indicating that they have little influence on the relative stability. The computed Θ_D values of the reference structures—bcc W, hcp Re, and hcp Os—correspond to 302, 261, and 310 K, respectively, which are in good agreement with the experimental room-temperature values of 319, 264, and 320 K, respectively [51]. The Θ_D data for the σ configurations ranges from 241 to 264 K, which are consistently lower than those of the pure reference structures. This trend was also observed in the Cr-Re σ phase [18].

TABLE I. The sublattice configuration number (No.), the elements of the Wyckoff sites with “x” representing Re/Os occupancy, the tungsten fraction x_W , and the formation enthalpy ΔH_f at 0 K and ΔF^{HA} at 1500 K in units of meV/atom. The zero-point energy in units of meV/atom and the Debye temperature Θ_D in units of K are computed for dynamically stable configurations. Configurations marked with “—” are dynamically unstable, while those marked “†” are both dynamically unstable and do not satisfy the Born stability criteria [34].

No.	Wyckoff sites					x_W	WRe				WOs			
	$2a$	$4f$	$8i_1$	$8i_2$	$8j$		ΔH_f	ΔF^{HA}	ZPE	Θ_D	ΔH_f	ΔF^{HA}	ZPE	Θ_D
1	W	W	W	W	W	1.00	173.1	106.5	25.6	262	173.1	106.5	25.6	262
2	x	W	W	W	W	0.93	142.0	79.8	25.6	263	137.2	67.7	25.5	262
3	W	x	W	W	W	0.87	196.7	118.7	24.6	252	238.3	134.7	24.0	244
4	x	x	W	W	W	0.80	170.1	95.4	24.6	252	211.5	109.8	23.9	248
5	W	W	W	W	x	0.73	167.9	98.9	24.7	253	235.4	—	—	—
6	W	W	W	x	W	0.73	58.1	2.8	25.4	260	34.0	−42.5	25.3	259
7	W	W	x	W	W	0.73	153.3	64.7	24.0	244	153.8	67.4	24.9	254
8	x	W	W	W	x	0.67	136.1	75.2	24.8	255	209.5	—	—	—
9	x	W	W	x	W	0.67	27.9	−15.7	25.7	264	6.3	−63.1	25.6	264
10	x	W	x	W	W	0.67	120.8	46.0	24.3	248	125.1	32.5	24.7	252
11	W	x	W	W	x	0.60	179.1	112.6	24.4	250	271.5	—	—	—
12	W	x	W	x	W	0.60	78.5	18.5	24.8	253	79.7	−14.3	24.5	250
13	W	x	x	W	W	0.60	179.7	103.5	24.0	244	268.7	—	—	—
14	x	x	W	W	x	0.53	154.9	92.4	24.4	250	269.4	—	—	—
15	x	x	W	x	W	0.53	51.5	−2.4	24.9	255	70.4	−12.2	25.0	256
16	x	x	x	W	W	0.53	151.3	85.6	24.3	247	238.8	—	—	—
17	W	W	W	x	x	0.47	59.9	20.5	25.2	259	151.8	—	—	—
18	W	W	x	W	x	0.47	144.8	93.6	24.7	253	221.7	—	—	—
19	W	W	x	x	W	0.47	67.8	16.7	24.9	253	147.6	43.8	24.4	248
20	x	W	W	x	x	0.40	36.5	0.6	25.1	258	171.0	—	—	—
21	x	W	x	W	x	0.40	116.4	67.5	24.6	252	195.9	—	—	—
22	x	W	x	x	W	0.40	40.3	−1.1	25.1	256	143.5	—	—	—
23	W	x	W	x	x	0.33	76.3	28.7	24.5	250	196.7	—	—	—
24	W	x	x	W	x	0.33	171.2	104.2	23.7	241	339.8	†	†	†
25	W	x	x	x	W	0.33	98.3	35.6	24.0	243	238.4	—	—	—
26	x	x	W	x	x	0.27	57.1	10.4	24.4	250	233.6	—	—	—
27	x	x	x	W	x	0.27	147.3	86.0	23.7	242	324.8	†	†	†
28	x	x	x	x	W	0.27	74.1	12.6	24.0	243	243.9	—	—	—
29	W	W	x	x	x	0.20	84.7	—	—	—	326.1	—	—	—
30	x	W	x	x	x	0.13	66.9	—	—	—	339.3	†	†	†
31	W	x	x	x	x	0.07	114.2	—	—	—	442.3	—	—	—
32	x	x	x	x	x	0.00	96.0	—	—	—	477.3	†	†	†

In Fig. 2, ΔH_f at 0 K and ΔF^{HA} & ΔF^{QHA} at 1500 K of the configurations are plotted as a function of the transmutation product content and numbered following Table I. The temperature of 1500 K was chosen as it lies in the expected operation temperature range of W-based plasma-facing components [4]. The convex hull is constructed using the common-tangent method. In Figs. 2(c) and 2(d), the convex hull was linearly extrapolated to high concentrations using the two dynamically stable configurations on the convex hull with the highest Re/Os concentration.

It is found that No. 9 is the most stable configuration. Here, the Re/Os atoms are positioned at two sites with low coordination numbers, $2a$ and $8i_2$, and the Re/Os content is 33.3 at.%, which is the ideal composition for the σ phase. While the No. 9 configuration has a positive value of ΔH_f at 0 K, at elevated temperatures, ΔF^{HA} becomes negative, indicating thermally induced stability relative to the reference bcc-W and hcp-Re/Os phases. This occurs at temperatures above 970 K for the WRe phase and above 80 K for the WOs phase. The

QHA, however, predicts the No. 9 configurations to become stable at temperatures above 1050 K for the WRe phase and 130 K for the WOs phase. The scatter in the formation energy of configurations with the same stoichiometry reduces at high temperatures. For example, the energy difference between the No. 5 and No. 6 configurations of the WRe phase is 110 meV/atom at 0 K and 96 meV/atom at 1500 K, corresponding to a 13% reduction, which is representative for the other configurations as well. This indicates increased substitutional disorder at high temperatures.

In Table II, the anharmonic contribution to the free energy, F^{anh} , is given for several configurations on the convex hull. Anharmonic effects contribute only marginally to the total free energy, as F^{anh} is about 0.1% of F^{QHA} . For the reference structures, anharmonic effects contribute more, especially for hcp Re, where F^{anh} constitutes about 0.2% of F^{QHA} . The relative stability, ΔF^{QHA} , differs only by a few meV/atom from the ΔF^{HA} values, meaning that the shape of the convex hull remains roughly unchanged, as seen in Figs. 2(c)

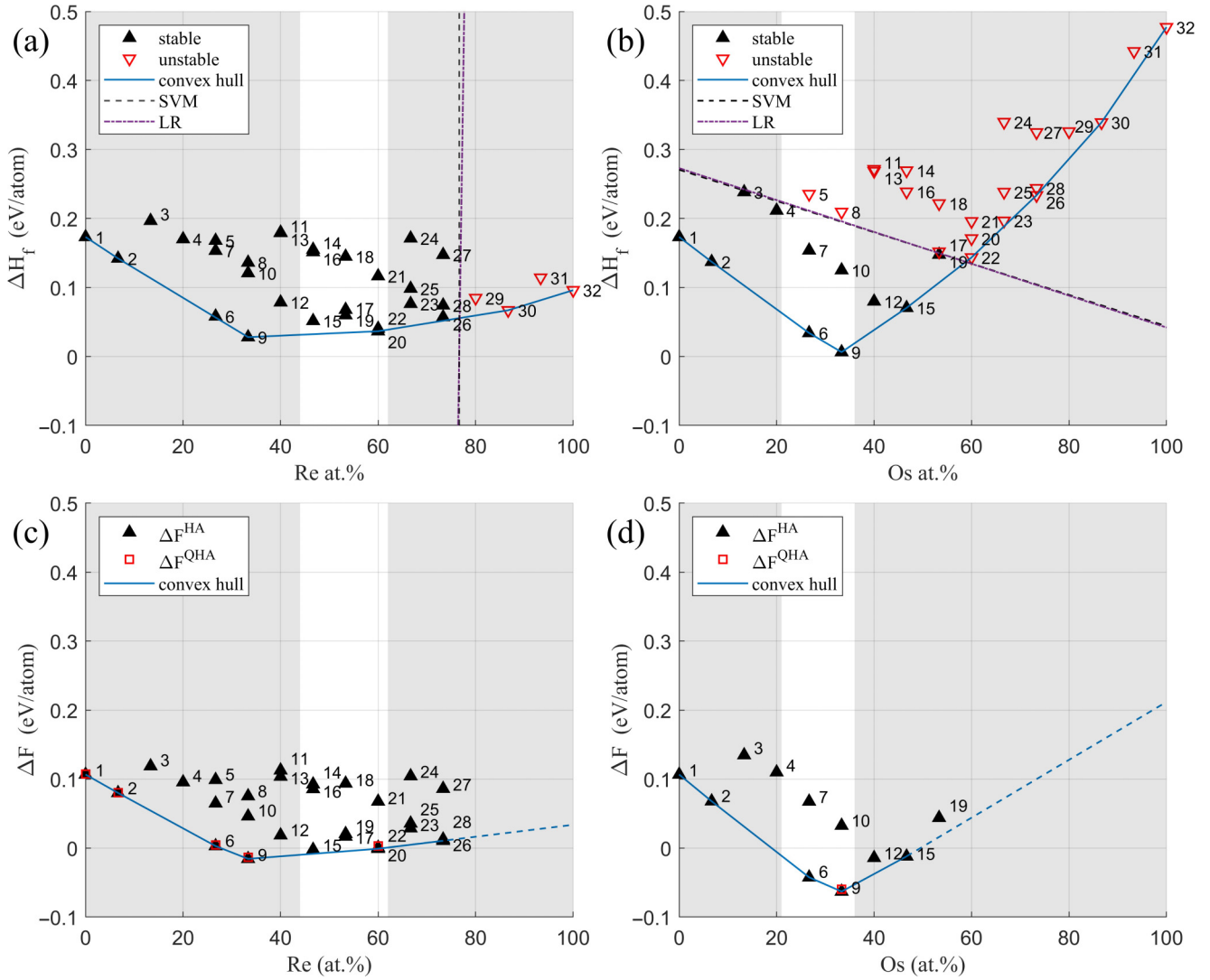


FIG. 2. Formation enthalpy for the 32 sublattice configurations of (a) WRe and (b) WOs at 0 K. The configurations are numbered according to Table I with filled, black upwards-pointing triangles indicating stable configurations and red downwards-pointing triangles indicating unstable configurations. The convex hulls are drawn with solid lines and the boundaries between the stable and unstable structures as classified by SVM and LR are plotted as dashed and dot-dashed lines, respectively. The ΔF^{HA} calculated at 1500 K is indicated by black triangles for (c) WRe and (d) WOs, while ΔF^{QHA} is indicated with red, hollow squares. The convex hull has been extended with dashed lines.

and 2(d). As the size of F^{anh} is larger for the reference structures, the difference $\delta = \Delta F^{QHA} - \Delta F^{HA}$ becomes positive. Hence, for the current study, we deem the anharmonic impact on the relative stability of the phases as small.

B. Dynamical stability

It was found that any configuration that did not satisfy the Born criteria was also dynamically unstable, as seen in Table I. There are no dynamically stable configurations above 73 at.% Re for the WRe phase and 53 at.% Os for the WOs; however, several unstable WOs configurations exist below this concentration. These unstable configurations typically have high values of ΔH_f compared to stable configurations at the same stoichiometry.

From Fig. 2, it is seen that the dynamically stable and unstable configurations are linearly separable. The boundaries were computed using the Support Vector Machine (SVM)

[52] and Logistic Regression (LR) [53] algorithms and drawn in Figs. 2(a) and 2(b). The predictions by SVM and LR are nearly identical, which suggests consistent results across models. In the case of WRe, the optimal boundary is a vertical line at 76.5 at.% Re, while for the WOs phase, it is the line $\Delta H_f = -0.23 x_{Os} + 0.27$. The regions containing the unstable configurations can be regarded as the regions of high ΔH_f and/or high Os content, illustrating the influence of both parameters.

The dynamically unstable WRe configurations exhibit one to three imaginary modes, while the unstable WOs configurations have between five and seven. For the WRe σ phase, the dynamic instability occurs for configurations where Re occupies all of the $8i_1$, $8i_2$, and $8j$ sites. They share a common imaginary mode that features vibrations of the site $8i_1$ in direction [001], $8i_2$ in direction [001], and $8j$ in directions [110] and $[1\bar{1}0]$. The WOs σ phase has multiple dynamically unstable configurations. Most of them have in common that

TABLE II. Anharmonic contribution to the free energy F^{anh} , ΔF^{QHA} , and δ in meV/atom and F^{QHA} in units of eV/atom for the reference structures and selected configurations on the convex hull at 1500 K.

No.	F^{anh}	F^{QHA}	ΔF^{QHA}	δ
WRe				
1	-14.2	-13.61	107.3	0.8
2	-15.2	-13.61	80.2	0.4
6	-15.3	-13.60	4.6	1.8
9	-15.2	-13.58	-13.5	2.2
20	-17.9	-13.45	3.2	2.6
W-Os				
9	-13.1	-13.21	-59.8	3.3
Reference structures				
bcc W	-15.3	-13.7		
hcp Re	-24.5	-13.3		
hcp Os	-19.4	-12.0		

Os occupies the $8j$ site, which seems to be sufficient to induce dynamic instability. This indicates that the W occupation of this site is crucial for the stability of the WOs phase. These configurations have an imaginary mode in common that includes small vibrations of the $8i_1$ and $8i_2$ sites in the $[001]$ direction accompanied by large vibrations of the $8j$ sites in the $[110]$ and $[1\bar{1}0]$ directions. In both modes, the $8j$ sites have larger amplitudes than the $8i_1$ and $8i_2$ sites, though for the WOs configuration, the difference in amplitude is considerable. The two imaginary modes and the resulting potential energy surfaces are shown in Fig. 3(a) for the four unstable WRe configurations and in Fig. 3(b) for selected unstable WOs configurations. The data points (shown as symbols)

provide a good fit to the Landau double-well potential (solid lines), which demonstrates the dynamic instability.

C. Crystallographic transformation

Owing to its association with the imaginary modes, it is possible that the vibration of the $8j$ -Os atoms in the WOs phase may facilitate the transformation into a new crystal structure. To test this hypothesis, a new stable crystal structure of lower energy was sought after, using the WOs No. 5 configuration as an example. Starting from the bottom of the left well in Fig. 3(b), a series of relaxations was performed for which the atomic positions, cell shape, and volume were allowed to change. A new stable structure was found with lower energy than the original No. 5 configuration. The subtle energy difference, ~ 10 meV/atom, is comparable to that reported for diamond and graphite structures of carbon, which amounts to 12 meV/atom [54].

The space group of the new structure is identified as $Pnn2$ using the spglib package [55] and the Bilbao Crystallographic Server [56,57] with a precision of 10^{-3} Å. This means that the phase transformation resulted in a reduction of crystal symmetry. The crystal structure and Wyckoff sites of the σ and orthorhombic phases can be seen in Tables III and IV, respectively. The computed diffraction patterns and unit cells of the two structures are visualized in Fig. 4. While the diffraction patterns are similar, the orthorhombic structure is distinct as it exhibits several cases of peak splitting due to the lower symmetry. As an example, we refer to the small peak at $2\theta = 45.95^\circ$, indicated by the arrow in Fig. 4(a), that splits into two peaks at 45.86° and 46.22° in Fig. 4(b). The difference should be large enough to distinguish experimentally. Among other structural changes is the displacement of the Os atoms, which can be seen by comparing the unit cells in Fig. 4. In the σ phase, the Os atoms belong to the $8j$ Wyckoff site,

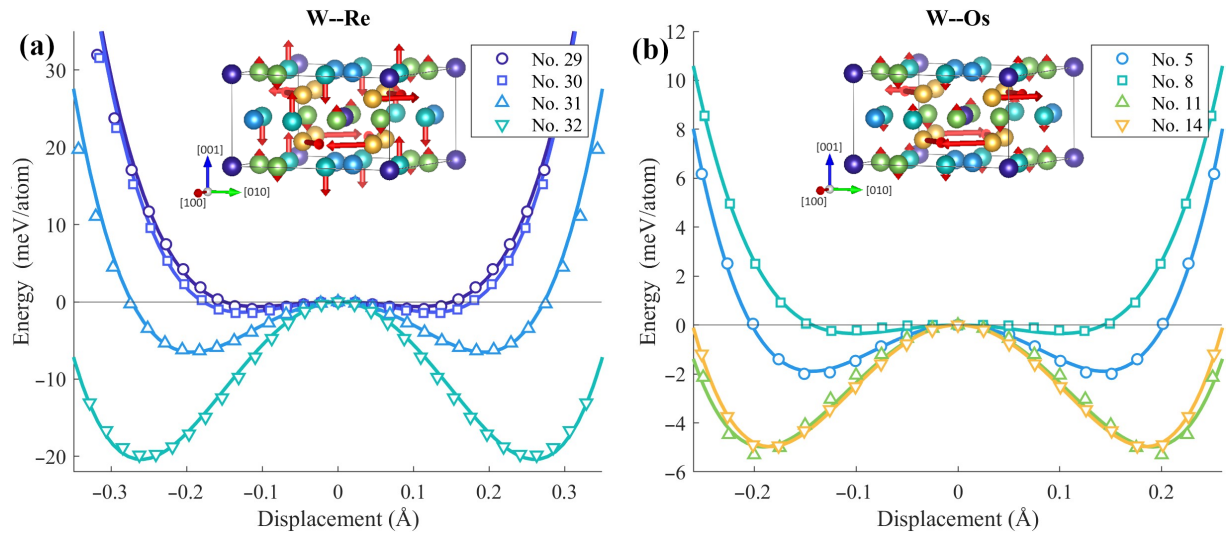


FIG. 3. Potential energy surfaces vs displacement along the imaginary mode shown in the insets (amplitudes have been scaled for clarity). The x axis indicates the displacement of the $8j$ atoms. The data points, indicated with symbols, provide a good fit for the Landau double-well potential drawn with solid lines.

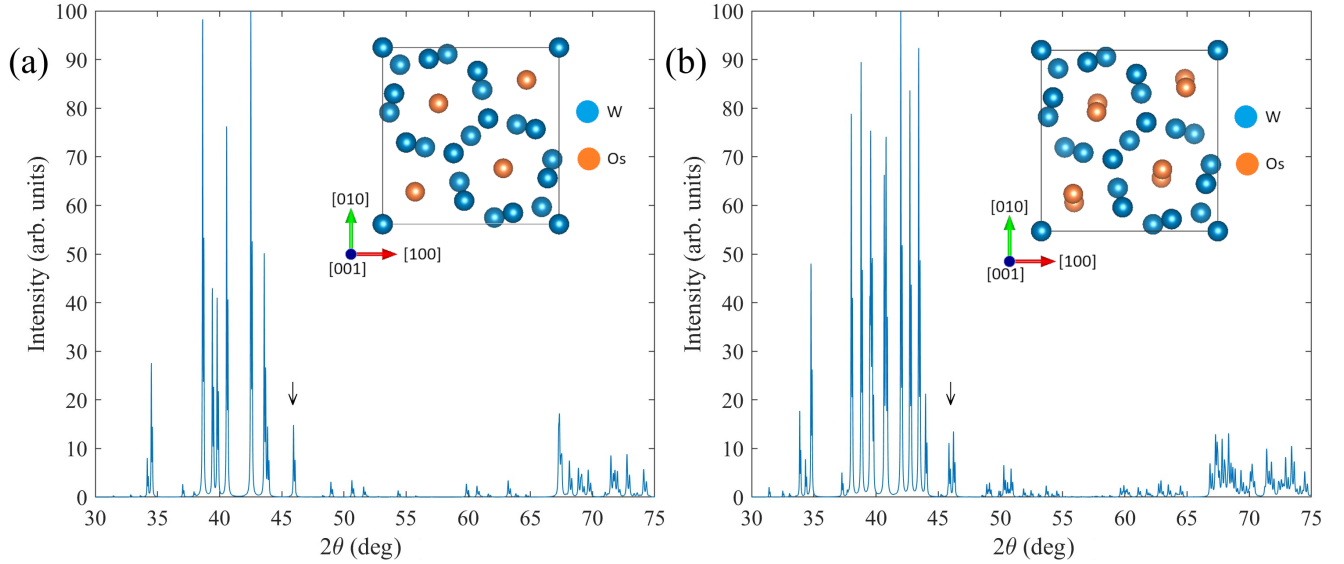


FIG. 4. Calculated diffraction pattern of the No. 5 configuration in (a) the tetragonal σ phase and (b) the orthorhombic phase. The unit cells of the two structures are inserted with color-coded W and Os atoms. The arrow indicates an example of peak splitting.

while in the new structure, they are split into two groups of $4c$ Wyckoff sites. As the multiplicity often indicates the order of symmetry, the splitting of $8j$ to $4c$ is indicative of a symmetry reduction.

D. Phonons and electronic density of states

To further investigate the cause of the dynamic instability, we analyze the phonon band structure, PDOS, and EDOS. In Fig. 5, we compare the phonon band structure and PDOS

of (a) the dynamically stable No. 5 configuration and (b) the unstable No. 30 configuration. The phonon band structure of the No. 5 configuration is similar to that found for the Cr-Re σ phase [58]. It contains 90 phonon modes, i.e., three acoustic and 87 optical branches contributing to a broad PDOS spectrum that is most dense in the 2–6 THz range. The No. 30 configuration contains three imaginary modes. According to the projected PDOS, these modes are structurally associated with the $8i_1$, $8i_2$, and $8j$ sites. The total and projected contributions from W and Re to the EDOS of the configurations

TABLE III. Crystal structure of the WOs No. 5 configuration at 0 K. The coordinates of the five nonequivalent sites are given in units of the cell parameters $a = 9.601$ Å and $c = 5.194$ Å. The ditto mark (") has been used to abbreviate the coordinates of sites with the same Wyckoff letter.

Tetragonal (σ) structure		
Wyckoff	Coordinates	
$2a$	$(0, 0, 0)$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
$4f$	$(x, x, 0)$	$(\bar{x}, \bar{x}, 0)$
	$(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2})$	$(\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2})$
	$x = 0.402$	
$8i_1$	$(x, y, 0)$	$(\bar{x}, \bar{y}, 0)$
	$(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2})$	$(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2})$
	$(y, x, 0)$	$(\bar{y}, \bar{x}, 0)$
	$(\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2})$	$(\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2})$
	$x = 0.462, y = 0.133$	
$8i_2$	"	
	$x = 0.739, y = 0.065$	
$8j$	(x, x, z)	$(\bar{x}, \bar{x}, z)$
	$(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z)$	$(\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z)$
	$(x, x, \bar{z})$	$(\bar{x}, \bar{x}, \bar{z})$
	$(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} - z)$	$(\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} - z)$
	$x = 0.184, z = 0.252$	

TABLE IV. Orthorhombic structure of the WOs No. 5 configuration at 0 K. The coordinates of the nonequivalent sites are given in units of the cell parameters, $a = 9.549$ Å, $b = 9.776$ Å, and $c = 5.155$ Å. The ditto mark (") has been used to abbreviate the coordinates of sites with the same Wyckoff letter.

Orthorhombic structure		
Wyckoff	Coordinates	
$2a$	$(0, 0, z)$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)$
	$z = 0.486$	
$4c_1$	(x, y, z)	$(\bar{x}, \bar{y}, z)$
	$(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$	$(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z)$
	$x = 0.096, y = 0.899, z = 0.498$	
$4c_2$	"	
	$x = 0.039, y = 0.632, z = 0.496$	
$4c_3$	"	
	$x = 0.133, y = 0.463, z = 0.000$	
$4c_4$	"	
	$x = 0.067, y = 0.738, z = 0.000$	
$4c_5$	"	
	$x = 0.238, y = 0.434, z = 0.489$	
$4c_6$	"	
	$x = 0.186, y = 0.159, z = 0.263$	
$4c_7$	"	
	$x = 0.181, y = 0.206, z = 0.761$	

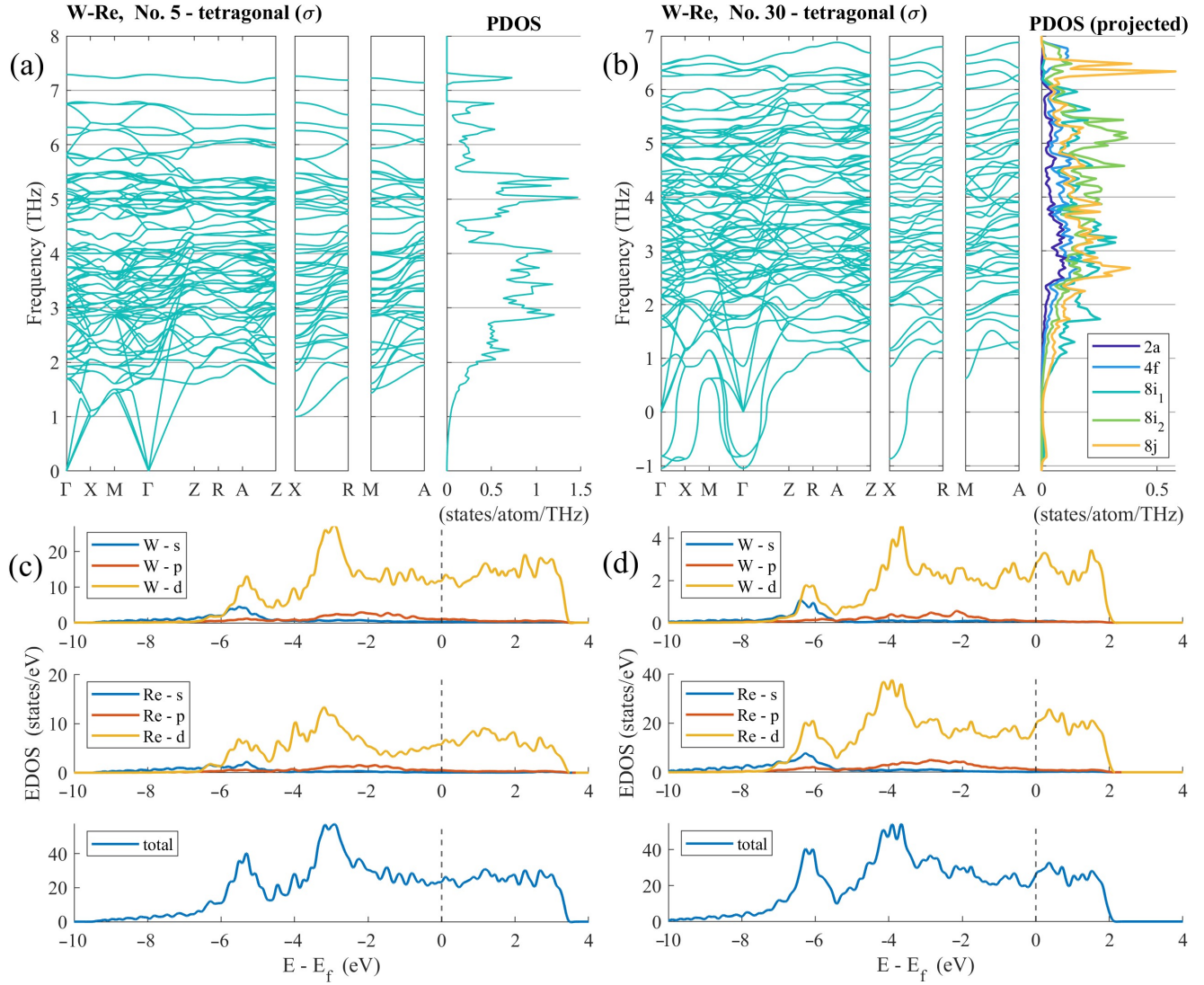


FIG. 5. Phonon band structure and PDOS of sublattice configurations (a) WRe No. 5 and (b) WRe No. 30. The points of high symmetry are $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $M = (1/2, 1/2, 0)$, $Z = (0, 0, 1/2)$, $R = (0, 1/2, 1/2)$, and $A = (1/2, 1/2, 1/2)$ in units of the reciprocal lattice vectors. For configuration WRe No. 30, the PDOS is projected onto the Wyckoff sites. The EDOS projected onto the five Wyckoff sites of (c) the stable No. 5 and (d) the unstable No. 30 WRe. The energy is shifted so that the zero reference corresponds to the Fermi level, E_f .

are shown in Figs. 5(c) and 5(d). The four unstable WRe configurations all have peaks in the EDOS coinciding with the Fermi level, as shown for configuration No. 30 in Fig. 5(d). Such peaks at the Fermi level have been linked to reduced structural stability since a small variation of the Fermi level will cause a large change in the number of electrons in its proximity; see, e.g., [59]. By comparison, for the stable No. 5 configuration, the Fermi level coincides with a relatively flat section of the EDOS spectrum, as seen in Fig. 5(c).

In Fig. 6, the phonon band structures of the No. 5 WO₅ configuration in its tetragonal σ and orthorhombic forms are shown. The unstable σ phase, shown in Fig. 6(a), contains six imaginary branches at the Γ point. The projected PDOS reveals that they are also structurally associated with the $8j$ sites and, to a lesser extent, the $8i_1$ and $8i_2$ sites.

The phonon band structure of the orthorhombic structure in Fig. 6(b) indicates the presence of a “mildly imaginary” mode in the proximity of the Γ point. However, since there

was no indication of dynamic instability when investigating the associated potential energy surface, it is believed to be a consequence of its relatively flat potential energy surface and attributed to numerical noise in the calculations. Thus, it is likely to be dynamically stable.

The EDOS of the unstable No. 5 σ configuration is shown in Fig. 6(c). Here, the EDOS of the $8j$ -Os atoms exhibits a distinct peak at the Fermi level, indicated by an arrow. We note that the stable No. 6 configuration, which has the same Os content as No. 5, did not exhibit any peak at the Fermi level. This demonstrates that the EDOS structure depends on Wyckoff site occupation in addition to the Os content. For the new orthorhombic structure, the Os contribution to the EDOS exhibits a shallow local minimum at the Fermi level located between two peaks marked with arrows in Fig. 6(d). This would indicate that the structural transformation has reduced the d -electron state degeneracy of the Os atoms near the Fermi level.

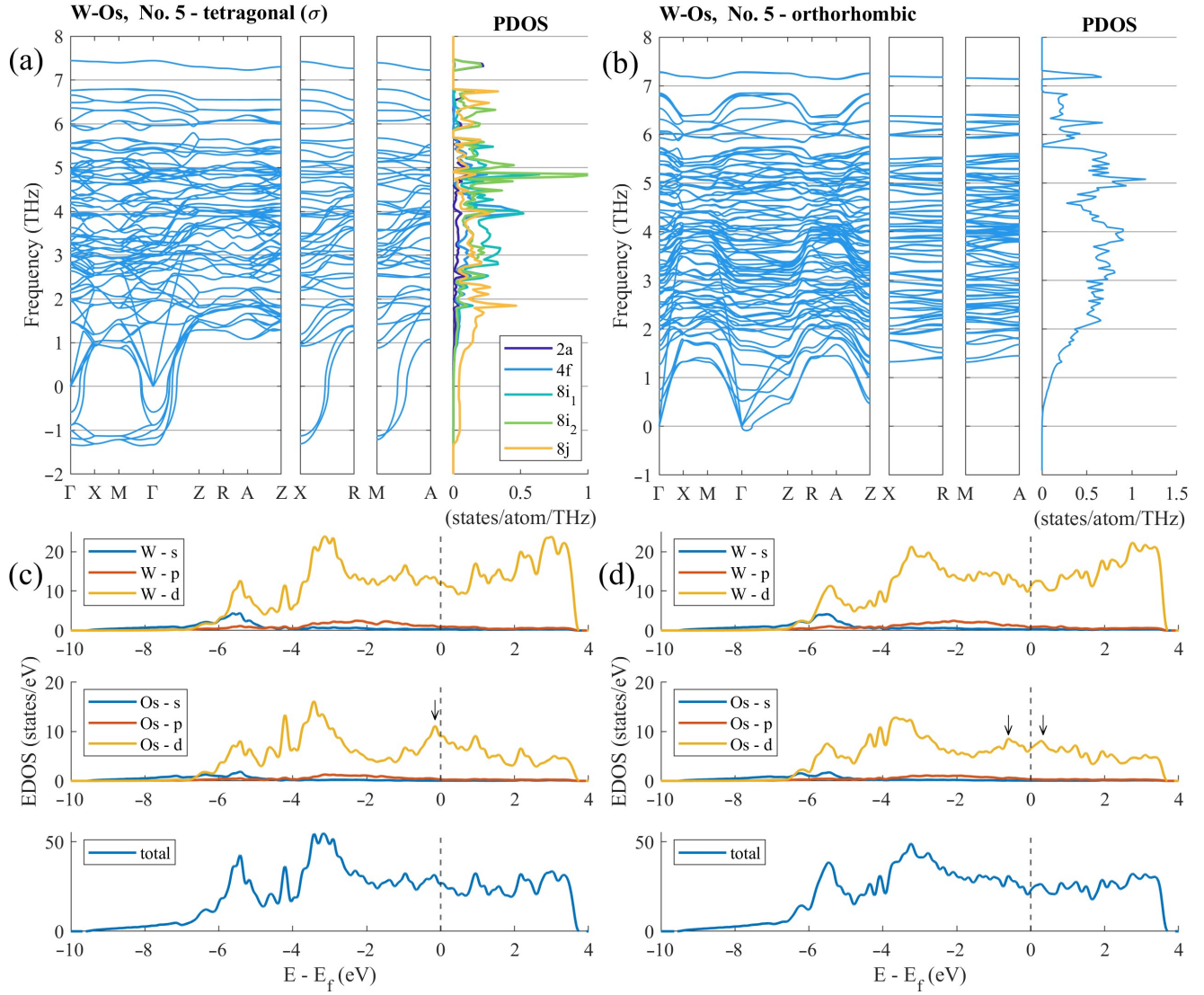


FIG. 6. Phonon dispersion structure and PDOS of the WOs configuration No. 5 in (a) the tetragonal σ phase and (b) the newly obtained orthorhombic phase. The points of high symmetry are $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $M = (1/2, 1/2, 0)$, $Z = (0, 0, 1/2)$, $R = (0, 1/2, 1/2)$, and $A = (1/2, 1/2, 1/2)$ in units of the reciprocal lattice vectors. For configurations WOs No. 5, the PDOS are projected onto the Wyckoff sites. The EDOS of the W and Os atoms projected onto the s , p , and d orbitals as well as the total EDOS for (c) the σ phase and (d) the orthorhombic phase. The arrows indicate peaks near the Fermi level.

IV. DISCUSSION

The sublattice model is frequently utilized to estimate the Wyckoff site occupations and the substitutional disorder of the σ phase and other TCP phases. While previous studies often neglect the phonon contribution to free energy, the present work computes it using the HA for all configurations and the QHA for selected configurations. When this contribution is included, the σ phase at the ideal composition becomes thermodynamically stable at elevated temperatures, that is, at 130 K for WOs and 1050 K for WRe, according to QHA. Furthermore, the energy scatter between configurations of the same stoichiometry is reduced at high temperatures, indicating that atom substitution between sublattices becomes less energetically expensive. This implies that studies based solely on zero-temperature calculations may underestimate

the amount of substitutional disorder in the σ phase at high temperatures. However, as the phonon contribution cannot be calculated for configurations with imaginary modes, it is difficult to quantify the amount of underestimation. We note that other intermetallic phases, such as the χ phase, have not been considered for the thermodynamic stability calculations. This would be required to calculate the complete WRe and WOs phase diagrams. We emphasize that the majority of the results of this study is based on the HA. However, based on the results in Table II, our assessment is that the anharmonicity only has a minor influence on the Helmholtz free energy for temperatures up to 1500 K. This is in line with results from previous investigations of the Cr-Re σ phase [58].

We investigated the dynamic stability of all the sublattice configurations for the WRe and WOs σ phases. A connection

between the stability of the configuration and the transmutation product concentration was observed, with generally high-Re and -Os content triggering instability. It is noted that the WOs phase also becomes mechanically unstable for Os contents exceeding 78 at.%, as it fails to satisfy the Born criteria [34]. Although we emphasize that the emergence of EDOS peaks at the Fermi level does not automatically mean instability [59], inspection of the EDOS of the dynamically unstable configurations reveals that they all exhibit peaks at the Fermi level. The Re and Os atoms have one and two more electrons in the d orbital than the W atom, respectively, and for transition metals, the stability and bonding are primarily determined by the d electrons [59]. For configurations with high Re/Os content, the additional d -orbital electrons may increase the density at the Fermi level in the form of peaks in EDOS. Besides the transmutation product concentration, the EDOS also depends on the Wyckoff site occupation. Critically, when Os occupies the $8j$ Wyckoff sites, it gives rise to a peak at the Fermi level, which also coincides with the WOs σ phase becoming dynamically unstable.

It was discovered that the dynamically unstable WRe configurations share an imaginary mode that featured notable vibrations of the $8i_1$, $8i_2$, and $8j$ sites. This was supported by projecting the PDOS onto the Wyckoff sites, which showed that the imaginary phonons were structurally associated with those sites. We note that an earlier study on the Cr-Re σ phase found a similar result where Re occupied $8i_1$, $8i_2$, and $8j$ sites vibrating in directions $[001]$, $[00\bar{1}]$, and $[110]$ caused instability [58]. The WOs configurations with Os occupying the $8j$ site exhibited a similar imaginary mode, but with noticeably larger vibration amplitudes for the $8j$ sites. The projected PDOS of the WOs No. 5 configuration showed that the imaginary modes were also structurally associated with the $8j$ site.

A new dynamically stable structure was identified for the WOs No. 5 configuration. The new structure had lower symmetry (orthorhombic) than the tetragonal σ phase. In particular, the unstable $8j$ sites were transformed into a pair of $4c$ Wyckoff sites, also indicating a symmetry reduction. Crystal transformation to lower symmetry structures is not uncommon, as it often represents lower-energy states. For example, this behavior is observed in iron-based superconductors, which undergo a transition from a tetragonal to orthorhombic structure at low temperatures [60,61]. Similar phase transitions are also found in rare-earth manganites [62,63]. Another example is the Jahn-Teller effect [64] observed in ZrH_x [65] and TiH_x [66], where degeneracies in the EDOS at the Fermi level are reduced by a tetragonal deformation of the face-centered-cubic phase [67–71]. By comparing the EDOS of the tetragonal and orthorhombic WOs phases in Figs. 4(c) and 4(d), we observe a behavior reminiscent of this effect. The peak at the Fermi level from the Os atoms is split into two peaks, thereby creating a shallow local minimum. This would imply that the degeneracy of the Os d electrons at the Fermi level is reduced after transitioning to the orthorhombic phase. Although investigating the precise role of d -electron hybridization in driving the orthorhombic transition lies beyond the scope of the present work, a future expanded investigation—accounting also for the effect

of spin-orbit coupling on the electronic structure and phonon spectrum—would be of significant interest, especially in the light of the emerging field of topological metals, whose unusual electronic properties emerge from the atoms' geometric arrangements in kagome lattices [72,73], which are the underlying patterns of TCP phases.

The existence of the orthorhombic phase may affect phase diagram studies, as it should be considered one of the possible stable phases of the WOs system. Even though the new structure is dynamically stable and has lower energy than the σ phase, it is likely only metastable due to a large positive value of ΔH_f . However, metastable phases may still form under the highly nonequilibrium conditions that neutron-irradiated plasma-facing components are subjected to. Further studies into how precipitates of these phases affect the mechanical properties, particularly the ductility, of W-based plasma-facing components are needed to assess their longevity.

V. CONCLUSIONS

In this study, the dynamic stability and thermodynamic properties of the WRe and WOs σ phases have been investigated. The phonon contribution to the free energy was calculated using the HA and the QHA. When this contribution is included, the σ phase becomes thermodynamically stable for temperatures above 1050 K for WRe and 130 K for WOs. The scatter in formation energy between configurations with the same stoichiometry reduces for high temperatures, indicating that models that exclude the phonon contribution may underestimate the amount of substitutional disorder in the σ phase at high temperatures.

The dynamic stability of the σ phase depends on the transmutation product content, with configurations containing more than 73 at.% Re and 53 at.% Os being dynamically unstable. We propose that the dynamic instability originates from the additional number of electrons in the d orbital of Re and Os, as compared to W, which causes a peak in the EDOS at the Fermi level. Furthermore, the dynamic stability also depends on the Wyckoff site occupation, as configurations where Os atoms occupy the $8j$ site and are dynamically unstable. The dynamically unstable configurations share an imaginary phonon mode that in particular features significant vibrations of the $8j$ sites along the $[110]$ and $[1\bar{1}0]$ directions. By using the aforementioned vibration mode, a new dynamically stable, orthorhombic crystal structure belonging to the spacegroup $Pnn2$ was identified for the WOs phase. Comparison of the EDOS of the original σ phase and orthorhombic structure revealed a reduction of d -electron degeneracy at the Fermi level following the transformation.

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A.V. contributed to the conceptualization, methodology, investigation, formal analysis, data curation, visualization, and writing (original draft, review, and editing). D.M. contributed to the methodology and writing (review and editing). T.H. contributed to the methodology and writing (review and editing). M.P. contributed to the methodology and writing (review and editing). P.A.T.O. contributed to the conceptualization, methodology, writing (review and editing), supervision, and funding acquisition.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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