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Ordered Structures in Rhenium Binary Alloys from First-Principles Calculations

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Abstract: Rhenium is an important alloying agent in catalytic materials and superalloys, but the experimental and computational data on its binary alloys are sparse. Only 6 out of 28 Re transition-metal systems are reported as compound-forming. Fifteen are reported as phase-separating, and seven have high-temperature disordered σ or χ phases. Comprehensive high-throughput first-principles calculations predict stable ordered structures in 20 of those 28 systems. In the known compound-forming systems, they reproduce all the known compounds and predict a few unreported ones. These results indicate the need for an extensive revision of our current understanding of Re alloys through a combination of theoretical predictions and experimental validations. The following systems are investigated: AgRe★, AuRe★, CdRe★, CoRe, CrRe★, CuRe★, FeRe, HfRe, HgRe★, IrRe, MnRe, MoRe, NbRe, NiRe, OsRe, PdRe, PtRe, ReRh, ReRu, ReSc, ReTa, ReTc, ReTi, ReV, ReW★, ReY, ReZn★, and ReZr (★ = systems in which the ab initio method predicts that no compounds are stable).

1. Introduction

The quantum mechanical description of material properties based on density functional theory (DFT) is currently a major tool of chemistry and materials science. It provides an understanding of the fundamental physical properties and increasingly serves as a tool for computer-assisted materials design (for a recent review, see ref 1). The advance in computational methods and hardware in recent years was followed by the development of high-throughput (HT) DFT-based calculations for comprehensive screening of properties of large sets of materials. These HT methods have been applied to theoretically guided material discovery and improvement.[2−12] They give insights into trends

in alloy properties and indicate possible existence of hitherto unobserved compounds. In this paper, we apply the HT approach to a comprehensive screening of rhenium intermetallic binary alloys. This choice is motivated by the wide array of technological applications of rhenium alloys in contrast with the sparsity of experimental data and the scant theoretical discussion in the literature.

The major uses of rhenium are in petroleum-reforming catalysts and in superalloys for high-temperature applications. As a catalyst, rhenium is highly resistant to chemical poisoning by nitrogen, phosphorus, and sulfur. It is used mostly in bimetallic platinum−rhenium catalysts for production of high-octane hydrocarbons and lead-free gasoline and in hydrogenation reactions.[13−15] Other rhenium bimetallic catalysts, for example, ReRh and RePd,[16−18] and rhenium−ceramics catalysts[19−22] have been recently investigated for uses in various additional

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reactions. In nickel-based superalloys, inclusion of a few percent of rhenium improves strength properties at high temperatures.[23] In alloys of the group VI metals, Cr, Mo, and W, it gives rise to the so-called rhenium effect, where the strength and plasticity of the metal increase simultaneously.[24] These alloys are used in turbine blades, crucibles, thermocouples, electrical contacts, temperature controls, etc.[15,26]

Guided by these applications, most of the experimental data on Re metallic binary systems are limited to platinum, nickel, and the group VI metals.[24] Of the 28 Re transition-metal binary systems,[25] 15 are reported as non-compound-forming and 7 are listed with disordered Frank−Kasper phases, σ and χ, at the lowest temperatures at which data are available.[27,28] In fact, at higher temperatures, the disordered σ phase is reported in eight systems, but in the Re−V system, it decomposes into a two-phase region above the lowest reported temperature of 800 °C. We, therefore, count it here among the 15 phase-separating systems. Rhenium is the element with the highest prevalence of these disordered phases in its binary metallic systems.[29,30] Of the six compound-forming systems, five (with Sc, Y, Ti, Zr, and Hf) are concentrated in columns IIIB and IVB of the periodic table and one, Pt, is listed with a single compound, Pt_3Re, with an unknown structure.[27,28]

DFT-based investigations of rhenium alloys are largely limited to cases where the rhenium effect is observed. Studies of rhenium-doped nickel-based superalloys deal with the bonding[31−37] and vacancy formation[38] mechanisms that might be related to the rhenium-induced improvement of the mechanical properties. The bonding mechanism was also investigated in bcc Cr−Re alloys.[39] Studies of Re−W alloys were concerned with the thermodynamic stability of random alloys,[40,41] the structure and thermodynamic properties of the σ and χ phases,[42−45] and the effect of rhenium doping on the dislocation structure and plasticity of tungsten.[46] Dislocation structure and mobility were also studied in bcc Mo−Re alloys.[47] In the Mo−Re system, it was found that a specific configuration of the χ phase is stable at low temperatures, relative to the pure elements.[45,48] This same configuration was found to be marginally stable in the Re−W system,[45] whereas all the configurations of the σ phase are unstable in both systems. Ordering effects in the Re−Ta σ phase were shown to be more pronounced than in the Re−W system.[42] Hexagonal Fe/Re multilayer structures were studied due to their peculiar magnetic properties.[49] Amorphization processes in the equilibrium immiscible Cu−Re system[50] and solid solution structures in the Re−Ti system[51] were also investigated using ab initio calculations. Rhenium's importance as a catalytic agent and the recent increased interest in intermetallic catalysts have led to DFT studies of its surface and nanoparticle properties, as well as of some alloys and surface alloys with platinum group metals (PGMs).[16−18,52,53] These studies emphasize the need to evaluate the stability of new potential alloy catalysts. All of these studies do not address the more general issue of the structure of rhenium binary phase diagrams and the phase stability of possible compounds. The importance of re-examining this issue is underscored by the sparsity of experimental data and the recent findings that certain surface alloys, of PGMs and other metals, might be better electrocatalysts than pure metals for hydrogen evolution reactions.[18,54]

2. Predictions via a High-Throughput Approach

We use high-throughput calculations[6,55−58] to explore the phase stability landscape of binary Re alloys. The formation enthalpies of a large number of structures are calculated in each system, and the minima at various component concentrations are identified. The corresponding convex hull of the binary system is constructed of these minima. The effectiveness of this

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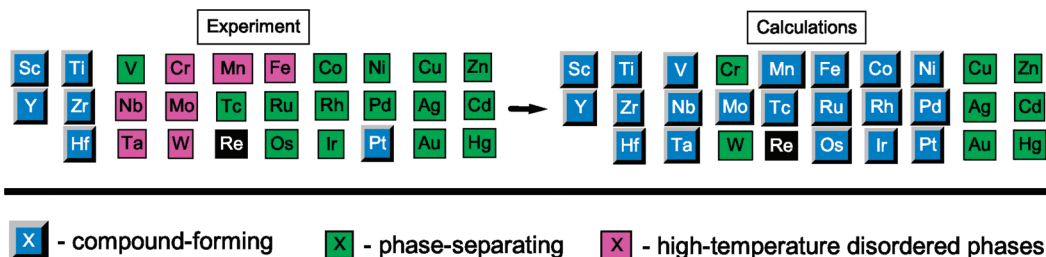
Figure 1. Phase-separating or compound-forming characteristics of 28 Re alloy systems as found in experiments (left) and in ab initio calculations (right).

approach in studying binary metallic systems for which experimental data are scarce and difficult to obtain has been recently demonstrated by comprehensive studies on rhodium[59] and hafnium alloys,[60] where a large number of new compounds have been identified.

The HT approach confirms phase ordering in all six rhenium binary intermetallic systems known to be compound-forming and predicts unreported compounds in three of them: Hf−Re, Re−Pt, and Re−Ti. Of the 22 systems that are reported either as phase-separating or as having only high-temperature disordered phases,[27,28] we show that 14 actually exhibit ordering tendencies, forming stable compounds at low temperatures. Of the seven systems reported with high-temperature disordered phases (σ, χ, or β-Mn), five are found to be compound-forming, with ordered realizations of the χ phase (the $Re_{24}Ti_5$ or $Al_{12}Mg_{17}$ prototypes) or β-Mn (the Mg_3Ru_2 prototype). These results are summarized in Figure 1, which depicts the phase-separating or compound-forming nature of the 28 rhenium binary systems with the transition metals.

3. Method

The calculations were performed using the high-throughput framework AFLOW[6,11,55] based on ab initio calculations of the energies by the VASP software.[61] We used projector augmented waves (PAW) pseudopotentials[62] and the exchange-correlation functionals parametrized by Perdew, Burke, and Ernzerhof[63] for the generalized gradient approximation (GGA). The energies were calculated at zero temperature and pressure, with spin polarization and without zero-point motion or lattice vibrations. All crystal structures were fully relaxed (cell volume and shape and the basis atom coordinates inside the cell). Numerical convergence to about 1 meV/atom was ensured by a high energy cutoff (30% higher than the highest energy cutoff for the pseudopotentials of the components) and dense 6000 k-point Monkhorst−Pack meshes. For each system, we calculated the energies of all the reported crystal structures[27,28] and approximately 200 additional structures from the AFLOW database[55] listed in refs 59 and 64−66. In systems where disordered χ or β-Mn phases are reported, we included their ordered realizations, the $Re_{24}Ti_5$ and $Al_{12}Mg_{17}$ prototypes or the Mg_3Ru_2 prototype, respectively (no corresponding prototype is known

for the σ phase). This approach gives reasonable results. In ref 6, it was shown that the probability of reproducing the correct ground state, if well-defined and not ambiguous, is $\eta_c^\star \sim 96.7\%$ (*"reliability of the method"*, eq (3)). There is no guarantee that the true ground states of a system will be found among the common experimentally observed structures or among small unit cell derivative structures. However, even if it is impossible to rule out the existence of an unexpected ground state, this protocol (searching many enumerated derivative structures and exhaustively exploring experimentally reported structures) is expected to give a reasonable balance between high-throughput speed and scientific accuracy to determine miscibility, or lack thereof, in Re alloys.

4. Results and Discussion

The results are summarized in Table 1. In the first column, the 28 alloying metals are ordered according to their Mendeleev number (or Pettifor's chemical scale).[67,68] The next two columns indicate whether the corresponding binary system is phase-separating or compound-forming, according to the experimental data[27,28] and the ab initio calculations reported here. Ordered in this way, five of the six experimentally reported compound-forming systems are grouped at the top of the table, and one, Pt−Re, is isolated near the bottom. The systems with reported disordered phases are grouped right below the compound-forming cluster at the center of the table. Our calculations find stable structures in most of the systems bridging the compound-forming ones.

The remaining phase-separating systems form a pair in the middle of the table, Re−W and Cr−Re (systems with disordered high-temperature phases, but no low-temperature stable compounds), and a cluster of six systems at the bottom of the table, which includes the noble metals Au, Ag, and Cu and their neighbors on the IIB column of the periodic table, Zn, Cd, and Hg. All of these systems are reported as phase-separating in the literature.[27,28] We found no example of a system reported as compound-forming but predicted to be phase-separating by the ab initio calculations. It should be noted that this prediction of phase separation is based on the screening of a database, of approximately 200 structures, in which none were found with negative formation enthalpy. As explained in the previous section, this approach is expected to be highly reliable but cannot completely rule out the existence of unexplored ground states.[6] The grouping of systems by predicted compound-formation or phase-separation characteristics essentially complements the trend indicated by the Pettifor chemical scale. The ratio of calculated phase-separating to compound-forming systems is reversed comparing with the experimental picture.

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Table 1. Compounds Observed in Experiments (exper.) or Predicted by ab Initio Calculations (calc.) in Re Binary Alloys (Structure Prototype in Parentheses)[a]
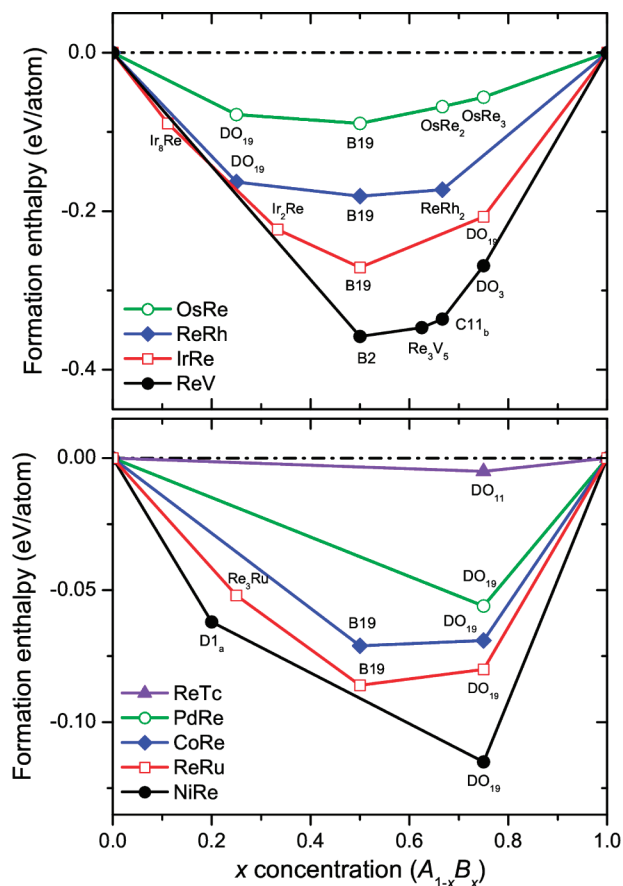
	compounds		
	exper.[27,28]	calc.	ΔH meV/atom
Y	Re_2Y (C14)	Re_2Y (C14)	−211
Sc	$Re_{24}Sc_5$ ($Re_{24}Ti_5$)	$Re_{24}Sc_5$ ($Re_{24}Ti_5$)	−220
	Re_2Sc (C14)	Re_2Sc (C14)	−341
Zr	$Re_{24}Zr_5$ ($Re_{24}Ti_5$)	$Re_{24}Zr_5$ ($Re_{24}Ti_5$)	−212
	Re_2Zr (C14)	Re_2Zr (C14)	−357
	$Re_{25}Zr_{21}$ ($Re_{25}Zr_{21}$)	$Re_{25}Zr_{21}$ ($Re_{25}Zr_{21}$)	−351
Hf		Hf_3Re ($Mo_3Ti\star$)	−200
	$HfRe$ (unkn.)		
	$Hf_{21}Re_{25}$ ($Re_{25}Zr_{21}$)	$Hf_{21}Re_{25}$ ($Re_{25}Zr_{21}$)	−407
	$HfRe_2$ (C14)	$HfRe_2$ (C14)	−394
	Hf_5Re_{24} (Ti_5Re_{24})	Hf_5Re_{24} (Ti_5Re_{24})	−252
Ti	$Re_{24}Ti_5$ ($Re_{24}Ti_5$)	$Re_{24}Ti_5$ ($Re_{24}Ti_5$)	−229
		Re_5Ti_3 (Ga_3Pt_5)	−391
	$ReTi$ (B2)	$ReTi$ ($MoTi\star$)	−431
		$ReTi_2$ ($ReTi_2\star$)	−316
		$ReTi_3$ ($Mo_3Ti\star$)	−252
Nb		Nb_3Re ($D0_3$)	−207
		Nb_2Re ($C11_b$)	−257
		$NbRe$ (B2)	−306
	$Nb_{0.25}Re_{0.75}$ (χ)	Nb_5Re_{24} ($Re_{24}Ti_5$)	−149
Ta	$Re_{0.7}Ta_{0.3}$ (χ)	$Re_{24}Ta_5$ ($Re_{24}Ti_5$)	−153
		$ReTa$ (B2)	−420
		$ReTa_2$ ($C11_b$)	−346
V	-	ReV (B2)	−358
		Re_3V_5 (Ga_3Pt_5)	−347
		ReV_2 ($C11_b$)	−336
		ReV_3 ($D0_3$)	−269
Mo	$Mo_{0.2}Re_{0.8}$ (χ)	Mo_5Re_{24} ($Re_{24}Ti_5$)	−2
W	$Re_{0.5}W_{0.5}$ (σ)	-	
	$Re_{0.75}W_{0.25}$ (χ)		
Cr	$Cr_{0.4}Re_{0.6}$ (σ)	-	
Tc	-	$ReTc_3$ ($D0_{11}$)	−5
Mn	$Mn_{0.55}Re_{0.45}$ (σ or χ)	$Mn_{24}Re_5$ ($Re_{24}Ti_5$)	−82
		Mn_2Re (C14)	−139
		$Mn_{12}Re_{17}$ ($Al_{12}Mg_{17}$)	−90
Fe	$Fe_{0.6}Re_{0.4}$ (σ)	Fe_2Re (C15)	−20
	$Fe_{0.4}Re_{0.6}$ (β-Mn)	Fe_2Re_3 (Mg_3Ru_2)	−25
		$FeRe_2$ (C16)	−24
Os	-	Os_3Re ($D0_{19}$)	−78
		$OsRe$ (B19)	−89
		$OsRe_2$ ($Sc_2Zr\star$)	−68
		$OsRe_3$ ($Re_3Ru\star$)	−56
Ru	-	Re_3Ru ($Re_3Ru\star$)	−52
		$ReRu$ (B19)	−86
		$ReRu_3$ ($D0_{19}$)	−80
Co		$CoRe$ (B19)	−72
		$CoRe_3$ ($D0_{19}$)	−70
Ir	-	Ir_8Re (Pt_8Ti)	−89
		Ir_2Re ($ZrSi_2$)	−223
		$IrRe$ (B19)	−271
		$IrRe_3$ ($D0_{19}$)	−207
Rh	-	Re_3Rh ($D0_{19}$)	−163
		$ReRh$ (B19)	−181
		$ReRh_2$ ($ZrSi_2$)	−173
Ni	-	Ni_4Re ($D1_a$)	−64
		$NiRe_3$ ($D0_{19}$)	−115
Pt	Pt_3Re (unkn.)	Pt_3Re ($BCC_{AB3}^{[001]}$)	−128
		$PtRe_3$ ($D0_{19}$)	−231
Pd	-	$PdRe_3$ ($D0_{19}$)	−56
Au	-	-	
Ag	-	-	
Cu	-	-	
Hg	-	-	
Cd	-	-	
Zn	-	-	

[a] A "$\star$" denotes unobserved prototypes described in ref 64. "-" denotes no compounds. ΔH is the formation enthalpy found in the present study.
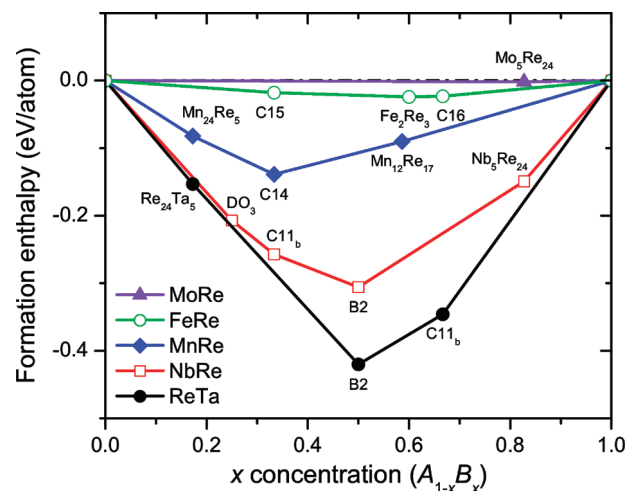
Figure 2. Ground-state convex hulls of the five Re–M binary systems reported with high-temperature disordered phases and predicted to be compound-forming by HT ab initio calculations.

Following these results, the predicted compound-forming Re binary systems may be divided into three types: (a) the systems reported with high-temperature disordered phases, σ, χ, or β-Mn, (b) systems reported as phase-separating, and (c) those reported as compound-forming. The first type includes five of the seven systems reported with disordered phases. Their convex hulls are shown in Figure 2. In four systems, the χ phase is reported at high temperatures and stable ordered structures of prototype $Re_{24}Ti_5$ are found. This structure is one of only two prototypes (the second is $Al_{12}Mg_{17}$) that are identical to one of the 16 possible ordered realizations of the disordered χ phase (*Strukturbericht* designation A12, space group #217). The χ phase is also reported in the Re–W system, where this prototype is found to be just slightly unstable, at 7 meV/atom above the pure elements tie line. A previous calculation of all the 16 ordered realizations of the χ phase in this system, with a different exchange-correlation functional (Perdew–Wang), found the same prototype to be marginally stable, at 3 meV/atom below the tie line.[45] As mentioned above, this structure was also identified as lying below the pure elements tie line in previous studies of the χ phase in the Mo–Re system,[45,48] in agreement with our calculations. The second prototype, $Al_{12}Mg_{17}$, is found to be stable in just one of these five systems, Re–Mn. A β-Mn disordered phase (*Strukturbericht* designation A13, space group $P4/mmm$ #213) is reported in Fe–Re. This phase also has a known ordered derivative, the Mg_3Ru_2 prototype, which is found to be stable in the Fe–Re system, at low temperatures. In the Cr–Re system, only the σ phase is reported and no compounds are found.
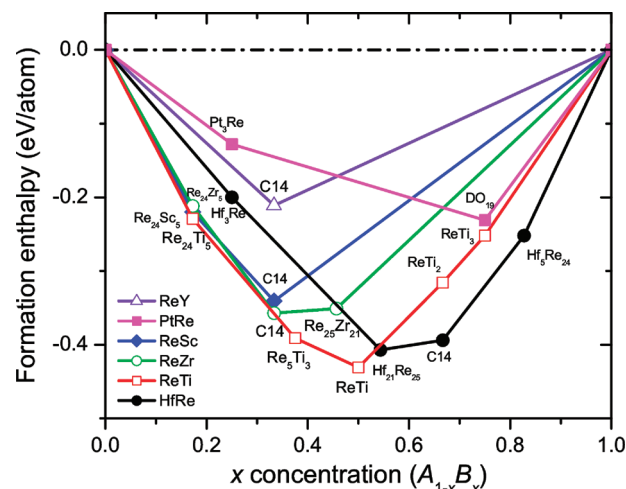
The convex hulls for the nine systems of the second type, those reported as phase-separating but predicted to be compound-forming, are shown in Figure 3. Two of these systems, Re–V and Re–Tc, lie within the cluster of systems reported with disordered phases. Re–Tc is predicted to have a single $ReTc_3$ compound. In the Re–V system, we find four compounds, two with structures B2 and $C11_b$, that appear in the adjacent systems Re–Ta and Nb–Re. The seven other systems in this group bridge the gap between the isolated compound-forming system, Pt–Re, and the predicted compound-forming systems of the first type. Interestingly, all of these systems, ordered from Os–Re to Pd–Re in Table 1, have a $D0_{19}$ compound, either Re_3M or M_3Re, where M denotes the alloying element. Five of them, Os–Re to Re–Rh, also have an MRe (B19) compound.

Figure 3. Ground-state convex hulls of the nine Re−M binary systems predicted to be compound-forming by HT ab initio calculations in contrast to phase separation reported in the literature.

Compounds with unobserved prototypes are found in the Os−Re and Re−Ru systems. These prototypes, $Sc_2Zr^{\star}$ and $Re_3Ru^{\star}$, are described in ref 64. Two compounds (prototypes $D1_a$ and DO_{19}) are predicted in the Ni−Re system. The Ni_4Re compound may be the underlying cause for the ordering tendencies recently found in ab initio simulations of $Ni_{400}Re_{100}$ molten alloy cells.[69]

It is interesting to note that, in systems with a magnetic alloying element, Fe−Re, Co−Re, and Ni−Re, the predicted ground states exhibit dramatically reduced moments, compared with the pure alloying element, or no magnetization at all. In the Fe−Re system, the Fe_2Re compound is predicted with a magnetic moment of 0.9 μ_B/atom, compared with 2.2 μ_B/atom calculated for pure bcc Fe. This reduction occurs due to a combined effect of reduced d-electron magnetization on the Fe ions and an antiferromagnetic contribution of the Re ions. The other two ground states, with higher rhenium concentrations, are predicted with vanishing magnetic moments. A similar effect occurs in the Co−Re system, where the CoRe compound is predicted with 0.1 μ_B/atom, compared with 1.6 μ_B/atom calculated for pure hcp Co. The $CoRe_3$ compound and the two ground states in the Ni−Re system are predicted with no magnetic moments. These results were verified by additional calculations on each of these structures with a few fixed finite magnetic moments. The calculations reproduced the energy minima, as a function of magnetization, with the predicted magnetic moments. These results show that rhenium effectively

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Figure 4. Calculated ground-state convex hulls of six Re−M binary systems experimentally reported as compound-forming. New structures are predicted in the Hf−Re, Re−Ti, and Pt−Re systems.

reduces or eliminates the magnetization when alloyed with magnetic d-electron metals.

In agreement with the experimental data, we find stable compounds in all the systems reported as compound-forming: Re−Y, Re−Sc, Re−Zr, Hf−Re, Re−Ti, and Pt−Re. The convex hulls of these systems are shown in Figure 4. The existence of all but one of the reported compounds with known prototypes is reproduced. The exception is the ReTi compound, reported with the B2 prototype, but predicted with the $MoTi^{\star}$ prototype.[64] The B2 prototype is found at 34 meV/atom higher energy. At high temperatures, it is perhaps stabilized by vibrational entropy. The experimental data are available at temperatures above 600 °C.[28] The Pt_3Re compound, reported with an unknown prototype, is found with a $fcc_{AB3}^{[001]}$ structure (space group $P4/mmm$ #123). In the Hf−Re system, the HfRe compound, reported with an unknown prototype, is replaced by the predicted Hf_3Re compound, while the three specified structures are reproduced. Additional unreported compounds are found in the Re−Ti and the Pt−Re systems: Re_5Ti_3, $ReTi_2$, $ReTi_3$, and $PtRe_3$.

5. Conclusion

The bulk phase behavior of alloys determines to a large extent the surface and small particle properties that dominate catalytic processes. A detailed understanding of Re alloys is crucial for a better realization of its potential as an alloying and catalytic agent in currently known applications and in developing new ones. This is demonstrated by the recent finding that surface alloys of ReRh, PdRe, and PtRe might be better electrocatalysts than pure PGMs for hydrogen evolution reactions.[17,18] The reported results for binary systems might also affect related ternary systems, for example, Re-doped Ni−Al alloys and the AlPdRe alloys recently investigated due to their very unusual semiconducting behavior.[70,71] The ternary phase diagrams would be considerably modified by predictions of compound formation in the constituent binary systems. The structure of the Al−Pd−Re diagram, for example, would be affected by the existence of

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the predicted PdRe$_3$ compound in a binary system previously believed to be phase-separating. As remarked in ref 72, the theoretical prediction of phase ordering and stability in these systems should be the starting point for designing desirable alloys for various applications.

The picture of Re alloys emerging from this study is very different from that depicted by current experimental data. Instead of many phase-separating systems, we predict that most (9 out of 15) form ordered structures. It is also shown that the existence of high-temperature disordered χ or β-Mn phases quite reliably indicates stable ordered structures at low temperatures. It should be emphasized that we consider the alloys in thermodynamical equilibrium, which can be difficult to reach

at low temperatures due to slow kinetics. At higher temperatures, configurational disorder and vibrational entropic promotion might destabilize the predicted compounds. The theoretical predictions presented here complement the woefully incomplete experimental picture. They would hopefully serve as a motivation for their experimental validation and as a guide for future studies of these important catalytic materials.

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