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2011-12-20

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Gus L. W. Hart
gus.hart@gmail.com

Lance J. Nelson

Michal Jahnátek

Ohad Levy

Roman V. Chepulsii

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Michal Jahnatek, Ohad Levy, Gus L. W. Hart, Lance J. Nelson*, Roman V. Chepulsii, J. Xue*, and Stefano Curtarolo, "Ordered phases in ruthenium binary alloys from high-throughput first principles," *Phys. Rev. B* 84, 21411 (Dec. 211). The original article may be found here: <http://prb.aps.org/abstract/PRB/v84/i21/e21411>

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Hart, Gus L. W.; Nelson, Lance J.; Jahnátek, Michal; Levy, Ohad; Chepulsii, Roman V.; Xue, J.; and Curtarolo, Stephano, "Ordered phases in ruthenium binary alloys from high-throughput first-principles calculations" (2011). *Faculty Publications*. 77.
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Authors

Gus L. W. Hart, Lance J. Nelson, Michal Jahnátek, Ohad Levy, Roman V. Chepulsii, J. Xue, and Stephano Curtarolo

Ordered phases in ruthenium binary alloys from high-throughput first-principles calculationsMichal Jahnátek,¹ Ohad Levy,^{1,2} Gus L. W. Hart,³ Lance J. Nelson,³ Roman V. Chepulskii,¹ J. Xue,¹ and Stefano Curtarolo^{1,*}¹*Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, USA*²*Department of Physics, NRCN, P.O. Box 9001, Beer-Sheva, Israel*³*Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602, USA*

(Received 9 June 2011; published 20 December 2011)

Despite the increasing importance of ruthenium in numerous technological applications, e.g., catalysis and electronic devices, experimental and computational data on its binary alloys are sparse. In particular, data are scant on those binary systems believed to be phase-separating. We performed a comprehensive study of ruthenium binary systems with the 28 transition metals, using high-throughput first-principles calculations. These computations predict novel unsuspected compounds in 7 of the 16 binary systems previously believed to be phase-separating and in two of the three systems reported with only a high-temperature σ phase. They also predict a few unreported compounds in five additional systems and indicate that some reported compounds may actually be unstable at low temperature. These new compounds may be useful in the rational design of new Ru-based catalysts. The following systems are investigated: AgRu*, AuRu*, CdRu*, CoRu*, CrRu*, CuRu*, FeRu*, HfRu, HgRu*, IrRu, MnRu, MoRu, NbRu, NiRu*, OsRu, PdRu*, PtRu, ReRu, RhRu, RuSc, RuTa, RuTc, RuTi, RuV, RuW, RuY, RuZn, and RuZr (a star denotes systems in which the *ab initio* method predicts that no compounds are stable).

DOI: [10.1103/PhysRevB.84.214110](https://doi.org/10.1103/PhysRevB.84.214110)

PACS number(s): 61.66.Dk, 64.75.Op, 82.65.+r, 82.40.Np

I. INTRODUCTION

Ruthenium is used extensively as an alloying agent in applications for the chemical and electronics industries.¹ It is an important catalyst in a wide variety of reactions, mostly used in platinum alloys or alloys of the other platinum group metals (PGM's) (rhodium, osmium, iridium, and palladium). Ruthenium alloys are used in electrodes of fuel cells and electrolytic cells. They are being researched as components in a number of developing solar energy technologies. Alloys of ruthenium with platinum and palladium make extremely durable electrical contacts and resistors. Ruthenium thin films are used in hard disk drives and plasma display panels. The addition of ruthenium improves the mechanical properties and corrosion resistance of titanium, platinum, palladium, and gold, and of nickel-based superalloys in jet engine turbine blades.² Gold-ruthenium alloys are used in jewelry and luxury items, of which a famous example is fountain pen nibs.

Ab initio studies of material properties based on density functional theory (DFT) are currently a major tool of chemistry and materials science. They provide an understanding of the fundamental physical properties and increasingly serve as a tool for computer-assisted materials design (for a recent review, see Ref. 3). The wealth of ruthenium's potential applications has motivated numerous DFT-based investigations of its properties, as a pure element and as an alloy component.

Ruthenium's practical importance as a catalytic agent has led to studies of its bulk properties⁴⁻⁶ and its behavior in various chemical reactions. It was recently found to be an excellent potential candidate for direct use of hydrocarbon fuels in solid-oxide fuel cells involving thermochemical and electrochemical reactions on electrocatalysts (H₂ electro-oxidation, CO electro-oxidation, and methane steam reforming).⁷ Experimental examples of this potential are the use of a PdRu catalyst as the anode of ethanol alkaline fuel cells⁸ and of Pt-Ru-Ni and Pt-Cr-Ru on carbon support as catalysts for direct methanol fuel cells.^{9,10}

Pt-Ru alloys are catalysts for proton exchange membrane fuel cells, in which Ru improves resistance to CO adsorption-poisoning compared to pure platinum.¹¹ They are also good substrates for water dissociation, sometimes used with a thin Pt-Ru-Co coating.¹² A recent computational screening of a large set of bimetallic catalysts identified Co-Ru alloys as highly active, though relatively expensive, for CO and CO₂ hydrogenation.^{13,14} Additional catalytic processes for which ruthenium or ruthenium alloys (e.g., Pt-Ru, Pd-Ru, Ni-Ru, Mn-Ru, and Ru-V) were studied include ammonia synthesis, ethanol steam reforming for hydrogen production, hydrogenation of methyl-propionate, methanol electro-oxidation, hydrogenation of chloronitrobenzene, oxidation of butanol and alcohol, hydrogenation of cinnamaldehyde, and hydrodechlorination of chlorobenzene.¹⁵⁻²⁰

Ruthenium surface properties, and diffusion and adsorption on them, were investigated for a wide variety of chemical species, e.g., H₂, O₂, N₂, CO, CH_x, water, BN, Cu, Pd, Ge, Li, and tetracene.²¹⁻³⁴ Pure Ru nanoparticles were studied³⁵⁻³⁷ as well as a few Ru-alloy nanoparticles, e.g., Pt-Ru³⁸ and Pd-Ru, which was suggested as a substrate for methanol oxidation in methanol fuel cells.³⁹

Studies of ruthenium doping of Ni-based superalloys include site preference of Ru in the alloy structure,^{40,41} effects of interface strengthening,^{42,43} and modification of dislocation dynamics⁴⁴ and elastic properties.⁴⁵ Similar issues were addressed for ruthenium-doped Nb-based superalloys,⁴⁶ as well as the relative stability of the several phases of NbRu shape memory alloys.⁴⁷⁻⁵⁰ The defect structure of NiRu and NiRuAl alloys was modeled by *ab initio* methods,⁵¹ and their phase diagram was investigated by thermal modeling assisted by *ab initio* calculations.^{52,53} Ru(0001) was shown to be a good catalyst for epitaxial growth of graphene.⁵⁴ In addition, Ru doping and Ru substrates were also shown to affect the properties of the grown graphene layers⁵⁵⁻⁵⁸ and carbon nanotubes.⁵⁹

The possible existence of stable alloys and ordered structures in the MoRu phase diagram was studied by thermodynamic and *ab initio* methods.^{60–63} This system is reported with a high-temperature σ phase, but experiments found a continuum of Ru-rich alloys with negative formation enthalpy.⁶⁴ A previous high-throughput study found a stable MoRu₃ compound.⁶⁵ The stability of disordered alloys was also discussed in a few of the reported immiscible systems, including FeRu, CuRu, NiRu, CoRu, AgRu, RuTa, and RuPd.^{66–72} Additional studies were carried out on the properties of the B2 phase of HfRu,⁷³ the site occupancy in the CrRu σ phase,⁷⁴ the electronic and magnetic properties of RuV thin films and superlattices,^{75,76} and the stability of RuV alloys.⁷⁷

The advances in computational methods and hardware in recent years were followed by the development of high-throughput computational methods for comprehensive screening of properties of large sets of materials. These high-throughput methods have been applied to theoretically guided material discovery and improvement.^{65,78–87} They give insights into trends in alloy properties and indicate the possible existence of hitherto unobserved compounds.

In this paper, we report on a comprehensive screening of ruthenium intermetallic binary alloys by high-throughput *ab initio* calculations. We explore the phase-stability landscape of binary Ru–transition-metal alloys, calculating the formation enthalpies of a large number of structures and identifying the minima at various component concentrations. A minimum-free-energy convex hull, i.e., the low-temperature phase diagram, is constructed for each binary system from the corresponding minimum-energy structures with negative formation enthalpies. The effectiveness of this approach in studying binary metallic systems for which experimental data are scarce and difficult to obtain has been demonstrated recently by comprehensive studies on hafnium,⁸⁸ rhodium,⁸⁹ and rhenium⁹⁰ alloys, where a large number of new compounds have been identified. As we will show in the following, this is also the case for ruthenium alloys.

The empirical data on Ru alloys are incomplete. Of the 28 Ru–transition-metal binary systems,⁹¹ 16 are reported to be non-compound-forming and 3 are listed with the disordered σ phase, at the lowest temperatures at which data are available.^{92,93} Of the nine compound-forming systems, eight are concentrated in columns IIIB, IVB, and VB of the Periodic Table, and one, Zn (listed with a single compound RuZn₆), is isolated in the IIB column^{92,93} (Fig. 1). The high-throughput approach confirms phase-ordering in the nine intermetallic systems known to be compound-forming, and predicts unreported compounds in five of them: Nb–Ru, Ru–Ta,

Ru–Ti, Ru–V, and Ru–Zn. Of the 19 systems that are either reported as phase-separating or having only a high-temperature disordered σ phase, we show that nine actually exhibit ordering tendencies, forming stable compounds at low temperature. These results are summarized in Fig. 1, which depicts the phase-separating or compound-forming nature of the 28 Ru binary systems with the transition metals.

II. METHOD

A. Formation enthalpy

The calculations were performed using the high-throughput framework AFLOW^{65,86,87,94} based on *ab initio* calculations of the energies by the VASP software.⁹⁵ We used projector augmented waves (PAW) pseudopotentials⁹⁶ and the exchange-correlation functionals parameterized by Perdew, Burke, and Ernzerhof⁹⁷ 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.⁹⁸

For each system, we calculated the energies of all the reported crystal structures^{92,93} and approximately 230 additional structures from the AFLOW prototypes database,⁹⁴ listed in Ref. 99. This protocol (of searching many enumerated derivative structures and exhaustively exploring experimentally reported structures) is expected to result in a reasonable balance between high-throughput speed and scientific accuracy to determine miscibility, or the lack thereof, in Ru alloys (a detailed discussion on the reliability of the method is presented in Refs. 65 and 100). However, there is no guarantee that the true ground states of a system are found among the common experimentally observed structures or among small-unit-cell derivative structures, and it is impossible to rule out the existence of additional unexpected ground states.

B. Phonon spectra

Depending on computational convenience, the vibrational properties (in the harmonic approximation) were calculated in one of two ways: (i) the direct force constant method (the so-called small displacement method)¹⁰¹ or (ii) the linear-response method¹⁰² for the calculation of the real-space dynamical matrices, as implemented in VASP 5.2. These

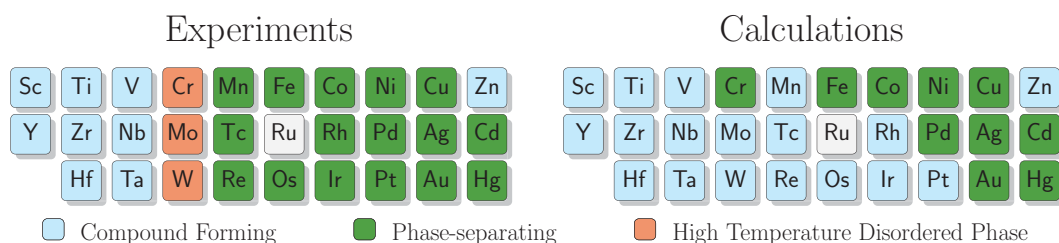


FIG. 1. (Color online) The phase-separating or compound-forming characteristics of 28 Ru-alloy systems as found in experiments (left) and in *ab initio* calculations (right).

calculations were performed using a newly implemented module of the AFLOW package, which operates in combination with VASP. The package also includes the nonanalytic part of the dynamical matrix^{103,104} for the correct splitting between longitudinal and transverse optical phonon frequencies (LO-TO splitting).

The phonon spectrum calculations require a preliminary run in which the primitive cell has to be fully relaxed with very fine settings. The energy cutoff in these runs has been set 40% higher than the highest-energy cutoff for the pseudopotentials of the components. The total energy was calculated with high precision and converged to 10^{-3} meV/atom. The calculation of very accurate forces was supported by the finer augmentation grid to avoid wrap errors (PREC=ACCURATE) and the inclusion of an additional (third) support grid for the reduction of the numerical noise (ADDGRID=TRUE). The structural relaxation was stopped when all forces acting on the atoms were converged to within 10^{-2} meV/Å and all components of the stress tensor were converged to within 0.01 GPa. The Brillouin zone (BZ) was sampled using dense 32 000 k-point Monkhorst-Pack meshes.⁹⁸

In Sec. IV, phonon calculations for the hcp elements Os and Ru and for the hcp-based B19 compound OsRu are presented. The spectra of the pure elements were determined with the direct force method with a $4 \times 4 \times 3$ supercell (96 atoms). The BZ was sampled by a Γ -centered 8000 k-point Monkhorst-Pack mesh. Six atomic displacements were required (because of the VASP selection) and the distortion magnitude was 0.015 Å.

The linear-response approach was used for the 4-atom/cell B19 compound. The phonon density of states (pDOS) was calculated by the linear tetrahedron method¹⁰⁵ on a $21 \times 21 \times 21$ q-point Monkhorst-Pack mesh. Using the DOS, the zero-point energy, the internal energy, the vibrational free energy, and the vibrational entropy were calculated based on the well-known expressions of Ref. 106.

III. RESULTS AND DISCUSSION

The convex hulls calculations are summarized in Table I. In the first column, the 28 alloying metals are ordered according to their Mendeleev number (or Pettifor's chemical scale).^{107,108} The next three columns indicate whether the corresponding binary system is phase separating or compound forming, according to the experimental data,^{92,93} a previous *ab initio* study,⁶⁵ and the calculations reported herein. The full data set of calculated formation energies and initial and relaxed unit cells for all the structures included in this study is accessible on the AFLOWLIB consortium repository.^{94,109}

Ordered by this chemical scale, almost all of these systems group into three clusters with distinct experimental characteristics: (i) compound-forming systems at the top, (ii) three systems with a high-temperature σ phase in the middle, and (iii) phase-separating systems at the bottom. The only exception to this clear separation is the compound-forming system Ru-Zn isolated at the bottom of the table. Our *ab initio* results complement this empirical tendency by predicting that most systems down to Ru-Pt (17 out of 21) are included in a large cluster of compound-forming systems. Only four systems within this cluster are predicted to be phase-separating, three with

the magnetic elements (Fe-Ru, Co-Ru, and Ni-Ru) and one (Cr-Ru) reported with a high-temperature disordered σ phase.

In the three systems of the σ -phase group, the alloying metals belong to the VIB column of the Periodic Table and share a bcc ground state. Our calculations find stable Ru_3M structures, of the DO_{19} prototype, in two of them. In the third, Cr-Ru, this structure is slightly metastable at 4 meV/atom above the pure elements tie line. Phase-ordering is also predicted in 7 of the 16 systems reported as phase-separating (see Fig. 2). In particular, these include four of the five binary systems of ruthenium with the other platinum group metals that are of special importance for chemical applications. A single ground state with the CdTi prototype is predicted for the Pt-Ru system, and multiple ground states are predicted for the Os-Ru, Rh-Ru, and Ir-Ru systems. A few of these predicted ground states do not have a known prototype or *Strukturbericht* designation. Those denoted by a ★ in Table I were found in previous studies and are described therein.^{65,88,99} The structures of $RuTc_5$ and $RhRu_5$, denoted by § in Table I, were found in this study and are described in Table II. The discrepancies between the current predictions and those of Ref. 65, e.g., the new predictions of $RuTc_5$ and $RhRu_5$ compounds, arise from the larger structure database scanned in this study. Six of the ten remaining phase-separating systems form a cluster, Pd-Ru to Cd-Ru, at the bottom of Table I. The other four, mentioned above, are dispersed among those for which compound formation is predicted.

In agreement with the experimental data, we find stable compounds in all the systems reported as compound-forming. The convex hulls of these systems are shown in Fig. 3. In the systems of the IIIB metals, Sc and Y, the calculations largely reproduce the multicomponent experimental phase diagrams,

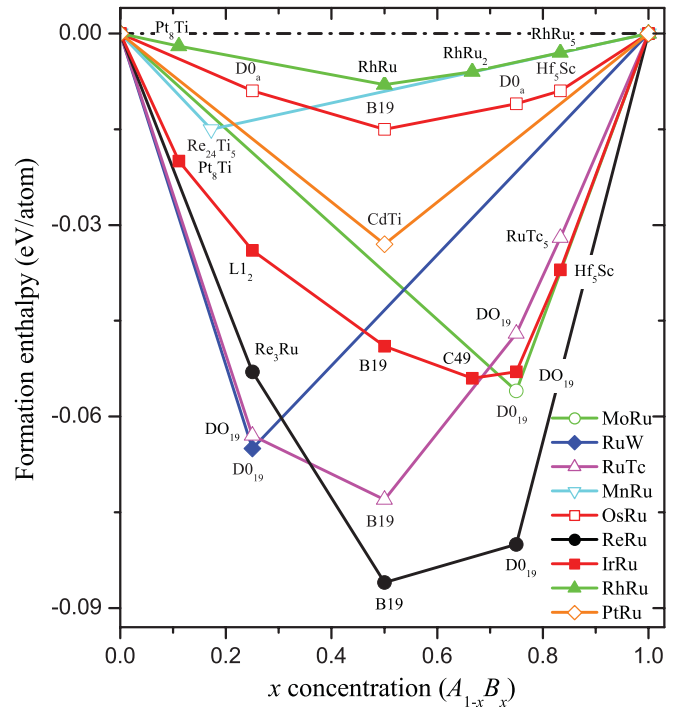


FIG. 2. (Color online) The ground-state convex hulls of the nine Ru-M binary systems reported to have no ordered phase but predicted to be compound-forming by high-throughput *ab initio* calculations.

TABLE I. Compounds observed in experiments (“Expt.”) or predicted by *ab initio* calculations (“Calc.”) in Ru binary alloys (structure prototype in parentheses). (Unkn.) denotes an unidentified structure. ★ denotes unreported prototypes described in Refs. 65, 88, and 99. § denotes new prototypes described in Table II. A blank space denotes no compounds, and “N/A” indicates no available data. ΔH is the formation enthalpy found in the present study. The energy difference between reported and calculated structures or between a reported structure (unstable in the calculation) and a calculated two-phase tie line is indicated in square brackets.

	Compounds			ΔH meV/ atom		Compounds			ΔH meV/ atom
	Expt. ^{92,93}	Calc. (Previous) ⁶⁵	Calc. (Present)			Expt. ^{92,93}	Calc. (Previous) ⁶⁵	Calc. (Present)	
Y	Ru ₂ Y(C14)	Ru ₂ Y(C14)	Ru ₂ Y(C14)	-313	Mo	σ	MoRu ₃ (D0 ₁₉)	MoRu ₃ (D0 ₁₉)	-56
	Ru ₂ Y ₃ (Er ₃ Ru ₂)			[79]	W	σ	N/A	Ru ₃ W(D0 ₁₉)	-65
	Ru ₂₅ Y ₄₄ (Ru ₂₅ Y ₄₄)		Ru ₂₅ Y ₄₄ (Ru ₂₅ Y ₄₄)	-342	Cr	σ	N/A		
		RuY ₂ (C16)		[21]	Tc		Ru ₃ Tc(D0 ₁₉)	Ru ₃ Tc(D0 ₁₉)	-63
	Ru ₂ Y ₅ (Mn ₅ C ₂)		Ru ₂ Y ₅ (Mn ₅ C ₂)	-334			RuTc(B19)	RuTc(B19)	-73
	RuY ₃ (D0 ₁₁)	RuY ₃ (D0 ₁₁)	RuY ₃ (D0 ₁₁)	-307			RuTc ₃ (D0 ₁₉)	RuTc ₃ (D0 ₁₉)	-47
Sc	Ru ₂ Sc(C14)	N/A	Ru ₂ Sc(C14)	-389				RuTc ₅ (RuTc ₅ [§])	-32
	RuSc(B2)		RuSc(B2)	-540	Re		N/A	Re ₃ Ru(Re ₃ Ru [*])	-53
	Ru ₃ Sc ₅ (D8 ₈)			[42]				ReRu(B19)	-86
	RuSc ₂ (NiTi ₂)		RuSc ₂ (C11 _b)	-484[84]				ReRu ₃ (D0 ₁₉)	-80
	Ru ₄ Sc ₁₁ (Ir ₄ Sc ₁₁)		Ru ₄ Sc ₁₁ (Ir ₄ Sc ₁₁)	-405	Mn		N/A	Mn ₂₄ Ru ₅ (Re ₂₄ Ti ₅)	-15
	Ru ₁₃ Sc ₅₇ (Rh ₁₃ Sc ₅₇)			[10]	Fe		N/A		
	Ru ₇ Sc ₄₄ (Mg ₄₄ Rh ₇)		Ru ₇ Sc ₄₄ (Mg ₄₄ Rh ₇)	-226	Os		N/A	Os ₃ Ru(D0 _a)	-9
								OsRu(B19)	-15
Zr	RuZr(B2)	RuZr(B2)	RuZr(B2)	-646				OsRu ₃ (D0 _a)	-11
		RuZr ₄ (D1 _a)		[7]				OsRu ₅ (Hf ₅ Sc [*])	-9
Hf	HfRu(B2)	N/A	HfRu(B2)	-819	Ru	(reference position)			
	HfRu ₂ (Unkn.)				Co		N/A		
Ti	RuTi(B2)	RuTi(B2)	RuTi(B2)	-763	Ir		N/A	Ir ₈ Ru(Pt ₈ Ti)	-20
		RuTi ₂ (C49)	RuTi ₂ (C49)	-532				Ir ₃ Re(L1 ₂)	-34
		RuTi ₃ (Mo ₃ Ti [*])	RuTi ₃ (Mo ₃ Ti [*])	-401				IrRu(B19)	-49
Nb			Nb ₈ Ru(Pt ₈ Ti)	-117				IrRu ₂ (C49)	-54
		Nb ₅ Ru(Nb ₅ Ru [*])	Nb ₅ Ru(Nb ₅ Ru [*])	-172				IrRu ₃ (D0 ₁₉)	-53
		Nb ₃ Ru(D0 ₃)	Nb ₃ Ru(L6 ₀)	-222[9]				IrRu ₅ (Hf ₅ Sc [*])	-37
			Nb ₅ Ru ₃ (Ga ₃ Pt ₅)	-249	Rh			Rh ₈ Ru(Pt ₈ Ti)	-2
	NbRu(Unkn.)		Nb ₃ Ru ₅ (Ga ₃ Pt ₅)	-240			RhRu(RhRu [*])	RhRu(RhRu [*])	-8
		NbRu ₂ (C37)		[11]			RhRu ₂ (RhRu ₂ [*])	RhRu ₂ (RhRu ₂ [*])	-6
	NbRu ₃ (L1 ₂)	NbRu ₃ (D0 ₂₄)		[8]			RhRu ₅ (RhRu ₅ [§])	-3	
Ta	Ru ₅ Ta ₃ (Unkn.)	N/A	Ru ₅ Ta ₃ (Ga ₃ Pt ₅)	-332	Ni		N/A		
	RuTa(Unkn.)				Pt		Pt ₃ Ru(fcc _{AB3} ^[001])		[4]
			Ru ₃ Ta ₅ (Ga ₃ Pt ₅)	-313			PtRu(fcc _{A2B2} ^[001])	PtRu(CdTi)	-33[1]
			RuTa ₃ (fcc _{AB3} ^[001])	-281	Pd				
			RuTa ₅ (Nb ₅ Ru [*])	-207	Au				
V		N/A	Ru ₃ V(Re ₃ Ru [*])	-145	Ag				
			Ru ₂ V(C37)	-192	Cu		N/A		
	RuV(B11)			[28]	Hg		N/A		
			Ru ₃ V ₅ (Ga ₃ Pt ₅)	-313	Cd				
			RuV ₂ (C11 _b)	-321	Zn		N/A	RuZn ₃ (L1 ₂)	-150
			RuV ₃ (Mo ₃ Ti [*])	-296				RuZn ₆ (RuZn ₆)	-132
			RuV ₄ (D1 _a)	-262					
			RuV ₅ (Nb ₅ Ru [*])	-230					
			RuV ₈ (Pt ₈ Ti)	-154					

TABLE II. Geometry of new prototypes marked by § in Table I. Atomic positions and unit-cell parameters are fully relaxed.

Formula	RuTc ₅	RhRu ₅
Lattice	Monoclinic	Orthorhombic
Space group (opt.)	<i>Cm</i> #8 (2)	<i>Amm</i> 2 #38
Pearson symbol	mS12	oS12
HT Lattice type/variation ⁸⁶	MCLC/MCLC1	ORCC/ORCC
Conv. cell		
<i>a, b, c</i> (Å)	9.997, 2.752, 6.484	4.323, 2.724, 14.195
α, β, γ (deg)	90 75.942 90	90, 90, 90
Wyckoff positions	Ru1 0,0,-0.00140 (2a) Tc1 0.390,0,-0.277 (2a)	Rh1 0,0,0 (2a) Ru1 1/2,0,-0.223 (2b)
(Refs. 110 and 111)	Tc2 -0.335,0,-0.331 (2a) Tc3 0.055,0,0.388 (2a) Tc4 0.334,0,0.334 (2a) Tc5 -0.278,0,0.055 (2a)	Ru2 0,0,-0.331 (2a) Ru3 1/2,0,0.444 (2b) Ru4 0,0,0.332 (2a) Ru5 1/2,0,0.112 (2b)
AFLOW label ⁹⁴	“128”	“141”

but show that two reported structures, Ru₂Y₃ and Ru₃Sc₅, are unstable at low temperatures. The calculations reproduce the B2 structure in the phase diagrams of the IVB metals, Ti, Zr,

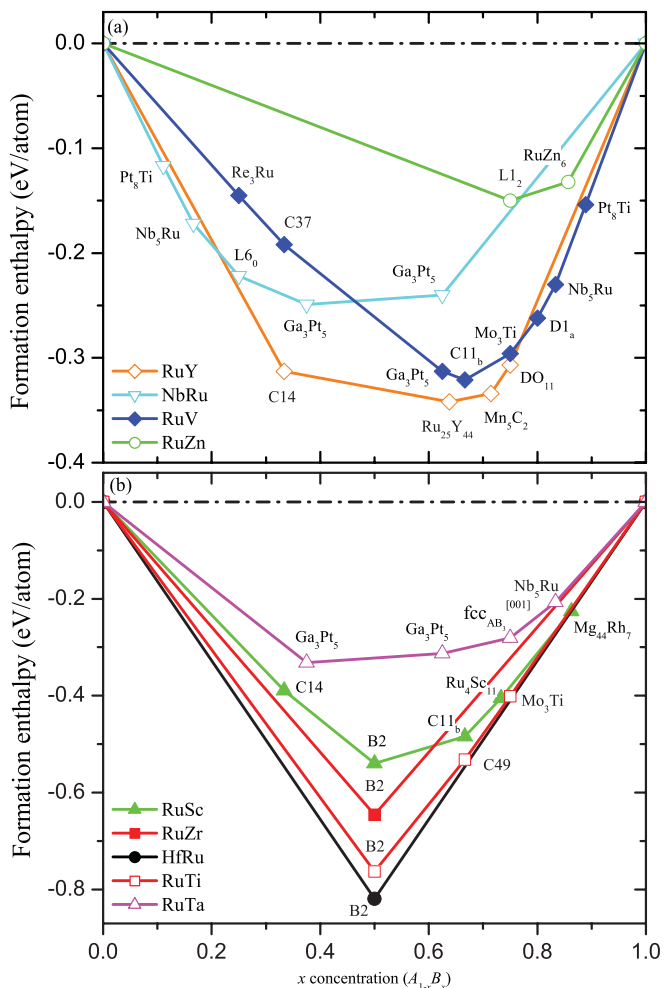


FIG. 3. (Color online) The calculated ground-state convex hulls of nine Ru-M binary systems reported experimentally, and confirmed by *ab initio* calculations, to be compound-forming. Unreported structures are predicted in five systems.

and Hf, and predict two additional structures, RuTi₂ and RuTi₃, in the RuTi system.

RuM equiatomic structures are reported in the experimental phase diagrams of the VB metals, V, Nb, and Ta, and only one additional structure is reported in the Nb-Ru and Ru-Ta systems. However, the calculations indicate a much more complex picture with many compounds in the phase diagrams and no stable RuM structures. The low-temperature phase diagrams of these systems are thus much richer than previously indicated by the experimental data.

The Nb-Ru system in particular is interesting due to the shape memory properties of its equiatomic composition alloy.⁴⁶⁻⁵⁰ This alloy undergoes two structural transformations at high temperature. Above 900 °C, it is a cubic B2 structure, the so-called β -phase. Below 900 °C, it transforms to a tetragonal L1₀ structure, called β' . Near 750 °C, another transformation takes place to the β'' phase, which is either orthorhombic or monoclinic. Our calculations show that none of these structures is stable at low temperature; however, their relative stability is consistent with that found in experiment, as a function of temperature. The orthorhombic B19 structure (space group *Pmma*) and the monoclinic structure reported in Ref. 50 (space group *P21/m*) are nearly degenerate at 30 meV/atom above the convex hull, defined at this concentration by the Nb₅Ru₃-Nb₃Ru₅ tie line. The relaxed monoclinic structure, with $\gamma = 91.4^\circ$, is barely distinguishable from the orthorhombic B19 structure. The L1₀ structure appears at 3 meV/atom higher energy and the B2 structure is 28 meV/atom above it.

IV. DISORDER AND VIBRATIONS

The convex hulls of the three systems Pt-Ru, Rh-Ru, and Os-Ru are relatively shallow. In these cases, it is possible that thermal contributions to the free energy may prevent ordering at ambient temperature despite negative formation enthalpies at zero temperature. The vibrational contributions can be estimated from first-principles calculations of the phonon spectra. In systems where the pure elements and the ground state share a common lattice, we can estimate the configurational entropy via a cluster expansion model

and Monte Carlo simulation. Using these methods, we may estimate the order-disorder transition temperature of the B19 predicted equiatomic ground state in Os-Ru. In the other shallow systems, Pt-Ru and Rh-Ru, a CE-based Monte Carlo approach is inapplicable because the lattices of the pure elements do not match.

Calculated via a cluster expansion,¹¹² the energy for the equiatomic random alloy of Os-Ru is ~ 7 meV/atom higher than the predicted ground state. Monte Carlo modeling using the same cluster expansion gives the order-disorder transition $T_c \approx 110$ K. The cluster expansion model, though, only includes *configurational* entropy. The vibrational contribution is usually smaller. It is calculated from the phonon-dispersion curves for Os, Ru, and OsRu, obtained as described in Sec. II B. In order-disorder transitions where the underlying lattice of both phases is the same, the vibrational effect on the transition temperature can be estimated by

$$T_{\text{config+vib}} \approx T_{\text{config}} \left(1 + \frac{\Delta S_{\text{vib}}}{\Delta S_{\text{config}}} \right)^{-1},$$

where $T_{\text{config+vib}}$ is the transition temperature adjusted by including both contributions, T_{config} includes only the configurational contribution, and ΔS_{vib} and ΔS_{config} are the corresponding contributions to the entropy.¹¹³

ΔS_{config} is estimated as the ratio of the energy difference between the ordered and disordered states and the transition temperature taken from the MC modeling. ΔS_{vib} is the difference between the entropy of the ordered state and the *average* entropy of the pure elements, both extracted from the phonon spectra. This gives a minor reduction in the transition temperature of $\sim 5\%$ to $T_{\text{config+vib}} = 105$ K.

The implication of this low transition temperature in OsRu-B19 is that the predicted ground state is unlikely to be observed experimentally. At such a low temperature, atomic diffusion is extremely sluggish, and it will be practically impossible to reach thermodynamic equilibrium. This may be a reason some of the compounds predicted in this study have not been observed in experiments. Similarly, the discrepancy between a predicted minimum energy structure and an observed high-temperature phase may be due to vibrational stabilization at high temperature. Small energy differences between the experimentally observed structure and *ab initio* results could be reversed at elevated temperature, e.g., a vibrational entropy difference was shown to stabilize the θ -Al₂Cu phase over the competing Al₂Cu- θ' phase, which has the lowest energy and is, therefore, stable at low temperatures.¹¹⁴ However, it should be emphasized that small formation enthalpies do not necessarily imply a low transition temperature, because the vibrational contributions may also act to stabilize the ordered phase relative to the disordered phase. An example is the case of the observed Hg₂Rh compound, which has a calculated formation enthalpy of only ~ 5 meV/atom.⁸⁹

Even if the bulk phases might not exist at room temperature, ordered structures might be stable at the nanoscale; i.e., for a few nanocatalysts (Fe-C, FeMo-C, Pt), it was shown that the surface-tension contribution to the free energy plays a fundamental role in stabilizing ordered structures, thereby causing catalytic deactivation.^{115–117} Thus, to design effective Ru-based catalytic nanosystems, it is necessary to be aware of all the possible competing phases, even if they are not kinetically accessible in the bulk.

V. CONCLUSION

To a large extent, the bulk phase behavior of alloys determines the surface and small particle properties that dominate catalytic processes. A detailed understanding of Ru alloys is crucial for a better realization of its performance as an alloying agent. This is demonstrated by the recent finding that alloys of Co-Ru, Pt-Ru, Pd-Ru, Ni-Ru, Mn-Ru, and V-Ru may be better electrocatalysts than pure PGM for various reactions.^{15–20}

The picture of Ru alloys emerging from this study is different from that depicted by current experimental data. We predict ordering in seven systems reported to be phase-separating and in two systems where only the disordered σ phase was reported. Even in the ordering systems, we find several cases in which far more phases are predicted to be stable than reported in the experimental phase diagrams. These *ab initio* results complement the empirical tendency implied by the Pettifor chemical scale by predicting that most compound-forming systems are included in a large cluster of 21 systems. Only four systems within this cluster are predicted to be phase-separating, and only one compound-forming system is separated from it.

It should be emphasized that we consider the alloys in thermodynamic equilibrium, which can be difficult to reach at low temperature due to slow kinetics. Configurational disorder and vibrational entropic promotion might also destabilize the predicted compounds. We demonstrate this in the case of Os-Ru, where our calculated transition temperature indicates that observation of ordering is highly unlikely. The theoretical predictions presented here complement the incomplete experimental picture and will hopefully serve as a motivation for their experimental validation and be a guide for future studies of these important catalytic systems.

ACKNOWLEDGMENTS

We thank Wahyu Setyawan, Shidong Wang, Richard Taylor, and Mike Mehl for fruitful discussions. Research was supported by ONR (N00014-07-1-0878, N00014-07-1-1085, N00014-09-1-0921, N00014-1-110136) and NSF (DMR-0639822, DMR-0650406). We are grateful for extensive use of the Fulton Supercomputer Center at Brigham Young University and Teragrid resources (MCA-07S005).

*stefano@duke.edu

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