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Small step graphs of cell data versus composition for ccp solid-solution binary alloys: Application to the (Pt,Ir), (Pt,Re) and (Pt,Ru) systems

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Abstract

It is shown here that crystallographic descriptions of hypothetical AB₆₃, AB₁₀₇, AB₁₂₇, AB₂₁₅ and especially AB₂₅₅ stoichiometric compounds with cell edge, respectively 4, 3, 4, 6 and four times the (A,B) fcc subcell edge stick out as convenient models for ab initio studies of cell data versus composition for ccp solid-solution alloys. Their Wyckoff positions can be combined to generate most binary alloy compositions from 0% to 100% in multiples of 1/64, 1/108, 1/128, 1/216 and 1/256 while retaining the same periodicity and, respectively the same *Fm* $\bar{3}$ *m*, *Pm* $\bar{3}$ *m*, *Im* $\bar{3}$ *m*, *Fm* $\bar{3}$ *m* and *Pm* $\bar{3}$ *m* space group symmetry. As an application, we model cell data for three cubic solid-solution alloys of Pt. (Pt,Ir) and (Pt,Ru) remain close to Vegard's law predictions with a slight convexity or concavity in the plot. That curvature is explainable by the magnitude and sign of the alloying energy. Modeling of (Pt,Re) between 0% and 45% Re in 50 steps of Re_{*n*}Pt_{108–*n*} stoichiometric compounds follows approximately non-Vegard experimental data but with large, unexplained spread. The method has been automated in *Materials Toolkit* (<http://www.tothcanada.com/toolkit>).
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Keywords: Intermetallics; Computer simulations; Fuel-cells

1. Introduction

Current fuel-cell research efforts hinge on the catalytic properties of a variety of platinum alloys, most of which are close-packed solid-solutions, either ccp or hcp. Experimental cell data for a few solid-solution alloys are well documented in the literature, while those for others are not. Sometimes, reported values turn out to be insufficiently precise or samples insufficiently characterized. It is then tempting to complement the existing experimental data with some modeling, either to support the data, fill composition gaps or clarify deviations from Vegard's law (Vegard [1]; Thorpe and Garboczi [2]).

We contributed before to the characterization of the slope of Vegard's law in (Pt,Ru) cell data (Bock et al. [3]). Ab initio modeling of cell data for solid-solution systems is performed by optimizing cell and coordinate data for hypothetical stoichiometric compounds within the known range of the solid-solution. This optimization is the essence of the Car and Parrinello [4]

algorithm. This algorithm, which is implemented in all density functional theory (DFT) packages, is at the base of the current explosion of applications of DFT to materials science and chemistry problems. It is well known that DFT quantum modeling can extract correctly tiny energy or stress differences between two models, while the value itself of that energy or stress may be affected by a much larger bias. This is why for example the routine calculation of accurate elastic coefficients for crystalline materials is feasible in the presence of a pressure bias that is commonly a GPa or so even with today's best pseudopotentials. Adequate precautions are therefore required in order to perform most modeling operations. If at all feasible, the atomic content of the primitive cell, the Cartesian components of its cell edges, the symmetry, the origin of atom coordinates and the k-mesh should be identical from simulation to simulation. For execution speed, symmetry should also be as high as possible. In the present contribution, we try to optimize the production of cell data versus composition plots around the above criteria. In performing this analysis, we somewhat extrapolate on what is economically feasible today with coarse steps and extend the analysis toward finer steps that will be reasonably achievable in 5–10 years provided that Moore's law goes on holding for that length of time.

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Table 1
Possible models with holohedral cubic symmetry for ab initio simulation of ccp alloys

Type	Wyckoff site	Site symmetry	Atom coordinates		
(a) Formula: AB ₇ , Z=4, Space group: $Fm\bar{3}m$, $a=2a_{\text{subcell}}$ ^a					
A	4a	$m\bar{3}m$	0	0	0
B	4b	$m\bar{3}m$	1/2	0	0
B	24d	$m\cdot mm$	0	1/4	1/4
(b) Formula: AB ₂₆ , Z=4, Space group: $Fm\bar{3}m$, $a=3a_{\text{subcell}}$ ^b					
A	4a	$m\bar{3}m$	0	0	0
B	24e	$4m\cdot m$	0.333333333	0	0
B	32f	$\cdot 3m$	0.333333333	0.333333333	0.333333333
B	48h	$m\cdot m2$	0	0.166666667	0.166666667
(c) Formula: AB ₆₃ , Z=4, Space group: $Fm\bar{3}m$, $a=4a_{\text{subcell}}$ ^c					
A	4a	$m\bar{3}m$	0	0	0
B	4b	$m\bar{3}m$	1/2	0	0
B	8c	$\bar{4}3m$	1/4	1/4	1/4
B	24d	$m\cdot mm$	0	1/4	1/4
B	24e	$4m\cdot m$	0.250000000	0	0
B	48h	$m\cdot m2$	0	0.125000000	0.125000000
B	48i	$m\cdot m2$	1/2	0.375000000	0.375000000
B	96k	$\cdot\cdot m$	0.125000000	0.125000000	0.250000000
(d) Formula: AB ₁₂₄ , Z=4, Space group: $Fm\bar{3}m$, $a=5a_{\text{subcell}}$ ^d					
A	4a	$m\bar{3}m$	0	0	0
B	24e	$4m\cdot m$	0.400000000	0	0
B	24e	$4m\cdot m$	0.200000000	0	0
B	32f	$\cdot 3m$	0.200000000	0.200000000	0.200000000
B	32f	$\cdot 3m$	0.400000000	0.400000000	0.400000000
B	48h	$m\cdot m2$	0	0.100000000	0.100000000
B	48h	$m\cdot m2$	0	0.200000000	0.200000000
B	96j	$m\cdot\cdot$	0	0.200000000	0.400000000
B	96k	$\cdot\cdot m$	0.400000000	0.400000000	0.200000000
B	96k	$\cdot\cdot m$	0.300000000	0.300000000	0.400000000
(e) Formula: AB ₂₁₅ , Z=4, Space group: $Fm\bar{3}m$, $a=6a_{\text{subcell}}$ ^e					
A	4a	$m\bar{3}m$	0	0	0
B	4b	$m\bar{3}m$	1/2	1/2	1/2
B	24d	$m\cdot mm$	0	1/4	1/4
B	24e	$4m\cdot m$	0.333333333	0	0
B	24e	$4m\cdot m$	0.166666667	0	0
B	32f	$\cdot 3m$	0.166666667	0.166666667	0.166666667
B	32f	$\cdot 3m$	0.333333333	0.333333333	0.333333333
B	48g	$2\cdot mm$	0.166666667	1/4	1/4
B	48h	$m\cdot m2$	0	0.166666667	0.166666667
B	48h	$m\cdot m2$	0	0.083333333	0.083333333
B	48i	$m\cdot m2$	1/2	0.333333333	0.333333333
B	48i	$m\cdot m2$	1/2	0.416666667	0.416666667
B	96j	$m\cdot\cdot$	0	0.083333333	0.250000000
B	96k	$\cdot\cdot m$	0.083333333	0.083333333	0.333333333
B	96k	$\cdot\cdot m$	0.083333333	0.083333333	0.166666667
B	192l	1	0.250000000	0.166666667	0.083333333
(f) Formula: AB ₃₁ , Z=1, Space group: $Pm\bar{3}m$, $a=2a_{\text{subcell}}$ ^f					
A	1a	$m\bar{3}m$	0	0	0
B	1b	$m\bar{3}m$	1/2	1/2	1/2
B	3c	$4/mm\cdot m$	0	1/2	1/2
B	3d	$4/mm\cdot m$	1/2	0	0
B	12i	$m\cdot m2$	0	0.250000000	0.250000000
B	12j	$m\cdot m2$	1/2	0.250000000	0.250000000
(g) Formula: AB ₁₀₇ , Z=1, Space group: $Pm\bar{3}m$, $a=3a_{\text{subcell}}$ ^g					
A (Atom 1)	1a	$m\bar{3}m$	0	0	0
B (Atom 2)	3c	$4/mm\cdot m$	0	1/2	1/2
B (Atom 3)	6e	$4m\cdot m$	0.333333333	0	0
B (Atom 4)	6f	$4m\cdot m$	0.333333333	1/2	1/2
B (Atom 5)	8g	$\cdot 3m$	0.333333333	0.333333333	0.333333333
B (Atom 6)	12h	$mm2\cdot\cdot$	0.166666667	1/2	0
B (Atom 7)	12i	$m\cdot m2$	0	0.333333333	0.333333333
B (Atom 8)	12i	$m\cdot m2$	0	0.166666667	0.166666667

Table 1 (Continued)

Type	Wyckoff site	Site symmetry	Atom coordinates		
B (Atom 9)	24l	$m\bar{c}$	1/2	0.333333333	0.166666667
B (Atom 10)	24m	$\bar{c}m$	0.166666667	0.166666667	0.333333333
(h) Formula: AB_{255} , $Z=1$, Space group: $Pm\bar{3}m$, $a=4a_{\text{subcell}}$ ^h					
A	1a	$m\bar{3}m$	0	0	0
B	1b	$m\bar{3}m$	1/2	1/2	1/2
B	3c	$4/m\bar{m}m$	0	1/2	1/2
B	3d	$4/m\bar{m}m$	1/2	0	0
B	6e	$4m\bar{m}$	0.250000000	0	0
B	6f	$4m\bar{m}$	0.250000000	1/2	1/2
B	8g	$\bar{3}m$	0.250000000	0.250000000	0.250000000
B	12h	$mm2\bar{c}$	0.250000000	1/2	0
B	12i	$m\bar{m}2$	0	0.125000000	0.125000000
B	12i	$m\bar{m}2$	0	0.250000000	0.250000000
B	12i	$m\bar{m}2$	0	0.375000000	0.375000000
B	12j	$m\bar{m}2$	1/2	0.125000000	0.125000000
B	12j	$m\bar{m}2$	1/2	0.250000000	0.250000000
B	12j	$m\bar{m}2$	1/2	0.375000000	0.375000000
B	24k	$m\bar{c}$	0	0.125000000	0.375000000
B	24l	$m\bar{c}$	1/2	0.125000000	0.375000000
B	24m	$\bar{c}m$	0.125000000	0.125000000	0.250000000
B	24m	$\bar{c}m$	0.375000000	0.375000000	0.250000000
B	48n	1	0.375000000	0.250000000	0.125000000
(i) Formula: AB_{15} , $Z=2$, Space group: $Im\bar{3}m$, $a=2a_{\text{subcell}}$ ⁱ					
A	2a	$m\bar{3}m$	0	0	0
B	6b	$4/m\bar{m}m$	0	1/2	1/2
B	24h	$m\bar{m}2$	0	0.250000000	0.250000000
(j) Formula: AB_{127} , $Z=2$, Space group: $Im\bar{3}m$, $a=4a_{\text{subcell}}$ ^j					
A	2a	$m\bar{3}m$	0	0	0
B	6b	$4/m\bar{m}m$	0	1/2	1/2
B	8c	$\bar{3}m$	1/4	1/4	1/4
B	12d	$\bar{4}m2$	1/4	0	1/2
B	12e	$4m\bar{m}$	0.250000000	0	0
B	24h	$m\bar{m}2$	0	0.125000000	0.125000000
B	24h	$m\bar{m}2$	0	0.250000000	0.250000000
B	24h	$m\bar{m}2$	0	0.375000000	0.375000000
B	48i	$\bar{c}2$	1/4	0.375000000	0.125000000
B	48j	$m\bar{c}$	0	0.125000000	0.375000000
B	48k	$\bar{c}m$	0.125000000	0.125000000	0.250000000

^a Compositions not achievable: (3, 4)/8.

^b Compositions not achievable: (2, 3, 4, 5, 10, 11)/27.

^c Compositions not achievable: (5, 11, 17, 23, 29)/64.

^d Compositions not achievable: (2, 3, 4, 5, 10, 11, 16, 17, 22, 23, 28, 29, 34, 35, 40, 41, 46, 47, 52, 53, 58, 59)/125.

^e Compositions not achievable: (3, 4, 5, 11)/216.

^f Compositions not achievable: (9, 10, 11)/16.

^g Compositions not achievable: (2, 5)/108.

^h All compositions that are integer multiples of 1/256 are achievable.

ⁱ Compositions not achievable: (2, 5, 6, 7, 8)/16.

^j Compositions not achievable: 2/128.

2. Optimal computational models

As shown below, all the above general precautions can be implemented in modeling of cell data versus alloy composition apart, of course, from the atomic content of the primitive cell. However, difficulties arise that are detailed below.

2.1. Sufficiently fine composition steps

A first difficulty arises with the composition step. If we want a composition step s , the primitive cell of our model must then

contain at least $1/s$ atoms. As we want s to be as small as possible, this means that our model must include many atoms. However, optimization of models becomes very slow above 70 atoms or so, depending on the symmetry. In the particular case of ccp solid-solutions, the maximum symmetry of compositional models is holohedral cubic. Preserving this cubic symmetry is then crucial for the optimizations to be feasible at all with 100 or more atoms per primitive cell, which is required for percent composition steps. We are then restricted to building $n \times n \times n$ supercells of one of three possible primitive cells: the 60° rhombohedron of the fcc lattice, the cubic cell of the primitive cubic lattice or the

109.54° rhombohedron built by body centering the cube of the $2 \times 2 \times 2$ supercell. No other holohedral cubic solution can exist. As the fcc rhombohedron contains one atom, its supercells with cubic symmetry then contain $1 \times n^3$ with n integer, i.e. 8, 27, 64, 125, 216, 343, 512, etc. atoms. The cube contains four atoms and its supercells then contain 32, 108, 256, 500, etc. atoms. The bcc rhombohedron contains 16 atoms and its supercells 128, 432, 1024, etc. atoms. The possibly useful and tractable numbers in the above list are 8, 16, 27, 32, 64, 108, 125, 128, 216 and 256. Simulations for the last five numbers of atoms are barely feasible with PCs today, but as they will presumably become tractable in just a few years, we include them in the analysis below. The next number, 343, is likely to remain both out-of-reach for a while, and of limited usefulness anyway.

2.2. Achievable compositions

A second difficulty is the alloy compositions that can be achieved while retaining holohedral cubic symmetry. The problem boils down to combinations of the multiplicities of the occupied Wyckoff positions. This problem is easily handled with the *Supercells* and *Symmetry* tools in *Materials Toolkit* (Le Page and Rodgers [5]; <http://www.tothcanada.com/toolkit/>). In Table 1, we accordingly report the cubic crystallographic descriptions for hypothetical AB₇, AB₁₅, AB₂₆, AB₃₁, AB₆₃, AB₁₀₇, AB₁₂₄, AB₁₂₇, AB₂₁₅ and AB₂₅₅ stoichiometric ccp compounds. AB₇, AB₁₅, AB₂₆ and AB₃₁, respectively shown in Table 1a, i, b and f all combine the drawbacks of coarse composition steps with huge gaps in the achievable compositions. AB₁₂₄ (Table 1d) turns out to be a poor choice because it displays both drawbacks of a relatively large number of atoms per primitive cell as well as significant gaps in the compositions that are achievable by selecting full occupancy at its Wyckoff positions by either just element A or just element B. In comparison, models based on the Wyckoff positions of AB₆₃ in *Fm* $\bar{3}$ *m* (Table 1c) then seem to constitute the compromise between sufficiently fine composition step (1.56%) and affordable computing effort. They do not allow generation of fractions 5, 11, 17, 23, 29, 35, 41, 47, 53 and 59/64, but those are equally spaced numbers, leaving no big composition gap empty or depleted. Similarly, AB₁₀₇, AB₁₂₇ and AB₂₁₅ in Table 1g, j and e appear to be acceptable selections, leaving only a few gaps for low percentage alloying, but otherwise covering nicely the intermediate range with no gaps. Finally, AB₂₅₅ (Table 1h) seems to be an excellent selection for the future, as it leaves no composition gap at all. Quantum optimizations involving 256 atoms with cubic symmetry are expensive today, but they will no longer be by 2010 provided that Moore's law holds until that date.

2.3. Degree of randomness

An ideal solid-solution displays randomness of its atom distribution, a fact translating in reciprocal space by a clean powder diffraction pattern of the simple structure type for the element, usually ccp or hcp, with no additional lines, not even diffuse ones. No periodic superstructure can be claimed to be random,

Table 2

Bonds per cell with first neighbours for each atom position in Table 1g are given as a row

Atom #	1	2	3	4	5	6	7	8	9	10
1								12		
2							12		24	
3						24		24		24
4				24	24				24	
5				24					48	24
6			24			24	24		24	48
7		12				24		12	48	48
8	12		24				12	48		48
9		24		24	48	24	48		72	48
10			24		24	48	48	48	48	48

Both rows and columns are in the order of Table 1g. The cell contains 648 bonds, each linking two atoms. Each bond is then counted twice in the table.

but some periodic distributions are further remote from randomness than others. For example, the ratios of the numbers of AA:AB:BB bonds in a random distribution of composition (A_xB_{1-x}) are $x^2:2x(1-x):(1-x)^2$. We then attempt to create superstructure models that approximate those proportions as closely as feasible. In the following discussion, we use the material AB₁₀₇ in Table 1g as an example. Table 2 shows in its cells the number of bonds per crystallographic cell linking atom *i* and its symmetry equivalents to atom *j* and its equivalents as numbered in Table 1g. Table 2 was produced by multiplication of the number of bonds originating from each atom as printed by the *Distances* and *Angles* tool in *Materials Toolkit* by the multiplicity of that atom printed in Table 1g. Apart from the compositions 1, 3, 4, 104, 105 and 107/108 for which there is no leeway in the selection of the atoms from the list giving the corresponding total number of atoms per cell, all other achievable compositions can be obtained through multiple selections. For example, composition 6/108 can be achieved in two ways, by selecting either atom #3 or atom #4. Those two ways are not equivalent because it can be read off Table 2 that the first generates no AA bond, 72 AB bonds and 576 BB bonds, while the second one generates 24 AA bonds, 48 AB bonds and 576 BB bonds. As the numbers expected from the random distribution of a composition in the proportion of six atoms A and 102 atoms B are 2:68:578, it is clear that the first selection approximates more closely a random distribution than the second one. Composition 9/108 can be achieved in three ways, by involving atom numbers (2,3), (2,4) and (1,5). Each time, we select that distribution of atoms which best approximates the distribution of bonds expected from a random distribution of atoms in the same atomic proportion. We report in Table 3 the optimum solution for the various achievable compositions. In most cases, several distributions achieve the same sum of the squares of the differences in numbers of AA, AB and BB bonds. We did not implement any additional criterion in the selection of the printed optimum solution. In order to fully implement the structures described in the various Table 1a–i, readers should then build the corresponding neighbour tables, similar to Table 2 here, and implement considerations above as in Table 3.

Table 3
Optimum occupancy by atom A of the various atom sites in Table 1g leading to alloy formula A_NB_{108-N} while minimizing the sum of the squares of the differences in numbers of AA, AB and BB bonds with respect to a random distribution of atoms A and B with same proportions

N	Occupancy of the 10 sites in Table 1g										Sqrt of sum of square of differences
	1	2	3	4	5	6	7	8	9	10	
1	1	–	–	–	–	–	–	–	–	–	0.136
3	–	1	–	–	–	–	–	–	–	–	1.225
4	1	1	–	–	–	–	–	–	–	–	2.177
6	–	–	1	–	–	–	–	–	–	–	4.899
7	1	–	1	–	–	–	–	–	–	–	6.668
8	–	–	–	–	1	–	–	–	–	–	8.709
9	1	–	–	–	1	–	–	–	–	–	11.023
10	1	1	1	–	–	–	–	–	–	–	13.608
11	–	1	–	–	1	–	–	–	–	–	16.466
12	–	–	–	–	–	1	–	–	–	–	9.798
13	1	–	–	–	–	1	–	–	–	–	6.396
14	–	–	1	–	1	–	–	–	–	–	26.672
15	–	1	–	–	–	1	–	–	–	–	1.225
16	1	1	–	–	–	1	–	–	–	–	5.443
17	–	1	1	–	1	–	–	–	–	–	39.328
18	–	–	–	1	–	1	–	–	–	–	14.697
19	1	–	–	1	–	1	–	–	–	–	9.662
20	–	–	–	–	1	–	–	1	–	–	4.355
21	–	1	–	1	–	1	–	–	–	–	1.225
22	1	1	–	1	–	1	–	–	–	–	7.076
23	–	1	–	–	1	–	–	1	–	–	13.200
24	–	–	–	–	–	–	–	–	1	–	9.798
25	1	–	–	–	–	–	–	–	1	–	3.130
26	–	–	–	1	1	–	1	–	–	–	3.810
27	–	1	–	–	–	1	–	1	–	–	11.023
28	1	1	–	–	–	1	1	–	–	–	10.887
29	–	1	–	1	1	1	–	–	–	–	3.130
30	–	–	–	1	–	–	1	1	–	–	4.899
31	1	–	1	–	–	–	–	–	–	1	13.200
32	–	–	–	–	1	–	–	–	–	1	21.773
33	–	1	1	–	–	–	–	–	1	–	1.225
34	1	1	1	–	–	–	–	–	1	–	10.342
35	–	1	1	1	1	1	–	–	–	–	9.662
36	–	–	1	1	–	–	–	–	1	–	0.000
37	1	–	–	–	–	1	–	–	1	–	9.934
38	–	–	1	–	1	–	–	–	1	–	9.254
39	–	1	–	–	–	–	–	1	1	–	1.225
40	1	1	–	–	–	1	–	–	–	1	11.975
41	–	1	–	1	1	–	–	–	–	1	22.998
42	–	–	–	1	–	–	–	1	1	–	4.899
43	1	–	–	1	–	1	–	–	1	–	12.928
44	–	–	–	–	1	1	–	–	–	1	1.089
45	1	–	–	–	1	1	–	–	–	1	11.023
46	1	1	–	1	–	–	–	1	–	1	5.988
47	–	1	–	–	1	–	–	1	–	1	6.668
48	–	–	1	1	–	1	–	–	1	–	9.798
49	1	–	1	1	–	–	–	1	1	–	3.402
50	–	–	1	–	1	1	–	–	1	–	12.520
51	1	–	1	–	1	–	–	1	1	–	1.225
52	1	1	1	1	–	–	–	1	1	–	14.153
53	–	1	1	–	1	–	–	1	1	–	0.136
54	–	–	1	–	–	1	1	–	1	–	14.697

Atom B occupies the sites denoted with a minus sign for easy legibility.

3. The cubic solid-solution alloys (Pt,Ir), (Pt,Re) and (Pt,Ru)

The alloys (Pt,Ir), (Pt,Re) and (Pt,Ru) are currently the subject of intense studies aiming at the optimization of their catalytic

activity and resistance to poisoning in fuel-cell operation. However, literature data for the characterization of these alloys using cell edge versus composition information remains spotty or in need of clarifications. We therefore attempt to apply the above considerations to the calculation of detailed cell data versus com-

position graphs based on the experimental observation that those alloys are ccp solid-solutions.

3.1. (Pt,Ir)

Both Pt and Ir are ccp elements. Cell data versus composition for (Pt,Ir) have been studied by Raub [6] and by Tripathi and Chandrasekharaiah [7] who report data for 13 compositions each. Tripathi reports significant deviations from Vegard's law, with the worst deviations under 50% Ir, but Raub's data points in this range follow rather nicely Vegard's straight line.

3.2. (Pt,Ru)

Gasteiger, Ross and Cairns [8] report numerical cell data values for four ccp alloys in the Pt–Ru system. They do not comment on the behaviour, but their data fits nicely on a straight line. For Ru content greater than 80%, the alloys are hcp. Bock et al. [3] report an ab initio low-resolution plot of the a cell edge versus Ru content, also plotting on a straight line with same slope as the experimental data. Strictly speaking, this straight line cannot be called Vegard's law because pure Ru is hcp. It is nevertheless interesting to note that the extrapolation of the straight line to pure Ru gives a cubic cell volume with precisely twice the volume of the hcp experimental cell, as it should. We nevertheless reinvestigate the (Pt,Ru) system at higher resolution in order to contrast the behaviour of the three alloy systems.

3.3. (Pt,Re)

The alloys of Pt and Re were studied using powder diffraction by Trzebiatowski and Berak [9] who report curves of cell data versus Re content. Their main conclusions are that they form cubic solid-solutions up to about 40% Re without obeying Vegard's law. Rhenium itself is hcp and its alloys with Pt remain hcp down to about 60% Re. Both phases coexist in the region from 40% to 60% Re. We accurately digitized the data points in their Fig. 2. In view of the lasting importance of this work 50 years later, we print their results in Table 4 below, including the hcp data. We transformed their results from kX units and rescaled them to $a_{\text{Pt}} = 3.9231 \text{ \AA}$ reported by Swanson and Tatge [10], which is probably still the most reliable cell edge value for Pt at 25 °C. Grgur, Markovic and Ross [11] as well as Rudman [12] report individual cell data–Re content pairs that more-or-less fit on Trzebiatowski and Berak's curve.

4. Modeling and results

4.1. Modeling parameters

In order to compare meaningfully simulation results, the VASP execution parameters must be preserved from run to run. For all simulations within this study, we used the following parameters.

We performed computations with VASP4.6.4 [13] on both Linux and Windows machines with medium-precision calculations using GGA PAW [14] potentials, electronic convergence

Table 4

Cell data for (Pt,Re) alloys, accurately digitized from Fig. 2 in Trzebiatowski and Berak [9] and rescaled to $a = 3.9231 \text{ \AA}$ for pure platinum at 25 °C (Swanson and Tatge, [10])

Re (%)	Cubic a	Hexagonal a	Hexagonal c
0	3.9231		
2.5	3.9195		
5	3.9172		
7.5	3.9151		
10	3.9127		
20	3.9076		
30	3.9020		
35	3.9012		
40	3.8990		
45	3.8986	2.7668	4.4314
50	3.8982	2.7670	4.4322
55	3.8982	2.7668	4.4317
60		2.7672	4.4272
70		2.7681	4.4181
80		2.7734	4.4193
90		2.7659	4.4355
95		2.7637	4.4465
100		2.7625	4.4596

Re values rescaled to Pt in this way also agree very well with 25 °C values for Re in Swanson and Fuyat [18].

at 10^{-7} eV level and energy cutoff 260 eV. The convergence for forces was 10^{-4} eV/Å. A Methfessel–Paxton [15] smearing scheme was used, with order 1 and width 0.2 eV. Calculations did not include spin polarization. A maximum of 40 SCF cycles were used per single point while 30 single points ensured convergence. Davidson's [16] blocked scheme was used in combination with reciprocal projectors. We used a uniform $2 \times 2 \times 2$ k-mesh with a Monkhorst–Pack scheme [17].

4.2. Calculation of the bond energy difference ε for alloying

Under the rough assumption that the cohesive energy U of an $(A_x B_{1-x})$ alloy is stored in its AA, AB and BB bonds, solid-solutions exist when the energy U_{AB} of the bond linking an atom of type A and an atom of type B is approximately the average of U_{AA} and U_{BB} , which can be written

$$2U_{AB} = U_{AA} + U_{BB} + 2\varepsilon \quad (1)$$

Provided that $|\varepsilon|$ is smaller than kT at alloy formation temperature, the elements will then display miscibility, but without formation of defined compounds where element A surrounds itself with element B and vice-versa. They lead instead to materials known as solid-solution alloys. Combined with the $x^2:2x(1-x):(1-x)^2$ distribution for, respectively AA:AB:BB bonds, Eq. (1) leads after rearrangement to

$$U = N(x^2 U_{AA} + (1-x)^2 U_{BB} + x(1-x)(U_{AA} + U_{BB} + 2\varepsilon))$$

from which,

$$U = N(-2\varepsilon x^2 + (U_{AA} - U_{BB} + 2\varepsilon)x + U_{BB}) \quad \text{follows,} \quad (2)$$

where N is the number of interatomic bonds per supercell. As the coefficient of the quadratic term is $-2N\varepsilon$, it follows

that the alloying energy ε can be read off as $-a/2N$ in the quadratic fit $U = ax^2 + bx + c$ obtained by least-squares regression of the experimental total energy data U versus the alloy composition x .

Derivation of cell data for RePt_{107} is then a matter of requesting cell and structure optimization based on the crystallographic description of Table 1h to VASP and running the computing job. With VASP4.6 running on an AMD Athlon 64 built beginning of 2005 and operated under Windows XP, and a $2 \times 2 \times 2$ k-mesh corresponding to $0.04 \text{ \AA}^{-1}$ reciprocal resolution, the execution time is about 1 week. We felt that a $1 \times 1 \times 1$ k-mesh would be too coarse for a metallic system while a $3 \times 3 \times 3$ k-mesh would lead to computation times that would be inordinately long. In spite of the borderline feasibility today, we decided to go ahead and implement the general method in Section 1 in the hope that, owing to Moore's law, the automated derivation of cell-composition graphs for ccp binary solid-solutions using modest computing equipment will be quite convenient as close as 5 years from now.

Fig. 1. (a) Cell data vs. Ir content x for $(\text{Pt}_{1-x}\text{Ir}_x)$ system. Triangles: Raub (1959); circles: Tripathi and Chandrasekharaiah (1983); plus signs: this work. Although superficially looking like a textbook case of Vegard's law, the calculated data actually displays a slight convexity, probably due to the item below. In order to clearly see the convexity after reduction for journal requirements, readers may have to look down the line, at an angle to the page. (b) Calculated values for the total energy per cell vs. Ir content for $(\text{Pt}_{1-x}\text{Ir}_x)$ alloys. The convexity is quite perceptible and due to the fact that the energy associated with a Pt–Ir bond is slightly higher than the average for a Pt–Pt bond and an Ir–Ir bond.

5. Results

5.1. $\text{Pt}_{1-x}\text{Ir}_x$

Cell data results are shown in Fig. 1a and total energy results in Fig. 1b. The ab initio cell data were corrected for the expected bias originating in approximations common to all DFT packages. The bias is known from the very accurate cell data measurements for pure Pt and Ir [10]. This linear rescaling was by a factor 0.9888 at Pt and 0.9900 at Ir. The Vegard-law fit is: $a(\text{Pt}_{1-x}\text{Ir}_x) = 3.9222 - 0.0714x - 0.0114x^2$ applicable to all values of x from 0 to 1. The “Vegard slope” is then $-0.0714 - 0.0228x$, corresponding to -0.0714 at Pt while it is -0.0942 at Ir. The least-squares fit to the energy data is $U = -30.721x^2 - 266.82x - 653.75$, meaning that alloying corresponds to an energy of +24 meV per AB bond.

5.2. $\text{Pt}_{1-x}\text{Ru}_x$

Cell data results are shown in Fig. 2a and total energy results in Fig. 2b. The Vegard-law fit is: $a(\text{Pt}_{1-x}\text{Ru}_x) =$

Fig. 2. (a) Calculated cell data vs. Ru content x for $(\text{Pt}_{1-x}\text{Ru}_x)$ system. This time, the calculated data actually displays a very slight concavity, seen clearly on full-page plots and extracted accurately by least squares, but probably difficult to see after the required size reduction. (b) Total energy per simulation cell for $\text{Pt}_{1-x}\text{Ru}_x$ alloys. The data displays a slight concavity due to the fact that the energy of a Pt–Ru bond is very slightly lower than the average of a Pt–Pt and a Ru–Ru bond.

Fig. 3. (a) Calculated cell data vs. Re content x for $(\text{Pt}_{1-x}\text{Re}_x)$ system. The calculated data displays considerable spread. Circles are Trzebiatowski and Berak's [11] data points over the ccp region for (Pt,Re) . (b) Total energy per simulation cell for $\text{Pt}_{1-x}\text{Re}_x$ alloys. Contrary to cell data in Fig. 3a, the energy plot displays no big spread and virtually no curvature.

$3.9231 - 0.1489x$ applicable to all values of x from 0 to about 0.8 because it is experimentally known that (Pt,Ru) alloys are in fact hcp in the range $0.8 < x \leq 1$. The least-squares fit to the energy data is $U = +11.536x^2 - 339.04x - 652.08$, meaning that alloying corresponds to an energy of -8.9 meV per AB bond.

5.3. $\text{Pt}_{1-x}\text{Re}_x$

Calculations were performed in the range $0 \leq x < 0.45$ because the (Pt,Re) alloys are known to be hcp in the range $0.6 < x \leq 1$, ccp in the range $0 \leq x < 0.4$ and two-phased for $0.4 < x < 0.6$. The plot of cell edge versus x shown in Fig. 3a displays considerable spread while roughly following the general trend indicated by experimental data. We performed those simulations using different starting points and obtained each time comparable spread with different data points. In view of the poor quality of plot 3a, we leave it to readers to derive their own conclusions. In contrast, the plot of the total energy U does not display any anomaly. The least-squares fit to the energy data is $U = 3.465x^2 - 686.67x - 654.39$ in eV, indicating a very small energy difference of -2.7 meV per AB bond.

6. Discussion

The (Pt,Ir) and (Pt,Ru) results are quite well behaved and in agreement with experimental results. The curvature of the total energy plot is very noticeable for (Pt,Ir) , which also displays a small but significant deviation of cell data with respect to Vegard's law. As far as we know, this small curvature of the cell data is a new observation. In fact, Raub's [6] triangles on Fig. 1a follow remarkably well the calculated data points from this work and could be interpreted as an experimental observation of the curvature. We feel that the two observations of the curvature of the energy and of the cell data versus composition are related and explainable as indicated below.

In a situation where ε would be zero, the alloy would be random, the plot of U versus x would be straight and Vegard's law would be accurately obeyed. The convexity of the plot of U versus x indicates that the energy of two AB bonds is greater than that of an AA bond plus a BB bond. In other words, the elements A and B are at a slight energy disadvantage if they mix than if they stay separate. However, this repulsion is overcome by the thermal energy kT at alloy formation time. Annealing at lower temperatures might cause nanoscale segregation within the alloy, but that would require very long times, and may not happen at room temperature due to the energy barrier for diffusion that is much higher than the small energy to be gained. At any rate, in the range of compositions around 50% Ir, the (Pt,Ir) is at a slight energy disadvantage with respect to an alloy for which ε would be zero because half of its bonds are AB bonds. An alloy with $\varepsilon = 0$ would follow Vegard's law. A slight lengthening of the a cell edge with respect to Vegard's law is then expected around 50% Ir because of the weaker cohesive energy. It is seen here clearly for the first time as a slight convexity in the plot of a versus x .

The opposite situation is seen on a smaller scale with Ru. Contrary to Ir, Ru has a very slight energy advantage to mix with Pt. A slight concavity in the plot of a versus x is then expected and observed here, but it is so slight that it could easily be missed.

The case of (Pt,Re) alloys is inconclusive for three reasons. First the curvature of the plot of U versus x is about three times smaller than for Ru, meaning that the expected deviation from Vegard's law would be barely noticeable. Second, our data extends only in the range $0 \leq x < 0.45$, where the curvature would be more difficult to see than in the full range from 0 to 1. The third and main reason is the large and unexplained spread in ab initio cell data. Additional convergence cycles did not fix this spread. Starting with a different cell edge or nudging atoms with respect to ideal fractional positions produced slightly different converged cell edges, a fact for which we have no explanation because we proceeded in exactly the same way as for Ir and Ru which did not display any such spread.

7. Conclusion

We systematized here a way to model cell edge versus finely stepped composition for ccp solid-solution binary alloys and implemented it as an automated tool in *Materials Toolkit*

(<http://www.tothcanada.com>). We applied this software to the (Pt,Ir), (Pt,Ru) and (Pt,Re) systems that are known to be solid-solution binary alloys. The corresponding jobs were distributed for execution among two Linux clusters and one 8-CPU Windows setup, all with VASP.4.6.4 running on state-of-the-art Intel or AMD CPUs.

Results for (Pt,Ir) and (Pt,Ru) indicate that Vegard's law is followed quite well, but with a previously unnoticed slight convexity or concavity that we relate here to, respectively a small positive or negative alloying energy. The ability to model binary alloys with small composition steps without altering the cell data or the space group symmetry was crucial in order to disclose this kind of small deviation with respect to Vegard's law.

Results for (Pt,Re) are consistent with experimental data, but with a wider spread for which we hope that DFT package developers will find a cure.

The above piece of work required a lot of computing time on many CPUs. In this respect, it may be somewhat ahead of what is easily feasible today, but assuming that Moore's law would hold for another 5 years, all computing times would be divided by a factor 10, making this type of work quite tractable with much more modest equipment.

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