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Thermodynamic stability of Pd–Ru alloy nanoparticles: Combination of density functional theory calculation, supervised learning, and Wang–Landau sampling

Electronic Supplementary Information

Yusuke Nanba,[a] *Michihisa Koyama*[a,b]

[a]Research Initiative for Supra-Materials, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

[b]Open Innovation Institute, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Excess energy of Pd–Ru alloys

The bulk models of a face-centered cubic (fcc) and hexagonal close-packed (hcp) structures consist of 32 atoms as shown in Figures 1 (a) and (b). The Warren–Cowley parameter was used to evaluate the homogeneity of the bulk model. The composition x/N (= c_{Pd}) of 0.09, 0.19, 0.31, 0.41, 0.5, 0.59, 0.69, 0.81, 0.91 was considered, where x and N represent the number of Pd atoms and whole atoms, respectively. Five configurations were considered at c_{Pd} = 0.09 and 0.91, while ten configurations were considered at other compositions. Tables S1 and 2 show the specific values of the excess energies, overall composition, bond fractions, and Warren–Cowley parameter in bulk models.

To investigate the size and composition dependences of the stability of Pd–Ru alloy NPs, the excess energies of solid-solution fcc Pd_xRu_{201-x}, hcp Pd_xRu_{238-x}, fcc Pd_xRu_{55-x}, and hcp Pd_xRu_{63-x} were calculated. The stability of $Pd_{0.5}Ru_{0.5}$ alloy NPs was focused because solid-solution $Pd_{0.5}Ru_{0.5}$ alloy NPs were synthesized.[S1] 40 and 30 configurations were prepared for solid-solution fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ alloy NPs, respectively. The compositions c_{Pd} of 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875 were considered and five configurations were considered except for fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ alloy NPs. The excess energy and information on NP models are summarized in Tables S3–6. Figure S1 shows the excess energies of solid-solution fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ alloy NPs as a function of the Ru composition in the surface layer. The excess energies of fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ were roughly proportional to Ru composition in the surface layer. Then, we considered the subcluster, Pd-rich surface, and Ru-rich surface segregated configurations of fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ alloy NPs as shown in Figure S2. The excess energy and information on NP models are summarized in Tables S7 and 8. Truncated octahedron and truncated hexagonal bipyramid are high-symmetry structure. However, the observed form of NP is not always high symmetry. There are the adatoms and vacancies on the surface of the observed NP. We investigated the variation of excess energy by increasing/decreasing atom. Pd or Ru atom was added/removed, which suggested eight kinds of Pd–Ru alloy NPs as shown in Figure S3. The site of adding/removing atom was randomly selected in fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$. Five configurations were considered for each case. Tables S9-16 show the specific values of the excess energy, overall composition, surface ratio to NP, composition in the surface layer, and the bond fractions in fcc $Pd_{100}Ru_{100}$, fcc $Pd_{101}Ru_{99}$, fcc $Pd_{102}Ru_{100}$, fcc $Pd_{101}Ru_{101}$, hcp $Pd_{118}Ru_{119}$, hcp $Pd_{119}Ru_{118}$, hcp $Pd_{120}Ru_{119}$, and hcp $Pd_{119}Ru_{120}$ alloy NPs.

Prediction of excess energy of Pd–Ru alloy NPs

Multiple regression analysis was used as machine learning (ML) in this study. The descriptors as shown in Table 1 were used. Hold-out validation was used, where 1/4 and 3/4 of the considered configurations were randomly selected as test and training sets, respectively. We estimated the coefficient of determination expressed as

$$R^2 = 1 - \Sigma_i (y_i - f_i)^2 / \Sigma_i (y_i -)^2 \qquad \text{(S1)}$$

where f_i and y_i represent the values of excess energies predicted by ML and calculated by DFT, respectively. is the average of y_i. Repeating the validation five times, the coefficients of determination in each case were estimated for both the test and training sets, respectively. Figure S4 shows four cases comparing the excess energy predicted by ML and that calculated by DFT. Note that the other case is shown in Figure 3

The obtained regression coefficient of Ru deviation in the surface layer was positive. To understand this property, we calculated the surface energies of the fcc (100) and (111) and hcp (0001), (100), and (110) surfaces for Pd and Ru. The slab models of the typical fcc and hcp surfaces were based on the 2 × 2 supercell and seven layers, as shown in Figure S5. The surface energy was used to evaluate the stability of the surface, which is expressed as follows.

$$\gamma = (\varepsilon_{slab} - (N_{bulk}/N_{slab}) \times \varepsilon_{bulk})/2A \qquad \text{(S2)}$$

ε_{bulk} and ε_{slab} are the energies of the bulk and slab models with the number of atoms N_{bulk} and N_{slab}, respectively. A represents the surface area of the slab model. The DFT calculations were conducted using the VASP code with the PBE exchange-correlation functional based on the GGA. PAW was used for the interaction between valence and core electrons. The cutoff energy for the plane wave was 400 eV and the Monkhorst–Pack k-points grids of the slab models with the fcc (100), (111) and hcp (0001), (100), (110) surfaces are 1 × 9 × 9, 1 × 6 × 6, 1 × 13 × 13, 1 × 13 × 8, and 1 × 8 × 7, respectively. The convergence of the self-consistent field and the geometry optimization were 1.0×10^{-5} and 1.0×10^{-4} eV, respectively. The estimated surface energies are shown in Table S17. The surface energy of Ru was higher than that of Pd for the identified surface. Thus, the composition in the surface layer affects the excess energy.

The regression equation was applied to the larger PdRu alloy NPs. The surface ratio to NP was one of the descriptors in the obtained regression equation and the corresponding coefficient was negative. With increasing number of atoms, the surface ratio to NP becomes lower. We considered solid-solution $Pd_{203}Ru_{202}$, solid-solution $Pd_{356}Ru_{355}$, and subcluster segregated $Pd_{356}Ru_{355}$ alloy NPs as shown in Figure S6. Table S18 shows the specific values of the excess energy, overall composition, surface ratio to NP, composition in the surface layer, and the bond fractions in these NP models. The calculated excess energies of solid-solution $Pd_{203}Ru_{202}$, solid-solution $Pd_{356}Ru_{355}$, and subcluster segregated $Pd_{356}Ru_{355}$ were 0.104, 0.105, and 0.026 eV/atom, respectively. The regression equation was applied to large Pd–Ru alloy NPs. The excess energies of solid-solution $Pd_{203}Ru_{202}$, solid-solution $Pd_{356}Ru_{355}$, and subcluster segregated $Pd_{356}Ru_{355}$ estimated by regression equation were 0.091, 0.090, and 0.034 eV/atom, respectively. The average errors of excess energy between ML and DFT were 0.012

eV/ atom for larger solid-solution and sub-cluster segregated Pd–Ru alloy NPs. Even if the number of samples is only three, the coefficient of determination is 0.847. The regression equation could explain the excess energy of large Pd–Ru alloy NPs.

Monte Carlo simulation of Pd–Ru alloy NPs

Wang–Landau sampling,[S1] which is one of multicanonical Monte Carlo (MC) algorithms, was used. In the well-known Metropolis method, the transition probability from energy level E_A to energy level E_B was expressed as $\exp(-(E_B - E_A)/k_BT)$ (k_B: Boltzmann constant, T: Temperature). Although this method was extensively used in MC simulation, overcoming energy barrier ΔE becomes exponentially more difficult. Large energy barrier results in the sampling concentrated at a local stable point. Instead of $\exp(-(E_B - E_A)/k_BT)$, transition probability in multicanonical MC simulation was based on reciprocal of configurational density of states $g(E)$ expressed as

$$p\,(E_A \rightarrow E_B) = \min(1.0,\, g(E_A)/g(E_B))\ . \qquad \text{(S3)}$$

The problem of multicanonical MC simulation is that the configurational density of states should be known initially. Then, Wang and Landau proposed new sampling. The configurational density of states was asymptotically obtained by repeating calculation until it convergences. The obtained configurational density of states results in partition function, Helmholtz free energy, internal energy, and specific heat expressed as

$$Z = \Sigma_E\, g(E)\exp(-E/k_BT), \qquad \text{(S4)}$$

$$F = -k_BT\ln(Z), \qquad \text{(S5)}$$

$$U = (\Sigma_E\, Eg(E)\exp(-E/k_BT))\ /Z, \qquad \text{(S6)}$$

$$C = (\langle E^2\rangle - \langle E\rangle^2)/\ k_BT^2. \qquad \text{(S7)}$$

In this study, the flatness criteria of the histogram were set to be 0.8. The initial modification factor f_0 was assumed to be logarithm e. When the histogram was flat, the modification factor was reduced from f to $f^{1/2}$. When the modification factor f was smaller than $\exp(10^{-8})$, the MC simulation finished.

To estimate the structural parameters α such as the bond fractions in the whole NP and surface layer and composition of atoms in each CN, two-dimensional density of states $g(E, \sigma)$ was considered. It is difficult for the NP model to satisfy the flatness criteria of the two-dimensional histogram. Less stringent criterion[S2] was used. When the number of entries larger than or equal to 2000 remains unchanged for $N \times 10^6$ trials. Because the flatness criteria of the two-dimensional histogram were less stringent than that of the one-dimensional histogram, the transition temperature may deviate. This point must be noted. The expected values of the structural parameters were obtained from the two-dimensional configurational density of states. The stable configurations were depicted based on these expected values.

For the bulk model, we considered the models consisting of 256 atoms in the fcc structure (4 × 4 × 4 supercell) and 288 atoms in the hcp structure (6 × 6 × 4 supercell). Figures S7 and 8 show the configurational density of states and the temperature dependence of the configurational specific heat, excess free energy, and excess internal energy in fcc Pd_xRu_{256-x} and hcp Pd_xRu_{288-x}. The expected values of structural parameters of fcc Pd_xRu_{256-x} and hcp Pd_xRu_{288-x}. are summarized in Figures S9 and 10. We considered fcc Pd_xRu_{201-x} and hcp Pd_xRu_{238-x} as the NP models. Figures S11 and 12 show the obtained configurational density of states and the temperature dependence of the configurational specific heat, excess free energy, and excess internal energy of fcc Pd_xRu_{201-x} and hcp Pd_xRu_{238-x} alloy NPs. The expected values of structural parameters are summarized in Figures S13 and S14. Figures S15 and 16 show stable configurations. Note that the configuration is one of the possible configurations where the structural parameters are close to the expected values. To investigate the size dependence, fcc Pd_xRu_{405-x} and fcc Pd_xRu_{711-x} alloy NP models were considered. The obtained configurational density of states and the temperature dependence of the configurational specific heat, excess free energy, and excess internal energy were shown in Figures S17 and 18. Figures S19 and 20 show the expected values of structural parameters. The stable configurations of fcc Pd_xRu_{405-x} and fcc Pd_xRu_{711-x} alloy NPs are depicted based on the expected values of structural parameters as shown in Figures S21 and 22.

(S1) F. Wang and D. P. Landau, *Phys. Rev. Lett.* 2001, **86**, 2050–2053.
(S2) S.-H. Tsai, F. Wang and D. P. Landau, *Phys. Rev. E* 2007, **75**, 061108.

Table S1. Excess energy (ε_{excess}), overall Ru composition (c_{Ru}), bond fractions, and Warren–Cowley parameter (α) in fcc Pd_xRu_{32-x} alloys in bulk state.

ε_{excess} (eV/atom)	c_{Ru}	Bond fractions		α
		Pd–Pd	Ru–Ru	
0.1309	0.9067	0.0104	0.8229	0.0192
0.1330	0.9067	0.0104	0.8229	0.0192
0.1353	0.9067	0.0052	0.8177	−0.0421
0.1375	0.9067	0.0052	0.8177	−0.0421
0.1254	0.9067	0.0156	0.8281	0.0805
0.1399	0.8125	0.0365	0.6615	0.0085
0.1421	0.8125	0.0365	0.6615	0.0085
0.1450	0.8125	0.0365	0.6615	0.0085
0.1543	0.8125	0.0365	0.6615	0.0085
0.1543	0.8125	0.0365	0.6615	0.0085
0.1486	0.8125	0.0365	0.6615	0.0085
0.1387	0.8125	0.0313	0.6563	−0.0256
0.1523	0.8125	0.0313	0.6563	−0.0256
0.1385	0.8125	0.0417	0.6667	0.0427
0.1399	0.8125	0.0417	0.6667	0.0427
0.1505	0.6875	0.0990	0.4740	0.0061
0.1532	0.6875	0.0990	0.4740	0.0061
0.1404	0.6875	0.0990	0.4740	0.0061
0.1583	0.6875	0.0990	0.4740	0.0061
0.1424	0.6875	0.0990	0.4740	0.0061
0.1436	0.6875	0.0990	0.4740	0.0061
0.1448	0.6875	0.0938	0.4687	−0.0182
0.1525	0.6875	0.0938	0.4687	−0.0182
0.1443	0.6875	0.1042	0.4792	0.0303
0.1513	0.6875	0.1042	0.4792	0.0303
0.1466	0.5937	0.1667	0.3542	0.0067
0.1574	0.5937	0.1667	0.3542	0.0067
0.1415	0.5937	0.1667	0.3542	0.0067
0.1507	0.5937	0.1667	0.3542	0.0067
0.1668	0.5937	0.1615	0.3490	−0.0148
0.1600	0.5937	0.1615	0.3490	−0.0148
0.1441	0.5937	0.1563	0.3437	−0.0364
0.1447	0.5937	0.1719	0.3594	−0.0364
0.1354	0.5937	0.1719	0.3594	0.0283
0.1355	0.5937	0.1719	0.3594	0.0283
0.1391	0.5000	0.2500	0.2500	0.000
0.1276	0.5000	0.2500	0.2500	0.000
0.1374	0.5000	0.2500	0.2500	0.000
0.1403	0.5000	0.2500	0.2500	0.000
0.1384	0.5000	0.2448	0.2448	−0.0208
0.1496	0.5000	0.2448	0.2448	−0.0208
0.1536	0.5000	0.2448	0.2448	−0.0208
0.1344	0.5000	0.2552	0.2552	0.0208
0.1385	0.5000	0.2552	0.2552	0.0208
0.1433	0.5000	0.2552	0.2552	0.0208
0.1217	0.4063	0.3542	0.1667	0.0067
0.1369	0.4063	0.3542	0.1667	0.0067
0.1198	0.4063	0.3542	0.1667	0.0067
0.1284	0.4063	0.3542	0.1667	0.0067
0.1500	0.4063	0.3490	0.1614	−0.0148
0.1301	0.4063	0.3490	0.1614	−0.0148
0.1352	0.4063	0.3438	0.1562	−0.0364
0.1236	0.4063	0.3594	0.1719	−0.0364
0.1086	0.4063	0.3594	0.1719	0.0283
0.1138	0.4063	0.3594	0.1719	0.0283
0.1091	0.3125	0.4740	0.0990	0.0061
0.1084	0.3125	0.4740	0.0990	0.0061
0.1044	0.3125	0.4740	0.0990	0.0061
0.1165	0.3125	0.4740	0.0990	0.0061
0.1040	0.3125	0.4740	0.0990	0.0061
0.1066	0.3125	0.4740	0.0990	0.0061
0.1084	0.3125	0.4688	0.0937	−0.0182
0.1070	0.3125	0.4688	0.0937	−0.0182
0.0966	0.3125	0.4792	0.1042	0.0303
0.1084	0.3125	0.4792	0.1042	0.0303
0.0714	0.1875	0.6615	0.0365	0.0085
0.0725	0.1875	0.6615	0.0365	0.0085
0.0721	0.1875	0.6615	0.0365	0.0085
0.0862	0.1875	0.6615	0.0365	0.0085
0.0862	0.1875	0.6615	0.0365	0.0085
0.0781	0.1875	0.6615	0.0365	0.0085
0.0723	0.1875	0.6563	0.0312	−0.0256
0.0812	0.1875	0.6563	0.0312	−0.0256
0.0627	0.1875	0.6667	0.0417	0.0427
0.0569	0.1875	0.6667	0.0417	0.0427
0.0365	0.0938	0.8229	0.0104	0.0192
0.0425	0.0938	0.8229	0.0104	0.0192

Table S2. Excess energy (ε_{excess}), overall Ru composition (c_{Ru}), bond fractions, and Warren–Cowley parameter (α) in hcp Pd_xRu_{32-x} alloys in bulk state.

ε_{excess} (eV/atom)	c_{Ru}	Bond fractions		α
		Pd–Pd	Ru–Ru	
0.0596	0.9067	0.0104	0.8229	0.0192
0.0568	0.9067	0.0104	0.8229	0.0192
0.0568	0.9067	0.0052	0.8177	−0.0421
0.0605	0.9067	0.0000	0.8125	−0.1034
0.0479	0.9067	0.0156	0.8281	0.0805
0.0998	0.8125	0.0365	0.6615	0.0085
0.1023	0.8125	0.0365	0.6615	0.0085
0.0977	0.8125	0.0365	0.6615	0.0085
0.0991	0.8125	0.0365	0.6615	0.0085
0.0995	0.8125	0.0365	0.6615	0.0085
0.1030	0.8125	0.0365	0.6615	0.0085
0.1039	0.8125	0.0313	0.6562	−0.0256
0.1030	0.8125	0.0313	0.6562	−0.0256
0.0989	0.8125	0.0417	0.6667	0.0427
0.0952	0.8125	0.0417	0.6667	0.0427
0.1455	0.6875	0.0990	0.4740	0.0061
0.1400	0.6875	0.0990	0.4740	0.0061
0.1221	0.6875	0.0990	0.4740	0.0061
0.1495	0.6875	0.0990	0.4740	0.0061
0.1403	0.6875	0.0990	0.4740	0.0061
0.1388	0.6875	0.0990	0.4740	0.0061
0.1404	0.6875	0.0938	0.4687	−0.0182
0.1272	0.6875	0.0938	0.4687	−0.0182
0.1347	0.6875	0.1042	0.4792	0.0303
0.1323	0.6875	0.1042	0.4792	0.0303
0.1327	0.5937	0.1667	0.3542	0.0067
0.1528	0.5937	0.1667	0.3542	0.0067
0.1526	0.5937	0.1667	0.3542	0.0067
0.1536	0.5937	0.1615	0.3490	−0.0105
0.1591	0.5937	0.1667	0.3542	0.0067
0.1435	0.5937	0.1667	0.3542	0.0067
0.1551	0.5937	0.1615	0.3490	−0.0105
0.1601	0.5937	0.1615	0.3490	−0.0105
0.1604	0.5937	0.1615	0.3490	−0.0105
0.1479	0.5937	0.1719	0.3594	0.0283
0.1442	0.5000	0.2500	0.2500	0.0000
0.1654	0.5000	0.2500	0.2500	0.0000
0.1595	0.5000	0.2500	0.2500	0.0000
0.1659	0.5000	0.2500	0.2500	0.0000
0.1565	0.5000	0.2552	0.2552	−0.0208
0.1705	0.5000	0.2448	0.2448	0.0208
0.1751	0.5000	0.2396	0.2396	−0.0417
0.1463	0.5000	0.2604	0.2604	0.0417
0.1708	0.5000	0.2500	0.2500	0.0000
0.1641	0.5000	0.2448	0.2448	−0.0208
0.1484	0.4063	0.3542	0.1667	0.0067
0.1517	0.4063	0.3542	0.1667	0.0067
0.1607	0.4063	0.3542	0.1667	0.0067
0.1624	0.4063	0.3490	0.1615	−0.0105
0.1599	0.4063	0.3542	0.1667	0.0067
0.1409	0.4063	0.3542	0.1667	0.0067
0.1644	0.4063	0.3490	0.1615	−0.0105
0.1597	0.4063	0.3490	0.1615	−0.0105
0.1675	0.4063	0.3490	0.1615	−0.0105
0.1451	0.4063	0.3594	0.1719	0.0283
0.1417	0.3125	0.4740	0.0990	0.0061
0.1515	0.3125	0.4740	0.0990	0.0061
0.1251	0.3125	0.4740	0.0990	0.0061
0.1463	0.3125	0.4740	0.0990	0.0061
0.1458	0.3125	0.4740	0.0990	0.0061
0.1440	0.3125	0.4740	0.0990	0.0061
0.1464	0.3125	0.4688	0.0938	−0.0182
0.1406	0.3125	0.4688	0.0938	−0.0182
0.1479	0.3125	0.4792	0.1042	0.0303
0.1329	0.3125	0.4792	0.1042	0.0303
0.1146	0.1875	0.6615	0.0365	0.0085
0.1096	0.1875	0.6615	0.0365	0.0085
0.1096	0.1875	0.6615	0.0365	0.0085
0.1061	0.1875	0.6615	0.0365	0.0085
0.1115	0.1875	0.6615	0.0365	0.0085
0.1118	0.1875	0.6615	0.0365	0.0085
0.1139	0.1875	0.6563	0.0312	−0.0256
0.1147	0.1875	0.6563	0.0312	−0.0256
0.1060	0.1875	0.6667	0.0417	0.0427
0.1032	0.1875	0.6667	0.0417	0.0427
0.0767	0.0938	0.8229	0.0104	0.0192
0.0757	0.0938	0.8229	0.0104	0.0192
0.0738	0.0938	0.8177	0.0052	−0.0421
0.0807	0.0938	0.8125	0.0000	−0.1034
0.0671	0.0938	0.8281	0.0156	0.0805

Table S3. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions, and Warren–Cowley parameter (α) in fcc Pd_xRu_{201-x} alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions		α
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru	
0.0241	0.8706	0.8770	0.8333	0.9444	0.8548	0.607	0.0190	0.7563	0.0175
0.0262	0.8706	0.8607	0.8750	0.8611	0.8548	0.607	0.0148	0.7595	−0.0157
0.0168	0.8706	0.8525	0.9167	0.7500	0.8871	0.607	0.0095	0.7637	−0.0598
0.0573	0.8706	0.9016	0.8750	1.0000	0.8548	0.607	0.0179	0.7373	−0.0018
0.0123	0.8706	0.8443	0.9167	0.7778	0.8548	0.607	0.0190	0.7764	0.0312
0.0465	0.7463	0.7295	0.8333	0.6389	0.7419	0.607	0.0591	0.5601	−0.0227
0.0681	0.7463	0.7869	0.7083	0.7778	0.8226	0.607	0.0749	0.5506	0.0429
0.0828	0.7463	0.7869	0.7500	0.8611	0.7581	0.607	0.0802	0.5475	0.0633
0.0906	0.7463	0.7869	0.8333	0.7778	0.7742	0.607	0.0622	0.5285	−0.0275
0.0375	0.7463	0.7213	0.7917	0.7222	0.6935	0.607	0.0781	0.5791	0.0793
0.0693	0.6219	0.6311	0.7083	0.5000	0.6774	0.607	0.1445	0.3861	0.0048
0.0594	0.6219	0.5984	0.6667	0.5278	0.6129	0.607	0.1350	0.3903	−0.0249
0.0804	0.6219	0.6475	0.7083	0.6667	0.6129	0.607	0.1561	0.3808	0.0396
0.0871	0.6219	0.5984	0.7917	0.5833	0.5323	0.607	0.1203	0.3629	−0.0974
0.0814	0.6219	0.6803	0.6667	0.6944	0.6744	0.607	0.1878	0.3998	0.1583
0.0570	0.4975	0.5082	0.5833	0.4722	0.5000	0.607	0.3049	0.2929	0.2002
0.0816	0.4975	0.5410	0.4583	0.6667	0.5000	0.607	0.3112	0.2774	0.2001
0.0446	0.4975	0.4836	0.5000	0.5000	0.4677	0.607	0.3006	0.3017	0.1998
0.0637	0.4975	0.4836	0.5000	0.5278	0.4516	0.607	0.2764	0.2753	0.0998
0.0994	0.4975	0.5246	0.6667	0.5556	0.4516	0.607	0.2848	0.2532	0.0998
0.0729	0.4975	0.5164	0.5000	0.5000	0.5323	0.607	0.2795	0.2669	0.0997
0.0641	0.4975	0.4754	0.5000	0.5556	0.4193	0.607	0.2753	0.2743	0.0956
0.0524	0.4975	0.4672	0.5417	0.6389	0.3611	0.607	0.2595	0.2753	0.0499
0.0757	0.4975	0.5000	0.5000	0.5278	0.4722	0.607	0.2648	0.2605	0.0499
0.0842	0.4975	0.5164	0.4583	0.4722	0.5278	0.607	0.2658	0.2532	0.0453
0.0736	0.4975	0.5082	0.3333	0.5278	0.4722	0.607	0.2542	0.2574	0.0152
0.0623	0.4975	0.4672	0.5000	0.5556	0.4444	0.607	0.2489	0.2627	0.0047
0.0802	0.4975	0.5000	0.5000	0.5000	0.5000	0.607	0.2532	0.2468	0.0013
0.0968	0.4975	0.5164	0.5417	0.5278	0.4722	0.607	0.2553	0.2395	0.0002
0.1059	0.4975	0.5410	0.4167	0.4167	0.5833	0.607	0.2574	0.2331	0.0002
0.1058	0.4975	0.5410	0.4583	0.4167	0.5833	0.607	0.2584	0.2300	0.0002
0.1063	0.4975	0.5410	0.6667	0.5556	0.4444	0.607	0.2595	0.2268	0.0001
0.1240	0.4975	0.5656	0.4583	0.4167	0.5833	0.607	0.2605	0.2236	0.0001
0.1200	0.4975	0.5492	0.6667	0.5556	0.4444	0.607	0.2605	0.2236	0.0001
0.1230	0.4975	0.5328	0.7500	0.5000	0.5000	0.607	0.2616	0.2205	0.0001
0.1344	0.4975	0.5820	0.5000	0.4444	0.5556	0.607	0.2627	0.2173	0.0001
0.0967	0.4975	0.5328	0.5833	0.6111	0.3889	0.607	0.2553	0.2363	−0.0029
0.1086	0.4975	0.5328	0.5833	0.6111	0.3889	0.607	0.2553	0.2352	−0.0040
0.0819	0.4975	0.5082	0.3750	0.4444	0.5556	0.607	0.2511	0.2468	−0.0050
0.0590	0.4975	0.4508	0.5833	0.6389	0.3611	0.607	0.2458	0.2627	−0.0050
0.0564	0.4975	0.4754	0.3750	0.5000	0.5000	0.607	0.2468	0.2595	−0.0050
0.0641	0.4975	0.4918	0.4583	0.5833	0.4167	0.607	0.2479	0.2563	−0.0050
0.0632	0.4975	0.4672	0.4583	0.5556	0.4444	0.607	0.2468	0.2595	−0.0050
0.1009	0.4975	0.5000	0.5000	0.3611	0.6389	0.607	0.2542	0.2373	−0.0050
0.0463	0.4975	0.4508	0.3750	0.5556	0.4444	0.607	0.2437	0.2690	−0.0050
0.0835	0.4975	0.5000	0.5000	0.4722	0.5278	0.607	0.2521	0.2437	−0.0050
0.1211	0.4975	0.5410	0.5417	0.3889	0.6111	0.607	0.2574	0.2226	−0.0101
0.0649	0.4975	0.4754	0.4583	0.5556	0.4444	0.607	0.2437	0.2542	−0.0200
0.0716	0.4975	0.4836	0.3750	0.5278	0.4722	0.607	0.2363	0.2468	−0.0500
0.1125	0.4975	0.5164	0.5833	0.5556	0.4444	0.607	0.2300	0.2141	−0.1000
0.0800	0.4975	0.4754	0.6667	0.7222	0.2778	0.607	0.2247	0.2321	−0.1001
0.1009	0.4975	0.4672	0.3750	0.4167	0.5833	0.607	0.1994	0.2099	−0.2000
0.1002	0.4975	0.4918	0.2083	0.3889	0.6111	0.607	0.1994	0.2099	−0.2000
0.0931	0.4975	0.4508	0.4167	0.6944	0.3056	0.607	0.1709	0.2036	−0.2998
0.0681	0.4975	0.4180	0.4583	0.5556	0.4444	0.607	0.1572	0.2131	−0.3407
0.0730	0.3781	0.3689	0.2917	0.5000	0.3226	0.607	0.3861	0.1445	0.0000
0.0927	0.3781	0.4016	0.3333	0.4722	0.3871	0.607	0.3903	0.1350	−0.0001
0.0533	0.3781	0.3525	0.2917	0.3333	0.3871	0.607	0.3808	0.1561	0.0000
0.0971	0.3781	0.4016	0.2083	0.4167	0.4677	0.607	0.3629	0.1203	−0.1001
0.0289	0.3781	0.3197	0.3333	0.3056	0.3226	0.607	0.3998	0.1878	0.1000
0.0663	0.2537	0.2705	0.1667	0.3611	0.2581	0.607	0.5601	0.0591	0.0002
0.0436	0.2537	0.2131	0.2917	0.2222	0.1774	0.607	0.5506	0.0749	0.0000
0.0317	0.2537	0.2131	0.2500	0.1389	0.2419	0.607	0.5475	0.0802	−0.0002
0.0439	0.2537	0.2131	0.1667	0.2222	0.2258	0.607	0.5285	0.0622	−0.1001
0.0537	0.2537	0.2787	0.2083	0.2778	0.3065	0.607	0.5791	0.0781	0.0999
0.0288	0.1294	0.1230	0.1667	0.0556	0.1452	0.607	0.7563	0.0190	0.0002
0.0371	0.1294	0.1393	0.1250	0.1389	0.1452	0.607	0.7595	0.0148	−0.0002
0.0498	0.1294	0.1475	0.0833	0.2500	0.1129	0.607	0.7637	0.0095	0.0005
0.0199	0.1294	0.0984	0.1250	0.0000	0.1452	0.607	0.7373	0.0179	−0.1003
0.0419	0.1294	0.1557	0.0833	0.2222	0.1452	0.607	0.7764	0.0190	0.0998

Table S4. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions, and Warren–Cowley parameter (α) in hcp Pd_xRu_{238-x} alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions		α
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru	
0.0499	0.8782	0.8815	0.7917	0.9524	0.8696	0.567	0.0151	0.7680	0.0005
0.00932	0.8782	0.8370	0.7500	0.9048	0.8261	0.567	0.0133	0.7964	0.0013
0.0312	0.8782	0.8741	0.8750	0.7619	0.9420	0.567	0.0142	0.7804	−0.0002
0.0717	0.8782	0.8963	0.9583	0.9286	0.8551	0.567	0.0044	0.7440	−0.0999
0.0489	0.8782	0.8889	0.9583	0.8810	0.8696	0.567	0.0267	0.7724	0.1001
0.1088	0.7521	0.8000	0.8333	0.7619	0.8116	0.567	0.0649	0.5413	0.0000
0.0638	0.7521	0.7259	0.6667	0.7381	0.7391	0.567	0.0596	0.5796	0.0003
0.0468	0.7521	0.7037	0.7500	0.7143	0.6812	0.567	0.0587	0.5876	0.0015
0.0945	0.7521	0.7481	0.7083	0.7381	0.7681	0.567	0.0427	0.5502	−0.0992
0.0630	0.7521	0.7556	0.7083	0.7143	0.7971	0.567	0.0800	0.5867	0.1016
0.0902	0.6260	0.5926	0.7083	0.5476	0.5797	0.567	0.1369	0.4027	−0.0017
0.1224	0.6260	0.6741	0.6250	0.6190	0.7246	0.567	0.1431	0.3787	0.0007
0.1046	0.6260	0.6296	0.6250	0.5952	0.6522	0.567	0.1404	0.3902	0.0007
0.0863	0.6260	0.5926	0.5000	0.5476	0.6522	0.567	0.1129	0.3902	−0.0983
0.1145	0.6260	0.6593	0.5417	0.7619	0.6377	0.567	0.1671	0.4000	0.0986
0.0724	0.5000	0.4963	0.6250	0.4524	0.4783	0.567	0.3013	0.2978	0.2010
0.1458	0.5000	0.5852	0.7083	0.5952	0.5362	0.567	0.3173	0.2604	0.2010
0.1312	0.5000	0.5556	0.4583	0.5952	0.5652	0.567	0.2827	0.2551	0.1003
0.0840	0.5000	0.4889	0.4167	0.5714	0.4638	0.567	0.2720	0.2764	0.0929
0.0891	0.5000	0.4815	0.4583	0.5238	0.4638	0.567	0.2613	0.2676	0.0519
0.1232	0.5000	0.5185	0.5833	0.5238	0.4928	0.567	0.2596	0.2418	0.0201
0.7712	0.5000	0.4593	0.3750	0.6429	0.3768	0.567	0.2471	0.2693	0.0109
0.1938	0.5000	0.6148	0.6667	0.5714	0.6232	0.567	0.2684	0.2018	0.0067
0.0381	0.5000	0.3926	0.5000	0.4048	0.3478	0.567	0.2364	0.2933	0.0028
0.0577	0.5000	0.4296	0.4583	0.5714	0.3333	0.567	0.2409	0.2800	0.0028
0.0052	0.5000	0.3481	0.3750	0.3333	0.3478	0.567	0.2276	0.3191	0.0020
0.1329	0.5000	0.5333	0.7500	0.4524	0.5072	0.567	0.2560	0.2329	0.0009
0.1037	0.5000	0.4889	0.6250	0.4762	0.4493	0.567	0.2507	0.2480	0.000
0.0760	0.5000	0.4593	0.3750	0.5238	0.4493	0.567	0.2436	0.2684	−0.0009
0.1826	0.5000	0.6000	0.5417	0.5000	0.6812	0.567	0.2613	0.2142	−0.0017
0.1005	0.5000	0.4815	0.4167	0.5476	0.4638	0.567	0.2471	0.2569	−0.0018
0.1016	0.5000	0.4741	0.6667	0.4286	0.4348	0.567	0.2489	0.2507	−0.0027
0.0986	0.5000	0.4741	0.7083	0.4524	0.4058	0.567	0.2480	0.2516	−0.0045
0.0906	0.5000	0.4815	0.5833	0.3810	0.5072	0.567	0.2471	0.2542	−0.0045
0.1073	0.5000	0.4963	0.5417	0.4762	0.4928	0.567	0.2489	0.2480	−0.0053
0.0690	0.5000	0.4593	0.4583	0.3810	0.5072	0.567	0.2418	0.2676	−0.0073
0.1489	0.5000	0.5333	0.7083	0.5476	0.4638	0.567	0.2542	0.2240	−0.0129
0.1340	0.5000	0.5259	0.5833	0.5476	0.4928	0.567	0.2507	0.2302	−0.0174
0.1097	0.5000	0.5037	0.3750	0.4762	0.5652	0.567	0.2364	0.2436	−0.0474
0.1180	0.5000	0.4963	0.4167	0.4524	0.5507	0.567	0.2240	0.2347	−0.0943
0.1033	0.5000	0.4519	0.5833	0.4524	0.4058	0.567	0.2213	0.2373	−0.1003
0.1261	0.5000	0.4667	0.4167	0.6190	0.3913	0.567	0.1973	0.2124	−0.1986
0.1026	0.5000	0.4370	0.3750	0.3810	0.4928	0.567	0.1911	0.2311	−0.2037
0.0872	0.5000	0.4148	0.4167	0.2381	0.5217	0.567	0.1653	0.2231	−0.2981
0.1007	0.5000	0.4074	0.3333	0.3571	0.4638	0.567	0.1573	0.2160	−0.3314
0.0993	0.3739	0.3778	0.2917	0.4286	0.3768	0.567	0.3920	0.1396	−0.0002
0.0804	0.3739	0.3481	0.3750	0.3333	0.3478	0.567	0.3884	0.1493	0.0025
0.1402	0.3739	0.4370	0.3333	0.4048	0.4928	0.567	0.3991	0.1209	−0.0042
0.1164	0.3739	0.3630	0.3750	0.3333	0.3768	0.567	0.3671	0.1182	−0.1020
0.1261	0.3739	0.4148	0.4583	0.5714	0.3043	0.567	0.4258	0.1413	0.0987
0.0962	0.2479	0.2667	0.3333	0.2143	0.2754	0.567	0.5707	0.0542	0.0022
0.0698	0.2479	0.2370	0.1667	0.3095	0.2174	0.567	0.5618	0.0667	−0.0025
0.0735	0.2479	0.2148	0.2917	0.3095	0.1304	0.567	0.5618	0.0667	−0.0025
0.0828	0.2479	0.2444	0.2083	0.1429	0.3188	0.567	0.5413	0.0507	−0.1041
0.0860	0.2479	0.2519	0.3750	0.3095	0.1739	0.567	0.5902	0.0711	0.1007
0.0493	0.1218	0.1259	0.0833	0.0952	0.1594	0.567	0.7707	0.0169	0.0059
0.0592	0.1218	0.1481	0.0417	0.0714	0.2319	0.567	0.7733	0.0124	0.0016
0.0355	0.1218	0.0889	0.1250	0.0476	0.1014	0.567	0.7636	0.0249	0.0014
0.0510	0.1218	0.1259	0.0417	0.0476	0.2029	0.567	0.7556	0.0098	−0.1032
0.0520	0.1218	0.1259	0.0833	0.2143	0.0870	0.567	0.7840	0.0222	0.0973

Table S5. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions, and Warren–Cowley parameter (α) in fcc Pd_xRu_{55-x} alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions		α
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru	
0.0272	0.8727	0.8571	0.7500	0.8750	1.0000	0.764	0.0139	0.7917	−0.0026
0.1143	0.8727	0.9048	0.9167	0.9167	0.8333	0.764	0.0185	0.7269	−0.0003
0.0246	0.8727	0.8333	0.9167	0.7500	1.0000	0.764	0.0139	0.7963	0.0004
0.0497	0.8727	0.8810	0.8333	0.9167	0.8333	0.764	0.0278	0.7685	0.0997
0.0574	0.8727	0.8810	0.6667	0.9583	1.0000	0.764	0.0046	0.7685	−0.1009
0.0715	0.7455	0.7381	0.7500	0.7917	0.5000	0.764	0.0648	0.5556	0.0000
0.1322	0.7455	0.7857	0.7500	0.7917	0.8333	0.764	0.0694	0.5231	−0.0004
0.0357	0.7455	0.7143	0.6667	0.7500	0.6667	0.764	0.0602	0.5880	0.0005
0.0416	0.7455	0.7381	0.5000	0.8750	0.6667	0.764	0.0787	0.6019	0.1014
0.0782	0.7455	0.7381	0.8333	0.7083	0.6667	0.764	0.0463	0.5324	−0.0998
0.0351	0.6182	0.5952	0.3333	0.6667	0.8333	0.764	0.1343	0.4306	−0.0004
0.1647	0.6182	0.6667	0.6667	0.7500	0.3333	0.764	0.1574	0.3333	0.0003
0.0126	0.6182	0.5714	0.5833	0.4583	1.0000	0.764	0.1343	0.4306	−0.0004
0.0634	0.6182	0.6190	0.6667	0.6250	0.5000	0.764	0.1713	0.3981	0.0992
0.0790	0.6182	0.6190	0.7500	0.5833	0.5000	0.764	0.1250	0.3426	−0.1008
0.0838	0.4909	0.5000	0.5000	0.4167	0.8333	0.764	0.2593	0.2407	0.0000
0.0233	0.4909	0.4524	0.4167	0.3750	0.8333	0.764	0.2454	0.2824	0.0011
0.0885	0.4909	0.5238	0.3333	0.5000	1.0000	0.764	0.2593	0.2407	0.0000
0.0758	0.4909	0.5000	0.4167	0.6250	0.1667	0.764	0.2870	0.2593	0.1008
0.1029	0.4909	0.5000	0.5000	0.5000	0.5000	0.764	0.2361	0.2083	−0.1011
0.0377	0.3818	0.3810	0.2500	0.3750	0.6667	0.764	0.3750	0.1620	0.0004
0.1007	0.3818	0.4048	0.4167	0.5000	0.0000	0.764	0.3935	0.1204	0.0000
0.0417	0.3818	0.3571	0.4167	0.2917	0.5000	0.764	0.3750	0.1620	0.0004
0.0126	0.3818	0.3810	0.1667	0.3750	0.8333	0.764	0.3935	0.1944	0.1000
0.0941	0.3818	0.3810	0.5000	0.2917	0.5000	0.764	0.3611	0.1157	−0.1002
0.0411	0.2545	0.2619	0.2500	0.2083	0.5000	0.764	0.5556	0.0648	−0.0004
0.0860	0.2545	0.2857	0.3333	0.2500	0.3333	0.764	0.5694	0.0410	0.0000
0.0209	0.2545	0.2143	0.2500	0.2083	0.1667	0.764	0.5417	0.0880	−0.0009
0.0982	0.2545	0.2619	0.5833	0.1250	0.1667	0.764	0.5926	0.0556	0.1007
0.0571	0.2545	0.2619	0.1667	0.3333	0.1667	0.764	0.5370	0.0463	−0.0980
0.0183	0.1273	0.1190	0.1667	0.0833	0.1667	0.764	0.7593	0.0185	−0.0030
0.0347	0.1273	0.1429	0.0000	0.2500	0.0000	0.764	0.7639	0.0139	0.0023
−0.0067	0.1273	0.0952	0.0833	0.0833	0.1667	0.764	0.7454	0.0370	−0.0008
0.0161	0.1273	0.1190	0.0833	0.1667	0.0000	0.764	0.7685	0.0324	0.0990
0.0127	0.1273	0.1190	0.0000	0.1667	0.1667	0.764	0.7407	0.0185	−0.0983

Table S6. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions, and Warren–Cowley parameter (α) in hcp Pd_xRu_{63-x} alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions		α
	Overall	Surface layer	CN < 6	CN = 7	7 < CN < 12		Pd–Pd	Ru–Ru	
0.0290	0.8730	0.8750	0.8667	0.8750	0.8888	0.762	0.0159	0.7659	0.0000
0.1197	0.8730	0.9375	0.9333	0.9167	1.0000	0.762	0.0198	0.7063	−0.0005
−0.0308	0.8730	0.8333	0.6000	0.9583	0.8888	0.762	0.0119	0.8254	0.0008
0.0448	0.8730	0.8750	0.9333	0.7917	1.0000	0.762	0.0278	0.7698	0.1013
−0.0024	0.8730	0.8542	0.6667	0.9167	1.0000	0.762	0.0040	0.8016	−0.1005
0.0978	0.7460	0.7500	0.8000	0.7917	0.5556	0.762	0.0675	0.5357	−0.0003
0.1390	0.7460	0.7917	0.8667	0.7500	0.7778	0.762	0.0714	0.5079	−0.0006
0.0375	0.7460	0.7083	0.6000	0.7917	0.6667	0.762	0.0595	0.5913	0.0004
0.0590	0.7460	0.7500	0.8000	0.6667	0.8888	0.762	0.0833	0.5754	0.0994
0.0702	0.7460	0.7500	0.6000	0.7917	0.8888	0.762	0.0437	0.5556	−0.1007
0.0837	0.6190	0.6250	0.4667	0.7083	0.6667	0.762	0.1429	0.3929	0.0000
0.1497	0.6190	0.6667	0.8667	0.5833	0.5556	0.762	0.1587	0.3254	0.0000
0.0504	0.6190	0.5625	0.8000	0.5417	0.2222	0.762	0.1429	0.3929	0.0000
0.0740	0.6190	0.6250	0.6000	0.6667	0.5556	0.762	0.1706	0.4008	0.1007
0.0751	0.6190	0.6250	0.5333	0.6667	0.6667	0.762	0.1190	0.3730	−0.0998
0.0721	0.4921	0.5000	0.4667	0.4583	0.6667	0.762	0.2540	0.2540	0.0000
0.0916	0.4921	0.5208	0.3333	0.5833	0.6667	0.762	0.2579	0.2421	−0.0003
0.0488	0.4921	0.4583	0.6000	0.4167	0.3333	0.762	0.2540	0.2540	0.0000
0.0802	0.4921	0.5000	0.6000	0.5000	0.3333	0.762	0.2897	0.2500	0.1002
0.1048	0.4921	0.5000	0.4667	0.4167	0.7778	0.762	0.2302	0.2262	−0.1005
0.0696	0.3810	0.3750	0.2667	0.4167	0.4444	0.762	0.3770	0.1587	−0.0004
0.1306	0.3810	0.4167	0.4000	0.5000	0.2222	0.762	0.3968	0.1151	0.0004
0.0024	0.3810	0.3333	0.3333	0.2500	0.5556	0.762	0.3611	0.1944	0.0000
0.0323	0.3810	0.3542	0.1333	0.5000	0.3333	0.762	0.3929	0.1984	0.1017
0.0617	0.3810	0.3750	0.2667	0.3750	0.5556	0.762	0.3492	0.1468	−0.1002
0.0562	0.2540	0.2500	0.2000	0.2083	0.4444	0.762	0.5476	0.0794	−0.0003
0.0884	0.2540	0.2917	0.0667	0.4167	0.3333	0.762	0.5595	0.0595	0.0000
0.0487	0.2540	0.2292	0.2000	0.2500	0.2222	0.762	0.5476	0.0794	−0.0003
0.0629	0.2540	0.2500	0.2667	0.2083	0.3333	0.762	0.5754	0.0833	0.0994
0.0646	0.2540	0.2500	0.2000	0.2500	0.3333	0.762	0.5317	0.0556	−0.1008
0.0563	0.1270	0.1250	0.2000	0.1250	0.0000	0.762	0.7659	0.0119	0.0023
0.0565	0.1270	0.1458	0.0667	0.2083	0.1111	0.762	0.7659	0.0119	0.0023
0.0307	0.1270	0.1042	0.0667	0.1250	0.1111	0.762	0.7500	0.0317	−0.0003
0.0674	0.1270	0.1250	0.3333	0.0417	0.0000	0.762	0.7857	0.0119	0.1015
0.0513	0.1270	0.1250	0.1333	0.0833	0.2222	0.762	0.7460	0.0119	−0.0993

Table S7. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions in fcc $Pd_{101}Ru_{100}$ alloy NPs of subcluster (SC), Pd-rich surface (PS), and Ru-rich surface (RS) segregated configurations.

	ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
		Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
SC	−0.0042	0.4975	0.5000	0.5000	0.5000	0.5000	0.607	0.4430	0.4367
PS1	−0.1598	0.4975	0.1721	0.0833	0.1111	0.2419	0.607	0.2764	0.4599
PS2	−0.1702	0.4975	0.1721	0.0000	0.0000	0.3387	0.607	0.2595	0.4589
RS1	0.2796	0.4975	0.8197	1.0000	1.0000	0.6452	0.607	0.4304	0.2278
RS2	0.2507	0.4975	0.8197	0.9167	0.8611	0.7581	0.607	0.4652	0.2743

Table S8. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions in hcp $Pd_{119}Ru_{119}$ alloy NPs of subcluster (SC), Pd-rich surface (PS), and Ru-rich surface (RS) segregated configurations.

	ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
		Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
SC	0.0198	0.5000	0.5037	0.5000	0.5000	0.5072	0.567	0.4453	0.4436
PS1	−0.1539	0.5000	0.1259	0.0833	0.1190	0.1449	0.567	0.2507	0.4578
PS2	−0.1622	0.5000	0.1259	0.0000	0.0000	0.2464	0.567	0.2400	0.4578
RS1	0.3245	0.5000	0.8815	1.0000	1.0000	0.7681	0.567	0.4596	0.2382
RS2	0.3224	0.5000	0.8815	0.8333	0.8571	0.9130	0.567	0.4551	0.2516

Table S9. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in fcc $Pd_{100}Ru_{100}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.0792	0.5000	0.4919	0.5000	0.5000	0.4844	0.620	0.2508	0.2444
0.0749	0.5000	0.5082	0.4615	0.5455	0.5079	0.610	0.2521	0.2436
0.0758	0.5000	0.5000	0.5000	0.5151	0.4921	0.610	0.2521	0.2436
0.0750	0.5000	0.5000	0.5385	0.4848	0.4921	0.610	0.2532	0.2436
0.0788	0.5000	0.5161	0.5000	0.5000	0.5313	0.620	0.2540	0.2444

Table S10. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in fcc $Pd_{101}Ru_{99}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.0779	0.4950	0.4919	0.5000	0.5000	0.4844	0.620	0.2572	0.2390
0.0775	0.4950	0.4839	0.5000	0.5000	0.4688	0.620	0.2572	0.2412
0.0741	0.4950	0.5000	0.5000	0.4848	0.5079	0.610	0.2561	0.2401
0.0751	0.4950	0.4839	0.5000	0.5000	0.4688	0.620	0.2572	0.2412
0.0766	0.4950	0.4839	0.5000	0.5000	0.4688	0.620	0.2572	0.2412

Table S11. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in fcc $Pd_{102}Ru_{100}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.0717	0.4950	0.4959	0.4800	0.4857	0.5079	0.609	0.2550	0.2413
0.0716	0.4950	0.4959	0.4800	0.5000	0.5000	0.609	0.2550	0.2413
0.0709	0.4950	0.4959	0.4583	0.5143	0.5000	0.609	0.2558	0.2410
0.0728	0.4950	0.4959	0.5000	0.5000	0.4921	0.609	0.2561	0.2413
0.0728	0.4950	0.4959	0.5000	0.5000	0.4921	0.609	0.2561	0.2413

Table S12. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in fcc $Pd_{101}Ru_{101}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.0786	0.5000	0.5041	0.5417	0.5000	0.4921	0.609	0.2540	0.2423
0.0755	0.5000	0.5041	0.5417	0.4857	0.5000	0.609	0.2537	0.2431
0.0850	0.5000	0.5041	0.5200	0.5143	0.4921	0.609	0.2540	0.2413
0.0841	0.5000	0.5041	0.5200	0.5000	0.5000	0.609	0.2540	0.2413
0.0765	0.5000	0.5041	0.5200	0.4857	0.5079	0.609	0.2540	0.2434

Table S13. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in hcp $Pd_{118}Ru_{119}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.1044	0.5021	0.4859	0.6538	0.4390	0.4533	0.578	0.2511	0.2448
0.1029	0.5021	0.4894	0.6154	0.4878	0.4459	0.578	0.2509	0.2446
0.1043	0.5021	0.4895	0.6154	0.4651	0.4595	0.578	0.2505	0.2450
0.1032	0.5021	0.4859	0.6400	0.4444	0.4583	0.578	0.2502	0.2448
0.1037	0.5021	0.4894	0.6538	0.4634	0.4459	0.578	0.2527	0.2446

Table S14. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in hcp $Pd_{119}Ru_{118}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.0991	0.4979	0.4823	0.4800	0.4857	0.3836	0.574	0.2543	0.2426
0.1016	0.4979	0.4823	0.5769	0.4878	0.4459	0.578	0.2547	0.2421
0.1040	0.4979	0.4859	0.6400	0.4667	0.4444	0.578	0.2547	0.2394
0.0968	0.4979	0.4786	0.5600	0.4878	0.4459	0.570	0.2541	0.2441
0.1007	0.4979	0.4857	0.6154	0.4762	0.4533	0.578	0.2543	0.2399

Table S15. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in hcp $Pd_{120}Ru_{119}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.0994	0.4979	0.4823	0.6000	0.4524	0.4595	0.569	0.2540	0.2424
0.0980	0.4979	0.4823	0.6000	0.4309	0.4667	0.569	0.2529	0.2422
0.0973	0.4979	0.4823	0.6000	0.4878	0.4400	0.569	0.2540	0.2424
0.0988	0.4979	0.4823	0.6000	0.4390	0.4667	0.569	0.2531	0.2424
0.0973	0.4979	0.4823	0.6000	0.4762	0.4459	0.569	0.2538	0.2422

Table S16. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, and bond fractions in hcp $Pd_{119}Ru_{120}$ alloy NPs.

ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions	
	Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru
0.1020	0.5021	0.4894	0.6400	0.4390	0.4667	0.569	0.2522	0.2442
0.1002	0.5021	0.4894	0.6400	0.4390	0.4667	0.569	0.2520	0.2449
0.0998	0.5021	0.4894	0.6400	0.4390	0.4667	0.569	0.2520	0.2449
0.1020	0.5021	0.4894	0.6400	0.4651	0.4521	0.569	0.2522	0.2442
0.1011	0.5021	0.4894	0.6400	0.4651	0.4521	0.569	0.2522	0.2442

Table S17. Surface energy of fcc and hcp surfaces for Pd and Ru.

		Pd	Ru
fcc	(100)	0.093 eV/Å^2	0.186 eV/Å^2
	(111)	0.082 eV/Å^2	0.147 eV/Å^2
hcp	(0001)	0.071 eV/Å^2	0.164 eV/Å^2
	(100)	0.081 eV/Å^2	0.184 eV/Å^2
	(110)	0.096 eV/Å^2	0.213 eV/Å^2

Table S18. Excess energy (ε_{excess}), Ru overall composition, ratio of surface atoms to total atoms in NP (R_{surf}), Ru composition in surface layer, bond fractions, and Warren–Cowley parameter (α) in solid-solution fcc $Pd_{203}Ru_{202}$ (SS405), solid-solution fcc $Pd_{356}Ru_{355}$ (SS711), and subcluster segregated fcc $Pd_{356}Ru_{355}$ (SC711) alloy NPs.

	ε_{excess} (eV/atom)	Ru composition					R_{surf}	Bond fractions		α
		Overall	Surface layer	CN < 6	CN = 7	7< CN < 12		Pd–Pd	Ru–Ru	
SS405	0.1038	0.4988	0.5049	0.375	0.5333	0.5167	0.5037	0.2470	0.2416	−0.0198
SS711	0.1048	0.4993	0.4771	0.375	0.5000	0.4798	0.4304	0.2486	0.2541	−0.0014
SC711	0.0257	0.4993	0.5000	0.5000	0.5000	0.5000	0.4304	0.4626	0.4609	0.8470

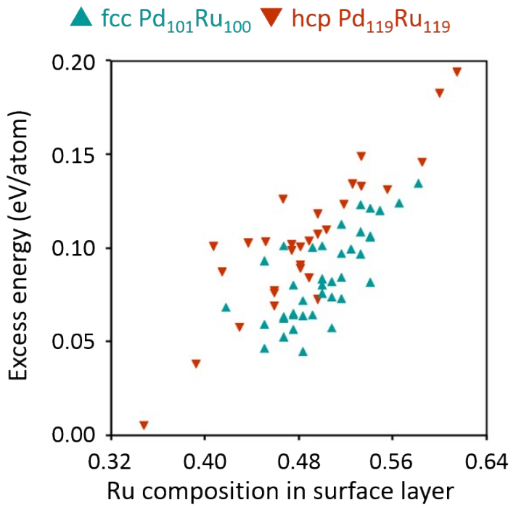

Figure S1 - Excess energies of fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ alloy NPs as a function of Ru composition in the surface layer.

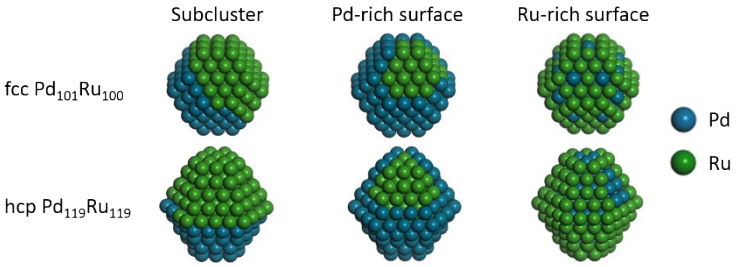

Figure S2 - Models of fcc $Pd_{101}Ru_{100}$ and hcp $Pd_{119}Ru_{119}$ alloy NPs for subcluster, Pd-rich surface, Ru-rich surface segregated configurations.

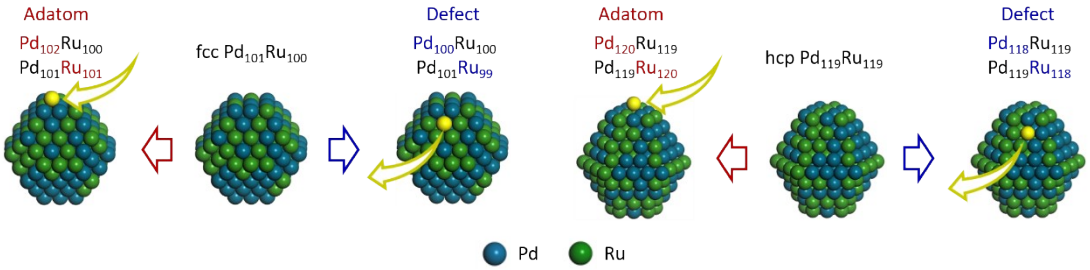

Figure S3 - Adatom and defect for PdRu alloy NPs (Top: fcc $Pd_{101}Ru_{100}$, Bottom: hcp $Pd_{119}Ru_{119}$).

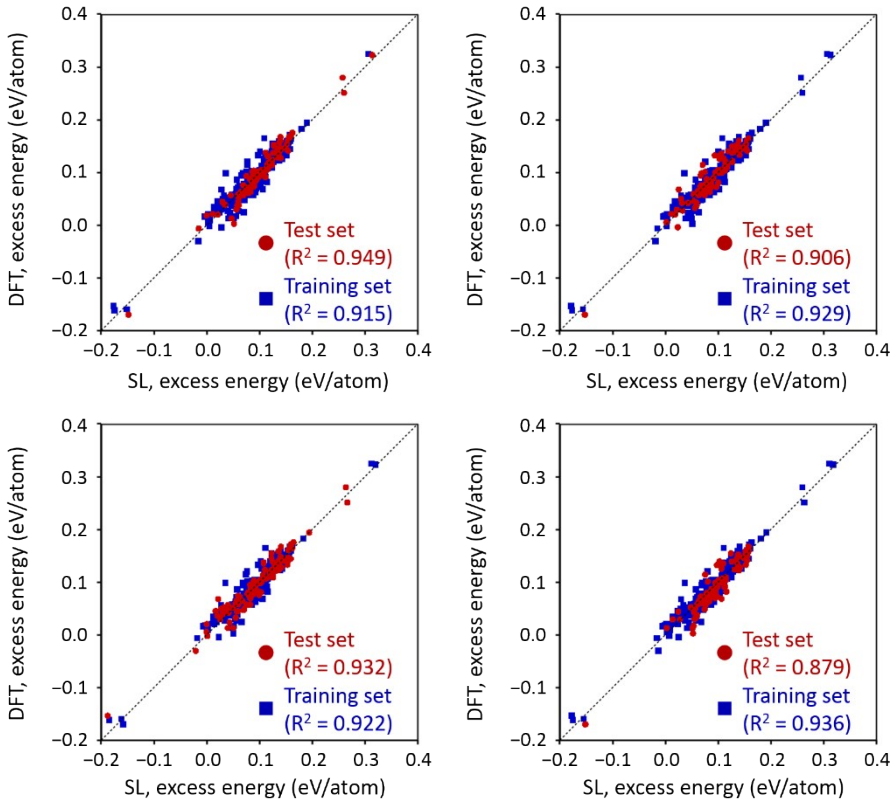

Figure S4 - Comparison of excess energy values determined by SL and DFT calculation for Pd–Ru alloy NPs. Descriptors used in SL are shown in Table2.

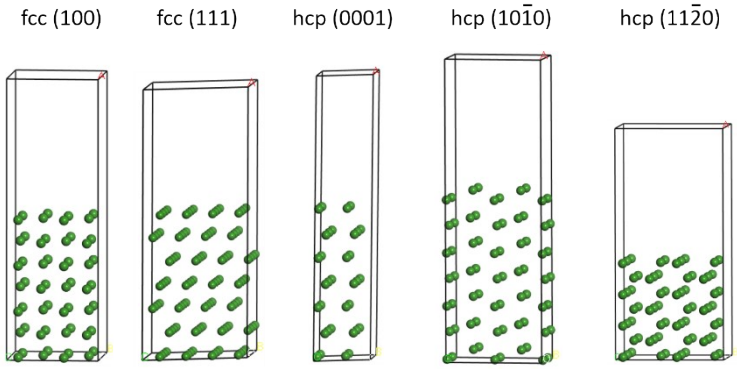

Figure S5 - Slab models of fcc (100) and (111) surfaces and hcp (0001), (100), and (110) surfaces. These models of fcc and hcp surfaces were prepared based on the 2 × 2 supercell and seven layers.

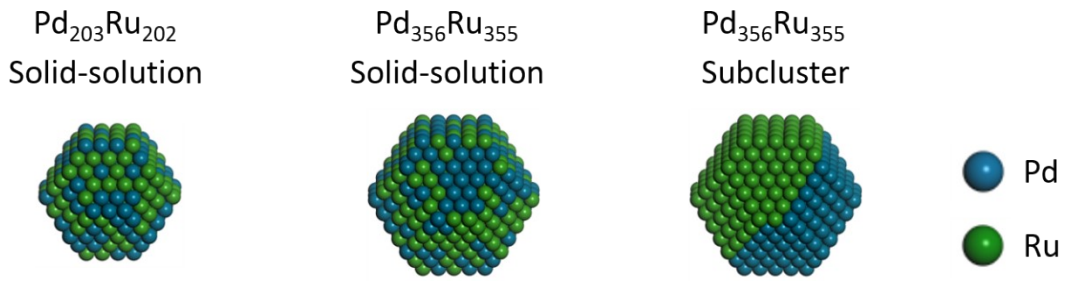

Figure S6 - Models of fcc $Pd_{203}Ru_{202}$ for solid-solution configuration, fcc $Pd_{356}Ru_{355}$ alloy NPs for solid-solution and subcluster segregated configurations.

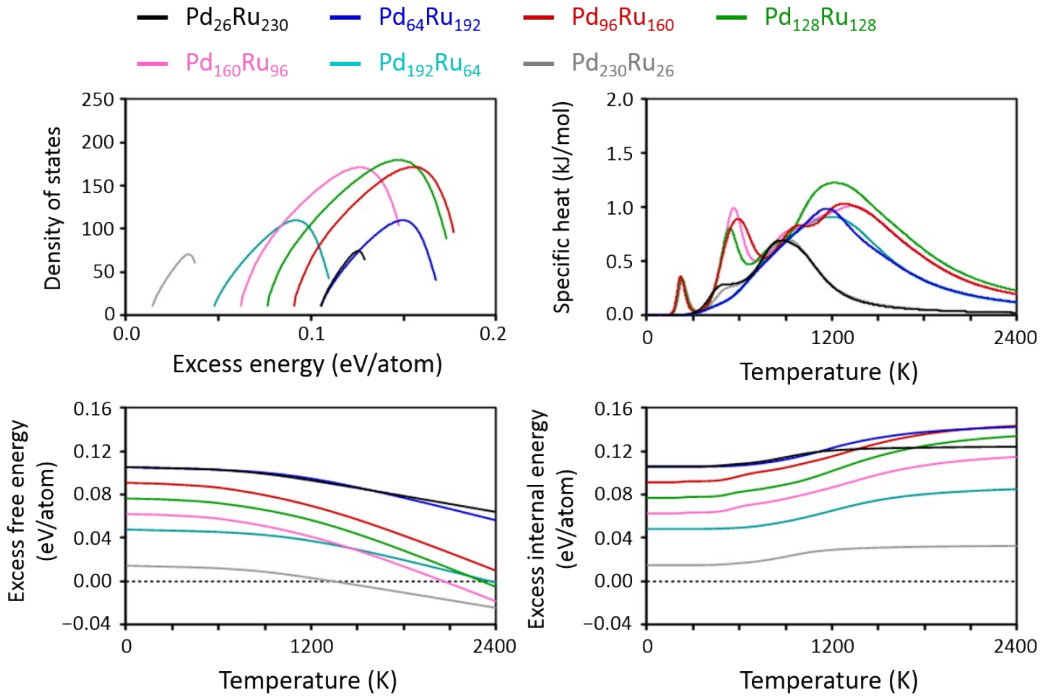

Figure S7 - Configurational density of states and temperature dependence of configurational specific heat, excess free energy, and excess internal energy in fcc Pd_xRu_{256-x} alloy.

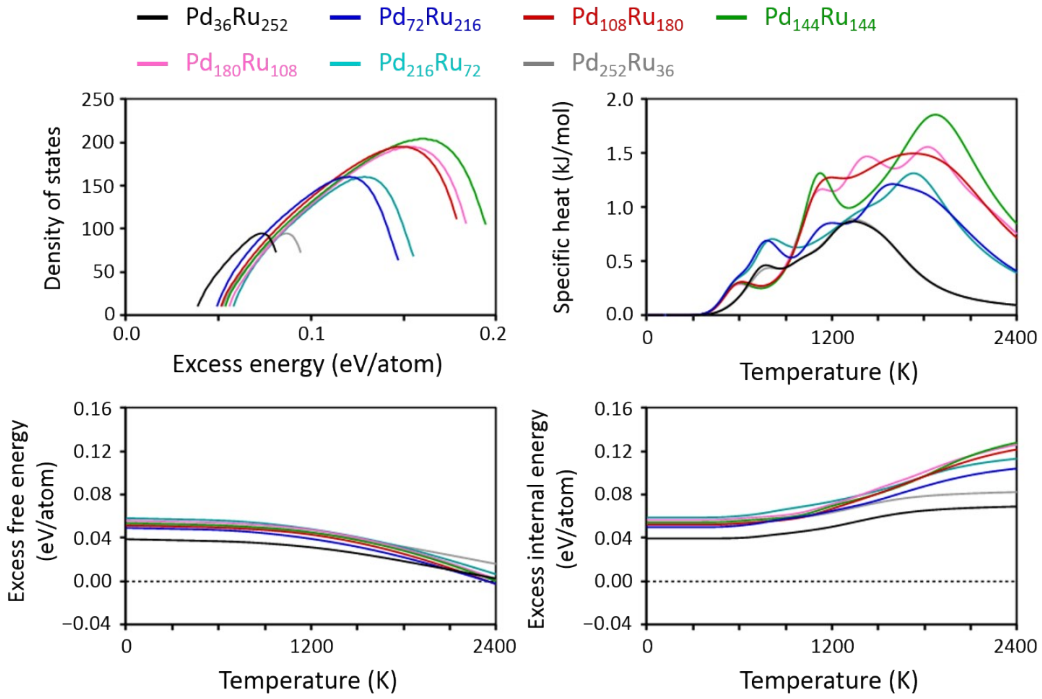

Figure S8 - Configurational density of states and temperature dependence of configurational specific heat, excess free energy, and excess internal energy in hcp Pd_xRu_{288-x} alloy.

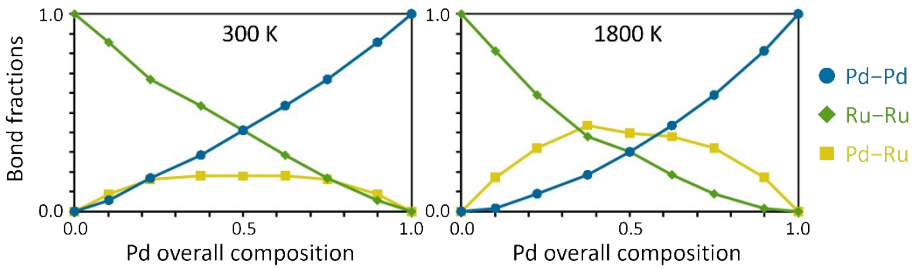

Figure S9 - Pd–Pd, Ru–Ru, and Pd–Ru bond fractions in fcc Pd_xRu_{256-x} alloy as a function of Pd overall composition.

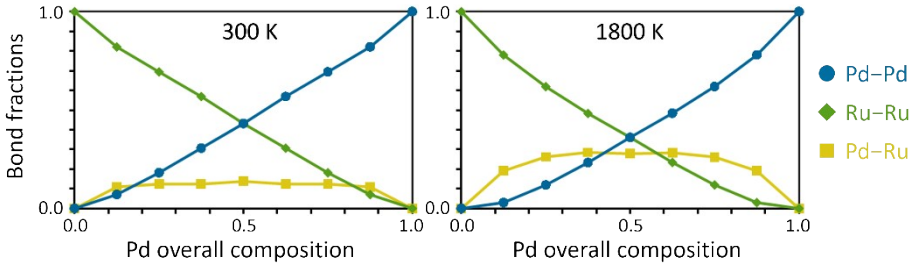

Figure S10 - Pd–Pd, Ru–Ru, and Pd–Ru bond fractions in fcc Pd_xRu_{288-x} alloy as a function of Pd overall composition.

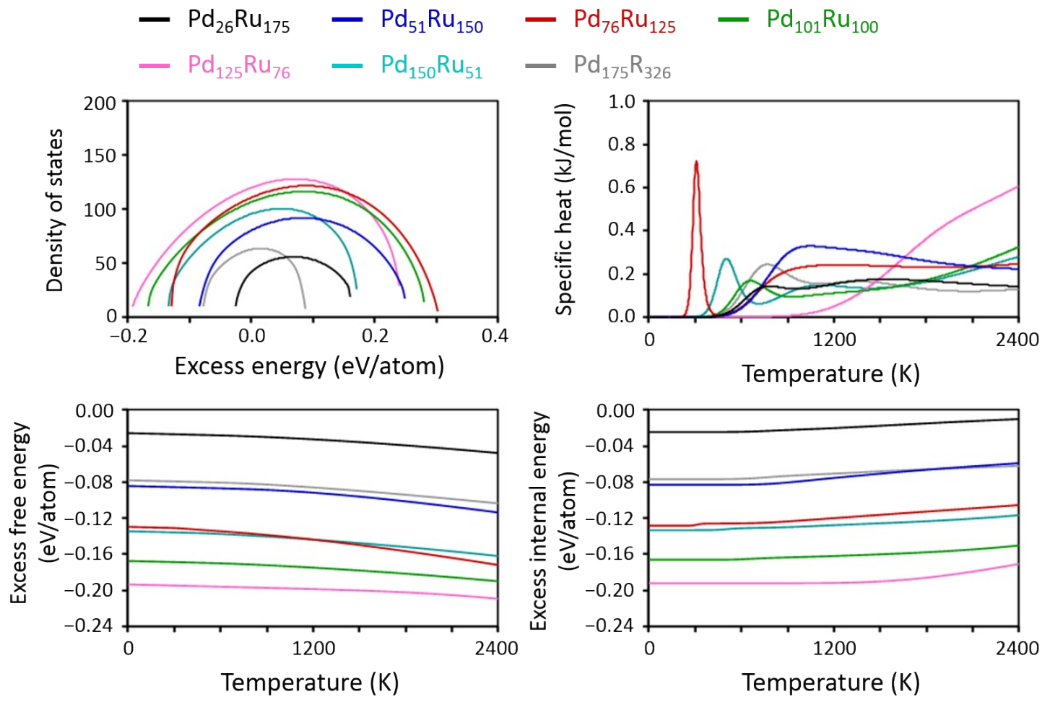

Figure S11 - Configurational density of states and temperature dependence of configurational specific heat, excess free energy, and excess internal energy in fcc Pd_xRu_{201-x} alloy NP.

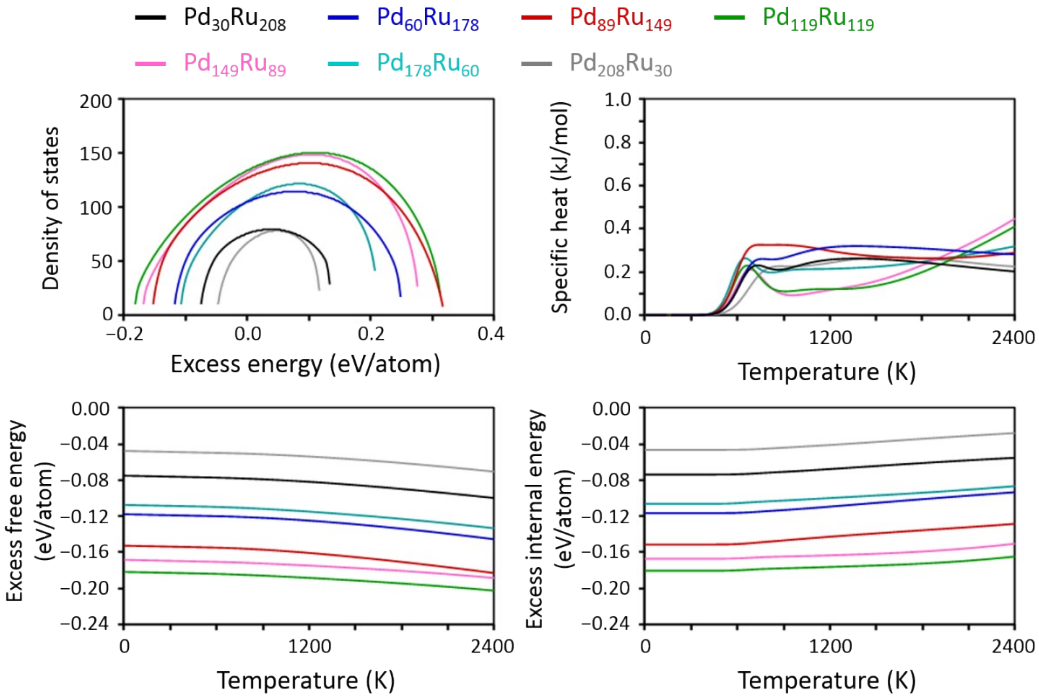

Figure S12 - Configurational density of states and temperature dependence of configurational specific heat, excess free energy, and excess internal energy in hcp Pd_xRu_{238-x} alloy NP.

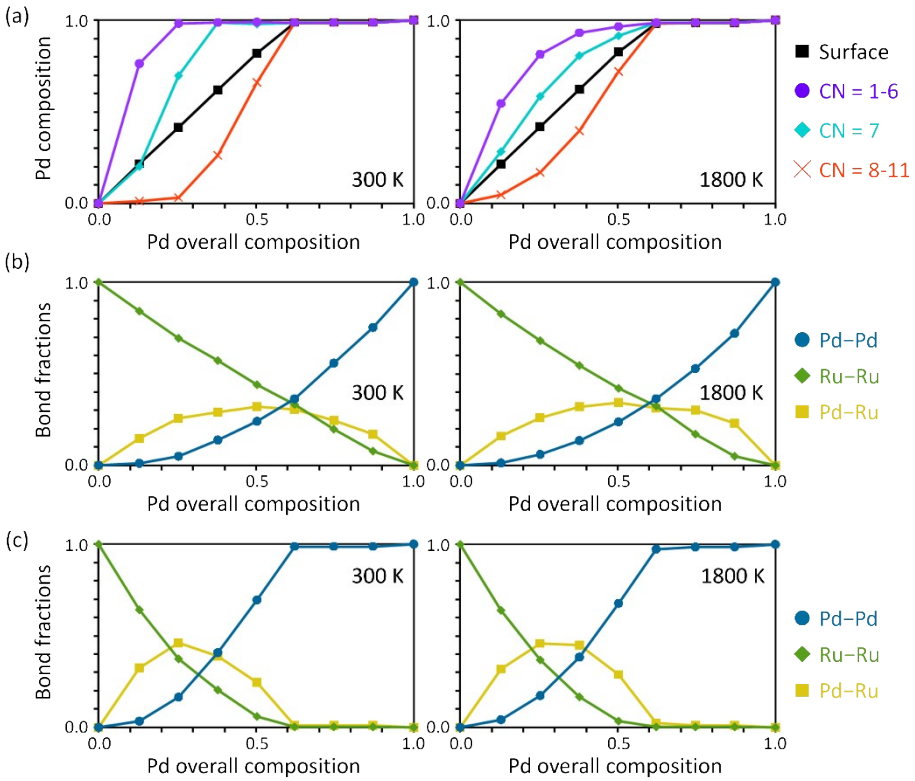

Figure S13 - Structural parameters of fcc Pd_xRu_{201-x} alloy NP as a function of Pd overall composition. The expected values of (a) Pd composition in the surface layer, (b) bond fractions, (c) bond fractions in the surface layer were estimated.

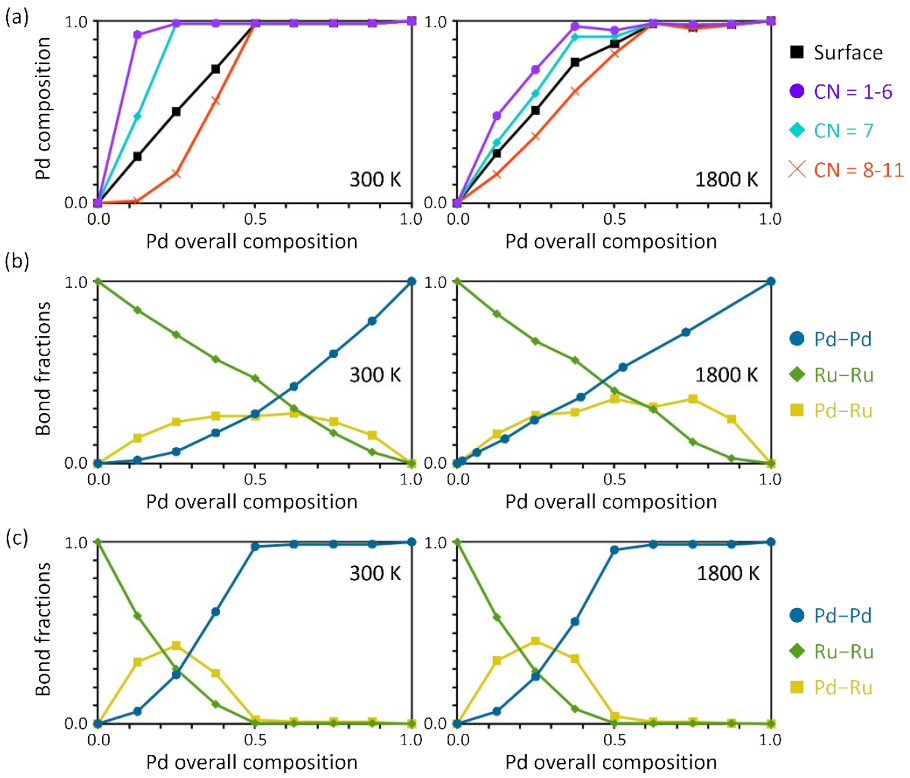

Figure S14 - Structural parameters of hcp Pd_xRu_{238-x} alloy NP as a function of Pd overall composition. The expected values of (a) Pd composition in the surface layer, (b) bond fractions, (c) bond fractions in the surface layer were estimated.

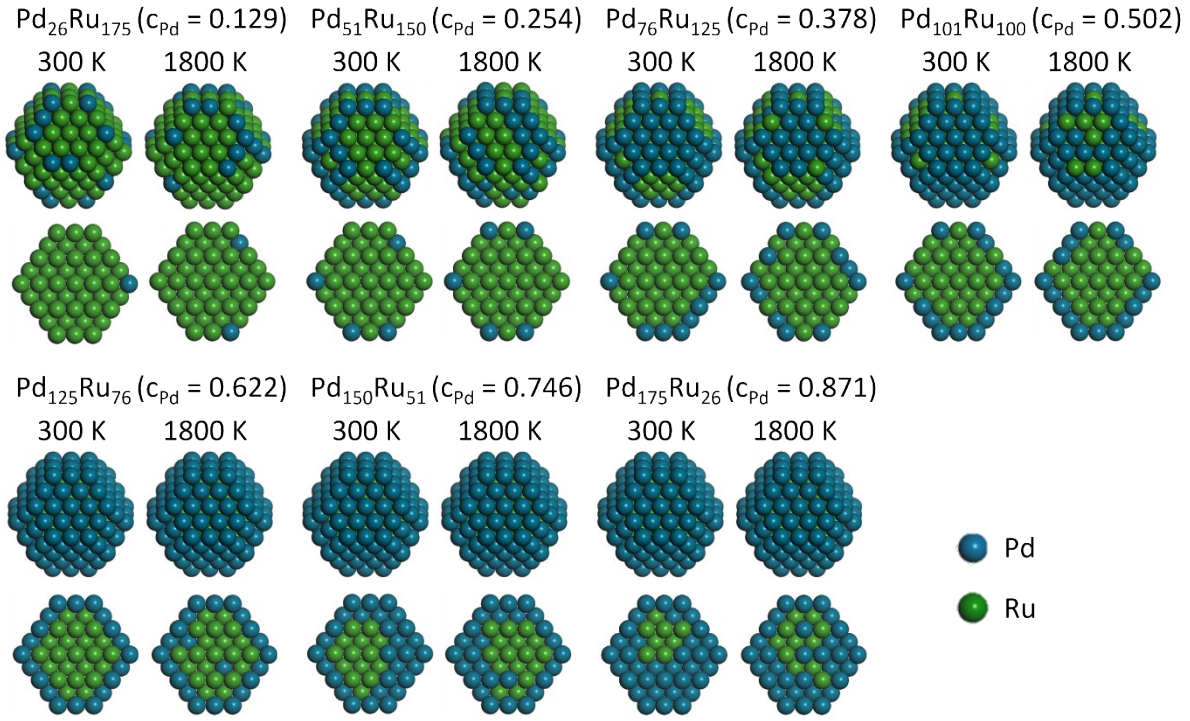

Figure S15 - Stable configurations of fcc Pd_xRu_{201-x} alloy NPs.

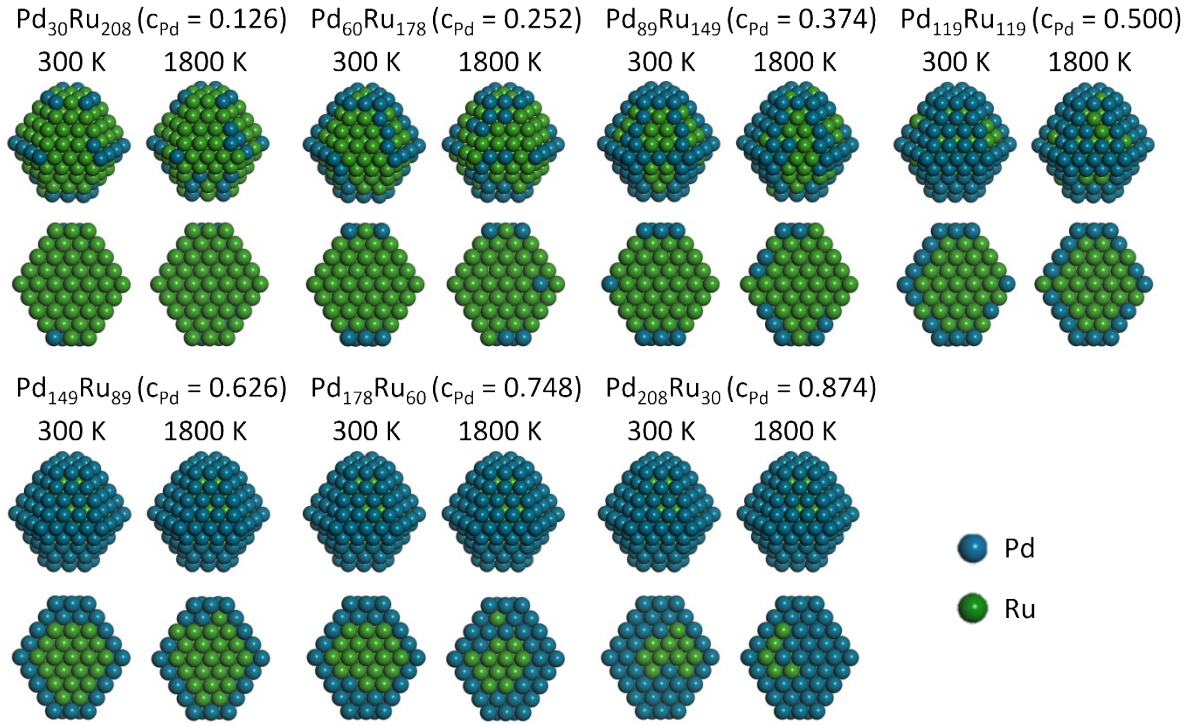

Figure S16 - Stable configurations of hcp Pd_xRu_{238-x} alloy NPs.

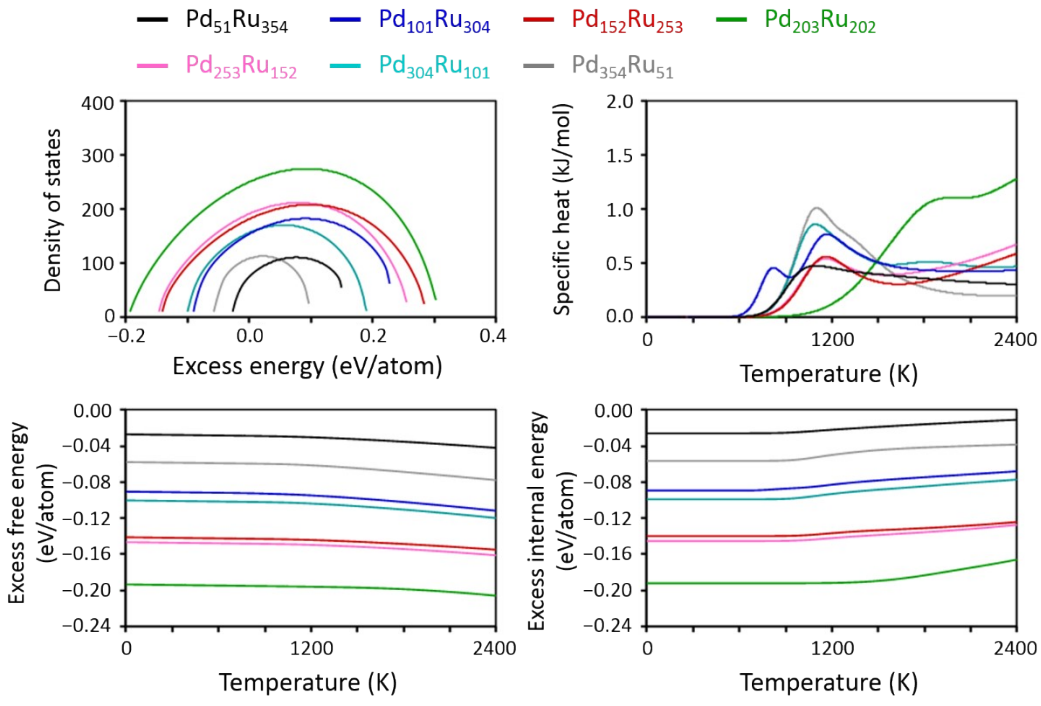

Figure S17 - Configurational density of states and temperature dependence of configurational specific heat, excess free energy, and excess internal energy in fcc Pd_xRu_{405-x} alloy NP.

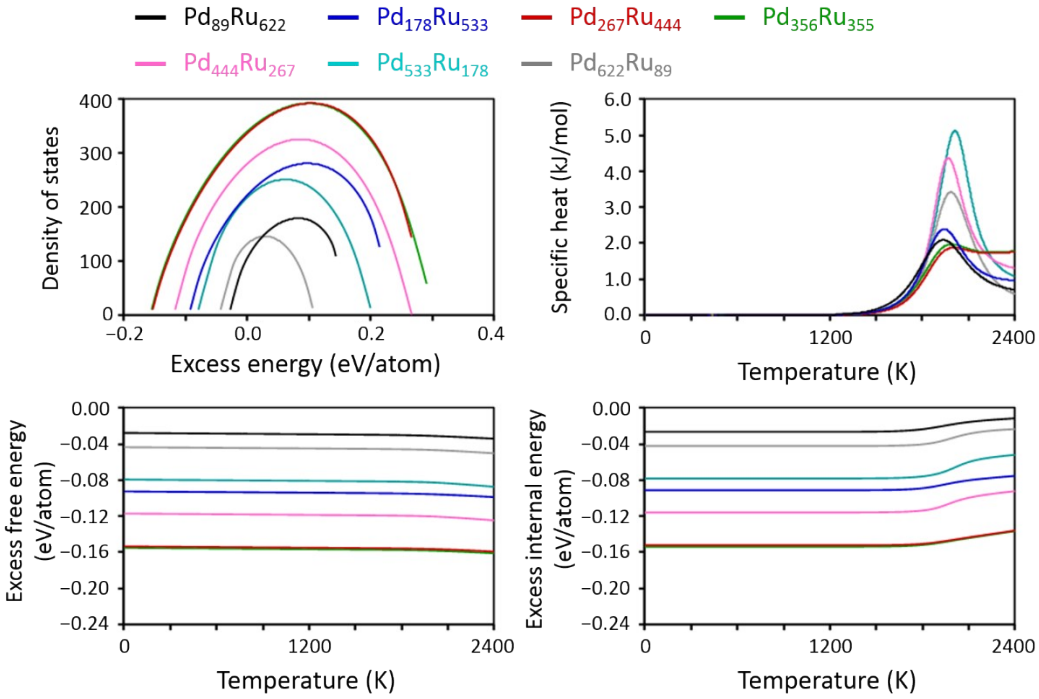

Figure S18 - Configurational density of states and temperature dependence of configurational specific heat, excess free energy, and excess internal energy in fcc Pd_xRu_{711-x} alloy NP.

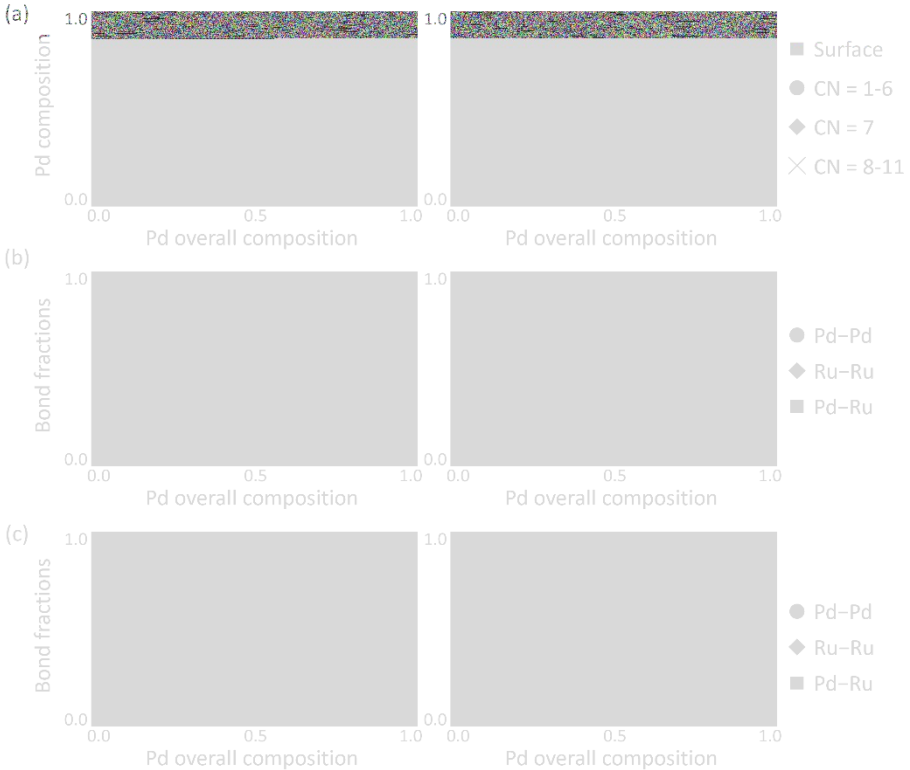

Figure S19 - Structural parameters of fcc Pd_xRu_{405-x} alloy NP as a function of Pd overall composition. The expected values of (a) Pd composition in the surface layer, (b) bond fractions, (c) bond fractions in the surface layer were estimated.

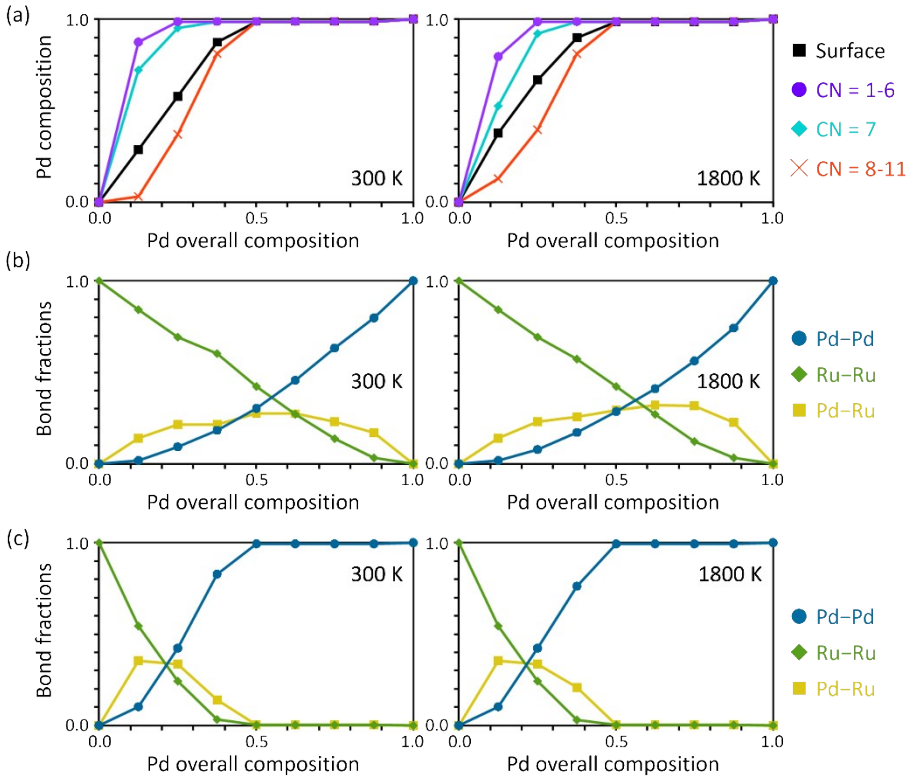

Figure S20 - Structural parameters of fcc Pd_xRu_{711-x} alloy NP as a function of Pd overall composition. The expected values of (a) Pd composition in the surface layer, (b) bond fractions, (c) bond fractions in the surface layer were estimated.

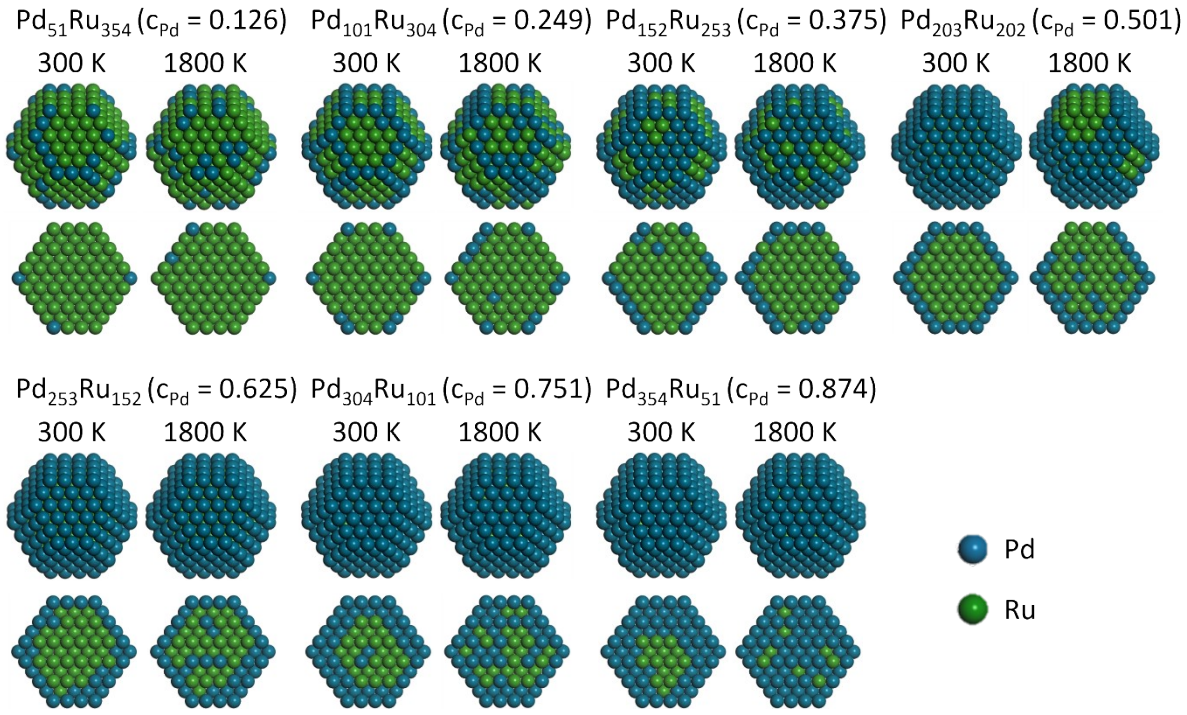

Figure S21 - Stable configurations of fcc Pd_xRu_{405-x} alloy NPs.

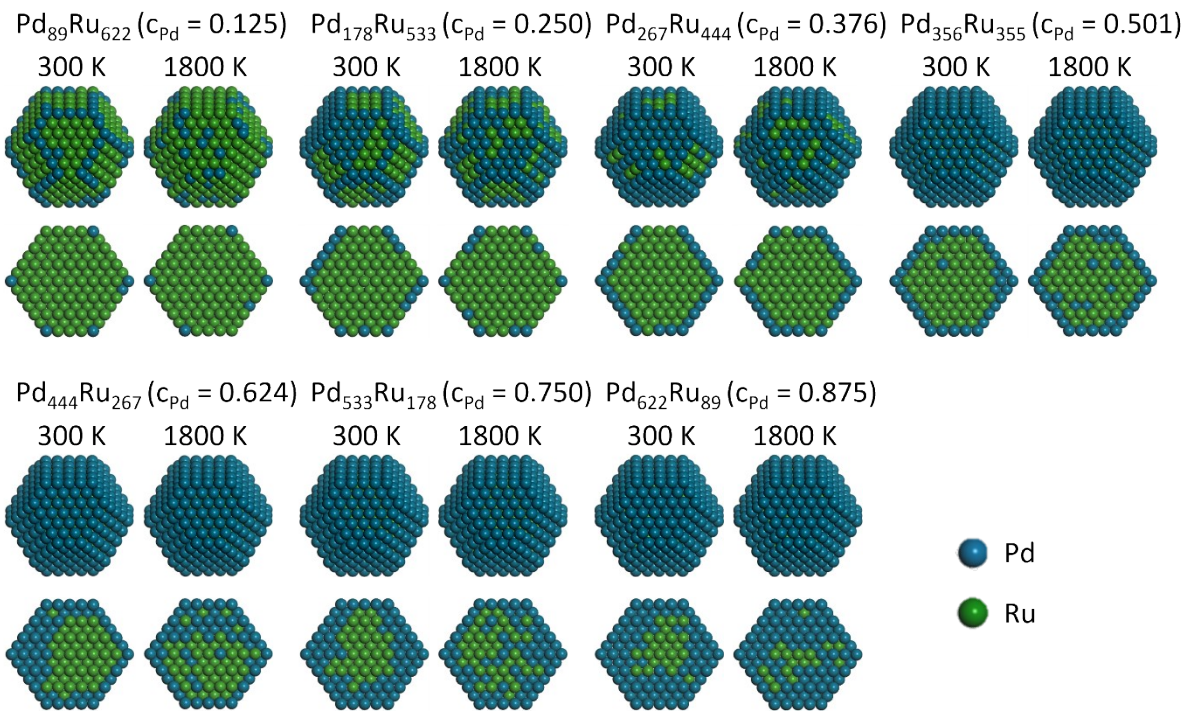

Figure S22 - Stable configurations of fcc Pd_xRu_{711-x} alloy NPs.