Supporting Information

DFT-based Global Optimization Of Sub-nanometre Ni-Pd Clusters

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Table S1: Total energies (taken from MEGA-VASP calculations), spin magnetic moments (SMM), binding energies (E_b) and excess energies (Δ) for 3-8-atom Ni, Pd and Ni-Pd clusters. Second differences in energy ($\Delta_2 E$) are also given for pure Ni and Pd clusters

Composition	E / eV	SMM / μ_B	E_b / eV	Δ / eV	$\Delta_2 E$ / eV
Pd_3	-8.32	2	1.30	0.00	-0.30
Ni_1Pd_2	-8.54	2	1.65	-0.46	
Ni_2Pd_1	-8.28	2	1.84	-0.44	
Ni_3	-7.61	4	1.89	0.00	-0.38
Pd_4	-12.66	2	1.69	0.00	0.55
Ni_1Pd_3	-12.82	2	1.94	-0.48	
Ni_2Pd_2	-12.45	2	2.05	-0.44	
Ni_3Pd_1	-11.79	2	2.09	-0.10	
Ni_4	-11.37	2	2.20	0.00	-0.36
Pd_5	-16.46	2	1.82	0.00	-0.35
Ni_1Pd_4	-16.71	2	2.03	-0.44	
Ni_2Pd_3	-16.47	2	2.15	-0.40	
Ni_3Pd_2	-16.44	2	2.31	-0.56	
Ni_4Pd_1	-16.01	2	2.39	-0.33	
Ni_5	-15.49	4	2.45	0.00	-0.33
Pd_6	-20.62	2	1.96	0.00	0.46
Ni_1Pd_5	-20.70	2	2.11	-0.19	
Ni_2Pd_4	-20.71	2	2.25	-0.32	
Ni_3Pd_3	-20.56	2	2.37	-0.28	
Ni_4Pd_2	-20.30	4	2.46	-0.13	
Ni_5Pd_1	-19.92	2	2.54	0.14	
Ni_6	-19.94	4	2.68	0.00	0.27
Pd_7	-24.31	2	2.00	0.00	-0.42
Ni_1Pd_6	-24.59	2	2.16	-0.31	
Ni_2Pd_5	-24.78	2	2.30	-0.52	
Ni_3Pd_4	-24.97	4	2.45	-0.74	
Ni_4Pd_3	-24.78	2	2.54	-0.58	
Ni_5Pd_2	-24.63	2	2.64	-0.45	
Ni_6Pd_1	-24.41	6	2.72	-0.26	
Ni_7	-24.13	6	2.80	0.00	-0.04
Pd_8	-28.43	4	2.08	0.00	-0.18
Ni_1Pd_7	-28.78	2	2.23	-0.36	
Ni_2Pd_6	-29.24	2	2.39	-0.82	
Ni_3Pd_5	-29.27	2	2.50	-0.87	
Ni_4Pd_4	-29.30	4	2.60	-0.90	
Ni_5Pd_3	-29.11	4	2.68	-0.73	
Ni_6Pd_2	-29.00	6	2.77	-0.63	
Ni_7Pd_1	-28.74	6	2.84	-0.38	
Ni_8	-28.35	8	2.90	0.00	-0.14

Table S2: Total energies (taken from MEGA-VASP calculations), spin magnetic moments (SMM), binding energies (E_b) and excess energies (Δ) for 9- and 10-atom Ni, Pd and Ni-Pd clusters. Second differences in energy ($\Delta_2 E$) are also given for pure Ni and Pd clusters. *Indicates that the spin magnetic moment is quasi-degenerate in energy with the quintet (SMM=4)

Composition	E / eV	SMM / μ_B	E_b / eV	Δ / eV	$\Delta_2 E$ / eV
Pd_9	-32.72	2*	2.16	0.00	0.20
Ni_1Pd_8	-33.18	2	2.31	-0.46	
Ni_2Pd_7	-33.53	4	2.44	-0.81	
Ni_3Pd_6	-33.85	2	2.56	-1.13	
Ni_4Pd_5	-33.67	2	2.64	-0.95	
Ni_5Pd_4	-33.70	2	2.73	-0.98	
Ni_6Pd_3	-33.75	2	2.83	-1.03	
Ni_7Pd_2	-33.50	6	2.89	-0.78	
Ni_8Pd_1	-33.18	4	2.95	-0.46	
Ni_9	-32.72	8	2.99	0.00	-0.12
Pd_{10}	-36.82	4	2.21	0.00	
Ni_1Pd_9	-37.27	2	2.34	-0.41	
Ni_2Pd_8	-37.79	4	2.47	-0.89	
Ni_3Pd_7	-38.12	6	2.59	-1.18	
Ni_4Pd_6	-38.33	4	2.69	-1.36	
Ni_5Pd_5	-38.45	4	2.78	-1.43	
Ni_6Pd_4	-38.65	8	2.89	-1.60	
Ni_7Pd_3	-38.36	4	2.94	-1.27	
Ni_8Pd_2	-38.02	2	2.99	-0.89	
Ni_9Pd_1	-37.64	4	3.03	-0.47	
Ni_{10}	-37.21	8	3.07	0.00	

Table S3: Calculated quantum molecular descriptors for free atoms, dimers and clusters, $N = 3 - 6$

Cluster	Δ_{HL}	I / eV	A / eV	χ / eV	μ / eV	η / eV	ω / eV
$N = 1$							
Ni_1	0.06	3.78	3.72	3.75	-3.75	0.03	218.63
Pd_1	0.67	3.88	3.21	3.54	-3.54	0.33	18.76
$N = 2$							
Ni_2	0.21	3.641	3.43	3.54	-3.54	0.10	59.96
Ni_1Pd_1	0.04	4.65	4.62	4.64	-4.4	0.02	613.81
Pd_2	0.37	4.42	4.05	4.23	-4.23	0.19	48.49
$N = 3$							
Ni_3	0.14	3.198	3.06	3.13	-3.13	0.07	70.93
Ni_2Pd_1	0.30	3.51	3.21	3.36	-3.36	0.15	37.64
Ni_1Pd_2	0.19	4.17	3.98	4.07	-4.07	0.10	85.68
Pd_3	0.14	4.57	4.43	4.50	-4.50	0.07	142.24
$N = 4$							
Ni_4	0.56	3.65	3.10	3.37	-3.37	0.28	20.483
Ni_3Pd_1	0.05	2.87	2.82	2.85	-2.85	0.02	166.72
Ni_2Pd_2	0.28	3.07	2.79	2.93	-2.93	0.14	30.70
Ni_1Pd_3	0.28	3.40	3.12	3.26	-3.26	0.14	38.01
Pd_4	0.04	3.61	3.57	3.59	-3.59	0.02	326.75
$N = 5$							
Ni_5	0.24	3.43	3.19	3.31	-3.31	0.12	45.44
Ni_4Pd_1	0.41	3.64	3.23	3.43	-3.43	0.20	28.88
Ni_3Pd_2	0.62	3.87	3.25	3.56	-3.56	0.31	20.41
Ni_2Pd_3	0.43	4.10	3.67	3.89	-3.89	0.22	34.77
Ni_1Pd_4	0.32	3.47	3.15	3.31	-3.31	0.16	34.25
Pd_5	0.07	3.53	3.46	3.50	-3.50	0.04	165.47
$N = 6$							
Ni_6	0.11	3.863	3.75	3.81	-3.81	0.06	128.10
Ni_5Pd_1	0.10	3.89	3.78	3.83	-3.83	0.05	141.97
Ni_4Pd_2	0.23	3.63	3.40	3.52	-3.52	0.12	53.32
Ni_3Pd_3	0.28	3.69	3.41	3.55	-3.55	0.14	45.04
Ni_2Pd_4	0.41	3.91	3.51	3.71	-3.71	0.20	33.84
Ni_1Pd_5	0.23	3.39	3.16	3.27	-3.27	0.12	46.31
Pd_6	0.11	3.39	3.28	3.34	-3.34	0.06	100.51

Table S4: Calculated quantum molecular descriptors for free clusters, $N = 7 - 10$

Cluster	Δ_{HL}	I / eV	A / eV	χ / eV	μ / eV	η / eV	ω / eV
$N = 7$							
Ni_7	0.13	3.89	3.76	3.82	-3.82	0.07	111.24
Ni_6Pd_1	0.41	3.64	3.23	3.43	-3.43	0.20	28.88
Ni_5Pd_2	0.23	3.76	3.54	3.65	-3.65	0.12	58.01
Ni_4Pd_3	0.23	3.90	3.67	3.79	-3.79	0.12	60.77
Ni_3Pd_4	0.13	3.88	3.75	3.82	-3.82	0.07	110.56
Ni_2Pd_5	0.20	3.88	3.68	3.78	-3.78	0.10	71.94
Ni_1Pd_6	0.10	3.81	3.71	3.76	-3.76	0.05	141.29
Pd_7	0.09	3.63	3.54	3.59	-3.59	0.04	145.73
$N = 8$							
Ni_8	0.10	3.69	3.59	3.64	-3.64	0.05	133.97
Ni_7Pd_1	0.10	3.89	3.78	3.83	-3.83	0.05	141.97
Ni_6Pd_2	0.13	4.08	3.95	4.02	-4.02	0.07	119.56
Ni_5Pd_3	0.14	3.83	3.69	3.76	-3.76	0.07	101.95
Ni_4Pd_4	0.26	3.67	3.42	3.54	-3.54	0.13	49.10
Ni_3Pd_5	0.24	3.65	3.41	3.53	-3.53	0.12	52.23
Ni_2Pd_6	0.24	3.80	3.56	3.68	-3.68	0.12	56.34
Ni_1Pd_7	0.06	3.73	3.66	3.70	-3.70	0.03	221.26
Pd_8	0.15	3.68	3.53	3.61	-3.61	0.08	86.00
$N = 9$							
Ni_9	0.05	3.52	3.47	3.50	-3.50	0.03	237.08
Ni_8Pd_1	0.09	3.79	3.70	3.74	-3.74	0.04	158.81
Ni_7Pd_2	0.07	3.81	3.74	3.78	-3.78	0.03	215.37
Ni_6Pd_3	0.07	3.96	3.89	3.93	-3.93	0.04	210.46
Ni_5Pd_4	0.10	3.96	3.86	3.91	-3.91	0.05	153.18
Ni_4Pd_5	0.10	3.80	3.69	3.74	-3.74	0.05	139.22
Ni_3Pd_6	0.24	3.67	3.44	3.55	-3.55	0.12	53.62
Ni_2Pd_7	0.06	3.51	3.45	3.48	-3.48	0.03	201.26
Ni_1Pd_8	0.28	3.96	3.68	3.82	-3.82	0.14	52.28
Pd_9	0.08	3.84	3.75	3.79	-3.79	0.04	170.69
$N = 10$							
Ni_{10}	0.30	3.60	3.30	3.45	-3.45	0.15	39.06
Ni_9Pd_1	0.27	3.66	3.39	3.52	-3.52	0.14	45.22
Ni_8Pd_2	0.26	3.78	3.52	3.65	-3.65	0.13	51.43
Ni_7Pd_3	0.26	3.95	3.69	3.82	-3.82	0.13	57.22
Ni_6Pd_4	0.27	3.93	3.65	3.79	-3.79	0.14	51.90
Ni_5Pd_5	0.26	3.89	3.63	3.76	-3.76	0.13	54.16
Ni_4Pd_6	0.19	3.87	3.67	3.77	-3.77	0.10	73.42
Ni_3Pd_7	0.12	3.86	3.75	3.80	-3.80	0.06	124.79
Ni_2Pd_8	0.06	3.84	3.78	3.81	-3.81	0.03	252.25
Ni_1Pd_9	0.10	3.88	3.78	3.83	-3.83	0.05	139.78
Pd_{10}	0.11	3.89	3.78	3.84	-3.84	0.06	134.96

Table S5: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 2 - 4$

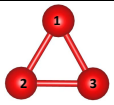
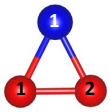
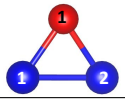
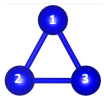
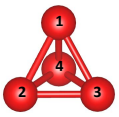
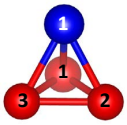
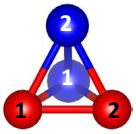
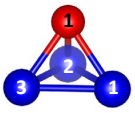
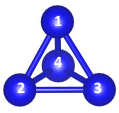
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Ni_2	1	Ni	-0.05	
	2	Ni	0.05	
Ni_1Pd_1	1	Ni	0.06	
	2	Pd	-0.06	
Pd_2	1	Pd	-0.01	
	2	Pd	0.01	
Ni_3	1	Ni	0.001	
	2	Ni	0.002	
	3	Ni	-0.003	
Ni_2Pd_1	1	Ni	0.10	
	2	Ni	0.09	
	1	Pd	-0.19	
Ni_1Pd_2	1	Ni	0.23	
	1	Pd	-0.12	
	2	Pd	-0.10	
Pd_3	1	Pd	-0.001	
	2	Pd	-0.002	
	3	Pd	0.003	
Ni_4	1	Ni	-0.01	
	2	Ni	0.004	
	3	Ni	-0.001	
	4	Ni	0.005	
Ni_3Pd_1	1	Ni	0.02	
	2	Ni	0.10	
	3	Ni	0.10	
	1	Pd	-0.22	
Ni_2Pd_2	1	Ni	0.17	
	2	Ni	0.17	
	1	Pd	-0.17	
	2	Pd	-0.17	
Ni_1Pd_3	1	Ni	0.26	
	1	Pd	-0.09	
	2	Pd	-0.09	
	3	Pd	-0.08	
Pd_4	1	Pd	0.002	
	2	Pd	-0.003	
	3	Pd	0.001	
	4	Pd	-0.0002	

Table S6: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 5$

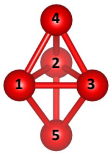
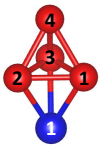
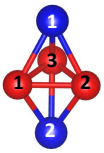
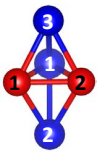
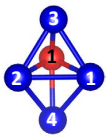
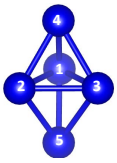
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Ni_5	1	Ni	0.09	
	2	Ni	0.09	
	3	Ni	0.09	
	4	Ni	-0.13	
	5	Ni	-0.13	
Ni_4Pd_1	1	Ni	0.14	
	2	Ni	0.14	
	3	Ni	0.15	
	4	Ni	-0.12	
	1	Pd	-0.31	
Ni_3Pd_2	1	Ni	0.21	
	2	Ni	0.21	
	3	Ni	0.21	
	1	Pd	-0.32	
	2	Pd	-0.32	
Ni_2Pd_3	1	Ni	0.27	
	2	Ni	0.27	
	1	Pd	-0.04	
	2	Pd	-0.25	
	3	Pd	-0.25	
Ni_1Pd_4	1	Ni	0.30	
	1	Pd	-0.05	
	2	Pd	-0.05	
	3	Pd	-0.10	
	4	Pd	-0.10	
Pd_5	1	Pd	0.09	
	2	Pd	0.09	
	3	Pd	0.09	
	4	Pd	-0.14	
	5	Pd	-0.14	

Table S7: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 6$

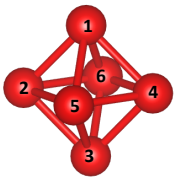
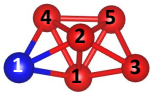
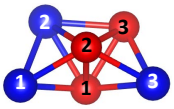
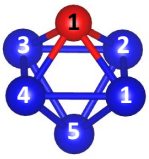
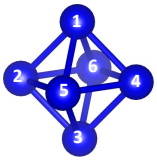
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Ni_6	1	Ni	-0.001	
	2	Ni	-0.002	
	3	Ni	0.002	
	4	Ni	-0.001	
	5	Ni	-0.001	
	6	Ni	0.002	
Ni_5Pd_1	1	Ni	0.17	
	2	Ni	0.17	
	3	Ni	-0.07	
	4	Ni	0.05	
	5	Ni	-0.03	
	1	Pd	-0.29	
Ni_3Pd_3	1	Ni	0.25	
	2	Ni	0.25	
	3	Ni	0.15	
	1	Pd	-0.22	
	2	Pd	-0.17	
	3	Pd	-0.26	
Ni_1Pd_5	1	Ni	0.28	
	1	Pd	-0.06	
	2	Pd	-0.07	
	3	Pd	-0.06	
	4	Pd	-0.07	
	5	Pd	-0.02	
Pd_6	1	Pd	-0.01	
	2	Pd	-0.01	
	3	Pd	-0.01	
	4	Pd	-0.01	
	5	Pd	0.02	
	6	Pd	0.02	

Table S8: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 7$

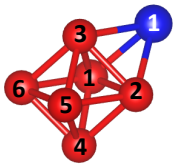
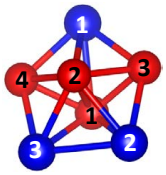
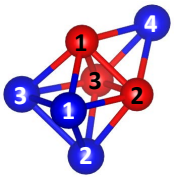
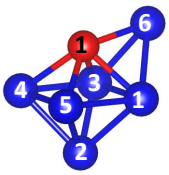
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Ni_7	1	Ni	0.04	
	2	Ni	0.03	
	3	Ni	0.04	
	4	Ni	-0.01	
	5	Ni	-0.06	
	6	Ni	-0.02	
	7	Ni	-0.01	
Ni_6Pd_1	1	Ni	0.08	
	2	Ni	0.10	
	3	Ni	0.11	
	4	Ni	0.00	
	5	Ni	-0.02	
	6	Ni	-0.01	
	1	Pd	-0.26	
Ni_4Pd_3	1	Ni	0.26	
	2	Ni	0.26	
	3	Ni	0.08	
	4	Ni	0.09	
	1	Pd	-0.25	
	2	Pd	-0.22	
	3	Pd	-0.22	
Ni_3Pd_4	1	Ni	0.25	
	2	Ni	0.25	
	3	Ni	0.25	
	1	Pd	-0.13	
	2	Pd	-0.14	
	3	Pd	-0.14	
	4	Pd	-0.34	
Ni_1Pd_6	1	Ni	0.35	
	1	Pd	0.004	
	2	Pd	-0.02	
	3	Pd	0.002	
	4	Pd	-0.07	
	5	Pd	-0.07	
	6	Pd	-0.19	

Table S9: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 7 - 8$

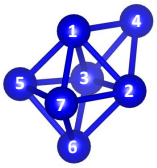
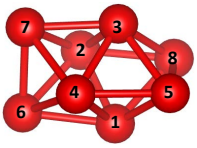
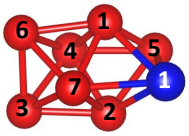
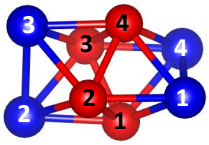
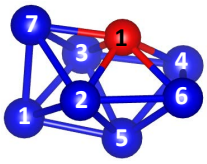
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Pd_7	1	Pd	0.05	
	2	Pd	0.03	
	3	Pd	0.05	
	4	Pd	-0.06	
	5	Pd	-0.04	
	6	Pd	-0.02	
	7	Pd	-0.02	
Ni_8	1	Ni	0.03	
	2	Ni	0.03	
	3	Ni	0.04	
	4	Ni	0.03	
	5	Ni	-0.03	
	6	Ni	-0.04	
	7	Ni	-0.03	
	8	Ni	-0.03	
Ni_7Pd_1	1	Ni	0.09	
	2	Ni	0.09	
	3	Ni	-0.03	
	4	Ni	0.02	
	5	Ni	0.03	
	6	Ni	-0.03	
	7	Ni	0.08	
	1	Pd	-0.25	
Ni_4Pd_4	1	Ni	0.22	
	2	Ni	0.21	
	3	Ni	0.21	
	4	Ni	0.22	
	1	Pd	-0.22	
	2	Pd	-0.22	
	3	Pd	-0.22	
	4	Pd	-0.22	
Ni_1Pd_7	1	Ni	0.35	
	1	Pd	-0.05	
	2	Pd	-0.02	
	3	Pd	-0.03	
	4	Pd	-0.10	
	5	Pd	0.04	
	6	Pd	-0.10	
	7	Pd	-0.09	

Table S10: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 8 - 9$

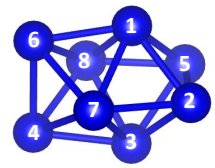
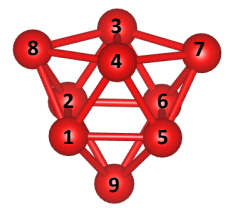
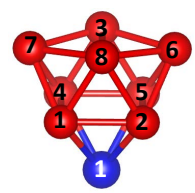
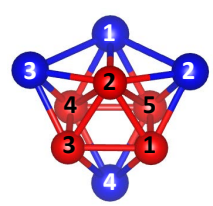
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Pd_8	1	Pd	0.03	
	2	Pd	-0.03	
	3	Pd	0.03	
	4	Pd	-0.03	
	5	Pd	-0.03	
	6	Pd	-0.03	
	7	Pd	0.03	
	8	Pd	0.04	
Ni_9	1	Ni	0.02	
	2	Ni	0.02	
	3	Ni	0.03	
	4	Ni	0.03	
	5	Ni	0.03	
	6	Ni	0.03	
	7	Ni	-0.06	
	8	Ni	-0.04	
	9	Ni	-0.05	
Ni_8Pd_1	1	Ni	0.08	
	2	Ni	0.08	
	3	Ni	0.02	
	4	Ni	0.08	
	5	Ni	0.08	
	6	Ni	-0.03	
	7	Ni	-0.04	
	8	Ni	0.02	
	1	Pd	-0.28	
Ni_5Pd_4	1	Ni	0.13	
	2	Ni	0.22	
	3	Ni	0.12	
	4	Ni	0.20	
	5	Ni	0.20	
	1	Pd	-0.16	
	2	Pd	-0.23	
	3	Pd	-0.22	
	4	Pd	-0.27	

Table S11: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 9 - 10$

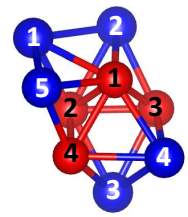
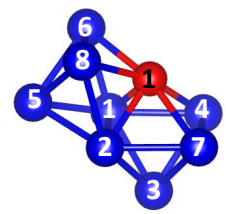
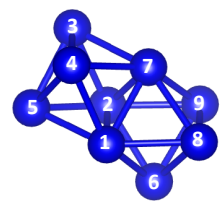
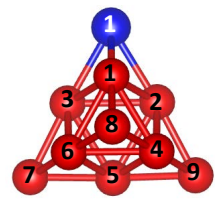
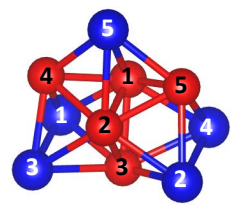
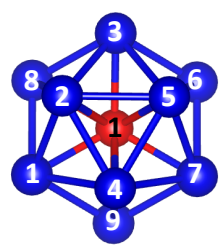
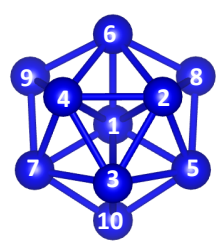
Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Ni_4Pd_5	1	Ni	0.27	
	2	Ni	0.24	
	3	Ni	0.19	
	4	Ni	0.20	
	1	Pd	-0.13	
	2	Pd	-0.21	
	3	Pd	-0.20	
	4	Pd	-0.15	
	5	Pd	-0.19	
Ni_1Pd_8	1	Ni	0.37	
	1	Pd	0.01	
	2	Pd	0.003	
	3	Pd	-0.04	
	4	Pd	-0.08	
	5	Pd	-0.04	
	6	Pd	-0.08	
	7	Pd	-0.07	
	8	Pd	-0.08	
Pd_9	1	Pd	0.02	
	2	Pd	0.02	
	3	Pd	-0.008	
	4	Pd	-0.01	
	5	Pd	-0.01	
	6	Pd	-0.007	
	7	Pd	0.02	
	8	Pd	-0.01	
	9	Pd	-0.01	
Ni_{10}	1	Ni	0.08	
	2	Ni	0.08	
	3	Ni	0.08	
	4	Ni	0.08	
	5	Ni	0.08	
	6	Ni	-0.12	
	7	Ni	0.07	
	8	Ni	-0.12	
	9	Ni	-0.12	
	10	Ni	-0.12	

Table S12: Bader charge distributions calculated for pure, monosubstituted and 50:50 composition for Ni-Pd nanoalloys, $N = m + n = 10$

Composition	Numbering of the atoms	Type of atom	Bader charge	Structure
Ni_9Pd_1	1	Ni	0.13	
	2	Ni	0.14	
	3	Ni	0.14	
	4	Ni	0.08	
	5	Ni	0.08	
	6	Ni	0.08	
	7	Ni	-0.10	
	8	Ni	-0.11	
	9	Ni	-0.11	
	1	Pd	-0.33	
Ni_5Pd_5	1	Ni	0.22	
	2	Ni	0.22	
	3	Ni	0.21	
	4	Ni	0.17	
	5	Ni	0.17	
	1	Pd	-0.17	
	2	Pd	-0.17	
	3	Pd	-0.17	
	4	Pd	-0.17	
	5	Pd	-0.29	
Ni_1Pd_9	1	Ni	0.41	
	1	Pd	-0.07	
	2	Pd	-0.002	
	3	Pd	-0.07	
	4	Pd	0.007	
	5	Pd	0.003	
	6	Pd	-0.07	
	7	Pd	-0.06	
	8	Pd	-0.07	
	9	Pd	-0.07	
Pd_{10}	1	Pd	0.09	
	2	Pd	0.02	
	3	Pd	0.02	
	4	Pd	0.01	
	5	Pd	-0.004	
	6	Pd	-0.008	
	7	Pd	-0.004	
	8	Pd	-0.04	
	9	Pd	-0.04	
	10	Pd	-0.04	