Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental material for The electronic structure of Ni-Pd particles: a clue to their special catalytic properties†

Linn Leppert,[a,b], Rhett Kempe,[c] and Stephan Kümmel[a‡]

In this supplemental material we discuss the effects of the exchange correlation (xc) functional approximation in greater detail and present the cluster structures and magnetic moments.

We start by discussing the influence of the xc functional approximation on the structure of 13-atom Ni_xPd_{13-x} ($x = 0-13$) clusters. Starting point of our considerations are three stable Pd_{13} clusters taken from Ref. 1 which are depicted in Fig. 1: an icosahedral cluster Pd_{13}(ico), a bilayered geometry Pd_{13}(bi) and a cluster with c3v symmetry Pd_{13}(c3v). For the clusters Ni_1Pd_{12} and Ni_2Pd_{11} we determined further stable geometries by simulated annealing. In Fig. 1, these geometries are labeled Ni_1Pd_{11}(ico), Ni_1Pd_{12}(geo4), Ni_1Pd_{12}(bcc), Ni_2Pd_{11}(ico), Ni_2Pd_{11}(geo2) and Ni_2Pd_{11}(geo3). For Ni_{13} two structures are reported in the literature: the icosahedron, which is the established ground state structure, and a bilayered structure with a binding energy around 50 meV higher than that of the icosahedron[2]. The binding energies of these systems as calculated with the PBE0 xc functional[3] used in the generalized Kohn-Sham framework[4] can be found in Tab. 1. The energetic ordering of the isomers is different when, e.g., the PBE[5] functional is used. This,

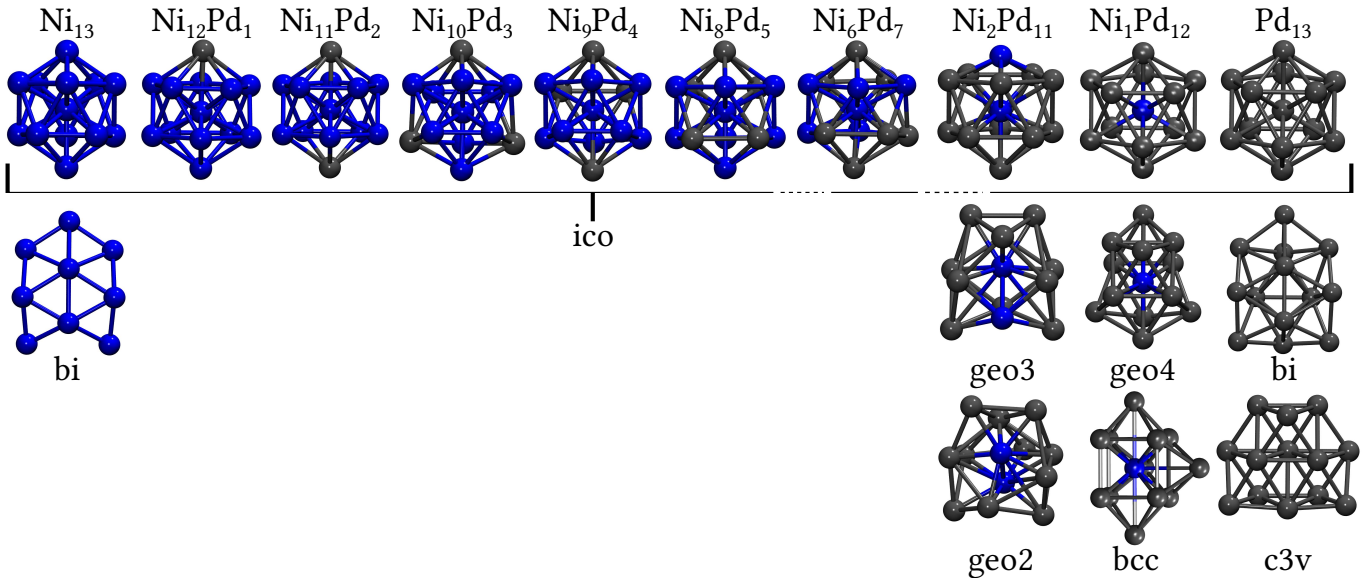

Figure 1 The structures of the 13-atom Ni_xPd_{13-x} ($x = 0-13$) clusters that were used in this work.

however, is no reason for concern in the present study as we are interested in electronic properties of Ni-Pd systems that are independent of the specific geometry and can be generalized over a wide size range as shown in the main manuscript. Furthermore, as argued in the main manuscript, studying the clusters' magnetic properties allows for a sensitive test of the xc functional.

[0a] *Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth, Germany*
[0b] *Present address: Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[0c] *Inorganic Chemistry II, University of Bayreuth, 95440 Bayreuth, Germany*
[0‡] Corresponding author: stephan.kuemmel@uni-bayreuth.de

Table 1 PBE0 binding energies and magnetic moments of Ni_{13}, Ni_2Pd_{11}, Ni_1Pd_{12} and Pd_{13} isomers. The binding energy is defined as $xE_{Ni} + (13-x)E_{Pd} - E_{Ni_xPd_{13-x}}$.

system	structure	binding energy (eV)	magnetic moment (μ_B)
Ni_{13}	ico	1.992	16
	bi	1.944	14
Ni_2Pd_{11}	ico	1.985	8
	geo2	2.001	8
	geo3	2.006	8
Ni_1Pd_{12}	ico	1.937	8
	bcc	1.898	8
	geo4	1.930	8
Pd_{13}	ico	1.815	8
	bi	1.820	6
	c3v	1.841	6

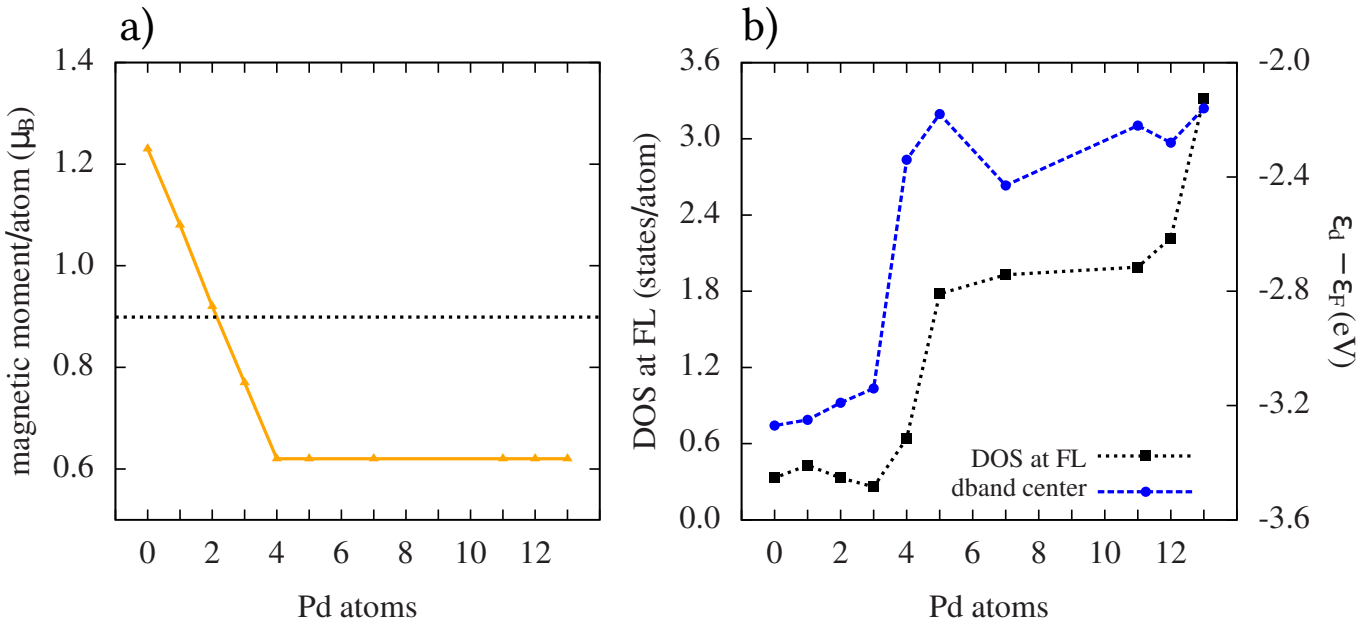

Figure 2 a) spin magnetic moment per atom of icosahedral 13-atom clusters as calculated with PBE0. The black dotted line marks the magnetic moment of Ni bulk calculated using the HSE06 functional. b) d-band center with respect to Fermi level (FL) and density of states at the Fermi level, obtained by integrating the total density of states from the Fermi level to 1 eV below it. All numbers refer to the "unrelaxed" icosahedral 13-atom clusters.

We determined the magnetic moment of all clusters by performing a set of geometry optimizations with fixed spin magnetic moments between 0 and 10 for $x = 0-2,6,8,9$ and between 8 and 18 for $x = 10-13$. The resulting magnetic moments per atom are shown as orange triangles in Fig. 2a) for the icosahedral clusters. The moments of all other isomers can be found in Tab. 1. Icosahedral Ni_xPd_{13-x} clusters with $x = 0-9$ have magnetic moments of $8\,\mu_B$, whereas for $x = 10-13$ the moment increases by $2\,\mu_B$ per Ni atom up to $16\,\mu_B$ for Ni_{13}. Note that this value, which is in excellent agreement with a recent experiment[6], is not obtained when the xc functional is approximated by a generalized gradient expression such as PBE. In

contrast, PBE results in a magnetic moment of 8 μ_B which is even lower than the moment of bulk Ni. This observation not only emphasizes the importance of choosing a proper xc functional approximation for these systems, but also independently confirms that the icosahedral geometry is most likely the ground state of Ni_{13}. A Mulliken population analysis relates the size dependence of the magnetic moment to considerable charge transfer from Ni to Pd. For clusters with $x = 0-9$ the local spin magnetic moments of Pd are reduced by charge transfer from Ni to Pd. The reduced local moments of Pd thus compensate the Ni local moments and the total spin moments remains at 8 μ_B. For $x > 9$ not enough Pd atoms are available for compensation any more and the spin moment begins to build up until it reaches a maximum of 16 μ_B in Ni_{13}.

The importance of choosing an xc functional that at least partly cancels the spurious effects of the self-interaction error becomes evident in several calculations. As a first example we mention that the *d*-band centers of Ni_{13} and Pd_{13} calculated with PBE are 1.4 eV and 1.6 eV below the Fermi level, respectively. This means that PBE not only predicts a *d*-band center much closer to the Fermi level than PBE0, but also reverses the energetic ordering of the *d*-band centers of Ni_{13} and Pd_{13}. Second, for the Pd_{13}(bi) cluster's DOS, see Methods section of main manuscript, using the PBE xc functional results in a value of 5.6 states/atom, whereas PBE0 and ωPBE give 3.5 and 3.4 states/atom, respectively. The DOS at the Fermi level shows a similar behaviour as the d-band center as a function of Ni-Pd ratio, as can be seen in Fig. 2b). There is no minimum for the Ni-Pd ratio for which a maximum of E_{diss} is observed.

To determine hydrogen binding on mixed Ni-Pd surfaces, we constructed a mixed Ni-Pd surface model with a Ni:Pd ratio of 1:1. In this surface slab, each surface layer consists of two Ni and two Pd atoms as can be seen in Fig. 3.

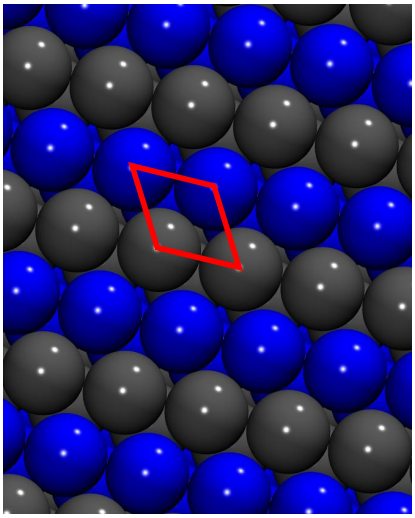

Figure 3 Ni-Pd(111) surface with Ni:Pd ratio of 1:1. The red rhombus marks the atoms in the top layer of one unit cell.

Finally, we report the optimized coordinates of our 13-atom (Tab. 2) and 38-atom (Tab. 3) clusters.

Pd_{13}	**bilayer**			**ico**			**c3v**		
element	x	y	z	x	y	z	x	y	z
Pd	1.0325	-0.0001	1.0515	0.0001	0.0000	0.0000	-1.3731	0.7232	1.2747
Pd	1.8986	-0.0003	-1.7293	2.3563	1.3881	-0.1063	-0.0253	2.9908	1.3003
Pd	-0.2610	2.3157	1.4313	2.3472	-1.4033	-0.1076	-2.5868	-1.5988	1.0590
Pd	-1.6544	0.0002	1.1521	1.5351	-0.0072	2.1187	-0.0060	0.0443	-1.0198
Pd	-0.2616	-2.3156	1.4316	-1.3345	0.0020	2.2464	1.2789	2.4089	-0.9330
Pd	-2.5714	-2.2345	0.0467	0.0605	-2.2157	1.3564	-1.3314	-2.2905	-1.1607
Pd	2.0199	2.1618	-0.0833	1.3342	-0.0025	-2.2466	-1.3828	2.3659	-0.8819
Pd	-2.5710	2.2351	0.0465	0.0706	2.2127	1.3606	1.3637	0.7600	1.2303
Pd	-2.6050	0.0003	-1.4290	-0.0763	-2.2126	-1.3606	2.6724	-1.5140	1.1078
Pd	2.0192	-2.1624	-0.0831	-2.3466	1.4040	0.1096	0.0371	-1.6330	1.1827
Pd	-0.3252	1.3614	-1.0651	-2.3558	-1.3889	0.1049	1.3713	-2.2885	-1.0664
Pd	-0.3256	-1.3611	-1.0649	-0.0561	2.2157	-1.3567	2.6784	0.0370	-1.0411
Pd	3.6048	-0.0004	0.2950	-1.5347	0.0077	-2.1188	-2.6965	-0.0053	-1.0517
Ni_1Pd_{12}	**ico**			**geo4**			**bcc**		
element	x	y	z	x	y	z	x	y	z
Pd	0.5138	-2.4900	-0.8088	0.0126	-1.3640	-2.3846	1.9888	1.3922	-0.4130
Pd	1.9884	1.5166	0.4563	1.3616	2.0544	-0.0284	-0.0021	1.4267	1.6667
Pd	-0.5084	2.4921	0.8051	-0.0017	2.1770	2.2957	-2.2575	0.0000	1.8582
Pd	0.5217	0.5594	2.5555	1.4368	0.0004	1.7822	-0.0020	-1.4266	1.6668
Pd	-1.9817	0.3173	1.5606	-1.4367	-0.0031	1.7819	-1.9878	-1.3923	-0.4175
Pd	1.9804	-0.3136	-1.5638	2.2050	0.0049	-1.5857	2.2528	0.0001	1.8635
Pd	0.4563	1.9432	-1.7673	-1.3512	2.0647	-0.0382	-1.9878	1.3922	-0.4176
Pd	-2.0213	1.1441	-1.0299	-2.2055	-0.0024	-1.5850	0.0027	1.4084	-2.3098
Pd	-0.4565	-1.9432	1.7674	0.0019	-2.1804	2.2923	0.0006	-3.2001	-0.3013
Pd	-0.5267	-0.5598	-2.5541	-0.0132	1.3678	-2.3827	0.0004	3.2000	-0.3014
Pd	-1.9852	-1.5208	-0.4531	-1.3613	-2.0545	-0.0315	0.0028	-1.4085	-2.3097
Pd	2.0199	-1.1443	1.0312	1.3517	-2.0648	-0.0413	1.9889	-1.3922	-0.4129
Ni	0.0004	0.0002	-0.0001	0.0003	0.0001	-0.1750	0.0004	0.0000	-0.3165
Ni_2Pd_{11}	**ico**			**geo2**			**geo3**		
element	x	y	z	x	y	z	x	y	z
Pd	-1.4160	0.4827	2.2007	-1.1061	0.0292	-2.1323	1.4604	-2.6196	-0.0185
Pd	0.6467	2.1196	1.3489	1.5920	0.1935	1.9024	-1.5049	-2.4516	0.7280
Pd	1.1369	-0.4316	2.2371	-2.2813	-1.2662	-0.0021	-0.4706	-1.4910	-1.5463
Pd	-1.6964	1.9605	-0.0486	-0.1844	-2.3993	-1.3553	-1.7928	0.3725	1.6743
Pd	1.4472	-2.0822	0.0491	1.5941	0.1919	-1.8997	0.8982	1.4669	1.5694
Pd	-0.9302	-2.1015	1.4227	-1.1092	0.0285	2.1308	-2.8454	-0.6177	-0.5572
Pd	-0.9204	-2.1549	-1.3457	-0.1878	-2.4003	1.3538	-1.2335	2.8251	0.7587
Pd	-1.3928	0.4005	-2.2422	-1.3400	1.6757	-0.0012	1.8707	-0.0462	-0.7798
Pd	0.6615	2.0648	-1.4179	0.0912	2.4218	-2.1680	0.9970	2.5001	-0.8744
Pd	2.4842	0.5536	0.0034	0.0870	2.4221	2.1678	2.5744	-0.6818	1.6637

Pd	1.1527	-0.5258	-2.2022	2.1204	-1.7532	0.0028	0.3682	0.7323	-2.8050
Ni	0.0910	-0.0340	-0.0001	1.1662	1.8211	0.0008	-0.8191	0.8148	-0.6263
Ni	-2.2101	-0.4860	-0.0070	0.1511	-0.2626	0.0008	0.2251	-0.7923	0.9705
Ni_6Pd_7	**ico**			**Ni_8Pd_5**	**ico**				
element	x	y	z	x	y	z			
Pd	2.2598	-1.4314	-0.1247	Pd	1.4428	0.0658	2.1265		
Pd	1.4472	0.1157	2.0841	Pd	0.0121	-2.2166	1.3028		
Pd	-1.3287	0.1319	2.1951	Pd	1.3257	-0.0407	-2.2104		
Pd	-0.0516	-2.2449	1.3123	Pd	-0.0502	2.2286	-1.2801		
Pd	1.2332	0.0032	-2.2904	Pd	-1.5376	-0.0272	-2.0629		
Pd	-0.0738	2.2667	-1.1553	Ni	-0.0088	0.0157	-0.0217		
Pd	-1.5211	-0.0443	-2.0903	Ni	2.0840	1.2738	-0.0693		
Ni	0.0154	-0.0570	-0.0499	Ni	2.0500	-1.2901	-0.0747		
Ni	2.1194	1.2393	-0.1468	Ni	-1.1488	-0.0031	2.0984		
Ni	0.0834	1.9929	1.3026	Ni	0.0715	2.0977	1.2927		
Ni	0.0779	-1.9806	-1.2043	Ni	-0.0745	-2.0743	-1.2917		
Ni	-2.1304	1.2765	0.0711	Ni	-2.0776	1.2733	0.1093		
Ni	-2.1306	-1.2680	0.0966	Ni	-2.0885	-1.3028	0.0813		
Ni_9Pd_4	**ico**			**$Ni_{10}Pd_3$**	**ico**				
element	x	y	z	x	y	z			
Pd	0.0541	-2.1818	1.3733	Pd	1.3275	-0.0500	-2.2234		
Pd	1.3260	-0.0569	-2.2257	Pd	-0.0556	2.2592	-1.2687		
Pd	-0.0489	2.2517	-1.2318	Pd	-1.5258	-0.0456	-2.0940		
Pd	-1.5182	-0.0489	-2.0986	Ni	-0.0008	0.0130	-0.0336		
Ni	-0.0003	0.0279	-0.0091	Ni	2.0466	1.2543	-0.0795		
Ni	2.0484	1.2876	-0.0857	Ni	2.0262	-1.2684	-0.0679		
Ni	2.0393	-1.2937	-0.0800	Ni	1.3152	-0.0554	2.0369		
Ni	1.3580	-0.0120	1.9914	Ni	-1.1299	-0.0477	2.1447		
Ni	-1.1745	-0.0051	2.1049	Ni	0.0538	-2.0294	1.3252		
Ni	0.0661	2.0738	1.3213	Ni	0.0656	2.0102	1.2896		
Ni	-0.0623	-2.0585	-1.2583	Ni	-0.0601	-2.0435	-1.2589		
Ni	-2.0410	1.2987	0.0984	Ni	-2.0380	1.2632	0.1095		
Ni	-2.0466	-1.2828	0.0999	Ni	-2.0247	-1.2600	0.1202		
$Ni_{11}Pd_2$	**ico**			**$Ni_{12}Pd_1$**	**ico**				
element	x	y	z	x	y	z			
Pd	1.4815	-0.0058	2.1099	Pd	1.4672	-0.0347	2.0889		
Pd	-1.4816	0.0058	-2.1099	Ni	-1.2021	0.0164	2.1067		
Ni	0.0000	0.0000	0.0000	Ni	0.0116	-2.0624	1.2469		
Ni	2.0681	1.2768	-0.1191	Ni	1.2505	0.0017	-2.1240		
Ni	2.0601	-1.2905	-0.1221	Ni	0.0408	2.0674	1.2681		
Ni	-1.2358	0.0007	2.1163	Ni	-0.0342	-2.1190	-1.2588		
Ni	0.0218	-2.0228	1.3007	Ni	-2.0533	1.2919	0.1266		
Ni	1.2358	-0.0007	-2.1163	Ni	-2.0911	-1.2744	0.1312		
Ni	0.0319	2.0205	1.3059	Ni	-0.0495	2.1063	-1.2496		

Ni	-0.0319	-2.0205	-1.3059	Ni	-1.3763	-0.0087	-2.0447		
Ni	-2.0601	1.2905	0.1221	Ni	-0.0379	0.0027	-0.0494		
Ni	-2.0680	-1.2768	0.1191	Ni	2.0353	1.2901	-0.1247		
Ni	-0.0217	2.0228	-1.3007	Ni	2.0391	-1.2773	-0.1172		
Ni_{13}	**ico**			**bilayer**					
element	x	y	z	x	y	z			
Ni	-0.0065	0.0000	0.0027	0.1031	-1.4148	-1.1250			
Ni	1.9647	1.2258	-0.0782	-2.1106	-1.0032	-0.4044			
Ni	1.9575	-1.2360	-0.0799	-2.3251	1.1123	0.7505			
Ni	1.3164	-0.0054	1.9430	-1.3581	-0.8898	1.7235			
Ni	-1.1097	0.0001	2.0323	0.8584	-1.3174	0.9937			
Ni	0.0609	-2.0362	1.2490	0.0434	0.9924	1.1111			
Ni	1.1169	-0.0015	-2.0360	-0.7236	0.8916	-1.0329			
Ni	0.0727	2.0329	1.2538	-0.8592	-2.8751	0.4709			
Ni	-0.0661	-1.9952	-1.2349	-1.0234	2.9539	0.1811			
Ni	-1.9531	1.2330	0.0805	2.4276	-1.6552	-0.7484			
Ni	-1.9612	-1.2218	0.0767	2.2951	0.4663	0.3708			
Ni	-0.0544	1.9981	-1.2311	1.5373	0.3580	-1.7570			
Ni	-1.3380	0.0063	-1.9779	1.1351	2.3809	-0.5339			

Table 2 xyz-coordinates in Ångström of the 13-atom clusters depicted in Fig. 1.

element	x	y	z
Pd	1.3273	1.3171	0.0605
Pd	3.9501	1.6061	-0.0030
Pd	1.5847	3.9827	0.0807
Pd	-1.4131	1.3889	-0.0007
Pd	-4.0749	1.1308	-0.0830
Pd	-0.9872	4.1400	-0.1030
Pd	-1.4232	-1.4132	0.1257
Pd	-4.1047	-1.4743	0.0539
Pd	-1.3237	-4.0444	0.1255
Pd	1.3963	-1.4392	0.0057
Pd	3.9839	-1.1837	-0.1298
Pd	1.3458	-4.0398	-0.1400
Pd	-0.0247	-0.0142	1.9902
Pd	2.7463	-0.0212	2.0635
Pd	-2.8254	0.0692	2.0769
Pd	-0.0484	2.7627	2.0596
Pd	0.1220	-2.7874	2.1065
Pd	2.6411	2.5602	2.2421
Pd	-2.7306	2.8445	1.6990
Pd	-2.6029	-2.6661	2.1169
Pd	2.8667	-2.7102	1.8387
Pd	-0.0126	-0.0199	-1.9443
Pd	2.6765	0.1132	-2.0814
Pd	-2.6878	-0.1080	-2.0481
Pd	0.1213	2.6722	-2.0388
Pd	-0.1507	-2.7044	-2.0346
Pd	2.8166	2.7563	-2.0431
Pd	-2.5516	2.6263	-1.9512
Pd	-2.7452	-2.8155	-1.9411
Pd	2.5980	-2.5804	-2.2077
Pd	1.1176	1.1556	4.1131
Pd	-1.6793	1.5895	4.0276
Pd	-1.2947	-1.0047	3.9546
Pd	1.4676	-1.6041	3.9451
Pd	1.3380	1.4047	-4.1034
Pd	-1.2348	1.3025	-4.0590
Pd	-1.4860	-1.4327	-3.9764
Pd	1.2863	-1.3332	-4.0375

Table 3 xyz-coordinates in Ångström of cuboctahedral Pd_{38}, Ni_5Pd_{33} and Ni_{38}. To construct Ni_5Pd_{33} the five Pd atoms that are marked by bold letters were replaced by Ni.

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