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

SUPPORTING INFORMATION

Atomic Order, Electronic Structure and Thermodynamic Stability of Nickel Aluminate

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Formation energies for phase diagram

Table S1. Formation energies of NiO, Al_2O_3 and $NiAl_2O_4$ using experimental data and different functionals. The tetragonal $P4_122$ structure for $NiAl_2O_4$, trigonal R-3m structure for NiO (antiferromagnetic) and trigonal R-3c structure for Al_2O_3 have been used.

	NiO (kJ mol^{-1})	Al_2O_3 (kJ mol^{-1})	$NiAl_2O_4$ (kJ mol^{-1})
PBE + U (U = 2.8 eV)	-237.9	-1663.7	-1920.2
PBE + U (U = 6.4 eV)	-242.4	-1655.0	-1920.6
OptB88-vdW	-200.5	-1722.9	-1923.3
Experimental	-239.7	-1675.7	-1920.5

Table S2. Experimental and calculated formation energy ($\Delta H_f^{NiAl_2O_4}$) of tetragonal $P4_122$ $NiAl_2O_4$ bulk structure using PBE and different van der Waals corrections.

	$\Delta H_f^{NiAl_2O_4}$ (kJ mol^{-1})
PBE	-1654.7
PBE-D2	-1732.5
PBE-D3	-1698.3
PBE-D3BJ	-1693.5

Effective Cluster Interaction

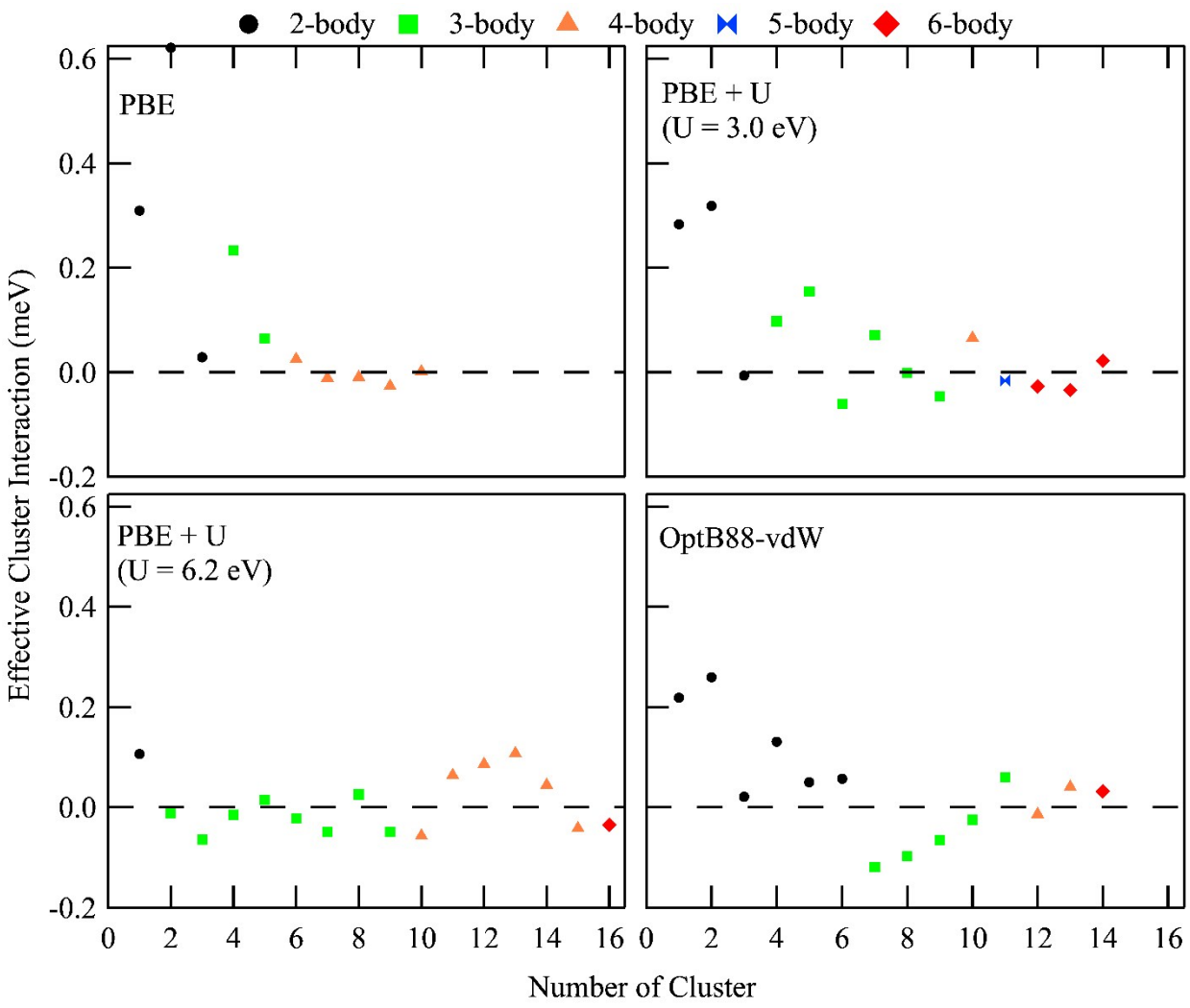

Figure S1. Effective cluster interaction for the clusters generated from cluster expansion of cubic Fd3m structure using 4 unit cells and different functionals. The zero and point cluster terms are not shown.

Fitting of Hubbard U for PBE + U

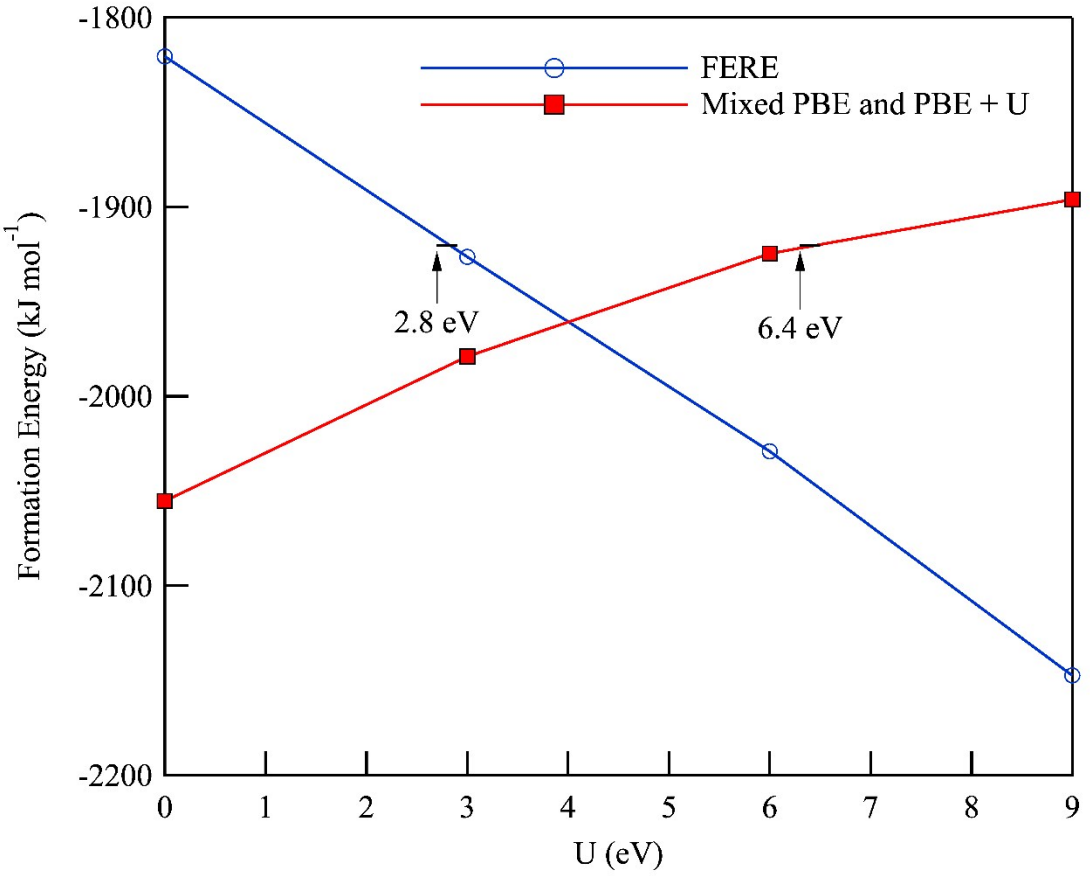

Figure S2. Formation energy of the tetragonal $P4_122$ $NiAl_2O_4$ structure with PBE + U functional using a range of Hubbard U values from 0.0 eV to 9.0 eV. Two methods, FERE and mixed PBE/PBE + U, were used. The use of U = 2.8 eV and U = 6.4 eV correctly reproduced the experimental formation enthalpy of -1920.5 kJ mol^{-1} using FERE and mixed PBE/PBE + U respectively.

Nickel aluminate Fd3m structure to initialize cluster expansion

$NiAl_2O_4$_Fd3m
1.0
0.00000000 4.02500000 4.02500000
4.02500000 0.00000000 4.02500000
4.02500000 4.02500000 0.00000000
O Al Ni
8 4 2
Direct
0.23830000 0.23830000 0.23830000
-0.21490000 0.23830000 0.23830000
0.23830000 -0.21490000 0.23830000
0.23830000 0.23830000 -0.21490000
0.76170000 0.76170000 0.76170000
0.21490000 0.76170000 0.76170000
0.76170000 0.21490000 0.76170000
0.76170000 0.76170000 0.21490000
0.00000000 0.00000000 0.00000000
0.50000000 0.00000000 0.00000000
0.00000000 0.50000000 0.00000000
0.00000000 0.00000000 0.50000000
0.37500000 0.37500000 0.37500000
0.62500000 0.62500000 0.62500000

Nickel aluminate $P4_122$ structure obtained from cluster expansion

$NiAl_2O_4$_$P4_122$
1.0
5.79850021 0.00000000 0.00000000
0.00000000 5.79850021 0.00000000
0.00000000 0.00000000 8.20031764
Al Ni O
8 4 16
Direct
0.00000000 0.25000000 0.00000000
0.00000000 0.75000000 0.50000000
0.75000000 0.00000000 0.25000000
0.25000000 0.00000000 0.75000000
0.25000000 0.25000000 0.37500000
0.25000000 0.75000000 0.12500000
0.75000000 0.25000000 0.62500000
0.75000000 0.75000000 0.87500000
0.50000000 0.25000000 0.00000000
0.50000000 0.75000000 0.50000000
0.75000000 0.50000000 0.25000000
0.25000000 0.50000000 0.75000000
0.25000000 0.48940000 0.99470000
0.25000000 0.51060000 0.50530000
0.75000000 0.48940000 0.00530000
0.75000000 0.51060000 0.49470000
0.51060000 0.75000000 0.25530000
0.51060000 0.25000000 0.24470000
0.48940000 0.75000000 0.74470000
0.48940000 0.25000000 0.75530000
0.75000000 0.98940000 0.49470000
0.75000000 0.01060000 0.00530000
0.25000000 0.98940000 0.50530000
0.25000000 0.01060000 0.99470000
0.01060000 0.25000000 0.75530000
0.01060000 0.75000000 0.74470000
0.98940000 0.25000000 0.24470000
0.98940000 0.75000000 0.25530000

Aluminium oxide R-3c structure

Al_2O_3

1.0

2.38010000 1.37415138 4.33110000

-2.38010000 1.37415138 4.33110000

-0.00000000 -2.74830275 4.33110000

O Al

6 4

Direct

0.55617000 -0.05617000 0.25000000

0.25000000 0.55617000 -0.05617000

0.94383000 0.25000000 -0.44383000

1.44383000 0.05617000 0.75000000

0.75000000 1.44383000 0.05617000

1.05617000 0.75000000 0.44383000

0.14782000 0.14782000 0.14782000

0.35218000 0.35218000 0.35218000

0.85218000 0.85218000 0.85218000

0.64782000 0.64782000 0.64782000

Nickel oxide R-3m structure

NiO

1.0

5.10718611 0.00000000 0.00000000

4.25598843 2.82310335 0.00000000

4.25598843 1.28322879 2.51460461

Ni O

2 2

Direct

0.00000000 0.00000000 0.00000000

0.50000000 0.50000000 0.50000000

0.25000000 0.25000000 0.25000000

0.75000000 0.75000000 0.75000000