

**Supporting Information:**

**Thermodynamics of Sodium-Lead Alloys for  
Negative Electrodes from First-Principles**

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# 1 Structure Characteristics of NaPb Intermetallics.

Table S1: Computed lattice parameters (in Å), space groups, and volume per atom (in Å<sup>3</sup> · atom<sup>-1</sup>) of all Na-Pb intermetallics.

Formula	Space Group	<i>a</i>	<i>b</i>	<i>c</i>	V	Ref.
Pb	<i>Fm</i> $\bar{3}m$	5.028	–	–	31.780	S1
NaPb <sub>3</sub>	<i>Pm</i> $\bar{3}m$	4.941	–	–	30.154	S2
NaPb	<i>I4</i> <sub>1</sub> / <i>acd</i>	10.661	–	18.039	32.035	S3
Na <sub>5</sub> Pb <sub>2</sub>	<i>R</i> $\bar{3}m$	5.546	–	23.224	29.462	S4
Na <sub>9</sub> Pb <sub>4</sub>	<i>P6</i> <sub>3</sub> / <i>mmc</i>	5.513	–	30.009	30.378	S5
Na <sub>13</sub> Pb <sub>5</sub>	<i>P6</i> <sub>3</sub> / <i>mmc</i>	5.551	–	40.439	29.977	S4
Na <sub>15</sub> Pb <sub>4</sub>	<i>I</i> $\bar{4}3d$	13.338	–	–	31.221	S6
Na	<i>Im</i> $\bar{3}m$	4.192	–	–	36.837	S7

Table S2: Experimental lattice parameters (in Å), space groups, and deviation from computed lattice parameters ( $\Delta$  in %) of all Na-Pb intermetallics.

Formula	Space Group	<i>a</i>	<i>b</i>	<i>c</i>	$\Delta$	Ref.
Pb	<i>Fm</i> $\bar{3}m$	4.950	–	–	+1.58	S1
NaPb <sub>3</sub>	<i>Pm</i> $\bar{3}m$	4.888	–	–	+1.08	S2
NaPb	<i>I4</i> <sub>1</sub> / <i>acd</i>	10.580	–	17.746	+1.21	S3
Na <sub>5</sub> Pb <sub>2</sub>	<i>R</i> $\bar{3}m$	5.540	–	23.150	–0.43	S4
Na <sub>9</sub> Pb <sub>4</sub>	<i>P6</i> <sub>3</sub> / <i>mmc</i>	5.470	–	30.410	–0.27	S5
Na <sub>13</sub> Pb <sub>5</sub>	<i>P6</i> <sub>3</sub> / <i>mmc</i>	5.510	–	40.390	+0.43	S4
Na <sub>15</sub> Pb <sub>4</sub>	<i>I</i> $\bar{4}3d$	13.020	–	–	+2.44	S6
Na	<i>Im</i> $\bar{3}m$	4.300	–	–	–2.51	S7

## 2 Spin-orbit coupling effects

Since Pb is a heavy element, spin-orbit effects might be present in the system. Using the determined ground state structures on the convex hull, we compared the differences between our PBE calculations and the spin-orbit coupling (SOC)-included calculations (Figure S1). These SOC effects also include the zeroth-order-regular approximation that accounts for the relativistic mass correction in the SOC operator. There is an average of –15.6 meV/atom difference between the SOC and PBE calculations. This difference is well within the range of DFT formation energy errors,<sup>S8,S9</sup> and the convex hull points were unaffected. Therefore,

we do not expect the inclusion of SOC effects to significantly change our results and have elected to perform the rest of our calculations without the inclusion of SOC effects.

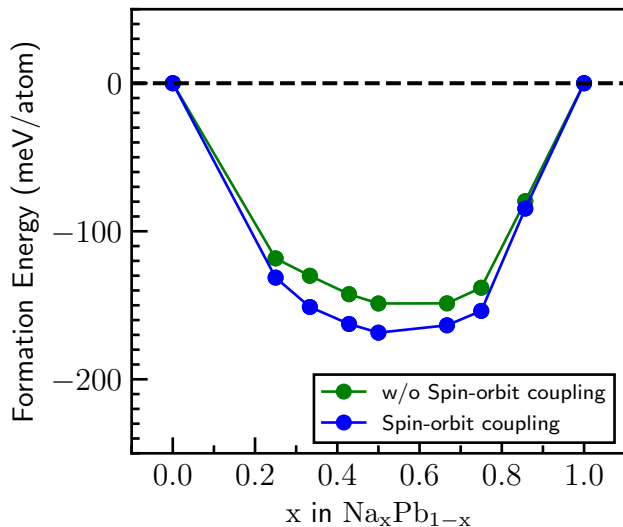


Figure S1: Formation energies of the ground state FCC orderings for the PBE calculations (green) and the PBE-SOC calculations (blue). The average difference between the formation energies obtained with the PBE-SOC and PBE calculations is  $-15.6$  meV/atom.

### 3 Cluster Expansion Coefficients

The 33 fitted effective cluster interactions (ECIs) are displayed in Table S3 and plotted in Figure S3. A negative ECI indicates energetically favorable interactions between Na and Pb for clusters while a positive ECI indicates unfavourable interactions between atoms of similar species.

Table S3: Effective cluster interactions (ECIs in meV) values of the Point, Pair, Triplet, and Quadruplet terms. Cell  $[0, 0, 0]$  is the reference cell. M refers to the multiplicity of each cluster. Maximum (Max.) and Minimum (Min.) cluster lengths are in Å.

Index	Cluster Index	Cluster type	Cell	M	Min.	Max.	ECI	ECI/M
0	0	Empty	-	1	0.000	0.000	-113.436	-113.436
1	1	Point	$[0, 0, 0]$	1	0.000	0.000	-14.220	-14.220
2	2	Pair	$[0, 0, 0][0, 1, 0]$	6	3.500	3.500	119.944	19.991
3	3	Pair	$[0, 0, 0][1, -1, -1]$	3	4.950	4.950	-1.687	-0.562
4	4	Pair	$[0, 0, 0][1, -2, 1]$	12	6.062	6.062	-11.092	-0.924
5	5	Pair	$[0, 0, 0][0, 2, 0]$	6	7.000	7.000	6.452	1.075
6	7	Pair	$[0, 0, 0][3, -1, -1]$	4	8.574	8.574	1.773	0.443
7	10	Pair	$[0, 0, 0][0, 3, 0]$	6	10.501	10.501	-2.864	-0.477
8	14	Triplet	$[0, 0, 0][0, 0, 1][0, 1, 0]$	8	3.500	3.500	9.574	1.197
9	15	Triplet	$[0, 0, 0][0, 0, 1][1, -1, 1]$	12	3.500	4.950	10.437	0.870
10	16	Triplet	$[0, 0, 0][0, 0, 1][1, 0, 1]$	24	3.500	6.062	-12.251	-0.510
11	17	Triplet	$[0, 0, 0][0, 1, 0][1, -1, 1]$	24	3.500	6.062	-18.552	-0.773
12	18	Triplet	$[0, 0, 0][0, 1, 1][1, 1, 0]$	24	3.500	6.062	4.501	0.188
13	20	Triplet	$[0, 0, 0][0, 1, -2][0, 2, -1]$	8	6.062	6.062	-2.336	-0.292
14	23	Triplet	$[0, 0, 0][0, 0, 1][0, 2, -1]$	48	3.500	7.000	24.069	0.501
15	24	Triplet	$[0, 0, 0][0, 1, 1][2, 0, 0]$	12	6.062	7.000	-6.514	-0.543
16	25	Triplet	$[0, 0, 0][0, 0, 2][0, 2, 0]$	8	7.000	7.000	-1.651	-0.206
17	28	Triplet	$[0, 0, 0][0, 1, -2][1, -1, -2]$	48	6.062	7.827	5.966	0.124
18	29	Triplet	$[0, 0, 0][0, 1, -1][2, 0, 0]$	24	3.500	7.827	7.520	0.313
19	31	Triplet	$[0, 0, 0][1, -2, 2][2, -2, 1]$	24	3.500	7.827	-3.592	-0.150
20	34	Quadruplet	$[0, 0, 0][0, 0, 1][0, 1, 0][1, 0, 0]$	2	3.500	3.500	1.178	0.589
21	35	Quadruplet	$[0, 0, 0][0, 1, -1][0, 1, 0][1, 0, 0]$	12	3.500	4.950	6.423	0.535
22	37	Quadruplet	$[0, 0, 0][0, 0, 1][1, 0, 0][1, 0, 1]$	12	3.500	6.062	6.600	0.550
23	40	Quadruplet	$[0, 0, 0][0, 0, 1][0, 1, -1][1, -1, 0]$	24	3.500	6.062	4.028	0.168
24	42	Quadruplet	$[0, 0, 0][0, 1, 0][1, -1, 1][1, 0, 1]$	6	3.500	6.062	2.417	0.403
25	44	Quadruplet	$[0, 0, 0][0, 1, -2][0, 1, -1][0, 2, -1]$	8	3.500	6.062	-3.835	-0.479
26	45	Quadruplet	$[0, 0, 0][0, 1, -1][0, 1, 0][2, 0, -1]$	8	3.500	6.062	3.397	0.425
27	47	Quadruplet	$[0, 0, 0][0, 1, 0][1, 1, -2][2, 0, -1]$	12	3.500	6.062	-4.748	-0.396
28	55	Quadruplet	$[0, 0, 0][0, 0, 1][0, 2, -1][1, 1, -1]$	24	3.500	7.000	-4.435	-0.185
29	61	Quadruplet	$[0, 0, 0][0, 0, 1][0, 1, -1][2, 0, -1]$	48	3.500	7.000	6.889	0.144
30	63	Quadruplet	$[0, 0, 0][1, -1, 1][1, -1][2, 0, 0]$	3	4.950	7.000	2.593	0.864
31	64	Quadruplet	$[0, 0, 0][1, -2, 1][1, 0, -1][2, -2, 0]$	12	3.500	7.000	-3.203	-0.267
32	68	Quadruplet	$[0, 0, 0][0, 0, 2][0, 2, 0][2, 0, 0]$	2	7.000	7.000	-0.720	-0.360

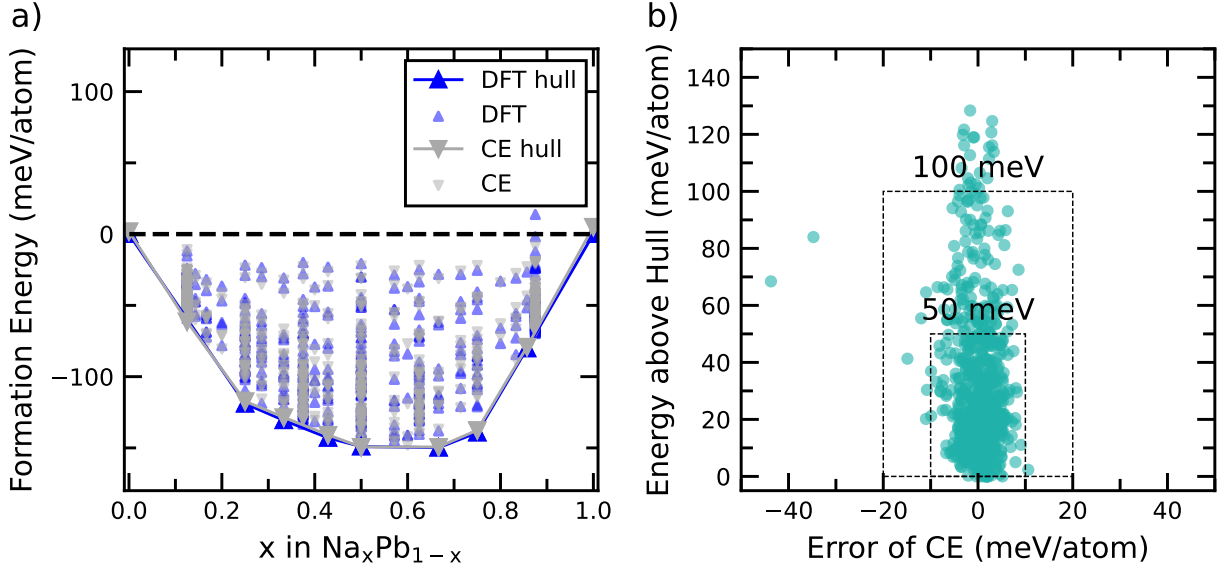


Figure S2: **a)** Formation energies of the FCC orderings (blue) and the formation energies predicted by the cluster expansion model (grey). The references used are the FCC crystal structure for pure Na and Pb. **b)** Error of the CE model with respect to DFT. The dashed lines are the confidence windows ( $\pm 10 \text{ meV}\cdot\text{atom}^{-1}$  and  $\pm 20 \text{ meV}\cdot\text{atom}^{-1}$  for the CE model).

## 4 Thermodynamic Integration

The grand canonical potential energy ( $\Phi$ ) is defined in Eq. 4:

$$\Phi = E - TS - \mu x \quad (1)$$

where  $E$  is the total energy predicted by the CE model,  $S$  is the configurational entropy, and  $\mu$  is the parametric chemical potential set in GCMC scans. From GCMC scans at fixed  $\mu$  and variable  $T$ ,  $\Phi$  is calculated using the thermodynamic integration of Eq. 2.

$$\beta\Phi(T, \mu) = \beta_0\Phi(T_0, \mu) + \int_{\beta_0}^{\beta} [E - \mu x] d\beta \quad (2)$$

where  $\beta$  is the reciprocal temperature,  $1/k_B T$ ,  $k_B$  is the Boltzmann constant, and  $\beta_0 = 1/k_B T_0$ .  $T_0$  is the reference temperature and is chosen to be 5K, in which entropic effects are negligible and hence  $\Phi(T_0, \mu) = E - \mu x$ . For GCMC scans at fixed  $T$  and variable  $\mu$ ,  $\Phi$

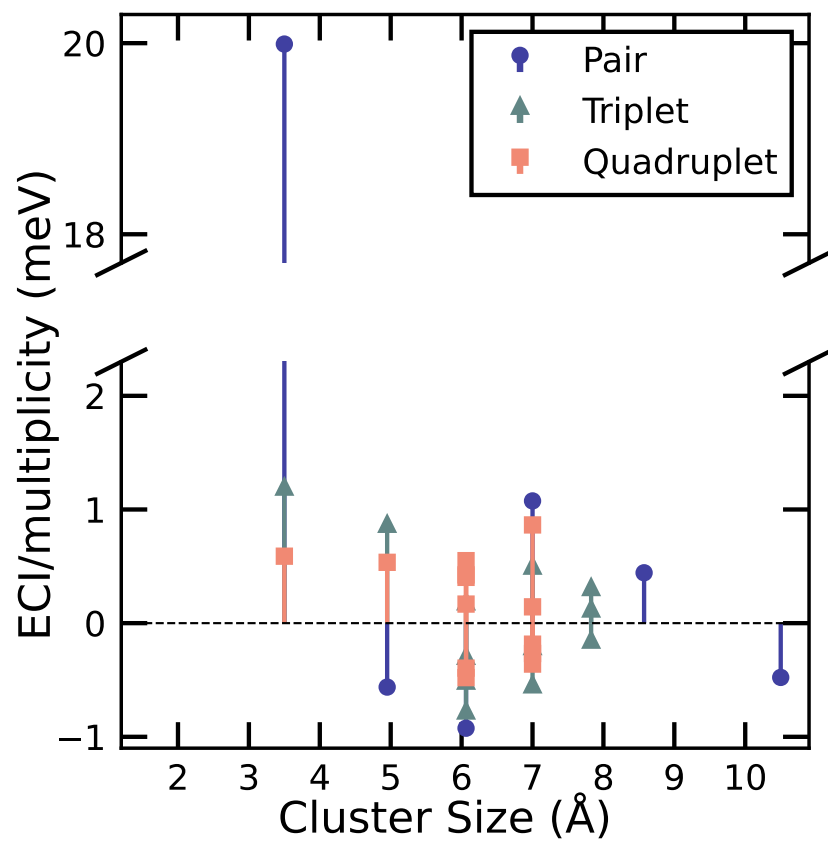


Figure S3: 33 effective cluster interactions in meV/multiplicity vs. their length (in Å,  $x$ -axis). Negative (positive) ECIs in pairs are favourable (unfavourable) interactions between Na-Pb (Na-Na, Pb-Pb).

is calculated using thermodynamic integration in Eq. 3:

$$\Phi(T, \mu) = \phi(T, \mu_0) - \int_{\mu_0}^{\mu} x d\mu \quad (3)$$

Thermodynamic integration was carried out numerically with the composite trapezoidal rule.

For ordered intermetallic phases, the grand-canonical free energy can be obtained directly from Eq. 4.

$$\Phi = E - \mu x \quad (4)$$

since the configurational entropy ( $S$ ) of an ordered phase is 0.

The grand canonical energies for each phase can be plotted on a single plot to determine the phase boundaries. The phase boundaries are identified from the intersections of  $\Phi$  for each phase in the  $\mu$  space and from the discontinuities in  $x$  vs.  $\mu$  plots.

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