Supplemental materials to the manuscript Search of stable structures in cation deficient (V,Nb)CoSb half-Heusler alloys by an atomic cluster expansion.

DFT SETTINGS

For the DFT calculations, we used the projector augmented wave method (PAW)[1] as implemented in the Vienna *ab-initio* simulations package [2, 3]. The energy cut-off for the expansion of the electronic wave function in plane waves was set to 390 eV, while the type of exchange-correlation functional chosen was the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA); an 8x8x8 Monkhorst-Pack k-mesh for the Brillouin integration was selected. Magnetic effects were considered throughout the spin-polarized electronic density of states within the local spin density approximation (LSDA). Structural optimization was taken into account by allowing the relaxation of the unit cell, ion positions, and lattice parameters. Any force larger than 6 meV/Å was relaxed with a maximum of twelve ionic steps. Energies below 0.1 meV were used as a self-consistency criterion to stop the calculations. The largest unit cell proposed by the cluster expansion was of 48 lattice sites. In practice, for DFT calculations, the number of atoms to be considered was reduced depending on the number of vacancies. Thus, for a 125 % of vacancies in the 48 lattices proposed cluster, the explicit number of atoms was 46 (16 Co, 16 Sb, and 14 M atoms).

$(Nb_{1-z}V_z)_xVac_xCoSb$	a(Å)	b(Å)	c(Å)	$A(^\circ)$	$B(^\circ)$	$C(^\circ)$	Vol. ($Å^3$)	CoM_2	CoM_3	CoM_4	$Nb_{overlap}$	$V_{overlap}$	Energy (eV)
$V_{0.8}CoSb$	7.04	7.04	7.04	99.70	99.70	131.54	238.32	0	4	1	0	4	-0.456
β-$Nb_{0.2}V_{0.6}CoSb$	7.12	7.12	10.10	118.32	118.32	33.37	244.91	1	2	2	3	0	-0.433
α-$Nb_{0.2}V_{0.6}CoSb$	7.12	7.12	10.03	117.97	117.97	33.50	244.87	1	2	2	3	3	-0.498
$Nb_{0.2}V_{0.6}CoSb$	7.11	7.10	7.08	99.77	99.77	131.58	243.46	0	4	1	4	3	-0.560
α-$Nb_{0.4}V_{0.4}CoSb$	7.14	7.14	7.15	99.78	99.87	131.46	249.03	0	4	1	7	0	-0.558
$Nb_{0.4}V_{0.4}CoSb$	7.12	7.12	7.12	99.59	99.89	131.25	249.05	0	4	1	9	0	-0.561
$Nb_{0.6}V_{0.2}CoSb$	7.18	7.17	7.20	99.70	99.87	131.35	253.98	0	4	1	12	0	-0.633
$Nb_{0.8}CoSb$	7.25	7.25	7.25	99.74	99.74	131.43	261.03	0	4	1	14	0	-0.717

TABLE I: Stuctural parameters, coordination number CoM_n, number of overlappings ($Nb_{overlap}$ and $V_{overlap}$), and structucral energies for a few alloys as discussed in the main text. The $Nb_{overlap}$ and $V_{overlap}$ are extracted from the electronic charge density (eCD) as the ones displayed in Fig. 1. It counts only when eCD is connecting one pair of Co and M atoms.

EFFECTIVE CLUSTER INTERACTIONS (ECI)

In the MC results, we took into account all the ECIs provided by the ACE. The ECIs were extracted from an equal weight fitting to all the DFT energies. For this case, the energy expression of the fitting expands to quadruplets. Fig 4a displays the set of ECIs with a total of 109 terms, which are composed of the three on-site energies, 16 pairs, 62 triples, and 28 quadruplets.

In addition to this fitting, we also tested others by setting, for instance, by using an energy expression that does not extend beyond triplets (Fig 4b). Under this criteria, we obtained a set of ECIs plotted in Fig 4b (a total of 82 terms which are composed of the three on-site energies, 16 pairs, and 62 triplets), and structures such as the one seen in Fig. 5. In Fig. 5 the alloy is at 1:1 V and Nb mixture composition; it is 0.06 eV higher in energy than the energy computed for the alloy of Fig. 10b of the main text, which has an identical composition. These high-energy systems strongly demix in regions with pure NbCoSb and regions containing simultaneously V, Nb, and vacancies. In the coexistence region of atoms and vacancies, the ordering is much weaker than the one observed in Fig. 8b of the main text. Here we see that the local number of vacancies around a vacancy has drastically increased, which gives, as a result, an increase in formation energy due to the increase of repulsive interactions among vacancies. Additionally, the high energy of formation of the pure NbCoSb HH inclusion helps to explain the higher energy.

We can conclude that by selecting only the largest ECI terms or discarding quadruplets, one may miss subtle information of key symmetries and interactions that are important to create the complex short- and longe- ranged order, and which are an essential feature of these type of HH [4].

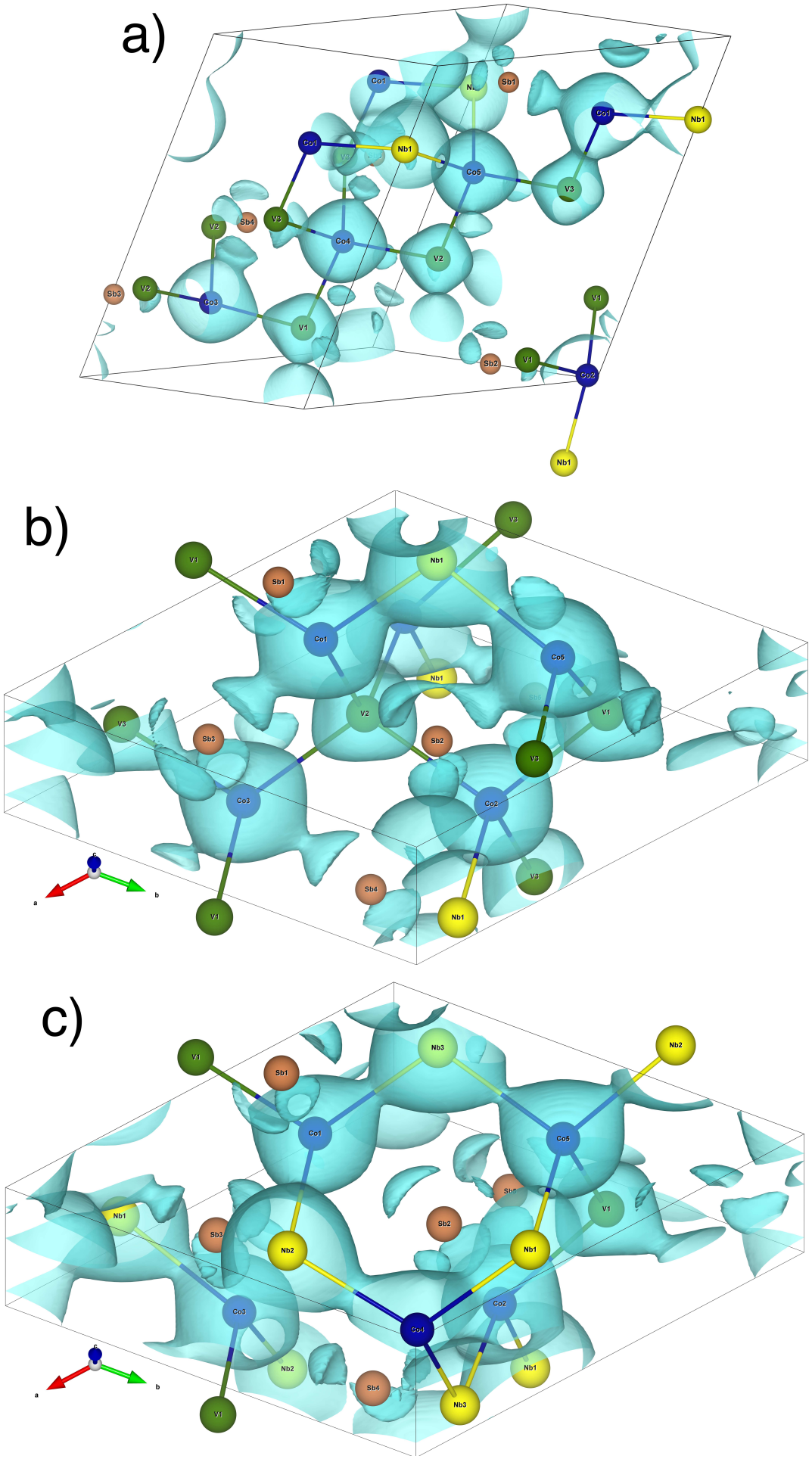

FIG. 1: Electronic charge density (eCD) in a) β-$Nb_{0.2}V_{0.6}CoSb$, b) $Nb_{0.2}V_{0.6}CoSb$ and c) $Nb_{0.6}V_{0.2}CoSb$. The V, Nb, Co and Sb atoms are depicted in green, yellow, dark blue and brown, respectevely. The charge density surface is defined by the 0.06 $e/\mathring{A}^3$(Color online).

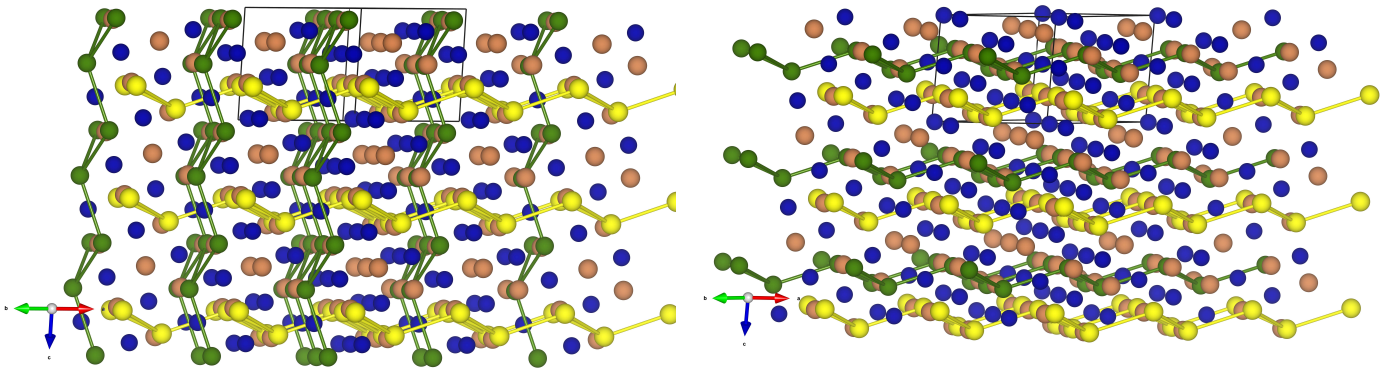

FIG. 2: Two Extended unit cells with $Nb_{0.2}V_{0.6}CoSb$ composition. The left figure corresponds to the structure labeled α $Nb_{0.2}V_{0.6}CoSb$ in Table 1, and right to the $Nb_{0.2}V_{0.6}CoSb$. The drawn bonds connect next nearest neighbor atoms corresponing to the FCC symmetry of the C sublattice within the half-Hesulers. (Color online).

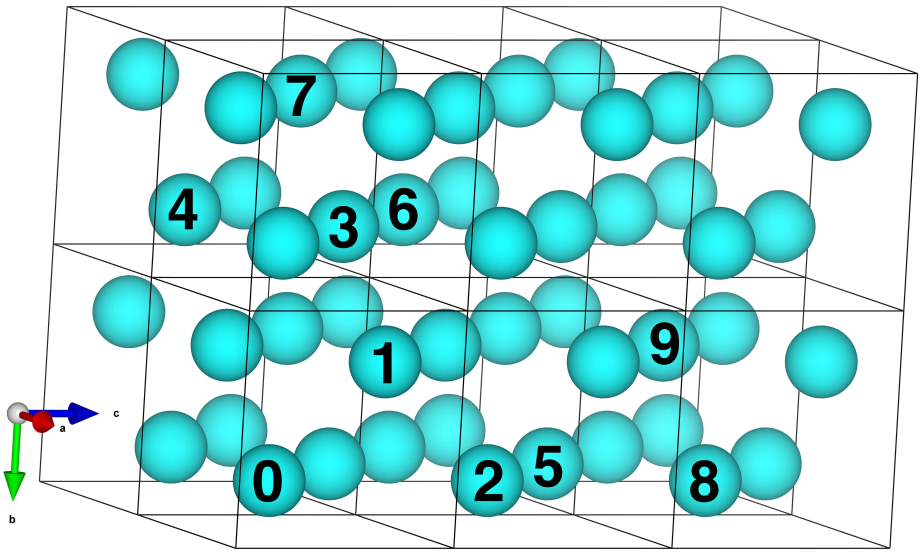

FIG. 3: 2x2x3 cubic cell for the B-sublattice of the HH structure (Fig. 1 main text). Numbers label one atom corresponding to i-shell (i=1,2,3 ... 9) around the lattice site marked as 0 (see Table 2 of main text). They also represent the position assigned to the i-order parameter discussed in the text. (Color online).

References

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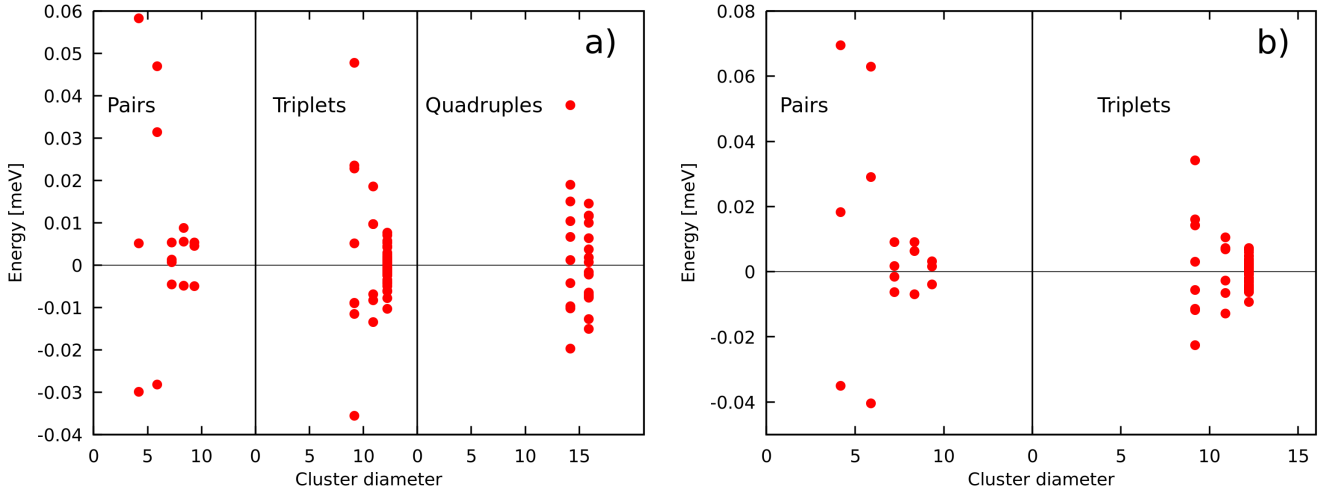

FIG. 4: a) ECIs used for all our alloys MC simulations, and b) ECI only considereing pairs and triplets (Color online).

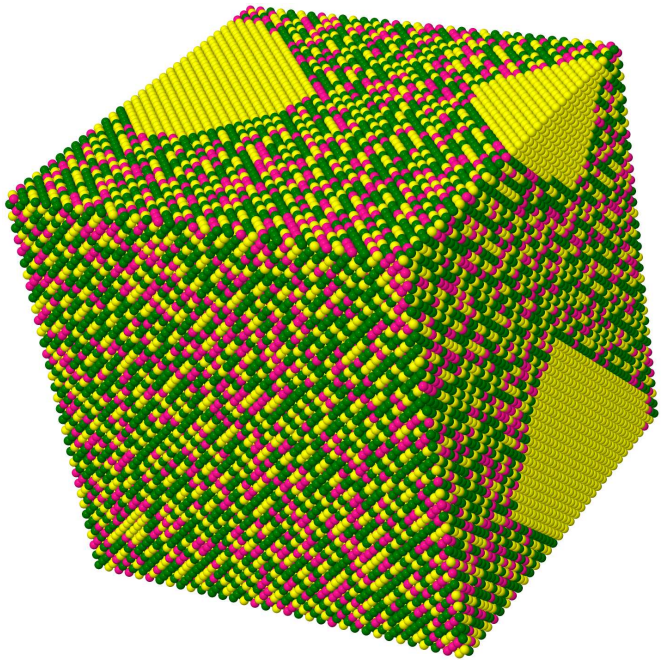

FIG. 5: High-energy configuration for $Nb_{0.4}V_{0.4}CoSb$ at 300 K obtained by the set ECIs displayed in Fig. 4b . It is 0.06 eV higher in energy than the configuration displayed in Fig 8b of the main text. The color code is, Vanadium:Green, Niobium:Yellow, and Vacancies:Magenta (color online).