Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information
Interplay Between Intrinsic Defects and Optoelectronic Properties of Semi-Heusler Gapped Metals

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Calculations of the formation enthalpy and phase diagram:

The formation enthalpy of each compound was calculated using the following equation:

$$\Delta H_f\left(Nb_{n_1}Co_{n_2}Sb_{n_3}\right) = E\left(Nb_{n_1}Co_{n_2}Sb_{n_3}\right) - n_1E(Nb) - n_2E(Co) - n_3E(Sb)$$

Here, $E\left(Nb_{n_1}Co_{n_2}Sb_{n_3}\right)$ is the total ground-state energy of the compound and $n_1E(Nb)$, $n_2E(Co)$, and $n_3E(Sb)$ are the total energies of the pure elements in their stable phases. While n_i represent the number of atoms of the ith element in a single formula unit.

We obtained the phase diagram by calculating the formation enthalpies of all Nb-Co-Sb phases as given in Table S1, and plotting them in a composition ratio versus energy space using doped package. It should be noted that for ternary phases, the composition ratio has two degrees of freedom, resulting in a three-dimensional phase diagram. The phase diagram is used to evaluate phase stability: stable structures lie on the convex hull, while metastable structures are above it.

Table S1. List of experimentally reported Nb-Co-Sb used for the calculations of energy phase diagram shown in Fig 2b. E_{hull} is the energy above the convex hull and H_f is the formation enthalpy**.**

No.	Material ID	Compositions	H_f (eV/atom)	E_{hull} (eV/atom)
1	mp-31460	NbCoSb	-0.2158	0.021
2	icsd_062111	$CoSb_3$	-0.1928	0.0
3	icsd_063553	$CoSb_2$	-0.1805	0.012
4	icsd_153504	$CoSb_3$	-0.1928	0.001
5	mp-570557	$NbCo_3$	-0.1723	0.0
6	mp-977426	$NbCo_3$	-0.1575	0.015
8	icsd_076118	CoSb	-0.1657	0.0
9	icsd_076120	$CoSb_2$	-0.1713	0.003
10	icsd_624900	CoSb	-0.1656	0.001
11	icsd_102548	$NbCo_2$	-0.1596	0.014
12	mp-1018021	$NbCo_3$	-0.1112	0.072
13	icsd_108305	Nb_6Co_7	-0.1760	0.0
14	icsd_018144	$NbSb_2$	-0.27691	0.0
15	icsd_057430	$NbSb_2$	-0.27691	0.0
16	icsd_076573	Nb_5Sb_4	-0.3121	0.0
17	icsd_077752	$NbSb_2$	-0.27691	0.001
18	icsd_645351	Nb_5Sb_4	-0.0501	0.262
19	icsd_645357	Nb_3Sb	-0.2838	0.0
20	mp-1220660	$NbCo_3$	-0.0999	0.061

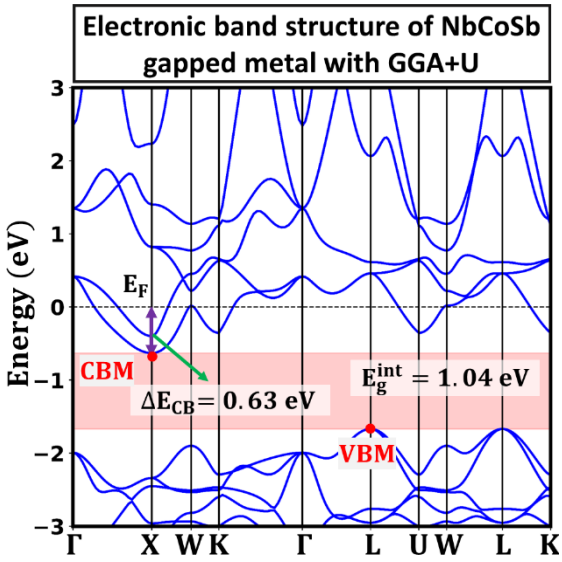

Figure S1: Calculated electronic band structure along the high-symmetry k-paths for NbCoSb using the GGA+U functional. Here, Fermi level is shown by dashed line, the internal band gap E_g^{int} is 1.03 eV, and the occupied width of the conduction band ΔE_{CB} is 0.63 eV.

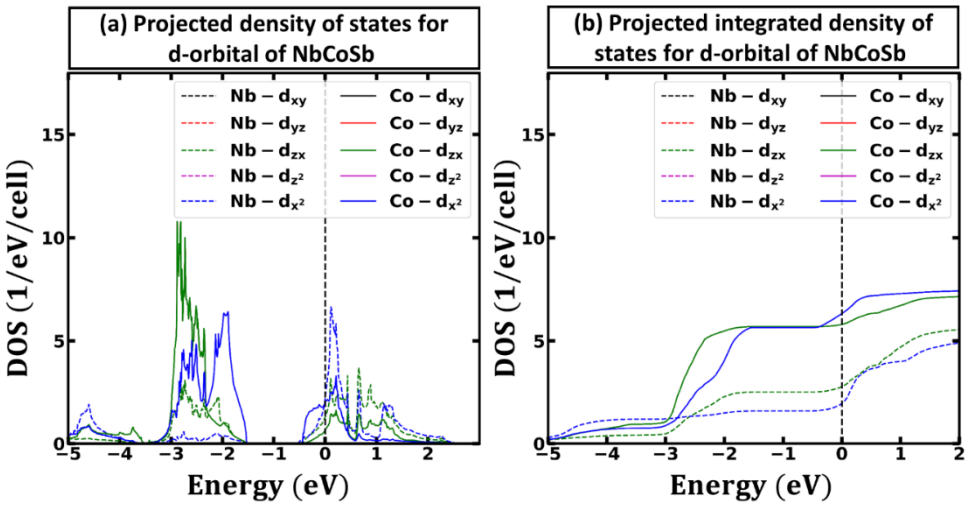

Figure S2: Projected density of state for NbCoSb half Heusler compound, indicating the main contribution from Nb-d and Co-d orbital at the conduction band minimum and valance band maximum, respectively.

List of the lowest ground state non-stoichiometric compositions			
No.	**Composition**	**E_{Form} (meV/ atom)**	**E_{hull} (meV/ atom)**
1	$NbCoSb$	- 216	184
2	$Nb_{0.95}CoSb$	- 256	133
3	$Nb_{0.90}CoSb$	- 297	82
4	$Nb_{0.85}CoSb$	- 332	34
5	$Nb_{0.80}CoSb$	- 357	0.0

Figure S3: Summary of the lowest ground state non-stoichiometric composition with their formation energies per atom (E_{Form}) and energy above the convex hull (E_{hull}).

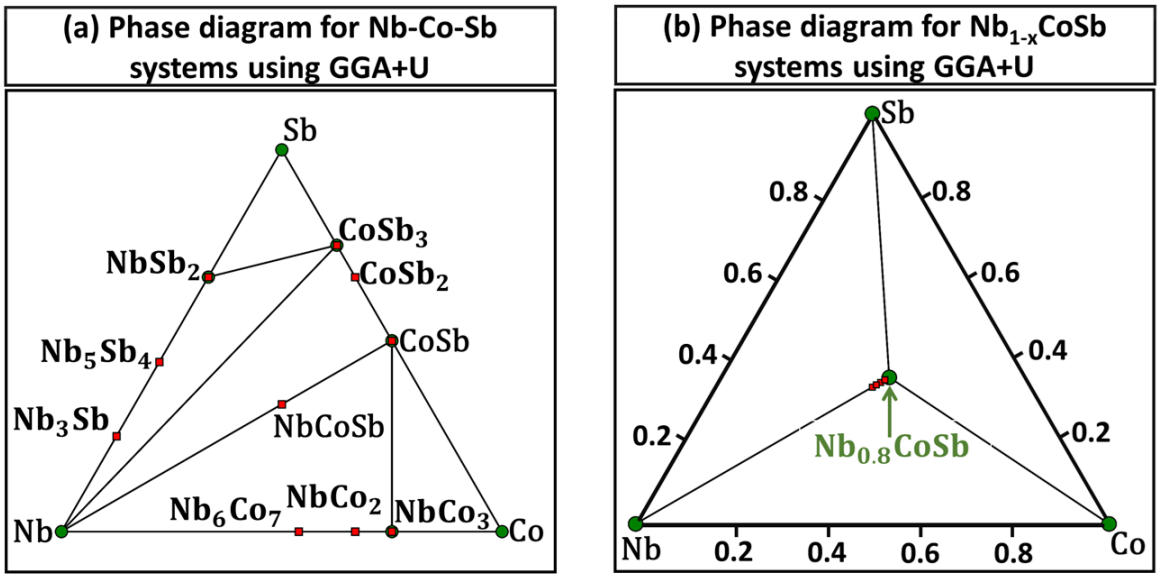

Figure S4: (a) Phase diagrams of Nb-Co-Sb systems using GGA+U functional (b) Phase diagram for $Nb_{1-x}CoSb$ system using GGA+U functional calculated by accounting the non-stoichiometric phases.

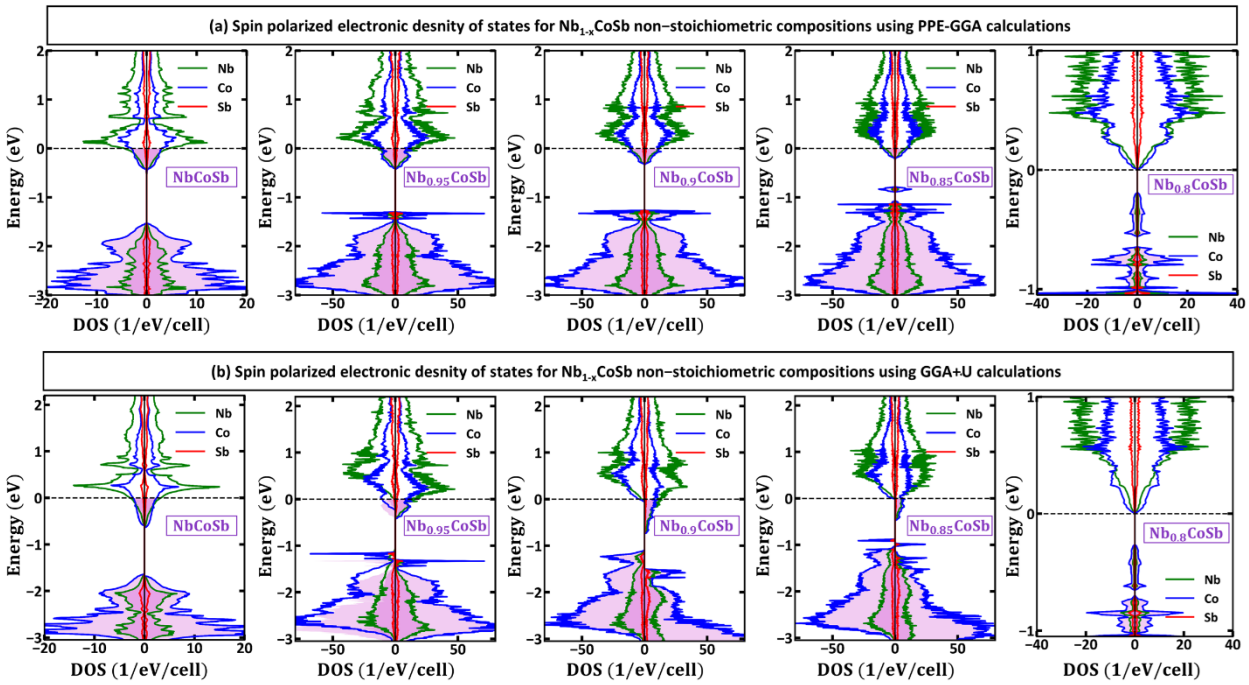

Figure S5: (a) Calculated spin polarized partial electronic density of states using PBE-GGA for NbCoSb, $Nb_{0.95}CoSb$, $Nb_{0.9}CoSb$, $Nb_{0.85}CoSb$, and $Nb_{0.80}CoSb$ (from left to right). (b) Calculated spin polarized partial electronic density of states using GGA+U for NbCoSb, $Nb_{0.95}CoSb$, $Nb_{0.9}CoSb$, $Nb_{0.85}CoSb$, and $Nb_{0.80}CoSb$ (from left to right). Black dotted line corresponds to Fermi level.

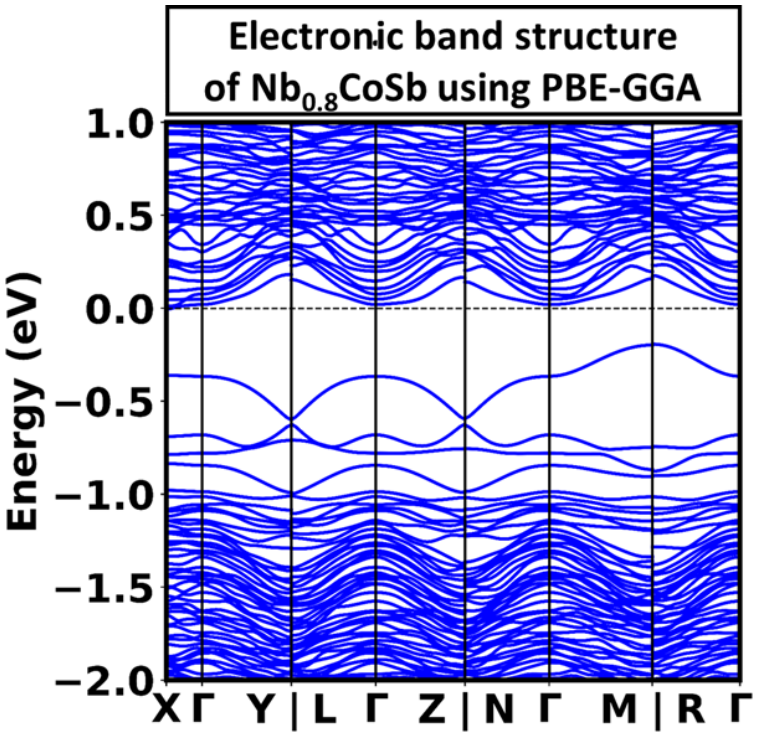

Figure S6: Calculated electronic band structure of $Nb_{0.8}CoSb$ non-stoichiometric composition. Here, black dotted line corresponds to Fermi level.