Supplementary Materials

Section 1 : Convex Hull Analysis

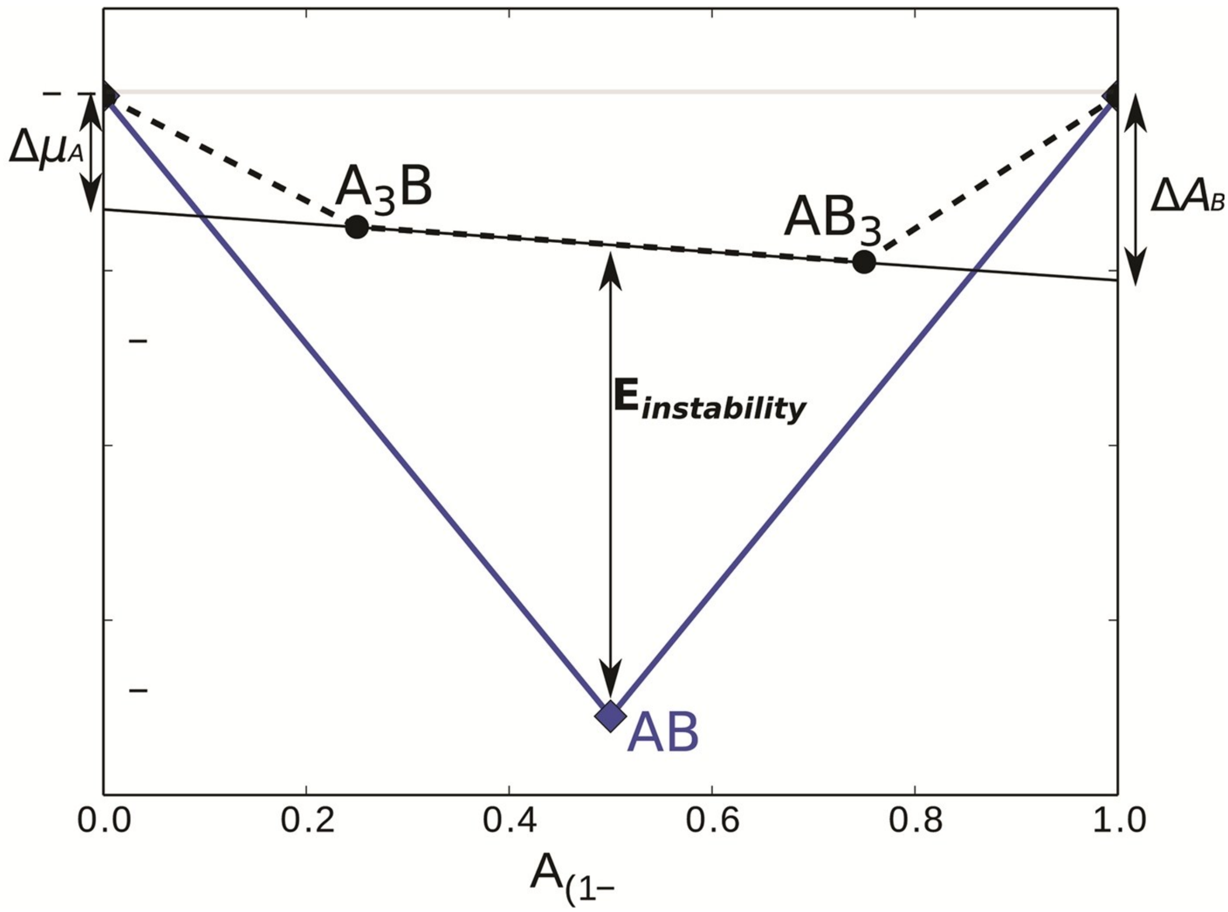
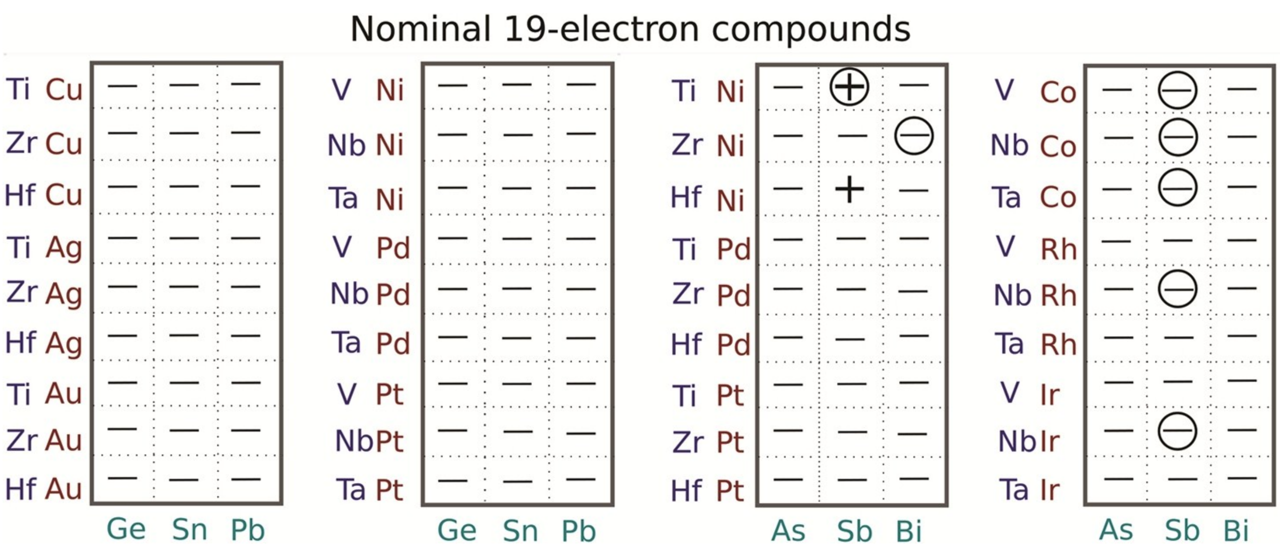


Figure S1 depicts a the convex hull construction for a model binary system A-B. The formation enthalpies (E_{Form}) of the compounds are calculated relative to the elemental chemical potentials of the components A (μ_A) and B (μ_B), which are simply the DFT-calculated total energies of the elements in their lowest energy bulk structures.

$$E_{Form} = E_{Compound} - \sum_{i=1}^{2} c_i \mu_i$$

where $E_{compound}$ is the DFT total energy of the compound of interest. Negative values of E_{form} (Figure S1) for all the three structures considered (A_3B, AB and AB_3) indicate their stability with respect to the elements A and B. However, stability with respect to the elemental components is not enough. For overall thermodynamic phase stability, the formation energy of the compound of interest needs to be compared against all other phases or combination of phases at that composition. This is accomplished by constructing the so-called convex hull for the phase space of interest. By definition, the convex hull connects phases that are lower in energy than any other phase or linear combination of phases *at that overall composition*. By extension, phases that lie on the convex hull are thermodynamically stable whereas the ones above it are metastable or unstable. For example, in the schematic binary system A-B considered here, all three binary phases—A_3B, AB, and AB_3—have negative formation energies, i.e., are stable with respect to the constituent elements. However, only the phase at AB is truly thermodynamically stable. Phases A_3B and AB_3 are unstable with respect to A–AB and AB–B mixture of phases (by visual inspection, we see that the energy of AB_3 (AB_3) is higher than the phase mixture of A–AB (AB–B) at the corresponding composition).

Further, we can quantify the degree of thermodynamic stability (or instability) of a given phase (referred to as $E_{instability}$) by comparing its energy to that of the decomposition products at that composition. To determine the lowest-energy decomposition products of a given phase, we construct the convex hull in the phase space *excluding the phase of interest*. For example, for A_3B, the convex hull excluding it is the same as the overall convex hull (solid blue lines in Figure S1). The lowest-energy decomposition products at the A_3B composition is A–AB. For the phase AB, the convex hull excluding it is given by the dashed black lines in Figure S1. The lowest-energy decomposition products at the composition AB is A_3B–AB_3. The phase equilibrium between the decomposition products (i.e., A–AB in the case of A_3B, and A_3B–AB_3 in the case of AB) determines the elemental chemical potentials μ_A and μ_B to be used in calculating $E_{instability}$ of the phase in question. Thus, a positive $E_{instability}$ indicates that the phase is thermodynamically metastable or unstable whereas a negative $E_{instability}$ indicates true overall thermodynamic stability.



Section 2: Predicted stability ignoring off-stoichiometry in the half-Heusler structure.