

## Electronic Supplementary Information for

### Defect energetics in high-entropy alloy fcc CoCrFeMnNi

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# 1. Chemical potentials for vacancy formation energy

In a crystal solid, a vacancy in a defective supercell with  $(N-1)$  atoms is created by removing an atom from a reference supercell with  $N$  atoms. Vacancy formation energy  $E_V^f$  given by:

$$E_V^f = E_d - E_0 + \mu \quad (1.1)$$

where  $E_d$  is the total energy of the defective supercell,  $E_0$  is the total energy of the defect-free supercell, and  $\mu$  is the chemical potential of the removed atom.

In the high-entropy alloys (HEAs), the vacancy formation energy  $E_{V,j,k}^f$  for the atom of the type  $j$  with the atomic site index  $k$  removed for vacancy creation, given by:

$$E_{V,j,k}^f = E_{d,j,k} - E_0 + \mu_{j,k} \quad (1.2)$$

where  $E_{d,j,k}$  is the total energy of the defective supercell that is the atom of the type  $j$  with the atomic site index  $k$  removed, and  $\mu_{j,k}$  is the chemical potential of the atom of the type  $j$  with the atomic site index  $k$ .

Summing all  $E_{V,j,k}^f$  from Eq. (1.2) over the atomic site index  $k$  with the same type  $j$  gives:

$$\sum_{k=1}^{N_j} E_{V,j,k}^f = \sum_{k=1}^{N_j} E_{d,j,k} - \sum_{k=1}^{N_j} E_0 + \sum_{k=1}^{N_j} \mu_{j,k} \quad (1.3)$$

where  $N_j$  is the number of the atomic site index  $k$  with the same type  $j$ . With sufficient

statistics,  $\sum_{k=1}^{N_j} E_{V,j,k}^f = N_j \langle E_V^f \rangle$ , where  $\langle E_V^f \rangle$  is the mean vacancy formation

energy which should be independent of the specific atom removed. Assuming the

chemical potentials of atomic type  $j$  with different atomic site index  $k$  are the same, rewriting Eq. (1.3) gives:

$$N_j \langle E_V^f \rangle = \sum_{k=1}^{N_j} E_{d,j,k} - N_j E_0 + N_j \mu_j \quad (1.3')$$

Then, this gives:

$$\mu_j = E_0 + \langle E_V^f \rangle - \frac{1}{N_j} \sum_{k=1}^{N_j} E_{d,j,k} \quad (1.4)$$

Continuing to sum all  $E_{V,j,k}^f$  from Eq. (1.3) over the type  $j$  gives:

$$\sum_{j=1}^M \sum_{k=1}^{N_j} E_{V,j,k}^f = \sum_{j=1}^M \sum_{k=1}^{N_j} E_{d,j,k} - \sum_{j=1}^M \sum_{k=1}^{N_j} E_0 + \sum_{j=1}^M \sum_{k=1}^{N_j} \mu_{j,k} \quad (1.5)$$

where  $M$  is the number of atomic type  $j$ . Using  $\sum_{j=1}^M \sum_{k=1}^{N_j} \mu_{j,k} = E_0$ , Eq. (1.5) becomes:

$$N \langle E_V^f \rangle = \sum_{n=1}^N E_{d,n} - NE_0 + E_0 \quad (1.5')$$

where  $N$  is the total number of the atoms in the perfect supercell, and  $E_{d,n}$  is the total energy of the defective supercell irrespective of the type of the atom removed. Thus, Eq. (1.5') gives:

$$\langle E_V^f \rangle = \frac{1}{N} \sum_{n=1}^N E_{d,n} - \frac{N-1}{N} E_0 \quad (1.6)$$

With the  $\langle E_V^f \rangle$  calculated from Eq. (1.6), the chemical potential for each component can be obtained using Eq. (1.4). Then the vacancy formation energy  $E_{V,j,k}^f$  can be obtained from Eq. (1.2). Finally the distribution of  $E_V^f$  can be obtained.

## 2. Chemical potentials for interstitial formation energy

In a crystal solid, an interstitial atom in a defective supercell with  $(N+1)$  atoms is created by adding an atom to a reference supercell with  $N$  atoms. Interstitial formation energy  $E_V^f$  given by:

$$E_V^f = E_d - E_0 - \mu \quad (2.1)$$

where  $E_d$  is the total energy of the defective supercell,  $E_0$  is the total energy of the defect-free supercell, and  $\mu$  is the chemical potential of the added atom.

In the high-entropy alloys (HEAs), the interstitial formation energy  $E_{I,j,k}^f$  for the

atom of the type  $j$  with the atomic site index  $k$  added for interstitial creation, given by:

$$E_{I,j,k}^f = E_{d,j,k} - E_0 - \mu_{j,k} \quad (2.2)$$

where  $E_{d,j,k}$  is the total energy of the defective supercell that is the atom of the type  $j$  with the atomic site index  $k$  added, and  $\mu_{j,k}$  is the chemical potential of the atom of the type  $j$  with the atomic site index  $k$ .

Summing all  $E_{I,j,k}^f$  from Eq. (2.2) over the atomic site index  $k$  with the same type  $j$  gives:

$$\sum_{k=1}^{N_j} E_{I,j,k}^f = \sum_{k=1}^{N_j} E_{d,j,k} - \sum_{k=1}^{N_j} E_0 - \sum_{k=1}^{N_j} \mu_{j,k} \quad (2.3)$$

where  $N_j$  is the number of the atomic site index  $k$  with the same type  $j$ . With sufficient

statistics,  $\sum_{k=1}^{N_j} E_{I,j,k}^f = N_j \langle E_I^f \rangle$ , where  $\langle E_I^f \rangle$  is the mean interstitial formation energy which should be independent of the specific atom added. Assuming the chemical potentials of atomic type  $j$  with different atomic site index  $k$  are the same, rewriting Eq. (2.3) gives:

$$N_j \langle E_I^f \rangle = \sum_{k=1}^{N_j} E_{d,j,k} - N_j E_0 - N_j \mu_j \quad (2.3')$$

Then, this gives:

$$\mu_j = \frac{1}{N_j} \sum_{k=1}^{N_j} E_{d,j,k} - E_0 - \langle E_I^f \rangle \quad (2.4)$$

Continuing to sum all  $E_{I,j,k}^f$  from Eq. (2.3) over the type  $j$  gives:

$$\sum_{j=1}^M \sum_{k=1}^{N_j} E_{I,j,k}^f = \sum_{j=1}^M \sum_{k=1}^{N_j} E_{d,j,k} - \sum_{j=1}^M \sum_{k=1}^{N_j} E_0 - \sum_{j=1}^M \sum_{k=1}^{N_j} \mu_{j,k} \quad (2.5)$$

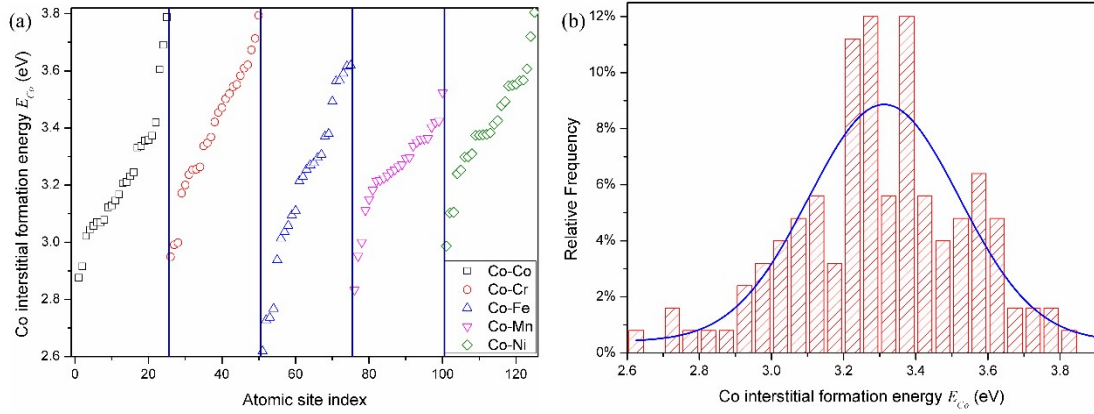
where  $M$  is the number of atomic type  $j$ . Using  $\sum_{j=1}^M \sum_{k=1}^{N_j} \mu_{j,k} = E_0$ , Eq. (2.5) becomes:

$$N \langle E_I^f \rangle = \sum_{n=1}^N E_{d,n} - N E_0 - E_0 \quad (2.5')$$

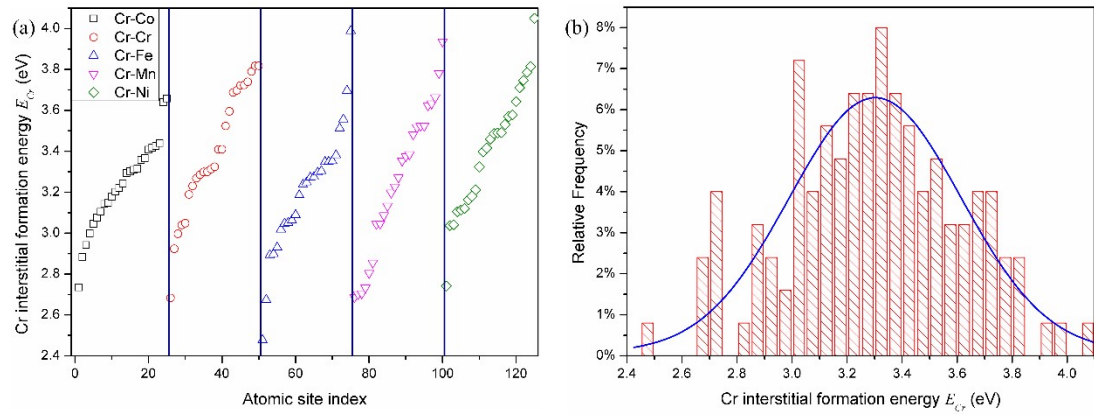
where  $N$  is the total number of the atoms in the perfect supercell, and  $E_{d,n}$  is the total energy of the defective supercell irrespective of the type of the atom added. Thus, Eq. (2.5') gives:

$$\langle E_I^f \rangle = \frac{1}{N} \sum_{n=1}^N E_{d,n} - \frac{N+1}{N} E_0 \quad (2.6)$$

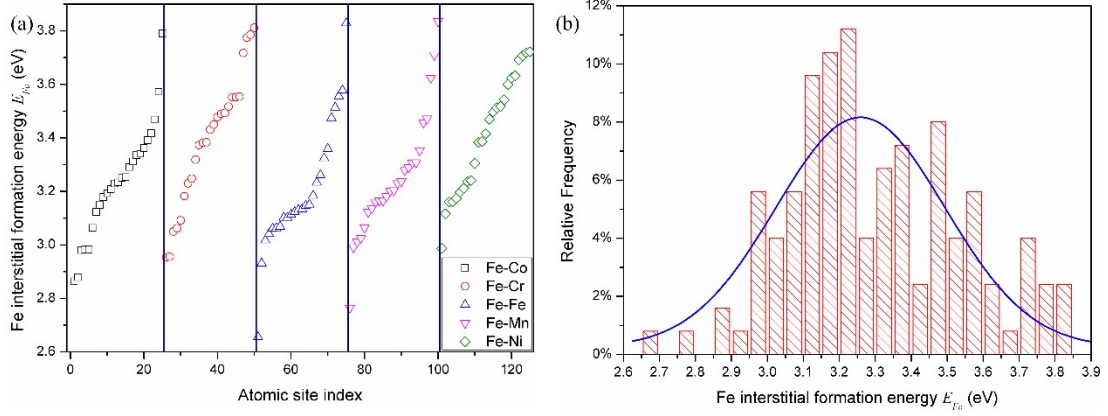
With the  $\langle E_I^f \rangle$  calculated from Eq. (2.6), the chemical potential for each component can be obtained using Eq. (2.4). Then the interstitial formation energy  $E_{I,j,k}^f$  can be obtained from Eq. (2.2). Finally the distribution of  $E_I^f$  can be obtained.



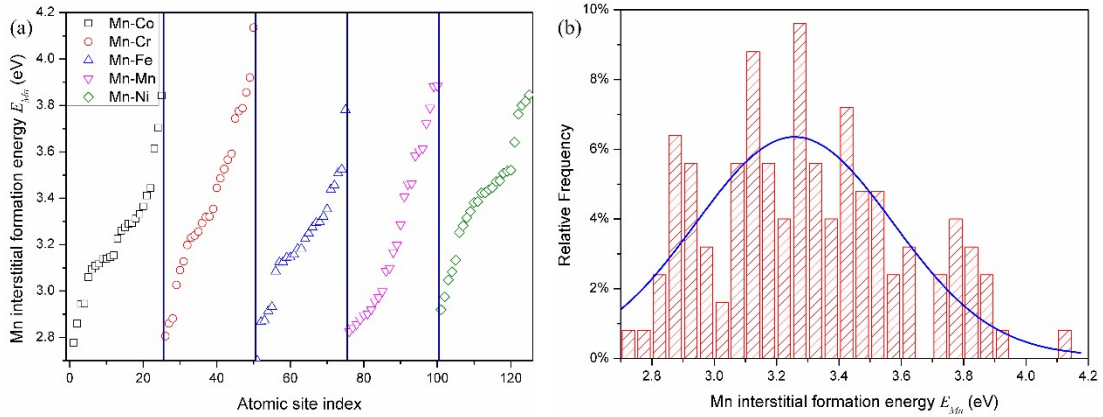
**Fig. S1.** (a) Co interstitial formation energy for [100] Co-Co, Co-Cr, Co-Fe, Co-Mn, Co-Ni dumbbell in fcc CoCrFeMnNi HEA. There are 25 different calculations for each dumbbell and these data are compiled in an ascending order. (b) Total distribution of Co interstitial formation energies of all 125 samples in fcc CoCrFeMnNi HEA. The blue line represents Gaussian function fit.



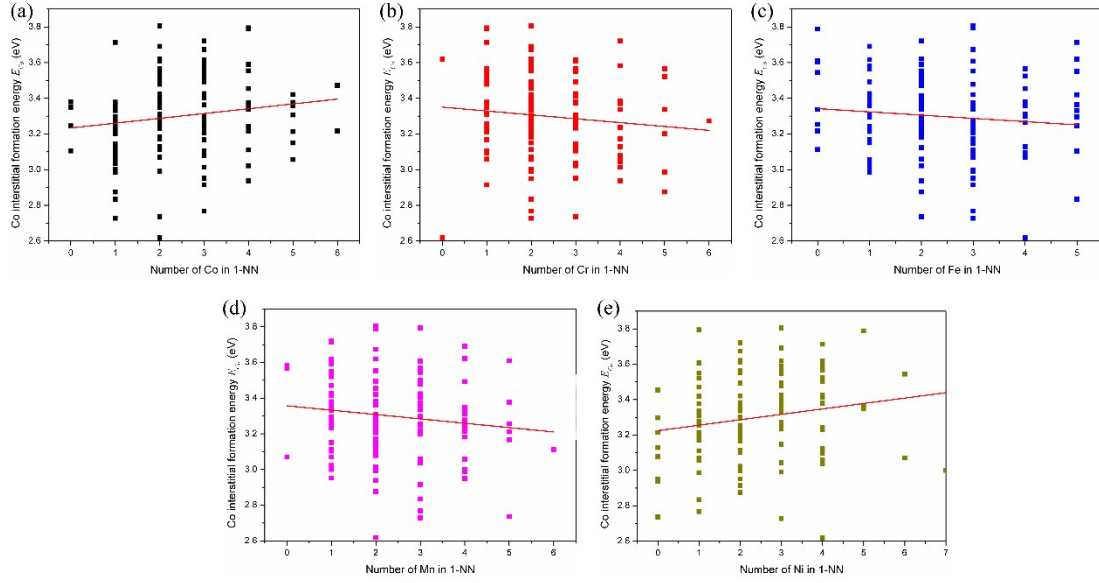
**Fig. S2.** (a) Cr interstitial formation energy for [100] Cr-Co, Cr-Cr, Cr-Fe, Cr-Mn, Cr-Ni dumbbell in fcc CoCrFeMnNi HEA. There are 25 different calculations for each dumbbell and these data are compiled in an ascending order. (b) Total distribution of Cr interstitial formation energies of all 125 samples in fcc CoCrFeMnNi HEA. The blue line represents Gaussian function fit.



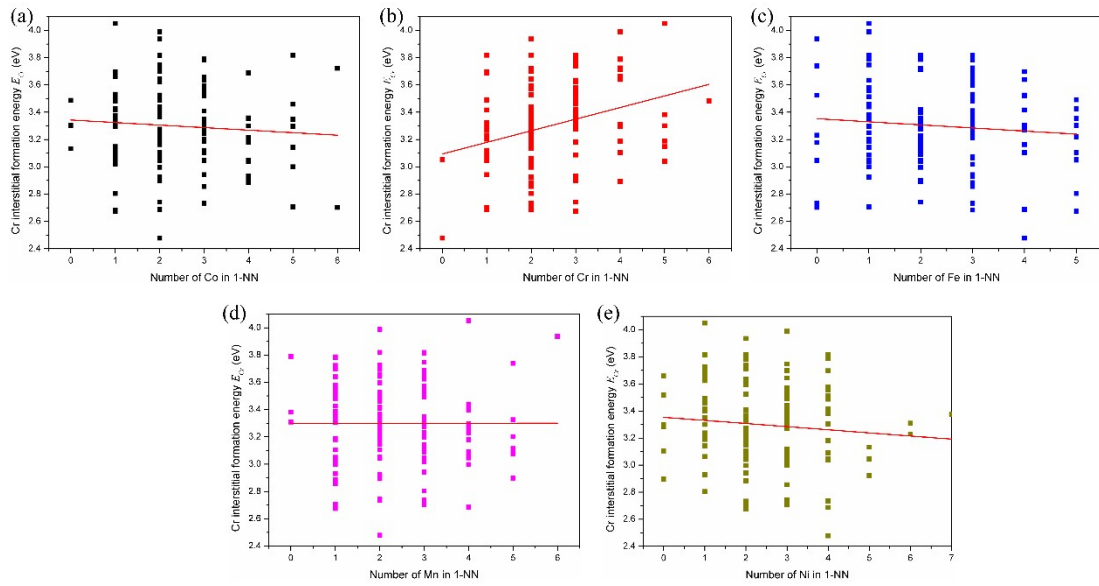
**Fig. S3.** (a) Fe interstitial formation energy for [100] Fe-Co, Fe-Cr, Fe-Fe, Fe-Mn, Fe-Ni dumbbell in fcc CoCrFeMnNi HEA. There are 25 different calculations for each dumbbell and these data are compiled in an ascending order. (b) Total distribution of Fe interstitial formation energies of all 125 samples in fcc CoCrFeMnNi HEA. The blue line represents Gaussian function fit.



**Fig. S4.** (a) Mn interstitial formation energy for [100] Mn-Co, Mn-Cr, Mn-Fe, Mn-Mn, Mn-Ni dumbbell in fcc CoCrFeMnNi HEA. There are 25 different calculations for each dumbbell and these data are compiled in an ascending order. (b) Total distribution of Mn interstitial formation energies of all 125 samples in fcc CoCrFeMnNi HEA. The blue line represents Gaussian function fit.

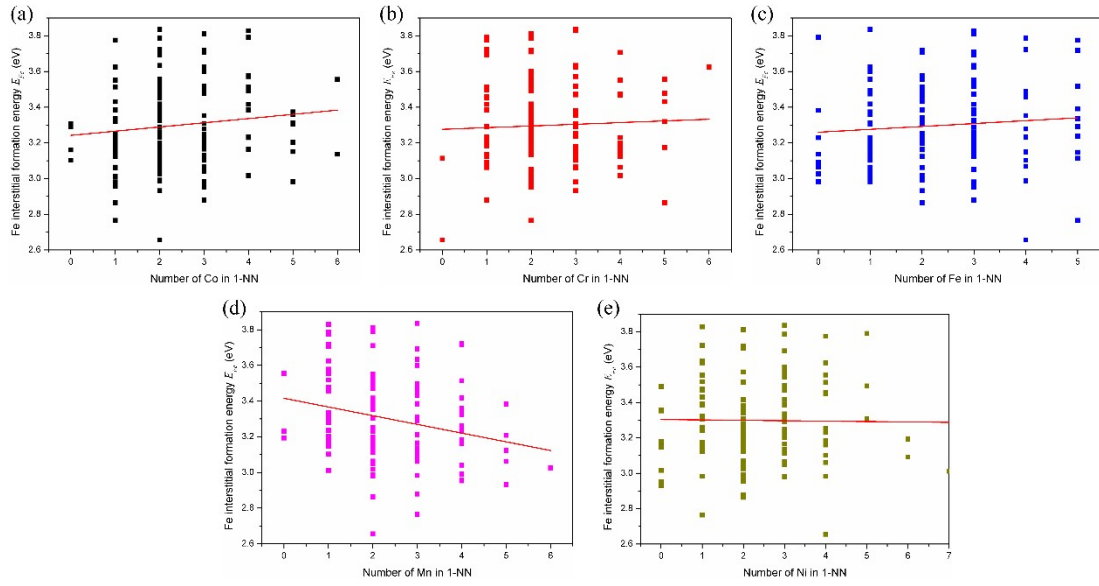


**Fig. S5.** Evolution of Co interstitial formation energy with the number of X atoms in the first nearest neighbor (1NN) in fcc CoCrFeMnNi HEA: (a) Co, (b) Cr, (c) Fe, (d) Mn, (e) Ni.

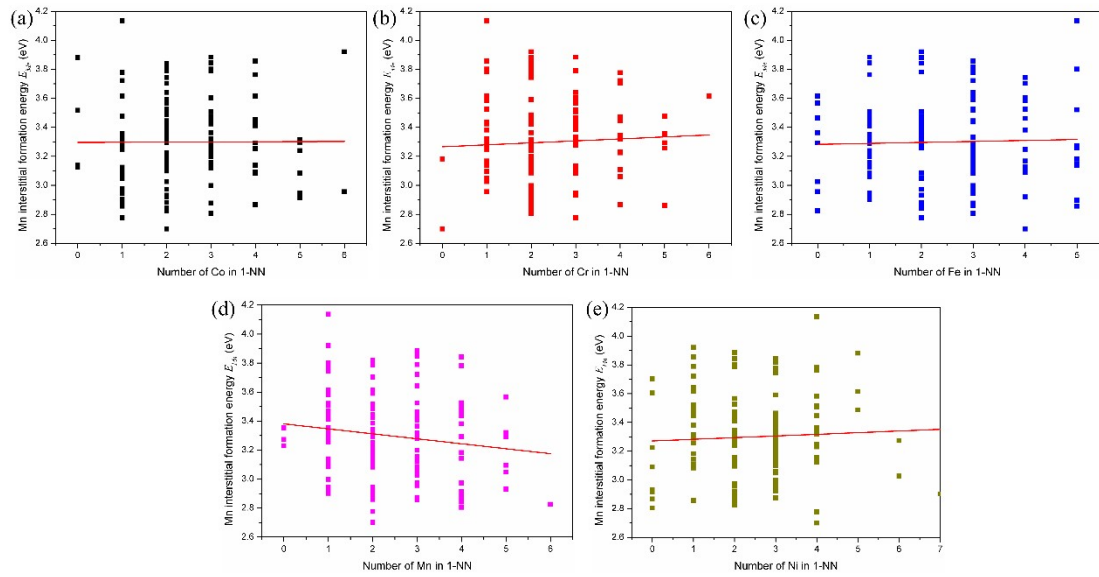


**Fig. S6.** Evolution of Cr interstitial formation energy with the number of X atoms in the first nearest neighbor (1NN) in fcc CoCrFeMnNi HEA: (a) Co, (b) Cr, (c) Fe, (d) Mn, (e) Ni.

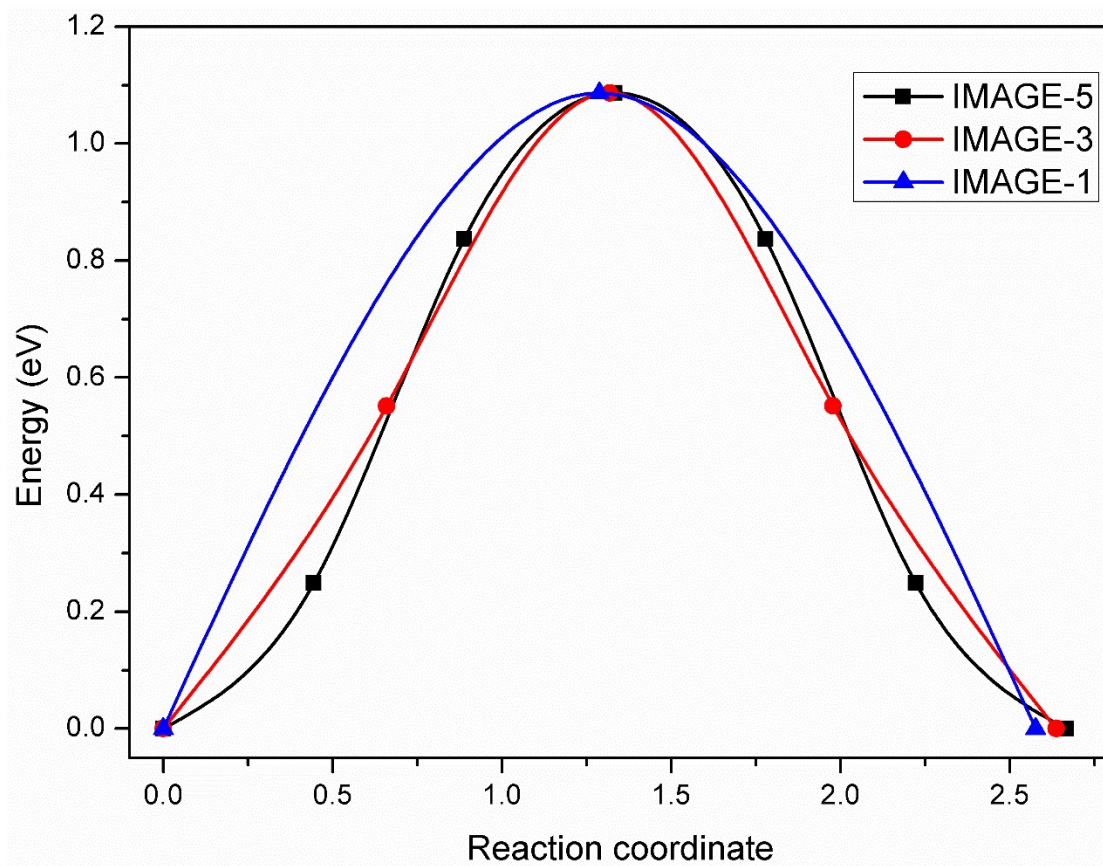




**Fig. S7.** Evolution of Fe interstitial formation energy with the number of X atoms in the first nearest neighbor (1NN) in fcc CoCrFeMnNi HEA: (a) Co, (b) Cr, (c) Fe, (d) Mn, (e) Ni.



**Fig. S8.** Evolution of Mn interstitial formation energy with the number of X atoms in the first nearest neighbor (1NN) in fcc CoCrFeMnNi HEA: (a) Co, (b) Cr, (c) Fe, (d) Mn, (e) Ni.



**Fig. S9.** Energy landscape of vacancy migration in pure Ni.