Thermodynamic Routes to Novel Metastable Nitrogen-Rich Nitrides

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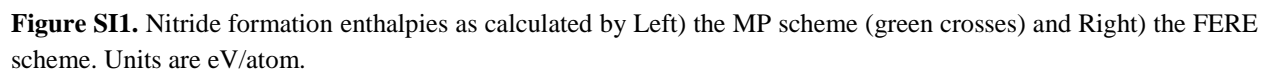[4] Department of Materials Science and Engineering, UC Berkeley, Berkeley, California 94720, USA

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Supplementary Information

SI.1. Formation Energy Correction Scheme Benchmarking

SI.1.1: Nitride formation energies in two formation energy correction schemes

Density functional theory calculations of formation energies for semiconducting and insulating compounds often differ significantly than formation energies obtained from experimental calorimetry. This arises primarily due to differences in bonding and electronic structure between the intermediate compounds, A_xB_y, and the pure elemental reference states, A and B, resulting in incomplete cancellation of errors in the total energies from DFT. Improved formation energy predictions can be attained from more sophisticated functionals in DFT, ranging from HSE[1] to RPA[2] and QMC[3], but these improvements in accuracy are often accompanied by a significant increase in computational expense. However, DFT formation energy errors are often systematic within a chemical space, enabling the construction of formation energy correction schemes, where the elemental reference energies are modified to yield predicted formation energies within a chemical space to achieve overall closer agreement with experiment.

We investigate the performance of two such correction schemes for use in the nitrides: the fitted-elemental reference scheme (FERE),[4] and the gas-fit reference scheme,[5] as currently employed in the Materials Project (henceforth referred to as the 'MP' scheme). In the FERE scheme, all elemental energies are determined simultaneously by a linear least-squares fit on *all* elemental-phase chemical potentials, to minimize formation energy errors. In the FERE scheme, all intermediate compounds are calculated from a GGA $+ U$ framework, with a $+ U$ value of 3 eV for all compounds. In the MP scheme for nitrides, only the error arising from GGA over-binding in the N_2 molecule is treated; by preserving the total energies of all the metal elemental references, and performing a linear least-squares fit on *only* the N_2 gas chemical potential to minimize formation energy errors. On the Materials Project, more sophisticated schemes are also employed in the transition metal oxides to attain a $+ U$ value for transition metals,[5] and for mixing GGA and GGA $+ U$ formation energies in ternary spaces,[6] but such an analysis has not been systematically carried out for the nitrides.

Figure SI1. Nitride formation enthalpies as calculated by Left) the MP scheme (green crosses) and Right) the FERE scheme. Units are eV/atom.

When benchmarked against the formation energies of binary nitrides with tabulated thermochemical data, the formation energies of both correction schemes perform similarly well. Figure

SI.1 shows the root-mean-squared-error (RMSE) of the MaterialsProject Scheme, and the FERE scheme, for a collection of binary nitrides. The overall RMSE for the MP scheme is 103 meV/atom (with a major outlier for the semiconductor Ta_3N_5), and is 117 meV/atom for the FERE scheme (with an outlier for the intermetallics VN, Mo_2N, and Fe_xN). It is somewhat counterintuitive that the FERE scheme, which is fit on all elements, has a slightly greater error than the MP scheme, which only fits the N_2 chemical potential. However, this may be because there are fewer nitrides than oxides, which means a FERE-scheme fitting of all compounds biases an accurate description for oxides over the nitrides, whereas the MP-scheme corrections are focused in the specific nitride space. However, the difference in formation energy errors between the two schemes is only 15 meV/atom, which is too small to distinguish between the thermochemical predictability of the two schemes.

Tabulated calorimetry data for the nitrides is most prevalent for nitrides with large negative formation energies. However, in chemical spaces with thermoneutral or small negative formation energies, there are significant and qualitative differences in the convex hulls as calculated from FERE and MP. Figure SI.2 highlights in the Fe-N system particularly prominent differences in the calculated convex hulls by the MP and FERE scheme. In the FERE scheme, all Fe_xN_y compounds have positive formation energy with respect to standard state conditions, whereas in the MP scheme, the Fe-N subnitrides have negative formation energy. The MP scheme prediction of negative formation energies in the iron subnitrides is consistent with experimental calorimetry measurements.[7] The positive formation energies in the FERE scheme for the subnitrides is likely due to the use of a DFT $+U$ value of +3 eV for all binary nitride compounds. Typically $+U$ is employed to increase the calculated band gap, which is underpredicted in DFT, giving a better description of electronic structure for semiconducting and insulating compounds. However, transition metal subnitrides tend to exhibit intermetallic electronic structure, and thus would be poorly described by a DFT $+U$ scheme. DFT $+U$ results in more positive formation energies, explaining why the calculated formation energies of the subnitrides in the Fe-N system are unphysically above the convex hull.
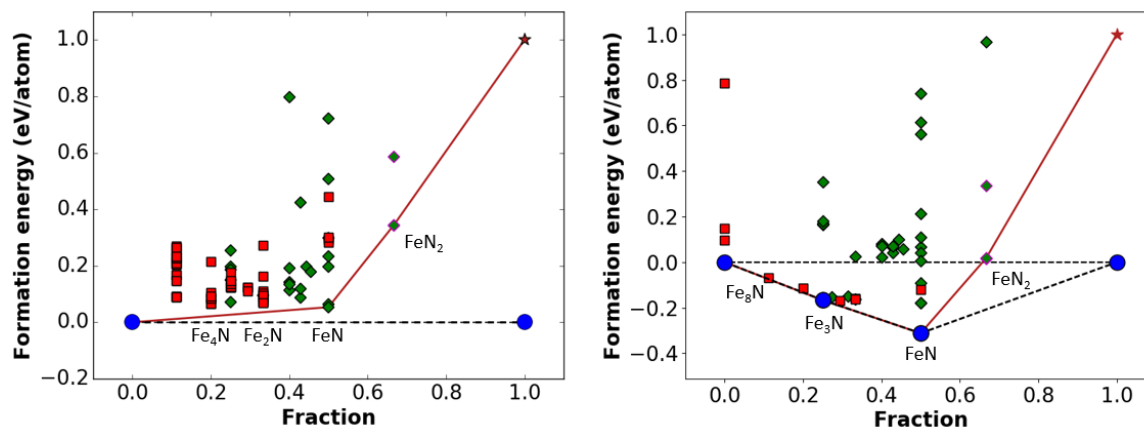
Figure SI2. Nitride formation enthalpies as calculated by Left) the FERE scheme (green crosses) and Right) the MP scheme. Units are eV/atom.

On the other hand, because the MP scheme uses only pure GGA-PBE calculations, the band gap of the *nitrogen-rich* nitrides, which are likely to be semiconductors and insulators, are probably underpredicted, resulting in overstabilized formation energies in the nitrogen-rich portion of the convex

hull. Figure SI3. shows the formation energy error as a function of oxidation state in the MP vs FERE schemes. For binary nitrides with oxidized metal cations, there is a consistent overbinding in a pure GGA scheme, which scales with the cation oxidation state.
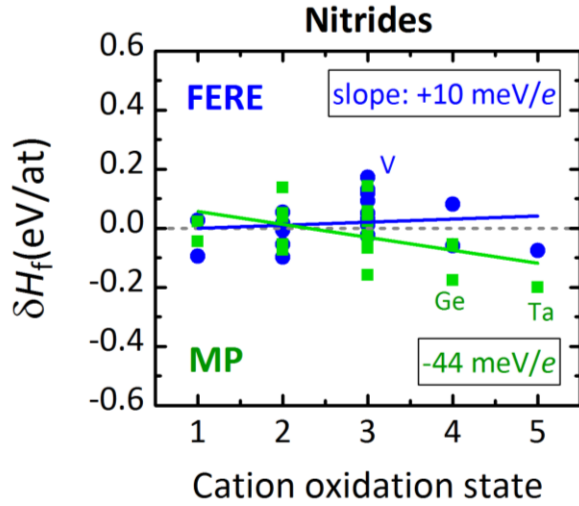
Figure SI3. Formation energy error in the FERE and MP schemes for nitrides with oxidized metal cations

The primary focus of this work is the determination of the critical $\Delta\mu N_2$ required to stabilize novel metastable nitrogen-rich binary nitrides. Accurate prediction of this value relies on correct formation energies for both the nitrogen-rich phase, and for the next-reduced nitride in composition space. Because of the errors inherent in both the MP and the FERE scheme, the predicted critical $\Delta\mu N_2$ can vary significantly and qualitatively between these two schemes. To illustrate this difference, Table SI.1. shows the energy above the hull and the critical $\Delta\mu N_2$ for three nitrogen-rich transition metal nitrides. In the MP scheme the overstabilization of the nitrogen-rich phase leads to small or zero energy above the hull results, resulting in zero or moderate critical $\Delta\mu N_2$ required to stabilize these phases. However, because these nitrogen-rich transition metal nitrides have never been experimentally observed in these well-explored chemical spaces, these stability predictions from the MP scheme are probably inaccurate. On the other hand, FERE understabilizes the next-reduced nitride, which in these three systems is likely an intermetallic mononitride. Coupled with a high, but probably accurate, formation energy of the nitrogen-rich phase, this can result in high, positive critical $\Delta\mu N_2$. As shown in Table SI.1., the difference in the critical $\Delta\mu N_2$ as calculated in the two schemes can differ by more than 2 eV/N, which is a qualitative difference in prediction between 'synthesizable' and 'not synthesizable'.

Table SI.1. Energy above the hull and critical $\Delta\mu N_2$ for several nitrogen-rich transition metal nitrides

Predicted Nitride	Decomposition Products	MP ΔH above hull (eV/atom)	FERE ΔH above hull (eV/atom)	MP Critical $\Delta\mu N_2$ (eV/N)	FERE Critical $\Delta\mu N_2$ (eV/N)
Cr_3N_4	$CrN+N_2$	Stable	0.340	0	2.38
Mn_3N_4	$MnN+N_2$	0.059	0.294	0.41	2.06
V_3N_4	$VN+N_2$	Stable	0.144	0	1.01

Despite the ability of the two schemes to accurately predict the formation energies of strongly exothermic binary nitrides, the deficiencies of both schemes at determining electronic structure consistently across the metal-nitrogen composition space yields widely varying predictions of critical

$\Delta\mu N_2$. By the use of $+U$ value in the FERE scheme, it is estimated that the critical $\Delta\mu N_2$ will generally be overpredicted, whereas the MP scheme will underpredict the critical $\Delta\mu N_2$. For the sake of experimental investigation, it was necessary to identify a more reliable critical $\Delta\mu N_2$ prediction scheme, that would provide a more accurate prediction of the formation energies over all metal-nitride compositions, from the intermetallic sub-nitrides to the semiconducting/insulting nitrogen-rich phases.

SI.1.2: Nitride formation energies in SCAN / gas-fit correction

The SCAN metaGGA functional was released in Fall 2016,[8] which by its construction, theoretically offers a superior description of electronic structure across compounds with diverse bonding.[9] We benchmarked the SCAN functional for prediction of nitride formation energies and critical $\Delta\mu N_2$. We benchmark the prediction capability of the SCAN functional against known experimental formation energies of binary nitrides, finding a root-mean-squared-error (RMSE) of 0.128 eV/atom when the N_2 reference state is calculated in DFT from a molecule-in-a-box. By fitting the energy of the SCAN N_2 gas phase to minimize formation energy errors, this RMSE was reduced to 0.099 eV/atom. This is a marginally lower error than in the pure GGA gas-fit scheme as implemented in the Materials Project, which has RMSE = 0.103 eV/atom, and from the FERE scheme, which has RMSE = 0.117 eV/atom. When the critical $\Delta\mu N_2$ is calculated with the gas-fit scheme in the SCAN functional, in general we obtain intermediate $\Delta\mu N_2$ as compared to the MP and FERE correction schemes, although specific systems may vary based on how MP and FERE schemes treat the electronic structure. Table SI.2 offers a comparison of the critical $\Delta\mu N_2$ as obtained from the three schemes. By manual investigation of the convex hulls, it appears that SCAN accurately reproduces negative formation energies in the subnitride region, while not overstabilizing the nitrogen-rich phases as from a PBE-GGA scheme. We therefore ultimately base our analysis in this work on a formation energy calculation scheme based on SCAN, with a gas-fit nitrogen chemical potential.

Table SI. 2. Critical $\Delta\mu N_2$ as calculated in the gas-fit 'MP' and FERE schemes, and the gas-fit scheme using a SCAN functional. A triple dash signifies critical $\Delta\mu N_2$ greater than +1.5 eV/N.

Predicted Nitride	MP Critical $\Delta\mu N_2$ (eV/N)	FERE Critical $\Delta\mu N_2$ (eV/N)	SCAN Critical $\Delta\mu N_2$ (eV/N)
BiN	0.655	---	1.437
CoN	---	0.704	0.227
Cr_3N_4	STABLE	---	0.917
Cr_3N_5	0.559	---	---
CrN_2	0.074	---	0.817
Cu_3N	**---**	**0.698**	**1.048**
FeN_2	0.536	0.619	0.537
IrN_2	0.240	0.701	0.568
Mn_3N_4	0.397	---	0.602
Mo_2N_3	0.699	0.972	1.199
Mo_3N_5	0.586	0.978	0.883
MoN_2	0.741	---	1.152
Nb_3N_5	0.830	---	0.925
Pb_3N_4	0.811	---	1.304
Re_3N_4	0.194	---	0.641
Re_3N_5	0.069	---	0.681
ReN	0.013	---	0.477
ReN_2	0.137	---	0.587
SbN	0.362	---	0.799

Ti_3N_4	0.705	0.669	0.602
V_3N_4	STABLE	---	0.756

SI.2. New SCAN Predicted Stable Nitride Polymorphs

For the FeN, TiN, Mn_3N_2, VN, CrN, and NbN compounds, our DFT-SCAN calculations on DMSP-suggested nitrides determine several new polymorphs that are lower in total energy than the lowest-energy known nitride phase. The observation of these lower-energy polymorphs may suggest that the ground-state crystal structures in these compounds have not yet been synthesized yet. However, DFT does have some notable failures in predicting accurate relative polymorph energetics,[10,11] although SCAN seems to have better polymorph energy rankings in some transition metal oxides,[12] potentially due to satisfaction of all known constraints appropriate to a semilocal exchange-correlation functional, and its accurate representation of all types of orbital overlap. We list below the lower-energy phases in these compounds, and urge readers to interpret their predicted stability within the context of potential DFT errors. We note that this list is significantly longer when total energies are calculated using a standard GGA-PBE functional.

While most predicted stable polymorphs are within -10 meV/atom of the known ground-state nitride, CrN and VN have significantly more stable predicted phases. Both CrN and VN are known to exhibit low-temperature dynamical instabilities,[13,14] which likely underlies the DFT-predicted metastability of the rocksalt phase, which is the stable phase at room temperature. More sophisticated sampling of temperature-dependent magnetic structure may also be required to calculate accurate relative free-energy differences between polymorphs.[14,15]

Composition	E. below known (meV/atom)	Original ICSD Number	Original ICSD Composition	Space Group Symbol
FeN	0	41258	FeN	F-43m
	-2.38	181079	CrN	F-43m
	-3.06	167513	OsN	Pmn2/1
	-10.3	162871	BN	R3m
TiN	0	64904	TiN	Fm-3m
	-2.28	162872	BN	P-6m2
	-3.3	162875	BN	P42/mnm
Mn_3N_2	0	152810	Mn_3N_2	I4/mmm
	-1.06	91273	Sr_2NiN_2	Pnma
VN	0	62468	VN	Fm-3m
	-7	162872	BN	P-6m2
	-36.3	162876	BN	Pnma
	-36.4	163951	AlN	Cmcm
	-76.6	99452	MoN	P63mc
	-81.7	76280	MoN	P1
	-109	150967	NbN	P63/mmc
	-109	76280	MoN	P1
	-111	99452	MoN	P63mc
	-216	181299	ReN	P-6m2
CrN	0	41827	CrN	Fm-3m
	-30.1	161754	CoN	F-43m
NbN	0	644536	NbN	P-6m2

| -0.1 | 169820 | VN | P-6m2 |
| -0.2 | 168368 | MoN | Pm |

SI.3: Select Nitride Convex Hulls

Calculated nitride convex hulls are shown for the Au, Ba, Bi, Ca, Cr, Cu, Fe, Hf, Ir, Mn, Mo, Na, Nb, Os, Pb, Pd, Pt, Re, Ru, Sb, Sn, Sr, Ta, Ti, V, W, and Zr systems, as calculated in the MP and FERE formation energy correction schemes. The SCAN formation energy correction scheme uses the same gas-fit elemental reference correction as the MP scheme, but total energies are calculated within the newly developed SCAN functional. FERE does not have fitted elemental reference energies for Pb, Re, and Ru, so their convex hulls are not shown here. The dashed line shows the convex hull under standard state N_2 gas, the red convex hull is with respect to a nitrogen chemical potential of +1 eV/N. Red squares are known ICSD phases, green diamonds are predicted phases. Orange squares are ICSD phases identified after 2012, and materials with magenta borders have N-N bond lengths corresponding to pernitrides.

Ba-N
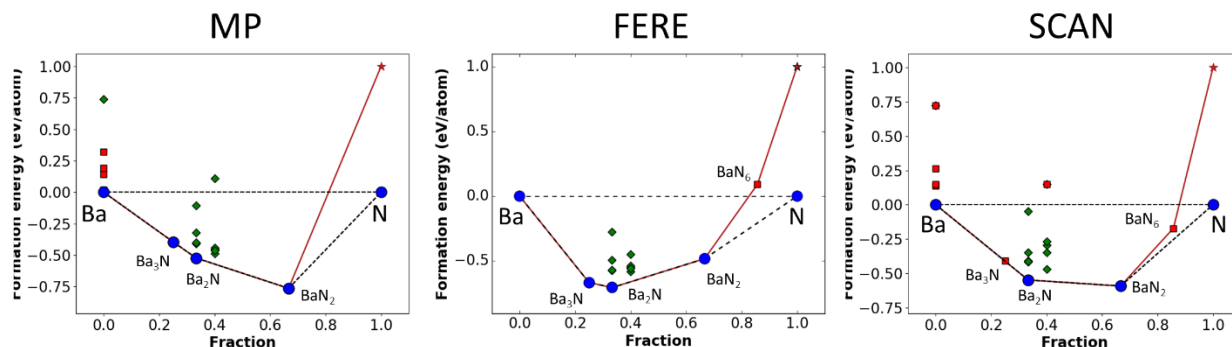
Bi-N

Ca-N

Cr-N

Cu-N

Fe-N

Hf-N

Ir-N

MP   FERE   SCAN

Mn-N

MP   FERE   SCAN

Mo-N

MP   FERE   SCAN

Na-N

MP   FERE   SCAN

Nb-N

MP FERE SCAN

Pb-N

MP FERE SCAN

No FERE correction for Pb

Pd-N

MP FERE SCAN

Pt-N

MP FERE SCAN

Re-N

MP
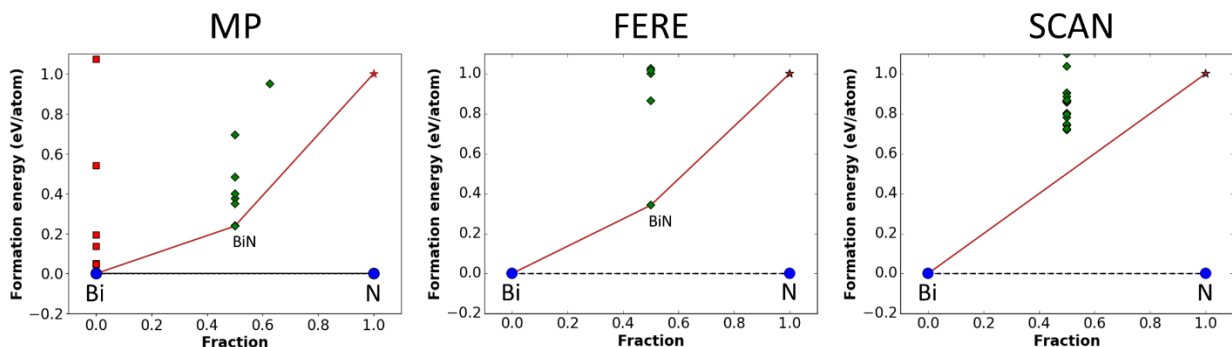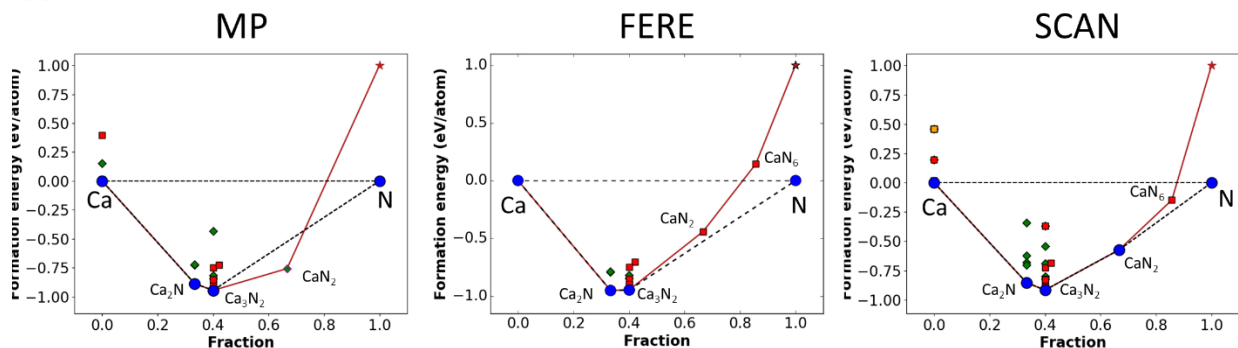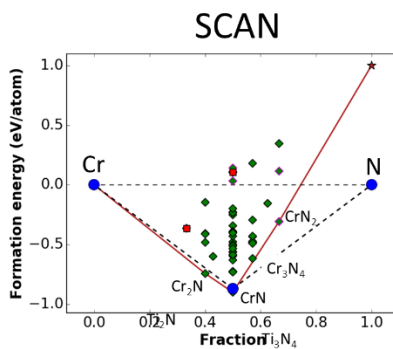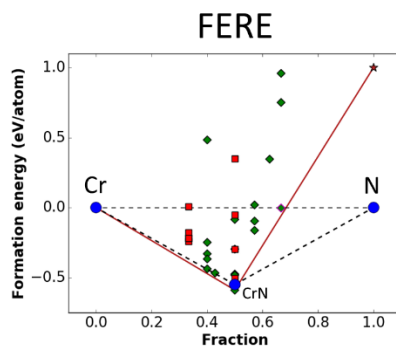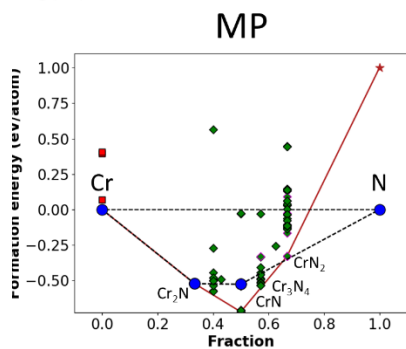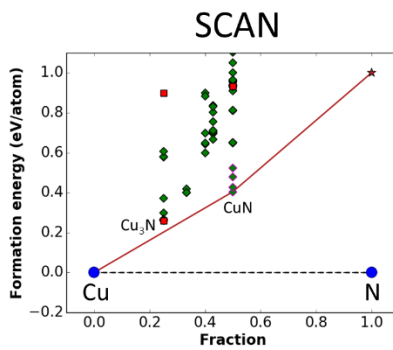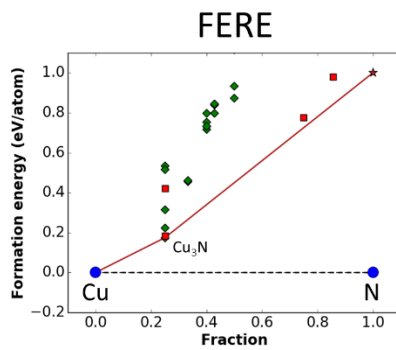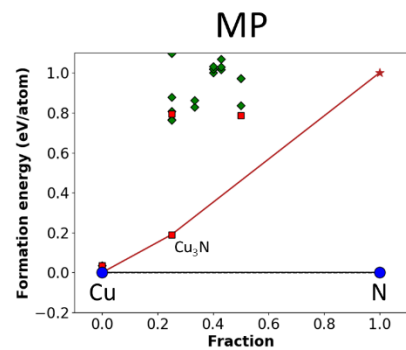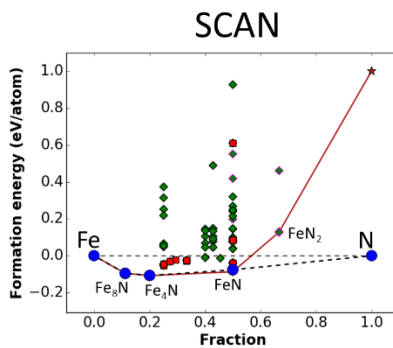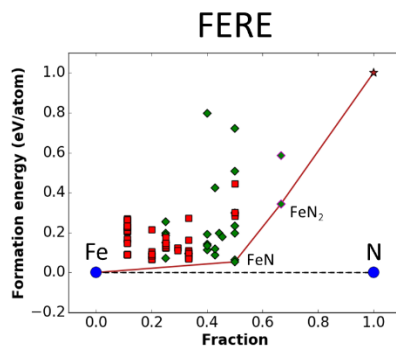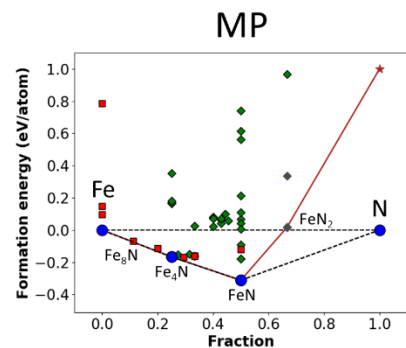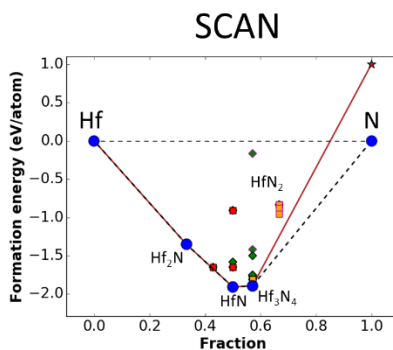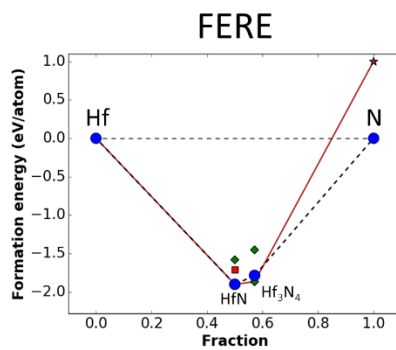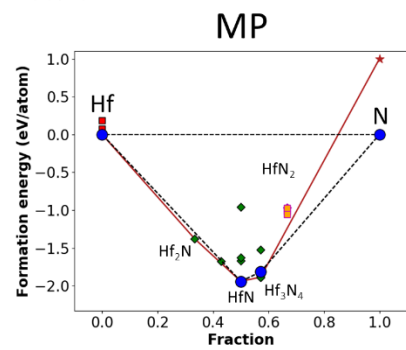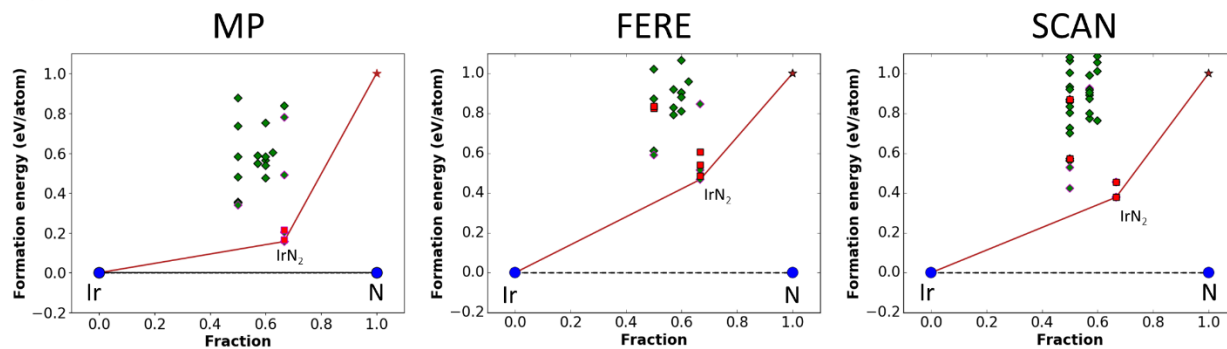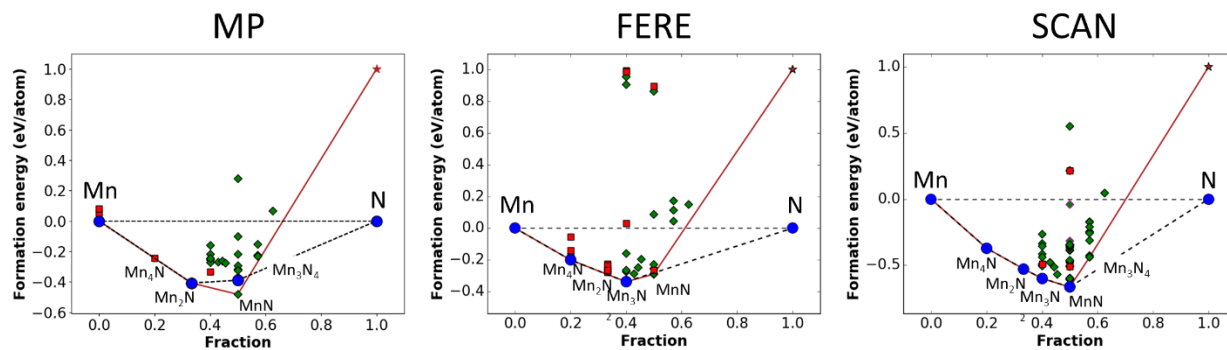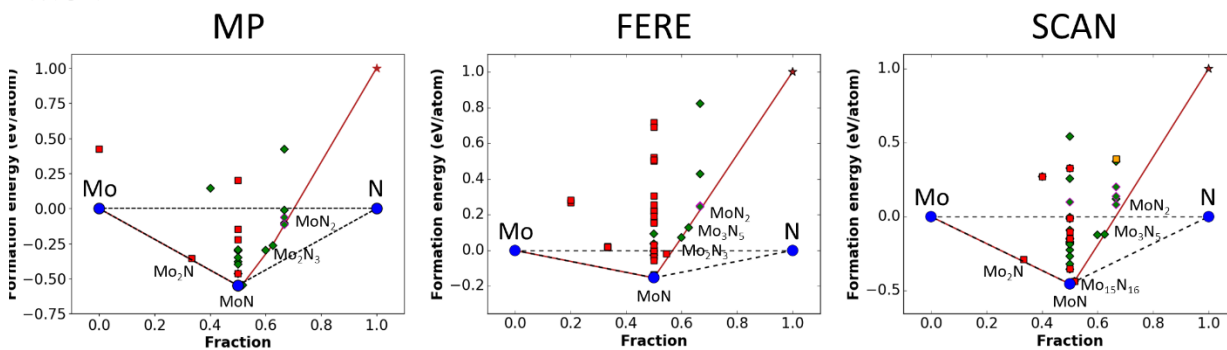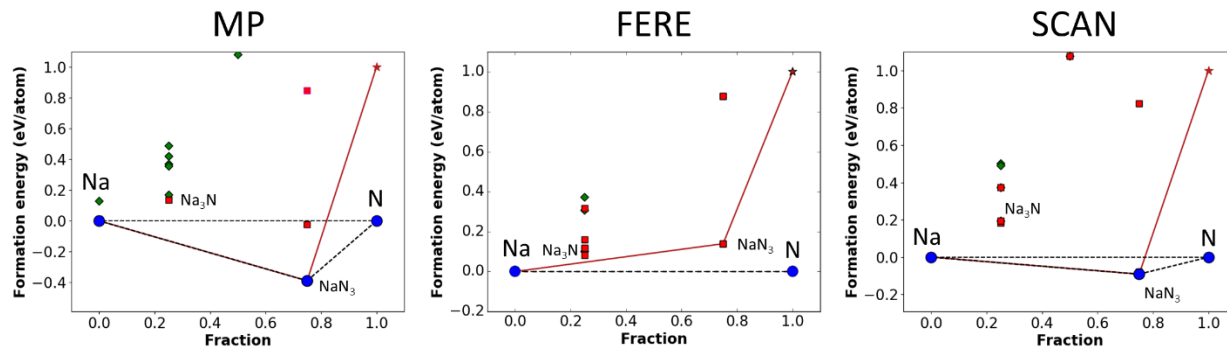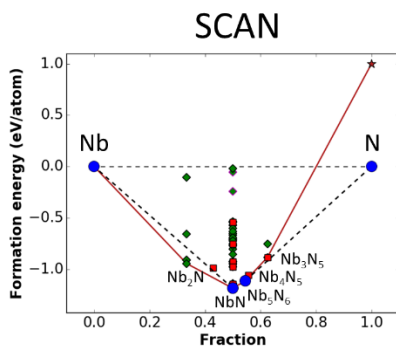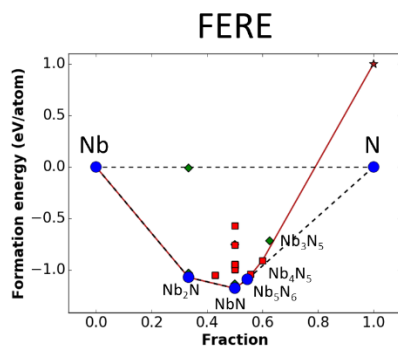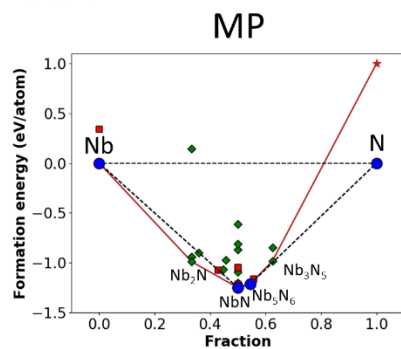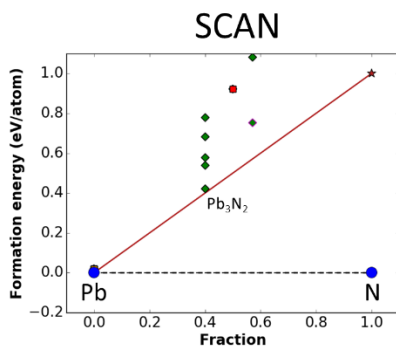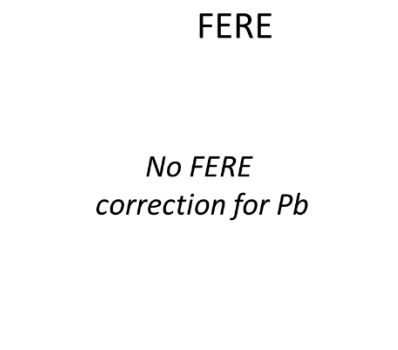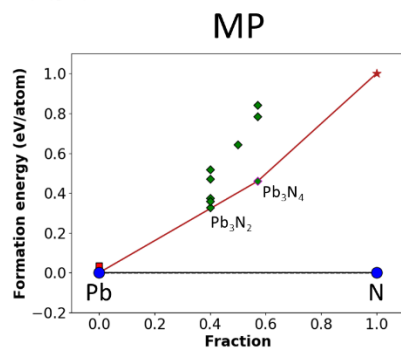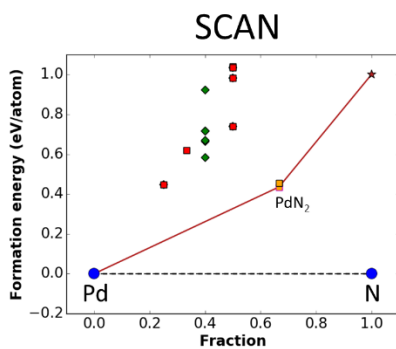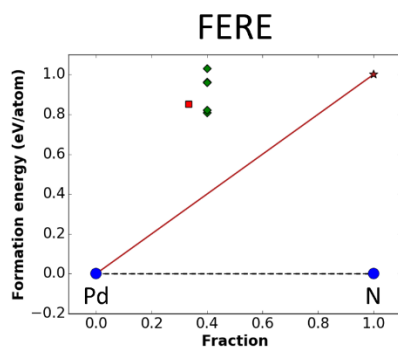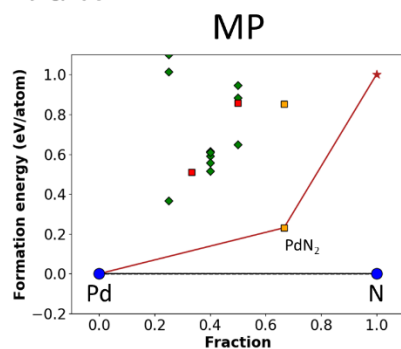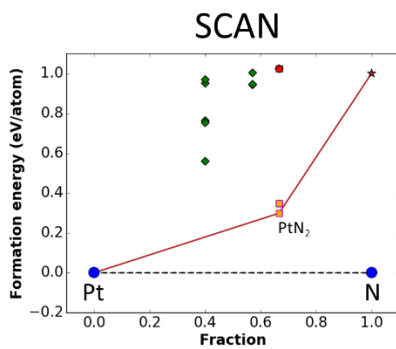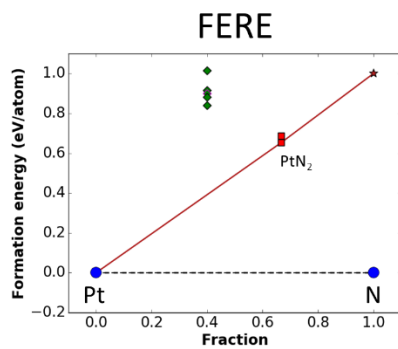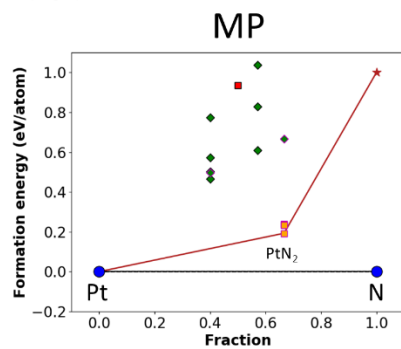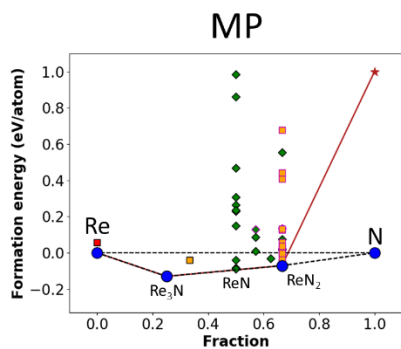
FERE

No FERE correction for Re

SCAN

Ru-N

MP
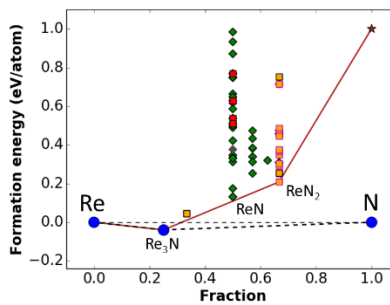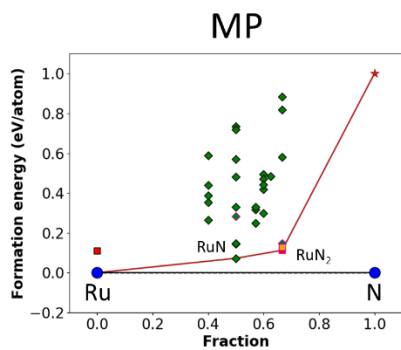
FERE

No FERE correction for Ru

SCAN

Sb-N

MP

FERE

SCAN

Sn-N

MP
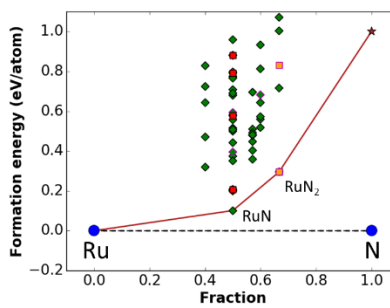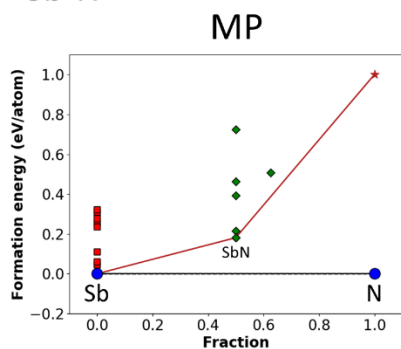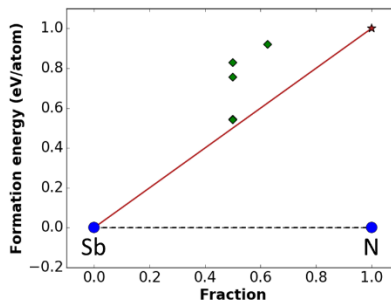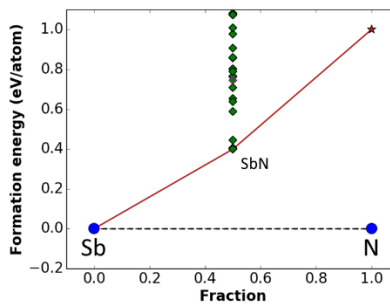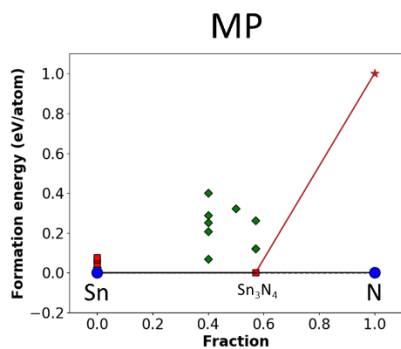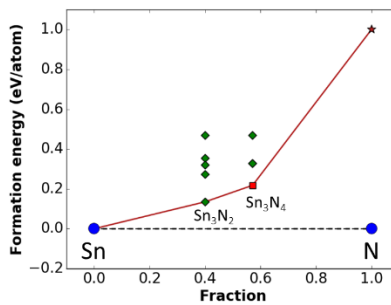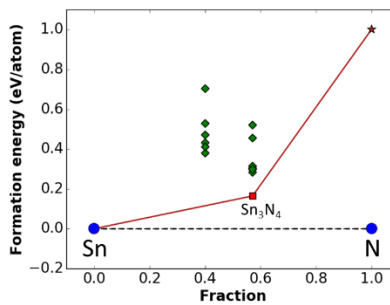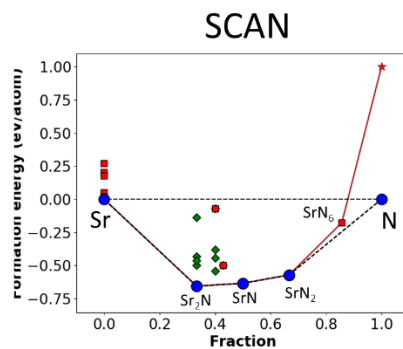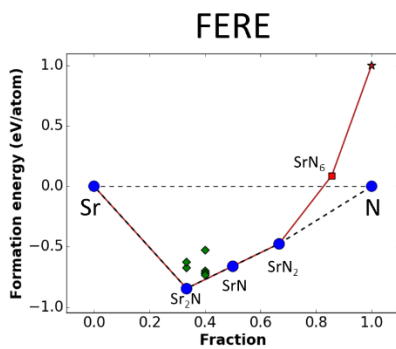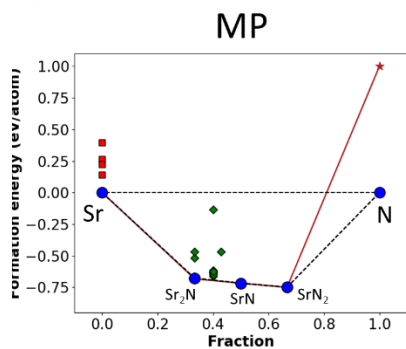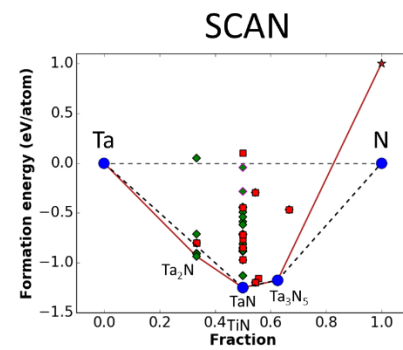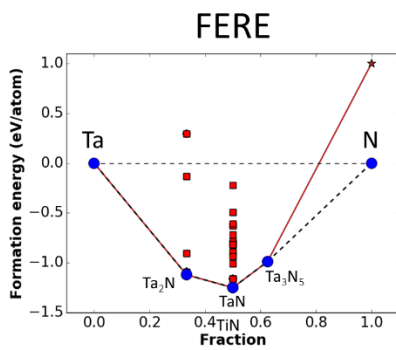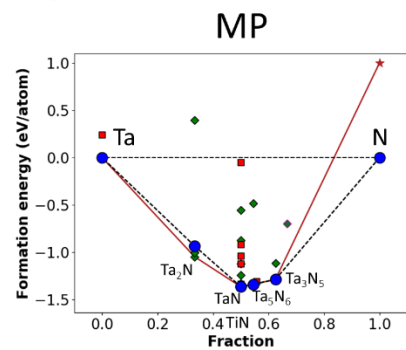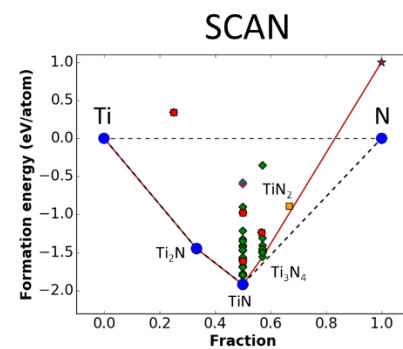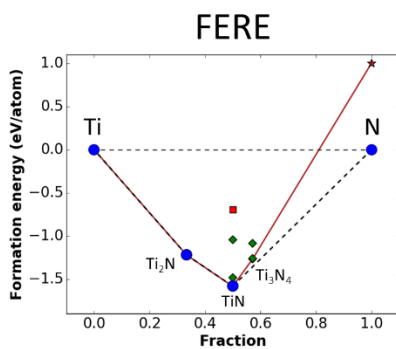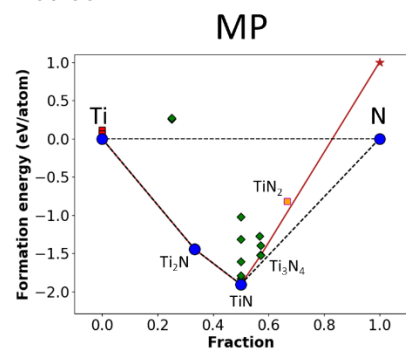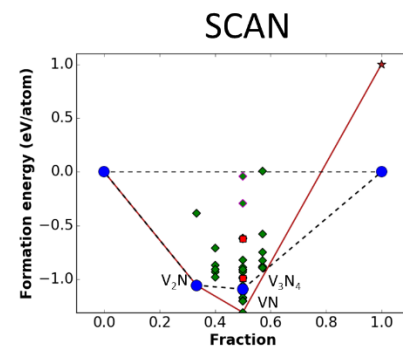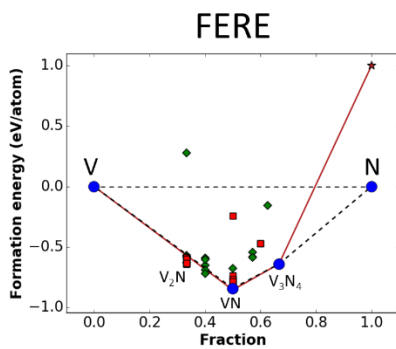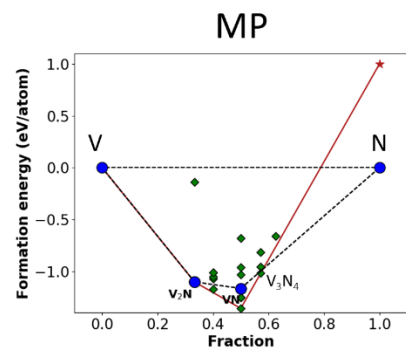
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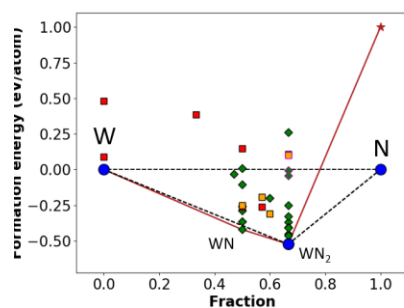
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Supplemental Information References
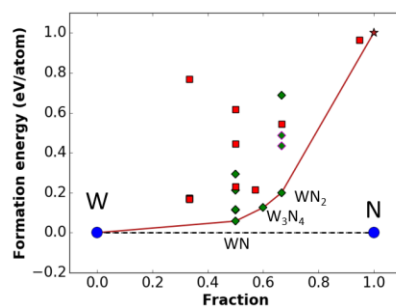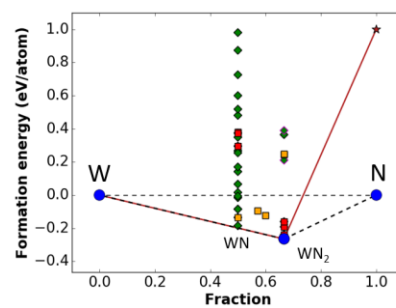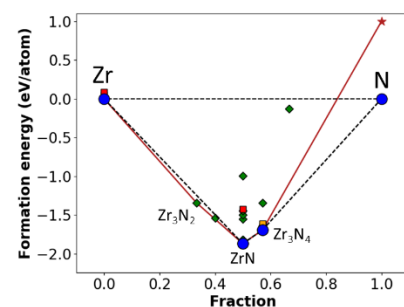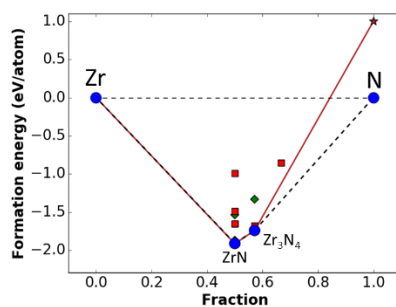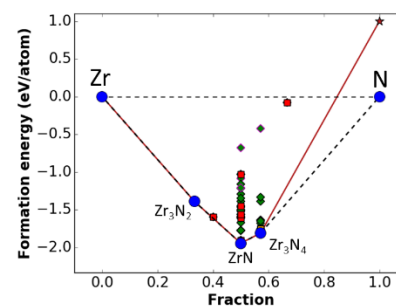
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