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Session 13.01.04: Materials for Quantum Information Science

Instability of Rock-salt Cubic NbN in Density Functional Calculations

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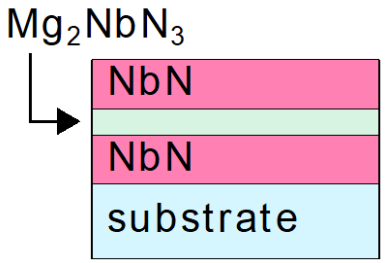
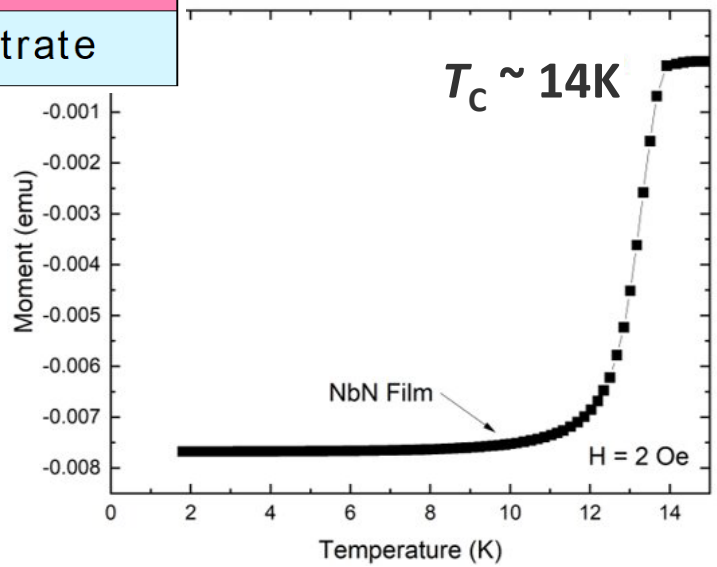
Cubic NbN for Superconducting Quantum Circuits

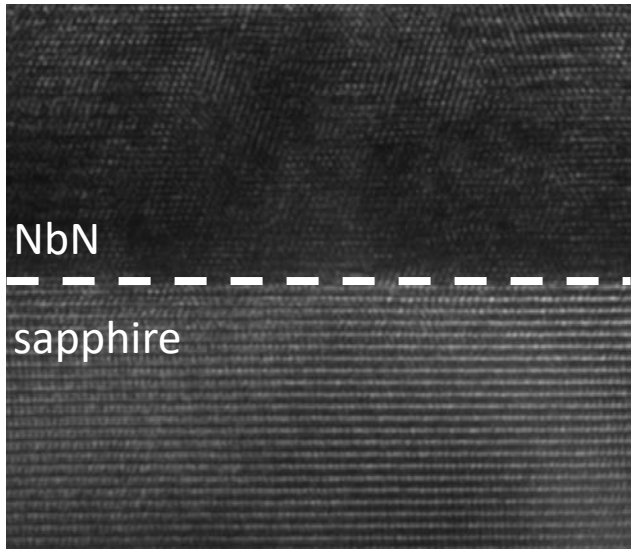
All nitride semi-/super-conductor heterojunctions[1] for Josephson Junction (superconducting quantum circuit)

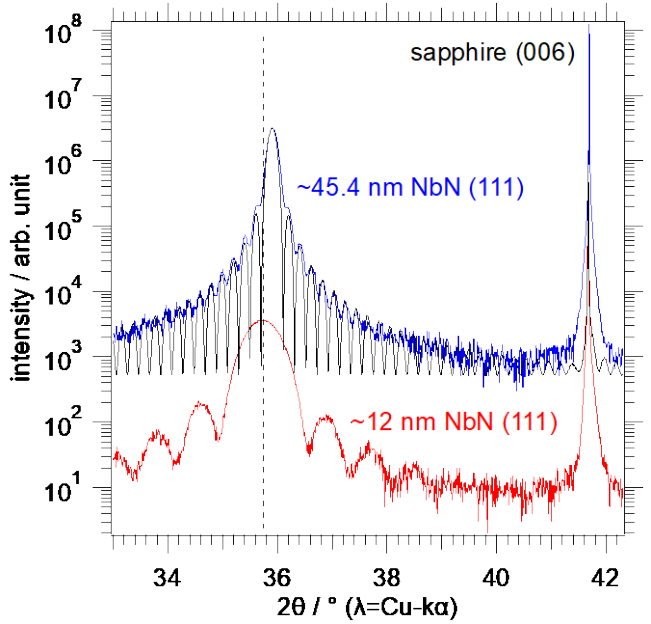


- Structurally commensurate (cubic)
- Chemically compatible (TMNs)



Experimental results courtesy Sage Bauers (NREL)





In thin-films, superconducting NbN stabilizes in the cubic (rock-salt) phase

[1]S. R. Bauers et al., PNAS 45, 116, 14829 (**2019**)

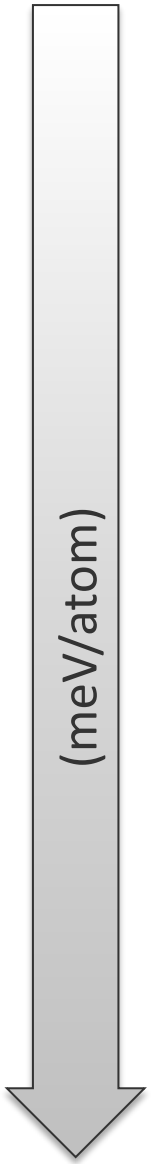
NbN Cubic Phase is Unstable in DFT Calculations

Bulk experiments[1]:

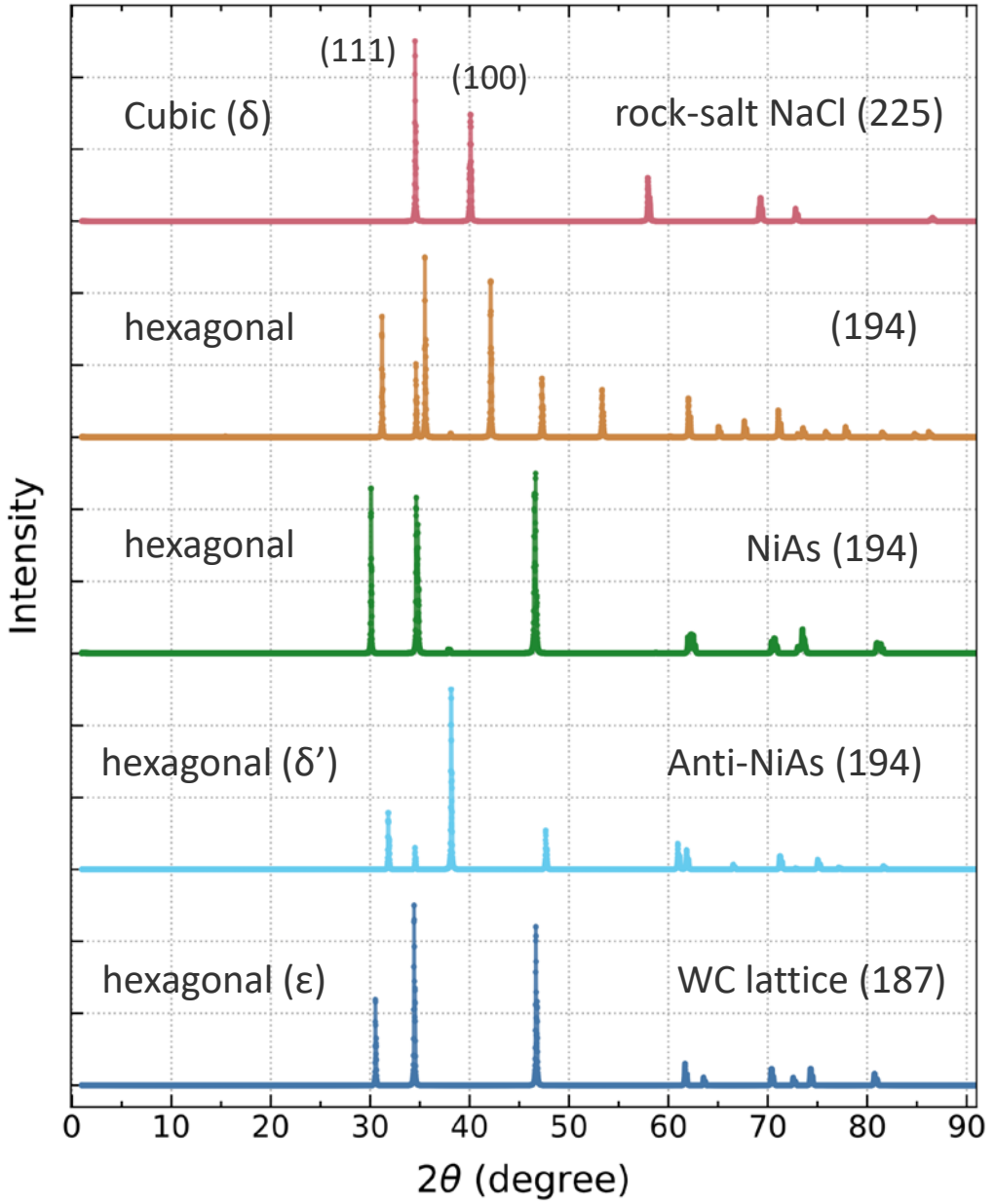
- Stoichiometric hexagonal ε-NbN stable below $T < 1330°C$
- δ-NbN_x, $0.72 < x < 0.86$, stable at $T > 1070 – 1225°C$

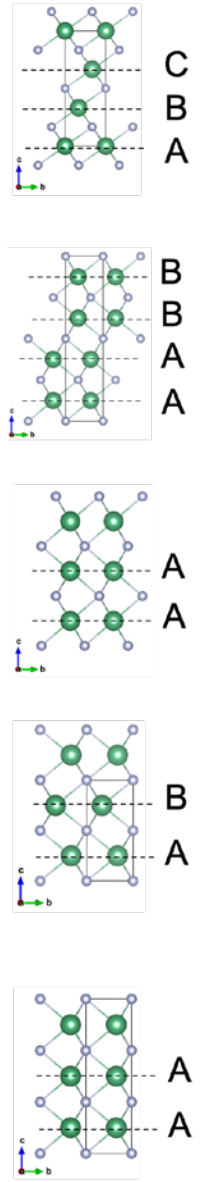
Similar energy ordering reported in DFT literature[2,3]

Energy ordering remains the same across different DFT functionals (PBE+*U*, SCAN) and Hybrid-DFT)



Modeled XRD patterns of known (ICSD) polymorphs of NbN





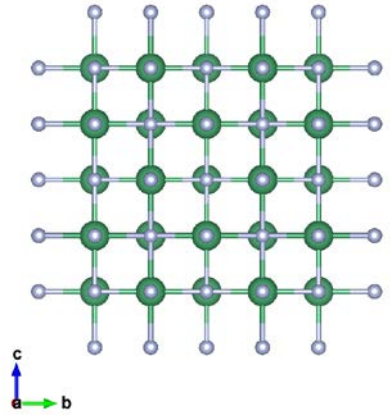
[1]G. Oya et al., J. Appl. Phys. 45, 3 (**1974**)
[2]V. I. Ivashchenko et al., Phys. Rev. B 82, 054109 (**2010**)
[3]K. R. Babu et al., Phys. Rev. B 99,104508 (**2019**)

Why is cubic phase stable in thin-film experiments?

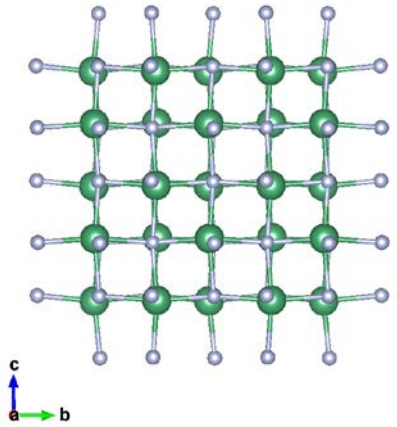
Hypothesis:

- Does there exists other **unknown low-energy polymorph**(s) of NbN with an average cubic symmetry?
- Can **off-stoichiometry** or **oxygen impurity doping** energetically stabilize rock-salt over WC lattice?
- Does **in-plane strain** due to lattice mis-match with the substrate stabilizes the cubic phase?

Cubic phase relaxes to lower energy monoclinic phase in DFT Calculations



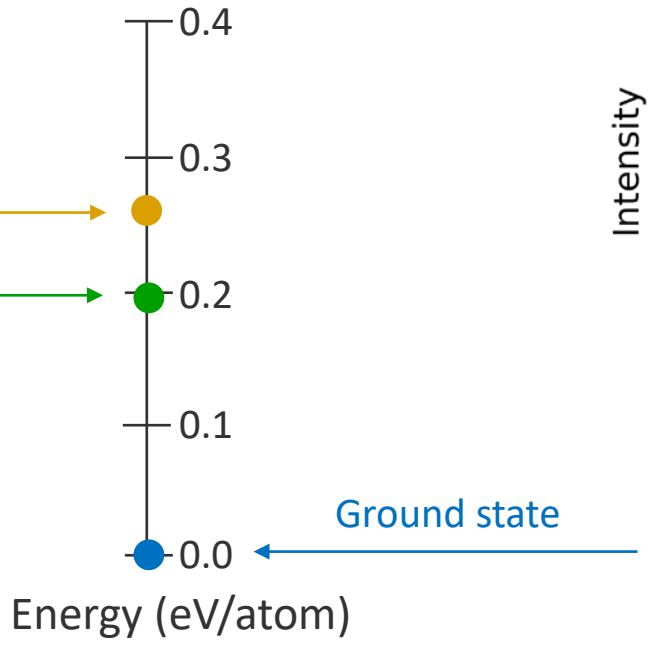
DFT relaxations

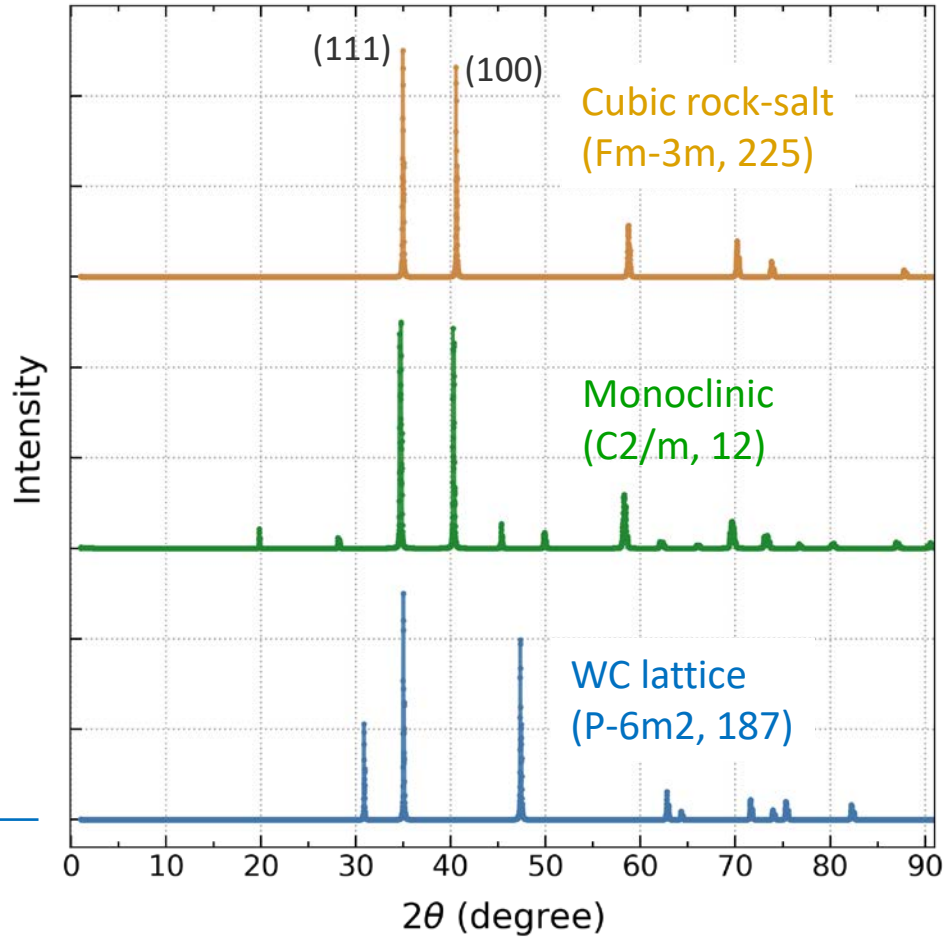


Cubic rock-salt is **dynamically unstable** and relaxes to monoclinic phase

Monoclinic phase (distorted rock-salt) approximate average cubic symmetry

Calculated Energy of NbN polymorphs

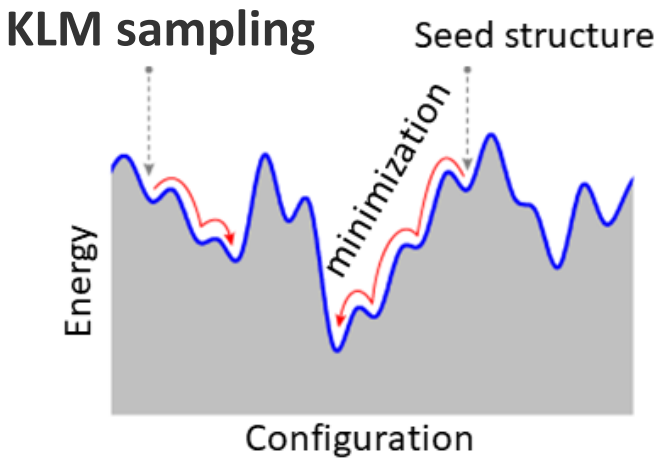




Monoclinic is still substantially higher in energy, ~0.195 eV/atom, above the ground state WC lattice

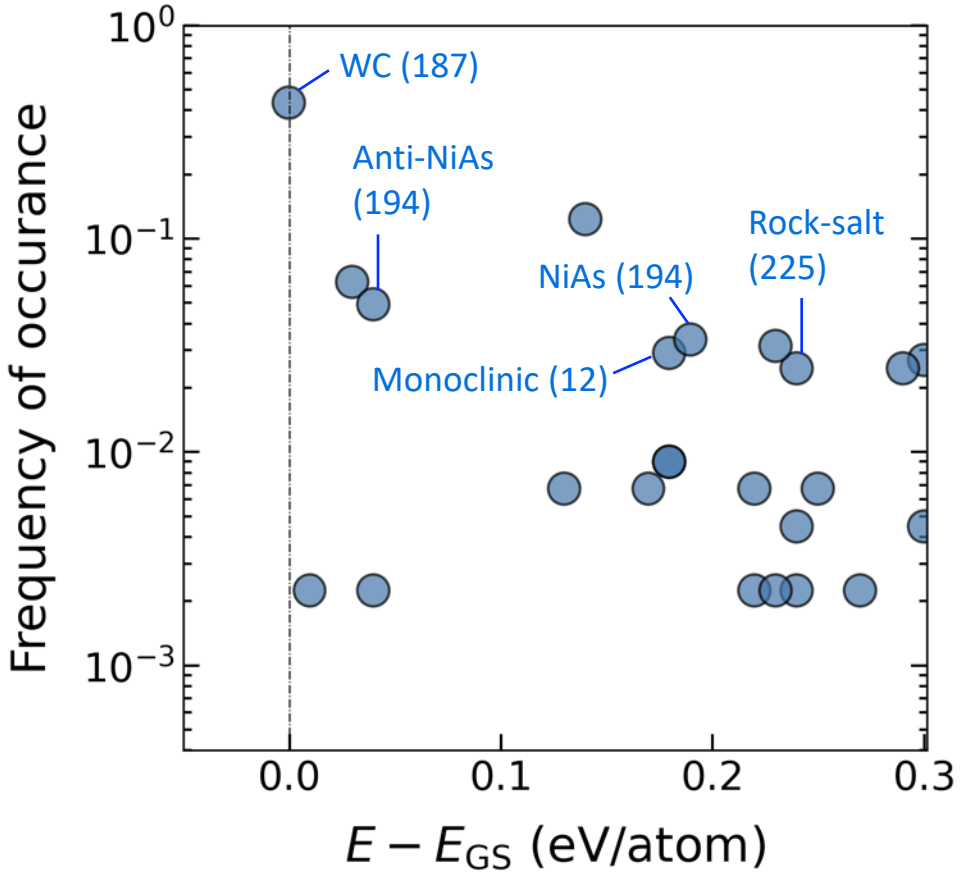
Search for NbN polymorphs using unconstrained structure prediction

Performed using **Kinetically limited minimization (KLM)**[1]



- Hybrid approach combines random sampling and basin hopping
- Well suited for metastable materials
- Application: nitrides[2], oxynitrides[3]
- Considered variable and constrained (c/a) cell shapes and sizes

Structures resulting from KLM sampling (N=4)



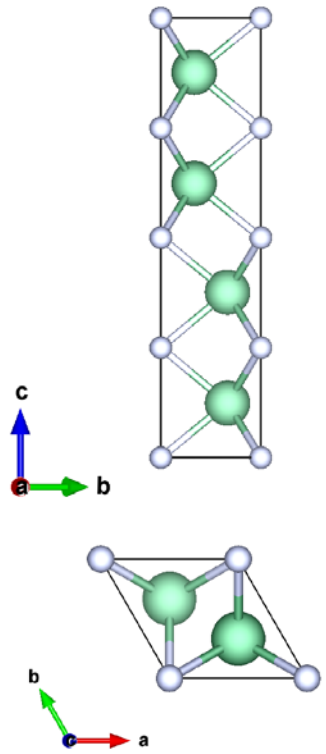
Do we find new (low-energy) polymorphs of NbN from structure prediction?

[1]E. Arca et al., J. Am. Chem. Soc. 140, 4293 (**2018**)
[2]W. Sun et al., Nat. Mater. 18, 732 (**2019**)
[3]A. Sharan and S. Lany, J. Chem. Phys. 154, 23406 (**2021**)

Low energy (< 100 meV/atom) polymorphs from structure prediction

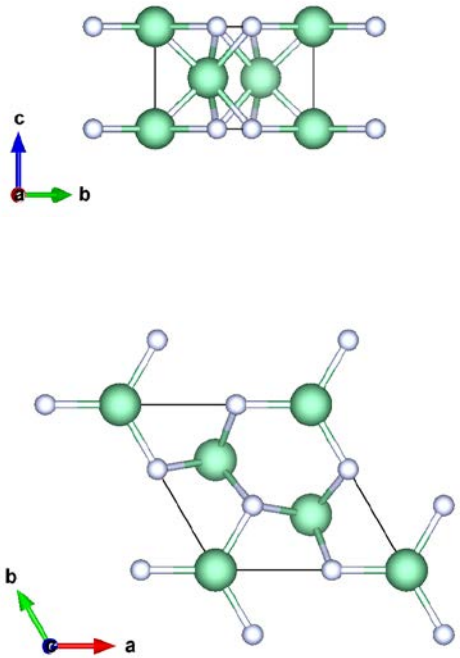
E- E_{GS} = 10.49 meV/atom | 16.62 meV/atom | 34.01 meV/atom | 95.38 meV/atom

Hexagonal
$P6_3mc$ (194)



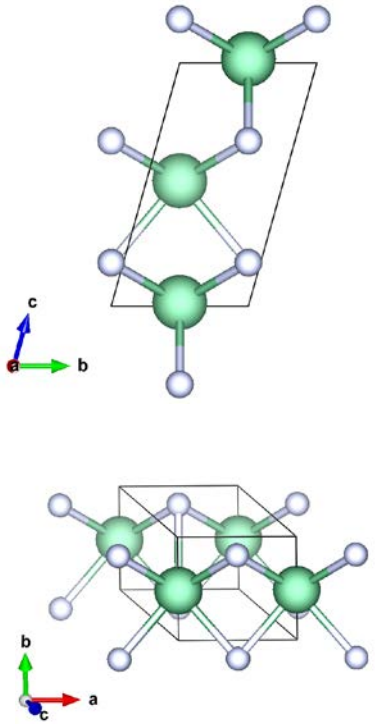
Primitive cell (8 atoms)

Hexagonal
P-62m (189)



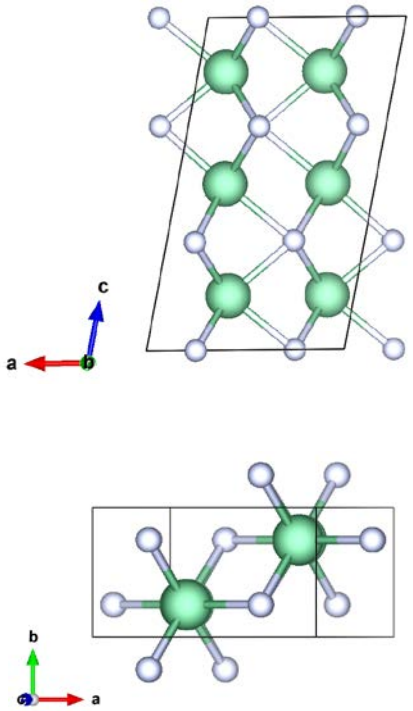
Primitive cell (6 atoms)

Tetragonal
$I4_1md$ (109)



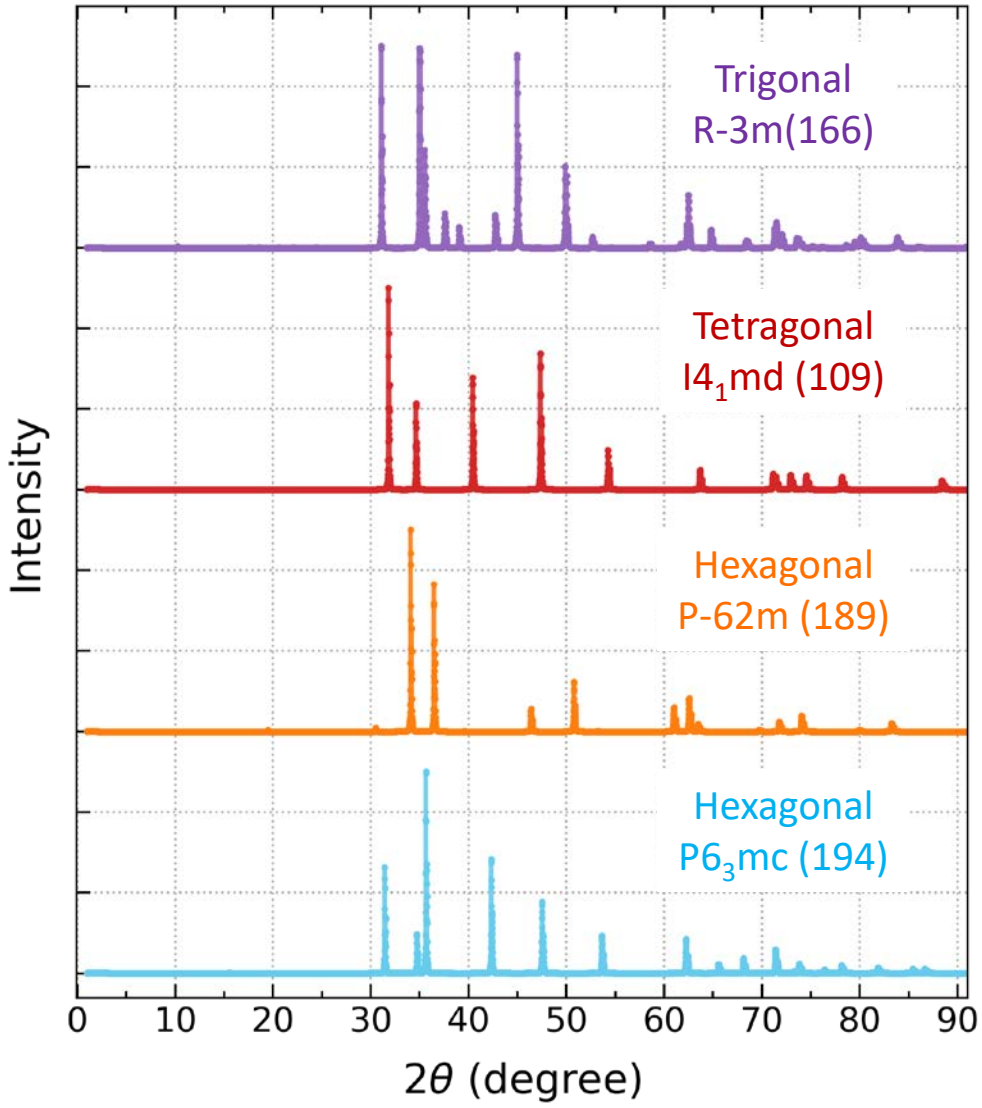
Primitive cell (4 atoms)

Trigonal
R-3m(166)

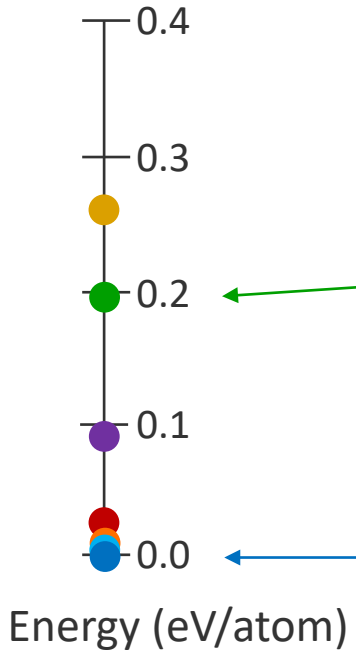


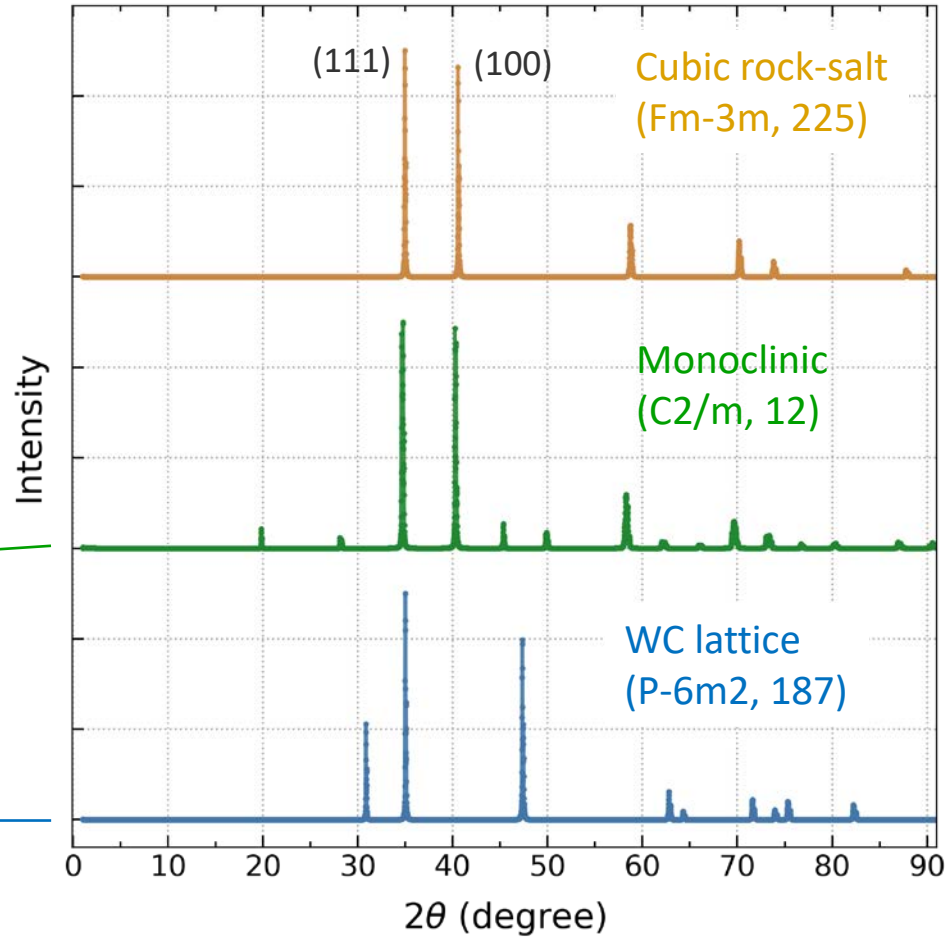
Primitive cell (12 atoms)

Low energy (< 100 meV/atom) polymorphs from structure prediction



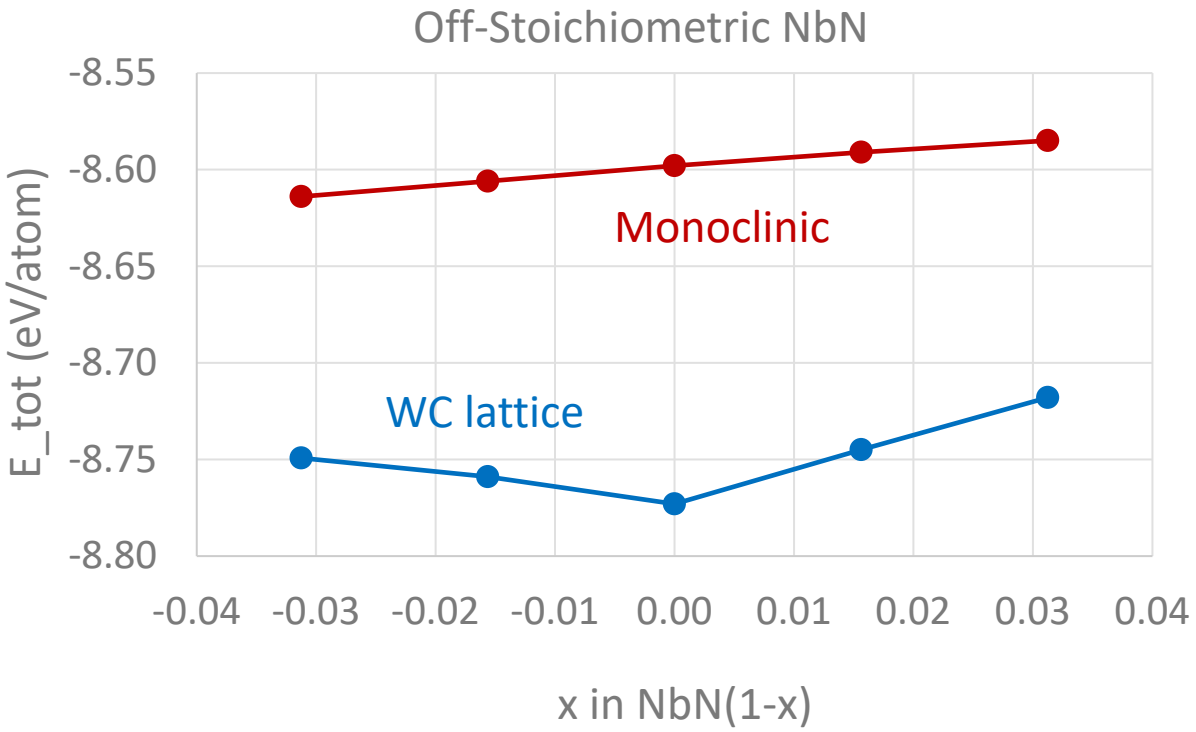
Calculated Energy of NbN polymorphs

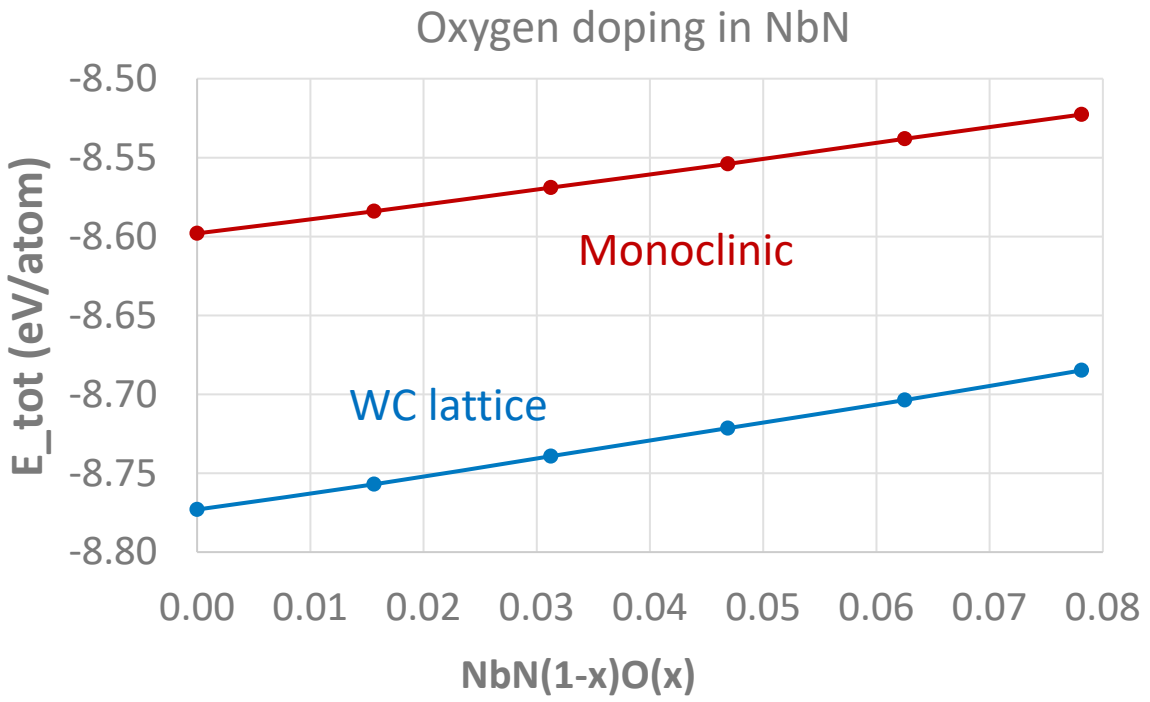




None of the discovered low energy polymorphs has a cubic symmetry. **Monoclinic still the best approximation**

Can off-stoichiometry or oxygen doping stabilize rock-salt over CW lattice?

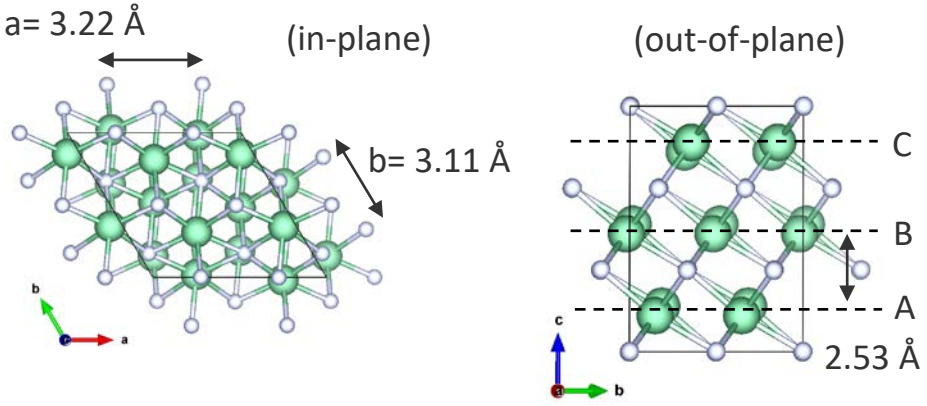




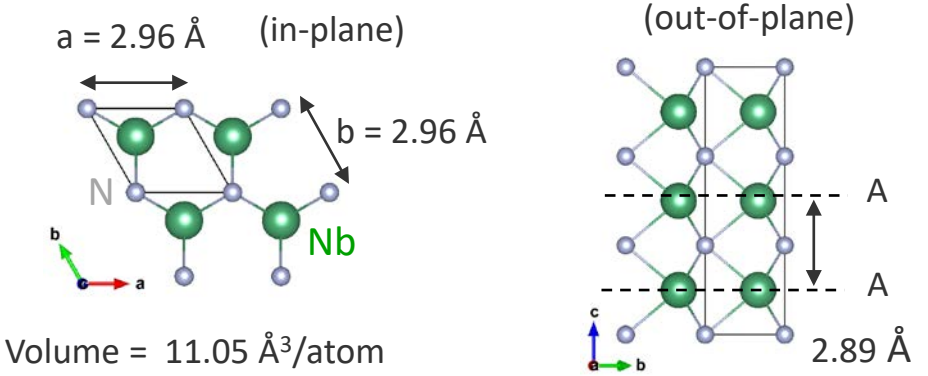
Energy ordering does NOT change for low off-stoichiometric or O impurity doping levels

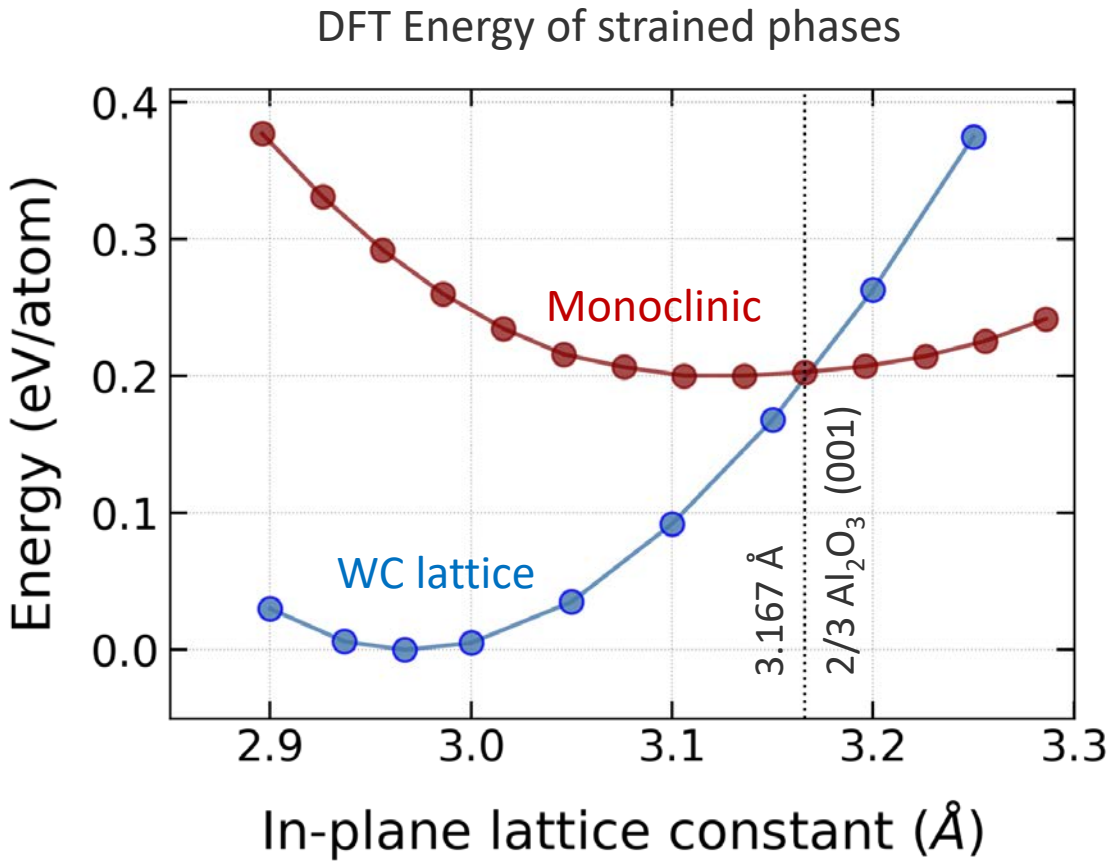
In-plane strain stabilizes the cubic NbN on sapphire (Al_2O_3) (001)

Monoclinic (C2/m, 12)



WC lattice (P-6m2, 187)





WC to monoclinic phase transition is predicted to occur ~3.17 Å

[1]F. Mercier et al., Surface & Coatings Tech. 260, 126 (**2014**)

Concluding Remarks

- **Rock-salt NbN** is energetically **unstable** and relaxes to a lower energy **monoclinic** phase
- Low **off-stoichiometry** or **oxygen doping** do NOT change the energy ordering
- **On sapphire** Al_2O_3 (001), **in-plane strain stabilizes** the cubic NbN phase
- **On MgO** (001), **other factors** (energy barrier) could possibly trap the metastable monoclinic phase

Questions and feedback: anuj.goyal@nrel.gov

Thank you!

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