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)

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

Experimental results courtesy Sage Bauers (NREL)

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\(^1\)S. R. Bauers et al., PNAS 45, 116, 14829 (2019)
NbN Cubic Phase is Unstable in DFT Calculations

Bulk experiments\(^1\):
- Stoichiometric hexagonal \(\varepsilon\)-NbN stable below \(T < 1330^\circ\text{C}\)
- \(\delta\)-NbN\(_x\), \(0.72 < x < 0.86\), stable at \(T > 1070 – 1225^\circ\text{C}\)

Similar energy ordering reported in DFT literature\(^2,^3\)

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

\(^1\)G. Oya et al., J. Appl. Phys. 45, 3 (1974)
Why is cubic phase stable in thin-film experiments?

Hypothesis:

• Does there exist 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 stabilize the cubic phase?
Cubic phase relaxes to lower energy monoclinic phase in DFT Calculations.

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

DFT relaxations

Cubic rock-salt (Fm-3m, 225)

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

Calculated Energy of NbN polymorphs

Ground state

Monoclinic (C2/m, 12)

WC lattice (P-6m2, 187)

Intensity

Energy (eV/atom)

Cubic 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

\(^1\)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)

Do we find new (low-energy) polymorphs of NbN from structure prediction?
Low energy (< 100 meV/atom) polymorphs from structure prediction

- Hexagonal P6_3mc (194): $E - E_{GS} = 10.49$ meV/atom
  - Primitive cell (8 atoms)

- Hexagonal P-62m (189): 16.62 meV/atom
  - Primitive cell (6 atoms)

- Tetragonal I4_1md (109): 34.01 meV/atom
  - Primitive cell (4 atoms)

- Trigonal R-3m (166): 95.38 meV/atom
  - Primitive cell (12 atoms)
Low energy (< 100 meV/atom) polymorphs from structure prediction

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$_2$O$_3$) (001)

Monoclinic (C2/m, 12)

- **a** = 3.22 Å (in-plane)
- **b** = 3.11 Å
- **c** = 2.53 Å
- Volume = 11.02 Å$^3$/atom

WC lattice (P-6m2, 187)

- **a** = 2.96 Å (in-plane)
- **b** = 2.96 Å
- **c** = 2.89 Å
- Volume = 11.05 Å$^3$/atom

DFT Energy of strained phases

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

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1F. 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** $\text{Al}_2\text{O}_3$ (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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