Exploring new phases in Ni-O binary system from ab initio

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INTRODUCTION

- Nickel with oxygen forms three binary phases: NiO, NiO_2 and Ni_2O_3.
- The only known and well scientifically studied nickel oxide phase is NiO (green nickel) and the other two phases are weakly characterized.
- In 1961, Aggarwal identified the crystal structure of Ni_2O_3 as a hexagonal structure [1].
- There are no mentions in literature regarding the Ni_2O_5 oxide - this phase is completely unexplored.
- We focus on **theoretical prediction** of crystal and electronic structure and dynamic stability of **Ni_2O_3 and Ni_2O_5** using **Density Functional Theory modelling (DFT)** and **Evolutionary algorithms (EA)**.

METHODS

- Spin-polarized DFT calculation were performed in program VASP [2] with GGA PBEsol functional and plane-wave cut-off energy 520 eV.
- Strong electron correlations were accounted for with LSDA+U method [3] with Hubbard parameter U_{Ni} = 5 eV in combination with Hund´s correction J_{Ni} = 1 eV.
- Lattice dynamics was calculated for supercells using direct phonon method and quasiharmonic approximation as implemented in the program PHONOPY. [5].
- EA calculations were performed in XTalOpt program [6] in combination with DFT calculations (with PBE functional and cut-off 530 eV) and 1000 structures was generated for Z=2.
- Visualization of crystal structures was done in VESTA [4].

CONCLUSIONS

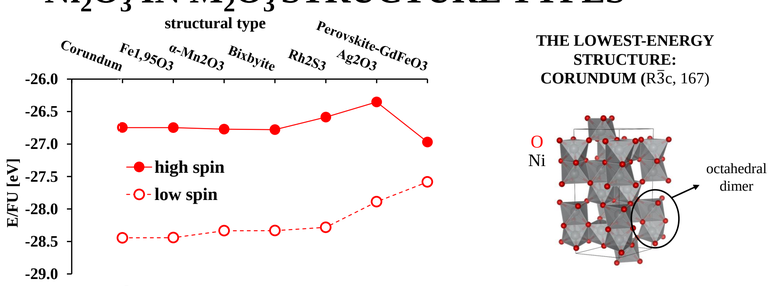
Ni_2O_3

- Considering the 7 structure types commonly taken by transition metal sesquioxides, corundum structure ($R\bar{3}c$) is favoured yet dynamically unstable.
- Dynamically stable Ni_2O_3 ground-state structure is predicted to be a non-centrosymmetric corundum type ($R\bar{3}$, 148) with two crystallographic Ni1 and Ni2 sites.
- Ni_2O_3 ground state structure is predicted to be ferromagnetic semiconductor with band gap equal to 1.4 eV.
- EA calculations confirm the corundum type ground state Ni_2O_3 structure.

Ni_2O_5

- Monoclinic structure (C2/c, 15) common to V, Nb and Ta pentoxides is favoured and predicted to be dynamically stable.
- O-O bridges are present in the monoclinic Ni_2O_5 structure contrary to the known V, Nb and Ta pentoxides.
- Ni_2O_5 in the C2/c structure is predicted to be ferromagnetic conductor.
- EA calculations further confirm the strong tendency for formation of O-O bonds in Ni_2O_5.
- Presence of O-O bonds in all Ni_2O_5 models suggest that it is unlikely to stabilize N^{i5+} cation at ambient conditions in the Ni_2O_5 oxide.

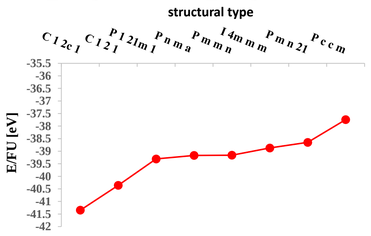
Ni_2O_3 IN M_2O_3 STRUCTURE TYPES

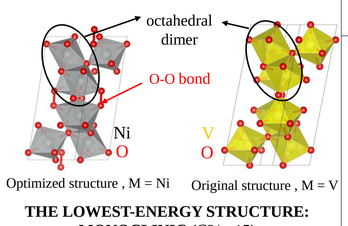


THE LOWEST-ENERGY STRUCTURE: CORUNDUM ($R\bar{3}c$, 167)

- Low-spin Ni^{3+} energetically preferred in all Ni_2O_3 models.
- The lowest energy structure is corundum type.
- Characteristic feature of corundum structure are **octahedral dimers** (in the c-direction) formed by MO_6 octahedrons that share a common face.

Ni_2O_5 IN M_2O_5 STRUCTURE TYPES





THE LOWEST-ENERGY STRUCTURE: MONOCLINIC (C2/c, 15)

M_2O_5	C2/c	C2	$P2_1/m$	Pnma	Pmmn	I4/m mm	$Pmn2_1$	Pccm
M	V, Nb, Ta	Nb, Ta	V	V	V	Nb	V	Ta

- The structure with lowest energy (C2/c, 15) is common for all known M_2O_5 oxides (see table above)
- $[NiO_6]$ octahedra from **octahedral dimers** by sharing a common edge. The dimers are interconnected by oxygen atoms in shared vertices.
- O-O bonds are being formed in all optimized Ni_2O_5 modes in contrary to the original structures commonly taken by V, Nb and Ta pentoxides.

REFERENCES

[1] P. S. Aggarwal, A. Goswami. J Phys Chem, 65, 2105 (1961).

[2] G. Kresse and J. Hafner, Phys. Rev. B 47 , 558 (1993); ibid. 49, 14251 (1994).

[3] G. Kresse and J. Furthmüller, Comput Mater Sci. 6, 15 (1996).

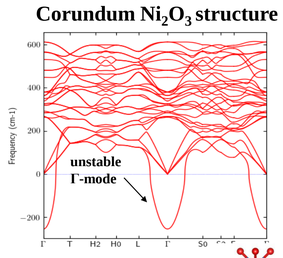
[4] K. Momma a F. Izumi, J. Appl. Crystallogr., 41, 653 – 658 (2008).

[5] A. Togo and I. Tanaka, Scr. Mater., 108, 1-5 (2015).

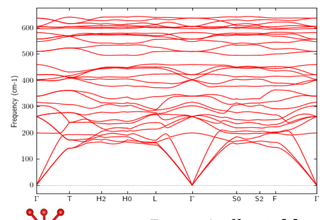
[6] D. C. Lonie, E. Zurek, Computer Physics Communications 182, 372-387 (2011).

Ni_2O_3 LATTICE DYNAMICS

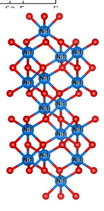
Nondisplaced $R\bar{3}c$ Corundum Ni_2O_3 structure

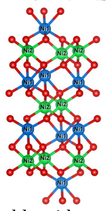


Γ-mode displaced $R\bar{3}$ Corundum Ni_2O_3 structure



Dynamically **unstable** corundum with **one** crystallographic **Ni site**: Ni1

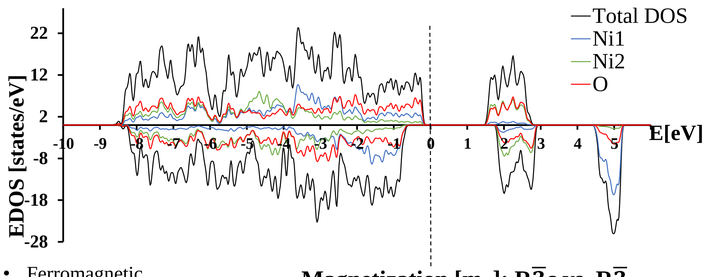




Dynamically **stable** corundum with **two** crystallographic **Ni sites**: Ni1 and Ni2

- The corundum structure is dynamically unstable with respect to phonon soft mode at Γ point of the Brillouin zone.
- This vibrational mode lowers the symmetry of the corundum structure from $R\bar{3}c$ (167) to $R\bar{3}$ (148) with two distinct crystallographic Ni sites.

ELECTRONIC STRUCTURE ($R\bar{3}$)



- Ferromagnetic semiconductor.
- Insulating band gap is **1.4 eV.**

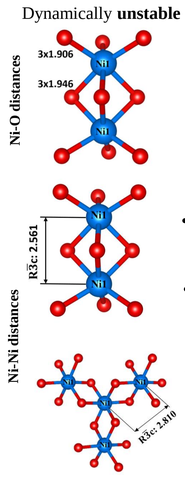
Magnetization [m_B]: $R\bar{3}c$ vs. $R\bar{3}$

	Ni1	Ni2	O
nondisplaced $R\bar{3}c$	1.138, 1.141	-	-0.072, -0.086, -0.099
displaced $R\bar{3}$	1.575	0.361	0.013, 0.016, 0.025

- **$R\bar{3}c$ corundum structure** - two magnetically slightly distinct nickel sites, which are organized into separated layers in the same fashion as Ni1 and Ni2 in the distorted $R\bar{3}$ corundum structure.
- **$R\bar{3}$ corundum structure** - magnetic moment on Ni1 is increased relative to the $R\bar{3}c$ corundum and magnetic moment on Ni2, which is characteristic of the very short Ni-O distances is severely reduced.

ANALYSIS OF GEOMETRY

Dynamically **unstable $R\bar{3}c$**



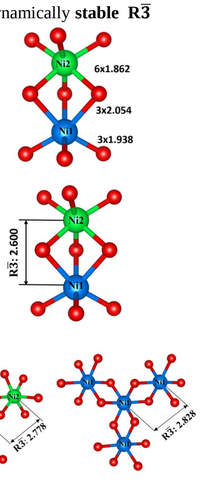
← $R\bar{3}c$ - the $[NiO_6]$ octahedron has three longer and three shorter Ni-O distance.

→ $R\bar{3}$ - two different octahedrons. Ni1: three longer and three shorter Ni-O distances.

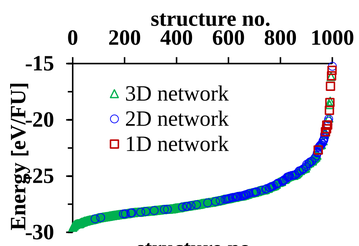
Ni2: six equivalent Ni-O distances.

- The intra-dimer Ni-Ni distance elongates upon symmetry lowering.
- The intra-layer Ni-Ni distance decreased within Ni1 layers and increased within the Ni2 layer upon symmetry lowering.
- The shortest Ni-Ni distance is in the octahedral dimer in both structures.

Dynamically **stable $R\bar{3}$**

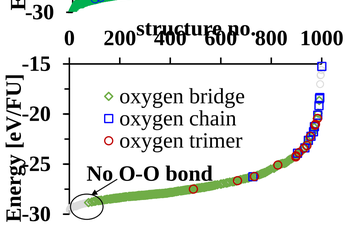


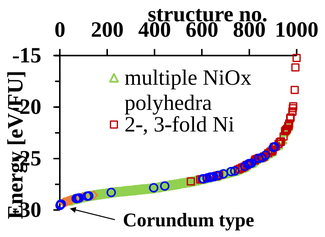
EVOLUTIONARY ALGORITHMS



Bonding networks

- Crystal structures with 3D connectivity are the most frequent and energetically preferred.





Formation of O-O bonds

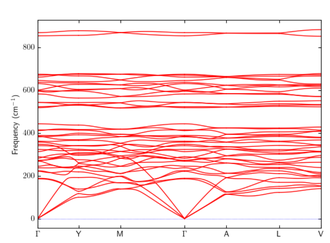
- Majority of structures contain oxygen-oxygen bonds.
- The lowest-energy structures do not contain oxygen-oxygen bonds.

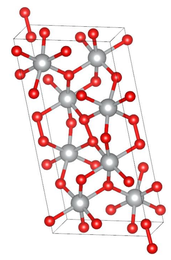
Topology

- Majority of EA structures contain multiple NiO_x polyhedra: *e.g.* octahedron, pyramid, square, butterfly.
- The lowest-E structure is corundum.

Ni_2O_5 LATTICE DYNAMICS

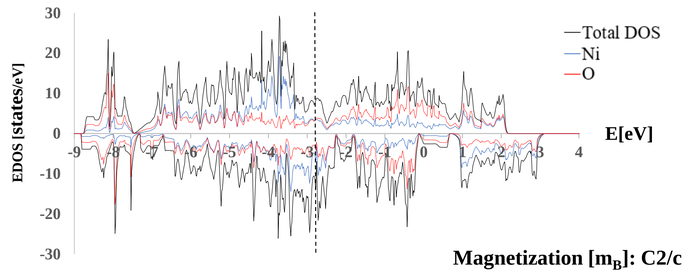
Monoclinic C2/c Ni_2O_5 structure





- The monoclinic (C2/c, 15) structure is dynamically stable, there are no negative frequencies present.

ELECTRONIC STRUCTURE (C2/c)

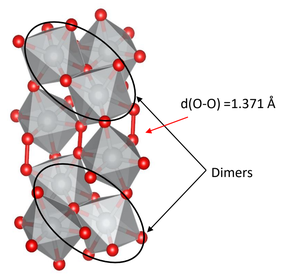


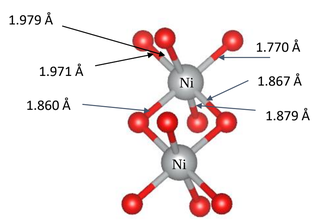
- This structure appears to be a ferromagnetic conductor

Magnetization [m_B]: C2/c

	Ni	O	
C2/c	0.678 – 0.688	0.211 – 0.213	-0.085 – -0.211

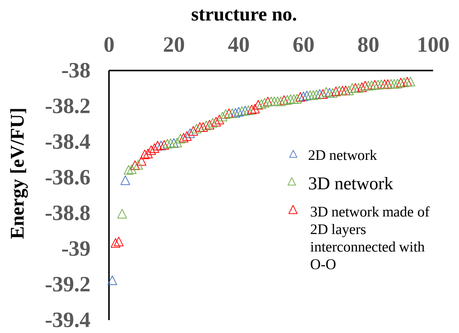
ANALYSIS OF GEOMETRY





- The intra-dimer Ni-Ni distance is 2.833 Å.
- Dimers are made of slightly distorted octahedrons - all distances between Ni and coordinating O atoms in one octahedron are different.
- Very short O-O distances are present in this structure.
- Octahedron dimers share vertices and are further interconnected by O-O bridges.

EVOLUTIONARY ALGORITHMS



Formation of O-O bonds

- The first 100 lowest-energy structures contain O-O bonds.

Bonding networks

- Lowest energy structure has 2D network
- Crystal structures with 3D connectivity are the most frequent, with majority of them being made of 2D layers interconnected with O-O bonds

Topology

- Majority of EA structures contain multiple NiO_x polyhedra, *e.g.* octahedron, pyramid, tetrahedron, planar square, planar triangle.
- Most of the polyhedra are distorted to various extent.

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