The search for the new superconductors in the Ni-N system

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Abstract. Transition metal nitrides show a unique combination of superconducting and mechanical properties. In this study we perform a theoretical search of the intermediate compounds in Ni-N system, determine their superconducting transition temperatures ($T_c$) and bulk moduli ($K_0$) in the wide range of pressures, from 0 to 300 GPa. We have revealed several nickel-rich interstitial compounds, Ni$_5$N$_2$, Ni$_3$N, and Ni$_6$N, and one nitrogen-rich compound, NiN$_2$, as stable structures. At pressures above 100 GPa, previously unknown NiN with antinickeline structure is also stabilized. All found compounds are non-magnetic. The most promising for superconductivity NiN$_2$ structure is stable against decomposition on the mixture of (Ni+N) from 3 to at least 300 GPa. The transition from marcasite-type NiN$_2$-P$_{nmm}$ to pyrite-type NiN$_2$-Pa$_3$ occurs at 70 GPa. NiN$_2$-P$_{nmm}$ is an insulator with the band gap of about 1 eV, while NiN$_2$-Pa$_3$ is a metallic phase. The calculated $T_c$ of NiN$_2$-P$_{nmm}$ equals to $10^{-2}$ K, and the bulk modulus ($K_0$) equals to 225 GPa at 10 GPa, which is in excellent agreement with available experimental data. The comparison of $T_c$ of compounds in the Ni-H and Ni-N systems with that of the Fe-H and Fe-N compounds, shows that hydrides and nitrides of nickel have lower $T_c$ than hydrides and nitrides of iron, which is explained by the significant differences in crystal structures.

1. Introduction

Nitrogen-rich transition metal (TM) nitrides (MN$_x$, $x > 1$), the so-called covalent conductors, are rare class of materials combining presence of both metallic and covalent bonds. Due to the low reactivity of nitrogen at ambient pressure, their synthesis requires high-temperatures, that usually decompose initial reagents. This obstacle can be overcome by application of high pressures, so that the number of new TM nitrides were synthesized in high-pressure apparatus in the pressure range of 20-100 GPa. These include first of all pernitrides PtN$_2$, PdN$_2$, IrN$_2$, OsN$_2$, TiN$_2$, CoN$_2$, FeN$_2$, RhN$_2$, and ReN$_2$ ([1] and reference therein), and NiN$_2$ [2], containing covalently bonded dumbbell N-N units. Similarly to other late metal nitrides, the NiN$_2$ is characterized by marcasite-type structure [2]. This structure does not have infinite 2D- or 3D-nets, typical for the conventional superconductors [3]. However, the available data on NiN$_2$ (as
well as on most of the other TM nitrides), is limited to 60 GPa [2]. At ultra high-pressures a transition from isolated covalently bonded units to chains, sheets and frameworks occurs. Calcium carbides [4] and carbonates [5] can be given as an example of such a structures. In the present investigation, we perform the search of \( \text{Ni}_x \text{N}_y \) structures up to the pressures of 300 GPa, describe the observed structural changes and make an assessment of their superconducting transition temperatures and elastic properties.

2. Details of calculations
To predict stable nickel nitrides, we have explored the Ni-N system using the variable-composition evolutionary algorithm technique, as implemented in the USPEX code [6, 7, 8, 9]. We performed crystal structure predictions in the pressure range from 50 to 300 GPa with up to 40 atoms in the primitive unit cell. First generation was produced randomly. 60% of the structures with the lowest enthalpy were selected after the optimization and then used for producing the next generation, with 40% of structures produced by heredity, 20% - by atomic mutation, 10% - by lattice permutation, and 30% - randomly. For the produced structures, structural relaxations and total energy calculations were performed within density functional theory (DFT) implemented in the VASP package [10, 11, 12]. The exchange-correlation interaction was taken into account in the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional [13]. The computation parameters were as follows: energy cut-off 450 eV; the density of the grid of Monkhorst-Pack [14] k-point mesh \(-0.5\, \text{Å}^{-1}\); electronic smearing - with Methfessel-Paxton scheme; parameter \(\sigma=0.2\, \text{eV}\). The most promising predicted structures were then optimized with higher accuracy at various pressures. In these calculations, the cut-off energy was 700 eV, the density of k-points was 0.2 \(\text{Å}^{-1}\), and parameter \(\sigma=0.1\, \text{eV}\).

Symmetry of the structures were analysed with FINDSYM program [15], and VESTA software [16] has been used for the structure visualisation.

To take into account the temperature effect and predict the phase diagram of NiN\(_2\), we used the method of lattice dynamics within the quasi-harmonic approximation (QHA), according to the standard technique [17]. For this task, the phonon frequencies were calculated with the PHONOPY code [18]. The energy cut-off in this case has been increased to 900 eV.

Calculations of \(T_c\) were performed using the QUANTUM ESPRESSO package [19, 20]. Phonon frequencies and electron-phonon coupling (EPC) coefficients were computed using density-functional perturbation theory, employing the plane-wave pseudopotential method and PBE exchange-correlation functional. In the calculations of the EPC parameter \(\lambda\), the energy cut-off was 70 Ry; the first Brillouin zone was sampled using \(2\times2\times2\) q-point mesh and a denser \(12\times12\times12\) k-point mesh for NiN\(_2\) (with Gaussian smearing and \(\sigma=0.05\, \text{Ry}\)). The \(T_c\) was estimated by using the McMillan equation by the standard scheme [21]. For empirical parameter \(\mu^*\), the lower and upper bound values of 0.10 and 0.15 were used.

3. Results and Discussion
3.1. Predicted phases
Performed calculations on crystal structure prediction show that there are no stable intermediate compounds in Ni-N system at 0 GPa (Figure 1). The phase Ni\(_3\)N was synthesized experimentally at ambient pressure [22]. According to our calculations, similar phase became stable starting from 2 GPa (Figure 2).

The difference between experimental and theoretical results is explained by the difference in synthesis conditions. In the experiment, Ni\(_3\)N was synthesized from Ni(NH\(_3\))\(_6\)Cl\(_2\) and NaNH\(_2\) at 523 K, while in our calculations the stability of Ni\(_3\)N against decomposition on (Ni+3α-N) at 0 K was considered. Also, there is some structural differences between synthesized and predicted phases. In the synthesized phase, nitrogen is disordered through two positions, \((0.333\ 0.667\ 0.5)\).
0.25) and (0.00 0.00 0.25), with 97% and 3% occupancies, while in the predicted phase all the nitrogen is in the first position (Table 1). This disorder likely increases the entropy and Gibbs energy, expanding the stability field of the phase.

Figure 1. Calculated convex hulls of the Ni-N system at 0, 50, 100, 200, 300 GPa (a) and corresponding phase transitions (b); stable structures are shown with blue squares, metastable with red triangles

Figure 2. Pressure-Enthalpy dependancies for Ni$_3$N (a) and NiN$_2$(b) relative to the mixture (3Ni+N) and (Ni$_3$N+N), respectively

At 50 GPa there are two stable intermediate phases on the convex hull of energy, mentioned Ni$_3$N and NiN$_2$-Pnm with marcasite-type structure (Figure 1).
Figure 3. PT diagram of NiN$_2$ phases

The calculated enthalpies shows that NiN$_2$-$Pnnm$ became stable against decomposition on (Ni$_3$N+5N) at 7 GPa and remains stable up the pressure of 300 GPa, undergoing phase transition from NiN$_2$-$Pnnm$ with marcasite-type structure to NiN$_2$-$Pa\overline{3}$ with pyrite-type structure at 70 GPa. Both phases are stable within the wide temperature range, the calculated PT boundary is shown in Figure 3.

At 100 GPa there are three stable phases, NiN$_2$, Ni$_3$N, and Ni$_6$N, at 200 GPa - NiN$_2$ and Ni$_5$N$_2$, and at 300 GPa - NiN$_2$, NiN, Ni$_5$N$_2$, and Ni$_3$N.

All nickel-rich phases, revealed in the calculations, Ni$_6$N, Ni$_3$N, and Ni$_5$N$_2$, are interstitial phases with nickel, forming hexagonal close-packed (hcp) structure, and nitrogen, occupying octahedral voids. NiN has the structure of anti-nickeline type, with N atoms forming hcp structure and Ni occupying octahedral voids. To the best of our knowledge, the NiN compound was previously unknown. It should be noted, that pure Ni at ambient pressure has fcc structure [23] and according to our calculations stays in this structure in through the over studied pressure range, while found interstitial compounds are characterized by 2-layered close packing. Thus, nitrogen addition energetically stabilises 2-layered close-packed structure (hcp) against 3-layered one (fcc).

3.2. Superconducting transition temperature and bulk modulus

The calculated density of states (DOS) of NiN$_2$-$Pa\overline{3}$ shows that this phase is a metal without a band gap in the pressure range of 100-200 GPa (Figure 4a), while NiN$_2$-$Pnnm$ is an insulator with the band gap equals to 1 eV at 50 GPa (Figure 4b). According to the calculations of Niwa and co-authors [2], the band gap of NiN$_2$-$Pnnm$ equals to 0.3-0.35 eV. Unfortunately, it is not specified to what pressure this band gap corresponds to, which obstacles the comparison of results.

The calculated $T_c$ for the NiN$_2$-$Pnnm$ is only slightly higher than 0 K and is less than $10^{-2}$ K. There is only a small electron-phonon coupling constant $\lambda$ of 0.188, showing a weak electron-phonon interaction Figure 5. Ni atomic vibrations in the low-frequency region (less than 20 THz) contribute approximately 55% to the total $\lambda$, whereas high-frequency modes of N atoms contribute 45% of $\lambda$.

The calculated bulk modulus ($K$) of NiN$_2$-$Pnnm$ equals to 225 GPa at 10 GPa. The approximation with third-order Birch-Murnaghan equation of state to 0 GPa yield value of 172.7 GPa. This is in excellent agreement with the ex-
The experimental value of 172(6) GPa. The NiN$_2$-Pa$\bar{3}$ is slightly more compressible than NiN$_2$-P$nnm$. At transition pressure, the difference of bulk moduli of these phases is 22.8 GPa (Figure 6).

**Figure 5.** Eliashberg function of NiN$_2$-P$_nnm$ at 100 GPa

**Figure 6.** The bulk moduli of NiN$_2$ phases

Comparison of the obtained value of $T_c$ with that of nickel hydrides [24] shows that both hydrides and nitrides of nickel do not reveal superconductivity down to almost 0 K. In this regard, they are different from iron hydrides and nitrides, with $T_c$ reaching 56 and 5 K, respectively [21, 25]. This difference is explained by the difference in their crystal structures. Iron hydrides, having the highest $T_c$ among related compounds, have structures with the frameworks of H-H bonds, iron nitrides - structures with chains of N-atoms or isolated N$_4$ groups, while hydrides and nitrides of nickel have isolated atoms or dumbbell groups of light element, which is not typical for the high-temperature superconductors.

**Table 1.** Structural data for the predicted phase

| Pr. (GPa) | Sp. gr., (formula) | Lattice parameters, Å, deg. | Species | Atomic coordinates |
|-----------|--------------------|-----------------------------|---------|--------------------|
|           |                    |                             |         | $x$                |
| 400       | $P$nnm (NiN$_2$, marcasite) | $a = 3.580$, $b = 4.385$, $c = 2.665$ | Ni | 0.140 -0.090 0.00 |
| 100       | $Pa\bar{3}$ (NiN$_2$, pyrite) | $a = 4.2197$, $b = 4.2197$, $c = 4.2197$ | Ni | 0.591 0.591 0.591 |
| 300       | $P$6$_3$/mmc (NiN) | $a = 2.382$, $b = 2.382$, $c = 4.404$ | Ni | 0.333 0.667 0.75 |
| 400       | $P$2$_1$/m (Ni$_3$N$_2$) | $a = 7.387$, $b = 2.228$, $c = 5.220$ | Ni1 | 0.8209 0.00 0.775 |
|           |                    |                             | Ni2 | 0.00 0.50 0.00 |
|           |                    |                             | Ni3 | 0.846 0.00 0.189 |
|           |                    |                             |       | 0.614 0.00 0.440 |
| 50        | $P$6$_3$22 (Ni$_3$N) | $a = 4.378$, $b = 4.378$, $c = 4.061$ | Ni | 0.333 0.667 0.750 |
|           |                    |                             |       | 0.320 0.00 0.00 |
\begin{align*}
300 & \quad C_{3cmc} \\
& (\text{Ni}_2\text{N}_2) \quad \alpha = 2.296 \quad \beta = 7.495 \quad c = 5.538 \quad \text{N1} \quad 0.00 \quad 0.741 \quad 0.250 \\
& \quad \text{Ni2} \quad 0.00 \quad 0.637 \quad -0.060 \\
100 & \quad R^3 \quad a = 4.058 \quad b = 4.058 \quad c = 11.654 \quad \text{N} \quad 0.00 \quad 0.00 \quad 0.00 \\
& (\text{Ni}_4\text{N}) \quad \alpha = 90 \quad \beta = 90 \quad \gamma = 120 \quad \text{Ni} \quad 0.350 \quad 0.350 \quad 0.087
\end{align*}

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