Effects of increasing the concentration of Cr in the alloys Nb$_{1-x}$Cr$_x$N

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Abstract. We investigate the effects of increasing in the concentration of Cr atoms on the structural and electronic properties of Nb$_{1-x}$Cr$_x$N alloys in the concentrations ($x = 0.0, 0.125, 0.25, 0.50, 0.75$ and $1.0$) in the NiAs phase. For NbN and CrN in all concentrations, the calculations were carried out using the Quantum ESPRESSO code through the pseudopotential method within the framework of density functional theory. Regarding the structural properties, it was found that the lattice constant of the alloys decreases while the concentration of Cr increases. The bulk modulus of the alloys changes slightly compared to the bulk modulus of the binary NbN compound. Furthermore, the density of states calculations shows that the incorporation of Cr into the NbN matrix gives magnetic properties to the NbN. All the alloys have a metallic-ferromagnetic character.

1. Introduction

Over the last few decades, the binary compound NbN has attracted the attention of many researchers due to its excellent physical properties, which include chemical inertia, high thermal stability, high melting point, and high corrosion resistance [1]. These properties open the door for applications in high-frequency and high-temperature devices, diffusion barriers in microelectronic devices, and hard coatings for cutting tools [1,2]. NbN crystallizes into different structures such as CW, AsNi, and NaCl. While CW is the most stable, NiAs and NaCl are metastable [3]. Some investigations have recently reported the results of alloys of the type MT$_{1-x}$Nb$_x$N, where MT is a transition metal. For example, Ou et al. [4] used density functional theory in 2015 to study the structural and elastic properties of T$_{1-x}$Nb$_x$N in the NaCl phase. Additionally, Inumaru, et al. [2] grew thin films of Nb$_{1-x}$Cr$_x$N epitaxially on a Si (001) substrate [5] through molecular beam epitaxy (MBE). Although reports of alloys of the MT$_{1-x}$Nb$_x$N type have been scarce and focus on the cubic structure. This prompted us to carry out a theoretical study to investigate the structural, electronic, and magnetic properties of the Nb$_{1-x}$Cr$_x$N alloy in the hexagonal structure type NiAs. This theoretical study will provide a better understanding of the physical processes that take place between the chromium atom (Cr) and the niobium (Nb) and nitrogen (N) atoms. Furthermore, the results of the calculations will deliver information on the origin of magnetism in the Nb$_{1-x}$Cr$_x$N alloy. It is expected that this research leads to the design and development of new devices for different technological applications.
2. Computational details

We carried out the total energy theoretical calculations within the framework of density functional theory [6] by means of the computational Quantum ESPRESSO package. The electron-electron interaction was included with the generalized gradient approximation (GGA-PBE) [7], while the electron-ion interaction was included with the Vanderbilt ultrasoft pseudopotential [8], which allows a fast convergence of the calculations. We used a cutoff energy of 40 Ry and a charge density at an energy of 320 Ry. We took a 10×10×6 k-point mesh generated with the Monkhorst-Pack method [9]. The unit cell of NbN in the NiAs structure has four atoms, two Nb and two N. So to reach the concentration (x = 0.0, 0.125, 0.25, 0.50, 0.75 and 1.0) in the Nb_{1-x}Cr_{x}N alloys, we used the supercell method. Therefore, for Nb_{0.875}Cr_{0.125}N, a 1x1x8 supercell with 32 atoms, for Nb_{0.75}Cr_{0.25}N and Nb_{0.25}Cr_{0.75}N a 1x1x4 supercell with 16 atoms, and for Nb_{0.50}Cr_{0.50}N a 1x1x2 supercell with 8 atoms were used. These four structures for and the binary NbN and CrN compounds were relaxed using relax-type calculations. The calculations were carried out with spin polarization. The relax calculations were concluded when the obtained forces became smaller than 10^{-4} eV/Å and the convergence energy was 10^{-5} eV.

3. Results and discussions

3.1. Structural properties

The main equilibrium structural parameters (lattice constants, c/a ratio, and bulk modulus) of NbN, CrN, and the Nb_{1-x}Cr_{x}N alloys (with x = 0.0, 0.125, 0.25, 0.50, 0.75 and 1.0) were calculated using the semi-empirical Murnaghan equations. Additionally, in order to estimate the stability of the Nb_{1-x}Cr_{x}N alloys, the formation energy was computed as Equation (1):

\[ \Delta E_f = E^{NiAs}_{Nb_{1-x}Cr_{x}N} - (1-x)E^{bulk-Na}_{Cr_{N}} - xE^{CW}_{Cr_{N}} \]  \hspace{1cm} (1)

Where \( E^{NiAs}_{Nb_{1-x}Cr_{x}N} \) is the total energy of each alloy, \( E^{bulk-Na}_{Cr_{N}} \) is the total energy of CrN, and \( E^{CW}_{Cr_{N}} \) is the total energy of NbN in its ground state. To guarantee the reliability of the formation energy calculations in the alloys, we calculated the formation energy of the NbN and CrN binary compounds, was computes as Equation (2):

\[ \Delta E_f = E_{XN}^{Total} - E_{X}^{atom} + E_{N}^{atom} \]  \hspace{1cm} (2)

Where \( E_{XN}^{Total} \) is the total energy of the binary NbN (or CrN) compound, \( E_{X}^{atom} \) is the total energy of the Nb (or Cr) free atoms, and \( E_{N}^{atom} \) is the total energy of the molecular nitrogen. Table 1 shows the calculated structural parameters and formation energy as well as the theoretical and experimental values reported by other authors.

The values calculated for the lattice constant at 2.92 Å, the c/a ratio at 1.99, and the bulk modulus at 300 GPa of NbN are consistent with the theoretical values reported in other articles referenced in Table 1. The maximum deviation of the calculated lattice constants stands at 0.02 Å. For the CrN binary compound, the calculated lattice constant was 4.190 Å and the bulk modulus was 308 GPa, which are in excellent agreement with theoretical and experimental data. The maximum deviation of the lattice constant was 0.11 Å. Similarly, the formation energies obtained for NbN (-1.83 eV) and CrN (-1.01 eV) are consistent with the referenced values of -1.72 eV and -0.98 eV respectively. The deviations between the computed and the referenced values are small, which guarantees the reliability of the results.

For the Nb_{1-x}Cr_{x}N alloys (x = 0.0, 0.125, 0.25, 0.5 and 0.75), we observe that the lattice constant of the alloys decreases with an increase in Cr concentration. This happens because the atomic radius of a Cr atom is less than the radius of a Nb atom. In addition, we note that bulk modulus of the four alloys is
very close to the bulk modulus of NbN (300 GPa); therefore, the inclusion of Cr atoms in the matrix of NbN does not affect the rigidity of NbN.

### Table 1. Equilibrium Structural parameters: lattice constant ($a_0$), c/a ratio, bulk modulus ($B_0$) and formation energy.

| Compound          | $a_0$ (Å) | c/a | $B_0$ (GPa) | $E_f$ (eV/atom) |
|-------------------|-----------|-----|-------------|----------------|
| NbN               | 2.920     | 1.99| 300         | -1.83          |
| NbN               | 2.940$^a$ | 1.99$^a$| 300$^a$    | -1.72$^a$      |
| Nb$_{0.875}$Cr$_{0.125}$N | 2.970     | 1.94| 299         | -1.34          |
| Nb$_{0.75}$Cr$_{0.25}$N | 2.900     | 1.92| 297         | -1.28          |
| Nb$_{0.50}$Cr$_{0.50}$N | 2.870     | 1.90| 293         | -1.16          |
| Nb$_{0.25}$Cr$_{0.75}$N | 2.790     | 1.87| 299         | -1.11          |
| CrN               | 4.190$^d$ |      | 308         | -1.01          |
| CrN               | 4.130$^d$ |      | 310$^d$    | -0.98$^d$      |
| CrN               | 4.080$^d$ |      |             |                |
| CrN               | 4.150$^e$ |      |             |                |

$^a,b,c,d$: theoretical reference [3,2,10,11].
$^e$: experimental reference [12].

The values of the formation energy for the NbN and CrN compounds calculated in this investigation were -1.83 eV and -1.01 eV, respectively. We note that these values are in good agreement with theoretical and experimental values reported by other researchers, the maximum deviation being 0.11 eV for NbN and 0.03 eV for CrN. These values are small, which again guarantees the reliability of calculations. The calculated formation energy of the Nb$_{0.875}$Cr$_{0.125}$N, Nb$_{0.75}$Cr$_{0.25}$N, Nb$_{0.50}$Cr$_{0.50}$N, and Nb$_{0.25}$Cr$_{0.75}$N alloys were -1.34 eV, -1.28 eV, -1.16 eV, and -1.11 eV, respectively. All the values of the formation energy are negative; this indicates that the alloys are stable. The Nb$_{0.875}$Cr$_{0.125}$N alloy is the most stable, because it has the lowest formation energy, -1.34 eV.

#### 3.2. Electronic properties

The spin polarized density of states (DOS) of the NiAs structure of Nb$_{1-x}$Cr$_x$N alloys ($x = 0.0, 0.125, 0.25, 0.50, \text{and} 0.75$) were calculated using the equilibrium parameters shown in Table 1. The DOS illustrated in Figure 1 of all four alloys, reached zero-point energy in the Fermi level.

![Figure 1](image-url)
Figures 1(a), Figures 1(b), Figures 1(c) and Figures 1(d) correspond to the density plots of the DOS states of the Nb$_{0.875}$Cr$_{0.125}$N, Nb$_{0.75}$Cr$_{0.25}$N, Nb$_{0.50}$Cr$_{0.50}$N and Nb$_{0.25}$Cr$_{0.75}$N alloys, respectively. Figure 1 reveals that all alloys exhibit a metallic behavior, because spin up and spin down channel cross the Fermi Level. Additionally, due to the inclusion of Cr atoms in the NbN matrix, all alloys exhibit ferromagnetic properties, given that the DOS spin up is not symmetrical with the DOS spin down. The ferromagnetic properties are induced by the hybridization and polarization between Cr-3d and N-2p states, resulting in magnetic moments of 3.24 µβ/cell for Nb$_{0.875}$Cr$_{0.125}$N, 2.98 µβ/cell for Nb$_{0.75}$Cr$_{0.25}$N, 2.54 µβ/cell for Nb$_{0.50}$Cr$_{0.50}$N, and 2.95 µβ/cell for Nb$_{0.25}$Cr$_{0.75}$N.

4. Conclusions
The structural, electronic, and magnetic properties of Nb$_{1-x}$Cr$_x$N alloys (x = 0.125, 0.25, 0.50, and 0.75) in the NiAs structure were studied by means of ultrasoft pseudopotentials and the PBE-GGA approximation. The structural analyses show that the lattice constant of the alloys decreases with an increase in Cr concentration, yet the bulk modulus of all alloys presents some slight changes compared to the bulk modulus of the binary NbN compound. Finally, the density of states calculations shows that the incorporation of Cr into the NbN matrix, gives magnetic properties to the Nb$_{1-x}$Cr$_x$N alloys.

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