Electronic structure and elasticity of Z-phases in Cr-Nb-V-N system

Dominik Legut\textsuperscript{1,2} and Jana Pavlu\textsuperscript{3,4}

\textsuperscript{1} Nanotechnology Centre, VSB-Technical University of Ostrava, 17. listopadu 15, CZ-708 33 Ostrava, Czech Republic
\textsuperscript{2} Chair of Atomistic Modelling and Design of Materials, Montanuniversität Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria
\textsuperscript{3} Central European Institute of Technology, CEITEC MU, Masaryk University, Kamenice 5, CZ-625 00 Brno, Czech Republic
\textsuperscript{4} Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic

E-mail: dominik.legut@vsb.cz

Abstract. Structural properties and energetics of Cr-based Z-phases (CrNbN, Cr(Nb,V)N, and CrVN) were investigated using the VASP (Vienna \textit{Ab initio} Simulation Package) code employing the PAW (Projector Augmented Wave) pseudopotentials by means of both LDA (Local Density Approximation) and GGA (Generalized Gradient Approximation) for exchange and correlation term. Geometry of all studied phases including NbN, VN and elemental constituents (nonmagnetic bcc Nb and V and antiferromagnetic bcc Cr) was fully relaxed providing the equilibrium structure parameters and energies. The calculated lattice parameters of Z-phases correspond very well with the experimental data and decrease with increasing molar fraction of vanadium. Enthalpies of formation show that all three Z-phases are stable at T=0K. The electronic structures of Z-phases including densities of states and charge densities were analyzed. The calculated bulk moduli and elastic constants were used to evaluate stability conditions and elastic anisotropy ratios. It was confirmed that Z-phases are mechanically stable. Additional information on ductility was obtained from Cauchy pressures, Pugh ratios, Young moduli and Poisson ratios. The ductility evaluated using Pugh ratio decreases with amount of vanadium atoms.

PACS numbers: 71.20.Be, 62.20, 82.60.Cx

Submitted to: \textit{J. Phys.: Condens. Matter}
1. Introduction

In recent years, the studies of Cr-containing austenitic and martensitic steels intensified due to the long term creep failure and rupture of steam power plant parts. The higher Cr content was demanded to increase an operating temperature of steels above 650°C and hence to improve turbine efficiency. Another reason for addition of Cr was to increase steam oxidation resistance and creep strength. However, it was found that in many martensitic steels with 11-12 wt.% of Cr a rupture and long-term creep strength failures appear. In steels with lower (9%) Cr content the creep instability is much lower.[1] It was shown that the Z-phase precipitates at higher rate in Cr-rich steels than in Cr depleted ones and this precipitation correlates with presence of Nb. The drawback of appearance of Z-phase is its ability to dissolve the MX carbonitrides, which are beneficial for creep stability.[1]

The Z-phase has been known since 1950.[2] However, its crystallographic structure was determined by Jack et al.[3] in Cr-containing steels in 1972, where particularly CrNbN Z-phase was formed. Later, the Cr(Nb,V)N Z-phase was identified in austenitic steels at higher temperatures.[4] The Cr(Nb,V)N phase has CrNbN-like structure where some of Nb atoms in 2c sublattice are replaced by V atoms and the ratio of particular elements is Cr:aNb:bV:N where a+b=1. Recently, the existence of a niobium free, i.e. CrVN Z-phase, was confirmed.[1, 5] The appearance of Z-phase is related to e.g. the steel composition, temperature, and creep exposure time. For instance, at lower temperature of circa 600°C, the Nb free Z-phase appears, whereas at about 800-850°C the Cr(Nb,V)N is stable. At higher temperatures of 1000-1250°C the Z-phase of CrNbN is formed in ferritic and austenitic steels.[1]

In this paper, the phase stability, electronic structure, and elastic properties (elastic constants) of Z-phases are studied to get deeper insight into their behaviour which is responsible for a failure of steam power plant turbines.[1] The paper is organized as follows: After the Introduction, the details on ab initio calculations and thermodynamic relations concerning the phase stability are given in Section 2. Section 3 reports on the enthalpy of formation at T=0K, electronic structure (density of states and valence charge density analysis), elastic constants and subsequently determined mechanical properties of Z-phases and discusses the ductility as a function of vanadium content. Section 4 concludes the paper and presents outlook.

2. Methodology

The ab initio calculations of electronic structure of Z-phases have been performed within the density functional theory (DFT) and by using the Projector-Augmented Wave (PAW) method[6, 7] as implemented in the Vienna Ab initio Simulation Package (VASP) code.[8] The exchange and correlation terms where treated within local density approximation (LDA) [9] and generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE).[10] These PAW pseudopotentials represent 2s22p3,
Electronic structure and elasticity of Z-phases in Cr-Nb-V-N system

3p\(^6\)d\(^1\)3d\(^4\), 4s\(^1\)3d\(^5\) and 4p\(^6\)5s\(^1\)4d\(^4\) valence electron configuration of N, V, Cr and Nb atoms, respectively. A plane-wave expansion up to 600 eV was used. The Brillouin zone was sampled using the k-point mesh generated by the Monkhorst-Pack scheme where the number of divisions in each direction of the reciprocal unit cell is 33x33x14, 34x34x14, and 35x35x14 for CrNbN, Cr(Nb,V)N, and CrVN, respectively. The combination of conjugate gradient energy minimization and quasi-Newton force minimization was used to optimize the geometry of structures. Lattice parameters and atomic positions [11] were relaxed until the convergence criterion of 10\(^{-4}\) eV/Å for forces and 10\(^{-6}\) eV for total energy was reached. After the full structural relaxation, a static total energy calculation was performed using the tetrahedron method with Blöchl corrections to obtain more accurate total energies and densities of states (DOS). The Z-phase in CrNbN and similarly in Cr(Nb,V)N system develops as a result of direct transformation of Nb(C,N), i.e. of nitrides and carbides. Therefore in our investigation the enthalpy of formation of Z-phases is evaluated with respect to the following reference states (RS): transition metal nitrides and pure transition metals in structures, which are stable at Standard Ambient Temperature and Pressure (SATP) (i.e. antiferromagnetic (AFM) body-centered cubic (bcc) Cr and nonmagnetic (NM) bcc V and Nb). The enthalpy of formation per formula unit (f.u.) of CrNbN and CrVN Z-phase at T=0K was calculated using total energies as:

\[
H_f^0 = E_{Z\text{-phase}} - E_{Cr} - E_{TmN},
\]

where \(E_{Z\text{-phase}}\) is the total energy of particular Z-phase, \(E_{Cr}\) corresponds to the total energy of AFM bcc Cr and \(E_{TmN}\) stands for the total energy of Nb or V cubic nitride.

For the mixed Cr(Nb,V)N Z-phase, the above mentioned formula changes into:

\[
H_f^0 = E_{Cr(Nb,V)N} - E_{Cr} - \frac{1}{2}E_{VN} - \frac{1}{2}E_{NbN}.
\]

On the other hand, the total energies of simple transition elements and gas phase of \(N_2\) were used in previous study of C. Kocer.[12] This approach can be described by the following equations:

\[
H_f^0 = E_{Z\text{-phase}} - E_{Cr} - E_{Tm} - \frac{1}{2}E_{N_2}
\]

and

\[
H_f^0 = E_{Cr(Nb,V)N} - E_{Cr} - \frac{1}{2}E_{Nb} - \frac{1}{2}E_{V} - \frac{1}{2}E_{N_2},
\]

where \(E_{Tm}\) stands for the total energy of NM bcc Nb or V similarly as \(E_{Nb}\) and \(E_{V}\). \(E_{N_2}\) corresponds to the total energy of gaseous \(N_2\).
Table 1. Equilibrium lattice parameters \(a\) (Å) of cubic nitride phases and pure transition metals (AFM bcc Cr, NM bcc V and Nb) calculated using both GGA (PBE) and LDA for exchange-correlation term. The results are compared with experimental data and \textit{ab initio} results based on full potential linearized augmented plane wave (FLAPW) and linear muffin-tin orbital (LMTO) method.

<table>
<thead>
<tr>
<th>phase</th>
<th>NbN (a) (PBE)</th>
<th>VN (a) (PBE)</th>
<th>Cr (a) (PBE)</th>
<th>V (a) (PBE)</th>
<th>Nb (a) (PBE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (LDA)</td>
<td>4.392</td>
<td>4.052</td>
<td>2.780</td>
<td>2.930</td>
<td>3.249</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Enthalpy of formation

Calculated equilibrium lattice parameters of cubic nitride phases (VN, NbN) and bcc structures of transition metals (Cr, V, Nb) are summarized and compared with literature data in table 1.

Our results are in very good agreement with full potential linearized augmented plane wave (FLAPW) and linear muffin-tin orbital (LMTO) calculations as well as with experimental data. The only structure possessing magnetic arrangement in this study is bcc Cr. The Cr structure analyzed using the GGA (PBE) reaches the lowest total energy for AFM ordering having the magnetic moment \(M = 1.06\mu_B\) per Cr atom. On the other hand, the calculations using the LDA predict the non-spinpolarized state as the most stable one. The results published by Guo [14] indicate that the lowest total energy of bcc Cr was obtained in the case of AFM ordering with \(M = 1.1\mu_B/\text{atom}\) and the lattice parameter \(a = 2.87\) Å which corresponds to the increase of cell volume by 0.7% in comparison with NM phase. In our calculations the energy gained by introducing AFM alignment is 11 meV/atom and the unit cell expands by 0.6%. The magnetic moments calculated in this work and those published by Guo [14] are slightly higher than values found in experimental studies where \(M = 0.5\mu_B/\text{atom}\).[19] This discrepancy is attributed to the imperfect description of exchange and correlation effects.[14] The magnetism of Cr is due to incommensurate spin density waves with different polarizations rather than due to local magnetic moment (see [20] and references therein). However, at very low temperatures, the so-called AF-0 structure exists, where the nearest-neighbor Cr atoms are antiparallelly aligned and spin-density wave is commensurate with lattice vectors.[20] Hence, our simplest model of local atomic magnetism for bcc Cr corresponds to this AF-0 phase, AFM bcc structure, exhibiting a
Table 2. Equilibrium lattice parameters \(a\) and \(c\) (Å) of Z-phases calculated using both GGA (PBE) and LDA for exchange-correlation term. The results are compared to available experimental data and \textit{ab initio} results.

<table>
<thead>
<tr>
<th>phase</th>
<th>CrNbN</th>
<th>Cr(Nb,V)N</th>
<th>CrVN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (PBE)</td>
<td>3.021</td>
<td>2.956</td>
<td>2.860</td>
</tr>
<tr>
<td>(a) (LDA)</td>
<td>2.999</td>
<td>2.922</td>
<td>2.811</td>
</tr>
<tr>
<td>(a) (GGA)[12]</td>
<td>3.041</td>
<td>-</td>
<td>2.857</td>
</tr>
<tr>
<td>(a) (exp.)[3]</td>
<td>3.037</td>
<td>2.860[1]</td>
<td>2.860[5]</td>
</tr>
<tr>
<td>(c) (PBE)</td>
<td>7.367</td>
<td>7.235</td>
<td>7.134</td>
</tr>
<tr>
<td>(c) (LDA)</td>
<td>7.234</td>
<td>7.096</td>
<td>6.986</td>
</tr>
<tr>
<td>(c) (GGA)[12]</td>
<td>7.387</td>
<td>-</td>
<td>7.125</td>
</tr>
<tr>
<td>(c) (exp.)[3]</td>
<td>7.391[3]</td>
<td>7.391[1]</td>
<td>7.390[5]</td>
</tr>
</tbody>
</table>

little bit higher magnetic moment per atom.

The equilibrium \(a\) and \(c\) lattice parameters of Z-phases calculated using both LDA and GGA (PBE) for the exchange-correlation term are given in table 2. Calculated equilibrium \(a\) and \(c\) lattice parameters are in very good agreement with experimental data. Nevertheless, using GGA (PBE) leads to better results, as it is widely known that using LDA overestimates crystalline bindings in solids leading to smaller lattice parameters. The structural parameters are also in very good agreement with the recent study of Kocer \textit{et al.} \[12\] Most of the lattice constants calculated by PBE are somewhat smaller than experimental ones, although GGA (PBE) usually overestimate lattice constants. However, this statement is not a rule of thumb as it was shown in \[21\].

According to equation 1 and 2 we arrived to the enthalpies of formation which are listed in table 3 and denoted by an asterisk. In this table, the values of enthalpy of formation are also recalculated according to equation 3 and 4 and are denoted by two asterisks. These data can be used for comparison with those published in \[12\].

In addition to values published in \[12\], the Cr(Nb,V)N Z-phase was analyzed in this work. The agreement between our GGA (PBE) enthalpies of formation (calculated according to equation 3 and 4 and given in the fourth and the fifth row of table 3) and those calculated in \[12\] is excellent as the deviation goes from -0.1% to 2.2% which corresponds to energy difference of 14.34 and -89.08 meV/f.u. The limits of deviation interval correspond to the data of CrVN based on \textit{ab initio} analysis of gas-N\(_2\) and CrNbN based on experimental gas-N\(_2\) cohesive energy.

To analyze our results listed in table 3, we can say that the results based on the GGA (PBE) (that also predicts correct antiferromagnetic (AFM) arrangement of bcc Cr) show that the lowest amount of energy is released by the formation of the mixed Z-phase \textit{i.e.} the least stable Z-phase.

Despite the V and Nb are isoelectronic, the pure Nb-based Z-phase shows the
Table 3. Enthalpies of formation of Z-phases (meV/f.u.) at T=0K calculated using both GGA (PBE) and LDA for exchange-correlation term. * AFM bcc Cr, NbN and VN were taken as RS according to equation 1 and 2. ** AFM bcc Cr, NM bcc V and Nb, and gaseous N\textsubscript{2} were taken as RS according to equation 3 and 4. These values were obtained by recalculation of our values by means of the formation enthalpies of NbN and VN published in table 1 in [12] where \textsuperscript{a} N\textsubscript{2} was studied using \textit{ab initio} calculations and \textsuperscript{b} experimental gas-N\textsubscript{2} cohesive energy was implemented.

<table>
<thead>
<tr>
<th>phase</th>
<th>CrNbN</th>
<th>Cr(Nb,V)N</th>
<th>CrVN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{f}^{0}$ (PBE)*</td>
<td>-351.0</td>
<td>-229.0</td>
<td>-278.7</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (LDA)*</td>
<td>-316.2</td>
<td>-154.4</td>
<td>-291.1</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (PBE)**\textsuperscript{a}</td>
<td>-2181.4</td>
<td>-2136.0</td>
<td>-2262.5</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (PBE)**\textsuperscript{b}</td>
<td>-2461.2</td>
<td>-2438.6</td>
<td>-2587.9</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (LDA)**\textsuperscript{a}</td>
<td>-2146.5</td>
<td>-2061.4</td>
<td>-2274.8</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (LDA)**\textsuperscript{b}</td>
<td>-2426.3</td>
<td>-2364.1</td>
<td>-2600.2</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (GGA)**\textsuperscript{a} [12]</td>
<td>-2192.0</td>
<td>—</td>
<td>-2260.4</td>
</tr>
<tr>
<td>$H_{f}^{0}$ (GGA)**\textsuperscript{b} [12]</td>
<td>-2515.4</td>
<td>—</td>
<td>-2586.9</td>
</tr>
</tbody>
</table>

The highest output of energy to form Z-phase with respect to the nitride phases and transition metal. On the other hand, using pure elements in structures stable at SATP (e.g. the N\textsubscript{2} gas) as reference states as done by Kocer \textit{et al.} predicts the highest energy gain for the CrVN Z-phase. Similar findings were reported by Stampfl \textit{et al.} [13], where the vanadium nitride was predicted to be more stable than niobium one. This analysis was based on enthalpy of formation calculated using the total energy of N\textsubscript{2} gas phase.

Furthermore, it is obvious from table 3 that the energy released by the formation of Z-phases from nitrides is much lower than the energy released by formation from pure elements, i.e. the highest energy change corresponds to the the formation of nitrides and the subsequent occurrence of Z-phases is driven by much smaller energy difference. This corresponds to experimental findings where a considerable heat treatment was required during the procedures providing Z-phases when carbides and nitrides were already present (the diffusion was so slow that it often seemed to be in thermodynamic equilibrium with Z-phases). [22, 23, 1]

Concerning the thermodynamic stability of mixed Cr(Nb,V)N Z-phase, it was found that the mixed Cr(Nb,V)N Z-phase is unstable with respect to the Z-phases of pure Nb and V at T=0K as the calculated enthalpy of formation related to these structures is positive, i.e. $H_{f}^{0} = 85.9$ (149.2) meV/f.u. calculated using GGA-PBE (LDA) for exchange-correlation energy. Nevertheless, it is known that all three Z-phases precipitate at higher temperatures and therefore entropy term stemming from lattice dynamics will significantly contribute to their stability. Hence, a complex investigation of the lattice vibrations (phonon stability) is desirable. [24]
3.2. Electronic structure

The electronic structure of various Z-phases was analyzed by means of DOS and by valence charge density. The results calculated using LDA and GGA (PBE) for exchange-correlation energy are very similar, hence the latter ones are discussed further. The total DOS of CrNbN, Cr(Nb,V)N and CrVN are depicted in figure 1. In general, lower number of states at Fermi level \((E_F)\) often indicates higher stability. The lowest DOS at \(E_F\) was found in case of CrNbN, while the highest value was obtained for CrVN and mixed Cr(Nb,V)N Z-phase, despite the fact that Nb and V Z-phases have isoelectronic valence shell. Similar order was reported for cubic nitrides in [25].

The total DOS of CrVN and Cr(Nb,V)N exhibit a higher peak around Fermi level than CrNbN phase, see figure 1. Similar situation is observed in the case of NbN and VN nitrides, where the latter one has higher number of states at \(E_F\) and exhibits a large sharp peak at Fermi level.[26, 27, 13] Partial atomic DOS of all three investigated Z-phases are shown in figure 2. We can draw an analogy between transition metal nitrides [13] and Z-phases, where DOS of N are predominately located at the bottom of the valence band with some admixture of 3d-transition metal states. Within the energy range from -8 eV to -4 eV, the Cr DOS is almost constant and not dominant in all three Z-phases investigated, see figure 2. However, nitrogen states dominate over metallic ones for pure Z-phases CrNbN and CrVN, while for Cr(Nb,V)N, the density of Nb states is higher at lower energy. Overall, this might suggest higher degree of interaction between nitrogen and vanadium (niobium) atoms. In the energy range from -4 eV to 1.5 eV, the transition-metal states dominate in all Z-phases, see figure 2. It is interesting that close to \(E_F\) the number of unoccupied as well as occupied V states in Cr(Nb,V)N is higher than number of Nb states in this structure. Also the number of both V and Nb states here is higher than in pure CrVN and CrNbN phases, see figure 2. This might indicate lower stability of the mixed phase, which is in accord to the \(H_0^9\) results. Also, overall DOS of Cr(Nb,V)N resembles the one of CrVN (see figure 1) and therefore we predict the Cr(Nb,V)N phase, despite having equal concentration of Nb and V atoms, to have character more similar to CrVN rather than to CrNbN phase.

The valence charge density at planes normal to [001] direction containing only Cr atoms and N-Nb or N-V atoms, are shown in figures 3-5. Valence charge distribution in Cr-Cr plane is slightly less spherical in CrVN than in CrNbN (see figures 3 and 5). A complete substitution of Nb by V atoms in Z-phases leads to less spherical valence charge density, i.e. higher charge anisotropy. Hence, the mixed Z-phase of Cr(Nb,V)N consists of planes with valence charge distributions that resemble the ones of pure Z-phases in corresponding planes, compare the left (right) panel of 4 with left panel of 3 (5). For instance, the Nb-N plane of mixed Z-phase has electron charge elongated towards N atom, while in V-N plane towards transition-metal atoms, both resembling the corresponding plane in pure Z-phases. The small difference occurs within pure Cr-Cr plane, where valence charge density is slightly less anisotropic, i.e. more spherical,

in Cr(Nb,V)N than in the same plane in pure CrVN and CrNbN phases, compare
Figure 1. Total DOS of CrNbN, Cr(Nb,V)N, and CrVN Z-phases calculated using GGA (PBE). Fermi energy ($E_F$) is chosen as reference energy.

middle panel of 4 with right panel of 5 and 3, respectively. This could slightly, but not dramatically, influence the response of the electronic cloud to the finite distortions needed to determine elastic behaviour.

3.3. Elastic constants and mechanical stability

The tetragonal symmetry of the Z-phase leads to six independent elastic constants ($C_{ij}$) which can be calculated using a Taylor expansion of the total energy for the system, with respect to the small strain of the lattice. The single distortions of the equilibrium structure were used according to those in [28, 29]. The values of elastic constants are proportional to the squared term of a fit (4th order) of the total energy with respect to the appropriate strain, for details see [28, 29]. The values of these constants calculated using GGA (PBE) are summarized in table 4 together with bulk moduli ($B$) derived according to equation:[28]

$$B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2).$$

The substitution of Nb atoms by V ones can influence particular elastic constants in different way. The highest effect can be found in case of $C_{12}$ and $C_{66}$ where the above mentioned substitution causes the decrease of 53 and 31 GPa, respectively. On the other hand, $C_{13}$ and $C_{11}$ are influenced minimally within the accuracy of our fitting of calculated data, i.e. their values increased by 4 and 6 GPa, respectively. The values of $C_{11}$ are rather high, two times higher than values of many compounds possessing tetragonal symmetry, e.g. covalent compounds as rutile (TiO$_2$), zircon (ZrSiO$_4$), or ceramic BaTiO$_3$. Interestingly, values of $C_{13}$ of Z-phases are very similar to those of TiO$_2$, ZrSiO$_4$, and BaTiO$_3$, see table 4. Hence, it must be $C_{44}$ that will change and therefore influence Cauchy pressure upon V alloying of Z-phase, see below.
Electronic structure and elasticity of Z-phases in Cr-Nb-V-N system

Figure 2. Partial DOS of Cr, Nb, V and N in CrNbN, Cr(Nb,V)N, and CrVN Z-phase calculated using GGA (PBE). Fermi energy ($E_F$) is chosen as reference energy.
Electronic structure and elasticity of Z-phases in Cr-Nb-V-N system

Figure 3. Valence charge density $(e/\text{Å}^3)$ calculated using GGA (PBE) of CrNbN normal to [001] direction in plane containing Nb-N (left) and Cr-Cr (right) atoms. Contours are in logarithmic scale. The values of minima (blue) and maxima (red/green) are 0.036 (0.034) and 1.094 (0.534) for Nb-N (Cr-Cr) plane.

Figure 4. Valence charge density $(e/\text{Å}^3)$ calculated using GGA (PBE) of Cr(Nb,V)N normal to [001] direction in plane containing Nb-N (left), Cr-Cr (middle) and V-N (right) atoms. Contours are in logarithmic scale. The values of minima (blue) and maxima (red/green) are 0.039, 0.035, 0.031 and 1.102, 0.527, 2.158 for Nb-N, Cr-Cr, V-N plane, respectively.

Elastic constants $C_{12}$, $C_{66}$, and $C_{33}$ show a clear decreasing tendency, except for value of $C_{33}$ of Cr(Nb,V)N phase, as the Nb atoms are replaced by V ones. The observed decrease of $C_{12}$, $C_{33}$, and $C_{66}$ is certainly the main cause of changes in elastic anisotropy, Young modulus $(E)$, Poisson ratio $(\nu)$ and ductility as discussed further. On the other hand, $C_{44}$, $C_{11}$, and $C_{13}$ show increasing tendency as Nb is substituted by V, except for value of $C_{11}$ and $C_{13}$ of Cr(Nb,V)N phase.

Cubic transition metal nitrides are parent phases of Z-phases in Cr-based steels and therefore it might be useful to compare their $C_{11}$, $C_{12}$, and $C_{44}$ elastic constants found in literature with corresponding ones of Z-phases (see table 4). The experimental values of $C_{11}$ and $C_{44}$ of NbN and VN are similar to those of all three investigated Z-phases.
Figure 5. Valence charge density (e/Å³) calculated using GGA (PBE) of CrVN normal to [001] direction in plane containing V-N (left) and Cr-Cr (right) atoms. Contours are in logarithmic scale. The values of minima (blue) and maxima (red/green) are 0.036 (0.036) and 2.158 (0.538) for V-N (Cr-Cr) plane.

Table 4. Elastic constants ($C_{ij}$) and bulk moduli ($B$) in GPa of CrNbN, Cr(Nb,V)N, and CrVN calculated using GGA (PBE) for exchange-correlation term compared with experimental elastic constants of tetragonal phases TiO$_2$, ZrSiO$_4$, BaTiO$_3$, and experimental and calculated (GGA) data for cubic nitrides.

<table>
<thead>
<tr>
<th>phase</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrNbN</td>
<td>537</td>
<td>243</td>
<td>145</td>
<td>528</td>
<td>120</td>
<td>268</td>
<td>296</td>
</tr>
<tr>
<td>Cr(Nb,V)N</td>
<td>532</td>
<td>212</td>
<td>139</td>
<td>497</td>
<td>124</td>
<td>250</td>
<td>282</td>
</tr>
<tr>
<td>CrVN</td>
<td>543</td>
<td>190</td>
<td>149</td>
<td>507</td>
<td>136</td>
<td>237</td>
<td>285</td>
</tr>
<tr>
<td>TiO$_2$-exp.[30]</td>
<td>271</td>
<td>178</td>
<td>150</td>
<td>484</td>
<td>124</td>
<td>194</td>
<td>220</td>
</tr>
<tr>
<td>ZrSiO$_4$-exp.[31]</td>
<td>259</td>
<td>179</td>
<td>154</td>
<td>381</td>
<td>73</td>
<td>111</td>
<td>208</td>
</tr>
<tr>
<td>BaTiO$_3$-exp.[32]</td>
<td>275</td>
<td>179</td>
<td>152</td>
<td>165</td>
<td>54</td>
<td>113</td>
<td>187</td>
</tr>
<tr>
<td>NbN-exp.[33] (34)</td>
<td>608 (556)</td>
<td>134 (152)</td>
<td>—</td>
<td>—</td>
<td>117 (125)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NbN-calc.[27]</td>
<td>498</td>
<td>212</td>
<td>—</td>
<td>—</td>
<td>89</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>VN-exp.[34]</td>
<td>533</td>
<td>135</td>
<td>—</td>
<td>—</td>
<td>133</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

On the other hand, the values of $C_{12}$ of NbN (VN) are by about 100 GPa (50 GPa) lower than corresponding elastic constants of CrNbN (CrVN).

The intrinsic mechanical stability of a solid is in general determined by certain conditions related to the crystal symmetry [35] and the following criteria based on relations between elastic constants have to be fulfilled for tetragonal phases: the $C_{11}$, $C_{33}$, $C_{44}$, and $C_{66}$ elastic constants have to be positive and $C_{11} > C_{12}$. These criteria
are satisfied for all Z-phases, see table 4. Further stability conditions are as follows:[36]

\[
C_{11} + C_{33} - 2C_{13} > 0, \quad (I)
\]

\[
2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0, \quad (II)
\]

\[
\frac{1}{3}(2C_{11} + C_{33}) - B > 0. \quad (III)
\]

The values of the left-hand sides of stability conditions I-III are summarized in table 5 and none of them is broken for any of investigated Z-phases. Therefore, Cr-based Z-phases are considered to be mechanically stable.

Furthermore, the shear resistance of system (the energy change in a crystal associated with the shear modes along different slip directions) is characterized by the elastic anisotropy factors.[37] There are three elastic anisotropy factors in tetragonal systems, defined as:

\[
A_1 = \frac{2C_{66}}{(C_{11} - C_{12})},
\]

\[
A_2 = \frac{4C_{44}}{(C_{11} + C_{33} - 2C_{13})},
\]

\[
A_3 = \frac{C_{44}}{C_{66}},
\]

and their values are presented in table 5. The denominator in the A1 anisotropy relation represents simple tension on the (001) plane shear while the A2 anisotropy relation corresponds to the shear along [011] direction on the (011) plane.[38] The $C_{66}$ and $C_{44}$ elastic constants then correspond to the shear resistance along [010] and [100] direction in the (001) and (010) plane, respectively.[38, 39] Therefore, the numerator (denominator) in the A3 ratio represents the shear of intra- (inter-) layer bonds.

The evident correlation between the values of elastic anisotropy ratios and number of V atoms in Z-phase was found: the A1 elastic ratio decreases with increasing number of V atoms whereas A2 and A3 elastic ratio increases. Therefore, it can be stated that all elastic anisotropy ratios go towards unity (They are equal to unity if a solid is elastically isotropic.) which means that the substitution of Nb atoms by V makes the Z-phases elastically more isotropic.

† The shear directions and planes for the $C_{44}$ and $C_{66}$ are interchanged in [38], p. 160. The correct reading is as follows: “$C_{44}$ corresponds to [100] shear in (010) plane and $C_{66}$ to [010] shear in (001) plane.”
Table 6. $C_1$ and $C_2$ Cauchy pressures, shear modulus $G_{RVH}$, Pugh ratio $B_{RVH}/G_{RVH}$, Poisson ratio $\nu$, Young modulus $E$, and elastic anisotropy $A$ of Z-phases studied. Cauchy pressures, Young and shear modulus are given in GPa.

<table>
<thead>
<tr>
<th>phase</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$G_{RVH}$</th>
<th>$B_{RVH}/G_{RVH}$</th>
<th>$\nu$</th>
<th>$E$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrNbN</td>
<td>-25</td>
<td>25</td>
<td>134</td>
<td>2.20</td>
<td>0.303</td>
<td>349</td>
<td>0.289</td>
</tr>
<tr>
<td>Cr(Nb,V)N</td>
<td>-38</td>
<td>15</td>
<td>135</td>
<td>2.08</td>
<td>0.293</td>
<td>350</td>
<td>0.264</td>
</tr>
<tr>
<td>CrVN</td>
<td>-47</td>
<td>13</td>
<td>141</td>
<td>2.02</td>
<td>0.287</td>
<td>363</td>
<td>0.243</td>
</tr>
</tbody>
</table>

3.4. Ductility and polycrystalline materials

The ductility behaviour was proposed to be related to the so-called Cauchy pressures.\cite{40} Although the interpretation of the Cauchy relations was questioned recently,\cite{39} they are still widely used. For phases with tetragonal symmetry, the Cauchy pressures are defined as:

$$C_1 = C_{12} - C_{66},$$
$$C_2 = C_{13} - C_{44}.$$  

Positive or negative values of $C_1$ and $C_2$ indicate ductile or brittle behaviour, respectively.

An empirical rule found by Pugh \cite{41} says that the $B/G$ (bulk modulus over shear modulus) ratio of value 1.75 separates ductile materials ($B/G > 1.75$) from brittle ones ($B/G < 1.75$). The inverse ratio $(G/B)$ indicates the relative degree of directional bonding (i.e. covalency of bonding) supposing that the bulk modulus corresponds to the average bond strength and the shear modulus to the resistance to changes in the bonding angles (see discussion in \cite{42}).

To account for a polycrystalline material, the upper and lower bounds (Reuss \cite{43} and Voigt \cite{44}) of bulk $(B_R, B_V)$ and shear $(G_R, G_V)$ moduli are found from single crystal elastic constants. Subsequently, a simple average of those bound values of $B_R$, $B_V$ and $G_R$, $G_V$ is calculated as proposed by Hill.\cite{45} For the detailed description of this issue concerning the polycrystalline materials see \cite{37, 46} and references therein. Further on, we refer to Hill’s averaged values of bulk and shear modulus $(B_{RVH}, G_{RVH})$ that are used for evaluation of quantities describing polycrystalline material \cite{37, 46} such as Pugh ratio $(B_{RVH}/G_{RVH})$, Poisson ratio $(\nu = (3B_{RVH} - 2G_{RVH})/(6B_{RVH} + 2G_{RVH}))$, Young modulus $(E = 9B_{RVH}G_{RVH}/(3B_{RVH} + G_{RVH}))$ and polycrystalline elastic anisotropy ratio $(A = (G_V - G_R)/(G_V + G_R))$ of all Z-phases studied which are summarized in table 6. The RVH subscript is omitted for simplification in further text.

Despite the fact that the Cauchy pressures $C_1$ are negative, that should indicate the brittle behaviour, both $C_1$ and $C_2$ exhibit general trend to have lower values as the vanadium content increases. This indicates that CrNbN will be always more ductile than CrVN or mixed Z-phase, see table 6.
Electronic structure and elasticity of Z-phases in Cr-Nb-V-N system

Similar trend of ductility/brittleness as found for C1 and C2 is showed by the Pugh $B_{RVH}/G_{RVH}$ ratio. Nevertheless, $B_{RVH}/G_{RVH}$ is higher than 1.75 even for CrVN and therefore all three Z-phases are considered to be ductile. The elastic anisotropy ratio $A$ decreases with higher V content and becomes further away from 1, indicating a larger overall polycrystalline elastic anisotropy for CrVN.

A lower Young modulus $E$ and $G_{RVH}$ and higher Poisson ratio $\nu$ in case of CrNbN Z-phase correlate with weaker and less directional interatomic bonding, and hence with an increase of ductile behaviour.[47] This is again in accord with trends following Cauchy pressures as well as Pugh criteria.

4. Conclusion

The enthalpy of formation, electronic structure and mechanical properties of Cr-based Z-phases were determined by means of first-principles calculations. All three Z-phases CrNbN, Cr(Nb,V)N, and CrVN are stable with respect to reference states from the thermodynamic point of view and are also mechanically stable considering mechanical stability conditions based on single elastic constants. A mixed Cr(Nb,V)N Z-phase is not stable with respect to the CrNbN and CrVN Z-phases. The largest polycrystalline elastic anisotropy ($A$) is found for CrNbN, whereas CrVN is more isotropic. The ductility behaviour was analyzed by evaluating Cauchy pressures, Pugh ratios, Young moduli and Poisson ratios. The increase of V-content in investigated Z-phases leads to a slight decrease of ductility, i.e. CrNbN is more ductile than CrVN.

Acknowledgments

This research was supported by the Grant Agency of the Czech Republic (Project No. P108/10/1908), Ministry of Education, Youth and Sports of the Czech Republic (Project No. MSM0021622410) and Academy of Sciences of the Czech Republic (Project No. AV0Z20410507). D. Legut acknowledges a partial support within the framework of the Nanotechnology Centre the basis for international cooperation project, Reg. No. CZ.1.07/2.3.00/20.0074 and the IT4Innovations Centre of Excellence project, Reg. No. CZ.1.05/1.1.00/02.0070, both supported by Operational Programme 'Education for competitiveness' funded by Structural Funds of the European Union and state budget of the Czech Republic. J. Pavlík was also supported by the Project "CEITEC - Central European Institute of Technology" (CZ.1.05/1.1.00/02.0068) from the European Regional Development Fund.

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