Structural stability, elasticity, thermodynamics, and electronic structures of $L1_2$-type $\text{Ni}_3X$ ($X =$ Al, Ti, V, Nb) phases under external pressure condition

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Abstract
In this paper, the effect of pressure on the structural stability, elasticity, thermodynamics, and associated electronic structure of $L1_2$-type $\text{Ni}_3X$ ($X =$ Al, Ti, V, Nb) phases is investigated using a first-principles approach. It is shown that pressure leads to volume compression of the $\text{Ni}_3X$ phase and reduction of the lattice parameters. The increase of pressure promotes the increase of elastic constants, bulk modulus, shear modulus, and Young’s modulus. And there is an extremely strong linear correlation between the pressure and the elastic constants. The calculated elastic constants indicate that the pressure leads to strong mechanical stability and ductility of the $\text{Ni}_3X$ phase. Mechanical anisotropy of the $\text{Ni}_3X$ phase also increases with increasing pressure. The electronic analysis shows that the increase in pressure leads to enhanced Ni-d-orbitals and X-d-orbitals hybridization and increased electron transfer. The order in terms of electron accumulation intensity is $\text{Ni}_3\text{Ti} > \text{Ni}_3\text{Nb} > \text{Ni}_3\text{V} > \text{Ni}_3\text{Al}$. It is more directly reflected in the charge density difference diagram. This is in agreement with the results of the enthalpy of formation ($\Delta H$) and Debye temperature ($\Theta_D$) analysis.

Keywords Ni$_3$X · Elastic constants · Thermodynamic · Electronic structures · First-principles

Introduction
Ni-based single-crystal superalloys are one the most important high-temperature materials, which are widely used for modern aircraft engines owning to high temperature strength [1], thermal stability [2–4], creep resistance [5, 6], and oxidation resistance [7–9] at high temperatures. These excellent mechanical properties of Ni-based single-crystal superalloys at high temperatures depend mainly on the effect of the $\gamma'$-Ni$_3\text{Al}$ strengthening phase in the alloy [10]. The large number of investigations on the $\gamma'$-Ni$_3\text{Al}$ strengthening phase found that the strengthening effect cannot meet the requirements for the performance of Ni-based single-crystal alloys under high temperature conditions [11–13]. Recent studies have proven the mechanical characteristics of Ni-based single-crystal alloys can be significantly reinforced by adding Ti, V, Nb, and Ta [11–13], and promote the formation of the $L1_2$-type $\gamma^\prime$-Ni$_3X$ ($X =$ Ti, V, Nb) phases.

Over the past decades, there are few reports on Ni$_3\text{Ti}$ (hexagonal), Ni$_3\text{V}$ (tetragonal), Ni$_3\text{Nb}$ (tetragonal), and Ni$_3\text{Ta}$ (tetragonal). Li et al. [14] investigated the mechanical properties of $\gamma^\prime$-Ni$_3\text{Ta}$ under variable pressure by means of theoretical simulations, and explored the internal mechanisms affecting its stability and mechanical strength. K. Santhy et al. [15] identified the phase of stability of Ni$_3\text{Ti}$ ($\text{V}$) through first-principles calculations. Tomasz Czeppe et al. [16] researched effects of Ti and high cooling rate on the phase equilibrium and properties of Ni$_3$(Ti, V) alloys. Gong et al. [17] analyzed the effect of alloying elements on the
occupation preference, structural stability, and mechanical performance of γ″-Ni₃Nb based on density functional theory.

In recent research, the calculation of phases based on density functional theory mainly focused on under fixed conditions. For example, Hou et al. [18] calculated the structural, elastic, thermodynamic, and electronic behavior of Ni₃Al, Ni₃Ga, and Ni₃Ge under assumed pressures. They found that the elastic properties, thermodynamic stability, lattice anisotropy, and Debye characteristic temperature of Ni₃X increase with increasing external pressure. Mao et al. [19] explored the mechanical stability, microscopic electronic structure, and thermodynamic properties of Mg₂Sr by applying different pressures. Liu et al. [20] investigated the impact of pressure on the microscopic crystal structure, electron distribution properties, and bonding ion configuration of the MgCu₂ Laves phase. Zhao et al. [21] showed that the variation of pressure could improve the mechanical stability, microscopic electronic structure, and thermodynamic properties of Ni₃V intermetallic compound, and the mechanical strength of the alloy. Chen et al. [22] performed first-principles calculations on D0₂₂-type Al₃V and Al₃Nb intermetallic compounds. They found that pressure has a profound effect on the structure, mechanical properties, and electronic properties of Al₃V and Al₃Nb. These studies are reported to provide new ideas and directions for the study of material properties, and they provide new theoretical approaches for the design, development, and stability of new materials.

Based on the above research reports, first-principles calculations was used to investigate the structural stability, elastic constants ($C_{ij}$), bulk modulus ($B$), Yong's modulus ($E$), shear modulus ($G$), Debye temperature ($\Theta_D$), and electronic structures of $LI_2$-type Ni₃X ($X$ = Al, Ti, V, Nb) phases under external pressure condition. The aim of this work is to provide theoretical basis for the exploration of material structure, organization, and properties of $LI_2$-type γ′-Ni₃X, and also provides important theoretical references for subsequent experimental studies and alloy design.

### Model and computational details

The $LI_2$ type γ′-Ni₃X ($X$ = Al, Ti, V, Nb) phase has a face-centered cubic structure [23] (FCC), and the space group is $Pm-3m$ (No. 221). As shown in Fig. 1, the γ′-Ni₃X unit cell contains 3 Ni atoms and 1 X atom. Ni atoms occupy six face center positions of the cubic structure, and X atoms occupy 8 vertices of the cubic structure. The lattice constants of γ′-Ni₃X at 0GPa are shown in Table 1.

In this study, all calculations are performed using the plane wave pseudo-potential method based on density functional theory [32]. The generalized gradient approximation of the Perdew-Burke-Ernzerhof functional [33] is used to express the electron exchange-related potential. The Broyden-Fletcher-Goldfarb-Shanno scheme [34] is used to
optimize the geometry of the original unit cell. The cutoff energy of the atomic wave function is set to 440 eV, and the $K$ point is set to $8 \times 8 \times 8$. The valence electron configurations of Ni-3d$^8$4s$^2$, Ti-3d$^2$4s$^2$, V-3d$^4$4s$^2$, Nb-4d$^4$5s$^1$, and Ta-4f$^{14}$5d$^6$6s$^2$ are considered. The convergence tolerance is set to $2.0 \times 10^{-6}$ eV/atom, the maximum residual stress on a single atom is less than 0.03 eV/Å, the stress deviation is less than 0.05 Pa, and the tolerance deviation is less than 0.001 Å. In order to study the influence of pressure on $\gamma'$-Ni$_3$X, the equivalent hydrostatic pressure applied ranges from 0 to 100 GPa in the geometric optimization process, with an interval of 20 GPa.

### Results and discussion

#### Structural properties

The stability of a material is closely related to the enthalpy of formation ($\Delta H$) of the crystals that make up the material. The enthalpy of formation is the total energy of the crystal minus the energy of the reactants. When the value of the $\Delta H$ is less than zero, it indicates that the crystal structure is thermodynamically stable; otherwise, the crystal structure is unstable. In this research, the $\Delta H$ of $L1_2$-type $\gamma'$-Ni$_3$X ($X = $ Al, Ti, V, Nb) can be determined by the following expression:

$$\Delta H_m = \Delta H^0_m (\text{product}) + \Delta_j H^0_j (\text{reactant})$$

(1)

where $E_{\text{Total}}^m$ represents the total energy of $L1_2$-type $\gamma'$-Ni$_3$X; $N_A$ stands for Avogadro’s constant; $e$ is the basic charge; and $E_{\text{Total}}^m$ and $E_{\text{Total}}^X$ are the energy per atom in the Ni and X crystals, respectively.

The values of the lattice parameters $a$, $b$, $c$, $\Delta H$, and $V$ at 0 GPa and experimental and theoretical data studied by other researchers are listed in Table 1. The calculated results of the lattice constant are consistent with the existing experimental results [24, 26, 28, 30] and theoretical data [15, 25, 27, 29], indicating that the calculated results are credible. In Table 1, the $\Delta H$ of Ni$_3$Ti at 0 GPa is $-53.05$ kJ/mol, which is close to $-47.1$ kJ/mol and $-45.14$ kJ/mol reported in the literature. The $\Delta H$ of Ni$_3$V at 0 GPa is $-20.49$ kJ/mol, which is close to $-14.9$ kJ/mol and $-16.27$ kJ/mol reported in the literature. The $\Delta H$ of Ni$_3$Nb is relatively close to the previous research result of $-16.45$ kJ/mol [15], which proves the reliability of the calculation. The $\Delta H$ of the $L1_2$ type $\gamma'$-Ni$_3$X ($X = $ Al, Ti, V, Nb) phase at 0 GPa are $-48.15$, $-53.05$, $-20.49$, and $-21.82$ kJ/mol, respectively. It shows that the $L1_2$ type $\gamma'$-Ni$_3$X phase is thermodynamically stable, and the stability order of $\gamma'$-Ni$_3$X is Ti > Al > Nb > V.

Figure 2 shows the curves of lattice constants and cell volume ($V$) of $L1_2$-type $\gamma'$-Ni$_3$X as a function of pressure. It can be seen that $a$ and $b$ decrease with the increase of pressure, indicating that the increase of pressure leads to the compression of cell volume and the atomic distances become smaller. However, as the pressure increases, the decrease in the interatomic distance slows down and the volume change becomes slow. This is due to the fact that the reduction of interatomic distances under high pressure disrupts the balance of interatomic interaction forces and leads to strong repulsion between atoms, which makes it difficult for the crystal to continue to be compressed under high pressure.

#### Elastic properties

The elastic constant is a physical quantity used to describe the elastic properties of a material. It can be seen from Table 2 that the stability of the Ni$_3$X phase under external pressure satisfies the following constraints on the mechanical stability of the cubic crystal [35, 36]:

$$C_{11} - C_{12} > 0, C_{11} > 0, C_{44} > 0, C_{11} + 2C_{12} > 0$$

(3)

which indicates they are mechanically stable under pressure. The Pearson correlation coefficient $R^2$ in Fig. 3 is almost
close to 1, indicating that there is a very high linear correlation between the elastic constant and the pressure. The fitting curve between elastic constant and pressure is shown in Fig. 3. It can be seen from Fig. 3 that $C_{11}$, $C_{12}$, and $C_{44}$ increase with pressure increasing. $C_{11}$ possesses relatively large values, which means that $C_{11}$ is more sensitive to the change of pressure than $C_{12}$, $C_{44}$. Among them, $C_{11}$ represents the elasticity in length, which is used to explain the longitudinal strain characteristics of cubic crystals. $C_{12}$ and $C_{44}$ represent the elasticity of shape of cubic crystals, and are
often used to characterize elastic shear characteristic \[37\]. Under zero pressure, the \(C_{44}\) value of Ni₃Nb is the smallest and close to zero; it shows that Ni₃Nb have almost no shape elasticity at 0GPa. The larger change in \(C_{11}\) is due to the strain on the length, which produces a certain volume change without changing the shape of the crystal. In addition, based on the fitted curves in Fig. 3, the elastic constants at pressures greater than 100GPa can be inferred, and further predictions of the elastic modulus at pressures greater than 100GPa can be made.

The bulk modulus (\(B\)), shear modulus (\(G\)), Yong’s modulus (\(E\)), and Poisson’s ratio (\(\nu\)) of Ni₃X (X = Al, Ti, V, Nb) at 0 to 100GPa can be calculated straightforwardly by the Voigt-Reuss-Hill method \[38–40\]. The calculation equations are as follows.

\[
B = \frac{1}{3}(C_{11} + 2C_{12})
\]

\[\tag{4}
\]

\[
G_{V} = \frac{1}{5}(C_{11} - C_{12} + 3C_{44})
\]

\[\tag{5}
\]

\[
G_{R} = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}}
\]

\[\tag{6}
\]

\[
G = \frac{1}{2}(G_{V} + G_{R})
\]

\[\tag{7}
\]

\[
E = \frac{9GB}{3B + G}
\]

\[\tag{8}
\]

\[
\nu = \frac{3B - E}{6B}
\]

\[\tag{9}
\]

According to the methods above, the \(B\), \(G\), \(E\), and \(\nu\) of Ni₃X (X = Al, Ti, V, Nb) at 0 to 100GPa can be obtained, as shown in Table 2 and Fig. 4. It is generally accepted that \(G\) is usually used to measure the resistance of a metallic material to its own deformation, while \(B\) is used to characterize the resistance of the material to volume change. Figure 4 clearly shows that the values of bulk modulus for Ni₃X at the same pressure are much larger than the shear modulus, implying that Ni₃X tends to
resist volume change more than shape change under high pressure. $E$ describes the resistance of a solid material to deformation. The larger the $E$, the less deformable and more rigid the material. Thus, Ni$_3$Al, Ni$_3$Ti, and Ni$_3$V are much stiffer than Ni$_3$Nb. The hardness decreases in the following order: Ni$_3$Ti $>$ Ni$_3$V $>$ Ni$_3$Al $>$ Ni$_3$Nb. It is clear that the values of $B$, $G$, and $E$ in Fig. 4a and c show an increasing trend with increasing pressure, which indicates that pressure can increase the elastic modulus of the material and thus improve the hardness of the metal material itself. Figure 4b, c, and d show $G/B$, $v$, and $A^U$. Pugh [41, 42] proposed a rough method for judging the toughness and tough-brittle transition behavior of materials using the ratio of $G/B$ after an in-depth study. The brittleness of a material is associated with high $G/B$ values, while low $G/B$ values lead to ductility of the material [38]. The critical value of $G/B$ to distinguish between ductility and brittleness of a material is about 0.57 [42]. Figure 4c shows that the calculated $G/B$ values for different pressures are below 0.57, indicating that Ni$_3$Ti, Ni$_3$V, Ni$_3$Al, and Ni$_3$Nb all show ductility. Meanwhile, the increase in pressure leads to smaller $G/B$ values for Ni$_3$Al, Ni$_3$Ti, and Ni$_3$V, indicating that the ductility of Ni$_3$X is improved at high pressure. Conversely, higher pressures resulted in worse ductility of Ni$_3$Nb. Poisson’s ratio furnishes pertinent information.
on bonding capabilities [43], and for metallic materials, \( v \) is usually between 0.25 and 0.5. The calculated values of Ni\(_3\)Al, Ni\(_3\)Ti, Ni\(_3\)V, and Ni\(_3\)Nb at different pressures are between 0.25 and 0.5, and the Poisson’s ratio values of Ni\(_3\)Al, Ni\(_3\)Ti, and Ni\(_3\)V increase correspondingly with increasing pressure, which translates into better ductility of the material. On the contrary, Ni\(_3\)Nb has poor ductility.

Elastic anisotropy is an important property of materials, which reveals the difference in mechanical properties in different directions. The anisotropy of the crystal can be characterized by the universal anisotropy index. It is defined as [44, 45]:

\[
A^U = \frac{5G_V}{G_R} + \frac{B_V}{B_R} - 6 \tag{10}
\]

When the value of universal anisotropy index is not equal to 1, it indicates that the material is anisotropic; otherwise, the crystal is isotropic. Figure 4d shows that the value of \( A^U \) is not equal to 1, which obvious that Ni\(_3\)X phases are anisotropic materials. For the Ni\(_3\)X (X = Al, Ti, V) phase, the value of \( A^U \) increases with pressure, which indicates that the pressure causes anisotropy. On the contrary, pressure causes the anisotropy of Ni\(_3\)Nb to decrease. Moreover, the anisotropy decreases in the following order at 0GPa, Ni\(_3\)Nb > Ni\(_3\)Al > Ni\(_3\)Ti > Ni\(_3\)V, which means Ni\(_3\)Nb exhibits stronger anisotropy at 0GPa than the other phases. This is closely related to its smallness \( C_{44} \) at zero pressure.

**Anisotropy of acoustic velocities and Debye temperature**

**Anisotropy of acoustic velocities**

The propagation of sound velocity is anisotropic in solid, which is contingent on the symmetry of the crystal structure and the direction of dissemination. The relationship is shown by the following formula [46, 47].

\[
\left| C_{ijk}n_in_j - \mu w^2 \delta_{il} \right| = 0 \tag{11}
\]

\[
v(k) = \frac{dw}{dk} \tag{12}
\]

In this work, only the pure propagation modes of the cubic structure crystal Ni\(_3\)X in [100], [110], and [111] directions are considered; the sound velocities in Eqs. (11) and (12) can be solved by the elastic constants and phonon frequencies. Equations (13)–(16) denote the sound velocities of crystals in different crystal directions, respectively.

Cubic crystal [47, 48]:

For [100] direction:

\[
[100]v_1 = \sqrt{C_{11}/\rho}; [010]v_{12} = [001]v_{23} = \sqrt{C_{44}/\rho} \tag{14}
\]

For [110] direction:

\[
[110]v_1 = \sqrt{(C_{11} + C_{12} + 2C_{44})/\rho}; [1\overline{1}0]v_{1} = \sqrt{(C_{11} - C_{12})/\rho}; [001]v_{23} = \sqrt{C_{44}/\rho} \tag{15}
\]

For [111] direction:

\[
[111]v_1 = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho}; [1\overline{1}2]v_{1} = v_{23} = \sqrt{(C_{11} - C_{12} + 3C_{44})/3\rho} \tag{16}
\]

where \( C_{ijkl} \) represents the elastic constant; \( n_i \) and \( n_j \) denote the polarization direction and the propagation direction of sound velocity, respectively; \( w \) is the vibration frequency of the sound wave per unit period; and \( v \) is the propagation velocity of sound \( (v_l) \), the propagation velocity of sound in the longitudinal direction; \( v_{l1} \), is the sound velocity of the first transverse wave; and \( v_{l2} \), the sound velocity of the second transverse wave). The calculated results of the sound velocity of Ni\(_3\)X along each direction and at varying pressures are illustrated in Fig. 5. The elastic anisotropy of the crystal can be reflected by the propagation rate of the sound velocity in different directions within the crystal. For example, \( C_{11} \) determines the longitudinal sound velocity along the [100] direction, \( C_{22} \) determines the longitudinal sound velocity along the [010] direction, \( C_{33} \) determines the longitudinal sound velocity along the [001] direction, while \( C_{44} \), \( C_{55} \), and \( C_{66} \) determine the transverse sound velocity of Ni\(_3\)X along the [100], [010], and [001] directions, respectively.

In Fig. 5, the outcome shows that the sound velocity in different directions increases of the \( Li_x \)-type \( \gamma’-Ni_3X \) (X = Ti, V, Nb) phase with the increase of pressure. Moreover, the speed increase rates in the [001], [110], and [111] directions are different, which indicates the existence of anisotropy of sound velocity. Among the three longitudinally propagating sound velocities in Fig. 5, the longitudinal wave velocity along the [111] direction
(111) \( v_r \) is the fastest, which may be due to the difference of \( C_{11} \) and \( C_{12} \), resulting in the difference in sound velocity propagation. This also explains the anisotropic variation of the \( \text{Ni}_3\text{X} \) phase.

**Debye temperature**

The Debye temperature \( \Theta_D \) is an important physical parameter that reflects the degree of dynamic distortion of the solid lattice and the strength of the interatomic bond. Many physical quantities of matter are connected with it, as elasticity, hardness, specific heat, and melting point, so it is essential to study the Debye temperature. \( \Theta_D \) can be calculated from the data of elastic constants in Table 2 according to the following equation [49–51]:

\[
\Theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( N_A \rho \right) \right]^{(1/3)} v_m
\]

\[ (17) \]

\[
v_m = \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_s^3} \right) \right]^{(-1/3)}
\]

\[ (18) \]

\[
v_l = \sqrt{\frac{3B + 4G}{3\rho}}
\]

\[ (19) \]
The \( h \) in Eq. (16) represents Planck’s constant, \( k_B \) stands for the Boltzmann’s constant, \( n \) is the number of atoms in a single \( \text{Ni}_3X \) cell, \( N_A \) is Avogadro’s number, \( \rho \) is the density of a single \( \text{Ni}_3X \) cell, \( M \) is the molecular weight of \( \text{Ni}_3X \), respectively. \( v_m \), \( v_l \), and \( v_s \) stand for the average, longitudinal, and shear sound velocities, respectively. Table 3 displays the dependence of \( v_m \), \( v_l \), and \( v_s \) with pressure interval from 0 to 100 GPa. The computed values of Debye temperature (\( \Theta_D \)) of \( \text{Ni}_3X \) at variable pressures are demonstrated in Fig. 6. The Debye temperatures of \( \text{Ni}_3\text{Al} \) and \( \text{Ni}_3\text{V} \) at 0 GPa are 461.45 K and 448.83 K, respectively, which is close to the existing experimental values derived from the measurement of elastic constants at chamber temperature [21], which are in line with the findings of this paper. It can be found that \( \text{Ni}_3\text{Ti} \) has the highest \( \Theta_D \) among the five phases. Debye temperature rises with incremental pressure for \( \text{Ni}_3X \) phases, and the growth rate gradually decreases.

In addition, as mentioned above, the Debye temperature (\( \Theta_D \)) can be utilized to depict the intensity of covalent bonds in solids. The larger the value of \( \Theta_D \), the stronger the covalent bonds. Therefore, the covalent bonds in \( \text{Ni}_3X \) become stronger as the pressure increases.

\[
v_s = \sqrt{\frac{G}{\rho}}
\]  

(20)

![Graph](image_url)

**Fig. 6** Sound velocity, Debye temperature (\( \Theta_D \)) of \( \text{Ni}_3X (X=\text{Al, Ti, V, Nb}) \) phases

| Phase  | Pressure | \( v_m (m/s) \) | \( v_l (m/s) \) | \( v_s (m/s) \) | \( \Theta_D (k) \) |
|--------|----------|-----------------|-----------------|-----------------|-----------------|
| \( \text{Ni}_3\text{Al} \) | 0        | 4207.93         | 6152.01         | 3162.58         | 461.45          |
|       | 20       | 4470.68         | 6880.14         | 3317.77         | 490.27          |
|       | 40       | 4849.46         | 7584.10         | 3586.32         | 531.81          |
|       | 60       | 5129.87         | 8220.99         | 3775.00         | 562.56          |
|       | 80       | 5340.12         | 8661.35         | 3920.81         | 585.61          |
|       | 100      | 5504.08         | 8937.02         | 4040.39         | 603.59          |
| \( \text{Ni}_3\text{Ti} \) | 0        | 4446.32         | 6132.45         | 3401.70         | 487.60          |
|       | 20       | 4900.93         | 7102.18         | 3692.49         | 537.45          |
|       | 40       | 5135.15         | 7660.46         | 3839.26         | 563.13          |
|       | 60       | 5393.67         | 8182.37         | 4016.07         | 591.48          |
|       | 80       | 5587.69         | 8605.96         | 4046.10         | 612.76          |
|       | 100      | 5749.31         | 8977.2          | 4253.29         | 630.48          |
| \( \text{Ni}_3\text{V} \)  | 0        | 4092.86         | 3053.58         | 6156.80         | 448.83          |
|       | Other calculation [21] | 3835.20 | 3432.78 | 6442.70 | 507.12 |
|       | 20       | 4442.07         | 3288.78         | 6909.67         | 487.13          |
|       | Other calculation [21] | 4196.65 | 3648.77 | 7248.24 | 570.23 |
|       | 40       | 4809.94         | 3551.61         | 7578.06         | 527.47          |
|       | 60       | 5088.3          | 3749.84         | 8094.33         | 558.00          |
|       | 80       | 5300.28         | 3910.35         | 8385.85         | 581.24          |
|       | 100      | 5516.44         | 4054.6          | 8896.58         | 604.95          |
| \( \text{Ni}_3\text{Nb} \) | 0 | 2079.96 | 1466.94 | 4981.47 | 228.09 |
|       | 20       | 2835.67         | 2015.41         | 6005.79         | 310.97          |
|       | 40       | 3263.52         | 2328.63         | 6588.92         | 357.89          |
|       | 60       | 3557.53         | 2542.98         | 7043.09         | 390.13          |
|       | 80       | 3976.12         | 2853.68         | 7563.29         | 436.03          |
|       | 100      | 4302.19         | 3099.52         | 7922.38         | 471.85          |
Electronic structure

In addition, to recognize the bonding traits and to look into the impact of stress on the digital structure, the whole density of states and partial density of states of Ni$_3$X are calculated in this paper, as proven in Fig. 7. Here, it is solely the TDOS of Ni$_3$X at 0, 40, and 80GPa that it has plotted to describe the hassle extra clearly.

As seen in Fig. 7, many energy states occupy the Fermi level, which means that the Ni$_3$X phase demonstrates metallic properties. In addition, the peak height of TDOS can be significantly reduced by increasing the pressure, and the distribution range of TDOS can be expanded. For Ni$_3$Al, Ni$_3$Ti, Ni$_3$V, and Ni$_3$Nb, the dominant bond-forming peaks in the vicinity of the Fermi level are dominated by the Ni-3d and Al-3p states, the Ni-3d and Ti-3d states, and the Ni-3d and V-3d states. In particular, the hybridization between Ni and X atoms is apparent, which forms a covalent bonding feature.

To reap perception into the chemical bonding homes of Ni$_3$X beneath pressure, Mulliken charges [52] as properly as bond lengths have been analyzed to quantitatively examine the impact of stress on structural, elastic, thermodynamic, and digital properties. The ionic configurations are listed in Table 4. At 0GPa, the charges transferred from X to Ni atoms for Ni$_3$Al, Ni$_3$Ti, Ni$_3$V, and Ni$_3$Nb are 0.25, 0.40, 0.30, and 0.28e, respectively. In addition, the charges transferred from X to Ni atoms expand with growing pressure. But the bond length size decreases with the ascending of pressure. This is the physical root of the impact of pressure on the structure, elastic constants, Debye temperature, etc. This offers an appropriate rationalization for the variant of lattice constant and volume with pressure.

To further analyze the difference interaction between Al, Ti, V, and Nb atoms and Ni atoms, this article studies the charge density (Fig. 8 is the charge density diagram of Ni$_3$X phases) distribution of Ni$_3$X on the [010] crystal plane. From the point of view of electron transfer between atoms, Ni atoms lose more electrons in Ni$_3$X ($X = \text{Ti, V, Nb}$), and the lost electrons are transferred to the space between Ni atoms and Ti, V, and Nb (the red part in Fig. 8). With the pressure increases, the electron transfer tendency increases. The order of electron aggregation strength between doping atoms is Ti > Nb > V > Al; therefore, the interaction between Ti atoms and Ni atoms is the strongest, and the interaction between Ta atoms and Ni atoms is the weakest. This is consistent with the analysis results of the enthalpy of formation, the Debye temperature, and the density of states.

Conclusions

In this paper, the structural stability ($\Delta H$), elastic constants ($C_{ij}$), bulk modulus ($B$), Yong’s modulus ($E$), shear modulus ($G$), Debye temperature ($\Theta_D$), and electronic structures of $L1_2$-type Ni$_3$X ($X = \text{Al, Ti, V, Nb}$) phases under external pressure condition were systematically studied by first principles calculations. The conclusion is as follows:

(1) The relationship between elastic constant, elastic modulus, $G/B$ value, and Poisson’s ratio under pressure shows that Ni$_3$X has good shear stability and ductility. And the $C_{ij}$, $B$, $G$, and $E$ values increase with the increase of pressure.

(2) All Ni$_3$X phases have the sound velocity anisotropy, and the increase of external pressure leads to the enhancement of anisotropy. The [111] direction has strong longitudinal anisotropy, which is closely related to the large $C_{ij}$ of Ni$_3$X phases.

Table 4 Mulliken charge, bond length of Ni$_3$X ($X = \text{Al, Ti, V, Nb}$) phases at 0 to 100GPa

| Pressure (GPa) | Ni$_3$Al | Ni$_3$Ti | Ni$_3$V | Ni$_3$Nb |
|----------------|----------|----------|----------|----------|
| Bond length (Å) | Bond length (Å) | Bond length (Å) | Bond length (Å) | Bond length (Å) |
| Mulliken charge (e) | Mulliken charge (e) | Mulliken charge (e) | Mulliken charge (e) | Mulliken charge (e) |
| 0 | 2.53 | 2.56 | 2.53 | 2.61 |
| | $\text{Ni}^{+0.08}\text{Al}^{+0.25}$ | $\text{Ni}^{-0.13}\text{Ti}^{+0.4}$ | $\text{Ni}^{-0.1}\text{V}^{+0.3}$ | $\text{Ni}^{-0.09}\text{Nb}^{+0.28}$ |
| 20 | 2.46 | 2.49 | 2.46 | 2.54 |
| | $\text{Ni}^{+0.07}\text{Al}^{+0.22}$ | $\text{Ni}^{-0.2}\text{Ti}^{+0.59}$ | $\text{Ni}^{-0.15}\text{V}^{+0.44}$ | $\text{Ni}^{-0.19}\text{Nb}^{+0.58}$ |
| 40 | 2.4 | 2.44 | 2.42 | 2.49 |
| | $\text{Ni}^{+0.06}\text{Al}^{+0.19}$ | $\text{Ni}^{-0.26}\text{Ti}^{+0.78}$ | $\text{Ni}^{-0.19}\text{V}^{+0.58}$ | $\text{Ni}^{-0.29}\text{Nb}^{+0.86}$ |
| 60 | 2.36 | 2.34 | 2.38 | 2.45 |
| | $\text{Ni}^{+0.05}\text{Al}^{+0.16}$ | $\text{Ni}^{-0.32}\text{Ti}^{+0.96}$ | $\text{Ni}^{-0.24}\text{V}^{+0.72}$ | $\text{Ni}^{-0.37}\text{Nb}^{+1.11}$ |
| 80 | 2.33 | 2.36 | 2.35 | 2.42 |
| | $\text{Ni}^{+0.04}\text{Al}^{+0.13}$ | $\text{Ni}^{-0.38}\text{Ti}^{+1.14}$ | $\text{Ni}^{-0.29}\text{V}^{+0.86}$ | $\text{Ni}^{-0.45}\text{Nb}^{+1.35}$ |
| 100 | 2.3 | 2.34 | 2.32 | 2.39 |
| | $\text{Ni}^{+0.03}\text{Al}^{+0.10}$ | $\text{Ni}^{-0.44}\text{Ti}^{+1.31}$ | $\text{Ni}^{-0.33}\text{V}^{+0.99}$ | $\text{Ni}^{+0.53}\text{Nb}^{+1.58}$ |
The sound velocity and Debye temperature increase of the Ni$_3$X phases with the increase of the applied pressure. The magnitude of the Debye temperature under the applied pressure is Ni$_3$Ti > Ni$_3$Al > Ni$_3$V > Ni$_3$Nb.

Electronic analysis shows that increase pressure results in improving the bond strength and crystal stability of Ni$_3$X phases. The degree of charge hybridization and Ni-X bond strength increases with increasing pressure. In those phases, the charge accumulation of Ni$_3$Ti is the largest and the crystal structure is the most stable.

Author contribution Y H Wu: investigation, methodology, formal analysis, validation, writing (original draft), writing (review and editing). J S Chen: writing (review and editing), validation. J Y Ji: formal analysis, methodology, validation. Y Z Zhang: conceptualization, methodology. Q Z Wang: writing (review and editing). K Xiong: conceptualization, methodology.

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Data availability The raw/processed data required to reproduce these findings can be shared upon request.

Code availability The code for the simulations can be provided upon request.

Declarations

Conflict of interest The authors declare no competing interests.

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