# First-principles study of mechanical stability and thermal properties of $M$NNi$_3$ ($M$=Zn, Mg, Al) under pressure*

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The mechanical stability, elastic, and thermodynamic properties of the anti-perovskite superconductors $M$NNi$_3$ ($M$=Zn, Mg, Al) are investigated by means of the first-principles calculations. The calculated structural parameters and elastic properties of $M$NNi$_3$ are in good agreement with the experimental and the other theoretical results. From the elastic constants under high pressure, we predict that ZnNNi$_3$, MgNNi$_3$, and AlNNi$_3$ are not stable at the pressures above 61.2 GPa, 113.3 GPa, and 122.4 GPa, respectively. By employing the Debye model, the thermodynamic properties, such as the heat capacity and the thermal expansion coefficient, under pressures and at finite temperatures are also obtained successfully.

**Keywords:** density functional theory, elasticity, thermodynamic properties

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## 1. Introduction

Soon after the discovery of Ni-rich intermetallic anti-perovskite superconductor MgCNi$_3$,[1] much attention has been directed to the isostructural cubic anti-perovskite superconductors for their puzzling physical properties and important technical applications. Many researchers have focused on the development of design principles, the synthesis, and the investigation of the related anti-perovskite type superconductors. So far, some cubic anti-perovskite $M$CNi$_3$ have been synthesized, and their physical properties have been investigated, such as (Mg, Zn) CNi$_3$,[2] (Al, Ga, Cd) CNi$_3$,[3−5] and In$_{0.95}$CNi$_3$.[6] It is noteworthy that only MgCNi$_3$ and CdCNi$_3$ indicate superconductivity.

Recently, the first new superconducting ($T_c \sim 3$ K) Ni-rich nitrogen-containing anti-perovskite ZnNNi$_3$ has been successfully synthesized by replacing the carbon with nitrogen.[7] The stoichiometric compound ZnNNi$_3$ has the same structure as that of ZnCNi$_3$ (space group $Pm$-3$m$). It provides another route for synthesizing superconducting compounds to study the Ni-based anti-perovskite superconductors. So far, some physical properties of cubic Ni-rich nitrides $M$NNi$_3$[8−16] have been investigated for ZnNNi$_3$, MgNNi$_3$, CdNNi$_3$, AlNNi$_3$, GaNNi$_3$, and InNNi$_3$[10−16] by means of different approximations at the ambient condition. The *ab initio* calculations have been performed to study the electronic structures, the phonon dispersion relations, and the electron–phonon interactions for cubic superconductors Mg$X$Ni$_3$, with $X$ = B, C, and N.[11] The mechanical and the electronic properties of anti-perovskite type superconductor ZnNNi$_3$ as well as its isostructural and isovalent counterparts MgNNi$_3$ and CdNNi$_3$ have been studied by using the first-principles calculations.[12] The structural, the elastic, and the electronic properties of the new ternary nitrides AlNNi$_3$, GaNNi$_3$, and InNNi$_3$

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with the cubic anti-perovskite-like structure have been predicted by using the full-potential linear augmented plane wave (FP-LAPW) method.[16] The investigations of mechanical stability and elastic properties of $ZnNNi_3$, $AlNNi_3$, and $MgNNi_3$ at zero pressure and zero temperature have already been conducted. However, to our knowledge, the mechanical stability, the elastic and the thermal properties of $M$NNi$_3$ ($M$=Zn, Al, Mg) under pressures and at finite temperatures have not been studied theoretically yet. Moreover, the available experimental and theoretical data have shown that the physical properties of $MgCNi_3$ as the isostructural counterpart of $ZnNNi_3$ are very sensitive to the external pressure, such as the superconducting transition temperature $T_c$, the mechanical stability, the electronic and the elastic properties.[17,18] Therefore, it attracts us to investigate the elastic constants, the mechanical stability and the thermal properties of $M$NNi$_3$ ($M$=Zn, Al, Mg) under pressures and at finite temperatures. The results are useful to understand the behaviors of $M$NNi$_3$ superconductors.

## 2. Theoretical methods

### 2.1. Total energy electronic structure calculations

In the electronic structure calculations, the ultrasoft pseudopotential introduced by Vanderbilt[19] has been employed for all the ion–electron interactions. The effects of the exchange–correlation interaction are treated within the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE).[20] A plane wave basis set with energy cutoff 800.0 eV is used. Pseudo atomic calculations are performed for Zn $3d^{10}4s^2$, Mg $2p^63s^2$, Al $3s^23p^1$, Ni $3d^84s^2$, and N $2s^22p^3$. As for the Brillion-zone sampling, we use 12×12×12 $k$ points. The self-consistent convergence criterion of the total energy is set at $10^{-7}$ eV/atom. The hydrostatic pressure, coupled with the variable cell approach, is applied within the Parrinello–Rahman method to perform a full optimization of the cell structure for each target external pressure. All these total energy electronic structure calculations are carried out by using the CASTEP code.[21,22]

### 2.2. Elastic properties

To calculate the elastic constants under pressure, we apply the non-volume conserving method. The complete elastic constant tensor is determined by calculating the stresses induced by small deformations of the equilibrium primitive cell. The elastic constants $c_{ijkl}$ are then determined as[23–25]

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}}\right)_X, \tag{1}$$

where $\sigma_{ij}$ and $e_{kl}$ are the applied stress and the Eulerian strain tensors, respectively, and $X$ and $x$ are the coordinates before and after the deformation, respectively. For the isotropic stress, the elastic constants are defined as[24–26]

$$c_{ijkl} = C_{ijkl} + \frac{P}{2}(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}), \tag{2}$$

$$C_{ijkl} = \left(\frac{1}{V(x)}\frac{\partial^2 E(x)}{\partial e_{ij}\partial e_{kl}}\right)_X, \tag{3}$$

where $C_{ijkl}$ is the second-order derivative with respect to the infinitesimal strain (Eulerian). For a cubic crystal $M$NNi$_3$, there are three independent elastic constants, i.e., $C_{11}$, $C_{12}$, and $C_{44}$.

For a cubic structure $M$NNi$_3$, bulk modulus $B$, shear modulus $G$, tetragonal shear modulus $G'$, and the Young's modulus $E$ are expressed as

$$B = (C_{11} + 2C_{12})/3, \tag{4}$$

$$G = (3C_{44} + C_{11} - C_{12})/5, \tag{5}$$

$$G' = (C_{11} - C_{12})/2, \tag{6}$$

$$E = \frac{9BG}{3B + G}. \tag{7}$$

The Debye temperature may be estimated from the average sound velocity $V_m$[27]

$$\Theta = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} V_m, \tag{8}$$

where $h$ is the Planck constant, $k$ is the Boltzmann constant, $N_A$ is the Avogadro number, $n$ is the number of atoms per formula unit, $M$ is the molecular mass per formula unit, $\rho$ is the density, and $V_m$ is obtained from[27]

$$V_m = \left[\frac{1}{3}\left(\frac{2}{V_s^3} + \frac{1}{V_l^3}\right)\right]^{-1/3}, \tag{9}$$

with $V_s$ and $V_l$ being the shear and the longitudinal sound velocities, respectively, which can be related to the shear and the bulk moduli by the Navier's equations[28]

$$V_s = \sqrt{\frac{G}{\rho}}, \quad V_l = \sqrt{\left(B + \frac{4}{3}G\right)/\rho}. \tag{10}$$

### 2.3. Thermodynamic properties

To investigate the thermodynamic properties of $M$NNi$_3$, we apply the quasi-harmonic Debye model,[29] in which the phononic effect is considered, and the non-equilibrium Gibbs function $G^*$ $(V; P, T)$ takes the form

$$G^*(V; P, T) = E(V) + PV + A_{\rm Vib}(\Theta(V); T), \quad (11)$$

where $E(V)$ is the total energy per unit cell, $PV$ corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and $A_{\rm Vib}$ is the vibrational Helmholtz free energy that can be written as

$$A_{\rm Vib}(\Theta; T) = nkT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1 - {\rm e}^{-\Theta/T}) - D(\Theta/T)\right], \quad (12)$$

with $D(\Theta/T)$ representing the Debye integral, $n$ denoting the number of atoms per formula unit, and $\Theta$ being the Debye temperature given by Eq. (8).

By solving the following equation with respect to $V$:

$$\left(\frac{\partial G^*(V; P, T)}{\partial V}\right)_{P,T} = 0, \quad (13)$$

we can obtain the thermal equation of state $V$ $(P, T)$ and the thermal expansion coefficient $\alpha$ as

$$\alpha = \gamma C_V/(B_T V), \quad (14)$$

where heat capacity $C_V$ is expressed as

$$C_V = 3nk\left[4D(\Theta/T) - \frac{3\Theta/T}{{\rm e}^{\Theta/T} - 1}\right]. \quad (15)$$

This method has been successfully applied to some crystals.[30–33]

## 3. Results and discussion

For the anti-perovskite type superconductors $M$NNi$_3$, a series of lattice constants are used to calculate the total energy $E$ and the corresponding primitive cell volume $V$, and then the obtained $E$–$V$ data are fitted to the Birch–Murnaghen equation of state (EOS).[34] The obtained equilibrium lattice constant $a$, zero-pressure bulk modulus $B_0$, and its pressure derivation $B_0'$ of $M$NNi$_3$ ($M$=Zn, Al, Mg) at $P = 0$ and $T = 0$ are summarized in Table 1, together with the other theoretical[12–16] and the experimental results.[7] From Table 1, it is easily found that the calculated values are well consistent with the theoretical[12–16] and the experimental[7] results in the literature.

**Table 1.** Calculated equilibrium parameter $a$ (Å), bulk modulus $B_0$ (GPa), pressure derivative bulk modulus $B_0'$, and bond lengths of ZnNNi$_3$, MgNNi$_3$, and AlNNi$_3$ at $P = 0$ and $T = 0$.

| $M$NNi$_3$ | | Present work | Other work |
|---|---|---|---|
| ZnNNi$_3$ | $a$ | 3.765 | 3.756[a], 3.77[b], 3.770[c], 3.719[d], |
| | $B_0$ | 192.1 | 3.769[e] |
| | $B_0'$ | 4.97 | 198.92[b], 225.61[d] |
| | $d_{\rm Zn-Ni}$ | 2.681 | 4.75[d] |
| | $d_{\rm N-Ni}$ | 1.896 | 2.666[b] |
| | | | 1.885[b] |
| MgNNi$_3$ | $a$ | 3.841 | 3.82[b], 3.815[c] |
| | $B_0$ | 169.3 | 188.53[b] |
| | $B_0'$ | 4.80 | |
| | $d_{\rm Mg-Ni}$ | 2.715 | 2.701[b] |
| | $d_{\rm N-Ni}$ | 1.920 | 1.915[b] |
| AlNNi$_3$ | $a$ | 3.794 | 3.777[c], 3.777[f] |
| | $B_0$ | 197.6 | |
| | $B_0'$ | 4.82 | |
| | $d_{\rm Al-Ni}$ | 2.683 | |
| | $d_{\rm N-Ni}$ | 1.897 | |

[a] Ref. [7] (experiment data); [b] Ref. [12]; [c] Ref. [13]; [d] Ref. [14]; [e] Ref [15]; [f] Ref. [16].

The bond lengths of Zn–Ni and N–Ni are also shown in Table 1, which are in agreement with those obtained by Li *et al.*[12] It is found that the relations of the bond lengths in $M$NNi$_3$ are $d_{\mathrm{Zn-Ni}} < d_{\mathrm{Al-Ni}} < d_{\mathrm{Mg-Ni}}$, $d_{\mathrm{N-Ni}}(\mathrm{ZnNNi_3}) < d_{\mathrm{N-Ni}}$ $(\mathrm{AlNNi_3}) < d_{\mathrm{N-Ni}}(\mathrm{MgNNi_3})$. Unfortunately, to our knowledge, no experiment values of bulk modulus and bond length of $M$NNi$_3$ are available to be compared with our theoretical results.

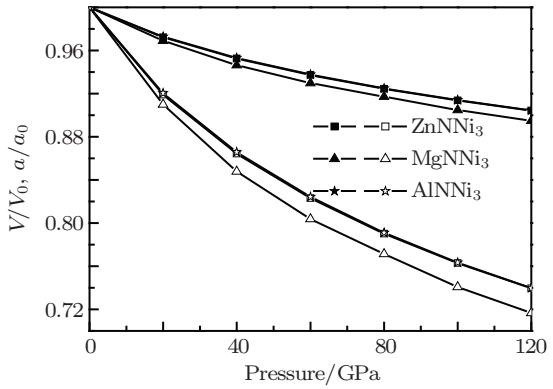



**Fig. 1.** Normalized parameters $V/V_0$ and $a/a_0$ of $M$NNi$_3$ versus the increasing pressure, where solid symbols represent $V/V_0$ and hollow ones represent $a/a_0$.

In addition, the normalized parameters $V/V_0$ and $a/a_0$ each as a function of pressure for $M$NNi$_3$ are plotted in Fig. 1. The $V/V_0$ and $a/a_0$ decrease almost linearly with the increasing pressure. And the normalized parameters $a/a_0$ of $M$NNi$_3$ vary less under pressures than that of the relative volumes $V/V_0$. When the applied pressure equals to 120 GPa, the relative volumes $V/V_0$ of ZnNNi$_3$, MgNNi$_3$, and AlNNi$_3$ become 73.94%, 71.65%, and 73.94%, respectively. It is interesting to find that ZnNNi$_3$ is compressed nearly the same as AlNNi$_3$. Among the three superconductors, MgNNi$_3$ is the most difficult to be compressed.

The elastic constants of solids provide a link between the mechanical and the dynamical behaviors of the crystals, and give important information concerning the nature of the forces operating in the solids. The elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ at zero pressure are listed in Table 2. It is shown that the differences between our results and those of Li *et al.*[12] are slightly large. Since there are no experimental data to compare with, we list the available theoretical data of ZnNNi$_3$. Among the three independent elastic constants of cubic $M$NNi$_3$, the value of $C_{44}$ represents the resistance to deformation with respect to the shear stress applied across the (1 0 0) plane in the [0 1 0] direction. In the present calculations, we find that $C_{44}(\mathrm{MgNNi_3}) > C_{44}(\mathrm{AlNNi_3}) > C_{44}(\mathrm{ZnNNi_3})$. Our calculated lattice parameters listed in Table 1 are closer to the experiment value than that of Li *et al.*[12] So we believe that our calculations of the elastic constants should be more reliable.

**Table 2.** Calculated elastic constants $C_{ij}$ (GPa), bulk modulus $B$, shear modulus $G$ (GPa), tetragonal shear modulus $G'$ (GPa), Young's modulus (GPa), $B/G$, and Debye temperature $\Theta_{\mathrm{D}}$ (K).

| | | $C_{11}$ | $C_{12}$ | $C_{44}$ | $B$ | $G$ | $G'$ | $E$ | $B/G$ | $\Theta^*_{\mathrm{D}}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| ZnNNi$_3$ | present | 321.7 | 125.1 | 35.4 | 190.6 | 54.1 | 98.3 | 251.6 | 3.52 | 315 |
| | literature | 354.28[a)] | 134.01[a)] | 48.06[a)] | 207.43[a)] | 48.06[a)] | 110.14[a)] | 229.1[a)] | | 336[a)] |
| | | 381.6[b)] | 116.5[b)] | 17.9[b)] | 179.1[b)] | | 132.5[b)] | 127.4[b)] | | 276.47[b)] |
| | | 364.2[c)] | 124.9[c)] | 32.69[c)] | | | | | | 271.57[c)] |
| | | 394.57[d)] | 140.28[d)] | 55.39[d)] | | | | | | 287.49[d)] |
| MgNNi$_3$ | present | 317.8 | 112.4 | 55.8 | 180.8 | 69.6 | 102.7 | 259.1 | | |
| | literature | 336.19[a)] | 125.31[a)] | 48.96[a)] | 195.60[a)] | 48.96[a)] | 105.44[a)] | | | |
| | | 319.9[b)] | 108.6[b)] | 96.9[b)] | 179.1[b)] | 100.3[b)] | 105.6[b)] | 253.6 | | |
| AlNNi$_3$ | present | 354.7 | 122.4 | 50.0 | 199.9 | 70.6 | 116.2 | 290.9 | 2.83 | 391 |
| | literature | 431.4[b)] | 96.1[b)] | 48.0[b)] | 207.8[b)] | 81.5[b)] | 167.7[b)] | 216.3[b)] | | |

[a)]Ref. [12]; [b)]Ref. [13]; [c)]Ref. [14]; [d)]Ref. [14] (GGA-WC); [e)]Ref. [14] (GGA-PBE); [f)]Ref. [14] (LDA).

*The Debye temperature of $M$NNi$_3$ is determined from the elastic constants.

It is acknowledged that the bulk modulus or the shear modulus can measure the hardness in an indirect way. The materials have often been used in polycrystalline aggregates. Therefore it is useful to estimate the corresponding parameters of the polycrystalline species. For this purpose, we utilize the Voigt–Reuss–Hill approximation to calculate the main mechanical parameters for cubic $M$NNi$_3$ (Table 2),

namely, bulk modulus $B$, shear modulus $G$, tetragonal shear moduli $G'$, and Young's modulus $E$, which can be calculated from the elastic constants of the single crystals via Eqs. (4)–(7). The bulk moduli of the $M$NNi$_3$ crystals increase in the sequence of $B$ (MgNNi$_3$) < $B$(ZnNNi$_3$) < $B$(AlNNi$_3$). The present bulk moduli of $M$NNi$_3$ ($M$=Zn, Al, Mg) are in good agreement with the ones obtained from the equation of state fitting. In addition, shear moduli $G$ are maximal and minimal for AlNNi$_3$ and ZnNNi$_3$, respectively. The tetragonal shear modulus $G'$, which represents the resistance to deformation by the shear stress applied across the (1 1 0) plane in the [1$\bar{1}$0] direction, increases in the same sequence as that of the shear modulus. For $M$NNi$_3$, there are similar characters in the mechanical behaviors, i.e., $B > G' > G$. This implies that the parameter limiting the mechanical stability of these materials is the shear modulus $G$. The Young's modulus $E$ is defined as the ratio between the stress and the strain, and is often used to provide a measure of the stiffness of the solid, i.e., the larger the value of $E$, the stiffer the material. From our calculations, the compounds with the maximal Young's moduli are AlNNi$_3$ (290.9 GPa) and MgNNi$_3$ (251.6 GPa), whereas the lowest $E$ is found in ZnNNi$_3$ (251.6 GPa). We note that there is a direct correlation between the Young's and the shear moduli of $M$NNi$_3$. Hence the above mentioned stiffest phases AlNNi$_3$ and MgNNi$_3$ with the highest $E$ also have the maximal shear moduli, whereas ZnNNi$_3$ with the minimal $E$ has the minimal shear ability.

The ratio between the bulk and the shear moduli, $B/G$, has been proposed by Pugh to predict brittle or ductile behavior of materials. The shear modulus $G$ represents their resistance to the plastic deformation, while $B$ represents their resistance to the fracture. A high $B/G$ ratio is associated with ductility, whereas a low one corresponds to the brittle nature. The critical value that separates ductile and brittle materials is around 1.75, i.e., if $B/G > 1.75$, the material behaves in the ductile manner, otherwise the material behaves in the brittle manner. We find that $B/G$ ratios are 3.52, 2.59, and 2.83 for $M$NNi$_3$ ($M$=Zn, Mg, Al) (also listed in Table 2), respectively, indicating that they are all ductile. Moreover, the ductile manner of ZnNNi$_3$ is the strongest.

The Debye temperature is one of the important thermodynamic parameters and is closely related to many thermophysical properties of the solids, such as specific heat, thermal expansion, vibrational entropy, sound velocities, hardness, and melting temperature. At low temperature, the vibrational excitations arise solely from the acoustic vibrations. Hence, at low temperature, the Debye temperature calculated from the elastic constants is the same as that determined from the specific heat measurement. The Debye temperatures $\Theta_{\rm D}$ of $M$NNi$_3$ are obtained from Eqs. (8)–(10), and are listed in Table 2 together with the experimental[7] and the other theoretical data.[12−14] The calculated Debye temperature of ZnNNi$_3$ is 315 K, which is more consistent with the experimental data than the other theoretical results. The Debye temperature gradually increases in ZnNNi$_3$, AlNNi$_3$, and MgNNi$_3$.

The elastic constants of $M$NNi$_3$ under pressure, obtained for the first time, are illustrated in Fig. 2. The changeable features of the elastic constants with pressures are very similar for $M$NNi$_3$ ($M$=Zn, Al, Mg). It is seen that $C_{11}$, $C_{12}$, and $C_{44}$ increase with the increase of the pressure. The $C_{11}$ is more sensitive to pressure than the others, while $C_{44}$ is the most insensitive one. Recently, elastic constants and mechanical stabilities of crystals have attracted lots of interest from physicists. In 2002, Sin'ko and Smirov[35] deduced the conditions of mechanical stability for elastic constants. As is known, for a cubic crystal, the mechanical stability under the isotropic pressure is judged from the following condition:

$$\tilde{C}_{44} > 0, \quad \tilde{C}_{11} > |\tilde{C}_{12}|, \quad \tilde{C}_{11} + 2\tilde{C}_{12} > 0, \qquad (16)$$

where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P$ ($\alpha = 1, 4$), and $\tilde{C}_{12} = C_{12} + P$. By fitting $\tilde{C}_{44}$ data to a second-order polynomial, we have the following relation:

$$\tilde{C}_{44} = \alpha + \beta P - \gamma P^2. \qquad (17)$$

Figure 3 shows $\tilde{C}_{44}$ versus pressure for $M$NNi$_3$ ($M$=Zn, Mg, Al). The $M$NNi$_3$ is not mechanically stable at pressures above the one of $\tilde{C}_{44} = 0$. The critical pressures of $M$NNi$_3$ ($M$=Zn, Mg, Al) are 61.2 GPa, 113.3 GPa, and 122.4 GPa, respectively. In the previous work, the obtained critical pressure of MgCNi$_3$ is 58.4 GPa,[18] which is reasonable comparing with the experimental data. In fact, according to our experience, the phase transition pressure should be smaller than the critical mechanical stable pressure.

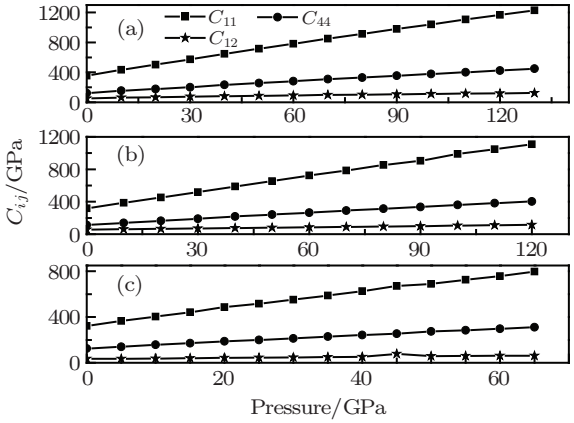



**Fig. 2.** Dependences of $C_{ij}$ on pressure for (a) $AlNNi_3$, (b) $MgNNi_3$, and (c) $ZnNNi_3$.

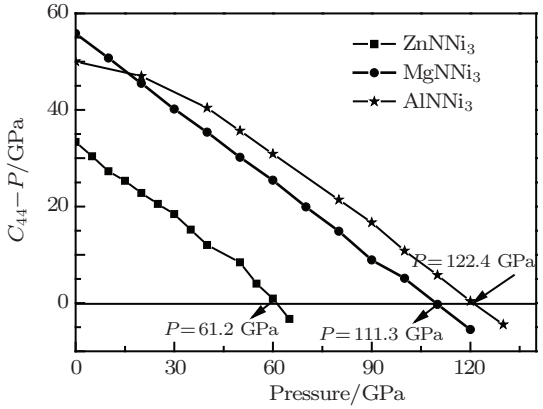



**Fig. 3.** Mechanical stability of $M$NNi$_3$ versus pressure at 0 K.

Through the quasi-harmonic Debye model, we can calculate the thermodynamic quantities of cubic $M$NNi$_3$ at any temperatures and any pressures from the $E$–$V$ data obtained at $T = 0$ and $P = 0$. In Fig. 4, we plot the thermal expansion coefficient $\alpha$ of $M$NNi$_3$ versus temperature under various pressures. It is shown that for a given pressure, especially at 0 GPa, the expansion coefficient increases with the increase of the temperature. And the increase gradually tends to a linear one at high temperature. With the increasing pressure, the increase of the thermal expansion coefficient with temperature becomes smaller. For a given temperature, the thermal expansion coefficient decreases strongly with the increasing pressure and remains very small at high temperatures and high pressures. Moreover, it is found that the thermal expansion coefficients of $ZnNNi_3$ and $MgNNi_3$ are nearly the same, and larger than that of $AlNNi_3$. At room temperature and zero pressure, the expansion coefficients of $ZnNNi_3$, $MgNNi_3$, and $AlNNi_3$ are $4.06\times10^{-5}$ K$^{-1}$, $4.17\times10^{-5}$ K$^{-1}$, and $3.62\times10^{-5}$ K$^{-1}$, respectively.

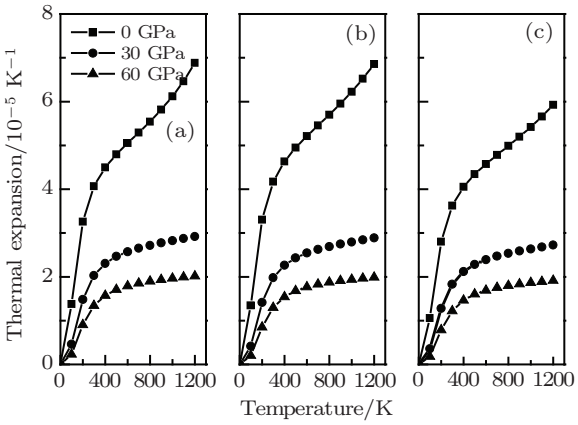



**Fig. 4.** Thermal expansion coefficient $\alpha$ versus temperature at various pressures for (a) $ZnNNi_3$, (b) $MgNNi_3$, and (c) $AlNNi_3$.

The knowledge of the heat capacity of a crystal not only provides essential information about its vibrational properties but also is mandatory for many applications. The relations of heat capacity $C_V$ with temperature and pressure are shown in Fig. 5. It is found that the variation of $C_V$ with pressure is similar to that of the thermal expansion coefficient below 400 K. At high temperature ($T > 400$ K), the heat capacity $C_V$ is strongly dependent on both temperature $T$ and pressure $P$, which is due to the used anharmonic approximation. However, when $T > 400$ K, the anharmonic effects are suppressed. The heat capacity $C_V$ of $M$NNi$_3$ at sufficient high temperature does not depend much on temperature $T$ and tends to approach a constant about 123 J/mol·K. The heat capacity $C_V$ is very close to the Dulong–Petit limit ($C_V(T) \sim 3R$ for mono-atomic solids), which is true to all solids at high temperature. At zero pressure and ambient temperature, $C_V$ of $M$NNi$_3$ ($M$=Zn, Mg, Al) are 105.79 J/mol·K, 104.65 J/mol·K, and 102.12 J/mol·K, respectively. This is probably the first report on them.

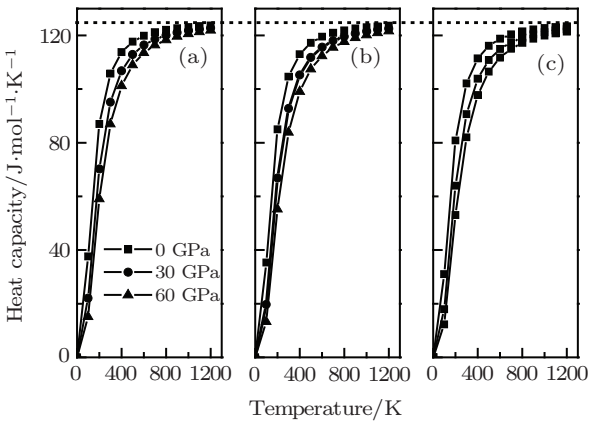



**Fig. 5.** Temperature dependences of heat capacity under various pressures for (a) $AlNNi_3$, (b) $MgNNi_3$, and (c) $ZnNNi_3$.

# 4. Conclusion

The structural and elastic properties, mechanical stability, and thermodynamic properties of the anti-perovskite superconductors $M$NNi$_3$ ($M$=Zn, Mg, Al) under pressure are investigated by using first-principles calculations with the generalized gradient approximation for exchange and correlation. The calculated structural parameters and the elastic constants of $M$NNi$_3$ are in good agreement with the experimental and the other theoretical results. Based on the elastic constants under high pressure, ZnNNi$_3$, MgNNi$_3$, and AlNNi$_3$ are predicted to be unstable at the pressures above 61.2 GPa, 113.3 GPa, and 122.4 GPa, respectively. The thermodynamic properties, such as the thermal expansion coefficient and the heat capacity, under pressures and at finite temperatures are also obtained successfully. We find that the mechanical behaviors of ZnNNi$_3$, MgNNi$_3$, and AlNNi$_3$ are very similar. It should be useful to stimulate future experimental and theoretical work.

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