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First-principles calculations of elasticity and thermodynamic properties of $LaNi_5$ crystal under pressure*

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This paper investigates the equilibrium lattice parameters, heat capacity, thermal expansion coefficient, bulk modulus and its pressure derivative of $LaNi_5$ crystal by using the first-principles plane-wave pseudopotential method in the GGA-PBE generalized gradient approximation as well as the quasi-harmonic Debye model. The dependences of bulk modulus on temperature and on pressure are investigated. For the first time it analyses the relationships between bulk modulus B and temperature T up to 1000 K, the relationship between bulk modulus B and pressure at different temperatures are worked out. The pressure dependences of heat capacity C_v and thermal expansion α at various temperatures are also analysed. Finally, the Debye temperatures of $LaNi_5$ at different pressures are successfully obtained. The calculated results are in excellent agreement with the experimental data.

Keywords: hydrogen storage, Debye temperature, thermodynamic properties, $LaNi_5$
PACC: 7115M, 6740K, 6155H

1. Introduction

The famous intermetallic compound $LaNi_5$ is of great importance to perform chemical, mechanical or thermodynamic works because of its easy activation, good hydrogen absorption- desorption kinetics and large hydrogen storage capacity. It is of great scientific and technological interest in view of its potential for applications such as paramagnetic materials,[1] electrodes for rechargeable nickel-metal hydride batteries,[2] hydrogen compressors[3] and thermodynamic projects[4,5] due to its outstanding ability to react reversibly with hydrogen and deuterium.

The elastic properties of solids are closely related to many fundamental solid-state properties, such as equation of state (EOS), thermal expansion, melting temperature and specific heat. A study of the elastic properties and thermodynamic properties for materials is well motivated by the understanding about the chemical bonds and the cohesion of material. Specifically for $LaNi_5$ alloy, the elastic properties are very useful for an evaluation of the elastic contribution to the hydrogen-hydrogen interaction energies and the elastic energy associated with the precipitation of hydrides. The cycle life of $LaNi_5$ has been attributed to hydrogen distributions and internal strains. Moreover, the elastic constants are also related to thermal properties according to the Debye theory. Because these effects are related to elastic and thermodynamic properties, there are good reasons to investigate the elastic properties of the $LaNi_5$ alloy.

The $LaNi_5$ alloy has a hexagonal $CaCu_5$ structure (space group P6/mmm). The La atom occupies 1a (0, 0, 0) Wyckoff site, the two nonequivalent Ni atoms occupy 2c (2/3, 1/3, 0) and 3g (0.5, 0, 0.5) sites. The elastic modulus of $LaNi_5$ intermetallic compounds have been measured over the temperature range 3∼415 K.[6] So far, no theoretical results and experimental data are available for elastic properties of $LaNi_5$ under high pressures and temperatures. In this paper, we investigate the structural and thermodynamic properties of $LaNi_5$ under high temperatures and high pressures through the plane-wave pseudopotential (PW-PP) method[7] and quasi-harmonic Debye

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model,[8] where the phononic effect is considered.

2. Theoretical method

2.1. Total energy calculations

Here we make a first-principles total energy electronic structure calculation. In our electronic structure calculation, we use the PW-PP method. The generalized gradient approximation (GGA) of PBE96[9] is used for the exchange-correlation energy functional and the ultrasoft pseudopotentials introduced by Vanderbilt[10] is applied to the interactions of the electrons with the ion cores. Initial convergence tests guided the choice of 400 eV for the plane wave cutoff energy, $E_{\rm cut}$. For the hexagonal Brillouin-zone sampling, we use the 10×10×12 Monkhorst–Pack mesh.[11] The electronic degrees of freedom are converged to 10^{-6} eV/cell and the force components on each atom are relaxed to less than 2×10^{-4} eV/Å(1Å= 0.1 nm)

2.2. Thermodynamic properties

The quasi-harmonic Debye model is employed to calculate the EOS and the thermodynamic properties which are constructed from the Helmholtz free energy at the temperature below the melting point in the quasi-harmonic approximation. This method is well established and many papers have been published recent years.[12,13] The bulk modulus B can be investigated under various pressures and temperatures using the quasi-harmonic Debye model. The non-equilibrium Gibbs function of the crystal phase $G*(V;P,T)$ can be written as[14]

$$G^*(V;P,T) = E(V) + pV + A_{\rm Vib}(V;T), \quad (1)$$

where $E(V)$ is the total energy per unit cell for $LaNi_5$, the second term, PV, corresponds to the constant hydrostatic pressure condition. The third term, $A_{\rm vib}$, is the vibrational Helmholtz free energy, which can be written as[15,16]

$$\begin{aligned} &A_{\rm vib}(\Theta_{\rm D};T) \\ &= nkT\left[\frac{9}{8}\frac{\Theta_{\rm D}}{T} + 3\ln(1-{\rm e}^{-\Theta_{\rm D}/T}) - D(\Theta_{\rm D}/T)\right], \end{aligned} \quad (2)$$

where $\Theta_{\rm D}$ is the Debye temperature, $D(\Theta_{\rm D}/T)$ represents the Debye integral, n is the number of atoms per formula unit. By solving the equation

$$\left(\frac{\partial G^*(V;p,T)}{\partial V}\right)_{p,T} = 0, \quad (3)$$

one could obtain the isothermal bulk modulus B

$$\begin{aligned} B_T(p,T) &= -V\left(\frac{\partial p}{\partial V}\right)_T \\ &= V\left(\frac{\partial^2 G^*(V;p,T)}{\partial V^2}\right)_{p,T}. \end{aligned} \quad (4)$$

According to the quasi-harmonic Debye model, the heat capacity C_v and the thermal expansion α can be obtained by

$$C_v = 3nk\left[4D(\Theta_{\rm D}/T) - \frac{3\Theta_{\rm D}/T}{{\rm e}^{\Theta/T}-1}\right], \quad (5)$$

$$\alpha = \frac{\gamma C_v}{B_T V}, \quad (6)$$

where γ is the Grüneisen parameter. For further details see Refs.[8, 17]. By using the method above, we can successfully obtain the elastic and thermodynamic properties of $LaNi_5$.

3. Results and discussion

Firstly, we make a first-principles calculation to find the most stable structure of $LaNi_5$. The geometric optimization and internal optimization are both applied. Then, a series of different cell volume V are set so as to calculate the corresponding total energy. The obtained relationship between primitive cell volume and total energy is illustrated in Fig.1. The zero pressure bulk modulus B_0 and its first order pressure derivative B_0' are determined by fitting the calculated energy–volume $(E-V)$ data points to the Birch–Murnaghan EOS[18]

$$\begin{aligned} &\Delta E(V) \\ &= E - E_0 \\ &= B_0 V_0\left[\frac{V_n}{B_0'} + \frac{1}{1-B_0'} + \frac{V_n^{1-B_0'}}{B_0'(B_0'-1)}\right], \end{aligned} \quad (7)$$

where E_0 is the equilibrium energy. The pressure P versus the normalized volume $V_n(=V/V_0$, where V_0 is the equilibrium volume at zero pressure) is obtained by

$$p = -\frac{{\rm d}E}{{\rm d}V} = \frac{B_0}{B_0'}\left[V_n^{-B_0'} - 1\right]. \quad (8)$$

Thus, we can obtain the lattice parameters, bulk modulus B_0 and its pressure derivative B_0' of $LaNi_5$, which are listed in Table 1, together with experimental data.

From Table 1, we know that agreement between experimental data and our calculated results is excellent.

From Fig.1, we found that the ratio c/a of 0.792 has the minimum energy, which corresponds to the most stable structure of $LaNi_5$ at $P = 0$ and $T = 0$. Clearly the most stable structure of $LaNi_5$ crystal corresponds to the total energy -281.16682 Hartree, and primitive cell volume $V_0 = 88.158\,\text{a.u.}^3$ (a.u. represents atomic units.). When $V < 88.158\,\text{a.u.}^3$, as volume V increases, the total energy decreases dramatically. When $V > 88.158\,\text{a.u.}^3$, the relationships between total energy and volume V are opposite.

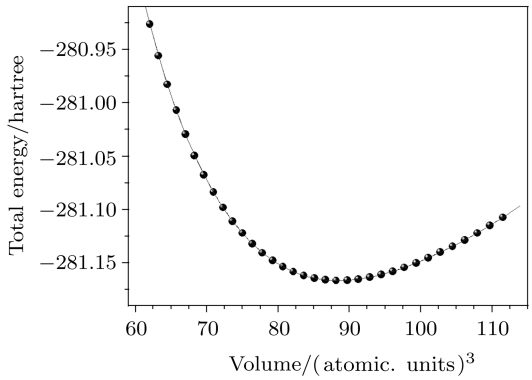


Fig.1. Energy-volume curves for $LaNi_5$. (1 hartree = 110.5×10^{-21} J).

Table 1. Calculated lattice parameters, bulk modulus B_0 and its pressure derivative B_0'.

	a/nm	c/nm	c/a	B_0/GPa	B_0'
Present work	0.5028	0.3982	0.792	137.3	4.82*
Ref.[19]	0.5018	0.39817	0.793	137.8[6]	5.0**
Ref.[20]	0.5016	0.3990	0.795	135.2	

*The calculated $B_0' = 4.82$ at $T = 285$ K **The experimental value $B_0' = 5.0$ at $T = 235 \sim 295$ K.

Now, applying the quasi-harmonic Debye model described above, we investigate the pressure dependence of bulk modulus B with the temperature varying from 0 to 1000 K. The calculated relationship of bulk modulus B as a function of temperature T is plotted in Fig.2(a). The relationships between bulk modulus B and pressure P at different temperatures $T = 0$, 300 K and 1000 K are plotted in Fig.2(b).

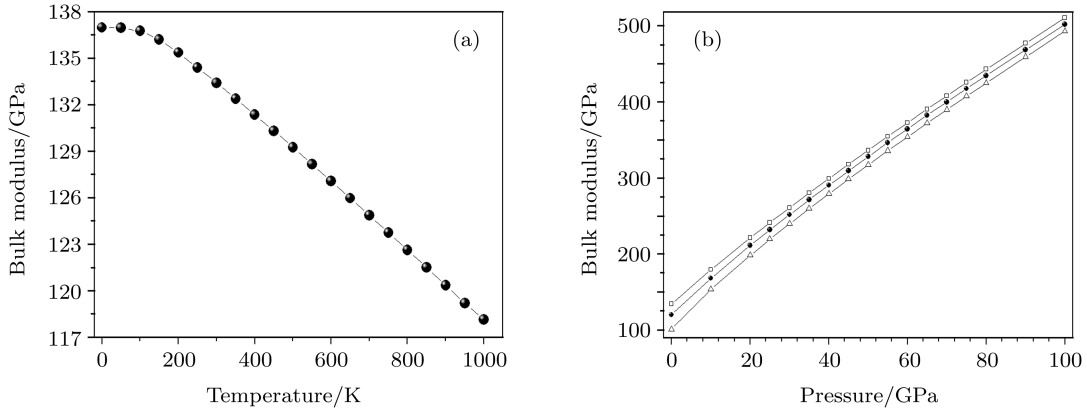


Fig.2. Bulk modulus B as a function of temperature T at pressure of zero pressure (a) and relationships between bulk modulus B as a function of pressure at $T = 0$ (square), 500(circle) and 1000 K (triangle) (b).

In Fig.2(a) we found that when $T < 100$ K, B nearly keeps constants. This indicates that the lattice constants a and c nearly keep constant. When $T > 100$ K, the bulk modulus B decreases dramatically as T increases, which means that the cell volume changes rapidly. The rapid volume variation makes rapid decrease of the bulk modulus B_0. By fitting the $B - T$ data points to third-order polynomial, we obtain

$$B = 137.3421 - 6.37 \times 10^{-3}T - 2.55783 \times 10^{-5}T^2 + 1.2898 \times 10^{-8}T^3, \quad \text{for } T < 1000\,\text{K}. \tag{9}$$

In Fig.2(b), it is clear that the bulk modulus B increases with pressure dramatically at a given temperature, B decreases with T at a given pressure. It shows the fact that the effect of increasing pressure on $LaNi_5$ is the same as decreasing its temperature. From Table 2, we find that the agreement between our calculated results and available experimental data is excellent.

Table 2. Calculated bulk modulus together with the experimental data at various temperatures.

Temperature	0K	100K	200K	300K	400K
B/GPa Expt.[6]	139.9	139.7	139.0	137.3	134.9
B/GPa Calc.	137.3	137.1	134.7	133.7	131.6
B/GPa Expt.[19]	135.3	134.6	133.7	132.0	129.6

From the quasi-harmonic Debye model, we can determine the heat capacity C_v and the thermal expansion coefficient α of $LaNi_5$ at simultaneous high pressure and temperature conditions, shown in Figs.3 and 4.

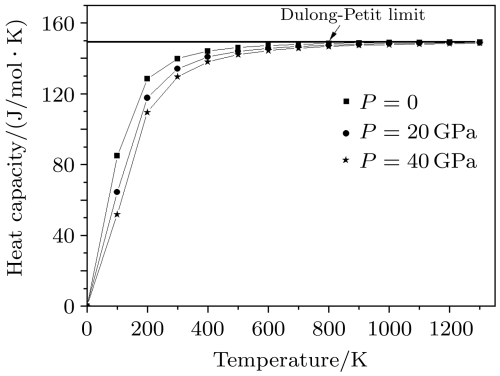


Fig.3. Heat capacity C_v of the $LaNi_5$ alloy at various pressures and temperatures.

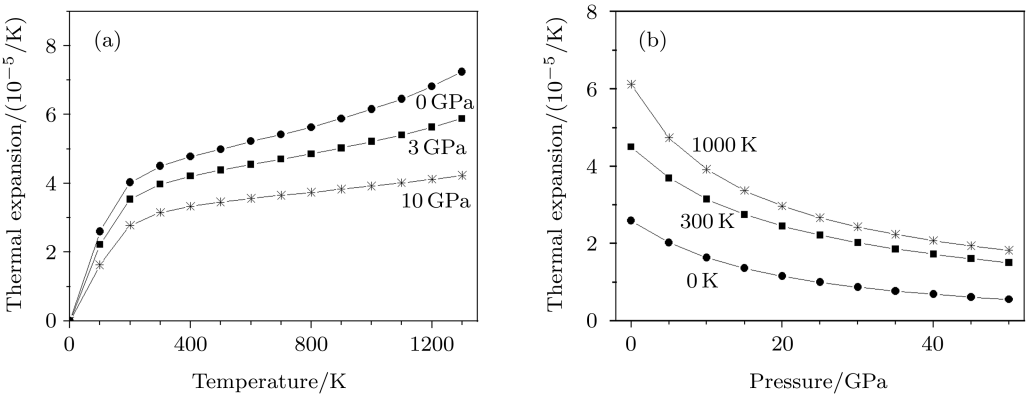


Fig.4. Thermal expansion versus temperature at $P = 0$, 3 GPa, 10 GPa (a) and thermal expansion versus pressure at $T = 0$ K, 300 K, 1000 K (b).

The calculated relationships between heat capacities and temperatures at different pressures are plotted in Fig.3. It is clear that when $T < 400$ K, the heat capacity C_v increases with temperature at a given pressure and decreases with pressure at a given temperature. The heat capacity C_v strongly depends on both temperature T and pressure P when $T < 400$ K. This is due to the anharmonic approximation of the Debye approximations used here. However, when $T > 400$ K, the anharmonic effect on heat capacity C_v is suppressed. The C_v value is very close to the Dulong–Petit limit, which is common to all solids at high temperature. These results show the fact that the interactions among ions in $LaNi_5$ crystal have big effect on heat capacity C_v especially at low temperatures. No phase transition appears in this region, which indicates that the thermodynamic properties of $LaNi_5$ crystal are stable. Unfortunately, there are no theoretical results or experimental data to check our calculated results.

In Fig.4(a), the variations of thermal expansion α versus temperature and versus pressure are clearly seen. The thermal expansion α increases with T^3 at low temperatures and gradually approaches a linear increase at high temperatures, and then the increasing trend becomes gentler. As the pressure increases, the increase of α with temperature becomes smaller, especially at high temperatures. It is noteworthy that the high-temperature dependence of the thermal expansion α is not linear at zero pressure, this is an indication of the inadequacy of the quasi-harmonic approximation at high temperatures and low pressures. In Fig.4(b), we found that for a given temperature, α decreases dramatically with increasing pressure. It is

shown that the thermal expansion α converges to a constant value at high temperatures and pressures. The higher the temperature is, the faster the thermal expansion α decreases. At 1000 K, the value $\alpha_1 = 2.96\times10^{-5}$/K (20 GPa) is much smaller than the value $\alpha_2 = 6.11\times10^{-5}$/K at zero pressure, this implies that the pressure influence on α is significant at high temperatures. When the pressure is above 50 GPa, the thermal expansion α at 1000 K is just little larger than that of 300 K, which means that the temperature dependence of α is very weak at higher temperatures and higher pressures. Our calculated value for α equals 3.729×10^{-5}/K at 235 K, which is in good agreement with the value $\alpha = 3.7\times10^{-5}$/K ($T = 235 \sim 295$ K) obtained through the powder diffraction methods.[20] These results are in agreement with the results of the Debye theory, which applies to many kinds of materials.

The Debye temperature $\Theta_{\rm D}$ is another important fundamental parameter of solids, which is closely related to specific heat, elastic constants and melting temperature. Finally, the pressure dependences of the Debye temperature $\Theta_{\rm D}$ with pressure increasing from 0 to 100 GPa are analysed and plotted in Fig.5.

At zero pressure, we found that the Debye temperature $\Theta_{\rm D} = 355$ K, this is in agreement with the Debye temperatures obtained by Yeheskel *et al* (359 K),[21] Bereznitsky *et al* (363 K)[22] and Chung *et al* (375 K).[23] It is shown that the Debye temperature $\Theta_{\rm D}$ increases with applied pressures. By fitting the data points to third-order polynomial, we obtained the following equation

$$\Theta_{\rm D} = 355.02021 + 5.26004P - 3.537\times10^{-2}P^2 + 1.34343\times10^{-4}P^3, \quad \text{for} \quad T = 300\,\text{K}. \quad (10)$$

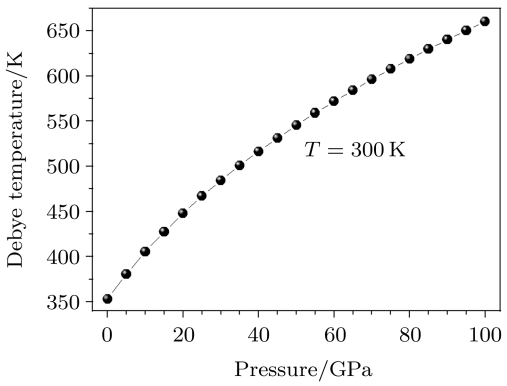


Fig.5. Relationships between the Debye temperature and pressure at 300 K.

4. Conclusions

The equilibrium structure, heat capacity C_v, thermal expansion coefficient α, bulk modulus and its pressure derivative of $LaNi_5$ alloy are investigated by using the first-principles PW-PP method as well as the quasi-harmonic Debye model. For the first time we analyse the bulk modulus of $LaNi_5$ up to 1000 K, and obtain the relationships between bulk modulus B and pressure at different temperatures. It is found that the bulk modulus B increases monotonically with the increasing pressure. The pressure dependences of heat capacity C_v and thermal expansion α at various temperatures are also analysed. Finally, the Debye temperatures of $LaNi_5$ at different pressures are successfully obtained. Our results are in excellent agreement with the experimental data. The calculation method used here seems to be available for one to investigate the elastic properties and the thermodynamic properties of solids.

References

[1] Kitagawa I, Terao K, Aoki M and Yamada H 1997 *J. Phys.: Cond. Matt.* **9** 231

[2] Cuevas F, Joubert J M, Latroche M and Percheron-Guégan A 2001 *Appl. Phys.* A **72** 225

[3] Dehouche Z, Grimard N, Laurencelle F, Goyette J and Bose T K 2005 *J. Alloys Compd.* **399** 224

[4] Chen D, Yu B H, Wang C L and Gao T 2007 *Chin. Phys.* **16** 2056

[5] Zhang X L, Huang Z, Chen B, Ma H F and Gao G Q 2007 *Acta Phys. Sin.* **56** 4039 (in Chinese)

[6] Atteberry J E, Agosta D S, Nattrass C E, Leisure R G, Jacob I, Rowman R C Jr and Yeheskel O 2004 *J. Alloys Compd.* **376** 139

[7] Segall M D, Lindan Philip J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Cond. Matt.* **14** 2717

[8] Blanco M A, Francisco E and Luaňa V 2004 *Comput. Phys. Commun.* **158** 57

[9] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[10] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892

[11] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[12] Rudin S P, Jones M D, Greeff C W and Albers R C 2002 *Phys. Rev.* B **65** 235114

[13] Wang H Y, Chen X R, Zhu W J and Cheng Y 2005 *Phys. Rev.* B **72** 172502

[14] Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1971 *Theory of Lattice Dynamics in the Harmonic Approximation* (New York: Academic)

[15] Francisco E, Recio J M and Blanco M A 2001 *Phys. Rev.* B **63** 094107
[16] Flórez M, Recio J M, Francisco E, Blanco M A and Martín Pendás A 2002 *Phys. Rev.* B **66** 144112
[17] Francisco E, Recio J M, Blanco M A and Pendás A M 1998 *J. Phys. Chem.* **102** 1595
[18] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* **30** 244
[19] Ryan C, http://www.engr.colostate.edu/ce/REU/sound/summer_2003/chris_ryan/REU_complete.htm, 2003
[20] Joubert J M, Ćrný R, Latroche M, Percheron-Guégan A and Yvon K 2005 *Intermetallics* **13** 227
[21] Yeheskel O, Nattrass C E, Leisure R G, Jacob I and Bowman R C Jr 2004 *J. Appl. Phys.* **95** 1809
[22] Bereznitsky M, Ode A, Hightower J E, Yeheskel O, Jacob I and Leisure R G 2002 *J. Appl. Phys.* **91** 5010
[23] Chung Y, Takeshita T, Mcmasters O D and Gschneidner K A Jr 1980 *J. Less-Common Metals* **74** 217