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Ab intio study of YNi_4Si under pressure

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In the framework of the density functional theory, we study conditions of formation of YNi_4Si and its electronic properties under pressure. Within the local density approximation (LDA) used in calculation, the equilibrium volume and the bulk modulus are obtained. The theoretical electronic specific heat coefficient γ (12.32 mJ/(f.u.·mol·K^2)) derived from the density of states at the Fermi energy at ambient pressure and the experimental value of γ (13 mJ/(mol·K^2)) are in a reasonable agreement.

Key words: *rare earth metals; transition metal compounds; equation of states; electronic specific heat coefficient*

1. Introduction

In recent years, interest has steadily increased in investigation of ternary compounds containing a rare earth metal and 3d transition element. These compounds may exhibit various ground state properties [1–4]. The studied compound YNi_4Si belongs to a wide class of ternary compounds with rare earth metal crystallising in the hexagonal $CaCu_5$ structure with the space group *P*6/*mmm*. In the $CaCu_5$ structure, Ni atoms occupy two kinds of crystallographic sites (2c) and (3g), the rare earth metal is located in (1a), and silicon occupies (3g).

By investigating the electronic structure of this class of materials, one can create the basis for understanding the majority of their physical properties. YNi_4Si is indeed useful as an isostructural nonmagnetic reference material. Therefore, it is important to characterise its ground state properties and to consider what happens in the electronic structure under pressure using *ab initio* method.

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2. Experimental and calculation details

The sample preparation procedure for YNi_4Si is almost the same as that for YNi_4Cu [6]. The compound was synthesized by the induction melting of stoichiometric amounts of the constituent elements in a water-cooled boat. Argon was used as a protective atmosphere. The ingot was inverted and melted several times to insure homogeneity. According to X-ray diffraction data, the crystal structure of YNi_4Si is of the hexagonal $CaCu_5$ structure with the space group *P6/mmm*. The experimental lattice constants are $a = 4.79$ Å and $c = 4.692$ Å.

The electronic structure was calculated by the spin polarised tight binding linear muffin tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [7]. The systematic errors due to the use of ASA get cancelled while determining the ground state energy differences such as formation energy as well as incorporating the so-called 'combined corrections' one can partly salvage the error due to spheridisation of potential and charge density [7, 8]. For the exchange-correlation potential, the von Barth–Hedin parameterisation [9] has been employed. The Langreth–Mehl–Hu nonlocal correction [10] was included. All total energy for above 1220 *k* points is contained in the irreducible Brillouin zone. The initial atomic configurations for each atom were taken as in the periodic table of elements. We assume for Y core(Kr) + $4d^15s^2$, for Ni: core(Ar) + $3d^84s^2$ and for Si: core(Ne) + $2s^22p^2$. The primitive cell consists of 6 atoms, where Y atom occupies (1a) site, four Ni atoms are in (2c), (3g) positions, and Si atom is in the (3g) or (2c) positions.

3. Results

Based on the self-consistent calculations, the ground state of YNi_4Si is concluded a paramagnetic one. The equilibrium lattice constants obtained by minimization procedure of the total energy of YNi_4Si are $a = 4.551$ Å, $c = 4.41$ Å, where Si atom occupied (3g) position in $CaCu_5$ structure. This result is in the acceptable range of LDA band structure calculations.

To analyze the stability of YNi_4Si, a possibility of occupation of (2c) position by Si atom was also considered in $CaCu_5$ structure. The results of the total energy calculations for YNi_4Si indicate that substitution of Ni by Si takes place in (3g) position rather than in the (2c) site. The corresponding difference in the total energy is 30.2 mRy/atom. We used the cohesive energy as an important physical quantity, expressing the strength of the force binding atoms together in the compound. Thus, it is correlative with the structural stability in the ground state. The cohesive energy per formula unit of YNi_4Si is obtained by

$$E_{\mathrm{coh}} = E(Y) + 4E(\mathrm{Ni}) + E(\mathrm{Si}) - E_{\mathrm{total}}(\mathrm{YNi_4Si}) \qquad (1)$$

where $E_{\mathrm{total}}(\mathrm{YNi_4Si})$ refers to the total energy of the intermetallic compound at equilibrium, and E(Y), E(Ni), E(Si) are the total energies of pure atomic components. The values of cohesive energy for YNi_4Si with two different positions of Si atom in the unit cell, listed in Table 1, show that the both occupations of Si are possible, but the (3g) position in $CaCu_5$ structure is more preferable.

Table 1. Equilibrium lattice parameters, cohesive energy and density of states at the Fermi energy of YNi_4Si for two possible occupations of Si atom in the unit cell

Position	3g	2c
a [Å]	4.551	4.567
c [Å]	4.410	4.425
E_{coh} [Ry/f.u.]	20.15	19.97
$N(E_F)$ [states/(Ry f.u.)]	71.21	106.14

The results of *ab initio* study allow us to predict the pressure behaviour of YNi_4Si at $T = 0$ K. We use the bulk modulus as a characteristic change in volume of a solid sample as the pressure on it is changed. The bulk modulus is defined as:

$$B_0 = -V\frac{\partial p}{\partial V} = V\frac{\partial^2 E_{\mathrm{tot}}(V)}{\partial V^2} \tag{2}$$

where p is the pressure and V is volume of the cell. The volume–energy dependence is fitted by the Murnaghan equation of state (EOS) [11]:

$$E_{\mathrm{total}}(V) = \frac{B_0 V}{B'(B'-1)}\left[\left(\frac{V_0}{V}\right)^{B'} + B'\left(1-\frac{V_0}{V}\right) - 1\right] + E_0 \tag{3}$$

Here $E_{\mathrm{total}}(V)$ is the total energy of the system at volume V, B_0 and B' are the bulk modulus and its pressure derivative at the equilibrium volume V_0, respectively. Thus, for YNi_4Si, the bulk modulus and its pressure derivative are $B_0 = 143$ GPa and $B' = 1.37$, respectively. The obtained value of B_0 for YNi_4Si is lower than that for earlier studied YNi_4B (about 162 GPa) [5] and YNi_4Cu (160 GPa) [6]. Thus, one can expect that YNi_4Si is more compressible material than isostructural YNi_4Cu and YNi_4B with $CeCo_4B$ structure. The difference between the values of the bulk moduli of YNi_4Si and earlier studied YNi_4B is connected with two features: 1) the structural differences between both compounds (the unit cell of YNi_4B contains two formula units); 2) one of constituents (B atom) in YNi_4B has the bulk modulus higher than a silicon atom. In the case of YNi_4Cu, the electronic structure and nearly filled 3d bands of Cu in particular have a significant influence on the value of compressibility.

The theoretical pressure–volume dependence for studied YNi_4Si calculated as the negative volume derivative of the total energy:

$$p = -\frac{\partial E}{\partial V} \tag{4}$$

is shown in Fig. 1. The picture of the isothermal (at $T = 0$ K) volume–pressure dependence shows that the applied hydrostatic pressure of 22.6 GPa caused the change of volume of YNi_4Si from equilibrium volume to 0.87 of its value.

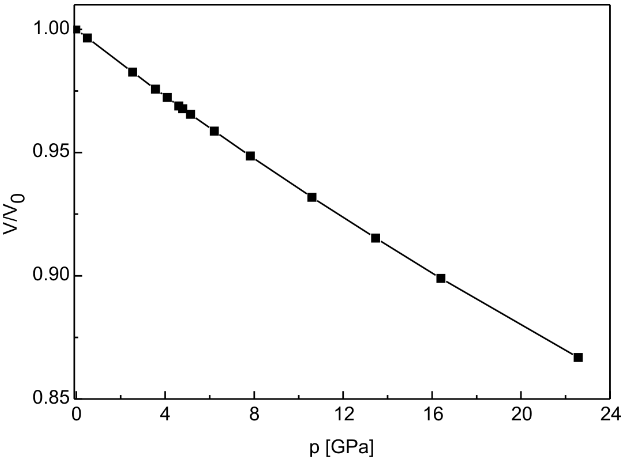

Fig. 1. Dependence of reduced atomic volume V/V_0 on pressure p for YNi_4Si

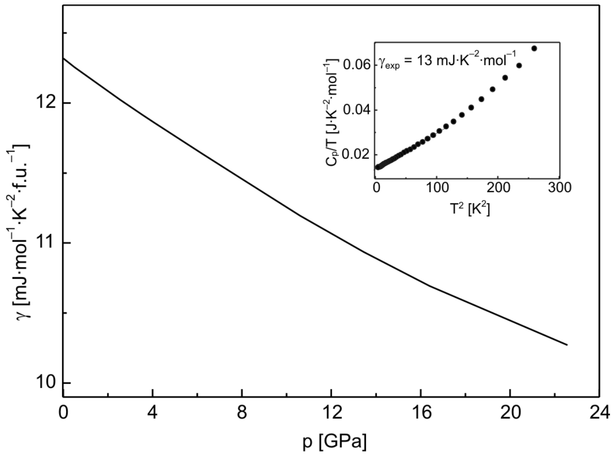

Fig. 2. The pressure dependence of the theoretical electronic specific heat coefficient γ for YNi_4Si. The inset presents the temperature dependence of the specific heat C_p

Using the results of calculations of the electronic structure, the electronic specific heat coefficient was estimated from the dependence:

$$\gamma = \frac{\pi^2 k_B^2}{3} N\left(E_F\right) \tag{5}$$

where k_B is the Boltzmann constant, $N(E_F)$ is the total electronic density of states. Dependence of the electronic specific heat coefficient on the applied hydrostatic pressure is shown in Fig. 2. The increase of pressure leads to a decrease of the density of states at the Fermi energy, implying a linear decrease of the electronic specific heat coefficient of YNi_4Si. At ambient pressure (0 GPa), the value of the electronic specific heat coefficient ($\gamma^{\text{theor}} = 12.32$ mJ/(mol·K^2)) is in a good agreement with the experimental value (γ^{exp}=13 mJ/(mol·K^2)). The experimental value of the electronic specific heat coefficient extracted from a linear fit to the low temperature part of C_p/T vs. T^2. The inset of Fig. 2 presents the low temperature dependence of the isobaric specific heat C_p. From theoretical calculations the pressure of about 22.6 GPa caused a small decrease of γ to 10.27 mJ/(mol·K^2). The obtained values of the electronic specific heat coefficient under pressure demonstrate that the paramagnetic YNi_4Si has been expected typical metallic behaviour.

4. Conclusions

We have described the pressure behaviour of YNi_4Si using the *ab initio* theoretical formalism together with the Murnaghan equation of state. The presented results reveal that the ground state of YNi_4Si is paramagnetic and the more stable is the unit cell of the compound with Si occupying (3g) position. The obtained bulk modulus B_0 of YNi_4Si suggests that the studied compound more compressible material than isostructural YNi_4Cu and YNi_4B with $CeCo_4B$ structure. Application of the pressure leads to a nearly linear decrease of the electronic specific heat coefficient of the compound. We obtained a good agreement between the theoretical (at the ambient pressure) and experimental values of the electronic specific heat coefficient. The hydrostatic pressure does not change the metallic character of YNi_4Si.

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