

Electronic Structure and Thermodynamic Properties of RNi_5Sn ($\text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) Compounds

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The electronic structure, pressure and temperature dependence of thermodynamic properties of RNi_5Sn ($\text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) compounds are calculated by *ab initio* full potential local orbital minimum-base (ver. 9 and ver. 14) method. These compounds crystallize in the hexagonal crystal structure (space group $P6_c/mmc$, No. 194). The band calculations were performed in the scalar-relativistic mode for the exchange correlation potentials in the form of the Perdew–Burke–Ernzerhof general gradient approximation. In this work we present the band structures of LaNi_5Sn , CeNi_5Sn , NdNi_5Sn and PrNi_5Sn compounds. The thermodynamic properties (bulk modulus, Debye temperature) are calculated in the Debye–Grüneisen model using the equation of states in the form of Birch–Murnaghan, Poirier–Tarantola and Vinet. Our results have shown that values of thermodynamic properties depend on the method of calculations.

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1. Introduction

The rare-earth RNi_5Sn compounds have been investigated in the recent years [1–8]. The crystal structure, magnetic and thermal properties were studied in [2–5]. These compounds were also investigated as a hydrogen storage materials. The hydrogen absorption and desorption properties of LaNi_5Sn and NdNi_5Sn were examined by Sato and Yartys [4, 5]. RNi_5Sn systems crystallize into hexagonal crystal structure (space group No. 194 ($P6_3/mmc$)). The crystal structure is presented in Fig. 1

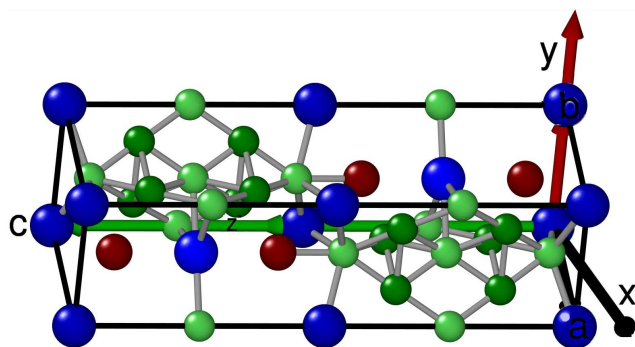


Fig. 1. The crystal structure of RNi_5Sn .

and the crystal structure parameters are listed in Table I.

The rare-earth R atoms (blue circles) are located in two different sublattices at 2c site ($1/3, 2/3, 1/4$) and 2a site ($0, 0, 0$). Nickel atoms (green circles) occupy four

sublattices: 2b site ($0, 0, 1/4$), 2d site ($1/3, 2/3, 3/4$), 4f site ($1/3, 2/3, z$) and 12k site (x, y, z). The Sn atoms (red circles) are located at 4f site ($1/3, 2/3, z$). The values of x, y and z for Ni and Sn in 4f site and Ni in 12k site are listed in Table I.

TABLE I

Crystal structure parameters for RNi_5Sn .

| Compounds RNi_5Sn | R = La [7] | R = Ce [1] | R = Pr | R = Nd |
|--------------------------------------|------------|------------|-----------|-----------|
| a [Å] | 4.95809 | 4.8845 | 4.9287 | 4.9225 |
| c [Å] | 19.9437 | 19.7026 | 19.7943 | 19.7628 |
| V [a.u.] | 2865.2451 | 2747.2046 | 2810.1671 | 2803.1015 |
| Ni3 z | 0.5437 | 0.5877 | 0.5424 | 0.5431 |
| Ni4 x | 0.8333 | 0.8338 | 0.8347 | 0.8340 |
| y | 0.6666 | 0.6676 | 0.6694 | 0.6680 |
| z | 0.1457 | 0.1455 | 0.1435 | 0.1455 |
| Sn z | 0.0863 | 0.0421 | 0.0870 | 0.0867 |

2. Method of calculations

The electronic structures of RNi_5Sn compounds were calculated by the full-potential local-orbital minimum-base (FPLO ver. 9 and 14) [9–12] method for 192 k -points in the irreducible Brillouin zone. We have performed the self-consistent band calculations in local density approximation (LDA) and exchange correlation potential was assumed in the form of Perdew, Burke and Ernzerhof (PBE) [13, 14]. The total energy versus volume was obtained in the scalar relativistic mode and the thermal properties were calculated in the Debye–Grüneisen model using the GIBBS2 code [15–18]. The band structures were computed for the values of lattice parameters listed in Table I. We have applied the different methods

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of calculation of the equation of states (EOS) (Murnaghan (murn) [19], Birch–Murnaghan (bm4 — four order) [20, 21], Poirier–Tarantola (pt5 — five order) [22], Vinet (vinet) [23, 24]. In the Debye–Grüneisen model we calculated the pressure and temperature dependence of the volume, bulk modulus B , Debye temperature θ_D and Grüneisen parameter γ . In the Debye–Grüneisen model the Debye temperature is determined by the Grüneisen parameter γ , and hence [16],

$$\gamma = -1/6 + 0.5dB_{\text{stat}}/dp,$$

$$\theta_D(V) = \theta_D(V_0)(B_{\text{sta}}/B_0)^b/(V/V_0)^a,$$

where V_0 , B_0 , B_{stat} are the static equilibrium volume, bulk modulus and static bulk modulus, respectively. In the Dugdale–McDonald approximation $a = -0.5$ and $b = 0.5$. The results are presented in Table II.

TABLE II

The values of bulk modulus (B) and Debye temperature (θ_D) and static equilibrium volume V_0 for RNi_5Sn ($R = \text{La, Ce, Nd, Pr}$) for the different models of EOS.

| R = La | bm4 | pt5 | vinet | murn |
|----------------|-----------|-----------|-----------|-----------|
| B [GPa] | 38.505 | 38.505 | 38.277 | 37.204 |
| θ_D [K] | 275.72 | 275.74 | 274.91 | 271.04 |
| V_0 [a.u.] | 2883.7461 | 2884.8197 | 2883.9728 | 2885.2343 |
| R = Ce | bm4 | pt5 | vinet | murn |
| B [GPa] | 37.411 | 37.985 | 38.100 | 35.935 |
| θ_D [K] | 270.44 | 272.47 | 272.93 | 265.04 |
| V_0 [a.u.] | 2818.4269 | 2816.0871 | 2819.1602 | 2817.5813 |
| R = Pr | bm4 | pt5 | vinet | murn |
| B [GPa] | 41.643 | 41.818 | 41.767 | 40.573 |
| θ_D [K] | 284.46 | 285.05 | 284.89 | 280.77 |
| V_0 [a.u.] | 2779.4321 | 2778.9075 | 2779.5723 | 2778.4403 |
| R = Nd | bm4 | pt5 | vinet | murn |
| B [GPa] | 40.748 | 39.913 | 41.398 | 40.278 |
| θ_D [K] | 280.17 | 277.32 | 282.42 | 278.54 |
| V_0 [a.u.] | 2757.1691 | 2759.1197 | 2758.3926 | 2756.4848 |

3. Results and discussion

The total densities of states (DOS) is presented in Fig. 2. The broad peaks below the Fermi level give the contribution from nickel atoms. Above the Fermi level we observe the peaks due to rare-earth R atoms. In the case of $R = \text{Pr}$ and Nd the Fermi level is located at large peak of $4f$ electrons. The values of densities of states at the Fermi level are 77.02, 53.77, 153.41, and 258.03 states/eV for $R = \text{La, Ce, Pr}$ and Nd , respectively. In Fig. 2 we plotted the dependence of the total energy versus volume. In Table II we listed the values of bulk modulus B (GPa), Debye temperature θ_D (K) and equilibrium volume V_0 obtained from the different models of equation of states (bm4, pt5, vinet and murn). The values in Table II indicate that different approximation for the EOS give the different values of bulk modulus and Debye temperatures. In Fig. 4 we plotted the dependence of specific

heat versus temperature for CeNi_5Sn . For all models this dependence is similar. Results presented in Fig. 4 are similar to the experimental results obtained for CeNi_5In by Rojas et al. (Fig. 2 in [6]).

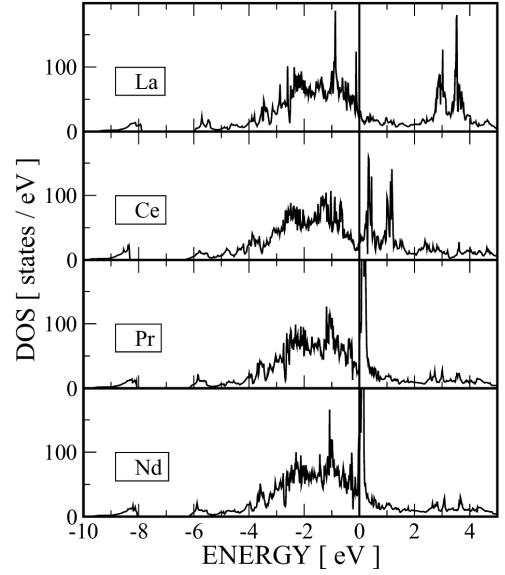


Fig. 2. Total density of states for RNi_5Sn ($R = \text{La, Ce, Pr, Nd}$).

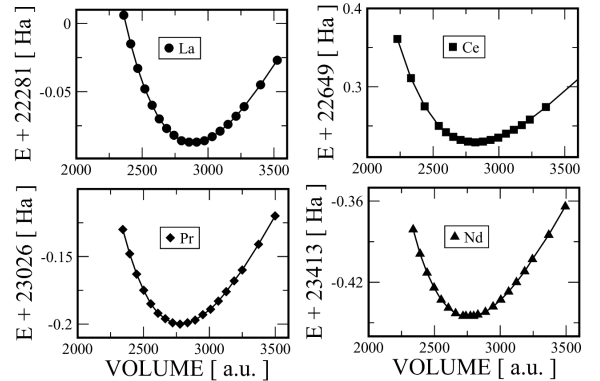


Fig. 3. The dependence of the total energy vs. volume for RNi_5Sn ($R = \text{La, Ce, Pr, Nd}$).

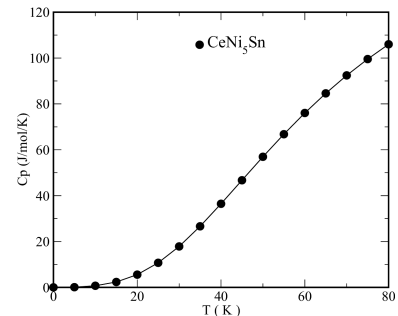


Fig. 4. Specific heat vs. temperature for CeNi_5Sn .

4. Conclusions

We have calculated the band structure and thermodynamic properties of RNi_5Sn compounds using the FPLO and GIBBS2 methods. The equation of states was assumed in the different forms. Our results indicate that the values of bulk modulus, Debye temperature and static equilibrium volume depend on the method of calculations, although the differences are small. We have also shown that the Debye–Grüneisen model gives the dependence of the specific heat versus temperature for $CeNi_5Sn$ similar to $CeNi_5In$ [6].

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