The Electronic Structure
and Specific Heat of YNi$_4$Si

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The studies of the electronic structure and the specific heat of YNi$_4$Si are reported. Below the Fermi energy ($E_F$) the density of states contains mainly the 3$d$ states of Ni, which hybridized with 4$d$ states of Y and 3$p$ states of Si. The theoretical electronic specific heat coefficient (12.32 mJ/(mol K$^2$)) obtained for equilibrium lattice parameters and the experimental value (13 mJ/(mol K$^2$)) are in a reasonable agreement.

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1. Introduction

In recent years ternary compounds RNi$_4$Si, containing the rare-earth metal (R), have been intensively studied [1–3]. These compounds have a variety of interesting properties such as a mixed-valence state of the Ce ion, a Kondo-like resistivity impurity in CeNi$_4$Si as well as a strong Mott-type scattering in resistance in YbNi$_4$Si [2, 3]. From the electronic structure point of view these compounds are of special interest due to the nearly filled Ni(3$d$) band implying that the Ni magnetic moment is negligible [1]. The YNi$_4$Si compound is indeed useful considered as the isostructural non-magnetic reference material. Therefore, it is important to characterize its ground-state properties such as electronic structure from \textit{ab initio} method and specific-heat experiments, which give information on magnetic properties and energy level distribution. The YNi$_4$Si belongs to a wide
class of compounds which crystallise in the hexagonal CaCu$_5$ structure (space group $P6/mmm$). In the CaCu$_5$ structure the Ni atoms occupy the crystallographic sites (2c) and (3g), while the rare-earth atoms are located in (1a) and Si atoms occupy (3g) sites.

2. Experimental details and calculation method

The electronic structure was calculated by using the tight-binding linear muffin-tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [4]. Details of calculation were the same as that for CeNi$_4$Si [1]. The sample preparation procedure for YNi$_4$Si is similar to that for CeNi$_4$Si [1]. The lattice constants are $a = 4.79$ Å and $c = 4.692$ Å (YNi$_4$Si). Specific heat measurements were performed by PPMS commercial device (Quantum Design) in the temperature range 4–300 K by relaxation method using two-$\tau$ model. The error of the measurement was about 2%.

3. Results

The electronic structure calculations for YNi$_4$Si have shown that its ground state is paramagnetic. The calculated densities of states (DOS) are shown in Fig. 1a. The DOS reflects a large separation of the low-lying bands and the main part of DOS (from $-0.497$ Ry to $E_F$) with respect to the corresponding band widths. Si 3$s$ band is located deeply at the lower part of DOS [$-0.73$ Ry; $-0.58$ Ry] below the $E_F$. In the upper part of the DOS (above $-0.497$ Ry) 3$d$

![Fig. 1](image-url)
Ni states overlap with 4d Y states. The hybridization of Si 3p, Y 4d and Ni 3d levels results in continuous DOS from the energy of ~0.5 Ry to the Fermi energy. The band structure of YNi$_4$Si along selected high-symmetry lines within the first Brillouin zone (BZ) is shown in Fig. 1b. The shape of the lowest band is strikingly similar to that of CeNi$_4$Si [1]. The bottom of the lowest band of YNi$_4$Si, which consists entirely Si 3s states, has the parabolic shape around the $\Gamma$ point of high symmetry in the $\Gamma-A$, $\Gamma-M$, $\Gamma-K$ direction (below ~0.7 Ry) as well as in the $A-H$ direction (below ~0.65 Ry). The group of bands formed between ~0.5 Ry and the $E_F$ is mainly dominated by Ni 3d states mixed with Si 3p states. $E_F$ is crossed in all main directions of the first BZ by the bands. The $K$, $L$, $\Gamma$, $M$ points of high symmetry bands do not cross $E_F$. The DOS at $E_F$ is 85.55 [st./(Ry f.u.)] for YNi$_4$Si. The electronic specific heat coefficient can be estimated from band calculations by using the relation:

$$\gamma = \frac{1}{3} \pi^2 k_B^2 N(E_F)$$

and is equal to 14.8 mJ/(mol K$^2$).

The electronic specific heat of YNi$_4$Si, plotted as $C_p/T$ versus $T^2$.

The temperature dependence of heat capacity $C_p$ measured for YNi$_4$Si is presented in Fig. 2. The total heat capacity consists of two contributions: the electronic specific heat $C_{el}$ characterized by the Sommerfeld coefficient $\gamma$ and the phonon contribution $C_{ph}$ which can be expressed as:

$$C_p = C_{el} + C_{ph} = \gamma T + \beta T^3.$$  

The Debye temperature is estimated using the relation:

$$\Theta_D = \left( \frac{12 \pi^4 R n}{5 \beta} \right)^{\frac{1}{3}},$$

where $n$ is a number of atom in the unit cell, $R$ is the gas constant. The experimental values are: $\gamma = 13$ mJ/(mol K$^2$); $\Theta_D = 388$ K. The value of $\gamma$ obtained from electronic structure for experimental lattice parameters is somewhat higher than the experimental $\gamma$. However, minimization procedure of the total energy
of YNi$_4$Si gives the equilibrium lattice constants of $a = 4.551$ Å, $c = 4.41$ Å and value of $\gamma = 12.32$ mJ/(mol K$^2$). Thus, the experimental value and the theoretical value of the electronic specific heat coefficient obtained at equilibrium lattice parameters are in good agreement. Moreover, the theoretical values of $\gamma$ obtained for YNi$_4$Si in this work are close to the value of 11.33 mJ/(mol K$^2$) determined for YNi$_4$B [6] and 13.42 mJ/(mol K$^2$) determined for YNi$_4$Cu [5].

4. Conclusions

*Ab initio* calculation has shown that the YNi$_4$Si is paramagnetic. Below the $E_F$ the total DOS contained mainly Ni 3$d$ states in (2c) and (3g) positions hybridized with Y 4$d$ states and Si 3$p$ states which formed the main part of the valence band. The theoretical electronic specific heat coefficient is in good agreement with that obtained from experiments.

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References


