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The Electronic Structure and Specific Heat of YNi_4Si

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The studies of the electronic structure and the specific heat of YNi_4Si are reported. Below the Fermi energy (E_F) the density of states contains mainly the $3d$ states of Ni, which hybridized with $4d$ states of Y and $3p$ 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_4Si, 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 $CeNi_4Si$ as well as a strong Mott-type scattering in resistance in $YbNi_4Si$ [2, 3]. From the electronic structure point of view these compounds are of special interest due to the nearly filled Ni($3d$) band implying that the Ni magnetic moment is negligible [1]. The YNi_4Si 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 *ab initio* method and specific-heat experiments, which give information on magnetic properties and energy level distribution. The YNi_4Si 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 $CeNi_4Si$ [1]. The sample preparation procedure for YNi_4Si is similar to that for $CeNi_4Si$ [1]. The lattice constants are $a = 4.79$ Å and $c = 4.692$ Å (YNi_4Si). Specific heat measurements were performed by PPMS commercial device (Quantum Design) in the temperature range 4–300 K by relaxation method using two-τ model. The error of the measurement was about 2%.

3. Results

The electronic structure calculations for YNi_4Si 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 $3s$ 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) $3d$

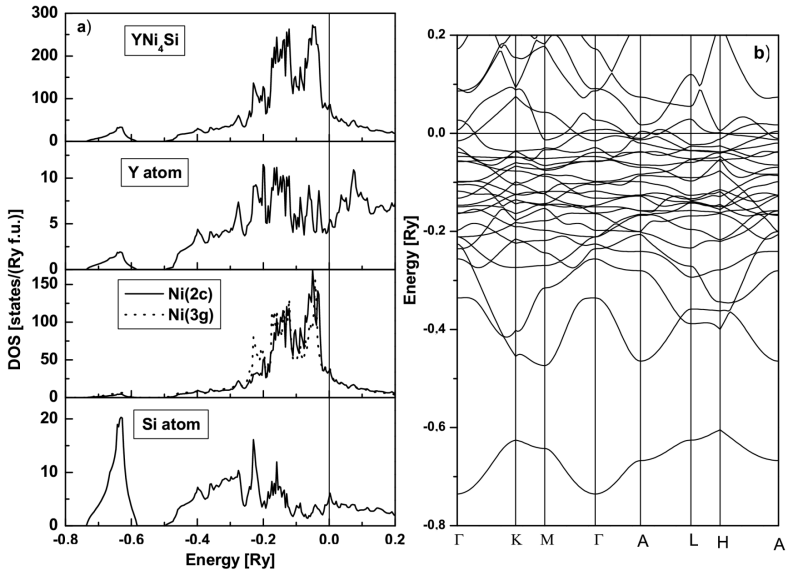

Fig. 1. (a) The calculated DOS for YNi_4Si: the total DOS; the contribution of Y; the contribution of Ni(2c) and Ni(3g); the contribution of Si. (b) The band structure of YNi_4Si along the high symmetry directions.

Ni states overlap with 4*d* Y states. The hybridization of Si 3*p*, Y 4*d* and Ni 3*d* levels results in continuous DOS from the energy of –0.5 Ry to the Fermi energy. The band structure of YNi_4Si 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 $CeNi_4Si$ [1]. The bottom of the lowest band of YNi_4Si, which consists entirely Si 3*s* states, has the parabolic shape around the Γ 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 3*d* states mixed with Si 3*p* states. E_{F} is crossed in all main directions of the first BZ by the bands. The K, L, Γ, 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_4Si. The electronic specific heat coefficient can be estimated from band calculations by using the relation:

$$\gamma = \frac{1}{3}\pi^2 k_{\mathrm{B}}^2 N(E_{\mathrm{F}}) \tag{1}$$

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

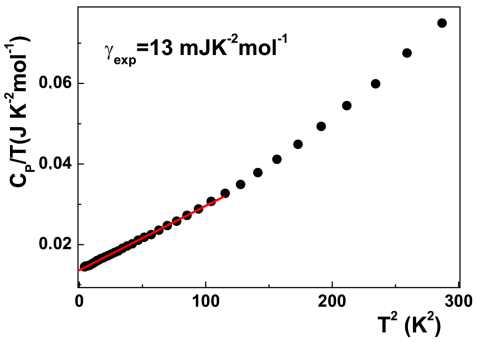

Fig. 2. Specific heat of YNi_4Si, plotted as C_p/T versus T^2.

The temperature dependence of heat capacity C_p measured for YNi_4Si is presented in Fig. 2. The total heat capacity consists of two contributions: the electronic specific heat C_{el} characterized by the Sommerfield coefficient γ and the phonon contribution C_{ph} which can be expressed as:

$$C_p = C_{\mathrm{el}} + C_{\mathrm{ph}} = \gamma T + \beta T^3. \tag{2}$$

The Debye temperature is estimated using the relation:

$$\Theta_{\mathrm{D}} = \left(\frac{12\pi^4 Rn}{5\beta}\right)^{\frac{1}{3}}, \tag{3}$$

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); $\Theta_{\mathrm{D}} = 388$ K. The value of γ obtained from electronic structure for experimental lattice parameters is somewhat higher than the experimental γ. However, minimization procedure of the total energy

of YNi_4Si 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 γ obtained for YNi_4Si in this work are close to the value of 11.33 mJ/(mol K^2) determined for YNi_4B [6] and 13.42 mJ/(mol K^2) determined for YNi_4Cu [5].

4. Conclusions

Ab initio calculation has shown that the YNi_4Si 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.

Acknowledgments

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References

[1] A. Kowalczyk, M. Falkowski, V.H. Tran, M. Pugaczowa-Michalska, *J. Alloys Comp.* **440**, 13 (2007).

[2] A. Kowalczyk, M. Falkowski, T. Toliński, G. Chełkowska, *Solid State Commun.* **139**, 5 (2006).

[3] A. Kowalczyk, M. Falkowski, T. Toliński, V.H. Tran, W. Miiller, M. Reiffers, M. Timko, *Mater. Res. Bull.* **43**, 185 (2008).

[4] O.K. Andersen, O. Jepsen, M. Sob, in: *Electronic Structure and Its Applications*, Ed. M.S. Yussouff, Springer, Berlin 1987, p. 2.

[5] M. Pugaczowa-Michalska, G. Chełkowska, A. Kowalczyk, *Acta Phys. Pol. A* **104**, 487 (2003).

[6] T. Toliński, M. Pugaczowa-Michalska, G. Chełkowska, A. Kowalczyk, *J. Electron. Spectrosc. Relat. Phenom.* **151**, 1 (2006).