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Specific Heat Study of $PrNi_4Si$

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Here we present the results of pilot polycrystalline study of $PrNi_4Si$. The X-ray study did not confirm the expected $CaCu_5$-type structure. Instead of this, the orthorhombic structure with the space group *Cmmm* was found. The zero-field specific heat was measured in the temperature range 2–300 K. The data were analyzed using the sum of the phonon, electronic, and magnetic contributions to specific heat, respectively. The magnetic part of the specific heat can be well described using the Schottky formula for the 9 crystal-field singlet levels of the $^3H_4$ ground-state multiplet of the Pr^{3+} ion.

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1. Introduction

Intermetallic compound $PrNi_4Si$ represents one of possible substitution compounds of $PrNi_5$. It was expected that Si ion randomly occupies the Ni positions of the $PrNi_5$ structure. To our best knowledge, this compound was not studied up till now. The parent compound $PrNi_5$ crystallizes in the hexagonal structure of the $CaCu_5$-type structure [1]. The aim of this study was to continue the specific heat analysis of the $RENi_5$ series (RE = rare earth) and their substituents [2] as a pilot study of Si substitution and its influence on magnetic properties of $PrNi_5$.

2. Experimental

The polycrystalline sample was prepared by arc-melting of stoichiometric composition of pure elemental constituents (Pr — 3N5, Ni — 4N and Si — 5N), the sample was several times turned and re-melted to ensure good homogeneity. Part of the sample was pulverized for X-ray identification. Surprisingly, the expected $CaCu_5$-type structure was not confirmed, instead of this an ordered orthorhombic structure has been found.

Diffraction pattern was indexed within a orthorhombic lattice using DicVol04 [3]. An analogous compound $LaNi_4Si$ was reported [4] to crystallize in an orthorhombic structure as well, but no details of crystal structure has been given.

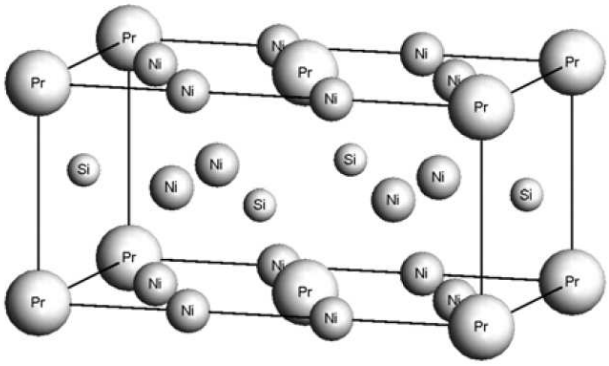

Fig. 1. Crystal structure of $PrNi_4Si$.

TABLE I

Details of crystal structure of $PrNi_4Si$.

Atom	$Cmmm$ (65)	$a = 5.136(1)$ Å	$b = 8.339(1)$ Å	$c = 3.976(1)$ Å
Pr	2a	0	0	0
Ni	4f	1/4	1/4	1/2
Ni	4i	0	0.338(2)	0
Si	2c	1/2	0	1/2

The space group $Cmmm$ was determined using systematic extinction rules from indexed diffraction pattern. The crystal structure (see Fig. 1) has been solved by means of Le Bail et al. procedure [5], Patterson map and differential Fourier maps in WinPlotR/FullProf software [6]; the details of the structure are summarized in Table I.

About 10 mg of the polycrystalline $PrNi_4Si$ was used for the specific heat study. The zero-field specific heat was measured using the PPMS apparatus (Quantum Design) in the temperature range 2–300 K by relaxation method. No indication of magnetic ordering was found on the specific heat data.

3. Results and discussion

The zero-field low-temperature specific heat has been analyzed as a sum of the phonon, electronic, and magnetic contributions, respectively. The electronic specific heat expected in the form $C_\mathrm{e} = \gamma T$ yields the γ-coefficient $\gamma = 7$ mJ/(mol K^2).

For the analysis of the phonon part, we use the approach described e.g. in [2], i.e. the sum of acoustic and optical parts, respectively. The phonon spectrum in $PrNi_4Si$ consists of 18 branches, 3 acoustic and 15 optical ones, all of them corrected for anharmonicity. The three acoustic and the 15 optical branches are described by the Debye term C_D and the Einstein approximation C_E, respectively.

$$C_{\rm ph} = R\left(\frac{9C_{\rm D}}{1-\alpha_{\rm D}T} + \sum_{i=1}^{15}\frac{C_{{\rm E}i}}{1-\alpha_{{\rm E}i}T}\right), \tag{1}$$

where R is a gas constant. The analysis yields the characteristic temperatures $\theta_{\rm D}$ and $\theta_{\rm E}$ and corresponding anharmonicity coefficients $\alpha_{\rm D}$ and $\alpha_{\rm E}$, respectively. To reduce the number of adjustable parameters, several optical branches were grouped into the degenerated one. The best grouping scheme and values of the fitted parameters are summarized in Table II.

TABLE II

Results of the phonon specific heat analysis, n denotes the degeneracy of Debye (D) and Einstein (E) branches, respectively.

Branch	n	θ [K]	α [10^{-4} K^{-1}]
D	3	176 ± 2	0.3 ± 0.1
E1	5	187 ± 2	0.7 ± 0.2
E2	6	312 ± 2	0.4 ± 0.1
E3	2	965 ± 5	0.4 ± 0.1
E4	2	1850 ± 10	0.2 ± 0.1

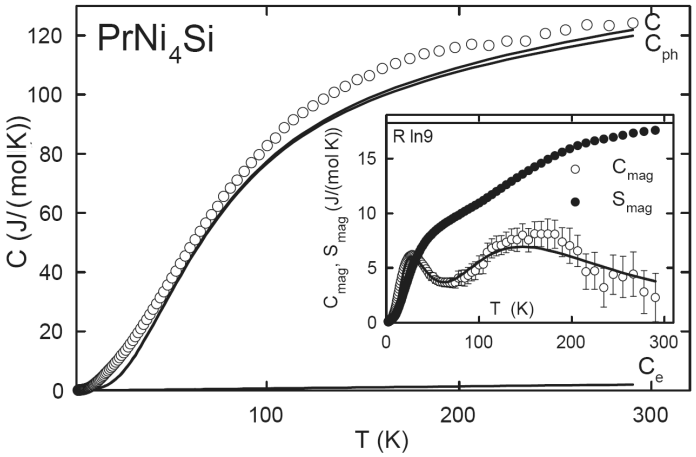

Fig. 2. Specific heat of $PrNi_4Si$ in comparison with the best fit of nonmagnetic, phonon and electronic parts. The inset shows the magnetic part of specific heat and the resulting magnetic entropy.

To obtain the magnetic specific heat, the nonmagnetic fit was subtracted from the measured data. This enabled us to fit the magnetic part to the Schottky

formula [2] because the orthorhombic crystal field splits the $^3H_4$ ground-state multiplet of the Pr^{3+} ion into 9 singlets. Taking the distances Δ_i of the 8 excited levels in K, the best fit yields Δ_i = 61, 87, 441, 444, 452, 460, 461, and 475 K, respectively.

As we were not able to prepare the non-magnetic analogue yet, this level scheme strongly depends on the validity of the phonon and electronic fit and the error of the individual levels may reach up to 10%.

Simultaneously, the magnetic entropy S_{mag} was calculated from the magnetic specific heat C_{mag}, numerically integrating C_{mag}/T (see inset in Fig. 2). As can be seen, the value of S_{mag} approaches the limit $R \ln 9$ at room temperature, which is in agreement with the maximum entropy value of the 9-level scheme. We have to stress out that this paper represents just the pilot study aimed mainly on the details of crystalline structure. In the next future we plan to grow a single crystal and to prepare an isostructural nonmagnetic analogue to obtain more reliable data. Such work is now in progress.

Acknowledgments

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