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Crystal structure and magnetic properties of the compound $CeNi_5Si$

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Abstract

The crystallographic structure of the compound $CeNi_5Si$ was studied by means of high-resolution neutron diffraction. The refinement results of the neutron powder diffraction pattern show that this compound crystallises in the hexagonal $TbCu_7$ type structure and that there is a distinct preference for the Si atoms to occupy the 3g site.

Keywords: Ternary rare earth nickel silicides; Cerium nickel silicides; Crystal structure; Magnetic susceptibility

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1. Introduction

The present investigation is a continuation of previous studies in which we have studied the preferential site occupation in rare earth based intermetallic compounds having a crystal structure in which more than one crystallographic site is available for the non-rare earth components [1–5]. Recent examples of such studies have dealt with the $TbCu_7$ structure type [6]. This structure type is a derivative of the $CaCu_5$ structure type and can be visualised as $TbCu_5$ in which part of the Tb sites are occupied by dumb bell pairs of Cu atoms [7]. Using high-resolution neutron diffraction we showed that the compounds $CeNi_4Cu_2$ and $CeNi_3Cu_3$ crystallise in the $TbCu_7$ structure, and that the Cu and Ni atoms are not statistically distributed over the three available sites but that there is a distinct preference of the Ni atoms to occupy the dumb bell sites. In the present investigation we have extended this investigation with $CeNi_5Si$ in order to obtain more experimental information on the origin of the preferred site occupancy in these materials.

2. Experimental

The $CeNi_5Si$ compound was prepared by arc melting from starting materials of at least 99.9% purity. After arc melting the sample was wrapped into Ta foil, sealed into an evacuated quartz tube and annealed for 3 weeks at 1050°C. After annealing the sample was quenched to room temperature by breaking the quartz ampoules in water. The X-ray diffraction diagram showed that the annealed sample is approximately single phase, its diffraction pattern corresponding to the hexagonal $TbCu_7$ structure type.

Neutron powder-diffraction experiments were performed at 295 K on the POLARIS high intensity powder diffractometer at the ISIS spallation neutron source [8]. Data were collected in the backscattering mode ($2\Theta=145°$) over the entire 20 ms time frame between ISIS pulses, providing a range of accessed d-spacings from 0.4 to 3 Å. The instrumental resolution, $\Delta d/d=0.005$, is constant over this range.

The magnetic properties were studied on a SQUID magnetometer in the temperature range 5–350 K. The magnetic susceptibility shows only a modest temperature dependence. At room temperature we find $\chi=2\times10^{-8}$ $m^3\ mol^{-1}$. Around 225 K there is a broad maximum and at low temperatures we find an upturn to $4.3\times10^{-8}\ m^3\ mol^{-1}$ at the lowest temperature measured. The latter feature is probably due to impurities.

3. Neutron-diffraction data analysis

The diffraction data collected for the $CeNi_5Si$ compound on the POLARIS diffractometer was analysed by the Rietveld technique [9], using the program TF15LS based on the Cambridge Crystallography Subroutine Library, CCSL [10]. This program is one that least-squares refines time-of-flight neutron powder diffraction data. It is based on a peak-shape function that is a convolution of a

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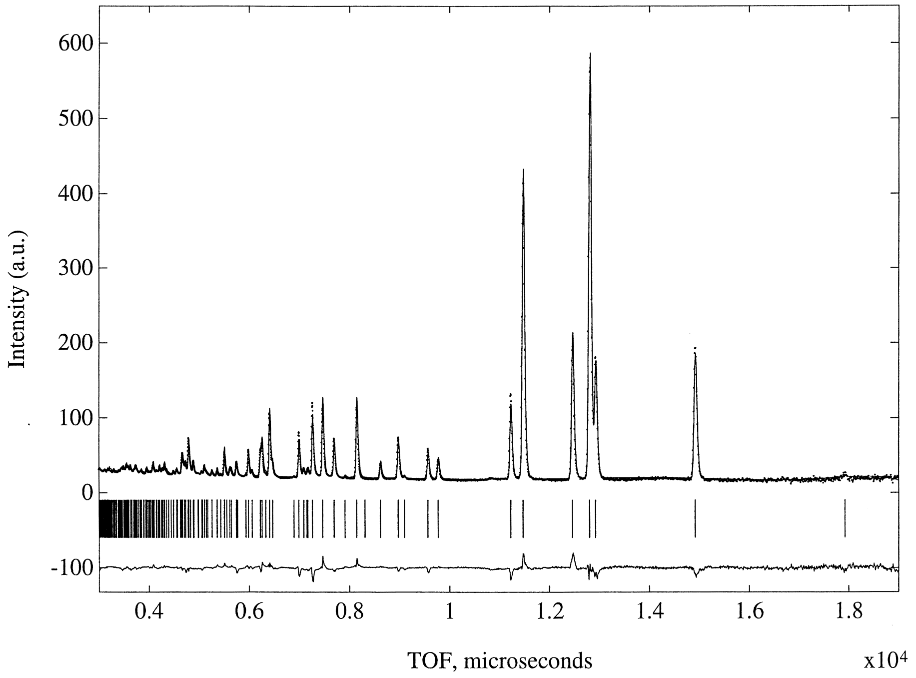

Fig. 1. Observed and calculated neutron diffraction pattern at 293 K for $CeNi_5Si$.

modified Ikeda–Carpenter lineshape and a Voigt function [11]. The appropriate nuclear scattering lengths employed in the refinement ($b_{Ce}=0.484\times10^{-12}$, $b_{Si}=0.4149\times10^{-12}$ and $b_{Ni}=1.03\times10^{-12}$ cm) were taken from the most up-to-date tabulation available [12].

The hexagonal $TbCu_7$ type (space group *P*6/*mmm*) was used as trial structure, with the assumption of a statistical distribution of the Si and Ni atoms over the 2c, 3g and 2e sites. The origin of the unit cell was chosen at the Ce position 1a (0, 0, 0). Consequently, only the following parameters were refined: unit cell constants, individual isotropic temperature factors for all sites, atomic position parameters and relative site populations of Si and Ni over the three sites, a scale factor, and peak profile and background parameters. As in our previous investigation we have excluded the possibility that 1a sites and adjacent 2e sites are simultaneously occupied by Ce atoms and dumb bell pair atoms, respectively. When taking account of the different multiplicities of both sites this leads to the constraint that the sum of the occupancies of the 1a and 2e sites must be equal to unity.

The observed and calculated diffraction pattern for the $CeNi_5Si$ compound is displayed in Fig. 1. The corresponding range in *d*-spacing for this pattern is approximately 0.5–2.9. The access to relatively small *d*-spacings implies a particularly accurate assessment of the thermal parameters.

4. Discussion

The refined structural and thermal parameters and the *R* factors for the $CeNi_5Si$ compound are listed in Table 1. It can be inferred from the data listed that the Si atoms occupy exclusively the 3g sites and completely avoid the 2c sites as well as the 2e or dumb bell sites. Bearing the structural relationship between $CeNi_5$ ($CaCu_5$-type) and Ce_2Ni_{17} (Th_2Zn_{17}-type) in mind, this result is in concord

Table 1
Refined parameters for the compound $CeNi_5Si$, space group *P*6/*mmm*, lattice constants: $a=4.83995(8)$ Å, $c=4.04093(1)$ Å

Atom	Position	*x*	*y*	*z*	Occupancy	Temp. Factor
Ce	1a	0.0000	0.0000	0.0000	0.88(4)	1.32(1)
Ni	2c	0.3333	0.6667	0.0000	1.00(1)	1.46(5)
Si	2c				0.00(1)	
Ni	3g	0.5000	0.0000	0.5000	0.68(1)	0.80(5)
Si	3g				0.32(1)	
Ni	2e	0.0000	0.000	0.3084	0.12(4)	1.16(5)
Si	2e				0.00(4)	

$R_{wp}=4.91\%$, $R_{exp}=1.21\%$, $\chi^2=16.46$.

with the observation that the Si atoms in $Ce_2Ni_{17-x}Si_x$ occupy exclusively the 9d site [13].

The results of the refinements reported previously for $Ce(Ni,Cu)_6$ compounds have shown that there is a strong preference of the Ni atoms to occupy the dumb bell sites and also a distinct preference for the Cu atoms to occupy the 2c sites [6]. This has led to the hypothesis that the dumb bell site occupation is size-controlled in the sense that the dumb bell site is preferentially occupied by the smaller type of non-rare earth atoms. The present results refute this hypothesis because they show that the dumb bell site is completely avoided by the Si atoms although these atoms are much smaller than the Ni atoms.

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