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Crystal structure and magnetic properties of $CeNi_{11-x}Si_x$ compounds

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Abstract

We have studied the crystallographic and magnetic properties of $CeNi_{11-x}Si_x$ compounds for $x = 2$ and $x = 2.5$. Both compounds have a structure that is derived from the tetragonal $BaCd_{11}$ structure. For the compound $CeNi_9Si_2$ we have studied the preferred site occupancies of Si and Ni in more detail by time-of-flight neutron diffraction at room temperature. A strong site preference of the Si atoms for the crystallographic 8d position was observed. From magnetic measurements it is derived that the Ce atoms in both compounds are close to tetravalent.

Keywords: Cerium nickel silicides; Crystal structure; Neutron diffraction; Magnetic properties; Ce valence

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1. Introduction

Cerium atoms frequently give rise to an unstable 4f-shell. In many intermetallic compounds this leads to anomalies in the temperature dependence of the magnetic susceptibility and the electrical transport properties. There are strong indications that the stability of the 4f-shell of Ce depends strongly on the extent to which the Ce electron states hybridise with the electron states of the surrounding atoms. For this reason the physical properties mentioned depend not only on the nature of the various elements with which Ce is combined in a given crystal structure but also on the crystal structure itself and on the extent to which the Ce atoms are surrounded by atoms of the composing elements. In the present investigation we have extended previous structural and magnetic investigations of ternary Ce compounds [1,2] to compounds of the tetragonal $BaCd_{11}$ structure type.

2. Experimental details

Samples of compounds with the nominal composition $Ce_2Ni_{17}Si_5$ and $CeNi_9Si_2$ were prepared by arc melting starting materials of at least 99.9% purity. Subsequently the samples were wrapped in Ta foil, sealed into an evacuated quartz tube and annealed for 4 weeks at 900°C. The X-ray diffraction diagrams showed that the annealed samples were approximately single phase and that their crystal structure corresponds to the tetragonal $BaCd_{11}$ structure type reported earlier by Bodak [3].

Neutron powder-diffraction experiments were performed for $CeNi_9Si_2$ and $Ce_2Ni_{17}Si_5$ on the POLARIS high intensity powder diffractometer at the ISIS spallation neutron source [4]. 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 diffraction data were collected at 295 K, at which temperature virtually only nuclear scattering is present, because it follows from magnetic measurements made on $CeNi_9Si_2$ that magnetic ordering is absent, even at 5 K (see below).

The magnetic measurements were made on a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 6 T.

3. Neutron-diffraction data analysis

The diffraction data collected on the POLARIS diffractometer were all analysed by the Rietveld

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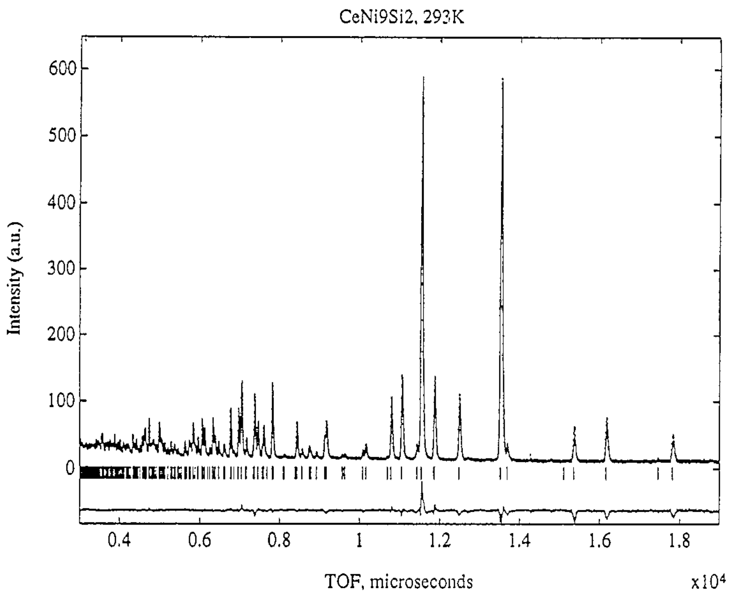

Fig. 1. Observed, calculated and difference neutron time-of-flight diffraction pattern of the compound $CeNi_9Si_2$ at 295 K. The vertical bars indicate calculated peak positions. The difference pattern has been divided by estimated standard deviations (EDSs).

technique [5], using the program TF15LS based on the Cambridge Crystallography Subroutine Library, CCSL [6]. 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 modified Ikeda–Carpenter lineshape and a Voigt function [7]. The appropriate nuclear scattering lengths employed in the refinement ($b_{Ce} = 0.484 \times 10^{-12}$ cm, $b_{Ni} = 1.03 \times 10^{-12}$ cm, $b_{Si} = 0.4149 \times 10^{-12}$ cm) were taken from the most up-to-date tabulation available [8]. The tetragonal $BaCd_{11}$ structure (space group *I41/amd*) was used as trial structure, with the assumption of a statistical distribution of the Si and Ni atoms over the 8d, 32i and 4b sites, and the additional constraint that the overall composition be fixed by the nominal composition. The origin of the unit cell was shifted in a way that the Ce position is at 4a (0, 0.750, 0.125). Consequently, only the following parameters were refined: unit cell constants, individual isotropic temperature factors for all sites, relative site populations of Si and Ni on the sites 8d, 32i and 4b, a scale factor, and peak profile and background parameters. A total of 732 overlapping and independent reflections were analysed.

4. Experimental results and discussion

The observed and calculated diffraction patterns for $CeNi_9Si_2$ are displayed in Fig.1. The corresponding ranges in *d*-spacing for these two patterns are approximately 0.5–1.5 and 1.5–2.9 respectively. The access to relatively small *d*-spacings implies a particularly accurate assessment of the thermal parameters.

The refined structural, thermal and *R* factors of $CeNi_9Si_2$ are listed in Table 1. It follows from these data that there is a very strong preference for the Si atoms to occupy the 8d site. These results confirm conclusions reached earlier by means of X-ray diffraction [3], showing that $CeNi_9Si_2$ can actually be classified as a true ternary compound.

The neutron data for $Ce_2Ni_{17}Si_5$ (or $CeNi_{8.5}Si_{2.5}$) was also refined in the same space group, but with less success than the corresponding $CeNi_9Si_2$ compound. The refined lattice parameters are $a = 0.979159(2)$ nm and $c = 0.623581(2)$ nm. The presence of a second phase, as well as a significant line broadening of peaks, made the refinement less stable than for the $CeNi_9Si_2$ compound. The final χ^2 value was 13.0 with the Si atoms fully occupying the 8d site but with some

Table 1
Site occupation and atomic position parameters and temperature factors of the compound $CeNi_9Si_2$; *I41/amd* No. 140; $a = 0.98116(1)$ nm, $c = 0.62130(1)$ nm; $R_{wp} = 6.86\%$, $R_{exp} = 2.37\%$; $\chi^2 = 8.36$

Site	Atom	*x/a*	*y/a*	*z/c*	*B* (Å)	Occupancy
4a	Ce	0.00000	0.75000	0.12500	0.65(5)	1.00
4b	Ni	0.00000	0.25000	0.37500	0.50(3)	0.92(1)
	Si	0.00000	0.25000	0.37500	0.50(3)	0.08(1)
32i	Ni	0.12364(7)	0.04645(7)	0.18670(4)	0.51(4)	1.00(1)
	Si	0.12364(7)	0.04645(7)	0.18670(4)	0.51(4)	0.00(1)
8d	Ni	0.00000	0.00000	0.50000	0.38(3)	0.00(1)
	Si	0.00000	0.00000	0.50000	0.38(3)	1.00(1)

additional disorder on the 32i sites. However, given the instability of the refinement for this compound, probably not much significance can be attached to these figures.

Results of magnetic measurements are shown in Figs. 2 and 3. It may be seen from Fig. 2 that the magnetic susceptibility of both compounds decreases with increasing temperature in the low-temperature region. Above about 120 K, the susceptibility of $CeNi_{8.5}Si_{2.5}$ slightly increases with temperature while the susceptibility of $CeNi_9Si_2$ becomes more or less temperature-independent. The upturn of χ in the lowest temperature range, which is particularly pronounced for $CeNi_{8.5}Si_{2.5}$, is probably due to small amounts of an impurity phase (probably Ce_2O_3) [9]. It can be inferred from the results shown that no Curie–Weiss behaviour is followed, which in turn indicates that the Ce atoms do not carry a localised moment. The tendency of the susceptibility of $CeNi_{8.5}Si_{2.5}$ to increase with temperature is reminiscent of mixed valence behaviour [10].

The field dependence of the magnetisation at 5 K is shown for both compounds in Fig. 3. Also, these data support the view that Ce does not carry a localised moment in both cases.

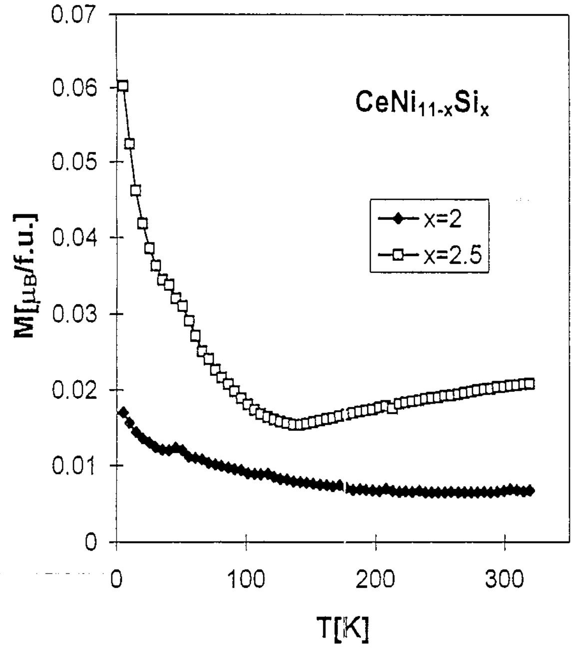

Fig. 2. Temperature dependence of the magnetic susceptibility for $CeNi_9Si_2$ and $CeNi_{8.5}Si_{2.5}$ measured in 5 T.

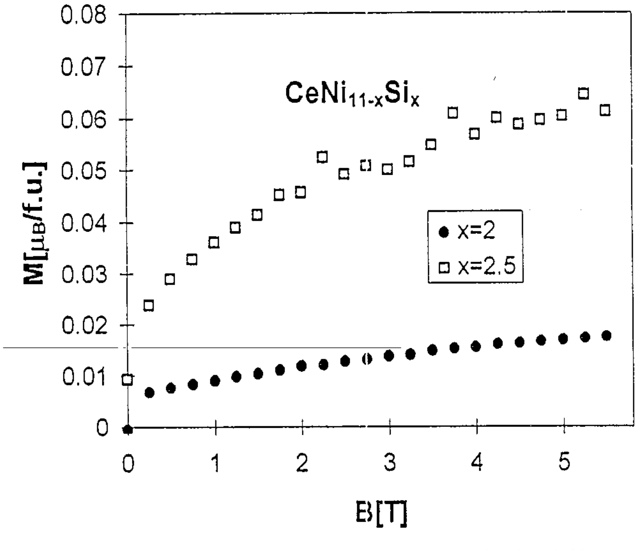

Fig. 3. Field dependence of the magnetic moment in $CeNi_9Si_2$ and $CeNi_{8.5}Si_{2.5}$ measured at 5 K.

4. Concluding remarks

We have investigated the crystallographic properties of $CeNi_{11-x}Si_x$ compounds for $x = 2$ and $x = 2.5$ and shown that they can be regarded as ternary compounds having a crystal structures derived from the tetragonal $BaCd_{11}$ type. The Si atoms are not distributed at random over the four available crystallographic sites but are restricted almost exclusively to one site, which they fully occupy. From magnetic measurements it is derived that Ce does not carry a localised magnetic moment. Indications were obtained that Ce has a mixed valence state in $CeNi_{8.5}Si_{2.5}$.

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