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Note on the crystal structure and magnetic properties of the compounds $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$

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Abstract

The crystal structures of the compounds $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ have been studied by time-of-flight neutron diffraction at room temperature. Both compounds have a tetragonal structure that is derived from the cubic $NaZn_{13}$ structure type. A strong site preference of the Si atoms was observed. From magnetic measurements it is derived that the Ce atoms in both compounds do not carry a magnetic moment.

Keywords: $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$; Intermetallic compounds; Crystal structure; Magnetic properties; Neutron diffraction

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 atoms surrounding it. 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 investigations of ternary Ce compounds [1,2] to the crystal structure and magnetic properties of two Ce compounds in which the Ce atoms are coordinated by polyhedra composed of a comparatively high number of neighbour atoms.

2. Experimental details

Samples of the compounds $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ were prepared by arc melting from starting materials of at least 99.9% purity. After arc melting the samples were wrapped into 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 $Ce_2Ni_{17}Si_9$ structure type reported by Bodak [3].

Neutron powder diffraction experiments were performed 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 these compounds that magnetic ordering is absent, even at 5 K (see below).

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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 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, $b_{Co} = 0.249 \times 10^{-12}$ cm, $b_{Si} = 0.4149 \times 10^{-12}$ cm) were taken from the most up-to-date tabulation available [8]. The tetragonal $Ce_2Ni_{17}Si_9$ structure (space group *I*4/*mcm*) was used as trial structure, with the assumption of a statistical distribution of the Si and Ni(Co) atoms over the 16k, 4d and the two 16l 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, 0.25). Consequently, only the following parameters were refined: unit cell constants, individual isotropic temperature factors for all sites, relative site populations of Si and Ni(Co) on the sites 16k, 4d, the two 16l sites, a scale factor, and peak profile and background parameters. A total of 886(877) overlapping and independent reflections for $Ce_2Ni_{17}Si_9$ ($Ce_2Co_{17}Si_9$)were analysed.

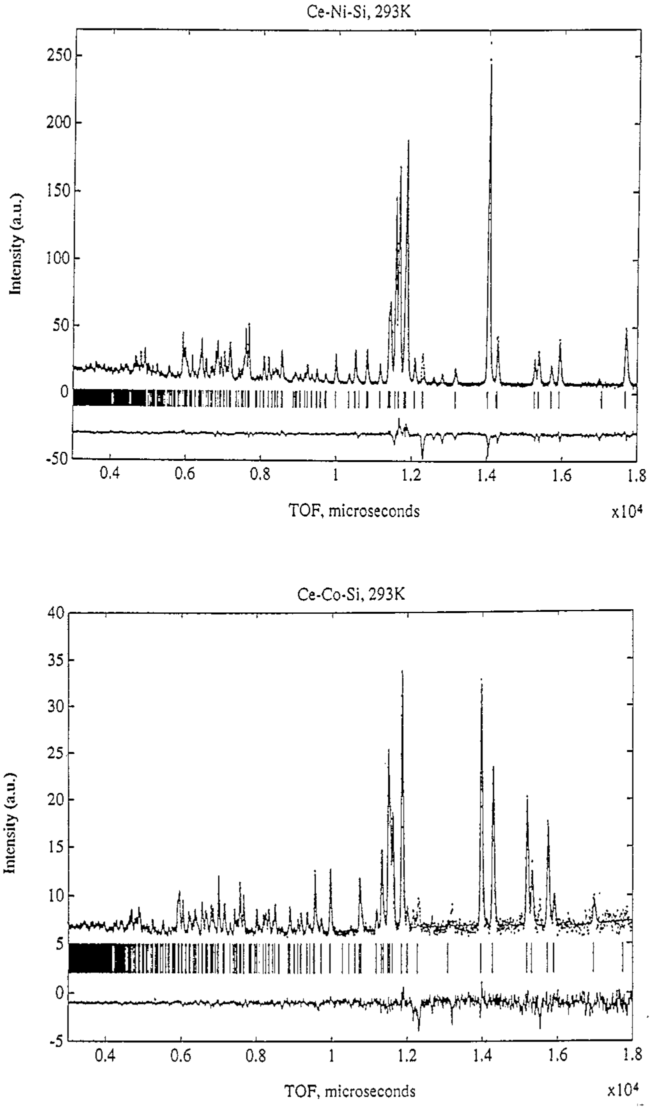

Fig. 1. Observed, calculated and difference neutron time-of-flight diffraction pattern at 293 K of the compounds (a) $Ce_2Ni_{17}Si_9$, (b) $Ce_2Co_{17}Si_9$. The vertical bars indicate calculated peak positions.

4. Experimental results and discussion

The observed and calculated diffraction pattern for the two compounds investigated are displayed in Figs. 1(a) and 1(b). The access to relatively small *d*-spacings implies a particularly accurate assessment of the thermal parameters.

The refined structural, thermal and *R* factors of the compounds $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ are listed in Tables 1 and 2 respectively. It follows from these data that there is a very strong preference for the Si atoms to occupy one of the 16l sites These results confirm conclusions reached earlier by means of X-ray diffraction [3] and show that the compounds $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ can actually be classified as true ternary compounds. Full site occupation by Si atoms of only this particular 16l site would correspond to the ternary compositions $Ce_2Ni_{18}Si_8$ and $Ce_2Co_{18}Si_8$. Apparently these ternary compounds only form with an excess Si concentration. Previous X-ray data have indicated that the excess Si atoms are accommodated in the 4d sites, which would then be equally filled by Si and 3d atoms [3]. The neutron data obtained in the course of the present investigation have shown, however, that the excess of Si atoms goes mainly into the 16k site. These sites are then occupied statistically by about 90% 3d atoms and 10% Si atoms. It is interesting to note that this refinement result was also reached when starting from a trial structure corresponding to the structure in which the excess Si atoms fill half of the 4d sites, as proposed originally by Bodak [3].

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 is nearly temperature-independent over almost the whole temperature range considered; the slight upturn of χ in the lowest temperature range probably being due to

Table 1
Site occupation and atomic position parameters of the compound $Ce_2Co_{17}Si_9$. *I4/mcm* No. 140; $a = 0.77889(1)$ nm, $c = 1.15273(2)$ nm; $R_{wp} = 1.6\%$, $R_{e_p} = 1.3\%$, $\chi^2 = 1.6$

Site	Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)	Occupancy
4a	Ce	0.00000	0.00000	0.25000	0.48(5)	1.00
16k	Co	0.06996(22)	0.20052(18)	0.00000	0.41(3)	0.88(2)
	Si					0.12(2)
16l	Co	0.62837(17)	0.12837(17)	0.18060(14)	0.25(4)	1.00(1)
16l	Si	0.16868(11)	0.66868(11)	0.12187(10)	0.46(3)	1.00(1)
4d	Co	0.00000	0.50000	0.00000	0.15(6)	1.00(1)

Table 2
Site occupation and atomic position parameters of the compound $Ce_2Ni_{17}Si_9$. *I4/mcm*; $a = 0.77837(1)$ nm, $c = 1.14869(1)$ nm; $R_{wp} = 3.4\%$, $R_{exp} = 1.4\%$, $\chi^2 = 5.8$

Site	Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)	Occupancy
4a	Ce	0.00000	0.00000	0.25000	0.59(5)	1.00
16k	Ni	0.06948(11)	0.20270(11)	0.00000	0.63(3)	0.89(2)
	Si					0.11(2)
16l	Ni	0.62971(7)	0.12971(7)	0.18319(10)	0.53(3)	1.00(1)
16l	Si	0.16887(20)	0.66887(20)	0.11903(17)	0.40(4)	1.00(1)
4d	Ni	0.00000	0.50000	0.00000	0.40(6)	1.00(1)

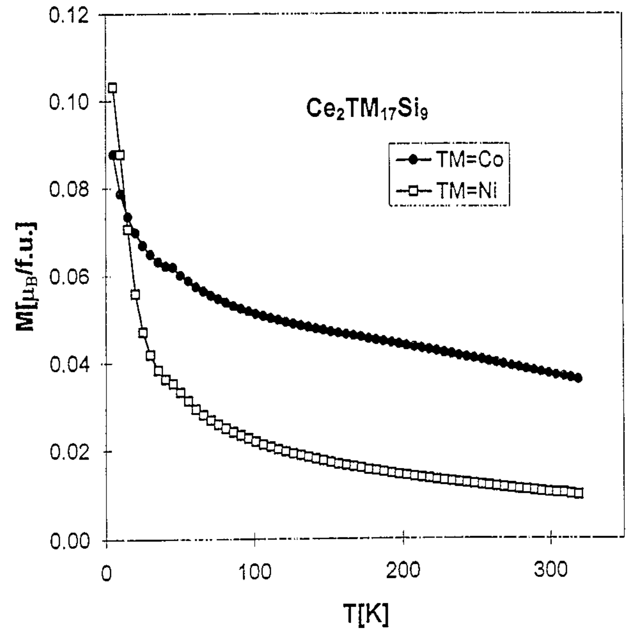

Fig. 2. Temperature dependence of the magnetic susceptibility for $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ measured in 1 T.

very small amounts of impurity phases (probably Ce_2O_3). 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 localized moment. If one corrects the susceptibility data for small amounts of Ce_2O_3 one obtains nearly temperature-independent susceptibilities of the order of 10^{-2} emu per mole Ce. This value is enhanced with respect to normal Pauli paramagnetism, but is of the same order of magnitude as found in Ce compounds where Ce is close to the tetravalent state [1].

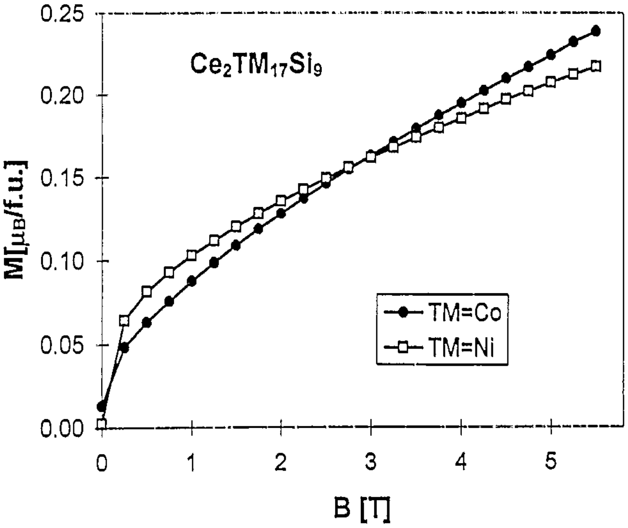

Fig. 3. Field dependence of the magnetic moment in $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ measured at 5 K.

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

5. Concluding remarks

We have shown that $Ce_2Ni_{17}Si_9$ and $Ce_2Co_{17}Si_9$ can be regarded as ternary compounds having crystal structures derived from the cubic $NaZn_{13}$ type. The Si atoms are not distributed at random over the four available crystallographic sites but are restricted primarily to one site, which they fully occupy. The excess Si atoms needed to stabilise this structure type in both ternary systems is fairly small. Also these excess Si atoms show a strong site preference and partially fill only one of the three remaining sites. From the fact that Ce adopts a localised moment in all Ce–Si compounds investigated thus far [9], it may be derived that coordination of Ce by Si is favourable for the formation of trivalent Ce. Apparently, such a situation can persist even in ternary compounds formed from Ce, Si and transition metals T in which the T concentration is equal (CeTSi, CeT_2Si_2) or higher (CeT_2Si) than the Si concentration [10]. The two compounds studied in the course of the present investigation are exceptional in as far as they give rise to Ce atoms having an unusually high coordination number (24), with most of the atoms in the coordination shell being T atoms. The concomitant strong hybridisation of the Ce valence electrons with the T valence electrons is probably the reason why the trivalent state of the Ce atoms can no longer be maintained.

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