Journal of Alloys and Compounds 279 (1998) 110–112

Neutron diffraction study of $CeNi_5Sn$

O. Moze[a], W. Kockelmann[b,c], E. Brück[d], K.H.J. Buschow[d]

[a]Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica, Universit'a di Modena, Via G. Campi 213/a, I-41100 Modena, Italy
[b]Mineralogical-Petrological Institute, University of Bonn, D-53115, Bonn, Germany
[c]ISIS, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK
[d]Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstr. 65, 1018 XE Amsterdam, Netherlands

Received 18 May 1998

Abstract

The crystal structure of the compound $CeNi_5Sn$ has been studied by time-of-flight neutron diffraction at room temperature. The hexagonal structure of this compound was confirmed and the site occupancy of the Ni and Sn compounds was studied in more detail. The neutron diffraction data show that only the 2b and 2c site are exclusively occupied by Ni atoms whereas Ni shares the other non-rare earth sites with Sn. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cerium nickel stannide; Crystal structure; Magnetic properties; Neutron diffraction

1. Introduction

In several previous investigations we have studied the crystal structure and site occupations of the constituent atoms in several ternary Ce compounds in order to study how far the valence of Ce is dependent on the nature of its nearest neighbour shell. In the present investigation we have extended previous structural investigations of ternary Ce compounds [1–3] to the crystal structure and magnetic properties of the compounds $CeNi_5Sn$.

2. Experimental procedures and results.

The $CeNi_5Sn$ compound was prepared by arc melting starting materials of at least 99% purity. After arc melting, the sample was wrapped into Ta foil and vacuum annealed inside an evacuated quartz tube at 850 °C for several weeks. The annealed sample was investigated by X-ray diffraction. The X-ray pattern was mostly single phase, and was indexed according to the hexagonal $CeNi_5Sn$ type of structure [4]. Indications were obtained of the presence of small amounts of Ni_3Sn as an impurity phase. From magnetic measurements made on a SQUID magnetometer in the temperature range 4.2–350 K it could be derived that there is a second impurity phase consisting of a $Ni_{1-x}Sn_x$ solid solution with $x \approx 0.09$, having a Curie temperature of about 350 K. From the saturation magnetisation we derived that only about 2.7% of this phase is present, although it dominates the magnetisation completely in the whole temperature range and makes it impossible to obtain reliable information on the magnetic properties of the main phase $CeNi_5Sn$.

The neutron powder diffraction experiments were made on the POLARIS high-intensity powder diffractometer, a facility present at the ISIS spallation neutron source [5]. Data were collected in the backscattering mode ($2\Theta = 145$ deg) over the entire 20 ms time frame between ISIS pulses, providing a range of accessed d-spacings from 0.4 to 1.8 Å. The instrumental resolution, $\Delta d/d = 0.005$, is constant over this range. The diffraction data were collected at 295 K.

3. Neutron diffraction data analysis

We analysed the neutron diffraction data collected on the POLARIS diffractometer by the Rietveld technique [6], using the programs TF15LS based on the Cambridge Crystallography Subroutine Library, CCSL [7] and GSAS. These programs are able to least-squares refinement of time-of-flight neutron powder diffraction data. They are based on a peak-shape function that is a convolution of a modified Ikeda–Carpenter lineshape and a Voigt function [8]. 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_{Sn} 0.6228×10^{-12} cm) were taken from the most up-to-date tabulation available [9]. The hexagonal

PII: S0925-8388(98)00669-0

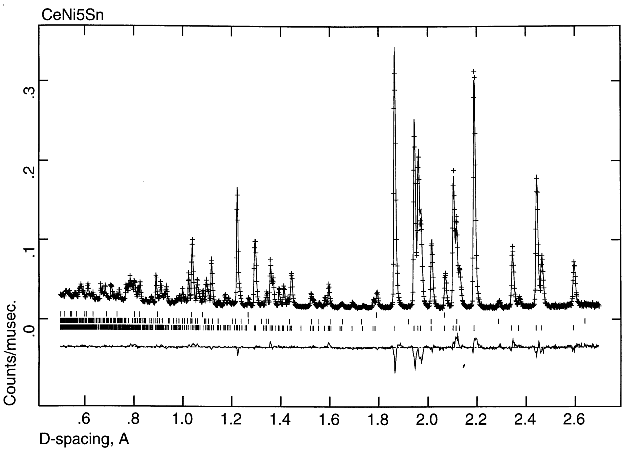

Fig. 1. Observed, calculated and difference neutron time-of-flight diffraction pattern of the $CeNi_5Sn$ compound at 293 K.The vertical bars indicate calculated peak positions. The bottom line of bars refer to calculated peak positions for the main phase, $CeNi_5Sn$, the middle row of lines refers to the second phase, hexagonal Ni_3Sn and the top row refers to the third impurity phase, cubic $Ni_{0.91}Sn_{0.09}$.

$CeNi_5Sn$ structure (space group $P6_3/mmc$, No.194) was used as trial structure, with Ce in 2a and 2d, the assumption of a statistical distribution of the Ni and Sn atoms over the $4f_1$, $4f_2$, 2c, 2b, and 12k sites, and the additional constraint that the overall composition be fixed by the nominal composition. The Ce position at 2a was chosen as origin of the unit cell. Consequently, only the following parameters were refined: unit cell constants, individual isotropic temperature factors for all sites, relative site populations of the Ni and Sn atoms over the $4f_1$, $4f_2$, 2c, 2b, and 12k sites, a scale factor, and peak profile and background parameters. A total of 1311 overlapping and independent reflections were analysed.

The initial refinement results were not very satisfactory. From the X-ray diagrams indications were obtained that small amounts of the hexagonal Ni_3Sn phase are present as an impurity. Similarly, from the magnetic measurements it was derived that about 2.7% of $Ni_{0.91}Sn_{0.09}$ are present. These two impurity phases were included in the refinement. The relative amounts of the two impurity phases derived from the refinement are 3.5 wt% for Ni_3Sn and 2.5 wt% for $Ni_{0.91}Sn_{0.09}$.

The results of the refinement are displayed in Fig. 1. Atomic position parameters and occupancies for $CeNi_5Sn$ are listed in Table 1. It follows from the data listed in the table that there is a strong preference for the Sn atoms to occupy only one ($4f_2$) of the four available sites. The Sn atoms avoid the 2c and 2b sites completely, and for the 12k site the interchange with Ni atoms is only very modest. These results only partially confirm conclusions reached earlier by means of X-ray diffraction [4] that indicated $CeNi_5Sn$ to be a true ternary compound.

Acknowledgements

The authors wish to thank R.M. Ibberson for assistance with the neutron diffraction experiments. Provision of neutron facilities by DRAL (Daresbury and Rutherford Laboratories) is gratefully acknowledged. This research has been supported by the Dutch Technology Foundation (STW).

References

[1] O. Moze, K.H.J. Buschow, J. Alloys Comp. 235 (1996) 62.
[2] O. Moze, S.A.M. Mentink, G.J. Nieuwenhuys, K.H.J. Buschow, J. Magn. Magn. Mater. 150 (1995) 345.
[3] O. Moze, L.D. Tung, J.J.M. Franse, K.H.J. Buschow, J. Alloys Comp. 256 (1997) 45.
[4] R.V. Skolozdra, V.M. Mandzyk, L.G. Akselrud, Sov. Phys. Crystallogr. 26 (1981) 272.

Table 1
Refined parameters for the compound $CeNi_5Sn$

Atom	Position	*x*	*y*	*z*	Occ.	Temp. Factor
Ce	2a	0.0000	0.0000	0.0000	1.00	0.51(6)
Ce	2d	0.3333	0.6667	0.7500	1.00	0.86(6)
Ni	$4f_1$	0.3333	0.6667	0.0421(1)	0.87	0.98(3)
Sn					0.13	
Ni	$4f_2$	0.3333	0.6667	0.5877(1)	0.17	0.70(3)
Sn					0.83	
Ni	2c	0.3333	0.6667	0.2500	1.00	1.08(4)
Sn					0.00	
Ni	2b	0.0000	0.0000	0.2500	1.00	0.86(4)
Sn					0.00	
Ni	12k	0.1662(1)	0.3325(3)	0.14550(4)	0.97	0.50(1)
Sn					0.03	

Space group $P6_3/mmc$ Lattice constants: a=4.88451(5) Å, c=19.7026(4) Å.
R_{wp}=3.1%, R_{exp}=0.94%, R_{Bragg}=3.6%, χ^2=10.87.

[5] S. Hull, J. Mayers, Rutherford Appleton Laboratory Report 89/118, 1989.
[6] H.M. Rietveld, J. Appl. Cryst. 2 (1969) 65.
[7] P.J. Brown, J.C. Matthewman, Rutherford Appleton Laboratory Report 85/112, 1985.
[8] W.I.F. David, S. Hull, R.M. Ibberson-Rutherford-Appleton Laboratory Report 90/000, 1990.
[9] V.F. Sears, Neutron scattering lengths and cross sections, Neutron News Vol 3, pp. 26, Gordon and Breach Science Publ. 1992.