Acta Cryst. (1952). **5**, 329

The Structure of Ni_2Si

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(*Received* 9 *October* 1951)

The structures of a low- and high-temperature modification of Ni_2Si are determined. The former is orthorhombic (*Pbnm*) with $a = 7{\cdot}03$, $b = 4{\cdot}99$, $c = 3{\cdot}72$ Å and with 4 Ni_2Si in the unit cell. The latter is hexagonal ($C6_3m$) with $a = 3{\cdot}805$, $c = 4{\cdot}890$ Å, and with 2 Ni_2Si in the unit cell.

Introduction

This paper is based on the equilibrium diagram of the system Ni–Si, published by Osawa & Okamoto (1939). In the latter paper Ni_2Si is considered to have two allotropic modifications, δ-Ni_2Si and θ-Ni_2Si. δ-Ni_2Si, with 19·3% Si, transforms at 1214° C. into θ-Ni_2Si. The transformation temperature is lowered to 806° C. by the presence of silicon in solid solution of the θ-phase. Osawa & Okamoto describe the low-temperature phase as orthorhombic with $a = 7{\cdot}39$, $b = 9{\cdot}90$, $c = 7{\cdot}06$ Å, and with 16 Ni_2Si in the unit cell; and the high-temperature phase as hexagonal with $a = 3{\cdot}797$, $c = 4{\cdot}892$ Å, and with 2 Ni_2Si in the unit cell. These statements are based on powder photographs only. The present study revises the results of Osawa & Okamoto and proposes new structures on the basis of measurements on monocrystals.

Structure of δ-Ni_2Si

Preparation of the crystals

The material for the determination of the structure of the δ phase was prepared by melting a mixture of nickel and silicon in stoichiometric ratio in a vacuum induction furnace. It was then crushed, and suitable prismatic fragments were selected under the microscope for further study. It was found that these fragments were actually monocrystals. Some were powdered and a debyegram proved to be identical with the debyegrams found by Osawa & Okamoto.

Dimensions and space group of the unit cell

Photographs were made using the rotating-crystal method (Cu $K\alpha$ radiation) and the Weissenberg goniometer about all three axes. Orthorhombic symmetry was established. The dimensions of the unit cell,

$$a = 7{\cdot}06,\ b = 4{\cdot}99,\ c = 3{\cdot}72 \text{ Å},$$

and the specific weight, 7·23 g.cm.$^{-3}$, point to the presence of 4 Ni_2Si in the unit cell. The unit cell is therefore four times smaller than that proposed in the work of Osawa & Okamoto (1939), where the a and b axes are approximately twice the length of the c and b axes determined in this study. The absence of reflexions $h0l$ when $h+l$ is odd and of $0kl$ when k is odd show that the space group must be either *Pbnm* or *Pbn*. In the case of *Pbnm* the atoms of nickel can be situated only in a special fourfold position in the planes of symmetry owing to the shortness of the c axis. It is possible to decide between the *Pbn* and *Pbnm* groups, as with NiSi (Toman, 1951), on the basis of the determination of $z_{1\,Ni}-z_{Si}$ and $z_{2\,Ni}-z_{Si}$.

Intensity measurements and determination of the structure

The intensity was estimated from oscillation photographs, taken about [001] with Cu $K\alpha$ radiation, using visual comparison with an intensity scale having exposures in the ratio 10:7·5:5·0:2·5:1·25:0·62. Measured intensities were corrected in the usual way by Lorentz and polarization factors. The absorption factor was relatively small on account of the small dimensions of the crystal (cross-section 0·06×0·04 mm.) and was estimated in the same way as for NiSi. The approximate structure was determined using Patterson's projection on (001). On the basis of this approximation the projection of the electron density on (001) was calculated. The systematic errors in the calculation of the atom coordinates due to the termination of the series were corrected by the method of Booth (1948). The z parameters were determined by trial and error. The final co-ordinates are given in Table 1.

Table 1. *The final atomic coordinates for* δ-Ni_2Si

	x	y	z
Ni_1	0·063	0·325	$\frac{1}{4}$
Ni_2	0·203	0·042	$\frac{3}{4}$
Si	0·386	0·236	$\frac{1}{4}$

The agreement between the observed and calculated values of the $hk0$ structure factors is clear from Table 2. The structure factors were calculated using a temperature factor $\exp[-2{\cdot}5\lambda^2/\sin^2\theta]$. The coefficient $2{\cdot}5\times10^{16}$ cm.$^{-2}$ in the temperature factor and the scale factor were calculated using the method of least squares. The reliability index for the $hk0$ reflections is 0·16.

Table 3 shows the agreement between the observed

Table 2. *Observed and calculated hk0 structure factors for* δ-Ni_2Si

*hk*0	F_o	F_c	*hk*0	F_o	F_c	*hk*0	F_o	F_c
020	10	11	250	Abs.	1	530	20	19
040	16	19	310	58	66	540	20	19
060	19	16	320	63	70	600	27	22
110	6	5	330	Abs.	0	610	51	46
120	Abs.	2	340	20	22	620	16	25
130	47	46	350	13	16	630	Abs.	6
140	64	57	400	Abs.	5	640	Abs.	5
150	Abs.	7	410	25	33	710	11	10
160	7	10	420	42	36	720	Abs.	6
200	4	6	430	21	27	730	34	37
210	17	27	440	Abs.	2	800	22	26
220	85	77	450	33	33	810	Abs.	1
230	36	32	510	42	48	820	7	6
240	30	21	520	20	22			

Table 3. *Observed and calculated h0l structure factors for* δ-Ni_2Si

h0l	F_o	F_c	*h0l*	F_o	F_c	*h0l*	F_o	F_c
200	4	6	501	19	25	103	Abs.	7
400	Abs.	5	701	13	15	303	56	62
600	27	22	002	152	152	503	Abs.	14
800	22	26	202	Abs.	3	004	59	53
101	16	12	402	Abs.	2	204	Abs.	1
301	114	126	602	24	19	404	Abs.	2

Table 4. *Observed and calculated structure factors for* θ-Ni_2Si

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
100	11	12	121	11	12	033	Abs.	0
101	17	18	203	15	12	031	Abs.	10
002	Abs.	10	104	15	7	022	Abs.	6
102	82	88	122	43	49	124	15	6
110	95	90	300	66	70	115	Abs.	0
111	Abs.	0	031	Abs.	0	132	29	42
200	13	7	114	82	65	025	Abs.	10
003	Abs.	0	032	Abs.	6	040	Abs.	6
021	Abs.	14	123	Abs.	6	233	Abs.	0
112	Abs.	7	024	Abs.	6	034	45	55
013	Abs.	13	005	Abs.	0	006	Abs.	6
202	71	75	220	66	60	041	Abs.	10
121	Abs.	7	125	Abs.	10	133	Abs.	10
113	Abs.	0	221	Abs.	0	016	29	39
004	90	70	130	Abs.	6	042	39	39

and calculated *h0l* structure factors, the reliability index being 0·17.

Structure of θ-Ni_2Si

The θ phase of Ni_2Si was prepared according to the equilibrium diagram of the system Ni–Si (Osawa & Okamoto, 1939) by quenching the alloy containing 24% silicon from 964° C. The debyegram (Cu $K\alpha$ radiation) of the quenched alloy shows a hexagonal lattice with parameters

$$a = 3{\cdot}805,\ c = 4{\cdot}890\ \text{Å}$$

differing only slightly from those of Osawa & Okamoto (1939). The specific weight, 6·85 g.cm.$^{-3}$, indicates the presence of 2 Ni_2Si in the unit cell. The pseudo-hexagonality of the projection of δ-Ni_2Si along the b axis and the approximately equal length of the b axis in δ-Ni_2Si and the c axis in θ-Ni_2Si gives the relation between the structures of the δ and θ phases. The position of the a axes of the hexagonal θ phase in relation to the structure of the δ phase is shown in Fig. 4.

It follows from the number of Ni_2Si in the unit cell that the silicon atoms must be situated in a special twofold position and the nickel atoms either in a special twofold or in a special fourfold position. In view of the structure of δ-Ni_2Si and of the fact that systematic absences of reflexions are observed

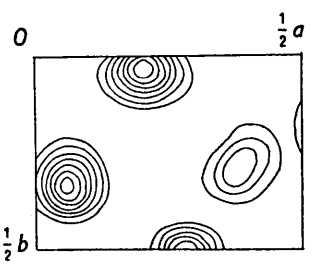

Fig. 1. δ-Ni_2Si, electron density, projection along [001].

only for $00l$ when l is odd, the space group C_{6h}^2 or D_6^6 with a special twofold position with no degree of freedom is most likely. The following parameters are then found:

Ni: 0, 0, 0; 0, 0, $\frac{1}{2}$; $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$.
Si: $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$.

The agreement between the observed and calculated structure factors is shown in Table 4.

The two projections θ-Ni_2Si along [110] (Fig. 6) and δ-Ni_2Si along [001] (Fig. 2) and the two projections θ-Ni_2Si along [001] (Fig. 5) and δ-Ni_2Si along [010] (Fig. 3) show the close relation between the two structures.

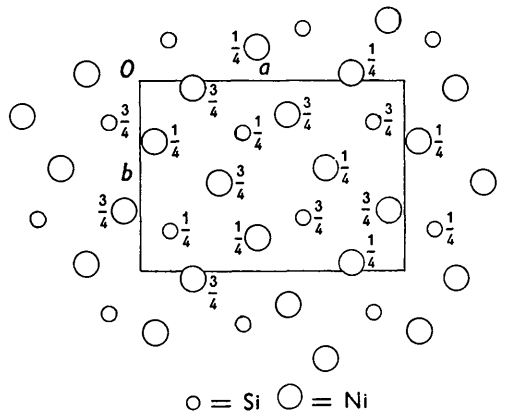

Fig. 2. δ-Ni_2Si, projection along [001].

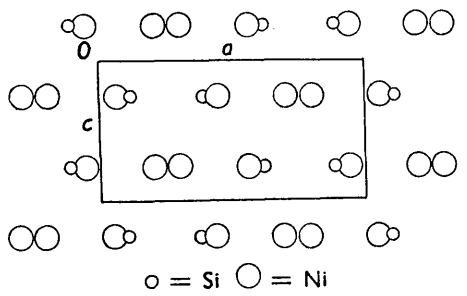

Fig. 3. δ-Ni_2Si, projection along [010].

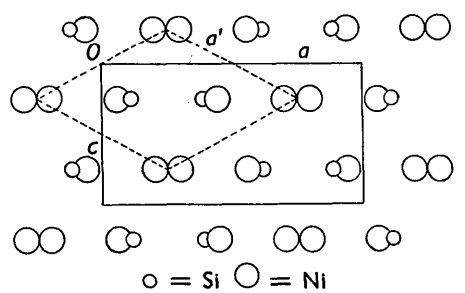

Fig. 4. The position of the a axis of the θ-Ni_2Si structure in relation to the δ-Ni_2Si structure.

Conclusions

The distances between atoms in δ-Ni_2Si are:

Ni–Ni 2·54, 2·62, 2·72 Å.
Si–Si 3·27 Å.
Ni–Si 2·28, 2·31, 2·34, 2·35, 2·41, 2·56, 2·62, 2·72 Å.

The distances between atoms in θ-Ni_2Si are:

Ni–Ni 2·45, 2·52 Å.
Si–Si 3·29 Å.
Ni–Si 2·23, 2·45, 2·52 Å.

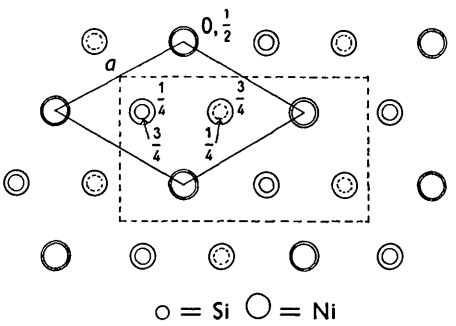

Fig. 5. θ-Ni_2Si, projection along [001].

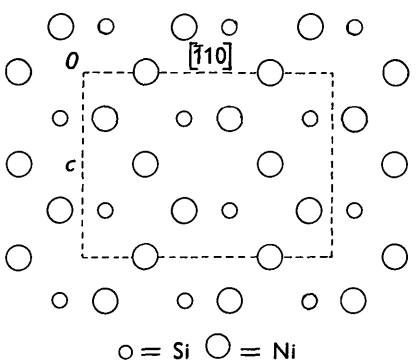

Fig. 6. θ-Ni_2Si, projection along [110].

The author wishes to express his thanks to The Research Institute of Metals for permission to publish this paper.

References

Booth, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis*. Cambridge: University Press.
Osawa, A. & Okamoto, M. (1939). *Sci. Rep. Tôhoku Univ.*, First Series, **27**, 326.
Toman, K. (1951). *Acta Cryst.* **4**, 462.