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# The Structure of NiSi

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The structure of NiSi has been determined from Weissenberg and rotating-crystal photographs using Cu $K\alpha$ radiation. Dimensions of the unit cell, determined by the powder method, are: $a=5{\cdot}62$, $b=5{\cdot}18$, $c=3{\cdot}34$ A. The space group is *Pbnm*, and there are four molecules in the unit cell. The structure is a deformed NiAs arrangement.

## Introduction

The structure of nickel silicide was first studied by the powder method by Borén (1933) who described this compound as cubic ($a=4{\cdot}437$ A.) of the FeSi type. Later work, also by the powder method, was undertaken by Osawa & Okamoto (1939). These authors, on the basis of thermic, dilatometric and metallographic investigations, revised the Ni–Si system and tried to measure the dimensions of the unit cells of individual phases. NiSi was found to be tetragonal ($a=7{\cdot}655$, $c=8{\cdot}45$ A.) with twenty molecules in the unit cell. The latest work dealing with the structure of NiSi is by Pauling & Soldate (1948), who determined once again the structure of FeSi, on the basis of work on single crystals, and discussed the interatomic distances for FeSi, CrSi, MnSi, CoSi and NiSi. The discussion of these silicides, other than that of FeSi, is based on the data of Borén (1933).

## Preparation of the crystals

A small block of alloy was prepared by melting very pure nickel and silicon in stoichiometric ratio in a vacuum induction furnace. After cooling in the furnace the block was broken, and inside there was found a cavity with imperfectly developed prismatic crystals whose constitution corresponded to the phase of NiSi. A powder photograph, prepared from the powdered crystal, was identical with that published by Osawa & Okamoto (1939).

## Unit-cell dimensions and the space group

On the basis of rotation and Weissenberg photographs (Cu $K\alpha$ radiation), orthorhombic symmetry was established. The dimensions of the unit cell, determined from rotation photographs and from powder photographs in a 19 cm. camera (Co $K\alpha$ radiation), after correction by the method of Heavens & Cheesman (1950), were found to be

$$a=5{\cdot}62, \quad b=5{\cdot}18, \quad c=3{\cdot}34 \text{ A.}$$

The absent reflexions, $(0kl)$ where $k=2n+1$, $(h0l)$ where $h+l=2n+1$, $(00l)$ where $l=2n+1$, indicate the probable space group *Pbn* or *Pbnm*.

The density is 5·86 g.cm.$^{-3}$ and the unit cell therefore contains four NiSi. In the case of the group *Pbnm* a special fourfold position with atoms in the plane of symmetry (001) satisfies, while in the case of the group *Pbn* the general fourfold position satisfies. The final decision is possible on the basis of the determination of $z_{Ni}-z_{Si}$, which for *Pbn* may have all the values from 0 to $\frac{1}{2}$, for *Pbnm* only 0 or $\frac{1}{2}$.

## Intensity measurements

For intensity measurements oscillation photographs were taken about the $c$ axis, with Cu $K\alpha$ radiation. Measurements were made in the planes $(hk0)$ using visual comparison with an intensity scale having exposures in the ratios 10:6·6:5·0:3·3:1·8:1·0. Measured intensities were corrected in the usual way using polarization and Lorentz factors. The measured

crystal was prismatic, the absorption factor for the cylinder circumscribed to the crystal ($r=0{\cdot}07$ mm., $\mu r=2{\cdot}2$) differed at most by 25% compared with the inscribed cylinder ($r=0{\cdot}06$ mm., $\mu r=1{\cdot}9$). As a correction the average value, which does not deviate from the correct value for single reflexions ($hk0$) by more than 15%, was taken. Structure factors, calculated from these measured intensities, were transferred to an absolute scale using the powder method. As reference substances aluminium and remelted KBr were chosen. Greater weight was attached to the results based on KBr because of the proximity of linear absorption coefficients of NiSi and KBr for the Co $K\alpha$ radiation used.

## Determination of the structure

The preliminary structure was determined on the basis of the two-dimensional Patterson projection along $c$. This projection (Fig. 1) has three well-distinguished maxima that correspond to Ni–Ni vectors, allowing the preliminary co-ordinates $x_{Ni}$ and $y_{Ni}$ to be determined.

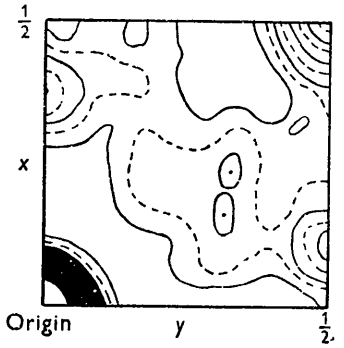


Fig. 1. Patterson projection on (001).

The preliminary co-ordinates $x_{Si}$ and $y_{Si}$ were found by trial. From these preliminary co-ordinates a two-dimensional Fourier projection along $c$ was computed in the usual way (Fig. 2). Divisions of $\frac{1}{60}$th of the identity period were used and the atom centres were determined by the paraboloid method (Booth, 1948). The co-ordinates thus found were:

$$x_{Ni}=0{\cdot}185, \quad y_{Ni}=0{\cdot}007,$$
$$x_{Si}=0{\cdot}078, \quad y_{Si}=0{\cdot}327.$$

Table 1 shows the agreement between observed and calculated structure factors ($hk0$). Structure factors were calculated with the temperature factor

$$\exp(-1{\cdot}5\sin^2\theta/\lambda^2).$$

The coefficient in the temperature factor was determined by the method of least squares from thirty-four values. The reliability index

$$R=\Sigma||F_o|-|F_c||\div\Sigma|F_o|$$

is 0·14.

Systematic errors in the determination of the atom co-ordinates, due to termination of the series, were determined by using the $F_c$ synthesis (Booth, 1948). The values obtained have been used as a correction. The magnitude of the influence of the random errors in the estimation of intensities upon the position of the atom was determined by the method of Cruickshank (1949). The corrected atom co-ordinates and their standard deviations are:

| | $x$ | $\sigma_x$ | $y$ | $\sigma_y$ |
|---|---|---|---|---|
| Ni | 0·184 | 0·0010 | 0·006 | 0·0008 |
| Si | 0·080 | 0·0018 | 0·330 | 0·0021 |

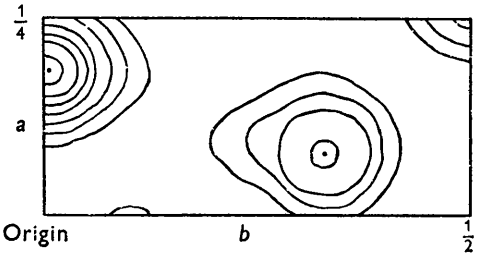


Fig. 2. Fourier projection on (001). Contours are drawn on an arbitrary scale.

For the complete determination of structure, it suffices to determine $z_{Ni}-z_{Si}$, which in the space group $Pbnm$ is 0 or $\frac{1}{2}$. The determination was carried out by trial and error on the basis of the first layer line of the oscillation photographs around $c$. The greatest weight was attached to plane (321), the absence of which, even on photographs with a long exposure, is explicable only for $z_{Ni}-z_{Si}=\frac{1}{2}$. On the basis of this result the space group $Pbnm$ was accepted.

Table 2 gives a survey of the observed plane intensities ($hk1$) and the calculated structure factors.

Table 1. *Observed and calculated structure factors*

| $hkl$ | $\|F_o\|$ | $\|F_c\|$ | $hkl$ | $\|F_o\|$ | $\|F_c\|$ | $hkl$ | $\|F_o\|$ | $\|F_c\|$ |
|---|---|---|---|---|---|---|---|---|
| 020 | 50 | 60 | 230 | 0 | 2 | 430 | 9 | 3 |
| 040 | 43 | 35 | 240 | 37 | 31 | 440 | 4 | 0 |
| 060 | 38 | 38 | 250 | 7 | 8 | 450 | 14 | 12 |
| 110 | 18 | 18 | 260 | 10 | 10 | 510 | 39 | 42 |
| 120 | 10 | 10 | 310 | 53 | 60 | 520 | 10 | 10 |
| 130 | 47 | 48 | 320 | 31 | 23 | 530 | 15 | 16 |
| 140 | 19 | 13 | 330 | 40 | 41 | 540 | 5 | 6 |
| 150 | 4 | 4 | 340 | 21 | 14 | 600 | 8 | 10 |
| 160 | 3 | 1 | 350 | 23 | 28 | 610 | 0 | 2 |
| 200 | 35 | 35 | 400 | 16 | 11 | 620 | 25 | 27 |
| 210 | 30 | 26 | 410 | 23 | 18 | | | |
| 220 | 57 | 55 | 420 | 9 | 4 | | | |

Table 2. *Observed intensities and calculated structure factors*

| *hkl* | *I* | $\lvert F_c \rvert$ | *hkl* | *I* | $\lvert F_c \rvert$ | *hkl* | *I* | $\lvert F_c \rvert$ |
|---|---|---|---|---|---|---|---|---|
| 021 | *m* | 24 | 221 | *w* | 12 | 411 | *m* | 30 |
| 041 | *w* | 18 | 231 | *w* | 15 | 421 | *vw* | 8 |
| 101 | *vs* | 59 | 241 | *w* | 9 | 431 | *s* | 72 |
| 111 | *m* | 27 | 251 | *m* | 30 | 441 | *w* | 12 |
| 121 | *vs* | 63 | 301 | *s* | 40 | 501 | *m* | 30 |
| 131 | *vw* | 2 | 311 | Abs. | 0 | 511 | *w* | 16 |
| 141 | *m* | 30 | 321 | Abs. | 3 | 521 | *vw* | 10 |
| 151 | *w* | 15 | 331 | Abs. | 0 | 611 | *m* | 24 |
| 211 | *vs* | 68 | 341 | *vw* | 9 | 621 | *w* | 16 |


## Summary

This work on the single crystal of nickel silicide, NiSi, shows it to be orthorhombic with space group *Pbnm*. There are four NiSi in the cell of dimensions

$$a=5{\cdot}62, \quad b=5{\cdot}18, \quad c=3{\cdot}34\,\text{A}.$$

The atomic co-ordinates are:

Ni: $x=0{\cdot}184$, $y=0{\cdot}006$, $z=0{\cdot}000$.

Si: $x=0{\cdot}080$, $y=0{\cdot}330$, $z=0{\cdot}500$.

The projection on (010) (Fig. 4) shows the structure to be pseudo-hexagonal and to be related to that of NiAs.

Interatomic distances are:

Ni–Ni: 2·66, 2·69 A.

Si–Si: 2·58 A.

Ni–Si: 2·29, 2·30, 2·38, 2·44 A.


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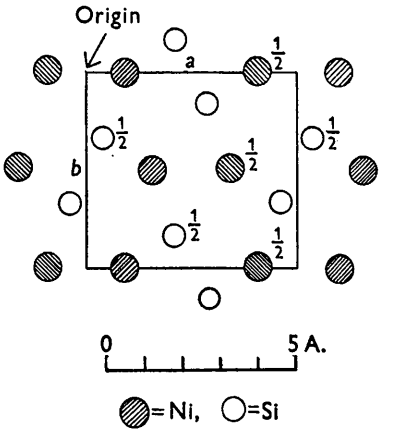


Fig. 3. Projection along *c*.

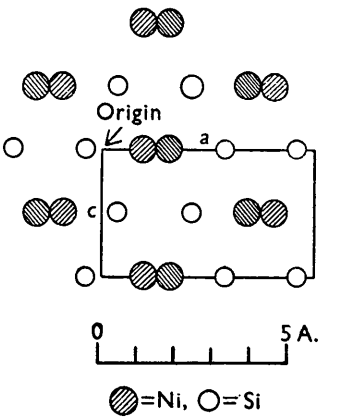


Fig. 4. Projection along *b*.