

## A Superstructure of Ni<sub>6</sub>Se<sub>5</sub>

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The crystal structure of Ni<sub>6</sub>Se<sub>5</sub> quenched from 420 °C has been determined by X-ray methods using 1750 reflections recorded by counter methods. The crystal system is orthorhombic, space group *Pca*2<sub>1</sub> with lattice constants  $a = 6.863 \pm 0.003$  Å;  $b = 17.09 \pm 0.01$  Å;  $c = 11.821 \pm 0.005$  Å. There are eight formula units per unit cell. The Se-atoms form a zig-zag pattern and the nickel atoms are situated in deformed tetrahedral, octahedral, or pyramidal positions in the selenium lattice. A number of possible nickel positions are vacant, so that the crystal lattice can be regarded as a superstructure of a ground cell with nickel atoms randomly distributed over some partly occupied nickel positions.

A compound Ni<sub>6</sub>Se<sub>5</sub> which is stable between 400 and 670 °C was reported by Kuznecov *et al.*<sup>1</sup> The structure was found to be hexagonal with  $a = 3.78$  Å and  $c = 15.89$  Å. Grønvold, Møllerud and Røst<sup>2</sup> reported that the structure of Ni<sub>6</sub>Se<sub>5</sub> is orthorhombic with  $a = 3.437$  Å,  $b = 11.86$  Å, and  $c = 17.06$  Å. X-Ray high temperature measurements indicated that this phase is stable between 400 and 640 °C. The existence of Ni<sub>6</sub>Se<sub>5</sub> with orthorhombic crystal structure has been confirmed by others.<sup>3,4</sup> In this phase tellurium can be partly substituted for selenium,<sup>5</sup> whereas a complete substitution of sulfur for selenium is possible.<sup>6</sup> Density measurements have been carried out on several ternary samples from the systems Ni—Se—Te<sup>6</sup> and Ni—S—Se.<sup>6</sup> In all cases the unit cells were found to contain 20 chalcogen atoms whereas the number of nickel atoms was found to vary within certain limits. A crystal structure determination of Ni<sub>6</sub>Se<sub>5</sub> has been carried out by Røst and Haugsten.<sup>7</sup> The phase has, however, shown a tendency of superstructure formation and the structure determination concerned only the subcell of the structure. Some of the nickel

positions were regarded as being only partly occupied. It was pointed out that some apparently short distances between nickel atoms could be due to an alternating occupancy of some nickel positions in a superstructure lattice. The crystal structure of Ni<sub>7</sub>S<sub>6</sub>, determined by Fleet,<sup>8</sup> seems to be isostructural to Ni<sub>6</sub>Se<sub>5</sub> as far as the subcell is concerned.

### EXPERIMENTAL

Samples of Ni<sub>6</sub>Se<sub>5</sub> were prepared by melting calculated amounts of the elements in evacuated and sealed silica tubes. The samples were annealed at 600 °C and quenched in water. Single crystals were obtained by annealing crushed samples in long silica tubes in an oven with a temperature gradient. Small amounts of iodine were added as a transport agent. After an annealing time of two weeks at 600 °C, very small crystals of Ni<sub>6</sub>Se<sub>5</sub> were found in the colder end of the tube. Several crystals were examined using Weissenberg X-ray cameras. Crystals which had been quenched from 600 °C showed weak and diffuse superstructure reflections corresponding to a doubling of two lattice constants. Crystals that had been slowly cooled to 420 °C and annealed at that temperature for two weeks showed, however, a second kind of superstructure corresponding to a doubling of only one lattice constant, the *a*-axis. In this case the superstructure reflections were sharp and relatively strong. A single crystal which had been quenched from 420 °C was used for further investigations. It was 0.07 mm long and had a cross section of 0.04 by 0.04 mm. The unit cell dimensions were calculated from measurements using a Picker manual single crystal diffractometer with CuKβ radiation. The intensity data were recorded on an automatic Picker four-circle diffractometer using MoKα radiation. About 3600 reflections with  $2\theta < 75^\circ$  were measured using the  $\omega - 2\theta$  scanning mode with  $2\theta$  scanning speed of  $1^\circ \text{ min}^{-1}$ . Background counts were taken for 20 s at each of the scan range limits. 1750 reflections with intensities larger than  $2\sigma(I)$  were considered to be observed.

Those with lower intensity were excluded from the final refinement procedure.

The computer programmes used in the present analysis are described in Ref. 9. Intensity data were corrected for absorption and for Lorentz and polarization effects. Atomic form factors were those of Hanson *et al.*<sup>10</sup>

## CRYSTAL DATA

Orthorhombic

Ni<sub>8</sub>Se<sub>8</sub>

$a = 6.863 \pm 0.003$  Å,  $b = 17.09 \pm 0.01$  Å,

$c = 11.821 \pm 0.005$  Å

Unit cell volume = 1368.4 Å<sup>3</sup>

Unit cell content: 40 Se and 48 Ni atoms.

Calculated density 7.16 g cm<sup>-3</sup>.

Linear absorption coefficient = 4.40 cm<sup>-1</sup>

Systematically absent reflections:

$0kl$  for  $l = 2n + 1$  and  $h0l$  for  $h = 2n + 1$

Possible space groups:  $Pca 2_1$  and  $Pcmb$

## STRUCTURE DETERMINATION

Preliminary crystal structure calculations were based on atomic parameters corresponding to the subcell structure of Ni<sub>8</sub>Se<sub>8</sub>.<sup>7</sup> In accordance with a unit cell content of 48 nickel and 40 selenium atoms the selenium atoms were arranged in ten fourfold positions, referring to the lowest symmetrical space group  $Pca2_1$ . The previous structure determination of the ground cell strongly indicated that six of the

nickel positions are completely occupied. In the present investigation (Fig. 1) these correspond to the positions Ni1,2,7,8,9 and 12. The remaining 24 nickel atoms must be distributed over 12 fourfold positions. Both reduced occupancy of the nickel positions, and a successive distribution between occupied and vacant positions were tried as a basis for least squares calculations.

The calculations led to a crystal structure in which the nickel atoms are arranged in twelve completely occupied positions leaving the rest of the possible nickel positions empty. The final positional parameters assuming anisotropic temperature factors are given in Table 1. The corresponding conventional  $R$ -factor is 0.060 ( $R_w = 0.053$ ). The  $R$ -factors found using isotropic temperature factors were 0.066 and 0.060, respectively. Further refinements assuming anomalous dispersion were also tried, but no significant improvement of the reliability factor was obtained.

This solution of the superstructure confirms a stoichiometric composition of Ni<sub>8</sub>Se<sub>8</sub> with eight formula units per unit cell.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A projection along the  $a$ -axis of Ni<sub>8</sub>Se<sub>8</sub> is found in Fig. 1. Selenium and nickel atoms are

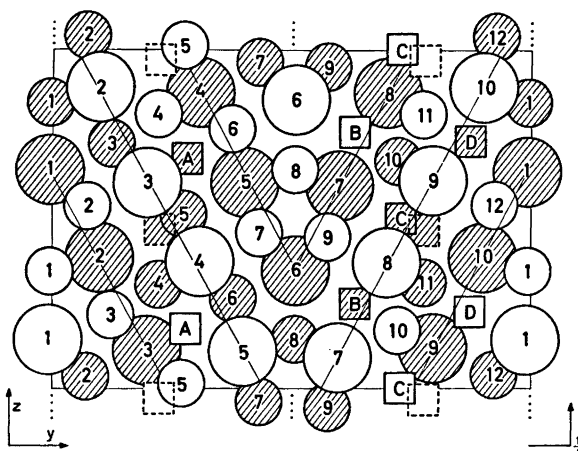


Fig. 1. A projection of the superstructure of Ni<sub>8</sub>Se<sub>8</sub> along the  $x$ -axis. Large and small circles show selenium and nickel atoms, respectively, and the squares represent vacant nickel positions. Only the atoms and vacancies with  $x$ -parameter  $\sim \frac{1}{2}$  and  $\sim \frac{3}{2}$  are presented. Atoms and vacancies in the layer with  $x \sim \frac{1}{2}$  are hatched. Glide planes along the  $x$ -direction and along the  $z$ -direction are indicated. The zig-zag pattern of the structure is indicated by thin lines,

shown as large and small circles, respectively. Vacancies corresponding to possible nickel positions are indicated as squares. The atoms are situated in layers perpendicular to the  $a$ -axis with  $x$ -parameters near  $1/8$ ,  $3/8$ ,  $5/8$ , and  $7/8$ . The deviations from these values are of the order of  $0.1 \text{ \AA}$ . Only two of the layers,  $x \sim 1/8$  and  $x \sim 3/8$ , are presented in the figure. Atoms and vacancies in the layer with  $x \sim 1/8$  are hatched. The rest of the unit cell can be visualized using the glide plane along the  $x$ -direction, which is indicated on the figure at the edges of the unit cell.

The selenium atoms form a zig-sag pattern parallel to the  $bc$  plane. Each selenium atom is surrounded by 11 or 12 other selenium atoms at distances between  $3.33 \text{ \AA}$  and  $4.0 \text{ \AA}$ . The nickel atoms are situated in deformed tetrahedral, octahedral, or square pyramidal positions in the selenium lattice. In addition, the nickel atoms are bound also to other nickel atoms. The distances from the different nickel atoms to the adjacent atoms are given in Table 2.

The nickel positions which were regarded as completely filled in the subcell correspond to the atoms Ni1,2,7,8,9, and 12. These are all

coordinated to five selenium atoms in a deformed square pyramidal arrangement at distances between  $2.31$  and  $2.59 \text{ \AA}$  and, in addition, to two or three nickel atoms at distances between  $2.5$  and  $2.8 \text{ \AA}$ . The rest of the nickel positions correspond to those which were regarded as partly occupied in the subcell. With respect to the surrounding selenium atoms, they can be divided into three kinds:

$\alpha$ : Ni5 and vacancy  $C$  are possible double positions, one on each side of the center of a deformed octahedron. The distance between the two positions is about  $1.0 \text{ \AA}$  only and both of them can obviously not be occupied at the same time.

$b$ : Ni3, Ni6, and vacancies  $B$  and  $D$  are surrounded by five selenium atoms in a deformed square pyramidal arrangement. The positions lie near the center of a deformed octahedron.

$c$ : Ni4,10,11 and vacancy  $A$  are tetrahedrally surrounded by selenium.

In this superstructure of  $\text{Ni}_6\text{Se}_8$ , only one of the type  $\alpha$  positions (Ni5) is occupied. It is obviously necessary that the nearest nickel position  $A$  must be empty as the distance from Ni5 would

Table 1. Positional and thermal parameters ( $\times 10^4$ ) with estimated deviations. The temperature factor is given by  $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$ .

| Atom  | $x$      | $y$     | $z$     | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|-------|----------|---------|---------|----------|----------|----------|----------|----------|----------|
| Se 1  | 1272(9)  | 9911(2) | 6440(0) | 38(7)    | 5(1)     | 12(2)    | 4(6)     | -2(10)   | -1(2)    |
| Se 2  | 1261(9)  | 956(2)  | 3869(4) | 31(6)    | 6(1)     | 17(2)    | -11(7)   | 18(10)   | 0(2)     |
| Se 3  | 1411(8)  | 1989(2) | 1124(5) | 38(7)    | 5(1)     | 11(2)    | -3(5)    | -1(9)    | -2(2)    |
| Se 4  | 1314(9)  | 3085(2) | 8743(4) | 24(6)    | 9(1)     | 18(2)    | 1(6)     | 19(10)   | -1(2)    |
| Se 5  | 1407(8)  | 3999(2) | 6124(4) | 48(7)    | 7(1)     | 12(2)    | 11(5)    | -29(7)   | 4(2)     |
| Se 6  | 1247(11) | 5058(2) | 3483(2) | 36(7)    | 10(1)    | 9(2)     | 4(5)     | 11(12)   | 1(2)     |
| Se 7  | 1304(8)  | 5994(2) | 5969(4) | 28(6)    | 7(1)     | 11(2)    | 1(6)     | 3(9)     | -3(2)    |
| Se 8  | 1280(9)  | 7009(2) | 8708(5) | 28(6)    | 8(1)     | 12(2)    | -12(5)   | 23(8)    | 1(2)     |
| Se 9  | 1126(8)  | 7971(2) | 1153(5) | 67(8)    | 6(1)     | 12(2)    | -5(5)    | -27(9)   | 1(2)     |
| Se 10 | 1168(9)  | 9006(2) | 3890(5) | 58(8)    | 6(1)     | 23(2)    | 11(7)    | 36(10)   | -3(2)    |
| Ni 1  | 1239(15) | 9957(3) | 8458(5) | 55(10)   | 8(1)     | 10(2)    | -5(6)    | 13(18)   | 5(3)     |
| Ni 2  | 1311(11) | 712(3)  | 360(5)  | 53(9)    | 5(1)     | 9(3)     | 6(9)     | 10(12)   | -1(3)    |
| Ni 3  | 1241(9)  | 1207(3) | 7187(5) | 76(10)   | 3(1)     | 20(3)    | -3(7)    | -3(12)   | -0(3)    |
| Ni 4  | 1415(11) | 2200(2) | 3089(4) | 58(10)   | 5(1)     | 10(2)    | 4(7)     | -21(10)  | -1(2)    |
| Ni 5  | 1283(8)  | 2726(2) | 5109(4) | 42(6)    | 10(1)    | 11(2)    | 0(6)     | 14(10)   | 6(2)     |
| Ni 6  | 1263(10) | 3751(3) | 2670(5) | 57(9)    | 10(1)    | 14(2)    | -3(7)    | 15(11)   | 5(3)     |
| Ni 7  | 1277(12) | 4306(3) | 9587(5) | 45(9)    | 7(1)     | 10(2)    | 1(8)     | 4(12)    | 1(3)     |
| Ni 8  | 1151(15) | 5058(3) | 1452(5) | 42(11)   | 7(1)     | 10(2)    | 5(6)     | -11(10)  | -1(3)    |
| Ni 9  | 1107(11) | 5764(3) | 9501(6) | 58(12)   | 7(1)     | 20(3)    | 15(7)    | -16(11)  | 6(3)     |
| Ni10  | 1242(9)  | 7241(3) | 6731(5) | 40(8)    | 8(1)     | 16(2)    | -6(7)    | 20(10)   | -4(3)    |
| Ni11  | 1081(10) | 7752(3) | 3127(5) | 48(10)   | 8(1)     | 14(3)    | -7(7)    | -10(10)  | 1(4)     |
| Ni12  | 1152(11) | 9241(3) | 400(5)  | 46(10)   | 6(1)     | 10(3)    | 3(7)     | 0(11)    | -1(3)    |

Table 2. Nearest neighbour interatomic distances (<2.8 Å) from the nickel atoms with  $x$ -parameter  $\sim \frac{1}{3}$ . The standard deviations are of the order of 0.01 Å. Atoms with negative  $x$ -parameter ( $\sim -\frac{1}{3}$ ) are marked with an asterisk.

|         |      |          |      |          |      |           |      |           |      |           |      |
|---------|------|----------|------|----------|------|-----------|------|-----------|------|-----------|------|
| Ni1-Se1 | 2.29 | Ni2-Se1* | 2.43 | Ni3-Se1  | 2.39 | Ni4-Se2   | 2.32 | Ni5-Se3   | 2.35 | Ni6-Se4   | 2.38 |
| Se2*    | 2.37 | Se1      | 2.50 | Se2      | 2.66 | Se3       | 2.35 | Se4       | 2.39 | Se5       | 2.47 |
| Se2     | 2.47 | Se2      | 2.46 | Se3      | 2.44 | Se4       | 2.31 | Se5       | 2.49 | Se6       | 2.43 |
| Se10*   | 2.48 | Se3      | 2.36 | Se9*     | 2.47 | Se8*      | 2.40 | Se8*      | 2.46 | Se7*      | 2.71 |
| Se10    | 2.46 | Se10*    | 2.48 | Se10*    | 2.63 | Ni3       | 2.57 | Se9*      | 2.38 | Se8*      | 2.50 |
| Ni2     | 2.59 | Ni1      | 2.59 | Ni1      | 2.61 | Ni5       | 2.55 | Ni4       | 2.55 | Ni8       | 2.66 |
| Ni3     | 2.61 | Ni12     | 2.52 | Ni4      | 2.57 | Ni6       | 2.70 |           |      | Ni10*     | 2.66 |
| Ni12    | 2.60 |          |      | Ni11*    | 2.63 |           |      |           |      |           |      |
|         |      |          |      | Ni12*    | 2.78 |           |      |           |      |           |      |
| Ni7-Se4 | 2.31 | Ni8-Se5* | 2.41 | Ni9-Se5* | 2.61 | Ni10-Se3* | 2.36 | Ni11-Se4* | 2.30 | Ni12-Se1* | 2.53 |
| Se5     | 2.47 | Se5      | 2.50 | Se6*     | 2.46 | Se7       | 2.31 | Se8       | 2.32 | Se1       | 2.44 |
| Se6     | 2.50 | Se6      | 2.40 | Se6      | 2.49 | Se8       | 2.37 | Se9       | 2.36 | Se2*      | 2.48 |
| Se6*    | 2.43 | Se7      | 2.44 | Se7      | 2.51 | Se9       | 2.30 | Se10      | 2.33 | Se9       | 2.35 |
| Se7*    | 2.46 | Se7*     | 2.53 | Se8      | 2.33 | Ni4*      | 2.61 | Ni3*      | 2.63 | Se10      | 2.59 |
| Ni8     | 2.55 | Ni6      | 2.66 | Ni7      | 2.50 | Ni6*      | 2.66 | Ni10      | 2.62 | Ni1       | 2.60 |
| Ni9     | 2.50 | Ni7      | 2.55 | Ni8      | 2.60 | Ni11      | 2.62 |           |      | Ni2       | 2.52 |
|         |      | Ni9      | 2.60 |          |      |           |      |           |      | Ni3*      | 2.78 |

be about 2.0 Å only. The distance to Ni4 (2.55 Å) is, however, acceptable. Around the completely vacant double position *C*, however, both the nearest nickel positions (Ni10 and Ni11) are occupied.

Compared to the subcell of Ni<sub>6</sub>Se<sub>6</sub>, the superstructure formation results in a doubling of the *a*-axis. Instead of a casual occupation of nickel positions a successive alternation between filled and empty sites is found. There are four such alternating pairs of positions in the *x*-direction: Vacancy *A* and Ni10; vacancy *B* and Ni6; vacancy *C* and Ni5; vacancy *D* and Ni3.

The atomic arrangements around the nickel atoms in Ni<sub>6</sub>Se<sub>6</sub> may be compared with those found in the neighbouring nickel selenides NiSe of the millerite- and of the NiAs-type and in Ni<sub>3</sub>Se<sub>2</sub>. In millerite (NiS) nickel is coordinated to five sulfur atoms in a deformed square pyramidal arrangement, and in addition, to two nickel atoms.<sup>11</sup> In the high temperature NiAs-type phase of NiSe nickel is octahedrally coordinated to selenium. According to the lattice constants of NiSe<sub>1.03</sub><sup>12</sup> the Ni–Se distances are 2.50 Å. In addition nickel is coordinated to two other nickel atoms at 2.68 Å. The Se–Se distances are 3.41 Å. In Ni<sub>3</sub>Se<sub>2</sub>, with rhombohedral crystal structure the nickel atoms are tetrahedrally surrounded by selenium at distances of 2.36 and 2.38 Å and, in addition, by four nickel atoms at about 2.60 Å. The shortest Se–Se distance in Ni<sub>3</sub>Se<sub>2</sub> is 3.67 Å.<sup>13,14</sup>

In Ni<sub>6</sub>Se<sub>6</sub> as well as in the nickel selenides referred to above there is no close Se–Se bonding contact. The shortest Se–Se distance in Ni<sub>6</sub>Se<sub>6</sub> is 3.31 Å whereas a corresponding bonding distance as found for example in NiSe<sub>2</sub><sup>12</sup> is 2.40 Å only. The shortest Ni–Ni distances found in Ni<sub>6</sub>Se<sub>6</sub> correspond well to those found in nickel metal (2.49 Å). The shortest Ni–Se distance in Ni<sub>6</sub>Se<sub>6</sub> (2.31 Å) is surprisingly short. This is, however, probably a consequence of the irregularity of the structure. Corresponding short metal-selenium distances are also observed in (Fe<sub>x</sub>Ni<sub>1-x</sub>)<sub>22</sub>Se<sub>16</sub><sup>15</sup> which also crystallizes in a kind of superstructure lattice.

The present superstructure of Ni<sub>6</sub>Se<sub>6</sub> was found in samples quenched from 420 °C. As mentioned above quenching from temperatures around 600 °C results in another type of superstructure. This structure is, however, not neces-

sarily stable at that temperature, but may be formed during the quenching procedure. The disorder in the atomic arrangement may possibly increase by increasing temperature, leading to a more casual occupation of some of the nickel positions. This will involve a possible variation in stoichiometry of the phase, just as has been observed for some ternary samples referred to above.<sup>5,6</sup>

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A copy of the intensity data from this investigation can be obtained from the authors.

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