

On the Structural Properties of the $\text{Nb}_{1+x}\text{Se}_2$ Phase

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The $\text{Nb}_{1+x}\text{Se}_2$ phase has a homogeneity range within the limits 60.8 (61.5 for samples quenched from 1000°C) and 66.67 atomic % Se. The structure is hexagonal and the lattice constants vary between the limits

$$\begin{aligned} \text{Nb}_{1.28}\text{Se}_2 : a &= 3.450 \text{ \AA}, c = 13.02 \text{ \AA}, c/a = 3.774 \\ (\text{Nb}_{1.25}\text{Se}_2 : a &= 3.425 \text{ \AA}, c = 12.92 \text{ \AA}, c/a = 3.743 \\ &\text{for samples quenched from } 1000^\circ\text{C}) \\ \text{Nb}_{1.00}\text{Se}_2 : a &= 3.446 \text{ \AA}, c = 12.55 \text{ \AA}, c/a = 3.643 \end{aligned}$$

Between ~ 63 and ~ 65.5 atomic % Se the existence of a superstructure has been observed.

As indicated by the formula $\text{Nb}_{1+x}\text{Se}_2$ the solid solution takes place by addition of niobium atoms as the niobium content increases from $\text{Nb}_{1.00}\text{Se}_2$ to $\text{Nb}_{1.28}\text{Se}_2$.

The crystal structure is of the NbS_2 (*H*) type. In terms of the space group $P6_3/mmc$ the unit cell contains $2+2x$ Nb and 4 Se in the positions:

$$\begin{aligned} 2 \text{ Nb in } (b) &\pm (0,0,\frac{1}{2}); 2x \text{ Nb in } (a) 0,0,0; 0,0,\frac{1}{2} \text{ and} \\ 4 \text{ Se in } (f) &\pm (\frac{1}{3},\frac{2}{3},z; \frac{2}{3},\frac{1}{3},\frac{1}{2}-z) \text{ with } z = \frac{1}{4}. \end{aligned}$$

A reaction between niobium and selenium was first observed by von Bolton.¹ However, no composition for the reaction product was given.

In a study of the reaction by diffusion in binary systems of the type metal-gas the niobium-selenium system among others was investigated by Arkharov *et al.*² Although no detailed analysis was carried out of the phase relationships in the niobium-selenium system, several phases were inferred from their characteristic X-ray patterns.

Recently Brixner³ has reported the existence of NbSe_2 and NbSe . Brixner suggests a continuous solid solution between NbSe_2 and NbSe . This is particularly interesting in relation to his reference to a corresponding observation in the TiTe_2 - TiTe system,⁴ which has recently been shown to be partly erroneous by Raaum *et al.*⁵ Brixner also reports data on the electrical, thermal and thermoelectric properties of NbSe_2 .

Recently unit cell dimensions for NbSe_2 have also been reported by Koerts.⁶

EXPERIMENTAL

Materials. The niobium metal used in this study was "Spectrographically standardized niobium" from Johnson, Matthey & Co., Ltd. Two batches of niobium, hereafter referred to as niobium I and niobium II, were purchased at different times. According to the supplied analysis niobium I contained 250 ppm of Ni and traces of Cu, Ag, Ti, Fe, and Si, whereas niobium II contained (in ppm): Fe (500), Si (100), Pb (80), Mg (2), Mn (1), and Ta (100).

A Guinier photograph of niobium I gave a lattice constant of 3.2999 Å, in close agreement with the value 3.300, Å, reported by Neuberger⁷ and Edwards *et al.*⁸ for pure niobium. Guinier photographs of niobium II on the other hand, contained diffuse reflections from a phase which could be identified as NbH_{0.89} described by Brauer *et al.*⁹ Niobium II was therefore carefully degassed in vacuum at 1000°C (final pressure 5×10^{-6} mm Hg). Guinier photographs of dehydrogenated niobium II did not contain reflections from NbH_{0.89}. The lattice constant of 3.3078 Å, however, indicated the presence of traces of hydrogen.

The highly purified selenium was a gift from Bolidens Gruvaktiebolag, Sweden. It carried the analysis (in ppm): Cu (2), Fe (0.8), K (0.3), Na (0.4) and non-volatile matter (12).

Preparations. Samples with composition 57.14, 58.33, 58.68, 59.02, 59.35, 59.68, 60.16, 60.78, 61.24, 61.54, 63.10, 64.29, 65.52, 66.10, 66.67, and 67.74 atomic % Se were made from niobium I and samples with 57.14, 58.33, 59.02, 59.68, 60.00, 60.16, 60.47, 60.78, 61.54, 62.26, 62.96, 64.29, 65.52, 65.75, 66.10, 66.67, 67.53, 67.74, and 68.25 atomic % Se were made from niobium II. The samples were prepared by heating the weighed quantities of niobium and selenium in evacuated and sealed silica tubes. In some cases crucibles of pure alumina were placed inside the silica tubes.

All samples were heated at 800°C for 8 days and cooled slowly to room temperature over a period of 2 days. Samples with 59.18, 61.54, 63.10, 64.29, 65.52, and 66.67 atomic % Se (and niobium II) were heated at 1000°C for 1 day and quenched in ice water. Samples with 64.29 and 65.52 atomic % Se were also heated at various temperatures between 500 and 1200°C, either quenched in ice water or cooled slowly.

X-Ray diffraction. All samples were crushed and X-ray photographs were taken in a Guinier camera of 80 mm diameter using strictly monochromatized CuK α_1 -radiation. X-Ray photographs were also taken in a Weissenberg camera of 57.3 mm diameter.

For the calculation of lattice constants by the Guinier method, potassium chloride (Analar, The British Drug Houses, Ltd. $a = 6.2919$ Å¹⁰) was added to the specimen as an internal standard. Lattice constants are expressed in Ångström units on the basis of $\lambda(\text{CuK}\alpha_1) = 1.54050$ Å.

Density measurements. The density of the samples was determined by the pycnometric method at 25°C with kerosene as displacement liquid. To remove gases adsorbed by the sample the pycnometer was filled with kerosene under vacuum. The samples weighed approximately 2 g.

RESULTS

In the niobium-selenium system the existence of one phase with a wide range of homogeneity has been established. The present paper gives an account of some structural properties of this phase, which has been designated Nb_{1+x}Se₂.

(i) *Limits of homogeneity.* The composition range, estimated using the disappearing phase method on the Guinier photographs, extends from ~60 to ~66.7 atomic % Se for slowly cooled samples and from ~62 to ~66.7 atomic % Se for samples quenched from 1000°C. The neighbouring phases are the Nb₃Se₄ phase and the "NbSe₄" phase reported elsewhere.^{11,12}

The strongest lines on the Guinier photographs of the Nb_{1+x}Se₂ phase could be indexed as hexagonal throughout the whole range of homogeneity, *cf.* Table 1. The lattice constants are listed in Table 2 for samples of various

Table 1. Guinier photograph data of the Nb_{1+x}Se₂ phase taken with strictly monochromatized CuK α_1 -radiation.

| <i>hkl</i> | $\sin^2\Theta \times 10^5 I_{\text{obs}}$ | | | | | | |
|------------|---|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| | Nb _{1.00} Se ₂ | Nb _{1.04} Se ₂ | Nb _{1.08} Se ₂ | Nb _{1.11} Se ₂ | Nb _{1.19} Se ₂ | Nb _{1.25} Se ₂ | Nb _{1.29} Se ₂ |
| 002 | 1498 m | 1501 m | 1489 st | 1519 st | 1438 st | 1429 st | 1404 st |
| 004 | | | | | | 5692 vw | |
| 100 | 6664 vw | 6664 vw | 6675 w | 6601 w | 6629 w | 6605 w | 6651 w |
| | | | | 6679 m | | | |
| 101 | 7027 vst | 7034 vst | 7036 st | 6987 st | 6987 vst | 6996 vst | 7003 st |
| | | | | 7430 vw | | | |
| 102 | 8174 st | 8150 vst | 8150 w | 8102 w | 8066 st | 8064 st | 8059 m |
| | | | 8980 vw | 8975 vw | | | |
| | | | 9302 vw | 9254 vw | | | |
| 103 | 10058 st | 10039 st | 10016 m | 9990 st | 9836 st | 9854 st | 9805 m |
| | | | 10786 vw | 10758 vw | | | |
| | | | 11217 vw | 11214 w | | | |
| 104 | 12709 st | 12671 vst | 12630 w | 12601 w | 12365 st | 12362 vst | 12262 st |
| 006 | 13593 w | 13498 w | 13441 w | 13555 w | | 12852 w | |
| | | | | 14203 vw | | | |
| 105 | 16060 w | 16047 w | 15951 vw | 16028 w | 15579 vw | 15585 m | 15402 w |
| 110 | 19993 vst | 19993 vst | 20003 vst | 19840 vst | 19909 vst | 19902 vst | 19941 vst |
| 106 | 20227 vw | 20168 w | | | | 19475 w | |
| 112 | 21489 m | 21471 w | 21443 m | 21332 m | 21353 w | 21335 m | 21325 w |
| 008 | 24110 w | | 23885 w | 24095 m | 22950 w | 22838 m | 22403 vw |
| 107 | 25121 w | 25049 m | | | | | 23786 w |

Table 2. Lattice constants of the Nb_{1+x}Se₂ phase in samples made from niobium I.

| Composition | <i>a</i> (Å) | <i>c</i> (Å) | <i>c/a</i> |
|---|--------------|--------------|------------|
| Nb _{1.00} Se ₂ | 3.446 | 12.55 | 3.643 |
| Nb _{1.03} Se ₂ | 3.446 | 12.56 | 3.645 |
| Nb _{1.04} Se ₂ | 3.446 | 12.58 | 3.651 |
| Nb _{1.05} Se ₂ | "3.446" | "12.61" | "3.659" |
| Nb _{1.11} Se ₂ | "3.459" | "12.55" | "3.629" |
| Nb _{1.17} Se ₂ ^a | 3.452 | 12.82 | 3.714 |
| Nb _{1.19} Se ₂ | 3.453 | 12.86 | 3.725 |
| Nb _{1.25} Se ₂ ^b | 3.453 | 12.89 | 3.733 |
| Nb _{1.27} Se ₂ | 3.451 | 12.96 | 3.755 |
| Nb _{1.29} Se ₂ | 3.450 | 13.02 | 3.774 |
| α -NbSe ₂ ^c | 3.449 | 12.998 | 3.769 |
| β -NbSe ₂ ^c | 3.439 | 25.188 | 7.324 |
| NbSe ₂ ^d | 3.43 | 12.51 | 3.647 |
| NbSe ^c | 3.437 | 13.030 | 3.791 |

^a Made from niobium II. Heated 1 day at 1000°C and quenched.^b For samples quenched from 1000°C the limiting lattice constants (found at this composition) are *a* = 3.452 Å, *c* = 12.92 Å.^c Quoted from Brixner.³^d Quoted from Koerts.⁶

composition. The changes in length of the a - and c -axis determined the composition at the selenium-rich phase limit. For the selenium-poor phase limit it is necessary to distinguish between the results from the two batches of niobium. Samples containing niobium I show large variations in the lattice constants with composition, whereas the corresponding values for the samples made from niobium II are almost constant.

The changes in unit cell dimensions with composition indicate that the selenium-poor limit of the phase is close to 60.8 atomic % Se for samples slowly cooled from 800°C (made from niobium I) and 61.5 atomic % Se for samples quenched from 1000°C (niobium II). In terms of the notation $Nb_{1+x}Se_2$ the corresponding phase limits are $0.00 \leq x \leq 0.29$ and $0.00 \leq x \leq 0.25$.

The same results were not obtained with the samples containing niobium II when these were treated as the samples containing niobium I, *cf.* Fig. 1. The difference between the two series of results is explained by the tendency of niobium to react with silica. According to Schäfer and Dohmann¹³ this reaction is catalysed by the presence of hydrogen, traces of which are present in niobium II. Samples with selenium content higher than ~ 65.5 atomic % Se are unaffected by the difference between the two batches of niobium. Attempts to synthesize niobium selenides from niobium II with selenium content lower than ~ 65.5 atomic % Se, however, invariably lead to a mixture of $\sim Nb_{1.05}Se_2$ (65.5 atomic % Se), Nb_5Si_3 and NbO (*cf.* Fig. 1). For samples with composition ≤ 62.5 atomic % Se the additional lines from Nb_5Si_3 and NbO are easily seen on the Guinier photographs. (For samples with composition ≤ 61 atomic % Se the silica tubes also show considerable crystallization.) Evidently equilibrium is reached at $\sim Nb_{1.05}Se_2$, the excess of niobium being transformed into Nb_5Si_3 and NbO. However, short heat treatment at relatively high temperatures (1 day at 1000°C) produces samples from niobium II which for a selenium content higher than ~ 61.5 atomic % Se resemble those made from niobium I.

(ii) *Symmetry and dimensional variations in the unit cell.* Although the strongest reflections on the Guinier photographs have been indexed as hexagonal throughout the homogeneity range, a pronounced difference in the appearance of the photographs is observed between ~ 63 and ~ 65.5 atomic % Se, *cf.* Table 1. The basic structure in this concentration range is different from that in the rest of the homogeneity range. The superstructure reflections, *cf.* Table 1, have not yet been reasonably indexed. The differences in the photographs are also noticed in the linepattern of the strong reflections. The lattice constants of for example $Nb_{1.11}Se_2$ (64.3 atomic % Se) fall far outside the smooth curves of the lattice constants variation in Fig. 1.

A comparison of the present results with those obtained by Brixner³ and Koerts⁶ is given in Table 2. The present data show reasonable agreement with Koerts' values for $NbSe_2$. The discrepancy between the present data and those of Brixner is obvious. By the experimental technique used in this study no indications of the dimorphism of $NbSe_2$ were observed. Brixner's article either contains a misprint in the value listed for the c -axis of α - $NbSe_2$ or the composition stated for this sample is considerably erroneous, *cf.* Table 2. (According to the present results a sample with those dimensions ought to have a composition $\sim Nb_{1.29}Se_2$.) The lattice constant values reported by Brixner for $NbSe$ are in close agreement with the present values for the selenium-poor phase limit. However, the composition $NbSe$ is apparently quite wrong. $Nb_{1.29}Se_2$ is the limit found in this study and according

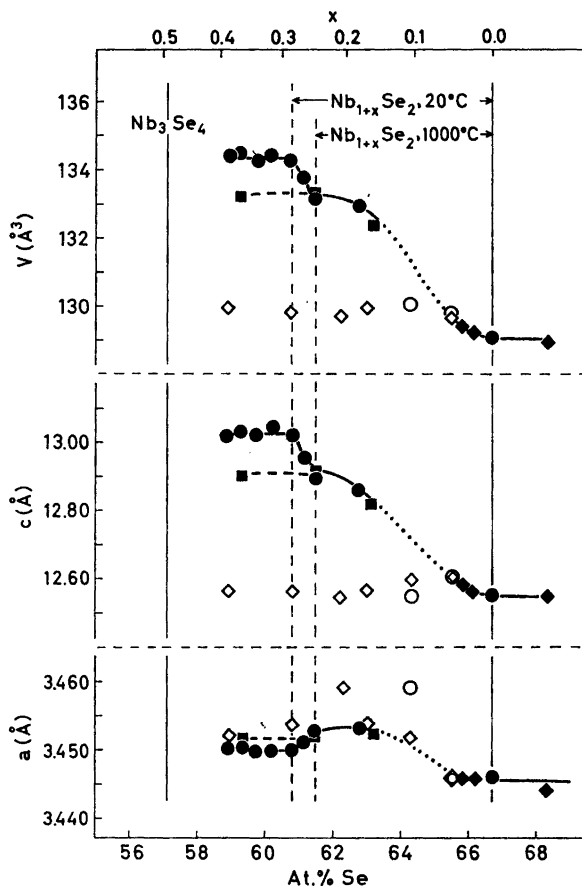


Fig 1. Variations in lattice constants of the $Nb_{1+x}Se_2$ phase as function of composition. Results both for the niobium I (●) and niobium II (◆ 8 days at 800°C, slowly cooled; ■ 1 day at 1000°C, quenched) series are shown. The occurrence of superstructure reflections in the Guinier photographs is indicated by the corresponding open symbols.

to Selte and Kjekshus¹¹ another phase, *i.e.* the Nb_3Se_4 phase, is present in samples with selenium content $50 \leq \text{atomic \% Se} \leq 60.8$.

(iii) *The crystal structure of $NbSe_2$.* Well formed, platy single crystals of hexagonal shape were obtained in samples with composition ~ 66.7 atomic % Se. A pronounced cleavage is observed parallel to the hexagonal faces.

Some of these crystals were investigated on the Weissenberg goniometer with the rotation axis along the hexagonal axis. The photographs confirmed the hexagonal symmetry of the crystals. Comparing the unit cell dimensions with those obtained from the Guinier photographs the composition of the crystals was estimated to be $Nb_{1.00}Se_2$.

The only systematic extinctions were of the type

$$hkl \text{ when } h-k = 3n \text{ and } l = 2n + 1.$$

The Laue symmetry is $6/mmm$ and the possible space groups are $P6_322$, $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$.

A hexagonal structure with this composition and similar unit cell dimensions has been observed in the niobium-sulfur system by Jellinek *et al.*¹⁴ The possibility of NbSe_2 and NbS_2 (*H*) being isostructural was therefore investigated. According to Jellinek *et al.* the atomic arrangement in the NbS_2 (*H*) structure in terms of the space group $P6_3/mmc$ is as follows, *cf.* Fig. 2:

$$\begin{aligned} 2 \text{ Nb in } (b) &\pm (0, 0, \frac{1}{4}) \\ 4 \text{ S in } (f) &\pm (\frac{1}{3}, \frac{2}{3}, z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z) \text{ with } z = \frac{1}{8} \end{aligned}$$

(This arrangement of the atoms can be obtained in all of the four possible space groups and an unambiguous space group determination accordingly cannot be given.)

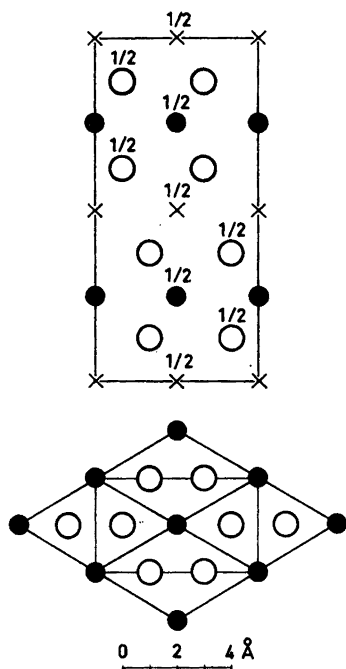


Fig. 2. The NbS_2 (*H*) structure. The structure is shown in two projections. Four unit cells are shown along $[001]$ (an orthohexagonal cell is also indicated in this projection) and above this there is a projection of the orthohexagonal cell along $[100]$. The numbers indicate fractional heights of atoms on the projection. Filled-in circles represent the niobium atoms and open circles the selenium atoms. Crosses indicate the positions of partially filled lattice sites.

Intensity measurement of the $hk0$, $hk1$ and $hk2$ -reflections were carried out visually on the Weissenberg photographs, using the multiple-film technique, and corrected for the combined Lorentz and polarization factor. For the calculation of F_c -values the atomic scattering factors were taken from *Internationale Tabellen*. No corrections for absorption, extinction or temperature factors were applied.

The agreement between F_o and F_c is expressed by the reliability index:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

All possible reflections were observed on the various Weissenberg photographs. The agreement between F_o and F_c was good, cf. Table 3, ($R(hk0)=0.084$, $R(hk1)=0.075$ and $R(hk2)=0.070$) and leaves no doubt about the correctness of the proposed structure. The small values of R show that the temperature and absorption factors nearly neutralize each other. For sym-

Table 3. Observed and calculated structure factors for NbSe₂.

| hkl | F_o | F_c | hkl | F_o | F_c | hkl | F_o | F_c |
|-------------|-------|-------|-------------------|-------|-------|-------------|-------|-------|
| $1\bar{1}0$ | 14.9 | 11.6 | $4\bar{1}0$ | 8.7 | 7.6 | 112 | 46.7 | -53.6 |
| 100 | 14.3 | 11.6 | $\bar{1}\bar{1}1$ | 64.9 | 67.1 | 222 | 54.2 | -49.8 |
| 110 | 135.2 | 141.6 | 101 | 59.7 | -67.1 | $2\bar{1}2$ | 52.4 | -53.6 |
| $2\bar{2}0$ | 17.2 | 9.6 | $2\bar{2}1$ | 53.5 | -49.7 | 202 | 48.9 | -49.8 |
| $2\bar{1}0$ | 133.9 | 141.6 | 201 | 48.1 | 49.7 | 212 | 43.9 | -42.6 |
| 200 | 16.6 | 9.6 | 211 | 42.3 | -42.4 | 222 | 40.2 | -36.6 |
| 210 | 9.8 | 8.0 | $3\bar{2}1$ | 46.3 | 42.4 | $3\bar{3}2$ | 37.0 | -39.8 |
| 220 | 92.3 | 95.2 | $3\bar{1}1$ | 45.3 | -42.4 | $3\bar{2}2$ | 47.7 | -42.6 |
| 330 | 96.6 | 104.0 | 311 | 40.4 | 34.8 | $3\bar{1}2$ | 46.8 | -42.6 |
| $3\bar{2}0$ | 11.2 | 8.0 | 431 | 28.6 | -34.8 | 302 | 38.3 | -39.8 |
| $3\bar{1}0$ | 12.6 | 8.0 | $4\bar{1}1$ | 36.1 | 34.8 | 312 | 38.9 | -35.6 |
| 300 | 95.8 | 104.0 | $\bar{1}\bar{1}2$ | 68.2 | -65.0 | $4\bar{3}2$ | 29.7 | -35.6 |
| 310 | 7.6 | 7.6 | 102 | 62.7 | -65.0 | $4\bar{2}2$ | 33.9 | -36.6 |
| $4\bar{3}0$ | 8.1 | 7.6 | | | | $4\bar{1}2$ | 34.6 | -35.6 |
| $4\bar{2}0$ | 95.9 | 95.2 | | | | | | |

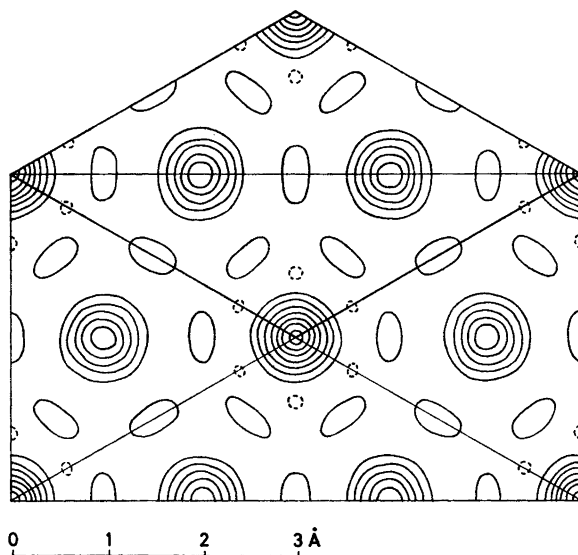


Fig. 3. Electron density projection of NbSe₂ on (001). Contours are at intervals of 10 e·Å⁻². The zero contours are broken. Both the hexagonal and orthohexagonal unit cell are indicated.

metry reasons only the 4 Se atoms in (f) contribute to the hkl -reflections. The z -coordinates of the 2 Nb atoms in (b) are tested by the $hk2$ -reflections to which both the Nb and Se atoms should contribute. The electron density projection on (001) is shown in Fig. 3.

(iv) *The structure of the $Nb_{1+x}Se_2$ phase.* Results of the density determinations are presented in Fig. 4. The observed values are in reasonable agreement with those calculated on the basis of addition of niobium atoms only with changing composition from $Nb_{1.00}Se_2$ to $Nb_{1.29}Se_2$. The lower density of samples with < 64.3 atomic % Se made by heating niobium II and selenium 8 days at $800^\circ C$ is explained by the fact that these samples consist of a mixture of $\sim Nb_{1.05}Se_2$, Nb_5Si_3 , and NbO (see section i).

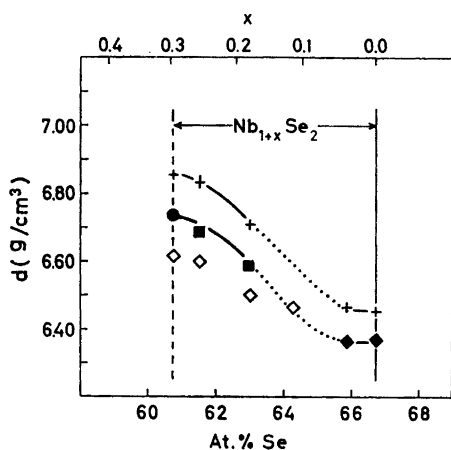


Fig. 4. Observed (●, ◆, ◁, ■; see caption to Fig. 1) and calculated (+) densities for the $Nb_{1+x}Se_2$ phase.

The $NbSe_2$ crystals have vacant positions which can accommodate the additional metal atoms. According to space group $P6_3/mmc$ the available empty positions are $2(a)$ $0,0,0$; $0,0,\frac{1}{2}$, indicated by crosses in Fig. 2. To test the hypothesis that the vacant positions are gradually filled up with niobium atoms the powder photograph data were considered, as single crystals were only available for $NbSe_2$. Reflections with $l = 2n$ should increase in intensity as more and more niobium atoms are added to position 2 (a). This was indeed confirmed by a careful visual inspection of Debye-Scherrer photographs.

(v) *Interatomic distances in the structure of the $Nb_{1+x}Se_2$ phase.* In the NbS_2 (H) type structure of $NbSe_2$, cf. Fig. 2, each Nb atom is coordinated to 6 Se atoms at the corners of a trigonal prism. Two selenium atoms form the top and bottom of an almost regular, trigonal bipyramid, cf. Fig. 5, with three niobium atoms at the corners of the triangle.

On adding Nb atoms to obtain the filled-in $Nb_{1+x}Se_2$ structure the coordination of the original Nb atoms remains unchanged. Each added Nb atom is coordinated to 6 Se atoms at the corners of a regular octahedron. Each Se atom is coordinated to $3+3x$ Nb atoms at the corners of a trigonal prism.

The interatomic distances between nearest neighbours are listed in Table 4.

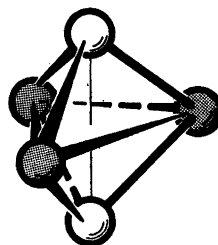


Fig. 5. The trigonal bipyramid formed by two selenium and three niobium atoms.

An ionic description of NbSe_2 would presumably correspond to the ions Nb^{4+} and Se^{2-} . The radius of the Nb^{4+} ion is difficult to assign. The distance 2.68 Å, being the sum of the Nb^{5+} and Se^{2-} radii according to Pauling,¹⁵ is larger than the observed distance, cf. Table 4. A more realistic ionic distance based on Nb^{4+} would be expected to be still larger, *i.e.* definitely larger than the observed distances, *cf.* Table 4.

Table 4. Interatomic distances in $\text{Nb}_{1+x}\text{Se}_2$ (Å).

| | | $x=0.00$ | $x=0.04$ | $x=0.19$ | $x=0.25$ | $x=0.29$ |
|------|-------------|----------|----------|----------|----------|----------|
| Nb — | x Nb | — | 3.145 | 3.215 | 3.223 | 3.255 |
| | 6 Nb | 3.446 | 3.446 | 3.453 | 3.453 | 3.450 |
| | 6 Se | 2.534 | 2.537 | 2.562 | 2.565 | 2.572 |
| Se — | $3 + 3x$ Nb | 2.534 | 2.537 | 2.562 | 2.565 | 2.572 |
| | 1 Se | 3.139 | 3.145 | 3.215 | 3.223 | 3.255 |
| | 6 Se | 3.446 | 3.446 | 3.453 | 3.453 | 3.450 |
| | 3 Se | 3.716 | 3.721 | 3.784 | 3.790 | 3.816 |

The observed interatomic distances can also be compared with the values predicted from the metallic radii. Using the single bond radius value of 1.342 Å for Nb and 1.17 Å for Se, with an electronegativity correction of -0.032 Å and bond number $\frac{2}{3}$, the estimated Nb-Se distance is 2.586 Å. This value is somewhat larger than the observed distance.

To account for this discrepancy one can assume a higher bond number for the Nb-Se bonds. Higher bond number would be found, according to Pauling,¹⁵ if one electron is transferred from the hyperelectronic Se atom to the hypoelectronic Nb atom thus increasing the valences.

If x is determined by the composition $\text{Nb}_{1+x}\text{Se}_2$ the selenium atoms have a valence number $v = 2 + (1 + x)/2 = 2.5 + 0.5x$ and coordination number $L = 3(1 + x) = 3 + 3x$. The calculated Nb-Se distances according to the formula

$$1.342 \text{ Å} + 1.17 \text{ Å} - 0.032 \text{ Å} - 0.600 \log \frac{2.5 + 0.5x}{3 + 3x}$$

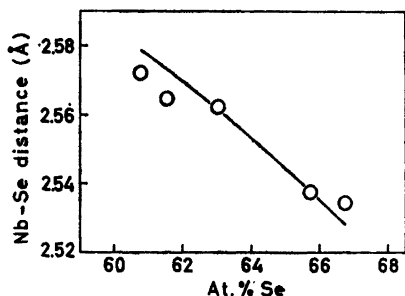


Fig. 6. Comparison of observed (O) and predicted Nb-Se distances.

are shown in Fig. 6 together with the corresponding observed interatomic distances, *cf.* Table 4. As seen from Fig. 6 a reasonable agreement is obtained. However, Paulings theory also predicts some short Nb-Nb distances (because of residual valence on the Nb atoms) which are not observed. On the contrary, relatively short Se-Se distances, *cf.* Table 4 and Fig. 5, are found. This short Se-Se distance is much shorter than the expected van der Waals distance of ~ 4 Å. Assuming that bonding orbitals are pointing from the selenium atoms towards the niobium atoms in Fig. 5, a fourth orbital concentrated in the middle of these three looks unlikely. One should therefore expect that the short Se-Se distance is caused by the geometry and that these two selenium atoms are in fact not bond to each other.

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