

## The Crystal Structure of Niobium Selenide Nb<sub>2</sub>Se<sub>9</sub> from Twin-Crystal Data

BY A. MEERSCHAUT, L. GUÉMAS, R. BERGER\* AND J. ROUXEL

Laboratoire de Chimie Minérale A, LA 279, 2 rue de la Houssinière, 44072-Nantes CEDEX, France

(Received 28 June 1978; accepted 10 April 1979)

### Abstract

Nb<sub>2</sub>Se<sub>9</sub> crystallizes in the triclinic system, space group *P*1̄, with  $a = 8.1829(6)$ ,  $b = 8.3230(6)$ ,  $c = 13.084(1)$  Å,  $\alpha = 120.893(6)$ ,  $\beta = 124.017(7)$ ,  $\gamma = 92.274(8)^\circ$ ,  $Z = 2$ ,  $d_m = 5.26(1)$ ,  $d_x = 5.29$  Mg m<sup>-3</sup>. The structure has been determined from a twinned crystal from 301 non-overlapping independent reflexions. The refinement of the positional and thermal parameters has yielded a reliability factor  $R = 0.11$ . The geometrical aspects of the structure reveal marked one-dimensional character. Channels between the niobium–selenium chains are observed.

### Introduction

Three niobium selenides with approximate composition NbSe<sub>4</sub> were initially reported (Selte & Kjekshus, 1964). However, it has recently been shown that two of these are in fact Nb<sub>2</sub>Se<sub>9</sub> (Guémas, Meerschaut & Palvadeau, 1975) and INb<sub>3</sub>Se<sub>12</sub> (Meerschaut, Palvadeau & Rouxel, 1977).

### Crystallographic characterization

Nb<sub>2</sub>Se<sub>9</sub> was prepared by direct combination of the elements in sealed silica tubes at temperatures ranging from 773 to 873 K (Guémas *et al.*, 1975). The resulting needle-shaped crystals permitted the determination of the symmetry and approximate lattice parameters. The latter were refined by the least-squares method using powder data obtained from a Guinier–Hägg focusing camera with strictly monochromatized Cr  $K\alpha_1$  radiation ( $\lambda = 2.28975$  Å). Silicon was used as an internal calibration standard, assuming  $a = 5.431065$  Å (Deslattes & Henins, 1973). The X-ray powder intensity data were obtained from measurements on films with a SAAB model 2 automatic film scanner adapted for this purpose (Malmros & Werner, 1973; SAAB, 1967). Table 1 shows the results of the refinement and intensity measurements.

\* Permanent address: University of Uppsala, Institute of Chemistry, Box 531 S-751 21 Uppsala, Sweden.

Table 1. Powder diffraction data for Nb<sub>2</sub>Se<sub>9</sub>

Data were measured using a Guinier–Hägg camera with Cr  $K\alpha_1$  radiation. Intensities are on a relative numerical scale.

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I/I_0$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I/I_0$
8.249	8.271	0 0 1	28	2.7411	2.7418	2 $\bar{2}$ 1	18
6.348	6.343	0 1 0	93	2.7363	2.7384	0 $\bar{3}$ 3	
6.030	6.024	1 0 0	49	2.7111	2.7111	0 $\bar{2}$ 4	8
5.940	5.939	1 1 0	42	2.5667	2.5678	1 $\bar{3}$ 3	21
5.649	5.648	1 1 $\bar{2}$	6	2.5572	2.5578	1 0 4	100
5.0452	5.0450	1 1 $\bar{1}$	5		2.5576	1 $\bar{3}$ 4	
4.9728	4.9702	1 1 1	4	2.5428	2.5434	3 1 4	15
4.1349	4.1357	0 0 2	3	2.5293	2.5304	3 0 4	8
4.0771	4.0781	2 0 2	24	2.5122	2.5129	3 1 3	16
3.7439	3.7447	1 $\bar{2}$ 1	2	2.4984	2.4992	0 1 4	32
3.5893	3.5880	1 0 3	5	2.4864	2.4867	0 $\bar{3}$ 4	42
3.5582	3.5595	2 0 3	3		2.4850	3 1 3	
3.5200	3.5211	1 2 2	4	2.4740	2.4743	0 2 1	2
3.4846	3.4828	0 1 3	30	2.3897	2.3899	1 2 0	17
3.4717	3.4701	0 $\bar{2}$ 3				2.3631	1 $\bar{3}$ 0
3.4520	3.4546	2 1 2	6	2.3630	2.3627	2 0 1	23
3.4071	3.4065	2 1 2	2	2.3446	2.3450	2 2 2	1
3.3016	3.3005	1 1 2	9	2.3357	2.3363	2 1 0	2
3.2795	3.2791	1 2 2	6	2.3283	2.3280	2 3 1	3
3.1731	3.1716	0 2 0	6	2.2973	2.2967	2 3 0	5
3.1134	{ 3.1135 3.1136 }	{ 1 2 4 1 1 4 }	53	2.2862	2.2860	3 1 2	4
3.0118	3.0119	2 0 0		3	2.2508	2.2512	3 2 2
2.9697	2.9693	2 2 0	3	2.2316	2.2321	3 1 0	21
2.8986	2.9003	2 1 1	1	2.2207	2.2211	3 2 4	40
2.8247	2.8242	2 2 4	7	2.1962	2.1954	3 1 4	9
2.8108	2.8099	2 2 3	40	2.1136	2.1135	2 3 1	13
2.7770	2.7775	2 1 3	34	2.1058	2.1050	1 3 4	21
2.7606	2.7605	2 1 1	14	2.0850	2.0850	2 2 3	5

In our attempts to determine the structure of Nb<sub>2</sub>Se<sub>9</sub>, we unfortunately found that all the crystals we tested exhibited twinning. Since the crystals are opaque and show a metallic lustre, an ordinary polarizing microscope was of no use in deciding which crystals might be non-twinned. Even after breaking the crystals into smaller fragments we could not select any which were not twinned, as was revealed by X-ray diffraction. Moreover, the crystals are ductile and were easily deformed by such treatment.

We therefore undertook a study by film techniques (Weissenberg multiple film) which allowed us to distinguish the relative intensities coming from the twin individuals, after having selected an arbitrary axis. In order to increase the resolution radiation with as long a wavelength as possible was required. However, this choice limits the number of diffracted lines. The

diffraction intensity data were recorded in equi-inclination Weissenberg geometry with Cu *K* $\alpha$  radiation. Photographs taken after a rotation about the *c* axis indicated the twin orientation. The two reciprocal lattices from the twin individuals are oriented as shown in Fig. 1. As the three axes must form a right-handed set, *C*<sub>1</sub><sup>\*</sup> is found to be upward and *C*<sub>2</sub><sup>\*</sup> downward. Thus the crystal was twinned by pseudo-merohedry.

The crystal used for the structure determination had the approximate dimensions 1.60 × 0.02 × 0.01 mm. Because of the twinning, no acceptable absorption correction could be performed. Since  $\mu = 54.7 \text{ mm}^{-1}$ , neglecting absorption is likely to have introduced systematic errors.

301 non-overlapped independent reflexions were measured with the aid of a Nonius microdensitometer. When the spots were not well separated, the intensities had to be estimated visually for some 50 reflexions. All intensities were corrected for Lorentz and polarization effects.

Interpretation of the three-dimensional Patterson function allowed us to identify all the atomic positions in the cell and to form a reasonable picture of the structure. The atoms were assigned to the 2(*i*) positions in space group *P* $\bar{1}$ .

The subsequent refinement of the structure was performed using the *SFLS-5* program (Prewitt, 1966). The atomic scattering factors were calculated according to the technique devised by Vand, Eiland &

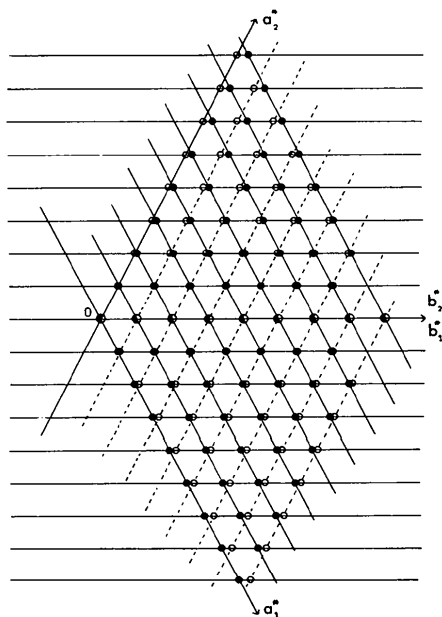


Fig. 1. *hk*0 reciprocal lattice section showing the twin type. The reciprocal lattice of unit (1) is drawn with full lines and full circles. That of unit (2) is drawn with dashed lines and open circles. The *b*<sup>\*</sup> axes are common to both.

Table 2. *Final structure data for Nb<sub>2</sub>Se<sub>9</sub>*

Standard deviations are given in parentheses. All atoms were assigned the position 2(*i*).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Nb(1)	0.049 (2)	0.034 (2)	0.136 (2)	0.3 (3)
Nb(2)	0.982 (2)	0.036 (2)	0.398 (2)	0.1 (3)
Se(1)	0.449 (3)	0.215 (3)	0.417 (3)	1.3 (5)
Se(2)	0.361 (3)	0.204 (3)	0.687 (3)	0.4 (4)
Se(3)	0.309 (2)	0.123 (3)	0.914 (2)	0.0 (3)
Se(4)	0.194 (3)	0.340 (3)	0.152 (3)	0.5 (4)
Se(5)	0.156 (3)	0.337 (3)	0.417 (3)	1.5 (5)
Se(6)	0.113 (3)	0.333 (3)	0.676 (3)	0.8 (4)
Se(7)	0.823 (3)	0.188 (3)	0.006 (3)	0.9 (4)
Se(8)	0.796 (2)	0.108 (2)	0.700 (2)	0.0 (3)
Se(9)	0.736 (3)	0.194 (3)	0.281 (2)	0.6 (4)

Pepinsky (1957), as modified by Forsyth & Wells (1959).

$$f_i = A_i \exp[-a_i(\sin \theta/\lambda)^2] + B_i \exp[-b_i(\sin \theta/\lambda)^2] + C_i$$

The constants in this formula corresponding to Nb<sup>0</sup> and Se<sup>0</sup> were taken from Moore (1963). Values for the anomalous-dispersion corrections were those in *International Tables for X-ray Crystallography* (1962).

The final refinement on *F* of the positional parameters, scale factors and isotropic temperature factors yielded the *R* value  $R = \sum (|F_o| - K|F_c|) / \sum |F_o| = 0.11$ .

The relatively high *R* value is probably due to the difficulties encountered in working with twin data. The absence of an absorption correction is also likely to have affected *R*. The systematic errors are partly reflected in the thermal parameters but do not affect the positional parameters to a large extent. It was not considered worth abandoning the centrosymmetrical description. Accordingly, the final coordinates and isotropic temperature factors as refined in space group *P* $\bar{1}$  are presented in Table 2.\*

### Description of the structure

Fig. 2 shows the projection of the structure on the *xy* plane, partly illustrating the channels in the structure.

The Nb atoms form non-linear chains along the *c* axis as illustrated in Fig. 3. In these, long (3.76 Å) and short (2.89 Å) intermetallic distances alternate. The shortest distance [Nb(1)–Nb(1') and Nb(2)–Nb(2')] characterizes a Nb–Nb pair. It is compatible with the value of 2.94 Å found in the ternary selenide Nb<sub>3</sub>Se<sub>5</sub>Cl<sub>7</sub> (Rijnsdorp, 1978). The Nb–Nb distances between

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34363 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

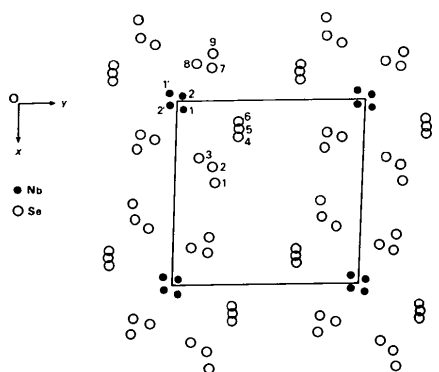


Fig. 2. Crystal structure of  $\text{Nb}_2\text{Se}_9$ , projected on the  $xy$  plane; superscript (i) refers to the centrosymmetric position  $\bar{x}, \bar{y}, \bar{z}$ .

neighbouring chains are equal to the  $a$  and  $b$  parameters, *i.e.* 8.1829 and 8.3230 Å, respectively.

The Se atoms appear as  $\text{Se}_2$  and  $\text{Se}_3$  units. The Se atoms lie more or less in planes approximately  $\frac{1}{4}c$  apart. Each Nb atom is surrounded by one  $\text{Se}_3$  and two  $\text{Se}_2$  units as illustrated in Fig. 3. According to the interatomic distances, given in Table 3, each Nb atom is coordinated to eight Se atoms. Although non-equivalent, Nb(1) and Nb(2) hardly differ as regards their coordination geometry, and the averages of their eight respective Nb–Se distances are equal (2.66 Å).

Nb can be considered to exhibit a bicapped-trigonal-prismatic coordination. Trigonal prisms are also found in the two binary selenides  $\text{NbSe}_2$  (Kadijk, 1969) and  $\text{NbSe}_3$  (Meerschaut & Rouxel, 1975). However, the coordination numbers and the linking of the prisms are different. As can be inferred from Fig. 3, the centrosymmetrically related prisms share one quadrilateral face and enable a short Nb–Nb distance to form. These  $\text{Nb}_2\text{Se}_{12}$  'double prisms' are in turn connected by sharing three Se atoms at each end, forming a plane perpendicular to the Nb chain in concordance with the overall composition  $\text{Nb}_2\text{Se}_9$ . The details of these connections are shown in Fig. 4.

The Se atoms taking part in the shared quadrilateral faces form  $\text{Se}_2$  units (probably  $\text{Se}_2^{2-}$ ) with shorter interatomic distances than are found in the buckled  $\text{Se}_3$  chain. The latter distances are quite compatible with those found in the other niobium selenides and are as expected from the Se covalent radius of 1.16 Å (Pauling, 1960).

### Comparison with other compounds

$\text{Nb}_2\text{Se}_9$  is a new example of a pseudo one-dimensional compound presenting Nb–Nb pairs forming a chain. In  $\text{NbSe}_3$ , the intermetallic distances are longer than the metallic contacts although the Nb atoms form an even-spaced chain. However, the corresponding sulphide  $\text{NbS}_3$  permits pair formation (Rijnsdorp, 1978).

In the ternary compound  $\text{INb}_3\text{Se}_{12}$  (Meerschaut *et al.*, 1977), there are also Nb chains broken up into metal-atom pairs. Nb is coordinated to eight Se atoms in a slightly distorted rectangular antiprismatic arrangement, the Se atoms being attributed to  $\text{Se}_2^{2-}$  units. The I atoms are incorporated between the chains.

Formally, a few 'one-dimensional' niobium selenides can be discussed from a common stand-point, all compounds being derived from the hitherto hypothetical compound  $\text{NbSe}_4$ , which is built up of Nb chains enclosed by  $\text{Se}_4$  units. With this description the chain can be written as  $\dots\text{NbSe}_4\text{NbSe}_4\dots$ . The chain in

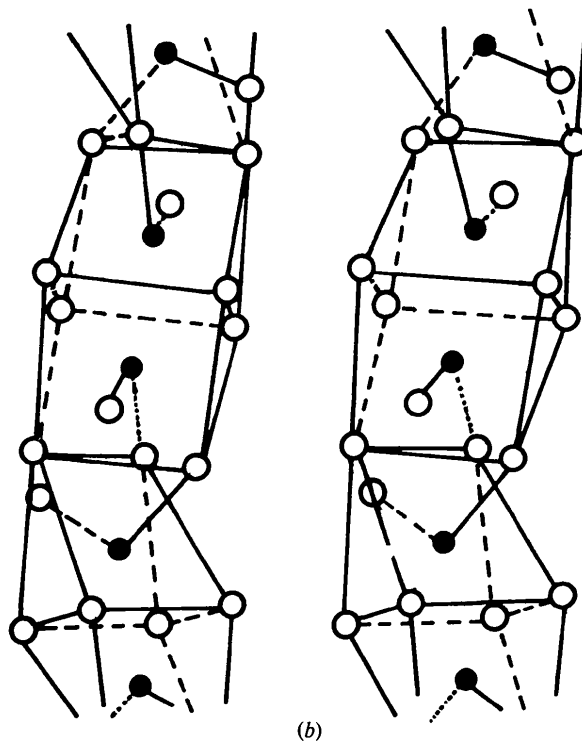
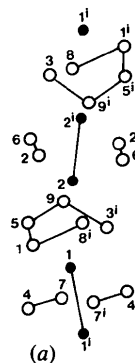


Fig. 3. (a) One chain of  $\text{Nb}_2\text{Se}_9$  projected along the  $c$  axis. Short Nb–Nb and Se–Se distances are denoted by full lines, emphasizing  $\text{Nb}_2$  pairs,  $\text{Se}_2$  and  $\text{Se}_3$  units. (b) Stereoscopic view as given by ORTEP Johnson (1965). The bicapped-trigonal-prismatic coordination is shown.

Table 3. *Interatomic distances (Å) in Nb<sub>2</sub>Se<sub>9</sub>*

Standard deviations are given in parentheses. The superscript (i) refers to the centrosymmetrical position.

Nb(1)—Nb(2)	3.76 (3)	Nb(2)—Se(2)	2.64 (2)	
Nb(1)—Nb(1 <sup>i</sup> )	2.89 (3)	—Se(5)	2.66 (4)	
Nb(2)—Nb(2 <sup>i</sup> )	2.88 (3)	—Se(6)	2.58 (2)	
		—Se(2 <sup>i</sup> )	2.62 (3)	
Nb(1)—Se(4)	2.62 (4)	—Se(6 <sup>i</sup> )	2.63 (3)	
—Se(5)	2.70 (3)	—Se(3 <sup>i</sup> )	2.72 (2)	
—Se(7)	2.63 (3)	—Se(8 <sup>i</sup> )	2.76 (3)	
—Se(4 <sup>i</sup> )	2.63 (2)	—Se(9)	2.64 (3)	
—Se(7 <sup>i</sup> )	2.60 (3)			
—Se(8 <sup>i</sup> )	2.70 (3)	Se(4)—Se(7)	2.28 (3)	} Isolated pairs
Se(1)	2.64 (2)	Se(2)—Se(6)	2.30 (3)	
—Se(3 <sup>i</sup> )	2.72 (3)			
		Se(8 <sup>i</sup> )—Se(1)	2.34 (3)	} Polyanion constituted by five Se atoms
		Se(1)—Se(5)	2.64 (4)	
		Se(5)—Se(9)	2.66 (3)	
		Se(9)—Se(3 <sup>i</sup> )	2.36 (3)	

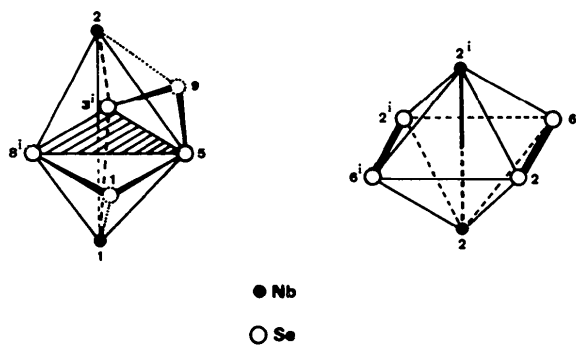


Fig. 4. The Se atom arrangement between Nb(1)—Nb(2) and Nb(2)—Nb(2<sup>i</sup>).

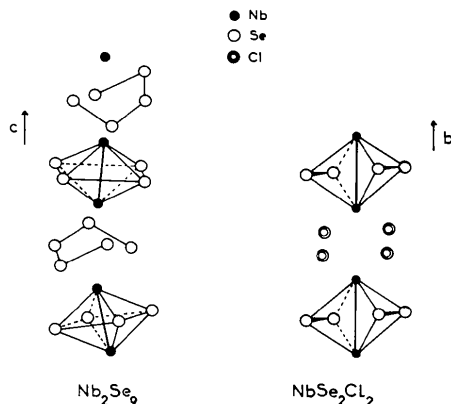


Fig. 5. The Nb<sub>2</sub>Se<sub>9</sub> and NbSe<sub>2</sub>Cl<sub>2</sub> structures (Rijnsdorp, 1978). 'Nb<sub>2</sub>Se<sub>4</sub>' cages which are common to both these structures are shown.

INb<sub>3</sub>Se<sub>12</sub> is written in a similar manner while that in Nb<sub>2</sub>Se<sub>9</sub> is described as ...NbSe<sub>4</sub>NbSe<sub>5</sub>.... The ternary selenide NbSe<sub>2</sub>Cl<sub>2</sub> (Rijnsdorp, 1978) also contains

chains, these being in the form ...NbSe<sub>4</sub>NbCl<sub>4</sub>.... A common structural unit for the existing compounds is an octahedral Nb<sub>2</sub>Se<sub>4</sub> 'cage' (*cf.* Fig. 5) built up of Se<sub>2</sub> and Nb<sub>2</sub> pairs.

The 'one-dimensional' compound is particularly interesting as regards the possibility for chemical intercalation in empty channels. Murphy, Trumbore & Carides (1977) have reported intercalation in Se-rich niobium selenides both by electrochemical and *n*-butyllithium preparative techniques. These results have been interpreted as being due to the formation of a new phase with the composition limit Li<sub>8</sub>Nb<sub>2</sub>Se<sub>9</sub>.

One of us (AM) would like to thank Professor Stig Rundqvist for useful discussions during the author's stay at the Inorganic Department of the Institute of Chemistry, University of Uppsala. We are also grateful to Dr Jaap Folmer, Laboratoria voor anorganische chemie, Rijksuniversiteit, Groningen, for his help in preparing the ORTEP plot.

#### References

- DESLATTES, R. D. & HENINS, A. (1973). *Phys. Rev. Lett.* **31**, 972.
- FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412–415.
- GUÉMAS, L., MEERSCHAUT, A. & PALVADEAU, P. (1975). *C. R. Acad. Sci.* **281**, 297–299.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 214. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KADIJK, F. (1969). PhD Thesis, Univ. of Groningen, The Netherlands.
- MALMROS, G. R. & WERNER, P. E. (1973). *Acta Chem. Scand.* **27**, 493–497.
- MEERSCHAUT, A., PALVADEAU, P. & ROUXEL, J. (1977). *J. Solid State Chem.* **20**, 21–27.
- MEERSCHAUT, A. & ROUXEL, J. (1975). *J. Less-Common Met.* **39**, 197–203.
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.
- MURPHY, D. W., TRUMBORE, F. A. & CARIDES, J. N. (1977). *J. Electrochem. Soc.* **3**, 325–329.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- PREWITT, C. T. (1966). SFLS-5. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- RIJNSDORP, J. (1978). PhD Thesis. Univ. of Groningen, The Netherlands.
- SAAB (1967). Film Scanner Manual SAAB AB, Datasaab Linköping, Sweden.
- SELTE, K. & KJEKSHUS, A. (1964). *Acta Chem. Scand.* **18**, 697.
- VAND, T., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303–306.