

double bond with osmium tetroxide.⁸ The mass spectrum of the silylated compound is shown in Fig. 2, and is analogous to the spectrum of the derivative of the 18-carbon homologue.⁹ The allylic double bond (Fig. 2) is indicated by fragments at m/e 229 and 331. The peak at m/e 159 is the base peak from the 18-carbon derivative and is probably derived from a three carbon unit including carbon atoms 3 and 4 (original allylic portion). This peak is absent when the hydroxylated double bond is in a non-allylic position.⁹ The peak at m/e 313 is present with a similar intensity in the spectrum of the 18-carbon derivative and therefore probably originates from the polar portion. Other fragments are indicated in Fig. 2.

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Phase Relations in the System Ni-S-Se at 500°C

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The phase relations at 500°C of the ternary system Ni-S-Se have been examined by X-rays and metallographic methods. The alloys were prepared by melting calculated amounts of the elements in evacuated silica tubes. The samples were then annealed for about a week at 500°C and quenched in water. 65 samples were synthesized for this investigation.

No isolated ternary phase was found at 500°C. However, in the phases existing in the binary systems, Ni-S and Ni-Se, complete mutual interchange of sulfur and selenium is possible.

In the phase $Ni_3(S,Se)_2$, with rhombohedral structure, the successive replacement of sulfur by selenium is accompanied by an increase of the lattice dimensions, linear to the S/Se-ratio; see Table 1a. The rhombohedral angle is less than 90° in the sulfur-rich and greater than 90° in the selenium-rich compounds. No variation from the stoichiometric composition $Ni_3(S,Se)_2$ could be observed.

A phase Ni_6S_5 with orthorhombic structure was first found by Lundqvist,¹ and later confirmed by others. According to different authors, this phase is stable between approximately 400 and 570°C. There are, however, some discrepancies concerning the composition of the phase. For instance, Kullerud and Yund² report the stoichiometry to be Ni_7S_6 , whereas Rosenqvist³ found a small homogeneity range including both the compositions Ni_6S_5 and Ni_7S_6 . A phase Ni_6Se_5 , with orthorhombic crystal structure similar to that of the phase mentioned above, has been reported by Grønvold *et al.*⁴

In the present investigation samples of Ni_6S_5 and Ni_7S_6 contained two phases; one on either side of the orthorhombic phase, whereas a sample with composition $Ni_{5.87}S_5$ appeared to contain this phase only. (The notation Ni_xS_5 is used in this paper for reasons given below). No variation of the lattice constants of the orthorhombic phase could be observed in these samples and therefore variation of the Ni/S ratio is assumed to be negligible.

Table 1. Lattice constants (in Å) of Ni-S-Se compounds.

a)			
Rhombohedral	<i>a</i>	angle α	
Ni ₅ S ₂	4.082	89.46°	
Ni ₃ (S _{0.75} Se _{0.25}) ₂	4.121	89.83°	
Ni ₃ (S _{0.625} Se _{0.375}) ₂	4.1405	90.00°	
Ni ₃ (S _{0.50} Se _{0.50}) ₂	4.160	90.17°	
Ni ₃ (S _{0.25} Se _{0.75}) ₂	4.204	90.46°	
Ni ₃ Se ₂	4.237	90.70°	
b)			
Orthorhombic	<i>a</i>	<i>b</i>	<i>c</i>
Ni _{5.730} (S ₅ Se ₅) ₅ ^a	3.342	11.612	16.62
Ni _{5.926} (S ₅ Se ₅) ₅	3.345	11.618	16.64
Ni ₆ (S ₅ Se ₅) ₅	3.351	11.634	16.66
Ni _{6.072} (S ₅ Se ₅) ₅	3.359	11.649	16.68
Ni _{6.246} (S ₅ Se ₅) ₅ ^a	3.364	11.662	16.68
c)			
Ni _{5.87} S ₅	3.254	11.338	16.43
Ni _{5.87} (S _{0.89} Se _{0.11}) ₅	3.290	11.410	16.43
Ni ₆ (S _{0.76} Se _{0.25}) ₅	3.316	11.514	16.54
Ni ₆ (S _{0.50} Se _{0.50}) ₅	3.351	11.634	16.66
Ni ₆ (S _{0.25} Se _{0.76}) ₅	3.393	11.757	16.83
Ni ₆ Se ₅	3.437	11.858	17.06
d)			
Hexagonal	<i>a</i>	<i>c</i>	
Ni _{5.50} S _{5.0}	3.439	5.352	
Ni _{5.60} S _{5.13} Se _{0.37} ^a	3.492	5.358	
Ni _{5.60} S _{5.25} Se _{0.25} ^a	3.555	5.361	
Ni _{5.60} S _{5.37} Se _{0.13} ^a	3.612	5.360	
Ni _{5.50} Se _{5.50} ^a	3.662	5.357	

^a Two phase samples.

In the ternary region, however, a certain variation of the nickel-chalcogen ratio is possible. This variation was examined for samples containing equal parts of sulfur and selenium, and the observed lattice constants are given in Table 1b. On the basis of these values the homogeneity range was found to extend from Ni_{5.9}(S₅Se₅)₅ to Ni_{6.12}(S₅Se₅)₅.

Using a vacuum-pycnometric method the densities of three samples of the orthorhombic phase were determined to be:

$$\begin{aligned} \text{Ni}_{5.87}\text{S}_5, & \quad d = 5.49 \text{ g cm}^{-3}, Z = 3.97 \\ \text{Ni}_{5.93}(\text{S}_5\text{Se}_5)_5, & \quad d = 6.38 \text{ g cm}^{-3}, Z = 3.98 \\ \text{Ni}_{6.07}(\text{S}_5\text{Se}_5)_5, & \quad d = 6.43 \text{ g cm}^{-3}, Z = 3.99 \end{aligned}$$

Within experimental errors all these compounds contain 20 chalcogen atoms per unit cell, whereas a small variation of the nickel content is possible. Table 1c shows lattice constants of the orthorhombic phase in samples with increasing Se/S-fraction, and, as can be seen, a smooth increase of the lattice constants was observed.

At about 500°C the hexagonal NiAs-(B8-C6) type structure has a range of homogeneity from 50.0 to 51.5 at.% S in the nickel-sulfur system,⁵ and from 50.5 to 56.5 at.% in the nickel-selenium system.⁶ When selenium is successively substituted for sulfur in samples along the nickel-rich limit of the phase, the *a*-axis increases considerably whereas the *c*-axis remains almost constant, as can be seen in Table 1d. At the chalcogen-rich limit of the phase the structure is hexagonal only for the most sulfur-rich samples, and by increasing selenium content a monoclinic deformation takes place.

In the pyrite-(C2) type phase region NiS₂-NiSe₂, we observed a continuous linear increase of the lattice constants from 5.688 to 5.965 Å. This is in good agreement with the results given by Klemm.⁷

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