

identified by chemical analysis as In_2O and by an unpublished X-ray powder pattern. Klemm and Vogel² used the same method and identified the reaction product as In_2O by chemical analysis. An X-ray powder pattern of In_2O and of In_2O_3 obtained with a Debye-Scherrer camera is represented diagrammatically. The intensities of the reflections are given as the height of the lines in the diagram and the positions of the reflections are given in the line diagram at the appropriate scattering angles. Gastinger³ reported that indium can be oxidised to In_2O by CO_2 at 850°C and 10 torr. The compound formed was not characterised by its X-ray powder pattern. By an electron diffraction study of In_2O vapour obtained from the reaction of indium oxide (In_2O_3) with indium metal, Rambidi and Tolmachev⁵ found an In—O distance of $2.02 \pm 0.01 \text{ \AA}$ and an In—O—In angle of $150^\circ \pm 10^\circ$. In_2O was also observed in the gas phase by Burns, De Maria, Drowart and Inghram.⁶

In order to characterise crystalline In_2O more thoroughly, preparations were tried by the method reported by Brauer.⁴ Three different samples of cubic In_2O_3 were used. One sample (I) was prepared from freshly precipitated indium trihydroxide by heating at 360°C for 60 h. A Guinier powder pattern of (I) proved that it was microcrystalline In_2O_3 . The second sample (II) was prepared by treating freshly precipitated indium trihydroxide with a 0.1 m NaOH solution in a pressure bomb at 373°C and 230 atm. for 40 h. A Guinier powder pattern of (II) had sharp lines all characteristic of In_2O_3 . The third sample (III) was prepared from (II) by ignition at 1100°C for 60 h. A Guinier powder pattern showed that (III) was still In_2O_3 .

The samples (I, II, III) were reduced with hydrogen at $380\text{--}425^\circ\text{C}$. The reduced samples were shown by Guinier powder patterns to be mixtures of In and In_2O_3 . These mixtures were sublimed at 650°C at a pressure of $10^{-4}\text{--}10^{-5}$ mm Hg, and the sublimed products were characterised by Guinier powder patterns. Five independent reductions and sublimations were performed. All products formed by the sublimation were proved by the Guinier powder pattern to be In or mixtures of cubic In_2O_3 and In. The experimental conditions are given in Table 1. Table 2 gives the powder pattern of the product formed in experiment No. 2 (see Table 1). All the lines in the powder pattern belong to the patterns of indium and cubic indium oxide, (In_2O_3).

The powder patterns of indium and indium oxide were obtained with the same Guinier camera as that used for the reaction products from the reductions. The patterns agreed well with the previously reported powder patterns for indium (ASTM 5-0642) and indium oxide (ASTM 6-0416). For comparison, the powder pattern of In_2O reported by Klemm and Vogel² has been calculated from the line diagram. This pattern is probably also a combination of the powder patterns of indium and indium oxide. To our knowledge an unambiguous proof for the existence of crystalline In_2O has not yet been given.

1. Thiel, A. and Luckmann, H. *Z. anorg. Chem.* **172** (1928) 353.
2. Klemm, W. and Vogel, H. U. v. *Z. anorg. Chem.* **219** (1934) 45.
3. Gastinger, E. *Naturwiss.* **42** (1955) 95.
4. Brauer, G. *Präparative anorganische Chemie*, Enke, Stuttgart 1960, p. 765.
5. Rambidi, N. G. and Tolmachev, S. M. *Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR* **3** (1965) 487; *Chem. Abstr.* **63** (1965) 17254.
6. Burns, R. P., De Maria, G., Drowart, J. and Inghram, M. G. *J. Chem. Phys.* **38** (1963) 1035.

Received August 25, 1966.

The High-Temperature Phases $\text{Ni}_{3\pm x}\text{Se}_2$ and Ni_6Se_5

FREDRIK GRØNVOLD, ROLF MØLLERUD
and ERLING RØST

*Kjemisk Institutt A, Universitetet i Oslo,
Blindern, Oslo 3, Norway*

In the nickel-selenium system a phase In_2O with rhombohedral (pseudocubic) structure and no appreciable range of homogeneity exists.¹⁻³ According to our high temperature X-ray study the rhombohedral deformation persists up to 600°C . Above this temperature transformation to a face-centered cubic structure takes place. In contrast to the rhombohedral phase, the high-temperature phase has a broad range of homogeneity, as indicated by the large variation in lattice constants with composi-

tion. The lattice constants determined from photographs taken at about 630°C are

NiSe _{0.50}	5.427 Å at 630°C
NiSe _{0.67}	5.421 » » 620 »
NiSe _{0.70}	5.385 » » 630 »
NiSe _{0.75}	5.343 » » 640 »

This high temperature phase cannot be quenched and must therefore be examined at high temperature. Photographs of NiSe_{0.50} contained additional reflections from metallic nickel, and those of NiSe_{0.75} contained lines from NiSe (hexagonal NiAs-type). The increase in lattice dimensions with increasing nickel content is indicative of a formula Ni_{3±x}Se₂ with a variation in nickel content from Ni_{2.7}Se₂ to Ni_{3.1}Se₂. Comparisons of observed and calculated intensities for the high temperature phase have been made on the basis of various metal distributions suggested for the structurally related chalcogenides of copper and silver⁴ and of the high temperature form of the mineral bornite, Cu₅FeS₄.⁵ No satisfactory accordance between observed and calculated intensities has yet been reached.

A similar face-centered cubic structure has been found for Ni_{3±x}S₂⁶ and Ni₃Te₂.⁷ The lattice constants found in the present investigation for the Ni_{3±x}S₂-phase at 580°C are 5.296, 5.230, and 5.149 Å for Ni_{3.39}S₂ (NiS_{0.59}), Ni₃S₂ (NiS_{0.67}), and Ni_{2.63}S₂ (NiS_{0.76}), respectively, which agrees well with the results by Liné and Huber.⁶ The hexagonal cell dimensions reported by Kuznecov *et al.*⁸ for Ni₃Se₂, $a = 7.62 \pm 0.01$ and $c = 6.23 \pm 0.01$ Å at 650°C are apparently not related to those reported here.

The X-ray photograph of the sample NiSe_{0.75} at 640°C showed that the high temperature phase Ni_{3±x}Se₂ exists in equilibrium with the B8-type NiSe at this temperature. At 635°C, however, another phase with composition Ni₆Se₅ appears. This phase is stable down to about 400°C, at which temperature it slowly decomposes into rhombohedral Ni₃Se₂ and B8-type NiSe. In contrast to the cubic high temperature phase Ni_{3±x}Se₂, Ni₆Se₅ is quenchable.

After annealing Ni₆Se₅ for about two months in evacuated silica tubes, some single crystals were obtained. Oscillation and Weissenberg photographs showed orthorhombic symmetry, which made indexing of the powder pattern possible, see Table 1. The orthorhombic lattice constants are $a = 3.437$ Å, $b = 11.856$ Å, and $c = 17.064$ Å.

Table 1. X-Ray powder pattern of Ni₆Se₅ taken with CuK α_1 -radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs.	calc.	
vw	818	815	0 0 2
w	2500	2503	0 2 2
m	3257	3260	0 0 4
vw	3526	3522	0 2 3
m	4946	4948	0 2 4
m	6753	6753	0 4 0
st	6780	6782	0 2 5
st	7275	7279	1 1 3
vw	7337	7335	0 0 6
vw	8705	8705	1 1 4
m	8816	8822	1 3 0
st	9020	9023	0 2 6
		9024	1 3 1
m	9634	9637	1 3 2

Systematic absent reflections: hkl when $h + k = 2n + 1$; $h0l$ when $l = 2n + 1$. The extinctions are characteristic for the space groups D_{2h}^{17} , C_{2v}^{16} , and C_{2v}^{12} .

The crystal structure of Ni₆Se₅ seems to be isotypic with that of the corresponding sulfide, Ni₆S₅ (Lundqvist⁹ and Kuznecov *et al.*⁸). A reinvestigation of the lattice constants of Ni₆S₅ gave $a = 3.254$, $b = 11.338$, and $c = 16.427$ Å.

According to Kuznecov *et al.*⁸ a phase with composition Ni₆Se₅ exists in the temperature range 400 to 670°C. The crystal structure of this phase is described as hexagonal with $a = 3.78 \pm 0.01$ and $c = 15.89 \pm 0.02$ Å. The powder pattern of Ni₆Se₅ found in the present investigation cannot be indexed on the basis of these hexagonal unit cell parameters.

- Jacobsen, E. *Thesis*. University of Oslo 1954.
- Agarwala, R. P. and Sinha, A. P. B. Z. *anorg. allgem. Chem.* **289** (1957) 203.
- Hiller, J. E. and Wegener, W. *Neues Jahrb. Mineral.* **94** (1960) 1147.
- Rahlfis, P. Z. *physik. Chem.* **31B** (1936) 157.
- Morimoto, N. *Acta Cryst.* **17** (1964) 351.
- Liné, G. and Huber, M. *Compt. Rend.* **256** (1963) 3118.
- Vestersjö, E. *Thesis* University of Oslo 1965.
- Kuznecov, V. G., Eliseev, A. A., Špak, Z. S., Palkina, K. K., Sokolova, M. A. and Dmitriev, A. V. *Voprosy Met. Fiz.* **1961** 159.
- Lundqvist, D. *Arkiv Kemi, Mineral. Geol.* **24 A** (1947) No. 21.

Received May 13, 1966.