identified by chemical analysis as \( \text{In}_2\text{O} \) and by an unpublished X-ray powder pattern. Klemm and Vogel used the same method and identified the reaction product as \( \text{In}_5\text{O}_7 \) by chemical analysis. An X-ray powder pattern of \( \text{In}_2\text{O} \) and of \( \text{In}_5\text{O}_7 \), 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. Gastinger reported that indium can be oxidised to \( \text{In}_2\text{O} \) by \( \text{CO}_2 \) at 850°C and 10 torr. The compound formed was not characterised by its X-ray powder pattern. By an electron diffraction study of \( \text{In}_2\text{O} \) vapour obtained from the reaction of indium oxide (\( \text{In}_2\text{O}_3 \)) with indium metal, Rambidi and Tolmachev found an \( \text{In}_5\text{O}_7 \) distance of 2.02 ± 0.01 Å and an \( \text{In}_2\text{O}_7 \) — \( \text{In}_5\text{O}_7 \) angle of 150° ± 10°. \( \text{In}_2\text{O} \) was also observed in the gas phase by Burns, De Maria, Drowart and Ingraham.

In order to characterise crystalline \( \text{In}_2\text{O} \) more thoroughly, preparations were tried by the method reported by Brauer. Three different samples of cubic \( \text{In}_2\text{O}_3 \) 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 \( \text{In}_2\text{O}_3 \). 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 characteristic of \( \text{In}_5\text{O}_7 \). 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 \( \text{In}_2\text{O}_3 \).

The samples (I, II, III) were reduced with hydrogen at 380–425°C. The reduced samples were shown by Guinier powder patterns to be mixtures of \( \text{In} \) and \( \text{In}_5\text{O}_7 \). These mixtures were sublimed at 650°C at a pressure of \( 10^{-4} - 10^{-5} \) 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 \( \text{In} \) or mixtures of cubic \( \text{In}_2\text{O}_3 \) and \( \text{In} \). 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, (\( \text{In}_2\text{O}_3 \)).

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 \( \text{In}_2\text{O} \) reported by Klemm and Vogel 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 \( \text{In}_2\text{O} \) has not yet been given.


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The High-Temperature Phases
\( \text{Ni}_5\text{Se}_2 \) and \( \text{Ni}_3\text{Se}_5 \)

FREDRIK GRØNVOLD, ROLF MØLLERUD and ERLING RØST

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

In the nickel-selenium system a phase \( \text{Ni}_5\text{Se}_2 \) with rhombohedral (pseudocubic) structure and no appreciable range of homogeneity exists. 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

\[
\begin{align*}
\text{NiSe}_{0.50} & \quad 5.427 \, \text{Å at 630°C} \\
\text{NiSe}_{0.67} & \quad 5.421 \, \text{Å at 620°C} \\
\text{NiSe}_{0.70} & \quad 5.385 \, \text{Å at 630°C} \\
\text{NiSe}_{0.75} & \quad 5.343 \, \text{Å at 640°C}
\end{align*}
\]

This high temperature phase cannot be quenched and must therefore be examined at high temperature. Photographs of NiSe\textsubscript{0.50} contained additional reflections from metallic nickel, and those of NiSe\textsubscript{0.75} contained lines from NiSe (hexagonal NiAs-type). The increase in lattice dimensions with increasing nickel content is indicative of a formula Ni\textsubscript{1-x}Se\textsubscript{x} with a variation in nickel content from Ni\textsubscript{1-x}Se\textsubscript{2} to Ni\textsubscript{1-x}Se\textsubscript{1.5}. 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 silver 4 and of the high temperature form of the mineral bornite, Cu\textsubscript{5}FeS\textsubscript{4}. 5 No satisfactory accordance between observed and calculated intensities has yet been reached.

A similar face-centered cubic structure has been found for Ni\textsubscript{1-x}Se\textsubscript{x} and Ni\textsubscript{1-x}Te\textsubscript{x}. The lattice constants found in the present investigation for the Ni\textsubscript{1-x}Se\textsubscript{x}-phase at 580°C are 5.296, 5.250, and 5.149 Å for Ni\textsubscript{34}Se\textsubscript{66}, Ni\textsubscript{3}Se\textsubscript{65} (NiSe\textsubscript{0.54}), and Ni\textsubscript{14}Se\textsubscript{34} (NiSe\textsubscript{0.76}), respectively, which agrees well with the results by Liné and Huber. 6 The hexagonal cell dimensions reported by Kuznetsov 7 for Ni\textsubscript{1-x}Se\textsubscript{x}, \(a = 7.62 \pm 0.01\) 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\textsubscript{0.75} at 640°C showed that the high temperature phase Ni\textsubscript{1-x}Se\textsubscript{x} exists in equilibrium with the B8-type NiSe at this temperature. At 635°C, however, another phase with composition NiSe\textsubscript{0.5} appears. This phase is stable down to about 400°C, at which temperature it slowly decomposes into rhombohedral NiSe\textsubscript{1.5} and B8-type NiSe. In contrast to the cubic high temperature phase Ni\textsubscript{1-x}Se\textsubscript{x}, NiSe\textsubscript{0.5} is quenchable.

After annealing NiSe\textsubscript{0.5} 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 \(a = 3.437 \, \text{Å}, \ b = 11.856 \, \text{Å}, \) and \(c = 17.064 \, \text{Å}.

Table 1. X-Ray powder pattern of Ni\textsubscript{1-x}Se\textsubscript{x} taken with CuKα\textsubscript{1} radiation.

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<th>(I_{\text{obs}})</th>
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<th>(k)</th>
<th>(l)</th>
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<tr>
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</tbody>
</table>

Systematic absent reflections: \(hkl\) when \(h + k = 2n + 1\); \(h0l\) when \(l = 2n + 1\). The extinctions are characteristic for the space groups \(D_{4h}^{17}, C_{4v}^{14}\), and \(C_{2v}^{5}\).

The crystal structure of Ni\textsubscript{1-x}Se\textsubscript{x} seems to be isotypic with that of the corresponding sulfide, Ni\textsubscript{1-x}S\textsubscript{x} (Lundqvist 8 and Kuznetsov et al. 4). A reinvestigation of the lattice constants of NiSe\textsubscript{0.5} gave \(a = 3.254\), \(b = 11.338\), and \(c = 16.427\) Å. According to Kuznetsov et al. 8 a phase with composition Ni\textsubscript{1-x}Se\textsubscript{x} 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 Ni\textsubscript{1-x}Se\textsubscript{x} found in the present investigation cannot be indexed on the basis of these hexagonal unit cell parameters.


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