

Short Communications

On Niobium Selenides with
Approximate Composition NbSe₄

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In continuation of our examination of niobium selenides¹⁻⁴ we here present some preliminary data on phases with approximate composition NbSe₄.

A variety of samples were prepared by heating accurately weighed quantities of niobium and selenium in different compositions in evacuated and sealed silica tubes. (Information about the purity of the elements is given by Selte and Kjekshus.³) The samples were heated at various temperatures between 400 and 800°C, and quenching in ice water as well as slow cooling was applied. X-Ray diffraction measurements (oscillation, Weissenberg, and Guinier photographs) were carried out as described in the preceding papers.¹⁻³

In the composition range 66.7-100 atomic % Se three previously unknown phases have been identified by X-ray powder methods. It is rather difficult to obtain consistent reproducible results in this composition range. Most samples contained a mixture of two of these phases and in some cases the presence of the NbSe₂ phase was furthermore established. The exact composition of these phases has therefore not been determined. Two of the phases have been designated the composition NbSe₄ (α - and β -NbSe₄) on the basis of the relationship in lattice dimensions between these phases and the NbTe₄ phase.⁵ Needle shaped single crystals were obtained of the α - and β -NbSe₄ phases.

Phase analytical work and crystal structure determination are still in progress and only a few of the observations will be mentioned here:

1) The α -NbSe₄ phase crystallizes in the tetragonal class with $a = 28.57 \text{ \AA}$, $c =$

3.836 \AA , $c/a = 0.1343$. As α -NbSe₄ is present in most of the samples prepared in this study, the formation of this phase is probably preferred for thermodynamical or kinetical reasons.

2) The β -NbSe₄ phase crystallizes in the tetragonal class with $a = 9.503 \text{ \AA}$, $c = 19.15 \text{ \AA}$, $c/a = 2.015$. Systematic extinctions in the X-ray photographs are hhl for $l = 2n + 1$ and $0kl$ for $k + l = 2n + 1$. The Laue symmetry is $4/mmm$ and the possible space groups are $P4nc$ and $P4/mnc$. The unit cell dimensions of β -NbSe₄ are closely related to those of NbTe₄ [$a(\beta\text{-NbSe}_4)$ corresponds to $(2)^{-1}a(\text{NbTe}_4)$, $c(\beta\text{-NbSe}_4)$ corresponds to $c(\text{NbTe}_4)$] and α -NbSe₄ [$a(\beta\text{-NbSe}_4) \approx (3)^{-1}a(\alpha\text{-NbSe}_4)$, $c(\beta\text{-NbSe}_4) \approx 5c(\alpha\text{-NbSe}_4)$]. The β -NbSe₄ phase has only been ascertained in one of the samples.

3) In addition to the α - and β -NbSe₄ phases a third phase (with approximately the same composition) with a very complex Guinier photograph has been identified. The X-ray data of this phase show no obvious relationship with those of α - and β -NbSe₄. Its X-ray pattern has not yet been indexed. This phase has been found in two of the samples.

The thermodynamical relationship between the three phases has not been established.

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