Short Communications

The Crystal Structures of \( \text{Nb}_5\text{Se}_4 \) and \( \text{Nb}_5\text{Te}_4 \)

Kari Selte and Arne Kjekshus

Kjemisk Institut A, Universitetet i Oslo, Blindern, Norway

In a recent study of niobium selenides and tellurides the existence of two previously unknown phases with composition \( \text{Nb}_5\text{Se}_4 \) and \( \text{Nb}_5\text{Te}_4 \) has been established.

Samples were prepared from spectrographically standardized niobium (Johnson, Matthey & Co., Ltd.), highly refined selenium (Bolidens Gruvatiekolag) and semiconductor grade tellurium (American Smelting and Refining Co.). Incidentally, one batch of purchased niobium consisted of niobium hydride (\( \text{NbH}_4 \)) instead of pure niobium, which although it was carefully degassed in vacuum at 1000°C caused certain difficulties in the preparation of the samples. A variety of samples were prepared by heating accurately weighed quantities of the components in different compositions in evacuated and sealed silica tubes. The samples were heated at various temperatures between 500 and 1350°C, and quenching in ice water as well as slow-cooling was applied.

All samples were crushed and X-ray photographs taken in a Guinier focusing camera of 80 mm diameter with strictly monochromatized \( \text{CuK}_\alpha \)-radiation. For the calculation of lattice constants potassium chloride (Analar, The British Drug Houses, Ltd., \( a = 0.2919 \text{ Å} \)) was added as an internal standard. Lattice constants are expressed in Angstrom units on the basis of \( \lambda (\text{CuK}_\alpha) = 1.54050 \text{ Å} \). Densities were determined by the pycnometric method at 25°C with kerosene as displacement liquid.

It seemed to be rather difficult to obtain consistent, reproducible results for metal content higher than \( \sim 50 \) atomic % Nb. Most samples in this concentration range contained a mixture of four phases, a \( \text{Nb}_5\text{X}_4 \) phase (\( X = \text{Se} \) or \( \text{Te} \)), a \( \text{Nb}_2\text{X}_4 \) phase,\(^a\) a NbO phase and a \( \text{Nb}_2\text{Si}_2 \) phase (the two last phases resulting from a reaction between niobium and the silica).\(^b\) The interfering reaction with silica could only be avoided by use of the hydrogen-free niobium. When this was done a mixture of the \( \text{Nb}_5\text{X}_4 \) and \( \text{Nb}_2\text{X}_4 \) phases with niobium metal was obtained. (Alumina crucibles placed inside the silica tubes which often have been used with

Table 1. Guinier photograph data of \( \text{Nb}_5\text{Se}_4 \) and \( \text{Nb}_5\text{Te}_4 \) taken with strictly monochromatized \( \text{CuK}_\alpha \)-radiation.

<table>
<thead>
<tr>
<th>hkl</th>
<th>( \sin^2 \Theta \times 10^4 )</th>
<th>( I_{obs} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(_5)Se(_4)</td>
<td>Nb(_5)Te(_4)</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>1.219 m</td>
<td>1.139 st</td>
</tr>
<tr>
<td>200</td>
<td>2.432 w</td>
<td>2.265 w</td>
</tr>
<tr>
<td>220</td>
<td>4.869 w</td>
<td>4.638 st</td>
</tr>
<tr>
<td>101</td>
<td>4.563 w</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>5.674 m</td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>8.021 m</td>
<td>7.135 vst</td>
</tr>
<tr>
<td>400</td>
<td>9.735 vw</td>
<td>9.060 vw</td>
</tr>
<tr>
<td>301</td>
<td>10.458 st</td>
<td>9.398 vst</td>
</tr>
<tr>
<td>330</td>
<td>10.968 m</td>
<td>10.213 st</td>
</tr>
<tr>
<td>420</td>
<td>12.187 m</td>
<td>11.333 vst</td>
</tr>
<tr>
<td>321</td>
<td>12.887 w</td>
<td>11.659 m</td>
</tr>
<tr>
<td>411</td>
<td>15.330 m</td>
<td>13.918 vst</td>
</tr>
<tr>
<td>510</td>
<td>15.839 w</td>
<td>14.737 vw</td>
</tr>
<tr>
<td>002</td>
<td>19.906 w</td>
<td>17.161 m</td>
</tr>
<tr>
<td>440</td>
<td>18.139 vw</td>
<td></td>
</tr>
<tr>
<td>501</td>
<td>20.185 vw</td>
<td>18.463 m</td>
</tr>
<tr>
<td>431</td>
<td>20.724 w</td>
<td>19.269 m</td>
</tr>
<tr>
<td>112</td>
<td>21.146 vw</td>
<td>20.742 w</td>
</tr>
<tr>
<td>521</td>
<td>22.669 vw</td>
<td>21.853 w</td>
</tr>
<tr>
<td>222</td>
<td>22.822 w</td>
<td></td>
</tr>
</tbody>
</table>
success in this institute did not lead to any improved results in this case.)

Attempts to obtain single crystals were unsuccessful, but all lines from the Nb₂X₄ phases on the Guinier photographs, cf. Table 1, could be indexed on the basis of tetragonal cells with dimensions:

\[
\begin{align*}
\text{Nb}_2\text{Se}_4: & \quad a = 9.871 \text{ Å}, \\
c & = 3.4529 \text{ Å}, \\
c/a & = 0.3498 \\
\text{Nb}_2\text{Te}_4: & \quad a = 10.231 \text{ Å}, \\
c & = 3.7194 \text{ Å}, \\
c/a & = 0.3635
\end{align*}
\]

The approximately constant lattice dimensions of these phases for samples of various originally different compositions show that the homogeneity range must be rather narrow.

Only reflections with \( h + k + l = 2n \) were present on the photographs, indicating that the unit cells are body-centered.

In order to determine the composition of the phases more exactly and also the contents of the unit cells, density measurements were made.

Compared with a reasonable unit cell content of ten niobium and eight selenium or tellurium atoms, respectively, per unit cell the observed densities are approximately 5% too low. These discrepancies are, however, explained by the presence of small quantities of the Nb₂X₄ phases, the NbO phase and the Nb₂Si₃ phase with considerably lower densities.

The formula Nb₂X₄ is thus assumed to be verified. A tetragonal structure with this composition has been observed in the titanium tellurium system by Gronvold et al.² As there were obvious relationships between the intensities of the reflections from Nb₂Se₄, Nb₂Te₄ and Ti₂Te₄, the possibility of the compounds being isostructural was investigated. According to Gronvold et al. the atomic arrangement in the Ti₂Te₄ structure in terms of the space group \( I4/m-C_{4h}\) is as follows:

\[
\begin{align*}
\text{Ti I in (a)} & \quad 0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \\
\text{Ti II in (h)} & \quad (x, y, 0; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2}; \\
y & \quad 0; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2}) \text{, with } x_1 = 0.31 \text{ and } y_1 = 0.38 \\
\text{Te in (b)} & \quad \text{with } x_2 = 0.06 \text{ and } y_2 = 0.28.
\end{align*}
\]

These parameters were used in the calculation of intensities on the Guinier photographs. A reasonable agreement between observed and calculated intensities was obtained indicating that the proposed structures are correct. The parameters, however, might need further refinement.

\[\text{Table 2. Interatomic distances in Nb}_2\text{Se}_4 \quad \text{and} \quad \text{Nb}_2\text{Te}_4 \text{ (Å).}\]

<table>
<thead>
<tr>
<th></th>
<th>Nb₂Se₄</th>
<th>Nb₂Te₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb I</td>
<td>2 Nb I : 3.453</td>
<td>2 Nb I : 3.719</td>
</tr>
<tr>
<td>-8 Nb II : 2.80</td>
<td>-8 Nb II : 2.95</td>
<td></td>
</tr>
<tr>
<td>-4 Se</td>
<td>2.82</td>
<td>4 Te : 2.92</td>
</tr>
<tr>
<td>Nb II</td>
<td>2 Nb I : 2.80</td>
<td>2 Nb I : 2.95</td>
</tr>
<tr>
<td>-2 Nb II : 3.13</td>
<td>-2 Nb II : 3.23</td>
<td></td>
</tr>
<tr>
<td>-2 Nb II : 3.27</td>
<td>-2 Nb II : 3.43</td>
<td></td>
</tr>
<tr>
<td>-2 Nb II : 3.453</td>
<td>-2 Nb II : 3.719</td>
<td></td>
</tr>
<tr>
<td>-1 Se</td>
<td>2.69</td>
<td>1 Te : 2.79</td>
</tr>
<tr>
<td>-2 Se</td>
<td>2.62</td>
<td>2 Te : 2.77</td>
</tr>
<tr>
<td>-2 Se</td>
<td>2.67</td>
<td>2 Te : 2.81</td>
</tr>
<tr>
<td>Se</td>
<td>-1 Nb I : 2.82</td>
<td>-1 Nb I : 2.92</td>
</tr>
<tr>
<td>-1 Nb II : 2.69</td>
<td>-1 Nb II : 2.79</td>
<td></td>
</tr>
<tr>
<td>-2 Nb II : 2.62</td>
<td>-2 Nb II : 2.77</td>
<td></td>
</tr>
<tr>
<td>-2 Nb II : 2.67</td>
<td>-2 Nb II : 2.81</td>
<td></td>
</tr>
<tr>
<td>-2 Se</td>
<td>3.453</td>
<td>2 Te : 3.719</td>
</tr>
<tr>
<td>-4 Se</td>
<td>3.62</td>
<td>4 Te : 3.79</td>
</tr>
<tr>
<td>-2 Se</td>
<td>3.99</td>
<td>2 Te : 4.14</td>
</tr>
<tr>
<td>-2 Se</td>
<td>4.20</td>
<td>2 Te : 4.37</td>
</tr>
</tbody>
</table>

For a detailed description of the structure reference is made to Gronvold et al.⁴ The shortest interatomic distances calculated on the basis of the above parameters are listed in Table 2. The parameters and thus the interatomic distances are probably not sufficiently accurate to justify a detailed comparison with "theoretical" bond distances. One significant observation should nevertheless be mentioned: The arrangement of atoms in the Ti₂Te₄ type structure is typical of the metallic state with correspondingly short metal-metal distances. The niobium coordination around the Nb I atoms is the same as in the cubic body-centered niobium structure. According to Neuberger³ and Edvards et al.⁵ the cube edge of niobium is 3.300 Å and the shortest interatomic distances 2.858 Å. In Nb₂Se₄ and Nb₂Te₄, the shortest interatomic Nb I—Nb II distances are 2.80 and 2.95 Å, respectively.

The relationship of the Ti₂Te₄ structure to the NiAs structure was discussed by Gronvold et al.⁴ and the relationship to the Nb₂X₄ structure \((X = \text{Se or Te})\) will be outlined in a forthcoming paper.⁶ Six phases are known at present with the Ti₂Te₄ structure, i.e. Ti₂Te₄, V₂S₄, V₂Se₄,

*Acta Chem. Scand.* 17 (1963) No. 9
The Mustard Oils of Dentaria pinnata Lmk.
PIERRE G. DELAVEAU
Laboratoire de Matière médicale, Faculté de Pharmacie, Université de Paris, France
ANDERS KJER*
Organic Chemistry Department, Royal Veterinary and Agricultural College, Copenhagen, Denmark

Recently the production of two volatile isothiocyanates subsequent to disintegration of rhizomes of the crucifer Dentaria pinnata Lmk. (Cardamine pinnata R.Br.) was reported. The major constituent was identified as isopropyl isothiocyanate (I), a mustard oil derived from the glucoside precursor glucoputranjivin and repeatedly encountered in higher plants (cf. Refs. 1, 2). We now wish to report that the minor isothiocyanate consists of (S)-2-methylbutyl isothiocyanate (II), which was only recently established as a mustard oil of natural derivation when it was identified as a minor constituent of the isothiocyanate fraction of seed kernels of Putranjiva Roxburghii Wall. (Euphorbiaceae). 3

The crude thiourea fraction (1.2 g), obtained from 250 g of rhizomes of D. pinnata, 4 was separated into isopropyl-thiourea and a minor amount of 'thiourea A' (0.25 g) by chromatography on cellulose powder as previously described. 5 Upon recrystallization, first from water and then from benzene : hexane, a pure specimen of 'thiourea A' was obtained as colourless needles, m.p. 73°, [α]D21 9° ± 1° (c 1.0, 96 % EtOH). These data, combined with the established elementary composition C11H14N2S, suggested its identity as (S)-1-(2-methylbutyl)-thiourea. 6 This was further substantiated upon critical comparison (mixed melting point, paper chromatography, UV., IR., and NMR-spectroscopy) with an authentic specimen. 7

Paper chromatography of the parent thioglucosides in rhizomes of Dentaria pinnata (70 % methanolic extract) in butanol : ethanol : water (4:1:4) and butanol:pyridine:water (6:4:3) revealed, as expected, a major spot of glucoputranjivin and a smaller spot of glucosiaputin, the plant precursor of 2-methylbutyl isothiocyanate. 8 When larger amounts of the glucoside mixture were applied to the paper, a trace of a third glucoside was noted at about the site of glucocochlearin, in keeping with the previously observed trace amounts of a thiourea, tentatively identified as a derivative of (S)-2-butyl isothiocyanate (III), in crude thiourea fractions of certain Dentaria collections. 9

* Part LII of a series of papers on naturally derived isothiocyanates. For part LI, see Acta Chem. Scand. 17 (1963) 2143.

* The employed material was collected in the field near Besse en Chandesse, Puy de Dôme (France).