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Short Communications

The Crystal Structures of Nb_5Se_4 and Nb_5Te_4

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In a recent study of niobium selenides and tellurides the existence of two previously unknown phases with composition Nb_5Se_4 and Nb_5Te_4 has been established.

Samples were prepared from spectrographically standardized niobium (Johnson, Matthey & Co., Ltd.), highly refined selenium (Bolidens Gruvaktiebolag) and semiconductor grade tellurium (American Smelting and Refining Co.). Incidentally, one batch of purchased niobium consisted of niobium hydride ($NbH_{0.9}$) 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 $CuK\alpha_1$-radiation. For the calculation of lattice constants potassium chloride (Analar, The British Drug Houses, Ltd., $a = 6.2919$ Å[1]) was added as an internal standard. Lattice constants are expressed in Ångström units on the basis of $\lambda(CuK\alpha_1) = 1.54050$ 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 Nb_5X_4 phase (X = Se or Te), a Nb_3X_4 phase,[2] a NbO phase and a Nb_5Si_3 phase (the two last phases resulting from a reaction between niobium and the silica).[3] The interfering reaction with silica could only be avoided by use of the hydrogen free niobium. When this was done a mixture of the Nb_5X_4 and Nb_3X_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 Nb_5Se_4 and Nb_5Te_4 taken with strictly monochromatized $CuK\alpha_1$-radiation.

hkl	$\sin^2\Theta \times 10^5$		I_{obs}	
	Nb_5Se_4		Nb_5Te_4	
110	1 219	m	1 139	st
200	2 432	w	2 265	w
220	4 869	w	4 538	st
101			4 863	w
310			5 674	m
211	8 021	m	7 135	vst
400	9 735	vw	9 060	vw
301	10 458	st	9 398	vst
330	10 968	m	10 213	st
420	12 187	m	11 333	vst
321	12 887	w	11 659	m
411	15 330	m	13 918	vst
510	15 839	w	14 737	vw
002	19 906	w	17 161	m
440			18 139	vw
501 431	20 185	vw	18 463	m
530	20 724	w	19 269	m
112	21 146	vw		
521	22 669	vw	20 742	w
222			21 683	w
312			22 822	w

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 Nb_5X_4 phases on the Guinier photographs, *cf.* Table 1, could be indexed on the basis of tetragonal cells with dimensions:

$$\begin{aligned} Nb_5Se_4: a &= 9.871 \text{ Å}, \\ c &= 3.4529 \text{ Å}, \\ c/a &= 0.3498 \\ Nb_5Te_4: a &= 10.231 \text{ Å}, \\ c &= 3.7194 \text{ Å}, \\ c/a &= 0.3635 \end{aligned}$$

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 Nb_3X_4 phases, the NbO phase and the Nb_5Si_3 phase with considerably lower densities.

The formula Nb_5X_4 is thus assumed to be verified. A tetragonal structure with this composition has been observed in the titanium tellurium system by Grønvold *et al.*[4] As there were obvious relationships between the intensities of the reflections from Nb_5Se_4, Nb_5Te_4 and Ti_5Te_4, the possibility of the compounds being isostructural was investigated. According to Grønvold *et al.* the atomic arrangement in the Ti_5Te_4 structure in terms of the space group $I4/m-C_{4h}{}^5$ is as follows:

2 Ti I in (a) $0,0,0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$,
8 Ti II in (h) $\pm (x, y, 0;\ \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2};\ \bar{y}, x, 0;\ \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2})$, with $x_1 = 0.31$ and $y_1 = 0.38$
8 Te in (h) with $x_2 = 0.06$ and $y_2 = 0.28$.

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.

Table 2. Interatomic distances in Nb_5Se_4 and Nb_5Te_4 (Å).

Nb_5Se_4		Nb_5Te_4	
Nb I	−2 Nb I :3.453	Nb I	−2 Nb I :3.719
	−8 Nb II:2.80		−8 Nb II:2.95
	−4 Se :2.82		−4 Te :2.92
Nb II	−2 Nb I :2.80	Nb II	−2 Nb I :2.95
	−2 Nb II:3.13		−2 Nb II:3.23
	−2 Nb II:3.27		−2 Nb II:3.43
	−2 Nb II:3.453		−2 Nb II:3.719
	−1 Se :2.69		−1 Te :2.79
	−2 Se :2.62		−2 Te :2.77
	−2 Se :2.67		−2 Te :2.81
Se	−1 Nb I :2.82	Te	−1 Nb I :2.92
	−1 Nb II:2.69		−1 Nb II:2.79
	−2 Nb II:2.62		−2 Nb II:2.77
	−2 Nb II:2.67		−2 Nb II:2.81
	−2 Se :3.453		−2 Te :3.719
	−4 Se :3.62		−4 Te :3.79
	−2 Se :3.99		−2 Te :4.14
	−2 Se :4.20		−2 Te :4.37

For a detailed description of the structure reference is made to Grønvold *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 Ti_5Te_4 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 Neuberger[5] and Edvards *et al.*[6] the cube edge of niobium is 3.300_7 Å and the shortest interatomic distances 2.858 Å. In Nb_5Se_4 and Nb_5Te_4 the shortest interatomic Nb I−Nb II distances are 2.80 and 2.95 Å, respectively.

The relationship of the Ti_5Te_4 structure to the NiAs structure was discussed by Grønvold *et al.*[4] and the relationship to the Nb_3X_4 structure (X = Se or Te) will be outlined in a forthcoming paper.[2] Six phases are known at present with the Ti_5Te_4 structure, *i.e.* Ti_5Te_4,[4] V_5S_4,[7] V_5Se_4,[8]

Nb_5Se_4, Nb_5Te_4 and Nb_5Sb_4,[9] while V_5Te_4[10] has a monoclinic structure of similar dimensions.

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1. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
2. Selte, K. and Kjekshus, A. *To be published.*
3. Schäfer, H. and Dohmann, K.-D. *Z. anorg. u. allgem. Chem.* **299** (1959) 197.
4. Grønvold, F., Kjekshus, A. and Raaum, F. *Acta Cryst.* **14** (1961) 930.
5. Neuberger, M. C. *Z. Krist.* **A 93** (1936) 158.
6. Edwards, J. W., Speiser, R. and Johnston, H. L. *J. Appl. Phys.* **22** (1951) 424.
7. Grønvold, F., Haraldsen, H., Pedersen, B. and Tufte, T. *To be published.*
8. Røst, E. and Gjertsen, L. *To be published.*
9. Furuseth, S. and Kjekshus, A. *To be published.*
10. Grønvold, F., Hagberg, O. and Haraldsen, H. *Acta Chem. Scand.* **12** (1958) 971.

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The Mustard Oils of *Dentaria pinnata* Lmk.

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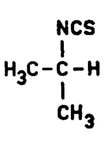
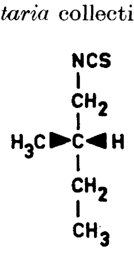
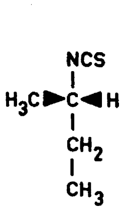
Recently [1] the production of two volatile isothiocyanates subsequent to disintegration of rhizomes of the crucifer *Dentaria pinnata* Lmk. (*Cardamine pinnata* R.Br.) was reported. The major constituent was identified as isopropyl isothiocyanate (I),[1] a mustard oil deriving from the glucosidic precursor 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*,* was separated into isopropylthiourea and a minor amount of 'thiourea A' (0.25 g) by chromatography on cellulose powder as previously described.[1] Upon recrystallization, first from water and then from benzene : hexane, a pure specimen of 'thiourea A' was obtained as colourless needles, m.p. 73°, $[\alpha]_D^{21} + 9° \pm 1°$ (*c* 1.0, 96 % EtOH). These data, combined with the established elementary composition $C_6H_{14}N_2S$, suggested its identity as (*S*)-1-(2-methylbutyl)-thiourea.[3] This was further substantiated upon critical comparison (mixed melting point, paper chromatography, UV-, IR-, and NMR-spectroscopy) with an authentic specimen.[3]

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 glucoputranjiv in and a smaller spot of glucojiaputin, the plant precursor of 2-methylbutyl isothiocyanate.[3] When larger amounts of the glucoside mixture was 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.[1]


I


II


III

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* 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 Bessé en Chandesse, Puy de Dôme (France).