On the Crystal Structure of TaSe$_3$

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TaSe$_3$ crystallizes monoclinically with

$a = 10.411$ Å, $b = 3.494$ Å, $c = 9.836$ Å, $\beta = 106.36°$.

In terms of space group $P2_1$ the unit cell contains Ta$_I$, Ta$_{II}$, Se$_I$, Se$_{II}$, Se$_{III}$, Se$_{IV}$, Se$_V$, and Se$_{VI}$ in (a) x, y, z; $\bar{x}$, $\tfrac{1}{2} + y$, $\bar{z}$:

$$
\begin{array}{llll}
\text{Ta}_I & \text{with } x_1 = 0.1968, & y_1 = \tfrac{1}{4}, & z_1 = 0.6287 \\
\text{Ta}_{II} & \text{with } x_2 = 0.3295, & y_2 = \tfrac{3}{4} + \varepsilon_1, & z_2 = 0.0498 \\
\text{Se}_I & \text{with } x_3 = 0.0813, & y_3 = \tfrac{3}{4} + \varepsilon_2, & z_3 = 0.4205 \\
\text{Se}_{II} & \text{with } x_4 = 0.1295, & y_4 = \tfrac{3}{4} + \varepsilon_3, & z_4 = 0.7972 \\
\text{Se}_{III} & \text{with } x_5 = 0.1542, & y_5 = \tfrac{1}{4} + \varepsilon_4, & z_5 = 0.0770 \\
\text{Se}_{IV} & \text{with } x_6 = 0.3668, & y_6 = \tfrac{3}{4} + \varepsilon_5, & z_6 = 0.5797 \\
\text{Se}_V & \text{with } x_7 = 0.3822, & y_7 = \tfrac{1}{4} + \varepsilon_6, & z_7 = 0.2563 \\
\text{Se}_{VI} & \text{with } x_8 = 0.4008, & y_8 = \tfrac{1}{4} + \varepsilon_7, & z_8 = 0.8797
\end{array}
$$

$(\varepsilon_1 \approx \varepsilon_2 \approx \varepsilon_3 \approx \varepsilon_4 \approx \varepsilon_5 \approx \varepsilon_6 \approx \varepsilon_7 \approx 0)$

The TaSe$_3$ structure is related to the ZrSe$_3$ and NbAs$_2$ type structures.

In continuation of the studies at this Institute of the polychalcogenide compounds of the transition metals of subgroups IV, V, and VI,[1-4] the present paper describes the determination of the crystal structure of TaSe$_3$. The particular interest in these polychalcogenide compounds centres on their apparently anomalous composition. A series of experiments is therefore being carried out to acquire information about the nature of their chemical bonding.

The existence of the TaSe$_3$ phase was first established by Ariya *et al.*[5] and has since been confirmed by Aslanov *et al.*[6] and the present authors.[2]

RESULTS

(i) *Unit cell and space group.* According to Bjerkelund and Kjekshus[2] TaSe$_3$ crystallizes monoclinically with the unit cell dimensions * (calculated from Guinier photograph data):

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* *Note added in proof.* The English translation of the second paper by Aslanov *et al.*[19] on the properties of TaSe$_3$ has come to hand since this manuscript was submitted for publication. The apparent differences in the values of a, c, and β reported by Aslanov *et al.* and those given here are explicable as a miscalculation. Using the tabulated $\sin^2\Theta$ values of Aslanov *et al.* the unit cell dimensions:

$a = 10.413$ Å, $b = 3.501$ Å, $c = 9.836$ Å, $\beta = 106.20°$

are obtained using their data for the reflections 400, 014, 41$\bar{3}$, and 020.

$a = 10.411$ Å, $b = 3.494$ Å, $c = 9.836$ Å, $\beta = 106.36°$.

No extended range of homogeneity of the $TaSe_3$ phase exists and the composition was unequivocally determined to be $TaSe_3$.

On the basis of the observed density, 7.913 g cm^{-3}, the unit cell contains 4 ($Z_c = 3.93$) $TaSe_3$-groups.

A large number of single crystals was obtained (grown from the vapour phase), of needle shape, with the diad axis along the needle axis.

Reflections of the type $(0k0)$ with $k = 2n + 1$ are absent in the X-ray photographs indicating that the space group is $P2_1$ or $P2_1/m$. (In view of the few $(0k0)$ reflections experimentally accessible, the possibility of the space group being $P2$, Pm, or $P2/m$ could not be excluded at this stage.)

(ii) *(010)-Projection.* Intensity measurements of the $h0l$ reflections were carried out microphotometrically using the multiple-film technique. (The X-ray photographs were obtained in an integrating Weissenberg camera of 57.3 mm diameter with CuK-radiation.) The intensities were corrected for the combined Lorentz and polarization factor. (No correction for absorption was carried out.) For the calculation of F_c-values the atomic scattering factors were taken from *International Tables*.[7] The agreement between F_o and F_c is expressed by the reliability index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

The four space groups $P2$, $P2_1$, $P2/m$, and $P2_1/m$ can be distinguished from the space group Pm by the presence or absence of a centre of symmetry in the (010)-projection. (The short b-axis excludes the general position $2(c)$ of Pm, which would lead to interatomic distances ≤ 1.7 Å. It was nevertheless still possible that all the atoms were in the special positions $1(a)$ and $1(b)$.) A statistical $N(z)$ test [8] was therefore applied to the intensities of the $h0l$ reflections, and the result is shown in Fig. 1. The observed distribution is consistent with a centrosymmetric projection and the space group Pm was therefore excluded.

As all the four remaining space groups have symmetry $p2$ in the (010)-projection, it was decided to start with a Patterson synthesis on the basis of the corrected $F_o^2(h0l)$-values. This projection is also specially suitable because of the short b-axis. (Furthermore, this projection corresponds to rotation about the needle axis, the crystal is easy to orient and most favourable with regard to absorption.) Attempts to derive trial structures from examination of the Patterson synthesis were, however, unsuccessful. (16 structure proposals
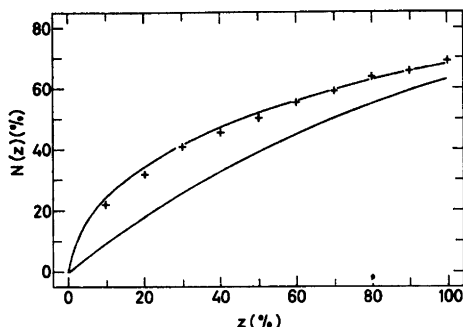

Fig. 1. Test for centre of symmetry in the (010)-projection.

Table 1. Observed and calculated structure factors for TaSe₃.

h	l	F_o	F_c	h	l	F_o	F_c
$\overline{1}\overline{2}$	1	37	48	$\overline{6}$	3	110	−102
$\overline{1}\overline{2}$	2	174	172	$\overline{6}$	4	35	− 27
$\overline{1}\overline{2}$	3	49	− 44	$\overline{6}$	5	88	88
$\overline{1}\overline{2}$	4	43	− 18	$\overline{6}$	6	54	− 57
$\overline{1}\overline{2}$	5	94	− 90	$\overline{6}$	7	99	−105
$\overline{1}\overline{2}$	6	113	−106	$\overline{6}$	8	94	− 90
$\overline{1}\overline{1}$	1	240	−223	$\overline{6}$	9	139	−148
$\overline{1}\overline{1}$	2	0	− 4	$\overline{6}$	10	45	− 43
$\overline{1}\overline{1}$	3	123	−131	$\overline{6}$	11	29	− 17
$\overline{1}\overline{1}$	4	100	− 88	$\overline{5}$	1	79	− 94
$\overline{1}\overline{1}$	5	78	61	$\overline{5}$	2	176	−215
$\overline{1}\overline{1}$	6	122	−137	$\overline{5}$	3	0	− 1
$\overline{1}\overline{1}$	7	67	52	$\overline{5}$	4	270	−352
$\overline{1}\overline{1}$	8	57	49	$\overline{5}$	5	121	−118
$\overline{1}\overline{0}$	1	88	−102	$\overline{5}$	6	61	− 49
$\overline{1}\overline{0}$	2	43	− 37	$\overline{5}$	7	40	− 48
$\overline{1}\overline{0}$	3	149	133	$\overline{5}$	8	191	194
$\overline{1}\overline{0}$	4	0	− 2	$\overline{5}$	9	74	− 58
$\overline{1}\overline{0}$	5	54	55	$\overline{5}$	10	78	62
$\overline{1}\overline{0}$	6	87	86	$\overline{5}$	11	121	145
$\overline{1}\overline{0}$	7	68	65	$\overline{4}$	1	61	58
$\overline{1}\overline{0}$	8	176	193	$\overline{4}$	2	77	− 87
$\overline{1}\overline{0}$	9	43	43	$\overline{4}$	3	202	239
$\overline{9}$	1	73	77	$\overline{4}$	4	0	18
$\overline{9}$	2	56	42	$\overline{4}$	5	0	− 28
$\overline{9}$	3	72	71	$\overline{4}$	6	266	290
$\overline{9}$	4	141	131	$\overline{4}$	7	0	− 10
$\overline{9}$	5	51	− 48	$\overline{4}$	8	136	119
$\overline{9}$	6	72	76	$\overline{4}$	9	72	81
$\overline{9}$	7	148	−152	$\overline{4}$	10	0	− 7
$\overline{9}$	8	140	−139	$\overline{4}$	11	86	89
$\overline{9}$	9	47	58	$\overline{3}$	1	113	140
$\overline{9}$	10	140	−157	$\overline{3}$	2	57	− 55
$\overline{8}$	1	0	7	$\overline{3}$	3	28	21
$\overline{8}$	2	154	−176	$\overline{3}$	4	157	153
$\overline{8}$	3	167	−165	$\overline{3}$	5	0	− 17
$\overline{8}$	4	85	83	$\overline{3}$	6	32	− 20
$\overline{8}$	5	64	− 69	$\overline{3}$	7	77	62
$\overline{8}$	6	39	− 24	$\overline{3}$	8	54	− 58
$\overline{8}$	7	0	18	$\overline{3}$	9	0	10
$\overline{8}$	8	73	− 75	$\overline{3}$	10	172	−162
$\overline{8}$	9	79	84	$\overline{3}$	11	165	−194
$\overline{8}$	10	34	− 30	$\overline{2}$	1	98	−121
$\overline{7}$	1	122	131	$\overline{2}$	2	56	− 55
$\overline{7}$	2	143	136	$\overline{2}$	3	57	22
$\overline{7}$	3	0	− 1	$\overline{2}$	4	48	− 40
$\overline{7}$	4	121	129	$\overline{2}$	5	95	− 75
$\overline{7}$	5	0	− 2	$\overline{2}$	6	228	−220
$\overline{7}$	6	69	69	$\overline{2}$	7	55	50
$\overline{7}$	7	51	60	$\overline{2}$	8	45	− 14
$\overline{7}$	8	35	− 23	$\overline{2}$	9	48	− 46
$\overline{7}$	9	0	− 2	$\overline{2}$	10	146	153
$\overline{7}$	10	126	130	$\overline{2}$	11	70	− 65
$\overline{7}$	11	31	26	$\overline{1}$	1	136	−169
$\overline{6}$	1	62	71	$\overline{1}$	2	156	168
$\overline{6}$	2	156	187	$\overline{1}$	3	0	− 1

h	l	F_o	F_c	h	l	F_o	F_c
$\bar{1}$	4	138	122	4	4	50	− 61
$\bar{1}$	5	284	318	4	5	0	− 8
$\bar{1}$	6	36	17	4	6	0	− 12
$\bar{1}$	7	59	33	4	7	0	− 13
$\bar{1}$	8	0	34	4	8	0	9
$\bar{1}$	9	0	− 13	4	9	81	− 77
$\bar{1}$	10	85	73	5	0	76	93
$\bar{1}$	11	64	− 53	5	1	100	− 93
0	1	51	45	5	2	56	54
0	2	117	96	5	3	63	75
0	3	94	95	5	4	73	65
0	4	126	−121	5	5	69	68
0	5	126	106	5	6	0	32
0	6	193	−178	5	7	40	24
0	7	80	− 94	5	8	170	168
0	8	0	− 14	5	9	47	58
0	9	91	− 82	6	0	111	112
0	10	58	− 57	6	1	122	132
0	11	30	− 25	6	2	0	− 6
1	0	36	− 28	6	3	260	288
1	1	33	− 30	6	4	44	46
1	2	176	−203	6	5	0	− 52
1	3	0	− 13	6	6	0	28
1	4	221	−219	6	7	167	−164
1	5	147	−154	6	8	26	− 49
1	6	44	41	7	0	82	−108
1	7	167	−147	7	1	131	125
1	8	98	− 87	7	2	210	−218
1	9	0	36	7	3	142	−170
1	10	58	52	7	4	39	− 15
1	11	143	158	7	5	148	−155
2	0	116	−155	7	6	42	29
2	1	67	67	7	7	145	−113
2	2	68	− 48	8	0	41	− 41
2	3	236	−251	8	1	0	9
2	4	143	142	8	2	43	− 18
2	5	34	− 6	8	3	82	− 72
2	6	207	193	8	4	75	81
2	7	169	185	8	5	0	23
2	8	0	− 12	8	6	35	− 32
2	9	190	202	9	0	0	11
2	10	70	− 42	9	1	33	14
2	11	0	11	9	2	82	67
3	0	0	20	9	3	0	31
3	1	66	64	9	4	53	− 56
3	2	208	243	9	5	148	129
3	3	0	− 1	10	0	68	54
3	4	124	101	10	1	66	− 45
3	5	92	− 58	10	2	31	− 45
3	6	86	−107	10	3	91	− 64
3	7	153	145	10	4	155	−145
3	8	104	− 96	11	0	0	− 14
3	9	40	− 64	11	1	115	− 65
3	10	29	− 16	11	2	0	− 13
4	0	212	−278	11	3	159	161
4	1	161	−206	12	0	0	3
4	2	57	58	12	1	132	137
4	3	126	−123				

were tried.) A sharpening of the Patterson synthesis did not lead to any improvement.

Direct methods for sign determination were then attempted. The intensities were converted to unitary structure factors and application of Harker-Kasper inequalities [9-11] and coincidence relations [11] gave signs (8 probable combinations) for 118 out of 227 structure factors. A Fourier synthesis, evaluated on the second set of signs tried, showed the atomic positions clearly, with a marked difference between tantalum and selenium atoms. Structure factors were calculated based on the atomic parameters deduced from this Fourier synthesis, giving $R = 0.24$, which was improved to 0.128 ($B = 0.5$ for all atoms) after two further Fourier syntheses.
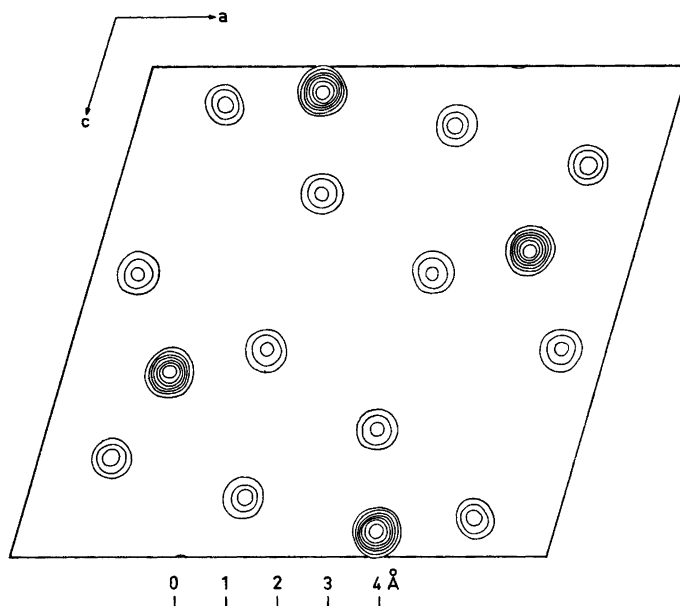
Fig. 2. Electron density projection of TaSe₃ along [010]. Contours are at intervals of 25 e.Å⁻². The zero contours are omitted.

The observed and calculated structure factors are listed in Table 1 and the final Fourier map is shown in Fig. 2.

(iii) *The three-dimensional structure.* By considering the interatomic distances on the basis of the parameters in the (010)-projection it appeared that only $y_i - y_j \approx 0$ or $\frac{1}{2}$ would lead to reasonable distances. The values exactly 0 or $\frac{1}{2}$ would suggest the space group $P2/m$ or $P2_1/m$, whereas values slightly different from 0 and $\frac{1}{2}$ would lead to $P2$ or $P2_1$. With a choice of y-parameters for the tantalum atoms the approximate y-parameters for the selenium atoms are fixed.

A comparison of $F_o(h1l)$ and $F_c(h1l)$ showed clearly that the space groups $P2$ and $P2/m$ could be excluded. This finding is in accordance with the indicated

extinction in the X-ray photographs. (The space groups $P2_1$ and $P2_1/m$ lead to approximately the same configuration of selenium atoms around each of the tantalum atoms which is more reasonable than the possibility of two different arrangements suggested from the space groups $P2$ and $P2/m$.)

The present set of $F_o(h1l)$-values was not considered to be accurate enough to justify a distinction between the space groups $P2_1$ and $P2_1/m$. The deviation from the fixed y-coordinates of space group $P2_1/m$, if any, must be rather small. In terms of the space group $P2_1$ one of the atoms may be given an arbitrary y-coordinate, and the deduced atomic arrangement may be described as follows:*

Ta_I, Ta_{II}, Se_I, Se_{II}, Se_{III}, Se_{IV}, Se_V, and Se_{VI} in (a) $x, y, z;$ $\bar{x}, \frac{1}{2} + y, \bar{z}$

$$
\begin{array}{llll}
Ta_I & \text{with } x_1 = 0.1968, & y_1 = \frac{1}{4}, & z_1 = 0.6287 \\
Ta_{II} & \text{with } x_2 = 0.3295, & y_2 = \frac{3}{4} + \varepsilon_1, & z_2 = 0.0498 \\
Se_I & \text{with } x_3 = 0.0813, & y_3 = \frac{3}{4} + \varepsilon_2, & z_3 = 0.4205 \\
Se_{II} & \text{with } x_4 = 0.1295, & y_4 = \frac{3}{4} + \varepsilon_3, & z_4 = 0.7972 \\
Se_{III} & \text{with } x_5 = 0.1542, & y_5 = \frac{1}{4} + \varepsilon_4, & z_5 = 0.0770 \\
Se_{IV} & \text{with } x_6 = 0.3668, & y_6 = \frac{3}{4} + \varepsilon_5, & z_6 = 0.5797 \\
Se_V & \text{with } x_7 = 0.3822, & y_7 = \frac{1}{4} + \varepsilon_6, & z_7 = 0.2563 \\
Se_{VI} & \text{with } x_8 = 0.4008, & y_8 = \frac{1}{4} + \varepsilon_7, & z_8 = 0.8797
\end{array}
$$

The notations $y_2 = \frac{3}{4} + \varepsilon_1$, etc. are introduced to facilitate a possible transfer from space group $P2_1$ to $P2_1/m$ when the space group question is finally solved. Three-dimensional X-ray data are now being collected in order to determine the values of $\varepsilon_1, \ldots \varepsilon_7$. Awaiting the results of this analysis the values $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = \varepsilon_7 = 0$ are adopted in the remainder of this paper.

(iv) *Interatomic distances and coordination.* The coordination around the tantalum and selenium atoms can be seen in Fig. 3; and the shortest interatomic distances are listed in Table 2.

Each tantalum atom (Ta_I and Ta_{II} have nearly the same configuration of near neighbours) is surrounded by eight selenium atoms. Six selenium atoms are at the corners of a triangular prism and two lie outside rectangular faces of the prism. The Se_I and Se_{II} atoms are coordinated to three tantalum atoms, the Se_{III}, Se_{IV}, and Se_V atoms are coordinated to two tantalum atoms and the Se_{VI} atoms are coordinated to four tantalum atoms. The arrangement of the selenium atoms produces longer and shorter Se—Se distances. The short Se—Se distances are found between Se_V and Se_{III} or Se_{IV} (cf. Fig. 3 and Table 2).

Table 2. Interatomic distances (< 3 Å) in $TaSe_3$ (Å).

$$
\begin{array}{llll}
Ta_I - 2Se_I & : 2.70 & \qquad Ta_{II} - 1Se_{II} & : 2.76 \\
- 1Se_I & : 2.80 & - 2Se_{III} & : 2.59 \\
- 2Se_{II} & : 2.64 & - 2Se_V & : 2.62 \\
- 2Se_{IV} & : 2.63 & - 2Se_{VI} & : 2.67 \\
- 1Se_{VI} & : 2.77 & - 1Se_{VI} & : 2.70
\end{array}
$$

$$
\begin{array}{ll}
Se_{III} - Se_V & : 2.53 \\
Se_{IV} - Se_V & : 2.66 \\
Se_I - Se_{IV} & : 2.94
\end{array}
$$

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* The only alternative arrangement in which the y-parameters of Ta_I and Ta_{II} have approximately the same value could be excluded by comparison of $F_o(h1l)$ and $F_c(h1l)$.
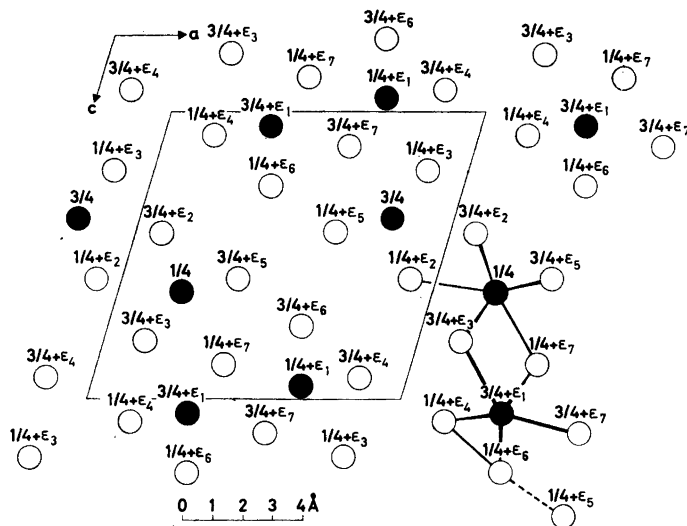
Fig. 3. The structure of $TaSe_3$ projected along [010]. In this and the following diagrams filled circles represent metal atoms and open circles represent metalloid atoms. The numbers indicate fractions of the projection axes.

$$(\varepsilon_1 \approx \varepsilon_2 \approx \varepsilon_3 \approx \varepsilon_4 \approx \varepsilon_5 \approx \varepsilon_6 \approx \varepsilon_7 \approx 0)$$

It is interesting to compare the atomic arrangement in the $TaSe_3$, $ZrSe_3$, and $NbAs_2$ structures [12,13] (cf. Figs. 3—5). The configuration of the metalloid atoms surrounding the metal atoms are nearly the same in the three cases
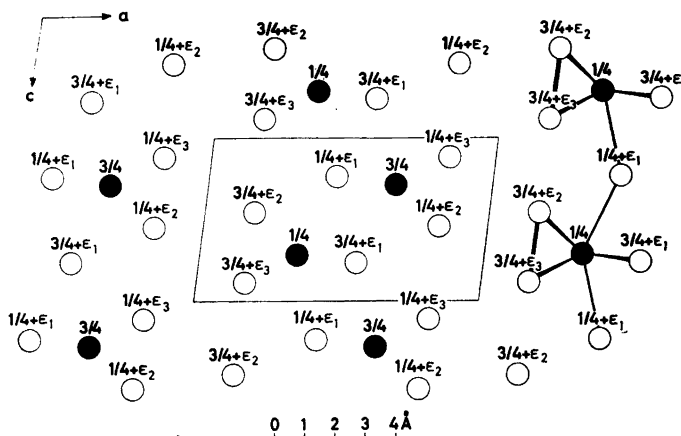
Fig. 4. The structure of $ZrSe_3$ projected along [010].

According to the latest results by Krönert and Plieth [20] it is shown that $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 0$.

and the structures have in common the feature of some short metalloid-metalloid distances. The $TaSe_3$ and $ZrSe_3$ structures may be regarded as distorted $NbAs_2$ structures with 1/3 of the positions for the metal atoms vacant. The distribution of these vacancies is somewhat different in the two cases and the effect of the distortion is that the short metalloid-metalloid distances are arranged differently in the three structures.
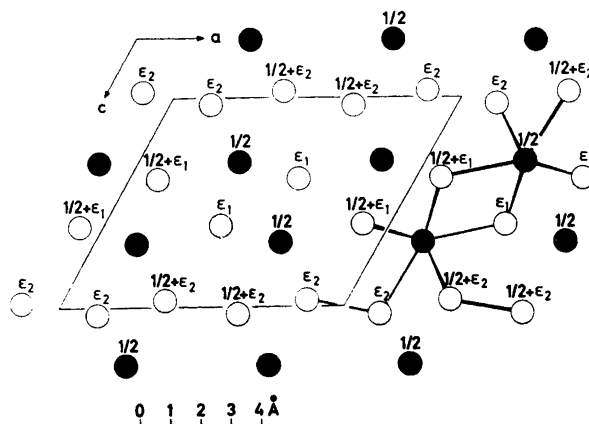

Fig. 5. The structure of $NbAs_2$ projected along [010].

$(\varepsilon_1 = 0.012, \quad \varepsilon_2 = 0.067)$

The short Se—Se distances observed (cf. Table 2 and Fig. 3) in the $TaSe_3$ structure indicate that bonding exists between selenium atoms. The effect of these Se—Se bonds on the outer electron configuration of the selenium atoms can be discussed in terms of the general (8—N) rule:[14-17]

$$(n + P - Q)/a = 8$$

where n is the total number of valence electrons (excluding any unshared electrons on the cations); a is the number of anions; P is the number of electrons involved in forming anion-anion bonds; Q is the number of electrons involved in forming cation-cation bonds, all these values being calculated per formula unit of the compound. (This rule is a mathematical formulation of the need for all the anions in the crystal to have complete octets.[17])

In $TaSe_3$ there are no localized unpaired d-electrons on the tantalum atoms [2] and their contribution to n must accordingly be either 5, 3, or 1 electron. Each selenium atom contributes 6 electrons, thus:

$n = 23, 21,$ or $19;$

$a = 3;$

$Q = 0$ (from the crystal structure);

and therefore

$P = 1, 3,$ or 5, respectively.

Consequently, each formula unit $TaSe_3$ must on average use either 1, 3, or 5 electrons in forming Se—Se bonds; *i.e.* in the whole cell (containing 4 $TaSe_3$ units) there must be 2, 6, or 10 Se—Se two-electron bonds. Examination of the crystal structure (*cf.* Table 2 and Fig. 3) shows that in each unit cell there are four short Se—Se distances (2.53 Å (2) and 2.66 Å (2)). Longer Se—Se distances exceed 2.9 Å. (Allowing $\varepsilon_1,....\varepsilon_7$ values slightly different from zero, or minor errors in the x- and z-parameters of the atoms, will not affect the general pattern of these figures.) In no way can more than four bonds be chosen from this set, the possibilities of 6 and 10 Se—Se two-electron bonds can therefore be ruled out. Assuming the four short Se—Se distances to be two-electron bonds the general (8—N) rule (predicting 2 Se—Se two-electron bonds per unit cell) is not satisfied. From the available data the following considerations may be made:

1) According to Aslanov *et al.*[6] the electrical conductivity of $TaSe_3$ is 150 $\Omega^{-1}cm^{-1}$ and the Seebeck coefficient coupled with aluminium is zero at room temperature. The comparatively high conductivity and low Seebeck coefficient may be taken as an indication of $TaSe_3$ being a metallic like conductor. There is accordingly no need for the general (8—N) rule to be satisfied. Under these conditions, however, it seems unnecessary for $TaSe_3$ to adopt its characteristic crystal structure. (The rule appears to be satisfied for compounds with the $ZrSe_3$ type structure.[18] The $ZrSe_3$ type structure being just as characteristic as the $TaSe_3$ structure.) Electrical conductivity measurements of $TaSe_3$ as a function of temperature will shortly be carried out to check this point.

2) The short Se—Se distances (Table 2) are larger than the expected distance of 2.35—2.45 Å from comparison with Se—Se distances observed in compounds of similar type. This may suggest that the bonds differ from the normal Se—Se single bond. In this connection it should be mentioned that "the general (8—N) rule" can be extended to include electron configurations around the anions other than octets:[17]

$$n + P - Q = \Sigma a_i N_i$$

where n, P, and Q have unaltered meanings and N_i is the number of electrons in the outer shell of the a_i anions of kind i. The $TaSe_3$ structure can be given a satisfactory explanation by allowing the Se_V atoms to have an outer shell of 10 electrons (all the other selenium atoms having an outer shell of 8 electrons). A ten electron configuration on Se_V would supposedly give rise to increased Se_V—Se_{III} and Se_V—Se_{IV} separations.

3) If only the distances Se_V—Se_{III} are considered as bond distances and the Se_V—Se_{IV} distances (dotted in Fig. 3) regarded as geometrical in origin, the general (8—N) rule may be satisfied in its simple form.

We are awaiting the results of the three-dimensional refinement of the structure and the electrical conductivity measurements before further considerations are presented.

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