On the Properties of TaS$_3$ and TaSe$_3$

E. BJERKELUND, J. H. FERMOR and A. KJEKSHUS

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

Electrical resistivities of TaSe$_3$ and TaS$_3$ are given, the results and discussion indicating TaSe$_3$ to be metallic and TaS$_3$ to be non-metallic. The results of least-squares refinements of the TaSe$_3$ crystal structure are given.

The compounds TaS$_3$ and TaSe$_3$, which have been classified among the transition metal polychalcogenides, have recently been the subject of several investigations.[1-9] Despite all these studies, little is known about the chemical and physical properties of TaS$_3$ and TaSe$_3$ since most of the previous studies have been concerned with establishing their existence and correct composition. Aslanov et al.[5] have described briefly the electrical properties of TaSe$_3$ at room temperature and structural and magnetic properties of both compounds have to some extent been reported by Bjerkelund and Kjekshus.[3,7] In the previous attempts [3,7] to explore the nature of the chemical bonding in these compounds, the need for more data was felt. Attempting to meet these requirements, we have accordingly measured the electrical resistivities of TaS$_3$ and TaSe$_3$ as functions of temperature, and carried out a further refinement of the TaSe$_3$ structure.

EXPERIMENTAL

Samples of TaS$_3$ and TaSe$_3$ were prepared from 99.92 % Ta (Johnson, Matthey & Co., Ltd.; impurities in (ppm): Nb($<$200), Fe(300), Si(100), Al(20), Cr(20), Sn(20), Mn(5), and Mg(1)), 99.999 + % S (American Smelting and Refining Co.; no impurities detected), and 99.999 + % Se (Bolidens Gruvaktiebolag; impurities in (ppm): Cu(2), Fe(0.8), K(0.3), Na(0.4), and non-volatile matter (12)). Ta and S or Se in the stoichiometric ratio were heated in evacuated and sealed silica tubes for 14 days at 800°C. The samples were then cooled to room temperature over a period of another 14 days. After the heat treatment, the samples were found to be sintered and comparatively large crystals of needle-shape had grown from the vapour phase.

A portion of each sample was crushed and the homogeneity was checked by an X-ray diffraction technique using a Guinier focusing camera of 80 mm diameter and strictly monochromatized CuKα_1-radiation. (KCl, a = 6.2919 Å,[10] was added to the specimen as an internal standard.) Lattice dimensions were calculated from Guinier photographic data by applying the method of least squares. The indicated error limits correspond to twice the standard deviation obtained in these calculations.

Three-dimensional X-ray data of TaSe$_3$ were collected using an integrating Weissenberg camera of 57.3 mm diameter with Mo-radiation. Intensity measurements were carried out microphotometrically using the multiple-film technique. The cross-section of the crystal used for these measurements was 0.017×0.018 mm^2. The intensities were corrected for the combined Lorentz and polarization factors, whereas the correction for absorption could be neglected. For the calculation of F_c-values, the atomic scattering factors were taken from *International Tables*.[11] The final atomic parameters were obtained by least squares refinements. The error limits indicated for atomic parameters and interatomic distances and angles correspond to twice the standard deviations deduced from the least-squares calculations.

The measurements of electrical resistance as a function of temperature were carried out by a four terminal method using a somewhat modified Dauphinee-Mooser[12] circuit. For a detailed description of the equipment used reference is made to Fermor and Kjekshus.[13] The samples of sintered material were ground to a prismatic shape and their dimensions together with the separation of the potential contacts were determined using a travelling microscope.

RESULTS AND DISCUSSION

A. The compound TaS₃

The temperature dependence of the electrical resistance of a sintered polycrystalline sample of TaS$_3$ was measured from 113 to 386°K. The upper temperature limit was chosen in order to avoid any possible decomposition of the sample. A plot of the logarithm of resistivity as a function of the reciprocal of the absolute temperature (Fig. 1) shows the sample to be extrinsically semiconducting. In the saturation range of the curve above 325°K substantially all extrinsic carriers are activated. (The sign of the carriers could not be deter-
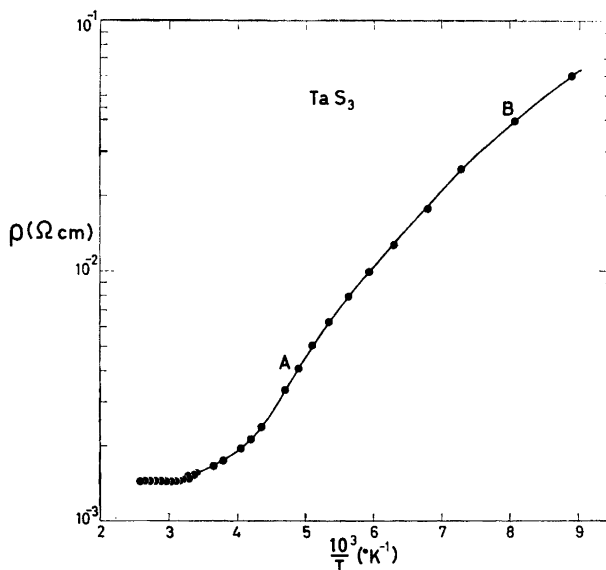

Fig. 1. Log ϱ versus $1/T$ plot for TaS$_3$.

mined since the Hall voltage was too small to be detected.) At lower tempera-
tures, the plot does not follow a simple expression of the form $\varrho = \varrho_0$ exp
$(\varepsilon/2kT)$ since the curve shows a gradual change in slope. This variation in
slope is due to the presence of extrinsic carriers available at more than one
activation energy, consistent with the high * impurity content of the sample.
The values of the slope at the points A and B correspond to activation energies
of 0.17 and 0.09 eV, respectively.

Although electrical conduction intrinsic to TaS_3 is not observed, metallic
conduction must be excluded. Further data are, however, needed in order
to classify the compound as being intrinsically ionic or semiconducting.

In connection with further exploration of the bonding scheme of TaS_3
(e.g. in terms of the generalized (8—N) rule) it is of great interest to establish
its crystal structure. Attempts are now being made to prepare single crystals
which are suitable for this purpose. It is expected that the structure deter-
mination will be a fairly complex problem, as the orthorhombic unit cell is
of considerable size ** with a cell content of 24 TaS_3-groups.

B. The compound $TaSe_3$

The main features of the atomic arrangement in the $TaSe_3$ structure have
previously been described by Bjerkelund and Kjekshus [7] and the further
details presented here constitute only minor adjustments.

The following unit cell dimensions:
$a = 10.402 \pm 0.004$ Å, $b = 3.495 \pm 0.002$ Å,
$c = 9.829 \pm 0.004$ Å, $\beta = 106.26 \pm 0.03°$

have been obtained by a least-squares refinement of the Guinier photographic
data.

Refinements of the three-dimensional structure factor data, according to
the method of least-squares, were first carried out assuming a description of
the atomic arrangement in terms of space group $P2_1$. These calculations showed
quite clearly that each of the atoms in the structure can be ascribed a fixed
y coordirate. (The difference between each of these calculated y values and
an assumed fixed value of $\frac{1}{4}$ or $\frac{3}{4}$ is considerably smaller than twice the corre-
sponding standard deviation of y. The deduced differences were considered to
be insignificant and they were accordingly neglected.) The mirror plane charac-
teristic of space group $P2_1/m$ was now definitely established and the only
serious ambiguity of the previous structure determination [7] was thus removed.

Further refinements were carried out with the atoms arranged
according to space group $P2_1/m$. These calculations were terminated at
$R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.081$, with the final coordinates (all atoms in
positions $2(e) \pm x, \frac{1}{4}, z$):

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* The impurity level (for which see experimental section) is relatively high only in connection
with electrical phenomena.

** The dimensions deduced from Guinier photographic data by applying the method of least-
squares are: $a = 36.791 \pm 0.015$ Å, $b = 15.177 \pm 0.004$ Å, $c = 3.340 \pm 0.001$ Å. The most
probable space group is $C222_1$.

Ta_I $x_1 = 0.1937 \pm 0.0008,$ $z_1 = 0.6250 \pm 0.0008$
Ta_{II} $x_2 = 0.6723 \pm 0.0008,$ $z_2 = 0.9518 \pm 0.0009$
Se_I $x_3 = 0.9154 \pm 0.0019,$ $z_3 = 0.5760 \pm 0.0020$
Se_{II} $x_4 = 0.8691 \pm 0.0019,$ $z_4 = 0.2011 \pm 0.0020$
Se_{III} $x_5 = 0.1512 \pm 0.0019,$ $z_5 = 0.0750 \pm 0.0020$
Se_{IV} $x_6 = 0.6338 \pm 0.0018,$ $z_6 = 0.4222 \pm 0.0019$
Se_V $x_7 = 0.3832 \pm 0.0018,$ $z_7 = 0.2582 \pm 0.0019$
Se_{VI} $x_8 = 0.4006 \pm 0.0020,$ $z_8 = 0.8820 \pm 0.0021$

The atomic arrangement is shown in Fig. 2, and interatomic distances and angles are listed in Table 1. For a description of the structure, reference is made to Bjerkelund and Kjekshus.[7]

The electrical resistance of $TaSe_3$ was determined between 80 and 415 °K. (The onset of decomposition was noticed at 430°K when a gradual fall in resistance at constant temperature was recorded.) Two samples were measured, the first being in a sintered polycrystalline form and the second a bunch of about twenty hair-like needle-crystals grown from a common base. These crystals had a parallel orientation along [010] with lengths of about 10 mm and their resistance was measured along the needle axis. The resistivities of the samples are shown in Fig. 3 as functions of temperature where the curve for the single
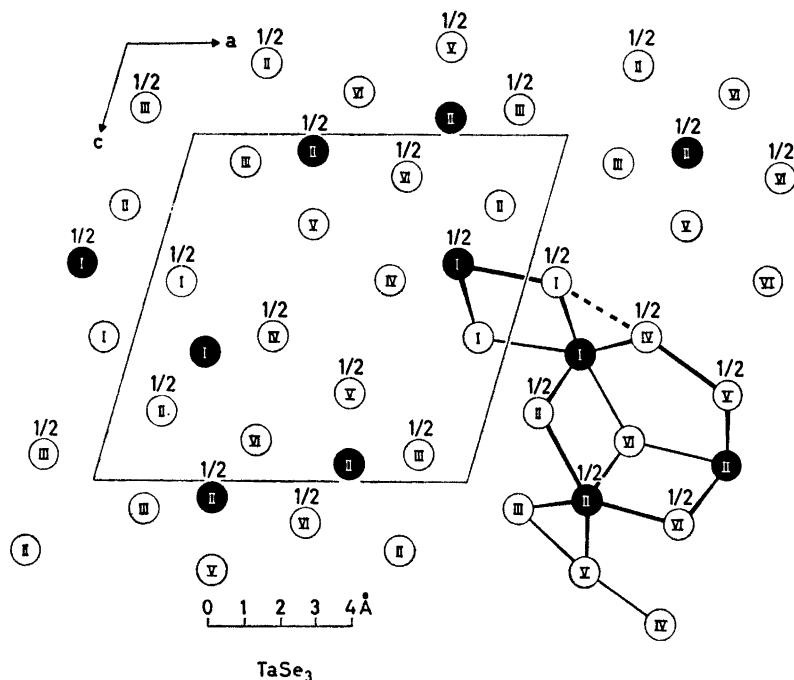

Fig. 2. The crystal structure of $TaSe_3$ projected along [010]. Filled circles represent tantalum atoms and open circles represent selenium atoms. The numbers indicate fractions of the projection axis. (The origin of this diagram has been shifted to $0,\frac{1}{4},0$ from that of the text.)

Table 1. Interatomic distances and angles in $TaSe_3$.

Interatomic distances (Å)					
Ta_I —$2Ta_I$	3.495 ± 0.002	Se_{II} —$1Ta_{II}$	2.718 ± 0.019	Se_{IV}—$2Se_V$	3.642 ± 0.023
—$2Se_I$	2.643 ± 0.015	—$2Se_I$	3.183 ± 0.021	—$2Se_{VI}$	3.395 ± 0.023
—$1Se_I$	2.799 ± 0.017	—$1Se_I$	3.580 ± 0.027		
—$2Se_{II}$	2.651 ± 0.014	—$2Se_{II}$	3.495 ± 0.002	Se_V —$2Ta_{II}$	2.642 ± 0.015
—$2Se_{IV}$	2.637 ± 0.013	—$2Se_{III}$	3.184 ± 0.022	—$1Se_{III}$	2.576 ± 0.024
—$1Se_{VI}$	2.823 ± 0.019	—$1Se_{III}$	3.491 ± 0.022	—$1Se_{IV}$	2.653 ± 0.023
		—$1Se_{IV}$	3.701 ± 0.023	—$2Se_{IV}$	3.642 ± 0.023
Ta_{II} —$2Ta_{II}$	3.495 ± 0.002	—$2Se_{VI}$	3.211 ± 0.019	—$2Se_V$	3.495 ± 0.002
—$1Se_{II}$	2.718 ± 0.019			—$2Se_{VI}$	3.427 ± 0.020
—$2Se_{III}$	2.601 ± 0.012	Se_{III} —$2Ta_{II}$	2.601 ± 0.012	—$1Se_{VI}$	3.753 ± 0.026
—$2Se_V$	2.642 ± 0.015	—$2Se_{II}$	3.184 ± 0.022		
—$2Se_{VI}$	2.644 ± 0.014	—$1Se_{II}$	3.491 ± 0.022	Se_{VI}—$1Ta_I$	2.823 ± 0.019
—$1Se_{VI}$	2.715 ± 0.017	—$2Se_{III}$	3.495 ± 0.002	—$2Ta_{II}$	2.644 ± 0.014
		—$2Se_{III}$	3.540 ± 0.020	—$1Ta_{II}$	2.715 ± 0.017
Se_I —$2Ta_I$	2.643 ± 0.015	—$1Se_V$	2.576 ± 0.024	—$2Se_{II}$	3.211 ± 0.019
—$1Ta_I$	2.799 ± 0.017	—$1Se_{VI}$	3.616 ± 0.023	—$1Se_{III}$	3.616 ± 0.023
—$2Se_I$	3.139 ± 0.019			—$2Se_{IV}$	3.395 ± 0.023
—$2Se_I$	3.495 ± 0.002	Se_{IV}—$2Ta_I$	2.637 ± 0.013	—$2Se_V$	3.427 ± 0.020
—$2Se_{II}$	3.183 ± 0.021	—$1Se_I$	2.896 ± 0.023	—$1Se_V$	3.753 ± 0.026
—$1Se_{II}$	3.580 ± 0.027	—$1Se_{II}$	3.701 ± 0.023	—$2Se_{VI}$	3.167 ± 0.021
—$1Se_{IV}$	2.896 ± 0.023	—$2Se_{IV}$	3.495 ± 0.002	—$2Se_{VI}$	3.495 ± 0.002
		—$2Se_{IV}$	3.939 ± 0.020		
Se_{II} — $2Ta_I$	2.651 ± 0.014	—$1Se_V$	2.653 ± 0.023		

Table 1. Continued.

Interatomic angles (°)			
Se_I —Ta_I —Se_I	70.4 ± 0.6	Se_{III}—Ta_{II} —Se_V	58.8 ± 0.6
—Se_I	82.8 ± 0.5	—Se_{VI}	87.2 ± 0.4
—Se_{II}	71.4 ± 0.5	Se_V —Ta_{II} —Se_V	82.8 ± 0.5
—Se_{II}	85.1 ± 0.4	—Se_{VI}	79.5 ± 0.5
—Se_{IV}	66.5 ± 0.5	—Se_{VI}	90.5 ± 0.5
—Se_{VI}	130.3 ± 1.1	Se_{VI} —Ta_{II} —Se_{VI}	72.4 ± 0.5
Se_{II} —Ta_I —Se_{II}	82.5 ± 0.5	—Se_{VI}	82.7 ± 0.5
—Se_{IV}	88.8 ± 0.4		
—Se_{VI}	71.8 ± 0.6	Ta_I —Se_I —Ta_I	109.6 ± 0.8
Se_{IV} —Ta_I —Se_{IV}	83.0 ± 0.4	Ta_I —Se_{II} —Ta_I	108.8 ± 0.9
—Se_{VI}	76.8 ± 0.5	Ta_I —Se_{VI} —Ta_I	105.9 ± 0.8
		Ta_I —Se_{VI} —Ta_{II}	134.8 ± 1.6
Se_{II} —Ta_{II}—Se_{III}	73.5 ± 0.5	Ta_{II} —Se_{VI} —Ta_{II}	107.6 ± 0.7
—Se_{VI}	73.6 ± 0.6		
—Se_{VI}	134.1 ± 1.2	Se_I —Se_{IV} —Se_V	174.4 ± 16.9
Se_{III}—Ta_{II}—Se_{III}	84.4 ± 0.4	Se_{III}—Se_V —Se_{IV}	173.5 ± 15.9

crystals has been added in an arbitrary position for purposes of comparison. (The resistivity, $\varrho = 66 \times 10^{-4}\ \Omega$ cm, at room temperature reported by Aslanov *et al.*[5] is greater than twice the value obtained in this study.) Both curves
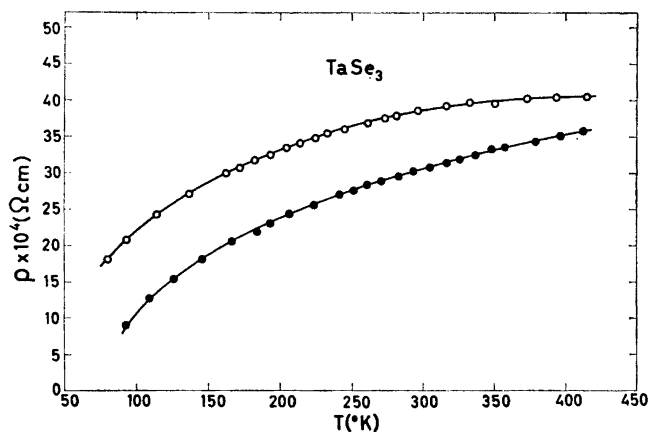
Fig. 3. ϱ *versus* T plot for TaSe$_3$. (Results marked ● are for the polycrystalline sample and ○ indicate those for the single crystals.)

are seen to have a positive temperature coefficient of resistance over the whole temperature range, the form of the curves showing either a saturation range of semiconductivity or metallic conductivity.

The following features point towards TaSe$_3$ being classified as a metallic compound:

(i) The shape of the curves in Fig. 3 and the resistivity level of the polycrystalline sample suggest metallic conduction. In addition, Aslanov *et al.*[5] report a Seebeck coefficient of zero against aluminium at room temperature. It should be noted however that the number of ∼10^{19} impurity atoms/cm^3 recorded for the present samples is sufficient to account for saturated semiconduction with a low activation energy.

(ii) Despite several unsuccessful attempts to arrive at a bonding scheme in which the observed crystal structure and magnetic properties of TaSe$_3$ could be accounted for, the discussion of Bjerkelund and Kjekshus [7] clearly showed that it was impossible to satisfy the generalized (8—N) rule with a reasonable assumption for the valences of tantalum and selenium. Since the generalized (8—N) rule is satisfied by all compounds known to be semiconductors, the negative finding for TaSe$_3$ indicates that the compound is metallic.

(iii) Considering the Se—Se distances of Table 1 (see also Fig. 2), those marked Se$_{III}$—Se$_V$ (2.576 ± 0.024 Å) and Se$_{IV}$—Se$_V$ (2.653 ± 0.023 Å) are too great to represent Se—Se single bonds (expectation value 2.40 ± 0.05 Å) whereas they are too short for there to be negligible bonding interaction. The collinearity of the atoms Se$_{III}$—Se$_V$—Se$_{IV}$ and the respective bond lengths suggest that delocalized electrons may be associated with this arrangement and thus available for metallic conduction.

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