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## Obtention of a new phase of the one-dimensional compound TaS<sub>3</sub> : X-Ray characterization and electrical measurements

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**Résumé.** — Une nouvelle variété de la phase TaS<sub>3</sub> a été observée. La maille est monoclinique :  $a = 9,515$  (2) Å,  $b = 3,341$  2 (4) Å,  $c = 14,912$  (2) Å,  $\beta = 109,99^\circ$  (2),  $V = 445,5$  Å<sup>3</sup> pour six motifs TaS<sub>3</sub> par maille. Une isotypie avec NbSe<sub>3</sub> est certaine. Les mesures électriques indiquent deux transitions, l'une métal-isolant de type Peierls à 210 K, l'autre à 160 K.

**Abstract.** — A new tantalum trisulfide with a monoclinic unit cell has been characterized :  $a = 9.515$  (2) Å,  $b = 3.341$  2 (4) Å,  $c = 14.912$  (2) Å,  $\beta = 109.99^\circ$  (2),  $V = 445.5$  Å<sup>3</sup> with  $Z = 6$ . The compound presents two transitions, one of a Peierls type metal-insulator at 210 K and the other at 160 K.

The existence of the trichalcogenide TaS<sub>3</sub> was first indicated by Biltz and Köcher [1]. Bjerkelund *et al.* [2] and Jellinek [3] established the symmetry and the parameters of the orthorhombic unit cell as given in table I. TaS<sub>3</sub> was obtained by heating tantalum and sulfur in stoichiometric proportions at 800 °C in a sealed silica tube followed by a very slow cooling (two weeks). Very recently, resistivity measurements have shown that TaS<sub>3</sub> exhibits a metal-insulator transition at 210 K which can be explained by a Peierls transition [4]. Evidence at low temperature of the commensurate Peierls superstructure has been

dependence of the CDW order parameter and the magnitude of the electronic gap opened by the CDW at the Fermi surface [7].

The observation of a second transition in our preliminary resistivity measurements on TaS<sub>3</sub> has incited us to re-examine the chemical and structural determination of TaS<sub>3</sub>. We have prepared TaS<sub>x</sub> compounds with  $2.6 < x < 4$  at different temperatures between 600 °C and 700 °C with different cooling speeds. The compounds with or near the composition TaS<sub>3</sub> are fibrous. The X-Rays pattern of the powdered TaS<sub>3</sub> compound prepared at 600 °C is the same as in reference [2], but with several reflexions due to TaS<sub>2</sub> and with very weak reflexions that we cannot index with the parameters given by Bjerkelund and Kjekshus [2]. A careful X-Ray examination of many single crystals showed that some of them presented a symmetry and cell parameters explaining the new set of lines. The new phase is monoclinic and the refined lattice parameters, determined from a Guinier photograph with Pb(NO<sub>3</sub>)<sub>2</sub> as internal calibration standard are given in table I. As can be seen also in this table the new compound is probably isostructural with NbSe<sub>3</sub> [8, 9], the cell parameters being very similar. In table II we compare observed and calculated interplanar spacings and relative intensities.

We have measured the electrical resistivity with the applied current along the fibers. The four electrical contacts were made with a conducting paint. For temperatures higher than room temperature, contacts were made with knots of very thin gold wire

Table I. — *Lattice parameters of TaS<sub>3</sub> and NbSe<sub>3</sub>.*

TaS <sub>3</sub> orthorhombic (references [2, 3])	TaS <sub>3</sub> monoclinic (this work)	NbSe <sub>3</sub> monoclinic (references [8, 9])
$a = 36.804$ Å	$a = 9.515$ (2) Å	$a = 10.009$ (1) Å
$b = 15.173$ Å	$b = 3.341$ 2 (4) Å	$b = 3.480$ 5 (6) Å
$c = 3.340$ Å	$c = 14.912$ (2) Å	$c = 15.629$ (2) Å
$V = 1\ 865.15$ Å <sup>3</sup>	$\beta = 109.99^\circ$ (2)	$\beta = 109.47^\circ$
$Z = 24$	$V = 445.5$ Å <sup>3</sup>	$V = 513.3$ Å <sup>3</sup>
Space group C 22 <sub>1</sub>	$Z = 6$	$Z = 6$
	likely space group P 2 <sub>1/m</sub>	Space group P 2 <sub>1/m</sub>

obtained by several groups by electron diffraction [4, 5], and X-ray measurements [6]. By Raman spectroscopy Tsang *et al.* have determined the temperature

(\*) L.A. 279 au C.N.R.S.

Table II. — Comparison of observed and calculated interplanar spacings and relative intensities from Guinier powder data.

$hkl$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I$
100	8.925 1	8.941 9	w
10 $\bar{2}$	6.752 9	6.747 8	w
101	6.579 4	6.585 9	vw
003	4.672 5	4.671 2	s
200	4.467 1	4.470 9	w
20 $\bar{3}$	3.981 6	3.980 4	m
10 $\bar{4}$	3.723 9	3.722 8	w
103	3.657 2	3.658 7	vw
20 $\bar{4}$	3.373 1	3.373 9	vvw
30 $\bar{3}$	3.025 3	3.025 0	vw
11 $\bar{2}$	2.995 3	2.994 2	s
10 $\bar{5}$		2.981 1	
111	2.981 2	2.979 6	s
300		2.980 6	
104	2.933 6	2.938 5	vw
20 $\bar{5}$	2.853 9	2.854 0	m
11 $\bar{3}$	2.756 7	2.757 1	w
21 $\bar{1}$	2.734 8	2.734 0	w
013	2.718 3	2.717 5	m
21 $\bar{2}$	2.691 3	2.690 4	m
210	2.675 9	2.676 4	w
21 $\bar{3}$	2.560 1	2.559 1	m
211	2.534 0	2.535 0	m
10 $\bar{5}$		2.446 4	
20 $\bar{6}$	2.445 3	2.440 7	m
006	2.334 8	2.335 6	vw
30 $\bar{6}$	2.250 1	2.249 2	vvw
31 $\bar{3}$	2.241 7	2.242 4	vvw
310		2.224 2	
11 $\bar{5}$	2.224 9	2.224 4	w
40 $\bar{5}$		2.140 4	
21 $\bar{3}$	2.140 7	2.140 9	m
20 $\bar{7}$	2.115 8	2.116 9	m
401	2.099 2	2.098 7	vvw
11 $\bar{6}$	1.990 5	1.989 4	m
21 $\bar{6}$	1.972 9	1.970 8	m
41 $\bar{2}$	1.936 9	1.937 4	m
31 $\bar{6}$	1.866 4	1.865 8	m
41 $\bar{6}$	1.710 0	1.709 8	m
408	1.686 4	1.686 9	m
020	1.669 2	1.670 6	s

around the samples. In figure 1, we show the logarithm of the resistivity of our TaS<sub>3</sub> samples as a function of  $1000/T$ . Sample labelled A is a bundle of fibers. The metallic behaviour at high temperatures is well observed. But we observed two transitions for  $1000/T_1 = 4.8$  ( $T_1 = 210$  K) and  $1000/T_2 = 6.2$  ( $T_2 = 160$  K), where the logarithm of the resistivity shows the sharpest increase. On the same plot the dashed line indicates the results obtained by Sambongi *et al.* [4] where only the transition at  $T_1$  was observed. Sample B is the single crystal for which

the X-Ray lattice parameters were determined and which correspond to the monoclinic phase. Transitions occur at the same temperature  $T_1$  and  $T_2$ . We have observed the same behaviour on all the samples we have measured (more than ten of different batches). However, the relative amplitudes of the sharp increase of the resistivity at  $T_1$  and  $T_2$  are sample dependent. Below 120 K, the resistivity can be well described in the form of  $\exp.(E/2kT)$ . But we found  $E = 55$  meV for sample A and 114 meV for sample B. Below 160 K, non-linear  $I-V$  characteristics were observed. DC and pulsed currents were used. The non-linear conductivity is not due to heating which can be directly observed on the shape of the voltage across the sample. Non-linearity is a common feature of pinned charge density waves and can be explained by the non-linear mode associated with the phase of the CDW [10]. Detailed results will be given in a further publication.

According to the preparation, both compounds, the orthorhombic one isolated by Bjerkelund and Kjekshus [2], and the monoclinic one, can be assigned a composition close to TaS<sub>3</sub>. The orthorhombic derivative was not submitted to a precise analysis. The B crystal used for X-Ray determination was also too small to lead the reliable quantitative analysis.

The relationship between both compounds does not appear to be a simple one as would be the case between a structure and its superstructure. It could be assumed that a slight deviation from stoichiometry occurs for, at least, one of the compounds without it being presently possible to establish which phase is non-stoichiometric. A non-stoichiometry in MX<sub>3</sub> chalcogenides as already been considered by F. Jellinek *et al.* [11]. A simple model can be proposed assuming a replacement of some (S<sub>2</sub>)<sup>2-</sup> groups by S<sup>-</sup> ions in the MX(X<sub>2</sub>) formula. This would lead to a chalcogen deficiency MX<sub>3-x</sub>. Considering (X<sub>2</sub>)<sup>2-</sup> pairs at the S<sup>-</sup> ions sites a chalcogen excess would be also possible as MX<sub>4</sub> chalcogenides exist. The coexistence of two different compounds of very similar composition may occur in the same batch due to small temperature gradients. However no precise structural determination has been made for both compounds and it is not to be excluded that they have related but different structural arrangements. A recent XPS study of the orthorhombic TaS<sub>3</sub> has shown evidence of the occurrence of two types of tantalum which is not to be expected in the classical MX<sub>3</sub> model [12].

After heating the orthorhombic phase under vacuum, a loss of sulfur was observed at 180 °C without a modification of the X-ray diffraction pattern. The sample was then heated up to 500 °C without further loss of sulfur. At that temperature a mixing of the orthorhombic and of the monoclinic phases was observed. At higher temperature (650 °C) the X-Ray lines of the TaS<sub>3</sub> monoclinic phase increased.

In conclusion we have shown that TaS<sub>3</sub> may exist

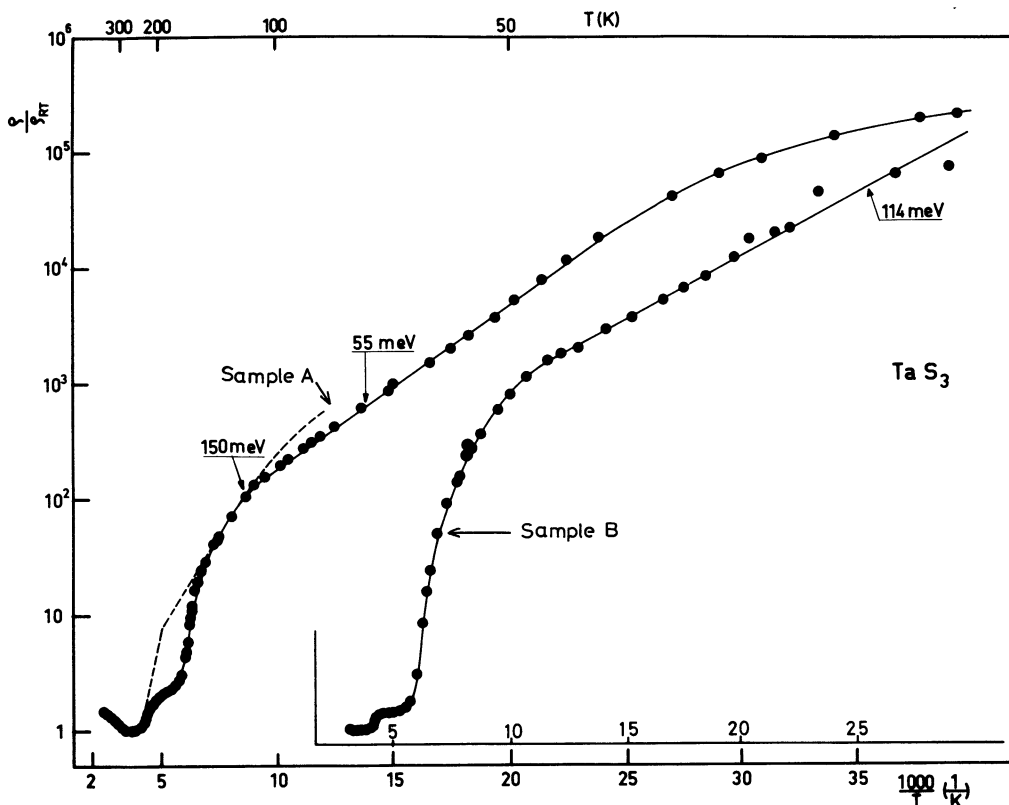


Fig. 1. — Semi-log plot of the resistivity of TaS<sub>3</sub> normalized to the room temperature as a function of  $1000/T$ . Sample A is a bundle of fibers. The dashed line indicates the results of Sambongi *et al.* (Ref. [4]). Sample B is the same monocrystal of TaS<sub>3</sub> on which the parameters of the monoclinic phase were determined.

in at least two phases. The monoclinic phase is isostructural with NbSe<sub>3</sub>. The Bjerkelund and Kjekshus derivative, with a bigger unit cell, is not a simple superstructure of the monoclinic form. The resistivity measurements on samples of the new TaS<sub>3</sub> monoclinic phase indicate two phase transitions: a metal-insulator transition at 210 K probably due to a Peierls transition which is observed also for the orthorhombic phase of TaS<sub>3</sub>, and another transition in the semi-conducting state at 160 K. Preliminary electronic diffraction measurements show diffuse scattering lines at room temperature which condense into superlattice spots below 210 K [13]. The vector of the distortion has a projection of 1/4 on the reciprocal

lattice along the chain axis ( $b^*$  for the monoclinic cell or  $c^*$  for the orthorhombic cell). We suggest that the components of this vector may be different at the  $T_1$  and  $T_2$  transitions or have a continuous variation between the two transitions. More work from the chemical point of view must be done in order to determine if there are other TaS<sub>3</sub> phases and experiments, in particular electronic diffraction measurements as a function of temperature, must be performed in order to study in more detail the nature of the two phase transitions.

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