

## High-Pressure Syntheses of TaS<sub>3</sub>, NbS<sub>3</sub>, TaSe<sub>3</sub>, and NbSe<sub>3</sub> with NbSe<sub>3</sub>-Type Crystal Structure

S. KIKKAWA,\* N. OGAWA, AND M. KOIZUMI

*The Institute of Scientific and Industrial Research, Osaka University,  
Osaka 565, Japan*

AND Y. ONUKI

*Saitama Institute of Technology, Fusaiji Okabe, Saitama 369-02, Japan*

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Transition metal trichalcogenides TaSe<sub>3</sub>, TaS<sub>3</sub>, NbSe<sub>3</sub> and NbS<sub>3</sub> were prepared under the reaction conditions of 2 GPa, 700°C, 30 min. NbSe<sub>3</sub> is exactly the same as that obtained in the usual sealed-tube method. The other products are modifications of each usual phase. They have crystal structures very similar to that of NbSe<sub>3</sub>. The lattice parameters are  $a = 10.02 \text{ \AA}$ ,  $b = 3.48 \text{ \AA}$ ,  $c = 15.56 \text{ \AA}$ ,  $\beta = 109.6^\circ$  for TaSe<sub>3</sub>,  $a = 9.52 \text{ \AA}$ ,  $b = 3.35 \text{ \AA}$ ,  $c = 14.92 \text{ \AA}$ ,  $\beta = 110.0^\circ$  for TaS<sub>3</sub>, and  $a = 9.68 \text{ \AA}$ ,  $b = 3.37 \text{ \AA}$ ,  $c = 14.83 \text{ \AA}$ ,  $\beta = 109.9^\circ$  for NbS<sub>3</sub>. In spite of the similarity in their crystal structures, these high-pressure phases show a variety of electrical transport properties. TaSe<sub>3</sub> is a superconductor having  $T_c$  at 1.9 K. TaS<sub>3</sub> is a semiconductor with two transitions at 200 and 250 K. NbS<sub>3</sub> is a semiconductor with  $E_a = 180 \text{ MeV}$ .

### Introduction

Many papers have appeared recently in connection with electronic properties of transition metal trichalcogenides  $MX_3$  ( $M$ : Ti, Zr, Nb, Ta;  $X$ : S, Se) (1). All these compounds are usually prepared in evacuated quartz tubes (2-4). They form needle-shaped crystals with the common structural feature that each metal atom lies at the center of the trigonal prism of chalcogen atoms (5). Successive prisms are arranged in infinite chains along the  $b$  axis. However, the transport properties are markedly different from each other. NbSe<sub>3</sub> and TaSe<sub>3</sub>

are highly anisotropic metals from room temperature down to helium temperatures. TaSe<sub>3</sub> is superconducting below 2.2 K (6-8). NbSe<sub>3</sub> shows two major resistivity anomalies at 145 and 59 K suggestive of charge density wave formation, although no such anomalies are observed in the resistivity of TaSe<sub>3</sub> (9). The group IV compounds and the group V sulfides are semiconductors (4, 6, 10-12). A Peierls metal-insulator transition has been observed at 270 K in TaS<sub>3</sub> (13). All these trichalcogenides have basically the same structural units, i.e., chains of  $MX_6$  trigonal prism. However, they are different from each other in the shape and the packing of the trigonal prism chains. These differences

\* To whom correspondence should be addressed.

may cause this large variation in electrical properties. An electron band structure has already been calculated to explain the variations considering the crystal structural differences (1, 14).

Tantalum trisulfide,  $TaS_3$ , prepared above  $800^\circ C$  crystallizes with an orthorhombic unit cell (2, 6). On the other hand, Meerschaut *et al.* have lately obtained a monoclinic modification of  $TaS_3$  as a minor phase in a sample synthesized between  $600$  and  $700^\circ C$  (15). Most of the product was a mixture of  $TaS_2$  and orthorhombic  $TaS_3$ . The monoclinic phase is probably isostructural with  $NbSe_3$ . Very recently, Kikkawa *et al.* have prepared monoclinic  $TaS_3$  as a single phase under high pressure (16).

In the present paper, we were able to obtain the respective niobium and tantalum trisulfides and triselenides with  $NbSe_3$  structure under high pressures. X-Ray diffraction and electrical resistivity measurements were carried out on the products. The results are discussed in connection with the data for the phases already reported.

## Experimental

Powders of each metal were mixed with powdered chalcogen in the molar ratio  $X/M = 3$ . Purities of Nb, Ta, S, and Se were, respectively, 99, 99.9, 99.5, and 99.9%. The mixtures were placed inside carbon heaters separated by BN sleeves 4 mm in diameter and 3 mm in height. These assemblages were inserted in pyrophyllite cubes and subjected to high-temperature and -pressure conditions ( $700^\circ C$ , 2 GPa) using a cubic anvil device. The duration of each reaction was 30 min. All products were black sintered masses. In order to grow single crystals, products were melted with various amounts of excess chalcogen and solidified under various cooling rates. However,

these trials failed. Products were identified by X-ray powder diffractometry. Lattice parameters were refined using a least-squares method. Electrical resistivity and magnetoresistivity of the sintered bodies were measured by the ordinary four-probe dc method. Electrical contacts for lead wires were made of indium ultrasonically soldered to the sample pellet on the glass plate.

## Results

### X-Ray Diffraction

X-Ray powder diffraction patterns are depicted in Fig. 1 for the respective trichalcogenides prepared under high pressures. The diffraction for  $NbSe_3$  was the same as that reported by Meerschaut and

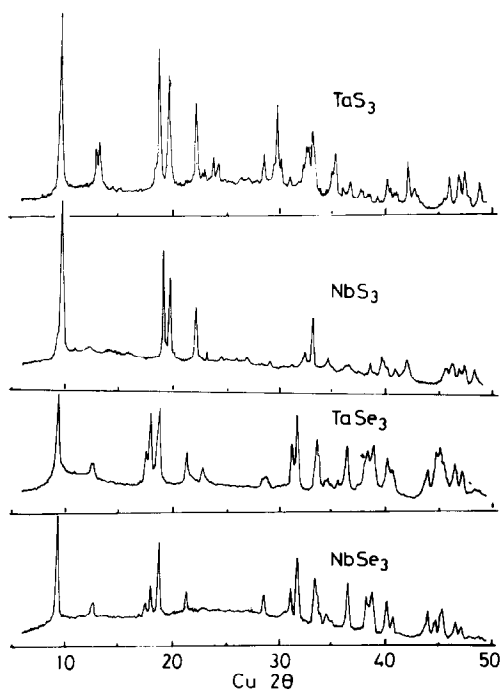


FIG. 1. X-Ray diffraction patterns for  $TaS_3$ ,  $NbS_3$ ,  $TaSe_3$ , and  $NbSe_3$  prepared under high pressure. No extra lines are observed.

Rouxel (3). They prepared NbSe<sub>3</sub> in a quartz tube and determined the crystal structure as having a monoclinic unit cell with dimensions  $a = 10.006 \text{ \AA}$ ,  $b = 3.478 \text{ \AA}$ ,  $c = 15.626 \text{ \AA}$ , and  $\beta = 109.5^\circ$ . On the other hand, the X-ray diffraction pattern for TaSe<sub>3</sub> was different from that reported by Bjerkelund and Kjekshus (2), and was very similar to that for NbSe<sub>3</sub>. Diffraction data are represented in Table 1. All diffraction peaks were indexed so that the high-pressure form of TaSe<sub>3</sub> has a monoclinic unit cell very similar to that of NbSe<sub>3</sub>:  $a = 10.02 \text{ \AA}$ ,  $b = 3.48 \text{ \AA}$ ,  $c = 15.65 \text{ \AA}$ , and  $\beta = 109.6^\circ$ .

TABLE I  
X-RAY DIFFRACTION DATA FOR TaSe<sub>3</sub> PREPARED  
UNDER HIGH PRESSURE

$hkl$	$d_{\text{obsd}}$ (\AA)	$d_{\text{calcd}}$ (\AA)	$I$
1 0 0	9.481	9.436	<i>vs</i>
1 0 $\bar{2}$	7.047	7.074	<i>w</i>
1 0 2	5.055	5.045	<i>m</i>
0 0 3	4.929	4.914	<i>s</i>
2 0 0	4.726	4.718	<i>s</i>
2 0 $\bar{3}$	4.179	4.175	<i>m</i>
1 0 4	3.910	3.906	<i>w</i>
1 1 $\bar{2}$	3.125	3.120	<i>w</i>
2 0 3	2.942	2.945	<i>vw</i>
3 0 1	2.859	2.885	<i>m</i>
2 1 0	2.806	2.799	<i>s</i>
2 1 $\bar{3}$	2.671	2.672	<i>m</i>
3 0 $\bar{5}$	2.656	2.638	<i>m</i>
3 0 2	2.593	2.595	<i>w</i>
2 0 4	2.524	2.522	<i>w</i>
0 0 6	2.459	2.457	<i>m</i>
3 0 $\bar{6}$	2.348	2.358	<i>m</i>
3 0 3	2.319	2.319	<i>m</i>
4 0 $\bar{5}$	2.247	2.246	<i>m</i>
2 0 $\bar{7}$		2.221	
1 0 $\bar{7}$	2.220	2.220	<i>m</i>
4 0 1		2.216	
4 0 2	2.063	2.055	<i>m</i>
4 1 $\bar{2}$	2.029	2.032	<i>m</i>
0 1 6	2.008	2.006	<i>m</i>
2 0 $\bar{8}$		1.953	
4 1 0	1.953	1.952	<i>m</i>
2 0 6		1.927	
3 1 3	1.927	1.930	<i>m</i>
0 2 0	1.740	1.738	<i>w</i>

Neither unreacted Ta nor Se could be observed. TaS<sub>3</sub> usually crystallizes as orthorhombic modification in evacuated tubes. In the present study, however, it was obtained as a monoclinic modification having a crystal structure similar to NbSe<sub>3</sub> as mentioned elsewhere (16). A refinement of the structure of monoclinic TaS<sub>3</sub> has been reported by Meerschaut *et al.* (17). The monoclinic structure had been related to that of NbSe<sub>3</sub>. NbS<sub>3</sub> also crystallized in a crystal structure different from that prepared by the conventional method (4, 18). Table 2 shows X-ray diffraction data for NbS<sub>3</sub> prepared under high pressures, which are similar to the diffraction data for monoclinic TaS<sub>3</sub> (15-17). The high-pressure modification of NbS<sub>3</sub> is identical with neither of the modifications reported by Cornelissens *et al.* (19) or by Boswell and Prodan (20). Its X-ray diffraction data could not be fully indexed due to the presence of characteristic diffraction peaks,  $d = 4.659$

TABLE II  
X-RAY DIFFRACTION DATA FOR NbS<sub>3</sub> PREPARED  
UNDER HIGH PRESSURE

$hkl$	$d_{\text{obsd}}$ (\AA)	$d_{\text{calcd}}$ (\AA)	$I$
1 0 0	9.110	9.095	<i>vs</i>
0 0 3	4.659	4.646	<i>s</i>
2 0 0	4.523	4.547	<i>s</i>
2 0 $\bar{3}$	4.031	4.003	<i>m</i>
1 0 3	3.658	3.662	<i>vw</i>
2 0 2	3.340	3.324	<i>vw</i>
3 0 $\bar{3}$	3.069	3.061	<i>vw</i>
1 1 2	2.745	2.757	<i>w</i>
2 1 0	2.690	2.707	<i>m</i>
2 1 3	2.582	2.577	<i>w</i>
0 0 6	2.324	2.323	<i>w</i>
3 1 0	2.261	2.254	<i>w</i>
3 1 1	2.141	2.141	<i>w</i>
3 0 4	1.978	1.978	<i>w</i>
2 1 4	1.956	1.954	<i>w</i>
5 0 2	1.927	1.928	<i>w</i>
0 1 6	1.909	1.912	<i>w</i>
3 1 $\bar{6}$	1.874	1.872	<i>w</i>
5 0 $\bar{5}$	1.836	1.837	<i>w</i>

and 4.031 Å and so on for NbSe<sub>3</sub>-type crystal structure. It was indexed as monoclinic very similar to monoclinic TaS<sub>3</sub>:  $a = 9.68$  Å,  $b = 3.37$  Å,  $c = 14.83$  Å, and  $\beta = 109.9^\circ$ .

For high-pressure forms of TaSe<sub>3</sub>, TaS<sub>3</sub>, and NbS<sub>3</sub>, their X-ray powder diffraction patterns were different from those of the corresponding normal phases. They could be indexed so that the high-pressure modifications have a crystal structure similar to that of NbSe<sub>3</sub>.

### Electrical Conductivity

TaSe<sub>3</sub> prepared under pressure was metallic below room temperature as shown in Fig. 2. The resistivity was  $2 \times 10^{-3} \Omega \cdot \text{cm}$  at room temperature. The compound became a superconductor below 1.9 K. In spite of the different crystal structure, the single crystal of conventional TaSe<sub>3</sub> was also metallic with a resistivity of  $5 \times 10^{-4} \Omega \cdot \text{cm}$  at room temperature and changed to a superconductor at 2.2 K (6–8). Scattering at the grain boundary of the polycrystalline sample may have raised the resistivity in the present study. In order to investigate the superconducting state of high-pressure modification, the resistivity was measured in changing magnetic field up to 12 kOe at 1.6 and 1.4 K. As shown in Fig. 3, the critical magnetic field  $H_{c2}$  was 2 kOe at 1.6 K and 6 kOe at 1.4 K.

NbSe<sub>3</sub> prepared under pressure showed a

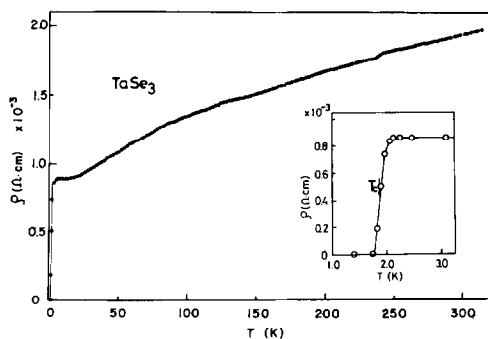


FIG. 2. Electrical resistivity of TaSe<sub>3</sub> prepared under high pressure.

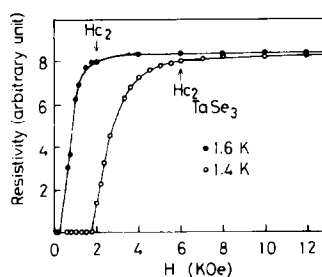


FIG. 3. Change of resistivity on TaSe<sub>3</sub> with the applied magnetic field at 1.4 and 1.6 K.

peculiar temperature dependence of electrical resistivity as depicted in Fig. 4. The resistivity was  $3 \times 10^{-3} \Omega \cdot \text{cm}$  at room temperature and decreased with temperature down to 150 K. Then, it showed two anomalous maxima at 120 and at 40 K. This anomalous behavior is similar to that of usual NbSe<sub>3</sub> due to the same crystal structure as that of the usual form. The resistivity maximum at 40 K, however, seems to be emphasized in the present study. Magnetoresistivity was measured at 1.4, 1.6, and 4.2 K, changing the magnetic field up to 24 kOe. Positive values were observed as shown in Fig. 5. Under a magnetic field of 24 kOe, they were large, amounting to 6.03, 5.29, and 0.73%, respectively.

TaS<sub>3</sub> was a semiconductor above liquid nitrogen temperature as mentioned elsewhere (16). Specific resistivity was  $8 \times 10^{-2} \Omega \cdot \text{cm}$  at room temperature. The activation energy was 120 MeV in the temperature

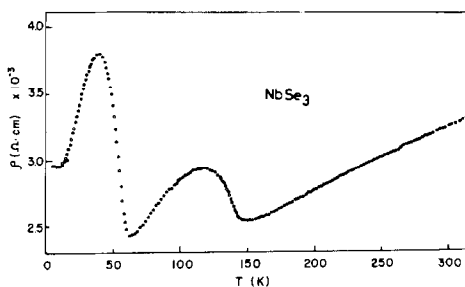


FIG. 4. Electrical resistivity of NbSe<sub>3</sub> prepared under high pressure.

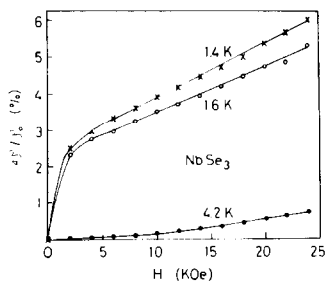


FIG. 5. Magnetoresistance of NbSe<sub>3</sub> at 1.4, 1.6, and 4.2 K.

range between 130 and 170 K. The resistivity decreased with temperature, showing a small anomaly at around 200 K. It seems to increase above room temperature. Metal–semiconductor transition has been observed around room temperature on the conventional modification of TaS<sub>3</sub> (13).

NbS<sub>3</sub> was a typical semiconductor having a resistivity of  $10^2 \Omega \cdot \text{cm}$  at room temperature as shown in Fig. 6. The activation energy was 180 meV. The usual modification of NbS<sub>3</sub> was also a semiconductor having resistivity of  $10^3 \Omega \cdot \text{cm}$  at room temperature (4).

The new modifications of TaSe<sub>3</sub>, TaS<sub>3</sub>, and NbS<sub>3</sub> prepared under high pressure

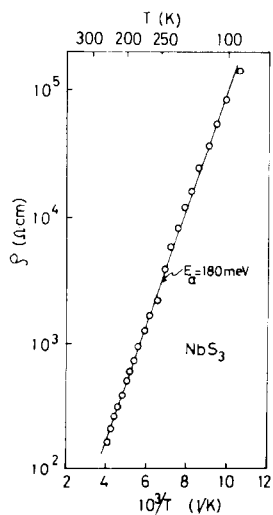


FIG. 6. Electrical resistivity of NbS<sub>3</sub> prepared under high pressure.

showed essentially the same electronic properties as those of conventional phases in spite of their different crystal structures. It is surprising that the electrical properties of the high-pressure forms of the compounds  $\text{MX}_3$  are so different from each other and resemble those of the corresponding normal forms. It was verified before and after measurements of the electrical properties that the samples actually were of the high-pressure form. Any phase transitions from the high-pressure form to the normal form were not observed during the electrical measurements. Electrical properties of these anisotropic compounds should be measured on single crystals. We are still trying to obtain single crystals of these modifications.

## Discussion

Transition metal trichalcogenides were prepared by heating the elements in quartz tubes. Their crystal structure consists basically of infinite chains of  $\text{MX}_6$  trigonal prisms. However, they are slightly different from each other. The structural differences are thought to be the cause of the variation of their electrical properties (1, 14).

The crystal structures of ZrSe<sub>3</sub>, TaSe<sub>3</sub>, and NbSe<sub>3</sub> are illustrated in Fig. 7. Their

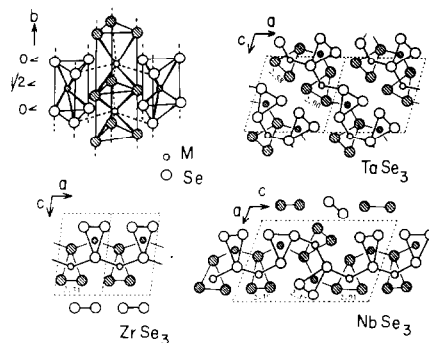


FIG. 7. Schematic crystal structure of triselenides. Stacking of prisms along the  $b$  axis and projections of the ZrSe<sub>3</sub>, TaSe<sub>3</sub>, and NbSe<sub>3</sub> structures in the  $ac$  plane are represented. Open and shaded circles are at 0 and at  $b/2$ , respectively.

structures are derived from that for  $ZrSe_3$ . In the  $ZrSe_6$  prism, two of the Se atoms in the base of each prism are bonded at a distance comparable to that in pure Se (2.30 Å) while the other Se–Se distances are considerably longer. The prisms share their tops and bottoms with each other, forming columns of  $ZrSe_6$  along the  $b$  axis. The columns are displaced by  $b/2$  with respect to each other. Each metal atom has two Se neighbors in adjacent columns at distances scarcely longer than those to its six intracolumn ligands. The one-dimensional columns are linked via the intercolumn bond, forming successive layers separated by a van der Waals gap.

The number of columns per unit cell increases from two in  $ZrSe_3$  to four in  $TaSe_3$ , and to six in  $NbSe_3$ . In  $ZrSe_3$  two columns of the chain  $ZrSe_6$  have the same dimension in a unit cell. They form a continuous  $M$ –Se– $M$ –Se pathway perpendicular to themselves. In  $TaSe_3$  four canted chains in a unit cell can be divided into two duos of columns. An inner duo of columns that are still in the  $ZrSe_3$  setting displays fairly substantial Se–Se pairing (2.58 Å). The flanking duo, however, has almost completely relaxed their Se–Se pairing (2.90 Å). Moreover, the intercolumn linkages terminate on these expanded columns instead of forming extended pathways. The structure of  $NbSe_3$  includes blocks of four columns similar to those in  $TaSe_3$ . However, these blocks are now interconnected through an additional duo of strongly canted  $ZrSe_3$ -like columns instead of being directly linked. The interchain  $M$ –Se pathways once again terminate at the expanded columns.

The crystal structure of  $NbS_3$  is closely related to the  $ZrSe_3$  structure type. The main difference with  $ZrSe_3$  is that the Nb atoms are shifted from the mirror planes of the surrounding bicapped trigonal prisms of sulfur atoms to form Nb–Nb pairs (Nb–Nb = 3.04 Å). The structure of  $TaS_3$  is not yet fully determined. It has been reported that

the unit cell contains 24 chains. There might be a more or less continuous spread of the S–S bonding in the different chains due to the large number of chains in the unit cell.

In the present study, the transition metal trichalcogenides  $TaSe_3$ ,  $TaS_3$ ,  $NbSe_3$ , and  $NbS_3$  were prepared under high chalcogen vapor pressure in a high-pressure reaction vessel. The present  $NbSe_3$  was the same in structure as that already reported (3). On the other hand, the remaining three compounds were different from those prepared in quartz tubes (2, 4). Applying high-pressure technique,  $TaSe_3$ ,  $TaS_3$ , and  $NbS_3$  were prepared as the modifications having probably  $NbSe_3$ -type crystal structure. Their powder X-ray diffraction patterns could be indexed so that the modifications have the same crystal structure as that of  $NbSe_3$ . The lattice parameters of the high-pressure phases are summarized in Table 3 in comparison with the data for the already reported phases (2, 3, 18). Densities were calculated using the X-ray data. High-pressure forms have slightly higher densities. The phase relations between high-pressure and normal forms will be discussed in the following paper (21). The high-pressure forms were stoichiometric  $MX_3$  and the normal forms were less-chalcogen phases.

Although the four trichalcogenides prepared under pressure had the same crystal structure, their electrical properties were different from each other. Their properties were basically the same as those of the products in quartz tubes.  $TaSe_3$  was a superconductor having  $T_c$  at 1.9 K.  $NbSe_3$  was a metal down to 1.2 K. Its temperature dependence of resistivity had two anomalies at 120 and at 40 K, which might be caused by formation of charge density wave.  $TaS_3$  seemed to change from metal to semiconductor around room temperature as observed in orthorhombic  $TaS_3$  (13). This change might be a Peierls transition, which is characteristic of one-dimensional

TABLE III  
LATTICE PARAMETERS OF TRANSITION METAL TRICHALCOGENIDES PREPARED UNDER HIGH PRESSURE AND IN SEALED TUBES

	NbS <sub>3</sub>	NbSe <sub>3</sub>	TaS <sub>3</sub>	TaSe <sub>3</sub>
		Prepared in sealed tubes		
Crystal system	Tricli. (17)	Monocli. (3)	Ortho. (2)	Monocli. (2)
Space group	$P\bar{1}$	$P2_1/m$	$Cmcm$	$P2_1/m$
Lattice constants	$a = 4.963 \text{ \AA}$ $b = 6.730 \text{ \AA}$ $c = 9.144 \text{ \AA}$ $\beta = 97.17^\circ$ $\alpha = \gamma = 90^\circ$	$a = 10.006 \text{ \AA}$ $b = 3.478 \text{ \AA}$ $c = 15.626 \text{ \AA}$ $\beta = 109.50^\circ$	$a = 36.804 \text{ \AA}$ $b = 15.117 \text{ \AA}$ $c = 3.340 \text{ \AA}$	$a = 10.402 \text{ \AA}$ $b = 3.495 \text{ \AA}$ $c = 9.829 \text{ \AA}$ $\beta = 106.26^\circ$
Unit cell volume ( $\text{\AA}^3$ )	303.0	513.3	1865.2	343.0
X-Ray density ( $\text{g/cm}^3$ )	4.14	6.41	5.92	8.08
		Prepared under high pressure		
Crystal system	Monocli.	Monocli.	Monocli.	Monocli.
Lattice constants	$a = 9.68 \text{ \AA}$ $b = 3.37 \text{ \AA}$ $c = 14.83 \text{ \AA}$ $\beta = 109.9^\circ$	$a = 10.02 \text{ \AA}$ $b = 3.47 \text{ \AA}$ $c = 15.63 \text{ \AA}$ $\beta = 109.5^\circ$	$a = 9.52 \text{ \AA}$ $b = 3.35 \text{ \AA}$ $c = 14.92 \text{ \AA}$ $\beta = 110.0^\circ$	$a = 10.02 \text{ \AA}$ $b = 3.48 \text{ \AA}$ $c = 15.65 \text{ \AA}$ $\beta = 109.6^\circ$
Unit cell volume ( $\text{\AA}^3$ )	454.3	512.8	446.8	513.4
X-Ray density ( $\text{g/cm}^3$ )	4.15	6.41	6.18	8.11

compounds. NbS<sub>3</sub> should be metallic, as is TaS<sub>3</sub>, but it was a semiconductor. Similar behavior was reported on normal NbS<sub>3</sub> already prepared in which Nb–Nb pairing was observed (18). However, there was no clear evidence of such pairing in X-ray powder diffraction patterns of the present phase. The similarities of electrical resistivities between the normal phases and the corresponding high-pressure phases suggest that the conduction along the  $[MX_6]$  chain plays the most important role in the electron transport in the compounds. Neither the manner of packing of the chains nor a minor change in the arrangement of chalcogen in the chain has much of an effect on the electron transport.

In conclusion, monoclinic modifications of TaSe<sub>3</sub>, TaS<sub>3</sub>, and NbS<sub>3</sub> having NbSe<sub>3</sub>-type crystal structure were obtained applying a high-pressure technique in the prepara-

tions. Their electrical transport properties were not much different from those of the corresponding normal phases.

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