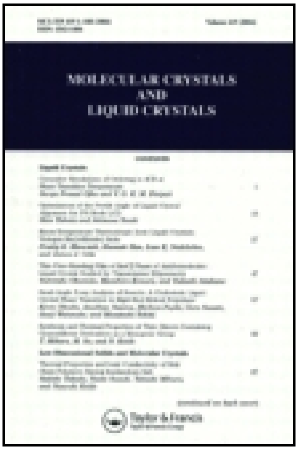

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New 1-D Chalcogen-Rich Niobium and Tantalum Chalcogenides

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NEW 1-D CHALCOGEN-RICH NIOBIUM AND TANTALUM CHALCOGENIDES

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A monoclinic form of TaS_3 has been characterized. It undergoes a metal-insulator transition at 240 K which structural effects will be discussed. A new iron-containing niobium selenide ($FeNb_3Se_{10}$) retains in its structure one type of $NbSe_3$ chains present in niobium triselenide. However the C.D.W. observed in this chain in the case of $NbSe_3$, has been replaced here by a metal-insulator transition at 140 K.
A second series of new chalcogenides concerns the X_xMY_4 derivatives (X = Cl, Br, I ; $0 < x < 0.50$; M = Nb, Ta ; Y = S, Se). In the structure MY_4 columns built up with MY_8 rectangular antiprisms, are separated by X chains. Long and short M-M distances may alternate in different ways with a related effect on the electrical properties.

TRANSITION METAL TRICHALCOGENIDES AND MONOCLINIC TaS_3

From a structural point of view, all of the transition metal trichalcogenides (T.M.T.C.) are built up with the same framework (Figure 1). In any case MY_3 trigonal prismatic chains are running along the monoclinic b axis giving a pseudo one-dimensional character to these compounds. Differences due to chalcogen-chalcogen bonds in the triangular base of the trigonal prismatic framework (Figure 2) lead to recognize three types of compounds :

- those with one kind of chains as represented by $ZrSe_3$[1].
- those with two kinds of chains such as $TaSe_3$[2].
- those with three kinds of chains as represented by $NbSe_3$[3].

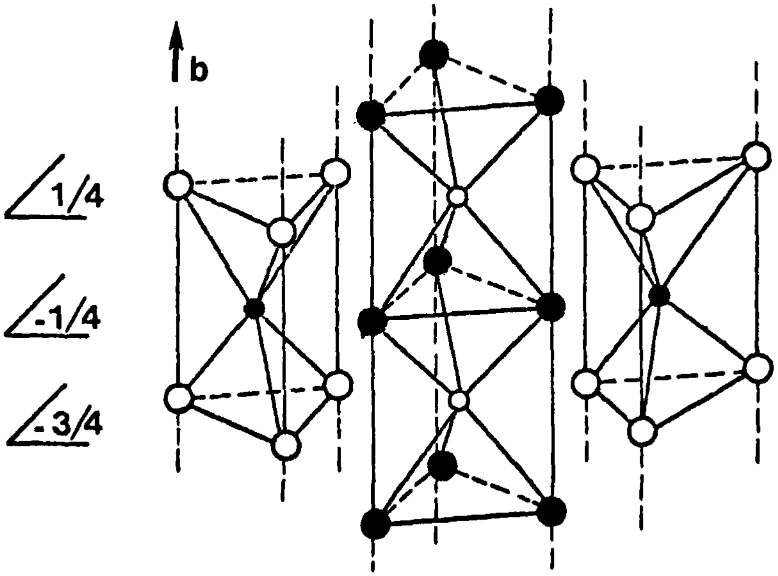


FIGURE 1 Trigonal prismatic frame in MY_3 chalcogenides

The two strong anomalies observed in the resistivity curve of $NbSe_3$[4] and, probably to a larger extent, the possible depinning of the corresponding C.D.W., explain the considerable interest devoted by physicists in the study of these compounds. Without any doubt $NbSe_3$ has considerably enlarged the field of research concerning structural instabilities before being the subject of theoretical studies.

The less or more 1 D character of these compounds is to be related to the strength of the lateral bondings associating the chains in ribbons, which in turn depends directly on the ionicity of the metal-chalcogen-bonds. $NbSe_3$ presents two C.D.W., which do not suppress the metallic state at low temperature, but orthorhombic TaS_3[5] with a more electropositive cation and a more electronegative anion presents a metal-insulator transition.

What distinguishes the three structural types of T.M.T.C. is the length of the Y-Y bond. A lengthening of such a pair corresponds to a weakening of the bonding and to a reinforcement of the neighbouring metal-chalcogen bond. Therefore we consider that the Y-Y pairs largely govern the properties of these compounds. It behaves as a reservoir of electrons giving rise to a related variation of the electron density from chain to chain.

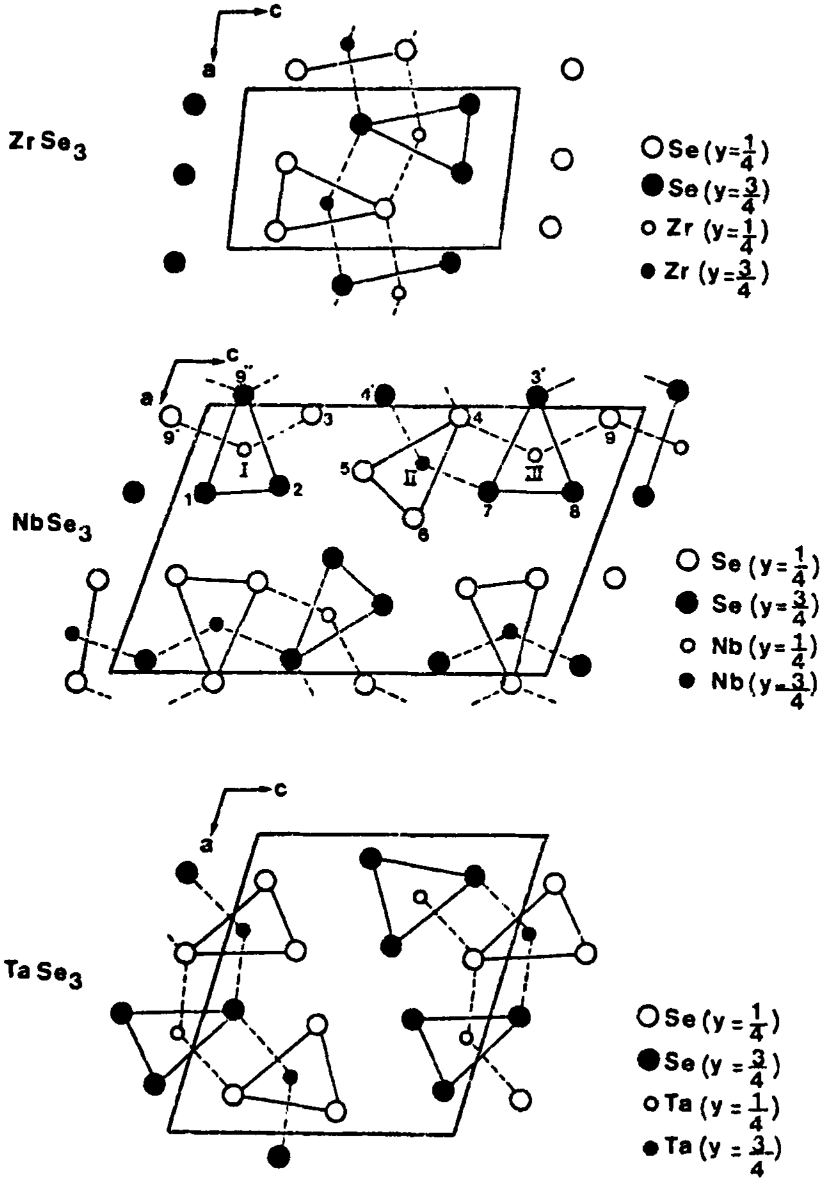


FIGURE 2 $ZrSe_3$, $TaSe_3$ and $NbSe_3$ structural types

The role of the chemist at this point is to prepare new MX_3 compounds or at least new Low Dimensional chalcogenides with chalcogen pairs in order to get a reasonable number of terms to draw general conclusions. The chemist is also able to modify the electronic density along the metallic chains by performing a well motivated intercalation chemistry.

Let us consider at first the trichalcogenides themselves. Comparing with transition metal dichalcogenides, it is clear that polytypism is to be expected associating various types of chains in new arrangements.

We have been able to prepare a new form of TaS_3[6] It presents a monoclinic structure, to be distinguished from the orthorhombic one of the previously known TaS_3. The structure (Figure 3) shows

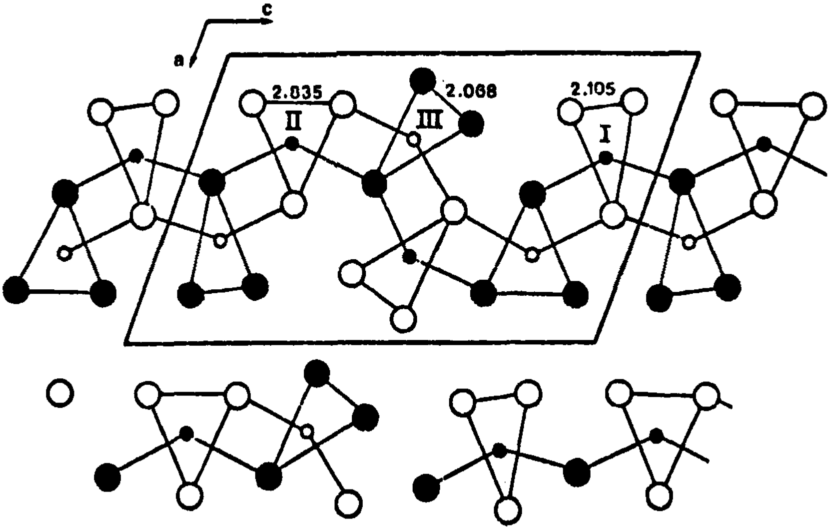


FIGURE 3 Structural arrangement in monoclinic TaS_3

three groups of chains as a function of the Y-Y distances in the anionic pairs. Two chains are concerned with short Y-Y distances of 2.068 and 2.105 Å, the third one exhibits a longer Y-Y distance of 2.835 Å. This is an important difference with $NbSe_3$ which shows short, mean, and long distances for the chalcogen pairs. Monoclinic TaS_3 undergoes two phase transitions[7] : the first one around 240K

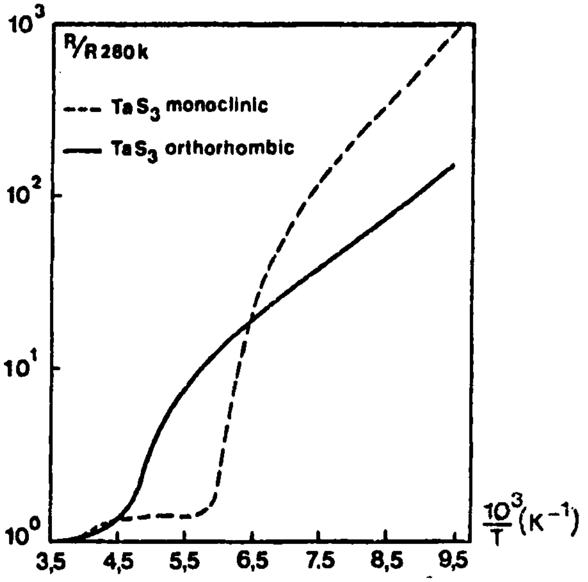


FIGURE 4 Metal-insulator transition in monoclinic TaS_3

is a metal insulator transition, the second one at 160K appears in the semi-conducting state (Figure 4). Electron diffraction observations show at room temperature, that is above the first transition, a pretransition effect which is indicated by the presence of diffuse lines in the direction perpendicular to the chain axis at around $\frac{1}{4}b^*$. When decreasing the temperature a first set of superlattice spots appears for $T < 240K$. The components of the wave vector distortion q_1 are $(0, 0.254 \pm 0.003, 0)$. After decreasing further the temperature ($T < 160K$) a second set of spots appears. The components of the q_2 wave vector are $(0.5, 0.245 \pm 0.003, 0.5)$. The occurence of these incommensurate superlattices is well connected with the two accidents observed in the resistance curve. Table 1 gives the components of the wave vectors associated to distortions in trichalcogenides.

Concerning chemistry the most important points are:
- polytypism has been found for the first time in a MX_3 compound. This new structural form represents a particular arrangement of TaS_3 chains. It has been recently remake under pressure by a Japanese group. Thermodynamically it is surprising that so many different chains exist in the same compound. All these compounds are probably metastable phases. Under higher pressure

NbSe$_3$ (monoclinic)	T_2= 59K 0, 0.241,0 ½, 0.259,½	T_1= 145K 0, 0.243,0	T 145K no diffuse lines
TaS$_3$ (monoclinic)	T_2= 160K 0, 0.254,0 ½, 0.245,½	T_1= 240K 0, 0.254,0	T 240K diffuse lines
TaS$_3$ (orthorhombic)	T = 210K $\frac{1}{2}, \frac{1}{8}, \frac{1}{4}$		

TABLE 1 Components of the wave vectors distortions in NbSe$_3$, monoclinic and orthorhombic TaS$_3$

and at higher temperatures highly symmetrical MY$_3$ compounds of the ZrSe$_3$ type should be obtained.
- the first type of chains presents a S-S distance of about 2.08 Å which is typically the bond length in the $(S_2)^{2-}$ anions.

Therefore it can be suggested that in these chains Tantalum would be Ta^{4+} with one d electron. We consider that the metal-insulator transition at 240K corresponds to the pairing of the tantalum atoms leading to a situation analogous to that found by Jellinek in NbS$_3$. No interpretation of the second transition is possible at the moment. We do not know yet if we have insulating chains (Ta^{5+} only) or chains containing statistically distributed Ta^{5+}-Ta^{4+} ions with the possibility of various mechanisms.
- orthorhombic TaS$_3$ presents also a Peierls transition at 210K, but not the second one[8]. This material, which structure is still unknown, contains chains of the first type with d^1- Ta^{4+}ions, and the same Ta-Ta distance, as illustrated by the fact that c orthorhombic = b monoclinic, which is precisely the M-M distance in the chains.

Concerning physics monoclinic TaS$_3$ is a very promissing materials. Preliminary studies show non linear effects as in the case of NbSe$_3$. Furthermore, comparing with orthorhombic TaS$_3$, depinning can be studied in the case of both commensurate and non commensurate transitions.

FeNb$_3$Se$_{10}$ STRUCTURAL TYPE

A way to change the electronic density and the properties of the compounds is to change the chemical composition either by atomic substitutions in the chains or by intercalation between the chains. Only very small amounts of

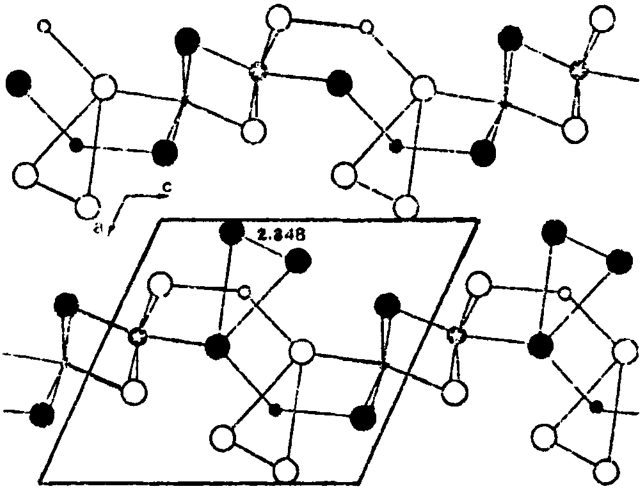


FIGURE 5 Structure of $FeNb_3Se_{10}$

tantalum have been substituted to niobium in $NbSe_3$[9]. However it is well known that in the case of dichalcogenides, first row transition metal can readily intercalate between the MY_2 slabs. Hillenius et al.[10] have recently prepared a compound $Fe_{0.25}Nb_{0.75}Se_3$ which is supposed to have the same structural type as $NbSe_3$. We prepared the same compound which is in fact $FeNb_3Se_{10}$ (and not Se_{12})[11]. The structure (Figure 5) is not as expected by Hillenius but represents a new fascinating structural type. It explains very well the chemical composition. Two groups of two types of chains are running along the b axis. One type corresponds to a trigonal prismatic frame of selenium around niobium, the other develops an octahedral surrounding of selenium around alternatively iron and niobium atoms. The trigonal prismatic chain corresponds exactly to the chain which exhibited the shortest Se-Se distance in $NbSe_3$. Electrical measurements indicate that $FeNb_3Se_{10}$ undergoes a metal-insulator transition below 140K. The question arises thus why a C.D.W. in the corresponding chain in $NbSe_3$ has been replaced here by a metal-insulator transition.

THE X_xMX_4 CHALCOGENIDES

In all these compounds the length of the chalcogen pair is to be directly associated with the structural instabilities observed in the corresponding chain. Chalcogen pairs begin to appear in MY_n chalcogen-rich chalcogenides when n = 3. Let us consider briefly a new series of original compounds with the formulation X_xMY_n where n = 4.

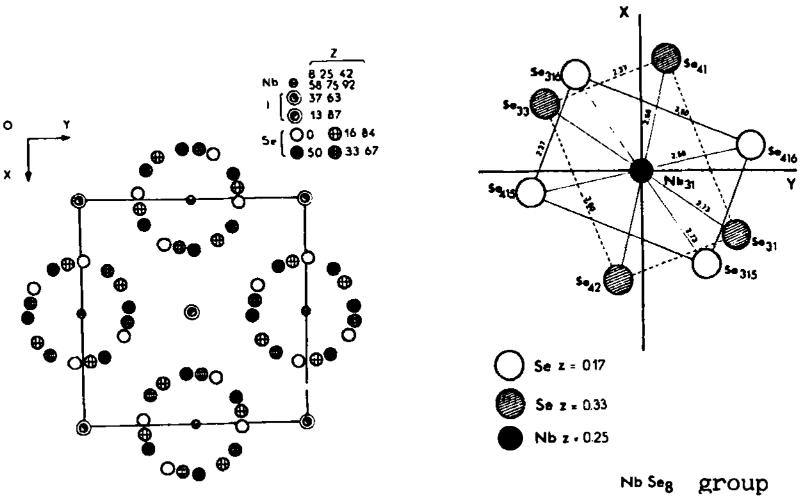
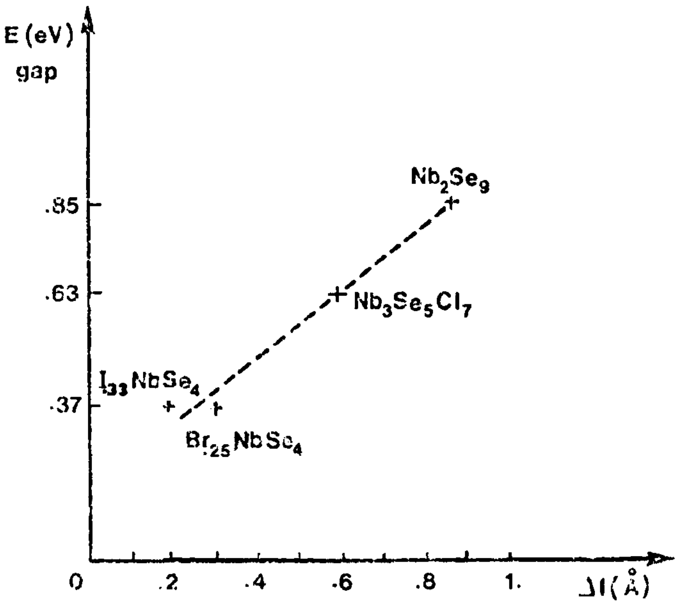


FIGURE 6 Structure of $I_{0.33}NbSe_4$

Figure 6 shows the structure of $I_{0.33}$ $NbSe_4$[12]. Niobium chains are running inside of a frame made of rectangular antiprisms built up with Se-Se pairs (2.34 Å), that is exactly $(Se_2)^{2-}$. There is a 3b superstructure along the chains according to the iodide sublattice and the presence of long and short Nb-Nb distances in the chains in agreement with the presence of $2Nb^{4+}$ for one Nb^{5+}. This can be represented by the formal scheme Nb_2^{4+} Nb_1^{5+} $I(Se_2)_6^{2-}$ corresponding to the formulation INb_3Se_{12}. This structure is not so far of the one of $(TSeT\text{-}I_x)$ determined by Delhaes[13]. Of interest is the fact that we were able to prepare a lot of similar compounds with Ta, Nb, and Br^-, Cl^-, I^-, for various x values. They all are semi-conductors with a narrow band gap. The activation energy (Figure 7) seems to be simply related to the value of the long and short M-M distances which is a feature already found in some conjugated organic polymers.

These materials are metals in which the metallic conducting chain has been cut by d°M $^{5+}$ ions due to the presence of I^- ions.



$I_{33}NbSe_4$	...L.L.S.L.L.S...	L = 3.25	S = 3.06 Å
Nb_2Se_9	...L.S.L.S...	L = 3.76	S = 2.89 Å
$Nb_3Se_5Cl_7$	...L.S.L.S...	L = 3.53	S = 2.94 Å
$Br_{25}NbSe_4$	?(L.L.S.S.LL.SS)	L = 3.4	S = 3.1 Å

FIGURE 7 Activation energies Vs Δl in X_xMY_4 series

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