Solid State Communications, Vol.64,No.4, pp.395-399, 1987.
Printed in Great Britain.

0038-1098/87 $3.00 + .00
Pergamon Journals Ltd.

THE CRYSTALLOGRAPHIC MECHANISM OF THE NbS_3 TO $Nb_{1.12}S_2$ TRANSITION

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(Received 2 June 1987 by E.F. Bertaut)

An electron diffraction study has allowed the crystallographic mechanism to be established for the thermally-induced transition from NbS_3 to $Nb_{1.12}S_2$, which belongs to the NbS_2 structural type. For the trisulfide, the structural unit is a bicapped trigonal prism [NbS(6+2)] (6 is for the prism, 2 is for the bicapping sulfur atoms). When heating NbS_3 one sulfur is removed from every (S_2) pair which leads to a (4+2) sulfur coordination for niobium. Atomic rearrangements are then needed for new [NbS_6] prisms to be reconstructed, perpendicular to the original bicapped ones, and for the NbS_2 structural type to establish. The Van der Waals gap orientation remains unchanged through the transition ; no strong bond is unnecessarily broken. The obtained disulfide is not stoichiometric ($Nb_{1.12}S_2$) due to the thermodynamic route followed.

INTRODUCTION

Niobium trisulfide NbS_3 is not thermally very stable. When heated under vacuum, it loses sulfur and $Nb_{1+x}S_2$ is obtained.

Niobium trisulfide can be schematically formulated as $Nb^{4+}(S_2)^{2-}S^{2-}$, with two thirds of the sulfur atoms involved in $(S-S)^{2-}$ pairs (1). Niobium is surrounded by eight sulfur atoms forming a bicapped trigonal prism (fig.1a). The bases of these prisms are not equilateral triangles but only isosceles ones due to the shorter distance between the paired sulfur atoms. The prisms share their triangular bases to constitute linear chains running along the b axis [1]. Every capping sulfur atom of a given chain also belongs to the next chain in which it occupies a non-paired position (S^{-2}) ; for instance, in fig. 1a, sulfur n° 8 is a capping atom for chain A and a non-paired sulfur atom for chain B (see also fig. 1b). Consequently, the chains are associated through sulfur atoms to form staggered layers. These layers are separated by an empty space, the Van der Waals gap, which spreads out along the ab plane (fig. 1b). In this way, NbS_3 has to be regarded as a two-dimensional compound.

$Nb_{1+x}S_2$ belongs to the NbS_2 structural type : niobium is still surrounded by a sulfur trigonal prism, but the bases of this prism are equilateral triangles, as sulfur pairs do not exist any longer. The prisms are associated into successive slabs [2] between which spreads the Van der Waals gap (fig. 2). For NbS_2 (x = 0) this gap is perfectly empty, for x ≠ 0 part of its sites is occupied, by the x niobium excess.

Comparing fig. 1a and 2a, it could be thought that the NbS_3 to $Nb_{1+x}S_2$ transition results from a breaking of the chains followed by the onset of a new arrangement of the prisms, without any important change of their orientation to occur. In this case the c axis of $Nb_{(1+x)}S_2$ would derive from the b axis of NbS_3. But such an hypothesis remained to be confirmed...

Due to the existence of the chains, the trisulfide crystallites appear as fibers. Due to the existence of the slabs, the disulfide crystallites appear as platelets. We did observe these two habits through an electron microscopy study (SEM) performed on several samples : fibers for NbS_3 and platelets for some $Nb_{(1+x)}S_2$ compounds (x ≠ or = 0) classically prepared at 1000°C from the elements in evacuated silica tubes. On the occasion of a catalytic study [3], we prepared by thermolysis (500°C) of NbS_3 a $Nb_{1.12}S_2$ sample and observed it by electron microscopy : instead of the expected platelets, we observed fibers. The fact that the thermally-induced $NbS_3 \rightarrow Nb_{1.12}S_2$ transition keeps the crystalline habit unchanged seems somewhat difficult to explain in the frame of the above outlined mechanism : effectively, according to this hypothesis, the Van der Waals gap of $Nb_{1.12}S_2$ should appear perpendicular to the b-axis of NbS_3. The onset of this new cleavage plane should induce the slicing of the original fibrous crystallites perpendicular to their growing direction so that platelets should be formed. We thus thought it of interest to elucidate the precise mechanism of this transition.

Another peculiar feature of the NbS_3 structure is the existence of $Nb^{IV}-Nb^{IV}$ pairing through d^1-d^1 bonds, which leads to semi-conducting properties. A metallic high

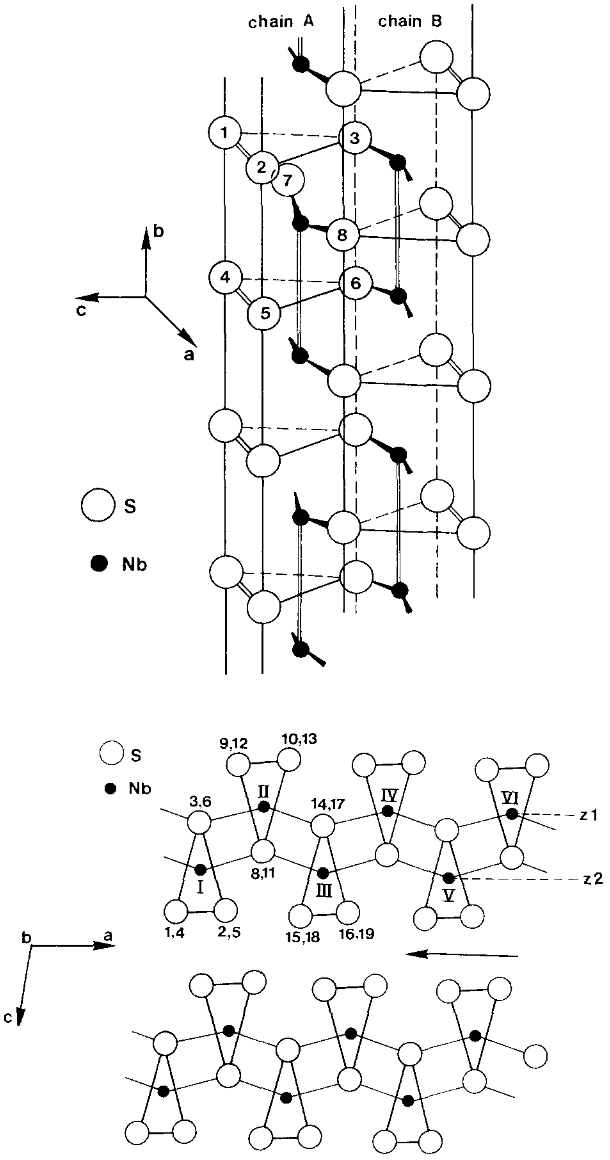

Fig. 1 : The structure of niobium trisulfide NbS_3.
a) Perspective view inspired by ref. [1].
b) Projection on the a-c plane. The arrow indicates the Van der Waals gap.

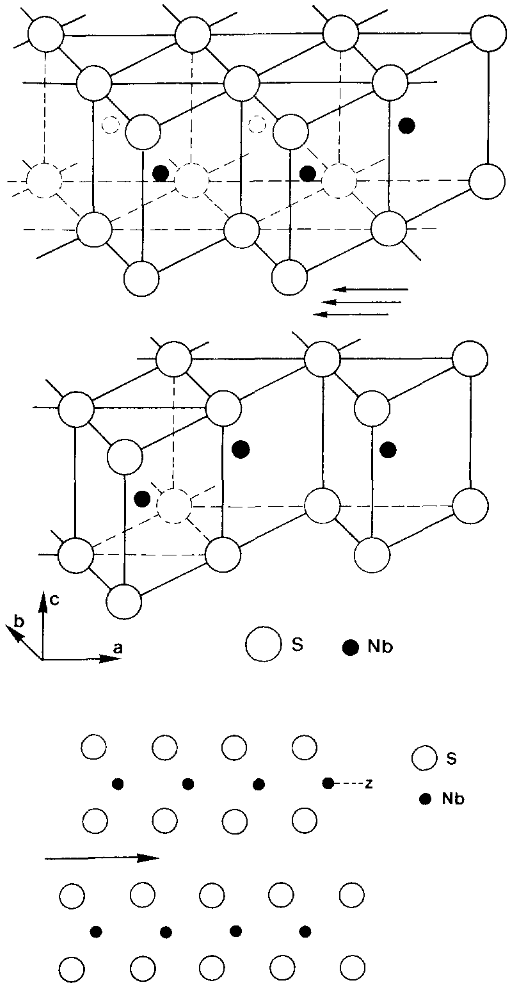

Fig. 2 : The structure of niobium disulfide NbS_2 (x = 0). The arrows indicate the Van der Waals gap.
a) Perspective view.
b) Projection on the $11\bar{2}0$ plane.

temperature state could be expected but it was never observed due to the compound decomposition [4,5].

EXPERIMENTAL

The NbS_3 starting material was prepared from the elements, at 650°C, in evacuated silica tubes. The powder X-ray diffraction pattern is consistent with the unit cell reported by Rijnsdorp and Jellinek [1]. The values deduced from the Guinier data least-square refinement are : $a = 4.961(4)$ Å, $b = 6.740(4)$ Å, $c = 9.136(5)$ Å, $\beta = 97.1(1)°$. Similarly, for the $Nb_{1.12}S_2$ compound prepared by thermolysis of NbS_3, the hexagonal cell parameters are found to be : $a = 3.332(1)$ Å, $c = 17.83(2)$ Å, which is consistent with the 3s-NbS_2 unit-cell [2] : $a = 3.33$ Å, $c = 17.81$ Å.

The experiments were carried out using a TEM JEOL device at an accelerating voltage of 120 kV. The starting material (NbS_3) was first examined with a classic sample holder (double tilt). Then, NbS_3 was heated in situ, using a heating holder which allows only a single tilt. Several diffraction patterns were so obtained from room temperature up to 500°C.

We tried to determine the exact formulation of the transformed crystal using the elemental X-ray microanalysis (EDX) technique. No correct measurements could be done because of the important overlapping of the Nb and S peaks. Hoowever, from the results of some NbS$_3$ thermolysis performed in the 450°C–650°C temperature range it can be estimated that the actual formula is well represented by Nb$_{1.12 \pm 0.03}$S$_2$.

RESULTS

For as-deposited NbS$_3$ fibers, a few degrees tilt of the sample is always found sufficient for the a*-b* diffraction pattern to be obtained, which means that the a-b crystallographical plane is always very close to the observation plane. b corresponds to the growing axis of the fibers and a to the wider dimension of their roughly rectangular cross-section : just as in lamellar chalcogenides, the larger face of the NbS$_3$ crystallites is found to be parallel to the Van der Waals gap (fig. 1b), which explains the preferred orientation of the crystallites. This orientation implies that the triangular bases of the bicapped trigonal prisms are perpendicular to the observation plane. Fig. 3a gives the a*b* diffraction pattern of NbS$_3$. For fig. 3 to be self-consistent we have chosen to show four diagrams successively obtained with the same crystal. As could be expected, it was impossible to find any suitable crystal properly orientated for the single tilt to be efficient. Consequently, the first pattern (fig. 3a) displays some discrepancies between the intensities of equivalent spots due to some disorientation (the a*-b* plane differs from the a-b one by 7°).

When heating, sulfur is progressively removed. Reflections with k = 2n+1, characteristic of the Nb-Nb pairing, weaken. Simultaneously, for k = 2n, streaks develop parallel to the a*-axis and gradually give rise to extra spots (fig. 3b). In our experimental conditions, the breaking of the niobium pairs seems to arise simultaneously with the chemical change, so that the non-paired niobium NbS$_3$ variety (if any) could not be evidenced. Then, the extra spots become stronger and stronger, the original ones become weaker and weaker and disappear (fig. 3c). After a 20 hours annealing at 500°C, the streaks have completely vanished. The diffraction pattern is then characteristic of the hexagonal symmetry of the a-b plane of Nb$_{1.12}$S$_2$ (fig.3d). The intensity discrepancies have disappeared with the disorientation (for Nb$_{1+x}$S$_2$, the a-b and a*-b* planes are common). Hereafter a$_h$, b$_h$, c$_h$ will refer to the Nb$_{1.12}$S$_2$ cell and a, b, c, to the NbS$_3$ one. Fig. 3 shows that all the Nb$_{1.12}$S$_2$ spots lie exactly on the hk0 (k=2n) NbS$_3$ rows, in accord with the parameter relationship $b \simeq 2a_h$. That means that in the complete metallic layer of Nb$_{1.12}$S$_2$, the Nb-Nb spacing (a$_h$) is similar to the mean Nb-Nb distance occuring in NbS$_3$ along the chains. Consequently, along this direction (b), the structural change just amounts to a breaking of the Nb-Nb pairs, as far as the niobium arrangement is concerned. Another striking feature is that the Van der Waals gap orientation is kept unchanged through the transition, since the a-b plane transforms into the a$_h$-b$_h$ one. This observation unambiguously rules out the mechanism roughly outlined in the introduction section, because such a mechanism would have needed a complete reconstruction of the Van der Waals gap. In fact, the only solution for the Van der Waals gap orientation to be preserved is to consider that the bicapped trigonal prisms are destroyed and that new prisms are formed, perpendicular to the former, i.e. with their 3-axis perpendicular to the observation plane.

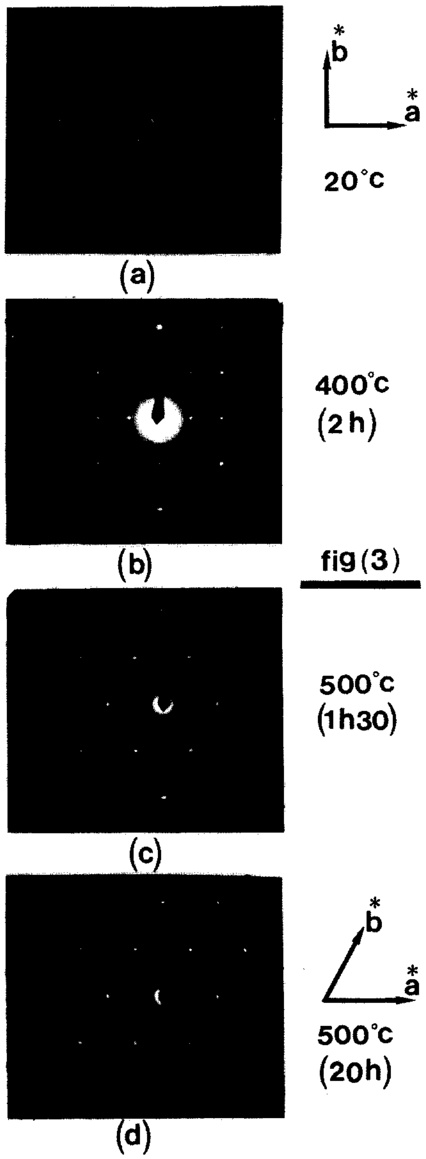

Fig. 3 : Thermal evolution of the diffraction pattern : 20°C (a), 400°C 2h (b) , 500°C 1h30 (c), 500°C 20 h (d).
The temperatures given here and in the text are only indicative because they were measured on the specimen holder. The precise temperature of the sample is not known (heating by electron irradiation, etc...).

THE CRYSTALLOGRAPHICAL MECHANISM OF THE TRANSITION

Fig. 4a represents three bicapped trigonal prisms which belong to three neighboring infinite chains. For a complete view of the structure, it has to be kept in mind that, along the b-axis, all the atoms here shown belong to homoatomic rows : three niobium ones (...,NbI,...), (...,NbII,...), (...,NbIII,...) and nine sulfur ones : (...,1,4,...), (...,2,5,...), (...,3,6,...), etc...

First, every anionic S_2^{2-} pair breaks and lets one sulfur atom escape (n° 2,5; 10,13; 16,19 and all the homologous atoms located on the same sulfur lines). A temporary pseudo-octahedral coordination of niobium can be imagined (fig. 4b), followed by the atomic rearrangements indicated by the arrows and commented hereafter. As sulfur 1 and 4 for instance belong to an infinite row, sulfur quadrilaterals such as (1,4,6,3), for instance, belong to a two sulfur-rows infinite ribbon (fig. 4b) which surrounds a niobium file (...,NbI,...) referred to by a roman numeral (fig. 1b and 4). If this numeral is even, the neighboring sulfur ribbon will be said to belong to the B-group -(...,8,11,12,9,...), for instance-, if not, to the A-group -(..,1,4,6,3,...), for instance-. As represented by the arrows (fig. 4b), ribbons A rotate around an axis parallel to $\underline{b}$ to become vertical, and ribbons B insert between their two nearest A neighbors (fig. 4b) and become vertical too (fig. 4c).

The niobium - sulfur slabs so undergo a drastic compaction : six not very dense atomic planes before the transition : S-Nb(z1)-S-S-Nb(z2)-S (fig. 1b and 4a), three dense atomic planes after the transition is achieved : S-Nb(z)-S (fig. 2b and 4c). The anfractuosities of the NbS_3 Van der Waals gap, roughly delimitted by three sulfur rows -(...,2,5,...), (...,8,11,...), (...,15,18,...), for instance, cf fig. 1b-, disappear.

On fig. 4b, it has been arbitrarily considered that NbIII moves to the right and that NbI does not move at all. In fact, which is important is the relative movement : the NbI-NbIII distance has to increase from a = 4.96 Å (NbS_3) to $a_h \sqrt{3}$ = 5.77 Å ($Nb_{1.12}S_2$). This obviously induces compression strains which can be responsible for the disorder evidenced by the diffuse streaks which develop along a* during the transition. Besides, these strains can explain why $Nb_{1.12}S_2$ is obtained, and not stoichiometric NbS_2, which is perfectly stable in the conditions of the study. As the transformation takes place, accumulated strains can locally become so important that a niobium atom such as NbII, instead of moving downwards as described above, can be ejected upwards into the Van der Waals gap located above the (3,6,9,12,17,14) sulfur slab (fig. 4c), two sulfur atoms of the (8,9,12,11) qualidrateral (fig. 4b) being eliminated for the $Nb_{1+x}S_2$ formulation to be obtained. Such a phenomenon necessarily induces a defect in the [S-Nb-S] layer where the ejected niobium is missing, but it occurs when

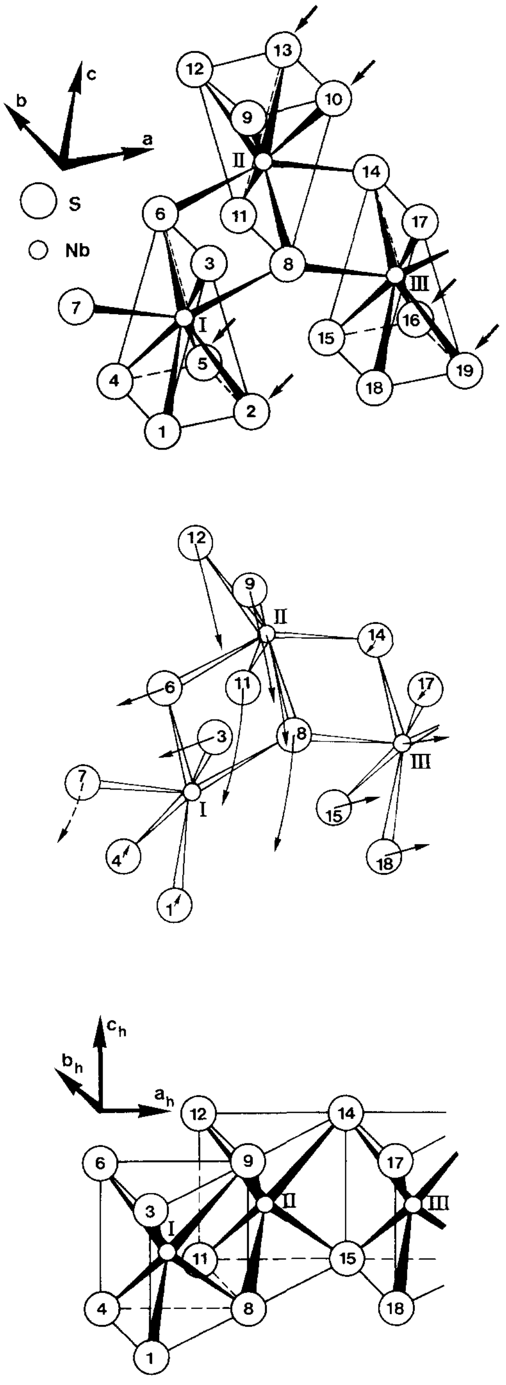

Fig. 4 : The crystallographical mechanism of the NbS_3 to $Nb_{1.12}S_2$ transition.

a) NbS_3. The sulfur atoms to be removed are indicated by arrows.

b) Every second sulfur atom has been removed from every S_2^{-2} pair. The atomic displacements which are going to occur are indicated by arrows.

c) $Nb_{1.12}S_2$ (the Van der Waals gap population is not represented).

the defect energy is lower than the compression strain one. Comparing the NbI-NbIII distance in the initial and final states (4.96x8 ∿ 5.77x7), it can be seen that for the crystal not to expend along that Nb-Nb direction, approximately every eighth niobium of NbS_3 has to be ejected into the $Nb_{1+x}S_2$ Van der Waals gap. It leads to 0.14 for the theoretical value of x, in good agreement with our 0.12 experimental value.

CONCLUSION

The NbS_3 to $Nb_{1+x}S_2$ transition here described well illustrates the concept of topotaxy as defined by I. Bonev [6]. The knowledge of this transition mechanism can be of some aid for the understanding of the catalytic behavior of some di or trisulfides in hydrodesulfurization reactions. What is remarkable in this transition is that the Van der Waals space is not affected a lot. Once the S_2^{2-} and Nb-Nb pairs have been broken, no strong bond is destroyed, some of them are redistributed (fig. 4b and 4c), but "strong bonds remain strong, weak bonds remain weak" [7].

Compared to the standard disulfide synthesis by reaction of the elements, the thermolysis of the trisulfide appears as an original thermodynamic route which involves a strain energy contribution responsible for the metal-excess formulation of the obtained disulfide.

Another striking feature is that, as previous authors [4,5], we did not observe the non-paired niobium NbS_3 state. It possibly means that the Nb pairing is necessary for NbS_3 to be stable due to the lowering of the electronic energy. For TaS_3, this pairing is not essential, it exists at low temperature and is destroyed by heating : the non-paired tantalum state is the stable one at room temperature [8,9,10]. But, when the Ta-pairs are broken, another stabilization factor takes place : electronic delocalization. This factor is not sufficient for non-paired niobium NbS_3 to exist, probably due to the less extended d-orbitals.

ACKNOWLEDGEMENT

The authors are indebted to Dr. A. Meerschaut for fruitful discussions, and to A. Barreau for SEM observations.

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