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Structural studies of the metal-rich region in the ternary Ta-Nb-S system

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Iowa State University, 1991

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Structural studies of the metal-rich region in the ternary Ta-Nb-S system

by

Xiaoqiang Yao

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TABLE OF CONTENTS

GENERAL INTRODUCTION

Early transition metal-rich chalcogenides ($n_M/n_X > 1$; M represents metals in Group IVB and VB, and X represents chalcogen elements) have played an important role in developing understanding of the nature of interactions in solids. They are different from conventional compounds, e.g., NaCl, CaF_2, in which metal and nonmetal are in direct contact only with each other. They form a class of compounds in which there are many metal-metal interactions and the metal-metal interactions run through the whole structure rather than being limited within isolated metal clusters, e.g., in some transition metal-rich halides, Sc_7Cl_{10},[1] Tb_2Cl_3[2] and Gd_2Cl_3.[3] Because metal can interact with metal directly to form so called metal-metal bonds and these play a dominant role in the structure, early transition metal-rich chalcogenides usually exhibit low volatility, high melting point and have typical metallic properties, e.g., high electrical conductivity, Pauli paramagnetism, and metallic luster. They are also typically hard and brittle. Unusual properties, one of which is the high coordination number of the chalcogen atoms, are exhibited by the metal-rich compounds because of the robust metal-metal bonding in the solids. The diverse structure types and stoichiometries of the metal-rich compounds also have their origin in the metal-metal bonding in the compounds. Early transition metal-rich chalcogenides usually have high melting points, so they are good candidates for refractory material applications.

Although the first early transition metal-rich chalcogenides, α-V_3S and β-V_3S,[4] were found as early as 1959 by Pedersen and Grønvold, little progress had been made in this area until in 1966 Franzen and coworkers successfully synthesized the third one, Hf_2S.[5] A large number of binary early transition metal-rich chalcogenides have been gradually found since 1966.

Now it is known that all of the early transition metals in Group IVB and VB can form metal-rich compounds with both sulfur and selenium and metals in Group IIIB and VIB apparently cannot form this kind of compound with chalcogen elements. The binary early transition metal-rich chalcogenides exhibit some common structural features, e.g., short metal-metal distances (comparable to those in the metallic elemental state) and high coordination number of the chalcogen atoms. Despite the common features exhibited by the binary early transition metal-rich chalcogenides, many different features, e.g., the polyhedron type around metals and nonmetals and the chemical compositions, have their origin in the ability of metals to form bonds with metals directly. From the point of view of structures the binary early transition metal-rich chalcogenides may be divided into four classes.

The number of binary early transition metal-rich chalcogenides belonging to first class is greater than that of the other ones. The compounds in this class include Ti_2S,[6] Zr_2S,[7] Ti_2Se,[8] Zr_2Se,[9] $Nb_{21}S_8$,[10] $Zr_{21}S_8$,[7] $Nb_{14}S_5$[11] and Ti_8S_3.[12] They belong to four different structure types, namely the Ta_2P,[13] $Nb_{21}S_8$, $Nb_{14}S_5$ and Ti_8S_3 types, respectively; but they exhibit some common features. Their structures can be viewed as modified bcc metal structures in which nonmetals substitute for the metals in some of the distorted body centered cubes or play a bridge role, connecting the metallic distorted body centered cubes to form a three dimensional network through the whole structure. The coordinations around the chalcogen atoms are capped trigonal prismatic, a dominant feature in this kind of metal-rich compound. The coordination number of the chalcogen atoms are 6, 7, 8 and 9 for noncapped, monocapped, bicapped and tricapped trigonal prisms, respectively. The coordinations around the metals are capped distorted cubic prismatic, and it may be thought that in the structures of these compounds there are a lot of distorted body-centerd cubes and they form three dimensional networks through the structures by sharing corners, or faces. In some cases the capped distorted cubic prisms have some corners substituted by chalcogen atoms, and it is not difficult to believe that the chalcogen elements exhibit some metallic character. This idea is supported by the high coordination numbers of the chalcogen atoms. Except for the coordinations around the metal atoms and nonmetal atoms the common features shared by this class of metal-rich compounds include the existence of a short axis (about 3.3 Å) which is perpendicular to a mirror plane, all of the metal atoms and nonmetal atoms are located on the mirror planes perpendicular to the short axis and separated from each other by half of the short axis (about 1.6 Å). The existence of short metal-metal distances comparable to those in the metallic elemental state and the metal coordination polyhedra which are more or less reminiscent of the coordination of metals in the bcc structure type (i.e., in the structure type of the high temperature form of the metal in the case of the Group IVB transition metals) are also common features of the structures in this class. Some binary early transition metal-rich phosphides, such as Ta_2P,[13] Hf_2P,[14] Nb_8P_5,[15] Nb_7P_4,[16] Nb_5P_3,[17] Zr_2P[18] and large varieties of other transition metal-rich phosphides synthesized by Rundqvist et al also belong to this class.

Binary early transition metal-rich chalcogenides belonging to the second class have only been found in the Ta-S system, namely Ta_2S,[19] α-Ta_6S (monoclinic form),[20] β-Ta_6S (triclinic form)[21] and Ta_3S_{2-x} ($x = 0.2$).[22] In the binary Ta-S system only these four metal-rich phases are known. The common feature of this class of compounds is the occurance of clusters made up of tantalum atoms. Although the structure types of the four binary tantalum-rich sulfides are different from each other, a common structural feature shared by all of them is that the structures can be viewed as tantalum clusters consisting of linear chains of face-sharing centered pentagonal antiprisms which interact via direct metal-metal interactions. Sulfur atoms play a bridging role in the structures. The centering atoms form linear chains that are surrounded by the face-sharing pentagonal antiprisms of tantalum atoms. The distances between two tantalum atoms in the linear chains are 2.79 Å, 2.64 Å, 2.62 Å and 2.80 Å in Ta_2S,[19] α-Ta_6S (monoclinic form),[20] β-Ta_6S (triclinic form)[21] and Ta_3S_{2-x} ($x = 0.2$),[22] respectively. The shortest distance between two metal atoms in elemental tantalum is 2.86 Å, thus strong metal-metal interactions undoubtedly exist in these compounds. The structural differences among the tantalum-rich sulfides is in the arrangement of the tantalum clusters, i.e., the arrangement of the linear chains of face-sharing pentagonal antiprisms in the structure and the resultant difference in the sulfur coordination. The coordination numbers of the sulfur atoms are 4 and 6, 7, 7 and 4 in Ta_2S,[19] α-Ta_6S (monoclinic form),[20] β-Ta_6S (triclinic form)[21] and Ta_3S_{2-x} ($x = 0.2$),[22] respectively. There are non-bonding orbitals on the sulfur atoms coordinated with four atoms. The coordination number of four is unusually low for binary early transition metal-rich chalaogenides and phospides and has been found only in Ta_2S, Ta_3S_{2-x} ($x = 0.2$) and Nb_2Se.[23] Hughbanks et al.[24] used a formula Ta_6S_n ($n = 1, 3, 4$ and 5) to represent all of the tantalum-rich sulfides known and assumed that ${}^{1}_{\infty}[Ta_5TaS_5]$ may be thought to be a building block for Ta_2S, and Ta_3S_2. In the Ta_6S_5 chain, tantalum atoms form a chain of fused, centered pentagonal antiprisms and sulfur atoms surround the $^{1}_{\infty}[Ta_5TaS_5]$ chain so as to cap alternate exposed triangular faces. Ta_2S and Ta_3S_2 may be thought to be three dimensional and two dimensional networks, respectively, built from condensed Ta_6S_5 chains.

The third class of early transition metal-rich chalcogenides includes α-V_3S,[4] β-V_3S[4] and Zr_9S_2.[25] In this class the principal structural feature is a 22 atom unit consisting of three six-membered rings forming two face-sharing (hexagonal faces) hexagonal antiprisms with atoms in their centers, and two capping atoms off the centers of the two hexagonal faces. There are four chalcogen atoms in these units, two in each of the two outer six-membered rings, and the remainder of the atoms are metals. The sulfur coordinations are square antiprismatic for these three metal-rich compounds. There are also some metal-rich phosphides belonging to this class, such as Ti_3P,[26,27] Nb_3P,[28] Ta_3P[29] and Fe_3P.[30]

The fourth class of metal-rich compounds consists of layered compounds. There are only two binary metal-rich compounds, Hf_2S[5] and Ta_2Se,[31] in this class. Hf_2S is the first layered compound found in which direct metal-metal interactions exist. The structure of Hf_2S is hexagonal with an ABACBC stacking sequence with the layers of Hf S Hf Hf S Hf. The coordinations of the metal atoms and nonmetal atoms are trigonal antiprismatic and trigonal prismatic, respectively. Recently a novel binary metal-rich compounds, Ta_2Se, was found by Harbrecht. The stacking sequence of Ta_2Se is Se-Ta-Ta-Ta-Ta-Se with a bcc basis instead of the hcp basis found for almost all of the layered transition metal chalcogenides and halides. In this novel layered compound van der Waals interactions are responsible for holding together the Se-4Ta-Se network with direct metal-metal interactions existing between the metal layers.

Finally there is a compound, Nb_2Se,[23] which may be included in the first class based on the capped distorted cubic prismatic coordination of the metal atoms, but the coordinations of the nonmetals are similiar to those in Ta_2S, i.e., incomplete trigonal prismatic. Van der Waals interactions exist between the selenium atoms.

Actually these four classes of metal-rich compounds also include all of the binary early transition metal-rich phosphides.[32]

The early transition metals of the fifth and sixth rows but in the same column of the periodic table are expected to exhibit very similiar properties because of the lanthanide contraction.[33] This is true for many of the compounds of niobium and tantalum with the metal-rich sulfides being a striking exception. Niobium and tantalum form many isostructural compounds with nonmetals or polyanionic clusters, even with sulfur in conventional valence compounds. But not one niobium-rich sulfide was found to be isostructural with a tantalum-rich sulfide, moreover there are striking differences between them, e.g., the coordination around the metals and nonmetals are totally different. They belong to two different classes of metal-rich compounds as mentioned above. The reason for the striking structural difference was discussed by Smeggil in his Ph.D thesis.[34] By considering the number of unpaired electrons on each electron configuration and the promotion energies for getting this electron configuration from the ground state, Smeggil concluded that the final electron configurations possessed by metals in the metal-rich sulfides are d^4s and d^5 for Nb and Ta, respectively; and that this is the reason for the striking structural difference between niobium-rich and tantalum-rich sulfides.

Consequently there is a natural question: what structures (if any) occur for ternary (Nb, Ta)-rich sulfides?

Although ternary metal-rich chalcogenides containing early transition metals were investigated as early as 1985, only little attention has been paid to these systems. There had been, prior to this work, only several ternary metal-rich compounds ($M_xM'_yX_z$; $(n_x + n_y)/n_z > 1$; M, M' are transition metals and at least one of them is an early transition metal; X is S or Se) found, namely $M_2Ta_9S_6$ (M = Fe, Co and Ni)[35] and $M'_xTa_{6-x}S$ ($x \approx 1$, M' = V and Cr).[36] In this research the metal-rich region of the ternary Ta-Nb-S system was explored.

The previously known ternary metal-rich chalcogenides exhibited new structure features. The structure of $M_2Ta_9S_6$ (M =

Fe, Co and Ni)[35] can be viewed as a hexagonal network of Ta_9 tricapped trigonal prisms with their centers occupied by M, sharing faces along the c-axis and sharing capping atoms with sulfur on the exterior of the network and surrounding a large channel.

The structure of $M'_xTa_{6-x}S$ ($x \approx 1$, M' = V and Cr) can be viewed as a substitutional solid solution of early 3-d transition metal in α-Ta_6S, i.e., some metal positions occupied by two kinds of metal elements. The tantalum clusters in the compounds are similiar to those in Ta_6S, i.e., a close packing of metal columns made up of interpenetrating icosahedra. The principal structural difference between $M'_xTa_{6-x}S$ and α-Ta_6S is the orientation of the tantalum clusters and a resultant difference in the sulfur coordination. In $M'_xTa_{6-x}S$ the sulfur is eight coordinate in a square antiprism, while in α-Ta_6S it is seven coordinate in a monocapped trigonal prism.

Since this research was initiated, several additional ternary compounds have been found by other researchers. They include a variety of substitutional ternary metal-rich chalcogenides and three novel patterns of condensed tricapped trigonal prismatic cluster type compounds, $M_2Ta_{11}Se_8$ (M = Fe, Co and Ni).[37]

In the structure of $M_2Ta_{11}Se_8$ the cluster of MTa_9, as in $M_2Ta_9S_6$, also exists, but hexagonal networks are not formed by the MTa_9 clusters in the selinide. The structure of $M_2Ta_{11}Se_8$ is built from clusters of MTa_9 condensed via trans-triangulated trigonal prism faces along the c direction and via one out of three capping tantalum atoms. In both the sulfides and selinides low coordination chalcogen atoms exist.

The substitutional solid solution type early transition metal-rich chalcogenides can be divided into two catagories. One catagory includes the compounds which are isostructural with known binary metal-rich compounds, e.g. $Hf_xTi_{21-x}S_8$ (x = 7.47)[38] ($Nb_{21}S_8$[10]-type), $Hf_{2-x}Ti_xS$[38] (Hf_2S[5]-type), $M_xNb_6S_{3-x}$ (M = Fe, Co and Ni; x ≈ 1)[39] and $Cu_xNb_6S_{3-x}$ (x = 0.46)[40] (Ta_2P[13]-type), $M_xTa_{6-x}S$ (M = V and Cr, x ≈ 0.32)[41] (β-Ta_6S[21]-type) and $V_xNb_{14-x}S_5$ (x = 3.14)[42] ($Nb_{14}S_5$[11]-type). The second catagory includes the compounds which exhibit new structure types, e.g. $M_xTa_{6-x}S$ (M = V and Cr, x ≈ 1)[36] and $Nb_9Ni_{2-x}S_{3+x}$ (x = 0.63).[39]

In the structure of $Nb_9Ni_{2-x}S_{3+x}$[39] clusters of $NiNb_9$ similiar to those in $M_2Ta_9S_6$ and $M_2Ta_{11}Se_8$ exist. The difference among these structures is the arrangement of the clusters on the plane parallel to the axes of centered trigonal prisms of MM'_9 (MTa_9, $NiNb_9$).

Unlike other ternary substitutional solid solution type metal-rich compounds in which metals partially substitute another kind of metal, 3-d transition metals partially occupy the positions of nonmetals in $M_xNb_6S_{3-x}$ (M = Fe, Co, Ni and Cu)[39,40] and $Nb_9Ni_{2-x}S_{3+x}$.[39]

The known binary and ternary early transition metal-rich chalcogenides are listed in Table 1.

Table 1 Summary of Substitutional Ternary Metal-rich Chalcogenides

Compound	Structure type	Space group	Lattice parameters Å	Reference
$Fe_xNb_6S_{3-x}$ ($x \approx 1$)	Ta_2P	Pnnm	a = 11.620 b = 14.512 c = 3.384	39
$Co_xNb_6S_{3-x}$ ($x \approx 1$)	Ta_2P	Pnnm	a = 11.606 b = 14.463 c = 3.390	39
$Ni_xNb_6S_{3-x}$ ($x \approx 1$)	Ta_2P	Pnnm	a = 11.625 b = 14.429 c = 3.394	39
$Cu_xNb_6S_{3-x}$ ($x \approx 0.46$)	Ta_2P	Pnnm	a = 11.613 b = 14.434 c = 3.395	40
$Hf_xTi_{21-x}S_8$ ($x \approx 7.47$)	$Nb_{21}S_8$	I4/m	a = 16.970 c = 3.362	38
$Hf_{2-x}Ti_xS$	Hf_2S	$P6_3/mmc$	a = 3.362 c = 11.751	38
$V_xNb_{14-x}S_5$ ($x \approx 3.14$)	$Nb_{14}S_5$	Pnma	a = 18.189 b = 3.326 c = 19.453	42

Table 1 (continued)

Compound	Structure type	Space group	Lattice parameters Å	Reference
$Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$)	$Nb_{21}S_8$	I4/m	a = 16.820 c = 3.341	this work
$Nb_xTa_{2-x}S$ ($x \approx 0.2$)	Ta_2S	Pbcm	a = 7.372 b = 5.576 c = 15.198	this work
$Nb_xTa_{6-x}S$	α-Ta_6S	C2/c	a = 14.121 b = 5.285 c = 14.833 β = 117.97°	this work
$Nb_xTa_{6-x}S$	β-Ta_6S	$P\bar{1}$	a = 5.258 b = 7.589 c = 7.626 α = 59.31° β = 68.67° γ = 77.36°	this work
$V_xTa_{6-x}S$ ($x \approx 0.32$)	β-Ta_6S	$P\bar{1}$	a = 5.205 b = 7.560 c = 7.609 α = 59.38° β = 68.59° γ = 77.74°	41

Table 1 (continued)

Compound	Structure type	Space group	Lattice parameters Å	Reference
$Cr_xTa_{6-x}S$ ($x \approx 0.34$)	β-Ta_6S	$P\bar{1}$	a = 5.143 b = 7.544 c = 7.602 α = 59.47° β = 68.47° γ = 78.14°	41
$Nb_xTa_{2-x}S$ ($x \approx 0.95$)	Ta_2Se	P4/nmm	a = 3.330 c = 9.093	this work
$V_xTa_{6-x}S$ ($x \approx 2.25$)	$V_xTa_{6-x}S$	C2/c	a = 7.431 b = 12.746 c = 4.977 β = 111.95°	36
$Cr_xTa_{6-x}S$ ($x \approx 0.96$)	$V_xTa_{6-x}S$	C2/c	a = 7.510 b = 12.911 c = 5.056 β = 111.31°	36
$Nb_9Ni_{2-x}S_{3+x}$ ($x \approx 0.63$)	$Nb_9Ni_{2-x}S_{3+x}$	Cmcm	a = 3.343 b = 14.928 c = 17.687	39

Table 1 (continued)

Compound	Structure type	Space group	Lattice parameters Å	Reference
$Nb_xTa_{11-x}S_4$	$Nb_xTa_{11-x}S_4$	Pnma	a = 31.210	this work
(x ≈ 4.92)			b = 3.351	
			c = 9.592	
$Nb_{12-x}Ta_xS_4$	$Nb_{12-x}Ta_xS_4$	Pnma	a = 9.591	this work
(x ≈ 5.26)			b = 3.364	
			c = 32.825	
$Nb_xTa_{5-x}S_2$	$Nb_xTa_{5-x}S_2$	I4/mmm	a = 3.320	this work
(x ≈ 1.72)			c = 21.619	

EXPLANATION OF DISSERTATION FORMAT

The thesis is in two parts. The first part includes the discussion of the general techniques used in the investigations, namely, high temperature techniques in preparative work and x-ray diffraction techniques in the characterization of the compounds. The first part also presents the structural chemistry of the metal-rich compounds, $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$), $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$), $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$), $Nb_xTa_{2-x}S$ ($x \approx 0.95$), $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$) and $Nb_xTa_{2-x}S$ ($x \approx 0.20$) found in the ternary Ta-Nb-S system.

The second part presents results of extended Hückel band calculations for two layered compounds, $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ (Ta_2Se-type) found in the ternary Ta-Nb-S system.

Future research activities to broaden the understanding and applicability of the chemistry of substitutional type ternary solids in the M-M′-X (M, M′ are early transition metals while X is nonmetal) system and of the new principle regarding the bonding in $(Nb,Ta)_xS_y$ ($x > y$) compounds are proposed in the last chapter.

PART I: SYNTHESIS AND CHARACTERIZATION OF NOVEL TERNARY METAL-RICH COMPOUNDS IN Ta-Nb-S SYSTEM

INTRODUCTION

Synthesis of new solid compounds is a central activity in the field of solid-state chemistry. All of the applications of materials depend on the successful synthesis of materials. If the material has not been synthesized, its properties cannot be measured. The high-temperature superconductors[43,44,45] had to be synthesized before their unusual properties could be found. Although not every compound synthesized exhibits useful properties, there is always the possibility of a new superconductor, a new catalyst that could revolutionize the petroleum industry, or something with entirely unprecedented properties could be found through continuing efforts in solid-state syntheses.

Since there are few rules governing the formation, stoichiometry and structure of solid compounds, the hunt for new solid compounds also helps us to understand basic solid-state chemistry. Professor DiSalvo of Cornell University says: "Every material that can possibly come our way is sitting there in the periodic table. It is a puzzle that has been given to us by God... and it is one of the most exciting brain teasers that science will ever have."[46] "Consequently, the synthesis of novel solids is as much an art as a science. Discoveries of new compounds and structure types highlight the versatility that nature has allowed with the relatively small number of elements."[47] Thus it is not hard to see the importance of synthesis in solid-state chemistry.

Based upon the above arguments an attempt was made to synthesize ternary metal-rich compounds in the Ta-Nb-S system. The purpose of this exploration is to enrich the body of information about the metal-metal bonding in compounds and hopefully to find some useful materials.

EXPERIMENTAL

A. Synthesis Techniques

All of early transition metal-rich chalcogenides have been synthesized using high-temperature techniques (> 1200°C). There are two kinds of reasons responsible for the requirement of high-temperatures, namely thermodynamic and kinetic reasons.

The standard change in Gibbs free energy can be obtained from the equation: $\Delta G° = \Delta H° - T\Delta S°$. If the formation of the solid from neighboring phases is endothermic and endoentropic, the reaction will not occur spontaneously at normal temperature because $\Delta G°$ is positive. When temperature is increased and reaches the critical point that entropy of the reaction plays a dominant role, i.e., $T = \Delta H°/\Delta S°$, the reaction will become spontaneous. At present thermodynic data for metal-rich compounds are extremely lacking. There are only two metal-rich chalcogenides, Ta_2S and Ta_6S, for which $\Delta H°_{f,298}/R$ (-21.0 and -24.5)[48] are known at present.

Another possible reason for using high-temperature techniques is kinetic. At temperatures below 1000°C the rate of diffusion of non-metals into metals and/or metals into compounds to form metal-rich compounds is too low to reach equilibrium in any experimentally feasible period. The activation energies for diffusion to form metal-rich compounds fall roughly in the range of 70 to 140 kJ mol^{-1}, and thus the formation process is approximately 200 to 50,000 times faster at 1500K than it is at 1000K. Reactions of forming ternary metal-rich compounds consisting of two metals have higher activation energies than those of forming binary metal-rich compounds, and thus increases of reaction temperatures have more notable effect on increasing the reaction processes for forming ternary metal-rich compounds.

There are two apparatuses traditionally used in our group to obtain high-temperatures (> 1200°C), the induction furnace and the arc-melter. Usually an initial reaction between sulfur and metals is carried out in a resistance furnace at lower temperature (< 900°C) to combine the sulfur with the metals to minimize loss of sulfur when the sample is taken to high temperatures.

The general procedures used in this work for the preparation of ternary metal-rich compounds in the Ta-Nb-S system are given below. More specific conditions are considered for each in their respective sections.

1. Synthesizing initial products at lower temperature (< 900°C)

The desired amounts of elements in powder form (metals were mixed well using a spatula) were introduced into a clean 8mm silica tube sealed at one end in a dry-box filled with argon. A long funnel was used to avoid samples sticking to the wall of the tube and complicating the sealing process. After the tube containing elements was evacuated by an oil diffusion pump backed by a mechanical pump, it was sealed off with a gas-oxygen torch. After the tube was checked for leaks, it was placed in a resistance furnace and the temperature was set at about 440°C (approximately the boiling point of sulfur). The temperature was increased to 800-900°C (above this temperature the sample would be contaminated by the silica tube) after all of the free sulfur was consumed, i.e., after the yellow vapor in the tube disappeared. The reaction was held at this temperature for three to five days. The sample was cooled by air. The products of these reactions were generally polyphasic consisting of higher sulfides coating metal powders. These polyphasic materials were treated either directly or after mixing with other initial products or metals at high temperatures by means of induction heating or arc-melting.

2. Annealing by means of an induction furnace

The technique used to achieve the high-temperature environment (1000°C - 2000°C) has generally been induction heating of a tungsten Knudsen cell in a high vacuum. The reason why tungsten was chosen to be a container in this processing for sulfide preparation is that there are no stable sulfides of tungsten, either solids or gases, at temperature above 900°C in high vacuum. The most serious problem in the synthesis of transition-metal sulfides in a tungsten container is the possible solid solution of transition metals into the solid crucible. For synthesizing ternary metal-rich sulfides in the Ta-Nb-S system the formation of solid solution of transition metals seems not to be a big problem.

The initial product or a stoichiometrically appropriate mixture of different kinds of initial products and metals was pressed into a pellet in order to improve the contact within the sample and eventually to increase the diffusion rate in the sample. The pellet was placed in a tungsten crucible in an induction furnace. Before the induction furnace was turned on, the residual pressure was lowered below 10^{-5} mmHg using an oil diffusion pump backed by a mechnical pump. The temperature of the crucible was then slowly increased to the desired one and the inductively heated crucible was held at this temperature for the desired time. The temperature of the tungsten crucible was read using a pyrometer. The equilibrium or near equilibrium states achieved at high temperatures were brought to room temperature by rapid cooling of the crucible, primarily by radiative heat loss. Usually after an initial sharp decline it takes about three hours for the crucible to cool to room temperature.

3. Arc-melting

Extremely high temperature (> 2000°C) can be achieved by means of an arc-melter. The advantages of this technique are the very simple principle and direct effect. It has been applied to synthesize many solid state compounds and some compounds, such as $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) and $Nb_xTa_{2-x}S$ ($x \approx 0.95$) can only be prepared using this techniquqe. The reactions are very fast using this technique and it is especially beneficial for initial studies of solid reactions. The disadvantages of this technique are material losses, especially for volatile elements like sulfur, and possible contaminants. The first disadvantage is overcome by reacting the sulfur with the metals first in a closed system at lower temperature (< 900°C) (as described above) with the addition of a few percent excess of sulfur, and the latter seems not to be a serious problem in the studies of the ternary Ta-Nb-S system.

The initial product, a sample annealed in an induction furnace, or a stoichiometrically appropriate mixture, was pressed into a pellet and placed on a water-cooled cooper hearth in an arc-furnace. The chamber was evacuated and purged with argon several times. Finally argon was filled into the chamber with a pressure greater than 1 atm. to minimize air entering into the chamber. This pressure was maintained through all of the operations, including the final cooling process. The arc was generated by touching the copper hearth with a nonconsumable tungsten electrode, then pointed to a zirconium ball for thirty seconds to getter contaminating gases and thus reduce the possibility of contamination of samples, and finally the arc was pointed to the sample with movement around the sample to heat it evenly. The process of arc-melting the sample lasted for about one minute. To ensure homogeneity of the sample, the arc-melted sample button was turned over, and the above procedure was repeated at least two times. The sample was cooled by the cooling water running through the copper hearth.

There is a temperature gradient within the arc-melted button generated by the temperature difference between the arc and the water-cooled copper hearth, and additional homogenization reaction (annealing) was usually required. If a small amount of sample (< 2 g) was synthesized once using this technique, the inhomogenity of the sample was not very serious.

There are no known intermetallic compounds of copper with either tantalum or niobium and there is only one known metal-rich sulfide consisting of copper and a VB metal, $Cu_xNb_6S_{3-x}$.[40] From the experimental results, it could be concluded that copper contamination was not a problem for studies of the Ta-Nb-S system.

B. Characterization Techniques

In this research the characterization techniques used are powder x-ray diffraction, single-crystal x-ray diffraction and energy dispersive analysis by x-rays.

The general pocedures used in this work for the characterization of ternary metal-rich compounds in the Ta-Nb-S system are given below. More specific conditions are considered for each in their respective sections.

1. Powder x-ray diffraction

Guinier powder diffraction was used as the primary characterization method to identify materials, obtain accurate lattice parameters, and estimate the relative yields. This method is known to have a high sensitivity and resolving power and only needs small amounts of sample. An Enraf-Nonius model FR552 Guinier camera and monochromatic Cu $K\alpha_1$ ($\lambda = 1.5405Å$) radiation was used. A detailed description of Guinier method can be found in Guinier.[49]

A small amount of well ground sample mixed with NBS silicon (SRM 640) as an internal standard was mounted on a sample holder by 3M tape. Subsequently the sample holder was mounted on a rotating motor to reduce preferred orientation and was exposed to x-rays for two to four hours.

The film obtained was read using an Enraf-Nonius Guinier film reader. The data were converted to 2θ and d-spacing values by calibrating with the known 2θ values of the standard silicon d-spacings using the program GUIN.[50]

The 2θ values, d-spacings and relative intensities of all reflections of known or postulated structures were calculated using the program PWDR.[51] The powder patterns with the same scale as the experimental ones were generated using the program PLOT[52] following the above calculations. The powder pattern of the sample was compared with the calculated powder patterns of known or postualted compounds to initially determine whether a new material had been prepared. However, it should be noted that intensities observed sometimes depend on grinding damage and prefered orientation which are commonly encountered in layered compounds with weak interactions between layers, e.g., van der Waals interactions. Also, intensities of high angle reflections always were weaker than calculated ones.

In cases where known phases were identified, accurate lattice parameters were determined by the least-squares method using the program LATT[53] after indices were assigned to the reflections observed in powder diffraction.

2. Single-crystal x-ray diffraction

The powder x-ray diffraction technique served only as a identifying tool, i.e., to find out if known or new phases existed in the sample. When a new phase with new structure type was discovered, the single-crystal x-ray diffraction technique was used to determine its structure. Sometimes the powder x-ray diffraction technique utilizing the Rieveld method,[54,55] can also be used to determine simple structure or solve problems with known structure types, but the single-crystal method remains the most efficient tool known today to determine new structures.

Some small pieces thought to be crystals by virtue of having at least one regular and shining face were picked form the sample, dipped in n-butylacetate in a watch glass to separate satellites from the crystals, and then mounted on one end of a glass fiber using EPOXY glue or APIEZON greese. Compounds formed in the Ta-Nb-S system are not usually air-sensitive. Before intensity data were collected on a single-crystal x-ray diffractometer, it is very helpful to check the quality of the crystal on a Weissenberg camera. If possible, the rotation and Weissenberg photographs of the aligned crystal were taken to obtain the rough cell parameters and to determine the space group of the crystal. A detailed description of rotation and Weissenberg methods can be found in Jeffery.[56] After the cell parameters and space group had been obtained, it could be reliably known if the crystal of interest had a new structure.

If the structure was a new one and the sample well crystallized, intensity data were collected on a rotating anode RIGAKU AFC6 single-crystal x-ray diffractometer with monochromatic MoKα (λ = 0.71069Å) radiation. The RIGAKU AFC6 single-crystal diffractometer is more automatic and has higher power than other diffractometers. Usual procedures include crystal centering, random search for 15-25 reflections, indexing of reflections obtained to determine primitive cell parameters, reduction of the cell to get the highest lattice symmetry possible, determination of Laue symmetry, collection of intensity data, and psi-scans for empirical absorption corrections.

This diffractometer has accompanying software, TEXSAN[57] for structure determination. The intensity data were processed with Lorentz-polarization corrections and an empirical absorption using psi-scan data, and then averaged in the proper Laue group.

Space groups were determined using rotation and Weissenberg photographs or the PROCESS program in TEXSAN.

Initial models were obtained by direct methods using SHELXS-86[58] and subsequent difference-Fourier syntheses of the electron density, or from known isostructure type. The full-matrix least-squares refinements were used to refine the structure. During the refinement one hundred percent occupancies were assumed for all of the atom positions of metals and nonmetals. The percentage of niobium and tantalum on each metal position was obtained by refering to one hundred percent sulfur occupancies on nonmetal positions. Usually after isotropic least-squares refinement, it was very helpful to apply another empirical absorption correction program, DIFABS[59] for lowering R-factors. Other procedures were mentioned in detail in respective sections of ternary metal-rich compounds.

3. Electron dispersive analysis by x-rays in SEM

A JEOL JSM-840 scanning electron microscope and a KEVEX EDX system were used for elemental analysis. A qualitative analysis, determining the presence of elements, can be easily done for compounds in the Ta-Nb-S system. For a quantitative EDAX analysis reference materials and a polished surface, i.e., a flat and smooth surface on the sample, were required. A piece of the sample was fixed on a copper tube with EPOXY glue and the sample surface was on the same level as the end of the copper tube holder. The sample surface was then polished on a series of sandpapers. Finally ash on a cloth was used to polish the sample surface to obtain the analytically required surface. Silver paste was used to electrically connect the sample with the wall of copper holder.

Samples were inspected in the compositional (back scattering) and topological modes to determine where to look for elemental analyses. This technique can easily tell how many phases exist in the sample. However, the ratios of metal and nonmetal were not accurately determined in the Ta-Nb-S system because sulfur is too light compared with either niobium or tantalum.

CRYSTAL STRUCTURE OF $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$)

A. Preparation and Characterization

The initial reactant, Ta_2S,[19] was synthesized by heating a mixture of tantalum (Alpha Products, M3N8) and sulfur (Fisher Scientific, lab grade) with a n_{Ta}/n_S ratio of 2 in a previously out-gassed quartz tube, first at 440°C to consume all of the free sulfur, and then at 800°C for three days. Cold pressed samples of Ta_2S and equimolar amounts of niobium (Alpha Products, M2N8) were arc-melted three times in an argon atmosphere. The sample was subsequently annealed for 10h at 1450°C in an inductively heated tungsten crucible. The resultant partially melted sample contained some small needle-like gray-colored crystals in addition to the bulk sample.

The x-ray powder pattern of the sample was very diffuse. If this melted sample was inductively annealed again at a slightly lower temperature (1350°C) for 5h, the powder pattern could be indexed as two phases, $Nb_xTa_{11-x}S_4$ [31.200(5), 3.3507(7), 9.592(2)Å, Pnma] and a 2s-$Nb_{1+x}S_2$[60] -type compound, according to the two-theta angles calculated with program PWDR[51] (using data from the structure solution for $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$)). The main product in this sample was $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$). In the diffuse pattern (only annealed at 1425°C) some reflections had originally been thought to belong to $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$), with the cell parameters determined to be 31.19(1), 3.350(1) and 9.602(6)Å. After the $Nb_xTa_{2-x}S$ (Ta_2Se^{31}-type) phase was found, it was determined that the reflections in the diffuse pattern of the melted sample belong to $Nb_xTa_{2-x}S$ (Ta_2Se-type). The critical temperature below which $Nb_xTa_{11-x}S_4$ is stable and above which $Nb_xTa_{2-x}S$ (Ta_2Se-type) is stable is close to 1425°C. Although the reflections in the diffuse pattern of the melted sample belong primarily to $Nb_xTa_{2-x}S$ (Ta_2Se-type), there were small amounts of $Nb_xTa_{11-x}S_4$ in the melted sample because 1425°C is close to that critical temperature. Powder diffraction data for $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) are presented in Table 2. Intensities were calculated using the computer program PWDR. Positional parameters were used from the refined structure.

A crystal from this sample was examined by electron dispersive analysis by x-rays (EDAX) in a scanning electron microscope, and the composition of this crystal was obtained as follows: S, 27.75 at.%; Nb, 32.24 at.% and Ta, 40.01 at.% ($Nb_{4.65}Ta_{5.77}S_4$).

After the structure and composition of $Nb_{4.92}Ta_{6.08}S_4$ were determined, an attempt was made to synthesize the title compound starting with the elements. A mixture of tantalum, niobium and sulfur ($n_{Ta}:n_{Nb}:n_S \approx 6:5:4$) was heated at 440°C in a previously out-gassed quartz tube until the yellow color of free sulfur disappeared. The temperature was increased to 800°C and the sample was held at this temperature for 3 days. The mixture was

Table 2 **X-ray powder diffraction of $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) (Cu $K\alpha_1$ radiation)**

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[a]	I_{calc}
2	0	0	5.58	5.66	MS	36.7
1	0	1	9.57	9.64	W	9.2
2	0	1	10.74	10.82	M	13.4
3	0	1	12.48	12.54	MS	27.0
4	0	1	14.60	14.62	VW	1.8
6	0	2	25.27	25.24	VW	0.7
1	0	3	27.87	28.03	VW	0.2
3	1	1	29.46	29.49	W	1.0
4	1	1	30.42	30.46	VW	0.6
5	1	1	31.66	31.68	MW	5.7
9	0	2	31.80	31.82	M	18.4
1	1	2	32.68	32.70	M	10.0
2	1	2	33.05	33.08	MS	19.9
10	0	2	34.23	34.25	M	9.3
12	0	0	34.39	34.45	VW	0.3
7	1	1	34.74	34.74	M	12.7
8	0	3	36.29	36.30	S	39.9
8	1	1	36.53	36.54	M	13.7
9	0	3	38.23	38.26	M	22.7
9	1	1	38.48	38.49	M	12.2
1	1	3	38.98	39.01	S	48.9
10	1	0	39.38	39.42	VVS	100.0
10	0	3	40.37	40.35	W	4.2
10	1	1	40.61	40.57	MW	6.9
6	0	4	41.40	41.43	W	7.5
5	1	3	41.60	41.60	VW	3.8
11	0	3	42.45	42.56	W	8.4
15	0	1	44.54	44.52	VW	3.2

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[a] V, very; W, weak; M, medium; S, strong.

Table 2 (continued)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	$I_{obs}{}^{b}$	I_{calc}
12	0	3	44.89	44.89	M	13.9
16	0	0	46.52	46.52	W	3.4
4	1	4	48.06	48.05	VW	1.6
4	0	5	48.85	48.85	W	2.0
14	0	3	49.89	49.82	VW	0.4
17	0	1	50.58	50.58	W	2.9
15	0	3	52.40	52.42	VW	0.9
18	0	1	53.66	53.67	W	5.1
0	2	0	54.73	54.74	S	29.0
19	0	1	56.82	56.81	w	4.5
1	0	6	57.68	57.69	W	2.8
3	0	6	58.32	58.35	W	4.9
20	0	0	59.17	59.15	W	6.0
20	0	1	60.02	60.01	W	2.5
6	0	6	60.55	60.54	VW	1.9
13	1	4	61.15	61.18	VW	1.6

arc-melted and then inductively annealed at 1250°C for 11h. The total mass loss after these processes was less than 0.5%. From comparison of the powder pattern of the final product with standard one of $Nb_{4.92}Ta_{6.08}S_4$ calculated using program PWDR, it is certain that almost all of the sample is $Nb_{4.92}Ta_{6.08}S_4$.

B. Single Crystal X-Ray Investigations

Some needle-like single crystals were selected from the gray colored product annealed at 1425°C and examined by a Weissenberg camera. The needle shaped crystal was easily aligned with the longest edge parallel to the rotating axis. From the rotation and Weissenberg patterns of several such crystals it was found that there were two kinds of crystals in the sample, $Ta_{6-x}Nb_xS$ (C 2/c, 14.1214(168), 5.2849(41), 14.8331(182)Å, β = 117.97° (5)) and $Ta_{6.08}Nb_{4.92}S_4$.

From preliminary Weissenberg and rotation photographs of $Nb_xTa_{11-x}S_4$ the conditions limiting the possible reflections were observed to be as follows: hkl, no conditions; 0kl, k + l = 2n; h0l, no conditions; hk0, h = 2n; h00, h = 2n; 00l, l = 2n. These conditions indicate two possible space groups, $Pna2_1$ and Pnma, differing by a center of symmetry.

Intensity data for a $Nb_xTa_{11-x}S_4$ crystal ($0.5x0.02x0.01mm^3$) were collected using a RIGAKU AFC6 single-crystal diffractometer and monochromated Mo Kα radiation, employing the ω scan technique up to 60° (2θ). From the total 3473 reflections (hkl, -hkl), 929 independent reflections with $F^2 > 3\sigma(F_o^2)$ were obtained and used for structure analysis. The observed intensities were corrected for Lorentz-polarization and absorption effects. No remarkable decay was observed during the data collection.

This structure was determined using program TEXSAN. First the empirical absorption correction was applied with an absorption coefficient (μ(Mo Kα)) being 711.53 cm^{-1}. The averaging of all F_o values of $Ta_{6.08}Nb_{4.92}S_4$ according to Pnma symmetry gave an internal factor R = 0.164 (including all reflections). Application of the direct method resulted in an electron map containing several strong peaks per asymmetric unit on the y = 1/4 section. These peaks were assigned as Ta and the refinement was initiated. After the refinement had converged for this trial structure, a difference Fourier map was calculated. From the difference Fourier map, some strong peaks were found and they were assigned as Ta. The above processes were then repeated. Finally, eleven metal positions and four sulfur positions were found. The distances and coordinations were chemically reasonable, e.g., by comparison with $Nb_{21}S_8$[10] and $Nb_{14}S_5$.[11]

The occupancies of the tantalum positions were then refined. From the calculated occupancies a rough combination of niobium and tantalum at each position was assumed and assigned on each metal position, and then the occupancies for the metal positions were refined by fixing the total occupancy at each position as 1. After this refinement had converged the isotropic temperature factors were refined with a secondary extinction correction applied (secondary extinction coefficient is 1.22405×10^{-7}).

F_o values of $Ta_{6.08}Nb_{4.92}S_4$ were corrected for absorption effects with the program DIFABS[59] in the mode that utilizes θ-dependent systematic deviations $|F_o| - |F_c|$. After this correction, the R and R_w dropped from 0.066 and 0.099 to 0.056 and 0.063, respectively, in isotropic refinement. The F_c values which entered into the calculations were obtained from refinement of the positional and isotropic thermal parameters in Pnma.

The anisotropic refinement was carried out, but it was not successful since some anisotropic thermal parameters were nonpositive definite. The refinement of the structure is complicated by the fact that the temperature factor at each position correlates with the occupancy of tantalum and niobium at that position.

The occupancy of tantalum and niobium at each metallic position was, therefore, changed arbitrarily to make as many anisotropic temperature factors positive as possible. $R = 0.051$ and $R_w = 0.068$ were finally obtained from the anisotropic refinement with the nonpositive-definite anisotropic temperature factors at the S1, S3 and S4 position. Information concerning the refinement is in Table 3. The final composition $Ta_{6.08}Nb_{4.92}S_4$ was obtained from the refinement. The atomic

Table 3 Crystal data for $Nb_xTa_{11-x}S_4$ (x ≈ 4.92)

Formula	$Nb_{4.92}Ta_{6.08}S_4$
Space group	Pnma(#62)
a, Å	31.210(5)[a]
b, Å	3.3507(6)[a]
c, Å	9.592(2)[a]
Z	4
d_{calc}, g/cm^3	11.160
Crystal size, mm^3	0.02x0.01x0.5
$\mu(MoK_\alpha)$, cm^{-1}	711.53
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ = 0.71069 Å)
Orientation reflections, number, range (2θ)	25,14-35
Temperature, °C	22
Scan method	ω
Octants measured	hkl,-hkl
Data collection range, 2θ, deg	0-60
No. refl. measured	3473
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	929
No. parameters refined	103
Secondary ext. coeff. (10^{-7})	1.224
Trans. factors, max., min.	1.000,0.376
R^b, R_w^c, GOF^d	0.051, 0.068, 1.71
Largest shift/esd, final cycle	0.00
Largest peak, e/Å^3	4.74 (1.79Å, M4)

[a] obtained from indexing of the powder pattern.

[b] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[d] $GOF = \Sigma((|F_o| - |F_c|) / \sigma_i) / (N_{obs} - N_{parameters})$.

positions, occupancies and isotropic temperature factors at each position are given in Table 4. The failure of anisotropic refinement may have arisen from the quality of the crystal. The powder pattern of the sample from which the crystals were selected was diffuse, i.e., the sample was not well crystallized. Observed and calculated structure factors are listed in Appendix A.

C. Results and Discussions

Figures 1 and 2 show the structure of $Nb_xTa_{11-x}S_4$. The coordinations of the sulfur and metal atoms in this compound are similar to those found in a broad class of transition metal compounds in which atoms are located in mirror planes perpendicular to short (about 3.5Å) axes. Some examples of compounds belonging to this class are $Nb_{21}S_8$,[10] $Nb_{14}S_5$,[11] Ti_2S,[6] Nb_7P_4,[16] Nb_5P_3,[17] Ta_2P[13] and Co_2P.[61] The metallic coordinations are capped, distorted cubic prismatic. The coordination of sulfur is capped trigonal prismatic. The distorted cubic prisms of M1, M2 and M4 contain only metal atoms. The capping atoms of the distorted cubic prism for M1 are M5, M8, M10 and S2. For other metal positions the distorted cubic prisms are partially substituted by sulfur, so there is more distortion for this kind of distorted cubic prism, e.g., two S4 occupy two corners of the distorted cubic prism for M3. The structure can be thought of as

Table 4 Positional, thermal parameters and occupancies for $Nb_xTa_{11x}S_4$ ($x \approx 4.92$)

Atom	Occupancy	x	y	z	B_{iso} (Å^2)
M1	76% Ta + 24% Nb	0.2177 (1)	1/4	0.5355 (2)	0.27 (7)
M2	76% Ta + 24% Nb	0.3268 (1)	1/4	0.8482 (2)	0.24 (7)
M3	72% Ta + 28% Nb	0.4247 (1)	1/4	0.7579 (2)	0.32 (7)
M4	70% Ta + 30% Nb	0.0254 (1)	1/4	0.0853 (2)	0.26 (7)
M5	66% Ta + 34% Nb	0.2357 (1)	1/4	0.2166 (2)	0.27 (7)
M6	54% Ta + 46% Nb	0.3401 (1)	1/4	0.1834 (2)	0.31 (8)
M7	50% Ta + 50% Nb	0.4207 (1)	1/4	0.4183 (2)	0.30 (8)
M8	48% Ta + 52% Nb	0.2150 (1)	1/4	0.8917 (2)	0.32 (8)
M9	46% Ta + 54% Nb	0.1350 (1)	1/4	0.1206 (2)	0.28 (8)
M10	44% Ta + 56% Nb	0.1102 (1)	1/4	0.4761 (2)	0.30 (9)
M11	6% Ta + 94% Nb	0.0233 (1)	1/4	0.7255 (3)	0.4 (1)
S1		0.4200 (4)	1/4	0.153 (1)	0.6 (4)
S2		0.3044 (4)	1/4	0.580 (1)	0.6 (4)
S3		0.1367 (3)	1/4	0.865 (1)	0.3 (3)
S4		0.0296 (3)	1/4	0.380 (1)	0.6 (4)

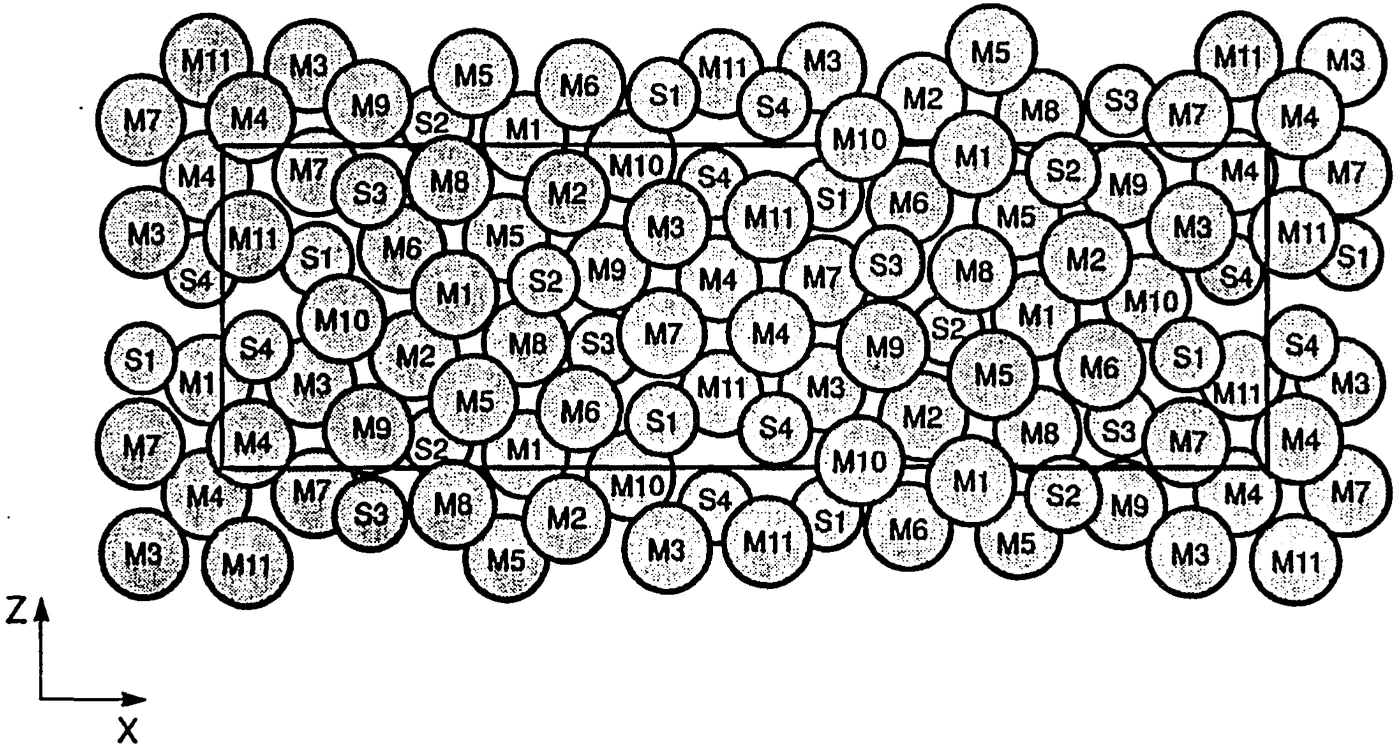

Figure 1 The crystal structure of $Nb_xTa_{11-x}S_4$ viewed along the b-axis. Unit cell is marked by solid lines

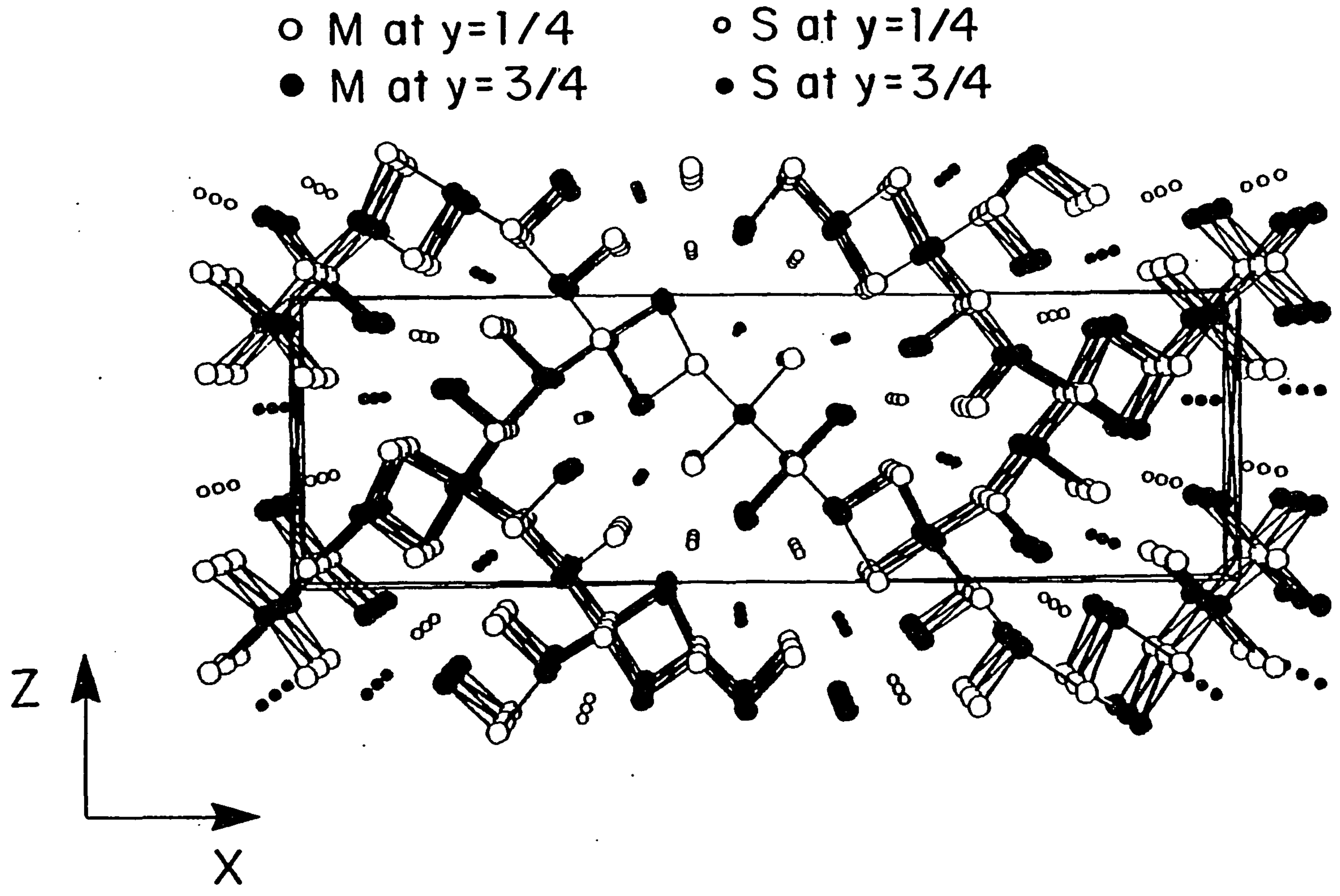

Figure 2 The projection of $Nb_xTa_{11-x}S_4$ on the xz-plane. Unit cell is marked by solid lines

a strongly modified bcc metal structure. The fragments of modified bcc metal networks can be easily recognized from Figure 2.

In the structure of $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) each metal position is fractionally occupied by niobium and tantalum and the metal positions have been labeled so that as the metal indicator increases, the n_{Nb}/n_{Ta} ratio on that position also increases, i.e., from M1 to M11 the n_{Nb}/n_{Ta} ratio on the metal position increases. The number of coordinating sulfur increases from M1 to M11, i.e., the more niobium on the metal position, the more sulfur bound to that metal position.

It is easy to recognize that the coordination of S2 is bicapped trigonal prismatic. The coordination polyhedra of S1 and S3 are trigonal prisms that are bisected by the mirror plane vertically rather than horizontally. The coordination of S4 is interesting and is shown in Figure 3. The coordination of S4 may be thought of as a trigonal prismatic with two of the six corners missing. This is similar to that of sulfur in Ta_2S.[19] The coordination of S4 is the typical case of the lower coordinated sulfur atoms in metal-rich compounds, i.e., there apparently are some structurally significant nonbonding orbitals on S giving rise to an incomplete trigonal prism. It can be seen that the

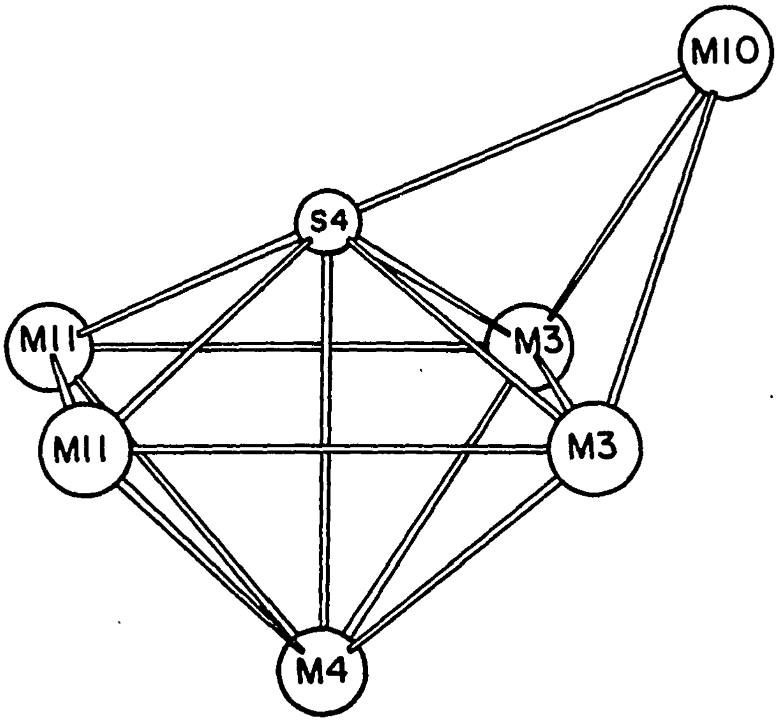

Figure 3 The coordination of S4 atom in $Nb_xTa_{11-x}S_4$

resulting van der Waals interactions lead to a void region surrounded by these atoms.

The shortest metal-metal distance in this compound is 2.82Å. There is no doubt that there are numerous strong metal-metal interactions in this solid. Table 5 gives the interatomic distances for $Ta_{6.08}Nb_{4.92}S_4$. If only distances less than 3.30Å (for S-S only distance less than 3.00Å) are considered, the metallic coordination number ranges from 9 to 12 and that for sulfur from 6 to 8.

In the structures of the tantalum-rich and niobium-rich sulfides there are pentagonal antiprisms or prisms. In the structure of this ternary (TaNb)-rich sulfide there are neither pentagonal prisms nor antiprisms. It is surprising that although the molar ratio of tantalum to niobium in this compound is larger than 1, the structure of this compound is more similar to that in the niobium-rich sulfides than to that in the tantalum-rich sulfides, e.g., there is a short axis (about 3.50Å) and the metallic coordinations are distorted cubic prismatic. Attempts were made to synthesize $Ta_{11}S_4$ and $Nb_{11}S_4$; but they failed and the products were β-Ta_6S[21] and Ta_2S[19] in the case of "$Ta_{11}S_4$", and $Nb_{21}S_8$[10] in the case of "$Nb_{11}S_4$".

Table 5 Interatomic distances (pm) for $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) (M-M < 330 pm, M-S < 300 pm)

M1	S2	1[a]	274 (1)	M5	S2	2	247.1 (8)
	M5	2	281.8 (2)		M1	2	281.8 (2)
	M2	2	282.1 (2)		M8	2	282.7 (2)
	M6	2	284.0 (2)		M2	2	286.4 (2)
	M8	2	302.0 (3)		M1	1	311.0 (2)
	M5	1	311.0 (3)		M8	1	318.3 (3)
					M6	1	327.3 (3)
M2	S2	1	267 (1)		M9	1	327.6 (3)
	M1	2	282.1 (2)				
	M10	2	286.1 (3)	M6	S1	1	251 (1)
	M5	2	286.4 (2)		S3	2	252.5 (7)
	M9	2	299.9 (2)		M1	2	284.0 (2)
	M3	1	317.7 (3)		M10	2	302.8 (3)
	M6	1	324.2 (3)		M8	2	312.4 (3)
					M2	1	324.2 (2)
M3	S4	2	249.2 (8)		M5	1	327.3 (3)
	M4	2	282.4 (2)				
	M9	2	283.1 (3)	M7	S3	2	250.6 (8)
	M10	2	289.4 (3)		S1	1	254 (1)
	M11	1	308.0 (4)		M4	2	286.4 (2)
	M2	1	317.7 (2)		M11	2	304.7 (4)
	M7	1	326.0 (3)		M9	2	309.8 (3)
					M3	1	326.0 (2)
M4	M3	2	282.4 (2)		M4	1	326.7 (3)
	M4	2	282.8 (3)				
	S4	1	283 (1)	M8	S3	1	246 (1)
	M7	2	286.4 (3)		S2	2	253.5 (8)
	M11	2	289.9 (3)		M5	2	282.7 (2)
	M7	1	326.7 (3)		M1	2	302.0 (2)

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[a] number of neighbors.

Table 5 (continued)

	M6	2	312.4 (2)
	M5	1	318.3 (2)
M9	S3	1	245.0 (9)
	S2	2	255.6 (9)
	M3	2	283.1 (2)
	M2	2	299.9 (2)
	M7	2	309.8 (2)
	M5	1	327.6 (2)
M10	S1	2	256.5 (8)
	S4	1	268 (1)
	M2	2	286.1 (2)
	M3	2	289.4 (2)
	M6	2	302.8 (2)
M11	S1	2	253.4 (9)
	S4	2	256.0 (8)
	M4	2	289.9 (3)
	M7	2	304.7 (3)
	M3	1	308.0 (4)
S1	M6	1	251 (1)
	M11	2	253.4 (8)
	M7	1	254 (1)
	M10	2	256.5 (8)
S2	M5	2	247.1 (8)
	M8	2	253.5 (8)
	M9	2	255.6 (9)
	M2	1	267 (1)
	M1	1	274 (1)
S3	M9	1	245.0 (9)
	M8	1	246 (1)
	M7	2	250.6 (7)
	M6	2	252.5 (7)
S4	M3	2	249.2 (8)
	M11	2	256.0 (8)
	M10	1	268 (1)
	M4	1	283 (1)

CRYSTAL STRUCTURE OF $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$)

A. Preparation and Characterization

High purity tantalum, niobium (Alpha Products) and sulfur (Fisher Scientific Co.) were put into a previously out-gassed silica tube at the molar ratio: $n_{Ta}:n_{Nb}:n_S = 6:12:7$ and were heated at 440°C until all of sulfur was consumed and then were held at 850°C for ten days. After being pressed into a pellet, the sample was annealed in a tungsten crucible at 1360°C for 16h in an induction furnace. The resultant partially melted sample contained some gray-colored crystals in addition to the bulk sample.

The Guinier x-ray powder pattern indicated that a new phase coexisted along with $Nb_{21-x}Ta_xS_8$ ($Nb_{21}S_8$[10]-type); (I4/m, a = 16.8237(31), c = 3.3428(7)Å). The reflections in the powder pattern, except for those belonging to $Nb_{21-x}Ta_xS_8$, could be indexed as $Nb_{6.74}Ta_{5.26}S_4$ (9.5912(26), 3.3637(10), 32.8251(74)Å, Pnma) according to the two-theta angles calculated with program PWDR (using data from the structure solution for $Nb_{6.74}Ta_{5.26}S_4$). Powder diffraction angles $2\theta < 55°$, estimated and relative intensities of $Nb_{6.74}Ta_{5.26}S_4$ calculated using the computer program PWDR (positional parameters used from the refined structure) are listed in Table 6.

Table 6 X-ray powder diffraction of $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$) (Cu $K\alpha_1$ radiation)[a] ($2\theta < 55°$)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[b]	I_{calc}
0	0	2	5.39	5.38	W	18
1	0	1	9.64	9.60	M	42
1	0	4	14.18	14.19	W	9
3	0	4	29.99	29.97	W	6
1	1	4	30.15	30.16	W	6
3	0	5		31.09		5
2 2	1 0	2 10	32.94	32.95 33.04	M[c]	5 7
2	1	3	33.55	33.53	W	13
3	0	7	33.92	33.91	M	24
2 2	1 0	5 11	35.35	35.31 35.40	M	25 21
3	0	8	35.57	35.58	W	11
0	1	9	36.29	36.30	M	56
2	1	6	36.50	36.50	W	14
1	1	9	37.50	37.53	W	36
2	0	12	37.86	37.83	S[c]	38
0	0	14	38.36	38.36	W	7
3	1	1	38.91	38.93	M	32
4 3 3	0 1 0	4 2 10	39.22	39.10 39.23 39.31	S	7 100 8
1	1	10	39.46	39.46	S	73
3	1	3	39.72	39.72	W	20
0	1	11	40.35	40.37	W	6

[a] 2θ values of reflections with relative intensities $I_{calc} \geq 5$ are listed.

[b] W, weak; M, medium; S, strong.

[c] Reflections also belong to $Nb_{21-x}Ta_xS_8$.

Table 6 (continued)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[b]	I_{calc}
2	1	9	41.03	41.03	W	12
3	0	11		41.35		6
1	1	11	41.47	41.50	W	12
4	0	7	42.33	42.30	M	21
1	0	15	42.33	42.33	W	9
4	0	8	43.77	43.69	W	20
2	0	15	45.56	45.52	W	5
5	0	3	48.12	48.12	W	6
1	0	18	50.91	50.93	W	5
5	0	8	52.60	52.62	W	5
1	0	19	53.90	53.87	W	7
0	2	0	54.53	54.51	M	41

A crystal of $Nb_{6.74}Ta_{5.26}S_4$ from this sample was examined by electron dispersive analysis by x-rays (EDAX) in a scanning electron microscope, and the composition of this crystal was determined to be as follows: S, 24.46 at.%; Nb, 49.35 at% and Ta, 26.19 at.% ($Nb_{8.07}Ta_{4.28}S_4$).

After the structure was solved and the composition of the title compound was known, an attempt was made to synthesize the title compound by using Ta_6S, "Nb_2S" or "$Nb_{1.5}S$" (there is no compound known with either the formula Nb_2S or the formula $Nb_{1.5}S$) and Nb as initial reactants. The initial reactant, Ta_6S, was synthesized by heating the mixture of tantalum (Alpha Products, M3N8) and sulfur (Fisher Scientific, lab grade) with the n_{Ta}/n_S ratio of 6 first at 440°C in a previously out-gassed quartz tube to consume all of free sulfur, and then at 860°C for one week. "Nb_2S" and "$Nb_{1.5}S$" were synthesized using a similiar method. The stoichiometrically appropriate mixture of Ta_6S, "Nb_2S" or "$Nb_{1.5}S$" and Nb was pressed into a pellet and arc-melted three times in an argon atmosphere. The total mass loss after the arc-melting process was less than 0.6%. From comparison of the powder pattern of the final product with that of the $Nb_{6.74}Ta_{5.26}S_4$ standard calculated using program POWDER, it is certain that major product in the sample is $Nb_{12-x}Ta_xS_4$.

B. Single Crystal X-ray Investigation

There were two kinds of crystals in the annealed sample ("$Nb_{12}Ta_6S_7$"). The thin needle-like crystals of $Nb_{6.74}Ta_{5.26}S_4$ could easily be distinguished from the larger trapezoidal-shaped $Nb_{21-x}Ta_xS_8$ crystal. A gray-colored crystal ($0.02 x 0.02 x 0.35 mm^3$) of the new compound was selected from the nearly melted sample and was examined using Cu Kα radiation on a Weissenberg camera. The needle shaped crystal was easily aligned with the longest edge parallel to the rotating axis.

Oscillation and Weissenberg photographs from the crystal, rotated along the b-axis (shortest axis), showed the following systematic extinctions: 0kl, k + l = 2n, hk0, h = 2n; h00, h = 2n; 00l, l = 2n. These conditions correspond to two possible space groups, $Pna2_1$, and Pnma, differing by a center of symmetry. The shortest axis corresponds to the b-axis, while longest one corresponds to the c-axis.

This crystal was placed on a RIGAKU AFC6 single-crystal diffractometer, and intensity data were collected using monochromatic Mo Kα radiation, employing the ω scan technique up to 60° (2θ). A total of 3943 (hkl, hk-l) reflections were monitored, and 721 unique reflections with $F^2 > 2\sigma(F_o^2)$ were obtained and used for structure determination. The observed intensities were corrected for Lorentz-polarization and absorption effects with an absorption coefficient of $611.61 cm^{-1}$.

Based on three standard reflections that were measured every 150 reflections there was no significant fluctuation or decay of the crystal. Subsequent data processing and structure calculations were performed with the program package TEXSAN.

The structure was solved by direct methods in the centrosymmetric space group Pnma. First the empirical absorption correction was applied with the max. and min. transmission factors of 1.000 and 0.767, respectively. Application of the direct method resulted in an electron map containing several strong peaks per asymmetric unit on the y = 1/4 section. These peaks were assigned as Ta and the refinement was initiated. More metal positions were then obtained from a subsequent difference-Fourier syntheses of the electron density after initial refinements, and they were assigned as Ta or S depending on the peak height and the distance to known atom positions. The above processes were then repeated. Finally, twelve metal positions and four sulfur positions were found. The distances and coordinations were chemically reasonable, e.g., by comparison with $Nb_{21}S_8$[10] and $Nb_{14}S_5$.[11]

First the structure was solved and the composition was determined to be $Nb_{8.08}Ta_{3.92}S_4$ using the following procedures: a. after twelve metal positions and four sulfur positions had been found, the metal positions were assigned as Ta and the occupancies of Ta were refined, b. according to the refinement result and the atomic numbers of Nb and Ta, the percentage of Ta and Nb was assigned to each metal position, c. isotropic refinement was done with concomitant refinement of the secondary extinction coefficient while the multiplicities of Ta and Nb were fixed on each metal position, d. the multiplicity on each metal position was changed so as to make the overall thermal parameters as positive and as nearly equal as possible, while 100% occupation was assumed for each position. Finally R, R_w and GOP were obtained as 0.059, 0.062 and 1.393; respectively. The isotropic parameters are similiar in value and range from 0.26 to 0.41 for metals, from 0.4 to 0.8 for sulfur; respectively. However, anisotropic refinement was not successful.

Another approach to solve this structure was also applied and the composition was determined to be $Nb_{6.74}Ta_{5.26}S_4$. The procedure was as follows: a. after twelve metal positions and four sulfur positions had been found, the multiplicities for twelve metal positions were refined after the assignment of 50% Ta and 50% Nb for each metal position, b. the isotropic refinement was done for the twelve metal positions and four sulfur positions with concomitant refinement of the secondary extinction coefficient while the multiplicities for metal positions were fixed, c. the isotropic refinement was then done again while the multiplicities for metal positions were allowed to vary, d. the isotropic refinement, the multiplicities for the twelve metal positions and the second extinction coefficient were refined at the same time. Finally R, R_w and GOP were obtained as

0.059, 0.066 and 1.31; respectively. However, the anisotropic refinement still was not successful. The B's differ very much for different atoms. The refinement of the structure is complicated by the fact that the temperature factor at each position correlates with the occupancy of Ta and Nb at that position. Another complication may be the disorder in the solid since the sample was heated at high temperature and nearly melted.

In the first calculation the physically reasonable, but nonetheless subjective, assumption of equal atomic thermal parameters is made. The second calculation is objective in the sense that no apriori physical restaint is assumed. In either case the calculated n_{Nb}/n_{Ta} ratio is within the range determined in this work (Section on the discussions of the metal-rich region in the ternary Ta-Nb-S system) and in both cases the n_{Nb}/n_{Ta} ratio increases with the S coordination number of the site. Thus the subjective and the objective calculations both result in the same conclusions as drawn in this study. The choice between these two calculations is a matter of personal preference, and the results of the objective calculations are arbitrarily chosen as the best results.

Information concerning the refinement is in Table 7. The atomic positions, multiplicities and isotropic temperature factors at each position are given in Table 8. The interatomic distances for $Nb_{6.74}Ta_{5.26}S_4$ are given in Table 9.

Table 7 Crystal data for $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$)

Formula	$Nb_{6.74}Ta_{5.26}S_4$
Space group	Pnma(#62)
a, Å	9.5911(26)[a]
b, Å	3.3637(10)[a]
c, Å	32.8251(74)[a]
Z	4
d_{calc}, g/cm^3	10.752
Crystal size, mm^3	0.02x0.02x0.35
$\mu(MoK_\alpha)$, cm^{-1}	611.61
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ = 0.71069 Å)
Orientation reflections, number, range (2θ)	25,14-35
Temperature, °C	22
Scan method	ω
Octants measured	hkl,hk-l
Data collection range, 2θ, deg	0-60
No. refl. measured	3493
No. unique data, total with $F_o^2 > 2\sigma(F_o^2)$	704
No. parameters refined	62
Trans. factors, max., min.	1.000,0.767
Secondary ext. coeff. (10^{-7})	1.292
R^b, $R_w{}^c$, GOF^d	0.059, 0.065, 1.292
Largest shift/esd, final cycle	0.00
Largest peak, e/Å^3	6.35 (0.48Å, M8)

[a] obtained from indexing of the powder pattern.

[b] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[d] $GOF = \Sigma((|F_o| - |F_c|) / \sigma_i)/ (N_{obs} - N_{parameters})$.

Table 8 **Positional, thermal parameters and occupancies for $Nb_{12-x}Ta_xS_4$ ($x \sim 5.26$)**

Atom	Occupancy	x	z	B_{iso} (Å^2)
M1	72.64% Ta + 27.36% Nb	0.3715 (3)	0.0726 (1)	0.27 (7)
M2	72.54% Ta + 27.46% Nb	0.4914 (3)	0.8706 (1)	0.54 (8)
M3	67.82% Ta + 32.18% Nb	0.4383 (3)	0.9691 (1)	0.34 (7)
M4	52.18% Ta + 47.82% Nb	0.1445 (4)	0.3139 (1)	0.46 (9)
M5	50.98% Ta + 49.02% Nb	0.2537 (3)	0.5123 (1)	0.29 (9)
M6	42.12% Ta + 57.88% Nb	0.2176 (4)	0.4102 (1)	0.6 (1)
M7	41.02% Ta + 58.98% Nb	0.2686 (4)	0.7505 (1)	0.5 (1)
M8	37.08% Ta + 62.92% Nb	0.3327 (4)	0.6090 (1)	0.5 (1)
M9	32.72% Ta + 67.28% Nb	0.1388 (4)	0.8426 (1)	0.3 (1)
M10	20.60% Ta + 79.40% Nb	0.0281 (5)	0.0391 (1)	0.4 (1)
M11	18.54% Ta + 81.46% Nb	0.3106 (5)	0.1772 (2)	0.5 (1)
M12	17.94% Ta + 82.06% Nb	0.4691 (5)	0.2708 (1)	0.6 (1)
S1		0.028 (2)	0.7125 (4)	0.4 (2)
S2		0.469 (2)	0.3885 (4)	0.1 (2)
S3		0.168 (2)	0.9601 (5)	0.5 (2)
S4		0.394 (2)	0.6826 (5)	0.7 (3)

y = 0.25.

Table 9 Interatomic distances (pm) for $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$) (M-M < 330 pm, M-S < 300 pm)

M1	M2	2[a]	283.1 (3)	M5	M1	2	286.2 (3)
	M3	2	283.3 (3)		M3	2	286.8 (3)
	M5	2	286.2 (4)		M3	1	308.6 (3)
	M8	2	284.5 (4)		M8	1	326.3 (6)
					M10	2	282.5 (5)
M2	M1	2	283.1 (3)		M10	1	312.6 (6)
	M3	1	326.8 (4)		S3	2	252 (1)
	M4	2	283.1 (4)				
	M6	2	292.0 (4)	M6	M2	2	292.0 (4)
	M11	2	298.6 (5)		M3	2	296.6 (4)
	S1	1	276 (1)		M4	1	324.1 (6)
					M9	2	310.8 (5)
M3	M1	2	283.3 (3)		S2	1	252 (2)
	M2	1	326.8 (4)		S3	2	259 (1)
	M3	2	289.0 (5)				
	M5	2	286.8 (4)	M7	M4	2	280.2 (5)
	M5	1	308.6 (4)		M9	1	327.0 (6)
	M6	2	296.6 (4)		M11	2	303.1 (6)
	S3	1	261 (2)		M12	2	291.1 (5)
					M12	2	310.6 (5)
M4	M2	2	283.1 (4)		S1	1	262 (2)
	M6	1	324.1 (6)		S1	1	277 (1)
	M7	2	280.2 (5)		S4	1	253 (2)
	M9	2	283.5 (4)				
	M11	1	321.6 (6)	M8	M1	2	284.5 (3)
	M12	1	324.9 (6)		M5	1	326.3 (4)
	S1	2	251 (1)		M10	2	314.3 (5)
					M11	2	312.0 (6)
					S2	2	254 (1)
					S4	1	249 (2)

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[a] number of neighbors.

Table 9 (continued)

M9	M4	2	283.5 (3)
	M6	2	310.8 (3)
	M7	1	327.0 (4)
	M12	2	307.3 (5)
	S2	2	248 (1)
	S4	1	249 (2)
M10	M5	2	282.5 (4)
	M5	1	312.6 (5)
	M8	2	314.3 (4)
	M10	2	311.4 (7)
	S2	1	245 (1)
	S3	2	252 (1)
	S3	1	292 (2)
M11	M2	2	298.6 (4)
	M4	1	321.6 (5)
	M7	2	303.1 (5)
	M8	2	312.0 (4)
	S1	2	256 (1)
	S4	2	259 (1)
M12	M4	1	324.9 (5)
	M7	2	291.1 (4)
	M7	2	310.6 (4)
	M9	2	307.3 (4)
	S1	2	255 (1)
	S4	2	262 (1)
S1	M2	1	276 (1)
	M4	2	251 (1)
	M7	1	262 (2)
	M7	1	277 (1)
	M11	2	256 (1)
	M12	2	255 (1)
S2	M6	1	252 (1)
	M8	2	254 (1)
	M9	2	248 (1)
	M10	1	245 (1)
S3	M3	1	261 (1)
	M5	2	252 (1)
	M6	2	259 (1)
	M10	1	292 (2)
	M10	2	252 (1)
S4	M7	1	253 (2)
	M8	1	249 (2)
	M9	1	249 (2)
	M11	2	259 (1)
	M12	2	262 (1)

Observed and calculated structure factors of $Nb_{6.74}Ta_{5.26}S_4$ are listed in Appendix B.

C. Results and Disscussions

In the structure of $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$) each metal position is fractionally occupied by niobium and tantalum and the metal positions have been labeled so that as the metal indicator increases, the n_{Nb}/n_{Ta} ratio on that position also increases, i.e., from M1 to M12 the n_{Nb}/n_{Ta} ratio on the metal position increases. Figures 4 and 5 show the structure of $Nb_{12-x}Ta_xS_4$. The structure can be thought of as a strongly modified bcc metal structure. The fragments of modified bcc metal networks can be easily recognized from Figure 5. All of the atoms lie on layers at $y = 1/4$ and $y = 3/4$. The coordinations of the sulfur and metal atoms in this compound are similar to those of $Nb_{21}S_8$ and $Nb_{14}S_5$; i.e., the coordinations of sulfur are capped trigonal prismatic, and the coordinations of metals are distorted capped cubic prismatic and capped pentagonal prismatic. The coordinations of S1 and S3 can be easily recognized as a tricapped trigonal prism and a bicapped trigonal prism, respectively. The coordination of S2 is a trigonal prism and that for S4 a monocapped trigonal prism, in both cases the trigonal prism axis lies in the mirror plane. The coordinations of M1 to M10 are distorted capped cubic prismatic, while the

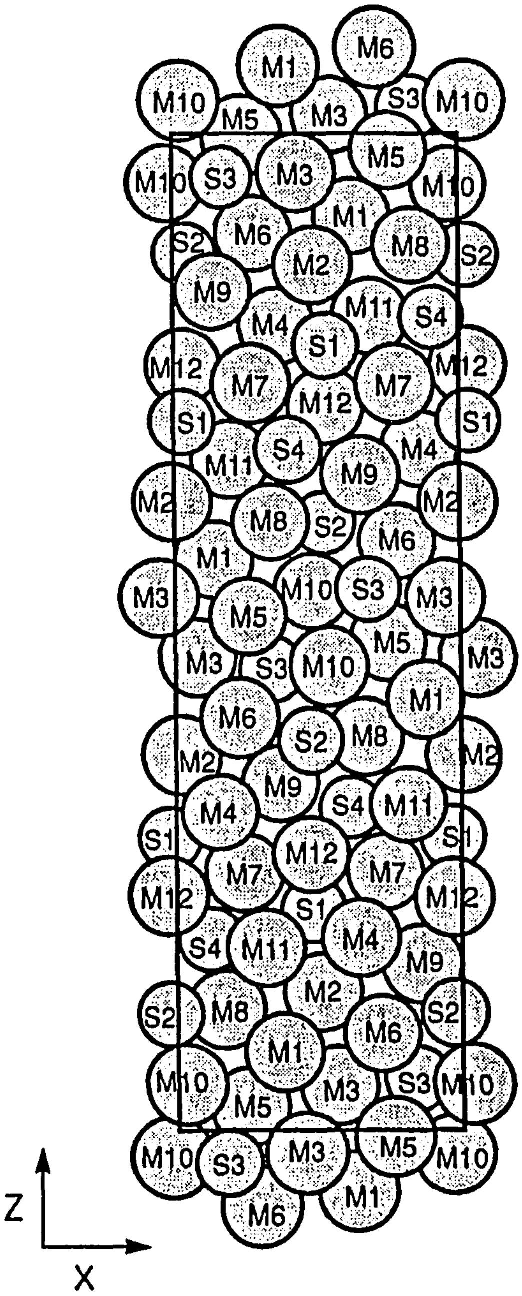

Figure 4 The crystal structure of $Nb_{12-x}Ta_xS_4$ viewed along the b-axis. Unit cell is marked by solid lines

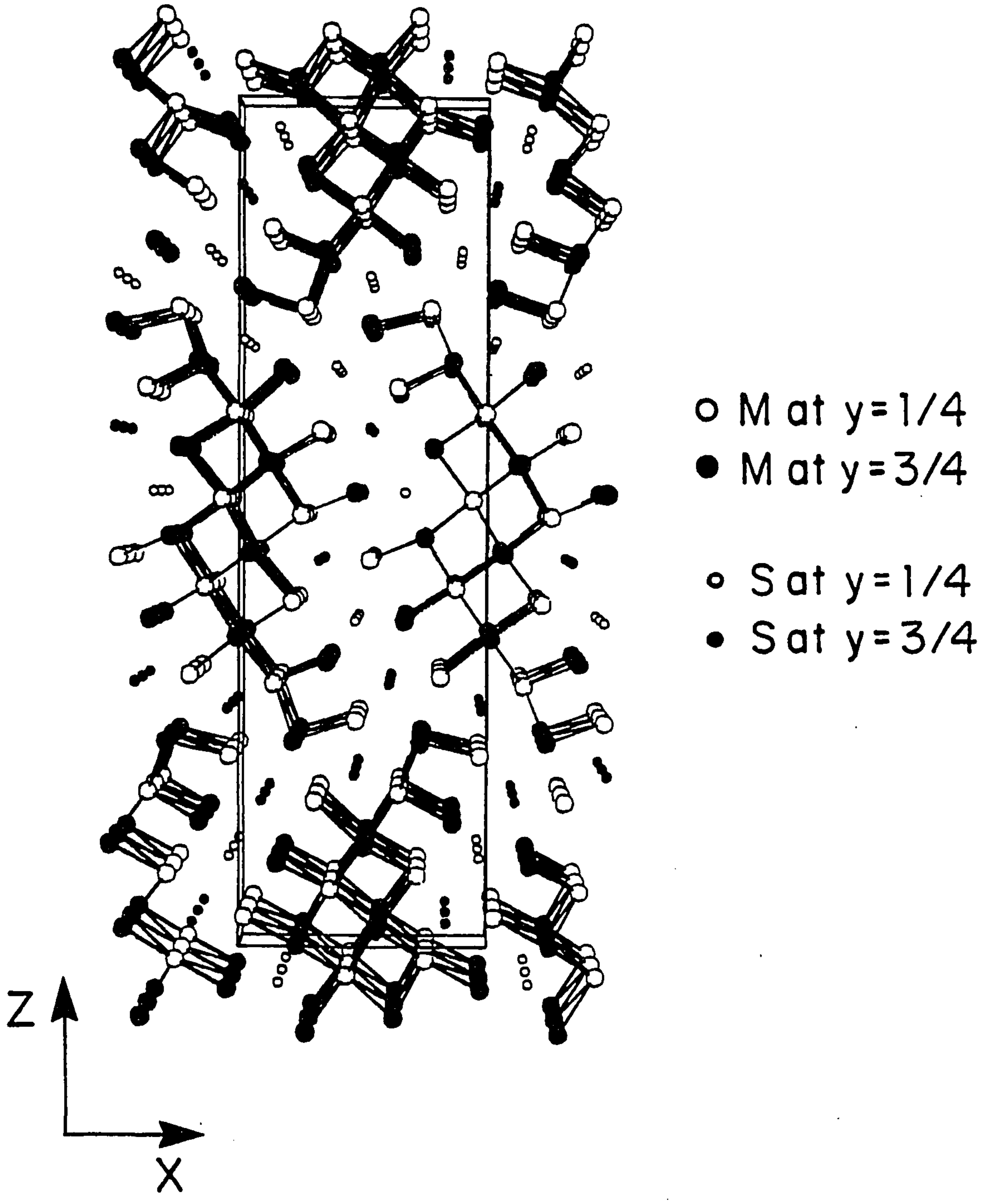

Figure 5 The projection of $Nb_{12-x}Ta_xS_4$ on the xz-plane. Unit cell is marked by solid lines

coordinations of M11 and M12 are capped pentagonal prismatic; e.g., for M1 the coordinating atoms are two M2, two M3, two M5 and two M8 while the capping ones are M3, M6, M10 and M11. The distorted capped cubes of M1, M2 and M3 consist only of metal atoms; while the distorted cubic coordinations and the pentagonal coordinations of other metal atoms consist of both metal atoms and sulfur atoms, i.e., sulfur atoms substitute for metal atoms at the corners of cubic and pentagonal prisms leading to increased distortion of the prisms. From Figure 4 it can be seen that the higher the metal indicator, the more sulfur is bound to the metal. The same result was also found in the compound $Nb_{4.92}Ta_{6.08}S_4$. Thus, it appears that in the metal-rich sulfides Nb-S binding is favored over that of Ta-S.

The shortest distance between the metal atoms is 2.80Å, compared with 2.82Å in $Nb_{4.92}Ta_{6.08}S_4$. There is no doubt that there are numerous strong metal-metal interactions in this solid. If only $d_{M-M} < 3.30$Å and $d_{M-S} < 3.00$Å are considered, the metallic and sulfur coordination numbers range from 8-11 and 6-9, respectively.

The characteristic features common for a broad class of transition metal-rich compounds are triangular prismatic metal atom coordinations about the nonmetal atoms, the dense packing of the metal atoms and the atoms located in mirror planes perpendicular to short axis (about 3.5 Å). This new compound, $Nb_{6.74}Ta_{5.26}S_4$ is also included in this class.

The ratio of metal and nonmetal for this new compound is 12:4; compared with 11:4 of $Nb_{4.92}Ta_{6.08}S_4$. Although the space group (Pnma) is the same and the cell parameters are similar for $Nb_{12-x}Ta_xS_4$ and $Nb_xTa_{11-x}S_4$ there are substantial differences between these two compounds, e.g., the longest axis is the c-axis in $Nb_{12-x}Ta_xS_4$ while the longest one in $Nb_xTa_{11-x}S_4$ is the a-axis. The coordinations of metals and nonmetals in $Nb_{12-x}Ta_xS_4$ and $Nb_xTa_{11-x}S_4$ are very similar except that there are pentagonal prisms for metals in the former compound and there is evidence for a volume effect resulting from nonbonding orbitals on sulfur in the latter compound. Thus, $Nb_{12-x}Ta_xS_4$ is more similar to the Nb-rich sulfides, $Nb_{21}S_8$[10] and $Nb_{14}S_5$;[11] than $Nb_xTa_{11-x}S_4$, i.e., there is capped pentagonal prismatic coordination around some metals in $Nb_{12-x}Ta_xS_4$.

CRYSTAL STRUCTURE OF $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$)

A. Preparation and Characterization

The initial reactant, Ta_2S,[19] was synthesized by heating a mixture of tantalum (Alpha Products, M3N8) and sulfur (Fisher Scientific, lab grade) with the n_{Ta}/n_S ratio of 2 at 440°C, first in a previously out-gassed quartz tube to consume all of free sulfur, and then at 800°C for three days. "Nb_2S" (there is no known compound with the formula Nb_2S) was synthesized using a similiar method. The cold pressed mixtures of Ta_2S and "Nb_2S" were arc-melted in an argon atmosphere, then annealed in an induction furnace. When $n_{Nb}:n_{Ta} = 1:4$, there were several unexplained reflections in the powder pattern of the arc-melted sample, one of them at very low diffraction angle. After annealing at 1350°C in an induction furnace, the unexplained reflections disappeared, and $Nb_xTa_{11-x}S_4$ appeared and was the major phase in the sample. When several mixtures of Ta_2S and "Nb_2S" ($n_{Ta2S}:n_{Nb2S} = 2$, 3 and 4, respectively) were arc-melted, these new reflections from the new phase also appeared in the powder pattern and it seemed the new phase was the major phase in the sample for n_{Ta2S}/n_{Nb2S} equal to 2 or 3.

The products in which the new phase was the major phase exhibited metallic luster and the facile shearing characteristic of layered compounds. It could be seen by the diffuse reflections in the powder pattern that the sample was not well crystallized.

The cell parameters of the new phase, $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$), were determined to be a = 3.3203, c = 21.619(12)Å in space group I4/mmm from the powder pattern of the arc-melted sample in the molar ratio: $n_{Ta2S}:n_{Nb2S} = 3:1$, according to the two-theta angles calculated with program PWDR[51] (using data from the structure solution for $Nb_{1.72}Ta_{3.28}S_2$). Powder diffraction data for this new compound are presented in Table 10. Intensities were calculated using the computer program PWDR. Positional parameters were used from the refined structure.

The arc-melted sample was examined by the EDAX method in a scanning electron microscope, and the major phase was found to consist of tantalum, niobium and sulfur elements with minor amounts of tungsten and copper originating from the arc-melting process and probably on the sample surface.

After the structure and composition of $Nb_{1.72}Ta_{3.28}S_2$ were determined, an attempt was made to synthesize the title compound starting with the elements. A mixture of Ta, Nb and S ($n_{Ta}:n_{Nb}:n_S \approx 3.28:1.72:2$) was heated at 440°C in a previously out-gassed quartz tube until the yellow color of free sulfur disappeared. The temperature was increased to 800°C and the sample was held at this temperature for 3 days. The mixture was then arc-melted three times and the mass loss was about 0.4% after the arc-melting. The powder pattern of this sample

Table 10 X-ray powder diffraction of $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) (Cu $K\alpha_1$ radiation)[a] ($2\theta < 75°$)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[b]	I_{calc}
0	0	2	8.17	8.17	S	78.0
1	0	5	34.05	34.02	M	39.2
1	1	0	38.28	38.31	S	65.0
1	1	2	39.18	39.24	W	8.6
1	0	7	39.93	39.83	S	100.0
0	0	12	50.61	50.62	W	7.6
2	0	0	55.28	55.29	M	24.7
0	0	14		59.84		5.4
1	1	12		65.22		16.6
2	1	5		66.53		15.0
2	1	7	70.31	70.28	M	49.2
1	1	14		73.32		14.1

[a] 2θ values of reflections with relative intensities $I_{calc} > 5$ are listed.

[b] W, weak; M, medium; S, strong.

indicated that the title compound was the main phase with less than 10% $Nb_xTa_{2-x}S$ (Ta_2Se[31]-type).

The same result was also obtained from arc-melting the mixture of Ta, TaS and "Nb_2S" with $n_{Ta}:n_{Nb}:n_S = 3.28:1.72:2$ overall. The quantitive analysis of the arc-melted sample using the EDAX method only found one phase for which the molar ratio of n_{Ta}/n_{Nb} was 1.87 cooresponding to $Nb_{1.74}Ta_{3.26}S_2$, although the Guinier x-ray powder pattern indicated that minor $Nb_xTa_{2-x}S$ (Ta_2Se[31]-type) coexisted with the title compound.

B. Single Crystal X-Ray Investigation

One gray-colored needle-shaped crystal ($0.02 \times 0.02 \times 0.25 mm^3$) was picked from the arc-melted mixture of Ta_2S and "Nb_2S" in which the molar ratio was 3:1; and placed on a Rigaku AFC6 single-crystal x-ray diffractometer for data collection. During the SEARCH only twelve peaks were found in the range of 14°-$45^\circ (2\theta)$. Seven peaks were indexed in the INDEX TWIN process as a body-centered cell with $a = 3.3129(30)$, $b = 3.3202(41)$, $c = 21.4348(214)$Å, $\alpha = 89.904(91)^\circ$, $\beta = 89.992(93)^\circ$ and $\gamma = 90.223(96)^\circ$. Intensity data were collected using monochromatic $MoK\alpha$ radiation, employing the 2θ-ω scan technique up to 60° (2θ). 955 reflections (hkl, -hkl, hk-l, -hk-l) were collected, and 124 unique reflections with $F^2 > 3\sigma(F_0^2)$ were obtained and used for structure determination. The observed intensities were corrected for Lorentz-polarization and absorption effects with an absorption coefficient of $795.13 cm^{-1}$. There was no significant fluctuation or decay of the crystal as determined by checking three standard reflections measured every 150 reflections. Subsequent data processing and structure calculations were performed with the program package TEXSAN.

First, the structure was solved using the direct method in the orthorombic centrosymmetric space group Immm obtained from automatic check in PROCESS. The empirical absorption correction was applied with the max. and min. transmission factor of 1.000 and 0.526, respectively. Application of the direct method resulted in finding three metal atoms and one sulfur atom in an asymmetric unit. The multiplicities for three metal positions were refined after each of them was assigned as 50%Nb and 50%Ta. Isotropic refinement was then done while the multiplicities were held fixed. Finally, the isotropic refinement was done with multiplicities for the metals also refined. The secondary extinction coefficient was also refined; but it was negative, i.e., there is no secondary extinction. Subsequently, the anisotropic refinement was done, first with the multiplicities for the metal positions were held fixed, and finally U_{ij} for all atoms and multiplicities for metals were refined altogether. R, R_w and GOF were obtained as 0.053, 0.054 and 1.36; respectively. The composition was determined to be $Nb_{2.17}Ta_{2.83}S_2$ from the refinement.

Since the a-axis and the b-axis are very nearly equal in length, the tetragonal space group I4/mmm was used to refine the structure. The final result of Immm was used as a basis for refinement in the space group of I4/mmm; after the space group and Laue group had been changed accordingly and the original data were averaged in the new Laue group 4/mmm with R_{ave} = 0.165 compared to 0.155 for Laue group mmm. R, R_w and GOF were finally obtained as 0.049, 0.058 and 1.52; respectively. The composition was determined to be $Nb_{1.97}Ta_{3.03}S_2$ from the refinement.

The DIFABS[59] correction was applied to the data, to which the empirical correction had been applied, but which had not been averaged. The max. and min. transmission factors were 1.272 and 0.731, respectively after the isotropic refinement in the space group I4/mmm had completed. For the above process (DIFABS) the original cell constants and orientation matrix were used. After the data were averaged (R_{ave} = 0.09), the same procedure as before was applied. Final R, R_w and GOF were obtained as 0.034, 0.038 and 1.43; respectively. The composition was determined to be $Nb_{1.72}Ta_{3.28}S_2$ by this approach. The refinement result of the last approach was adopted because of the lower R-factors.

The crystal was also examined by the Weissenberg technique and some streaking was observed. Thus, the crystal was not of optimum quality for refininement and the precision of the results could be adversely effected. However, the R factor was indicative of satisfactory refinement.

The refinement result, crystal data, and bond distances are given in Tables 11, 12, and 13; respectively. Figures 6 and 7 show representations of this compound.

Observed and calculated structure factors are listed in Appendix C.

C. Results and Discussions

In the structure of $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) each metal position is fractionally occupied by niobium and tantalum and the metal positions have been labeled so that as the metal indicator increases, the n_{Nb}/n_{Ta} ratio on that position also increases, i.e., from M1 to M3 the n_{Nb}/n_{Ta} ratio on the metal position increases. The structure can be viewed as a bcc-type Nb-Ta solid solution in which two neighboring layers in every seven are replaced by sulfur. Some distortions relative to bcc are observed; e.g., the cube consisting of eight M2 contracts along the c-axis while the cube of four M1 and four M3 expands along the c-axis, with M2 deviating slightly from the center of the cube. This novel layered structure is reminisent of Ta_2Se[31] which is composed of six layers in the sequence Se-Ta-Ta-Ta-Ta-

Table 11 Positional, thermal parameters and occupancies for $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$)

		occupancy	z	B_{eq} ($Å^2$)	U_{11}	U_{33}
M1	2a	88.3% Ta + 11.7% Nb	0	0.98 (9)	0.011 (1)	0.015 (2)
M2	4e	82.6% Ta + 17.4% Nb	0.4248(1)	0.68 (5)	0.0098 (7)	0.006 (1)
M3	4e	37.3% Ta + 62.7% Nb	0.1560 (1)	0.74 (8)	0.009 (1)	0.010 (2)
S	4e		0.3024 (4)	0.7 (2)	0.011 (4)	0.005 (6)

x, y = 0 for all atoms; $U_{22} = U_{11}$, $U_{ij} = 0$. $B_{eq} = 8\pi^2/3\ (U_{11} + U_{22} + U_{33})$.

Table 12 Crystal data for $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$)

Formula	$Nb_{1.72}Ta_{3.28}S_2$
Space group	I4/mmm
a, Å	3.3203(9)[a]
c, Å	21.6190(116)[a]
V, $Å^3$	238.34(16)[a]
Z	2
d_{calc}, g/cm^3	11.513
Crystal size, mm^3	0.02x0.02x0.25
$\mu(MoK_\alpha)$, cm^{-1}	795.13
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ = 0.71069 Å)
Orientation reflections, number, range (2θ)	12,14-45
Temperature, °C	22
Scan method	2θ-ω
Octants measured	hkl,-hkl,hk-l,-hk-l
Data collection range, 2θ, deg	0-60
No. refl. measured	955
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	124
No. parameters refined	15
Trans. factors, max., min.	1.000,0.526
R^b, R_w^c, GOF^d	0.035, 0.038, 1.43
Largest shift/esd, final cycle	0.00
Largest peak, e/$Å^3$	4.99 (1.06Å, M2)

[a] obtained from indexing of the powder pattern.

[b] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[d] $GOF = \Sigma((|F_o| - |F_c|) / \sigma_i) / (N_{obs} - N_{parameters})$.

Table 13 Interatomic distances (pm) for $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) (< 340pm)

M1	M1	4[a]	332.03 (9)
	M2	8	285.6 (2)
	M3	2	337.4 (3)
M2	M1	4	285.6 (2)
	M2	1	325.1 (6)
	M2	4	332.03 (9)
	M3	4	292.7 (3)
	S	1	264.6(9)
M3	M1	1	337.4 (3)
	M2	4	292.7 (3)
	M3	4	332.03 (9)
	S	4	251.4 (3)
	S	1	316.4 (9)
S	M2	1	264.6 (9)
	M3	4	251.4 (3)
	M3	1	316.4 (9)
	S	4	326 (1)
	S	4	332.03 (9)

[a] number of neighbors.

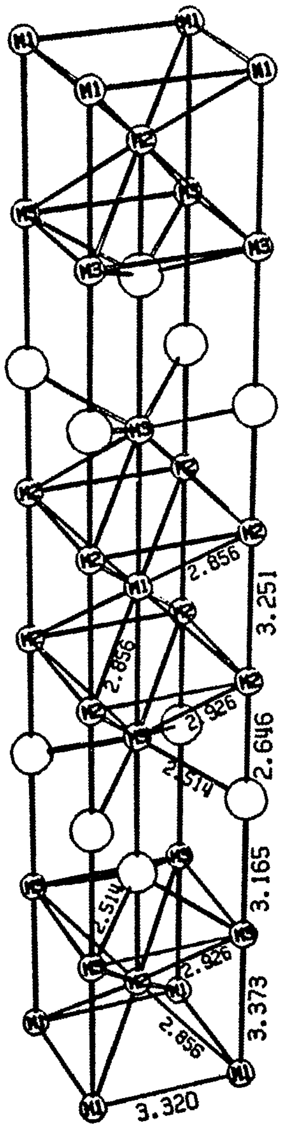

Figure 6 Picture of one unit cell for $Nb_xTa_{5-x}S_2$. Larger circle represents S. Vertical is z-direction

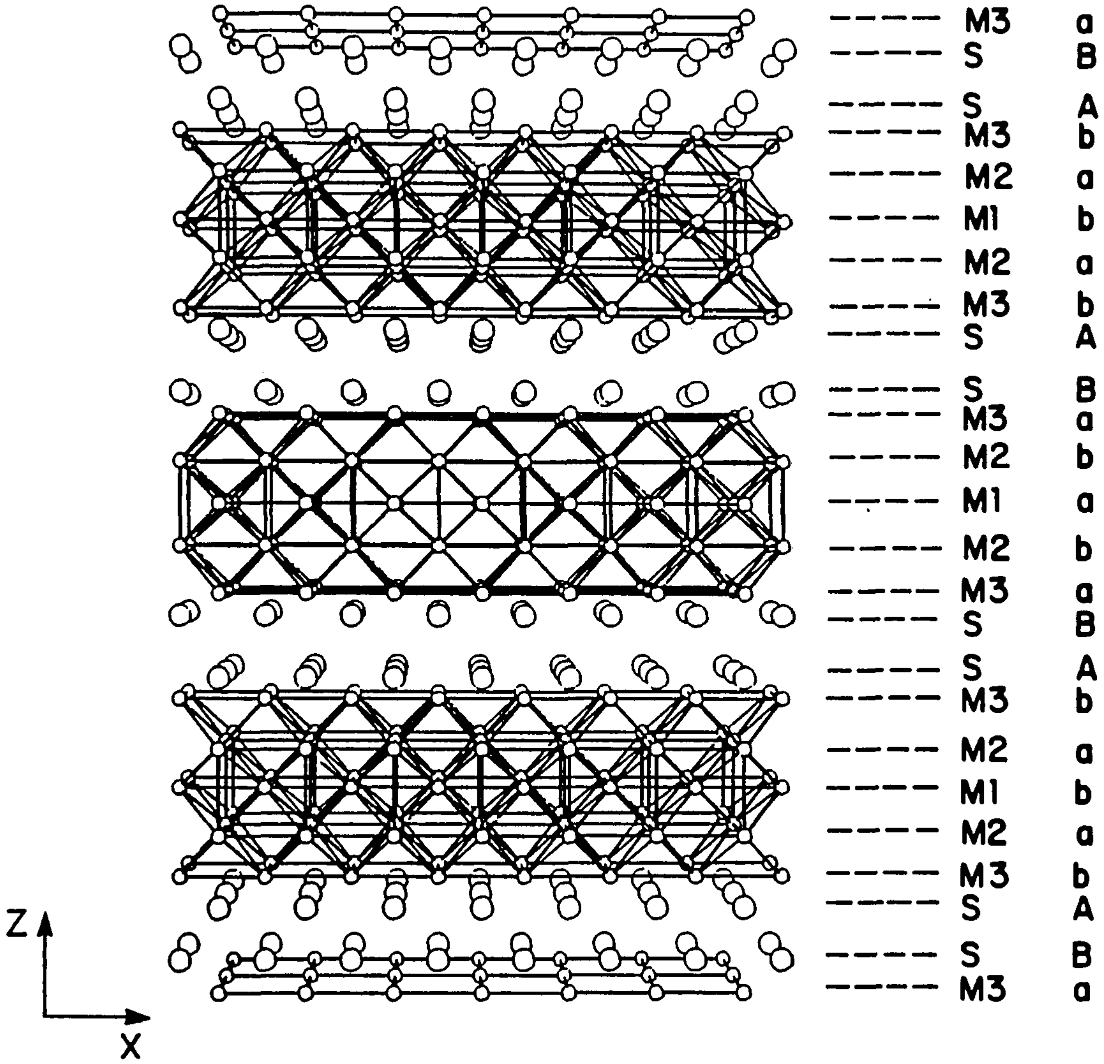

Figure 7 The projection of $Nb_xTa_{5-x}S_2$ on the xz-plane. Larger circle represents S. Vertical is z-direction

Se, also in bcc-type packing. In ZrCl-type[62] and ZrBr-type[63] compounds the sequence of the layers is X-Zr-Zr-X (X = Cl, Br) and the homoatomic analogue structure is ccp-type. The structure can also be thought of as a modified bcc metal structure. The fragments of modified bcc metal networks can be easily recognized from Figure 7.

The shortest distance between metal and metal is 2.856Å compared with 2.86Å in elemental niobium or tantalum, and thus it is clear that there is robust metal-metal bonding in this compound.

The coordination of M1 is as follows: eight M2 (2.856Å) at the corners of a distorted capped cube with four M1 (3.320Å) and two M3 (3.373Å) as capping atoms. Around M2 there are four M1 (2.856Å) and four M3 (2.926Å) at the corners of a distorted capped cube with five M2 (four at 3.320Å and one at 3.251Å), and one S (2.646Å) as capping atoms. The corners of the distorted capped cube around M3 are four M2 (2.926Å) and four sulfur (2.514Å) while the capping atoms are one M1 (3.373Å) and four M3 (3.320Å), respectively.

As the identifying number of the metal increases, the Nb/Ta ratio on that position also increases. The number of coordinating sulfurs for M1, M2 and M3 are 0, 1 and 4, respectively; i.e., the more Nb in the position, the more sulfur bound to this position. The shortest distance between sulfur atoms (3.26Å) in neighboring layers indicates interlayer van der Waals interactions, consistant with the graphitic character and the tendency of the compound to disorder. This is the first van der Walls layered compound with such high ratio of $n_{metal}/n_{nonmetal}$, 2.50.

The layered disulfides (TiS_2, MoS_2, NbS_2, etc.) have been studied extensively[64] because they intercalate both organic and inorganic substances into the interlayer van der Waals gaps between adjacent sulfur layers. The compound reported here introduces the possibility of studying intercalates in a new setting, namely, in a compound with a robustly metallic region separating van der Waals layers. This compound also raises again the intriguing chemical question posed previously by $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) and $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$), namely: what are the properties of mixed Nb-Ta that cause compounds of the mixed metals to differ substantially in M/S ratio and structure from the binary sulfides of niobium and tantalum?

CRYSTAL STRUCTURE OF $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

A. Preparation and Characterization

High purity Nb (Alpha Products) and S (Fisher Scientific Co.) were put into a previously out-gassed silica tube in the molar ratio: $n_{Nb}:n_S = 2:1$ and were heated at 440°C first and then held at 800°C for 5 days in a tube furnace. TaS was synthesized using a similiar method. The mixture of "Nb_2S" (there is no known compound with the formula Nb_2S), TaS and Ta with $n_{Ta}:n_{Nb}:n_S =$ 3:2:2.17 was pressed into a pellet and arc-melted three times in an argon atmosphere. The Guinier x-ray powder pattern indicated that a new phase existed together with less than 2% NbS-type[65] compound in the sample; but the powder pattern of the arc-melted sample was diffuse, which indicated that the sample was not well crystallized (if the sample was arc-melted longer, $Nb_xTa_{5-x}S_2$ was also found in the sample). An attempt was made to anneal the arc-melted sample to improve the crystallinity of the sample. First the sample was annealed for 10 hours in an induction furnace at 1350°C, but the new phase disappeared to yield $Nb_xTa_{11-x}S_4$ and unknown phases. The arc-melted sample was put in a previously out-gassed silica tube and annealed for 5 weeks at a lower temperature (850°C) in a tube furnace. Many needle-like crystals were found in the annealed sample. The x-ray powder pattern of the annealed (850°C) sample was the same as that of the nonannealed sample. The cell parameters of the new phase, $Nb_xTa_{2-x}S$ ($x \approx 0.95$), were determined to be $a = 3.3304(7)$, $c = 9.0928(94)$Å in tetragonal space group P4/nmm according to the two-theta angles calculated with program PWDR[51] (using data from the structure solution for $Nb_{0.95}Ta_{1.05}S$). Powder diffraction data for this new compound are presented in Table 14. Intensities were calculated using the computer program PWDR. Positional parameters were used from the refined structure.

After the structure and composition of $Nb_{0.95}Ta_{1.05}S$ were determined, an attempt was made to synthesize the title compound from a stoichiometrically appropriate mixture of Ta, TaS and "Nb_2S" by means of the arc-melting method. The total mass loss after the arc-melting process was less than 1%. Two phases, $Nb_xTa_{2-x}S$ and about 50% $Nb_{1-x}Ta_xS$ (NbS-type[65]), were found to coexist in the product from the x-ray powder diffraction. The ratios of n_{Ta}/n_{Nb} were determined to be 1.29 and 0.81 for $Nb_xTa_{2-x}S$ and $Nb_{1-x}Ta_xS$, respectively, by the EDAX method in a scanning electron microscope. These values correspond to $Nb_{0.87}Ta_{1.13}S$ ($Nb_xTa_{2-x}S$) and $Nb_{0.55}Ta_{0.45}S$ ($Nb_{1-x}Ta_xS$).

A mixture of the elements tantalum, niobium and sulfur with $n_{Ta}:n_{Nb}:n_S \approx 1.15:0.85:1$ were heated at 440°C, first in a previously evacuated silica tube to consume all of the free sulfur and then were held at 800°C for three days. Finally the pressed sample was arc-melted three times in an argon atmosphere. The total mass loss after the arc-melting process was less than

Table 14 X-ray powder diffraction of $Nb_xTa_{2-x}S$ ($x \approx 0.95$) (Cu $K\alpha_1$ radiation)[a] ($2\theta < 75°$)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[b])	I_{calc}
0	0	1	9.63	9.72	S	71.9
1	0	2	33.35	33.32	S	40.8
1	1	0	38.21	38.18	S	66.1
1	1	1	39.46	39.49	W	11.1
1	0	3	40.19	40.19	S	100.0
0	0	5		50.12		6.9
2	0	0	55.10	55.10	M	24.9
0	0	6		61.10		5.5
1	1	5	64.48	64.71	W	14.9
2	1	2	65.95	65.94	W	15.1
2	1	3	70.34	70.37	M	49.7
1	1	6	74.32	74.37	W	14.7

[a] 2θ values of reflections with relative intensities $I_{calc} > 5$ are listed.

[b] W, weak; M, medium; S, strong.

0.8%. The Guinier powder pattern of the sample indicated that about 5% NbS-type compound coexisted with the major product, $Nb_xTa_{2-x}S$. When the initial amounts of sulfur were decreased to $n_{Ta}:n_{Nb}:n_S$ = 1.15:0.85:0.9 and the same procedure of synthesis was used, the amount of NbS-type compound decreased to less than 5%. The products of a stoichiometrically appropriate mixture with $n_{Ta}:n_{Nb}:n_S \approx 1.10:0.90:0.85$ were $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ when the same synthesis produre was used.

This means that samples in this range of n_{Ta}/n_{Nb} favor the formation of solid solutions of $Nb_{1-x}Ta_xS$ (NbS-type) and $Nb_xTa_{2-x}S$ and with increasing ratio of quantity of metals to sulfur the amounts of NbS-type solid solution decreased.

B. Single Crystal X-Ray Investigation

Many crystals were found in the annealed (850 °C) sample. A gray-colored crystal ($0.03 \times 0.04 \times 0.15 mm^3$) was picked from the annealed sample and attached to a glass fiber using APIEZON grease (the crystal was deformed when EPOXY glue was used). First the quality of the crystal were checked using a Weissenberg camera. Then intensity data were collected using monochromatic Mo Kα radiation, employing the 2θ-ω scan technique up to 65°(2θ) on a RIGAKU AFC6 single-crystal diffractometer. A total of 763 reflections (hkl, -hkl, hk-l, -hk-l) were monitored, and 104 unique reflections with $F^2 > 3\sigma(F_o^2)$ were obtained and used for the structure determination. The observed intensities were corrected for Lorentz-polarization and absorption effects with an empirical absorption coefficient of 622.93cm^{-1}. Based on three standard reflections measured every 150 reflections, there was no significant fluctuation or decay of the crystal. Subsequent data processing and structure calculations were performed with the program package TEXSAN.

The space group was determined to be P4/nmm using the program PROCESS. First an empirical absorption correction was applied with the max. and min. transmission factors of 1.000 and 0.301, respectively. Application of direct methods resulted in an electron map containing three strong peaks per asymmetric unit on the x, y = 1/4 sections. Two of these peaks were much higher than the 3rd one. The two stronger peaks were taken to be at Ta positions, and the 3rd peak to be at a S position; and the refinement was initiated. The multiplicities for the metal positions were refined after 50%Ta and 50%Nb was assigned to each metal position. Finally the isotropic thermal parameters were refined with the concomitant refinement of the multiplicities for the metal positions, and the final R, R_w and GOF were 0.048, 0.046 and 1.647, respectively. The composition was determined to be $Nb_{0.59}Ta_{1.41}S$ from the isotropic refinement (because the secondary extinction coefficient became negative when refined, it is concluded that there is no significant secondary extinction in the compound).

After isotropic refinement, F_c values for $Nb_{0.59}Ta_{1.41}S$ were calculated and used for a DIFABS[59] absorption correction for the F_o values in the mode that utilizes θ-dependent systematic deviations $|F_o| - |F_c|$. The ratio of the highest to the lowest transmission was 1.385. An anisotropic refinement was then carried out, and the final R, R_w and GOF were 0.048, 0.048 and 1.054, respectively. The composition was determined to be $Nb_{0.95}Ta_{1.05}S$ from the anisotropic refinement. (The R, R_w and GOF were obtained as 0.048, 0.049 and 1.069, respectively, if the multiplicities for the metal positions were fixed (i.e., the composition was $Nb_{0.59}Ta_{1.41}S$ during the anisotropic refinement). However, the first approach appears to be more reasonable. There are two impurity peaks higher than $5e^-/Å^3$ (5.695 and 5.267 $e^-/Å^3$) in the result of the second approach, compared to only one impurity peak higher than $5e^-/Å^3$ ($5.291e^-/Å^3$ in the result of the first approach). In addition the ratio of U_{33}/U_{11} for the sulfur atom was about 10 in the second case, compared to about 3 in the first case. The trend that niobium preferentially occupies the metal positions bound to more sulfur is true for the results of both approaches. Based on the above arguments the result of the first approach is preferred.

The crystal data, atom parameters and bond distances are given in Tables 15, 16 and 17, respectively.

Figures 8 and 9 show representations of $Nb_xTa_{2-x}S$ (x = 0.95).

Table 15 Crystal data for $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

Formula	$Nb_{0.95}Ta_{1.05}S$
Space group	P4/nmm(#129)
a, Å	3.3304(7)[a]
c, Å	9.0928(94)[a]
V, Å^3	100.85(11)[a]
Z	2
d_{calc}, g/cm^3	10.275
Crystal size, mm^3	0.03x0.04x0.15
$\mu(MoK_\alpha)$, cm^{-1}	622.93
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ = 0.71069 Å)
Orientation reflections, number, range (2θ)	23,14-40
Temperature, °C	22
Scan method	2θ-ω
Octants measured	hkl,-hkl,hk-l,-hk-l
Data collection range, 2θ, deg	0-65
No. refl. measured	763
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	104
No. parameters refined	12
Trans. factors, max., min.	1.000,0.301
R[b], R_w[c], GOF[d]	0.048, 0.048, 1.069
Largest shift/esd, final cycle	0.00
Largest peak, e/Å^3	5.29 (0.74Å, S)

[a] obtained from indexing of the powder pattern.

[b] $R = \Sigma\left|\left|F_o\right| - \left|F_c\right|\right| / \Sigma\left|F_o\right|$.

[c] $R_w = [\Sigma w(\left|F_o\right| - \left|F_c\right|)^2 / \Sigma w\left|F_o\right|^2]^{1/2}$; $w = 1/\sigma^2(\left|F_o\right|)$.

[d] $GOF = \Sigma((\left|F_o\right| - \left|F_c\right|) / \sigma_i) / (N_{obs} - N_{parameters})$.

Table 16 Positional, thermal parameters and occupancies for $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

Atom	site	occupancy, %	z	B_{eq}	U_{11}	U_{33}
M1	2c	76.6Ta + 23.4Nb	0.4146(1)	0.22(3)	0.0031(6)	0.0020(6)
M2	2c	28.2Ta + 71.8Nb	0.7761(2)	0.37(5)	0.0041(7)	0.006(1)
S	2c		0.119(1)	0.6(2)	0.005(2)	0.014(4)

x,y = 1/4 for all atoms; $U_{22} = U_{11}$, $U_{ij} = 0$. $B_{eq} = 8\pi^2/3(U_{11} + U_{22} + U_{33})$.

Table 17 Interatomic distances (pm) for $Nb_xTa_{2-x}S$ ($x \approx 0.95$) (< 340 pm)

M1	M1	4[a]	333.04 (7)
	M1	4	282.1 (2)
	M2	4	292.5 (2)
	M2	1	328.7 (4)
	S	1	269 (1)
M2	M1	4	292.5 (2)
	M1	1	328.7 (4)
	M2	4	333.04 (7)
	S	4	254.1 (4)
	S	1	312 (1)
S	M1	1	269 (1)
	M2	4	254.1 (4)
	M2	1	312 (1)
	S	4	320 (1)
	S	4	333.04 (7)

[a] number of neighbors.

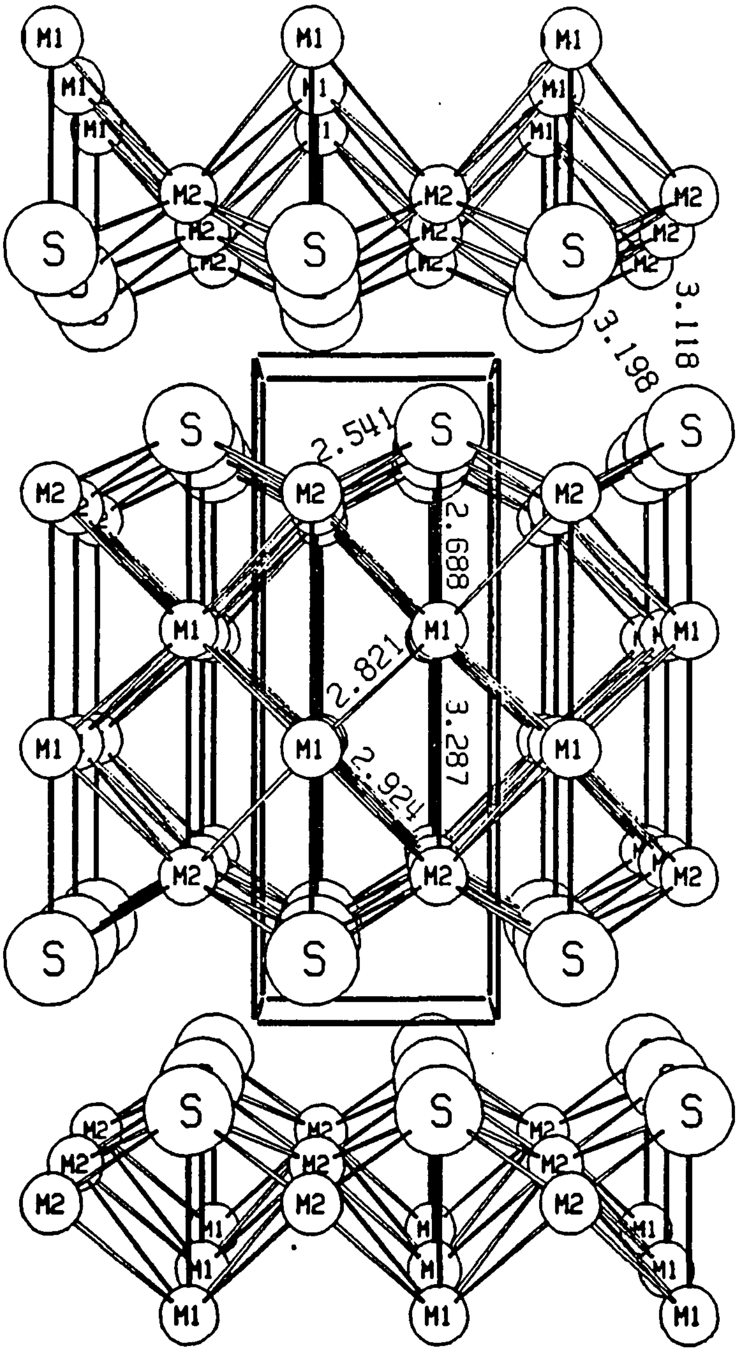

Figure 8 The projection of $Nb_xTa_{2-x}S$ (Ta_2Se-type[31]) on the xz-plane. Vertical is z-direction. Unit cell is marked by solid lines

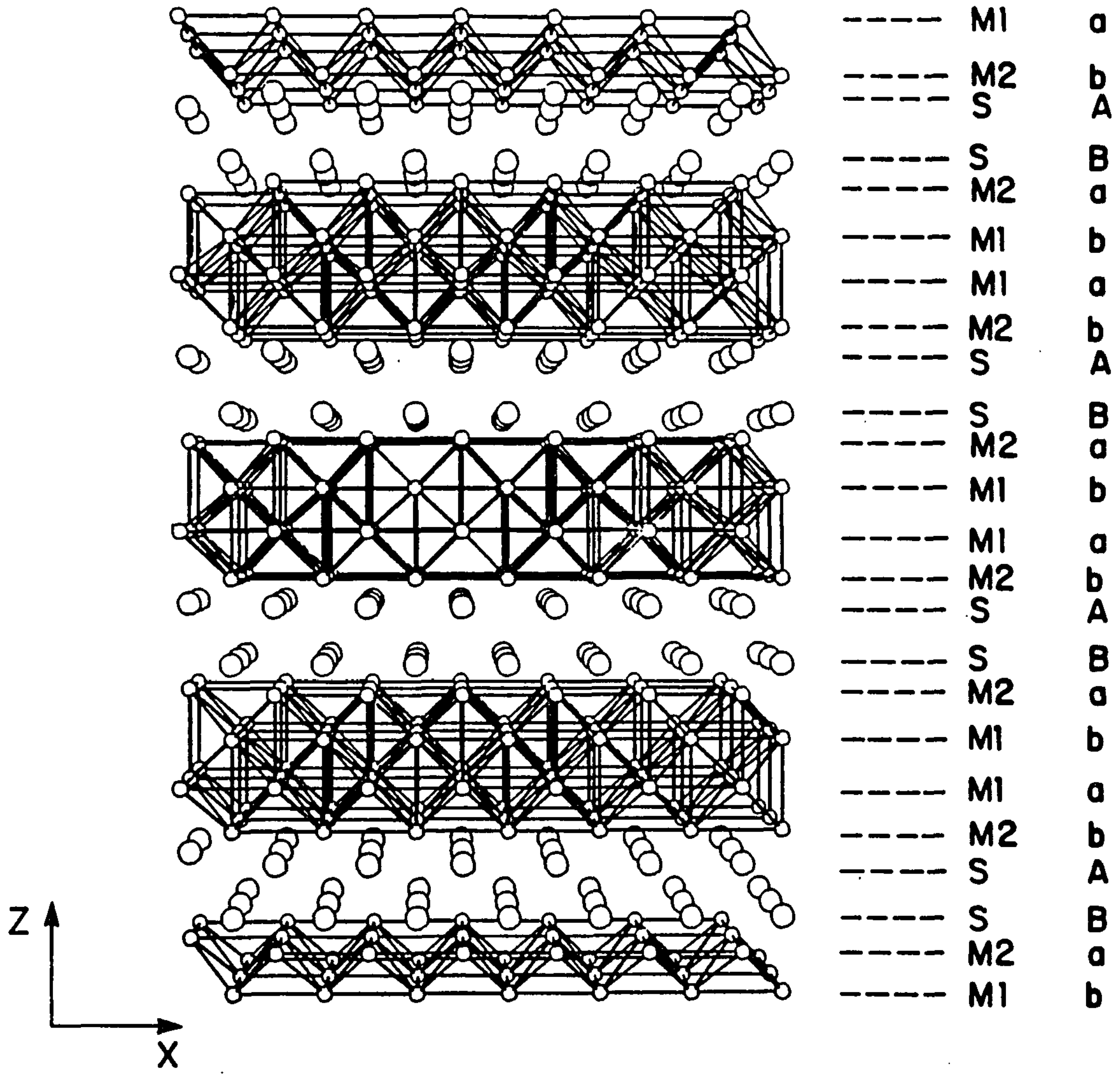

Figure 9 The projection of $Nb_xTa_{2-x}S$ (Ta_2Se-type[31]) on the xz-plane. Larger circle represents S. Vertical is z-direction

Observed and calculated structure factors are listed in Appendix D.

C. Results and Discussions

$Nb_xTa_{2-x}S$ is isostructural with Ta_2Se.[31] In the structure of $Nb_xTa_{2-x}S$ each metal position is fractionally occupied by niobium and tantalum and the metal positions have been labeled so that as the metal indicator increases, the n_{Nb}/n_{Ta} ratio on that position also increases, i.e., from M1 to M2 the n_{Nb}/n_{Ta} on the metal position increases. Figure 8 is a projection of the structure onto the xz-plane. The unit cell is marked using solid lines. The structure of $Nb_xTa_{2-x}S$ is similiar to that of $Nb_xTa_{5-x}S_2$ in that the structure can be viewed as a bcc-type Nb-Ta solid solution in which two neighboring layers in every six (compared to every seven in $Nb_xTa_{5-x}S_2$) are replaced by S. Some distortions relative to bcc-type structure are observed, e.g., there is a contraction of the cube consisting of four M1 and four M2 along the c-axis with M1 deviating slightly from the center of the cube. The structure can also be thought of as a modified bcc metal structure. The fragments of modified bcc metal networks can easily be recognized from Figure 9.

The shortest distance between metal and metal is 2.821Å compared with 2.86Å in elemental niobium or tantalum, thus it is clear that strong metal-metal bonding plays an important role in stablizing the structure.

The coordinations around each atom may be approximately thought of as capped distorted cubes. The M1 atom is surrounded by fourteen atoms: four M1 atoms (2.821Å distant) and four M2 atoms (2.925Å distant) at the corners of a distorted cube; and four M1 atoms (3.3304Å distant), one M2 atom (3.287Å distant) and one S atom (2.69Å distant) as capping atoms. For M2 the surrounding atoms are as follows: four M1 atoms (2.925Å distant) and four S atoms (2.541Å distant) at the corners of a distorted cube; one M1 atom (3.287Å distant), four M2 atoms (3.3304Å distant) and one S atom (3.12Å distant) as the capping atoms. The corners of the distorted cube around the S atom are four M2 atoms (2.541Å distant) and four S atoms (3.20Å distant) with one M1 atom (2.69Å distant), one M2 atom (3.12Å distant) and four S atoms (3.3304Å distant) as the capping atoms. The shortest distance between two sulfur atoms in two neighboring layers is 3.20Å, and apparently van der Waals interactions hold together the S-4M-S sandwiches. Van der Waals interactions lead to graphitic properties and the observed tendency of the crystal of the compound to be deformed by the drying of EPOXY glue.

Because there are one and five coordinating sulfur atoms around the M1 and M2 atom, respectively; this is the fifth example (along with $Nb_{21-x}Ta_xS_8$, $Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$ and $Nb_xTa_{5-x}S_2$) in which it has been found that the niobium percentage of a site occupied by both niobium and tantalum increases with the number of S atoms in the first coordination sphere of that position.

$Nb_xTa_{2-x}S$ and $Nb_xTa_{5-x}S_2$ belong to a new class of layered compounds with two characteristics, namely layered compounds with robustly metallic regions separating the van der Waals layers and with a bcc basis. The robustly metallic region between two van der Waals layers can be easily seen in Figure 9. Inorganic and organic intercalation studies of layered transition metal disulfides, e.g., TiS_2, NbS_2 and MoS_2 (hcp setting), have been of interest for many years,[64] and many useful properties have been found. Because there is a vital difference between this new class of the layered compounds and the transition metal disulfides, i.e., the previously discussed robustly metallic regions between the two settings of van der Waals layers, it can be expected that some new properties may be found from the organic and inorganic intercalation studies of the two new layered compounds, $Nb_xTa_{2-x}S$ and $Nb_xTa_{5-x}S_2$.

CRYSTAL STRUCTURE OF $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$)

A. Preparation and Characterization

As previously described the reaction of Nb + Ta_2S[19] (n_{Nb}:n_{Ta2S} = 1:1) was studied and a new ternary phase, $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) was found. In this section the reaction of Ta + "Nb_2S" (n_{Ta}:n_{Nb2S} = 1:1) was desired. This reaction was studied using a method similiar to that previously described for the reaction of Nb + Ta_2S, i.e., arc-melting the cold pressed mixture of the reactants in an argon atmosphere and then annealing the sample at 1350°C for several hours in an induction furnace. From the Guinier powder pattern three phases were found in the sample; $Nb_{21-x}Ta_xS_8$, NbO[66] and unreacted Ta; respectively. The reflections of $Nb_{21-x}Ta_xS_8$ were similiar to those of $Nb_{21}S_8$[10] except for changes in the intensity of some reflections (the most obvious change was observed for the [110] reflection).

The structures of Ta_6S[20,21] and $Nb_{21}S_8$[10] are different, and thus there was a motivation to know what products would be obtained from the reaction of Ta_6S + $Nb_{21}S_8$. This reaction was carried out using the same method as before (annealing temperature and time were 1350°C and 42h., respectively). Many gray-colored crystals were found in the annealed sample. The powder pattern could be indexed as one phase, $Nb_xTa_{21-x}S_8$ [16.817(2), 3.3450(9)Å, I4/m], according to the two-theta angles calculated with program PWDR[51] (using data from the structure solution for $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$)). Powder diffraction data for this new compound are presented in Table 18. Intensities were calculated using the computer program PWDR. Positional parameters were used from the refined structure.

The quantitive analysis of the product from the reaction of $Nb_{21}S_8$ + Ta_6S using EDAX in SEM indicated the presence of Nb-Ta-S ternary phase (Nb 52.08 at.%, Ta 17.94 at.% and S 27.83 at.% corresponding to the $Nb_{14.97}Ta_{5.16}S_8$).

B. Single Crystal X-Ray Investigation

A single crystal (0.4mm x 0.3mm x 0.2mm) was picked from this sample and its quality was checked on a Weissenberg camera first.

Intensity data were collected using monochromatic Mo Kα radiation, employing the 2θ-ω scan technique up to 50°(2θ) on a RIGAKU AFC6 single-crystal diffractometer. A total of 1045 reflections (hkl, -hkl) were monitored, and 416 unique reflections with $F^2 > 3\sigma(F_o^2)$ were obtained and used for the structure determination. The observed intensities were corrected for Lorentz-polarization and absorption effects with an empirical absorption coefficient of 443.03cm^{-1}. Based on three standard reflections measured every 150 reflections, there was no significant fluctuation or decay of the crystal. Subsequent data

Table 18 X-ray powder diffraction of $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$) (Cu $K\alpha_1$ radiation)[a] ($2\theta < 55°$)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[b]	I_{calc}
1	1	0	7.35	7.43	M	43.1
2	0	0	10.46	10.51	W	6.1
3	1	0	16.60	16.66	W	5.0
2	1	1	29.17	29.19	W	5.1
3	5	0	30.93	30.98	W	8.4
2	3	1	32.90	32.92	M	14.7
2	6	0	33.68	33.68	M	30.7
1	4	1	34.61	34.68	M	9.3
5	5	0	37.80	37.79	S	8.9
1	7	0		37.79		29.0
4	3	1	37.90	37.90	S	77.0
5	0	1		37.90		26.5
5	2	1	39.44	39.44	S	100.0
3	7	0	40.83	40.83	M	28.1
5	4	1	43.78	43.79	W	8.6
8	2	0	44.38	44.38	W	6.0
8	4	0	48.37	48.37	W	7.3
0	0	2	54.85	54.84	M	24.6

[a] 2θ values of reflections with relative intensities $I_{calc} \geq 5$ are listed.

[b] W, weak; M, medium; S, strong.

processing and structure calculations were performed with the program package TEXSAN.

After processing the intensity data, the structure model of $Nb_{21}S_8$ was used to initialize the refinement. After the refinement had converged and 50%Nb and 50%Ta was assigned on each metal position the multiplicities of metal positions were refined. The isotropic thermal parameters were refined with the concomitant refinement of the multiplicities for the metal positions and the secondary extinction coefficient.

The DIFABS[59] correction was applied to the data, which had been corrected with the empirical absorption correction, but had not been averaged after the isotropic refinement had completed. Finally the anisotropic refinement was carried out and the final R, R_w and GOF were 0.027, 0.043 and 1.17, respectively. The composition was determined to be $Nb_{14.8}Ta_{6.2}S_8$ from the refinement. The crystal data, atom coordinates, thermal parameters and bond distances are given in Tables 19, 20, and 21, respectively.

Observed and calculated structure factors are listed in Appendix E.

C. Results and Discussions

Figures 10 and 11 are the projections of the structure onto the xy-plane. This is a solid solution type compound having the

Table 19 Crystal data for $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$)

Formula	$Nb_{14.8}Ta_{6.2}S_8$
Space group	I4/m(#87)
a, Å	16.817(2)[a]
c, Å	3.3450(9)[a]
V, $Å^3$	946.0(5)[a]
Z	2
d_{calc}, g/cm^3	9.665
Crystal size, mm^3	0.4x0.3x0.2
$\mu(MoK_\alpha)$, cm^{-1}	443.03
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ = 0.71069 Å)
Orientation reflections, number, range (2θ)	25,14-35
Temperature, °C	22
Scan method	2θ-ω
Octants measured	hkl,-hkl
Data collection range, 2θ, deg	0-50
No. refl. measured	1045
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	416
No. parameters refined	45
Trans. factors, max., min.	1.000,0.807
Secondary ext. coeff. (10^{-7})	2.9658
R[b], R_w[c], GOF[d]	0.027, 0.043, 1.17
Largest shift/esd, final cycle	0.00
Largest peak, e/$Å^3$	3.44 (0.12Å, M6)

[a] obtained from indexing of the powder pattern.

[b] $R = \Sigma\left|\left|F_o\right| - \left|F_c\right|\right| / \Sigma\left|F_o\right|$.

[c] $R_w = [\Sigma w(\left|F_o\right| - \left|F_c\right|)^2 / \Sigma w\left|F_o\right|^2]^{1/2}$; $w = 1/\sigma^2(\left|F_o\right|)$.

[d] $GOF = \Sigma((\left|F_o\right| - \left|F_c\right|) / \sigma_i) / (N_{obs} - N_{parameters})$.

Table 20 Positional, thermal parameters and occupancies for $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$)

Atom	Occupancy	x	y	B_{eq} (Å^2)	U11	U22	U33	U12
M1	92% Nb + 8% Ta	0.45032(7)	0.63579(8)	0.32(5)	0.0041(7)	0.0041(6)	0.0040(7)	0.0005(5)
M2	89% Nb + 11% Ta	0.19231(7)	0.80247(7)	0.34(5)	0.0060(7)	0.0035(7)	0.0034(7)	0.0005(5)
M3	86% Nb + 14% Ta	0	0	0.42(5)	0.0053(8)	0.0053(8)	0.005(1)	0
M4	75% Nb + 25% Ta	0.27740(6)	0.98218(6)	0.32(5)	0.0037(6)	0.0042(6)	0.0042(7)	-0.0011(4)
M5	54% Nb + 46% Ta	0.38325(5)	0.81483(5)	0.25(4)	0.0027(5)	0.0032(5)	0.0036(6)	0.0005(3)
M6	39% Nb + 61% Ta	0.08199(5)	0.54896(4)	0.22(4)	0.0027(5)	0.0027(5)	0.0029(6)	-0.0006(3)
S1		0.2132(2)	0.6338(2)	0.2(1)	0.001(2)	0.004(2)	0.003(2)	0.000(1)
S2		0.1372(2)	0.9363(2)	0.3(2)	0.005(2)	0.002(2)	0.003(2)	0.000(1)

z = 0, U13, U23 = 0.

Table 21 **Interatomic distances (pm) for $Nb_{21-x}Ta_xS_8$ ($x = 6.2$) (M-M < 330 pm, M-S < 300 pm)**

M1	M2	2[a]	310.3 (2)
	M3	2	295.1 (1)
	M4	2	312.4 (2)
	M5	1	321.5 (2)
	S2	4	253.7 (3)
M2	M1	2	310.3 (1)
	M2	2	311.1 (2)
	M5	2	288.2 (1)
	M5	1	321.8 (2)
	S1	2	254.3 (3)
	S1	1	285.8 (4)
	S2	1	243.4 (4)
M3	M1	8	295.1 (1)
	S2	4	254.4 (4)
M4	M1	2	312.4 (1)
	M5	2	288.4 (1)
	M5	1	333.0 (2)
	M6	2	294.3 (1)
	S1	2	257.5 (3)
	S2	1	248.0 (4)
M5	M1	1	321.5 (1)
	M2	2	288.2 (1)
	M2	1	321.8 (1)
	M4	2	288.4 (1)
	M4	1	333.0 (1)
	M6	2	289.6 (1)
	M6	1	328.3 (1)
	S1	2	248.5 (3)
M6	M4	2	294.3 (1)
	M5	2	289.6 (1)
	M5	1	328.3 (1)
	M6	4	282.1 (1)
	M6	1	321.2 (2)
	S1	1	262.8 (4)
S1	M2	2	254.3 (3)
	M2	1	285.8 (4)
	M4	2	257.5 (3)
	M5	2	248.5 (3)
	M6	1	262.8 (4)
S2	M1	4	253.7 (3)
	M2	1	243.4 (4)
	M3	1	254.4 (4)
	M4	1	248.0 (4)

[a] number of neighbors.

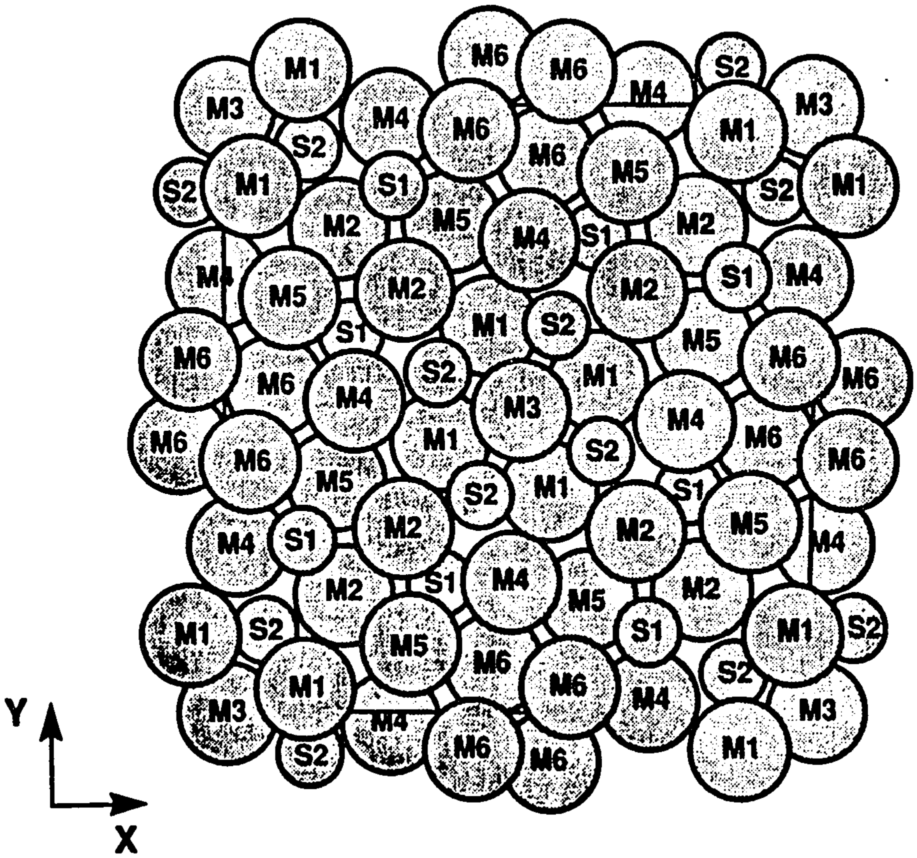

Figure 10 The crystal structure of $Nb_{21-x}Ta_xS_8$ viewed along the z-axis. Unit cell is marked by solid lines

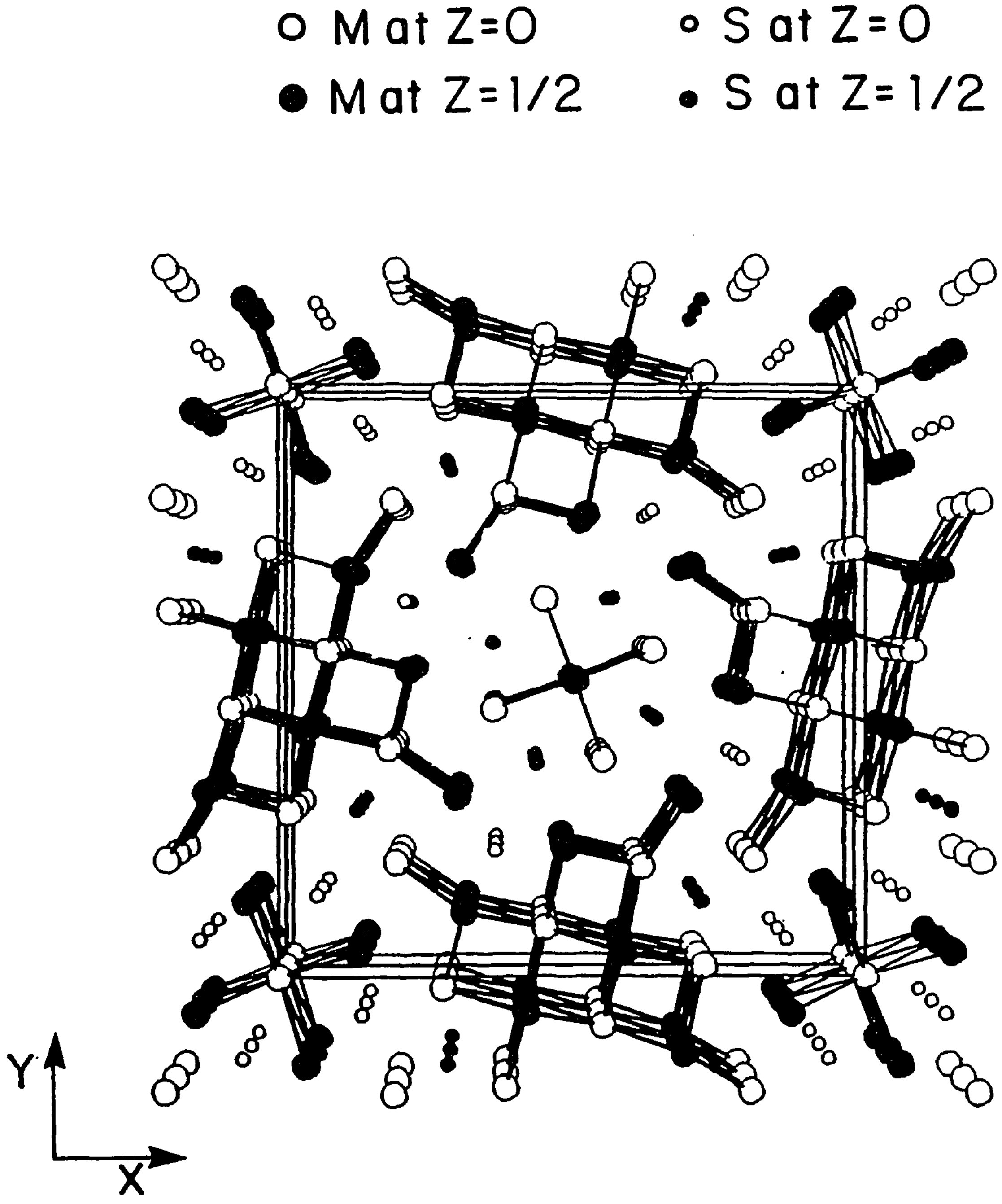

Figure 11 The projection of $Nb_{21-x}Ta_xS_8$ on the xy-plane. Unit cell is marked by solid lines

$Nb_{21}S_8$-type structure in which tantalum partially substitutes for niobium, i.e., the metal coordinations are capped pentagonal and capped cubic prismatic while the sulfur coordinations are capped trigonal prismatic. The structure can be thought of as a modified bcc metal structure. The fragments of modified bcc metal networks can be easily recognized from Figure 11.

In the structure of $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$) each metal position is fractionally occupied by niobium and tantalum and the metal positions have been labeled so that as the metal indicator increases, the n_{Ta}/n_{Nb} ratio on that position also increases, i.e., from M1 to M6 the n_{Ta}/n_{Nb} ratio on the metal position increases. The numbers of coordinating atoms for M1, M2, M3, M4, M5 and M6 are 4, 4, 4, 3, 2 and 1, respectively, i.e., they follow the trend that niobium preferentially occupies the metal site bound to more sulfur atoms compared with tantalum.

The cell constants (a, b = 16.817; c = 3.345Å) of $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$) differ slightly from those (a, b = 16.794; c = 3.359Å) of $Nb_{21}S_8$. The radius of niobium and tantalum are nearly the same and Nb and Ta are in the same column of the periodic table, so the above similiarity is not unexpected. Because the atomic positions and cell constants of $Nb_{14.8}Ta_{6.2}S_8$ and $Nb_{21}S_8$ are nearly the same, it is not surprising that the bond distances in $Nb_{14.8}Ta_{6.2}S_8$ are nearly the same as those in $Nb_{21}S_8$.

CRYSTAL STRUCTURE of $Nb_xTa_{2-x}S$ ($x \approx 0.2$)

A. Preparation and Characterization

High purity niobium (Aldrich Products) and sulfur (Fisher Scientific Co.) were put into a previously out-gassed silica tube in the molar ratio: $n_{Nb}:n_S = 2:1$ and the mixture was heated at 440°C until the yellow color of free sulfur disappeared and was then held at 800°C for 3 days in a tube furnace. TaS was synthesized using a similiar method. The mixture of "Nb_2S" (there is no known compound with the formula Nb_2S), TaS and Ta with $n_{Ta}:n_{Nb}:n_S \approx 1.5:0.2:1$, was pressed into a pellet and arc-melted three times in an argon atmosphere. The Guinier x-ray powder pattern of the arc-melted sample using Cu $K\alpha_1$ and silicon as an internal standard indicated that the major phase was a Ta_2S[19]-type compound with a minor phase, 2s-$Nb_{1+x}S_2$[60]-type compound. If the n_{Ta}/n_{Nb} was 4, keeping the molar ratio of metals and the nonmetal unchanged, the main product in the arc-melted sample was $Nb_xTa_{5-x}S_2$ and no Ta_2S-type compound was found in the powder pattern. After the arc-melted sample was annealed at 1400°C for 11h in an induction furnace, the powder pattern was nearly unchanged except that weak reflections from a β-Ta_6S-type compound appeared, possibly as the result of loss of sulfur during the annealing process. The cell parameters of $Nb_xTa_{2-x}S$ ($x \approx 0.20$) were determined to be $a = 7.3724(11)$, $b = 5.5757(11)$

and c = 15.1981(23)Å in space group Pbcm according to the two-theta angles calculated with program PWDR[51] (using data from the structure solution $Nb_{0.20}Ta_{1.80}S$). Powder diffraction data for this new compound are presented in Table 22. Intensities were calculated using the computer program PWDR. Positional parameters were used from the refined structure.

The quantitive analysis of the annealed sample using the electron dispersive analysis by x-rays method in a scanning electron microscope showed that two phases coexist in the sample. The ratio of n_{Ta}/n_{Nb} of major phase was determined to be 12.75, which corresponds to be $Nb_{0.15}Ta_{1.85}S$.

B. Single Crystal X-Ray Investigation

Many crystals were found in the inductively annealed sample. After their qualities were examined on a Weissenberg camera, one of them (0.03x0.01x0.2 mm^3) was used for collecting intensity data.

Intensity data were collected using monochromatic Mo Kα radiation, employing the 2θ-ω scan technique up to 70°(2θ) on a RIGAKU AFC6 single-crystal diffractometer. A total of 6334 reflections (hkl, -hkl, hk-l, -hk-l) were monitored, and 581 unique reflections with $F^2 > 3\sigma(F_o^2)$ were obtained and used for the structure determination. The observed intensities were corrected for Lorentz polarization and absorption effects with an

Table 22 X-ray powder diffraction of $Nb_xTa_{2-x}S$ ($x \approx 0.2$) (Cu $K\alpha_1$ radiation)[a] ($2\theta < 55°$)

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}[b]	I_{calc}
0	0	2	11.58	11.64	S	100.0
1	0	0	11.93	12.00	S	64.7
2	1	1	29.60	29.64	W	7.8
1	1	4	30.95	30.96	W	7.4
2	1	2	31.36	31.39	M	9.9
0	2	1	32.63	32.67	S	47.3
2	0	4	33.83	33.88	W	13.1
2	1	3	34.08	34.11	S	55.3
1	2	1	34.88	34.92	M	17.1
0	0	6	35.42	35.44	W	14.7
1	1	5	35.76	35.78	M	63.5
3	0	0	36.55	36.57	M	16.8
0	2	3	36.78	36.81	S	29.7
1	0	6	37.50	37.54	S	18.7
2	1	4		37.63		29.3
3	0	2	38.49	38.50	S	35.0
1	2	3	38.80	38.85	S	79.4
3	1	0	40.05	40.10	M	29.4
3	1	1	40.53	40.56	M	38.6
1	1	6	40.98	41.01	S	52.0
2	2	1		41.04		44.5
2	0	6	43.30	43.34	M	35.9
3	1	3	44.01	44.06	M	13.0
2	2	3	44.46	44.51	M	15.6
1	1	7	46.51	46.55	M	21.1
3	1	4	46.90	46.95	M	13.1
0	0	8	47.83	47.88	W	6.0

[a] 2θ values of reflections with relative intensities $I_{calc} \geq 5$ are listed.

[b] W, weak; M, medium; S, strong.

empirical absorption coefficient of 951.01cm^{-1}. Based on three standard reflections measured every 150 reflections, there was no significant fluctuation or decay of the crystal. Subsequent data processing and structure calculations were performed with the program package TEXSAN.

The space group was assigned to be Pbcm, the same as that of Ta_2S. First an empirical absorption correction was applied with the max. and min. transmission factors of 1.000 and 0.350, respectively. Application of direct methods resulted in an electron map containing four strong peaks per asymmetric unit. These peaks were assigned as Ta and the refinement was initiated. Two sulfur positions were then obtained from a subsequent difference-Fourier syntheses of the electron density after initial refinements, and the multiplicities for the metal positions were refined after 50%Ta and 50%Nb was assigned on each metal position. Finally the isotropic thermal parameters were refined with the concomitant refinement of the multiplicities for the metal positions and the secondary extinction coefficient.

After isotropic refinement, F_c values for $Nb_{0.2}Ta_{1.8}S$ were calculated and used for a DIFABS[59] absorption correction for the F_o values in the mode that utilizes θ-dependent systematic deviations $|F_o| - |F_c|$. The ratio of the highest to the lowest transmission was 1.142. An anisotropic refinement was then carried out with the concomitant refinement of the multiplicities for the metal positions and the secondary extinction coefficient, and the final R, R_w and GOF were 0.040, 0.043 and 0.911, respectively. The composition was determined to be $Nb_{0.2}Ta_{1.8}S$ from the refinement.

The crystal data, atom coordinates, thermal parameters and interatomic distances for $Nb_xTa_{2-x}S$ ($x \approx 0.20$) are given in Tables 23, 24, 25 and 26, respectively.

Observed and calculated structure factors are listed in Appendix F.

C. Results and Discussions

Figure 12 is a projection of the structure onto the xz-plane. This is a solid solution type compound having the Ta_2S-type[19] in which niobium partially substitute for tantalum, i.e., the structure can be viewed as linear chains of body-centered pentagonal antiprisms of metal atoms sharing faces in one direction and interconnected principally via sulfur atoms in the other two directions.

In the structure of $Nb_xTa_{2-x}S$ ($x \approx 0.20$) three out of four asymmetrical metal sites are fractionally occupied by niobium and tantalum and the metal positions have been labeled so that as the metal indicator increases, the n_{Nb}/n_{Ta} ratio on that position also increases, i.e., from M2 to M4 the n_{Nb}/n_{Ta} ratio on the metal position increases. The metal site where only tantalum resides is surrounded by pentagonal antiprism consisting of metal

Table 23 Crystal data for $Nb_xTa_{2-x}S$ ($x \approx 0.2$)

Formula	$Nb_{0.20}Ta_{1.80}S$
Space group	Pbcm(#57)
a, Å	7.3724(11)[a]
b, Å	5.5757(11)[a]
c, Å	15.1981(23)[a]
Z	12
d_{calc}, g/cm^3	12.029
Crystal size, mm^3	0.03x0.01x0.2
$\mu(MoK_\alpha)$, cm^{-1}	951.01
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ = 0.71069 Å)
Orientation reflections, number, range (2θ)	12,14-35
Temperature, °C	22
Scan method	2θ-ω
Octants measured	hkl,-hkl,hk-l,-hk-l
Data collection range, 2θ, deg	0-70
No. refl. measured	6334
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	581
No. parameters refined	49
Trans. factors, max., min.	1.000,0.350
Secondary ext. coeff. (10^{-8})	5.227
R[b], R_w[c], GOF[d]	0.040, 0.043, 0.911
Largest shift/esd, final cycle	0.00
Largest peak, e/Å^3	4.87 (1.43Å, Ta)

[a] obtained from indexing of the powder pattern.

[b] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[d] $GOF = \Sigma((|F_o| - |F_c|) / \sigma_i) / (N_{obs} - N_{parameters})$.

Table 24 Positional, thermal parameters and occupancies for $Nb_xTa_{2-x}S$ ($x \approx 0.2$)

Atom	Occupancy	x	y	z	B_{eq} (Å^2)
Ta1		0.0084(3)	0.1320(4)	0.25	0.42(5)
M2	92% Ta + 8% Nb	0.3523(3)	0.8715(4)	0.25	0.49(6)
M3	90% Ta + 10% Nb	0.7165(2)	0.8949(3)	0.34614(7)	0.53(4)
M4	83% Ta + 17% Nb	0.0964(2)	0.8941(3)	0.41025(7)	0.50(4)
S1		0.179(2)	0.25	0.5	0.6(3)
S2		0.412(1)	0.768(1)	0.4030(5)	0.9(3)

Table 25 Anisotropic thermal parameters for $Nb_xTa_{2-x}S$ ($x \approx 0.2$)

Atom	U11	U22	U33	U12	U13	U23
Ta1	0.0051(8)	0.0047(6)	0.0060(5)	0.0006(8)	0	0
M2	0.0068(5)	0.0057(6)	0.0065(5)	0.0000(8)	-0.0001(4)	0.0001(5)
M3	0.0074(6)	0.0073(5)	0.0053(4)	-0.0004(8)	0.0011(4)	0.003(6)
M4	0.0051(8)	0.0071(8)	0.0065(6)	-0.001(1)	0	0
S1	0.007(4)	0.014(3)	0.013(3)	-0.002(4)	0.002(3)	0.005(2)
S2	0.015(6)	0.003(4)	0.004(3)	0	0	0.001(3)

Table 26 **Interatomic distances (pm) for $Nb_xTa_{2-x}S$ ($x \approx 0.2$) (M-M < 330 pm, M-S < 300 pm)**

Ta1	Ta1	2[a]	278.7 (1)
	M2	1	284.5 (2)
	M2	1	284.7 (2)
	M2	1	294.0 (2)
	M2	1	294.2 (2)
	M3	1	289.4 (3)
	M3	1	289.6 (3)
	M3	1	291.4 (3)
	M3	1	291.6 (3)
	M4	1	291.9 (3)
	M4	1	297.3 (3)
M2	Ta1	1	284.5 (2)
	Ta1	1	294.2 (2)
	M2	2	312.6 (2)
	M2	1	316.2 (3)
	M2	1	329.3 (3)
	M3	1	296.3 (3)
	M3	1	325.2 (3)
	M3	1	325.9 (3)
	M4	1	308.1 (2)
	S1	1	243 (1)
	S2	1	248.2 (4)
	S2	1	257 (1)
M3	Ta1	1	289.6 (2)
	Ta1	1	291.4 (2)
	M2	1	296.3 (2)
	M2	1	325.2 (2)
	M2	1	325.9 (2)
	M3	1	292.0 (2)
	M4	1	305.7 (3)
	M4	1	307.0 (3)
	M4	1	330.0 (3)
	S1	1	244.3 (9)
	S1	1	250 (1)
	S2	1	258.8 (5)
M4	Ta1	1	291.9 (2)
	Ta1	1	297.3 (2)
	M2	2	308.1 (2)
	M3	2	305.7 (2)
	M3	1	307.0 (2)
	M3	1	307.2 (2)
	M3	1	329.8 (2)
	M3	1	333.0 (2)
	S1	1	243.4 (8)
	S1	1	243.4 (8)
S1	M2	1	243 (1)
	M3	1	244.3 (9)
	M3	1	250 (1)
	M4	1	243.4 (8)
	S1	1	295 (2)
S2	M2	2	248.2 (4)
	M2	2	257 (1)
	M3	2	258.8 (5)

[a] number of neighbors.

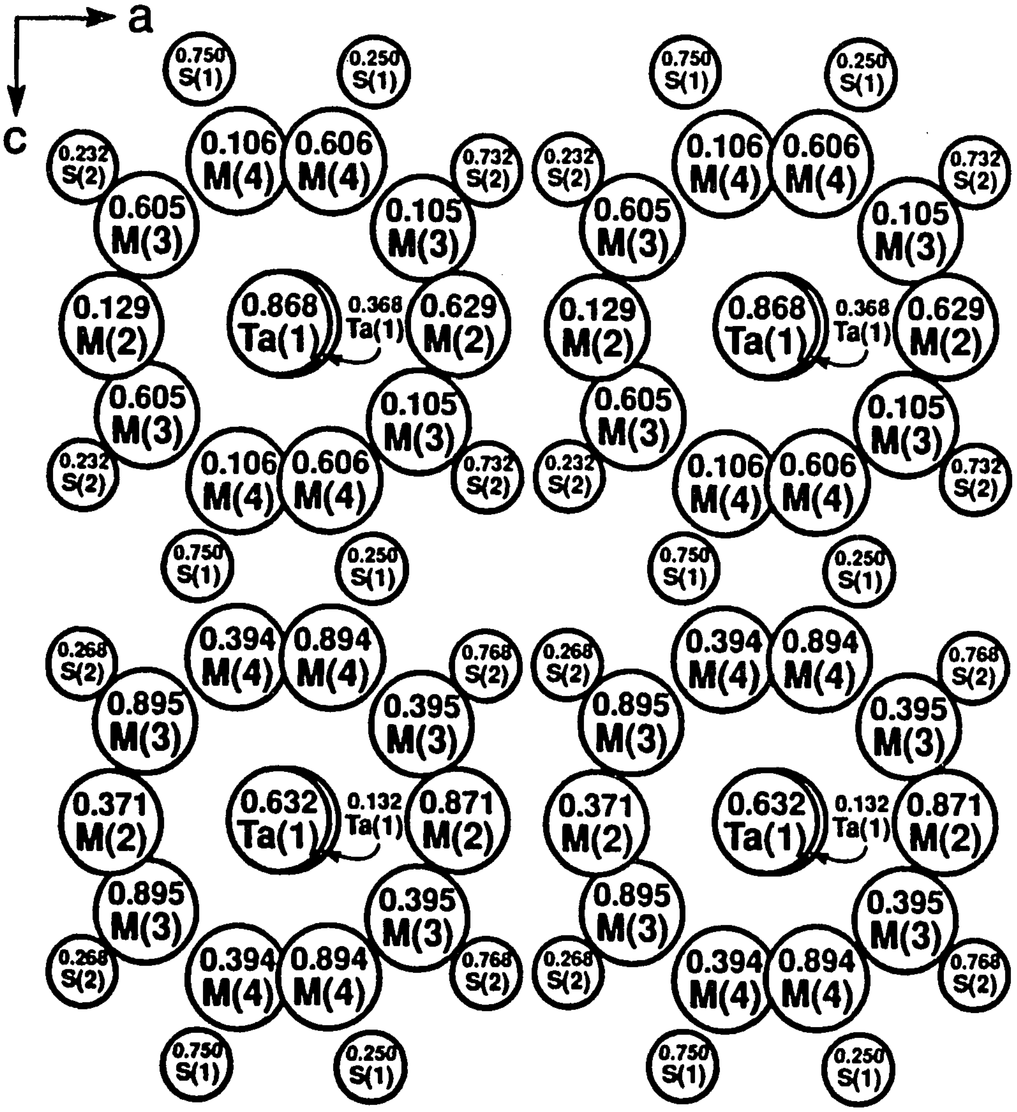

Figure 12 The projection of $Nb_xTa_{2-x}S$ (Ta_2S-type[19]) on the xz-plane

atoms, i.e., the center columns running through the pentagonal antiprisms of metals consist of only tantalum atoms. It can be expected that there are no coordinating sulfur atoms ($d_{M-S} < 3Å$) for metal sites surrounded by pentagonal antiprisms of metals. The niobium-content increase with sulfur-coordination number is in agreement with the observed trend that niobium preferentially occupies the metal position bound to more coordinating sulfur compared with tantalum in the metal-rich compounds of the ternary Ta-Nb-S system. The numbers of coordinating sulfur atoms for Ta1, M2, M3 and M4 are 0, 2, 3 and 3, respectively.

The cell constants (a = 7.372, b = 5.576, c = 15.198Å) of $Nb_xTa_{2-x}S$ ($x \approx 0.20$) differ slightly from those (a = 7.379, b = 5.574, c = 15.19Å) of Ta_2S. The radius of niobium and tantalum are nearly the same and they are in the same column of periodic table, so the above similiarity is not unexpected. Because the atomic positions and cell constants of $Nb_{0.20}Ta_{1.80}S$ and Ta_2S are nearly the same, it is not surprising that the bond distances in $Nb_{0.20}Ta_{1.80}S$ are nearly the same as those in Ta_2S.

DISCUSSIONS OF THE METAL-RICH REGION IN THE TERNARY Ta-Nb-S SYSTEM

$Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$, $Nb_xTa_{5-x}S_2$, $Nb_xTa_{2-x}S$ (Ta_2Se-type), $Nb_{21-x}Ta_xS_8$, and $Nb_xTa_{2-x}S$ (Ta_2S-type) were found using the single crystal method. $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$), $Nb_xTa_{2-x}S$ ($x \approx 0.95$) (Ta_2Se-type), $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$), $Nb_xTa_{2-x}S$ ($x \approx 0.2$) (Ta_2S-type) and $Cu_xNb_6S_{3-x}$ ($x \approx 4.6$)[40] (Ta_2P-type[13]) were sucessfully refined anisotropically, while $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$) and $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$) could only be refined isotropically. The crystals of the last two compounds were obtained from the melted sample heated inductively while crystals of other compounds were obtained from the arc-melted samples for the layered compounds, $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) and $Nb_xTa_{2-x}S$ ($x \approx 0.95$) and from the non-melted samples for $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$) and $Nb_xTa_{2-x}S$ ($x \approx 0.20$). The crystal of $Cu_xNb_6S_{3-x}$[40] was obtained from a sample initially inductively melted and then annealed for three hours at a temperature slightly lower than its melting point. Thus the failure of the anisotropic refinements of the last two compounds may stem from disorder in the solids because the samples do not crystalize well from the melt.

The compound $Nb_xTa_{6-x}S$ (α-Ta_6S-type[20] and β-Ta_6S-type[21]) was also found during the study of the ternary Ta-Nb-S system. A crystal of $Nb_xTa_{6-x}S$ (α-Ta_6S-type) was found in the sample mentioned in the section of crystal structure of $Nb_xTa_{11-x}S_4$. The structure was refined to $R/R_w = 0.191/0.249$ and the composition was determined to be $Nb_{1.6}Ta_{4.4}S$. However, single crystals of this compound with good quality has not yet been obtained. One possible reason is that α-Ta_6S[20]-type and β-Ta_6S[21]-type phases coexisted in the sample, and thus intergrowth crystals were formed in the sample. $Nb_xTa_{6-x}S$ (α-Ta_6S-type and β-Ta_6S-type) can be found in the sample with $n_{Ta}/n_{Nb} > 4$ and $(n_{Ta} + n_{Nb})/n_S > 3$. The cell parameters were determined to be C2/c, 14.1214(168), 5.2849(41), 14.8331(182)Å, $\beta = 117.97°$ (5) (determined by single crystal method on a CAD-4 diffractometer); and 5.258(13), 7.589(21), 7.626(26)Å, 59.31(20)°, 68.67(28)°, 77.36° for α-Ta_6S-type and β-Ta_6S-type $Nb_xTa_{6-x}S$, respectively. Because the radii of niobium and tantalum are nearly equal, the cell parameters show negligible change with x in $(Nb_xTa_{1-x})_yS_z$.

It is not surprising that in the Ta-Nb-S system solid-solution type compounds, $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$), $Nb_xTa_{2-x}S$ ($x \approx 0.2$) and $Nb_xTa_{6-x}S$ isostructural with the respective binary niobium-rich sulfides or tantalum-rich sulfides, are formed because of the chemical and size similiarities between the niobium and tantalum. What is surprising is the finding of four new compounds; $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$), $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$), $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) and $Nb_xTa_{2-x}S$ ($x \approx 0.95$) in which the first three exhibit totally new structure types and the last one is isostructural with Ta_2Se^{31}, i.e., the finding that these compounds are not isostructural with Ta_2S or other binary metal-rich compounds in the Ta-S or Nb-S system. The general formulae for the metal-rich compounds found in the Ta-Nb-S system and unknown in the respective two-component systems (Ta-S and Nb-S) are M_8S_4 ($Nb_xTa_{2-x}S$ ($x \approx 0.95$)), $M_{10}S_4$ ($Nb_xTa_{5-x}S_2$ ($x \approx 1.72$)), $M_{11}S_4$ ($Nb_xTa_{11-x}S_4$ ($x \approx 4.92$)) and $M_{12}S_4$ ($Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$)).

Fragments of the distorted elemental metal structures of tantalum and niobium (bcc-type structure) are common features in the structures of the compounds, $Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$, $Nb_xTa_{5-x}S_2$, $Nb_xTa_{2-x}S$ (Ta_2Se-type^{31}) and $Nb_{21-x}Ta_xS_8$. Metal-metal distances comparable to those of the nearest neighbors in the elemental metal state, tantalum and niobium, were found in the solid-solution type metal-rich compounds in the ternary Ta-Nb-S system, and thus there is no doubt that there are numerous strong metal-metal interactions in these solids. These compounds are, in effect, modified intermetallic compounds in which the nonmetal bonds in such a way as to facilitate new metal-metal interactions.

Figure 13 is a plot showing the relation between sulfur coordination numbers and percentages of niobium on same metal

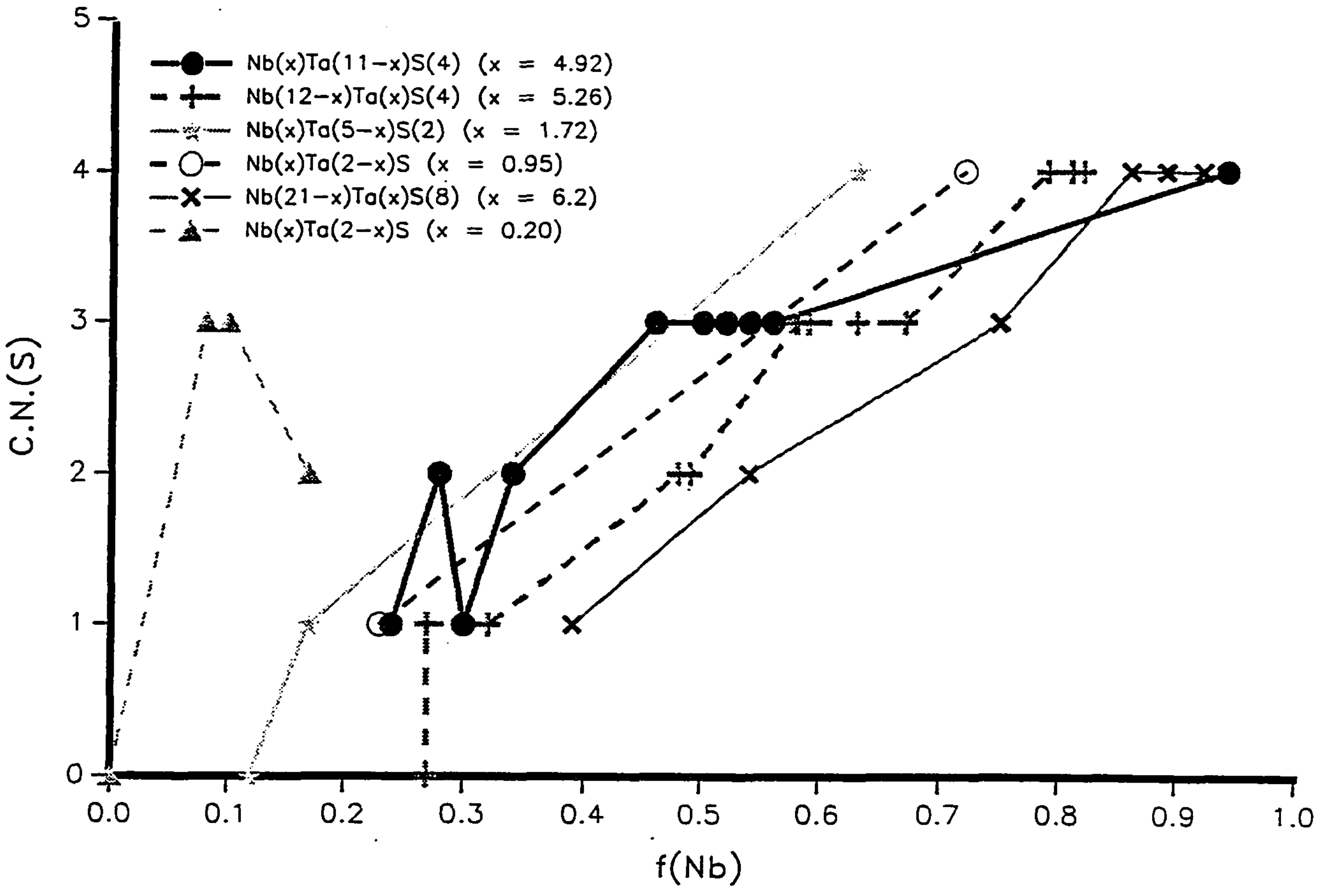

Figure 13 Plot of # of coordinating sulfur (C.N.(S)) vs. Nb% (f(Nb)) on metal sites for the ternary metal-rich compounds in the Ta-Nb-S system

positions for the ternary metal-rich compounds found in the Ta-Nb-S system. A general trend that niobium compared with tantalum preferentially occupies the metal positions bound to more sulfur atoms was observed. In $Nb_xTa_{11-x}S_4$ and $Nb_xTa_{2-x}S$ (Ta_2S-type) there were two positions (M2 and M3 in $Nb_xTa_{11-x}S_4$, and M3 and M4 in $Nb_xTa_{2-x}S$ (Ta_2S-type)) contradicting the general trend; these contradictions probably stem from the close niobium percentages between respective two metal positions in each compound and represent the experimental uncertainty.

In Part II the hypothetical binary Ta-S compounds isostructural with $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ (Ta_2Se-type) were calculated to have lower average energies than those for the corresponding Nb-S hypothetical binaries, i.e., the binding energy of Ta-S is greater than that of Nb-S. Thus the principle: if in a metal-rich compound M-S has a greater binding energy than does M′-S, then new metal-rich structures and stoichiometries can be stabilized by metal-metal bonding in compounds in which M′-S bonding is numerically more important than M-S bonding was found regarding the $(Nb,Ta)_xS_y$ ($x > y$) compounds.

Because the compounds found in this research are solid-solution type compounds, they exist over a range instead of at a specific composition. Because of the chemical and size similiarities of tantalum and niobium, it is very hard to determine the exact percentage of niobium or tantalum by means of changes of the cell parameters or other means. In this research the fractions of tantalum and niobium were changed while the ratios of $(n_{Ta} + n_{Nb})/n_S$ (2.75, 3, 2.5, 2, 2.625 and 2 for $Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$, $Nb_xTa_{5-x}S_2$, $Nb_xTa_{2-x}S$ (Ta_2Se-type[31]), $Nb_{21-x}Ta_xS_8$ ($Nb_{21}S_8$-type[10]) and $Nb_xTa_{2-x}S$ (Ta_2S-type[19]) respectively) were fixed, and then ranges in which the major components (> 90%) were of the desired phases were taken to be the approximate corresponding ranges of the respective solid-solution type compounds. Although the compounds found in this research were prepared using high-temperature techniques, the compounds vary in their temperature ranges of stability.

$\underline{Nb_xTa_{11-x}S_4}$ This phase can exist when $n_{Ta}/(n_{Ta} + n_{Nb})$ is between 50% and 70% ($x \approx 3.3 - 5.5$) and the compound is synthesized using the method mentioned previously in the section on the crystal structure of $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$). This phase is stable at temperatures below 1425°C, above which $Nb_xTa_{11-x}S_4$ will disproportionate to $Nb_xTa_{2-x}S$ (Ta_2Se[31]-type) and other phases.

$\underline{Nb_{12-x}Ta_xS_4}$ This phase can exist when $n_{Ta}/(n_{Ta} + n_{Nb})$ is between 35% and 60% ($x \approx 4.2 - 7.2$) and the compound is synthesized using the method mentioned previously in the section on the crystal structure of $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$).

$\underline{Nb_xTa_{5-x}S_2}$ This phase can exist when $n_{Ta}/(n_{Ta} + n_{Nb})$ is between 70% and 80% ($x \approx 1.0 - 1.5$) and the compound is synthesized using the method mentioned previously in the section on the crystal structure of $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$). This phase is stable at very high temperatures and the major product of disproportionation is $Nb_xTa_{2-x}S$ (Ta_2Se-type) and $Nb_xTa_{11-x}S_4$ at temperatures between 1425°C - 1450°C and below 1425°C, respectively. Because $Nb_xTa_{5-x}S_2$ was synthesized by the arc-melting method and its melting point is around 1450C, the specific temperature above which this phase is stable has not been determined.

$\underline{Nb_xTa_{2-x}S}$ ($\underline{Ta_2Se\text{-type}}$[31]) This phase can exist when $n_{Ta}/(n_{Ta} + n_{Nb})$ is between 55% and 60% ($x \approx 0.8 - 0.9$) and the compound is synthesized using the method mentioned previously in the section on the crystal structure of $Nb_xTa_{2-x}S$ ($x \approx 0.95$). This phase is stable at temperatures above 1425°C, below which it will disproportionate to $Nb_xTa_{11-x}S_4$ and other phases.

$\underline{Nb_{21-x}Ta_xS_8}$ ($\underline{Nb_{21}S_8\text{-type}}$[10]) This phase can exist when $n_{Ta}/(n_{Ta} + n_{Nb})$ is less than 30% ($x < 6.3$) and the compound is synthesized using the method mentioned previously in the section on the crystal structure of $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$).

$\underline{Nb_xTa_{2-x}S}$ ($\underline{Ta_2S\text{-type}}$[19]) This phase can exist when $n_{Ta}/(n_{Ta} + n_{Nb})$ is greater than 90% ($x < 0.2$) and the compound is synthesized using the method (annealing the arc-melted samples at 1300°C for 10h.), similiar to that mentioned previously in the section on the crystal structure of $Nb_xTa_{2-x}S$ ($x \approx 0.2$).

When $n_{Ta}/(n_{Ta} + n_{Nb})$ is between 60% and 70% and $(n_{Ta} + n_{Nb})/n_S$ between 2 and 2.7, arc-melted samples consist of the two layered compounds, $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ (Ta_2Se-type). Because ranges for ternary metal-rich compounds in the Ta-Nb-S system were determined by the method mentioned above, it is difficult to know if both of the layered compounds, $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ (Ta_2Se-type) can be formed in the above range or if first one is formed in the range of 70% - 80% for $n_{Ta}/(n_{Ta} + n_{Nb})$ and then the latter one formed in the range of 55% - 60% for $n_{Ta}/(n_{Ta} + n_{Nb})$. The same is true for the sample with the ratio $n_{Ta}/(n_{Ta} + n_{Nb})$ between 50% and 55% and the ratio $(n_{Ta} + n_{Nb})/n_S$ of 2 ($Nb_xTa_{2-x}S$ (Ta_2Se-type) and $Nb_{1-x}Ta_xS$ (NbS-type[65]) coexisted).

In the experiments to determine the range for each solid solution, the smallest change in $n_{Ta}/(n_{Ta} + n_{Nb})$ was 5%.

It is amusing to note that early chemists spent several decades to separate tantalum and niobium and that now when these two metal elements are mixed on atom sites, totally new compounds are found to result. When neither tantalum nor niobium is the dominant metallic element, mixed Ta-Nb has been shown to exhibit new chemical properties different from either tantalum metal or niobium metal. Presumably because of the high reaction temperatures and the great similiarities between tantalum and niobium, the compounds in which metal positions are occupied by both tantalum and niobium were formed.

Measurements of electrical properties (superconductivity and electrical conductivity) of $Nb_xTa_{2-x}S$ (Ta_2Se[31]-type) and $Nb_xTa_{5-x}S_2$ are being carried out by colleagues in Dr. Jonston's group of physics department at ISU. The compound $Nb_xTa_{2-x}S$ has been found to go superconducting below 5K.

PART II: EXTENDED HÜCKEL BAND CALCULATIONS ON TWO NOVEL LAYERED COMPOUNDS: $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) and $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

INTRODUCTION

Concepts of bonding and antibonding play a central role in the molecular orbital (MO) interpretation of chemical phenomena. For a diatomic molecule bonding and antibonding MO's are formed as in-phase and out-of-phase combinations of atomic orbitals, respectively. A bonding MO leads to a buildup of electron density in the region between two nuclei, while an antibonding MO causes charge withdrawal from this region. Thus electron occupation of the former results in bond strengthening, but that of the latter leads to bond weakening. These conclusions are valid for polyatomic molecules as well. They can be given a perburbation theoretical justification and form the basis of a general set of rules governing orbital interaction.[67]

Valuable information of electronic structures of compounds, such as the electron configurations, constituting orbitals in a formed bond, the electron distribution on each atom, the strength of a bond of specific type, Fermi energy, density of states and so on can be obtained through theoretical studies, such as band calculations. From the information of electronic structure, some properties of a compound can be predicted.

Early transition metal-rich chalcogenides form a very important class with many new characteristics. Those have been discussed in the General Introduction section of this dissertation. However, only a few band calculations have been carried out for this kind of compound, e.g., $M_2Ta_9S_6$ (M = Fe, Co, Ni)[68] and Ta_6S_n (n = 3, 4, 5)[24] and much work needs to be done in this area.

Two novel layered metal-rich compounds, $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ found in this research exhibit a striking difference from the normal layered transition metal disulfides, e.g., TiS_2,[69] NbS_2[70] and MoS_2,[71] i.e., the van der Waals gaps are separated by robustly metallic regions. These novel materials can be expected to have some useful properties. Thus it is very interesting to see what kind of electronic structure they have and this will be helpful for the understanding of these two layered compounds. In addition the general trend that niobium preferentially occupies the metal positions bound to more sulfur atoms compared with tantalum was also observed for these two layered compounds. Thus an attempt was made to understand the reason for that trend from the point of view of their electronic structures. The effects of occupancies of niobium or tantalum on the electronic structure and the nature of chemical bonding interactions were elucidated by means of band calculations.

CALCULATION METHOD

The calculations used through this research are extended Hückel type,[72,73,74] using the tight-binding method.[75,76]

A program, BIG5, written by Professor Burdett's group at University of Chicago was used to calculate the electronic structures of solids. Density of states (DOS) diagrams, crystal orbital overlap population (COOP) curves, and energy bands in reciprocal space can be obtained in the results.

Usually a primitive cell is used for this kind of calculations in order to save computer time. In this research three kinds of elements, tantalum, niobium and sulfur were involved. The parameters used for band calculations are given in Table 27. The atomic parameters of sulfur were from Clementi and Roetti.[77] The valence-state ionization energies (H_{ii}'s) for tantalum and niobium were obtained from a charge-iterative calculation[78] on Nb_5S_2 and Ta_5S_2 in the $Nb_xTa_{5-x}S_2$ structure.

Because band theory cannot deal explicitly with the compounds in which one position is occupied by two kinds of elements, some assumptions were made to enable the calculation.

The overall atomic ratios of Ta/Nb are observed to be close to 1.1 and 1.9 for $Nb_xTa_{2-x}S$ ($x \approx 0.95$) (Ta_2Se-type[31]) and $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$), respectively; and the atomic ratio of Nb/Ta on the metal site increases with the increase of the metal indicator in these two layered compounds. Thus (the layer

Table 27 Atomic parameters used in the calculations

atom	orbital	H_{ii}, eV	ξ_1[a]	ξ_2[a]	c_1[b]	c_2[b]
Ta	5d	-11.21	4.76	1.94	0.6815	0.6815
	6s	-12.22	2.28			
	6p	-7.97	2.24			
Nb	4d	-11.97	4.08	1.64	0.6401	0.5516
	5s	-10.41	1.89			
	5p	-6.44	1.85			
S	3s	-20.00	1.82			
	3p	-13.30	1.82			
	3d	-8.00	1.50			

[a] Exponent in the double ξ function for d orbitals.

[b] Slater-type orbitals exponents.

sequence of M1, M2 and S is M1M2S in $Nb_xTa_{2-x}S$) the arrangement $Ta_2Nb_2S_2$ is closer to the real one than is $Nb_2Ta_2S_2$ for $Nb_xTa_{2-x}S$, and (the layer sequence of M1, M2, M3 and S is M1M2M3S in $Nb_xTa_{5-x}S_2$) the arrangement $TaTa_2Nb_2S_2$ is closer to the real one than is $TaNb_2Ta_2S_2$ for $Nb_xTa_{5-x}S_2$ (If Nb were to be put on the M1 site and Ta on M2 and M3 sites, the atomic ratio of Ta/Nb would be 4 and this is not as close to the real ratio (1.9) as that (1.5) for the two arrangements listed above). The assumptions made are listed in Table 28 for these two layered compounds.

The k-points used for calculations can be calculated using the program BTET and STET[79] after the information about space group, lattice type and ratios of axes of the compound were known. The more k-points used for band calculations, the more accurate the results obtained; and also the more computer time needed. In program NEW5 there is a restraint on the number of k-points used and the number of atomic orbitals used, i.e., the product of these two numbers must be less than 5000. For both of these two layered compounds seventy-two k-points were used for the band calculations.

To avoid becoming bogged down in too many system-specific details, we will stick to a presentation of the total density of states (DOS) plots, overlap populations, charge distributions, the crystal orbital overlap population (COOP) plots for the metal-metal bonding, and average energies in these systems.

Table 28 Assumptions in extended Huckel band calculations for $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$

$Nb_xTa_{5-x}S_2$ (x ≈ 1.72) I4/mmm

atom	site	occupancy %	C.N.[a]	arrangement 1[b] $TaTa_2Nb_2S_2$	arrangement 2 $TaNb_2Ta_2S_2$
M1	2a	88.3 Ta + 11.7 Nb	0	Ta	Ta
M2	4e	82.6 Ta + 17.4 Nb	1	Ta	Nb
M3	4e	37.3 Ta + 62.7 Nb	4	Nb	Ta
S	4e		8	S	S

$Nb_xTa_{2-x}S$ (x ≈ 0.95) P4/nmm

atom	site	occupancy %	C.N.[a]	arrangement 1[b] $Ta_2Nb_2S_2$	arrangement 2 $Nb_2Ta_2S_2$
M1	2c	76.6 Ta + 23.4 Nb	1	Ta	Nb
M2	2c	28.2 Ta + 71.8 Nb	4	Nb	Ta
S	2c		8	S	S

[a] number of coordinating sulfur atoms.

[b] arrangement 1 is closer to the real compound than arrangement 2.

BAND STRUCTURES OF $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) AND $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

A. Band Structure of $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$)

The total density of states (DOS) for "Ta_5S_2", "$TaTa_2Nb_2S_2$", "$TaNb_2Ta_2S_2$" and "Nb_5S_2" are almost the same in shape and value. Although there is a local minimum in the DOS at the Fermi level, clearly there is no gap in the DOS around the Fermi level. Thus, $Nb_xTa_{5-x}S_2$ is expected to exhibit metallic properties, e.g., metallic electrical conductivity. As previously discussed in the Method Section, $TaTa_2Nb_2S_2$ is the model structure closest to the real arrangement. A plot of the DOS for $TaTa_2Nb_2S_2$ is given in Figure 14.

Information about the strength of a bond can be obtained from the corresponding overlap population. The difference in bonding between the two arrangements, $TaTa_2Nb_2S_2$ and $TaNb_2Ta_2S_2$ can be analyzed with the aid of the overlap population, the average energes, the values of the charge (valence electron) on each atom position and the crystal orbital overlap population (COOP) plots in these two arrangements.

The values of OP (overlap population) for each symmetry-unique pair of atoms, the average energies and the values of the charge on each atom position for the two arrangements are given

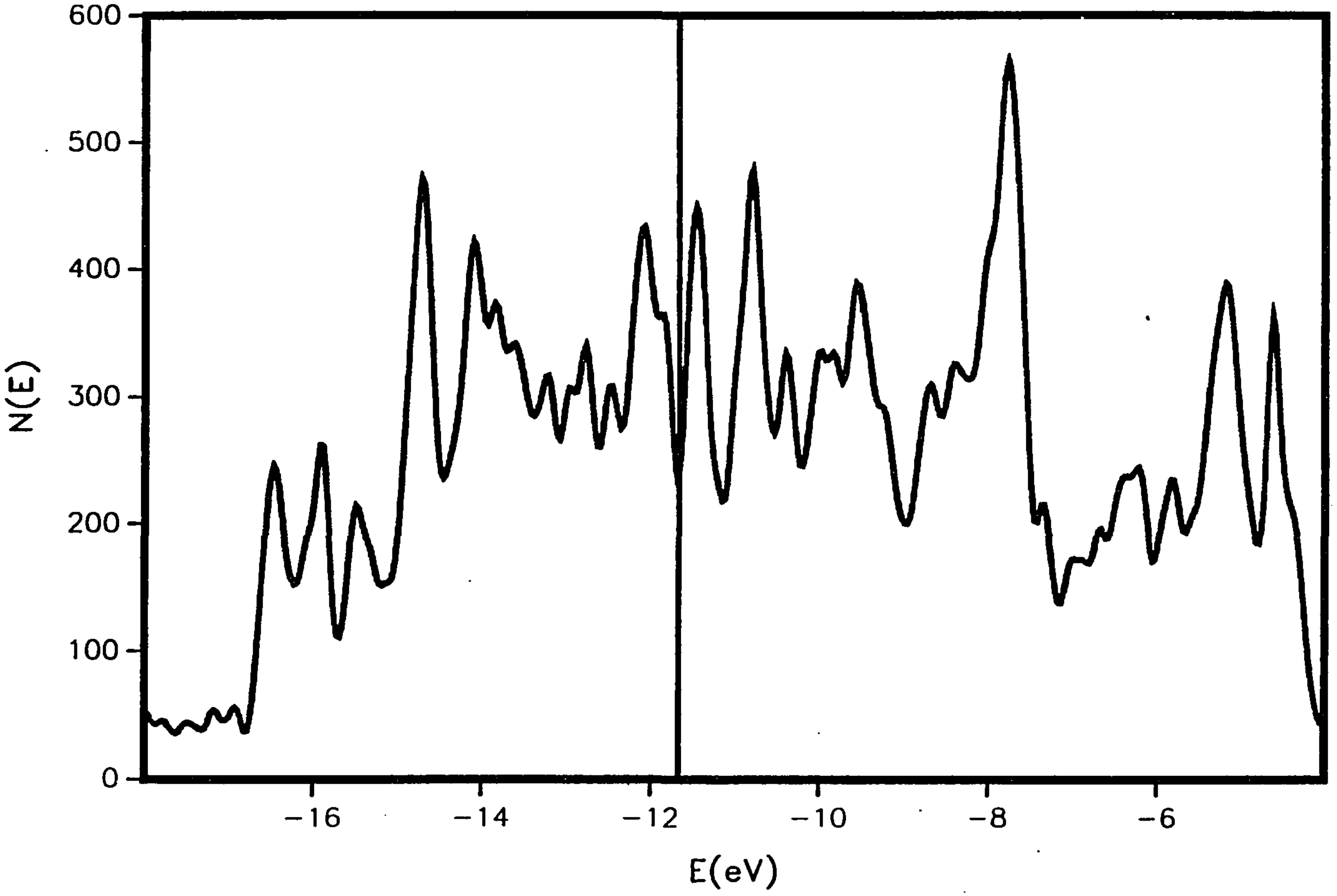

Figure 14 Total DOS curve of $TaTa_2Nb_2S_2$ ($Nb_xTa_{5-x}S_2$-type). Fermi level is marked by the vertical line

in Tables 29 and 30, respectively. The sums of OP's for all metal-metal bonds and for all bonds in the structure for the two arrangements, appropriately weighted to reflect the number of each symmetry-unique bond, are also listed in Table 29.

The values of summations (6.79 and 12.66 for metal-metal bonds only and all kinds of bonds, respectively) for arrangement 1 ($TaTa_2Nb_2S_2$) are greater than the corresponding values (6.43 and 12.53) for arrangement 2 ($TaNb_2Ta_2S_2$). This fact means that the metal-metal bonding and overall bonding are more effective in arrangement 1 than those of arrangement 2. The charges on the metal positions are more nearly equal in arrangement 1 ($TaTa_2Nb_2S_2$) than in arrangement 2 ($TaNb_2Ta_2S_2$). The smaller the difference between the valences of two atoms, the smaller the fraction of the bonding that is ionic in character. For two metals the smaller fraction of the bonding that is ionic in character, the larger the fraction of the metal-metal bonding. Thus the more effective metal-metal bonding in arrangement 1 compared to arrangement 2 can be seen from the charge distribution on the metal atoms in the two arrangements.

The difference (0.35) between summation of the OP's for all metal-metal bonds of the two arrangements is much greater than the corresponding value (0.13) for summation of the OP's for all bonds, i.e., including metal-metal, metal-sulfur and sulfur-

Table 29 Average energy, Fermi energy and overlap populations for two arrangements of $Nb_xTa_{5-x}S_2$

	arrangement 1 ($TaTa_2Nb_2S_2$)	arrangement 2 ($TaNb_2Ta_2S_2$)
average energy, eV	-555.655	-555.640
Fermi level, eV	-11.669	-11.817
overlap population		
M1-M1 (332pm) (2)[a]	0.15607	0.17597
M1-M2 (286pm) (8)	0.41355	0.36500
M1-M3 (337pm) (2)	0.10567	0.13679
M2-M2 (325pm) (1)	0.17752	0.11758
M2-M3 (293pm) (8)	0.24414	0.25704
M2-S (265pm) (2)	0.42815	0.29986
M3-S (251pm) (8)	0.55271	0.61847
M3-S (316pm) (2)	0.12611	0.13502
S-S (332pm) (4)	0.01855	0.01007
S-S (326pm) (4)	0.06746	0.05990
M2-M2 (332pm) (4)	0.18026	0.10231
M3-M3 (332pm) (4)	0.02581	0.07608
sum. of OP (M-M)[b]	6.78680	6.43298
sum. of OP[c]	12.66104	12.53038

[a] the number of symmetry-unique bonds in one primitive cell.

[b] the summation of OP for all metal-metal pairs in one primitive cell.

[c] the summation of OP for all pairs of atoms in one primitive cell.

Table 30 **Charges on each atomic position for two arrangements in $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) and $Nb_xTa_{2-x}S$ ($x \approx 0.95$)**

$Nb_xTa_{5-x}S_2$

site	arrangement 1 ($TaTa_2Nb_2S_2$)	arrangement 2 ($TaNb_2Ta_2S_2$)
M1	5.101	4.888
M2	4.989	5.681
M3	5.292	4.737
S	5.669	5.638

$Nb_xTa_{2-x}S$

site	arrangement 1 ($Ta_2Nb_2S_2$)	arrangement 2 ($Nb_2Ta_2S_2$)
M1	5.267	5.572
M2	5.117	4.830
S	5.616	5.597

sulfur bonds, between two arrangements in $Nb_xTa_{5-x}S_2$, and this fact means that the metal-metal bonding is facilitated by a trade off for a lesser amount of metal-sulfur and sulfur-sulfur bonding in arrangement 1 of $Nb_xTa_{5-x}S_2$ and presumably in $Nb_xTa_{5-x}S_2$ resulting in an increases in the overall bonding in arrangement 1 and in $Nb_xTa_{5-x}S_2$.

Thus, because arrangement 1 ($TaTa_2Nb_2S_2$) is closer to that of the real compound for $Nb_xTa_{5-x}S_2$, the calculations provide a basis for understanding why Nb preferentially occupies the metal position bound to more coordinating S. The fact that the average energy for arrangement 1 (-555.655 eV) is slightly lower than the corresponding one (-555.640 eV) for arrangement 2 in $Nb_xTa_{5-x}S_2$ also supports the explanation given above.

A COOP curve can yield information about the bonding (or antibonding) character of the system's crystal orbitals with respect to any specific symmetry-unique pair of atoms in the structure. There are many symmetry-unique metal-metal bonds in $Nb_xTa_{5-x}S_2$ and we are more interested in the overall metal-metal bonding in the structure. Thus the COOP curves are averaged over all the short metal-metal bonds in the structure and appropriately weighted to reflect the number of each symmetry-unique bond for $Nb_xTa_{5-x}S_2$. There is no big difference in averaged COOP curves between two arrangements, $TaTa_2Nb_2S_2$ and $TaNb_2Ta_2S2$, i.e., the Fermi levels lie in the bonding region and they are very close to the dividing lines between the bonding and antibonding regions in the two arrangements. Figure 15 is the plot of averaged COOP (Crystal Orbital Overlap Population) for $TaTa_2Nb_2S_2$. Thus the maximum metal-metal bonding is nearly achieved in $Nb_xTa_{5-x}S_2$.

The difference between the plots of COOP for arrangement 1 ($TaTa_2Nb_2S_2$) and arrangement 2 ($TaNb_2Ta_2S_2$) is hardly discernable. Thus the fact that arrangement 1 is favored over arrangement 2 cannot be explained from COOP curves, and thus it is not difficult to understand why there is a mixed metal occupation type ($Nb_xTa_{5-x}S_2$) formed rather than a segragated atom type ($TaTa_2Nb_2S_2$) formed.

B. Band Structure of $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

There are striking resemblances between the band structures of $Nb_xTa_{2-x}S$ and $Nb_xTa_{5-x}S_2$.

There are no big difference among the DOS plots of "Ta_4S_2", "$Ta_2Nb_2S_2$", "$Nb_2Ta_2S_2$" and "Nb_4S_2". As previously discussed, $Ta_2Nb_2S_2$ is the closest model to the real arrangement. A DOS plot for $Ta_2Nb_2S_2$ is included in Figure 16. Metallic properties can be expected for $Nb_xTa_{2-x}S$ because there is no gap at the Fermi level in the DOS plot.

The values of OP (overlap population) for each symmetry-unique pair of atoms, the average energies and the values of the charge on each atom position for the two arrangements are given

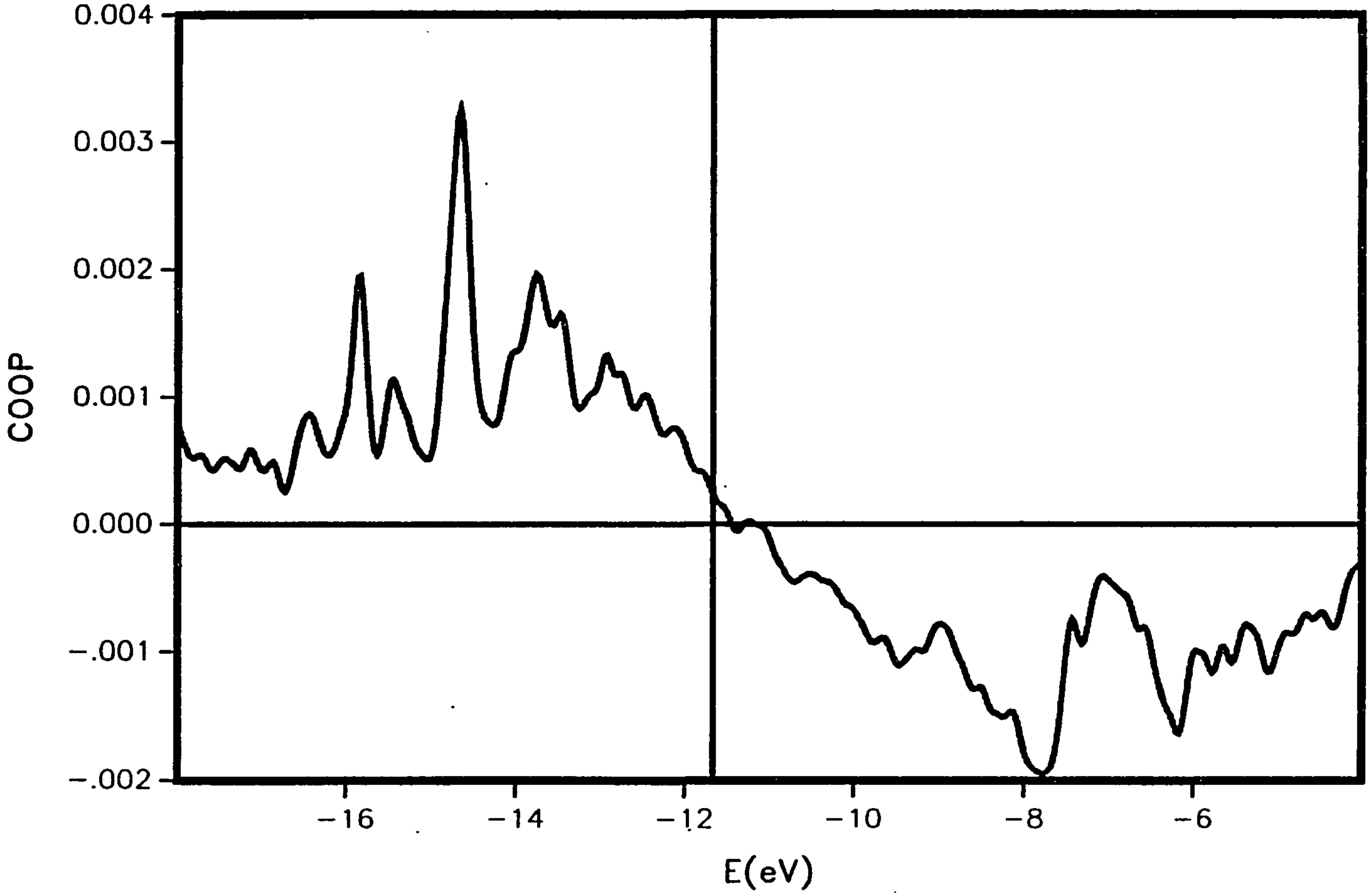

Figure 15 Averaged metal-metal COOP curve of $TaTa_2Nb_2S_2$ ($Nb_xTa_{5-x}S_2$-type). Fermi level is marked by the vertical line

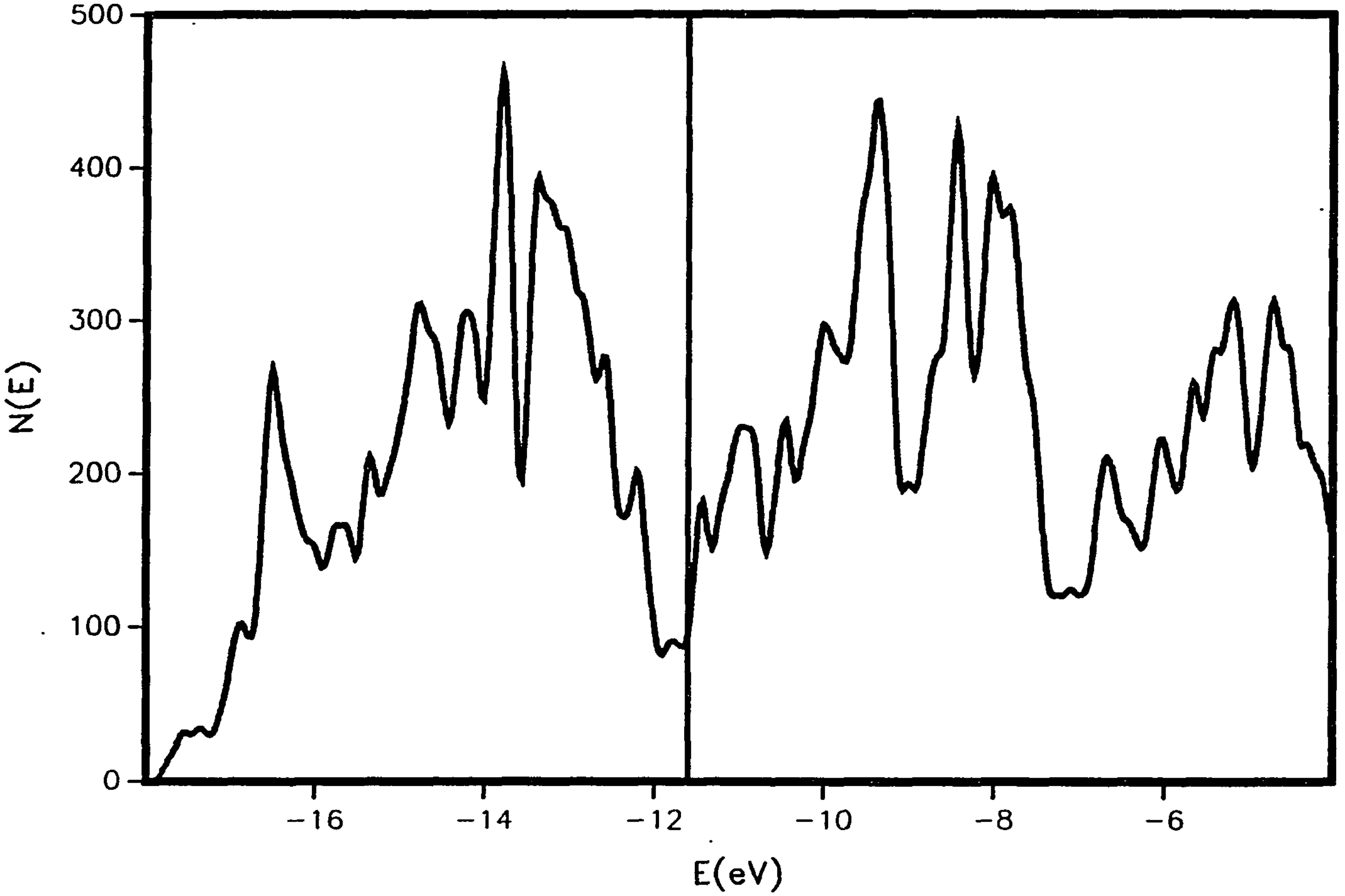

Figure 16 Total DOS curve of $Ta_2Nb_2S_2$ (Ta_2Se-type[31]). Fermi level is marked by the vertical line

in Tables 31 and 30, respectively. The sums of OP's for all metal-metal bonds and for all bonds in the structure for the two arrangements, appropriately weighted to reflect the number of each symmetry-unique bond, are also listed in Table 31.

The values of summations (2.80 and 5.73 for metal-metal bonds only and all kinds of bond, respectively) for arrangement 1 ($Ta_2Nb_2S_2$) are greater than the corresponding ones (2.57 and 5.64) for arrangement 2 ($Nb_2Ta_2S_2$). The charges on the metal positions are closer to each other in arrangement 1 ($Ta_2Nb_2S_2$) than in arrangement 2 ($Nb_2Ta_2S_2$). Thus the metal-metal bonding and overall bonding are more effective in arrangement 1 than those in arrangement 2.

The difference (0.23) for summation of OP for all metal-metal bonds between two arrangements is much greater than the corresponding value (0.09) for summation of OP for all bonds, i.e., including metal-metal, metal-sulfur and sulfur-sulfur bonds, between two arrangements in $Nb_xTa_{2-x}S$, and thus there is, relative to a completely random solid-solution, a bonding trade-off of metal-sulfur and sulfur-sulfur bonding in arrangement 1 and presumably in $Nb_xTa_{2-x}S$ as well. The trade off increases the overall bonding in arrangement 1 and presumably in $Nb_xTa_{2-x}S$.

Thus, because arrangement 1 ($Ta_2Nb_2S_2$) is closer to that of the real compound for $Nb_xTa_{2-x}S$, the calculations on this layered

Table 31 Average energy, Fermi energy and overlap populations for two arrangements of $Nb_xTa_{2-x}S$

	arrangement 1 ($Ta_2Nb_2S_2$)	arrangement 2 ($Nb_2Ta_2S_2$)
average energy, eV	-486.215	-486.180
Fermi level, eV	-11.603	-11.670
overlap population		
M1-M1 (333pm) (2)[a]	0.17346	0.11336
M1-M1 (282pm) (2)	0.51574	0.38513
M1-M2 (293pm) (4)	0.28520	0.29818
M1-M2 (329pm) (1)	0.16613	0.18757
M1-S (269pm) (1)	0.42488	0.29101
M2-M2 (333pm) (2)	0.05542	0.09862
M2-S (254pm) (4)	0.51506	0.58972
M2-S (312pm) (1)	0.18847	0.20213
S-S (333pm) (2)	0.03007	0.01936
S-S (320pm) (2)	0.09833	0.08735
sum. of OP (M-M)[b]	2.79617	2.57451
sum. of OP[c]	5.72656	5.63995

[a] the number of symmetry-unique bonds in one primitive cell.

[b] the summation of OP for all metal-metal pairs in one primitive cell.

[c] the summation of OP for all pairs of atoms in one primitive cell.

compound again provided a basis for understanding why Nb preferentially occupies the metal position bound to more coordinating S. The conclusion was also supported by the fact that the average energy for arrangement 1 (-486.215 eV) is slightly lower than the corresponding one (-486.180 eV) for arrangement 2 in $Nb_xTa_{2-x}S$.

As previously discussed for $Nb_xTa_{5-x}S_2$, the averaged COOP curve for $Nb_xTa_{2-x}S$ was calculated. There is no big difference in averaged COOP curves between two arrangements, $Ta_2Nb_2S_2$ and $Nb_2Ta_2S_2$, i.e., the Fermi levels lie on the dividing line of the bonding region and the antibonding regions in the two arrangements. Figure 17 is the plot of averaged COOP (Crystal Orbital Overlap Population) curve for $Ta_2Nb_2S_2$. Thus the maximum metal-metal bonding is achieved in $Nb_xTa_{2-x}S$.

The difference between the plots of COOP for arrangement 1 ($Ta_2Nb_2S_2$) and arrangement 2 ($Nb_2Ta_2S_2$) is hardly discernable. Thus the fact that the arrangement 1 is favored over arrangement 2 cannot be explained from COOP curves, and thus it is not difficult to understand why there is a mixed metal occupation type ($Nb_xTa_{2-x}S$) formed rather than a segragated atom type ($Ta_2Nb_2S_2$) formed.

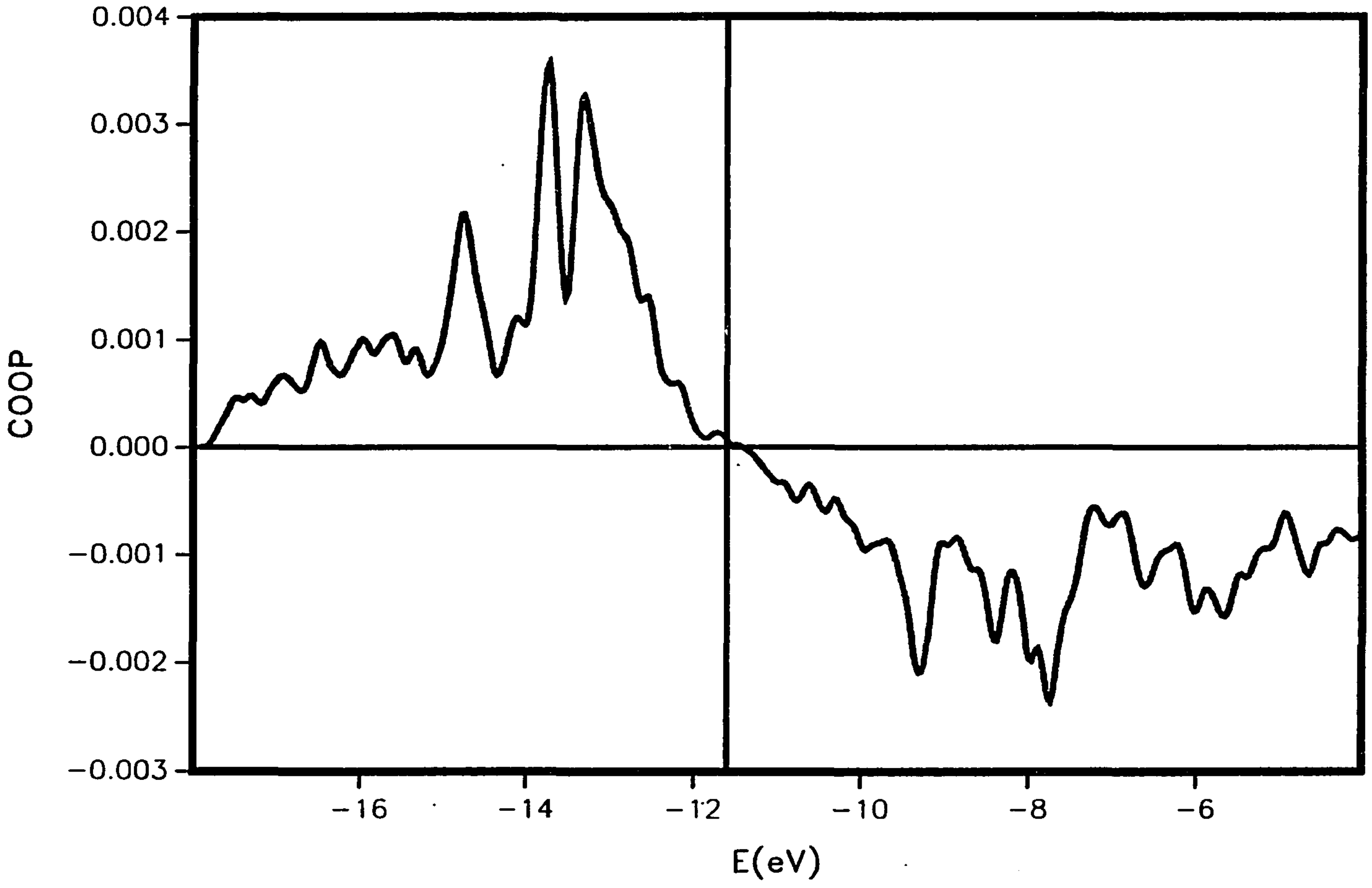

Figure 17 Averaged metal-metal COOP curve of $Ta_2Nb_2S_2$ (Ta_2Se-type[31]). Fermi level is marked by the vertical line

C. Comparison of Band Structures of $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$) and $Nb_xTa_{2-x}S$ ($x \approx 0.95$)

Both $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ are expected to exhibit metallic properties from the band calculations. Although there are no gaps in the plots of DOS around the Fermi level, a decrease of the DOS values at the Fermi level was observed from $Nb_xTa_{5-x}S_2$ to $Nb_xTa_{2-x}S$. This sort of behavior seems to be a common characteristic of systems in which the extension of the metal-metal bonded network is reduced. The number of metal layers between two sulfur van der Waals layers decreases from five in $Nb_xTa_{5-x}S_2$ to four in $Nb_xTa_{2-x}S$. The maximum metal-metal bonding is nearly achieved in $Nb_xTa_{5-x}S_2$ and achieved in $Nb_xTa_{2-x}S$. The decrease of DOS values at the Fermi levels and the formation of maximum metal-metal bonding in the metal-rich compounds were also observed in Ta_6S_n ($n = 3, 4, 5$).[24]

Band calculations carried out for the two novel layered compounds, $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ were approximate ones because band theory cannot deal explicitly with solid solution type compounds, i.e., compounds in which some symmetry-unique metal positions are occupied by two kinds of elements; nevertheless these calculations provided us with qualitative information about metal-metal bonding and explanation of the observed general trend that niobium compared with tantalum preferentially occupies the metal positions bound to more sulfur atoms in these two layered compounds.

That the metal-metal bondings are more effective in arrangements 1 ($TaTa_2Nb_2S_2$ and $Ta_2Nb_2S_2$) than the corresponding ones in arrangements 2 ($TaNb_2Ta_2S_2$ and $Nb_2Ta_2S_2$) in $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$, respectively; can also be understood in terms of electronegativity. The electronegativities of Ta, Nb and S are 1.5, 1.6 and 2.5,[82] respectively. The difference of electronegativities between Ta and S (1.0) is greater than that between Nb and S (0.9), i.e., Ta would lose more electron density to S than would Nb were they equivalently bound to S. Thus Nb in comparison with Ta is more effective in forming metal-metal bonds when equivalently bound to S. Thus the arrangements 1 are favored over arrangements 2 by the enhanced metal-metal bonding of arrangements 1 for both $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$.

The average energy differences between two arrangements (0.015 and 0.035 eV) are so small and the reacting temperatures (above 2000°C) are so high that entropic stabilization drives fractional occupancy of each metal position, rather than the idealized $TaTa_2Nb_2S_2$ and $Ta_2Nb_2S_2$ arrangements in $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$, respectively.

Although band calculations were not carried out for non-layered metal-rich compounds found in the ternary Ta-Nb-S system,

$Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$, $Nb_{21-x}Ta_xS_8$ and $Nb_xTa_{2-x}S$ (Ta_2S[19]-type); the observed general trend mentioned in the last paragraph can also be explained in terms of electronegativity.

From the band calculations it was found that the hypothetical binary Ta-S compounds isostructural with $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$, respectively, have lower average energies ("Ta_5S_2", -556.571 eV; "Ta_4S_2", -487.661 eV) than those for niobium corresponding ones ("Nb_5S_2", -552.676 eV; "Nb_4S_2", -484.253 eV). Thus it is the more effective metal-metal bonding that controls the arrangements of tantalum and niobium rather than the Ta-S and Nb-S binding energy in these two layered compounds.

GENERAL SUMMARY

The metal-rich compounds, $Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$, $Nb_xTa_{5-x}S_2$, $Nb_xTa_{2-x}S$ (Ta_2Se-type[31]), $Nb_{21-x}Ta_xS_8$ and $Nb_xTa_{2-x}S$ (Ta_2S-type[19]) that have resulted from this research in high temperature chemistry have played an important role in developing understanding of the nature of interactions in solids. The structures of $Nb_xTa_{11-x}S_4$, $Nb_{12-x}Ta_xS_4$, $Nb_xTa_{5-x}S_2$ and $Nb_xTa_{2-x}S$ (Ta_2Se-type[31]) are not found for the pure niobium sulfides and tantalum sulfides, i.e., an inherent feature of these sulfide structures is that the metal atom positions are fractionally occupied by niobium and tantalum, and thus the mixture niobium plus tantalum is seen to have a different structural chemistry than do the pure elements themselves. In particular they have demonstrated the role that the metal-metal bond can play in stabilizing novel structures and stoichiometries.

The ternary compounds mentioned above taken together are representative of an entirely new chemistry, namely the formation of site averaged intermetallic, metal-rich sulfides. These compounds exhibit regions in which the extensive metal-metal bonding that is characteristic of intermetallics and alloys together with regions in which there is metal-sulfur bonding. They open the door to the development of new materials with novel structures, with properties characteristic of intermetallics and solid-solution alloys and with the potential of modifying the electronic properties by altering the nature and quantity of the nonmetal components.

FUTURE WORK

In view of this new principle found for ternary solid solution type metal-rich compounds in the Ta-Nb-S system, a series of M-M′-X (M and M′ are early transition metals; and X is P, As, S or Se) should be investigated to prove the validity of this new principle in ternary solid-solution type metal-rich compounds. A generalization of the ideas regarding the bonding in $(Nb,Ta)_xS_y$ $(x > y)$ compounds presented above is: if in a metal-rich compound M-S has a greater binding energy than does M′-S, then new metal-rich structures and stoichiometries can be stabilized by metal-metal bonding in compounds in which M′-S bonding is more important than M-S bonding.

This work is only the beginning of the investigation of ternary metal-rich compounds with mixed metal occupations, and it is certain that many new compounds can be found in this area. Here only a few suggestions are listed.

As for the (Nb, Ta) pair, many early transition metal pairs, such as (Ti, Zr), (Zr, Hf) and (Ti, Hf) in Group IVB can form binary metal-rich pnictides and chalcogenides with different structure type. Thus they are good targets to be investigated in the ternary M-M′-X systems for finding compounds with new structure types and exploring the range of validity of the principle found in this research.

In a ternary M-M′-X system around the ratio $n_M/(n_M + n_{M'})$ of 0.5 there is a possiblity of forming new solid-solution type compounds different from the respective binary compounds because around that ratio the "mixed metal" or "hybrid metal" has the greatest difference from either M or M′. Thus maybe one day new layered compounds with new or variable numbers of metal layers and with new or variable metal occupation between the van der Waals gaps will be synthesized.

It is worthwhile to try to synthesize $Nb_xTa_{5-x}S_2$-type or $Nb_xTa_{2-x}S$-type layered compounds in M-M′-X (M = Ta or Nb; M′ = Ti, Mo, W; X = S or Se) systems because TiS_2, MoS_2 and WS_2 have been proven to be a useful battary material and useful catalytic materials in the petrolum industry, respectively. New materials in these systems would have the applications mentioned above and exhibit new properties because of the robustly metallic regions separating the van der Waals gaps.

Because $Nb_xTa_{2-x}S$ ($x \approx 0.95$, P4/nmm) is isostructural with Ta_2Se, rather than with any known binary Nb-rich sulfides or Ta-rich sulfides, an attempt should be made to synthesize "$Ta_{11}Se_4$" ($Nb_xTa_{11-x}S_4$-type), "$Ta_{12}Se_4$" ($Nb_{12-x}Ta_xS_4$-type) and "Ta_5Se_2" ($Nb_xTa_{5-x}S_2$-type).

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APPENDIX A OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (x10) FOR $Nb_xTa_{11-x}S_4$ ($x \approx 4.92$)

k	l	Fo	Fc	sigF
******* h = 0 *******				
0	2	1013	1179	34
0	4	1272	1358	80
0	6	3079	2994	84
0	8	1883	1734	97
1	-11	2247	2015	119
1	-9	5650	5355	147
1	-3	2703	3071	72
1	7	865	810	58
2	-6	2126	2433	118
2	0	18384	18833	463
2	4	998	982	78
2	8	1410	1471	80
3	-9	4083	4130	140
3	-1	525	397	82
3	7	611	570	71
4	-6	1567	1584	64
4	0	12064	11432	310
******* h = 1 *******				
0	-12	776	676	90
0	-11	2885	2604	91
0	-5	6694	6924	244
0	-4	1340	1499	45
0	1	1470	1246	41
0	3	428	599	35
0	6	4459	4442	115
0	7	2120	2069	69
0	8	834	832	65
0	10	937	707	117
1	-4	1528	1779	49
1	-3	8577	8988	216
1	1	869	829	44
1	2	3276	3352	85
1	8	3932	3691	106
1	9	2262	2239	79
1	12	2665	2328	118
2	-11	2469	2295	91
2	-6	3092	3652	84
2	-5	5136	5544	132
2	-4	1219	1173	97
2	-1	959	941	39
2	7	1607	1757	111
3	-9	1602	1725	73
3	-8	2501	2773	80
3	-4	1234	1226	85
3	-2	2284	2286	230
3	1	492	533	77
4	-7	1189	1219	55
4	-6	2325	2423	173
4	1	671	582	59
4	5	3644	3620	107
******* h = 2 *******				
0	-12	3665	3367	108
0	-9	4354	3872	210
0	-3	546	576	36
0	-1	1895	1700	50
0	0	1393	2072	41
0	6	3936	3947	105
0	7	2067	1878	93
1	-13	2030	1805	77
1	-5	782	863	36
1	-3	9684	10347	243
1	1	672	568	53
1	2	4593	4847	117
1	8	2547	2474	79
1	10	1884	1791	118
1	12	4427	3922	123
2	-12	3327	3012	103
2	-7	1370	1566	127
2	-6	2866	3251	80
2	-1	1391	1368	49
2	0	1520	1626	60
2	9	3458	3374	125
3	-8	1603	1852	172
3	-3	6310	6766	508
3	-2	3453	3168	212
3	10	1512	1412	63
4	-7	980	1036	69
4	0	1043	1055	59
4	1	823	890	87
4	3	633	284	102
4	6	2220	2182	87
******* h = 3 *******				
0	-12	767	724	97
0	-11	2306	2103	83
0	-10	2033	1923	104
0	-7	736	708	57
0	-6	5560	5892	189
0	-1	3333	2833	85
0	3	822	799	35
0	4	1409	1601	90
0	5	2024	2476	104
0	9	4922	4576	166
1	-11	1014	908	103
1	-10	2208	2079	78
1	-6	1818	2049	84
1	-4	795	761	46
1	-3	576	551	47
1	1	984	965	38
1	2	968	898	37
1	7	1555	1657	60
1	8	3487	3444	95
1	9	2029	2053	83
1	12	2034	1789	191
2	-11	1951	1847	111
2	-10	1740	1693	67
2	-6	4547	4874	118
2	-4	1294	1205	77
2	-1	2286	2291	65
2	5	2028	1968	68
2	9	3907	3956	107
3	-10	1731	1627	125
3	-9	1515	1569	74
3	-8	2262	2595	149
3	-7	1056	1216	55
3	-4	623	559	79
3	2	702	506	105
3	6	1538	1464	61
4	-6	3304	3295	101
4	1	1415	1484	82
4	4	756	746	122
4	5	1286	1264	65
******* h = 4 *******				
0	-12	984	939	80
0	-11	2148	1998	116
0	-10	1677	1433	124
0	-8	1353	1240	56
0	-6	3368	3807	88
0	-5	2898	3237	77
0	-1	887	912	120
0	0	447	362	46
0	2	601	591	39
0	4	1893	2020	55
0	9	1129	1018	54
0	13	2846	2638	244
1	-12	1064	1041	85
1	-11	2969	2680	211
1	-9	1660	1684	171
1	-6	3658	4008	96
1	-4	2058	2060	62
1	-3	3296	3177	86

k	l	Fo	Fc	sigF
1	0	1552	1546	54
1	1	763	688	35
1	2	683	642	49
1	7	1697	1945	115
1	8	1915	2048	73
1	13	1793	1588	69
2	-12	858	835	92
2	-11	1935	1758	90
2	-10	1280	1252	83
2	-9	776	868	68
2	-4	1655	1556	95
2	-1	732	736	80
2	2	431	399	67
2	5	2837	2661	82
2	6	3102	3127	154
2	8	868	1069	50
3	-9	1187	1334	124
3	-8	1464	1534	61
3	-7	1360	1442	58
3	-6	3029	2925	91
3	0	982	1016	52
3	3	2193	2171	288
3	4	1538	1452	59
4	-6	2128	2084	74
4	-4	1149	981	145
4	5	1824	1783	71

******* h = 5 *******

k	l	Fo	Fc	sigF
0	-11	1420	1366	60
0	-7	1201	1262	47
0	-6	2518	2820	69
0	-3	1362	1398	50
0	5	681	621	76
0	8	1322	1310	55
0	9	2603	2408	80
0	10	1532	1545	62
0	12	2664	2418	167
1	-12	973	846	97
1	-10	1932	1900	77
1	-9	2245	2274	75
1	-7	2421	2887	69
1	1	2420	2449	65
1	3	2656	2627	72
1	6	3659	3762	97
1	8	3413	3682	94
1	13	1614	1401	69
2	-12	2313	2141	93
2	-11	1303	1197	65
2	-9	2008	2108	72
2	-8	924	1121	47
2	-7	983	1075	48
2	-6	2380	2321	75
2	3	1117	1055	47
2	10	1393	1349	57
3	-10	1337	1476	86
3	-6	2806	2714	120
3	-3	1698	1717	151
3	1	1603	1527	88
3	7	2133	2162	266
3	8	2533	2785	81
3	9	1683	1789	71
4	-6	1495	1562	66
4	-3	712	679	90
4	7	862	739	118

******* h = 6 *******

k	l	Fo	Fc	sigF
0	-13	899	723	92
0	-11	3963	3615	111
0	-5	1212	1233	48
0	-3	3039	2960	80
0	-2	938	898	44
0	0	1087	1022	51
0	4	5507	5381	140
0	6	3652	3865	95
0	7	863	956	41
0	8	1255	1287	52
0	9	3338	3260	127
1	-13	2332	2152	114
1	-10	1757	1535	62
1	-7	986	1057	43
1	-3	814	832	38
1	-1	645	564	35
1	0	2994	2948	80
1	4	784	666	54
1	5	1020	974	63
1	6	2252	2208	69
1	8	1557	1837	149
2	-11	3358	3205	162
2	-7	701	812	63
2	-3	2544	2407	122
2	0	771	814	52
2	2	670	650	49
2	4	4482	4307	118
2	5	1011	978	54
2	6	3401	3214	185
2	8	1088	1100	47
2	9	2567	2838	79
3	-10	1208	1197	147
3	-8	1341	1415	58
3	0	1899	1906	78
3	5	758	709	72
3	6	1654	1611	64
3	7	815	798	72
4	-4	2708	2813	345
4	0	607	525	95
4	3	1631	1584	68
4	6	2160	2182	115

******* h = 7 *******

k	l	Fo	Fc	sigF
0	-13	1107	1005	125
0	-12	2602	2312	108
0	-10	1731	1669	78
0	-9	553	597	81
0	-4	3603	3456	94
0	-3	2881	2837	76
0	-2	584	505	40
0	6	2387	2483	69
0	7	2193	2499	64
0	8	1527	1622	61
0	11	3064	2771	94
1	-9	3003	3244	85
1	-8	1118	1227	70
1	-7	1725	1904	63
1	-3	822	849	38
1	-1	4034	4071	103
1	2	879	800	35
1	4	453	375	72
1	6	6069	5778	155
1	11	2730	2531	90
2	-12	2240	2082	92
2	-11	2583	2435	283
2	-8	1301	1378	50
2	-7	2197	2088	95
2	-3	2445	2271	71
2	4	2864	2776	91
2	6	2212	2036	111
2	10	1349	1460	56
3	-9	2289	2500	76
3	-7	1552	1426	73
3	-1	2749	2755	78
3	2	546	509	68
3	6	4393	4223	185
3	8	830	917	119
4	-6	1361	1348	65
4	-3	1632	1463	106
4	4	1752	1835	102

k	l	Fo	Fc	sigF
******* h = 8 *******				
0	-8	680	784	61
0	-7	1750	1824	61
0	-5	1572	1596	90
0	-2	1247	1237	45
0	3	11017	10632	276
0	4	1058	975	71
0	6	603	574	98
0	10	2289	2263	91
0	12	3720	3251	235
1	-11	847	831	78
1	-9	2472	2598	74
1	-6	6179	5867	198
1	-5	781	732	51
1	-2	1126	1152	47
1	0	1701	1802	57
1	1	4457	4502	113
1	4	1444	1419	62
1	7	1136	1101	47
1	8	1098	1171	66
1	12	3184	2818	202
2	-10	1780	1996	196
2	-5	1334	1274	53
2	-2	994	993	41
2	3	8457	8270	214
2	4	705	779	87
2	7	1625	1545	66
3	-9	1910	2054	68
3	-8	887	860	74
3	-1	2990	3024	124
3	0	1431	1357	78
3	2	806	712	59
3	4	1111	992	51
3	6	4466	4274	192
3	7	909	806	75
4	3	5579	5258	148
4	5	840	828	77
******* h = 9 *******				
0	-13	1392	1265	70
0	-9	1052	1062	48
0	-6	834	748	57
0	2	6512	6323	164
0	3	8916	8527	224
0	5	1072	981	46
0	8	4283	4891	111
1	-11	2158	2121	83
1	-8	764	855	53
1	-2	891	857	36
1	-1	4418	4431	112
1	4	1630	1476	56
1	5	3045	2786	84
1	6	3987	3779	134
1	7	2461	2453	75
2	-8	4043	4197	175
2	-6	625	595	93
2	2	5084	5040	130
2	3	6913	6715	176
2	9	830	924	116
2	11	769	698	82
3	-6	2859	2760	149
3	-5	1928	1961	76
3	-1	2973	2925	116
3	4	1077	1007	81
3	7	1925	1848	71
4	2	3348	3262	97
4	3	4620	4335	125
******* h = 10 *******				
0	-6	1202	1031	64
0	-4	1319	1288	60
0	-3	3906	3808	101
0	-1	584	503	60
0	2	4887	4862	124
0	5	488	468	72
0	9	4776	5364	124
0	11	1532	1434	60
0	12	662	563	106
1	-9	980	1256	60
1	-7	744	666	108
1	-6	3266	3050	103
1	-2	1135	1147	42
1	0	18013	18353	452
1	1	3407	3535	88
1	4	1120	1117	55
1	8	1613	1717	60
1	11	1315	1327	60
2	-11	1239	1282	59
2	-9	4234	4677	113
2	-4	1046	1030	56
2	-3	3013	2954	84
2	-2	3807	3765	100
2	6	934	844	82
3	-9	935	960	67
3	-8	1162	1286	63
3	-6	2292	2212	82
3	-2	771	724	95
3	0	11229	12044	285
3	1	2341	2342	119
3	4	709	780	70
4	-3	1980	1869	83
4	2	2537	2404	84
******* h = 11 *******				
0	-12	3441	3196	103
0	-10	1083	1119	53
0	-9	2255	2596	68
0	-3	6021	5773	152
0	-2	1299	1305	46
0	-1	1808	1785	52
0	4	3353	3312	89
0	7	1887	1771	69
0	8	1605	1707	64
0	11	1600	1537	81
1	-7	1142	1091	108
1	-5	8240	7606	208
1	-3	1407	1398	52
1	6	3137	2966	87
1	10	2229	2335	72
1	11	3354	3229	117
1	12	970	1016	76
2	-11	1363	1356	72
2	-10	876	994	127
2	-7	1525	1498	59
2	-4	2782	2681	79
2	-3	4683	4577	121
2	1	1356	1370	56
2	2	1112	1065	46
2	8	1501	1458	60
2	9	1979	2269	74
3	-7	893	850	102
3	-6	2332	2182	80
3	-5	5492	5484	144
3	-1	950	986	88
3	3	902	928	50
4	-4	1557	1749	62
4	2	706	701	84
4	3	3047	2962	95
******* h = 12 *******				
0	-12	3623	3377	113
0	-10	1467	1595	148
0	-8	1879	1967	87
0	-7	3250	3025	90
0	-6	800	684	104

k	l	Fo	Fc	sigF
0	-5	527	639	74
0	-4	1308	1242	63
0	-3	8257	7848	208
0	0	1330	1356	54
0	2	6131	6160	183
1	-12	3208	3139	97
1	-11	1723	1739	63
1	-9	3151	3301	109
1	-1	737	642	42
1	0	870	855	42
1	3	1879	1833	58
1	4	2396	2310	95
1	5	1441	1322	57
1	6	1882	1717	68
1	7	1858	1845	70
1	8	864	778	121
2	-10	1262	1405	54
2	-7	2758	2584	84
2	-4	1050	986	105
2	-3	6335	6212	162
2	0	1042	1122	51
2	2	4810	4863	124
2	8	1643	1696	62
3	-9	2543	2583	88
3	-7	1529	1374	57
3	-6	1282	1266	139
3	-3	1148	1244	47
3	0	641	532	85
3	4	1604	1605	59
4	-3	4100	3996	114
4	2	3296	3129	98
******* h = 13 *******				
0	-10	1451	1484	53
0	-8	5678	5520	146
0	-4	1265	1177	49
0	1	890	1044	81
0	3	1041	1022	41
0	6	864	798	55
0	9	2108	2414	114
1	-12	971	951	70
1	-9	3864	4073	104
1	-7	786	702	60
1	-6	3118	2855	88
1	-5	2479	2403	73
1	-4	2508	2402	72
1	-2	889	813	38
1	-1	1050	931	39
1	8	787	706	77
1	10	2417	2812	74
2	-7	568	538	88
2	-6	676	668	70
2	-1	890	829	42
2	4	848	926	55
2	8	5020	4788	133
2	9	2060	2104	77
2	10	1203	1325	160
3	-8	636	515	95
3	-6	2235	2141	78
3	-5	1883	1744	71
3	2	558	555	71
3	4	1710	1674	64
3	9	2943	3152	254
******* h = 14 *******				
0	-8	1696	1609	68
0	-4	590	575	69
0	0	2676	2807	75
0	2	418	315	53
0	3	1574	1497	65
0	6	3526	3289	96
0	7	1776	1762	126
0	11	859	865	119
1	-11	2268	2458	77
1	-6	3194	3054	89
1	-5	5490	5173	141
1	-4	2655	2551	75
1	-1	1302	1290	54
1	0	699	654	48
1	9	1704	1822	70
1	10	987	1165	51
2	-11	722	786	70
2	-8	1453	1391	60
2	-6	2847	2790	84
2	-4	589	445	70
2	0	2195	2189	73
2	3	1277	1226	51
2	7	1678	1509	65
3	-5	3803	3819	105
3	-4	1855	1819	126
3	-1	949	882	49
3	6	2144	2255	95
4	-3	1006	817	160
4	0	1464	1361	75
******* h = 15 *******				
0	-8	4723	4477	124
0	-7	4027	3816	108
0	-6	3394	3053	93
0	-5	807	768	52
0	-4	638	622	54
0	1	3886	3743	113
0	2	1452	1466	50
0	3	2345	2313	66
0	9	1126	1192	50
0	10	764	858	54
1	-12	2472	2695	151
1	-7	706	624	67
1	-6	749	623	64
1	-5	1254	1188	50
1	-4	800	699	49
1	-2	828	808	101
1	3	1080	1024	42
1	8	1312	1152	55
1	9	1486	1519	59
1	11	1813	2167	148
2	-9	1040	1061	74
2	-6	2580	2573	80
2	-2	1245	1200	49
2	-1	2855	2932	79
2	3	1895	1857	65
2	5	571	637	75
2	7	3487	3298	98
2	8	4060	3892	183
3	-8	911	893	78
3	3	592	704	69
4	1	1918	1876	98
4	3	1256	1199	58
******* h = 16 *******				
0	-10	1261	1374	48
0	-7	2895	2618	84
0	-6	707	623	66
0	-5	535	401	69
0	-2	1645	1637	101
0	0	5666	5667	145
0	3	1172	1146	82
0	4	550	441	62
0	8	1786	1827	72
0	11	693	815	73
1	-11	2415	2768	88
1	-9	2849	2833	85
1	-5	1373	1327	94
1	-4	6154	5866	157
1	-3	856	847	43
1	0	497	481	67

k	l	Fo	Fc	sigF
1	1	655	594	49
1	6	2658	2450	138
2	-7	2356	2264	79
2	-2	1432	1366	60
2	-1	1764	1732	61
2	0	4536	4519	121
2	3	935	949	82
2	8	1606	1599	102
2	10	1169	1215	156
3	-9	2112	2227	103
3	-5	1006	963	66
3	-4	4211	4297	114
3	3	582	634	68
3	6	1913	1839	77
4	-2	1028	927	64
4	-1	1151	1134	111
4	0	2858	2920	102
4	3	674	634	112
******* h = 17 *******				
0	-10	1649	1723	67
0	-9	1407	1338	59
0	-7	2189	2021	74
0	-6	4031	3803	108
0	-1	4687	4014	656
0	5	4859	4585	126
0	8	1123	1112	81
0	11	2075	2248	75
1	-9	819	820	67
1	-7	1803	1756	175
1	-4	4737	4540	123
1	-3	3244	3170	151
1	1	1481	1439	57
1	5	697	689	61
1	6	1700	1576	61
1	8	790	875	70
1	11	2744	3118	84
2	-11	1799	1997	68
2	-10	1421	1541	109
2	-7	1648	1755	135
2	-5	3853	3857	111
2	-2	1276	1253	134
2	1	3276	3268	88
2	6	3259	3249	92
2	9	1217	1175	60
3	-7	1341	1305	61
3	-4	3342	3356	95
3	-1	920	1037	52
3	3	2235	2296	73
3	6	1132	1161	106
4	-1	2199	2183	165
******* h = 18 *******				
0	-12	1893	1978	88
0	-9	1154	1059	54
0	-8	1184	1159	71
0	-3	703	729	72
0	0	1263	1256	66
0	1	6555	5715	812
0	4	2294	2137	69
0	6	6834	6324	174
0	10	832	917	59
0	11	636	806	105
1	-7	1880	1788	75
1	-5	1804	1736	67
1	-3	7083	7344	686
1	0	1120	1126	54
1	1	1387	1306	201
1	8	1861	1832	105
1	9	863	924	67
1	10	2149	2357	77
2	-8	902	996	70
2	-6	5215	5412	389
2	-4	1872	1787	68
2	-2	1718	1706	145
2	-1	4686	4695	164
2	0	965	937	58
2	3	623	610	103
3	-7	1343	1398	215
3	-2	1500	1479	58
3	-1	1026	974	48
3	0	762	809	81
3	3	5086	5309	141
3	5	1248	1284	56
4	-1	3136	3144	167
4	2	1230	1124	105
4	4	1113	1189	76
******* h = 19 *******				
0	-7	2389	2226	76
0	-6	2609	2431	93
0	2	2145	1999	258
1	-11	807	930	112
1	-8	5057	4878	197
1	-6	1330	1255	51
1	2	7269	6640	606
2	-2	1682	1659	62
2	-1	4529	4563	118
2	7	1989	1941	77
3	-8	3858	3785	125
3	-6	906	924	67
3	-5	901	879	64
3	-3	2488	2539	148
3	2	4688	4831	124
4	-1	2965	3075	195
4	2	1160	1130	96
******* h = 20 *******				
0	-7	1064	992	83
0	-6	3574	3544	98
0	0	9712	9474	246
0	4	984	934	48
0	8	1685	1619	92
0	9	992	870	61
1	-7	1900	1715	71
1	-6	1142	1128	111
1	1	2425	2368	69
1	3	4100	4230	417
1	9	4743	4541	127
2	-8	1371	1400	59
2	-2	1133	1045	45
2	0	7719	7798	198
2	1	3582	3572	96
2	4	922	807	51
2	9	704	763	93
3	-2	3740	3794	103
3	-1	1729	1706	70
3	3	3044	3061	209
3	4	1155	1115	51
3	6	783	840	77
3	7	1453	1341	59
4	0	5088	5197	143
4	1	2337	2399	94
******* h = 21 *******				
0	-10	3003	3161	122
0	-8	906	842	142
0	-5	6419	6007	164
0	4	1821	1857	291
1	-11	1934	2064	103
1	-8	804	763	98
1	7	2134	2250	280
2	-10	2608	2827	379
2	-4	1644	1586	137
2	-2	1063	1124	57

k	l	Fo	Fc	sigF
2	3	1698	1681	105
2	5	5240	5147	137
3	-7	1656	1757	67
3	-1	1051	1072	63
3	2	690	524	68
3	3	982	842	55
3	4	1939	2015	173
3	6	940	947	67
4	-3	1071	1122	65
4	2	785	734	77
******* h = 22 *******				
0	-9	1661	1662	64
0	-8	1453	1432	81
0	-6	1395	1428	89
0	0	3254	3300	92
0	3	3002	2886	84
0	7	1362	1334	115
1	-10	1417	1534	217
1	-3	3401	3209	93
1	0	2326	2378	77
1	2	4280	4101	112
1	7	3419	3540	562
2	-7	948	1159	152
2	-6	1214	1225	125
2	0	2762	2731	87
2	1	658	607	57
2	3	2370	2422	116
2	4	2269	2202	74
3	0	1790	1784	89
3	2	3062	3024	89
3	3	2344	2375	77
3	4	1220	1211	95
3	7	2765	2770	100
4	0	1792	1823	84
******* h = 23 *******				
0	-10	1904	2225	206
0	2	1273	1158	49
0	9	2409	2703	344
1	-11	906	1034	134
1	-8	6053	5868	158
1	4	1181	1261	111
2	-4	1463	1249	241
2	-2	932	980	50
3	-5	970	933	66
3	2	1085	1023	54
3	4	914	926	58
******* h = 24 *******				
0	-5	5806	5745	255
0	-4	2205	2409	275
0	-1	1100	1117	43
0	0	695	702	72
1	-9	1377	1488	203
1	-6	1469	1653	126
1	0	2751	2886	86
2	-5	5109	4984	134
2	-4	2254	2069	191
2	-1	939	939	137
2	0	708	600	75
3	-4	665	633	74
3	-1	764	747	63
3	0	2203	2095	91
3	6	1220	1288	60
******* h = 25 *******				
0	-10	1810	1762	137
0	-3	2467	2349	113
0	-2	2083	1996	137
1	-8	3141	3122	245
1	-1	2331	2241	197
1	2	2080	1913	221
1	5	934	1024	88
2	-8	1785	1817	96
2	-7	1425	1485	127
2	-3	1998	1999	109
2	-2	1721	1707	73
3	-7	2696	2748	88
3	-5	709	763	89
3	-2	1413	1439	62
3	-1	1564	1674	61
3	3	993	1012	59
******* h = 26 *******				
0	-4	4695	4625	124
0	0	797	793	69
1	-4	1349	1177	82
1	-2	3235	3102	303
1	-1	2805	2669	308
1	0	5501	5502	145
2	-2	1559	1409	66
2	0	687	680	85
2	4	4290	4020	131
2	6	1097	1111	91
2	8	1454	1526	68
3	-4	922	884	60
3	-2	2375	2378	80
3	-1	1930	2010	78
3	0	4167	4115	121
3	5	727	635	104
******* h = 27 *******				
0	1	2151	2113	121
1	-5	6381	6243	164
2	-9	1344	1242	76
2	-3	1657	1623	193
2	1	1818	1817	77
3	-2	1185	1216	58
3	-1	1946	1872	75
3	5	5082	4851	136
******* h = 28 *******				
0	-10	2037	2096	83
0	-3	5196	5132	255
0	-1	2950	2910	138
0	0	2824	2827	88
0	2	3404	3033	494
0	5	1479	1437	180
1	0	4375	4385	120
1	1	4222	4176	252
1	2	2249	2032	270
1	6	4646	4607	124
2	-8	2488	2837	264
2	-2	2794	2628	82
2	0	2288	2445	88
2	1	2416	2526	264
2	3	4337	4440	188
3	-2	1568	1542	107
3	-1	3152	3215	93
3	0	3255	3291	106
3	4	904	854	63
******* h = 29 *******				
0	-8	4801	4724	214
0	2	5453	5179	389
0	6	714	787	75
1	-9	935	1026	78
1	-1	3833	3881	588
1	3	1535	1529	60
1	4	2986	2820	109
1	5	1082	993	58

```
k    l     Fo     Fc sigF  k    l     Fo     Fc sigF  k    l     Fo     Fc sigF

1    7   1512   1584   61  2   -2   1998   1989  168  2   -3   1679   1693  141
2   -8   4335   4186  284  2   -1    781    774   87  2   -2   3063   2983  162
2    2   4449   4501  162  2    0   2769   2695   97  2   -1   1985   1961   81
3   -4   2054   2218   86  3   -2    727    737   86  2    0   3362   3426  111
3   -3   1148   1170   63  3    0   2683   2669  103
3   -1   2859   3033   91  3    3   2029   2111   83  ******* h = 37 *******
3    2   1533   1593  175
                           ******* h = 33 *******     0   -4   2220   2119  262
******* h = 30 *******                                0   -3   2398   2422  166
                           0   -5   1540   1359   96  0    5   5841   5564  154
0   -9   3734   3583  108  0    8   4986   4943  234  1   -5   1236   1087   97
0   -7   2075   2225   81  1   -8   1823   1756  253  1    4   3116   3255  308
0   -6    917    831   68  1    2   1511   1393   88  2   -4   1786   1876  153
0   -4   1223   1093  183  1    6   2860   2501  444  2    3   2166   2171  305
0    1   3492   3587   95  2    5   1198   1190  113
0    3   4457   4561  117  3   -2   1104   1113  100  ******* h = 38 *******
1   -9    870    804  130
1    0   2706   2513   89  ******* h = 34 *******     0    0   5916   6129  160
1    6   3280   3274  166                             0    1   2016   2118  201
2   -4    845    948  105  0   -3   2348   2515   76  0    6   3273   3216  143
2   -1   3083   3123   89  0   -1   1761   1824   97  1   -2   1891   1795  114
2    0    647    444   98  0    0   1750   1841   89  1    0   3746   3823  114
2    3   3878   3955  106  1   -7   1563   1505  215  1    1   2988   3061  155
3    0   1920   1927   99  1   -5   4379   4170  121  1    3   2949   3168  176
3    1   1815   1912  197  1    0    706    761  102  2    0   5321   5429  150
                           1    4   1293   1286  204  2    1   1756   1886  157
******* h = 31 *******     2    0   1724   1604   94
                           2    1   1663   1625   62  ******* h = 39 *******
0   -7   2366   2194  177  2    3   2058   2219   79
0    6   2691   2541   84                             0   -4   3268   3585   95
0    8   2290   2238  243  ******* h = 35 *******     0   -3   2154   2138  123
1   -8    937    872   75                             0   -2   1465   1415  170
1   -2   1676   1617  167  0   -8   1509   1406   93  0   -1   1701   2020   99
1    4   2042   1787  145  0   -7   2801   2568  314  1    2   2252   2254  113
1    5   3355   2935  439  0   -6   1449   1357  114  2    1   1665   1821  130
2    6   2231   2243   85  1   -6   1847   1830  277  2    2   1271   1287   92
3    2   1231   1244   60  1   -2   2578   2506   81
3    3   1368   1391  159  1    1   1130   1117   57  ******* h = 40 *******
3    4   1413   1437   61  2    2   1377   1397  179
                                                      0   -5   1673   1723   76
******* h = 32 *******     ******* h = 36 *******     1   -3   3953   3972  314
                                                      1   -1   3206   3241   96
0   -8   1812   1826  123  0   -7   2816   2459  440  1    0   1098   1122   88
0   -2   2265   2276  154  0   -3   1745   1919  258
0   -1    920    900   90  0   -2   3354   3355  195  ******* h = 41 *******
0    0   2991   3066   94  0    0   3928   3907  115
0    7   2492   2246  350  0    1   2273   2231  129  0   -4    832    808   71
0    9   1905   1852  105  1    0   2211   2281   99  0   -2   1307   1401  100
1   -3   2608   2686  210  1    3   2877   2926  157  0    3   1208   1291  162
1    0   3531   3456  105  2   -4   1385   1488   67  1    2   1935   1926   75
```

```
  k    l   Fo     Fc  sigF  k    l   Fo     Fc  sigF  k    l   Fo     Fc  sigF

******* h =  42 *******

  0   -4    985   1044 112
  0   -3   2085   2047  85
  0    0   2748   2759 102
  0    1   1429   1382  60
  1    0   2746   2880 108
  1    1   1353   1365 136

******* h =  43 *******

  0   -2   1447   1568  65
  0   -1   1406   1543  67

******* h =  44 *******

  0    0   1013   1256 100
```

APPENDIX B OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (x10) FOR $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$)

k	l	Fo	Fc	sigF
^^^^^^^ h = 0 ^^^^^^^				
0	12	1793	1836	79
0	14	5657	5542	98
0	18	3024	2990	80
0	20	3384	3433	85
0	24	840	757	0
0	26	2073	2050	75
0	28	2744	2907	0
0	32	2570	2524	0
0	34	2869	2834	91
0	36	2125	2143	0
0	40	1492	1400	0
0	42	4096	4201	0
0	44	2007	1901	96
0	46	1541	1401	0
1	-33	2504	2515	96
1	-29	920	876	0
1	-25	3369	3253	98
1	-21	6627	6391	0
1	-9	11735	10843	0
1	5	2066	2050	78
1	7	1639	1661	56
1	11	3988	3884	81
1	13	788	749	94
1	17	895	633	0
1	23	3814	3668	0
1	27	1385	1311	0
1	31	1454	1271	0
1	35	2066	2081	79
1	39	3038	2901	0
1	41	3883	3742	0
2	-40	1230	1256	0
2	-32	2179	2177	92
2	-28	2421	2525	79
2	-18	2455	2439	79
2	-2	1205	1082	0
2	0	17685	18979	0
2	12	1283	1448	0
2	14	4180	4205	95
2	20	2797	2821	0
2	26	1704	1783	0
2	34	2657	2513	97
2	36	2040	1902	86
3	-33	1941	1925	95
3	-31	1113	1017	0
3	-29	884	741	0
3	-25	2352	2455	88
3	-21	4641	4544	0
3	-11	2660	2642	0
3	-9	7006	7139	0
3	-5	1144	1301	0
3	23	2653	2593	96
3	35	1437	1567	0
4	-12	903	900	0
4	0	10723	11568	0
4	14	2530	2618	0
4	16	976	321	0
4	18	1762	1590	96
4	20	1808	1887	0
^^^^^^^ h = 1 ^^^^^^^				
0	-44	1217	860	0
0	-41	2457	2214	91
0	-38	1927	1788	0
0	-30	6147	5926	0
0	-9	1005	1042	68
0	1	2270	2328	0
0	4	1618	1590	0
0	15	5022	5012	0
0	33	2597	2466	0
0	37	1778	1511	0
1	-42	1739	1122	0
1	-40	2562	1466	0
1	-39	3006	2720	0
1	-36	2067	2197	84
1	-35	1386	515	0
1	-31	2013	1478	0
1	-28	2809	2426	0
1	-22	3300	3399	0
1	-18	1142	960	0
1	-16	870	861	95
1	-9	6508	6271	0
1	-6	1307	1291	57
1	1	1011	1111	77
1	4	1982	1997	0
1	8	1616	1683	56
1	10	10044	9375	0
1	11	3979	4010	0
1	12	1029	1122	0
1	13	1494	1473	58
1	25	2312	2362	0
1	29	3583	3238	0
1	32	1715	1567	0
1	38	1911	654	94
1	41	2624	2555	94
1	45	1418	923	0
2	-35	1385	1242	0
2	-34	1598	1312	0
2	-33	2366	2144	0
2	-32	1664	1328	0
2	-28	1134	438	0
2	-21	2103	1973	0
2	-20	3890	4052	0
2	-15	3984	3913	0
2	-11	1270	1180	0
2	1	2111	1892	0
2	10	687	377	0
2	13	1141	1066	87
2	17	1171	1057	0
2	18	3592	3745	0
2	19	4773	4719	0
2	23	1601	1545	77
2	25	1382	1345	91
2	30	5456	5128	0
2	38	1980	1587	95
2	39	1515	1401	0
2	41	2169	1983	0
3	-22	2523	2480	88
3	-21	2608	2452	92
3	-20	2008	2022	79
3	-11	2534	2661	0
3	-4	1257	1256	0
3	-3	837	219	0
3	8	1189	1205	0
3	9	4159	4091	0
3	10	6252	6160	0
3	13	997	1041	0
3	17	835	592	0
3	25	1874	1802	0
3	28	1911	1853	0
3	29	2672	2472	0
4	-20	2935	2700	0
4	-15	2708	2511	93
4	-1	1014	1196	0
4	18	2704	2518	0
4	19	3125	3200	0
4	21	1305	1343	0
^^^^^^^ h = 2 ^^^^^^^				
0	-30	4925	5041	0
0	-26	3145	3101	0
0	-23	2174	2000	0
0	-20	4548	4289	0
0	-12	9839	9231	0
0	-11	6726	6470	0
0	-10	3313	3427	0
0	0	928	856	68

k	l	Fo	Fc	sigF
0	9	828	772	0
0	13	2814	2926	0
0	15	3316	4062	0
0	44	1157	1249	0
1	-43	2306	2183	89
1	-42	1629	371	0
1	-40	2693	2791	0
1	-35	1839	1723	0
1	-21	6090	5860	0
1	-18	990	386	0
1	-17	1493	1380	0
1	-13	2024	2140	0
1	-7	1609	1653	98
1	-6	3892	3789	0
1	-5	4827	4802	0
1	-3	3376	3279	0
1	-2	2082	2137	0
1	0	2671	2709	81
1	8	1390	1330	58
1	9	4041	3981	0
1	16	1688	1656	0
1	37	1854	1847	0
2	-38	2684	2326	0
2	-15	3370	3250	0
2	-13	2237	2305	80
2	-12	7377	7165	0
2	-11	5227	5082	0
2	10	2628	2681	0
2	14	829	988	0
2	16	1884	1928	0
2	19	2679	2834	0
2	20	3428	3512	0
2	23	1841	1708	0
2	26	2427	2623	0
2	27	1299	1235	0
2	30	4268	4349	0
2	37	2378	2175	0
2	39	2743	2577	0
3	-32	2347	2184	0
3	-22	2045	1871	81
3	-20	2788	2771	0
3	-6	2666	2556	0
3	-5	3302	2996	0
3	-3	2262	2065	0
3	0	1746	1759	0
3	2	1730	1536	0
3	9	2538	2533	99
3	13	1461	1503	98
3	14	1008	283	0
3	17	1124	938	0
3	21	4337	4280	0
3	27	1905	1798	0
3	28	3179	3101	99
3	29	3292	3225	0
3	30	1653	1513	0
3	31	2351	2226	90
4	-16	1359	1299	0
4	-14	819	519	0
4	-11	3550	3313	0
4	10	1829	1688	96
4	12	4704	4570	0
4	13	1632	1493	0
4	15	2052	2145	0
4	19	1908	1907	0
4	20	2256	2303	91
4	23	1233	1208	0

^^^^^^^ h = 3 ^^^^^^^

k	l	Fo	Fc	sigF
0	-43	2584	2440	0
0	-40	2680	2957	0
0	-37	3114	2976	0
0	-16	924	638	90
0	-14	1714	1687	88
0	-13	1529	1579	0
0	4	2835	2886	0
0	5	2611	2667	0
0	6	1419	1548	0
0	7	6566	6495	0
0	8	4570	4752	0
0	9	2961	2956	0
0	10	4425	4437	0
0	11	3836	3991	0
0	12	2585	2599	0
0	19	3288	3889	0
0	21	2651	2281	0
0	25	1148	1159	0
0	27	2922	2857	0
0	31	1533	1408	0
1	-42	1796	1933	0
1	-40	2550	2581	0
1	-28	1722	1752	80
1	-17	3489	4092	0
1	-9	721	249	0
1	-3	5018	4928	0
1	-2	11407	10916	0
1	1	6226	6169	0
1	5	1057	1115	0
1	6	1508	1488	66
1	7	1361	1408	69
1	10	824	771	0
1	12	1822	1792	0
1	13	1654	1581	64
1	20	2183	2128	0
1	22	2238	2211	0
1	32	2027	1902	0
1	34	1954	2138	0
2	-37	2711	2625	90
2	-28	868	482	0
2	-27	2517	2474	95
2	-19	3339	3199	0
2	-17	1325	1357	90
2	-13	1415	1249	79
2	-10	3521	3514	0
2	-9	2430	2333	0
2	-6	1243	1244	0
2	4	2194	2209	0
2	5	2083	2031	71
2	7	5062	5054	0
2	8	3726	3746	0
2	11	3074	3160	0
2	12	2100	2147	0
2	14	1508	1373	0
2	18	1670	1631	0
2	20	1146	1188	0
2	21	1810	1873	0
2	22	1294	1285	0
2	23	902	895	0
2	40	2529	2646	0
3	-25	1752	1512	94
3	-12	1177	1215	0
3	-10	888	489	0
3	-7	908	937	0
3	-3	3380	3264	0
3	1	3885	4152	0
3	2	7283	7138	0
3	16	1522	1509	96
3	17	2923	2896	0
3	18	1516	1377	97
3	20	1634	1483	0
3	22	1620	1645	0
3	26	1273	1373	0
3	28	1241	1362	0
3	31	1194	1142	0
3	32	1820	1504	0
3	34	1617	1695	0
4	-19	2144	2160	94
4	-13	1121	763	0
4	-12	1383	1505	0
4	-5	1298	1178	0

k	l	Fo	Fc	sigF
4	-4	1353	1362	0
4	7	3427	3209	0
4	8	2454	2447	91
4	9	1622	1481	0
4	10	2294	2307	92
4	11	2248	2039	0
4	20	1181	812	0
4	21	1344	1220	0

------- h = 4 -------

k	l	Fo	Fc	sigF
0	-35	2239	2293	0
0	-24	4218	3781	0
0	-12	1891	1971	0
0	-9	3307	3293	0
0	-8	7904	7727	0
0	-4	3897	3995	0
0	-1	1426	1523	0
0	0	2816	2700	0
0	3	1735	1571	0
0	6	1764	1857	0
0	7	7585	7499	0
0	18	1343	1448	78
0	26	4469	4354	0
0	28	2737	2443	0
0	33	1171	959	0
0	38	3692	3628	0
1	-43	2194	2181	0
1	-37	1354	1715	0
1	-12	912	813	0
1	-5	1101	1169	83
1	-4	662	616	0
1	-2	1158	1226	79
1	-1	1381	1435	71
1	0	1578	1640	65
1	17	9221	9365	0
1	22	1586	1564	0
1	25	2635	2534	0
2	-29	1264	730	0
2	-28	2197	2110	0
2	-23	2274	2338	0
2	-12	1590	1627	80
2	-7	5963	5848	0
2	-6	1374	1348	0
2	0	1940	2029	0
2	1	1035	1158	0
2	4	3147	3119	0
2	8	6250	6153	0
2	9	2769	2651	0
2	18	1094	1172	0
2	21	2933	2967	0
2	22	2152	2314	0
2	24	3395	3210	0
2	26	3582	3766	0
2	35	1905	2028	0
2	38	3179	3236	0
3	-28	2373	2299	87
3	-25	1911	1905	0
3	-22	1277	1105	0
3	-17	6985	6842	0
3	1	1117	1020	0
3	16	1862	2004	0
3	18	1966	1843	0
3	19	1704	1744	0
3	29	1504	1491	0
3	32	2186	2330	0
4	-7	3653	3757	0
4	-4	1991	2043	0
4	0	1090	1203	0
4	8	4205	4022	0
4	9	1769	1763	0
4	12	1359	1135	0

------- h = 5 -------

k	l	Fo	Fc	sigF
0	-42	1896	1999	0
0	-36	1543	1522	0
0	-27	4971	4318	0
0	-18	1098	1154	0
0	-10	1048	1172	0
0	-6	1817	1807	64
0	2	1719	1814	63
0	3	4288	4400	0
0	4	4009	4018	95
0	5	693	612	0
0	7	2175	2264	0
0	8	4574	4618	0
0	11	1691	1748	0
0	12	1076	998	91
0	15	1239	1375	0
0	16	1148	1215	91
0	24	2476	2513	0
0	34	3456	3289	0
1	-32	2868	2836	0
1	-27	2139	1998	0
1	-21	1296	1434	0
1	-14	2326	2266	83
1	-13	8333	7984	0
1	-12	3701	3792	0
1	-9	742	551	0
1	2	1240	1272	81
1	10	1471	1728	0
1	11	1271	1278	85
1	15	1589	1445	75
1	16	1074	1170	0
1	22	1147	1063	0
1	24	1444	1367	90
1	29	1874	2027	0
2	-34	3066	2916	0
2	-28	3135	2870	0
2	-10	990	936	0
2	-8	3784	3720	0
2	-7	1923	1849	0
2	-3	3423	3508	0
2	-2	1289	1455	0
2	1	801	467	0
2	4	3135	3291	95
2	6	1489	1438	88
2	11	1513	1378	0
2	12	918	820	0
2	15	1207	1134	0
2	22	2436	2440	0
2	23	3454	3126	0
2	24	2137	2213	0
2	27	3798	3758	0
2	36	1400	1339	0
3	-22	1172	815	0
3	-19	1314	1481	0
3	-18	1591	1505	0
3	10	1266	1143	0
3	13	5798	5804	0
3	14	1763	1627	0
3	15	1004	1133	0
3	27	1601	1534	0
4	-8	2548	2465	89
4	3	2141	2283	0
4	4	1992	2231	0

------- h = 6 -------

k	l	Fo	Fc	sigF
0	-33	3162	3161	0
0	-29	1115	668	0
0	-28	890	471	0
0	-26	2339	2284	84
0	-19	2583	3111	0
0	-15	3007	2998	0
0	-13	1010	821	0
0	-11	2227	2245	0
0	-9	2722	2746	0
0	-3	5612	5633	0

k	l	Fo	Fc	sigF
0	0	2887	2865	0
0	2	2394	2415	77
0	4	5704	5690	0
0	5	3369	3430	0
0	8	1369	1407	81
0	12	3222	3246	0
0	18	2671	2562	0
0	23	5125	5266	0
0	36	1389	1263	0
0	38	2733	2839	0
1	-29	2506	2564	0
1	-17	2755	2791	97
1	-10	1633	1606	76
1	-8	2866	2740	0
1	-7	4377	4427	0
1	-4	1345	1384	85
1	-1	778	836	0
1	0	2590	2618	80
1	2	4072	4131	97
1	3	3133	3051	96
1	5	4030	4066	0
1	6	3871	3996	0
1	13	3994	4025	0
1	14	3597	3416	0
1	24	1792	1856	0
1	27	898	898	0
1	32	1925	1891	0
1	33	1373	618	0
1	38	1967	1849	0
2	-11	1908	1908	0
2	-9	2300	2279	0
2	-4	4817	4702	0
2	0	2257	2315	83
2	1	792	597	0
2	2	1876	2007	80
2	3	4672	4620	0
2	5	2810	2847	0
2	8	1246	1180	0
2	12	2749	2704	0
2	15	2466	2555	88
2	23	4529	4569	0
2	26	2025	2002	88
2	33	2662	2817	0
3	-23	1166	888	0
3	-10	1398	1136	0
3	-7	3030	3205	0
3	-6	2704	2941	90
3	-5	2732	2943	0
3	0	1814	1857	94
3	2	2987	2913	97
3	3	2028	2111	89
3	8	1915	2022	0
3	13	2574	2983	0
3	14	2229	2591	0
3	17	2136	2128	87
3	25	991	438	0
3	29	2006	2014	0
4	-12	1670	1796	0
4	-9	1594	1541	0
4	-4	2785	3182	0
4	0	1631	1500	0
4	3	2676	3085	0

^^^^^^^ h = 7 ^^^^^^^

k	l	Fo	Fc	sigF
0	-29	1174	77	0
0	-25	1108	1243	0
0	-17	3094	3182	97
0	-16	2822	2905	0
0	-12	1289	1195	99
0	-10	1786	1735	0
0	-6	978	1268	0
0	3	1507	1372	83
0	4	1135	1070	0
0	14	1498	1455	0
0	15	6459	6450	0
0	18	3641	3703	0
0	32	2118	1984	0
0	35	3692	3396	0
1	-13	2214	2256	81
1	-10	1724	1853	83
1	-9	2013	2017	0
1	-3	2260	2434	0
1	1	1929	1950	76
1	5	3235	3255	0
1	6	2556	2760	0
1	7	2974	3039	0
1	8	2065	2131	0
1	17	1031	1116	0
1	19	1759	1816	85
1	24	4807	4987	0
1	26	4092	3722	0
1	28	1420	1441	0
1	35	1818	1219	0
2	-3	1148	1152	0
2	1	1175	1127	0
2	4	908	938	0
2	6	923	1063	0
2	10	1484	1453	0
2	12	1100	972	0
2	15	5406	5540	0
2	31	1158	286	0
3	-24	3988	3924	0
3	-23	2441	2511	0
3	-19	1205	1388	0
3	-13	1641	1680	0
3	-8	1573	1592	0
3	-7	2185	2281	0
3	-5	2385	2471	0
3	-1	1690	1435	0
3	3	1874	1860	93
3	6	1824	2061	0
3	10	1450	1417	0
3	26	3096	2928	0
4	1	1339	751	0
4	3	1166	767	0

^^^^^^^ h = 8 ^^^^^^^

k	l	Fo	Fc	sigF
0	-36	2717	2731	0
0	-31	1811	1468	0
0	-25	1240	1619	0
0	-13	1621	1424	0
0	-11	3096	3031	0
0	-7	2320	2359	86
0	-3	1597	1583	89
0	-1	1553	1583	90
0	0	3487	3510	0
0	5	1937	1986	0
0	12	2106	2337	0
0	14	3957	3969	0
0	15	3227	3102	0
0	16	3537	3652	0
0	28	1856	1687	0
0	30	1688	1236	0
0	34	5097	4859	0
1	-25	5766	5567	0
1	-23	1811	2030	0
1	-11	1091	824	0
1	-10	2568	2606	92
1	-9	2313	2385	0
1	-6	3415	3451	0
1	-5	3294	3362	0
1	1	1492	1386	93
1	3	2144	2221	0
1	4	2848	2984	91
1	8	2256	2178	0
1	14	1767	1760	0
1	16	1168	1142	0
1	28	2049	2003	0

```
k   l   Fo    Fc   sigF
1  30  2064  1760  0
1  32  2370  2108  0
1  34  1752  1853  0
2 -31  1475  1294  0
2 -30  1504  1109  0
2 -27  1341   661  0
2 -16  2572  3181  0
2 -11  2472  2592 91
2  -7  2071  2007 82
2   0  2866  3024  0
2   1   952  1343  0
2   3  1041  1325  0
2   5  1743  1665  0
2  12  1964  2060  0
2  14  3108  3470  0
3  -9  1465  1839  0
3  -6  2549  2609 92
3  -5  2557  2583  0
3   3  1566  1714  0
3   4  2248  2258 92
3   8  1577  1649  0
3  10  1718  1986  0
3  20  1333  1301  0

^^^^^^^ h =  9 ^^^^^^^

0 -33  1936  1716  0
0 -30  3049  2958  0
0 -20  1161  1116  0
0 -16  3051  3215  0
0 -10  1231  1245  0
0  -9  2099  2045  0
0  -5  4739  4625  0
0  -2  1571  1528 92
0  -1  1681  1654 91
0   3  1745  1688  0
0   4  5620  5632  0
0   6  2018  2033 81
0  15   976  1145  0
0  26  1157   782  0
1 -31  1759  1772  0
1 -17  2196  2306  0
1 -14  2854  2998  0
1 -11  1995  2063 84
1   4  2200  2206 82
1   5  4014  4065  0
1   6  2823  2779 97
1   9  2381  2428 85
1  25  3312  3276  0
2  -9  1813  1756 93

k   l   Fo    Fc   sigF
2  -6  1803  1806  0
2  -5  3786  4004  0
2  -2  1435  1312  0
2  -1  1463  1414  0
2   3  1431  1469  0
2   4  4806  4891  0
2  10  1085  1093  0
2  16  2714  2836 93
3 -14  2129  2321  0
3  -9  1733  1941  0
3   4  1512  1728  0
3   5  3046  3133  0
3   6  1945  2155  0
3  11  1598  1626  0

^^^^^^^ h = 10 ^^^^^^^

0   0  3278  3216  0
0   2  1296  1142  0
0   4  2911  2834 96
0   6  1256  1139  0
0  13  1435  1414  0
0  15  2338  2347  0
0  17  1762  1705 99
0  19  2972  3140  0
0  25  4855  4944  0
0  31  1953  1788  0
1 -21  2311  2463  0
1 -14  2381  2851  0
1  -8  1867  1641  0
1  -2  1230  1345  0
1   4  1389  1285  0
1   5  1298  1305  0
1   6  2428  2514 92
1   9  1635  1667  0
1  13  3014  3222  0
1  16  3499  3772  0
1  29  1142   827  0
2 -22  1746  2048  0
2 -19  2739  2774  0
2 -17  1348  1486  0
2   0  2851  2866  0
2   4  2407  2476  0
2  15  1960  2074  0
3  -6  1801  2008  0
3   2  1055  1005  0

^^^^^^^ h = 11 ^^^^^^^

0 -26  2337  2413  0

k   l   Fo    Fc   sigF
0 -24  2093  2133  0
0 -14  1335  1135  0
0 -11  2242  2230 89
0  -8  2588  2663 93
0  -6  3452  3456  0
0   3  1631  1369  0
0   7  3119  3112  0
0  10  1891  1904  0
0  22  2282  2637  0
1 -10  1938  2041 98
1  -2  2157  2031  0
1  -1  1332  1465  0
1  12  1183  1241  0
2 -10  1616  1683  0
2  -8  2162  2344  0
2  -7  2370  2771  0
2   3   988  1216  0
2   6  2917  3062  0

^^^^^^^ h = 12 ^^^^^^^

0  -1  2102  1918 93
0   3  1710  1657  0
0   5  1956  1950  0
0   8  3403  3161  0
0  13  3068  3047  0
1  -6  1480  1550  0
1  -4  3421  3447  0
1  -3  2693  2901  0
1  -2  2587  2549  0
1  -1  2314  2352 93
1   5  1722  1610  0
1  10  1643  1671  0
2  -3  1338  1463  0
2  -1  1558  1687  0
2   5  1780  1729  0
2   8  2846  2832 99

^^^^^^^ h = 13 ^^^^^^^

0 -12  3360  3468  0
0  -8  1935  1973  0
0  -2  1452  1618  0
0   6  1393  1340  0
1  -3  1254  1058  0
1  -1  1663  1767  0
```

APPENDIX C OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (x10) FOR $Nb_xTa_{5-x}S_2$ ($x \approx 1.72$)

k	l	Fo	Fc	sigF
^^^^^^^ h = 0 ^^^^^^^				
0	2	1654	1610	26
0	4	705	713	19
0	6	999	789	55
0	8	1064	1047	28
0	12	3190	3247	64
0	14	3043	3112	51
0	22	1180	1133	34
0	24	834	882	30
0	26	2327	2360	42
0	28	560	580	44
1	-29	624	623	24
1	-23	310	211	52
1	-21	1374	1436	29
1	-13	644	640	28
1	-7	4576	4723	0
1	-5	2316	2534	97
1	3	479	460	23
1	9	552	611	28
1	11	381	395	56
1	15	1295	1281	31
1	17	549	546	30
1	19	2870	2854	67
2	-26	1999	2026	57
2	-24	744	749	23
2	-22	936	966	22
2	-14	2462	2489	39
2	-12	2629	2554	57
2	-8	739	765	23
2	-4	504	505	22
2	0	4864	4443	74
2	2	1253	1218	25
2	6	380	520	45
3	-21	1120	1039	44
3	-19	2157	2040	61
3	-15	879	893	29
3	-9	408	393	42
3	-7	2901	2931	67
3	-5	1502	1576	33
3	13	442	420	72
4	-14	1491	1512	36
4	-12	1484	1529	59
4	-8	383	454	53
4	0	2387	2467	41
4	2	652	674	41
^^^^^^^ h = 1 ^^^^^^^				
-4	-5	1053	1125	35
-3	-14	1937	1907	36
-3	-12	1978	1934	57
-3	0	3117	3189	49
-3	4	340	374	40
-3	6	359	369	34
-3	22	860	778	36
-2	-9	472	486	56
-2	-5	1965	1951	32
-2	7	3668	3600	56
-2	15	1067	1054	26
-2	17	463	446	34
-1	-12	2880	2860	0
-1	-8	792	872	33
-1	-4	526	581	44
-1	0	5424	5182	0
-1	2	1318	1379	74
-1	24	843	811	30
-1	28	593	539	34
1	-22	1033	1044	39
1	-14	2740	2764	92
1	6	577	614	19
1	26	2223	2185	0
2	-21	1210	1212	37
2	-13	481	505	34
2	-3	423	363	50
2	19	2463	2391	59
3	-2	885	877	29
3	8	580	574	68
4	7	2008	2102	47
^^^^^^^ h = 2 ^^^^^^^				
-4	-2	568	578	39
-3	-5	1320	1319	31
-3	13	393	355	54
-3	19	1833	1762	34
-2	-24	606	644	96
-2	-12	2102	2107	59
-2	0	3779	3517	86
-2	2	1099	971	0
-2	8	609	626	37
-2	22	844	835	30
-1	-15	1056	1054	48
0	-8	728	765	62
0	-6	485	519	44
0	-4	461	504	61
0	-2	1166	1217	45
0	0	4352	4439	76
0	12	2539	2554	42
2	-14	2062	2068	38
3	-17	364	310	49
3	7	2456	2459	40
3	15	785	767	35
4	0	2128	2115	38
^^^^^^^ h = 3 ^^^^^^^				
-3	-12	1438	1425	34
-3	0	2228	2285	39
-3	2	610	624	28
-3	4	354	284	58
-2	15	718	768	31
-1	-14	1908	1905	37
-1	-6	342	369	41
-1	0	3219	3186	51
-1	12	1950	1931	37
0	-21	1053	1039	62
0	-15	881	892	37
0	-5	1505	1575	34
0	-3	343	298	52
0	7	2810	2928	62
0	9	381	393	42
0	19	2070	2040	68
1	-8	503	573	71
1	-2	867	876	54
1	22	730	778	99
2	-5	1275	1315	32
^^^^^^^ h = 4 ^^^^^^^				
-2	-2	609	578	51
-2	0	2143	2117	41
-2	8	378	393	61
-1	-5	1158	1124	54
0	-14	1468	1511	94
0	-12	1542	1528	53
0	0	2691	2464	52
0	2	727	673	39
1	-7	2122	2098	45

APPENDIX D OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (x10) FOR $Nb_xTa_{2-x}S$ ($x = 0.95$)

k	l	Fo	Fc	sigF
^^^^^^^ h = 0 ^^^^^^^				
0	13	206	201	14
1	-9	636	680	52
1	-5	123	118	8
1	-4	378	373	23
2	-11	907	869	69
2	-9	355	414	35
2	-6	971	1059	75
2	1	552	557	24
3	3	1081	1241	0
4	-6	687	744	68
^^^^^^^ h = 1 ^^^^^^^				
-4	-3	947	975	36
-3	-5	783	804	46
-3	-1	449	437	10
-3	7	178	180	22
-3	9	335	348	26
-2	5	89	91	15
-1	-11	969	915	0
-1	-6	1143	1149	91
-1	-5	1120	1087	93
-1	-3	388	398	24
-1	0	2066	2005	31
-1	2	181	184	12
-1	12	298	349	32
0	-6	538	557	38
0	-3	1738	1835	0
0	1	65	66	10
0	2	879	975	54
0	7	309	354	26
0	8	1114	1106	99
0	10	199	190	21
0	11	239	232	19
0	12	247	255	32
0	13	443	475	25
1	-9	427	441	64
1	-7	231	224	23
1	1	611	614	30
1	10	394	439	54
1	13	202	193	26
2	-2	808	787	31
3	-6	813	872	49
3	-3	264	272	12
3	-2	112	110	13
4	4	221	226	12
4	7	225	224	10
^^^^^^^ h = 2 ^^^^^^^				
-4	-5	621	621	30
-3	-9	512	499	13
-3	-3	1093	1091	44
-3	6	365	362	17
-2	-11	970	788	64
-2	-6	934	925	66
-2	-3	290	293	28
-2	0	1466	1444	48
-2	1	481	469	27
-2	5	883	856	56
-2	10	348	376	39
-1	-12	251	229	16
-1	-10	184	172	17
-1	-6	447	469	33
-1	3	1461	1456	65
-1	4	312	317	20
-1	8	969	969	66
-1	11	212	211	19
0	-12	334	335	15
0	-10	328	416	41
0	-7	193	211	14
0	-4	129	149	13
0	-3	307	351	26
0	-2	133	154	11
0	0	1808	1750	41
0	5	919	993	71
1	7	275	309	25
1	9	556	606	40
2	-9	358	368	51
^^^^^^^ h = 3 ^^^^^^^				
-3	-7	172	152	15
-3	-6	754	708	78
-3	3	212	213	31
-2	-8	773	783	58
-2	-7	237	247	16
-2	-2	587	586	19
-2	4	247	248	17
-1	-10	399	358	12
0	-11	206	194	19
0	-9	496	547	42
0	-8	848	866	69
0	-7	259	275	31
0	2	613	667	45
0	4	215	277	31
0	6	380	409	27
1	-4	134	125	9
1	0	1377	1340	31
3	-5	663	651	28
3	0	998	1051	45
3	1	359	350	22
^^^^^^^ h = 4 ^^^^^^^				
-2	-1	328	334	12
-1	-6	318	324	12
-1	2	518	526	16
0	-5	656	683	65
0	-1	365	367	8
0	0	1129	1110	19
0	2	111	88	13
0	3	210	225	19
0	7	157	158	17
2	0	935	997	48
2	3	204	201	6
2	6	644	676	25

APPENDIX E OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (x10) FOR $Nb_{21-x}Ta_xS_8$ ($x \approx 6.2$)

```
   k    l    Fo    Fc sigF    k    l    Fo    Fc sigF    k    l    Fo    Fc sigF

******* h =     0 *******  -13   -1  3517  3585  92   15    2  3939  3981 102
                           -12   -2  2088  2089  58   17    0  1046   997  72
   0    2 14953 15337 376  -12    0  2322  2467 131   17    2   931   874  37
   2    2   782   802  37  -10   -2  3278  3180 154
  11    1  9693  9203 243  -10    0  3771  3883 202 ******* h =     4 *******
  11    3  6935  6796 175   -9   -1   682   701  26
  12    0  3782  3703 123   -6   -2  1271  1226  56  -18    0  1852  2001  54
  13    1  1137  1173  36   -6    0  1400  1524  87  -16   -2  4652  4640 120
  14    2   711   735  30   -5   -3  7586  7590 192  -16    0  5139  5252 163
  16    0  3106  3071  92   -4    0   387   176  37  -14    0   757   830  29
  19    1  3578  3470 148   -3   -1  1864  1894  48  -10   -2  2644  2565 167
                            -2   -2   548   512  25   -7   -3   880   822  34
******* h =     1 *******   -2    0   629   685  66   -6    0   478   483  22
                             0    0   999  1001  42   -5   -3  2667  2675  72
 -16   -1   806   794  31    6    0  7928  7541 433   -4   -2   915   912  44
 -15    0  1473  1486  76    7    1  2771  2793 102   -4    0  1134  1186  76
 -12   -3  3870  3896 101    7    3  1829  1907  60   -2    0   450   376  19
 -12   -1  5028  5111 166    8    2  3657  3602  94    0    0   292   143  18
 -10   -3  1267  1250  45   11    1   538   489  34    1    1  2728  2747  70
 -10   -1  1554  1643  67   11    3   463   381  38    3    3  6410  6464 163
  -9    0  1066  1106  66   14    0  4878  4769 492    5    3  1408  1399  46
  -8   -3   695   659  65   14    2  4170  4121 107    7    3   790   795  32
  -7   -2  1019   984  37   16    2   610   609  33    8    0  4320  4112 170
  -7    0  1257  1314  61   17    1  1887  1731 145    8    2  3159  3255 128
  -4   -3  1921  1882  56   18    0  1105  1153  93    9    1  2301  2242  60
  -3   -2  1127  1134  37                              10    2  1182  1168  42
  -3    0  1322  1432  94 ******* h =     3 *******   11    1   716   738  29
  -2   -3  1179  1178 107                              11    3   546   532  40
  -2   -1  1791  1863  47  -17   -2  1999  1999  59   15    1  1003   976  42
  -1    0  1994  1907  87  -15   -2  4482  4407 115   16    2  1588  1596  51
   0    1   505   529  18  -11   -2   461   433  34   17    1   606   576  38
   1    2  1667  1597  48  -11    0   536   549  24
   2    1   952  1027  30   -9   -2  1835  1755  51 ******* h =     5 *******
   3    0   609   322  62   -6   -3   561   544  32
   3    2   443   344  33   -6   -1   678   669  32  -16   -1  2189  2242  61
   4    1  2802  2955  72   -5    0   335   248  22  -15   -2  3609  3574  94
   4    3  1919  1832  99   -4   -1 10057  9666 252  -14   -1  3226  3229  84
   6    3   736   789  34   -2   -3  2264  2247  67  -12   -1  2668  2648  70
   7    0  8956  8434 335   -2   -1  3333  3512  84  -11   -2  1239  1173  72
   7    2  6632  6651 167    0   -1  1124  1056 100  -11    0  1416  1430  42
   8    3  1194  1168  44    0    3   726   718  90   -9   -2  7087  6994 447
  10    3   613   580  41    2    3  1309  1329  48   -6   -1   628   639  35
  15    2  2727  2787 105    4    1  1254  1249  36   -5    0  4610  4599 312
  16    1   571   589  69    4    3   741   704  31   -4   -1  2013  2076  76
                             7    0  9380  8783 732   -3   -2  2605  2674  68
******* h =     2 *******    7    2  6739  6932 170   -3    0  3482  3543 301
                             9    2  2006  1977  56   -1   -2   552   528  71
 -19   -1  1248  1237  46   13    0  2304  2290 255   -1    0   539   553  21
 -17   -1  3178  3247  83   13    2  1939  1978  56    0   -3  3690  3572 132
 -14   -2   743   725  39   15    0  4591  4531 533    0   -1  5481  5516 148
```

```
   k    l     Fo     Fc sigF   k    l     Fo     Fc sigF   k    l     Fo     Fc sigF

   1    0    442    322  25   0   -3   1151   1162  52  18    0   3887   3882 497
   2    1  12363  11353 669   0   -1   1617   1642  42
   4    1   3863   3827 112   3    0   4942   5021 125 ******* h =    9 *******
   5    2   3501   3566  90   3    2   3910   3860 100
   6    1   2191   2109  83   4    1   1217   1188  79 -14   -1   4382   4360 112
   6    3   1446   1457  48   5    0   3839   3916 124 -13   -2   1027    948  52
   7    0   1272   1233 117   5    2   3204   3161 106 -13    0   1103   1084  75
   7    2    957   1000  35   7    2    515    557  63 -12   -1   3365   3208 146
   8    1   1448   1420  54   8    1   2587   2550  86  -9   -2    316    177  45
  11    0   5393   5066 276  12    1   3048   3049 185  -8   -1   1295   1276  53
  11    2   4344   4275 111  14    1   1689   1690  51  -6   -3   4902   5164 174
  13    2   3762   3702  98  15    2    439    322  57  -6   -1   7430   6972 213
                              17    0   1137   1056  70  -5   -2   1014   1051  66
******* h =    6 *******                                -5    0   1309   1302  61
                           ******* h =    8 *******     -4   -3   1633   1646  74
 -11   -1   1880   1885  53                             -3    0   2474   2420 123
  -9   -3   1369   1462  48 -16    0   1978   2051  56  -2   -1    561    505  25
  -9   -1   2028   2025  55 -15   -1   1011    908  39  -1   -2    505    532  59
  -8    0   3603   3645  99 -14    0    407    405  46  -1    0    629    628  45
  -7   -3    505    511  34 -13   -1   4502   4472 115   1    2    896    862  68
  -7   -1    704    649  54 -12   -2   1649   1622  51   2    3    549    531  32
  -4    0    463    428  29 -12    0   1792   1865  51   3    0   2111   2189  70
  -3   -3   1357   1393  47 -11   -1    850    883  87   5    0   8654   8454 217
  -3   -1   1924   2058  76 -10   -2   1582   1574  62   7    2   3415   3349 132
  -2   -2   5905   5927 157  -9   -3   2038   2073  58   8    1   2749   2741 181
  -1   -1   1193   1240  51  -8   -2    611    613  30  11    2   2383   2285 139
   0   -2    574    548  23  -8    0    739    720  25  13    0   3235   3204 163
   0    0    804    814  25  -7   -3   1747   1857 112  17    0   2939   3032 284
   1    1   1014    981  44  -6    0    930    882  52
   1    3    549    598  49  -5   -3    944    985  43 ******* h =   10 *******
   4    2    373    327  35  -3   -3    435    418  50
   5    3    433    469  38  -3   -1    630    595  43 -14   -2   2448   2438  94
   8    2    711    715  29  -2    0   4630   4412 198 -13   -1   1091   1061  43
  12    0   1118   1106 122  -1   -1   1638   1682  44 -12   -2   2061   2003 132
  14    0    683    660  81   0   -2   2353   2289  62 -12    0   2248   2302  80
  15    1   1657   1688 129   0    0   2904   2831  81 -10   -2   2487   2445 135
  17    1   1001    977 125   1    1    851    914  31 -10    0   2730   2850  95
  18    0   1666   1669 188   2    0   4320   4402 242  -9   -1   1199   1170 112
                               2    2   3572   3451 184  -8   -2    523    538  64
******* h =    7 *******       3    1    895    893  49  -8    0    646    639  49
                               3    3    607    605  30  -7   -3   3491   3649 211
 -17    0   1593   1640  50   4    0   5275   5333 133  -7   -1   4849   4809 346
 -16   -1    559    588  68   4    2   4378   4327 132  -6   -2   1430   1445  46
 -15    0   1452   1482  45   6    2   3067   3039 118  -6    0   1804   1744  82
 -10   -1   1715   1737  53   9    3    986   1008 104  -5   -3   4595   4742 137
  -9    0   3988   3978 102  11    1    415    341  35  -5   -1   6647   6350 302
  -8   -3   3505   3754 129  12    0   1589   1647 154  -4    0   1514   1464  77
  -8   -1   5316   5208 188  13    1   1685   1592  77  -3   -3   2455   2426  68
  -7    0    665    717  68  14    2    394    311  45  -3   -1   3363   3328  86
  -4   -1   1106   1169  65  17    1   5167   5085 362  -2   -2    844    848  62
```

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
-2	0	1022	1021	69	-6	-2	903	916	35	0	0	863	843	82
-1	-1	937	923	32	-4	-2	864	868	34	1	1	470	401	56
0	-2	1508	1556	43	-4	0	1019	1007	103	2	0	859	859	34
0	0	1910	1915	75	-3	-3	1228	1195	97	3	1	985	1014	36
3	1	498	536	25	-3	-1	1632	1578	89	4	2	755	746	31
4	0	2952	3072	138	-2	-2	647	610	48	6	0	1713	1846	88
5	1	2500	2439	66	-2	0	781	711	62	6	2	1562	1590	50
5	3	1770	1806	53	-1	-1	371	318	34	7	1	3744	3705	97
6	0	4090	4173	104	0	-2	3017	3126	87	10	0	2699	2746	72
6	2	3676	3538	216	4	0	2287	2326	97	12	0	447	360	36
7	3	1287	1330	46	4	2	1999	1969	65					
8	0	1892	1871	52	5	3	1998	2028	58	******* h = 15 *******				
11	1	626	580	29	7	1	4775	4706	122					
12	2	5190	5065	249	11	1	1716	1665	51	-13	0	1336	1352	47
14	0	1640	1567	50	12	2	648	549	35	-12	-1	2270	2231	97
14	2	1488	1404	58	13	1	2104	2133	60	-9	0	1297	1335	152
15	1	1256	1196	124	14	0	788	787	50	-8	-1	1288	1267	74
16	0	1286	1199	109						-2	-1	477	420	30
					******* h = 13 *******					-1	0	3184	3222	412
******* h = 11 *******										0	1	2266	2329	89
					-11	-2	3557	3575	229	1	2	1343	1305	45
-14	-1	523	509	55	-11	0	3958	4039	127	2	1	674	677	27
-13	-2	564	473	38	-10	-1	3497	3445	184	3	0	4941	5037	195
-13	0	487	527	36	-9	-2	2880	2815	137	4	1	1016	1074	53
-11	0	5664	5645	151	-7	-2	927	910	43	5	0	3986	4079	151
-9	0	2621	2642	136	-6	-1	1519	1483	84	6	1	1317	1369	45
-7	-2	1351	1363	137	-5	0	4387	4283	578	7	2	1290	1313	48
-7	0	1592	1593	103	-4	-1	1987	1998	110	9	0	579	532	31
-6	-3	1653	1691	70	-2	-1	1030	1013	38	10	1	2479	2472	68
-6	-1	2176	2185	135	0	-3	900	918	32	11	0	643	685	54
1	0	736	728	80	1	0	1012	1055	73					
1	2	635	594	28	1	2	869	885	33	******* h = 16 *******				
2	1	4845	4849	123	3	2	400	332	38					
2	3	3562	3598	93	4	1	2534	2539	67	-9	-1	3344	3287	194
6	3	1345	1400	93	5	0	582	620	27	-7	-1	4597	4492	318
9	0	622	642	79	6	1	3003	3019	79	-5	-1	2347	2342	150
9	2	619	566	32	7	0	2002	2107	55	-4	0	1800	1804	177
10	1	1887	1892	54	7	2	1810	1827	95	-3	-1	3510	3467	200
11	2	5022	4938	304	13	0	1158	1130	44	-2	0	709	693	101
12	1	1963	1987	70	14	1	1585	1514	51	0	2	2691	2699	89
15	0	926	918	38						2	0	3907	4010	135
					******* h = 14 *******					2	2	3529	3537	92
******* h = 12 *******										6	0	1268	1254	44
					-14	0	1137	1137	46	6	2	1175	1102	46
-15	-1	1504	1472	133	-9	-1	1922	1906	104	10	0	2601	2677	70
-13	-1	571	525	34	-6	-2	607	564	33					
-12	0	556	601	34	-5	-1	2607	2637	152	******* h = 17 *******				
-10	0	5839	5761	239	-4	-2	5636	5528	143					
-9	-1	823	834	92	-4	0	6569	6368	706	-1	-2	1308	1367	131
-8	-2	1467	1412	56	-3	-1	337	319	41	-1	0	1477	1553	145

```
 k    l    Fo     Fc   sigF  k    l    Fo     Fc   sigF  k    l    Fo     Fc   sigF

 0    1  2816   2842   90
 1    0  2044   2142   97
 1    2  1927   1890   57
 3    0  2173   2244   66
 5    0   824    849   35
 6    1  1414   1457   48
 9    0  2491   2544   68

******* h =  18 *******

-7   -1  1771   1785  127
-3   -1  3261   3215  213
-1   -1  5071   4970  220
 0    0   804    778   44
 1    1  1788   1741   53
 2    0   598    580   31
 3    1  2079   2105   59
 6    0  1345   1364   46
 7    1  1131   1119   47
 8    0  1406   1409   98

******* h =  19 *******

-3    0   952   1037   72
-2   -1  1575   1608  150
 1    0   992   1083   96
```

APPENDIX F OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (x10) FOR $Nb_xTa_{2-x}S$ ($x \approx 0.2$)

k	l	Fo	Fc	sigF
^^^^^^^ h = 0 ^^^^^^^				
0	2	4159	4151	67
0	4	1894	1889	51
0	6	5296	5202	90
0	8	4461	4479	83
0	10	3753	3717	82
0	12	8918	8844	0
0	14	1584	1521	72
0	16	2359	2389	0
0	18	3775	3688	0
0	20	5152	5238	0
0	22	1355	1329	0
0	24	1980	2097	95
2	-19	2931	2942	0
2	1	6060	6019	99
2	3	5614	5501	0
2	4	1578	1569	50
2	5	2976	2896	75
2	7	1061	916	0
2	9	1090	1037	0
2	11	3157	3164	83
2	13	2578	2444	78
2	15	4621	4678	0
2	17	2155	2086	83
2	19	2976	2943	0
4	-20	3172	3366	0
4	-18	3168	3338	0
4	-16	1241	1321	0
4	-15	1593	1719	0
4	-14	1398	1395	0
4	-13	1217	924	0
4	-12	5646	5665	0
4	-11	1352	1515	0
4	-10	4081	4113	0
4	-8	2625	2599	95
4	-3	1567	1532	81
4	-2	4011	3917	0
4	0	8895	8971	0
4	1	2228	2272	61
4	2	3771	3918	0
4	3	1456	1532	89
4	5	1037	992	94
4	6	3593	3462	0
4	8	2659	2600	98
4	10	4084	4115	0
4	11	1474	1516	0
4	12	5650	5669	0
4	15	1668	1720	0
4	18	3370	3340	0
4	20	3145	3367	0
6	-16	2503	2612	0
6	-15	2449	2399	0
6	-11	1628	1554	0
6	-5	1457	1349	0
6	0	3563	3467	0
6	1	2417	2347	66
6	3	2182	2179	67
6	4	2757	2855	78
6	5	1405	1349	0
6	11	1409	1555	0
6	12	1876	1850	0
6	15	2480	2400	0
6	16	2614	2614	0
8	-11	1452	1507	0
8	-10	1674	1506	0
8	-8	1667	1916	0
8	0	4452	4372	0
8	1	2484	2426	76
8	2	1584	1600	0
8	3	1910	1878	0
8	6	1945	1940	90
^^^^^^^ h = 1 ^^^^^^^				
-8	-6	1217	1258	0
-7	-14	1619	1570	0
-7	-4	1202	994	0
-7	6	3729	3683	0
-7	10	2176	2149	0
-7	14	1820	1569	0
-6	-11	2190	2029	0
-6	-10	1444	1351	0
-6	-5	1287	1186	0
-5	-13	1258	1571	0
-5	-11	1418	1416	0
-5	-5	3993	3987	0
-5	-4	1197	1396	0
-5	11	1342	1415	0
-5	13	1646	1570	0
-4	-14	1192	1163	0
-4	-13	1306	1255	0
-4	-10	1782	1675	0
-4	-6	3956	3956	0
-4	-5	1115	1169	0
-4	-3	1050	959	0
-4	0	3072	2952	0
-3	-22	1749	1703	0
-3	-17	1241	1230	0
-3	-16	1987	1985	0
-3	-13	1516	1513	81
-3	-7	2509	2475	82
-3	-6	4972	5052	0
-3	-4	2943	2897	79
-3	7	2642	2474	0
-3	10	3336	3249	0
-3	22	1366	1702	0
-2	-23	2057	2006	91
-2	-21	3086	2973	0
-2	-17	1907	1922	0
-2	-9	5774	5949	0
-2	-6	1479	1473	55
-2	-5	1609	1650	0
-2	-4	1218	1158	96
-2	-3	6594	6685	0
-2	9	6098	5947	0
-2	17	1956	1922	0
-1	-11	1338	1373	0
-1	-9	2385	2391	63
-1	-7	4020	4086	0
-1	-4	1630	1583	47
-1	11	1302	1373	98
0	-22	1090	1270	0
0	-18	2017	1924	83
0	-10	1922	1875	74
0	-6	4455	4453	0
0	-2	984	912	88
0	0	3630	3511	83
0	12	2644	2551	0
0	24	1395	1404	0
1	-10	2144	2136	77
1	5	5365	5460	0
1	6	5607	5664	0
1	10	2056	2137	75
1	13	1788	2115	0
1	21	1737	1553	88
2	-21	2922	2972	0
2	1	2784	2750	97
2	11	3088	3135	0
2	15	3390	3356	82
3	-16	1813	1984	0
3	2	1341	1335	0
3	5	3012	2978	80
3	10	3113	3251	93
3	14	1740	1721	0
3	18	1355	1393	0
4	-18	1557	1648	0
4	-14	1196	1162	0
4	-12	2030	2003	97
4	-7	1574	1525	0

k	l	Fo	Fc	sigF
4	7	1566	1526	95
4	12	2033	2004	97
5	-15	1411	1576	0
5	-9	2109	2205	0
5	-7	2873	2948	0
5	6	1056	1084	0
5	7	2858	2949	0
5	9	2251	2206	88
6	-15	2298	2279	0
6	-11	2106	2027	0
6	-9	3801	3550	0
6	1	1594	1516	81
6	3	3753	3779	0
6	9	3525	3552	0
6	12	1107	607	0
6	15	2131	2281	0
7	6	3692	3685	0
7	10	2271	2150	0

^^^^^^^ h = 2 ^^^^^^^

k	l	Fo	Fc	sigF
-8	5	1928	1891	0
-8	6	1574	1967	0
-6	-9	2929	2955	0
-6	-6	1819	1766	0
-6	-2	1164	1020	0
-6	11	2768	2674	0
-5	-18	1441	730	0
-5	-9	2257	2324	93
-5	-3	3879	3864	0
-5	-1	1711	1706	0
-5	15	2961	2901	0
-4	-7	1300	1192	0
-4	-6	3961	4006	0
-4	-4	2888	2957	0
-3	-15	1906	1838	0
-3	-14	1316	1325	0
-3	-12	2220	2066	0
-3	-10	2607	2607	84
-3	-5	1303	1354	84
-3	-3	2548	2571	93
-3	-2	2687	2654	93
-3	15	1813	1837	0
-3	16	3565	3555	0
-2	-11	4777	4714	98
-2	-1	5298	5258	0
-1	-15	3247	3192	0
-1	-14	1200	1512	0
-1	-8	2183	2206	70
-1	-3	4735	4852	0
-1	-2	1783	1894	86
-1	-1	1517	1584	0
-1	4	3868	3914	0
0	-24	1435	1399	0
0	-22	1316	1170	0
0	-20	1397	746	0
0	-18	1964	1904	99
0	-16	2300	2245	88
0	-6	6955	7058	0
0	4	3366	3327	0
0	10	2904	2846	0
0	14	2982	2994	98
1	-15	3212	3191	0
1	4	3898	3915	0
1	5	1743	1726	52
1	9	2629	2697	67
1	10	1386	1338	70
1	16	2753	2823	75
2	3	3364	3391	0
2	9	5412	5508	0
2	19	1552	1637	0
2	21	3308	3413	0
2	23	1773	1738	0
3	-3	2534	2570	0
3	0	4065	4124	0
3	4	4490	4441	0
3	8	1257	1262	78
3	9	1759	1666	88
3	16	3465	3557	0
4	-16	2182	2202	0
4	-14	1904	1802	0
4	-10	1807	1739	97
4	5	1951	1855	75
4	8	948	824	0
4	10	1775	1740	98
4	14	1792	1803	0
4	16	2115	2203	0
4	17	1352	777	0
5	-17	1414	1382	0
5	-9	2315	2323	0
5	4	1724	1717	95
5	5	1049	1048	0
5	15	2952	2903	0
6	-10	1905	1969	0
6	-9	2898	2953	0
6	1	2739	2790	89
6	3	1890	1837	0
6	11	2529	2676	0
7	0	1638	1864	0
7	4	2373	2534	0
8	5	1862	1891	0
8	6	1867	1967	0

^^^^^^^ h = 3 ^^^^^^^

k	l	Fo	Fc	sigF
-8	-9	1350	1009	0
-8	-4	1234	1347	0
-8	8	1702	1592	0
-7	-4	2495	2466	0
-7	0	3976	4054	0
-5	-15	2752	2636	0
-5	-11	2023	2258	0
-5	-7	1217	986	0
-5	-1	3491	3509	0
-5	11	2304	2257	0
-5	19	2010	2228	0
-4	-12	2775	3005	0
-4	-10	4189	4250	0
-4	-4	2517	2661	0
-4	-2	3779	3829	0
-4	0	4499	4474	0
-4	2	3866	3829	0
-4	8	3190	3363	0
-4	12	2790	3003	0
-4	14	1383	1388	0
-4	20	2669	2549	0
-3	-20	1743	1541	0
-3	-14	1259	1021	0
-3	-12	3088	3092	0
-3	-3	1227	1109	0
-3	0	5542	5414	0
-3	16	2811	3022	0
-2	-21	1433	1252	0
-2	-11	1367	1430	96
-2	-7	1724	1720	61
-2	-1	1208	1229	0
-1	-16	2692	2669	0
-1	-11	2666	2654	0
-1	-6	1207	1243	70
-1	-5	942	886	98
-1	-4	3237	3257	0
-1	0	5904	5890	0
-1	19	2557	2557	0
0	-22	3369	3243	0
0	-18	1987	1864	98
0	-16	1375	1339	0
0	-14	2122	2133	85
0	-12	3269	3280	0
0	-10	6268	6236	0
0	-2	6144	6190	0

k	l	Fo	Fc	sigF
0	0	5940	5746	0
0	4	2539	2595	0
0	6	1261	1380	0
0	8	3785	3831	0
0	20	2816	2819	77
1	1	4742	4818	99
1	3	3049	3083	82
1	7	1600	1621	59
1	12	2888	2917	0
1	13	2352	2378	70
1	15	2678	2732	0
1	19	2743	2557	0
2	5	2627	2604	0
2	9	1769	1766	0
3	-19	1531	1511	0
3	1	2611	2599	73
3	4	3193	3280	0
3	7	1217	1245	0
3	11	1582	1502	0
3	13	1657	1544	0
3	16	2832	3024	0
4	8	3521	3365	0
4	16	1598	1632	0
4	20	2550	2551	0
5	-15	2671	2635	0
5	-13	1890	1845	0
5	3	2396	2462	0
5	13	1988	1846	0
5	19	2154	2229	0
6	-6	1557	1425	0
6	6	1442	1426	0
7	12	2210	2426	0
8	0	1943	1923	0
8	2	2251	2255	0

------- h = 4 -------

k	l	Fo	Fc	sigF
-8	-2	1363	787	0
-6	-15	1318	1675	0
-6	-7	3169	3295	0
-6	-6	2110	2145	97
-6	-5	3552	3585	0
-6	3	1535	1325	0
-5	-9	2048	2071	0
-4	-10	2677	2760	0
-4	-2	1553	1611	0
-3	-18	1615	1455	0
-3	-14	1638	1628	0
-3	-13	1171	1162	0
-3	-5	2138	2124	0
-2	-13	3984	4207	0
-2	-7	5752	5904	0
-2	-1	2908	3039	82
-1	-9	1855	1861	0
-1	-6	2465	2523	0
-1	-4	1481	1510	0
-1	-2	1158	982	0
-1	13	1901	1839	0
0	2	2756	2770	0
0	6	4593	4671	0
0	8	989	989	0
0	10	4547	4574	0
0	22	2323	2387	0
1	5	3700	3745	0
1	7	3146	3129	0
1	10	1710	1860	0
1	13	1974	1839	97
1	19	1078	932	0
1	21	1293	1210	0
2	5	6251	6395	0
2	15	2232	2363	0
2	17	2734	2719	0
2	19	2766	2597	0
3	-18	1524	1455	0
3	2	1173	1117	0
3	6	4652	4679	0
3	7	1763	1813	0
3	10	2912	2892	0
4	6	2662	2814	0
5	5	2977	3018	0
5	7	2589	2686	0
5	17	1336	1079	0
6	-15	1781	1674	0
6	-13	2515	2523	0
6	13	2345	2524	0
7	6	2203	2394	0

------- h = 5 -------

k	l	Fo	Fc	sigF
-8	-3	1636	1686	0
-6	-13	2290	2128	0
-6	-1	3141	3168	90
-6	13	1986	2126	0
-5	-2	1289	1222	0
-4	-16	3905	4035	0
-4	-14	1822	1912	0
-4	-4	4424	4643	0
-4	-2	2091	2144	92
-4	-1	1571	1539	0
-4	0	3588	3537	0
-4	16	3883	4033	0
-3	-12	1598	1600	0
-3	-10	2253	2158	0
-3	-9	1279	1245	0
-3	0	2925	2768	0
-3	8	1761	1565	0
-2	-15	2217	2365	0
-2	-7	2184	2218	96
-2	-3	2061	1999	0
-2	0	2395	2440	0
-2	19	3290	3206	0
-1	-22	1217	1395	0
-1	-12	1468	1313	0
-1	0	2114	2144	0
0	-14	2624	2561	76
0	-12	1677	1759	84
0	-6	1536	1585	0
0	-2	2026	1939	0
0	0	3843	3798	0
0	4	6009	6135	0
0	8	2317	2342	0
0	16	4993	5025	0
1	1	1934	1908	78
1	2	2453	2431	78
1	4	1010	982	0
1	9	1705	1842	0
1	10	2551	2716	0
1	11	1623	1708	0
1	21	1245	1234	0
2	1	5592	5587	0
2	11	3626	3632	0
2	13	2988	3120	0
2	19	3133	3207	0
2	21	1542	1257	0
3	-20	1494	1541	0
3	-12	1369	1600	0
3	2	1723	1696	98
3	20	1684	1542	0
4	-12	1721	1700	0
4	3	1967	1896	0
4	8	1469	1380	0
4	10	1607	1675	0
4	12	1565	1700	0
5	0	1671	1746	0
5	1	1541	1502	0
5	8	1394	1355	0
6	7	1638	1640	0
6	11	2246	2073	0
7	-10	1381	1704	0
8	4	2042	2035	0

```
  k   l    Fo    Fc sigF      k   l    Fo    Fc sigF      k   l    Fo    Fc sigF

                             -5  -9  2013  1926    0     -1  11  2208  2066    0
------- h =  6 -------       -4 -10  2396  2566    0      0  -6  2350  2368    0
                             -4  -6  2751  2765    0      0  -4  1810  1721    0
 -7  -5  1259   946    0     -4   9  1615  1431    0      0   0  1779  1603    0
 -5 -11  2229  2211    0     -4  10  2564  2565    0      0   2  1836  1819   98
 -5  -1  2022  1828    0     -3  -3  1567  1560    0      0   8  1719  1492    0
 -4 -16  2935  2964    0     -3   0  1472  1413    0      0  10  1457  1390    0
 -4 -10  2478  2615    0     -3  10  1325  1113    0      0  12  1564  1321    0
 -4  -6  1316  1471    0     -2 -17  2614  2879    0      0  14  1648  1558    0
 -4  -3  1152  1081    0     -2 -15  2994  3090    0      1   0  4052  4000    0
 -3 -10  3072  3077    0     -2 -13  2860  2846    0      1   3  1941  1828    0
 -3  -9  1998  2002    0     -2  -7  4116  4424    0      1  10  1770  1652    0
 -3  -6  2882  2971    0     -2  -5  5267  5516    0      1  11  2013  2066    0
 -3  -2  1509  1620    0     -1 -10  1345  1456    0      1  12  2688  2728    0
 -3  -1  1749  1752    0     -1  -9  2331  2281   83      1  15  2011  2127    0
 -3   0  1666  1644    0     -1  -6  1596  1748    0      2  12  1225    88    0
 -2  -1  2569  2518    0     -1   0  2230  2089    0      3   0  5195  5423    0
 -1 -21  2134  2191   96      0 -16  1160  1339    0      3   1  1623  1552    0
 -1 -10  2373  2441    0      0 -10  2829  2905    0      5  11  1674  1906    0
 -1  -9  3212  3211    0      0  -2  1438  1413    0      5  12  1376  1335    0
 -1  -6  1665  1818    0      0   0  2028  1973    0
 -1  -3  1599  1632    0      0   6  3190  3225    0    ------- h =  9 -------
 -1  -1  2547  2476   75      1   3  2474  2459   81
  0  -4  5841  5914    0      1  12  1540  1448    0     -5  -3  1440  1678    0
  0  -2  3716  3740    0      2 -17  2872  2878    0     -4  -5  1198  1152    0
  0   8  3025  3066    0      2   3  2255  2302   86     -3  -9  1573  1761    0
  0  10  3511  3681    0      2  19  1775  1541    0     -3  -3  1790  1814    0
  0  14  2025  2072   87      3   4  1191   983    0     -2  -7  1459  1257    0
  0  16  4512  4597    0      3   6  2031  2074    0     -2  -1  1608  1428    0
  1   2  1514  1518    0      5   3  2117  1986    0     -1 -15  1468  1221    0
  1   5  1583  1559   97      6   5  3176  3368    0     -1  -4  1408  1026    0
  1  11  2551  2617    0      6   7  2852  2911    0     -1  -1  1266   881    0
  2 -15  1448  1805    0                                  0 -14  2397  2348    0
  2   3  2335  2432    0    ------- h =  8 -------        0  -4  2312  2292    0
  2   7  1614  1738   97                                  0   6  5124  4831    0
  2   9  1391  1229    0     -5  -3  2313  2033    0      0  16  1633  1701    0
  2  13  1859  1933    0     -5  -1  3038  2975   90      1   3  2012  2260    0
  2  15  1707  1805    0     -5   0  1860  1924    0      1   9  2319  2368   98
  2  19  2058  1957   94     -5  11  1599  1905    0      1  10  1649  1545    0
  4 -10  2619  2614    0     -4  -8  1682  1521    0      2   3  1278  1362    0
  4   2  3002  2996    0     -4  -4  1319  1549    0      2   5  2053  1808    0
  4   4  3493  3540    0     -4   0  1931  1841    0      2   9  2643  2778    0
  4   8  2151  2253    0     -3 -16  2219  2240    0      2  11  1871  1912    0
  4  14  2322  2341    0     -3 -13  1344   838    0      3   2  1214  1091    0
  5   9  2442  2745    0     -3 -12  3204  3323    0      4   4  1900  1932    0
  6   1  1464  1255    0     -3  -6  1488  1455    0      4   6  3590  3670    0
  7   6  1748  1922    0     -3  -4  1936  2071    0
                             -1 -13  1699  1590    0    ------- h = 10 -------
------- h =  7 -------       -1  -2  1421  1270    0
                             -1  -1  3046  3082    0     -2  -9  2833  2781   91
```

```
  k   l    Fo    Fc  sigF  k    l    Fo     Fc  sigF  k    l    Fo     Fc  sigF

 -2  -3  3994  3958  0
 -1 -11  1260  1276  0
 -1  -6  1481  1558  0
 -1  -5  1323  1106  0
  0   0  3224  3094  0
  0   4  2048  2153  0
  2  -5  2159  2259  0
  2   5  2240  2259  0
  3   6  2100  1934  0
  4   0  2091  1906  0
^^^^^^^ h =  11 ^^^^^^^

 -2  -3  2223  1846  0
  0   0  4219  4222  0
  0   6  1598  1533  0
  1   5  1197   929  0
```