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Structural Studies of the Metal-rich Region in the Ternary
Ta-Nb-S System

by

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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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1991

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

Xiaoqiang Yao

**Under the Supervision of Hugo F. Franzen
from the Department of Chemistry
Iowa State University**

Six new solid solution type compounds have been prepared using high temperature techniques and characterized by means of single crystal x-ray techniques during a study of the metal-rich region of the ternary Ta-Nb-S system.

The structures of $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$; Pnma; $Z = 4$; $a = 31.2100(54)$, $b = 3.3507(7)$ and $c = 9.5918(19)\text{\AA}$) and $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$; Pnma; $Z = 4$; $a = 9.5911(26)$, $b = 3.3637(10)$ and $c = 32.8251(74)\text{\AA}$) are reminiscent of niobium-rich sulfides, rather than of tantalum-rich sulfides. The coordinations of sulfur are capped trigonal prismatic while the metal coordinations are capped distorted cubic prismatic for $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, and capped distorted cubic prismatic and pentagonal prismatic for $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$.

The structures of $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$; $I4/mmm$; $Z = 2$; $a = 3.3203(9)$ and $c = 21.619(12)\text{\AA}$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$; $P4/nmm$; $Z = 2$; $a = 3.3304(7)$ and $c = 9.0928(94)\text{\AA}$) contain homoatomic layers sequenced S-M3-M2-M1-M2-M3-S (M is mixed Nb, Ta) generating

seven-layer sheets and S-M2-M1-M1-M2-S generating six-layer sheets, respectively, stacked along [001]. Both of the structures are closely related to bcc. Weak S-S interactions at 3.26 and 3.19 Å between sheets contrast with the M-M binding within and between the sheets in these two novel layered compounds. The former are presumably responsible for the observed graphitic slippage of the samples.

$\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$; I4/mmm; $Z = 2$; $a = 16.817(2)$ and $c = 3.3450(9)$ Å) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$; Pbcm; $Z = 12$; $a = 7.3724(11)$, $b = 5.5757$ and $c = 15.1981(23)$ Å) are isostructural with Nb_{21}S_8 and Ta_2S , respectively.

Extended Hückel band calculations were carried out for two layered compounds, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$). Based upon band calculations metallic properties can be expected for these two layered compounds. The relative preference of the metal sites for the two metal elements (Ta, Nb) in two layered compounds is explained by the results of the band calculations.

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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, CaF₂, 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, Sc₇Cl₁₀,¹ Tb₂Cl₃,² and Gd₂Cl₃.³ 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 -V₃S and β -V₃S,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, Hf₂S.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-centered 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 $\alpha\text{-Ta}_6\text{S}$ (monoclinic form),²⁰ $\beta\text{-Ta}_6\text{S}$ (triclinic form)²¹ and $\text{Ta}_3\text{S}_{2-x}$ ($x = 0.2$).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 occurrence 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 $\alpha\text{-Ta}_6\text{S}$ (monoclinic form),²⁰ $\beta\text{-Ta}_6\text{S}$ (triclinic form)²¹ and $\text{Ta}_3\text{S}_{2-x}$ ($x = 0.2$),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 $\alpha\text{-Ta}_6\text{S}$ (monoclinic form),²⁰ $\beta\text{-Ta}_6\text{S}$ (triclinic form)²¹ and $\text{Ta}_3\text{S}_{2-x}$ ($x = 0.2$),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 chalcogenides and phosphides and has been found only in Ta_2S , $\text{Ta}_3\text{S}_{2-x}$ ($x = 0.2$) and Nb_2Se .²³ Houghbanks 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 $\frac{1}{\infty}[\text{Ta}_5\text{TaS}_5]$ 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 $\infty^1[\text{Ta}_5\text{TaS}_5]$ 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 $\alpha\text{-V}_3\text{S}$,⁴ $\beta\text{-V}_3\text{S}^4$ 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 similar 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 similar 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 Ta₉ 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 -Ta₆S, i.e., some metal positions occupied by two kinds of metal elements. The tantalum clusters in the compounds are similar to those in Ta₆S, 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 -Ta₆S 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 -Ta₆S 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, M₂Ta₁₁Se₈ (M = Fe, Co and Ni).³⁷

In the structure of M₂Ta₁₁Se₈ the cluster of MTa₉, as in M₂Ta₉S₆, also exists, but hexagonal networks are not formed by the MTa₉ clusters in the selenide. The structure of M₂Ta₁₁Se₈ is built from clusters of MTa₉ 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 selenides low coordination chalcogen atoms exist.

The substitutional solid solution type early transition metal-rich chalcogenides can be divided into two categories. One category includes the compounds which are isostructural with known binary metal-rich compounds, e.g. $\text{Hf}_x\text{Ti}_{21-x}\text{S}_8$ ($x = 7.47$)³⁸ (Nb_{21}S_8 ¹⁰-type), $\text{Hf}_{2-x}\text{Ti}_x\text{S}_8$ (Hf_2S_5 -type), $\text{M}_x\text{Nb}_6\text{S}_{3-x}$ ($\text{M} = \text{Fe}, \text{Co}$ and Ni ; $x \approx 1$)³⁹ and $\text{Cu}_x\text{Nb}_6\text{S}_{3-x}$ ($x = 0.46$)⁴⁰ (Ta_2P^{13} -type), $\text{M}_x\text{Ta}_6\text{S}_{6-x}$ ($\text{M} = \text{V}$ and Cr , $x \approx 0.32$)⁴¹ ($\beta\text{-Ta}_6\text{S}_8$ ²¹-type) and $\text{V}_x\text{Nb}_{14-x}\text{S}_5$ ($x = 3.14$)⁴² (Nb_{14}S_5 ¹¹-type). The second category includes the compounds which exhibit new structure types, e.g. $\text{M}_x\text{Ta}_6\text{S}_{6-x}$ ($\text{M} = \text{V}$ and Cr , $x \approx 1$)³⁶ and $\text{Nb}_9\text{Ni}_{2-x}\text{S}_{3+x}$ ($x = 0.63$)³⁹.

In the structure of $\text{Nb}_9\text{Ni}_{2-x}\text{S}_{3+x}$ ³⁹ clusters of NiNb_9 similar to those in $\text{M}_2\text{Ta}_9\text{S}_6$ and $\text{M}_2\text{Ta}_{11}\text{Se}_8$ 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 $\text{M}_x\text{Nb}_6\text{S}_{3-x}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ and Cu)^{39,40} and $\text{Nb}_9\text{Ni}_{2-x}\text{S}_{3+x}$.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
$\text{Fe}_x\text{Nb}_6\text{S}_{3-x}$ ($x \approx 1$)	Ta_2P	Pnnm	$a = 11.620$ $b = 14.512$ $c = 3.384$	39
$\text{Co}_x\text{Nb}_6\text{S}_{3-x}$ ($x \approx 1$)	Ta_2P	Pnnm	$a = 11.606$ $b = 14.463$ $c = 3.390$	39
$\text{Ni}_x\text{Nb}_6\text{S}_{3-x}$ ($x \approx 1$)	Ta_2P	Pnnm	$a = 11.625$ $b = 14.429$ $c = 3.394$	39
$\text{Cu}_x\text{Nb}_6\text{S}_{3-x}$ ($x \approx 0.46$)	Ta_2P	Pnnm	$a = 11.613$ $b = 14.434$ $c = 3.395$	40
$\text{Hf}_x\text{Ti}_{21-x}\text{S}_8$ ($x \approx 7.47$)	Nb_{21}S_8	I4/m	$a = 16.970$ $c = 3.362$	38
$\text{Hf}_{2-x}\text{Ti}_x\text{S}$	Hf_2S	$\text{P}6_3/\text{mmc}$	$a = 3.362$ $c = 11.751$	38
$\text{V}_x\text{Nb}_{14-x}\text{S}_5$ ($x \approx 3.14$)	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
$\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$)	Nb_{21}S_8	I4/m	$a = 16.820$ $c = 3.341$	this work
$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$)	Ta_2S	Pbcm	$a = 7.372$ $b = 5.576$ $c = 15.198$	this work
$\text{Nb}_x\text{Ta}_{6-x}\text{S}$	$\alpha\text{-Ta}_6\text{S}$	C2/c	$a = 14.121$ $b = 5.285$ $c = 14.833$ $\beta = 117.97^\circ$	this work
$\text{Nb}_x\text{Ta}_{6-x}\text{S}$	$\beta\text{-Ta}_6\text{S}$	P $\bar{1}$	$a = 5.258$ $b = 7.589$ $c = 7.626$ $\alpha = 59.31^\circ$ $\beta = 68.67^\circ$ $\gamma = 77.36^\circ$	this work
$\text{V}_x\text{Ta}_{6-x}\text{S}$ ($x \approx 0.32$)	$\beta\text{-Ta}_6\text{S}$	P $\bar{1}$	$a = 5.205$ $b = 7.560$ $c = 7.609$ $\alpha = 59.38^\circ$ $\beta = 68.59^\circ$ $\gamma = 77.74^\circ$	41

Table 1 (continued)

Compound	Structure type	Space group	Lattice parameters Å	Reference
$\text{Cr}_x\text{Ta}_{6-x}\text{S}$ ($x \approx 0.34$)	$\beta\text{-Ta}_6\text{S}$	PI	$a = 5.143$ $b = 7.544$ $c = 7.602$ $\alpha = 59.47^\circ$ $\beta = 68.47^\circ$ $\gamma = 78.14^\circ$	41
$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)	Ta_2Se	P4/nmm	$a = 3.330$ $c = 9.093$	this work
$\text{V}_x\text{Ta}_{6-x}\text{S}$ ($x \approx 2.25$)	$\text{V}_x\text{Ta}_{6-x}\text{S}$	C2/c	$a = 7.431$ $b = 12.746$ $c = 4.977$ $\beta = 111.95^\circ$	36
$\text{Cr}_x\text{Ta}_{6-x}\text{S}$ ($x \approx 0.96$)	$\text{V}_x\text{Ta}_{6-x}\text{S}$	C2/c	$a = 7.510$ $b = 12.911$ $c = 5.056$ $\beta = 111.31^\circ$	36
$\text{Nb}_9\text{Ni}_{2-x}\text{S}_{3+x}$ ($x \approx 0.63$)	$\text{Nb}_9\text{Ni}_{2-x}\text{S}_{3+x}$	Cmcm	$a = 3.343$ $b = 14.928$ $c = 17.687$	39

Table 1 (continued)

Compound	Structure type	Space group	Lattice parameters Å	Reference
$\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$)	$\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$	Pnma	a = 31.210 b = 3.351 c = 9.592	this work
$\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$)	$\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$	Pnma	a = 9.591 b = 3.364 c = 32.825	this work
$\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)	$\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$	I4/mmm	a = 3.320 c = 21.619	this work

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, $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$), $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$), $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$), $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$), $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$) found in the ternary Ta-Nb-S system.

The second part presents results of extended Hückel band calculations for two layered compounds, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (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 $(\text{Nb}, \text{Ta})_x\text{S}_y$ ($x > y$) 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 ($> 1200^{\circ}\text{C}$). 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: $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$. If the formation of the solid from neighboring phases is endothermic and endoentropic, the reaction will not occur spontaneously at normal temperature because ΔG° is positive. When temperature is increased and reaches the critical point that entropy of the reaction plays a dominant role, i.e., $T = \Delta H^{\circ}/\Delta S^{\circ}$, the reaction will become spontaneous. At present thermodynamic data for metal-rich compounds are extremely lacking. There are only two metal-rich chalcogenides, Ta_2S and Ta_6S , for which $\Delta H^{\circ}_{f,298}/R$ (-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 $800\text{--}900^{\circ}\text{C}$ (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 mechanical 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 ($> 2000^{\circ}\text{C}$) 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) can only be prepared using this technique. 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 ($< 900^{\circ}\text{C}$) (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 copper 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 inhomogeneity 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, $\text{Cu}_x\text{Nb}_6\text{S}_{3-x}$.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 procedures 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 $K\alpha_1$ ($\lambda = 1.5405\text{\AA}$) 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 PLOT⁵² following the above calculations. The powder pattern of the sample was compared with the calculated powder patterns of known or postulated 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 preferred 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 LATT⁵³ 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 Rietveld 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 from 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 MoK α ($\lambda = 0.71069\text{\AA}$) 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, TEXSAN⁵⁷ 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-86⁵⁸ 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 referring 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, DIFABS⁵⁹ 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$)

A. Preparation and Characterization

The initial reactant, Ta_2S_5 ,¹⁹ was synthesized by heating a mixture of tantalum (Alpha Products, M3N8) and sulfur (Fisher Scientific, lab grade) with a $n_{\text{Ta}}/n_{\text{S}}$ 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_5 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, $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ [31.200(5), 3.3507(7), 9.592(2)Å, Pnma] and a $2\text{s-Nb}_{1+x}\text{S}_2$ ⁶⁰ -type compound, according to the two-theta angles calculated with program PWDR⁵¹ (using data from the structure solution for $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$)). The main product in this sample was $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$). In the diffuse pattern (only annealed at 1425°C) some reflections had originally been thought to belong to $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$), with

the cell parameters determined to be 31.19(1), 3.350(1) and 9.602(6) Å. After the $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($\text{Ta}_2\text{Se}^{31}$ -type) phase was found, it was determined that the reflections in the diffuse pattern of the melted sample belong to $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type). The critical temperature below which $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ is stable and above which $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type) is stable is close to 1425°C. Although the reflections in the diffuse pattern of the melted sample belong primarily to $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type), there were small amounts of $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ in the melted sample because 1425°C is close to that critical temperature. Powder diffraction data for $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$) 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.% ($\text{Nb}_{4.65}\text{Ta}_{5.77}\text{S}_4$).

After the structure and composition of $\text{Nb}_{4.92}\text{Ta}_{6.08}\text{S}_4$ were determined, an attempt was made to synthesize the title compound starting with the elements. A mixture of tantalum, niobium and sulfur ($n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} \approx 6:5:4$) 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x = 4.92$) (Cu $K\alpha_1$ radiation)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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

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

Table 2 (continued)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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 $\text{Nb}_{4.92}\text{Ta}_{6.08}\text{S}_4$ calculated using program PWDR, it is certain that almost all of the sample is $\text{Nb}_{4.92}\text{Ta}_{6.08}\text{S}_4$.

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, $\text{Ta}_{6-x}\text{Nb}_x\text{S}$ ($C 2/c$, $14.1214(168)$, $5.2849(41)$, $14.8331(182)\text{\AA}$, $\beta = 117.97^{\circ}$ (5)) and $\text{Ta}_{6.08}\text{Nb}_{4.92}\text{S}_4$.

From preliminary Weissenberg and rotation photographs of $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ 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, $\text{Pna}2_1$ and Pnma , differing by a center of symmetry.

Intensity data for a $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ crystal ($0.5 \times 0.02 \times 0.01 \text{mm}^3$) were collected using a RIGAKU AFC6 single-crystal diffractometer and monochromated $\text{Mo K}\alpha$ radiation, employing the ω scan technique

up to 60° (2θ). From the total 3473 reflections (hkl , $-hkl$), 929 independent reflections with $F^2 > 3\sigma(F_0^2)$ 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 ($\mu(\text{Mo K}\alpha)$) being 711.53 cm^{-1} . The averaging of all F_0 values of $\text{Ta}_{6.08}\text{Nb}_{4.92}\text{S}_4$ 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 DIFABS⁵⁹ 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}S₄ (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
μ(MoK _α), 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 > 3σ(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.

$$^b R = \sum \left| \left| F_o \right| - \left| F_c \right| \right| / \sum \left| F_o \right|$$

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

$$^d GOF = \sum ((\left| F_o \right| - \left| F_c \right|) / \sigma_i)^2 / (N_{obs} - N_{parameters})$$

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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$. 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$
($x \approx 4.92$)

Atom	Occupancy	x	y	z	B_{iso} ($\text{\AA}^2$)
M1	75% 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ viewed along the b -axis. Unit cell is marked by solid lines

Figure 2 The projection of $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$) 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 $n_{\text{Nb}}/n_{\text{Ta}}$ ratio on that position also increases, i.e., from M1 to M11 the $n_{\text{Nb}}/n_{\text{Ta}}$ 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$

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 $\text{Ta}_{6.08}\text{Nb}_{4.92}\text{S}_4$. 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 $\beta\text{-Ta}_6\text{S}^{21}$ and Ta_2S^{19} in the case of " Ta_{11}S_4 ", and $\text{Nb}_{21}\text{S}_8^{10}$ in the case of " Nb_{11}S_4 ".

Table 5 Interatomic distances (pm) for $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \sim 4.92$) (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)

^a number of neighbors.

Table 5 (continued)

	M6	2	312.4 (2)		M1	1	274 (1)
	M5	1	318.3 (2)				
				S3	M9	1	245.0 (9)
M9	S3	1	245.0 (9)		M8	1	246 (1)
	S2	2	255.6 (9)		M7	2	250.6 (7)
	M3	2	283.1 (2)		M6	2	252.5 (7)
	M2	2	299.9 (2)				
	M7	2	309.8 (2)	S4	M3	2	249.2 (8)
	M5	1	327.6 (2)		M11	2	256.0 (8)
					M10	1	268 (1)
M10	S1	2	256.5 (8)		M4	1	283 (1)
	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)				

CRYSTAL STRUCTURE OF $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$)

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: $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} = 6:12:7$ 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 $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($\text{Nb}_{21}\text{S}_8^{10}$ -type); ($I4/m$, $a = 16.8237(31)$, $c = 3.3428(7)\text{\AA}$). The reflections in the powder pattern, except for those belonging to $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$, could be indexed as $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ ($9.5912(26)$, $3.3637(10)$, $32.8251(74)\text{\AA}$, Pnma) according to the two-theta angles calculated with program PWDR (using data from the structure solution for $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$). Powder diffraction angles $2\theta < 55^\circ$, estimated and relative intensities of $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ 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 $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$) (Cu $K\alpha_1$ radiation)^a ($2\theta < 55^\circ$)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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	1	2	32.94	32.95	M^c	5
2	0	10		33.04		7
2	1	3	33.55	33.53	W	13
3	0	7	33.92	33.91	M	24
2	1	5	35.35	35.31	M	25
2	0	11		35.40		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	0	4		39.10		7
3	1	2	39.22	39.23	S	100
3	0	10		39.31		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 $I_{\text{calc}} \geq 5$ are listed.

^b W, weak; M, medium; S, strong.

^c Reflections also belong to $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$.

Table 6 (continued)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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 $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ 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.% ($\text{Nb}_{8.07}\text{Ta}_{4.28}\text{S}_4$).

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 " $\text{Nb}_{1.5}\text{S}$ " (there is no compound known with either the formula Nb_2S or the formula $\text{Nb}_{1.5}\text{S}$) 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 $n_{\text{Ta}}/n_{\text{S}}$ 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 " $\text{Nb}_{1.5}\text{S}$ " were synthesized using a similar method. The stoichiometrically appropriate mixture of Ta_6S , " Nb_2S " or " $\text{Nb}_{1.5}\text{S}$ " 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 $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ standard calculated using program POWDER, it is certain that major product in the sample is $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$.

B. Single Crystal X-ray Investigation

There were two kinds of crystals in the annealed sample ("Nb₁₂Ta₆S₇"). The thin needle-like crystals of Nb_{6.74}Ta_{5.26}S₄ could easily be distinguished from the larger trapezoidal-shaped Nb_{21-x}Ta_xS₈ crystal. A gray-colored crystal (0.02x0.02x0.35mm³) of the new compound was selected from the nearly melted sample and was examined using Cu K α 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, Pna2₁, 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 K α radiation, employing the ω scan technique up to 60° (2 θ). 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 611.61cm⁻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 similar 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 restraint is assumed. In either case the calculated $n_{\text{Nb}}/n_{\text{Ta}}$ 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 $n_{\text{Nb}}/n_{\text{Ta}}$ 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 $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ are given in Table 9.

Table 7 Crystal data for $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$)

Formula	$\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$
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
$\mu(\text{MoK}\alpha)$, cm ⁻¹	611.61
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo $\text{K}\alpha$ ($\lambda = 0.71069$ Å)
Orientation reflections, number, range (2 θ)	25, 14-35
Temperature, °C	22
Scan method	ω
Octants measured	hkl, hk-l
Data collection range, 2 θ , 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 (0.48 Å, M8)

^a obtained from indexing of the powder pattern.

$$b \quad R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

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

$$d \quad \text{GOF} = \frac{\sum (|F_o| - |F_c|)^2 / \sigma_i^2}{(N_{\text{obs}} - N_{\text{parameters}})}$$

Table 8 Positional, thermal parameters and occupancies for $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$
($x \approx 5.26$)

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 $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$) (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)
M2	M1	2	283.1 (3)	M6	M10	2	282.5 (5)
		1	326.8 (4)		M10	1	312.6 (6)
		2	283.1 (4)		S3	2	252 (1)
		2	292.0 (4)		M2	2	292.0 (4)
		2	298.6 (5)		M3	2	296.6 (4)
		1	276 (1)		M4	1	324.1 (6)
M3	M1	2	283.3 (3)	M7	M9	2	310.8 (5)
	M2	1	326.8 (4)		S2	1	252 (2)
	M3	2	289.0 (5)		S3	2	259 (1)
	M5	2	286.8 (4)		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)
M4	M2	2	283.1 (4)	M8	M12	2	310.6 (5)
		1	324.1 (6)		S1	1	262 (2)
		2	280.2 (5)		S1	1	277 (1)
		2	283.5 (4)		S4	1	253 (2)
		1	321.6 (6)		M1	2	284.5 (3)
		1	324.9 (6)		M5	1	326.3 (4)
		2	251 (1)		M10	2	314.3 (5)
					M11	2	312.0 (6)
					S2	2	254 (1)
					S4	1	249 (2)

^a number of neighbors.

Table 9 (continued)

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

Observed and calculated structure factors of $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ are listed in Appendix B.

C. Results and Discussions

In the structure of $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$) 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 $n_{\text{Nb}}/n_{\text{Ta}}$ ratio on that position also increases, i.e., from M1 to M12 the $n_{\text{Nb}}/n_{\text{Ta}}$ ratio on the metal position increases. Figures 4 and 5 show the structure of $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$. 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 $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ viewed along the b -axis. Unit cell is marked by solid lines

Figure 5 The projection of $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ 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 $\text{Nb}_{4.92}\text{Ta}_{6.08}\text{S}_4$. 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 $2.80\text{\AA}$, compared with $2.82\text{\AA}$ in $\text{Nb}_{4.92}\text{Ta}_{6.08}\text{S}_4$. There is no doubt that there are numerous strong metal-metal interactions in this solid. If only $d_{\text{M-M}} < 3.30\text{\AA}$ and $d_{\text{M-S}} < 3.00\text{\AA}$ 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, $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ is also included in this class.

The ratio of metal and nonmetal for this new compound is 12:4; compared with 11:4 of $\text{Nb}_{4.92}\text{Ta}_{6.08}\text{S}_4$. Although the space group (Pnma) is the same and the cell parameters are similar for $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ and $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ there are substantial differences between these two compounds, e.g., the longest axis is the c-axis in $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ while the longest one in $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ is the a-axis. The coordinations of metals and nonmetals in $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ and $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ 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, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ is more similar to the Nb-rich sulfides, Nb_{21}S_8 ¹⁰ and Nb_{14}S_5 ;¹¹ than $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, i.e., there is capped pentagonal prismatic coordination around some metals in $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$.

CRYSTAL STRUCTURE OF $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)

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 $n_{\text{Ta}}/n_{\text{S}}$ 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 similar 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 $n_{\text{Nb}}:n_{\text{Ta}} = 1:4$, 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ appeared and was the major phase in the sample. When several mixtures of Ta_2S and " Nb_2S " ($n_{\text{Ta}_2\text{S}}:n_{\text{Nb}_2\text{S}} = 2, 3$ 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 $n_{\text{Ta}_2\text{S}}/n_{\text{Nb}_2\text{S}}$ 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, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$), were determined to be $a = 3.3203$, $c = 21.619(12)\text{\AA}$ in space group $I4/mmm$ from the powder pattern of the arc-melted sample in the molar ratio: $n_{\text{Ta}_2\text{S}}:n_{\text{Nb}_2\text{S}} = 3:1$, according to the two-theta angles calculated with program PWDR⁵¹ (using data from the structure solution for $\text{Nb}_{1.72}\text{Ta}_{3.28}\text{S}_2$). 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 $\text{Nb}_{1.72}\text{Ta}_{3.28}\text{S}_2$ were determined, an attempt was made to synthesize the title compound starting with the elements. A mixture of Ta, Nb and S ($n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} \approx 3.28:1.72:2$) 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) (Cu $K\alpha_1$ radiation)^a ($2\theta < 75^\circ$)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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 $I_{\text{calc}} > 5$ are listed.

^b W, weak; M, medium; S, strong.

indicated that the title compound was the main phase with less than 10% $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($\text{Ta}_2\text{Se}^{31}$ -type).

The same result was also obtained from arc-melting the mixture of Ta, TaS and " Nb_2S " with $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} = 3.28:1.72:2$ overall. The quantitative analysis of the arc-melted sample using the EDAX method only found one phase for which the molar ratio of $n_{\text{Ta}}/n_{\text{Nb}}$ was 1.87 corresponding to $\text{Nb}_{1.74}\text{Ta}_{3.26}\text{S}_2$, although the Guinier x-ray powder pattern indicated that minor $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($\text{Ta}_2\text{Se}^{31}$ -type) coexisted with the title compound.

B. Single Crystal X-Ray Investigation

One gray-colored needle-shaped crystal ($0.02 \times 0.02 \times 0.25 \text{ mm}^3$) 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 $14^\circ - 45^\circ (2\theta)$. Seven peaks were indexed in the INDEX TWIN process as a body-centered cell with $a = 3.3129(30)$, $b = 3.3202(41)$, $c = 21.4348(214) \text{ \AA}$, $\alpha = 89.904(91)^\circ$, $\beta = 89.992(93)^\circ$ and $\gamma = 90.223(96)^\circ$. Intensity data were collected using monochromatic $\text{MoK}\alpha$ radiation, employing the 2θ - ω scan technique up to $60^\circ (2\theta)$. 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 795.13cm^{-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 orthorhombic 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 $\text{Nb}_{2.17}\text{Ta}_{2.83}\text{S}_2$ 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 DIFABS⁵⁹ 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 refinement 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) 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 $n_{\text{Nb}}/n_{\text{Ta}}$ ratio on that position also increases, i.e., from M1 to M3 the $n_{\text{Nb}}/n_{\text{Ta}}$ 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 reminiscent of $\text{Ta}_2\text{Se}^{31}$ which is composed of six layers in the sequence Se-Ta-Ta-Ta-Ta-

Table 11 Positional, thermal parameters and occupancies for $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)

	occupancy	z	$B_{\text{eq}} (\text{\AA}^2)$	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; $U_{22} = U_{11}$, $U_{ij} = 0$. $B_{\text{eq}} = 8\pi^2/3 (U_{11} + U_{22} + U_{33})$.

Table 12 Crystal data for $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)

Formula	$\text{Nb}_{1.72}\text{Ta}_{3.28}\text{S}_2$
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
$\mu(\text{MoK}\alpha)$, cm ⁻¹	795.13
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K α ($\lambda = 0.71069$ Å)
Orientation reflections, number, range (2 θ)	12, 14-45
Temperature, °C	22
Scan method	2 θ - ω
Octants measured	hkl, -hkl, hk-l, -hk-l
Data collection range, 2 θ , 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 (1.06 Å, M2)

^a obtained from indexing of the powder pattern.

$$b \quad R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

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

$$d \quad \text{GOF} = \frac{\sum (|F_o| - |F_c|)^2 / \sigma_i^2}{(N_{\text{obs}} - N_{\text{parameters}})}$$

Table 13 Interatomic distances (pm) for $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x = 1.72$) ($< 340\text{pm}$)

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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$. Larger circle represents S. Vertical is z-direction

Figure 7 The projection of $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ on the xz -plane. Larger circle represents S. Vertical is z -direction

Se, also in bcc-type packing. In ZrCl-type⁶² and ZrBr-type⁶³ 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, consistent with the graphitic character and the tendency of the compound to disorder. This is the first van der Waals layered compound with such high ratio of $n_{\text{metal}}/n_{\text{nonmetal}}$, 2.50.

The layered disulfides (TiS_2 , MoS_2 , NbS_2 , etc.) have been studied extensively⁶⁴ 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$) and $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$), 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)

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: $n_{\text{Nb}}:n_{\text{S}} = 2:1$ 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 $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} = 3:2:2.17$ 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-type⁶⁵ 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, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ 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, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$), were determined to be $a = 3.3304(7)$, $c = 9.0928(94)\text{\AA}$ in tetragonal space group $P4/nmm$ according to the two-theta angles calculated with program PWDR⁵¹ (using data from the structure solution for $\text{Nb}_{0.95}\text{Ta}_{1.05}\text{S}$). 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 $\text{Nb}_{0.95}\text{Ta}_{1.05}\text{S}$ 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, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ and about 50% $\text{Nb}_{1-x}\text{Ta}_x\text{S}$ (NbS -type⁶⁵), were found to coexist in the product from the x-ray powder diffraction. The ratios of $n_{\text{Ta}}/n_{\text{Nb}}$ were determined to be 1.29 and 0.81 for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ and $\text{Nb}_{1-x}\text{Ta}_x\text{S}$, respectively, by the EDAX method in a scanning electron microscope. These values correspond to $\text{Nb}_{0.87}\text{Ta}_{1.13}\text{S}$ ($\text{Nb}_x\text{Ta}_{2-x}\text{S}$) and $\text{Nb}_{0.55}\text{Ta}_{0.45}\text{S}$ ($\text{Nb}_{1-x}\text{Ta}_x\text{S}$).

A mixture of the elements tantalum, niobium and sulfur with $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} \approx 1.15:0.85:1$ 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) ($\text{Cu K}\alpha_1$ radiation)^a ($2\theta < 75^\circ$)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	$I_{\text{obs}}^{\text{b)}$	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 $I_{\text{calc}} > 5$ 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, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$. When the initial amounts of sulfur were decreased to $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} = 1.15:0.85:0.9$ 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 $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} \approx 1.10:0.90:0.85$ were $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ when the same synthesis procedure was used.

This means that samples in this range of $n_{\text{Ta}}/n_{\text{Nb}}$ favor the formation of solid solutions of $\text{Nb}_{1-x}\text{Ta}_x\text{S}$ (NbS-type) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ 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 ($0.03 \times 0.04 \times 0.15 \text{ mm}^3$) 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 $\text{Mo K}\alpha$ radiation, employing the 2θ - ω scan technique up to $65^\circ(2\theta)$ 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 $\text{Nb}_{0.59}\text{Ta}_{1.41}\text{S}$ 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 $\text{Nb}_{0.59}\text{Ta}_{1.41}\text{S}$ were calculated and used for a DIFABS⁵⁹ 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 $\text{Nb}_{0.95}\text{Ta}_{1.05}\text{S}$ 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 $\text{Nb}_{0.59}\text{Ta}_{1.41}\text{S}$ during the anisotropic refinement). However, the first approach appears to be more reasonable. There are two impurity peaks higher than $5\text{e}^-/\text{\AA}^3$ (5.695 and $5.267\text{ e}^-/\text{\AA}^3$) in the result of the second approach, compared to only one impurity peak higher than $5\text{e}^-/\text{\AA}^3$ ($5.291\text{e}^-/\text{\AA}^3$ 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x = 0.95$).

Table 15 Crystal data for Nb_xTa_{2-x}S (x ≈ 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
μ(MoK _α), 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 > 3σ(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 (0.74 Å, S)

^a obtained from indexing of the powder pattern.

$$^b R = \sum \left| \left| F_o \right| - \left| F_c \right| \right| / \sum \left| F_o \right|$$

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

$$^d GOF = \sum ((\left| F_o \right| - \left| F_c \right|) / \sigma_i)^2 / (N_{obs} - N_{parameters})$$

Table 16 Positional, thermal parameters and occupancies for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$
($x \approx 0.95$)

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

Table 17 Interatomic distances (pm) for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) (< 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta₂Se-type³¹) on the xz-plane. Vertical is z-direction. Unit cell is marked by solid lines

Figure 9 The projection of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta₂Se-type³¹) 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

$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ is isostructural with Ta_2Se .³¹ In the structure of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ 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 $n_{\text{Nb}}/n_{\text{Ta}}$ ratio on that position also increases, i.e., from M1 to M2 the $n_{\text{Nb}}/n_{\text{Ta}}$ 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ is similar to that of $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$) 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 stabilizing 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 $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$, $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ and $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$) 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.

$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ and $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ 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, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ and $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$.

CRYSTAL STRUCTURE OF $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$)

A. Preparation and Characterization

As previously described the reaction of $\text{Nb} + \text{Ta}_2\text{S}^{19}$ ($n_{\text{Nb}}:n_{\text{Ta}_2\text{S}} = 1:1$) was studied and a new ternary phase, $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$) was found. In this section the reaction of $\text{Ta} + \text{"Nb}_2\text{S"}$ ($n_{\text{Ta}}:n_{\text{Nb}_2\text{S}} = 1:1$) was desired. This reaction was studied using a method similar to that previously described for the reaction of $\text{Nb} + \text{Ta}_2\text{S}$, 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; $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$, NbO^{66} and unreacted Ta ; respectively. The reflections of $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ were similar to those of $\text{Nb}_{21}\text{S}_8^{10}$ except for changes in the intensity of some reflections (the most obvious change was observed for the $[110]$ reflection).

The structures of $\text{Ta}_6\text{S}^{20,21}$ and $\text{Nb}_{21}\text{S}_8^{10}$ are different, and thus there was a motivation to know what products would be obtained from the reaction of $\text{Ta}_6\text{S} + \text{Nb}_{21}\text{S}_8$. 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, $\text{Nb}_x\text{Ta}_{21-x}\text{S}_8$ [$16.817(2)$, $3.3450(9)\text{\AA}$, $I4/m$], according to the two-theta angles

calculated with program PWDR⁵¹ (using data from the structure solution for $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$)). 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 quantitative analysis of the product from the reaction of $\text{Nb}_{21}\text{S}_8 + \text{Ta}_6\text{S}$ 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 $\text{Nb}_{14.97}\text{Ta}_{5.16}\text{S}_8$).

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 $K\alpha$ radiation, employing the 2θ - ω scan technique up to $50^\circ(2\theta)$ 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 $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$) (Cu $K\alpha_1$ radiation)^a ($2\theta < 55^\circ$)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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 $I_{\text{calc}} \geq 5$ 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 DIFABS⁵⁹ 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 $\text{Nb}_{14.8}\text{Ta}_{6.2}\text{S}_8$ 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_xS₈ (x ≈ 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
μ(MoK _α), 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 > 3σ(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.

$$^b R = \sum \left| \left| F_o \right| - \left| F_c \right| \right| / \sum \left| F_o \right|$$

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

$$^d GOF = \sum ((\left| F_o \right| - \left| F_c \right|) / \sigma_i) / (N_{obs} - N_{parameters})$$

Table 20 Positional, thermal parameters and occupancies for Nb_{21-x}Ta_xS₈ (x ≈ 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 $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$) (M-M < 330 pm, M-S < 300 pm)

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

^a number of neighbors.

Figure 10 The crystal structure of $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ viewed along the z-axis. Unit cell is marked by solid lines

○ M at Z=0

○ S at Z=0

● M at Z=1/2

● S at Z=1/2

Figure 11 The projection of $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ 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 $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$) 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 $n_{\text{Ta}}/n_{\text{Nb}}$ ratio on that position also increases, i.e., from M1 to M6 the $n_{\text{Ta}}/n_{\text{Nb}}$ 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 , $b = 16.817$; $c = 3.345\text{\AA}$) of $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$) differ slightly from those (a , $b = 16.794$; $c = 3.359\text{\AA}$) 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 similarity is not unexpected. Because the atomic positions and cell constants of $\text{Nb}_{14.8}\text{Ta}_{6.2}\text{S}_8$ and Nb_{21}S_8 are nearly the same, it is not surprising that the bond distances in $\text{Nb}_{14.8}\text{Ta}_{6.2}\text{S}_8$ are nearly the same as those in Nb_{21}S_8 .

CRYSTAL STRUCTURE of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$)

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: $n_{\text{Nb}}:n_{\text{S}} = 2:1$ 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 similar method. The mixture of " Nb_2S " (there is no known compound with the formula Nb_2S), TaS and Ta with $n_{\text{Ta}}:n_{\text{Nb}}:n_{\text{S}} \approx 1.5:0.2:1$, 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 $\text{Cu K}\alpha_1$ and silicon as an internal standard indicated that the major phase was a Ta_2S^{19} -type compound with a minor phase, $2\text{s-Nb}_{1+x}\text{S}_2^{60}$ -type compound. If the $n_{\text{Ta}}/n_{\text{Nb}}$ was 4, keeping the molar ratio of metals and the nonmetal unchanged, the main product in the arc-melted sample was $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ 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 $\beta\text{-Ta}_6\text{S}$ -type compound appeared, possibly as the result of loss of sulfur during the annealing process. The cell parameters of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$) were determined to be $a = 7.3724(11)$, $b = 5.5757(11)$

and $c = 15.1981(23)\text{\AA}$ in space group Pbcm according to the two-theta angles calculated with program PWDR⁵¹ (using data from the structure solution $\text{Nb}_{0.20}\text{Ta}_{1.80}\text{S}$). 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 quantitative 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 $n_{\text{Ta}}/n_{\text{Nb}}$ of major phase was determined to be 12.75, which corresponds to be $\text{Nb}_{0.15}\text{Ta}_{1.85}\text{S}$.

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 ($0.03 \times 0.01 \times 0.2 \text{ mm}^3$) was used for collecting intensity data.

Intensity data were collected using monochromatic Mo $K\alpha$ radiation, employing the 2θ - ω scan technique up to $70^\circ(2\theta)$ 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 $F^2 > 3\sigma(F_0^2)$ 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \sim 0.2$) ($\text{Cu K}\alpha_1$ radiation)^a ($2\theta < 55^\circ$)

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	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 $I_{\text{calc}} \geq 5$ 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 $\text{Nb}_{0.2}\text{Ta}_{1.8}\text{S}$ were calculated and used for a DIFABS⁵⁹ 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 $\text{Nb}_{0.2}\text{Ta}_{1.8}\text{S}$ from the refinement.

The crystal data, atom coordinates, thermal parameters and interatomic distances for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$) 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 -type¹⁹ 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$) 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 $n_{\text{Nb}}/n_{\text{Ta}}$ ratio on that position also increases, i.e., from M2 to M4 the $n_{\text{Nb}}/n_{\text{Ta}}$ 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 = 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
μ (MoK _α), 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 > 3σ(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.

$$b \quad R = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$$

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

$$d \quad GOF = \frac{\sum (|F_o| - |F_c|)^2 / \sigma_i^2}{(N_{obs} - N_{parameters})}$$

Table 24 Positional, thermal parameters and occupancies for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$
($x \approx 0.2$)

Atom	Occupancy	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \sim 0.2$)

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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$) (M-M < 330 pm, M-S < 300 pm)

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

^a number of neighbors.

Figure 12 The projection of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta₂S-type¹⁹) 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 ($d_{M-S} < 3\text{\AA}$) 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 ($a = 7.372$, $b = 5.576$, $c = 15.198\text{\AA}$) of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$) differ slightly from those ($a = 7.379$, $b = 5.574$, $c = 15.19\text{\AA}$) 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 similarity is not unexpected. Because the atomic positions and cell constants of $\text{Nb}_{0.20}\text{Ta}_{1.80}\text{S}$ and Ta_2S are nearly the same, it is not surprising that the bond distances in $\text{Nb}_{0.20}\text{Ta}_{1.80}\text{S}$ are nearly the same as those in Ta_2S .

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

$\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type), $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$, and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2S -type) were found using the single crystal method. $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$), $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) (Ta_2Se -type), $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$), $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$) (Ta_2S -type) and $\text{Cu}_x\text{Nb}_6\text{S}_{3-x}$ ($x \approx 4.6$)⁴⁰ (Ta_2P -type¹³) were successfully refined anisotropically, while $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$) and $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$) 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, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) and from the non-melted samples for $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.20$). The crystal of $\text{Cu}_x\text{Nb}_6\text{S}_{3-x}$ 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 $\text{Nb}_x\text{Ta}_{6-x}\text{S}$ ($\alpha\text{-Ta}_6\text{S}$ -type²⁰ and $\beta\text{-Ta}_6\text{S}$ -type²¹) was also found during the study of the ternary Ta-Nb-S system. A crystal of $\text{Nb}_x\text{Ta}_{6-x}\text{S}$ ($\alpha\text{-Ta}_6\text{S}$ -type) was found in the sample

mentioned in the section of crystal structure of $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$. The structure was refined to $R/R_w = 0.191/0.249$ and the composition was determined to be $\text{Nb}_{1.6}\text{Ta}_{4.4}\text{S}$. However, single crystals of this compound with good quality has not yet been obtained. One possible reason is that $\alpha\text{-Ta}_6\text{S}^{20}$ -type and $\beta\text{-Ta}_6\text{S}^{21}$ -type phases coexisted in the sample, and thus intergrowth crystals were formed in the sample. $\text{Nb}_x\text{Ta}_{6-x}\text{S}$ ($\alpha\text{-Ta}_6\text{S}$ -type and $\beta\text{-Ta}_6\text{S}$ -type) can be found in the sample with $n_{\text{Ta}}/n_{\text{Nb}} > 4$ and $(n_{\text{Ta}} + n_{\text{Nb}})/n_{\text{S}} > 3$. The cell parameters were determined to be $C2/c$, $14.1214(168)$, $5.2849(41)$, $14.8331(182)\text{\AA}$, $\beta = 117.97^\circ$ (5) (determined by single crystal method on a CAD-4 diffractometer); and $5.258(13)$, $7.589(21)$, $7.626(26)\text{\AA}$, $59.31(20)^\circ$, $68.67(28)^\circ$, 77.36° for $\alpha\text{-Ta}_6\text{S}$ -type and $\beta\text{-Ta}_6\text{S}$ -type $\text{Nb}_x\text{Ta}_{6-x}\text{S}$, respectively. Because the radii of niobium and tantalum are nearly equal, the cell parameters show negligible change with x in $(\text{Nb}_x\text{Ta}_{1-x})_y\text{S}_z$.

It is not surprising that in the Ta-Nb-S system solid-solution type compounds, $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$), $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$) and $\text{Nb}_x\text{Ta}_{6-x}\text{S}$ isostructural with the respective binary niobium-rich sulfides or tantalum-rich sulfides, are formed because of the chemical and size similarities between the niobium and tantalum. What is surprising is the finding of four new compounds; $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$), $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$), $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) in which the first

three exhibit totally new structure types and the last one is isostructural with $\text{Ta}_2\text{Se}^{31}$, 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 ($\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)), M_{10}S_4 ($\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)), M_{11}S_4 ($\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$)) and M_{12}S_4 ($\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$)).

Fragments of the distorted elemental metal structures of tantalum and niobium (bcc-type structure) are common features in the structures of the compounds, $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type³¹) and $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$. 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2S -type) there were two positions (M2 and M3 in $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, and M3 and M4 in $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2S -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 $(\text{Nb,Ta})_x\text{S}_y$ ($x > y$) 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 similarities 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 -type³¹), $Nb_{21-x}Ta_xS_8$ ($Nb_{21}S_8$ -type¹⁰) and $Nb_xTa_{2-x}S$ (Ta_2S -type¹⁹) 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.

$Nb_xTa_{11-x}S_4$ 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.

$Nb_{12-x}Ta_xS_4$ 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 $Nb_{12-x}Ta_xS_4$ ($x \approx 5.26$).

$\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ This phase can exist when $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$). This phase is stable at very high temperatures and the major product of disproportionation is $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type) and $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ at temperatures between $1425^\circ\text{C} - 1450^\circ\text{C}$ and below 1425°C , respectively. Because $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ was synthesized by the arc-melting method and its melting point is around 1450°C , the specific temperature above which this phase is stable has not been determined.

$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type³¹) This phase can exist when $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$). This phase is stable at temperatures above 1425°C , below which it will disproportionate to $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ and other phases.

$\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ (Nb_{21}S_8 -type¹⁰) This phase can exist when $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ 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 $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$).

$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2S -type¹⁹) This phase can exist when $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ 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.), similar to that mentioned previously in the section on the crystal structure of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$).

When $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ is between 60% and 70% and $(n_{\text{Ta}} + n_{\text{Nb}})/n_{\text{S}}$ between 2 and 2.7, arc-melted samples consist of the two layered compounds, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (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, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type) can be formed in the above range or if first one is formed in the range of 70% - 80% for $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ and then the latter one formed in the range of 55% - 60% for $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$. The same is true for the sample with the ratio $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ between 50% and 55% and the ratio $(n_{\text{Ta}} + n_{\text{Nb}})/n_{\text{S}}$ of 2 ($\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type) and $\text{Nb}_{1-x}\text{Ta}_x\text{S}$ (NbS -type⁶⁵) coexisted).

In the experiments to determine the range for each solid solution, the smallest change in $n_{\text{Ta}}/(n_{\text{Ta}} + n_{\text{Nb}})$ 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 similarities 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($\text{Ta}_2\text{Se}^{31}$ -type) and $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ are being carried out by colleagues in Dr. Jonston's group of physics department at ISU. The compound $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ has been found to go superconducting below 5K.

PART II: EXTENDED HÜCKEL BAND CALCULATIONS

ON TWO NOVEL LAYERED COMPOUNDS:

$\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)

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 perturbation 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 calculation⁷⁸ 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 -type³¹) 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$) the arrangement $\text{Ta}_2\text{Nb}_2\text{S}_2$ is closer to the real one than is $\text{Nb}_2\text{Ta}_2\text{S}_2$ for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$, and (the layer sequence of M1, M2, M3 and S is M1M2M3S in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$) the arrangement $\text{TaTa}_2\text{Nb}_2\text{S}_2$ is closer to the real one than is $\text{TaNb}_2\text{Ta}_2\text{S}_2$ for $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ (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 STET⁷⁹ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$

$\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) $I4/\text{mmm}$						
atom	site	occupancy %	C.N. ^a	arrangement 1 ^b $\text{TaTa}_2\text{Nb}_2\text{S}_2$	arrangement 2 $\text{TaNb}_2\text{Ta}_2\text{S}_2$	
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	

$\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$) $P4/\text{mmm}$						
atom	site	occupancy %	C.N. ^a	arrangement 1 ^b $\text{Ta}_2\text{Nb}_2\text{S}_2$	arrangement 2 $\text{Nb}_2\text{Ta}_2\text{S}_2$	
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
 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) AND $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)**

A. Band Structure of $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)

The total density of states (DOS) for " Ta_5S_2 ", " $\text{TaTa}_2\text{Nb}_2\text{S}_2$ ", " $\text{TaNb}_2\text{Ta}_2\text{S}_2$ " 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, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ is expected to exhibit metallic properties, e.g., metallic electrical conductivity. As previously discussed in the Method Section, $\text{TaTa}_2\text{Nb}_2\text{S}_2$ is the model structure closest to the real arrangement. A plot of the DOS for $\text{TaTa}_2\text{Nb}_2\text{S}_2$ 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, $\text{TaTa}_2\text{Nb}_2\text{S}_2$ and $\text{TaNb}_2\text{Ta}_2\text{S}_2$ can be analyzed with the aid of the overlap population, the average energies, 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 $\text{TaTa}_2\text{Nb}_2\text{S}_2$ ($\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ -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 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$) are greater than the corresponding values (6.43 and 12.53) for arrangement 2 ($\text{TaNb}_2\text{Ta}_2\text{S}_2$). 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 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$) than in arrangement 2 ($\text{TaNb}_2\text{Ta}_2\text{S}_2$). 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$

	arrangement 1 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$)	arrangement 2 ($\text{TaNb}_2\text{Ta}_2\text{S}_2$)
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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)

$\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$		
site	arrangement 1 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$)	arrangement 2 ($\text{TaNb}_2\text{Ta}_2\text{S}_2$)
M1	5.101	4.888
M2	4.989	5.681
M3	5.292	4.737
S	5.669	5.638

$\text{Nb}_x\text{Ta}_{2-x}\text{S}$		
site	arrangement 1 ($\text{Ta}_2\text{Nb}_2\text{S}_2$)	arrangement 2 ($\text{Nb}_2\text{Ta}_2\text{S}_2$)
M1	5.267	5.572
M2	5.117	4.830
S	5.616	5.597

sulfur bonds, between two arrangements in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$, 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and presumably in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ resulting in an increase in the overall bonding in arrangement 1 and in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$.

Thus, because arrangement 1 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$) is closer to that of the real compound for $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$, 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$. There is no big difference in averaged COOP curves between two arrangements, $\text{TaTa}_2\text{Nb}_2\text{S}_2$ and $\text{TaNb}_2\text{Ta}_2\text{S}_2$, 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 $\text{TaTa}_2\text{Nb}_2\text{S}_2$. Thus the maximum metal-metal bonding is nearly achieved in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$.

The difference between the plots of COOP for arrangement 1 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$) and arrangement 2 ($\text{TaNb}_2\text{Ta}_2\text{S}_2$) 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 ($\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$) formed rather than a segregated atom type ($\text{TaTa}_2\text{Nb}_2\text{S}_2$) formed.

B. Band Structure of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)

There are striking resemblances between the band structures of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ and $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$.

There are no big difference among the DOS plots of " Ta_4S_2 ", " $\text{Ta}_2\text{Nb}_2\text{S}_2$ ", " $\text{Nb}_2\text{Ta}_2\text{S}_2$ " and " Nb_4S_2 ". As previously discussed, $\text{Ta}_2\text{Nb}_2\text{S}_2$ is the closest model to the real arrangement. A DOS plot for $\text{Ta}_2\text{Nb}_2\text{S}_2$ is included in Figure 16. Metallic properties can be expected for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ 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 $\text{TaTa}_2\text{Nb}_2\text{S}_2$ ($\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ -type). Fermi level is marked by the vertical line

Figure 16 Total DOS curve of $\text{Ta}_2\text{Nb}_2\text{S}_2$ (Ta₂Se-type³¹). 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 ($\text{Ta}_2\text{Nb}_2\text{S}_2$) are greater than the corresponding ones (2.57 and 5.64) for arrangement 2 ($\text{Nb}_2\text{Ta}_2\text{S}_2$). The charges on the metal positions are closer to each other in arrangement 1 ($\text{Ta}_2\text{Nb}_2\text{S}_2$) than in arrangement 2 ($\text{Nb}_2\text{Ta}_2\text{S}_2$). 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$, 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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ as well. The trade off increases the overall bonding in arrangement 1 and presumably in $\text{Nb}_x\text{Ta}_{2-x}\text{S}$.

Thus, because arrangement 1 ($\text{Ta}_2\text{Nb}_2\text{S}_2$) is closer to that of the real compound for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$, the calculations on this layered

Table 31 Average energy, Fermi energy and overlap populations for two arrangements of $\text{Nb}_x\text{Ta}_{2-x}\text{S}$

	arrangement 1 ($\text{Ta}_2\text{Nb}_2\text{S}_2$)	arrangement 2 ($\text{Nb}_2\text{Ta}_2\text{S}_2$)
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 $\text{Nb}_x\text{Ta}_{2-x}\text{S}$.

As previously discussed for $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$, the averaged COOP curve for $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ was calculated. There is no big difference in averaged COOP curves between two arrangements, $\text{Ta}_2\text{Nb}_2\text{S}_2$ and $\text{Nb}_2\text{Ta}_2\text{S}_2$, 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 $\text{Ta}_2\text{Nb}_2\text{S}_2$. Thus the maximum metal-metal bonding is achieved in $\text{Nb}_x\text{Ta}_{2-x}\text{S}$.

The difference between the plots of COOP for arrangement 1 ($\text{Ta}_2\text{Nb}_2\text{S}_2$) and arrangement 2 ($\text{Nb}_2\text{Ta}_2\text{S}_2$) 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 ($\text{Nb}_x\text{Ta}_{2-x}\text{S}$) formed rather than a segregated atom type ($\text{Ta}_2\text{Nb}_2\text{S}_2$) formed.

Figure 17 Averaged metal-metal COOP curve of Ta₂Nb₂S₂ (Ta₂Se-type³¹). Fermi level is marked by the vertical line

**C. Comparison of Band Structures of
 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$) and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)**

Both $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ to $\text{Nb}_x\text{Ta}_{2-x}\text{S}$. 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ to four in $\text{Nb}_x\text{Ta}_{2-x}\text{S}$. The maximum metal-metal bonding is nearly achieved in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and achieved in $\text{Nb}_x\text{Ta}_{2-x}\text{S}$. 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, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ 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 ($\text{TaTa}_2\text{Nb}_2\text{S}_2$ and $\text{Ta}_2\text{Nb}_2\text{S}_2$) than the corresponding ones in arrangements 2 ($\text{TaNb}_2\text{Ta}_2\text{S}_2$ and $\text{Nb}_2\text{Ta}_2\text{S}_2$) in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$, 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$.

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 $\text{TaTa}_2\text{Nb}_2\text{S}_2$ and $\text{Ta}_2\text{Nb}_2\text{S}_2$ arrangements in $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$, respectively.

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

$\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$, $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($\text{Ta}_2\text{S}^{19-}$ 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 $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$, 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, $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$, $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type³¹), $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2S -type¹⁹) 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 $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$, $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$, $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ and $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ (Ta_2Se -type³¹) 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 possibility 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 battery material and useful catalytic materials in the petroleum 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 ($\times 10$) FOR $\text{Nb}_x\text{Ta}_{11-x}\text{S}_4$ ($x \approx 4.92$)

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

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
1	0	1552	1546	54	2	-8	924	1121	47	3	-8	1341	1415	58
1	1	763	688	35	2	-7	983	1075	48	3	0	1899	1906	78
1	2	683	642	49	2	-6	2380	2321	75	3	5	758	709	72
1	7	1697	1945	115	2	3	1117	1055	47	3	6	1654	1611	64
1	8	1915	2048	73	2	10	1393	1349	57	3	7	815	798	72
1	13	1793	1388	69	3	-10	1337	1476	86	4	-4	2708	2813	345
2	-12	858	835	92	3	-6	2806	2714	120	4	0	607	525	95
2	-11	1935	1758	90	3	-3	1698	1717	151	4	3	1631	1584	68
2	-10	1280	1252	83	3	1	1603	1527	88	4	6	2160	2182	115
2	-9	776	868	68	3	7	2133	2162	266	***** h = 7 *****				
2	-4	1655	1556	95	3	8	2533	2785	81					
2	-1	732	736	80	3	9	1683	1789	71					
2	2	431	399	67	4	-6	1495	1562	66	0	-13	1107	1005	125
2	5	2837	2661	82	4	-3	712	679	90	0	-12	2602	2312	108
2	6	3102	3127	154	4	7	862	739	118	0	-10	1731	1669	78
2	8	868	1069	50	***** h = 6 *****					0	-9	553	597	81
3	-9	1187	1334	124						0	-4	3603	3456	94
3	-8	1464	1534	61	0	-13	899	723	92	0	-3	2881	2837	76
3	-7	1360	1442	58	0	-11	3963	3615	111	0	-2	584	505	40
3	-6	3029	2925	91	0	-5	1212	1233	48	0	6	2387	2483	69
3	0	982	1016	52	0	-3	3039	2960	80	0	7	2193	2499	64
3	3	2193	2171	288	0	-2	938	898	44	0	8	1527	1622	61
3	4	1538	1452	59	0	0	1087	1022	51	0	11	3064	2771	94
4	-6	2128	2084	74	0	4	5507	5381	140	1	-9	3003	3244	85
4	-4	1149	981	145	0	6	3652	3865	95	1	-8	1118	1227	70
4	5	1824	1783	71	0	7	863	956	41	1	-7	1725	1904	63
***** h = 5 *****					0	8	1255	1287	52	1	-3	822	849	38
0	-11	1420	1366	60	0	9	3338	3260	127	1	-1	4034	4071	103
0	-7	1201	1262	47	1	-13	2332	2152	114	1	2	879	800	35
0	-6	2518	2820	69	1	-10	1757	1535	62	1	4	453	375	72
0	-3	1362	1398	50	1	-7	986	1057	43	1	6	6069	5778	155
0	5	681	621	76	1	-3	814	832	38	1	11	2730	2531	90
0	8	1322	1310	55	1	-1	645	564	35	2	-12	2240	2082	92
0	9	2603	2408	80	1	0	2994	2948	80	2	-11	2583	2435	283
0	10	1532	1545	62	1	4	784	666	54	2	-8	1301	1378	50
0	12	2664	2418	167	1	5	1020	974	63	2	-7	2197	2088	95
1	-12	973	846	97	1	6	2252	2208	69	2	-3	2445	2271	71
1	-10	1932	1900	77	1	8	1557	1837	149	2	4	2864	2776	91
1	-9	2245	2274	75	2	-11	3352	3205	162	2	6	2212	2036	111
1	-7	2421	2887	69	2	-7	701	817	63	2	10	1349	1460	56
1	1	2420	2449	65	2	-3	2544	2407	122	3	-9	2289	2500	76
1	3	2656	2627	72	2	0	771	814	52	3	-7	1552	1426	73
1	6	3659	3762	97	2	2	670	650	49	3	-1	2749	2755	78
1	8	3413	3682	94	2	4	4482	4307	118	3	2	546	509	68
1	13	1614	1401	69	2	5	1011	978	54	3	6	4393	4223	185
2	-12	2313	2141	93	2	6	3401	3214	185	3	8	830	917	119
2	-11	1303	1197	65	2	8	1088	1100	47	4	-6	1361	1348	65
2	-9	2008	2108	72	2	9	2567	2838	79	4	-3	1632	1463	106
					3	-10	1208	1197	147	4	4	1752	1835	102

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

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

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

k	l	fo	fc	sigF	k	l	fo	fc	sigF	k	l	fo	fc	sigF
2	3	1698	1681	105						2	8	1454	1526	68
2	5	5240	5147	137	*****	h = 24	*****			3	-4	922	884	60
3	-7	1656	1757	67						3	-2	2375	2378	80
3	-1	1051	1072	63	0	-5	5806	5745	255	3	-1	1930	2010	78
3	2	690	524	68	0	-4	2205	2409	275	3	0	4167	4115	121
3	3	982	842	55	0	-1	1100	1117	43	3	5	727	635	104
3	4	1939	2015	173	0	0	695	702	72					
3	6	940	947	67	1	-9	1377	1488	203	*****	h = 27	*****		
4	-3	1071	1122	65	1	-6	1469	1653	126					
4	2	785	734	77	1	0	2751	2886	86	0	1	2151	2113	121
*****	h = 22	*****			2	-5	5109	4984	134	1	-5	6381	6243	164
0	-9	1661	1662	64	2	-4	2254	2069	191	2	-9	1344	1242	76
0	-8	1453	1432	81	2	-1	939	939	137	2	-3	1657	1623	193
0	-6	1395	1428	89	2	0	708	600	75	2	1	1818	1817	77
0	0	3254	3300	92	3	-4	665	633	74	3	-2	1185	1216	58
0	3	3002	2886	84	3	-1	764	747	63	3	-1	1946	1872	75
0	7	1362	1334	115	3	0	2203	2095	91	3	5	5082	4851	136
1	-10	1417	1534	217	*****	h = 25	*****			*****	h = 28	*****		
1	-3	3401	3209	93						0	-10	2037	2096	83
1	0	2326	2378	77	0	-10	1810	1762	137	0	-3	5196	5132	255
1	2	4280	4101	112	0	-3	2467	2349	113	0	-1	2950	2910	138
1	7	3419	3540	562	0	-2	2083	1996	137	0	0	2824	2827	88
2	-7	948	1159	152	1	-8	3141	3122	245	0	2	3404	3033	494
2	-6	1214	1225	125	1	-1	2331	2241	197	0	5	1479	1437	180
2	0	2762	2731	87	1	2	2080	1913	221	1	0	4375	4385	120
2	1	658	607	57	1	5	934	1024	88	1	1	4222	4176	252
2	3	2370	2422	116	2	-8	1785	1817	96	1	2	2249	2032	270
2	4	2269	2202	74	2	-7	1425	1485	127	1	6	4646	4607	124
3	0	1790	1784	89	2	-3	1998	1999	109	2	-8	2488	2837	264
3	2	3062	3024	89	2	-2	1721	1707	73	2	-2	2794	2628	82
3	3	2344	2375	77	3	-7	2696	2748	88	2	0	2288	2445	88
3	4	1220	1211	95	3	-5	709	763	89	2	1	2416	2526	264
3	7	2765	2770	100	3	-2	1413	1439	62	2	3	4337	4440	188
4	0	1792	1823	84	3	-1	1564	1674	61	3	-2	1568	1542	107
*****	h = 23	*****			3	3	993	1012	59	3	-1	3152	3215	93
0	-10	1904	2225	206						3	0	3255	3291	106
0	2	1273	1158	49	*****	h = 26	*****			3	4	904	854	63
0	9	2409	2703	344	0	-4	4695	4625	124	*****	h = 29	*****		
1	-11	906	1034	134	0	0	797	793	69					
1	-8	6053	5868	158	1	-4	1349	1177	82	0	-8	4801	4724	214
1	4	1181	1261	111	1	-2	3235	3102	303	0	2	5453	5179	389
2	-4	1463	1249	241	1	-1	2805	2669	308	0	6	714	787	75
2	-2	932	980	50	1	0	5501	5502	145	1	-9	935	1026	78
3	-5	970	933	66	2	-2	1559	1409	66	1	-1	3833	3881	588
3	2	1085	1023	54	2	0	687	680	85	1	3	1535	1529	60
3	4	914	926	58	2	4	4290	4020	131	1	4	2986	2820	109
					2	6	1097	1111	91	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	***** h = 37 *****				
3	-1	2859	3033	91	3	3	2029	2111	83	***** h = 33 *****				
3	2	1533	1593	175	***** h = 30 *****					0	-4	2220	2119	262
***** h = 30 *****					0	-5	1540	1359	96	0	-3	2398	2422	166
0	-9	3734	3583	108	0	8	4986	4943	234	0	5	5841	5564	154
0	-7	2075	2225	81	1	-8	1823	1756	253	1	-5	1236	1087	97
0	-6	917	831	68	1	2	1511	1393	88	1	4	3116	3255	308
0	-4	1223	1093	183	1	6	2860	2501	444	2	-4	1786	1876	153
0	1	3492	3587	95	2	5	1198	1190	113	2	3	2166	2171	305
0	3	4457	4561	117	3	-2	1104	1113	100	***** h = 38 *****				
1	-9	870	804	130	***** h = 34 *****					0	0	5916	6129	160
1	0	2706	2513	89	0	-3	2348	2515	76	0	1	2016	2118	201
1	6	3280	3274	166	0	-1	1761	1824	97	0	6	3273	3216	143
2	-4	845	948	105	0	0	1750	1841	89	1	-2	1891	1795	114
2	-1	3083	3123	89	1	-7	1563	1505	215	1	0	3746	3823	114
2	0	647	444	98	1	-5	4379	4170	121	1	1	2988	3061	155
2	3	3878	3955	106	1	0	706	761	102	1	3	2949	3168	176
3	0	1920	1927	99	1	4	1293	1286	204	2	0	5321	5429	150
3	1	1815	1912	197	2	0	1724	1604	94	2	1	1756	1886	157
***** h = 31 *****					2	1	1663	1625	62	***** h = 39 *****				
0	-7	2366	2194	177	2	3	2058	2219	79	0	-4	3268	3585	95
0	6	2691	2541	84	***** h = 35 *****					0	-3	2154	2138	123
0	8	2290	2238	243	0	-8	1509	1406	93	0	-2	1465	1415	170
1	-8	937	872	75	0	-7	2801	2568	314	0	-1	1701	2020	99
1	-2	1676	1617	167	0	-6	1449	1357	114	1	2	2252	2254	113
1	4	2042	1787	145	1	-6	1847	1830	277	2	1	1665	1821	130
1	5	3355	2935	439	1	-2	2578	2506	81	2	2	1271	1287	92
2	6	2231	2243	85	1	1	1130	1117	57	***** h = 40 *****				
3	2	1231	1244	60	2	2	1377	1397	179	0	-5	1673	1723	76
3	3	1368	1391	159	***** h = 32 *****					1	-3	3953	3972	314
3	4	1413	1437	61	***** h = 36 *****					1	-1	3206	3241	96
***** h = 32 *****					0	-7	2816	2459	440	1	0	1098	1122	88
0	-8	1812	1826	123	0	-3	1745	1919	258	***** h = 41 *****				
0	-2	2265	2276	154	0	-2	3354	3355	195	0	-4	832	808	71
0	-1	920	900	90	0	0	3928	3907	115	0	-2	1307	1401	100
0	0	2991	3066	94	0	1	2273	2231	129	0	3	1208	1291	162
0	7	2492	2246	350	1	0	2211	2281	99	1	2	1935	1926	75
0	9	1905	1852	105	1	3	2877	2926	157					
1	-3	2608	2686	210	2	-4	1385	1488	67					
1	0	3531	3456	105										

k	l	Po	Pc	sigF	k	l	Po	Pc	sigF	k	l	Po	Pc	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 ($\times 10$) FOR $\text{Nb}_{12-x}\text{Ta}_x\text{S}_4$ ($x \approx 5.26$)**

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

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
0	9	828	772	0	3	21	4337	4280	0	1	10	824	771	0
0	13	2814	2926	0	3	27	1905	1798	0	1	12	1822	1792	0
0	15	3316	4062	0	3	28	3179	3101	99	1	13	1654	1581	64
0	44	1157	1249	0	3	29	3292	3225	0	1	20	2183	2128	0
1	-43	2306	2183	89	3	30	1653	1513	0	1	22	2238	2211	0
1	-42	1629	371	0	3	31	2351	2226	90	1	32	2027	1902	0
1	-40	2693	2791	0	4	-16	1359	1299	0	1	34	1954	2138	0
1	-35	1839	1723	0	4	-14	819	519	0	2	-37	2711	2625	90
1	-21	6090	5860	0	4	-11	3550	3313	0	2	-28	868	482	0
1	-18	990	386	0	4	10	1829	1688	96	2	-27	2517	2474	95
1	-17	1493	1380	0	4	12	4704	4570	0	2	-19	3339	3199	0
1	-13	2024	2140	0	4	13	1632	1493	0	2	-17	1325	1357	90
1	-7	1609	1653	98	4	15	2052	2145	0	2	-13	1415	1249	79
1	-6	3892	3789	0	4	19	1908	1907	0	2	-10	3521	3514	0
1	-5	4827	4802	0	4	20	2256	2303	91	2	-9	2430	2333	0
1	-3	3376	3279	0	4	23	1233	1208	0	2	-6	1243	1244	0
1	-2	2082	2137	0						2	4	2194	2209	0
1	0	2671	2709	81	----- h =	3	-----			2	5	2083	2031	71
1	8	1390	1330	58						2	7	5062	5054	0
1	9	4041	3981	0	0	-43	2584	2440	0	2	8	3726	3746	0
1	16	1688	1656	0	0	-40	2680	2957	0	2	11	3074	3160	0
1	37	1854	1847	0	0	-37	3114	2976	0	2	12	2100	2147	0
2	-38	2684	2326	0	0	-16	924	638	90	2	14	1508	1373	0
2	-15	3370	3250	0	0	-14	1714	1687	88	2	18	1670	1631	0
2	-13	2237	2305	80	0	-13	1529	1579	0	2	20	1146	1188	0
2	-12	7377	7165	0	0	4	2835	2886	0	2	21	1810	1873	0
2	-11	5227	5082	0	0	5	2611	2667	0	2	22	1294	1285	0
2	10	2628	2681	0	0	6	1419	1548	0	2	23	902	895	0
2	14	829	988	0	0	7	6566	6495	0	2	40	2529	2646	0
2	16	1884	1928	0	0	8	4570	4752	0	3	-25	1752	1512	94
2	19	2679	2834	0	0	9	2961	2956	0	3	-12	1177	1215	0
2	20	3428	3512	0	0	10	4425	4437	0	3	-10	888	489	0
2	23	1841	1708	0	0	11	3836	3991	0	3	-7	908	937	0
2	26	2427	2623	0	0	12	2585	2599	0	3	-3	3380	3264	0
2	27	1299	1235	0	0	19	3288	3889	0	3	1	3885	4152	0
2	30	4268	4349	0	0	21	2651	2281	0	3	2	7283	7138	0
2	37	2378	2175	0	0	25	1148	1159	0	3	16	1522	1509	96
2	39	2743	2577	0	0	27	2922	2857	0	3	17	2923	2896	0
3	-32	2347	2184	0	0	31	1533	1408	0	3	18	1516	1377	97
3	-22	2045	1871	81	1	-42	1796	1933	0	3	20	1634	1483	0
3	-20	2788	2771	0	1	-40	2550	2581	0	3	22	1620	1645	0
3	-6	2666	2556	0	1	-28	1722	1752	80	3	26	1273	1373	0
3	-5	3302	2996	0	1	-17	3489	4092	0	3	28	1241	1362	0
3	-3	2262	2065	0	1	-9	721	249	0	3	31	1194	1142	0
3	0	1746	1759	0	1	-3	5018	4928	0	3	32	1820	1504	0
3	2	1730	1536	0	1	-2	11407	10916	0	3	34	1617	1695	0
3	9	2538	2533	99	1	1	6226	6169	0	4	-19	2144	2160	94
3	13	1461	1503	98	1	5	1057	1115	0	4	-13	1121	763	0
3	14	1008	283	0	1	6	1508	1488	66	4	-12	1383	1505	0
3	17	1124	938	0	1	7	1361	1408	69	4	-5	1298	1178	0

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
4	-4	1353	1362	0	2	21	2933	2967	0	1	2	1240	1272	81
4	7	3427	3209	0	2	22	2152	2314	0	1	10	1471	1728	0
4	8	2454	2447	91	2	24	3395	3210	0	1	11	1271	1278	85
4	9	1622	1481	0	2	26	3582	3766	0	1	15	1589	1445	75
4	10	2294	2307	92	2	35	1905	2028	0	1	16	1074	1170	0
4	11	2248	2039	0	2	38	3179	3236	0	1	22	1147	1063	0
4	20	1181	812	0	3	-28	2373	2299	87	1	24	1444	1367	90
4	21	1344	1220	0	3	-25	1911	1905	0	1	29	1874	2027	0
----- h = 4 -----					3	-22	1277	1105	0	2	-34	3066	2916	0
0	-35	2239	2293	0	3	-17	6985	6842	0	2	-28	3135	2870	0
0	-24	4218	3781	0	3	1	1117	1020	0	2	-10	990	936	0
0	-12	1891	1971	0	3	16	1862	2004	0	2	-8	3784	3720	0
0	-9	3307	3293	0	3	18	1966	1843	0	2	-7	1923	1849	0
0	-8	7904	7727	0	3	19	1704	1744	0	2	-3	3423	3508	0
0	-4	3897	3995	0	3	29	1504	1491	0	2	-2	1289	1455	0
0	-1	1426	1523	0	3	32	2186	2330	0	2	1	801	467	0
0	0	2816	2700	0	4	-7	3653	3757	0	2	4	3135	3291	95
0	3	1735	1571	0	4	-4	1991	2043	0	2	6	1489	1438	88
0	6	1764	1857	0	4	0	1090	1203	0	2	11	1513	1378	0
0	7	7585	7499	0	4	8	4205	4022	0	2	12	918	820	0
0	18	1343	1448	78	4	9	1769	1763	0	2	15	1207	1134	0
0	26	4469	4354	0	4	12	1359	1135	0	2	22	2436	2440	0
0	28	2737	2443	0	----- h = 5 -----					2	23	3454	3126	0
0	33	1171	959	0	0	-42	1896	1999	0	2	24	2137	2213	0
0	38	3692	3628	0	0	-36	1543	1522	0	2	27	3798	3758	0
1	-43	2194	2181	0	0	-27	4971	4318	0	2	36	1400	1339	0
1	-37	1354	1715	0	0	-18	1098	1154	0	3	-22	1172	815	0
1	-12	912	813	0	0	-10	1048	1172	0	3	-19	1314	1481	0
1	-5	1101	1169	83	0	-6	1817	1807	64	3	-18	1591	1505	0
1	-4	662	616	0	0	2	1719	1814	63	3	10	1266	1143	0
1	-2	1158	1226	79	0	3	4288	4400	0	3	13	5798	5804	0
1	-1	1381	1435	71	0	4	4009	4018	95	3	14	1763	1627	0
1	0	1578	1640	65	0	5	693	612	0	3	15	1004	1133	0
1	17	9221	9365	0	0	7	2175	2264	0	3	27	1601	1534	0
1	22	1586	1564	0	0	8	4574	4618	0	4	-8	2548	2465	89
1	25	2635	2534	0	0	11	1691	1748	0	4	3	2141	2283	0
2	-29	1264	730	0	0	12	1076	998	91	4	4	1992	2231	0
2	-28	2197	2110	0	0	15	1239	1375	0	----- h = 6 -----				
2	-23	2274	2338	0	0	16	1148	1215	91	0	-33	3162	3161	0
2	-12	1590	1627	80	0	24	2476	2513	0	0	-29	1115	668	0
2	-7	5963	5848	0	0	34	3456	3289	0	0	-28	890	471	0
2	-6	1374	1348	0	1	-32	2868	2836	0	0	-26	2339	2284	84
2	0	1940	2029	0	1	-27	2139	1998	0	0	-19	2583	3111	0
2	1	1035	1158	0	1	-21	1296	1434	0	0	-15	3007	2998	0
2	4	3147	3119	0	1	-14	2326	2266	83	0	-13	1010	821	0
2	8	6250	6153	0	1	-13	8333	7984	0	0	-11	2227	2245	0
2	9	2769	2651	0	1	-12	3701	3792	0	0	-9	2722	2746	0
2	18	1094	1172	0	1	-9	742	551	0	0	-3	5612	5633	0

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
0	0	2887	2865	0	3	3	2028	2111	89	2	15	5406	5540	0
0	2	2394	2415	77	3	8	1915	2022	0	2	31	1158	286	0
0	4	5704	5690	0	3	13	2574	2983	0	3	-24	3988	3924	0
0	5	3369	3430	0	3	14	2229	2591	0	3	-23	2441	2511	0
0	8	1369	1407	81	3	17	2136	2128	87	3	-19	1205	1388	0
0	12	3222	3246	0	3	25	991	438	0	3	-13	1641	1680	0
0	18	2671	2562	0	3	29	2006	2014	0	3	-8	1573	1592	0
0	23	5125	5266	0	4	-12	1670	1796	0	3	-7	2185	2281	0
0	36	1389	1263	0	4	-9	1594	1541	0	3	-5	2385	2471	0
0	38	2733	2839	0	4	-4	2785	3182	0	3	-1	1690	1435	0
1	-29	2506	2564	0	4	0	1631	1500	0	3	3	1874	1860	93
1	-17	2755	2791	97	4	3	2676	3085	0	3	6	1824	2061	0
1	-10	1633	1606	76	~~~~~ h = 7 ~~~~~					3	10	1450	1417	0
1	-8	2866	2740	0	0	-29	1174	77	0	3	26	3096	2928	0
1	-7	4377	4427	0						4	1	1339	751	0
1	-4	1345	1384	85	0	-25	1108	1243	0	4	3	1166	767	0
1	-1	778	836	0						~~~~~ h = 8 ~~~~~				
1	0	2590	2618	80	0	-17	3094	3182	97	0	-36	2717	2731	0
1	2	4072	4131	97	0	-16	2822	2905	0					
1	3	3133	3051	96	0	-12	1289	1195	99	0	-31	1811	1468	0
1	5	4030	4066	0	0	-10	1786	1735	0	0	-25	1240	1619	0
1	6	3871	3996	0	0	-6	978	1268	0	0	-13	1621	1424	0
1	13	3994	4025	0	0	3	1507	1372	83	0	-11	3096	3031	0
1	14	3597	3416	0	0	4	1135	1070	0	0	-7	2320	2359	86
1	24	1792	1856	0	0	14	1498	1455	0	0	-3	1597	1583	89
1	27	898	898	0	0	15	6459	6450	0	0	-1	1553	1583	90
1	32	1925	1891	0	0	18	3641	3703	0	0	0	3487	3510	0
1	33	1373	618	0	0	32	2118	1984	0	0	5	1937	1986	0
1	38	1967	1849	0	0	35	3692	3396	0	0	12	2106	2337	0
2	-11	1908	1908	0	1	-13	2214	2256	81	0	14	3957	3969	0
2	-9	2300	2279	0	1	-10	1724	1853	83	0	15	3227	3102	0
2	-4	4817	4702	0	1	-9	2013	2017	0	0	16	3537	3652	0
2	0	2257	2315	83	1	-3	2260	2434	0	0	28	1856	1687	0
2	1	792	597	0	1	1	1929	1950	76	0	30	1688	1236	0
2	2	1876	2007	80	1	5	3235	3255	0	0	34	5097	4859	0
2	3	4672	4620	0	1	6	2556	2760	0	1	-25	5766	5567	0
2	5	2810	2847	0	1	7	2974	3039	0	1	-23	1811	2030	0
2	8	1246	1180	0	1	8	2065	2131	0	1	-11	1091	824	0
2	12	2749	2704	0	1	17	1031	1116	0	1	-10	2568	2606	92
2	15	2466	2555	88	1	19	1759	1816	85	1	-9	2313	2385	0
2	23	4529	4569	0	1	24	4807	4987	0	1	-6	3415	3451	0
2	26	2025	2002	88	1	26	4092	3722	0	1	-5	3294	3362	0
2	33	2662	2817	0	1	28	1420	1441	0	1	1	1492	1386	93
3	-23	1166	888	0	1	35	1818	1219	0	1	3	2144	2221	0
3	-10	1398	1136	0	2	-3	1148	1152	0	1	4	2848	2984	91
3	-7	3030	3205	0	2	1	1175	1127	0	1	8	2256	2178	0
3	-6	2704	2941	90	2	4	908	938	0	1	14	1767	1760	0
3	-5	2732	2943	0	2	6	923	1063	0	1	16	1168	1142	0
3	0	1814	1857	94	2	10	1484	1453	0	1	28	2049	2003	0
3	2	2987	2913	97	2	12	1100	972	0					

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
1	30	2064	1760	0	2	-6	1803	1806	0	0	-24	2093	2133	0
1	32	2370	2108	0	2	-5	3786	4004	0	0	-14	1335	1135	0
1	34	1752	1853	0	2	-2	1435	1312	0	0	-11	2242	2230	89
2	-31	1475	1294	0	2	-1	1463	1414	0	0	-8	2588	2663	93
2	-30	1504	1109	0	2	3	1431	1469	0	0	-6	3452	3456	0
2	-27	1341	661	0	2	4	4806	4891	0	0	3	1631	1369	0
2	-16	2572	3181	0	2	10	1085	1093	0	0	7	3119	3112	0
2	-11	2472	2592	91	2	16	2714	2836	93	0	10	1891	1904	0
2	-7	2071	2007	82	3	-14	2129	2321	0	0	22	2282	2637	0
2	0	2866	3024	0	3	-9	1733	1941	0	1	-10	1938	2041	98
2	1	952	1343	0	3	4	1512	1728	0	1	-2	2157	2031	0
2	3	1041	1325	0	3	5	3046	3133	0	1	-1	1332	1465	0
2	5	1743	1665	0	3	6	1945	2155	0	1	12	1183	1241	0
2	12	1964	2060	0	3	11	1598	1626	0	2	-10	1616	1683	0
2	14	3108	3470	0	----- h = 10 -----					2	-8	2162	2344	0
3	-9	1465	1839	0	0	0	3278	3216	0	2	-7	2370	2771	0
3	-6	2549	2609	92	0	2	1296	1142	0	2	3	988	1216	0
3	-5	2557	2583	0	0	4	2911	2834	96	2	6	2917	3062	0
3	3	1566	1714	0	0	6	1256	1139	0	----- h = 12 -----				
3	4	2248	2258	92	0	13	1435	1414	0	0	-1	2102	1918	93
3	8	1577	1649	0	0	15	2338	2347	0	0	3	1710	1657	0
3	10	1718	1986	0	0	17	1762	1705	99	0	5	1956	1950	0
3	20	1333	1301	0	0	19	2972	3140	0	0	8	3403	3161	0
----- h = 9 -----					0	25	4855	4944	0	0	13	3068	3047	0
0	-33	1936	1716	0	0	31	1953	1788	0	1	-6	1480	1550	0
0	-30	3049	2958	0	1	-21	2311	2463	0	1	-4	3421	3447	0
0	-20	1161	1116	0	1	-14	2381	2851	0	1	-3	2693	2901	0
0	-16	3051	3215	0	1	-8	1867	1641	0	1	-2	2587	2549	0
0	-10	1231	1245	0	1	-2	1230	1345	0	1	-1	2314	2352	93
0	-9	2099	2045	0	1	4	1389	1285	0	1	5	1722	1610	0
0	-5	4739	4625	0	1	5	1298	1305	0	1	10	1643	1671	0
0	-2	1571	1528	92	1	6	2428	2514	92	2	-3	1338	1463	0
0	-1	1681	1654	91	1	9	1635	1667	0	2	-1	1558	1687	0
0	3	1745	1688	0	1	13	3014	3222	0	2	5	1780	1729	0
0	4	5620	5632	0	1	16	3499	3772	0	2	8	2846	2832	99
0	6	2018	2033	81	1	29	1142	827	0	----- h = 13 -----				
0	15	976	1145	0	2	-22	1746	2048	0	0	-12	3360	3468	0
0	26	1157	782	0	2	-19	2739	2774	0	0	-8	1935	1973	0
1	-31	1759	1772	0	2	-17	1348	1486	0	0	-2	1452	1618	0
1	-17	2196	2306	0	2	0	2851	2866	0	0	6	1393	1340	0
1	-14	2854	2998	0	2	4	2407	2476	0	1	-3	1254	1058	0
1	-11	1995	2063	84	2	15	1960	2074	0	1	-1	1663	1767	0
1	4	2200	2206	82	3	-6	1801	2008	0	----- h = 11 -----				
1	5	4014	4065	0	3	2	1055	1005	0	0	-26	2337	2413	0
1	6	2823	2779	97										
1	9	2381	2428	85										
1	25	3312	3276	0										
2	-9	1813	1756	93										

APPENDIX C OBSERVED AND CALCULATED STRUCTURE FACTOR
AMPLITUDES ($\times 10$) FOR $\text{Nb}_x\text{Ta}_{5-x}\text{S}_2$ ($x \approx 1.72$)

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

APPENDIX D OBSERVED AND CALCULATED STRUCTURE FACTOR
AMPLITUDES ($\times 10$) FOR $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.95$)

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

APPENDIX E OBSERVED AND CALCULATED STRUCTURE FACTOR
AMPLITUDES ($\times 10$) FOR $\text{Nb}_{21-x}\text{Ta}_x\text{S}_8$ ($x \approx 6.2$)

k	l	Po	Pc	sigF	k	l	Po	Pc	sigF	k	l	Po	Pc	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	***** h = 4 *****				
11	1	9693	9203	243	-10	0	3771	3883	202					
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
***** h = 1 *****														
				-2	0	548	512	25	-7	-3	880	822	34	
				0	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	***** h = 5 *****				
2	1	952	1027	30	-9	-2	1835	1755	51					
3	0	609	322	62	-6	-3	561	544	32	-16	-1	2189	2242	61
3	2	443	344	33	-6	-1	678	669	32	-15	-2	3609	3574	94
4	1	2802	2955	72	-5	0	335	248	22	-14	-1	3226	3229	84
4	3	1919	1832	99	-4	-1	10057	9666	252	-12	-1	2668	2648	70
6	3	736	789	34	-2	-3	2264	2247	67	-11	-2	1239	1173	72
7	0	8956	8434	335	-2	-1	3333	3512	84	-11	0	1416	1430	42
7	2	6632	6651	167	0	-1	1124	1056	100	-11	-2	7087	6994	447
8	3	1194	1168	44	0	3	726	718	90	-9	-1	628	639	35
10	3	613	580	41	2	3	1309	1329	48	-6	0	4610	4599	312
15	2	2727	2787	105	4	1	1254	1249	36	-5	-1	2013	2076	76
16	1	571	589	69	4	3	741	704	31	-4	-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
										-5	0	1309	1302	61
*****	h =	6	*****		*****	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
-17	0	1593	1640	50	4	3	607	605	30	-7	-3	3491	3649	211
-16	-1	559	588	68	4	0	5275	5333	133	-7	-1	4849	4809	346
-15	0	1452	1482	45	6	2	4378	4327	132	-6	-2	1430	1445	46
-10	-1	1715	1737	53	9	3	3067	3039	118	-6	0	1804	1744	82
-9	0	3988	3978	102	11	1	986	1008	104	-5	-3	4595	4742	137
-8	-3	3505	3754	129	12	0	415	341	35	-5	-1	6647	6350	302
-8	-1	5316	5208	188	13	1	1589	1647	154	-4	0	1514	1464	77
-7	0	665	717	68	14	2	1685	1592	77	-3	-3	2455	2426	68
-4	-1	1106	1169	65	17	1	394	311	45	-3	-1	3363	3328	86
							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 = 11 *****					***** h = 13 *****					-1	0	3184	3222	412
-14	-1	523	509	55	-11	-2	3557	3575	229	0	1	2266	2329	89
-13	-2	564	473	38	-11	0	3958	4039	127	1	2	1343	1305	45
-13	0	487	527	36	-10	-1	3497	3445	184	2	1	674	677	27
-11	0	5664	5645	151	-9	-2	2880	2815	137	3	0	4941	5037	195
-9	0	2621	2642	136	-7	-2	927	910	43	4	1	1016	1074	53
-7	-2	1351	1363	137	-6	-1	1519	1483	84	5	0	3986	4079	151
-7	0	1592	1593	103	-5	0	4387	4283	578	6	1	1317	1369	45
-6	-3	1653	1691	70	-4	-1	1987	1998	110	7	2	1290	1313	48
-6	-1	2176	2185	135	-2	-1	1030	1013	38	9	0	579	532	31
1	0	736	728	80	0	-3	900	918	32	10	1	2479	2472	68
1	2	635	594	28	1	0	1012	1055	73	11	0	643	685	54
2	1	4845	4849	123	1	2	869	885	33	***** h = 16 *****				
2	3	3562	3598	93	2	2	400	332	38	-9	-1	3344	3287	194
6	3	1345	1400	93	4	1	2534	2539	67	-7	-1	4597	4492	318
9	0	622	642	79	5	0	582	620	27	-5	-1	2347	2342	150
9	2	619	566	32	6	1	3003	3019	79	-4	0	1800	1804	177
10	1	1887	1892	54	7	0	2002	2107	55	-3	-1	3510	3467	200
11	2	5022	4938	304	7	2	1810	1827	95	-2	0	709	693	101
12	1	1963	1987	70	13	0	1158	1130	44	0	2	2691	2699	89
15	0	926	918	38	14	1	1585	1514	51	2	0	3907	4010	135
***** h = 12 *****					***** h = 14 *****					2	2	3529	3537	92
-15	-1	1504	1472	133	-14	0	1137	1137	46	6	0	1268	1254	44
-13	-1	571	525	34	-9	-1	1922	1906	104	6	2	1175	1102	46
-12	0	556	601	34	-6	-2	607	564	33	10	0	2601	2677	70
-10	0	5839	5761	239	-5	-1	2607	2637	152	***** h = 17 *****				
-9	-1	823	834	92	-4	-2	5636	5528	143	-1	-2	1308	1367	131
-8	-2	1467	1412	56	-4	0	6569	6368	706	-1	0	1477	1553	145
					-3	-1	337	319	41					

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 ($\times 10$) FOR $\text{Nb}_x\text{Ta}_{2-x}\text{S}$ ($x \approx 0.2$)

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

k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF	k	l	Fo	Fc	sigF
4	7	1566	1526	95	-1	-2	1783	1894	86	8	5	1862	1891	0
4	12	2033	2004	97	-1	-1	1517	1584	0	8	6	1867	1967	0
5	-15	1411	1576	0	-1	4	3868	3914	0	----- h = 3 -----				
5	-9	2109	2205	0	0	-24	1435	1399	0					
5	-7	2873	2948	0	0	-22	1316	1170	0					
5	6	1056	1084	0	0	-20	1397	746	0	-8	-9	1350	1009	0
5	7	2858	2949	0	0	-18	1964	1904	99	-8	-4	1234	1347	0
5	9	2251	2206	88	0	-16	2300	2245	88	-8	8	1702	1592	0
6	-15	2298	2279	0	0	-6	6955	7058	0	-7	-4	2495	2466	0
6	-11	2106	2027	0	0	4	3366	3327	0	-7	0	3976	4054	0
6	-9	3801	3550	0	0	10	2904	2846	0	-5	-15	2752	2636	0
6	1	1594	1516	81	0	14	2982	2994	98	-5	-11	2023	2258	0
6	3	3753	3779	0	1	-15	3212	3191	0	-5	-7	1217	986	0
6	9	3525	3552	0	1	4	3898	3915	0	-5	-1	3491	3509	0
6	12	1107	607	0	1	5	1743	1726	52	-5	11	2304	2257	0
6	15	2131	2281	0	1	9	2629	2697	67	-5	19	2010	2228	0
7	6	3692	3685	0	1	10	1386	1338	70	-4	-12	2775	3005	0
7	10	2271	2150	0	1	16	2753	2823	75	-4	-10	4189	4250	0
----- h = 2 -----					2	3	3364	3391	0	-4	-4	2517	2661	0
					2	9	5412	5508	0	-4	-2	3779	3829	0
					2	19	1552	1637	0	-4	0	4499	4474	0
-8	5	1928	1891	0	2	21	3308	3413	0	-4	2	3866	3829	0
-8	6	1574	1967	0	2	23	1773	1738	0	-4	8	3190	3363	0
-6	-9	2929	2955	0	3	-3	2534	2570	0	-4	12	2790	3003	0
-6	-6	1819	1766	0	3	0	4065	4124	0	-4	14	1383	1388	0
-6	-2	1164	1020	0	3	4	4490	4441	0	-4	20	2669	2549	0
-6	11	2768	2674	0	3	8	1257	1262	78	-3	-20	1743	1541	0
-5	-18	1441	730	0	3	9	1759	1666	88	-3	-14	1259	1021	0
-5	-9	2257	2324	93	3	16	3465	3557	0	-3	-12	3088	3092	0
-5	-3	3879	3864	0	4	-16	2182	2202	0	-3	-3	1227	1109	0
-5	-1	1711	1706	0	4	-14	1904	1802	0	-3	0	5542	5414	0
-5	15	2961	2901	0	4	-10	1807	1739	97	-3	16	2811	3022	0
-4	-7	1300	1192	0	4	5	1951	1855	75	-2	-21	1433	1252	0
-4	-6	3961	4006	0	4	8	948	824	0	-2	-11	1367	1430	96
-4	-4	2888	2957	0	4	10	1775	1740	98	-2	-7	1724	1720	61
-3	-15	1906	1838	0	4	14	1792	1803	0	-2	-1	1208	1229	0
-3	-14	1316	1325	0	4	16	2115	2203	0	-1	-16	2692	2669	0
-3	-12	2220	2066	0	4	17	1352	777	0	-1	-11	2666	2654	0
-3	-10	2607	2607	84	5	-17	1414	1382	0	-1	-6	1207	1243	70
-3	-5	1303	1354	84	5	-9	2315	2323	0	-1	-5	942	886	98
-3	-3	2548	2571	93	5	4	1724	1717	95	-1	-4	3237	3257	0
-3	-2	2687	2654	93	5	5	1049	1048	0	-1	0	5904	5890	0
-3	15	1813	1837	0	5	15	2952	2903	0	-1	19	2557	2557	0
-3	16	3565	3555	0	6	-10	1905	1969	0	0	-22	3369	3243	0
-2	-11	4777	4714	98	6	-9	2898	2953	0	0	-18	1987	1864	98
-2	-1	5298	5258	0	6	1	2739	2790	89	0	-16	1375	1339	0
-1	-15	3247	3192	0	6	3	1890	1837	0	0	-14	2122	2133	85
-1	-14	1200	1512	0	6	11	2529	2676	0	0	-12	3269	3280	0
-1	-8	2183	2206	70	7	0	1638	1864	0	0	-10	6268	6236	0
-1	-3	4735	4852	0	7	4	2373	2534	0	0	-2	6144	6190	0

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

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