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X-RAY DIFFRACTION STUDIES OF METAL-RICH TRANSITION METAL SULFIDES AND SELENIDES FORMED AT HIGH TEMPERATURES

1. THE TANTALUM SULFUR SYSTEM

2. THE GROUP IV-B DIMETAL SELENIDES

by

John George Smeggil

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

### Approved:

Signature was redacted for privacy.

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Signature was redacted for privacy.

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Dean of Graduate College

Iowa State University Ames, Iowa

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#### I. INTRODUCTION

#### A. General Background

The transition metal-sulfur and selenium systems have been the objects of a large number of studies by many investigators. Jellinek (1) and Haraldsen (2) have reviewed work by Biltz and Köcher (3, 4, 5, 6), Ehrlich (7, 8, 9), Hahn (10, 11, 12, 13, 14, 15), Jellinek (16), McTaggert and Wadsley (17), Selte and Kjekshus (18) and many others.

Three general methods were used by the early workers to prepare metal-rich sulfides and selenides. The first method involved placing stoichiometric mixtures of metal powder filings and chalcogen in clean fused silica tubes which were evacuated, sealed, and placed in resistance furnaces heated to between 800°C and 1300°C for periods of time varying from a few days to several weeks. The second method of preparation involved the thermal degradation of chalcogen-rich phases, and the third method employed H<sub>2</sub>S gas which was passed over the heated metal.

The results of these preparations were phases with C/M ratios, where C is the chalcogen and M is the appropriate transition metal, greater than or equal to 1, and in no case were metal-rich chalconides (C/M  $\leq$  1/2) produced by these techniques. This failure to prepare equilibrium samples containing metal-rich phases may be due to kinetic

It has been generally observed that the metalfactors. chalcogen reaction results in the coating of the metal by a chalcogen-rich phase which, at the temperatures used, is relatively impervious to further diffusion of the chalcogen, thereby blocking the complete reaction of chalcogen with the metal. The degradation method, on the other hand, results in phases with negligible chalcogen partial pressures at the reaction temperatures, resulting in a negligible rate of chalcogen loss. If the temperature of the furnace containing the sample preparation tubes is significantly raised above 1000°C in an attempt to increase the reaction rates, the principal effect is an increase in the interaction of the transition-metal with the silica of the preparation tubes to form metal silicides and oxides. For example, Jellinek (1) reported that a claim by Biltz for the preparation of a titanium subsulfide formed by reaction of the elements in fused silica tubes was incorrect, and that the phase actually prepared was Ti<sub>5</sub>Si<sub>3</sub>.

Recent work in the V-S system (19), the Ti-S system (20), the Hf-S system (21), and Nb-S system (22) demonstrated that new metal-rich chalconide phases were prepared at temperatures greater than 1300°C in containers that did not interact seriously with the sample. With these successful preparations in mind, it was decided to investigate the Ta-S system and the Group IVB transition metal-selenium systems with the

specific purposes of preparing metal-rich phases in these systems by high temperature techniques, characterizing the structures of these phases by X-ray crystallographic techniques and comparing the structures of these phases with structures of known metal-rich phases.

B. Incentives for Future Investigation

An understanding of the phase relations and structural chemistry of the metal-rich chalconides is important for several reasons. A knowledge of the phases in these systems at elevated temperatures is necessary if one is to evaluate the high temperature chemical compatibility of a metal with a given environment. Thermodynamic data for these condensed phases would also be highly useful for such an evaluation. Vaporization studies require as a basis an understanding of the condensed phases present. In addition, these phases may well possess some properties of interest in material science since they are all refractory in nature and exhibit properties indicative of metallic conduction at room temperature.

The determination of the structure is important from the viewpoint of understanding the nature of bonding in the condensed state which may in turn be useful in understanding the relationship between the properties and structure of a given phase. For example, one of the structural features of the

metal-rich chalconides, which suggests that the bonding of chalcogens in these solids is different from that usually assumed for sulfur or selenium, is the high chalcogen coordination, namely between seven and nine. Other new structural features were found in the metal-rich tantalum sulfides, and these will be discussed in a later section.

C. Pertinent Background Literature

#### 1. The tantalum-sulfur system

Biltz and Köcher (4) originally investigated the tantalum-sulfur system in 1938. Their method of sample preparation involved heating the elements in evacuated quartz tubes to 1100°C. They reported four phases present: a "tantalum-rich" subsulfide, TaS<sub>0.3-1.0</sub>; a "sulphur-rich" subsulfide, TaS<sub>1.0-1.9</sub>; a tantalum disulfide, TaS<sub>2</sub>; and a tantalum trisulfide, TaS<sub>3</sub>.

Hägg and Schönberg (23) later studied this system in 1954. They prepared samples by heating the elements in evacuated silica tubes and by passing  $H_2S$  gas over the metals heated to between 500°C and 900°C. They reported the existence of only a hexagonal tantalum disulfide, TaS<sub>2</sub>, which was found in four modifications  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . The forms  $\beta$ ,  $\gamma$  and  $\delta$ were found only with the TaS<sub>2</sub> stoichiometry. The  $\alpha$  form was found to have the Cd(OH)<sub>2</sub> structure type, and was observed to exist over a homogeneity range with a metal-rich boundary

given by S/Ta = 1.6. They found no evidence for intermediate phases existing between Ta and TaS<sub>2</sub>, nor for any phase corresponding to TaS<sub>3</sub>. Bjerkelund, Fermor and Kjekshus (24) reported that the phase TaS<sub>3</sub> is orthorhombic with space group  $C_{222_3}$ .

Jellinek (16) also prepared a series of tantalum disulfide polytypes:  $1s-TaS_2$ ,  $2s-TaS_2$ ,  $3s-TaS_2$ ,  $6s-TaS_2$ and random -  $TaS_2$  with 1, 2, 3, 6 and a random number of  $TaS_2$  repeat slabs per unit cell, respectively. Jellinek's findings with regard to the  $TaS_2$  polytypes are summarized in the following paragraph.

The structure of  $1s-TaS_2$  is of the Cd(OH)<sub>2</sub> structure type, with space group  $P\overline{3}m$ . In this structure the metal atoms are all octahedrally coordinated by sulfur atoms. This phase is the  $\alpha$ -TaS<sub>2</sub> phase reported by Hägg and Schönberg, and also the only TaS<sub>2</sub> phase reported by Biltz and Köcher. The phase 2s-TaS<sub>2</sub> is isostructural with NbS<sub>2</sub> (16), and belongs to the space group P6<sub>3</sub>/mmc. The metal atoms all have trigonal prismatic coordination in this structure. The phase  $\beta$ -TaS<sub>2</sub> reported by Hägg and Schönberg is the same as the 2s-TaS<sub>2</sub> phase. The 3s-TaS<sub>2</sub> phase is isostructural with the rhombohedral form of NbS<sub>2</sub>, and belongs to the space group R3m. The metal atoms all have trigonal prismatic coordination. The 6s-TaS<sub>2</sub> structure is rhombohedral and belongs to the space group R3m. The metal atom coordination is of

two types, one half of them are octahedrally coordinated and the other half are trigonal prismatically coordinated. The  $6s-TaS_2$  phase is the  $\delta-TaS_2$  phase reported by Hägg and Schönberg.

Jellinek reported obtaining from a sample which had been heated for a relatively short period of time a diffraction pattern which could only be indexed on a unit cell containing approximately one third of the volume of ls-TaS<sub>2</sub>. This phase, labelled random - TaS<sub>2</sub>, on further annealing yielded a mixture of ls-TaS<sub>2</sub>, 2s-TaS<sub>2</sub>, and 6s-TaS<sub>2</sub>.

Jellinek also investigated some metal-rich tantalum disulfudes of the general form  $Ta_{1+\alpha}S_2$ ,  $\alpha>0$ ; and his findings with respect to these phases are summarized in the following paragraph.

The phase  $2s-Ta_{1+2}S_2$ ,  $0.35 \ge z \ge 0.20$ , is isostructural with hexagonal  $2s-Nb_{1+x}S_2$  (1) and belongs to space group  $P6_3$ /mmc. The additional metal atoms (compared with  $2s-TaS_2$ ) are randomly inserted into octahedral positions. The structure of  $3s-Ta_{1+x}S_2$ ,  $x\simeq 0.15$ , is isostructural with rhombohedral  $3s-Nb_{1+x}S_2$  (1), belonging to space group R3m. The additional tantalum atoms in this phase (with respect to  $3s-TaS_2$ ) randomly occupy octahedral positions. The structure of  $6s-Ta_{1+y}S_2$ ,  $y\simeq 0.20$ , is rhombohedral, belonging to space group R3m. It was suggested that this phase is not closely related to the structure of  $6s-TaS_2$ , but is based on another

type of layer structure. The phases called  $\gamma$ -TaS<sub>2</sub> and  $\alpha$ -TaS<sub>2</sub> by Hägg and Schönberg and the two subsulfides reported by Biltz and Köcher were, according to Jellinek, mixtures of 2s-Ta<sub>1+z</sub>S<sub>2</sub>, 3s-Ta<sub>1+x</sub>S<sub>2</sub>, and 6s-Ta<sub>1+y</sub>S<sub>2</sub>. Jellinek makes no mention of any tantalum sulfide more metal-rich than 2s-Ta<sub>1+z</sub>S<sub>2</sub>, z = 0.35.

As discussed previously, the lack of knowledge concerning the existence of metal-rich phases in the Ta-S system was thought to result primarily from the techniques previously used for sample preparation. It was therefore decided to investigate this system using high temperature techniques with the purpose of preparing metal-rich phases. It was a further purpose to characterize any new solids, especially by the techniques of x-ray crystallography.

The lattice parameters, symmetry and space group for both the tantalum sulfides known prior to this research and the new tantalum sulfide phases known as a result of this research are listed in Table 1.

### 2. The Group IVB - transition metal - selenium systems

a. <u>The titanium - selenium system</u> The titaniumselenium system has been investigated by McTaggert and Wadsley (17), who report finding an hexagonal  $\text{TiSe}_2$ , an hexagonal  $\text{Ti}_2\text{Se}_3$  and an hexagonal TiSe. These samples were prepared by either combination of the elements in evacuated

| Phase   | Lattice<br>Symmetry | Lattice<br>Parameter      | S                      | Space<br>Group       | Reference |
|---|---------------------|---------------------------|------------------------|----------------------|-----------|
| TaS <sub>3</sub>                              | Monoclinic          |                           |                        |                      | l         |
|   | Orthorhombic        | a=36.79Å<br>c=3.340Å      | b=15.18Å               | C2221                | 24        |
| ls-TaS <sub>2</sub>                           | Trigonal            | a=3.36Å                   | c=5.90Å                | P3m                  | l         |
| 2s-TaS <sub>2</sub>                           | Hexagonal           | a=3.315Å                  | c=12.10Å               | P6 <sub>3</sub> /mmc | : 1       |
| 3s-TaS <sub>2</sub>                           | Rhombohedral        | a=3.32Å                   | c=17.9Å                | R3m                  | l         |
| 6s-TaS <sub>2</sub>                           | Rhombohedral        | a=3.335Å                  | c=35.85Å               | R3m                  | 1         |
| random TaS                                    | 2                   | a=1.92Å                   | c=5.99Å                |                      | l         |
| 2s-Tal+z <sup>S</sup> 2                       | Hexagonal           | °<br>a=3.295A<br>(z=0.20) | c=12.45Å               | P63/mmc              | 2 1       |
| 0.35 <u>&gt;</u> z <u>&gt;</u> 0.20           | )                   | a=3.29Å<br>(z=0.35)       | c=12.65Å               |                      |           |
| 3s-Ta <sub>1+x</sub> S <sub>2</sub><br>x=0.15 | Rhombohedral        | a=3.31Å                   | c=18.2Å                | R3m                  | , l       |
| 6s-Ta <sub>l+y</sub> S <sub>2</sub><br>v=0.20 | Rhombohedral        | a=3.315Å                  | c=36.2Å                | R3m                  | 1         |
| Ta <sub>2</sub> S                             | Orthorhombic        | a=7.381A<br>c=15.19A      | b=5.574A               | Pbcm                 | _a        |
| Ta <sub>6</sub> S                             | Monoclinic          | 。<br>a=14.16A<br>c=14.79Å | b=5.284Å。<br>β=118.01Å | C/2c                 | _a        |

Table 1. Summary of phases in the Ta-S system

<sup>â</sup>This research.

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sealed silica tubes or by thermal degradation of the chalcogenrich phases to yield the more metal-rich phases.

Grønvold and Langmehr (25) reported the existence of a  $TiSe_{0.95}$  with a MnP structure, a  $TiSe_{1.05}$  with a NiAs structure and the phase  $TiSe_{1.20-2.00}$  which is hexagonal at the metal-rich limit, becomes monoclinic upon addition of selenium, and then reverts to a hexagonal structure in the composition range  $TiSe_{1.40-2.00}$ . Their samples were prepared by heating the elements in alumina boats placed in silica tubes which were then evacuated, sealed and subsequently heated to between 600°C and 800°C.

Bernusset (26) reported a trigonal  $\text{TiSe}_2$ , a monoclinic  $\text{TiSe}_{1.60}$ , a monoclinic  $\text{TiSe}_{1.33}$  and a hexagonal  $\text{TiSe}_{1.09-1.20}$ . His samples were prepared by heating of the elements in evacuated and sealed silica tubes at temperatures between 500°C and 1100°C.

Chevreton and Brunie (27) report a monoclinic  $\text{TiSe}_{1.60}$ which is isostructural with  $V_5S_8$  and  $V_5Se_8$ . They prepared their samples by heating the elements at 800°C in evacuated and sealed silica tubes which first had a carbon coating deposited on them in an attempt to minimize interaction between the silica and metal. Brunie and Chevreton (28) reported finding an orthorhombic phase of unknown structure with the stoichiometry  $\text{Ti}_9Se_4$  with the lattice parameters a =  $3.43\text{\AA}$ , b =  $11.68\text{\AA}$  and c =  $14.47\text{\AA}$  belonging to the space group Pnn2

or Pnnm. As result of the work described in this thesis, this phase has been shown by single-crystal X-ray techniques to have the stoichiometry Ti<sub>2</sub>Se and will be discussed later in this thesis.

b. <u>The zirconium - selenium system</u> McTaggert and Wadsley (17) reported a monoclinic ZrSe<sub>3</sub>, whose structure has been determined by Krönert and Plieth (29), an hexagonal ZrSe<sub>2</sub> and an hexagonal ZrSe<sub>3</sub>.

Hahn and Ness (14) reported the existence of  $2rSe_3$ , a hexagonal  $2rSe_2$ , a tetragonal  $2r_4Se_3$ , a  $2rSe_{1.0-1.4}$  with a WC structure. Their samples were prepared by reaction of the elements in evacuated and sealed silica tubes heated from 700°C to 1000°C.

Solomons and Wiegers<sup>1</sup> investigated the composition range between ZrSe and  $\text{ZrSe}_2$  at temperatures between 800°C and 1200°C. They found  $\text{Zr}_{1+x}\text{Se}_2$  with the  $\text{Cd}(\text{OH})_2$  structure, the  $\text{Zr}_3\text{Se}_4$  phase reported by Hahn and Ness and a new phase  $\text{Zr}_2\text{Se}_3$ . The  $\text{Zr}_2\text{Se}_3$  structure was determined and was found to be intermediate between NaCl and  $\text{CdI}_2$ . The  $\text{Zr}_2\text{Se}_3$ structure was found to be isotypic with  $\text{Ti}_2\text{S}_3$ . They reported that the tetragonal phase  $\text{Zr}_4\text{Se}_3$  reported by Hahn and Ness

<sup>&</sup>lt;sup>1</sup>Solomons, W. and Wiegers, G. A., Laboratorium voor anorganische chemie, Rijksuniversitat, Groningen, The Netherlands. The System Zirconium-Selenium: The Structures of the Phases  $Zr_3Se_4$  and  $Zr_2Se_3$ . Private communication. 1969.

is actually ZrSiSe.

c. <u>The hafnium - selenium system</u> McTaggert and Wadsley (17) reported the existence of a monoclinic HfSe<sub>3</sub>, a hexagonal HfSe<sub>2</sub>, and possibly a hexagonal Hf<sub>2</sub>Se<sub>3</sub>. They reported that a powder pattern of HfSe could not be reliably indexed.

The noticeable lack of knowledge, pointed out earlier, concerning the existence of metal-rich phases  $(C/M \leq \frac{1}{2})$  in the Ti-Se, Zr-Se, and Hf-Se systems probably resulted primarily from the previously used techniques of sample preparation. The investigation of these metal-selenium systems was conducted with the purpose of preparing metal-rich phases and characterizing any new metal-rich phases found, especially by x-ray crystallography techniques.

The lattice parameters, symmetry and space group for both phases in the Ti-Se, Zr-Se, and Hf-Se systems known prior to this research and new phases known as a result of this research are listed in Table 2.

| Phase                                     | Lattice Symmetry | Lattice Parameters  | Reference          |
|---|------------------|---|--------------------|
| TiSe <sub>2</sub> Ti-Se System            | hexagonal        | a=3.535Å, c=6.004Å  | 17, 26             |
| <sup>Ti</sup> 2 <sup>Se</sup> 3           | hexagonal        | a=3.595Å, c=5.99Å   | 17                 |
| TiSe                                      | hexagonal        | a=7.15Å, c=12.00Å   | 17                 |
| TiSe <sub>0.95</sub>                      | hexagonal        | a=3.494Å, c=6.462Å  | 25                 |
| TiSe <sub>1.05</sub>                      | hexagonal        | a=3.571Å, c=3.539Å  | 25                 |
| TiSe1.60                                  | monoclinic       | a=3.608Å, b=6.19Å,<br>c=11.94Å, β=90.33°                  | 26                 |
| TiSe<br>1.33                              | monoclinic       | a=13.66Å, b=3.571Å<br>c=12.02Å, $\beta$ =152.92°          | 26                 |
| TiSe1.09-1.20                             | hexagonal        | a=3.572Å, c=6.205Å  | 26                 |
| TiSe1.60                                  | monoclinic       | a=12.39Å, b=7.19Å,<br>c=11.95Å, $\beta$ =90.60°           | 27                 |
| $\text{Ti}_{2}$ Se (Ti $_{9}$ Se $_{4}$ ) | orthorhombic     | $a=11.744\Lambda$ , $b=14.517\Lambda$<br>$c=3.456\Lambda$ | 28, - <sup>a</sup> |

Table 2. Summary of phases in the Group IVB metal-selenium systems

<sup>a</sup>This research.

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| Phase                            | Lattice Symmetry | Lattice Parameters                          | Reference      |
|----------------------------------|------------------|---|----------------|
| ZrSe <sub>3</sub> Zr-Se Syste    | monoclinic       | a=3.42Å, b=9.45Å<br>c=3.74Å, $\beta$ =98.2° | 17, 29         |
| ZrSe <sub>2</sub>                | hexagonal        | a=3.770Å, c=6.137Å                          | 17             |
| ZrSe1.0-1.4                      | rhombohedral     | a=5.337Å, α=89.39°                          | 14, 30         |
| ZrSe0.6-0.8                      | hexagonal        | a=3.55Å, c=3.61Å                            | 14             |
| Zr <sub>2</sub> Se               | orthorhombic     | a=12.640Å, b=15.797Å<br>c=3.602Å            | _ <sup>a</sup> |
| Hf-Se Syste<br>HfSe <sub>3</sub> | monoclinic       | a=3.55Å, b=3.72Å<br>c=9.47Å, $\beta$ =98.3° | 17             |
| HfSe2                            | hexagonal        | a=3.748Å, c=6.159Å                          | 17             |
| Hf <sub>2</sub> Se               | Hexagonal        | a=3.4502A, $c=12.260A$                      | _a             |

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#### II. EXPERIMENTAL TECHNIQUE

## A. Source and Purity of Metals and Chalcogen Used

The tantalum sulfides investigated in this research were prepared using 99.999% sulfur acquired from the American Smelting and Mining Company and 99.99% tantalum from the National Research Corporation.

The Group IVB transition-metal selenides were prepared using 99.999% selenium obtained from Alfa Inorganics Inc. and 99.93% titanium metal from the Chicago Development Corporation, 99.90% zirconium metal from the Westinghouse Electric Corporation and 99.9% hafnium metal containing 0.02% zirconium metal purified at the Ames Laboratory of Iowa State University.

#### B. General Sample Preparation

The metal in the form of sheet or bar was filed using a flat bastard file. The filing process was done in a plastic glove bag filled with argon. Before the file was used, it was cleaned by rinsing with dilute HCl, then rinsed with distilled water and finally rinsed with ethanol. The file was then immediately inserted into the argon filled glove bag. A strong magnet was kept in the glove bag during the filing and periodically passed over the metal filings to remove any chips which may have broken off the file during the

filing operation. The metal filings were stored until used in small sample vials with an argon atmosphere. When sulfides were prepared the metal filings were weighed, and 1.05 times the stoichiometric amount of sulfur was added. The sulfur above that needed for stoichiometry was added to allow for sulfur loss in transferring. In the case of the selenide preparations, the selenium was first weighed since it was in the form of rather large pieces of shot, and then stoichiometric guantities of metal filings were added. These mixtures were introduced by means of a funnel into clean 8mm Vycor tubes sealed at one end. The tube with the chalcogen and metal filings was evacuated by a mechanical pump to about  $10^{-2}$  torr and was sealed off with a gas-oxygen torch. After the tube was cooled by air or water guenching, the tube was checked for leaks with a Tesla coil. If there were no leaks, the tube was placed in a resistance furnace at 400°C, and the temperature was raised to about 500°C after approximately one day. The tube was kept at 500°C until there was no visual indication of unreacted chalcogen in the sample tube. Next the sample tube was withdrawn from the furnace, air or water guenched to room temperature and broken open taking care to avoid contaminating the sample with Vycor fragments. A microscope using low power (X45) was used to examine the sample and to aid in the removal of pieces of Vycor. The samples were stored, until use, in sample vials.

Only in the case of the hafnium-selenium preparations was it found necessary to displace the air above the sample. The sample vial was, in this case, filled with argon to avoid reaction of the preparation with air. In cases in which hafnium-selenium samples were stored in air reaction of the sample was evidenced by a red color, presumably due to selenium, coating the walls of the sample vial. The products of the preparations in the silica tubes were a mixture of higher chalconides and unreacted metal. There in no cases evidence of interaction of the metal with was the silica of the tubes. No attempt was made at this stage of the sample preparation to use x-ray techniques to identify the phases present.

#### C. High Temperature Annealing

In all preparations, the samples prepared in the silica tubes were annealed in a tungsten Knudsen cell heated by radio-frequency induction in the arrangement shown in Figure 1. The temperature, duration of the heating and any other specifics pertaining to the preparation of a specific phase are given in a later section. The tungsten Knudsen cell and sample were maintained in a dynamic vacuum of  $10^{-6}$  torr by an oil diffusion pump backed by a mechanical pump. The residual pressure of the vacuum system was measured by a hot cathode ionization gauge. The temperatures of the Knudsen cells were

Figure 1. Vacuum line used for high temperature annealing



measured by sighting on a small channel in the bottom of the cell with a Leeds and Northrup optical pyrometer. The observed temperatures were corrected for window and prism effects. The samples prepared in this fashion were quenched by radiation loss when the power to the coils was turned off. The sample and Knudsen cell were left in the vacuum for 24 hours after heating to insure that they cooled to room temperature before being exposed to the atmosphere. The vacuum was broken with an inert gas such as argon or nitrogen, and the sample was stored in a sample vial. In the case of the hafniumselenium preparations, it was found necessary to keep the sample under an argon atmosphere to avoid slow decomposition. All other phases discussed in this research were stable in air.

#### D. Results of Spectroscopic Analyses

Three typical samples, one of  $Ta_2S$ , one of  $Ta_6S$ , and one of Ta metal filings, were submitted for spectroscopic analyses to determine the impurities present, especially iron from the filing process, silicon from the preparation tubes and tungsten from the high temperature annealing in the Knudsen cell. The concentration of iron in each of the samples  $Ta_2S$  and  $Ta_6S$  was about 200 ppm whereas analysis of the filed metal indicated less than 100 ppm iron. Magnetic data, discussed below, suggest that the iron concentrations in the  $Ta_2S$  and  $Ta_6S$  samples are considerably less than these values. There were 200 ppm of silicon in the  $Ta_2S$  and  $Ta_6S$ samples compared with less than 50 ppm of silicon in the filed metal. No tungsten was observed in any of the three samples. There were only negligible concentrations (< 20 ppm) of other metallic impurities present in the three samples.

## E. Analyses for Oxygen, Nitrogen, and Hydrogen in Metals

Samples of Ti, Zr, and Ta metal filings were analyzed by a vacuum fusion method for the presence of oxygen, nitrogen, and hydrogen. The results of these analyses are summarized in Table 3. The concentrations for nitrogen are minimum values. The concentration of oxygen in the hafnium filings was probably not greatly different from 250 ppm, as reported by Graham (30) for filings obtained in a similar fashion from the same hafnium bar.

| Metal | Oxygen (ppm) | Hydrogen (ppm) | Nitrogen (ppm) |
|-------|--------------|----------------|----------------|
| Ti    | 567          | 171            | 43             |
| Zr    | 521          | 39             | 34             |
| Hf    | 250          | · _            | -              |
| Ta    | 167          | 8              | 25             |

Table 3. Impurities in metals

## III. X-RAY EXAMINATION OF POWDER SAMPLES PRODUCED BY HIGH TEMPERATURE ANNEALING

X-ray examination of powder samples annealed at high temperatures was performed by the Debye-Scherrer and Guinier techniques. The Debye-Scherrer and Guinier cameras used had diameters of 114.6mm and about 80mm, respectively. For a description of the Guinier cameras see Guinier (31). The radiation used to obtain the Debye-Scherrer patterns was nickel filtered  $CuK_n$  radiation and to obtain the Guinier patterns was monochromatic  $CuK_{\alpha_1}$  radiation ( $\lambda$ =1.5405Å). An internal standard, KCl with  $a=6.29300+0.00009\mathring{A}$  (32), was mixed with the samples in the powder patterns obtained by the Guinier method. The method, involving the use of the internal standard, and the method of reading the Guinier films has been discussed by Westman and Magneli (33) and Graham (30). The dispersion values ( $l/\theta$  in which l is the distance between the primary beam and reflected beam and  $\theta$  is the Bragg angle for the same reflection) are 2.80 mm/degree for the Guinier method and 2.00 mm/degree for the Debye-Scherrer method. Thus the resolution of relatively close lines is significantly better on Guinier patterns than on Debye-Scherrer patterns. Also, there are no systematic errors in the diffraction angles obtained from Guinier patterns due to absorption effects, as are encountered with diffraction angles obtained by the Debye-Scherrer method.

Guinier patterns were used to obtain  $\sin^2 \theta$  values in the low reflection region ( $2\theta \leq approximately 60^\circ$ ). A least squares program by Williams (34) was used to obtain accurate lattice parameters from the  $\sin^2 \theta$  data. These lattice parameters and  $\sin^2 \theta$  data are reported in later sections. All diffraction data obtained in this research were obtained by room-temperature diffraction techniques.

#### IV. THE TANTALUM-SULFUR SYSTEM

A. The Structural Determination of Ta2S

## 1. Collection of intensity data

The Ta<sub>2</sub>S phase was prepared as outlined in sections II,A and B. The final annealing temperature of 1600°C was maintained for 3 hours.

A single crystal of Ta<sub>2</sub>S, picked from an arc-melted sample containing both Ta<sub>2</sub>S and Ta<sub>6</sub>S, was mounted on the end of a glass fiber by Duco cement. A Charles G. Supper Co. Weissenberg camera was used to take a rotation photograph and  $0k\ell$ ,  $lk\ell$ , and  $2k\ell$  layer photographs about the a-axis. Reciprocal lattice plots drawn from these layer photographs indicated that the lattice is orthorhombic. The following systematic conditions on the Miller indices were deduced for reflections to be observed: hk 2, no conditions; hk0, no conditions; hol, l = 2n; 0kl, k = 2n; h00, h = 2n; 0k0, k = 2n; 00l, $\ell$ =2n. These reflection conditions indicate that the centrosymmetric space group is Pbcm. The Guinier powder pattern of a sample which exhibited diffraction lines attributed only to the Ta2S phase yielded data which resulted in the following lattice parameters:  $a=7.381\pm0.002\text{\AA}$ ,  $b=5.574\pm0.001\text{\AA}$ , and c=15.195+0.003Å. A pycrometric determination of the density of this sample using water at 24°C as the displaced medium yielded a value of 12.39 g/cc. The calculated density

of  $Ta_2S$  based on 12  $Ta_2S$  units per unit cell is 12.46 g/cc. The hk $\ell$  indices,  $\sin^2\theta_{(obs)}, \sin^2\theta_{(calc)}$  and the estimated relative intensities of reflections for the  $Ta_2S$  phase obtained from a Guinier powder pattern are listed in Table 4.

| Table 4. | X-rav | diffraction | data | for | Ta <sub>s</sub> , | λ=l. | .5405A |
|----------|-------|-------------|------|-----|-------------------|------|--------|
|----------|-------|-------------|------|-----|-------------------|------|--------|

|                   |  | <u> </u>                               |                       |
|-------------------|--|--|-----------------------|
| h k <b>l</b>      | sin <sup>2</sup> 0 (obs) ×10 <sup>-5</sup> | $\sin^2\theta$ (calc) $\times 10^{-5}$ | I/I <sub>O</sub> x100 |
| 0,0,2             | 1032                                       | 1028                                   | 50                    |
| 1,0,0             | 1085                                       | 1089                                   | 50                    |
| 1,0,2             | 2124                                       | - 2116                                 | 10                    |
| 0,0,4             | 4116                                       | 4112                                   | 10                    |
| 2,1,1             | 6521                                       | 6521                                   | 15                    |
| 1,1,4             | 7106                                       | 7110                                   | 10                    |
| 2,1,2             | 7295                                       | 7295                                   | 18                    |
| 0,2,1             | 7887                                       | 7896                                   | 80                    |
| 2,1,2             | 8573                                       | 8577                                   | 80                    |
| 1,2,1             | 8789                                       | 8784                                   | 35                    |
| 0,0,6             | 9244                                       | 9249                                   | 25                    |
| 1,1,5             | · 9416                                     | 9421                                   | 80                    |
| 3,0,0             | 9792                                       | 9802                                   | 25                    |
| 0,2,3             | 9943                                       | 9953                                   | 40                    |
| 1,0,6             | 10354                                      | 10338                                  | 50                    |
| 3,0,2             | 10826                                      | 10832                                  | 50                    |
| 1,2,3             | 11033                                      | 11038                                  | 100                   |
| 3,1,0             | 11726                                      | 11709                                  | 40                    |
| 2,2,1             | 12242                                      | 12253                                  | 100                   |
| $\perp, \perp, 6$ |  | 12247                                  |                       |
| 2,1,5             | 12680                                      | 12691                                  | 5                     |
| 2,0,6             | 13593                                      | 13605                                  | 40                    |
| 3,1,3             | 14027                                      | 14021                                  | 20                    |
| 2,2,3             | 14307                                      | 14307                                  | 20                    |
| 1,2,5             | 15148                                      | 15154                                  | 5                     |
| 2,1,6             | 15532                                      | 15519                                  | 35                    |
| 2,1,4             | 15817                                      | 15824                                  | 25                    |
| 0,0,8             | 16440                                      | 16446                                  |                       |
| 4,4,5             |  |  | T2                    |
| 1,3,2             |  | · 19300                                | 5                     |
| ∠, , ∪            |  | 21543                                  | 18<br>7 F             |
| 1,3,4             | 22389                                      | 22389                                  | 15                    |
| 2,3,2             | 22372                                      | 22371                                  | CT<br>O C             |
| L · + · O         | 11131                                      |  | 111                   |

Using the crystal of Ta<sub>2</sub>S previously described to determine the proper space group for this phase, single crystal intensity data were initially collected using a General Electric spectrogoniometer and nickel filtered Cu K<sub> $\alpha$ </sub> radiation. After the single crystal orienter angles were obtained for three linearly independent reflections, the computer program SCO-6 by D. E. Williams<sup>1</sup> was used to calculate the orienter angles for all other reflections. Data were collected for 767 reflections in the range:  $0^{\circ} < 2\theta < 160^{\circ}$ . A second set of integrated peak intensity data was collected using a Hilger-Watts diffractometer coupled with an SDS (910)-IBM(1401) computer configuration described elsewhere (35). Mo K<sub> $\alpha$ </sub> radiation with a Zr filter was used to collect data for 1104 reflections in the range  $0^{\circ} < 2\theta < 60^{\circ}$ .

## 2. Absorption correction

The calculation of accurate structure factors from intensity data required that corrections be made for absorption of the incident and diffracted radiation. The absorption corrections are calculated in the form of a transmission factor, A\*, for each reflection by an evaluation of the integral.

<sup>&</sup>lt;sup>1</sup>Williams, D. E., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Single Crystal Orienter Program SCO-6. Private communication. 1964.

$$A^{*} = 1/V \int_{0}^{V} \exp\left[-\mu \left(r_{\alpha} + r_{\beta}\right)\right] dV$$
(1)

in which V is the volume of the crystal used to collect the data,  $r_{\alpha}$  and  $r_{\beta}$  are the path lengths of the primary and diffracted beam, respectively, through the crystal and  $\mu$  is the linear absorption coefficient of the material comprising the crystal. The transmission factor coefficients were obtained using a computer program by Busing and Levy (36) in which the integral is evaluated for each Bragg reflection by a Gaussian approximation. The calculation is based on the dimensions and orientation of the crystal. The dimensions and orientations of the crystal were obtained in the form of a set of linear equations, with one for each face of the crystal, expressed in the form

$$Ax + By + Cz - D = 0$$
 (2)

in which A, B and C are the direction cosines of a normal from a chosen origin within the crystal to a given face and D is the length of that normal from the origin to that face.

The single crystal of  $Ta_2^S$  was approximated by a volume which had six faces, requiring six equations relating direction cosines and normals from the origin to the six faces. A Bausch-Lomb Stereozoom microscope which had in one eyepiece a reticle calibrated against a series of lines 20  $\mu$ apart etched into a glass slide was used to measure the dimensions of the crystal. The measured dimensions were

approximately  $15\mu \times 20\mu \times 140\mu$ .

The linear absorption coefficient initially used in the solution of the structure with the Cu data had a value of  $2330.9 \text{cm}^{-1}$  based on a guess that the structure had 14 Ta<sub>2</sub>S units per unit cell. Subsequent determination of the structure led to the value of 12 as the correct number of Ta<sub>2</sub>S units per unit cell. The correct values for the linear absorption coefficients were  $1110.7 \text{cm}^{-1}$  for the Mo data and  $1997.5 \text{cm}^{-1}$  for the Cu data. The transmission factor coefficients ranged from 0.1152 to 0.2156 and from 0.01402 to 0.1713, respectively, for the Mo and Cu data.

## 3. Lorentz and polarization effects

The Lorentz effect results from the disparity in the time during which the conditions for reflection are met for reflections with different Bragg angles. The polarization effect results from the fact that the diffracted beam is partially polarized while the primary beam is not. These two effects are generally accounted for in one factor, a Lorentz-polarization factor Lp, of the form for single crystal intensity data taken on a diffractometer

$$Lp = \frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$$
(3)

where  $\theta$  is the Bragg angle of a particular reflection.

4. Structural solution

a. The specific problem The intensity, I(hk l), of a given reflection, with Miller indices hk l, can be expressed by the relationship:

$$I(hkl) = kLp A^* |F(hkl)|^2, \qquad (4)$$

in which k is a scale factor, Lp is the combined Lorentzpolarization factor, A\* is the transmission factor and  $|F(hk\ell)|$  is the magnitude of the structure factor.

The structure factor for a reflection hk(, F(hk), is. related to the scattering powers of the j atoms composing the unit cell by the relationship:

$$F(hk k) = \sum_{j=1}^{j} \cos 2\pi (hx_j + ky_j + kz_j)$$

+ 
$$i\Sigma f_j$$
 sin  $2\pi$  (hx<sub>j</sub>+ky<sub>j</sub>+ $\{z_j\}$ )

in which  $f_j$  is the scattering power of the jth atom at the fractional coordinates x, y, z in the unit cell. For atoms related by a center of symmetry the sine terms of the above equations will cancel, and the relationship for a structure containing a center of symmetry reduces to:

$$F(hkl) = \sum_{j j} \cos 2\pi (hx_j + ky_j + lz_j).$$
(5)

Thus the various  $F(hk\ell)$  are not complex numbers in the centrosymmetric case but are real numbers, either less than
or greater than zero. The appropriate assignment of signs to the structure factors, the magnitudes of which are obtained from the observed intensities, constitutes the problem in a centrosymmetric crystal structure determination. For the space group Pbcm, the equation describing the structure factor,  $F(hk\ell)$ , may be expanded and rewritten in the form (37):

$$F(hk\mathbf{k}) = 8 \sum_{j} cos 2\pi (hx_{j} + \frac{k}{4}) cos 2\pi (ky_{j} - \frac{k+\mathbf{k}}{4})$$

$$\times cos 2\pi (z_{j} + \frac{\mathbf{k}}{4}) .$$
(6)

b. The general method of solution A graphical method of obtaining unsigned unitary structure factors outlined by Woolfson (38) was used in the solution of the structure of  $Ta_2S$ .

The unitary structure factor for a reflection hk l, U<sub>hkl</sub>, is related to the structure factor by the following relation:

$$|U_{hk\ell}| = |F(hk\ell)| / \sum_{j j} , \qquad (7)$$

where  $f_j$  is the atomic scattering factor uncorrected for thermal effects of the jth atom in the unit cell. The magnitude of  $\Sigma f_j$  is the maximum value for the magnitude of  $f_{j}$ , Clearly,

$$0 \leq |U_{hk}| \leq 1$$
 (8)

Harker and Kasper (39) derived a series of inequalities for unitary structure factors based on the Cauchy inequality:

$$\left| \sum_{j=1}^{\Sigma} a_{j} b_{j} \right|^{2} \leq \left( \sum_{j=1}^{\Sigma} a_{j} \right|^{2} \left( \sum_{j=1}^{\Sigma} b_{j} \right)^{2} \right).$$
(9)

In the case of a centrosymmetric structure the structure factor possesses no imaginary component, and a very useful result of the Cauchy inequality can be obtained (38). This result is that, for sufficiently large structure factors:

$$s(h,k,l)s(h',k',l')s(h+h',k+k',l+l') = +1 and/or (10a)$$

$$s(h,k,l)s(h',k',l')s(h-h',k-k',l-l') = +1$$
 (10b)

in which s(h,k,l) refers to the sign of the unitary structure factor  $U_{hkl}$ . The minimum value of  $|U_{hkl}|$  suggested by Woolfson for use in these relations is 0.40, which was also the minimum value of  $|U_{hkl}|$  used in the solution of the structures of the Ta<sub>2</sub>S phase and the Ta<sub>6</sub>S phase. The above two equations (10a and 10b) have been called triple-product relations (38).

Therefore, if a sufficient number of unitary structure factors are sufficiently large in magnitude; and, if their signs can be interrelated by the triple-product relations, then positive or negative signs can be assigned to the

structure factors (38). These signed structure factors can then be used to calculate an election density map using the equation:

$$\rho(XYZ) = \frac{1}{\nabla} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} F(hk\ell) \exp\left[-2\pi i (hX+kY+\ell Z)\right]$$
(11)

where p(XYZ) is the election density at the grid point X,Y,Z in the mapping and V is the volume of the unit cell. This equation can be reduced in the special case of a centrosymmetric structure to

$$\rho(XYZ) = \frac{1}{V} \sum \sum \sum F(hkl) \cos 2\pi (hX+kY+lZ).$$
(12)  
h k l

This map yields a trial structure. If this trial structure makes "chemical sense," e.g. there are no unrealistically short interatomic distances, then this trial structure, which may not contain all of the atoms in the structure, can be used to obtain signs for more structure factors than those assigned signs by the direct method. This enlarged set of signed structure factors may then be used to calculate another electron density function, possibly locating additional atoms in the structure. Once all the atoms in the structure are found by repetition of this procedure, then refinement of the structure which will be discussed in section IV,5 can be accomplished. c. The specific solution of the structure of  $Ta_2S$ The Cu data were used to solve the  $Ta_2S$  structure. It was decided to accept those data as "observed" for which

 $\sigma I/I \simeq \sqrt{A+B} / (B-A) \leq 0.25$ ,

in which oI is the estimated standard deviation in the intensity, I, and in which B and A equal, respectively, the integrated peak intensity and the background intensity. All other reflections were considered "unobserved." According to this criterion, there were 366 observed reflections, or about 17 data per variable, in the final refinement, using the Cu data and 435 observed reflections, or about 21 data per variable, using the Mo data.

The graphical method used to obtain unitary structure factors involved the calculation of the magnitude of the unitary structure factors from the intensity data. The ratio of the squares of the magnitude of the unitary structure factor to the intensity,  $I_{corr}$ , of a given Bragg reflection corrected for absorption and Lorentz and polarization effects was computed. This ratio,  $\phi^2$ , is a function of  $\theta$  which combines a scale factor, k, and an overall thermal parameter, B, for all the atoms of the unit cell.

In detail, the  $|U_{hk\ell}|$  values were obtained as per the following description. The unitary structure factor is

defined by the relation:

$$U_{hk} = \sum_{j \neq j} \left[ \sum_{j=1}^{f} \exp[2\pi i (hx_j + ky_j + \ell z_j)] \right]$$
(13)

where  $f_j$  is the atomic scattering factor uncorrected for thermal motion and  $x_j$ ,  $y_j$ ,  $z_j$  are the positional parameters for the jth atom in the unit cell. The square of the magnitude of the unitary structure factor,  $|U_{hk}\ell|^2$ , is the product of  $U_{hk}\ell$  and its complex conjugate,  $\tilde{U}_{hk}\ell$  given by:

$$|\mathbf{U}_{hk}|^{2} = \mathbf{U}_{hk} \cdot \tilde{\mathbf{U}}_{hk}$$
(14)

$$= \sum_{j \in I_{j}} \left[ \exp\left[2\pi i \left(hx_{j} + ky_{j} + \ell z_{j}\right)\right] \right]$$
  

$$\cdot \sum_{i \in I_{i}} \left[\frac{f_{i}}{\sum f_{i}} \exp\left[-2\pi i \left(hx_{i} + ky_{i} + \ell z_{i}\right)\right] \right] . \quad (15)$$

This product can be simplified by substituting the unitary atomic scattering factor defined as:

$$n_{j} = f_{j} / \sum_{j=1}^{n} f_{j}.$$
 (16)

Combining terms,

$$|\mathbf{U}_{hk}\boldsymbol{\ell}|^{2} = \sum_{j}^{n} \sum_{\substack{i \ j \\ i \neq j}}^{2} + \sum_{\substack{i \ j \\ i \neq j}}^{2} n_{i}^{n} \sum_{\substack{i \ j \\ i \neq j}}^{n} \exp[2\pi i [h(\mathbf{x}_{j}^{-\mathbf{x}_{i}}) + k(\mathbf{y}_{j}^{-\mathbf{y}_{i}})] + k(\mathbf{y}_{j}^{-\mathbf{y}_{i}})] + k(\mathbf{y}_{j}^{-\mathbf{y}_{i}})]$$

$$(17)$$

For a general reflection, the term containing the crossproduct will not equal zero. However, for most distributions of unitary scattering factors, if values of  $|U_{hk}|^2$ are summed over a sufficiently large number of reflections with phases varying between 0 and  $\pi$ , the second term on the right of equation 17 will tend to zero since there will be as many positive terms as negative terms in the sum (40, 41). This is equivalent to requiring that the distance between any two atoms be greater than one half the minimum spacing of the reflections considered (41). Therefore, to a first approximation, the average for a sufficiently large number of reflections is given by:

$$\overline{|\mathbf{U}_{\mathrm{hk}}\boldsymbol{\ell}|^2} = \overline{\boldsymbol{\Sigma} \mathbf{n}_{\mathrm{j}}^2} .$$
 (18)

The average square of the magnitude of the unitary scattering factor,  $|U_{hk}|^2$ , the average of the square of the unitary scattering factor,  $\Sigma n_j^2$ , and the average corrected intensity,  $\overline{I_{corr}}$ , for a given region of  $\theta$  sufficiently small such that  $\phi^2$  is essentially constant, are related by:

$$\overline{|\mathbf{U}_{hk}\boldsymbol{\ell}|^2} = \overline{\boldsymbol{\Sigma} \mathbf{n}_j^2} = \phi^2 \cdot \overline{(\mathbf{I}_{corr})}$$
(19)

Thus  $\phi^2$  can be readily calculated as a function of  $\theta$  using tabulated atomic scattering factors,  $f_j$ , and the observed corrected intensities. Woolfson (38) suggests that a range of  $\pm$  0.05 in sin $\theta$  for the calculation of  $|U_{hk}\ell|^2$  and  $\overline{I_{corr}}$ 

is both sufficiently large that the interval contains sufficiently many data that Equation 19 is valid and is sufficiently small that  $\phi^2$  is essentially constant over the interval for most distributions of structure factors.

Values of corrected intensity data, I corr, for all reflections for the Cu data were serialized in increasing order of  $\sin\theta$ , where  $\theta$  is the Bragg angle. The intensity value for each first octant reflection was multiplied by its relative weight in the total reciprocal lattice: 1 for an h00,0k0, or 00 $\ell$  reflection; 2 for an hk0, h0 $\ell$ , or  $0k\ell$  reflection and 4 for an  $hk\ell$  reflection for which  $h\neq 0$ ,  $k \neq 0$ , and  $\ell \neq 0$ . The weighted intensity data for regions of  $sin\theta = +0.05$  starting with  $sin\theta = 0.05$  were summed. If an allowed reflection had an observed intensity of zero, it was assigned one half of the minimum intensity observed in its sin0 range and the adjacent two sin0 ranges. The average of the weighted intensities was computed for each sinf region by dividing the weighted intensity sum by the weighted number of reflections in the sin $\theta$  region. The number of reflections, the weighted number of reflections and the average weighted intensity for the various  $\sin\theta$  ranges are listed in Table 5. The data for neighboring  $\sin \theta$  regions were combined to determine the average  $\sin\theta$  and average weighted intensity values which are listed in Table 6. The average weighted intensity value,  $\overline{I_{corr}}$ , for sin $\theta$  equal to

|         | -                        |                                   |                               |
|---------|--------------------------|-----------------------------------|-------------------------------|
| Sinθ    | Number of<br>Reflections | Weighted Number<br>of Reflections | Average Weighted<br>Intensity |
| 0.0-0.1 | 1                        | 2                                 |                               |
| 0.1-0.2 | 11                       | 20                                | 5,950                         |
| 0.2-0.3 | 23                       | 54                                | 15,840                        |
| 0.3-0.4 | 36                       | 105                               | 47,960                        |
| 0.4-0.5 | 60                       | 176                               | 8,742                         |
| 0.5-0.6 | 88                       | 273                               | 18,485                        |
| 0.6-0.7 | 110                      | 352                               | 12,532                        |
| 0.7-0.8 | 141                      | 477                               | 6,882                         |
| 0.8-0.9 | 186                      | 630                               | 6,666                         |
| 0.9-1.0 | 187                      | 637                               | 3,704                         |
|         |                          |                                   |                               |

Table 5. Number of reflections, weighted number of reflections and the average weighted intensity per Sin0 region

0.10 was not determined due to lack of sufficient data in the sint region 0.0 to 0.10.

The evaluation of  $|U_{hk} l|^2$  by means of Equation 18 requires a knowledge of the number and kinds of atoms in the unit cell. In the case of the Ta<sub>2</sub>S structure, it was initially guessed that there were 14 Ta<sub>2</sub>S units per unit cell. Using this supposition, the values of  $|U_{hk} l|^2$  were calculated for values of  $\overline{\sin\theta}$  in increments of 0.10 starting with  $\sin\theta=0$ . The atomic scattering factors used in this research were given by Hanson, Herman, Lea and Skillman (42). The results of the evaluation of  $\overline{|U_{hk}|^2}$  are listed in Table 7. Values of  $\overline{\sin\theta}$ ,  $\phi^2$  and  $\phi$  are listed in Table 8. A plot of  $\phi$  versus sin $\theta$  (data from Table 8) is given in Figure 2. Magnitudes of unitary structure factors,  $U_{hk}$ , were calculated from the relation  $U_{hk} \rho = \phi \sqrt{T_{corr}}$ , using interpolated values of  $\phi$  from Figure 2. These magnitudes were only evaluated for reflections for which  $\sin\theta > 0.300$  because the region of the graph for which  $\sin\theta \leq 0.300$  was poorly determined, presumably a result of an insufficient number of observed reflections for this portion of the low angle region.

The Cu data yielded 41 unitary structure factors with magnitudes greater than or equal to 0.40 for Bragg angles,  $\theta$ , such that sin $\theta$  > 0.30. These unitary structure factors comprised approximately 11% of the observed reflections.

In the solution of the structure by the direct method, it is possible to assign signs to one, two or three unitary structure factors, subject to restrictions discussed below. This arbitrary selection of signs fixes the origin at one of the centers of symmetry. In a centrosymmetric triclinic unit cell, there are eight possible independent centers of symmetry in the unit cell which can serve as origins. These centers are located at 0,0,0; 1/2,0,0; 0,1/2,0; 1/2,1/2,0; 1/2,0,1/2; 0,1/2,1/2; and 1/2,1/2,1/2 in a given unit cell. The effect of arbitrarily choosing structure-factor signs

| Average sin0<br>Region | Mean Weighted<br>Intensity |
|------------------------|----------------------------|
| 0.20                   | 13,135                     |
| 0.30                   | 37,038                     |
| 0.40                   | 23,390                     |
| 0.50                   | 14,667                     |
| 0.60                   | 15,132                     |
| 0.70                   | 9,281                      |
| 0.80                   | 6,759                      |
| 0.90                   | 5,176                      |
|                        |                            |

Table 6. Mean weighted intensity per average sin $\theta$  region for  $\text{Ta}_2S$ 

| sin0 | f <sub>s</sub> | f <sub>Ta</sub> | 14f <sub>s</sub> | 28f <sub>Ta</sub> | `Σf<br>j | n <sub>Ta</sub><br>(x10 <sup>-2</sup> ) | n <sub>s</sub><br>(x10 <sup>-3</sup> ) | n <sub>s</sub> <sup>2</sup><br>(x10 <sup>-5</sup> ) | n <sup>2</sup> Ta<br>(x10 <sup>-3</sup> ) | $14n_{\rm S}^2$<br>(x10 <sup>-4</sup> ) | $28n_{Ta}^{2}$ (x10 <sup>-2</sup> ) | $\frac{ v ^2}{(x10^{-2})}$ |
|------|----------------|-----------------|------------------|-------------------|----------|---|--|---|---|---|-------------------------------------|----------------------------|
| 0.2  | 13.4           | 66.8            | 188.             | 1870.             | 2058.    | 3.25                                    | 6.51                                   | 4.20  | 1.06                                      | 5.90                                    | 2.97                                | 3.03                       |
| 0.3  | 11.6           | 62.4            | 162.             | 1747.             | 1909.    | 3.27                                    | 6.08                                   | 3.70  | 1.07 .                                    | 5.20                                    | 3.00                                | 3.05                       |
| 0.4  | 9.9            | 57.8            | 139.             | 1618.             | 1757.    | 3.29                                    | 5.63                                   | 3.20  | 1.08                                      | 4.50                                    | 3.02                                | 3.07                       |
| 0.5  | 8.8            | 53.6            | 123.             | 1501.             | 1624.    | 3.30                                    | 5.42                                   | 2.90  | 1.09                                      | 4.10                                    | 3.05                                | 3.09                       |
| 0.6  | 8.1            | 49.6            | 113.             | 1389.             | 1502.    | 3.30                                    | 5.39                                   | 2.90  | 1.09                                      | 4.10                                    | 3.05                                | 3.09                       |
| 0.7  | 7.5            | 45.4            | 105.             | 1271.             | 1376.    | 3.30                                    | 5.45                                   | 3.00  | 1.09                                      | 4.20                                    | 3.05                                | 3.09                       |
| 0.8  | 6.9            | 42.2            | 97.              | 1182.             | 1279.    | 3.30                                    | 5.39                                   | 2.90  | 1.09                                      | 4.10                                    | 3.05                                | 3.09                       |
| 0.9  | 6.3            | 39.2            | 88.              | 1098.             | 1186.    | 3.30                                    | 5.31                                   | 2.80 /  | 1.09                                      | 3.90                                    | 3.05                                | 3.09                       |
|      |                |                 |                  |                   |          |   |  |   |   |   |                                     |                            |

Table 7. Calculation of  $\overline{|U|^2}$  for Ta<sub>2</sub>S (Cu data)

i

ω 9 Figure 2. Graph of phi,  $\phi$ , vs. sin $\theta$  for Ta<sub>2</sub>S (Cu data)

-----



| 1~2  |                                   |                       |  |
|------|-----------------------------------|-----------------------|--|
| Sinð | φ <sup>2</sup> x 10 <sup>-6</sup> | $\phi \times 10^{-3}$ |  |
| 0.20 | 2.31                              | 1.52                  |  |
| 0.30 | 0.82                              | 0.91                  |  |
| 0.40 | 1.31                              | 1.14                  |  |
| 0.50 | 2.11                              | 1.45                  |  |
| 0.60 | 2.04                              | 1.42                  |  |
| 0.70 | 3.33                              | 1.82                  |  |
| 0.80 | 4.57                              | 2.14                  |  |
| 0.90 | 5.97                              | 2.44                  |  |
|      |                                   |                       |  |

Table 8.  $\phi^2$  and  $\phi$  values for an average  $\overline{\sin\theta}$  region for Ta<sub>2</sub>S

(phases) is shown in the following specific example. Consider the general structure factor for a centrosymmetric structure:

$$F(hk\ell) = \Sigma f_{j} \cos 2\pi (hx_{j} + ky_{j} + \ell z_{j}), \qquad (20)$$

with the origin initially at 0,0,0. The effect of shifting the origin from 0,0,0 to 0,0,1/2 is to change the structure factor to

$$F'(hkl) = \Sigma f_{j} \cos 2\pi [hx_{j} + ky_{j} + l(z_{j} + 1/2)]$$
(21)

which can be rewritten as

$$F'(hkl) = \Sigma f_{j} \cos 2\pi (hx_{j}+ky_{j}+lz_{j})\cos(\pi l)$$
$$-\Sigma f_{j} \sin 2\pi (hx_{j}+ky_{j}+lz_{j})\sin(\pi l) \qquad (22)$$

for which  $\sin \pi l = 0$  for all integral values of l and  $\cos(\pi) = (-1)^{\ell}$ . Therefore,  $F'(hkl) = (-1)^{k} F(hkl)$ , and changing the origin from z=0 to z=1/2 alters the sign of F(hk $\ell$ ) when  $\ell$  is odd. Shifts from an origin 0,0,0 to the other sites mentioned above vield similar results. Thus structure factors with all indices even are unaffected by any of these shifts, and structure factors with odd indices, after a shift of one half along the corresponding axes, are changed in signs. Shifts involving a translation of one half with respect to two or three axes result in a change in sign of the structure factor if the sum of the Miller indices of the affected axis are odd and in no changes if this sum is even. Table 9 summarizes the sign changes from an initially positive set of reflections for the origin 0,0,0 for all possible sets of parities, even(e) or odd(o), of  $hk\mathcal{L}$ reflections (38).

As a result of the variety of possible origins in the crystallographic unit cells it is possible to assign arbitrary signs to one, two or three structure factors subject to certain restrictions. No sign assignment can be made to a structure factor whose indices are all even since the signs of the group of structure factors are structure invariant,

| Origin                                  | eee | eeo      | e0e | e00 | 0ee | 0e0 | 00e | 000 |  |
|---|-----|----------|-----|-----|-----|-----|-----|-----|--|
| 0,0,0                                   | +   | +        | +   | +   | ÷   | +   | +   | +   |  |
| $\frac{1}{2}, 0, 0$                     | +   | ÷        | ÷   | ÷   | -   | -   | -   | -   |  |
| $0, \frac{1}{2}, 0$                     | +   | +        | -   | -   | +   | ÷   | _   | -   |  |
| $0, 0, \frac{1}{2}$                     | ÷   | <u> </u> | · + | -   | ÷   | -   | +   | -   |  |
| $\frac{1}{2}, \frac{1}{2}, 0$           | ÷   | +        | · _ | -   | -   | _   | ÷   | ÷   |  |
| $\frac{1}{2}, 0, \frac{1}{2}$           | ÷   | -        | ÷   | -   | -   | +   | -   | ÷   |  |
| $0, \frac{1}{2}, \frac{1}{2}$           | +   | -        | -   | +   | +   | -   | -   | ÷   |  |
| $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ | +   | -        | -   | +   | -   | +   | +   | -   |  |
|   |     |          |     |     |     |     |     |     |  |

Table 9. Parities of hk & reflections

i.e., the signs of these reflections are independent of the origin chosen for the cell. Signs cannot be assigned to more than one reflection from each parity group of Table 9, and the parity of these three assigned reflections cannot be linearly related.

The origin in the structure of  $Ta_2S$  was fixed by assigning phases to three unitary structure factors from the set of unitary structure factors for which  $|U_{hk}| \ge 0.40$ . These three unitary structure factors had the following respective Miller indices, parities and assigned signs: 1,2,3,(0e0),(+); 2,5,3(e00),(+); 2,3,4,(e0e),(-). The assignment of signs to additional unitary structure factors in this set was accomplished by use of the triple product relations:

$$s(h,k,l)s(h',k',l',)s(h+h',k+k',l+l') = +1$$
 (10a)

and

$$s(h,k,l)s(h',k',l')s(h-h',k-k',l-l') = +1$$
 (10b)

described earlier.

In detail, this procedure can be exemplified by using these relations to assign a few signs, s(hk l) for reflections in this set. Thus, for example,

$$s(\overline{1},2,\overline{3}) \cdot s(1,2,3) = s(0,4,0),$$
 (23)

where

$$s(1,2,3) = +$$
 by assignment (24)

and where

$$s(\overline{1},2,\overline{3}) = -s(1,2,3)$$
 (25)

by symmetry conditions of the space group Pbcm. Therefore,

$$s(0,4,0) = -$$
 (26)

Furthermore, by combining the signs for  $U_{1,2,3}$  and  $U_{0,4,0}$ , the sign for  $U_{1,6,3}$  can be obtained:

$$s(1,2,3) \cdot s(0,4,0) = s(1,6,3).$$
 (27)

Therefore, s(1,6,3) = (+)(-) = -.

Similarly, using the signs of  $U_{1,2,3}$  and  $U_{1,2,3}$  and noting that

$$s(1,\overline{2},3) = -s(1,2,3)$$
 (28)

due to space group symmetry,

$$s(2,0,6) = s(1,2,3) \cdot s(1,\overline{2},3),$$
 (29)

and

$$s(2,0,6) = (+)(-) = -$$
 (30)

By continuing this procedure, it was possible to assign signs to all 41 unitary structure factors in the set.

A Fourier electron density function was obtained using a computer program by D. Dahm<sup>1</sup> and the 41 structure factors with assigned signs. This function indicated the presence of five strong peaks in the asymmetric unit cell: one half of the length of the a-axis, the full length of the b-axis, and one quarter of the length of the c-axis. A "trial structure" was proposed with five Ta atoms in the positions of the five peaks. An electron density function was calculated on the basis of this trial structure, and this function clearly indicated the presence of two possible sulfur positions in the asymmetric unit cell.

## 5. Structure refinement for Ta<sub>2</sub>S

The structure thus obtained was refined by least-squares computation (43). The scattering factors given by Hanson, Herman, Lea and Skillman (42) were corrected for both real and imaginary dispersion for both the Cu and Mo sets of data

<sup>&</sup>lt;sup>1</sup>Dahm, D., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. General Fourier Program. Private communication. 1967.

using the values given in the <u>International Tables for</u> Crystallography (44).

In the case of the data obtained using Cu radiation and refinement using isotropic temperature factors, the structure refined until the unweighted reliability index, defined by

$$R = \Sigma ||F_{O}| - k|F_{C}|| / \Sigma |F_{O}|$$
(31)

where k is the scaling factor and F and  $F_c$  are the observed and calculated structure factors, respectively, was 0.100 for the 366 observed reflections. The data obtained with Mo data were refined using isotropic temperature factor coefficients until the unweighted reliability index was 0.095 for 435 observed reflections. The positional and thermal parameters for both Mo and Cu data are listed in Tables 10 and 11, respectively. Graph 1, written using a computer program written by S. Porter<sup>1</sup>, lists the observed and approximately 40% of the unobserved structure factors, indicated by an asterisk (\*), for the Mo data. The unweighted reliability index for these data is 9.8%.

All signs assigned by the direct method agreed with those obtained for the structure.

<sup>&</sup>lt;sup>1</sup>Porter, S., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. A Computer Listing Program. 1967.

|       | radiat              | ion for T           | <sup>a</sup> 2 <sup>5</sup> |                     |                      |
|-------|---------------------|---------------------|-----------------------------|---------------------|----------------------|
| Atom  | Wyckoff<br>Notation | 10 <sup>4</sup> X/a | 10 <sup>4</sup> Y/b         | l0 <sup>4</sup> Z/c | в (Å <sup>+2</sup> ) |
| Ta(l) | e .                 | 966 <u>÷</u> 4      | 8933 <u>+</u> 8             | 901 <u>+</u> 2      | 0.36 <u>+</u> 5      |
| Ta(2) | е                   | 2843 <u>+</u> 4     | 3945 <u>+</u> 8             | 1542 <u>+</u> 2     | 0.28 <u>+</u> 5      |
| Ta(3) | d                   | -93 <u>+</u> 7      | 6307 <u>+</u> 11            | 2500                | 0.22 <u>+</u> 6      |
| Ta(4) | d                   | 3526 <u>+</u> 6     | 8742 <u>+</u> ll            | 2500                | 0.41 <u>+</u> 7      |
| S (l) | С                   | 1834 <u>+</u> 33    | 2500                        | 0                   | 0.29 <u>+</u> 31     |
| S (2) | е                   | 4092 <u>+</u> 29    | 7724 <u>+</u> 42            | 939 <u>+</u> 12     | 1.13 <u>+</u> 28     |

Table 10. Positional and thermal parameters from Mo radiation for Ta<sub>2</sub>S

Table 11. Positional and thermal parameters from Cu radiation for  ${\rm Ta}_6{\rm S}$ 

| Atom  | Wyckoff<br>Notation | 10 <sup>4</sup> X/a | 10 <sup>4</sup> Y/b | 10 <sup>4</sup> Z/c | В                              |
|-------|---------------------|---------------------|---------------------|---------------------|--------------------------------|
| Ta(l) | e                   | 969 <u>+</u> 4      | 8930 <u>÷</u> 9     | 900 <u>+</u> 2      | 1.01 <u>+</u> 7 Å <sup>2</sup> |
| Ta(2) | e                   | 2841 <u>+</u> 5     | 3952 <u>+</u> 9     | 1541 <u>+</u> 2     | 1.06 <u>+</u> 8                |
| Ta(3) | d                   | -90 <u>+</u> 7      | 6305 <u>+</u> 15    | 2500                | 0.94 <u>+</u> 8                |
| Ta(4) | d                   | 3528 <u>+</u> 7     | 8709 <u>+</u> 13    | 2500                | 1.09 <u>+</u> 9                |
| S (l) | с                   | 1809 <u>+</u> 38    | 2500                | 0                   | 1.36 <u>+</u> 39               |
| S (2) | e                   | 4132 <u>+</u> 27    | 7651 <u>+</u> 49    | 955 <u>+</u> 14     | 1.63 <u>+</u> 29               |
|       |                     |                     |                     |                     |                                |

 
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Graph 1. F and F for Ta2S (Mo data) (\*=unobserved <u>cf</u>. text)

### 6. Weighting scheme for intensities

A weighting scheme based on the estimated reliability of each reflection was used in the refinement of the structure of  $Ta_2S$ . A weighting scheme based on estimated errors, primarily, was used in the least squares treatment of both sets of data. The weights were assigned by calculating a relative error in the magnitude of the structure factor for each reflection, namely, the weights were taken to be  $(\sigma F)^{-2}$ , where

$$\sigma F = \left[ \left( \frac{\partial F}{\partial I} \right)^{2} \left( \sigma I \right)^{2} + \left( \frac{\partial F}{\partial A} \right)^{2} \left( \sigma A \right)^{2} \right]^{2} + \left( \frac{\sigma F}{\partial Lp} \right)^{2} \left( \frac{\sigma Lp}{D} \right)^{2} \right]^{\frac{1}{2}}.$$
(32)

In this expression  $\sigma I$  is the estimated error in the measured intensity of a reflection and is taken as  $\sqrt{A + B}$  in which A and B are respectively the total peak count and background peak count for a given reflection. The term  $\sigma A$  is the estimated error in the reciprocal of the transmission factor coefficients and was taken to be 0.05 for all reflections in both Cu and Mo sets of data. The term  $\sigma \overline{Lp}$  is the estimated error in the reciprocal of the combined Lorentz and polarization corrections and was evaluated by the expression:

$$\sigma \overline{Lp} = (\partial \overline{Lp} / \partial (2\sigma)) \sigma (2\sigma), \qquad (33)$$

for which the estimated error in  $2\theta$ ,  $\sigma(2\theta)$ , was taken as 0.02°. Equation 32 was obtained using the propagation of errors treatment for the relationship:

$$I = kA^*Lp |F|^2, \qquad (34)$$

where I is the measured intensity, Lp is the combined Lorentz-polarization correction factor, A\* is the transmission factor coefficient,  $|\mathbf{F}|$  is the magnitude of the structure factor and k is a scale factor. The weights calculated in this fashion were revised using a computer program written by S. Porter<sup>1</sup>, so that the line obtained when  $(|\mathbf{F}_0| - |\mathbf{kF}_c|)^2 / (\sigma \mathbf{F})^2$  was plotted versus  $|\mathbf{F}_0|$  had approximately zero slope. After refinement, the quantity referred to as the standard deviation of an observation of unit weight, defined by:

$$\{\Sigma[(|F_{o}|-|kF_{c}|)^{2}/(\sigma F)^{2}]/(m-n)\}^{\frac{1}{2}},$$
(35)

for which m is the number of observed reflections and n is the number of variables, were 1.051 and 0.871, respectively, for the observed reflections in the Mo and Cu cases. For the data in Graph 1, the value of this quantity is 0.938.

<sup>&</sup>lt;sup>1</sup>Porter, S., Department of Chemistry. Iowa State University of Science and Technology, Ames, Iowa. A Weights Change Computer Program. Private communication. 1967.

### 7. Fourier difference analyses

A difference Fourier function was calculated for each set of data using all observed reflections. In the case of the Mo data, the synthesis indicated an approximately 2 electron peak above the position occupied by Ta(1), i.e., x=0.097, y=0.893, z=0.090, and a second peak of the order of 1.8 electrons at x=0.328, y=0.611, and z=0.032. All other residual peaks were less than 1.7 electrons in magnitude. In the case of the Cu data, there were 2 peaks at x=0.109, y=0.889, z=0.145 and at x=0.297, y=0.389, z=0.097, corresponding to a peak height of 3 electrons. Each of these peaks was within 1 Å of the center of a Ta atom. All other peaks from the Cu data corresponded to scattering by less than 2.6 electrons. It was concluded from the absence of common residual peaks in the difference Fourier synthesis for the Cu and Mo data that the residual peaks in the difference Fourier maps were due to errors in the data.

# 8. Drawing of the structure of Ta<sub>2</sub>S and the interatomic distances

The Thermal Ellipsoid Plot computer program written by Johnson (45) was used to draw a projection of the structure down the b-axis with the radius of the atoms arbitrarily chosen to be proportional to Slater's radii (46) for the elements. This view is illustrated in Figure 3. The interatomic

Figure 3. Projection of the Ta<sub>2</sub>S structure on the XZ plane



distances obtained using Johnson's program are listed in Table 12. The upper limits to the uncertainties in these interatomic distances are estimated to have the following values: 0.008Å (Ta-Ta), 0.02Å (Ta-S), and 0.03Å (S-S). The results from the Mo data were used for these calculations.

B. The Determination of the Structure of Ta<sub>6</sub>S

### 1. Collection of intensity data

The  $Ta_6S$  phase was prepared as described in sections II,B and C with a very important modification. The tungsten cell used in this preparation did not have an orifice in the lid as it did for most preparations. This modification in the construction of the cell resulted from the observation that samples of the approximate stoichiometry  $Ta_6S$  tended to lose a sulfur bearing vapor species on heating to about 1600°C, leaving behind proportionately large amounts of metallic tantalum in the condensed phase. The final annealing temperature for the  $Ta_6S$  preparation was 1620°C.

Due to a very high incidence of twinning in this phase, a single crystal suitable for the determination of the structure was found only after numerous attempts. This crystal was mounted on the end of a glass fiber by Duco Cement. A Charles C. Supper Co. Weissenberg camera was used to take a rotation photograph and  $h0\ell$ ,  $hl\ell$ , and  $h2\ell$ Weissenberg layer photographs with rotation about the b-axis. Reciprocal lattice plots from these layer photographs indi-

| Table 12.         | Bond distances for | Ta <sub>2</sub> S      |              |
|-------------------|--------------------|------------------------|--------------|
| Reference<br>Atom | Neighbor           | Number of<br>Neighbors | Distance (Å) |
| Ta(l)             | S(2)               | 1                      | 2.403        |
|                   | S(1)               | l                      | 2.497        |
|                   | S(1)               | l                      | 2.604        |
|                   | Ta(3)              | l                      | 2.840        |
|                   | Ta(3)              | 1                      | 2.942        |
|                   | Ta(2)              | 1                      | 2.975        |
|                   | Ta(4)              | 1                      | 3.079        |
|                   | Ta(1)              | 2                      | 3.131        |
|                   | Ta(1)              | l                      | 3.169        |
|                   | Ta(2)              | 1 .                    | 3.255        |
|                   | Ta(2)              | l                      | 3.267        |
|                   | Ta(l)              | 1                      | 3.307        |
| Ta(2)             | S(2)               | l                      | 2.475        |
|                   | S(2)               | l                      | 2.534        |
|                   | S(1)               | l                      | 2.587        |
|                   | Ta(3)              | 1                      | 2.897        |
|                   | Ta(2)              | l                      | 2.910        |
|                   | Ta(3)              | · l                    | 2.923        |
|                   | Ta(1)              | l                      | 2.975        |
|                   | Ta(4)              | l                      | 3.051        |
|                   | Ta(4)              | l                      | 3.085        |
|                   |                    |                        |              |

| Table 12 (Continued | ued) |
|---------------------|------|
|---------------------|------|

| Reference<br>Atom | Neighbor | Number of<br>Neighbors | Distance (Å) |
|-------------------|----------|------------------------|--------------|
|                   | Ta(1)    | 1 ·                    | 3.255        |
|                   | Ta(l)    | l                      | 3.267        |
|                   | Ta(4)    | l                      | 3.284        |
| Ta(3)             | Ta(3)    | 2                      | 2.790        |
|                   | Ta(1)    | 2                      | 2.840        |
|                   | Ta(2)    | 2                      | 2.897        |
|                   | Ta(4)    | l                      | 2.908        |
|                   | Ta(2)    | 2                      | 2.923        |
|                   | Ta(1)    | · 2                    | 2.942        |
|                   | Ta(4)    | l                      | 2.995        |
| Ta(4)             | S(2)     | 2                      | 2.474        |
|                   | Ta(3)    | l                      | 2.908        |
|                   | Ta(3)    | l                      | 2.995        |
|                   | Ta(2)    | 2                      | 3.051        |
|                   | Ta(1)    | 2                      | 3.079        |
|                   | Ta(2)    | 2                      | 3.085        |
|                   | Ta(2)    | 2                      | 3.284        |
| S(1)              | Ta(l)    | 2                      | 2.497        |
|                   | Ta(2)    | 2                      | 2.587        |
|                   | Ta(1)    | 2                      | 2.604        |

|                   |          |                        | •            |
|-------------------|----------|------------------------|--------------|
| Reference<br>Atom | Neighbor | Number of<br>Neighbors | Distance (Å) |
| S(2)              | Ta(1)    | l                      | 2.403        |
|                   | Ta(4)    | 1                      | 2.474        |
|                   | Ta(2)    | l                      | 2.475        |
|                   | Ta(2)    | l                      | 2.534        |

Table 12 (Continued)

cated that the lattice is monoclinic. The following systematic conditions on the Miller indices for reflections were observed:

 $hk\ell$ , h+k=2n; hk0, h+k=2n;  $h0\ell$ , h=2n,  $\ell=2n$ ; 0k0, k=2n.

These conditions for the observation of reflections indicated that the centrosymmetric space group is C2/c.

Single crystal diffraction data were collected using the Hilger-Watts diffractometer with an SDS (910) - IBM (1401) computer configuration previously described in section IV,A,1 in conjunction with the data collection for the Ta<sub>2</sub>S phase. MoK<sub> $\alpha$ </sub> radiation was used with a Zr filter to collect data for all reflections in the range 0°<20≤60° in octants hkl, hkl, hkl, and hkl. Lorentz and polorization corrections were applied as described in section IV,A,3. Absorption corrections, based on the crystal's rectangular prismatic shape (about 40µ x 30µ x 10µ) determined from

photographs taken of the crystal by H. Baker, were computed as described earlier (Section IV,A,2). A linear absorption coefficient of 1413  $\rm cm^{-1}$  for MoK<sub>q</sub> radiation was used to obtain the integrated absorption corrections. The values of the transmission factor coefficients ranged from 0.0830 to 0.2352.  $F_{obs}$  values for hk $\ell$  and  $\overline{h}k\ell$  were averaged for common h, k, and  $\mathcal L$  indices in the symmetrically equivalent octants. The lattice parameters were determined at 25°C from a Guinier powder photograph indicating lines attributable only to  $Ta_6S$  using KCl, a=6.29300+0.00009Å (32) as an internal standard and CuK radiation,  $\lambda$ =1.5405Å. The lattice parameters determined by least squares treatment of the powder data are: a=14.158 $\pm$ 0.0040Å, b=5.284 $\pm$ 0.001Å,  $c=14.789\pm 5^{\circ}$  and  $\beta=118.01^{\circ}\pm 0.02^{\circ}$ . The hk $\ell$  indices,  $\sin^2\theta_{(obs)}$ ,  $\sin^2\theta_{(calc)}$  and the estimated relative intensities of reflections for the Ta<sub>6</sub>S phase obtained from a Guinier powder photograph are listed in Table 13. A pyconometric determination of the density of this sample using water at 24°C as the displaced medium yielded a value of 15.18 g/cc. The calculated density of Ta<sub>6</sub>S on the basis of % formula units per unit cell is 15.20 g/cc.

|  |  |                             |  | 0  |   |
|--|--|-----------------------------|--|--|---|
| h  | k  | 2                           | sin <sup>2</sup> 0 (obs) ×10 <sup>5</sup>  | $\sin^2\theta$ (calc) $\times 10^5$  | I/I <sub>o</sub> ×100   |
| $ \begin{array}{c}     11 \\     0 \\     2 \\     -3 \\     -3 \\     0 \\     3 \\     0 \\     3 \\     -1 \\     -5 \\     2 \end{array} $ | 001101221110   | 2012410125534               | 1388<br>1524<br>4871<br>5561<br>6923<br>8480<br>8863<br>8992<br>9118<br>9508<br>9621<br>9813                     | 1392<br>1519<br>4867<br>4886<br>5569<br>6914<br>8499<br>8848<br>8982<br>9123<br>9498<br>9631<br>9318             | 10<br>5<br>1<br>1<br>25<br>60<br>25<br>70<br>20<br>25<br>20             |
| -556203021460  | 0<br>2<br>1<br>1<br>0<br>2<br>2<br>1<br>0<br>2<br>1<br>2<br>0<br>2<br>1<br>2<br>0<br>2 | r 2 1 4 2 3 3 3 6 4 5 3 6 4 | 9885<br>10263<br>10375<br>10951<br>11110<br>11631<br>11743<br>12523<br>12854<br>12919<br>13617<br>13912<br>14082 | 9396<br>10258<br>10359<br>10968<br>11104<br>11636<br>11748<br>12529<br>12854<br>12913<br>13611<br>13906<br>14069 | 20<br>100<br>80<br>55<br>85<br>90<br>60<br>1<br>1<br>50<br>70<br>5<br>1 |

Table 13. X-ray diffraction data for  $Ta_{c}S$ ,  $\lambda=1.5405$ Å

# 2. <u>Structural solution</u>

The method used to determine the structure of  $Ta_6S$  was analogous to that employed in solving the structure of  $Ta_2S$ .

It was decided to accept those data as "observed" for which  $\sigma I/I$ , as defined in section IV,A,4,c, was less than or equal to 0.40. The remainder of the reflections were considered to be "unobserved." According to this criterion, there were 668 "observed" reflections. The graphical method, as described in section IV,A,4,c, was used to calculate the magnitude of the unitary structure factors from the intensity data.

The method of evaluation of  $|U|^2$  for a given range in values of  $\sin\theta$  was modified slightly to account for the fact that that space group of  $Ta_6^S$  was centered and not primitive as was the case in  $Ta_2^S$ .

The unitary scattering factor, n<sub>j</sub>, for a primitive cell was defined by the relationship:

$$n_{j} = f_{j} / \sum_{j=1}^{N} f_{j}$$
(36)

for the N atoms in the unit cell. However, in a centered cell, this relationship can be slightly modified to account for the centering condition which, in the case of the space group C2/c, places an atom at 1/2+x, 1/2+y, z in the unit cell for each at x,y,z. This can be expressed as:

$$n_{j} = f_{j} / 2 \sum_{j=1}^{N/2} f_{j}$$
(37)

Accordingly  $\overline{|U|^2}$  for a centered cell, call this value,  $\overline{|U_c|^2}$  can be evaluated from the expression:

$$\frac{1}{|U_c|^2} = 2\sum_{j=1}^{N/2} \sum_{j=1}^{2} j^2 , \qquad (38)$$

$$= 2 \sum_{j=1}^{N/2} (f_j/2 \sum_{j=1}^{N/2} f_j)^2, \qquad (39)$$

$$= \frac{1}{2} \sum_{j=1}^{N/2} (f_j / \sum_{j=1}^{N/2} f_j)^2.$$
(40)

But the contents of the entire centered unit cell can be divided into two equivalent halves, each of which is a simple primitive cell containing one half of the total number of atoms in the centered cell, in which the atoms in one primitive cell are related to those in the other primitive cell by the centering condition, and  $|U|^2$  for the primitive cell, call this value  $|U_p|^2$ , can be written as:

$$\frac{1}{|v_{p}|^{2}} = \sum_{j=1}^{N/2} (f_{j} / \sum_{j=1}^{N/2} f_{j})^{2}.$$
(41)

Combining equations 40 and 41,  $|U_c|^2$  and  $|U_p|^2$  are related by the relationship:

$$\overline{|\mathbf{U}_{c}|^{2}} = \overline{1/2|\mathbf{U}_{p}|^{2}} .$$
 (42)

Consequently,  $\phi_{\rm C}$  for a centered cell is given by the relationship:

$$\phi_c^2 = \overline{|U_c|^2} / (\overline{I_{corr}}) , \qquad (43)$$

$$= \frac{\left| U_{p} \right|^{2}}{(2 \cdot \overline{I_{corr}})} \quad . \tag{44}$$

Therefore,

$$\overline{|\mathbf{U}_{p}|} = \phi_{c} \sqrt{2 \cdot \overline{\mathbf{I}_{corr}}} .$$
 (45)

Values of corrected intensity data, I<sub>corr</sub>, for all reflections were serialized in increasing order of sin8 (8 is the Bragg angle). The intensity datum for each

reflection was multiplied by its relative weight in the reciprocal lattice according to the following scheme: 2 for an h00,0k0, or 00L reflection, 4 for an 0kL reflection, 2 for an hk0,  $\overline{h}k0$ , h02, or an  $\overline{h}02$  reflection, and 4 for an hkl or an  $\overline{hkl}$  reflection for which h $\neq 0$ , k $\neq 0$ , and  $l\neq 0$ . The weighted intensity data for regions of  $sin\theta+0.05$ , starting with  $sin\theta=0.05$ , were averaged. If an allowed reflection had an observed intensity of zero, it was assigned one half of the minimum intensity observed in its sind range and the adjacent two sint ranges. The average of the weighted intensities was computed for each sint region by dividing the weighted intensity sum by the weighted number of reflections in the sind region. The number of reflections and the average weighted intensities for the various sing ranges are listed in Table 14. The data for neighboring sind regions were combined to determine average weighted intensity values for ranges of average sing. These data are listed in Table 15.

The evaluation of  $|U_{hk} g|^2$  requires a knowledge of the numbers and kinds of atoms in the unit cell. In the case of the Ta<sub>6</sub>S structure, it was guessed that there were 8 Ta<sub>6</sub>S units per unit cell of the centered cell. Using this supposition, the value of  $|U_{hk} g|^2$  for a centered cell were calculated for values of sing in increments of 0.100 starting

| 202 32.00 205200 |                          |                                   |                               |
|------------------|--------------------------|-----------------------------------|-------------------------------|
| Sinð             | Number of<br>Reflections | Weighted Number<br>of Reflections | Average Weighted<br>Intensity |
| 0.0-0.1          | 34                       | 80                                | 16.44                         |
| 0.1-0.2          | 186                      | 596                               | 354.44                        |
| 0.2-0.3          | 530                      | 1756                              | 215.38                        |
| 0.3-0.4          | 938                      | 3266                              | 162.52                        |
| 0.4-0.5          | 1566                     | 5588                              | 111.56                        |

Table 14. Number of reflections, weighted number of reflections and the average weighted intensity per sin0 region

Table 15. Mean weighted intensity per sin8 region

| Average Sin0 | Mean Weighted Intensity |
|--------------|-------------------------|
| 0.10         | 312.29                  |
| 0.20         | 249.51                  |
| 0.30         | 181.00                  |
| 0.40         | 130.36                  |
|              |                         |

with  $\sin\theta=0$ . The results of the evaluation of  $|U_c|^2$  are listed in Table 16. Values of  $\sin\theta$ ,  $\phi_c^2$  and  $\phi_c$  are listed in Table 17. A plot of  $\phi_c$  versus  $\sin\theta$  (data from Table 17) is given in Figure 4. The magnitudes of the unitary structure factors,  $\overline{|U_{hk}\chi|}$ , were calculated from the relation:

 $|U_{hk}|_{c} = \phi_{c} \sqrt{(I_{corr})_{hk}}$ (45)
|      |                |         | · · c           | 6                 |                 |                                     |
|------|----------------|---------|-----------------|-------------------|-----------------|-------------------------------------|
| sinð | f <sub>s</sub> | f<br>Ta | 4f <sub>S</sub> | 24f <sub>Ta</sub> | Σf <sub>j</sub> | (x10 <sup>n</sup> Ta <sub>2</sub> ) |
| 0.10 | 13.00          | 66.00   | 52.0            | 1584.0            | 1636.0          | 4.034                               |
| 0.20 | 9.45           | 56.50   | 37.8            | 1356.0            | 1393.8          | 4.054                               |
| 0.30 | 7.73           | 47.25   | 30.9            | 1134.0            | 1164.9          | 4.056                               |
| 0.40 | 6.60           | 40.00   | 26.4            | 960.0             | 986.4           | 4.055                               |
| 0.50 | 5.59           | 34.25   | 22.4            | 822.0             | 844.4           | 4.056                               |

Table 16. Calculation of  $|U|_c^2$  for Ta<sub>6</sub>S

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| <del></del>                |                   | <u>_</u>                               |            |         |              |                      |
|----------------------------|-------------------|--|------------|---------|--------------|----------------------|
| $\frac{n_{s}}{(x10^{-2})}$ | n <sup>2</sup> Ta | $\binom{n^2 S}{(x \downarrow 0^{-4})}$ | $24n^2$ Ta | $4n^2s$ |              | U _2                 |
|                            | (x10)             |  | (x10 )     | (X10))  | $(x10^{-4})$ | (x10 <sup>-4</sup> ) |
| 0.795                      | 16.273            | 0.632                                  | 390.55     | 2.53    | 393.08       | 196.54               |
| 0.678                      | 16.435            | 0.460                                  | 394.44     | 1.84    | 396.27       | 198.14               |
| 0.564                      | 16.451            | 0.441                                  | 394.82     | 1.76    | 396.59       | 198.29               |
| 0.669                      | 16.443            | 0.448                                  | 394.63     | 1.79    | 396.42       | 198.21               |
| 0.662                      | 16.451            | 0.438                                  | 394.82     | 1.75    | 396.58       | 198.29               |
|                            |                   |  |            |         |              |                      |

| sin0 | $\phi_c^2 \times 10^{-4}$ | ¢c x 10 <sup>-2</sup> |  |
|------|---------------------------|-----------------------|--|
| 0.10 | 0.6294                    | 0.793                 |  |
| 0.20 | 0.7941                    | 0.891                 |  |
| 0.30 | 1.0955                    | 1.047                 |  |
| 0.40 | 1.5204                    | 1.233                 |  |

Table 17.  $\phi_c^2$  and  $\phi_c$  for an average sin $\theta$  region

using the interpolated values from Figure 4.

The Mo data yielded 105 unitary structure factors with magnitudes greater than or equal to 0.40. These unitary structure factors comprised approximately 16% of the observed reflections.

As discussed in section IV,A,4,c, signs can be assigned to one, two, or three structure factors subject to certain restrictions. In the solution of the structure of  $Ta_6S$ , due to the existence of centering in the unit cell, only two unitary structure factors could be assigned signs to fix the origin. These two unitary structure factors from the set of those for which  $|U_{hk\ell}| \ge 0.40$  had the following respective Miller indices, parities and assigned signs: 2,2,3,(e,e,o), (+) and 3,1,3,(o,c,o), (+). The assignment of signs to additional unitary structure factors in this set was accomplished by use of the triple product relations as discussed in section II,A,4,c. One unitary structure factor Figure 4. Graph of phi,  $\phi_c$ , vs. sin $\theta$  for Ta<sub>6</sub>S

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possessing the set of Miller indices 4,2,5 was assigned the variable sign b. Accordingly, by using the triple product relations, it was possible to assign signs to all 106 unitary structure factors of this set with one variable sign.

Two Fourier electron density functions were computed using a computer program by D. Dahm<sup>1</sup> and the 106 structure factors with assigned signs and with the variable sign, b, positive for one function and negative in the other function. Both maps contained six strong peaks per asymmetric unit. There was an unreasonably short Ta-Ta distance  $(2.13\text{\AA})$  in the asymmetric cell obtained with the variable sign positive. Accordingly, the atomic positions implied with the variable sign negative were used as atomic positions in a trial structure. The electron density map calculated on the basis of this trial structure clearly showed one possible sulfur position in the asymmetric unit.

#### 3. Structure refinement

The structure thus obtained was refined by least-squares computation (43). The scattering factors given by Hanson, Herman, Lea and Skillman (42) were corrected for both real and imaginary dispersion using the values given by the <u>International Tables for Crystallography</u> (44).

<sup>1</sup>Dahm, <u>ibid</u>.

The structure was refined until the unweighted reliability index, R, using isotropic temperature factors was 6.6% for the 668 "observed" reflections, about 23 reflections per variable in the refinement. The positional and thermal parameters for  $Ta_6S$  are listed in Table 18. Graph 2, written using a computer program written by S. Porter<sup>1</sup>, lists the "observed" and approximately 14% of the unobserved reflections. The unweighted reliability index for these data is 6.8%. The positional and thermal parameters for these two sets of  $F_{obs}$ data agree within the standard deviation of the related parameters in Table 18. All signs assigned by the direct method agreed with those obtained for the structure.

### 4. <u>Weighting scheme for intensities</u>

A weighting scheme analogous to that described for  $Ta_2S$  in section IV,A,6 was used. The standard deviation of an observation of unit weight, as defined by Equation 35, was 1.29 for the 668 "observed" reflections.

### 5. Fourier difference analyses

A difference Fourier synthesis was performed using all observed reflections. The synthesis indicated a peak attributable to approximately 1.3 electrons at x=0.410, y=0.826, and z=0.200. An examination of the  $F_{obs}$  Fourier

<sup>1</sup>Porter, <u>op</u>. <u>cit</u>., a computer listing program.

Graph 2. Observed and calculated structure factors (x0.10) for Ta<sub>6</sub>S (\*="unobserved", <u>cf</u>. text)

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| $\underline{x} \underline{y} \underline{z}$ of the space group C2/c |   |  |   |   |  |  |  |
|---|---|--|---|---|--|--|--|
| 10 <sup>4</sup> X/a   | 10 <sup>4</sup> Y/b   | l0 <sup>4</sup> z/c  | $\underline{B}(A^2)$  |   |  |  |  |
| 2480 <u>+</u> 3   | 4067 <u>+</u> 7   | 2518 <u>+</u> 3  | 0.04+5.   |   |  |  |  |
| 3401 <u>+</u> 2   | 6568 <u>+</u> 9   | 4547 <u>+</u> 3  | 0.26 <u>+</u> 5   |   |  |  |  |
| 4364 <u>+</u> 2   | 1628 <u>+</u> 8   | 4051 <u>+</u> 2  | 0.13 <u>+</u> 5   |   |  |  |  |
| 358 <u>÷</u> 2  | 1460 <u>+</u> 8   | $1740 \pm 3$   | 0.12 <u>+</u> 5   |   |  |  |  |
| 2111 <u>+</u> 2   | 1475 <u>+</u> 8   | 3969 <u>+</u> 3  | 0.06 <u>+</u> 5   |   |  |  |  |
| 1063 <u>+</u> 2   | 6793 <u>+</u> 7   | 3173 <u>+</u> 3  | C.06 <u>÷</u> 5   |   |  |  |  |
| 3920 <u>+</u> 15  | 9189 <u>+</u> 41  | 437 <u>+</u> 16  | 0.51 <u>+</u> 30  |   |  |  |  |
|   | <u>x y z of the</u><br>$10^{4}$ x/a<br>$2480\pm3$<br>$3401\pm2$<br>$4364\pm2$<br>$358\pm2$<br>$2111\pm2$<br>$1063\pm2$<br>$3920\pm15$ | <u>x y z of the space group</u><br>$10^{4}$ x/a $10^{4}$ Y/b<br>$2480\pm3$ $4067\pm7$<br>$3401\pm2$ $6568\pm9$<br>$4364\pm2$ $1628\pm8$<br>$358\pm2$ $1460\pm8$<br>$2111\pm2$ $1475\pm8$<br>$1063\pm2$ $6799\pm7$<br>$3920\pm15$ $9189\pm41$ | <u>x y z</u> of the space group C2/c<br>$10^{4}$ X/a $10^{4}$ Y/b $10^{4}$ Z/c<br>$2480\pm3$ $4067\pm7$ $2518\pm3$<br>$3401\pm2$ $6568\pm9$ $4547\pm3$<br>$4364\pm2$ $1628\pm8$ $4051\pm2$<br>$358\pm2$ $1460\pm8$ $1740\pm3$<br>$2111\pm2$ $1475\pm8$ $3969\pm3$<br>$1063\pm2$ $6799\pm7$ $3173\pm3$<br>$3920\pm15$ $9189\pm41$ $437\pm16$ | $\underline{x \ y \ z} \text{ of the space group C2/c}$ $10^{4} \text{X/a} \qquad 10^{4} \text{Y/b} \qquad 10^{4} \text{Z/c} \qquad \underline{B}(\text{Å}^{2})$ $2480\pm3 \qquad 4067\pm7 \qquad 2518\pm3 \qquad 0.04\pm5^{\circ}$ $3401\pm2 \qquad 6568\pm9 \qquad 4547\pm3 \qquad 0.26\pm5$ $4364\pm2 \qquad 1628\pm8 \qquad 4051\pm2 \qquad 0.13\pm5$ $358\pm2 \qquad 1460\pm8 \qquad 1740\pm3 \qquad 0.12\pm5$ $2111\pm2 \qquad 1475\pm8 \qquad 3969\pm3 \qquad 0.06\pm5$ $1063\pm2 \qquad 6798\pm7 \qquad 3173\pm3 \qquad 0.06\pm5$ $3920\pm15 \qquad 9189\pm41 \qquad 437\pm16 \qquad 0.51\pm30$ |  |  |  |

Table 18. Refined positional and thermal parameters for  $Ta_6S$  using the 668 "observed" reflections. All atoms occupy eightfold general positions (f) x v z of the space group C2/c

synthesis at this position indicated no positive peak. All other peaks corresponded to one electron or less. These small peaks found in the difference Fourier synthesis do not necessarily lie on positions of positive electron concentration in the  $F_{\rm obs}$  Fourier. It was therefore concluded that the small peaks in the difference Fourier synthesis were due to errors in the data.

# 6. Drawing of the structure of Ta<sub>6</sub>S and the interatomic <u>distance</u>

The Thermal Ellipsoid Program written by Johnson (45) was used to draw a projection of the structure down the b-axis with the radii of the Ta and S atoms chosen to be proportional to Slater's radii (46) for the elements, this view is illustrated in Figure 5. The interatomic distances, listed in Table 19, were also obtained using this program. The Oak Ridge Fortran Function and Error Program by Busing, Martin, and Levy (47) was used to determine the errors in the interatomic distances. The average error in the Ta-Ta distance is 0.005Å; the average error in the Ta-S distance is 0.020Å.

| Та | ble | e 19 | • | Bond | distances | in | Ta,S |
|----|-----|------|---|------|-----------|----|------|
|----|-----|------|---|------|-----------|----|------|

|                   |          | 0                      |              |
|-------------------|----------|------------------------|--------------|
| Reference<br>Atom | Neighbor | Number of<br>Neighbors | Distance (Å) |
| Ta-l              | Ta-l     | 2                      | 2.644        |
|                   | Ta-5     | ī                      | 2.795        |
|                   | Ta-5     | 1                      | 2.828        |
|                   | Ta-3     | ī                      | 2.873        |
|                   | Ta-3     | 1                      | 2.890        |
|                   | Ta-6     | 1                      | 2.953        |
|                   | Ta-2     | <u>1</u>               | 2.964        |
|                   | Ta-6     | 1                      | 2.979        |
|                   | Ta-4     | 1                      | 3.001        |
|                   | Ta-4     | 1                      | 3.004        |
|                   | Ta-2     | 1                      | 3.008        |
| Ta-2              | S-l      | 1                      | 2.525        |
|                   | Ta-l     | ī                      | 2.964        |
|                   | Та-б     | 1                      | 2.966        |
|                   | Ta-1     | 1                      | 3.008        |
|                   | Ta-3     | 1                      | 3.010        |
|                   | Ta-5     | · <u>1</u>             | 3.055        |
|                   | Ta-5     | 1                      | 3.071        |
|                   | Ta-4     | <u>]</u>               | 3.138        |
|                   | Ta-5     | 1                      | 3.140        |
|                   | Ta-3     | 1                      | 3.188        |
|                   | Ta-6     | l                      | 3.208        |
|                   | Ta-3     | 1                      | 3.237        |

| Table 19 | (Continued) |
|----------|-------------|
|----------|-------------|

| Reference<br>Atom | Neighbor   | Number of<br>Neighbors | Distance (Å)  |
|-------------------|--|------------------------|---|
| Ta-3              | S-1<br>S-1<br>Ta-1<br>Ta-1<br>Ta-4<br>Ta-2<br>Ta-6<br>Ta-3<br>Ta-3<br>Ta-4<br>Ta-5<br>Ta-5<br>Ta-2<br>Ta-6<br>Ta-5<br>Ta-6 |                        | 2.448<br>2.529<br>2.873<br>2.890<br>2.911<br>3.010<br>3.055<br>3.055<br>3.069<br>3.138<br>3.188<br>3.227          |
| Ta-4              | Ta-2<br>S-1<br>Ta-4<br>Ta-3<br>Ta-1<br>Ta-1<br>Ta-1<br>Ta-2<br>Ta-5<br>Ta-6<br>Ta-6<br>Ta-6<br>Ta-6                        |                        | 3.237<br>2.503<br>2.869<br>2.911<br>3.001<br>3.004<br>3.058<br>3.069<br>3.094<br>3.138<br>3.143<br>3.2_2<br>3.387 |
| Ta-5              | S-1<br>S-1<br>Ta-1<br>Ta-1<br>Ta-6<br>Ta-6<br>Ta-5<br>Ta-2<br>Ta-2<br>Ta-2<br>Ta-2<br>Ta-2<br>Ta-2<br>Ta-2<br>Ta-2         |                        | 2.485<br>2.489<br>2.795<br>2.828<br>2.839<br>2.921<br>3.055<br>3.058<br>3.071<br>3.138<br>3.140<br>3.140<br>3.143 |

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Table 19 (Continued)

| Reference<br>Atom | Neighbor | Number of<br>Neighbors | Distance (Å) |
|-------------------|----------|------------------------|--------------|
| Ta-6              | S-1      | 1                      | 2.465        |
|                   | Та-б     | 1                      | 2.722        |
|                   | Ta-5     | 1                      | 2.839        |
|                   | Ta-l     | 1                      | 2.953        |
|                   | Ta-2     | 1                      | 2.966        |
|                   | Ta-l     | 1                      | 2.979        |
|                   | Ta-3     | 1                      | 3.055        |
|                   | Ta-4     | 1                      | 3.094        |
|                   | Ta-5     | 1                      | 3.140        |
|                   | Ta-2     | 1                      | 3.208        |
|                   | Ta-4     | 1                      | 3.222        |
|                   | Ta-3     | 1                      | 3.227        |
|                   | Ta-4     | 1                      | 3.387        |
| S-1               | Ta-3     | 1                      | 2.448        |
|                   | Та-б     | l                      | 2.465        |
|                   | Ta-5     | l                      | 2.485        |
|                   | Ta-5     | l                      | 2.489        |
|                   | Ta-4     | l                      | 2.503        |
|                   | Ta-2     | l                      | 2.525        |
|                   | Ta-3     | 1                      | 2.529        |

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Figure 5. Projection of the Ta<sub>6</sub>S structure on the XZ plane



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## V. THE PREPARATION AND X-RAY CHARACTERIZATION

OF THE GROUP IVE DIMETAL SELENIDES:

1. Collection of intensity data

The Ti<sub>2</sub>Se phase was prepared as outlined in sections II, A and B. The annealing temperature was 1580°C. maintained for 3 hours.

A Charles G. Supper Co. Weissenberg camera was used to take rotation photographs and hk0 and hk $\ell$  Weissenberg layer photographs about the c-axis of a crystal of Ti<sub>2</sub>Se. Reciprocal lattice plots from these layer photographs indicated that the lattice is orthorhombic. The following systematic conditions on the Miller indices were observed: hk $\ell$ , no conditions; 0k $\ell$ , k+ $\ell$ =2n; h0 $\ell$ , h+ $\ell$ =2n; hk0, no conditions; h00, h=2n; 0k0, k=2n; 00 $\ell$ ,  $\ell$ =2n. These systematic conditions for observed reflections indicated that the centrosymmetric space group is Pnnm. A comparison of the Weissenberg layer photographs for Ti<sub>2</sub>Se and for Ti<sub>2</sub>S (20), which exhibits the Ta<sub>2</sub>P (48) structure type, indicated that the two phases Ti<sub>2</sub>S and Ti<sub>2</sub>Se are isostructural.

Single crystal diffraction data were collected using the G. E. spectrogoniometer for the  $\text{Ti}_2\text{Se}$  phase as described in section IV,A,1. CuK<sub>a</sub> radiation was used with a Ni filter to collect data for hk0, hk1, h0l, and 0kl reflections for

0°<28<90°. Lorentz and polarization corrections were applied as described in section IV, A, 3. Absorption corrections, based on the crystal's rectangular prismatic shape (approximately 35µ x 28µ x 100µ) determined from photographs by H. Baker, were computed as described earlier. A linear absorption correction of 271.8 cm<sup>-1</sup> for CuK<sub>2</sub> radiation was used to calculate the absorption correction using Busing and Levy's program (36). The lattice parameters, determined at 25°C from a Guinier powder photograph, using KCl, a=6.29300 $\pm$ 0.00009Å (32) as an internal standard and CuK $\alpha_1$ radiation,  $\lambda$ =1.5405Å, were: a=11.744+3Å, b=14.517+3Å,  $c=3.4564\pm 8$ Å. The hkl indices,  $\sin^2\theta_{(obs)}$ ,  $\sin^2\theta_{(calc)}$  and estimated relative intensities from a Guinier powder photograph are listed in Table 20. The calculated density for Ti<sub>2</sub>Se on the basis of 12 Ti<sub>2</sub>Se units per unit cell is 5.91 g/cc.

After the intensity data were taken, it was discovered that the crystal used to collect the data was twinned. The examination of the Weissenberg layer photographs indicated that the crystal was twinned and that both twins were almost equal in size. Single crystal intensity data were taken for about 25 reflections from both crystals comprising the twin, and the magnitude of the respective intensities for these reflections were approximately equal. Despite the fact that the crystal was twinned, it was decided to attempt to refine

|       |                                       | Z  |        |
|-------|---------------------------------------|--|--------|
| h k L | $\sin^2_{\theta}_{(obs)} \times 10^5$ | $\sin^{2}\theta$ (calc) ×10 <sup>5</sup> | I xl00 |
| 2 2 0 | 2848                                  | 2845                                     | l      |
| 140   | 4924                                  | 4935                                     | 5      |
| 320   | 4988                                  | 4996                                     | 10     |
| 0 1 1 | 5242                                  | 5246                                     | 10     |
| 101   | 5402                                  | 5394                                     | 8      |
| 2 4 0 | 6218                                  | 6227                                     | · l    |
| 3 3 0 | 6401                                  | 6405                                     | l      |
| 2 1 1 | 6981                                  | 6967                                     | 15     |
| 410   | 7173                                  | 7164                                     | 8      |
| 031   | 7510                                  | 7501                                     | 8      |
| 2 2 1 | 7798                                  | 7812                                     | 30     |
| 301   | 8828                                  | 8838                                     | 20     |
| 3 1 1 | 9118                                  | 9118                                     | 30     |
| 2 3 1 | 9218                                  | 9218                                     | 30     |
| 141   | 9890                                  | 9901                                     | 30     |
| 060   | 10152                                 | 10137                                    | 10     |
| 3 5 0 | 10908                                 | 10908                                    | 13     |
| 510   | 11575                                 | 11580                                    | 10     |
| 2 4 1 | 11181                                 | 11192                                    | 100    |
| 331   | 11369                                 | 11369                                    | 100    |
| 440   | 11391                                 | 11000                                    | TOO    |

Table 20. X-ray diffraction data for Ti<sub>2</sub>Se,  $\lambda$ =1.5405Å

| h k <b>l</b> | sin <sup>2</sup> 0 (obs) x10 <sup>5</sup> | $\sin^2\theta$ (calc) $\times 10^5$ | I ×100 |
|--------------|---|-------------------------------------|--------|
| 151          | 12437                                     | 12431                               | 20     |
| 421          | 12972                                     | 12977                               | 30     |
| 530          | 13290                                     | 13319                               | 20     |
| 341          | 13343                                     |                                     |        |
| 360          | 13991                                     | 14009                               | 10     |
| 170          | 14228                                     | 14222                               | 25     |
| 540          | 15255                                     | 15261                               | 15     |
| 511          | 16015                                     | 16002                               | 20     |
| 1 8 0        | 18466                                     | 18466                               | 18     |
| 0 0 2        | 19867                                     | 19861                               | 70     |
| 461          | 21990                                     | 21983                               | 10     |
| 631          | 23017                                     | 22988                               | 5      |

Table 20 (Continued)

the structure using the intensity data.

### 2. Structure refinement of Ti<sub>2</sub>Se

It was decided to accept those data as observed for which cI/I, as defined in section IV,A,6, was less than or equal to 0.25. The remainder of the reflections were considered to be "unobserved." According to this criterion, there were 205 "observed" reflections.

Using the positions of the respective Ti and S atoms in

 ${\rm Ti}_2 {\rm S}$  as initial positions for the respective Ti and Se atoms in  ${\rm Ti}_2 {\rm Se}$ , the structure of  ${\rm Ti}_2 {\rm Se}$  was refined by least-squares techniques (43) using one isotropic thermal parameter for the Ti atoms and one isotropic thermal parameter for the Se atoms. The unweighted reliability index for this refinement of the structure of 7.2%. There were 20 variables in this refinement, resulting in about 10 reflections per variable parameter. The thermal and positional parameters obtained from this refinement are listed in Table 21. Table 22 lists the hk $\ell$ ,  ${\rm F}_{\rm obs}$ , and  ${\rm F}_{\rm calc}$  values for the 205 "observed" reflections.

The interatomic distances were calculated using a program written by D. Bailey<sup>1</sup>, these values are listed in Table 23.

### 3. <u>Weighting scheme for intensities</u>

The weights for the refinement of the structure of  $Ti_2Se$  were based on a statistical treatment of the intensity data similar, but not identical, to that used in the structure determination of  $Ta_2S$  and  $Ta_5S$ .

According to Equation 4:

 $I = kLp A * |F|^2$ ,

<sup>&</sup>lt;sup>1</sup>Bailey, D., Department of Matallurgy, Iowa State University of Science and Technology, Ames, Iowa. Bond Distances Computer Program. Private communication. 1967.

| エエスションションションション  | 13'                   | Table                  | Se (3)          | Se(2)    | Se(1)    | Ti (6)  | Ti (5)           | Ti (4) | Ti (3)           | Ti (2) | Ti (1)         | Atom                | Table          |
|--|-----------------------|------------------------|-----------------|----------|----------|---------|------------------|--------|------------------|--------|----------------|---------------------|----------------|
| 0000004444400000   | *                     | 22.                    |                 | -        | -        | -       |                  |        |                  |        |                |                     | 21.            |
| 20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>2    | 1 Fobs F              | Table of Fo            | 6867 <u>+</u> 6 | 2446+6   | 4327+6   | 8830+11 | 8102 <u>+</u> 11 | 4687+9 | 5841 <u>+</u> 10 | 01-968 | 1516+10        | 10 <sup>4</sup> X/a | Positional a   |
| <ul> <li>□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □</li></ul>                           | calc <sup>h</sup>     | bs and Fcalc           | 3496+4          | 4134+4   | 2079±4   | 4525+8  | 2055+8           | 3947+7 | 754+8            | 2602+8 | 195 <u>+</u> 7 | 10 <sup>4</sup> Y/b | ind thermal pa |
| ИИШШ Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф Ф   | ж Л н                 | for Ti <sub>2</sub> Se | 0               | 0        | 0        | 0       | 0                | 0      | 0                | 0      | O              | 2                   | rameters       |
| ЧЧ Ч2<br>22<br>22<br>22<br>22<br>22<br>22<br>22<br>22<br>22<br>22<br>22<br>22<br>2 | obs <sup>F</sup> calc |                        | 0.42+5          | 0 • 42+5 | 0 • 42+5 | 0.62+5  | 0.62+5           | 0.62+5 | 0.62+5           | 0.62+5 | 0.62+5         | B (Å <sup>2</sup> ) | For Ti2Se      |
|  | 1                     | I I                    |                 |          |          |         |                  |        |                  |        |                |                     |                |

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|  |  |                                      |   |                                       |  |   | 1            | 1        |

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Table 22 (Continued)

| h  | k  | 2   | Fobs  | Fcalc   | hk,  | 2 F <sub>obs</sub>   | Fcalc  |
|--|--|---|---|---|--|--|--|
| 12340634797012358357237023581234580113468151 | 5555556666677777788888888888000000000000 | רו הו | 23<br>912341905528831370008101152364348541515952<br>12212212364348541515952 | $\begin{array}{c} -22 \\ -8 \\ 9 \\ 11 \\ -17 \\ 12 \\ 15 \\ 21 \\ 8 \\ -9 \\ -12 \\ 13 \\ -8 \\ 15 \\ 12 \\ -10 \\ 20 \\ 16 \\ -7 \\ 11 \\ -22 \\ -12 \\ -10 \\ -22 \\ -12 \\ -10 \\ -10 \\ -10 \\ -10 \\ -10 \end{array}$ | 0 13<br>1 13<br>2 13<br>3 15<br>9 15<br>1 17<br>2 18<br>9 1 15<br>2 18<br>7 2 18<br>7 2 10<br>6 0 0 12<br>1 16<br>8 0 0 12<br>1 16<br>9 15<br>1 17<br>2 18<br>9 0 0 12<br>1 16<br>1 17<br>2 0 0 0 12<br>1 16<br>1 17<br>2 0 0 0 12<br>1 16<br>1 17<br>1 17<br>1 17<br>1 17<br>1 17<br>1 18<br>1 17<br>1 19<br>1 0 0 0 12<br>1 16<br>1 17<br>1 19<br>1 0 0 0 12<br>1 16<br>1 17<br>1 16<br>0 0 12<br>1 16<br>0 0 12<br>1 16<br>0 0 0 12<br>1 16<br>0 0 0 12<br>1 16<br>0 0 0 12<br>1 3 7<br>0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 1       23         1       17         1       17         1       10         1       16         1       15         1       16         1       16         1       17         1       16         10       17         11       16         12       17         23       94         10       17         23       17         23       17         23       17         23       17         23       17         23       17         23       17         23       17         23       15         13       15         13       17         9       10         15       13         16       13         17       15         17       15         17       15         17       15         17       15         17       15         17       15         17       15 | $ \begin{array}{c} -23 \\ -18 \\ 17 \\ 11 \\ 20 \\ -16 \\ 18 \\ -17 \\ -18 \\ -14 \\ -17 \\ -15 \\ -14 \\ -17 \\ -15 \\ -14 \\ 10 \\ 20 \\ -15 \\ -14 \\ -12 \\ -10 \\ -13 \\ 14 \\ 15 \\ 7 \\ 32 \\ -10 \\ 8 \\ -17 \\ -11 \\ 15 \\ 1$ |

| Reference<br>Atom | Neighbor<br>Atom  | Number of<br>Neighbors               | Distance (Å)   |
|-------------------|---|--------------------------------------|--|
| Ti(l)             | Se(2)<br>Se(3)<br>Ti(4)<br>Ti(4)<br>Ti(5)<br>Ti(6)<br>Ti(3)                   | 2<br>2<br>2<br>1<br>2<br>1           | 2.64<br>2.64<br>2.91<br>3.05<br>3.31<br>3.35<br>3.40                 |
| Ti(2)             | Se(1)<br>Se(3)<br>Se(2)<br>Ti(3)<br>Ti(5)<br>Ti(4)<br>Ti(5)<br>Ti(6)          | 2<br>2<br>1<br>2<br>2<br>2<br>1<br>1 | 2.59<br>2.64<br>2.88<br>2.95<br>3.18<br>3.19<br>3.38<br>3.40         |
| Ti(3)             | Se(2)<br>Se(1)<br>Ti(6)<br>Ti(6)<br>Ti(2)<br>Ti(3)<br>Ti(5)<br>Ti(4)          | 2<br>1<br>2<br>2<br>1<br>1<br>1      | 2.58<br>2.62<br>2.85<br>2.94<br>2.95<br>2.99<br>3.26<br>3.40         |
| Ti(4)             | Se(3)<br>Se(2)<br>Se(1)<br>Ti(1)<br>Ti(5)<br>Ti(1)<br>Ti(4)<br>Ti(2)          | 1<br>1<br>2<br>2<br>2<br>1<br>2      | 2.64<br>2.67<br>2.75<br>2.91<br>2.96<br>3.05<br>3.16<br>3.19         |
| Ti(5)             | Se(3)<br>Se(1)<br>Se(2)<br>Ti(4)<br>Ti(2)<br>Ti(3)<br>Ti(6)<br>Ti(1)<br>Ti(2) | 1<br>2<br>2<br>2<br>1<br>1<br>1      | 2.54<br>2.59<br>2.60<br>2.96<br>3.18<br>3.26<br>3.30<br>3.31<br>3.38 |

Table 23. Bond distances in Ti<sub>2</sub>Se

| Referen <b>ce</b> | Neighbor   | Number of             | Distance (Å)                                 |
|-------------------|--|-----------------------|--|
| Atom              | Atom   | Neighbors             |  |
| Ti(6)             | Se(3)  | 1                     | 2.57   |
|                   | Se(1)  | 2                     | 2.68   |
|                   | Se(2)  | 1                     | 2.81   |
|                   | Ti(3)  | 2                     | 2.85   |
|                   | Ti(3)  | 2                     | 2.94   |
|                   | Ti(5)  | 1                     | 3.30   |
|                   | Ti(1)  | 2                     | 3.35   |
|                   | Ti(2)  | 1                     | 3.40   |
| Se(l)             | Ti(2)  | 2                     | 2.59   |
|                   | Ti(5)  | 2                     | 2.59   |
|                   | Ti(3)  | 1                     | 2.62   |
|                   | Ti(6)  | 2                     | 2.68   |
|                   | Ti(4)  | 1                     | 2.75   |
| Se(2)             | Ti(3)<br>Ti(5)<br>Ti(1)<br>Ti(4)<br>Ti(6)<br>Ti(2) | 2<br>2<br>1<br>1<br>1 | 2.58<br>2.60<br>2.64<br>2.67<br>2.80<br>2.38 |
| Se(3)             | Ti(5)<br>Ti(6)<br>Ti(4)<br>Ti(1)<br>Ti(2)          | 1<br>1<br>2<br>2      | 2.54<br>2.56<br>2.64<br>2.64<br>2.64         |

Table 23 (Continued)

where all the terms have been previously defined. If k, L, p and A\* are assumed to be constant, then I and |F| are the only variables. Therefore, on differentiating Equation 4:

 $dI = 2kLp A * |F| d |F|. \qquad (46)$ If dI is assumed to equal  $\sigma I$  and d|F| is assumed to equal  $\sigma |F|$ , on rearranging terms:

$$\sigma[F] = \sigma I / (2kLp A^* |F|) .$$
(47)

The term oI can be evaluated using the expression:

$$\sigma I = [A+B+(0.05xA)^{2} + (0.05xB)^{2}]^{\frac{1}{2}}$$
(48)

where A and B are the total peak count for a given reflection and the background count for the same reflection. The terms  $(0.05xA)^2$  and  $(0.05xB)^2$  are inserted into Equation 48 to reflect and account for instrumental instability.

The value of the standard deviation of a reflection of unit weight for the refinement of Ti<sub>2</sub>Se using the above weighting scheme was 1.34.

## B. Zr<sub>2</sub>Se

### 1. Structure determination

The Zr<sub>2</sub>Se phase was prepared by the method outlined in sections II,A,B. The final annealing temperature and time were 1550°C and 3 hours.

A Charles G. Supper Co. Weissenberg camera was used to take rotation photographs and hk0 and hk1 Weissenberg layer photographs about the c-axis. The diffraction pattern and extinction conditions again indicated that the centrosymmetric space group is Pnnm. A comparison of the Weissenberg layer photographs of  $Zr_2Se$  with those of  $Ti_2S$ and  $Ti_2Se$  indicated that all three of these phases are isostructural with  $Ta_2P$ . Later, L. J. Norrby (49) used this crystal to refine the structure of  $Zr_2Se$ . He obtained an unweighted reliability index of 10.6% for 438 reflections. The lattice parameters for this phase at 25°C obtained from a Guinier powder photograph using KCl, a=6.29300±0.00009Å (32), as an internal standard and CuK<sub>a</sub>radiation,  $\lambda$ =1.5405Å, are: a=12.640±3Å, b=15.797±3Å, c=3.602±1Å. The hk½ indices,  $\sin^2\theta_{(obs)}$ ,  $\sin^2\theta_{(calc)}$  and estimated relative intensities for  $Zr_2Se$  are listed in Table 24. The calculated density of  $Zr_2Se$  is 7.24 g/cc. The refined atomic and thermal parameters are listed in Table 25.

C. Hf<sub>2</sub>Se

### 1. Structure determination

The Hf<sub>2</sub>Se phase was prepared by the methods outlined in sections II,A and B. The sample was annealed at 1500°C for about 2 hours.

A Charles G. Supper Co. Weissenberg camera was used to take rotation and Weissenberg layer photographs about the a-axis. Reciprocal lattice plots of these layer photographs indicated that the lattice is hexagonal. The following extinction conditions were observed: hkL, no conditions; hhL, no conditions; hhL,L=2n. In addition, the condition that, if h-k=3n, L=2n was observed. These systematic conditions for reflections to be observed indicated that the

| $\begin{array}{c c c c c c c c c c c c c c c c c c c $   |  |  |  |  |
|--|--|--|--|--|
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$  | h k 🕺  | sin <sup>2</sup> 0 <sub>obs</sub> x10 <sup>5</sup>   | $\sin^2_{\theta}$ calc x10 <sup>5</sup>  | I/I <sub>0</sub> × 100   |
| Table 25. Positional and thermal parameters for $2r_2Se$ Atom $10^4x/a$ $10^4y/b$ $Z$ $B(A)^2$ $2r(1)$ $1522\pm5$ $242\pm4$ $0$ $0.52\pm12$ $2r(2)$ $755\pm5$ $2534\pm5$ $0$ $0.64\pm11$ $2r(3)$ $5829\pm5$ $801\pm4$ $0$ $0.20\pm10$ $2r(4)$ $4681\pm5$ $3912\pm4$ $0$ $0.35\pm11$ $2r(5)$ $7988\pm5$ $2028\pm4$ $0$ $0.18\pm11$ $2r(6)$ $8767\pm5$ $4221\pm4$ $0$ $0.23\pm11$ $Se(1)$ $4206\pm5$ $2083\pm4$ $0$ $0.22\pm11$ $Se(2)$ $2447\pm5$ $4191\pm4$ $0$ $0.38\pm12$ $Se(3)$ $ 6306\pm5$ $3476\pm4$ $0$ | 2 1 1 1 2 2 1 2 2 0 1 0 1 1 0 1 2 0 1 0 1  | 6294<br>7016<br>7910<br>8162<br>8563<br>8759<br>8863<br>9289<br>9534<br>9359<br>10232<br>10514<br>11469<br>13083<br>14082<br>15582 | 6299<br>7012<br>7915<br>8152<br>8558<br>8749<br>8868<br>9284<br>9524<br>9854<br>10237<br>10519<br>11469<br>13089<br>14094<br>15587 | 5<br>10<br>30<br>30<br>70<br>15<br>30<br>40<br>100<br>30<br>60<br>50<br>30<br>20<br>15                     |
| Atom $10^4 \text{X/a}$ $10^4 \text{Y/b}$ Z $B(\text{\AA})^2$ Zr(1) $1522\pm5$ $242\pm4$ 0 $0.52\pm12$ Zr(2) $755\pm5$ $2534\pm5$ 0 $0.64\pm11$ Zr(3) $5829\pm5$ $801\pm4$ 0 $0.20\pm10$ Zr(4) $4681\pm5$ $3912\pm4$ 0 $0.35\pm11$ Zr(5) $7988\pm5$ $2028\pm4$ 0 $0.18\pm11$ Zr(6) $8767\pm5$ $4221\pm4$ 0 $0.23\pm11$ Se(1) $4206\pm5$ $2083\pm4$ 0 $0.22\pm11$ Se(2) $2447\pm5$ $4191\pm4$ 0 $0.38\pm12$ Se(3) $-6306\pm5$ $3476\pm4$ 0 $9.13\pm11$   | Table 25.  | Positional and   | thermal parameters   | for Zr <sub>2</sub> Se   |
| $Zr(1)$ $1522\pm5$ $242\pm4$ $0$ $0.52\pm12$ $Zr(2)$ $755\pm5$ $2534\pm5$ $0$ $0.64\pm11$ $Zr(3)$ $5829\pm5$ $801\pm4$ $0$ $0.20\pm10$ $Zr(4)$ $4681\pm5$ $3912\pm4$ $0$ $0.35\pm11$ $Zr(5)$ $7988\pm5$ $2028\pm4$ $0$ $0.18\pm11$ $Zr(6)$ $8767\pm5$ $4221\pm4$ $0$ $0.23\pm11$ $Se(1)$ $4206\pm5$ $2083\pm4$ $0$ $0.22\pm11$ $Se(2)$ $2447\pm5$ $4191\pm4$ $0$ $0.38\pm12$ $Se(3)$ $6806\pm5$ $3476\pm4$ $0$ $0.13\pm11$   | Atom   | 10 <sup>4</sup> x/a  | l0 <sup>4</sup> Y/b Z  | B(Å) <sup>2</sup>  |
|  | Zr (1)<br>Zr (2)<br>Zr (3)<br>Zr (3)<br>Zr (5)<br>Zr (5)<br>Zr (6)<br>Se (1)<br>Se (2)<br>Se (3) | 1522+5<br>755+5<br>5829+5<br>4681+5<br>7988+5<br>8767+5<br>4206+5<br>2447+5<br>6306+5  | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$  | 0.52÷12<br>0.64+11<br>0.20+10<br>0.35+11<br>0.18+11<br>0.23+11<br>0.22+11<br>0.38+12<br>0.38+12<br>0.13+11 |

Table 24. X-ray diffraction data for  $2r_2Se$ ,  $\lambda=1.5405 Å$ 

centrosymmetric space group is P6,/mmc.

The lattice parameters for this phase were obtained at 25°C from a Guinier photograph using KCl, a=6.29300 $\pm$ 0.00009Å, (32) as an internal standard and CuK radiation,  $\lambda$ =1.5405Å. These parameters are: a=3.4502 $\pm$ 9Å, c=12.640 $\pm$ 3Å.

The hkl indices,  $\sin^2\theta_{(obs)}$ ,  $\sin^2\theta_{(calc)}$  and the estimated relative intensities from a Guinier photograph are listed in Table 26.

A comparison of the Weissenberg layer photographs and Guinier photographs for  $Hf_2S$  and  $Hf_2Se$  indicated that  $Hf_2Se$  is isostructural with  $Hf_2S$  (31). The calculated density of  $Hf_2Se$  is 11.45 g/cc.

It was found that the  $Hf_2Se$  phase had to be kept under vacuum or in an inert atmosphere to avoid reaction of the phase with air. Neither  $Ti_2Se$  nor  $Zr_2Se$  exhibited this tendency to react with air.

| h k 🙎 | sin <sup>2</sup> 8 (obs) x10 <sup>5</sup> | $\sin^2\theta_{(calc)} \times 10^5$ | I/I <sub>o</sub> x100 |
|-------|---|-------------------------------------|-----------------------|
| 0 0 2 | 1582                                      | 1580                                | 1                     |
| 0 0 4 | 6320                                      | 6316                                | 10                    |
| 1 0 1 | 6651                                      | 6647                                | 20                    |
| 1 0 2 | 7043                                      | 7039                                | 20                    |
| 1 0 3 | 3238                                      | 8224                                | 70                    |
| 1 0 4 | 10211                                     | 10200                               | 100                   |
| 0 1   | 12948                                     | 12960                               | 75                    |
| 0 1   | 14203                                     | 14209                               | 15                    |
| 0 1   | 19916                                     | 19937                               | 50                    |

Table 26. X-ray diffraction data for  $Hf_{2}Se$ ,  $\lambda=1.5405Å$ 

VI. DISCUSSION OF POSSIBLE ERRORS INVOLVED IN THE CALCULATION OF THE MAGNITUDE OF UNITARY STRUCTURE FACTORS BY THE GRAPHICAL METHOD AS USED IN THE DETERMINATION OF THE STRUCTURES OF Ta<sub>2</sub>S and Ta<sub>6</sub>S A. The Structure of Ta<sub>2</sub>S

Figure 6 is a graph of the calculated  $\phi$  values for Ta<sub>2</sub>S (determined on the basis of 12 Ta<sub>2</sub>S units per unit cell) vs. sin<sup>2</sup>. The interpolated  $\phi$  values obtained from this graph are, on the average, 7.6% greater than those calculated using the graph in Figure 2 for which the  $\phi$  values were calculated on the basis of 14 Ta<sub>2</sub>S units per unit cell.

Figures 7 and 8 contain the interpolated curves of the calculated  $\diamond$  versus sint for Ta<sub>2</sub>S (with 12 Ta<sub>2</sub>S units per unit cell) as the solid line with the individual observed values plotted for unitary structure factors having magnitude greater than or equal to 0.40 and 0.30, respectively.

In Figure 7, the dotted lines drawn on either side of the solid line represent the boundaries within which observed values occur, except for two points one above the upper dotted line and one below the lower dotted line. The lower dotted line represents the boundary of values about 10% low on the basis of the theoretical curve. The upper dotted line represents the boundary of values about 60% greater than would be expected from the theoretical  $\phi$  curve. The point,

Figure 6. Interpolated curve of calculated phi values for Ta<sub>2</sub>S (determined on the basis of 12 Ta<sub>2</sub>S units per unit cell) vs. sin0

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Figure 7. Interpolated curve of the calculated phi values for Ta<sub>2</sub>S (determined on the basis of 12 Ta<sub>2</sub>S units per unit cell) vs. sin0 as the solid line. Points represent unitary structure factors with magnitudes greater than 0.40. Upper and lower dotted lines represent the boundaries of the region about the calculated phi curve in which all the observed unitary structure factors, except for two points, with magnitudes greater than 0.40 lie

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Figure 8. Interpolated curve of calculated phi values for Ta<sub>2</sub>S (determined on the basis of 12 Ta<sub>2</sub>S units per unit cell) vs. sin0 as the solid line. Points represent unitary structure factors with magnitudes greater than 0.30


representing the 0,6,0 reflection, in Figure 7 below the lower dotted line exhibits a value for the magnitude of its unitary structure factor about 22% lower than the value which would be calculated on the basis of the solid curve. The behavior of this reflection with respect to calculated and observed values for the magnitude of its unitary structure factor points out a source of difficulty in the method used to make sign assignments in this research. Explicitly, if a reflection were determined by the method previously discussed to have a unitary structure factor of sufficient magnitude (say  $\geq$  0.4) and if, in fact, the true value of the magnitude of the unitary structure factor were 22% lower, then the use of the triple product relations to assign a sign to this reflection could lead to erroneous results. This follows from the fact that the triple-product relations are strictly valid as equalities only if the magnitudes of the unitary structure factors for the three reflections are sufficiently large.

# B. The Structure of Ta<sub>6</sub>S

Figures 9 and 10 are plots of the interpolated curves of the calculated  $\phi_c$  values for Ta<sub>6</sub>S listed in Table 17 versus sin0 as solid lines with the plotted values of  $\phi_c$ at the appropriate sin0 value for reflections having unitary structure factors greater than 0.40 and 0.30, respectively.

# Figure 9. Interpolated curve of phi, $\phi_c$ , values for Ta<sub>6</sub>S vs. sint as the solid line. Points represent unitary structure factors with magnitudes greater than 0.40. Upper and lower dotted lines represent the boundaries

lower dotted lines represent the boundaries of the region about the calculated phi curve in which all the observed unitary structure factors with magnitudes greater than 0.40 lie



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Figure 10. Interpolated curve of the calculated phi,  $\phi_c$ , values for Ta<sub>6</sub>S vs. sint as the solid line. Points represent unitary structure factors with magnitudes greater than 0.30



In Figure 9, the dotted lines drawn on either side of the solid line represent the boundaries within which all the observed  $\phi_c$  values occur. The lower dotted line lies approximately 120 below the solid line while the upper dotted line lies approximately 190 higher than the solid line.

# C. Comparison of the Calculated $\phi$ Versus Sin9 Curves for Ta $_2S$ and Ta $_6S$ with Respect to the Calculation of Unitary Structure Factors

The graph of the calculated  $\phi$  values versus sind is better characterized for the structure of Ta<sub>6</sub>S, Figure 9, than for the structure of Ta<sub>2</sub>S, Figure 7. This difference is probably in large part due to the fact that only about 350 "observed" reflections were used in the case of the Ta<sub>2</sub>S structure to characterize the curve from sin $\theta$ =0.0 to sin $\theta$ =0.90 while for the Ta<sub>6</sub>S structure there were about 670 "observed" reflections used to characterize the curve from sin $\theta$ =0.0 to sin $\theta$ =0.50.

The low sing regions of the graphs, Figures 7 and 9, for  $Ta_2S$  and  $Ta_6S$  respectively, are poorly characterized in comparison to the remainder of the sing regions. In  $Ta_2S$ , the graph in Figure 7 is undefined in the region below sing=0.35 whereas for  $Ta_6S$  the graph is undefined below sing=0.15. Accordingly, use of these graphs to calculate magnitudes for unitary structure factors in the poorly characterized regions of the graph could be expected to yield dubious values for the calculated magnitudes of these unitary structure factors. Also, in the case of the Cu data for the Ta<sub>2</sub>S structure, intensity data were only taken for Bragg reflections for which  $2\theta \le 160^\circ$  or  $\sin\theta \le 0.985$ . Therefore, the set of intensity data for the  $\sin\theta$  range:  $0.90 < \sin\theta \le 1.0$  is incomplete, and it can be expected that the region of the curve of calculated  $\phi$  values versus  $\sin\theta$  above  $\sin\theta = 0.85$  is not as well characterized as it would have been if the data for the region of  $1.0 \ge \sin\theta > 0.985$  had been obtained and utilized.

In future structural determinations involving the graphical method of calculating the magnitude of unitary structure factors, the initial set of reflections which are given signs in order to fix the origin of the unit cell, should be selected from the well characterized region of the calculated versus sin0 curve.

#### D. Analysis of the Assumption of a Gaussian Distribution of Unitary Structure Factors

Assuming a Gaussian distribution of unitary scattering factors, Wilson (50) has shown for a centrosymmetric structure that the probability of a unitary structure having a value between U and U + dU is given by

$$P(U) dU = (2\pi\epsilon)^{-\frac{1}{2}} \exp(-U^2/2\epsilon) dU, \qquad (49)$$

in which:

$$\varepsilon = (\overline{\upsilon^2}). \tag{50}$$

From tables of the probability integral (51), it is seen that 10% of the area of a normal distribution will be beyond the values of  $\pm 1.6\sqrt{\epsilon}$ . Woolfson (38) claims that structures that have 10% or more of the U's with magnitudes greater than 0.40 will be solvable by inequalities. Thus according to the above:

$$1.6\sqrt{\varepsilon} = 0.40 \text{ or} \tag{51}$$

$$\varepsilon = 0.0625$$
 . (52)

This value of  $\varepsilon$  sets an approximate upper limit to the complexity of a structure which might be solved by an inequalities treatment. The value of  $\varepsilon$  is 0.0361 for Ta<sub>2</sub>S and 0.0398 for the primitive cell associated with Ta<sub>6</sub>S. Both of these values are substantially lower than the value suggested as the lower limit by Woolfson for solving a structure by an inequalities approach.

Woolfson (38) states that structures having a value of  $\varepsilon$ less than 0.0625 may have high structural, if not crystallographic, symmetry and abnormal U distributions and still be solvable by an inequalities treatment. The graphs in Figures 11 and 12 are plots of U versus the number of U

Figure 11. An interpolated curve of the number of unitary structure factors between U and U+dU for  $\text{Tra}_2^S$  for Bragg reflections  $0^{\circ} < 20 \le 160^{\circ}$  (Cu data)

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Figure 12. An interpolated curve of the number of unitary structure factors between 0 and 04d0 for  $\text{Ta}_6S$  (centered cell) for Bragg reflections  $0^\circ < 20 \le 60^\circ$ 

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values in a given range of  $U \pm 0.025$  for  $Ta_2S$  and  $Ta_6S$ , respectively. In the  $Ta_2S$  and  $Ta_6S$  structures, only 5.5% and 3%, respectively, of the unitary structure factors exhibit magnitudes greater than or equal to 0.40.

# VII. DESCRIPTION OF THE STRUCTURES REPORTED IN

### THIS RESEARCH

## A. Ta<sub>2</sub>S and Ta<sub>6</sub>S

The Ta atoms in both  $Ta_2S$  and  $Ta_6S$  structures are all contained in chains of slightly distorted body-centered pentagonal antiprisms sharing faces. These chains run parallel to the b-direction in both structures. In  $Ta_2S$ , the average Ta-Ta distance from the central Ta atom to the Ta atoms forming the pentagonal antiprisms is 2.91Å, in  $Ta_6S$  this distance is slightly larger, 2.93Å. In  $Ta_2S$ , the distance from a central Ta atom to the next such atom is 2.79Å while in  $Ta_6S$ this distance is 2.64Å, a remarkably short Ta-Ta distance. Thus in both structures each central Ta atom is surrounded by 12 Ta atoms in a slightly distorted icosahedron in which each central Ta atom is also an apical Ta atom in the next icosahedron in the chain. The average Ta-Ta distance on the face of the antiprism is 3.14Å in  $Ta_2S$  and 3.09Å in  $Ta_6S$ .

The coordination about the sulfur atoms is totally different in the two phases.

In Ta<sub>2</sub>S, the two sulfur atoms serve structurally different roles. The first type, S(1), is bonded to six Ta atoms forming the faces of two of the antiprisms with an average Ta-S distance of 2.56Å. The coordination polyhedron about S(1) can be described as a distorted octahedron. This is the

only known metal-rich chalconide structure ( $M_{n}C$  and M and C are the metal and chalcogen, respectively, and  $n\geq 2.00$ ) in which a chalcogen is found in a coordination polyhedron which cannot possibly be considered as distorted trigonal prismatic. The second type of sulfur atom, S(2), is bonded to three Ta atoms forming the face of one antiprism in one column of Ta atoms and to a Ta atom at the corner of an antiprism in another column. The average Ta-S(2) distance is 2.47Å. The coordination polyhedron about S(2) can be described as fragment of a trigonal prism with two atoms from one of the triangular faces of the prism missing. The average Ta-S(2) distance in Ta<sub>2</sub>S is 2.53Å.

The arrangement of S atoms in  $Ta_2S$  leads to a very striking structural feature of this phase. The sulfur atoms are localized in regions of the unit cell in such a manner as to describe an octahedral configuration without an atom located in the interior of the octahedron. The octahedra run parallel to the b-axis through the structure resulting in an empty channel. The dimensions of the octahedron, and in effect the dimensions of the channel, are 5.40Å from S(1) to S(1), 4.20Å from S(2) to S(2) diagonally, and 3.09Å and 2.86Å for the two S(1)-S(2) distances. These distances are from the center of one atom to the center of the next atom. The diagonal S(2)-S(2) distance effectively represents the width of the channel. If the radii of the

sulfur atoms comprising this distance are subtracted, using the Slater radius (46) of the sulfur atom  $(1.00\text{\AA})$ , the net width of the channel is  $2.20\text{\AA}$ .

In  $Ta_6S$  the chains of Ta antiprisms are bridged in the a- and c-directions by sulfur atoms. The sulfur atoms are bonded to seven Ta atoms from three chains of antiprisms. Two chains each supply two Ta atoms to the arrangement, and the third chain supplies three Ta atoms. The average Ta-S distance, 2.49Å, in  $Ta_6S$  is slightly closer to the sum of the Slater (46) radii (2.45Å) for Ta and S than is the average Ta-S distance in  $Ta_2S$ , 2.53Å. The shortest distance between sulfur atoms is 3.93Å in  $Ta_6S$  while in  $Ta_2S$  the shortest distance between sulfur atoms is 2.86Å. The structure of  $Ta_6S$  lacks the large channel present in the  $Ta_2S$  structure.

The coordination polyhedron around the sulfur in  $Ta_6S$  can be described from two different points of view although each describes a distorted capped trigonal prism. From the first viewpoint indicated in Figure 13, six of the Ta atoms describe a distorted trigonal prism with an average Ta-S distance of 2.48Å. The seventh Ta atom, Ta(2), is off one of the rectangular faces at a distance of 2.53Å. This trigonal prismatic coordination about the sulfur atom in  $Ta_6S$  is similar to that about the sulfur atom in  $\alpha$ -V<sub>3</sub>S (19) except that there is an additional atom off another rectangular

Figure 13. Coordination polyhedron about the sulfur atom in  ${\rm Ta}_6{\rm S}$  . View I



8TT

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face in  $\alpha$ -V<sub>3</sub>S. From this viewpoint, the sulfur coordination polyhedron in both structures are distorted in a similar fashion, namely, two short edges of the ideal trigonal prism are slightly rotated relative to each other such that they remain at least approximately perpendicular to the three-fold axis of the ideal prism.

From the second point of view, shown in Figure 14, six of the Ta atoms describe a trigonal prism with an average Ta-S distance of 2.49Å with the seventh Ta atom, Ta(3), at a distance of 2.53Å off one of the rectangular faces. The trigonal prism described from this point of view is less distorted than the one described previously.

In the Ta<sub>2</sub>S and Ta<sub>6</sub>S structures there is a metal atom in a unique environment for a metal atom in the metal-rich chalconide and pnictide structures. The metal atom in the center of the pentagonal antiprism is too far away from the nearest sulfur atom to be considered to be bonded to it. This Ta-S distance is  $3.74\text{\AA}$  and  $3.97\text{\AA}$  in Ta<sub>2</sub>S and Ta<sub>6</sub>S, respectively.

B. The Group IVB Dimetal Selenides

1. Ti2Se and Zr2Se

The  $\text{Ti}_2\text{Se}$  and  $\text{Zr}_2\text{Se}$  (49) phases are isostructural with  $\text{Ti}_2\text{S}$  (20) and  $\text{Zr}_2\text{S}$  (52) all of which exhibit the  $\text{Ta}_2\text{P}$  structure type.

Figure 14. Coordination polyhedron about the sulfur atom in  ${\rm Ta}_6{\rm S}.$  View II



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Each Se atom in both  $\text{Ti}_2\text{Se}$  and  $\text{Zr}_2\text{Se}$  is found in an augmented trigonal prismatic environment with between one and three augmenting metal atoms off the rectangular faces of a slightly distorted trigonal prism. There are no close Se-Se distances in either  $\text{Ti}_2\text{Se}$  or  $\text{Zr}_2\text{Se}$ . The shortest Se-Se distance is 3.48Å in  $\text{Ti}_2\text{Se}$  and 3.61 in  $\text{Zr}_2\text{Se}$ .

2. Hf<sub>2</sub>Se

 ${\rm Hf}_2{\rm Se}$  is isostructural with  ${\rm Hf}_2{\rm S}$  (28). The chalcogen atoms in both the  ${\rm Hf}_2{\rm S}$  and  ${\rm Hf}_2{\rm Se}$  structures are in trigonal prismatic environments while the hafnium atoms in each structure are in a distorted octahedral environment of three hafnium atoms and three chalcogen atoms.

# VIII. MAGNETIC PROPERTIES OF Ta2S and Ta5S

As a result of the uncommon structural characteristics of the TapS and TapS structures as compared with other known metal-rich chalconide and pnictide phases, i.e., the segregation of metal and non-metal atoms intr different regions of the unit cell in both structures, the columns of metal atoms in both structures, and the empty channel in the Ta<sub>2</sub>S structure, it was decided that it would be worthwhile to measure the magnetic susceptibilities of Ta2S and Ta2S. A Faraday balance constructed by Professor R. E. McCarley and co-workers (53) was used to measure the magnetic susceptibilities of the Ta<sub>2</sub>S and Ta<sub>2</sub>S phases from room temperature, approximately 25°C, down to the temperature of liquid nitrogen, 77°K. The samples of these phases were the same ones used to measure the densities of the respective phases. The magnetic susceptibilities were calculated by a least squares Honda-Owen treatment of the data using a computer program written by J. Greiner.<sup>1</sup> The magnetic susceptibilities of both Ta2S and Ta2S are temperature independent paramagnetic from 77°K to 298°K and have values of

<sup>&</sup>lt;sup>1</sup>Greiner, J., Department of Metallurgy. Iowa State University of Science and Technology, Ames, Iowa. Magnetic Susceptibilities Program. Private communication. 1969.

73.12( $\pm$ 5.32) x 10<sup>-6</sup> cc/g-atom and 427.1( $\pm$ 9.6) x 10<sup>-6</sup> cc/g-atom, respectively.

The amount of ferromagnetic impurity present in the samples was also determined by the Honda-Owen treatment of the data. Assuming iron to be the only ferromagnetic constitutent present in the samples measured, the maximum of iron concentration present was approximately 3 ppm.

## IX. DISCUSSION

#### A. Introduction

A number of points concerning the nature of the chemical bonding in transition metal chalconides are raised by the structures reported here. In order to discuss the bonding in  $Ta_2S$  and  $Ta_6S$ , and the interrelation between these compounds and other metal-rich chalconides, a general discussion of the bonding in chalconides will be presented. This discussion will include consideration of general bonding schemes advanced by Pauling, Rundle, Slater, the applications of these schemes to transition metal chalconides by Franzen and an application of the Brewer-Engel correlation to the consideration of metal coordination polyhedra in metal-rich chalconides.

### B. General Bonding Considerations

Since band theories of the solid state have not progressed sufficiently to allow treatment of structures and bonding from this point of view, more qualitative discussions are usually given. Such discussions of the bonding in the condensed state are essentially concerned with accounting for the characteristics of the free atoms which lead to interactions between atoms to stabilize a given structure.

A description of bonding in the metal-rich chalconide

phases must account for the physical properties observed in these phases: the metallic luster, the relatively high electrical conductivity and a very high degree of brittleness.

Metals are generally characterized as exhibiting a high luster, high thermal and electrical conductivities, high malleability and high ductility. Although these properties vary from metal to metal, they are not generally found for non-metals which are characterized by low luster, low thermal and electrical conductivities, low malleability and low ductility. The metal-rich chalconide phases discussed in this thesis possess properties of both metals and non-metals, a fact which must be accounted for in a bonding description.

Metals can be thought of as having more orbitals available for bonding than valence electron pairs. The high electrical conductivity and high thermal conductivity derive from the ability of valence electrons to move more or less freely, subject to certain core potentials, through the metal lattice. The high malleability and high ductility of metals arise from the fact that if one or more bonds between atoms are broken by mechanical work done on the metal, due to the large surplus of available orbitals suitable for bonding, other orbitals become involved in bonding and new

bonds are formed.

The non-metals, on the other hand, do not possess a surplus of orbitals available for bonding in comparison to the number of valence electron pairs present. In fact, in non-metals the valence band is filled, consequently electrons in the non-metal structures are not free to move through the lattice, as is the case in the metal lattice, and accordingly the electrical conductivity and thermal conductivity of non-metals are significantly lower than they are for metals. Due to the lack of surplus orbitals to form suitable alternate bonds, when bonds are ruptured due to mechanical work done on the non-metallic materials, the substance will fracture under stress, resulting in low malleability and low ductility.

Three approaches have been proposed to describe the bonding in the inter-metallic and metal-rich composition range of metal-non-metal systems. The first way of viewing these structures is as the insertion of non-metal atoms into available interstices in the metal lattice (54, 55, 56, 57). Accordingly atoms are viewed as inert spheres occupying a certain volume, and structures are considered to be stabilized primarily by a high packing efficiency with regard to the insertion of an atom into an interstice of a particular size. In the second description, structures are considered in terms of arrangements of cations and anions which

form stable structures by a minimization of energies due to coulombic interactions. The third approach to bonding considers structures to be composed of atoms sharing electrons covalently.

With respect to the consideration of structures as interstitial compounds, i.e., the non-metal simply occupies available vacancies in the metal lattice, there is a minimum consideration given to atomic orbitals, their respective symmetry or availability from energy or spatial considerations except in so far as any of these factors may influence the value of the atomic radius. In this approach an important factor in bonding is the minimization of void spaces in the unit cell. From the interstitial viewpoint, the high electrical conductivity of metal-non-metal systems is due to an essentially undisturbed metal lattice in which inert spheres (non-metal atoms) are placed. The continuously variable compositions exhibited by metallic interstitial compounds are considered to be merely the result of the ease of insertion or withdrawal of the "inert" non-metal atoms from the host metal lattice.

Arguments could be made for describing the structure of the phases with the  $Ta_2P$  structure type, <u>i.e.</u>,  $Ti_2S$ ,  $Ti_2Se$ ,  $Zr_2S$ ,  $Zr_2Se$ ,  $Hf_2P$  (58),  $Hf_2As$  (59), in this manner, however the structures of the closely related compounds  $Ta_2S$  and  $Ta_6S$  suggest that factors other than packing are

important in determining the structures of the metal-rich compounds. Consider, for example, the fact that  $Ta_2P$  and  $Ta_2S$  exhibit such radically different structures in spite of having very nearly equal radius ratios. Since there is no reason to consider  $Ta_2S$  and  $Ta_6S$  to be radically different from other metal-rich chalconides, it must be concluded that this approach is not entirely sufficient to explain the occurrence of metal-rich chalconide structures.

The second approach to a bonding description based on an ionic description does not seem appropriate when applied to metal-rich chalconide structures because of the very large number of short metal-metal contacts. If all of the metal atoms were positively charged, a very large destabilizing potential energy would result, making the metalrich phases unstable with respect to the elemental metal and phases with structures having far fewer short metalmetal distances. On the basis of the electrostatic or ionic model of structures and structural models consistent with this basis, Moody and Thomas (60), using an equation by Kapustinskii to calculate lattice energies, computed values of 1H2 for Ti2S of 144-123 kcal/mole and for Ti2Se of 182-162 kcal/mole. Accordingly, Ti<sub>2</sub>S and Ti<sub>2</sub>Se would exhibit a great tendency toward disproportionation to either TiC(s) + Ti(s) or 2 Ti(s) + C(s) where C is S or Se. However it is important to note that Moody and Thomas acknowledge that

a structure with pronounced covalent character could exist even though the calculated  $\Delta H_{\tilde{I}}^{\circ}$  using Kapustinskii's equation for lattice energies is a relatively large positive value.

Pauling (61) proposed a covalent description of the bonding in metallic and intermetallic compounds which was recently critically discussed by Rundle (62). From this point of view, bonding between atoms in metallic and intermetallic compounds is fractional in character, <u>i.e.</u>, the bonds are not two electron bonds between atoms. The electrons in these fractional bonds are thought to be delocalized throughout the entire structure in a conduction band. The general physical properties of metals, <u>i.e.</u>, high malleability and high electron conductivity, derive from the fractional bonds and delocalized electrons. Pauling proposed an empirical relation:

 $D(n) = D(1) - 0.600 \log n$  (50)

where the bond distance, D, is related to its order, n, which can be used to calculate both the order of a given bond and valences for the various atoms in the structure.

In 1948, Rundle (62) pointed out that metallic carbides, oxides and nitrides with the NaCl structure formed this structure irrespective of the structure or radius of the metal: all the monoxides and all the reliably known monocarbides and mononitrides of the third, fourth and fifth

group metals possess the NaCl structure whereas only Sc, La, Ce and Th exhibit a cubic closest packed structure (63). In view of this tendency to form the NaCl structure type, according to Rundle, some effect, other than mere insertion of the non-metal into the metal lattice, must be occurring to cause the rearrangement of metal atoms to form the octahedral "interstices" for the non-metal atoms.

Rundle reasoned that any theory attempting to account for bonding in the MX phases must account for:

- preferential formation of the NaCl structure in MX compounds, irrespective of the metal lattice;
- 2. high melting points of the MX phases despite an increase in metal-metal distances in the MX phases as compared with those found in the metal;
- 3. the brittle character of the MX phases as compared with the malleability of pure metal;
- the relatively high electrical conductivity of the MX phases.

Using the valence bond approach of Pauling, Rundle deduced that these physical properties could be explained in terms of the non-metal atoms using either three <u>p</u> orbitals or an sp hybrid and two <u>p</u> orbitals. For example, according to this bonding there are, for the TiO phase with the NaCl structure type, a total of 6 or 8 bonding electrons, depending on whether or not the two <u>s</u> valence electrons of 0 were involved in bonding, per TiO unit. These electrons are involved in the formation of six  $\sigma$  bonds. In other words there would be six bonds of order 1/2 or 2/3 between the metal and non-metal atoms in the TiO structure.

The resulting octahedral coordination of metal atoms about non-metal atoms, and vice-versa, accounts for the NaCl structure observed in these phases. The brittleness found in the MX phases derives, according to Rundle's arguments, from the directional nature of the covalent bonds. The high electrical conductivity is due to the fact that the bonding orbitals in these phases do not contain two electrons each, allowing for a delocalization of electrons throughout the structure. The very high melting points observed for the MX phases are a result of the strengthening of the MX structure relative to the metal by the formation of strong metal-non-metal bonds.

In broad outline, Rundle, using the Pauling valence bond approach and delocalized electrons, explained many of the physical properties of MX phases from the viewpoint of covalently interacting atoms. However, Rundle did not consider the fact that many of these transition metal monoxides, monocarbides and mononitrides exhibit significant vacancy concentrations for example, as high as 15% vacancies are observed for both Ti and 0 sites in stoichiometric Ti0<sub>1.00</sub> (64). Denker

(54) has recently accounted for this propensity as a result of a tendency of a given MX phase to depopulate antibonding states with consequent stabilization of the NaCl structure. Denker postulates that for MX phases with the NaCl structure the metal atom uses  $d^2sp^3$  hybrid orbitals and the nonmetal atom uses its valence <u>p</u> orbitals and an <u>sp</u> hybrid to bond together by means of both  $\sigma$  and  $\pi$  bonding molecular orbitals for an MX<sub>6</sub> octahedral configuration.

Slater (46) has discussed the suitability of a covalent bonding description for compounds which have classically been considered ionic in nature. As an example, he has considered KCl and adequately described both the interatomic distances between atoms in terms of atomic radii and the coordination symmetry about the component atoms in this compound. Slater further suggests that the covalent effects are the dominant factor in determining interatomic distances in compounds, even in "typically ionic" ones such as KCl.

Franzen (65) has described the tendency of sulfur, selenium and tellurium to be found in a trigonal prismatic environment in transition metal monochalconides under certain conditions. The conditions are on the metal associated with the chalcogen, namely, that, first of all the metal possess enough valence electrons to donate four electrons to six bonds and secondly the metal possess six empty valence orbitals to be used in bonding to non-metals. The initial

condition was derived from the fact that the application of Pauling's empirical equation (Equation 50) to representative structures of monochalconides in which the chalcogen is in a trigonal prism yielded calculated valences of the metal atoms which were approximately four. This criterion rules out finding a transition metal monochalconide in which the chalcogen is in a trigonal prism for those transition metals having less than four valence electrons, such as in the case for Group IIA metals, Sc, Y, La, the rare earths and the actinides. The second condition rules out metals in Groups IB and IIB, i.e., Cu, Ag, Au and Zn, Cd, Hg, respectively, since these metals will not have six free valence orbitals for bonding to the chalcogen. The use of Pauling's empirical relation (Equation 50) to determine the valence of the chalcogen in transition metal monochalconides has yielded values between 3 and 4. Consequently, if these values are to be believed, the chalcogen must employ outer orbitals resulting in delocalized electron bonding. The outer orbitals involved might either be d orbitals or the next valence level s orbital. However the use of d orbitals seems to be indicated since these d orbitals, unlike the s orbital, have directional properties associated with them.

Group theory calculations based on an ideal trigonal prism having D<sub>3h</sub> symmetry indicate that possible hybrid orbital configurations <u>utilizing six orbitals</u> would involve

either three d orbitals and three p orbitals or one s orbital, three p orbitals and two d orbitals. The chalcogen involved in bonding to metal atoms coordinated about it in a trigonal prism could use, in the formation of six bonds, four of its valence electrons and four electrons from the six metal atoms to make six bonds of order 2/3. Another possible hybrid orbital configuration for the chalcogen bonded to six metals atoms in a trigonal prismatic coordination symmetry would involve one s and two p orbitals. The metal atoms comprising the trigonal prism would then conceptually  $\pi$  bond to the hybrid sp<sup>2</sup> chalcogen orbitals, however the difficulty with this bonding proposal is that for a calculated valence of 3 these bonds would contain two electrons each. The electrons in these bonds would not be delocalized and so would not contribute to electrical conduction. Also, the amount of metal-metal bonding to electrically conducting compounds such as HfS is relatively low [Pauling bond order of 0.15 (Equation 50) for a Hf-Hf bond in HfS] indicating that electrical conduction does not primarily occur as a result of metal-metal bonding. This, and similar results for other monochalconides, suggests that the description of bonding involving sp<sup>2</sup> hybrids by the chalcogen is incapable of explaining the high electrical conductivity in the transition metal monochalconides. The inability to explain bonding in transition metal monochalconides

in terms of delocalized electrons by using the  $\underline{sp}^2$  hybrid orbitals by the chalcogen seems to indicate that outer orbitals on the chalcogen are involved in bonding.

Transition metal monosulfides are also found to exhibit the NaCl structure type, e.g., ScS (66), US (67),  $\alpha$ -MnS (68). Franzen has pointed out, for example, that the bonding in  $\alpha$ -MnS, with six Mn-S distances of 2.61Å, corresponding to a bond order of 0.23 according to Pauling's empirical relation (Equation 50), can be understood in terms of sulfur using its three <u>p</u> orbitals to bond to Mn and that these six bonds contain four electrons: two from sulfur and two from Mn. This explanation is totally analogous to that described by Rundle for the transition metal monoxides, mononitrides and monocarbides with the NaCl structure type.

With the chalcogen atom either trigonal prismatically or octahedrally coordinated by metal atoms, the bonding according to this viewpoint would involve delocalized electrons in directional bonds, thereby accounting for the same physical properties observed in these phases which Rundle observed in the MX compounds with the NaCl structure.

A question, which must be answered in conjunction with the postulate that the chalcogen atom in the transition metal monochalconide structures has access to outer orbitals, in particular the empty d orbitals, is whether or not the empty outer orbitals are accessible from the viewpoint of the amount
of energy required to excite an electron into such an orbital as compared with the amount of energy returned on bond formation.

Recent work by Webster (69) and by Coulson and Gianturco (70), using Hartree-Pock SCF calculations, determined that for sulfur the lowest valence state involving <u>d</u> orbitals, namely the  ${}^{5}D(\underline{s^2p^3d^1})$  state, lies 166.20 kcal/mole and 167.58 kcal/mole, respectively, above the ground state,  ${}^{3}P(\underline{s^2p^4})$ . Moore (71) reports on the basis of spectroscopic data that the energy from the ground state to the  ${}^{5}D(\underline{s^2p^3d^1})$  state for sulfur is 193.93 kcal/mole.

In determining energetically whether or not sulfur can use its 3<u>d</u> orbitals in bonding, a fruitful comparison can be made by taking a look at this same situation with respect to carbon. The ground state for the carbon atom is the  $\frac{s^2w^2}{s}$  state, consequently due to the pairing of the <u>s</u> electrons in this configuration carbon would be expected to exhibit a normal valence of 2. This valence is certainly not the normal valence for carbon which generally forms four bonds directed toward the corners of a tetrahedron. Moore (71) lists the excitation energy in going from the  $\frac{s^2w^2}{s}$  ground state to the energetically lowest configuration of the <u>sw</u><sup>3</sup> valence state, namely the <sup>5</sup>S, as 95.38 kcal/mole.

This promotion energy for carbon to the lowest valence

 $sp^3$  state is approximately one half that for sulfur to the lowest  $s^2p^3d^1$  valence state, consequently it is meaningful to ask what effects can be expected to return energy as a result of bonding in the condensed state to offset the rather high promotion energy to the  $s^2p^3d^1$  state for sulfur. Two effects which will return energy in the condensed state, and accordingly tend to offset the high promotion energy, are crystal field splitting and delocalization energy. A rather naive assumption has been made in assuming that the energy required to form a given valence state is the same irrespective of whether the atom is in the gas or solid states. This assumption essentially implies that the various electronic states of an atom are effectively unperturbed due to interactions with electronic configurations of neighboring atoms in the condensed state.

Crystal field theory (72) states that under the influence of an electrostatic field of a certain geometry the <u>d</u> orbitals of a given atom in that field will have their degeneracy removed with respect to energy: some of the orbitals will be raised, some will be lowered and some will remain effectively the same with respect to the energy of the orbitals in the isolated atom. Various geometries about a central atom will split the degeneracy of the <u>d</u> orbitals in their own particular manner. In the case of a chalcogen atom in a trigonal prismatic environment, one of the d orbitals is dropped in energy in comparison to the other four d orbitals (73). In the case of an octahedral symmetry three of the d orbitals have their energies lowered with respect to the other two d orbitals. The metal atoms can also be expected to have the degeneracy of the <u>d</u> orbitals split with respect to the energy levels of the isolated This splitting of the d orbitals to remove their atom. degeneracy will result in the subsequent lowering of the energies of certain orbitals. Figgis (74) lists values of the electrostatic splitting of the energy levels for the first row transition metal oxides, sulfides, selenides and tellurides from Ti to Cu calculated on the basis of an electrostatic model for MX compounds consisting of M<sup>+2</sup> cations and  $x^{-2}$  anions. The average crystal field splitting for these MX compounds is 59 kcal/mole with extreme values of 114 kcal/mole as a high and 29 kcal/mole as a low value. Orgel (72) lists spectroscopically determined crystal field splittings for transition metal complexes the average of which is 54 kcal/mole with high and low values of 97 kcal/ mole and 10 kcal/mole, respectively. Although the ionic model was rejected earlier as an explanation of bonding in metal-chalcogen systems, the consideration of crystal field splittings for various solids might be useful as an indication of the approximate energy involved in this effect. Both the calculated crystal field splitting energies of

Figgis and the observed ones of Orgel suggest that crystal field splitting energies are not trivial and can well be expected to be effective in lowering the energy of the  $\underline{d}$  orbitals thereby making them more accessible for bonding.

The second effect to stabilize the type of structure postulated for the transition metal monochalconides is the energy gained from the delocalization of electrons throughout the structure. The resonance energy of benzene is 36 kcal/ mole (75) or 6 kcal/mole per C-C bond. This amount of energy, 6 kcal/mole per C-C bond, is by no means insignificant. And, if this energy per bond is assumed to be the same order of magnitude in the transition metal monochalconides, this effect could be expected to be important in stabilizing structures of transition metal monochalconides.

Unfortunately experimental values for the crystal field stabilization and delocalization energies are not available to corroborate what has been postulated with respect to their effect on stabilizing the transition metal monochalconide structures. However a simple series of calculations can be made to give an approximate measure of the sum of these two effects with respect to offsetting the rather high promotion energy to the  $\frac{s^2p^3d^1}{s^2p^3d^1}$  valence state of sulfur. Consider, for example, solid TiS (1) with the NiAs structure type. The chalcogen, S, in this structure is in a trigonal prism formed by six metal atoms. The calculated valence of S

in TiS, according to Pauling's empirical relation (Equation 50), is approximately 4. Therefore, according to the bonding model under discussion, in TiS there are six bonds of approximately 2/3 order from the S atom to the metal atoms composing the trigonal prism, this bonding from the S atom can be conceptually considered to involve 4 single bonds. Therefore the energy (AH°), involved in the reaction:

$$TiS(s) = Ti(g)(\underline{a}^{3}s) + S(g)(\underline{s}^{2}p^{3}\underline{a}^{1})$$
(51)

is that needed to break 4 single Ti-S bonds, assuming to a first order approximation that there is no Ti-Ti bonding in TiS(s), and yield the gaseous atoms in their supposed valence states. The energy involved in this process will include the 4 single Ti-S bond energies, the crystal field stabilization energy and the delocalization energy. The value of (LH°), can be calculated from the following reactions:

$$\operatorname{TiS}(s) = \operatorname{Ti}(g)\left(\underline{s^2 d^2}\right) + S(g)\left(\underline{s^2 v^4}\right), \quad (\Delta H^\circ)_2$$
(52)

$$Ti(g)(\underline{s^2d^2}) = Ti(g)(\underline{d^3s}),$$
 (AH°)<sub>3</sub> (53)

$$S(g)\left(\underline{s^{2}p^{4}}\right) = S(g)\left(\underline{s^{2}p^{3}a^{1}}\right), \qquad (\Delta H^{\circ})_{4}. \qquad (54)$$

The values of  $(\Delta H^{\circ})_2$  (76),  $(\Delta H^{\circ})_3$  (71) and  $(\Delta H^{\circ})_3$  (71), are, respectively, 128 kcal/mole, 19 kcal/mole and 194 kcal/mole. Accordingly the value for  $(\Xi H^{\circ})_1$  is given by

$$(\Delta H^{\circ})_{1} = (\Delta H^{\circ})_{2} + (\Delta H^{\circ})_{3} + (\Delta H^{\circ})_{4} \text{ or } (55)$$

$$(\Delta H^{\circ})_{7} = 341 \text{ kcal/mole}$$
 (56)

Now consider the dissociation energy of the diatomic molecule TiS according to the following reaction:

$$TiS(g) = Ti(g)(\frac{s^2 a^2}{a}) + S(g)(\frac{s^2 p^4}{a}), \quad (\Delta H^{\circ})_5. \quad (57)$$

The value of  $(\Delta H^{\circ})_{5}$  is 106 kcal/mole (76) and is the energy required to rupture the bonds holding the gaseous molecule together. It seems plausible to suggest that, at least to a first approximation, two single bonds are involved in the TiS gaseous molecule. This derives from the fact that the Ti atom by donating two electrons to the S atom fills the <u>p</u> orbitals of the chalcogen. No promotion energy is needed in Equation 57 since the dissociated atoms are already in the valence state capable of forming two bonds.

It is assumed in this simple approximation that the bond energy is proportional to the bond number. The apparent energy difference between a single Ti-S bond in the condensed TiS phase according to Equation 56 and a single Ti-S bond in the TiS gaseous molecule according to Equation 57 will then be a measure of the sum of the crystal field and delocalization effects in solid TiS. The apparent energy of a single Ti-S bond in the condensed phase is  $(AH^{\circ})_{1}/4$  or 85 kcal/mole, and the same Ti-S single bond in the gaseous TiS

molecule is  $(\Delta H^{\circ})_5/2$  or 53 kcal/mole. The difference in these energy values is 32 kcal/mole which represents a considerable, but not unbelievable, stabilization energy in solid TiS per mole of Ti-S single bonds involved in resonance and crystal field effects.

In the case of the metal-rich chalconides, the same general physical properties are observed as those discussed by Rundle in the MX compounds, e.g., metallic luster and electrical conductivity, brittleness and high melting points. Consequently, it seems plausible to extend Rundle's bonding interpretation for MX compounds, i.e., delocalized electrons in directional bonds, to these metal-rich phases. The coordination of the chalcogen in these phases is, with few exceptions, trigonal prismatic with from zero to three augmenting atoms off the rectangular faces of the trigonal These augmenting atoms, if they are bonded to the prism. chalcogen and are not merely close non-bonded atoms, could result from the increased participation of outer orbitals of the chalcogen atoms, the promotion energy in turn being compensated by increased bonding, crystal field stabilization and delocalization energies. If in Ti<sub>2</sub>S one of the sulfur atoms is using all six of its valence electrons to form bonds each of order 2/3 to nine metal atoms arranged in an augmented trigonal prism about the chalcogen and if to a first approximation each Ti-S single bond formed in Ti<sub>2</sub>S returns 85

kcal/mole due to bonding, crystal field stabilization and delocalization effects, then the amount of energy returned by the sulfur in bonding to nine metal atoms in this manner will be 510 kcal/mole. This amount of energy compares quite favorably with the promotion energy listed by Webster (69) from a Hartree-Fock SCF calculation for the valence state  ${}^{7}F(\underline{sl_{p}3d^{2}})$ , namely 564 kcal/mole. This valence configuration will allow maximum bond formation for the chalcogen, in this case sulfur, by making six unpaired electrons available for bonding.

### C. A Discussion and Comparison of the Metal-Rich Sulfides and Selanides of the Group IVB and VB Transition Metals

The known phases of metal-rich chalconides i.e.,  $M_nC$  where M and C are the appropriate metal and chalcogen, respectively, and  $n\geq 2.00$ , are Ti<sub>2</sub>S (20), Ti<sub>2</sub>Se, Zr<sub>2</sub>S (52), Zr<sub>2</sub>Se,  $2r_{21}S_8^{-1}$ ,  $Mf_2S$  (21) and  $Mf_2Se$  for the Group IVB metals and  $\alpha-V_3S$  (19),  $3-V_3S$  (19),  $Nt_{21}S_8$  (22),  $Nb_2Se$  (77), Ta<sub>2</sub>S and Ta<sub>6</sub>S for the Group VB metals. There exists a claim by Eremenko and Listovnichii (73) for the possible existence in the Ti-S system of a Ti<sub>6</sub>S phase with the Ti<sub>2</sub>P (79)

<sup>&</sup>lt;sup>1</sup>Conard, B. R., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Discussion of the Zirconium-Sulfur System. Private communication. 1969.

structure type. B. R. Conard<sup>1</sup> has recently claimed the existence of a phase in the Zr-S system with the approximate stoichiometry  $Zr_5S$ . However, additional comments on the  $Ti_3S$  and  $Zr_5S$  phases must await the result of further careful work in these respective systems.

In connection with the known structures of the metal-rich sulfides and selenides of the Group IVB and VB metals, three distinct structural features of these phases will be discussed in this section. The first point will deal with the noticeable absence of an  $M_{2}C$  structure, in which C is the chalcogen and M is a Group VB metal, exhibiting the  $Ta_2^P$ structure type. A continuation of the discussion of this point will deal with an explanation for the presence of the channels devoid of atomic centers running through the crystal lattices of the  $Ta_2S$  and  $Nb_2Se$  (77) structures. The second point will deal with the tendency toward aggregation by metal atoms to form the metal columns observed in Ta<sub>p</sub>S and  $\operatorname{Ta}_{S}S$ . This tendency is not exhibited by any other known metal-rich chalconide or pnictide structure. The third point of this section will be concerned with the disparity in behavior of the coordination polyhedra about the Hf atoms in  $\mathrm{Hf}_2\mathrm{S}$  and  $\mathrm{Hf}_2\mathrm{Se}$  as compared with that found in  $\mathrm{Hf}_2\mathrm{P}$  and HfpAs, noting the similarity in behavior for Ta in TapS

<sup>1</sup>Conard, <u>ibid</u>.

as compared with that found in Ta<sub>2</sub>P.

1. The non-existence of an  $M_2S$  or  $M_2Se$  phase, with M a Group VB metal, exhibiting the Ta<sub>2</sub>P structure

The Group IVB metals, with the exception of Hf, form dimetal sulfides and selenides with the Ta<sub>2</sub>P structure type which is structurally characterized by a trigonal prismatic coordination polyhedron about the chalcogen and a more or less distorted body-centered cubic (bcc) environment about each metal atom. The coordination number for the chalcogen atoms in these phases isostructural with Ta<sub>2</sub>P is quite high, namely six to nine. The calculated valence using Pauling's empirical relation (Equation 50) for the chalcogen atoms in these phases is quite high, namely about 4. The densities of these phases are comparable in magnitude to the densities of the metals, <u>e.g.</u>, for Ti<sub>2</sub>S,  $\rho$ =4.8 g/cc and for Ti,  $\rho$ =4.5 g/cc (20, 80).

The Group VB metal-rich chalconides can profitably be viewed as belonging to either one of two groups, Group I and Group II, neither of which exhibit the  $Ta_2P$  structure type. The first group, Group I, is characterized by phases with the stoichiometry  $M_nC$  for which n>2.00. For these phases the coordination of the chalcogen atom is high, between six and nine, and the valence of the chalcogen atom, calculated using Pauling's empirical equation (Equation 50), is high, about 4. The densities of these phases are guite high in comparison with those of the metals: for  $Nb_{21}S_8$  and Nb (22, 80), p=8.8 g/cc and 8.6 g/cc, respectively, for  $\alpha - V_3 S, \ \beta - V_3 S$  and V (19, 80),  $\rho = 5.90$  g/cc, 5.94 g/cc and 6.0 g/cc, respectively, for  $Ta_6S$  and Ta, p=15.18 g/cc and 16.7 g/cc, respectively (80). The second group, Group II, is characterized by phases exhibiting a stoichiometry  $\rm M_2C$  . The members of this group include the  $\rm Ta_2S$  and  $\rm Nb_2Se$ phases. The coordination number about the chalcogen atom in these phases is between four and six. The calculated valence of the chalcogen in these phases is significantly lower than 4, generally about 3. The densities of these phases are lower than the densities of the parent metals: for Ta<sub>2</sub>S and Ta (SO), p=12.39 g/cc and 16.7 g/cc, respectively, and for  $\rm Nb_2Se$  and Nb (77, 80),  $\rho=7.88$  g/cc and 8.6 g/cc, respectively.

The differences in densities can be more profitably viewed as the percentage of void regions in the respective unit cells assuming the atoms to be approximated by hard spheres with the respective radii given by Slater (46). For  $\alpha$ -V<sub>3</sub>S,  $\beta$ -V<sub>3</sub>S, Nb<sub>21</sub>S<sub>8</sub> and Ta<sub>6</sub>S, the percentage of void regions are 32%, 32%, 36% and 34%, respectively. And for Ta<sub>2</sub>S and Nb<sub>2</sub>Se, both Group II phases, the percentage of void region in the respective unit cells is 43% for both structures. The percentage of void space is significantly higher for the Group II phases than for the Group I phases.

The Group II phases,  $Ta_2S$  and  $Nb_2Se$ , are both structurally characterized by channels devoid of atomic centers which run through the respective unit cells. These empty channels are surrounded by arrangements of non-bonded chalcogen atoms in  $Ta_2S$  and  $Nb_2Se$ . In  $Ta_2S$  the shortest S-S distance is 2.86Å, and in  $Nb_2Se$  the shortest Se-Se distance is 3.43Å (77).

The structures of Group IVB dimetal sulfides and selenides can profitably be considered from the viewpoint of valence electron concentration (v.e.c.) per M<sub>2</sub>C unit. For Ti<sub>2</sub>S, Ti<sub>2</sub>Se, Zr<sub>2</sub>S and Zr<sub>2</sub>Se, the v.e.c. is equal to 2 x 4 + 6 or 14 electrons. For  $Hf_2P$ ,  $Hf_2As$  and  $Ta_2P$ , the v.e.c.'s are 13, 13 and 15 electrons, respectively. The v.e.c. for both Ta2S and Nb2Se is 16 electrons. Therefore, it seems reasonable to suggest that for a hypothetical M2C phase exhibiting a v.e.c. greater than 15 the Ta<sub>2</sub>P structure is destabilized with the resultant structure becoming either a Group I or a Group II structure. For the formation of the Group I phases, it is suggested that the hypothetical  $M_2C$ phase with the Ta<sub>2</sub>P structure type disproportionates to yield one phase more chalcogen-rich than M<sub>2</sub>C and one phase, possessing the structural properties described for the Group I phases, more metal-rich than M2C. As for the Group II phases, the stoichiometry of the phase remains M2C. However,

in this case it is suggested that the additional electrons in excess of 15 valence electrons per  $M_2C$  unit are located in non-bonding orbitals directed into the region of the unit cell through which the empty channel runs. According to this suggestion the void channels in Ta<sub>2</sub>S and Nb<sub>2</sub>Se are not really void regions at all, but are rather occupied by electrons in orbitals directed into these regions. In other words, the sulfur-sulfur and selenium-selenium contacts across the channels are the typical van der Waal's contacts of non-bonded atoms.

# 2. The motal column formations in the Ta<sub>2</sub>S and Ta<sub>5</sub>S structures

The bonding in motal-chalcogen systems has been discussed, as pointed out earlier in this section, in terms of radius ratios. In fact in a recent review article, Hulliger (73) states with regard to metal-rich chalconides and pnictides that: "In these phases an optimal filling of space is aimed at and their structures are therefore in most cases determined by the radius ratios of the constituent elements." Admittedly for the phases exhibiting the Ta<sub>2</sub>P structure type, Hf<sub>2</sub>S, Hf<sub>2</sub>Se,  $\alpha$ - and  $\beta$ -V<sub>3</sub>S, Nb<sub>2</sub>Se and Nb<sub>21</sub>S<sub>8</sub> the directional nature of the bonding about the metal atoms in these structures is not self evident. Accordingly some investigators have described these structures on the basis of radius

ratio arguments.

However in both the Ta<sub>2</sub>S and Ta<sub>6</sub>S structures, the directional bonding in the interpenetrating icosahedra forming the metal columns is clearly evident. The difference in structure between Ta<sub>2</sub>S and Ta<sub>2</sub>P cannot be explained on the basis of radius ratios and an optimal filling of space in the Ta<sub>2</sub>S structure. The atomic radius of sulfur is the same as that for phosphorus, namely 1.00Å (46). Accordingly the radius ratios of sulfur to tantalum and phosphorus to tantalum are identical. Secondly the structure of Ta2S cannot be said to be optimally filling space since the percentage void space in Ta<sub>2</sub>S is 43%, compared with 35% for Ta, P. Since the general physical properties observed in TapS and TagS do not differ from those observed for other metal-rich chalconides and pnictides, it can be suggested that the same type of bonding is present in all metal-rich chalconids and pnictide phases, namely, as described earlier in this discussion, a directional covalent bonding between atoms involving delocalized electrons. However, this general bonding description doesn't account for the difference in metal coordination found in Ta<sub>2</sub>S and Ta,P.

The metal coordination in structures exhibiting that Ta<sub>2</sub>P structure type is high, 10 to 11, with eight of these forming a more or less distorted bcc environment about each

metal atom. Remnants of this bcc structure can be seen around the metal atoms in both Nb<sub>2</sub>Se and Nb<sub>21</sub>S<sub>8</sub>. The metal coordination about V in both  $\alpha$ - and  $\beta$ -V<sub>3</sub>S is quite complex and not easily described. The coordination polyhedron about Hf in Hf<sub>2</sub>S and Hf<sub>2</sub>Se is a distorted octahedron composed of three Hf atoms and three chalcogen atoms, while the Hf atoms in Hf<sub>2</sub>P and Hf<sub>2</sub>As, both of which exhibit the Ta<sub>2</sub>P structure type, are found in a bcc environment. More will be said about Hf in the four phases Hf<sub>2</sub>S, Hf<sub>2</sub>Se, Hf<sub>2</sub>P and Hf<sub>2</sub>As, but first the Ta coordinations are considered. The configuration of Ta atoms in both Ta<sub>2</sub>S and Ta<sub>6</sub>S is unique for any metal in any metal-rich chalconide or pnictide phase.

It has already been pointed out that attempts to interpret this strange ability of Ta to form columnar aggregations of metal atoms on the basis of radius ratio arguments were totally unfruitful. Accordingly it was decided to consider this behavior not as a simple size effect, but rather the result of the specific behavior of electrons on the Ta atom.

Brewer (81) has discussed the ideas of Engel correlating the tendency of a metal to be found in a given coordination polyhedron in the condensed state with the promotion energy required to obtain the gaseous metal atom in a given electronic configuration. Accordingly Brewer and Engel

correlate the electronic configuration of the metal with one valence <u>s</u> electron in the gas state with a bcc structure and one valence <u>s</u> and one valence <u>p</u> electron with a hexagonal closest packed (hcp) structure for the metal in the condensed state. If two excited states have the same number of unpaired electrons available for bonding, and if the bond energies for the two excited states are comparable, then the state with the lowest promotion energy will be favored in the condensed state. Table 29 lists the promotion energies, according to Moore (71), for the Group VB metals for the lowest  $\frac{d^3s^2}{ds}$ ,  $\frac{d^4s}{ds}$ ,  $\frac{d^5}{and}$   $\frac{d^3sp}{sp}$  states with the maximum electron multiplicity for the gaseous atoms. On the basis of the Brewer-Engel correlation, one would expect the bcc structure to be found for the elements in the condensed state, and this is the structure observed for these metals.

| <u>:</u> | ccal/mole           | <u></u>                           |                                  |                                    |  |
|----------|---------------------|-----------------------------------|----------------------------------|------------------------------------|--|
| Metal    | $d^{3}s^{2}(^{4}F)$ | ā <sup>4</sup> s( <sup>6</sup> D) | a <sup>5</sup> ( <sup>6</sup> s) | d <sup>3</sup> sp( <sup>6</sup> G) |  |
| V7       | 0                   | б                                 | 58                               | <u>4</u> 7                         |  |
| Nb       | З                   | 0                                 | 32                               | 43                                 |  |
| Ta       | 0                   | 28                                | 34                               | 50                                 |  |
|          |                     |                                   |                                  |                                    |  |

Table 27. Promotion energies for the Group VB metals in kcal/mole

Furthermore, in both the Nb<sub>2</sub>Se and Nb<sub>21</sub>S<sub>8</sub> structures, the metal atoms can be observed to be at the center of a more or less distorted bcc environment consisting of both metal and

non-metal atoms. Extending the Brewer-Engel correlation to chalconides, this behavior can be related to the promotion energy from the ground state to the d<sup>4</sup>s state for the gaseous metal atoms. According to Table 27, the d<sup>4</sup>s state is the ground state for the Nb atom in the gas state. The  $d^3s^2$ state is not very interesting from the viewpoint of bonding since there are only three unpaired electrons available for bond formation. The next two excited states, the  $d^{2}$  and the  $d^3sp$ , are energetically quite removed, namely by 32 kcal/mole and 48 kcal/mole, respectively, from the d<sup>4</sup>s ground state. Accordingly, the d<sup>4</sup>s state will make an important contribution to the valence state of Nb in condensed phases. Therefore it is no surprise to find that in the  $Nb_{21}S_8$  and  $Nb_2Se$  structure and in a metal-rich phosphide  $Nb_7P_4$  (82) many Nb atoms are in a more or less distorted bcc arrangement of atoms.

With respect to the situation for Ta, the ground state of the gaseous atom is  $\frac{d^3s^2}{s}$ , a rather uninteresting state from the point of bonding consideration. The first excited state is not unexpectedly the  $\frac{d^4s}{s}$  state, 28 kcal/mole above the ground state. However, the second excited state, the  $\frac{d^5}{s}$  state, is 34 kcal/mole above the ground state or only 6 kcal/mole above the first excited state, the  $\frac{d^4s}{s}$  state. Therefore it can well be expected that the  $\frac{d^4s}{s}$  and the  $\frac{d^5}{s}$ configurations can interact in the condensed state. It is suggested that indeed this is the case with regard to the valence configurations of the Ta atoms in  $Ta_2S$  and  $Ta_2S$ .

In conjunction with the use of the  $d^{\frac{5}{2}}$  state by Ta in bonding, Brewer (81) suggests that for two of the polymorphic forms, a and 3, of Mn metal, in addition to various atoms having the  $\frac{d^5}{ds}$  and  $\frac{d^5}{sp}$  configurations in which the majority of the bonding would be done by electrons in the valence s and p orbitals, some of the Mn atoms could have the  $\frac{d^5s^2}{d^5s^2}$  configuration in which all the bonding interaction, since the two valence s electrons are unavailable for bonding, would arise from the  $\frac{d^5}{d}$  portion of the  $\frac{d^5s^2}{s}$  configuration. Consequently, the metal columns in TapS and TapS can be considered to be similar to the situation in a- and  $\beta-Mn$  where presumably the  $d^{\frac{5}{s}^2}$  configuration is important in stabilizing these polymorphic structures of Mn. It can be suggested that Mn metal has both the available orbitals to form complex metal structures and the electrons necessary to stabilize these structures, and that Ta metal itself has only the available orbitals to form a complex metal structure as is found in the Ta<sub>2</sub>S and Ta<sub>5</sub>S structures but not the electrons necessary to stabilize this type of metal framework. The sulfur could well be imagined to supply a sufficient number of valence electrons to stabilize the metal chains found in Ta,S and Ta,S.

With regard to this suggested explanation, an explanation

for the disparity between the  $Ta_2S$  and  $Ta_2P$  structures can also be suggested. An interpretation for the lack of Ta chains in the case of  $Ta_2P$  could be suggested in terms of a valence electron concentration: the sulfur atom supplies a sufficient number of valence electrons to make the  $\frac{d^5}{2}$ configuration of Ta important in bonding, while in the case of phosphorus the  $\frac{d^5}{2}$  state of Ta is not involved in bonding in the  $Ta_2P$  structure as a consequence of an insufficient number of valence electrons on phosphorus as compared with sulfur. Accordingly, in  $Ta_2P$  only the valence  $\frac{d^4s}{2}$  configuration is involved in bonding, and this state is associated with the boc environment found about the Ta atom in  $Ta_2P$ .

3. A sugrested interpretation for the anomalous metal coordination found in  $Hf_2S$  and  $Hf_2Se$  as compared with that observed in  $Fi_2S$ ,  $Fi_2Se$ ,  $Zr_2S$ ,  $Zr_2Se$  and  $Zr_{21}S_3$ 

All the dimetal sulfides and selenides of Zr and Ti are isostructural with the  $Ta_2P$  structure type. The phase  $Zr_{21}S_8$  is isostructural with  $Nb_{21}S_8$ . Of concern is the fact that the boordination about each metal atom in both  $2r_{21}S_8$ and the structures isostructural with  $Ta_2P$  is more or less distorted boo, whereas in both  $Hf_2S$  and  $Hf_2Se$  the metal atoms are in a distorted octahedron composed of three metal atoms and three non-metal atoms. Surprisingly, however, both  $Hf_2P$  and  $Hf_2As$  are isostructural with  $Ta_2P$ . Obviously any attempt to account for the variance of the  $Hf_2S$  and  $Hf_2Se$  structures from the  $Ta_2P$  structure exhibited by  $Zr_2S$ ,  $Zr_2Se$ ,  $Ti_2S$ ,  $Ti_2Se$ ,  $Hf_2P$  and  $Hf_2As$  on the basis of radius ratio arguments is doomed to failure since the atomic radii of Hf and Zr are equal (1.45Å) and the atomic radii of S and P and of Se and As are also equal, namely 1.00Å and 1.15Å, respectively, according to Slater (46).

Therefore an interpretation of this disparate behavior of Hf will be suggested on the basis of the Brewer-Engel correlation, as was the case for Ta in the Ta<sub>2</sub>S and Ta<sub>2</sub>P structures. Table 28 lists the promotion energies, according to Moore (71), to the lowest spectroscopic  $\frac{d^2s^2}{ds}$ ,  $\frac{d^3s}{ds}$ and  $\frac{d^2sp}{ds}$  states with the maximum electron multiplicity for

| Metal | d <sup>2</sup> s <sup>2</sup> ( <sup>3</sup> F) | d <sup>3</sup> s ( <sup>5</sup> F) | d <sup>2</sup> sp ( <sup>5</sup> G) | · · · · · · · · · · · · · · · · · · · |
|-------|---|------------------------------------|-------------------------------------|---------------------------------------|
| Ti    | 0   | 19                                 | 45                                  |                                       |
| Zr    | 0   | 14                                 | 42                                  |                                       |
| Hf    | 0   | 40                                 | 51                                  |                                       |

Table 28. Promotion energies for the Group IVB metals in kcal/mole

the gaseous atoms of the Group IVB metals. It is interesting to note that the stable form of the Group IVB metals at room temperature is the hexagonal closest packed arrangement of atoms which, according to the Brewer-Engel correlation, is associated with the  $\underline{d^2}\underline{sp}$  configuration, the second excited state above the ground state, while the body centered cubic arrangement associated with the first excited state, the  $\underline{d^4s}$  configuration, of the metal is the high temperature form of the element. The hep to bee transition temperatures arel155°K for Ti, 1150°K for Zr and 2023°K for Hf (83). This inversion of the hep and bee configurations for the elements, as would be predicted by the Brewer-Engel correlation, means that in the elementary form <u>p</u> orbitals afford stronger bonds than do d orbitals for these metals.

For 9i and Zr, according to the Brewer-Engel correlation, the  $\underline{d^3s}$  state is the lowest interesting valence state and would be expected to be the valence configuration of the metal in the condensed state since the  $\underline{d^2st}$  state lies 26 kcal/mole and 28 kcal/mole, respectively, above the  $\underline{d^3s}$ state. To a first approximation, the  $\underline{d^2st}$  and  $\underline{d^3s}$  valence states can be assumed to yield approximately equal bond energies in metal-non-metal systems. Accordingly, in  $\text{Pi}_2\text{S}$ ,  $\text{Ti}_2\text{Se}$ ,  $\text{Zr}_2\text{S}$ ,  $\text{Zr}_{21}\text{S}_8$  and  $\text{Zr}_2\text{Se}$ , the bod environment is found about each metal atom.

For Hf the  $\underline{d^3s}$  state lies 1 rest at 40 kcal/mole above the  $\underline{d^2s^2}$  ground state. However the second excited state lies at 51 kcal/mole above the ground state or only 11 kcal/mole above the  $\underline{d^3s}$  state. Therefore, assuming the

promotion energies to the various valence states in the gaseous atoms do not drastically differ in energy nor in relative position for the atom in the condensed state, a certain amount of interaction could be expected to occur between these two levels, the  $\frac{d^3s}{ds}$  and the  $\frac{d^2sp}{ds}$ , for Hf. The existence of the two phases Hf2As and Hf2P with the Ta<sub>2</sub>P structure type indeed suggests that, as was the situation for Ta in Ta<sub>2</sub>S and Ta<sub>2</sub>P, this is what is happening here. For Hf in Hf<sub>2</sub>P and Hf<sub>2</sub>As, there are an insufficient number of valence electrons to effectively use the  $d^2sp$ state of Hf in bonding. Consequently for Hf,P and Hf,As only the  $d^3s$  state of Hf is involved in bonding, and so the Hf atoms in Hf\_P and Hf\_As are all found in a more or less bcc environment. However, since the chalcogen atom has one more valence electron than does the pnicogen atom, in Hf<sub>2</sub>S and Hf<sub>2</sub>Se the metals atoms are effectively using the second excited state, the  $\frac{d^2sp}{dsp}$  configuration, in addition to the  $d^3s$  state in bonding. In other words, Hf in Hf<sub>2</sub>S and Hf<sub>2</sub>Se is using a considerable amount of p valence orbitals in bonding while the metal in Hf2P and Hf2As is using primarily only the valence s and d orbitals.

The Brewer-Engel correlation also suggest an explanation for the difference in metal coordination in the  $Hf_2S$  and  $Ta_2S$ structures. The  $\underline{d}^3s$  and  $\underline{d}^4s$  states for Hf and Ta, respectively, lie lowest in energy for both metals in the gas state, and in the case that higher valence states are not involved in bonding, the atomic configuration about both Hf and Ta atoms in metal-non-metal systems could be expected to be the same, namely bod, as is the case in  $\text{Hf}_2\text{P}$  and  $\text{Ta}_2\text{P}$ . However if symmetrically different higher valence states of Hf and Ta became involved in bonding, then the coordination symmetry about the two metals, Hf and Va, could be expected to be different. Accordingly this is the behavior that seems to be indicated for Ta in Ta<sub>2</sub>S where the  $\frac{d^4s}{d^4s}$  and  $\frac{d^5}{d^5}$  states are important in bonding while for Hf in Hf<sub>2</sub>S the  $\frac{d^3s}{d^2sp}$  valence states are important in bonding.

### X. CONCLUSIONS

There exists in the metal-rich region of the tantalumsulfur system two phases, Ta<sub>2</sub>S and Ta<sub>6</sub>S, which have not been previously reported. In the metal-rich regions of the titanium-, zirconium-, and hafnium-selenium systems, there exists three new phases: Ti<sub>2</sub>Se, Zr<sub>2</sub>Se and Hf<sub>2</sub>Se, respectively.

The physical properties of these phases are explained in terms of delocalized electrons in directional bonds as was originally proposed by Rundle to explain bonding in transition metal monoxides, mononitrides and monocarbides exhibiting the NaCl structure. It was proposed that the chalcogen atoms uses outer <u>d</u> orbitals in bonding in metalrich chalconide phases.

The occurrence of the two metal-rich chalconide structures for the Group VB metals was proposed to be the result of a valence electron concentration effect. An explanation for the coordination about the metal atoms in the metal-rich chalconide structures was suggested in terms of both the Brewer-Engel correlation and a valence electron concentration effect.

## XI. SUGGESTIONS FOF FURTHER RESEARCH

In view of the uncommon configuration of metal atoms in  $Ta_2S$  and  $Ta_6S$ , the tantalum-selenium system should be investigated to determine if the phases present there resemble those found in the Ta-S system with respect to the coordination about the metal atoms. If metal-rich phases in the Ta-Se system were found to be similar from the point of view of metal coordination, this would corroborate the bonding explanation proposed in this thesis for the metal columns found in  $Ta_2S$  and  $Ta_6S$ .

It would be interesting to determine if there exist phases  $V_2S$ ,  $Nb_2S$  and a phase more metal-rich than  $Nb_2Se$ , and to determine the structures of these phases to check the validity of the bonding scheme proposed in this thesis for the two general types of metal-rich Group VB chalconide structures.

In view of the disparity in the metal coordination found for Hf in  $Hf_2P$  and  $Hf_2S$  structures and for Ta in the  $Ta_2P$ and  $Ta_2S$  structures for which an explanation has been suggested in terms of a valence electron concentration difference between S and P, it would be very interesting to prepare and determine the structure of a phase having the stoichiometry  $Hf_4PS$  or  $Ta_4PS$ .

A more thorough knowledge of the electrical and magnetic

properties of the metal-rich chalconides would be most useful in formulating a more quantitative bonding description for these phases.

During the study of the metal-rich region of the Ta-S system, it became evident that there exists a previously unreported Ta-S vapor species of considerable importance. The determination of the precise nature of this vapor species, both with regards to a determination of its stoichiometry and thermodynamic properties, would constitute a very worthwhile project.

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#### XIII. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. H. F. Franzen for his encouragement, suggestions, direction and patience during the course of this research. The many illuminating discussions with him have added immensely to the author's scientific background and for this, the author is extremely grateful.

To his wife, Marilynn, for her encouragement, patience, love and understanding during the course of this work, the author gives his special thanks.