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EXPERIMENTAL STATION

PIGMENTS DEPARTMENT

February 8, 1963

THERMOELECTRIC PROPERTIES OF SELENIDES AND TELLURIDES
OF GROUPS VB AND VIB METALS AND THEIR SOLID SOLUTIONS

NObs-84824

Index No. SR-007-12-01

Task 802

Sixth Quarterly Report
by

W. T. Hicks, H. Valdsaar

approved by

D. G. Kelemen

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This report covers the period October 1, 1962 to December 30, 1962.

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It is planned to incorporate tantalum-doped tungsten diselenide (p-type) in a practical thermoelectric module, cascaded with p-type lead telluride and encapsulated in a ceramic-coated constantan can which will also serve as the n-leg of the couple. Experimentation with the details of construction is underway.

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ABSTRACT

Improved procedures in synthesis and in measurements have eliminated unreproducibilities in tantalum-doped tungsten diselenide preparations, giving a well-substantiated Figure of Merit of about $0.5 \times 10^{-3}/\text{deg}$ in the 500-1000°C range. An apparatus for direct efficiency measurements is under construction.

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A. INTRODUCTION - D. G. Kelemen

In earlier reports on this project, we presented our work in two major sections. Dr. W. T. Hicks gave an account of a fundamental study of the thermoelectric parameters for a variety of refractory metal selenides and tellurides and their solid solutions, while Dr. Valdsaar dealt primarily with practical problems such as encapsulation and electrical contacts. We hope that by the end of the present contract (June 30, 1963), we shall have useful thermoelectric modules based on our best material, tantalum-doped tungsten diselenide. Therefore, we have been turning our attention increasingly to the practical problems, and both Dr. Hicks and Dr. Valdsaar plan to work in this area for the next six months.

Dr. Hicks has elucidated the causes of some unreproducibilities mentioned in our earlier reports. Thorough mixing at an intermediate stage in the synthesis seems to reduce resistance variations between repeated preparations, and careful attention to chemical reactions between thermocouple leads and tungsten diselenide results in reliable Seebeck coefficient measurements. (As one would expect from the history of thermoelectric materials research, the confirmed Seebeck coefficient values always turn out to be the lowest ones.) The Figure of Merit of tantalum-doped tungsten diselenide according to our

latest and, we hope, final data stands at about $.5 \times 10^{-3}/\text{deg}$ in the 500-1000°C range. While this is not an outstandingly high value, it is at least comparable to well-established data for the best materials known in this temperature range. Dr. Hicks is now engaged in the construction of a device which will measure the efficiency of thermoelectric modules directly.

Dr. Valdsaar has continued his work intended to lead to a design and fabrication process for practical modules. At the present time, his thinking centers around a construction involving a segmented p-leg with lead telluride on the 100-500°C side and tungsten diselenide on the 500-1000°C side, encased in a constantan tube with flame-sprayed ceramic coatings on both inside and outside surfaces. The constantan will act as the return leg of the module and will provide some additional output, on account of its own fair thermoelectric properties. This construction, with a theoretical conversion efficiency of about 10%, seems more practical than one using semiconductors for both the n- and p-elements. During this past quarter, Dr. Valdsaar made considerable progress in gathering information on metallic encapsulation.

The last section of this report deals with thermal conductivity measurements on tungsten diselenide and its analogues.

This information has been gathered over several years, and none of it is new. It was not, however, conveniently available in one place and, therefore, we have summarized it here at the request of Mr. B. B. Rosenbaum of the Bureau of Ships.

B. THERMOELECTRIC PROPERTIES OF TUNGSTEN DISELENIDE - W. T. Hicks

Extreme variations in the resistivity of tantalum-doped tungsten diselenide, reported in the past, are eliminated by thorough mechanical mixing of the reaction mixture, and discrepancies between older and more recent Seebeck coefficient values have been resolved by several methods in favor of the new (lower) values. Using these improved techniques, the effects of a number of variables such as stoichiometry, tungsten source and molding pressure were studied.

Electrical measurements on tungsten diselenide were extended to 1000°C through the use of platinum versus platinum-10% rhodium thermocouples. Construction of a device to measure directly the efficiency of encapsulated modules has been started.

Material Improvement

Reproducibility of Electrical Properties

Table B-I illustrates electrical data collected at 600°C on a number of samples of $W_{0.99}Ta_{0.01}Se_2$. All these samples nominally had a ratio of two parts of selenium for one atom of metal within an accuracy of two parts in ten thousand. This data was included in the last quarterly report but is reproduced here for convenience. As noted previously, even samples made from the same source of tungsten show variations in resistivity by as much as a factor of two. In addition, with

TABLE B-I

ELECTRICAL PROPERTIES AT 600°C OF $W_{0.99}Ta_{0.01}Se_2$
SAMPLES MADE WITH MANUAL SHAKING

<u>Sample</u>	<u>W Source</u>	<u>S(μV/deg)</u>	<u>ρ(mΩ-cm)</u>	<u>S²/ρ (w/deg²-cm) · 10⁵</u>
382	Fansteel	372	9.3	1.48
478	M & R	353	8.0	1.52
483	M & R	305	8.3	1.12
549	M & R	300	9.8	.92
603	M & R	298	14.3	.62
604	M & R	300	19.6	.46
606	Fansteel	370	16	.85
630	Fansteel	320	10.6	.96

TABLE B-II

RESISTIVITIES (m Ω -cm) AT ROOM TEMPERATURE OF $W_{0.99}Ta_{0.01}Se_y$

SAMPLES MADE USING MECHANICAL SHAKING

<u>W Source</u>	Nominal Values of y		
	<u>1.998</u>	<u>2.000</u>	<u>2.002</u>
Fansteel	12.95	13.73	13.49
	12.92	14.10	13.57
	13.22		13.61
			13.64
M & R		10.53	9.01
			8.52
			9.14

one exception, all samples made recently have Seebeck coefficients close to 300 microvolts/degree, while the first two samples made had Seebeck coefficient values measured in excess of 350 microvolts/degree. As the following detail will show, both sources of uncertainty were eliminated during the last quarter.

1. Effects of Mechanical Mixing •

Up to this time, samples were prepared as follows. Appropriate amounts of the elements were weighed out in quartz tubes. The tubes were evacuated and sealed, and to prevent explosion, the samples were initially reacted at 600° without premixing the selenium and metals. After this reaction, a loose powder product was obtained. The powder was then manually shaken while still in the sealed tube before the final reaction was carried out by heating the samples overnight at 1150°C. It was suspected that the manual shaking might have been inadequate and subject to considerable variation and thus might account for the lack of reproducibility. Therefore, the practice was substituted of mechanically shaking all samples on a vibrating table for five minutes after the initial reaction while the powders were still sealed in the tubes. The materials were then given a final reaction at 1150°C as previously. After this final reaction, the capsules were broken open, the powder removed and sieved as usual before being pressed into bars at 40 tsi. The resulting

resistivities measured at room temperature on samples made by this technique are shown in Table B-II as a function of stoichiometry and tungsten source. Reproducibility is shown by these accurate measurements to be excellent and similar effects of variation of stoichiometry and tungsten source are shown.

Another experiment was attempted to achieve even better mixing. A large 100 gm batch of the above composition was weighed into a quartz tube, sealed and reacted at 600°C overnight. The tube was then opened and the sample was mixed for one hour in a solids-solids blender. The product was resealed into quartz tubes for the final reaction at 1150°C. When these samples were pressed into bars, they all had resistivity values of around 20 milliohm-cm. This deterioration in electrical conductivity is probably due to the pickup of moisture or oxygen by the powders while their surfaces are still in an activated state. Reaction of the powders at 1150°C probably yields a powder having a smoother and less reactive surface.

2. Seebeck Coefficient Measurements

It was considered possible that the lower values of Seebeck coefficients recently measured might have been caused by a variation in sample preparation not thus far detected. Therefore, electrical properties were remeasured as a function of temperature on a sample of $W_{0.99}Wb_{0.01}Se_2$ on which the

following properties were measured with wire chromel-alumel thermocouples at 600° approximately one year ago: $S = 337$ microvolts/deg, $\rho = 7.8$ milliohm-cm and $S^2/\rho = 1.47 \times 10^{-5}$ watts/deg²-cm. The new measurements yielded $S = 289$ microvolts/deg, $\rho = 8.7$ milliohm-cm and $S^2/\rho = 0.95 \times 10^{-5}$ watts/deg²-cm. Thus, it was shown that the discrepancies in Seebeck coefficient values are not a result of changes in sample preparation but result from errors in the measuring technique.

It remained, then, to verify recent methods used to measure Seebeck coefficient as a function of temperature. Reaction has been observed at 600° between the chromel-alumel thermocouples and the sample material. Therefore, the following procedure was used to check for inaccuracies arising from thermocouple contamination. Measurements were made at 600°C with a varying temperature gradient through the sample while maintaining the same average temperature. In this way, it was found that the trouble did not arise from uneven reaction of the two Megapak chromel-alumel thermocouples with the same material.

Recently, sheathed Megapak chromel-alumel thermocouples have been used in place of wire chromel-alumel thermocouples to reduce the reaction of the thermocouples with the sample and reduce the necessity of replacing thermocouples. Therefore, as an additional verification of the measurements, Seebeck coefficients were measured as a function of temperature on the same

sample using three types of thermocouples: Megapak chromel-alumel, wire chromel-alumel, and platinum vs. platinum-10% rhodium wire thermocouples. The results obtained on two separate samples made from different sources of tungsten are summarized for 600°C in Table B-III. All Seebeck coefficients were corrected to absolute values by accounting for the absolute Seebeck coefficients of the reference thermocouple leads: chromel in the case of the chromel-alumel thermocouples and platinum in the case of the platinum vs. platinum-10% rhodium thermocouples. The results agree within experimental error for both the measurement of Seebeck coefficients and resistivities at these temperatures. The recently measured lower values for the Seebeck coefficient of the composition $W_{0.99}Ta_{0.01}Se_2$ are thus confirmed and the earlier measured higher values must be attributed to thermocouple-sample reaction for the unprotected wire thermocouples. In the future, better control will be maintained by varying the temperature gradient of the measurement at 600° on some samples and by occasionally rechecking the measurements made with chromel-alumel Megapaks by using platinum vs. platinum-10% rhodium thermocouples.

Effect of Variations in Stoichiometry

In Table B-II, accurate resistivity measurements at room temperature show effects of slight variations in stoichiometry on the composition $W_{0.99}Ta_{0.01}Se_2$. Table B-IV illustrates

sample using three types of thermocouples: Megapak chromel-alumel, wire chromel-alumel, and platinum vs. platinum-10% rhodium wire thermocouples. The results obtained on two separate samples made from different sources of tungsten are summarized for 600°C in Table B-III. All Seebeck coefficients were corrected to absolute values by accounting for the absolute Seebeck coefficients of the reference thermocouple leads: chromel in the case of the chromel-alumel thermocouples and platinum in the case of the platinum vs. platinum-10% rhodium thermocouples. The results agree within experimental error for both the measurement of Seebeck coefficients and resistivities at these temperatures. The recently measured lower values for the Seebeck coefficient of the composition $W_{0.99}Ta_{0.01}Se_2$ are thus confirmed and the earlier measured higher values must be attributed to thermocouple-sample reaction for the unprotected wire thermocouples. In the future, better control will be maintained by varying the temperature gradient of the measurement at 600° on some samples and by occasionally rechecking the measurements made with chromel-alumel Megapaks by using platinum vs. platinum-10% rhodium thermocouples.

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TABLE B-III

SEEBECK COEFFICIENTS FOR $W_{0.99}Ta_{0.01}Se_2$ AT $600^\circ C$
MEASURED WITH DIFFERENT THERMOCOUPLES

<u>Sample</u>	<u>Thermocouples</u>	<u>S ($\mu V/deg$)</u>	<u>ρ (mΩ-cm)</u>	<u>S^2/ρ (w/deg²-cm) $\cdot 10^5$</u>
660	Chromel-Alumel Megapaks	281	8.5	0.93
	Chromel-Alumel Wire	290	8.2	1.03
	Pt. vs. Pt-10%Rh Wire	284	8.1	1.00
662	Chromel-Alumel Megapaks	308	9.9	0.96
	Chromel-Alumel Wire	294	9.6	.90
	Pt. vs. Pt-10%Rh Wire	318	9.8	1.03

TABLE B-IV

EFFECTS OF STOICHIOMETRY ON ELECTRICAL PROPERTIES
OF $W_{0.99}Ta_{0.01}Se_y$ AT $600^\circ C$

<u>Sample</u>	<u>Tungsten Source</u>	<u>y</u>	<u>Dens. (gm/cc)</u>	<u>S ($\mu V/deg$)</u>	<u>ρ (mΩ-cm)</u>	<u>$\frac{S^2}{\rho}$ (w/deg²-cm) $\cdot 10^5$</u>
661	Fansteel	1.998	8.768	307	10.2	0.93
662	"	1.998	8.759	309	9.9	.96
675	"	1.998	8.645	309	10.9	.88
676	"	2.000	8.708	307	10.4	.91
682A	"	2.000	8.754	305	11.4	.82
657	"	2.003	8.789	310	10.3	.94
658	"	2.003	8.763	304	11.3	.82
663	"	2.002	8.668	312	10.8	.90
679	M & R	2.000	8.604	291	9.8	.86
659	"	2.002	8.749	280	9.0	.87
660	"	2.002	8.746	281	8.5	.93
680	"	2.002	8.682	288	8.5	.97

electrical properties measured on these same samples at 600°C. In the case of the samples made from Fansteel tungsten, the slight variations in resistivity observed at room temperature are not apparent in the less accurate high-temperature measurements. Similar differences in resistivities of samples made from Metals and Residues tungsten are also less obvious at 600°C. For the samples made from Metals and Residues, there is some evidence that a slightly higher resistivity measured for the stoichiometric samples is compensated by a higher Seebeck coefficient, yielding S^2/ρ values which are not significantly different. Thus, variations in stoichiometry cannot be considered an effective method of improving the Figure of Merit of $W_{0.99}Ta_{0.01}Se_2$.

Effect of Tungsten Source

A number of samples of $W_{0.99}Ta_{0.01}Se_2$ were made with mechanical shaking using tungsten powder from a number of sources. Properties measured on these samples are summarized in Table B-V. Considering the experimental uncertainty of the properties, one must be cautious in interpreting the data of this table. However, differences in electrical conductivity of the samples made from these sources are obvious. In general, higher conductivities are compensated by lower Seebeck coefficients resulting in only a small spread in S^2/ρ values measured

at 600°C. In this particular batch of samples, all made at the same time, best results were obtained on samples made from **General Electric** and **Wah Chang tungsten powder**.

The compensating effects of Seebeck coefficient and resistivities observed for these samples suggest a relatively constant carrier mobility and a carrier concentration which varies with the source of tungsten used. This suggests that variations are the result of impurity levels in the tungsten rather than particle size distribution. Analyses were supplied with several of these batches of tungsten, but no gross differences in impurity levels are apparent from any of these analyses. More samples will be made from the more promising tungsten sources to see if any actual improvement in Figure of Merit can be confirmed.

Effects of Molding Pressure

Up to this time, all reacted powders were pressed in a 1/4" x 2" die at a standard pressure of 40 tsi. To test the effects of varying the molding pressure, an 80 gram batch of material was divided into four parts, and bars were pressed in the same die at pressures of 40, 50, 60 and 75 tsi. In the case of the highest pressure, diagonal faults were created in the sample, and it broke up while being removed from the die.

Table B-VI summarizes the resulting properties measured on the

TABLE B-V

EFFECT OF TUNGSTEN SOURCES ON PROPERTIES
OF $W_{0.99}Ta_{0.01}Se_2$

W Source	25 °C		600 °C	
	ρ	S ($\mu V/deg$)	ρ (m Ω -cm)	S^2/ρ (w/deg ² -cm) $\cdot 10^5$
Fansteel	13.61	312	10.8	0.90
General Electric	12.37	313	9.6	1.02
Sylvania	10.78	293	9.9	.87
Cleveland	9.58	292	9.0	.95
Wah Chang	9.79	292	8.6	.99
Wah Chang	10.65	275	9.9	.77

TABLE B-VI

EFFECT OF MOLDING PRESSURE ON PROPERTIES
OF $W_{0.99}Ta_{0.01}Se_2$

Pressure (tsi)	25 °C		600 °C		
	% of x-ray Dens.	ρ (m Ω -cm)	S ($\mu V/deg$)	ρ (m Ω -cm)	S^2/ρ (w/deg ² -cm) $\cdot 10^5$
40	93.1	14.10	305	11.4	0.82
50	93.8	13.49	299	11.0	.81
60	94.3	13.03	310	10.7	.90

other three samples. It is seen that the higher molding pressure resulted in an approximately 1% increase in apparent density of the bars. This increase was accompanied by a 7% increase in electrical conductivity at room temperature. This variation is also reflected in high temperature measurements which show approximately a 10% increase in truncated Figure of Merit at 600°C for the sample pressed at the highest pressure over that of the sample pressed at the lowest pressure. Unfortunately the Figure of Merit of the control sample is lower than that usually measured on samples made from the Fansteel tungsten powder. Similar experiments will be conducted on samples made from a different source of tungsten.

In any case, it is quite probable that the increase in electrical conductivity is compensated by a similar increase in thermal conductivity for these materials. However, it is possible that a variation in anisotropy ratios obtained with samples of varying density might result in an improvement of Figure of Merit. (See also Section D on thermal conductivity measurements.)

Data for Module Construction

Extension of Measurements to High Temperatures (1000°C)

Electrical measurements were made on a sample of $W_{0.99}Ta_{0.01}Se_2$ made from Fansteel tungsten up to 1000°C. Platinum vs. platinum-10% rhodium thermocouples were in direct contact with

the sample and current was supplied to platinum electrodes at the end of the sample through platinum leads. A protective, static argon atmosphere of approximately 1 atm was used in these measurements. In the course of the measurements, the platinum lead wires which supplied current for the resistivity measurements were corroded through while the sample was at a temperature of only 800°C. However, the thermocouples remained intact, and the Seebeck measurements were thus carried out up to 1000°C and continued to be measured as the sample was step-cooled down to lower temperatures. Measurements were carried out as rapidly as possible and only a slight deposition of a dark material, probably selenium, was noted in the cooler parts of the tube. However, the sample did undergo a 4% loss in density during the measurements. Considerable reaction between the platinum electrodes and the sample was observed; a hard white material being formed between the electrodes and the sample. A bright blue deposit, possibly platinum selenide, was easily brushed off the end of the sample which had been at the higher temperatures. The results of the measurements are shown by the points in Figure B-1. It is seen that the Seebeck coefficients measured while cooling from the highest temperature are slightly higher than those made while the temperature was increasing. This is probably due to contamination of the thermocouples but does not seem to have

been a serious effect. Thermal conductivities previously measured for this material below 600°C were extrapolated to 1000°C.¹ These values were used with the measured Seebeck coefficients and the resistivity extrapolated from 800°C to 1000°C to calculate the Figure of Merit to 1000°C. Since only a slight decrease in thermal conductivity is expected above 600°C, this extrapolation should not cause serious error. The resulting Figure of Merit shows a peak of $0.51 \times 10^{-3} \text{ deg}^{-1}$ between 700 and 800°C.

Measurement of Thermocouple Efficiency

Direct measurement of the efficiency of a thermocouple made using tantalum-substituted tungsten diselenide would provide confirmation of the thermoelectric parameters which have been measured and reported for this material and also show the practical value of using this material in a working device. To obtain a useful efficiency, we plan to use it in combination with readily available commercial thermoelectric materials.

For the p-leg of the thermocouple a segmented leg is planned with lead telluride being used between 25 and 500°C and tungsten diselenide being used between 500 and 1000°C. For the n-leg of the thermocouple, constantan is contemplated, as discussed in Section C of this report by Dr. Valdsaar.

Exact calculations of the efficiencies of segmented thermocouples having temperature dependent thermoelectric

¹ L. H. Brixner, J. Electrochem. Soc., To be published.

parameters will be made, using a computer program developed for an IBM 704 computer by Dr. R. G. Moore, Jr., formerly of Texas Instruments Inc. This program has been kindly supplied to us by Texas Instruments. Such calculations will enable the selection of the best doping levels for the PbTe and WSe₂ used in the p-leg of the thermocouples.

For the purpose of the efficiency measurements, the semiconductor leg of the thermocouple will be encapsulated in an iron-nickel capped forsterite tube 1/4" dia. x 2" long and will be spring loaded to keep the semiconductor material in contact with the hot temperature. The measurement will be carried out using the following device now under construction: Metered power will be supplied to a small nichrome heater located in the center of a furnace surrounded by approximately 6" of "Tipersul"* insulation. At one side of the device, the encapsulated thermocouple with a constantan lead wire will be inserted in a hole in the insulation. The DC power output of the thermocouple will be measured with the optimum load resistance. The heat input into the thermocouple will be measured by determining the power needed to take the device to a certain temperature with an insulating plug of known thermal resistance inserted in place of the thermocouple and comparing this quantity with the power needed

* Registered du Pont trademark

to take the device to the same temperature with the thermocouple in place. Water will be passed over the cold end of the thermocouple and the temperature rise and flow rate of the water will also be used to calculate the heat loss from the cold end of the thermocouple. The efficiency will be calculated as the power output divided by either the heat input or the sum of power output and heat loss.

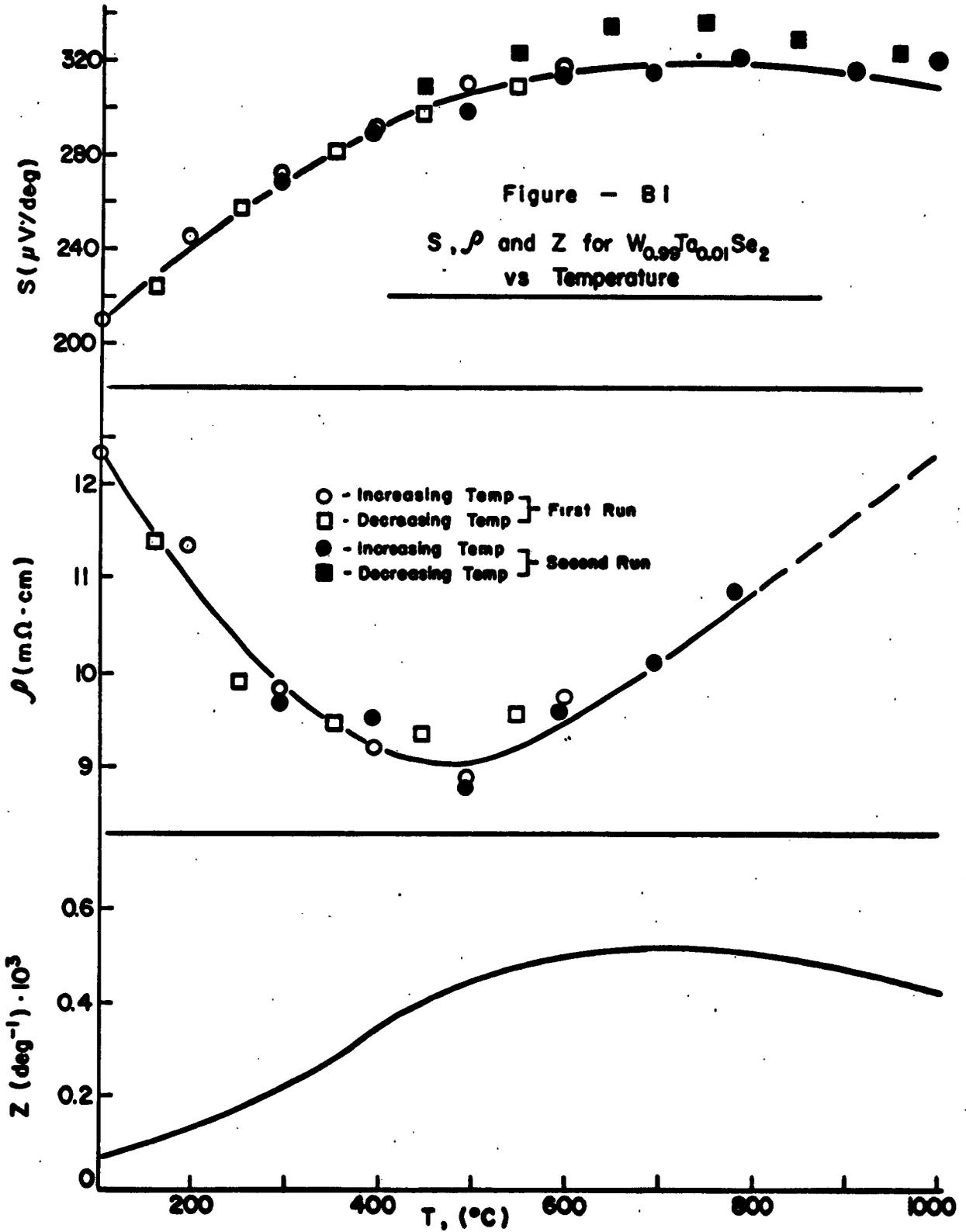
Contact Reactions

To test the effect of contamination of tungsten diselenide in contact with an iron, copper or nickel bearing hot junction electrode, the following experiment was performed. Samples of tungsten diselenide were synthesized both with 1 and 3 at.% iron, copper and nickel. Low-temperature thermoelectric parameter measurements show that the copper and nickel had little effect. These materials yielded properties comparable with that of undoped tungsten diselenide. A sample doped with iron, however, showed a substantial higher resistivity than undoped tungsten diselenide. Thus, it is concluded that copper and nickel are not appreciably soluble in tungsten diselenide, but iron is sufficiently soluble to impart an n-type compensating effect on p-type tungsten diselenide, thus resulting in the extremely low electrical conductivity. Thus, iron may have a deleterious effect when used as a hot junction contact

material. However, the solubility of iron is much lower than that of tantalum in tungsten diselenide and, therefore, may have little effect on tantalum-doped tungsten diselenide. Experiments will be carried out to confirm this speculation.

Acknowledgement

Electrical measurements and sample preparation were carried out by A. R. Sohodski.



C. THERMOELECTRIC DEVICES - H. Valdsaar

In the past Quarter, our work was directed primarily toward experiments on auxiliary materials and fabrication techniques intended to serve as the basis for a final module design. Some information on WSe_2 doping levels and composition methods was also obtained.

Choice of Doping Level and Compaction Method

In Table C-I of the Fifth Quarterly Report, the peak performances of $W_{.980}Ta_{.020}Se_2$ and $W_{.985}Ta_{.015}Se_2$ pressed at 40 tsi were compared in the standard test module. The results for the composition $W_{.990}Ta_{.010}Se_2$ are given in Table C-I of the present report, with the first two sets of data repeated for the sake of completeness. From the point of view of device efficiency, the performance of $W_{.990}Ta_{.010}Se_2$ would be the best within the tested range. For maximum power, 1.5 percent tantalum-doped material may be preferred.

We tested three practical approaches to producing powder compacts in the needed shapes. The information is summarized in Table C-II.

(a) Rectangular steel molds in which the longitudinal axis is normal to the favored pressing direction. When the bars had to be filled into circular modules, the edges were filed off

TABLE C-I

PEAK PERFORMANCE OF MATERIALS WITH VARYING DOPING LEVELS⁽¹⁾

Composition	W. _{0.980} Ta. _{0.020} Se ₂	W. _{0.985} Ta. _{0.015} Se ₂	W. _{0.990} Ta. _{0.010} Se ₂
Resistivity, mΩ-cm	3.2	5.5	10.7
Temperature Interval °C	985-105	1025-125	1050-128
Open Circuit Voltage, mV	108	137	204
Power into Matched Load, mw	82	173	123
Approx. Contact Resistance, mΩ	15	5	15

(1) Pressed at 40 tsi normal to current flow, in 0.3 cm²
x 2 cm ceramic capsules with sealed nickel caps on
hot end, copper wire return leg.

TABLE C-II
CHARACTERISTICS OF POWDER COMPACTS

<u>Shape of Compact*</u>	<u>Dimensions</u>		<u>Pressure</u>	<u>Current vs. Pressing Dir.</u>	<u>Density % Theor.</u>	<u>Resistivity mΩ-cm</u>
	<u>Length</u>	<u>Cross-Section</u>				
Rectangular						
Standard	2"	1/4" x 1/4"	40	⊥	90.8	10.3
Large	4 1/2"	5/8" x 5/8"	15	⊥	84.8	40.0
Circular	1"	3/4" diam.	40		89.2	21.7
	1"	1/2" diam.	40		87.8	42.2
	1/2"	1/2" diam.	40		89.0	35.1
Hydrostatic	1"	5/8" diam.	35	random	87.7	17.0

* All material was $W_{.99}Ta_{.01}Se_2$ from identical preparations.

manually. In this category, a 2" x 1/4" x 1/4" die is being used routinely at 40 tsi. It produces fairly consistent density values provided that the powder is distributed uniformly across the length of the mold before pressing.

A larger mold of the same type has the dimensions 4-1/2" x 5/8" x 5/8". For this mold, 35 tsi was the maximum pressure available. At this pressure, the bars usually cracked. At 15 tsi, whole bars could be obtained, but they possessed low density and high resistivity. An intermediate size mold, 1" x 1/2" x 1/2", is being constructed.

(b) Cylindrical steel molds in which the longitudinal axis is parallel to the crystallographical c axis.

This is a convenient shape to use with circular modules and a full range of pressures is available. Density depends to some extent on the length/diameter ratio. Longer and narrower bars have a lower density. The electrical resistivity, however, is about three times higher in the c (longitudinal) direction than in a direction (radial). Because of a corresponding change in thermal conductivity, the Figures of Merit are probably - accurate measurements are not yet complete - similar in either direction; thus the possibility of using cylindrically pressed modules is not ruled out.

(c) Hydrostatic pressing produces compacts in which no crystallographic direction clearly dominates. The technique is flexible, and any size below 1" diameter can be handled in the available equipment. Final shaping after pressing is done by hand.

The few compacts, so far made, have not indicated improved characteristics over the compacts produced in steel molds, but further attempts will be made to exploit the flexibility of the hydrostatic techniques.

(d) Melting of tungsten selenide - A sample of $W_{.98}Ta_{.02}Se_2$ (see Figure 1) was melted (the test was performed in the Central Research Department under the supervision of Mr. H. S. Young) in a boron nitride crucible at about 1700°C and 15 kilobars. The identity of the product was established by x-ray diffraction. Because of equipment limitations, only small samples (0.5 grams) can be melted.

Module Design

Our basic thermoelectric material, doped tungsten-selenide, is inherently p-type. There is no readily available n-type semiconductor which would properly match the thermoelectric properties of tungsten selenide. Some cerium sulfide compositions, for example, are likely candidates, but these materials are still in development and not available in the market. Under these

circumstances, it is preferable to employ a metal for the other arm in the construction of a device. Particularly if constantan (Figure of Merit: $\sim 0.2 \times 10^{-3}/\text{deg}$) can be used, there would be a considerable contribution (about 50 mV) to the total voltage of the thermocouple, and the metal-semiconductor couple provides higher efficiency than two semiconductors which do not have a comparable Figure of Merit. (R. R. Heikes and R. W. Ure, "Thermoelectricity" Interscience, 1961, p. 513.)

For practically useful modules, the encapsulation of the thermoelectric material in a metal can (e.g. constantan) with insulated walls which would also serve as the n-leg of the couple (see Figure 2) is an attractive possibility. Such a design would offer the utmost weight saving combined with minimal unproductive heat transfer. This approach was actively studied and tested on a number of experimental modules during the last quarter. Ultimately, we propose to use a segmented p-leg (WSe_2 on the hot end, PbTe-based material on the cold end); in this phase of the program, however, we did not concern ourselves with the segmented construction.

1. Choice of Can Material and Dimensions

Ideally, the metal chosen for the can should have good thermoelectric properties and should be both oxidation resistant and selenium resistant. Constantan, which has desirable thermo-

electric properties, does not satisfy either of the chemical requirements in the intended temperature region (up to about 1000°C). Stainless steel and special nickel alloys have the desired oxidation resistance but gradually corrode in a selenium atmosphere (see Figure 3).

In a stability comparison between metals, thin strips were sealed individually in quartz envelopes with $W_{.99}Ta_{.01}Se_2$ powder under partial argon atmosphere (180 mm at 25°C). The sealed tubes were held at $1000^\circ \pm 25^\circ C$ for 70 hours. Constantan, iron and stainless steel (#321) reacted with the selenide. Molybdenum and niobium were seemingly unaffected with no loss of weight. The same result was obtained with Mo and Nb strips covered by a silicide layer. Tantalum, however, had visibly reacted in several spots.

Thus, for durable metal can construction, the following possibilities may be considered:

1. Constantan walls with Mo or Nb end caps, which in turn are protected by a suitable layer against oxidation. Possibly nickel plating of the end caps may be satisfactory. An alternative lies in the application of silicide coatings.
2. A constantan can, with a protective nickel layer on the bottom outside region and a Mo (Nb) coating on the bottom inside.
3. A stainless steel can, with Mo or Nb layer inside, sacrificing the constantan contribution in favor of simplicity of construction. The arrangement has been used for testing tungsten-selenide performance.

In all these cases, of course, the side walls of the metal can have to be electrically insulated from the p-type semiconductor core.

It is well known that the cross-section of the metal has to stand in a certain ratio to the cross-section of the encapsulated thermoelectric material in order that optimum efficiency or optimum power be realized for the thermocouple.

The appropriate formulas are (see e.g., I. B. Cadoff and E. Miller, "Thermoelectric Materials and Devices" Reinhold Pub. Co., pp. 227-237 (1960)):

$$\frac{A_n l_p}{A_p l_n} = \sqrt{\frac{\rho_n k_p}{\rho_p k_n}} \quad \text{for optimum efficiency}$$
$$\frac{A_n}{A_p} \sqrt{\frac{l_p}{l_n}} = \sqrt{\frac{\rho_n}{\rho_p}} \quad \text{for optimum power per unit area}$$

where A = cross-sectional area, cm²; ρ = resistivity, Ω-cm;
k = thermal conductivity, watt/°C.cm; l = length of arm, cm;
n = subscript designating n-type material; p = subscript designating p-type material.

The average values of ρ and k for the three materials W_{0.99}Ta_{0.01}Se₂, constantan (the material actually used was Advance Alloy of Driver-Harris; the physical characteristics of Advance (43% Ni) and constantan (45% Ni) are practically the same for thermoelectric purposes), and stainless steel (#321) in the

temperature range 100-1000°C are the following (in round figures):

	ρ <u>mΩ-cm</u>	k <u>mwatt/°C·cm</u>
W _{.99} Ta _{.01} Se ₂ (p)	10.0	20
Constantan (n)	0.05	400
Stainless Steel	0.10	200

The desired cross-sectional ratios of the individual arms in the constantan-selenide thermocouple are 1:63 for optimum efficiency and 1:14 for optimum power. For the stainless steel-selenide couple, the corresponding ratios are 1:32 and 1:10.

In Table C-III, the numerical values are calculated for realistic cross-sections of the selenide-constantan thermocouple. Three diameters, 1/2", 5/8", 3/4", are given for the tungsten selenide core. In designing for optimum efficiency, the theoretically required wall-thickness is quite thin (about 2-3 mils) and may prove difficult to work with. In practice, a reasonable compromise may be found between power and efficiency needs at about 5 mil wall-thickness.

2. Experimental

At the start, no thin wall tubing was available and the modules were constructed from heavy sheet with rough welds on the sides. The primary purpose was to observe the stability of the materials in the system WSe₂-insulator-metal. A summary of electrical measurements is given in Table C-IV.

TABLE C-III

AREA RATIOS FOR W.₉₉Ta.₀₁Se₂-CONSTANTAN THERMOCOUPLES

Cylindrical W. ₉₉ Ta. ₀₁ Se ₂			
diameter, cm (inches)	1.27 (1/2")	1.59 (5/8")	1.90 (3/4")
W. ₉₉ Ta. ₀₁ Se ₂ , area, cm ²	1.26	1.99	2.76
Constantan, area, cm ²			
optimum efficiency	0.020	0.032	0.044
optimum power	0.090	0.143	0.197
Diameter* of metal can, cm (in.)	1.59 (5/8")	1.90 (3/4")	2.22 (7/8")
Wall thickness**, mm			
optimum efficiency	0.040	0.053	0.063
optimum power	0.180	0.238	0.282

* Allowing for 1/16" thick insulating layer

** Assuming a cylindrical shape with uniform wall thickness

TABLE C-IV

CHARACTERISTICS OF METAL ENCAPSULATED MODULES

Module No.	#14	#16	#18	#20
Wall thickness, mil	25	25	10	10
Wall Material	Const.	Const.	S. Steel	Const.
Cross-Section (3/4")	square	square	circular	square
Length, inches	1-3/8	1-3/8	1	1-3/8
Ta-doping level, %	1.5	1.0	1.0	1.0
Resistivity, mΩ-cm	6	10	40 (a)	18 (b)
Resistance for complete module, mΩ	16-32	30-35	47-50	74-100 (c)
Max. open circuit voltage, mV	236 (d)	200	274	289
Temperature Interval, °C	~900	~800	~1000	~1000

(a) Current flow parallel to pressing direction, high resistivity reflects crystallographic anisotropy due to preferred orientation.
 (b) Pressed at 15 tsi (standard is 40 tsi).
 (c) No iron powder at the bottom, high contact resistance.
 (d) 1.5% Ta-doped WSe₂ has inherently a lower Seebeck coefficient than W₉₉Ta₀₁Se₂.

The hot end contact was WSe_2 to stainless steel, usually with some iron powder. This type contact is good for several days at $900^\circ C$ but fails within hours above $1000^\circ C$. Mo or Nb are good candidates for the hot end contact of durable modules. Comments on other details of construction for the specific modules follow.

Module #14 - Welded from 25 mil constantan sheet in square cross-section $3/4$ " on the edge. Length of the module was $1-3/8$ ". The hot end was of stainless steel. For side-wall insulation, three thin layers of Sauereisen #1 were applied. Because of the difficulties experienced in pressing large sections, four individual $W_{.985}Ta_{.015}Se_2$ bars side by side were fitted into the can with a total cross-section of about 2 cm^2 . Down the center of the can, a protected thermocouple was inserted. The cool end was closed by Pb-Sn solder. A water-cooled copper block pressed against this end. There was no water-cooling on the metal envelope.

The current drawn through a matched load resistance was initially 6 amperes, with a ΔT of about $700^\circ C$ (power 0.5 watts). Testing was terminated when a hole had corroded through the hot end plate on the third day; by that time, the resistance of the module, initially $16 \text{ m}\Omega$, had doubled.

Module #16 - The construction was similar to Module #14 except that a copper cooling coil (1/4") was soldered around the can at the open end. The coil turned out to be too heavy, and the hot end could not reach temperatures above 800°C.

Module #18 - A cylindrical bar, 3/4" diameter, was fitted into a stainless steel can. This was seamless tubing with 10 mil wall thickness and Sauereisen insulation inside. In contrast to the other modules, current flow was parallel to the pressing direction giving relatively high electrical resistance (see Section D of this report). A 1/8" diameter copper cooling coil was soldered to the can. Inner resistance remained fairly steady at 50 mΩ. Maximum open circuit voltage on the first day was 274 mV, on the second day 245 mV.

Module #20 - Square can of 3/4" x 3/4" cross-section, constantan walls 10 mil thick, stainless steel bottom, Sauereisen insulation. The $W_{.99}Ta_{.01}Se_2$ bar, 5/8" x 5/8" in cross-section, 1-3/8" long, had been pressed at 15 tsi; hence, its resistivity was rather high. The maximum current through a matched load was 1.6 amperes.

Acknowledgement

Sample handling and electrical measurements were performed by S. E. Clark

FIGURE 01. MELTED TUNGSTEN SELENIDE IN BORON NITRIDE CRUCIBLE



Cross-section of the boron nitride crucible (3 mm I.D.) with $W_{.98}Ta_{.02}Se_2$ crystals frozen from a melt at approx. 1700°C and 15 kilobars.

FIGURE - C2
METAL CAN ENCAPSULATION

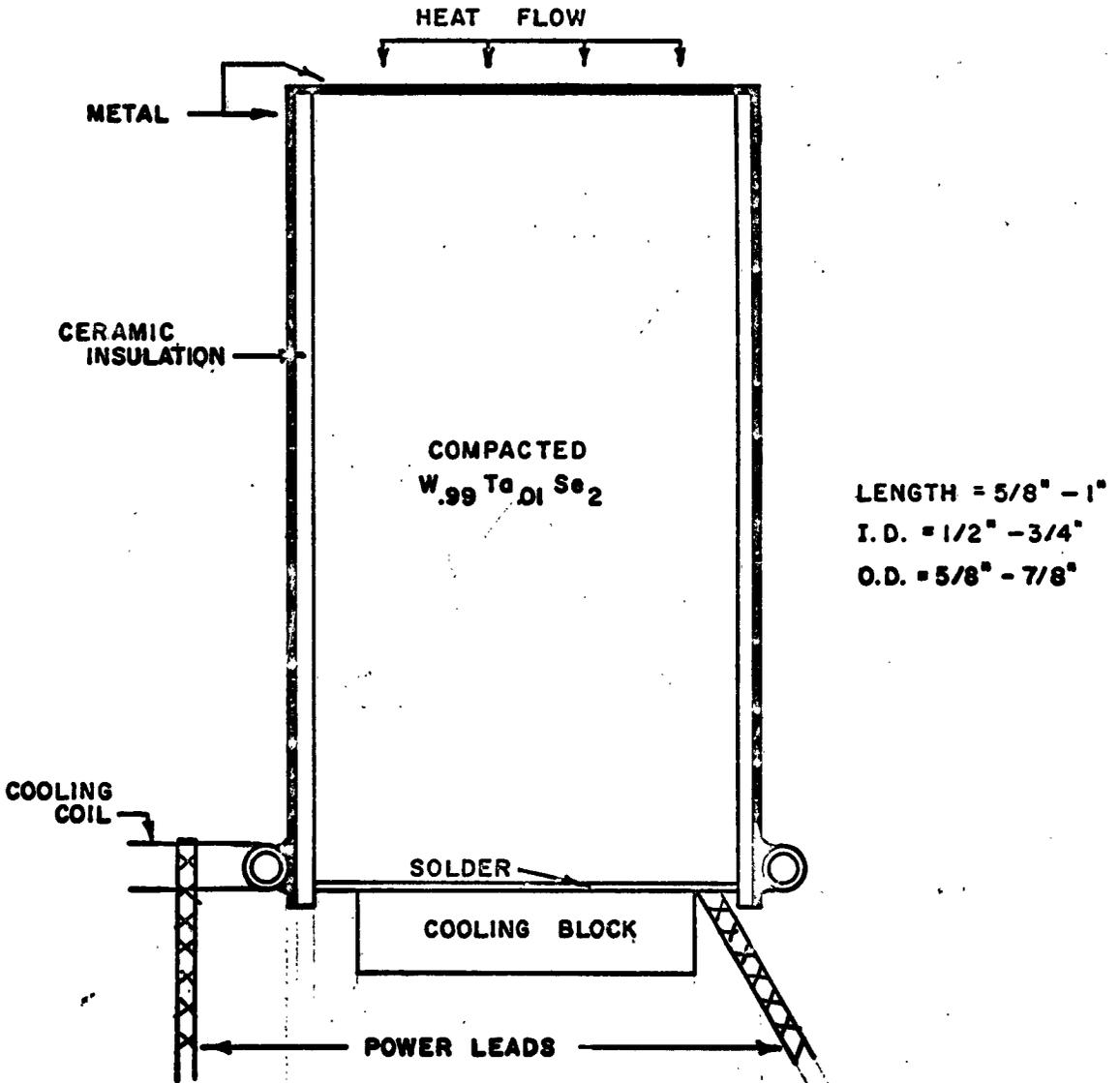
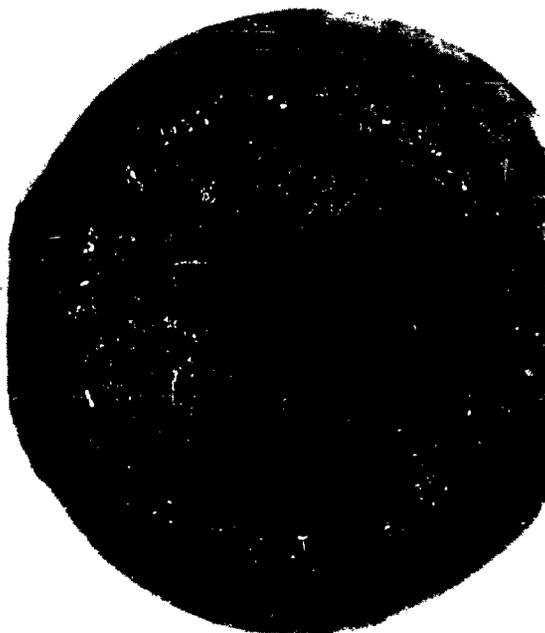


FIGURE C3. TUNGSTEN SELENIDE REACTION WITH STAINLESS STEEL



A rectangular $W_{.99}Ta_{.01}Se_2$ bar, 6 x 8 mm cross-section, inserted in stainless steel tube $3/8$ " I.D. with no wall insulation. Heated for 20 hours at $1000^\circ C$ under argon atmosphere. Most of the crystalline deposit on the walls had formed without physical contact between the selenide and the steel.

D. SUMMARY OF THERMAL CONDUCTIVITY DATA - D. G. Kelemen

Most of the thermal conductivity measurements on tungsten diselenide and its analogues were performed by Dr. L. H. Brixner in work related to but not supported by our Bureau of Ships contract. While the data were quoted occasionally, a general summary seems appropriate at this time.

Experimental

In view of the notorious unreliability of most thermal conductivity measurements, we used three different methods for our measurements.

A device patterned after one described to us by R. O. Carlson of the General Electric Co., Knolls Research Laboratory, shown schematically in Figure D-1, gave the most reliable data but was usable only at room temperature. Many similar devices have also been reported in the literature; see for example, H. Weiss, Ann. Phys., Lpz. 4, 121 (1959).

An instrument described in principle by J. Franci and W. D. Kingery (J. Am. Ceram. Soc. 37, No. 2, 80-84 (1954), sketched in Figure D-2, was our tool for high temperature measurements up to 700°C. It differed from the original mainly in that the wall temperature was controlled automatically to give identical temperatures on the two sides of the appropriate interfaces in the sample-standard stack and at the wall of the four guard heater sections.

Finally, we constructed an exact duplicate of the thermal comparator developed by K. G. Skinner of the Naval Research Laboratory. K. G. Skinner kindly supplied us with some standards to use with his apparatus.

Comparison of our measurements with data reported in literature on various compositions and also a few direct cross-checks on our materials by Dr. Carlson of GE lead us to believe that our data obtained by Carlson's method are accurate within about $\pm 5\%$, while those determined in the Francl-Kingery apparatus can be relied on within about $\pm 20\%$. We have no firm opinion on the accuracy of the NRL apparatus and shall not quote any data obtained with it; the results did not cause us to question the reliability of our other data.

Measurements

Figure D-3 shows Dr. Brixner's results for 3% tantalum-doped tungsten diselenide as a function of temperature. The anisotropy of the electrical conductivity, incidentally, results in a better high-temperature Figure of Merit for the high thermal conductivity direction (\perp to the pressing direction) as discussed in earlier reports.

In Figure D-4, Dr. Brixner plotted the experimental results at room temperature for the undoped system $W_xMo_{1-x}Se_2$ as a function of x measured both parallel to the pressing direction and normal to it. Table D-I shows that, even for the lowest-

thermal-conductivity member of this series, the tantalum doping level has little effect on the results. On the other hand, the thermal conductivities given in Table D-II for an even more complex system containing isoelectronic substitutions in both the cation and the anion sites may include (according to a Wiedemann-Franz law calculation) an electronic contribution in the order of 20%, and the same is true for $W_{1-x}Ta_xSe_2$ above 600°C.

Figure D-5 repeats a plot Dr. Hicks presented before, based partly on his own data and partly on Dr. Brixner's (Fourth Quarterly Report, Fig. B-3), to illustrate the point that the reduction of thermal conductivity by isoelectronic substitution does not manifest itself at high temperatures and has, therefore, no practical value.

TABLE D-I

THERMAL CONDUCTIVITY IN THE SYSTEM $W_{(1-x)/2}Mo_{(1-x)/2}Ta_xSe_2$

x	0.01	0.02	0.03
k, milliwatts/cm-deg	39	34	36

Measured at room temperature, normal to pressing direction.

TABLE D-II

THERMAL CONDUCTIVITY IN THE SYSTEM $W_{.47}Mo_{.47}Ta_{.06}Se_{2-y}Te_y$

y	0.5	1.0	1.5
k_{\perp}	19	18	19
k_{\parallel}	not meas.	10	not meas.

k_{\perp} : Normal to pressing direction

k_{\parallel} : Parallel to pressing direction, both at room temperature

FIGURE - D1
CARLSON APPARATUS

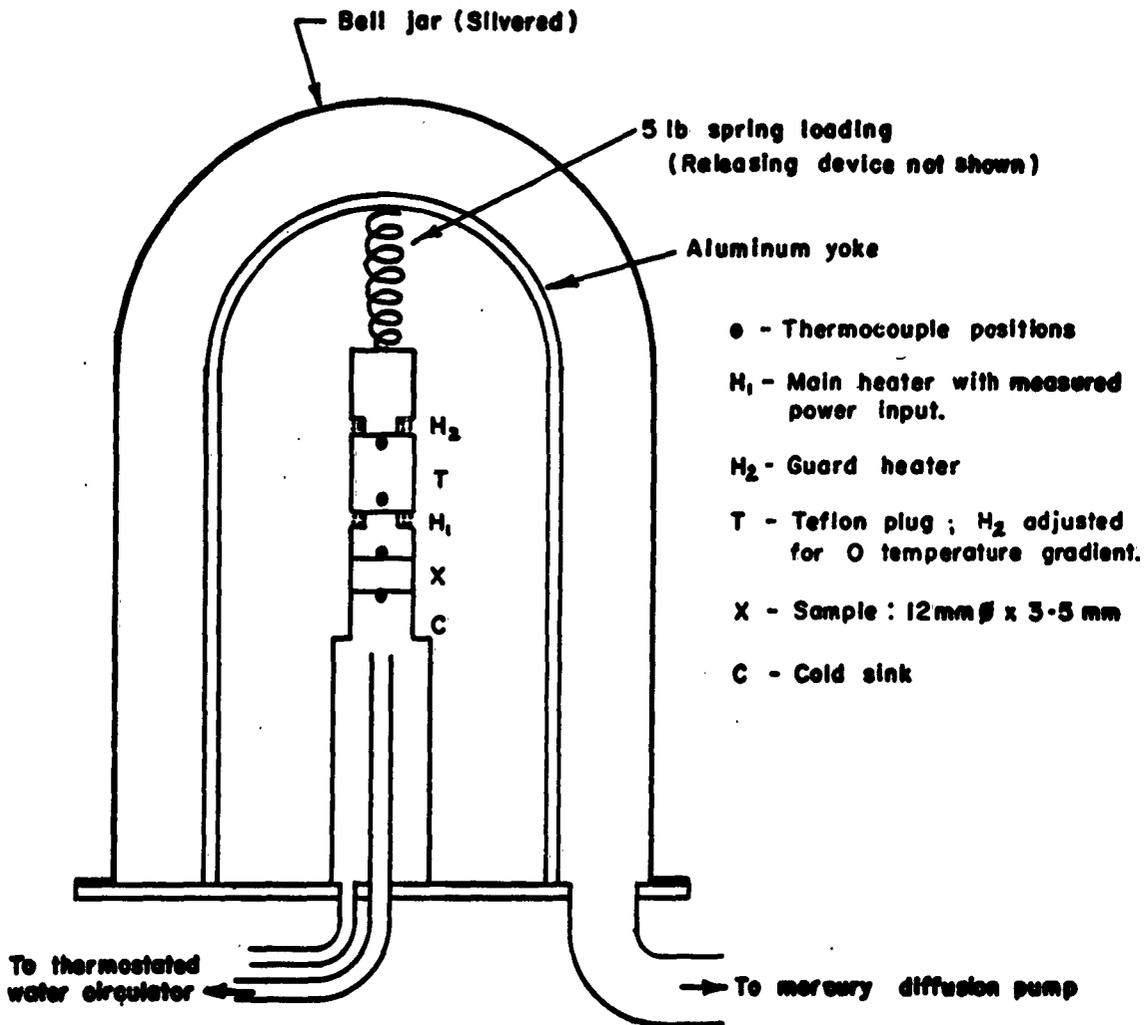
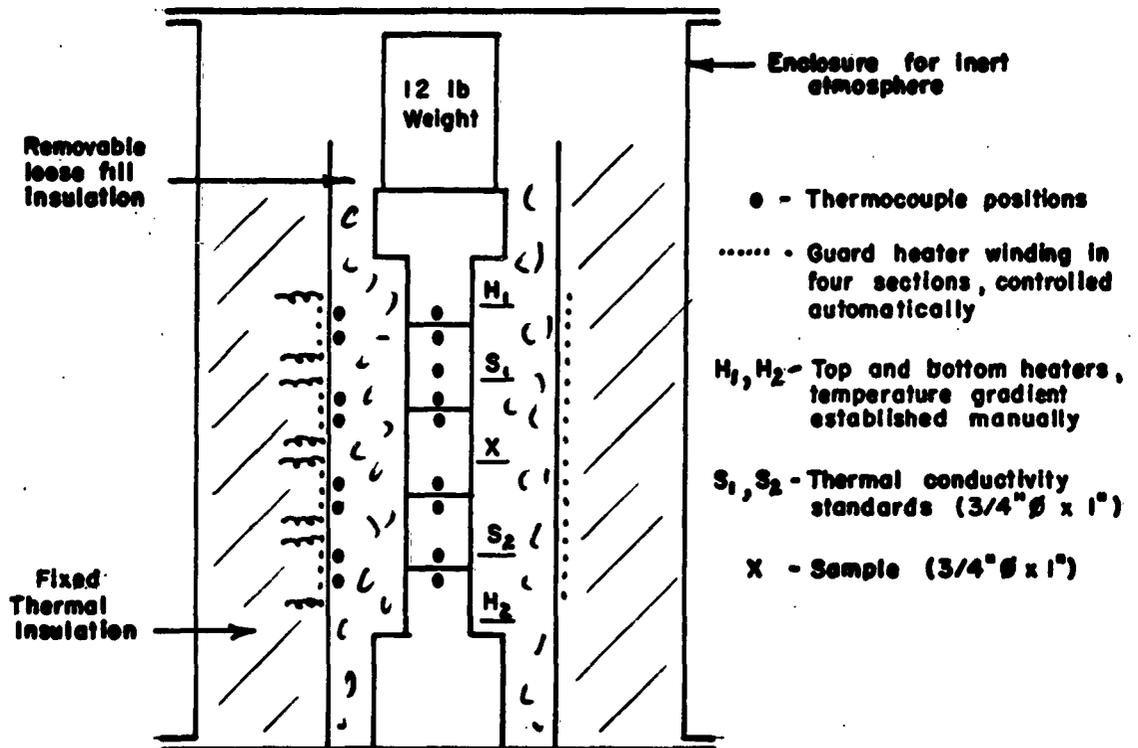


FIGURE - D2
FRANCL - KINGERY APPARATUS



THERMAL CONDUCTIVITY OF $W_{.97}Ta_{.03}Se_2$
AS A FUNCTION OF TEMPERATURE
IN a and c DIRECTION

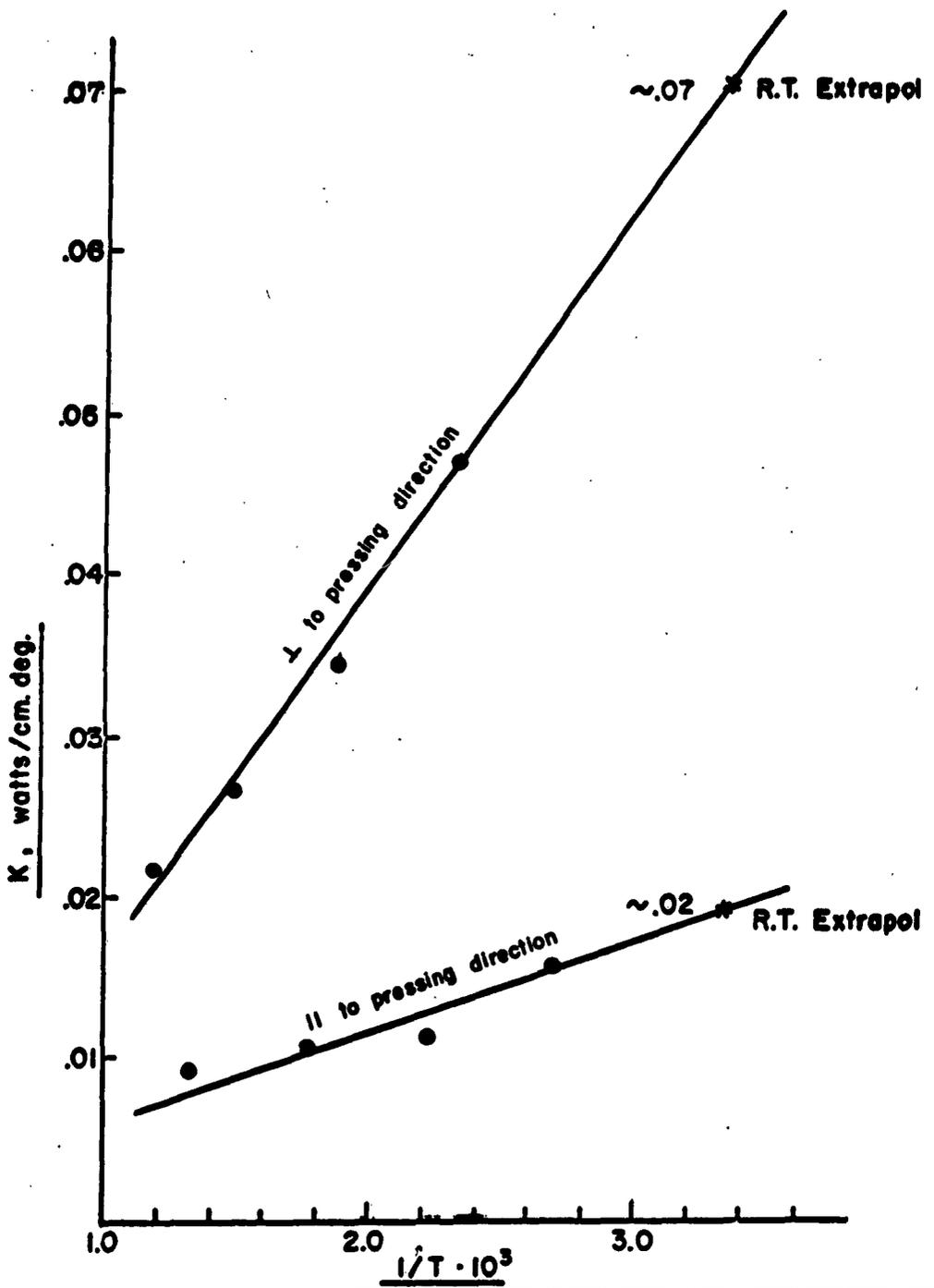


FIGURE - D 3

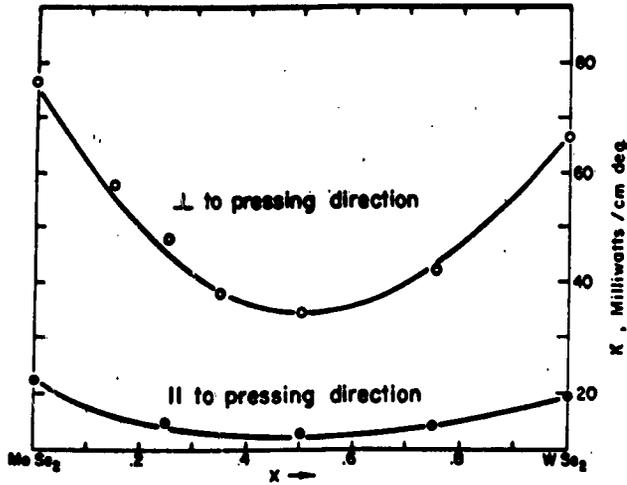


Figure - D4 Thermal Conductivity for the $W_xMo_{1-x}Se_2$ System as a Function of x .

THERMAL CONDUCTIVITY (pressing direction) vs 1/T

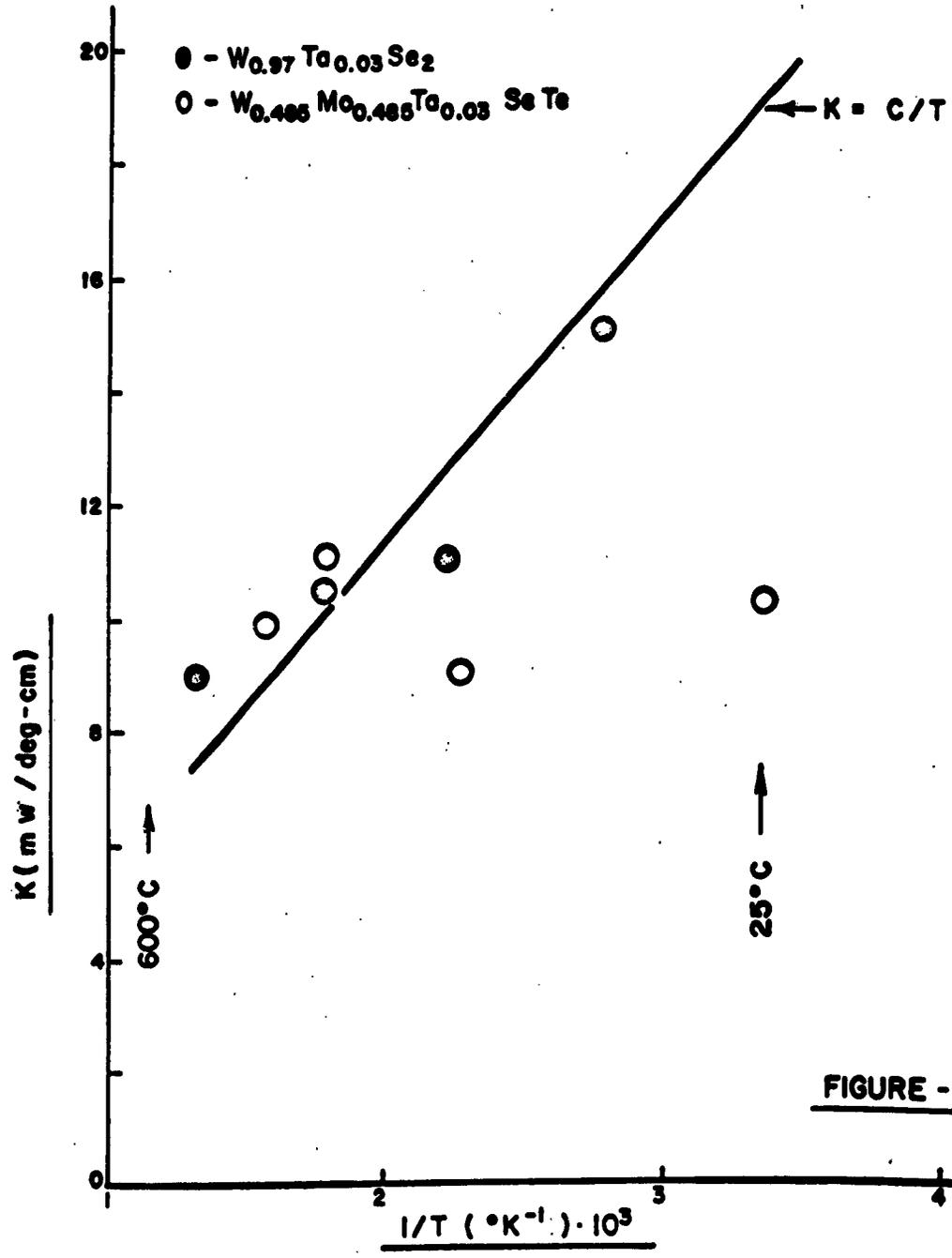


FIGURE - D5