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THERMOELECTRIC MATERIALS EVALUATION PROGRAM
ANNUAL TECHNICAL REPORT FOR FISCAL YEAR 1979

OCTOBER 1979

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by
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J. D. Hinderman

Program Manager

Prepared Under
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for the
Power System Section
Advanced Nuclear Systems and
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MINNESOTA MINING AND MANUFACTURING COMPANY

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St. Paul, Minnesota 55101

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FOREWORD

The primary objective of the Thermoelectric Materials Evaluation Program is the design and development of a high efficiency thermoelectric couple consisting of a TPM-217 P-element and an N-element which has a hot segment based on rare earth selenide technology and a lead telluride cold segment. The design is to be based on operation at a hot strap temperature of 850°C or higher and a cold junction of 150°C which will be capable of stable operation up to 50,000 hours. A long term objective is the development of a thermoelectric couple with a goal of 13% couple efficiency when operated at a hot junction temperature of 900°C and a cold junction temperature of 150°C and a high efficiency couple with operation up to 1200°C.

An additional objective is the generation of data with, and the demonstration of the thermoelectric performance of couples of P-TPM-217 and N-neodymium selenide materials in geometries necessary for operation in a radioisotope thermoelectric generator. A further objective is the design, development and performance demonstration of thermoelectric modules consisting of P-TPM-217 and N-rare earth selenide couples in geometries necessary for operation in a radioisotope thermoelectric generator.

ABSTRACT

Optimization was initiated with respect to performance, operating temperatures and thermoelectric properties of an N-type material based on rare earth (neodymium and gadolinium) selenide technology. Effort was expanded to experimentally describe the chemical, electrical and physical behavior of P-type thermoelectric material over a range of temperatures. Emphasis was changed in P-type material research from basic properties to sublimation suppression by wrapping, and to the understanding of contact resistance problems at the hot end. Analytical performance calculations were made as an aid in couple development. In the area of module development an evaluation of the reduction of bypass-heat loss was made and module M-22R was placed on test. Parts were fabricated for M23R. Data on long term operating characteristics, ingradient compatibility, and reliability of elements and couples was obtained.

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INTRODUCTION

This Annual Technical Report was prepared under Contract EY-76-C-02-2331 with the United States Department of Energy and covers the performance period which extends from October 1, 1978 to September 30, 1979.

HIGHLIGHTS

TASK 1.0 – N-TYPE MATERIAL DEVELOPMENT

1.1 OBJECTIVE

The objective of this task is to optimize with respect to performance, operating temperatures and thermoelectric properties an N-type thermoelectric material, based on gadolinium-selenide technology, for use with P-type TPM-217 thermoelectric material.

During this reporting period, emphasis was originally placed on improvement in synthesis and fabrication of gadolinium selenide legs in support of the Galileo program. Midway in the program emphasis was switched to include fabrication of neodymium selenide legs, which is similar in structure to gadolinium selenide but is more homogeneous and sinters more uniformly and conventionally.

1.2 MATERIAL SYNTHESIS

Data derived from the LTR and RQC steps are recorded in Table 1, with sintering treatments and electrical properties listed in Table 2.

GADOLINIUM SELENIDE SYNTHESIS

From Table I it will be noted that all 420 gm GdSe_x batches lost selenium during the RQC step, the change in Se/Gd ratio being from 1.4908 mean ($\sigma = .00043$) to 1.4898 mean ($\sigma = .00065$) or only 0.067%.

A glance at Table 2 indicates that much larger batch-to-batch variations exist in electrical characteristics of sintered legs:

ρ_{RT}	3.7 – 5.2 ($\text{m}\Omega\text{-cm}$)	~	29%
ρ_{500}	11.9 – 15.8 ($\text{m}\Omega\text{-cm}$)	~	25%
S_{500}	205 – 218 $\mu\text{V}/^\circ\text{C}$	~	6%
Density	6.69 – 7.21 g/cc	~	7%

It seems clear that much of the variability in Galileo batches stems from ingot inhomogeneity and sintering problems due to oxidation, temperature variations and so forth together with measurement errors, rather than from selenium loss in the formation of the ingot in the initial synthesis

Neodymium Selenide Synthesis

From Tables I, II and III, it will be noted that the selenium loss in 140 gm. batches is much larger and more variable than in the case of gadolinium-selenide.

Se/Gd ratio LTR — 1.4910 (σ .000087)

RQC — 1.4759 (σ .0060)

(neglecting # 2686, which is of different composition)

This difference in means corresponds to a variation of $\frac{1.4910 - 1.4759}{1.4910 \times 100}$ or 1.01%, about

fifteen times greater for NdSe_x than for GdSe_x ; the standard deviation of the RQC compositions is about 9 times greater also.

This effect seems to be due to the greater difficulty of completely reacting Nd and Se; it will be noted that batch # 2690, which used foil neodymium and exhibited no pellets of unreacted material had better results:

Se/Gd ratio LTR — 1.4914

RQC — 1.4877

Corresponding to a difference in means of $\frac{1.4914 - 1.4877}{1.4914 \times 100} = 0.248\%$

which is a factor of 4 worse than gadolinium and may be merely a reflection of the larger surface/volume ratio of a 180 gm ingot compared to a 420 gm ingot.

Electrical property variation are:

ρ_{RT}	1.59 — 2.34	32%
ρ_{500}	4.0 — 6.5	38%
S_{500}	135 — 164	21%
Density	6.07 — 6.67	9%

(Neglecting # 2688 (No binder) which may have oxidized.

In general, the property variation is not much greater than in gadolinium-selenide, except for Seebeck coefficient; extraneous resistance values are generally better, particularly for the highest density batch #2685 — $0\% \pm 10$. The only samples exhibiting extraneous resistance values greater than 30% were the control (or non-binder) pellets from batch #2688. These were exposed to glovebox atmosphere for about a week while debonding experiments were in process: it is encouraging to note that the bonded samples from batch #2688 exhibited good properties, suggesting that the binder may act as an oxidation barrier as well as yielding better density. The conclusion from this is that in contrast to Gadolinium Selenide, the variation is a result of loss of selenium in the initial synthesis rather than sintering abnormalities.

TABLE I

Compositional Data — Gadolinium Selenide Batches

"N" No.	Ames Gadolinium No.	Sample Weight (grams)	Composition — GdSe _x	
			LTR	RQC
2662	61478*	420	1.4901	1.4888
2664	12478	420	1.4911	not RQC'd
2665	61478*	380	1.4705	1.4700
2667	73178*	420	1.4903	1.4898
2668	73178*	420	1.4910	1.4898
2669	73178*	420	1.4910	1.4893
2670	73178*	420	1.4911	1.4907
2671	73178*	390	1.4912	1.4895
2672	81478*	420	1.4912	not RQC'd
2673	81478*	420	1.4909	not RQC'd
2674	81478*	420	1.4911	not RQC'd
2675	81478*	420	1.4910	not RQC'd
2676	91578*	420	1.4909	not RQC'd
2677	91578*	420	1.4911	not RQC'd
2678	91678*	420	1.4911	not RQC'd
2679	91678*	420	1.4911	not RQC'd
2680	102878*	420	1.4911	not RQC'd
2681	102878*	420	1.4911	not RQC'd
2682	102878*	420	1.4912	not RQC'd

***Galileo" N-Type batch — gadolinium procured by DoE.

NdSe_x Compositional Data

"N" No.	Ames Nd. No.	Batch Size (grams)	NdSe _x	
			LTR	RQC
2683	11375	140	1.4910*	1.4682
2684	71878	140	1.4911*	1.4781
2685	71878	140	1.4911*	1.4817
2686	71878	140	1.5005*	1.4788
2687	71878	140	1.4910*	1.4805
2688	71878	140	1.4909*	1.4709
2690	71878	180	1.4914	1.4877

*Several very small hard pellets present in LTR material —
RQC done on all material.

TABLE II Gadolinium Selenide Processing

Batch	Wt. (g)	RQC GdSe _x X	Grind- ing	Pre- pressing Pressure (psig)	pressing Pressure (psig)	Sintering Cycle			Location in Sintering Chamber	Density (g/cc)	ρ RT (m Ω -cm)	ρ 500 (m Ω -cm)	S500 (μ V/ $^{\circ}$ C)	Calc. Ext. Res. (%)
						Rate ($^{\circ}$ C/min)	To: Soak Temp. ($^{\circ}$ C)	For: (hrs)						
2662	420	1.489	Dry	200	20,000	30	1000	1						
						0.5	1350	2						
						0.5	1630	8						
									T2-10	7.21	3.7	12.2	206	35
									T3-5	7.18	4.1	13.0	208	40
									T4-7	7.18	4.3	12.6	208	35
2665	420	1.470	Dry	200	20,000				T5-21	7.16	4.2	12.6	210	33
									T6-6	7.18	4.4	12.2	210	29
						30	1000	1	T2		2.3	5.5	152	23
						0.5	1350	2	T3		2.1	6.2	149	43
						0.5	1630	8	T4		2.2	6.4	149	48
									T5		2.2	5.5	148	28
2667	420	1.490	Dry	200	20,000				T6		2.1	5.1	148	19
						30	1000	1	T2-1		4.2	12.1	207	33
						0.5	1350	2	T3-5		4.1	12.4	206	37
						0.5	1630	8	T4-15	7.11	4.3	12.1	208	31
									T5-14	(σ ,045)	4.6	11.9	205	33
									T6-12		4.4	12.2	206	34
2668	420	1.490	Dry	200	20,000	30	1000	1	T2-9		4.9	14.5	218	37
						0.5	1350	2	T3-3	6.89	5.2	14.4	218	37
						0.5	1630	8	T4-7		5.1	14.8	218	41
									T5-18	(σ ,13)	5.1	15.8	218	50

TABLE III Summary of Neodymium Selenide Properties

Batch No.	Batch Size (grams)	Composition NdSe_x		Average Density (g/cm^3)		Sample	ρ r.t. ($\text{m}\Omega\text{-cm}$)	ρ 500°C ($\text{m}\Omega\text{-cm}$)	$S_{500^\circ\text{C}}$ ($\mu\text{V}/^\circ\text{C}$, rel. to aba)	% Extraneous
		LTR	RQC							
N-2683	140	1.4910	1.4682	6.08	Sinter 3	T2-1	**	5.3	144	30
						T2-2	**	4.0	135	9
						T4-1	**	4.6	138	20
						T4-2	**	5.1	142	30
N-2684	140	1.4911	1.4781	6.21		T3-2*	2.03	6.5	162	26
						T4-2	2.07	6.5	161	27
						T4-3	1.76	6.1	164	16
						T5-2*	**	6.3	162	22
N-2685	140	1.4911	1.4817	6.67		T3-3	1.71	4.1	154	-10
						T3-4	1.65	4.2	153	-8
						T4-1	1.66	5.2	156	8
						T4-2	1.59	5.1	156	6
N-2686	140	1.5005	1.4788	6.35		T3-1	2.25	5.5	160	11
						T3-3	2.18	6.0	159	20
						T4-1	2.08	6.2	160	22
						T4-3	1.99	6.2	160	22
N-2687	140	1.4910	1.4805	6.37		T3-2	2.34	6.4	163	24
						T3-3	2.10	***	163	
						T4-2	2.25	5.8	164	9
						T4-3	2.50	****	—	—
N-2688	140	1.4909	1.4709	6.07	Binder	T3-2	1.70	3.5	138	-7
						T3-3	1.64	4.1	138	9
				5.61	No Binder	T4-3	2.45	7.0	152	54
						T4-4	2.48	5.8	147	36

*Elements prepared from powder ground extra two hours

**Measurement not done

***Sample loaded into high temp. fixture with high resistance

****Sample broke as it was being loaded into high temp. ρ fixture - no high temp. measurements done

1.3 MATERIAL ANALYSES

1.3.1 Chemical, Crystal Structure, and Metallurgical Analyses

Chemical analyses were performed on raw materials, on atmosphere for control of the synthesis process, on element contact structure, on doping studies, and on isothermal chemical compatibility experiments as required. In Top Summary Report No. 117, several phases identified in the gadolinium-selenium-type system were tabulated and remarked upon. Further work reported in Top Summary Report 121 elucidated the nature of the black phase of composition approximately $\text{GdSe}_{1.5}$ with orthorhombic crystal structure. A crystal model was built to demonstrate the crystal structure arrangement of the orthorhombic phase. It is essentially a molecular structure made up of double molecules $(\text{Gd}_2\text{Se}_3)_2$ arranged in layers. From samples of various compositions and heat treatments, it was observed that the cubic orthorhombic transformation appears to be initiated at free surfaces in the presence of oxygen, with oxidation of the sample increasing the proportion of orthorhombic phase so that samples with optically detectable oxide skins were stable as single phase orthorhombic at 900°C .

Heat treatment experiments were performed during the period of this contract on samples N2645/48 T3 and T5 in a vacuum of 10^{-6} Torr and at a temperature of 900°C . It was observed that after 100 hours, this heat treatment at 10^{-6} Torr pressure produced a structure consisting of a core of cubic phase material surrounded by an orthorhombic phase with grains extending inwards from the surface. The cubic material exhibited visible cracks and was surrounded by a kind of "river pattern" of microcracks at the cubic-orthorhombic interface; these microcracks extended a little way into the orthorhombic and then appeared to heal in such a way that no continuous crack extended to the surface. Rather short sections of crack were isolated from each other, often separating orthorhombic grains in different orientations. If it is assumed that the orthorhombic phase is less dense than the cubic phase, a possible explanation for this effect is that elastic strain at the interface causes cracking in the cubic phase (which is in tension), while the compressive stresses remaining in the orthorhombic phase close the cracks and allow healing.

A eutectic phase which occurred in the attempted sintering of N-2659 led to melting instead of sintering. The eutectic was present in sufficient concentration for SEM analyses. The composition derived from this analysis was $\text{GdSe}_{1.40.5}$, suggesting that the compound may be essentially GdSe_2 with substitution of some oxygen for selenium. There was insufficient material for x-ray diffraction characterization.

1.3.2 Thermoelectric Properties

Samples of N and P material were measured for Seebeck coefficient and resistivity on a routine basis.

1.4 MATERIAL PROCESSING

1.4.1 Processing of Gadolinium Selenide

Two pressing/sintering experiments were conducted to evaluate an alternative grinding process to produce a smaller particle size, hence more sinterable, powder. It has previously been reported that the large RQC ingots are inhomogeneous, with considerable amount of a red material which is both insulating and of lower melting point than the bulk GdSe_x phase. Analysis of this red material indicates that it is very close to stoichiometric Gd_2Se_3 . In the standard sintering process, high density sintering appears to be promoted by the formation of some liquid phase material which would be expected to concentrate at grain boundaries. To develop an alternative to the present process which avoids liquid sintering, either more homogeneous starting material must be used or the sintering must be carried out at a lower temperature. The data in Figure I summarizes earlier data indicating that a lower temperature sintering cycle which avoids liquid sintering is effective in

decreasing extraneous resistance. The difficulty with this process is that it is difficult to obtain the high densities needed. The standard procedure in a situation like this is simply to produce a more sinterable powder by alternative or extended grinding cycles. This was the procedure described in the experiments summarized in Table IIIa.

In P/S experiment 119, the low temperature reaction product (LTR) was milled directly in a ball mill for 48 hours without going through the usual ingot forming step. By starting from the LTR product, the red phase was avoided and a more homogeneous sintering powder was obtained. Previous experiments using the LTR material directly had resulted in low extraneous resistance for the low density obtained (Figure 1) so this was a logical candidate for an alternative grinding procedure. The ball milling operation was successful in producing a powder with about twice the surface area of standard material. The attempted sintering caused melting of the material. Metallographic examination of the melt showed a eutectic previously associated with oxidation during processing, and subsequent analysis (section 1.3) indicated a eutectic composition of $\text{GdSe}_{1.40.5}$.

Pressing/sintering experiment P/S 120 represented a repetition of experiment P/S 119, but using a conventional RQC ingot (N2647) instead of the LTR product. Again, a higher surface area powder was obtained but melting occurred during attempted sintering. The conclusion drawn from these experiments is that surface area can be increased but that the ball milling approach resulted in oxidation of the GdSe_x powder.

In addition to the experiments aimed at improving the sintering process of the gadolinium selenide, experiments were conducted on post sintering heat treatment of the gadolinium selenide to form the orthorhombic phase.

Cubic as sintered legs from batches #2662 and #2665 were annealed at 800°C for 200 hours in vacuo in order to estimate the electrical properties to be expected from orthorhombic GdSe_x . In earlier experiments annealing was performed using a horizontal furnace so that the samples together with a titanium/zirconium getter experienced a temperature gradient: the legs themselves were subject to a fairly uniform temperature of 800°C , but the getter chips ran considerably cooler $\sim 400^\circ\text{C}$.

While this technique was found to yield orthorhombic material of low extraneous resistance, it was not suitable for preparing larger numbers of legs simultaneously: for production in quantity it was found necessary to use larger silicon tubes and a vertical furnace, which meant, inter-alia, that the getter chips would have to be in the isothermal 800°C zone of the furnace.

Results of initial annealing experiments on batches 2662 and 2665, using both techniques are listed in Table IV. Three features of interest are apparent:

1. The Seebeck values for #2665 hardly changed during annealing, unlike those for #2662 which fell dramatically.
2. Extraneous resistance values for vertically annealed samples were inferior to those of horizontally annealed ones.
3. There is a suspicion that a tube-to-tube variation exists both in vertical and horizontal anneals.

FIGURE 1: Low Temperature Sintering

TABLE IIIa Gadolinium Selenide Processing

P/S Exp. No.	Batch	Wt. (g)	RQC GdSe _x X	Grind- ing	Pre- pressing Pressure (psig)	Pressing Pressure (psig)	Sintering Cycle			Location in Sintering Chamber	Density (g/cc)	RT (mΩ-cm)	500 (mΩ-cm)	S ₅₀₀ (μV/°C)	Calc. Ext. Res. (%)
							Rate (°C/min)	To: Soak Temp. (°C)	For: (hrs)						
119	2659	340	1.50***	Dry*	200	20,000	{ 0.5	1630	0.5 }	TEST SINTERS ONLY: ALL MELTED					
120	2647	420	1,490	Dry**	200	20,000	0.5	1630	0.5	TEST SINTERS ONLY: ALL MELTED					

NOTE:

* Ball-milled 48 hours in ceramic jar with iron balls.

** Ball-milled ½ hour in tungsten carbide jar with tungsten carbide balls, then 48 hours in ceramic jar with iron balls.

*** LTR ground directly; no RQC ingot formed.

Metallographic examination revealed that batch 2662 legs were all transformed, while batch 2665 legs showed very little transformation, and then only at the surface. This indicates that the transformation must be composition-dependent, such that a $\text{GdSe}_{1.47}$ material does not transform at 800°C , unlike the $\text{GdSe}_{1.49}$ material.

The difference between vertical and horizontal annealing was traced to impurities in the getter chips which evidently could volatilise at 800°C though not at 400°C .

For this reason, all later experiments used getter chips which had been baked in high vacuum at 1000°C to remove impurities.

The suspected tube-to-tube variation was ascribed to oxidation caused by very slight leaks in the welded seals in the silica tubes, and for that reason a much greater concern for seal integrity was generated.

The improved technique was employed to make 0.2" diameter N-legs from batch N-2669 to be used in preparing segmented elements. Since these samples were too small to yield data similar to that derived from 0.3" diameter material, electrical property measurements will be discussed in a later section of this report concerning bonded elements.

TABLE IV Annealing Experiment

Sample	Tube #	Seebeck 500	Resistivity 500	Extraneous	
Batch 2665		149.2 ($\sigma = 1.6$)	5.74 ($\sigma = .54$)	32.2 ($\sigma = 12.6$)	
Annealed	1	152.4 152.1	5.8 5.8	28 27	26, $\sigma = 2.6$
Vertical	2	151.3	5.5	23	
Annealed	3	150.7 150.0	4.4 4.9	-1 11	12.5, $\sigma = 10.2$
Horizontal	4	149.4 150.7	5.1 5.4	17 23	

Sample	Tube #	S500	P500	Extraneous %	
Batch 2662		208.4 ($\sigma = 1.67$)	12.52 ($\sigma = 0.33$)	34.4 ($\sigma = 3.97$)	
Horizontal	1	112.7 111.5	3.0 3.2	10 19	19, $\sigma = 9.4$
Anneal	2	113.4 109.8	3.6 3.0	32 15	
Vertical	3	113.4 111.1	3.6 2.9	32 10	40.3, $\sigma = 37$
Anneal	4	116.2 115.0	3.6 5.5	25 94	

1.4.2 Preparation of Lead Telluride

Much of the development of segmented N-legs was performed using 0.2" diameter lead-telluride pellets of 2N composition purchased from Global Thermoelectrics Co., but in addition some lead telluride batches were made in our laboratory.

Details of fabrication variables and associated electrical properties of different lead-telluride materials are given in Table V.

The main conclusion of this work is that 3M material is equivalent to that purchased from Global Thermoelectrics.

1.4.3 Bonding Experiments

In order to prepare segmented N-legs, some kind of diffusion barrier between the $GdSe_x$ and PbTe components is necessary, and since nickel is customarily used for the hot-end of $GdSe_x$ it is natural to use it for segmented applications. This approach cannot be applied to PbTe, unfortunately, since nickel diffuses into it at operating temperatures ($\sim 400^\circ C$). Iron foils are needed in this case based on the technology base for contacting PbTe developed in the SNAP Programs. However, the iron-foil must be prior sputtercoated with nickel, since PbTe will not bond directly to iron, but will to nickel.

Thus we arrive at the "four-foil" concept:

FIGURE 1a Four Foil Concept

Here, the two bonded segments remain to be joined together, and a pure indium solder may be employed.

Clearly this process is rather tedious, so a technique was developed to cut out several steps — the "three-foil" concept.

TABLE V PbTe Synthesized During Fiscal Year 1979

Batch No.	Weight - In Comp. (Weight %)			Synthesis Cycle	Electrical Charac. of Sintered Pellets		
	Pb	Te	PbI ₂		E _{oc} (mv)	$\rho_{r.t.}$ ($\mu\Omega$ -1)	
102578	62.1318	37.8388	0.02942	} 300g Forming gas atmosphere, Vit. carbon cruo. Heat to 327°C, hold until exotherm over & temp starts to drop – 8 min. Heat to 350°C, soak for 30 min. Heat to 950°C, soak for 30 min. Furnace cool to 800°C, air cool to room temp.	2-11	62.6	286
					2-12	61.5	238
					2-13	62.9	267
					2-14	61.9	256
51479	62.1310	37.8390	0.0299	} 200g Forming gas atmosphere, Vit. carbon cruo. Heat to 327°C, exotherm, temp. drops Heat to 350°C, soak for 30 min Heat to 950°C, soak for 30 min. Furnace cool to 800°C, air cool to room temp.	2-11	Pressed w/old press, .187" die multiple filling of cavity, pressed to 1000 lb.	
					2-12	Pressed w/new press, .210" die multiple filling of cavity, pressed to 1000 lb.	
					2-13	Pressed w/old press, .250" die multiple filling of cavity, pressed to 600 lb.	
					2-14	Pressed w/old press, .250" die multiple filling of cavity, pressed to 1000 lb.	
52979	62.1314	37.8387	0.02986	} 250g Forming gas, Vit. carbon Heat to 327°C, exotherm, temp drops - 7 min. Heat to 350°C, soak for 30 min. Heat to 950°C, soak for 30 min. Furnace cool to 800°C, air cool to room temp.	Still in ingot form		
6579	62.1311	37.8390	0.02992	} 250g Forming gas, Vit. carbon Heat to 327°C, exotherm, temp. drops - 6 min. Heat to 350°C, soak for 30 min. Heat to 950°C, soak for 30 min. Furnace cool to 800°C, air cool to room temp.	Still in ingot form		

Global PbTe M1085/T214130

This is a comparison of our measurements to those done by Global -
Samples labeled "Test Sample" were measured by Global prior to shipment
of batch and then measured in our Seebeck fixture. Other two samples
were only measured in our Seebeck fixture.

	E _{oc} (mv) 3M Measured	E _{oc} (mv) Global Measured
Test Sample 1-E	60.6	66.8
1-7	57.1	
Test Sample 1-D	58.8	66.3
1-6	59.8	

In this case the superfluous nickel foil at the cooler end of the GdSe_x was omitted, and the n-leg bonded in one operation using pre-bonded GdSe_x , but no solder.

Electrical measurements made on bonded segments of the 4-foil version are quoted in Table VI, along with measurements of bonded legs. The data are still quite preliminary, but it does seem clear that the major component of n-leg resistance is due to the GdSe_x segment (roughly $5.6 \text{ m}\Omega$ out of 6.9) and that the GdSe_x material itself is responsible for most of the variability observed (mean resistance $5.6 \text{ m}\Omega$ with $\sigma = 4.1 \text{ m}\Omega$) in the bonded legs: this is not conforming in view of the fact that the orthorhombic GdSe_x is known to contain partly-healed transformation cracks.

1.5 ELEMENT CONTACTING

The sputter coating process is sensitive to sputtering atmosphere impurities and sample preparation. Poor adhesion and high contact resistances has occurred in the sputtercoating of GdSe . A definite cause and effect relationship was not positively established, but repair of the dark space shield and correction of several leaks resulted in a return to proper operation of the system. After these repairs, the contact resistances of eight nickel sputter coated elements from batch N2649 were measured at $1.3 \pm 0.2 \text{ m}\Omega$. Metallographic examination showed the nickel sputtercoating to be about $20,000 \text{ \AA}$ thick. The initial measurements of nickel sputter coated legs yielded contact resistances of $0.7 \text{ m}\Omega$, while three fold extension of the sputtering cycle to build up a thick nickel coating produced a nickel contact as low as $0.35 \text{ m}\Omega$ (2639, T4-7). The uniformity, quality, and capacity of the sputtering operation could be improved by a new sputtering system; a purchase justification was written on a new sputtering system for the Galileo Program, and the system was purchased and installed.

The alternative approach of using a vendor for sputtering was investigated. Koral Labs sputtercoated nine legs in a process normally duplicating our cycle. The contact resistances was very high ($10.3 \pm 5 \text{ m}\Omega$), rendering this approach unacceptable. To maintain better control of the atmosphere during the sputtering, a partial pressure analyzer was attached to the sputtering system. Some water and organics were detected, but no air leaks.

Experimentation with Freon grinding and cleaning of the legs showed promise in reducing pumpdown time, but was abandoned in favor of the established procedures.

TABLE VI (a) Summary of Q.C. of Bonded GdSe_x Segments

Sample	Total Length (in.)	Diameter (in.)	Flatness (in.)	Total Resistance (mΩ)	Contact Resistance (mΩ)	Contact Resistance (mΩ)
N-2669-I-1	.178	.206	.002	4.3	.30	.15
-2	.178	.200	.002	2.8	.34	.23
-3	.177	.204	.003	3.9	.59	.36
-4*	.180	.195	.002	3.1	.32	.36
-5	.179	.202	.003	3.6	.27	.41
-6	.177	.205	.003	4.0	.36	.29
-7	.177	.204	.003	3.7	.34	.49
-8	.177	.200	.003	2.6	.37	.29
-9	.176	.203	.004	3.2	.28	.19
-10	.178	.206	.002	4.0	.34	.48
-11	.177	.202	.003	3.5	.32	.28
N-2669-I-13**	.177	.205	.004	3.3	.46	.44
-14	.176	.200	.004	2.8	.52	.37
-15	.178	.204	.005	4.1	.48	1.15
-16	.176	.205	.004	4.1	.64	.40
-17	.177	.202	.003	6.4	.80	2.45
-18	.178	.202	.005	3.5	.38	.86
-19	.178	.202	.004	3.1	.42	.47
-20	.177	.205	.004	4.4	.36	.70
-21	Stuck together during bonding					
-22						
-25	.174	.205	.004	4.1	.68	.72
-26	.176	.203	.006	3.4	.54	.46
-27	.183	.203	.010	3.9	.36	.64
-28	.187	.205	.004	5.0	1.15	1.15
-30	.164	.205	.010	4.0	1.05	.77
-31	.174	.205	.006	4.2	.60	2.20
-32	.182	.208	.004	4.3	.55	.62
-33	.178	.204	.004	3.6	.42	1.35
-34	.162	.205	.008	Foil separated		
-35	.177	.200	.006	2.7	.48	1.15
-36	.170	.202	.004	3.5	1.10	.66
N-2669-I-37	.188	.198	.000	2.8		
-38	.187	.204	.002	4.0		
-39	.188	.203	.001	3.9		
-40	.187	.200	.002	3.0		
-41	.185	.200	.002	2.8		
-42	.187	.200	.000	3.3		
-43	.188	.204	.002	3.8		
-44	.188	.200	.001	3.2		
-45	.188	.203	.002	3.2		
-46	.187	.201	.000	2.9		
-47	.187	.203	.002	3.0		
-48	.186	.204	.002	3.9		
-50	.188	.198	.001	2.7		
-51	.187	.202	.004	3.0		
-52	.188	.198	.001	2.1		
-53	.189	.203	.002	3.0		
-54	.188	.198	.002	2.4		
mean = 0.187				mean = 0.201	mean = 0.002	mean = 3.1
σ = 0.001				σ = 0.002	σ = 0.001	σ = 0.5

*Sample Cracked

** — No.'s 13 - 22 machined by Knight Tool, No.'s 25 - 36 ground by operator just prior to sputtering.

TABLE VI (b) Summary of Q.C. of Bonded PbTe Segments

Sample	Total Length (in.)	Diameter (in.)	Flatness (in.)	Total Resistance (mΩ)	Contact Resistance – Cold End (mΩ)	Contact Resistance – Hot End (mΩ)
M1085-1-14	.162	.207	.004	1.2	.24	.23
-15	.162	.207	.004	1.23	.38	.30
-16	.163	.207	.006	1.2	.31	.34
-17	.163	.208	.004	1.1	.21	.23
-18	.161	.208	.004	1.1	.23	.24
-19	.161	.208	.005	1.12	.25	.24
-20	.161	.208	.004	1.13	.23	.29
-21	.165	.207	.010	1.35	.50	.26
-22	.161	.207	.004	1.25	.26	.35
-23	.163	.208	.004	1.16	.35	.26
-24	.163	.208	.008	1.17	.20	.32
-25	.159	.208	.002	1.21	.30	.34
-26	.165	.208	.012	1.18	.20	.40
-27	.163	.207	.006	1.08	.29	.27
M1085-1-12	.166	.208	.014	1.00	.24	.24
-28	.168	.206	.013	1.15	.26	.26
-29	.163	.208	.010	.97	.32	.32
-30	.163	.207	.002	1.03	.28	.34
-31	.163	.207	.004	1.05	.28	.27
-32	.163	.206	.004	1.20	.26	.26
-33	.163	.208	.007	.96	.26	.26
-34	.161	.206	.005	5.1	.32	.20
-35	.163	.207	.007	1.12	.24	.35
-36	.165	.206	.010	1.20	.26	.25
-37	.163	.208	.009	1.00	.24	.28
-38	.156	.208	.006	.85	.25	.30
M1085-1-50	.162	.207	.001	1.04	.35	.30
-51	.162	.207	.002	1.12	.34	.34
-52	.163	.208	.003	1.12	.32	.32
-53	.162	.208	.002	1.14	.32	.28
-54	.162	.208	.002	1.24	.28	.30
-55	.163	.207	.002	1.21	.38	.40
-56	.162	.208	.008	1.18	.25	.34
-57	.162	.208	.004	1.16	.42	.36
-59	.162	.208	.003	1.51	.42	.36
-60	.162	.208	.002	1.14	.35	.52
-61	.161	.207	.003	1.13	.30	.42
M1085-1-63	.144	.208	.000			
-64	.143	.208	.000			
-65	.142	.208	.001			
-66	.144	.208	.000			
-67	.143	.208	.000			
-68	.142	.208	.000			
-69	.142	.208	.000			
-70	.144	.208	.000			
-71	.144	.208	.000			
-72	.144	.208	.000			
-73	.144	.208	.000			
-74	.144	.208	.000			
-75	.142	.208	.000			
-76	.143	.208	.000			

TABLE VI (c) Summary of Q.C. of Segmented N-Legs

Sample	Total Length (in.)	Leg Flatness (in.)	Total Resistance (mΩ)	Contact Resistance Cold End (mΩ)	Contact Resistance Hot End (mΩ)	Resistance Across Center Bond* (mΩ)	Comments
S-1-1	.341	.004	5.2	.48	.62	1.4	
-2	.347	.008	3.7	.31	.44	1.05	Gap in center bond
-3	.340	.004	4.6	.47	.60	1.35	
-5	.341	.002	4.5	.30	.42	1.05	GdSe _x is slightly cracked near center bore
-6	.341	.006	5.1	.30	.50	1.6	
-7	.341	.008	4.5	.38	.46	1.2	
-8	.341	.006	3.4	.42	.35	1.15	
-9	.337	.004	4.0	.37	.43	1.00	
-10	.342	.004	5.1	.45	.55	1.2	
S-2-1**	.350	.014	5.5	.42	.49	.84	
-3	.347	.012	5.2	.36	.52	1.6	
-4**	.348	.010	5.1	.33	.48	.84	
-5	.339	.004	5.3	.28	.66	.75	
-8	.334	.003	3.8	.36	.60	.70	
-9	.341	.004	4.3	.36	.62	.84	
-10	.340	.004	4.3	.45	.53	1.6	
-11	.341	.002	4.2	.34	.42	1.3	

*Measured across bond using fixed probes — spacing .105"

**Gap in center bond

TABLE VI (d) Summary of Q.C. of Segmented N-Legs, S-5

Sample	N-2669-1 GdSe _x Sample No.	M1085-1 PbTe Sample No.	Total Length (in.)	Ends Parallel (in.)	Total R (mΩ)	R GdSe _x Segment (mΩ)	R GdSe _x Material Only (mΩ)	R PbTe Segment (mΩ)
S-1	37	63	.339	.010	4.8	3.26	1.96	1.0
-2	38	64	.336	.004	11.0	9.8	8.6	.8
-3	39	65	.337	.002	11.5	10.2	9.6	.8
-4	40	66	.339	.008	5.2	3.9	3.4	.8
-5	41	67	.338	.004	5.3	3.0	2.4	1.4
-6	42	68	.338	.005	5.7	4.4	4.1	.8
-7*	43	69	.338	.002	19.9	18.3	16.4	**
-8*	44	70	.339	.002	8.3	7.0	5.9	.8
-9	45	71	.342	.000	6.2	4.4	3.7	1.3
-10	46	72	.335	.000	5.3	3.4	2.9	.8
-11*	47	73	.337	.002	6.5	4.9	4.7	1.0
-12	48	74	.339	.002	10.9	9.4	9.1	1.0
-13*	50	75	.328	.000	9.5	8.9	1.9	1.3
-14	51	76	.338	.008	6.6	5.6	3.4	.7
mean =			.337	.004	8.3	6.9	5.6	1.0
σ =			.003	.003	4.1	4.2	4.1	0.2

*PbTe segment separated from middle foil, leg was rebonded prior to Q.C.

**Not measureable

TASK 2.0 – P-TYPE MATERIAL CHARACTERIZATION

2.1 OBJECTIVE

The objective of this task is to experimentally describe the chemical, electrical, and physical behavior of P-type thermoelectric material at temperatures to 1100°C.

The past twelve months have seen a change in emphasis in P-type material research, from basic properties to sublimation suppression by wrapping, and to the understanding of contact resistance problems at the hot-end.

Thus, this contract period has seen the use of WRe end-caps (as opposed to thin or thick foils) which yielded a threefold improvement in suppression properties; studies of wrap improvement by removal of binder; electrophoretic deposition of slurry; vacuum drying; and use of deionized water.

In addition, current effects on carrier concentration in the basic material were investigated, and a start made on instrumenting wrapped legs to aid in the analysis of contact problems, which were also studied by S.E.M. examination of contact surfaces.

2.2, 2.3 MATERIAL PREPARATION AND ANALYSIS

Electrical measurements on p-legs from various batches are recorded in Table VII, from which it will be seen that the great majority fell inside specification.

2.4 MATERIAL PROCESSING

In this reporting period several different techniques were employed to increase the yield of end cap bonded P legs. Some batches were cast "right" side up, others "right" side down, some with different tiers alternately "up" and "down"; some batches were cast in fresh molds, some in pre-used molds; some were cast with standard plugs, some with special tight plugs; some were cast with plain end-caps, some with grooved end-caps.

None of these variants in technique seemed capable of consistently improving yields, and it currently seems that the problem may lie in the de-flashing procedure, since bonds mostly remain intact until the p-material flashing is removed, whether they be considered 'good' or 'bad'; the latest batches gave good yields, when a new fixture was employed to hold the legs in the sand-blaster.

It may therefore be that all bonds are marginal at the casting stage, and the overall yield is more dependent on subsequent handling than on any particular casting technique.

2.4.1 Wrap Processing

In this reporting period the wrapping technique was refined for p-legs (with stepped WRe caps), comprising an Astroquartz fiber wrap infiltrated with a Min-K slurry during wrapping. Most sublimation suppression would be expected to occur by mean free path curtailment by the dried slurry, with the Astroquartz fiber providing overall strength to the composite.

TABLE VII P-Type Seebeck Measurements

Sample No.	Seebeck ($\mu\text{V}/^\circ\text{C}$, rel. to abs.)	Sample No.	Seebeck ($\mu\text{V}/^\circ\text{C}$, rel. to abs.)
R-64	Tier 1 No. 1 +241	R-79	Tier 1 No. 3 +247
	Tier 4/5 No. 1 +246		Tier 5/6 No. 1 +248
	Tier 10 No. 1 +245		Tier 12 No. 1 +250
	Tier 1 No. 3 +244	R-80	Tier 1 No. 1 +244
	Tier 3 No. 2 +241		Tier 5/6 No. 1 +243
	Tier 4/5 No. 3 +240		Tier 12 No. 1 +249
	Tier 9 No. 1 +241	R-81	Tier 1 No. 1 +246
	Tier 7 No. 2 +241		Tier 5/6 No. 1 +245
	Tier 8 No. 5 +244		Tier 12 No. 1 +249
	Tier 10 No. 4 +245	R-82	Tier 1 No. 1 +243
R-68*	Tier 1 No. 1 +261*		Tier 6 No. 1 +238
	Tier 4/5 No. 1 +258*		Tier 13 No. 1 +242
	Tier 10 No. 1 +260*	R-84	Tier 1 No. 1 +241
R-70	Tier 1 No. 1 +246		Tier 5/6 No. 1 +238
	Tier 4/5 No. 1 +246		Tier 12 No. 1 +250
	Tier 12 No. 1 +249	R-83	Tier 1 No. 1 +240
R-73	Tier 1 No. 1 +249		Tier 5/6 No. 3 +243
	Tier 5/6 No. 1 +250		Tier 12 No. 1 +235
	Tier 12 No. 1 +255	R-87	Tier 1 No. 1 +244
	Tier 1 No. 3 +252		Tier 5/6 No. 1 +247
	Tier 3 No. 2 +252		Tier 12 No. 1 +250
	Tier 3 No. 3 +254	R-74	Tier 1 No. 3 +244
	Tier 5/6 No. 3 +252		Tier 1 No. 4 +244
	Tier 9 No. 4 +253		Tier 3 No. 3 +243
	Tier 9 No. 5 +250		Tier 3 No. 4 +245
	Tier 12 No. 3 +256		Tier 4/5 No. 5 +247
R-74	Tier 1 No. 1 +247		Tier 8 No. 4 +248
	Tier 10 No. 1 +254		Tier 8 No. 5 +248
	Tier 4/5 No. 3 +245	R-80	Tier 1 No. 3 +250
R-75	Tier 1 No. 1 +249		Tier 4 No. 1 +247
	Tier 5/6 No. 1 +249		Tier 5/6 No. 3 +249
	Tier 12 No. 1 +252		Tier 5/6 No. 4 +249
R-77	Tier 1 No. 1 +249		Tier 9 No. 4 +250
	Tier 5/6 No. 1 +248		Tier 10 No. 1 +247
	Tier 12 No. 1 +250		Tier 12 No. 3 +251
R-78	Tier 1 No. 1 +246	R-91	Tier 1 No. 1 +248
	Tier 5/6 No. 1 +248		Tier 5/6 No. 1 +249
	Tier 12 No. 1 +249		Tier 12 No. 1 +252

*Tube broken during synthesis — batch rejected.

TABLE VII P-Type Seebeck Measurements (Continued)

Sample No.		Seebeck ($\mu\text{V}/^\circ\text{C}$, rel. to abs.)	Sample No.		Seebeck ($\mu\text{V}/^\circ\text{C}$, rel. to abs.)
R-88	Tier 1 No. 1	+242	R-58	Tier 3 No. 3	+245
	Tier 5/6 No. 1	+243			
	Tier 12 No. 1	+247	R-59	Tier 9 No. 3	+245
R-90	Tier 1 No. 1	+241	R-82	Tier 1 No. 3	+236
	Tier 5/6 No. 1	+243		Tier 4 No. 1	+236
	Tier 12 No. 1	+247		Tier 5 No. 1	+236
R-84	Tier 12 No. 3	+247		Tier 6 No. 3	+240
R-88	Tier 1 No. 3	+243		Tier 9 No. 4	+241
	Tier 4 No. 2	+240		Tier 11 No. 1	+237
	Tier 4 No. 3	+241		Tier 13 No. 3	+242
	Tier 5/6 No. 3	+243	R-83	Tier 1 No. 3	+242
	Tier 9 No. 4	+242		Tier 4 No. 2	+240
	Tier 10 No. 1	+242		Tier 5/6 No. 4	+243
	Tier 12 No. 3	+248		Tier 5/6 No. 5	+243
R-90	Tier 1 No. 3	+242		Tier 9 No. 4	+243
	Tier 4 No. 2	+242		Tier 10 No. 1	+241
	Tier 4 No. 3	+240		Tier 12 No. 3	+243
	Tier 5/6 No. 3	+242	R-90	Tier 1 No. 3	+240
	Tier 9 No. 4	+242		Tier 1 No. 3*	+242
	Tier 10 No. 1	+242		Tier 4 No. 2	+240
	Tier 12 No. 3	+247		Tier 4 No. 2*	+241
R-94	Tier 1 No. 1	+260		Tier 4 No. 3	+237
	Tier 4 No. 1	+263		Tier 4 No. 3*	+239
	Tier 12 No. 1	+262		Tier 5/6 No. 3	+242
R-96	Tier 1 No. 1	+248		Tier 5/6 No. 3*	+243
	Tier 5 No. 1	+250		Tier 9 No. 4	+242
	Tier 12 No. 1	+252		Tier 9 No. 4*	+243
				Tier 10 No. 1	+241
				Tier 10 No. 1*	+244
				Tier 10 No. 1	+242
				Tier 10 No. 1*	+243
				Tier 12 No. 3	+248
				Tier 12 No. 3*	+249
				Tier 12 No. 3	+248
				Tier 12 No. 3*	+248

*Pressure to bellows increased from standard 40 psig to 60 psig without removing leg from fixture following immediately preceding run.

TABLE VII P-Type Seebeck Measurements (Continued)

Sample No.		Seebeck No. ($\mu\text{V}/^\circ\text{C}$, rel. to abs.)
R-84	Tier 1 No. 3	+241
	Tier 4 No. 2	+239
	Tier 4 No. 3	+240
	Tier 5/6 No. 3	+242
	Tier 9 No. 4	+241
	Tier 10 No. 1	+242
	Tier 12 No. 4	+244
R-93	Tier 4 No. 2*	+280
R-94	Tier 4 No. 2*	+275
R-98	Tier 1 No. 1	+240
	Tier 5/6 No. 1	+243
	Tier 11 No. 1	+239

* Sample measured to complete characterization of batch. First three samples measured did not meet specifications. It was not necessary to measure more than one additional sample since these values are out of specification and will not be used.

Obviously any gaps in the wrap would be expected to increase the sublimation of selenium by short-circuiting the slurry, and the stepped WRe endcap was intended as an improvement over the thick-foil end-cap in this regard.

Isothermal accelerated current tests at 940°C, reported in Table VIII, show rather convincingly that the machined WRe caps yield about three times the sublimation suppression of thick foils, namely about 0.17 mg/cm²/hours as opposed to 0.42 mg/cm²/hours.

Further wrap improvements were sought by removing the binder from the Astroquartz. Since it was found that the fiber outgassed various hydrocarbons, CO₂, and water vapor at temperatures up to 650°C. However, the outgassed fiber exhibited a lower tension strength than the as-received material, which necessitated lower wrap tension and consequently higher selenium loss rates.

Attempts to bake out the finished wrap at 650°C and thereby remove the binder in situ also led to a degradation of sublimation suppression, so final drying of the wrapped elements was performed at 150°C.

Use of deionized water in the slurry preparation, in preference to tap-water, led to no change in wrap effectiveness, nor to any noticeable improvement in element behavior in module tests.

Variation of drying atmosphere - from humid air through dry air to vacuum - did demonstrate a significant effect, since the vacuum-dried legs had superior baffling properties to air-dried ones. S.E.M. examination suggests that this effect correlates with the reduction in the tendency of vacuum dried slurries to exhibit "mud cracking".

Data supportive of these statements is included in Section 2.9 of this report dealing with high-temperature operation of p-elements.

2.5 THERMODYNAMIC STABILITY

Alternative copper cold-end bonding techniques include ultrasonic welding, which was investigated in this reporting period.

Initially a sample was made with a Sonics and Materials ultrasonic welder with 2500 watts power, in air at ambient temperatures.

Clearly this process is much more convenient than the high-temperature vacuum operation normally employed, provided an equivalent bond can be achieved. The above sample was run in ATT 537 at 850°C/150°C without a wrap, to see the effects of larger copper extension due to sublimation; the observed weight loss was 42mg, yet post test examination showed uniform good contact between the cap and leg despite copper extrusion.

In view of this encouraging result, two more ultrasonically bonded samples were tested in ATT 609 and ATT 610, as reported in Table IX - again without wraps to maximize copper extrusion.

As can be seen from the start and end A/l ratios, there was severe creep at the hot end which "mushroomed" the diameter there; lengths decreased by about one-third as well. While ATT 609 showed signs of extruded copper pushing off the copper electrode and possessed a 2-4mΩ resistance at the P-material copper interface, ATT 610 was solidly in one piece with the extruded copper coming out uniformly at the copper electrode. There was a 0.6 mΩ resistance between P-material and extruded copper but no apparent resistance between extruded copper and copper electrode on ATT 610.

All in all, these results suggest that ultrasonic welding may provide a worthwhile improvement when better developed.

TABLE VIII Isothermal Accelerated Current Tests of P-Legs
With Thick Foil at Hot End

<u>Leg Identification</u>	<u>Temp (°C)</u>	<u>i^L/A (amp/cm)</u>	<u>Rate (mg/cm² - Hr)</u>
598, 3-A	940	22.0	0.44
598, 2-A	940	22.0	0.54
598, 4-A	940	22.0	0.41
585, 4-C	940	22.3	0.34
592, 2-A	940	22.0	0.62
598, 5-A	940	22.0	0.18
597, 3-A	940	22.0	0.50
597, 1-A	940	22.0	0.33
598, 8-C	941	22.0	0.60
608, 3-A	941	22.0	0.25
608, 6-B	941	22.0	0.27
592, 4-B	943	22.0	0.79
592, 3-C	941	22.0	0.99
609, 8-D	940	22.0	0.27
609, 5-A	940	22.0	0.54
609, 1-D	940	22.0	0.38
609, 4-B	940	22.0	0.20
609, 4-C	940	22.0	0.33
Mean:			0.44 ± 0.21

Isothermal Accelerated Current Tests of P-Legs with Machined W-Re Caps

<u>Leg Identification</u>	<u>Temp (°C)</u>	<u>i^L/A (amp/cm)</u>	<u>Rate (mg/cm² - Hr)</u>
618, 4-B	939	22.0	0.10
618, 4-A	941	22.0	0.13
618, 3-B	942	22.0	0.21
618, 4-C	941	22.0	0.087
618, 9-D	941	22.0	0.18
618, 7-A	939	22.0	0.12
618, 6-D	940	22.0	0.23
618, 4-D	940	22.0	0.19
618, 3-D	940	22.0	0.16
618, 6-B	942	22.0	0.16
618, 8-D	940	22.0	0.17
618, 9-A	941	22.0	0.19
619, 3-C	940	22.0	0.23
Mean:			0.17 ± 0.04

TABLE IX Physical Properties and Performance
of Ultrasonically Copper Bonded P-Legs

ATT No.	A/ ℓ ratio (cm)		Weight Lost (g)
	Start	End	
609	0.45	0.89	0.128
610	0.45	0.89	0.142

Conditions: nominal 900°C/150°C; 5.0 amperes, 150 psi load pressure, high vacuum atmosphere; 400 hours at temperature.

2.7 PERFORMANCE MAPPING OF CONTACTED AND NON-CONTACTED ELEMENTS

The model used by 3M for the effect of current on carrier concentration has been described in earlier reports (e.g. Technical Task Report 35, Top Summary Report 51). This model is routinely used by 3M to successfully predict changes in the operating electrical characteristics of p-legs as a function of current. A more stringent application of this model is in the prediction of acceleration conditions, since it is then only the carrier concentration in the vicinity of the hot junction rather than the average carrier concentration which is important.

Direct measurements of the carrier concentration at the hot end of operating p-legs performed this year by resistivity probe techniques dramatically confirmed the model predictions.

These measurements were performed on two separate samples with voltage probes near the hot end. A four probe a.c. resistance measurement was used. At each hot and cold end junction temperature, the current was scanned through several different values, and the data taken after steady state was obtained for each current value.

The data is plotted in Figures 4 - 9 for the first sample, and Figures 10 - 13 for the second sample as inverse resistance normalized to the value of resistance at the nominal load current ($i^{\ell}/A = 8.5 \text{ amp/cm}$).

According to the dopant migration model, this plot should be linear, with the slope given approximately by

$$\frac{R_{\text{nominal}}}{R} = 1 + \frac{(0.0095) (i^{\ell}/A - (i^{\ell}/A)_{\text{nominal}})}{N_{\text{nominal}}}$$

with $N_{\text{nominal}} = N_0 + 0.0095 (i^{\ell}/A)_{\text{nominal}}$

The slopes determined by these relations are plotted in the figures.

The conclusions drawn from this data are:

1. The linearity prediction is confirmed. Previous measurements had shown a current dependence of Seebeck coefficient and resistance averaged over the entire leg which was in accordance with the dopant migration model. It had been suggested that some other effect (e.g., semiconductor junction phenomena) may have influenced the behavior of the average Seebeck coefficient and resistivity. These new measurements show that the resistance change also occurs within a region near the hot junction, as predicted, so the alternative conjectures seem yet more improbable.
2. The quantitative agreement of the measurement with prediction is good. An objective of this testing is to determine more precisely the current acceleration factor which occurs during ingradient operation at higher than nominal current. The measurement so far indicates that the acceleration factor predicted from the previously published equations with the previously determined nominal values for the coefficients predicts the acceleration factor to about 10%. This is well within the previously estimated uncertainty, and is adequate for accelerated testing.

Figure 4

CURRENT EFFECT ON CARRIER CONCENTRATION AT P LEG HOT END

CURRENT EFFECT ON CARRIER CONCENTRATION AT P LEG HOT END

Figure 5

Figure 6

CURRENT EFFECT ON CARRIER CONCENTRATION AT P LEG HOT END

Figure 7

CURRENT EFFECT ON CARRIER CONCENTRATION AT P LEG HOT END

CURRENT EFFECT ON CARRIER CONCENTRATION AT P LEG HOT END

Figure 8

CURRENT EFFECT ON CARRIER CONCENTRATION AT P LEG HOT END

Figure 9

FIGURE 10 Carrier Concentration Experiment: P-Leg Hot End 800–150°C

FIGURE 11 Carrier Concentration Experiment: P-Leg Hot End 850 - 150°C

FIGURE 12 Carrier Concentration Experiment: P-Leg Hot End 800 - 200°C

FIGURE 13 Carrier Concentration Experiment: P-Leg Hot End 850 - 200°C

2.8 ELEMENT PARTITIONING AND CONTACTING DEVELOPMENT

This effort involved evaluation of the nature and extent of the hot-end bond, as well as attempts to use third metals and mechanical interlocking bonding techniques.

2.8.1 Evaluation of hot-end Bonds

Examination of as-fabricated P-legs was made by optical microscopy and SEM analysis. Tentative conclusions drawn from observations of both "good" and "bad" castings (i.e. castings which resulted in bonding, and non-bonding, of W-Re caps to P-material) are as follows:

1. If bonding is by the adherence of P-material to W-Re end-caps, then it appears that a bond is formed only at the circumference of the P-material in contact with the end-cap.
2. "Good" and "bad" castings seem only to differ in the proportion of the circumference which is bonded; "good" castings show P-material sticking to the end-cap over a majority of its circumference while "bad" castings exhibit P-material adhesion only over short arcs of the circumference.
3. The surface texture of the center of the P-leg is on a different scale to the surface texture of the end-cap, suggesting that only a very poor mechanical bond exists in central regions of the P-material/end-cap interface. Certainly there appears to be no "coining" of the P-material which might be expected if a good mechanical bond had ever existed.
4. Certain samples exhibited bubbles in the P-material adjacent to the end-cap: these bubbles contained finely divided graphite and most probably are associated with pick-up of mold material during casting. This effect may only be present in the case of samples cast with the end-cap above the mold cavity since graphite would be expected to float upwards and possibly desorb gas to form the bubbles.
5. In some cases a layer of copper/silver alloy was found on the end-cap, presumably exsolved from the P-material during the casting process. A strong variation in silver content from one area to another suggests that the alloy was present in the liquid state, and segregation of silver took place by normal eutectic formation during cooling.

The main conclusion from these examinations is that the P-material, when cast onto a tungsten-rhenium alloy end-cap, does not form an intimate bond except at the circumference. It was therefore decided to examine samples of wrapped P-legs annealed at elevated temperatures in vacuum, with the thought that any creep caused by thermal expansion stresses might lead to better mechanical contact between the P-material and the end-cap.

Examination of P-leg 592, experiment 4B, which had been annealed at 900°C with applied axial stress of 150 psi, led to the following tentative conclusions:

1. The surface texture of the P-material was generally on a different scale to the surface texture of the end-cap, except possibly in small isolated patches.
2. The surface of the P-material generally appeared eroded due to sublimation, the erosion pattern appearing to depend on the crystallographic orientation of different grains to an extent, although deep radially oriented grooves formed at the very edge of the P-material.

3. In very localized areas of the end-cap there appeared reaction zones containing either barium or titanium (the SEM being unable to distinguish between the two elements). Most likely the reaction zone contained titanium which could come from the Min-K wrap; silicon was not observed, but may be outside the resolution of the SEM.

The main conclusion from these examinations appears to be that even in isothermal tests, no very intimate contact between P-material and end-cap is achieved in the case of wrapped legs.

It therefore became of interest to look at the WRe/P-leg interface in tested unwrapped legs which had undergone extensive compression, and hence might be expected to show good mechanical contact due to creep; ATT 610 (previously mentioned in Section 2.5) seemed a likely candidate.

Optical examination of the contacting surfaces at the time of prying off the cap showed that the end-cap appeared cleaner than usual; SEM examination showed that the surface textures of P-material and end-cap were similar.

It is concluded that "coining" of the P-material into the W-Re end-cap does occur ingradient provided creep of the P-material is occurring at a sufficient rate, and the case for attempting to improve contact properties by using higher spring pressures is reaffirmed.

Since creep rates are typically related to stress levels by a power law

$$\dot{\epsilon} \propto \sigma^n$$

where n lies in the range 2 - 4 for metals, it is suggested that applied pressures of the order 300-600 psi might be needed to ensure intimate contact between P-material and end caps during high-temperature operation.

2.8.2 Use of Third Metal Foils

It has become apparent that a reaction between end-cap and p-material may occur in tested p-legs, resulting in a layer of dark material (identified as WSe₂) being formed on the end-cap. The use of a foil between end-cap and p-material as a diffusion barrier was considered, but no successful application of this concept has yet been made, for three reasons:

1. Most transition metals are known to diffuse into p-material at rapid rates in operation.
2. Almost all other metals are likely to react with selenium, and thus fail to act as diffusion barriers.
3. The one metal which seemed most promising - rhenium - could not be made to bond to p-material at reasonable pressures and temperatures.

This idea has not been abandoned, and it remains to be seen if solids such as graphite, W-Re-Ta and Ir, or liquids such as bismuth, could provide good electrical contact behavior.

FIGURE 3 Patterns cut into W/25Re Caps Used in Run No. 637

2.8.3 Mechanical Interlocking Bonding Devices.

Ten elements in run 637 were cast on to caps with grooves and holes cut in them to promote mechanical retention of cap and p-leg. Figure 3 demonstrates the patterns cut into the experimental caps. Other elements in run 635 had been cast on to end-caps with annular grooves, and while the as-fabricated bond seemed good, a simple test on #635, 3-A demonstrated that the selenium loss rate of the wrapped leg was higher than that measured on non-grooved capped elements. This result is described in Section 2.9.

Overall there has yet to be seen any clear evidence that mechanical interlocking bonding techniques serve any valuable purpose.

In general it may be said that future progress will depend on an understanding of the exact nature of the contact resistance problem in wrapped legs; it does appear that creep of the p-material in unwrapped legs may suffice to maintain low contact resistance, which makes it seem dubious that the problem stems from WSe_2 formation; although this might of course exacerbate it.

2.9 HIGH TEMPERATURE OPERATION OF P-ELEMENTS

2.9.1 In-Gradient Comparison of Partitioned and Non-Partitioned Legs.

Test series ATT 571-576 was initiated in the six station test fixture to compare performance of partitioned and non-partitioned P-legs. Both types of legs had thick foils at the hot end rather than machined W-Re caps. The tests operated for about 900 hours at a nominal temperature interval $900^{\circ}C/150^{\circ}C$ in a dynamic vacuum of 10^{-6} Torr. The weight loss measurements after test are summarized in Table X. Comparison of the mean weight loss for partitioned and non-partitioned legs indicates a factor of two different in weight loss, but there is considerable scatter to the data. The average creep for all six tests was less than $\frac{1}{2}\%$.

2.9.2 Mass-Spectrometer Analysis

Time of flight mass spectrometer analysis was performed on both a wrapped and non-wrapped P-leg to temperatures in excess of $1000^{\circ}C$. The results dramatically indicated the wrap effectiveness — no selenium or silver was observed on the wrapped sample with an estimated sensitivity of 3.4×10^{-5} Torr at $1000^{\circ}C$. Water, hydrocarbons and CO_2 were observed for both with the wrapped sample producing only slightly higher levels. At $650^{\circ}C$, the water and hydrocarbons did not appear above background levels in either sample.

From the limit of detectability and measured control selenium pressure at $1000^{\circ}C$, along with spectrometer orifice size, a wrap baffling factor of at least 500 can be calculated. The comparable factor calculated from isothermal tests is approximately 300.

TABLE X Ingradient Accelerated Testing of Partitioned and Non-Partitioned Wrapped P-Legs at 900°C/150°C and, i^L/A of 11 amp/cm.

Test No.	Description	Measured Weight Loss Rate, Accelerated Conditions (10^{-6} gm/hr-cm ²)
571	Partitioned, Min-K/H ₂ O Slurry, astro-quartz wrap, thick foil	4.2
572	" " "	7.6
573	" " "	11.8
574	Non-partitioned, Min-K/H ₂ O slurry, astroquartz wrap, thick foil	16.1
575	" " "	16.3
576	" " "	11.5

Mean weight loss rate:

Partitioned	7.9 ± 3.8
Non-Partitioned	14.6 ± 2.7

Acceleration factor relative to nominal 850°C/150°C and $i^L/A = 8.5$ amp/cm operation: 5.

2.9.3 Definition of P-Leg Wrap Process

A program to improve the effectiveness of the Astroquartz/MIN-K slurry sublimation barrier on P-legs has been completed. Investigations were carried out on removal of Astroquartz binder, substitution of deionized water for tap water and variations in drying atmosphere. Table XI lists the data collected in isothermal, current accelerated testing.

The first of two series of tests used low binder content Astroquartz yarn and MIN-K slurry formulated with deionized water to study the effect of various drying conditions on wrap sublimation suppression effectiveness. No. 630, 7-B and 7-C used the controlled humidity of a small closed container for two days prior to air exposure. No. 630, 8-A and 9-C was air dried as usual while No. 630, 3-D and 5-D were vacuum dried immediately after wrapping. While the controlled humidity and air dried samples displayed similar loss rates (0.20_5 and $0.18_5 \times 10^{-3}$ g/cm²-hr) which are close to or greater than the average loss rate of 0.16×10^{-3} g/cm²-hr ($\sigma = .04$) observed for the standard wrap, the vacuum dried samples were both lower than standard and on the edge of a statistically significant difference (0.12×10^{-3} g/cm²-hr). This result is supported by visual observations of greater wrap cohesiveness for vacuum dried samples and SEM photographs revealing less severe cracking of the vacuum dried slurry.

The second round of testing centered on the separation of variables responsible for the increased sublimation effectiveness observed in vacuum dried samples in the first round. Only one change from the standard wrap was made for each type sample tested. No. 630, 9-A and 4-D were vacuum dried; No. 630, 2-C and 3-A were prepared with deionized water slurry; No. 630, 1-C and 1-B were wrapped with low binder Astroquartz yarn and No. 630, 1-A and 2-B were standard wraps for reference. The standard wraps measured $0.13_5 \times 10^{-3}$ g/cm²-hr. — slightly lower but within the range of the many similarly wrapped legs previously tested. The deionized water slurry samples compared well with the accepted standard loss rate with a $0.15_5 \times 10^{-3}$ g/cm²-hr. loss rate. Merely substituting low binder Astroquartz yarn in the wrap yielded a $0.26_5 \times 10^{-3}$ g/cm²-hr. loss rate — well above the accepted standard rate. It is surmised that the decreased wrapping tension needed for the lower strength, low binder Astroquartz yarn was responsible for the decreased effectiveness of sublimation suppression even though wrap and turns density values do not show a decrease. While vacuum drying and a 150°C vacuum bakeout of wrapped P-legs removes most of the wrap water vapor, a 650°C bakeout is necessary to reduce residual water vapor and organic species below background levels as measured by time-of-flight mass spectrometry. Samples of wrapped P-legs were baked out at 650°C under vacuum for approximately 15 hours with 0.5 amperes maintained through the legs to prevent copper migration throughout the thermoelectric material from the copper electrode. The only observable change in the wrapped legs as a result of the bakeout was a dimensional shift which conserved the volume of thermoelectric material while increasing the length by approximately 3%. The dimensional change is essentially the same as that observed during normal isothermal, accelerated current testing. The four samples (No. 631, 2-A, 2-B, 4-B, and 7-B) reported in Table XII had an average loss rate of 0.25×10^{-3} g/cm²-hr ($\sigma = 0.06$) which is 50% higher than the established rate for air dried wrapped P-legs using a 150°C bakeout. The conclusion based on this series is that a 650°C vacuum bakeout cannot be used to remove residual wrap impurities without significantly effecting the wrap performance.

As a separate exercise, two P-legs (No. 598, 6-C and 6-D) with an oversized WRe foil on the hot end and a thick WRe foil on the cold end were MgO vapor coated before wrapping to further decrease sublimation of the leg. The results of isothermal, current accelerated testing show an average loss rate of 0.36×10^{-3} g/cm²-hr, $\sigma = 0.04$, which is more than twice the rate observed on capped, wrapped P-legs. No direct visual observations could account for the increased loss rate.

TABLE XI Isothermal Current Accelerated P-Leg Tests with Machined WRe Caps

Leg Ident- ification	Temp. (°C)	il/a (A/cm)	Rate (x10 ⁻³ g/ cm ² -hr.)	Resistance in Fixture (mΩ) BTAT		Spring Force (lbs.)	Wrap Density (g/cc)	Turns Density (x10 ⁴ cm ²)	Wrap Thickness (")	Length Change (")	Diameter Change (")	Weight Loss (grams)	Type of Dry
630 Tier 7-B Astroquartz* Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	936	22.0	.24	38	7.5	7.5	1.29	2.2	.028	+0.008	-.002	.0063	Closed Container for 2 days
630 Tier 7-C Astroquartz* Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	936	22.0	.17	50	9.3	8.0	1.38	2.3	.026	+0.006	-.003	.0047	Closed Container for 2 days
630 Tier 8-A Astroquartz* Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	940	22.0	.16	67	6.8	7.0	1.38	2.4	.0255	+0.006	-.003	.0047	Air
630 Tier 9-C Astroquartz* Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	940	22.0	.21	40	7.5	7.3	1.38	2.3	.026	+0.011	-.002	.0061	Air
630 Tier 3-D Astroquartz* Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	938	22.0	.11	34	9.4	7.7	1.43	2.5	.024	+0.006	-.003	.0035	Vacuum
630 Tier 5-D Astroquartz* Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	941	22.0	.13	40.5	8.1	7.3	1.3	2.2	.027	+0.006	-.003	.0044	Vacuum
630 Tier 9-A Astroquartz Min-K/H ₂ O, .020 WRe cap (+), .030" Copper Foil (-)	936	22.0	.12	38	6.6	8.0	1.5	2.3	.025	+0.006	-.005	.0030	Vacuum
630 Tier 4-D Astroquartz Min-K/H ₂ O, .020" WRe cap (+), .030" Copper Foil (-)	940	22.0	.19**	46	6.3	8.0	1.4	2.1	.028	+0.008	-.003	.0057	Vacuum

TABLE XI Isothermal Current Accelerated P-Leg Tests with Machined WRe Caps (Continued)

Leg Ident- ification	Temp. (°C)	il/a (A/cm)	Rate ($\times 10^{-3}$ g/ cm ² -hr.)	Resistance in Fixture (m Ω)		Spring Force (lbs.)	Wrap Density (g/cc)	Turns Density ($\times 10^4$ cm ²)	Wrap Thickness (")	Length Change (")	Diameter Change (")	Weight Loss (Grams)	Type of Dry
630 Tier 1-A Astroquartz Min-K/H ₂ O, .020" WRe cap (+), .030" Copper Foil (-)	941	22.0	.15	60	7.5	5.5	1.35	1.9	.031	+.010	-.004	.0044	Air
630 Tier 2-C Astroquartz Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	941	22.0	.17	38	8.4	6.8	1.4	2.2	.0265	+.011	-.005	.0044	Air
630 Tier 3-A Astroquartz Min-K/Deionized H ₂ O, .020" WRe Cap (+), .030" Copper Foil (-)	941	22.0	.14	73	8.6	7.5	1.44	2.3	.026	+.009	-.003	.004	Air
630 Tier 1-C Astroquartz* Min-K/H ₂ O, .020" WRe cap (+), .030" Copper Foil (-)	941	22.0	.29	40	7.3	7.0	1.4	2.1	.029	+.008	-.004	.0081	Air
630 Tier 1-B Astroquartz* Min-K/H ₂ O, .020" WRe cap (+), .030" Copper Foil (-)	941	22.0	.24	31	8.4	7.3	1.27	1.9	.0325	+.007	-.003	.0084	Air
630 Tier 2-B Astroquartz Min-K/H ₂ O, .020" WRe cap (+), .030" Copper Foil (-)	942	22.0	.12	39	8.4	7.3	1.36	2.1	.0275	+.005	-.004	.0034	Air

* Low binder Astroquartz yarn

** Anomalous copper end erosion - not valid test

TABLE XII Isothermal Current Accelerated P-Leg Tests with Machined WRe Caps

Leg Ident- ification	Temp. (°C)	il/a (A/cm)	Rate ($\times 10^{-3}$ g/ cm ² -hr.)	Resistance in Fixture (m Ω)		Spring Force (lbs.)	Wrap Density (g/cc)	Turns Density ($\times 10^4$ cm ⁻²)	Wrap Thickness (")	Length Change (")	Diameter Change (")	Weight Loss (grams)
No. 631 tier 2-A, Astroquartz Min-K/deionized H ₂ O, .020" W-Re cap (+), .050" copper foil (-) (high temp. bakeout)	941	22.0	.22	38	6.5	7	1.38	1.87	.024	+.010	-.005	.0072
No. 631 tier 2-B, Astroquartz Min-K/deionized H ₂ O, .020" W-Re cap (+), .050" Copper foil (-) (high temp. bakeout)	940	22.0	.24	23.5	7.2	7.3	1.31	1.75	.026	+.010	-.005	.0070
No. 631 4-B Astroquartz Min-K/deionized H ₂ O, .020" W-Re cap (+), .050" Copper foil (-) (high temp. bakeout)	940	22.0	.24	18	6.2	6.9	1.27	1.7	.027	+.009	-.003	.0075
No. 631 7-B Astroquartz Min-K/deionized H ₂ O, .020" W-Re cap (+), .050" Copper foil (-) (high temp. bakeout)	941	22.0	.34	65	7.2	6.9	1.23	1.54	.030	+.010	-.004	.0097
No. 635 tier 3-A, Astroquartz Min-K/H ₂ O, .020" W-Re Cap (+), .030" Cu foil (-) Air Dry*	939	22.0	.28	46	7.7	1.41		1.96	.023	+.007	-.003	.0071
No. 598 Tier 6-C, Astroquartz Min-K/deionized H ₂ O, .002 W-Re foil (+), .020" W-Re foil (-) Air Dry, (vapor coated)	941	22.0	.43	28	5.7	6.5	1.2	1.64	.028	+.003	-.003	.0118
No. 618 tier 2-C, Astroquartz Min-K/H ₂ O, .020" W-Re cap (+), .030" Cu foil (-)	940	22.0	.16	34	5.4	6.5	1.3	2.3	0.28	+.008	-.004	.0050
No. 598 tier 6-D, Astroquartz Min-K/deionized H ₂ O, .002" W-Re foil (+), .020" W-Re foil (-), (Vapor coated)	941	22.0	.35	36	18.5	7	1.3	1.9	.024	+.006	-.002	.0089

*Annular grooved WRe cap

The conclusions of this program are:

1. The average of all vacuum dried samples shows a $0.11\text{-}0.12 \times 10^{-3}\text{g/cm}^2\text{-hr.}$ loss rate — a lower, more consistent rate than the standard.
2. Astroquartz binder removal alone has a detrimental effect on loss rate.
3. Deionized water MIN-K slurry has no effect on sublimation loss rate.
4. A single test of a wrapped P-leg with annular grooved WRe cap (No. 635, 3-A) produced a higher loss rate than that measured for legs with non-grooved caps ($0.28 \times 10^{-3}\text{g/cm}^2\text{-hr.}$). The annular grooves on the thermoelectric material interfacial side of the cap were being tested for improved mechanical bonding of cap to thermoelectric material. In contrast to flat faced, capped legs, the annular grooved cap on this sample did remain bonded to the material after testing.

TASK 3.0 — COUPLE DEVELOPMENT

3.1 OBJECTIVE

The objectives of this task are to design, obtain data, demonstrate performance, and predict long-term performance of thermoelectric couples using experimental elements from Tasks 1.0 and 2.0 of this report.

3.2 ANALYTICAL PERFORMANCE CALCULATIONS

Through a cooperative effort between the Pioneering Lab and the ES&T division of 3M, a new computer program was developed in support of the Galileo program in order to evaluate performance of couple designs. This program was used to perform analytical studies on the Thermoelectric Materials Evaluation Program contract and a description of these studies is contained in the following paragraphs.

The program obtains approximate solutions to a one-dimensional conservation of energy equation applied to the elements themselves. User imposed constraints include thermal boundary conditions, current flow and couple geometry. The program is also sufficiently general to accommodate consideration of contact resistances and segmented legs. Subroutines for calculating thermoelectric properties contain models for TPM-217, cubic phase NdSe_x and GdSe_x , orthorhombic phase GdSe_x , 2N and 2P PbTe, N and P type SiGe (new and aged) and advanced N and P type SiGe. The program is capable of obtaining optimum couple geometries, optimum efficiency load current and load current required to obtain a specified load voltage. Typical output data for any given solution includes integrated average property values for both N and P-materials, leg resistances, leg heat fluxes, leg power outputs, leg and couple efficiencies, segment interface temperatures, current flow, load voltage and P-leg acceleration factor. Since demonstrating the accuracy of the computer program, it has been used for several studies, some of which are described in the next few paragraphs.

A comparative analysis of various thermoelectric materials was performed and the results are presented in Figure 14. It should be noted that in general no contact resistance was assumed for the generation of these curves; however, the curve labeled M-9 includes the characteristics of the couple

as actually measured in the module and therefore does include contact resistance. The data for the advanced SiGe was extrapolated above 600°C, because until recently, 3M had no data above 600°C. The maximum temperature for the selenides is shown as 900°C, although a selenide couple could be operated above that temperature by utilizing a high temperature segment on the P-leg. It is clear that the selenides offer significant performance advantages for thermoelectric power generation over competing systems. Figure 15 and 16 illustrate the additional benefit in coupling the selenides with PbTe.

In June, a question arose concerning the validity of using the hot junction temperature and current as parameters with which to characterize sublimation. The argument was made that the effect of temperature and current produce a weight loss variation along the P-element and that the actual variation must be integrated to compare two cases with one another (e.g., a nominal and an accelerated case).

A calculation was performed to evaluate that argument. The weight loss rate for two cases (nominal: 860/160, 8.57 amp/cm, accelerated: 913/160, 12.8 amp/cm) was calculated using the couple performance computer program. The normalized weight loss rate for these two cases is shown in Figure 17 as a function of position. It can be seen that the two curves have very similar shapes and that the area under the curves differs by less than 1%. As a result the weight loss at the hot junction characterizes the integrated weight loss when comparing the two cases. Thus, the simplified approach of using hot junction temperature and current to calculate acceleration factor is valid. Another interesting point which is observed in Figure 17 is that most of the weight loss occurs in 10% of the length at the hot end.

A study was performed to assess the effects of component variations on performance. This information has been used to assess whether existing tolerance specifications should be changed. For purposes of this study, "performance" was taken to mean thermoelectric efficiency and P-leg weight loss rate. Parameters that were allowed to vary are listed in Figure 18. To study the effects of variables on efficiency, load voltage was held fixed while load current adjusted, and to study the effects on P-leg weight loss rate the load current was held fixed. The results indicate that with present tolerance specifications, couple to couple variations could account for converter thermoelectric efficiencies that are .63% below nominal and for P-leg weight loss rates 3.48 times higher than nominal. By changing the specification of N-leg diameter from $\pm .005$ in. to $\pm .002$ in., these figures can be cut to .59% and 2.79 respectively. This change can be made without large increases in waste or manufacturing time requirements.

FIGURE 14 A Comparison of Couple Efficiency for Various Thermoelectric Material Pairs ($T_C = 160^\circ\text{C}$, No Contact Resistance)

FIGURE 17

FIGURE 18 Variables Influencing Performance

- D_N — N-leg Diameter
- L_{1N} — N-leg Hot Segment Length
- L_{2N} — N-leg Cold Segment Length
- D_p — P-leg Diameter
- L_p — P-leg Length
- Y_{Nd} — $NdSe_x$ Doping Level ($x = 1.5 - Y_{Nd}$)
- R_{Nd} — $NdSe_x$ Material Extraneous Resistance
- R_{ENH}, R_{TNH} — N-leg Hot End Electrical, Thermal Contact Resistance
- R_{ENC}, R_{TNC} — N-leg Cold End Electrical, Thermal Contact Resistance
- R_{EPH}, R_{TPH} — P-leg Hot End Electrical, Thermal Contact Resistance
- R_{EPC}, R_{TPC} — P-leg Cold End Electrical, Thermal Contact Resistance
- Q — Heat Flux per Couple
- I — Current per Couple

3.3.1 P-Element Contacting

In January, a test program was devised to learn more about P-leg resistance increases observed in Module M-21 and to suggest ways of eliminating them.

ATT Nos. 600, 602, 604, 606, 608 and 612, hereafter referred to collectively as Series 1, were designed to help explain the presence of the resistance increases. In particular, the roles of angular misalignment, low contact pressure, foreign matter at an interface and the loss of mechanical bond at the hot end of the P-material were to be characterized. Table XIII describes Series 1 test configurations.

Series 1 was the first group of tests to be run. The results of these tests were used in deciding on the focus of the second series of P-leg tests. Series 2 comprised ATT Nos. 628, 630, 632, 636, 640, 642 and 648. The purpose of this series was to evaluate some potential solutions to the P-leg problem. In particular, ideas such as increasing the contact pressure, changing the cap material, mechanically bonding the cap to the leg, and employing a gimbal were all evaluated. Table XIV describes the Series 2 test configurations.

The legs used in all tests were assembled with a stepped cap of WRe, and were wrapped with the standard Astroquartz thread/Min-K slurry for sublimation suppression. Standard hot end and cold end hardware was used in every test. Figure 19 shows how the leg/hardware assembly was instrumented.

The desired operating condition for each test was 913/160°C, 15.4A/cm. This operating condition was selected to provide a sublimation rate approximately 1.6 times greater than that of M-21. Tables XV and XVI show the mean operating conditions and acceleration factors (w.r.t. M-21) of each test in Series 1 and 2. Deviations from the desired operating conditions were caused by fixture limitations.

Weight loss measurements are shown in Tables XV and XVI. These numbers should be interpreted with some caution for two reasons. These are:

- (1) The presence of voltage probes in the legs influenced the weight measurement in some cases.
- (2) The presence of voltage probes in the leg can influence the weight loss (wrapping around the probe is a difficult task and introduces a potential sublimation leak). This can be seen by comparing weight loss for ATT 630 and ATT 642, which are nominally identical tests.

The approach which appears to be most promising is the increase of contact pressure. A test with 600 psi contact pressure (ATT 632) maintained a low resistance for more than 2800 hours of actual test time (equivalent to more than 67,000 hours of operation at the reference conditions of 815/160°C, 8.57 amp/cm). This test was still in operation at the end of the reporting period. A summary of the performance for this test is contained in Table XVII.

The conclusions that have been made from these tests are listed below:

- (1) The P-leg problem occurs at the interface between the stepped cap and the P-material.
- (2) The problem can be described as a gradually increasing resistance (and gradually decreasing Seebeck coefficient) which continues until a "critical point" is reached. At times after the critical point is reached, the interface seeks a high resistance operating mode. Therefore, the P-leg behavior can usually be characterized by two numbers: initial resistance degradation rate, and hours to critical point. The high electrical resistance is accompanied by a high thermal resistance. Figure 20, a graph of leg resistance vs. time for ATT 600, illustrates the occurrence of the critical point.
- (3) Thermal cycling seems to repair the hot end interface, at least temporarily. This point is also illustrated in Figure 20.
- (4) If left undisturbed for a long time (a few hours), temporarily opening the circuit will jar the hot end interface into a low resistance operating condition. However, the interface resistance will inevitably degrade to the high resistance condition after some span of time, the length of which is unaffected by additional externally imposed disturbances. Usually, the low resistance mode is maintained anywhere from a few minutes to a few hours.
- (5) Misalignment and low applied load do not cause the problem, but can aggravate it.
- (6) Foreign matter between the hardware and the TE elements causes high but steady contact resistances.
- (7) Electrical contact resistances are lower than expected and are not overly sensitive to misalignment nor to contact pressure. The hot end thermal contact resistance appears to be moderately dependent on contact pressure. Tables XVIII and XIX show compilations of contact resistance data from Series 1 and Series 2 tests.
- (8) Increased load and a P-leg gimbal both seem to affect lower resistance degradation rates and longer lifetimes. A mechanically bonded cap with increased load pressure also performed admirably. Table XX shows degradation rates and hours to critical point for series 2 tests as compared to those of ATT 600. The behavior of ATT 600 was comparable to that of the P-legs of Module M-21.
- (9) WSe_2 was found at the hot end interface of the P-leg. A first attempt at the use of a Re cap was unsuccessful.

TABLE XIII Series 1 Test Descriptions

ATT No.	Loose Cap	10° Wedge	Min-K	Contact Pressure	Desired Operating Conditions
600				150 psi	913/160°C, 15A/cm
602		x		" "	" " " "
604	x			" "	" " " "
606	x	x		" "	" " " "
608	x			100 "	" " " "
612			x	150 "	" " " "

TABLE XIV Series 2 Test Descriptions

ATT No.	Bonded Cap	Rhenium Cap	Gimbal	Contact Pressure	Desired Operating Conditions
628				300 psi	913/160°C, 15.0 A/cm
630				800 "	" " " "
632				600 "	" " " "
636	x			150 "	" " " "
640	x			300 "	" " " "
642				800 "	" " " "
646			x	150 "	" " " "
648		x		150 "	" " " "

FIGURE 19 Instrumentation Lay-out for Series 1 & 2 Tests

TABLE XV Series 2 Test Status, 9/25/79

Att No.	Duration (Hrs.)	Termination Date	Mean Operating Conditions	Mean Norm. M.L. Power* (W)	Expected Wt. Loss (mg)	Actual Wt. Loss (mg)	Accel. Factor (M-21)
628	765	6/26/79	915/138°C. 15.1 A/cm	.55	26.0	36.0	2.0
630	550	6/22/79	905/165°C. 15.0 A/cm	.68	11.0	~ 200	1.2
632	2800	—	905/160°C. 15.0 A/cm	.60	—	NYA	1.3
636	900	7/29/79	929/174°C. 15.0 A/cm	.57	27.0	< 46.0**	1.8
640	900	7/29/79	900/170°C. 15.0 A/cm	.61	17.0	< 43.0**	1.1
642	500	7/11/79	915/173°C. 15.2 A/cm	.56	12.0	~ 12	1.4
646	800	7/27/79	905/175°C. 14.8 A/cm	.48	15.0	16.0	1.1
648	160	7/5/79	913/170°C. 15.0 A/cm	.54	—	—	1.4

NYA - Not yet available

* - Before failure (Normalization is to 913/160°C, matched load)

** - These values are less than the amount shown because of problems with the voltage probe in the leg influencing the weight measurement. Additional evaluations of the amount of copper extrudant will be performed to obtain a better estimate of weight loss.

TABLE XVI Series 1 Test Status, 9/25/79

Att No.	Duration (Hrs.)	Termination Date	Mean Operating Conditions	Mean Norm. M.L. Power* (W)	Expected Wt. Loss (mg)	Actual Wt. Loss (mg)	Accel. Factor (M-21)
600	1000	4/27/79	897/158°C, 16.9 A/cm	.51	—	—	1.6
602	560	4/20/79	870/142°C, 15.0 A/cm	.41	8.0	< 18**	.85
604	660	4/27/79	922/155°C, 15.2 A/cm	.41	—	—	1.9
606	570	4/27/79	877/139°C, 15.1 A/cm	.26	—	—	1.0
608	670	5/2/79	907/162°C, 15.1 A/cm	.42	15.0	< 77**	1.3
612	840	5/23/79	858/170°C, 15.2 A/cm	.27	—	—	.53

* — Before Failure (Normalization is to 913/160°C, matched load)

** These values are less than the amount shown because of problems with the voltage probe in the leg influencing the weight measurement. Additional evaluations of the amount of copper extrudant will be performed to obtain a better estimate of weight loss.

TABLE XVII Performance of P-Leg at 600 psi
Contact Pressure (ATT 631)

TIME (Hr.)	T _H (°C)	T _C (°C)	R (mΩ)	S (μ V/°C, Pt)
4	903	151	11.3	232
100	908	155	11.5	235
208	904	157	11.8	235
304	907	157	12.1	234
400	903	158	12.4	233
508	905	161	13.3	233
604	902	159	11.2	236
700	904	159	11.5	237
808	908	159	11.8	236
904	910	160	11.8	236
1000	915	160	11.9	236
1108	915	163	11.9	237
1204	923	164	12.2	239
1300	907	162	11.7	239
1408	897	160	12.0	237
1504	893	160	11.9	237
1600	890	160	11.8	237
1708	904	163	11.8	240
1804	892	161	11.7	238
1900	903	161	11.7	238
2008	916	163	11.7	241
2104	915	164	11.9	241
2200	914	165	12.0	242
2308	914	165	11.8	242
2392	912	164	11.8	242
2524	912	165	11.1	243
2713	908	166	11.6	242
2800	904	165	11.5	243

TABLE XVIII Series 1 Contact Resistances

ATT No.	Hot Strap - Cap		Disc - Cold Strap	
	$\Delta T(^{\circ}\text{C})$	$R(\text{m}\Omega)$	$\Delta T(^{\circ}\text{C})$	$R(\text{m}\Omega)$
600	42./50.	.25/.40	2./4.	.05/.20
602	14./16.	.17/.22	3./5.	.12/.13
604	8./18.	.15/.26	3.	.08
606	—	.14/.32	11./14.	.17
608	21./33.	.14/.45	2./3.	.14
612	29./37.	6.6/8.3	—	.15

TABLE XIX Series 2 Contact Resistances

ATT No.	Hot Strap - Cap		Disc - Cold Strap	
	$\Delta T(^{\circ}\text{C})$	$R(\text{m}\Omega)$	$\Delta T(^{\circ}\text{C})$	$R(\text{m}\Omega)$
628	9./19.	.09/.19	5./7.	.05
630	13.	.07/.08	—	.08
632	12./15./	.10	1./2.	.06
636	4./10.	.11/.17	1./3.	.13
640	8./10.	.15/.16	0./1.	.09/.10
642	0./5.	.09/.12	9./11.	.09/.10
646	3./6.	.17/.19	5./6.	.06/.07
648	—	—	—	—

TABLE XX Series 2 Details of Resistance Increases

Att No.	Initial Rate (% per 1000 hrs.)	# Hrs.to Critical Pt.
628	28.	480
630	53.	—
632	30.	—
636	—	0
640	12.	630
642	36.	NYA
646	39.	800
648	0	100
600	85.	200

NYA — Not yet available

3.3.2 N-Element Contacting

The four segmented N-legs that were tested (refer to Section 3.6.2) brought to light a problem with single element N-leg tests in the 12 station. Each leg suffered severe resistance and Seebeck coefficient increases immediately upon heatup. Post test examinations confirmed that oxidation of the legs was responsible. The results of a number of experiments that were performed to find the source of the oxygen suggested that the absence of a pretest bake out process resulted in a liberation of residual water vapor from the thermal insulation during heatup.

Presently, at the start of any N-leg test the fixture is wrapped with heating tape, allowing a 60°C bakeout of the insulation. This additional processing step has significantly reduced the occurrence of leg oxidation, thereby substantially reducing the degradation rates. Table XXI illustrates these improvements. Higher temperature bakeouts (100-150°C) have been examined for any further improvements.

3.3.3 Cold End Thermal Resistance Reduction

Between October and December of 1978, a new test fixture was designed and built for the purpose of accurately and expeditiously measuring the thermal resistances of cold end hardware and hardware interfaces. This fixture was intended to be used not only for characterization studies, but hopefully also for non-destructive QC testing of cold end hardware assemblies. Figures 21 and 22 describe the test fixture.

A number of experiments have been conducted to characterize the thermal resistance of the interface between the cold frame segment and the outer housing. For all experiments, the outer housing was modeled by a 6064 Al chill block tailored to match the convex surface of the cold frame segment and polished to a 16 μ " RMS surface finish. Temperature drops across the interface were measured with Teflon insulated .003" D Iron-Constantan thermocouples embedded .030 in. from the interface on either side. The results are compiled in Table XXII. The contact pressures shown in the table correspond to the use of six 24 lb. N-leg springs and six 8.5 lb. P-leg springs.

A few conclusions can be drawn from these results. Firstly, the switch from 2024 to 6061 Al apparently has no effect on thermal resistance at the interface. Secondly, the presence of a ductile intermediate layer in test number 3 significantly reduces the thermal resistance. The relatively wide spread in the data could be attributed to a number of things: differences in mean temperature, variability in degree of oxidation of the aluminum surfaces from test to test, and large uncertain ($\pm 10\%$) in the contact pressure.

Thermal resistance with an intermediate ductile layer needs to be better characterized. Presently the effect of the ductile layer on the variability of thermal resistance is not known.

A number of tests have been conducted to study the magnitude and reproducibility of the thermal resistance of the SN-1 cold hardware. These measurements were made along with the cold end interfacial ΔT measurements. All specimens were X-rayed before the test in order to provide some indication of bond quality. The results, which are displayed in Table XXIII show that whereas there does seem to be some correlation between bond quality and thermal resistance, it isn't strong enough to warrant using X-rays alone as a QC inspection tool. (This is not to say that X-ray couldn't be used for detecting grossly flawed assemblies.) In any event, the data indicates that reproducibility of thermal resistance is not a problem.

TABLE XXI Summary of N-Leg Ingradient Performance

ATT No.	Description	dR/dt (Milliohms/hr.)	dS/dt (μ V/ $^{\circ}$ C/hr.)
626	Segmented GdSe _x /PbTe; No bakeout	.21	.20
638	Unsegmented, Cubic Phase GdSe _x ; 15 hr. Bakeout at 60 $^{\circ}$ C	.0051	.0049
643	Unsegmented Cubic Phase NdSe _x ; 15 hr. Bakeout at 60 $^{\circ}$ C	.002	.006
644	Segmented GdSe _x /PbTe; 15 hr. Bakeout at 60 $^{\circ}$ C	.015	.032
650	Segmented GdSe _x /PbTe; Not yet on ingradient test; resistance measured during bakeout at 150 $^{\circ}$ C, 175 $^{\circ}$ C, and 100 $^{\circ}$ C	.037 at Bakeout Temp. of 200 $^{\circ}$ C	

FIGURE 21 Cold End Hardware QC Testing

SCHEMATIC OF THERMAL RESISTANCE TEST ASSEMBLY

FIGURE 22 Cold End Hardware QC Testing

TABLE XXII A Compilation of Interfacial ΔT Results

Test No.	Segment Material	Intermediate Material	Contact Pressure (psi)	Mean Temperature ($^{\circ}\text{C}$)	Heat Flux (W)	Mean ΔT ($^{\circ}\text{C}$)	No. of ΔT Readings	Contact Resistance ($^{\circ}\text{C}/\text{W}$)
1	2024-T7	None	65.0	142	26.7	5.8	1	.217
2	6061-T6	None	65.0	119	35.4	7.7	1	.218
3	6061-T6	.001 Sn foil	65.0	236	32.6	5.2	3	.160
4	6061-T6	None	65.0	58.1	49.9	12.8	3	.257
5	6061-T6	None	65.0	47.7	53.8	19.0	3	.353
6	6061-T6	None	65.0	128	40.4	11.3	2	.280
7	6061-T6	None	65.0	133	41.2	9.3	1	.226
8	6061-T6	None	65.0	139	37.0	7.8	1	.211

TABLE XXIII A Compilation of Cold End Hardware
Thermal Resistance Data

<u>Assembly No.</u>	<u>Thermal Resistance ($^{\circ}\text{C}/\text{W}$)</u>	<u>Bond Quality</u>
1	5.04	Good
2	7.08	Poor
3	7.92	Fair
4	6.40	Poor
5	6.42	Good
6	6.22	Poor

3.4.1 Spring Load Relaxation

A compilation of spring load relaxation data appears in Figure 23. In the course of 20,000 hours of exposure, M-7 springs experienced an almost complete loss of load. This degree of load relaxation was far in excess of existing load relaxation vs. time data available in the literature. Springs from other modules had higher than expected load losses, though none were as dramatically high as M-7. The fundamental differences between the conditions in which the module springs and the literature springs were tested were that the module springs were operated in an oxygen free environment (either vacuum or inert backfill, depending on the module) and were also subjected to selenium vapor. Spring tests described in the literature took place in air.

A series of load relaxation tests were planned and run. These tests, which were intended to be diagnostic tests, are described and their results displayed in Table XXIV. The air data is in acceptable agreement with the literature, and the vacuum plus selenium data is in good agreement with the module data. Comparison of the vacuum only data with the vacuum plus selenium data tells us that the presence of selenium is not the key. This conclusion has been backed up by a number of chemical analyses. X-ray fluorescence tests were conducted to obtain an overall selenium content measurement, and whereas there was selenium present on all springs, there was no correlation between selenium pickup and load relaxation. Oakridge Labs determined that all of the selenium pickup occurs at the surface in the form of a very thin film of iron selenide. The fact that this film is not a contributor to load relaxation was demonstrated with dip tests performed at 3M.

Microhardness tests performed by both 3M and Oak Ridge National Labs (ORNL) showed that hardness changes occurred throughout the crosssections of the springs. Also, metallographic analysis performed by ORNL showed grain enlargement throughout the crosssection, an observation consistent with the microhardness tests.

It is important to mention that M-7 springs were a bit underdesigned with respect to load relaxation considerations. In addition an overtemperature did occur for a short period of time. It is estimated that the BOL corrected stress in the N-leg springs was 130 ksi. This could be the reason why M-7 springs relaxed more than other modules, but the amount of relaxation is significantly higher than one would estimate based on the 130 ksi stress level. It appears that one reason all module springs relaxed more than expected was that the absence of oxygen seemed to accelerate load relaxation rate, but again, at present there is not enough information to explain why this occurs.

The observation of grain enlargement in the module springs that were examined indicates that the operating temperature was too high for ASTM A-401 Cr-Si steel, the material used for modules M-7 through M-18. Presently, 17-7 PH stainless steel is being used for module springs. Test data indicates that 17-7 relaxes only about 50% as much as Cr-Si under identical conditions and test durations. Even though 17-7 is showing superior performance with respect to Cr-Si, other materials are being looked into, e.g. Inconel X, MP-35N and Elgiloy. To date springs of these materials have not been tested.

3.4.2 Solder Bond Strength Tests

Tests were conducted to determine the strength of the solder connection between the followers and the rails. The test was designed to provide a load in pure tension. Results indicate a strength of about 800 psi. A total of fifteen specimens were tested. There appeared to be some correlation between bond strength and contact area as shown in X-ray photographs that were taken on all specimens prior to the full tests.

FIGURE 23 A Compilation of Load Relaxation Data

Environment: $T = 150 - 175^{\circ}\text{C}$
Vacuum + Partial Pressure of Se

TABLE XXIV A Compilation of Load Relaxation Data

<u>Material</u>	<u>Corrected Stress (ksi)</u>	<u>Temperature (°C)</u>	<u>Environment</u>	<u>Duration (hrs)</u>	<u>% Load Loss</u>	<u>No. of Springs</u>
Cr-Si	100	150	Air	274	4.6	6
302 Stainless	100	150	Air	274	5.9	6
17-7 PH (R.T. Set)	100	150	Air	274	3.1	6
17-7 PH (H.T. Set)	100	150	Air	274	2.9	6
Cr-Si	73.4	179	Vacuum + Se	283	8.0	6
17-7 PH (R.T. Set)	85.1	179	Vacuum + Se	283	7.0	6
Cr-Si	100	175	Vacuum + Se	360	8.3	12
17-7 PH (R.T. Set)	100	175	Vacuum + Se	360	3.1	12
Cr-Si	100	175	Vacuum	300	9.1	12
17-7 PH (R.T. Set)	100	175	Vacuum	300	4.3	12

3.6 SEGMENTED ELEMENT STRUCTURES

3.6.1 Multicouple Tests

A six couple module, ATT 590, which used segmented $\text{GdSe}_x/\text{PbTe}$ N-legs was assembled and tested between December and March. The test has been terminated and a post test analysis report has been written (Section 5.4.4.2). Some brief comments appear in the following paragraph, and a tabulated performance history appears in Table XXV.

While at temperature two of three N-leg couples increased in resistance throughout the test. The third N-leg couple was stable. In the last 100 hours of at-temperature operation, two of the P-leg couples began to exhibit sporadic increase in resistance and drops in Seebeck coefficient. The third P-leg couple was stable in terms of resistance and Seebeck. The test was terminated after power output dropped approximately 20% from peak. Delta T and current for at-temperature testing was from flight design, $\Delta T = T_h - T_c = 850^\circ\text{C} - 150^\circ\text{C} = 700^\circ\text{C}$ and $I = 8$ amperes. Post cooldown resistance probing from the external fixture connectors indicate at least one electrical short to ground of less than one ohm. The following observations were made following the removal of the converter assembly from the test fixture:

1. Appearance of orange bands on GdSe segments of N-legs correlates with increased resistance in N-legs, which was the main cause of performance degradation prior to $t = 1400$ hours of ingradient testing.
2. Several low resistance shorts appeared across BeO discs which degraded electrical performance from $t = 1400$ hours to end of test.
3. The P-legs were not tested long enough to enter their characteristic unstable resistance mode; however, PTA resistance measurements correlate high P-material to WRe interface resistance with the relative amount of black deposit on WRe cap. The significance of this correlation should not be overemphasized, however, because the data base is small.
4. PbTe hot ends were not adhered to segment foils; two N-legs had high resistance ($38\text{ m}\Omega$ and $30\text{ m}\Omega$) at this interface.

3.6.2 Single Element Tests

Seven single element segmented N-legs were placed on test this year. Four of the seven tests suffered severe oxidation shortly after heatup, preventing extensive analysis of thermoelectric performance. However, it was possible to obtain measurements of the interfacial temperatures. Predictions of the interface temperature for each test were generated with the couple performance program, based on the individual leg geometries and thermal boundary conditions. A comparison of predicted and observed temperatures appears in the first two columns of Table XXVI.

Other available data (including K measurements of unsegmented PbTe legs) suggested that the discrepancies between expected and measured interfacial temperatures were caused by a discrepancy between expected and predicted PbTe thermal conductivities. Notice that the discrepancies with this data (illustrated in Table XXVII) are in good agreement with the discrepancies shown in Table XXVI. This is very likely due to a difference in doping between these PbTe materials and the 2N material which was used as a reference for the segmented leg design.

As a result of these observations, several new segmented N-legs having different geometrics were designed and manufactured. To date only one of these redimensioned legs has been tested, and the results haven't been thoroughly analyzed. Work on PbTe will be deferred for the next fiscal year but when it is continued good measurements of the PbTe properties for the materials we are using must be obtained.

TABLE XXV ATT 590 6-Couple Performance

Total Test Time (Hours)	P-Leg								N-Leg							
	Leg No. 1		Leg No. 3		Leg No. 5		Mean		Leg No. 2		Leg No. 4		Leg No. 6		Mean	
	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)	S (uv/°C)	R (mΩ)
5.9	229.6	10.05	223.3	9.62	221.0	9.25	224.6	9.64	170.5	7.43	179.8	7.72	173.0	6.96	174.6	7.37
21	221.4	9.00	218.8	8.55	212.9	8.00	217.7	8.52	175.9	7.64	182.5	7.74	178.3	7.21	178.9	7.53
42	214.7	8.44	212.2	7.95	206.0	7.31	211.0	7.90	176.1	7.58	181.5	7.61	178.8	7.19	178.8	7.46
94	214.5	8.38	210.6	7.55	205.4	7.09	210.2	7.68	178.0	7.61	183.4	7.76	117.6	7.03	179.7	7.47
164	219.4	8.61	215.3	7.82	211.3	7.55	215.3	7.99	182.0	8.06	188.4	8.36	180.3	7.31	183.6	7.91
210	217.9	8.48	215.1	7.78	211.0	7.46	214.7	7.91	183.3	8.16	188.2	8.36	180.2	7.27	183.9	7.93
258	218.4	8.56	214.1	7.67	210.0	7.43	214.0	7.89	185.1	8.35	191.4	8.67	180.5	7.28	186.0	8.10
308	217.2	8.57	215.4	7.78	210.5	7.85	214.0	8.06	188.0	8.63	193.8	8.96	184.4	7.58	189.0	8.39
379	217.2	8.51	214.7	7.70	210.0	7.44	214.0	7.88	188.3	8.76	195.7	9.21	183.7	7.53	189.0	8.50
428	217.7	8.59	213.2	7.85	206.8	7.55	213.0	8.00	189.8	8.93	197.0	9.39	182.0	7.40	190.0	8.57
474	214.9	8.92	213.5	7.83	208.9	7.29	212.0	8.02	190.2	9.05	196.2	9.38	182.9	7.46	190.0	8.63
527	218.4	8.68	215.1	7.94	213.5	7.27	216.0	7.96	193.4	9.46	201.9	10.04	187.4	7.89	194.0	9.13
619	214.9	8.53	213.2	7.86	209.6	7.55	213.0	7.98	191.5	9.48	198.6	9.94	185.2	7.72	191.0	9.05
670	213.1	8.35	209.8	7.57	208.9	7.48	211.0	7.80	194.0	9.89	199.5	10.17	186.2	7.79	193.0	9.28
717	211.7	8.41	211.5	7.74	209.6	7.08	211.0	7.74	191.3	9.79	198.5	10.18	186.7	7.85	192.0	9.27
882	211.2	8.25	208.1	7.51	208.7	7.58	209.0	7.78	193.3	10.39	199.1	10.67	187.0	7.90	193.0	9.66
955	208.7	8.17	208.3	7.58	210.7	7.47	209.2	7.74	190.8	10.52	199.4	10.96	187.3	7.96	192.5	9.81
978	210.1	8.24	208.2	7.60	210.4	7.62	209.6	7.82	190.7	10.59	197.9	10.90	187.1	7.97	191.9	9.82
1002	206.3	8.24	209.0	7.63	212.7	7.83	209.3	7.90	191.3	10.67	198.6	11.01	187.8	8.04	192.6	9.91
1027	209.5	8.38	209.2	7.67	212.8	7.87	210.5	7.98	191.4	10.76	200.1	11.19	187.9	8.05	193.2	10.00
1123	213.1	8.79	209.9	8.00	212.7	7.40	211.9	8.06	199.4	11.39	204.0	11.58	189.4	8.17	197.6	10.38
1170	215.0	8.49	210.5	7.74	212.8	8.11	212.8	8.11	200.1	11.59	204.6	11.75	188.3	8.08	197.7	10.47
1218	213.3	8.68	207.4	7.87	211.6	7.73	210.7	8.10	201.4	11.88	204.5	11.91	190.0	8.25	198.6	10.68
1291	212.9	8.43	205.7	7.83	213.9	7.64	210.9	7.97	200.8	11.98	205.4	12.20	190.8	8.33	199.6	10.84
1339	212.2	8.55	209.6	7.73	213.7	7.66	211.8	7.98	204.6	12.64	205.2	12.32	190.6	8.33	200.2	11.10
1386	216.3	8.80	210.5	7.97	213.2	7.73	213.3	8.16	204.3	12.39	206.2	12.50	190.2	8.29	200.2	11.06
1459	213.7	8.51	207.9	8.26	213.3	8.27	211.6	8.35	205.9	13.08	206.3	12.74	191.9	8.48	201.4	11.43
1506	215.6	8.79	208.4	7.95	213.9	8.11	212.6	8.28	209.0	13.70	206.9	12.97	192.4	8.53	202.8	11.73
1530	213.7	8.73	209.5	7.99	213.7	7.76	212.3	8.16	208.7	13.80	208.0	13.17	192.2	8.53	203.0	11.83
1562	202.3	7.78	200.8	7.51	214.9	8.00	206.0	7.76	188.6	12.58	196.4	12.40	191.6	8.46	192.2	11.15
1626	201.5	7.59	195.7	8.39	214.3	7.98	203.8	7.99	192.3	12.67	200.0	13.02	192.7	8.59	195.0	11.43
1650	199.2	7.44	200.6	7.34	214.6	8.10	204.8	7.63	188.5	12.30	196.2	12.64	192.9	8.61	192.5	11.18
1674	199.1	7.69	198.9	7.44	214.4	8.15	204.1	7.76	185.5	12.46	196.0	12.79	192.8	8.61	191.4	11.29

TABLE XXVI A Compilation of Comparisons of Predicted to Measured Values of the Interface Temperature for Segmented Legs (PbTe/Orthorhombic GdSe_x)

Test No.	Interface Temperature (°C)		Correction Factor for K PbTe	Seebeck Coefficient (μV/°C)		
	Measured	Predicted		W/O Correction	W/Correction	Measured
PM 055	398	350	0.70	165	176	174
PM 057	458	408	0.70	178	189	200
PM 063	484	392	0.55	174	192	186
ATT 616	447	380	0.65	172	186	173
ATT 618	437	387	0.74	173	183	183
ATT 622	431	369	0.65	169	183	220
ATT 624	411	363	0.73	168	178	197
			$\bar{x} = 0.67$			
			$\sigma = 0.07$			

TABLE XXVII A Comparison of Predicted to Measured Conductivities
for PbTe Legs

Test No.	Thermal Conductivity (mw/cm-°C)		Correction Factor
	Predicted	Measured	
PM 056	16.5	12.3	0.75
PM 060	16.4	12.8	0.78

TASK 4.0 -- MODULE DEVELOPMENT

4.1 EVALUATION OF REDUCTION OF BYPASS--HEAT LOSS

4.1.1 Aerosol Injection of Insulation

The purpose of this evaluation was to improve the assembly technique of inserting insulation and to reduce bypass-heat loss. A test fixture, including four (4) six-couple assemblies, was set up to evaluate the results of this technique under vibration. Using air as the vehicle, powdered MIN-K was injected to a density of 14.0 pcf. (close to the density to which Hi-Fi paper is packed). Initially, the insulation was very evenly distributed around the legs with no visible voids. The assembly was vibrated at approximately 19 g's for about thirty (30) minutes, ten (10) minutes on each major axis. By the end of the test, several large air pockets taking up as much as 20% of the cross-sectional area had appeared. It may be possible to correct this problem by increasing the density pack. Further evaluation would have to be completed to determine if the density required interfered with hardware conformity.

4.1.2 Thermal Conductivity vs. Packing Density

A series of tests was completed at Dynatech R/D Co. to evaluate the effect of packing density on thermal conductivity of Hi-Fi 660 paper. Densities ranged from 12.0 pcf (nominal) to approximately 20.0 pcf. Samples were tested over a temperature range of 100-1000°C. The results show that over the given density range, thermal conductivity decreases with increasing density.

4.2 DEVELOPMENT OF IMPROVED ASSEMBLY TECHNIQUES

Techniques for improving module assembly were developed in conjunction with Module M-22R described in Section 4.3.1.

4.3 DESIGN AND DEVELOPMENT OF MODULES

4.3.1 M22-R Module Design

A twelve couple diagnostic module similar to M-21 was placed on test during June 1979. The testing of this module is described in Section 5.4.4.1. A description of some of the design features is contained below.

(1) Design steps to control leg and spring alignment.

- The cold frame was redesigned so that compression forces on springs and legs are axial.
- Assembly tooling was redesigned to help maintain proper alignment during assembly.
- Design changes were made to have the converter held in compression by three tantulum rods, rather than four, to provide easier stack height adjustment and a more even distribution of load. Design changes were also made to eliminate the need of shimming to obtain correct stack heights which required successive de-compression and compression of the converter.

- The above steps taken to control alignment were successful. Measurements taken before and after module operation indicated that the amount of mis-alignment that occurred was within the tolerance of our measurement technique.
- (2) Platinum heaters were used to reduce contamination of the system. This design change was successful. Post operation analysis concluded that the M22-R module exhibited a much lower degree of contamination compared to previous modules.
- (3) Platinum foils were placed between the P-leg caps and hot current straps to increase conductivity between these surfaces.
- (4) Springs forces on P-legs in one segment were increased to determine what effect this would have on contact resistance and alignment.

4.3.2 Module M-23R Individually Isolated Cold-End Hardware

The purpose of module M-23R was to compare performance of the isolated cold end hardware design to that of the compliant cold end hardware design. The couple configuration is shown in Figure 24. Voltage and temperature measurements were to be made at various locations in the module to measure electrical and thermal resistances between various components during operation. The degree of misalignment, spring relaxation, leg degradation and chemical contamination was to be compared with data from the M-22R test to determine the most effective cold end hardware design.

The design for module M-23R was essentially completed and parts were fabricated; however, due to lack of funding it was not assembled and placed on test.

FIGURE 24 M23R Stack Configuration

Capped wrapped P-leg 240 psi

Non-segmented N-Leg Gdse_x cubic 300 psi

TASK 5.0 – EVALUATION OF LIFETIME AND RELIABILITY OF IMPROVED MATERIALS, HARDWARE COMPONENTS AND MODULES.

5.1 OBJECTIVE

The objective of this task is to obtain data on long term operating characteristics, ingradient compatibility, and reliability of elements, couples, and modules.

5.2 CHEMICAL COMPATIBILITY, OUTGASSING AND REACTIVE ATMOSPHERES OF CONVERTER COMPONENTS.

Multifoil Compatibility Test

A single couple test was placed on test during October, 1978, to evaluate the effect of P-leg sublimation on multifoil insulation effectiveness. The test was to operate at 850/150°C for 2000 hours. Thermocouples were attached to the multifoil at three (3) different ingradient locations. These indicate that the multifoil operated at a lower temperature than desired (approximately 600°C). Additional testing was planned with a fixture which would maintain multifoil temperatures at the desired value; however, these additional tests were not completed because of a refocus of priorities after the Galileo Stop Work Order.

5.3.1 Dynamic Testing

Parts for a test fixture to be used for characterizing the damping behavior of converter hardware were designed and fabricated. Three (3) sub-miniature piezo-electric accelerometers would be used to measure motion in each of the three axes. Signals would be picked up through a B and K charge amplifier and read out on an oscilloscope. A description of the output waveforms would be stored in a digital transient recorder for easy recall. Hard copies of waveforms would be obtained by photographing the screen of the oscilloscope. The apparatus would house two (2) opposing six-couple assemblies. The simulation heater block would be supported in between the two assemblies and therefore the motion of the block would depend entirely on the transmissibility of the six-couple assemblies. These tests also were not completed because of a refocus of priorities after the Galileo Stop Work Order.

The single-couple vibration test CV-5 was completed and suffered no significant power degradation on any of the three (3) axis. Upon disassembly, it was discovered that two (2) of the rods retaining the spacer had broken and thus reduced the contact pressure on the P-leg 32 psi and N-leg 38 psi. These results demonstrated that the legs could survive the dynamic loading even with a decrease in contact pressure. The sixth in a series of single-couple vibration tests was performed in December, 1978. Test CV-6 contained compliant cold end hardware and a segmented N-leg. The test was interrupted by an electrical failure after vibration along the first axis, which was parallel to the rail. This assembly survived a total of five (5) minutes at 23 g's before failing. Upon disassembly, the N-leg was found to be fractured at the Ni-GdSe_x bond.

Computer modeling was initiated in January. The ANSYS finite element structural analysis program was used. A finite element model of the cold frame segment was constructed and in the model linked to the hot frame via spring-dashpot elements in place of the compliant followers. This was done to avoid excessive storage requirements. At some later point, output from this model can be used as input for a second model, which would be of the compliant subassemblies themselves. This second model should permit an assessment of dynamic stresses in the foils as compared to their endurance limit.

Work continued on the dynamic characterization of the SN-1 design. Although SN-1 is not going to be built, the study should be beneficial in that it provides a baseline from which new potential designs can be judged. In April the solution for natural response of the converter ring was obtained. The finite element model included both axial and lateral spring stiffness, but didn't include damping. The results obtained were descriptions of several vibration mode shapes and their corresponding natural frequencies. The mode shapes which included both rigid body and non-rigid body motions, had natural frequencies ranging between 100 and several thousand cps.

5.4 LIFE TESTING OF IMPROVED MATERIALS, COUPLE COMPONENTS AND MODULE DESIGN

The assembly of twelve (12) new test fixtures was initiated in February. These fixtures have water cooling and cartridge heating, and are sufficiently flexible to accommodate both single-element and single-couple tests. Test to be performed in these fixtures include performance mapping, sublimation suppression, hardware evaluation and electrical/thermal contacting.

5.4.1 TPM-217 N-Material Ingradient Compatibility and Life Testing

Two (2) N-leg tests (ATT 364 and 385) are shown in Table XXVIII. ATT 385 experienced thermal-cycles during 1978 and was not restarted during FY, 1979. This leg test had been started in July, 1975 to evaluate tungsten and silver sputtering techniques on the leg electrodes. ATT 364 was designed to demonstrate the status of M-6 materials and contacts including using a gadolinium foil; it was started in April 1975. It had experienced a number of thermal cycles and the leg resistance value had increased and performance was greatly degraded; accordingly, the test was terminated in July, 1979 after 28,258 hours.

N-Legs with Pb-Ag Bonded Contacts

A series of Pb-Ag bonded N-legs were placed on long term test. Two of these (ATT 504/505) continued this year until they were terminated in March, 1979 after 15,243 hours. Table XXIX summarizes their performance. The other tests of the series were terminated earlier but are shown for comparison purposes.

Transformed N-Leg

An N-leg was placed on test during April, 1978, (ATT 539) which had an orthorhombic structure. The performance is summarized in Table XXX. The test was terminated March, 1979 after 7888 hours.

Neodymium-Selenide Testing

A total of nine (9) neodymium-selenide (NdSe_x) N-legs (ATT 658-666) were placed on ingradient life test during August, 1979. Two (2) of these elements (ATT 658, 660) were from a low density NdSe_x batch (batch N-2683 described in Table XXXI) and the other seven (7) elements were from a higher density batch (batch N-2685, also described in the above reference). The tests ATT 661-666 were placed on test in a six-station fixture to fulfill the August milestone. A summary of the room temperature resistance for the elements from batch N-2685 in various stages is shown in Table XXXII. A summary of the performance of these tests in the fixture at operating conditions is shown in Table XXXIII. It can be seen that the performance of the higher density material is superior to the lower density material both from the standpoint of the magnitude of Seebeck and resistivity as well as the stability of those parameters. This is consistent with observations on cubic GdSe_x and with the fact that reactivity with oxygen or other reactive gases should be greater for less dense material.

TABLE XXVIII Life Test Performance Summary

Key to Parenthetical Numbers (1) Terminated (2) Temporarily Shut Down (3) Instrumentation Problems			Nominal $T_H/T_C (^{\circ}\text{C})$	Theoretical $S(\mu\text{V}/^{\circ}\text{C}, \text{rel. to Pt})$	Theoretical $R(\text{m}\Omega)$	SEPTEMBER 1979				AUGUST 1979				JULY 1979				JUNE 1979			
						S (mean) $(\mu\text{V}/^{\circ}\text{C}, \text{rel. to Pt})$	S (Std. Dev.)	R (mean) $(\text{m}\Omega)$	R (Std. Dev.)	S (mean) $(\mu\text{V}/^{\circ}\text{C}, \text{rel. to Pt})$	S (Std. Dev.)	R (mean) $(\text{m}\Omega)$	R (Std. Dev.)	S (mean) $(\mu\text{V}/^{\circ}\text{C}, \text{rel. to Pt})$	S (Std. Dev.)	R (mean) $(\text{m}\Omega)$	R (Std. Dev.)	S (mean) $(\mu\text{V}/^{\circ}\text{C}, \text{rel. to Pt})$	S (Std. Dev.)	R (mean) $(\text{m}\Omega)$	R (Std. Dev.)
	Hours	ATT No.																			
P	91266	127	700/280	285	35.8	269	27.0	25.8	5.7	306	1.2	17.5	2.9	305	0.6	20.5	9.6	305	1.5	17.1	2.3
	91266	128	700/280	285	35.8	104	0.4	0.8	0.2	107	1.5	0.6	0.3	111	1.0	0.3	0.4	121	1.2	.5	0.3
	91147	129	700/280	285	35.8	233	2.3	1.2	1.3	235	0.6	3.5	17.	236	0.6	1.71	1.3	233	0.7	2.5	1.2
	80083	132	600/260	270	31.4	(2)				(2)				(2)				(2)			
	91266	133	600/260	270	31.4	276	17.2	20.0	7.0	303	0.5	8.8	0.7	304	0.3	7.5	1.2	303	0.6	6.9	0.7
	91266	136	500/210	244	24.4	257	21.0	27.6	7.7	291	0.7	38.7	2.2	231	0.0	35.6	2.1	289	0.7	38.5	1.7
	91266	137	500/210	244	24.4	197	1.1	13.1	0.6	201	2.5	11.8	1.7	200	1.4	11.2	1.5	200	1.6	14.7	7.7
	70985	192	700/260	276	32.8	291	13.3	30.9	19.9	313	0.5	1.4	1.2	312	1.0	3.9	4.7	312	1.1	1.3	0.6
	71261	195	700/260	276	32.8	278	6.7	39.6	18.2	290	0.6	10.3	1.1	291	0.4	9.4	1.2	289	0.6	8.5	0.9
	60199	196	800/300	297	40.1	(2)				(2)				(2)				(2)			
	38840	287	565/200	250	13.2	(2)				(2)				(2)				(2)			
	55223	288	565/200	250	13.2	242	.4	17.4	0.3	242	0.5	17.4	0.3	243	0.1	17.6	0.1	242	0.5	17.3	0.1
	55223	289	565/200	250	13.2	243	3.9	18.5	0.2	256	1.4	18.7	0.2	245	1.5	18.8	0.1	245	0.5	19.0	0.4
	27890	292	565/200	250	13.2	(2)				(2)				(2)				(2)			
Partitioned P	64858	210	800/270	297	40.7	(3)				(3)				(3)				(3)			
	59284	241	800/270	314	53.4	269	13.7	63.3	26.7	279	11.4	17.5	15.2	293	2.2	3.1	1.4	296	1.3	3.3	1.6
	22245	371	800/200	277	18.3	(1)				(1)				(1)				(1)			
	21945	372	800/200	277	18.3	(1)				(1)				(1)				(1)			
	22445	373	800/200	277	18.3	(1)				(1)				(1)				(1)			
	27245	374	800/200	277	18.3	(1)				(1)				(1)				(1)			
	27245	375	800/200	277	18.3	(1)				(1)				(1)				(1)			
	22025	376	800/200	277	18.3	(1)				(1)				(1)				(1)			
P Bonding	40130	237	800/250	285	35.3	(2)				(2)				(2)				(2)			
	56641	272	775/240	278	35.6	(3)				(3)				(3)				(3)			
Couple P N	12400	413	800/200	255	13.4	(2)				(2)				(2)				(2)			
	12400	417	800/200	177	10.8	(2)				(2)				(2)				(2)			
N M-6 Eval.	11934	385	800/200	195	14.2	(2)				(2)				(2)				(2)			
	28258	364	800/200	195	13.5	(2)				(2)				(2)				276	125.3	754.4	32.1

TABLE XXVIII (Continued)

Key to Parenthetical Numbers (1) Terminated (2) Temporarily Shut Down (3) Instrumentation Problems			Nominal T_H/T_C (°C)	Theoretical $S(\mu V/°C)$ rel to Pt	Theoretical R (m Ω)	MAY 1979				APRIL 1979				MARCH 1979				FEBRUARY 1979			
						S (mean) ($\mu V/°C$ rel to Pt)	S (Std Dev)	R (mean) (m Ω)	R (Std Dev)	S (mean) ($\mu V/°C$ rel to Pt)	S (Std Dev)	R (mean) (m Ω)	R (Std Dev)	S (mean) ($\mu V/°C$ rel to Pt)	S (Std Dev)	R (mean) (m Ω)	R (Std Dev)	S (mean) ($\mu V/°C$ rel to Pt)	S (Std Dev)	R (mean) (m Ω)	R (Std Dev)
P	Hours	ATT No																			
		127	700/280	285	35.8	303	2.2	18.4	3.2	264	17.5	29.4	9.5	256	1.7	26.2	1.10	257	2	27.1	66
		128	700/280	285	35.8	129	6.9	2.0	6.8	124	17.1	68.5	10.6	177	1.5	64.8	4.0	182	1.2	56.1	2.35
		129	700/280	285	35.8	231	1.0	2.3	1.6	226	1.6	1.0	0.2	225	0.6	1.2	0.08	224	4	1.2	0.7
		132	600/260	270	31.4	(2)				(2)	18.9	22.5	5.7	(2)				(2)			
		133	600/260	270	31.4	303	6	7.4	7	260	26.1	22.4	8.7	252	0.5	19.9	0.62	251	4	19.6	0.6
		136	500/210	244	24.4	289	4	38.4	1.9	232	1.0	13.6	0.4	219	0.7	17.9	0.05	217	4	17.8	0.4
		137	500/210	244	24.4	204	7	13.5	3.5	206	15.1	52.3	13.7	206	0.7	13.7	0.01	206	8	13.7	0.8
		192	700/260	276	32.8	311	1.8	2.9	1.9	278	7.5	48.2	2.1	273	0.3	53.8	5.08	273	2	53.7	2.68
		195	700/260	276	32.8	290	6	9.2	1.0	275	(3)			271	0.44	47.3	0.18	272	2	46.9	1.8
		196	800/300	297	40.1	(2)				(2)				(2)				(2)			
		287	565/200	250	13.2	(2)				(2)				(2)				(2)			
		288	565/200	250	13.2	242	3	17.3	1	242	0.9	17.4	16	242	0.4	17.3	0.07	243		17.5	
		289	565/200	250	13.2	245	3	20.6	1	245	0.2	20.5	14	244	0.1	20.5	0.08	245	3	20.6	10
		292	565/200	250	13.2	(2)				(2)				(2)				(2)			
Partitioned P		210	800/270	297	40.7	(3)				275	2.8	174	19.2	278	6	160.1	23.3	278	6	147	
		241	800/270	314	53.4	296	3.7	5.6	2.4	283	4.3	77.9	4.5	282	6	82.2	1.2	284	1.7	82	85
		371	800/200	277	18.3	246	8.5	12.2	25	244	10.2	12.3	35	243	9.9	12.3	0.29	249	9.0	12.1	32
		372	800/200	277	18.3	291	0	176.3	77.7	291	0.6	74.8	9.9	291	3	73.9	13.1	291	7	55.7	9.47
		373	800/200	277	18.3	386	17.1	13.9	72	334	56.1	12.3	1.6	306	47.3	11.9	1.7	291	7	10.6	
		374	800/200	277	18.3	259	1.4	12.6	0.6	260	1.8	12.8	0.21	260	1.1	12.8	0.8	261	1.6	12.9	14
		375	800/200	277	18.3	279	12.9	18.7	4	281	16.8	18.6	0.68	274	14.6	18.6	5.2	259	9.0	18.9	6
P Bonding		237	800/250	285	35.3	(2)				(2)				(2)				(2)			
		272	775/240	278	35.6	(3)				245	1.7	5.1	2.2	245	1.1	4.2	1.91	247	5	1.7	19
Couple P N		413	800/200	255	13.4	(2)				(2)				(2)				(2)			
		417	800/200	177	10.8	(2)				(2)				(2)				(2)			
N M 6 Eval		385	800/200	195	14.2	(2)				(2)				(2)				(2)			
		364	800/200	195	13.5	186.0	2.1	747.7	16.3	220	73.1	735.6	7.8	193	12.1	697.1	27.6	168	1.53	649.4	

TABLE XXVIII (Continued)

Key to Parenthetical Numbers				Theoretical S ($\mu\text{V}/^\circ\text{C}$, rel. to Pt)	Theoretical R ($\text{m}\Omega$)	JANUARY 1979				DECEMBER 1978				NOVEMBER 1978				OCTOBER 1978			
(1) Terminated	(2) Temporarily Shut Down	(3) Instrumentation Problems	Nominal T_h/T_c ($^\circ\text{C}$)			S (mean) ($\mu\text{V}/^\circ\text{C}$, rel. to Pt)	S (Std. Dev.)	R (mean) ($\text{m}\Omega$)	R (Std. Dev.)	S (mean) ($\mu\text{V}/^\circ\text{C}$, rel. to Pt)	S (Std. Dev.)	R (mean) ($\text{m}\Omega$)	R (Std. Dev.)	S (mean) ($\mu\text{V}/^\circ\text{C}$, rel. to Pt)	S (Std. Dev.)	R (mean) ($\text{m}\Omega$)	R (Std. Dev.)	S (mean) ($\mu\text{V}/^\circ\text{C}$, rel. to Pt)	S (Std. Dev.)	R (mean) ($\text{m}\Omega$)	R (Std. Dev.)
	Hours	ATT No.																			
P		127	700/280	285	35.8	257	.2	26.9	.41	256	0.5	26.3	0.6	273	24.5	25.3	3.2	256	0.4	25.6	0.4
		128	700/280	285	35.8	189	1.5	55.3	1.15	195	0.8	53.8	5.0	227	40.9	(3)		207	1.2	31.0	1.4
		129	700/280	285	35.8	222	.8	0.8	.46	221	0.4	1.6	0.05	221	1.7	2.1	1.5	214	1.4	1.8	0.0
		132	800/260	270	31.4	(2)				(2)				(2)				(2)			
		133	660/260	270	31.4	251	.3	19.5	.06	252	0.5	19.7	0.09	270	23.7	20.2	0.5	251	6.8	19.4	0.2
		136	500/210	244	24.4	212	1.1	17.3	.18	212	0.1	17.1	0.03	217	1.4	17.8	0.4	211	0.5	16.4	0.2
		137	500/210	244	24.4	207	.6	13.8	.02	206	0.5	13.8	0.01	206	2.1	13.9	0.7	205	0.8	13.6	0.1
		192	700/260	276	32.8	274	.3	38.8	2.68	274	0.0	33.3	1.44	288	20.2	31.1	2.7	273	0.6	34.5	2.6
		195	700/260	276	32.8	273	.4	47.0	.18	273	0.3	46.7	0.23	276	6.4	45.8	1.6	262	8.9	27.9	0.5
		196	800/300	297	40.1	(2)				(2)				(2)				(2)			
		287	565/200	250	13.2	(2)				(2)				(2)				(2)			
		288	565/200	250	13.2	244	.2	17.8	.03	244	0.0	17.8	0.05	243	0.4	17.6	0.1	243	0.4	17.5	0.1
		289	565/200	250	13.2	244	.3	20.5	.11	243	0.2	20.4	0.11	242	0.4	20.1	0.1	242	0.6	20.0	0.2
	292	565/200	250	13.2	(2)				(2)				(2)				(2)				
Partitioned P		210	800/270	297	40.7	272	8.2	123.6	28.0	280	6.7	(3)		289.3	9.8	(3)		283	1.8	106.5	9.9
		241	800/270	314	53.4	286	1.7	74.2	2.4	285	1.8	70.0	2.26	289	6.6	65.0	5.8	284	0.0	69.1	0.0
		371	800/200	277	18.3	248	9.4	12.1	.22	246	13.2	12.4	0.53	252	4.4	11.9	0.4	247	5.6	11.7	0.3
		372	800/200	277	18.3	289	.5	44.9	7.91	288	0.6	34.1	4.75	263	2.0	15.9	0.5	247	15.4	16.2	1.4
		373	800/200	277	18.3	314	53.5	11.8	1.42	256	8.9	10.3	0.28	251	10.9	10.3	0.8	255	4.9	9.9	0.2
		374	800/200	277	18.3	259	1.6	12.7	.07	259	1.5	12.8	.06	260	1.9	12.8	0.2	261	1.3	12.6	0.1
		375	800/200	277	18.3	262	5.7	18.1	.88	253	11.2	18.0	1.07	265	10.6	17.7	0.6	270	8.9	17.4	0.5
		376	800/200	277	18.3	270	2.0	11.0	.10	271	1.6	11.2	.07	270	1.7	11.3	0.1	271	2.0	11.5	0.2
P Bonding		237	800/250	285	35.3	(2)				(2)				(2)				(2)			
		272	775/240	278	35.6	249	.8	(3)		248	0.8	(3)		247	1.8	17.4	5.3	111	2.0	692.1	49.6
Couple P N		413	800/200	255	13.4	(2)				(2)				(2)				(2)			
		417	800/200	177	10.8	(2)				(2)				(2)				(2)			
N M-6 Eval.		385	800/200	195	14.2	(2)				(2)				(2)				(2)			
		364	800/200	195	13.5	157	.8	584.6	35.7	159	2.1	(3)		165	165	(3)		174	5.0	567.3	33.21

TABLE XXIX Summary of Long Term Testing of N-Legs with Bonded Cold End Contacts (Pb-Ag Foil)

ATT No.	Test Time (hrs)	Environment	Beginning of Test (4)				Most Recent Data				Best Performance			
			T_h/T_c ($^{\circ}\text{C}$)	S ($\mu\text{V}/^{\circ}\text{C}$, Pt)	R ($\text{m}\Omega$)	% ext.	T_h/T_c ($^{\circ}\text{C}$)	S ($\mu\text{V}/^{\circ}\text{C}$, Pt)	R ($\text{m}\Omega$)	% ext.	T_h/T_c ($^{\circ}\text{C}$)	S ($\mu\text{V}/^{\circ}\text{C}$, Pt)	R ($\text{m}\Omega$)	% ext.
490	495	Ar(3)	824/181	217	26.0	39	748/170	213	29.9	68	824/181	217	26.0	39
491	495	Ar(3)	824/173	216	28.5	54	748/164	207	32.3	94	824/173	216	28.5	54
494	650	Ar(3)	853/203	202	22.0	36	807/187	196	40.4	170	853/203	202	22.0	36
495	650	Ar(3)	852/186	205	27.9	65	808/189	194	33.0	126	854/189	200	25.5	61
497	450	Ar(3)	856/201	162	12.8	32	866/204	154	15.0	71	857/202	157	12.0	31
498	450	Ar(3)	856/189	158	12.3	34	866/193	153	14.0	62	856/189	158	12.3	34
499	6420	Ar	856/194	216	26.5	36	772/180	255	219.0	540	856/194	216	26.5	36
500	6420	Ar	856/201	213	25.4	36	772/183	245	214.3	628	856/201	213	25.4	36
504	15243	Vac	848/221	197	23.5	54	806/208	159	16.8	80.2	855/218	177	17.6	53
505	15243	Vac	848/212	199	27.0	73	807/200	159	17.1	86.0	829/195	166	16.3	63

- (1) Test still operating.
(2) Test temporarily shut down.
(3) No getter was used.
(4) After one day of seat in.

TABLE XXX Performance of Orthorhombic Leg – ATT 539

<u>Time</u>	<u>T_h</u> <u>(°C)</u>	<u>T_c</u> <u>(°C)</u>	<u>Seebeck</u> <u>(μV/ °C, Pt)</u>	<u>Resistance</u> <u>(mΩ)</u>	<u>%</u> <u>Ext.</u>
3	820	130	86	4.3	12
159	830	134	98	5.6	28
483	838	140	107	6.5	30
1010	810	131	102	6.4	35
1707	830	145	99	6.6	40
2523	819	148	94	5.2	22
3267	826	149	102	6.1	29
4011	829	154	114	7.2	32
4779	813	138	116	7.1	23.9
5547	808	147	121	7.7	27.0
6291	808	152	120	9.2	56.3
7107	804	155	127	10.2	58.3
7779	796	145	132	11.0	56.5
7888	804	143	133	12.4	77.7

TABLE XXXI Summary of Neodymium Selenide Processing Experimental Results

Batch No.	Batch Size (grams)	Composition		Average Density (g/cm ³)	Sample	ρ r.t. (m Ω -cm)	ρ 500°C (m Ω -cm)	$S_{500^\circ\text{C}}$ ($\mu\text{V}/^\circ\text{C}$, rel. to Abs.)
		LTR	NdSe _x RQC					
N-2683	140	1.4910	1.4682	6.08	Sinter 3 T2-1	**	5.3	144
					2-2	**	4.0	135
					4-1	**	4.6	138
					4-2	**	5.1	142
N-2684	140	1.4911	1.4781	6.21	T3-2*	2.03	6.5	162
					4-2	2.07	6.5	161
					4-3	1.76	6.1	164
					5-2*	—	6.3	162
N-2685	140	1.4911	1.4817	6.67	T3-3*	1.71	4.1	154
					3-4	1.65	4.2	153
					4-1	1.66	5.2	156
					4-2*	1.59	5.1	156
N-2686	140	1.5005	1.4788	6.35				
N-2687	140	1.4910						
N-2688	140	1.4909						
N-2689	140	1.4910						

* Elements prepared from powder ground extra two hours.

** Measurement not done.

TABLE XXXII Summary of Room Temperature Resistance Measurements —
N-2685 NdSe_x Elements on TestRoom Temperature Resistances — (m Ω)

Sample No.			After Sputtering *			After Pb/Ag Bonding *			Loaded in test Fixture
		ATT No.	Total R	Ni Contact	Ag Contact	Total R	Ni Contact	Pb/Ag Contact	Total R
N-2685	T3-1	661	4.8	1.4	.62	4.6	1.2	.60	4.7
	T3-2	662	4.5	1.0	.81	4.2	1.1	.58	3.9
	T3-6	659	4.2	.61	.28	5.1	.95	.58	—
	T5-4	664	4.2	.95	.21	4.4	1.1	.58	6.6
	T5-5	665	3.8	.75	.39	3.9	1.1	.64	4.1
	T5-6	666	3.9	1.5	.10	4.2	1.5	.32	5.6
	T5-8	663	3.3	.48	.38	4.0	1.0	.38	5.5

*It should be noted that these measurements include contact resistances between the fixture and leg surfaces — they are not four-probe measurements. In addition, the measured contact resistances will vary in relation to the probe placement from the end of the leg.

TABLE XXXIII Performance of Neodymium Selenide Ingradient Tests

Time (Hrs.)	ATT 658				ATT 659				ATT 660**				ATT 661				ATT 662				ATT 663			
	T _h (°C)	T _c (°C)	R (mΩ)	S(μV/°C, Pt)	T _h (°C)	T _c (°C)	R (mΩ)	S(μV/°C, Pt)	T _h (°C)	T _c (°C)	R (mΩ)	S(μV/°C, Pt)	T _h (°C)	T _c (°C)	R (mΩ)	S(μV/°C, Pt)	T _h (°C)	T _c (°C)	R (mΩ)	S(μV/°C, Pt)	T _h (°C)	T _c (°C)	R (mΩ)	S(μV/°C, Pt)
2	847	158	17.0	124	835	185	7.7	136	848	156	17.1	125	836	173	7.5	134	842	166	7.3	130	834	160	7.4	135
14	853	158	18.9	125	843	185	7.5	138	845	155	18.4	125	836	174	7.3	134	837	167	7.2	131	828	161	7.1	136
50	856	158	2.13	126	851	186	7.4	140	840	152	20.5	125	836	174	7.3	135	837	167	7.2	132	833	161	7.0	137
98	860	159	22.9	127	853	185	7.4	141	841	151	22.2	125	827	172	7.2	135	830	165	7.1	132	822	160	6.9	137
146	861	159	23.9	128	854	184	7.4	141	840	149	23.5	125	845	176	7.3	137	845	169	7.2	134	846	163	7.0	139
206	865	160	24.8	128	855	184	7.4	141	840	148	24.7	125												
266	866	160	25.5	129	854	183	7.4	142	843	149	25.8	125												
302	868	160	26.1	129	856	186	7.5	142	840	147	26.3	125												
362	868	161	26.4	129	855	185	7.5	142	840	147	27.2	125	841	153	7.4	135	849	161	7.3	135	787	159	6.7	135
410	859	158	26.5	128	854	183	7.4	142	839	145	28.0	125	***				***				***			
448	861	158	26.8	129	855	181	7.5	142	840	146	28.3	125												
508	—	—	—	—	—	—	—	—	850	149	29.3	127												
580	863	158	27.7	129	856	180	7.5	143	846	142	31.6	126												
747	864	159	28.5	130	857	181	7.5	143																
795	866	158	28.7	130	858	179	7.5	143																
847	864	159	28.8	130	*																			
891	866	159	29.0	130	854	170	8.4	142																
940																								
988																								

* Cycle to room temperature to change light bulb heater.

** Test ATT 660 cycled to room temperature because of a light bulb heater failure.

*** Tests ATT 661-666 were exposed to an oxidizing environment at 380 hours because of a leak. They were subsequently cooled down and terminated.

TABLE XXXIII Performance of Neodymium Selenide Ingradient Tests (Continued)

[illegible]

5.4.2 TPM-217 P-Material Ingradient Compatibility and Life Testing

The performance of partitioned and non-partitioned P-legs on life test is summarized in Table XXVIII. All of the tests were shut down during November, 1976, for the move to new facilities. Instrumentation and contacts were cleaned and repaired before the tests were restarted.

5.4.2.1 Non-Partitioned P-Legs

The first six tests in Table I have been on test for approximately 91,300 hours. Their performance has been degrading markedly in recent months with erratic performance which may be indicative of poor contact and/or instrumentation problems. Of the other non-partitioned legs shown in Table XXVIII, ATT 192 and ATT 195 remain on test although their performance has been degrading in recent months. ATT 288 and ATT 289 continue to operate in a quite stable manner.

5.4.2.2 Partitioned P-Legs

ATT 210 experienced degradation (increase in resistance) and instrumentation problems during the year. It was started in September, 1971, and was the first leg with a tungsten foil. It is operating in an argon atmosphere. ATT 241 was initiated in April, 1972, and is a three segment element with tungsten-rhenium barriers and has a copper silver cold end electrode. It continues to operate in a quite stable manner.

Six partitioned P-leg tests were started in April 1975, (ATT 371 through 376). The test series suffered a number of thermal cycles and there had been instrumentation problems as well as temperature and current variations. The series was shut down in May, 1979.

5.4.3 TPM-217 Couple Life Testing

5.4.3.1 Design and Development of TPM-217/Gadolinium-Selenide Rare Earth Chalcogenide Couple

The effort continues to utilize chemical, physical, and thermoelectric data which have been obtained on TPM-217 and gadolinium-selenide to develop effective couples appropriate to RTG operation.

Couple Test ATT 421/422:

The objective of couple test ATT 421/422, initiated in May, 1976, was to evaluate the hardware to be incorporated into Module M-7. A summary of the test performance is contained in Table XXXIV. The performance of the P-leg degraded during November, 1978, with a severe increase in resistance. The N-leg performance has remained relatively stable. The test was terminated June 13, 1979, and the data reported is up to that date.

5.4.3.2 Design and Development of TPM-217/3N-PbTe Couples

Couple Test ATT 275:

Couple test ATT 275 was initiated in October, 1972, to evaluate the performance of a P-TPM-217/3N-PbTe couple which utilized a ball-socket cold end and pivoting hot end. It has now operated for a total of 46,337 hours.

5.4.4.1 TPM-217 Module Life Testing

Module M-8 — Twenty-Watt Module

The design characteristics and processing procedures for the twenty-watt module, M-8, were described in Top Summary Report No. 103. A summary of the module performance is contained in Table XXXV. The performance degraded about 42% through June with an increase in module resistance; in July, however, leg set resistance decreased particularly in circuit one; consequently, power increased to about 60% of the maximum power performance point. The module has continued to perform at this higher power level for the last three months of the year.

Module M-9 — Two-Couple Module

The design characteristics and test objectives of Module M-9, a two-couple module placed on test in December, 1976, were described in Top Summary Report No. 105. The performance of the module is summarized in Table XXXVI. The thermoelectric efficiency which is calculated based on measured properties is in the range of 9 to 9.5%. This module has operated more than 24,000 hours having normalized output power of more than 0.7 watts per couple from the time of test of 2,303 hours.

TABLE XXXIV Performance of Couple ATT 421/422

<u>Time (hr)</u>	<u>S_n (μv/°C, Pt)</u>	<u>R_n (mΩ)</u>	<u>S_p (μv/°C, Pt)</u>	<u>R_p (mΩ)</u>
54	144	28.1	270	20.7
270	146	22.9	269	19.8
510	146	22.1	268	20.6
699	145	21.3	263	20.4
700	Thermal cycle to room temperature			
1000	145	21.4	261	22.0
1251	146	20.6	266	22.7
2010	146	19.8	270	22.8
2200	Thermal cycle to room temperature			
2202	148	19.4	270	22.6
2598	149	21.6	267	24.2
3039	146	20.8	270	24.5
3414	148	20.4	270	24.2
3660	149	20.4	269	25.0
3700	Shut down for move to new facilities			
3800	147	30.7	265	25.0
4500	147	28.6	268	26.3
5310	148	27.4	267	27.2
6050	148	26.7	268	27.3
6510	148	26.4	267	27.3
7280	149	26.4	267	26.8
8290	143	25.5	268	27.0
8840	146	24.9	261	27.1
9390	147	24.9	265	27.2
10300	147	24.6	265	25.8
11020	147	24.7	264	26.4
11720	145	24.4	265	26.7
12400	146	24.3	264	26.4
13060	145	24.0	265	26.3
13900	144	23.8	265	26.3
14570	143	23.7	265	25.9
15270	Instrumentation Problems		265	25.1
16090	146	24.8	266	24.7
16829	143	24.6	265	24.9
17573	140	24.3	264	24.2
18341	139	24.5	265	24.9
19109	140	24.6	167	25.0
19853	140	24.8	168	169.1
20405	140	25.1	166	187.3
21341	140	24.9	Instrumentation problems	
22085	140	24.9	174	153.1
22721	140	25.2	165	184.2
23549	140	25.7	166	180.0
23849	143	26.6	178	167.8

TABLE XXXV Summary of Module M-8 Performance

	Time (hrs)	Open Circuit Voltage (volts)		Resistance (mohms)		Measured Power Output (watts)	
		Total	Average Couple	Total	Average Couple	Total	Average Couple
850°/150°C (nominal)	17	3.71	0.309	196	49.0	17.5	0.486
	71	3.63	0.303	170	42.5	19.4	0.539
	166	3.60	0.300	161	40.3	20.0	0.556
	328	3.60	0.300	152	38.0	21.3	0.592
	521	3.57	0.298	148	37.0	21.5	0.597
	833	3.45	0.288	139	34.8	21.4	0.594
Shut down for repair	905	3.34	0.278	135	33.8	20.7	0.575
Restart after repair	906	3.56	0.297	250	62.5	12.7	0.353
	1045	3.53	0.294	181	45.3	17.2	0.478
	1239	3.45	0.286	176	44.0	16.6	0.461
	1545	3.42	0.285	171	42.8	17.0	0.472
	1840	3.39	0.283	169	42.3	16.9	0.469
	1935	3.14	0.262	160	40.0	15.2	0.422
	2441	3.31	0.276	161	40.3	16.9	0.469
	2508	3.32	0.277	163	40.8	16.8	0.467
	3206	3.40	0.283	154	38.5	18.5	0.514
	3281	3.10	0.258	147	36.8	16.0	0.444
	3779	3.09	0.258	144	36.0	16.1	0.447
	4520	3.04	0.253	140	35.0	16.0	0.444
	5270	3.08	0.257	142	35.5	16.2	0.450
843°/163°C	5550	3.08	0.257	141	35.3	16.3	0.453
870°/169°C	6035	3.20	0.267	140	35.0	18.2	0.506
	6370	3.04	0.253	132	33.0	17.5	0.486
	6705	3.29	0.274	138	34.5	19.6	0.544
	7045	3.23	0.269	138	34.5	18.9	0.525
	7380	3.28	0.273	139	34.8	19.4	0.539
	7890	2.91	0.243	128	32.0	16.5	0.458
	8050	3.26	0.272	136	34.0	19.5	0.542
	8890	3.18	0.265	135	33.8	18.7	0.519
	9230	3.37	0.281	141	35.3	20.0	0.556

TABLE XXXV Summary of Module M-8 Performance (Continued)

Time (hrs)	Open Circuit Voltage (volts)		Resistance (mohms)		Measured Power Output (watts)	
	Total	Average Couple	Total	Average Couple	Total	Average Couple
9390	3.40	0.283	143	35.8	20.0	0.556
9900	3.28	0.273	138	34.5	19.5	0.542
10230	3.06	0.255	139	34.8	16.8	0.467
10910	3.11	0.259	130	32.5	18.7	0.519
11240	3.12	0.260	130	32.5	18.6	0.517
11580	3.17	0.264	129	32.3	19.5	0.542
11940	3.18	0.265	131	32.8	19.3	0.536
12420	3.15	0.263	132	33.0	18.7	0.519
12920	3.12	0.260	133	33.3	19.2	0.533
13170	3.13	0.261	136	34.0	18.0	0.500
13600	3.08	0.257	132	33.0	18.0	0.500
13810	3.11	0.259	135	33.8	17.9	0.497
14802	3.06	0.255	153	38.2	15.2	0.422
15610	3.13	0.261	132	33.0	18.2	0.506
16281	3.18	0.353	137	34.2	18.4	0.511
17002	3.21	0.357	138	34.5	18.6	0.517
17801	3.13	0.348	147	36.7	16.6	0.461
18465	3.15	0.263	144	36.0	17.2	0.478
19137	3.22	0.268	192	48.0	13.0	0.360
19977	3.16	0.263	220	55.0	10.5	0.292
20674	3.18	0.265	218	54.5	10.7	0.297
21322	3.11	0.259	250	62.5	8.8	0.244
22162	2.97	0.248	166	41.5	13.15	0.365
22835	3.11	0.259	171	42.8	13.8	0.383
23506	3.10	0.258	185	46.2	12.6	0.350

TABLE XXXVI Summary of Module M-9 Performance

Time (Hrs)	T _h (°C)	T _c (°C)	Open Circuit Voltage (volts)		Resistance (mohms)		Measured Power Output (watts)		Normalized Power Output (watts)	
			Total	Average Couple	Total	Average Couple	Total	Average Couple	Total	Average Couple
1	844	184	0.299	0.299	21.9	43.8	0.94	0.47	1.14	0.57
115	834	134	0.294	0.294	17.6	35.2	1.02	0.51	1.23	.61
210	854	160	0.301	0.301	17.6	35.2	1.05	0.53	1.26	.63
309	8.67	187	0.298	0.298	18.2	36.4	1.22	0.61	1.30	.65
353	863	146	0.297	0.297	18.9	37.8	1.16	0.58	1.23	.61
376	846	142	0.282	0.282	14.8	29.6	1.32	0.66	1.32	.66
449	848	152	0.282	0.282	15.1	30.2	1.32	0.66	1.33	.67
1007	865	185	0.288	0.288	15.9	31.8	1.31	0.66	1.38	.69
1342	834	142	0.272	0.272	13.8	27.6	1.34	0.67	1.37	.69
1508	881	151	0.295	0.295	14.5	29.0	1.49	0.75	1.38	.69
2008	843	152	0.275	0.275	14.0	28.0	1.35	0.68	1.39	.69
2303	861	136	0.278	0.278	12.9	25.8	1.46	0.73	1.39	.70
2378	862	136	0.279	0.279	13.0	26.0	1.46	0.73	1.39	.70
2974	861	147	0.290	0.290	14.5	29.0	1.44	0.72	1.40	.70
3743	858	147	0.279	0.279	13.3	26.6	1.43	0.72	1.41	.71
4242	871	165	0.286	0.286	13.9	27.8	1.44	0.72	1.44	.72
4990	831	182	0.266	0.266	14.3	28.6	1.24	0.62	1.44	.72
5660	850	152	0.276	0.276	13.3	26.6	1.41	0.71	1.45	.72
6020	853	155	0.276	0.276	13.2	26.4	1.41	0.71	1.50	.75
6660	858	164	0.278	0.278	13.1	26.2	1.48	0.74	1.50	.75
6830	859	164	0.277	0.277	12.9	25.8	1.48	0.74	1.50	.75
7170	887	169	0.291	0.291	13.5	27.0	1.56	0.78	1.49	.74
7510	862	166	0.278	0.278	13.2	26.4	1.47	0.74	1.48	.74
7840	859	161	0.278	0.278	13.1	26.2	1.47	0.74	1.48	.74
8350	862	160	0.278	0.278	13.1	26.2	1.48	0.74	1.47	.74
8510	857	152	0.275	0.275	12.7	25.4	1.49	0.75	1.47	.73
9350	837	150	0.264	0.264	12.4	24.8	1.41	0.71	1.46	.73
9690	852	154	0.272	0.272	12.7	25.4	1.45	0.73	1.46	.73
10020	856	155	0.275	0.275	12.9	25.8	1.46	0.73	1.46	.73
10360	856	155	0.273	0.273	12.8	25.6	1.46	0.73	1.45	.73
10700	851	150	0.270	0.270	12.6	25.2	1.45	0.73	1.44	.72
11030	872	199	0.280	0.280	14.5	29.0	1.34	0.67	1.46	.73
11370	852	143	0.271	0.271	12.6	25.2	1.46	0.73	1.42	.71
11710	855	156	0.272	0.272	12.8	25.6	1.43	0.72	1.45	.72
12040	855	151	0.272	0.272	12.8	25.6	1.44	0.72	1.43	.72
12400	859	161	0.276	0.276	13.2	26.4	1.44	0.72	1.45	.73
12880	856	156	0.273	0.273	12.9	25.8	1.44	0.72	1.44	.72
13290	859	160	0.276	0.276	13.2	26.4	1.44	0.72	1.44	.72
13630	859	160	0.276	0.276	13.2	26.4	1.44	0.72	1.44	.72
14270	845	151	0.267	0.267	12.7	25.4	1.40	0.70	1.43	.71
15265	848	159	0.269	0.269	13.0	26.0	1.39	0.70	1.44	.72
16073	837	135	0.264	0.264	12.3	24.6	1.41	0.71	1.40	.70
16744	855	147	0.272	0.272	12.6	25.2	1.46	0.73	1.43	.71
17465	846	140	0.266	0.266	12.3	24.6	1.43	0.72	1.41	.76
18264	844	138	0.266	0.266	12.2	24.4	1.44	0.72	1.42	.71
18927	851	158	0.270	0.270	12.8	25.6	1.41	0.71	1.45	.72
19600	848	151	0.268	0.268	12.7	25.4	1.40	0.70	1.42	.71
20440	856	147	0.272	0.272	12.6	25.2	1.46	0.73	1.43	.71
21137	857	151	0.270	0.270	12.6	25.2	1.45	0.72	1.43	0.71
21785	851	155	0.269	0.269	12.8	25.6	1.41	0.71	1.43	.71
22625	849	143	0.267	0.267	12.6	25.2	1.41	0.71	1.42	0.71
23298	852	156	0.269	0.269	12.9	25.8	1.40	0.70	1.42	0.71
23969	844	139	0.263	0.263	12.4	24.8	1.40	0.70	1.37	0.69

Module M-11 — Fifty-Four Couple Module

The design characteristics and processing procedures for the fifty-four couple module, M-11, were described in Top Summary Report No. 112. A summary of the module performance is contained in Table XXXVII. The unit was shut down April 20 with a total test time of 15,496 hours at operating temperature.

Module M-15C and M-15D — Two Couple Modules

Modules M-15C and M-15D were placed on test August 23, 1978, to demonstrate sublimation inhibition methods at elevated hot end temperature (900°C). Both modules, M-15C and M-15D are similar in construction detail to M-15A and M-15B. Module M-15C uses an oversize W-Re foil with astroquartz wrap/slurry as a P-leg sublimation suppression method. Module M-15D has P-legs having a thick (.020") W-Re foil also with astroquartz wrap/slurry. Their performance is summarized in Tables XXXVIII and XXXIX. Both modules open circuited and were terminated during October.

Module M-16 — Eighteen Couple Module

Module M-16 is a tracking module for GDS-I. It has been tested in xenon at 850/150°C. It was placed on test during March, 1978, and the performance is summarized in Table XL. The performance is compared with that of recent modules in Table XLVIII. The internal resistance increased greatly during April to an open circuit condition. The unit was shut down April 26 after 9593 hours at temperature.

Module M-17 — Eighteen Couple Module

Module M-17 was placed on test during April, 1978. It is identical to module M-16 described above. The performance is summarized in Table XLI. Basically, it is performing in a similar manner to module M-16. It did exhibit a short seat-in period compared with M-16 which is probably due to a slightly different processing temperature history. The unit was shut down April 23 after 8242 hours at operating temperature.

Module M-18 — Eighteen Couple Module

Module M-18 was placed on test August 4, 1978. The performance is summarized in Table XLII. This unit incorporates a configuration similar to that of M-16 and M-17; however, the module operates under vacuum at 850°/150°C as the lead unit in a three module vacuum test series. These modules incorporated second generation wrapped P-legs to demonstrate operation in a vacuum. The performance of module M-18 began to degrade after 800 hours of operation and the test was terminated October 26, 1978.

[illegible]

TABLE XXXVIII Summary of Module M-15C Performance

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit Voltage (volts)	Resistance (mohms)	Average Couple	Measured Power Output (watts)		Normalized Power Output (watts)	
				Average Couple	Total		Total	Average Couple	Total	Average Couple
7	895	154	0.317	0.317	20	39.0	1.3	0.65	1.12	.56
24	895	150	0.315	0.315	19	37.2	1.3	0.66	1.15	.57
48	890	154	0.312	0.312	18	36.2	1.3	0.66	1.22	.61
120	890	150	0.308	0.308	17	34.8	1.4	0.68	1.25	.62
175	899	155	0.310	0.310	17	34.6	1.4	0.69	1.25	.62
338	899	153	0.307	0.307	18	35.0	1.4	0.68	1.15	.57
824	897	148	0.305	0.305	19	37.2	1.3	0.63	1.07	.53
1127	898	146	0.303	0.303	24.6	49.2	0.76	0.38	.81	.40

TABLE XXXIX Summary of Module M-15D Performance

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit Voltage (volts)	Resistance (mohms)	Average Couple	Measured Power Output (watts)		Normalized Power Output (watts)	
				Average Couple	Total		Total	Average Couple	Total	Average Couple
7	904	157	0.318	0.318	27	53.6	0.9	0.47	.82	.41
24	896	157	0.308	0.308	26	51.2	0.9	0.46	.82	.41
48	890	153	0.305	0.305	25	49.4	0.9	0.47	.84	.42
120	883	150	0.299	0.299	22	43.4	1.0	0.51	.93	.46
175	886	150	0.281	0.281	26	51.6	0.5	0.24	.69	.34
338	903	148	0.260	0.260	36	71.2	—	—	.40	.20
824	897	155	0.260	0.260	29	57.6	—	—	.52	.26

No readings available in October

Test terminated October 25, 1978

Module remained heated up through October 24, 1978 — Total heat up time: 1510 hours

[illegible]

[illegible]

TABLE XLII Summary of Module M-18 Performance

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit Voltage (volts)		Resistance (mohms)		Measured Power Output (watts)		Normalized Power Output (watts)	
				Average Couple	Total	Average Couple	Total	Average Couple	Total	Average Couple	Total
.3	876	157	2.75	0.305	237	52.7	8.0	0.44	7.53	.42	
1	877	157	2.62	0.291	212	47.1	8.0	0.44	8.09	.45	
62	837	154	2.51	0.279	182	40.6	8.6	0.48	8.64	.48	
92	851	162	2.55	0.283	183	40.6	8.9	0.49	8.88	.49	
134	842	152	2.49	0.277	169	37.6	9.2	0.51	9.18	.51	
230	860	159	2.54	0.282	159	35.4	10.1	0.56	10.1	.56	
302	846	154	2.46	0.274	152	33.8	10.0	0.56	10.2	.57	
566	854	154	2.46	0.274	143	31.9	10.6	0.59	10.6	.59	
814	873	179	2.37	0.264	148	32.9	9.47	0.53	9.67	.54	
980	872	143	2.44	0.271	398	88.4	2.50	0.13	3.45	.19	
1270	876	148	2.43	0.270	230	51.1	5.65	0.31	5.92	.33	
1406	860	139	2.03	0.226	262	58.2	0.23	0.013	3.71	.21	
1573	840	136	1.98	0.220	188	41.8	4.03	0.22	5.15	.29	
1670	847	168	2.19	0.243	241	53.6	4.27	0.24	5.29	.29	

Test Terminated October 26, 1978

Module remained heated up through October 25, 1978 — Total heat up time 1982 hours.

TABLE XLIII Summary of Module M-19 Performance

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit Voltage (volts)		Resistance (mohms)		Measured Power Output (watts)		Normalized Power Output (watts)	
				Average Couple	Total	Average Couple	Total	Average Couple	Total	Average Couple	Total
0.1	850	188	2.547	0.283	246.0	54.8	6.55	0.36	7.34	.41	
25.6	848	184	2.541	0.282	244.8	54.4	6.56	0.36	7.33	.41	
89.6	841	191	2.510	0.279	239.8	53.3	6.53	0.36	7.62	.42	
162.4	840	200	2.492	0.277	236.3	52.5	6.52	0.36	7.87	.44	
257.5	826	190	2.440	0.271	210.9	46.9	6.94	0.39	8.54	.47	
450	854	202	2.511	0.279	212.9	47.3	7.30	0.41	8.53	.47	
644	844	198	2.462	0.274	229.8	51.1	6.53	0.36	7.73	.43	
762	858	196	2.488	0.276	240.2	53.4	6.43	0.36	7.19	.40	
1099	867	208	2.292	0.255	301.4	66.9	4.33	0.24	4.92	.27	
1433	852	197	1.810	0.101	300.1	66.7	2.71	0.15	3.11	.17	
1770	853	190	1.733	0.192	317.8	70.6	2.34	0.13	2.63	.15	
1865	861	189	1.612	0.179	377.4	83.9	1.67	0.09	1.87	.10	

Test Terminated December 18, 1978

Total heat up time 1939 hours.

Module M-19 — Eighteen Couple Module

Module M-19 was placed on test September 28, 1978. The performance of this module is summarized in Table XLIII. This module is similar to Module 18 and is part of the vacuum test series which include N-leg hot foil. The heat transfer path in the cold end hardware was apparently high because the cold end temperatures were higher than desired. The module performance degraded after 450 hours with an increase in resistance and subsequent loss of power. The unit was shut down December 18 and will be subjected to a post test analysis as the time permits.

Module M-20 — Eighteen Couple Module

Module M-20 was placed on test October 6, 1978. The performance of this module is summarized in Table XLIV. Module M-20 is the same as modules M-18 and M-19 and as was the case for M-19, the cold end temperature is higher than anticipated. The output power is somewhat higher than that produced by Module M-19; however, the performance degraded after 600 hours and the test was terminated April 25 after 4845 hours at operating temperature; a post-test analysis will be performed as conditions permit.

Module M-21 — Eighteen Couple Module

This module was an 18 couple, 3-segment implementation of the November, 1978 reference design of a selenide-based thermoelectric generator. The main features of the design include a non-partitioned, stepped capped, sublimation suppression wrapped P-leg and compliant cold end hardware. The module is operated at an increased ΔT and current combination intended to accelerate the P-leg sublimation rate factor by 10.5. The module was shut down January 19 after about 1000 hours of operation at temperature. During the first 450 hours on test, the measured power was stable at slightly more than 6 watts or half of its predicted power level. During the following 550 hours, power output declined as module resistance increased. The module was subjected to extensive post test analysis reported on in 3M Document No. 2331-0578. A summary of daily module performance is given in Table XLV.

Module M-22R, Twelve-Couple Diagnostic Module

A twelve-couple diagnostic module similar to M-21 was designed and processed and placed on test June 19, 1979, at the accelerated test conditions of T_h at 913 and T_c at 160 with a nominal 12 ampere test current. A detailed description of the design and purpose of this module was issued as a topical report and was also described in Top Summary Report No. 135.

The total performance of the two six-couple section of M-22R (ATT 633-240 psi P-leg spring pressure and ATT 634 - 150 psi P-leg spring pressure) is summarized in Tables XLVI and XLVII: the test was terminated after 1,000 hours on July 31, 1979. Figures 25 through 37 show M22R operating performance characteristics. A post test analysis has been initiated and a report of findings will be issued.

Module Summary Information

A summary of information about modules for fiscal year 1978 is contained in Table XLVIII. This table is updated as appropriate and time for peak performance of active tests has been added.

The general characteristic of the behavior of all recent modules has been a degradation in performance which is caused by an increase in P-leg resistance. It has been learned (Section 3.3.1) that this degradation is occurring at the junction between the hot end electrode (W-Re cap) and the P-leg hot end. The contact pressure has been shown to have a significant effect on this degradation and continuing investigations will more completely define the effect of increasing contact pressure on minimizing P-leg degradation.

It has been observed that type of hardware, assembly procedures, etc. don't have a significant effect on the ultimate degradation mode, although they can influence BOL contact resistances and performance. This is exemplified by a comparison between the performance of modules M-21 and M-22R. A modification of assembly procedures and tooling was accomplished between M-21 and M-22R such that alignment control was improved in M-22R. This was reflected in an improved BOL performance in M-22R even though the P-leg degradation made ultimately occurred.

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit		Measured		Normalized		
				Voltage (volts)	Resistance (mohms)	Power Output (watts)	Power Output (watts)			
				Average Couple	Total	Average Couple	Total	Average Couple	Total	
4	849	215	2.616	0.291	232.1	51.6	7.34	0.41	8.98	0.50
21	846	214	2.568	0.285	224.9	49.9	7.33	0.41	9.00	0.50
93	837	205	2.525	0.281	207.8	46.2	7.67	0.43	9.41	0.52
189	839	205	2.515	0.279	203.4	45.2	7.76	0.43	9.47	0.53
285	851	205	2.568	0.285	201.7	44.8	8.14	0.45	9.59	0.53
309	854	204	2.594	0.288	204.3	45.4	8.04	0.45	9.55	0.53
479	842	198	2.508	0.279	196.0	43.6	7.84	0.44	9.48	0.53
597	848	197	2.515	0.279	191.7	42.6	8.22	0.46	9.53	0.53
1268	851	201	2.450	0.272	225.8	50.2	6.63	0.37	8.98	0.50
1989	851	182	2.463	0.274	214.8	47.7	7.02	0.39	7.72	0.43
2788	845	177	2.463	0.274	216.3	48.1	6.97	0.39	7.70	0.43
3451	849	174	2.349	0.261	385.7	85.7	3.41	0.19	3.84	0.21
4124	847	169	2.417	0.269	485.9	107.9	2.69	0.15	3.20	0.18
4797	848	173	2.497	0.277	520.5	115.6	3.25	0.18	3.22	0.18
4845	TERMINATED APRIL 25, 1979									

TABLE XLV Summary of Module M-21 Performance

Time (Hrs.)	Time Accelerated Hours	T _h (°C)	T _c (°C)	Open Circuit Voltage (volts)		Resistance (mohms)		Measured Power Output (Watts)		Normalized Power Output (Watts)	
				Total	Average Couple	Total	Average Couple	Total	Average Couple	Total	Average Couple
Ref.		853	145	2.545	0.283	205.3	45.6	7.89	0.438	7.69	0.427
0	0	913	154	2.733	0.304	214.6	47.7	1.90	0.106	7.40	0.411
1.7	17.9	914	154	2.722	0.302	208.5	46.3	2.63	0.146	7.53	0.418
2.2	23.1	913	153	2.712	0.301	205.6	45.7	2.92	0.162	7.58	0.421
69.9	734	910	138	2.633	0.293	172.9	38.4	6.72	0.373	8.24	0.458
73.1	768	913	142	2.626	0.292	173.8	38.6	6.51	0.362	8.19	0.455
91.8	964	914	152	2.621	0.291	175.2	38.9	6.24	0.347	8.28	0.460
115.6	1214	912	156	2.607	0.290	173.7	38.6	6.30	0.350	8.38	0.467
140	1470	910	153	2.598	0.289	172.2	38.3	6.41	0.356	8.37	0.466
164	1722	910	156	2.595	0.288	173.0	38.4	6.26	0.348	8.38	0.467
236	2478	908	152	2.584	0.287	171.2	38.0	6.39	0.355	8.36	0.465
260	2730	922	154	2.651	0.295	174.4	38.8	6.74	0.374	8.37	0.466
283	2972	918	153	2.633	0.293	174.5	38.8	6.51	0.362	8.33	0.463
307	3224	912	154	2.602	0.289	174.7	38.8	6.11	0.339	8.26	0.459
332	3486	911	149	2.605	0.289	174.7	38.8	6.15	0.342	8.20	0.455
361	3790	909	148	2.591	0.288	175.4	39.0	5.89	0.327	8.10	0.450
383	4022	910	148	2.612	0.290	173.4	38.5	6.42	0.357	8.29	0.461
434	4557	914	150	2.622	0.291	182.0	40.4	5.32	0.296	7.92	0.440
452	4746	917	152	2.645	0.294	179.1	39.8	6.01	0.334	8.19	0.455
476	4998	917	152	2.626	0.292	188.9	42.0	4.371	0.243	7.64	.424
499	5240	908	152	2.593	0.288	183.5	40.8	4.760	0.264	7.87	.437
534	5607	917	151	2.682	0.298	186.5	41.4	5.40	0.300	8.06	.448
552	5796	916	150	2.681	0.298	187.1	41.6	5.29	0.294	8.03	.446
596	6258	917	153	2.673	0.297	198.2	44.0	3.61	0.201	7.58	.421
626	6573	917	153	2.65	0.294	197.8	44.0	3.31	0.184	7.42	.412
646	6783	917	153	2.66	0.296	188.8	42.0	4.79	0.266	8.08	.448
650.8	6833	909	151	2.687	0.299	196.5	43.7	4.02	0.293	7.85	.436
667.8	7012	907	150	2.647	0.294	182.5	40.6	5.54	0.308	8.21	.456
694.6	7293	908	151	2.659	0.295	188.0	41.8	4.89	0.272	8.04	.447
724.1	7603	904	151	2.648	0.294	191.2	42.5	4.31	0.239	7.93	.441
739.6	7766	906	153	2.647	0.294	191.8	42.6	4.21	0.234	7.89	.438
763.5	8017	907	156	2.667	0.296	193.5	43.0	4.22	0.234	7.97	.442
788.1	8275	911	156	2.684	0.298	197.0	43.8	3.92	0.218	7.86	.437
813.5	8542	909	150	2.689	0.299	202.4	45.0	3.20	0.178	7.82	.434
836.1	8779	916	149	2.718	0.302	198.8	44.2	4.07	0.226	7.74	.430
907.9	9533	924	148	2.815	0.313	250.9	55.8	—	—	6.41	.356
931.6	9782	912	152	2.736	0.304	321.8	71.5	—	—	4.94	.274
956.1	10039	913	149	2.763	0.307	300.8	66.8	—	—	5.33	.296
980	10290	911	151	2.732	0.304	331.4	73.6	—	—	4.77	.265
990	10395	910	150	2.722	0.302	328.1	72.9	—	—	4.79	.266
1003	10532	912	147	2.736	0.304	287.4	63.9	—	—	5.46	.303
1005	10552	846	149	2.443	0.271	271.0	60.2	—	—	5.56	.309

TABLE XLVI Summary of Module M-22R Performance ATT 633H

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit Voltage (Volts)	Resistance (mohms)	Average Couple	Measured Power Output (watts)		Normalized Power Output (watts)	
				Average Couple	Total		Total	Average Couple	Total	Average Couple
0.27	913	156	0.971	0.324	58.4	38.9	3.28	0.55	3.45	0.57
23.4	915	156	0.960	0.320	53.3	35.5	3.80	0.63	3.68	0.61
48.8	915	159	0.955	0.318	52.0	34.7	3.95	0.66	3.76	0.63
70.6	915	155	0.954	0.318	50.7	33.8	4.13	0.69	3.81	0.64
136.4	915	157	0.955	0.318	51.4	34.3	4.03	0.67	3.79	0.63
162.3	915	156	0.957	0.319	50.8	33.9	4.09	0.68	3.83	0.64
187.6	915	167	0.958	0.319	53.2	35.5	3.77	0.63	3.78	0.63
211.4	914	144	0.964	0.321	51.5	34.3	4.07	0.68	3.72	0.62
239.6	915	152	0.970	0.323	52.8	35.2	3.95	0.66	3.74	0.62
260.6	915	151	0.970	0.323	53.6	35.7	3.84	0.64	3.68	0.61
283.6	915	150	0.971	0.324	52.6	35.1	4.06	0.68	3.75	0.62
304.5	915	150	0.983	0.328	54.4	36.3	3.94	0.66	3.72	0.62
328.7	915	151	0.978	0.326	55.9	37.3	3.67	0.61	3.59	0.60
354.2	914	151	0.973	0.324	61.7	41.1	2.90	0.48	3.23	0.54
377.2	913	153	0.976	0.325	66.3	44.2	2.56	0.43	3.05	0.51
400.3	912	145	0.970	0.323	63.5	42.3	2.16	0.36	3.09	0.52
451.3	912	144	0.987	0.329	67.7	45.1	2.11	0.35	2.99	0.50
472.3	912	144	0.980	0.327	72.0	48.0	1.50	0.25	2.77	0.46
498.5	912	152	0.995	0.332	70.9	47.3	1.87	0.31	2.96	0.49
551.3	912	153	0.997	0.332	90.6	90.6	—	—	2.33	0.39
569.0	912	151	0.984	0.328	109.7	73.1	—	—	1.87	0.31
640.6	913	151	0.999	0.333	105.2	70.1	—	—	2.00	0.33
664.7	913	152	0.990	0.330	106.1	70.7	—	—	1.96	0.33
688.5	912	152	0.998	0.333	114.5	76.3	—	—	1.84	0.31
712.7	913	157	0.990	0.330	105.8	70.5	—	—	1.98	0.33
736.5	913	160	0.995	0.332	118.4	78.9	—	—	1.81	0.30
808.7	914	160	1.027	0.342	131.1	87.4	—	—	1.73	0.29
832.4	915	159	1.000	0.333	137.2	91.5	—	—	1.56	0.26
864.8	916	160	0.999	0.333	134.8	89.9	—	—	1.59	0.26
888.9	915	156	1.010	0.337	131.7	87.8	—	—	1.64	0.27
904.5	916	156	0.992	0.331	118.2	78.8	—	—	1.77	0.29
976.5	915	157	1.001	0.334	131.3	87.5	—	—	1.62	0.27
1001.1	915	156	0.997	0.332	133.1	88.7	—	—	1.59	0.26

TABLE XLVII Summary of Module M-22R Performance ATT 634L

Time (Hrs)	T _h (°C)	T _c (°C)	Total	Open Circuit Voltage (Volts)	Resistance (mohms)	Average Couple	Measured Power Output (Watts)	Average Couple	Normalized Power Output (Watts)	Average Couple
				Average Couple	Total		Total		Total	
0.27	909	159	0.925	0.308	54.1	36.1	3.34	0.56	3.44	0.57
23.4	911	160	0.908	0.303	49.0	32.7	3.80	0.63	3.66	0.61
48.8	911	163	0.900	0.300	47.8	31.9	3.91	0.65	3.72	0.62
70.6	910	159	0.896	0.299	46.6	31.1	4.04	0.67	3.74	0.62
136.5	911	163	0.889	0.296	46.7	31.1	3.92	0.65	3.71	0.62
162.3	911	161	0.889	0.296	45.9	30.6	4.00	0.67	3.76	0.63
187.6	912	172	0.891	0.297	46.6	31.1	3.93	0.66	3.82	0.64
211.5	910	148	0.885	0.295	44.6	29.7	4.14	0.69	3.70	0.62
239.6	910	157	0.901	0.300	45.0	30.0	4.28	0.71	3.89	0.65
260.7	909	155	0.899	0.300	45.5	30.3	4.19	0.70	3.83	0.64
283.6	909	154	0.897	0.299	44.7	29.8	4.31	0.72	3.87	0.65
304.5	909	155	0.898	0.299	44.8	29.9	4.30	0.72	3.87	0.65
328.7	908	155	0.895	0.298	45.7	30.5	4.15	0.69	3.78	0.63
354.3	908	154	0.884	0.295	49.8	33.2	3.46	0.58	3.38	0.56
377.2	909	158	0.891	0.297	51.5	34.3	3.42	0.57	3.35	0.56
400.3	908	150	0.905	0.302	44.6	29.7	4.31	0.72	3.91	0.65
452.2	909	148	0.876	0.292	51.0	34.0	3.00	0.50	3.19	0.53
472.4	908	148	0.885	0.295	52.0	34.7	3.17	0.53	3.19	0.53
498.4	912	156	0.906	0.302	48.6	32.4	3.78	0.63	3.62	0.60
551.4	911	155	0.885	0.295	86.9	57.9	—	—	1.93	0.32
569.0	909	155	0.894	0.298	54.5	36.3	2.87	0.48	3.16	0.53
640.6	910	154	0.902	0.301	63.3	42.2	1.68	0.28	2.75	0.46
664.7	910	156	0.905	0.302	55.4	36.9	2.86	0.48	3.17	0.53
688.5	913	155	0.917	0.306	96.7	64.5	—	—	1.85	0.31
712.7	910	160	0.894	0.298	86.6	57.7	—	—	2.01	0.34
736.6	912	164	0.885	0.295	113.1	75.4	—	—	1.51	0.25
808.9	916	164	0.933	0.311	94.5	63.0	—	—	2.00	0.33
832.5	916	162	0.896	0.299	105.8	70.5	—	—	1.64	0.27
864.8	917	163	0.931	0.310	122.7	81.8	—	—	1.52	0.25
888.9	914	158	0.927	0.309	105.2	70.1	—	—	1.75	0.29
904.5	915	160	0.937	0.312	79.4	52.9	—	—	2.37	0.40
976.7	912	160	0.938	0.313	100.0	66.7	—	—	1.91	0.32
1001.1	912	161	0.901	0.300	99.1	66.1	—	—	1.78	0.30

TABLE XLVIII

Summary of Test Conditions and Measured Performance of Multi-Couple Modules

Module	On Test	Purpose of Test	No. of Cou- ples	Cou- ples in par- allel	Config- uration Cyl. on Rect.	Hot End Temp. (°C)	Cold End Temp. (°C)	Envi- ronment	Power Out** per Couple (watts)	Eoc** per Couple (volts)	Total Test Time (hours)	Time for Peak Perf. (hours)
M-1	7/11/74	Module demonstration (processing, computer)	2	1	Rect.	800	200	Vacuum	0.27	0.27	22,430	
M-2	7/27/74	Assembly Techniques developed, compatibility	10	1	Rect.	800	200	Vacuum	0.27	0.29	630	
M-3	11/11/74	Hot end gimbel on N-leg	10	1	Rect.	800	200	Vacuum	0.30	0.28	3,400	
M-4	6/9/75	Cyl. configuration larger scale leg production	72	1	Cyl.	800	200	Vacuum	0.31	0.29	700	
M-5	7/29/75	Ag sputter on N leg, Fiberfrax H-Blanket	10	1	Rect.	800	200	Vacuum	0.44	0.26	8,900	1,701
M-6	5/4/76	Improved hardware, BeO sockets	10	1	Rect.	800	200	Vacuum	0.43	0.26	5,200	
M-7	6/22/76	Advanced hardware, bonded BeO insulation	10	1	Rect.	850	125	Xenon	0.625	0.259	18,945	981
M-8	10/15/76	Cyl. config. 3 parallel elements, gas getter	36	3	Cyl.	850	125	Xenon	0.565	0.289	23,506*	521
M-9	12/29/76	Plasma sprayed Al ₂ O ₃ insulation, MoS ₂ material	2	2	Rect.	250	150	Xenon	0.752	0.282	23,969*	6,830
M-10A	4/11/77	GDS segment design	18	2	Cyl.	850	150	Xenon	0.55	0.279	8,050	1,769
M-11	7/13/77	Full GDS ring, POCO hot frame, Hi-Fi paper	54	2	Cyl.	850	150	Xenon	0.554	0.284	15,496	1,790
M-12A	6/20/78	Partial GDS ring, random vibration tests	18	2	Cyl.	850	150	Xenon	0.524	0.252	450	400
M-13	9/11/77	Min-K sleeve sublimation suppression	18	2	Cyl.	900	150	Vacuum	0.570	0.274	1,170	335
GDS/M14	6/4/78	Ground demonstration unit	156	2	Cyl.	850	150	Xenon	0.556	0.285	1,752	768
M-15A	1/20/78	Astroquartz wrap, 1st Gen. Wrap.	2	2	Rect.	900	150	Vacuum	0.607	0.284	935	405
M-15B	1/20/78	Min-K block sleeve, 1st Gen. Wrap	2	2	Rect.	900	150	Vacuum	0.611	0.276	935	240
M-15C	8/13/78	Large dia. foil, Min-K/H ₂ O slurry	2	2	Rect.	900	150	Vacuum	0.615	0.292	1,510	175
M-15D	8/13/78	Thick foil, Astroquartz wrap	2	2	Rect.	900	150	Vacuum	0.470	0.286	1,510	119
M-16	3/22/78	Tracking for GDS Xenon data base	18	2	Cyl.	850	150	Xenon	0.573	0.286	9,593*	280
M-17	4/7/78	Identical to M-16 " " "	18	2	Cyl.	850	150	Xenon	0.577	0.281	8,242*	1,027
M-18	8/4/78	Vacuum accelerated test series, N-leg hot foil	18	2	Cyl.	850	150	Vacuum	0.588	0.274	1,952	566
M-19	9/28/78	" " " " " " "	18	2	Cyl.	850	150	Vacuum	0.475	0.298	1,939	257
M-20	10/6/78	" " " " " " "	18	2	Cyl.	850	150	Vacuum	0.533	0.300	4,245*	597
M-21	12/8/78	Non-partitioned P-leg, SN Hardware	18	2	Cyl.	913	150	Vacuum	0.466	0.268	1,005	116
M-22R	6/19/79	Diagnostic Module	12	2	Rect.	913	150	Vacuum				
								ATT633H	0.638	0.294	1,001	152
								ATT 634L	0.652	0.279	1,001	400

* Current active tests

** Normalized Peak performance for M-7 and later models.
$$P_n = \frac{E_{oc}^2}{4M} \times \left(\frac{700}{\Delta T} \right)^2 \quad \& \quad E_{oc_n} = E_{oc} \times \frac{700}{\Delta T}$$

FIGURE 25 M 22R PERFORMANCE
ATT 633 - H

FIGURE 26
M 22R PERFORMANCE
ATT 634-L
(913/160°C - 12 AMPS)

FIGURE 28 M 22R PERFORMANCE
N LEG MEAN VALUES
(913/160°C - 12 AMPS)

FIGURE 29 M 22R Performance (913/160°C – 12 AMPS)
ATT 633H – Leg 6A

FIGURE 31
M 22R PERFORMANCE (913/160°C — 12 AMPS)
P LEG MEAN/ONE S.D. ATT 634L

FIGURE 32
M 22R PERFORMANCE (913/160°C — 12 AMPS)
P LEG MEAN/ONE S.D. — ATT 633H

FIGURE 33
M 22R PERFORMANCE (913/160°C – 12 AMPS)
P LEG MEAN/ONE S.D. – ATT 634L

5.4.4.2 TPM-217 Module Post Test Analyses

Intensive post test analyses were conducted on a number of modules in order to obtain data on long-term operating characteristics, ingradient compatibility and reliability of elements, couples and modules. While additional post analyses work was done the following reports intensively characterize the results of this task.

Converter M-12 Summary Report
3M No. 2331-0572, February 22, 1979.

Converter M-21 Summary Report
3M No. 2331-0578, March 9, 1979.

Converter ATT #590 Summary Report
3M No. 2331-0611, May 30, 1979

5.5 RELIABILITY

The analytical models which were developed to predict the long-term performance of an all-selenide thermoelectric converter system are described in Section 3.2.

5.6 QUALITY ASSURANCE

A quality assurance plan (MMM-2331-0605) for technology modules was prepared, issued and implemented. This plan has as its objectives:

- To support system design, integrity and reliability.
- To support and document design conformance of the 3M milestone modules, together with all sub-assemblies, components, raw material, facilities and test operation where safety or integrity of the modules or components could be jeopardized.
- To monitor and document the fabrication of thermoelectric materials to be used in covered modules.
- To monitor and document tests, when the purpose of the test is to support system integrity and reliability. Tests which are initiated to investigate a theory of a new engineering concept are not covered by this Plan.
- To include all Government furnished equipment.
- To provide highly trained and skilled personnel from the Quality organization who have sufficient, well-defined responsibility, authority, and the organization freedom, together with an unimpeded route to higher management, to identify and evaluate quality problems and to initiate, recommend or provide solutions.

The assembly and documentation of Modules M-20, M-21 & M-22R were maintained by QA personnel as per this plan. In addition, QA personnel from Sandia Labs audited the plan for compliance and found it adequate.

TASK 6.0 — LIAISON WITH THE JET PROPULSION LABORATORY (JPL) AND MATERIAL SUPPLY

6.1 OBJECTIVE

The objective is to provide technical liaison and limited amounts of TPM-217 thermoelectric material to the Jet Propulsion Laboratory of the California Institute of Technology.

6.3 MATERIAL SUPPLY

Two shipments of material were made to JPL this year.

- (1) Ten wrapped P-legs with stepped caps were shipped to JPL on January 22, 1979.
- (2) A total of one-hundred and twenty (120) TPM-217 selenide thermoelectric elements (50 N-type and 70 P-type) was shipped to the Jet Propulsion Laboratory for evaluation during April, 1979.

TASK 7.0 — LIAISON WITH GENERAL ATOMIC COMPANY (GA) AND MATERIAL SUPPLY

7.1 OBJECTIVE

The objective is to provide technical liaison and limited amounts of TPM-217 thermoelectric material to the General Atomic Company.

7.3 MATERIAL SUPPLY

Two shipments of material were made to GA this year.

- (1) Ten N-legs were sent on December 19, 1978.
- (2) A total of seventy (70) TPM-217 selenide thermoelectric elements (30 N-type and 40 P-type) was shipped to General Atomic Company for evaluation during April, 1979.

TASK 8.0 — LIAISON WITH BATTELLE COLUMBUS LABORATORIES (BCL) AND MATERIAL SUPPLY

8.1 OBJECTIVE

The objective is to provide technical liaison and limited amounts of TPM-217 selenide thermoelectric material to Batelle Columbus Laboratories.

8.3 MATERIAL SUPPLY

Eight porous stainless steel replica P-legs were received from BCL and subsequently wrapped with Astroquartz/MIN-K according to current specification. The eight samples were sent back to BCL for testing in February, 1979. BCL used these samples to measure the wrap effectiveness via a diffusion experiment. In addition, two N-legs and two P-legs were shipped to BCL.

TASK 9.0 — PROGRAM MANAGEMENT

9.1 GENERAL

Work under this task included technical direction and overall coordination of activities associated with the program and liaison with DoE.

9.1.1 Meetings with DoE and other DoE Contractors.

A number of meetings were held during the last year. A summary of these is contained below.

- (1) Representatives from Fairchild Industries and Sandia were at 3M on November 6-10 to observe module teardown.
- (2) Representatives from Fairchild Industries, BMI and Sandia, attended a program review at 3M on November 16-17, 1978.
- (3) A review of the TPM P-leg theory was held at 3M on November 17, 1978, with representatives from MIT and Teledyne Energy Systems in attendance.
- (4) A design review was held at DoE/ASMP on November 28-30, 1978, with representatives from DoE and 3M in attendance.
- (5) The monthly interface meeting was held at 3M on November 15, 1978, with representatives from Teledyne Energy Systems.
- (6) Representatives from Teledyne Energy Systems and ORNL were at 3M, December 13-18 to discuss post test diagnostics.
- (7) A technology work effort review meeting was held at DoE/ASMP on February 15, 1979.
- (8) A technology work effort review meeting was held at DoE/ASMP on March 16, 1979.
- (9) A technology review meeting was held at 3M Company on March 22-23, 1979, with a representative from Fairchild Company in attendance.
- (10) A review of the Quality Assurance Program was held at 3M Company on April 23-25, 1979, with a representative from Sandia Laboratory.
- (11) A meeting was held at the Department of Energy Headquarters on May 1, 1979, for the purpose of providing a program status update.
- (12) A representative of Sandia Laboratory was at 3M on June 4-6, 1979, and on June 11-13, 1979, to monitor the assembly and documentation of module M-22R.
- (13) A meeting was held at 3M on June 13-19, 1979, to review the status of the Technology program. Personnel from DoE, Fairchild Industries and JPL were in attendance.

- (14) A meeting was held at 3M on June 20, 1979, to review the status of selenide work at Oak Ridge National Lab (ORNL). A representative of that organization presented a summary of his hot-pressing work on GdSe_x as well as some evaluations of the W-Re P-leg hot cap. Two (2) samples of hot pressed N-legs were left at 3M. We subsequently measured the Seebeck and resistivity of these legs. The room temperature resistance of each of the samples was in the range of 60 to 70 $\text{m}\Omega\text{-cm}$ (approximately 1 $\text{m}\Omega\text{-cm}$ would be expected). The high temperature Seebeck of one of the samples was $S_{500} = 121 \mu\text{V}/^\circ\text{C}$ (approximately as expected). The other sample cracked during loading into the Seebeck fixture. These samples were returned to ORNL for additional evaluations. The conclusion of these measurements is that additional work needs to be done before isostatic hot pressing can contribute significantly to selenide fabrication methods.
- (15) A meeting was held with a representative of DoE on June 25-26, 1979, to discuss programmatic issues.
- (16) A meeting was held at DoE/Germantown, Md., on July 26, 1979, to review the technical and programmatic status of the Technology program. Personnel from 3M, DoE and Fairchild Industries were in attendance.

9.1.2 Other Liaison Activities

Additional GdSe_x samples which were isostatically hot pressed at Oak Ridge National Lab (ORNL) were received during July. Resistance measurements were made on these elements and a summary is contained in Table XLIX. The sample which was measured at high temperature cracked during heat-up and the resistivity increased suddenly. After cooldown and disassembly it was clear that it had cracked. The room temperature resistivities are high and variable around the periphery indicating a certain amount of cracking, as fabricated. Thus, additional work needs to be done to refine isostatic hot pressing techniques.

A number of P-leg and hot cap samples were sent to Oak Ridge National Laboratory for evaluation during May. The evaluations involve verification of WSe_2 coating on the cap and evaluation of hot pressing methods to improve the intimacy of the contact at the TPM-217/W-Re cap interface.

Metallic foils of an alloy W-74%, Re-25%, Ta-1% have been fabricated at the Oak Ridge National Lab (ORNL) and were received this last month. Hot end contacting caps for the P-leg will be fabricated from these foils and they will be used as a replacement for the W-Re foil. This is being done to determine if the contact resistance at the hot cap/P-leg interface is reduced (it is known that tantalum-selenide has a lower contact resistance than tungsten-selenide).

9.1.3 Property Management

Several items of equipment under 3M control were transferred to General Electric Company in April. This transfer was accomplished with Transfer Order No. 79-069 on a GSA Standard Form 122.

Eight electrical cartridge heaters were received from Teledyne Energy Systems in April. These heaters have a platinum sheath and will eliminate the outgassing problems we have seen with our present heaters. This transfer was accomplished with Transfer Order No. 79-001 on a Form 122.

A "Report of Excess Personal Property" and Property Retirement Notice list pertaining to government capital equipment not needed on this program were processed by DoE Chicago Operations Office.

TABLE XLIX Summary of Measurements on Isostatically
Hot Pressed NdSe_x

<u>Sample</u>	<u>Room Temperature Resistance (m-Ω)</u>		<u>S₅₀₀ (<μV/°C, abs.)</u>	<u>ρ₅₀₀ (mΩ-cm)</u>
	<u>Average</u>	<u>Range</u>		
T3-8	5.2	4.8-5.3	228	19.0*
T3-12	5.6	4.1-8.3	223	—
T3-16	5.2	3.2-9.0	—	—

* Discontinuous increase to ρ₅₀₀ = 28.0 occurred during heat up of test.

SUMMARY AND CONCLUSIONS

N TYPE MATERIAL DEVELOPMENT

During the reporting period emphasis was originally placed on improvement in synthesis and fabrication of gadolinium selenide leg, as well as segmented $\text{GdSe}_x/\text{PbTe}$ legs.

Development of segmented N-legs was performed using lead telluride pellets of 2N composition purchased from Global Thermoelectrics as well as fabricated in our laboratory. It was found that 3M fabricated material is equivalent to that purchased from Global Thermoelectrics.

The gadolinium selenide segment development required transforming the sintered pellets from the cubic phase to the orthorhombic one, only the latter being truly stable at operating temperatures. Heat-treatment experiments were therefore performed at temperatures up to 950°C , and for times as long as 200 hours, using vacuum atmosphere of 10^{-6} Torr in evacuated silica capsules. The treatment produced orthorhombic material with large grains extending in from the surface of the pellets, together with partly-healed transformation cracks. Samples of cubic material were given to O.R.N.L. in order to see if transformation under pressure would eliminate the cracks.

Midway in the program emphasis was changed to include fabrication of neodymium selenide legs. This material is similar in structure, and properties, to cubic gadolinium selenide but offers the advantage of being stable at operating temperatures. In addition, it seems less susceptible to segregation during the RQC step, and hence does not exhibit the marked liquid-phase sintering observed in the case of gadolinium selenide.

The absence of liquid-phase sintering called for a re-optimization of sintering procedures, which is still in process. Further improvements in fabrication technique were begun also; these included extra grinding, addition of binder and plasticiser, and the building of a double-acting press.

P TYPE MATERIAL DEVELOPMENT

During the period a change in emphasis in P-type material development took place from basic properties to sublimation suppression by wrapping and to the understanding of contact resistance problems at the hot end. The use of W Re end caps yielded a threefold improvement in suppression properties. Current effects on carrier concentration in the basic material were investigated and a start made on instrumenting wrapped legs to aid in the analysis of contact problems, which were also studied by S.E.M. examination of contact surfaces.

The wrapping technique has been refined for P-legs comprising an astroquartz fiber wrap infiltrated with a Min-K slurry during wrapping. Most sublimation suppression would be expected to occur by mean free path curtailment by the dried slurry, with the astroquartz fiber providing overall strength to the composite.

Ultrasonic welding for cold end bonding was investigated in air ambient temperatures.

Direct measurements at the hot end of operating P-legs by resistivity probe techniques have confirmed the 3M model predictions. These measurements were performed on samples with voltage probes near the hot end. A four probe A.C. resistance measurement was used. At each hot and cold end junction temperature, the current was scanned through several different values, and the data taken after steady state was obtained for each current value. The conclusions drawn from the data are: 1) The linearity prediction is confirmed and 2) The quantitative agreement of the measurement with prediction is good.

COUPLE DEVELOPMENT

A new computer program was developed in order to evaluate performance of couple designs. The program obtains approximate solutions to a one dimensional conservation of energy equation applied to the elements themselves. A study was performed to evaluate the effects of component variations on performance to assess whether existing specifications should be changed. The results indicate that converter performance can be improved significantly by controlling element dimensions more carefully. These controls can be implemented without significant cost or schedule impact.

A test fixture was designed and built for the purpose of accurately measuring the thermal resistances of cold end hardware and hardware interfaces. This fixture was intended to be used not only for characterization studies but also for non-destructive testing of cold end hardware assemblies.

MODULE DEVELOPMENT

Aerosol injection of insulation was evaluated for the purpose of improving the assembly technique of inserting insulation and to reduce bypass heat loss. Using air as the vehicle, powdered MIN-K was injected into six couple assemblies to a density of 14.0 pcf. Initially the insulation was evenly distributed around the legs with no visible voids. At the end of vibration testing several large air pockets had appeared. The problem can be corrected by increasing the density of the pack.

A series of tests was completed at Dynatech R/D Company to evaluate the effect of packing density on thermal conductivity of Hi-Fi 660 paper over a temperature range of 100-1000°C. The results showed that over the given density range, thermal conductivity decreases with increasing density.

A twelve couple diagnostic module M22-R was constructed and placed on test at the accelerated test conditions of T_H at 913°C and T_C at 160°C with a nominal 12 ampere test current. A detailed description of the design and purpose of this module was issued as a topical report.

Module M-23R design was completed and parts were fabricated; however due to lack of funding it was not assembled and placed on test.