Theoretical and Experimental Research
in Thermoelectricity, 1959

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TECHNOLOGY

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Status Report No. 3

Theoretical and Experimental Research in Thermoelectricity

Covering Period
15 January 1959 - 15 April 1959

Contract No. AF 19(604)-4153
with
Electronics Research Directorate
Air Force Cambridge Research Center
Air Research and Development Command

1.0 ALLOYS OF SEMINCONDUCTING COMPOUNDS (John Blair)

Sample preparation work is now in progress for the characterization of the CdTe-HgTe-HgSe alloy system. Initially, samples with known amounts of the starting material are reacted in an evacuated quartz tube and are solidified by quenching. These samples are then used to calibrate the size of the unit cell over the composition range. X-ray diffraction equipment with a temperature controlled camera is available to make these measurements to four decimal places with a high degree of reliability. These measurements will be used to establish the alloy composition of slowly grown samples in case the composition in the solid and liquid phases are not the same because of segregation. A quenched control sample will be run and evaluated for each crystal grown at a given alloy composition.

A Bridgeman furnace was designed and constructed. The furnace winding has four separately controlled winding sections to allow a control of the temperature distribution. The temperature profile is satisfactory for growing crystals in the melting point range of the system under investigation, namely between 670°C and 1045°C. See Figure I for furnace design.

During the next quarter the sample preparation work will continue. In addition, the evaluation of the optical, electrical and thermal properties will shortly begin along the lines indicated in Progress Report No. 1.

2.0 HALL COEFFICIENT AND ELECTRICAL CONDUCTIVITY

The design and construction of a sample holder for measuring the Hall coefficient and electrical conductivity at elevated temperatures is completed. This device consists of a vacuum chamber in which the sample is held by pressure contacts. The springs activating the pressure contacts are placed in a water-cooled section of the assembly. The heater wires are surrounded by a water jacket to protect the magnet pole pieces from overheating. This sample holder will be used in the study of lattice scattering in the alloy system over a wide composition range. See Figure 2 for design of sample holder.

3.0 THERMAL CONDUCTIVITY MEASUREMENTS (Paul Gray)

During this quarter the apparatus for measurement of thermal conductivity at room temperature and below has been set up with the necessary auxiliary equipment and been placed in operation. The apparatus has been calibrated for thermal losses both at room temperature and liquid nitrogen temperature and is used

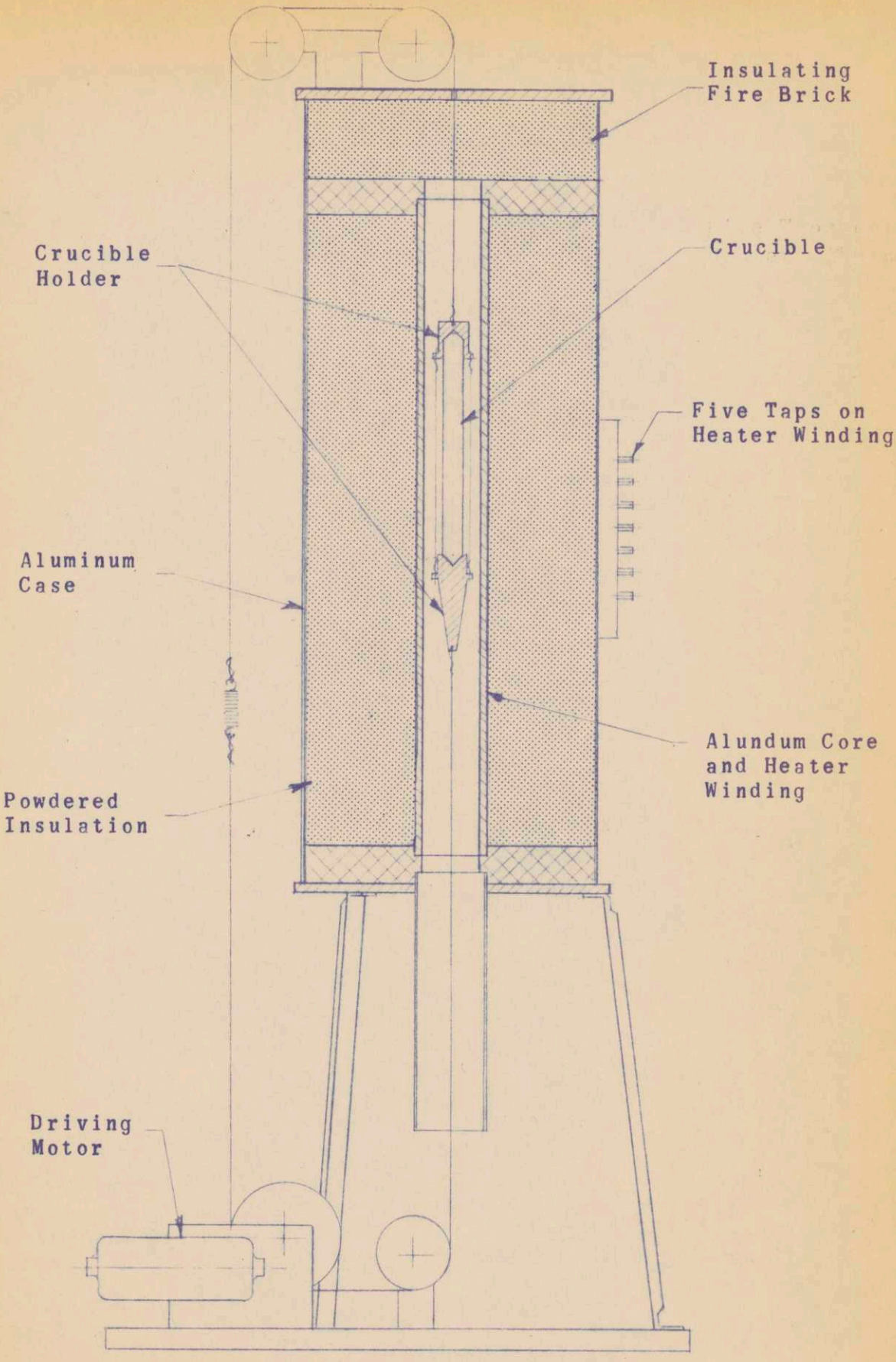


Fig. 1 Bridgman Furnace

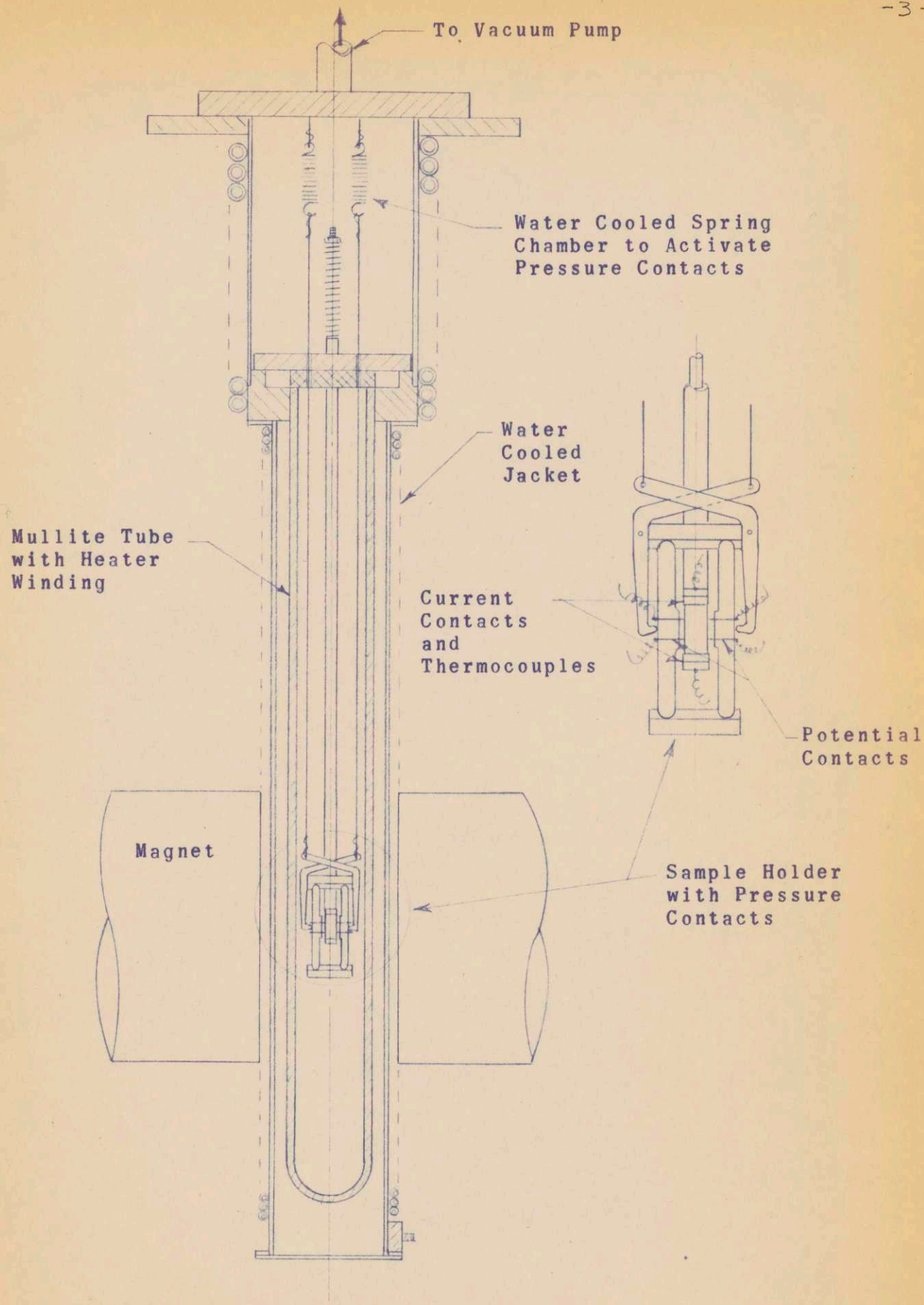


Fig. 2 High Temperature Hall Sample Holder

almost daily in the evaluation of materials for device work. The measurement cannot be made as rapidly as was originally hoped because the time required for the temperature distribution to come to equilibrium is of the order of an hour or two. Nevertheless, a measurement can be made without elaborate sample preparation or extensive set-up time. Measurements made to date indicate that the accuracy of the measurement is 3% or better.

The possibility of determining thermal conductivity in a crystal by measuring the attenuation of a longitudinal acoustic wave has been studied. In the light of present theoretical understanding of the various loss mechanisms which operate on high-frequency acoustic waves, and the current VHF acoustic measurement techniques, it does not appear possible to relate the acoustic loss directly to the thermal conductivity. Basically, the difficulties arise because measurements cannot be made at a sufficiently high frequency to distinguish between the thermoelastic losses and the other lossses (principally dislocation losses). Furthermore, additional losses have been observed whose behavior with frequency is not known.

4.0 THERMAL EXPANSION MEASUREMENTS

A literature search and study of our requirements for the measurement of coefficients of thermal expansion have indicated that the most suitable method would be to use a quartz tube dilatometer. This is preferable to the use of an optical interferometer since the greatsensistivity of the interferometer is not required for our purposes. Also, the quartz tube dilatometer can be made more rugged and can produce an electrical output suitable for recording.

In the measurement system now under construction the expansion of the sample will be transferred by means of the quartz tubes to a parallel-plate capacitor of variable spacing. This capacitor is used in the tuned circuit of a radio-frequency oscillator, the output frequency of which is compared to a crystal-controlled reference oscillator in a mixer. The resulting difference frequency, which is (approximately) linearly related to the expansion of the sample is converted to a potential which can be used to actuate a recorder. Since temperature can be recorded simultaneously, the coefficient of expansion can readily be determined as a function of temperatures. If an x-y recorder is used the expansion versus temperature curve can be plotted directly by the recorder.

5.0 BRIDGEMAN FURNACE

Several modifications to the Bridgeman furnace have been made during this quarter:

a. An RF induction heater has been added coaxial with and below the main resistance heater. This has facilitated the thorough mixing of the samples before they are raised into the main heater for crystal growth, and has eliminated crucible breakage due to excessive cooling of the sample during its transfer from a separate mixing furnace to the Bridgeman furnace.

b. A water-cooled sleeve has been added at the bottom of the main resistance heater for the purpose of improving the temperature gradient within the furnace. Measurement of the temperature profile before and after the addition of this sleeve indicate that the gradient at the melting temperature has been increased by a factor of about four. It is too soon to determine the effect of this improvement on the crystals grown in the furnace.

c. The steel guide rod and crucible chuck used previously in the furnace have been replaced. The high temperatures in the furnace annealed the guide rod sufficiently so that it could not be kept straight and the chuck became so corroded after a few passes through the furnace that the sample could not be clamped tightly. We are presently experimenting with a quartz rod fused directly to and coaxial with the crucible. This provides a much more rigid and satisfactory support for the sample and will probably be used regularly from now on.

6.0 EFFICIENCY OF THERMOELECTRIC GENERATORS (Jose Borrego)

The optimization of the efficiency of a thermoelectric generator using a single thermoelectric material is a very well known procedure. The recent developments of thermoelectric materials has made available for the designer materials with thermoelectric properties which are best suited to specific temperature ranges. This has brought up the problem, that given a temperature range, to choose within it a set of thermoelectric materials from those available which will give

the best efficiency. The solution of this problem is being undertaken, and the advances toward its solution are presented in this part of the report.

6.1 DEFINITION OF AN EFFICIENCY DENSITY

The efficiency of a thermoelectric generator is usually written using total quantities, such as total power output, total power input, etc. However, as is shown in what follows, it is possible to define an efficiency density so that the efficiency of the device is related to the integral along the length of the device of the efficiency density.

The starting point are the equations for coupled flows from the theory of irreversible thermodynamics:

$$I_p = -\frac{A}{\rho e^2}\nabla\mu - \frac{SA}{\rho e^2}\nabla T$$

$$I_q = STI_p - KA\nabla T$$

$$I_w = I_q + I_p\mu$$

where:

I_p = particle current

I_q = heat current

I_w = energy current

μ = electrochemical potential per particle of charge $+e$

T = temperature

S = entropy per particle

K = thermal conductivity

ρ = electrical resistivity

e = charge per particle

A = cross sectional area

∇ = one-dimensional gradient = $\frac{d}{dx}$

The efficiency density $\underline{\eta}$ can be defined as:

$$\eta = \frac{I_p \nabla \mu}{I_q}$$

Steady state conditions require:

$$\nabla \cdot I_w = 0 \quad \nabla \cdot I_p = 0$$

and it is shown, by the above three equations, that the relation between the total efficiency η_T and the efficiency density is given by:

$$\eta_T = 1 - \exp - \int_0^{\ell} \eta \, dx$$

where ℓ is the length of the device.

Making use of the equations for coupled flows, the efficiency density can be expressed as:

$$\eta = \frac{-\frac{\ell}{A} e^2 I_p^2 - S I_p \nabla T}{S I_p T - KA \nabla T} = -\frac{\nabla T}{T} \cdot \frac{1 + \frac{\rho e^2 I_p}{AS \nabla T}}{1 - \frac{KA \nabla T}{I_p S T}}$$

The terms in the above expression are interpreted as follows. The term:

$$\frac{\rho e^2 I_p}{AS \nabla T} = \frac{\rho e^2 I_p^2}{AS I_p \nabla T}$$

represents the relation between the power dissipated as heat by Joule effect to the power generated by the Seebeck voltage.

The term: $\frac{KA \nabla T}{I_p S T}$

is a relation between the heat carried by the lattice to the heat carried by the particle current. Finally, the term

$$\frac{\nabla T}{T}$$

represents a differential carnot efficiency.

6.2 APPLICATION OF THE EFFICIENCY DENSITY EXPRESSION

As an application of the above results, the optimum loading and optimum efficiency are found for the case of $\underline{T}$ independent of the particle current. This assumption is valid if the Joule heat and the Thompson heat are small compared to the conduction heat. Under the assumption of temperature independent of I_p, the procedure is straight forward and leads to the results: —

$$I_p = -\frac{KA\nabla T}{ST}\left[\sqrt{1+\frac{S^2T}{K\rho e^2}} - 1\right]$$

$$\eta = -\frac{\nabla T}{T}\,\frac{\sqrt{1+\frac{S^2T}{K\rho e^2}} - 1}{\sqrt{1+\frac{S^2T}{K\rho e^2}} + 1}$$

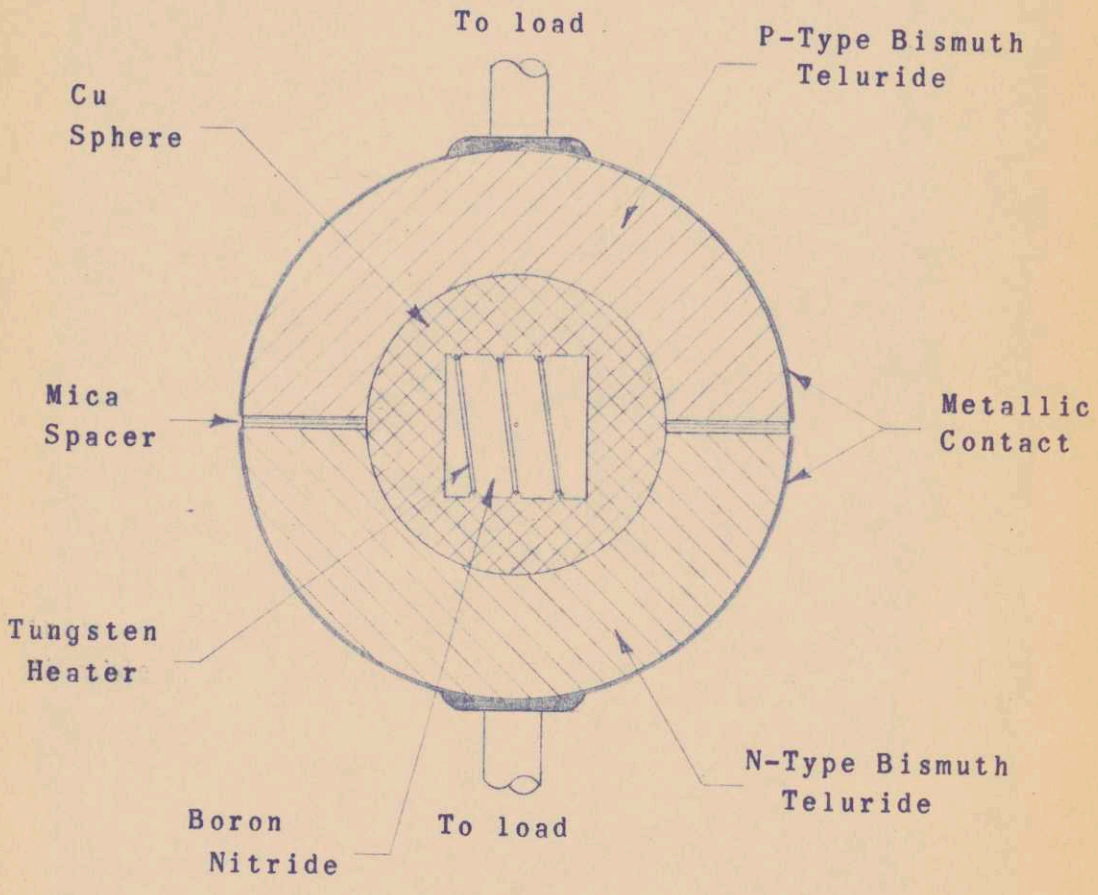
The last expression is a function of the figure of merit of the material and it can be used as a criterion for choosing the most appropriate material in a certain temperature range. This result was previously reported in the literature. The use of this criterion for designing thermoelectric generators leads to impractical configurations since the particle current along the generator does not remain constant. This is shown by the equations obtained for the optimum particle current.

6.3 CONCLUSIONS AND FUTURE WORK

An efficiency density has been defined which shows that the criterion which is now available for solving the problem of cascading thermoelectric materials gives impractical results. Future work in this area will be concerned with the solution of the cascading problem.

7.0 DESIGN AND CONSTRUCTION OF A THERMOELECTRIC GENERATOR (R. Schwartz)

The construction of a thermoelectric generator, which may be used for evaluation purposes, has been started. The geometry of the generator differs from that of the more common pi configuration in that the thermoelements consist of two hemispherical shells which entirely enclose the heat source. The reason for choosing such a geometry is that it allows one to evaluate the performance of such a device without the necessity of constructing and calibrating a highly controllable heat source,



Spherical Geometry Thermoelectric Generator

Fig. 3

such as would be necessary in the evaluation of a pi configuration generator.

The core, or heat source, is a copper sphere which contains a tungsten heater wound upon a boron nitride cylinder. Since the thermal conductivity of copper and boron nitride is orders of magnitude larger than the bismuth telluride shells, the inner core will become essentially an isothermal volume under steady state operation. Also, since the heat source is entirely surrounded by thermal elements, any heat which is removed from the core must be transferred through the thermal elements (with the exception of the small fraction of heat conducted away through the mica spacer and the small diameter wires connected to the core). Thus, measuring the electrical power input to the heater and the hot and cold junction temperatures, while the generator is open circuited, one is able to determine the thermal conductivity of the thermal elements. At the same time a measurement of the open circuit voltage allows one to calculate the total thermal electric power of the generator. A measurement of the output current under short-circuit conditions allows the calculation of the internal resistance of the generator.

The temperature measurements are made by means of a thermocouple imbedded in the core and a thermocouple placed in the cold bath in which the generator is to be immersed.

The above procedures allow the determination of all of the parameters which are contained in the efficiency expression derived by Ioffe. (1)

$$\eta = \frac{T_1 - T_o}{T_1} \; \frac{\frac{M}{M+1}}{1 + \frac{K_r}{\alpha^2} \frac{M+1}{T_1} - \frac{1}{2} \frac{(T_1 - T_o)}{T_1} \frac{1}{M+1}}$$

where T_1 = heat source temperature

M = ratio of external to internal resistance

K = thermal conductance of the generator

r = generator resistance

The above expression was originally derived for a pi configuration generator, but it is also valid for spherical geometry if one makes the same assumptions with regard to thermal electric

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1. Ioffe, A. F., "Semiconductor Thermoelements and Thermoelectric Cooling," London, Infosearch Limited, 1957.

power, thermal conductivity, and resistivity, as were made in the original derivation.

The highest possible efficiency for a given material is obtained when the radii of the two hemispherical shells are related by the following equation:

$$\left[\frac{1}{R_{1n}} - \frac{1}{R_{2n}}\right] = \sqrt{\frac{\rho_p K_n}{\rho_n K_p}} \left[\frac{1}{R_{1p}} - \frac{1}{R_{2p}}\right]$$

where R = radius
K = thermal conductivity
ρ = resistivity

and the subscripts 1 and 2 refer to the inner and outer radii respectively and n and p refer to the type of material.

Because of the ease with which single crystal or polycrystalline samples of bismuth telluride are separated at the cleavage planes it would be quite difficult to machine the required hemispherical shells. For this reason the shells are being constructed by powder metalurgy techniques. Bismuth telluride of the proper impurity concentration is powdered then pressed in molds of suitable shape. This is found to result in the degradation of the figure of merit for the material by a minimum of a factor of three. The best results to date have been obtained by heating the sample to 300°C during the application of pressure. It is expected that the performance of the powdering and pressing operation in a reducing atmosphere will return the figure of merit to that of the original sample.

Tin-indium solder applied by ultrasonic soldering techniques has been found to make a suitable contact for the low temperature junction (outer surface) and electroplated nickel has been found to be suitable for the high temperature junction (inner surface).

It is expected that the construction of the generator will be completed and the evaluation begun during the next interval.

8.0 CONTACTS (Dave Caplan)

The purpose of this work is to investigate techniques for establishing suitable metal contacts to semiconductor material.

Directly associated with this work is the investigation of the electrical and mechanical properties of the contact.

The method of measuring the contact resistance is essentially that of determining the potential profile of a sample of uniform cross-section and containing the two end contacts. The procedure used was fully described in the last report.

An indication of the mechanical rigidity of the contact can be readily obtained by allowing the contact to adhere to only one face of the sample crystal, and measuring the force required to separate a connected lead from the crystal surface. Contact must not be made with any of the adjacent faces, as otherwise additional adhesion will occur, which is undesirable for evaluation purposes.

For electroplated contacts to cylindrically shaped Bismuth Telluride, a plastic is formed over the curved crystal surface, such that one face of the crystal sample is flush with the adjacent plastic face. Any overlapping of either the plastic or crystal is removed on a lathe. This end face is immersed in the plating bath; and current is applied through a connection, which is not exposed to the bath, and which is remote from this end face. When a sufficient plate thickness has been obtained, the plastic is dissolved, thus leaving the cylindrically-shaped sample with a plated deposit on one face only, and with no overlapping to the adjacent surface. A tin-lead rosin core solder is then used to connect a copper lead to the sample.

This method of electroplating is also used for contact resistance evaluation purposes, where an overlap of the deposited plate onto the adjacent surface would be highly undesirable.

The metal-semiconductor contacts can be divided into two classes. One type lacks mechanical rigidity, and requires an external supporting structure for stability. This is commonly referred to as a pressure type contact. The other class of contacts rely on a good bond between the metal and semiconductor for mechanical rigidity, and requires no external support.

In the class of pressure contacts, a wetting agent is used between the metal and semiconductor. To date, two such agents have been found which exhibit excellent electrical properties, in addition to being easily applied. The use of an indium-gallium alloy as the wetting agent allows the contact resistance, between copper and p-type Bismuth Telluride, to be reduced to

approximately 0.10×10^{-3} ohm - cm^2. With indium amalgam as the wetting agent, an almost equally low contact resistance may be obtained at room temperature. However, the deterioration of the latter type wetting agent at slightly elevated temperatures necessitates the use of the rather expensive indium-gallium alloy, for temperatures up to 250°C.

Recently it has been found that an indium-tin solder will alloy with the indium gallium wetting agent to provide a bond which has fair mechanical rigidity. Investigation is presently continuing so as to improve the mechanical properties of this type of contact.

For the second class of contacts, one method for obtaining a mechanically stable metal-semiconductor bond is through electroplating techniques. A nickel plate on a semiconductor surface has been obtained by using an electroless nickel sulphate plating bath heated to 95°C. Prior to plating, the surface of the semiconductor sample was sandblasted, and was chemically cleaned with dilute hydrochloric acid. In addition, the rapid evolution of hydrogen gas from the bath aided in further cleaning the surface. The chemical composition of the plating bath is as follows:

Nickel sulphate	80 gm/ℓ.
Sodium hypophosphite	24 gm/ℓ.
Sodium acetate	12 gm/ℓ.
Boric Acid	8 gm/ℓ.
Amonium chloride	6 gm/ℓ.

The contact resistance to p-type Bismuth Telluride was found to be approximately 0.20×10^{-3} ohm cm^2 If the nickel plate is allowed to adhere to the adjacent surfaces of the sample, a reasonably good bond is obtained.

At present, investigation is continuing to determine the effects of temperature and time on the contacts; as well as contact agents for n-type Bi_2Te_3. Investigation has also been undertaken on a thermopressure type contact to sintered semiconductor material. The intentions of each of these investigations is to establish techniques for obtaining contacts to semiconductor material with favorable electrical, mechanical, and temperature properties.

9.0 DIFFUSION OF IMPURITIES IN Bi_2Te_3 (Oscar Manley)

Some semiquantitative experiments pertinent to the penetration of Cu into Bi_2Te_3 have been carried out. The amount

of Cu which penetrated Bi_2Te_3 was estimated spectroscopically for the temperature range 300°C - 470°C. Except for sample No. 3 the experimental arrangement was as described in the previous report. The results are tabulated in Table II.

TABLE II
Estimated Cu Concentration
after Baking at Temperature T°C

	T°C	~%Cu	Baking Time
Sample No. 1	Starting	.0028	---
	305	.0105	8 d.
Sample No. 2	Starting	.0005	---
	401	.35	4 d.19h
	470	.7	4 d. 6h
Sample No. 3	Starting	.001	---
	295	.04	4 d. 1h

NOTE: Sample No. 3 was a single crystal of p-type Bi_2Te_3 (α = 100 μv/°C.

Copper was plated on all the surfaces. After baking the plating was removed with aqua-regia and all the surfaces sandblasted. Thermoelectric power measured on a freshly exposed cleavage plane was $\alpha \simeq$ - 100 μv//C) indicating conversion to n-type material.

In addition to the above, one sample of Bi_2Te_3 was baked at 300°C for 8 days in the presence of Ni shot. While no significant amount of Ni penetrated the sample, spectroscopic analysis of the shot used in the experiment showed that Bi penetrated Ni. As yet, no quantitative data are available on this phenomenon.

During the next phase of this experimental program it is planned to extend the range of observation to room temperature. It is expected that in this range diffusion rather than chemical reaction is of primary importance. To implement this phase of the program a thermostat has been constructed. The temperature range extends from about 0°C to 150°C. The temperature can be regulated to within $\pm$ .05°C.

Visitors to Project:

March 13, 1959 -- International Business Machines

Mr. B. J. Greenblott
Mr. I. H. Lohman
Mr. W. E. Swanton
Mr. J. E. Wallace

March 23, 1959 -- Texas Instruments Inc.

Mr. Haggarty, President
Mr. Olson, V.P., Research & Engineering