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THERMAL PROPERTY MEASUREMENT TECHNIQUES
AND SOME RESULTS FOR CdTe

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SUMMARY

The objective of this study is to measure the thermal properties of several semiconductor materials. Some of the materials of interest are mercury telluride, cadmium telluride and gallium arsenide. The thermal properties to be measured include thermal conductivity, specific heat, coefficient of expansion, heat of fusion and emissivity. These properties are to be measured over a range of temperature levels.

Because of the range of temperature levels required, some modification of equipment is underway.

A literature review has been made to find existing data on the thermal properties of semiconductors; it has been found that little data exists.

The thermal properties are being measured in the laboratory using equipment described in the report. The thermal conductivity is measured using the guarded hot plate method, the specific heat and heat of fusion is measured using a gradient layer calorimeter, the expansion coefficient is measured using a quartz dilatometer and the emissivity is measured using a two disc system that is described in the report.

Thus far, measurements have been made on cadmium telluride at the

room temperature level. Values of 0.061 BTU/lb°F ($0.061 \frac{\text{cal}}{\text{gm}^\circ\text{C}}$) for the specific heat and 2.3 BTU/hrft²°F/ft (4.0 W/m K) for the thermal conductivity have been obtained.

Experiments are continuing, to measure the thermal properties of cadmium telluride. Samples are currently being studied using the quartz dilatometer for measurement of the expansion coefficient.

A ceramic gradient layer calorimeter is being constructed to make specific heat measurements at higher temperatures. Emissivity measurements will also begin shortly.

In conclusion, it has been found that little data exist in the literature on the thermal properties of semiconductors. Experimental measurements of these properties are continuing.

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I. INTRODUCTION

In order to improve the manufacturing techniques for semi-conductor materials as well as establishing their operating performance characteristics, information on thermal properties is required. Typical materials of interest are mercury telluride, cadmium telluride and gallium arsenide. The primary thermal properties of interest are the thermal conductivity, specific heat, expansion coefficient, heat of fusion and emissivity.

Geoscience's responsibility is to make these measurements under a range of environmental conditions and specimen size limitations. This quarterly report 1) outlines the measurement techniques, 2) reviews some general information on semi-conductor materials, 3) presents some measurement results on cadmium telluride and 4) discusses some equipment modification efforts.

II. THERMAL PROPERTY MEASUREMENT TECHNIQUES

In the manufacture of semi-conductor materials as well as in their use, information on their thermal properties is required; specifically, thermal conductivity, specific heat, heat of fusion, thermal expansion and gray body emissivity are of interest. The methods that are being used are described briefly in the following paragraphs.

A. Thermal Conductivity

One method that is used to measure the thermal conductivities of crystalline materials is the axial heat flow or comparative method as it is sometimes called. Figure 1 shows the elements of the technique. Heat flows from a heat source (a resistance heater) through thermal conductivity standards positioned on both sides of a test sample. These elements consist of short cylinders. The heat is removed from the other end of this composite rod by a cooling system. There are also guard heater windings around the composite rod to minimize radial surface heat losses. The outer structure of the system consists of annular insulation. Thermocouples are positioned axially along the composite rod as shown in the figure. The system may or may not be located in a vacuum environment. A classical heat balance at steady state involving known measured temperature gradients and thermal conductivities of the standard materials makes it possible to determine the thermal conductivity of the test sample.

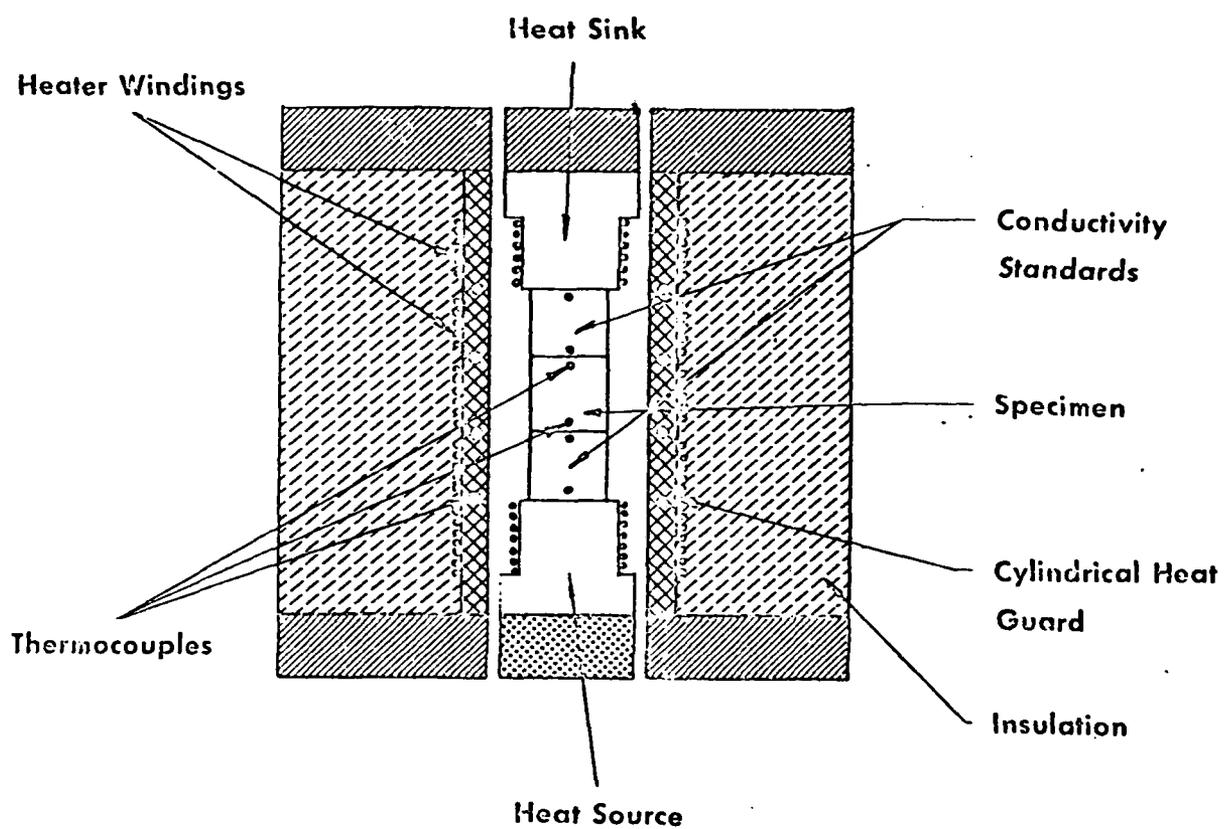


Figure 1. Rod heat conduction (comparative) thermal conductivity system.

A second method for measuring the thermal conductivities of crystalline materials is the guarded hot plate or twin-plate method. Figure 2 illustrates the major elements of the system. Heat from a central, flat plate heater flows through two hot plates, through two test slabs to two cooling plates. The temperature differences across the two test samples are determined from thermocouples that are embedded in the hot and cold plates or in the test samples. As shown in the figure, the central heater is surrounded by a guard heater. A thermopile is positioned between the central hot plates and the guard hot plates. At steady state, when the central heater and guard heater have been adjusted so that the thermopile output is very small (yielding unidirectional heat flow), a data set is obtained. From a heat balance on the system involving heater power inputs, heat transfer areas, temperature differences and sample thicknesses, the thermal conductivity can be determined. Figure 3 shows a photograph of a typical guarded hot plate measurement system in use at Geoscience.

B. Specific Heat

One convenient way of measuring the specific heat of crystalline materials is by utilizing a gradient layer calorimeter. The elements of such a system are shown in Figure 4. A test sample is positioned inside of the heat flux measuring envelope that is housed in a fluid cooled heat sink. The heat sink in turn is

Thermal Conductivity

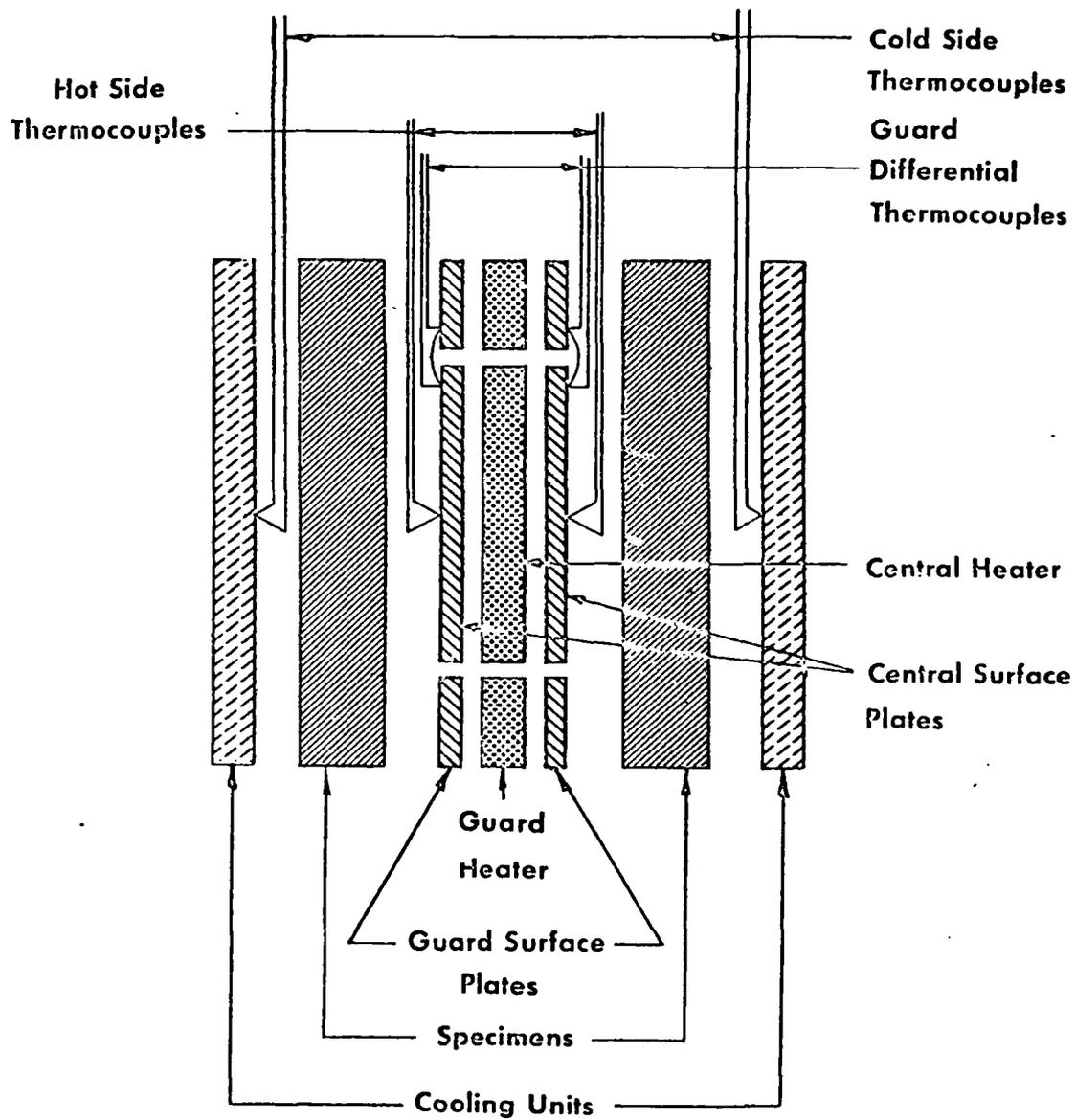


Figure 2. Guarded Hot Plate (Twin Plate) Thermal Conductivity System.

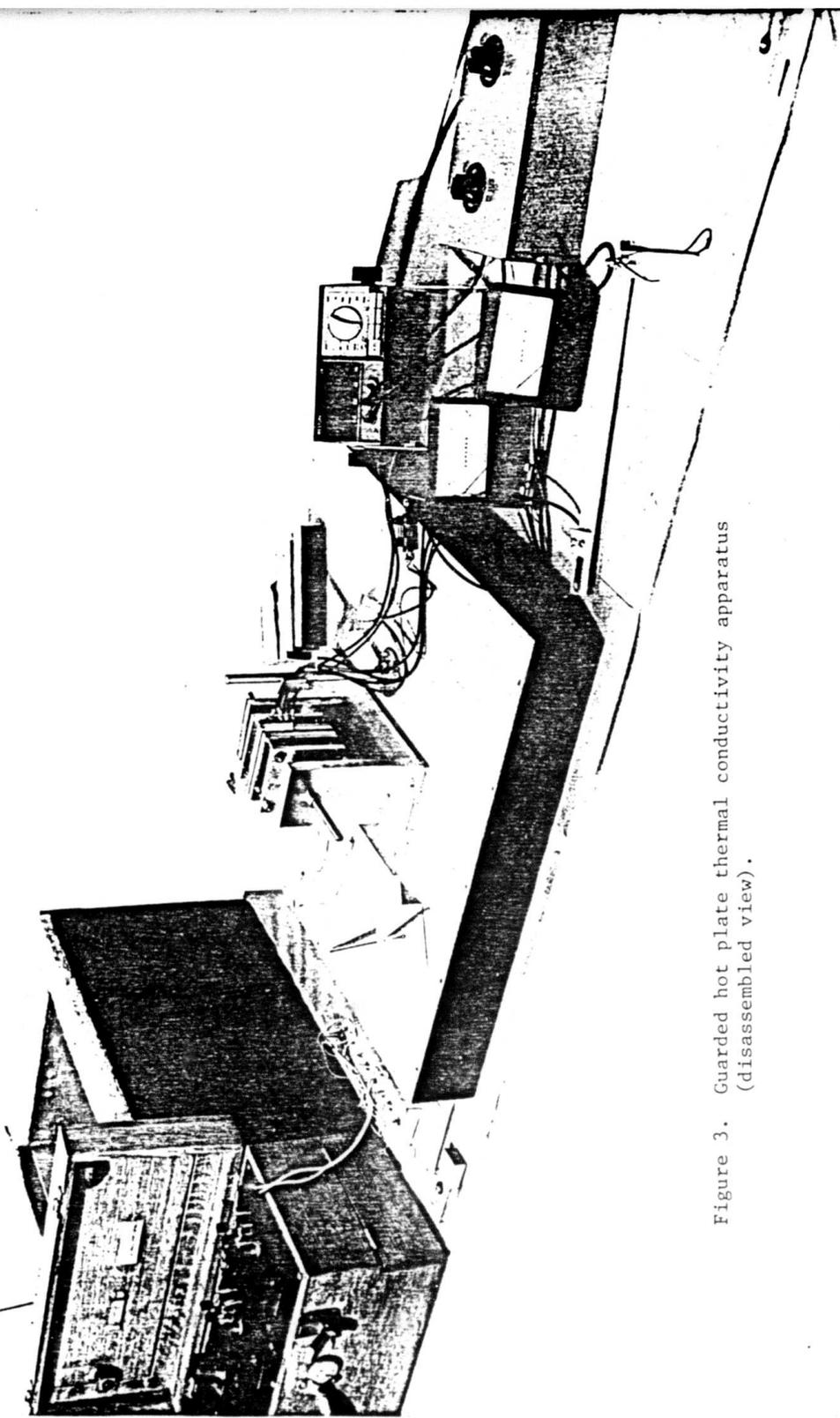


Figure 3. Guarded hot plate thermal conductivity apparatus
(disassembled view).

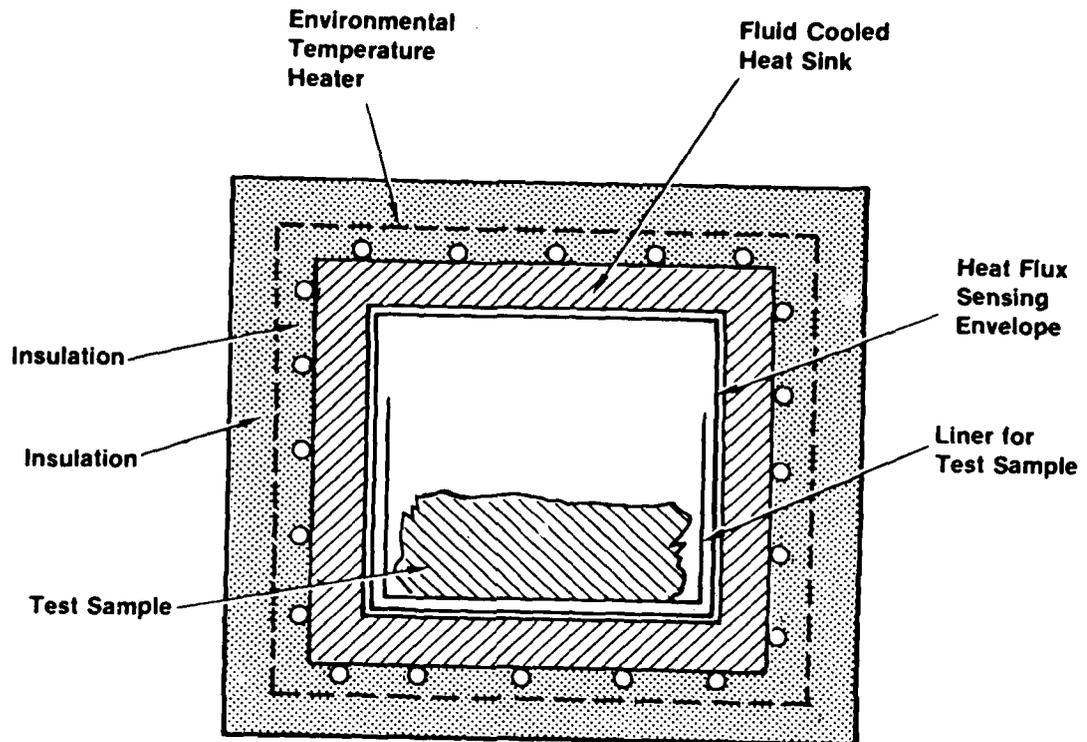


Figure 4. Elements of a gradient layer calorimeter system.

surrounded by thermal insulation. Figures 5 and 6 show photographic views of an unassembled and assembled gradient layer calorimeter, respectively.

This calorimeter is based on the principle that all of the heat flow into or out of the calorimeter must pass through its walls where the temperature gradient sensors are located. Therefore, the calorimeter envelope integrates the total heat flow in the system on an instantaneous basis. The calorimeter walls consist of special thermoelectric heat flux transducers* that yield a DC voltage output signal. The calorimeter walls are thin so that low time constants are involved. As heat flows through the walls, a small temperature difference is established; this temperature difference is directly proportional to the heat flow. In a properly designed calorimeter, the output signal is affected only by the rate of heat flow.

The utilization of the calorimeter to measure the specific heat of a material is done as follows: An unloaded calorimeter that has come to thermal equilibrium at temperature level t_1 is suddenly exposed to a new temperature level, t_2 . The heat flow trace as the transient process proceeds from the initial steady state condition to the final steady state condition can be obtained with a

* A heat flux transducer is composed of a thermopile system that has "hot" junction sets at one depth within the sensor and "cold" junction sets at another depth.

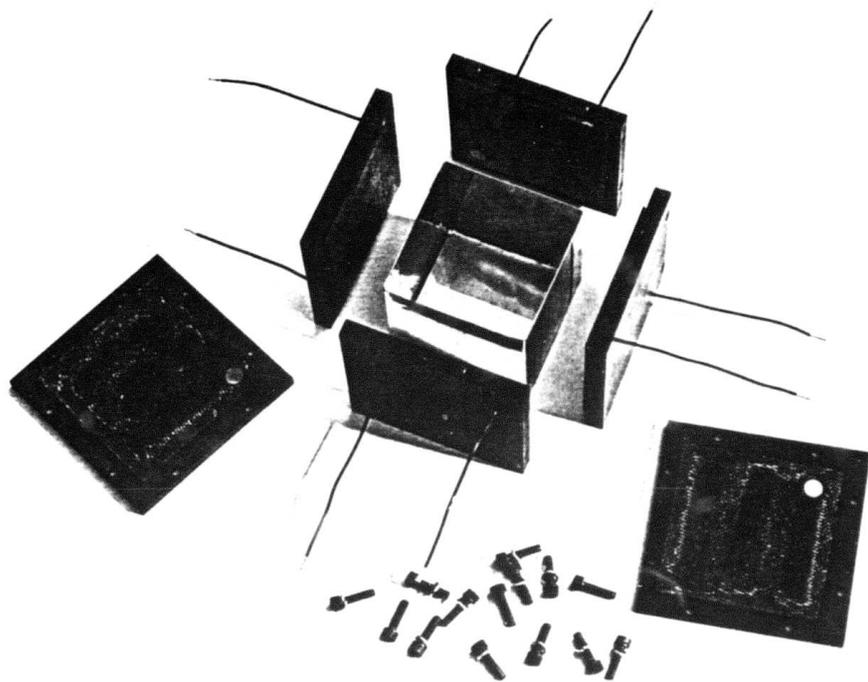


Figure 5. Photograph of a disassembled gradient layer calorimeter.

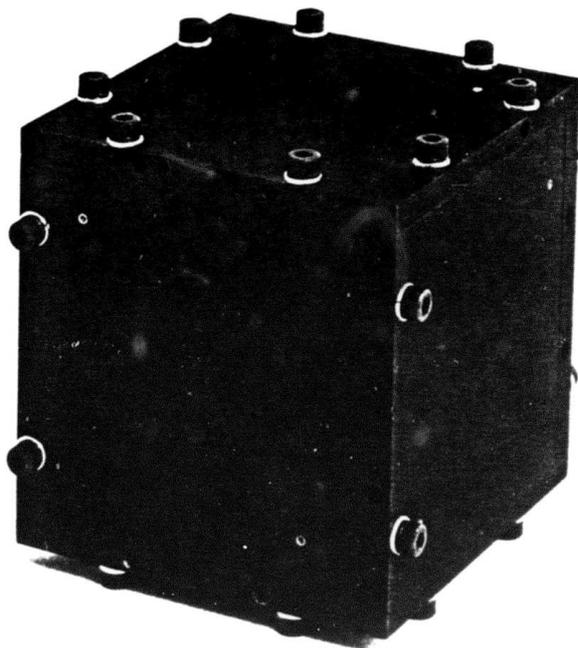


Figure 6. Photograph of an assembled gradient layer calorimeter.

recording potentiometer. The area under this curve is equal to the heat added to or extracted from the calorimeter and its liner for the superposed temperature perturbation. Next, the calorimeter is loaded with the specimen to be investigated and again exposed to the original temperature t_1 and allowed to equilibrate. Then the loaded calorimeter is suddenly exposed to the new temperature datum t_2 , allowed to reach equilibrium and the corresponding transient heat flow trace recorded. The area under this curve is equal to the heat added to or given up by the calorimeter, its liner and the specimen. Subtraction of the areas under the two transient traces yields the desired heat flow for the specimen alone. The trace area is related to an energy flow per unit time by means of an accurate resistance heating calibration for the calorimeter. The heat capacity for the specimen is obtained from the classical definition (heat transferred divided by the product of the mass and temperature perturbation). The defining equation for the specific heat, c_{p_s} , is

$$c_{p_s} = \frac{\int_0^{\theta_e} (q(\theta) - q(\theta)_e) d\theta}{m_s (t_2 - t_1)} \quad (1)$$

where:

$q(\theta)$, time dependent heat flow through calorimeter when loaded with test sample

$q(\theta)_e$, time dependent heat flow through calorimeter without the test sample

θ , time

- θ_e , the equilibrium time period (no further heat flow)
 m_s , mass of the test sample
 t_1 , initial temperature datum
 t_2 , final temperature datum

C. Thermal expansion Coefficient

The thermal coefficient of expansion for materials is normally measured by the classical dilatometer method. Specifically, the differential length change between a test rod of the material being investigated and a low expansion coefficient standard rod or tube (such as a quartz) is measured. Figure 7 illustrates three typical geometrical arrangements. Each system is surrounded by a constant temperature furnace that allows the temperature datum to be controlled. The relative expansion between the test specimen and the quartz is measured with an accurate, highly sensitive dial gauge. From the differential expansion measurement and the known expansion coefficient of the quartz, the expansion coefficient of the test material is determined.

D. Gray Body Emissivity

From classical radiation theory, it is possible to write net radiation transport expressions including inter-reflections that relate fourth power absolute temperature differences, surface areas and surface emissivities. The two geometries usually considered are parallel planes and concentric tubular or spherical shells. These classical net radiation exchange expressions are presented below.

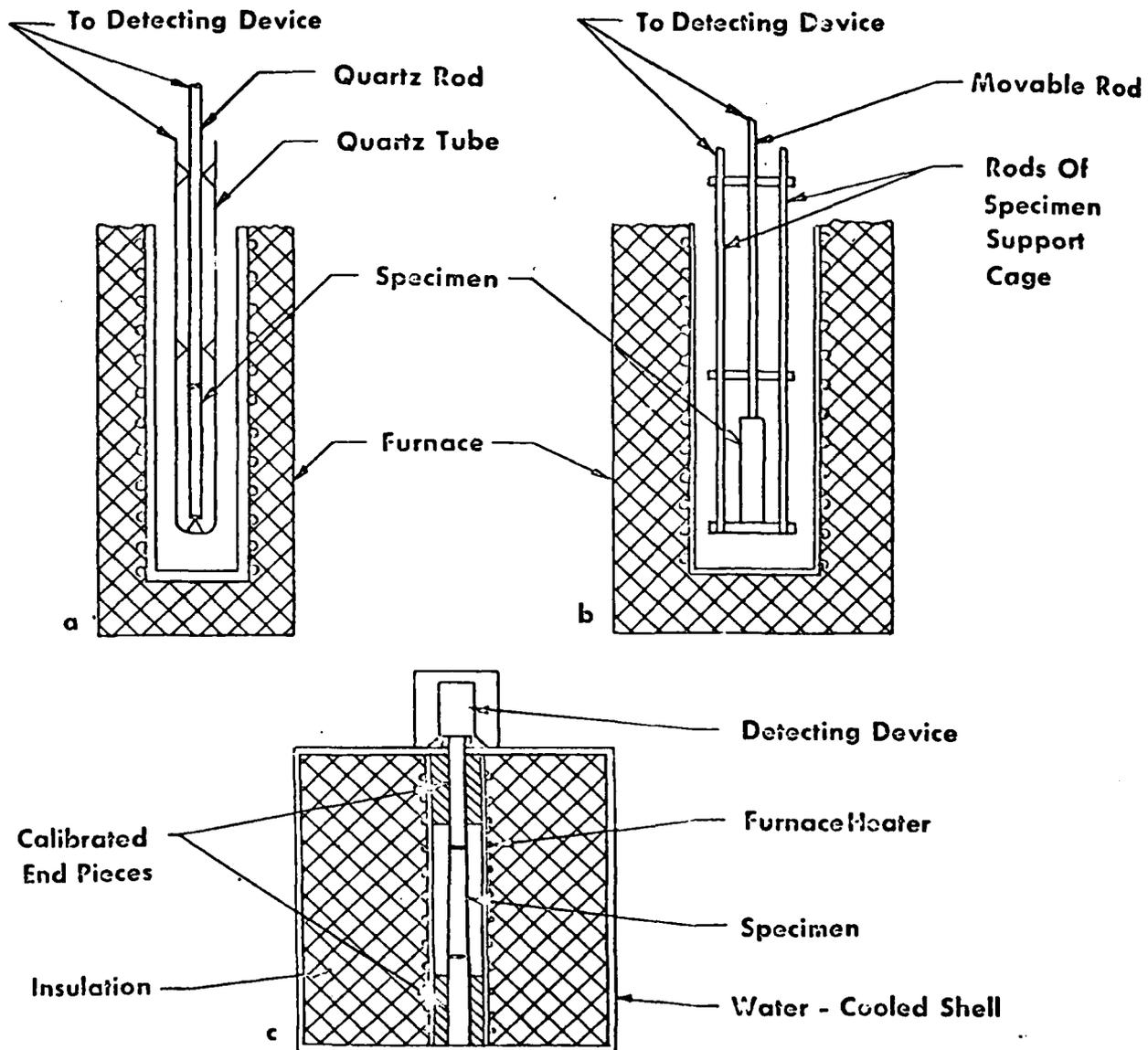


Figure 7. Thermal expansion coefficient (dilatometer) system (three arrangements).

For a parallel planes system, in a vacuum, the net radiation flux,

$\left(\frac{q}{A}\right)_{\text{rad}}$, is given by,

$$\left(\frac{q}{A}\right)_{\text{rad}} = \frac{\sigma}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1} \left[T_1^4 - T_2^4 \right] \quad (2)$$

where:

σ , Stefan Boltzmann constant

ϵ_1 , gray body emissivity of plane 1

ϵ_2 , gray body emissivity of plane 2

T_1 , absolute surface temperature of plane 1

T_2 , absolute surface temperature of plane 2

In the case of a long cylindrical shell system or concentric spherical shells, in a vacuum, the corresponding net radiant flux at area A_1 is given by,

$$\left(\frac{q}{A}\right)_{\text{rad}} = \frac{\sigma}{\frac{1}{\epsilon_1} + \frac{A_1}{A_2} \left(\frac{1}{\epsilon_2} - 1 \right)} \left[T_1^4 - T_2^4 \right] \quad (3)$$

where:

A_1 , radiating area for shell 1

A_2 , radiating area for shell 2

In both radiation systems, multiple inter-reflections are included and gray body emissivities are postulated.

Geoscience will utilize a flat disc system to perform the emissivity measurements as shown in Figure 8. A central, flat heater is covered by two flat test specimens which in turn are covered by two additional flat test specimens or reference discs. The discs are spaced from each other by thin spacers as shown in the figure. Surface thermocouples are attached as shown. This system is positioned in a hard vacuum where the heater is activated. At steady state, the system temperatures and heater power are measured. The sum of the heat flowing through the left and right hand radiation circuits in Figure 8 equal the electrical heat input. This relation together with Equation (2) yield a final equation containing the unknown test sample emissivity, ϵ_1 , and the measured system parameters.

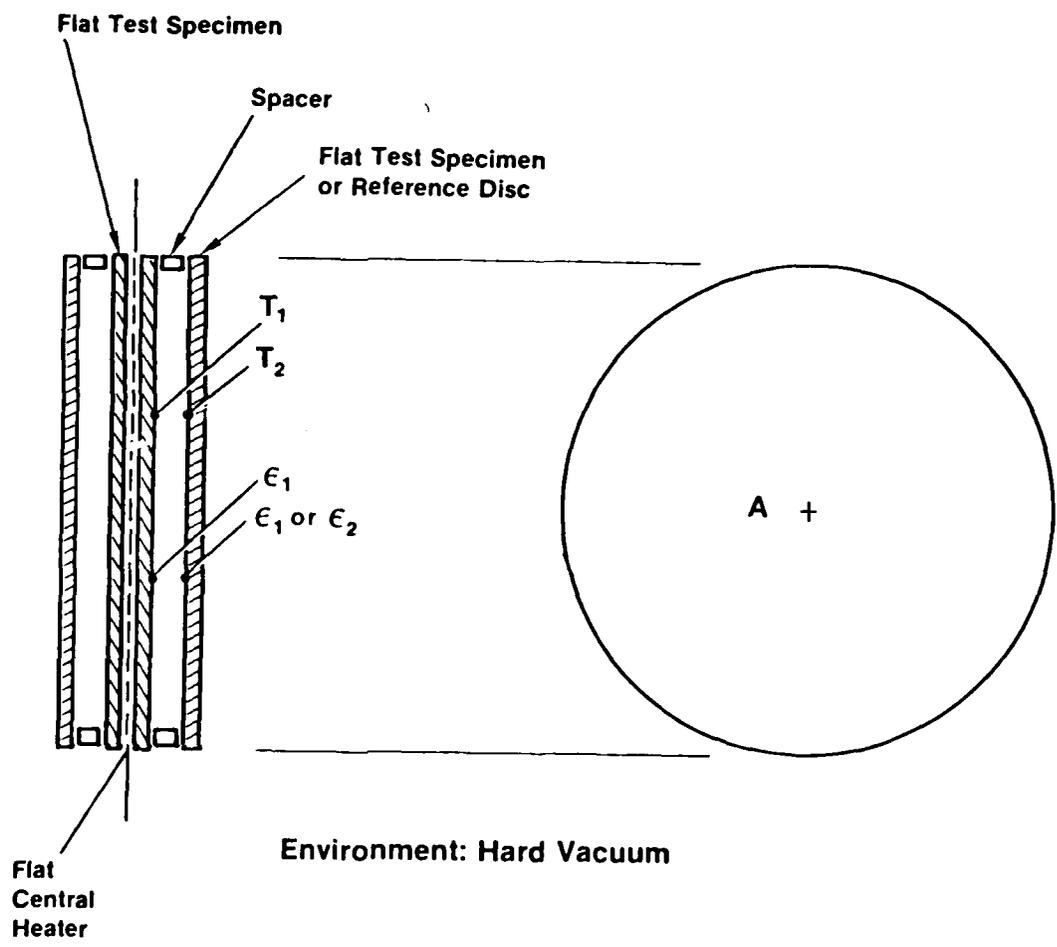


Figure 8. A gray body emissivity measurement system.

III. SOME GENERAL INFORMATION ON CADMIUM TELLURIDE

The first semi-conductor material being studied by Geoscience is cadmium telluride. Apparently, this material is used in optical and thermal radiation systems. It is also a base for mercury-cadmium-telluride which is used as an infrared detector. It has a high transmissivity in the long wavelength infrared region and is used for lenses in infrared detecting devices.

Figure 9 shows a binary phase diagram for cadmium telluride. Note that the pure compound has a composition of equal parts of cadmium and tellurium with a melting point of 1097°C. In other combinations, the compound exists with either cadmium rich or tellurium rich solids or liquids.

There is some difficulty in handling cadmium telluride because it is somewhat toxic. It cannot be machined by Geoscience because local officials require that the cuttings be disposed of as hazardous waste. The literature indicates that cadmium telluride is a possible carcinogen. It also shows that the material is somewhat toxic and gives off hydrogen telluride when it is exposed to moisture or acids. It is flammable and is a moderate explosion hazard. It is also volatile at higher temperatures as shown by the vapor pressure curve given in Figure 10. The vapors are toxic. Therefore, cadmium telluride presents some handling problems.

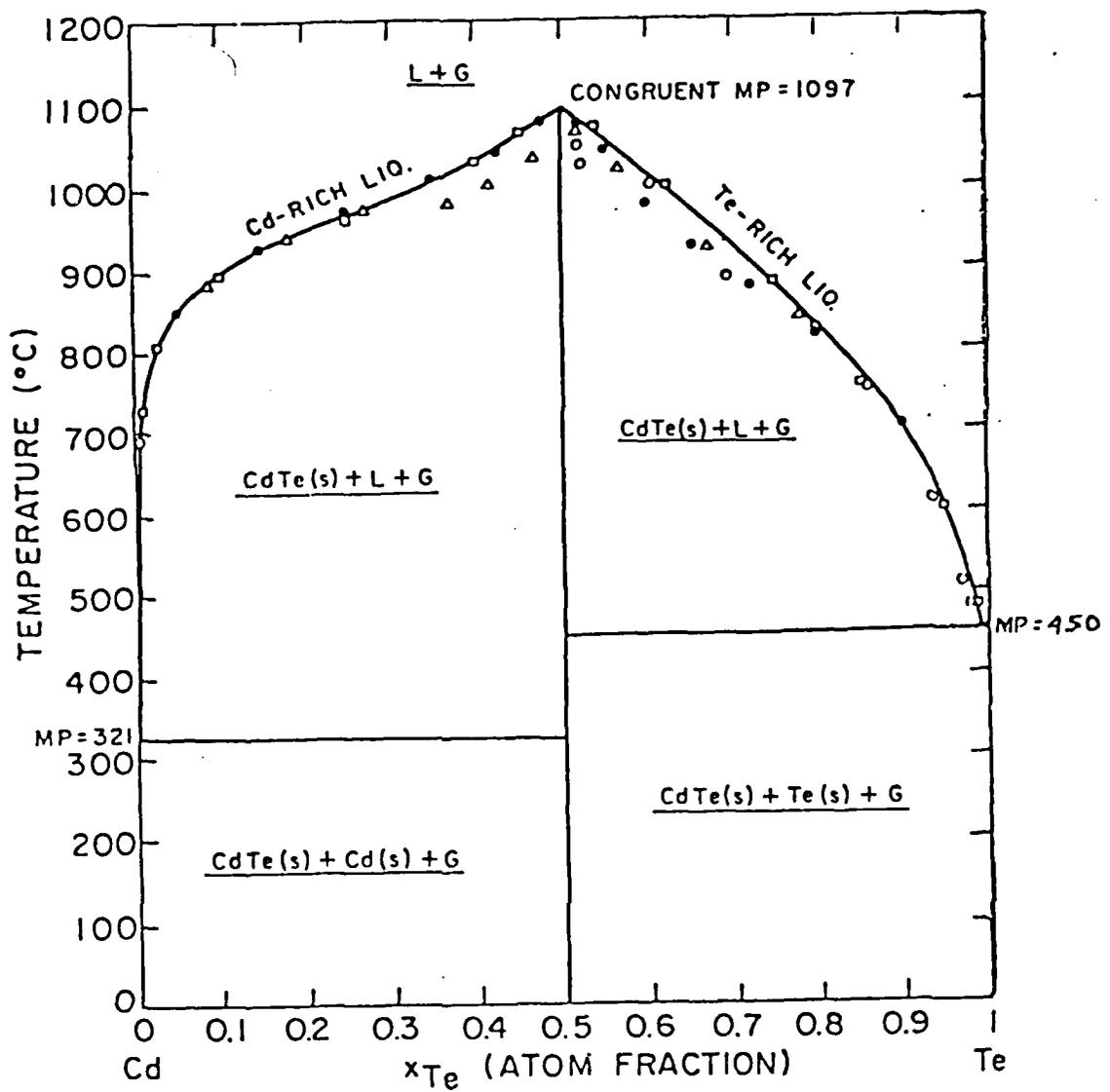


Figure 9. Phase Diagram Of The Cd-Te System.
 (Taken from: A. R. Hilton, Large Plate CdTe Synthesis by Sealed Vessel Transport", Quarterly Technical Report No. 4, Amorphous Materials, Inc.)

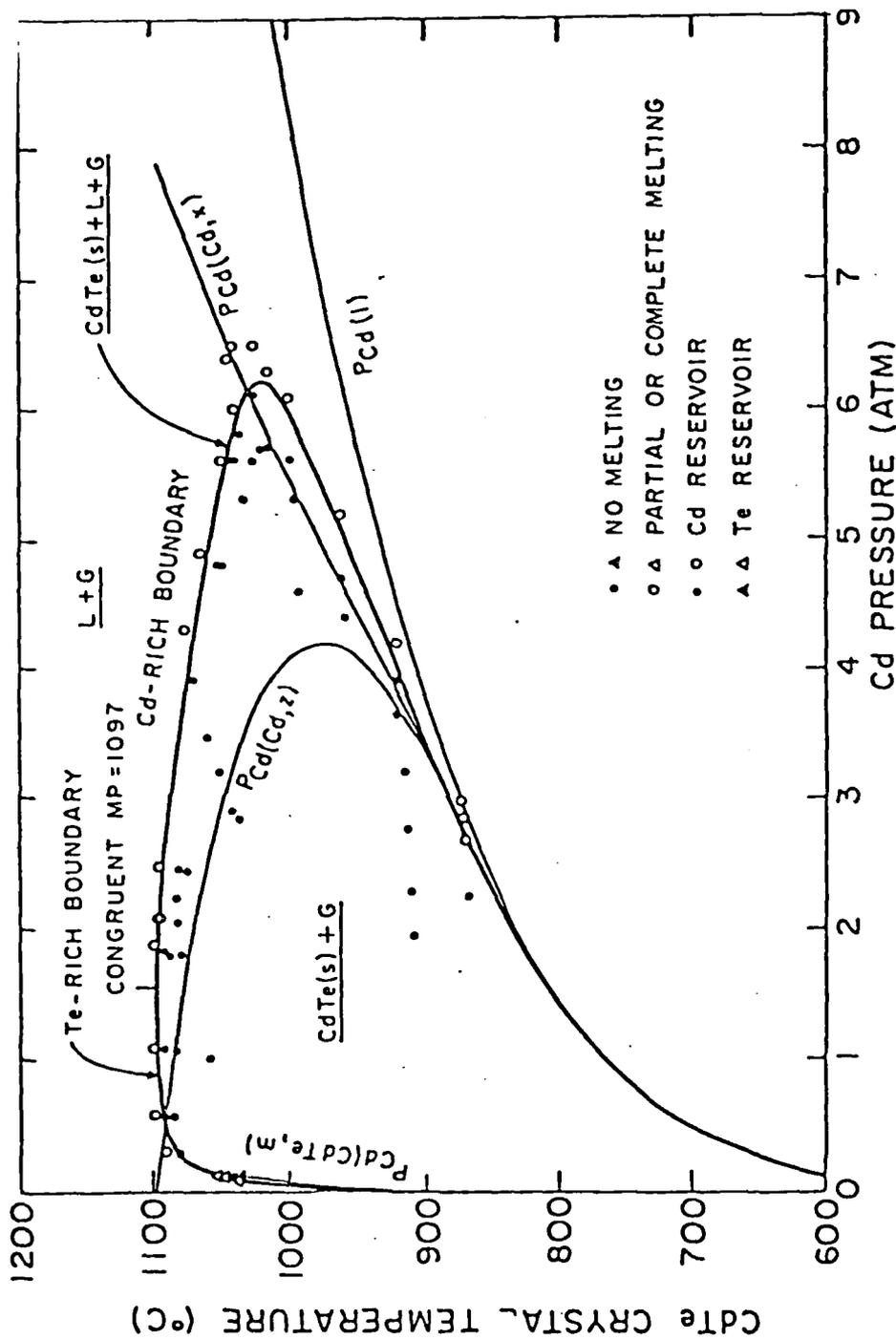


Figure 10. Cd-Rich Boundary Of The Solid CdTe Stability Field; Pressure-Temperature Projection. Taken from: A. R. Hilton, "Large Plate CdTe Synthesis by Sealed Vessel Transport", Quarterly Technical Report No. 4, Amorphous Materials, Inc.)

IV. CURRENT MEASUREMENTS MADE ON CADMIUM TELLURIDE

It has been suggested that Geoscience first study the properties of cadmium telluride. Dr. A. R. Hilton of Amorphous Materials, Inc., has kindly supplied a number of CdTe test samples having specific geometries required for the property measurements described previously.

A. Specific Heat

The specific heat of cadmium telluride was measured using the gradient layer calorimeter method. First the calorimeter was calibrated with an electric heat source. Next, runs were made with the calorimeter empty and loaded with the test samples. The calorimeter empty and loaded with the test samples. The calorimeter temperature datum was raised to 120°F using an external environmental furnace. The furnace was then removed and the calorimeter cooled gradually to room temperature. The output voltage of the calorimeter was traced on a potentiometer recorder.

The first sample studied was a copper slug at a mean temperature of 100°F. The resulting specific heat was within 5 percent of the literature value. This measurement was a system verification test. The next measurement was made for the CdTe sample; the specific heat of this material was found to be 0.061 BTU/lb°F $\left[0.061 \frac{\text{cal}}{\text{gm}^\circ\text{C}} \right]$ at a mean temperature of 100°F. This value compares reasonably with the values of cadmium and tellurium alone.

B. Thermal Conductivity

The thermal conductivity of cadmium telluride was measured using the guarded hot plate system (ASTM C-177 method) shown in Figure 2. The power input to the central heater is carefully measured at steady state. Each test sample has two 0.0003 inch diameter thermocouples placed, one on each surface in the central region. The thermocouples were pressed into position by thin sheets of gasket material. The temperature drop across the test samples alone were determined by making small temperature drop corrections in the gasket material. The thermal conductivity was then determined from the heat flux and temperature drop measurements.

The resulting thermal conductivity at a mean temperature of 100°F was found to be $2.3 \text{ BTU/hrft}^2 (\text{°F/ft}) \left[4.0 \text{ W/m.k.} \right]$.

V. WORK CURRENTLY UNDERWAY

There are several efforts currently being pursued that will extend into the next quarterly period. This work is briefly outlined below.

A. Expansion Coefficient

The test specimen for the CdTe will shortly be inserted into the dilatometer apparatus for thermal expansion measurement. It is believed that data can be obtained up to about 400°F without having excessive, undesirable gas generation.

B. Gray Body Emissivity

The two emissivity test samples prepared by Amorphous Materials, Inc., will be assembled with two reference plates as shown in Figure 8. The surface thermocouples are fine gauge and will be mounted in a shallow groove with a cement. The test matrix will be mounted in the environmental chamber shown in Figure 11.

C. High Temperature Calorimeter

As some of the specific heat values of interest are at the higher temperature levels, a high temperature gradient layer calorimeter has been designed and its tubular elements readied for thermopile installation. A sample container that can sustain significant pressure levels is also being considered.

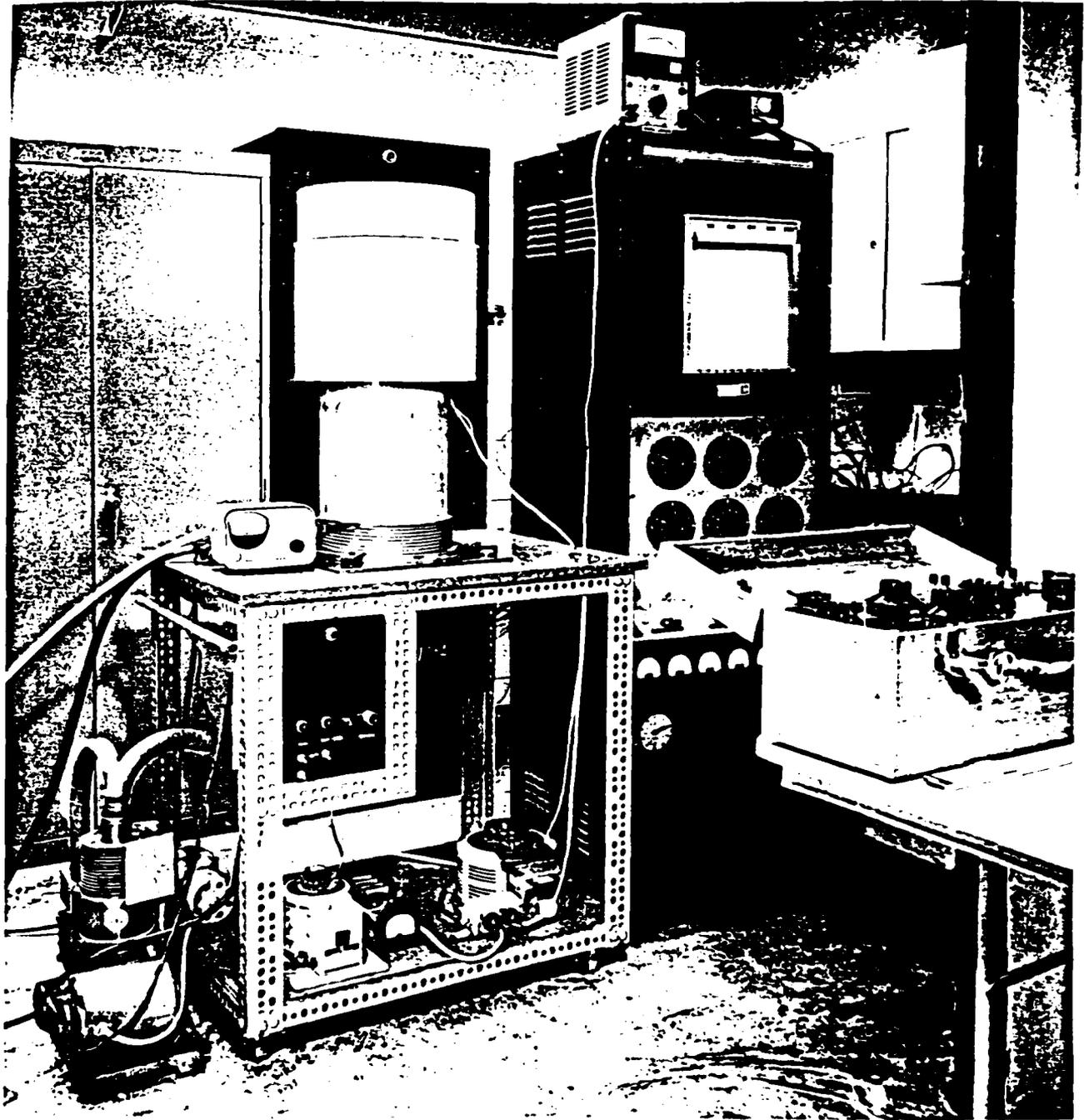


Figure 11. View of stainless steel vacuum jacket, thermal insulator, cooling water coil, environmental and sample heater power supplies and instrumentation and thermocouple measurement equipment.