TECHNICAL REPORT: PHYSICAL ELECTRONICS

A RAPID METHOD OF CRYSTAL GROWTH AND EVALUATION OF THERMOELECTRIC COMPOUND SEMICONDUCTORS

by

V. J. KING,

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NOTICE

FOREWORD

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Section 1

INTRODUCTION

During the past two years, the Solid State crystal laboratory has been concerned with two principal responsibilities:

- Supplying single-crystal specimens of compound semiconductor materials to the research group for basic studies and to the device group for evaluation and device applications
- Concurrently developing the techniques, apparatus, and facilities that are necessary to the first objective and which can be extended or diverted to searching out processes or materials of propietary interest to LMSD

The results of the first activity are contained in reports and papers originating from the research or device groups. This report summarizes accomplishments pertinent to the second responsibility and outlines the plans for integrating the several techniques to study multi-element systems which are interesting as potential thermoelectric material.

The plan of future work is based on four principal factors which have emerged while applying semiconductor theory to thermoelectric energy conversion.

- Because of the present state of theory, materials work is of primary importance in assembling necessary data.
- New techniques are necessary to permit more expedient processing of large numbers of materials of widely diversified characteristics.
- The ultimate thermoelectric material will probably come from careful work with multi-element semiconductor systems to achieve specific types of structural defects in a crystal lattice.

- Composition-temperature equilibrium diagram construction will play a predominant role in establishing the stoichiometry of congruently melting or peritectically formed compounds and the range of composition of solid solutions resulting from alloying two or more components.

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Section 2
THE HAND FLAME TECHNIQUE

The hand flame technique developed by this laboratory is a new method of growing crystals from the melt. It is a particularly applicable to material development problems because of its versatility and simplicity of operation. A brief description of the factors that affect crystal growth from the melt is helpful in understanding the operation.

- Thermal strains and inhomogeneities are the inevitable result of crystal growth from the melt. Such imperfections are best removed by proper annealing of the solid crystal.

- The degree of single-crystal growth obtained initially is, to a large extent, determined by the mean rate of advance of the solid-liquid interface R (cm/sec) and the magnitude of the thermal gradient across the interface G ($^\circ$C/cm). Optimum values of R and G for a given crystal type may be considered as empirical quantities, which must be determined by the practical magnitudes obtainable. In all cases, the instantaneous rate of temperature fluctuation at the interface β ($^\circ$C/cm) must be equal to or less than the product of R and G, that is, $RG > \beta$.

These contentions indicate that satisfactory single-crystal materials may frequently be achieved by annealing crystals grown rapidly with a large gradient and without the necessity of precise temperature regulation. Large RG conditions may produce other problems associated with rapid growth, but in many cases they may be of secondary importance or eliminated by annealing.

The hand flame technique for crystal growth from the melt consists of using a hand-held hydrogen-oxygen torch to melt or react the material in a quartz crucible. This is

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followed by rapid cooling under a strong gradient achieved by manual manipulation of the torch. The RG values achieved are approximately 10° C/sec, which is larger than the temperature fluctuation existing during crystal growth under these conditions. Initial seeding is controlled by melting back to the tip of the coned crucible. The atmosphere over the crucible is controlled by an interlocking valve system to a vacuum pump or selected gases. Except for an outlet to the vacuum pump, protected by a liquid nitrogen trap, and one well-ventilated gas outlet, the system is entirely enclosed

The hand flame technique, which permits observation of the charge throughout the operation, enables the operator to:

- Control the rate and completeness of reaction when compounds are synthesized by direct fusion. Violent reactions are readily controlled by proportioning heat from the hand torch to preferentially melt one of the elements of the compound or heat a small localized area. Inhomogeneous specimens resulting from slow or incomplete reactions are avoided by observing thermally induced convection currents and noting any layering or separation in the melt.
- Evaluate the tendency of the material to decompose, reflux, or sublime at high temperatures.
- Degas a melt or selectively remove volatile components by application of a vacuum
- Observe crystal growth, remelt, and alter growing conditions as necessary to produce the best ingot
- Detect solid-solid phase changes by observing contraction and expansion phenomena during cooling of the solid
- Estimate and establish the pertinent factors conducive to good material preparation

The technique has also been used to achieve significant material purification. The element or compound is melted under a controlled atmosphere (usually hydrogen), degassed under a hard vacuum, cooled under a positive head of an appropriate inert

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gas, and the surfaces of the ingot removed by machining in a metal lathe. In addition to the reducing action of the hydrogen gas at white heat and removal of the volatile components under vacuum, the remaining impurities tend to float to the surface of the ingot, to adhere to the quartz, or to be partially excluded by the growth process. Pb and Te processed in this way yield PbTe material with a carrier concentration of less than $5 \times 10^{16}/cm^3$.

The hand flame technique can be used with more sophisticated methods of crystal growth or compound formation. Homogeneous but polycrystalline ingots which are quickly prepared by the hand flame can be transferred to other apparatus and single crystals growth carried out under special conditions. By observing the behavior of elements which do not react, or react with difficulty, the conditions necessary for complete reaction may be ascertained.

The hand flame technique has been tested on more than 35 different binary and ternary compounds of varying stoichiometry and their constituent elements with excellent success. Single crystals of p and n type PbTe , for example, exhibit homogeneities and mobilities which are equal to or greater than those prepared by the Bridgman technique. For thermoelectric energy conversion evaluations, materials were synthesized and evaluated with a minimum of sophistication. Although as many as two different compounds have been processed per man day with frequent use of polycrystalline specimens, the values observed were in excellent and consistent agreement with the best results obtained in other laboratories. The range of materials prepared by this simple technique is indicated as follows:

Binaries				Ternaries	
CuTe	ZnTe	Tl_2Te_3	Sb_2Te_3	$AgSbTe_2$	$AuSbSe_2$
Cu_2Te	CdTe	SiTe	Sb_2Se_3	$AgBiTe_2$	$AuBiTe_2$
Ag_2Te	HgTe	GeTe	Bi_2Te_3	$AgGaTe_2$	$AuGaTe_2$
Ag_2Se	Al_2Te_3	SnTe	VTe	$AgInTe_2$	$AuInTe_2$
$AuTe_2$	GaTe	PbTe	MnTe	$AgTlTe_2$	$AuTlTe_2$
$AuSb_2$	InTe	As_2Te_3	FeTe	$AuSbTe_2$	$CuGaTe_2$

The high quality of crystals obtained is demonstrated by the magneto-oscillatory effects which have been observed in this laboratory on PbTe .

Section 3
THE CONE FURNACE

A cone-shaped furnace was developed for growing crystal from the melt at low RG values and with the temperature control required by the RG $> \beta$ relationship.

In a cone furnace, the magnitude of G is determined (Fig. 1) by shaping the outer shell to vary the amount of insulation around a resistance-type heat source cylinder containing the crucible and charge. The furnace is contained in an environmental oven which is maintained at a given temperature somewhat higher than ambient. Power to the furnace is supplied by a variable voltage power supply.

In a steady-state condition, heat input is exactly equal to heat losses, but the temperature will increase from the bottom to the top of the crucible due to the geometric configuration and the thermal gradient will go according to the expression,

$$G \propto (T_z - T_1) \frac{\text{Tan } \theta}{\ell \text{n Tan } \theta}$$

During operation the cone furnace is placed on its small base and the crucible held stationary. By progressively decreasing the voltage from the power supply, a melting point isothermal surface is forced upward through the crucible with nucleation occurring at the lower tip of the coned crucible. If the crucible is lowered through the furnace held at a constant temperature, then crystal growth by the Bridgeman technique is achieved.
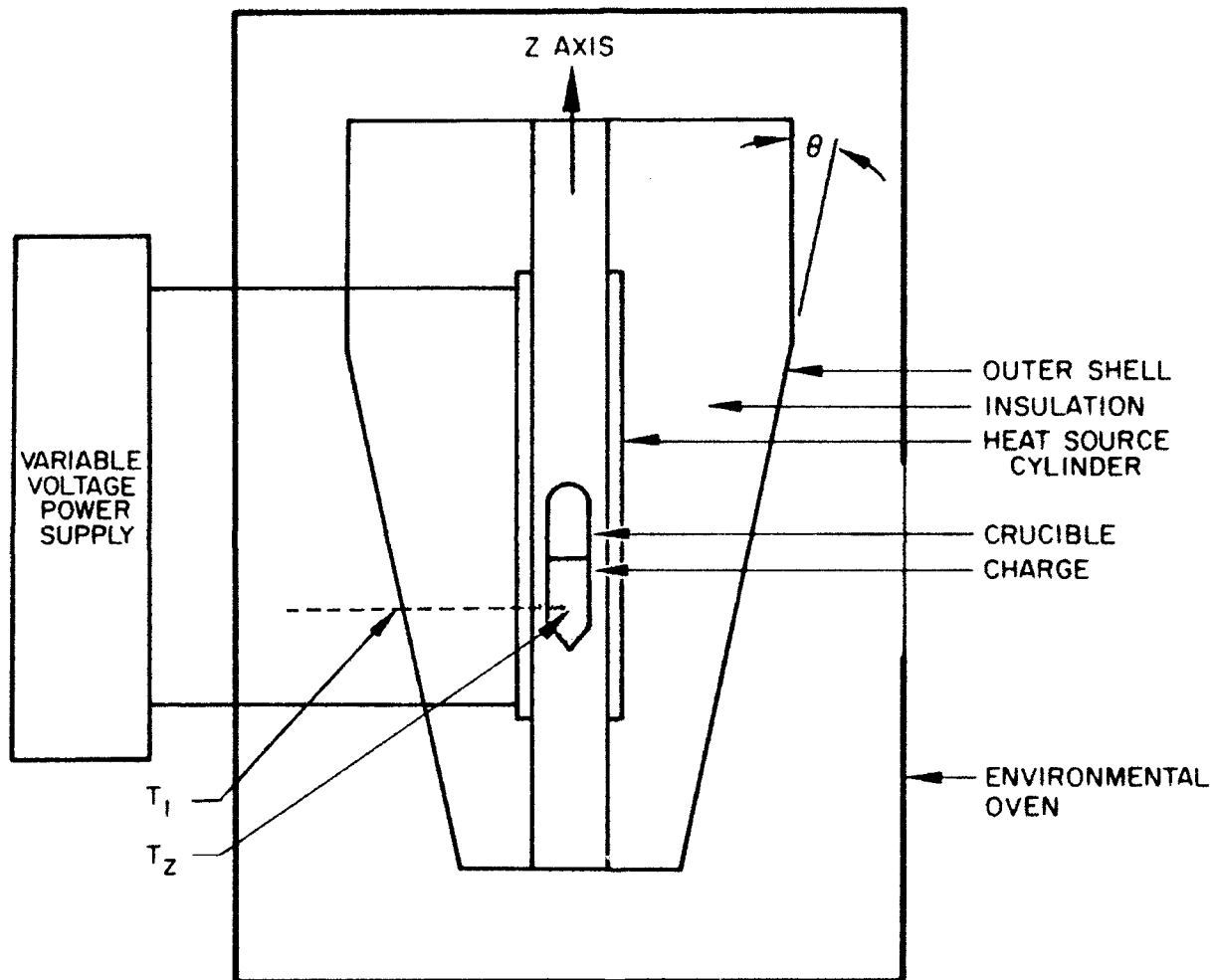
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Fig. 1 The Cone Furnace

Should the furnace be inverted and the power to the heaters decreased, nucleation would occur at the top and crystal growth from the vapor phase is possible. Variations of the Kyropoulus or Czochralski method is achieved by seeding the melt at the top, of by "pulling."

The fluctuations in the temperature at the heaters is directly proportional to fluctuations in the voltage impressed across the heaters, or $dT_z/dV \propto V$. Experience indicates that attenuation between the heaters and crucible in a small furnace results in the condition $\Delta T_z \cong \Delta V$. With voltage regulation of ± 0.01 percent, we deduce that the cone furnace is capable of operating over extended periods of time with T_z fluctuations of less than $0.02°$ C. These fluctuations must have a time duration of the order of several hundred seconds so that β can be estimated at less than 10^{-4} ° C/sec. For G values near $30°$ C/cm, growth rates as slow as 10^{-5} cm/sec are possible within the conditions $RG > \beta$.

A variation of the cone furnace has been conceived for crystal growth at temperatures above $2000°$ C (Fig. 2). The charge would be held in a cavity within a graphite or refractory electrode and the electrode protected by a radiation shield. A temperature gradient would be established along the crucible segment of the electrode by inductively heating the shield cylinder to provide a high-temperature ambient and then passing a large current through the electrode. The smaller cross section at the upper end of the crucible cavity would result in increased I^2R heating, to produce a temperature gradient across the charge. Reduction of heat input would result in crystal growth by solidification of the melt from bottom to top.
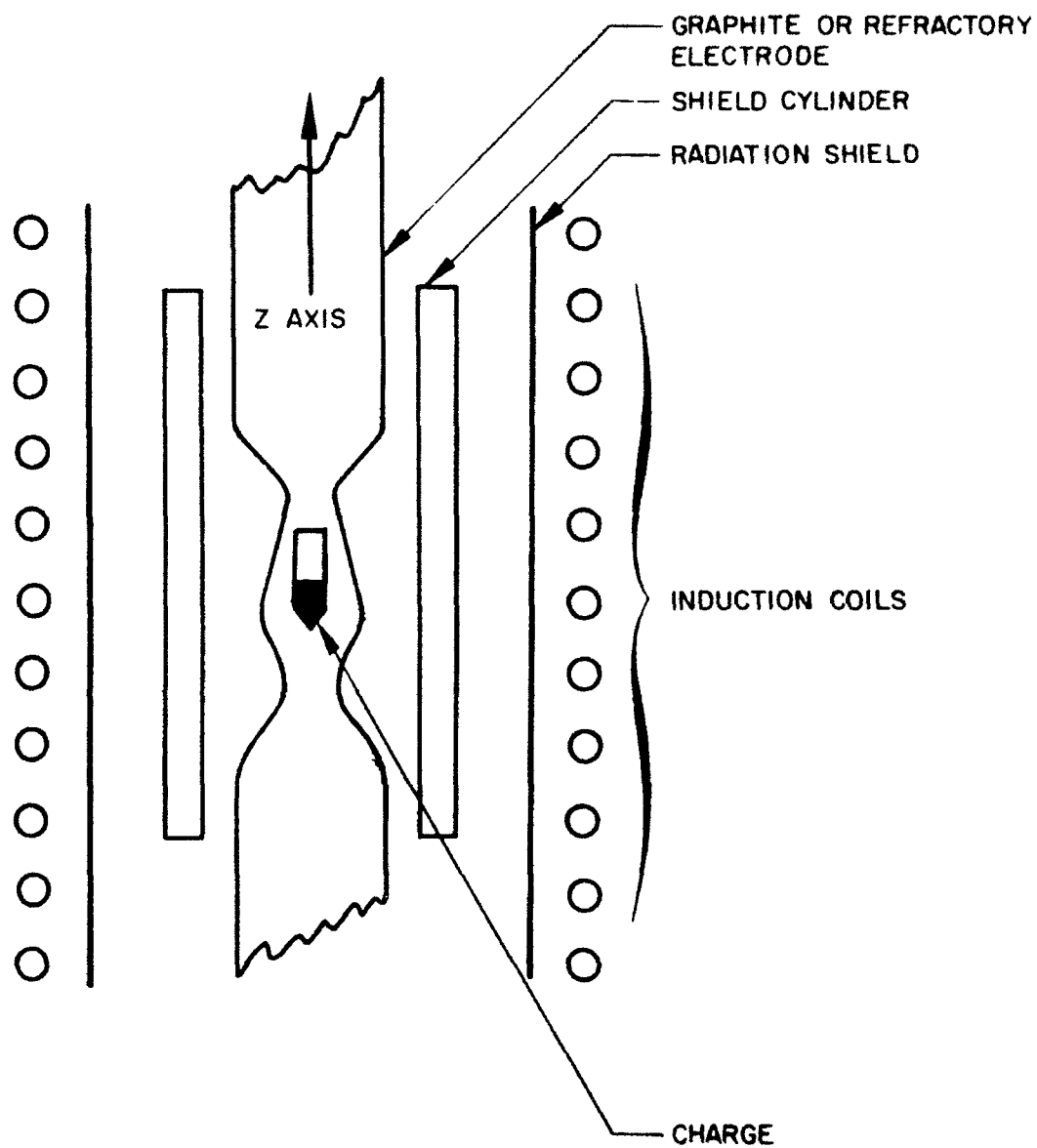
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Fig. 2 High-Temperature Modification of the Cone Furnace

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Section 4
MACHINING SINGLE CRYSTAL MATERIALS

The tendency of crystal ingots to fracture or cleave makes it difficult to size and shape specimens of suitable dimensions. Losses of time and frequently total loss of valuable ingots occur when improper or inadequate machining is attempted.

The general sequence of machining operations carried out in this laboratory consists of:

- Trimming ingots of the elements used for crystal growing or for formation of compounds to remove surface impurities
- Trimming the crystal ingot to remove surface impurities and to show grain or crystal orientation in the ingot
- Slicing the crystal ingot into oriented slabs
- Shaping and sizing of the specimen

Cylindrical ingots are trimmed on a lathe which is sturdy and accurate. A diamond saw, with an indexing table, is used for oriented slicing. Final shaping and sizing are done on an S. S. White Airbrasive cutter.

The Airbrasive cutter is used for limited machining of extremely brittle material. A stream of fine particles of a refractory material is jetted by air pressure through a small nozzle, each particle removing a small volume from the material. Materials too brittle to withstand the usual mechanical operations can be successfully machined. Surfaces left by the sandblasting may be examined under the microscope and minute crystal imperfections detected. This provides for rapid selection of good specimens for measurements.
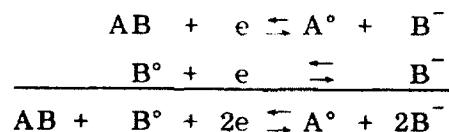
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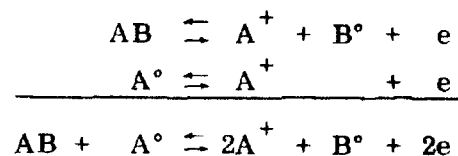## ETCHING AND ELECTRODING COMPOUND SEMICONDUCTORS*

Etching is used as a nonmechanical method of removing surface imperfections and impurities from single crystal specimens. A properly etched surface may be studied under a microscope or examined with x-ray to establish crystal perfection, type, lattice constants, etc. Etching is also used to clean a surface without imparting mechanical damage.

Etching of compound materials is more difficult than single element materials. For example, the lead may be removed from lead telluride using a suitable reagent, but the tellurium will remain as a troublesome film, whereas removal of the tellurium results in an equally troublesome film of lead.

It has been found that PbTe , and it is hoped other compound semiconductors, may be etched by making the sample one electrode of an electrolyte cell and applying a shaped AC waveform conducive to the half cell reaction:

$$AB \;+\; e \;\rightleftharpoons\; A° \;+\; B^-$$
$$B° \;+\; e \;\rightleftharpoons\; B^-$$
$$\overline{AB \;+\; B° \;+\; 2e \;\rightleftharpoons\; A° \;+\; 2B^-}$$

and

$$AB \;\rightleftharpoons\; A^+ \;+\; B° \;+\; e$$
$$A° \;\rightleftharpoons\; A^+ \;+\; e$$
$$\overline{AB \;+\; A° \;\rightleftharpoons\; 2A^+ \;+\; B° \;+\; 2e}$$

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*Patent Disclosure D-03-616.

During the first part of the cycle, atom A is reduced to its elemental form, and ion B^- is rejected from the sample surface. During the second phase of the cycle, the sample behaves as an anode, and atom B^- is oxidized to its elemental form, while ion A^+ is rejected. For ideal operating conditions, the magnitude and time of the voltage applied during each half cycle are adjusted so that equal amounts of A and B are removed. The upper frequency of the applied AC voltage is limited by the distance ions A^+ and B^- must be moved into the solution to prevent redeposition. To insure dispersion, a high-frequency sonic field is used to agitate the electrolyte.

Although only minor effort has been devoted to the project, the possible advantages of the above technique as applied to the problem of obtaining intimate low resistance contacts to intermetallic materials, particularly compound semiconductors, are apparent. The technique described above would be altered only to favor electrolytic deposition of the selected electrode material onto the semiconductor surface. The advantages over simple DC electrolytic deposition appear in recognizing the probable effect of the work functions. During the first part of the cycle, the surface would be etched; during the second part, electrode material would be deposited. In the subsequent etching operation that part of the deposited material which is strongly bonded would remain, while the portion weakly bonded would be removed. This repetitive deposition and etching would result in an exceptionally strong and uniformly intimate electrode.

Section 6
THE HgInTl LIQUID SOLDER*

To measure properly the electrical and thermal properties of semiconductor materials, uniform ohmic contacts to metal electrodes must be obtained without damage to the specimen. Hot soldering, spot welding, or pressure contacts are generally unsatisfactory. Application of heat can cause diffusion, phase changes, or composition changes, while pressure is associated with mechanical damage to fragile crystals.

Most of these difficulties were eliminated when it was discovered that a HgInTl alloy, liquid at room temperature, possesses an outstanding ability to wet such diversified materials as glass, plastic, metal, paper, refractories, and the many different compounds prepared in this laboratory.

Temporary contacts are achieved by wetting the contact area with the alloy and touching to a metal electrode. The alloy solidifies at $-35°$ C to $-40°$ C and can be treated as a conventional solder below these temperatures. Permanent contacts are obtained by using the alloy as a "tinning agent" and dropping molten commercial solder onto the alloy-wetted surface. Contact resistance to PbTe , for example, has been found to be between 10^{-5} and 10^{-6} ohm-cm^2 .

Many advantages, in addition to those already experienced in achieving measurement apparatus of simple design and operation, are expected on further exploitation of this unusual material.

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*Patent Disclosure D-03-595.

Section 7

RAPID MEASUREMENTS OF THE THERMOELECTRIC
PROPERTIES OF MATERIALS

An apparatus which utilizes the liquid HgInTl alloy to measure the resistivity ρ and thermoelectric power α is shown schematically in Fig. 3a. Both ends of a specimen of cross-sectional area A and length L are wetted with the liquid alloy and positioned between the two massive electrodes E and E'. An AC voltage passes a current through the meter and the specimen. The IR drop across contacts V^o and V^+ is read on a suitable voltmeter and the resistivity of the material calculated from the relationship; $\rho = \frac{AR}{L}$ ohm-cm. With the AC voltage disconnected and DC voltage supplying power to the resistance heater H, a temperature difference $T_H - T_C$ is imposed across the specimen and a thermoelectric voltage is produced across V^+ and V^o. The thermoelectric power of the material is calculated from $\alpha = \frac{V^+ - V^o}{T_H - T_C} \mu v/°C$.

This apparatus is being modified to give thermal conductivity values k and extend the temperature range of the α and ρ measurements (Fig. 3b). In this apparatus, $\Delta T = T_H - T_C$ is to be maintained constant over a wide range of temperatures and to a high degree of accuracy by two separate temperature controls C and C' signalled by the temperature-sensitive element 1 and 1'. Power supplied to the heater elements H and H' is to be monitored by the power meters P and P'.

The power required to maintain the insulated electrodes E and E' at temperature T_H and T_C are noted before and after the specimen is inserted. Because the specimen provides a heat path between electrodes, P will increase and P' decrease by the amounts $+ \Delta P$ and $- \Delta P'$ where ΔP is the power conducted from surface 2 and $\Delta P'$ the power conducted to surface 2'. Due to radiation losses, $|\Delta P|$ will be larger than $|\Delta P'|$, but at low temperature this difference is small and the thermal conductivity is calculated from $k = (L/A)(\Delta P/\Delta T)$.
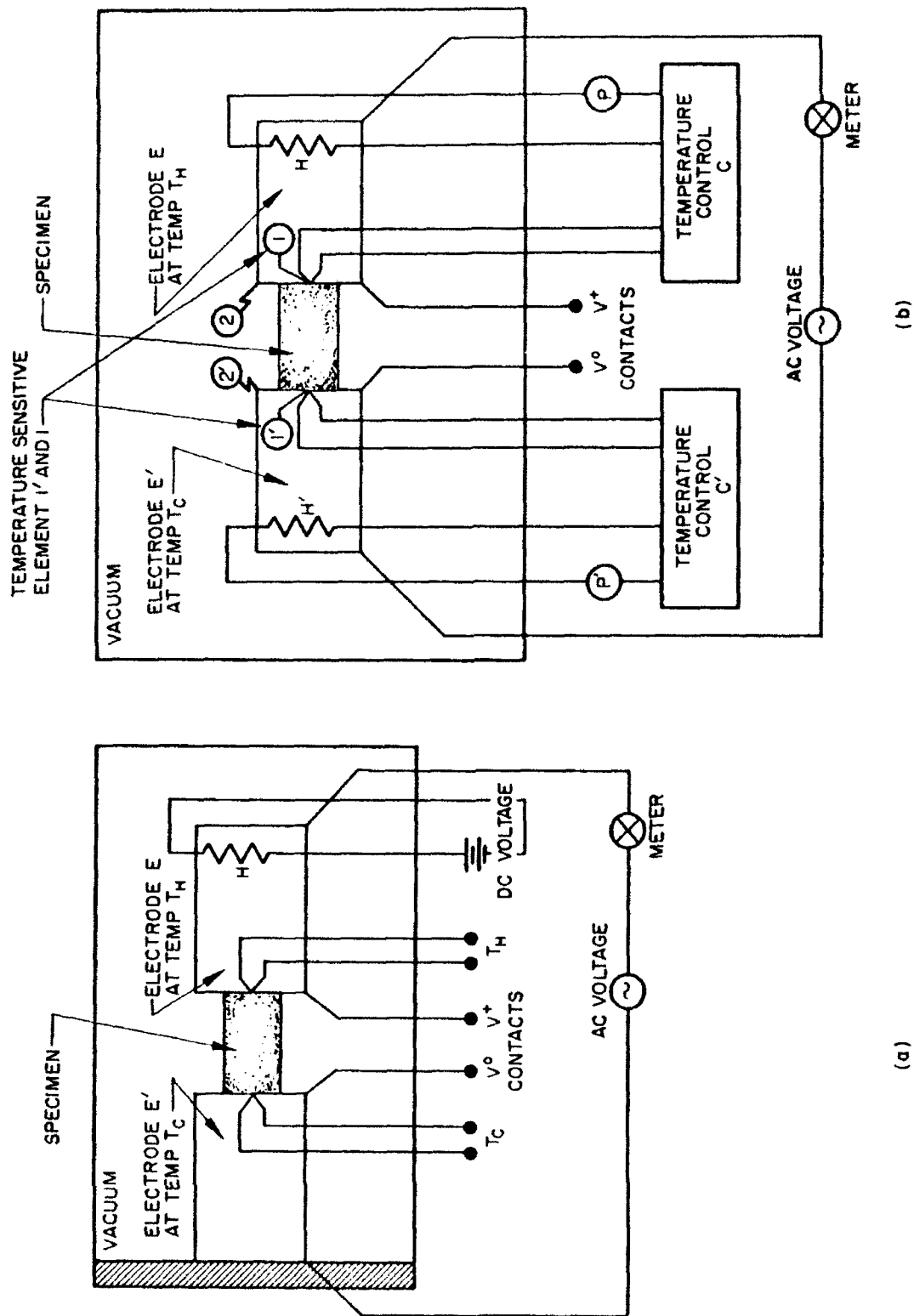
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Fig. 3 Apparatus for Measuring Thermoelectric Properties

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This apparatus is designed to evaluate rapidly, but with sufficient accuracy, the thermoelectric properties of a material including temperature dependence near room temperature. This constitutes a means of screening classes or groups of materials preliminary to more sophisticated and detailed studies on selected systems.

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Section 8
THERMAL ANALYSIS

Thermal analysis is the principal technique used in constructing composition temperature equilibrium diagrams. Such diagrams are essential to an understanding of multicomponent systems because of the many valency combinations possible to compound formation, the stability ranges of the compounds, the solid solutions formed, and the phase transitions that may occur in a solid. For semiconductor studies, it is frequentl important to establish these diagrams over narrow selected ranges of composition.

It is possible from a study of the temperature-time curves obtained on cooling a melt to determine temperatures of initial and final solidification and to detect the temperature at which various transformations or transitions occurred. Used in conjunction with Gibb's Phase Rule, the number of phases produced by a given mixture of components can be ascertained. Correctly interpreted, a succession of these curves can be used to establish equilibrium or phase diagrams.

Gross cooling curves are obtained by us by heating 10 to 20 grams of a material in an open quartz test tube with a hydrogen-oxygen hand torch. The test tube is slagged to give cooling rates of approximately 50°C per min on free cooling. Temperature-time traces are recorded on a 10-mv-scale recorder as signalled by thermocouples protected by a quartz sleeve immersed in the melt. Although the cooling rate used is high, the technique is rapid and determines whether a mixture is single or polyphase. Calibrated against elements and compounds of known melting points, this assembly is accurate within ±5 percent.

A more versatile and precise thermal analysis system (Fig. 4) has been designed and is being constructed to facilitate the hand flame technique in locating and studying single-phase compositions in complex multi-component systems.
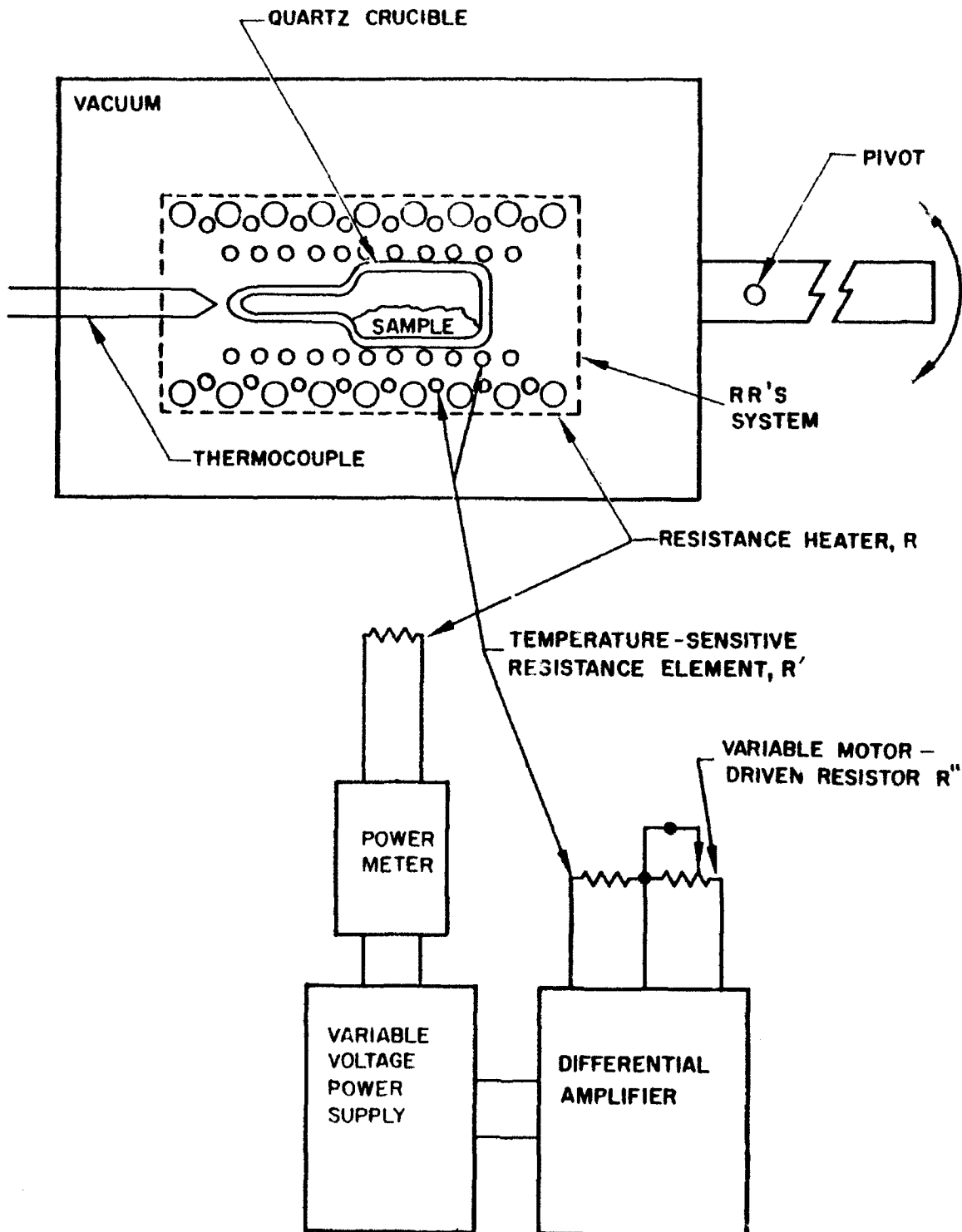
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Fig. 4   New Thermal Analysis System

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The sample is contained in a closed quartz crucible. A resistance heater R and temperature-sensitive resistance element R' , together with the sample S, constitute a discrete mass of high thermal conductivity well insulated from the ambient. A thermocouple monitors the temperature of this RR'S system.

Power, monitored by a power meter, is supplied to the resistance heater by a variable voltage power supply. The output of the power supply is controlled by the output of a differential amplifier which compares the magnitudes of the temperature-sensitive resistance element and a variable motor-driven resistor so that the temperature-sensitive resistance element will be heated until it has a value dictated by the variable motor-driven resistor.
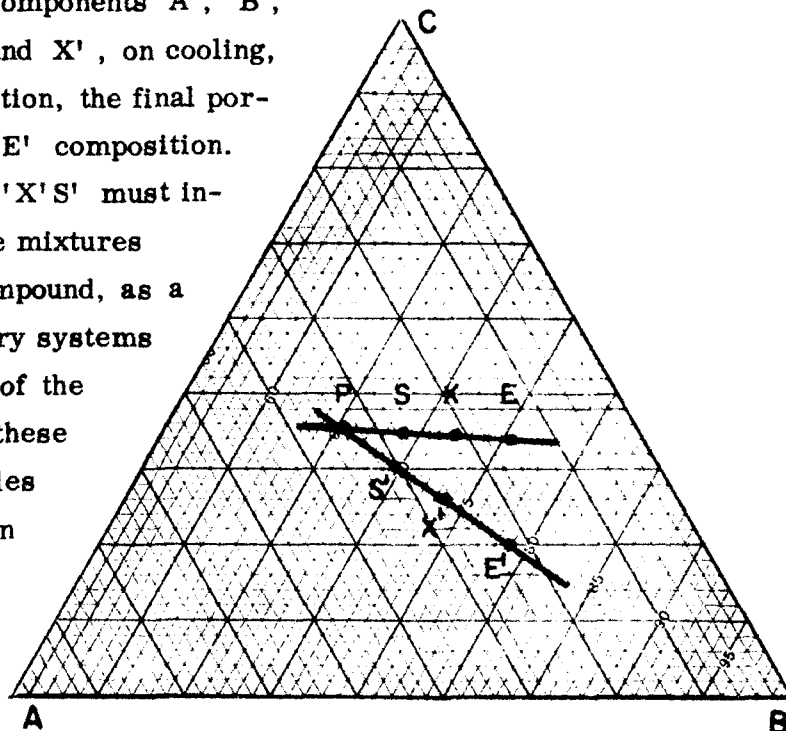
Operation is as follows: The insulated RR'S system is heated and maintained at a temperature determined by the variable motor-driven resistor. When no other power generating source is involved (that is, the sample is thermally inert), a reference time trace of the temperature and power is obtained by either progressively increasing or decreasing the value of the variable motor-driven resistor. When the sample becomes thermally active, the quantity of power required from the variable power supply is changed and the power-time trace will be deflected from the reference trace by an amount and for a time that is directly proportional to the quantity of heat involved in the thermal transition. The integrated area of this deflection gives the quantity of heat involved.

This design predicts that short-term temperature variations in the RR'S system as small as 10^{-5} °C will be detected and that minute heat changes in small samples will be detected without contamination or deterioration. The thermocouple monitors the temperature in the usual way, but deflections of the power input detects the occurrence of thermal activities that are qualitatively much smaller than is possible to detect from variations in the thermocouple output.

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Although the absolute accuracy of the temperature readings by the thermocouple are not improved by this design, small qualitative differences in temperature can be detected. From these data and with the qualitative measurements of the heats of fusion and transition, the details of an equilibrium diagram may be determined for narrow composition ranges.

Considerable information concerning the nature of a compound and its behavior can be deduced from heats of formation (ΔH) data. For example, the ΔH values of the binary compounds AB , BC , and AC can indicate the probable tendency for two of the elements to form a complex in a companion ternary mixture, ABC . Changes in ΔH also indicate changes in free energy; the magnitude and direction of change providing additional evidence as to the existence or location of a single phase.

In addition to the heat of formation, fusion, and transition, the crucible configuration and pivot arrangement provides for samples to be taken for chemical analysis of the first and last portions of a melt that solidifies on cooling. The accompanying figure shows one manner in which chemical analysis would minimize the effort required to locate and establish the composition of a ternary compound, which is not predictable on the basis of the valency of the components A , B , and C . The composition X and X' , on cooling, first yields S and S' composition, the final portion of the melt having E and E' composition. The extensions of EXS and E'X'S' must intersect at P if X and X' are mixtures having P , the sought after compound, as a common constituent to two binary systems with these extensions as part of the composition base lines. Under these conditions, as few as two samples are needed to locate the unknown ternary compound.

Section 9
CONCLUSIONS

Concurrent to providing material to the research and device groups of the Solid State organization during the past two years, the crystal laboratory has developed a facility which has the ability to produce, process, and evaluate compound semiconductor materials with a minimum expenditure of effort.

The maximum value of this facility will probably be realized by intensified application to material problems, which require evaluation of large numbers of materials of diversified and unknown behavior.

Future work in the crystal laboratory is to be directed to the preparation and study of semiconductors of the multi-element compound and solid solution type, particularly for the purpose of locating more efficient thermoelectric materials. Specifically, we intend to extend the hand flame and associated techniques and the special thermal analysis method to establish the stoichiometry and behavior of the ternary $A_x B_y C_z$ compounds.

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