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THE THERMOELECTRIC POWER OF AU-NI
THIN FILM THERMOCOUPLES

MASTER

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I. INTRODUCTION

A. History of the Thermoelectric Effect

In 1822, Seebeck⁽¹⁾ discovered that if two junctions were made between wires of two dissimilar metals as shown in Figure 1, and a temperature difference was established between the two junctions, a voltage would be developed across the points A and B. He further noted that for small changes in temperature this voltage difference was proportional to the temperature difference between the two junctions. The derivative $\frac{dV}{dT}$ relating the infinitesimal voltage increment to an infinitesimal temperature gradient was thus found to be a property of the two metals forming the couple. In honor of his contribution $\frac{dV}{dT}$ is called the Seebeck coefficient and is given the symbol ΔS . Subsequent theories of Peltier and Thomson were concerned with thermoelectric effects in the presence of a current flow and their developments are discussed elsewhere.⁽²⁾ The Seebeck coefficient, also called the thermoelectric power, is accurately determined only under conditions where there is no flow of electric current through the junctions.

The thermoelectric power of a junction can be expressed in terms of the absolute thermoelectric powers of the component metals.⁽³⁾ This parameter, S , only recently was found to be capable of experimental determination. That S is a property of the individual metals and not of the junction can be demonstrated by several simple experiments. We express the thermoelectric power of a junction by

$$\Delta S_{ab} = S_a - S_b \quad (1)$$

where S_a and S_b are the absolute thermoelectric powers of the component

metals. If a junction consists of two identical wires

$$\Delta S_{aa} = S_a - S_a = 0 \quad (2)$$

which is readily observed to be true. This is why the absolute thermoelectric power cannot be determined by direct measurement on a single metal. However if another metal c is chosen and from an a - b junction ΔS_{ab} is determined, and from an a - c junction ΔS_{ac} is determined, then

$$\Delta S_{bc} = \Delta S_{ac} - \Delta S_{ab} = S_b - S_c \quad (3)$$

This has been observed to be universally true, and has resulted in the law of intermediate metals.⁽¹⁾ If in a thermoelectric circuit (as in Figure 2) metal c is placed as shown, then as long as the temperature at both ends of metal c is the same, the voltage produced at A - B will be that of the a - b junctions only.

Recently, methods have been developed whereby the absolute thermoelectric power of a metal can be measured directly by forming a junction between the metal under consideration and a superconductor.⁽²⁾ Because superconductors have a zero absolute Seebeck coefficient,⁽⁴⁾ the observed thermoelectric properties between a metal and a superconductor are those of the non-superconducting metal alone. In this way S may be determined experimentally up to $\sim 18^\circ\text{K}$, but from this point upwards theoretical calculations must be relied upon.

The general theory of the thermoelectric power is developed for individual component metals of the junction, but most experimental observations of the effect measure the difference between the absolute thermoelectric powers of the component metals.

The Seebeck effect provides a reliable method of thermometry as evidenced by the large scale use of thermocouples as laboratory and industrial thermometers.

B. Thermodynamic Justification

A theoretical justification of the thermoelectric EMF can be provided through irreversible thermodynamics. While a detailed treatment is outside the scope of this work, a brief discussion of the relevant concepts is given. Detailed treatments may be found in many references among which are Nye,⁽⁵⁾ Lee, Sears and Turcotte⁽⁶⁾ and de Groot.⁽⁷⁾

One of the most important concepts in irreversible thermodynamics is that of entropy production, a phenomenon easily demonstrated. Suppose a rod with isotropic thermal and electrical conductivities is immersed in an isothermal bath and an electric current I is passed through the rod under the influence of a small potential δV . Since the entire rod is kept at a constant temperature T , all its state properties (internal energy, U and entropy, $\bar{S}$) remain constant with time. The heat flux out of the rod in time dt then equals the work

$$\delta Q = I \delta V dt \quad (4)$$

done on the rod, and the increase entropy of the reservoir absorbing the heat is

$$\delta \bar{S} = \frac{\delta Q}{T} \quad (5)$$

We now consider an entropy and energy balance for the system. Since the state of the system does not change, U and $\bar{S}$ must remain constant. An

energy balance is obtained since the heat flux from the rod equals the work flux into the rod. While an "outflow" of entropy exists, there is no corresponding entropy influx, and thus entropy must be created within the rod at a rate equal to the rate at which it flows to the reservoir. This rate is

$$\frac{d\bar{S}}{dt} = \frac{\delta Q/T}{dt} = \frac{I\delta V}{T} \quad (6)$$

Similarly it may be shown⁽⁶⁾ that if a rod is placed between two isothermal reservoirs of different temperature and steady state is reached, the constant heat flux, J_q , flowing through the rod results in an entropy flux, J_s , which is given at any point by

$$J_s = J_q/T \quad (7)$$

where T is the temperature of the point under consideration. For this case one obtains

$$\frac{d\bar{S}}{dt} = \frac{J_s \delta T}{T} \quad (8)$$

where δT is the temperature difference across the element under consideration. If both an electric current and a heat flux are present, then

$$\frac{d\bar{S}}{dt} = I \frac{\delta V}{T} + J_s \frac{\delta T}{T} \quad (9)$$

It was shown by Onsager⁽⁷⁾ that the "fluxes" conjugate to the "forces" δV and δT are the electric current and the entropy flux. By conjugate forces and fluxes, it is meant that each flux in Equations 10 and 11 has a force associated with it which satisfies the property expressed in Equation 12 below. It was further suggested by Onsager that these forces and fluxes are related by the equations

$$I = L_{11} \delta V + L_{12} \delta T \quad (10)$$

$$J_s = L_{21} \delta V + L_{22} \delta T \quad (11)$$

and that the matrix of phenomenological coefficients is symmetric, i. e.,

$$L_{12} = L_{21} \quad (12)$$

These expressions are considered in more detail by de Groot.⁽⁷⁾

Consider a rod in which there is an entropy current but I is zero, then from the above

$$\delta V \Big|_{I=0} = - \frac{L_{12}}{L_{11}} \delta T \quad (13)$$

Further, for $\delta T = 0$

$$I \Big|_{\delta T=0} = L_{11} \delta V \quad (14)$$

$$J_s \Big|_{\delta T=0} = L_{21} \delta V \quad (15)$$

The ratio of the entropy flux to the electric current at zero temperature gradient is then given by

$$\frac{J_s}{I} \Big|_{\delta T=0} \equiv Z = \frac{L_{12}}{L_{11}} \quad (16)$$

and finally it follows that

$$\frac{\delta V}{\delta T} \Big|_{I=0} = -Z \quad (17)$$

Thus the Seebeck effect for a single material has been given thermodynamic justification, although from this treatment the magnitude of the effect cannot be determined. It is generally true that thermodynamics predicts what is capable of happening, while specific models must be chosen to examine the magnitude of the effects.

C. Simple Free Electron Model and Justification

From the free electron theory of metals, a particularly simple treatment can be given to demonstrate the existence of the Seebeck effect in a single conductor. The electrons under consideration are assumed to have the energy scheme shown in Figure 3. Electrons occupy states from the bottom of the valence band to the region of the Fermi level, ξ . The distribution of these electrons follows Fermi-Dirac statistics. The surface of the metal is above the Fermi level by an energy $e\phi$ where ϕ is the work function of the metal in volts. Thus the depth of the potential well, E_b , is given by

$$E_b = \xi + e\phi \quad (18)$$

Suppose that this hypothetical piece of metal has a temperature T . Then it can be shown⁽¹⁸⁾ that the Fermi energy as a function of T is approximately given by

$$\xi = \xi_0 \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\xi_0} \right)^2 \right] \quad (19)$$

where ξ_0 is the Fermi energy of the metal at absolute zero. If another identical piece of the same metal at temperature $T + \delta T$ is brought in close proximity to the first piece, it will have a different Fermi energy given by $\xi + \frac{\partial \xi}{\partial T} \delta T$. Therefore there exists a driving force for electron flow, since in thermal equilibrium the Fermi levels must be the same in both rods. If electrons are transferred between the rods until the Fermi energies are equal, a potential difference will exist between the rods given by the difference in their work functions. Thus

$$\delta V = \phi_1 - \phi_2 = \frac{1}{e} \frac{\partial \xi}{\partial T} \delta T \quad (20)$$

and therefore

$$S \equiv \lim_{\delta T \rightarrow 0} \frac{\delta V}{\delta T} = \frac{1}{e} \frac{\partial \xi}{\partial T} \quad (21)$$

Using the relation for the temperature dependence of the Fermi level, the Seebeck coefficient for a pure metal is found to be

$$S = - \frac{\pi^2}{6} \frac{k^2 T}{e \xi_0} \quad (22)$$

This treatment is quite straightforward but lacks rigor in that no mention is made of the process by which the Fermi energy changes with temperature. This equation, (22), is applied satisfactorily only to the alkali metals, for which the free electron approximation is most accurate. Its failure when applied to other "monovalent" metals (copper for example) shows the extreme sensitivity of the effect to the behavior of the electrons at the Fermi surface.

D. Results of More Detailed Developments

The conventional treatment of thermoelectricity begins with an effect not yet discussed. In 1884, Thompson⁽²⁾ postulated the existence of what is now known as the Thomson heat of a conductor. If an electric current of density J is passing through metal isotropic with respect to electrical and thermal conductivity and a temperature gradient $\frac{dT}{dx}$ is also present in the same direction as J then the net heat produced by the conductor per unit volume per second, $\dot{Q}$, is given by

$$\dot{Q} = \frac{J^2}{\sigma} - \mu J \frac{dT}{dx} \quad (23)$$

where σ is the conductivity of the metal and μ is the Thomson coefficient for the conductor. The first term in Equation 23 is the irreversible Joule heat, while the second is the reversible Thomson heat.⁽²⁾

Thomson was able to demonstrate that

$$\mu = T \frac{dS}{dT} \quad (24)$$

From this relation the absolute thermoelectric power of a conductor is given by

$$S(T) - S(0) = \int_0^T \frac{\mu}{T} dT \quad (25)$$

where $S(0)$ vanishes according to the third law of thermodynamics. Thus

$$S(T) = \int_0^T \frac{\mu}{T} dT \quad (26)$$

The theory of S follows from a theory for μ . This is convenient since μ is interpreted as the heat absorbed per unit positive charge and unit temperature difference when the charge is transported quasi-statically (so that the Joule term in Equation 23 becomes vanishingly small) in the direction of increasing temperature. This parameter can thus be determined using transport theory.

The development of this theory is far beyond the scope of the present work, but is found in detail in Mott and Jones.⁽⁹⁾ There are two conclusions from this theory that have relevance to this work. The first is that S depends on the mean free path of conduction electrons, and that in general

$$S = \frac{\pi^2}{3} \frac{k^2 T}{e} \left(\frac{\partial (\ln \sigma(E))}{\partial E} \right)_{E = \xi} \quad (27)$$

where

$$\sigma(E) = \frac{2e^2}{\hbar^2} \int \left(\frac{\partial E}{\partial k} \right)^2 \tau(\vec{k}) \frac{dS}{|\nabla E|} \quad (28)$$

In the above $\vec{k}$ is a wave vector in momentum space, $E(k)$ is the electron energy and $\tau(\vec{k})$ is the relaxation time of the electrons. The integration (28) is carried out over the Fermi surface.

That S depends on mean free path allows the prediction that the thermoelectric power will be a size effect. By this it is meant that once some critical dimension of the conductor is reduced to a size smaller than the electron mean free path, the Seebeck coefficient should be a function of the specimen dimensions.

E. Thermoelectric Power as a Size Effect

Size effects in the present context are conventionally defined as those whose magnitude is dependent upon the mean free path of conduction electrons in the substance under consideration. The electrical conductivity, for example, is a size effect since it is a function of the electron relaxation time, τ . The mean free path is given by

$$\lambda = v\tau \quad (29)$$

where the velocity, v , is that of the conduction electrons near the Fermi surface and is given by

$$v = \sqrt{\frac{2\xi}{m^*}} \quad (30)$$

where m^* is the effective mass of a conduction electron. As mentioned in the previous section, S will be a size effect because of the appearance of τ in Equation 28.

A convenient method for studying size effects involves the preparation of thin films, i.e., films of a conductor which are of macroscopic dimensions in two directions, but which are only a few hundred to a few thousand angstroms thick.

Conduction electrons are usually scattered by the thermal vibrations of the lattice and by interactions with various impurities and defects. If the film is thinner than the electron mean free path, surface scattering will effectively shorten the distance an electron travels before it is scattered, and thus will cause the mean free path to be a strong function of film thickness. It is convenient for the purpose of this discussion to describe three regions of film thickness. Region I films are much thicker than λ so that surface scattering plays a minor role. Such films exhibit a behavior characteristic of the bulk metal. Region II films are of such thickness that electron scattering from the surfaces of the film becomes important. Region III films are films which are in the nucleation stage and have not yet coalesced to form a continuous layer of metal.

Thus far the theory of the Seebeck coefficient has been restricted to region I films. The properties of region II films will now be discussed and region III films will not be considered at all. The reason for not considering region III films is that the mechanism of electrical conduction in these films has not been conclusively determined and to the knowledge of the author there is no theoretical description of the Seebeck coefficient in these films against which experimental data could be compared.

The theory of size effects represents a field in which much work is being done. The treatment presented here follows Mayer⁽¹⁰⁾ (which is often referenced by other workers in the field). Equation 27 may be re-written in terms of the electron mean free path as

$$S_{\infty} = - \frac{1}{e} \frac{\pi^2}{3} \frac{k^2 T}{\xi} \left[1 + \left(\frac{d \ln \lambda}{d \ln E} \right)_{E=\xi} \right] \quad (31)$$

where S_{∞} is the absolute thermoelectric power of a region I (bulk) film. Since λ depends on film thickness, then so does S . From Equation 31 and the theory of size effects, Mayer obtained the thermoelectric power of a region II film as measured against a suitable (i.e., constant thickness) reference film of a different metal. The expression given is

$$\Delta S \cdot d = \alpha d + \beta \quad (32)$$

where

$$\alpha = - \left\{ \frac{\pi^2 k^2 T}{3 e \xi} \left[1 + \left(\frac{d \ln \lambda}{d \ln E} \right)_{E=\xi} \right] + S_o \right\} \quad (33)$$

$$\beta = \frac{\pi^2 k^2 T}{8 e \xi} \lambda_o \left(\frac{d \ln \lambda}{d \ln E} \right)_{E=\xi} \quad (34)$$

d is the film thickness of the metal under observation, λ , is its bulk mean free path, and S_o is a constant thermoelectric contribution due to the second metal. From a plot of $\Delta S \cdot d$ vs. d , one should obtain a straight line whose intercept and slope give information regarding the variation of mean free path with electron energy at the Fermi surface. The above equation assumes that the films under consideration are isotropic with regard to electrical and thermal conductivity.

F. Survey of Previous Work

A brief overview of the current literature regarding the thermoelectric power of film metal films shows a wide variation in the results obtained. Notable trends in the data seem to indicate that the Seebeck coefficient approaches zero for vanishing film thickness, and levels off to some constant value for thick films.

Early studies on sputtered Sb and Bi film by Johnson and Harris⁽¹¹⁾ indicate that S was a function of Bi thickness for films thinner than $10,000 \text{ \AA}$. More recent observations on Bi indicate a thickness dependence of ΔS occurs for films less than $1500 \text{ \AA}$ thick.^(12, 13) It is unfortunate that what appears to be an exhaustive study of many metals, performed by Reimer,⁽¹²⁾ is thrown into doubt by his inclusion of data for films $20 \text{ \AA}$ thick. Such films, deposited on glass, are likely to be region III films, and should not display the smooth behavior he has observed.⁽¹⁰⁾ Furthermore, it is characteristic of some papers in the field that much useful information is missing. Such information as identification of the metal against which measurements are being made, metallurgical treatment of the films during manufacture and vacuum during deposition typify the information not reported.

Rather than list the myriad of papers which characterize the above problems, it is worth noting that some detailed work has been performed. Studies on the alkali metals vs. platinum by Nossek⁽¹⁴⁾ are notable since they provide experimental confirmation of Mayer's theory (see previous section). Heubener⁽¹⁵⁾ studied the thermoelectric power in thin gold foils and wires to investigate the role of quenched-in defects in determining the magnitude of the Seebeck coefficient. A study of the absolute thermoelectric power of gold thin films was made by Worobey⁽¹⁶⁾ for films in the temperature range from 1.4 to 9°K .

The use of thin film thermocouples as practical temperature measuring devices has had a parallel history. Fabrication techniques and thermal EMF vs. temperature curves are described by Harris and Johnson,⁽¹⁷⁾ Morrison and Lechenmayer,⁽¹⁸⁾ Marshall, et al.,⁽¹⁹⁾ Belous and Wayman⁽²⁰⁾ and Chopra, et al.⁽²¹⁾ The work of Belous and Wayman provided the basis for the current study and the essential elements of their work will be discussed later. The work of Chopra et al. on copper-constantan thin film thermocouples typifies the average work performed in this field. A dependence for ΔS vs. copper thickness is observed for films less than 1400 Å thick, but scatter in the data and a paucity of data points makes true definition of the thickness dependence difficult.

G. Purpose of the Present Work

It was the opinion of this author that the quality of the data available on thin film thermoelectric power was questionable in that only a few investigators had performed an exhaustive study on a single system. Since preliminary work had been performed in this laboratory on Au-Ni thin film thermocouples, it was decided that a more detailed study would be performed on this system in order that questions regarding reproducibility, stability and thickness dependence of the thermal EMF might be answered.

It was found that even the thinnest of the films examined approached bulk material in thermoelectric power. This characteristic suggested that these devices might be useful as thermometers with ultra-fast response times. With this in mind some measurements were made to determine the response time of our thin film thermocouples. Experimental details are given in Appendix B.

II. EXPERIMENTAL METHODS

A. Selection of a Suitable Bimetallic System

The selection of component metals for the thin film thermocouples was based on several criteria. The component metals should be readily available in pure form, be fairly easy to evaporate from a resistance heated source and should be resistant to oxidation at room temperature. Once these conditions have been met, the two metals should be chosen so that the Seebeck coefficient of their junction is as large as possible. Gold and nickel were two metals which maximized the above requirements and were thus selected.

The starting material was obtained in wire form and was rated by the manufacturer as being 99.999% pure. Both metals were washed in dilute nitric acid and rinsed in ethanol to remove surface impurities. The nominal impurity level of the metals thus treated was believed to be on the order of 10 ppm.

Gold is readily deposited from a tungsten source. Nickel is more difficult to deposit from tungsten due to the large solubility of tungsten in nickel;⁽²²⁾ however, residual gas analysis performed with an Ultek Quad 150 RGA during a nickel evaporation indicated that no tungsten was present in the vapor stream. The mass range scanned was from 1 to 250 AMU. Ni evaporations were performed from sources made of "Vaporite-X" (Thermionic Products Co., Plainfield, N.J.). While the composition of this proprietary alloy is not known, residual gas analysis of a Ni evaporation from this source showed no detectable impurities in the vapor stream other than those originally in the system. This source was found to embrittle much more slowly than tungsten during the course of an evaporation.

The selection of substrate material was based on preliminary experiments. In the initial study of substrate temperatures using Au-Ni thin film thermocouples, ⁽²⁰⁾ mica was used as the substrate material. Mica was found to be unsatisfactory for the current study since during the heat treatment of the films (to be described in the next section), trapped gases produced bubbles in the mica and thus caused severe distortions in the thin films. Other substrates considered were: lapped Al_2O_3 ceramic plates, polished quartz, and Corning 7059 substrate glass. The last of these was selected because it displays high bulk electrical resistivity (greater than 10^{20} ohm-cm at 25°C), has an excellent surface finish, is of moderate cost and can withstand prolonged treatment at elevated temperatures (300°C).

B. Preparation of Specimens

The thin film thermocouples used in this study were fabricated with the vacuum system shown in Figures 4 and 5. This system has an ultimate pressure of about 5×10^{-8} Torr which is achieved by using a water cooled 6 inch oil diffusion pump backed by a 12 CFM rotary pump. The system has an 18 inch bell jar fitted with a Viton-A seal, and the baseplate is provided with numerous electrical feedthroughs.

A variac powered high current transformer provided power for the wire baskets used as evaporation sources. A substrate furnace was incorporated in this system to allow the substrate to be outgassed prior to the deposition of the thin films, and to allow these films to be subsequently annealed without breaking the vacuum. This furnace, shown in detail in Figure 6, consists of a G. E. Quartzline lamp (type Q500T3/CL) placed at the focus of a stainless steel parabolic cylinder. This reflector was then

mounted on an OFHC copper block which served as the heat source for the substrate. The substrate was affixed to this copper plate by two tantalum clips. The temperature could be closely controlled by adjusting the input power to the lamp with a variac. After the initial outgassing was completed, this furnace could be taken to 300°C in the 10^{-7} Torr range without any appreciable increase in system pressure.

A thermocouple gauge was used to measure system pressure during the roughing out period of the pump down. Once the diffusion pump was opened to the system, a NRC ionization gauge was used. Both gauge tubes are situated midway between the optical baffle of the diffusion pump and the baseplate of the system.

A resistance thickness monitor (RTM) was constructed so that film thicknesses could be monitored during the course of the evaporation. A schematic of the RTM is shown in Figures 7 and 8. The operation of this device is as follows. A portion of the vapor stream passes through a slit and condenses on a glass substrate which has two gold strips spaced $3/4$ " apart. The slit is positioned so that the condensing vapor bridges these two strips. The resistance of the resulting thin film bridge is then measured. By determining the actual thickness of the bridge by interferometric techniques, and assuming ohmic behavior for the film, one can plot resistance vs. film thickness for many metals. The geometry of the substrate holder must, of course, remain constant.

Specimens were prepared in the following manner. Pieces of 7059 substrate glass ($1" \times 3" \times 0.030"$) were cleaned in deionized water and dusted with a Static-Master radioactive brush. A stainless steel mask was clipped

to the substrate with phosphor bronze slips and this assembly was mounted on the furnace plate. During all handling operations silk gloves were worn. A charge of nickel was placed in a Vaporite-X basket located about three inches from the specimen, and the system was evacuated.

When the pressure reached $\sim 10^{-6}$ Torr, the substrate was outgassed at 300°C for one hour and was furnace cooled to room temperature (requiring about six hours). By this time the system pressure was 3×10^{-7} Torr. The Ni evaporation was then performed at a rate of about $300 \text{ \AA}/\text{min}$ and the specimen was removed from the system after allowing sufficient time for the substrate to cool down. The system was always backfilled with dry nitrogen prior to removing the specimen.

After the desired number of specimens had been brought to this stage, the vacuum system was cleaned and a tungsten basket was installed for the Au evaporations. The specimen was mounted on the furnace plate as before, excepting that the stainless steel mask was inverted so that the second arm of the thermocouple would be formed (Figure 9 shows the specimen at various stages of manufacture). The system was pumped to the high 10^{-7} Torr range and the specimen was outgassed at 300°C for one hour before furnace cooling to room temperature.

The heating served two purposes. It both outgassed the Ni film and the substrate prior to the deposition of Au, and annealed the Ni film. The importance of both the outgassing and annealing procedures was demonstrated experimentally, and the basis for these procedures will be discussed in the section on results and conclusions.

The Au film was deposited at a rate of $300 \text{ \AA}/\text{min}$ after the substrate had cooled to room temperature. The completed specimen was then annealed at 300°C for one hour under a pressure of $1 \text{ to } 3 \times 10^{-7}$ Torr and was furnace cooled to room temperature. The specimen was then removed from the vacuum chamber.

C. Data Acquisition

Two types of data were determined for each specimen: the film thickness and the Seebeck coefficient for the thin film thermocouples. While means could have been devised to determine the Seebeck coefficient directly, it was decided to determine the thermocouple calibration curve (thermocouple EMF vs. temperature difference between the two ends) and from this determine ΔS , the Seebeck coefficient for the couple.

A system was designed whereby the region of Au-Ni overlap of the thin film thermocouple was heated slowly from room temperature to about 150°C , while the other end of the specimen was held at ambient temperature. By measuring the temperature difference between the ends of the thermocouple and using this to drive the X axis of an X-Y plotter, while the thin film thermocouple output was connected to the Y axis of the plotter, a calibration curve for the thermocouple was obtained. A block diagram of the data acquisition system is shown in Figure 10.

The specimen chamber (Figure 11) consisted of two massive copper blocks mounted on a teflon base. The specimen was inserted into slits in these blocks and electrical connections were made with copper wires fed through Al_2O_3 insulators. The leads were tacked onto the specimen with silver paint. Chromel-alumel thermocouples were placed directly on the

heated junction and in close proximity to the junction held at room temperature. A nichrome heater was wound around the base of one block and was connected to a programmable power supply which fed a predetermined current to the heater for about 30 minutes, and then turned off the current to allow the block to cool down. During the heating cycle, the temperature of the neighboring copper block was observed to vary only 1-2°C. Since the X axis of the recorder plotted the temperature difference between the hot and cold end of the specimen, and the calibration curve was almost linear for all specimens tested, this temperature change did not introduce any noticeable error into the data.

Chromel-alumel thermocouples were chosen to measure the temperature of the specimen since their calibration curve is linear over the region of interest and their output is almost 1 mV/25°C which corresponds to a convenient scale on the X-Y plotter. The plotter calibration was adjusted so that a temperature difference of 100°C corresponded to an X displacement of eight inches. The reference ends of these thermocouples were thermostated in an ice water bath and copper leads were run from this bath to a Leeds and Northrup thermocouple switch so that either actual temperature (referenced to 0°C) or relative temperature (between the hot and cold ends of the specimen) could be displayed along the X axis of the plotter.

A Honeywell model 520 X-Y plotter was selected for this work because of its high sensitivity (up to 0.1 mV/in) and potentiometric inputs to both axes. Since no current is drawn from the specimen at balance, the calibration curve obtained is as accurate as that obtained by more conventional potentiometric techniques. In fact, since data were obtained automatically,

the possibility of reading errors was eliminated. A further advantage of this system was that all measurements were guarded, i. e., the recorder was constructed in such a manner that any stray voltages picked up between the specimen and the recorder were canceled and only those developed by the specimen and the associated chromel-alumel thermocouples were plotted. A typical calibration plot for a thin film thermocouple is shown in Figure 16.

The heater power supply circuit is shown in Figure 12. The operation of this unit is as follows. The output of a full wave rectified and filtered 10 volt power supply is connected to a series pass element (two 2N669 transistors wired in a Darlington configuration). Bias for this element is provided by the ten turn potentiometer connected as shown. The heater was connected between the emitter of the pass element and the positive side of the 10 volt supply. In this manner close control of heater current could be obtained. Heater current could be varied from 0 to 5 amperes.

Remote automatic control was provided by the time delay system shown in Figure 13. A unijunction transistor timer with a period of 30 minutes drives a silicon controlled rectifier connected in series with a relay. When the "reset" switch is depressed, the relay opens and the unijunction transistor timer is started. The opening of the relay causes the heater power supply to be biased by an amount set on the ten turn potentiometer provided with the remote programmer. In this manner current is caused to flow through the heater. The pen of the X-Y plotter is also controlled by the "reset" button. After 30 minutes have elapsed, the unijunction transistor sends a pulse to the gate of the silicon controlled rectifier, thus causing the relay to close. The closing of the relay turns the heater power off and lifts the pen from the paper. Once the timing period is completed, the unit remains off until it is manually reset.

The construction of this system allowed several runs to be made daily - a task which would have been most difficult if data were taken point by point.

The specimen chamber was located in the vacuum system which was flushed and backfilled to atmospheric pressure with dry nitrogen. By taking data in a atmosphere of dry nitrogen, good thermal contact of the heater with the copper block was insured, and the thin films were protected from oxidation.

D. Measurement of Film Thickness

The RTM previously described gives only a rough indication of the film thickness, and it is necessary to make a direct observation of the thin film in order to evaluate this parameter accurately. The method chosen utilized a Zeiss interferometer. This instrument resembles a metallographic microscope, but differs from it in two important ways. The incident beam of light is monochromatic. Before the light enters the objective to illuminate the specimen, it is passed through a beam splitting mirror. One half of the beam is focused on the specimen, while the other half of the beam is passed through identical optics and is focused on a perfectly flat mirror. The reflected beam from the specimen "interferes" with the reflected beam from the mirror in such a way as to produce a series of alternating light and dark fringes. These fringes appear superimposed on the image of the specimen.

In order for these fringes to appear, the specimen must be tilted slightly with respect to the reference mirror. In this way the path length of the two beams of light varies slightly as one moves across the field of view.

When these beams interact, their electric fields add vectorially to create the beam seen by the observer. If the field vectors of the two beams are in phase, constructive interference occurs and the line is bright. If the field vectors of the two beams are out of phase by 180° , the interference is destructive and no visible light is produced. The increase of specimen height with displacement across the field of view is directly related to the fringe spacing. For the geometry of the instrument used, the distance between two like fringes corresponds to a height change of $\lambda/2$, the half wavelength of the monochromatic light.

Any local height changes in the specimen, such as at the edge of an evaporated film, will cause a shift in the fringes. One can determine the height of this step by measuring the fringe displacement and dividing this by the measured distance between like fringes. The resulting number, when multiplied by $\lambda/2$ yields the step height. This procedure is demonstrated in Figure 14. The Zeiss interferometer was provided with a thallium lamp for which $\lambda/2$ is $2700 \text{ \AA}$.

Photographs of the interference patterns were made for Au and Ni edges at the junction area. From these one could determine the absolute thickness of a film to better than $100 \text{ \AA}$ accuracy.

E. Data Analysis

The plots of EMF vs. temperature difference were analyzed by selecting a series of data points at fixed intervals and passing a smooth second order curve through these points. Noting that the raw data passes through the origin and by using least squares techniques, the coefficients a and b were determined so that

$$E(\Delta T) = a \Delta T + b \Delta T^2 \quad (35)$$

where $E(\Delta T)$ is the thermocouple EMF and ΔT is the difference between the temperature of the hot junction and the fixed temperature of the cold junction. Thus if the cold junction were at $\bar{T}^0\text{C}$, then expansion of the above yields E at temperature T given by

$$E(T) = b\bar{T}^2 + (a - 2b\bar{T})T + bT^2 \quad (36)$$

The thermoelectric power is found by taking the derivative of this expression

$$\Delta S(T) = a + 2b(T - \bar{T}) \quad (37)$$

It is the latter expression which is most important for comparisons with theory, while $E(T)$ is most valuable when these thermocouples are used as practical temperature measuring devices.

The least squares method is discussed in Appendix A. An alternative method of determining ΔS by using finite difference techniques was abandoned since this method amplifies the "noise" in the data, while the least squares method compensates for small random fluctuations. It is impossible to place an error bound on ΔS when it is determined in this fashion, since the least squares curve should give a perfect fit if the data contains on random (Gaussian) errors. Any discrepancies in ΔS must then reflect properties of the specimen, and with the exception of roundoff errors, should not be cause by the data analysis.

It was convenient to chose data intervals of 3.125°C which correspond to major markings on the recording graph paper. By choosing this interval, at least 44 data points were available for analysis from each specimen.

The film thicknesses were determined in the manner previously described and ΔS was evaluated at 25°C . Since for this study the gold films were all in the thickness region where bulk behavior is observed, a plot a ΔS vs. Ni thickness was made. The interpretation of this curve is made in the next section.

III. RESULTS AND CONCLUSIONS

The initial investigations of the thermoelectric power of Au-Ni thin film thermocouples was performed on specimens prepared on mica substrates. No annealing treatment of the films was used during the fabrication process, and it was subsequently observed that a series of calibration runs, prepared over a period of a few days, showed the thermal EMF, vs. temperature curve increasing slightly in slope for each run. This instability eventually leveled out, and an important result was obtained. It is suggested that recrystallization may have been taking place during the period of the calibration run which was causing EMF to vary, thus producing spurious results. Cold rolled Ni wire identical to that used as the evaporant in this study, was found to be completely softened by treatment at 300°C for 1 hour at $\sim 10^{-5}$ Torr. Hoffman et al.⁽²³⁾ studied the thermal treatment of Ni films on mica substrates and found that maximum stress relief occurred for a treatment in vacuum of 250°C for 15 minutes.

The next step was to anneal the films prior to calibration. This was performed in a vacuum furnace external to the bell jar. The treatment consisted of heating the specimen to 300°C for 1 hour at $\sim 10^{-5}$ Torr, followed by furnace cooling to room temperature. This treatment required exposure of the specimen to air at each stage of the preparation. While this treatment yielded specimens with stable calibration curves, it was observed that thermocouples of identical film thickness had significantly different thermoelectric powers. Since trapped gases in the mica are a possible source of impurities in the thin films, Corning 7059 glass was chosen as the new substrate material.

A series of specimens was prepared on this material by use of the above technique. The gold films were about $2700 \text{ \AA}$ thick and were well in the region of bulk behavior so that variations of Au thickness between specimens would not effect the Seebeck coefficient. The nickel films ranged from 140 to $1400 \text{ \AA}$ thick. Nineteen specimens were prepared in this series. The Seebeck coefficients for these specimens is shown plotted vs. the logarithm of the Ni thickness in Figure 15. The results from a Au-Ni 30 gauge wire thermocouple are shown as the horizontal line marked "wire". As can be seen from this plot, there is considerable scatter in the data. Furthermore there is no appearance of the expected downward trend of ΔS with decreasing Ni thickness as predicted by Mayer.⁽¹⁰⁾ These somewhat puzzling results prompted a close examination of the thermocouples themselves. Microscopic examination showed that in some cases trapped gases had severely strained the films during the annealing procedure. It was this observation that resulted in the specimen preparation ^{and process of} procedure described in section II. These preliminary experiments nevertheless served a very useful purpose, since several possible sources of scatter were identified, if not subsequently eliminated.

A series of 30 specimens was then made by the technique described in section II. A typical calibration curve for one of these specimens is shown in Figure 16. The general appearance of this curve is typical of all specimens prepared on 7059 glass. There is a small negative curvature at the beginning of the run caused by non-uniform heating of the junction area. Once the temperature distribution has equilibrated, the curve extends smoothly to a temperature difference of about 125°C , where the curve undergoes a slight increase in slope and continues upward. This change in slope

is only observed on glass substrates and was shown to be a property of the thermocouple and not of the measuring apparatus by performing a run on the same specimen heated in an oil bath. The cause of this break is not known, however since the desired data for this study was the value of the Seebeck coefficient at 25°C , the least squares analysis was performed on the temperature region below the break.

A plot of ΔS vs. Ni thickness is shown for this series in Figure 17. for which the gold films averaged $1400 \text{ \AA}$ thick, placing them still in the region of bulk behavior.⁽²⁴⁾ Nickel thicknesses ranged from 230 to $2700 \text{ \AA}$. Again, data for a wire thermocouple are shown as a horizontal line. The scatter in this data is seen to be far less than that of the previous specimens (Figure 15), thus indicating the importance of outgassing the substrate prior to deposition of the films.

It is evident from Figure 17 that the thickness dependence of the Seebeck coefficient is very slight. There appears to be some breaking from the bulk behavior for films less than $500 \text{ \AA}$ thick, but from this graph little quantitative information may be gained. In order to compare these results with the theoretical prediction of Mayer, a plot of $\Delta S \cdot d_{\text{Ni}}$ vs. d_{Ni} was prepared and is shown in Figure 18. The apparent reduction of scatter in the data results from the fact that all of the data points for ΔS are fairly closely clustered around the bulk value, and that the observed thickness dependence is slight. A least squares straight line was passed through this data and is the solid line shown. The negative intercept is a result of plotting $\Delta S_{\text{Au-Ni}} \cdot d_{\text{Ni}}$ instead of the proper parameter, $\Delta S_{\text{Ni-Au}} \cdot d_{\text{Ni}}$. Since these terms are just the negative of each other, the sign of the intercept is simply reversed for comparison with theory.

Prediction of $(\partial \ln \lambda) / \partial \ln E)_{\epsilon = \xi}$ by this intercept is difficult since λ_0 and ξ must be known. The value of this intercept does, however, correspond in range to that obtained by Nossek⁽¹⁰⁾ for alkali metals. The cluster of data about the straight line provides further correspondence with Mayer's theory.

In conclusion, it was found that there are several sources of potential error in performing thermoelectric power studies on thin films. It is believed that the majority of these sources have been identified and eliminated. The lack of exact reproducibility between specimens indicates that there are further causes of scatter which have not yet been identified.

For example, it is common knowledge that very thin region II films deposited on glass are not necessarily smooth, but can have open channels running through them. If this channel structure is present, the conditions for which Mayer's theory is developed are violated. Such random channeling would be expected to cause scatter in ΔS data for small film thicknesses. Such scatter is observed in Chopra's data⁽¹⁹⁾ and in the present (Figure 17). This type of scatter probably results from non-uniformities in the degree of channeling between films with identical average thicknesses. Provided that a large amount of data is available, it is supposed that statistical treatments (such as least squares analysis) are capable of compensating for such fluctuations.

The principle issue involved in studies of thin film thermoelectric power is that of accuracy. One must start with accurate calibration curves and must accumulate data from many specimens in order to accurately measure what appears (in the present case) to be a small effect.

The increased thickness dependence observed by Chopra results from his choice of a different system (copper-constantan) which will, of course, behave differently than Au-Ni. It is the opinion of this author however, that while Chopra does observe a significant size effect, the accuracy of his results is thrown into some question by the scatter in his thermocouple calibration curves and the small number of points with which he tries to define the effect.

The work on alkali metals by Nossek⁽¹⁰⁾ shows a pronounced thickness dependence for ΔS when the film thickness is reduced below 500 Å. His work was based on a large amount of data, and thus the conclusions he draws are well founded. It is to be noted that data from Chopra, Nossek and from this project all seem to fit Mayer's theory well, even though it is felt that in the first case the accuracy of the data is questionable. This leads to the disturbing thought that perhaps the present work is merely confirming a theory which is insensitive to scatter in the data. If this is the case, then the caution taken in the preparation of our specimens becomes all the more important.

There appears to be very little thickness dependence for the thermal EMF of Au-Ni thin film thermocouples in the Ni thickness region studied. While the exact cause of this phenomenon is not known, some insight to this effect may be obtained from an examination of Equation 32. If this equation is rewritten in the form

$$\Delta S = \alpha + \frac{\beta}{d} \quad (38)$$

then it becomes evident that the thickness for which ΔS starts to vary significantly will depend on the relative magnitude of α and β . Since α contains

a constant parameter which is a property of the reference (Au) film, one may interpret the lack of strong thickness dependence to be a consequence of the choice of reference metal. This is not the only parameter of concern however, and examination of the coefficients α and β ((33) and (34)) show that the magnitude and behavior of the mean free path of electrons near the Fermi surface in Ni is also important.

It may be safely concluded that correlation with Mayer's theory is insufficient guarantee of careful work and that in light of the observations we have made an Au-Ni, other bimetallic systems should be carefully studied in order to further define the nature of the thickness dependence of the Seebeck coefficient. It may also be concluded that for any region II Ni film deposited of a bulk (region III) Au film, the thermoelectric power of the resulting junction will approach the bulk value.

IV. APPENDICES

A. Derivation of Normal Equations for a Least Squares Second Order Curve

The X-Y plots of the thermocouple EMF vs. temperature were such that the data passed through the point (0, 0). Because of the theoretical prediction that this plot should be second order, it was decided that a least squares fit of the data by a second order curve would provide the most accuracy. The EMF was then expressed as a function of the temperature difference between the hot and cold ends of the specimens, and was given as

$$E(\Delta T) = a\Delta T + b\Delta T^2 \quad (39)$$

In order to obtain the best fit for a second order curve, the method of least squares is superior as long as the distribution of the data around the curve is Gaussian.⁽²⁵⁾ This last criterion can only be tested after the analysis is performed, but a typical histogram for one of the runs in this study shows this criterion to be satisfied (Figure 19).

The normal equations are obtained in the following manner. It is desired to fit a set of data to the curve

$$f(x) = ax + bx^2 \quad (40)$$

Data points were chosen at equal intervals, h , so that

$$x_i = ih \quad (41)$$

Since in this project h was equal to 3.125°C , i ranged to 40, thus making $x_{\max} (\Delta T_{\max})$ equal to 125°C . For each x_i there is a data point f_i . The error for each point is thus

$$e_i = f_i - ahi - bh^2i^2 \quad (42)$$

Since it is desired to minimize the sum of the squares of the individual errors, H is defined such that

$$H = \sum_{i=1}^N e_i^2 = \sum_{i=1}^N (f_i - \alpha i - \beta i^2)^2 \quad (43)$$

where $\alpha = ah$ and $\beta = bh^2$.

By taking the partial derivative of H with respect to α and β , one obtains

$$\frac{\partial H}{\partial \alpha} = -2 \sum_{i=1}^N i(f_i - \alpha i - \beta i^2) \quad (44)$$

$$\frac{\partial H}{\partial \beta} = -2 \sum_{i=1}^N i^2(f_i - \alpha i - \beta i^2) \quad (45)$$

The normal equations are obtained when each of the above derivatives is set to zero:

$$\sum_{i=1}^N i f_i = \alpha \sum_{i=1}^N i^2 + \beta \sum_{i=1}^N i^3 \quad (46)$$

$$\sum_{i=1}^N i^2 f_i = \alpha \sum_{i=1}^N i^3 + \beta \sum_{i=1}^N i^4 \quad (47)$$

By defining A, B, C, D, and E as

$$A = \sum_{i=1}^N i f_i$$

$$B = \sum_{i=1}^N i^2 f_i$$

$$C = \sum_{i=1}^N i^2$$

$$D = \sum_{i=1}^N i^3$$

$$E = \sum_{i=1}^N i^4$$

then it follows that

$$a = \frac{EA - BD}{h(CE - D^2)} \quad (48)$$

and

$$b = \frac{CB - DA}{h^2(CE - D^2)} \quad (49)$$

To assist in the numerous computations involved, tables of C, D and E for N ranging from 1 to 100 were compiled with the aid of a Monroe EPIC 3000 calculator.

The standard deviation of the calculated from the observed value is given by

$$\sigma = \left(\frac{\sum_{i=1}^N (f_i - f(x_i))^2}{N} \right)^{1/2} \quad (50)$$

B. Determination of Response Time for Thin Film Thermocouples

Whenever a body is placed in contact with a heat reservoir, a certain amount of time is required for this body to achieve thermal equilibrium. Furthermore, if the heat source is not infinite, then the temperature of the source will be modified when both bodies attain equilibrium. When the temperature of an object is to be measured, it is desired that the thermometer interfere as little as possible with the system under observation. A fast response time is another desirable characteristic of a thermometer.

An examination of the thermometric properties of thin film thermocouples was initiated in order to determine the potential applicability of these devices as high speed temperature sensors.

If one assumes Newton's law of cooling describes the behavior of the average temperature of a body subjected to a step function heat input, then the response time of the body is defined as the time it takes for the average temperature to attain $1/e$ of its final value. It will be shown that this concept of response time is applicable to thin film thermocouples and that these devices have theoretical response times on the order of 10^{-10} sec.

The object of this work was to determine the theoretical response time of a thin film thermocouple and to then experimentally determine the various factors which influence the applicability of this device as a practical temperature sensor.

The response time of a thin metal film to a heat pulse was studied by Gutfeld and Nethercot⁽²⁶⁾ on indium films deposited on insulating substrates. Their analysis utilizes the black body phonon radiation model which is applicable at low temperature where phonon mean free paths are long.

At higher temperatures (room temperature for example), short phonon mean free paths suggest that diffusive heat flow will provide the basis for a correct analysis of the temperature distribution in the film.

The Fourier heat equation was solved for the two dimensional configuration shown in Figure 20. In this two dimensional configuration the film thickness is represented by d . It is assumed that the temperature distribution in the third direction is uniform so that a two dimensional analysis will suffice. The heat source is represented by the image line extending from the origin to the point $-d$. This line has a temperature distribution such that the initial conditions for the problem are:

$$T(x, y, t) = \delta(x) \quad ; y=0, t=0, -a \leq x \leq a \quad (51a)$$

$$T(x, y, t) = 2(1 - H(y)) \quad ; x=0, t=0, -d \leq y \leq d \quad (51b)$$

Where $T(x, y, t)$ is the temperature of the body, $\delta(x)$ is the Dirac delta function and $H(y)$ is the unit Heaviside step function. Boundary conditions are based on the assumption that the film under consideration is adiabatically enclosed, and that since the vector heat flux, $\vec{Q}$, in a body isotropic with respect to thermal conductivity, k , is given by

$$\vec{Q} = -k \nabla T \quad (52)$$

then we have $\nabla T = 0$ at all boundaries. The heat flow equation

$$\nabla^2 T = \frac{c \rho}{k} \frac{\partial T}{\partial t} \quad (53)$$

where ρ is the density, and c is the specific heat, was then solved for the

above configuration by the use of Fourier techniques. The result of these calculations is given as

$$T(x, y, t) = \left[B_0 + \sum_{n=1}^{\infty} B_n \cos \frac{n\pi x}{a} \exp \left(-\frac{n^2 \pi^2 k t}{c \rho d^2} \right) \right] \left[1 + \sum_{m=0}^{\infty} C_m \sin \frac{(2m+1)\pi y}{d} \exp \left(-\frac{(2m+1)^2 \pi^2 k t}{c \rho d^2} \right) \right] \quad (54)$$

where the B_1 and C_1 are the Fourier coefficients for the appropriate series representation of the initial conditions. Since they are not needed in this analysis their derivation will not be included.

Since the thermoelectric output of a thermocouple depends on the average temperature of the junction, ⁽²⁷⁾ the average of Equation 54 over x and y is the desired parameter. The average value of $T(x, y, t)$ is given by

$$\langle T \rangle = \frac{\int_{-a}^a \int_{-d}^d T(x, y, t) dy dx}{\int_{-a}^a \int_{-d}^d dy dx} \quad (55)$$

When the indicated calculations are performed, one obtains

$$\langle T \rangle = B_0 \left[1 + \sum_{n=0}^{\infty} \frac{2 C_n}{(2n+1)\pi} \exp \left(-\frac{(2n+1)^2 \pi^2 t k}{c \rho d^2} \right) \right] \quad (56)$$

In this equation C_n is negative and thus this expression may be rewritten in the simpler form

$$\langle T \rangle = B_o \left[1 - \sum_{n=0}^{\infty} G_n \exp\left(-\frac{t}{\tau_n}\right) \right] \quad (57)$$

where G_n and τ_n are readily identified by comparison with Equation 56. This equation (57) is almost identical to Newton's law of cooling, and thus the response time, τ , may be determined. For large t only the first term in the series retains significance, thus we define the response time by

$$\tau = \frac{c \rho d^2}{k \pi^2} \quad (58)$$

As an example, it can be shown by substitution of handbook values for c , ρ , and k for Bi that

$$\tau = 1.49 d^2 \quad (59)$$

where d is measured in cm. For a 1000 Å film the response time is on the order of 10^{-10} sec. This is in agreement with the results of Gutfeld and Nethercot. (26)

Since the theoretical response time and heat capacity of a thin film thermocouple is very small, many practical applications for this device may be anticipated. It was decided to perform some experiments to determine the response time characteristics of this device in order to assess the effect of the substrate (which was excluded from the theoretical analysis). Arrangements were made to utilize a Q-switched CO_2 laser as a source of pulsed heat. By making the thin film thermocouple with a Ag-Bi junction, good heat transfer properties were expected since the absorptive properties of Bi are

superior to Au at 10.6 microns, the laser wavelength. The thermocouples were fabricated on mica using the general technique described in section II. The various stages of preparation are illustrated in Figure 21. The finished thermocouple was mounted in the specimen chamber shown in Figure 22. The fine collimation of the laser beam made it unnecessary to mask the junction area. The laser spot was directed on the junction and covered it entirely. To this extent the geometrical configuration paralleled that for which the theoretical study was made.

Preliminary observations of response time were made with thin film thermocouples $2000 \text{ \AA}$ thick through the junction. These thermocouples were heated by laser pulses whose rise time was determined to be 150 nsec by means of a cryogenically cooled Ge detector. Thermocouple response times were found to vary from 200 nS to about $5 \mu \text{ sec}$. While in general it was found that response time shortened for thinner substrates, anomalies were observed which prevented a clear description of the response time as a function of substrate thickness. It was established however, that the substrate plays a very important role in determining the response time, and further investigations should put this effect on a quantitative framework.

LIST OF REFERENCES

- 1) W. F. Magie, A Source Book in Physics, Harvard Univ. Press, pp. 461-464, 1963
- 2) D.K.C. MacDonald, Thermoelectricity: An Introduction to the Principles, J. Wiley and Sons, Inc., 1962
- 3) P. Egghi, Thermoelectricity, J. Wiley and Sons, Inc., 1958
- 4) J. W. Christian, J.P. Jan, W. B. Pearson and I. Templeton, Proc. Roy. Soc. (London), A245, pp. 213-221 1958
- 5) J. F. Nye, Physical Properties of Crystals, Oxford, p. 195 ff, 1957
- 6) J. Lee, F. Sears, D. Turcotte, Statistical Thermodynamics, Addison Wesley Publishing Co., Inc., 1963
- 7) S. de Groot, Thermodynamics of Irreversible Processes, North-Holland Publishing Co., 1951
- 8) A. Dekker, Solid State Physics, Prentice Hall, Inc., p. 216, 1957
- 9) N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys, Dover Publications, Inc., 1958
- 10) H. Mayer in Neugebauer, Newkirk and Vermilyea, eds., Structure and Properties of Thin Films, J. Wiley and Sons, Inc., p. 225 ff, 1959
- 11) E. Johnson and L. Harris, Phys. Rev., 44, 944-5 (1933)
- 12) L. Reimer, Z. Naturforsch., 12A, 525-6 (1957)
- 13) G. A. Efendiev et al., Izr. Akad. Nauk Azerb. SSR, 1963(4), 65-9 (1963)
- 14) R. Nossek, Z. Physik, 174, 296-300 (1963)
- 15) R. P. Huebener, Phys. Rev., 136 (6A), 1740-4 (1964)
- 16) W. Worobey et al., Phys. Lett., 16(1), 15-16 (1965)
- 17) L. Harris and E. Johnson, Rev. Sci. Instr., 5, 153-8 (1934)
- 18) R. Morrison and R. Lechemayer, Rev. Sci. Instr., 34, 106-7 (1963)
- 19) R. Marshall et al., J. Sci. Instr., 43, 144-9 (1966)
- 20) M. V. Belous and C. M. Wayman, J. Appl. Phys., 38, 5119-24 (1967)

- 21) K. L. Chopra et al., J. Appl. Phys., 39, 1525-8 (1968)
- 22) M. Hansen, Constitution of Binary Alloys, McGraw-Hill Book, Co., 1958
- 23) R. M. Hoffman et al., Proc. Phys. Soc. (London), B67, 497 (1954)
- 24) K. L. Chopra and L. C. Bobb, Acta Met., 12, 807 (1964)
- 25) A. Ralston, A First Course in Numerical Analysis, McGraw-Hill Book, Co., 1965
- 26) R. M. Gutfeld and A. Nethercot, Jr., J. Appl. Phys. 37, 3767-71 (1966)
- 27) G. Koerber, Properties of Solids, Prentice Hall, Inc., P.229 ff, 1962

Figure 1 Thermoelectric junction of two dissimilar metals

Figure 2 Thermoelectric junction with a third metal added

Figure 3 Free electron model for thermoelectric power

- A. basic energy distribution for electrons obeying the free electron theory of metals
- B. two pieces of the same metal at different temperature prior to attaining equal Fermi energies
- C. two pieces of the same metal at different temperature with equal Fermi energies

Figure 4 Schematic of the vacuum system

1. bell jar	5. nitrogen cold trap
2. air release valve	6. roughing valve
3. vacuum gauges	7. fore line valve
4. gate valve	8. oil diffusion pump
9. mechanical pump	

Figure 5 View of the evaporation setup

1. bell jar	4. base plate for furnace
2. tungsten basket	5. quartz lamp furnace
3. high current leads	6. substrate
	7. vacuum system baseplate

Figure 6 Detail of the annealing furnace

Figure 7 Schematic of the resistance thickness monitor

Figure 8 RTM blank before and after an evaporation

Figure 9 Thin film thermocouple in various stages of manufacture

from left to right: stainless steel mask, Ni film, completed thin film thermocouple

Figure 10 Block diagram of the data acquisition system

Figure 11 Detail of the specimen chamber

A. top view

1. Ni lead (-)

2. cold junction thermocouple

3. Au lead (+)

4. hot junction thermocouple

B. side view

$$d (\text{\AA}) = 2700 \frac{a}{b}$$

Figure 14 Method of analysis of an interferogram

top: actual interferogram

bottom: schematic showing method of analysis

Figure 15 Data for G100 series: ΔS vs. $\log d_{\text{Ni}}$

Figure 16 EMF vs. ΔT calibration curve for G230

Figure 17 Data for G200 series; ΔS vs. $\log d_{\text{Ni}}$

Figure 18 Data for G200 series: $\Delta S \cdot d_{Ni}$ vs. d_{Ni}

Figure 19 Histogram for G230

Figure 20 Heat equation model

Figure 21 Various stages of Ag-Bi thin film thermocouple preparation
from left to right: stainless steel mask, silver leads,
completed set of five thin film thermocouples

Figure 22 Specimen chamber for laser studies