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THERMAL DIFFUSIVITY BY THE MODIFIED ANGSTROM TECHNIQUE

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ABSTRACT

The modified Angstrom technique is applied in measurements of the thermal diffusivity of thermoelectric materials in bulk and thin film forms. Correction terms to McNeill's procedure¹ which are required for its application to thin films are calculated and their relative importance is discussed. Finally, preliminary experimental results on $\text{Bi}_{1-x}\text{Sb}_x$ thin films are presented.

Introduction

The thermal conductivity is an important factor in the figure of merit of thermoelectric materials. However, it is often more convenient to measure the thermal diffusivity instead. The advantages of convenience and accuracy of the measurement usually outweigh the disadvantage, i.e., the need to know the material's heat capacity. Moreover, it is possible to account for radiation corrections in well-designed diffusivity experiments. This is especially important in thin films for which the corrections are relatively large, even at room temperature.

One established technique is that due to Angstrom.² In this technique one end of a long sample is periodically heated and allowed to cool. The resulting periodic temperature excursions at points along the sample can be analyzed to yield values of the thermal diffusivity. In 1962, McNeill¹ introduced a variation of the Angstrom method by exploiting the considerable Peltier heat produced at the junction between a current-carrying lead and a thermoelectric material. Periodic reversal of the current changes the sign of the Peltier heat and establishes symmetrical temperature variations, which depend upon the thermal diffusivity.

McNeill's method is particularly attractive for the study of thin films because radiation and Joule heating effects can readily be taken into account. We have evaluated the method for this application and have obtained preliminary results for the thermal properties of Bi-Sb films. The general theory of the technique is reviewed in the next section of this paper, where several modifications or corrections for thin films are presented. The following sections describe our apparatus and experimental procedures, the results to date, and the potential of the method for future studies of thin film thermoelectric materials.

Theory

In one convenient geometry, the specimen under study is suspended in vacuum by metallic leads attached to each end. If an electrical current is directed through the sample, one junction will be heated and the other will be cooled by the Peltier effect. If the current is periodically reversed, then temperatures along the length of the sample will vary periodically as well.

The essential aspects of the analysis may be obtained from a model geometry. An infinitely long, rectangular sample is heated or cooled by a source at the origin. The temperature of the sample must obey the following equation:

$$\frac{\partial \theta}{\partial t} - D \frac{\partial^2 \theta}{\partial x^2} + H \theta = \frac{I \Pi}{c \rho w t} \delta(x) \quad (1)$$

Here $\theta(x,t) = T(x,t) - T_0$ where T_0 is the ambient temperature. D is the thermal diffusivity of the sample, c its heat capacity per unit mass, ρ the density, and w and t the width and thickness respectively. In addition, $I(t)$ is the current, Π the Peltier coefficient of the thermoelectric relative to that of the support leads, and $\delta(x)$ is the Dirac function. Finally, the coefficient which appears in the linearized radiation term has the following form:

$$H = \frac{2(w+t)}{wt} \frac{4\sigma\epsilon T_0^3}{c\rho} \quad (2)$$

where σ is the Stefan-Boltzmann constant and ϵ is the emissivity of the sample. Joule heating is neglected here, but is easily incorporated as will be discussed below.

For the special case of a square-wave current of amplitude I_0 and fundamental frequency ω , Eq. 1 has the following solution:

$$\theta(x,t) = \sum_{n \text{ odd}} A_n [\exp(-g_n x)] \sin(n\omega t - g_n' x + \gamma_n) \quad (3)$$

where

$$A_n = \frac{2\pi I_0}{\pi D c \rho t \omega n} (g_n'^2 + g_n^2)^{-1/2} \quad (4)$$

$$g_n = (2D)^{-1/2} (H + (H^2 + n^2 \omega^2)^{1/2})^{1/2} \quad (5)$$

$$g_n' = (2D)^{-1/2} (-H + (H^2 + n^2 \omega^2)^{1/2})^{1/2} \quad (6)$$

and

$$\gamma_n = -\text{arc tan}(g_n'/g_n). \quad (7)$$

For experimental rectangular samples of sufficient length, the solution of Eq. 3 will describe the temperature at distance x from the nearest end if multiplied by a factor of 2 since we assume a semi-infinite sample.

Depending on whether or not $\omega \gg H$, there are two approaches to obtaining the thermal diffusivity.

If the frequency of the current reversals is such that $\omega \gg H$. Then the higher harmonics in Eq. 3 will be small in comparison to the fundamental. In this limit, the amplitude of the temperature excursions assumes the following simple form:

$$\ln(\sqrt{\omega} |\theta|) \simeq C' - x \sqrt{\omega/2D} \quad (8)$$

where C' is a constant. Thus, a semi-log plot against $\omega^{1/2}$ of the temperature amplitudes weighted by $\omega^{1/2}$ will yield a straight line with slope = $x/(2D)^{1/2}$.

For a particular experiment several possible complications should be addressed. The assumption $\omega \gg H$ must be examined. One should also estimate the size of the third harmonic which is reduced at high frequencies and/or at large distances from the sample ends.

The second approach for analysis of the data is to assume that x_1 and x_2 are large enough that θ_1 and θ_2 have negligible higher harmonic content (or Eq. 3 is valid for $n=1$ only). Then the thermal diffusivity is given by³

$$D = \frac{\pi (x_2 - x_1)^2}{\tau \beta \ln \left(\frac{\theta_1}{\theta_2} \right)} \quad (9)$$

where τ is the period and β is the phase shift (see Fig. 1). It can be shown that Eq. 9 is independent of the relative values of ω and H . Since H is generally large for thin films, it is to be expected that this approach is more useful for thin films.

In both cases, the heat capacity of the thermometer, C_T , has also been neglected, as has the effect of thermal conductance through its electrical leads. A similar situation arises in heat-pulse calorimetry where corrections depend, to first order, on the ratio of C_T to the heat capacity of the entire sample.⁴ In general, the thermometer should be minute and well-isolated to justify neglecting these factors.

Joule heating adds the term

$$- \frac{I^2 \rho_0}{c\rho(wt)^2}$$

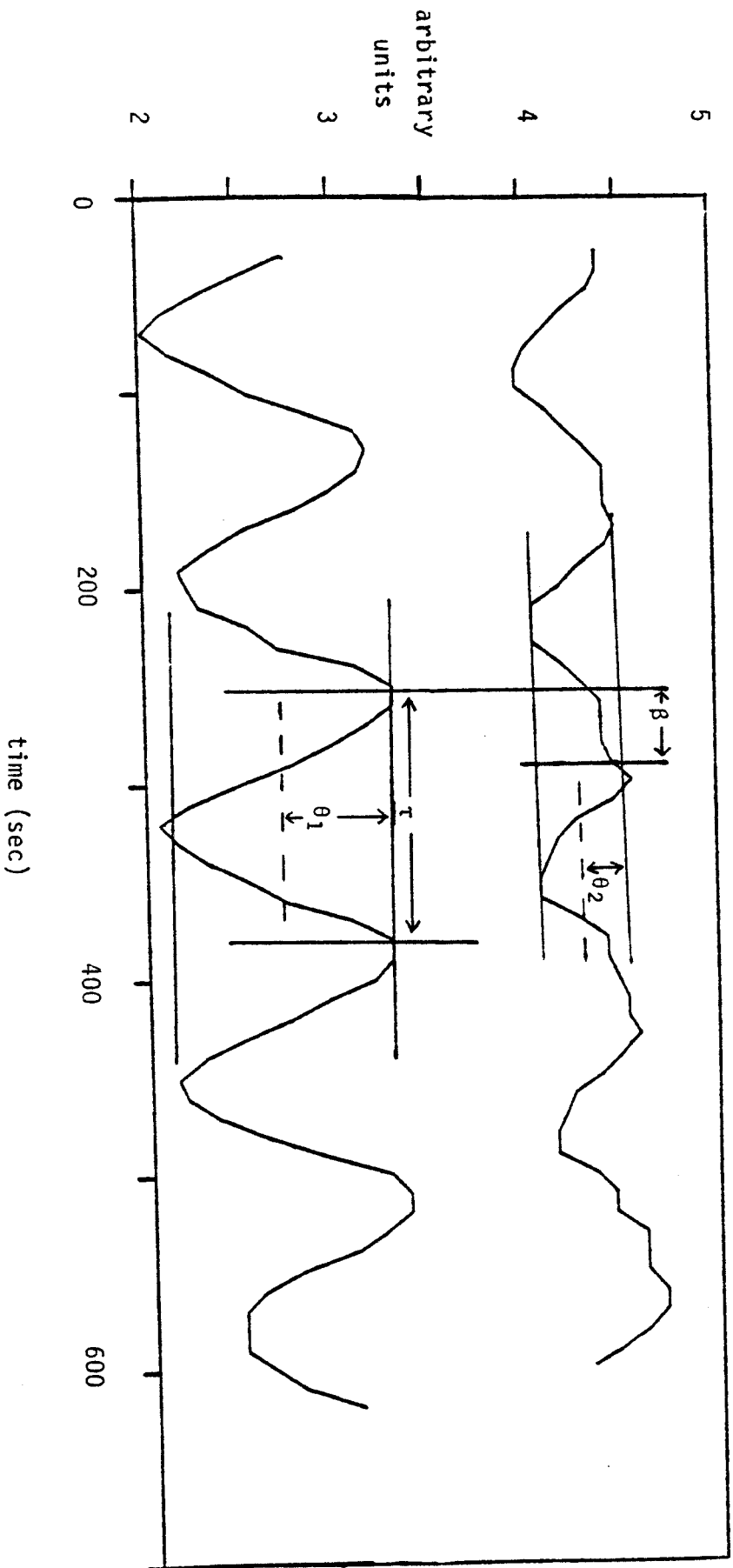


Fig. 1 Example of trace defining, ω , β , θ_1 , θ_2

to the left side of Eq. 1 where ρ_0 is the resistivity of the sample. For square-wave currents the term is constant. Its effect is simply to heat the sample by the following amount:

$$\Delta T = \frac{I^2 \rho_0}{wt 2(w+t) 4\sigma\epsilon T_0^3} \quad (10)$$

In practice, it is possible to limit this temperature rise to a few degrees.

Finally, for thin films, the presence of the substrate must be taken into account. This is done by defining the following effective quantities:

$$\bar{\epsilon} = \frac{(2t_s + w)\epsilon_s + (2t_{ss} + w)\epsilon_{ss}}{2t_s + 2w} \quad (11)$$

$$\bar{c\rho} = (c_s \rho_s t_s + c_{ss} \rho_{ss} t_{ss})/t_s \quad (12)$$

and

$$\bar{K} = (K_s t_s + K_{ss} t_{ss})/t_s \quad (13)$$

Here the subscripts s and ss refer to sample and substrate respectively, and K denotes thermal conductivity. The consequence of these substitutions is that the analysis will now yield an effective diffusivity:

$$\bar{D} = D_s \frac{1 + \frac{K_{ss} t_{ss}}{K_s t_s}}{1 + \frac{c_{ss} \rho_{ss} t_{ss}}{c_s \rho_s t_s}} \quad (14)$$

For appropriate choice of substrate material and thickness, the numerator of the correction factor will be of the order of unity. The denominator, however, is typically 3 or more, even in the best circumstances.⁴ Thus, for an accurate determination of the sample diffusivity a knowledge of the substrate's and sample's heat capacity and density and of the substrates' thermal diffusivity is needed. Both sides of equation 14 depend on the sample's diffusivity. Rearranging gives

$$K_s = \overline{D} (c_s \rho_s + c_{ss} \rho_{ss} t_{ss}/t_s) - K_{ss} t_{ss}/t_s \quad (15)$$

Experimental

A diagram of the experimental apparatus is shown in Fig. 1. The sample is placed in a copper box with its end pulse wires and thermocouples in place. Measurements are made under vacuum (4×10^{-3} Torr) to eliminate heat losses due to convection and conduction. The pulse generator provides square waves of bipolar current through the sample. Due to the Peltier effect this produces a series of one dimensional temperature waves travelling down the sample. These are picked up by the two thermocouples amplified and fed to a two-pen x-y recorder, which plots the voltage of each thermocouple (θ_1 and θ_2), as a function of time.

Since the required current reversals occur relatively slowly, the pulse generator is essentially a relay, an isolated power supply and the appropriate timing circuit.

The films are prepared by a single source evaporation and possess a nominal composition of $\text{Bi}_{88}\text{Sb}_{12}$. The substrates are polyimide Kapton* films, nominally 127 μm (5 mil.) thick. The Seebeck coefficient and conductivity of each of the films are measured utilizing standard techniques. Only samples possessing high $S^2\sigma$ are selected for further evaluation.

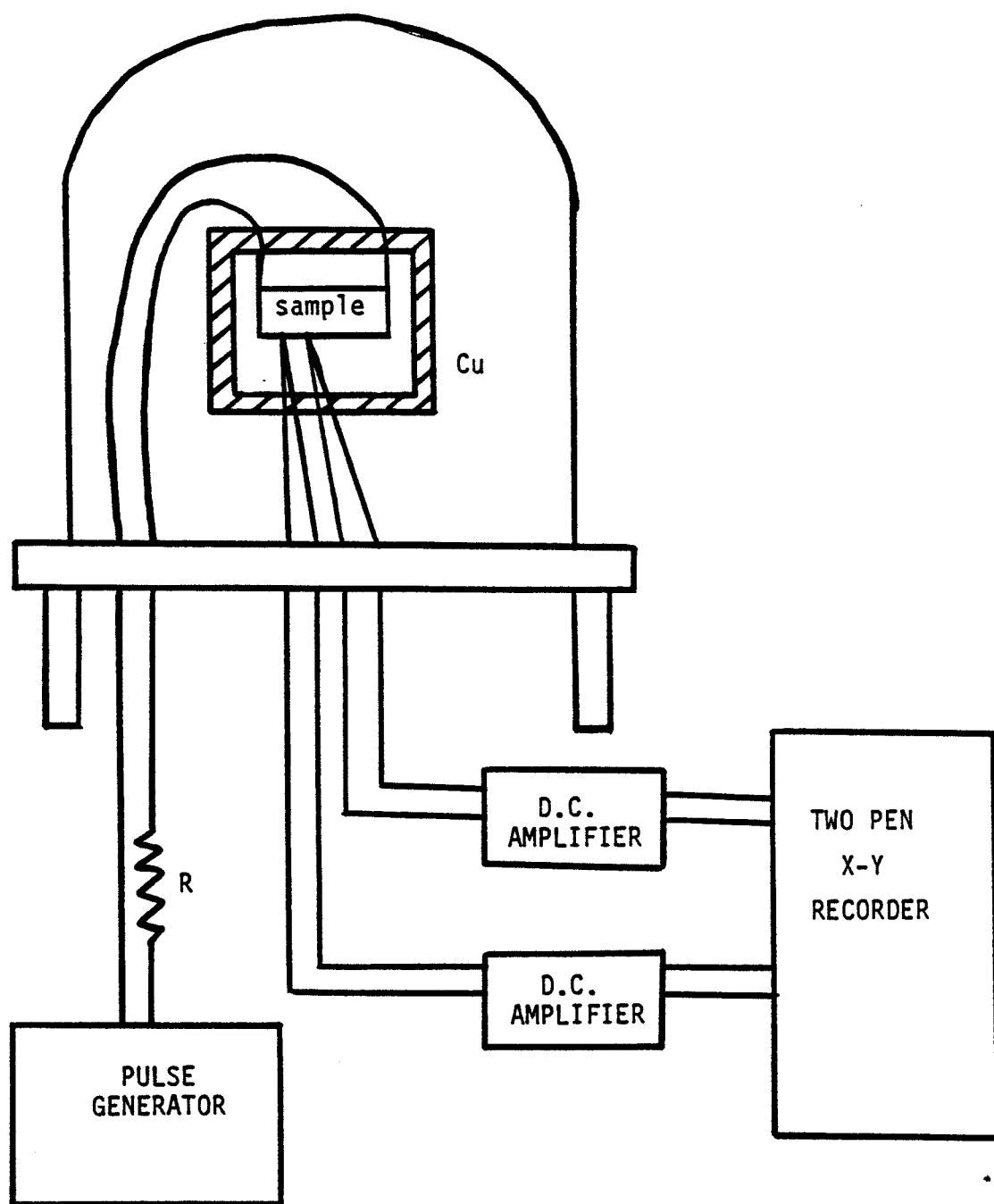


Figure 2

The current leads (see Fig. 2) are fixed to the ends of the film using silver paste. Thermocouples are prepared using 3 mil wire to minimize heat conduction down their length. The thermocouples are attached to the film using a ceramic cement.** The wires with the sample are soldered into the copper box in the modified Angstrom system.

A series of runs is carried out in which θ_1 and θ_2 are measured as a function of input current and switching frequency.

Results and Discussion

Typical data for a 10 μ m thick bismuth-antimony film is shown in Table 1. The trace for the experiment summarized in the third line of Table 1 is shown in Fig. 1. The film in this case is 5.73 cm long by 2.54 cm wide and the two thermocouples are placed at 0.94 and 1.75 cm, respectively, from one end of the sample. Relatively high currents had to be used to minimize the error in measuring the amplitude and phasing of the voltages from the thermocouples.

*Kapton is a trademark of Dupont Co. for polyimide plastic film. It is thermal conductivity and heat capacity are respectively, 1.55 mW/cm⁰ K and 1.09 J/gm⁰ K.

**Ceramabond is a trademark of Aremco Products Inc. for ceramic cement.

The value of ω/H for this film was less than 1. This is not sufficiently large that equation 8 can be employed. The values of \bar{D} tabulated in Table 1 were calculated utilizing the second approach, equation 9 instead.

The effect of errors in the measurement of the various parameters, x_1 , x_2 , θ_1 , θ_2 , and β , of the calculation of D can be evaluated by a propagation of error treatment of equation 9. The tabulated variances reflect this procedure. For higher frequencies and lower currents the apparent thermal diffusivity becomes large due to the lack of sensitivity of the equipment. Higher currents and lower frequencies reduce the error in the measurement of θ and β . Higher currents increase, however, the average temperature of the sample by Joule heating. (At $I=0.6$ amps the average temperature of the sample is 42°C). There is also a penalty when low frequencies are employed; higher harmonics begin to become important. The variances in the table do not reflect the effect of higher harmonics, which is estimated to be 10% for the lowest frequency data reported in the table. Employing the method of least squares the weighted average of \bar{D} is $(5.8 \pm 2.2) \times 10^{-3} \text{ cm}^2/\text{sec}$.

For thin film samples on a substrate, such as these, to calculate the thermal diffusivity of the film, it is important to consider the correction factor due to the substrate. This is done utilizing equation 15. For the film under consideration the second term in the expression is dominant; it is approximately twenty times the magnitude of the first. The third term is a constant $20\text{mW}/\text{cm}^0\text{K}$. In addition to the variance associated with \bar{D} , there are other measurement errors in the calculation of K_s . Since the substrate thermal properties are known relatively accurately from the manufacturer, the largest source of error is due to the measurement of the thickness of the bismuth-antimony thin film. Its variance however, is much smaller than the variance in \bar{D} so the relative variance of K_s is increased only slightly. For the film of Table 1, the estimate for the thermal conductivity is $K_s = 100 \pm 50\text{mW}/\text{cm}^0\text{K}$. This preliminary result does not include corrections for harmonics. For comparison, the K_s for bulk single

crystal bismuth-antimony of a similar composition ranges from 50 to 80mW/cm⁰K depending on the crystal orientation.⁶

The variance can be decreased. The most important improvement would be to employ a better arrangement for fixturing the samples wherein one could handle very thin substrates with reasonably thicker films. This would reduce the size of the substrate correction factor in equation 15 and, most importantly would increase the magnitude of the θ . Replacement of the wire thermocouples with thin film thermocouples is also needed. Further investigation of the sample geometry to determine ideal placement of thermocouples is needed to standardize the measurement and to minimize the effects of higher harmonics. Alternatively, a method to calculate the effects of the third harmonic can be developed from the theory.

CONCLUSION

We have discussed the theory of utilizing the modified Angstrom method for thin films. As a demonstration of the technique we report the thermal diffusivity of a 10 μ m thick bismuth-antimony film. The measured values are in reasonable agreement with those of bulk single crystals, but the variances are not sufficiently small to determine how, if any, the thermal conduction of the thin films differs from that of bulk crystals. It can be concluded that it is possible to measure the thermal conductivity of thin films along their length using the modified Angstrom method. Techniques can, and should be, developed to make the measurement more precise.

We would like to acknowledge the assistance of Steve Dudzinski and Gary Fournier in preparing the films.

TABLE 1

Data for computing the diffusivity of a
Bismath-antimony thin film

<u>I(amps)</u>	<u>$\omega(\text{sec}^{-1})$</u>	<u>$\theta_1(\text{mV})$</u>	<u>$\theta_2(\text{mV})$</u>	<u>β</u>	<u>$\bar{D} \times 10^3 (\text{cm}^2/\text{sec})$</u>
0.2	0.050	0.250	0.070	2.252	2.2 \pm 1.6
0.6	0.058	0.550	0.125	1.862	3.1 \pm 2.4
0.6	0.048	0.625	0.250	1.966	9.1 \pm 4.8

$$\bar{D}_{\text{ave}} = 5.8 \pm 2.2$$

$$K_s(\text{ave}) = 100 \pm 50 \text{ mW/cm}^0\text{K}$$

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0293r/E11a

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