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THE THERMAL CONDUCTIVITY OF SILVER-ION SUPERIONIC CONDUCTORS

By

Michael Carl Goetz

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

THE THERMAL CONDUCTIVITY OF SILVER-ION SUPERIONIC CONDUCTORS

By

Michael Carl Goetz

The thermal conductivity for several samples of AgI, $AgI_{0.96}Br_{0.04}$, and $PyAg_5I_6$ was determined between 120 K and 500 K using the transient-hot-wire method. In the experimental set-up the temperature excursion of a nickel wire resistively heated by a current pulse and surrounded by sample material is determined many times a second. The logarithmic time dependence of the temperature excursion is used to calculate the thermal conductivity.

All of the sample materials have phase transitions above which they are superionic conductors with the characteristic high ionic conductivity. Below these phase transitions in AgI and $AgI_{0.96}Br_{0.04}$ the temperature dependence of the thermal conductivity is interpreted in terms of multiphonon scattering processes, while above the transition temperatures the data is analyzed using a form of the thermal conductivity that assumes a minimum phonon mean free path. These data suggest that the mobile ions play no direct part in thermal conduction in these materials.

The $PyAg_5I_6$ data is difficult to interpret because of the scatter and because the quality of the samples is questionable. This thesis is dedicated to my wife, Arlene.

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CHAPTER I

INTRODUCTION

The thermal conductivity is a transport property which relates the amount of heat per unit area that flows per unit time to the temperature gradient which produces this heat flow. A formulation of the differential equation that describes thermal conduction was published by Fourier¹ in 1822.

Measurements² of the thermal conductivity of dielectric solids early in this century indicated a T^{-1} dependence above 77 K. To explain this behavior, Debye³ suggested that traveling waves could carry heat in an elastic medium and that these waves would be scattered by anharmonicities in the material. Peierls⁴ quantized these waves, and rigorously treated the anharmonicities of the crystalline structure. He found that only those scattering processes that do not conserve crystal momentum contribute directly to the T^{-1} dependence of the thermal conductivity at high temperatures.

Since the treatment of Peierls many other theories considering additional scattering mechanisms have been used to explain the results of these, and other, thermal conductivity

experiments. Reviews and books dealing with the thermal conductivity of solids have been written by the prominent workers in the field--Berman⁵, $Slack^{6}$, $Klemens^{7,8}$, and $Ziman^{9}$.

Many different methods have been used to measure thermal conductivity. One particular technique used originally to measure the thermal conductivity of fluids is the transient hot wire technique.

Stalhåne and Pyk¹⁰ pioneered the transient hot wire method by determining empirically the time dependence of the temperature increase of a thin wire located in a known liquid and heated by the passage of an electric current. Van der Held¹¹ related their result to a solution of the differential equation of Fourier under appropriate boundary conditions. Since then the transient hot wire method has been used by several groups of experimenters to measure the thermal conductivity of fluids with each group, in turn, refining the mathematical solution¹².

With the advent of high precision measuring techniques¹³, the transient hot wire method has been used to measure thermal conduction in solids. The method has been applied with success to $\mathrm{NH}_4\mathrm{C}\ell$ ¹⁴ and ice¹⁵ where the structural changes in the materials can be studied by measuring the thermal conductivity.

The effects of the high ionic disorder of superionic conductors upon thermal conduction have not been studied previously. The classification "superionic conductor" includes all solids (for example, AgI, PbF_2 , β -alumina)

with a melt-like ionic conductivity and a low activation energy for ionic diffusion. The high ionic conductivity of these materials suggests using them as electrolytes in solid state batteries and in solid electrolyte coulometers.

Due partly to the relatively low temperature of the first order phase transition to the superionic phase, silver iodide has been investigated intensely since the discovery of the high-ionic-conductivity silver-conducting phase by Tubandt and Lorenz in 1914¹⁶. From X-ray diffraction studies of the superionic phase of AgI Strock¹⁷ determined that the iodine ions have a simple b.c.c. structure and identified forty-two available sites for the two silver ions in each unit cell. He concluded that the mobile silver ions hopped from site to site within this structure. Recent neutron diffraction studies¹⁸ have modified this picture by establishing that some sites are unoccupied and by indicating clearly the conduction pathways in the open structure.

The technological need for room-temperature superionic conductors has motivated the substitution of impurity ions for some of the silver ions in silver iodide in order to open up the structure¹⁹. One such room-temperature superionic conductor is based on the partial substitution of the pyridinium ion $C_5H_5NH^+$ into silver iodide. In this compound-- $(C_5H_5NH)Ag_5I_6$ --a phase transition near 310 K makes available an additional number of sites for the silver ions without changing the structure of the other atoms²⁰.

Another high ionic conductivity material is created by the replacement of some of the iodine ions in silver iodide by bromine ions. The increase in the ionic conductivity (in some mixtures by a factor of a thousand) occurs not in the superionic phase but rather in the low-temperature mixtures²¹. This increase is attributed not to an increase in the number of available sites but to an increase in the number of ions activated to the interstitial sites in the material.

The entire subject area of superionic conductors has been extensively reviewed $^{22-26}$ with emphasis not only upon the measurements of the properties of the materials but also on the theory of transport of the ions through the open structure.

The major objectives of the work that follows are:

- a) the construction of a transient hot wire method apparatus;
- b) the measurement of the thermal conductivity of some high ionic conductivity materials; and
- c) the subsequent interpretation of the data with emphasis upon the ionic disorder.

CHAPTER II

SUPERIONIC CONDUCTIVITY AND THE SAMPLE MATERIALS

The sample materials are superionic conductors, so that the experimental results must be interpreted in terms of processes that allow a high ionic conductivity. The following section describes

- a) the ionic disorder of these materials,
- b) the principal measurements which investigate this ionic disorder, and
- c) specific detail concerning the materials.

Ionic Disorder

The superionic conducting phase of a solid has an ionic conductivity near that of the melt and a low activation energy for the mobile ions. The conducting ions move freely along extended pathways between the stationary ions of the solid.

X-ray and neutron diffraction experiments establish that the stationary ions in a superionic conductor form a regular sub-lattice and that the mobile ions are spread over many possible sites within the unit cell. These sites can

be divided into several sets of locations with the same symmetry, and the mobile ions can be pictured as hopping from site to site in the solid.

The passageways through the solid consist of interconnected inequivalent sites. The easy movement of the mobile ions through the passageways requires that the energy barriers between the sites be low. In other words, the activation energy for diffusion must be small.

The hopping diffusion in superionic conductors is not the same as ionic conduction in a normal (non-superionicconducting) solid. The mobile ion in a normal solid can occupy its own lattice site, move into a vacancy left by another ion, or occupy an interstitial position. In a superionic conductor the mobile ion can occupy any of several sites--the number of available sites is much larger than the number of ions that can occupy them.

The idea of a few ions with many possible sites per ion forms the theoretical basis of the ionic disorder within superionic conductors. Interactions between these mobile ions are suggested by investigations of phase transitions in these materials.

The phase transition from a normal solid to a superionic conductor can be considered as a sublattice melting transition--the mobile ions of the superionic conductor melt from a separate rigid structure in the normal solid. The extent to which the mobile ions are liquid-like demands some knowledge about the interactions between the mobile ions.

Some superionic conductors have phase transitions in which the occupancy of certain sets of sites becomes allowed without other structural change. Although both phases are disordered, some set of restrictions on the movement of the ions disappears at the transition. This removal of restrictions also suggests that long-range correlations affect apparently free disordered ions.

Several theoretical models for superionic conductors are suggested by this general discussion:

- a) hopping models, where the ions are considered as hopping from site to site;
- b) lattice gas models, which stress the statistics of n ions spread over N sites;
- c) free-ion models, which treat the charged ions like the free electrons of the Drude model for metals; and
- d) hydrodynamic models, which emphasize the melt-like characteristics of the superionic phase.

Measurements and Disorder

In order to learn about the ionic disorder and how it occurs in each superionic conductor, three principal experiments are done:

- a) measurement of the ionic conductivity;
- b) X-ray diffraction experiments; and
- c) measurement of the heat capacity.

Since they provide a basic working knowledge of the materials, these are generally the first experiments done on a new superionic conductor. In this section the information that each set of measurements provides will be discussed.

The ionic conductivity of a solid identifies the material as a superionic conductor. It is usually 3-4 orders of magnitude larger than that of a normal solid (such as NaCl) immediately below the melting temperature and approaches that of the melt ($\sim 1 \ \Omega^{-1} \text{cm}^{-1}$).

Measurements of the ionic conductivity can be analyzed to provide the activation energy for charged ion diffusion when only one ionic species is mobile. Simple arguments then indicate that the ionic conductivity σ has a temperature T dependence like²⁷

$$\sigma = \frac{A_{I}}{T} \exp \left(-E_{I}/k_{B}T\right)$$
(1)

where A_I is a temperature-independent prefactor, k_B is the Boltzmann constant, and the slope energy E_I is obtained from the slope of plots of log(σT) against T^{-1} .

The slope energy E_I is an empirically determined energy that is equal to, or greater than, the activation energy for ionic diffusion. The activation energy is the height of the energy barrier that restricts the motion of the mobile ion.

Any difference between the slope energy and the activation energy is generally ascribed to the formation of

either Frenkel or Schottky defects. The silver halides principally form Frenkel defects (the combination of a vacancy and an interstitial) in the normal phase²⁸, and diffusion occurs by the movement of interstitials through the solid.

In the normal solid at low temperatures, frozen-in interstitials control the ion motion, and so

$$E_{I} = E_{A}$$
(2)

where E_A is the activation energy for the diffusion process. At higher temperatures in the normal solid, temperatureactivated Frenkel defects form, and the slope energy E_I increases to

$$E_{I} = E_{A} + \frac{1}{2}E_{f}$$
(3)

where E_f is the energy of formation for the Frenkel defects. As a result, the plot of $log(\sigma T)$ vs T^{-1} will show a sharp increase in the slope at the temperature where the Frenkel defects begin to control the ionic conductivity.

Ideally the slope energy $\mathbf{E}_{\mathbf{I}}$ determined for the superionic state will obey

$$E_{I} = E_{m}$$
(4)

where E_m is the migration (activation) energy for the diffusion of the mobile ions through the rigid open structure. Since equation (4) assumes that none of the interactions

noted earlier are present, if some set of restrictions inhibits mobile ion conduction, then

$$E_{I} - E_{m} > 0 \tag{5}$$

because a formation energy will contribute to the slope energy. Supplementary measurements (such as the thermopower²⁵) have shown that the statement of equality, equation (4), holds for many but not all superionic conductors.

Another of the set of principal experiments is the determination of the rigid structure within the superionic conductor using X-ray diffraction. The data is analyzed by identifying the Bragg (or Debye) peaks, assigning a rigid structure consistent with the scattering, and finally determining the locations within the structure where mobile ions might be located. Three considerations guide this determination of the mobile ion sites²⁹:

- a) there must be many more sites than ions to fill them;
- b) the sites must form a connected conduction pathway; and
- c) movement along this pathway must require a low activation energy.

The positions for the mobile ions within the superionic conductor ideally can be checked by analysis of the diffuse X-ray scattering. The diffuse X-ray scattering contains a coherent scattering part that can be separated from Compton scattering, thermal vibrations, and the general background. The coherent scattering intensity, once isolated, can provide the radial distribution functions of the mobile ions about other mobile ions and of the mobile ions about the stationary ions.

The two radial distribution functions are difficult to separate, and when separated using other X-ray techniques, do not indicate much beyond nearest-neighbor distances³⁰. As a result, supplementary experiments such as neutron diffraction and EXAFS (Extended X-ray Absorption Fine Structure) are done to detail the locations of the mobile ions.

The last of the principal set of experiments done on superionic conductors is measurement of the heat capacity. The object of these measurements is the determination of phase transitions and of disorder from both the location of peaks in and the anomalous contributions to the heat capacity.

The heat capacity C_p measured at constant pressure can be written in terms of temperature derivatives of the entropy S and the Gibbs free energy G.

$$C_{p} = T\left(\frac{\partial S}{\partial T}\right)_{p} = -T\left(\frac{\partial^{2}G}{\partial T^{2}}\right)_{p} , \qquad (6)$$

where T is the absolute temperature. The Gibbs free energy is a thermodynamic state function, and changes in G describe energy changes associated with thermodynamic processes.

By definition³¹, changes in G that produce a step discontinuity in $\frac{\partial G}{\partial T}$ (and hence an infinity in C_p) indicate

first-order phase transitions. If $\frac{\partial G}{\partial T}$ changes its slope continuously, then humps or discontinuities in C_p indicate higher-order phase transitions. Anomalous increases in the heat capacity near phase transitions are due to increased disorder (increased entropy S) in the material.

In the sections that follow, the sample materials will be characterized primarily through this set of three experiments, with supplementary data included where it clarifies details.

Silver Iodide

Silver iodide AgI is one of the most interesting superionic conductors for several reasons:

- a) its simple chemical formula and structure suggest
 that the mechanism of superionic conduction should
 be uncomplicated;
- b) half of the ions (the cations Ag⁺) are mobile and therefore are the current carriers;
- c) the ionic conductivity σ increases by a factor of 10^4 to ~1.3 Ω^{-1} cm⁻¹ (one of the largest ionic conductivities for any solid) in the superionic phase at the first-order transition at 420 K;
- d) the ionic conductivity decreases upon melting at830 K; and
- e) the temperature range over which it is a superionic conductor (420 K to 830 K) is a large fraction of the temperature range over which it is solid.

The plot of $\log(\sigma T)$ vs T^{-1} (see Figure 1) indicates the features noted above. The slope energies associated with these data are given in Table 1.

Silver iodide has three phases at atmospheric pressure:

- a) the superionic α -phase above 420 K;
- b) the stable β -phase below 420 K; and
- c) the metastable γ -phase below 420 K.

The metastable γ -phase forms rather easily under extremes of pressure such as powdering and pelletizing³⁴, so that precautions must be taken to insure a pure sample of the stable β -phase. Two procedures that eliminate γ -AgI are:

a) annealing the sample between 400 K and 420 K for about one week³⁵; or

Table 1. Slope Energies E_{T} for AgI

Phase	Range T(K)	E _I (ev)	Sample Type	Meas. Freq. (Hz)	Reference
a-AgI	420 → 820	0.051	Powder	0	16
	1 250 + 420	0.58	Crystal	10)
	200 → 250	0.38	⊥ c-axis		
β-AgI	250 + 420	0.73	Crystal	10	
	200 → 250	0.41	c-axis		J
γ-AgI	3 00 + 4 00	0.26	Powder	10 ⁴	33

Figure 1. The ionic conductivity data for AgI (after Tubandt and Lorenz¹⁶, Govindacharyulu, et al.³², and Hoshino and Shimoji³³).

.



b) heating the sample to 450 K or above, and subsequently cooling the material slowly back through the phase transition.

Samples of Y-AgI heated just through the phase transition at 420 K will be Y-AgI when cooled back through the phase transition, and the samples must be heated well above the phase transition to produce β -AgI when cooled³⁶.

The values of E_I given for β -AgI indicate that the crystals are anisotropic and that the few mobile ions will be channeled along certain preferred directions. The γ -AgI results do not show any dependence on crystal anisotropy since these measurements were taken on powder samples. The ionic conductivity for both phases is due to the movement of silver ions through interstitial locations^{32,37}.

The value of E_I for α -AgI is significantly smaller than the values for β -AgI and Y-AgI, and indicates a low activation energy. The high value for the ionic conductivity σ and the low value for the slope energy E_I are sufficient to label α -AgI as a superionic conductor.

The structure of these phases has been determined by X-ray diffraction:

- a) the superionic conductor α-AgI has a b.c.c. rigid structure;
- b) stable $\beta\text{-AgI}$ has a wurtzite structure; and

c) metastable γ -AgI has a zincblende structure. The existence of two room-temperature phases (β -AgI and γ -AgI) was first shown by Wilsey³⁸, who found both structures in a set of several samples.

According to the X-ray diffraction measurements of Strock¹⁷, the iodine ions for α -AgI are arranged in a bodycentered-cubic lattice while the mobile silver ions can be found at any of forty-two possible crystallographic sites (one set of six octahedral sites, one set of twelve tetrahedral sites, and one set of twenty-four trigonal sites) in the unit cube (see Figure 2). Although the rigid structure has been repeatedly verified, neutron diffraction studies¹⁸ indicate that the octahedral sites for the mobile ions are not occupied. These neutron diffraction studies show that the mobile silver ions in α -AgI move from tetrahedral site to tetrahedral sites as intermediate bridging sites.

To understand the nature of the superionic phase transition in AgI one can look at the heat capacity data of Nölting³⁹ (see Figure 3). The curve clearly shows that the superionic transition at 420 K, like the melting transition at 830 K, is first order. No additional features are seen in this heat capacity data either above or below the superionic phase transition.

Many other material properties have been measured and are catalogued in the reviews indicated in the introduction.

The reasons for measuring the thermal conductivity κ of AgI can be stated as follows:

- a) the relative abundance of information concerning the material allows calculations to be done;
- b) its structure is simple;

Figure 2. Sites for AgI in the Strock Model.



- 6 (octahedral)
- 12 (tetrahedral)
- 24 (trigonal)

.

Figure 3. The heat capacity C_p for AgI (after Nölting³⁹).



- c) its superionic phase is conveniently set apart from the room-temperature phases by the transition at 420 K; and
- d) the thermal conductivity κ is an unmeasured transport coefficient that either directly (if κ is due to the ions) or indirectly should continue the characterization of this compound.

Silver Iodide/Silver Bromide Mixtures

In order to learn more about ionic disorder, changes in the ionic conductivity may be monitored when impurity ions are introduced. The effects of these impurities will fall into two categories:

- a) size effects, such as occur when a smaller ion substitutes for a larger ion; and
- b) charge effects, such as occur when one ion substitutes for another ion with a different charge.

Charge effects will lead to increased or decreased numbers of vacancies or interstitials in order to achieve charge neutrality in ionic conductors. For example, a Cd⁺⁺ impurity in AgI will be compensated by a silver ion vacancy.

Size effects can be viewed as opening or closing the structure to the mobile ions. The partial substitution of bromine ions (using silver bromide) for some of the larger iodine ions in silver iodide should change the ionic conductivity through size effects alone. A plot of the ionic conductivity against concentration for silver iodide/silver bromide mixtures at room temperature²¹ (see Figure 4) can be used to gauge some of these effects. The data shows a peak at 20 atomic percent AgBr where the ionic conductivity of the mixture is 3 orders of magnitude greater than the ionic conductivity of either component.

Figure 4 also shows the single-phase and multi-phase regions of composition for these materials⁴⁰. β -AgI dissolves up to 5 atomic percent AgBr to form one of the two single-phase regions, while AgBr dissolves up to 30 atomic percent AgI to form the other. The multi-phase mixtures consist of combinations of the two single-phase materials and any leftover component compounds.

Two points on the maximum dissolved concentration of AgBr in AgI vs. temperature curve have been described by Shahi and Wagner⁴⁰. They find that AgI dissolves up to ~ 5 atomic percent AgBr at room temperature, and up to ~ 10 atomic percent at the superionic transition temperature. The discussion that follows will focus upon single-phase material (because the properties of the multi-phase materials are difficult to interpret) and so will be restricted to concentrations up to 10 atomic percent AgBr.

The temperature dependence of the ionic conductivity for several different concentrations of AgBr in AgI is shown in Figure $5^{16,40,41}$. These powder sample data show that with increasing bromine concentration:
Figure 4. The room-temperature ionic conductivity of AgI/AgBr mixtures (after Shahi and Wagner²¹).



Figure 5. The ionic conductivity of several concentrations of AgBr in AgI (after Shahi and Wagner⁴⁰ Tubandt and Lorenz⁴¹, and Tubandt and Lorenz¹⁶).



- a) the temperature of the superionic phase transition
 decreases (see also Table 2);
- b) the temperature of the melting transition decreases;
- c) the ionic conductivity of the melt and of the superionic phase is nearly the same; and
- d) the ionic conductivity of the wurtzite phase (the room temperature phase) increases.

Shahi and Wagner⁴⁰ verified that the structure of their samples was like β -AgI after heat treatment similar to that required for AgI.

The nearly identical curves of $\log(\sigma T)$ vs. T^{-1} in the superionic phase of Figure 5 indicates that the slope energy for this phase does not change with increasing concentration

Transition Temperature	Concentration
T _c (K)	C (atomic percent)
420.5	0
416.0	2
412.3	4
408.3	6
401.0	10

Table 2. Depression of the superionic phase transition temperature with increasing concentration of AgBr (after Shahi and Wagner⁴⁰).

of AgBr. The slope energy E_{I} for an ideal superionic conductor should obey (equation(4))

$$E_{I} = E_{m}$$

where E_m is the migration energy for the mobile ions, and so the lack of any change in E_I indicates no dependence on defects for the conduction of the mobile ions in this phase for low concentrations of the impurity.

A more interesting feature of the ionic conductivity data of Figure 5 is the decrease, with increasing bromine concentration, of the slope energy below the superionic phase transition. Since (equation(3)).

$$E_{I} = E_{A} + \frac{1}{2}E_{f}$$
,

one can interpret the results as showing (with increasing bromine concentration):

- a) a decrease in the activation energy E_{Λ} ;
- b) a decrease in the defect formation energy E_f ; or
- c) a decrease in both E_{Δ} and E_{f} .

Shahi and Wagner⁴⁰ suggest that increasing bromine concentration lowers the formation energy E_f , and that the increase in the ionic conductivity is due primarily to increased numbers of mobile ions in the room-temperature phase. This suggestion also indicates why the slope energy in the super-ionic phase does not change. Since the conduction ions are already mobile, no new conducting ions can be thermally activated.

Shahi and Wagner⁴⁰ also suggest that the phase transition to the superionic phase is driven by a critical number of defects in the room-temperature material. Thus, since the critical number is passed at a lower temperature, the temperature of the phase transition should decrease with increasing bromine concentration.

Measurements using a low concentration of AgBr in AgI should establish some idea of the dependence of the thermal conductivity upon the number of defects within the material. The concentration should be close to 5 atomic percent AgBr, since this material is single phase at room temperature and has a room temperature ionic conductivity ten times larger than that for pure AgI.

Pyridinium Penta-Silver Hexa-Iodide

One way to make a low-temperature superionic conductor is to open up the structure of a high-temperature superionic conductor using large organic ions to replace some of the mobile ions. An example of a near-room-temperature superionic conductor prepared by the insertion of organic ions into AgI is the pyridinium ion $(Py^+ = C_5H_5NH^+)$ compound $PyAg_5I_6$.

The single crystal ionic conductivity data⁴² for $PyAg_5I_6$ (see Figure 6) indicates that:

- a) some small differences in the ionic conductivity
 due to crystal anisotropy exist;
- b) a definite change in the slope of the ionic conductivity curve occurs near 310 K;

Figure 6. The ionic conductivity of $PyAg_5I_6$ (after Hibma⁴²).

-



- c) the slope energy E_{I} is less above 310 K than below 310 K; and
- d) below 310 K the ionic conductivity curves show no sharp features.

The high ionic conductivity for $PyAg_5I_6$ coupled with the sharp decrease in the slope energy E_I suggests that the phase above 310 K is a superionic conductor.

X-ray diffraction measurements 20,43 indicate the following set of phases:

- a) a superionic phase above ~310 K;
- b) a high conductivity hexagonal phase between 230 K
 and ~310 K where the silver ions gradually disorder
 with increasing temperature;
- c) a monoclinic phase between 180 K and 230 K; and
- d) a second monoclinic phase below 180 K.

These measurements also indicate that the transition near 310 K is not accompanied by a change in the rigid structure consisting of pyridinium ions and iodine ions. Rather, this transition seems to involve the gradual removal of restrictions upon the mobile silver ions.

The evolution of the silver-ion disordering process can be traced from the silver-ion ordered material in the room-temperature phase at 230 K. The structure²⁰ at this temperature has the space group P6/mcc (D_{6h}^2) with two formula units per unit cell. The ten silver ions occupy ten sites--6f tetrahedral sites and 4c octahedral sites-with 24m tetrahedral sites unoccupied. The iodine ions are arranged to form long pipe-like tunnels which detour around pyridinium ions.

The mechanism of the disorder can be illustrated using Figure 7^{42} . At 230 K only the c and f sites are occupied, and the connecting m sites are unoccupied. The m sites are tetrahedral sites, but one of the paths from each site is blocked by a pyridinium ion, so that only three conduction paths are available. As the temperature is increased, the ions move into m sites until ~310 K where the ions are completely disordered and are spread over all three sets of sites.

This sort of transition is quite different from the superionic transition at 420 K in AgI. The structural phase transition in AgI provides a sharp break between the normal phase and the superionic phase. The rigid structure of the pyridinium ions and the iodine ions in $PyAg_5I_6$ does not change at the phase transition to the superionic phase, and so the change in the ionic conductivity is much smoother.

Heat capacity measurements 42 show:

- a) no feature for the transition at 180 K;
- b) a small peak near 230 K which indicates the presence of a higher-order phase transition; and

c) a very broad feature centered near 310 K. This broad feature suggests a higher order phase transition associated with gradual disordering in the material.

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Figure 7. Schematic of the silver-ion sites and conduction paths in $PyAg_5I_6$ above ~310 K (after Hibma⁴²).

Within the PyI/AgI system another superionic conductor, $Py_5Ag_{18}I_{23}$, exists. This single-phased compound is a twodimensional superionic conductor with an order of magnitude lower ionic conductivity than $PyAg_5I_6$. Deviations from stoichiometry during preparation of $PyAg_5I_6$ may produce $Py_5Ag_{18}I_{23}$, and subsequently problems with data interpretation may develop.

The thermal conductivity of $PyAg_5I_6$ is measured to investigate the phase transition near 310 K.

CHAPTER III

THEORY FOR THE TRANSIENT HOT WIRE METHOD

A mathematical description of the transient hot wire method will be derived and discussed in this section. The final results are important not only for an understanding of how the thermal conductivity is obtained by this method, but for the restrictions that these results place on the sample geometry.

Diffusion Equation

The thermal conductivity κ is formally defined by

$$\bar{q} = -\kappa \bar{\nabla} T \tag{7}$$

where \overline{q} is the heat flux (heat/area.time) through the material due to the temperature gradient $\overline{\nabla}T$. The continuity equation for heat flow (with no internal sources or sinks)

$$\overline{\nabla} \cdot \overline{q} + \rho c \frac{\partial T}{\partial t} = 0$$
(8)

(where ρ is the density and c is the heat capacity at constant volume) can be combined with equation (7) to give the diffusion equation

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$$\nabla^2 T - \frac{1}{D_{TH}} \frac{\partial T}{\partial t} = 0$$
⁽⁹⁾

with the thermal diffusity $D_{TH} = \kappa / \rho c$.

The diffusion equation is a second-order partial differential equation generally solved using a particular set of coordinates and at least one boundary condition. In what follows, the symmetry of the system under consideration is used to eliminate space derivatives, and Laplace transformations are used to remove the time derivative. Laplace transformations are discussed in Appendix A.

The Boundary Value Problem

To a good approximation the geometry of the transienthot-wire-method system consists of an infinitely long cylindrical heat source of near-zero radius surrounded by a sample of infinite radius. The symmetry of the system geometry allows the three cylindrical coordinates (r, θ, z) to be reduced to the single coordinate (r). In other words, system variables such as the temperature T will be a function only of the radius r and the time t.

In the calculation of the working equation for the transient hot wire method, one considers a cylindrical wire of radius a, density ρ_w , and gram heat capacity c_w surrounded by sample material of thermal diffusity D_{TH} , thermal conductivity κ , density ρ , and gram heat capacity c. The temperature within the wire can be written $T_1 = T_1(r,t)$, and the temperature of the sample material outside the wire

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can be written $T_2 = T_2(r,t)$. Heat is produced in the wire by a current pulse of duration t_p .

Following the discussion of Blackwell⁴⁴ and Carslaw and Jaeger⁴⁵, the diffusion equation within the sample (r > a, t > 0) can be written (because of the symmetry) as

$$\frac{\partial^2 T_2}{\partial r^2} + \frac{1}{r} \frac{\partial T_2}{\partial r} - \frac{1}{D_{TH}} \frac{\partial T_2}{\partial t} = 0$$
(10)

The initial condition (t=0) for the system is

$$T_1 = T_2 = T_0$$
 (11)

Since one is interested only in temperature changes, T_0 is set equal to zero.

The first of the two boundary conditions at r = a is

$$\dot{Q} - \pi a^2 \rho_w c_w \frac{\partial T_1}{\partial t} = -2\pi a \kappa \left. \frac{\partial T_2}{\partial r} \right|_{r=a}$$
(12)

where \dot{Q} is the heat power supplied per unit length. This expression states that the heat supplied to the wire (\dot{Q}) . less the heat retained by the wire $(\pi a^2 \rho_w c_w \frac{\partial T_1}{\partial t})$ leaks away to the outside sample through thermal conduction $(-2\pi a\kappa \frac{\partial T_2}{\partial r} \Big|_{r=a})$.

The second boundary condition approximates the effects of thermal resistance. The heat that leaks away from the wire $(-2\pi a\kappa \frac{\partial T_2}{\partial r} \Big|_{r=a}$ above) may be assumed to cross a boundary layer which retains extra heat in the wire and so increases the temperature of the wire. If \dot{Q}_{BL} is the total heat power flowing through the boundary layer, then one many write the simple expression for thermal conduction

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$$\dot{Q}_{BL} = \kappa_{BL} A_{BL} \frac{(T_1 - T_2)}{\Delta x_{BL}}$$

where, for the boundary layer (subscript BL), A_{BL} is the area, Δx_{BL} is the thickness, and κ_{BL} is the effective thermal conductivity. As a result, the power per unit length flowing through the boundary layer may be written

$$\frac{\dot{Q}_{BL}}{\ell} = \kappa_{BL} \left(\frac{A_{BL}}{\Delta x_{BL} \ell} \right) (T_1 - T_2) = \frac{1}{R_T} (T_1 - T_2)$$

where ℓ is the length along the wire and R_T , the inverse of κ_{BL} multiplied by a dimensionless constant, has the units of a thermal resistivity. Thus, the second boundary condition is

$$-2\pi \alpha \kappa \left. \frac{\partial T_2}{\partial r} \right|_{r=\alpha} = \frac{1}{R_T} (T_1 - T_2) \qquad (13)$$

At this point, one takes the Laplace transform of the differential equation (equation (10)) and the two boundary conditions (equations (12) and (13)) using $T_0 = 0$ for the initial condition (equation (11)). This gives the three equations

$$\frac{d^{2}\bar{T}_{2}}{dr^{2}} + \frac{1}{r} \frac{d\bar{T}_{2}}{dr} - \frac{p}{D_{TH}} \bar{T}_{2} = 0$$
(14)

$$\frac{\dot{Q}}{p} - \rho \pi a^2 \rho_w c_w \bar{T}_1 = -2\pi a \kappa \left. \frac{d\bar{T}_2}{dr} \right|_{r=a}$$
(15)

$$2\pi a\kappa \left. \frac{d\bar{T}_2}{dr} \right|_{r=a} + \frac{1}{R_T} (\bar{T}_1 - \bar{T}_2) = 0$$
(16)

where \bar{T}_1 and \bar{T}_2 are the Laplace transforms of T_1 and T_2 , and where p is the complementary variable to the time t in the Laplace transform and has the dimensions t^{-1} .

If the parameter $q = \sqrt{p/D_{TH}}$ is substituted into equation (14), the solution to this differential equation involving the modified Bessel functions may be written:

$$\bar{T}_2 = c_1 I_0(qr) + c_2 K_0(qr)$$

Since $K_0(qr)$ is finite as qr goes to ∞ and $I_0(qr)$ is not⁴⁶, the coefficient c_1 must vanish, and

$$\bar{T}_2 = c_2 K_0(qr)$$
 (17)

Finally, if \bar{T}_2 and the derivative of \bar{T}_2

$$\frac{\mathrm{d}\bar{\mathrm{T}}_2}{\mathrm{d}\mathrm{r}} = \mathrm{c}_2(-\mathrm{q} \ \mathrm{K}_1(\mathrm{q}\mathrm{r}))$$

are substituted into the two boundary condition expressions (equations (15) and (16)), the resulting two equations in the two unknowns c_2 and \overline{T}_1 may be solved to give the expression

$$\overline{T}_{1} = \frac{\dot{Q}}{p} \frac{K_{0}(qa) + q2\pi a \kappa R_{T}K_{1}(qa)}{2\pi \kappa qaK_{1}(qa) + p\pi a^{2}\rho_{w}c_{w}K_{0}(qa) + 2\pi^{2}a^{3}p\rho_{w}c_{w}q\kappa R_{T}K_{1}(qa)} .$$
(18)

One must use the formal integral expression for the inverse Laplace transform (see Appendix A) of \overline{T}_1 since \overline{T}_1 is a complicated function of the complementary variable p. The integration can be performed, but the solution is not experimentally useful since it is weighted heavily towards extremely small times (large p). To find a solution valid at comparatively large times (small p), the expression for \overline{T}_1 (equation (18)) must be re-written in ascending powers of p, and then this re-written expression can be integrated using the formal inverse Laplace transform in the leading powers of p.

Because $q^2 = p/D$, the modified Bessel functions $K_0(qa)$ and $K_1(qa)$ must be expanded to terms involving q^2a^2 to be first order in p. These expansions are⁴⁵:

$$K_0(qa) = -(ln \frac{Cqa}{2})(1 + \frac{q^2a^2}{4}) + \frac{q^2a^2}{4} + \dots$$
 (19a)

$$qaK_1(qa) = 1 - \frac{q^2a^2}{4} + (ln \frac{Cqa}{2})(\frac{q^2a^2}{2}) + \dots$$
 (19b)

where $ln \ C = \gamma = 0.5772 \dots$ is Euler's constant. These expansions are substituted into the expression for \overline{T}_1 (equation 18) keeping only the terms which are first order in p. Using the binomial expansion for \overline{T}_1 , after the subsequent algebra one obtains

$$\bar{T}_{1} = \frac{\dot{Q}}{2\pi\kappa} \left[\frac{1}{p} \left\{ 2\pi\kappa R_{T} - \ell n \frac{Cqa}{2} \right\} + \frac{a^{2}\rho_{w}c_{w}}{2D_{TH}^{\rho_{c}}} \left\{ \frac{\rho_{c}}{\rho_{w}c_{w}} - (2\pi\kappa R_{T})^{2} + (\ell n \frac{Cqa}{2})(4\rho\kappa R_{T} - \frac{\rho_{c}}{\rho_{w}c_{w}}) + (\frac{\rho_{c}}{\rho_{w}c_{w}} - 1)(\ell n \frac{Cqa}{2})^{2} \right\} \right].$$

$$(20)$$

If one defines the quantities

$$H = 2\pi\kappa R_{T}$$
$$\alpha = 2\rho c / \rho_{w} c_{w}$$

then by using the inverse Laplace transform (see Appendix A) one obtains

$$T_{1} = \frac{\dot{Q}}{4\pi\kappa} \left\{ 2H + \ln \frac{4D_{TH}t}{Ca^{2}} - \frac{a^{2}}{2D_{TH}t} \left(\frac{4H-\alpha}{\alpha}\right) + \frac{a^{2}}{2D_{TH}t} \left(\frac{\alpha-2}{\alpha}\right) \ln \frac{4D_{TH}t}{Ca^{2}} \right\}$$
(21)

as the solution to the boundary value problem for large times.

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The Working Equation for the Transient Hot Wire Method

The solution to the boundary value problem (equation (21)) may be written

$$T_1 = \Delta T + \delta T_H + \delta T_{\alpha}$$

where

$$\Delta T = \frac{\dot{Q}}{4\pi\kappa} \ln \frac{4D_{\rm TH}t}{Ca^2}$$
(22)

$$\delta T_{\rm H} = \frac{\dot{Q}}{4\pi\kappa} \{2H\} = \frac{\dot{Q}}{4\pi\kappa} (4\pi\kappa R_{\rm T})$$
(23)

$$\delta T_{\alpha} = \frac{\dot{Q}}{4\pi\kappa} \left(- \frac{a^2}{2D_{\text{TH}}t} \right) \left(\frac{4H-\alpha}{\alpha} - \frac{\alpha-2}{\alpha} \ln \frac{4Dt}{Ca^2} \right) \quad . \tag{24}$$

Consider each of these terms in order. The leading term ΔT , equation (22), will turn out to be the working equation for the transient hot wire method. The thermal conductivity κ of the sample can be found from the slope of the wire temperature increase ΔT against the logarithm of the time ln t.

The expression for $\delta T_{\rm H}$ (equation (23)) is independent of t and suggests that the thermal resistance should not affect the measurement of the slope that determines κ .

The expression for δT_{α} estimates the error in the measurement due to the heat capacity of the wire. The parameter α appearing in this expression contain the ratio of the heat capacity c of the sample to the heat capacity c_w of the wire. The relative contribution due to this

correction can be written

$$\frac{\delta T_{\alpha}}{\Delta T} = -\frac{a^2}{2D_{TH}t} \frac{1}{\ell n \left(\frac{4D_{TH}t}{Ca^2}\right)} \left[\frac{4H-\alpha}{\alpha} - \frac{\alpha-2}{\alpha} \ell n \left(\frac{4D_{TH}t}{Ca^2}\right)\right].$$

A crude approximation for this ratio follows. The value $\alpha \approx 2$ can be used if one assumes that the density and the heat capacity of the wire are of the same order of magnitude as for the sample. If one also assumes that the heat capacity of the wire has a much larger effect than the thermal resistivity (effectively H \approx 0), then the term in brackets is about -1. So, if one evaluates

$$\frac{\delta T_{\alpha}}{\Delta T} = \frac{a^2}{2D_{TH}t} \left(\frac{1}{\ell n \left(\frac{4D_{TH}t}{Ca^2} \right)} \right)$$
(25)

at t = 1 sec using

$$a \approx 10^{-4} \text{ m}$$

 $D_{\text{TH}} \approx 10^{-7} \text{ m}^2/\text{s}$
 $C \approx 2$

for the parameters, then the relative error that results if the term δT_{α} is ignored is

$$\frac{\delta T}{\Delta T} \approx 0.017 \quad .$$

The time dependence for $\frac{\delta T_{\alpha}}{\Delta T}$ indicated by equation (25) suggests that this relative error will decrease as t increases.

Effect of the Finite Outer Boundary

The outer boundary of the sample was earlier assumed to be located at infinity. Since the sample size for practical measurement systems is limited, the effect of this finite outer boundary upon the measurement of the thermal conductivity κ must be discussed.

The effect of the finite outer boundary can be estimated for the system where the wire cylinder is compressed between flat disks of the sample 47 (see Figure 8). This approach approximates the heating of the wire cylinder due to a heat pulse that travels from the wire cylinder to the flat outer boundary of the sample and back again to the wire cylinder. Since the heat pulse travels along the "slice" of the sample, the temperature increase of the wire due to the heat pulse from the wire can be treated using a one-dimensional diffusion equation. This approach over-estimates the effect, since all heat is assumed to flow along the slice of sample material. In the following discussion, x is the distance along a slice of material which is 2b in length (b is the sample disk thickness).

The one-dimensional diffusion equation is

$$\frac{\partial^2 T}{\partial x^2} - \frac{1}{D_{TH}} \frac{\partial T}{\partial t} = 0$$
 (26)

Figure 8. The finite outer boundary of the sample system.



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which, for the same initial conditions as the boundary value problem

$$T = T_0 , \qquad (27)$$

can be Laplace transformed using $T_0 = 0$. One obtains (see Appendix A)

$$\frac{\mathrm{d}^2\bar{\mathrm{T}}}{\mathrm{dx}^2} - \frac{\mathrm{p}}{\mathrm{D}}\bar{\mathrm{T}} = 0 \tag{28}$$

where p is the complementary variable to t in the Laplace transform.

If the parameter $q = \sqrt{p/D}$ is introduced as before, the solution has the general form

 $\bar{\mathbf{T}} = \mathbf{d}_1 \mathbf{e}^{\mathbf{q}\mathbf{x}} + \mathbf{d}_2 \mathbf{e}^{-\mathbf{q}\mathbf{x}}$

Since e^{qx} approaches infinity as x approaches infinity, the coefficient d_1 vanishes, and so

$$\bar{\mathbf{T}} = \mathbf{d}_2 \mathbf{e}^{-\mathbf{q}\mathbf{x}} \quad . \tag{29}$$

The boundary condition is

$$T = f(t) \tag{30}$$

at x = 0 for t > 0. If this is Laplace transformed,

$$\overline{T} = \overline{f}(p)$$
,

so that for all x

 $\bar{\mathbf{T}} = \bar{\mathbf{f}}(\mathbf{p}) e^{-\mathbf{q}\mathbf{X}} \tag{31}$

The inverse Laplace transform can be performed using Duhamel's theorem (see Appendix A). One obtains

$$T = \int_{0}^{t} f(\tau) \left\{ \frac{x}{2\sqrt{\pi D_{TH}}} \frac{1}{(t-\tau)^{3/2}} e^{-\frac{x^{2}}{4D_{TH}(t-\tau)}} \right\} d\tau$$

where the bracketed quantity is the inverse Laplace transform of e^{-qx} . This expression can be rewritten using the parameter

$$u = \sqrt{\frac{x^2}{4D_{\text{TH}}(t-\tau)}}$$

to give

$$T = \frac{2}{\sqrt{\pi}} \int_{\frac{x}{\sqrt{4D_{TH}t'}}}^{\infty} f\left(t - \frac{x^2}{4D_{TH}u^2}\right) e^{-u^2} du .$$
(32)

Since the integral can be evaluated⁴⁶ in terms of the error function erf(x) if

 $f(t) = kt \tag{33}$

this form for f(t) is used to overestimate the actual time dependence for the transient hot wire $f(t) = k \ell n t$ (see equation (22)). Upon substitution and integration the expression for T (equation (32)) becomes at x = 2b

$$T = kt \left\{ \left[1 - erf\left(\frac{b}{\sqrt{D_{TH}t}}\right) \right] \left(1 + \frac{2b^2}{D_{TH}t} \right) + \frac{2}{\sqrt{\pi}} \frac{b}{\sqrt{D_{TH}t}} e^{-b^2/D_{TH}t} \right\}$$
(34)

Because a factor of the same form as f(t) appears in the final solution for T, its time dependence can be divided out to give the percent increase in the temperature of the wire cylinder due to "reflection" at the outer boundary.

The procedure at this point is to evaluate the factor in the braces in equation (34) for several values of $b/\sqrt{D_{TH}t}$ until the percent increase in the wire cylinder temperature falls below some acceptable level. Since for $b/\sqrt{D_{TH}t} = 3$ the percent increase falls below 0.1%, this condition is used as a criterion for choosing the thickness of the sample disks.

Using the same order of magnitude estimate for D_{TH} as is used in the calculation of $\left|\delta T_{\alpha}/\Delta T\right|$ (equation (25)), one obtains, for $D_{TH} \approx 10^{-7} \text{ m}^2/\text{sec}$,

$$b = 3\sqrt{D_{TH}t_p} = 2\sqrt{t_p/10} mm$$
 (35)

with the pulse time t_p given in seconds. Sample disks 3 mm thick should permit pulse times up to ten seconds for $D_{TH} \approx 10^{-7} \text{ m}^2/\text{sec.}$

If the sample disk thickness b is fixed by this procedure, then changes in $D_{TH} = \kappa / \rho c$ will require that changes be made in t_p so that the percent increase (the bracketed portion of equation (34)) will stay below 0.1% (see Table 3). As a result, because of the increase in κ (due to the T^{-1} law explained in Chapter IV) and the decrease in c (due to the Debye T^3 law) as the temperature is decreased, one must expect to reach a temperature where the data becomes unusable.

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D _{TH} (m ² /sec)	t _p (sec)	
5x10 ⁻⁷	2	
1x10 ⁻⁷	10	
5x10 ⁻⁸	20	

Table 3. The effect of changes in the thermal diffusivity D_{TH} upon the acceptable pulse time t_p for 3 mm thick sample disks.

The pulse time becomes too small to include a sufficiently long straight-line portion of the ΔT vs. lnt plot needed to determine κ .

Larger sample disks can minimize this problem, but require more material and larger equipment. Larger equipment can accommodate larger diameter samples which are needed in order to maintain adequate material between the wire and the outer diameter of the sample disk.

Cooling from the Potential Leads

Practically, the heat dissipated by the wire is generated resistively by means of a pulse of current I which lasts for the time t_p . One determines the temperature of the wire by

- a) measuring the potential difference V across a length of the wire,
- b) determining the resistance $R_w = V/I$, and

c) converting the resistance to a temperature using a calibration curve.

The details of this procedure can be found in Chapter V.

The potential leads spotwelded to the wire will cool the wire at its ends. A steady-state approximation due to Horrocks and McLaughlin⁴⁸ overestimates the error in the electrical resistance R_w due to this cooling by fixing the temperature at the spotwelds at T = T₀ and by calculating the temperature distribution along the wire.

The model considers the temperature distribution along a wire cylinder of length ℓ , radius a, and volume V and surface area S defined to be

$$V = \pi a^2 \ell \tag{36a}$$

$$S = 2\pi a \ell \qquad (36b)$$

The wire has a thermal conductivity κ_w , a density ρ_w , a heat capacity c_w , and so a thermal diffusivity $D_w = \kappa_w / \rho_w c_w$. This wire is surrounded by material of "thermal conductivity per unit length" H.

The power \dot{Q}_{I} is supplied to the wire by means of resistive heating. Part of \dot{Q}_{I} escapes to the sample material and the rest flows through the wire to its ends. One can write a continuity equation including \dot{Q}_{I} as a source and the escaped heat power as a sink (see equation (8)):

$$\overline{\nabla} \cdot \overline{q} + \rho_{w} c_{w} \frac{\partial T_{w}}{\partial t} = \frac{\dot{Q}_{I}}{V} - \frac{HS}{V} (T_{w} - T_{0})$$
(37)

where T_w is the temperature in the wire and the last term is an approximation for the escaped heat power/volume. Since our geometry is one-dimensional, if y describes the distance along the wire, then, using the definition for the thermal conductivity (equation 7), the symmetry of the system, and the definitions of V and S (equations (36a) and (36b)), one can write

$$-\kappa_{w} \frac{\partial^{2} T_{w}}{\partial y^{2}} + \rho_{w} c_{w} \frac{\partial T_{w}}{\partial t} = \frac{\dot{Q}_{I}}{\pi a^{2} \ell} - H \frac{2}{a} (T_{w} - T_{0}) \quad .$$
(38)

Finally, if the steady state is assumed $(\frac{\partial T_w}{\partial t} = 0)$, the differential equation may be written

$$0 = \frac{d^2 T_w}{dy^2} + g_1 - g_2^2 (T_w - T_0)$$
(39)

where

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$$g_{1} = \frac{\dot{Q}_{I}}{\pi a^{2} \ell \kappa_{w}}$$
(40a)

$$g_2^2 = \frac{2H}{\kappa_w a} \qquad (40b)$$

The solution of the differential equation (equation (39)) is

$$T_w - T_0 = j_1 e^{g_2 y} + j_2 e^{-g_2 y} + \frac{g_1}{g_2^2}$$
, (41)

where j_1 and j_2 are constants to be determined. The boundary conditions are

$$T = T_0$$

at y = 0 and y = 2 ℓ . If one sets $T_0 = 0$ as before, and uses the half-length L = $\ell/2$, the two constants are found to be

$$j_1 = -\frac{g_1}{g_2^2} \frac{e^{-g_2 L}}{2\cosh(g_2 L)}$$
 (42a)

$$j_{2} = -\frac{g_{1}}{g_{2}^{2}} \frac{e^{g_{2}L}}{2\cosh(g_{2}L)} \qquad (42b)$$

The solution for T_w (equation (41)) can then be written

$$T_{w} = \frac{g_{1}}{g_{2}^{2}} \left(1 - \frac{\cosh g_{2}(L-y)}{\cosh g_{2}L} \right)$$

The average electrical resistance ${\rm R}_{_{\rm W}}$ of the wire can be expressed as

$$R_{w} = \int_{0}^{2L} (1 + \alpha T_{w}) dR_{0}$$

where R_0 is the initial resistance and α is the linear temperature coefficient of resistance. If the electrical conductivity of the wire is σ_w , then

$$dR_0 = \frac{dy}{\sigma_m \pi a^2}$$

and

$$R_{w} = R_{0} + \alpha \int_{0}^{2L} \frac{1}{\sigma_{w} \pi a^{2}} T_{w} dy \qquad (44)$$

Substituting the expression for T_w (equation (43)) into the expression for R_w , one can define the wire temperature error E by

$$\frac{R_w - R_0}{R_0} = \alpha \frac{g_1}{g_2^2} (1 - E)$$

where E is found by integration to be

$$E = \frac{1}{g_2 L} \tanh g_2 L \quad . \tag{45}$$

Because g_2 depends on H (equation (40b)), this error E can be evaluated only if some approximation for the "thermal conductivity per unit length" can be made. To begin with, the temperature T_w at the center of the wire (y = L) can be approximated from equation (43)

$$T_{w} \approx \frac{g_{1}}{g_{2}^{2}} = \frac{(\dot{Q}_{I}/\ell)}{2\pi aH}$$
 (46)

Also, the temperature distribution across a hollow cylinder of inner radius a and outer radius b can be expressed as 45

$$T(a) - T(b) = \frac{(\dot{Q}_{I}/\ell)}{4\pi\kappa} (2 \ln \frac{b}{a})$$

using \dot{Q}_{I}/ℓ as the heat input per unit length at the inner surface and κ as the thermal conductivity of the hollow cylinder sample material. Finally, setting T(b) = T₀ = 0, and T(a) = T_w from equation (46), one finds

$$H = \frac{\kappa}{a \ln \left(\frac{b}{a}\right)}$$

and

$$g_2 = \sqrt{\frac{2\kappa}{\kappa_w} \frac{1}{a^2} \frac{1}{\ln b/a}} \quad . \tag{47}$$

To determine E (equation (45)), g_2 must be evaluated. Using a $\approx 10^{-4}$ mm as before, b = 3.0 mm as determined by the finite outer boundary expression (equation (35)), $\kappa_w = 91$ W/mK from the CRC Handbook⁴⁹, and $\kappa = 0.35$ W/mK from the data (see Chapter V), at room temperature $g_2 = 480$ m⁻¹. If ℓ is chosen to be 50 mm (L = 25 mm), the error E is calculated to be 0.08.

The value E = 8% must be considered against the assumptions that

a) the wire leads maintain the ends of the wire at

 $T_w = T_0 = 0$, and

b) the wire is in the steady state.

The first assumption guarantees that E will be over-estimated by this calculation, and the second assumption indicates that these effects will not become important until reasonably late in the current pulse. Summary

The working equation of the transient hot wire method (equation (22))

$$\Delta T = \frac{\dot{Q}}{4\pi\kappa} \ln \frac{4D_{TH}t}{Ca^2}$$
$$= \frac{\dot{Q}}{4\pi\kappa} \ln t + \frac{\dot{Q}}{4\pi\kappa} \ln \frac{4D_{TH}}{Ca^2}$$
(48)

can be obtained from a boundary value problem which includes the effects of a thermal resistance at the surface of the wire (equations (13) and (23)) and the heat capacity of the wire (equations (12) and (24)).

The sample thickness and the pulse length were calculated by considering the effects of the finite outer boundary of the sample (equation (35)). The heater wire must be long enough to reduce the effects of potential lead cooling upon the resistance of the heater wire (equations (45) and (47)).

CHAPTER IV

THEORY OF THERMAL CONDUCTION

In this section the theory of thermal conduction for non-metals at high temperatures will be discussed in order to form a basis for the interpretation of the data. The semi-quantitative treatment of the theory will emphasize the temperature dependence of the thermal conductivity for the superionic conductors and for normal solids.

The Kinetic Theory Expression

The simple expression for the thermal conductivity κ derived from the kinetic theory is qualitatively useful since it allows the straightforward interpretation of results.

This expression²⁸ is derived by considering the flux of particles traveling along the x-axis in response to the temperature gradient δT (see Figure 9). If a particle travels with a velocity v_x an average distance x_0 between collisions, then

$$\delta T = \frac{dT}{dx} dx = \frac{dT}{dx} x_0 = \frac{dT}{dx} v_x \tau$$

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Figure 9. The particle flux and the temperature gradient for the kinetic theory.



where τ is the average time between collisions. If at each collision each particle releases an energy $\xi = c \delta T$ (c = heat capacity/particle), then for n particles/volume the heat flux q can be written

$$q = -n\xi v_{x} = -nc\delta T v_{x} = -nc(v_{x})^{2}\tau \frac{dT}{dx} , \qquad (49)$$

where the minus sign indicates that the heat flow is towards lower temperatures. Since the definition of the thermal conductivity along one direction is (see equation (7))

$$q = -\kappa \frac{dT}{dx} ,$$

and since, on the average, the three-dimensional particle velocity v obeys $\langle v_x^2 \rangle = \langle v^2 \rangle/3$, the thermal conductivity can be written

$$\kappa = \frac{1}{3} \operatorname{ncv}^{2} \tau = \frac{1}{3} \operatorname{Cv}^{2} \tau = \frac{1}{3} \operatorname{Cv}^{2}$$
 (50)

where C is the heat capacity per unit volume and $\ell = v\tau$ is the mean free path.

Quantities such as the particle mean free path generally are not useful in a solid. However, one may relate a "phonon gas" to the quantities written down in equation (50).

Phonons may be considered as propagating transverse or longitudinal waves in the solid. The atoms may be pictured as moving in a coordinated fashion about the equilibrium lattice positions under the influence of spring-like restoring forces. The normal mode frequencies for the propagating waves can be described by dispersion curves²⁸ that relate the phonon frequency ω to the phonon wave-vector <u>k</u>. Two types of normal modes appear in these dispersion curves-low frequency acoustic modes which for <u>k</u> = 0 have ω = 0, and high frequency optic modes which for <u>k</u> = 0 have $\omega \neq 0$.

In their particle $aspect^{28}$, phonons are considered to be the quantized unit of lattice vibrations. The displacement and momentum variables for the atom are re-written in terms of phonon creation and destruction operators obtained from a harmonic oscillator Hamiltonian. Thus, the solid can be considered to be equivalent to a large number of phonons each of which travels an average distance ℓ (the phonon mean free path) between interactions.

Equation (50) can be re-written as a sum over the phonon wave-vectors, and then further re-written as an integral over the phonon frequencies using the Debye approximation.

The Debye approximation estimates the actual distribution of the acoustic modes in the solid using $\omega = vk$ (where v is the sound velocity) to describe the dispersion curve up to a cut-off frequency ω_D . The Debye approximation is applicable here because the low-frequency acoustic modes carry much more heat through the solid than the optic modes. If C is the heat capacity of the lattice, v is the sound velocity, and τ is the phonon relaxation time, the thermal conductivity can be written in the Debye approximation as

$$\kappa = \frac{1}{3} \int_{0}^{\omega_{\rm D}} C(\omega) [v(\omega)]^2 \tau(\omega) d\omega$$
 (51)

where the integral is taken over the phonon frequency spectrum up to the Debye frequency $\omega_{\rm D}$.

In the Debye approximation the heat capacity can be written (ω = frequency, f = Planck's constant/2 π , k_B = Boltzmann's constant)²⁸

$$C(\omega) = \frac{3k_B\omega^4}{2\pi^2 v^3} \left(\frac{\pi}{k_BT}\right)^2 \frac{\frac{\hbar\omega/k_BT}{e}}{\frac{e}{\pi\omega/k_BT}-1}^2$$
(52)

The Debye approximation was formulated to give low-temperature results, but the high-temperature form for $C(\omega)$ (using $e^{\mu} \approx 1+\mu$ in equation (52))

$$C(\omega) \approx \frac{3k_B\omega^4}{2\pi^2 v^3} \left(\frac{\hbar}{k_B T}\right)^2 \frac{1}{(\hbar\omega/k_B T)^2} = \frac{3k_B\omega^2}{2\pi^2 v^3}$$
(53)

can be integrated to give the Dulong-Petit rule for the heat capacity C per unit volume at high temperature (T > A)

$$C = \int_{0}^{\omega_{D}} C(\omega) d\omega$$

$$= \frac{3k_{B}}{2\pi^{2}v^{3}} \frac{\omega_{D}^{3}}{3} = \frac{3Nk_{B}}{V}$$
(54)

using²⁸ $\omega_D^3 = 6\pi^2 v^3 N/V$ where N/V is the number of unit cells per unit volume.

As a result the high temperature lattice thermal conductivity can be written (using equations (51) and (53))

$$\kappa = \frac{k_{\rm B}}{2\pi} \int_0^{\omega_{\rm D}} \tau(\omega) \frac{\omega^2}{v} d\omega$$
 (55)

in the Debye approximation. Since v changes very slightly with temperature, the temperature dependence of the relaxation time $\tau(\omega)$ will determine the temperature dependence of κ .

The relaxation time $\tau(\omega)$ is related to the relaxation times $\tau_i(\omega)$ due to different scattering mechanisms through

$$\tau^{-1} = \sum_{i} \tau_{i}^{-1}$$

Thus, the general strategy is to determine the τ_i , and then to write out the thermal conductivity κ .

The T⁻¹ Law

The relaxation time τ_u appropriate to the temperature dependence of non-metals at high temperatures $(T > \theta_D = h\omega_D/k_B)$ has been calculated in many ways^{5,7-9}. The discussion that follows indicates the essential points of some of the calculations^{7,8} by concentrating upon the determination of the temperature dependence of τ_u while ignoring the additional theory required to obtain the magnitude of τ_u .

If N gives the number of normal modes of frequency ω in a solid, and if n is the departure of N from its

equilibrium value N^0 , then the relaxation time can be defined by

$$\frac{dN}{dt}\bigg|_{scatt} = -\frac{n}{\tau_{u}} = -\frac{N-N^{0}}{\tau_{u}}$$
(56)

which gives an exponential decay law to the time rate of change of N due to scattering processes. The derivative $\frac{dN}{dt}$ can be related to transition probabilities obtained scatt from perturbation theory.

The unperturbed Hamiltonian is the harmonic oscillator Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x$$

where p and x are the momentum and displacement of a particle of mass m vibrating at a lattice site with frequency ω . The solution to the unperturbed Hamiltonian can be expressed in terms of the creation and annihilation operators a⁺ and a where

$$a^+ | N > = \sqrt{N+1} | N+1 >$$

$$a | N > = \sqrt{N} | N - 1 >$$

and where the ket vectors |N> represent the wavefunctions corresponding to the Nth energy eigenstate.

The perturbation Hamiltonian is

$$H' = \phi x^3$$

where ϕ is a proportionality constant. If the displacement x is written in terms of the creation and destruction operators (non-essential factors will not be included from here until the end of this section)

 $x \sim a + a^{\dagger}$,

then the perturbation must look like

H' ~
$$(a_1 + a_1^+)(a_2 + a_2^+)(a_3 + a_3^+)$$

~ $a_1 a_2 a_3^+ + a_1^+ a_2^+ a_3^+ + \dots$

where terms like $a_1a_2a_3$ and $a_1^{\dagger}a_2^{\dagger}a_3^{\dagger}$ cannot satisfy conservation of energy. Thus, only three-phonon processes such as the annihilation of two phonons to form a third and the breakdown of one phonon into two other phonons can contribute to the calculation using the perturbation theory.

The transition probability obtained from time-dependent perturbation theory involves the square of the matrix element due to the perturbation. As a result the derivative $\frac{dN}{dt}$ must involve terms like scatt

$$\frac{dN}{dt} \bigg|_{scatt} \sim \left[N_1 N_2 (N_3^{+1}) - (N_1^{+1}) (N_2^{+1}) N_3 \right] \\ \sim \left[N_1 (N_2^{-1} N_3) - N_3 (N_2^{+1}) \right] .$$
(57)

Before this factor can be evaluated, the three-phonon processes must be separated into normal processes (N-processes) and Umklapp processes (U-processes). For both sets of processes energy conservation

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 \tag{58}$$

is observed. However, for N-processes the momenta \underline{k}_i obey

$$\frac{k_1}{2} + \frac{k_2}{2} = \frac{k_3}{2}$$
,

while for U-processes the momenta obey

$$\underline{\mathbf{k}}_1 + \underline{\mathbf{k}}_2 = \underline{\mathbf{k}}_3 + \underline{\mathbf{G}}$$

where \underline{G} is a reciprocal lattice vector. These processes are compared pictorially in Figure 10.

The N-processes, in the absence of other scattering mechanisms, cannot produce any thermal resistance. These processes maintain the equilibrium distribution of the phonons, so that a heat-flow distribution of phonons would also be maintained. The N-processes, although generally ignored mathematically, are important physically because these processes maintain the phonon distribution in which U-processes contribute to the thermal resistance.

In order to evaluate the derivative $\frac{dN}{dt}$ (see equation (58)), one must define the equilibrium distribution

$$N_{i}^{0} = [e^{\hbar \omega_{i}/k_{B}T} - 1]^{-1}$$

and the change from equilibrium

$$n_i = N_i - N_i^0$$

for the k_i mode. So using equation (58), one can write

Figure 10. Normal processes and Umklapp processes.



Umklapp Process



$$\frac{dN_1}{dt} \sim [n_1[N_2^0 - N_3^0] + N_1^0[N_2^0 - N_3^0] - N_3^0[N_2^0 + 1]]$$

where the non-equilibrium part is contained in the term $n_1[N_2^0-N_3^0]$. Using the equilibrium distributions (with $e^{\mu} \approx 1+\mu$) one can write (see equation (57))

$$\frac{1}{\tau_{u}} = -\frac{1}{n_{1}} \frac{dN_{1}}{dt} \sim [N_{2}^{0} - N_{3}^{0}]$$

$$\sim \frac{k_{B}T}{f_{1}} \frac{\omega_{1}}{\omega_{2}\omega_{3}}$$
(59)

where the frequency factor follows from energy conservation (equation (58)).

Finally, all the various factors can be lumped together into one constant D such that

$$\frac{1}{\tau_{\rm u}} = DT \tag{60}$$

and, with constant v,

$$\kappa = \frac{k_B}{2\pi^2 v} \frac{1}{T} \int_0^{\omega} \frac{\omega^2}{D} d\omega \qquad (61)$$

The integral is independent of T so that the lattice thermal conductivity at high temperatures should go as T^{-1} if three-phonon Umklapp scattering is the dominant scattering mechanism.

Other Scattering Mechanisms

Although three-phonon Umklapp scattering dominates the temperature dependence of the thermal conductivity at high temperatures, other contributions due to

a) boundary scattering

b) impurity scattering,

c) four-phonon processes,

d) thermal expansion, and

e) optical phonon scattering

must also be considered.

In order to argue that some of these contributions are negligible at high temperatures, one might assume that at the melting phase transition temperature T_{MELT} the phonon mean free path ℓ is one lattice spacing long. Since $\ell = v\tau$ and $\tau = \frac{1}{DT}$ (see equation (60)), if $T_{MELT} = 840$ K (similar to that for AgI) then at T = 140 K the phonon mean free path will be six lattice spacings.

With this assumption both boundary scattering and impurity scattering can be ignored at high temperatures. Boundary scattering, which refers to phonon scattering from the crystal walls, can become important only if the crystallite size is smaller than the phonon mean free path. For powder a few microns in diameter the phonon mean free path (for the T_{MELT} given above) is much smaller than the powder particle size. Impurity scattering is also negligible. For a sample of 99.9% purity, an impurity will be encountered only once in a thousand atoms, so that the impurities will

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be $\sqrt[3]{1000}$ = 10 lattice spacing apart on the average. For the assumed value of T_{MELT} impurity scattering should not affect high temperature data.

Practically speaking, the Debye temperature θ_D ($\theta_D \approx 120$ K for AgI) usually is the lower limit on the hightemperature region, with both the impurity and boundary scattering of no importance above $\theta_D/5$.

Calculations involving perturbation Hamiltonians like

$$H'' = \psi x^4$$

lead to a consideration of four-phonon processes. Ideally, the four-phonon relaxation time τ_4 will have 50

a) a temperature dependence $\frac{1}{\tau_A} = D'T^2$, and

b) a much smaller magnitude than the relaxation time

 $\boldsymbol{\tau}_n$ due to three-phonon Umklapp processes.

In most non-metals no evidence of a T^{-2} contribution appears in the high-temperature thermal conductivity data. A few exceptions have been found, and are listed in the references to the paper by Klemens and Ecsedy⁵⁰.

The contributions due to thermal expansion and to optical phonon scattering also affect the thermal conductivity in this temperature range. These are considered in some detail in the following sections.

Thermal Expansion Correction

To determine the effect of volume changes upon the temperature dependence of the thermal conductivity, one may write

$$\kappa = \frac{G(V)}{T} = \frac{M}{T^{1+\varepsilon}TH}$$
(62)

where G(V) is a volume dependent proportionality constant, M is a volume and temperature independent quantity, and ε_{TH} is a correction to the temperature power law due to the volume dependence. The assumption here is that, since V = V(T), the coefficient determined for the T⁻¹ law (equation (62)) will have a hidden temperature dependence.

To determine ε_{TH} , one first takes temperature derivatives of equation (62):

$$\frac{d\kappa}{dT} = -\frac{\kappa}{T} (1+\varepsilon_{TH}) = -\frac{\kappa}{T} + \frac{1}{T} \frac{dG(V)}{d\ell n V} \frac{d\ell n V}{dT} .$$
(63)

Using

$$3\alpha = \frac{d\ell n\kappa}{dT}$$

where α is the coefficient of linear expansion and defining $g \;=\; -\; \frac{d\ell n\kappa}{d\ell n V} \quad,$

equation (63) can be manipulated (using equation 62) to give

$$\varepsilon_{\rm TH} = -\frac{1}{\kappa} \frac{dG(V)}{d\ell n V} \frac{d\ell n V}{dT} = -\frac{3\alpha}{\kappa} \frac{dG(V)}{d\ell n V}$$
$$= -\frac{3\alpha}{\kappa} \frac{d(\kappa T)}{d\ell n V} = 3\alpha T \left(-\frac{\partial \ell n \kappa}{\partial \ell n V}\right)$$
$$= 3\alpha g T \qquad . \tag{64}$$

The correction ε_{TH} to the temperature dependence of the thermal conductivity is small both at low temperatures and

for materials with a small thermal expansion if g is not too large.

Optic Phonon Scattering

Optic phonons contribute to the thermal conductivity not by carrying heat (from the phonon dispersion curves, $v = \frac{d\omega}{d\kappa}$ is near zero²⁸) but by scattering acoustic phonons. This effect can be approximated in the following way⁶.

One assumes that the thermal resistivity $W = \frac{1}{\kappa}$ is proportional to the number of acoustic phonons scattered by each set of modes, and that this scattering is proportional to the total energy in each set of modes.

Since the heat capacity at high temperatures is constant (see equation (54)) one can write for the acoustic modes

$$E_{A} = N_{A}k_{B}T$$
(65)

where E_A is the total energy in the acoustic modes and N_A is the number of acoustic phonons. If an Einstein oscillator approximation is used for the optic modes, then

$$E_0 = N_0 \hbar \omega_0 \left(\frac{1}{\frac{h\omega_0 / k_B T}{e} - 1} \right)$$
(66)

where E_0 is the total energy of the optic modes, N_0 is the number of optic phonons, and ω_0 is the maximum optic phonon frequency. The expression for E_0 (equation (66)) can be re-written in terms of

$$x_0 = \frac{\pi \omega_0}{k_B T} = \frac{\theta_{op}}{T}$$
$$Z = \frac{x_0}{e^{\alpha_0} - 1}$$

to give

$$E_0 = N_0 k_B T \frac{x_0}{e^{0} - 1}$$
$$= N_0 k_B T Z$$
(67)

If one assigns f as the ratio of the number of acoustic phonons scattered by acoustic phonons to the total number of scattered acoustic phonons, and takes η as a proportionality constant, then one can write

$$W = f\eta T + (1-f)\eta TZ$$
(68)

where the first term has the temperature dependence of E_A and the second term of E_0 . If S is defined to be the ratio of the number of acoustic phonons scattered by optic phonons to the number of acoustic phonons scattered by acoustic phonons, then $S = \frac{1-f}{f}$ and $f = \frac{1}{1+S}$. Equation (68) may be written using this definition to give

$$W = \eta T \frac{1+SZ}{1+S} = \eta T^{1+\varepsilon} op$$
(69)

where ε_{op} is the correction to the temperature dependence due to optic phonon scattering.

Through differentiation of equation (69) one obtains

$$\frac{\partial \ell n W}{\partial \ell n T} = 1 + \epsilon_{op} = 1 + \frac{ST}{1+SZ} \frac{\partial Z}{\partial T}$$

which gives

$$\varepsilon_{\rm op} = \frac{\rm ST}{1+\rm SZ} \frac{\partial Z}{\partial T} = \frac{\rm SZ}{1+\rm SZ} (Z+x-1) \quad . \tag{70}$$

This correction to the power law for the thermal conductivity is a complicated function of the temperature and of the maximum optic mode frequency.

Minimum Thermal Conductivity

At high temperatures the thermal conductivity of nonmetals becomes temperature independent. This region of minimum thermal conductivity occurs when the phonon mean free path reaches its minimum value. The discussion will follow Slack⁶, except that some numerical factors will be changed to insure clarity in the discussion.

The minimum thermal conductivity κ_{Min} is obtained from the kinetic theory expression for the thermal conductivity (see equation (50))

$$\kappa = \frac{1}{3} C v \ell$$

by substituting appropriate values for the parameters. If the number of atoms per unit cell is n = 2, then both optic and acoustic phonons must be considered. Since the heat capacity C can be written (see equation (54))

$$C = \frac{3k_B}{2\delta^3}$$

where δ^3 is the volume per atom, the minimum thermal

conductivity κ_{Min} can be expressed as

$$\kappa_{\rm Min} = \frac{k_{\rm B}}{2\delta^3} \left(v_{\rm A} \ell_{\rm A} + v_0 \ell_0 \right) \tag{71}$$

where the subscripts A and O refer to acoustic phonons and optic phonons respectively.

The acoustic phonon velocity v_A can be set equal to the sound velocity v. The acoustic phonon mean free path ℓ_A can be written in terms of the sound velocity v and the Debye frequency $v_D = \omega_D/2\pi$:

$$\ell_{\rm A} = v/v_{\rm D} \qquad (72)$$

For the optic phonons, the mean free path ℓ_0 is taken to be δ and the frequency $v_0 = \omega_0/2\pi$ to be the largest optic mode frequency. As a result the optic phonon velocity v_0 can be expressed as

$$\mathbf{v}_0 = \mathbf{v}_0 \delta \quad . \tag{73}.$$

Finally the minimum thermal conductivity κ_{Min} can be expressed as

$$\kappa_{\text{Min}} = \frac{1}{2} \frac{k_{\text{B}}}{\delta^3} \left[(\mathbf{v}) (\frac{\mathbf{v}}{\nu_{\text{D}}}) + (\nu_{0}\delta)(\delta) \right]$$
$$= \frac{k_{\text{B}} \mathbf{v}^2}{2\delta^3 \nu_{\text{D}}} + \frac{k_{\text{B}} \nu_{0}}{2\delta}$$
(74)

for a system with n = 2 atoms per unit cell.

Thermal Conductivity: Superionic Conductors

Two theories out of the several available treatments of the transport properties of superionic conductors deal with the thermal conductivity--the hydrodynamic model^{26,51} and the free-ion model⁵².

The hydrodynamic theory considers the collective excitations of a material at low frequencies and long wavelengths. The idea is to look at a slowly changing system, to treat the system as if it were in local thermal equilibrium, and finally to write the variations of the system in terms of the local thermodynamic variables and the transport coefficients. One obtains time-dependent correlation functions which can be related directly to the scattering crosssections for neutrons and photons. Although the thermal conductivity is used as a parameter in the calculation, no way of obtaining κ from the scattering data exists. It is possible only to verify that κ has the correct order of magnitude (Zeyher⁵¹ uses a T⁻³ dependence for κ to obtain results from his calculations).

By contrast the free-ion theory of Rice and Roth⁵² derives an explicit expression for thermal conductivity. The details of this model are presented in the next section.

The Free-Ion Model

The mobile ions in the model of Rice and Roth⁵² are treated as free ions which have been excited above an energy gap ε_0 in the superionic conductor. The threshold energy ε_0

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is the minimum energy for ion motion in the solid, and the energy spectrum for ion energy $\varepsilon_m \ge \varepsilon_0$ is continuous while for $\varepsilon_m < \varepsilon_0$ it is zero. The ion energy ε_m can be written in terms of an ion velocity v_m such that $\varepsilon_m = \frac{1}{2} M v_m^2$ where M is the ion mass. The ions travel for a time τ_m before they de-activate, which gives an ion mean free path $\ell_m = v_m \tau_m$.

For each of the free-ion states of energy ε_m one can define a thermal occupation n_m such that the total number of N of thermally excited free-ion states per unit volume can be expressed by

$$N = \frac{1}{V} \sum_{m} \int \frac{d\Omega}{4\pi} n_{m}$$
(75)

where V is the volume of the conductor and Ω is a solid angle. This statement can be refined by defining a densityof-states function $g(\varepsilon_m)$ such that $g(\varepsilon_m)\delta\varepsilon_m$ gives the number of free-ion states per unit volume between ε_m and $\varepsilon_m + \delta\varepsilon_m$. In this case the density-of-states function is

$$g(\varepsilon_{m}) = \begin{cases} 0 & \varepsilon_{m} < \varepsilon_{0} \\ \vdots & \vdots \\ \frac{n}{k_{B}T} & \varepsilon_{m} \ge \varepsilon_{0} \end{cases}$$
(76)

where n is the number of potentially mobile ions per unit volume.

Expressions for the ionic current (Ze = charge of the conducting ion)

$$\overline{I}(\overline{r},t) = Ze \int_{0}^{\infty} d\varepsilon_{m} g(\varepsilon_{m}) \int \frac{d\Omega}{4\pi} \overline{v}_{m} n_{m}(\overline{r},t)$$
(77)

and the heat flux

$$\bar{q}_{\rm H}(\bar{r},t) = \int_0^\infty d\varepsilon_{\rm m} g(\varepsilon_{\rm m}) \int \frac{d\Omega}{4\pi} \varepsilon_{\rm m} \bar{v}_{\rm m} n_{\rm m}(\bar{r},t)$$
(78)

can be written if n_m is a function of position \bar{r} and time t unless the system is at equilibrium. At equilibrium, both \bar{I} and \bar{q}_H will vanish because n_m will be isotropic and so the integral over $d\Omega$ will vanish. The quantities \bar{I} and \bar{q}_H appear in the equations for the ionic transport coefficients:

$$\bar{I} = \sigma_{\tau} \bar{E}$$
(79a)

$$\bar{\mathbf{E}} = -\theta \bar{\nabla} \mathbf{T} \tag{79b}$$

$$\bar{q}_{TOT} = \kappa_L \bar{\nabla}T + \bar{q}_H = -(\kappa_L + \kappa_I)\bar{\nabla}T$$
(79c)

where σ_{I} is the ionic conductivity, \bar{E} is the applied electric field, θ is the thermopower, $\bar{\nabla}T$ is a temperature gradient, \bar{q}_{TOT} is the total heat flux, κ_{L} is the lattice thermal conductivity, and κ_{I} is the ionic thermal conductivity.

The finite lifetime τ_m for the free-ion states can be introduced by writing a Boltzmann transport equation

$$\frac{\partial n_{m}(\bar{r},T)}{\partial t} + \bar{v}_{m} \cdot \frac{\partial n_{m}(\bar{r},t)}{\partial \bar{r}} = -\frac{n_{m}(\bar{r},t) - n_{m}^{0}}{\tau_{m}}$$
(80)

where the left-hand side describes the evolution of $n_m(\bar{r},t)$ due to the propagation of the free-ions and the right-hand side describes the decay of the free-ion states due to interaction with the solid.

For weak $\overline{E}(\overline{r})$ and small uniform $\overline{\nabla}T(\overline{r})$ the thermal occupation n_m can be written

$$n_{\rm m}(\bar{\mathbf{r}}) = n_{\rm m}^0(\bar{\mathbf{r}}) + \delta n_{\rm m}$$
(81)

where $\delta n_m << n_m^0(\bar{r})$ and where (using $\phi(\bar{r})$ defined by $\bar{E} = -\bar{\nabla}\phi$)

$$n_{\rm m}^0(\bar{\mathbf{r}}) = \exp\{-[\varepsilon_{\rm m} + Ze\phi(\bar{\mathbf{r}})]/k_{\rm B}T(\bar{\mathbf{r}})\} \qquad (82)$$

If equations (81) and (82) are substituted into the Boltzmann transport equation (equation (80)), then $\frac{\partial n_m}{\partial t} = 0$ and

$$\delta n_{\rm m} = n_{\rm m}^0 \tau_{\rm m} \overline{v}_{\rm m} \cdot \left[\mathbb{Z} e \overline{E} + \frac{\varepsilon_{\rm m}}{T} \overline{\nabla} T \right] \frac{1}{k_{\rm B} T}$$
(83)

The ionic current \overline{I} (see equation (77)) calculated from $n_{m}(\overline{r})$ defined by equations (81), (82), and (83) can be expressed as

$$\overline{\mathbf{I}} = \overrightarrow{\sigma}_{\mathbf{I}} \cdot \overline{\mathbf{E}} + \overrightarrow{\sigma}_{\mathbf{T}} \cdot \overline{\nabla}\mathbf{T}$$

where $\overrightarrow{\sigma}_{I}$ and $\overrightarrow{\sigma}_{T}$ are the tensors

$$\vec{\sigma}_{I} = \frac{(Ze)^{2}}{k_{B}T} \int_{0}^{\infty} d\varepsilon_{m} g(\varepsilon_{m}) \int \frac{d\Omega}{4\pi} n_{m}^{0} \bar{v}_{m} \bar{v}_{m} \tau_{m}$$
(84)

$$\vec{\sigma}_{T} = \frac{(Ze)}{k_{B}T^{2}} \int_{0}^{\infty} d\varepsilon_{m} g(\varepsilon_{m}) \int \frac{d\Omega}{4\pi} n_{m}^{0} \tau_{m} \varepsilon_{m} \bar{v}_{m} \bar{v}_{m}$$
(85)

The trace of the tensor $\overleftrightarrow{\sigma}_{I}$ (equation (84)) can be taken to give the ionic conductivity

$$\sigma_{I} = \frac{1}{3} \frac{\left(\frac{Ze}{k_{B}T}\right)^{2}}{k_{B}T} \langle v_{m}\ell_{m} \rangle$$
(86)

under isotropic conditions. The average $\langle f_m \rangle$ for a function f_m can be expressed as

$$\langle f_{m} \rangle = \int_{0}^{\infty} d\varepsilon_{m} g(\varepsilon_{m}) f_{m} e^{-\varepsilon_{m}/k_{B}T}$$
 (87)

The ionic thermal conductivity can be obtained by calculating the heat flux $\bar{q}_{\rm H}$ (see equation (78)) using the expression for $n_{\rm m}$ (equation (81), (82), and (83)) and by taking a trace similar to that for the ionic conductivity above (equation (86)). One obtains

$$\kappa_{I} = \frac{1}{3} \frac{\langle \varepsilon_{m}^{2} v_{m} \ell_{m} \rangle}{k_{B} T^{2}} \left\{ 1 - \frac{\langle \varepsilon_{m} v_{m} \ell_{m} \rangle^{2}}{\langle v_{m} \ell_{m} \rangle \langle \varepsilon_{m}^{2} v_{m} \ell_{m} \rangle} \right\}.$$
(88)

To evaluate the averages (equation (87)) the form of $g(\epsilon_m)$ (equation (76)) is used to give

$$\langle f_{m} \rangle = \frac{n}{k_{B}T} \int_{\varepsilon_{0}}^{\infty} d\varepsilon_{m} f_{m} e^{-\varepsilon_{m}/k_{B}T}$$
 (89)

which can be repeatedly integrated by parts to give

$$\langle f_{m} \rangle = nf(\varepsilon_{0})e^{-\varepsilon_{0}/k_{B}T} \left\{ 1 + C_{1}\left(\frac{k_{B}T}{\varepsilon_{0}}\right) + \dots + C_{N}\left(\frac{k_{B}T}{\varepsilon_{0}}\right)^{N} + \dots \right\}$$
(90)

where the coefficients C_N are

$$C_{N} = \left[\frac{\varepsilon_{0}^{N}}{f(\varepsilon_{0})}\right] \left[\frac{d^{N}f(\varepsilon)}{d\varepsilon^{N}}\right]_{\varepsilon=\varepsilon_{0}}$$
(91)

The expansion for $\langle f_m \rangle$ (equation 90) can be terminated to

$$\langle f_{m} \rangle = nf(\varepsilon_{0})e^{-\varepsilon_{0}/k_{B}T}$$
 (92)

if the gap energy ε_0 is much larger than the thermal energy k_B^T . Rice and Roth⁵² use this approximation in their calculations because it allows the transport coefficients to be evaluated. They indicate that the results are applicable only at low temperatures (T << ε_0/k_B^T).

Using the simple statement for the averages (equation (92)), one can write

$$\sigma_{I} = \frac{1}{3} \frac{(Ze)^{2}}{k_{B}T} nv_{0}\ell_{0}e^{-\epsilon_{0}/k_{B}T}$$

Since the simple statement for the averages gives a zero κ_{I} , the next term in the expansion (see equations (90) and (91)) is required. One obtains

$$\kappa_{I} = \frac{\alpha'}{2} n k_{B} v_{0} \ell_{0} \frac{\varepsilon_{0}}{k_{B}T} e^{-\varepsilon_{0}/k_{B}T}$$
$$= \sigma_{I} L_{I}$$

where

$$\alpha' = 1 + \frac{2\varepsilon_0}{3\ell_0} \left(\frac{d\ell(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}$$
$$L_I = \frac{3\alpha' k_B \varepsilon_0}{2Z^2 e^2} \quad .$$

As a result, the free-ion model suggests that the ionic thermal conductivity should have the same sort of temperature dependence as the ionic conductivity. The total thermal conductivity of the superionic phase should be the sum of the lattice thermal conductivity κ_L and the ionic thermal conductivity κ_T .

CHAPTER V

APPARATUS AND MEASUREMENT

To measure the thermal conductivity of the samples, one must

- a) prepare the sample with its heater wire,
- b) compress the sample to its final form,
- c) control the temperature of the sample,
- d) create current pulses through the heater wire within the sample, and
- e) measure the potential difference between two points on the heater wire and so obtain the temperature increase of the heater wire.

Making the Sample

The initial step in the manufacture of a sample ensemble was the creation of a suitable heater wire from thin Nickel wire (diameter d \approx 0.1 mm). The Nickel wire used was made a) by drawing larger diameter MARZ grade Nickel wire⁵³ through diamond dies, and b) by then annealing the smaller diameter wire. Precut pieces of this wire were spotwelded together to form a heater wire approximately 50 mm long with four 10 mm long leads. Larger diameter wire

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(d' \approx 0.2 mm) was attached to each of the four leads in order to withstand the stresses of assembly and compression.

A second step was the manufacture of thermocouples in order to measure the sample temperature. Two iron-constantan thermocouples⁵⁴ were spotwelded together, and a teflon sheath was fitted over each exposed spotweld. Thermocouples used in preliminary runs did not have such protection and corroded during data-taking.

Finally, sample disks were made by compressing a premeasured amount of sample powder to ~1 kbar in the sample cell. These disks, about 3 mm thick and 30 mm in diameter, were strong enough to permit both the removal of material from the circumference of the disk (in order to ease the insertion of the completed sample ensemble into the sample cell) and drilling through the disks for the thermocouple and heater-wire leads.

Figure 11 is an exploded diagram of the assembled sample ensemble. The notations TOP and BOTTOM refer to the orientation of the sample during data-taking.

Sample Cell

The sample cell (Figure 12) is used for three purposes: a) to compress the sample disks from powder;

b) to compress the sample ensemble; and

c) to act as a sample cell during the data-taking.

The sample ensemble compression insures both a single-crystallike density for the material⁵⁵ and close contact between the heater wire and the sample material.

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Figure 11. An exploded diagram of the sample ensemble.



Figure 12. Cross-sectional view of the sample cell and of the pressure-related pieces.



The pieces shown in Figure 12 are axially symmetric about the pressure axis except for the cell body. This piece has four slots on its bottom in order to preserve the wire leads during compression as well as two holes for pins in order to prevent movement of the assembled sample cell with respect to its base (the bottom brass plate described in a later section).

Three materials were used to build the sample cell:

- a) type 304 stainless steel for the pistons and the cell body;
- b) Teflon for the disks and for one pressure ring; and
- c) a glass-filled phenolic for the rest of the pressure rings.

The design of the sample cell follows that of Andersson and Bäckström⁴⁷, and has been used to pressures of 5 kbar. The particular dimensions of the sample cell were restricted by the maximum pressure as well as the sample size. The outer diameter of the cell body was computed by multiplication of the inner diameter by a safety factor of 3.5⁵⁶.

Sample Placement

Centering the sample ensemble axially within the cell and attaching leads that do not break or short under pressure figure significantly in run preparation. A procedure for these tasks follows.

1) Invert the cell body with the top piston protruding

 $\sim \frac{3}{4}$ inch onto any form that will maintain this relative position.

- 2) Fit the inverted sample ensemble (Figure 11) into the central bore of the cell body (sample ensemble TOP toward cell TOP) and press the sample ensemble carefully downward until contact is made with the top piston.
- 3) Place the top phenolic ring and the teflon ring into the central bore of the cell body.
- 4) Spotweld leads to the heater wire (and to the thermocouples if needed). Use copper wire (AWG34) for the current leads and enameled nickel wire⁵⁷ for the potential leads.
- 5) Carefully press all leads into position and place the bottom phenolic ring into position. The leads last longer if equally spaced around the ring, and the spotwelds break less often if the lead from the sample and the lead to the outside are laid side-by-side.
- 6) Center the thin teflon disk over the spotwelds and leads, and then slowly drop the bottom piston into the central bore of the cell body.
- 7) Gather two leads at a time and pull them into a slot on the cell body bottom. Tug on the leads enough to remove excess wire from the annulus between the bottom piston and the cell body.

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8) Finally, position some teflon spacers (~0.006 inch thick) within the annulus to minimize any rocking motion of the bottom piston.

Experimental Set-Ups

In order to produce the sample disks and to compress the sample ensemble, pressure was applied to the sample cell using a hydraulic ram⁵⁸ confined within a steel rack (see Figure 13). Brass plates were used where high stress occurred--above and below the sample cell and between the lower beams of the rack. Transite plates slowed heat flow along the pressure axis.

The design of the bottom brass plate (see Figure 14) solves several problems. The four slots, which are continued in the bottom transite pieces, channel the wire leads away from the sample cell at a safe distance from the refractory oven elements in the high temperature set up. The two holes line up with the holes in the bottom of the cell body, and when the cell body and the bottom brass plate are connected with copper pins any rocking motion of the bottom piston is prevented. Finally, the four radial screw holes allow handles to be attached to the bottom brass plate for the transport of the sample cell and the bottom brass plate. Such transportation requires flipping the sample cell/bottom brass plate to the run orientation (TOP up). Figure 13. Pressure set-up for pelletizing. Internal set-up for high-temperature runs.


Figure 14. Top view of bottom brass plate.



The manufacture of the sample disks required only the set up of Figure 13. However, sample ensemble compression usually took place immediately before a high-temperature run. The set up for a high-temperature run required in addition to the set up of Figure 13 both some quartz wool packing to protect the leads and fitting the refractory oven around the column of plates and sample cell before positioning the hydraulic ram. The refractory oven (see Figure 15) essentially consists of two semi-circular refractories (wound with heating coils)⁵⁹ surrounded by firebrick. The high-temperature system easily reached the temperature of 500 K needed for our measurements.

During sample ensemble compression (pressure $p_{MAX} \approx 5$ kbar) the electronics were turned on in order to monitor the wires. During compression the sample warmed causing a noticeable rise in the voltage across the heater wire. Both compression and de-compression were done slowly to preserve the insulation on the leads and so to prevent shorts to the stainless steel cell body.

For the low-temperature data, a slightly different arrangement was used (see Figure 16). Usually no sample compression was required since low-temperature data-taking followed a high-temperature run.

The coil is a length of $\frac{3}{8}$ thick square copper tubing wound helically with an inner coating of soft solder. A layer of vacuum grease (Dow Corning silicone lubricant) helped to make good contact between the coil and the cell body and aided in slipping the coil in place. The tight Figure 15. Oven (bolts and electrical connection not shown).



Figure 16. Low-temperature set-up.



fit of the coil required that a plastic mallet be used to pummel the coil into final position on the sample cell. To protect the leads the sample cell was inverted during the "delicate" procedure.

The sample cell was lowered into the foam bucket using the detachable handles for the bottom brass plate. After the hydraulic ram was positioned on top of the sample cell, quartz wool was stuffed into open spaces in the bucket in order to keep any water condensed by the ram out of the foam bucket.

The cooling agent, cold gaseous nitrogen, was boiled off from inside a liquid nitrogen storage dewar using a 100 Ω power resistor hooked to a variac for a heat source. The gas was transferred to the coil through a short length of rubber hose.

Cooling by means of liquid nitrogen poured into the foam bucket was tried for all the samples. The effectiveness of this procedure was limited since

- a) the thermocouples indicated temperatures several degrees below 77 K,
- b) heat pulse reflection destroyed the linear portion of the $\Delta T/\dot{Q}$ vs. lnt plots at low temperatures, and
- c) any data obtained after such cooling did not match earlier data.

No data taken below 120 K was found to be useful.

Hot and cold running water were used sometimes to obtain additional data near room temperature using the low-temperature set up. Data could be obtained between 285 K and 325 K.

Nickel Wire Calibration

In order to determine accurately the small temperature excursions of the heater wire, the resistivity of the wire as a function of the temperature was determined. For this calibration a nickel wire sample ($\ell_{wire} = 13.35$ cm; $d_{wire} = 0.012$ cm) was mounted in a small vycor tube using G.E. varnish. An iron-constantan thermocouple was mounted inside this tube in contact with the wire sample.

The sample resistance was determined from 77 K to 300 K using a cryostat provided by Dr. P. A. Schroeder. The current was supplied by a Helwett-Packard 6920B meter calibrator while the voltage across the sample was measured using a Keithley 180 Digital Nanovoltmeter. A by-product of the low-temperature calibration of the nickel wire was the simultaneous calibration of the thermocouple against a Platinium resistance thermometer. The thermocouple read approximately 1.5 K high near 77 K, but only ~0.5 K high above 150 K.

The high-temperature calibration (290 K to 540 K) was determined with the same sample and electronics. The sample temperature was maintained using an oven. The sample was held by a piece of firebrick. Figure 17 shows the entire calibration from 77 K to 500 K.

The calibration curve was fitted to a ninth order polynomial using the FORTRAN IV program GOATFIT (see Appendix B) on the CDC 7600 computer.

Figure 17. Nickel wire calibration.

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Electronics

The experimental setup for the electronics and the computer is shown in Figure 18. The setup can be divided into two sections:

- a) temperature control, including the thermocouples and their electronics; and
- b) data-taking, which is overseen by the PDP-8 mini-computer.

The major tasks for the PDP-8 are considered below (the programs are found in Appendix B).

First, the PDP-8 controls the current pulse generated by the power supply (a Hewlett-Packard 6259B DC Power Supply). The mini-computer sends to the power supply a timed 10 volt pulse which regulates the length of the output current pulse. Hardwire programming on the back panel of the power supply--a variable voltage divider for the input, a sensing resistor with the output--converts the mini-computer voltage to a constant current level.

Second, the PDP-8 collects the voltage readings from the DVM (a Dana Digital Multimeter Model 5900) through an interface. The inferface was designed and constructed in the electronics shop by D. Edmunds with input from M. Haerle. The software which runs this portion of the experiment (see Appendix B) was originally written by D. Edmunds, but has been modified by the author and contains some contributions from M. Haerle. The DVM/interface system could measure either the voltage across a 1 Ω power resistor (in order to Figure 18. Circuit diagram.



measure the current) or the potential difference across the heater wire, and collected twenty readings per second during the current pulse.

Both of these tasks, as well as the storing of data files on disk, were contained in the FORTRAN II data-taking program. Other tasks were undertaken by a FORTRAN IV analysis program which

- a) generated an initial resistance R_0 by extrapolation from the first five data points,
- b) calculated the temperature differences using R_0 and the ninth order polynomial fit corrected to the heater wire dimensions,
- c) displayed the $\Delta T/\dot{Q}$ vs. lnt data,
- d) permitted the removal of spurious data points (such as the points that are due to heat pulse reflection from the finite outer boundary), and
- e) calculated the thermal conductivity and χ^2 using a least squares fit, and displayed the differences between the actual data and the fit.

Data Taking

In order to relate the electronics to the other apparatus a summary of the data-taking procedure follows.

 The temperature controlling variac was adjusted to give a temperature drift of ~8 K/hr by setting the variac at the voltage for an equilibrium temperature ~30 K ahead in the drift direction.

- 2) The two thermocouples were monitored to judge the temperature drift and to insure that their difference was 1 K or less. Larger differences indicated thermal non-equilibrium.
- 3) The current could be varied between 0.18 Amp and 1.0 Amp using the resistive pot in the voltage divider circuit on the power supply. This pot was adjusted to give a maximum temperature excursion near 1.6 K.
- 4) Using the FORTRAN II data-taking program:
 - a) a set of voltages across the 1 Ω resistor were taken in order to measure the current;
 - b) a set of voltages from the heater wire were measured in order to monitor the temperature excursion; and
 - c) the heater wire voltages and the parameters (including the temperature and the current) were written onto the disk for storage.
- 5) The data was analyzed with the FORTRAN IV analysis program to give the thermal conductivity κ . Two sets of $\Delta T/\dot{Q}$ data points were eliminated consistently during the analysis:
 - a) the initial curved section of the data due to the heat capacity of the wire; and
 - b) the upward curving section towards the end of the data due to heat pulse reflection from the finite outer boundary (especially important at low temperatures).

A typical set of $\Delta T/\dot{Q}$ vs. *lnt* data is shown in Figure 19.

System Calibration

In order to verify the accuracy and precision of the total system it was calibrated against known materials. The system calibration proceeded in several steps.

First, the thermal conductivity of glycerol at room temperature was measured to test the electronics without computer programs. The data obtained was not analyzed by computer but rather was analyzed by plotting numbers from an x-y plotter trace. The value of 0.24 W/mK obtained by such data manipulation was near the value of 0.29 W/mK obtained by Sandberg, et al. 60 Some of the difference between the two numbers could be due to absorbed water in the glycerol.

Second, the thermal conductivity of teflon was measured as a function of pressure and compared to the data of Andersson and Bäckström⁴⁷. The pressure was measured using a resistance pressure gauge consisting of Manganin wire wound on a teflon form. This gauge was substituted for one of the thermocouples during these pressure runs. One set of the data (see Figure 20) indicates the agreement with the data of Andersson and Bäckström.

There are two difficulties with this data. First, the sample was not under hydrostatic pressure. Second, continual compression and decompression destroyed the wire leads. This last problem was due to the wire rubbing

Figure 19. A typical set of $\Delta T/\dot{Q}$ vs. Lnt data.

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Figure 20. The thermal conductivity of teflon (compared to data from Andersson and $B\ddot{a}ckstr\ddot{o}m^{47}$).



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against surfaces during the pressure cycles and shorting to the metal cell body.

As a final calibration, the thermal conductivity κ' of NH₄Cl was measured as a function of the temperature T. The data was measured at a pressure of ~0.8 kbar and fits the line (see Figure 21)

 $ln\kappa' = 6.882 - 1.167 lnT$.

The standard deviation of the points about this fit is about 3%. The data of Ross and Sandberg¹⁴ fits the line

 $ln\kappa' = 6.219 - 1.049 lnT$

for data taken between 250 K and 298 K at ~0.5 kbar. The data for the two curves meet at 300 K and differ by only 1%.

AgI Sample Preparation

Silver Iodide may exist as either stable β -AgI or metastable Y-AgI below the phase transition at 420 K. Metastable Y-AgI forms under extremes of pressure such a occur during powdering and pelletizing³⁴. Since both of these techniques are used to prepare the sample disks, any AgI sample must be considered to be primarily Y-AgI unless it is converted to β -AgI by heat treatment.

To obtain the β -AgI sample used in the experiments a pressed powder compact was annealled <u>in situ</u> between 400 K and 420 K for one week³⁵. By the procedure the material in the sample was changed to greater than 95% β -AgI.

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Figure 21. The thermal conductivity of NH_4C\ell (compared to data from Ross and Sandberg<sup>14</sup>).
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AgI0.96^{Br}0.04 Sample Preparation

The sample material containing AgI + 4 atomic percent AgBr (written $AgI_{0.96}Br_{0.04}$) was prepared by the following procedure:

- a) appropriate amounts of 99.999% AgBr and 99.999% AgI were mixed, and subsequently sealed within coaxial vycor tubes evacuated to 10^{-4} torr;
- b) the system was heated in a furnace to near 900 Kin order to melt both the AgI and the AgBr;
- c) the melt was shaken vigorously within the furnace using a wire connected to a loop on the outer vycor tube; and

d) the material was cooled slowly to room temperature. The solid at room temperature was purplish on the outside and nearly the same yellow as AgI on the inside.

Two items of information are needed in order to understand the sample preparation. First, since the sample material expands as it cools both through and below the phase transition, the inner vycor tube shatters. Two vycor tubes were required in order to prevent contamination of the sample material. Second, since AgI dissolves up to 5 atomic percent AgBr at room temperature, a sample with proportionally less AgBr will have the bromine ions well distributed throughout the sample. As a result, the sample does not need to be quenched.

$PyAg_5I_6$ Sample Preparation

The sample preparation for the sample material PyAg₅I₆ begins with the manufacture of the component compound PyI. PyI precipitates from a stoichiometric mixture of HI and pyridine in the form of white flakes. This precipitate must be re-crystallized several times by dissolving the flakes in hot ethanol and cooling the ethanol/PyI solution. The re-crystallizations remove any leftover pyridine and HI.

The $PyAg_5I_6$ sample material was made in the following way:

- a) stoichiometric amounts of PyI and AgI were ground together, compressed into small pellets, and sealed in an evacuated vycor tube;
- b) this sample system was annealled near 125^oC for 12-16 hours;
- c) the ionic conductivity of the pellets was measured, and as long as the ionic conductivity continued to increase strongly, the pellets were crushed and steps a) through c) were repeated.

Typically the ionic conductivity of the $PyAg_5I_6$ samples leveled off after 5-6 anneals at values about an order of magnitude below the reported value²⁰ of $(8)(10^{-2})\Omega^{-1}$ cm⁻¹ (except for one sample that had an ionic conductivity of $(1.3)(10^{-2})\Omega^{-1}$ cm⁻¹). The low ionic conductivity may have been due to:

a) decomposition (the decomposition temperature is 440 K 20);

- b) water and oxidation;
- c) excess reactants; and
- d) the formation of $Py_5^{Ag}18^{I}23$.

The measurements of the ionic conductivity suggest that the samples of $PyAg_5I_6$ are below the quality of the other samples.

CHAPTER VI

DATA AND INTERPRETATION

The measurements of the thermal conductivity and the interpretation of the data are presented in this section. The samples at room temperature consisted of:

- a) β -AgI
- b) Y-AgI
- c) β -AgI with four atomic percent AgBr; and
- d) predominantly PyAg₅I₆.

The measurements were taken between 120 K and 500 K. Since

 $\kappa = C_0 T^{-\varepsilon}$

where C_0 is a constant, these data are plotted on a $ln\kappa$ vs. lnT graph in order to determine the temperature exponent ε from the slope of the plotted data.

β-AgI

The thermal conductivity results (see Figure 22) for one sample of 99.999% AgI predominantly in the β -phase at room temperature show three linear regions in the thermal conductivity:

a) region I between 120 K and 180 K where $\kappa \sim T^{-1.3\pm0.1}$; Figure 22. The thermal conductivity of $\beta\text{-AgI}.$

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- b) region II between 300 K and 420 K where $\kappa \sim T^{-1.8\pm0.1}$; and
- c) region III above 420 K where $\kappa \sim T^{+0.5\pm0.1}$.

All of region III lies above the phase transition at 420 K and corresponds to superionic α -AgI. Regions I and II and the intermediate curving region correspond to stable β -AgI.

Two sets of data are shown within region II:

- a) the first set of data (•) taken between the anneal temperature and room temperature, and then through the phase transition at 420 K; and
- b) the second set of data (•) taken while cooling from the phase transition at 420 K after taking the α -AgI data.

The latter set of points have slightly lower values of the thermal conductivity compared to the freshly annealed sample since no pressure was placed on the sample during the phase transition at 420 K. A 5% volume increase occurs as AgI is cooled through the transition, so that either the heater wire pulled away from the sample material or the material density was less for the second set of data (\bullet). In any case, the effect was small so that no correcting compression was desirable. Had such a compression been used, it could have changed some significant fraction of the β -AgI to γ -AgI.

Interpretation of the β -AgI Data

If the temperature dependence of the thermal conductivity is written as $\kappa = CT^{-\varepsilon}$, three processes should contribute to the exponent $\varepsilon = \varepsilon_u + \varepsilon_{th} + \varepsilon_{op}$ for the normal solid:

- a) three phonon Umklapp scattering gives $\varepsilon_u = 1$ (equation (61));
- b) thermal expansion gives $\varepsilon_{th} = 3\alpha gT$ (equation (64)); and
- c) optical phonon scattering gives $\varepsilon_{op} = \frac{SZ}{1+SZ} (Z+x_0-1)$ (equation (70)).

The quantity α is the coefficient of thermal expansion,

$$g = -\frac{\partial \ell n \kappa}{\partial \ell n V}$$
, $x_0 = \theta_{op}/T$ where $\theta_{op} = \frac{\hbar \omega_0}{k_B}$, $Z = x_0/(e^{X_0}-1)$,

and S relates the scattering by the optic phonons to the scattering from the acoustic phons.

Consider first the contribution $\varepsilon_{\rm th}$. The coefficient of thermal expansion α for Y-AgI has been measured by many workers, but measurements of the lattice constant by Lawn⁶¹ using X-ray techniques indicate the coefficient of thermal expansion for the two polymorphs is similar. As a result, one can use the value $\alpha \approx (2)(10^{-6})/K$ determined by Bienenstock and Burley⁶² for Y-AgI. The derivative g can be taken to be ≈ 7 as for the potassium halides⁶. One can then calculate $\varepsilon_{\rm th}$, and the results for three temperatures are given in Table 4.

Also in Table 4 are the results of the calculations for $\varepsilon_{\rm op}$. The parameter x_0 can be determined from the maximum optical mode wavenumber $(\lambda_{\rm op}^{-1} \approx 124 \ {\rm cm}^{-1})$ determined by Raman scattering⁶³. The quantity S is between 0.6 and 1.4 for many materials⁶, so that one can use S \approx 1.

T(K)	^ε th	ε op	ε	
150	-0.01	0.24	1.23	
300	-0.01	0.14	1.13	
420	-0.02	0.10	1.08	

Table 4. Calculated values for $\varepsilon = 1 + \varepsilon_{th} + \varepsilon_{op}$ at 150 K, 300 K, and 420 K for β -AgI.

These sets of calculations indicate that this theory explains the data near 150 K (ϵ (I) = 1.3±0.1) but not the data at higher temperatures (ϵ (II) = 1.8±0.1, ϵ (III) = -0.5±0.1).

In order to explain the temperature exponent $\varepsilon(II)$, one can look at the temperature dependence of the average square deviation $\langle \bar{x}^2 \rangle$ of the ions about their lattice positions. In a purely harmonic potential, $\langle \bar{x}^2 \rangle$ will be proportional to the temperature T at high temperatures $(T \gg \theta_D)$.²⁸ The quantity $\langle \bar{x}^2 \rangle$ may be obtained from measurements of the Debye-Waller factor in X-ray or neutron diffraction experiments.

However, the determination of $\langle \bar{x}^2 \rangle$ from the thermal parameters of neutron scattering¹⁸ for β -AgI between 290 K and 420 K suggests a temperature dependence like T^{1.4} for $\langle \bar{x}^2 \rangle$ that is becoming even stronger at higher temperatures. Since most materials obey $\langle \bar{x}^2 \rangle \sim T$ at high temperatures, this evidence implies increasing lattice anhamonicity and so motivates the addition of $H'' = \psi x^4$ to the potential energy in region II.

The addition of the x⁴ term in the potential energy permits the inclusion of the four-phonon relaxation time $\tau_4 = \frac{1}{D'T^2}$ in the temperature dependence of the thermal conductivity :

$$\kappa \sim \tau = \frac{1}{\tau_{u}^{-1} + \tau_{4}^{-1}} = \frac{1}{DT + D'T^{2}}$$
$$= \frac{1}{DT} \left(\frac{1}{1 + T/T_{p}} \right) .$$
(94)

The proportionality constant $T_p = \frac{D}{D'}$ has the units of temperature and measures the relative strength of the three-phonon processes to the four-phonon processes.

The theory of Klemens and Ecsedy⁵⁰ uses a factor like T_p such that $|T/T_p|$ is the "mean square thermal shear". Their factor has a magnitude around 50,000 K for many non-metals, so that four-phonon processes should contribute little to the thermal conductivity at room temperature since (300 K)/ $T_p \approx 10^{-2}$.

However, for a few materials the experimentally determined T_p is much smaller^{65,66}. The temperature exponent $\epsilon(II)$ can be used to estimate T_p for β -AgI by the following procedure. The slope of the data in region II is $-\epsilon(II)$ between the end points at 300 K and at 420 K. One can write

$$-\varepsilon(II) = -1.8 = \frac{\ln\tau(420 \text{ K}) - \ln\tau(300 \text{ K})}{\ln(420 \text{ K}) - \ln(300 \text{ K})}$$
$$= \frac{\ln[\tau(420 \text{ K})/\tau(300 \text{ K})]}{\ln(420/300)}$$

for this slope using the expression for τ given in equation (94). The constant T_p is found to be near 140 K. At room temperature the four-phonon processes appear to contribute a large portion of the scattering since (300 K)/ $T_p \approx 2$.

In region III, using the free-ion model of Rice and Roth, the ionic thermal conductivity κ_{I} may be written (equation (93))

 $\kappa_{I} = \sigma_{I}L_{I}$

where $\boldsymbol{\sigma}_{T}$ is the ionic conductivity and

$$L_{I} = \frac{3\alpha' k_{B} \varepsilon_{0}}{2Z^{2} e^{2}}$$

where α' is nearly 1, Ze = (1)e is the charge on the mobile ion Ag⁺, and ε_0 is the gap energy in the free-ion model. According to Rice and Roth⁵² the gap energy ε_0 may be identified with the migration (activation) energy $E_m = 0.051 \text{ eV}$ obtained from the slope of the ionic conductivity data for α -AgI ¹⁶. For α -AgI at 420 K ¹⁶, $\sigma_I = 1.3 \ \Omega^{-1} \text{cm}^{-1}$ and $L_I \approx (6.6)(10^{-6}) \text{W} \ \Omega/\text{K}$, so that $\kappa_I \approx (8.6)(10^{-4}) \text{ W/m}\cdot\text{K}$. When compared to the data at 425 K ($\kappa \approx 0.16 \text{ W/m}\cdot\text{K}$), the ionic thermal conductivity is seen to be more than three orders of magnitude lower than the meassured total thermal conductivity.
As a result, the discontinuity and change in the temperature dependence at 420 K suggest that further shortening of the phonon mean free path due to scattering from the mobile ions occurs in the superionic phase. A direct calculation of the lattice thermal conductivity for α -AgI cannot be made due to the lack of appropriate data for this phase. However, a calculation of the minimum thermal conductivity at 420 K using β -AgI parameters can be made, and this calculation can be drawn upon to interpret the α -AgI data.

The minimum thermal conductivity κ_{MIN} may be expressed as (see equation (74))

$$\kappa_{\rm MIN} = \frac{k_{\rm B} v^2}{2\delta^3 v_{\rm D}} + \frac{k_{\rm B} v_{\rm O}}{2\delta}$$

where δ^3 is the volume per atom, $\nu_0 = \frac{\omega_0}{2\pi}$ is the largest optic mode frequency ($\lambda_0^{-1} \approx 124 \text{ cm}^{-1}$ from Raman scattering⁶³), $\nu_D = \omega_D/2\pi$ is the Debye frequency calculated from $\theta_D \approx 120$ K, and v is the sound velocity.

The sound velocity can be re-created from the elastic constants 64 C₁₁ and C₄₄ at room temperature using 6

$$v = \frac{1}{3\sqrt{\rho}} \left(\sqrt{C_{11}} + 2\sqrt{C_{44}}\right)$$
(94)

where ρ is the mass density. One finds that

$$\kappa_{\rm MIN} \approx 0.17 + 0.08 = 0.25 \ W/m \cdot K$$

using β -AgI parameters, which agrees quite well with the measured value for β -AgI at 420 K ($\kappa \approx 0.20$ W/m·K).

The thermal conductivity of β -AgI does not become temperature-independent immediately below the phase transition, so the phonon mean free path in β -AgI at 420 K is not at its minimum value. However, the weak temperature dependence of κ for the superionic phase supports the extrapolation of the minimum thermal conductivity idea to α -AgI since the introduction of temperature-dependent quantities into $\kappa_{\rm MIN}$ can produce a weakly increasing thermal conductivity at temperatures roughly 3-4 times $\theta_{\rm D}^{-6}$.

In short, our data shows that the mobile ions in α -AgI affect the thermal conductivity not by carrying heat but by truncating the phonon mean free path.

<u> Y-AgI</u>

The thermal conductivity results (see Figure 23) for two samples of 99.9% AgI predominately in the α -phase at room temperature show three straight-line regions in the thermal conductivity:

- a) region I' between 120 K and 180 K, where $\kappa \sim T^{-1.3\pm0.1}$;
- b) region II' between 300 K and 420 K, where $\kappa \sim T^{-1.7\pm0.1}$; and

c) region III' above 420 K, where $\kappa \sim T^{+0.2\pm0.1}$. All of region III' lies above the phase transition at 420 K,

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Figure 23. The thermal conductivity of $\gamma\text{-AgI}.$

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and corresponds to α -AgI. Region I' and the curve between regions I' and II' corresponds to γ -AgI because this data was taken on an unannealed sample. Region II' corresponds to mixtures of β -AgI and γ -AgI.

Within region I' sample 1 (•) was estimated to contain at least 90% γ -AgI. Within region II' the exact percentage of γ -AgI for this sample changes since this portion of the data represents several traversals between room temperature and just below 420 K. Since γ -AgI slowly converts to β -AgI above 400 K ³⁵, some γ -AgI will anneal out at the high temperatures. However, this sample is estimated to contain more than 50% γ -AgI ³⁵ for all the data below the phase transition in Figure 23. Over the range of temperature and composition in region II' no dependence on the amount of γ -AgI is seen in this sample, and the collective data appear linear.

Within region II' the initial composition of sample 2 (\blacksquare) was also near 90% γ -AgI, but this data repesents only one traversal from room temperature to the phase transition.

Two parallel lines of data appear at room temperature for sample 1 (\bullet) in Figure 23 due to an additional compression after taking the low-temperature data. This compression insured that the nickel heater wire was in close contact with the sample material after the apparatus change-over. The compression increased the magnitude of the thermal conductivity while preserving the slope of the $ln\kappa$ vs. lnTplot.

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Interpretation of the Y-AgI Data

The temperature exponents for the three regions I', II', and III'' in the γ -AgI samples match up with the values obtained for the corresponding data of the β -AgI sample. The temperature exponents $\epsilon(III) = -0.5\pm0.1$ for β -AgI and $\epsilon(III') = -0.2\pm0.1$ for γ -AgI show the largest difference, but the discrepancy can be attributed to the scatter in the data.

The similarities between the temperature exponents for the two phases indicate that the same scattering mechanisms dominate the thermal conductivity over the same ranges of temperature. Especially important is the observation that $\epsilon(II)$ for β -AgI and $\epsilon(II')$ for γ -AgI are nearly the same. Because the ionic conductivity for the two phases is so different (two orders of magnitude at room temperature; see Figure 1), the thermal conductivity in regions II and II' cannot depend on either the ionic conductivity or the number of defects in the material but only upon the anharmonicity of the lattice. The number of defects is contained in the prefactor for the ionic conductivity, and so should affect the relative magnitude of the ionic conductivity of γ -AgI compared to β -AgI.

The thermal conductivity data in Figure 23 has a lower magnitude than the β -AgI of Figure 22. The maximum pressure used during the sample ensemble compression was smaller, so that the decreased magnitude is probably due to either a lower sample density or poorer wire contact. It cannot be

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attributed to differences between γ -AgI and β -AgI because of the mixed phase data in region II.

AgI0.96^{Br}0.04

This sample was compressed to nearly the same gauge pressure as the β -AgI sample, and was heated through the phase transition in order to determine immediately the temperature of the phase transition. Once above the phase transition, the superionic phase data were taken, and then the remaining data for the stable β -phase were taken. The data (see Figure 24) for AgI_{0.96}Br_{0.04} show the following when compared to the data from the pure AgI sample:

- a) the phase transition is reduced 6 K from 420 K for
 AgI to 414 K for the mixed sample;
- b) the mixed sample data is lower in magnitude than the β -AgI data; and
- c) the mixed sample data has the same temperature dependence as the β -AgI data.

The reduction of the superionic transition temperature by 6 K would seem to indicate that the sample is near 3 atomic percent AgBr in AgI (see Table 2). Because the concentration of AgBr was not determined by other methods, the exact concentration is unknown. In either case the sample can be used to judge the effect of Br⁻ impurities in AgI solid solution. Figure 24. The thermal conductivity of AgI + 4 atomic percent AgBr.



Interpretation of the AgI_{0.96}Br_{0.04} Data

The mixed sample data and the pure AgI data may be interpreted using the same set of scattering processes since the temperature dependence of the thermal conductivity of both samples is nearly identical. Because the data of Shahi and Wagner²¹ shows that this amount of bromine impurity increases the ionic conductivity at room temperature by a factor of ten, the two curves indicate that the ionic conductivity (which is related to the number of defects) is not connected with the temperature dependence of κ .

The mixed sample data and the pure AgI data would be expected to have nearly the same magnitude since the pressure used in the manufacture of the two samples was nearly identical. Although the difference in the magnitude of the two samples might be attributed either to the contact between the wire and the sample or to the number of defects, the difference in the density that results from the substitution of bromine ions is probably responsible. The thermal conductivity κ should depend on the density ρ as

 $\kappa \sim (\rho)^{g}$

where g is defined by

$$g = -\frac{\partial ln\kappa}{\partial lnV}$$

as was used to determine the correction for thermal expansion (equation (64)). If $g \approx 7$ as for the potassium halides⁶, then a one percent decrease in the density could account for a seven percent reduction in the thermal conductivity.

PyAg5^I6

The thermal conductivity data for several samples of $PyAg_5I_6$ prepared as described in Chapter V are shown in Figure 25. Because of the scatter in the data and because no sharp phase transitions appear, the temperature dependence of the thermal conductivity cannot be uniquely determined. One interpretation is that

- a nearly temperature-independent region exists
 between ~140 K and ~260 K,
- b) the thermal conductivity goes as $T^{-0.6}$ between ~260 K and ~350 K, and
- c) another nearly temperature-independent region exists between 350 K and 440 K.

None of the transitions between regions in this interpretation corresponds to a phase transition determined by other methods.

Interpretation of the $P_y Ag_5 I_6$ Data

The thermal conductivity data for $PyAg_5I_6$ are difficult to analyze because of

- a) the poor quality of the samples, and
- b) the ambiguous temperature dependence.

Figure 25. The thermal conductivity of $PyAg_5I_6$.

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Overall, the data looks similar to that found for amorphous solids where no strong temperature dependence occurs⁶.

The interpretation of the data which suggests a temperature dependence for some portions of the thermal conductivity curve hints that the gradual phase transition at ~310 K shortens the phonon mean free path over a broad range of temperature. As indicated earlier, this interpretation is not unambiguous.

Overall Summary

The data for the several samples of AgI and $AgI_{0.96}^{Br}0.04$ show three regions of temperature dependence which can be explained by:

- a) three-phonon Umklapp scattering between 120 K and 180 K;
- b) four-phonon Umklapp processes between 300 K and the superionic phase transition; and
- c) a minimum phonon mean free path above the superionic phase transition.

The introduction of the bromine impurity reduces the temperature of the superionic phase transition but does not seem to affect the temperature dependence of the thermal conductivity.

The mobile ions in all phases $(Ag^+ \text{ interstitials in } \beta-AgI \text{ and in } \gamma-AgI \text{ and the free ions in } \alpha-AgI) do not participate directly in thermal conduction. In the normal phases this is to be expected since the number of mobile$

ions is small. However, in the superionic phase the number of mobile ions is half the total number of ions, and one would expect a correspondingly larger effect. The data indicates that the ions transport no heat, but rather truncate the phonon mean free path. The ions can be described as continually disturbing the lattice during their passage through the open structure.

A negligible ionic thermal conductivity also results in the free-ion model postulated by Rice and Roth^{52} . However, their restriction that

 $k_BT \ll \epsilon_0 = E_m$

is not obeyed--the thermal energy is instead nearly equal to the migration (activation) energy for α -AgI. The violation of this restriction probably nullifies their expression for the ionic thermal conductivity, but since this is the only explicit calculation of the thermal conductivity for superionic conductors it is worthwhile to make the comparison.

The data for $PyAg_5I_6$ is featureless and reflects the poor quality of the samples. Reliable data could be obtained by growing single crystals⁴² of $PyAg_5I_6$, and by powdering these crystals.

The system could be improved in many ways, including:

- a) better pressure measurement systems, including
 a hydrostatic pressure cell for the sample;
- b) high-temperature plastics for the rings and protective teflon disks;

- c) a larger sample cell so that a straight heater wire could be used instead of an "S" shaped heater wire with a large radius of curvature;
- d) a vacuum system around the sample cell to prevent contamination by the air and to permit the handling of water-sensitive samples;
- e) one single computer program for data-taking and analysis; and
- f) a good method of determining the thermal diffusivity $D_{TH} = \frac{\kappa}{\rho C}$ from the intercept of the $\Delta T/\dot{Q}$ vs. ℓnt plot. The intercept of the $\Delta T/\dot{Q}$ vs. ℓnt plot includes several additive components that need to be removed before D_{TH} can be determined. A determination of both κ and D_{TH} would permit the product of the density ρ and the heat capacity C to be determined.

APPENDICES

APPENDIX A

LAPLACE TRANSFORMATIONS

The Laplace transform of a function v(x,y,z,t) is defined to be

$$\overline{v}(x,y,z,p) = L\{v\} = \int_0^\infty e^{-pt}v(x,y,z,t)dt$$

where p is the complementary variable to t. Several Laplace transforms 67 important to the discussion are given in Table 5.

The inverse Laplace Transform is usually determined by means of inspection from tables such as Table 5, or by using the inversion theorem for the Laplace transform

$$v(t) = \frac{1}{2i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{pt} \bar{v}(p) dp$$

where γ is large enough to enclose all the singularities of $\overline{v}(p)$ on the negative side of the line drawn parallel to the imaginary axis through $+\gamma$.

The boundary value problem of Chapter III can only be solved using the inversion theorem. Since there is a branch point at the origin, the contour of Figure 26 must be used for the integral in the complex plane. The contour

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v	ī
с	c p
Т	Τ
$\frac{\partial \mathbf{T}}{\partial \mathbf{t}}$	р Т – Т _О
$\frac{\partial^{n}T}{\partial r^{n}}$	<u>∂ⁿT</u> ∂r ⁿ
$\frac{r}{2\sqrt{\pi K t^3}} e^{-r^2/4K t}$	$e^{-\sqrt{p/K^{1}r}}$

Table 5. Some Laplace Transforms

includes the line parallel to the imaginary axis through $+\gamma$ as well as a cut that starts just below the negative axis, circles the origin, and ends just above the negative axis (line BC).

The procedure⁶⁸ that is followed for problems such as the boundary value problem is to show that the integral vanishes for all of the contour except for the cut (line BC) from $-\infty$ to the origin, and then to evaluate the integrals along this cut. These integrals can be written

$$v(t) = \frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{pt} \overline{v}(p) dp$$

and have been evaluated for several functions 67 (Table 6).

Figure 26. The contour for the inverse Laplace transform of the boundary value problem.

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$$\frac{1}{2\pi i} \int_{-\infty}^{(0+)} \frac{1}{p} e^{pt} dp = 1$$

$$\frac{1}{2\pi i} \int_{-\infty}^{(0+)} \frac{1}{p} e^{pt} \ln(kp) dp = -\ln\left(\frac{Ct}{k}\right)$$

$$\frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{pt} dp = 0$$

$$\frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{pt} [lnkp] dp = -\frac{1}{t}$$

$$\frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{pt} [\ell n k p]^2 dp = \frac{2}{t} \ell n \left(\frac{Ct}{k}\right)$$

Duhamel's theorem (also known as the Superposition theorem) is

$$L\{\int_{0}^{t} f_{1}(\tau)f_{2}(t-\tau)d\tau\} = L\{f_{1}(t)\} L\{f_{2}(t)\}$$

which essentially states that the product of two Laplace transforms can be written in terms of the Laplace transform of a convolution integral.

APPENDIX B

COMPUTER PROGRAMS

The computer programs used in the determination of the thermal conductivity using the transient hot wire method can be separated into two classifications:

- a) data-taking and file-storage programs written in FORTRAN II and SABR (an assembly language for FORTRAN II) for the PDP-8; and
- b) analysis and curve fitting programs written in FORTRAN IV for the PDP-8 and for the CDC 7600.

The two sets of programs are connected by the data files organized as in Table 7. The data files have space for up to 85 data points and 12 parameters.

The hub of the data-taking programs is IGUANA·FT. (see Table 8). IGUANA·FT calls three subroutines in the following order:

- a) RM16SB·FT to measure the voltage across a nominal 1 Ω resistor during the pulse to measure the current (the actual resistance is given as the scale factor);
- b) RM16SB.FT to measure the voltage across the heater wire during a second pulse;

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I	SV(I)
1	Data Taken = 1
2	
3	
4	
5	
•	
83	
84	\rangle Data Points (Maximum Number = 85)
85	
86	
87	End of Data = Negative Number
88	Open
89	Parameters Included = 1
90	Open
91	Resistance Zero
92	Temperature
93	Pressure
94	Current
95	Open
96	Scale Factor
97	Wire Length
98	Wire Diameter
99	Time Interval
100	Date

Table 7. Data File Arrangement

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- c) PARMSD.FT (called PARMSB by IGUANA.FT) to attach the parameters such as the sample temperature and pressure; and
- d) SHOFIL.FT to write the completed data file onto the disk storage device.

RM16SB·FT is given in Table 9, PARMSD·FT is given in Table 10, and SHOFIL·FT is given in Table 11.

The program RM16SB·FT is a long program principally written in SABR. The letter S appears before the SABR lines. RM16SB·FT performs the following tasks:

- a) to obtain the number of data points from the user;
- b) to control the power supply;
- c) to wait for 51.4 msec between data points;
- d) to take the data points and to store them temporarily; and finally

e) to convert the data points into usable numbers. The final values are stored in COMMON.

PARMSD'FT defines the array PAR(I) which stores the parameters entered in this subprogram. Using comment statements the user can decide which parameters are to be printed out and entered during data-taking. This decision usually takes place immediately prior to the run when the parameters (such as the wire length) are changed using the system EDITOR.

SHOFIL.FT allows the user to assign a six-symbol name (with no spaces since the file would be irretrievable) to the file written on the disk. It also checks to make sure that the data and the parameters have been included in SV(I) before the file is written:

The analysis program GOATSV.FT (see Table 12):

- a) reads the data and the parameters from the file;
- b) calculates the array of points D(I) which are the temperature excursions divided by the instantaneous power dissipated per unit length;
- c) calculates the array C(I) of the *lnt* values corresponding to D(I);
- d) displays the data points;
- e) permits the elimination of spurious data points; and
- f) calculates the thermal conductivity and the χ^2 with a linear least-squares regression and displays the differences E(I) between the fit and the data points.

The program sections that control the manipulation of the displayed data points have been given line numbers between 400 and 699.

One section of GOATSV.FT requires additional explanation--the section that extrapolates an initial potential difference from the first five potential differences measured (line 800). This extrapolation fits the measured points to an internally generated set of orthogonal Legendre polynomials⁶⁹. This procedure is a least-squares approximation that quickly converges to a solution because of the orthogonality of the polynomials. The array AA(I) in GOATSV.FT stores the coefficients of the nickel wire calibration calculated by GOATFIT (see Table 13) on the CDC 7600. GOATFIT calculates these coefficients by writing a matrix equation that minimizes χ^2 , and then by solving the matrix equation using Cramer's rule⁷⁰. Table 8. Listing for IGUANA.FT

С	IGUANA.FT
С	THERMAL CONDUCTIVITY MEASUREMENTS
č	TRANSIENT HOT WIRE METHOD
	DIMENSION SV(100);PAR(12)
	DO 100 I=1,100
100	SV(I)=0.0
	DD 102 I=1,12
102	PAR(I)=0.0
1	READ(1+2) IGO
5	FORMAT(' GD=0.0UT=FLSE: '.I3)
-	
C	
L.	
200	WRI1E(1)2017
201	FORMAT(' DATA TAKING: OUT=0; MAX 85 PTS; I BEFORE V')
208	CALL RM16SB
	IF(ATT) 1,1,205
205	SV(1)=1.0
	IATT=IFIX(ATT)+2
	SU(TATT) = -1.0
	TE(TATT-87) 207-210-201
207	
207	
	DU 207 1-12EK/B/
209	50(1)=0.0
210	DO 212 J=1,IATT,5
	WRITE(1,213) (SV(K+J-1),K=1,5)
212	CONTINUE
213	FORMAT(' ',5E13.6)
218	READ(1,214) ISW
214	FORMAT(' CURRENT DATA=-1,D.FOINT CHANGE=0,VOLTAGE DATA=+1:',I3)
·	TE(TSW) 250-215-400
215	FEAT(1-212) THEC
217	COMMAT/, DECIMAL POINT CHANGE! MULTICLIED-1044 (-13)
217	PORTHIC DECIMAL FOIRT CHARGE, MCCIFEIER-10** 9137
225	
227	SV(1)=SV(1)*(10:0**10PC)
	GO TO 218
С	CURRENT DATA
250	IAT=IATT-1
	SUMCU=0.0
	DO 252 I=2,IAT
	SUMCU=SUMCU+SV(T)
252	
232	
260	WRI(E(1,261) CUR
261	FORMAT(' CURRENT =';E14.6)
	SV(94)=CUR
	PAR(6)=CUR
	GD TD 200
C	PARAMETERS
400	CALL PARMSB
C.	FILE
000	
c	
L.	END -
999	STUP
	END

Table 9. Listing for RM16SB.FT

	SUBROUTINE RM16SB
C	GOETZ SABR,F2
C C	TRANSIENT HOT HIDE METHOD
0	COMMON SV,ATT
	DIMENSION SVX(100)
	DIMENSION SVY(100)
_	DIMENSION SV(100)
5	OPDEF DACS 6551
5	OPDEF CLAR 6133
S	OPDEF CLSA 6135
S	SKPDF CLSK 6131
S	OPDEF CLDE 6132
S	OFDEF DGUT 6113
5	0FDEF DGIN 6144 READ(1.15A) TOUR
150	FORMAT(' NUMBER OF POINTS = ',13)
	IF(ICHR) 460,460,151
151	IF(ICHR-85) 152,152,999
152	CONTINUE
	JC=ICHR+2
	SUX(ID)=0.0
	SVY(JD)=0.0
5	SV(JI)=0.0
	VEX=0.0
200	CONTINUE
G	LLA LLL TAD (3777
S	DACS
S	CLA CLL
220	CONTINUE
	DD 300 JM=1, JC
SMEECE,	DO 300 JM=1,JC CLA CLL
SMEECE, S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ
SMEECE, S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1
SMEECE, S S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL
SMEECE, S S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO
SMEECE, S S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUT2 CONTINUE
SMEECE, S S S 300 C	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE ZPOWER DEF
SMEECE, S S S 300 C SPWDFF,	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER DFF CLA CLL
SMEECE, S S S 300 C SPWOFF, S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS
SMEECE, S S S 3000 C SPWDFF, S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL
SMEECE, S S S 300 C SPWOFF, S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUTO=0.0 AUT2=0.0
SMEECE, S S S 300 C SPWDFF, S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE
SMEECE, S S S 300 C SPWDFF, S S 400	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUTO=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC
SMEECE, S S S 300 C SPWDFF, S S 400	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM)
SMEECE, S S S 300 C SPWDFF, S S 400	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM)
SMEECE, S S S 300 C SPWDFF, S S 400 SCECIL,	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL MES CNUT
SMEECE, S S S 300 C SPWDFF, S S 400 SCECIL, S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNVT JMS PNTD
SMEECE, S S S 300 C SPWDFF, S S 400 SCECIL, S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNVT JMS PNTD CLA CLL
SMEECE, S S S 300 C SPWDFF, S S 400 SCECIL, S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DD 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNVT JMS PNTD CLA CLL SV(JM)=VEX/((10.0)**5)
SMEECE, S S S 300 C SPWDFF, S S 400 SCECIL, S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNVT JMS PNTD CLA CLL SV(JM)=VEX/((10.0)**5) VEX=0.0
SMEECE, S S S S S S S S S S S S S S S S S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNVT JMS PNTD CLA CLL SV(JM)=VEX/((10.0)**5) VEX=0.0 CONTINUE IATT=ICHE+2
SMEECE, S S S S S S S S S S S S S S S S S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNUT JMS PNTD CLA CLL SV(JM)=VEX/((10.0)**5) VEX=0.0 CONTINUE IATT=ICHR+2 SV(1)=1.0
SMEECE, S S S S S S S S S S S S S S S S S S S	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNUT JMS PNTD CLA CLL SV(JM)=VEX/((10.0)**5) VEX=0.0 CONTINUE IATT=ICHR+2 SV(I)=1.0 SV(IATT)=-1.0
SMEECE, SSSS SS 400 SCECIL, SS 450 460	DO 300 JM=1,JC CLA CLL JMS STTM JMS READ JMS WTTM1 CLA CLL SVY(JM)=AUTO SVX(JM)=AUTO SVX(JM)=AUT2 CONTINUE /POWER OFF CLA CLL DACS CLA CLL AUT0=0.0 AUT2=0.0 CONTINUE DO 450 JM=1,JC AUT0=SVY(JM) AUT2=SVX(JM) CLA CLL JMS CNUT JMS PNTD CLA CLL SV(JM)=VEX/((10.0)**5) VEX=0.0 CONTINUE IATT=ICHR+2 SV(I)=1.0 SV(IATT)=-1.0 ATT=FLOAT(ICHR)

Table 9. (continued)

С	SUBROUTINES
SMASK1,	0017
STEMP.	0000
SK1750,	0764
SUGI1,	0000
SDOI21	0000
SUGTA	0000
SDGT5.	0000
SUGT6,	0000
C	START TIMER SUBROUTINE
SSTTM,	0000
S	CLA CLL
S	CMA
S	CLZE
S	CLA CLL
3	
3	
3	TAD K1750
s	
S	CLAB
S	CLA CLL
S	TAD (1400
S	CLDE
S	JMP I STTM
С	/WAIT TIMER 1 SUB.
SWTTM1,	0000
5011	
5	
а с	IMP T UTTM1
č	/READ DVM SUR.
SREAD,	0000 /START
S	CLA CLL /DVM
S	TAD (0300
5	DGOT
S	NOP
S	NOP
5	NUP
а <u>,</u>	
5	NOP
S	NOP
Ŝ	CLA CLL
S	DGOT
S	CLA CLL
S	TAD (0400 /LOOK FOR
S	DGOT /DATA READY
S	NOP
5	NUP
3	
S	NOP
SRDE,	NOP
S	NOP
S	CLA CLL
S	DGIN
S	AND (0001
S	SZA
5	JMP RDE
3	ULA ULL /REAU DVM
с С	
u	

.

S	DGOT
S	NOP
5	
S	NOP
S	CLA CLL
S	DGIN
S	DCA NAUTO
S	CLA CLL
5	
5	NOP
Š	NOP
S	NOP
5	
5	
5	
S	DGOT
s	JMP I READ
č	/CONVERT SUBROUTINE
SCNVT,	0000
S	CLA CLL
S	TAD NAUTO
5	DCA TEMP
5	DTD
S	RTR
S	RTR
S	RTR
S	DCA DGT1
S	TAD TEMP
S	RTR
8	RTR
5	JUA JUIZ TAD TEMP
5	DCA DGT3
5	
Ś	DCA TEMP
S	TAD TEMP
S	RTR
S	RTR
S	RTR
5	
5	TAD TEMP
5	RTR
Š	RTR
S	DCA DGT5
S	TAD TEMP
S	DCA DGT6
S	CALL O, CLEAR
S	JMP I CNVT
	ADDLITET BY TEN SUBR.
STULIENS	
Š	CLA CLL

Table 9. (continued)

Table 9. (continued)

S	TAD (0012
ŝ	CALL OFFLOT
- -	CALL 1.EMP
5 e	APG VUEY
5	
3	ADD NIEY
5	HRU IVEA
5	JMP I MULTEN
C	ADD SUBR.
SADD,	0000
S	AND (0017
5	CALL 0,FLOT
S	CALL 1,FAD
S	ARG VEX
S	CALL 1,STO
S	ARG VEX
ŝ	IMP T ADD
r.	/PLACE DATA SUBR.
GPNTD.	0000
6	
5	TAD DGT1
0 C	INC ADD
5	
5	JAS AULIEN
S	CLA CLL
5	TAD DGT2
S	JMS ADD
S	JMS MULTEN
S	CLA CLL
S	TAD DGT3
S	JMS ADD
ŝ	JMS MULTEN
ŝ	CLA CLL
ŝ	TAD DGT4
č	IMS ADD
3 C	INC MULTEN
5	
5	TAD DOTS
5	TAD DOTS
5	JAS AUD
S	JMS MULTEN
S	CLA CLL
S	TAD DGT6
S	JMS ADD
S	JMP I PNTD
999	CONTINUE
	RETURN
	END

Table 10. Listing for PARMSD.FT

	SUBROUTINE PARMSB
С	GOETZ F2
С	PARAMETER ACQUISITION
C '	SITES SV(88),SV(90),SV(95) DPEN
С	DATE=SV(100)=PAR(12)
С	TIME INTERVAL=SV(99)=PAR(11)
Ĉ	WIRE DIAMETER=SV(98)=PAR(10)
č	WIRE LENGTH=SU(97)=PAR(9)
Ē	SCALE FACTOR=SU(96)=PAR(8)
ř	CURRENT = SU(94) = PAR(4)
č	PRESS(RE=SU(93)=PAR(5))
č	TEMPERATURE=SU(92)=PAR(4)
č	RESISTANCE $7ERD=SU(91)=PAR(3)$
r r	PARAMETER FULLESU(89) \pm PAR(1)
ř	
0	COMMON SULATT
	COMMON BAR
	DIMENSION SU(100).PAR(12)
r	DADAMETEDS ENTEDED EADLIED WITH EDITAD
L	PARAMETERS ENTERED EMALTER WITH EDITOR
	PAR(8)=1.022
	PAR(9)=5.00
	PAR(10) = 4.2
	PAR(11)=51.4
	PAR(12)≠9.2481
	WRITE(1,405) PAR(12)
	WRITE(1,406) PAR(11)
	WRITE(1,407) PAR(10)
	WRITE(1,408) PAR(9)
	WRITE(1,409) PAR(8)
0	CURRENT SUPPLIED BY AVERAGE
	WRITE(1,410) PAR(6)
С	WRITE(1,411) PAR(5)
	READ(1,412) PAR(4)
C	READ(1,413) PAR(3)
	PAR(7)=0.0
	PAR(2)≖0.0
	PAR(1)=1.0
413	FORMAT(' RESISTANCE ZERO(OHM)= '+E14.6)
412	FORMAT(' TEMPERATURE(K)= ',E14.6)
411	FORMAT(' PRESSURE(KBAR)= ',E14.6)
410	FORMAT(' CURRENT(AMP)= ',E14.6)
409	FORMAT(' SCALE FACTOR= ',E14.6)
408	FORMAT(' WIRE LENGTH(CM)= ',E14.6)
407	FORMAT(' WIRE DIAMETER(MIL)= ',E14.6)
406	FORMAT(' TIME INTERVAL(MILLESEC) = ',E14,6)
405	FORMAT(' PARAMETERS DATE(MONTH.DAY)= ',F8.4)
456	DO 457 I=1+12
457	SV(I+88)=PAR(I)
1	RETURN
-	END

Table 11. Listing for SHOFIL.FT

	SUBROUTINE SHOFIL
С	GOETZ F2
С	MAKES SINGLE DATA SET FILES
	COMMON SV,ATT
	DIMENSION SV(100)
	IF(SV(1)) 9,9,11
9	WRITE(1,10)
10	FORMAT(' NO DATA SET FOR SHORT FILE')
	GO TO 999
11	IF(SV(89)) 12,12,20
12	WRITE(1,14)
14	FORMAT(' NO PARAMETER SET FOR SHORT FILE')
	GD TD 999
20	READ(1,56) ISH
56	<pre>FORMAT(' SHORT FILE: OUT=-1,LIST=0,DISK WRITE=+1: ',I3)</pre>
	IF(ISH) 999,58,630
57	FORMAT(' ',4(2X,E14.6))
58	DO 59 I=1,100,4
	WRITE(1,57) (SV(I+J),J=0,3)
59	CONTINUE
	GO TO 20
630	WRITE(1,633)
633	FORMAT(' PROGRAM ATTACHES .DA')
	WRITE(1,634)
634	FORMAT(' ENTER SIX CHARACTERS, NO SPACES')
	READ(1,638) ENAME
638	FORMAT(' FILE NAME: '#A6)
	CALL OOPEN('DSK',ENAME)
	DO 650 I=1,100,5
	WRITE(4,659) (SV(I+J),J=0,4)
650	CONTINUE
659	FORMAT(5E14.6)
,	CALL OCLOSE
999	RETURN
	END

Table 12. Listing for GOATSV.FT

•

С	GOATSV
C C	THERMAL CONDUCTIVITY CALCULATIONS
č	USES INFUT DATA FILE
	LOGICAL PABST DIMENSION A(100)-C(85)-AA(10)-FL(10)-XL(10)
	DIMENSION E(85),SV(100),BUFFER(100),D(85)
	DIMENSION PL(10,10),SL(10),BL(10),CL(10),DL(10)
	DO 1 I=1,100,5
	READ(1,2) (SV(I+J),J=0,4)
2	FORMAT(5E14.6)
9	FORMAT (/ 1,5(G12.6,2X))
13	IX=0
	DO 14 I=2,86
	IF(SV(I), GI, 0, 0) GU U 14 IX=I-2
	GO TO 15
14	CONTINUE TX=85
15	CONTINUE
	IXT=IX DO 17 T=1-84
17	A(I)=SV(I+1)
18	DO 18 I=89,100 A(T)=SU(T)
c	FARAMETER ACQUISITION
19	CONTINUE
	WRITE (4,21) A(99)
	WRITE (4,26) A(98)
	WRITE (4,27) A(76)
	WRITE (4,22) A(94)
	WRITE (4,24) A(92)
	WRITE (4,25) A(91)
	VSF=A(96)
	RH=A(98)
	CU=A(94)
	TNIL=A(92)
	ZERD=A(91)
20	GO TO 800
20	FORMAT (' TIME INTERVAL= ',G12.6,' MILLESEC')
22	FORMAT (' CURRENT= ',G12.6,' AMPS')
24	FORMAT (' TEMPERATURE= ',G14.6, K')
25	FORMAT (' RESISTANCE ZERO= ',G12.6,' OHMS')
27	FORMAT (' WIRE LENGTH= ',G12.6,' CM')
29	FORMAT (' VOLTAGE SCALE FACTOR= ',G12.6)
37 38	CONTINUE
	IX=IXT
С	TEMP DIFFS + DATA PREP
С	T VS & PARAMETERS FROM CDC GOATFIT
	WLN=KH#1.0E-3#2.54E-2/2.0

•
	R0=13.35
	CO=(60/WL)*(8H/DO)*(6H/DO)
	AA(2)=481.459*C0
	AA(3)=-609.070*CD*CD
	AA(4)=1243.07*CD**3
	AA(5)=-1950.50*CD**4
	AA(6)=2055.55*CD**5
	AA(7)=-1386.91*CO**6
	AA(8)=569.210*CD**7
	AA(9)=-128.789*CO**8
	AA(10)=12.2872*CD**9
	REZER=RNIL*VSF
	TEZER=0.0
	DO 42 I=1,10
42	TEZER=TEZER+AA(I)#REZER##J
	$DO = 50 = 1 + 1 \times 1000$
	IF(1,E(,IX) - IM REPT=USE#A(T)/CH
	DD 45 K=1.10
	JEK-1
45	TEPT=TEPT+AA(K)#REPT##.I
	DIET=TEPT-TEZER+DELTT
	IF(I.EQ.IX) XX=DIET
50	D(I)=DIET*WL*VSF/(A(I)*CU*100.0)
	IP=IX
	LASH=1.1*D(1)
	BASH=1.1*C(1)
	CASH=1.1*C(IP)
	ASH=1.1*D(IP)
	DO 57 I=1,100
57	
	LALL SUHLE(BHSH)LHSH)LHSH)HSH)
	CALL ELATING BOFFER/
C	DATA POINT MANTPULATION
۲ 45	WRITE (4.44)
44	FORMAT(' START=1.FND=2.PT.FLIM=3.FIT=4.CUESOR=5.LIST=6: ',\$)
00	READ (4,106) IND
	IF(IND.LE.O) GO TO 65
	IF(IND.GT.6) GO TO 65
	GD TD(401,501,601,80,550,650),IND
C	TRIPLE DOTS
80	CONTINUE
	HGT=(LASH+ASH)/2.0
	DU 83 1=28;30 Re-EL DAT(I)(10 0
	CALL PLOT(1.C. HCT)
07	
65	B=0.0
	DO 84 I=1+3
	H=LASH+FLOAT(T)/10.0
	CALL PLOT(1+G+H)
84	CONTINUE
С	LINEAR REGRESSION
90	AXM=0.0
	BYM=0.0
	AXMM=0.0
	BYMM=0.0
	ABMM=0.0

	DO 93 I=1,IP
	AXM=AXM+C(I)
	BYM=BYM+D(I)
	AXMM=AXMM+C(I)*C(I)
	BYMM=BYMM+D(I)*D(I)
93	ABMM=ABMM+C(I)*D(I)
	S2X=AXMM/IP-(AXM/IP)*(AXM/IP)
	S2Y=BYMM/IP-(BYM/IF)*(BYM/IF)
	SLOPE=((ABMM/IP)-(AXM/IP)*(BYM/IF))/S2X
	TNTC=(BYM/IP)-SLOFE*AXM/IP
	COCD=SLOPE*S2X/S2Y
С	CALCULATIONS AND FRINTOUT
	WK=1.0/(4.0*FI*SLOFE)
	DTH=0.4453*WLM*WLM*EXP(TNTC/SLOPE)
	CHI=0.0
	EX=0.0
	NO 98 I=1,IP
	EIO=D(I)-SLOPE*C(I)-TNTC
	CHI=CHI+EIO*EIO
	E(I)=EID*10.0+HGT
	IF(ARS(EIO)-EX) 98,98,97
97	EX=ABS(EID)
	IFD=I
98	CONTINUE
	CHI=CHI/(IP-2)
	FRAC=SQRT(CHI)/TNTC
	WRITE(4,100) WK
	WRITE(4,101) DTH
	WRITE(4,102) CHI,FRAC
	WRITE(4,109) EX,IFD
	WRITE(4,110) XX,TT
	CALL PLOT(IP,C,E)
	WRITE(4,105)
100	FORMAT(' ',5X,'KAPPA= ',G14.6)
101	FORMAT(' ',5X,'DTH= ',G14.6)
102	FORMAT(' ',5X,'CHI SQ= ',G14.6,': CHI/TNTC=',G14.6)
105	FORMAT(' FIT DIFFS #10 CENTERED ON AVE TEMF')
106	FORMAT(13)
109	FORMAT(' MAX FIT DIFF = ',G14.6,' AT POINT ',I3)
110	FORMAT(' TEMP DIFF MAX = ',G14.6,' AT ',G14.6,' SECS')
С	DECISIONS
300	WRITE(4,301)
301	FORMAT(' CHANGE=1,RE-ANALYZE=2,DONE=3: ',\$)
	READ(4,106) IND
	IF(IND.LE.O) GD TD 300
	IF(IND.GE.4) GD TO 300
	GO TO(420,38,999),IND
С	NEW START
401	WRITE (4,402)
402	FORMAT(' START : REMOVE THRU I= ',\$)
	READ (4,106) INS
	IF(INS.LE.O) GO TO 65
	IF(INS.GE.IP) GO TO 65
	IPSS=IP-INS
	DO 403 I=1,IFSS
	C(I)=C(I+INS)
	D(I)=D(I+INS)
403	CONTINUE
	IP=IPSS
	DD 407 I=1,100
4.7	BUFFER(I)=0.0
	CALL CLRPLT(100,BUFFER)
	CALL FLOT(IF,C,I)
	GO TO 65

С	NEW END
501	WRITE (4,502)
502	FORMAT (' END AT I= ',\$)
	READ (4,106) INE
	IF(INE.GE.IF) GO TO 65
	IF(INE.LE.O) GO TO 65
	DD 507 T=1.100
507	BUFFER(I)=0.0
	CALL CLRPLT(100, BUFFFR)
	CALL PLOT(IF,C,D)
_	GO TO 65
C	POINT ELIM
601	WKIIE (47602) EDEMAT (/ ELIM III (A)
802	FURNHI (* ELIM I= ',\$) REAN (A.104) TRE
	IF(IPE.LE.0) GO TO 65
	IF(IPE.GT.IP) GO TO 65
	DO 603 I=IPE,IP
	C(I)=C(I+1)
	D(I)=D(I+1)
603	CUNTINUE
	1 = 1 = 1 = 1 = 1 = 1 = 1 = 1 = 1 = 1 =
607	BUFFER(I)=0.0
	CALL CLRPLT(100,BUFFER)
	CALL PLOT(IP,C,D)
•	GO TO 601
450	UATA PUINT LISTING
651	FORMAT(' LISTING')
•••	BO 654 I=1,IXT,5
	WRITE(4,9) (A(I+J),J=0,4)
654	CONTINUE
-	GO TO 65
	PARAMETER CHANGE
420	FORMAT(/ PARAMETER CHANGE: NONE=0.CURR=1.TEMP=2.T INTVL=3/)
768	WRITE(4,422)
422	FORMAT(' R ZERD=4,WIRE LGTH=5,WIRE DIAM=6,SCALE FCTR=7: ',\$)
	READ (4,106) IPCH
	IF(IPCH.LE.0) GO TO 300
	IF(IPCH.GE.8) GU IU 300
▲25	ENRMAT (/ NEW VALUE= (.\$)
720	READ (4,13) CHASM
	IF(IPCH.EQ.1) CU=CHASM
	IF(IPCH.EQ.2) TZERO=CHASM
	IF(IPCH.EQ.3) DT=CHASM
	IF(IFCH.EQ.4) RNIL=CHASM
	IF(IFCH.EQ.5) WL=CHASM
	TE(TECH.EQ.7) VSE=CHASM
	GD TD 300
С	CURSOR
550	CONTINUE
	WRITE (4,551)
551	FORMAT(' CURSOR I= ';\$)
	TE(ICUR.GT.IP) GO TO 65
	IF(ICUR.LE.O) GO TO 65
	CALL PLOT(1,C(ICUR),D(ICUR))
	CALL PLOT(1,C(ICUR),D(ICUR))
	GO TO 65

-

С	LEGENDRE POLYNOMIAL EXTRAPOLATION
с	GENERATES N-1 ORTHOGONAL POLYNOMIALS TO FIT N POINTS
Ċ	THEN EXTRAPOLATES FROM THE FIT; HERE PRODUCES RNIL.
С	THEORY FROM CONTE AND DE BOOR
800	N=5
	DO 802 I=1,N
802	FL(I)=(A(5)-A(I))/(A(5)*CU)
	NN=N-1
	NF=N+1
	DO 810 I=1,NP
·	SL(I)=0.0
	BL(I)=0.0
	CL(I)=0.0
	DL(I)=0.0
	PL(I,1)=1.0
	DD 810 J=2,N
810	PL(I,J)=0.0
	ID 840 J=1,NN
	DO 830 K=1,N
830	SL(J)=SL(J)+PL(K,J)*FL(K,J)
	DD 832 K=1,N
832	BL(J)=BL(J)+XL(K)*PL(K,J)*PL(K,J)/SL(J)
	IF(J-1) 840,837,834
834	CL(J)=SL(J)/SL(J-1)
	DO 838 K=1,N
838	PL(K;J+1)=(XL(K)-BL(J))*PL(K;J)-CL(J)*PL(K;J-1)
	GO TO 840
837	DO 839 K=1,N
839	PL(K,2)=XL(K)-BL(1)
840	CONTINUE
	DO 850 J=1,NN
	DO 850 K=1,N
850	DL(J)=FL(K)*PL(K;J)/SL(J)+DL(J)
	XZ=0.0
	L=1
	RZ=DL(1)+DL(2)*(XZ-BL(1))
	DO 860 J=2,NN
	PL(L,J+1)=(XZ-BL(J))*PL(L,J)-CL(J)*PL(L,J-1)
	IF(J+1-NN) 858,858,860
858	RZ=RZ+DL(J+1)*FL(L,J+1)
860	CONTINUE
	RNIL=A(5)*(1.0-RZ*CU)/CU
	WRITE(4,870) RNIL
870	FORMAT(' EXTRAPOLATED RESISTANCE ZERO= ',G12.6,' OHMS')
	GO TO 38
С	
999	STOP
	END

Table 13. Listing for GOATFIT

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~		F(R (6	6 7	i /			E	C	A '	TI	F	1	(1	N	P	U	Ţ	•	ĊI	١	1	V	1)																	
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.

51	DC 54 L=1.NTERPS DC 54 K=1.NTERPS
54	N=L+K-1 ARRAY(J,K)=SLMX(A) DELTA=CETERM(ARRAY+NTEF#S)
57	
59	CC 55 J=1+NTER#S A(L)=0+(
61 62	GC TC E DC 70 L=10NTERMS DC 66 J=10NTERMS DC 65 K=10NTERMS
65 66 70 71	N=_+K-1 ARRAY(J,K)=SLMX(N) ARRAY(J,L)=SLMY(J) A(L)=CETERM(ARRAY,NTERPS)/DELTA DO 7 J=1.NTERMS
••	CFISG=CFISO-2.C+A(J)+SLMY(J) CC 75 K=1.NTERMS
75 76 77 8 0	N=J+K-1 CFISG=CFISQ+A(J)+A(K)+SLPX(N) FREE=NPIS-NTERPS CHISGF=CFISG/FREE RETURN
	ENC Double frecision function deterp(Array+Nterps)
ç	CALCULATE DET OF SQUARE MAT
10 11	IPPLICIT COUELE FRECISION (A-H+O-Z) DIMENSION ARRAY(10+1() DETERM=1+0 DETERM=
21	16 (ARFAY(ROK)) 41021041 DO 23 J=RONTERPS
23	IF(ARRA)(K.J)) 31,23,31 Continue Determ=(.0
31	GC 1G E + NTERMS GC 34 I=+ NTERMS SAVE=ARF/Y(I,J) ARRAY(I,J)=ARRAY(I,K) ARRAY(I,J)=SAVF
34	CCNTINUE
41	UEIERF=LEIERF+ARFAY(K+K) DETERF=LETERF+ARFAY(K+K) TE(K+AT5BVC) A3,50,50
43	17 (R-RIEPRA) 43930931 K1=K+1 R0 A/ Y-M4 MTEBME
46 50 65	UU 4E IERIONIERIS DC 4E JEKIONTERIS ARRAY(IOJ)-ARRAY(IOK)+ARRAY(KOJ)/ARRAY(KOK) CCATIIOE RETURN
	ENC

LIST OF REFERENCES

LIST OF REFERENCES

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