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SPECIFIC HEAT OF LIF AND KI

by

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A THESIS
SUBMITTED TO THE FACULTY
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REQUIREMENTS FOR THE DEGREE OF
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Specific Heat of LiF and KI

INTRODUCTION

For a number of years a group at this laboratory has been carrying on experimental work designed to supply measurements needed for a fundamental understanding of phenomena in solids. In recent years there has been a combined effort to measure at low temperatures certain related physical properties of alkali halides. Briscoe and Squire \(^1\) (1957) reported some of the first elastic constants measurements to be extended to the low temperature range. Their work has been continued to other alkali halides by Norwood.\(^2\) The present work, which is to be tied in theoretically with the before mentioned results, is a low temperature measurement of the specific heat of LiF and KI.

In a sense, the specific heat of a substance is one of its most fundamental measurable properties. It is an indication of the internal energy and the forces which bind the substance together. For dielectric crystals such as the alkali halides, there should be at low temperatures only one contribution to the specific heat, that due to thermal vibrations in the lattice. The form of the dependence of this contribution upon temperature has been well established by Debye\(^3\) and others\(^4,5\) who show that at sufficiently low temperatures

\[ C_V = 464.3(T/\theta)^3 \text{ cal/deg at. wt.} \]  \hspace{2cm} (1)
where $C_V$ is the specific heat at constant volume and $\Theta$ is a constant characteristic of the substance. The $\Theta$ will in general be a function of the forces between particles of the lattice and thus will be basic to the understanding of phenomena in solids.

The expression just given may be viewed in another way. It might be said that $\Theta$ is a parameter in Debye's theory of specific heat. For a given $C_V$ at a given $T$, $\Theta$ is determined by the Debye function, whose low temperature limit is given by (1). Experimentally values of $\Theta$ determined in this way are not found to be constant but show a marked dependence on temperature. Only at low temperatures, quite often in the liquid helium range, does $\Theta$ become temperature independent.

At the outset of the present work, the situation was somewhat as shown in Fig. 1. The Debye $\Theta$ for both KI and LiF had been measured over a wide range of temperatures, but as yet there was no clear indication that the $\Theta$ as a function of $T$ had leveled off. There was also no certain estimate of the value that $\Theta$ would assume near $T = 0$. The present experiment was set up to find these values. Moreover, the findings were to be used to verify determinations of the $\Theta$ by other means, and thereby help to tie together more tightly an extensive body of theory. Further, just such measurements as these are needed to shed light on recent attempts to extend the simple Debye theory. (Cf. Barron and Morrison\textsuperscript{12} and Ludwig,\textsuperscript{11} and also Conclusion.)
The question of how low in temperature one must go before the true $T^3$ region is reached was partially answered by Born and von Karman$^4$ and by Born.$^{13}$ They showed that the $T^3$ dependence of specific heat is a low temperature limit independent of crystal structure and independent of any special assumptions concerning isotropy. They showed that the frequency distribution function for crystals such as the alkali halides involving two different masses will have two different "branches". One of these will relate to modes of vibration of high frequency, on the order of Reststrahlen frequencies in the infrared. These modes will not be excited above their ground states at low temperatures where only low energies are available. The other branch will have as its limiting form a frequency squared dependence, leading to the $T^3$ dependence of specific heat.

The problem has been further considered by Blackman.$^5$ On the basis of semi-qualitative arguments along with detailed calculations of actual frequency distribution functions, he concludes the following: the true $T^3$ region is attained only at a temperature on the order of $\Theta/50$ where $\Theta$ is the low temperature limit of the Debye constant. For LiF with a $\Theta$ of about 723 this is a temperature of $14^\circ$K. All the measurements reported in this work were made well below this limit. It is thus expected that the specific heat of LiF will obey a $T^3$ law very well for all the data here reported. For KI, on the other hand, with a $\Theta$ of about
the Blackman criteria leads to a temperature of about 3 °K. Thus, while on Debye's model a \( T^3 \) law should be obeyed throughout these measurements, we may expect according to Blackman to detect some variation of \( \Theta \) with \( T \) down to low temperatures. In either case, however, both for LiF and KI the present experiment should be able to indicate the true limiting value of the Debye \( \Theta \) for \( T \) approaching zero.

**APPARATUS**

The specimens on which the measurements were performed were large single crystals obtained from the Harshaw Chemical Company. They were optically clear and shaped in the form of cylinders about three inches long and an inch in diameter. This gave a mass of 104 grams for the LiF and 125 grams for KI.

The calorimeter employed made use of a mechanical "heat switch" by which the salt could be put into direct mechanical contact with the constant temperature bath or could be isolated from it. It was similar in design to one reported by Ramanathan and Srinivasan. The calorimeter cooling is brought about by direct conduction without the need of helium exchange gas. This obviates the possibility that helium vapor may be adsorbed upon the sample as it is cooled and subsequently boil off during heating with an accompanying heat of desorption. For very low specific heats, such as with LiF,
this could lead to a significant error in the results. The temperature rise for a given input of heat would be smaller than expected and the measured specific heat therefore spuriously high.

A schematic diagram of the apparatus is depicted in Plate 1. The salt hangs freely in its normal position inside a brass can large enough to be one-half to three-quarters of an inch distant at closest approach. This can, the calorimeter, is attached at its top to a thin-walled monel tube which secures it rigidly to the top-plate at the room temperature end of the gear. The calorimeter is surrounded by a double Dewar flask arrangement which can be filled with liquid helium to form a constant temperature bath. The interior of the inner Dewar is connected to a high speed N.R.L. vacuum pump capable of reducing the pressure above the liquid helium to a fraction of a mm of Hg. This allows the bath temperature to be reduced from the normal boiling point of helium, 4.2 °K, to about 1.3 °K. Inside the calorimeter a high vacuum is produced by pumping out through the monel tube.

In practice it was found that quite adequate vacua could be obtained merely by pumping out at room temperature with an ordinary Welch forepump, the liquid helium itself then freezing out what air remained. The vacuum obtained in this way was ordinarily on the order of 10^{-5} mm. of Hg, as measured by an ion gauge at the top of the apparatus. The calorimeter can had a low melting point indium solder seal which allowed it to be opened easily when adjustments were to be made.
The salt specimen was suspended by nylon threads from a brass plate shown in the diagram. The plate was attached to a small stainless steel rod which extended up the inside of the monel tubing. At the top the rod was attached to a Sylphon bellows, which gave a vacuum tight connection with freedom of vertical motion of about an inch. The bellows was activated by a hand screw so that any vertical position within the limits of extension could be achieved and held. In this way the specimen could be lowered from a position in which it hung freely in vacuum to a position in which it was being pressed tightly by the rod to the bottom of the can. Pressures upon the salt which were obtainable by hand tightening the bellows screw were adequate to bring the salt from several degrees above the liquid helium bath temperature to an equilibrium with the bath in about fifteen minutes. The initial cooling from liquid air temperatures down to liquid helium temperatures took about forty-five minutes. Upon breaking the contact some heating occurred so that there was initially a very rapid rise in the temperature of the salt. Thus the lowest temperatures at which accurate measurements could be made were higher than the lowest bath temperatures obtainable by about a degree for LiF and about half that for KI.

Temperatures of the sample were measured with a carbon resistance thermometer, which was imbedded in a groove at the upper edge of the salt itself. A constantan heater wrapped directly on the salt over about three-quarters of its
length provided a means for admitting measurable amounts of heat. Good thermal contact between the salt and the heater and thermometer was assured by a very thin coating of red glyptal. The resistor was of the Allen-Bradley type. It had a room temperature resistance of 57 ohms, a resistance at 4.2 °K of about 1000 ohms, and a resistance at 2 °K of about 10,000 ohms. This thermometer was calibrated after each run by admitting helium exchange gas to the calorimeter and comparing resistance readings of the thermometer to vapor pressure readings of the bath as read from manometer and cathetometer. By-pass pumping lines with suitable valves allowed regulation of the pumping speed to such a degree that the bath could be held at essentially constant temperature (within a millidegree) for ten minutes or more for each calibration point so that equilibrium was assured. Extrapolation between the points directly determined was made using the formula suggested by Clement and Quinell;\textsuperscript{16} i.e.

\[ \log R + \frac{K}{\log R} = B + \frac{A}{T} \]

where \( R \) is the resistance, \( T \) the temperature, and \( A, B, \) and \( K \) are constants to be determined by calibration.

All measurements were made in point by point fashion using two Leeds and Northrup Type K potentiometers. One measured the voltage drop across the thermometer or heater directly, and the other measured the voltage drop across a standard resistance in the same circuit. In this way data were obtained for compiling plots of temperature vs. time through a drift period on either side of period of heating.
Energy was supplied to the sample via the heating coil from a wet cell battery. Suitable variable resistance in the circuit allowed the temperature rise for a fixed period of heating to be kept reasonably constant on the order of several hundredths of a degree. The heating period was fixed by a cam operated microswitch driven by a clock motor. This was calibrated using a scalar circuit set to read the peaks of the 60 cycle laboratory current. By this arrangement the time of the heating period was determined to be 30.63 ± 0.04 seconds.

In order to prevent heat leaking to or from the sample through the leads to the heater and thermometer two things were done. First, the leads themselves were brought out of the calorimeter can through kovar seals in its top, so that the leads outside the calorimeter passed through the liquid helium bath. The kovar seals gave quite adequate performance, although twice during the course of the work superfluid leaks around the solder connections to the kovars did develop and had to be repaired. Inside the calorimeter long leads of #38 manganin wire, about 50 cm. in length, were used. The salt was protected from radiation by a concentric-cup baffle at the end of the monel tube, and also by the plate from which it was suspended. The rod leading from the bellows was thermally linked to the bath by two flexible copper wires soldered to the lower end of the rod and to the top of the can. This was found necessary to prevent heat from leaking down the rod and reaching the specimen. The overall heat leak to the
sample could be determined by measuring the rate of temperature rise during drift periods. When this was done it was found always to be positive; i.e., heat leak to the sample. It was also found not to be strongly dependent on temperature. Generally the heat leak was on the order of several hundred ergs per minute. In view of the arrangement it seems reasonable to ascribe most of this to conduction down the rod and radiation to the salt.

METHOD OF ANALYSIS AND CORRECTIONS

The data taken were converted by the resistance-temperature relation into a set of values of temperature as a function of time. These corresponded to a period of heating, when a measurable amount of power was being delivered to the heater, and a preceding and following period of drift, when no power was delivered to the heater. A typical set of data is exhibited in Fig. 7. The data from these curves were put into an IBM 650 computer made available through the generosity of the Shell Development Company and a least squares fit to a parabola was made for each drift curve. These parabolas were then extrapolated to the midpoint of the heating period to determine the rise in temperature for the measured heat input. Provided the heat leak to or from the sample involves terms of no higher temperature dependence than the first, this is correct to a high order, as will be
shown later. In any case it is a closely correct procedure if the drift curves are very nearly linear, as was the case in this work.

Several corrections were necessary. In the first place, since the leads to the heater were of manganin and of rather long length, they had a rather high resistance of about twenty ohms apiece, compared to the heater resistance itself of about 295 ohms. In order to account for heat developed in the leads which might subsequently leak into the sample, the potential leads measuring the voltage drop across the heater were arranged after the manner suggested by Logan, Clement, and Jeffers. Under the assumption that heat developed in the leads flows either into the sample or into the bath via the lead itself this correction is adequate; namely, for balanced leads half the heat developed goes into the sample. However, with substances of very poor thermal conductivity, such as manganin, the impedance to heat flow may be sufficiently great that the lead becomes hot and loses a significant amount of energy by radiation. With this in mind a separate experiment was carried out to determine the amount of heating caused by the leads alone. It was determined, as is discussed later, that only 19% of the heat developed in the leads went into the sample (rather than 50%) and that this number was essentially independent of the sample temperature. Furthermore, the heat leaking
in from the leads may do so with a long time constant due to the low conductivity. The upper drift curve in this case should be extrapolated back from a point many seconds after the heating has stopped. This is also discussed in more detail later. With this effect taken into account the slopes of the two drift curves were found to be very nearly the same.

The heat input was calculated from the measured heater resistance and measured heater current with a correction being made as mentioned for lead heating. The heat capacity was then obtained using the relation

\[ C = \frac{\Delta Q}{\Delta T} \]

A correction to the heat capacity was made for the heat capacity of the glyptal. Taking the formula for specific heat of glyptal suggested by Pearlman and Keesom,\textsuperscript{21} i.e., \(0.22 T^2 \times 10^4\) erg/gm deg, this quantity was calculated for every point and subtracted off the heat capacity as determined above. For the LiF the correction to the heat capacity ranged from about 8% at the lowest temperatures to about 3% at the highest. For the KI the correction was a fraction of 1% at all temperatures. A separate experiment was made with the salt sample replaced by a thin aluminum shell to check this correction. The results indicated that the correction for the heat capacity of the addenda to the salt was quite reasonably accounted for by the glyptal correction alone.
The calibration of the thermometer deserves further comment. Whenever one refers temperatures to the vapor pressure of a surrounding bath of liquid helium one is faced with a situation having two limiting cases. Either there is poor convection in the bath so that a temperature gradient is established; one needs then to make a correction to the measured vapor pressure for the head of liquid helium above the thermometer. Or else there is good convection and the bath has essentially a uniform temperature throughout. This question is described in detail by Muench. An experimental determination of what head correction is necessary is afforded by the lambda-point transition in liquid helium. Liquid He II with its high heat conductivity is certainly at a uniform temperature. Hence one can plot resistance of thermometer vs. vapor pressure temperatures, making no correction to the temperatures below the lambda-point transition at 2.18 K, and demand a smooth transition across the lambda-point. In the present work this was done and always the indication was that no correction should be made to the vapor pressure measurements for the head of liquid helium. The Leyden vapor pressure tables were used throughout.

It was found that the parameters involved as constants in the calibration equation of Clement and Quinnell differed systematically depending on the range of temperature from which calibration points were chosen. This is no surprise,
of course, in light of the fact that the formula is only an extrapolation formula and is semi-empirical in nature. It merely indicates that the formula does not quite give an exact fit to the calibration points over the entire temperature range. The only time a difference of any consequence resulted so far as the derived temperatures were concerned was for the temperatures above those obtainable with the bath, where no calibration points could be determined. For these it was deemed adequate to extrapolate the Clement-Quinnell formula using constants determined from calibration points made between the lambda-point and the normal boiling point of helium. In this range the resistance is a comparatively slowly varying function of the temperature and seemed to be very well described by the formula over the whole range.

The results reported here are for $C_v$, the specific heat at constant volume. The actual measured quantities related to $C_p$, the specific heat at constant pressure. At sufficiently low temperatures, and this is certainly true in the liquid helium range, the two are negligibly different as can be seen from the following arguments. The two specific heats are related thermodynamically by

$$C_p - C_v = \beta^2 VT/k$$

where $\beta$ is the volume coefficient of thermal expansion and $k$ is the isothermal compressibility. At low temperatures $k$ approaches a constant finite value, while $\beta$ diminishes toward zero. For $\lambda$ the pertinent calculations were made
by Berg and Morrison and they find that at 25 K $C_p$ differs from $C_v$ by less than one part per thousand. Below 20 K the difference is negligible. A similar calculation can be roughed out for LiF. The compressibility for low temperatures has been deduced by Briscoe and Squire. The expansion coefficient has been measured to liquid air temperatures by Adenstedt and can be extrapolated in plausible fashion to low temperatures using Gruneisen's relation. Again one finds that below 20 K $C_p$ is negligibly different from $C_v$.

When making temperature measurements on substances such as these salts which have very low thermal conductivities, the question of thermal equilibrium arises. How long does it take for heat put in at one point to diffuse throughout the specimen so that the thermometer, at another point, will read a reliable average temperature? This is considered in detail in a later section. The conclusion is that on a theoretical basis fortified by experimental verification one need consider no time lag between the heater and the thermometer for the two salts and the arrangement used in this experiment.

RESULTS AND CONCLUSIONS

The results of the present investigation are presented in Figs. 2 and 3, where the specific heat as a function of $T^3$ is shown. The LiF is seen to be linear in $T^3$ throughout the range of measurements, while the KI veers from the line determined by the lowest temperature values and rises
from this line as the temperature is increased. More sensitive plots are shown in Figs. 4 and 5. (See also Fig. 10.) Here the value of θ from $C_V = 464.3(T/θ)^3$ is drawn as a function of T. For LiF the values are seen to cluster about a constant value which may be taken to be the $T = 0$ value of θ. An average of the 42 points along with the average deviation is $θ_{LiF} = 722 \pm 6.0K$. In Fig. 6 the LiF data are repeated along with the results of Clusius and Eichenauer and also Martin. Martin's data are seen to be somewhat consistently higher, although there are a number of points in excellent agreement. The work of Clusius and Eichenauer in a slightly higher temperature range are in excellent agreement. The present work forms a complementary extension of their work to liquid helium temperatures. Values of $θ_D$ reported by Martin and Clusius respectively, are $737 \pm 9.0K$ and $723 \pm 7.0K$. Briscoe and Squire derive a $θ_D$ from low temperature measurements on the elastic constants of LiF. They report a value of $θ_D$ calculated using DeLaunay's tables of $θ_D = 734 \pm 5.0K$. This is felt to be in agreement with the θ determined by specific heat measurements.

Also shown in Fig. 5 are data reported by Berg and Morrison derived from low temperature specific heat measurements. The agreement is seen to be good, but with an important difference in implication. From their data there is no indication that θ has yet begun to level off toward a constant value. The present work, however, indicates a
leveling off in the neighborhood of 3 \(^0\)K with an approach to \(T = 0\) at a value between 128 and 129 \(^0\)K. The average of the ten points below 3.5 \(^0\)K and the average deviation gives \(\Theta = 128.3 \pm 3\) \(^0\)K. The value of 3 \(^0\)K is in rough agreement with Blackman's criteria of \(\Theta/50 = 2.6\) \(^0\)K.
Norwood\(^2\) has measured the low temperature elastic constants of KI and again comparison of the elastic constants \(\Theta\) with specific heat \(\Theta\) may be made. He reports two values, depending on the method of calculation. Using DeLaunay's\(^3\) tables he derives \(\Theta = 131 \pm 2\). Using Houston's\(^9\) method as extended by Betts, Bhatia, and Wyman\(^10\) he gets \(\Theta = 129 \pm 2\). The agreement with either is felt to be good.

In light of a recent paper by Ludwig\(^11\) the agreement may be even better between the elastic constants data and the specific heat data. He indicates that due to anharmonic terms in the crystal potential which are normally neglected, there will generally be a slight difference between the \(\Theta_D\) derived in the normal way from elastic constants data and that derived from specific heat data. For LiF he reports, as for certain other alkali halides, this should have the effect of making \(\Theta\)-elastic a per cent or two higher than \(\Theta\)-specific heat. Barron and Morrison\(^12\) by another approach consider the effect of anharmonic terms retained in the frequency distribution and find a slight relative change of the same nature in the specific heat \(\Theta\).
The present work adds confirmation to the not very extensive body of low temperature data that the Debye $\Theta$ as derived by elastic means and by thermal means do, in fact, substantially agree. It is hoped, further, that this work coupled with the elastic constants experiments, will contribute to the increasing effort being made to evaluate anharmonic terms and their influence on the physical properties of crystals. More work of this nature is needed to test the recent extensions of the simple Debye model.
APPENDIX I

Frequency Distribution Function and the T-Cubed Dependence

At the basis of the theoretical explanation of the specific heat of solids is the view that a crystal is a collection of particles vibrating about equilibrium positions in a lattice. In dielectric crystals such as we are considering the only important contribution made to the specific heat is that made by the lattice. To a good approximation, at least insofar as specific heat is concerned, the vibratory motion may be taken to be simple harmonic. The lattice is then a collection of simple harmonic oscillators. A mole of an element has Avogadro's number, \( N \), particles each with three degrees of freedom so that it may be considered to be \( 3N \) simple harmonic oscillators.

In order to get the specific heat one must assign an energy to each oscillator so that the total energy of the crystal can be found. This energy can then be differentiated with respect to the temperature to get the specific heat. Initially, the classical average energy of an harmonic oscillator, \( kT \), was assigned to each oscillator, and this yielded

\[
C = 3Nk = 3R
\]

the Dulong-Petit value. This had the failing of not falling toward zero as the temperature was lowered, as experimental evidence indicated was true.

A great advance was the suggestion by Einstein\(^ {27} \) that the classical average energy be replaced by the quantum
mechanical average energy

\[ \bar{E} = \frac{1}{2} hv + \frac{hv}{e^{hv/kT} - 1} \]

This led to a specific heat from

\[ C = \frac{d}{dT} \ 3N \ \bar{E} \]

or

\[ C = 3N \ \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2} \ \frac{h^2 v^2}{kT^2} \]

where \( x = hv/kT \) and \( R \) is the gas constant, \( Nk \). For high temperatures where \( x \) might be considered small \( C \) should approach

\[ C_{\text{high } T} = 3R \ \frac{x^2}{(1 + x - 1)^2} = 3R \]

as desired. At low temperatures, however, where \( x \) is large the behavior should be like

\[ C_{\text{low } T} = 3R \ x^2 \ e^{-x} \]

with a nearly exponential approach to zero in \( 1/T \). Quantitatively this approach to zero turned out to be too rapid.

The next point of attack was the tacit assumption made in the above analysis that every oscillator is vibrating with the same frequency so that the crystal is merely 3N identical oscillators. There was introduced, instead, a distribution function, \( g(v) \), which specified the number of oscillators vibrating with a given frequency \( v \).
Generally $g(v)$ would be a function of $v$. In this light the total energy of the crystal would be

$$E = \sum_v g(v) \overline{E}(v)$$

where the summation is to be taken over all the frequencies involved, and

$$\sum_v g(v) = 3N$$

Then

$$C = \frac{d}{dT} E = \sum_v \frac{(\frac{h}{kT})^2 e^{\frac{hv}{kT}}}{(e^{\frac{hv}{kT}} - 1)^2} k g(v)$$

The whole problem now is finding, or at least finding an approximation to, the distribution function $g(v)$.

Debye\(^3\) suggested an approach which, though the approximations seem severe, yields a simple $g(v)$ function, giving particularly good agreement with experimentally determined specific heat values at low temperatures. First Debye assumes the medium to be, rather than a discrete crystalline medium, a continuum, isotropic and non-dispersive. Certainly the difference between a crystal and a continuum so far as propagation of waves is concerned diminishes as the waves become long enough to span many lattice dimensions. The details of structure are then not important. In brief Debye's reasoning was similar to the following. Consider a cube of material. It will support in the steady state modes of oscillation which set up
standing waves. A particular plane wave from which standing waves would be built could be put in the form of

\[ \vec{u}_\vec{r} = \vec{u}_k e^{i\vec{k} \cdot \vec{r}} e^{i\omega t} \]

where \( \vec{u}_\vec{r} \) is the displacement of a particle located by a position vector \( \vec{r} \), \( \vec{k} \) is a propagation vector of the plane wave with magnitude equal to \( 2\pi \) divided by the wavelength \( \lambda \) and the direction of \( \vec{k} \) is the direction of propagation of the wave. If this is to contribute to a standing wave, \( \vec{k} \) must be limited to certain values. In particular if \( L \) is one dimension of the cube of material then

\[ k_\chi L = n 2\pi \]

where \( n \) is an integer. Thus

\[ k_i = n \frac{2\pi}{L} \]

Hence we might construct a "k-space" having points distributed uniformly on a cubic lattice with spacing \( 2\pi/L \). Each point in this k-space is representative of an allowed mode of oscillation. The angular frequency \( \omega \) is taken to be a function of the magnitude of \( \vec{k} \) but not of its direction, since the medium is assumed isotropic. Therefore, the number of modes giving rise to the same frequency is essentially the number of points in k-space within a shell of thickness \( dk \) and radius \( k \). The spacing of points in k-space is quite close compared to dimensions of the actual lattice spacing since \( L \) is equal to a great number of lattice units.
Hence it is assumed that the number of points within the shell is very closely the volume of the shell times the density of points in k-space; i.e.

Number of points in shell = \((4\pi k^2 \, dk)/(2\pi L)^3\)

Thus, letting \(V\) be the volume of material,

\[ g'(\nu)\,d\nu = 4\pi \, \frac{1}{\lambda^2} \, d(1/\lambda)V \]

From the assumption of non-dispersiveness we can take

\[ \nu \lambda = c \]

where \(c\) is the velocity of sound in the material and is constant for all frequencies. Then

\[ g'(\nu) = 4\pi \, V \, \left( \frac{\nu^2}{c^3} \right) \]

However, we have neglected the fact that there are three polarizations of waves, two transverse and one longitudinal for each frequency, and these may have different velocities of propagation. Hence for the total density we arrive at

\[ g(\nu) = 4\pi \left( \frac{1}{c^2} + \frac{2}{c^3} \right) \, V \, \nu^2 \]

or

\[ g(\nu) = a \nu^2 \]

Debye brings in at this point cognizance of the fact that the material is not a continuum but is instead \(N\) oscillators each with three degrees of freedom. He does this by saying
\[ \int g(v) dv = 3N \]

where the integral is taken from zero up to some value \( v_{\text{max}} \) which is imposed to cut the integral off. Thus

\[ v_{\text{max}}^3 = 9N/a \]

The whole question of frequency distribution was given a different treatment by Born and von Karman,\(^4\) who again find at low temperatures a \( v^2 \) dependence. Their work shall only be outlined here, since the final result is essentially the same as Debye's and the method is much more involved. The important feature is that the method establishes, formally at least, to what degree Debye's approximation is an approximation. Born begins with the equations of motion of a particle in the lattice

\[ \ddot{u}_a = \sum_b A_{ba} (\bar{u}_b - \bar{u}_a) \]

where \( \bar{u}_a \) is the displacement of a particle designated by a set of indices symbolized by \( a \) and \( A_{ba} \) is a force constant of the Hooke's law type connecting particles \( b \) and \( a \). The summation extends over all values of \( b \); i.e., all the particles of the crystal. If the crystal is such, as alkali halides, that it contains particles of two differing masses, one has two equations similar to the one shown, and it is convenient to break up the summation to allow \( b \) to run over particles of only one type. One attempts to find solutions in the form of plane waves
\[ \overline{u}_a = \overline{U}_k e^{i(\omega t - \overline{k} \cdot \overline{a})} \]

where the amplitudes may be a function of \( k \), the propagation vector, and the plane waves run through only one type of particle. One then has six equations, a set of three for each type of particle, the three arising from the three components of vectors involved. For a non-trivial solution of these equations to exist in general, the six by six determinant of the coefficients of the \( U_k \) must be identically zero. This then gives a sixth order equation in \( \nu^2 \) to be solved for \( \nu^2 \) as a function of \( k \) for each particular direction. If this can be done, one has the frequency distribution function. The general solution is very involved. For low temperatures, however, one can make the assumption of long wave length or small \( k \), and make certain simplifications. Born\textsuperscript{13} expands \( \nu^2 \) and \( \nu \) as a power series in \( k \), as he also does \( U_k \) and various coefficients involving \( e^{i\overline{k} \cdot \overline{a}} \). He finds

\[ \nu = A + Bk + Ck^2 \]

with solutions falling into two types. For one \( A \neq 0 \) so that \( \nu \) does not approach zero as \( k \) does. These branches, three in number, are all of relatively high frequency. The Reststrahl frequency in KI, for instance, can be cited to give the order of magnitude of this branch. It is about \( 3 \times 10^{12} \) cps. Consequently these modes remain in their ground states at low temperatures. The other case is one in which \( A = 0 \). There are three of these branches. For these branches \( \nu \) approaches zero with \( k \) and for small \( k \),
v is proportional to k. The proportionality constant in general is a function of direction. From this point the analysis is closely parallel to Debye's and one arrives again with a \( v^2 \) frequency distribution. The directional dependence of the proportionality constant \( a \) in \( g(v) = av^2 \) can be removed by an appropriate averaging over all directions. The frequency distribution then, as we have seen, determines the specific heat. A peak in the distribution function, representing a large number of oscillators at a given frequency, would manifest itself in the behavior of the specific heat as a function of temperature. In particular, as will be shown now, the \( v^2 \) form for \( g(v) \) leads to the \( T^3 \) dependence in the specific heat.

\[
C = \sum_v \frac{(hv/kT)^2 e^{hv/kT}}{(e^{hv/kT} - 1)^2} k g(v)
\]

becomes

\[
C = \int_0^{v_m} \frac{(hv/kT)^2 e^{hv/kT}}{(e^{hv/kT} - 1)^2} k a \, v^2 \, dv
\]

Define \( x = hv/kT \).

\[
C = \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \cdot ka(kT)^3
\]

Remove \( a \) by using the normalization relation

\[
a \, v_m^3 = 9N
\]

\[
C = 9N \frac{k(kT)^3}{h^2v_m} \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} \, dx
\]
Define a parameter

\[ \Theta = \frac{h \nu_m}{k} \]

We see

\[ x_m = \frac{h \nu_m}{kT} = \frac{\Theta}{T} \]

and

\[ C = \mathcal{O}\left(\frac{T^3}{\Theta^3}\right) \int_0^{\Theta/T} \frac{e^x x^4}{(e^x - 1)^2} \, dx \]

The integral is one that cannot be evaluated exactly but may in general be expanded in series and evaluated term by term. It is not very sensitive to the value \( \Theta/T \) provided \( \Theta/T \) is large. Hence, for low temperatures, \( T \ll \Theta \), one may replace \( \Theta/T \) by infinity as an upper limit of the integral, and the integral can then be evaluated exactly. It yields \( 4/15 \pi^4 \). Thus one concludes that the limiting form of the dependence of specific heat upon temperature for very low temperatures is

\[ C = \frac{12}{5} \pi^4 R \left(\frac{T}{\Theta}\right)^3 = 464.3 \left(\frac{T}{\Theta}\right)^3 \text{cal/gm at. wt.} \]

It is exactly this \( T^3 \) region in which this present work is interested.

**Consideration of Approximations in Theory**

Considerable attention has been paid the approximations mentioned in the preceding section. The replacement of the upper limit on the Debye integral by infinity
is not severe. The Debye function is defined by

\[ D(x) = 3R x^3 \int_0^x \frac{e^y y^4}{(e^y - 1)^2} \, dy \]

which is the same as

\[ D(x) = 3R x^3 \int_0^x \frac{e^{-y} y^4}{(1 - e^{-y})^2} \, dy \]

For large \( x \) expand in powers of \( e^{-y} \) and obtain

\[ \frac{D(x)}{3R} = \frac{4\pi^4}{5} \frac{1}{x^3} - \frac{3x}{e^x - 1} - 12x \sum_{n=1} \left( \frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4} \right) \]

Recalling that \( x = \theta/T \), the lead term gives the \( T^3 \) dependence. The ratio of the second term to the lead term is given in the following table:

<table>
<thead>
<tr>
<th>( x )</th>
<th>( 4\pi^4/5x^3 )</th>
<th>( 3x/(e^x - 1) )</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.79 x 10^{-2}</td>
<td>13.66 x 10^{-4}</td>
<td>17.53 x 10^{-3}</td>
</tr>
<tr>
<td>11</td>
<td>5.85</td>
<td>5.51</td>
<td>9.41</td>
</tr>
<tr>
<td>12</td>
<td>4.51</td>
<td>2.21</td>
<td>4.91</td>
</tr>
<tr>
<td>13</td>
<td>3.55</td>
<td>.88</td>
<td>2.49</td>
</tr>
<tr>
<td>14</td>
<td>2.84</td>
<td>.34</td>
<td>1.23</td>
</tr>
<tr>
<td>15</td>
<td>2.31</td>
<td>.14</td>
<td>.60</td>
</tr>
</tbody>
</table>

Thus for an accuracy of better than 1% we could neglect all terms after the first for \( T \) less than \( \theta/12 \). In the case of KI this would be for a temperature of about \( T = 110^\circ K \).

As mentioned earlier, Blackman\(^5\) has established,
nevertheless, that for actual crystals the $T^3$ region is not reached until temperatures on the order of $\theta/50$ are reached. Moreover, he shows that the initial deviation from the $T^3$ law as $T$ is increased will be a decrease in the value of $\theta$ as a function of $T$.

The question of boundary conditions and their influence on the distribution function has also been considered in detail. Both Lederman$^{28}$ and Peierls$^{29}$ have worked on the problem and have shown, for reasonable sizes of materials at least, the particular boundary conditions imposed on the equations of motion have very slight effect on the resulting frequency distribution.
APPENDIX II.

Calculation of Specific Heat

Basically the heat capacity of the specimen is determined by injecting a measured quantity of heat, ΔQ, noting the temperature rise of the sample, ΔT, and defining the heat capacity as

\[ C = \frac{\Delta Q}{\Delta T} \]

In practice this is complicated by the fact that perfect isolation of the sample from its environment is never achieved. Moreover, since the heat is admitted over a finite length of time, t, there is always the possibility that some of the heat input leaks out to the bath during the heating period. Also, some of the temperature rise may be attributed to heat influx from sources other than the heater. For this reason the temperature is observed during drift periods, when no heat is being applied by the heater, in order to determine the contribution made by heat leaks. By proper extrapolation of these drift curves a true ΔT for the input ΔQ can be determined.

The method used in this work was to fit parabolas to the drift curves and extrapolate to the midpoint time of the heating period. Under reasonable assumptions pertaining to the heat leak this is correct to a high degree of accuracy as is shown below.

The data yield curves of the temperature T versus time t. Fig. 7 shows a typical set of drift and heating curves. At the left, the temperature is rising slowly due
to heat leak into the sample from its environment. At the arrow near 4.3 minutes the heat was turned on and the temperature begins to rise abruptly with a discontinuity in slope. At the arrow near 5.2 minutes the heat was turned off and the curve returns to its original form.

If we let $T$ represent the time derivative of the temperature and $Q$ the rate of heat input we have

$$C \frac{dT}{dt} = Q$$

where $C$ is the specific heat. $Q$ may have a temperature dependence. It can be expressed as partly due to a constant heat leak in (as by radiation from the room temperature end of the gear, mechanical vibration, etc.) and by a heat leak out from the sample, which will depend on the difference in temperature between the specimen and the surrounding bath. Conduction out of the leads, for instance, would have the form $k(T_S - T_B)$ where $k$ is the thermal conductivity of the lead material, $T_S$ is the specimen temperature, and $T_B$ is the temperature of the bath.

Similarly, conduction through the very rare gas about the sample would have this form as dominant term, as would radiation from the sample. Hence we may take

$$\dot{Q} = a - bT$$

where $a$ and $b$ are simply constants. $C$ will also have a temperature dependence, very nearly $T^3$ in this case (see Fig. 2). However, as will be shown below, if the overall rise in temperature is kept small, $C$ may be considered constant with little introduction of error. Hence we wish
to consider the behavior of $T$ governed by

$$C \frac{dT}{dt} = a - bT$$  \hspace{1cm} (1)$$

where $C$ is constant. Take for the origin of time the midpoint of the heating period. Let the temperature at the beginning of heating be $T_0$ and the temperature at the end of the heating be $T_e$. Let the two points at which extrapolations of the drift curves intersect a vertical through the midpoint time of the heating be $T_1$ and $T_2$ respectively, where $T_2$ is the larger temperature. Then integrating Eq. (1) and inserting the boundary conditions, we have

$$C \ln \frac{a - bT_1}{a - bT_0} = -b\tau/2$$  \hspace{1cm} (2)$$

$$C \ln \frac{a - bT_2}{a - bT_e} = +b\tau/2$$  \hspace{1cm} (3)$$

when $\tau$ is the length of time the heater is on. The same Eq. (1) holds for the curve obtained during heating, provided the constant term $a$ is increased by the amount of the heater input. From that integration we get

$$C \ln \frac{a' - bT_0}{a' - bT_e} = b\tau$$  \hspace{1cm} (4)$$

The problem is to eliminate the unknowns $a$ and $b$ from these equations and endeavor to find a simple expression for $C$ in terms of $T_1$, $T_2$, and $\tau$. Eqs. (2) and (3) can be solved for $a$ in terms of $b$ and the temperatures.

$$a = b \frac{T_1T_2 - T_0T_e}{T_1 + T_2 - T_0 - T_e}$$  \hspace{1cm} (5)$$
Eq. (4) can be solved for $a'$

$$a' = b \frac{T_e - T_0 e^{-b \tau / C}}{1 - e^{-b \tau / C}} \tag{6}$$

The difference between $a'$ and $a$ is simply the power input to the heater, $P$. Thus $b$ can be found in terms of measurables, and through Eq. (5) $a$ can be found. Putting these values into (2) and (3) we have

$$c = \frac{Pr}{\ln \left( \frac{T_2 - T_0}{T_e - T_1} \right)^2 \left\{ \frac{(T_2 - T_0)^2 T_e - (T_e - T_1)^2 T_0}{(T_2 - T_0)^2 - (T_e - T_1)^2} - \frac{T_1 T_2 - T_0 T_e}{(T_2 - T_0) - (T_e - T_1)} \right\}} \tag{7}$$

This, so far, is exact under the assumptions but is also unmanageable. However, due to the low heat leak, $T_1$ is only slightly larger than $T_0$ and $T_2$ is only slightly smaller than $T_e$. Also experimentally $T_2 - T_1$ is kept small by limiting the heater input. Thus we define

$$T_1 - T_0 = d_1$$
$$T_e - T_2 = d_2$$
$$T_2 - T_1 = D$$

and expand the various terms in (7). We get

$$c = \frac{Pr}{D} \left\{ 1 + \frac{1}{6} \frac{(d_1 - d_2)^2}{D} + \frac{(d_1 + d_2)}{12 D^2} \right\} (5 \frac{d_1^2}{D} - 16 d_1 d_2 + 5 d_2^2) + \ldots \}$$

From Fig. 7 we get

$$d_1 = .0004 \, ^\circ\text{K}$$
$$d_2 = .0003 \, ^\circ\text{K}$$
$$D = .0392 \, ^\circ\text{K}$$

and the second term in the sum is $4.2 \times 10^{-8}$, completely negligible.
The drift curves by the above analysis have an exponential dependence on time, \( t \),

\[
\frac{a - bT}{a - bT_0} = e^{-bt/C}
\]

In practice it is easier to handle a power series. We see by looking at Fig. 7 that the curvature of the drift curves is very slight. Hence \( b/C \) must be small, and we can expand the exponential in powers of \( bt/C \) and get rapid convergence

\[
\frac{a - bT}{a - bT_0} = 1 - \frac{b}{C} t + \left( \frac{bt}{C} \right)^2 + \ldots
\]

Rearranging

\[
T = T_0 + \left( \frac{a - bT_0}{C} \right) t - \left( \frac{a - bT_0}{C} \right) \left( \frac{b}{C} \right) t^2 + \ldots
\]

We can estimate the magnitude of the coefficients of the powers of \( t \) by returning to Fig. 7. The slope at \( T_0 \) gives the value of \( (a - bT_0/C) \) and is \( .00295 \) deg/min, while the curvature is \( 2 \left( \frac{a - bT_0}{C} \right) \left( \frac{b}{C} \right) \) and \( .000126 \) deg/min\(^2\). Thus \( b/C \) has the value \( .0213 \) and we see we are certainly justified in neglecting the next term in \( t^3 \) whose coefficient would be \( 1.34 \times 10^{-5} \) deg/min\(^3\). Thus the drift curves were fitted with a power series in \( t \) retaining only quadratic terms.

A final consideration must be given to the approximation that \( C \) is constant over the temperature interval. Taking the salt to obey the \( T^3 \) law perfectly, set

\[ C = AT^3 \]

where \( A \) is a constant involving the Debye \( \Theta \) which we wish
to determine.

Assuming no heat leak

\[ AT^3 \cdot T = p \]

Integrate to get

\[ \frac{AT^4}{4} \bigg|_{T_1}^{T_2} = pT \]

and solve for \( A \)

\[ A = \frac{4pT}{T_2 - T_1} \]

Also assign the measured specific heat, \( pT/T_2 - T_1 \), to the midpoint temperature

\[ \frac{pT}{T_2 - T_1} = A' \left( \frac{T_1 + T_2}{2} \right)^3 \]

We seek to determine to what degree the \( A' \) from this approximate determination differs from the \( A \) from the more exact procedure. Let \( T^* \) be the midpoint temperature and \( T_2 - T_1 = D \) again. Further let \( D/2T^* \) be \( p \). Then we have

\[ T_2 = T^* + D/2 = T^* (1 + p) \]
\[ T_1 = T^* - D/2 = T^* (1 - p) \]

\[ A = \frac{pT}{T^*^4} \left( \frac{4}{(1+p)^4} - \frac{4}{(1-p)^4} \right) \]
\[ A' = \frac{pT}{T^*^4} \cdot \frac{1}{2p} \]

Therefore

\[ \frac{A'}{A} = \frac{(1+p)^4 - (1-p)^4}{8p} = \frac{8p + 8p^3}{8p} = 1 + p^2 \]

Hence \( A' \) is the same as \( A \) if we can neglect \( p^2 \) compared to
1, which is to say \((T_2 - T_1/T_2 + T_1)^2 \ll 1\). Thus \(T_2 - T_1\) could be of the order of 10% of \(T_2 + T_1\), i.e., \(8^\circ\)K at \(4^\circ\)K, without introducing but 1% error. In practice \(T_2 - T_1\) was kept down to a few hundredths of a degree.

A precaution must be taken, however, due to the long time constant connected with the heat influx from the leads. The analysis just given supposes the heat input to the specimen from the heater to begin immediately when the heater is turned on and to cease immediately when the heater is turned off. The determination of lead heating is considered in a later section. Suffice it to say here, however, that Fig. 8 represents data taken to emphasize the possible error involved. One sees in that diagram that when the heat is turned on there is an abrupt change in slope of the \(T\) vs. \(t\) curve, as assumed in the analysis. When the heat is turned off, however, the temperature continues to rise for a number of seconds at a rate intermediate between the heating slope and the drift slopes. One concludes that heat is continuing to flow in from the hot leads. The final drift rate, for the validity of the above analysis, is not to include this source of heat. Consequently the drift curve must be extrapolated from a point after this source has become negligible; i.e., from a point many seconds after the heater has been turned off. The extrapolation to \(T_2\) in Fig. 8 represents the valid case. The open circles on the upper drift curve represent a plausible set
of data points. The extrapolation through them (overlooking the effect being discussed) would lead to the spurious temperature $T_S$. It is easy to see how an error of some size could be introduced.
APPENDIX III.

Thermal Relaxation

The question naturally arises when dealing with a substance of very poor thermal conductivity, such as the salts in question at these low temperatures, as to what sort of times are involved between the input of heat at the heater on the surface of the salt and the distribution of this heat in a more or less uniform way throughout the body of the sample. As will be shown below the important quantity in this process is not the thermal conductivity, $k$, alone but rather the ratio of the thermal conductivity to the specific heat, $k/C$. Despite very low values of $k$, the specific heat may be so small that $k/C$ is rather large and equilibrium in temperature is rapidly attained. This is the case for the two salts of this experiment.

An approach to this problem is the following. Suppose the salt to have a uniform temperature hot compared to the bath and that suddenly one end is placed in very good thermal contact with the bath. How much time elapses before the temperature of the other end comes to within 1% of the bath temperature? This is the same as plunging a slab of material of thickness twice the length of the salt into a bath and asking what is the midpoint temperature. The heat flow equation in one dimension is

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{a^2} \frac{\partial T}{\partial t}$$

where $a^2 = k/Cp$, $k$ is the thermal conductivity, $C$ the specific heat per gram, and $p$ is the density. The boundary
conditions are that $\partial T/\partial x$ be zero at the center ($x = 0$) for all times and that the temperature at the surface be $T_B(x = \pm L)$ for all times. For simplicity we may take the bath temperature $T_B$ to be zero without changing the problem. The initial conditions are that the temperature be a step function:

$$
T(x, 0) = \begin{cases} 
T_1 & |x| \leq L \\
0 & |x| > L 
\end{cases}
$$

The solution is easily expressible in this case and is

$$
T(x, t) = \frac{1}{2} T_1 \left\{ \overline{\mathcal{G}} \left( \frac{L - x}{2a \sqrt{t}} \right) + \overline{\mathcal{G}} \left( \frac{L + x}{2a \sqrt{t}} \right) \right\}
$$

where $\overline{\mathcal{G}}$ is the error integral

$$
\overline{\mathcal{G}}(t) = \frac{2}{\sqrt{\pi t}} \int_0^\infty e^{-x^2} \, dx
$$

and is tabulated. We are interested in the point $x = 0$ so that

$$
T(0, t) = T_1 \overline{\mathcal{G}} \left( \frac{L/2}{a \sqrt{t}} \right)
$$

As $t$ approaches infinity the argument of $\overline{\mathcal{G}}$ approaches zero, $\overline{\mathcal{G}}$ approaches zero, and hence $T$ approaches zero; i.e., the salt temperature approaches the bath temperature. When is $T(0, t) = 1\% T_1$? or when is $\overline{\mathcal{G}}(t) = 1\%$? Referring to the normal error table in the Handbook and converting to our notation, it is when

$$
\frac{L/2}{a \sqrt{t}} = 3.67
$$

or letting $d = L/2$ be the length of the salt, it is when
\sqrt{t} = \left(\frac{d}{3.67\ a}\right) \\
\sqrt{t^2} = \left(\frac{d^2}{13.5}\right)(cp/k)

We have tacitly assumed that C is a constant independent of temperature, but for small changes in temperature this is not a gross assumption. For a salt three inches long, or 7.6 cm., we have then for the "equilibrium time"

\[ t = 4.3\ cp/k \]

For LiF the specific heat per gram at 4.2 °K is about \(3.80 \times 10^3\) erg/gm deg, p is 2.33 gm/cc, and k is about \(5 \times 10^7\) erg/sec cm deg.\(^{23}\) Hence the "equilibrium time" is

\[ t = 7.6 \times 10^{-4}\ \text{sec}. \]

For KI the case is not quite as clear cut since the low temperature thermal conductivity has not yet been measured. However, both KBr\(^{24}\) and KCl\(^{24}\) have been measured with values respectively at 4.2 °K of 1.1 and 2.7 watts/cm deg. There is no reason to suppose KI to be radically different from these two, so as an order of magnitude choose the less favorable of the two values and say \(k = 1.1 \times 10^7\) erg/cm deg sec. The specific heat at 4.2 °K is about \(C = 7.0 \times 10^5\) erg/gm deg and \(p = 3.13\) gm/cc. Hence

\[ t = .86\ \text{sec} \]

In either case the time for thermal relaxation is seen to be of no great consequence. An experimental check on the relaxation time is seen in Fig. 8 which shows a discontinuity in the slope of temperature of the sample vs. time.
when the heat is switched on. The data point just below the arrow indicates the temperature at the instant the heat is applied. It is seen to lie smoothly on both the drift curve and the heating curve. Had there been a time lag of the thermometer following the turning on of the heater current the two curves would have intersected at some point to the right of the arrow. A time lag as great as five seconds would have been easily detectable. Accordingly, we have assumed throughout this work that there is no lag of consequence between application of heat and the distribution of this heat throughout the sample.
APPENDIX IV.

Lead Heating

It was stated earlier that although a comparatively large amount of heat is developed in the leads to the heater, less than a quarter of this heat finds its way into the sample. In this section it will be shown first that this is very plausible on a theoretical basis and second that it is supported experimentally.

There are two limiting cases which will be considered. First, suppose that heat from the leads is carried away by conduction along the leads only. In this event the differential equation to be solved is

\[
\frac{dq}{dx} = j^2 r
\]

where \( q \) is the thermal current density, \( j \) is the electrical current density, and \( r \) is the electrical resistivity of the wire. This yields

\[
q = j^2 r x + q_0 \quad (1)
\]

where \( x = 0 \) is the end of the lead at the bath. Setting \( q = -k \frac{dT}{dx} \), where \( k \) is the thermal conductivity, and integrating again, we get

\[
-k \frac{dT}{dx} = \frac{1}{2} j^2 r x^2 + q_0 x
\]

or

\[
q_0 = -\frac{1}{2} j^2 r L - \frac{K}{L} \quad (2)
\]

where \( K = \int k \frac{dT}{dx} \) and \( L \) is the length of the lead. Eliminating \( q_0 \) from Eq. (1) using Eq. (2) we have
\[ q_L = \frac{1}{2} j^2 r L - K/L \]
\[ q_0 = -\frac{1}{2} j^2 r L - K/L \]  (3)

In Eqs. (3) \( q_L \) is the heat flow into the sample \( (x = L) \) and \( q_0 \) is the heat flow into the bath \( (x = 0) \).

Eqs. (3) show that superimposed on the flow of heat due to the temperature gradient between the salt and the bath is a flow of the Joule heat, one half going in either direction.

As a second limiting case, consider the coefficient of thermal conductivity to be so low that no heat is carried by conduction into the sample and the wire merely heats up until it can radiate all the Joule heat away. We ask what is its temperature. The equation now, neglecting radiation to the wire from the bath, is

\[ s S T^4 = i^2 r \]

where now \( i \) is the current in amps, \( r \) the resistance per unit length, \( S \) the surface area per unit length, and \( s \) is a radiation constant dependent on the surface. Thus

\[ T^4 = i^2 r / s S \]

Now put in reasonable values. Fifty centimeters of wire had about twenty ohms resistance, so \( r = .4 \) ohms/cm. (The resistance is very nearly temperature independent. The heater resistance changed only from 304 ohms at 83 \( ^\circ \)K to 294 ohms at 4 \( ^\circ \)K.) Take \( i \) to be .85 ma. The diameter of the wire may be taken as .020 cm., so that \( S = .0628 \) cm\(^2\). For \( s \) take the Stefan-Boltzman constant \( 5.65 \times 10^{-5} \) erg/cm\(^2\) deg\(^4\) sec. Then
\[ T^4 = 81 \times 10^4 \text{ deg}^4 \]
\[ T = 30 \text{ }^\circ\text{K} \]

which is quite plausible.

Thus the situation existing in practice is most likely a combination of the two extreme cases. The solution of the problem when loss by both radiation and conduction is considered is almost intractable.\textsuperscript{25,26} Instead resort was made to an experimental determination of the heat flow into the sample from the leads. The heater was by-passed by an arrangement allowing the heater current to pass through the heater leads only. Values of temperature as a function of time were then taken with and without current in the leads. Fig. 9 shows a typical plot obtained. The central portion between the arrows represents the period of heating. The portion to either side represents the drift period. Several things can be noted, considering that the slope of the curve is a measure of the rate at which heat flows into the sample. First, the heat flow begins immediately upon turning on of the current, but its rate increases in time, reaching a steady value some minutes after heating began. Second, it continues to flow, with steadily decreasing rate, some minutes after the current has stopped. Third, the upper drift curve approaches the same slope as the lower, as one would expect for small temperature increments. By supposing the heat capacity to be known, the rate of heat input per minute and the total heat input can be calculated. For the plot shown
a temperature rise of $2.85 \times 10^{-2}$°K at a temperature of 3.659°K represents an input of $1.91 \times 10^4$ ergs of heat. This was developed, however, by $8.6 \times 10^{-4}$ amps flowing through a resistance of 36.2 ohms for 6.5 minutes or $10.2 \times 10^4$ ergs. Thus only $1.91/10.2 = 19\%$ of the Joule heat developed in the leads was carried by conduction into the specimen. Similar measurements at other temperatures showed that there was no significant dependence of this number on temperature.
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To Mr. Arthur Thorsen for many hours of assistance during the summer of 1957;

To Mr. Clarence Belcher for making the liquid helium and liquid air and assisting in technical details;

To Mr. J. F. Van der Henst for his help in constructing the equipment.
REFERENCES

DEBYE THETA
KI

$\Theta_D$ (°K)

T (°K)

$\times$ 2/3/58
$\bullet$ 2/11/58
$\circ$ 2/18/58
$\Delta$ BERG AND MORRISON

FIG. 5
DEBYE THETA
LiF

FIG. 6

T (°K)

Θ₀ (°K)

○ MARTIN
△ CLUSIUS AND EICHENAUER
X PRESENT WORK
## DATA

### I. LiF

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LiF, continued
### II. KI

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