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Atomic Heats of Normal and Superconducting Thallium

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The atomic heats of thallium have been measured in the liquid helium temperature range. In the normal state the atomic heat varies with temperature according to the form: $C_n=\gamma T+464.4(T/\theta)^3$ cal/mole deg in which $\gamma=6.11\times 10^{-4}$ cal/mole deg^2 and $\theta=86.6°$. In the superconducting state, at temperatures below $0.9T_c$, the electronic specific heat obeys the relationship: $C_{SE}=\gamma T_c A\exp(-\alpha T_c/T)$ cal/mole deg, in which $A=5.8$ and $\alpha=1.3$. These results lend support to the suggestion made in consequence of recent measurements of the atomic heats of aluminum, vanadium, and tin that the electronic specific heat may in general be an exponential function of temperature. They do not confirm, however, the suggestion that there exists a law of corresponding states among superconductors.

1. INTRODUCTION

In the light of recent revisions[1] of the temperature scale between 1°K and 4.2°K and the evidence[2–4] which has been published supporting an exponential relationship between the electronic specific heat of a superconductor and the temperature, it has been considered appropriate to measure the heat capacity of a sample of thallium metal between 1.1°K and 4.2°K both in the normal and in the superconducting states. Although the magnetic properties of this metal have received considerable attention,[5,6] the calorimetric properties below 4.2°K were last investigated by Keesom and Kok[7] in 1934. The fact that the metal has a relatively high lattice specific heat so that the ratio of the electronic contribution to the lattice contribution at the transition temperature is only 0.24 makes the accurate determination of the electronic contribution somewhat difficult and may account for the paucity of data on this particular property of the metal. Moreover, since the transition temperature is 2.36°K it is not possible with conventional techniques to perform measurements at a temperature lower than approximately $0.5T_c$. Since the results published on Al, V, and Sn indicate that the exponential temperature dependence of the superconducting electronic specific heat may only be valid below $0.7T_c$, it may be expected that measurements to a temperature no lower than 1.15°K may serve only to indicate whether a similar relationship exists in the case of thallium or not.

2. EXPERIMENTAL

The thallium sample was provided by A. D. Mackay, Inc., New York, New York with a stated purity of 99.999%. The metal was cast, *in vacuo*, in a Pyrex tube lined with magnesium oxide[8] to prevent the metal sticking to the glass. The sample was then cooled over a period of several hours from its melting temperature to ensure proper annealing although the softness of the metal probably made this unnecessary. After removal from the mould the metal was polished superficially to remove the few traces of magnesia adhering to its surface and coated with Glyptal lacquer to inhibit the formation of a surface layer of oxide, a process which occurs very rapidly on exposure to the atmosphere.

The thermometer employed was an Allen-Bradley 10-ohm, ½-w carbon resistor, the properties of which have been described by Clement and Quinnell.[9] This was cemented with Glyptal lacquer into a hole drilled into the metal specimen. The heater consisted of a length of No. 40 Advance wire wound around the sample and insulated from it by a layer of lens tissue, the whole being coated with Glyptal. The final sample was a cylinder of diameter 22 mm and length 44 mm. The mass of thallium was 199.20 g and the total mass of addenda, thermometer, heater, lens tissue, and Glyptal, was 0.49 g. Throughout the entire temperature range the estimated heat capacity of the addenda never exceeded 0.3% of that of the thallium, and accordingly the presence of these components was neglected in calculating the heat capacity of the specimen.

The sample was suspended by nylon fibers in a vacuum calorimeter surrounded by liquid helium. Only at the lowest temperatures, below 1.5°K, was there any positive indication of incomplete thermal isolation and then the heat leak into the sample never exceeded 2% of the power input during a heating cycle. Since the resistance changes of the thermometer were recorded in the manner reported by Horowitz, Silvidi, Malaker,

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and Daunt[10] accurate allowance could be made for any temperature drift. Electrical connections, of No. 40 Advance wire, to the heater and thermometer were conducted via glass-metal seals into the helium bath. Within the calorimeter the heater current leads were coated with lead solder to minimize the generation of heat.

The measurements of heater power and thermometer resistance were made by standard techniques. For the former, Rubicon potentiometers Type 2730 were employed in the measurement of heater current and potential. The thermometer current (constant) and thermometer potential difference were measured with a Rubicon Type B potentiometer. The error signal generated across the thermometer in the course of a heating cycle was amplified by a dc amplifier[11] and recorded on a Brown recording potentiometer. Thereafter, by the application of a calibration signal from the Type B potentiometer to the dc amplifier, the exact values of potential across the thermometer before and after the heating cycle could be obtained. The corresponding resistance values of the thermometer were thus calculated and in consequence the temperatures of the sample by use of a calibration equation of the type to be described. Power dissipation in the thermometer varied between 0.05 and 1 μw and was negligible in comparison with the heater input.

The calibration of the resistance thermometer was performed by measuring the resistance at various temperatures between 4.2°K and 1.2°K. The temperatures were obtained from measurements of the vapor pressure of the liquid helium bath and the use of the helium vapor-pressure temperature scale published by Clement, Logan, and Gaffney.[12] The use of the symbol T in the following will imply a temperature based on this scale. Separate calibrations were obtained whenever the thermometer current was changed or the external magnetic field was applied. Resistance measurements were made with an estimated inaccuracy of less than 0.03%. The resistance measurements taken during calibration were plotted as a function of temperature in an equation of the form[9]: $\log R+k(\log R)^{-1}=AT^{-1}+B$. On substituting into this equation a value for R, the value of the temperature so obtained was designated T_R. A curve of the deviation, (T_R-T), was plotted against T_R and employed to correct the values of T_R to the temperature T. It is believed that temperatures, T, determined in the above manner were accurate to within 0.002°.

The measurements of heater current, heater voltage, and heating cycle duration were such that the estimated inaccuracy in computing the total heat input during a cycle was less than 0.1%. The greatest source of error lay in computing the change in resistance of the thermometer, and accordingly the change in temperature (approximately 1% of the mean temperature) which occurred during a heating cycle. An analysis of all the relevant factors permits the inaccuracy in this measurement to be set at 2%. Accordingly it is estimated that the over-all experimental error in the computed values of specific heat as a function of temperature should be set at 2.5%. With the exception of measurements below 1.4°K, over 90% of the total specific heat values deviate by less than 2% from the smooth curves to be mentioned. For a few points at lower temperatures the deviation is as much as 5%.

3. RESULTS

The results reported here were obtained in a total of 184 heating cycles. Of these, 68 cy were performed with the metal in the superconducting state and the remainder in the normal state. Of the latter group, 61 cy were carried out in zero magnetic field above the transition temperature, 35 in a longitudinal magnetic field of 200 oe, sufficient to remove all traces of superconductivity at temperatures below the normal transition temperature, and 20 in the same field above the transition temperature.

Since it is expected that the total normal atomic heat, C_n, will be expressible as the sum of terms linear and cubic in temperature the data were plotted in the form C_n/T *vs* T^2. The curve so obtained is given in Fig. 1. It will be seen that the experimental points fit a straight line extremely well over the entire temperature range. Eighty-five percent of the points deviate from the straight line by less than 2% and except at the extremes of the temperature range, the scatter is random. At temperatures above $T^2=15$ deg^2 and below $T^2=2$ deg^2, it may perhaps be claimed that the deviations are other than random although the experimental scatter makes it difficult to make a categorical statement to this effect. On the assumption, following Debye[13] and Sommerfeld,[14] that the total normal specific heat is of the form:

$$C_p=C_v=C_n=\gamma T+464.4(T/\theta)^3$$

the values of the constants obtained from a least-squares evaluation of the C_n/T *vs* T^2 data are

$$\gamma=6.11\times10^{-4}\pm0.84\times10^{-4}\text{ cal/mole deg}^2,$$

$$\theta=86.6°\pm0.3°.$$

The fiducial limits in both cases are stated for a 99% confidence level.

If it is assumed that the total observed specific heat, in the superconducting state, C_{ST}, may be expressed as the sum of the lattice specific heat, C_L, and the superconducting electronic specific heat, C_{SE}, then

$$C_{SE}=C_{ST}-464.4(T/\theta)^3.$$

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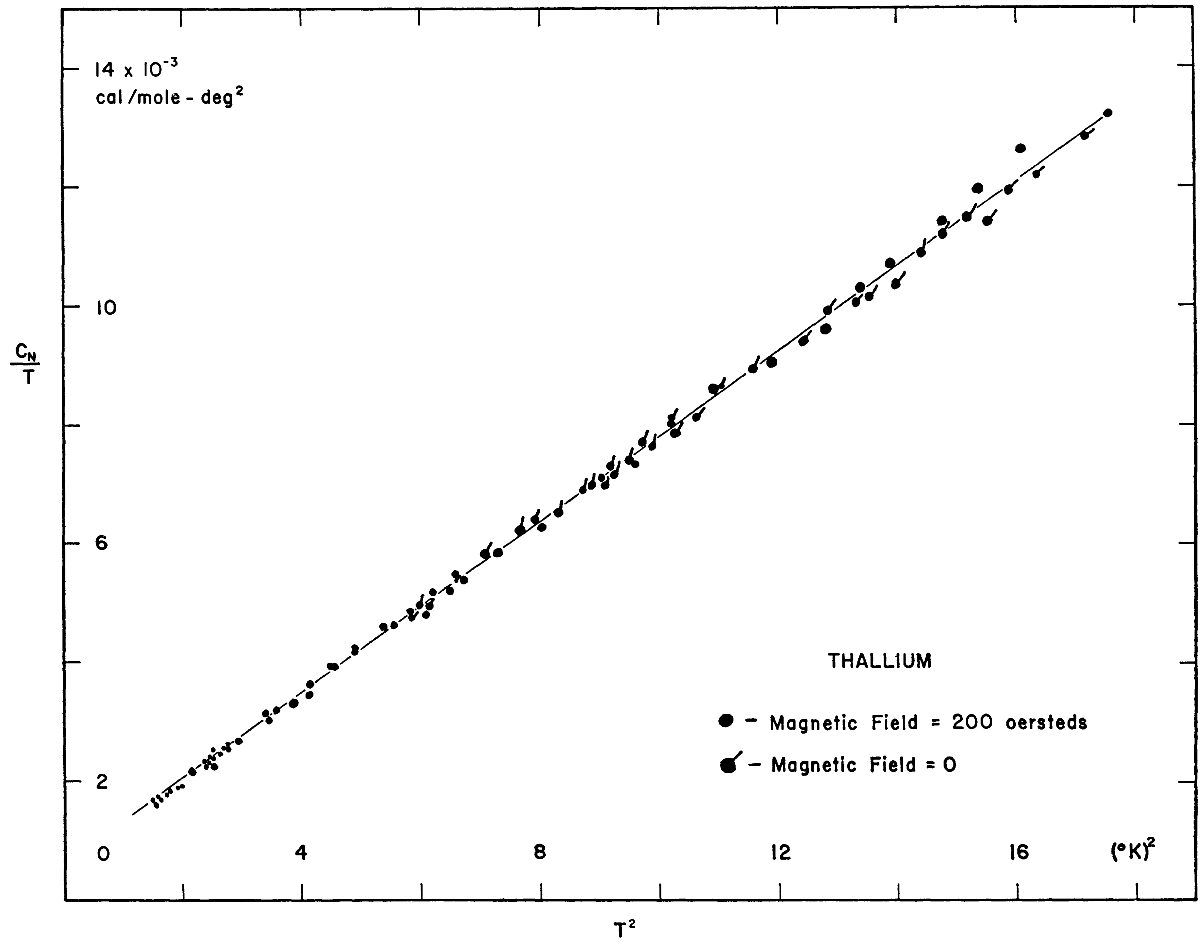

FIG. 1. Atomic heat of thallium in the normal state. The solid line represents: $C_n/T=0.000715T^2+0.000611$, where C_n is in cal/mole deg and T in deg K.

Using the constant value of θ obtained above, C_{SE} was computed for each value of C_{ST} measured experimentally. The values of the superconducting electronic specific heat so determined are plotted as a function of temperature in Fig. 2.

If the electronic specific heat is of the form

$$C_{SE}=\gamma T_c A \exp(-\alpha T_c/T), \tag{1}$$

the hypothesis may be tested by plotting the logarithm of the electronic specific heat *vs* T^{-1}. This analysis has been performed and it is apparent that at temperatures below 2.15°K (i.e., $0.9T_c$) the experimental points indicate a linear relationship. A least-squares analysis yields the following formula for the variation of C_{SE} with temperature:

$$C_{SE}=5.8\gamma T_c \exp(-1.3T_c/T) \text{ cal/mole deg}$$

in which $\gamma=6.11\times10^{-4}$ cal/mole deg² and $T_c=2.36°$.

4. DISCUSSION

The experimental results are in agreement with those of Keesom and Kok[7] throughout the temperature range which they investigated. The transition temperature and the magnitude of the specific heat discontinuity at the transition were also in agreement with data based upon the magnetic measurements of Misener[5] and Maxwell and Lutes[6] although scatter in the immediate vicinity of the transition prevented a precise determination of either quantity.

The information presented in Fig. 1 suggests that the Debye temperature is constant within the temperature range of the experiments, with the possible exception of the temperature range above $T^2=15\,(°\text{K})^2$. In this latter region, the value of θ was computed from the smoothed specific heat data using the value $\gamma=6.11\times10^{-4}$ cal/mole deg². Up to a temperature of 4.10°K, the value of θ so obtained agrees with that already quoted, 86.6°±0.3°. However there is evidence of a slow reduction of θ with further increase of temperature, since the following values are obtained: at 4.15°K, $\theta=85.9°$ and at 4.20°K, $\theta=85.1°$. This behavior is consistent with the results of previous investigations. The data of Keesom and Kok, have been reanalyzed by plotting C_n/T *vs* T^2. Between the transition temperature and 4.2°K, a straight line is obtained consistent with a constant value of $\theta = 89.6°$ with again possibly a slight tendency for θ to diminish in the vicinity of 4.2°K although the experimental data are insufficient to justify a more definite statement. Below the transition temperature very few values of the normal specific heat were obtained by Keesom and Kok and it is difficult to reach conclusions generally consistent with the data obtained above the transition temperature. It is possible that at least part of this difficulty arises from inaccuracies in the temperature scale employed by them. Measurements of the specific heat of thallium at higher temperatures have been performed by Clusius and Vaughen[15] and by Hicks.[16] They are agreed that above 17°K, θ is constant at approximately 94°, but that θ diminishes to 84° in the vicinity of 11°K. It therefore seems permissible to conclude that θ remains constant at 86.6° up to a temperature of 4.1°K and then diminishes slowly to a minimum between 4.2°K and 11°K. Thereafter it rises to a relatively constant value of approximately 94° at temperatures above 20°K. This over-all picture is qualitatively in agreement with that presented by some other hexagonal metals—e.g., Zr[17] and La.[18]

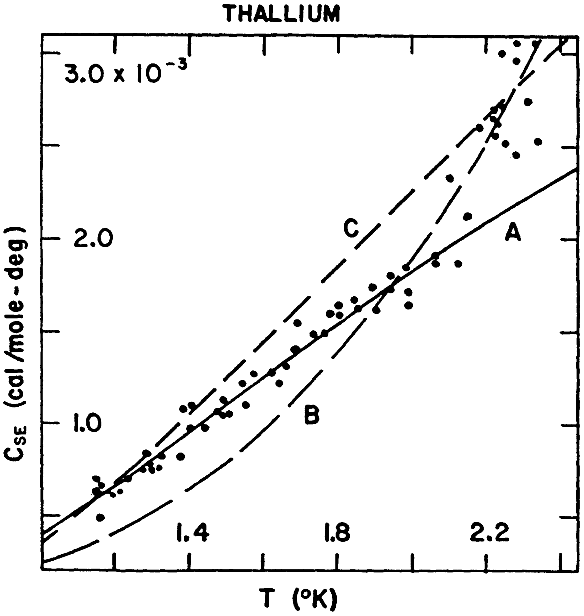

FIG. 2. Electronic specific heat of superconducting thallium *vs* temperature. The solid curve (A) represents: $C_{SE} = 5.8\gamma T_c \exp(-1.3T_c/T)$. The broken curves represent, (B): $C_{SE} = 0.000238T^3$, and (C): $C_{SE} = 9.17\gamma T_c \exp(-1.5T_c/T)$. In ($A$) and ($C$), $\gamma = 6.11\times10^{-4}$ cal/mole deg² and $T_c = 2.36$°K.

The value obtained for the electronic constant γ, 6.11×10^{-4}, is considerably closer to that obtained from the magnetic measurements, 2.8 to 3.65×10^{-4}, than is the calorimetric value, 14×10^{-4}, quoted by Shiffman[19] and also obtained from our analysis of the data of Keesom and Kok.

The analysis of the superconducting electronic specific heat confirms for thallium the conclusion already reached for aluminum, vanadium, and tin, that this parameter is an exponential function of temperature. There is therefore agreement with the predictions of the two-fluid model of the "energy-gap" superconductor recently discussed by Lewis.[20] Moreover, the values of the constants, $A = 5.8$, $\alpha = 1.3$ [Eq. (1)], are not incompatible with the criterion which is suggested in his Eq. (20). For comparison, the corresponding values in the case of aluminum[2] are $A = 6.9$ and $\alpha = 1.28$. On the other hand, the constants differ from those obtained by Corak *et al.* for both vanadium and tin and therefore are in disagreement with the suggestion that there exists a law of corresponding states for superconductors. In Fig. 2, there has been inserted the curve (marked C) which is predicted if $A = 9.17$ and $\alpha = 1.5$, the values obtained for vanadium and tin. This curve differs from the experimental data between 1.45°K and 2.1°K by an amount greater than the experimental scatter. In the plotting of these curves the values $\gamma = 6.11\times10^{-4}$ and $T_c = 2.36°$ have been employed. If it is assumed that this value of γ is in error and the most recent "magnetic" value of γ, 3.65×10^{-4}, is used instead, no better agreement with the experimental results is obtained.

In Fig. 2 there is drawn a curve (marked B) representing the equation:

$$C_{SE} = 0.000238T^3 \text{ cal/mole deg.}$$

This curve was chosen by fitting a T^3 function as suggested by the Gorter-Casimir theory[21] to the experimental points above 2°K. Clearly the data deviate considerably and consistently from this curve at lower temperatures.

We have performed an analysis of the specific heats of indium obtained by Clement and Quinnell[22] and find that their values for C_{SE} between 2.3°K and 1.8°K (their lowest temperature) agree closely with Eq. (1), with $A = 9.6$ and $\alpha = 1.6$. However the small number of experimental points within this temperature region renders this description somewhat tentative until further measurements at lower temperatures are performed.

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In conclusion, the evidence available from measurements on aluminum, vanadium, tin, and thallium (possibly also indium) strongly supports the contention that the electronic specific heat in the superconducting phase is an exponential function of temperature. However, the variation in the values of the constants A and α does not yet permit the existence of a law of corresponding states to be concluded without reservation.

5. ACKNOWLEDGMENTS

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Ionization Rates for Holes and Electrons in Silicon

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The ionization rates for holes and electrons in silicon at high electric fields have been evaluated from data on the multiplication of reverse-biased junctions. In Si, electrons have a higher ionization rate than holes. The variation of ionization rate with field strength is in good agreement with theory.

INTRODUCTION

It has been demonstrated that in both germanium and silicon, reverse biased junctions break down as a result of a solid state analog of the Townsend β-avalanche theory.[1-3] In germanium it was possible to detect the difference between the roles of holes and electrons in the breakdown process.[3] Differences in the functional form of multiplication *vs* reverse voltage, depending on whether the initial current entering the junction consisted of holes or electrons, were analyzed to give the ionization rates for holes and electrons as a function of field strength. In the case of the silicon experiments,[2] the initial currents entering the junction were composed of both holes and electrons; and the detection of a difference between their ionization rates was rendered either difficult or impossible.

In the work reported here for silicon, initial current consisted of predominantly one carrier type; and differences between the ionization rates for holes and electrons were detected.

It is interesting that in silicon the ionization rate is higher for electrons than for holes, while the opposite holds in germanium.

As in Ge, the ionization rates, as a function of field, could be brought into agreement with Wolff's[4] theoretical treatment of the problem by a suitable choice of parameters.

THEORY

The Townsend β-discharge theory for solids, pictures multiplication and breakdown of *pn* junctions as occurring when electrons and/or holes are accelerated to energies sufficient to create hole-electron pairs by collisions with valence electrons. This can occur in the high fields in the depletion region of a reverse biased junction. Electrons or holes, entering the depletion region from the p or n side of the junction, respectively, create electron-hole pairs. These collision products are then accelerated until they have sufficient energy for pair production and so on. This gives a multiplication of the original current appropriate to every field distribution and therefore every voltage for a given junction. This multiplication, for an original current composed of only one type of carrier, is given by[3]

$$1-\frac{1}{M}=\int_0^w \alpha_i(E)\exp\left[-\int_0^x [\alpha_i(E)-\beta_i(E)]dx'\right]dx, \quad (1)$$

where M is the multiplication, w is the width of the depletion region, and $\alpha_i(E)$ and $\beta_i(E)$ are, respectively, the ionization rates for the initial and secondary particles.

For a complementary set of step junctions consisting of a pn^+ and np^+ with the same net density of impurity centers on the high resistivity side, it is possible to solve for the ionization rates for holes and electrons separately if the multiplication of initial current coming from the high-resistivity side *vs* voltage conforms to the empirical law

$$M=\frac{1}{1-(V/V_B)^n}. \quad (2)$$

Then the expression for the ionization rate of the initial

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