Table I it is seen that the present work favors the theories developed by Landau[4] and by Spitzer.[8] However, no attempt is made to compare the present results with the theory (of transport phenomena) by Cohen, Spitzer, and Routly[35] and by Spitzer and Harm[36] because of the different nature of the problem involved.[37] The values of $C_1$ and $C_2$ determined by Anderson and Goldstein[11] are extremely good considering that they only did the experiment at one temperature (i.e., 300°K). Yet the present experiment clearly demonstrates the temperature dependence of electron-ion collision frequency for momentum transfer in an isothermal plasma.

In conclusion, the method of microwave diagnosis a decaying weakly ionized neon plasma at different gas temperatures provides a unique means of studying the fundamental processes of electron-neon atom and electron-ion collisions at very low energies.


## ACKNOWLEDGMENTS

It is a great pleasure to acknowledge the cooperation and assistance given by Dr. P. D. Goldan on the electron temperature measurements in the early part of the investigation. The author enjoyed the many stimulating and beneficial discussions with Professor L. Goldstein, Professor J. H. Cahn, and Professor M. Raether during the course of the work. He also thanks the members of the Atomic Physics group in Westinghouse Research Laboratories for their reading of the manuscript. In particular, the author would like to express his sincere gratitude to Dr. A. V. Phelps for his criticism and suggestions of this paper.


[35] R. S. Cohen, L. Spitzer, and P. McR. Routly, Phys. Rev. **80**, 230 (1950).

[36] L. Spitzer and R. Härm, Phys. Rev. **89**, 977 (1953).

[37] For a Lorentz gas, the dc resistivity $\eta_L$ cannot simply be written as $\eta_L=m\nu_{ei}/ne^2$. [See L. Spitzer, *Physics of Fully Ionized Gases* (Interscience Publishers, Inc., New York, 1956), p. 82.] It can be shown from the Boltzmann transport equation that, in the case of $Q_m(v)=bv^{-4}$

$$\eta_L=m\nu/\pi ne^2,$$

where $\nu=nb\langle v\rangle^{-3}$ may be identified as $\nu_{ei}$ and $\langle v\rangle=[8kT_e/\pi m]^{1/2}$ is the mean thermal velocity of the electrons. To equate $\eta_L$ so obtained to Spitzer's (Refs. 35, 36) more rigorous derivation of $\eta_L$ yields

$$\nu_{ei}=3.36\frac{n}{T_e^{3/2}}\ln\frac{1.25\times10^4T_e^{3/2}}{n^{1/2}}.$$

There is an apparent discrepancy of $\nu_{ei}$ so derived to that derived from $\tau_{eq}$. (Ref. 8) Because of the approximate nature in the treatment to deduce $\nu_{ei}$ from $\eta_L$, we think that it is improper to compare the present result with the dc resistivity theory.

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# Specific Heat of Mercury and Thallium between 0.35 and 4.2°K†

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The specific heat of mercury and thallium were measured between 0.35 and 4.2°K. In the normal state below 0.7°K the mercury results are given by: $C_n=1.79T+5.23T^3$ mJ/mole deg. The coefficient $\alpha$ of the $T^3$ term corresponds to a value of the Debye parameter $\Theta_0$ of 71.9°K. For temperatures higher than 0.7°K, the lattice specific heat deviates above the $T^3$ law. A plot of $\Theta(T)$ is given. Below 0.6°K, the specific heat of thallium in the normal state is given by: $C_n=1.47T+4.03T^3$ mJ/mole deg. The corresponding value of $\Theta_0$ is 78.5°K. Above 0.6°K, the lattice specific heat of thallium shows a deviation below the pure $T^3$ law, a result contrary to that found for most solids. This would imply a deviation in the dispersion curve above the linear portion. A similar effect was observed in the specific heat of graphite which was explained on the basis of bond-bending modes of vibration. It is suggested that similar modes may explain this behavior for thallium. In the superconducting state the specific heat of both materials can be represented by a sum of the normal lattice term and a superconducting electronic term $C_{es}$ of the form $a\gamma T_c\exp(-bT_c/T)$. For mercury, values are obtained for $a=15$ and $b=1.64$ with $T_c=4.16$°K; for thallium $a=9$ and $b=1.52$ with $T_c=2.38$°K. In the case of thallium the critical field as a function of temperature $H_c(T)$ is determined, with $H_c(0)=176.5$ G.

## INTRODUCTION

EARLIER measurements in this laboratory,[1] as well as independent measurements by O'Neal *et al.*[2] indicate an anomaly in the low-temperature specific heat of indium. At very low temperatures the superconducting-state specific heat drops below the lattice specific heat as obtained from normal-state measurements. For a while there were indications that niobium showed a similar effect,[3] but newer measurements[4]

† Work supported by U. S. Army Research Office.

[1] C. A. Bryant and P. H. Keesom, Phys. Rev. **123**, 491 (1961).

[2] H. R. O'Neal, N. M. Senozan, and N. E. Phillips, *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1963).

[3] A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).

[4] B. J. C. van der Hoeven and P. H. Keesom, Phys. Rev. **134**, A1320 (1964).

show this not to be the case. It was of interest to measure several other superconductors with low Debye parameters $\Theta_0$ and large $T_c/\Theta_0$ ratios, where $T_c$ is the critical temperature for a superconductor. Therefore the specific heat of lead was measured.[5] No anomalous behavior for the lattice specific heat was observed, but the measurements yielded values of the electronic specific heat in the superconducting state $C_{es}$, much larger than one would expect on the basis of the BCS theory of superconductivity.

Critical field determinations for mercury by Finnemore[6] and for lead by Decker *et al.*[7] have shown that both mercury and lead have the opposite deviation of the critical field from a parabolic law than is observed for other superconductors. In addition both of these metals have very similar values for $T_c/\Theta_0 \sim 0.07$. Thus it seemed interesting to measure the low-temperature specific heat of Hg.

The other superconductor chosen for investigation was thallium. Thallium is very similar to indium in that it is also a group III element with a low $\Theta_0$ value and a ratio of $T_c/\Theta_0 \sim 0.03$. Moreover, Tl has given indication of being an exception among soft superconductors, possessing an anomalous sign of $dH_c/dP$, the effect of pressure on the critical field.[8]

The results show that both Hg and Tl exhibit typical superconducting properties, following a dependence of $C_{es}$ on temperature consistent with the predictions of the BCS theory, and having equal lattice specific heats in the normal and superconducting states. For both materials, however, the Debye parameter $\Theta$ as a function of temperature is interesting, and for the case of Tl may shed some light on its exceptional behavior.

## EXPERIMENT

The apparatus used was the $He^3$ cryostat described previously.[9] A germanium thermometer, similar in composition to one discussed in an earlier publication[10] was used for the mercury measurements and preliminary thallium measurements. For the final Tl measurements a nominal 10 Ω, $\frac{1}{10}$ W Allen-Bradley carbon resistance thermometer was used. The calibration of the thermometers between 0.4 and 1.2°K was based on the 1962—$He^3$ temperature scale of Sydoriak and Roberts,[11] in conjunction with a paramagnetic salt thermometer below 0.5°K, and above 1.0°K, the 1958-$He^4$ temperature scale.[12] An expansion of $1/T$ in powers of $\log R$ up to $(\log R)^3$ was done in double precision arithmetic on an IBM-7090 digital computer, using the method of least squares described by Moody and Rhodes.[13]

The measurements of Hg were done in zero magnetic field and in a field of 1000 G. For Tl the measurements were done in zero field, 600 G, and 17 000 G. The 600 and 17 000 G measurements yielded identical results within experimental accuracy. Provision for the high magnetic field measurements was made with the use of a new set of cans incorporating a superconducting $Nb_3Zr$ wire solenoid of inner diameter 2.5 cm. The working volume was 1.5 cm in diameter and 3.5 cm long.

The germanium thermometer used in the mercury measurements followed a calibration curve very similar to that found for previous runs. Thus a small constant correction was applied to the value of $\ln R$ in the calibration curve of $1/T$ versus $\ln R$, after checking points at 4.2, 1.0, and 0.5°K. As the magnetoresistance correction for this thermometer was known, one was able to determine the calibration curve in 1000 G by making the appropriate shift from the zero field curve. The reproducibility of this thermometer from run to run was excellent—less than 0.05 Ω at 4.2°K (where $R$ was equal to 35 Ω) during a three-month period including four cyclings from room temperature to helium temperature. The magnetoresistance in 1000 G ranged from minus 1% at 4.2°K, to minus 0.6% at 1.0°K, and 0% at 0.5°K.

In preliminary measurements of Tl a germanium thermometer was mounted, but for the final results a carbon resistance thermometer was substituted. The carbon resistance was used since the magnetoresistance of the germanium was rather large in very high magnetic fields, namely, in 17 000 G, $\Delta\rho/\rho$ varied from minus 2% at 4.2°K to plus 8% at 0.4°K. This is to be compared with the carbon resistance for which $\Delta\rho/\rho$ varied from minus 1.2% at 4.2°K to less than plus 0.5% at 0.4°K in the same field. For zero field the two thermometers gave identical results, and thus low-temperature points from measurements in zero field using both thermometers have been used. The carbon thermometer was calibrated in separate runs at zero field, 600 G, and at 17 000 G. All measurements and calibrations for both Hg and Tl were done in a sequence of increasing field so that any possibility of trapped flux was avoided.

The systematic error in specific heat due to inaccuracies in the temperature scale and calibration, as well as addenda corrections, heater resistance, current, and timing errors should not exceed ±2% at the lowest temperature, and ±1% at 4°K. Error limits stated for experimental quantities are those found from random

[5] P. H. Keesom and B. J. C. van der Hoeven, Phys. Letters **3**, 360 (1963).
[6] D. K. Finnemore, Ph.D. thesis, University of Illinois, 1961 (unpublished).
[7] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **118**, 127 (1960).
[8] H. Rohrer, Helv. Phys. Acta **33**, 675 (1960), review article.
[9] G. M. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).
[10] B. J. C. van der Hoeven and P. H. Keesom, Phys. Rev. **130**, 1318 (1963).
[11] S. G. Sydoriak, T. R. Roberts, and R. H. Sherman, *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963).
[12] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).
[13] D. E. Moody and P. Rhodes, Cryogenics **3**, 77 (1963).

scatter of the data, which is observed to be ±1% over the entire temperature range.

## SAMPLES

The Hg sample (1.155 moles) was of 99.996% purity, triple-distilled Hg from Goldsmith Brothers. It was poured into a cup which was ultrasonically machined out of a solid piece of pure silicon. A central rod of 0.6 cm diameter was left standing in the center of the 3 cm inner diameter cup. The cup had a depth of 3.4 cm. The thermometer was glued with glyptal to the top of the rod, and the constantan heater wire glued around the outside of the cup. Total correction for the heat capacity of the addenda was less than 3% of the total heat capacity of the mercury in the superconducting state at the lowest temperature. As the specific heat of silicon is well known,[14] this should introduce less than 0.1% error in the measurements. The good thermal contact developed between the Hg and the cup gave very rapid heat distribution over the system, but also introduced strains in the Hg.

The first measurements of Tl were done with a sample (1.302 moles) prepared in a graphite boat in a vacuum furnace. As Tl oxidizes very rapidly in air, this sample was dipped in glyptal immediately after removal from a vacuum. It was then mounted and measured. Difficulties were experienced in the magnetic field measurements. At the time these were speculated to be due either to impurities or inaccuracy involving a large glyptal addenda correction. This proved later to be due to the magnetoresistance of the germanium thermometer.

A new sample (0.2116 moles) of 99.9907% purity was obtained from the Fairmont Chemical Company having a diameter of 1.3 cm and a length of 3.2 cm. The oxide layer was easily removed by scrubbing in distilled water. Thus this sample was stored in distilled water until just prior to mounting, then dried in helium gas and mounted, quickly pumping the surrounding space to a vacuum. Subsequent removal of an oxide layer before another run indicated a loss of weight due to oxidation of less than 0.1 mg. The results of measurements of this sample, both with germanium thermometer in zero field, and carbon thermometer for all three fields, are those reported here. Zero field measurements for both samples gave identical results. Total correction for heat capacity of the addenda was less than 1.5% of the heat capacity of Tl in the superconducting state at the lowest temperature.

## RESULTS

### Mercury

The specific heat of a superconductor in the superconducting state $C_s$ and in the normal state $C_n$ may be expressed as

$$C_s=C_{es}+C_{ls},$$
$$C_n=\gamma T+C_{ln},$$

where $C_{es}$ represents the superconducting electronic specific heat, $C_{ln}$ and $C_{ls}$ the lattice specific heat in the normal and superconducting states, respectively, and $\gamma T$ the normal-state electronic specific heat. The BCS theory of superconductivity contains the assumption that the lattice term be equal in the two states, or that $C_{ls}$ is equal to $C_{ln}$, and derives that $C_{es}$ be of the form:

$$C_{es}=\gamma T_c a \exp(-bT_c/T),$$

when $2<T_c/T<6$ and where $a=8.5$ and $b=1.44$. Furthermore, for low temperatures, the theory of lattice specific heats concludes that the temperature dependence of the lattice term can be represented by the following expansion:

$$C_l=\alpha T^3+\beta T^5+\mu T^7+\cdots.$$

For sufficiently low temperatures one expects the lattice term to have a pure $T^3$ behavior. Thus a plot of $C_n/T$ versus $T^2$ should have a limiting slope $\alpha$, and an intercept $\gamma$ at $T^2=0$. In Fig. 1 both $C_n/T$ and $C_s/T$ have been plotted as a function of $T^2$ up to $T^2=1.0$. Representative values of the specific heat over the entire temperature range are listed in Table I. Below $T^2=0.5$, $C_n$, measured in a magnetic field of 1000 G, may be given by:

$$C_n=(1.79\pm0.02)T+(5.23\pm0.04)T^3 \text{ mJ/mole deg.}$$

The coefficient of the linear term, $\gamma$, is in excellent agreement with critical field results by Finnemore[6] of 1.81 mJ/mole deg$^2$. The coefficient of the $T^3$ term $\alpha$ yields a value of the Debye parameter at 0°K, $\Theta_0$, of 71.9±0.2°K. Calorimetric measurements by Douglass

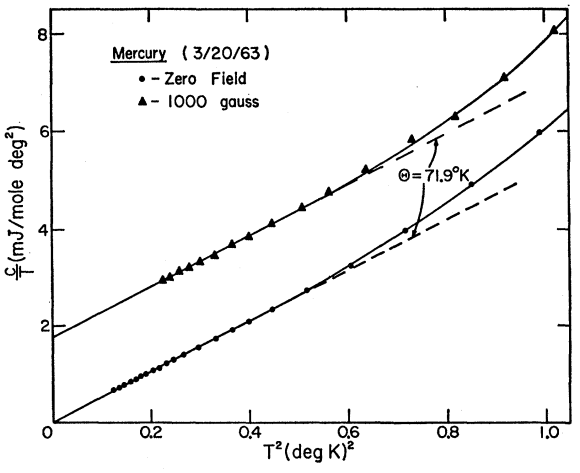


FIG. 1. Specific heat of mercury between 0.35 and 1.0°K.

[14] P. H. Keesom and G. M. Seidel, Phys. Rev. 113, 33 (1959).

TABLE I. Specific heat of mercury. ($C$ is in mJ/mole deg.)

| $T$, °K | $C$ ($H=0$) | $T$, °K | $C$ ($H=1000$ G) |
|---|---|---|---|
| 0.3522 | 0.233 | 0.4745 | 1.406 |
| 0.3669 | 0.263 | 0.5069 | 1.592 |
| 0.3968 | 0.336 | 0.5470 | 1.828 |
| 0.4243 | 0.406 | 0.6044 | 2.230 |
| 0.4529 | 0.488 | 0.6684 | 2.750 |
| 0.4809 | 0.587 | 0.7505 | 3.583 |
| 0.5173 | 0.729 | 0.7984 | 4.179 |
| 0.5766 | 1.001 | 0.8538 | 4.993 |
| 0.6328 | 1.323 | 0.9005 | 5.677 |
| 0.7189 | 1.968 | 0.9580 | 6.825 |
| 0.7790 | 2.535 | 1.021 | 8.249 |
| 0.8480 | 3.383 | 1.172 | 12.99 |
| 0.9228 | 4.542 | 1.284 | 18.26 |
| 0.9947 | 5.943 | 1.399 | 25.20 |
| 1.178 | 11.33 | 1.554 | 37.69 |
| 1.286 | 16.62 | 1.738 | 57.70 |
| 1.451 | 27.33 | 1.896 | 80.25 |
| 1.665 | 47.93 | 2.092 | 115.7 |
| 1.822 | 68.71 | 2.301 | 162.4 |
| 2.000 | 98.15 | 2.535 | 226.2 |
| 2.241 | 150.3 | 2.837 | 326.2 |
| 2.485 | 216.0 | 3.139 | 446.8 |
| 2.842 | 335.6 | 3.534 | 627.6 |
| 3.230 | 495.6 | 3.948 | 852.0 |
| 3.499 | 626.8 | 4.341 | 1084.3 |
| 3.746 | 754.8 | | |
| 3.956 | 874.7 | | |
| 4.121 | 965.6 | | |
| 4.273 | 1036.7 | | |

*et al.*[15] in the superconducting state have yielded a value of $\Theta_0$ of 73°K.

The electronic specific heat of mercury in the superconducting state $C_{es}$ becomes negligible compared with the lattice specific heat $C_{ls}$, for values of $T_c/T>5$. Below $T^2=0.7$, therefore, the total specific heat in the superconducting state should be equal to the lattice specific heat. Because the $T^5$ term dies out below $T^2=0.5$, the pure $T^3$ region is reached, and then the limiting slopes of $C_s/T$ and $C_n/T$ in Fig. 1 should be equal. Indeed this is the case. Therefore the assumption that $C_{ls}$ is equal to $C_{ln}$ is correct for Hg. As a result

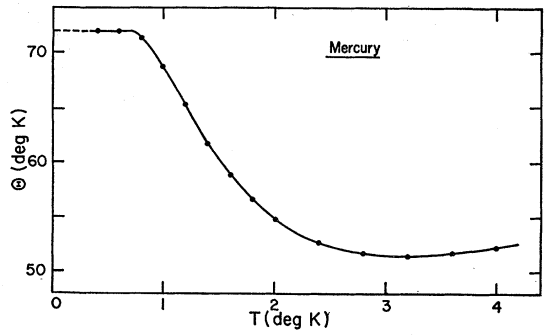


FIG. 2. $\Theta$ versus $T$ for mercury.

[15] R. L. Douglass, R. G. Petersen, and N. E. Phillips, *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1961).

$C_{es}$ may be calculated by the following method:

$$C_{es}=C_n-C_s+\gamma T.$$

Taking smoothed curves through the data, values of $C_{es}$ are obtained. A plot of $\ln(C_{es}/\gamma T_c)$ versus $(T_c/T)$, when $2<T_c/T<4.5$, yields values of $a=15\pm1$ and $b=1.64\pm0.10$.

Following Goodman,[16] the specific heat energy gap for Hg at 0°K, $2\epsilon(0)$, may be estimated by assuming $b$ as a measure of this energy gap:

$$2\epsilon(0)=(b/1.44)(3.50kT_c)=3.98kT_c. \quad (1)$$

This compares very favorably with $3.96kT_c$ found from critical field measurements by Finnemore and reasonably with $4.6kT_c$ from infrared absorption measurements by Richards and Tinkham.[17] All three determinations indicate a larger gap than that predicted by the BCS theory.

As a result of strains developed while cooling the sample the transition from the superconducting to normal state in zero magnetic field was spread out from 4.11 to 4.21°K. The average value of $T_c$ is 4.16°K, in good agreement with 4.154°K found by Finnemore.

TABLE II. Specific heat of thallium. ($C$ is in mJ/mole deg.)

| $T$, °K | $C$ ($H=0$) | $T$, °K | $C$ ($H=600$ G) | $T$, °K | $C$ ($H=17\,000$ G) |
|---|---|---|---|---|---|
| 0.4110 | 0.279 | 0.5159 | 1.341 | 0.6407 | 2.019 |
| 0.4325 | 0.324 | 0.5589 | 1.526 | 0.7250 | 2.565 |
| 0.4691 | 0.415 | 0.5868 | 1.677 | 0.7944 | 3.101 |
| 0.4895 | 0.478 | 0.6223 | 1.883 | 0.9167 | 4.251 |
| 0.5154 | 0.561 | 0.6556 | 2.084 | 0.9925 | 5.065 |
| 0.5662 | 0.758 | 0.7106 | 2.423 | 1.109 | 6.588 |
| 0.6015 | 0.917 | 0.7709 | 2.875 | 1.204 | 8.057 |
| 0.6442 | 1.157 | 0.8499 | 3.575 | 1.318 | 10.03 |
| 0.6886 | 1.421 | 0.9431 | 4.486 | 1.604 | 16.33 |
| 0.7274 | 1.691 | 1.036 | 5.519 | 1.852 | 23.59 |
| 0.8124 | 2.408 | 1.162 | 7.333 | 2.073 | 31.76 |
| 0.8591 | 2.865 | 1.222 | 8.266 | 2.259 | 39.65 |
| 0.9297 | 3.640 | 1.289 | 9.405 | 2.361 | 45.07 |
| 0.9779 | 4.213 | 1.382 | 11.15 | 2.443 | 49.22 |
| 1.031 | 4.955 | 1.434 | 12.22 | 2.600 | 58.64 |
| 1.140 | 6.682 | 1.538 | 14.57 | | |
| 1.260 | 8.907 | 1.647 | 17.28 | | |
| 1.421 | 12.63 | 1.718 | 19.25 | | |
| 1.519 | 15.12 | 1.798 | 21.67 | | |
| 1.599 | 17.46 | 1.932 | 26.30 | | |
| 1.726 | 21.41 | 2.154 | 34.76 | | |
| 1.839 | 25.44 | 2.233 | 38.53 | | |
| 1.932 | 29.15 | 2.520 | 53.69 | | |
| 2.014 | 32.80 | 2.778 | 70.08 | | |
| 2.133 | 38.20 | | | | |
| 2.232 | 43.63 | | | | |
| 2.327 | 48.66 | | | | |
| 2.370 | 50.88 | | | | |
| 2.419 | 48.49 | | | | |
| 2.487 | 52.43 | | | | |
| 2.572 | 56.93 | | | | |
| 2.738 | 67.80 | | | | |
| 3.001 | 87.96 | | | | |
| 3.280 | 114.6 | | | | |
| 3.670 | 160.5 | | | | |
| 4.103 | 224.9 | | | | |

[16] B. B. Goodman, C. R. Acad. Sci. (France) **244**, 2899 (1957).
[17] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

TABLE III. Results of measurements on mercury and thallium.

| Measurement | Temp. range (deg K) | $\gamma$ (mJ/mole deg$^2$) | $\Theta_0$ (deg K) | $a$ | $b$ | $T_c$, °K (1958 scale) | $H_0$ (G) | $-(dH_c/dT)_{T_c}$ (G/deg) |
|---|---|---|---|---|---|---|---|---|
| Mercury | | | | | | | | |
| These results | 0.35–4.2 | 1.79 ±0.02 | 71.9±0.2 | 15 | 1.64 | 4.16 | 380 ±60 | |
| Finnemore[a] | 0.30–4.2 | 1.809±0.012 | | | 1.63[b] | 4.154±0.001 | 410.88± 0.12 | 203.3[b] |
| Douglass *et al.*[c] | 0.1 –0.5 | | 73 | | | | | |
| Richards and Tinkham[d] | 1.0 –4.2 | | | | 1.9[b] | | | |
| Thallium | | | | | | | | |
| These results | 0.40–4.2 | 1.47 ±0.02 | 78.5±0.2 | 9 | 1.52 | 2.38 | 176.5 ± 3.8 | 128 |
| Maxwell and Lutes[e] | 1.2 –4.2 | 1.53 | | | | 2.38 | 172.8 ± 1.4 | 125.8±5.6 |
| Snider and Nicol[f] | 1.1 –4.2 | 2.56 ±0.35 | 86.6±0.3 | | | 2.36 | | |

[a] Reference 6.
[b] Calculated or estimated from data.
[c] Reference 15.
[d] Reference 17.
[e] Reference 19.
[f] Reference 18.

It is of interest to calculate the entropy difference, $\Delta S(T)$, between the normal and superconducting states, as this in turn may be integrated to yield the critical field as a function of temperature $H_c(T)$. The thermodynamic relations are

$$H_c^2(T)=\left(\frac{8\pi}{V_m}\right)\int_{T_c}^{T}\Delta S(T)dT,$$

where

$$\Delta S(T)=S_n(T)-S_s(T)=\int_0^T\left[\frac{(C_n-C_s)}{T}\right]dT.$$

$V_m$ is the molar volume which for Hg is 13.85 cm$^3$/mole. For the purposes of entropy calculation, the smoothed curves of a plot of $C_s/T$ and $C_n/T$ versus $T$ were used. At $T_c$ the difference in the specific heats in the two states is represented by the Rutgers equation:

$$\left(\frac{\Delta C}{T}\right)_{T_c}=\left[\frac{(C_s-C_n)}{T}\right]_{T_c}=\left(\frac{V_m}{4\pi}\right)\left[\left(\frac{dH_c}{dT}\right)_{T_c}\right]^2.$$

A value of $(dH_c/dT)_{T_c}$ can be calculated from Finnemore's data and is found to be $-203.3$ G/deg. This corresponds to $(\Delta C/T)_{T_c}=4.56$ mJ/mole deg$^2$. The curves have been drawn using this value of $(\Delta C/T)_{T_c}$. Within the accuracy of the measurements, a value of $\Delta S(T_c)=0$ is found, consistent with a second-order phase transition.

As the lattice specific heat of Hg is large compared with the electronic specific heat, the maximum value of $\Delta S(T)$ amounts to approximately 2% of the total entropy of the Hg at this temperature. The random scatter in the data is about 1%. Therefore $\Delta S(T)$ becomes increasingly inaccurate above 1°K. A very rough estimate of $H_c(0)$ can be calculated by integration of $\Delta S(T)$ from $T_c$ to 0°K, yielding a value of 380±60 G. This range includes Finnemore's value of 410.88 G.

One of the more interesting facets of these measurements is the behavior of the Debye parameter $\Theta$ as a function of temperature. As mentioned earlier the lattice specific heat $C_l$ is normally expressed as an expansion in odd powers of temperature. It may also be represented by

$$C_l=1944[T/\Theta(T)]^3 \text{ J/mole deg},$$

where the deviation of $C_l$ from a $T^3$ law is given by the temperature variation of $\Theta(T)$. In Fig. 2 is plotted $\Theta(T)$ versus $T$ up to 4.2°K for Hg. At $T=0.7$°K, $\Theta$ begins to deviate from the value of 0°K to a lower value, corresponding to the onset of a positive $T^5$ term. A minimum of $\Theta=51.5$°K occurs at $T=3.2$°K. It then begins to increase to a value at $T=4.2$°K of $\Theta=52.6$°K.

## Thallium

Representative values for the specific heat of Tl are listed in Table II. A plot of $C_s/T$ and $C_n/T$ versus $T^2$ is given in Fig. 3. As the normal-state data exhibit a deviation from the $T^3$ law at a rather low temperature,

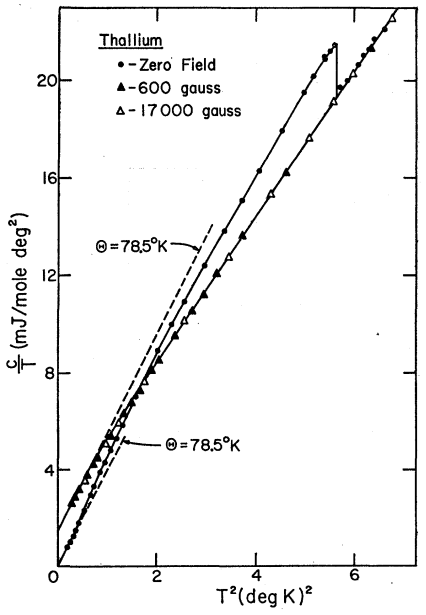


FIG. 3. Specific heat of thallium between 0.4 and 2.7°K.

below which only four points have been measured, a much more accurate determination of the slope $\alpha$ may be made using $C_s/T$. The zero intercept of $C_s/T$ is well defined, and more points are available at lower temperatures. A line of the same slope is then drawn through the four lowest points of the $C_n/T$ data in order to determine $\gamma$, the intercept at $T^2=0$. In order to use this method of obtaining $\alpha$, one must be certain that $C_{ln}$ is equal to $C_{ls}$, and this the data support.

Below $T^2=0.4$, the normal-state specific heat is given by

$$C_n=(1.47\pm0.02)T+(4.03\pm0.04)T^3 \text{ mJ/mole deg.}$$

The coefficient of the $T^3$ term corresponds to a value of $\Theta_0$ of 78.5±0.2°K. Both the value of $\gamma$ of 1.47 mJ/mole deg$^2$ and that of $\Theta_0$ are in disagreement with results of Snider and Nicol[18] for Tl. This discrepancy seems reasonable, however, since they measured only down to 1.2°K. Due to the deviation of the lattice specific heat from the pure $T^3$ law, any evaluation of $\gamma$ and $\Theta_0$ from data above $T^2=0.4$ will yield values much larger than those given above.

Calculation of $C_{es}$ for Tl is done in a manner similar to that for Hg. This leads to values for $a=9\pm1$ and $b=1.52\pm0.10$ in the range where $1.6<T_c/T<4$. Using Eq. (1), this yields a value of the energy gap at 0°K of $3.69kT_c$.

A sharp transition in the zero field specific heat occurs at a value of $T_c=2.38$°K, identical with the value determined from critical field measurements by Maxwell and Lutes[19] of 2.38°K (corrected to the 1958 He$^4$ temperature scale). Snider and Nicol found a value of 2.36°K. The jump in the specific heat at $T_c$, $(\Delta C/T)_{T_c}$, is 2.21 mJ/mole deg$^2$. Making use of the Rutgers formula, where $V_m=16.9$ cm$^3$/mole, one finds a value of $(dH_c/dT)_{T_c}$ of 128 G/deg. This is well within the limits of the measurements of Maxwell and Lutes who find a value of $(dH_c/dT)_{T_c}$ of 125.8±5.6 G/deg.

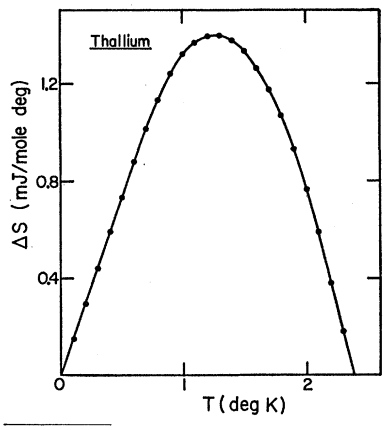


FIG. 4. Entropy plot for thallium.

[18] J. L. Snider and J. Nicol, Phys. Rev. **105**, 1242 (1957).
[19] E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).

Using the thermodynamic relations discussed earlier, a plot of $\Delta S(T)$ is given in Fig. 4. The value of $\Delta S(T_c)$ is zero, consistent with a second-order phase transition. Integration of this smoothed curve gives values for $H_c(T)$. The value obtained for $H_c(0)$ is 176.5±3.8 G compared with the value of Maxwell and Lutes of 172.8 G. The deviation of $H_c(T)$ from the parabolic law is shown in Fig. 5.

Goodman[20] derived an expression for the energy gap at 0°K as a function of the critical field and the electronic specific heat:

$$2\epsilon(0)/kT_c=7.256\eta^{1/2}, \quad \text{where} \quad \eta=V_mH_c^2(0)/(8\pi\gamma T_c^2).$$

Using the value of $H_c(0)$ of Maxwell and Lutes and the $\gamma$ and $T_c$ values found for this work, it is found that

$$2\epsilon(0)=3.64kT_c.$$

This value is in agreement with the specific heat energy gap, $3.69kT_c$.

Using values of the energy gap determined in this manner, Goodman[20] also found a linear relation between the energy gap, $2\epsilon(0)$, and $\ln(T_c/\Theta_0)$ for all superconductors. Tl was the only superconductor which fell far outside the range of this plot. These newer values of $2\epsilon(0)$ and $\Theta_0$ remove the discrepancy.

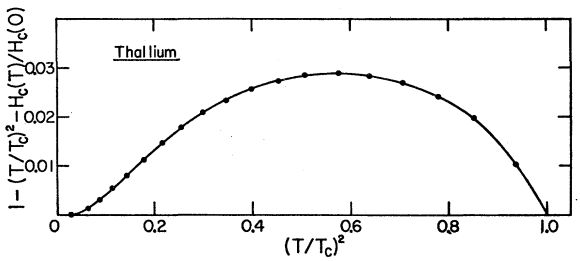


FIG. 5. Deviation of critical field of thallium from parabola.

It was noted previously that the variation of the Debye parameter $\Theta$ with temperature is a measure of the departure of the lattice specific heat from a $T^3$ law. In Fig. 6 has been plotted $\Theta$ as a function of $T$ for Tl. The positive deviation of $\Theta$ from $\Theta_0$, at $T=0.7$°K, indicates a negative deviation from the $T^3$ law. $\Theta$ reaches a maximum value of 85.6°K at $T=2.8$°K, decreasing thereafter to a value of 85.0°K at $T=4$°K. From the graph it becomes clear that Snider and Nicol could draw a straight line through their data, as in their temperature range, $\Theta$ is nearly constant, although different from $\Theta_0$.

## DISCUSSION

The negative deviation of the normal-state specific heat of Tl from a $T^3$ law is unusual. Many solids show deviations from a $T^3$ law at similar values of $\Theta_0/T$,

[20] B. B. Goodman, C. R. Acad. Sci. (France) **246**, 3031 (1958).

but in a positive direction. One might inquire if the negative deviation for Tl is electronic in origin. The relation between the electronic specific heat in the normal state $\gamma T$ and the superconducting state $C_{es}$ has been calculated by the BCS theory. It is highly unlikely that any extra terms in the normal-state electronic specific heat would not drastically alter the form of $C_{es}$ without completely violating predictions of the very successful BCS theory. Other causes, such as nuclear contributions, crystalline phase changes, or impurity effects appear unlikely and therefore one is forced to conclude that the negative deviation from the $T^3$ law is a lattice effect.

In a discussion of the low-temperature specific heat of solids, Blackman[21] made some observations about the expected temperature dependence. If one examines a typical dispersion curve for acoustic phonons ($\omega$ versus $k$), the low-frequency end of the curve is a straight line. Deviations from the linear relation between $\omega$ and $k$ should be in such a direction as to intersect the boundary of the Brillouin zone in a perpendicular direction $(\partial\omega/\partial k|_{BZ}=0)$. For the simplest case, this implies a gradual reduction of the slope of the dispersion curve to a value of zero slope at the Brillouin zone boundary. In terms of the phonon density of states [$g(\nu)$ versus $\nu$], the linear portion of the dispersion curve corresponds to a $\nu^2$ dependence. Deviations from the $\nu^2$ dependence are inversely related to $\partial\omega/\partial k$, and thus the portion of decreasing slope of the dispersion curve corresponds to a deviation above the $\nu^2$ dependence. A pure $\nu^2$ frequency density yields a $T^3$ law for the specific heat, and deviations above the $\nu^2$ curve correspond to positive deviations from the $T^3$ law. In this manner Blackman shows that one should expect the initial deviation from the pure $T^3$ law to be positive, as is observed for nearly all solids.

There is no restriction, however, which prevents the dispersion curve from having an upward deviation from the linear portion, which would lead to a negative deviation from the $T^3$ law, as is observed for Tl. It is only required that such a trend in the dispersion curve reverse itself so that the slope goes to zero at the Brillouin zone boundary.

An example of another material which shows a similar negative deviation from the $T^3$ law is graphite. For graphite this effect was explained on the basis of valence bond-bending modes (out-of-plane modes), as distinct from the usual transverse and longitudinal modes associated with the low-temperature continuum model. Bond-bending modes are introduced because the interaction between planes in the hexagonal graphite lattice is weak as compared to forces in the planes. This leads to a term proportional to $k^2$ in the dispersion equation. A quadratic term in the dispersion equation at low frequency will introduce an upward deviation from the linear portion to the dispersion curve, as described in the preceeding paragraph. Consequently, the phonon spectrum for these bending modes goes from a $\nu^2$ to $\nu$ dependence, and yields a negative deviation from the $T^3$ law for the specific heat. For graphite this transition occurs at a temperature corresponding to $\Theta_0/300$.

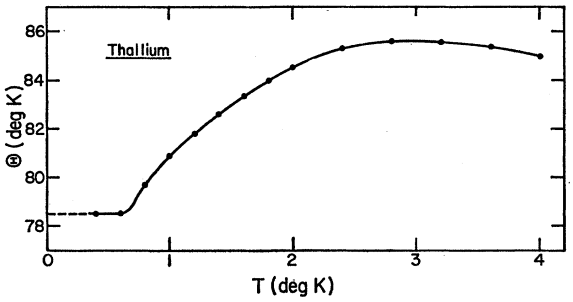


FIG. 6. $\Theta$ versus $T$ for thallium.

Naturally for Tl the atomic bonding is metallic and not covalent as for graphite. However, it is felt that similar out-of-plane modes may occur for Tl if the interplane interaction is weak, even though the nature of atomic bonding is different. There are indications that Tl does have a weak interaction between planes. Crystal anisotropy of this sort has been proposed by Cody[22] to explain the direction dependence of the volume change between the normal and superconducting states. The temperature at which the deviation from a $T^3$ law appears corresponds to a value of $\Theta_0/100$, a reasonable value for such bending modes.

Since the specific heat measures only bulk properties of a material, it is impossible to make any definite conclusions, but only suggest possible explanations. Other methods offer a more promising measure of lattice anisotropy. Velocity of sound measurements give values for the elastic constants, but will not observe dispersive effects. Neutron diffraction yields a method for determining the dispersion curve, but at too high frequencies. Since the increase of $\Theta$ from $\Theta_0$ for Tl occurs over a rather narrow temperature range, the corresponding drop in the phonon density spectrum could be sharp. If such is the case, tunneling measurements may be able to observe this discontinuity in the phonon spectrum.

[21] M. Blackman, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Part 1.

[22] G. D. Cody, Phys. Rev. **111**, 1078 (1958).