

Atomic Heats of Cesium, Rubidium, and Lithium Between 0.35 and 2°K*

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The electronic and lattice contributions to the atomic heat of lithium, rubidium, and cesium have been determined from heat capacity measurements on large high-purity samples between 0.35 and 2°K. The linear contribution to the heat capacity yields a value for γ of 1.71 for Li, 4.07 for Rb, and 6.29 for Cs in mJ/mole-(°K)². Interpreting this linear contribution to the heat capacity in terms of the density of single-excitation states at the Fermi level, a thermal effective mass $C_{el}/C_0 = \gamma/\gamma_0 = m/m_0$ is obtained. The value is $m/m_0 = 2.31$ for Li, 2.14 for Rb, and 2.82 for Cs. These values for the thermal effective mass suggest considerable anisotropy for the Fermi surface and are compared with the band calculations of F. S. Ham, and a calculation by Silverstein which combines the results of the band calculation with electron-electron interaction. The value for Li is in good agreement with that of Martin, but the effective mass for rubidium and cesium are considerably larger than the values of 1.26 and 1.43 obtained by Lien and Phillips. The lattice contribution to the very low-temperature heat capacity is described by a value of $\Theta_0 = 58.7$ for Rb and $\Theta_0 = 40.6$ for Cs. The dependence of Θ on temperature is given and the values at 2°K are in good agreement with the data of Lien and Phillips and the data of McCollum and Silsbee.

INTRODUCTION

THE active theoretical interest during the past few years in the alkali metals has indicated the need of improved experimental measurements on those properties associated with the conduction electrons and the lattice. This paper reports on the low-temperature atomic heat of cesium, rubidium, and lithium metals. If the electronic properties are described by a single-excitation model the electronic heat is given by^{1,2}

$$C_{el} = \gamma T = \frac{1}{3} \pi^2 k^2 T n(E_F), \quad (1)$$

where the density of single-excitation states at the Fermi level is

$$n(E_F) = \frac{1}{4\pi^3} \int_{S(E)} \frac{dS}{|\nabla_k E|}. \quad (2)$$

In order to avoid numerical constants, it is conventional to compare various models with the Sommerfeld free-electron model density of states $n_0(E_F)$ and use the following ratio:

$$n(E_F)/n_0(E_F) = C_{el}/C_0 = m/m_0 \quad (3)$$

in the discussion of experimental and theoretical data on electronic heat. Ham³ discussed the Fermi surface for the alkali metals in considerable detail in a recent paper. Since the nearly free-electron model predicts a general form for the constant energy surface which is in agreement with more rigorous calculations for the alkali metals,⁴ he introduced an interpolation procedure for calculating the energy for arbitrary \mathbf{k} . For the bcc

structure of the alkali metals the constant energy surface is almost spherical with bulges in the twelve [110] directions toward the zone faces. This procedure permits an evaluation of the effect of the crystal structure or lattice on the density of states at the Fermi surface and the calculated values of m_i/m_0 are given by Ham.³ His calculation does not include electron-electron and electron-phonon interactions. Silverstein⁵ extended the interpolation calculation for the correlation energy of Nozieres and Pines⁶ to evaluate the electronic heat capacity for electron densities characteristic of the alkali metals. The correlation enhancement of the density of states, $C_c/C_0 = m_c/m_0$, is given as a function of the atomic spacing or electron density. In a subsequent paper Silverstein⁷ combined the correlation enhancement of the density of states, m_c/m_0 , with the thermal effective mass, m_i/m_0 , which was given by Ham in order to account for the influence of the lattice on his correlation calculation. The electronic heat was given as $C^*/C_0 = (m/m^* + C_0/C - 1)^{-1}$. Inverting this expression and using the notation of this paper, this can be written as

$$1/m' = 1/m_i + 1/m_c - 1/m_0 \quad (4)$$

for the effective masses or density of states. Neither of the above papers included the electron-phonon interaction. Buckingham and Schafroth⁸ found an increase in density of states from this interaction. Jones⁹ has shown that some care is necessary in interpreting the linear term in the heat capacity. If the Fermi surface is near a zone boundary the elastic shear constants of the metal are sensitive to the electron distribution and the lattice vibrations may depend on temperature in a

* This work was supported by a grant from the National Science Foundation.

¹ L. D. Landau, *Zh. Eksperim. i Teor. Fiz.* **30**, 1058 (1956) [English transl.: *Soviet Phys.—JETP* **3**, 920 (1957)]; J. M. Luttinger, *Phys. Rev.* **119**, 1153 (1960).

² L. M. Falicov and V. Heine, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd. London, 1961), Vol. 10, p. 57.

³ F. S. Ham, *Phys. Rev.* **128**, 2524 (1962).

⁴ F. S. Ham, *Phys. Rev.* **128**, 82 (1962).

⁵ S. D. Silverstein, *Phys. Rev.* **128**, 631 (1962).

⁶ P. Nozieres and D. Pines, *Phys. Rev.* **109**, 762 (1958).

⁷ S. D. Silverstein, *Phys. Rev.* **130**, 912 (1963).

⁸ M. J. Buckingham and M. R. Schafroth, *Proc. Phys. Soc. (London)* **A67**, 828 (1954).

⁹ H. Jones, *Proc. Roy. Soc. (London)* **A240**, 321 (1957).

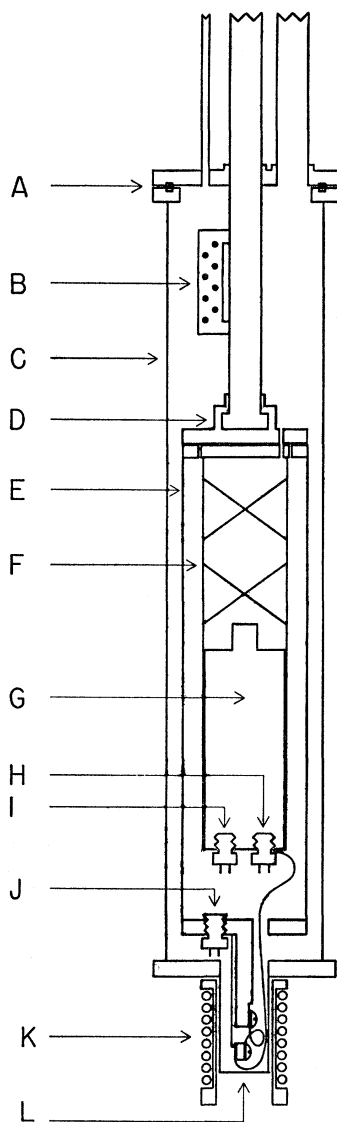


FIG. 1. Calorimeter used for experimental measurements. A—0.050 in. indium gasket; B—terminal board; C—external container; D—He³ container; E—lead plated copper thermal shield; F—0.014 in. stainless-steel tubing frame; G—sample; H—sample thermometer; I—sample heater; J—shield thermometer; K—control coil for thermal valve; L—lead thermal valve.

manner such that an additional linear term in the heat capacity occurs. Other lattice contributions to the heat capacity are discussed later.

Heat capacity measurements on lithium, cesium, and rubidium have been reported previously and reference to this work is included in a comparison with the work reported in this paper.

EXPERIMENTAL

A low-temperature calorimeter which was cooled to 0.35°K by a He³ cryostat was used for the heat-capacity measurements. Heat cycles were observed by means of a potentiometer-recorder system which measured the change in resistance of a carbon resistance thermometer. The calorimeter, thermometer calibration, the preparation of large high-purity samples, and the experimental procedures are discussed in the following subsections.

Calorimeter

The low-temperature calorimeter is shown in Fig. 1. A He⁴ cryostat provided cooling of the outer container wall to 1.05°K and a He³ cryostat¹⁰ was used to cool the copper shield to a temperature of 0.35°K. This shield was introduced to reduce the pressure of any residual He⁴ exchange gas to such a small value that heat transfer by this means was negligible. Since the thermal shield was the coldest part of the apparatus, the residual gas was adsorbed on the shield rather than the sample. The shield isolates the sample from other gas fluxes and from electromagnetic radiation. A lead coating on the copper isolates the sample from low frequency electrical disturbances. The sample is rigidly mounted to the thermal shield by using a frame of No. 28 gauge stainless-steel tubing. This frame has three vertical members making contact with the He³ container and numerous cross braces to provide a rigid structure. The heat leak through the stainless-steel sample supports is less than 0.05 μW for a sample temperature of 0.7°K and a He³ temperature of 0.35°K. Thermal contact between the sample and the shield is made by means of a lead thermal valve.¹¹ Fifteen 4 in. No. 36 gauge copper wires connect the bottom of the sample container to the lead thermal valve. An area/length ratio of 4×10^{-5} cm was used for the valve. A superconducting molybdenum-rhenium coil is mounted in the He⁴ bath and is used to control the thermal valve.

The sample heater and the sample thermometer are inserted in threaded holes in the copper sample container. A manganin wire coil potted with varnish in a threaded brass sleeve is used as a heater. The sample thermometer is an IRC 270 Ω—1/3 W carbon resistor with part of the insulation removed and then potted with varnish into a brass sleeve. A similar thermometer is inserted at the bottom of the copper shield in order to monitor the temperature of the He³ reservoir. The heater and thermometers are connected to a terminal board by 0.003 in. superconducting niobium wires. These niobium wires are in good thermal contact with the He³ container in order to provide good thermal isolation for the sample. A third carbon resistor is located in the He⁴ cryostat for measurement of the bath temperature.

The voltage across the carbon resistors, which was produced by a constant current of 10 μA, was continuously measured with a potentiometer-amplifier-recorder system. A Leeds and Northrup K-3 potentiometer was placed in series with a Keithley 150A microvolt-ammeter to measure the voltage. Variations of 0–100 μV were measured by the self-balancing Keithley and recorded on a Leeds and Northrup Speedomax H recorder. At 1°K the noise on this system was less than 0.1 μV.

¹⁰ G. Seidel and P. H. Keesom, *Rev. Sci. Instr.* **27**, 606 (1958).

¹¹ C. V. Heer, C. B. Barnes, and J. G. Daunt, *Rev. Sci. Instr.* **25**, 1088 (1954); C. V. Heer and J. G. Daunt, *Phys. Rev.* **76**, 854 (1949).

Below 0.5°K considerable noise was encountered and was found to be caused by transmission of radio-frequency power to the sample and erratic heating of the sample and thermometer. Since the sample was surrounded by a superconducting shield this source of rf heat was somewhat of a puzzle. This source of thermal noise was removed by observing that the electrical leads for the thermometer entered the calorimeter through a small stainless-steel capillary and served as a coaxial cable for transmission of rf power into the shield enclosure. The capacitance between the thermometer which was connected to the center wires of the coaxial cable and the enclosure which was connected to the capillary provided a path for rf heating of the thermometer. This heating appeared as 1 to 10 μ V noise on the recorder. Proper external shielding reduced this noise to less than 0.1 μ V.

Thermometer Calibration and Heating Cycles

The sample thermometer was calibrated against He⁴ vapor pressures between 1.05 and 3°K using the T_{68} scale.¹² For this calibration thermal contact between the sample and the He⁴ bath was made with He⁴ exchange gas. The exchange gas was removed by a high-vacuum pump and a pumping interval of 12 h with the sample at 4°K was used. The sample was then cooled by the He³-thermal valve system. Between 1.2 and 0.4°K the thermometers were calibrated against the He³ vapor pressures based on the scale of Sydorik and Roberts.¹³ Since corrections for pressure differences along the pumping tube are difficult to make, and as a precaution, a separate run was made to calibrate the vapor pressure measurements and the carbon resistor thermometers against the magnetic susceptibility measurements of cerium magnesium nitrate. The sample thermometer was found to obey the equation $T = a + b \exp(cR)$. Least-square analysis of 42 calibration points for Cs gave $a = 0.20^\circ\text{K}$, $b = 5443.3^\circ\text{K}$ and $c = -0.015632 \Omega^{-1}$. Seventy points for Rb gave $a = 0.23^\circ\text{K}$, $b = 6596.4^\circ\text{K}$ and $c = -0.016288 \Omega^{-1}$. Thirty-two points were used for Li. Calibration points were taken over the entire temperature range both before and after the heat capacity measurements. The He³ cryostat has a very remarkable property in that it is possible to transfer He⁴ to the external bath and keep the sample below 0.7°K during the transfer. Although these experiments lasted for more than four days, it was never necessary to raise the temperature of the sample above the highest heat capacity measurement. The calibration points obtained at the end of the experiment were in excellent agreement with those taken at the beginning. Cycling to room temperature caused a change in the thermometer constants and this is indicated by the difference between Cs and Rb.

¹² F. G. Brickwedde, H. Van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *J. Res. Natl. Bur. Stds.* **64A**, 1 (1960).

¹³ S. G. Sydorik and T. R. Roberts, *Phys. Rev.* **106**, 175 (1957).

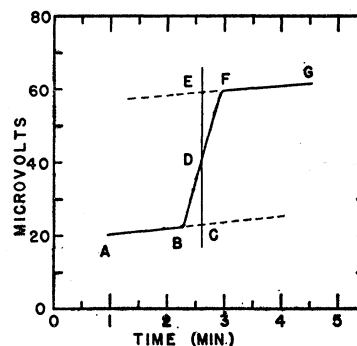


FIG. 2. Heating cycle for cesium showing recorder trace of voltage across the sample thermometer versus time. AB and FG show the joule heating introduced by the thermometer. BF is the change introduced by 1.992 μ W for a period of 39.00 sec and CE is the corresponding temperature change of 17.63 m°K. Cycle No. 71 is shown.

At the lowest temperatures and with the sample isolated the dominant source of heating was the 0.06 μ W joule heating of the sample thermometer. In order to ensure that this heating did not introduce an error in the calibration, some calibration points and heating cycles were taken with the 10 μ A current reduced to 5 μ A. No difference was noted in either the calibration curve or the measured heat capacity. The observed heating rates indicate an additional and almost constant heat input of 0.01 μ W for the Cs experiment and 0.04 μ W for Rb and Li.

Heat-capacity measurements were made from the change in the normal cooling rate with the introduction of known amounts of joule heating.¹⁴ A heating cycle for Cs is shown in Fig. 2 and the voltage across the thermometer resistance as displayed by the recorder is shown as a function of time. The normal heating rate at the beginning of the measurement is shown as AB and after the heating cycle as FG. Heat is supplied by the manganin heater from B to F. The temperature change upon heating is proportional to C-E. Although approximately 200 heating cycles were taken for the Cs and Rb samples, only those cycles which were smooth and indicated very little noise were used to evaluate the heat capacity. Even then great care was necessary in the graphical determination of the temperature difference. Thus for cesium it was possible to reduce the experimental scatter to less than 1% by careful graphical analysis and the use of good heating cycles. For cycle No. 71 shown in Fig. 2 and listed in Table I, the heater supplied 1.9925 μ W power for a period of 39.00 sec and caused a temperature rise of 17.632 m°K. This gives a heat capacity of 4.407 mJ/°K at 0.5116°K. The heating rate AB was 0.0568 μ W and the rate FG was 0.0510 μ W. This observed change in heating rate agrees well with the calculated change in heat transport through the stainless-steel supports due to the small increase in temperature.

¹⁴ J. K. Logan, J. R. Clement, and H. R. Jeffers, *Phys. Rev.* **105**, 1427 (1957).

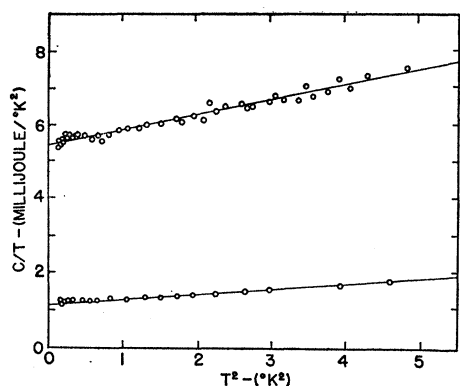


FIG. 3. C/T in $\text{mJ}/(^{\circ}\text{K})^2$ versus T^2 for lithium sample plus container (upper curve) and container alone (lower curve).

Sample Preparation

The large high-purity Cs, Rb, and Li samples were prepared by Davis, Jones, and the New Products Section, and the sample analysis was carried out by Farquhar and the Analytical Section of the Trona Research Laboratories of the American Potash and Chemical Corporation. Each copper container was tared weighed in an argon-filled vacuum dry box, filled with molten metal from a storage container, closed, reweighed, and sealed with solder. Samples of molten metal were also placed in glass ampoules before and after filling the copper container, and the glass ampoule samples were subsequently used for analysis by the method described by Farquhar and Hill.¹⁵ Each container was sealed with a known amount, approximately

TABLE I. Some typical experimental data for cesium.

No.	\bar{T} ($^{\circ}\text{K}$)	Q (μJ)	ΔT (m°K)	C ($\text{mJ}/^{\circ}\text{K}$)
138	0.3611	12.154	5.161	2.355
142	0.4007	24.508	8.610	2.847
63	0.4032	18.630	6.528	2.854
132	0.4578	33.295	9.328	3.570
149	0.4928	31.880	7.736	4.121
135	0.4978	50.142	12.079	4.151
76	0.6068	98.031	15.832	6.192
38	0.7216	189.41	20.711	9.145
41	0.8083	276.95	22.774	12.160
44	0.9017	316.21	19.524	16.196
99	0.9515	580.42	31.484	18.435
14	0.9655	443.60	22.676	19.563
15	1.0309	623.40	26.171	23.820
16	1.0973	887.20	31.910	27.803
48	1.1229	1319.0	44.072	29.929
101	1.1352	1406.2	45.244	31.081
103	1.2424	1331.0	32.916	40.437
51	1.2947	2747.0	59.036	46.531
19	1.3311	1536.7	30.411	50.531
52	1.4333	2836.6	44.821	63.286
53	1.4876	4974.1	68.234	72.898
21	1.5058	2879.9	37.660	76.472
22	1.6147	3838.9	40.579	94.602
54	1.6272	5066.5	51.760	97.885
71	0.5116	77.708	17.632	4.407

¹⁵ M. C. Farquhar and J. A. Hill, *Anal. Chem.* **34**, 222 (1962).

4 g, of 63%–37% tin-lead solder. The detailed information on each sample is given later.

A separate experimental run was made on an empty copper container to determine the heat capacity of the container, solder, thermometer, heater, etc. The experimental data are shown in Fig. 3 and the data follow the equation

$$C'/T = 1.166 + 0.136T^2 \text{ mJ}/^{\circ}\text{K}. \quad (5)$$

This is in excellent agreement with the heat capacity estimated from the known weights of the material and the known heat capacities.¹⁶ Since the weight of copper and solder differed by a small amount for each container, these corrections are included for each sample.

EXPERIMENTAL RESULTS

Cesium

The heat capacity measurements¹⁷ were made on a 71.62-g sample of Cs, 0.539 moles, and was 99.98% pure by assay. The sample contained 0.002% Rb and less than 0.001% of K, Na, and Li. A plot of C/T versus T^2 for the cesium sample plus container is shown in Fig. 4, and some typical data points are shown in Table I. Since the Debye Θ depends on temperature, no simple curve fits the data. A least-square fit of 44 points of the data below 0.8°K indicates the linear line is given by the first two terms on the right side of

$$C/T = 4.494 + 15.739T^2 + f(T^2) \text{ mJ}/^{\circ}\text{K}. \quad (6)$$

The heat capacity of the sample container is estimated

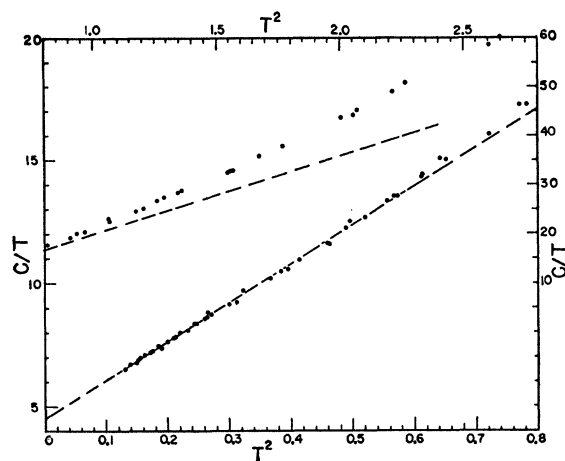


FIG. 4. C/T in $\text{mJ}/(^{\circ}\text{K})^2$ versus T^2 for cesium sample plus container. The scale for the lower curve is given on the bottom and left; and the scale for the upper points is given at the top and right of the figure.

¹⁶ I. Esterman, S. A. Freidberg, and J. E. Goldman, *Phys. Rev.* **87**, 582 (1952); W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, *ibid.* **98**, 1699 (1955); J. Rayne, *ibid.* **95**, 1428 (1954).

¹⁷ B. D. Martin and C. V. Heer, *Bull. Am. Phys. Soc.* **9**, 250 (1964).

on the basis of known weights as $C'/T = 1.104 + 0.129T^2$ mJ/°K. The effect of the $f(T^2)$ term is shown in Fig. 5, in which Θ is plotted as a function of T . The molar heat capacity is, to a good approximation, given by

$$C = 6.291T + 28.97T^3 + 1.48T^5 + 0.945T^7 \text{ mJ/mole-}^\circ\text{K.} \quad (7)$$

At 0°K the cubic coefficient yields a $\Theta_0 = 40.64$ and at higher temperatures the data is in good agreement with that of McCollum and Silsbee.¹⁸

Using the density of cesium at 5°K, as determined from the x-ray data of Barrett,¹⁹ $a = 6.045 \times 10^{-10}$ m for bcc structure, the linear term yields a thermal effective mass ratio of

$$m/m_0 = 2.82.$$

This value is considerably larger than the value of 1.43 reported by Lien and Phillips.²⁰ In view of the good agreement with their value of the Debye theta at 0°K, 39.7, no simple explanation of the difference is apparent. Their sample was considerably smaller and more sensitive to the estimate of the effect of the sample container and sample support on the heat capacity. Also the oxides of cesium are very soluble in cesium metal²¹ and considerable care is necessary in the sample preparation. To avoid the formation of these oxides great care was used in the preparation of the sample which was used in this experiment.

The low-temperature x-ray measurements and metallographic studies by Barrett¹⁹ on cesium indicate that cesium metal does not undergo a martensitic phase transformation down to temperature of 1.2°K. In the experiments reported above the heat capacity measure-

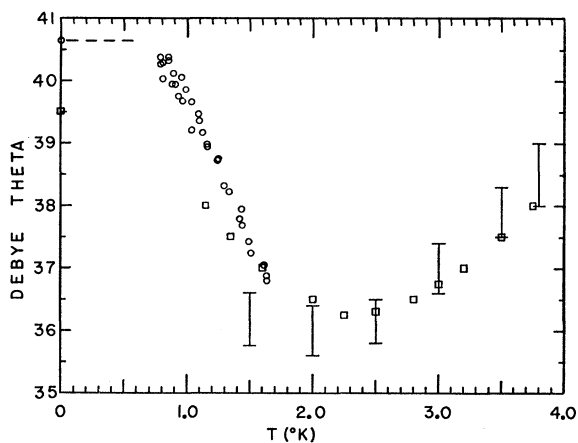


Fig. 5. Debye Θ of cesium as a function of T . The work reported here is indicated by \circ , the work of Lein and Phillips (Ref. 20) by \square , and that by McCollum and Silsbee (Ref. 18) by \square .

¹⁸ D. C. McCollum, Jr., and H. B. Silsbee, Phys. Rev. **127**, 119 (1962).

¹⁹ C. S. Barrett, Acta Cryst. **9**, 671 (1956).

²⁰ W. H. Lien and N. E. Phillips, Phys. Rev. **133**, A1370 (1964).

²¹ G. Brauer, Z. Anorg. Allgem. Chem. **255**, 101 (1947).

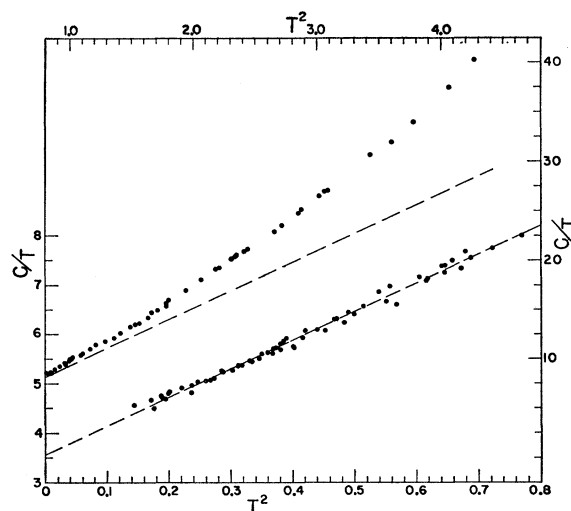


Fig. 6. C/T in mJ/(°K)² versus T^2 for rubidium sample plus container. The scale for the lower curve is given on the bottom and left; and the scale for the upper points is given at the top and right of the figure.

ments were made over a period of four days and the sample was cycled between 0.38 and 2.2°K five times. No difference in heat capacity was noted for the various cycles and suggests that no phase transformation occurs down to temperatures of 0.38°K.

Earlier work on the electrical resistance²² of cesium suggested a Debye theta of 30 in the 2–4°K temperature range and 45 at somewhat higher temperatures. A comparison with the values determined from heat capacity measurements requires a detailed model for electron-phonon interactions. Heat capacity measurements were made previously at higher temperatures,²³ and are in reasonable agreement with the data shown in Fig. 5.

Rubidium

The heat-capacity measurements were made on a 50.43-g sample of rubidium, 0.590 moles, of 99.90% purity by assay. The sample contained 0.071% Cs, 0.068% K, and less than 0.001% of Na and Li. In Fig. 6 the data points are plotted as C/T versus T^2 and a least-squares analysis of the 60 points below 0.8°K, indicates the data are fit by

$$C/T = 3.566 + 5.799T^2 + f(T^2) \text{ mJ/}^\circ\text{K.} \quad (8)$$

The heat capacity of the container is estimated as $C'/T = 1.163 + 0.136T^2$. Again the $f(T^2)$ term is shown by plotting Θ versus T as shown in Fig. 7. The molar

²² D. K. C. MacDonald, G. K. White, and S. B. Woods, Proc. Roy. Soc. (London) **235**, 358 (1956).

²³ T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas, Proc. Roy. Soc. (London) **133**, 214 (1955–1956).

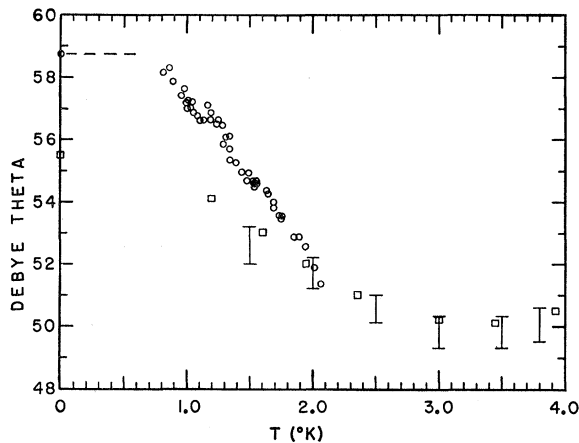


FIG. 7. Debye Θ of rubidium as a function of T . The work reported is indicated by \circ , the work of Lien and Phillips (Ref. 20) by \square , and that by McCollum and Silsbee (Ref. 18) by Δ .

heat capacity is, to a good approximation, given by

$$C = 4.075T + 9.599T^3 + 0.765T^5 + 0.0714T^7 \text{ mJ/mole-}^\circ\text{K}. \quad (9)$$

At 0°K the cubic coefficient yields a value of $\Theta_0 = 58.72^\circ\text{K}$ and at higher temperatures the value of Θ decreases to a value in good agreement with that of McCollum and Silsbee.¹⁸

Using the known density of rubidium at 5°K , as determined from the x-ray data of Barrett,¹⁹ $a = 5.585 \times 10^{-10}$ m for bcc structure, the linear term for the electronic heat yields a value of thermal effective mass of

$$m/m_0 = 2.14.$$

This value is again considerably larger than the value of 1.26 reported by Lien and Phillips.²⁰ Their value of Debye theta of 55.3 is somewhat lower than the value reported here. Again no simple explanation for this very large difference in effective mass is apparent. As for cesium, a large carefully prepared rubidium sample was used in the measurements reported in this paper. The linear heat capacity of the sample container and supports was less than 1/3 of the total heat capacity at the lower temperatures and an error of no larger than 1 to 2% is expected in estimating the heat capacity of the sample container. This estimate is of course based on a separate experiment and on measurements of other workers on similar materials.¹⁶ The linear term for the atomic heat of copper determined in this separate run is in good agreement with the accepted value.¹⁶ A separate experiment with a cerium magnesium nitrate magnetic susceptibility thermometer lends considerable support to the low-temperature calibration procedure. Even if the lowest temperature data were omitted the data between 0.6 to 0.8°K would suggest almost the same value for the linear term in cesium and rubidium. Since a direct extrapolation of the He^4 and the He^3

calibration points of the resistance thermometer above 0.8°K to a temperature of 0.6°K would be reasonably correct, we do not feel that an important calibration error is possible in this work. This is supported by the experiment on lithium discussed in the next section and the measurements on the copper container. Further indication of correct calibration can be obtained if the form of the heat capacity curve is known. Thus, if it is assumed that the correct C/T versus T^2 curve is a straight line at low temperatures, then the observation of a linear line for the experimental data as shown in Fig. 4 for cesium and Fig. 6 for rubidium is an indication that the calibration temperature is approximately the same as the thermodynamic temperature. Small deviations cause a curvature away from the correct form. Of course this argument is only valid if the correct form is known for the atomic heat.

Other high-²³ and low-²⁴ temperature heat-capacity measurements and electrical resistance measurements²² were made on rubidium. The lattice contribution to the heat capacity is in reasonable agreement with the values shown in Fig. 7.

Lithium

The 17.29-g sample of lithium was of high purity and analysis indicated less than 0.001% of Na, K, Rb, and Cs. The salts from which the metal was derived came from Atomic Energy Commission tailings and are believed to have a lower Li^6 content than natural lithium. The calculations are based on a Li^6 content of 4% and a sample of 2.48 moles. The results for the heat capacity of the lithium sample²⁵ and container are shown in Fig. 2 and the molar atomic heat as a function of temperature is shown in Fig. 8. The experimental data for lithium are reasonably fitted by the equation

$$C = 1.71T + 0.114T^3 \text{ mJ/mole-}^\circ\text{K}. \quad (10)$$

The quality of these data is not comparable with that on cesium and rubidium, but the experimental scatter

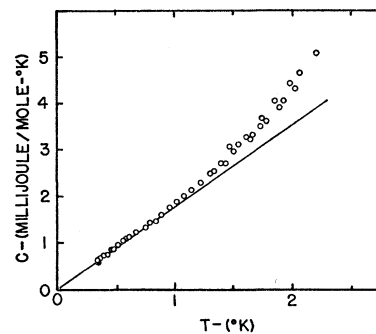


FIG. 8. Heat capacity of lithium versus temperature in $\text{mJ/mole-}^\circ\text{K}$.

²⁴ F. D. Manchester, *Can. J. Phys.* **37**, 525 (1959).

²⁵ D. A. Zych and C. V. Heer, *Bull. Am. Phys. Soc.* (to be published).

is considerably less than the previously reported work on lithium.

Using the density of lithium at 77°K, $a = 3.491 \times 10^{-10}$ m for bcc structure,¹⁹ the ratio of the experimental electronic heat to that calculated from free electron theory gives an experimental thermal effective mass ratio of m/m_0 of 2.31. This value is somewhat greater than the value of 2.20 reported by Martin²⁶ on natural lithium from measurements between 0.4 and 1.5°K. The agreement for the electronic heat is better with that obtained by Roberts,²⁷ 2.35, from data between 2.4 and 4.5°K. A value of $\Theta_0 = 260 \pm 10^\circ\text{K}$ is obtained from the slope shown in Fig. 3 and is considerably less than the value of 335 ± 40 obtained by Martin and 369°K obtained by Roberts from data above 2.4°K. MacDonald and Mendelssohn found that a value of $\Theta = 240$ was required to bring the electrical resistance of lithium between 10–20°K into agreement with the $(T/\Theta)^5$ law and that for a temperature of 80°K the value of Θ approached a value near 330.

Measurements on lithium are always troubled by the existence of a martensitic-type phase transformation from bcc to hcp at low temperatures. It is difficult to determine the amount of phase transformation and the experimental data up to now are given with the degree of phase transformation unknown. This is unfortunate since the density remains constant during the phase change and it would appear to be an excellent example for the study of the dependence of the thermal effective mass on crystal structure. The lithium sample used in this experiment was cooled to 77°K and held to this temperature for a period of several days before the heat capacity measurements were started. The data shown in Figs. 3 and 8 are the results of the second run and the thermal effective mass is essentially the same as that obtained in an earlier run. The earlier run on lithium was the first in the sequence of experiments on the alkali metals. Since the experimental scatter was twice as great as that shown in Fig. 2 these data are not reported. In subsequent experiments an improved dc amplifier and the reduction of random heating greatly improved the heat-capacity measurements. In view of the experimental scatter in the data given here and that reported by earlier workers, it would seem appropriate to regard the differences in thermal effective mass of experimental origin rather than due to a difference in degree of martensitic transformation. Although the experimental scatter in Martin's data is quite large, it is difficult to reconcile the large difference in the values of Θ . The first run indicated a Debye theta more nearly in agreement with that of Martin and this may indicate that further investigation of the martensitic transformation on the lattice heat is warranted.

TABLE II. Thermal effective masses for the alkali metals.

	Li	Na	K	Rb	Cs
γ (mJ/mole-deg ²) ^a	1.71			4.08	6.29
γ (other)	1.68 ^b	1.38 ^c	2.08 ^d	2.41 ^d	3.20 ^d
a for bcc (10^{-10} m) ^e	3.491	4.225	5.225	5.585	6.045
γ/γ_0 or m/m_0	2.31 ^a	1.27	1.25 ^d	2.14 ^a	2.82 ^a
m_i/m_0 (Band theory) ^f	1.66	1.00	1.09	1.21	1.76
m_e/m_0 (electron-electron interactions) ^g	1.10	1.15	1.21	1.23	1.28
m'/m_0 [Eq. (4)] ^h	1.96	1.15	1.35	1.56	2.86
m_p/m_0 (electron-phonon interaction) ⁱ	1.35	1.45	1.59	1.61	1.69

^a Reported in this paper.

^b An average of 1.63 reported by Martin (Ref. 26) and 1.74 by Roberts (Ref. 27).

^c An average of 1.32 reported by Gaumer and Heer [R. E. Gaumer and C. V. Heer, Phys. Rev. 118, 955 (1960)], 1.44 by Lien and Phillips (Ref. 20) and 1.38 by Martin [D. L. Martin, Phys. Rev. 124, 438 (1961)].

^d Reference 20.

^e Reference 19.

^f Reference 4.

^g Reference 5.

^h Reference 7.

ⁱ Reference 30.

DISCUSSION OF RESULTS

A summary of the thermal effective masses which are obtained from the linear term in the heat capacity in accordance with the definitions given in Eqs. (1) and (3) are shown in Table II. Comparison of the linear term with the values obtained by other workers has been discussed in detail in the previous section. The cause of the large difference between the values reported here for cesium and rubidium and those reported by Lien and Phillips is not apparent. The samples used in our experiments were large and of high purity. Considerable care was used in the preparation of the samples to avoid the formation of the soluble oxides. The large size of the samples reduced the errors introduced by unavoidable heating or cooling of the sample. Even though the samples were quite large the heat transfer throughout the sample was very rapid and this is indicated by the absence of "over shoot" in the heat cycle shown in Fig. 2. The rubidium sample of Lien and Phillips contained 3% potassium and the cesium sample contained approximately 1% of other alkali metals. Soluble oxides were not discussed. It is not possible at this time to assess the importance of alloying with other alkali metals and of the soluble oxides.

Although a knowledge of the density of states at the Fermi surface is the only quantity needed for the comparison of the experimental heat capacity with those derived from theoretical calculations, the theoretical problem is sufficiently difficult that it is not presently possible to treat the complete problem. Ham has made extensive calculations on the energy bands of the alkali metals using the quantum defect method and the Green's function method³ for selected axes and symmetry points in the Brillouin zone. Using the general form of the Fermi surface given by the nearly free electron model to suggest the general form of an interpolation formula, he was able to extend the earlier

²⁶ D. L. Martin, Proc. Roy. Soc. (London) A263, 378 (1961).

²⁷ L. M. Roberts, Proc. Phys. Soc. (London) B70, 744 (1957).

calculations to arbitrary \mathbf{k} and obtain an expression for the density of states at the Fermi surface. His values are shown in Table II as m_i/m_0 . It is expected that these calculations introduce the effect of lattice periodicity and of the proximity to zone boundaries on the density of states in an approximately correct manner. A large lattice effect is suggested for Li and Cs and this is in accord with our observations. Our value for Rb suggests a larger lattice effect than given by the theory. Unfortunately this band calculation does not include electron-electron interactions and electron-phonon interactions. Silverstein⁵ has calculated the density of single particle excitation states or heat capacity of an intermediate density electron gas by the use of a momentum transfer interpolation procedure analogous to that used by Nozieres and Pines⁶ in the calculation of the correlation energy. His values are shown in Table II as m_c/m_0 . A small increase in density of states with atomic separation is given by these calculations. In order to include the effect of the lattice periodicity and electron-electron interactions an addition formula equivalent to Eq. (4) was suggested by Silverstein.⁷ These values are shown as m'/m_0 in Table II. The agreement for Cs is excellent and certainly better than can be expected. The addition procedure given by Eq. (4) places considerable emphasis on the deviation of m_i/m_0 from unity. Thus for Rb an increase of m_i/m_0 from 1.21 to 1.53 would increase m'/m_0 to the value of 2.14 reported here.

Electron-phonon interactions have been considered as a separate problem by Buckingham and Schafroth⁸ and by Quinn.²⁸ The increase in the density of states at the Fermi surface which is caused by the electron-phonon interaction given by Quinn is shown in Table II as m_p/m_0 . A monotone increase in the density of states from Li to Cs or with increased atomic spacing is given by these calculations. No procedure is suggested for combining the m_i , m_c , and m_p , but the theoretical calculations indicate that a monotonic increase in the density of states with atomic spacing occurs for electron-electron and electron-phonon interactions. A deviation from this monotonic dependence of the density of states on the lattice spacing must be regarded as due to the band structure and a measure of the anisotropy of the Fermi surface. The heat-capacity measurements reported here suggest considerable anisotropy of the Fermi surface for Li, Rb, and Cs.

It is interesting to compare these values for the density of states at the Fermi surface with the calculations of Ziman²⁹ on a parameter which he refers to as the reduced resistivity. The reduced resistivity is a measure of the anisotropy of the Fermi surface and he has shown that it depends on the (area of the Fermi

surface)⁻². Values of 1.63 for Li, 1.04 for Na, 1.61 for Rb, and 2.78 for Cs are given. These values are obtained from the high-temperature data, but unfortunately are very sensitive to the choice of the average of the square of the phonon scattering frequency or Θ^2 . His analysis suggests considerable anisotropy of the Fermi surface for Li, Rb, and Cs. Ziman also analyzed the thermoelectric power measurements of the alkali metals which were made by MacDonald, Pearson, and Templeton³⁰ and concluded that the Fermi surface is nearly spherical for Na but is distorted for Li, Rb, and Cs. Recent measurements using the deHaas-van Alphen effect when interpreted in terms of an effective mass suggest a value of 0.9 for potassium³¹ and a value considerably less than given in this paper for cesium.³² A detailed model is necessary for comparison with the thermal effective mass.

Regarding the linear term in the heat capacity as due to the electrons, and the remaining heat capacity as the lattice contribution, the heat capacity of the lattice may be expressed as

$$C = (12\pi^4 R/5)(T/\Theta)^3, \quad (11)$$

where Θ is a function of temperature. The temperature dependence of Θ is shown in Fig. 4 for Cs and Fig. 6 for Rb. The data are in reasonable agreement with those of Lien and Phillips and McCollum and Silsbee. The rise from the minimum is steeper in the data reported here. If the frequency spectrum of the lattice has a spectral density³³

$$g(\omega) = a_2\omega^2 + a_4\omega^4 + \dots = a_2\omega^2\{1 + (a_4/a_2)\omega^2 + \dots\} \quad (12)$$

then the molar heat capacity can be approximately expressed as

$$C = (12\pi^4 R/5)(T/\Theta_0)^3 \times \{1 + (20\pi^2 k^2/7\hbar^2)(a_4/a_2)T^2 + \dots\}. \quad (13)$$

Using the data reported here, the heat capacity given by Eqs. (7) and (9) can be rewritten as

$$\text{Cs} \quad C = 28.97T^3\{1 + 0.051T^2 + 0.0326T^4 + \dots\} \quad (7a)$$

$$\text{Rb} \quad C = 9.599T^3\{1 + 0.080T^2 + 0.0074T^4 + \dots\}. \quad (9a)$$

In the notation of Eq. (13), this yields a value for cesium of $\Theta_0 = 40.6$ and 0.051 for the coefficient of the T^2 term or $(a_4/a_2)(20\pi^2 k^2/7\hbar^2)$. For Rb $\Theta_0 = 58.2$ and the coefficient of the T^2 term is 0.080. Further analysis of the data requires the use of the higher temperature data and an analysis procedure which is able to treat sharp peaks and a finite cutoff frequency in the spectral

³⁰ D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A256**, 334 (1960).

³¹ A. C. Thorsen and T. G. Berlincourt, Phys. Rev. Letters **6**, 617 (1961).

³² I. M. Templeton and K. Okumura, Bull. Am. Phys. Soc. **9**, 238 (1964).

³³ See the review article by A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Solid State Phys. Suppl. **3** (1963) for general references regarding the lattice.

²⁸ J. J. Quinn, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 63.

²⁹ J. M. Ziman, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 296.

distribution. The rapid rise from the minimum for cesium suggests a rapid increase in the spectral distribution. Rubidium indicates a slower increase. Further analysis does not seem warranted in this paper. Also no procedure is apparent for examining the suggestion by Jones⁹ that the lattice may contribute a linear term to the heat capacity and it has been assumed that the linear heat capacity is associated with the electrons.

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Longitudinal Correlation Function of the Heisenberg Ferromagnet*

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The correlation function of the z components (parallel to the net magnetization) of two spins in a Heisenberg ferromagnet is computed by a Green function analysis. The results extend spin-wave theory to higher temperatures, although they are not satisfactory near the Curie temperature. The Fourier transform of the correlation function varies as $1/k$ for small k , with a more complicated behavior at large k .

1. INTRODUCTION

THE spin-wave theory of the Heisenberg ferromagnet, valid at low temperatures, previously has been extended to arbitrary temperature by the method of double-time, temperature-dependent Green functions.¹⁻⁴ This theory yields both the magnetization and the transverse correlation function $\langle S_{\mathbf{m}\alpha} S_{\mathbf{p}\beta} \rangle$, where \mathbf{m} and \mathbf{p} label lattice sites and α, β can be either x or y (the external magnetic field being parallel to the z axis). The longitudinal correlation function $\langle S_{\mathbf{m}z} S_{\mathbf{p}z} \rangle - \langle S^z \rangle^2$, which is somewhat more difficult to analyze, is the subject of this paper.

The longitudinal correlation function is of direct physical interest in several connections as, for example, the thermodynamic energy and specific heat, the magnetic scattering of neutrons, and the magnetic susceptibility.

Several studies of the correlation function have been carried out. Van Hove,⁵ by analogy with the classical, phenomenological, Ornstein-Zernicke⁶ theory of fluctuations, postulated that the longitudinal correlation function has the Yukawa form $e^{-\kappa r}/r$, both above and below the Curie temperature, and thereby analyzed

the critical scattering of neutrons. To discuss the same problem, De Gennes⁷ used a generalized (wavelength-dependent) molecular field model, and Elliott and Marshall⁸ employed a Bethe-Peierls-Weiss model; these models give the same functional dependence on distance as postulated by van Hove. However, at low temperatures the spin-wave theory yields a different form, the Fourier transform of the correlation function varying as $1/k$ rather than as $1/(k^2 + \kappa^2)$. Recently, Kawasaki and Mori⁹ have given a very thorough investigation of the generalized susceptibility

$$\chi(k) = \mu^2 \beta \left[\beta^{-1} \int_0^\beta d\lambda \langle S_{\mathbf{k}z} S_{-\mathbf{k}z}(i\hbar\lambda) \rangle - \langle S_{\mathbf{k}z} \rangle \langle S_{-\mathbf{k}z} \rangle \right] \quad (1)$$

for the special case of spin $\frac{1}{2}$. Here $S_{\mathbf{k}z}$ is the Fourier transform of $S_{\mathbf{m}z}$, $S_{\mathbf{k}z}(i\hbar\lambda)$ is the Heisenberg operator $\exp(-\lambda\mathcal{H}) S_{\mathbf{k}z} \exp(\lambda\mathcal{H})$, and $\beta = (k_B T)^{-1}$. Although $\chi(k)$ is not directly related to the correlation function for general k , in the limit of small k the quantity $\chi(\mathbf{k})/\mu^2\beta$ approaches the Fourier transform of the correlation function. Kawasaki and Mori find the functional form $1/k(k + \kappa_1) \sim \chi(k)$ below T_c (with $\kappa_1 \rightarrow 0$ as $T \rightarrow T_c^-$), agreeing with spin-wave theory in the limit of low k , and they find $\chi(k) \sim 1/(k^2 + \kappa^2)$ above T_c .

By a Green function approach, we find the correlation function for arbitrary spin. In the limit of low k the

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¹ S. V. Tyablikov, *Ukr. Mat. Zh.* **11**, 287 (1959).² R. A. Tahir-Kheli and D. ter Haar, *Phys. Rev.* **127**, 88 (1962).³ H. B. Callen, *Phys. Rev.* **130**, 890 (1963).⁴ R. A. Tahir-Kheli, *Phys. Rev.* **132**, 589 (1963).⁵ L. van Hove, *Phys. Rev.* **95**, 1374 (1954).⁶ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), Sec. 116.⁷ P. G. de Gennes, Report to the C. E. A. de Saclay No. 923 (1959) (unpublished); P. G. de Gennes and J. Villain, *Phys. Chem. Solids* **13**, 10 (1960).⁸ R. J. Elliott and W. Marshall, *Rev. Mod. Phys.* **30**, 75 (1958).⁹ K. Kawasaki and H. Mori, *Progr. Theoret. Phys. (Kyoto)* **28**, 690 (1962).