

Debye Temperature for Cadmium Derived from Low-Temperature Specific-Heat Measurements*

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(Received June 21, 1962)

The low-temperature specific heat of cadmium in its normal state has been measured between 1.5 and about 4.2°K and may be expressed in the form $C = \gamma T + \alpha T^3 + \beta T^5$. Using as the electronic specific-heat coefficient, γ , the value of 0.6845 ± 0.0109 mJ deg⁻² (mole)⁻¹ recently reported by Martin for the temperature range 0.4 to 1.5°K, the other coefficients are: $\alpha = 0.1837 \pm 0.0070$ mJ deg⁻⁴ (mole)⁻¹ and $\beta = 0.0098 \pm 0.0010$ mJ deg⁻⁶ (mole)⁻¹. The calorimetric Debye temperature, Θ_0^C , is $219.5 \pm 2.7^\circ\text{K}$ which agrees satisfactorily with the elastic value, Θ_0^E , of $213 \pm 1^\circ\text{K}$. In the light of this agreement, the apparent discrepancies between Θ_0^C and Θ_0^E for cadmium cited in earlier literature are probably not significant.

INTRODUCTION

GENERALLY, excellent agreement has been reported¹ to exist between Debye characteristic temperature values derived from low-temperature specific-heat measurements, Θ_0^C , and those obtained from elastic constant data extrapolated to 0°K, Θ_0^E , except in the case of some hexagonal close-packed metals (beryllium,² cadmium,³ magnesium,⁴ and zinc⁵) and vanadium.⁶ At temperatures sufficiently low so that the thermal vibrations are of long wavelength and the lattice does indeed behave as a elastic continuum, the usual lattice theory of specific heats⁷ predicts that Θ_0^C and Θ_0^E should be identical for a given substance. However, because of the marked anisotropy of the hexagonal metals, it has been observed⁸ that the calorimetric measurements have to be extended to much lower temperatures than for cubic metals with similar Debye temperatures, in order to ensure that the continuum region has been reached. Recently, however, Garland and Silverman⁹ have demonstrated that, in the case of zinc in its normal state, this discrepancy in Debye temperatures may be essentially eliminated by considering that there is a T^5 contribution, in addition to the usual linear and cubic terms, in the expression for the low-temperature specific heat of this material. Likewise, Zimmerman and Crane¹⁰ and Seidel and Keesom¹¹ have specified that such an additional T^5 term is necessary for the proper representation of their specific-heat data

for both single-crystal and polycrystalline zinc samples in the liquid-helium range. Thus, if cognizance is taken of the fact that the T^5 term should be included in the lattice specific heat, C_L , for hexagonal metals at low temperatures when the T^3 term alone is insufficient [because the contribution to the density of normal lattice vibrations is proportional to $g(\nu)$ where $g(\nu) = a\nu^2 + b\nu^4 + \dots$ and, therefore, $C_L = \alpha T^3 + \beta T^5 + \dots$], then the Debye temperature values Θ_0^C and Θ_0^E can be brought into close and satisfactory agreement.

Martin⁸ has recently reported on some measurements on the specific heat of cadmium (in its normal state) in the range 0.52 to 1.5°K, from which he derived an electronic specific-heat coefficient, γ , equal to 0.6845 mJ deg⁻² (mole)⁻¹ and a Debye characteristic temperature value, Θ_0^C , of $204 \pm 3^\circ\text{K}$. This latter value is in good agreement with the elastic value of $213 \pm 1^\circ\text{K}$ given by Garland and Silverman.⁹ In contrast, however, the Debye temperature values, Θ_0^C , derived from the low-temperature specific-heat data on cadmium of Smith and Wolcott¹² and Srinivasan¹³ are, respectively, 188°K and $189 \pm 4^\circ\text{K}$, which are in substantial disagreement with both Garland and Silverman's⁹ elastic value and Martin's⁸ calorimetric value.

In this paper, we report on the results of measurements of the specific heat of cadmium in the temperature range 1.5 to about 4.2°K where discrepancies have been observed between Θ_0^E and Θ_0^C . The present results may be expressed in the form

$$C = \gamma T + \alpha T^3 + \beta T^5, \quad (1)$$

where C is the specific heat, γ the linear term is the usual electronic contribution for cadmium in its normal state, and the lattice specific-heat contribution includes a T^5 term. The calorimetric data reported here, have been analyzed in the aforementioned manner and the conclusion is drawn that there is no real discrepancy between the calorimetric Debye temperature value derived from the coefficient α in Eq. (1) and the elastic constant value. No quantitative account is advanced for the observed magnitude of the β coefficient.

* This research was supported by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

¹ G. A. Alers and J. R. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

² J. F. Smith and C. L. Arbogast, *J. Appl. Phys.* **31**, 99 (1960).

³ C. W. Garland and J. Silverman, *Phys. Rev.* **119**, 1218 (1960).

⁴ L. J. Slutsky and C. W. Garland, *Phys. Rev.* **107**, 972 (1957).

⁵ C. W. Garland and R. Dalven, *Phys. Rev.* **111**, 1232 (1958).
G. A. Alers and J. R. Neighbours, *J. Phys. Chem. Solids* **7**, 58 (1958).

⁶ G. A. Alers, *Phys. Rev.* **119**, 1532 (1960).

⁷ M. Blackman, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, p. 325.

⁸ D. L. Martin, *Proc. Phys. Soc. (London)* **78**, 1482 (1961).

⁹ C. W. Garland and J. Silverman, *J. Chem. Phys.* **34**, 781 (1961).

¹⁰ J. E. Zimmerman and L. T. Crane, *Phys. Rev.* **126**, 513 (1962).

¹¹ G. Seidel and P. H. Keesom, *Phys. Rev.* **112**, 1083 (1958).

¹² P. L. Smith and N. M. Wolcott, *Phil. Mag.* **1**, 854 (1956).

¹³ T. M. Srinivasan, *Proc. Indian Acad. Sci. A* **49**, 61 (1959).

EXPERIMENTAL

Because the cryostat and calorimetric technique employed in the present measurements have been described in detail by both Clement and Quinnell¹⁴ and Janninck,¹⁵ only a few details of particular interest need to be mentioned here.

In the present experiments, a 1/2-W, uninsulated Allen-Bradley carbon-composition resistor, with a nominal room-temperature resistance of 56 Ω , served both as heater and thermometer. In the temperature range of interest here, the temperature dependence of the carbon resistance thermometer, positioned within a cylindrical hole in the sample is determined from the vapor pressure of He⁴ ($T_{55\text{ }^\circ\text{F}}$ scale) using the following empirical temperature-resistance relation given by Keesom and Pearlman¹⁶

$$[(\log_{10} R)/T]^{1/2} = a + b \log_{10} R, \quad (2)$$

where R is the resistance of the carbon resistance thermometer in ohms, T is the corresponding temperature, and a and b are constants. The temperature calibration of the carbon thermometer is made at ten to twelve points over the temperature range of interest prior to each heat capacity experiment.

The heat capacity sample, measuring about 2 cm in diameter by 4 cm in length, was prepared from Johnson-Matthey cadmium of 99.999% spectrographic purity by melting in an evacuated, flat-bottom quartz capsule. Following a rapid air quench to room temperature from the melting range, a close-fitting hole is machined along the axis of the sample to accommodate the heater-thermometer which is cemented in position with the aid of Glyptal type 7031 adhesive. This adhesive not only serves to prevent undesirable contact between the helium exchange gas and the carbon resistor, but also to act as a thermal conductor and electrical insulator between the resistor and specimen.

The heat capacity measurements are performed in the manner described by Clement and Quinnell,¹⁴ by observing the resistance change of the thermometer while adding a known pulse of heat to the sample. The calculations of the temperature and specific heat of the sample are carried out from these raw data, taking proper account of the heat capacity of the addenda (thermometer and adhesive, which is about 5 to 10% of the total heat capacity) in the specific-heat calculations. In this latter connection, the heat capacity of the heater thermometer was calculated from data obtained for a similar carbon-composition resistor,¹⁷ and that for

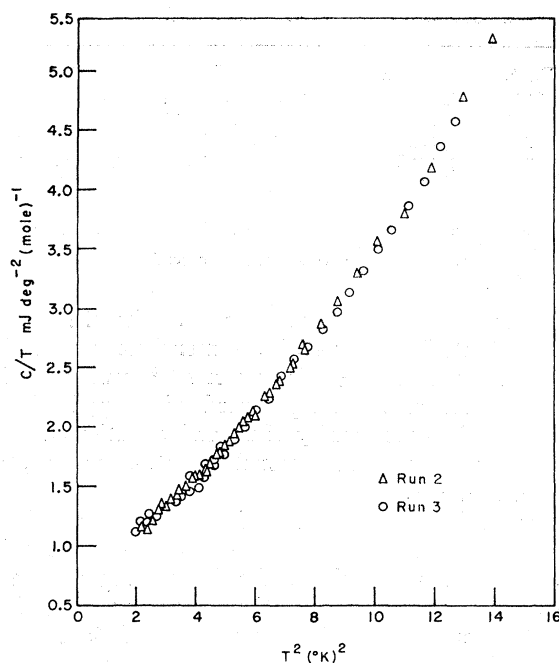


FIG. 1. Specific heat of polycrystalline cadmium plotted as C/T vs T^2 .

the Glyptal adhesive was calculated from the results given by Pearlman and Keesom¹⁸ for that material.

As a preliminary check on the present heat-capacity technique, Janninck¹⁵ performed specific-heat measurements on several silver samples of high purity and obtained an electronic specific-heat coefficient, γ , of 0.660 ± 0.007 mJ deg⁻² (mole)⁻¹ and a Debye characteristic temperature of $228.7 \pm 0.5^\circ\text{K}$, in satisfactory agreement with results reported by other investigators¹⁹ using different calorimetric techniques.

RESULTS AND DISCUSSION

It is quite apparent from an examination of Fig. 1, where C/T is plotted vs T^2 and a nonlinear plot results, that the specific heat of cadmium in the temperature range of interest here, is really not expressible in the usual manner as $C = \gamma T + \alpha T^3$. As had been pointed out previously for zinc⁹⁻¹¹ and gallium,¹¹ the lattice specific heat in such a circumstance is no longer proportional to T^3 only and the low-temperature specific heat of the substance can be best expressed by an equation of the form of Eq. (1) where the first term on the right side of this expression is taken to be the electronic specific heat, C_e , and the last two terms together are

¹⁴ J. R. Clement and E. H. Quinnell, *Low-Temperature Physics*, National Bureau of Standards Circular No. 519 (U. S. Government Printing Office, Washington, D. C., 1952).

¹⁵ R. F. Janninck, M. S. thesis, Northwestern University, Evanston, Illinois, 1961 (unpublished).

¹⁶ P. H. Keesom and N. Pearlman, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 282.

¹⁷ J. R. Clement and E. H. Quinnell, Naval Research Laboratory Document No.-106435, 1953 (unpublished).

¹⁸ N. Pearlman and P. H. Keesom, *Phys. Rev.* **88**, 398 (1952).

¹⁹ P. H. Keesom and N. Pearlman, *Phys. Rev.* **98**, 548 (1955); W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, *ibid.* **98**, 1699 (1955); J. Rayne, *Proc. Phys. Soc. (London)* **B69**, 482 (1956); F. E. Hoare and B. Yates, *Proc. Roy. Soc. (London)* **A240**, 42 (1957); J. E. Zimmerman, in *Low-Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 392; F. J. DuChatenier and J. DeNobel, *Physica* **28**, 181 (1962).

TABLE I. Summary of present results for cadmium.^a

Expt. run	α [mJ deg ⁻⁴ (mole) ⁻¹]	Θ_0^c (°K)	β [mJ deg ⁻⁶ (mole) ⁻¹]
2	0.1805±0.0051	220.8±2.0	0.0106±0.0008
3	0.1889±0.0060	217.5±2.2	0.0087±0.0009
2 and 3 ^b	0.1837±0.0070	219.5±2.7	0.0098±0.0010

^a Calculated using $\gamma = 0.6845$ mJ deg⁻² (mole)⁻¹ and an atomic weight = 112.41 g (see reference 8).

^b Least-squares analysis values computed for combined data from two experiments.

considered as an empirical expression for the lattice specific heat, C_L , below 4.2°K. As mentioned above, the need for expressing C_L as a sum of a T^3 term and a T^5 term for a lattice exhibiting marked anisotropy has been attributed¹¹ to the density of normal vibrations at low frequencies being proportional to $g(\nu)$, where $g(\nu) = a\nu^2 + b\nu^4 + \dots$.

Since it is generally recognized that specific-heat measurements conducted at lower temperatures should give a more reliable value of the electronic specific-heat coefficient, γ , than observations made at somewhat higher temperatures, the γ value ($= 0.6845 \pm 0.0109$ mJ deg⁻² (mole)⁻¹) for cadmium reported by Martin⁸ from measurements made between 0.52 and 1.5°K was employed in analyzing the present data by means of Eq. (1).

Thus, the data of Fig. 1 are replotted in Fig. 2 in the form $(C - \gamma T)/T^3$ vs T^2 which should yield a linear plot of intercept α and slope β if Eq. (1) is obeyed in the present instance. The coefficient α is proportional to $(\Theta_0^c)^{-3}$ where Θ_0^c is the usual calorimetric Debye temperature extrapolated to 0°K. The values found for

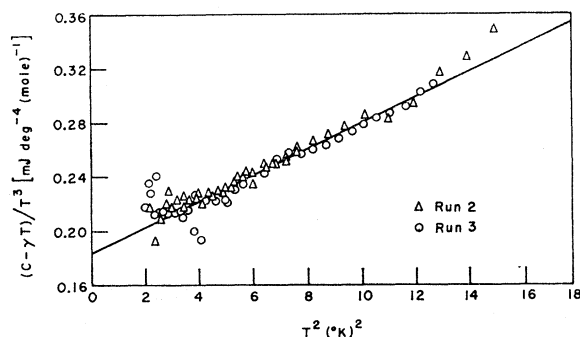


FIG. 2. Specific-heat data for polycrystalline cadmium plotted as $(C - \gamma T)/T^3$ vs T^2 . See text for explanation.

the coefficients α and β , together with the values of Θ_0^c calculated from the present data, are listed in Table I. The data of Fig. 2 were analyzed by the methods of least squares²⁰ and the limits set forth in Table I are the usual 95% confidence limits.

For comparison purposes, the results of this investigation are expressed in terms of the calorimetric Debye temperature Θ_0^c and given in Table II along with those values reported by previous investigators based upon their measurements in the liquid-helium temperature range. It is apparent that the present Θ_0^c value agrees well with both Martin's and the elastic constant value, but all of these are in substantial disagreement with the values derived from measurements by Smith and

TABLE II. Comparison of results for cadmium.

Specific heat results	Purity of material (%)	Temperature range over which Θ is assumed constant (°K)	Debye Θ (°K)
Samoilov ^a	99.95	0.45–0.95	300
Smith and Wolcott ^b	99.99+	1.3–3.0	188
Srinivasan ^c	99.95	1.3–2.5	189±4
Martin ^d	99.9999	0.52–1.5	204±3
Present work	99.999	1.5–4.0	219.5±2.7
Elastic constant results			
Garland and Silverman ^e			213±1

^a See reference 21.

^b See reference 12.

^c See reference 13.

^d See reference 8.

^e See reference 3.

Wolcott,¹² Srinivasan,¹³ and Samoilov²¹ using the usual relation $C = \gamma T + \alpha T^3$. Thus, it would appear that inclusion of the T^5 term in the lattice specific heat is important for anisotropic cadmium at helium temperatures which are slightly above its true continuum region because the T^3 term alone is insufficient to describe the thermal behavior of the lattice there.

ACKNOWLEDGMENTS

The authors are indebted to Dr. R. F. Janninck for assistance in the experimental phases of this work as well as for several valuable suggestions.

²⁰ See, for example, F. S. Acton, *Analysis of Straight Line Data* (John Wiley & Sons, Inc., New York, 1959), pp. 11, 21, and 240.

²¹ B. N. Samoilov, *Doklady Akad. Nauk, U.S.S.R.* **82**, 281 (1952).