

Extension of the Range of Validity of Thirring's Expansion for the Specific Heat of Crystals

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In 1913, Thirring obtained an expansion for the vibrational contribution to the specific heat of a crystalline solid in powers of $1/T^2$. The coefficients of this series are proportional to successive moments of the frequency spectrum. In its original form, Thirring's expansion converges only for $T > T_a$, where $T_a = \hbar\omega_L/2\pi k$ and ω_L is the maximum normal mode frequency, and because of slow convergence, it is useless from a numerical point of view for $T < 4T_a/3$. The range of convergence of the expansion can be extended to absolute zero and its computational usefulness down to $T \approx 2T_a/3$ by means of an Euler transformation, which effectively converts it into an expansion in $1/(T^2 + T_b^2)$ with $T_b \approx T_a$. The improvement in convergence is so efficient that, usually, only the first 6 or 7 even moments are required to obtain four-figure accuracy at $T = T_a$. Alternatively, nonlinear transformations can be applied if the specific heat is to be calculated for a few values of temperature only. Some examples of the use of these methods are presented. Conversely, Euler's transformation provides a means for a more detailed description of the frequency distribution from specific heat measurements.

1. INTRODUCTION

FOR a system of coupled harmonic oscillators, the thermal properties are uniquely determined by the frequencies of its normal modes, each frequency contributing to the energy E , free energy F , and specific heat C_v according to Planck's law. The accurate calculation of the frequency spectrum may present great difficulties; in a periodic lattice, this involves the evaluation of the eigenvalues of matrices, the dimensions of which are equal to the number of degrees of freedom of the unit cell and the elements of which depend on the components of the wave vector. With automatic computers such secular equations can be solved rather easily; nevertheless, any method by which the thermal properties may be calculated from the force constants without such machinery is of great importance. Even if the frequency distribution is known, the calculations usually necessitate a separate numerical integration for each temperature, and methods which circumvent this laborious process are desirable.

Such a method has first been derived by Thirring,¹ who expressed the vibrational contribution to the specific heat as a series in inverse powers of the absolute temperature T . The coefficients of successive terms involve the even moments of the frequency distribution. A major drawback in the application of Thirring's expansion is that it converges only for temperatures above $T_a = \hbar\omega_L/2\pi k$ where ω_L is the maximum normal

mode frequency. For practical purposes, the temperature range is even more restricted; even for $T = \frac{4}{3}T_a$, ten terms are required to give three-figure accuracy. Since, on the other hand, the thermal properties exhibit no singularities at any finite temperature, Thirring's series should be summable by any of the methods which sum divergent series and improve the convergence of slowly convergent sequences.²

For practical purposes, any numerical process for evaluating the sums should satisfy two conditions:

(I) Each term in the transformed sequence should depend on as small as possible a number of terms of the original sequence, and hence of moments.

(II) The resulting expressions should contain the temperature as an explicit parameter so that a single numerical process will yield an expansion applicable over a whole range of temperatures.

A procedure satisfying both the above conditions is Euler's transformation^{3,4} which converts the independent variable in a power series from $-x$ to $x/(1+x)$, the new coefficients being obtained from the old ones by differencing. In Sec. 2, this transformation is applied to Thirring's expansion for the specific heat, and the convergence of the new series is discussed in terms of the

² K. Knopp, *Theory and Applications of Infinite Series* (Blackie and Son, Ltd., London, 1951), 2nd ed., Chap. 13.

³ L. Euler, *Institutiones Calculi Differentialis cum eius usu in analysi finitorum ac doctrina serierum* (Impensis Academiae Imperialis Scientiarum, St. Petersburg, 1755), Pars Posterior, Caput I; *Opera Omnia* (B. G. Teubner, Leipzig, 1913), Part I, Vol. 10, p. 217.

⁴ D. R. Hartree, *Numerical Analysis* (Clarendon Press, Oxford, 1952).

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¹ H. Thirring, *Physik. Z.* **14**, 867 (1913); **15**, 127, 180 (1914).

analytical behavior of the function. A nonlinear summation method (sometimes known as exponential extrapolation^{5,6}) will be described in Sec. 3; for a given number of terms, it may give more accurate values than Euler's transformation; on the other hand, it violates condition (II) above, a separate numerical process being required for each temperature considered.

The converse problem, that of determining the frequency distribution from experimental measurements of the specific heat, can equally be facilitated by the use of Euler's transformation. This aspect will be discussed in the Appendix.

2. THIRRING'S SERIES AND ITS EULER TRANSFORMATION

The internal energy of a set of coupled harmonic oscillators is given by

$$E(T) = \sum_{i=1}^N \left\{ \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{\exp(\hbar\omega_i/kT) - 1} \right\} = \sum_{i=1}^N \frac{\hbar\omega_i}{2} \coth\left(\frac{\hbar\omega_i}{2kT}\right), \quad (1)$$

where the ω_i are the normal mode frequencies and N is the total number of degrees of freedom of the system. The specific heat is derived from (1) as

$$C_v(T) = \left(\frac{\partial E(T)}{\partial T} \right)_v = k \sum_i \frac{(\hbar\omega_i/2kT)^2}{\sinh^2(\hbar\omega_i/2kT)}. \quad (2)$$

The expansion of $\coth x$ as a power series yields⁷

$$x \coth x = 1 - \sum_{n=1}^{\infty} (-4x^2)^n B_{2n}/(2n)! = 1 - 2 \sum_{n=1}^{\infty} (-1)^n \zeta(2n) (x/\pi)^{2n}, \quad (3)$$

where $\zeta(2n)$ is Riemann's zeta function

$$\zeta(2n) = \sum_{m=1}^{\infty} m^{-2n}, \quad 2n > 1, \quad (4)$$

and the B_{2n} are the (absolute values of the) Bernoulli numbers

$$B_2 = 1/6, \quad B_4 = 1/30, \quad B_6 = 1/42, \quad B_8 = 1/30, \\ B_{10} = 5/66, \quad B_{12} = 691/2730, \quad B_{14} = 7/6, \quad \text{etc.}$$

Substitution of (3) in (1) leads to

$$E(T) = NkT + 2kT \sum_{i=1}^N \sum_{n=1}^{\infty} (-1)^{n+1} \zeta(2n) (\hbar\omega_i/2\pi kT)^{2n} \quad (5)$$

$$= NkT + 2NkT \sum_n (-1)^{n+1} \zeta(2n) \mu_{2n} (\hbar/2\pi kT)^{2n}. \quad (6)$$

⁵ D. R. Hartree, Proc. Cambridge Phil. Soc. **45**, 230 (1949).

⁶ D. Shanks, J. Math. and Phys. **34**, 1 (1955).

⁷ See, for example, E. P. Adams, *Smithsonian Mathematical Formulae and Tables of Elliptic Functions* (The Smithsonian Institution, Washington, D. C., 1957), p. 127. Note that Adams denotes by B_n what we have called B_{2n} .

Here the μ_{2n} are the moments of the frequency spectrum

$$\mu_{2n} = \sum_{i=1}^N \omega_i^{2n} / N = \int_0^{\omega_L} \omega^{2n} f(\omega) d\omega, \quad (7)$$

where $f(\omega)$ is the frequency distribution function of the system (normalized to unity).

From (2) and (6) we obtain

$$C_v/Nk = 1 + 2 \sum_n (-1)^n (2n-1) \zeta(2n) \mu_{2n} (\hbar/2\pi kT)^{2n}, \quad (8)$$

or in terms of Bernoulli numbers

$$\frac{C_v}{Nk} = 1 + \sum_n (-1)^n \frac{2n-1}{(2n)!} B_{2n} \mu_{2n} \left(\frac{\hbar}{kT} \right)^{2n}. \quad (9)$$

Equations (8) and (9) are alternative formulations of Thirring's expansion.

Its radius of convergence is given by the ratio test

$$(\hbar/2\pi kT)^2 < \lim_{n \rightarrow \infty} (\mu_{2n}/\mu_{2n+2}), \quad (10)$$

or

$$T > T_a = \hbar\omega_L/2\pi k, \quad (11)$$

as stated in the Introduction.

The squares of the normal mode frequencies are the roots of the secular equation

$$|\mathbf{D}_N - \omega^2 \mathbf{I}| = 0, \quad (12)$$

where \mathbf{D}_N is the dynamical matrix for the vibrating system, so that we can write (7) in the form

$$\mu_{2n} = \text{Tr}(\mathbf{D}^n)/N. \quad (13)$$

For an infinite 3-dimensional lattice with s degrees of freedom per unit cell, the matrix \mathbf{D} is reducible by a Fourier transformation to a set of $3s$ -dimensional matrices $D_{3s}(\theta_1, \theta_2, \theta_3)$ with elements containing only positive powers of $\sin\theta_k$ and $\cos\theta_k$ (the θ_k are components of the wave vector taken along, and measured in units of the axes of the reciprocal lattice). The moments can then be expressed as

$$\mu_{2n} = \frac{1}{3s(2\pi)^3} \int_0^{2\pi} \text{Tr}[D_{3s}^n(\theta_1, \theta_2, \theta_3)] d\theta_1 d\theta_2 d\theta_3. \quad (14)$$

In some simple cases, it is possible to solve for the frequencies in the form

$$\omega_j^2 = F_j(\theta_1, \theta_2, \theta_3), \quad (15)$$

where j labels the branch of the frequency spectrum; then the moments can be written

$$\mu_{2n} = \frac{1}{3s(2\pi)^3} \sum_{j=1}^{3s} \int_0^{2\pi} F_j^n(\theta_1, \theta_2, \theta_3) d\theta_1 d\theta_2 d\theta_3. \quad (16)$$

It will depend on the precise nature of the information provided whether the μ_{2n} are best evaluated from (7), (14), (16) or (13).

TABLE I. Difference table of the coefficients in Thirring's expansion for a Debye frequency distribution,
 $\gamma = 1, y_n = \frac{6(2n-1)}{2n+3} \zeta(2n).$

n	y_n	Δy_n	$\Delta^2 y_n$	$\Delta^3 y_n$	$\Delta^4 y_n$	$\Delta^5 y_n$	$\Delta^6 y_n$
0	1.000000						
1	1.973920	0.973920					
2	2.783117	0.809197	-0.164723				
3	3.391144	0.608027	-0.201170	-36 447			
4	3.833750	0.442606	-0.165421	+35 749	+72 196		
5	4.157977	0.324227	-0.118379	+47 042	+11 293	-60 903	
6	4.401083	0.243106	-0.081121	+37 258	-9784	-21 077	+39 826
7	4.588516	0.187433	-0.055673	+25 448	-11 810	-2026	+19 051
8	4.736892	0.148376	-0.039057	+16 616	-8832	+2978	+5004

An alternative form of Thirring's series is provided by the introduction of the dimensionless variable z and relative moments u_{2n}

$$z = T_a/T; \quad u_{2n} = \mu_{2n}/\omega_L^{2n}, \quad (17)$$

in which (8) becomes

$$C_v/Nk = 1 + 2 \sum_n (-1)^n (2n-1) z^{2n} \zeta(2n) u_{2n}. \quad (18)$$

The analytic nature of E and C_v is best determined from (1) and (2). For each contribution associated with a frequency ω_i , the only singularities occur for imaginary values of T for which $\hbar/2kT = m\pi i/\omega_i$ ($m = \pm 1, \pm 2, \dots$). For a continuous distribution of frequencies, the singularities will extend all along the imaginary axis where $|\hbar/2kT| > \pi\omega_L^{-1}$, i.e., for all imaginary values of T and z for which $|T_a/T| = |z| > 1$. We transform the independent variable to

$$\xi = T_b^2/(T^2 + T_b^2) = z^2/(\gamma + z^2), \quad (19)$$

where T_b is a temperature chosen such that $\gamma = T_a^2/T_b^2$ lies between 0 and 2, but is otherwise arbitrary. The singularities for the new variable come to lie along the real axis with $|\xi| > 1$. The corresponding power series in ξ converges thus for all temperatures from $T = \infty$ ($\xi = 0$) to $T = 0$ ($\xi = 1$).

The explicit form of C_v as a series in ξ is most easily obtained by means of Euler's transformation, according to which an infinite power series with numerically given coefficients y_n

$$F(x) = \sum_{n=0}^{\infty} (-x)^n y_n = S_{l-1}(x) + R_l(x), \quad (20)$$

where S_{l-1} is the partial sum up to the term $n = l-1$, the remainder $R_l(x)$ can be transformed to

$$R_l(x) = \frac{(-x)^l}{1+x} \sum_{\lambda=0}^{\infty} \left(\frac{-x}{1+x} \right)^{\lambda} \Delta^{\lambda} y_l, \quad (21)$$

with the differences $\Delta^{\lambda} y_l$ defined by

$$\Delta^0 y_n = y_n, \quad \Delta^{\lambda+1} y_n = \Delta^{\lambda} y_{n+1} - \Delta^{\lambda} y_n. \quad (22)$$

The function $F(x)$ in (20) can be identified with C_v/Nk in (8) or (18) and (19) on putting

$$x = z^2/\gamma = T_b^2/T^2, \quad \xi = x/(1+x), \quad (23)$$

$$y_n = 2(2n-1)\gamma^n \zeta(2n) u_{2n} = 2(2n-1)\zeta(2n) \times \mu_{2n} (\hbar/2\pi k T_b)^{2n}. \quad (24)$$

The explicit dependence on temperature becomes

$$\frac{C_v}{Nk} = 1 + \sum_{n=1}^{l-1} (-1)^n \frac{T_b^{2n}}{T^{2n}} y_n + (-1)^l \sum_{\lambda=0}^{\infty} \frac{(-1)^{\lambda} T_b^{2l+2\lambda} \Delta^{\lambda} y_l}{T^{2l-2} (T_b^2 + T^2)^{\lambda+1}}. \quad (25)$$

This expression with the definitions (24) and (22) for the coefficients satisfies both requirements listed in the Introduction; it represents an expansion in which the individual terms have a simple dependence on T , and the coefficients $\Delta^{\lambda} y_l$ depend only on the moments from μ_{2l} to $\mu_{2l+2\lambda}$. As shown above, for a suitable γ or T_b , (25) converges for all temperatures, though near $T = 0$ the convergence is poor. The best choice of γ is that which makes the individual terms in the second sum of (25) decrease most rapidly; if the relative moments u_{2n} were constant, the optimal value would be $\gamma = 1$; as the u_{2n} usually form a slowly decreasing sequence, a slightly bigger value of γ (say, 1.05 or 1.1) may be preferable. With the chosen value of γ , a table of the coefficients y_n and their differences is constructed according to (24) and (22); the best choice for the index l can usually be inferred from an inspection of the difference table. The use of the method is best demonstrated by an actual example.

TABLE II. Partial sums of the Thirring series and its Euler transformation for the Debye frequency distribution.

θ/T	4	6	8	10
x	0.405285	0.911891	1.621139	2.53303
ξ	0.288400	0.476958	0.618487	0.716957
S_1	0.200000	-0.800000	-2.2	-4.
S_2	0.657143	1.514286	+5.11428	13.8571
S_3	0.431393	-1.057144	-9.33372	-41.2576
S_4	0.534827	1.593766	+17.1455	116.570
S_5	0.489362	-1.028013	-29.4113	
S_6	0.508865	1.502545	+50.4766	
S_7	0.500669	-0.903323	-84.5484	
S_8	0.504117	1.361508	-141.4241	
S_1+R_{20}	0.525303	0.410470	0.590500	1.054343
S_1+R_{21}	0.504807	0.284337	0.213445	0.262663
S_1+R_{22}	0.503199	0.267970	0.150000	0.108241
S_1+R_{23}	0.503067	0.265750	0.138835	0.076756
S_1+R_{24}	0.503059	0.265530	0.137405	0.072061
S_1+R_{25}	0.503060	0.265552	0.137589	0.072758
S_1+R_{26}	0.503060	0.265578	0.137870	0.073992
Accurate	0.503059	0.265597	0.138187	0.075821

Example: The Debye Frequency Distribution

The Debye frequency spectrum is of the form

$$\begin{aligned} f(\omega)d\omega &= 3\omega^3 d\omega / \omega_L^3, \quad \omega < \omega_L, \\ f(\omega)d\omega &= 0, \quad \omega > \omega_L, \end{aligned} \quad (25)$$

and the reduced moments u_{2n} are thus

$$u_{2n} = 3/(3+2n). \quad (26)$$

In view of (10), Thirring's series in its original form (8) and (9) converges for temperatures $T > T_a = \theta/2\pi$ where θ is the Debye temperature of the distribution. For the choice of $\gamma = 1 (T_b = T_a)$ in (19), the values of the terms y_n in (24) and their differences are given in Table I. Inspection indicates that the expansion in terms of differences $\Delta^l y_l$ is best carried out for $l=2$ or $l=3$. Thus with

$$x = (\theta/2\pi T)^2,$$

$l=2$, and ξ defined in (19) the specific heat can be expanded as

$$\begin{aligned} C_v/kT &= 1 - 1.973920x + 2.783117x\xi - 0.608027x\xi^2 \\ &\quad - 0.165421x\xi^3 - 0.047042x\xi^4 - 0.009784x\xi^5 \\ &\quad + 0.002026x\xi^6 + 0.005004x\xi^7. \end{aligned} \quad (27)$$

The partial sums of the original and transformed series are tabulated in Table II for several values of θ/T and compared with the value for C_v/Nk calculated by Beattie.⁸ The moments have been purposely limited to 8 and the calculations to six decimals, although in the given case, a greater accuracy could have been achieved. It can be seen that even in the region where the original series converges, the gain in convergence on applying Euler's transformation is appreciable. The values of θ/T from 5 upward lie outside the useful range of convergence of the original series, but even for $\theta/T=8$,

C_v can be calculated to nearly four figures from the first eight even moments. Only for values of θ/T greater than 9, the error occurs in the second significant figure and the method breaks down. The useful range of Thirring's expansion as a function of inverse temperature has thus been approximately doubled.

The Euler transformation can equally be applied to the series (6) for the thermal energy or its dimensionless form

$$E/Nk = T + 2T \sum_n (-1)^n \zeta(2n) u_{2n} z^{2n}, \quad (28)$$

and since the variables z , x and ξ defined in (17), (19) and (23) are all simple functions of T , the specific heat can be obtained from a term-by-term analytic differentiation of the transformed series. In the same way, the corresponding series for the logarithm of the partition function (i.e., essentially the free energy) can be transformed, and the energy and specific heat calculated by a single or twofold term-by-term differentiation.

3. NONLINEAR TRANSFORMATIONS

Of the various possible nonlinear transformations of a slowly convergent or divergent sequences, the simplest is the method denoted by Hartree as exponential extrapolation, which has been discussed in great detail by Shanks.⁶ From three successive partial sums S_n of the sequence an extrapolated value S_n' is derived

$$S_n' = \frac{S_{n-1}S_{n+1} - S_n^2}{S_{n+1} + S_{n-1} - 2S_n}, \quad (29)$$

which is equal to the sum of the infinite geometric progression which has S_{n-1} , S_n and S_{n+1} as successive partial sums. The expression (29) can be written somewhat more simply using the terms of the series

$$v_n = S_{n+1} - S_n, \quad (30)$$

in addition to the partial sums,

$$S_n' = S_{n-1} + \frac{v_n^2}{v_n - v_{n+1}} = S_n + \frac{v_n v_{n+1}}{v_n - v_{n+1}}. \quad (31)$$

By a process analogous to (29) a second sequence of extrapolated values S_n'' can be derived, etc.

Table III shows the original and extrapolated partial sums for the specific heat of the Debye distribution for $\theta/T=8$. The results clearly demonstrate the advantages and drawbacks of this method compared with Euler's transformation. If only a very small number of moments are given, the extrapolation method yields a considerably more accurate result (compare the results 0.1500 and 0.1369, which both make use of the moments up to order 8); effectively, it optimizes the value of γ in (19) for every value of T , instead of using a preset (and somewhat arbitrary) value for all temperatures. On the other hand, it exhibits a number of drawbacks, of which the most obvious is that for each temperature the

⁸ J. Beattie, J. Math. and Phys. 6, 1 (1926).

TABLE III. Exponential extrapolation for the partial sums of the Thirring expansions of the Debye frequency distribution at $T = (1/8)\theta$.

n	S_n	S_n'	S_n''	S_n'''	S_n''''
-1	0.				
0	1.	0.238095			
1	-2.2	0.026087	0.136918		
2	5.11428	0.258322	0.139234	0.138462	
3	-9.33372	0.013892	0.138076	0.137022	0.137584
4	17.1455	0.266325	0.137524	0.137945	0.138433
5	-29.4113	0.003337	0.139295	0.138264	
6	50.4766	0.284808	0.136828		
7	-84.5484	-0.027214			
8	141.4241				

process must be redone *ab initio*. Secondly, for temperatures at which the original sequence diverges, the partial sums S_n may have to be given to a greater accuracy than the knowledge of the moments warrants in order to retain adequate accuracy in S_n'' or S_n''' , whereas in Euler's method, very large terms can be avoided by applying the differencing at the start. This difficulty can be overcome by attributing an increased accuracy to the moments, and carrying out the calculations consistently with these values. The effect of the extra figures will cancel out in the extrapolated sums, but it will ensure that the rounding off errors will be kept to a minimum. Most serious is the limitation that the regular alternation of partial sums may be interrupted in some order so that the extrapolations in the next higher order are less, instead of more, accurate. This occurs in the sequence S'' , S''' of Table III.

It would thus appear that, on balance, the Euler transformation is the more preferable method of extending the usefulness of Thirring's series, unless the number of known moments is very small.

Other transformations of the Thirring series are possible, such as the Padé table, expansions in continued fractions, or the higher-order summations discussed by Knopp and Shanks.^{2,6,9} As these involve heavier computations than the methods presented in Secs. 2 and 3, they will not be discussed here.

APPENDIX

Calculation of Moments from Specific Heat Measurements¹⁰

In accordance with Thirring's expansion, it has been customary to express the high temperature specific heat as a power series in $1/T^2$

$$C_v/Nk = 1 - A_1/T^2 + A_2/T^4 + \dots, \quad (A1)$$

from which the moments of the frequency distribution can be calculated by comparison with (8) and (9)

⁹ O. Perron, *Die Lehre von den Kettenbrüchen* (B. G. Teubner, Leipzig, 1957), 3rd ed., Vol. 2.

¹⁰ The analysis of this Appendix follows from that of Sec. 2 and is omitted. For the benefit of readers interested in this part of the problem only, the Appendix is made self-contained.

$$\mu_{2n} = \frac{A_n}{2(2n-1)\zeta(2n)} \left(\frac{2\pi k}{h} \right)^{2n}. \quad (A2)$$

The values of the Riemann zeta function $\zeta(2n)$ and $2(2n-1)\zeta(2n)$ for n up to 10 are tabulated in Table IV. The values for $\zeta(2n)$ were taken from the tables of Davis.¹¹

The coefficient A_1 determines the high-temperature value of the Debye temperature θ_h . For reasons discussed in Sec. 2, the usefulness of the series (A1) is limited to temperatures higher than $\frac{1}{4}\theta_h$, and hence only a few coefficients A_n can be determined accurately. The useful range of this expansion can be considerably increased by choosing as the independent variable

$$\xi = T_b^2/(T^2 + T_b^2), \quad (A3)$$

where T_b is an auxiliary temperature of the order $\theta_h/6$, but otherwise arbitrary. The experimental results should then be presented in one of the following forms

$$(1 + T_b^2/T^2)C_v/Nk = 1 - a_{01}\xi + a_{02}\xi^2 - a_{03}\xi^3 + \dots, \quad (A4)$$

or

$$C_v/Nk = 1 - a_{10}\xi + a_{11}\xi^2 - a_{12}\xi^3 + \dots, \quad (A5)$$

or

$$(1 - C_v/Nk)(T/T_b)^2 = a_{10} - a_{20}\xi + a_{21}\xi^2 - a_{22}\xi^3 + \dots. \quad (A6)$$

Set up a table

1	a_{01}	a_{02}	a_{03}	a_{04}
a_{10}	a_{11}	a_{12}	a_{13}	a_{14}
a_{20}	a_{21}	a_{22}	a_{23}	
a_{30}	a_{31}	a_{32}		
a_{40}	a_{41}			
a_{50}				

(A7)

in which one row of coefficients has been determined from (A4), (A5), or (A6) and the elements of succeeding rows are obtained by the recurrence relations

$$a_{i,k} = a_{i-1,k} + a_{i-1,k+1}; \quad (A8)$$

i.e., each element is the algebraic sum of the element above and that above to the right. The even moments

TABLE IV. Values of Riemann's zeta function for the first ten even integers.

$2n$	$\zeta(2n)$	$2(2n-1)\zeta(2n)$
2	1.644934067	3.289868134
4	1.082323234	6.493939402
6	1.017343062	10.17343062
8	1.004077356	14.05708299
10	1.000994475	18.01790055
12	1.000246087	22.00541390
14	1.000061248	26.00159245
16	1.000015282	30.00045847
18	1.000003817	34.00012978
20	1.000000954	38.00003625

¹¹ H. T. Davis, *Tables of the Higher Mathematical Functions* (Principia Press, Bloomington, Indiana, 1935), Vol. 2.

of the frequency distribution are then given in terms of elements of the first column of (A7)

$$\mu_{2n} = \frac{a_{n0}}{2(2n-1)\zeta(2n)} \left(\frac{2\pi k T_b}{\hbar} \right)^{2n}. \quad (\text{A9})$$

The expansions (A4), (A5), and (A6) are valid over a larger range of the inverse temperature than (A1), and in consequence their coefficients can be determined with greater accuracy, and hence, the moments μ_{2n} can be calculated to a higher value of n .

Specific Heat of a Body-Centered Cubic Cr-Fe Alloy between 30° and 110°K*

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The specific heat of a body-centered cubic alloy, $\text{Cr}_{80.6}\text{Fe}_{19.4}$, was determined between 30° and 110°K. The electronic specific heat coefficient γ and the Debye characteristic temperature were evaluated between 40° and 60°K to be $(46 \pm 5) \times 10^{-4} \text{ cal mole}^{-1} \text{ deg}^{-2}$ and $472 \pm 14^\circ\text{K}$, respectively. The origin of a sharp peak occurring at $37 \pm 2^\circ\text{K}$ is discussed.

THE specific heats of a number of body-centered cubic Cr-Fe alloys between 1.6° and 4.2°K were measured by Wei *et al.*¹ Near 19 at. % Fe there appeared to be a high peak in the coefficient γ of the linear term in temperature. It may be asked whether this high γ peak has its origin in a magnetic transformation. Should the Curie point of such an alloy occur near 4.2°K, the extra heat absorbed in the course of ferro-paramagnetic transition might appear to be linear in T in such a small temperature range. It is the purpose of the present work to investigate the heat capacity of a body-centered cubic alloy, $\text{Cr}_{80.6}\text{Fe}_{19.4}$, in the temperature range where a possible magnetic transition is likely to occur to see whether the high γ peak may be attributed to a magnetic transition.

The alloy was induction melted, homogenized at 1175°C for three days, and water quenched. X-ray diffraction and microscopic examination indicated that it was a single-phase, body-centered cubic alloy with no more than 1% in the total amount of oxides and foreign materials. Table I gives the chemical analysis of the

specimen, which weighed 17.38 g. The calorimetric equipment used in this work was the same as that used for specific heat measurements between 1.6° and 4.2°K.² A copper resistance thermometer, which was calibrated at 0°C, 78°K, and 4.2°K against the Dauphinee and Preston-Thomas scale,³ was used for the temperature measurement. The correction for the heat capacity of the copper body of the heater-thermometer assembly was calculated from Dockerty's heat capacity data⁴ for copper.

The measurement was carried out between 30° and 110°K. The thermal coefficient of the copper thermometer became small below 30°K, making accurate measurements of the specific heat difficult. Above 110°K the thermal relaxation time became long so that the present scheme was not suitable. Figure 1 shows the C_p vs T curve. The λ -shaped portion of the curve resembles that of a Curie type transition. The transition temperature is well defined and is $37 \pm 2^\circ\text{K}$. To check how the heat capacity as a function of temperature deviates from the relationship $C_p = \gamma T + \beta T^3$, a conventional C_p/T vs T^2 plot is shown in Fig. 2. Between 40° and 60°K this relationship still holds approximately. From the straight-line portion of the curve in Fig. 2, γ and β are evaluated to be $\gamma = (46 \pm 5) \times 10^{-4} \text{ cal mole}^{-1} \text{ deg}^{-2}$, $\beta = (0.0440 \pm 0.0004) \times 10^{-4} \text{ cal mole}^{-1} \text{ deg}^{-4}$. The corresponding Debye temperature is $472 \pm 14^\circ\text{K}$ which is not unreasonable when compared with $\Theta_{\text{Cr}} = 418^\circ\text{K}$ ⁵ and

² C. T. Wei, C. H. Cheng, and P. A. Beck, *Phys. Rev.* **112**, 696 (1958).

³ T. M. Dauphinee and H. Preston-Thomas, *Rev. Sci. Instr.* **25**, 884 (1954).

⁴ S. M. Dockerty, *Can. J. Research* **15A**, 59 (1937).

⁵ S. A. Friedberg, I. Esterman, and J. E. Goldman, *Phys. Rev.* **85**, 375 (1952).

TABLE I. Chemical analysis of the specimen (weight percent).

Cr	79.00
Fe	20.40
Al	0.01
Si	0.01
Mn	0.01
O ₂	0.137
N ₂	0.263

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¹ C. T. Wei, C. H. Cheng, and P. A. Beck, *Phys. Rev. Letters* **2**, 95 (1959).