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Heat Capacities from 1 to 30 K of Zn, Cd, Sn, Bi, and Y†

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The specific heats of the anisotropic metals zinc, cadmium, tin, bismuth, and yttrium have been measured from 1 to 30 K with an accuracy in most instances of 0.5%. Each of these materials showed a relatively rapid decrease in equivalent Θ_D with increasing temperature, a characteristic of anisotropic solids. The present results are in agreement with other similar quality data where overlaps exist. The results for the yttrium sample are somewhat ambiguous because of the existence of an anomaly which becomes important below 4 K and which is believed to be due to magnetic ordering of the rare-earth and transition-metal impurities in the sample. Low-temperature parameters, tabulated smoothed results, and reduced $\Theta_D(T)$ plots are given for each of these metals.

INTRODUCTION

THE low-temperature thermodynamic properties of anisotropic metals have not been investigated to any great extent in the temperature region 1–30 K. In part, this has been another example of the general scarcity of precision data in this temperature region due to thermomentry problems, but to a greater extent it has been due to a lack of theoretical interest in these complicated systems. In the past several years, White and his collaborators have published the results of thermal-expansion measurements on single crystals of several anisotropic metals (β-Sn, Bi[1]; Mg, Zn, Cd[2]; and In[3]) at liquid-helium temperatures. At the same time, Barron and Munn have looked closely at the formal analysis of these data in terms of single-crystal parameters and anisotropic Grüneisen constants.[4–6]

Our plans are to eventually measure with higher accuracy the thermal expansion of the Zn, Cd, β-Sn, and Bi samples for which we report heat-capacity data in the following. These heat-capacity data, which are needed to interpret the thermal-expansion results, were obtained at the same time as previously published heat-capacity measurements on copper and four III-V compounds,[7] and sapphire.[8] The heat capacity of the yttrium sample was measured to complement inelastic neutron scattering measurements which were concurrently being made at the Ames Laboratory research reactor.[9] Zinc is the only one of these metals for which comparable high-precision heat-capacity data exist over the same temperature range,[10] so the present data are reported as being of interest in themselves, independent of their utility for the interpretation of thermal-expansion or neutron-diffraction data.

EXPERIMENTAL

General details. The present data were taken with a tray calorimeter using the heat-pulse method. An earlier paper[7] describing measurements taken concurrently with the present ones discusses fully the apparatus, experimental details, thermometry, and error analysis. The heat capacity of the addenda never exceeded 25% (usually considerably less) of the total heat capacity of any of these samples, and hence the 1% addenda uncertainty reported in an earlier paper[7] does not introduce any significant error here. The germanium resistance thermometer is calibrated against the helium-vapor-pressure scale,[11] T_{58}, between 1.6 and 4.2 K, against a constant-volume gas thermometer scale between 3.7 and 20 K, and against the NBS platinum-resistance scale above 20 K.[12] These latter two are continuous and are hereafter referred to as T_{618} after one of our standard thermometers. The temperature scale was extended to 0.9 K by using the results of the specific heat of copper.[7] Since T_{58} and T_{618} are discontinuous at 4 K by ∼8 mK,[12] we have analyzed our data in terms of the two scales independently and have made no attempt to smooth through the discontinuity. This problem is discussed in detail in an earlier paper.[7]

Samples. The relevant characteristics of the samples are shown in Table I, with an indication of the nominal purity of each. A qualitative emission-spectrographic analysis which was made on these metals following the specific-heat measurements agreed with that supplied by the manufacturer and showed that no contamination had occurred upon casting. Approximately equivalent amounts of gaseous impurities (60 ppm O_2, 1 ppm H_2, and 4 ppm N_2, all by weight) were found in the Cd, Sn, and Bi samples, and it has been assumed that these play little part in the low-temperature heat capacities.

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TABLE I. Summary of the physical characteristics of the samples used.

	Zn	Cd	Y	Sn	Bi
Length (cm)	10.0	5.3	10.1	10.5	8.7
Mean diameter (cm)	1.0	0.8	1.0	1.0	0.9
Mass (g)	26.603	20.909	34.805	24.838	46.012
Crystal grain size[a]	(single)	large	small	(single)	large
Structure	hcp	hcp	hcp	tetr.	rhomb.
Atomic weight	65.37	112.40	88.905	118.69	208.980
No. of Moles	0.4070	0.1860	0.3915	0.2093	0.2202
Resistivity ratio[b]	···	3000[c]	27.4	>1700[d]	52
Nominal purity (%)	99.999+	99.999+	99.5	99.999+	99.999+
Source	ASARCO	ASARCO	Ames Lab.	···	ASARCO

[a] See text.
[b] $R_{300/4.2}$.
[c] Sample strained while making this measurement, but probably relatively unstrained for specific-heat measurement.
[d] Minimum value.

No gaseous analysis was run on the Zn sample, and much better yttrium now is available than when ours was produced. As will be pointed out below, the 99.5% purity[13] of our sample definitely is not adequate to establish the low-temperature specific heat of yttrium within the precision possible with modern techniques. This is not true of any of our other samples, with the possible exception of Bi.

RESULTS AND DISCUSSION

The low-temperature heat capacity of a metal usually can be represented by an expression of the form

$$C=\sum_n a_n T_n \quad (n=1,\,3,\,5,\,\cdots). \tag{1}$$

Here $a_1=\gamma$ and is associated with the electronic contribution to the specific heat, and $a_3=233.78R/\Theta_0{}^3$, with R being the gas constant and Θ_0 the limiting value of the Debye temperature. Higher-order terms are associated primarily with dispersion in the phonon spectrum, although they could also be due to deviations from T^3 behavior within the Debye theory. Since the terms a_5, a_7, etc., have no easily identifiable physical significance, and, in general, many terms are required to fit experimental data over the range in which we are interested, we have chosen in the following to report only the coefficients for Eq. (1) which pertain to the liquid-helium region and to list smoothed results [obtained from computer fits to Eq. (1)] for both this region and the higher-temperature region.[14] Equivalent values of the Debye temperature Θ_D (defined in terms of the specific heat, the temperature, and the Debye function) are given also to assist in interpolation between the stated temperatures. The estimated accuracy of the tabulated results is 0.5%,[7] which is at least twice the scatter of the data. A major contribution to this estimated uncertainty involves temperature-scale uncertainties.[12] The results of the individual metals are discussed below in some detail. C_p is given without conversion to C_v, both because the difference is small and because it has little meaning for anisotropic materials.[5]

Zinc. A rather complete comparison of our data for zinc and those of Martin[10] is given in an earlier paper.[7] The agreement within the region of overlap, 3–25 K, is within 0.4% everywhere. Our copper data and Martin's show a discrepancy of 1% near 26 K,[7] and it is unfortunate that the present zinc data do not extend to 30 K to give a further check of any possible systematic differences between his results and ours. Martin's zinc data[10] also show a gap between 1.5 and 3 K owing to the different apparatus which he used, and our data should be useful to fill in this gap. Unfortunately, our data on this sample show significantly higher scatter than usual (1.5%) below 2 K and are just this amount greater than his data between 1.0 and 1.5 K. Within this precision, our data interpolate smoothly between his data in the 1.5–3-K region.

Table II gives a comparison of the coefficients obtained for Eq. (1) for our data between 1 and 4 K and those reported by Martin for the 3–8-K region[10] as calculated by Barron and Munn.[4] Martin's value for a_1 came from low-temperature measurements, and a_3 was calculated from the acoustic value for Θ_0. The other coefficients were determined with these restrictions. With additional temperature-scale uncertainties, it is not surprising that these coefficients give an extrapolated value for the heat capacity at 1.5 K which is too large by 3% when compared with Martin's low-temperature data. In general, the present results agree with those given by Martin to within our experimental accuracy. Tables III and IV contain smoothed values for the present zinc data, while Fig. 1 shows these data in reduced form.

Cadmium. This metal has a relatively low value of Θ_0, and hence requires either many terms in Eq. (1) or a limited temperature range in which this equation

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[13] The indicated impurities in the yttrium sample in ppm by weight are approximately: Al, 20; Fe, 120; Cu, 40; Gd, 200; Tb, 50; Dy, 40; Ho, 40; Er, 60; Lu, 30; Ta, 300; O_2, 220; H_2, 21; N_2, 9. 10 ppm by weight or less was found for C, F, Na, Cl, Sc, Ti, Cr, Ni, Zn, Zr, Ag, Ce, Pr, Nd, W, and Pb.

[14] The actual experimental data may be obtained from C. A. Swenson, Physics Division, Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University, Ames, Iowa 50010.

TABLE II. Comparison of the coefficients for Eq. (1) for zinc. The units of C are μJ/K mole.

	a_1	a_3	a_5	a_7	Θ_0^{calc} (K)
Martin[a] (3–8 K)	653	55.7	0.640	0.0385	327
Present work[b] (1–4 K)	643.3±10	56.4±1.8	0.711±0.07	···	325.4±3.5

[a] Reference 10. These values as reported in calorie units have been converted here using the conversion factor given in this reference.
[b] These coefficients reproduce the present data to within 1%.

TABLE III. Smoothed values for the specific heats and the equivalent Debye Θ for the samples in the T_{58} region. Units are mJ/K mole for C and K for Θ.

	Zn		Cd		Sn[a]		Bi	
T_{58}	C_p[b]	Θ[c]	C_p[b]	Θ[c]	C_p[b]	Θ[c]	C_p[b]	Θ[c]
1.0	0.7004	324.1	0.9032	207.8	2.012	195.4	1.117	120.5
1.5	1.161	322.4	1.779	206.2	3.510	195.1	3.784	120.3
2.0	1.760	320.2	3.261	202.0	5.620	194.4	9.284	118.8
2.5	2.559	317.3	5.734	196.3	8.632	192.6	19.15	116.7
3.0	3.625	313.8	9.740	189.8	12.99	189.3	35.64	113.8
3.5	5.043	310.3	16.13	182.4	19.46	184.2	61.87	110.5
3.8	6.102	307.8	21.68	177.5	24.87	180.3	83.84	108.4
4.0	6.910	306.2	26.30	174.1	29.35	177.3	101.7	107.0
4.2	7.809	304.4	31.70	171.0	34.71	174.0	122.7	105.5

[a] These values are calculated from the equation given in Ref. 19.
[b] C_p is the total specific heat as measured.
[c] $\Theta(T)$ is obtained from $C_p - a_1T = D(\Theta/T)$, where $D(\Theta/T)$ is the Debye specific-heat function and a_1 is given in the text for the particular sample.

TABLE IV. Smoothed values for the specific heats and the equivalent Debye Θ for the samples in the T_{618} region. Units are mJ/K mole for C and K for Θ.

	Zn		Cd		Sn		Bi	
T_{618}	C_p[a]	Θ[b]	C_p[b]	Θ[b]	C_p[a]	Θ[b]	C_p[a]	Θ[b,c]
3.8	6.097	308.9	21.50	178.1	···	···	83.21	108.7
4.0	6.908	307.0	26.07	174.8	29.17	177.7	101.00	107.2
4.2	7.809	305.1	31.55	171.3	34.44	174.6	121.7	105.8
5.0	12.52	297.2	64.93	158.1	66.88	161.1	237.3	100.8
6.0	21.96	285.5	140.9	145.4	141.5	147.5	464.0	96.7
7.0	37.56	272.4	265.9	136.7	263.9	138.4	783.8	94.7
8.0	62.45	259.1	446.7	131.2	438.8	132.8	1188	94.0
9.0	100.20	246.8	682.7	127.9	663.4	129.8	1656	94.3
10.0	154.2	236.1	969.1	126.2	929.7	128.5	2164	95.3
11.0	227.4	227.4	1298	125.7	1229	128.5	2695	96.7
12.0	320.7	220.6	1661	125.8	1553	129.2	3236	98.4
13.0	435.7	215.4	2053	126.5	1896	130.5	3777	100.3
14.0	572.4	211.5	2417	127.3	2257	132.0	4314	102.2
15.0	731.3	208.6	2908	128.4	2629	133.6	4846	104.2
16.0	912.7	206.4	3360	129.5	3013	135.4	5372	106.2
17.0	1116	204.8	3822	130.7	3407	137.1	5892	108.0
18.0	1339	203.7	4292	131.9	3810	138.8	6406	109.9
19.0	1578	203.1	4762	133.2	4215	140.6	6912	111.6
20.0	1829	202.9	5230	134.5	4623	142.3	7408	113.3
21.0	2091	203.1	5698	135.7	5031	144.0	7892	114.9
22.0	2368	203.4	6162	137.0	5441	145.6	8364	116.4
23.0	2660	203.7	6620	138.2	5851	147.1	8828	117.9
24.0	2948	204.4	7073	139.4	6262	148.6	9286	119.3
25.0	3246	205.2	7520	140.6	6673	150.0	9741	120.5
26.0	···	···	7960	141.7	7082	151.3	10 190	121.6
27.0	···	···	8394	142.8	7489	152.5	10 640	122.7
28.0	···	···	8823	143.8	7891	153.7	11 060	123.7
29.0	···	···	9243	144.8	8289	154.9	11 480	124.6
30.0	···	···	9656	145.7	8686	155.9	11 890	125.4
31.0	···	···	10 060	146.5	···	···	···	···
32.0	···	···	10 450	147.4	···	···	···	···
33.0	···	···	10 840	148.2	···	···	···	···
34.0	···	···	11 220	148.9	···	···	···	···
35.0	···	···	11 590	149.5	···	···	···	···

[a] See footnote b of Table III.
[b] See footnote c of Table III.
[c] Here the electronic term was negligible, so a_1 was set to zero.

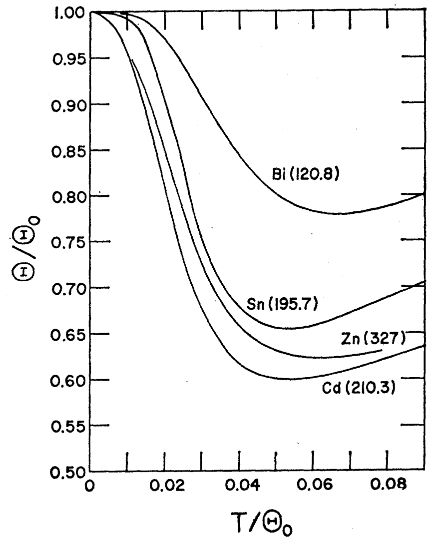

FIG. 1. Reduced plot of the temperature dependence of the equivalent Debye Θ for the present heat-capacity data for Bi, Sn, Zn, and Cd. The value of Θ_0 which was assumed for each curve is shown in parentheses. The data for Sn for $T/\Theta_0 \leq 0.02$ were taken from Wilkes (Ref. 19).

is used. Phillips[15] has compared his low-temperature data on cadmium with those of other workers. The excellent agreement between our data and his is illustrated by the comparison of the coefficients for Eq. (1) in Table V for low temperatures. This table also shows the excellent agreement of both sets of data with the acoustic value for Θ_0.[16] Our data show an unexplained inflection and discontinuity at about 2 K which has a magnitude of approximately 1.2% and appears to be superimposed on a smooth curve. Values of C_p calculated from this curve agree within our precision with other cadmium data[15] regardless of whether we used data in the region of the discontinuity or omitted it. We have assumed it to be experimental in origin and have chosen to ignore it in constructing the smoothed values of C and Θ_D which appear in Tables III and IV. The reduced Θ-versus-T relationship for cadmium is given also in Fig. 1, where it can be compared with that for zinc.

TABLE V. Comparison of the coefficients for Eq. (1) for cadmium. The units for C are μJ/K mole.

	a_1	a_3	a_5	Θ_0 (K)
Phillips[a]	688±6	213±7	5.32±0.5	209.0±2.3
Present work (1–1.8 K)	687±6	209±5	5.94±0.5	210.3±2
Elastic value[b]	···	···	···	213

[a] Reference 15.
[b] Reference 16.

These smoothed values can be compared with data between 1.3 and 20 K given by Smith and Wolcott.[17] In general, these early data are higher than ours by an average of 6%. Craig *et al.*[18] have measured the specific heat of cadmium from 12 to 320 K with results which agree with ours to within 0.8% above 14 K.

β-tin. These data are complicated by the superconducting transition in this metal. We have no means for applying a magnetic field, and excellent superconducting-state data exist for tin, so our data are restricted to the temperature region above $T_c = 3.73$ K. The most recent liquid-helium-temperature measurements of the heat capacity of white tin have been made by Wilkes,[19] who summarizes previous measurements. Our results join smoothly onto his normal-state results (obtained in a magnetic field) and at 4 K lie about 0.4% below the extrapolation of the equation which he uses to fit his data. The normal-state data of Corak and Satterthwaite[20] (1.2–4 K) are about 0.8% greater than ours in the 3.7–4-K region. In view of these rather extensive low-temperature data and the relatively high temperature at which we terminated our data taking, no effort was made to analyze our data in terms of Eq. (1). We have used the normal-state data of Wilkes[19] to complete the tin tabulation in Table III and to obtain the value $\Theta_0 = 195.7$ K used in constructing the tin curves for Fig. 1.

TABLE VI. Comparison of the coefficients for Eq. (1) for various low-temperature heat-capacity measurements on bismuth. The units of C are μJ/K mole.

	$a_1 = \gamma$	a_3	a_5	Θ_0 (K)
Phillips[a] (0.4–2 K)	21	1114	+16.7	120.4
Taylor[b]	7	1108	−12	120.6
Present (1.1–2 K)	51	1037	+27.4	123.4

[a] Reference 23. The above values of a_3 and a_5 were deduced from the expression given in this reference for the lattice contribution, $1944(T/\Theta)^3$ J/K mole, with $\Theta = 120.4 - 0.6T^2$.
[b] Reference 24.

The high-temperature (4–30 K) data for tin are summarized in Table IV in smoothed form. Apparently there have been no measurements on white tin in this temperature region since the early work of Keesom and van den Ende[21] and of Lange.[22] These earlier data lie (3±3)% above the present results.

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Bismuth. The Debye temperature of bismuth is sufficiently small (121 K) that our lowest temperature (1 K) is relatively high, and it is difficult to analyze our data in terms of physically meaningful coefficients in Eq. (1). Bismuth as a semimetal has a very small electronic contribution to its low-temperature heat capacity. This electronic contribution cannot be uniquely determined because of the relatively large lattice contribution and the possible effects of impurities. Low-temperature heat-capacity data have been given recently by Phillips[23] (0.1–2 K) and by Taylor[24] (0.5–1.1 K). The values of the a_n [Eq. (1)] and Θ_0 which relate to these experiments are listed in Table VI together with those given by an attempt to fit our lower-temperature (1.1–2 K) data using the first three terms in Eq. (1). When actual data rather than computer fits are compared, our data are about 1% larger than those of Taylor at 1 K and 3% smaller than those of Phillips from ~1–2 K. The difference between our data and Phillips's decreases slightly from 1.5 to 2 K and possibly would disappear somewhere between 3 and 4 K if the extrapolation of his data is valid.

The reasons for these discrepancies are not clear. The almost identical values of Θ_0 for the two low-temperature experiments (our data obviously cannot be extrapolated to low temperature) could be fortuitous in view of the very different values of γ (or a_1), or the differences in γ could be due to an impurity effect which does not influence Θ_0. Taylor[24] ascribes his anomalous negative value for a_5 to a thermometry problem, but indeed it is this negative contribution which causes his data to agree with Phillips's at low temperature and with the present data at 1 K. Phillips[25] has more recent data on another sample which agree with his older data in the range above 0.4 K. Since all of these measurements could be expected to produce 1% or better data near 1 K (and common measurements bear this out), we must tentatively ascribe the differences to unknown sample problems and conclude that the low-temperature lattice and electronic properties of bismuth are not known to the accuracy which is possible with modern calorimetric techniques.

Our results for bismuth in the temperature region below 4 K are summarized in Table III, and in reduced form in Fig. 1. The values of Θ were calculated assuming Taylor's value for γ because of the agreement in magnitude between our data and his at 1 K. This may not be a valid procedure for our sample. The higher-temperature data are summarized in Table IV. Our data are about (0.8±0.8)% larger than those given by DeSorbo[26] from 20 to 32 K, and by Franzosini and Clusius[27] above 16 K.

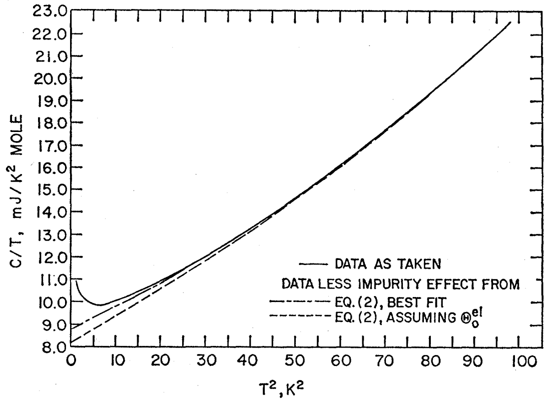

FIG. 2. Plot of the low-temperature behavior of the yttrium data. The solid line gives the temperature dependence of the data as taken. The other curves give estimates of the heat capacity of pure yttrium metal which depend on whether the best fit to Eq. (2) from 4 to 10 K is assumed or whether the fit of the data to Eq. (2) is forced to give the elastic-constant value of Θ_0.

Yttrium. The heat capacity of our yttrium sample as measured showed an anomalous behavior at low temperature which appeared as a positive curvature on a C/T-versus-T^2 plot. This is shown as the solid line in Fig. 2. This behavior undoubtedly is due to magnetic ordering of the rather large magnetic impurities (mostly rare earths and iron) in our sample.[13] Similar problems were observed in recent work on scandium metal,[28] and these may be responsible for the qualitative differences in earlier measurements of the specific heat of yttrium metal.[29,30] This anomaly, the relatively large value of γ (or a_1), and the non-Debye-like nature of the lattice contribution make it it very difficult to determine unambiguously the various contributions to our measured heat capacity for yttrium. The elastic constants of yttrium have been measured at low temperature[31] and can be used to predict an elastic-constant value for Θ_0.[32] Our original analysis contained a lattice contribution which differed considerably from that predicted by this elastic-constant work, but the difference possibly could be ascribed to these ambiguities in the analysis of the data.

Equation (1) can be modified slightly to include a heat-capacity contribution due to the initial stages of magnetic ordering:

$$C=a_{-2}T^{-2}+\sum_n a_nT^n \quad (n=1,3,5,7,\cdots). \qquad (2)$$

The temperature region in which this expression is valid can be tested graphically by a plot of CT^2 versus T^3, and our data appear to follow this relationship to within experimental scatter above about 2.3 K. This

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TABLE VII. Comparison of the coefficients for Eq. (2) for yttrium. The "computer-fit" coefficients reproduce the present data to within the stated rms deviation. The units of C are mJ/K mole.

	Graphical[a] (2.3–4.2 K)	Computer fits[a] (4–10 K) First	Computer fits[a] (4–10 K) Second	Montgomery and Pells[b]	Morin and Maita[c]
a_{-2}	7.4 ±0.5	7.4±1	28.5±3	...	...
a_1	8.78±0.02	8.748	8.180	10.1	10
a_3	...	0.0925	0.1159[d]	0.072	0.150
$10^4 \times a_5$	...	4.917	1.471	...	...
$10^6 \times a_6$	...	...	1.686	...	...
rms deviation	...	0.15%	0.25%	...	...
Θ_0	...	276±3 K	256[d]	300±10	235

[a] See text. [b] Reference 29. [c] Reference 30. [d] Reference 32. Elastic-constant value from data of Ref. 31.

graphical method was used with the 2.3–4-K data (T_{58} scale) to obtain values for a a_{-2}, γ $(=a_1)$, and a_3 by successive approximations. The resulting coefficients are given in column 2 of Table VII. This value for a_{-2} then was assumed and the higher-temperature data were used to obtain other independent values for γ, a_3, a_5, etc., using least-squares computer fitting procedures. The values for γ and a_3 which resulted from these analyses appeared to be independent of the temperature range (4–6 K, 4–8 K, 4–10 K, etc.) and the coefficients resulting from a 4–10-K fit are given in column 3 of Table VII. The agreement between the γ values obtained using only the 2.3–4-K data or only the 4–10-K data is excellent, and gives some confidence in the uniqueness of the coefficients. The exact value of the a_{-2} coefficient has little effect on the higher-temperature data analysis. A computer fit to Eq. (2) from 2.5 to 10 K essentially gave the same coefficients as appear in column 3 of Table VII. As a result of these analyses, it would appear that the most likely parameters which would describe our sample in the absence of magnetic impurities would be $\gamma = 8.75 \pm 0.05$ mJ/K^2 mole and $\Theta_0 = 276 \pm 3$ K.

Unfortunately, the low-temperature elastic-constant data[31] can be used to calculate $\Theta_0^{el} = 256$ K with an uncertainty of approximately 1%.[32] The coefficients for the "second" analysis listed in column 4 of Table VII were obtained by forcing a_3 to have the value associated with Θ_0^{el}. A reasonable fit is obtained which shows a much larger magnetic term, a smaller γ (by 6.7%), and the need for a T^7 term in Eq. (2). The deviations from this forced fit are not quite random, although they are well within the experimental uncertainties. The two values of γ obtained from the present measurements also are compared in Table VII

TABLE VIII. Smoothed values for the specific heats and the equivalent Debye Θ for yttrium for both methods of analysis. See the text for further explanation. The results below 4 K are extrapolations omitting the anomalous specific heat. The units are mJ/K mole for C and K for Θ.

T	First analysis[a] C_p[c]	First analysis[a] Θ[d]	Second analysis[b] C_p[c]	Second analysis[b] Θ[d]
1.0	8.841	275.5	8.295	255.9
2.0	18.25	274.1	17.29	255.5
3.0	28.86	271.7	27.71	254.9
4.0	41.42	268.6	40.31	254.0
5.0	56.84	264.7	55.97	252.6
6.0	76.29	260.3	75.72	250.7
7.0	101.2	255.5	100.9	248.2
8.0	133.5	250.3	133.1	245.0
9.0	175.2	244.9	174.9	241.0
10.0	229.2	239.4	229.3	236.2
11.0	297.6	234.3	297.6	231.9
12.0	383.4	229.4	383.4	227.6
13.0	489.0	224.9	489.0	223.5
14.0	616.4	221.0	616.4	219.9
15.0	766.9	217.7	766.9	216.7
16.0	941.2	214.8	941.2	214.0
17.0	1139	212.5	1139	211.8
18.0	1360	210.7	1360	210.1
19.0	1602	209.2	1602	208.7
20.0	1864	208.1	1864	207.7
21.0	2146	207.3	2146	206.9
22.0	2445	206.7	2445	206.2
23.0	2761	206.2	2761	205.8
24.0	3091	205.8	3091	205.4
25.0	3433	205.6	3433	205.2
26.0	3784	205.5	3784	205.1

[a] See text. $\Theta_0 = 276$ K.
[b] See text. $\Theta_0 = 256$ K.
[c] The specific heats do not include the anomalous contribution but do include the electronic specific heats.
[d] See footnote c of Table III.

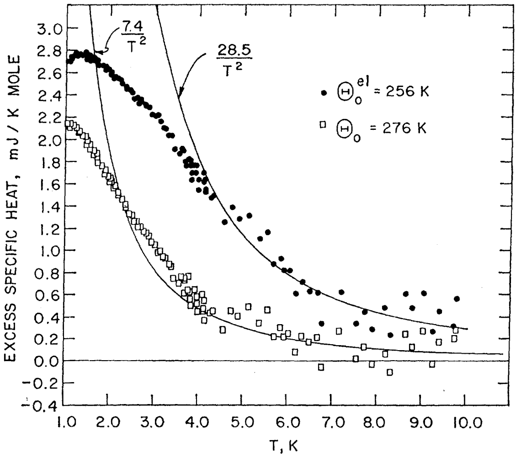

FIG. 3. Plot of the excess low-temperature heat capacity for the yttrium sample as determined by the two analyses. The two solid lines give the "high-temperature" estimates of the impurity contribution which were used in the data analysis. See the text for details.

with those obtained in earlier measurements.[29,30] The present sample is expected to be better (of higher purity) than those used for these measurements.

Figure 2 shows both the original data (solid line) and the specific heats calculated from each of the computer fits of Table VII. The increased "magnetic" contribution due to the smaller assumed value of Θ_0 (that is, steeper slope) can be estimated qualitatively from these plots. The "anomaly" is shown in detail in Fig. 3, where the difference between the actual data and each of the computer fits is plotted as well as the assumed $a_{-2}T^{-2}$ term. The discontinuity in our temperature scale at 4.2 K should appear as a 0.2% (or 0.08 mJ/K mole) increase in specific heat going from the T_{58} to the T_{618} region. This is not apparent due to the scatter of the data. The entropy content in this anomaly is of the same order of magnitude as would be expected for the magnetic ordering of the impurities.

Table VIII gives smooth C_p and Θ values for "pure" yttrium as obtained for both our analyses. The high-temperature data can be compared with the results of Jennings *et al.*[33] above 15 K, and our data lie roughly 2% lower than theirs in this region. The results of our two analyses as well as a corresponding curve for scandium metal[28] are given in the reduced Θ plot of Fig. 4.

We cannot make a firm statement as to the most likely values of γ and Θ_0 for yttrium. There is no reason to mistrust the elastic-constant data, and a discrepancy of the indicated magnitude between values of Θ_0 derived from calorimetric and elastic-constant measurements is quite unexpected. Our original analysis is internally self-consistent, with results that are independent of the temperature range used, while the fit to the data must be forced in a sense to obtain Θ_0^{el}. A comparison of Figs. 1 and 4 shows that scandium and yttrium behave quite differently from the other two hexagonal metals, zinc and cadmium, so the shape of these reduced curves cannot offer any guidance. This problem will be resolved only when measurements of comparable quality are made on much higher purity yttrium to remove the complications caused by the magnetic ordering.

CONCLUSIONS

The major objective of this research was to obtain good-quality heat-capacity data for these anisotropic solids in the temperature range 4–30 K, and we believe that the data summarized in Tables IV and VIII have an accuracy of 0.5%. The basis for this conclusion involves our good agreement with comparable measurements on zinc[10] and copper[7] as discussed in an earlier paper.[7] The data obtained below 4 K have indicated that for bismuth and yttrium, at least, and possibly for cadmium, impurity effects can be important. The comparisons which we have made between the various data by way of reduced Θ plots (Figs. 1 and 4) are in a sense meaningless except to point out the very rapid deviations from Debye-like behavior for Sn, Zn, and Cd as the temperature is increased and the more moderate behavior for Bi, Y, and Sc.

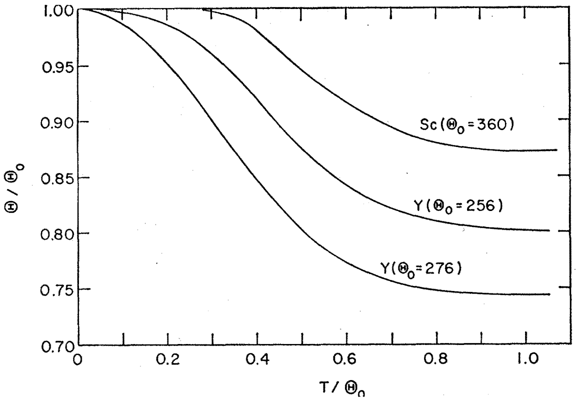

FIG. 4. Comparison of the reduced plots for the temperature dependence of the equivalent Debye Θ for the two analyses of the present data for yttrium metal and also for scandium metal (see Ref. 28).

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[33] L. D. Jennings, R. E. Miller, and F. H. Spedding, J. Chem. Phys. 33, 1849 (1960).