Atomic Heats of Normal and Superconducting Tin between 1.2° and 4.5°K

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(Received January 23, 1956)

Atomic heat measurements on tin in the normal and superconducting states revealed that the electronic contribution to the atomic heat in the superconducting state, C_{es}, could be represented below about $0.7T_c$ by the same exponential expression found applicable to vanadium: $C_{es}/\gamma T_c = ae^{-bT_c/T}$, with $a=9.17$ and $b=1.50$. The deduced curve of critical field *vs* temperature was in good agreement with H_c-T curves reported from magnetic measurements. The critical field extrapolated to the absolute zero, H_0, was 303.4 oersteds and the transition temperature was 3.722°K. Below 2.5°K the normal atomic heat could be represented by the Sommerfeld-Debye expression with $\gamma=1.75\times10^{-3}$ joule mole^{-1} deg^{-2} and $\Theta=195.0$°K; above 2.5°K deviation from this expression indicated that Θ decreased with increasing temperature.

I. INTRODUCTION

IN the preceding paper it was shown that an exponential function in $1/T$ [Eq. (4) of that paper] refresented the electronic contribution, C_{es}, to the atomic heat of vanadium in the superconducting state below about $0.7T_c$. In view of this result it was of interest to find whether an exponential temperature dependence of C_{es} was applicable to other superconductors and, if so, to what extent they obeyed a law of corresponding states. The elements for which corroborative evidence exists, V, Ta, and Nb, are all "hard" superconductors and in many other respects are quite similar since they fall in the same group of the periodic table. It was, therefore, desirable to extend this study to one of the "soft" superconductors.

Tin was considered the best choice among the soft superconductors since it has a high $C_{es}/C_{\text{lattice}}$ ratio, 1.23 at the transition temperature, and a fairly high transition temperature, 3.73°K; thus it was possible to study a wide range of reduced temperature with liquid helium techniques. Furthermore, tin is probably the most widely studied superconductor and exhibits almost ideal superconducting behavior. Previously published data on tin,[1–3] while showing deviation from a T^3 dependence of C_{es}, are not accurate enough to shed much light on the applicability of an exponential dependence.

II. EXPERIMENTAL

The specimen used in this investigation, a cylinder one inch in diameter and two inches long, was obtained from the Vulcan Detinning Company of Sewaren, New Jersey. By the analysis of the supplier it was 99.999+% tin. It was considered unnecessary to anneal the sample at an elevated temperature since tin is known to self-anneal at room temperature. The residual resistivity at 4.2°K of unannealed turnings from the same batch of tin was approximately 0.0002 of their room temperature resistivity.

The calorimetric apparatus and techniques were identical with those used in work previously published.[4] A permanent magnet was used to maintain a uniform field of 800 oersteds over the volume of the sample for the normal state measurements. For the superconducting state measurements, the magnetic field in the vicinity of the sample was held below 0.05 oersted by counteracting the earth's magnetic field with a pair of Helmholtz coils.

The individual determinations were spaced at approximately 0.1°K and temperature increments of about 0.03°K were used over most of the temperature range. From 1.2 to 1.4°K the measurements were spaced more closely, about every 0.03°K, for both the normal and superconducting state since the uncertainty of the measurements was somewhat higher in this region. In order to observe the nature and breadth of the superconducting transition, both the spacing and the temperature increments were reduced to 0.01°K in the vicinity of T_c for the superconducting state measurements.

III. RESULTS AND DISCUSSION

The experimental atomic heat data for tin in both the normal and superconducting states are given in Table I. They are reported on both the 1948 helium vapor pressure scale[5] and the corrected scale, T_w, described in the previous paper, because although the former is well defined and generally accepted, the latter, it is believed, approximates more closely the thermodynamic scale. The experimental data are shown graphically in Fig. 1, a C/T *vs* T^2 plot showing both normal and superconducting state data together with similar data of Keesom and Van Laer. The data of Fig. 1 were calculated on the basis of the T_w scale as were subsequent derived results.

The probable error of an individual determination of the atomic heat has been estimated in connection with earlier work[4] using the same apparatus and techniques. The probable error due to random uncertainties was

[1] W. H. Keesom and J. A. Kok, Commun. Phys. Lab. Univ. Leiden, No. 221e (1932).
[2] W. H. Keesom and P. H. van Laer, Physica **4**, 487 (1937).
[3] K. G. Ramanathan and T. M. Srinivasan, Phil. Mag. **46**, 338 (1955).
[4] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. **98**, 1699 (1955).
[5] H. van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

TABLE I. Atomic heat of tin in magnetic fields of 0 and 800 oersteds.

T_{48} (°K)	C_{48} (millijoule mole^{-1} deg^{-1})	T_w (°K)	C_w (millijoule mole^{-1} deg^{-1})
	Magnetic field—800 oersteds		
1.130	2.33	1.130	2.33
1.164	2.46	1.164	2.46
1.200	2.58	1.200	2.59
1.235	2.65	1.235	2.66
1.270	2.74	1.270	2.75
1.306	2.85	1.306	2.86
1.404	3.10	1.403	3.11
1.497	3.47	1.495	3.49
1.476	3.42	1.474	3.44
1.590	3.44	1.587	3.46
1.686	4.23	1.682	4.26
1.763	4.50	1.758	4.55
1.857	4.94	1.851	4.99
1.965	5.38	1.958	5.46
2.073	5.86	2.065	5.96
1.980	5.37	1.973	5.45
2.069	5.82	2.061	5.92
2.166	6.28	2.156	6.41
2.266	7.12	2.259	6.90
2.373	7.78	2.369	7.59
2.476	8.36	2.474	8.23
2.570	9.16	2.569	9.04
2.681	10.01	2.680	9.94
2.767	10.54	2.766	10.51
2.886	11.67	2.885	11.69
2.985	12.61	2.983	12.69
3.082	13.70	3.080	13.82
3.184	14.76	3.180	14.92
3.277	16.1	3.272	16.3
3.388	17.7	3.382	17.9
3.473	18.9	3.466	19.0
3.584	20.9	3.577	21.0
3.689	22.7	3.682	22.6
3.787	25.0	3.781	24.5
3.884	27.4	3.880	26.8
3.985	29.6	3.982	29.0
	Magnetic field—0 oersted		
1.122	0.810	1.122	0.811
1.148	0.903	1.148	0.904
1.177	0.939	1.177	0.940
1.208	1.052	1.208	1.054
	Magnetic field—0 oersted—*Continued*		
1.229	1.128	1.229	1.130
1.263	1.211	1.263	1.213
1.289	1.351	1.289	1.354
1.313	1.395	1.312	1.399
1.368	1.64	1.367	1.64
1.401	1.77	1.400	1.78
1.519	2.38	1.517	2.40
1.600	2.80	1.597	2.82
1.689	3.37	1.685	3.40
1.787	4.04	1.782	4.08
1.882	4.74	1.876	4.80
1.969	5.38	1.962	5.45
1.992	5.46	1.985	5.54
2.081	6.25	2.072	6.36
2.277	8.30	2.270	8.05
2.375	9.26	2.371	9.04
2.472	10.44	2.470	10.25
2.573	11.69	2.572	11.54
2.691	13.07	2.690	12.99
2.764	14.23	2.763	14.19
2.878	15.8	2.877	15.8
2.982	17.4	2.980	17.5
3.084	19.2	3.082	19.4
3.180	20.8	3.176	21.0
3.273	22.8	3.268	23.0
3.375	25.1	3.369	25.4
3.469	27.2	3.462	27.5
3.575	29.9	3.568	30.0
3.686	33.0	3.679	32.9
3.706	33.3	3.699	33.1
3.718	33.4	3.711	33.1
3.730	29.9	3.723	29.6
3.741	24.6	3.734	24.3
3.754	23.9	3.748	23.6
3.766	24.1	3.760	23.8
3.779	24.6	3.773	24.2
3.805	25.2	3.799	24.8
4.005	29.7	4.003	29.1
4.113	32.4	4.112	32.1
4.191	34.3	4.191	34.3
4.343	38.2	4.341	39.1

estimated at 0.8%. Additional error amounting to possibly 0.5% could have arisen from uncertainties in the corrected temperature scale which would not be random. The probable errors calculated from scatter of experimental data about smooth curves for the normal and superconducting state were 0.6% and 0.9%, respectively. In earlier work,[4] systematic errors of 2% or less were suspected below 1.4°K due to residual exchange gas adsorbed on the sample at the lowest temperatures and gradually driven off as the temperature was increased. Particular care was taken during these experiments to pump off the exchange gas before starting measurements and the absence of time dependent drift rates after heating, observed in the earlier experiments, indicated that errors from this source were not significant in the present work.

In a magnetic field of 800 oersteds, sufficient to completely quench superconductivity, the data could be represented by the Sommerfeld-Debye expression,

$$C_n=\gamma T+(12/5)\pi^4 R(T/\Theta)^3, \qquad (1)$$

only for temperatures below about 2.5°K. From data in this range of temperature the following values for the constants were obtained by the method of least squares:

$$\gamma=(1.75\pm0.01)\times10^{-3}\text{ joule mole}^{-1}\text{ deg}^{-2},$$
$$\Theta=195.0\pm0.6\text{°K}$$

From the curvature in the C/T *vs* T^2 plot for the normal state data above 2.5°K in Fig. 1, it is evident that Eq. (1) is no longer adequate. It is assumed that this deviation is due to the lattice and can be represented by a temperature variation of Θ as shown in Fig. 2. The following qualitative arguments can be given for making this assumption: (1) It is unlikely that any deviation from a linear temperature dependence of the electronic specific heat should occur so far below the degeneracy temperature ($\sim2\times10^4$ °K for tin); and (2) although, for a cubic metal, one would not expect a temperature variation of Θ at so low a temperature relative to Θ [e.g., no deviation from Eq. (1) was

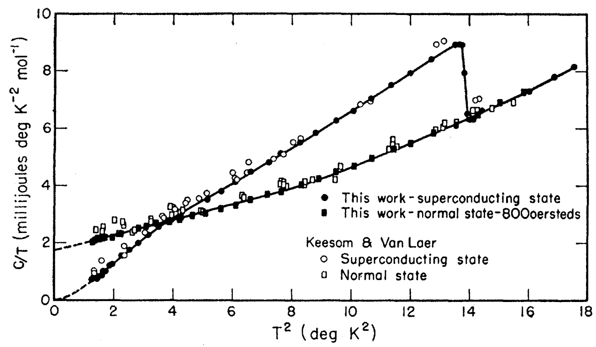

FIG. 1. Atomic heat of tin in the normal and superconducting state.

found for gold[4] below 5°K even though Θ for gold, 169°K, is lower than that for tin], for an anisotropic metal like tin the measured Θ is undoubtedly an average of two or more Θ's, characteristic of the lattice constants in different directions in the crystal, one of which may be quite low.

In accord with the above assumption, C_{es} was derived by subtracting from the superconducting state measurements, the lattice contribution, C_L, deduced from the normal state data, $C_L = C_n - \gamma T$. As in the case of vanadium, C_{es} for tin could be well represented, particularly below about $0.7T_c$ by an exponential expression of the type

$$C_{es}/\gamma T_c = ae^{-bT_c/T}. \tag{2}$$

Furthermore within the experimental error the same expression with constants, $a = 9.17$ and $b = 1.50$, represented C_{es} for both tin and vanadium. In Fig. 3 the values of C_{es} are shown on a semilogarithmic scale plotted against the reciprocal of the reduced temperature, $1/t = T_c/T$. The straight line represents Eq. (2) with the above constants. Values of C_{es} derived from the work of Keesom and Van Laer[3] are also plotted, showing that the precision of their data was not adequate to distinguish between a cubic and an exponential temperature dependence.

It should be pointed out that the total atomic heat in the superconducting state, C_s, approximated, quite

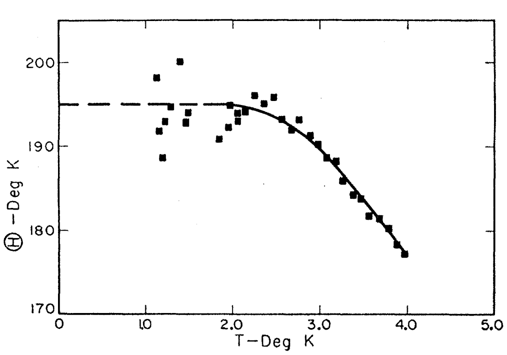

FIG. 2. Variation of the Debye Θ of tin with temperature.

closely, a T^3 dependence. It is unfortunate that in the case of tin, the superconductor on which earlier theories of the specific heat were based, deviations from a cubic temperature dependence in the electronic contribution were compensated by deviations in the opposite direction in the lattice contribution. Thus, if it was assumed that a T^3 law described the lattice, it was logical to conclude that the temperature dependence of C_{es} was also cubic.

In Fig. 4 the values of C_{es} for vanadium and tin are shown together to show their striking similarity. The vertical scale is expanded relative to Fig. 3 by multiplying by $\exp(1.5T_c/T)$ as indicated, with the result that Eq. (2) appears as a horizontal straight line. It is of interest to note that, on this reduced scale, the results for tin and vanadium are essentially identical even in the temperature region near T_c where appreciable deviation from Eq. (2) occurs.

The entropies of both the normal and superconducting states were derived from the atomic heat data for

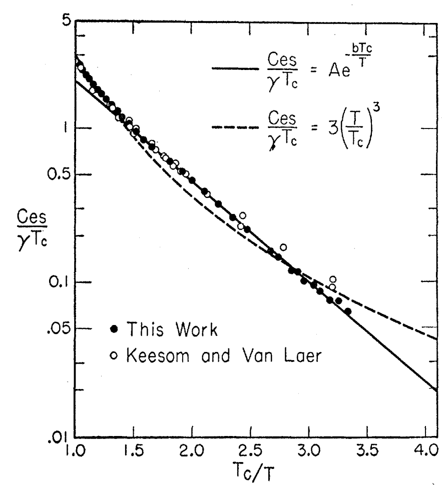

FIG. 3. Electronic contribution to the atomic heat of tin.

the individual states by graphical integration of smooth C/T *vs* T plots. The difference in entropy between the normal and superconducting state $(S_n - S_s)$, extrapolated to the absolute zero, vanished within the limit of experimental accuracy (i.e., ±0.2%), consistent with the third law of thermodynamics.

The critical field-temperature relationship was derived by graphical integration of the following expression:

$$H_c^2 = \frac{8\pi}{V}\int_T^{T_c}(S_n - S_s)dT, \tag{3}$$

where V is the atomic volume. The resulting $H_c - T$ curve is compared in Fig. 5 with those obtained from magnetic measurements by Lock, Pippard, and Shoen-

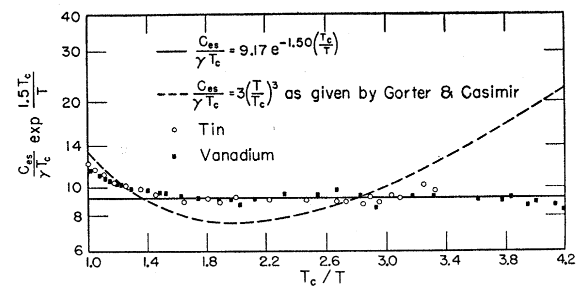

FIG. 4. Comparison of C_{es} for tin and vanadium.

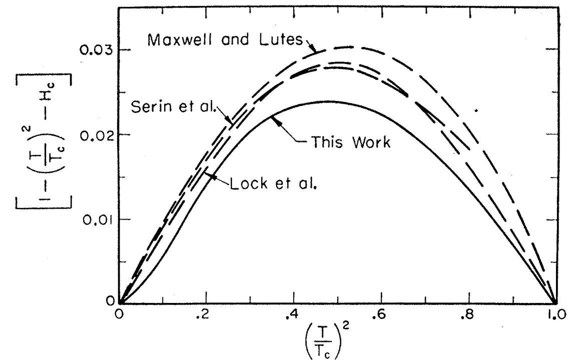

FIG. 5. Deviation of the critical field of tin from the parabolic law, $H_c = H_0[1-(T/T_c)^2]$.

berg,[6] Serin, Reynolds, and Lohman,[7] and Maxwell and Lutes.[8] The curves of Fig. 5 show deviations from the parabolic expression, $H_c = H_0[1-(T/T_c)^2]$, where H_0 is the critical field at 0°K and T_c is the transition temperature. The curves for the magnetic data were taken from polynomial expressions of the above authors giving H_c in powers of T. Most of the magnetic data were taken on samples enriched in one of the isotopes of tin, but the polynomials are applicable to normally occurring tin by adjusting H_0 and T_c. The differences among the curves ($\sim$1% or less), is largely due to differences in H_0 and T_c of the various measurements. These are compared in Table II.

In view of the similarity in C_{es} for tin and vanadium, two superconductors with otherwise quite different properties, it is of interest to review the calorimetric and magnetic data for other superconductors, first, to see what further evidence there is for a predominantly exponential temperature dependence of C_{es} and, second, to see to what extent this similarity may be extended to a law of corresponding states for all superconductors.

The available calorimetric data for superconductors for which the ratio C_{es}/C_L is large enough to allow reasonably accurate determinations of C_{es} have been reviewed in connection with the vanadium work in the preceding paper. For tantalum C_{es} could be represented by the same exponential expression applicable to V and Sn. Preliminary results on Al suggest a similar exponential temperature dependence for this metal, also. C_{es} for Nb could be represented over the same range of reduced temperature by an exponential with slightly different constants.

For a number of the soft superconductors, the ratio C_{es}/C_L is so small that accurate determinations of C_{es} from calorimetric data are impossible without considerably improved calorimetric techniques. However, for those for which precise magnetic measurements exist, a comparison can be made between the magnetically determined H_c-T curves and those for Sn and V derived from calorimetric measurements. For such a comparison, it is convenient to plot deviations of the reduced critical field from the parabolic law against the reduced temperature squared as was done for tin in Fig. 5. The magnetic data of Maxwell and Lutes[8] for In, Tl, and Hg are compared with corresponding derived results for Sn and V in Fig. 6.

The similarity between the H_c-T relationships for In and Tl and those for V and Sn is evidence that they must have quite similar electronic specific heats in the superconducting state. On the other hand, mercury exhibits quite different behavior, showing no deviation from the parabolic law within the experimental accuracy. This result is in agreement with the earlier work of Reynolds, Serin, and Nesbitt.[9] Thus, by the thermo-

TABLE II. Values of extrapolated critical field H_0 and transition temperature T_c.

	H_0 (oersteds)	T_c (deg K)
This work	303.4	3.722
Serin *et al.*	304	3.752
Lock *et al.*	304.5[a]	3.726
Maxwell and Lutes	306.9[a]	3.742

[a] Adjusted to normal isotopic mass from measurements on enriched samples.

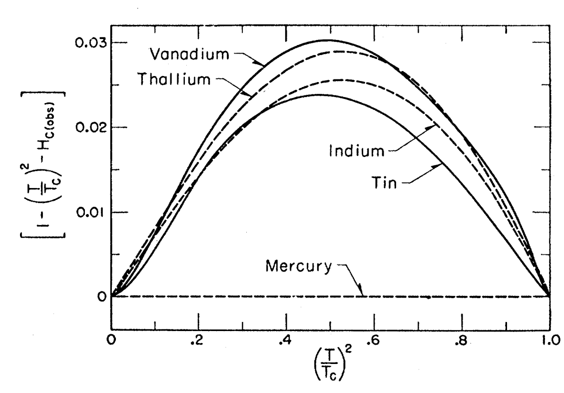

FIG. 6. Comparison of the deviations from the parabolic law for Sn, V, In, Tl, and Hg.

[6] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).
[7] Serin, Reynolds, and Lohman, Phys. Rev. **86**, 162 (1952).
[8] E. Maxwell, Phys. Rev. **86**, 235 (1952); E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).
[9] Reynolds, Serin, and Nesbitt, Phys. Rev. **84**, 691 (1951).

dynamic treatment of Gorter and Casimir[10] C_{es} must follow a very nearly cubic temperature dependence over the range of temperature covered by the magnetic measurements. It should be pointed out, however, that at low reduced temperatures the critical field is a very insensitive measure of C_{es}. Assuming that the lattice contribution is the same in the normal and superconducting state,

$$C_{es}=\gamma T+\frac{VT}{4\pi}\left[H_c\frac{d^2H_c}{dT^2}+\left(\frac{dH_c}{dT}\right)^2\right]. \tag{4}$$

At low reduced temperatures, C_{es} decreases much more rapidly than γT and therefore becomes a small difference between two larger quantities. Furthermore, at low reduced temperature, H_c varies slowly with temperature so that the temperature derivatives are not easily obtained from magnetic measurements. It is, therefore, possible that below some temperature C_{es} for mercury may also assume an exponential temperature dependence.

IV. CONCLUSIONS

The experimental evidence of this paper strongly supports the suggestion of the previous paper that a predominantly exponential temperature dependence of C_{es} is a characteristic property of superconductors. Furthermore, there is evidence that a number of superconductors obey a law of corresponding states. Mercury, alone, of the superconductors for which there are published data of sufficient accuracy to make a reliable comparison, deviates appreciably from the reduced relationships found applicable to vanadium and tin.

Recent measurements[11] have shown that, in mercury, not only is the Debye Θ very low but it is also varying rapidly with temperature in the superconducting temperature region, rising from a minimum of 50°K at 3°K to a low-temperature limiting value of 75°K at 1°K. In view of recent evidence suggesting that superconductivity arises from electron-lattice interactions, it may be that the anomalous superconducting behavior of mercury is related to the fact that Θ is low and/or varying rapidly with temperature. If so, one might expect to find similar behavior in lead which also has a low Debye Θ in its superconducting temperature range. However the variation of Θ with temperature is not as great as in mercury. The minimum in Θ, approximately 87°K, occurs at 12°K and the low-temperature limiting value of 96°K is reached at about 4°K. (Existing H_c-T data for lead are not sufficiently accurate to make a significant comparison with other superconductors.) Unfortunately, for both mercury and lead, C_{es} would be expected to make a very small contribution to the total atomic heat ($<3\%$ for mercury and $<7\%$ for lead) so that an accurate determination of C_{es} from calorimetric measurements would be extremely difficult.

ACKNOWLEDGMENTS

The authors are happy to acknowledge the continued interest and helpful suggestions of M. P. Garfunkel and B. B. Goodman.

[10] C. J. Gorter and H. B. G. Casimir, Physica 1, 306 (1934).

[11] P. L. Smith, Conference de Physique des Basses Temperatures, Paris, 1950, proceedings, pp. 281–283.