PHYSICAL REVIEW VOLUME 102, NUMBER 3 MAY 1, 1956

Atomic Heats of Normal and Superconducting Vanadium

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(Received January 23, 1956)

The atomic heats of vanadium, in the normal and superconducting states, have been determined from just above the transition temperature, $T_c=5.03$°K, down to 1.1°K. After corrections to the 1948 temperature scale had been made, the normal state atomic heat could be represented by $C_n=\gamma T+(12/5)\pi^4R(T/\Theta)^3$, with $\gamma=(9.26\pm0.03)\times10^{-3}$ joule mole^{-1} deg^{-2} and $\Theta=338\pm5$°K. The entropy difference, S_n-S_s, between the normal and superconducting states, extrapolated to 0°K, was found to vanish, in accordance with the third law of thermodynamics. The critical field values deduced from S_n-S_s gave $H_0=1310$ oersteds; at higher temperatures they were in agreement with initial penetration fields previously reported.

The most interesting result of this work was that below about $0.7T_c$ the electronic contribution to the atomic heat of the metal in the superconducting state could be represented by an exponential expression of the form $C_{es}/\gamma T_c=ae^{-bT_c/T}$ with $a=9.17$ and $b=1.50$; such an exponential relation is consistent with a single-electron model of a superconductor involving a gap of the order of kT_c per electron in the spectrum of available energy levels.

INTRODUCTION

FOR a metal in the superconducting state it is customary to separate the total atomic heat, C_s, into a lattice contribution, which is assumed to take the same values as in the normal state, and an electronic contribution, C_{es}. Until recently the available experimental evidence suggested a T^3 dependence for C_{es}. This was thermodynamically consistent with the parabolic temperature dependence found for the critical magnetic field, H_c. These features were incorporated into the Gorter-Casimir[1] two-fluid model for superconductors.

More recently, departures from this T^3 dependence of C_{es} have been observed in niobium,[2] tantalum,[3] and vanadium,[3] and corresponding departures from the parabolic H_c-T relationship have been noted.[4] Furthermore, measurements on the electronic thermal conductivity of superconducting tin[5] suggested that at very low reduced temperatures C_{es} might decrease much more rapidly than as T^3. Since detailed information on the temperature dependence of C_{es} may give a clue to the correct description of the superconducting state, accurate measurements of C_{es} were considered to be desirable.

Accurate determinations of C_{es} can be made from calorimetric measurements only on those superconductors for which C_{es} is a large fraction of the total atomic heat. From the approximate values of $(C_{es}/C_{\text{lattice}})_{T=T_c}$ shown in Table I, it can be seen which superconductors are best suited for such a study.

Vanadium was chosen for the present work because of its large value for $(C_{es}/C_{\text{lattice}})_{T=T_c}$; furthermore, while still using conventional liquid helium techniques, C_{es} could be measured at lower values of the reduced temperature, T/T_c, than previously investigated. Vanadium was also of interest in order to determine the H_c-T relationship for a typical "hard" superconductor, and in particular to compare the results with the measurements of its initial penetration field made by Wexler and Corak.[6] A brief preliminary account of the present work has already appeared.[7]

EXPERIMENTAL

The calorimetric apparatus and techniques have been fully described in a recent paper,[8] here designated as I. The present measurements differed from those described in I only in that a magnetic field was necessary to maintain the specimen in the normal state. An electromagnet capable of producing a field of 6200 oersteds uniform to 3% over the volume of the sample, was used for this purpose.

The sample was a cylinder 1 in. long and 1 in. in diameter, containing 1.674 moles. The ingot from which it was machined had been arc-melted from crystals produced by the van Arkel iodide process.[9] A spectrographic analysis showed it to be 99.8% vanadium with major impurities Fe, Al, Cr, and Ni. The specimen was annealed in vacuo ($p<3\times10^{-6}$ mm Hg) at 850°C for 6 hours, and then cooled slowly at about 50°C per hour. While internal strains and interstitial impurities may have a marked effect on the superconducting properties of vanadium, the low values of the hardness (121±11 diamond pyramid hardness) and residual resistivity (0.08 of its ice-point resistivity) of the specimen after annealing indicated that it was comparable in purity with the best specimens so far described.

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[1] C. J. Gorter and H. B. G. Casimir, Physik. Z. **35**, 963 (1934).

[2] Brown, Zemansky, and Boorse, Phys. Rev. **92**, 52 (1953).

[3] Worley, Zemansky, and Boorse, Phys. Rev. **99**, 447 (1955).

[4] P. M. Marcus and E. Maxwell, Phys. Rev. **91**, 1035 (1953); P. L. Bender and C. J. Gorter, Physica **18**, 597 (1952); B. Serin, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North Holland Publishing Company, Amsterdam, 1955), Vol. 1, pp. 142–148.

[5] B. B. Goodman, Proc. Phys. Soc. (London) **A66**, 217 (1953); S. J. Laredo, Proc. Roy. Soc. (London) **A229**, 473 (1955).

[6] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).

[7] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **96**, 1442 (1954).

[8] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. **98**, 1699 (1955).

[9] This ingot was prepared for us by the Battelle Memorial Institute.

TABLE I. Ratio of the electronic to lattice contributions to the atomic heats of a number of superconductors at their transition temperatures.

Element	T_c (°K)	$(C_{es}/C_{\text{lattice}})_{T=T_c}$
Ti	0.29	520
Zr	0.55	148
Zn	0.91	168
Al	1.20	155
Re	1.70	~50
V	5.03	19
Ta	~4.4	7.0
Nb	~9.0	3.3
La	~5.0	1.41
Sn	3.73	1.23
In	3.40	0.31
Tl	2.39	0.28
Pb	7.2	0.068
Hg	4.15	0.028

Heat capacity measurements were made at intervals of approximately 0.1°K over most of the range of temperature for both the normal and superconducting states. However, from 1.2 to 1.4°K, and in the region of the transition temperature, in zero field, measurements were made at intervals of approximately 0.03°K. Temperature increments of about 0.03°K were used throughout. The addenda (thermometer, heater, etc.) were identical to those used in I, and their thermal capacity values determined in that study were used here.

In I, it was shown that the use of the 1948 helium vapor pressure temperature scale[10] leads to systematic errors in specific heat several times larger than the uncertainties in the measurements themselves. Consequently, for the present work a corrected temperature scale (T_w) was constructed from a knowledge of these systematic errors, the resulting scale was thus an average of the three T_w scales of I. The temperature correction curve (A), and the fractional error curve (B), used for correcting the atomic heats, are shown in Fig. 1. A discussion of these temperature scale corrections appears in the appendix.

RESULTS

The results for the normal and superconducting atomic heats of vanadium are given in Table II. These are given both on the 1948 scale, which is still generally accepted, and also on the present corrected scale, which, on the other hand, is believed to represent more closely the thermodynamic temperature scale; all the derived results are given here on the latter scale.

The results on the corrected scale are also plotted in Fig. 2. The solid symbols represent results obtained with the specimen either wholly normal or wholly superconducting, except in the neighborhood of T_c. The open symbols represent results obtained in magnetic fields inadequate for complete quenching of superconductivity.

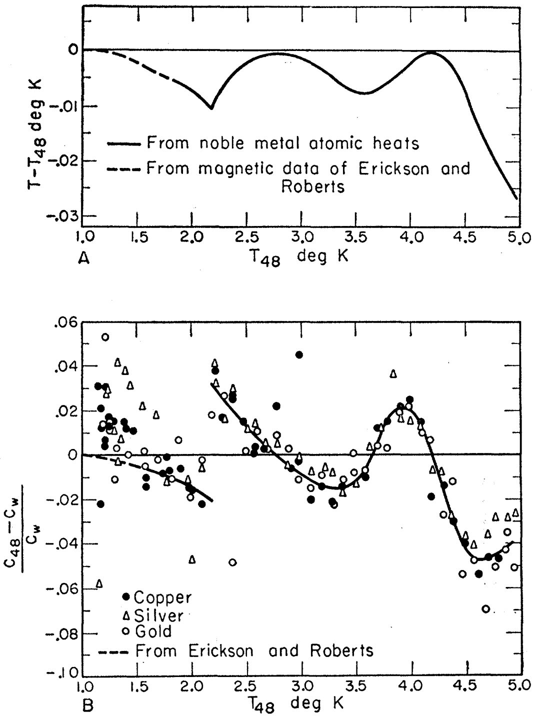

FIG. 1. Correction curves used to correct the present results from the T_{48} to the T_w scale. (A) The temperature; (B) The atomic heat.

A detailed discussion of the probable errors, both random and systematic, due to uncertainties in the various measurements and to errors in the corrected temperature scale, appeared in I. The probable error in an individual determination of C_n or C_s, estimated from the scatter of the points around smooth curves, was of the order of 0.8%, in agreement with an estimate based on the known limitations of the measuring apparatus. In addition, systematic errors of about 0.5% may have resulted from inaccuracies in the corrected temperature scale.

It can be seen that the superconducting state atomic heat, C_s, departs markedly from a T^3 law; the significance of this departure will be considered in detail later. The transition temperature, T_c, taken as the midpoint of the atomic heat discontinuity, was 5.03°K; the breadth of the zero field transition was 0.05°K. This transition temperature is only slightly different from the value $(T_c)_{48}=5.13$°K of the best specimen previously studied[6]; of this discrepancy, 0.03°K can be attributed to temperature scale discrepancies. In view of the large effect of impurities on the transition temperature of vanadium the remaining discrepancy in T_c between these two specimens may be due to quite small differences in purity.

In magnetic fields, large enough to quench superconductivity completely, the atomic heat could be represented within experimental error by

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

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[10] H. Van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

TABLE II. Atomic heat of vanadium in various magnetic fields. The absence, above 4.9°K, of results on the 1948 scale, and the meaning of the T_w scale in this temperature range, are discussed in the appendix.

T_{48} (°K)	C_{48} (millijoule mole^{-1} deg^{-1})	T_w (°K)	C_w (millijoule mole^{-1} deg^{-1})
	Zero magnetic field		
1.199	0.784	1.199	0.786
1.255	1.096	1.255	1.098
1.311	1.469	1.310	1.473
1.391	1.982	1.390	1.990
1.584	3.84	1.581	3.86
1.783	6.49	1.778	6.55
1.981	9.85	1.974	10.00
2.179	13.84	2.169	14.13
2.377	18.79	2.373	18.34
2.573	23.70	2.572	23.39
2.769	29.07	2.768	29.01
2.986	35.59	2.984	35.80
3.189	40.28	3.185	40.76
3.378	48.77	3.372	49.36
3.402	49.84	3.396	50.44
3.601	58.07	3.594	58.24
3.780	66.35	3.774	65.29
3.995	74.84	3.993	73.34
4.193	83.19	4.193	83.19
4.402	90.13	4.398	93.10
4.575	97.68	4.564	102.27
4.784	108.4	4.763	113.0
...	...	4.940	122.0
...	...	5.101	55.0
1.214	0.860	1.214	0.862
1.272	1.165	1.272	1.167
1.326	1.523	1.325	1.528
1.517	3.130	1.515	3.146
1.718	5.616	1.714	5.661
1.887	8.537	1.881	8.639
2.066	11.19	2.058	11.37
2.286	16.65	2.280	16.15
2.482	20.47	2.480	20.10
2.678	26.41	2.677	26.23
2.891	32.58	2.890	32.68
3.096	39.14	3.094	39.53
3.301	46.46	3.296	47.06
3.483	53.14	3.476	53.62
3.608	58.41	3.601	58.59
3.904	71.33	3.900	69.83
4.110	80.25	4.109	79.37
4.305	86.4	4.304	88.0
4.508	94.0	4.500	98.1
4.685	102.6	4.669	107.4
4.815	109.8	4.797	114.3
...	...	4.893	119.6
...	...	4.923	120.5
...	...	4.953	121.9
...	...	4.983	118.0
...	...	5.017	96.1
...	...	5.055	58.3
...	...	5.098	54.6
...	...	5.151	55.1
...	...	5.189	55.6
...	...	5.302	57.1
...	...	5.403	58.5
	3000 oersteds		
1.131	8.73	1.131	8.74
1.161	9.77	1.161	9.79
	3000 oersteds—*Continued*		
1.391	13.11	1.390	13.17
1.591	16.40	1.588	16.42
1.789	19.70	1.783	19.84
1.983	23.17	1.976	23.49
2.202	29.15	2.192	28.10
2.384	32.86	2.380	32.10
2.577	32.93	2.576	32.50
2.780	26.90	2.779	26.85
2.986	29.05	2.984	29.22
2.887	27.97	2.886	28.05
2.988	28.73	2.986	28.90
3.085	29.80	3.083	30.07
3.186	30.74	3.183	31.11
3.283	32.12	3.278	32.64
3.392	33.27	3.386	33.67
3.479	34.12	3.472	34.46
3.584	35.38	3.577	35.52
3.677	36.80	3.670	36.65
3.781	37.68	3.775	37.08
3.946	40.26	3.943	39.41
4.051	41.78	4.050	41.08
4.191	42.23	4.191	42.23
4.279	43.37	4.278	43.98
4.383	43.57	4.380	44.92
4.473	44.27	4.467	46.09
4.560	44.52	4.553	46.57
4.662	46.23	4.647	48.40
4.753	46.71	4.734	48.77
4.844	47.71	4.821	49.57
...	...	4.947	51.62
...	...	5.060	53.03
...	...	5.097	54.01
...	...	5.142	54.78
...	...	5.221	54.93
...	...	5.358	54.94
	5200 oersteds		
1.353	13.05	1.352	13.09
1.662	16.08	1.657	16.11
2.428	23.45	2.425	22.96
2.577	24.31	2.576	23.99
2.719	26.03	2.718	25.89
2.864	27.41	2.863	27.46
3.078	29.32	3.076	29.58
...	...	4.978	51.88
...	...	5.095	53.25
...	...	5.288	56.37
...	...	5.383	57.11
1.149	11.94	1.149	11.95
1.278	12.98	1.278	13.02
1.520	15.00	1.515	15.03
1.824	17.55	1.818	17.69
2.255	22.17	2.247	21.46
1.959	18.88	1.952	19.13
2.127	20.04	2.118	20.42
	6200 oersteds		
1.114	10.38	1.114	10.39
1.399	12.92	1.398	12.97
1.639	15.65	1.635	15.78
1.957	18.42	1.950	18.68

with $\gamma = (9.26 \pm 0.03) \times 10^{-3}$ joule mole^{-1} deg^{-2} [11] and $\Theta = 338 \pm 5$°K. The values of γ and Θ and their probable errors were obtained by fitting values of C_n/T and T^2 to Eq. (1) by the method of least squares. The values for γ and Θ recently published by Worley, Zemansky, and Boorse[3] ($\gamma = 8.96 \times 10^{-3}$ joule mole^{-1} deg^{-2} and $\Theta = 274$°K for their sample of highest purity), while similar to the values obtained from this work, are well outside the probable errors quoted here. It is believed that the present values should take precedence over

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[11] In our previous publication[7] there appeared a typographical error; the values of γ should have contained the factor 10^{-4} instead of 10^{-3}.

theirs since, in addition to their somewhat lower precision, the range of temperature in which they were able to completely quench superconductivity was limited to between 3.5 and 5.0°K. Furthermore, errors in the 1948 temperature scale, which they used below 4.2°K, could introduce some error into their values of γ and Θ.

DISCUSSION

A. Comparison with Magnetic Measurements

In order to derive the true thermodynamic critical field-temperature relationship for vanadium from the present results, the entropies of the normal and superconducting states were calculated as a function of temperature. For the normal state

$$S_n=\gamma T+\frac{1}{3}\left(\frac{12}{5}\pi^4 R\right)\left(\frac{T}{\Theta}\right)^3, \qquad (2)$$

and for the superconducting state the necessary integration was carried out graphically from a smoothed plot of C_s/T vs T. The entropy difference (S_n-S_s), extrapolated to 0°K, vanished to within ±0.2%, in accordance with the third law of thermodynamics.

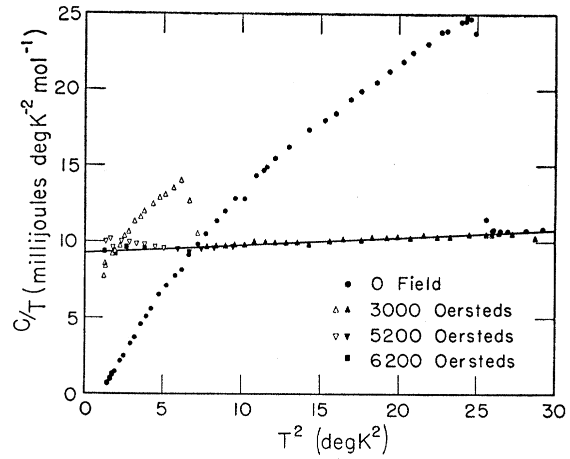

FIG. 2. C/T vs T^2 for normal and superconducting vanadium. The open symbols indicate incomplete quenching of superconductivity by the magnetic field.

The critical field-temperature relationship was then deduced by graphical integration of the relation

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

where $V=8.34$ cm^3 is the atomic volume. The resulting H_c-T curve is shown in Fig. 3, together with the initial penetration fields found experimentally by Wexler and Corak.[6] It can be seen that their results are in agreement with the present work. The discrepancy between their value for H_0 (1190 oersteds) and the present value (1310 oersteds) is due to the fact that they used a parabolic expression for extrapolating their results to 0°K. This procedure also led them to a value for γ (6.28×10^{-3} joule mole^{-1} deg^{-2}) which is somewhat in error. In the reduced plot of Fig. 4, the deviation of the critical field-temperature relationship from $H_c=H_0[1-(T/T_c)^2]$ is shown.

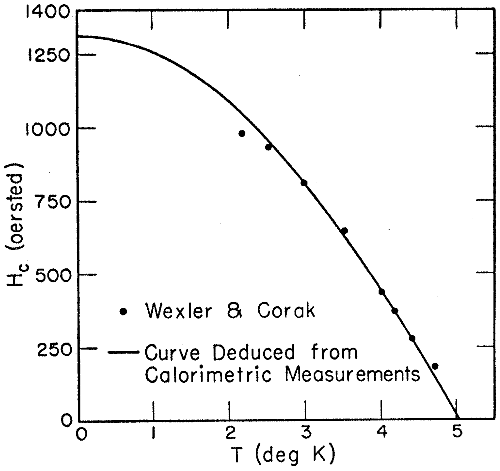

FIG. 3. Critical field-temperature relationship for vanadium.

In connection with the present work magnetization curves were also obtained, by the Shoenberg technique,[12] for a small specimen of vanadium taken from the calorimetric specimen. These measurements were not intended for comparison with the H_c-T relationship derived from the calorimetric measurements, but merely to determine what magnetic field would be necessary to maintain the specimen normal. At 4600 oersteds and down to 1.2°K the diamagnetic susceptibility of the specimen was less than 0.2% of the value for a completely superconducting specimen, suggesting that at least 99.8% of the volume of the specimen was in the normal state.

On the other hand, it may be seen from Fig. 2 that in a field of 5200 oersteds below 2.2°K the specific heat

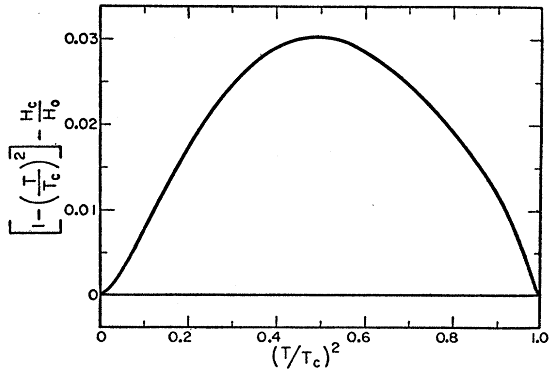

FIG. 4. Deviation of the H_c from the expression $H_c=H_0[1-(T/T_c)^2]$.

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[12] D. Shoenberg, *Report of an International Conference on Fundamental Particles and Low Temperatures*, Cambridge, 1946 (The Physical Society, London, 1947), Vol. 2, p. 85.

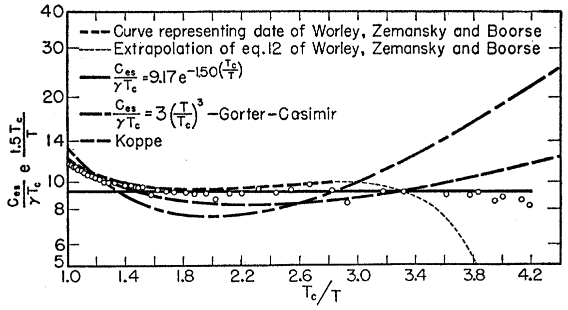

FIG. 5. Comparison of the present results for vanadium (open circles) with the exponential Eq. (4) and the work of other authors.

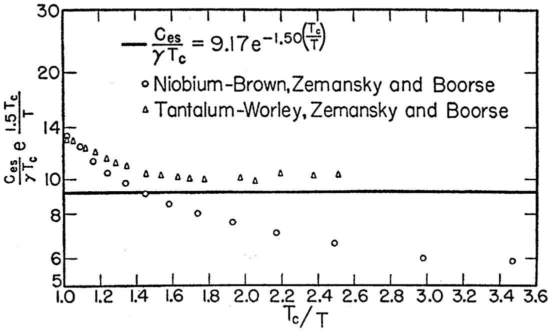

FIG. 6. Comparison of C_{es} for niobium and tantalum with Eq. (4).

was greater than that for the completely normal material in 6200 oersteds, thus indicating a lower entropy for the specimen in the lower field. An independent estimate of the fraction of normal material in the specimen could be obtained by assuming that the entropy was a linear combination of the contributions from normal and superconducting regions. The resulting estimate that 4% of the volume of the specimen was superconducting at 1.2°K in 5200 oersteds was in clear disagreement with the magnetic observations. The origin of this apparent discrepancy was not investigated, and in fact it may possibly have arisen from a genuine difference between the behavior of the small specimen and the calorimetric specimen, resulting from inhomogeneities in the latter. But let us suppose, as may be the case,[13] that superconducting filaments of very high critical field persisted above 4600 oersteds in the calorimetric specimen. Then, because of their high critical fields, these may possibly have contributed appreciably to the calorimetric properties of the specimen, while at the same time, because of their small size, they may have made only a negligible diamagnetic contribution to the susceptibility.

B. Temperature Dependence of C_{es}

On the basis of the assumption that C_{lattice} in the superconducting state was identical with that in the normal state, C_{es} was deduced by subtracting from C_s the last term in Eq. (1). Over the temperature range covered by these experiments, C_{es} constituted 85 to 95% of the total atomic heat, so that the probable error in the deduced values of C_{es} was comparable with the probable error in the results themselves, and therefore of the order of 1%.

It was immediately evident that C_{es} was not proportional to T^3, as suggested by the Gorter-Casimir theory, but could be well represented below about $0.7T_c$ by an exponential relation of the following form:

$$C_{es}/\gamma T_c = ae^{-bT_c/T}. \qquad (4)$$

The final values of the constants, $a=9.17$ and $b=1.50$, are slightly different from those published previously[7] due to temperature scale corrections and better normal-state data. In Fig. 5, the experimental values for C_{es} are plotted in such a way that, if Eq. (4) held exactly with the above values for the constants, the horizontal line shown would result.

A curve representing the data of Worley, Zemansky, and Boorse[3] is also shown. This curve was derived from their Eqs. (3) and (12) using the constants reported for their sample V–II. It can be seen that over the range of temperature covered by both investigations the values of C_{es} are not greatly different. However, if their Eq. (12) is extended to lower temperatures the difference becomes quite large. The predictions of the Gorter-Casimir theory and the calculations of Koppe[14] based on Heisenberg's theory are also shown.

Although previous calorimetric data have not been treated in terms of an exponential temperature dependence of C_{es}, it should be pointed out that none is inconsistent with this representation, particularly in view of the scatter of the earlier data.

Representative experimental points for tantalum and niobium shown in Fig. 6 indicate that on this reduced scale the tantalum results are similar to those for vanadium, while those for niobium may be represented by a similar exponential expression with slightly modified constants. The best data for tin so far published are not sufficiently accurate to distinguish between an exponential and a cubic temperature dependence; however recent measurements for this metal described in the following paper are, on a reduced scale, in close agreement with the present work.

Furthermore, preliminary results for aluminum,[15] over an even wider range of reduced temperature than that covered here, indicate that a similar exponential temperature dependence of C_{es} also holds for this metal.

It therefore seems quite probable that a predominantly exponential temperature dependence of C_{es}, may be a fundamental property of superconductors, par-

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[13] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition, pp. 37–47.

[14] H. Koppe, Ann. Physik 1, 405 (1947).

[15] B. B. Goodman, Conférence de Physique des Basses Températures, Paris, 1955, Proceedings, pp. 506–511.

ticularly below about $0.7T_c$. However, it is not yet clear whether this similarity in behavior between superconductors may be extended to a law of corresponding states for all superconductors. A discussion of some further evidence for the temperature dependence of C_{es}, obtained from critical magnetic field measurements, will appear in the following paper.

On any single-electron model of a superconductor, with a gap ϵ in the energy level spectrum immediately above the ground state levels, the expression for the specific heat would be expected to be dominated, at sufficiently low temperatures, by the term $\exp(-\epsilon/kT)$. The present experiments support the concept of such an energy gap, a concept which has received theoretical consideration recently.[16]

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to Dr. M. P. Garfunkel for his contribution to the techniques used in this work and for his continued interest.

APPENDIX

If the atomic heats are determined on the basis of a temperature scale which is incorrect (as the 1948 scale is known to be), errors arise, not only from errors in the temperature scale itself, but to an even greater extent from errors in its gradient. If T_{48} and C_{48} represent respectively the 1948 temperature scale and an atomic heat based on this scale, and if T_w and C_w are similar quantities for a new scale, it readily can be shown that

$$C_{48}/C_w = dT_w/dT_{48}. \qquad \text{(X-1)}$$

It may be noted that while errors in the 1948 scale are believed to be of the order of a few millidegrees, never exceeding 0.5% of T, the gradient of this scale may be in error by as much as 3–4%, thus introducing errors of a similar magnitude in atomic heats.

If the true atomic heat, C_w, is known for a given material for which there exist accurate measurements of C_{48}, the correct temperature scale can be constructed by integrating the foregoing expression:

$$T_w = \int \frac{C_{48}}{C_w} dT_{48}; \qquad \text{(X-2)}$$

or, by rearranging, a difference function may be obtained:

$$T_w - T_{48} = \int \frac{C_{48} - C_w}{C_w} dT_{48}. \qquad \text{(X-3)}$$

It is necessary to tie down one point on the T_w scale for the purpose of evaluating the constant of integration, and for this purpose the normal boiling point of helium was chosen.

A treatment of this sort was shown in I to yield a temperature scale for each of the noble metals, copper, silver, and gold in very close agreement, above about 1.6°K, with the corrections to the 1948 scale proposed by Erickson and Roberts[17] and Berman and Swenson.[18]

For the present work, the smooth deviation curve in Fig. 1(B) was fitted to the results for all of the noble metals in such a way that on carrying out the integration of Eq. (X-3) the resulting scale T_w, the smooth curve in Fig. 1(A), was in close agreement, between 1.6 and 4.9°K, with the corrections suggested by the above authors. Below 1.6°K, where errors of the order of a few percent were suspected in the values of C_{48} for the noble metals, the temperature scale was selected to agree with the magnetic data of Erickson and Roberts.

Above 4.9°K, where calibration of the resistance thermometer against the helium bath was difficult, the resistance-temperature relation was extrapolated so that the normal state data continued to scatter randomly about the theoretical expression for C_n [Eq. (1)] found applicable below 4.9°K. Since any contribution to C_n from higher power terms than T^3 below 4.9°K is negligible within the experimental accuracy, it is estimated that errors of less than 1% in C_s between 4.9°K and T_c could have arisen from neglecting such terms in C_n in this extrapolation of the temperature scale.

The present T_w scale is in close agreement with that proposed recently by Clement *et al.*[19]

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