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Low-Temperature Thermodynamic Properties of Vanadium. I. Superconducting and Normal States*

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The specific heat of vanadium (resistivity ratio = 140) has been measured in the superconducting and normal states between 0.5 and 5.4°K. The normal-state specific heat is given by $C_n = 9.82T + 0.035T^3 + C_{\mathrm{nuc}}$ mJ mole^{-1} deg^{-1}, where the term C_{nuc} arises from the interaction of the nuclear magnetic moments with the applied magnetic field. The coefficient of the cubic term corresponds to a Debye temperature Θ_0 at 0°K of (382±10)°K, which is slightly less than the value 399.3°K obtained from elastic measurements. The superconducting specific heat contains a term linear in T which is 0.52% of the normal-state linear term. This indicates the presence of a very small energy gap at the Fermi surface in addition to the normal gap. At all but the lowest temperatures the specific heat is governed by the normal energy gap and is in fair agreement with the BCS prediction. The agreement becomes excellent if the normal energy gap is assumed to be anisotropic with a maximum value of $3.52kT_c$ and a minimum of $3.20kT_c$, which is consistent with ultrasonic measurements. The superconducting transition temperature for this sample is (5.379±0.004)°K with a total transition width of only about 1 mdeg. The intrinsic transition temperature for vanadium is estimated to be (5.414±0.010)°K.

I. INTRODUCTION

PREVIOUS measurements[1–3] on the normal state specific heat of vanadium at liquid-helium temperatures gave widely varying values of both the electronic coefficient γ and the Debye temperature Θ_0 at 0°K. All values of Θ_0 were considerably lower than the value 399.3°K determined from velocity-of-sound measurements.[4] In addition, many different transition temperatures T_c have been reported[1,2,5–7]; however, T_c is dependent on purity. The superconducting specific heat[2,8] has shown very good agreement with the Bardeen-Cooper-Schrieffer[9] (BCS) theory. This is to be expected since vanadium is a weak coupling superconductor and the impurity contents in previous measurements were sufficiently high to produce an isotropic energy gap. For higher purity samples the energy gap becomes anisotropic,[10] and so small deviations from the BCS specific heat should occur.

The present investigation was begun when a single crystal vanadium sample of much higher purity than that used in previous work was kindly loaned to us by the Ford Scientific Laboratory. Preliminary results[11] showed that the sample had higher values for T_c, γ, and Θ_0 then reported before. A large deviation from the BCS specific heat has been found at very low temperatures comparable to that found in niobium by Shen *et al.*[12] This can be explained by the existence of two energy gaps. Also the presence of a mixed state showed that the sample was a type-II superconductor. Properties of this mixed state will be discussed separately.[13]

II. EXPERIMENTAL DETAILS

Measurements of the specific heat were done using the He^3 cryostat described previously.[14] An L-shaped thermometer was cut from a highly doped (gallium) and highly compensated (phosphorus) germanium crystal of 5×10^{19} cm^{-3} total impurities. About 6.3×10^{16} excess carriers were present[15] after compensation, which gave a room-temperature resistivity of 0.047 Ω cm. The thermometer was glued to the top of the sample using Glyptal lacquer with the measuring leg of the thermometer situated parallel to the magnetic field to decrease the magnetoresistance effect. A thin strip of pure germanium provided electrical insulation between the sample and thermometer while maintaining good thermal contact. Total weight of the thermometer was 0.035 g. Typical resistances were 1800 Ω at 0.5°K and 120 Ω at 4.2°K. The heater consisted of 20 cm of 0.0445-mm constantan wire wound around the sample and

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[1] R. D. Worley, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **99**, 447 (1955).

[2] W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **102**, 656 (1956).

[3] N. M. Wolcott, *Conference de Physique des Basses Temperatures, Paris, 1955* (Institut International du Froid, Paris, 1955), p. 286.

[4] G. A. Alers, Phys. Rev. **119**, 1532 (1960).

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

[6] G. Busch and J. Müller, Helv. Phys. Acta **30**, 230 (1957).

[7] J. Müller, Helv. Phys. Acta **32**, 141 (1959).

[8] B. B. Goodman, Compt. Rend. **244**, 2899 (1957).

[9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[10] H. V. Bohm and N. H. Horwitz, in *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 191.

[11] P. H. Keesom and Ray Radebaugh, Phys. Rev. Letters **13**, 685 (1964).

[12] L. Y. L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Letters **14**, 1025 (1965); N. E. Phillips (private communication).

[13] Ray Radebaugh and P. H. Keesom, following paper, Phys. Rev. **149**, 217 (1966).

[14] G. M. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).

[15] M. P. Mathur, Ph.D. thesis, Department of Physics, Purdue University, Lafayette, Indiana, 1966 (unpublished).

TABLE I. Specific heat of vanadium in the normal state at different magnetic fields. (C_n is in mJ mole^{-1} deg^{-1}).

			$H=14$ kOe			
H (Oe)	T (°K)	C_n	T (°K)	C_n	T (°K)	C_n
3055	0.8144	8.03	0.4082	4.588	1.197	11.93
3055	0.9620	9.49	0.4161	4.670	1.247	12.38
3055	1.135	11.21	0.4245	4.704	1.305	13.02
2841	0.9727	9.61	0.4329	4.747	1.371	13.65
2841	1.192	11.75	0.4447	4.910	1.436	14.31
2841	1.446	14.28	0.4603	4.993	1.496	14.84
2700	1.415	13.93	0.4730	5.088	1.578	15.70
2700	1.758	17.37	0.4885	5.305	1.665	16.58
2700	2.197	21.90	0.5095	5.472	1.747	17.37
2418	2.401	24.17	0.5300	5.633	1.844	18.38
1996	2.867	29.06	0.5508	5.859	1.892	18.90
1996	3.446	35.36	0.5896	6.198	2.152	21.46
1792	3.124	31.84	0.6065	6.342	2.235	22.25
1792	3.575	36.89	0.6290	6.538	2.324	23.58
1418	3.902	40.83	0.6549	6.803	2.421	24.42
1150	4.251	44.05	0.6796	7.011	2.502	25.56
1040	4.294	44.86	0.7133	7.351	2.618	26.82
937	4.136	43.11	0.7615	7.787	2.760	28.20
937	4.427	46.47	0.8092	8.23	2.907	29.96
937	4.343	45.33	0.8531	8.69	3.096	32.11
700	4.760	50.74	0.8881	8.97	3.293	34.24
552	4.964	53.50	0.9198	9.26	3.498	36.82
552	4.908	52.46	0.9498	9.58	3.686	38.57
250	5.075	55.03	0.9769	9.78	3.843	40.26
			1.006	10.08	4.016	42.26
			1.052	10.50	4.234	44.75
			1.119	11.14	4.462	47.20

cemented with Glyptal lacquer. The data of Ho *et al.*[16] were used for the heat capacity of the constantan wire. For the sample in the superconducting state the correction due to the heat capacity of the addenda (Glyptal, heater, and thermometer) varied from about 15% at the lowest temperature to about 0.5% just below the transition temperature. In the normal state the addenda correction varied from 0.1% at 0.5°K to about 1.2% at the transition temperature. Calibration of the thermometer was based on the 1962 He^3 temperature scale[17] for the range 0.5 to 1.2°K and the 1958 He^4 temperature scale[18] for the range between 1.0 and 5.2°K. An IBM 7094 digital computer was used to expand $1/T$ in powers of $\log R$ up to $(\log R)^3$ using the method of least squares described by Moody and Rhodes.[19] Two calibration regions were used which overlapped 0.6 at 1.5°K. Calibration in different fields indicated that the magnetoresistance of the thermometer could be neglected for fields less than 3000 Oe.

The specific-heat measurements in a field of 14 kOe were done using a set of high-field cans described in an earlier publication.[20] All other measurements were made using the original set of low-field cans wound with copper-plated Nb-25% Zr wire. The earth's magnetic field was canceled with a double Helmholtz coil for measurements of the superconducting specific heat. Heating and cooling curves were also take to determine the transition temperature very precisely. A heating or cooling rate of about 0.02°K/min was used and gave approximately a 45° slope on the recorder chart.

The systematic error in the specific heat due to inaccuracies in the temperature scale, addenda corrections, heater resistance, current, and timing errors should not exceed 2% at the lowest and highest temperatures. Between 1 and 4.2°K this error should be less than 1%. Error limits stated for experimental quantities are those found from random scatter of the data and represent the standard deviation.

The single crystal vanadium had been prepared by the electron beam floating zone technique and was in the form of a cylinder 7 mm in diameter by 19 mm long containing 0.08529 moles. The sample had a resistance ratio R_{295}/R_0 of 140 measured potentiometrically. A field of about 2600 Oe was used to quench superconductivity for measuring R_0 at 4.2°K. Before zone refining the sample was 99.95% pure and had a resistance ratio of 40. The zone refining probably increased the purity to at least 99.99%.

III. RESULTS AND DISCUSSION

A. Normal-State Specific Heat

The normal-state specific heat C_n is listed in Table I. The data were obtained in a field of 14 kOe as well as in 13 different magnetic fields used for the study of the mixed state.[13] Except in the case of $H=14$ kOe, most of the points listed in this table represent averages of T^2 and C/T for anywhere from 3 to 10 individual points and span temperature intervals ranging from about 0.1°K at the lowest temperature to about 1°K at the highest temperature. The number of points chosen were such that each average value of C/T would have about the same standard deviation. These large number of points with a small ΔT were obtained from measurements[13] pinpointing the transition temperature in different fields.

In the normal state the specific heat can be expressed in the form

$$C_n=\gamma T+\alpha T^3+C_{\mathrm{nuc}}\,, \qquad (1)$$

where γ and α are coefficients of the electronic and lattice contributions, respectively, and C_{nuc} is the contribution due to the interaction of the nuclear magnetic moments with the applied field. The Debye temperature Θ_0 at 0°K is found from the relationship

$$\alpha=(12/5)\pi^4R/\Theta_0{}^3=1944/\Theta_0{}^3\ \mathrm{J\ mole^{-1}\ deg^{-4}}, \qquad (2)$$

which follows from the Debye theory of lattice specific heat. A term of the type βT^5 in C_n would determine the temperature dependence of Θ at low temperatures. However, for vanadium the lattice specific heat is so small compared to the electronic contribution that the

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[16] J. C. Ho, H. R. O'Neal, and N. E. Phillips, Rev. Sci. Instr. **34**, 782 (1963).

[17] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U. S.) **68A**, 579 (1964).

[18] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U. S.) **64A**, 1 (1960).

[19] D. E. Moody and P. Rhodes, Cryogenics **3**, 77 (1963).

[20] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. **134**, A1320 (1964).

TABLE II. Results of specific-heat measurements on vanadium.

Measurement	$R_{295}/R_{4.2}$	Purity	T_c (°K)	γ (mJ mole^{-1} deg^{-2})	Θ_0 (°K)
Worley *et al.*[a]		99.8%	4.99	8.83	273
Corak *et al.*[b]	14	99.8%	5.03	9.26	338
Wolcott[c]		>99.98%		9.20	380
This work	140	>99.99%	5.379	9.82	382

[a] Reference 1.
[b] Reference 2.
[c] Reference 3.

T^5 term is hidden by experimental error. The results of the normal state specific heat are displayed in Fig. 1. The high-temperature data in a field of 14 kOe are not shown in this figure since these data are not as precise and, therefore, do not represent the normal state as well as the data in the lower fields. For magnetic fields less than 3100 Oe, the specific heat can be represented by

$$C_n = (9.82\pm0.03)T + (0.035\pm0.003)T^3 \text{ mJ mole}^{-1}\text{ deg}^{-1}.$$

The values of γ and α and their standard deviations were obtained by the method of least squares.

The coefficient of the cubic term corresponds to a Θ_0 of (382±10)°K. This is slightly lower than the value 399.3°K derived from velocity of sound measurements,[4] which is shown in Fig. 1 for comparison. The error of ±10°K is not enough to account for the difference in the two values; however, this error includes only the standard deviation associated with random scatter of the data. Systematic errors in Θ_0 (calorimetric) might possibly be large enough to account for the difference, but there is some reason to believe that the difference is real. Specific-heat measurements on niobium[20,21] have shown that Θ changes quite abruptly at about 3°K and below this temperature agrees with Θ_0 (elastic). A similar change may very well occur in vanadium at a slightly lower temperature. Unfortunately, the scatter of the data is too great to determine whether this is indeed the case. Another explanation for the difference in Θ_0 (calorimetric) and Θ_0 (elastic) which cannot be completely ruled out is the fact that the latter was deduced from measurements on a sample with a resistance ratio of only 15. Judging from hardness measurements made by other authors,[2,5–7] the hardness of this sample would be about twice that of the higher purity sample used in the present investigation. It is conceivable, then, that the lower purity sample may have higher elastic constants, which give rise to a larger Θ_0 (elastic), though the effect is usually very small. Corak *et al.*[2] found values for γ and Θ_0 of (9.26±0.03) mJ mole^{-1} deg^{-2} and (338±5)°K. Further comparison with other work is shown in Table II in order of increasing sample purity.

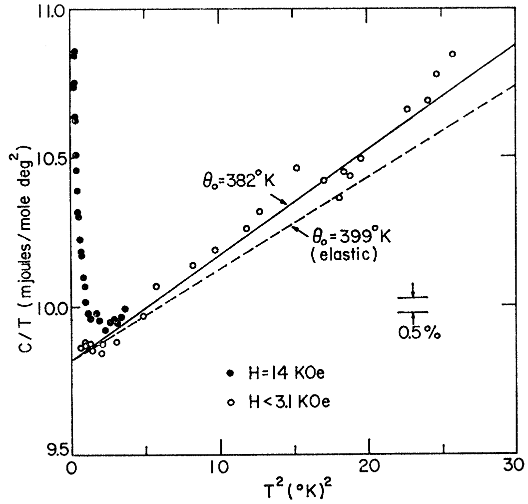

FIG. 1. Specific heat of vanadium in the normal state plotted as C/T versus T^2.

In a field of 14 kOe the normal state specific heat for $T<2.0$°K shows the T^{-2} behavior of a Schottky anomaly. This anomaly arises from the splitting of the nuclear energy levels as a result of the interaction of the nuclear magnetic moments ($\mu=5.14$ nuclear magnetons) with the external field. For vanadium the nuclear spin is $\frac{7}{2}$, so a magnetic field gives rise to eight separate energy levels. Experimentally we find that $C_{\text{nuc}}=0.8\times10^{-9}H^2/T^2$ mJ mole^{-1} deg^{-1}, where H is in Oe, but this value is accurate to only about a factor of 2 because of the limited temperature range and uncertainty in the applied field. Theoretically the specific heat is given by[22]

$$C_{\text{nuc}}=\tfrac{1}{3}I(I+1)R(\mu H/kT)^2, \tag{3}$$

where I is the nuclear spin. For $I=\frac{7}{2}$ this becomes $C_{\text{nuc}}=1.54\times10^{-9}H^2/T^2$ mJ mole^{-1} deg^{-1}.

B. Superconducting-State Specific Heat

The superconducting specific heat should have the form

$$C_s=C_{\text{ls}}+C_{\text{es}}. \tag{4}$$

The first term is the superconducting lattice contribution and is assumed to be the same as the normal lattice term, αT^3. The second term is the superconducting electronic contribution, which, according to the BCS theory, may be approximated by

$$C_{\text{es}}=a\gamma T_c\exp(-bT_c/T). \tag{5}$$

The results of the superconducting specific heat are given in Table III and shown in Fig. 2. As can be seen, C_{es} contains a small additional term linear in temperature: γ_sT, where $\gamma_s=0.051$ mJ mole^{-1} deg^{-2}. The presence of this linear term indicates that a fraction

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[21] H. A. Leupold and H. A. Boorse, Phys. Rev. **134**, A1322 (1964).

[22] W. Marshall, Phys. Rev. **110**, 1280 (1958).

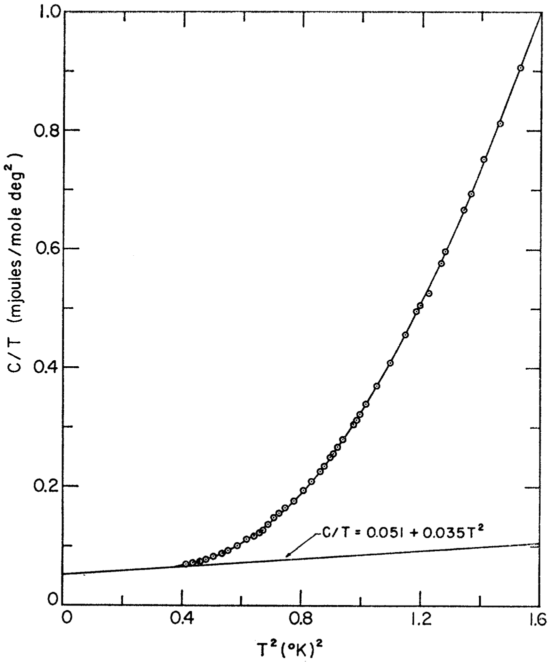

FIG. 2. Specific heat of vanadium in the superconducting state below 1.2°K plotted as C/T versus T^2.

of the material behaves as if normal. Since the earth's magnetic field was compensated, this cannot be a result of trapped flux. Any impurity which could give rise to a linear specific heat would constitute considerably less than 0.5% of the total sample and, thus, would be unable to cause such a large value of γ_s. A similar term was first noted[20] in Nb and recently by Shen *et al.*[12] in high purity Nb and Ta and moderately pure V. Shen *et al.* attributed this to the existence of two energy gaps as predicted by Suhl *et al.*[23] when extending the BCS theory to the case of overlapping *s* and *d* bands. Using a similar approach, Garland[24] showed that a two-gap model of superconductivity is appropriate only for clean superconductors and degenerates to a single-gap model in the dirty range. This mean free path of the *d* electrons in our vanadium sample is about five times the coherence length[13]; thus, by Anderson's[25] criterion the sample is well within the clean superconductor range. The existence of the linear term in the specific heat down to the lowest temperature of 0.65°K ($T/T_c = t = 0.12$) indicates that kT at this temperature is still larger than the smaller of the two energy gaps. The total electronic specific heat can be written[26] as

$$C_{es}=\frac{N_d}{N_s+N_d}C_{es}{}^d+\frac{N_s}{N_s+N_d}C_{es}{}^s\,, \qquad (6)$$

TABLE III. Specific heat of vanadium in zero magnetic field. (C_s is in mJ mole^{-1} deg^{-1}.)

T (°K)	C_s	T (°K)	C_s	T (°K)	C_s
0.9296	0.207	2.009	10.03	0.7445	0.0690
0.9364	0.219	2.121	11.98	0.7653	0.0769
0.9422	0.234	2.208	13.88	0.7855	0.0878
0.9514	0.243	2.301	15.84	0.8015	0.0927
0.9591	0.256	2.438	19.08	0.8122	0.0991
0.9729	0.276	2.592	22.68	0.8205	0.1046
0.9861	0.300	2.759	27.41	0.8298	0.1133
0.9968	0.321	2.954	32.89	0.8416	0.1235
1.010	0.347	3.133	38.39	0.8535	0.1320
1.025	0.378	3.373	46.51	0.8646	0.1415
1.045	0.426	3.621	55.42	0.8812	0.1540
1.070	0.489	3.883	65.14	0.8989	0.1745
1.087	0.539	4.231	80.07	0.9125	0.1896
1.106	0.582	4.661	98.90	0.9283	0.209
1.130	0.676	5.116	122.6	0.9484	0.237
1.157	0.772	5.201	127.6	0.9690	0.270
1.186	0.893	5.445	85.5	0.9914	0.309
1.209	0.987	5.808	65.7	1.007	0.341
1.236	1.119			1.024	0.378
1.273	1.305	0.6415	0.0445	1.046	0.427
1.308	1.508	0.6426	0.0446	1.070	0.488
1.349	1.769	0.6465	0.0452	1.093	0.554
1.393	2.090	0.6533	0.0467	1.124	0.648
1.433	2.401	0.6619	0.0476	1.167	0.810
1.483	2.820	0.6717	0.0501	1.208	0.983
1.533	3.280	0.6801	0.0502	1.267	1.273
1.567	3.634	0.6864	0.0522	1.307	1.495
1.629	4.333	0.6932	0.0539		
1.697	5.132	0.7027	0.0561		
1.760	5.931	0.7116	0.0584		
1.830	6.948	0.7214	0.0622		
1.912	8.272	0.7338	0.0651		

where N_d and N_s are the density of electronic states at the Fermi level in the *d* and *s* bands. The terms $C_{es}{}^d$ and $C_{es}{}^s$ are the specific heats due to the larger and smaller gaps, respectively. It is to be expected for a very small energy gap and for temperatures not too low that $C_{es}{}^s=\gamma T$, which then gives $N_s/(N_s+N_d) = \gamma_s/\gamma = 0.0052$. Therefore, according to the theory of Suhl *et al.*,[23] the smaller energy gap should be about an order of magnitude lower than the larger gap. Sung and Shen[26] were able to fit the specific-heat data[12] of high-purity niobium very well by using the two gap theory of Suhl *et al.* They used: $2\Delta_s(0)=0.32kT_c$, $\eta=0.5$, and $N_s/(N_s+N_d)=0.015$, where $\Delta_s(0)$ is the smaller energy gap at 0°K and η is related[27] to the coupling constant between the *s* and *d* bands. To fit our data on vanadium the theory must predict a contribution to the specific heat which is linear in T down to about $t=0.12$. This can be satisfied by using $2\Delta_s(0) \lesssim 0.10kT_c$ and $\eta \lesssim 1.0$. Measurements at lower temperatures need to be made to determine $\Delta_s(0)$ more precisely. The term $C_{es}-\gamma_s T$ should then be the contribution to the specific heat from the larger energy gap only, i.e., $N_dC_{es}{}^d/(N_s+N_d)$.

Figure 3 shows both the total superconducting electronic specific heat C_{es} and the term $C_{es}-\gamma_s T$. Actually the term γ_s was found by trial and error from this type of plot. As γ_s varies from 0.048 to 0.053 mJ

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[23] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Letters 3, 552 (1959).

[24] J. W. Garland, Jr., Phys. Rev. Letters **11**, 111 (1963).

[25] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[26] C. C. Sung and L. Yun Lung Shen, Phys. Letters **19**, 101 (1965).

[27] See Ref. 26. Their α is our η.

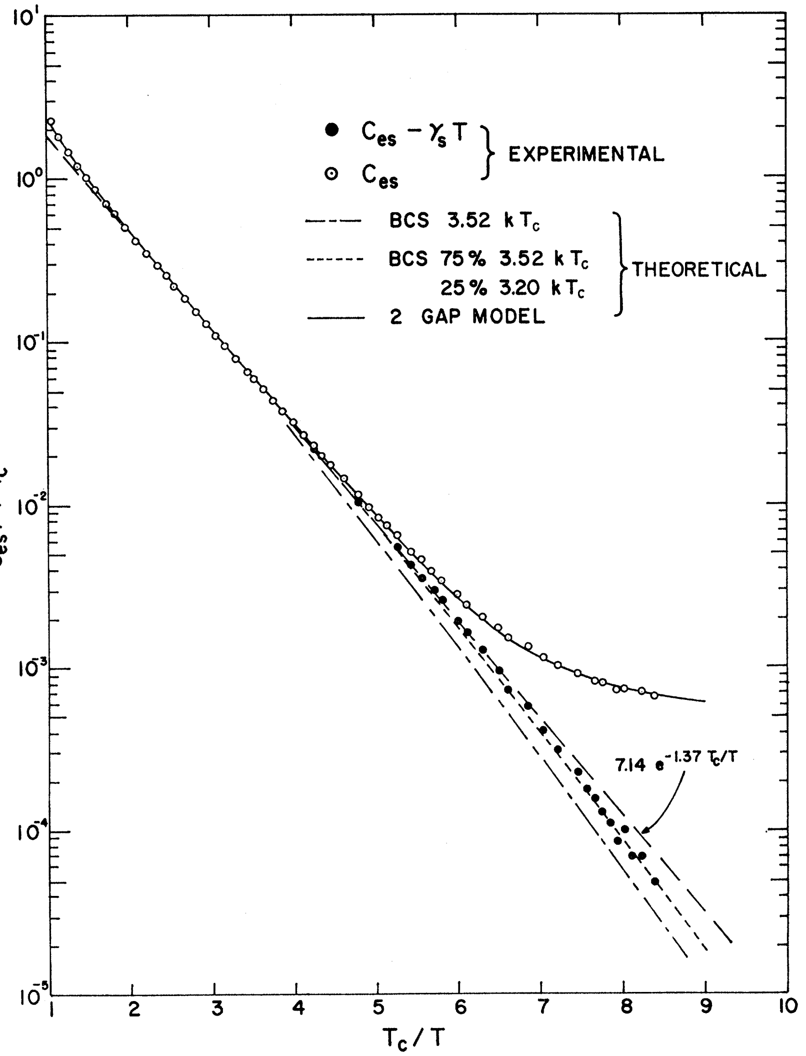

FIG. 3. Comparison of the superconducting electronic specific heat of vanadium with various theoretical predictions. The two-gap model includes the anisotropy of the larger gap.

mole^{-1} deg^{-2}, the low-temperature data change from perfect exponential behavior ($7.14e^{-1.37T_c/T}$) to a much stronger function of temperature. The value 0.051 mJ mole^{-1} deg^{-2} for γ_s was chosen to give an approximate BCS type behavior for $C_{es}-\gamma_s T$. Several different theoretical methods of describing $C_{es}-\gamma_s T$ were tested: (a) BCS theory (isotropic gap of $3.52kT_c$), (b) modified BCS theory using an isotropic gap of different value, (c) modified BCS theory using an anisotropic gap. Method (a) is shown in Fig. 3 and, as can be seen, does not agree with experiment at low temperatures. Method (b) is not represented in this figure but was unable to give a good fit of the data at all temperatures. As the figure shows, method (c) gives an excellent fit for all temperatures when it is assumed that 75% of the Fermi surface has a gap of $2\Delta_d(0)=3.52kT_c$, and the remainder of the surface has a gap of $2\Delta_d(0)=3.20kT_c$. Each of the gaps was assumed to have a BCS temperature dependence. These are given as possible values but certainly are not unique since so many variable parameters are used. The specific heat due to this anisotropic energy gap is taken as

$$C_{es}{}^d(t)=\sum_{i=1}^{N} A_i C_{es}(\Delta_d{}^i,t)\,, \qquad (7)$$

with

$$\sum_{i=1}^{N} A_i=1\,, \qquad (8)$$

where A_i is the fraction of the Fermi surface with the gap $\Delta_d{}^i$. We have chosen the simple case of $N=2$. The BCS theory leads to the following equation for $C_{es}(\Delta_d{}^i,t)$:

$$C_{es}(\Delta_d{}^i,t)=\frac{6}{\pi^2}\frac{1}{t^2}\int_0^\infty \frac{\exp[(x^2+u_i{}^2)^{1/2}/t]}{\{\exp[(x^2+u_i{}^2)^{1/2}/t]+1\}^2} \times\left[x^2+u_i{}^2-\frac{t}{2}\frac{d(u_i{}^2)}{dt}\right]dx\,, \qquad (9)$$

where $u_i = \Delta_d^i(t)/kT_c$. This equation was integrated numerically with the aid of a digital computer. The value for $[C_{es}/\gamma T_c]_{T_c}$ from these measurements is 2.49 compared with the anisotropic gap value of 2.38 and the normal BCS value of 2.43. The curve in Fig. 3 representing the two gap model is the theoretical prediction for the total superconducting electronic specific heat C_{es} as determined from Eq. (6) by using $C_{es}{}^s = \gamma T$; $N_s/(N_s+N_d) = 0.0052$, and from Eqs. (7), (8), and (9) for $C_{es}{}^d$.

For our sample, $C_{es}/\gamma T_c$ deviates from the expression $7.14\, e^{-1.37T_c/T}$ for $T_c/T > 4$. Measurements by Shen *et al.*[12] on a vanadium sample with a resistance ratio ten times smaller than our sample showed that $C_{es}/\gamma T_c$ deviated from exponential behavior only for $T_c/T > 7$, which implies that the specific-heat contribution due to the smaller energy gap is also about ten times smaller than in our case. The apparent increase of $N_s/(N_s+N_d)$ with purity has already been observed in niobium and tantalum.[12] Calculations[28] show that $N_s/(N_s+N_d) = 0.046$ for vanadium when assuming a parabolic s band and 0.5 s electrons per atom. Our value of 0.0052 is about ten times smaller than the calculated value, but it may very well be that this number will approach 0.046 in much purer samples.

C. Energy Gap

According to BCS, the energy gap $2\Delta_d(0)$ may be estimated from free-energy considerations by the relation

$$\frac{2\Delta_d(0)}{kT_c} = (4\pi/\sqrt{3})\left(\frac{H_c^2(0)V}{8\pi\gamma T_c^2}\right)^{1/2}. \tag{10}$$

Actually $\gamma - \gamma_s$ should be used in place of γ, but in this calculation γ_s is negligible. Using the values of γ and T_c found before and the value of $H_c(0)$ to be discussed later gives $2\Delta_d(0)/kT_c = 3.52 \pm 0.02$, which is just the value predicted by the BCS theory. Following Goodman,[8] $\Delta_d(0)$ may also be estimated from the coefficient b in Eq. (5) by the relation

$$2\Delta_d(0)/kT_c = 3.52(b/1.44), \tag{11}$$

which results in $2\Delta_d(0)/kT_c = 3.35 \pm 0.02$. This is somewhat lower than the value just obtained from free-energy considerations but can be expected when the energy gap is anisotropic. The coefficient b is determined for $T_c/T > 2.0$, and at these lower temperatures the minimum of the energy gap becomes more effective in determining C_{es}. The value obtained from free-energy considerations is more sensitive to the high-temperature specific heat so that 3.52 would be close to the maximum value of the gap. As discussed previously, the specific heat showed the need for an anisotropic gap with a maximum of $3.52kT_c$ and a minimum of $3.20kT_c$. Corak *et al.*[2] obtained the value 3.58 from Eq. (10) and 3.66 from Eq. (11), but their sample had sufficient impurities to eliminate most of the energy gap anisotropy.

Bohm and Horwitz[10] measured ultrasonic values for the energy gap in planes normal to three different crystal directions in vanadium with a resistance ratio of 130. Their values for the energy gap in units of kT_c are 3.1±0.2 in the $\langle 100\rangle$ direction, 3.4±0.2 in the $\langle 110\rangle$, and 3.2±0.2 in the $\langle 111\rangle$. Our results for the anistropy of the larger energy gap are certainly consistent with their measurements. Ultrasonic measurements by Brewster *et al.*[29] showed that the energy gap in the $\langle 110\rangle$ direction varied from 3.4±0.2 in dirty samples to 3.5±0.2 in a clean sample. Infrared-absorption[30] and tunneling[31] measurements both give a value of 3.4 for the energy gap. Toxen[32] pointed out that the relationship

$$\frac{2\Delta(0)}{kT_c} = \frac{2T_c}{H_c(0)}\left(\frac{dH_c}{dT}\right)_{T_c} \tag{12}$$

holds for nearly all superconductors. With vanadium one would take $\Delta(0) = \Delta_d(0)$ in this equation. For our sample the right-hand side of Eq. (12) becomes 3.55, which indicates the relationship holds very well for vanadium.

D. Transition Temperature and Gap Anisotropy

Extremely sharp reproducible changes in slope occurred in the heating and cooling curves when passing through the superconducting-normal transition in zero field. The earth's magnetic field was not compensated during these measurements. Cooling curves were not used in the determination of the transition temperature since they showed an appearance of supercooling of about 3 mdeg and required about 1 min for the sample to come back to thermal equilibrium after leaving the supercooled state. Since the measuring sensitivity was about 0.5 mdeg, further details of the cooling curves could not be obtained. In a true zero field no supercooling should occur, but for these heating and cooling curves the earth's field was still present and would give rise to a mixed state[13] 1 or 2 mdeg in width between the superconducting and normal states. A resistance to flux motion exists in the mixed state near $H_{c1}(T)$[13] which can delay entry of the sample into the superconducting state during cooling. During heating, however, the resistance to flux motion acts to decrease the width of the mixed state. The transition for the heating curves had a total width of only about 1 mdeg and occurred at (5.379±0.004)°K. The total transition

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[28] D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, D. W. Pracht, and T. J. Rowland, Phys. Rev. **135**, A455 (1964).

[29] J. L. Brewster, M. Levy, and I. Rudnick, Phys. Rev. **132**, 1062 (1963).

[30] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

[31] I. Giaever, in *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 171.

[32] Arnold M. Toxen, Phys. Rev. Letters **15**, 462 (1965).

TABLE IV. Energy-gap anisotropy of several elements.

Element	$\langle a^2\rangle$	Reference
V	0.016	this work
Sn	0.019	a
In	0.021	a
Al	0.011	a
Zn	0.047	b
Ta	0.011	c

[a] Reference **35**.

[b] D. Farrell, J. G. Park, and B. R. Coles, Phys. Rev. Letters **13**, 328 (1964).

[c] D. P. Seraphim, D. T. Novick, and J. I. Budnick, Acta Met. **9**, 446 (1961). (A value $S/S_f = 0.6$ was used for the Fermi surface area of Ta.)

width was taken as the interval wherein the heating curve slope changed from one constant value to another. The major source of error in T_c comes from the uncertainty in the calibration of the germanium thermometer. The highest calibration point was at 5.186°K, which is just below the critical temperature of He^4. The transition temperature, therefore, had to be obtained by extrapolating the calibration curve, which results in an uncertainty of about 3 mdeg. Any error inherent in the 1958 He^4 temperature scale is not included.

The transition temperature of this sample is higher than that reported by other investigators[2,5–7] due to better purity. A measure of the purity is given by $1/\rho_r$ which is proportional to the mean free path and defined by $\rho_r = R_0/(R_{295} - R_0)$ where R_{295} is the room temperature resistance and R_0 is the residual resistance. Figure 4 shows the variation of the transition temperature with ρ_r. Extrapolating to infinite mean free path yields a value of $T_{c0} = (5.414 \pm 0.010)$°K for the intrinsic transition temperature of vanadium. Anderson[25] proposed that the initial decrease of T_c for small impurity concentrations arises from the removal of the anisotropy of the energy gap by impurity scattering of the electrons. Until the gap anisotropy is removed the change in T_c is independent of the impurity. According to Anderson the gap anisotropy should be nearly removed when the mean free path l becomes comparable with the coherence length ξ_0, but there is experimental evidence[33,34] that the anisotropy is not completely removed until l is reduced to a few percent of ξ_0. Beyond this region the change in T_c depends on the specific impurity. For vanadium $l = \xi_0$ when $\rho_r = 0.039$ and is indicated by the arrow in Fig. 4. In view of the preceding discussion most of the data in Fig. 4 should be in the anisotropy region. Consequently, the slope $dT_c/d\rho_r$ may be used to calculate the anisotropy of the energy gap as shown by several authors.[35–37]

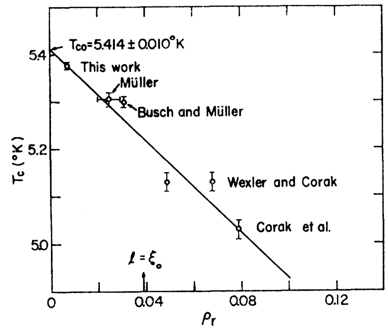

FIG. 4. Variation of T_c with normal-state electronic mean free path.

Markowitz and Kadanoff[35] (MK) take the anisotropy into account by introducing a simple factorized form for the matrix elements coupling pairs formed from states with momenta $\pm\mathbf{p}$ and $\pm\mathbf{p}'$:

$$V_{\mathbf{pp}'} = [1 + a(\hat{\Omega})]V[1 + a(\hat{\Omega}')], \tag{13}$$

where $\hat{\Omega}$ and $\hat{\Omega}'$ are unit vectors along $\mathbf{p}$ and $\mathbf{p}'$ and $a(\hat{\Omega})$ describes the anisotropy of the interaction. The terms $a(\hat{\Omega})$ are chosen so that their average is

$$\langle a\rangle = \int \frac{d\Omega}{4\pi} a(\hat{\Omega}) = 0. \tag{14}$$

The energy gap then has an angular dependence given by $[1 + a(\hat{\Omega})]$. Hence, the mean-square deviation $\langle a^2\rangle$ is a measure of the anisotropy of the energy gap. MK show that the change in transition temperature from that of the pure metal can be given by

$$\Delta T_c = \langle a^2\rangle T_{c0} I(\chi) + K^i\chi, \tag{15}$$

where K^i depends on the impurity (denoted by i) and the host. The function $I(\chi)$ is calculated by MK with $\chi = \hbar/kT_c\tau_a$, where τ_a is a relaxation time characteristic of the effect of electron scattering on energy-gap anisotropy. If τ_a is assumed to be the same as the relaxation time associated with electrical conduction, then the value $\chi = 142\rho_r$ is obtained for vanadium using a Fermi surface area of 0.714 times the free-electron area.[13] In the anisotropy region the term $\langle a^2\rangle T_{c0} I(\chi)$ should dominate Eq. (15), and in the limit of infinite mean free path $I(\chi)$ is given by MK as $I(\chi) = -(\pi/8)\chi$. The anisotropy $\langle a^2\rangle$ can then be obtained from the experimentally determined value of $dT_c/d\rho_r$ for large mean free paths. From Fig. 4 it follows that $dT_c/d\rho_r = 4.8$°K. An equivalent expression for $\langle a^2\rangle$ is given by

$$\langle a^2\rangle = \lim_{l\to\infty} 0.458 \frac{d(T_c/T_{c0})}{d(\xi_0/l)}, \tag{16}$$

in which the relation between $\langle a^2\rangle$ and the ratio ξ_0/l is easily seen. The values of $\langle a^2\rangle$ for vanadium and several other elements are displayed in Table IV. These values show that the energy-gap anisotropy of vanadium is approximately the same as for the other elements listed with the exception of zinc. The ultra-

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[33] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. **137**, A103 (1965).

[34] B. B. Goodman, Rev. Mod. Phys. **36**, 198 (1964).

[35] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[36] C. Caroli, P. G. de Gennes, and J. Matricon, J. Phys. Radium **23**, 707 (1962).

[37] T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **28**, 857 (1962).

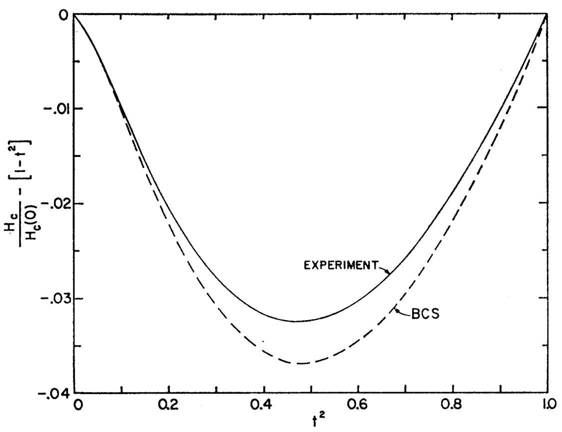

FIG. 5. Deviation of the thermodynamic critical field of vanadium from the parabolic law.

sonic work of Bohm and Horwitz[10] gives only a rough indication of $\langle a^2\rangle$, which is not inconsistent with the result $\langle a^2\rangle = 0.016$. Using the gap values $3.52kT_c$ and $3.20kT_c$ occupying 75% and 25% of the Fermi surface, as determined from the specific-heat measurements, leads to the value $\langle a^2\rangle = 0.006$. However, this result should also be regarded as only a rough indication of the true value, since specific-heat measurements do not determine a unique behavior of the energy gap at the Fermi surface.

E. Thermodynamic Critical Field H_c

The difference in entropy, $\Delta S(T)$, between the normal and superconducting states was derived from the specific heat, neglecting the nuclear contribution, through the thermodynamic relation

$$\Delta S(T) = S_n(T) - S_s(T) = \gamma T + \tfrac{1}{3}\alpha T^3 - \int_0^T (C_s/T)dT, \quad (17)$$

where the integration was carried out numerically. The entropy difference at the transition temperature was made to vanish in accordance with a second order phase transition, which also was consistent with the experimental error in smoothed values of C_s. This further supports the choice of values for γ and α.

The thermodynamic critical field $H_c(T)$ was then deduced by numerical integration of the relation

$$H_c^2(T) = (8\pi/V)\int_T^{T_c} \Delta S(T)dT, \quad (18)$$

where $V = 8.34$ cm^3 mole^{-1} is the molar volume for vanadium.[2] Equation (18) leads to a value for $H_c(0)$ of 1421±5 Oe. If nuclear entropy is included, $H_c(T)$ will be lowered in the order of 50 Oe below about 10^{-4}°K. The discrepancy between the present value of $H_c(0)$ and the value 1310 Oe found by Corak *et al.*[2] can be attributed to the difference in purity of the samples. The deviation of $H_c(T)$ from the parabolic law is shown in Fig. 5 and is in good agreement with the BCS prediction for weak-coupling superconductors. The quantity $(dH_c/dT)_{T_c}$ has the value (-469.3 ± 1.9) Oe deg^{-1} as deduced from the jump in the zero-field specific heat through the Rutgers formula,

$$\left(\frac{\Delta C}{T}\right)_{T_c} = \frac{V}{4\pi}\left(\frac{dH_c}{dT}\right)_{T_c}^2. \quad (19)$$

A large part of the error arises from an uncertainty in the molar volume V.

IV. CONCLUSIONS

The value (382±10)°K for Θ_0 (calorimetric) found in these measurements is higher than that arrived at from previous calorimetric investigations and also is in closer agreement with the value 399.3°K deduced from elastic measurements. The error of ±10°K is not enough to account for the difference between the two values; however, this error includes only the standard deviation associated with random scatter of the data. There is reason to believe the difference may be real and not due entirely to systematic errors in Θ_0 (calorimetric). The difference may be a result of a sudden change in Θ at about 3°K or below, as in niobium, or it may be due to a decrease of Θ_0 with purity. Further work is necessary to make any definite conclusions.

The low-temperature superconducting specific heat cannot be explained by the BCS theory alone. Instead, a modification which predicts two energy gaps, such as the theory of Suhl *et al.*,[23] is necessary to explain the data. The existence of a linear term down to $t = 0.12$ in the superconducting specific heat places an upper bound of about 0.10 for the smaller energy gap $2\Delta_s(0)/kT_c$, which is considerably less than the value 0.32 for niobium.[26] The linear term is about ten times larger than that previously seen[12] in a less pure sample of vanadium. The results also indicate that the larger energy gap for this sample is slightly anisotropic. Because of this anisotropy, the transition temperature increases with increasing electronic mean free path and approaches the intrinsic value $T_{c0} = (5.414\pm0.010)$°K.

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