refractive index change and of the dispersion change found experimentally for the gamma-ray-irradiated specimen 907, 30% smaller than that calculated from Eqs. (8) and (9).

It is apparent that the results are in good agreement with the modified dispersion theory introduced here, which assumes that the vacancies are generated during irradiation and are stabilized by the trapping of electrons to form color centers. The assumptions that the vacancies pre-empt a volume of the crystal about that of an equivalent number of occupied lattice sites and that the oscillator strength of the F centers is nearly unity, appear to be correct within the estimated precision of the work, about 20%. The results lend additional confirmation to the dispersion theory first introduced into the subject by Smakula⁵ and modified somewhat here, and about which some question has recently been raised.¹⁰ The advantage of also measuring the real part of the complex refractivity which was done here, is that it is sensitive to the whole spectrum of effects which take place in the crystal, whereas the imaginary part of the refractivity which has been used exclusively in the past investigations is sensitive only to particular oscillators under investigation. Although

the relative precision obtained here was low, it is quite evident that there are no important contributions to the effects from oscillators outside of the range of the instruments used other than those that are summed by considering the refractivity changes in the "base material," nor from very broad bands of small absorption coefficient within the wavelength range of the instruments. Since unknown effects were being investigated, the experiments were not designed to obtain specific information, but rather to elucidate the phenomena. It should now be possible to design experiments which would give specific information about the relationship of the number of centers to the dilatation and the absorption, and to the refractivity changes in the rest of the crystal, the "base material."

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Specific Heat of Gallium and Zinc in the Normal and Superconducting States*†

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By using a He³ cryostat the specific heat of gallium has been measured between 0.35°K and 4.3°K, and that of zinc between 0.42°K and 4.2°K. Measurements on Ga in the normal state indicate that the coefficient of the electronic specific heat, γ , is 0.601 millijoule/mole (°K)² while the Debye characteristic temperature θ at 0°K is 317°K. For Zn, $\gamma = 0.640$ millijoule/mole (°K)²; $\theta = 309$ °K. The electronic specific heat in the superconducting state, C_{es} , for both metals for T well below the transition temperature, T_c can be represented by the expression $C_{es} = a\gamma T_c e^{-bT_c/T}$. For Ga, $T_c = 1.087$ °K, a = 7.0, and b = 1.35. The zinc sample measured has a broad transition, T_c taken as 0.852°K. Also for Zn, a = 6.4 and b = 1.27. The magnetic threshold field curves are calculated from these specific heat results. The critical field at 0°K for Ga is 59.4 gauss and for Zn, 53.4 gauss.

In comparing these measurements with the calorimetric results of other superconductors a definite variation is noted in the parameters a, b, $(C_{es}-C_{en})/\gamma T_e$ at T_e , and $\gamma T_e^2/V_m H_0^2$. There appears to be a correlation between the magnitudes of these quantities and the transition temperature.

INTRODUCTION

 \mathbf{I} N the past few years a great deal of evidence has been presented in support of the idea that in the superconducting state there exists an energy gap in the single electron energy spectrum. One of the first experiments of this kind was the measurement by Corak *et al.*¹ of the specific heat of vanadium. They found that in the temperature region $T < 0.7T_c$ (T_c being the transition temperature), the electronic specific heat in the superconducting state could be represented by an equation of the form

$$C_{es} = a\gamma T_c e^{-bT_c/T},\tag{1}$$

where γ is the coefficient of the electronic specific heat in the normal state. They also suggested that there may, indeed, be a law of corresponding states for superconductors in which case the constants *a* and *b* would be the same for all superconductors. For vanadium and

^{*} This work was supported in part by a Signal Corps contract. † This paper is based partly on a thesis submitted by George M. Seidel to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. 96, 1442 (1954); 102, 656 (1956).

for tin² the values found for these constants are a=9.2and b=1.50. When analyzed for an exponential temperature dependence, the data on the specific heat of superconductors,³ niobium,^{4,5} tantalum,^{6,7} other indium,8 and thallium,9 can also be fitted within experimental error by the same constants. However, the results on aluminum^{10,11} are quite different, the best values of the constants being a=7.6 and b=1.32, and it appears that the law of corresponding states is of only approximate validity. The question then arises: Do the values of the constants for other superconductors show a similar variation, and if so does there appear to be any regularity in the variation?

Many of the measurements mentioned above suffer from the fact that the lattice contribution is a major fraction of the total specific heat, thus making it difficult to obtain the electronic specific heat with sufficient accuracy. To avoid this difficulty, gallium and zinc were selected for investigation as the lattice specific heat of these metals is only a small part of the total specific heat in the superconducting state. However, since both Ga and Zn have low transition temperatures, only relatively low values of T_c/T can be obtained with the present apparatus.

The theory of superconductivity recently proposed by Bardeen, Cooper, and Schrieffer¹² leads to an energy gap model of the superconducting state in agreement with many different types of experiments. One consequence of the energy gap is that for T well below T_c the electronic specific heat is given by Eq. (1). The theory also predicts a law of corresponding states with a=8.5and b = 1.44, values in quite reasonable agreement with experiment considering the approximations made in the theory.

EXPERIMENTAL

Temperatures down to 0.3°K are obtained in a cryostat employing a bath of liquid He³ as a coolant. Since the cryostat is described in detail in a previous paper,¹³ only a few points of particular interest need to be mentioned here.

The temperature dependence of a carbon resistance

(1958).
⁴ Brown, Zemansky, and Boorse, Phys. Rev. 92, 52 (1953).
⁵ Chou, White, and Johnston, Phys. Rev. 109, 788 (1958).
⁶ Worley, Zemansky, and Boorse, Phys. Rev. 99, 447 (1955).
⁷ White, Chou, and Johnston, Phys. Rev. 109, 797 (1958).
⁸ J. R. Clement and E. H. Quinnell, Phys. Rev. 92, 258 (1953).
⁹ J. L. Snider and J. Nicol, Phys. Rev. 105, 1242 (1957).
¹⁰ B. B. Goodman, Conference de Physique des Basses Temperatures, Paris, 1955 (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956).
¹¹ N. E. Phillips, Proceedings of the Fifth International Conference of Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957 (University of Wisconsin Press, Madison, Wisconsin, 1957 Wisconsin, 1958). (University of Wisconsin Press, Madison,

¹² Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

¹³ G. Seidel and P. H. Keesom, Rev. Sci. Instr. 29, 606 (1958).

thermometer attached to the sample is determined in different ways depending on the temperature range. Above 1°K the temperature is determined from the vapor pressure of He⁴ (T_{55E} scale). The He³ vapor pressure measurements of Sydoriak and Roberts14 (based, in turn, on the T_{55E} scale) are used for calibration between 0.5°K and 1.0°K. Below 0.5°K the susceptibility of a paramagnetic salt is relied on for temperature calibration.

The carbon thermometer used in these measurements is a 0.1-watt, nominal 10-ohm, Allen Bradley resistor which has a remarkable sensitivity below 1°K. At 1.0°K the resistance is 400 ohms while at 0.30°K the resistance is approximately 60 000 ohms.

On the average, 40 calibration points are taken in the course of each heat capacity experiment, 20 points above and 20 below 1°K. For convenience in handling the calculations the resistance R versus temperature Tcurve is broken up into two sections, one from 0.3°K to 1.3°K and the other, slightly overlapping the first, from 1.0°K to 4.2°K. Each section is then fitted by digital computer with the best curve in the least-

TABLE I. Specific heat of zinc, in millijoules/mole (°K).

T (°K)	С	<i>Т</i> (°К)	С	<i>T</i> (°K)	С	
Before heat		Before	Before heat		Before heat	
treatment		treatr	treatment		treatment	
0.4207	0.277	0.7952	1.138	3.295	4.57	
0.4236	0.279	0.8063	1.160	3.541	5.40	
0.4253	0.285	0.8064	1.157	3.756	6.02	
0.4279	0.288	0.8187	1.210	3.847	6.29	
0.4365	0.302	0.8232	1.201	3.940	6.94	
0.4458	0.317	0.8306	1.227	4.043	7.31	
0.4654	0.352	0.8396	1.221	4.145	7.80	
0.4735	0.366	0.8432	1.170	4.239	8.19	
0.4816	0.380	0.8492	1.027	After	heat	
0.4900	0.396	0.8591	0.749	treatr	nent	
0.4970	0.408	0.8627	0.748	0 7331	0.964	
0.5163	0.451	0.8735	0.639	0.7450	0.997	
0.5278	0.473	0.8891	0.632	0.7566	1.033	
0.5387	0.499	0.8892	0.630	0.7866	1.102	
0.5474	0.515	0.9053	0.630	0.7981	1.136	
0.5556	0.526	0.9183	0.642	0.8196	1.195	
0.5651	0.550	0.9462	0.665	0.8244	1.214	
0.5762	0.581	0.9723	0.087	0.8352	1.227	
0.5982	0.619	0.9915	0.723	0.8463	1.136	
0.6087	0.055	1.079	0.770	0.8521	0.967	
0.0191	0.074	1.141	0.829	0.8689	0.648	
0.0393	0.721	1.195	0.070	0.8761	0.632	
0.0557	0.752	1.200	1.020	0.8946	0.639	
0.0072	0.797	1,331	1.020	0.9104	0.646	
0.0009	0.820	1.570	1 252	0.9405	0.670	
0.0938	0.839	1.505	1 265	2.054	1.881	
0.7047	0.885	1.577	1.205	2.078	1.917	
0.7103	0.920	1.875	1.658	2.099	1.953	
0.7280	0.940	2 322	2 30	2.506	2.68	
0 7440	1 001	2.352	$\frac{2.00}{2.40}$	2.548	2.74	
0 7579	1 022	2.794	3 29	2.606	2.89	
0.7712	1.071	2.841	3.40	2.678	3.02	
0.7826	1.108	2.884	3.49	3.270	4.63	
0.7851	1.110	3.126	4.12	3.304	4.97	
0.7948	1.116	3.214	4.38	3.452	3.24 6 77	
				3.831	0.11	
				3.913	1.55	

¹⁴ S. G. Sydoriak and T. R. Roberts, Phys. Rev. 106, 175 (1957).

² W. S. Corak and C. B. Satterthwaite, Phys. Rev. 102, 662 (1956).

³ For an extensive discussion of these previous specific heat measurements see the recent review article by Biondi, Forrester Garfunkel, and Satterthwaite, Revs. Modern Phys. 30, 1109 (1958).

squares sense of the form

$$(\log R)/T = a_0 + a_1 \log R + a_2 (\log R)^2 + a_3 (\log R)^3 + a_4 (\log R)^4.$$
 (2)

Deviations of the individual points from the computed curves are at most 0.003°K at 4.2°K, 0.001°K, at 1°K, and 0.0004°K at 0.5°K.

The heat capacity measurements are performed in the usual manner, by observing the resistance change of the thermometer while adding a known pulse of heat to the sample. From these raw data the calculations of the temperature and the specific heat of the sample are all performed by computer. The heat capacity of the addenda (thermometer, heater wire and adhesive) is estimated to be less than 0.3% of the total heat capacity of either the gallium or zinc sample used, and is accounted for in the calculations.

Although a temperature of 0.3° K can be obtained with this He³ cryostat, the specific heat measurements on zinc extend only down to 0.42° K and on gallium only to 0.35° K. Because of the degree of thermal isolation of the sample required for reliable heat capacity measurements, the small amount of heat developed in the thermometer (approximately 0.1 erg/sec) is sufficient to keep the sample considerably above the temperature of its surroundings.

To remove the possibility of the earth's magnetic field affecting the measurements on the superconducting state, one of the vacuum cans surrounding the sample is coated with a layer of normal solder (50% lead, 50%)

TABLE II. Specific heat of gallium, in millijoules/mole (°K).

T (°K)	С	T (° K)	С	<i>Т</i> (°К)	С
0.3532	0.0734	0.6745	0.560	1.327	0.935
0.3535	0.0744	0.6902	0.592	1.359	0.975
0.3567	0.0761	0.6965	0.606	1.385	1.001
0.3601	0.0801	0.7215	0.661	1.630	1.246
0.3712	0.0914	0.7366	0.697	1.683	1.310
0.3750	0.0957	0.7565	0.741	1.940	1.626
0.3926	0.1108	0.7631	0.758	1.951	1.645
0.3997	0.1203	0.7882	0.821	2.264	2.17
0.4030	0.1221	0.8411	0.937	2.287	2.17
0.4057	0.1257	0.8522	0.975	2.308	2.20
0.4204	0.1403	0.8616	1.004	2.552	2.65
0.4363	0.1673	0.8867	1.067	2.577	2.70
0.4387	0.1659	0.9015	1.124	2.610	2.74
0.4450	0.1726	0.9259	1.168	2.638	2.83
0.4657	0.202	0.9615	1.287	2.854	3.32
0.4690	0.204	0.9769	1.323	2.892	3.44
0.4821	0.221	1.012	1.432	2.948	3.54
0.4855	0.228	1.028	1.476	3.049	3.82
0.4886	0.232	1.041	1.508	3.154	4.08
0.5103	0.262	1.052	1.536	3.290	4.50
0.5138	0.266	1.056	1.557	3.458	5.02
0.5370	0.302	1.061	1.590	3.577	5.45
0.5402	0.310	1.070	1.599	3.716	5.98
0.5434	0.310	1.074	1.620	3.815	6.41
0.5723	0.634	1.091	1.040	3.867	6.63
0.5753	0.365	1.103	0.748	3.984	7.15
0.6028	0.420	1.124	0.767	4.060	7.54
0.6064	0.430	1.125	0.762	4.143	7.90
0.6268	0.466	1.150	0.789	4.227	8.43
0.6357	0.483	1.177	0.808	4.309	8.86
0.6559	. 0.515	1.199	0.830	4.378	9.23



FIG. 1. C/T vs T^2 . Specific heat of gallium in the normal and superconducting states.

tin). This solder becomes superconducting somewhere above 4.2° K thus completely eliminating any magnetic field inside the can in the temperature range of these measurements.

The gallium sample used is a 250-gram ingot obtained from Eagle-Picher Company and has a stated minimum purity of 99.999%. The zinc, weighing 200 grams, also has a stated purity of 99.999% and was obtained from American Smelting and Refining Company. Since the superconducting transition was not very sharp for zinc (discussed below), an attempt was made to anneal the sample. The sample was maintained at 340°C for 40 hours and then returned to room temperature in 60 hours.

The results are given in Tables I and II.

RESULTS AND DISCUSSION

(a) Normal State

As can be seen in Figs. 1 and 2 where C/T is plotted against T^2 , the specific heat of both gallium and zinc in the normal state is not expressible simply as $C = \gamma T + \alpha T^3$. This means, in effect, that the lattice specific heat is not proportional to T^3 at these low temperatures where one would normally expect this to be the case. Consequently, the data are fitted by the best curve in the least-squares sense of the form

$$C_n = \gamma T + \alpha T^3 + \beta T^5. \tag{3}$$

The first term on the right-hand side of this equation



FIG. 2. C/T vs T^2 . Specific heat of zinc in the normal and superconducting states.

is assumed to be the electronic specific heat, C_{en} , while the last two terms together are taken as an empirical expression for the lattice specific heat, C_L , below 4.2°K. (The T^5 term is included in the lattice specific heat at low temperatures when the T^3 term is insufficient alone since the density of normal lattice vibrations, $g(\nu)$, at the low end of the frequency spectrum can be expressed as $g(\nu) = a\nu^2 + b\nu^4 + \cdots$. Thus $C_L = \alpha T^3 + \beta T^5 + \cdots$.)

The values found for the coefficients of Eq. (3)together with 70% confidence level limits are given in Table III. The large limits for zinc reflect the fact that the scatter of the results on zinc above 3°K is, for some inexplicable reason, larger than normally obtained. Nonetheless, these measurements are sufficiently accurate for the purpose, namely, to obtain a reasonable estimate of the lattice specific heat in the superconducting state. The limits on the coefficients account for all the random error in the experiment but, of course, do not include any systematic error of measurement. A possible systematic error of significance could arise from inaccuracies in the temperature scale and in fitting the R vs T curve as is done by Eq. (2). But since it is felt that these errors should be no larger than 0.5%, they are not included in the limits of error.

For comparison, the results of this work are expressed in terms of the Debye characteristic temperature θ and listed in Table IV along with previous measurements

TABLE III. Specific heat of Ga and Zn in the normal state. Coefficients of the equation $C_n = \gamma T + \alpha T^3 + \beta T^5$.

	$\left(\frac{\text{millijoules}}{\text{mole } (^{\circ}\text{K})^{2}}\right)$	$\left(\frac{\text{millijoules}}{\text{mole (°K)}^4}\right)$	$ \begin{pmatrix} \beta \\ \frac{\text{millijoules}}{\text{mole } (^{\circ}\text{K})^{6}} \end{pmatrix} $		
Ga	0.601 ± 0.003	0.0608 ± 0.0008	$\substack{0.00092 \pm 0.00004\\ 0.00039 \pm 0.00014}$		
Zn	0.640 ± 0.008	0.0660 ± 0.0025			

performed in the liquid helium temperature region. As can be seen from the table, these results on zinc agree reasonably well with the previous measurements, the differences being within the combined experimental errors. Unfortunately, nothing can be said concerning the disagreement in the value of γ of gallium as Wolcott in his short abstract gives no information upon which to judge the accuracy of his work.

(b) Superconducting State

Before discussing the results of the specific heat measurements on the superconducting state, it should be pointed out that the measurements on gallium are more satisfactory than those made on zinc. This is not due to inaccuracies in the zinc measurements but is due rather to the following: (1) Considerably lower values of reduced temperature, $t = T/T_c$, were obtained for Ga than for Zn, a fact that makes the analysis of the exponential temperature dependence of the electronic specific heat much more certain. And (2) the

TABLE IV. Specific heat of Ga and Zn in the normal state expressed in terms of the Debye characteristic temperature θ .

	$\left(\frac{\text{millijoules}}{\text{mole }(^{\circ}K)^{2}}\right)$	θ (0°K) (°K)	θ (4°K) (°K)
Ga: This work	0.601	317	295
Wolcotta	0.75	333	
Zn: This work	0.640	309	300
Smith ^b		306	300
Silvidi and Daunt ^e	0.66	296	296
Keesom and Van den Ende	0.65	321	321

^a N. M. Wolcott, Bull. Am. Phys. Soc. Ser. II, 1, 289 (1956).
 ^b P. L. Smith, Phil. Mag. 46, 744 (1955).
 ^c Data recalculated by P. H. Keesom and N. Pearlman, Handbuch der Physik, edited by S. Flugge (Springer-Verlag, Berlin, 1956), Vol. 14.

transition from the normal to the superconducting state is much sharper for Ga than for Zn. As can be seen from the data listed in Table I, on decreasing the temperature the specific heat of the zinc sample begins rising at 0.90°K but does not reach a maximum until approximately 0.84°K. The attempt to anneal the sample, described in the foregoing, did not change this broad transition whatsoever. While the temperature of the onset of the superconducting transition is in good agreement with the value of 0.905°K found by Goodman and Mendoza,¹⁵ T_c was chosen as 0.852°K for this sample. This is the temperature at which the specific heat is the average of the maximum value in the superconducting state and the minimum value in the normal state.

The gallium sample, on the other hand, has an extremely sharp transition. The transition is complete, as far as these measurements can tell, in at least 0.006°K, between 1.084°K and 1.090°K. Thus T_c is assumed to be 1.087°K for this sample, a value slightly lower than the 1.103°K reported by Goodman and

¹⁵ B. B. Goodman and E. Mendoza, Phil. Mag. 42, 594 (1951).

Mendoza.¹⁵ (It will be noted that in Table II there is a point which has an average temperature of 1.091°K but has a large heat capacity. This is due to the fact that while the average temperature of the point is above T_c , the temperature before the heat pulse was added is below T_c .)

To determine the electronic specific heat in the superconducting state, C_{es} , the lattice specific heat, C_L , deduced from the measurements on the normal state above the transition temperature, is subtracted from the total specific heat, C_s ; i.e., $C_{es} = C_s - C_L$. Since C_L is at most 5% of C_s for both Ga and Zn in the temperature range measured, the accuracy of C_{es} is essentially that of C_s . When C_{es} is plotted as indicated in Fig. 3, the measurements on Zn for $T_c/T > 1.6$ and those on Ga for $T_c/T > 1.9$ can be seen to satisfy the equation

$$C_{es} = a\gamma T_c e^{-bT_c/T}.$$
 (1')

The values found for the constants a and b for Ga and Zn are listed in Table V along with reliable values found for other superconductors. For comparison, the predictions of the theory of Bardeen, Cooper, and Schrieffer (BCS) are also tabulated. While the results for Ga and Zn are in reasonable agreement with the measurements of Phillips on Al, the differences in the constants appear to be outside experimental error. Of greater significance, however, is the larger difference between the values of the constants for Al, Ga, and Zn and those found for other superconductors. Therefore, there can be no doubt that the law of corresponding states does not hold exactly in its present statement.

To check the accuracy of these measurements, the electronic entropy in the normal state, S_{en} , and in the superconducting state, S_{es} , are derived from the specific



FIG. 3. $C_{es}/\gamma T_o$ vs T_c/T . Triangles—zinc. Circles—gallium. To avoid confusion only representative points are indicated for low values of T_c/T .

heat data. Since $S = \int_0^T (C/T) dT$, one has $S_{en} = \gamma T$. S_{es} is obtained by graphically integrating the smoothed C_{es}/T vs T curve which is extrapolated to $T=0^{\circ}K$ in accordance with Eq. (1) using the appropriate constants listed in Table V. It follows that $(S_{en}-S_{es})/S_{en}$ evaluated at T_c is less than $\pm 0.4\%$, in good agreement with the fact that in the absence of a magnetic field the superconducting transition is not of the first order. This check does not imply, however, that C_{es} necessarily decreases to zero according to Eq. (1). Serious deviations from this equation could exist at temperatures lower than those measured without appreciably affecting the entropy.

	θ (0°K) (°K)	$\left(rac{\gamma}{\mathrm{millijoules}} ight)$	(°K)	H ₀ (gauss)	a	b	$\frac{C_{es}-C_{en}}{\gamma T_c}\bigg _{T_c}$	$\left(\frac{\gamma T_{c^2}}{V_m H_{0^2}}\right)$
Cdb	300	0.71	0.54	28.7			1.2	0.19
Zn°	309	0.640	0.852	53.4	6.4	1.27	1.30	0.177
Ga°	317	0.601	1.087	59.4	7.0	1.35	1.41	0.170
Ald	420	1.36	1.17	104	7.6	1.32	1.4	0.18
Tle	88	2.8 ?	2.36				<1.0 ?	
Inf	109	1.81	3.396	278			1.62	0.176
Sng	195	1.75	3.722	303	9.2	1.50	1.62	0.159
Tah	255	5.7	4.39	780	10	1.5	1.7	0.167
V ⁱ	338	9.26	5.03	1310	9.2	1.50	1.60	0.164
Phi	95	3.0	7.23				2.4	0.101
Ñb⊧	320	7.7	9.17	1944			2.0	0.159
BCS1					8.5	1.44	1.52	0.170

TABLE V. Tabulation of thermodynamic data determined from calorimetric measurements.^a

* The values of T_e and H_0 may differ somewhat from those quoted by other authors since calorimetric and magnetic results are in variance for some superconductors, e.g., Nb. In almost all cases the quantities $(C_{ee} - C_{en})/\gamma T_e|_{T_e}$ and $\gamma T_e^2/V_m H_0^2$ are our calculations from the original data. ^b See reference 16. Since the transition found by Samoilov is rather broad, T_e is re-estimated in the manner used for zinc in this work.

b See reference 16. Since the transition found by Gamonov is fature block, if the end of the work.
d See references 10 and 11. As both these references are preliminary reports we can expect better results on Al in the near future.
e See reference 9. Also, W. H. Keesom and J. A. Kok, Physica 1, 175, 503, 595 (1934).
f See reference 2.
b See reference 2.
b See reference 1.

¹ See reference 7.
 ¹ See reference 1.
 ¹ J. R. Clement and E. H. Quinnell, Phys. Rev. 85, 502 (1952); Horowitz, Silvidi, Malakker, and Daunt, Phys. Rev. 88, 1182 (1952).
 ^k See reference 5. In view of the inaccuracies in this measurement, we feel that the quoted deviations for Nb of C_{ee} from an exponential dependence on 1/T at high T_e/T (see Fig. 6 of reference 7) are not significant.
 ¹ See reference 12.



FIG. 4. $[1-(T/T_c)^2-H_c/H_0]$ vs $(T/T_c)^2$: deviation of the critical fields from quadratic temperature dependence. The curve for vanadium is taken from reference 1. The curve for tin is taken from reference 2.

The magnetic threshold field curve is determined for these superconductors by graphically integrating the expression

$$H_{c}^{2} = (8\pi/V_{m}) \int_{T}^{T_{c}} (S_{en} - S_{es}) dT, \qquad (4)$$

where V_m is the molar volume. To illustrate the temperature dependence of the resulting critical field, the quantity $[1-(T/T_c)^2-H_c/H_0]$ is plotted against $(T/T_c)^2$ in Fig. 4. This quantity is a measure of the deviation of the critical field from a quadratic temperture dependence

$$H_{c} = H_{0} [1 - (T/T_{c})^{2}], \qquad (5)$$

 H_0 being the critical field at 0°K. While the magnitudes of the deviations are somewhat larger, the general shape of the curves for Ga and Zn in Fig. 4 is quite similar to that found for many other superconductors.

The only extensive magnetic measurements on gallium and zinc are those of Goodman and Mendoza¹⁵ who found that, to the accuracy of their data, the critical field of both metals could be represented by a quadratic temperature dependence, Eq. (5). For Zn they obtained $H_0=52.5$ gauss whereas we find 53.4 gauss, values in good agreement. However, for Ga they obtained $H_0=50.3$ gauss while these measurements yield 59.4 gauss. This large discrepancy is likely due, in part, to the fact that Goodman and Mendoza extrapolate H_c to 0°K by using a quadratic temperature dependence. It is, nonetheless, surprising that the discrepancy in H_0 for Ga is so large since the calorimetric determinations of H_0 for Zn, Cd,¹⁶ and Al ¹⁰ agree quite

well with the magnetic values obtained for these metals by Goodman and Mendoza.

The data on the superconductors listed in Table V for comparison with these measurements on gallium and zinc are the results of calorimetric determinations only. Magnetic measurements of the critical field curve are, for the most part, of insufficient accuracy to be of use in this comparison.

The quantities $(C_{es}-C_{en})/\gamma T_c|\tau_c$ and $\gamma T_c^2/V_m H_0^2$ are tabulated for reference to the BCS theory. In terms of this theory $(C_{es}-C_{en})/\gamma T_c|\tau_c$ is a measure of the rate of change of the size of the energy gap with temperature at T_c , and $\gamma T_c^2/V_m H_0^2$ is primarily dependent upon the size of the gap at absolute zero. While the theory in its present form predicts that these quantities should be the same for all superconductors (law of corresponding states), this is definitely not the case. In fact, there appears to exist a tendency for a, b, and $(C_{es}-C_{en})/\gamma T_c|\tau_c$ to increase and for $\gamma T_c^2/V_m H_0^2$ to decrease with increasing transition temperature. Although these trends are not without deviation, there seems to be a correlation between the transition temperature and these various parameters.

The explanation of these variations is not immediately obvious. The simplest picture one can construct does not appear to be adequate; namely, to assume that the energy gap expressed in units of kT_c is not a universal function as predicted by BCS. Using the experimentally determined variation of $\gamma T_c^2 / V_m H_0^2$ and the expression for this quantity given by the BCS theory, a dependence of the energy gap at 0°K on T_c can then be calculated. The resulting variation of *a* and *b* with T_c , while having the correct sign, is much smaller than that observed.

Perhaps a more serious concern, however, is the following. While the majority of specific heat measurements on superconductors, including these on Ga and Zn, indicate that C_{es} is exponentially dependent on 1/T for T well below T_c , there exists some experimental evidence that this may not be the case for large values of T_c/T . The measurements of Goodman¹⁷ on aluminum and of both Goodman¹⁷ and Zavaritskii¹⁸ on tin indicate that C_{es} does not obey a simple 1/T exponential dependence. But as Biondi *et al.*³ carefully point out, these measurements for various reasons lack the precision necessary to make the results convincing. The answer to the question—what really is the correct temperature dependence.

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¹⁷ B. B. Goodman, Compt. rend. 244, 2899 (1957).

¹⁸ N. V. Zavaritskii, J. Exptl. Theoret. Phys. S.S.S.R. 33, 1085 (1957).