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Superconductivity of α- and β-Mercury*

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Precise critical field measurements and a direct measurement of $(\partial H/\partial P)_T$ as a function of temperature were made on physically identical samples of α- and β-Hg. The purpose of these measurements was to obtain data on the effects of crystal structure on the properties of superconductors, and to permit calculation of various thermodynamic quantities difficult to obtain in any other way. The critical fields of the two phases were found to be identical when expressed in terms of the reduced variables H/H_0 and T/T_c. No generalizations of this type could be found to explain the pressure effects. The advantages of an H^2 vs T^2 and $(\partial H^2/\partial P)$ vs T^2 analysis for extrapolation to absolute zero are stressed. The critical fields of several representative superconductors are compared with the critical field predicted by the Bardeen-Cooper-Schrieffer theory, using a plot that emphasizes the detailed shape of the curves at low temperatures. This plot also can be interpreted in terms of the θ/T_c dependence of the width of the energy gap. The agreement between calorimetric and critical field determinations of the electronic specific heat in the normal state is shown to be improved by using the H^2-T^2 extrapolation. The volume dependence of the reduced energy gap is shown to be very small for those superconductors for which pressure effect data are available.

INTRODUCTION

THE β-Hg phase, which is a stress-induced modification of solidified mercury, is stable at zero pressure below 79°K.[1] A solid-solid transition was first observed in mercury by Bridgman above 200°K at pressures in excess of 10 000 atm.[2] Extrapolation of his data to zero pressure indicated that the transition should have been observed near 80°K, but specific heat,[3] metallographic[4] and x-ray diffraction studies[4] gave no indication of such behavior down to liquid helium temperatures. The work of Jennings and Swenson[5] on the effect of pressure on the zero-field superconducting transition of mercury showed anomalous effects depending upon the thermal and mechanical history of the sample. Subsequent work by Swenson showed that this behavior could be understood on the basis of a polymorphic transition in mercury requiring stress to initiate formation of the β phase at all temperatures.[1] Preliminary work on the zero-pressure superconducting properties of the two phases was reported elsewhere.[6]

β-Hg crystallizes in a body-centered tetragonal lattice[7] which is close to a linear chain structure, while ordinary mercury (α-Hg) possesses a rhombohedral structure[4] which is almost close-packed. The great difference in the symmetry of the two lattices suggests quite different thermal and electrical properties for the two phases. A Debye θ for β-Hg of 93°K at 79°K can be estimated from the phase transition data and the corresponding Debye θ for α-Hg, 87°K. These values of θ are consistent with a resistivity ratio of 1.70 which was observed at 79°K.

Mercury is the only known example of a superconductor which exists in two crystallographic modifications, both of which exhibit nearly ideal superconducting behavior. A comparison of data on the two phases offers an opportunity to investigate the effect of structure upon superconducting properties. The Bardeen-Cooper-Schrieffer (BCS) theory,[8] for example, suggests that the superconducting properties of a metal should be relatively insensitive to crystal structure and should obey a law of corresponding states; that is, the critical fields of all superconductors should be given by a common curve when the data are expressed in the reduced variables $t=T/T_c$ and $h=H/H_0$. (T_c is the critical temperature at $H=0$; and H_0, the critical field at $T=0$.) In addition to a check of these predictions for this simple case of two modifications of a single metal, a knowledge of the critical field of a superconductor as a function of temperature and pressure allows the calculation of electronic contributions to the specific heat and thermal expansions, which are, in many cases, difficult to obtain in any other manner. This is particularly true in the case of mercury where the Debye θ is unusually low, so that lattice effects almost completely overshadow the electronic contributions. With the above purpose in mind, critical fields for both phases of mercury were obtained as functions of temperature and pressure on physically identical samples.

These measurements involved two experiments, the direct measurement of the zero-pressure critical field and a two-sample (one at zero pressure, the other under pressure) method of obtaining $(\partial H/\partial P)_T$. In the latter measurement, the pressure was transmitted by solid He^4. The magnitude of the pressure was obtained by calculating the pressure drop from the melting curve to operating temperatures using the data of Dugdale

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* Contribution No. 1000. This work was done in the Ames Laboratory of the Atomic Energy Commission.

[1] C. A. Swenson, Phys. Rev. **111**, 82 (1958).

[2] P. W. Bridgman, Phys. Rev. **48**, 896 (1935).

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[4] C. S. Barrett, Acta Cryst. **10**, 58 (1957).

[5] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).

[6] J. E. Schirber and C. A. Swenson, Phys. Rev. Letters **2**, 296 (1959).

[7] M. Atoji, J. E. Schirber, and C. A. Swenson, J. Chem. Phys. **31**, 1628 (1959).

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

and Simon on the phase diagram of solid He[4,9] and subtracting this value from the fluid pressure initially imposed on the sample. This determination was checked using the "known" value of $(\partial H/\partial P)_{T_c}$ for Sn to calculate the pressure difference between two small Sn samples mounted with the mercury samples.[5] The two pressure determinations were found to agree to within 2%. The apparatus and experimental procedures used in these measurements are described in the preceding paper by Hinrichs and Swenson.[10]

EXPERIMENTAL DETAILS

The β-Hg samples used in the zero pressure critical field work were formed at 77°K by extrusion through a hole sufficiently small (0.016 in.) so that pressures in excess of 7000 atm were required to initiate flow, thus assuring formation of the β phase in the chamber. Extrusion rates had to be kept low (about an inch an hour) so as not to anneal the wire back to the α phase. The samples consisted of 2-cm lengths of this wire, which had been, in some cases, stored under liquid nitrogen for several months.

As described by Hinrichs and Swenson, the pressure work involved the measurement of the critical fields of two similar samples, one under pressure, the other at zero pressure.[10] Samples used in this work were formed by inserting mercury into an Al foil holder (0.019-in. diam by $\frac{3}{8}$ in. long) with a hypodermic needle. The β-Hg samples were formed *in situ* in the pressure chamber. Difficulty was encountered in initiating the formation of the β phase with purely hydrostatic pressure, and indications that the α-β transformation may be martensitic in character will be discussed in a subsequent paper.[11]

As was described in an earlier paper, a 33-cps mutual inductance technique was used to observe the superconducting transitions.[10] The large paramagnetic susceptibility of the intermediate state was observed in every case, and indeed was more pronounced than in the tantalum measurements.[10] This aided greatly in the precise determination of the transition. For both the zero-pressure and the high-pressure experiments, single instances were observed in which individual samples showed discrete transitions corresponding to both the α- and β-Hg phases. This behavior also had been observed in the x-ray work where superimposed α and β powder patterns were obtained for one sample.[7] In each of the cases where the α- and β-Hg superconducting transitions occurred in the same sample, they were separate and distinct, and agreed with monophase sample data, whereas Jennings and Swenson[5] had observed single, rather poorly defined (0.05° wide) transition temperatures in their deformed samples which were intermediate between the T_c's now established for the two phases. A possible explanation for this behavior may lie in the sizes of the crystallites of the mixed samples. Pippard has suggested on the basis of skin depth determinations and the sharpness of the superconducting transition that a long-range order effect must exist between the electrons of a superconductor.[12] Homogeneous distributions over distances of 10^{-4} cm satisfy the theory. If the samples formed in the work of Jennings and Swenson possessed many small crystallites randomly distributed between the α and β phases, over regions of this critical size, one might expect an average transition temperature depending upon the proportion of each phase appearing.

It was not feasible to mount a β-Hg sample in the zero-pressure chamber, so the direct isothermal comparison of two transitions was not possible for this phase. In α-β-Hg run I (which used a mixed sample), the carbon resistance thermometer was used to obtain critical field data at precisely the same temperatures for a run at 28 000-psi gauge pressure, and one at 3000 psi, so that the pressure effect could be obtained by subtraction. The thermometer did not warm above 20°K during these two runs. This procedure was tedious, however, and in β-Hg run I, an α-Hg sample was mounted in the zero-pressure chamber, and the differences in critical fields of the α sample and the β sample were obtained for two pressures on the β sample. Thus, the zero-pressure sample served as a precise secondary thermometer with the same characteristics as the property of the sample being measured.

TABLE I. Zero-pressure critical field data for α-Hg.[a]

Run I		Run II		Run III	
T (°K)	H_c (gauss)	T (°K)	H_c (gauss)	T (°K)	H_c (gauss)
4.0986	11.43	4.0907	12.65	4.0894	13.18
4.0122	28.32	3.9264	44.98	3.9585	39.49
3.8950	51.31	3.7706	74.53	3.8955	51.59
3.7687	74.78	3.5650	111.32	3.7588	77.15
3.6026	104.86	3.2493	163.99	3.5747	109.61
3.4465	131.45	3.0014	201.79	3.2180	168.59
3.1177	184.16	2.7370	238.65	3.0199	198.72
2.7660	234.61	2.4727	271.45	2.7352	238.40
2.4069	279.57	2.2811	293.67	2.5081	267.08
2.2656	295.37	2.0570	316.81	2.3331	287.56
2.0712	315.47	1.8221	337.99	2.0480	317.49
1.8572	335.16	1.5597	358.22	1.6320	352.84
1.5709	357.57	1.4371	366.46	1.9088	330.46
1.3739	370.50	1.2858	375.54	1.5963	355.75
1.3441	372.14	1.1721	381.94	1.4803	363.75
1.2844	375.57	1.1402	383.54	1.3851	369.78
1.2016	380.05			1.3464	372.19
1.1414	383.13			1.1576	383.06
				1.3120	374.28
				1.1921	381.13
				1.1565	383.21

[a] $T_c = 4.153 \pm 0.001$ °K; $H_0 = 412 \pm 1$ gauss.

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[9] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

[10] C. H. Hinrichs and C. A. Swenson, preceding paper (Phys. Rev. **123**, 1106 (1961)].

[11] J. E. Schirber and C. A. Swenson (to be published).

[12] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950).

The data taken on the α-β samples and the usual procedure of taking the β data (transforming the sample to α by warming it above 93°K and repeating the experiment) ensured identical conditions for comparing the properties of the two phases. All the mercury used in these experiments was obtained from Goldsmith Brothers Smelting and Refining Company, and was described on the container as "chemically pure, triply distilled, impurities less than 0.004%." The ratio of the resistance of the α-Hg at 215°K to that at 4°K was about 600.

RESULTS

The zero-pressure critical field data consisted of three runs for each phase; these data are tabulated in Tables I and II. The results of the pressure work are given in Tables III and IV. The pressure data were normalized to runs in which tin pressure calibrations were obtained. Runs at several pressures showed $(\partial H/\partial P)_T$ for Sn, Hg, and Ta to be independent of pressure to within our experimental uncertainties. The T_{55E} vapor-pressure scale was used throughout.

It has been customary to express critical field data in terms of power series expansions in $t^2=(T/T_c)^2$, since critical field curves are so nearly parabolic. The data then can be displayed conveniently in terms of a deviation from parabolic behavior, $\delta h(=h-1+t^2)$ vs t^2. This has been done in Fig. 1, where the deviations of least-squares power series fits to 4th order in t^2 of the critical field data are shown for each phase. The values of T_c of 4.153±0.001 and 3.949±0.001°K for α- and β-Hg, respectively, were obtained from these power series; the corresponding values of H_0, 412±1 and 339±1 gauss, were found using the analysis described below. A typical run has been shown for each phase to indicate the scatter. The α- and β-Hg critical fields

TABLE II. Zero-pressure critical field data for β-Hg.[a]

Run I		Run II		Run III	
T (°K)	H_c (gauss)	T (°K)	H_c (gauss)	T (°K)	H_c (gauss)
3.9428	1.21	3.8863	10.90	3.8851	11.47
3.8786	12.56	3.7605	32.51	3.7616	32.44
3.8033	25.21	3.5674	64.04	3.5511	66.61
3.7240	38.55	3.4081	88.80	3.3972	90.37
3.6063	57.54	3.2384	113.70	3.2149	116.98
3.4545	81.50	3.0343	142.31	3.0165	144.14
3.3176	101.90	2.7616	177.18	2.7318	180.51
3.0782	135.96	2.5475	202.45	2.5097	206.32
3.0067	145.51	2.3253	226.45	2.3705	221.58
2.8373	167.20	2.0531	252.45	2.0495	252.53
2.6796	186.49	1.8237	271.77	1.8116	272.31
2.4361	214.35	1.5613	290.69	1.6198	286.53
2.2631	231.92	1.3037	306.14	1.4596	297.00
2.0765	249.77	1.2863	307.12	1.1766	312.34
1.8479	269.15	1.1706	313.08	1.2910	306.65
1.5649	289.48	1.1381	314.75	1.1454	314.13
1.3832	301.25	1.3764	302.08		
1.3566	302.65				
1.2748	307.10				
1.1235	314.33				
1.1282	314.19				
1.2141	310.10				

[a] $T_c=3.949\pm0.001$°K; $H_0=339.3\pm1$ gauss.

TABLE III. Pressure data for α-Hg.

T(°K)	ΔH (gauss)	$-(\partial H/\partial P)_T$ $\times10^3$ (gauss/atm)	T (°K)	ΔH (gauss)	$(\partial H/\partial P)_T$ $\times10^3$ (gauss/atm)
α-Hg[a]—Run I					
3.4297	11.88	7.60	2.5273	16.87	7.40
3.1375	11.79	7.60	2.1670	16.72	7.34
2.5790	11.41	7.35	2.0449	16.84	7.38
2.2027	11.63	7.49	1.8636	16.74	7.34
2.0201	11.45	7.38	1.5990	16.59	7.28
1.5572	11.11	7.16	1.1416	16.48	7.23
1.2134	10.91	7.03	4.0222	17.35	7.61
α-β Hb[b]—Run I			α-Hg[c]—Run II		
3.7296	17.27	7.58	3.4716	18.70	7.39
3.4397	17.13	7.51			
3.2022	17.29	7.58			
3.0028	17.16	7.53			
2.7451	16.87	7.40			

[a] Gauge pressures 28 000 psi and 3000 psi.
[b] Gauge pressures 40 000 psi and 3000 psi.
[c] Gauge pressure 40 000 psi; ΔH_{Tc} for Sn, 18.50 gauss.

TABLE IV. Pressure data for $\beta-$Hg.

T (°K)	ΔH (gauss)	$-(\partial H/\partial P)_T$ $\times10^3$ (gauss/atm)	T (°K)	ΔH (gauss)	$-(\partial H/\partial P)_T$ $\times10^3$ (gauss/atm)
$\alpha-\beta$ Hg—Run I				ΔH_2	
3.7296	19.37	8.50	3.7271	19.39	8.51
3.4397	18.95	8.31	3.6467	19.37	8.50
3.2022	18.80	8.25	3.5424	19.25	8.44
3.0028	18.70	8.21	3.0809	18.03	8.17
2.7451	18.04	7.91	2.9135	18.58	8.15
			2.5785	18.11	7.95
2.5273	17.76	7.79			
2.1670	17.40	7.63	2.3061	17.75	7.79
2.0449	17.44	7.65	2.1157	17.45	7.66
1.8636	17.25	7.56	2.0485	17.26	7.57
1.5990	16.76	7.35	1.9737	17.09	7.50
1.1416	16.49	7.23	1.6571	16.69	7.32
$\beta-$Hg[a]—Run I			1.5149	16.44	7.21
	ΔH_1		1.319	16.39	7.19
3.7283	19.42	8.52	1.1958	16.20	7.10
3.5375	19.28	8.46	1.1795	16.26	7.13
3.3309	19.03	8.35			
3.0810	18.68	8.19		ΔH_1	
2.8600	18.49	8.11	3.3469	19.01	8.34
			2.9695	18.61	8.16
2.5862	18.05	7.92	1.9124	17.08	7.49
2.3110	17.80	7.81	1.6618	16.58	7.27
2.1607	17.32	7.60	1.3585	16.43	7.21
1.9069	17.11	7.50	1.2037	16.30	7.15
			1.4595	16.53	7.25

[a] ΔH_{Tc} for tin, 16.40 gauss.

$$\Delta H_1=(H_\beta{}^{2480\text{ atm}}-H_\alpha{}^{0\text{ atm}})-(H_\beta{}^{200\text{ atm}}-H_\alpha{}^{0\text{ atm}})^*,$$

$$\Delta H_2=(H_\beta{}^{2480\text{ atm}}-H_\alpha{}^{0\text{ atm}})^*-(H_\beta{}^{200\text{ atm}}-H_\alpha{}^{0\text{ atm}}),$$

where * denotes values as obtained from smooth curves through the experimental points.

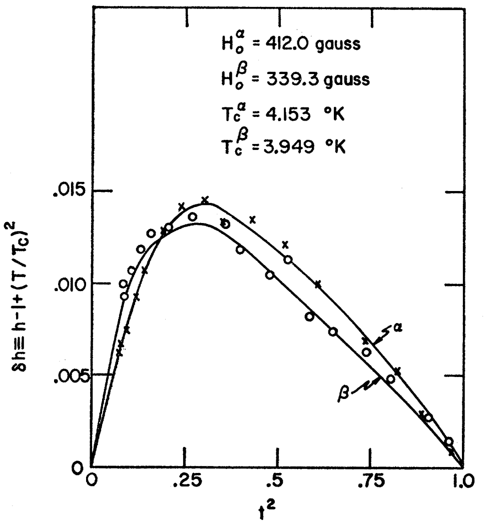

FIG. 1. A plot of the deviation from parabolic behavior of the critical field curves for α- and β-Hg. The solid curves are the results of least-squares power series fits to all the experimental data, while the points shown represent typical runs. The maximum difference between the two curves corresponds to, roughly, 0.4 gauss.

appear to be identical to within experimental uncertainties.

The pressure data are illustrated in Fig. 2, where the curves are least-squares fits to all the data, and data for a typical run for each phase are given to show the experimental scatter. The error bars constitute the uncertainty in ΔH, and additional uncertainty of about 3% is inherent in the determination of ΔP.

In spite of the convenience of displaying the data as in Fig. 2, very little insight is given to the primary problem of extrapolating the data to absolute zero to obtain values for H_0, γ, and the volume dependence of γ (γ being the coefficient of the electronic specific heat in the normal state). A method of extrapolation which is different from that which has been employed by most current investigators, although not entirely original,[10] was used in this work. A brief discussion of this method is given below.

The difference in the free energies of the superconducting and normal states can be expressed as[13]

$$F_n - F_s = H_c^2 V / 8\pi. \tag{1}$$

If it is assumed that the lattice contributions are identical in the normal and superconducting states, and that the electronic contribution to the entropy in the normal state is γT, the free energy of the electrons in the superconducting state can be expressed as

$$F_s = -H_c^2 V / 8\pi - \gamma T^2 / 2. \tag{2}$$

In the low temperature limit, the BCS theory of superconductivity predicts an $\exp(-1/t)$ dependence for the heat capacity of the superconducting state,[8] so the quantity F_s could be expected to approach its limiting value of $-H_0^2 V/8\pi$ much more rapidly than T^2. In this limit, then, Eq. (2) becomes

$$H^2 = -4\pi\gamma T^2 / V + H_0^2. \tag{3}$$

If this equation is simplified and differentiated with respect to pressure at constant temperature, one obtains

$$(\partial H^2/\partial P)_T = (4\pi\gamma K/V)[(d\ln\gamma/d\ln V) - 1]T^2 + dH_0^2/dP, \tag{4}$$

where K is the isothermal compressibility at absolute zero. The slopes at $T^2=0$ of Eqs. (3) and (4) (when plotted against T^2) yield γ and $d\ln\gamma/d\ln V$, and the intercepts at $T^2=0$ give H_0 and dH_0^2/dP.

This analysis seemed to be appropriate in the case of mercury, since the data below $t^2=0.15$ could be fitted to a straight line on the H^2 vs T^2 plot. Least-squares power-series expansion in t^2 to the lowest order which would fit the data to within the estimated experimental uncertainties were obtained for h^2, $2h(\partial H/\partial P)/(dH_0/dP)$ and h using an IBM-650 computer. The coefficients of the series are shown in Table V and are denoted by a_{2n}, b_{2n}, and A_{2n}, respectively. A disadvantage of the latter two series [h^2 and $2h(\partial H/\partial P)/(dH_0/dP)$ vs t^2] is that the considerable curvature of these functions makes these quantities more difficult to fit than the h and $\partial H/\partial P$ vs t^2 functions. However, in the regions of the validity of these series ($0.08 \leqslant t^2 \leqslant 0.75$ for Hg), one is able to give analytical expressions for the free energy, the electronic specific heat in the superconducting state, and the electronic contribution to the thermal expansion in the superconducting state. Equation (2) can be written in dimensionless form by

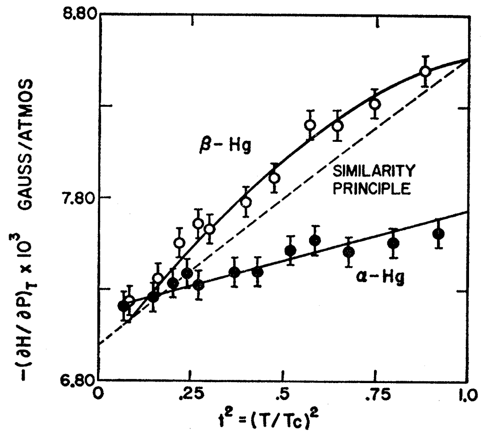

FIG. 2. $(\partial H_c/\partial P)_T$ for α- and β-Hg. The solid curves are the results of least-squares power-series fits to the experimental data while the points shown represent typical runs. Each run was made at a fixed pressure, the magnitude of which was uncertain to 3%.

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[13] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), 2nd ed., Chap. 3.

defining $f_s = F_s/F_{s0}$ and $\gamma_p = H_0{}^2V/2\pi T_c{}^2$, to give

$$f_s = h^2 + 2\gamma t^2/\gamma_p = \sum_{n=0} a_{2n}t^{2n} + 2\gamma t^2/\gamma_p. \quad (5)$$

Differentiating twice with respect to temperature and putting in dimensionless terms gives:

$$\begin{aligned} C_s{}^{\mathrm{el}}/\gamma T_c &= (t\gamma_p/4\gamma)(\partial^2 f_s/\partial t^2) \\ &= (\gamma_p/4\gamma)\Big[\sum_{n=0} 2n(2n-1)a_{2n}t^{2n-1} + 4\gamma t/\gamma_p\Big]. \quad (6) \end{aligned}$$

Finally, differentiating Eq. (1) with respect to T and P, and using the Maxwell relation $\partial S/\partial P = -\partial V/\partial T$, one obtains:

$$\begin{aligned} \beta_s{}^{\mathrm{el}}T_c &= (-H_0{}^2K/4\pi T_c{}^2) \\ &\times \sum_{n=0} n[(d\ln H_0/d\ln V)b_{2n} + a_{2n}]t^{2n-1} + \beta_n{}^{\mathrm{el}}T_c, \quad (7) \end{aligned}$$

where $\beta_n{}^{\mathrm{el}}$ can be shown to be equal to

$$(K\gamma T/V)d\ln\gamma/d\ln V.$$

If the power series used were to give the proper values for the extrapolations to absolute zero, a_0 would equal unity and the t^2 terms would drop out in Eq. (5). Similarly, the terms linear in t would cancel in Eq. (6); in Eq. (7), the β_n factor and the term linear in t would disappear. In practice the machine extrapolations are not correct, so these terms must be included.

The values of γ, T_c, and H_0 obtained in this work are shown in Table VI. The values of $\gamma = 1.91 \pm 0.05$ mjoules/mole-deg² and $H_0 = 412 \pm 1$ gauss obtained for α-Hg may be compared with the corresponding values of 2.1±0.15 mjoules/mole-deg and 415±1 gauss reported by Finnemore *et al.*[14] and with Chambers and Park's value of $\gamma = 2.04 \pm 0.03$.[15] The difference in the methods of extrapolation is sufficient to account for the discrepancies since the actual data agree to about 0.2%. Accurate calorimetric determinations of γ are difficult because of the overpowering lattice contribution to the specific heat, but Goodman has obtained a value of $\gamma = 2.1 \pm 0.1$ for α-Hg.[16]

TABLE V. Coefficients of machine power series in t^2.

	α-Hg	β-Hg
${}^a a_0$	0.99889	1.0060
a_2	−1.7788	−1.8438
a_4	0.2915	0.4446
a_6	0.7856	0.6430
a_8	−0.2983	−0.2506
${}^b b_0$	1.955	1.970
b_2	−1.315	−1.140
b_4	−1.185	−0.639
b_6	0.559	−0.926
b_8		0.759
${}^c A_0$	0.9981	1.0021
A_2	−0.8651	−0.9027
A_4	−0.3746	−0.2892
A_6	0.3978	0.3104
A_8	−0.1561	−0.1209

[a] $h^2 = \sum_{n=0}^{4} a_{2n}t^{2n}$.

[b] $2h(\partial H/\partial P)_T/(dH_0/dP) = \sum_{n=0}^{4} b_{2n}t^{2n}$.

[c] $h = \sum_{n=0}^{4} A_{2n}t^{2n}$.

TABLE VI. Summarized properties of α- and β-Hg.

	α-Hg	β-Hg
T_c (°K)	4.153±0.001	3.949±0.001
H_0 (gauss)	412.0 ±1	339.3 ±1
γ (mjoules/mole deg²)	1.91 ±0.05	1.37 ±0.04
K (atm^{-1}×10^6)	2.63 ±0.1	2.2 ±0.1
V (cc/mole)	13.79	13.59
dH_0/dP (gauss/atm×10^3)	−7.2 ±0.3	−7.0 ±0.3
$d\ln T_c/d\ln V$	3.4 ±0.1	5.5 ±0.1
$d\ln H_0/d\ln V$	6.7 ±0.3	9.4 ±0.3
$d\ln\gamma/d\ln V$	7.3 ±0.3	8.6 ±0.3
$\beta_N{}^{\mathrm{el}}/T\times10^8$ (°K^{-2})	2.6 ±0.1	1.9 ±0.1

The agreement of the pressure work with the $\Delta L/L$ results of Rohrer[17] is not, however, as good. Our value of $d\ln\gamma/d\ln V = 7.3 \pm 0.3$ differs from his value of 3.3 by more than the estimated experimental errors. Extrapolation procedures are again very important, and, furthermore, Rohrer's data were obtained from single-crystal $\Delta L/L$ measurements which were converted to $\Delta V/V$ (and $\partial H_c{}^2/\partial P$) for comparison with pressure-effect data. For anisotropic substances such as mercury, there may be some difficulty in combining properly the values of $\Delta L/L$ in the various crystallographic directions to obtain $\Delta V/V$.

The results of the calculation of $d\ln T_c/d\ln V$, $d\ln H_0/d\ln V$, $\beta_n{}^{\mathrm{el}}/T$, and the parameters V_s and K used in these calculations are also listed for both phases in Table VI. Equation (6) was used to calculate $C_s{}^{\mathrm{el}}/\gamma T_c$ for both phases over the temperature range of its validity ($0.08 < t^2 < 0.8$). Derivatives of the h vs t^2 expressions were used to obtain this quantity for the region $t^2 > 0.8$. The various contributions to the specific heat are shown in Fig. 3, where the lattice contribution shown is as given by Smith and Wolcott.[3] The α- and β-Hg fit the same $C_s{}^{\mathrm{el}}/\gamma T_c$ plot as would be expected from Eq. (6), since the critical fields are identical in terms of reduced variables.

A plot of the contributions to the thermal expansions of the two phases is given in Fig. 4. The lattice term was calculated from the specific heat values of Smith and Wolcott,[3] using the relationship $\beta^L = -(KC^L/V)\,d\ln\theta/d\ln V$, and an estimated value of $-d\ln\theta/d\ln V = 2$ (Grüneisen's constant).[10] It is to be noted that the

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[14] D. K. Finnemore, D. E. Mapother, and R. W. Shaw, Phys. Rev. **118**, 127 (1960).

[15] R. G. Chambers and J. G. Park, *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960*, edited by G. M. Graham and A. C. Hollis (University of Toronto Press, Toronto, 1960).

[16] B. B. Goodman, *Proceedings of Kammerlingh Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958* [Physica **24**, S149 (1958)].

[17] H. Rohrer, Helv. Phys. Acta, **33**, 675 (1960).

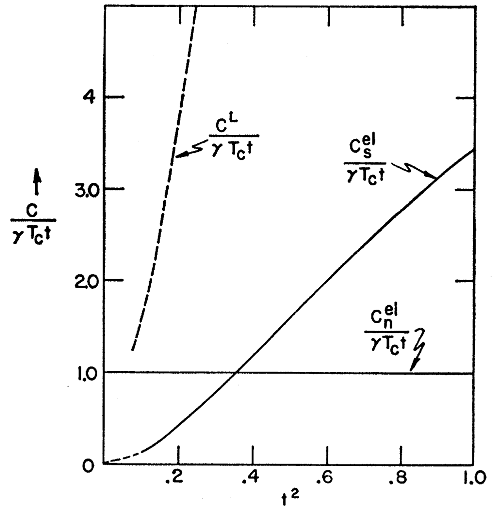

FIG. 3. Contributions to the specific heats of α- and β-Hg. The electronic contributions are identical for the two phases on this plot which is expressed in reduced variables. The lattice contribution is given by Smith and Wolcott (reference 3).

superconducting contributions to the electronic thermal expansions are negative for both α- and β-Hg. Similar calculations using the available data[18] for Sn,[19] In,[19] Pb,[20] and Ta[10] indicate that only tantalum differs in sign from this result. A possible explanation may lie in the fact that Ta is one of the transition metals which possess characteristically high values of γ. It would be of interest to examine Nb and V to corroborate this hypothesis.

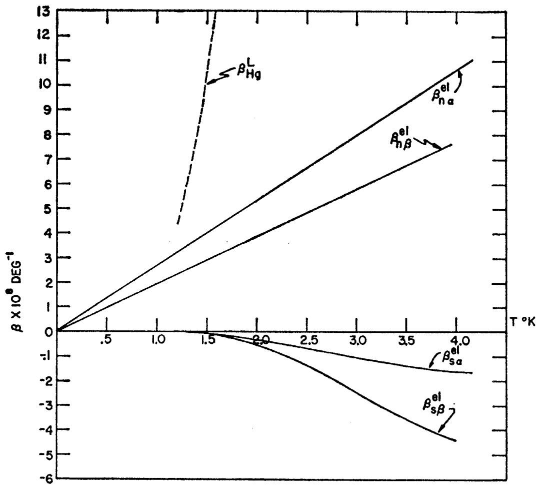

FIG. 4. Comparison of the various contributions to the thermal expansion of α- and β-Hg. The lattice contribution was calculated from experimental specific heat data using an estimated Grüneisen constant of 2.

DISCUSSION

The BCS theory of superconductivity assumes as a first approximation that the superconducting properties of the metal are independent of the crystal structure.[8] Our zero-pressure critical field data on mercury seem to bear this out. It is of interest to see if the differences in H_0, T_c, and γ between α and β Hg can be explained using the observed pressure effects and the volume difference (about 1.5%) between the two phases. The observed and calculated values of these differences are compared in Table VII and do not appear to agree except as to order of magnitude, showing the effect of the crystal structure.

The pressure effect data show that the similarity principle which would require that the h vs t^2 curve and the ratio of H_0/T_c be independent of pressure is not valid. A more general principle, that the h vs t^2 curve does not change shape with pressure (H_0 and T_c varying independently), appears to apply to α-Hg, but not to β-Hg. This is indicated by the dashed line in Fig. 2. Hence, the critical field parameters (A_{2n} and a_{2n}) for β-Hg in Table V can be expected to be functions of volume.

Critical field data have been used to check the BCS prediction of an $\exp(-1/t)$ dependence of the specific heat in the superconducting state. The theory, however, basically gives an expression for the critical field curve[8] so it would appear to be more fundamental to compare directly the experimental and theoretical critical field curves. The BCS expression has been evaluated by numerical integration using the ISU Cyclone computer[21] in order to make this comparison. A convenient method of representing both the theoretical and experimental critical field curves in the region of greatest interest ($t^2<0.3$) is by means of a plot of $[(1-h^2)/t^2]$ vs t^2, since this plot is extremely sensitive to slight experimental inaccuracies in this region, and approaches a horizontal line in the limit where the contribution of the superconducting state is negligible.

Figure 5 shows this plot for a parabolic critical field curve, for the BCS theory and for several superconductors for which precise critical field data are available.

TABLE VII. A comparison of the experimental shifts of T_c, H_0, and γ between α- and β-Hg with those calculated from the pressure data.

	Experimental	As calculated from $(\partial H_{c\alpha}/\partial P)_T$	$(\partial H_{c\beta}/\partial P)_T$
$\Delta T_c=T_{c\alpha}-T_{c\beta}$ (°K)	0.20	0.22	0.32
$\Delta H_0=H_{0\alpha}-H_{0\beta}$ (gauss)	73	41	48
$\Delta\gamma=\gamma_\alpha-\gamma_\beta$ (millijoules/deg²)	0.43	0.20	0.17

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[18] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **33**, 872 (1960).

[19] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

[20] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).

[21] The authors are grateful to Dr. D. R. Fitzwater and R. Dillon for the programming. The results of these calculations will appear in an ISU report.

The shape of the experimental curves is very sensitive to the value of H_0 which is chosen, and we have used a linear extrapolation of the H^2 vs T^2 relationship [Eq. (3)] to obtain the H_0's which were used. These, except for lead, where the different extrapolations made no difference in the value of H_0, are appreciably lower than those which have been reported in the literature. This method of extrapolation appears to be on fairly sound theoretical grounds, and has the more pragmatic justification that it removes much of the disagreement which has been reported in the past between calorimetric[16,22–25] and critical field determinations of γ. A comparison of the γ's from these two sources has been made in Table VIII for those metals for which precise calorimetric and critical field data are presently available.

The deviations of the critical field curves from parabolic behavior ($\delta h = h - 1 + t^2$) are indicated in the plot of Fig. 5, with the BCS curve showing the greatest negative deviation, and lead the maximum positive deviation. From this plot, it appears that the low temperature exponential contribution to the specific heat (since the curvature of the plots is related to this quantity) becomes less pronounced as one approaches lead-like behavior. This has been commented on by Mapother.[20] Even for tantalum, where this contribution appears to be greatest, it is difficult to visualize experiments which are sufficiently precise to determine the detailed nature of the exponential dependence because of the stringent requirements of both the temperature and critical field measurements. The error bars in Fig. 6 illustrate the effect of a change of 0.05% in H_0 (or H) for various values of t^2.

Figure 5 indicates that the usual deviation plot has little basic significance, especially at the lowest temperatures where the shape is extremely sensitive to the value of H_0 which is assumed. Indeed, an anomalous deviation plot of the type suggested by Bryant and Keesom[25] for indium (where δh passes through zero and the deviations have both positive and negative values) would follow naturally from this plot if the experimental critical field data for indium had been interpreted to give a slightly lower value for H_0. It would appear, however, that the calorimetric value for γ is too low for this substance, since our extrapolation should, if incorrect, give values which are on the low side.

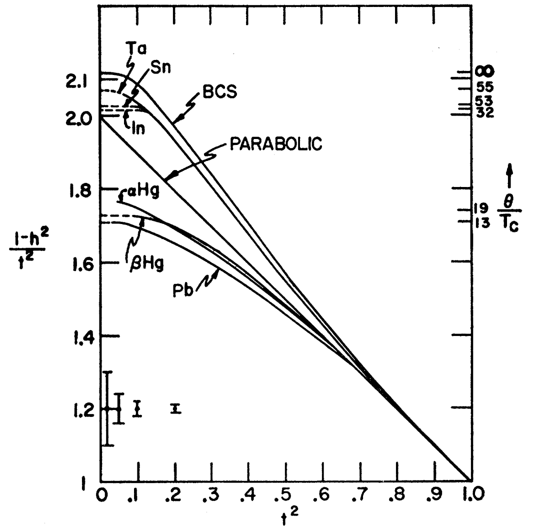

FIG. 5. $[(1-h^2)/t^2]$ vs t^2 for the BCS critical field curve and for α- and β-Hg, Pb, Sn, In, and Ta. The values of θ/T_c corresponding to the intercepts at $t^2=0$ of the various curves are plotted on the right-hand ordinant. The error flags in the lower left-hand corner demonstrate the effect of a change of H_0 of 0.05% at those values of t^2.

Equation (5) for the reduced critical field curve can be written as

$$(1-h^2)/t^2 = (1-f_s)/t^2 + 2\gamma/\gamma_p. \tag{8}$$

The intercept at $t^2=0$ of the curves in Fig. 6, which is $2\gamma/\gamma_p$, corresponds in the BCS theory to[8]

$$2\gamma/\gamma_p = 4\pi T_c^2\gamma/H_0^2 V = (kT_c/2\epsilon_0)^2 8\pi^2/3. \tag{9}$$

Goodman has shown that the reduced widths of the energy gap at absolute zero, $2\epsilon_0/kT_c$, as calculated from Eq. (10), are a fairly smooth function of θ/T_c.[26] Figure 6 shows a smooth variation in the shapes of the critical field curves from the BCS expression (which assumes θ/T_c approaches infinity) and lead ($\theta/T_c = 13$).[27] This correlation, which is identical with Goodman's, has been indicated on the right-hand ordinate of Fig. 6 where the corresponding values of θ/T_c have been given. Richards and Tinkham[28] have compared their

TABLE VIII. Comparison of γ's obtained by our extrapolation method with calorimetric values.

	Our method	Calorimetric
Ta	6.0 ±0.2	5.69(22)
Sn	1.78±0.05	1.75(23)
In	1.70±0.05	1.61(25)
α-Hg	1.91±0.05	2.1±0.1(16)
β-Hg	1.37±0.04	...
Pb	3.09±0.05	3.13(24)

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[22] D. White, C. Chou, and H. L. Johnston, Phys. Rev. **109**, 797 (1958).

[23] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

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[25] C. A. Bryant and P. H. Keesom, *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960*, edited by G. M. Graham and A. C. Hollis (University of Toronto Press, Toronto, 1960).

[26] B. B. Goodman, Compt. rend. **246**, 3031 (1958).

[27] This correlation corresponds to the dependence of the magnitude of the deviation from parabolic behavior on θ/T_c which has been discussed by Mapother. See references 14 and 20.

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

experimental values of $2\epsilon_0/kT_c$ with those of Goodman, and have found fair agreement except for mercury and the transition elements. The deviation for mercury is explained on the basis that it (and lead) show anomalous structure in the energy gap. Recent work with tantalum would seem to make any measurements of the superconducting properties of the transition elements suspect if these show anomalous properties, since small amounts of impurities seem to produce large effects.

Within this framework of the BCS theory, the pressure effect data and Eq. (9) can be used to determine the volume dependence of ϵ_0/kT_c. Using the values for $d\ln\gamma/d\ln V$, $d\ln H_0/d\ln V$, and $d\ln T_c/d\ln V$ given in Table VI, $d\ln(\epsilon_0/kT_c)/d\ln V$ is found to be zero within experimental uncertainties for the two mercuries. A survey of other available data show that this is also true for Ta,[10] Pb,[29] and Sn.[30]

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[29] M. Garfinkel and D. E. Mapother, Phys. Rev. **121**, 459 (1961)

[30] Unpublished data this laboratory.

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Pressure Dependence of the Microwave Resonance Properties of Some Spinel and Garnet Ferrites*†

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The anisotropy field, g value, and linewidth of several spinel and garnet ferrites have been measured at X band and room temperature as functions of hydrostatic pressure to 10^4 kg/cm^2. The crystals studied include yttrium, ytterbium, and erbium iron garnet; magnesium ferrite (with different distributions of Mg^{2+} ions on A and B sites); and $Ni_{1-z}Co_zFe_2O_4$ with $z=0$, 0.05 and 0.10. The pressure dependence of magnetization was measured using magnetostatic mode methods in the narrow linewidth materials, yttrium iron garnet and magnesium ferrite.

The complexity of the crystal structure and magnetic interactions makes any quantitative interpretation very difficult. However, the observations can be understood qualitatively in terms of the volume dependence of the crystalline fields and the exchange interactions. In the case of erbium iron garnet, the volume dependence of the ferric-rare-earth exchange constant is calculated; and, in the case of nickel cobalt ferrite, a simple explanation is offered for the observed volume dependence of the Co^{2+} anisotropy.

The contribution of thermal lattice vibrations to the linewidth in yttrium iron garnet is discussed, and the possibility of an anisotropic spin-orbit interaction is considered.

INTRODUCTION

THE two dominant factors determining the magnetic properties of ferrimagnetic oxides, the superexchange and crystalline field interactions, are sensitively related to the interionic spacings in the crystalline unit cell. When hydrostatic pressure is applied to a cubic crystal, such as a spinel or garnet ferrite, the unit cell will remain cubic (provided no phase change occurs[1]) and the lattice constant will be reduced in proportion to the compressibility. As a result of the compression, one would expect the superexchange interaction, which arises from the overlap of neighboring wave functions, to become more pronounced. Moreover, the crystalline electric fields at the metal ions, produced by neighboring oxygen ions, would also be expected to increase in intensity. Changes in local crystalline fields would be manifested mainly by variations in magnetic anisotropy, and changes in superexchange fields would cause variations in magnetization. These macroscopic properties, magnetization and anisotropy, as well as g value and linewidth, can be measured at room temperature to 10^4 kg/cm^2 (about 10^4 atm) with the high-pressure microwave resonance apparatus described below. It is found that the 0.2% reduction in lattice constant occurring in the ferrites at 10^4 kg/cm^2 produces rather large changes in the resonance properties.

Although the prospect of varying the exchange and crystalline field interactions directly is quite attractive, a number of difficulties arise in analyzing the results of pressure measurements. Despite the fact that the pressure dependence of the lattice constant may be determined from the compressibility by symmetry considerations, the pressure dependence of the oxygen parameters, which determine the relative positions of oxygen ions in the complex unit cell, cannot be determined except by x-ray analysis at high pressure. The simplest assumption, which is often a poor approximation, is to suppose that all interionic distances vary in proportion to the compressibility, i.e.,

$$(\partial \ln\xi/\partial P)=\tfrac{1}{3}(\partial \ln v/\partial P)=-\tfrac{1}{3}\chi, \qquad (1)$$

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* Supported by an Air Force contract.

† Based on a thesis presented by I. P. K. to the Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts, May 1960, in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

‡ Now at Bell Telephone Laboratories, Holmdel, New Jersey.

[1] Experimentally, no abrupt changes, no hysteresis, and no variations in symmetry of measured quantities are observed as a function of pressure.