ascertain whether or not a single anharmonic model could account for the infrared absorption and a number of other anharmonic effects. On the basis of the results summarized in Table I we reach an affirmative conclusion. A consequent conclusion is that in the case of GaP it is not *necessary* to invoke the second order electric moment mechanism (charge deformation) to explain the observed infrared combination bands.

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Critical Field Curve of Superconducting Mercury*

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The critical field curve of mercury has been precisely measured in a range of reduced temperature, $t=T/T_c$, from 1 to 0.27. The observed H_c values show an appreciable deviation from a parabolic temperature dependence, lying above the parabola which passes through the experimental values of H_0 and T_c. The general behavior is similar to that previously observed in the case of lead. Values of the temperature coefficient of the normal electronic specific heat, γ, are derived, but are somewhat uncertain since the H_c data indicate an appreciable entropy contribution from the superconducting electrons at the lowest temperature of measurement. The qualitative behavior of $H_c(T)$ for lead and mercury is in accord with recent infrared measurements which give direct indication that the energy gap value for these elements is anomalously large.

ONE of the best known regularities of superconductivity is the fact that the critical field curves of all superconducting elements can be approximately represented by the "parabolic law"

$$H_c(T)=H_0(1-t^2); \quad t=T/T_c, \tag{1}$$

where H_0 and T_c are, respectively, the critical field at $T=0°K$ and the critical temperature. Precise measurements of $H_c(T)$ for a particular element generally exhibit small deviations from (1) which may be described by the function

$$D(T)=[H_c(T)-H_c^p(T)]/H_0, \tag{2}$$

where $H_c(T)$ is the experimentally observed critical field and $H_c^p(T)$ is the value computed for the same temperature from (1) using the experimental constants, H_0 and T_c. The maximum value of $D(T)$ is never greater than a few percent and, until recently, $D(T)$ also seemed to be negative for all superconducting elements—a circumstance attributed to the fact that the superconducting electronic specific heat, C_{es}, had an exponential dependence on T [rather than the well known T^3 dependence which follows thermodynamically from (1)].[1]

Recent measurements of Pb show this element to be exceptional in exhibiting a positive $D(T)$.[2] From this behavior it follows that C_{es} for Pb cannot be exponential above a reduced temperature $t=T/T_c\sim0.3$. It was also noted that the maximum value of $D(T)$ for various elements shows a correlation with the ratio T_c/θ_D, where θ_D is the limiting value of the Debye temperature as $T\rightarrow 0°K$. The same correlation indicated that Hg, hitherto considered to be the one true "parabolic" superconductor,[3] should also show a positive $D(T)$. We have measured $D(T)$ for Hg and find it to be not only positive but of greater maximum amplitude than expected from the empirical correlation with T_c/θ_D.

Specimens of reagent grade Hg[4] were cast in graphite molds as nearly single crystals in the form of cylinders (0.160 cm diam×3.05 cm long). After removal from the mold, the specimens were annealed for 8 hours about 20°K below the melting point of Hg. The specimens were freely suspended in a liquid helium bath and the critical field measured by a ballistic induction method.[5] Values were obtained down to a temperature of about 1.1°K ($t\sim0.27$) by pumping over the helium bath. The specimen temperature was determined from a vapor pressure thermometer bulb with large copper fins which sampled the temperature of the helium bath immediately adjacent to the specimen. This procedure eliminates some of the uncertainty due to the hydrostatic head correction required when the vapor pressure

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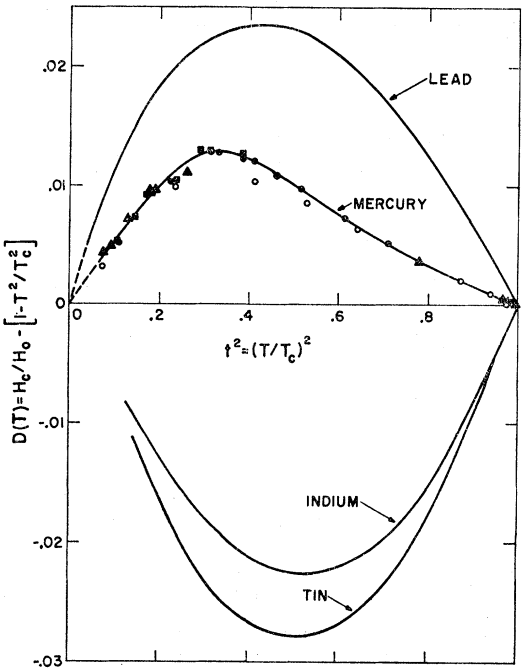

FIG. 1. Experimental determinations of $D(T)$ for four mercury specimens. The open circles indicate the points for sample Hg-4. $D(T)$ behavior of three other elements is shown for comparison.

is measured over the bath.[6] Absolute temperatures were computed according to the 1958 vapor pressure temperature scale.[7]

The magnetic transitions were characterized by an experimental demagnetizing factor of 0.005, in satisfactory agreement with the value expected on the basis of the specimen dimensions. There were no hysteretic effects of the sort which gave difficulty in the Pb measurements.[2]

Results of measurements on four different specimens are given in Table I, and the shape of $D(T)$ vs t^2 is shown in Fig. 1. One specimen shows a slightly lower $D(T)$ than the other three, but this specimen (Hg-4) showed a clear anomaly in its magnetic transition (a strange and incompletely understood flux trapping effect). However, it is clear that even for a specimen with obvious peculiarties neither the critical field constants nor $D(T)$ are seriously affected.

The values of γ are deduced following the analysis of Daunt and Mendelssohn[8] which is based on the thermodynamic relation

$$\Delta S=-(V/4\pi)H_c(dH_c/dT), \tag{3}$$

where $\Delta S=S_n-S_s$ is the difference in molar entropies of the superconducting and normal phases, and V is the molar volume (13.85 cc/mole in the case of Hg).[9] In the limit as $T\rightarrow 0°\text{K}$, ΔS is dominated by the normal electronic entropy with the result that

$$\lim_{T\rightarrow 0°\text{K}} \Delta S=\gamma T, \tag{4}$$

where γ is the temperature coefficient of the normal electronic specific heat.

Unfortunately it appears that the present data do not extend to sufficiently low temperatures to permit a reliable estimate of γ from (4). This can be seen in Fig. 2 where values of ΔS computed from (3) are plotted against t. A tangent to the ΔS curve at the lowest temperature of measurement extrapolates to a point significantly larger than zero, indicating that an appreciable entropy contribution from the superconducting electrons remains at this temperature. Under these circumstances, the value of γ deduced will depend on the way in which the critical field curve is extrapolated to 0°K. Assuming a parabolic extrapolation of H_c to 0°K, the values γ listed in Table I are obtained. However, while agreement between different specimens is within 1.4%, the uncertainty

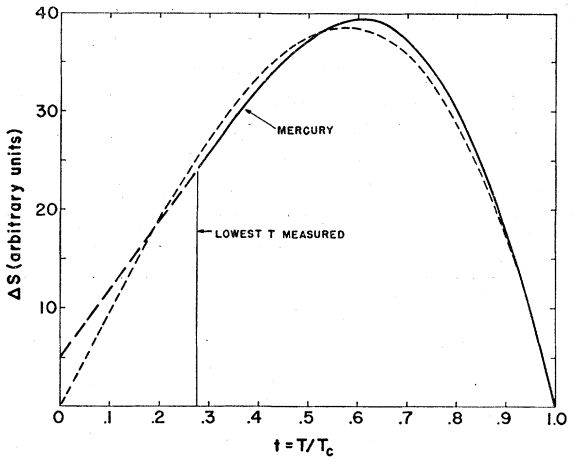

FIG. 2. Temperature dependence of the molar entropy difference, S_n-S_s, for mercury. The dashed portion of the curve is a linear extrapolation of the experimentally determined curve below the lowest temperature of observation. The light dashed curve shows ΔS expected for a parabolic critical field curve.

TABLE I. Critical constants for superconducting mercury.

Sample	T_c (°K)	H_0 (gauss)	γ millijoules/mole°K²
Hg-1	4.1535±0.0006	415.4+0.5, −1.5	2.103+0.01, −0.04
Hg-3	4.153 ±0.001	415.1±0.5	2.088±0.01
Hg-4	4.1531±0.0005	414.9+0.5, −1.5	2.108+0.01, −0.04
Hg-5	4.1532±0.0005	414.4±0.4	2.079±0.01

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of this extrapolation may be as much as 7%.[10] No reliable calorimetric determination of γ is available of Hg because of the very large low-temperature lattice specific heat of this element.

The temperature dependence of the superconducting electronic specific heat, C_{es}, may be deduced from the relation[2]

$$C_{es}(T)=\gamma T+(VT/4\pi)d^2(H_c^2)/dT^2.$$

However, the aforementioned uncertainty in γ leads to a rapidly increasing uncertainty in $C_{es}(T)$ below $t=0.5$. The only definite conclusion is that, in the temperature range immediately below T_c, C_{es} for Hg drops much more rapidly than the nearly exponential behavior predicted by the theory of Bardeen, Cooper, and Schrieffer.[11]

[10] It should be pointed out that $\lim(dH_c/dT)$ as $T\rightarrow 0°\text{K}$ is much more sensitive to the extrapolation error than is H_0. Thus the present ambiguity regarding γ does not have a serious effect on the form of $D(T)$ shown in Fig. 1. This problem with γ did not arise in the earlier measurements on Pb (reference 2) because of the lower value of t attained in that work.

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The critical field measurements on Pb and Hg establish that these elements are (a) qualitatively similar, and (b) conspicuously anomalous among the superconducting elements in the character of their electronic excitation spectrum. A more detailed thermodynamic analysis suggests that the positive values of $D(T)$ arise from values of the superconducting energy gap which are substantially larger than the BCS value of 3.52 kT_c. Thus the present results seem to compliment recent observations on Pb and Hg by infrared techniques which show that the sudden onset of absorption in these superconductors occurs at anomalously high frequencies.[12]

Precise measurements of $D(T)$ are being made on other superconducting elements and will be extended to the temperature range below 1°K. Further results will be reported shortly.

We are pleased to acknowledge the assistance of D. C. Hopkins with these measurements, and also D. M. Ginsberg for valuable discussions.

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Harmonic Spin Coupling in Ruby

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A new mode of maser pumping which makes use of harmonic spin coupling in ruby has been demonstrated. In addition higher order harmonic spin coupling effects in ruby have been found experimentally.

IN ruby a new mode of maser pumping has been demonstrated. This new mode of pumping makes use of harmonic spin coupling in ruby and indicates the possibility of operating a maser with pumping at frequencies lower than the signal frequency. Coupling between spins possessing the same transition frequency has been demonstrated by Feher and Scovil[1]. They found a reduced relaxation time associated with a gadolinium transition if the transition frequency coincides with that of the cerium transition, both ions being simultaneously present in a diamagnetic ethyl sulfate host crystal. Harmonic spin coupling in ruby was found by Mims and McGee.[2] They found an accelerated relaxation rate associated with a resonance transition in ruby whenever orientation and magnitude of the applied magnetic field were such that there was a 1:1, 2:1 or 1:2 ratio between two transition frequencies in the energy level scheme. In addition Mims and McGee[3] suggested that the harmonic spin coupling effect they observed in their relaxation experiments was only the first in a sequence of higher order processes and they further suggested that harmonic spin coupling might be used to advantage for pumping masers at frequencies beyond the range of existing signal sources.

This note contains experimental results which verify the existence of the higher order harmonic spin coupling processes as suggested by Mims and McGee.[3] Also we have demonstrated that harmonic spin coupling processes can be used in maser pumping. Consider four energy levels in ruby with transition frequencies as indicated in Fig. 1(a). For simultaneous observation of essentially all ruby transitions, a ruby sample in the shape of a rod was placed inside a shorted X-band waveguide with a helical transmission line wound on the sample. Signal transmission through the helix permits the study of lower microwave transition frequencies whereas transition frequencies in the

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