Pressure Effect on Superconducting Lead*

M. GARFINKEL† AND D. E. MAPOTHER
Department of Physics, University of Illinois, Urbana, Illinois
(Received November 29, 1960)

Techniques are described for measuring the effect of hydrostatic pressure on the critical field, H_c, of superconducting Pb. Pressures up to 650 atm were applied using solid helium as the pressure fluid. Observations were made from about 7 to 1°K, and values of dH_0/dP, dT_c/dP, and the temperature variation of $(\partial H_c/dP)_T$ are reported. From these data the value of $(1/\gamma^*)(d\gamma^*/dP)$ is deduced, where γ^* is the temperature coefficient per unit volume of the normal electronic specific heat. The observed data are accurately represented over the full range of measurement by the equation $H_c(P,T) = H_0(P)f(t)$ where $t = T/T_c$ and $f(t)$ is independent of pressure. The "similarity principle" requirement, $H_0(P)/T_c(P) = \text{const}$, is shown to be invalid for Pb. The results provide the basis for a discussion of the pressure effects on the net interaction potential, V, of the Bardeen, Cooper, Schrieffer theory and the density of electronic states near the Fermi surface.

I. INTRODUCTION

IT has long been recognized that the superconducting transition may be displaced by the application of hydrostatic pressure.[1] However, the effect is very small and, until recently, experimental work has been largely confined to the changes in critical field, H_c, near the critical temperature, T_c, or the displacement of T_c itself. The present work describes the results of measurements of the pressure variation of H_c for lead over the temperature range from T_c (7.175°K) to about 1°K.

In fundamental physical terms the analysis of the observed effect is complicated by several concurrent effects which result from the application of pressure. A theoretical approach to the situation is provided by the expression

$$kT_c = 1.14\hbar\omega \exp[-1/N(0)V], \qquad (1)$$

from the theory of Bardeen, Cooper, and Schrieffer (hereafter BCS).[2] In Eq. (1), ω is a characteristic phonon frequency (proportional to the Debye θ), $N(0)$ is the density of states at the Fermi level, and V characterizes the net electron-electron interaction. Each of these parameters is sensitive to pressure.

Reduction of the specific volume under pressure changes the lattice vibrational frequency, ω, leading to a displacement in T_c as seen in the simpler isotope effect.[3] The change in phonon spectrum may also affect V since that term contains the electron-phonon interaction responsible for superconductivity. Finally, the reduction in specific volume affects $N(0)$ in a manner which may be separated (at least formally) as follows: (a) an increase in the spatial density of electrons, and (b) a modification of the electronic band structure due to the reduced interatomic spacing.

In the present case, the total change in $N(0)$ with pressure can be obtained from γ, the temperature coefficient of the normal electronic specific heat. The value of γ can be deduced thermodynamically from the temperature dependence of the critical field as $T \rightarrow 0°K$. A somewhat analogous measurement (but presumably without the complication of changes in the phonon spectrum) has recently been described where the changes in $N(0)V$ were due to dilute impurity additions (which have the effect of depressing T_c of the impure superconductor).[4,5]

From an experimental standpoint, Pb should be a favorable element on which to study the effect of pressure upon γ. Because of its high critical temperature, a reduced temperature $t = T/T_c = 0.14$ is readily achieved with Pb without recourse to the special techniques necessary to make measurements below 1°K. It is thus convenient to obtain a relatively close approximation to the limiting low-temperature behavior of H_c from which γ must be derived.

II. EXPERIMENTAL

A. Apparatus and Procedure for Work Near T_c

The experimental procedure followed in this work was different above 4.2°K from what it was in the liquid helium range. For the work above 4.2°K the apparatus and general procedure were similar to that described by Hake and Mapother.[6] We will therefore give only a brief outline.

Two identical samples were placed in an isothermal container whose temperature was regulated electronically to about $10^{-4}°K$. One of the samples had pressure applied to it while the other served as a comparison sample. The critical field values of the two samples were alternately measured and the results plotted with time. In this way temperature drifts were readily apparent

[1] C. A. Swenson, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960) Vol. 11, p. 41.
[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[3] See, for example, B. Serin, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XV, p. 237.

[4] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids, **3**, 165 (1957).
[5] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).
[6] R. R. Hake and D. E. Mapother, J. Phys. Chem. Solids **1**, 199 (1956).

and it could be ascertained whether the two samples were drifting together. The drift curve for the sample under pressure was subtracted from that for the standard sample. This procedure gave, in a very direct manner, ΔH_c, the shift in critical field due to pressure.

For these measurements the pressure was kept below the solidification pressure of helium corresponding to the temperature at which the data were taken. The pressure of gaseous helium at the specimen was read directly on a high-precision Bourdon gauge at room temperature. This gauge was calibrated by the manufacturer and is accurate to ± 15 psi.[7]

B. Apparatus and Procedure for Work Below 4.2°K

Another apparatus was used for the work done below 4.2°K, which differed from the one used at higher temperatures in two respects. Most important, it was possible in this apparatus to measure the pressure in the helium surrounding the sample even though the helium had solidified. The second difference was the absence of a comparison sample. This made it necessary to measure the temperature to high precision, but was advantageous in that, aside from the sample under observation, there was no diamagnetic material about and therefore no magnetic field distortions at the sample.

A detailed drawing of this apparatus is shown in Fig. 1. The sample, marked A, is held by Teflon spacers on the axis of a tellurium copper fitting G. The tellurium copper piece serves to introduce the sample into the pressure chamber and to position it with respect to the external magnetic field. By virtue of its fairly high thermal conductivity, the tellurium copper piece provides an isothermal shield around the sample and communicates its temperature to the lower carbon resistor, M. The pressure vessel, B, is made of beryllium copper, heat treated to an ultimate tensile strength of approximately 200 000 psi. A second carbon resistor, F, was clamped at the top of the bomb to check for temperature gradients.

The seal against high pressure is made by compressing a Teflon gasket, H, against a flange on the tellurium-copper piece (G) and the wall of the pressure vessel. This gasket is compressed by a hardened beryllium-copper ring, N, clamped in position by the large beryllium-copper plug, E, which is bolted to the bottom of the bomb. At low temperatures this seal proved tight up to pressures of about 13 000 psi, but above this pressure leakage occurred.[8]

Fig. 1. Cross-section view of the pressure bomb assembly. Parts shown are: A—Pb specimen; B—beryllium copper bomb; C—capacitor plates for pressure measurement; D—specimen pickup coil; E—clamping plug and dummy pickup coil; F—upper carbon thermometer; G—tellurium copper specimen holder; H—Teflon pressure gasket; J—pressure line; K—Teflon insulator; L—split copper support for upper capacitor plate; M—lower carbon thermometer; N—beryllium copper clamping ring; O—heater coil.

---

[7] The gauge was obtained from Heise Bourdon Tube Company, Newton, Connecticut.

[8] Although Teflon is a satisfactory gasket material at helium temperatures, one must design to allow for the large thermal shrinkage of Teflon. This is handled straighforwardly by compressing the Teflon to a sufficiently high pressure that it won't "unload" at low temperatures. For this reason, the large surface area of the present gasket (necessitated by the low strength of the tellurium-copper flange) is a weakness of the present design.
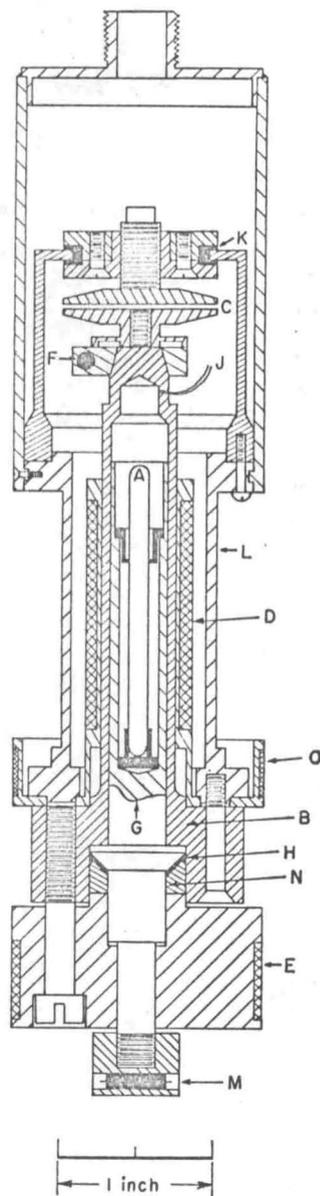
Helium gas, the pressure-transmitting fluid, is admitted to the pressure vessel by means of one of the stainless steel capillaries, J. The second capillary goes to the high precision Bourdon gauge at room temperature which measures the pressure. These capillaries, having inner and outer diameters of 0.008 and 0.016 inch, are soft soldered into the beryllium-copper chamber. The use of two lines, an inlet and a return, enables one to know whether the pressure is actually being transmitted to the sample or whether the lines are blocked.

At the top of the pressure vessel is a capacitor assembly, C, which serves to measure the pressure when the helium is solid. The top plate of the capacitor is threaded into an insulating bushing which is rigidly fixed with respect to the bomb, while the bottom plate is attached to the top of the bomb. Elastic extension of

the bomb due to internal pressure decreases the capacitor gap. This change is detected by a capacity bridge and is balanced out with an external capacity in parallel with the bomb.

The bomb capacitor is directly calibrated against the pressure readings of an external Bourdon tube gauge which measures the pressure of gaseous helium within the bomb. The calibration is done by raising the temperature of the bomb to a value such that the helium remains gaseous at the highest pressure reached. At the temperatures of calibration (about 10 to 15°K) the elastic properties of the bomb's walls are essentially temperature independent and it is assumed that the calibration is valid down to the lowest temperature of measurement.

The pressure sensitivity of the bomb capacitor depends upon the adjustment of the initial (zero pressure) spacing between the capacitor plates. In the present work, with a spacing of about 0.015 inch, the sensitivity was about 2×10^{-4} $\mu\mu f$/psi.

The assembly shown in Fig. 1 is suspended in a can filled with helium gas, and this can is surrounded by a second can immersed in liquid helium. A schematic diagram of a cryogenically similar apparatus and the method of temperature regulation have been described.[6]

Critical fields were determined by a ballistic induction method. A complete description and analysis of this method, as well as a detailed description of the Dewars, solenoids, and a cryostat substantially the same as the one used for this experiment have been given elsewhere.[9]

Temperatures were obtained in two ways. For Run No. 1 the temperature was measured using a carbon resistor calibrated against the critical field of lead at zero pressure. Calibrations were made at the beginning, at the end, and in the middle of the run which lasted for one week. Differences between the calibrations varied from 1 millidegree at 4.2°K to about 4 millidegrees at the lowest temperatures obtained. These differences introduce an uncertainty of about 0.1 gauss in ΔH_c which is about the same size as the scatter in the data, and we therefore ignore it. For Runs 2 and 3 liquid helium was condensed in the inner can and the temperature was obtained from measurement of its vapor pressure.

The experimental procedure was as follows. The inner can was raised to a temperature somewhat greater than the solidification temperature of helium at the pressure desired. Pressure was then applied to the sample by means of helium gas and a bomb calibration obtained. After the high-pressure gas inlet blocks with solid helium, the entire bomb assembly is cooled slowly allowing the helium in the pressure vessel to solidify. During the cooling the bomb capacitor is measured as a function of temperature. A typical cooling curve is shown in Fig. 2. The initial decrease in pressure of the bomb with
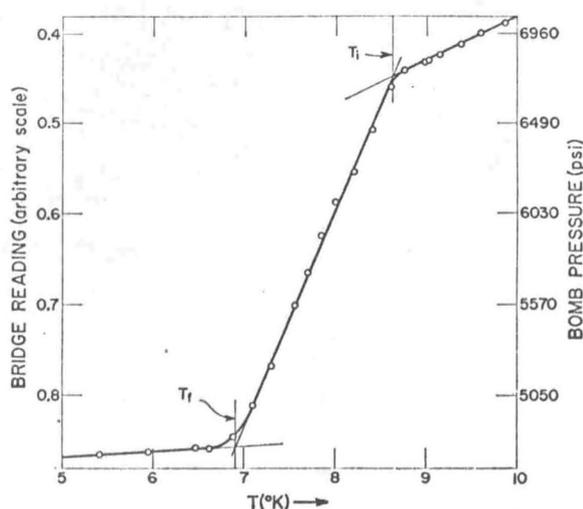

FIG. 2. Typical pressure variation in bomb during solidification of helium (which occurs at approximately constant volume). Bridge readings give the value of a balancing capacitor in parallel with the bomb capacitor. Pressure calibration is indicated on the right-hand scale.

decreasing temperature is caused by thermal contraction of the gas. A slight reduction in pressure with decreasing temperature is observed following solidification ($T < T_f$), but this causes no difficulty since the bomb capacitance can be measured at the temperature of the critical field measurements. Below 4°K the thermal expansion of solid He is negligible[10] and the bomb pressure remains constant.

At T_i the gas begins to solidify, with the solidification complete at T_f. In the region $T_f < T < T_i$ the helium in the bomb presumably follows the melting curve, the solidification taking place at essentially constant volume. The final pressure of the solid helium around the Pb specimen is given directly by the calibration of the bomb capacitor. However it is also possible to check the pressure obtained from the capacitor reading by using the observed value of T_f to check for self-consistency with the existing data on the thermodynamic properties of helium along the melting curve.[10] The directly measured and thermodynamically inferred values agree within about 3%.

The cooling described above is done over a period of one or two hours. It appears that this rate is slow enough so that no inhomogeneous strains are set up in the solid helium. Recent work has shown that, when subjected to inhomogeneous strain, lead exhibits large magnetic hysteresis in the superconducting transition.[11] The details of the magnetic transitions of our sample do not vary with pressure in any way. We take this fact to be a confirmation of the absence of inhomogeneous strain in

[9] J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. 103, 1657 (1956).

[10] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) A218, 291 (1953); R. L. Mills and E. R. Grilly, Phys. Rev. 99, 480 (1955).
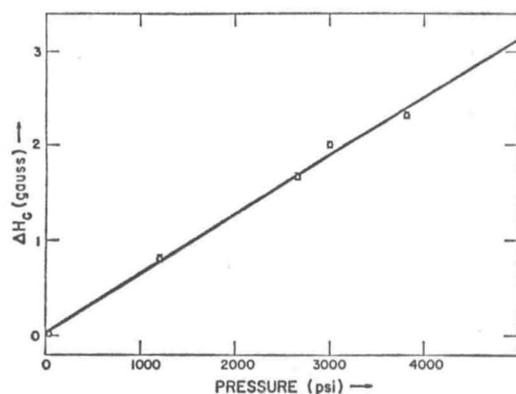
[11] R. W. Shaw and D. E. Mapother, Phys. Rev. 118, 1474 (1960).

FIG. 3. Shift of critical field with pressure. Measurements at $T=6.86°K$, $H_e=72$ gauss when $P=0$.

the specimen despite the use of solid helium as the pressure fluid.

C. Specimens and Details of the Magnetic Transitions

The specimens used in this work were in the form of long thin cylinders. The samples used in the measurements near T_c were 5.5 cm long and 0.24 cm in diameter. The sample used for the low-temperature measurements was 5.1 cm long by 0.32 cm in diameter. All the samples were vacuum cast in graphite-coated glass tubes which were subsequently etched away. The cooling from the melt was done in a gradient furnace at a rate of about 20°C per hour. The Pb from which the samples were grown was nominally 99.999% pure, obtained from the American Smelting and Refining Company. Etching showed a grain size of about 1 cm.

The magnetic transitions in the measurements below 4.2°K showed the same type of hysteresis which has been discussed in some detail in recent articles from this laboratory. The hysteresis observed here is somewhat smaller in magnitude than in the best previous specimens[11] but is identical in all other respects. The H_c values at low temperatures were corrected for this effect in the manner described in previous articles by taking the average of the apparent H_c values observed in the S-N and N-S transitions.[11,12]

III. EXPERIMENTAL RESULTS

A. Measurements Near the Critical Temperature

Data obtained in a series of isothermal measurements at $T=6.86°K$ are shown in Fig. 3. The pressure shift, ΔH_c, is defined by the equation

$$\Delta H_c(P,T)=H_c(0,T)-H_c(P,T), \quad (2)$$

and, as shown in Fig. 3, ΔH_c varies linearly with the applied pressure. When defined according to (2), ΔH_c is always positive since the application of pressure always

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

reduced H_c under conditions of constant temperature. The equation of the line in Fig. 3, as determined by a least-squares analysis, is

$$\Delta H_c(P)=(0.04\pm0.03)+(6.18\pm0.10)\times10^{-4}P, \quad (3)$$

where ΔH_c is in gauss and P is in psi. This gives

$$(\partial H_c/\partial P)_{T=6.86°K}=-(6.18\pm0.10)\times10^{-4} \text{ gauss/psi.}$$

Extrapolation of $(\partial H_c/\partial P)_T$ to the value characteristic of T_c requires knowledge of the pressure and temperature dependence of H_c which is obtained experimentally in the following section. Discussion of this extrapolation and the calculation of dT_c/dP will be deferred until after the presentation of the results of the measurements at low temperatures.

B. Measurements Below 4.2°K

1. *Effect of Pressure on H_0*

The data in the liquid helium range were taken in a series of isobaric measurements. Since the pressure shifts are small, a convenient way to display the data is to subtract off the known critical field of lead at zero pressure. The difference, ΔH_c, is defined by Eq. (2) where $H_c(O,T)$ is the function reported by Decker et al.[12] The ΔH_c values are plotted in Fig. 4(a) and 4(b) from which it may be seen that, within the scatter, the points vary linearly with T^2. The solid lines shown on the figure were determined by a least squares analysis of the values obtained for each pressure.

The intercept at $T^2=0$ in Fig. 4 defines ΔH_0, the shift in the critical field at the absolute zero. The variation of H_0 with pressure is shown in Fig. 5. The equation of the straight line fitting the data is

$$\Delta H_0=(0.14\pm0.09)+(5.36\pm0.14)\times10^{-4}P \text{ gauss}, \quad (4)$$

yielding

$$dH_0/dP=-(5.36\pm0.14)\times10^{-4} \text{ gauss/psi}$$
$$=-(7.90\pm0.21)\times10^{-3} \text{ gauss/atm.}$$

2. *Effect of Pressure on the Electronic Specific Heat*

As first shown by Daunt and Mendelssohn,[13] it is possible to deduce γ, the temperature coefficient of the normal electronic specific heat, from knowledge of the limiting temperature variation of H_c as T approaches 0°K. The relevant equation is

$$\lim_{T\to0°K}\frac{\Delta S}{v}=\gamma^*T=\left(\frac{\gamma}{v}\right)T=-\left(\frac{1}{4\pi}\right)\lim_{T\to0}H_c\left(\frac{\partial H_c}{\partial T}\right)_P, \quad (5)$$

where v is the molar volume of the superconductor.

At constant pressure the critical field of Pb can be accurately expressed as a polynomial in powers of T^2

[13] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) A160, 127 (1937); also J. G. Daunt, A. Horseman, and K. Mendelssohn, Phil. Mag. 27, 754 (1939).

as follows:

$$H_c(P,T) = H_0(P) + A_1(P)T^2 + A_2(P)^4 + \cdots. \quad (6)$$

Since the terms of higher power than T^2 become negligible as T approaches $0°K$, evaluation of (6) yields $\gamma^* = (H_0 A_1)/2\pi$.[14] Both H_0 and A_1 are sensitive to
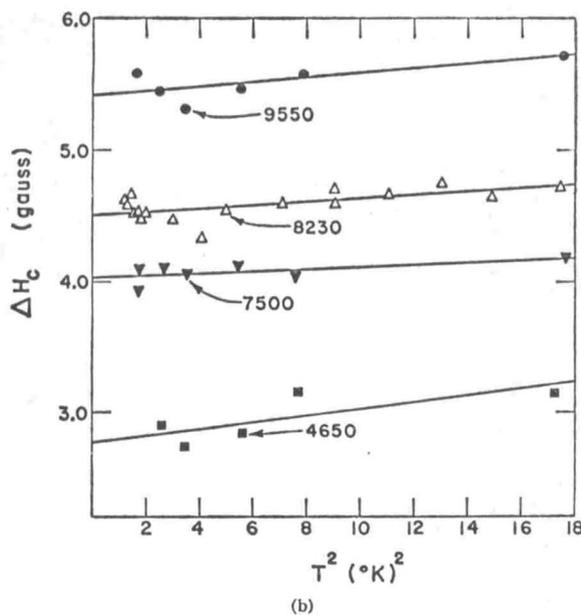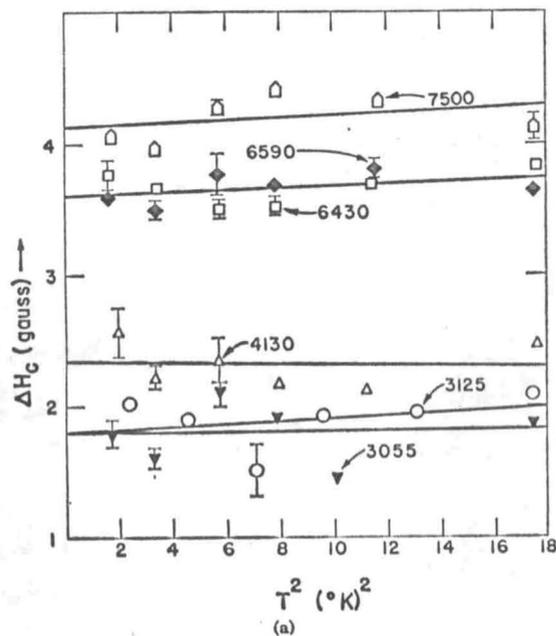

(a)

FIG. 4. Temperature variation of isobaric pressure shift for different pressures. Numbers identifying coded symbols give the pressure of measurement in pounds per square inch. (a) Run No. 1, six isobars at pressures from 3055 to 7500 psi. (b) Runs 2 and 3, four isobars at pressures from 4650 to 9550 psi.

FIG. 5. Variation of the critical field intercept, H_0, with pressure. o—Run 1; ●—Run 2; △—Run 3.

pressure so that

$$(1/\gamma^*)(d\gamma^*/dP) = (1/H_0)(dH_0/dP)$$
$$+ (1/A_1)(dA_1/dP). \quad (7)$$

Determination of (dA_1/dP) should, in principle, be done by measuring the limiting slope of a plot of H_c vs T^2 at the lowest temperature. Unfortunately, the experimental scatter, as well as the scarcity of points at the lowest temperatures of measurement, makes such an analysis unreliable in the present case. Instead, the following approximate method was used.

From (6) it follows that ΔH_c may be written as

$$\Delta H_c = H_c(0,P) - H_c(P,T)$$
$$= \Delta H_0 + \Delta A_1 T^2 + \Delta A_1 T^2 + \Delta A_2 T^4 \cdots. \quad (8)$$

In the temperature range below $4.2°K$ ($t = 0.585$), the contribution of terms involving T to a higher power than T^2 is small and decreases rapidly as T decreases. Accordingly, an approximately linear variation of ΔH_c with T^2 is expected, with a slope about equal to $\Delta A_1(P)$. The data of Fig. 4 were analysed by least squares to obtain the slope, which was interpreted as ΔA_1. Adding the estimated ΔA_1 values to the value of $A_1(P=0)$ from previous work,[12] and plotting against pressure gives the results shown in Fig. 6. While the scatter of the points in Fig. 6 is considerable, a perceptible decrease in A_1 with increasing pressure seems to be present. From the slope of Fig. 6 the following value is obtained

$$(dA_1/dP) = -(1.39 \pm 1.17) \times 10^{-6} \text{ gauss/psi deg}^2.$$

Using previously reported values of H_0 and A_1,[12] Eq. (7) may be evaluated with the result that

$$(1/\gamma^*)(d\gamma^*/dP) = -(5.65 \pm 1.05) \times 10^{-7} \text{ (psi)}^{-1}$$
$$= -(8.31 \pm 1.54) \times 10^{-6} \text{ (atm)}^{-1}.$$

As might be expected, there seems little doubt that

___

[14] It should be expressly noted that the validity of this analysis requires that data at sufficiently low temperatures be available to define a va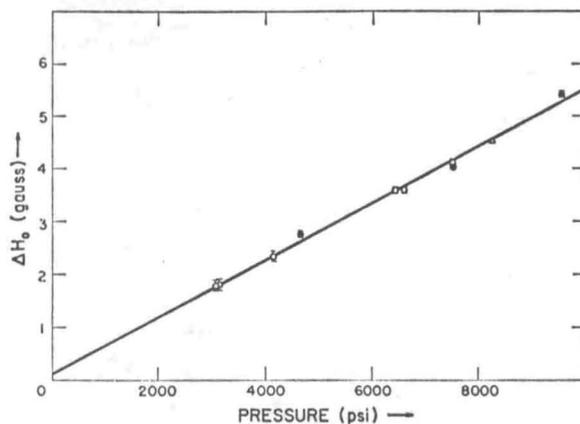lue of A_1 which does not vary with the lowest measuring temperature. For most superconductors this necessitates measurements below $1°K$, but because of the relatively high T_c of Pb, it appears that the limiting value of A_1 can be obtained with reasonable reliability from measurements no lower than $1.2°K$.
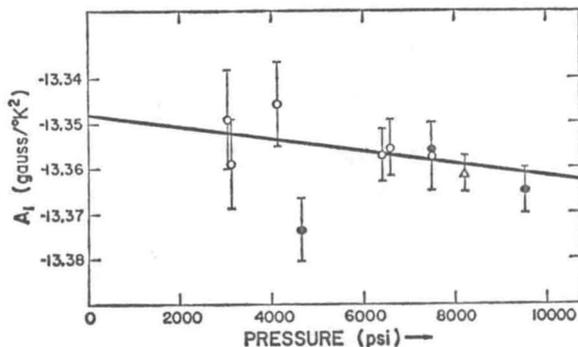
FIG. 6. Variation of the coefficient A_1 with pressure.
o—Run 1; •—Run 2; △—Run 3.

A_1 is rather insensitive to pressure. Unfortunately, despite the apparently small magnitude of (dA_1/dP) and its consequent experimental uncertainty, the (dA_1/dP) term in (7) makes a contribution of the same order of magnitude as the more accurately known (dH_0/dP) term. Accordingly, the possible error in (dA_1/dP) introduces a substantial uncertainty into the calculation of $(1/\gamma^*)(d\gamma^*/dP)$.

It seems possible that more measurements at lower temperatures will permit a more direct and accurate determination of (dA_1/dP). However, such measurements on Pb will be complicated by uncertainties introduced by the hysteresis correction which becomes more acute as 0°K is approached.

3. The H_c-T-P Surface for Lead

The present measurements permit a determination of the analytical form of the thermodynamic surface which separates the superconducting and normal regions above the P-T plane for the case of Pb. The critical field of Pb may be expressed in terms of reduced coordinates as follows.

$$h(P,t) = H_c(P,t)/H_0(P) = \sum_{n=0}^{5} a_n(t^2)^n, \quad (9)$$

where $a_0 = 1$ and $t = (T/T_c)$. We find that the data for all isobars measured in the present work are precisely represented by this expression. The differences between $h(P,t)$ at all temperatures and pressures of measurement and $h(0,t)$ as previously reported by Decker et al.[12] are of the order of 1 or 2×10^{-4} which is about the limit of precision of the present critical field measurements. Thus, to present experimental accuracy, the coefficients, a_n, in (9) are independent of pressure. This property (the invariance of the a_n under pressure) will be designated hereafter as "*geometrical similarity*" which, as shown later, is one (but not the only) condition of the familiar "similarity principle."

If our results are idealized by the assumption that geometrical similarity is exactly obeyed, the critical field

surface may be described by the following expression

$$H_c(P,T) = H_0(P)f(t), \quad (10)$$

where $H_0(P)$ is the linear function of P described above and $f(t)$ is the reduced critical field curve of Decker et al.[12] In the following discussion we offer further evidence to support the suitability of this representation for the H_c-T-P surface of Pb.

(a) *Temperature variation of* $(\partial H_c/\partial P)_T$. The consistency of the assumption expressed in (10) with experimental observations may be demonstrated by comparing the results which it predicts with the observed temperature dependence of $(\partial H_c/\partial P)_T$.

Differentiation of (10) yields

$$(\partial H_c/\partial P)_T = f(t)(dH_0/dP) \\ - (H_0/T_c)(dT_c/dP)t(df/dt), \quad (11)$$

and (dT_c/dP) may be evaluated from the general relation

$$(\partial T/\partial P)_{H_c} = -(\partial H_c/\partial P)_T(\partial T/\partial H_c)_P.$$

At $T = T_c$ and $P = 0$, this becomes

$$dT_c/dP = -\frac{(\partial H_c/\partial P)_{T=T_c}}{(\partial H_c/\partial T)_{P=0}}. \quad (12)$$

For comparison with experimental data, it is convenient to cast (11) into a dimensionless form by dividing through by (dH_0/dP). The resulting equation is

$$\Delta H_c(P,t)/\Delta H_0(P) = (\partial H_c/\partial P)_T/(dH_0/dP) \\ = f(t) - Bt(df/dt), \quad (13)$$

where

$$B = \frac{H_0(dT_c/dP)}{T_c(dH_0/dP)} = \frac{d \ln T_c/dP}{d \ln H_0/dP},$$

and $\Delta H_c(P,t)$ and $\Delta H_0(P)$ are the shifts resulting from the same applied pressure at the temperature corresponding to t and at 0°K, respectively.

Accurate evaluation of B involves an extrapolation to determine $(\partial H_c/\partial P)_{T_c}$. We shall defer comment on this point until later since the extrapolation depends on the validity of (10) which is presently under consideration. For the moment we simply assert that B is practically independent of pressure.[15] Thus, it follows that (13) describes a relation which is independent of the pressure of measurement. The comparison between experimental values of $\Delta H_c/\Delta H_0$ for various pressures and the predictions of (13) via (10) is shown in Fig. 7. The agreement is quite satisfactory.

---

[15] Irrespective of its actual magnitude, the invariance of B with respect to change in pressure follows from the fact that it is determined by the ratio of the derivatives (dT_c/dP) and (dH_0/dP). Within the range of pressure employed here, H_c varies linearly with pressure at all temperatures. Thus, the pressure derivatives in the expression for B [which are computed from the limiting values of $(\partial H_c/\partial P)_T$ at $T=0$ and $T=T_c$] must be independent of pressure and the same must be true of B.
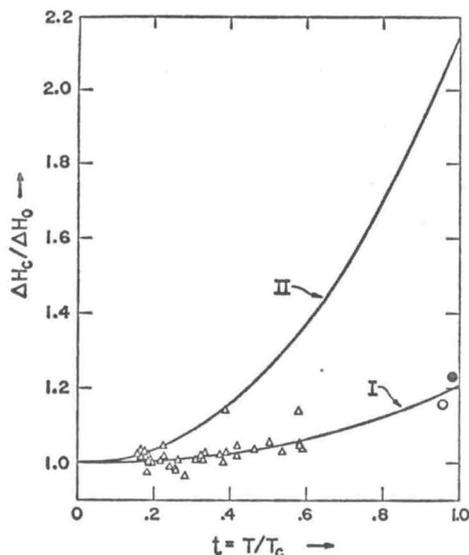
FIG. 7. Normalized variation of pressure shift with temperature. Curve I is obtained using the assumption of geometrical similarity and measured values of dH_0/dP and dT_c/dP. Curve II assumes geometrical similarity and also $H_0/T_c = $ const (i.e., the similarity principle). $\triangle$'s give results at various pressures up to 9550 psi which, in this representation, should be independent of the pressure. $\circ$ (present work) and $\bullet$ (reference 6) are results of measurements using gaseous helium near T_c.

It is interesting to compare the results shown in Fig. 7 with the "similarity principle"—a term generally understood to describe the simultaneous validity of the following two conditions: (a) geometrical similarity (as previously defined) and (b) the requirement that $H_0(X)/T_c(X)$ is independent of X, where X is an independent variable such as the pressure or the isotopic mass.[16] Although these two conditions are independent, available evidence as well as theoretical considerations indicate that both apply in the case of the isotope effect (in which connection the term "similarity principle" was first introduced).[17,18] Previous pressure effect results have suggested that the similarity principle was obeyed in the case of tin but not in the case of indium.[16]

The condition of a constant value of H_0/T_c is definitely not fulfilled in the case of Pb. If H_0/T_c were constant, it would follow that

$$\frac{(dH_0/dP)}{(dT_c/dP)} = \frac{H_0}{T_c},$$

which gives the value $B=1$ in Eq. (13). The value, $B=1$, leads to the curve marked II in Fig. 7 which is clearly beyond the limit of the experimental uncertainty, especially near T_c. (Curve I, which fits the experimental data, corresponds to a value of $B=0.562$.) Even though

the scatter of the experimental points in Fig. 7 is appreciable, the data seem good enough to provide reasonable confirmation of the hypothesis which underlies curve I.

It will be noted that the slopes of curves I and II differ by a factor of almost 6 at T_c. This is enough to introduce appreciable error into the extrapolation of experimental values of $(\partial H_c/\partial P)_T$ to T_c if such extrapolation were made according to the similarity principle.

(b) *Pressure effects on T_c.* The value of dT_c/dP is of interest for comparison with theory and to permit the calculation of the constant B introduced in (13). As shown in (12), dT_c/dP requires knowledge of the values of $(\partial H_c/\partial P)_T$ and $(\partial H_c/\partial T)_P$, both evaluated at $T=T_c$. An accurate value of $(\partial H_c/\partial T)_P$ is available from earlier work,[12] but determination of $(\partial H_c/\partial P)_{T=T_c}$ involves extrapolation of measurements made at temperatures below T_c and is somewhat sensitive to the analytic form of the H_c-T-P surface.

Assuming the validity of (10) it follows quickly from (11) and (12) that

$$(\partial H_c/\partial P)_{T_c} = (T_c/H_0)(1/t)(dt/df)(\partial H_c/\partial T)_{T_c}$$
$$\times [(\partial H_c/\partial P)_T - f(t)(dH_0/dP)], \quad (14)$$

where $(\partial H_c/\partial P)$ is the experimental value obtained at the temperature $T=T_c t$.

The value obtained from (14) in the present work is

$$(\partial H_c/\partial P)_{T_c} = -(6.23\pm0.10)\times10^{-4} \text{ gauss/psi}$$
$$= -(9.15\pm0.15)\times10^{-3} \text{ gauss/atm,}$$

and, using (12),

$$dT_c/dP = -(3.84\pm0.07)\times10^{-5} \text{ deg/atm.}$$

These values are about 6% smaller than a similarly corrected value derived from earlier measurements near T_c by Hake and Mapother.[19] For reasons not clearly understood, this difference is greater than the reported experimental error, but the discrepancy does not seriously complicate the picture as can be seen from Fig. 7. The two experimental points nearest T_c in Fig. 7 were obtained by calculating $\Delta H_c/\Delta H_0 = (\partial H_c/\partial P)_T/(dH_0/dP)$ using experimental values of the derivatives obtained in the present work and from the corrected value of $(\partial H_c/\partial P)_T$ of the previous pressure effect work.[6] The scatter of these points is not substantially worse than that apparent in some of the lower temperature measurements shown in the same figure. Thus, this uncertainty does not compromise the previous conclusions regarding the validity of curve I.

---

[16] N. L. Muench, Phys. Rev. 99, 1814 (1955).
[17] J. M. Lock, A. B. Pippard, and D. Shoenberg, Proc. Cambridge Phil. Soc. 47, 811 (1951).
[18] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. 121, 86 (1961).

[19] Corrections must be applied to the earlier reported value in the light of recently improved accuracy in the knowledge of the superconducting constants of Pb. These corrections affect the earlier values of the temperature of measurement, T_c, $(\partial H_c/\partial T)_P$, and also the earlier assumption that the similarity principle was valid. The final corrected value is $(\partial H_c/\partial P)_T = -(6.63\pm0.12)\times10^{-4}$ gauss/psi $= -(9.75\pm0.18)\times10^{-3}$ gauss/atm and $dT_c/dP = -(4.09\pm0.08)\times10^{-5}$ deg/atm.

The quantity B in Eq. (13) is defined as

$$B = \frac{H_0(dT_c/dP)}{T_c(dH_0/dP)}.$$

Substituting experimental values yields $B=0.545\pm0.037$ from the data of the present work, and $B=0.580\pm0.041$ using the data of the earlier measurements. The cumulative effect of experimental uncertainty in the quantities used in the calculations has magnified the uncertainty in B to a point where the errors overlap. Under the circumstances, it seems reasonable to use the average value of $B=0.562$, which is what was done in computing curve I in Fig. 7. The average value of dT_c/dP becomes $-(3.97\pm0.10)\times10^{-5}$ deg/atm.

(c) *Derivation of* $(1/\gamma^*)(d\gamma^*/dP)$ *from the* H_c-T-P *surface.* The internal consistency of our representation of the H_c-T-P surface for Pb may also be exhibited by calculation of $(1/\gamma^*)(d\gamma^*/dP)$ from (10). By comparison of coefficients in (6) and (9) it is seen that

$$A_1 = H_0 a_1/T_c{}^2. \tag{15}$$

The quantity $(1/A_1)(dA_1/dP)$ may be evaluated by differentiation of (15) and inserted in (7) to give

$$(1/\gamma^*)(d\gamma^*/dP) = 2[(1/H_0)(dH_0/dP)$$
$$- (1/T_c)(dT_c/dP)] + (1/a_1)(da_1/dP). \tag{16}$$

According to (10) we set $da_1/dP=0$, and substituting the average of the (dT_c/dP) values from the previous section, we obtain

$$(1/\gamma^*)(d\gamma^*/dP) = -(5.88\pm0.80)\times10^{-7} \text{ (psi)}^{-1},$$

which, aside from the appreciable uncertainties involved, is within 4% of the value obtained by experimental determination of dA_1/dP at the lowest temperature.

It must be emphasized that this agreement does not improve the accuracy of our knowledge of the pressure variation of γ^*. It only shows that the assumption, $da_1/dP=0$, is consistent with the best experimental determination of (dA_1/dP). A more rigorous experimental test of the pressure independence of a_1 encounters the same problems and is, in fact, identical with the problem of more accurate measurement of (dA_1/dP).

4. Comparison with Other Measurements

Values of $(\partial H_c/\partial P)_T$ may also be deduced from measurements of the change in length which occurs at the superconducting transition. Results of such measurements on Pb have been previously reported by other workers and are listed below for comparison.

Olsen and Rohrer report[20]

$$(dH_0/dP) = -(6.4\pm0.3)\times10^{-3} \text{ gauss/atm}$$
$$(\partial H_c/\partial P)_{T_c} = -(11.2\pm1.0)\times10^{-3} \text{ gauss/atm}$$

[20] J. L. Olsen and H. Rohrer, Helv. Physics Acta. 30, 49 (1957).

while Cody gives[21]

$$(dH_0/dP) = -(9.23\pm0.5)\times10^{-3} \text{ gauss/atm}$$
$$(\partial H_c/\partial P)_{T_c} = -(11.0\pm1.1)\times10^{-3} \text{ gauss/atm}.$$

As described above we obtain

$$(dH_0/dP) = -(7.90\pm0.21)\times10^{-3} \text{ gauss/atm}$$
$$(\partial H_c/\partial P)_{T_c} = -(9.45\pm0.30)\times10^{-3} \text{ gauss/atm},$$

where the latter value is obtained by averaging the values of $(\partial H_c/\partial P)_{T_c}$ from the two available measurements of the pressure effect near T_c.

The values derived from the length change observations are obtained by extrapolation of data observed in the temperature range from about 1.5 to 4.7°K, using the relation $(\partial H_c/\partial P)_T = a+bt^2$, where a and b are experimental constants. While the best available expression for $f(t)$ of Pb which was used in (14) shows small departures from a linear dependence of $(\partial H_c/\partial P)_T$ upon t^2, such deviations are beyond the limit of accuracy of any experimental measurements undertaken thus far and thus $(\partial H_c/\partial P)_T = a+bt^2$ is an adequate approximation.

Comparing values of dH_0/dP, the agreement between the present directly measured values and those deduced from length changes is fair. Olsen and Rohrer's value is about 19% smaller, while Cody's value is about 15% larger than our value. The temperature dependence of $(\partial H_c/\partial P)_T$ is roughly indicated by the ratio $(\partial H_c/\partial P)_{T_c}/(dH_0/dP)$ which has the value 1.76 from Olsen and Rohrer and 1.20 from Cody. The average value obtained from curve I of Fig. 7 is 1.20 which agrees very well with Cody's result though not with Olsen and Rohrer's.

We believe that the values obtained from our direct measurements are more reliable than those deduced from the length changes. However, it must be realized that the length change in the superconducting transition is extraordinarily small ($\Delta L/L \sim 10^{-7}$) and therefore very difficult to measure with precision. In view of this, we think that the agreement between the two types of measurement is remarkably good.

IV. DISCUSSION

The experimental values for lead, expressed in terms of both pressure and volume derivatives, have been collected in Table I. In converting the observed pressure

TABLE I. Summary of results.

X	$(d\ln X/dP)\times10^{-6}$ $(\text{atm})^{-1}$	$d\ln X/d\ln v$
H_0	-9.85 ± 0.26	$+5.90\pm0.16$
T_c	-5.53 ± 0.15	$+3.31\pm0.09$
γ^*	-8.31 ± 1.54	$+4.97\pm0.92$
θ_D	$+2.79$	-1.67

[21] G. D. Cody, Phys. Rev. 111, 1078 (1958).

derivatives to volume derivatives the value, $\kappa = 1.67 \times 10^{-6}$ per atm, calculated from the elastic constants,[22] was used for the compressibility of lead. The derivatives of the Debye temperature for lead, θ_D, are computed from the work of Dheer and Surange.[23]

These experimental data may be used in the formulas of the BCS theory to determine the pressure variation of V, the BCS interaction parameter. However, in making such a calculation it must be recognized that Pb is a special case among the superconducting elements for which the original BCS treatment of the cutoff frequency is probably incorrect. For this reason it is preferable to work from the BCS theoretical expression valid at $T = 0°K$ instead of Eq. (1).[24] Although Eq. (1) expresses the same result at T_c, it implies a law of corresponding states between superconducting elements which is known experimentally to be invalid for Pb.[12]

From BCS's Eq. (2.42) we write

$$H_0^2/8\pi \simeq 2N(0)(h\omega)^2 \exp[-2/N(0)V]. \quad (17)$$

Differentiating and replacing $[d \ln N(0)/dP]$ by $(d \ln\gamma^*/dP)$ we obtain

$$\frac{d \ln V}{dP} = N(0)V \left[\frac{d \ln H_0}{dP} - 0.5 \frac{d \ln\gamma^*}{dP} - \frac{d \ln\theta_D}{dP} \right] - \frac{d \ln\gamma^*}{dP}. \quad (18)$$

Evaluating (18) from the experimental data [and, for reasons discussed below, using $N(0)V = 0.66$] we obtain $d \ln V/dP = 3.4 \times 10^{-6}$ per atm (or $d \ln V/d \ln v = -2.04$). With the same value of $N(0)V$, an analogous calculation proceeding from Eq. (1) gives the result $d \ln V/dP = 2.8 \times 10^{-6}$ per atom which is not significantly different from the result of (18).

It is difficult to place limits on the precision of our calculated value of $(d \ln V/dP)$. Because of the present inadequacy of the theoretical understanding of Pb, there is doubt regarding a suitable value for $N(0)V$. The value $N(0)V = 0.41$, obtained by solving Eq. (1) using experimental values of T_c and θ_D, implies a cutoff frequency corresponding to $0.75\theta_D$. For the case of Pb, estimates based on lifetime effects[25] indicate that the cutoff frequency may be of the order of $\theta_D/3$ or even less. In evaluating (18) we have used Morel's calculation[20] for Pb, $N(0)V = 0.66$, which corresponds to a cutoff frequency of $0.3\theta_D$. A value of $N(0)V$ greater than unity is required to reverse the sign of $(d \ln V/dP)$, the positive sense of which is a noteworthy feature of the present results.

The BCS criterion for superconductivity requires that

V be positive, and the application of pressure increases V. An increase in V, if acting alone, favors superconductivity, and so would shift T_c to higher temperatures. However, the change in $N(0)$ must over-ride the changes associated with V and θ_D to produce a net decrease in T_c if the theory is to be in accord with experiment.

Morel has described detailed calculations of the pressure effect[26] based on the BCS theory via Eq. (1). His theoretical expressions are not in good agreement with the results described above. In addition to predicting a negative value of $(d \ln V/dP)$, Morel's results are very sensitive to the value $(d \ln\gamma^*/dp)$ employed in the calculation. For Pb he uses a value of about 1.2×10^{-6} per atm deduced from earlier results,[20] but this is considerably smaller than the value of the present work. Revising his calculations using the experimental values listed above does not improve the agreement with experiment. Such revision increases his calculated value of $(d \ln T_c/dP)$ from about half the observed value to a new result which is 3.8 times larger than the observed value.

A theoretical estimate of the experimental constant, B, is possible from BCS's Eq. (3.39) which is valid at $0°K$, and according to which

$$H_0^2 \propto N(0)\epsilon_0^2, \quad (19)$$

where ϵ_0 is the energy gap at $0°K$. Despite the abnormally large value of ϵ_0 characteristic of Pb ($4.1kT_c$[27] vs $3.5kT_c$ for the BCS theory), it seems likely that ϵ_0/T_c is independent of pressure; particularly so in view of the observed geometrical similarity expressed by (10). If it is assumed that ϵ_0/T_c is independent of pressure, (19) gives

$$H_0^2 \propto \gamma^* T_c^2. \quad (20)$$

[The same relation follows by eliminating common factors between Eqs. (1) and (17) since they implicitly contain the assumption, $\epsilon_0 T_c = \text{const}$. However, this approach is less fundamental than (19)]. Differentiation of (20) leads to the following expression

$$B = \frac{d \ln T_c/dP}{d \ln H_0/dP} = 1 - (0.5)\frac{d \ln\gamma^*/dP}{d \ln H_0/dP}. \quad (21)$$

Substituting experimental values in (21) gives $B(\text{calc}) = 0.58$ which is in very good agreement with the directly measured value, $B(\exp) = 0.562$.

We turn now to the effect of pressure upon γ^*. In general[28]

$$\gamma^* = \tfrac{2}{3}\pi^2 k^2 N(0), \quad (22)$$

where k is Boltzmann's constant. From Eq. (22) {which was the basis for the replacement of $[d \ln N(0)/dP]$ by

[22] E. Goens, Ann. Physik 38, 456 (1940).
[23] P. N. Dheer and S. L. Surange, Phil. Mag. 3, 665 (1958).
[24] J. Bardeen (private communication).
[25] J. Bardeen and J. R. Schrieffer, *Progress in Low-Temperature Physics*, edited by J. C. Gorter (to be published), Vol. III.

[26] P. Morel, J. Phys. Chem. Solids 10, 277 (1959).
[27] D. M. Ginsberg and M. Tinkham, Phys. Rev. 118, 990 (1960); P. L. Richards and M. Tinkham, Phys. Rev. 119, 575 (1960).
[28] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1954), Chap. VI.

$(d \ln\gamma^*/dP)$ in (18)}, we obtain

$$d \ln N(0)/dP = d \ln\gamma^*/dP = -8.31 \times 10^{-6} \text{ per atm.} \quad (23)$$

This result is very different from that expected from the free-electron model, according to which $N(0) \propto n^{\frac{2}{3}}$, where n is the number of electrons per unit volume. However, in general,

$$d \ln n/dP = -d \ln v/dP = \kappa, \quad (24)$$

where v is the molar volume and κ is the compressibility, and so the free electron model predicts

$$[d \ln N(0)/dP]_{\text{fr. el.}} = \frac{1}{3}(d \ln n/dP)$$
$$= \kappa/3 \simeq +5.6 \times 10^{-7} \text{ per atm}, \quad (25)$$

a result 15 times smaller than the measured value and of the wrong sign. The implication is clear that the free-electron model is not very satisfactory for dealing with the pressure effect in the case of Pb.

Consider now a density of states curve having the shape near the Fermi energy as suggested by Gold.[29] On the basis of Steele's measured values of the absolute thermoelectric power of Pb,[30] Gold obtains

$$\frac{1}{N(E_F)}\left(\frac{\partial N(E)}{\partial E}\right)_{E_F} = -0.90 \text{ per ev}, \quad (26)$$

where $N(E_F)$ is the density of states for both spins, i.e., $N(E_F) = 2N(0)$. The Fermi energy, E_F, is defined by the equation

$$\int_0^{E_F} N(E)dE = n. \quad (27)$$

Differentiating (27) with respect to pressure

$$\frac{dn}{dP} = n\kappa = \int_0^{E_F} \frac{\partial N(E)}{\partial P}dE + N(E_F)\frac{dE_F}{dP} \quad (28)$$

and, solving for (dE_F/dP), we obtain

$$\left(\frac{dE_F}{dP}\right) = \frac{n\kappa}{N(E_F)} - \frac{1}{N(E_F)}\int_0^{E_F}\frac{\partial N(E)}{\partial P}dE. \quad (29)$$

[29] A. V. Gold, Phil. Mag. 49, 73 (1960).
[30] M. C. Steele, Phys. Rev. 81, 262 (1951).

A detailed calculation is required to evaluate $[\partial N(E)/\partial P]$, but, as a rough approximation, we shall take it to be zero. We thus obtain from (20)

$$\frac{dE_F}{dP} \simeq \frac{n\kappa}{N(E_F)} = 5.15 \times 10^{-5} \text{ ev/atm}, \quad (30)$$

where we have used the values, $N(E_F) = 1.30$ per ev per atom from the value of γ given by Decker[12] and $n = 4$ per atom.

A general expression for the pressure variation in the density of states at the Fermi surface is

$$\frac{dN(E_F)}{dP} = \left(\frac{\partial N(E)}{\partial P}\right)_{E_F} + \left(\frac{\partial N(E)}{\partial E}\right)_{E_F}\frac{dE_F}{dP}. \quad (31)$$

According to the present approximation $[\partial N(E)/\partial P] = 0$, and so we finally obtain

$$\frac{d \ln N(E_F)}{dP} \simeq \frac{1}{N(E_F)}\left(\frac{\partial N(E)}{\partial E}\right)_{E_F}\frac{dE_F}{dP}$$

$$= -4.6 \times 10^{-6} \text{ per atm} \quad (32)$$

upon inserting the values from (26) and (30).

The approximate result in (32) compares reasonably well with the experimental value of -8.31×10^{-6} per atm. Moreover it can be seen from (29) and (31) that the effect of including the neglected $[\partial N(E)/\partial P]$ term would make $[dN(E_F)/dP]$ more negative. Since pressure decreases the interatomic distance and therefore broadens the energy bands, it is to be expected that $[\partial N(E)/\partial P]$ is negative. It is thus possible that an improved calculation will result in still better agreement with our experimental result.

ACKNOWLEDGMENTS