*Research supported by the Defence Research Board of Canada, Grant No. 9510-104.
[1]P. S. Swartz and C. P. Bean, J. Appl. Phys. **39**, 4991 (1968).
[2]S. L. Wipf, Phys. Rev. **161**, 404 (1967).
[3]K. Yamafuji, M. Takeo, J. Chikaba, N. Yano, and F. Irie, J. Phys. Soc. Jap. **26**, 315 (1969).
[4]B. B. Goodman and M. R. Wertheimer, Phys. Lett. **18**, 236 (1965).
[5]M. R. Wertheimer and J. le G. Gilchrist, J. Phys. Rev. Chem. Solids **28**, 2509 (1967),
[6]L. S. Wright, D. C. Baird, and M. R. Wertheimer in *Proceedings of the Twelfth International Conference on Low-Temperature Physics*, edited by Eizo Kauda (Academic of Japan, Kyoto, 1971), p. 465.
[7]Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. 139, A1163 (1965).
[8]F. W. Grover, *Inductance Calculations* (Van Nostrand, Princeton, N.J., 1946), p. 35.
[9]R. B. Harrison, L. S. Wright, and M. R. Wertheimer (unpublished).

PHYSICAL REVIEW B VOLUME 7, NUMBER 5 1 MARCH 1973

Superconducting Energy Gaps from Magnetization Measurements: Pb-In System

C. T. Rao* and L. W. Dubeck
Physics Department, Temple University, Philadelphia, Pennsylvania 19122

F. Rothwarf
Electronics Technology and Devices Laboratory, Fort Monmouth, New Jersey 07703
(Received 19 May 1972)

Isothermal-magnetization data have been obtained for a series of well-annealed chrome-plated Pb-In alloys of In composition between 30 and 80 at.% in the temperature range 1.90 °K to the appropriate transition temperature. The empirical relation proposed by Toxen involving the thermodynamic-critical-field data and the energy gap has been found to be valid over a wide range of values of the Ginzburg–Landau parameter κ, the electron mean free path l, and for both weak and strong coupling alloys. Consequently, it may be used to obtain the energy gap at $T=0$ from the critical-field measurements both in the case of elemental and alloy superconductors. The experimentally determined Ginzburg–Landau parameters $\kappa_1(T)$ and $\kappa_2(T)$ show a stronger temperature dependence and are generally larger than predicted by existing weak coupling theories.

I. INTRODUCTION

One of the characteristic features of superconductivity as described by the BCS theory is the existence of a gap $\Delta(T)$ in the energy spectrum of single-particle Fermion excitations from the ground state. According to the BCS theory, for the weak coupling case the gap at $T=0$ °K is $2\Delta(0) = 3.52k_BT_c$, where k_B is Boltzmann's constant and T_c is the transition temperature. In the so-called strong coupling superconductors $2\Delta(0)$ assume values as large as $4.6k_BT_c$. Thus a measurement of $2\Delta(0)$ for a superconductor provides an estimate of the strength of the electron-phonon interaction.

An interesting relationship between the critical field of a superconductor and its energy gap was pointed out by Toxen.[1] This empirical relation states that

$$\left|\frac{dh}{dt}\right|_{t=1} = \frac{\Delta(0)}{k_BT_c} , \tag{1}$$

where $h=H_c(T)/H_c(0)$ is the reduced critical field, and $t=T/T_c$ is the reduced temperature. $H_c(T)$ and $H_c(0)$ are the thermodynamic critical fields at temperatures T and 0 °K, respectively. Relation (1) can be rewritten

$$\frac{T_c}{H_c(0)}\left|\frac{dH_c}{dT}\right|_{T=T_c} = \frac{\Delta(0)}{k_BT_c} . \tag{1'}$$

Toxen,[1] using measured superconducting parameters, has shown that relation (1) is very well satisfied by both weak coupling and strong coupling elemental superconductors. It should be emphasized that $|dh/dt|_{t=1}$ and $\Delta(0)/k_BT_c$ depart from the values predicted by the BCS theory for weak coupling superconductors, but their ratio does not. Whereas BCS[2] predict $|dh/dt|_{t=1} = 1.736$ and $\Delta(0)/k_BT_c = 1.764$, one finds for Pb[3,4] $|dh/dt|_{t=1} = 2.13$ and $\Delta(0)/k_BT_c = 2.17$. Thus both these parameter increase as the coupling strength increases. There have been arguments[5] that relation (1) is just a numerical coincidence. Theoretically, Rothwarf[6] has shown that Toxen's proposed relation is consistent with the BCS theory if one uses the temperature dependence of the effective electron-electron interaction.

The BCS expression for the gap involves the effective electron-electron interaction V in the form

$$\Delta_k(T) = -\tfrac{1}{2}\sum_{k'} \left[V_{kk'}/E_{k'}(T)\right]\Delta_{k'}(T)\tanh\tfrac{1}{2}\beta E_{k'}(T) , \tag{2}$$

where

$$B=1/k_BT, \quad E_k^2=\epsilon_k^2+\Delta^2(T) \quad ,$$

$$E_k^2=\hbar^2k^2/2m-E_F \quad .$$

$V_{kk'}$ is the matrix element for the scattering of a pair of electrons from the state $(k\uparrow, -k\downarrow)$ to $(k'\uparrow, -k\downarrow)$. $V_{kk'}$ may be composed of two terms, the first describing the attractive electron-electron interaction mediated by phonons and the second resulting from the screened Coulomb interaction. The phonon contribution $V_{kk'}^{\mathrm{ph}}$ in the superconducting state has been calculated by Eliashberg[7] to be of the form

$$V_{kk'}^{\mathrm{ph}}=\frac{2(E_{k'}+\hbar\Omega)\left|M(k,k')\right|^2}{(E_{k'}+\hbar\Omega)^2-E_k^2} \quad , \tag{3}$$

where Ω is a characteristic phonon frequency, and $M(k,k')$ is the electron-phonon interaction in the normal state. Expression (3) implies that $V_{kk'}$ is dependent on temperature through the E's. In the BCS theory $V_{kk'}$ is replaced by a constant V. Starting from (3) for the electron-electron interaction and taking into account the Coulomb repulsion, Rothwarf[6] was able to show that relation (1) can be valid over the entire range of effective coupling strengths (weak to strong). Sheahen[8] had also modified the BCS model with certain semiempirical corrections so that the BCS "laws of corresponding states" for sets of reduced quantities were found to apply to even strong coupling elemental superconductors. Sheahen showed that this extension of the BCS model could be justified by discarding the BCS assumptions that (a) the interaction is independent of temperature, and (b) the cutoff energy is the Debye temperature times Boltzmann's constant.

Although the Toxen relation has been verified to hold in a large number of elemental superconductors, there exists relatively little evidence of its validity in the case of superconducting alloys. It should be noted, however, that Sekula and Kernohan[9] assume the validity of relation (1) to calculate the Ginzburg-Landau parameter $\kappa_1(T)$ in their studies on Pb-Tl alloys up to 27-at.% Tl. On the other hand, Fischer and Maki[10] find a serious discrepancy in Toxen's equality in their studies on Pb+17-at.%-In alloy when they use the $\Delta(0)/k_BT_c$ values measured by Adler, Jackson, and Will.[3] They attribute this disagreement, in part, to the large ratios of $\Delta(0)/k_BT_c$ recorded by Adler *et al.* using unannealed, inhomogeneous alloy films. It is interesting to note that no such discrepancy was observed within experimental error over the range 0–28-at.% In in Pb by Rothwarf, Dubeck, and Aston,[11] who also used the same data for $\Delta(0)/k_BT_c$.

The Pb-In alloys examined in this work are particularly suited to test the validity of the Toxen relation for a variety of reasons. Firstly, energy-gap measurements for these alloys are available for comparison with critical-field measurements. Secondly, there is a wide variation in the strength of the electron-phonon interaction and the electron mean free path in these alloys. Pure Pb and pure In, with transition temperatures of 7.19 and 3.40 °K, respectively, are both type-I superconductors. Pb, with four electrons per atom, is a strong coupling superconductor and In, with three electrons per atom, is weak coupling. The mass of Pb is about twice that of In. Thus in these alloys both the solute mass and the electron concentration play an important role in determining the electron-phonon interaction. Thirdly, these non-transition-metal alloys are easy to prepare. Both the metals, with a fcc crystal structure, form a series of solid solutions, except in the composition range of approximately 70–88-at.% In where they form a homogeneous intermediate α phase. This phase is face-centered tetragonal. The width of the two-phase region between the two phases is extremely uncertain, but rough estimates[12] give a value of 1.5-at.% In.

II. EXPERIMENTAL METHODS

A. Sample Preparation

The samples were made from ingots of Pb, 99.95% purity, and In, 99.9999% purity, supplied by Bram Metallurgical Company. They were melted together in a Pyrex tube with a propane flame whose temperature exceeded 500 °C, under a vacuum of better than 5×10^{-5} mm of mercury. The molten metals were rotated and shaken thoroughly for about 20 min to ensure homogeneity, and then rapidly cooled in an ice and brine solution.

The slug was then transferred to another Pyrex tube bent at the bottom into a narrow (nearly 0.1-in.-i.d.) capillary in which the sample was formed. The geometry of this tube was so chosen as to minimize the possibility that air bubbles might be trapped inside the sample. The slug was then remelted again using the propane torch while continually shaking by hand. After homogenizing the melt for 20–30 min, the sample was quenched in brine. The inside of each tube had been rinsed with a solution of 0.01% mineral oil in carbon tetrachloride. A thin film of oil remaining after evaporation of the solvent facilitated the removal of the finished sample. Dipping the tube in liquid nitrogen allowed the sample to be removed from the tube by cracking the glass. It was then cut to the desired length using a clean razor blade. The specimen was immediately polished chemically with a mixture of 80% acetic acid with 20% hydrogen peroxide for about a minute, and then electroplated in a chromium bath. This plating suppresses surface superconductivity and serves to seal the surface against absorption of gases.

Each sample was vacuum annealed for periods ranging from 3 to 5 weeks in an oven at a temperature of 5–10 °C below its solidus point. The annealed samples were placed into clear Teflon holders for subsequent measurements, thus minimizing the risk of cold working during handling.

B. Measurement Techniques

The magnetization measurements were carried out using two highly sensitive magnetometers, a commercial FM-1 Foner vibrating-sample magnetometer manufactured by the Princeton Applied Research Corporation, and a homemade ballistic-galvanometer magnetometer. In the Foner apparatus the magnetic field, provided by a Magnion electromagnet with 12-in. pole faces, was applied in a direction transverse to the axis of the cylindrical sample and consequently it had a finite (approximately 0.5) demagnetization coefficient, whereas in the ballistic-galvanometer magnetometer the field, provided by a superconducting solenoid, was along the length of the sample and hence the demagnetization coefficient was nearly zero. The shapes of the magnetization curves obtained from these two magnetometers for a given sample at a given temperature will be different, owing to the different demagnetization effects, but the superconducting parameters obtained from them are the same.

Nearly reversible magnetization curves were obtained from the ballistic-galvanometer magnetometer after jarring the sample a number of times between the pick-up coils. The corresponding curves from the Foner magnetometer resulted when a small oscillatory magnetic field was superimposed on the sample in a direction mutually perpendicular to its axis and to the dc field. (For details, refer to the Appendix.)

A 68-Ω Allen-Bradley carbon resistor was used for temperature measurement in the range 1.60–7.25 °K. The thermometer was calibrated by measuring the vapor pressure of liquid helium and using the 1954 He^4 temperature scale of the NBS.

Resistivity measurements were made using the standard four-probe technique. Four leads were independently attached to the sample and the voltage developed by an appropriate transport current was measured by a Honeywell potentiometer.

C. Data Analysis and Errors

In analyzing the magnetization data the following procedure was used.

(i) The upper critical field H_{c2} was measured directly from the magnetization curve. There was little ambiguity in this measurement since the curves were perfectly reversible near H_{c2}.

(ii) $\kappa_2(T)$ was obtained from the slope of the magnetization curve near H_{c2} using the Cape–Zimmerman relation

$$4\pi\left(\frac{dm}{dH}\right)_{H=H_{c2}}=\frac{1}{1.16(2\kappa_2^2-1)+D}\ ,$$

where D was determined from the dimensions of the sample.

(iii) The area under the constructed "reversible" magnetization curve[13] was measured using a planimeter and $H_c(T)$ was determined from the relation

$$\int_0^{H_{c2}} M\,dh = H_c^2/8\pi\ .$$

(iv) $\kappa_1(T)$ was determined from the relation $\kappa_1(T)=H_{c2}(T)/\sqrt{2}\,H_c(T)$.

(v) The lower critical field $H_{c1}(T)$ was taken as the point of first observable departure from the initial Meissner slope for samples with $D=0$. For nonzero D this point corresponds to $(1-D)H_{c1}$.

(vi) The Foner-magnetometer data depend on the magnetic field sweep rate. This was corrected appropriately to zero-sweep rate in order to eliminate rate-dependent effects when comparing with theory. The corrected experimental data agreed, within the experimental error, with the ballistic-galvanometer data. These effects will be the subject of a future publication.

(vii) Errors: (a) The value of H_{c2} is reliable within the instrumental errors inherent in the process of obtaining the magnetization curves which were estimated to be less than 3%. (b) The magnitude of H_c obtained by integrating the reversible magnetization curve is believed to be reliable within a maximum error of 5%. (c) The error in H_{c1} is estimated to be less than 5%, which stems from the fact that the transition was not sharp. (d) The error in dM/dH near H_{c2} was 5–6%. Hence the error to $\kappa_2(T)$ is estimated to be about 3%. (e) The value of $\kappa_1(T)$, which was determined from the ratio of H_{c2} and H_c has a maximum error of 7–8%. (f) The accuracy of the temperature measurements is better than 0.5%. The width of the transition at T_c was typically 100 m °K, with T_c chosen to be the midpoint of the transition.

III. RESULTS

A. Transition Temperature

The transition temperature T_c was determined by plotting the three critical fields H_c, H_{c1}, and H_{c2} as a function of temperature. The value thus obtained agreed with the T_c from resistivity measurements. The T_c's determined this way are plotted as a function of indium concentration in Fig. 1. With increasing indium concentration in lead the transition temperature monotonically decreases. Within the uncertainty (± 50 m°K) of our measurements there is no indication of a change of slope near 30-at.% In, in disagreement with the observa-

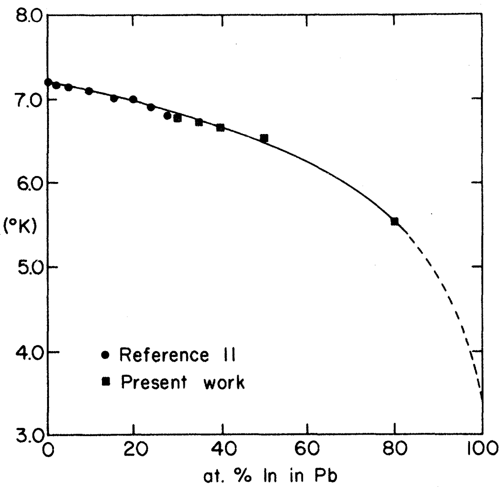

FIG. 1. Transition temperature vs at.% indium for Pb-In alloys.

tions of Farrell *et al.*[14] but in agreement with Culbert *et al.*[15] This variation of T_c with In composition is similar to that observed by Bon Mardion, Goodman, and Lacaze[16] for Pb-Tl alloys with increasing Tl concentration.

Recently, McMillan[17] has obtained an expression for the transition temperature within the framework of the strong coupling theory. According to this theory T_c is given by

$$T_c = \frac{\Theta}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) , \tag{4}$$

where Θ is a temperature corresponding to a characteristic phonon frequency, λ is the electron-phonon coupling parameter, and μ^*, which is generally found to be 0.10 ± 0.02 for nontransition metals, is the Coulomb pseudopotential of Morel and Anderson.[18]

McMillan's formula (4) can be approximated in a simplified form as

$$T_c \simeq \Theta\, e^{-(1+\lambda)/\lambda} .$$

Rewriting the coupling constant in terms of Θ as suggested by McMillan[17] this reduces to

$$T_c \simeq \Theta\, e^{-\Theta^2/C} , \tag{4a}$$

where C is a constant. This relationship predicts that Θ should increase with decreasing T_c for a given class of materials. Assuming that $\Theta = \Theta_D$, the Debye Θ, (4a) gives good agreement between the measured T_c and Θ_D for a large number of superconducting alloys.[17] However, for the Pb-In alloys, from the specific-heat measurements of Culbert *et al.*[15] it is found that the Debye temperature drops rapidly as indium is alloyed into lead from 104.11 °K for pure Pb to 78.65 °K for Pb+60-at.% In, while T_c also drops from 7.19 °K to 6.25 °K in that composition range. Pure indium, on the other hand, has a Θ_D of 111.00 °K. A similar behavior is noticed in Pb-Tl alloys also.[9] Thus it is incorrect to substitute Θ_D for Θ in (4a) for the Pb-In and Pb-Tl alloy systems. This is due to the fact that *different* averages of the phonon frequency go into Θ_D and the Eliashberg–McMillan theory.

B. Impurity Parameter

Gorkov[19] introduced a parameter ρ to characterize the purity of a superconductor; ρ is proportional to the ratio of the coherence length ξ to the electron mean free path l. This quantity is identical to λ used by Helfand and Werthamer[20] and α used by Tewordt[21] and the ratio ξ/l used by Eilenberger.[22] It is defined as

$$\rho = \hbar/2\pi k_B T_c \tau = 0.882\, \xi_0/l ,$$

where τ is the relaxation time for normal-state processes, and ξ_0 is the BCS coherence length at $T=0$ for the pure material. Gorkov calculated the ratio κ/κ_0 as a function of ρ, where κ_0 is the Ginzburg–Landau parameter in the pure limit.

The impurity parameter can also be calculated from the normal-state residual resistivity ρ_n independent of κ. This relationship is

$$\rho = 8.85\times10^{-3}\, \gamma^{1/2}\, \rho_n/\kappa_0 , \tag{5}$$

where γ, the coefficient of electronic specific heat, is in erg/cm^3 °K^2, ρ_n is in $\mu\Omega$ cm. Hence ρ can be determined from this relation provided κ_0 is known. Using Gorkov's work and (5) one can derive the well-known Goodman relation[16]

$$\kappa = \kappa_0 + 7.53\times10^{-3}\, \rho_n \gamma^{1/2} . \tag{6}$$

A plot of $\kappa_2(T_c)$ vs $\rho_n\gamma^{1/2}$ for the Pb-In alloys is a straight line, in qualitative agreement with relation (6). The γ's used here were the experimentally measured values of Culbert *et al.*[15] The experimental slope of this straight line, however, was 6.0×10^{-3} with an intercept of $\kappa_0 = 0.29 \pm 0.03$. This value of κ_0 is in good agreement with the calculated value of 0.28–0.30 by Farrell *et al.*[14] for these alloys, and the experimental value of 0.30 ± 0.02 by Kumpf,[23] who made a similar plot for Pb-Tl alloys. Sekula and Kernohan[9] also made a similar observation on Pb-Tl alloys. They have obtained a value of 6.1×10^{-3} for the slope and 0.2 for κ_0. These slopes differ from the Goodman slope of 7.53×10^{-3} as well as the Rauckhorst and Farrell[24] computation of 7.9×10^{-3}.

Using the experimental value of κ_0 and the specific-heat data of Culbert *et al.*[15] the impurity parameter for each specimen up to 50-at.% In was determined by means of relation (5). Since no measured value of γ for the Pb+80-at.%-In sample was available, ρ in this case was calculated using the relationship

TABLE I. Sample characteristics.

In comp. (at.%)	T_c (°K)	$H_c(0)$ (Oe)	$\kappa_1(T_c)$	$\kappa_2(T_c)$	ρ_n (Ω cm)	ρ	l (Å)	$\frac{\kappa_2(0)}{\kappa_2(T_c)}$	$\left(\frac{dh}{dt}\right)_{t=1}$	$\Delta(0)/k_B T_c$ (Ref. 3)	$\Delta(0)/k_B T_c$ (Ref. 31)
30	6.78	815	4.12	4.20	15.82	19.8	48	1.33	2.18	2.20	2.23
35	6.74	840	4.65	4.67	17.33	21.7	34	1.27	2.25	2.18	2.26
40	6.66	810	4.75	5.00	18.00	22.6	32	1.29	2.25	2.16	2.26
50	6.53	785	4.25	4.87	17.80	22.5	33	1.34	2.19	2.10	2.23
80	5.53	610	2.60	2.69	11.01	11.8	62	1.26	2.05	...	2.12

$$\frac{0.5807}{\kappa_0 H_c(0)}\left(\frac{dH_{c2}}{dt}\right)_{t=1}=\frac{12}{7\zeta(3)}+\frac{12}{\pi^2}\rho \qquad (7)$$

given by Helfand and Werthamer.[20] Here $\zeta(3)$ is the Riemann ζ function. These values of ρ are summarized in Table I and will be used in Sec. III C below.

The electron mean free path in these alloys was determined using the calculated values of ρ and the Gorkov definition of the impurity parameter. These values are also listed in Table I.

C. Ginzburg-Landau Parameters

The magnitude of the Ginzburg-Landau (GL) parameters $\kappa_1(T)$ and $\kappa_2(T)$ both increase with decreasing temperature for all the alloys tested. This increase is found to be significantly greater than predicted by theories. The values of these parameters at T_c appear to coincide within the combined experimental error of 10%. Such variations of both $\kappa_1(T)$ and $\kappa_2(T)$ in alloy specimens have been noted by several workers.[10,14,25,26] Measurements of $\kappa_2(T)$ by Farrell *et al.*[14] from bulk Pb-In magnetization studies have shown that it increases faster with decreasing temperature than theory predicts even in alloys close to the dirty limit. In their investigation, however, there was considerable irreversibility in the magnetization curves leading to uncertainties in the values of $\kappa_2(T)$ deduced from them.

The values of $\kappa_2(T)$ are found to be significantly larger than $\kappa_1(T)$ over the entire temperature range $0 < T < T_c$, for all the alloys investigated here. This is consistent with the results of Evetts and Wade,[27] who found this to be the case at 4.2 °K for Pb-In and and Pb-Bi alloys with roughly $\kappa(T) < 7$. Sekula and Kernohan[9] also found that $\kappa_2(T) > \kappa_1(T)$ for $T < T_c$ in Pb-Tl alloys.

Culbert *et al.*[15] on the other hand, observed that $\kappa_1(T_c) > \kappa_2(T_c)$ for Pb-In alloys. This result is in disagreement with our present results and all theoretical predictions, as well as previous experimental results. This discrepancy may be attributed to the procedure used by Culbert *et al.* to indirectly determine $\kappa_1(T_c)$.

Figures 2 and 3 give the reduced parameter $\kappa_2(t)/\kappa_2(1)$ as a function of t for the specimens investigated. The solid lines give the theoretical predictions of Eilenberger[28] for $\rho = 20$ and $\rho = 10$ in Figs. 2 and 3, respectively, with $\tau/\tau_{tr} = 1$ in the upper curve, 1.5 in the middle curve, and 2 in the lower curves, where τ_{tr} is the transport lifetime, and τ is the s-wave scattering lifetime. The experimental values are found to be larger than the predicted values. Such an effect was noted by Zoller and Dillinger,[29] also in Pb-In alloys. The results of French and Lowell[30] on Nb-Mo alloys with nearly reversible magnetization curves are in general agreement with Eilenberger's predictions near the dirty limit, but show increasing departure from theory as ρ increases. As shown in Table I, ρ for our samples varies from 11.8 to 22.6.

Further comparison of experiment with theory

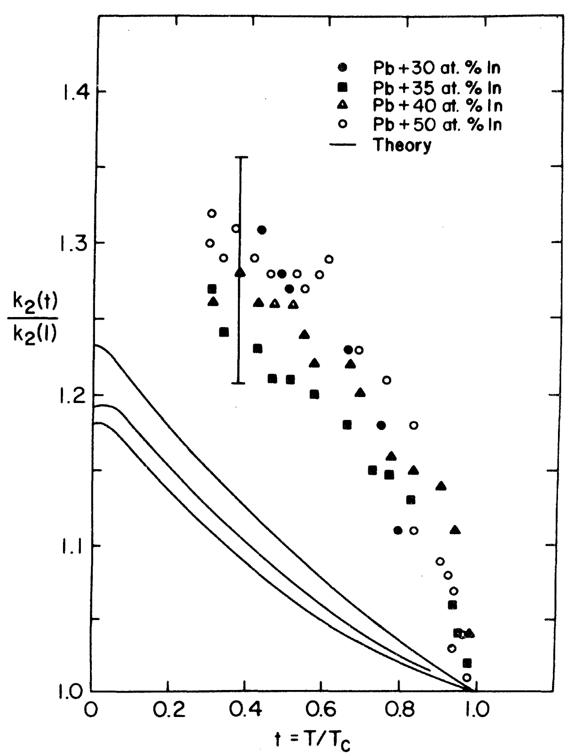

FIG. 2. Ratio of GL parameter $\kappa_2(t)$ to $\kappa_2(1)$ vs the reduced temperature $t = T/T_c$. The continuous lines are the theoretical curves of Eilenberger for $\rho = 20$ and $\tau/\tau_{tr} = 1$ for the upper curve, 1.5 for the middle curve, and 2 for the lower curve (Ref. 28).

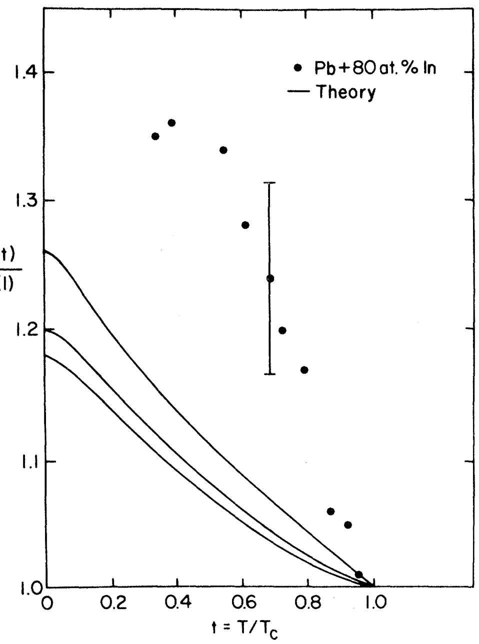

FIG. 3. Ratio $\kappa_2(t)$ to $\kappa_2(1)$ vs the reduced temperature $t = T/T_c$ for Pb+80-at.% In sample. The continuous lines are the theoretical curves of Eilenberger for $\rho = 10$, and $\tau/\tau_{tr} = 1$ for upper curve, 1.5 for the middle curve, and 2 for the lower curve (Ref. 20).

was facilitated by the normalized GL parameter $\kappa_2(0)/\kappa_2(T_c)$. Eilenberger's computation[28] of this ratio as a function of the impurity parameter for the three values of τ/τ_{tr} shows that although it initially decreases rapidly with increasing impurity content in the sample, it levels off to a constant value for approximately $\rho > 10$. These values are of the order of 1.2 and 1.15 for $\tau/\tau_{tr} = 1$ and 2, respectively. The experimental values of $\kappa_2(0)/\kappa_2(T_c)$ are shown in Table I. The values of $\kappa_2(0)$ were obtained by linear extrapolation to $T = 0$ of the lowest-temperature data of $\kappa_2(T)$. The general variation of $\kappa_2(0)/\kappa_2(T_c)$ with ρ is in qualitative agreement with the calculation of Eilenberger. However, it is clear that the experimental values are generally higher, and the increase of $\kappa_2(T)$ at low temperatures is much larger than what theory predicts. Such deviations of $\kappa_2(0)/\kappa_2(T_c)$ from theory were also noted in Nb-Ti alloys by Fietz and Webb[25] and in Pb-In alloys by Farrell *et al.*[14]

D. Thermodynamic Critical Field

Experimentally determined thermodynamic critical fields showed positive deviations from the parabolic dependence $H_c(t) = H_c(0)(1 - t^2)$ for all the samples. Such deviations, which are generally attributed to a strong coupling interaction, have also been observed by Decker and co-workers,[4] Sekula and Kernohan,[9] and Fietz and Webb[25] on various superconducting alloys.

The critical fields values at 0 °K were obtained from the plots of $H_c(t)$ vs t^2 by extrapolating the low-temperature values of $H_c(t)$ to $t = 0$. These data are listed in Table I and plotted in Fig. 4 as functions of indium concentration. Also shown for comparison in this figure are the values obtained by Culbert *et al.*[15] from specific-heat measurements. These two independent measurements seem to agree within experimental errors further substantiating the procedure[13] that was employed in transforming an irreversible magnetization curve into a reversible curve.

E. Toxen Relation

Table I illustrates the various quantities needed to test the Toxen relation. The energy-gap data presented are those of Adler *et al.*[3] and Brandli and Trofimenkoff.[31] The $(dh/dt)_{t=1}$ values were calculated using the measured values of T_c, the slopes of $H_c(T)$ vs T near T_c, and $H_c(0)$. The critical-field data and the energy-gap data are plotted as a function of indium concentration in these alloys in Fig. 5. These results show that there is little variation in both $|dh/dt|_{t=1}$ and $\Delta(0)/k_B T_c$ up to about 50-at.% In, indicating that lead-indium alloys exhibit a strong electron-phonon interaction even at these high concentrations of indium. Also shown in Fig. 5 are the $|dh/dt|_{t=1}$ values calculated from the data of Zoller and Dillinger[29] for In + 7.05-at.% Pb, and the data of Gygax *et al.*[32] for In + 4- and In + 6-at.%-Pb alloys.

The error in the $(dh/dt)_{t=1}$ measurements is estimated to be approximately 8%. This arises from the estimated error of 5% in the measurement of $H_c(0)$, an error of 3% in $(dH_c/dT)_{T=T_c}$, and the un-

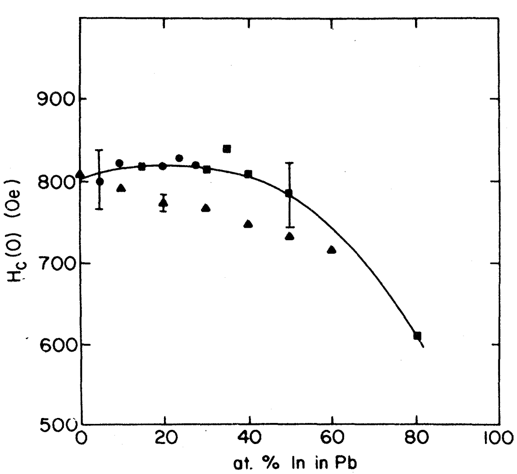

FIG. 4. Thermodynamic critical field at $T = 0$ °K, $H_c(0)$, as a function of indium concentration in lead. ■, present work; ●, Rothwarf *et al.* (Ref. 11); ▲, Culbert *et al.* (Ref. 15).

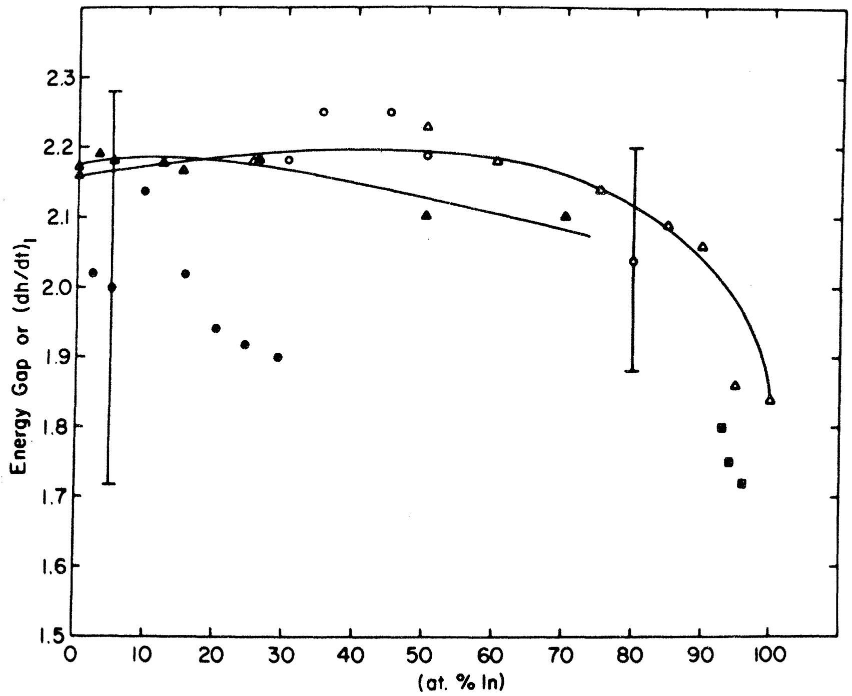

FIG. 5. Energy-gap ratio $\Delta(0)/k_BT_c$ [▲, Adler *et al.* (Ref. 3); Δ, Brandli *et al.* (Ref. 31)] and slope of the reduced critical field $h(t) = H_c(t)/H_c(0)$ at $t=1$ [●, Rothwarf *et al.* (Ref. 11); ○, present work; ■, Zoller *et al.* (Ref. 29); and Gygax *et al.* (Ref. 32)] as a function of indium concentration in lead.

certainty in T_c of 0.5%. These measurements have about one-half the uncertainty of the measurements of Rothwarf *et al.*,[11] since these earlier measurements were not made sufficiently close to T_c and were not corrected for magnetic field sweep-rate effects. Adler *et al.*,[3] although presenting their data up to three significant figures, do not state the accuracy of the tunneling measurements. Brandli and Trofimenkoff have recently repeated energy-gap measurements using a far-infrared-absorption technique. They report an error of less than 2% for their measurements.

From Fig. 5 it is clear that although small deviations between tunneling and magnetization measurements occur, the general agreement with the Toxen relation is remarkably good. It is important to note that the $(dh/dt)_{t=1}$ data for the samples reported here agrees with Brandli and Trofimenkoff measurements to within about 3%.

IV. DISCUSSION

The over-all purpose of this investigation of the Pb-In alloy system has been twofold. Firstly, to examine the validity of the Toxen relation, and secondly to make a comparison of the experimentally measured magnetic properties of type-II superconductors (the critical fields and the GL parameters) with the predictions of the presently available theories.

The Pb-In alloys show a wide variation in the electron-phonon coupling strengths, the electron mean free paths, the critical fields, and the GL parameters. These alloys appear to exhibit strong coupling behavior up to 50-at.% In, and intermediate coupling in the range 50–80-at.% In. Further addition of indium leads gradually to the weak coupling regime. The Toxen relation is satisfied substantially, within the experimental error, over the entire system. Since this relation has already been established for a variety of elemental superconductors, it is believed that it should apply to all types of presently known superconductors. The overwhelming experimental proof for the validity of this relation, together with our prescription for transforming an irreversible magnetization curve into a reversible one, allows one to determine energy gaps from the easier to make magnetization measurements, both in elemental and alloy superconductors. Furthermore, the Toxen relation allows one to extract more information from magnetization measurements than has heretofore been believed possible.

The apparent general validity of the Toxen relationship suggests that it is more than a mere numerical coincidence. Since it has already been shown[6] that the Toxen relationship follows from assuming a temperature-dependent effective electron-electron interaction, it would seem that further theoretical work incorporating this assumption would be fruitful.

The variation with temperature of both $\kappa_1(T)$ and $\kappa_2(T)$ for all the alloys is larger than predicted by present theories. In addition $\kappa_1(T) \neq \kappa_2(T)$ for $T < T_c$. Both these results suggest that further

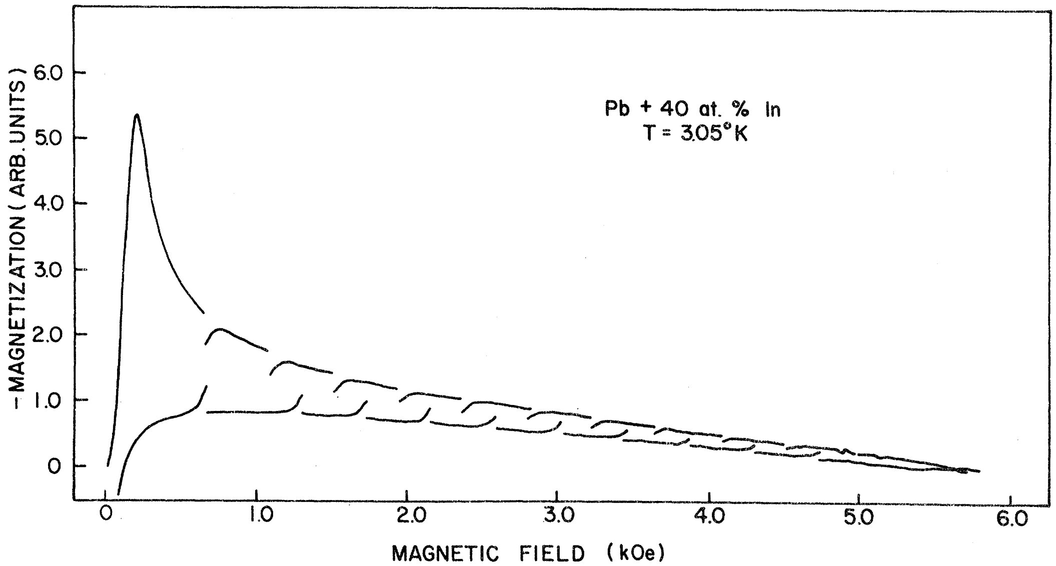

FIG. 6. Magnetic moment as a function of applied magnetic field for the Pb + 40-at.%-In sample at 3.05 °K.

theoretical work is needed to fully take account of strong coupling effects.

ACKNOWLEDGMENT

We thank Dr. Allen Rothwarf for helpful discussions and comments.

APPENDIX

In order to reduce the hysteresis effects in the magnetization curves, two experimental approaches were employed. A ballistic-galvanometer magnetometer was employed in which the measured deflection was proportional to the magnetic moment of the sample, which was moved between two pickup coils. The applied magnetic field was maintained constant while the sample was moved, and the resulting deflections recorded several times. At first, the measured moment decreased until an equilibrium value was obtained after three or four strokes of the plunger rod on which the sample was mounted. In decreasing fields the moment increased with successive strokes of the rod until the equilibrium moment, *identical* to that obtained in increasing field, was attained. Further strokes produced no additional changes in moment. Obviously, the jarring of the sample by moving it repeatedly depinned flux lines which then assumed their equilibrium distribution for a given field.

A similar result was produced in the PAR vibrating-sample magnetometer (VSM) by applying an ac magnetic field perpendicular to both the dc field and to the sample axis. The amplitude of the 400-Hz ac field was about 10–20 Oe. Figure 6 illustrates the results. All magnetization curves used in this study were at least as good as that shown in the figure. In increasing magnetic field (the upper curve), if the dc magnetic field was maintained constant, and the ac field applied, the moment decreased to an equilibrium value. Further application of the ac field did not result in any further change in moment. If the ac field was turned off and the dc field was further increased (at a rate of 500 Oe/min for Fig. 6), the moment returned to the nonequilibrium field curve as illustrated in the figure. The opposite effect was observed in decreasing field; namely, the ac field increased the measured magnetic moment. Note that the series of points corresponding to the maximum decrease of moment in increasing field or to the maximum increase in moment in decreasing field all lie on the same line for applied fields from H_{c2} down to nearly the peak in the magnetization curve. The area under the reversible magnetization curve has agreed with specific-heat data for $H_c(0)$ for a number of Pb-In alloys[17] to within 5%. Note that the κ values of the samples used in this study are comparable to those in Ref. 17 (i.e., intermediate κ values). The uncertainty in $H_c(0)$ would be somewhat greater for low-κ (~ 1) samples.

It may be that the error in the value determined for H_{c1} is larger than the 5% estimated. However, values of H_{c1} are not used in a comparison of experiment with theory described in the paper. Furthermore, H_c is rather insensitive to the point selected as corresponding to $H_{c1}(1-D)$, which we assumed to be the point of first observable departure from the initial Meissner slope.

The rate-dependent effects of the VSM measurements were small for the samples used in this study. If, at a given temperature, one obtained a series of magnetization curves at different sweep rates, the values of H_c, H_{c1}, and H_{c2} each varied linearly with sweep rate. Their values at 1000 Oe/min were each about 3–4% larger than their values at 100 Oe/min. The ballistic-galvanometer data corresponded virtually exactly with the VSM data extrapolated to zero-sweep rate. All VSM data were corrected for the rate effects, which are still being investigated. Preliminary results indicate that these effects are dependent on the κ of the sample.

---

*Based on a thesis submitted in partial fulfillment of the requirement for the Ph. D. degree at Temple University, Philadelphia, Pa. 19122.

[1]A. M. Toxen, Phys. Rev. Lett. 15, 462 (1965).
[2]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[3]J. G. Adler, J. E. Jackson, and T. A. Will, Phys. Lett. 24A, 407 (1967).
[4]D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. 112, 1888 (1958).
[5]J. Grunzweig-Genossar and M. Revzen, Phys. Rev. Lett. 16, 131 (1966).
[6]A. Rothwarf, Phys. Lett. 26A, 43 (1967); 28A, 430 (1968).
[7]G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 38, 966 (1960) [Sov. Phys. JETP 11, 696 (1960)].
[8]T. P. Sheahen, Phys. Rev. 149, 370 (1966).
[9]S. T. Sekula and R. H. Kernohan, J. Phys. Chem. Solids 27, 1863 (1966).
[10]G. Fisher and K. Maki, Phys. Rev. 176, 581 (1968).
[11]F. Rothwarf, L. W. Dubeck, and D. R. Aston, in *Proceedings of the International Conference on Superconductivity, Stanford*, 1970, edited by F. Chilton (North-Holland, Amsterdam, 1970), p. 636.
[12]M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
[13]L. W. Dubeck, D. R. Aston, and F. Rothwarf, J. Appl. Phys. 41, 1593 (1970); L. W. Dubeck, C. T. Rao, and F. Rothwarf, J. Appl. Phys. 42, 5196 (1971).
[14]D. E. Farrell, B. S. Chandrasekhar, and H. V. Culbert, Phys. Rev. 177, 694 (1969).
[15]H. V. Culbert, D. E. Farrell, and B. S. Chandrasekhar, Phys. Rev. B 3, 794 (1971).
[16]G. Bon Mardion, B. B. Goodman, and A. Lacaze, J. Phys. Chem. Solids 26, 1143 (1965).
[17]W. L. McMillan, Phys. Rev. 167, 331 (1968).
[18]P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).
[19]L. P. Gorkov, Zh. Eksp. Teor. Fiz. 36, 1918 (1959) [Sov. Phys. JETP 9, 1364 (1959)]; 37, 1407 (1959) [10, 998 (1960)].
[20]E. Helfand and N. R. Werthamer, Phys. Rev. Lett. 13, 686 (1964); Phys. Rev. 147, 288 (1966).
[21]L. Tewordt, Z. Physik 184, 319 (1965).
[22]G. Eilenberger, Z. Physik 190, 142 (1966).
[23]U. Kumpf, Phys. Status Solidi 44, 6 (1971).
[24]W. K. Rauckhorst and D. E. Farrell (private communication).
[25]W. A. Fietz and W. W. Webb, Phys. Rev. 161, 423 (1967).
[26]S. T. Sekula and R. H. Kernohan, J. Appl. Phys. 36, 2895 (1955).
[27]J. E. Evetts and J. M. A. Wade, J. Phys. Chem. Solids 31, 973 (1970).
[28]G. Eilenberger, Phys. Rev. 153, 584 (1967).
[29]P. Zoller and J. R. Dillinger, Phys. Rev. Lett. 20, 1154 (1968).
[30]R. A. French and J. Lowell, Phys. Rev. 173, 504 (1968).
[31]G. Brandli and D. N. Trofimenkoff, Phys. Lett. 36A, 431 (1971).
[32]S. Gygax, J. L. Olsen, and R. H. Kropschot, Phys. Lett. 8, 228 (1964).

PHYSICAL REVIEW B VOLUME 7, NUMBER 5 1 MARCH 1973

Superconductivity in $Pb_{0.9}Bi_{0.1}$

P. Vashishta*
Argonne National Laboratory, Argonne, Illinois 60439

J. P. Carbotte†
Physics Department, McMaster University, Hamilton 16, Ontario, Canada

(Received 18 July 1972)

We present results of strong coupling calculations of the superconducting properties of the alloy $Pb_{0.9}Bi_{0.1}$. The kernels in the Eliashberg equations are taken from quasiparticle-tunneling data which has been inverted by Dynes according to the method of McMillan and Rowell. The finite-temperature gap equations are solved by successive iteration to obtain solutions at several temperatures. The solutions are then employed to calculate select thermodynamic properties of $Pb_{0.9}Bi_{0.1}$.

I. INTRODUCTION

Recently, a considerable amount of effort has gone into obtaining accurate values of the electron-phonon part $\alpha^2(\omega)F(\omega)$ and the Coulomb pseudopotential U_C for some strong coupling superconductors.[1] These parameters enter directly into the Eliashberg[2,3] gap equations. They refer, respectively, to the phonon-mediated pair interaction for electrons at the Fermi surface and to their effec-