Properties of Superconducting Lead-Indium Alloys and the Generalized Ginzburg-Landau Parameter κ_2*

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(Received 7 August 1968)

Magnetization measurements have been made on a series of lead-indium alloys containing from 5 to 60 at.% indium. The upper and lower critical fields together with the generalized Ginzburg-Landau parameter κ_2 have been obtained at temperatures between $0.2T_c$ and T_c. Residual resistivities and transition temperatures have also been measured. It is found that κ_2 increases with decreasing temperature, the magnitude of the increase being much higher than that expected from existing theory. However, the increase as a function of the Gor'kov impurity parameter ρ closely follows available data for niobium alloys. This result lends support to the view that, despite the present conflict between experiment and theory, an experimental parameter $\kappa_2(\rho,T)$ does exist which is independent of the detailed characteristics of the alloy system being investigated. Temperature-independent characteristics of the lead-indium system are collected together, and some evidence is found for a modification of the electronic structure at an indium concentration of about 30 at.%.

I. INTRODUCTION

SINCE the original Abrikosov[1] solution of the Ginzburg-Landau[2] equations, a great deal of theoretical and experimental activity has focussed on obtaining a more complete understanding of the magnetic behavior of type-II superconductors. The entire range of temperature and mean-free-path variation has now been treated by at least one of the very many theoretical calculations, most of which are conveniently summarized by Fietz and Webb.[3] However, on the experimental side, data available for comparison with theory are not so extensive. Most experiments have been performed on transition-metal alloys. Moreover, in some investigations the ranges of temperature and mean-free-path variation have been too small to be useful, while in others the essential normal state parameters have not been ascertained. However, a recent investigation[3] of the niobium-titanium alloy system allowed a thorough comparison with theory and revealed substantial systematic disagreement. It seemed desirable to perform a similar extensive check on a nontransition-metal alloy system and we have investigated cubic lead-indium alloys. The range of compositions studied in our work carries the electron mean free path from $0.23\xi_0$ to about $0.05\xi_0$, where ξ_0 is the coherence length in pure lead

A major difficulty encountered with nontransition-metal alloys is that their magnetization always appears to exhibit rather more hysteresis than that of transition-metal alloys. We have managed to reduce this hysteresis somewhat with a careful annealing technique, but unfortunately it is still too great to permit an evaluation of the bulk thermodynamic field $H_c(t)$ with the precision necessary to obtain reliable values for the generalized Ginzburg-Landau parameters κ_1 and κ_3. Nonetheless, we have measured both H_{c2} and H_{c1}. At $t\equiv T/T_c=1$ the ratio of these quantities depends only on the impurity parameter, as will be explained, and so may be used to extract the parameter κ from the measurements, where $\kappa=\kappa_1(1)=\kappa_2(1)=\kappa_3(1)$.

Our basic set of temperature-dependent data relates to κ_2 which is associated with $(dM/dH)_{H=H_{c2}}$. A recent calculation of this parameter in the general case (arbitrary temperature and mean free path) has been made by Eilenberger,[4] his work subsuming previous treatments[5–8] as limiting cases. A number of assumptions enter this calculation, for example, that of a spherical Fermi surface and weak electron-phonon interaction. In addition, paramagnetic effects were neglected. Hence, the data presented here for κ_2 form a complementary set to those for the niobium alloys,[3] since the present system is dissimilar in all three qualitative aspects bearing on the assumptions mentioned.

II. EXPERIMENTAL METHODS

Apart from the general considerations given above, lead-indium alloys were selected for this investigation for a number of practical reasons. An unusually wide primary fcc phase exists, up to 65 at.% indium,[9] within

* Work supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under AFSOR Grant No. 565-66, and by the Atomic Energy Commission.

[1] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].

[2] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **2**, 1064 (1950).

[3] W. A. Fietz and W. W. Webb, Phys. Rev. **161**, 423 (1967).

[4] G. Eilenberger, Phys. Rev. **153**, 584 (1967).

[5] K. Maki and T. Tsuzuki, Phys. Rev. **139**, A868 (1965).

[6] L. Neumann and L. Tewordt, Z. Physik **191**, 73 (1966).

[7] K. Maki, Physics **1**, 21 (1964). Contains an error corrected in Ref. 8.

[8] C. Caroli, M. Cyrot, and P. G. de Gennes, Solid State Commun. **4**, 17 (1966).

[9] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).

which the transition temperature drops to only about 6°K so that an extensive reduced temperature range is available for investigation over the whole alloy system. A certain number of scattered results already exist in the literature, in fact data on the system were appealed to by Abrikosov in his original paper.[1] Finally, the preparation of homogeneous polycrystalline samples presents no difficulties.

The starting materials employed were 99.999% pure lead and indium. Using Pyrex glass containers and a vacuum always better than 10^{-4} Torr, each melt was thoroughly shaken for ~30 min and then quenched into cylindrical polycrystalline ingots ~3 mm in diameter. Samples ~13 mm long were cut from these ingots and the ends sanded down to a hemispherical shape. The specimen was then worked over with a fine emery cloth, lightly etched in concentrated nitric acid and finally polished with a mixture of 90% acetic acid with 10% hydrogen peroxide (by volume). The precise solidus point for each alloy was established using a section of the original ingot and each specimen was vacuum annealed for a week at a temperature of 3±1°C below its solidus point using an electronically controlled furnace. No weight loss was recorded after the casting procedure and so for simplicity the nominal composition was assumed without further analysis to be the actual composition. None of the arguments to be presented depend on this assumption but comparisons that will be made with some data in the literature demonstrate that no gross errors in composition are likely to have occured.

The magnetic properties were obtained using a vibrating coil magnetometer, previously described by one of us.[10] A brief outline of the essential features will be given here. The inner specimen chamber of the magnetometer is shown schematically in Fig. 1. The sample (1) is varnished onto a copper block (2). A small 99.9999% pure lead sample which serves as a temperature reference (3) and a germanium resistance thermometer (4) are set into the block with the same varnish (GE 7031). The surrounding copper can (5) is evacuated during an experiment and the whole assembly rests inside an outer brass can (not shown) immersed in liquid helium. An electric heater (6) can raise the temperature of the copper block and over the range 1.5–8°K it is controlled with an electronic regulator[11] used in conjunction with the germanium thermometer to maintain temperatures constant to ±0.001°K. The zero-field superconducting transition of the lead reference sample is monitored inductively and serves as a check on the stability of the thermometer. Magnetic fields uniform to 1 part in 10^5 over the sample are applied using a standard 12-in. electromagnet. The vibrating coil assembly is described in detail elsewhere.[10] A representative magnetization curve is shown in Fig. 2.

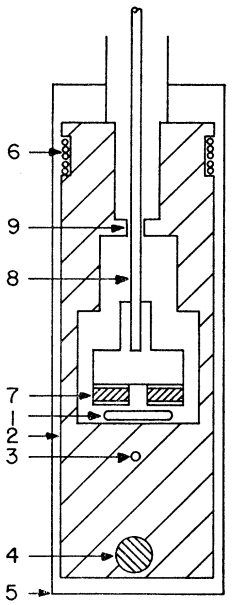

FIG. 1. Specimen chamber of the vibrating coil magnetometer.

Transition temperatures of all the samples were obtained from the intercept of the plot of H_{c1} against temperature very close to $T_c(0.99<t<1)$. After the magnetic measurements had been completed, residual resistivities of the samples at 4.2°K were obtained in the usual way, employing fields in excess of H_{c3} to completely quench superconductivity in each case. The electronic specific heats for alloys over the whole range of composition employed here have been measured in a related investigation.[12] The result obtained was that for the whole alloy phase the specific heat varies by less than 3% about the value $\gamma=3$ mJ mole^{-1} deg^{-2}.

III. ANALYSIS OF RESULTS

It is possible to proceed by a number of different routes when analyzing experimental data on type-II superconductors and this section outlines the procedures used in the present work. The observed quantities H_{c2} and $(dM/dH)_{H=H_{c2}}$ are related to the generalized Ginzburg-Landau parameters, κ_1 and κ_2, by the expressions

$$H_{c2}=\sqrt{2}\kappa_1 H_c(t)\,, \tag{1}$$

$$-4\pi(dM/dH)_{H=H_{c2}}=\{\beta[2\kappa_2(t)^2-1]\}^{-1}\,, \tag{2}$$

where H_c is the thermodynamic critical field and β is a parameter depending on the geometry of the fluxoid lattice. The value $\beta=1.16$ has been adopted here, in accord with the theoretical result due to Kleiner *et al.*[13] for a triangular lattice. Expressions (1) and (2) are quite general and theoretical calculations exist[4,14] for

[10] D. E. Farrell, Rev. Sci. Instr. **39**, 1452 (1968).
[11] C. Blake and C. E. Chase, Rev. Sci. Instr. **34**, 984 (1963).
[12] Harvey V. Culbert, D. E. Farrell, and B. S. Chandrasekhar (to be published).
[13] W. H. Kleiner, L. M. Roth, and S. H. Autler, Phys. Rev. **133**, A1226 (1964).
[14] E. Helfand and N. R. Werthamer, Phys. Rev. Letters **13**, 686 (1964); Phys. Rev. **147**, 288 (1966).

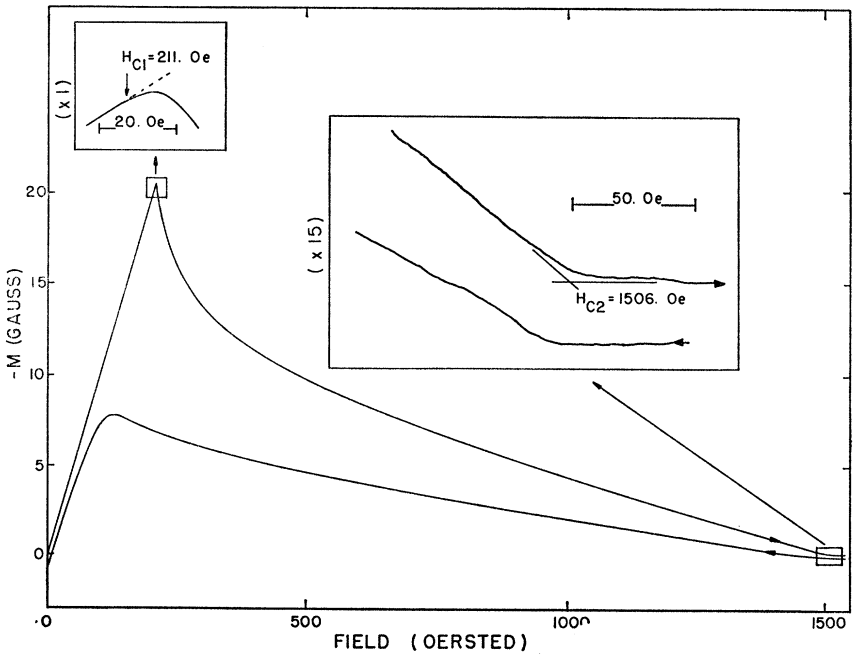

FIG. 2. Magnetization curve for Pb 10 at.% In at 4.93°K. Insets show regions of curve near H_{c1} and H_{c2} with increased sensitivity indicated.

both κ_1 and κ_2 over the whole range of reduced temperature and ξ_0/l, from the pure to the dirty limit. In the case of H_{c1} we may write

$$H_{c1}(t)=\ln\kappa_3(t)H_c(t)/\sqrt{2}\kappa_3(t)\,, \tag{3}$$

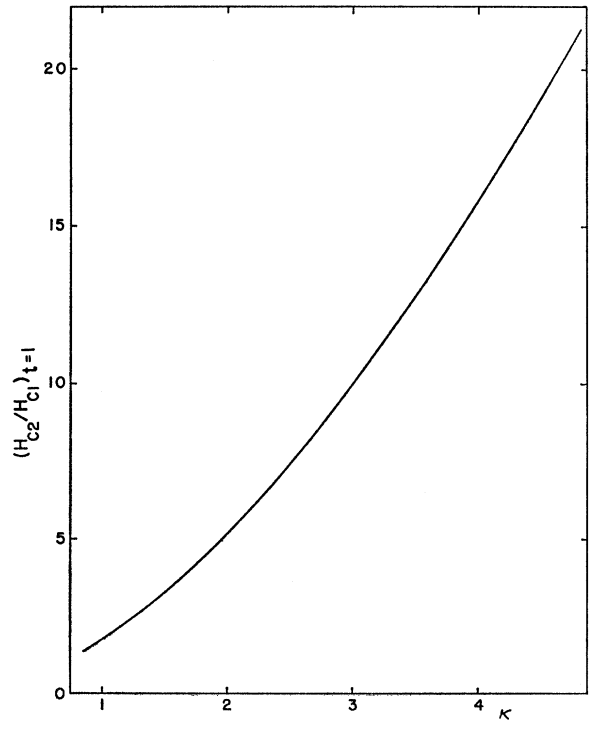

FIG. 3. Theoretical relationship (Ref. 16) between $(H_{c2}/H_{c1})_{t=1}$ and κ.

where κ_3 is a third generalized Ginzburg-Landau parameter, given explicitly by Maki[15] in the dirty limit. Unfortunately, no calculations exist for $\kappa_3(t)$ over the whole range of ξ_0/l. However, Neumann and Tewordt[16] have developed the theory of H_{c1} in the region close to $t=1$, for arbitrary values of ξ_0/l. At $t=1$ the ratio obtained for H_{c1}/H_c is equal to that originally obtained by Harden and Arp[17] directly from Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory. Hence, using (1) for all impurity concentrations we have

$$(H_{c2}/H_{c1})_{t=1}=\sqrt{2}\kappa(H_c/H_{c1})_{t=1}\,. \tag{4}$$

Together with the data given by Neumann and Tewordt for $(H_c/H_{c1})_{t=1}$ in terms of κ, this expression yields the dependence of $(H_{c2}/H_{c1})_{t=1}$ on κ shown on Fig. 3. Hence, by plotting H_{c2}/H_{c1} against t and extrapolating to $t=1$ we can obtain a value for κ for each alloy. A further connection with theory is obtained via the parameter $h^*(t)$ defined by

$$h^*(t)=H_{c2}(t)\div(-dH_{c2}/dt)_{t=1}\,. \tag{5}$$

Helfand and Werthamer[14] (1966) have given the form of $h^*(t)$ for all ξ_0/l.

IV. RESULTS AND ACCURACY

The basic parameters established will now be set out together with estimates of the accuracy with which they are known.

[15] K. Maki, Physics 1, 127 (1964).
[16] L. Neumann and L. Tewordt, Z. Physik 189, 55 (1966).
[17] J. L. Harden and V. Arp, Cryogenics 3, 105 (1963).

TABLE I. Basic parameters for all the alloys studied.

Specimen \ Parameter / Source	T_c (°K) expt	γ (erg cm^{-3} °K$^{-2}\times10^{-3}$) Ref. 12	ρ_n ($\mu\Omega$ cm) expt	ρ_n* ($\mu\Omega$ cm) Eq. (16)	κ_0 Eq. (12)	$\kappa_2(1)$ Fig. 8	κ_{expt} Figs. 3, 7	$\kappa_{theoret}$ Eqs. (7), (12), (13)	$\kappa_{expt}/\kappa_{theoret}$	ρ Eq. (13)	ρ Eq. (16)
Pb	7.19	1.69	...	...	0.28	...	...	...		...	...
Pb-5 In	7.12	1.70	3.40	3.50	0.28	1.25	1.40	1.37	1.02	4.42	4.55
Pb-10 In	7.05	1.71	6.30	5.41	0.29	2.17	2.05	2.30	0.89	8.1	7.0
Pb-20 In	6.91	1.72	11.0	9.1	0.29	3.50	3.25	3.77	0.86	14.0	11.6
Pb-30 In	6.76	1.74	15.6	11.0	0.29	4.22	3.90	5.20	0.75	19.8	14.0
Pb-40 In	6.57	1.76	17.5	13.1	0.29	4.52	4.55	5.79	0.78	22.1	16.4
Pb-50 In	6.39	1.78	17.8	12.8	0.30	4.62	4.55	5.93	0.77	22.4	16.2
Pb-60 In	6.21	1.80	15.8	11.4	0.30	4.15	4.07	5.32	0.77	19.6	14.1

A. Specific-Heat Coefficient

These data for the alloys are sufficiently precise ($\pm1\%$) to show some small changes from the pure lead value of $\gamma=3.00$ mJ (mole)$^{-1}$ (°K)$^{-2}$. However, all the alloys exhibit that value to within 3%. Since analysis of the small changes is reserved for a related paper[12] the pure lead value was that used to obtain the data in Table I.

B. Transition Temperature T_c

The germanium resistance thermometer was used over the whole temperature range. For $T\leqslant4.2$°K it was immersed in liquid helium and calibrated against the T-58 helium vapor-pressure scale, while for $T\geqslant4.2$°K the manufacturer's calibration was used. At $T=4.2$°K a permanent shift of $+0.03$°K was observed from that calibration, while the apparent T_c of the pure lead reference sample showed a similar shift of 0.03° from the commonly accepted value of $T_c=7.19$°K. However, the apparent T_c of the reference sample varied by less than 0.005°K over our whole sequence of experimental runs. In view of the stability of the fixed points, each measured temperature for $T\geqslant4.2$°K was corrected by subtracting the 0.03°K shift noted at the fixed points. The absolute temperature measurement is then conservatively considered accurate to 0.02°K over the whole range. Transition temperatures obtained from a plot of H_{c1} against temperature near T_c are shown in Table I and also Fig. 4, where they are compared with some results obtained in a careful study by Nembach.[18] The agreement is excellent, the maximum discrepancy being only 0.05°K for Pb-10 at.% In. However, it can be seen that our results give clear indication of a change in slope at around 30 at.% In.

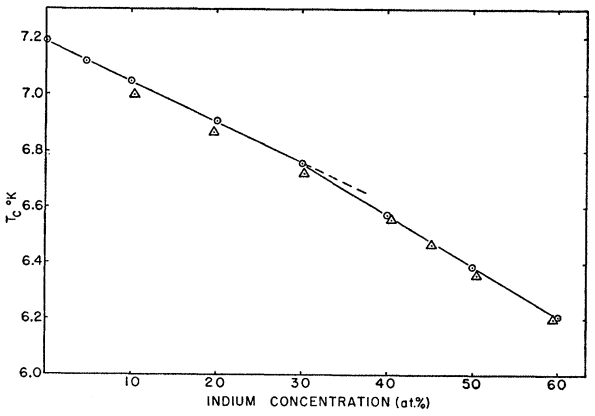

FIG. 4. Transition temperature for the Pb-In alloy system. ⊙ This work. △ Nembach (Ref. 18).

C. Residual Resistance

A conventional four-probe technique was employed to measure the resistivity at 4.2°K and the results shown in Table I were estimated accurate to 5% or better. Figure 5 shows ρ_n/x as a function of x, the indium concentration. As can be seen, some small changes of slope appear to occur around 30 at.% In.

D. Ginzburg-Landau Parameter κ

This parameter is obtained from values of H_{c2}/H_{c1} and three considerations arise in discussing the precision with which it is known.

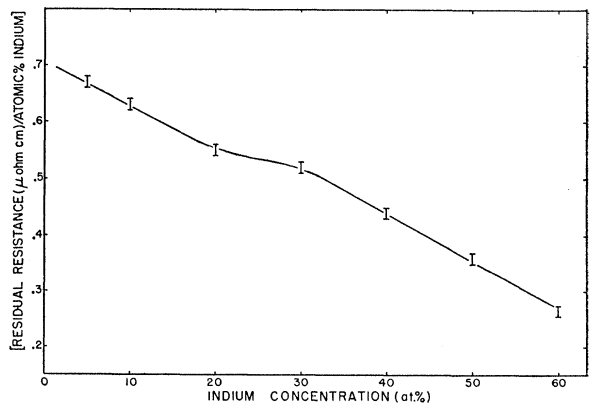

FIG. 5. Residual resistance per atomic percent indium for the Pb-In alloy system.

[18] E. Nembach, University of California, Report No. UCRL-17905 (unpublished) and to be published.

1. Nonzero Demagnetization Factor n

For a nonzero n, the observed value of H_{c1} differs from the true value H_{c1}^* according to the well-known result $H_{c1}^*=H_{c1}(1-n)$. Approximating our samples to ellipsoids of revolution and using Stoner's calculations[19] gives demagnetization factors ranging from 0.053 to 0.083. The corresponding correction to H_{c1} was made on all the measurements.

2. Irreversibility

Figure 2 displays the methods employed in this work for defining H_{c1} and H_{c2} from the slightly rounded curves observed at both transition points in an increasing field. The difference in the upper critical field point on decreasing the field is very small and the defining procedure gave a value for H_{c2} which was independent of surface treatment to 1%. The surface treatments involved will be discussed in the section on κ_2. However, in the case of the lower critical field, irreversibility has serious consequences and choice of H_{c1} is not completely obvious. It is clear that surface effects may delay flux penetration until the applied field reaches some value higher than the true bulk lower critical field H_{c1}. Indeed, for a given sample in an increasing or decreasing field, the points at which (dM/dH) changes sign were found to be strongly influenced by the surface conditions. The increasing field point was observed to be variable by up to 30% while the decreasing field point varied by factors of up to 5 for the changes in surface conditions studied. However, H_{c1} defined as the field for the first detectible change in (dM/dH) in increasing field was found to be independent of these changes to 5%.

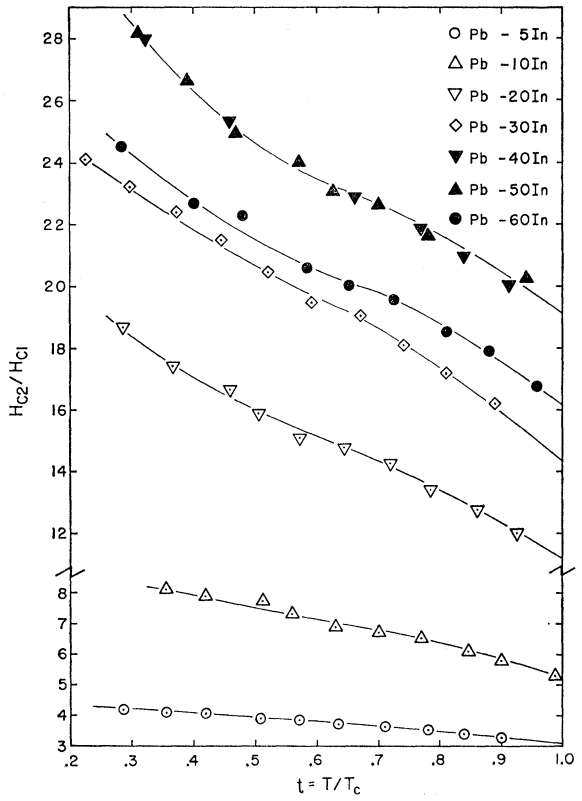

FIG. 6. H_{c2}/H_{c1} as a function of reduced temperature, $t=T/T_c$, for the Pb-In alloy system.

3. Instrumentation

All fields were measured to 1% and temperature instabilities of ~0.001°K lead to quite negligible error.

To summarize, it is considered that the ratio H_{c2}/H_{c1} is known to ±5% at all temperatures. Using (4) this leads to errors in κ of the order of ±5% for $\kappa=1$, but only ±1% for $\kappa=5$. Hence, it is believed that the κ values shown in Table I are accurate to ±5% over the whole alloy range. In Fig. 6 are plotted the results for H_{c2}/H_{c1} for all our alloys. The extrapolated value $(H_{c2}/H_{c1})_{t=1}$ was used together with the theoretical results exhibited in Fig. 3 in order to establish the value of κ_{expt} given in Table I.

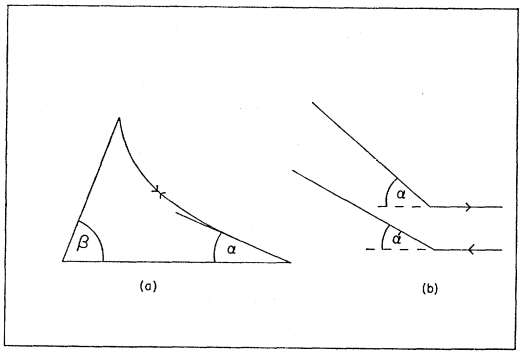

FIG. 7. Schematic features of magnetization curves: (a) complete reversibility, (b) irreversibility near H_{c2}.

E. Second Generalized Ginzburg-Landau Parameter $\kappa_2(t)$

A number of detailed points arise when one turns to extract numbers for $\kappa_2(t)$ from the raw data. As with κ, these may be conveniently divided into three categories.

1. Nonzero Demagnetization Factor

Consider the completely reversible magnetization curve indicated in Fig. 7(a). Both angles α and β are influenced by non-zero values of n. It may be shown[20] that the modifications result in an expression for κ_2 in terms of the directly observable parameter z:

$$\kappa_2=(1/2.32)[z-n(z+1)+1.16]^{1/2}, \quad (6)$$

[19] E. C. Stoner, Phil. Mag. 36, 803 (1945).

[20] J. A. Cape and J. M. Zimmerman, Phys. Rev. 153, 416 (1967).

where

$$z=(\tan\alpha/\tan\beta).$$

For $n=0$, (6) reduces to (2). For nonzero n, the small fractional correction to κ_2 is approximately $\frac{1}{2}n[(z+1)/(z+1.16)]\sim\frac{1}{2}n$, i.e., essentially *independent* of κ_2, and having a maximum value of about 5% for our samples. This correction was made and errors in κ_2 arising from it are considered insignificant compared with the other sources.

2. Irreversibility

The actual magnetization curves observed near H_{c2} nearly always exhibited irreversibility as shown in Fig. 2 and schematically in Fig. 7(b). A surface-sheath magnetization above H_{c2} of magnitudes up to about 1% the magnetization at H_{c1} was observed for nearly all the samples. This is known[21] to be an intrinsically irreversible magnetization and it appears likely that surface effects are introducing a major portion of the irreversibility in the mixed state of these very-well-annealed alloys. Some evidence for this point of view already exists[22] and we have accumulated a good deal more in the course of this work. Our results on the hysteretic properties will be published elsewhere but some significant findings may be enumerated here:

(a) The alloys measured exhibited diverse degrees of surface oxidation acquired in the different times that elapsed after annealing and before measurement. This diversity of surface condition was extended by copper plating and also repolishing some of the samples. In all these experiments a correlation emerged between the magnitude of the surface sheath magnetization just above H_{c2}, expressed as a fraction f of the magnetization at H_{c1}, and the fractional difference in the slopes, $\delta=[(\tan\alpha'-\tan\alpha)/\tan\alpha]$ [Fig. 7(b)]. For example, the 5 at.% In sample as measured initially was quite heavily oxidized and gave $f=0.1\%$, $\delta=7\%$: Chemically polishing the surface lightly, as described in the section on specimen preparation, drastically *increased* both parameters giving $f=5\%$, $\delta=100\%$. However, despite this large increase of irreversibility, H_{c2} remained the same to 1%—and, most importantly, the *average* value of the slope, $\frac{1}{2}(\tan\alpha+\tan\alpha')$, remained unchanged to 10%. These results held for all the varied changes in surface conditions investigated.

(b) By applying a small alternating magnetic field while measuring the magnetization the average slope defined above again remained unchanged to 10% but the observed values of both f and δ could be reduced essentially to zero and a nearly perfectly reversible magnetization curve produced. The nature of the magnetization in the presence of an alternating field is of course not completely clear, but it is tempting to see the role of the field as one of simply reducing in some way the surface barrier to the entrance and exit of flux lines. Certainly, the observable consequences are very similar to the effect of changes in surface conditions discussed in (1).

(c) By adopting the average slope defined above, values of $\kappa_2(t)$ are obtained from which we can extract $\kappa_2(1)$ by a small extrapolation to $t=1$. These values are shown in Table I. It can be seen that to an accuracy of better than 10%, $\kappa_2(1)=\kappa$ where κ is obtained entirely independently from Eq. (4).

3. Instrumentation

These instrumental errors are discussed in detail elsewhere.[10] The intrinsic sensitivity (10^{-4} emu) and the temperature stability (0.001°K) allow both $\tan\alpha$ and $\tan\alpha'$ to be determined to $\sim1\%$ so that any instrumentation errors are indeed negligible compared with uncertainties introduced by the irreversibility discussed above.

In summary, accepting the arguments in category 2 leads us to believe that $\kappa_2(t)$ itself is known to within 5%. [κ_2 depends on the square root of the slope from Eq. (6).] The situation is rather better in regard to the ratio $\kappa_2(0.2)/\kappa_2(1)$, which will be extracted in a later section for comparison with theory. Since it is observed that δ itself is independent of temperature to 5% or better, the ratio $\kappa_2(0.2)/\kappa_2(1)$ is essentially independent of our choice of which slope to use in extracting κ_2 from Eq. (6): The parameters $\kappa_2(t)$ are displayed in Fig. 8 for all the alloys. As previously remarked $\kappa_2(1)=\kappa$ to the uncertainty of our measurements.

F. Upper Critical Field $h^*(t)$

H_{c2} appears to be quite independent of the difficulties attendent on $(dM/dH)_{H_{c2}}$ and H_{c1}. H_{c2} is known to 1% and $h^*(t)$ is known with a precision of 5% or better, the error arising from uncertainty in measurement of $(dH_{c2}/dt)_{t=1}$. Figure 9 shows $H_{c2}(t)$ values for all our alloys and Fig. 10 shows values for h^* defined by Eq. (5). Data for all the alloys from 10 to 60 at.% In lie very close together within the shaded area shown while the circled points identify data for Pb 5 at.% In.

V. COMPARISON OF RESULTS WITH THEORY

A. Temperature-Independent Parameters

The theoretical situation for γ is to be discussed in a related paper.[12] We confine our attention here to the relation of κ to T_c, γ, and ρ_n.

The theoretical value of κ has been obtained by Gor'kov[23] in the form

$$\kappa_{\text{theoret}}=\kappa_0[\chi(\rho)]^{-1}. \quad (7)$$

[21] L. J. Barnes and H. J. Fink, Phys. Rev. **149**, 186 (1966).
[22] L. J. Barnes and H. J. Fink, Phys. Letters **20**, 583 (1966).
[23] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **10**, 998 (1960)].

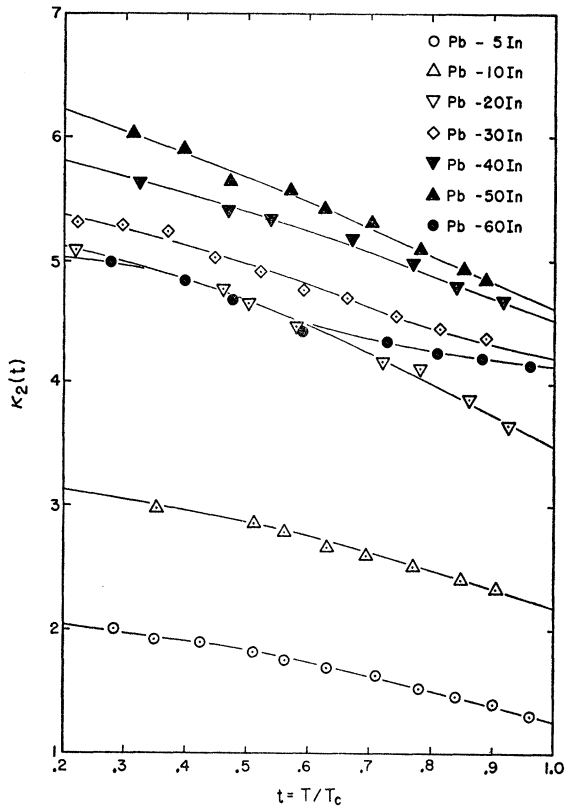

FIG. 8. κ_2 as a function of reduced temperature $t=T/T_c$ for the Pb-In alloy system.

In this expression, κ_0 is the Ginzburg-Landau parameter in the clean limit, and

$$\chi(\rho)=0.949\sum_0^\infty \frac{1}{(2n+1)^2(2n+1+\rho)}. \qquad (8)$$

The quantity ρ was introduced by Gor'kov to characterize the purity of a superconductor. It can be expressed as $\rho=0.882\xi_0/l$, where ξ_0 formally represents the coherence length of the superconductor for $l\to\infty$ and l is the average electron mean free path. To obtain $(\kappa_0)_{Pb}$, the value of κ_0 for pure lead, we utilize the basic expression due to Gor'kov[23]

$$(\kappa_0)_{Pb}=2\sqrt{2}eH_c\lambda_L^2/\hbar, \qquad (9)$$

where e is the electronic charge, $H_c(t)$ is the bulk thermodynamic critical field for pure lead and λ_L is the London penetration depth in small fields. At temperatures sufficiently close to T_c, λ_L is large compared with the coherence length and then is identical to the observable penetration depth λ. From the BCS[24] theory we have $\lambda(t)=\frac{1}{2}\lambda(0)(1-t)^{-1/2}$; hence,

$$(\kappa_0)_{Pb}=-\frac{eT_c\lambda(0)^2}{\sqrt{2}\hbar}\left(\frac{dH_c}{dT}\right)_{T=T_c}. \qquad (10)$$

Using the observed values[25] of $\lambda(0)=(3.9\pm0.3)\times10^{-6}$

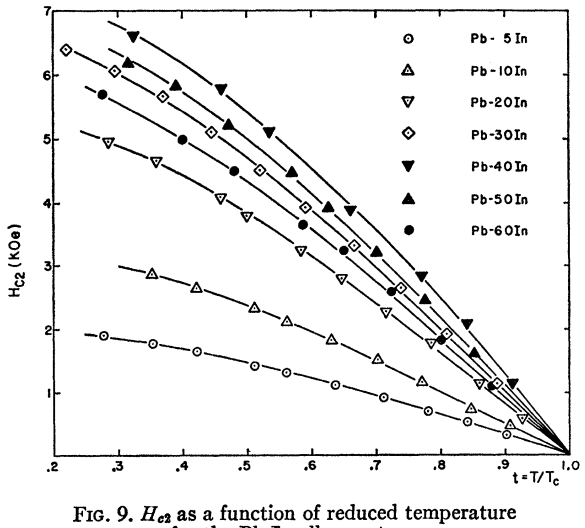

FIG. 9. H_{c2} as a function of reduced temperature for the Pb-In alloy system.

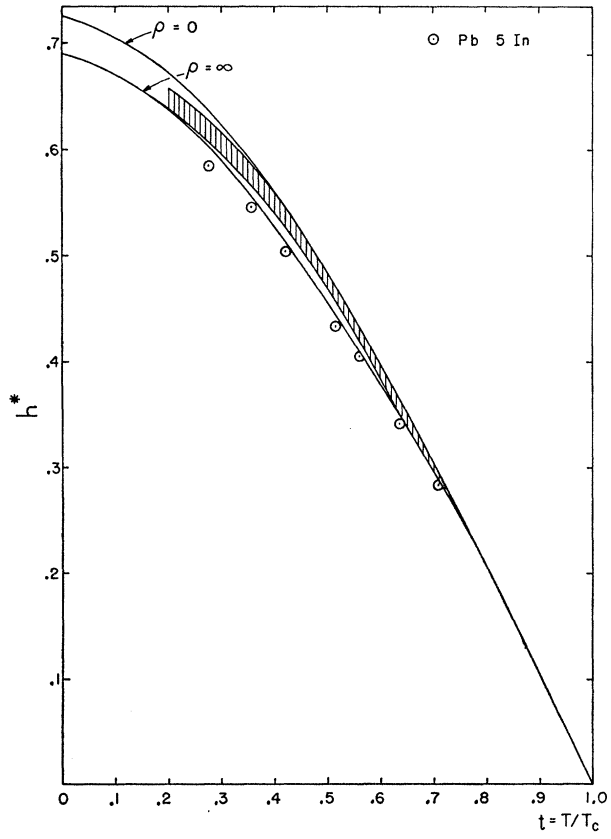

FIG. 10. The parameter $h^*=-H_{c2}(t)/(dH_{c2}/dT)_{T=T_c}$ as a function of reduced temperature $t=T/T_c$ for the Pb-In alloy system. Cross-hatched region, Pb: 10, 20, 30, 40, 50, and 60 at.% In. ⊙, Pb: 5 at.% In. The upper and lower lines are the theoretical predictions (Ref. 14) for $h^*(t)$ in the extreme cases of $\rho=0$ and $\rho=\infty$, respectively.

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

[25] J. M. Lock, Proc. Roy. Soc. (London) **A208**, 391 (1951).

cm and $(dH_c/dT)_{T=T_c}=-238$ Oe/deg,[26] we obtain $(\kappa_0)_{Pb}=0.28\pm0.04$, the value employed in our work. A simple plot of our observed κ values against indium concentration gives an extrapolated value at zero concentration of $\kappa=0.30\pm0.03$, comfortably inside the error limits for the theoretical value of $(\kappa_0)_{Pb}$. We now require expressions for both ρ and κ_0 in the alloys in terms of observable quantities so that $\kappa_{theoret}$ may be extracted from (7). The quantity κ_0 has been given by Berlincourt and Hake[27] as

$$\kappa_0=1.61\times10^{24}T_c\gamma^{3/2}[(n_e)^{4/3}(S/S_F)^2]^{-1}. \quad (11)$$

In this expression, n_e is the effective conduction-electron density in electrons per cm^3, obtained by assuming that lead and indium supply four and three electrons, respectively, to the conduction band. S is the area of the Fermi surface, while S_F is the area for the free-electron model at the same density. If we make the further assumption that the ratio S/S_F is the same for all the alloys, a value of κ_0 can be obtained for each alloy from (11), viz,

$$\kappa_0=(\kappa_0)_{Pb}\frac{T_c}{(T_c)_{Pb}}\left(\frac{\gamma}{\gamma_{Pb}}\right)^{3/2}\left(\frac{n_e}{(n_e)_{Pb}}\right)^{-4/3}. \quad (12)$$

Values for κ_0 obtained from (12) are displayed in Table I. A value of ρ for each alloy was then obtained from the expression[3]

$$\rho=8.85\times10^{-3}\gamma^{1/2}\rho_n/\kappa_0. \quad (13)$$

Here, γ is in erg cm^{-3} deg^{-2} and ρ_n is in $\mu\Omega$ cm. Resulting values for ρ are displayed in Table I. Returning to Eq. (7), the theoretical value $\kappa_{theoret}$ was then calculated with the help of the results assembled for ρ and κ_0. For comparison with the experimental value of κ, the ratio $\kappa_{expt}/\kappa_{theoret}$ is evaluated and displayed in Table I and plotted in Fig. 11 as a function of at.% In. Again a distinct change of slope is visible at around 30 at.%. This then is the third member of the trio of properties, T_c, ρ_n, and κ, each of which gives some evidence for a change of electronic structure at around a concentration of 30 at.% In. At first sight it might seem that a likely reason for the departure of κ from the theoretical calculation could be a breakdown of the assumption made in going from Eq. (11) to Eq. (12), i.e., that S/S_F is a constant for the alloys: To see clearly that this cannot be the case, we recall that to an accuracy of a few percent, Goodman has shown[28] that Eq. (7) may be rewritten in the form

$$\kappa_{theoret}=\kappa_0+7.5\times10^{-3}\rho_n\gamma^{1/2}. \quad (14)$$

Hence, to the accuracy of this expression, κ_0 is merely an additive constant which would be required to assume

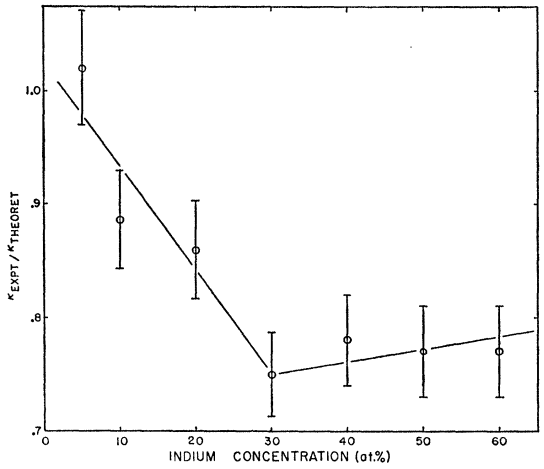

FIG. 11. $\kappa_{expt}/\kappa_{theoret}$ for alloys in the Pb-In alloy system.

negative values, as large as -1.3, in order to fit to data. Since κ_0 is essentially positive no possible change in its value can explain the results.

Reverting to the exact expressions, further progress can be made in analyzing this discrepancy by eliminating κ_0 between Eq. (7) and Eq. (13) to yield

$$\rho\chi(\rho)=8.85\times10^{-3}\gamma^{1/2}\rho_n/\kappa. \quad (15)$$

This is an implicit relation for ρ in terms of the directly observable parameters γ, ρ_n, and κ. However, substitution of these data in Eq. (15) leads to values of ρ very much higher than those calculated from Eq. (13), with the exception of the Pb-In 5 at.% sample which is quite close. To ensure self-consistency, we therefore require another parameter for each alloy to express the departures from the simple models on which all the previous equations are based. This is introduced as an effective resistivity ρ_n^*, and Eqs. (13) and (15) are rewritten as

$$\rho\chi(\rho)=8.85\times10^{-3}\gamma^{1/2}\rho_n^*/\kappa$$

and (16)

$$\rho=8.85\times10^{-3}\gamma^{1/2}\rho_n^*/\kappa_0.$$

In the alloys, it was then found possible to adjust ρ_n^* until the two values of ρ determined from both equations of (16) were equal. Values for ρ_n^* and ρ determined in this manner are shown in Table I. Hence, the introduction of an adjustable parameter multiplying ρ_n is a sufficient step to obtain consistency between experiment and theory. It is not, of course, a unique step since one might instead assume some adjustable parameter multiplying γ or some combination of adjustable parameters. At this point there appears to be no strong physical grounds dictating one choice over the other. However, any adjustment to γ will not only affect Eq. (13) and Eq. (15) but also Eq. (11) and so, on the grounds of simplicity alone, the choice was made to adjust ρ_n. The ρ values deduced from Eq. (16) are

[26] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).
[27] T. G. Berlincourt and R. R. Hake, Phys. Rev. **131**, 140 (1963).
[28] B. B. Goodman, IBM J. Res. Develop. **6**, 63 (1962).

somewhat lower than those obtained from Eq. (13) but will be those used in subsequent comparisons with theory.

B. Temperature-Dependent Parameters

1. Function $h^*(t)$

Figure 10 gives the experimental results and theoretical predictions[14] for this quantity for the pure limit and also the dirty limit. As remarked previously, data for all the alloys from 10 to 60 at.% In lie within the shaded area shown so that, over this range, the change of $h^*(t)$ with ρ is certainly weak in both theory and experiment. The deviation for the 5 at.% sample is outside experimental error, however, and interestingly is in the opposite direction expected from the impurity effect. Recent work[29] on strong coupling alloys gave an implicit expression for $H_{c2}(t)$ which was not evaluated, but which might contain an explanation of this small discrepancy.

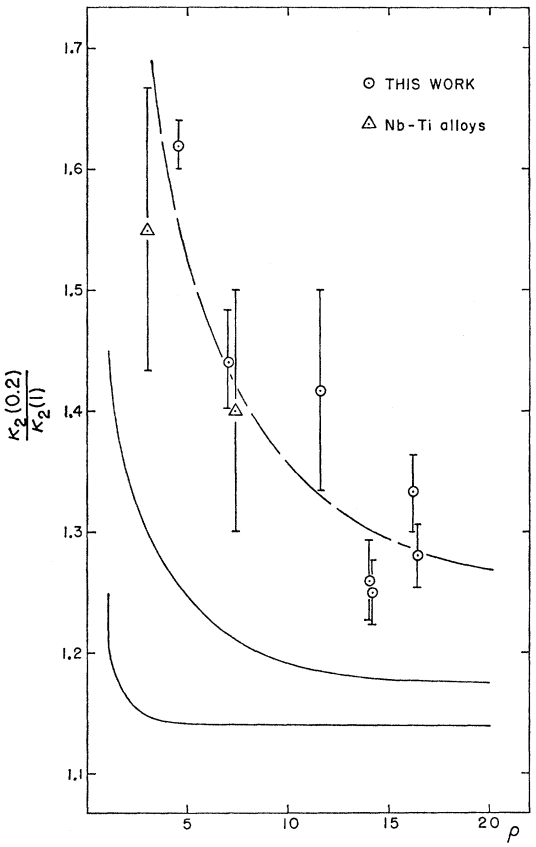

FIG. 12. The ratio $\kappa(0.2)/\kappa(1)$ as a function of the Gor'kov impurity parameter ρ for alloys in the Pb-In–alloy system (data for Nb-Ti alloys taken from Ref. 3). Dotted line is drawn through the points. The full lines are the theoretical predictions (Ref. 4) taking two extreme values for the ratio of transport mean free path to total mean free path (one and two for the higher and lower lines, respectively).

2. Second Generalized Ginzburg-Landau Parameter

The data for $\kappa_2(t)$ have been displayed in Fig. 8. In order to facilitate further discussion it is convenient to extract the normalized parameter $\kappa_2(0.2)/\kappa_2(1)$ which is displayed in Fig. 12 as a function of ρ, the impurity parameter. The temperature $t=0.20$ was chosen instead of $t=0$ because the lowest reduced temperature at which data are available is $t=0.21$ and extrapolation to $t=0$ would introduce a measure of uncertainty. The choice is guided by the theoretical results[4] which show substantial curvature below $t=0.1$ but between $t=0.2$ and $t=0.4$ are linear to a few percent over the range of ρ studied in this investigation. A number of points emerge from an examination of Figs. 8 and 12. First, the shapes of the curves in Fig. 8 are in excellent qualitative agreement with Eilenberger's predictions.[4] For low ρ alloys (5 at.% and 10 at.%), we have a simple convex curve with $d^2\kappa_2/dt^2<0$ for all t, whereas for the higher ρ samples there is evidence for a change in character with the appearance of positive values for this quantity. This change is most clearly seen by comparing data for the 20 at.% In and 60 at.% In samples. However, turning to Fig. 12 it is clear that there is a serious discrepancy for the actual magnitude of the increase of κ_2 between $t=1$ and $t=0.2$. For a given ρ the experimental data show a much stronger temperature dependence than expected from the theory. Again, the qualitative shape of the curve is as predicted[4] but it would need a change in ρ by an order of magnitude to bring the data into agreement with theory and this seems to be out of the question. Also plotted on Fig. 12 are data[3] for the niobium-titanium–alloy system which show a very similar departure from the theory.

VI. DISCUSSION

We have remarked that the trio of parameters T_c, ρ_n, and κ (Figs. 4, 5, and 11) all seem to give some evidence that an electronic structure change occurs around 30 at.% In. A large number of alloy systems investigated by Merriam[30] have exhibited T_c-composition plots of the type shown in Fig. 4 and these have been attributed by him to discontinuous changes in electronic structure. It is thought that such changes might occur if the conduction-electron density is changed sufficiently so as to change the topology of the Fermi surface. No quantitative theory exists for T_c under such conditions but it seems possible that the changes observed might be explicable qualitatively on such a basis. If the rigid band model holds for these alloys then one would expect an electronic structure change effect at ~45 at.% In.

[29] A. Eilenberger and V. Ambegaokar, Phys. Rev. **158**, 332 (1967).

[30] M. F. Merriam, M. A. Jensen, and B. R. Coles, Phys. Rev. **130**, 1719 (1963).

Our critical composition is somewhere around 30 at.% In, but in view of the sort of assumptions involved this is perhaps not a great disparity. Further, turning to κ, we have expressed the discrepancy with theory in terms of an effective resistivity ρ_n^*. In the approximations leading to Eq. (13), the equivalence of certain averages of the Fermi velocity over the Fermi surface is assumed. These will only be strictly true for a spherical Fermi surface and one would certainly anticipate that the departures from sphericity suggested above might lead to a breakdown of this averaging procedure.

Finally, we turn to examine the over-all situation with respect to $\kappa_2(\rho,t)$. The only other detailed set of data for this parameter in the literature, apart from niobium alloys,[3] is that for the lead-thallium system by Bon Mardion *et al.*[31] which gives $\kappa_2(0)/\kappa_2(1)=1.30\pm0.05$ for alloys of lead with thallium covering roughly the range of impurity parameter reported on here. Apart from the region below $\rho=10$ in which this investigation was restricted to two alloys over a limited temperature range, viz., $t<0.6$, the data of Ref. 31 show no systematic deviation from the present results. However, some recent data on niobium and niobium-tantalum alloys reported by Ikushima *et al.*[32] exhibit large, apparently systematic deviations. In their letter, data are displayed for the ratio $\kappa_2(0)/\kappa_2(1)$ which deviate very greatly from those found by Fietz and Webb[3] for the niobium-titanium system and at $\rho\sim1$ which actually fall 50% *below* Eilenberger's predictions. On the basis of their own data Ikushima *et al.* have suggested that these deviations from the theory are closely related to anisotropy of the energy gap. However, such anisotropy is unlikely to provide an explanation for the behavior reported here. Anisotropy of the energy gap is extremely small for lead[33] and will further be practically eliminated[34] by impurity scattering for $\rho\sim\xi_0/l>1$, i.e., for all the alloys discussed in this work.

VII. SUMMARY

(1) The temperature-independent parameter κ for lead-indium alloys can be incorporated within the framework of the GLAG theory by introducing an adjustable parameter which it has been suggested is related qualitatively to departures from sphericity of the Fermi surface in the alloys.

(2) Evidence has been presented for the occurence of some modification of electronic structure in the Pb-In system at a concentration of about 30 at.% In.

(3) $\kappa_2(\rho,t)$ for the whole Pb-In alloy system from 5 to 60 at.% In increases with decreasing t and ρ. The qualitative form of the dependence on both t and ρ agrees very well with present theory but there exists serious quantitative disagreement with the dependence on both parameters being stronger than predicted. Despite the conflict with theory, comparison with available data for other alloy systems supports the view that an experimental parameter $\kappa_2(\rho,t)$ does exist independent of the detailed characteristics of the alloy system being investigated.

Note added in proof. Two further investigations have come to our attention which do not appear to support our final suggestion. A survey of the Pb-Tl system[35] yielded generally higher values of $\kappa_2(0.2)/\kappa_2(1)$ than found here, whereas some very recent work on Nb-Mo alloys[36] reported rather lower values. It is known, however, that the ballistic technique used in both these investigations can produce non-negligible effects on the observed magnetization of type-II superconductors.[10] Such effects may have played some role in both the above investigations. In view of the present experimental situation, it is clear that, if genuine effects do exist (strong coupling or otherwise), a great deal of systematic work will be needed to distinguish them from experimental uncertainties.

[31] G. Bon Mardion, B. B. Goodman, and A. Lacaze, J. Phys. Chem. Solids **26**, 1143 (1965).
[32] A. Ikushima, T. Mizusaki, and T. Odaka, Phys. Letters **26A**, 582 (1968).
[33] H. Gamari-Seale and B. R. Coles, Proc. Phys. Soc. (London) **86**, 1199 (1965).
[34] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[35] S. T. Sekula and R. H. Kernohan, J. Phys. Chem. Solids **27**, 1863 (1966).
[36] R. A. French and J. Lowell, Phys. Rev. **173**, 504 (1968).