Effect of Antimony, Indium, and Zinc Impurities on the Critical-Field Curve of Tin*

F. V. BURCKBUCHLER,† D. MARKOWITZ, AND C. A. REYNOLDS
Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Connecticut
(Received 5 April 1968)

Measurements have been made of the superconducting critical field and the residual resistivity of oriented single-crystal tin samples containing In, Sb, and Zn impurities up to 2.2 at.%. The theory of Markowitz and Kadanoff is found to describe the variation of transition temperature with resistivity reasonably well. From the comparison, we obtain a value of 0.020 for the mean squared anisotropy of the superconducting energy gap in tin. Linear variations of ΔT_c, ascribable to impurity-induced variations of the gross parameters of the superconducting system, are determined to be 141, 135, and 58 m°K/$\mu\Omega$ cm for Zn, Sb, and In impurities, respectively. These results are in good agreement with previous measurements on polycrystalline material. It is found that the impurity-induced variation of the critical-field parameters, H_0/T_c and $(dH_c/dT)_{T_c}$, is in accord with Clem's theoretical calculations based on the washing out of gap anisotropy by impurity scattering. Comparison of the data with this theory suggests that the average density of states at the Fermi surface in tin is not seriously altered by the addition of up to 2 at.% impurity. Linear variations of ΔH_0 with $\rho_{0\perp}$ are found to be similar to those of ΔT_c. These linear variations of ΔH_0 and ΔT_c are correlated in a way predicted by BCS.

INTRODUCTION

THE effect of nonmagnetic impurities on the superconducting transition temperature T_c has been studied experimentally by several authors.[1–5] Markowitz and Kadanoff[6] (hereafter referred to as MK) calculated the effect of impurity scattering on T_c using a BCS-like model[7] which includes anisotropy. MK separated the effect into two parts (1) a nonlinear mean-free-path effect which produces an initial rapid decrease of T_c because of reduction of energy-gap anisotropy and (2) an effect linear in impurity concentration which results from small modifications of the average parameters of the superconducting system. They calculate the former theoretically and name it the "anisotropy effect." The latter is obtained empirically by effectively subtracting the anisotropy effect from experimental data, and is simply called the "linear effect." The essential features of the theory were verified by comparison with the existing experimental data on three superconductors with many impurities. Our data will be compared to the theory using the mechanics set up by MK, but only up to a point where, as will be shown, our lowest-impurity data will permit the removal of a weak link in the earlier analysis. The weak link consisted in estimating the conversion between a theoretical parameter and the resistivity; in view of the uncertainty in the quantities which were used to estimate this conversion, we believed a direct determination from T_c data to be very desirable. Further, a single-crystal study, taking into account residual resistance anisotropy, was available only for the cadmium-in-tin system. We therefore thought it worthwhile to undertake a single-crystal study of several other impurities in tin.

The effects of impurities on parameters of the critical-field curve such as the zero-temperature critical field H_0 and the slope near T_c, $(dH_c/dT)_{T_c}$, have been studied previously. Toxen *et al.*[8] found that both H_0/T_c and the reduced slope $(dh/dt)_1$, remained sensibly constant with the addition of tin to indium. The constancy of these two quantities has been known as the "similarity conditions" of the critical-field curve. Gueths *et al.*,[2] working with the cadmium-in-tin system, were the first to find that both of these parameters varied as impurity was added to the host metal, and in a manner which was in agreement with a theoretical treatment by Clem[9] predicting the sense and total size of the effects. Later, Blech and Serin[10] found a similar result for the tin-in-indium system. Recently, Clem[11] has extended his theoretical work to include calculation of the form of the variations of H_0/T_c and of $h(t)$ with impurity density. These calculations will allow us to make a detailed quantitative comparison of our data to the theory. Recently, we have learned that Mont-

* Supported by U.S. Air Force Office of Scientific Research Grant AF-AFOSR-474-67 and Office of Naval Research Contract NONR 2967(00). Portions of this work constitute a part of a thesis submitted by F. V. Burckbuchler in partial fulfillment of the requirements for the Ph.D. degree at the University of Connecticut.

† Present address: Bell Telephone Laboratories, Murray Hill, N.J.

[1] C. A. Reynolds, F. V. Burckbuchler, and D. Markowitz, Bull. Am. Phys. Soc. **13**, 76 (1968).

[2] J. E. Gueths, C. A. Reynolds, and M. A. Mitchell, Phys. Rev. **150**, 346 (1966).

[3] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

[4] D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta Met. **9**, 861 (1961).

[5] P. R. Doidge, Phil. Trans. Roy. Soc. (London) **A248**, 553 (1956).

[6] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

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

[8] A. M. Toxen, M. J. Burns, and D. J. Quinn, Phys. Rev. **138**, A1145, (1965).

[9] J. R. Clem, Ann. Phys. (N.Y.) **40**, 268 (1966).

[10] H. J. Blech and B. Serin, Bull. Am. Phys. Soc. **12**, 38 (1967).

[11] J. R. Clem, Phys. Rev. **153**, 449 (1967).

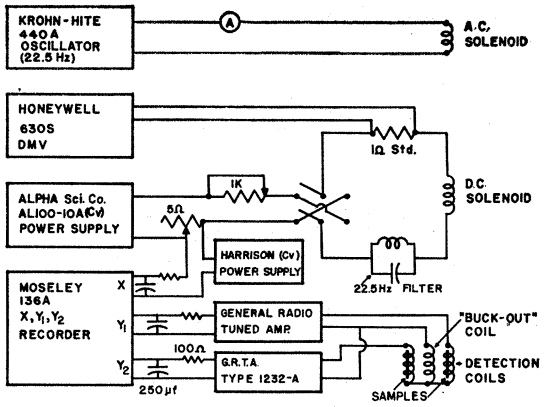

FIG. 1. Circuit used to measure the critical-field curve. The detection coils are ~15 000 turns of No. 40 Teflon-coated copper wire wound on a form 4 cm long with i.d. 0.09 in. and o.d. 0.5 in. The dc solenoid produces 344 G/A. The ac solenoid produces 34 G/A with the dc winding open.

gomery[12] has conducted a study of the indium-in-tin system and compared his results with Clem's predictions.

EXPERIMENTAL DETAILS

Seventy-seven tin single crystals in the tetragonal phase containing antimony, indium, or zinc impurity were grown and annealed at ~190°C for a period of six to 30 days to relieve strains and homogenize the impurity distribution. The methods of crystal growth and orientation were essentially those described by Gueths *et al.*[2] and will not be repeated here. The description of a new device used as an aid in the orientation of these crystals will be published elsewhere.

For this work it was necessary for us to have an experimental parameter which was proportional to the impurity density. The residual resistivity in a particular crystallographic direction fills this requirement, whereas the resistivity ratio used in some previous investigations is not entirely satisfactory owing to the impurity type and the temperature dependences of the anisotropy of the tin resistivity. We have chosen $\rho_{0\perp}$, the residual resistivity perpendicular to the tin tetrad axis, as the plotting parameter. This work was concurrent with a study of resistivity anisotropy which is described in the following paper; the details of the resistivity determinations will be given there.[13]

The superconducting critical field H_c of each sample was measured at several points in the temperature intervals 3.7–3.5°K and 1.9–1.1°K. A low-frequency ac method of measurement similar to that described by Reynolds *et al.*[14] was employed using the cryostat, solenoids, and detection coils described by Gueths *et al.*[2] The circuit used in this measurement is shown in Fig. 1 and contained two identical detection channels, which permitted the simultaneous measurement of an alloy sample and a standard sample. Errors resulting from small temperature drifts were thus eliminated and a direct determination of the difference in critical field ΔH_c was obtained. All alloys were measured relative to the standard sample, which itself contained ~0.01% Cd impurity; ΔH_c was later corrected to a pure tin reference. In the circuit of Fig. 1 a voltage proportional to the change in dc solenoid current appeared on the recorder X axis, and Y deflection signified a phase transition. Since the ac field (<0.15 Oe) was always less than the transition width (<1 Oe) the centroid of the recorded transition was taken as H_c. Inhomogeneous alloys were identified by broad transitions with a temperature-dependent shape, and were rejected on that basis.

Sample graphs used in the data reduction are shown in Fig. 2. Since the critical-field curve of tin is nearly linear near T_c, it is easily demonstrated that the intercept and slope in Fig. 2(a) may be used to obtain ΔT_c and $\delta(dH_c/dT)_{T_c}$, respectively. We shall consistently use the symbol Δ to mean a change and the symbol δ to mean a fractional change, both relative to pure tin. In the reduction of the lower temperature data from which we obtained ΔH_0 it was assumed that the reduced critical field h could be written as a function of the reduced temperature t in a form

$$h=1+At^2+Dt^4+\cdots, \qquad (1)$$

where A, B, etc., and t are slowly varying functions of impurity density. Under these assumptions it may be shown that a graph of the type shown in Fig. 2(b) will

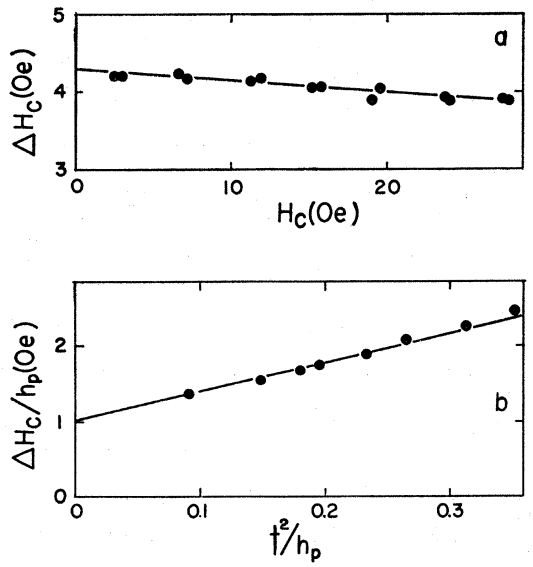

FIG. 2. Sample of the data and form of data reduction. In (a) $\Delta H_c[=H_c(\text{pure})-H_c(\text{alloy})]$ is plotted versus $H_c(\text{alloy})$ and was used to determine ΔT_c and $\delta(dH_c/dT)_{T_c}$. The graph in (b) was used to determine ΔH_0; $h_p=H_c(t)/H_0$ for pure tin; $t_p=T/T_c$, also for pure tin.

[12] D. C. Montgomery, Ph.D. Thesis, University of Illinois, 1967 (unpublished).

[13] F. V. Burckbuchler and C. A. Reynolds, first following paper, Phys. Rev. **175**, 550 (1968).

[14] C. A. Reynolds, B. Serin, and L. Nesbitt, Phys. Rev. **84**, 691 (1951).

be linear for the range of our data and it extrapolates to ΔH_0 as $t \rightarrow 0$. The subscript p in Fig. 2(b) denotes pure tin for which the critical field data of Finnemore and Mapother[15] were used in obtaining $h_p(t_p)$.

It is estimated that the ΔT_c of a sample relative to our standard sample was accurate to ± 0.0002°K plus $\pm 1\%$ of ΔT_c. By extrapolation from our least impure samples, we obtain T_c (pure tin) $= 3.7230 \pm 0.0010$°K, which is in reasonable agreement with Finnemore and Mapother's[15] value of 3.7216 ± 0.0010°K. The measurement of $\delta(dH_c/dT)_{Tc}$, estimated to be accurate within ± 0.003, was particularly sensitive to errors arising from sample inhomogeneity and a nonzero demagnetization coefficient. To ΔH_0 we assign an uncertainty of ± 0.3 Oe. Since the samples were held at room temperature between measurements, the room temperature solubility of impurities limited the range of accessible impurity concentration. Residual resistivity measurements indicated that approximately 1.8 at.% antimony and less than 0.1 at.% zinc were soluble in tin.

The precipitation of zinc occurred slowly, however, and results for zinc impurity are presented below which correspond to impurity densities approaching 0.5 at.%. The resistivities of zinc impurity samples were extrapolated (by $\leq 5\%$) to the time at which the critical-field measurements were made. Solubility limited the zinc data and the high-temperature antimony data. The low-temperature antimony data, and the high- and low-temperature indium data were limited by another effect however. This effect was a change in the character of the superconducting transition, which we tentatively ascribe to a superconducting sheath for some range of applied field $H > H_c$. This limited the high-temperature indium data to < 2.2 at.%, and the low-temperature indium and antimony data to < 1.8 and 1.4 at.%, respectively.

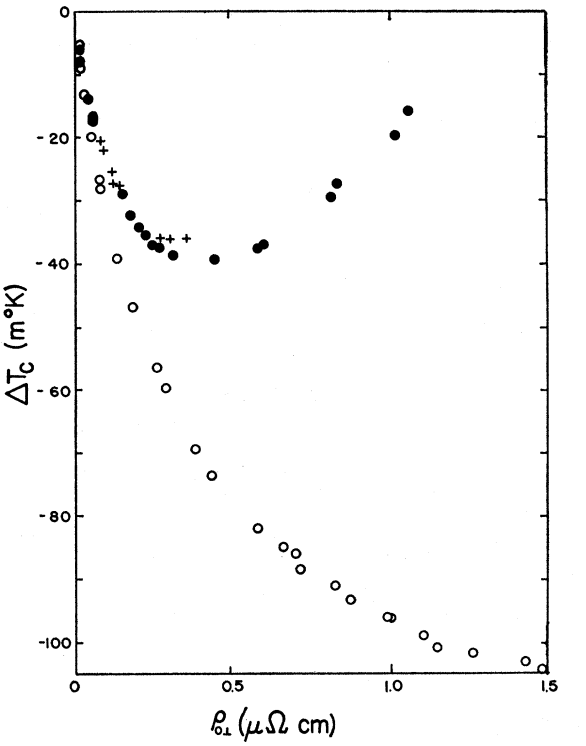

FIG. 3. Change in transition temperature, ΔT_c, versus $\rho_{0\perp}$ for antimony (●), indium (○), and zinc (+) impurity samples measured in this work.

RESULTS

Transition Temperature

The results of the T_c measurements on our samples containing antimony, indium, or zinc impurity are shown in Fig. 3. It is this data that we have compared to the theory of Markowitz and Kadanoff,[6] according to which the change in transition temperature is given by

$$T_c = K^i \chi + \langle a^2 \rangle T_c I_c(\chi), \qquad (2)$$

in which K^i is the coefficient of the linear effect and is dependent on the impurity type i. $\langle a^2 \rangle$ is the mean-squared energy-gap anisotropy in pure tin, and $I_c(\chi)$ is a function obtainable from their Fig. 4. χ is a theoretical variable defined in terms of a mean collision time τ_a which averages over scattering events in such a way as to take account of their effect in washing out gap anisotropy. τ_a is not to be identified with the relaxation time for transport τ except for the special case of isotropic scattering. It is sufficient for our purposes to know that χ is proportional to the impurity density as is $\rho_{0\perp}$. We have therefore defined a constant $C(=\chi/\rho_{0\perp})$, which we have determined from our data along with $\langle a^2 \rangle$, K^{Sb}, K^{In}, and K^{Zn}. Conceptually, C might be a function of impurity type; however MK found this not to be the case for tin, and we have come to the same conclusion. Assuming C to be independent of impurity type, Eq. (2) declares that the data of one impurity can be mapped onto the data of another impurity by the addition of a constant to the quantity $\Delta T_c/\rho_{0\perp}$. In this analysis we confine our attention to the impurities for which our data cover a wide range, viz., antimony and indium. The constant 0.077°K/$\mu\Omega$ cm has been added to each indium data point. That this mapping of indium data onto antimony data is successful is clearly shown in Figs. 4 and 5. Numerical results are obtained by comparing the data with two approximations to Eq. (2). In the high and intermediate impurity range of these data the approximate expression

$$\Delta T_c/\rho_{0\perp} = [K^i - (0.36 + 0.078 \ln C) \langle a^2 \rangle T_c] C + 0.078 \langle a^2 \rangle T_c C \ln \rho_{0\perp} \qquad (3)$$

was used by MK. In the limit of low impurity concen-

[15] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A507 (1965).

TABLE I. Linear-effect coefficients and their separation into coefficients for isotropic mean-free-path effect and charge effect.

	(a) Linear-effect coefficients K^iC (°K/$\mu\Omega$ cm)[a] In	Cd	InSb	Sb	Zn
MK	0.057	0.075	0.100	0.134	0.088
Present[b]	0.059	0.071[c]	...	0.136	0.142
	...	(0.068)	(0.101)	...	(0.051)

	(b) Ginsberg-Markowitz[d]	Gueths[e]	Ginsberg[f]	Glover and Sherill[g]	Present
$\langle a^2 \rangle$	0.019	0.023	...	...	0.020
α (K°/$\mu\Omega$ cm)[a]	0.102[h]	...	0.087[i]	...	0.10_1
β (K°/at.%)	0.020[h]	...	...	0.018[i]	0.022_4

[a] Resistivity ratios (ρ_r) used in some previous studies have been converted to $\rho_{0\perp}$ by the relationship $\rho_r/\rho_{0\perp} = (1+a_0\cos^2\theta)/9.05(1+0.55\cos^2\theta)$ using the a_0's of Ref. 13 and taking $\cos^2\theta \sim 0.2$ for a polycrystalline sample.
[b] Measured values, except that values in parentheses were calculated from our α and β.
[c] Estimated from the data of Gueths *et al.* (Ref. 2).
[d] Reference 18.
[e] Reference 2.
[f] D. M. Ginsberg, Phys. Rev. 138, A1409 (1965).
[g] R. E. Glover, III, and M. D. Sherill, Phys. Rev. Letters 5, 248 (1960).
[h] These estimates are based on six impurities in tin.
[i] This is a theoretical estimate based on a simple model of the effect of mean free path on the electron-electron interaction.
[j] Measured directly by charging a thin film of tin.

tration Clem[11] has suggested the approximate form

$$\Delta T_c/\rho_{0\perp} = (-0.393\langle a^2\rangle T_c + K^i)C + 0.0557\langle a^2\rangle T_c C^2 \rho_{0\perp}. \quad (4)$$

These two expressions plot linearly onto the scales of Figs. 4 and 5, respectively, in which the straight lines shown have been interpreted in the light of Eqs. (3) and (4), respectively. In plotting Fig. 5, the highest few points were corrected to compensate for the small difference ($\leq 4\%$) which exists in that range between the more exact function I_c and its approximate form contained in Eq. (4). Also, the lowest few points afforded a sensitive means of correcting the absolute ΔT_c of all samples in that a deviation from linearity of the form (const/$\rho_{0\perp}$) would result from any additive-constant error in all of the ΔT_c values. This resulted in a 0.0005°K correction to our initial estimate of T_c(pure). The line shown in Fig. 5 is a best fit to the low-impurity data and not an extension of the line or curve shown in Fig. 4.

Combining the information from Figs. 4 and 5, we have found that $C=15.1$ per $\mu\Omega$ cm; our results for $\langle a^2\rangle$ and the linear-effect coefficients are listed in Table I along with those from previous work. We estimate the uncertainty in C and in $\langle a^2\rangle$ to be $\pm 15\%$. The linear-effect coefficients are expected to be accurate to within ± 0.01°K/$\mu\Omega$ cm, but the differences between different impurities are much better known, within ± 0.002°K/$\mu\Omega$ cm.

We note that there is very good agreement between our results and those of MK. This is a consequence of (1) the agreement of the data of Lynton *et al.*[3] (used by MK) with our own, and (2) our obtaining of a result for C which is in good agreement with the value used by MK.

In view of the conclusion drawn in Ref. 13 that scattering is not isotropic in tin in the residual-resistance regime, it is surprising that our value of C agrees

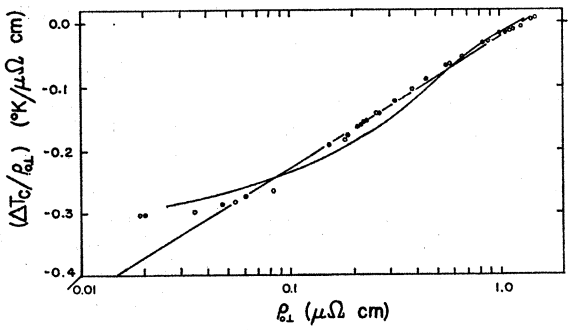

FIG. 4. Antimony and indium impurity data of Fig. 3 replotted on different scales; a constant $\Delta T_c/\rho_{0\perp}=0.077$°K/$\mu\Omega$ cm has been added to the indium data points to superpose them onto antimony data. Only samples for which the tetrad axis is nearly perpendicular ($\theta>75°$) to the sample axis are shown here. The straight line is drawn to facilitate comparison to Eq. (3). The curve represents Eq. (2).

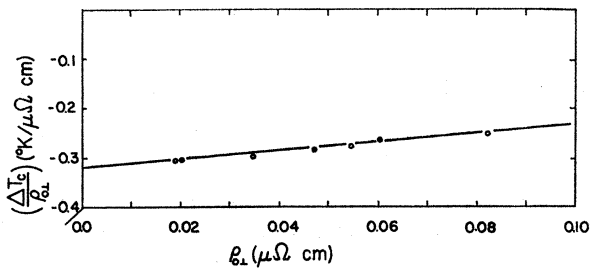

FIG. 5. Low-impurity data of Fig. 3 but plotted on a different abscissa scale. The straight line is drawn to facilitate comparison with Eq. (4).

with MK's value; they were forced to assume isotropic scattering. We note, however, that their computation of C involved the Fermi velocity v_F and the ratio of conductivity to mean free path σ/Λ. Neither of these quantities is well known for tin (estimates differ by as much as a factor of 2) owing to their large anisotropies. We must therefore conclude that the agreement concerning C is fortuitous. Our experimental value of C contains information about the ratio of the mean free times appropriate to energy-gap anisotropy washout and electrical transport, viz., τ_a/τ; any attempt to determine this ratio is premature however, since the uncertainty in v_F and σ/Λ permits estimates of τ_a/τ that range between 2 and $\frac{1}{2}$. It is also surprising that C is independent of impurity type when the anisotropy of ρ_0 is clearly dependent on impurity type.[13] We believe that the apparent constancy of C is a consequence of the choice of $\rho_{0\perp}$ as the plotting parameter, in that this component of the resistivity is primarily determined by large-angle scattering, as is also the washing out of energy-gap anisotropy. (Zavaritskii[16] has found that the directions of maximum and minimum gap values are separated by essentially 90°.) The resistivity parallel to the tetrad axis, $\rho_{0||}$, is determined by small-angle as well as large-angle scattering. Had $\rho_{0||}$ been used in our analysis, C would have varied with impurity type, and we would *not* have been able to map the data of one impurity onto that of another.[17]

In Fig. 4 we have plotted Eq. (2) with $C=15.1$, $\langle a^2\rangle=0.020$, and $K^{Sb}=0.136$. It is seen that the theoretical curve weaves about the data and reasonably describes its general behavior, but that the fit is far from perfect; the maximum deviation of the theoretical curve from the data exceeds 0.005°K, which is well in excess of the experimental uncertainty. A variation of the parameters C, $\langle a^2\rangle$, and K^i does not appear to materially improve the fit, and the authors believe that the difficulty is rooted in the assumption of isotropic scattering made in the theory. As has been pointed out by one of us (DM, see Ref. 6), a more exact solution can be obtained once the detailed variations of energy gap and relaxation time over the Fermi surface are known. Such detailed knowledge is not yet available however.

Markowitz and later Ginsberg[18] have resolved the linear effect coefficients into a term proportional to the resistivity, with coefficient α, and a term proportional to the valence excess of the impurity, with coefficient β. We have followed their procedure exactly using our antimony and indium impurity data, and so we will not repeat their arguments here. The results of this analysis using our results are given in Table I(b) and are in good agreement with the earlier work.

Variation of H_0/T_c

In the analysis of transition temperature we obtained values of $\langle a^2\rangle$ and C, which we may now use to compare variations in the other critical-field parameters to the predictions of Clem. Using the anisotropic BCS-like model introduced by MK, Clem[11] has calculated the effect of energy-gap anisotropy on the critical-field curve. As in the MK theory, impurity scattering reduces the effective $\langle a^2\rangle$. Clem noted that the critical field is expected to exhibit linear impurity-induced effects similar to those of T_c. For the particular case of H_0 this may be seen from the isotropic BCS[7] relations for T_c and H_0:

$$k_B T_c = 1.14\hbar\omega_D \exp[-1/N(0)V], \tag{5}$$

$$H_0 = 1.75[4\pi N(0)]^{1/2} k_B T_c. \tag{6}$$

$N(0)$ is the average density of states of one spin direction at the Fermi surface in the normal metal. V is the attractive electron-electron interaction, and $\hbar\omega_D$ is some average phonon energy. The major part of the linear effects will come from variation of $\exp[-1/N(0)V]$, which is common to both T_c and H_0; the similarity condition, $H_0/T_c=$constant, is therefore seen to be predicted by BCS under the restriction that $N(0)^{1/2}$ is slowly varying. In order to avoid linear effects, Clem worked with a quantity $\tilde{H}_0$, where

$$\tilde{H}_0^2 = H_0^2/8\pi\gamma T_c^2. \tag{7}$$

This quantity is strictly free of linear effects in the BCS context since γ, the normal-state electronic specific-heat coefficient, is proportional to $N(0)$. Clem calculated the impurity-induced change in H_0 and tabulated δ_H:

$$\delta_H = [\tilde{H}_0(\chi) - \tilde{H}_0(0)]/\langle a^2\rangle \tilde{H}_0(0). \tag{8}$$

As the changes in H_0/T_c due to all origins are small, we may separate them according to

$$\delta(H_0/T_c) = \langle a^2\rangle \delta_H + \tfrac{1}{2}\delta N(0). \tag{9}$$

The second term in this expression, which represents a fractional variation in the density of states, is expected to be small and linear in $\rho_{0\perp}$. We therefore compare our experimental values of H_0/T_c with the first term in Eq. (9), being mindful of any linear separation of the experimental points from the theoretical prediction. This comparison appears in Figs. 6(a), 7(a), and 8(a), where our results for $\langle a^2\rangle$ and C have been used in conjunction with δ_H from Fig. 3 of Ref. 11 in order to

[16] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **48**, 837 (1965) [English transl.: Soviet Phys.—JETP **21**, 557 (1965)].

[17] We expect that the resistivity ratio (ρ_r) of polycrystalline samples used in some previous investigations will be much more strongly influenced by $\rho_{0\perp}$ than $\rho_{0||}$ for three reasons. (1) An average residual resistivity is given by $\bar{\rho}_0=(2\rho_{0\perp}+\rho_{0||})/3$. (2) It is our experience that cast specimens grow in the perpendicular orientation preferentially, i.e., more often than would be expected on a statistical basis. (3) In a truly polycrystalline sample there will be parallel regions of different crystallographic orientation; a current will be shunted by crystallites with $\theta\sim 90°$ due to their lower resistance.

[18] D. Markowitz, Ph.D. thesis, University of Illinois, 1963 (unpublished); D. M. Ginsberg, Phys. Rev. **136**, A1167 (1964).

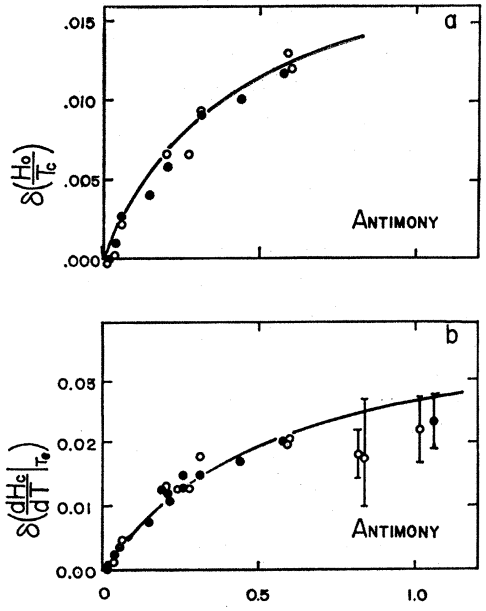

FIG. 6. Antimony impurity in tin. Fractional change in (a) H_0/T_c, (b) $(dH_c/dT)_{T_c}$ as functions of $\rho_{0\perp}$. The curves are predicted by Clem (Ref. 11) using $\langle a^2\rangle=0.02$ and $\chi=15\ \rho_{0\perp}$. Filled circles have $\theta>75°$, open circles have $\theta<75°$.

plot the theoretical curve. We postpone discussion of this comparison for a moment.

Slope of the Critical-Field Curve near T_c

In the case of $(dH_c/dT)_{T_c}$, we may use Clem's[11] Eq. (24) in order to obtain an expression for the fractional variation of the slope due to the reduction of energy-gap anisotropy. A variation due to $\delta N(0)$ is also expected from the BCS[7] expression [their Eq. (3.52)] for the slope near T_c. Combining these contributions, we have

$$\delta(dH_c/dT)_{T_c}=\langle a^2\rangle[X_H(1,0)-X_H(1,\chi)]+\tfrac{1}{2}\delta N(0), \tag{10}$$

in which $X_H(t,\chi)$ is a function given in Fig. 1 of Ref. 11. The comparison of experimental and theoretical slope variations is handled the same way as was done for H_0/T_c and is shown in Figs. 6(b), 7(b), and 8(b).

Examination of Figs. 6–8 reveals that there is good agreement between theory and the experimental data especially in view of the smallness of the effects. For antimony impurity the agreement is excellent, suggesting that $N(0)$ is held very nearly constant as this impurity is added to tin. In the case of indium it is seen that H_0/T_c systematically falls below the theoretical curve, though by an amount which is comparable to the experimental uncertainty, and it is doubtful that the discrepancy is due to a variation of $N(0)$. If $N(0)$ were changing, we would expect the separation of theory and data to increase linearly with the addition of impurity; this does not appear to be the case. Further, we would expect that both H_0/T_c and $(dH_c/dT)_{T_c}$ would depart from the theory in a similar way if $N(0)$ were responsible. In contrast to H_0/T_c, the slope measurements depart in the opposite sense, if they depart at all, from the theoretical prediction. We are led to conclude that the discrepancy in H_0/T_c is a consequence

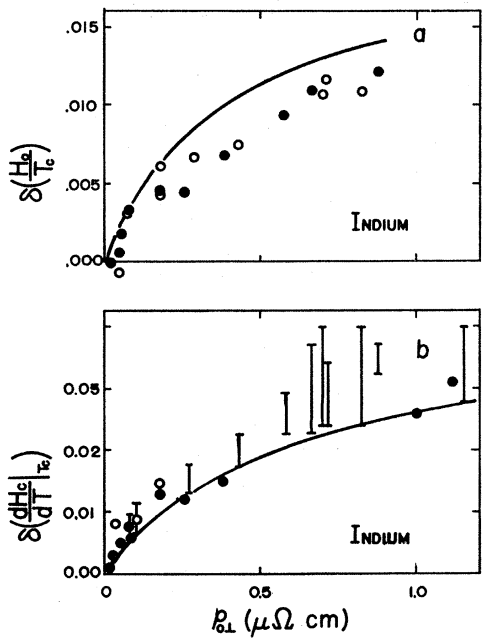

FIG. 7. Indium impurity in tin. Otherwise the same as Fig. 6.

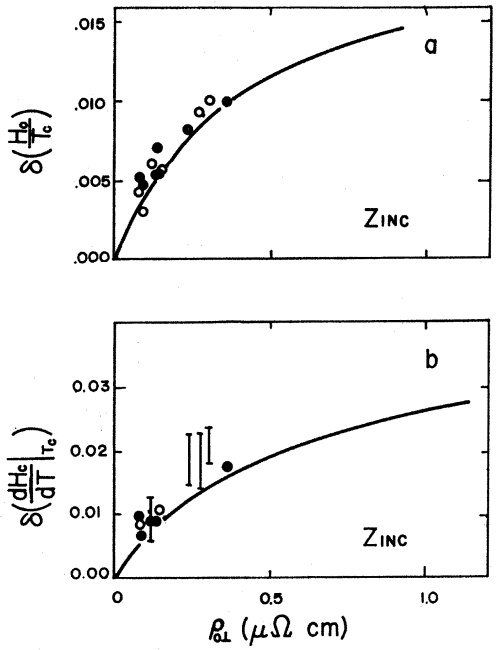

FIG. 8. Zinc impurity in tin. Otherwise the same as Fig. 6.

of a systematic experimental error of about 0.2%, which is not to be considered serious. For zinc impurity we find the data and theoretical curve to be in satisfactory accord. The small positive displacement is within our estimated experimental uncertainty.

Montgomery[12] has estimated $\langle a^2 \rangle$ to be 0.014 ± 0.001 from results on $H_0^2/T_c^2 N(0)$ for a small set of quasi-single-crystal tin samples with indium impurity. Indeed, our own indium impurity H_0/T_c data might lead us to believe that $\langle a^2 \rangle$ was somewhat lower than 0.020. All of our other graphs however, including $(dH_c/dT)_{T_c}$ for indium impurity, favor the estimate $\langle a^2 \rangle = 0.020$.

Similarity Conditions

We mentioned similarity conditions above, viz., the alleged constancy of $(dh/dt)_1$ and H_0/T_c. The latter is obviously violated in the graphs of Figs. 6(a), 7(a), and 8(a). The former requires that the slope and H_0/T_c change by the same amount. We see that the variation of slope exceeds that of H_0/T_c by about a factor of 2. We concur with Gueths *et al.*[2] in saying that neither similarity condition is applicable when impurities are added to tin. From the agreement shown by our comparison to Clem's theory,[11] we conclude that this is a consequence of reduction of the effect of gap anisotropy due to impurity scattering. We may set an upper limit of 0.5% on the change of $N(0)$ with the addition of 1 at.% of indium, antimony, or zinc impurity to tin. While some of our data indicate that the change is even much less, we believe that the scatter in the indium-impurity data indicates that we should be cautious in making this estimate. The method is not a sensitive test for small changes in $N(0)$, nor was it intended to be.

Linear Effects on H_0

It is implicit in the agreement of the data with Clem's theory that the second similarity condition is obeyed *by the linear effects* of alloying on H_0 and T_c. The relative insensitivity of the ratio of these quantities to changes in $N(0)$, V, and ω_D is embodied in the BCS Eqs. (5) and (6). However, it is instructive to look at the linear effect in H_0 explicitly. We have subtracted the anisotropy effect ($\Delta H_{0,\text{anis}}$) from $\Delta H_{0,\text{total}}$ by use of the expression

$$\Delta H_{0,\text{anis}}(\chi) = H_0(0)\,\langle a^2 \rangle [I_c(\chi) + \delta_H(\chi)]. \quad (11)$$

This function is independent of impurity type and is displayed in the lower curve in Fig. 9. The ΔH_0 data are also shown here, but with $\Delta H_{0,\text{anis}}$ subtracted out. The most important feature of the data is that they vary linearly with $\rho_{0\perp}$, and at a rate which depends on the particular impurity. We may predict the rates from the linear-effect coefficients ($C\mathrm{K}^i$) of ΔT_c. The

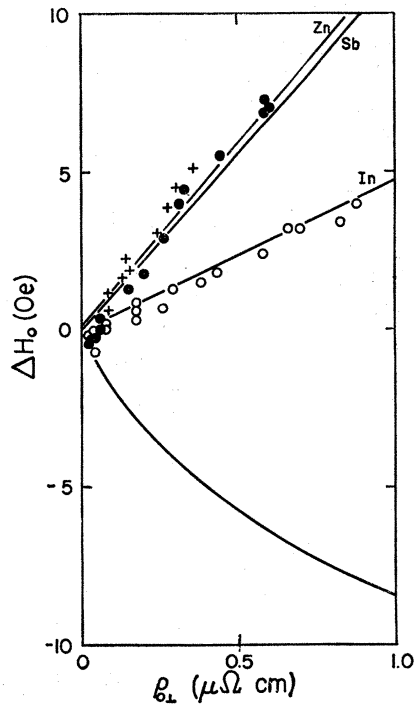

FIG. 9. The lower curve is the change in H_0 resulting from the reduction of gap anisotopy as predicted by Clem (Ref. 11) for $\langle a^2 \rangle = 0.02$ and $\chi/\rho_{0\perp} = 15$. The points were obtained by subtracting the theoretical curve from the measured change in H_0. The straight lines are drawn consistent with the similarity principle that H_0/T_c=constant (the effect of $\langle a^2 \rangle$ having also been subtracted from T_c). (●), antimony; (○), indium; (+), zinc impurities.

similarity condition may be written in the form

$$\Delta H_0{}^i = \Delta H^i{}_{0,\text{total}} - \Delta H_{0,\text{anis}}$$
$$= [H_0(0)/T_c(0)]C\mathrm{K}^i\rho_{0\perp} \quad (12)$$

for each impurity type i. The straight lines in Fig. 9 were obtained from this equation. It is clearly demonstrated that the linear effects in H_0 and T_c are highly correlated. It is pointless to speculate on improving the agreement in Fig. 9 since we have used rather imprecise estimates of $\langle a^2 \rangle$, C, and K^i to subtract a major contribution from $\Delta H_{0,\text{total}}$, which was less precisely measured than ΔT_c.

SUMMARY

In comparing our ΔT_c data to the Markowitz-Kadanoff theory, we have determined $\langle a^2 \rangle = 0.020$, and impurity-induced variations of the parameters $\hbar\omega_D$, $N(0)$, and V are found to be responsible for linear transition temperature variations of 141, 135, and 58 m°K/$\mu\Omega$cm for Zn, Sb, and In impurity, respectively.

We have found that the impurity-induced variation of the critical-field parameters H_0/T_c and $(dH_c/dT)_{T_c}$ are in accord with the theoretical calculations of Clem

based on the washing out of energy-gap anisotropy by impurity scattering; this point is thus established for four impurities in tin. Additional linear variations of H_0 with $\rho_{0\perp}$ are correlated with similar variations of T_c, as predicted by BCS. Our results suggest that $N(0)$ is held nearly constant as In, Sb, and Zn impurities are added.

General and consistent agreement between theory and experiment is found for all of the parameters of the critical-field curve studied. Because of the relative inaccuracy of the measurements of H_0 and $(dH_c/dT)_{T_c}$, no more can be said of their comparison to theory. The greater accuracy of the T_c measurement, however, shows that there are yet unresolved discrepancies in the detailed shape of the variation of this quantity when impurities are added to tin.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. E. Gueths for several interesting discussions during the course of this work. We also wish to thank H. Taylor, E. Singsen, and R. Palermo for technical assistance; Miss Elizabeth Zub-Zdanowicz for handling much of the computational work; and R. Linz for preparing the illustrations. The computational part of this work was carried out in the Computer Center at the University of Connecticut, which is supported in part by Grant GP-1819 of the National Science Foundation.

PHYSICAL REVIEW VOLUME 175, NUMBER 2 10 NOVEMBER 1968

Anisotropy of the Residual Resistivity of Tin with Sb, In, Zn, and Cd Impurities, and the Ideal Resistivities and Deviations from Matthiessen's Rule at 77 and 273°K*

F. V. BURCKBUCHLER† AND C. A. REYNOLDS

Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Connecticut

(Received 5 April 1968)

Measurements have been made of the orientation and of the electrical resistivities at 4.2, 77, and 273°K of single-crystal tin samples containing In, Sb, Zn, and Cd impurity up to 2.2 at.%. The superconducting transition temperature was used as a measure of impurity concentration. The anisotropy of the residual resistivity is found to be dependent on impurity type. Defining a_0 as the ratio of residual resistivities parallel and perpendicular to the tin tetrad axis ($a_0=\rho_{0\parallel}/\rho_{0\perp}$), it is found that $a_0=1.21\pm0.05$, 1.30 ± 0.07, 1.53 ± 0.07, and 1.60 ± 0.07 for In, Sb, Zn, and Cd impurities, respectively. These results indicate that impurity scattering in tin is not isotropic, and a qualitative discussion of these results is offered. It is found that $\rho_{0\perp}$ varies linearly with impurity content x for indium and antimony impurity; we determine $(\rho_{0\perp}/x)=0.54\pm0.02$ and 0.63 ± 0.03 $\mu\Omega$ cm/at.% for these two impurities, respectively. For zinc impurity this quantity is estimated to be at least 0.82 $\mu\Omega$ cm/at.%. For the $\theta=90°$ orientation, it is found that the deviations from Matthiessen's rule at 77 and 273°K vary linearly with $\rho_{0\perp}$ and are, within experimental uncertainty, the same for Sb, In, and Zn impurity. At the ice point the deviation is approximately 1.7 times larger than at 77°K where the deviation is $(10\pm1)\%$ of $\rho_{0\perp}$. Determinations of the ideal resistivity at 77 and 273°K are in good agreement with previous determinations made by Gueths.

INTRODUCTION

THIS paper is the result of an experimental investigation of the anisotropic electrical resistivities of impure tin at 4.2, 77, and 273°K. Approximately 80 oriented tin single crystals containing cadmium, antimony, indium, and zinc were measured. The purity of the samples (0.03–2.2 at.%) was such that the 4.2°K measurements yielded the residual resistivities. The resistivity per unit of impurity density ρ_0/x has been found as a function of crystal orientation and impurity type. From the 77 and 273°K measurements we have determined the ideal resistivity of tin at these temperatures and the deviations from Matthiessen's rule.

The orientation dependence of the resistivity of a tetragonal crystal such as tin may be written in the form

$$\rho(\theta)=\rho_{\perp}(1+(a-1)\cos^2\theta), \qquad (1)$$

in which θ is the angle between the current direction and the tetrad axis. By $\rho_{\perp}$ we mean $\rho(90°)$ and a, which we call the anisotropy, is the ratio $\rho(0°)/\rho(90°)$.

Previous measurements of the anisotropy a_0 of the residual resistivity have appeared to be inconsistent with each other.[1–3] The values of this quantity as found

* Supported by U.S. Air Force Office of Scientific Research Grant No. AF-AFOSR-474-67 and Office of Naval Research Contract No. NONR 2967(00). Part of a thesis submitted by F. V. Burckbuchler to the University of Connecticut in partial fulfillment of the requirements for the Ph.D. degree in Physics.

† Present address: Bell Telephone Laboratories, Murray Hill, N.J.

[1] J. E. Gueths, C. A. Reynolds, and M. A. Mitchell, Phys. Rev. **150**, 346 (1966).

[2] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

[3] V. B. Zernov and Yu. V Sharvin, Zh. Eksperim. i Teor. Fiz. **36**, 1038 (1959) [English transl.: Soviet Phys.—JETP **9**, 737 (1959)].