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Superconducting Properties and Anisotropic Electrical Resistivities of Pure and Cadmium-Doped Tin*

J. E. GUETHS, C. A. REYNOLDS, AND M. A. MITCHELL
Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Connecticut

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Approximately 60 cylindrically shaped single crystals of pure and cadmium-doped ($<\%1$ Cd) tin in the tetragonal phase were prepared. Electrical-resistivity determinations were made at 373, 273, 77, and 4.2°K. An investigation was made of the variation of the superconducting critical-field parameters with impurity content. The anisotropy of the temperature-dependent electrical resistivity $\rho(T)$ for pure tin was determined. $\rho_{\parallel}(T)/\rho_{\perp}(T)$ is found to be 1.53 ± 0.01 at 373°K, 1.555 ± 0.009 at 273°K, and 1.684 ± 0.010 at 77°K. $\rho_{\perp}(T)$ is 13.25 ± 0.05, 9.05 ± 0.03, and 1.772 ± 0.006 $\mu\Omega$-cm at 373, 272, and 77°K respectively. The anisotropy of the residual resistivity ρ_0 for cadmium impurity was determined at 4.2°K by two different experimental methods in different regions of impurity concentration x. $\rho_{0\parallel}/\rho_{0\perp}$ is found to be 1.6 ± 0.1 in both regions. The residual resistivity for any specific crystal orientation is found to vary linearly with x ($\rho_{0\perp}/x=1.39$ $\mu\Omega$ cm/at.%). Deviations from Matthiessen's rule are found to vary linearly [$\rho(T)_{\text{impure}}-\rho(T)_{\text{pure}}=0.16\rho_{0\perp}$] with impurity concentration and appear to be temperature-independent for $77°\text{K}\leq T\leq 373°\text{K}$. The general features of the data relating the change in superconducting transition temperature (T_c) with doping are in good agreement with the data of Lynton, Serin, and Zucker. However, there is evidence for anomalous T_c behavior in the region of composition ($x\approx0.3\%$) at which a lattice-spacing anomaly was reported by Lee and Raynor. The development of vacant sites as reported by Lee and Raynor in this region is not observed in plots of $\rho_{0\perp}$ versus x, however. The theory of Markowitz and Kadanoff is applied to the data relating T_c to impurity concentration. Reasonable agreement between the theory and experiment is found. The mean-squared relative anisotropy of the superconducting energy gap parameter $\langle a^2\rangle$, is found from this analysis to be 0.023. A recent theoretical treatment due to Clem which describes the change in the critical-field parameters with doping is compared to our experimental results. The so-called "similarity conditions" are found not to be satisfied. The shape of the reduced critical-field curve is found to be a function of impurity concentration. The value of $\langle a^2\rangle$ obtained from our data employing Clem's equations is 0.022, in good agreement with the value obtained from the T_c data alone. The data describing the reduced critical-field curve of pure tin is in good agreement with the results od Shaw *et al.* The change in shape of the reduced critical-field curve can be understood both qualitatively and quantitatively in terms of the reduction of the effects of $\langle a^2\rangle$ with doping as given by Clem's theoretical treatment.

INTRODUCTION

THE introduction of nonmagnetic impurities into superconducting metals such as tin has experimentally been found to systematically alter T_c, the superconducting transition temperature.[1-4] The effects of doping have also been noted on parameters associated with the critical-field curve such as H_0 and $(dH_c/dT)_{T=T_c}$.[1,3] The effect of doping on T_c has been theoretically treated by Markowitz and Kadanoff[5] (hereafter referred to as MK) with a reasonable degree of success. Contributing factors causing a change in T_c are (1) a decrease in the effectiveness of $\langle a^2\rangle$, the mean-squared relative anisotropy of the superconducting energy gap, and (2) all other effects which are grouped into a so-called "valence" effect varying approximately linearly with impurity concentration. MK apply their theory to data existing at that time and show that an appropriate value of $\langle a^2\rangle$ for tin is ≈0.02. More recently, Clem[6] has theoretically treated the effects of $\langle a^2\rangle$ on portions of the superconducting-critical-field curve. His results indicate that one expects the shape of the reduced critical-field curve to be a function of impurity concentration if the host material has a nonvanishing $\langle a^2\rangle$. The ratio T_c/H_0 is also expected to change with doping since $\langle a^2\rangle$, whose influence is impaired by doping, affects each quantity in the ratio to a different degree. This is equivalent to saying that the two so-called "similarity conditions"[3,7] are expected to fail when a metal like tin is doped.

These theories are formulated in terms of the electronic mean free path which is inversely proportional to the residual resistivity (ρ_0) of the normal metal in very dilute alloy systems. However, the resistivity of a metal such as tin is generally anisotropic, while quantities like T_c are not. The anisotropy of the resistivity must properly be accounted for if ρ_0 is to be used as a meaningful plotting parameter.

There is another interesting feature of dilute alloys of tin with cadmium and indium. Lee and Raynor[8] have

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[1] J. E. Gueths, M. A. Mitchell, and C. A. Reynolds, Bull. Am. Phys. Soc. **11**, 74 (1966).

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

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

[4] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).

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

[6] J. R. Clem, Ph.D. thesis, University of Illinois, 1965 (unpublished); Bull. Am. Phys. Soc. **11**, 89 (1966).

[7] A. M. Toxen, Phys. Rev. Letters **15**, 463 (1965).

[8] J. A. Lee and G. V. Raynor, Proc. Phys. Soc. (London) **B67**, 737 (1954).

reported anomalies in plots of lattice spacing and percentage of filled sites versus impurity concentration for Cd in Sn (at ~0.29% cadmium) and In in Sn (at ~2% indium). The cause for these effects is not precisely known, but it is almost certainly rooted in some sort of Fermi-surface–Brillion-zone boundary interaction and the change of their relative positions as the Fermi radius is altered by a change in electron/atom ratio. Ridley,[9] upon re-examination of these tin systems, found no evidence for the anomalies reported by Lee and Raynor. In an investigation of the superconducting properties of the In-Sn system,[10] anomalous behavior was not noted at ~2% indium. Recent investigations[11] of the impurity-dependent superconducting properties of other alloy systems having lattice-spacing anomalies have revealed many interesting effects which are presumably due to electronic structure alterations with composition. We chose cadmium as an impurity type in this work because the suspected anomaly occurs at rather low impurity concentrations, and single crystals with up to ~1% cadmium impurity could be prepared.

The purpose of this paper is to report experiments performed to gain information about:

(1) The anisotropic electrical resistivity of tin. We are interested in the anisotropy of the temperature-dependent resistivity as well as of the residual resistivity. Deviations from Matthiessen's rule are investigated.

(2) The variation of the superconducting critical-field curve and the associated parameters $[T_c, H_0, (dH_c/dT)_{T=T_c}]$ with cadmium impurity concentration. We wish to test the theoretical predictions of MK and Clem which pertain to the variation of these parameters as the effectiveness of $\langle a^2 \rangle$ is impaired with increased doping.

(3) The suspected lattice-spacing anomaly. In particular, is there any evidence for this as reflected in anomalous behavior in a plot of T_c versus composition at 0.29% cadmium, or in a plot of ρ_{01} versus composition, which should suggest the occurrence of vacant sites?

EXPERIMENTAL DETAILS

Approximately 60 crystals were prepared using a variation of the Bridgman method. 99.999% pure tin and cadmium were weighed in the desired quantities and melted together under a vacuum to form a slug of the approximate Cd concentration desired. The melt was shaken periodically to obtain a more uniform impurity concentration in the slug. Portions of the slug were then etched in 4*N* HCl, remelted in an oven and poured, under vacuum, into an evacuated section of precision-bore Pyrex tubing[12] that had been previously coated with a thin layer of a 1:1 solution of CCl_4-mineral oil in a manner described by Bridgman.[13] The tubing, which served as a mold, and the molten metal were then slowly lowered out of the oven by a motor-driven mechanism. The lowering rate was 0.5 mm/min, as suggested by the crystal-preparation experiments of Goss.[14]

The specimens were extracted from the mold by gently removing small sections of the glass tubing from each end of the specimen, plunging the specimen and mold into liquid N_2, and gently pulling the specimen from one end. All specimens were subsequently annealed for 72 h at ~200°C. A subsequent brief etching in 4*N* HCl made visual examination of the crystal structure possible. The first few cm of the specimen to crystallize generally consisted of many small crystallites, but in most cases the main portion of the specimen consisted of one or two large single crystals varying from 2 to 15 cm in length. Sections of single crystal were cut from the specimen and the angle θ between the tetrad axis of the tin crystal and the cylindrical axis of the specimen was determined from data taken with an optical goniometer constructed along the lines of one discussed by Chalmers.[15] Calculations of possible errors from the geometrical uncertainties of the goniometer arrangement indicated that the error in θ was less than $\pm 1°$.

Resistance determinations were made with the potentiometric method employing a microvolt potentiometer for voltage determinations and an integrating voltmeter with five-significant-figure readout continuously monitoring the voltage drop across a 1-Ω standard resistor for current determinations. The current passing through the crystals was varied from 50 to 300 mA, and the direction of current flow subsequently reversed. The average slope of the two *V*-versus-*I* lines was taken to be the resistance. While a set of *V*-versus-*I* data on a particular crystal was being obtained, all switching was done on the gold-plated switches in the potentiometer, thus minimizing the effects of nonreproducible error voltages that occur during normal switching procedures. The voltage and current lead connections to the crystal were by mechanical contact, so as to eliminate errors arising from polycrystalline portions of the specimen being formed around solder connections. Measurements of the cross-sectional area of the crystals indicated that it was generally that of the mold in which the specimens were cast,[12] and this value was subsequently used, except on rare occasions, when a crystal was etched for an extraordinarily long time. Length determinations were made either with a traveling microscope or vernier

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[9] N. Ridley, J. Inst. Metals **92**, 123 (1963–4).

[10] S. L. Wipf, Cryogenics **3**, 225 (1963).

[11] M. F. Merriam, Rev. Mod. Phys. **36**, 152 (1964); M. F. Merriam, M. A. Jensen, and B. R. Coles, Phys. Rev. **130**, 1719 (1963); M. F. Merriam, Phys. Letters **17**, 16 (1965); Phys. Rev. **144**, 300 (1966).

[12] Supplied by Wilmad Glass Company, Buena, New Jersey. Supplier specifications; i.d. = 2.000±0.005 mm.

[13] P. W. Bridgman, Proc. Am. Acad. Sci. **60**, 305 (1925).

[14] A. J. Goss, Proc. Phys. Soc. (London) **66**, 65 (1953).

[15] B. Chalmers, Proc. Phys. Soc. (London) **47**, 733 (1935).

calipers. Errors in the resistivity resulting from geometrical uncertainties were felt not to exceed 0.7%. Errors resulting from uncertainties in the resistance determination were not larger than 0.1% for $\rho > 1 \mu\Omega$ cm and 1% for $1 > \rho > 10^{-2} \mu\Omega$ cm. Superconducting critical-field determinations were made using an ac method similar to that described by Reynolds *et al.*[16] Six specimens, each surrounded by a detection coil of ~20 000 turns of No. 40 Teflon-coated copper wire, were arranged in a circle ~3 cm in diam and suspended in a Lucite holder in a helium Dewar. A seventh empty coil was located at the center of the circular arrangement. A solenoid consisting of two sets of windings, one for the dc field, the other for the ac field, was located in the surrounding nitrogen Dewar. A calibrated germanium thermometer was fixed ~2 cm below the specimens in the helium bath.

The dc field (H_{dc}) could be varied by means of a rheostat on the magnet current supply. The ac field (H_{ac}) was fixed at a frequency of 24 cps and an amplitude of ~0.15 Oe. The emf generated by each detection coil in opposition with the empty central coil was filtered and amplified and the time-averaged 24-cps $|\text{emf}|$ detected on a frequency-sensitive null detector. The temperature in the vicinity of the specimens was determined with the germanium thermometer. Corrections were made for small calibration shifts of the order of several millidegrees Kelvin from run to run. Absolute temperature determinations were periodically made using a mercury or oil manometer and the 1958 He vapor-pressure scale of temperatures along with appropriate pressure head corrections for temperatures above the λ point.

The experimental procedure was to lower the temperature of the helium bath to some $T < T_c$ and stabilize it with a Walker-type[17] regulator. Looking at the emf generated in the coil surrounding each specimen in turn, H_{dc} was varied in increasing and decreasing field until the value at which the time averaged 24 cps $|\text{emf}|$ was maximized. This corresponds to the value of H_{dc} at which the amount of flux entering and leaving the specimen in each cycle of H_{ac} is a maximum. This value of H_{dc} was taken to be H_c.

A specimen containing ~0.01% Cd was measured during each run and served as a standard. Absolute curves for the critical field for this specimen were obtained from the collective data from all runs. The differences in H_c from the standard specimen were plotted and extrapolated to $H_c = 0$ and $T = 0$ to determine differences in T_c and H_0, respectively. The differences in T_c were determined from linear extrapolations of data with $H_c < 30$ Oe. Differences in H_0 were determined from nonlinear extrapolations of data with $1 < T < 1.5$°K. The quality of the data is illustrated along with typical extrapolations of the latter type shown in Fig. 1. The magnetic field H is given in terms of solenoid current, and we follow this convention throughout this work. We are concerned with dimensionless quantities ($h = H/H_0$) and small fractional changes to compare our results to theory. For these purposes, the absolute value of H ($H/I \sim 0.34$ Oe/mA) is not necessary. Corrections were applied to the data for observable bath drifts and the component of the earth's magnetic field directed along the solenoid axis. Typical transitions were 1 or 2 mdeg wide, and the rare instances when they were wider will be discussed later. The differences in T_c as defined above were reproducible to about $\pm\frac{1}{2}$ mdeg. Extremely accurate absolute values for the T_c's are not needed for the analysis presented, but our value for T_c of pure tin with an estimated error is 3.724 ± 0.002°K. Differences in H_0 were felt to be accurate to ±1 mA, or ±0.3 Oe.

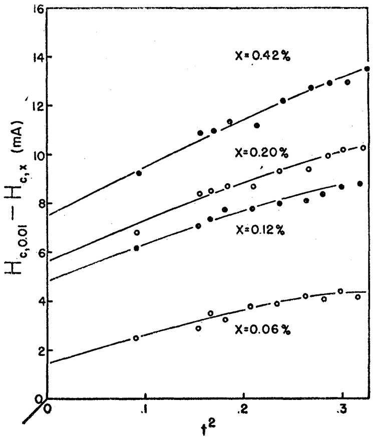

FIG. 1. The difference in critical-field curves as a function of impurity content in the limit of the lowest temperatures attained. The extrapolation to $t^2 = 0$ is felt to be accurate to ±1 mA (±0.3 Oe). (H is given in terms of solenoid current I; $H/I \approx 0.34$ Oe/mA.)

Effects rooted in the kinetics of the phase transition, trapped flux, and, on occasion, supercooling, were noted in our experiments. The choice of $H_{ac} = 0.15$ Oe was made subsequent to a systematic investigation of the dependence of the signal shape, size, and location on H_{ac}. From examination of these dependences, we concluded that lowering H_{ac} further did not change the location of the signal maximum (which we denote as H_c) and the shape of the signal. No evidence for negative interphase surface energy such as that observed by Wipf[10] for indium in tin concentrations greater than ~2% was found in the range of cadmium impurity investigated (<1%).

Cadmium impurity concentrations x given are those obtained from analysis performed by Jarrell-Ash Company.[18] In most cases, analysis for impurity content was performed on two end sections of the same crystal, and the mean value is the one used. Impurity concentration gradients were small, and evidence was obtained from ρ_0-versus-x data that they were approximately linear over the small lengths of crystal (~5 cm) used

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

[17] E. J. Walker, Rev. Sci. Instr. **30**, 834 (1959).

[18] 590 Lincoln Street, Waltham, Massachusetts.

in this work. $\delta x/x$ was typically 0.03 per cm of crystal length.

In the preliminary stages of the investigation, some measurements were directed toward determining the state of our crystals as reflected in the resistivity at 4.2°K, a temperature at which the presence of point imperfections, such as vacancies and impurity sites, and perhaps defects such as slip planes, are marked by an increase in resistivity. The resistivity at 4.2°K for the pure tin crystals was $\leqslant 10^{-3}\mu\Omega$ cm, a value to be expected for tin of the purity used in this work. Crystals prepared in a glass mold with and without the CCl_4–mineral-oil film were both found to have resistivities of this order. It is concluded that the influence of possible stray contaminants on the low-temperature resistivities is negligible.

Resistivity determinations made on two crystals before and after extraction from the glass mold were, within experimental error, identical. This, along with the results of careful visual examinations of the crystals which revealed no macroscopic defects (such as slip planes), indicates that the crystals were not noticeably damaged in the extraction process. The resistivity convention used here is as follows: ρ_T = total resistivity at temperature T, $\rho(T)$ = temperature-dependent part of the resistivity, and ρ_0 = residual resistivity = ρ_T at $T=0$.

The $\rho_{4.2}$ determinations are listed in this work as ρ_0. Little error is expected from this approximation for $x \geqslant 0.01\%$ Cd.[19] Resistivity determinations made on two crystals ($x \approx 0.01\%$) before and after the 72-h anneal indicated that ρ_0 had increased by $\sim 5\%$. This is interpreted in terms of a small radial impurity-concentration gradient that decreases upon anneal. Similar effects have previously been noted.[20] To summarize, we feel confident that the crystals used in this work are reasonably homogeneous and free from macroscopic defects and unwanted impurities.

RESULTS AND DISCUSSION

The anisotropic properties of the electrical resistivity as well as absolute values for $\rho(T)$, were determined by measuring nine pure tin crystals of varying orientations. The resistivity of these specimens at 4.2°K was $\leqslant 0.001$ $\mu\Omega$ cm. Resistivity determinations were made at 373, 273, and 77°K. The results of these measurements are plotted in Fig. 2. θ, as previously defined, is the angle between the tetrad axis and the direction of current flow. Best straight lines were determined by a least-squares fit to an equation of the form

$$\rho(T) = \rho_\perp(T)[1+\alpha(T)\cos^2\theta]. \qquad (1)$$

TABLE I. The anisotropic temperature-dependent resistivity of pure tin.

T(°K)	$\rho_\perp(T)$ ($\mu\Omega$ cm)	$\alpha(T)$	Standard deviation of $\rho(T)$ ($\mu\Omega$ cm)
373	13.25 ±0.05	0.53 ±0.01	0.11
273	9.05 ±0.03	0.555±0.009	0.06
77	1.772±0.006	0.684±0.010	0.01

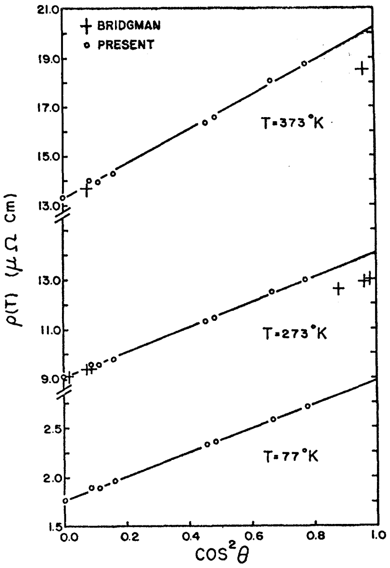

FIG. 2. Plot of the specific resistance of pure tin exhibiting the anisotropy of $\rho(T)$ at various temperatures for specimens having negligible impurity resistances. The +'s are the data of Bridgman (Refs. 13 and 22).

The results of these calculations are given in Table I. The uncertainties in $\rho_\perp(T)$ and the anisotropy $\alpha(T)$ are obtained from standard deviations in the slope and intercept of the straight-line fit.[21] The standard deviation in $\rho(T)$ is also tabulated. It should be noted that the standard deviation in $\rho(T)$ divided by $\rho_\perp(T)$ is approximately constant, which suggests that the main sources of error in $\rho(T)$ are geometrical and/or in the θ determination.

We have also plotted the results of Bridgman[13,22] in Fig. 2. Although we agree very well with his determinations in the perpendicular direction, our results in the parallel direction are $\sim 8\%$ higher. The reason for the discrepancy is not understood, although the determination of the orientation for crystals of low θ is certainly more difficult, and a misinterpretation of the optical reflection pattern could easily lead to an error this size. We double-checked the reflection data and calculations used to obtain the orientations for our crystals with low θ values to insure that errors of this type were not made. If low-angle grain boundaries were present in Bridgman's samples, this could lower the value of the specific resistance, but one would hardly expect it to be so systematic.

The anomaly in the lattice-spacing parameters ob-

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[19] The temperature-dependent resistivity of pure tin at 4.2°K is $\sim 10^{-4}\mu\Omega$ cm (Ref. 24).

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

[21] D. C. Baird, *Experimentation: An Introduction to Measurement Theory and Experiment Design* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), Chap. 6.

[22] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **68**, 95 (1933).

served by Lee and Raynor[8] could possibly mark a change in the electronic structure of this dilute alloy system. Thus, it was felt necessary to determine the anisotropy of ρ_0 both above and below the impurity concentration at which the anomaly occurred ($\sim 0.29\%$ Cd). For $x>0.29\%$, it was felt that the analytical results of Jarrell-Ash Company would give a reasonably accurate determination of x. For small x, however, the analysis becomes more difficult and uncertain. The results of Goss[14] suggest that small amounts of Cd might precipitate on the surface layer of the crystal, causing an overestimate of the impurity concentration through the main body of the crystal. For these reasons, we employed another technique in this dilute region.

Presumably, the superconducting transition temperature (the extrapolation of the H_c data as $H_c \rightarrow 0$) is isotropic (i.e., it depends only on the amount of impurity present in the specimen and various properties of the host but not on field direction). In the dilute region, barring any anomalous electronic behavior, we expect, however, ρ_0 to be a function of θ and x. ρ_0 in any specific direction, say $\rho_{0\perp}$, should be proportional to x. Thus we expect that $T_c=T_c(x)$, $\rho_0=\rho_0(\theta,x)$, and $\rho_{0\perp}\propto x$, so that $T_c=T_c(\rho_{0\perp})$. By measuring the transition temperatures (T_c) as well as $\rho_0(\theta,x)$ of many single crystals, we expect to be able to infer the θ dependence of $\rho_0(\theta)$ by minimizing the scatter in the data of a plot of $\rho_0(\theta)$ versus T_c to a particular value of the anisotropy. Since most of our impure crystals had $\theta \approx 90°$, we chose to refer all crystals to this direction ($\rho_{0\perp}$). We profit from the fact that in the very dilute region, T_c is very sensitive to x, in approximately a linear fashion, for dilute alloy systems with tin as a host.[2]

A set of 20 slightly impure specimens ($0.02\%<x<0.12\%$) were selected and measured. Their pertinent properties are given in Table II. Since we must treat the dependence of T_c on $\rho_{0\perp}$ in this region as unknown, we choose to expand T_c in terms of $\rho_{0\perp}$:

$$T_c=A+B\rho_{0\perp}+C\rho_{0\perp}^2, \tag{2}$$

where

$$\rho_{0\perp}=\rho_0/(1+\alpha\cos^2\theta). \tag{3}$$

Here α is the anisotropy of ρ_0. α was then varied from 0.0 to 1.0 in increments of 0.1, and the data were fitted by the method of least squares to Eq. (2). The standard deviation of the data (STD) was taken to be a measure of the appropriateness of the choice of α. The value of α for which STD was minimized was taken to be the proper one. We tabulate the results of the analysis in Table III. A, B, and C are the determined values of the coefficients in Eq. (2) for the choice of α. Although the minimum in STD is perhaps not very pronounced, a minimum certainly exists in this range. This analysis then leads us to conclude that

$$\rho_0=\rho_{0\perp}(1+0.6\cos^2\theta), \tag{4}$$

for $x<0.15\%$.

The anisotropy of ρ_0 in the more impure region ($x>0.29\%$) was determined by more direct means. Four crystals of widely differing orientations in the impurity range $0.3\%<x<0.4\%$ were used. We expect that in this limited range of impurity, $\rho_{0\perp}\propto x$, so that

$$\rho_0/x=(\rho_{0\perp}/x)(1+\alpha\cos^2\theta)=\mathrm{const}(1+\alpha\cos^2\theta). \tag{5}$$

Thus a value for α can be derived from a plot of ρ_0/x versus $\cos^2\theta$. Figure 3 is such a plot, and the value of α obtained is again 0.6.

Both of the determinations of the anisotropy of ρ_0 rest heavily on several low-θ crystals, but there is no obvious reason to suspect that the values (T_c, ρ_0, x) for these crystals are in error by a larger amount than those of higher θ. Although the error in both of these determinations is rather large ($\alpha=0.6\pm0.1$) the agreement of both determinations is evidence that the anisotropy of ρ_0 is the same in both regions and is approximately 0.6. This is to be compared with the value of 0.14 determined for the system[23] In-in-Sn and

TABLE II. Orientations, 4.2°K electrical resistivities, and superconducting transition temperatures of some slightly impure tin crystals.

Sample No.	$\cos^2\theta$	$\rho_0(\mu\Omega\text{ cm})$	$T_c(°\text{K})$
104	0.022	0.0545	3.7054
204	0.112	0.0435	3.7073
304	0.059	0.0575	3.7035
404	0.043	0.0695	3.7011
504	0.036	0.086	3.6980
604	0.001	0.073	3.6996
704	0.036	0.0545	3.7047
804	0.003	0.081	3.6986
904	0.015	0.060	3.7059
1004	0.250	0.0705	3.7011
1104	0.128	0.065	3.7013
1204	0.165	0.068	3.7025
1304	0.185	0.062	3.7045
1404	0.003	0.061	3.7052
10-5	0.076	0.040	3.7081
10-6	0.001	0.087	3.6960
10-7	0.748	0.090	3.7035
4-9	0.371	0.042	3.7090
10-4	0.101	0.149	3.6886
9-8	0.152	0.173	3.6845

TABLE III. Anisotropy determination in low-impurity range.

α	A(°K)	B(°K$\mu\Omega^{-1}$ cm^{-1})	C(°K$\mu\Omega^{-2}$ cm^{-2})	STD (10^{-3}°K)
0.0	3.718	−0.260	0.402	1.76
0.1	3.719	−0.277	0.464	1.56
0.2	3.719	−0.286	0.497	1.39
0.3	3.719	−0.290	0.518	1.27
0.4	3.719	−0.294	0.525	1.19
0.5	3.719	−0.293	0.495	1.19
0.6	3.719	−0.289	0.480	1.15
0.7	3.718	−0.281	0.434	1.16
0.8	3.718	−0.270	0.393	1.22
0.9	3.717	−0.258	0.332	1.27
1.0	3.717	−0.246	0.250	1.32

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[23] T. E. Faber, Proc. Roy. Soc. (London) **A214**, 392 (1952); **219**, 75 (1953); **223**, 174 (1954).

0.30 for an unknown impurity type in Sn.[24] The suggestion that the anisotropy of ρ_0 is dependent upon impurity type is an obvious one. Equally obvious is the need for a systematic investigation to shed further light on the dependence, if it exists.

We have assumed thus far that $\rho_{0\perp} \propto x$ for those limited regions of x that we have considered. In Fig. 4 we plot $\rho_{0\perp}$ versus x for the full range of impurity concentration. We have plotted the very dilute region separately to properly display the data. The results of Lynton *et al.*[2] have been introduced in the following way: They measured

$$\rho_r = \frac{R_0}{(R_{273}-R_0)} = \frac{\rho_0}{(\rho_{273}-\rho_0)}.$$

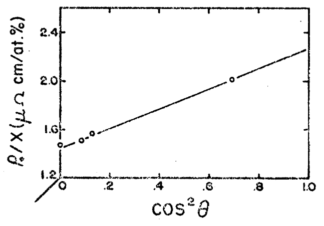
From our anisotropy values in Eq. (4) and Table I,

$$\rho_r = \left[\frac{1+0.6\cos^2\theta}{1+0.55\cos^2\theta}\right]\frac{\rho_{0\perp}}{\rho_\perp(273)}, \qquad (6)$$

where we have ignored possible deviations to Matthiessen's rule. For any sample of unknown orientation or for a polycrystalline aggregate, we assume it possible to define an "effective" value for θ. To a first approximation, the θ dependence cancels, and, using our value of $\rho_\perp(273)$ for pure tin, we find $\rho_{0\perp} \approx 9\times10^{-6}\rho_r$. In Fig. 4, we see that the data of Lynton *et al.* systematically appears to exhibit $\rho_{0\perp}/x$ values that are lower than our results would indicate. This is not unreasonable, as the x that they report is the impurity concentration added to the melt, which, because of losses on the specimen surface and on grain boundaries, might be expected to be too large.

If the vacancies observed by Lee and Raynor ($\sim$0.3% vacancies in the case of indium impurity in tin) are present in our crystals within a certain range of x, they would contribute to $\rho_{0\perp}$ but not to x, causing a systematic deviation from the straight line. The contribution to $\rho_{0\perp}$ from vacancies can be estimated[25] and is expected to be $\sim 1\mu\Omega$ cm/%. We see no evidence in Fig. 4 that vacancies have occurred. There is also no evidence of a discontinuity in $\rho_{0\perp}$ versus x sometimes seen in a Fermi-surface–Brillion-zone boundary crossing.[11] Also, the slopes of the lines are identical (1.39 $\mu\Omega$ cm/at.%) in the dilute and more concentrated regions. We then suppose that the only significant contribution to $\rho_{0\perp}$ is that of x, and we will use $\rho_{0\perp}$ as a measure of x in the subsequent discussions.

FIG. 3. The determination of the anisotropy of ρ_0 for $x \approx 0.35\%$ Cd. ρ_0/x is plotted versus $\cos^2\theta$ to account for variations in the (approximately) 0.35% Cd impurity.



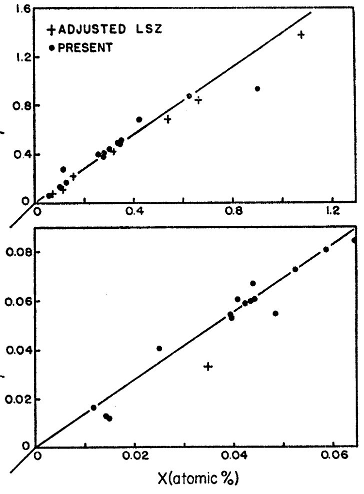


FIG. 4. The residual resistivity in the perpendicular direction as a function of impurity concentration. The adjusted (see text) data of Lynton *et al.* are the +'s. The very dilute region is shown on the bottom portion of the figure to better illustrate the data. The two lines drawn have the samel sopes.

The deviation from Matthiessen's rule is defined as

$$\Delta(T) = (\rho_T - \rho_0)_{\text{impure}} - \rho(T)_{\text{pure}}, \qquad (7)$$

where $\rho(T)_{\text{pure}}$ is taken from Fig. 2 using the appropriate temperature and the value of θ of the impure specimen. The dependence of $\Delta(T)$ on $\rho_{0\perp}$ can be seen in Fig. 5. We find that Δ is, within experimental uncertainty, independent of T, and linear in $\rho_{0\perp}$ ($\Delta = 0.16\,\rho_{0\perp}$). This is to be compared to the value reported by Pippard[26] ($\Delta = 0.12\rho_0$) for the system In-in-Sn at $T = 273$°K. The size of Δ at $T = 77$°K is certainly not negligible, since $\Delta(77)/\rho_\perp(77) \approx 9\%$. There appears to be no notable change in Δ at $\rho_{0\perp} \approx 0.4\mu\Omega$ cm ($x \approx 0.3\%$ Cd), which we might expect if a sudden electronic alteration had occurred. It should be noted that Δ appears to be roughly independent of θ and, because

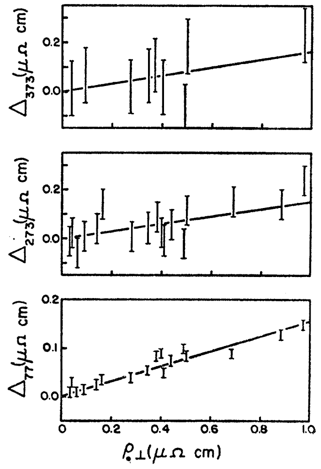


FIG. 5. Deviations from Matthiessen's rule $[\Delta_{273} = \rho(273)_{\text{impure}} - \rho(273)_{\text{pure}}]$ as a function of $\rho_{0\perp}$ at three temperatures. Note that the scale is changed in the lower figure. The three lines have the same slopes.

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

[25] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 344.

[26] A. B. Pippard, Proc. Roy. Soc. (London) **A248**, 13 (1955).

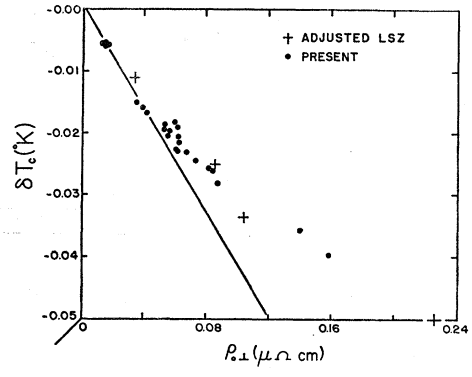

FIG. 6. Change in transition temperature [$\delta T_c = T_c$(impure) $-T_c$(pure)] with increasing $\rho_{0\perp}$ in the dilute region. The line drawn in the very dilute range indicates a seemingly linear portion of the data. The +'s are the data of Lynton *et al.* The data between $\rho_{0\perp}=0.03$ and 0.16 were used to determine the anisotropy of ρ_0 in the dilute region.

$\Delta > 0$, this means that the anisotropy of $\rho(T)$ is decreasing slightly as impurities are added to the crystal.

The uncertainties represented by the bars in Fig. 5 are twice the statistical errors in the pure-tin data presented in Table I. They are not the limits of error of the measurement. The nine points used to obtain the data in Table I can hardly be considered a large statistical sample, but measurements on 28 other pure and slightly impure ($x<0.04\%$) specimens at $T=273$°K exhibited a standard deviation of 0.06 $\mu\Omega$ cm about the 273°K line in Fig. 2. This is the same as the standard deviation of $\rho(T)$ in Table I. Thus we feel justified in using this value as a probable error in any $\rho(T)$ determination.

The linear dependence of Δ on $\rho_{0\perp}$ and its independence of T would indicate that it is to be understood in terms of the scattering of electrons originating from two zones of the Fermi surface, as discussed by Jones.[27] The criterion that $\rho(T) \gg \rho_0$ is hardly satisfied for the case when $T=77$°K, however, since ρ_0 and $\rho(T)$ are comparable. The size of $\Delta(77)$ is also larger than one might expect, but it is not without precedent, since other experiments[28] have resulted in values for $\Delta/\rho(T)$ that are of a similar order of magnitude when dilute alloys with $\sim 1\%$ impurity are measured at temperatures such that $\rho_0 \approx \rho(T)$.

We see the dependence of T_c on $\rho_{0\perp}$ in the very dilute region in Fig. 6. The behavior, generally speaking, is that T_c is strongly depressed initially with increasing $\rho_{0\perp}$ in approximately a linear fashion, and then less rapidly as $\rho_{0\perp}$ increases further. The data indicate that initially, $\delta T_c/\rho_{0\perp} = -0.41$°K/$\mu\Omega$ cm. We note the excellent agreement with the several adjusted data points of Lynton *et al.*, although the initial linear portion of the δT_c-versus-$\rho_{0\perp}$ data appears to be steeper in slope and shorter in extent than the previous data would indicate.

In Fig. 7, we show δT_c versus $\rho_{0\perp}$ for the complete range of impurity in this work. There appears to be an anomalous region in this curve at $\rho_{0\perp} \approx 0.4$. This impurity concentration ($x \approx 0.29\%$) is the concentration at which a lattice-spacing anomaly was reported.[8] We note also that this region is uniquely marked by the presence of apparently very wide transitions. The general features of a Fermi-surface–Brillion-zone boundary interaction are just these, namely, a discontinuous change in $\delta T_c/\delta x$, and double transitions corresponding to different parts of the specimen having different electronic structure because of inhomogeneties in x.[11] A double transition would appear, in our methods of measurement, as a very broad signal with possibly two peaks or at least an extended, flat peak. Admittedly, the effect is annoyingly small, but the general behavior of the data makes it difficult to reach any conclusion other than that some sort of anomalous behavior of this type has occurred.

According to the theory of MK, the variation of T_c with $\rho_{0\perp}$ can be employed to obtain an estimate of $\langle a^2 \rangle$. The change in T_c with doping is expected to be described by

$$\delta T_c(\chi)/\chi = K^i + \langle a^2 \rangle T_c [I_c(\chi)/\chi], \qquad (8)$$

where χ is a quantity inversely proportional to the electronic mean free path, and $\langle a^2 \rangle$ and T_c are properties of the host metal. $I_c(\chi)$ is a function which they calculate and can be extracted from their Fig. 4. In the region $1<\chi<100$, they note the useful approximation

$$\delta T_c(\chi)/\chi = [K^i - 0.36 \langle a^2 \rangle T_c] + 0.78 \langle a^2 \rangle T_c \ln\chi. \quad (9)$$

The residual resistivity ratio ρ_r, like χ, is inversely proportional to the electronic mean free path, and MK rewrite Eq. (9) in terms of ρ_r using the relationship (for tin) $\chi=135\,\rho_r$. We want to put Eq. (9) in terms of $\rho_{0\perp}$, and this is most simply done by using our result that $\rho_{0\perp}=9\rho_r \mu\Omega$ cm, which means that $\chi=15\,\rho_{0\perp}$, if we

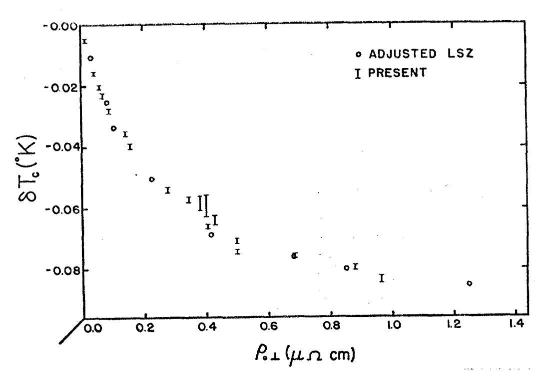

FIG. 7. Change in transition temperature with increasing $\rho_{0\perp}$ for the full range of impurity concentration measured. The widths of the bars are a measure of the widths of the transitions. For a more complete description of the data for $\rho_{0\perp}<0.2$, see Fig. 6. The region at $\rho_{0\perp} \approx 0.4$ ($x \approx 0.3\%$ Cd) appears to be slightly anomalous.

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[27] H. Jones, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, Chap. 3.

[28] D. H. Damon and P. G. Klemens, Phys. Rev. **138**, A1390 (1965); P. Alley and B. Serin, *ibid.* **116**, 334 (1959).

drop units and work in the $\mu\Omega$ cm system. Equation (9) then becomes

$$\delta T_c(\rho_{0\perp})/\rho_{0\perp}=15.0[K^i-0.15\langle a^2\rangle T_c]+1.17\langle a^2\rangle T_c \ln\rho_{0\perp} \qquad (10)$$

for intermediate $\rho_{0\perp}$ values.

In Fig. 8, we plot $\delta T_c/\rho_{0\perp}$ versus $\rho_{0\perp}$. From the slope of the straight line drawn through the data for intermediate concentrations and Eq. (10), we obtain

$$1.17\langle a^2\rangle T_c=0.102. \qquad (11)$$

Inserting $T_c=3.72$, we obtain $\langle a^2\rangle=0.023$. The appropriate value for K^i is similarly obtained and is given by $15K^i=0.14$. We then expect that the appropriate exact solution might be obtained by substituting $\chi=15\ \rho_{0\perp}$ and our determined values of K^i and $\langle a^2\rangle T_c$ into Eq. (8), obtaining

$$\delta T_c/\rho_{0\perp}=0.14+(3.72)(0.023)I_c(\rho_{0\perp})/\rho_{0\perp}, \qquad (12)$$

where $I_c(\chi)$, hence $I_c(\rho_{0\perp})$ is given by MK. The smooth dashed curve in Fig. 8 is a plot of Eq. (12).

It is seen that the exact solution does approximate the data in Fig. 8, and little is to be gained by adjusting the parameters K^i, $\langle a^2\rangle$, and $\chi/\rho_{0\perp}$ any further. It is noted, however, that a better smooth curve could be drawn through the data than the theoretical expression derived by MK, but the possibility of an electronic transition previously discussed at $\rho_{0\perp}\approx 0.4$ confuses the issue. The gross features of the data do appear to indicate the essential validity of their expression.

We now turn to the critical-field data. Shown in Fig. 9 are H_0 and $(dH_c/dT)_{T=T_c}$ as a function of $\rho_{0\perp}$. Both quantities exhibit the general behavior of the T_c-versus-$\rho_{0\perp}$ data. The rate of change is initially very large with increasing $\rho_{0\perp}$ and becomes smaller as $\rho_{0\perp}$ increases through the region in which the electronic mean free path is approximately equal to the coherence distance ($\rho_{0\perp}\approx 0.4$).

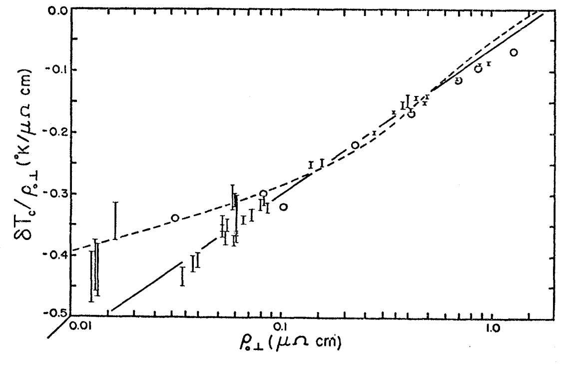

FIG. 8. $\delta T_c/\rho_{0\perp}$ versus $\rho_{0\perp}$ for the full range of impurity concentration. The O's are data of Lynton *et al.* The stright line through the data for intermediate values of $\rho_{0\perp}$ is used to obtain $\langle a^2\rangle$. The dotted line represents the more exact equation in MK's theory.

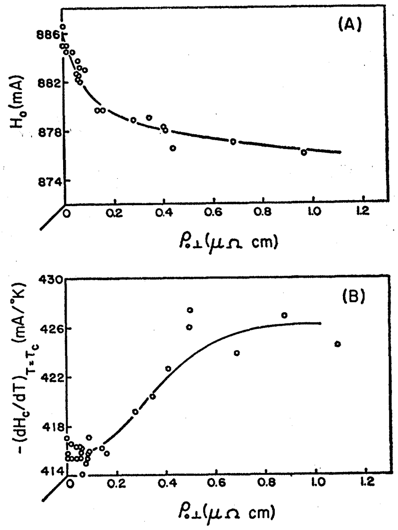

FIG. 9. (A) is a plot of the critical field at absolute zero (H_0) versus $\rho_{0\perp}$. (B) is a plot of the initial slope of the critical-field curves as a function of $\rho_{0\perp}$. The solid lines are smooth curves drawn through the data. (H is in terms of solenoid current I; $H/I\approx 0.34$ Oe/mA).

In Fig. 10 we test the validity of the so-called "similarity conditions." Both of the conditions are found to be violated by the specimens in this impurity system. T_c/H_0 is obviously not a constant for these specimens. The quantity T_c^2/H_0^2 changes rapidly as $\rho_{0\perp}$ is first increased and falls less rapidly as $\rho_{0\perp}$ is increased further. The initial slope of the reduced critical field curve $(dh/dt)_{t=1}$ behaves in a similar fashion. Previous investigations[2,3] of the influence of impurities on the critical field curves had suggested that one or both of the similarity conditions were valid.

In the treatment of the effects of $\langle a^2\rangle$ on the superconducting critical field curve, Clem[6] arrives at two equations that are pertinent to the discussion of the data in Fig. 10. They are:

$$\gamma T_c^2/H_0^2=[\gamma(0)T_c^2(0)/H_0^2(0)]\times[1+2\langle a^2\rangle(\lambda-1)] \qquad (13)$$

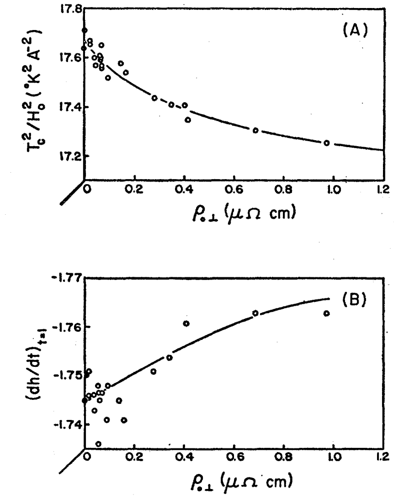

FIG. 10. (A) is a plot of T_c^2/H_0^2 and (B) a plot of the initial slope of the reduced critical-field curve as a function of $\rho_{0\perp}$. These curves demonstrate the failure of the two similarity conditions. The solid lines are only intended as visual aids.

and

$$h(t) = 1.7367(1-\langle a^2\rangle)(1-t) \times[1-(0.2730-0.908\langle a^2\rangle)(1-t) - (0.0949-0.037\langle a^2\rangle)(1-t^2)+\cdots] \quad (14)$$

for $t^2 \geqslant 0.7$. Here the argument (0) denotes zero impurity concentration and γ is the coefficient in the normal-state electronic specific heat. λ in Eq. (13) is a function of impurity concentration and is expected to be roughly similar to $I_c(X)$ in MK's theory. The numerical restrictions on λ are that λ be 1 in the absence of impurities and that it approach 0 as the host material becomes "infinitely dirty." We introduce the impurity dependence of the effectiveness of $\langle a^2\rangle$ on $h(t)$ by substituting $\langle a^2\rangle\lambda$ for $\langle a^2\rangle$ in Eq. (14). Then $(dh/dt)_{t=1}$ is given by

$$(dh/dt)_{t=1} = -1.7367(1-\langle a^2\rangle\lambda) \approx[(dh/dt)_{t=1}]_{(0)}(1-(\lambda-1)\langle a^2\rangle). \quad (15)$$

We wish to see if the variation of T_c^2/H_0^2 and $(dh/dt)_{t=1}$ with impurity concentration (in Fig. 10) is consistent with Eqs. (13) and (15). However, our ignorance of the proper way to fit theory to the data is considerably greater than in the case of the variation of T_c with $\rho_{0\perp}$. Besides the uncertainty of the constant relating X and $\rho_{0\perp}$, there are two other sources of ignorance.

We do not know the exact relation between λ and $I_c(X)$. If we assume that the two are exactly similar, then we can reasonably write[29]

$$\lambda(\rho_{0\perp}) = [(I_c(\rho_{0\perp})+4.0)/4.0], \quad (16)$$

where 4.0 is the limiting value of $I_c(\rho_{0\perp})$ for tin as $\rho_{0\perp}$ approaches infinity. In essence, we are assuming that the effectiveness of $\langle a^2\rangle$ for temperatures other than T_c is regulated by a function exactly similar to one derived in a calculation specialized to the critical temperature. This assumption is almost certainly not valid, but we expect it to be true as an approximation.

We are also ignorant of any so-called "valence" effects. They presumably cancel to a degree in the ratios T_c/H_0 and $(dH_c/dT)_{T=T_c}$ but the cancellation may not be complete. Information on other dilute alloy systems of tin is needed to realistically account for this effect.

For these reasons, we will deal with only the data in the range of very small impurity concentrations in which "valence" effects should be small. We will consider the fractional change in T_c^2/H_0^2 and $(dh/di)_{t=1}$ as doping decreases the electronic mean free path to a value approximately that of the superconducting coherence distance. In this region [$\rho_{0\perp}$ going from 0 to $\sim$0.4 and λ, which is defined by Eq. (10), going from 1.0 to 0.67], we expect the "anisotropy" effects to dominate the behavior in Fig. 10.

The fractional change in T_c^2/H_0^2 as $\rho_{0\perp}$ changes from 0 to 0.4 is seen in Fig. 10(A) to be 1.5%. There is experimental evidence[30] that the change in γ as small amounts of impurity are added to tin is very small, so we set $\gamma=\gamma(0)$. Using $\lambda=0.67$ in Eq. (13), we see that $\langle a^2\rangle \approx 0.022$, which is in excellent agreement with the value obtained in Eq. (11) with the analysis of the T_c data using the theory of MK.

We note that Eq. (15) does not describe the data in Fig. 10(B) in an absolute sense. As $\rho_{0\perp}$ is increased, $(dh/dt)_{t=1}$ approaches a value somewhat more negative than -1.737. This discrepancy cannot be considered to be serious, however, as the theory is derived with many simplifying assumptions which cannot reasonably be expected to be exactly satisfied by real superconductors. If we assume, however, that the fractional change in $(dh/dt)_{t=1}$ with increasing impurity concentration is reasonably defined by Eq. (15), we can make an estimate of $\langle a^2\rangle$. As $\rho_{0\perp}$ changes from 0.0 to 0.4 (λ from 1.0 to 0.67) the fractional change in $(dh/dt)_{t=1}$ is seen from Fig. 10(B) to be $\sim$0.007. From Eq. (15), we see that $0.33\ \langle a^2\rangle = 0.007$, or $\langle a^2\rangle \approx 0.021$. Thus the behavior of both T_c^2/H_c^2 and $(dh/dt)_{t=1}$ can be understood both qualitatively and quantitatively in terms of the effects of doping on λ.

In Fig. 11 we plot the differences between the reduced critical-field curves for different impurity concentrations and the curve describing the data for tin with 0.01% cadmium. The deviation from parabolicity of the 0.01% Cd curve itself was in good agreement with the results of Shaw *et al.*,[31] who measured the curve of pure tin in a temperature interval similar to ours. Finnemore *et al.*[32] have extended the critical-field measurements to much lower temperatures and obtain a better value of H_0 [thus, a better $h(t)$] by properly

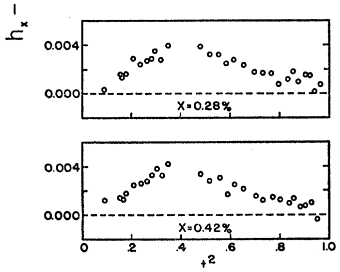

FIG. 11. The difference of the reduced critical-field curve from the curve for $x=0.01\%$ Cd as a function of composition. Not too much emphasis should be placed on the exact shape of this difference due to uncertainties in the determination of the respective H_0's. We do note, however, an increasingly large difference as x is increased. As impurities are introduced to the specimen, the reduced critical-field curve becomes more parabolic.

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[29] We wish to thank J. R. Clem for some helpful calculations pertinent to this point.

[30] R. I. Gayley, Jr., E. A. Lynton, and B. Serin, Phys. Rev. **126**, 43 (1962).

[31] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

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

TABLE IV. The anisotropic resistivity[a] of tin.

Reference	13	22	33	24	23	Present
$\rho_\perp(373)$	13.29		13.59			13.25 $\pm$0.05
$(\rho_\parallel/\rho_\perp)(373)$	1.43		1.17			1.53 $\pm$0.01
$\rho_\perp(273)$	9.05	9.088	9.27			9.05 $\pm$0.03
$(\rho_\parallel/\rho_\perp)(273)$	1.45	1.44	1.18			1.555$\pm$0.009
$\rho_\perp(77)$						1.772$\pm$0.006
$(\rho_\parallel/\rho_\perp)(77)$		1.35[b]				1.684$\pm$0.010
$\rho_\perp(4.2)$				7.1×10^{-5}		
$(\rho_\parallel/\rho_\perp)(4.2)$				1.5–1.6		
$(\rho_{0\parallel}/\rho_{0\perp})$				1.3[c]	1.14[d]	1.6 $\pm$0.1[e]

[a] All resistivities are in $\mu\Omega$ cm. The $\rho(T)$ values listed are those for tin in the absence of impurities.
[b] The temperature at which this measurement was made was ~90°K.
[c] This value is for an unknown impurity type in tin.
[d] This value is for indium impurity in tin.
[e] This value is for cadmium impurity in tin.

taking into account the curvature in the H_c-versus-t^2 curve for $t^2 \leqslant 0.1$. Our ignorance of H_c for $t^2 < 0.1$ makes an error of $\sim 1\%$ in the absolute values of H_0 possible, but its effect should be negligible in Fig. 11 since the relative values of H_0 used to reduce the H_c data are obtained from the extrapolations in Fig. 1. Thus, if we are making an error, it is of the same size and in the same direction for each specimen and the differences in $h(t)$ are little affected.

Since $D(t) = h(t) - 1 + t^2$ is always negative for tin, we see from Fig. 11 that the effects of doping on $h(t)$ are to make the reduced critical-field curve more parabolic. This is consistent with the theoretical development of Clem. Presumably, as one dopes tin the effectiveness of $\langle a^2 \rangle$ is impeded, and the deviation from parabolicity of the reduced-critical-field curve is decreased and approaches that of tin-like superconductor with $\langle a^2 \rangle = 0$.

One then expects to observe similar effects as one dopes other superconductors having a nonvanishing $\langle a^2 \rangle$. MK's analysis of existing data on dilute indium alloy systems indicates that indium has an $\langle a^2 \rangle$ similar to tin. The experimental results of Toxen *et al.*[3] for Sn impurity in In do not preclude behaviors of the critical-field parameters with doping similar to the ones we observe. There is some evidence in their data supporting a behavior similar to ours in tin of the quantity T_c^2/H_0^2, while the scatter in their values of $(dh/dt)_{t=1}$ is too large to clearly resolve an effect of the order of $\langle a^2 \rangle$

SUMMARY AND CONCLUSION

The primary findings and conclusions to be made from this work are summarized below.

(1) The anisotropies and absolute resistivities determined in this work are compared with the experimental results of all other investigations (Refs. 13,22–24, 33) known to the authors in Table IV. $\rho_{0\parallel}/\rho_{0\perp}$ for cadmium impurity is found by two different experimental methods to be ~ 1.6. The anisotropy of $\rho(T)$ increases as the temperature decreases. The deviation from Matthiessen's rule is found to be approximately 0.16 $\rho_{0\perp}$ and is, within experimental uncertainty, independent of temperature for $77°\text{K} < T < 373°\text{K}$. This type of deviation can be understood in terms of the two-zone model[27] although this may not be a unique interpretation. The size of the deviation at 77°K is perhaps larger than one would expect, but deviations of a similar order of magnitude have previously been observed.[28]

(2) The variation of each of the parameters describing the superconducting critical-field curve $[T_c, H_0, (dH_c/dt)_{T=T_c}]$ with composition is initially rather rapid, and the change is slower with composition as the electronic mean free path decreases below the superconducting coherence distance. The features of MK's theoretical treatment of the change in T_c with impurity concentration appears to be roughly satisfied, and the value of $\langle a^2 \rangle$ obtained from the data is 0.023. The variation of $(dh/dt)_{t=1}$ and the ratio T_c^2/H_0^2 with impurity concentration is consistent with the theoretical developments of Clem and MK. Thus the failure of the "similarity conditions" is understood, both qualitatively and quantitatively, in terms of the reduction of the effects of $\langle a^2 \rangle$ with doping.

(3) There is no evidence for a systematic development of vacant sites in a plot of $\rho_{0\perp}$ versus x at the cadmium concentration ($\sim 0.3\%$ Cd) associated with the previously reported[8] lattice-spacing anomaly. However, there is evidence of anomalous behavior at this same impurity concentration in a plot of T_c versus $\rho_{0\perp}$. This suggests that some sort of electronic alteration has occurred, but little more information about the situation can be obtained from our data.

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[33] B. Chalmers and R. H. Humphrey, Phil. Mag. **25**, 1108 (1938).