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

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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

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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

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† 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)].

by three different authors are 1.6 by Gueths *et al.*[1] for cadmium impurity, 1.14 by Pippard[2] for indium impurity, and 1.3 by Zernov and Sharvin[3] for a trace amount of unknown impurity. If, as it appeared, this anisotropy was impurity-type–dependent, then it was thought that knowing the systematics of the dependence would shed light on either the nature of tin solid solutions, or relaxation time anisotropy. We have found a_0 to be markedly dependent on impurity type, and provisionally interpret our results in terms of relaxation time anisotropy as suggested by Klemens.[4]

The anisotropy $a(T)$ of the ideal resistivity $\rho(T)$ was found by Gueths *et al.*[1] to increase as the temperature is lowered from 373 to 273 and then to 77°K. Presumably this is due either to an increase in importance of small-angle scattering at the lower temperatures, or to a temperature-dependent anisotropy of the phonon spectrum. Measurements by Gueths *et al.*,[1] by Bridgman,[5] and by Chalmers and Humphrey[6] agree on $\rho_\perp(273)$, but fail to agree on the anisotropy at this temperature. Our measurements support the results of Gueths *et al.* at both 273 and 77°K.

Deviations from Matthiessen's rule in tin have been noted by Pippard,[7] by Alley and Serin,[8] and by Gueths *et al.*[1] We note some points of agreement as well as disagreement between the earlier results and our own.

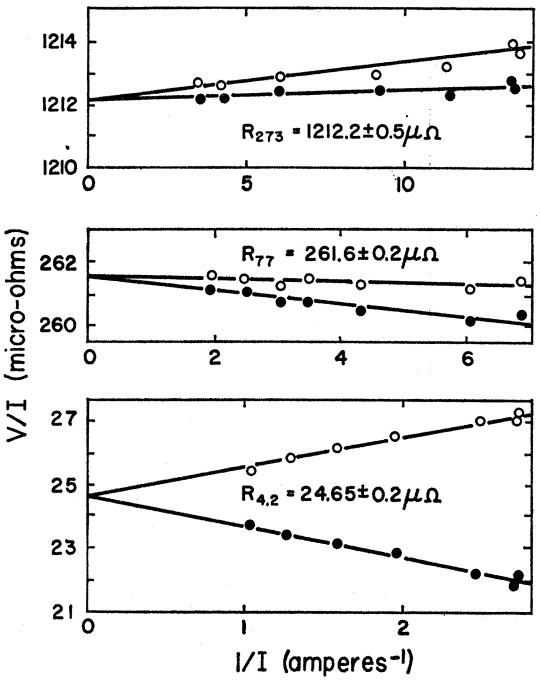

FIG. 1. Typical resistance determinations at 273, 77, and 4.2°K; this sample contained approximately 0.35% Sb. Filled and unfilled circles represent the two current polarities.

EXPERIMENTAL DETAILS

The techniques of sample preparation and orientation are the same as those described by Gueths *et al.*[1] and will not be repeated here. The samples used in this study were also part of a study of certain superconducting parameters in tin-rich binary alloys on which we are making a separate report.[9] We shall use the superconducting transition temperature T_c as a measure of the impurity concentration x in our residual resistivity anisotropy analysis. Actually, the difference in T_c between pure tin and an alloy ΔT_c was measured directly and described elsewhere (Ref. 9).

Each sample was a single-crystal cylinder with a diameter of 2±0.005 mm and a length of at least 7 cm. Current leads were attached to the ends of the sample by means of small alligator clamps, and brass knife-edge contacts separated by approximately 4 cm served as potential contacts. After the resistance measurements had been made on a sample the transition temperature of the portion of crystal between potential contacts was measured. Inhomogeneous alloys could be identified by the nature of their superconducting transition and such samples were discarded. Resistance measurements were made by the four-terminal potentiometric method which may be considered as standard. However, when small quantities such as deviations from Matthiessen's rule are measured, some explanation of technique is required to establish the credibility of the results.

A discrete set of measuring currents between 0.07 and 1 A was available and roughly spaced in equal increments of reciprocal current. The voltage drop across a 0.1-Ω standard resistor in series with the sample was continuously monitored by a Dymec model 2401B DVM. The voltage drop between the sample potential contacts was measured to ±0.005 μV with a Honeywell model 2783 potentiometer using a Keithley model 147 nanovoltmeter as the null detector. A measurement consisted of a set of six or seven voltage and current (V, I) readings after which the current polarity was reversed and the set repeated. The effect of error voltages was avoided by extrapolating a set of measured V/I ratios to infinite current in order to obtain the resistance. A typical set of data and the form of data reduction are shown in Fig. 1. With this form of reduction and taking both current polarities, any adverse effects from Joule heating in the leads or sample became readily apparent. The resistance measurement introduced an uncertainty into the resistivity of 0.1% of value, plus±0.0002 μΩ cm. The limit of error from geometrical factors is estimated to be 0.7% but will partially cancel in analyses which employ resistance ratios.

[4] P. G. Klemens, C. Van Baarle, and F. W. Gorter, Physica **30**, 1470 (1964).
[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **68**, 95 (1933); **60**, 305 (1925).
[6] B. Chalmers and R. H. Humphrey, Phil. Mag. **25**, 1108 (1938).
[7] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A248**, 97 (1955).
[8] P. Alley and B. Serin, Phys. Rev. **116**, 334 (1959).
[9] F. V. Burckbuchler, D. Markowitz, and C. A. Reynolds, preceding paper, Phys. Rev. **175**, 543 (1968).

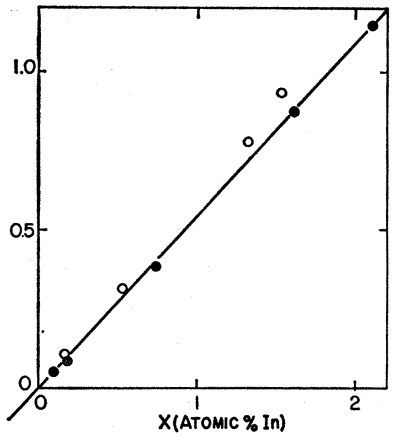

FIG. 2. Residual resistivity of indium impurity samples versus at.% impurity determined from spectroscopic analysis. (●) represents samples for which $\theta \sim 90°$. (○) represents samples for which the orientation is not close to 90°, and will be used in the anisotropy analysis.

RESULTS AND DISCUSSION

Ten indium impurity samples were analyzed spectroscopically for indium content by the Jarrell-Ash Company.[10] Half of these samples had their orientations near perpendicular ($\theta = 90°$); the rest were chosen to have $\cos^2\theta$ appreciably different from zero, so that their properties might be used in the resistivity anisotropy analysis. Figure 2 displays the results obtained for these ten samples. Using only the perpendicular crystals we obtained $\rho_{0\perp}/x = 0.54 \pm 0.02$ $\mu\Omega$ cm/at.% from this graph. Had we used the impurity concentration added to the melt we would have obtained the same result though with somewhat less certainty. It may be dangerous however to generalize from this case to other impurities in tin.

For antimony impurity we have used the impurity concentration added to the melt to plot the graph in Fig. 3. This graph contains only samples whose orientations were nearly perpendicular, and from it we obtained $\rho_{0\perp}/x = 0.63 \pm 0.03$ $\mu\Omega$ cm/at.%.

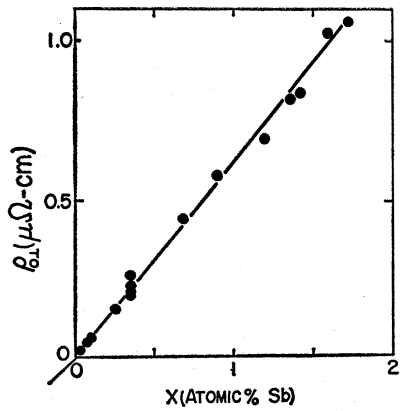

FIG. 3. Residual resistivity of antimony impurity samples versus at.% impurity added to the melt. All samples plotted here have orientations close to $\theta = 90°$.

[10] 590 Lincoln Street, Waltham, Mass.

For zinc impurity we could not obtain $\rho_{0\perp}/x$ with much confidence since all of our samples contained impurity in excess of the solubility limit. All of our samples containing zinc impurity exhibited ρ_0's which decreased with time when the samples were held at room temperature. We interpreted this as impurity precipitation. Beads of zinc on the surfaces of the most impure samples (0.5 at.%) were evident within a month. From the least impure samples ($\sim$0.1 at.% Zn, for which ρ_0 decreased at a rate of approximately 5% per month) we obtained 0.82 $\mu\Omega$ cm/at.%, which is to be regarded as a lower limit for this quantity.

We have not obtained $\rho_{0\perp}/x$ for cadmium impurity, since Gueths *et al.*[1] had already obtained 1.39 $\mu\Omega$ cm/at.% in a similar single-crystal study.

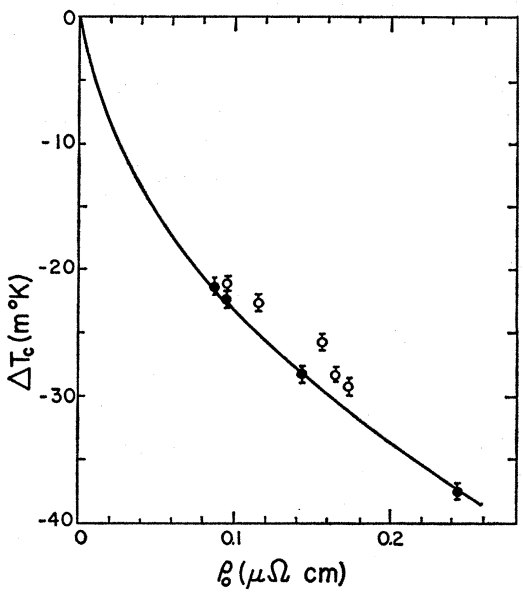

FIG. 4. Graph used in the determination of $\rho_{0\perp}$ for samples containing zinc impurity in tin. (●) represents samples whose orientation is nearly perpendicular to the tin tetrad axis. (○) represents samples whose orientation is not nearly perpendicular.

ρ_0 Anisotropy

It is evident from the scatter in Fig. 3 that melt impurity concentration is not sufficiently indicative of sample impurity concentration to be useful in a study of resistivity anisotropy. Nevertheless it is necessary to have a sensitive measure of impurity concentration and homogeneity. This is furnished over a limited range of concentration by the shift in T_c relative to pure tin. The transition temperature is independent of crystal orientation.

Our method is a strictly empirical one in which we have obtained $\rho_{0\perp}$ from the measurement of ΔT_c. We illustrate our method using our zinc impurity data set, which is small. Figure 4 shows the working diagram.

In this figure the perpendicular samples, shown as filled circles, are used to plot out the ΔT_c versus $\rho_{0\perp}$ variation. The curve shown here was obtained by small perturbations from a linear variation between data points so that the slope variation was continuous. The samples represented by open circles in this diagram have $\cos^2\theta$ appreciably different from zero, and are seen to lie to the right of the curve, indicating that $a_0>1$. $\rho_{0\perp}$ was obtained from the curve for each of the nonperpendicular crystals. The lowest graph in Fig. 5 displays the resulting variation of $\rho_0/\rho_{0\perp}$ with $\cos^2\theta$, which is seen to be linear in accord with Eq. (1), and from which we estimate $a_0=1.53\pm0.07$.

The results of the same type of analysis for samples containing cadmium, antimony, and indium impurities are also shown in Fig. 5. Anisotropies of 1.60 ± 0.07, 1.30 ± 0.07, and 1.22 ± 0.05 are found for these three impurities, respectively.

For a few indium impurity samples we had an alternative method to determine a_0. By use of spectroscopically obtained impurity concentrations we found $a_0=1.20\pm0.04$, which is in good agreement with our determination based on ΔT_c. Our residual resistivity results are summarized in Table I.

We set out to find whether a_0 is a function of impurity type in tin. The results in Table I clearly demonstrate that it is. Our result for cadmium impurity is in excellent agreement with that of Gueths *et al.* However, Pippard's result for indium impurity is outside of our experimental limits for reasons that we do not understand. Nevertheless we do agree with Pippard that the anisotropy for this impurity is small.

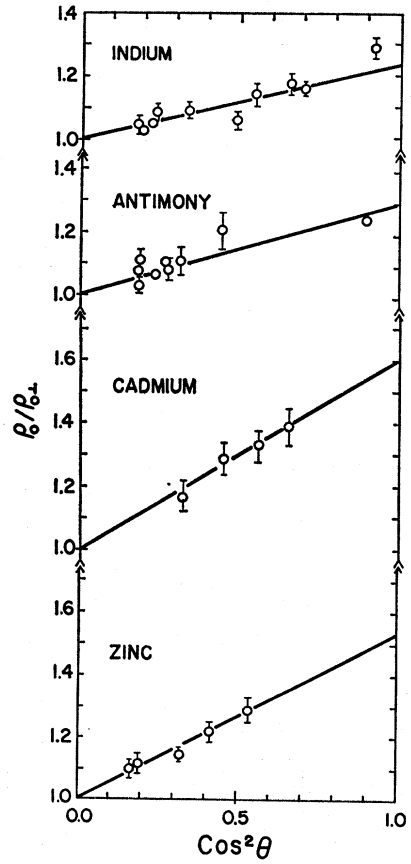

FIG. 5. Graphs used in the determination of the residual resistance anisotropy of tin with Zn, Cd, Sb, and In impurity.

TABLE I. Residual resistivity of tin with four impurities.

Impurity	Indium	Antimony	Zinc	Cadmium
$\rho_{0\perp}/x$[a]	0.54±0.02	0.63±0.03	0.82	1.39[b]
a_0	1.21±0.05	1.30±0.07	1.53±0.07	1.60±0.07
	1.14[c]			1.60±0.1[b]

[a] In units of $\mu\Omega$ cm/at.%.
[b] See Ref. 1.
[c] See Ref. 2.

It should be noted that the results of Table I are systematic in two ways: (1) As the resistivity per unit of impurity concentration (in any crystal direction) increases, so does the resistivity anisotropy. (2) The impurities which differ in valence by two from tin (Cd and Zn) produce larger resistivity anisotropies than the impurities which differ in valence by one from tin (Sb and In).

The latter feature of the results suggests an explanation of the effect which is based on a model of resistivity anisotropy proposed by Klemens.[4] Considering a free-electron Fermi sphere that is intersected by the zone boundaries of nonzero structure factor in tin, Klemens estimated the resistivity anisotropy by neglecting electrons on the small segments of Fermi surface defined by zone boundaries, and by taking the relaxation time to be constant on the larger free areas. The idea is that electrons close to zone boundaries may be brought to them by small-angle scattering and will therefore have short relaxation times. Klemens estimated $a_0>1$ since the electrons contributing to c-axis conductivity are more sensitive to small-angle scattering than the electrons contributing to a-axis conductivity.

The relation of these ideas to our results is that impurities which produce longer-range perturbations will tend to favor the small-angle scattering which increases resistance anisotropy. Since the longer-range part of the perturbation around an impurity is primarily due to valence difference, we would expect cadmium and zinc to produce a larger a_0 than the impurities indium and antimony.

Resistivity at 77 and 273°K

In the analysis of measured sample resistivity ρ_T at each of these two temperatures we determined the ideal resistivity $\rho(T)$ and the deviation from Matthiessen's rule, $\Delta(T)$. The expression

$$\rho_T=\rho(T)+\rho_0+\Delta(T) \qquad (2)$$

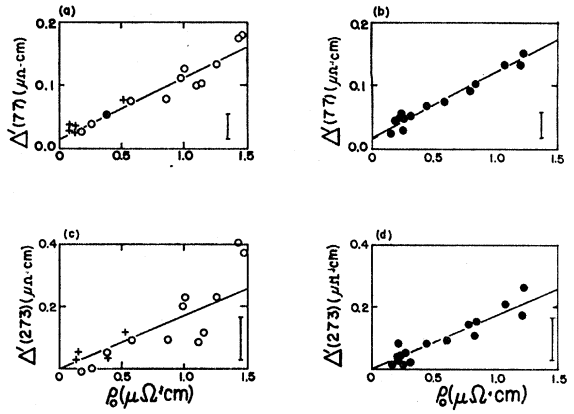

FIG. 6. Deviations from Matthiessen's rule for nearly perpendicular crystals using $\rho(T)$ determined by Gueths *et al.* (Ref. 1) (○) Indium impurity; (●) antimony impurity; (+) zinc impurity. Error bars in the lower right corner of each graph are the size of the anticipated experimental limits of error.

defines Δ. We have taken the values of $\rho(T)$ reported by Gueths *et al.*[1] for pure tin in order to calculate initial estimates of Δ from Eq. (2) for our alloy samples. These initial estimates we label Δ′. The Δ′s obtained are only a small fraction of $\rho(T)$ and are not much larger than our experimental error. We therefore confine our attention to samples for which $\theta > 75°$. This region has the advantage of being represented by a large number of samples, and here, where $\cos^2\theta$ varies slowly with θ, small errors in orientation are not serious. Figure 6 exhibits Δ′ versus ρ_0 for the nearly perpendicular crystals. At 77°K it is seen that the data are described by straight lines with a small but nonzero intercept. We interpret the latter feature as a small 0.015 μΩ cm underestimate of $\rho_\perp(77)$. No such discrepancy is found at 273°K, indicating that our data support Gueths's determination of $\rho_\perp(273)$. From Fig. 6 we conclude that $\Delta = \Delta'$ at 273°K, and $\Delta = \Delta' - 0.015$ μΩ cm at 77°K for perpendicular crystals. At 77°K we obtained Δ (not Δ′) per unit of residual resistivity from the slopes of the lines drawn in Figs. 6(a) and 6(b). At 273°K we follow a different procedure however.

If in Fig. 6 one compares the patterns of scatter at 77 and 273°K for either antimony or indium, one notes that they are similar at these two temperatures (though the scatter is aggravated at 273°K where Δ is fractionally smaller). This probably results from the geometrical errors which are common to resistivity measurements at both temperatures. Based on this interpretation, we have taken the ratios $\Delta(273)/\Delta(77)$ for samples with $\rho_0 > 0.5$ μΩ cm. Detailed examination shows that one may expect roughly one-half of the geometrical error to cancel in this ratio. Averaging the individual ratios we obtain

$$\Delta(273) = (1.71 \pm 0.15)\Delta(77) \qquad (3)$$

for antimony impurity, and

$$\Delta(273) = (1.8 \pm 0.5)\Delta(77) \qquad (4)$$

for indium impurity. The tolerances are rms deviations.

TABLE II. Deviations from Matthiessen's rule in tin, Δ/ρ_0.

T (°K)	Pippard[a]	Alley and Serin[b]	Gueths *et al.*[c]	This work
273	0.12	0.12±0.01	0.16	0.17±0.02
77	···	0.08±0.01	0.16	0.10±0.01

[a] Three single crystals with In impurity; see Ref. 7.
[b] Polycrystalline samples containing In, Sb, and Bi impurity; see Ref. 8.
[c] Predominantly perpendicular single crystals with Cd impurity. They give their result as a fraction of $\rho_{0\perp}$; see Ref. 1.

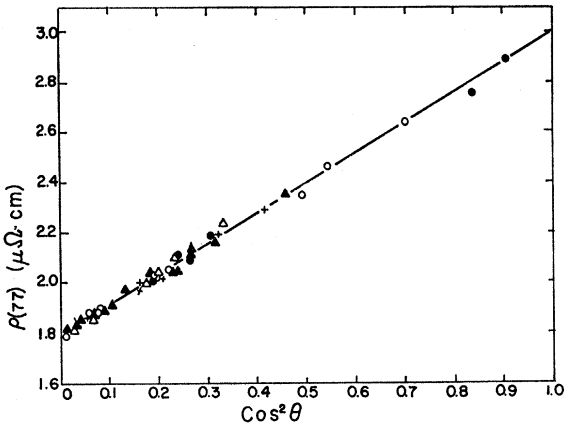

FIG. 7. Ideal resistivity of tin at 77°K obtained from impure samples as described in the text. Triangles and circles represent samples for which ρ_0 is less or greater than 0.5 μΩ cm, respectively. Filled and open figures represent antimony and indium impurity samples, respectively. + indicates zinc impurity samples for which ρ_0 is small.

There is no question but that $\Delta(273) > \Delta(77)$ though in the case of indium impurity their ratio is rather uncertain. So far as we can determine, Δ for indium impurity at both temperatures is identical to that for antimony impurity, which is somewhat better known from our data. The data for zinc impurity are limited, but from the few zinc points in Fig. 6 this impurity appears to behave similarly to both indium and antimony. Our results, as well as those of other investigators, are given in Table II. Agreement is seen to be poor in some cases. We note that the work of Alley and Serin was done with polycrystalline samples in which we might expect effects comparable to Δ in magnitude rooted in the differences of the anisotropies of ρ_0, $\rho(T)$, and $\Delta(T)$. Pippard's result is based on three samples, which is perhaps an insufficient number for the measurement of so small an effect. The differ-

ence between our result at 77°K and that of Gueths is appreciable and may be due to the difference in impurity type.

It is to be remembered that our results in Table II are for current nearly perpendicular to the tin symmetry axis. The anisotropy of Δ has not been determined and would require a group of crystals, in addition to our own, of varying impurity content and $\theta \sim 0°$. While a two-zone[11] type of model might be invoked to interpret our results, the authors feel that such an interpretation is premature in view of the experimental information which is yet lacking, viz., the temperature dependence of Δ over a wide range, and its anisotropy.

Having obtained Δ for perpendicular crystals, we now *assume* that its anisotropy is the same as that of ρ_0 for each impurity individually. The results are displayed in Figs. 7 and 8 where the points have been coded according to the size of Δ. We see no systematic difference between data of high and low impurity content, thus exonerating our assumption about Δ to within the scatter of the data. The ideal resistivities, $\rho(77°\text{K}, \theta)$ and $\rho(273°\text{K}, \theta)$, are now found from the straight lines in Figs. 7 and 8; these are collected in Table III along with the results of other investigators. It is to be noted that our results are in very good agreement with those of Gueths *et al.*[1] but differ appreciably from those of the two earlier measurements of a (273). In defense of the latest two works we wish to point out that both have demonstrated a linear variation of $\rho(273)$ with $\cos^2\theta$. This point was not made by the earlier works, which relied on crystals for which $\theta \sim 90°$ and $\theta \sim 0°$. We also note that parallel ($\theta \sim 0°$) pure tin crystals are very apt to twin under slight tension as pointed out by the work of Chalmers,[12] thus reducing the apparent resistivity anisotropy. We have noted this to happen for the one parallel crystal which we measured.

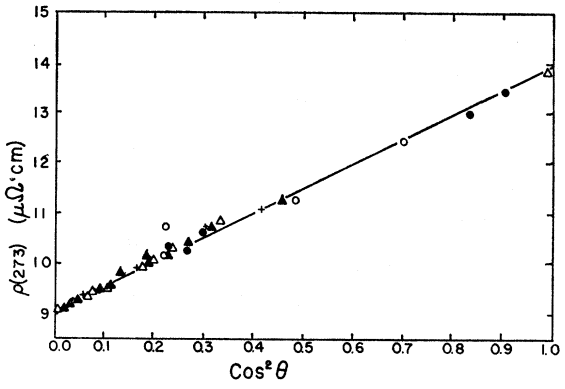

FIG. 8. Ideal resistivity of tin at 273°K. Same symbolism as in Fig. 7.

TABLE III. Ideal resistivity of tin.[a]

	Bridgman[b]	Chalmers and Humphrey[c]	Gueths *et al.*[d]	Present[e]
$\rho_\perp(77)$	...	...	1.772±0.006	1.787±0.01
$a(77)$	...	...	1.684±0.01	1.683±0.015
$\rho_\perp(273)$	9.088	9.27	9.05±0.03	9.05±0.02
$a(273)$	1.44	1.18	1.555±0.009	1.54±0.015
$\rho_\perp(373)$	13.29	13.59	13.25±0.05	...
$a(373)$	1.43	1.17	1.53±0.01	...

[a] Resistivities are given in $\mu\Omega$ cm.
[b] Reference 5.
[c] Reference 6.
[d] Reference 1. Tolerances are standard deviations.
[e] Tolerances are estimated limits of error.

SUMMARY

We have measured the effects of impurities on the resistivity of tin; principally indium, antimony, and zinc, and to a lesser extent cadmium. These effects include the residual resistivity and deviations from Matthiessen's rule at two fixed temperatures. In addition we have obtained the ideal resistivities at these two temperatures. For each of these quantities, except Δ, we have found the anisotropy.

The authors believe that the principal contribution of this work is in having for the first time studied the systematics of the anisotropy of the residual resistivity. The residual resistivity anisotropy is dependent on impurity type, which clearly demonstrates that impurity scattering in tin is not isotropic.

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[11] H. Jones, in *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1956), Vol. 19, Chap. 3.
[12] B. Chalmers, Proc. Phys. Soc. (London) **47**, 733 (1935).