remaining at 300°K are 8, 10, and 10 for Cu, Ag, and Au, respectively.

VII. ACKNOWLEDGMENT

Measurements of Electrical Conductivity and Magnetoresistance of Gray Tin Filaments*

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A method for the preparation of gray tin filaments suitable for electrical measurements is described. Results of measurements of the temperature dependence of the electrical conductivity and of the magnetoresistance on pure gray tin and on alloys containing various amounts of Sb, As, In, Al, and Zn are reported. For 99.998 percent pure tin the activation energy is 0.082 ev and the conductivity at 0°C is 2090 ohm^{-1} cm^{-1}. Addition of impurities results in an increase in the "intrinsic" activation energy and a decrease in the absolute value of the conductivity in the "intrinsic" range. Samples doped with n-type impurities exhibit a positive temperature coefficient of resistance at low temperatures whereas the low-temperature conductivity of p-type samples becomes temperature-independent at high impurity concentrations. The three p-type impurities In, Zn, and Al show marked differences in their effectiveness in producing p-type conductivity, In being 40 times more effective than Al. The magnetoresistance coefficient in the lattice-scattering region shows a stronger temperature dependence than is predicted by the simple theory. Impurity scattering appears to be relatively more important in p-type than in n-type material.

I. INTRODUCTION

IN 1950 Busch, Wieland, and Zoller[1] found that gray tin is a semiconductor similar to the other Group IV elements, carbon (in the form of diamond), silicon, and germanium. The subsequent investigations by Busch and his collaborators[2-4] and by Kendall[5,6] have revealed many of the semiconducting properties of gray tin. The measured values of some of the most important quantities have remained uncertain, however, because of the difficulty of preparing suitable specimens. The only method of obtaining gray tin is through the well known phase transition from the metallic phase. More direct methods, such as evaporation onto a cold substrate or electrolytic deposition at reduced temperatures, though tried by several investigators, have not proved successful. Using the phase transition method one generally obtains gray tin as a powder because of the large volume expansion associated with the white-to-gray transformation. Using such powder samples, Busch and his co-workers have measured the Hall coefficient, the magneto-

resistance coefficient, the temperature dependence of the conductivity and the magnetic susceptibility. They conclude however that neither high-frequency loss measurements nor direct conductivity measurements made on powder are suited to an exact determination of the absolute value of the conductivity. Kendall has used two types of samples, lumps selected from a large quantity of powder and rods of compressed powder. Only an approximate value of the conductivity could be determined using the first type because of the difficulty in measuring the cross section and electrode areas. While this difficulty was eliminated through the use of compressed-powder rods, measurements on these samples yielded an unusually low value of the activation energy and therefore the value of the specific conductivity obtained using them is also open to question. In view of these difficulties, need for an improved method of preparing gray tin samples has been recognized. More suitable specimens were needed both to establish precise and reliable values of previously measured quantities, especially the value of the specific conductivity, and to extend the investigation to include phenomena such as the thermoelectric effect and photoelectric effect.

In searching for an improved method of preparation one of us[7a] found that fine wires of metallic tin would transform to the gray phase without the usual crumbling

* Parts of this material were reported at the North Carolina and Michigan meetings of the American Physical Society [Phys. Rev. 91, 244 (1953); Phys. Rev. 94, 1428 (1954)].
[1] Busch, Wieland, and Zoller, Helv. Phys. Acta 23, 528 (1950).
[2] Busch, Wieland, and Zoller, Helv. Phys. Acta 24, 49 (1951).
[3] G. Busch and E. Mooser, Helv. Phys. Acta 26, 611 (1953).
[4] G. Busch and J. Wieland, Helv. Phys. Acta 26, 697 (1953).
[5] J. T. Kendall, Proc. Phys. Soc. (London) B63, 821 (1950).
[6] J. T. Kendall, Phil. Mag. 45, 141 (1954).

[7a] A. W. Ewald, Phys. Rev. 91, 244 (1953).

to a powder. Filaments of gray tin approximately 0.1 mm in diameter and up to several centimeters in length are readily obtained.[7b] These filaments are free of cracks and other gross imperfections and are mechanically strong. X-ray Laue patterns show well defined spots indicating that the filaments are probably single crystals. Because of their relative dimensions, these specimens have proved to be well suited to measurements of the electrical conductivity, its change in a magnetic field, and the thermoelectric power. It is anticipated that under the proper conditions of purity and low-temperature photoelectric effects should also be observable.

II. PREPARATION OF GRAY TIN FILAMENTS

Filaments of metallic tin are first prepared by a modified form of the Taylor technique.[8] A glass capillary of approximately 0.5-mm inside diameter is drawn from the center portion of a 10-mm diameter glass tube one end of which has been closed. Approximately one gram of tin is inserted in the open end and rests at the upper end of the capillary portion when the tube is mounted vertically and attached to a vacuum line. After pumping out (rough vacuum), the tin pellet is melted by heating with a flame and the molten tin is forced down the capillary by collapsing the evacuated tube just above it. Having the closed segment of 10-mm tubing at the lower end of the capillary prevents any appreciable increase in pressure on the advancing side of the tin column as the tin is forced downward. This bulb is removed by sealing off the capillary after the latter has been filled. The filled capillary is then drawn out to reduce the core diameter to about 0.1 mm by heating short segments ($\sim$1 cm) and pulling. Some care is necessary to prevent fracture of the glass due to expansion of the metal upon melting. Cracking can be avoided by softening the glass at the lower seal-off point first and then working upward step by step keeping the tin in the lower end of the undrawn capillary molten. The result of the drawing operation is a chain of small-diameter segments, 10 to 20 cm in length, separated by nodules having the original capillary diameter. The segments are broken apart keeping a nodule at one end of each, and a hook is formed at the other end. The glass is conveniently removed by hanging the segments in a wax-lined test tube containing hydrofluoric acid. The filaments are then dipped in distilled water, in sulfuric acid, and in distilled water

again. The nodules serve as sinkers to prevent doubling up of the filaments as they are lowered into the baths.

The metallic tin filaments are buried in gray tin powder and stored in a cold chest at $-30°C$ to transform them to gray tin. In the earlier work the transformation was stopped when segments a few millimeters long had converted to the gray phase so that the remaining metallic portions could be used as electrical leads, contact to them being made through spring-loaded clamps. Later, when tin of higher purity was obtained, this method was abandoned because during measurements on the samples the transformation of the metallic portions would proceed at an appreciable rate when the temperature was in the vicinity of $-30°C$. The current procedure is to allow the transformation to go to completion and to solder the samples to the holder with a low melting-point solder. The time required for complete transformation varies depending upon the purity, but is of the order of one day for the samples of highest purity.

III. APPARATUS AND PROCEDURE

The apparatus was designed to permit simultaneous measurement of the conductivity and its change in a magnetic field as well as determination of the sign of the thermal emf in the temperature range from 77 to 273°K. The sample holder consisted of two brass blocks which when insulated from each other and fastened together formed a block measuring $1 \times 1 \times 2\frac{1}{2}$ cm. To reduce strains set up by the differential thermal contraction of the sample and brass, the sample was connected to the two insulated blocks through flexible strips of silver foil. The connection of the sample to these strips was made using solder composed of one part indium to four parts gallium which is liquid at room temperature and solid at the measurement temperatures. The sample diameter and the distance between soldered contacts were measured after the sample was mounted using a microscope equipped with a filar eyepiece. The effective length, approximately fixed by the dimensions of the sample holder, was about 3 mm for all samples. A $\frac{1}{2}$-watt carbon resistor imbedded in one of the brass blocks served as a heater for the thermal emf determinations. The sample temperature was varied by means of a liquid nitrogen bath and a heating coil wound on a copper tube surrounding the sample holder. To prevent excessive heat loss to the nitrogen bath this tube was surrounded by another constructed of lead, both tubes being closed at the lower ends.

A dc, constant current method was used for the conductivity measurements. The sample current, which ranged from 0.25 to 10 ma depending upon sample diameter, was monitored by a microammeter. The sample voltage as well as the voltages generated in two thermocouples imbedded in the two blocks of the sample holder were measured potentiometrically through suitable switching arrangements which also allowed for

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[7b] *Note added in proof.*—Groen and Burgers have recently reported the formation of large compact pieces of gray tin of the order of 1 mm thick by 25 mm² in area. [L. J. Groen and W. G. Burgers, Proc. Koninkl. Ned. Akad. Wetenschap. (Amsterdam) **B57**, 79 (1954)]. However, subsequent investigations [L. J. Groen, Nature **174**, 836 (1954)] indicated the presence of mercury in the tin and that at least 0.2 atomic percent mercury was necessary for the formation of the large compact pieces. Our starting material was free of mercury and there was no possibility of contamination during preparation since only oil pumps were used in the vacuum system.

[8] G. F. Taylor, Phys. Rev. **23**, 655 (1924).

reversal of sample current direction so that thermal emf effects could be cancelled out of the conductivity measurements. Separate current and potential leads were connected between the sample holder and the external measuring circuit. Because of the small sample dimensions it was not convenient in routine work to make separate connections to the sample itself. A check measurement made with a third potential lead soldered directly to the midpoint of the sample established that the different methods of connection gave the same value for the conductivity.

Conductivity measurements with and without a magnetic field were made in a single temperature run. The sample was positioned approximately perpendicular to the magnetic field and then adjusted for maximum magnetic resistance change. To stay within the square-law range of the magnetoresistance effect the field intensity was readjusted at each temperature to the minimum value that would produce an accurately measurable effect. The determination of the magnetic resistance change $\Delta\rho/\rho_0$ was accomplished graphically

TABLE I. Analyses of two lots of tin used. Values given in percent by weight.

Impurity	Lot I	Lot II
Lead	0.0012%	0.0001%
Antimony	0.001	...
Iron	0.00027	0.001
Arsenic	0.0002	...
Sulfur	0.00003	...
Copper	0.0002	0.0003
Bismuth	0.00012	0.0001
Tin (by difference)	99.997	99.998

since it was in general impossible to get readings of the sample resistance with and without the magnetic field at exactly the same temperatures.

The present investigation was started in 1952 using 99.997 percent pure tin from Johnson, Matthey & Company, Ltd. The analysis supplied by the manufacturer is given in Table I under the heading Lot I. In 1953 a second supply of tin, Lot II, was obtained from the same supplier but from a new manufacturer's lot. The absence of antimony and arsenic and the reduction in concentration of lead in Lot II as compared to Lot I is noteworthy since these elements are active impurities in gray tin. Thus, although the total impurity content of the two lots is about the same, the second is more pure in the sense that it contains less of the known active impurities.

IV. RESULTS

A. Conductivity of Pure Gray Tin

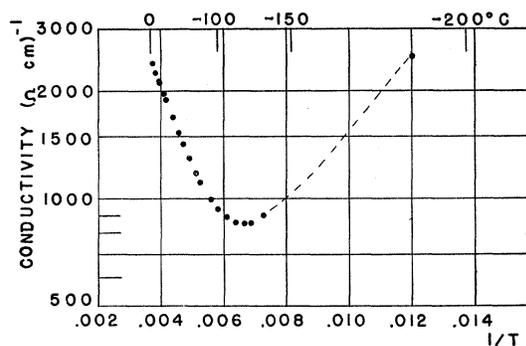Figure 1 shows a typical curve of the temperature dependence of the conductivity of filaments prepared

FIG. 1. Conductivity of pure gray tin prepared from Lot I.

from tin of Lot I.[9] Measurements on five samples yielded the values 2250 ohm^{-1} cm^{-1} for the conductivity at 0°C and 0.088 ev for the activation energy determined in the usual manner. In Fig. 2, which shows the conductivity of a sample prepared from tin of Lot II, the effect of higher purity is quite apparent. In addition to a marked reduction of the conductivity at low temperatures and disappearance of the minimum there is a change in slope of the "intrinsic" line and in the high temperature conductivity. Tin of this lot yielded the values 0.082 ev for the activation energy and 2090 ohm^{-1} cm^{-1} for the conductivity at 0°C. The dependence of the conductivity at all temperatures upon purity suggested further work along two different lines: further purification and doping with various known amounts of different impurities. Attempts thus far at purification by recrystallization and zone refining have not produced a significant change in the shape of the conductivity curve. Work along this line is continuing, however.[10] The effects of alloying are described in the next section.
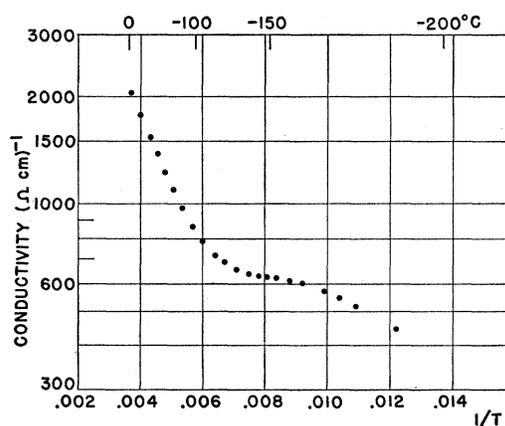
FIG. 2. Conductivity of pure gray tin of Lot II.

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[9] These early measurements, made with a cryostat different from that described above, did not include the temperature range immediately above liquid nitrogen temperature.

[10] Tanenbaum, Goss, and Pfann have recently reported the reduction in concentration of certain impurities in metallic tin by an order of magnitude through extensive zone refining. [J. Metals 6, 762 (1954).]
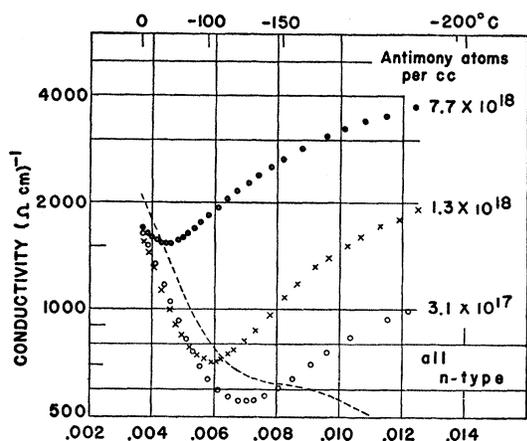
FIG. 3. Conductivity of Sb-Sn alloys. Impurity concentrations were calculated from amount of impurity added to melt. Pure tin curve (broken line) reproduced from Fig. 2 for comparison. Letters p and n designate conductivity types. Arrows indicate approximate temperatures at which conductivity changes type.
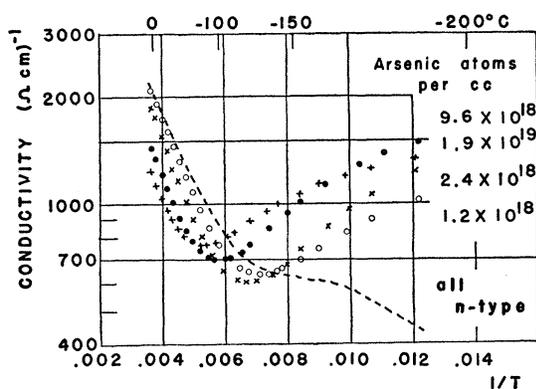

FIG. 4. Conductivity of As-Sn alloys.

B. Conductivity of Gray Tin Alloys

The conductivity curves for gray tin containing various amounts of Sb, As, In, Al, and Zn are shown in Figs. 3 to 7. Impurity concentrations specified in the figures were calculated from the amount of impurity added to the melt taking into account the larger specific volume of the gray phase. All specimens were prepared using tin of Lot II and the corresponding curve (of Fig. 2) is reproduced in each figure for comparison. The conductivity types as determined by thermal emf measurements are designated on the curves by the letters p and n, and the approximate cross-over points from one type to the other are indicated by arrows. It will be noted that Sb and As leave the material n-type whereas In, Al, and Zn in sufficiently high concentrations produce excess hole conduction.

The series of curves shown in these figures all exhibit, in varying degree, two new features. Addition of increasing amounts of any impurity results in (1) an increase in slope in the "intrinsic" temperature range and (2) a decrease in absolute value of the conduc-

tivity within this temperature range. Values of the activation energy determined from the slopes wherever possible together with conductivity values at $T = -50°C$ are given in Table II. In the cases of the highest impurity concentrations showing a straight-line behavior, e.g., 1.9×10^{19} As atoms/cc or 2.6×10^{18} In atoms/cc, the activation energies must be considered only lower limit values as it is impossible to ascertain in the limited temperature range available whether these curves have attained their steepest slope. There seems no question, however, that the pure sample slopes have reached a constant value since pure filaments stabilized by the addition of germanium to prevent the gray-to-white transformation at the normal temperature maintained the same slope to the limit of measurement at $+60°C$.[11]

At low temperatures doped samples of n-type show a positive temperature coefficient of resistance whereas the conductivity of p-type samples become temperature independent with increasing impurity content. For samples doped with n-type impurities the conductivity in this temperature range increases with increasing impurity content. For those doped with p-type impurities it decreases with the addition of small amounts of impurity (due to the neutralization by the added acceptors of the donors originally present) and then increases with further increase in impurity concentration. The three p-type impurity elements show striking differences in their effectiveness in producing excess hole conduction. The concentrations required to bring the material to the neutral condition are approximately 1.2×10^{19} atoms/cc of Al, 1.4×10^{18} atoms/cc of Zn and 2.9×10^{17} atoms/cc of In. Thus
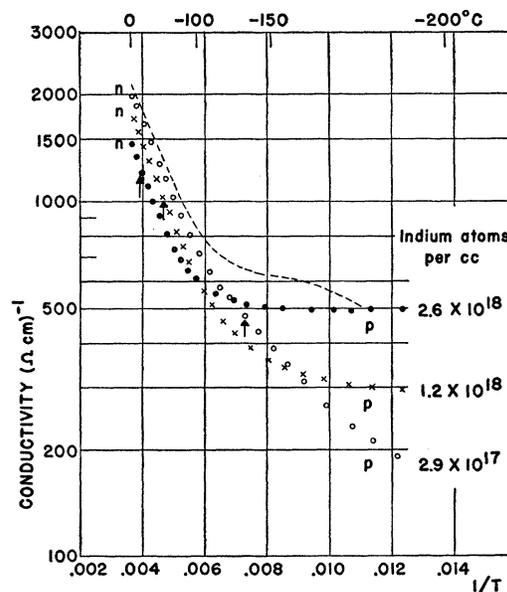

FIG. 5. Conductivity of In-Sn alloys.

[11] A. W. Ewald, J. Appl. Phys. (to be published).

In is 40 times more effective than Al for these concentrations. At higher concentrations this ratio is considerably reduced because of the remarkable increase in conductivity (a factor of 10) of the Al-doped samples as the concentration is increased from 1.2×10^{19} to 1.8×10^{19} atoms/cc.

C. Magnetoresistance

The magnetoresistance coefficient, $B(T)$, was calculated using the relation

$$\Delta\rho/\rho_0 = 3.8\times10^{-17}B(T)H^2,$$

where H is in gauss and $B(T)$ in cm⁴/(volt sec)². The values obtained for several typical specimens are plotted in Figs. 8, 9, and 10. Pure samples show the largest coefficient throughout the temperature range as is to be expected. Doping with the n-type impurities Sb and As reduces somewhat the magnetoresistance effect at low temperatures. Curves obtained for the three Sb-Sn alloys (two of which are shown) are essentially the same and agree with the values for the lowest concentration of As. Higher concentrations of As reduce the effect still further but not as much as even the lowest concentrations of p-type impurities such as Zn. With high concentration of p-type impurities the magnetoresistance change becomes too small for accurate measurement. For example, the maximum value of $B(T)$ for the sample containing 5.7×10^{18} Zn atoms/cc was 10^6 cm⁴/(volt sec)². Results for the In-Sn alloys were very similar to those of the Zn-doped samples and therefore are not included in the figures. The irregular variation of conductivity

with impurity content of Al-Sn alloys was reflected in the magnetoresistance effect. For the lowest concentration (6.6×10^{18} Al atoms/cc) the plot of $B(T)$ was practically identical to that for the pure material, whereas for a concentration of 2.4×10^{19} atoms/cc, $B(T)$ was less than 5×10^5 cm⁴/(volt sec)² throughout the temperature range.

V. DISCUSSION

It is of interest to compare the above values of the conductivity and activation energy for pure material
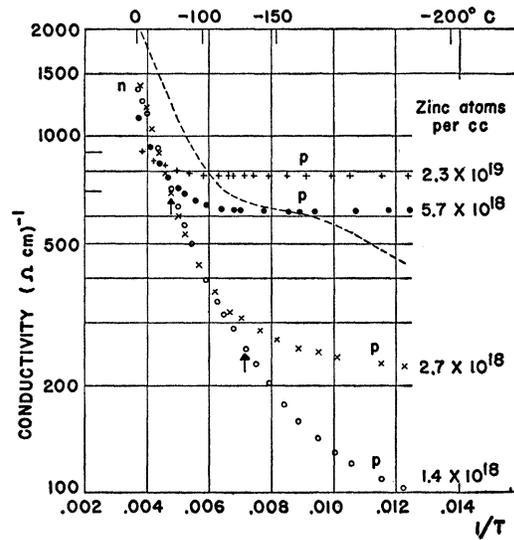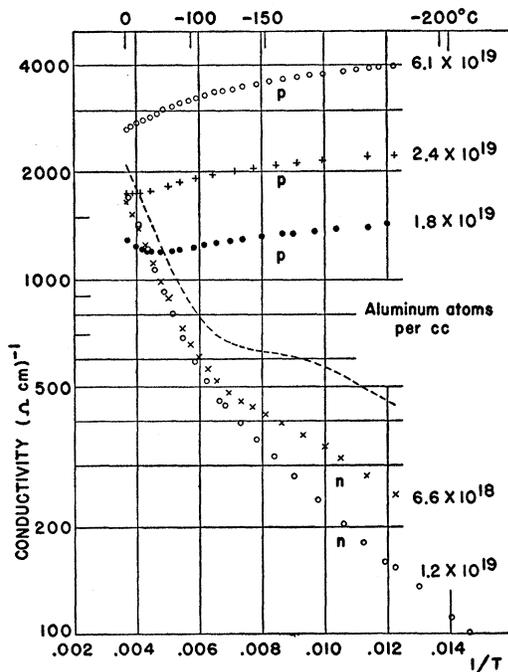
FIG. 7. Conductivity of Zn-Sn alloys.

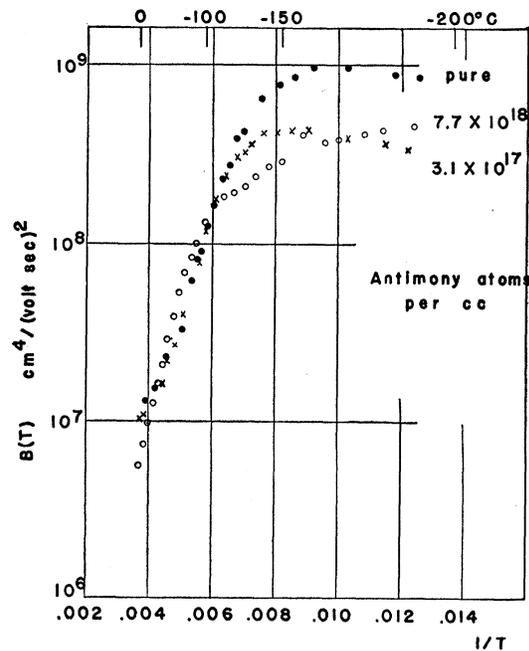FIG. 6. Conductivity of Al-Sn alloys.

FIG. 8. Magnetoresistance coefficient of pure gray tin of Lot II and of alloys with Sb.

TABLE II. Variation of conductivity and activation
energy with impurity content.

Impurity	Impurity atoms added per cc	ΔE(ev)	σ at $-50°C$ (ohm^{-1} cm^{-1})
Pure	...	0.0820	1405
Aluminum	6.6×10^{18}	0.0844	1116
	1.2×10^{19}	0.0936	1124
Zinc	1.4×10^{18}	0.1010	850
	2.7×10^{18}	0.1203	810
Antimony	3.1×10^{17}	0.0862	1102
	1.3×10^{18}	0.0941	1018
Indium	2.9×10^{17}	0.0881	1317
	1.2×10^{18}	0.0944	1125
	2.6×10^{18}	0.1032	899[a]
Arsenic	1.2×10^{18}	0.0912	1349
	2.4×10^{18}	0.0983	1160
	9.6×10^{18}	0.0969	910[a]
	1.9×10^{19}	0.0908	766[a]

[a] Values extrapolated from straight line portion of conductivity curve.

with those found by other investigators. Since our Lot I tin was identical in purity to that used by Kendall,[6] differences in results are probably due to different methods of preparing specimens. Kendall found 0.064 ev for the activation energy which is remarkably low in comparison with all other results, and 4100 ohm^{-1} cm^{-1} for the conductivity at 0°C which is almost twice our value for tin of the same purity. After extensive measurements on gray tin powder obtained from three different lots, Busch and Wieland[4] conclude that the activation energy is (0.08 ±0.008) ev in good agreement with our values, especially with that for tin of Lot II. As mentioned in the introduction these authors conclude that measurements on powder do not yield a reliable value for the
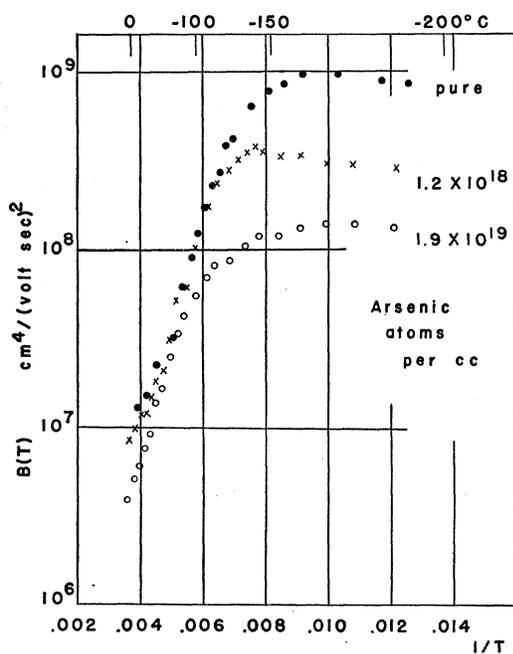

FIG. 9. Magnetoresistance coefficient of As-Sn alloys.

absolute magnitude of the conductivity. Through the assumption of a particular model they have calculated the value 2700 ohm^{-1} cm^{-1} for the conductivity at the transition temperature (13.2°C). When reduced to 0°C this value is about 20 percent higher than our value for tin of Lot II.

The variation with impurity content of the temperature dependence and the absolute value of the conductivity in the "intrinsic" range noted in Sec. IVB has not, to the authors' knowledge, been observed previously in gray tin. Kendall[6] has noted slightly different values of σ_0 (in the relation $\sigma = \sigma_0 \exp[-\Delta E/2kT]$) for different alloys but the smallest value was found
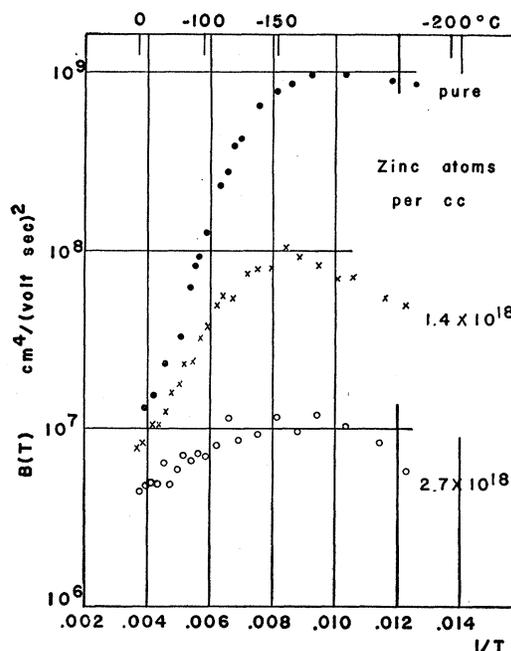

FIG. 10. Magnetoresistance coefficient of Zn-Sn alloys.

for the purest material which is the reverse of the effect noted above. An increase in the optical energy gap of InSb with increasing impurity content has been observed by Tanenbaum and Briggs[12] and attributed by Burstein[13] to the degeneracy of the material at relatively low charge-carrier densities. Whether or not this is also the explanation of the anomalous behavior of gray tin can best be decided after suitable optical measurements have been made. According to the present work the conductivity decreases as the slope increases suggesting that this decrease might be due entirely to the decrease in carrier concentration associated with the increased activation energy. That a decrease in carrier concentration does occur is also indicated by the Hall data of Busch and Wieland[4] and of Kendall[6] which, at high temperatures, show an increasing Hall coefficient with increasing impurity

[12] M. Tanenbaum and H. B. Briggs, Phys. Rev. 91, 1561 (1953).
[13] E. Burstein, Phys. Rev. 93, 632 (1954).

content. To investigate quantitatively the relationship between increased activation energy and decreased conductivity two quantities were calculated for various impurity concentrations and are compared in Fig. 11: (1) δE_c, the increase in activation energy required to account for the decrease in conductivity (at $-50°C$) observed between the pure sample and the doped sample in question and (2) δE_s, the observed increase in activation energy determined from the slopes of the corresponding conductivity curves. The displacement of some points from the 45-degree line is considerably larger than the experimental uncertainty, indicating that the added impurities influence the charge-carrier mobility as well as the activation energy. It should be mentioned that the measurements on germanium-stabilized gray tin referred to above gave the same slope as for pure material but a conductivity only 72 percent as large. The addition of an inactive impurity such as Ge apparently influences only the mobility.

There is considerable evidence that the pronounced minima displayed in Figs. 3 and 4 are characteristic of doped n-type material. In addition to the present data on Sb and As alloys, Busch and Wieland[4] have found this behavior in a Bi-doped specimen. This hypothesis would account for the minimum of Fig. 1 as well as that found by Busch, Wieland, and Zoller[2] in earlier work. In both cases the material contained 0.001 weight percent Sb in addition to smaller amounts of As and Bi. Since Sb is a very active impurity the minima in these cases are probably due primarily to it. If so, one would expect that the activation energy determined using tin of Lot I should compare favorably with that for the bottom curve of Fig. 3 and this is seen to be true. There is, however, a difference in conductivity which remains unexplained.

The temperature dependence of the magneto-resistance coefficient has been of considerable interest. According to usual theory based upon a number of simplifying assumptions,[14] the transverse magneto-resistance coefficient $B(T)$, defined in Sec. IVC, should be equal to the square of the charge-carrier mobility where carriers of only one sign are present. In the more complex situation involving the presence of carriers of both signs which we must consider in the high-temperature region of measurement for our samples, $[B(T)]^{\frac{1}{2}}$ should give the temperature dependence of the mobilities although more information is required to obtain absolute values.

For relatively pure material in this high-temperature range Busch and Wieland[4] have found a dependence of

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[14] An up-to-date summary of the standard theory and assumptions involved is given by C. Goldberg, Westinghouse Research Reports R-94416-3-0, 1953; and R-94416-3-P, 1953 (unpublished).
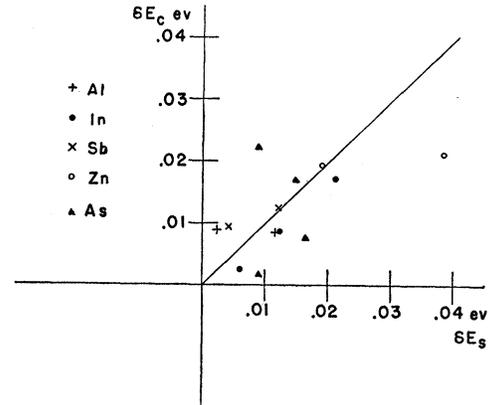

FIG. 11. Relationship of decrease in conductivity upon addition of impurities to the corresponding increase in activation energy observed. δE_c is the calculated increase in activation energy required to account for the observed decrease in conductivity at $-50°C$. δE_s is the increase in activation energy determined from slopes of the conductivity curves. Individual points correspond to different amounts of the added impurities shown in the legend.

the form

$$[B(T)]^{\frac{1}{2}} = AT^{-x},$$

with values of x between 3 and 3.5. This has led them to conclude that in particular the simplifying assumption of spherical energy surfaces in momentum space made in the theory is not justified since a $T^{-1.5}$ dependence is predicted for the mobility due to the scattering of the charge carriers by lattice vibrations. Our curves for pure tin as well as for alloys with Sb and As confirm their results and thus also their conclusion. However, comparison of absolute values for pure material shows that those of Fig. 8 are higher (by almost an order of magnitude) than those given by the above authors.

The rapid decrease of the magnetoresistance coefficient with increasing impurity content shown in Fig. 10 and the similar behavior of In-Sn and Al-Sn alloys was previously observed in Al-Sn alloys[2] and now appears to be characteristic of p-type gray tin. The reasons for the distinctly different behavior of p-type and n-type material are not entirely clear but the indications are that the addition of p-type impurity causes a greater tendency toward degeneracy and an increased importance of impurity scattering.

More quantitative analysis and interpretation of the conductivity and magnetoresistance data await the completion of Hall measurements now in progress. A method of mounting filaments to allow Hall coefficient determination has recently been devised, but only preliminary measurements have been completed.