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Specific Heats of Tin Alloys and Their Relation to the Superconducting Transition Temperature*†

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The specific heat between 1.2° and 2.2°K of a number of alloys of tin was measured. The alloys studied were Sn+Bi, Sn+In, and Sn+(InSb). These measurements enabled us to deduce the effect of alloying on the Sommerfeld γ and Debye Θ of tin. We find that the changes in the former are compatible with the simple rigid parabolic band model of alloying, and that the latter depends only on the electron per atom ratio. The expression for the superconducting transition temperature given by the Bardeen-Cooper-Schrieffer theory was then used to estimate the changes in T_c to be expected from the measured changes in γ and Θ. This accounts for only a part of the observed changes in transition temperature and we conclude that the increase in T_c at high solute concentrations is mainly due to effects of alloying on the mean electron-electron interaction energy, V, of the theory.

I. INTRODUCTION

A NUMBER of experiments in this laboratory on very dilute alloys,[1–3] on plastically deformed aluminum,[4] and on indium foils[5] seem to establish that as the electronic mean free path in superconductors decreases, the transition temperature also decreases. This behavior is evident in alloys, however, only in the range of extreme dilution. As the impurity concentration is increased in tin, indium, or aluminum, the superconducting critical temperature T_c soon becomes dependent on the valence of the added elements. As shown in Fig. 4 for tin alloys, impurities with more electrons than the host produce a minimum in T_c at relatively low concentrations, and then force the transition temperature to values higher than that of the solvent. Impurities with fewer electrons continue to decrease T_c with increasing concentration, but do so at a steadily diminishing rate. The data for alloys containing indium antimonide[6] in which the electron per atom ratio is unchanged fall in between these two extremes. Recent work by Seraphim *et al.*[7] showed that the distinction between the two valence groups is only a matter of degree, since for tin, indium, or aluminum containing sufficiently high concentrations of solute elements of lower valence, T_c also goes through a minimum and finally becomes greater than the value for the solvent superconductor. Moreover, these authors showed that all the data can be fitted to an empirical formula containing two constants (which depend on the solute for a given solvent), suggesting that there is some universal type of impurity behavior, at least in the three superconductors so far investigated.

According to the Bardeen-Cooper-Schrieffer (BCS) theory,[8] the superconducting critical temperature is given by

$$T_c = 1.14\hbar\omega \exp[N(0)V]^{-1}. \qquad (1)$$

In this expression, V is the mean electron-electron interaction energy, ω is an average phonon frequency and thus proportional to the Debye temperature Θ, and $N(0)$ is the density of electron states at the Fermi surface and hence proportional to the Sommerfeld electronic specific heat constant γ. All three quantities, V, ω, and $N(0)$, are likely to be affected by the addition of impurities to the solvent metal. Thus the impurity effects on T_c just described could be due to changes in all three. From the point of view of the theory of superconductivity of alloys, it seems interesting to determine how much of the variation in T_c is due to changes in γ and Θ, so that one can perhaps determine how V changes on alloying. From (1) it follows that

$$\left.\frac{d\ln T_c}{dx}\right|_{V=\text{const}} = \frac{d\ln\Theta}{dx} + [N(0)V]^{-1}\frac{d\ln\gamma}{dx}, \qquad (2)$$

where x is the atomic concentration of impurities. Using this to obtain the changes in T_c due to measured changes in γ and Θ, and subtracting these from the total impurity effects on T_c, one is then left with the change in T_c attributable to the variation in V. We attempted an analysis of this sort some years ago.[3] The changes in γ were inferred from the critical magnetic-field curves of the alloys. These changes appeared to

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

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

[3] B. Serin, *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1961), p. 391.

[4] W. Joiner and B. Serin (private communication). See also reference 3.

[5] E. A. Lynton and D. McLachlan, preceding paper [Phys. Rev. **126**, 40 (1962)].

[6] S. Wipf, thesis, Imperial College, University of London, 1961 (unpublished). We are grateful to Dr. Coles and Dr. Wipf for lending us a copy of this dissertation. See also B. R. Coles, IBM J. Research Develop. **6**, 68 (1962).

[7] D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta Met. (to be published).

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

TABLE I. The alloys measured, and the observed fractional changes in electronic specific heat constant and Debye temperature.

Specimen	$\Delta\gamma/\gamma$ (%)	$\Delta\Theta/\Theta$ (%)
Sn+2.9% In	−1.4	−3.8
+3.9% In	−0.9	−4.5
+5.6% In	−2.3	−6.4
Sn+1.0% Bi	+0.4	−1.8
+3.6% Bi	+0.6	−5.4
+5.3% Bi	+2.4	−6.6
Sn+1.9% (InSb)	−0.2	−1.3
+4.1% (InSb)	+0.5	−1.3
+4.9% (InSb)	+0.2	−1.2

be large and always to increase the electron specific heat independently of the valence of the solute. As we shall show, the present measurements contradict the earlier inferences concerning γ. Furthermore, in some of the systems the changes in Debye temperature on alloying are reasonably large.

In this investigation the impurity effects on Θ and γ were inferred from measurements of the normal phase specific heat of pure tin and of a number of tin alloys listed in Table I. The experiments were carried out between 1.2° and 2.2°K, and at these low temperatures one can express the specific heat of the normal metal by

$$C=\gamma T+a(T/\Theta)^3, \tag{3}$$

where $a=1.944\times10^6$ mjoules/°K mole. By fitting the specific heat data to this expression, we obtain the values of γ and Θ for our specimens.

II. SPECIMENS

The specimens were prepared from tin and alloying metals, all of purity better than 99.99%. Starting ingots were cast in Pyrex tubes under a vacuum of better than 5×10^{-6} mm Hg. The melts were mechanically stirred and outgassed for about 12 hr, and then cooled in a few minutes. Cylindrical specimens about $1\frac{5}{8}$ in. long and $\frac{3}{4}$ in. diameter were machined from the ingots. These had a mass of about 85 g, corresponding to 0.7 mole. After machining, the specimens were annealed at 185°C for at least 27 days. The specimens were usually measured within a day after removal from the annealing oven.

The most recent phase diagrams[9] indicate that at the annealing temperature about 6.5 at. % Bi is soluble in tin, and that for In the limit is about 11 at. %. Both these figures exceed the maximum concentrations (5.6 at. % In and 5.3 at. % Bi) in our specimens. At room temperature, the solubility of In exceeds 6 at. %, but the solubility of Bi in tin is only about 0.5 at. %. There is thus a chance that some bismuth precipitated out of solution in the interval between the removal of the specimens from the oven and the measurements. However, the data for the specimens containing bismuth were of just as good quality and consistent with those for the specimens containing indium. Moreover, in earlier investigations of alloys, we showed that after long annealing tin specimens containing high concentrations of bismuth are quite well behaved.[10] We therefore do not believe that there was much bismuth precipitation in our method of specimen preparation. As for Sn+(InSb), Zitter[11] gives a solubility of about 7 at. % at 185°C, and Rayson *et al.*[12] state that the room temperature solubility is 6 at. %, so that it would appear that there is little danger that our maximum concentration of 4.9% (InSb) exceeded the limit of solubility.

As a check on the concentration of our alloys, the residual resistivity of a few specimens was measured at 4.2°K, and the values agreed with those to be expected from our measurements on more dilute alloys.[3] The magnetic field needed to restore completely the normal resistance at 1.5°K was determined and found to be about 600 oe, which is more than double the critical magnetic field of pure tin.

The fact that the critical field to restore the resistance of alloys is much larger than that of pure metal is well known, and Abrikosov[13] and Goodman[14] have suggested that this behavior is to be expected on fundamental grounds and is not necessarily associated with inhomogeneities of composition. Even if there are inhomogeneities contributing to the retention of low resistance in high fields, it is generally agreed[15] that this is due to fine superconducting threads in a matrix of normal metal. The volume of such threads would be small enough to affect but little our specific heat determinations which give an average value for the specimen as a whole.

All the measurements reported here were made in external fields exceeding 650 oe. In the few runs where the field was initially too small, the specimen temperature showed erratic jumps on warming similar to those reported by Yaqub.[16] This condition was corrected by merely increasing the field until the jumps disappeared.

III. APPARATUS AND PROCEDURE

The essential parts of the calorimeter used in this investigation are shown schematically in Fig. 1. This apparatus is sufficiently different from those usually used to warrant brief description. While not useful for

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[9] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed.

[10] E. A. Lynton and B. Serin, Phys. Rev. **112**, 70 (1958).

[11] R. N. Zitter, Trans. Met. Soc. AIME **212**, 31 (1958).

[12] H. W. Rayson, C. W. Goulding, and G. V. Raynor, Metallurgia **59**, 57 (1959).

[13] A. A. Abrikosov, Soviet Phys.—JETP **5**, 1174 (1957).

[14] B. B. Goodman, Phys. Rev. Letters **6**, 597 (1961); IBM J. Research Develop. **6**, 63 (1962).

[15] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), pp. 39 *ff*.

[16] M. Yaqub, Cryogenics **1**, 1 (1961).

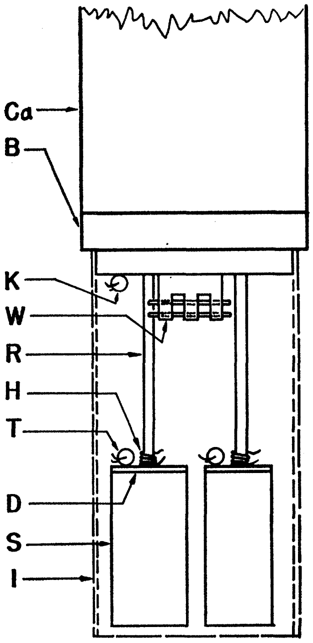

FIG. 1. A schematic diagram of the calorimeter. The letter symbols are defined in the text.

a wide range of investigations, it proved suitable for our particular purposes.

The calorimeter held two specimens in symmetrical arrangement. Each specimen *S* was cemented with GE 7031 varnish to a thin copper disk *D* to which was also attached a carbon resistance thermometer *T* and a heater *H*. The specimens could be removed from *D* or attached to it without disturbing either thermometer or heater. The disk was permanently soldered to a thin-walled stainless steel tube *R* and the upper end of this tube was attached to the copper base *B* of the stainless can *Ca* which held liquid helium. Also attached to *B* was another carbon resistor *K* used to monitor the temperature of the helium bath, and a copper heat station *W* at which the copper leads coming down from room temperature were terminated. All wires connecting *W* to *T* and *H* were of low thermal conductivity.

The thermometers were 56-ohm Allen Bradley $\frac{1}{2}$-w resistors with the ceramic coating partly removed. Each was cemented with the same varnish into thin copper sleeves, and the sleeve was then soldered to the disk, *D*. Current and potential leads of No. 40 constantan wire were attached to the thermometers. The heaters were wound noninductively from constantan wire and each had a resistance of about 200 ohms. The current leads to the heater were of superconducting niobium, and potential leads were attached to the niobium at *W*.

The specimens and associated parts were surrounded by the radiation shield, *I*, which was thermally connected to the helium bath, and which also had baffles in the bottom to permit the sample space to be evacuated. Can *Ca* was terminated at the top with appropriate pumping and vent tubes which passed through a liquid nitrogen shield and a cap at room temperature. The whole assembly was placed in a standard double glass Dewar system, which was inside a large solenoid. Exchange gas could be admitted to the inner of the two Dewars and evacuated through a side arm in the cap. O rings were used to seal the cap to the Dewar. Leads were brought in through wax seals in the cap.

Both the heater current and voltage drop and the thermometer current and voltage drop were measured potentiometrically. In the case of the thermometer, the potential leads were connected to a microvolt potentiometer whose output went to a dc amplifier connected to a recording voltmeter. The potential across the thermometer was roughly balanced by appropriate dial settings, and the off-balance was read off the recorder trace. A current of 1 μa was sent through the thermometers when their resistance was less than 10^4 ohms, and this was reduced to 0.1 μa when the resistance exceeded this value, so that the power dissipated in the thermometers never exceeded 10^{-8} w.

In order to obtain an accurate thermometer calibration, all measurements were taken at temperatures less than the λ point of liquid helium. Moreover, to insure that the thermometers were at the same temperature as the liquid in *Ca*, the exchange gas pressure was made great enough so that liquid He II was condensed in the inner Dewar. Under these circumstances, the specimens and thermometers are covered with a superfluid film in contact with the helium bath in *Ca*. Eight calibration points were taken between 1.23° and 2.14°K, by holding the temperature of the bath in *Ca* constant to about 0.5 mdeg with help of the resistor, *K*, and measuring the thermometer resistances and the vapor pressure over the helium bath. This pressure was determined by means of an oil manometer and cathetometer. The pressures were converted to absolute temperatures using the 1958 scale,[17] and resistance values as a function of temperature were fitted to the standard two-constant formula.[18] A correction curve relating the temperatures as given by the formula to the measured temperature was then plotted. The correction curves for the various runs were all smooth and all had the same shape. We estimate our error in temperature measurement to be about 0.5 mdeg.

After calibration, in order to facilitate removal of the exchange gas and provide sufficient running time, the bath was warmed to 4.2°K, *Ca* was refilled with liquid, and the exchange gas pressure reduced to about 5 μ. The temperature of the bath was reduced to 1.2°K, and the exchange space was evacuated until the pressure at room temperature was less than 10^{-6} mm Hg. The magnetic field needed to quench the superconductivity was then turned on. Throughout the remainder of a run, the bath was kept at 1.2°K.

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[17] H. van Dijk, H. Durieux, J. R. Clement, and J. K. Logan, Natl. Bur. Standards Monograph 10 (1960).

[18] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952); see also P. Lindenfeld, *ibid.* **32**, 9 (1961).

The specific heat C of a specimen was determined by sending power P through the heater for a time Δt, and measuring the resistance change of the thermometer as indicated by the change in off-balance of the recorder. From calibration measurements this resistance change could be connected to a temperature change ΔT, so that

$$C=(1/n)(P\Delta t/\Delta T), \tag{4}$$

where n is the number of moles in a specimen. The time Δt was measured by an electric timer of rated accuracy ± 2 msec, which was turned on by the same switch that controlled the heater current. The heat pulses were of about 30 sec duration, and the power was adjusted so as to give a total temperature change of about 0.1°K.

It is clear that with the bath at 1.2°K, as the specimen is warmed by the heat pulses, there will develop a considerable heat leak to the bath through the stainless steel tube, R. To take account of this heat leak, we adopted a different procedure from that used in the usual calorimeter where every effort is made to isolate the specimen adiabatically. Our procedure is similar to that used by Logan *et al.*,[19] but differs from it in detail. Whenever the specimen was at a higher temperature than the bath, and before a heat pulse was taken, the current through the heater was adjusted to the appropriate value I_1 to maintain the specimen temperature constant as indicated by the recorder trace. A heat pulse was initiated by switching the heater current to a new value, $I_2>I_1$, and the pulse was terminated by switching the current back to its initial value I_1. The specimen then would cool very slowly (at a rate $\leqslant 3\%$ of the heating rate during the pulse) toward its initial temperature. Because the rate of temperature change before and after the pulses was small, the temperature curves in these periods could be extrapolated to the mid-time of the pulses to find the temperature change produced by heater power during the pulse. In this method, the value of the power used in Eq. (4) is the difference between the power during the pulse and the initial (or final) power. Our heat pulses generally showed no detectable initial delay or later overshoot, indicating that the thermometer and heater were in good thermal contact with the specimen. Specific heat determinations were made at about 10 temperatures in the interval 1.2° to 2.2°K.

The heat capacity of the addenda (disk, thermometer, varnish, and heater) as a function of temperature was measured in separate runs. Because of their small heat capacity, the accuracy of these measurements was only about 10%. However, since the addenda formed only about 3% of the total heat capacity with specimen present, this uncertainty contributes an error of only about 0.3% to the value of the specimen specific heat. The addenda heat capacity was subtracted from the total heat capacity before the specific heat was calculated.

TABLE II. The results of several runs on pure tin specimens and the results of two other independent investigations.

Sample	γ(mjoule/mole °K)	Θ(°K)
1	1.80	198
2	1.81	197
1	1.78	196
2	1.79	196
2	1.80	196
Combined	1.80	196.5
Corak and Satterthwaite[a]	1.75	195
Bryant and Keesom[b]	1.80	200

[a] See reference 20. [b] See reference 21.

Considering all sources of error, we estimate the accuracy of our specific heat values to be about 1%.

IV. RESULTS

A. Pure Tin

To check on our accuracy both absolute and relative, we made five determinations of the specific heat as a function of temperature of two different pure tin specimens. The results of fitting each set of data by the method of least squares to Eq. (3) are listed in Table II. The entry labeled "combined" is the result of fitting all the data to this same equation. Also listed are the results of two recent detailed investigations of the low-temperature specific heat of tin.[20,21]

Because of the limited temperature range of our measurements, we could not detect higher order terms in the temperature dependence of the lattice specific heat. We consider the agreement between our values of γ and Θ and the others listed in Table I to be satisfactory.

In order to show the self-consistency and the scatter of the data on a magnified scale, we made plots of the quantity

$$\delta\equiv\frac{C-C_p}{T}=(\gamma-\gamma_p)+aT^2\left(\frac{1}{\Theta^3}-\frac{1}{\Theta_p{}^3}\right), \tag{5}$$

as a function of T^2. C is the measured specific heat, and C_p is the value given by Eq. (3) for the "combined" or average values for γ and Θ for the pure specimens, i.e., $\gamma_p=1.80$ mjoule/mole °K and $\Theta_p=196.5$°K. Such a plot is shown in Fig. 2(b), where it can be seen that the deviations from the average are satisfactorily small. The data shown in Fig. 2(b) are by no means our best, but they were chosen to illustrate the fact that in some runs δ tended to deviate systematically upwards at both the low and high ends of the temperature interval. This systematic behavior probably stemmed from our lack of knowledge of the thermometer

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[19] J. K. Logan, J. R. Clement, and H. R. Jeffers, Phys. Rev. **105**, 1435 (1957).

[20] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

[21] C. A. Bryant and P. H. Keesom, Phys. Rev. **123**, 491 (1961).

resistance vs temperature curve at the ends of the calibration interval. In any case, the determination of γ became more difficult in those runs in which the deviation was evident, the uncertainty in a few cases approaching 2%.

B. Alloy Specimens

For each of the specimens listed in Table I the quantity δ was fitted by the method of least squares to an equation of the form (5). The data for the Sn+3.5% Bi specimen are shown in Fig. 2(a) along with the line giving the least-squares fit. Three things are clear from this figure: the scatter in the data is quite small; there is an appreciable change in Θ because of the positive slope of the line; and the change in γ, if any, is very small as evidenced by the small intercept.

By treating the data as outlined in the foregoing paragraph, we obtained the values listed in Table I for the fractional changes in γ and in Θ of the alloy specimens which we will now discuss.

Three facts emerge concerning the electronic specific heat constant. The changes produced by alloying are very small, being comparable to our experimental error. Despite the poor resolution one can infer that γ is increased by alloying tin with bismuth, and decreased by alloying it with indium. The changes in γ produced by alloying with (InSb) are probably negligible. This last result is to be expected since the net valence of (InSb) is zero, and the volume change is quite small.[12] The first two results are in disagreement with the values which we indirectly deduced[3] from the critical magnetic field curves of dilute tin alloys, where we seemed to find that γ always increased regardless of the valence of the impurity. The magnitude of the rate of increase of γ with concentration also appeared to be several times greater than in the current investigation. We are now convinced that the γ values of alloys deduced from our magnetic data were wrong because one or the other of the implicit assumptions were unjustified. We believe that the γ values determined calorimetrically in the current investigations are much more reliable. This obtains support from the measurements on a Sn+1% In alloy by Yaqub,[16] who could not detect any change in γ within his experimental uncertainty of 2%.

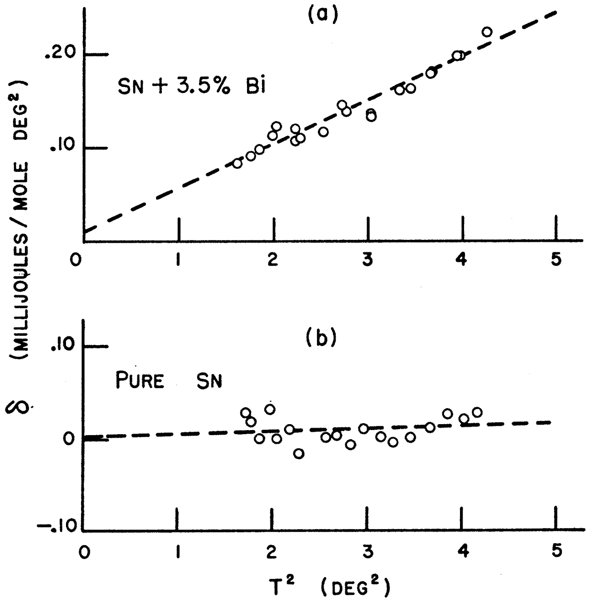

FIG. 2. A plot of the quantity δ, as defined by Eq. (5), as a function of T^2 for (a) a sample of Sn+3.5 at. % Bi, and (b) a sample of pure tin.

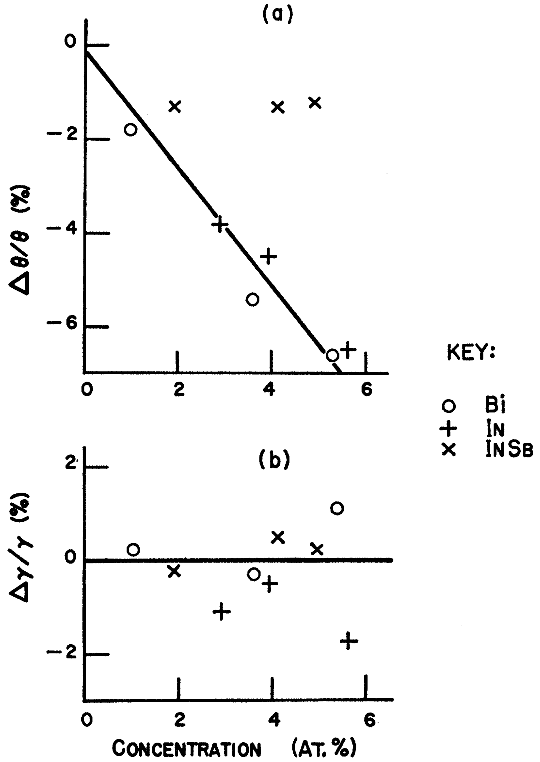

FIG. 3. (a) $\Delta\Theta/\Theta$ and (b) $\Delta\gamma/\gamma$, plotted as a function of solute concentration, in atomic percent, for tin samples containing bismuth, indium, and indium antimonide. For $\Delta\gamma$, the changes to be expected from the rigid band model of alloying have been subtracted from the measured values.

As nearly as we can tell, the changes in electronic specific heat constant are comparable to what would be expected from the rigid parabolic band model of alloying,[22] according to which

$$\gamma \propto V^{\frac{2}{3}} Z^{\frac{1}{3}},$$

where V is the atomic volume, and Z is the average number of free electrons per atom. From the determinations by Lee and Raynor[23] of the volume changes produced in these alloys, and assuming that Bi has a

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[22] J. Friedel, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

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

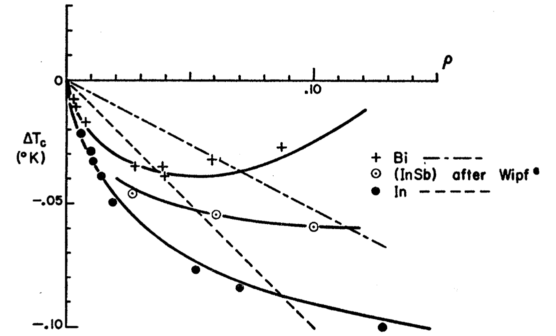

FIG. 4. The full lines show the change in critical temperature plotted against residual resistivity as measured by LSZ[1] for Sn+Bi and Sn+In, and by Wipf[6] for Sn+(InSb). The two dotted lines show the change in T_c for Sn+Bi and for Sn+In, respectively, deduced from Eq. (2) and the observed changes in γ and Θ.

valence of 5 and In of 3, one can use this expression to calculate the changes in γ expected on this model, and subtract them from the measured values. The results of this subtraction are shown in Fig. 3(b), where it is clear that all data cluster about zero, and that the maximum deviation is less than 2%. We therefore feel that within our experimental error the effect of alloying on the electronic specific heat of tin can be represented by this very simple model.

This result is somewhat surprising considering the complicated shape of the Fermi surface of tin.[24] It seems appropriate to point out, however, that γ can be written[25]

$$\gamma \propto A v_0^{-1},$$

where A is the *total* area of the Fermi surface in momentum space. v_0 is an appropriate average of the electron velocity on this surface. Thus γ is determined only by the gross properties of the Fermi surface. On this basis it does not seem so improbable that impurities, while perhaps drastically affecting particular small parts of the Fermi surface, could leave its total area only slightly changed. This appears particularly reasonable in view of the fact, pointed out by Harrison,[26] that in spite of its complications, the Fermi surface of tin can be reassembled into a nearly spherical body with small "bumps" each covering not more than 6° of arc. As further supporting evidence for our conclusion, we wish to point out that measurements[27] of the change in γ of tin with volume also yield a value close to that expected from a free electron model.

The changes in Debye temperature listed in Table I are comfortably greater than our experimental error. Θ decreased with increasing impurity concentration at the rate of about -1.2% per atomic percent and seems to depend only on the magnitude of the electron to atom ratio as shown in Fig. 3(a). We are not sure whether the small decrease of Θ exhibited by the (InSb) alloys is real or due to some small systematic error; since the change is comparable to our experimental error, we consider any changes in Θ in these alloys to be negligible. The result that the change in Θ produced by alloying depends on the electron per atom ratio agrees with the measurements of Rayne[28] on copper alloys. We know of no theory of this effect.

IV. SUPERCONDUCTING TRANSITION TEMPERATURES OF TIN ALLOYS

In using the results of this investigation to estimate the changes in transition temperature to be expected from changes in γ and Θ, we assume that the foregoing conclusions apply to our tin alloy systems. These are: (a) the changes in electronic specific heat constant are given by the rigid parabolic band model of alloying, and (b) the Debye temperature depends only on the magnitude of electron per atom ratio, and changes at the rate $d\ln\Theta/dx = -1.2$ as determined from Fig. 3(a).

Using these assumptions and the changes in atomic volume determined by Lee and Raynor,[23] the changes in transition temperature given by Eq. (2) were calculated assuming $[N(0)V]^{-1} = 3.8$. The results are shown by the dashed lines in Fig. 4 for the alloys of bismuth and indium. The reason that the slope of the line is smaller in the case of bismuth than for indium is that in the first instance the effect of γ on T_c is opposite to the effect of Θ, whereas in the latter case the two effects are in the same direction. For the (InSb) alloys, we expect no change in transition temperature due to Θ and γ effects because the electron per atom ratio is unchanged in these alloys.

Assuming that the initial decrease in transition temperature is determined by the decreasing electron mean free path, it seems clear from Fig. 4 that the subsequent rise of T_c at higher concentrations cannot be accounted for by the changes in density of electronic states and Debye temperature which result from alloying. Anderson[29] has suggested that the initial decrease of T_c is caused by the superconducting energy gap becoming isotropic when the electron mean free path about equals the range of coherence, and Richards[30] has obtained direct experimental evidence for this effect. Since according to Anderson's theory the gap has become isotropic at a concentration corresponding to about the minimum in the curve in Fig. 4 for bismuth alloys,[5] it follows that the increase in T_c cannot on this basis be due to a change from an anisotropic to a more isotropic energy gap.

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[24] A. V. Gold and M. G. Priestley, Phil. Mag. **5**, 1089 (1960).

[25] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).

[26] W. Harrison, IBM Conference on Superconductivity, 1961 (unpublished).

[27] For a review of measurements of the effect of pressure on γ, see: J. L. Olsen and H. Rohrer, Helv. Phys. Acta **33**, 872 (1960).

[28] J. Rayne, Phys. Rev. **110**, 606 (1958).

[29] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[30] P. L. Richards, Phys. Rev. Letters **7**, 412 (1961); see also Y. Masuda and A. Redfield, reference 3, p. 413; Y. Masuda, Phys. Rev. (to be published).

Within the framework of Eq. (1), we seem to have to conclude that alloying appreciably affects the mean electron-electron interaction V.[31] It is interesting to note the effect of algebraically subtracting the dashed lines in Fig. 4 from the appropriate solid curves. The curve of ΔT_c vs (residual resistance ratio) for the (InSb) alloys remains unchanged, and the shape of the curve for the Bi alloys is little altered, being pushed toward increasing values of T_c at the higher concentrations. The form of the curve for the In alloys is changed, however, and closely resembles that for bismuth, with a minimum and a subsequent upward trend. Thus our specific heat results lead to very similar curves for the alloying effect on T_c of tin, once the effect of changes in γ and Θ has been taken into account. This conclusion is already implicit in the work of Seraphim *et al.*[7] It would appear, therefore, that in tin alloys (and by inference in indium and aluminum alloys as well) the effect of alloying on V is such as to result in an increasing T_c once the electronic mean free path becomes less than the range of coherence. To determine this residual effect on V one must subtract small quantities of comparable magnitude. Unfortunately, the accuracy of our present data does not permit us to determine whether V depends only on electronic mean free path, or whether there is a residual dependence on valence.

In conclusion, it may be useful to emphasize that the solute concentrations used and the resulting changes in T_c are much smaller than those considered in various recent surveys of binary and ternary compounds.[32,33] Consequently our conclusions concerning small changes in V do not directly affect the question of the relative insensitivity of V to large-scale variations in composition.

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[31] According to P. Morel, J. Phys. Chem. Solids **10**, 277 (1959), a change in V is expected to arise from variations in lattice spacing. However, the changes in lattice parameters for these alloys are so small[23] that even the largest resulting change in V is about an order of magnitude smaller than the total alloying effect which we observe.

[32] B. B. Goodman, J. Hillairet, J. J. Veyssié, and L. Weil, reference 3, p. 350.

[33] J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

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Mössbauer Study of Hyperfine Fields and Isomer Shifts in Fe_4N and $(Fe,Ni)_4N$

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Mössbauer measurements of Fe^{57} were made on ferromagnetic Fe_4N, which has a face-centered cubic arrangement of iron atoms with nitrogen at the body-center position. The hyperfine fields are 345 koe for the corner Fe and 215 koe for the three face-center Fe, approximately proportional to their magnetic moments, $3\mu_B$ and $2\mu_B$. The isomer shifts, measured against a stainless steel source, are 0.30 mm/sec for the corner Fe and 0.45 mm/sec for the face-center Fe. These values are in line with their proposed electronic configurations of $3d^74s$ and $3d^84s$, which are derived on the assumption that the nitrogen at the body-center position acts as an electron "donor" to the face-center Fe. The Mössbauer spectra of $(Fe_{3.6},Ni_{0.4})N$ and $(Fe_3Ni)N$ are consistent with their ordered structures in which Ni replaces the corner Fe preferentially.

INTRODUCTION

THE magnetic properties of Fe_4N have been the subject of several investigations in recent years, since its simple structure offers an ideal case for the study of the effects of local environment on electronic configuration and magnetic moments. The crystal structure may best be visualized as a face-center γ iron lattice with nitrogen at the body-center position[1] (see Table I). The corner Fe atom, Fe I, is surrounded by 12 Fe nearest neighbors at 2.96 A, while the face-center Fe atom, Fe II, has two nitrogens at 1.90 A as the nearest neighbors. The body-center nitrogen is surrounded by an Fe II octahedron.

Guillaud and Creveaux[2] have reported a saturation moment of 2.2 Bohr magneton per Fe atom for Fe_4N approximately $9\mu_B$ for the formula unit. Wiener and Berger[3] have proposed a magnetic structure, in which $3\mu_B$ and $2\mu_B$ are assigned to Fe I and Fe II, respectively. This model was based on the assumption that nitrogen acts as a "donor" of electrons, giving one electron to each of the three nearest Fe II atoms. This gives electronic configurations of $3d^74s$ for Fe I and $3d^84s$ for

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[1] K. H. Jack, Proc. Roy. Soc. (London) **A195**, 34 (1948).

[2] C. Guillaud and H. Creveaux, Compt. rend. **222**, 1170 (1946).

[3] G. W. Wiener and J. A. Berger, J. Metals **7**, 360 (1955).