Superconductivity in Tin-Bismuth and Tin-Antimony Alloys*

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(Received April 27, 1953)

The Meissner effect in a series of spherically shaped solid solution alloys of tin with bismuth and antimony has been investigated. Magnetization curves have been obtained as a function of temperature and composition, from which critical field curves and transition temperatures have been derived. Increasing breadth of the magnetization curves and frozen in moment have been observed with increasing solute concentration. Thermodynamic analysis of the critical field data has shown an interesting variation of the electronic specific heat coefficient γ with solute concentration, which has been interpreted in terms of the overlapping band structure of tin.

I. INTRODUCTION

A STUDY of superconductivity in tin-bismuth and tin-antimony alloys is of interest because the electron-atom ratio can be increased by alloying bismuth and antimony, which have a valence of five, with tin, whose valence is four. In this manner, one can hope to obtain the influence of electron concentration on the superconductive properties of these alloys.

II. PREPARATION OF SAMPLES

Although bismuth and antimony are not soluble in tin to any appreciable extent at room temperature, the limits of solubility are increased considerably at higher temperatures.[1] Consequently, the samples studied must be kept in an annealing oven at temperatures sufficient to keep them in solid solution and must be rapidly quenched in a low temperature bath just prior to taking any measurements on them.

The samples were prepared from spectroscopically pure metals supplied by Johnson-Mathey, Ltd. The component metals were weighed in an analytical balance and melted over a Bunsen burner in a closed graphite crucible. The crucible was shaken vigorously to homogenize the melt and was quenched in running water. The resulting slug was remelted into a graphite mold made in two halves so that spherical specimens could be obtained. The mold was placed in a shallow pan of cool water so that the melt cooled from the bottom. This technique gives single crystals of pure tin most of the time, but results only in a large-grained polycrystalline sample for the alloys.

The tin-bismuth samples were kept in an annealing oven at 135°C where the limit of solid solubility is 12 atomic percent. Most of the samples were annealed for several weeks before any measurements were taken. The tin-antimony alloys were annealed at 225°C for 24 hours. At this temperature, antimony is soluble in tin up to 10 atomic percent. The tin-bismuth samples were quenched in liquid air just prior to taking the measurements. The tin-antimony samples were quenched in a bath of dry ice and acetone.

* This research has been carried out with the support of the U. S. Atomic Energy Commission.

[1] *Metals Handbook* (American Society for Metals, Cleveland, 1948), pp. 1180 and 1239.

III. EXPERIMENTAL TECHNIQUE

The method of taking measurements is the same as reported in an earlier paper.[2] The sample is displaced from the center of one pick-up coil to the center of another wound in opposition to the first, both coils located in a bath of liquid helium along the axis of an external solenoid surrounding the liquid helium dewar. When the sample acquires a magnetic moment in the field of the external solenoid and is displaced from one pick-up coil to the other, the flux changes in the coils add up to produce a deflection of an external galvanometer in series with the coils proportional to the magnetic moment of the sample.

IV. EXPERIMENTAL RESULTS

A set of typical magnetization curves for different alloys of tin-bismuth are shown in Figs. 1–3. The ratio of the galvanometer deflection to the maximum deflection at any field ($D/D_{\max}$) is plotted against H/H_{c2}, where H_{c2} is taken to be the value of the external field at which penetration by that field is complete. H_{c1} will denote the field which first penetrates the specimen and is obtained by multiplying the field corresponding to the maximum in the magnetization curve by $\frac{3}{2}$ to account for the enhancement of the field at the equator of a sphere. Although H_{c1} and H_{c2} are the same for a pure metal, H_{c2} can be much greater than H_{c1} for an alloy. This fact, together with the much larger frozen in flux (irreversibility in the magnetization curve), constitutes the main difference in behavior between alloys and pure metals. The spread in the magnetic transition, as evidenced by the degree of "tailing" in the magnetization curves, increases with increasing bismuth content. The frozen in flux in general increases, but it also depends on the grain structure in the specimen. It is felt that the field H_{c1} is more indicative of the critical field characterizing the bulk of the sample and that H_{c2} is a measure of the inhomogeneity of composition or internal strain in the material. This supposition is given support by the influence of annealing on the magnetization curve of a tin+5 atomic percent bismuth alloy, as shown in Fig. 4. In this

[2] Love, Callen, and Nix, Phys. Rev. 87, 844 (1952).

figure, two magnetization curves are shown, corresponding to annealing times of 1 day and 45 days. Although the value of H_{c1} is uninfluenced by the prolonged annealing, H_{c2} and the frozen in moment are reduced considerably by this process. This shows that inhomogeneity of composition, which is removed by annealing, has a considerable effect on the breadth of transition, as one would expect. However, any further annealing no longer affects the magnetization curve even though some spread in the transition remains. This would indicate that even the most homogeneous alloy still has a considerable breadth of transition. This "inherent" breadth of transition could be due to internal strains caused by size differences between tin and bismuth atoms. Such effects have been observed by Wexler and Corak[3] who found that the breadth of transition in the hard superconductor vanadium was due to internal strains caused by dissolved interstitial impurity atoms of oxygen and nitrogen.

By taking magnetization curves at different temperatures, critical field data for alloys up to 10 atomic percent of Bi has been obtained. Critical field curves

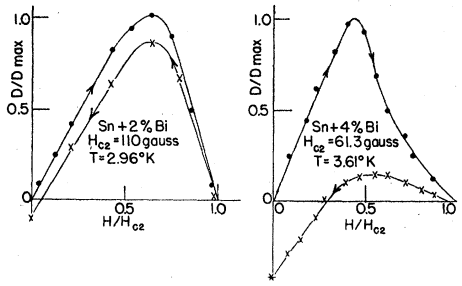


FIG. 1. Typical magnetization curves for Sn+2 atomic percent B and Sn+4 atomic percent Bi.

for alloys containing 2, 4, 6, and 8 atomic percent Bi are shown in Fig. 5, where both H_{c1} and H_{c2} are plotted against T^2. As can be seen from these curves, both of these fields can be represented fairly closely by a straight line.

The temperature breadth of transition of these alloys is represented in Fig. 6, where the galvanometer deflection in a small field (usually 2 gauss) is plotted as a function of temperature. There is a fair amount of breadth to these transitions as one would expect from the magnetization curves. However, the greater part of the transition takes place within one-tenth of a degree, indicating that the bulk of the material has a fairly well defined transition temperature.

The transition temperature T_c, obtained from the transition curves, is plotted as a function of the atomic percent of bismuth in Fig. 7.[4] T_c was obtained from the transition curves by extrapolating the linear portion

[3] A. Wexler and W. S. Corak, Phys. Rev. 85, 85 (1952).

[4] In a private communication to the author, B. Serin has pointed out that T_c actually passes through a minimum around 0.1 atomic percent bismuth.

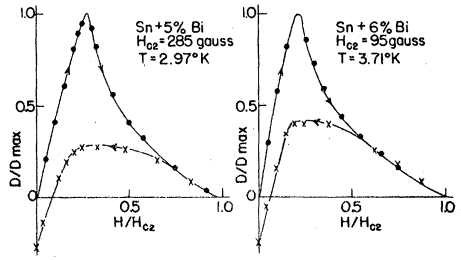


FIG. 2. Typical magnetization curves for Sn+5 atomic percent Bi and Sn+6 atomic percent Bi.

of the curves to zero deflection, and thus corresponds to the temperature at which the first appreciable sign of superconductivity appears. The behavior is in accordance with the known behavior of bismuth, that of raising the transition temperature when alloyed

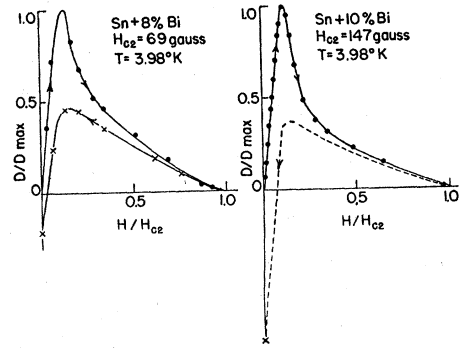


FIG. 3. Typical magnetization curves for Sn+8 atomic percent Bi and Sn+10 atomic percent Bi.

with other superconducting elements. It behaves as if bismuth would be a superconductor with a high transition temperature if it were to crystallize into the tetragonal white tin structure.

A less extensive survey of tin-antimony has been carried out in order to see what similarities exist

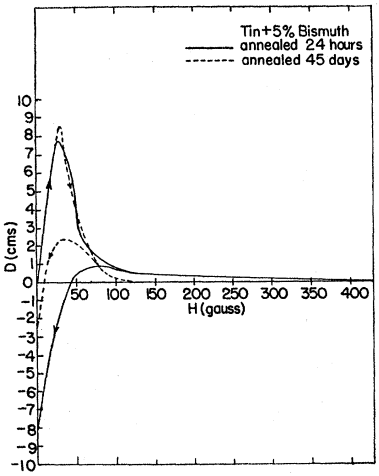


FIG. 4. Effect of annealing on the magnetization curve for Sn+5 atomic percent Bi.

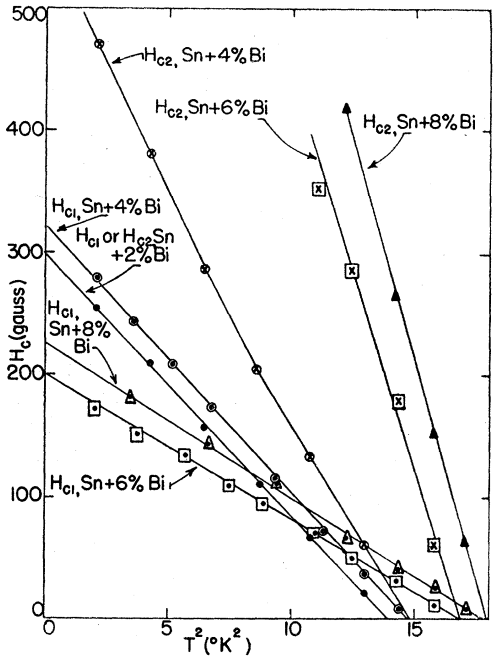


FIG. 5 Critical field curves for Sn-Bi alloys.

between tin-antimony and tin-bismuth alloys. Since both antimony and bismuth have the same valence, one can reasonably suppose that any similarities in behavior would be caused by the concentration of valency electrons, which is the same for alloys of the two systems having the same composition.

Similar measurements on the tin-antimony alloys were carried out and the results of these measurements are shown in Figs. 8 to 12. Figures 8 and 9 show typical

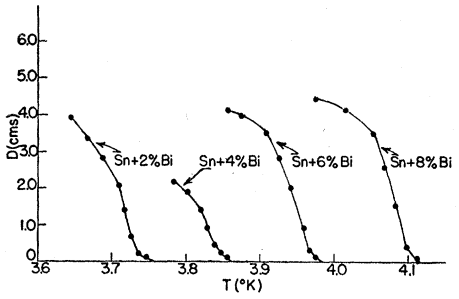


FIG. 6. Temperature transition curves for Sn-Bi alloys.

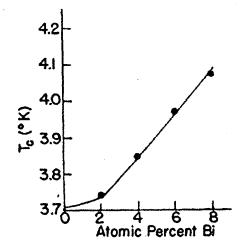


FIG. 7. Transition temperature as a function of atomic percent composition for Sn-Bi alloys.

magnetization curves for the alloys studied. The behavior is quite similar to the tin-bismuth alloys in that the breadth of transition and frozen in moment increase with increasing antimony content. However, for corresponding compositions, the tin-antimony alloys show somewhat sharper transitions. Figure 10 shows the critical field curves observed for these alloys. Figure 11 shows the transition temperature curves, and Fig. 12 shows the T_c *versus* composition curve obtained from the temperature transition curves by the same method as was used on the tin-bismuth alloys. It should be noted that the transition temperature for the tin-antimony alloys behaves diffently from that for the tin-bismuth alloys. In particular, the peak at around 6

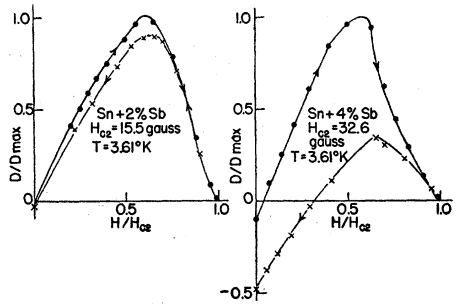


FIG. 8. Typical magnetization curves for Sn+2 atomic percent Sb and Sn+4 atomic percent Sb.

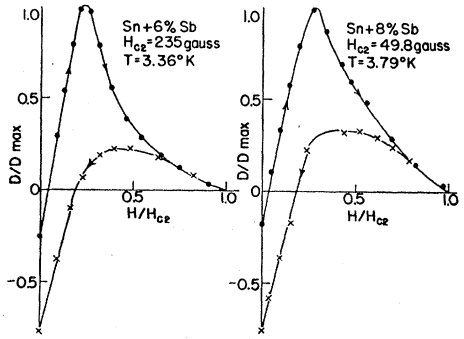


FIG. 9. Typical magnetization curves for Sn+6 atomic percent Sb and Sn+8 atomic percent Sb.

atomic percent antimony does not exist in the tin-bismuth alloys.

V. ANALYSIS OF EXPERIMENTAL RESULTS

An important parameter which can be derived from the critical field data is the Sommerfeld electronic specific heat coefficient γ, which gives the linear term γT in the specific heat of the normal state. Provided that there is no linear term in the specific heat of the superconducting state, one can then assume that the linear term in the formula for the difference in specific heats of the normal and superconducting states, as derived from the application of thermodynamics to the threshold field curve, represents the true electronic

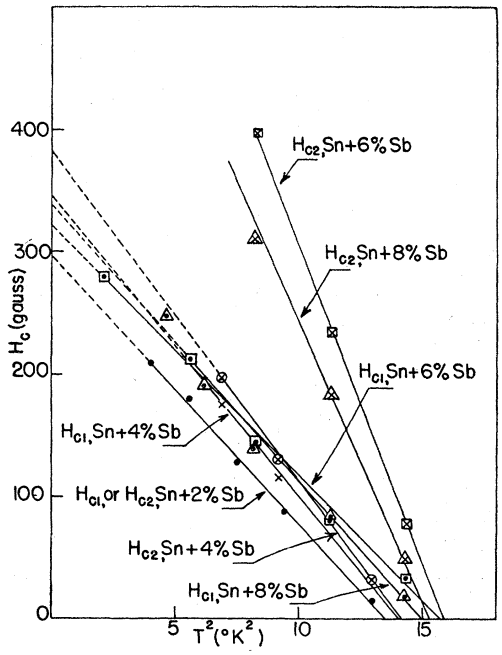


FIG. 10. Critical field curves for Sn-Sb alloys.

specific heat. If the threshold field is a parabola, as given by the formula

$$H_c = H_0[1-(T/T_c)^2],$$

then one can obtain[5]

$$\gamma = \tfrac{1}{2} V_m H_0^2/T_c^2, \text{ where } V_m = \text{molar volume.}$$

The validity of this relation is also based on the perfect reversibility of the superconducting-normal transition (Meissner effect). This, of course, is not the case in the alloys studied in this investigation. However, it seems reasonable to assume that H_{c1} represents the "true" critical field for these alloys. By "true" critical field, we mean that the greatest part of the sample has this value for its critical field and that if it were possible to remove the small volume of material responsible for the observed broadening of the transition and frozen in moment, the remaining part would show a sharp reversible transition at the "true" critical field. Some strong evidence in support of this assertion is obtained by comparing the predicted difference in specific heats at the transition temperature for the tin plus 4 atomic percent bismuth alloy with the actual value as observed by Mendelssohn and Moore.[6] They measured a $\Delta C_v = 3.42\times10^{-3}$ cal/mole deg, whereas the ΔC_v predicted from the H_{c1} threshold curve for this alloy is 3.39×10^{-3} cal/mole deg. The H_{c2} threshold curve predicts a value of 7.11×10^{-3} cal/mole deg. It would thus seem that the thermodynamic properties are more accurately predicted by the H_{c1} curve. However, one can only ascribe qualitative significance to any thermodynamic parameters derived from H_{c1}.

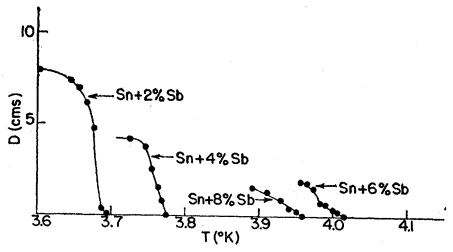


FIG. 11. Temperature transition curves for Sn-Sb alloys.

FIG. 12. Transition temperature as a function of composition for Sn-Sb alloys.

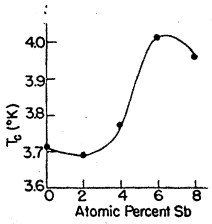
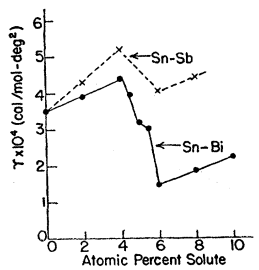


TABLE I. Critical field data for tin-bismuth and tin-antimony alloys.

Composition (atomic percent)	Sn-Bi T_c (°K)	Sn-Bi H_{c1} (gauss)	Sn-Bi $\gamma\times10^4$ cal per mole deg^2	Sn-Sb T_c (°K)	Sn-Sb H_{c1} (gauss)	Sn-Sb $\gamma\times10^4$ cal per mole deg^2
2	3.85	297	3.90	2.64	304	4.32
4	3.86	325	4.39	3.76	345	5.23
4.5	3.88	310	3.95	...	...	...
5	3.93	282	3.19	...	...	...
5.5	3.94	274	3.00	...	...	...
6	4.10	200	1.47	3.96	321	4.06
8	4.15	228	1.87	3.89	330	4.47
10	4.18	251	2.22	...	...	...

A summary of all the significant data on the two alloy systems is shown in Table I. This table gives the values of the parameters which best fit the observed data on the threshold fields by means of the relation $H_c = H_0[1-(T/T_c)^2]$. H_0 represents the critical field at 0°K and the subscripts 1 and 2 correspond to the fields at which penetration begins and is complete, respectively. The γ values given were derived from H_{c1}.

FIG. 13. γ *vs* atomic percent composition for Sn-Bi and Sn-Sb alloys.



[5] See F. London, *Superfluids* (John Wiley & Sons, New York, 1950), Vol. 1, p. 22.

[6] K. Mendelssohn and J. R. Moore, Proc. Roy. Soc. (London) A152, 34 (1935).

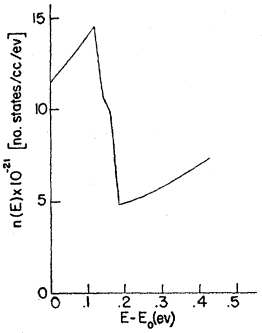


FIG. 14. Density of states curve derived from the Sn-Bi data.

A plot of γ *versus* atomic percent of solute is shown in Fig. 13 for the two alloy systems. There is a strong similarity in the two curves. In both cases, there is a linear rise in γ up to around 4 atomic percent of solute followed by a sharp drop between 4 and 6 atomic percent solute, and then a linear rise beyond this point. The shape of these curves has a natural explanation according to the band theory of metals. γ is proportional to the density of states at the surface of the Fermi distribution, and since the value of the Fermi surface is increased by adding bismuth or antimony atoms to the tin lattice, one should expect γ to vary in a manner closely related to the density of states curve for tin. Since tin is known to conduct by virtue of a small overlapping of energy bands, which leaves an incompletely filled Brillouin zone, one might expect that, on adding more electrons to the system, the first zone would be filled and the next outer zone would start to fill. Since the density of states is high at the top of a filled band and low at the bottom of the next higher band, one would expect a fairly sharp drop in the value of γ upon the completion of the filling of the lower band, and this is observed to be the case. One can obtain the density of states curve by integrating the observed data to get the change in Fermi energy. This can be done in the following way: we have $V=\frac{2}{3}\pi^2k^2V_mn(E)$ (cal/mole deg^2),[7] where k=Boltzmann's constant, V_m =molar volume, $n(E)$=density of states per unit volume at the Fermi level E. Let $C=\frac{2}{3}\pi^2k^2V_m$, so that $\gamma=Cn(E)$. Let N=total number of electrons per mole in the alloy. Then $N=(4+f_B)A$, where f_B=fraction of bismuth atoms in the alloy, and A=Avogadro's number. Hence, $dN=Adf_B$. We can also write $dN=V_mn(E)dE$. Here dN denotes the number of electrons per mole added to the system to change the Fermi level by an amount dE. Combining these two results, we have

$$dE=dN/V_mn(E)=Adf_B/V_mn(E).$$

Hence,

$$E=E_0+\int_0^{f_B}\frac{Adf_B}{V_mn(E)},$$

where E_0=Fermi level in pure tin. Since $n(E)=\gamma/C$, we have

$$E=E_0+\int_0^{f_B}\frac{CAdf_B}{V_m\gamma(f_B)},$$

where $\gamma(f_B)$ is the experimentally determined value of γ as a function of f_B. The two preceding formulas allow one to obtain $n(E)$ *versus* $(E-E_0)$. This integration has been carried out for the Sn-Bi alloys, and the resulting curve is plotted in Fig. 14. This curve cannot be assumed to represent the true density of states curve for pure tin for two reasons: (1) The γ values are subject to the uncertainty of the validity of the thermodynamic theory as applied to alloys; (2) The values of $n(E)$ were obtained from the alloys of tin and should be corrected for the effects of alloying on the $n(E)$ curve for pure tin. However, it seems reasonable to assume that qualitatively the shape of the curve resembles the shape of the true $n(E)$ curve. The fact that the curves of γ *versus* atomic percent solute in the Sn-Bi and Sn-Sb systems are different quantitatively indicates that bismuth and antimony have different effects on the electronic energy spectrum of tin.

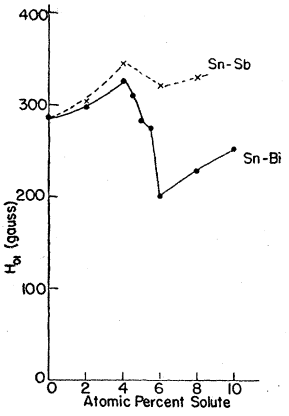


FIG. 15. H_{01} *vs* atomic percent composition for Sn-Bi and Sn-Sb alloys.

In Fig. 15, we show a plot of H_{01}, the critical field at absolute zero, for the Sn-Bi and Sn-Sb alloys as a function of atomic percent composition. The fact that H_{c1} behaves so similarly to $n(E)$, whereas there seems to be no corresponding behavior regarding T_c, indicates that H_{01} is determined to a large extent by the density of states. Of course, since $n(E)\propto H_{01}^2/T_c^2$ under the assumption made previously, then either H_{01} or T_c or both depend on $n(E)$. The observed behavior indicates that it is H_{01} which contains the dependency on $n(E)$, and that whatever other factors affect H_{01}, such as the magnitude of the interaction between electrons and lattice vibrations, also affect T_c in the same manner. This latter statement is supported by the isotope effect[8] which shows experimentally that H_{01} and T_c

[7] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 179.

[8] Reynolds, Serin, and Nesbitt, Phys. Rev. 84, 691 (1951).

depend on isotopic mass in the same manner. This dependency of H_{01} on the density of states appears quite logical if one assumes that only the electrons in a narrow band of width ΔE at the surface of the Fermi distribution are involved in the superconductive transition. Then at absolute zero the energy difference between the normal and superconducting states will be $\bar{\epsilon}n(E)\Delta E$, where $\bar{\epsilon}$ = average energy difference per electron. Since this energy difference is also $H_{01}^2/8\pi$, it follows that $H_{01} \propto [n(E)]^{\frac{1}{2}}$, which is in accordance with the observed behavior of H_{01}.

VI. ACKNOWLEDGMENTS

The author is indebted to Professor F. C. Nix, whose interest and valuable advice have helped considerably in the execution of this research. He would also like to express his thanks to Messrs. W. B. Teutsch and F. Witt for much help in taking the necessary data.

PHYSICAL REVIEW VOLUME 92, NUMBER 2 OCTOBER 15, 1953

Superconductivity of Titanium

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(Received May 4, 1953)

Critical magnetic fields of two specimens of titanium have been measured down to 0.23°K. The first specimen was a cold worked Ti wire having a purity of 99.98 percent. It was found to be superconducting at 0.37°K in zero magnetic field and the initial slope of the critical field curve was 465 gauss per degree. The second specimen was a Ti crystal bar with a purity greater than 99.99 percent. Its transition temperature was 0.49°K, and the initial slope of the critical field curve was 400 gauss per degree.

INTRODUCTION

THE superconductivity of titanium is of particular interest because of the large spread in reported transition temperatures. Meissner[1] first reported titanium to be superconducting at 1.13°K. Several subsequent investigations[2] on this metal have yielded transition temperatures from 0.53°K to 1.72°K.[3] The reported magnetic threshold values have also differed[3] by factors of two or more. In light of these circumstances, it was felt that additional data on the superconductivity of titanium would perhaps serve to clarify the situation. Before undertaking these measurements we sought to obtain titanium samples of the highest purity, since it is known that the properties of hard superconductors are very sensitive to even small amounts of impurity.

EXPERIMENTAL DETAILS

(A) Specimens

Two specimens of titanium were made available to us by E. J. Chapin of the Metallurgy Division, Naval Research Laboratory. Both were prepared by deposition from the iodide onto a titanium core.

(1) The first specimen was Ti wire with a diameter of 0.6 mm. The wire was prepared by cold swaging the original crystal bar (diameter 1.6 mm). No annealing followed this reduction in size. This wire was divided into lengths of 3–5 mm, and the pieces were then mixed with powdered chrome potassium alum. The mixture was compressed into a cylindrical pill having a diameter of 10 mm and a length of 12 mm. Spectrographic analysis showed that the Ti wire was 99.98 percent pure. The major impurities were oxygen and chromium, each of which appeared to the extent of 0.01 percent. The original crystal bar had a hardness of 70 on the Vickers scale.

(2) The second specimen was a Ti crystal bar with a diameter of 13 mm and a length of 13 mm. The purity of this sample exceeded 99.99 percent. The major impurity was oxygen which comprised ~0.005 percent of the total. Faint traces of silicon were also detected (~0.0001 percent). The hardness of this crystal bar was also ~70 on the Vickers scale. It was not annealed.

(B) Methods of Measurement

Because of the differences in the dimensions of the two specimens, we employed two distinct experimental arrangements for measuring the superconducting properties.

Ti Wire

For the Ti wire, thermal contact between the salt and metal was achieved by forming the pill described above. Temperatures below 1°K were obtained by the magnetic method, using a Bitter type solenoid to supply

[1] W. Meissner, Z. Physik **60**, 181 (1930).
[2] Meissner, Franz, and Westerhoft, Ann. Physik **13**, 555 (1932); W. J. de Haas and P. M. van Alphen, Proc. Amsterdam Akad. Sci. **34**, 70 (1931); R. T. Webber and J. M. Reynolds, Phys. Rev. **73**, 640 (1948); D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940); J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 715 (1949).
[3] This was the status at the time the present work was undertaken. Since then two additional papers have reported transition temperatures of 0.56°K and 0.39°K, respectively, for titanium; T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952); Smith, Gager, and Daunt, Phys. Rev. **89**, 654 (1953).