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

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Superconductivity of Titanium

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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).

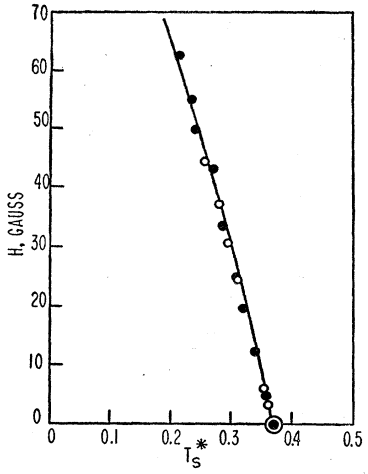

FIG. 1. Critical magnetic field of Ti wire as a function of T_s^*. ○—Oct. 23, 1952; ●—Nov. 6, 1952.

the magnetic fields. The temperature was determined from the magnetic susceptibility of the salt as measured by the ballistic mutual inductance technique.[4]

In order to obtain the extrapolated temperatures, T_s^*, based on Curie's law for a spherical salt specimen, we had to correct for the shape and filling factor of the salt. The value of Δ, obtained from $\Delta=cf(4\pi/3-N)$, where c is the Curie constant, N is the demagnetization factor of the specimen, and f is the filling factor of the specimen, was found to be 0.01 degree. The occurrence of superconductivity in the titanium was also detected from these susceptibility measurements. Details of this procedure have already been given.[5]

Ti Crystal Bar

The existing apparatus was not large enough to allow us to press the salt around the Ti crystal bar. Further, it was thought advisable to avoid straining this specimen in order to be able to compare the results with those of the wire. Therefore, we achieved thermal contact in this case by suspending the crystal bar from the salt pill by means of a copper rod. The paramagnetic salt (again chrome potassium alum) was pressed onto an assembly consisting of a brass base to which a copper fin is silver soldered. Then a copper screw was threaded into tight fitting threads in the brass base of the salt pill. The Ti specimen was then tapped to accommodate the lower end of the copper screw.[6]

The copper screw was about 35 mm in length and 3 mm in diameter. Halfway between the salt pill and the Ti metal, we attached a thermometer holder to the copper rod. The holder consisted of a flat piece of copper, silver soldered to the rod, and then wrapped around a carbon composition resistor. The thermometer was cemented into this copper sleeve so formed with GE 7031 adhesive. This adhesive was also used in connecting the copper rod to both the salt pill and the metal sample. The thermal contact obtained with this arrangement seemed to be very satisfactory for the first time the apparatus was brought to liquid helium temperatures.

Our experience has shown that the thermal contact deteriorates to some extent once the apparatus is allowed to warm up from liquid helium temperatures to room temperature. It seems most likely that this difficulty is due to the salt's breaking away from the copper fin, although macroscopic examination did not reveal any cracks in the pill. In order to circumvent the possibility of having a poor thermal contact, we prepared new pills each time for the data to be reported here. On several occasions we did reuse an assembly, and found that the results for the transition temperature and critical field values were not reproducible. When new assemblies were used, the results were quite reproducible. In general, we found that poor thermal contact resulted in too low an apparent transition temperature and too flat a critical field curve. Independent magnetic measurements were made on the salt and metal in this arrangement. After demagnetization, we observed the susceptibility of both the salt and the metal as a function of time. The ballistic mutual inductance method was again employed here.

The superconductivity of Ti was evidenced by a large deflection of the galvanometer, indicating a diamagnetic susceptibility. By noting the time at which the metal returned to essentially zero susceptibility, we obtained the required transition temperature from the susceptibility of the salt. The value of Δ for these pills, needed to obtain T_s^*, was again 0.01 degree. Repeating this procedure with externally applied magnetic fields present during the warmup gave the critical field as a function of temperature.

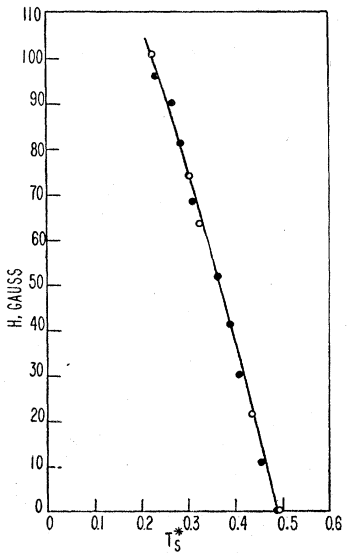

FIG. 2. Critical magnetic field of Ti crystal bar as a function of T_s^*. ○—Feb. 5, 1953; ●—Feb. 12, 1953.

[4] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A149**, 152 (1935).
[5] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 1324 (1949).
[6] This arrangement is similar to that employed by B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1951).

The carbon resistance thermometer served to indicate the goodness of the thermal connection between the salt and metal. Thus, by calibrating the carbon thermometer previously and ascertaining its reproducibility to about 1 percent, we could be reasonably sure of good thermal contact if the carbon thermometer agreed with the temperature of the salt. On those occasions when we reused a given assembly it was observed that the carbon thermometer always read a higher temperature than the salt.

We used a gold ring seal to obtain vacuum tightness in the can containing the sample. This type of seal has proved to be most reliable and convenient for adiabatic demagnetization work. Vacuum tightness is maintained even after allowing the apparatus to warm up to room temperature. The coil system which surrounded the vacuum can consisted of three secondary coils and one primary coil. There was a secondary coil around the salt, another for the Ti metal, and a third one which was empty and could be connected in series opposition to either of the other two. The primary coil extended over all the secondaries. With this arrangement, we could switch either the salt system or the metal system to the ballistic galvanometer.

RESULTS

(A) Ti Wire

The critical magnetic field as a function of T_s^* for the Ti wire is shown in Fig. 1. We found a zero field transition temperature of 0.37 ± 0.01°K for both runs on the same specimen. The slope of the critical field curve at the transition temperature,

$$(dH/dT)_{T=T_c}=465 \text{ gauss/degree.}$$

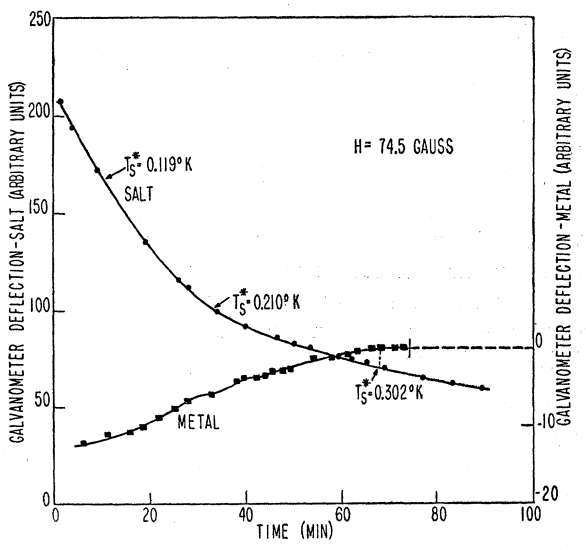

FIG. 3. Portion of a typical run with the Ti crystal bar.

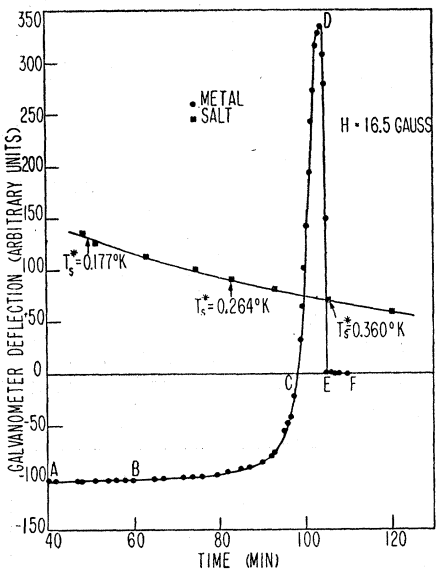

FIG. 4. Typical run with Cd rod, showing the "apparent" paramagnetism.

The curve in Fig. 1 could be represented adequately by the parabolic equation

$$H=H_0[1-(T/T_c)^2], \tag{1}$$

where H_0, the critical field at $T=0$°K, is 86 gauss and T_c, the zero field transition temperature, is 0.37°K. It took about two hours for the specimen to warm from 0.1°K to 0.5°K. From this it is estimated that the heat influx was less than 1 erg per second. The relatively slow warmup probably meant that the salt and metal were in good thermal contact. This supposition is made more plausible by the good reproducibility of the two runs on the same specimen.

(B) Ti Crystal Bar

The results for the Ti crystal bar are shown in Fig. 2, where the critical magnetic field is plotted as a function of T_s^*. Here the zero field transition temperature was found to be 0.49 ± 0.01°K. The slope of the curve,

$$(dH/dT)_{T=T_c}=400 \text{ gauss/degree.}$$

The curve in Fig. 2 could not be represented by the parabolic relation given in Eq. (1).

The warm-up times for these experiments were again of order two hours in going from 0.1°K to 0.5°K. The measurements in zero magnetic field can be used to estimate the percent of the Ti which actually is superconducting. Within experimental limits (±10 percent) this was found to be 100 percent. A portion of a typical run, with an applied field of 74.5 gauss, is depicted in Fig. 3, where the galvanometer deflections (in arbitrary units) of both the salt system and the metal system are plotted as functions of time after demagnetization. The deflections for the metal are adjusted so that zero

indicates the normal state. The time corresponding to the return to zero for the metal system deflection gives the desired temperature from the synchronous salt system deflection. For the applied field of 74.5 gauss this temperature was 0.302°K. The curve for the metal in Fig. 3 does not show the "apparent" paramagnetism which has been observed for soft superconductors such as zinc.[5] The Ti wire also failed to show this characteristic. The absence of this feature probably indicates that the magnetization curves for both Ti specimens are quite different from that of an ideal superconductor. This supposition is based on the explanation previously given by one of us.[7] We do not know if previous workers[2,3] observed the "apparent" paramagnetism in

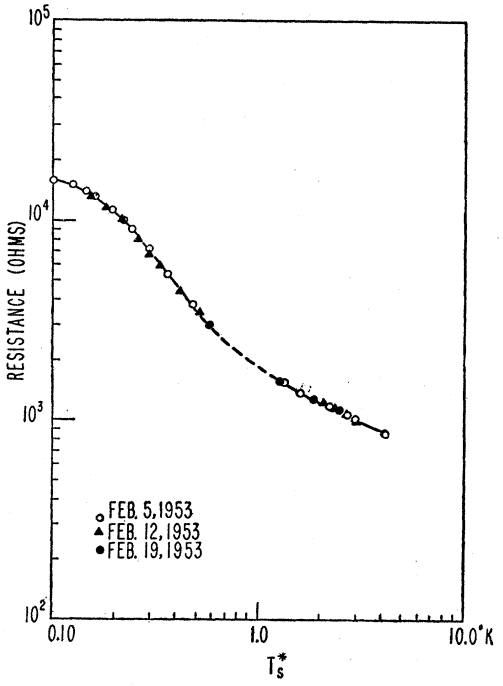

FIG. 5. Resistance-temperature curve for the carbon composition thermometer. Data from three separate experiments are shown.

their experiments with Ti. Actually, the presence of this effect may be a good measure of how close the sample comes to being an ideal superconductor. In order to ascertain that our experimental arrangement was not responsible for the absence of this effect, we decided to conduct an experiment with a cadmium rod (Johnson Matthey Lab. No. 4753, 7 mm diam×20 mm long). The Cd was suspended from the salt pill by the same technique described for the Ti crystal bar. Figure 4 gives the results obtained for Cd in an applied field of 16.5 gauss. The galvanometer deflection (for the metal) is again adjusted so that zero indicates the normal state. From A to B the Cd had a constant differential diamagnetic susceptibility corresponding to the superconducting state. From B to C the diamagnetic susceptibility gradually decreased to zero as the Cd approached the intermediate state. In the portion CDE the Cd shows a paramagnetic *differential* susceptibility. Finally, the line EF represents the normal state again. The steepness of the line DE permits a very accurate determination of the temperature at which the Cd becomes normal in the particular applied field. The shape of the entire curve is consistent with the particular geometry of the sample and the previous analysis.[7] Complete results for Cd will be given in a subsequent paper. A comparison of Figs. 3 and 4 serves to confirm our belief that the Ti specimens differ appreciably from an ideal superconductor. Because of this, no attempt will be made to compute the thermodynamic properties of Ti from the critical field data.

A measure of the goodness of the thermal contact between the salt and the metal can be obtained from the carbon thermometer readings taken during a particular experiment. If the superconducting transition temperatures obtained from the salt's susceptibility and the carbon resistance agree from one run to another, we probably had good thermal contact on each occasion. Figure 5 gives the resistance *versus* temperature plot for the carbon thermometer.[8] Three sets of data are shown, of which two were obtained during the same runs that gave the critical field values for the Ti crystal bar. The reproducibility of results in both Figs. 2 and 5 indicates that the thermal contact was good. When the thermal contact between the salt and metal is poor, the values for both T_c and the critical field curve will be erroneous. In fact, for three experiments with poor contact we found results which varied from apparently no superconductivity for Ti (down to 0.20°K) to a T_c having a value of 0.37°K and 0.42°K, respectively. The apparent lowering of the transition temperature when the thermal contact is poor can be explained by the following argument. Immediately after the demagnetization has been completed, the salt will be at a lower temperature, T_s, than the metal, T_m. This direction for the thermal gradient, $\Delta T = T_m - T_s$, results from two factors. First, the salt is the agent which is cooled by demagnetization, and secondly, the metal is actually heated by eddy currents induced during the time the field is being removed. The behavior of the gradient ΔT as a function of time is then determined by the nature of the thermal connection between the salt and metal. For good contact we believe that in the order of minutes after demagnetization ΔT becomes essentially zero[9] (more specifically ΔT would be less than

[7] M. C. Steele, Phys. Rev. **87**, 1137 (1952).

[8] This particular thermometer had a nominal room temperature resistance of 270 ohms. Although we do not know the manufacturer of this resistor, we believe that they are no longer being made. The characteristic feature of this type of resistor is the white ceramic covering. This resistance thermometer is *not* of the same composition as the type described in detail by J. Clement and E. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[9] This estimate is in agreement with the results of Goodman and Mendoza (reference 6).

0.01°K). However, for very poor thermal contact ΔT could be (and was found to be) as large as 0.5°K even an hour after demagnetization. With such a situation one would find the superconducting transition at too low a temperature. By exactly the same argument the critical field curve would be too flat, since in the presence of a field the time after demagnetization at which the metal becomes normal would be less and hence ΔT would be larger (assuming that ΔT decays toward zero with increasing time). It then follows that if the thermal contact for a particular assembly deteriorates between two runs, the two sets of data would not be in agreement. In fact, with this arrangement the most reliable results for a *given metal specimen* would be the highest reproducible transition temperature and the steepest reproducible critical field curve. The data shown in Fig. 2 met both these conditions within experimental limits.

(C) Discussion and Comparison with Previous Results

The comparison to previous work will be restricted to those measurements which found T_c for Ti to be below 1°K. In general, the agreement between different laboratories on measurements relating to hard superconductors has been poor. This is due, in large measure, to the sensitivity of the results to the characteristics peculiar to the particular specimen available. However, the measurements of Daunt and Heer[2] on unannealed Ti pieces (linear dimensions of about 2–3 mm) can be compared to our results for the Ti wire. Whereas their value of $T_c=0.53$°K differs considerably from ours, they found $(dH/dT)_{T=T_c}=470$ gauss/degree, which is in good agreement with the present results. The difference in T_c may easily be due to the fact that our Ti wire had been made by cold swaging without further annealing. Subsequent measurements by Smith and Daunt[3] on the same Ti (as used by Daunt and Heer[2]) in the annealed state did not reveal any significant differences from their earlier work. Both of these previous experiments used an experimental arrangement similar to that described in the present paper for the Ti wire; i.e., the metal (in the form of small pieces) was mixed with the paramagnetic salt and the mixture compressed into a pill. Kurti and Simon[10] have given arguments to show that such an arrangement probably gave better thermal contact between the metal and salt than other techniques. To our knowledge there are no experimental data to prove conclusively that the thermal contact is good at these temperatures.

Our results for the Ti crystal bar are in serious disagreement with the recent work of Smith, Gager, and Daunt.[3] They have reported $T_c=0.39$°K and $(dH/dT)_{T=T_c}=89.5$ gauss/degree for a very pure Ti crystal bar. Although their specimen was annealed subsequent to production, a comparison of the chemical purity and measured hardness shows that our specimen (unannealed) was similar to theirs. Therefore, it seems unlikely that the large differences, particularly in $(dH/dT)_{T=T_c}$, can be attributed to the specimens. It should be emphasized that our experimental technique for the Ti crystal bar was different from that of Smith *et al.*[3] It would appear that they pressed the paramagnetic salt around the Ti crystal bar to form an ellipsoidal pill,[11] whereas our specimen was suspended from the salt by the technique described above. Kurti and Simon[10] had considered the technique of Smith *et al.*[3] and had concluded that due to the thermal expansion coefficient of the salt being larger than that of the metal, there is danger that the salt will crack. This danger becomes greater as the size of the enclosed metal becomes larger. Whether or not these considerations can explain the difference between the two results would depend upon the reproducibility of each specimen from run to run.

Results from the two specimens used in the present experiments probably indicate that cold working the Ti has the effect of lowering T_c and making $(dH/dT)_{T=T_c}$ larger. The difference in making thermal contact between metal and salt may also be responsible in some way for this effect. In any event the observed trend is similar to other hard superconductors.[12] Finally, there is the question of the effect of annealing. Wexler and Corak[12] have pointed out that vacuum heat treatment of the hard superconductors only removes the internal strains due to cold work, and leaves unchanged the effects of the interstitially located foreign atoms such as oxygen and nitrogen. Even small amounts of such impurities can have appreciable effects upon the properties of the superconductor. Thus, although our Ti crystal bar contained only 0.005 percent oxygen, it is clear from the results obtained that the specimen is still far from being an ideal superconductor.

[10] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A151**, 610 (1935).

[11] The letter by Smith *et al.* (reference 3) does not give explicitly the technique used. However, their statement, "by methods previously reported," led us to believe that the salt was pressed around the metal.

[12] See, for example, the work of A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952) which contains a detailed discussion of the properties of hard superconductors.