From a comparison of our curve at 14 Mev with the theoretical curves of Buckingham and Massey[5] at 11.5 Mev, one may make the following general statements. The theoretical and the experimental curves agree in features of marked angular asymmetry with a minimum at about 110° and a forward scattering peak larger than the backward scattering peak. However, regardless of how the curves are normalized the experimental curve differs at some angles by factors of several from the various theoretical curves. As is pointed out by Massey and Buckingham,[4] their "exchange force" calculations will probably come into better agreement with experimental *total* cross-section values[7] in the region of 14 Mev when they take into account the contributions of higher than p angular momentum states, which were ignored in their original calculations. Such a refinement in the "exchange force" theory may also bring it into better agreement with our angular distribution data. If such an extension of the theory gives favorable results, the *over-all* evidence will be somewhat more in favor of "exchange forces" than "ordinary forces." However, as Darby and Swan[8] point out, their angular distribution data at 2.5 Mev agrees very closely with the "ordinary force" curve of Buckingham and Massey, whereas the data of Coon and Barschall[6] at this energy fits better with the "exchange force" curve. Obviously more accurate and complete data are necessary.

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Some Properties of Superconductors below 1°K. I. Titanium

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Magnetic measurements on titanium metal of purity 99.95 percent have been carried out down to 0.3°K. The titanium was found to be superconductive with a transition temperature of 0.53°K. Measurements of the magnetic threshold curve were made for which the initial slope was found to be 470 gauss per degree.

INTRODUCTION

In carrying out investigations on techniques required for the observation of nuclear paramagnetism, the properties of some superconductors have been studied below 1°K. Details of the results obtained with high purity titanium are given herewith.

Titanium of stated purity approximately 99.75 percent was found by Meissner[1] in 1930 to become superconductive by observation of the resistance of a single crystal specimen. The transition point in zero magnetic field was found to be 1.13°K. Subsequent resistance measurements by Meissner, Franz, and Westerhoff[2] on other titanium samples showed superconductive transitions at higher temperatures, one being as high as 1.77°K. de Haas and van Alphen[3] using titanium of unstated purity found by resistance measurements a superconductive transition at about 1.72°K, with a broad transition region. Webber and Reynolds[4] in 1948 observed an anomaly in the resistance of a titanium specimen, prepared in a different manner from the above, the resistance showing a marked decrease over a broad temperature range between 3°K and 1°K without, however, showing superconductivity.

Measurements by Shoenberg,[5] on the other hand, on the magnetic properties of titanium of purity 99.9 percent revealed no sign of superconductivity, defined by the establishment of zero magnetic induction throughout the entire specimen, down to temperatures of about 1.0°K. Shoenberg[5] reported, however, the occurrence of a very small diamagnetic anomaly at about 1.5°K and suggested that the previous observations of zero resistance at about this temperature were due to very small regions in the specimen becoming superconductive where chemical or physical impurity might have been concentrated. Such a view is supported by the considerable scatter in the values of transition points observed.[1–3]

The experiments reported in this paper were undertaken in order to clarify the question of the possible occurrence of superconductivity in titanium which in view of Shoenberg's work appeared doubtful. From the position of titanium in the periodic table it would appear that it should become superconductive, since the other metals in the same sub-group are super-

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[1] W. Meissner, Zeits. f. Physik **60**, 181 (1930).
[2] Meissner, Franz, and Westerhoff, Ann. d. Physik **13**, 555 (1932).
[3] W. J. de Haas and P. M. van Alphen, Proc. Amst. Roy. Akad. Sci. **34**, 70 (1931).
[4] R. T. Webber and J. M. Reynolds, Phys. Rev. **73**, 640 (1948).
[5] D. Shoenberg, Proc. Camb. Phil. Soc. **36**, 84 (1940).

conductors.[6] This view is supported by consideration of its atomic volume.[7] It seemed of interest, therefore, to extend magnetic measurements on a titanium sample of higher purity than previously used to the temperature region below 1°K.

EXPERIMENTAL METHODS AND RESULTS

A special sample of titanium of 99.95 percent purity was kindly furnished us by the Battelle Memorial Institute. The method of preparation by the thermal decomposition of the iodide on a hot wire has been fully described elsewhere.[8]

Cooling to liquid helium temperature was carried out by the use of a Simon-type[9] expansion liquefier having provision for withdrawing the liquid helium into external cryostats.[10] Temperatures below 1°K were obtained by the magnetic methods,[11] using chromium potassium alum as the working substance, the magnetic field being produced by a large permanent magnet giving a field of 8000 gauss in a 2-inch gap.

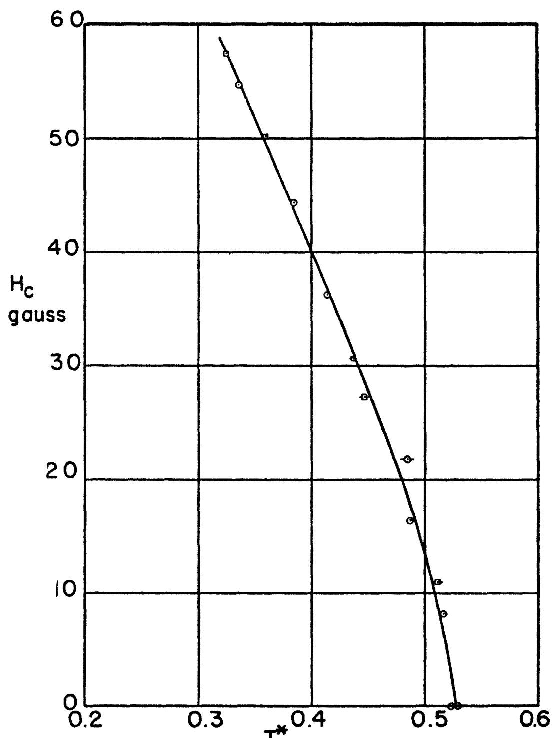

FIG. 1. The measured magnetic threshold as a function of temperature (Curie scale).

Thermal contact between the chromium potassium alum and the titanium metal was achieved mechanically, as previously carried out by Kurti and Simon.[6(b)] The metal was divided into small pieces of linear dimensions approximately 2–3 mm and these pieces were distributed at random in the powdered salt and the mixture compressed under a pressure of 200–300 atmos. into an ellipsoidal pill having major and minor axes of length 27 mm and 13 mm, respectively. This direct method of making thermal contact was found to be satisfactory down to the lowest temperatures used (0.3°K), as previously found by Kurti and Simon.[6(b)]

The filling factor, f, of the specimen, i.e., the ratio of the distributed density of the powder to the crystalline density, was 0.79. Hence, the calculated value of Δ, given by $\Delta = cf(4\pi/3 - N)$, where c is the Curie constant per cc and N the demagnetizing factor of the specimen, was taken to be 0.011 degrees. This value has been taken in calculating T_s^*, i.e., the extrapolated temperature based on Curie's law for a spherical specimen.[12]

The temperature was calculated in the usual manner from observations of the magnetic susceptibility of the sample, the latter being measured by the ballistic mutual inductance method.[13] These susceptibility measurements served also to detect the occurrence of the transition from the superconductive to the normal state of the titanium, such transitions producing sudden changes in the observed total susceptibility of the specimen, due to the perfect diamagnetic properties of the superconductive state.

The measurements were made by allowing the speciment to warm up slowly either in a small externally applied magnetic field (<60 gauss) or in zero field, susceptibility measurements being taken at regular time intervals. Superconductivity, evident by strong diamagnetism of the titanium, was observed at temperatures below 0.53 degrees. Details of the kind of transitions observed will be given in a subsequent publication. From the measurements in zero magnetic field, an assessment could be made of the percentage volume of the titanium which became superconductive. Within experimental error this was 100 percent, indicating that the superconductive effects were not due to impurities. The rate of warm-up was sufficiently slow to ensure satisfactory temperature equilibrium between the salt and the metal, approximately one hour being required for the specimen to warm from 0.3°K to 0.6°K. This warm-up time corresponded to an average heat influx of 350 ergs per minute.

The transition temperature for the titanium was found to be 0.527±0.006, with a slope for the magnetic

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[6] (a) W. Meissner, Ergeb. d. exakt. Naturwiss. **11**, 222 (1932); (b) N. Kurti and F. Simon, Proc. Roy. Soc. **A151**, 610 (1935); and (c) D. Shoenberg, *Superconductivity* (Cambridge University Press, London 1938), p. 2.

[7] See, for example, Burton, Grayson-Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 94.

[8] Campbell, Jaffee, Blocher, Gurland, and Gonser, J. Electrochem. Soc. **93** 271 (1948).

[9] F. Simon, Physik Zeits. **34**, 232 (1933).

[10] R. B. Scott and J. W. Cook, Rev. Sci. Inst. **19**, 889 (1948).

[11] P. Debye, Ann. d, Physik **81**, 1154 (1926); and W. F. Giaque J. Am. Chem. Soc. **49**, 1864 (1927).

[12] See N. Kurti and F. Simon, Phil. Mag. **26**, 849 (1938).

[13] See N. Kurti and F. Simon, Proc. Roy. Soc. **A149**, 152 (1935); and W. J. de Haas and Wiersma, Physica **2**, 335 (1935).

threshold of

$$(dH_c/dT)_{H=0}=470 \text{ gauss/degree.}$$

No traces of minor magnetic anomalies at temperatures between 0.53 and 4.2°K were observed. A plot of the measured magnetic threshold curve is given in Fig. 1, the temperatures being plotted on the Curie scale, T_s^*. The possible error in interpreting the observed results is given by the lines drawn through the points in Fig. 1. Within the temperature range concerned, the deviations of the values of T_s^* from the absolute temperature would be small and not greater than the experimental error of observation.

DISCUSSION

The low value found for the superconducting transition point of titanium (0.53) confirms the work of Shoenberg[5] who found no sign of complete superconductivity down to 1.0°K, and indicates that the results previously obtained by resistance measurements were probably due to physical or chemical impurity effects rather than being characteristic of pure titanium metal. The low transition point also lends some support to the considerations put forward by de Launay and Dolecek.[14]

The high value for the slope of the magnetic threshold curve is comparable with that for the "hard" superconductors, e.g., Ta and Cb.[15] The magnetic threshold curve for Zr, in the same sub-group of the periodic table as Ti, also has a high slope, being approximately 400 gauss per degree.[6(a)] For very pure thorium, however, the only other superconductor in Group IVa for which the magnetic threshold curve has been measured,[5] is as small as 190 gauss per degree, a figure comparable with those for the "soft" superconductors.[15,16] On the other hand, measurements[5] on less pure and on cold-worked thorium showed much higher slopes for the threshold curve, a result which made the subdivision between hard and soft superconductors appear artificial, the high slopes possibly being due to impurity effects or physical strain. This view is supported by the work of Lasarew and Galkin[17] on the effect of strain, and it would consequently be desirable to extend the magnetic measurements on the hard superconductors to include systematically the effects of annealing, etc.** In summation, it is certainly not possible to regard the magnetic threshold curves of the hard superconductors as forming a basis for the calculation of the thermodynamical properties, such as entropy difference, etc., with the same confidence as those for the soft superconductors. In view of this and because of the limited temperature range of our measured curve for titanium, no calculations have been made of thermodynamical properties.

[14] J. de Launay and R. L. Dolecek, Phys. Rev. **72**, 141 (1947).
[15] Daunt, Horseman, and Mendelssohn, Phil. Mag. **27**, 754 (1939).
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** Measurements of the magnetic properties of superconducting tantalum in various physical states have been made by R. T. Webber (Phys. Rev. **72**, 1241 (1947)). However the observed slopes of the threshold curves even for the annealed specimens were not smaller than that previously reported by Daunt and Mendelssohn (see reference 16).