PHYSICAL REVIEW VOLUME 112, NUMBER 1 OCTOBER 1, 1958

Effects of Pressure on the Superconducting Transition Temperatures of Sn, In, Ta, Tl, and Hg†

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(Received June 9, 1958)

Solid parahydrogen has been used as a transmitter of approximately hydrostatic pressure to study the effects of pressures up to 10 000 atmos on the superconducting transition temperatures of polycrystalline tin, indium, tantalum, thallium, and mercury. The technique which was used allowed an approximate evaluation of the effects of sample deformation and pressure gradients, and the results are considerably more accurate than the high-pressure data previously available. The transition temperature data for tin and indium showed considerable curvature when plotted *vs* pressure, but gave a roughly linear relationship when plotted against volume. No curvature was found for tantalum. The thallium data agree qualitatively with previous work, and show a maximum in the transition temperature *vs* pressure curve at about 2000 atmos. The mercury results were anomalous in that two distinct transition temperature *vs* pressure curves (with different zero-pressure transition temperatures) were found; one when the pressure was kept below 4000 atmos, and the other when the sample was cycled from zero to 10 000 atmos. Other experiments have shown that these results are due to two different modifications of solid mercury, each of which can exist at liquid helium temperatures.

INTRODUCTION

EXPERIMENTALLY, the phase boundary surface for a superconductor is defined by specifying the transition temperature as a function of magnetic field and pressure (or molar volume).[1] Theoretically, this surface is thought to be determined by an interaction between the electrons and the phonons in the metal, and the form of the interaction proposed in the recent Bardeen-Cooper-Schrieffer[2] (BCS) theory has had considerable success in describing many of the properties of superconductors. However, the volume dependence of the transition temperature, according to this theory, can be understood only if one has information as to the effects of volume changes on the phonon vibration energies, the density of states of the electrons in the normal metal, and the coupling between these two.[3] The BCS theory links these by means of the equation [reference 2, Eq. (3.29)]

$$T_c = 1.14\hbar\omega \exp[-1/N(0)A],$$

where $N(0)$ is the density of states of the electrons at the Fermi surface in the normal metal, and A is a parameter which measures the average interaction between electrons which arises through a coupling with the lattice vibrations. $\hbar\omega$ is an average phonon energy which is presumably proportional to θ_D, and it is this term which gives the isotope effect, since the terms in the exponential presumably are independent of the mass of the ions. If these terms are also ignored as a first approximation to the pressure effect, and Grüneisen's expression for the variation of θ_D with volume is assumed, the following relationship is obtained:

$$(d \ln T_c/d \ln V) = -\eta_0,$$

where $\eta_0 = (V\beta/C_v k)$ is of the order of 2 and is the Grüneisen constant for the metal in question.[4,5] This relationship predicts the wrong sign for the pressure effect for all of the metallic elements for which it is known, with the exception of thallium at low pressures. It is, however, of the right order of magnitude in absolute value. It would thus seem that the major contribution to the change in T_c with pressure is from the effect of volume changes on the $N(0)$ and A terms in the exponential, and in order to be able to understand the experimental values quantitatively, it will be necessary to evaluate these explicitly for each of the superconductors studied. In its current state, the theory does not attempt to do this.

Three experimental techniques have been used to study the pressure (and thence the volume) dependence of the superconducting transition temperature. Firstly, a measurement of the volume change associated with the transition at zero pressure in a magnetic field yields $(\partial H_c/\partial P)_T$.[1,6,7] The pressure dependence of the transition temperature may then be calculated with the aid of critical field data. The magnitude of the volume change

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† Contribution No. 642. This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition, Chap. 3.

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).

[3] D. Pines, Phys. Rev. **109**, 280 (1958).

[4] Earlier treatments of the pressure effect [see P. M. Marcus, Phys. Rev. **91**, 216(A) (1953) and reference 5 for a discussion] gave this relationship with a plus sign, in agreement as to sign and order of magnitude with the experimental data. This arose from the assumption that the interaction which produced superconductivity was basically between the mean square amplitude of the lattice vibrations and the electrons. The BCS theory, however, implies that in the absence of changes in $N(0)$ and A, the transition temperature is directly proportional to the zero-point energy. This (as well as the earlier theories) gives the correct isotope effect, but a pressure effect which is opposite in sign. We are indebted to Dr. D. E. Mapother for discussions on this subject.

[5] R. R. Hake and D. E. Mapother, J. Phys. Chem. Solids **1**, 199 (1956).

[6] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **30**, 49 (1957).

[7] G. D. Cody, Phys. Rev. **111**, 1078 (1958). We are indebted to Dr. Cody for a preprint of this paper.

is, however, very small (a few parts in 10^6) and may be anisotropic. The values for the relative changes in length found for various orientations of single crystals may be correlated directly with the changes in critical field which are found by the application of uniaxial stress along these same directions.[8,9] There seems to be a fair agreement between the two sets of measurements, and also, after suitable averaging over the various crystallographic directions, with the directly measured values for the effects of a truly hydrostatic pressure.

Secondly, one may measure the effect of hydrostatic pressure directly.[5,9–11] The maximum such pressure which may be transmitted is determined by the solidification pressure of helium which varies from 25 atmos at 1°K to 140 atmos at 4.2°K. The shift in transition temperature with pressure may be measured directly, but, since the maximum temperature shift is small (about 0.01°), it cannot be measured with high precision. Alternatively, it is feasible to make relatively precise measurements of the isothermal dependence of critical field on pressure, $(\partial H_c/\partial P)_T$, which, when again combined with the critical-field data at zero pressure, may then be used to calculate the pressure dependence of the transition temperature. The work by Fiske[9] demonstrates an ingenious method of compensating for temperature drifts.

These two techniques can give only an initial slope for the transition temperature-pressure curve. Since the behavior at high pressures yields further information (in thallium, for instance), various techniques for obtaining appreciable temperature shifts with approximately hydrostatic pressures have been devised.

The first was the ingenious method due to Lasarew and Kan,[12] who used the expansion of water upon freezing to produce pressures of the order of two thousand atmos. This technique and the clamp method originated by Chester and Jones[13] were not too satisfactory since the pressures produced were essentially applied at room temperature, and could not be varied at low temperature. There was also some doubt as to the exact value of the pressure generated in each case.

The initial approach to applying to a metal a pressure which was variable at liquid helium temperatures was made by Hatton,[14] who placed a wire of the metal of interest in a high-pressure cylinder, with four electrical lead ins. The cylinder was cooled and filled with solid hydrogen, and the pressure in the solid hydrogen was varied by applying force to its surface with a closely fitting piston and a hydraulic press. Previous work on the compressibility of solid hydrogen had shown that it was quite plastic at liquid helium temperatures, and that it was possible to produce pressures of up to 10 000 atmos by using this technique.[15,16] Hatton observed the onset of superconductivity by measuring the resistance of the wires at constant pressure as the temperature was decreased, with a maximum sample pressure of roughly 5000 atmos available.

While Hatton's experiments were valuable in demonstrating the feasibility of the use of solid hydrogen and in confirming previous work, their accuracy was not high due to various experimental limitations. The work which will be described below was based essentially on Hatton's technique, although several modifications were made which served to improve the accuracy of the results. Probably the most important of these were the use of a nonmagnetic piston and cylinder so that the Meissner effect could be used to detect the superconducting transition, and the use of an independent method for determining the friction in the sample holder. The use of a mutual inductance method for determining the transition temperatures made it possible to work with a smaller-area cylinder, and hence, at pressures (11 000 atmos) which were limited only by the strength of the cylinder material. In addition, the availability of liquid hydrogen in this laboratory meant that pure parahydrogen could be used as a pressure transmitter. Hatton pointed out that the unknown effects of pressure on the rate of the ortho-para conversion in solid normal hydrogen introduced an uncertainty in the actual temperature of the sample which was imbedded in the hydrogen. This difficulty was overcome through the use of solidified HD in some of his experiments.

APPARATUS

A sketch, roughly to scale, of the sample holder which was used is given in Fig. 1. The sample holder was inserted into the bottom end of a press which had long compression and tension members, and which furnished the force shown in the diagrams. The room-temperature part of the press consisted of a commercial (Blackhawk) four-ton hydraulic button ram which had been modified by the substitution of an "O"-ring for the leather packings. The oil pressure on the ram was kept constant by the direct use of a dead-weight gauge. By changing the weights on the dead-weight gauge pan, the oil pressure could be varied by discrete large units of 50 atmos (called "one weight") or by small steps of 5 atmos. Thus, it was possible to ensure the monotonic increase or decrease in the pressure which is so necessary in work of this kind. The maximum pressure used in the sample holder was roughly 11 000 atmos, and was determined by the strength of the hardened beryllium copper (Berylco 25) piston and cylinder at liquid helium temperatures. Stainless steel

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[8] Grenier, Spondlin, and Squire, Physica **19**, 833 (1953). C. Grenier, Compt. rend. **238**, 2300 (1954); **240**, 2302 (1955); **241**, 1275 (1955).

[9] M. D. Fiske, J. Phys. Chem. Solids **2**, 191 (1957).

[10] N. L. Muench, Phys. Rev. **99**, 1814 (1955).

[11] M. Garber and D. E. Mapother, Phys. Rev. **94**, 1065 (1954).

[12] B. G. Lasarew and L. Kan, J. Phys. (U.S.S.R.) **8**, 193 (1944).

[13] P. F. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953).

[14] J. Hatton, Phys. Rev. **100**, 1784 (1955).

[15] J. W. Stewart and C. A. Swenson, Phys. Rev. **94**, 1096 (1954).

[16] J. W. Stewart, Phys. Rev. **97**, 578 (1955).

(18–8) was used exclusively for the construction of the press because it is roughly nonmagnetic, and has both a low thermal conductivity and a relatively high strength.

The data were recorded in terms of weights (see Fig. 2 where these units are used). In order to convert from this unit to pressure on the sample it is necessary to know the ratio of the area of the ram piston to that of the sample holder piston. These areas could be calculated with precision at zero pressure, but the beryllium copper cylinder has a rather low Young's modulus, and the sample holder area must increase appreciably with pressure. Previous experience with sample holders which were made from this metal indicated that this expansion is about one percent in area at 10 000 atmos.[17] This correction was applied to the area of the sample holder in the calculation of the pressures which are given, and the error should be at most one percent at maximum pressure. The correction is quadratic in pressure and has little effect below 5000 atmos where one weight yields 1000 atmos at the sample.

The necessity for the potassium gasket which was used to seal the piston in the cylinder has been discussed previously.[15,16] The hydrogen-filling capillary led out of the Dewar system to a small gas container, whose volume was known and which could be evacuated and then filled with the vapor from a storage vessel of pure liquid parahydrogen which was boiling under a pressure of 12 psig. This storage vessel contained a quantity of charcoal as a catalyst in direct contact with the liquid hydrogen, and an analysis showed that pure parahydrogen existed in the container within one day after it was filled. A filling lasted approximately three weeks. Another check showed that there was negligible back-conversion in the gas container over the period of about an hour during which the gas was stored before it was condensed into the sample holder.

In order to be able to control the condensation of the hydrogen and also to cool the rather massive press efficiently, a metal "bottom filling" helium Dewar was used. By controlling the liquid helium transfer rate, the sample holder could be held at a temperature near 15°K until the desired amount of liquid hydrogen (about 1 cm^3, as shown by the pressure drop in the room-temperature gas volume) had been condensed into the sample holder. This technique removed the possibility of a solid hydrogen block during the condensation. The liquid helium Dewar had a 2½-liter capacity which was sufficient for an eight-hour run, and it could be refilled if desired without loss of the solid hydrogen around the sample. The 0.010-in. brass disk (lightly greased) served as a vacuum and pressure seal, and the amount of force needed to punch it out at 4.2°K (roughly 1000 lb) served to seat the potassium gasket initially.

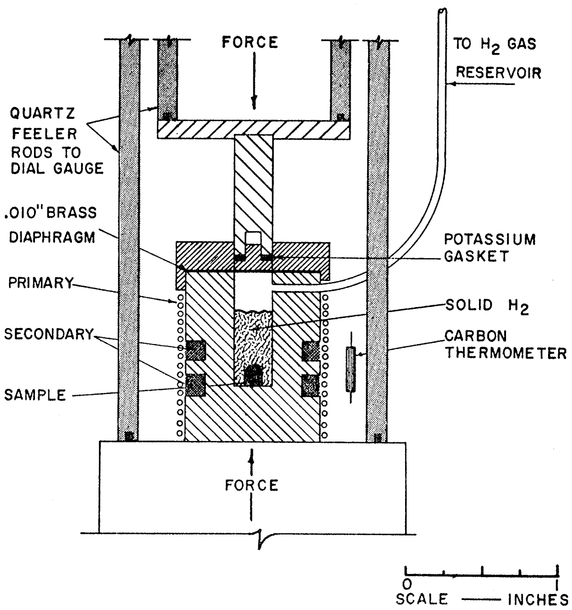

FIG. 1. A sketch of the high-pressure sample holder. The hydraulic press which furnished the forces indicated, as well as the liquid helium Dewar in which the press was placed, are not shown.

The quartz feeler rods connected the sample holder piston and cylinder to the frame and pin, respectively, of a commercial dial gauge (0.100 in./rev., 1.000-in. total travel) at room temperature. This dial gauge indicated the amount of solid hydrogen in the sample holder after compression, and also showed the compression of the solid hydrogen upon the application of pressure. When readings were taken with increasing and decreasing pressures, the separation of the two curves at any given value of the dial gauge reading gave twice the frictional effect, with the true internal pressure in the solid hydrogen being, presumably, the mean of the two pressure readings.[16,17] Such readings were made for each superconducting transition pressure determination, and in the discussion that follows, the "dial gauge friction" will be considered as just one-half the pressure difference between the pressure-increasing and pressure-decreasing displacement curves.

The temperature of the sample holder essentially was determined by the T_{55E} liquid helium vapor pressure scale. However, in order to take into account the potentially large hydrostatic head effects, a carbon resistance thermometer (Allen Bradley, 47 ohm) was mounted in the liquid helium close to the sample holder. The resistance was measured using a Rubicon No. 2780 Type B potentiometer and a current of either 10 or 100 microamperes. The resistance was monitored continuously during an isothermal run by means of a 0–100-microvolt Brown Recorder which was used with the potentiometer in place of a galvanometer. The resistance thermometer was calibrated at the end of a run when the liquid helium level was quite low.

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[17] C. A. Swenson, Phys. Rev. 99, 423 (1955).

TABLE I. A summary of the sources and purity of the metals used. The residual resistivities and unstrained transition temperatures are listed for comparison with other work.

Metal	Source	Purity percent	Impurities[a]	$R_{300}/R_{4.2}$	T_c (unstrained) °K
Tin	Baker, reagent	99.95	Fe, In; Ca, Cu, Mg, Pb, Si	500	3.725
Tin	Vulcan detinning, spec. pure	99.999+	Fe; Ca, Mg, Si	16 800	3.728
Indium	American Smelting and Refining	99.999	···	3900	3.404
Thallium	American Smelting and Refining	99.98	(Pb, Cu, Cd)	875	2.384
Mercury	Goldsmith, triple distilled	99.995	Traces: Ca, Cu, Mg, Si	···	4.153
Tantalum	Fansteel	99.+	0.07% zirconium	···	4.304

[a] Except for the thallium and the indium, where the supplier's analysis was accepted, the impurities are as determined by the Ames Laboratory Spectroscopic Analysis Group. The first elements in each analysis were classified as weak to very weak; those in the second group were present only in trace amounts. The analysis of the Vulcan tin did not agree well with the supplier's analysis, the major difference being the presence of some iron.

The vapor pressure of the bath was kept constant by a differential manometer-photoelectric cell regulator based on a design by Fiske.[18] This regulator uses a servo-operated valve for proportional control, and it proved invaluable in these experiments where an increase in the hydraulic oil pressure caused a burst of heat due to friction in the sample holder. The regulation was very good as measured by the constancy of the vapor pressure, but drifts in the resistance thermometer readings were observed which were real (as indicated by the transitions) and which could not be explained except on the basis that the temperature inside a liquid bath is basically determined by the competing hydrostatic head and convection effects. The addition of a small amount of heat to the bottom of the Dewar usually assisted in attaining an equilibrium temperature that was steady. The stability of the bath temperature as given by the resistance thermometer was usually about 2×10^{-4} deg above 3°K, but was quite poor just above the λ point in the thallium experiments. The error bars in the thallium and tantalum results (Figs. 5 and 6) are mostly due to uncertainties in the temperature measurements in these experiments.

The superconducting transitions were observed by means of the mutual inductance coils which are shown in Fig. 1 (primary, 10 turns/cm; secondary, 400 turns, wound in two parts to increase the strength of the sample holder). A Hartshorn bridge operating at 33 cps was used to measure the mutual inductance, and sufficient sensitivity was obtained through the use of a tuned amplifier. The units of M which are shown in Fig. 2 are roughly 0.2 microhenry, and the measuring field was 0.18 oersted rms, or 0.5 oersted peak to peak. The sensitivity of the measuring setup was such that changes in mutual inductance of 0.02 unit (Fig. 2) could be detected, although conditions were seldom such that this sensitivity could be used, or was actually needed.

The samples were generally in the form of cylinders, with rounded, almost hemispherical, ends (Fig. 1). In the preliminary runs, square-ended cylinders, 0.200 in. diam and 0.200 in. long, were used, but the size was reduced to 0.160 in. diam and 0.120 in. long, and one end was rounded when the need for less deformation became apparent, and the excess sensitivity was found. In general, except for mercury, the dimensions of the samples were measured before and after each run so that the deformation experienced by the sample could be determined.

EXPERIMENTAL AND DATA ANALYSIS PROCEDURES

The metals which were used, together with information as to their purity, source, etc., are given in Table I. Where there was any doubt as to the purity of a metal, a qualitative spectroscopic analysis was obtained from the Ames Laboratory Spectrochemistry Group. The impurities are listed as they appeared in this analysis, and have little quantitative significance. The zirconium content of the tantalum was determined in a quantitative analysis which supplemented the spectroscopic analysis.

The residual resistivities are also given for annealed wires of tin, indium, and thallium which were extruded from the same stock as the superconducting samples. The indium and thallium were annealed for two hours at 100°C, while the tin was annealed for the same time at 175°C. All of the samples which were used in the superconducting work were annealed for two hours in boiling water, with very little emphasis placed on this procedure since the samples were inevitably deformed by the solid hydrogen during the course of an experiment. For the same reason, no attempts were made to use single-crystal specimens. The details of the procedures which were used with mercury and tantalum will be given below in the discussion of the results.

At the beginning of each experiment, the superconducting transition temperature was determined for the sample in the annealed state before the application of pressure. This served as a check that the equipment was working properly, and also gave a means for comparing the states of the samples in different runs with the same metal. The widths of the unstrained mercury, thallium, indium, and tantalum transitions were about 0.01°, as were the strained widths. A rough computation of the effect of the demagnetization factor,

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[18] M. D. Fiske, General Electric Research Laboratory Memo 137, November, 1954 (unpublished). We are indebted to Dr. Fiske for supplying us with a copy of this memorandum.

taking into account the effects of the earth's field and the measuring field, showed that this was quite reasonable for indium, thallium, and mercury, although not for tantalum, which is a hard superconductor. The transition width for tin was greater by a factor of two (0.02°), and was probably due to the creation of stresses in the polycrystalline samples in the cooling process. The excess width of 0.01° could be explained by internal stresses up to 250 atmos in magnitude, and from the tin deformation which was observed in these experiments, this seems to be a reasonable figure for the yield stress of our tin at liquid helium temperatures. Indium and thallium are also quite anisotropic, but since they both have yield strengths much less than this (of the order of a factor of ten), and values for $\partial T_c/\partial P$ which are less than for tin, this effect would not be expected to appear. Although the mechanical properties of mercury are not known at liquid helium temperatures, it is presumably also quite soft, with a low yield strength.

A typical initial transition curve for the high-purity tin is given by the right-hand, bottom curve ($P_{\text{unc}}=-0.15$) in Fig. 2. The change in the mutual inductance for this run ($\Delta M=M_n-M_s$) was quite different from that found for the same sample after cycling to full pressure several times (see the curve, $P_{\text{unc}}=0$). This effect arises from the fact that for the high-purity tin the skin depth in the normal state at 33 cps is only about 0.1 mm at liquid helium temperatures and the interior of the sample is shielded even in the normal state. When the deformation of the sample on its initial compression in solid hydrogen raises its resistivity, the penetration of the magnetic field into the sample is increased, giving a larger ΔM. Much of this deformation may have been on the surface of the samples, and may not have been a bulk effect. The shape of the sample also changed slightly. However, after the first cycle, no appreciable further change in ΔM was observed.

Two types of experiments were used to determine the effects of pressure on the superconducting transition temperature. These were isotherms (increasing and decreasing pressure at constant temperature) and isobars (decreasing temperature at constant pressure). It was generally verified that these gave the same results when the data were properly interpreted. Typical isotherms and isobars are shown in Fig. 2. The data for tin VII were chosen because the greatest (and most consistent) number of points were taken for this sample, although many of the conclusions apply to all the samples tested.

The criterion for the superconducting transition pressure (or temperature) as used in this work was the pressure (or temperature) at which, neglecting any rounding of the transition curve, the sample first became superconducting, or at which the last of the samples became normal, depending on the direction in which the transition took place. This criterion is illustrated by the solid lines in both the isotherms and isobars of Fig. 2.

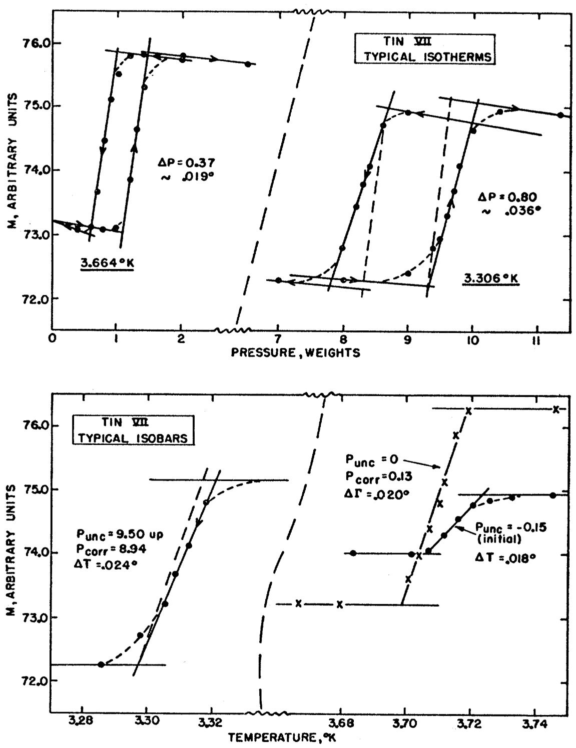

FIG. 2. Typical experimental isobars and isotherms obtained from the high-purity tin VII sample. The pressures are in arbitrary units (deadweight gauge weights) of roughly 1000 atmos. The minimum pressure available was about 150 atmos due to the weight of the dead-weight gauge pan, and all pressures above are calculated from this value as a nominal zero. The solid lines are fitted to the data and the dashed lines are corrected for the effects of pressure gradients. The subscripts "unc" and "corr" refer to pressures which are uncorrected or corrected for friction.

The problems which are involved in analyzing these curves will be illustrated by first discussing the isotherms (Fig. 2). The apparent friction in the system is evaluated by observing the transition for both increasing and decreasing pressure (both a high-pressure and a low-pressure cycle are shown). The friction, as given by the dial gauge readings (taken simultaneously), and also by the difference between the two superconducting transition pressures, generally increased slowly with pressure. For low pressures, the superconducting friction was identical with the dial gauge friction, but at high pressures the superconducting friction increased more rapidly. At low pressures the widths of the isothermal and isobaric transitions $[\Delta T_c=\Delta P_c(dT_c/dP)]$ were identical, so it was assumed that the low-pressure width was characteristic of the transition. However, at high pressures, the width became considerably larger for the isotherms (Fig. 2), and this was attributed to pressure gradients existing along the length of the sample.

The existence of these pressure gradients can also explain the greater increase of the superconducting friction as compared with the dial gauge friction. The upper knee which is found upon the increase of pressure corresponds to the transition at the bottom (and lower-pressure) end of the sample, while the upper knee which is found on the pressure-decreasing curve corresponds to the initiation of the transition at the top end of the sample. At low pressures, if there is no gradient, the curves refer to the sample as a whole, and the dial gauge friction is found. If it is assumed that the true width of the transition is unchanged by the application of the pressure, then the true transition pressure at, say, the top of the sample can be obtained by drawing a line parallel to the low-pressure transition curve through the lower knee on the pressure-increasing curve (see the dashed lines in Fig. 2), and through the upper knee on the pressure-decreasing curve. The resulting separation of these two lines, so drawn, was always identical with the dial gauge friction to within experimental accuracy (±50 atmos). The transition pressure was then taken as being the average of these two values.

The widening which was observed at high pressure was reversible; the 3.306°K curve in Fig. 2 was taken before the 3.664° curve. Thus, this widening gives a clue that pressure inhomogeneities in the solid hydrogen are about 400 atmos along the sides of this sample at 10 000 atmos. It should be emphasized that one isotherm can give the transition pressure quite unambiguously for a given temperature, without recourse to the dial gauge readings, provided that a low-pressure isotherm and a sufficiently accurate value of the ratio $(\partial T_c/\partial P)_P/(\partial T_c/\partial P)_{P=0}$ are available.

A similar effect should exist for the isobars, except that here the actual pressure on the sample depends on the direction of the force of friction, or, in other words, whether the applied force was generated with the piston moving down (pressure increasing), or with the piston moving upwards (pressure decreasing). Ideally, it is necessary to make two measurements, with opposite piston motions, to determine the frictional correction. The effects of pressure gradients should still exist, and should manifest themselves as an increase in the width (ΔT_c) of the transitions.

For the pressure-increasing case, the top knee of the transition curve corresponds to the transition at the bottom of the sample, and to obtain the transition temperature corresponding to the top of the sample, it is necessary to draw a line through the bottom knee which is parallel to the transition curve obtained at low pressures. This is done for the lower left-hand curve in Fig. 2, and is shown by the dashed line. Similarly, the top knee for a pressure-decreasing isobar gives the true transition temperature for the top of the sample. The usual technique was to correct the isobar data in this manner, and to assume the friction correction as determined from the dial gauge readings in order to reduce the apparent pressure to the true pressure.

As can be seen from Fig. 2, the change in width of the transition at high pressure was much greater for the tin isotherms than it was for the isobars. This effect is undoubtedly connected with an effect which was most pronounced for the tantalum runs, but which was observed in all of the isotherms which were taken at high pressure. There seemed to exist a very long equilibrium time (of the order of ten minutes) during which the mutual inductance drifted at constant external temperature after the pressure on the hydrogen was changed. This effect was observed when the pressure was such that the sample was in the middle of the transition curve, and was particularly apparent for tantalum since ΔM was large (12 units) and $(\partial T_c/\partial P)_H$ small. These time effects were always in a direction consistent with the hypothesis that the sample was hotter than the bath after a pressure change, and, thus, they could be interpreted as due to annealing in the solid hydrogen, with the subsequent release of heat (and change in pressure). In fact, it was almost impossible to obtain reliable isotherm data at the highest pressures for tantalum, and isobars were relied upon almost exclusively.

If these are annealing effects (or something related to them), then the difference between the isotherm and isobar curves becomes clear. Usually from fifteen to twenty minutes elapsed from the time that the pressure was applied in an isobaric run until the data covering the transition were taken, while it was never feasible to wait this long after each change in pressure during an isothermal run. The assumption of annealing seems to be strange, but no other hypothesis seems possible in view of the consistency of the results which were given by the two methods.[19]

Additional observations seemed to indicate that data taken during the initial pressure cycle after breaking the diaphragm were unreliable; one "seasoning" cycle was necessary. Also, the pressure inhomogeneities appeared to be greater at 4000 atmos for a sample that had not been taken to a higher pressure (the data on tin IV, Fig. 3) than for a sample which had been cycled to 11 000 atmos and then run at 4000 atmos. The reason for these effects is not clear, but it must be emphasized that the systematic analysis of the data, making the corrections for apparent pressure gradients as outlined above, gave no systematic difference between isotherm and isobar data which were taken at either increasing or decreasing pressure. This consistency is shown best in the results of the tin VII run which are given in Fig. 3.

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[19] We have been informed by Mr. L. Nesbitt of the General Electric Research Laboratories (private communication) that he and Dr. M. D. Fiske have also observed such annealing effects in extrusion experiments with solid hydrogen at liquid helium temperature. These observations were made considerably previous to ours.

TABLE II. The experimental results for Sn, In, Ta, and Hg at zero pressure in the earth's field, together with the Grüneisen constant η_0.

	Sn	In	Ta	Hgα	Hgβ
$-10^5(\partial T_c/\partial P)_{H=0}$ deg/atmos	4.95	4.36	0.26	3.4	4.4
$(\partial T_c/\partial V)_{H=0}$ deg-mole/cm^3	1.92	1.16	0.59	0.91	1.6
$(\partial \ln T_c/\partial \ln V)_{H=0}$	8.1	5.2	1.5	3.0	5.5
η_0	1.8[a]	2.35[b]	1.75[a]	2.2[c]	...

[a] See reference 23.
[b] See reference 22.
[c] See reference 24.

For the samples other than tin, the data were again consistent when treated in the above manner. The only other run in which the gradients were observed definitely was for mercury α, although the time effects in the isothermal measurements were observed for all samples. For tantalum, $(\partial T_c/\partial P)_H$ is so small that a pressure gradient of 400 atmos would be scarcely noticeable. For thallium, where the pressures were held below 6000 atmos, the unusual behavior of the T_c *vs* P curve is such that gradients would be difficult to see. For the mercury β phase, the natural width of the transitions appeared to be very broad and indicative of a strained sample. For indium, the data at high pressures were difficult to interpret, but no reasonable technique could be applied which gave more consistent results than the technique used for tin.

RESULTS

Tin

The results of two of the runs on tin are given in Fig. 3, and these data can be represented by the expression

$$T_c = (3.732 - 4.95\times10^{-5}P + 3.9\times10^{-10}P^2), \qquad (1)$$

where T_c is in °K and P in atmos.

The data for tin VII have a mean deviation from this curve of 0.0012° (25 atmos), and a maximum deviation of 0.002°. The tin IV run was intentionally held to quite low pressures (below 4000 atmos) initially, although at the end of the run at high-pressure (6000-atmos) run was made. The fit of the data for this run was not quite as good, with a mean deviation of 0.002° and a maximum deviation of 0.004°.

Both of these samples were polycrystalline (crystal size about 0.5 mm), and were made from the high-purity (Vulcan) tin. Their diameters were identical (0.160 in.), but the tin IV sample was 0.200 in. long as compared with the 0.120-in. length of tin VII. In spite of this difference in length, and the difference in the pressure range used, both samples showed a deformation of roughly two percent when inspected after their respective runs. The data shown in Fig. 3 were obtained from both isotherms and isobars in random order, and no systematic deviations were observed.

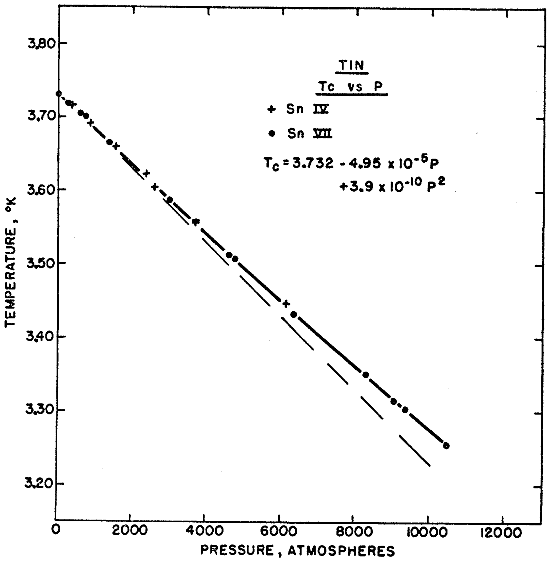

FIG. 3. The experimental results for two samples of tin. The solid curve is a plot of the quadratic equation given in the figure, whereas the dashed curve represents the linear term only.

This equation also represents moderately well earlier data on samples of the less pure tin (tin II and III) which were larger (0.200 in. diam and 0.200 in. long) and which suffered much greater (8%) deformation. These data, when recalculated using the above corrections, showed a mean deviation of 0.0018° and a maximum deviation of 0.005° from the above equation.[20] The extrapolation of this curve to higher pressure also agrees with the results of Chester and Jones[13] at 17 500 atmos. Thus, it is possible to conclude that the pressure dependence of the transition temperature for polycrystalline tin is relatively independent of the purity and the amount of deformation, as well as the technique used by the earlier workers.

It is of interest to try to interpret the curvature of the transition temperature *vs* pressure curve in terms of the change in volume with pressure. An extrapolation to absolute zero of Bridgman's data for the compressibility of single crystals of tin[21] gives

$$\Delta V/V_0 = -0.165\times10^{-5}P + 0.14\times10^{-10}P^2. \qquad (2)$$

When this is combined with (1), it is found that the variation of the transition temperature with volume can be expressed as a straight line by the relationship

$$T_c = (3.732 + 30.0\Delta V/V_0), \qquad (3)$$

where $V_0 = 15.6$ cm^3/mole, based on a density of 7.647 g/cm^3 at absolute zero. The values for various derivatives are summarized in Table II, which also lists the

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[20] The preliminary results reported at the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August, 1957 (unpublished), were obtained with the large samples, and were analyzed before the significance of the pressure gradients was realized.

[21] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949), p. 161.

values of the Grüneisen constant, η_0.[22-24] The uncertainty in $(\partial T_c/\partial P)_{H=0}$ is considered to be a maximum of 2%, while the other derivatives depend on the above extrapolation and are probably reliable to no better than 5%.

These data are only in fair agreement with the accurate low-pressure work of Fiske.[9] Our value of $(\partial T_c/\partial P)_{H=0}=(4.95\pm0.1)\times10^{-5}$ deg/atmos does not overlap with the value of $(-4.64\pm0.15)\times10^{-5}$ deg/atmos which can be calculated from his single-crystal results, and which agrees with other data for tin single crystals.[10,11] The difference may be due to an unexplained systematic error in either set of experiments, since far more serious disagreements occur for mercury and tantalum. Or, it may be due to a real difference which is caused by a difference in behavior between polycrystalline and single crystal samples. This difference is probably just significant enough so that it should be explored at greater length.

As can be seen from Table I and Fig. 3, the extrapolated zero-pressure superconducting transition temperature for tin showed a permanent shift to higher temperatures at the end of the runs, presumably due to the technique which was used. It is interesting, however, that the shift is so slight (0.004°) for the two-percent deformation which was suffered by tin IV and VII, and was not much greater for the tin II and III samples which had been deformed four times as much. We could detect no appreciable effect on the transition temperature due to initial annealing of the samples for several hours at 100°C.

The early experiments on tin II and III were made with large, rather impure samples, so that the change in mutual inductance (ΔM) was quite large (20 units). As was mentioned above, the sample deformations were also large, probably due to the small amount of solid hydrogen surrounding the samples. In any event, it was possible with these samples to observe quite accurately the effect of pressure cycling on the mutual inductances in the superconducting (M_s) and normal (M_n) states. The main factor influencing M_s is the motion of the piston (about 5 mm), although changes in sample shape will have some effect also. M_n is also influenced by the piston motion, but mostly by changes in the normal skin depth caused by changes in the resistivity due to deformation and hydrostatic pressure. The effects of piston motion can be compensated for by subtracting the variation of M_s with pressure (obtained from a cycle at 2.8°K, for instance) from the variation of M_n with pressure obtained for temperature above 3.73°K. The difference must be due to pressure and deformation effects.

This was done in detail for one tin run, and curves of M_n (corrected) as a function of pressure were obtained for successive cycles which resembled those obtained by Hatton for the resistivity of tin at 4.2°K. Here, however, it could easily be verified by later measurements at room temperature that the sample had been deformed, and undoubtedly was being deformed during these cycles. Thus, the increase in the zero-pressure value of M_n was attributed to an increase of the residual resistivity due to deformation. The initial slope of the M_n *vs* pressure curve was always in the direction of decreasing resistance with increasing pressure, although the curve passed through a minimum and the slope reversed sign at higher pressures where, undoubtedly, deformation was beginning to take place. Thus, we can say that our results are certainly not in contradiction with Hatton's hypothesis that the resistivity of a superconductor in the normal state decreases with pressure.

Indium

The results for indium III are given in Fig. 4, and can be represented by the equation

$$T_c=(3.403-4.36\times10^{-5}P+5.2\times10^{-10}P^2). \qquad (4)$$

The mean deviation of the data from this expression is 0.003°, with a maximum deviation of 0.011° (250 atmos) at the highest pressures. Indium is much softer than tin, and a total deformation of the order of twenty percent was found upon inspection of the sample after the run. The relative lack of consistency of these data, when compared with the tin data, can probably be explained in terms of this deformation. The indium III sample was identical in shape with the tin VII sample. Two earlier runs used the 0.200-in. right cylindical samples, and, while the data showed considerable scatter, the above relationship seems to express them reasonably well. The increase in ΔM upon cycling

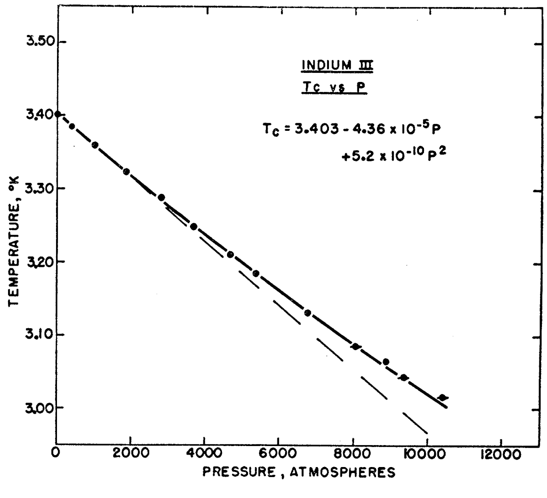

FIG. 4. The experimental results for the most reliable indium sample. The solid curve is a plot of the quadratic equation given in the figure, whereas the dashed curve represents the linear term only.

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[22] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).

[23] M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1957), fourth edition, p. 274.

[24] C. A. Swenson, Phys. Rev. **111**, 82 (1958).

(which should be indicative of the work hardening) was much less for the indium III sample than for the other two, so only the later run has been considered in plotting the data.

The change in volume with pressure for indium at 4.2°K can be estimated as

$$\Delta V/V_0=-0.247\times10^{-5}P+0.33\times10^{-10}P^2, \qquad (5)$$

where $V_0=15.370$ cm^3/mole. The total compression data at 4.2°K have been used here,[22] along with the assumption that the curvature in the $\Delta V/V_0$ *vs* pressure curve is the same as 4.2°K as to room temperature.[25] These data can give only an approximate relationship, but it is interesting to note that the transition temperature *vs* pressure curve is again more nearly linear when plotted *vs* this estimated volume than when plotted *vs* pressure. The variation of T_c with volume can be expressed as:

$$T_c=(3.403+17.6\Delta V/V_0). \qquad (6)$$

The relevant derivatives are given in Table II.

The data above 8000 atmos in Fig. 4 showed the only inconsistencies between isobar and isotherm determinations of T_c which we observed. Even without taking into account these inconsistencies, the data were not of the same quality as for tin. Perhaps this effect could be explained if our sample were not truly polycrystalline, so that the pressure inhomogeneities were more serious for the isotherms than for the isobars. The experiments on the change in sample length at the transition indicate that indium is anisotropic in its superconducting behavior.[6,7] However, the exact effect of pressure inhomogeneities in such a case is difficult to ascertain. This must be considered as a remote possibility, since the sample was formed initially in a die (although it was subsequently annealed), and, in addition, was deformed by twenty percent at liquid helium temperature.

An attempt was made to correlate the increase in ΔM (of about a factor of four) with earlier data on the change in the resistivity of indium upon deformation at 4.2°K,[22] since both the initial resistivity (Table I) and the amount of deformation were known. In general, the changes in ΔM seem to be much greater than the calculated changes in the skin depth would predict when the bulk deformation is assumed. The reason for this could lie in a greater relative deformation of the surface of the metal due to the slipping of the solid hydrogen during the compression process.

The initial slope $[(\partial T_c/\partial P)_{H=0}=(-4.36\pm0.10)\times10^{-5}$ deg/atmos$]$ agrees within experimental error with the previous pressure work of Hatton[14] and Muench,[10] and the volume change data of Olsen.[6] The difference between the initial value for the superconducting transition temperature and the extrapolated zero-pressure value is very small, again showing little dependence on deformation at 4.2°K.

Tantalum

The results of the run on tantalum II are given in Fig. 5. These results can be represented by the expression

$$T_c=(4.3010-0.26\times10^{-5}P), \qquad (7)$$

with a mean deviation of 0.0005° (200 atmos) and a maximum deviation of 0.0018°. The small changes in the transition temperature which were observed (0.027° over all) necessitated the use of the resistance thermometer, and the reduction of these resistance thermometer data to absolute temperature using a calibration which was taken at the end of the run. The scatter in the points is doubtless due to the difficulties in determining the temperature of the sample holder by means of a thermometer which was not attached to it directly. The permanent decrease in the transition temperature at zero pressure which was observed (0.003°) may or may not be real. The points shown on Fig. 5 were obtained from both isotherms and isobars, and were taken in random order. The only exception to this statement is that at high pressures the annealing effects were so great as to make the taking of isotherms impractical.

The curvature in the pressure *vs* volume curve for tantalum at room temperature is so small[21] that it is not surprising (if our results on tin and indium are to be interpreted as being general) that no curvature was found in the transition temperature *vs* pressure curve. This fact (as well as the slope) is in excellent agreement with the work of Bowen up to, roughly, twice the pressure.[26] No sign of the curvature mentioned by Hatton in his resistive transitions was found.

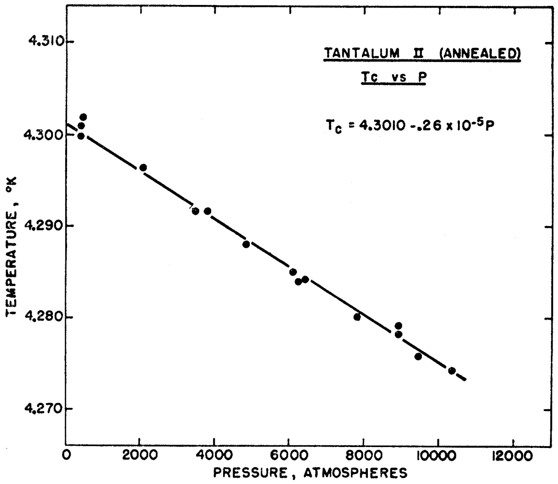

FIG. 5. The experimental results for tantalum annealed for a short time at 2300°C.

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[25] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 1 (1945).

[26] D. H. Bowen, Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August, 1957 (unpublished).

Bridgman's room-temperature data suggest an extrapolated compressibility at absolute zero of $(4.0\pm0.2)\times10^{-7}$ atmos^{-1},[21] and this gives a value for $(d\ln T_c/d\ln V)=1.5°$, which is less than for any of the other metals. The temptation exists to conclude that, since the only other cubic superconductor which has been studied (lead) also shows a small value for this quantity, the pressure effect is fundamentally smaller for the isotropic metals than for the more complicated anisotropic metals. Unfortunately, as will be pointed out below, tantalum, being a hard superconductor, offers many problems which are not understood. The value for dT_c/dV for tantalum in Table II was calculated assuming that the molar volume at absolute zero is 11.0 cm^3.

Our zero-pressure transition temperature and the shape of the transition temperature *vs* pressure curve seemed to depend very strongly on annealing in vacuum. Tantalum I (not shown) was run with the same piece of tantalum as the above, but was only annealed in high vacuum at 1300°C for a few minutes. The transition temperature was 4.27°K, and the mutual inductance *vs* temperature curves were quite rounded. The variation of the transition temperature with pressure, however, agreed in slope with tantalum II, but with some indication of a rounding at high pressures.

Tantalum I was then annealed at 2300°C in a high vacuum until the outgassing stopped and the pressure dropped to 10^{-6} mm Hg. The results of Fig. 5 were then obtained, with the transitions resembling closely those of Fig. 2, but with a width of 0.01°. The resulting transition temperature (4.304°K) is much lower than the accepted value of 4.38°K, although the sample was pure (the spectroscopic and a later quantitative analysis gave as the only impurity 0.07% zirconium) and well annealed by most standards. No sign of deformation was found upon inspection of the sample after the runs.

The value for the slope of the curve of Fig. 5 $(-0.26\times10^{-5}$ deg/atmos) is in definite disagreement with the value of -1.1×10^{-5} deg/atmos which can be deduced from Fiske's data.[9] Fiske's samples were subjected to a rigorous annealing process by being held at 2800°C for 25 hours, and recent work on the thermal properties of normal and superconducting tantalum seems to imply that the superconducting properties of tantalum can be made to approach those of a soft superconductor by such an annealing treatment.[27] However, none of the works on tantalum reported in the literature give the impurities present in the samples, and the term "high purity" is quite ambiguous for this metal. In any event, the status of the pressure (and volume) effects measurements is quite confused, with the current work (sample moderately annealed) agreeing with Bowen (sample as received) and Hatton (moderately annealed), but disagreeing with Fiske (well annealed) and Olsen (sample as received). There seems to be no consistency in these various sets of measurements, since Hatton and Olsen, while disagreeing on the magnitude of $(\partial T_c/\partial P)_{H=0}$, agree that it should pass through zero at some pressure (or temperature in a magnetic field). Fiske presumably did not see this effect. It is obvious that some careful work will be required to clear up these differences, and it would be of interest if the various techniques could be used on samples from the same initial source which had been heat treated in exactly the same manner. Our data are suspect in any event because of the low value for the zero-pressure transition temperature, and the transition width which is larger by a factor of two than would be expected from the estimated demagnetization factor.

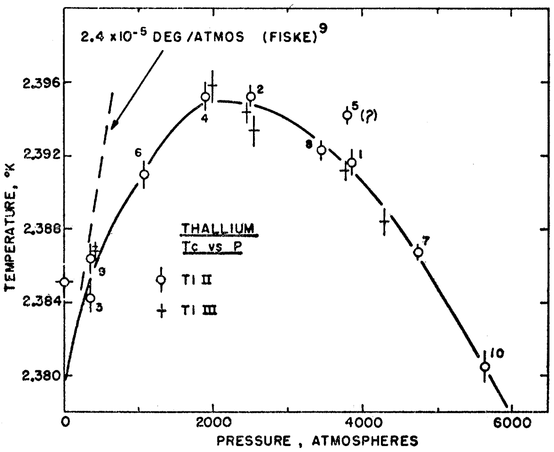

FIG. 6. The experimental results for two thallium runs. The numbers on the thallium II experimental points indicate the order in which the data were taken, and show the lack of systematic effects due to pressure cycling. The point numbered (5) showed an anomalous excess width which was reproducible but which was not present for previous or succeeding points. The dashed curve shows the initial slope of the curve found by Fiske.

Thallium

The experimental behavior of the transition temperature *vs* pressure curve for thallium was not understood for some time, since there appeared to be a change in the sign of the slope of the curve at high pressures. This discrepancy was first resolved by Hatton, and our data (Fig. 6) are in qualitative agreement with his. Again, because the temperature shifts are so small and the temperature region a difficult one due to large hydrostatic head effects, the resistance thermometer was relied upon almost exclusively. The agreement between thallium II and III was excellent. The individual thallium II points are numbered in the order in which they were taken to show the reproducibility and independence of cycling. In order to reduce the deformation to a minimum, the pressures were kept below 4000 atmos initially, with essentially only isobar data being taken for both increasing and decreasing

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[27] White, Chou, and Johnston, Phys. Rev. **109**, 797 (1958).

pressure. Late in the run, the pressures were raised to higher values and the results were consistent with those at low pressures. The total deformation $(\Delta L/L_0)$ was about 6% for thallium II and 4% for thallium III, showing the relatively greater softness of thallium as compared with tin at these temperatures.

The shift in the extrapolated zero-pressure transition temperature could be real, or could (if point 3 is ignored) be spurious. If Fiske's value for the initial slope is accepted, as is shown, the shift must be real. Certainly, it is impossible to make a definite decision as to whether or not the low-pressure value is correct from our data. An extrapolation of our curve to 13 400 atmos is in excellent agreement with the high-pressure shift of 0.06° observed by Chester and Jones.[13]

The recent work by Olsen[6] and by Cody[7] on the volume change at the superconducting transition in a magnetic field seems to offer a clue as to the reason for the maximum in the T_c *vs* P curve for thallium. Previous work had shown that it was probably not due to a crystallographic transformation.[22] Both Olsen and Cody found that the change in length at the transition is dependent on the crystallographic direction (as was also found for tin and indium), and, in fact, is of different sign depending on whether the ΔL is measured parallel or perpendicular to the C axis. This would imply that tensile stress along one crystallographic axis would produce a decrease in T_c, but the same stress would produce an increase in T_c along the other direction. If, now, these two coefficients $[(\partial T_c/\partial\sigma)_{H=0}$, where σ is the stress$]$, which must be suitably averaged to obtain the shift in T_c with hydrostatic pressure, vary with hydrostatic pressure, then any sign would be possible for $(\partial T_c/\partial P)_{H=0}$, dependent on the pressure. It would seem that the only positive method of verifying such an hypothesis would be to investigate the change in transition temperature produced by elastic stress along the crystallographic directions of a single crystal of thallium as a function of hydrostatic pressure. This would be a very difficult experiment.

An initial run with thallium was completely unsuccessful, in that it gave data which were impossible to interpret consistently using methods outlined above. These results have been neglected in the above discussion, since the sample was highly deformed (20%), and there was evidence of excessively large pressure gradients in both the isotherms and isobars for those runs which were made with increasing pressure. The pressure-decreasing runs were quite consistent among themselves, and agreed qualitatively with Fig. 6.

Mercury

The data which were obtained from three samples of mercury are given in Fig. 7. The liquid mercury was placed initially in a cylindrical Scotch tape container, 0.16-in. inside diameter, to form a sample 0.2 in. long with a top which was assumed rounded by surface tension. The initial transition temperature was found to be independent of the rate of cooling. The container was weak enough so that it presumably disintegrated upon the first application of pressure. The mercury was kept from amalgamating with the beryllium copper cylinder when it was warmed back to room temperature by coating the inside of the cylinder initially with mineral oil. This seemed to have no effect on the friction, and the loss of a sample holder by amalgamation in one of the first runs showed this precaution to be necessary.

The basic problem which was raised (and resolved) in these experiments is demonstrated by the data for mercury II, where the numbers indicate the order in which the points were taken. The indication seemed to be that there was a permanent shift in the transition temperature at zero pressure of 0.12° after the high-pressure cycling. Along with the gradual downward shift in transition temperature, there was a widening of the transitions from about 0.01° to about 0.05°, which would be expected for a highly strained sample. The run with mercury III confirmed this, with the added factor that the friction was considerably greater for this run.

Finally, on the hypothesis that it was the deformation of the sample which was important, the mercury IV run was made in which the data were obtained almost solely by means of isobars, with the pressures kept below 4000 atmos. The transitions remained sharp for all these points $(\Delta T_c = 0.01°$, plus a reversible increase due to pressure gradients). The extrapolated zero-

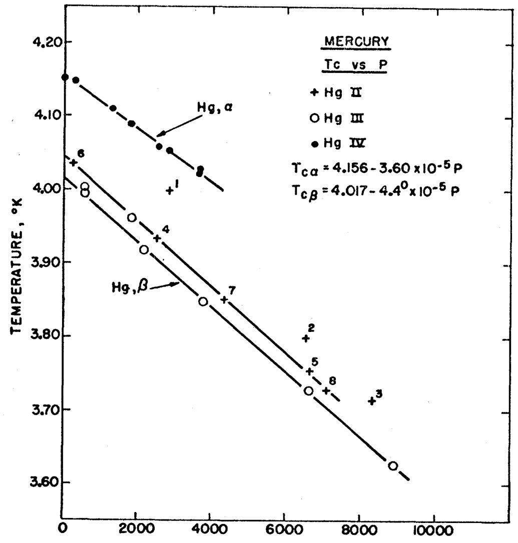

FIG. 7. The experimental results for the mercury runs. The numbers on the mercury II experimental points indicate the order in which these data were taken, and show the gradual decrease in the transition temperature with cycling. The anomalous mercury III point at 1800 atmos was taken between the unstrained point and the points which lie on the curve. Hence, it corresponds with the mercury II points labeled (1), (2), and (3).

pressure transition temperature was 0.003° higher than the original transition temperature. These data are shown in the upper (Hg_α) curve of Fig. 7. Thus, it seems that two transition temperature *vs* pressure curves could be obtained for mercury, one of which was characteristic of pressures below 4000 atmos, and a second which was much less clearly defined, but which was characteristic of cycling to much higher pressures. No further conclusions could be drawn from these experiments.

A second, independent, series of experiments were undertaken in which a much higher temperature phase transition in solidified mercury was investigated as a function of pressure.[24] These experiments showed that mercury ordinarily exists in a metastable state below 79°K. It can be forced into its stable form by the application of pressure, and this is presumably the reason why two superconducting transition curves were obtained. The postulate must be made, however, that at liquid helium temperatures it is deformation rather than pressure (or, perhaps, a combination) which is necessary to cause the transition. Thus, there is no reason for concluding that the lowest value of the transition temperature of the β phase which was observed here has any real significance. The difference between the two mercury β curves could well be due to the larger friction (and, hence, larger deformation?) which occurred in the mercury III run. The true transition temperature of this new phase must be determined in other experiments.

The data in Fig. 7 can be expressed by the relationship,

$$T_c = (4.156 - 3.60 \times 10^{-5} P), \tag{8}$$

for the α phase of mercury with a mean deviation of 0.002° and a maximum deviation of 0.004°. The lower curve for the β phase can be represented by

$$T_c = (4.017 - 4.40 \times 10^{-5} P), \tag{9}$$

with a mean deviation of 0.005° and a maximum deviation of 0.009°. The transitions for the β phase were generally very broad, and hard to fix accurately.

The same experiments in which the phase transition in mercury was studied also gave the pressure *vs* volume curves for mercury as a function of temperature for each of the phases. The transition temperatures of Fig. 7 show sufficient scatter so that no improvement in fit was found when they were plotted against volume rather than pressure. A summary of the various derivatives which could be calculated is given in Table II, although it must be emphasized that the data for the superconducting properties of the β phase of mercury are open to question since the phase transition may not have been complete.

The slope of the transition pressure *vs* temperature curve for mercury $\alpha[(-3.60\pm0.2)\times10^{-5}$ deg/atmos$]$ does not agree with the low-pressure value of $(-4.24\pm0.16)\times10^{-5}$ deg/atmos which can be deduced from Fiske's data,[9] nor with the value from the tensile data of Grenier (-2.9×10^{-5}).[9] The cause of this discrepancy is not known, in view of the relatively better agreement for tin. Our results are based solely on one run with one sample (which was cooled slowly overnight), and difficulties may have arisen due to pressure gradients if our sample was not truly polycrystalline. The apparent gradient amounted to less than 400 atmos, which is, nevertheless, relatively large when it is realized that the maximum pressure was 4000 atmos, and no gradients were observed at this pressure for tin VII. A similar behavior was found for the tin IV sample, however, when its pressure was kept low initially, and the results for the two tin runs agreed quite well.

The existence of the new mercury phase does not seem to offer a direct explanation for the results of Buckel and Hilsch[28] in their work with thin films of mercury which were deposited at liquid helium temperatures. The behavior of mercury was found to be anomalous in their experiments in that the superconducting transition temperature for the films was lower than the normal value, while it was increased for all the other substances studied. The possibility exists that the β phase of mercury is deposited at these temperatures, but currently there is little evidence upon which to base a decision.

SUMMARY

The major conclusions given by these experiments can be summarized as follows:

1. Solid hydrogen may be used satisfactorily as a transmitter of approximately hydrostatic pressure up to 10 000 atmos. The pressure gradients which were observed were of the order of several hundred atmos at the maximum pressure, although larger gradients may have existed as transients when the pressure was changed in large steps. Apparent annealing effects were observed in the solid hydrogen at 4.2°K.
2. The variation of the superconducting transition temperatures which was found for tin and indium are more nearly linear when plotted against the volume than when plotted against pressure.
3. The superconducting transition temperatures for the soft superconductors tin, indium, and thallium do not seem to depend very strongly on deformation at liquid helium temperatures.
4. The transition temperature *vs* pressure curve for tantalum is a straight line with a slope an order of magnitude less than that for tin or indium. This can be understood partially on the basis of the small compressibility of tantalum as compared with the other metals, although the discrepancies between results of various workers make definite conclusions difficult.
5. Previous data on thallium which showed first an

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[28] W. Buckel and R. Hilsch, Z. Physik **138**, 109 (1954).

increase of the transition temperature with pressure, then a decrease, have been confirmed.

6. The existence of two superconducting transition temperature *vs* pressure curves for mercury, depending on its history at liquid helium temperatures, have given the first indication that mercury normally exists in a metastable state at low temperatures.

7. The ratio $(d \ln T_c/d \ln V)$ varies considerably from one metal to another, with the values for tantalum (1.5) and tin (8.1) representing the extremes. Except for thallium at low pressures, this ratio was always positive. In order to obtain the true effects of compression on the density of states of the electrons at the Fermi surface and on the interaction matrix, it is necessary to add the Grüneisen constant to these values, since the effect of compression on the lattice vibrations alone is to produce a shift in the opposite direction (see the Introduction). In general the data summarized in Table II gave a straight line when T_c was plotted *vs* V, but an appreciably curved line when $\ln T_c$ was plotted *vs* $\ln V$. This means that the values tabulated in the third line of Table II refer only to zero pressure and magnetic field, and should not be used for extrapolation.

The most acceptable check on the thermodynamic consistency of these results would be given by an extension of the techniques to transitions in magnetic fields. This was not possible with the current experimental apparatus. Several problems must be investigated before such experiments can be undertaken with any hope of success. For instance, our results seem to show that there is little effect on the zero-field transition temperature due to the deformation which inevitably accompanies measurements on the softer metals made under pressure in a bath of solid hydrogen. It is not known whether a similar statement can be made with respect to the effects of deformation on the critical field curve at zero pressure, and it is hoped that this point will be investigated in the near future. There is also some question as to whether or not it is necessary to use single crystals of the anisotropic metals in order to obtain correct results, and whether, even in this case, the pressure gradients which we observed would cause anomalous results for certain crystal orientations. We, again, hope to look into this question. The disagreements between our work and Fiske's for tin and mercury are examples where these two effects may have come into play. In any event, it does not seem profitable to attempt the measurements in a magnetic field by our technique until the effects on the critical field curve of deformation, crystalline state (whether polycrystalline or single crystal), and demagnetization factor (due to the sample shape) have been investigated. The effect of impurities and annealing must also be investigated in the case of tantalum.

One interesting sidelight can be inferred from our data. Considerable work has been done with the ice bomb technique, and it is of interest to note that the ratio of the temperature shifts which were found by Lazarew and Kan for tin and indium agrees well with our data.[12] The pressures which were generated at liquid helium temperatures were assumed to be 1370 kg/cm^2 and 1750 kg/cm^2, while our data suggest that the pressures should be closer to 1750 atmos and 1950 atmos, respectively. These differences are not important, although the origin of the miscalculation might be. It must be emphasized that the value of the ice bomb technique lay not so much in obtaining accurate results, but in the fact that it outlined the problems which existed in this region of high-pressure and low-temperature physics. It is useful to note that once the transition temperature *vs* pressure curve for tin has been established, then tin can be used as a secondary pressure measuring device at these low temperatures.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. V. W. Hesterman who measured the residual resistivities and also assisted in the taking of some of the superconducting data. The tantalum was obtained from Dr. A. H. Daane, who also graciously undertook the annealing of the sample. The spectroscopic analyses of the samples were performed by Mr. E. L. Dekalb of the Spectrochemistry Group of the Ames Laboratory.