PHYSICAL REVIEW VOLUME 103, NUMBER 5 SEPTEMBER 1, 1956

Effect of Pressure on Superconducting Transitions and on Electrical Resistance at Low Temperatures

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(Received April 12, 1956)

Measurements have been made on the shift of the superconducting transition temperatures of Sn, In, Hg, Tl, and Ta by pressures up to 5000 kg/cm². For thallium, $\Delta T_c/\Delta P$ is initially positive but becomes negative above 1200 kg/cm². The effect of pressure on the normal resistance of all these metals, except Hg, has been investigated just above their transition temperatures. In all cases the resistance decreases under pressure.

INTRODUCTION

In recent years there has been a growth of interest in the effect of pressure on superconducting transitions. This has been due largely to the realization that the lattice plays an important role in the superconductivity of a metal, as suggested by the theories of Frohlich[1] and Bardeen[2] and confirmed by experiments on the isotope effect.[3,4] Measurements on the shift of superconducting transition temperature due to reduction of the lattice spacings by pressure should provide valuable guidance for the construction of any detailed atomic theory of superconductivity.

In the experiments to be described here, the method of applying high pressure to the superconducting specimen has the great advantage of enabling the pressure to be continuously varied at liquid helium temperatures. The importance of this is that it makes possible a check on the reversibility of the pressure effects. Hitherto, the only experiments which fulfilled this condition have been those in which pressure was transmitted to the superconductor by liquid helium, and which consequently were limited by solidification of the helium to maximum pressures in the neighborhood of 100 atmos.

In addition to measuring the shift of transition temperature under pressure, we have thought it profitable to examine how the normal electrical resistance of superconductors slightly above their transition temperatures is influenced by pressure. From measurements of this kind one might hope to find evidence for the nature of the electron-lattice interaction that differentiates superconductors from normal metals.

EXPERIMENTAL METHOD

The method used was to immerse the specimen in solid hydrogen contained in a stout cylinder, and to generate pressure by a close-fitting piston activated by a hydraulic ram. The piston and cylinder were immersed in liquid helium whose temperature could be varied. Insulated electric leads passed through the walls of the cylinder in order to make electrical resistance measurements on the specimen. The apparatus was identical with that used for earlier measurements[5] on the effect of pressure on the electrical resistance of metals at low temperature. The piston and cylinder arrangement is illustrated in Fig. 1.

The dimensions of the specimens were roughly 0.1–0.2 mm in diameter and about 5 mm long. For studying the superconducting transitions, the electrical resistance was measured by the voltage drop across the specimen due to a current of approximately 6×10^{-3} amp. The measuring procedure was as follows:

Keeping the pressure on the solid hydrogen at some constant value, the vapor pressure of the liquid helium was reduced very slowly and simultaneous readings made of the specimen resistance and of the vapor pressure. About a dozen readings were taken in the region of rapid fall of resistance, so that the shape of the transitions was accurately determined. The temperature of the helium bath was subsequently allowed to rise above the transition temperature of the specimen

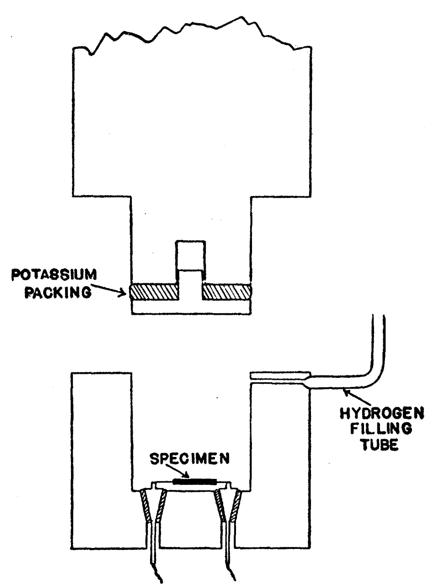

FIG. 1. The piston and cylinder. Only two of the four insulated leads are shown.

[1] H. Frohlich, Phys. Rev. 79, 845 (1950).
[2] J. Bardeen, Phys. Rev. 80, 567 (1950).
[3] Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. 78, 487 (1950).
[4] E. Maxwell, Phys. Rev. 78, 477 (1950).
[5] J. Hatton, Phys. Rev. 100, 681 (1955).

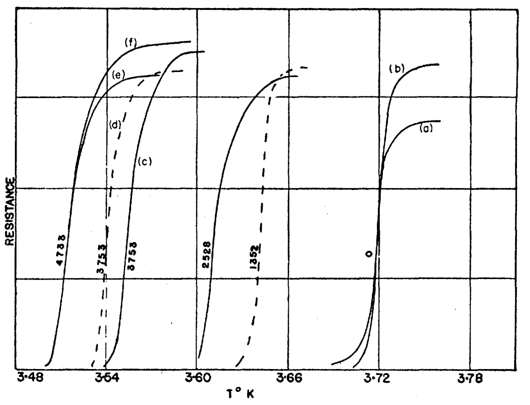

FIG. 2. Transitions in tin at different pressures. The measurements were made in the sequence: 0(a), 2528, 3753(c), 4733(e), 3753(d), 1352, 0(b), 4733(f).

and the observations repeated with a different pressure on the solid hydrogen.

Values quoted for the pressure applied to the specimens are derived from the measured thrust on the piston and its cross-section area, and are therefore in error on account of friction. Evidently, when a particular pressure has been reached by increasing from a lower value the true pressure on the specimen is less than the quoted value, and conversely for pressures reached by decreasing from a higher value. From measurements made with increasing and decreasing pressure, the effect of friction can be allowed for.

For measurements on the normal resistance of the superconductors above their transition temperatures, currents of the order of 0.5 amp were used. The temperature of the helium bath was maintained at a constant value and the resistance of the specimen measured at different pressures.

EXPERIMENTAL RESULTS

In the various figures showing the experimental results, full curves refer to observations made on the increasing part of a pressure cycle and dotted curves to the pressure-decreasing part of the cycle. Resistance values refer to the directly measured resistance (in arbitrary units) and not to the specific resistance. The value of a superconducting transition temperature, T_c, is taken to be the temperature at which the specimen resistance has fallen to half its normal value. With this definition, the precision of the measurements enables the value of T_c for each transition to be determined to within about 0.001 deg, except in the case of mercury for which the transitions were not followed to completion. An indication of the scatter of experimental points is provided in an earlier note on thallium.[6] In deducing values for the pressure coefficient of the transition temperature, negligible error arises from the uncertainty in T_c derived from the individual transition curves. The chief sources of uncertainty will be dealt with in the detailed presentation of results.

Tin.—The specimen was polycrystalline wire of high purity tin. The transitions at different pressures are shown for two complete pressure cycles in Fig. 2. It is observed that the transitions exhibit no appreciable broadening under pressure and that the pressure effects are reversible. In particular, there seems to be no permanent shift of the zero-pressure transition, contrary to the observations of Garber and Mapother.[7]

From these curves the values of T_c at different pressures are deduced and plotted in Fig. 3, in which the lower curve is drawn through points obtained at pressures reached by decreasing from higher values. The slope is greater than corresponds to the true dependence of T_c on P, being enhanced by the effects of ortho-para hydrogen conversion in the pressure cylinder, as will be explained later. In separate experiments we have investigated the effects of the ortho-para conversion and so are able to apply the appropriate corrections. From Fig. 3 we find that at 3753 kg/cm², the values of T_c corresponding to increasing and decreasing pressure differ by 0.015 deg. Taking the mean of these two values of T_c we get for the change between zero pressure and 3753 kg/cm² $\Delta T_c = -0.171 \pm 0.007$ deg. The effect of ortho-para hydrogen conversion accounts for an apparent shift of -0.012 deg, though this estimate might be in error by as much as 50%. Accordingly, we have for the true change of T_c under 3753 kg/cm², $\Delta T_c = -0.159$ deg with a possible error of ± 0.013 deg, giving $\Delta T_c/\Delta P = -4.3 \times 10^{-5}$ deg/(kg/cm²)$\pm$8%.

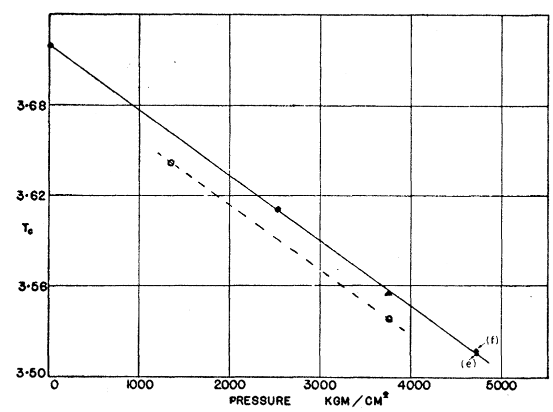

FIG. 3. Transition temperature *vs* pressure for tin, uncorrected for effect of ortho-para hydrogen conversion. Points on the upper curve correspond to pressures reached by increasing from lower values, those on the lower curve to pressures reached by decreasing from higher values. Letters on the points at 4733 kg/cm² indicate the curves of Fig. 2 from which they are derived.

In Fig. 4 we show the effect of pressure on the normal resistance of tin 4.2°K, for two complete pressure cycles. Initially the resistance is seen to decrease under pressure.

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

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

Indium.—The specimen was polycrystalline wire of high purity. Transitions at different pressures are shown for two complete pressure cycles in Fig. 5.

As in the case of tin, there is no significant broadening of the transition at high pressure. Apart from a small shift of the zero-pressure transition, the behavior under pressure is strictly reversible. The variation of T_c with pressure is shown in Fig. 6. From Fig. 6 we get for zero pressure and 2528 kg/cm², $T_c=3.399\pm0.001$ deg and $T_c=3.290\pm0.003$ deg, respectively. The effect of ortho-para hydrogen conversion is estimated at -0.012 deg, with an uncertainty of about 50%. Therefore, for the true change of T_c under 2528 kg/cm² we have $\Delta T_c=-0.097\pm0.01$ deg, giving $\Delta T_c/\Delta P=-3.8\times10^{-5}$ deg/(kg/cm²)$\pm$10%.

The variation with pressure of the normal resistance at 4.2°K is shown for two complete cycles in Fig. 7. The initial behavior is for the resistance to decrease under pressure.

Mercury.—For the measurements on mercury, there was some difficulty in devising a suitable holder for the specimen. The arrangement finally used consisted of a very thin tube made from a single thickness of cigarette paper. This was filled with distilled mercury and small iron electrodes were inserted in the ends. There was an appreciable contact resistance. The transitions appeared to be rather broad and were not followed to completion, but only far enough to enable their positions to be located with sufficient accuracy. The results are shown in Fig. 8, in which it is to be noted that the lowest value of ordinates does not correspond to zero resistance. In further experiments with mercury, much larger contact resistance and much broader transitions were encountered, but we were able to make measurements over a complete pressure cycle. These measurements were in reasonable agreement with the results given in Fig. 8 and showed the behavior under pressure to be substantially reversible. In view of the uncertainties associated with the measurements on mercury it does not seem worthwhile to apply corrections for the ortho-para hydrogen conversion. The results give $\Delta T_c/\Delta P\approx-4\times10^{-5}$ deg/(kg/cm²), with an estimated uncertainty of $\pm$25%.

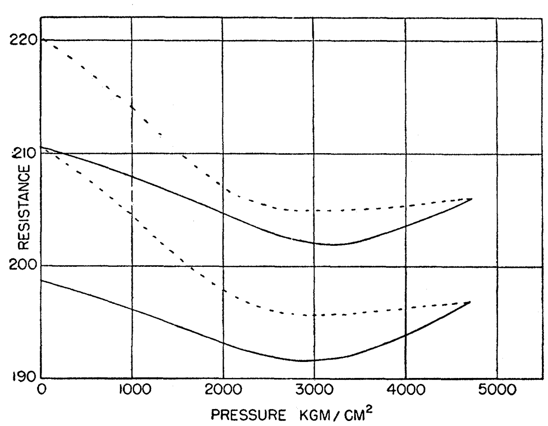

FIG. 4. The normal resistance of tin at 4.2°K *vs* pressure.

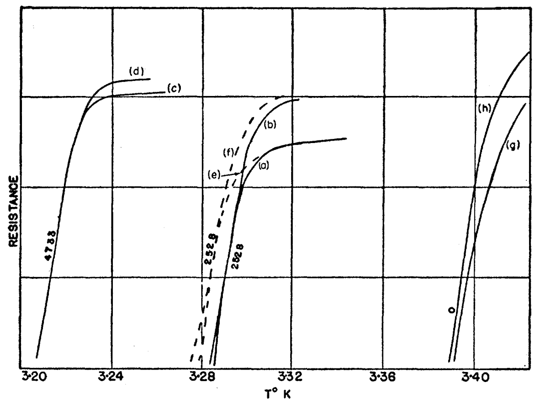

FIG. 5. Transitions in indium at various pressures. The measurements were made in the sequence: 2528(a), 4733(c), 2528(e), 0(g), 2528(b), 4733(d), 2528(f), 0(h).

No attempt has been made specifically to measure the effect of pressure on the normal resistance of mercury. It is worthwhile to point out, however, that in the experiments discussed above the measured overall resistance of the specimens in the normal state decreased markedly under pressure. Although it would be rash to ascribe this entirely to a decrease in the resistance of the mercury itself, the observations make it seem very probable that the true resistance does decrease under pressure.

Thallium.—Some heavy gauge wire of pure thallium was kindly made available to me by C. A. Swenson of Iowa State College. This was reduced to a thin ribbon from which a suitably sized specimen was prepared under distilled water. The specimen was surrounded by an inert atmosphere during mounting in the pressure cylinder. In the course of these operations the surface of the thallium became slightly tarnished, but since the ratio of the resistance at room temperature to that

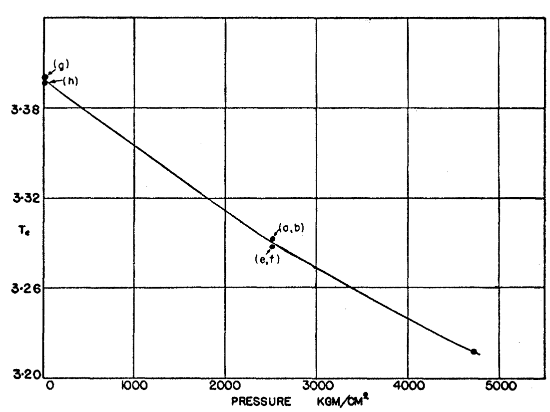

FIG. 6. Transition temperature *vs* pressure for indium, uncorrected for effect of ortho-para hydrogen conversion. Points at 0 and 2528 kg/cm² are lettered to indicate the curves of Fig. 5 from which they are derived.

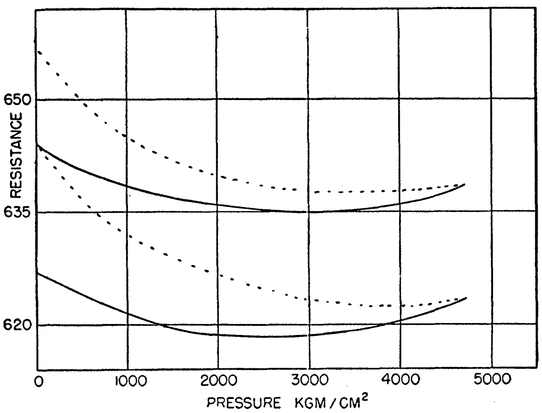

FIG. 7. The normal resistance of indium at 4.2°K *vs* pressure.

at liquid helium temperature was greater than 300, we conclude that there could have been no serious contamination of the specimen.

In studying the superconducting transitions of thallium, the medium used for transmitting pressure to the specimen was solid HD rather than solid H_2. As pointed out in an earlier note on thallium,[6] this was made necessary by the observation that in the case of solid H_2 (presumably having an ortho-para ratio of 3:1) the ortho-para conversion rate increases appreciably under pressure. The heat liberated by this conversion produces a pressure-dependent temperature drop between the position of the specimen inside the cylinder and the helium bath (where the temperature is measured). Owing to the smallness of the true shift of transition temperature with pressure for thallium, it is necessary to make the measurements using some modification of hydrogen in which there is no complication from ortho-para conversion. Actually a number of experiments were performed using solid H_2 and solid HD and from a comparison of the results obtained we have been able to determine, approximately, the effect of the conversion in H_2 and so to apply appropriate corrections to the results for tin and indium.

The transitions of thallium, using HD as the pressure-

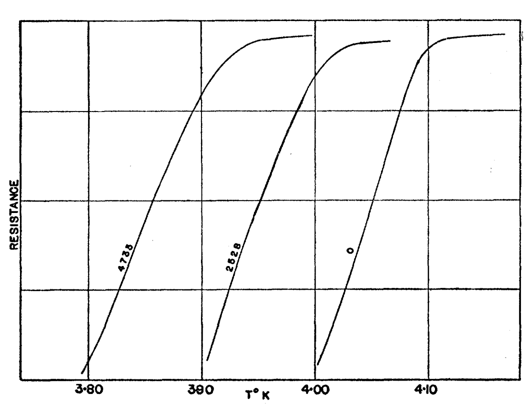

FIG. 8. Transitions in mercury at different pressures.

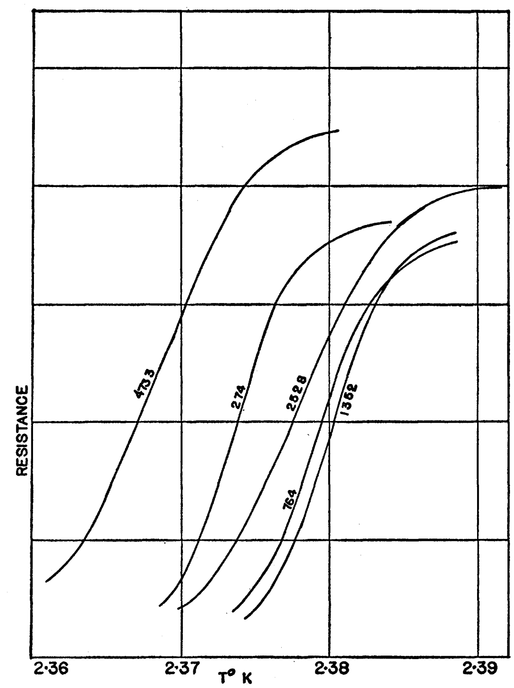

FIG. 9. Transitions of thallium at various pressures.

transmitting medium, are shown in Fig. 9. The variation of T_c with pressure deduced from Fig. 9 is remarkable in that the sign of $\Delta T_c/\Delta P$ changes from positive to negative at about 1200 kg/cm^2, as shown in Fig. 10. Evidence of such behavior has also been found by Bowen and Jones.[8] The effect of pressure on thallium is reversible in the sense that the shape of the T_c *vs* P curve is reproduced when the pressure is reduced to zero, though the curve for decreasing pressure lies below that for the first application of pressure and returns to a zero-pressure transition temperature somewhat lower than the original value. On a second application of pressure, the transition

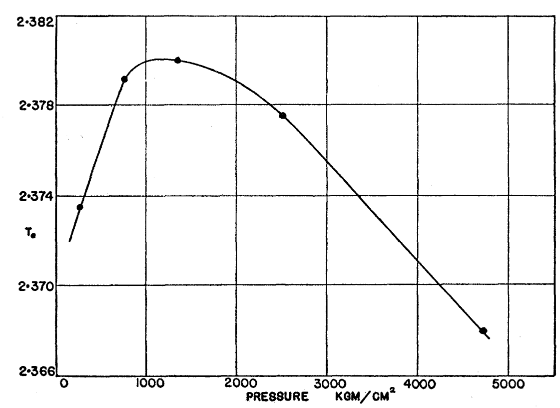

FIG. 10. Transition temperature *vs* pressure for thallium.

[8] D. H. Bowen and G. O. Jones, *Conference de Physique des Basses Temperatures* (Centrenational de la Recherche Scientifique and UNESCO, Paris, September, 1955), p. 514.

temperature again shows an initial rise. From Fig. 10 we get

$(P<800 \text{ kg/cm}^2)$:

$$\Delta T_c/\Delta P = +1.3\times10^{-5} \text{ deg/(kg/cm}^2\text{)},$$

$(P>2000 \text{ kg/cm}^2)$:

$$\Delta T_c/\Delta P = -0.43\times10^{-5} \text{ deg/(kg/cm}^2\text{)}.$$

Measurements made on a number of different specimens of thallium yielded different values for these coefficients, although the behavior was qualitatively always the same. The evidence from several experiments indicates that the values of $\Delta T_c/\Delta P$ lie in the range:

$(P<800 \text{ kg/cm}^2)$: $\Delta T_c/\Delta P$ from $+0.9$ to $+1.5\times10^{-5}$ deg/(kg/cm^2),

$(P>2000 \text{ kg/cm}^2)$: $\Delta T_c/\Delta P$ from -0.35 to -0.45×10^{-5} deg/(kg/cm^2).

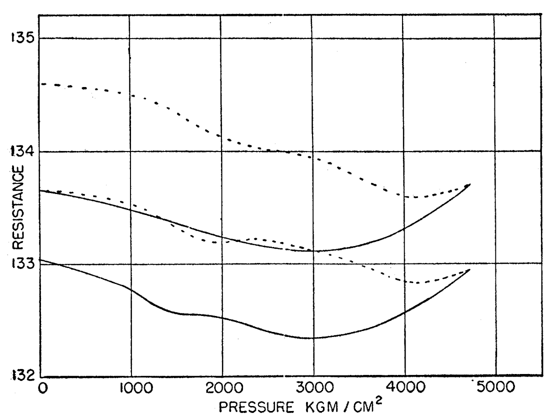

FIG. 11. The normal resistance of thallium at 3.0°K *vs* pressure.

The variation of normal resistance with pressure is of particular interest in this case, and the results for thallium at 3.0°K are shown in Fig. 11. The principal characteristic of this curve is the initial decrease of resistance under pressure, but we wish to point out the suggestion of a change in curvature evident at intermediate pressures. The precision of the measurements is not really great enough to make this change of curvature absolutely certain, but similar behavior has been apparent in several measurements on thallium and is probably not spurious. It may well be connected with the change in sign of $\Delta T_c/\Delta P$.

Tantalum.—The tantalum wire used for these experiments had been vacuum annealed at 2000°C and was kindly made available to me by Dudley Buck of M.I.T. Electrical connections were made via thin nickel wires spot-welded to the tantalum. The superconducting transitions at various pressures, using solid HD as the pressure transmitting medium, are shown in Fig. 12. In Fig. 13 the variation of T_c with P for two complete pressure cycles is shown. In this

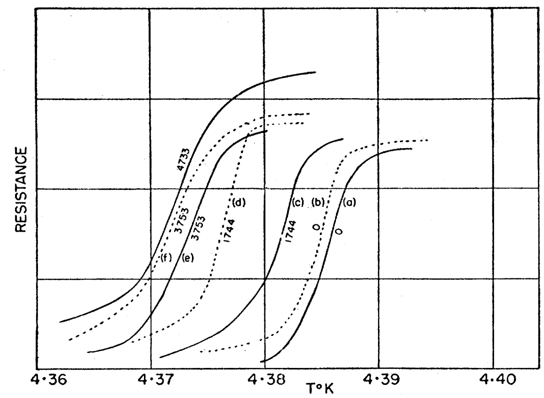

FIG. 12. Transitions of tantalum at various pressures. The measurements were made in the sequence: 0(a), 1744(c), 3753(e), 4733, 3753(f), 1744(d), 0(b).

figure, we have drawn smooth curves through all the experimental points in order to show up the indications of a minimum value of T_c in the neighborhood of 5000 kg/cm^2. Measurements to higher pressures will be required to establish the existence of such a minimum beyond all doubt. From Fig. 13 we find that the change of transition temperature between zero pressure and 1744 kg/cm^2 lies between -0.0042 deg and -0.0098 deg, or $\Delta T_c = -0.0070\pm0.0028$ deg. Therefore, $\Delta T_c/\Delta P = -0.4\times10^{-5}$ deg/(kg/cm^2)$\pm40\%$.

Measurements on the normal resistance of tantalum at 4.7°K are shown in Fig. 14. Initially the resistance decreases with pressure, but as would be expected for such a hard metal, the total change is very small.

Values of $\Delta T_c/\Delta P$ for the above superconductors are presented together in Table I.

DISCUSSION

A notable feature of the experiments presented above is that the width of the superconducting transitions at the highest pressures used is not significantly greater than the width at zero pressure. From this observation

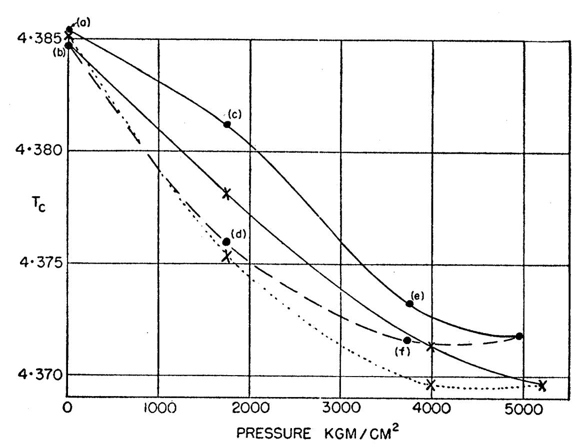

FIG. 13. Transition temperature *vs* pressure for tantalum. Points derived from the curves of Fig. 12 are lettered correspondingly.

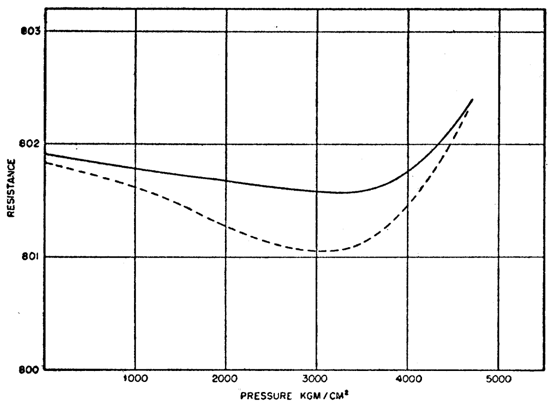

FIG. 14. The normal resistance of tantalum at 4.7°K *vs* pressure.

we draw the important conclusion that the pressure to which the specimens are subjected in this apparatus is substantially uniform; previously, we had been able to infer only from rather indirect evidence[5] that this was so. This conclusion, together with the fact that the values of $\Delta T_c/\Delta P$ we obtain for tin and indium agree quite well with those found by other workers,[9] gives us some confidence in our results for the variation of normal resistance with pressure.

The most interesting result for the variation of T_c with pressure is for thallium. The change in sign of $\Delta T_c/\Delta P$ occurring near 1200 kg/cm² is a novel feature and it is natural to inquire if it is associated with a phase change in the metal. Measurements on the low temperature compressibility of thallium by Swenson[10] give no evidence of any phase transition accompanied by appreciable volume change. If, on the other hand, the observed behavior resulted from a modification of the electronic configuration under pressure, then we would expect to see evidence of this in the measurements on the normal resistance of thallium. From Fig. 11 it is apparent that the normal resistance shows no striking variation with pressure, though as we have already pointed out, there is some evidence for a kink in the curve at intermediate pressures.

It would be of great interest to carry the experiments on tantalum to higher pressure in view of the indication our results give for a change in sign of $\Delta T_c/\Delta P$ in the region of 5000 kg/cm². If such a sign change were confirmed it would be in the opposite sense from that occurring in thallium, and from a comparison of the two metals it might be hoped that some clue to the underlying cause might be forthcoming. As yet, theoretical estimates[11,12] of $\Delta T_c/\Delta P$ based on electron-lattice interaction theory have met with little quantitative success, though they are of the right order of magnitude.

[9] N. L. Muench, Phys. Rev. **99**, 1814 (1955) gives a convenient table of published results.
[10] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).
[11] P. M. Marcus, Phys. Rev. **91**, 216 (1953).
[12] S. Mase, Busseiron Kenkyu, No. 53, 10 (1952).

In measurements on the variation of normal resistance with pressure, the magnitude of the observed effect differed by a factor of about 2 among different specimens of the same metal. Enough measurements were made, however, to exclude any doubt about the qualitative behavior—in particular, about the initial slope of the resistance *vs* pressure curves. A result which we feel may be of considerable significance is that for each of the four superconductors studied, the normal resistance decreases under pressure. Now it is readily shown that if we use as a model for the electrical conduction process at low temperatures a free degenerate electron gas scattered by a fixed number of scattering sites, then the resistance should increase under pressure. Such behavior is indeed found for relatively simple metals like copper and silver,[5] and the observed increase is of the expected order of magnitude.

In the case of antimony and bismuth, which are preceded in the Periodic Table by the superconducting elements tin and lead, respectively, we find[5] that the low temperature resistance decreases initially under

TABLE I. Values of $\Delta T_c/\Delta P$.

	Pressure kg/cm²	$10^5\times\Delta T_c/\Delta P$ deg/(kg/cm²)
Tin	3753	$-4.3\pm8\%$
Indium	2528	$-3.8\pm10\%$
Mercury	4733	$-4\pm25\%$
Thallium	<800	$+0.9$ to $+1.5$
	>2000	-0.35 to -0.45
Tantalum	1744	$-0.4\pm40\%$

pressure. It is tempting to ask if the interactions which are responsible for superconductivity also lead to the decrease of normal resistance with pressure.

The effects of electron-lattice interaction on the low temperature behavior of metals have been the subject of theoretical considerations by Bhatia[13] and by Schafroth and Buckingham.[14] It has been pointed out to the author by G. D. Cody of this laboratory that according to these theories the electrical resistance at low temperature contains a term which would decrease under pressure. This could account for the observed decrease of resistance with pressure for superconductors in the normal state, where presumably the interaction is larger than in ordinary metals.

The author wishes to express his gratitude to Ray Sawyer and George Cody for taking vapor pressure readings in the measurements on the superconducting transitions. Thanks are due also to Archie Grant who prepared the HD and to Earl Wilkie for help in a variety of ways. Grateful acknowledgement is made to Linde Air Products Company for their generous gift of liquid nitrogen.

[13] A. B. Bhatia, Phys. Rev. **95**, 914 (1954).
[14] M. R. Schafroth and M. J. Buckingham, Proc. Phys. Soc. (London) **A67**, 828 (1954).