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Superconductivity at Very High Pressures

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ABSTRACT

A method is described for the realization of very high pressures at liquid helium temperatures. First results are given of its application to studies of superconductivity under pressures up to 44 000 atm. Bismuth is shown to become superconducting under pressure. T_c for tin is shown to vary approximately linearly with volume up to 17 500 atm. The value of dT_c/dp for thallium is found to be negative, in disagreement with previous work.

§ 1. INTRODUCTION

RECENT theories of the origin of superconductivity make it desirable to obtain more experimental information on the effect of varying the pressure on the properties of superconductors, to supplement the growing mass of data on the effect of varying the isotope in a given superconducting metal. Indeed, the pressure (or volume) and the mass number would seem to be the only variables whose effect might be capable of immediate theoretical interpretation. In particular, it is of interest to determine the influence of pressure on the transition temperature, T_c, and on the value of the quantity dH_c/dT at T_c (where H_c is the threshold field at temperature T), and also to find whether the application of high pressures can destroy superconductivity, or cause it to appear in metals not normally superconducting.

The present paper describes some experiments of this kind which we have carried out at pressures up to about 40 000 atm.—over twenty times higher than the maximum pressures previously employed in similar investigations. The increase in the working range of pressure has been made possible by the use of a technique due to Bridgman adapted in a special way for use in low-temperature enclosures.

In a further paper the implications of some of the results obtained will be examined from the general standpoint adopted in the theories of Fröhlich (1950 a, b, 1951) and Bardeen (1950 a, b, 1951 a, b, c), in which superconductivity is attributed to interactions between electrons *via* their interactions with the lattice.

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* Communicated by the Authors.

§ 2. Summary of Previous Work

The earliest systematic study of the effect of compression on the properties of superconductors was carried out by Sizoo and Onnes (1925), who applied pressure to wires of tin and indium by compressing helium into the vessel in which they were mounted. For both metals the transition temperature (T_c), at which the resistance fell to half its residual value, was found to be depressed. However, the maximum pressures used were no greater than 300 atm., and the maximum observed depression of T_c was about 0·005°. The later discovery by Keesom (1926) of the solidification of helium under pressure threw doubt on the results obtained by Sizoo and Onnes for all but the lowest pressures used, and removed the last hope of using a transmitting fluid for the application of conventional high-pressure techniques to experiments at liquid helium temperatures.

An advance in technique which enabled appreciably higher pressures to be reached at low temperatures was made by Lazarew and Kan (1944), who generated pressures of about 1750 atm. by allowing water to freeze in a thick-walled ' bomb '. Electrical leads leading out of the ' bomb ' made it possible to measure the resistance of wires mounted in it as they were cooled, under pressure, to liquid helium temperatures. Of the metals (thallium, indium, tin, mercury, tantalum and lead) subsequently investigated by Kan, Sudovstov and Lazarew (1948, 1949), all but thallium showed a depression of T_c under pressure. Using the same technique, Alekseyevski and Brandt (1949, 1952) investigated the non-superconducting metal bismuth and its superconducting compounds $RhBi_4$, $NiBi_3$, KBi_2, LiBi and Au_2Bi. No signs of superconductivity could be observed in metallic bismuth at pressures up to 1050 atm. Compression lowered the transition temperatures of LiBi and Au_2Bi but raised those of the other compounds named. The absolute magnitude of the quantity dT_c/dp in these experiments ranged from $5{\cdot}8\times10^{-11}$ deg. dyne^{-1} cm^2 for tin to almost zero for $RhBi_4$. The maximum observed change in T_c was therefore about 0·1° ; in most cases the total change was much smaller. The fact that the transitions observed were fairly sharp was taken to imply that the pressure was uniform throughout the volume of the superconductor.

A number of other experiments, on specimens under non-uniform distributions of stress (such as linear extension), have also been carried out by the authors named above, but we do not discuss the results here.

§ 3. Experimental Method

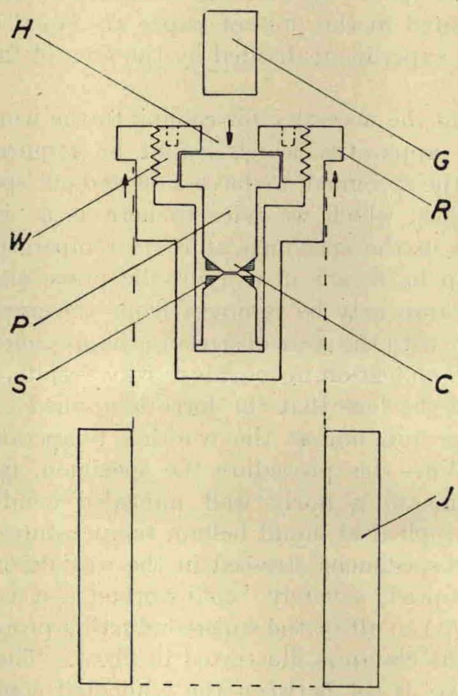
In order to reach much higher pressures it was decided to adapt for our purpose the technique due to Bridgman (1935 a, 1949, 1950, 1952) by which quasi-hydrostatic pressures up to about 400 000 atm. may be generated in thin solid specimens. This technique depends on the fact that a small area of a massive block of metal is able to withstand stresses far greater than the normal breaking stress of the bulk material, because of the support afforded by the surrounding metal. In applying this principle to the study of the shear strength or electrical resistance of metals under very high pressures, Bridgman interposes a disc-shaped specimen between the plane faces of two truncated conical bosses, each machined on massive blocks of steel or Carboloy. As the blocks are forced together, very intense stresses are developed over the small area of contact, and the specimen and compressing surfaces deform in such a way that the pressure in the specimen approaches a hydrostatic distribution locally, with a value which decreases radially from the centre to the perimeter. The actual form of the variation is difficult to estimate, but it was believed by Bridgman that a large central part of such a specimen would be under fairly uniform pressure. This question is discussed elsewhere (Chester 1953), and we shall only mention here certain indications arising from the present results which suggest that this is true for the metallic specimens so far investigated by us. (The values of mean pressure quoted in the present paper are equal to the total force applied in a given experiment divided by the area of the specimen under stress.)

In order to avoid the necessity for cooling to the working temperature the rather bulky apparatus which would be required to transmit a sufficient force to the specimen, we have mounted our specimens in a small self-contained device, which we refer to here as a ' clamp '. Pressure may be generated in the spec men at room temperature by applying a force to the clamp by means of a hydraulic press, and after a suitable adjustment the clamp may be removed from the press and transferred to a small cryostat, with the state of stress in the specimen still maintained. Apart from the simplification in technique wich results, there is an important advantage in the fact that the force is applied to the specimen at room temperature, and not at the working temperature in the liquid helium region. With this procedure the specimen, particularly if of a soft metal, remains in a fairly well annealed condition throughout. If the force were applied at liquid helium temperatures, annealing would not occur and the specimens stressed in the way described would be, if not actually disrupted, severely ' cold-worked '—a condition which is known (Hilsch 1951) to affect the superconducting properties profoundly.

The design of the clamp is illustrated in fig. 1. The specimen, in the form of a thin disc, is set between the truncated compressing cones C. For the application of pressure, the clamp is supported by its rim R in the cylindrical jig J, a plunger G is inserted in the axial hole H in the screw W, and the whole unit placed between the rams of the press. When force is applied between the plunger and the base of the jig, the pistons P of the clamp—and therefore the specimen—are put under compression, whilst the outer wall of the clamp is put into tension. The various members can now be ' locked ' in their state of stress by tightening the screw.

In practice it is not possible to preserve the full stress because of friction in the screw-thread, and the following procedure is adopted to ensure that the fraction preserved is as large as possible and is accurately known : When a suitable value of the force is reached, the screw is tightened progressively and the hydraulic press relaxed at such a rate as to keep constant the strain in the clamp—as indicated by a resistance strain-gauge cemented to its outer wall. As the press is relaxed further, the screw becomes more difficult to turn and after a certain stage no further tightening is attempted. At this point the press is relaxed completely and the fraction of the original strain which has been retained (in practice never less than 90%) is noted from the indication of the strain-gauge. The clamp is now transferred to the cryostat. No change in the pressure applied to the specimen is to be expected on subsequently cooling the clamp to the working temperature because its load-bearing members are made wholly of one material, and therefore contract equally.

Fig. 1



Schematic diagram of clamp (for explanation of symbols see text).

The superconducting transition of the compressed specimen is observed by a magnetic method. This is to be preferred to a method depending on the measurement of resistance, because it avoids the difficulties of electrical insulation at high pressure, and is less likely to lead to the spurious effects associated with the existence of filaments of abnormally high critical field—as reported by Lazarew and Galkin (1944) for inhomogeneously strained superconductors and by de Haas and Voogd (1930) for inhomogeneous superconducting alloys. The method best suited to the geometry of the clamp is to wind secondary coils S, in series, round each cone and to apply an alternating field along the axis of the clamp by means of a solenoid coaxial with it. The e.m.f. induced in the secondary coils is amplified, rectified and displayed on a micro-ammeter. Because of the large demagnetizing factor of a transverse disc, reasonably sharp transitions are to be expected only if the alternating field is of small amplitude. We have found also that it is not possible to make use of the increased sensitivity to be expected of high-frequency measurements because of skin effects in the material of the clamp. In consequence, most of the work has been done with alternating fields of amplitude about 0·1 gauss and frequency 30 c/s.

Preliminary investigations, made with clamps of various steels, indicated that the proximity of ferromagnetic materials complicated the transition of the superconductor and made accurate determination of T_c difficult. All the quantitative work to be described has therefore been carried out with a clamp of beryllium-copper—a material which remains weakly paramagnetic down to liquid helium temperatures. For experiments up to mean pressures of 16 000 atm., the circular area in contact with the specimen was about 5 mm in diameter, and the thickness of the specimen after compression was usually less than 0·01 mm. Some rough work up to higher pressures (about 40 000 atm.), has been carried out, using conical tips of smaller area, of ‘ Vibrac ’ steel.

Because of the existence of a radial pressure gradient in the specimen it was expected that for most superconductors under pressure the outer part of the disc would become superconducting at a higher temperature than would the centre part, and it was thought that the superconducting rings thus formed might tend to mask the transition of the centre. To avoid this complication a small wedge of a metal, known to be not superconducting under the conditions of the experiments, is inserted into a suitable cut in the circumference of the disc before compression, to prevent the formation of complete superconducting rings in the periphery. Aluminium, normally a superconductor below 1·2°K, has been found suitable for use with the metals so far studied. (An independent test was carried out to ensure that aluminium did not become superconducting under pressure above 2°K—the lower limit of temperature of the present experiments.) This precaution was not, of course, necessary in the exploratory work on non-superconductors.

A Helmholtz pair located outside the cryostat, with the axis of its coils in the plane of the specimen, permitted transitions to be observed in known magnetic fields. The demagnetizing factor of the disc in this direction appears to be sufficiently small to be ignored, because the form of transition curve obtained—though not of course its location on the temperature axis—is not sensibly altered by varying the field (see fig. 4).

Temperature control in the region 2° to 4·2°K was effected by varying the pressure over a bath of liquid helium in which the clamp was immersed, the temperature being deduced from the value of vapour pressure. Above 4·2°K a charcoal desorption method was used and temperatures measured by means of a carbon resistance thermometer of the type described by Clement and Quinnell (1952).

§ 4. Experimental Results and Discussion

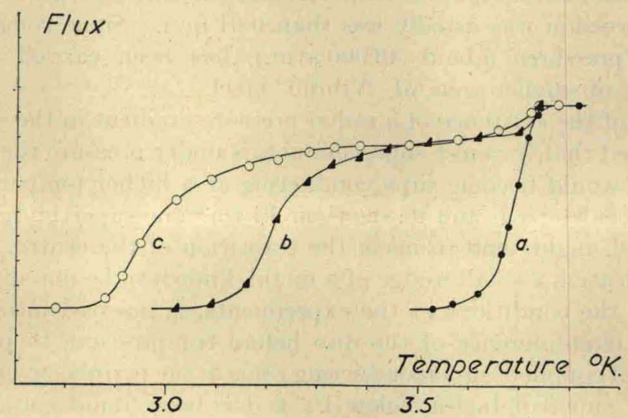
The results on the metals studied are now presented and discussed separately.

Tin

Tin, according to the Russian workers, shows the largest change in T_c under pressure. It is the most extensively studied superconductor, having its transition temperature in a range where very accurate control of temperature is possible, and it was therefore the obvious choice for a first detailed investigation.

Superconducting transitions were observed by cooling through the transition temperature under mean pressures of 1, 10 500 and 16 000 atm. The results are shown in fig. 2, where the alternating flux in the secondary

Fig. 2



Transitions of tin in zero field at differing pressures : (*a*) 1 atm., (*b*) 10 500 atm., and (*c*) 16 000 atm. mean pressure. Flux in arbitrary units.

coils is plotted, in arbitrary units, against temperature. The width of the curve at 1 atm. provides a reasonable measure of the limit of resolution of the method for a given alternating field, and we then interpret the spreading of the curves at high pressure as due to the pressure gradient in the specimen. Inspection of the curves suggests that over about three-quarters of the area the pressure is uniform within our limits of resolution (the small drop in flux at the high-temperature end of the curves is probably due to metal extruded beyond the area of the compressing cones). By assuming a linear gradient over the remaining area we can arrive at estimates of the maximum pressure in the specimen. For a mean pressure of 16 000 atm., for instance (curve c), we estimate that the pressure over the central three-quarters of the specimen lies between 16 000 and

19 000 atm., which we write as 17 500$\pm$1 500 atm. We believe the results may fairly be stated as follows :

At 1 atm., the value of T_c determined by us agrees with the normal value (3·73°K), within experimental error.

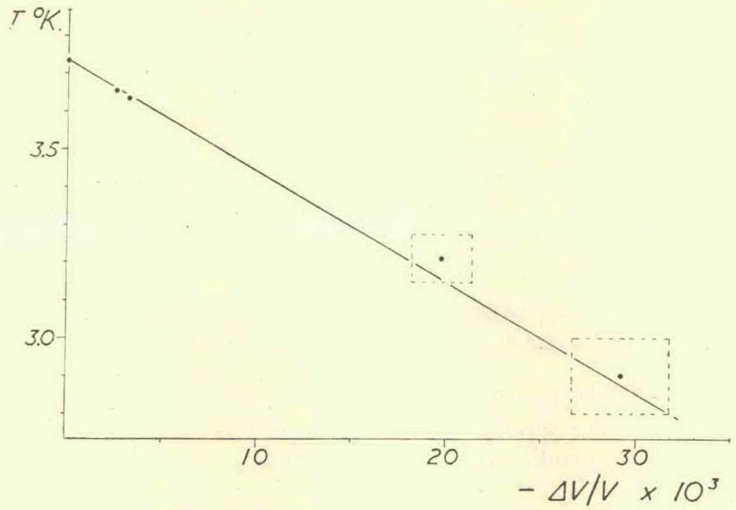
At 11 500$\pm$1000 atm., T_c=3·21$\pm$0·07°K.

At 17 500$\pm$1500 atm., T_c=2·9$\pm$0·1°K.

It is important to emphasize that the curves represent reversible behaviour and the effects shown are therefore not due to work-hardening (or ' cold-working '). After relaxing the pressure the curve obtained with a given specimen is indistinguishable from that obtained before the application of pressure.

Combining these with the results of Kan, Sudovstov and Lazarew (1948), and making use of Bridgman's values (Bridgman 1949) for the compressibility of tin, it is possible to plot T_c against $\Delta V/V$, where ΔV is the change in volume due to the increase in pressure. This is done in fig. 3, where it

Fig. 3



Relation between transition temperature and change in volume for tin under pressure. The areas enclosed by the dotted lines indicate the estimated experimental uncertainty in the present work.

may be seen that the variation is linear, within experimental error, and that the earlier and the present results lie on the same line.

The relation derived from the graph is

$$T_c\,(°\mathrm{K})=3{\cdot}73+29\,(\Delta V/V)$$

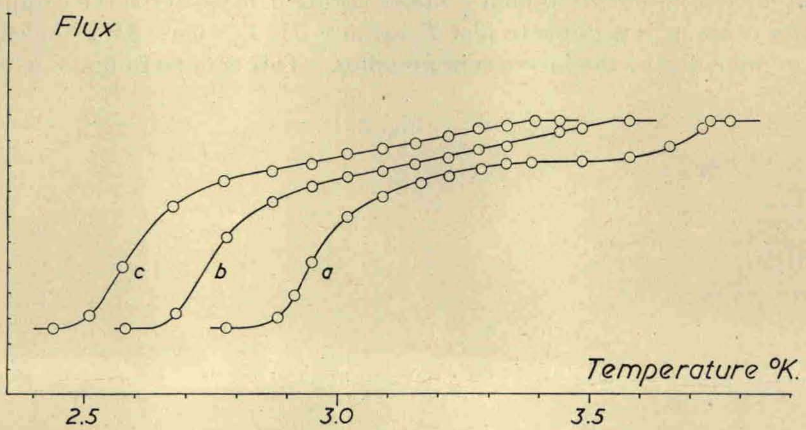
where the coefficient of $\Delta V/V$ may be in error by $\pm$10% at the lower pressures and by $\pm$20% at the higher pressures.

We have also observed transitions under the highest of these pressures for a number of differing values of magnetic field (in the plane of the disc).

The curves obtained are shown in fig. 4. A field of 50 gauss depresses the foot of the curve by about 0·37°. The corresponding depression at 1 atm. (see for instance Shoenberg 1952) would be 0·35°. Thus the quantity dH_c/dT at the temperature T_c remains substantially constant under pressure. At a given temperature H_c is of course lowered by pressure.

The magnitude of the quantity H_0, equal to $(H_c)_{T=0}$, is of theoretical significance since it is related to the difference in energy between the normal and superconducting states at absolute zero. Our experiments have not yet been carried to a sufficiently low temperature to determine the form of the curve of H_c against T, but we may point out that if it has

Fig. 4



Transitions of tin under 16 000 atm. mean pressure in differing magnetic fields : (*a*) zero field, (*b*) 23·6 gauss, (*c*) 47·2 gauss. Flux in arbitrary units.

the approximately parabolic form characteristic of tin at 1 atm., then the present results imply that H_0—and therefore the energy difference between the normal and superconducting states—is lowered by compression.

Lead

We have confirmed that T_c for lead is lowered by compression, but have not yet obtained detailed results on this metal.

Thallium

Because of the anomalous behaviour reported for thallium by the previous workers (Kan, Sudovstov and Lazarew 1949), using resistance measurements, we have investigated it by our method up to higher pressures.

In two runs under mean pressures of 11 700 atm. and 13 400 atm. respectively, no signs of superconductivity could be observed above 2·35°K although an uncompressed specimen began to show superconductivity at 2·39°K. The whole transition curve was displaced by pressure to a lower temperature, T_c being lowered by about 0·06° under 13 400 atm. The change is much smaller than that observed for tin, but is in the same direction. This result disagrees with the observation of Kan, Sudovstov and Lazarew; we may mention that the behaviour of thallium in the experiments of these workers was stated to be very sensitive to the method of mounting the specimen.

Bismuth

Bismuth, though not normally a superconductor, is obviously very close to being one. Hilsch (1951) has shown that very thin films of bismuth deposited from the vapour on to a surface at liquid helium temperatures exhibit superconductivity, with T_c at about 5°K (although annealing at room temperature destroys this property of the film) and a large number of alloys containing bismuth have been found to be superconductors. The positive value of dT_c/dp found by Alexeyevski for the bismuth-rich compounds $RhBi_4$, $NiBi_3$ and KBi_2, together with the vanishingly small electronic specific heat of the pure metal at low temperatures led him to suggest that bismuth might be a 'virtual' superconductor and that sufficient pressure might bring its transition temperature into the liquid helium region. Another interesting pointer arises from the curve of atomic volume of the elements plotted against atomic number; the superconducting metals are found to occupy a fairly well defined range of atomic volumes intermediate between the peaks and troughs of the curve (see for instance Mendelssohn 1952). Bismuth at ordinary pressures would appear to have just too great an atomic volume to take its place in this group.

A number of runs were made under pressure with samples of bismuth of purity stated to exceed 99·999%. No signs of superconductivity could be observed (down to 2°K) at mean pressures less than 20 000 atm., but at all pressures tried between 20 000 atm. and 41 000 atm., a superconducting transition was observed at about 7°K, the value of T_c not varying by more than 0·1°K throughout the range of pressures covered. This behaviour was reversible; that is, after relaxation of the pressure at room temperature the specimen was again non-superconducting.

It is of interest to consider this result in conjunction with the phase-equilibrium diagram for bismuth at high pressures determined by Bridgman (1935 b), in which polymorphic transitions are shown at room temperature at about 25 500 atm. and 27 000 atm. In view of the uncertainty about the distribution of pressure in our experiments, it seems reasonable to associate the onset of superconductivity with the changes to more close-packed crystalline forms of bismuth discovered by Bridgman.

Calcium and Strontium

Strontium satisfies the criteria for superconductivity arising in the theories of Fröhlich and Bardeen, and although calcium does not satisfy these criteria, both metals are exceptional in that their electrical resistance at room temperature increases with pressure (Bridgman 1949, 1952)—a property which would be expected to favour the appearance of superconductivity at high pressure.

We have subjected samples of calcium of purity 97% and strontium of purity 99·85% to mean pressures of 44 000 and 42 000 atm. respectively, and examined them down to 2·1°K. No signs of superconductivity could be observed in either metal.

The work is to be extended to other superconductors and non-superconductors, and to higher pressures.

Acknowledgments

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