SUPERCONDUCTIVITY AT HIGH PRESSURES

N. B. BRANDT and N. I. GINZBURG

Physics Faculty, Moscow State University

1. INTRODUCTION

IT is now over 40 years since the first experiments[1] on the effect of pressure on superconductivity. At first these investigations aroused no special interest because the effect was very small at the pressures which could then be achieved (the pressures were produced by liquefied gases and did not exceed 100 bar); superconducting transition temperatures, T_c, only changed by a few thousandths of a degree. It was only half-way through this 40-year period that the subject took a further step forward after the development of methods[2] for obtaining substantially higher pressures (up to 2 kbar) at low temperatures. Great interest in studying superconductivity at high pressures was aroused after the microscopic theory of superconductivity was propounded by Bardeen, Cooper and Schrieffer (the BCS theory).[3] Recently this interest has grown even greater. The limit to pressures which can be achieved at low temperatures has expanded appreciably and the temperature range of experiments has also widened, including the extremely low temperature region. It is now possible to obtain uniform pressures up to 300 000 bar at temperatures down to $0.1°K$ and, as a result, a number of new questions can be posed.

It is known, for example, that the transition temperature of all superconducting non-transition metals is lowered by pressure, while it is raised for a number of transition metals and their alloys. The question then arises: how far and according to what relation is the critical temperature reduced on applying still higher pressures? Can superconductivity for a given crystalline modification disappear purely as the result of pressure? On the other hand, it is uncertain how far the superconducting transition temperature will increase for metals and alloys for which it is raised by pressure. This problem is now of special interest in relation to finding an upper temperature limit for the occurrence of superconductivity in ordinary three-dimensional structures.

The relation between the experimentally measured parameters of superconductors and the characteristics of the metal in the normal state has been established by the microscopic theory of superconductivity. The establishment of such a relationship opens up the possibility of explaining the mechanism responsible for the effect of pressure on superconductivity and of determining the reasons for the change of T_c with pressure. Finally, high pressures enable new superconductors to be obtained and their properties studied. The discovery of superconductivity under pressure in silicon, germanium, antimony, tellurium, selenium and phosphorus represents a great success in this last direction which has substantially increased the number of superconducting elements in the periodic system.

In this article we discuss mainly work published during the last three to four years, together with some earlier work which has recently been extended. A more detailed description of much of the earlier work is given in [4-7].

2. FURTHER DEVELOPMENTS OF METHODS FOR OBTAINING HIGH PRESSURES AT LOW TEMPERATURES

All methods which have so far been proposed for producing high pressures at low temperatures can be divided into two main groups:

1. Methods of 'conserving' or 'freezing-in' the pressure, in which the pressure is applied at high temperatures and the apparatus is then cooled to liquid helium temperatures.

2. Methods in which the pressure is applied directly at low temperatures.

In both groups of methods apparatus is used in which the pressure is transmitted either directly to the specimen or through some intermediate medium surrounding the specimen. Details of apparatus based on these methods are given by Swenson[4] and Brandt and Ginzburg.[6] The maximum pressure which could be reached at low temperatures before 1964 was not more than 30 to 40 kbar. The more recent development of high-pressure techniques for low temperatures showed that the first group of methods offers more hope for reaching higher pressures. So far the second group of methods has not yielded appreciable results in increasing the pressure range at low temperatures. The main difficulty in this approach is, on the one hand, that the plasticity of pressure-transmitting media decreases sharply on lowering the temperature while, on the other hand, if the pressure is applied directly at low temperatures without an intermediate medium, great internal strains arise in the specimens.

We will only consider here methods which enable an appreciable increase in the limits of obtainable pressures to be achieved. We should first examine the method of Wittig[8] whose apparatus is shown in Figs. 1(a) and (b). The pressure is applied at room temperature in the special chamber 9 placed between the hardened tungsten carbide anvils 6, by compressing the whole system in an hydraulic press with a maximum load of 7000 kg. After the compression the pressure is retained by nut 2 and the system is placed in a cryostat and cooled to the required temperature. The main advance lies in the design of the high-pressure chamber (Fig. 1(b)). The chamber consists of the 0.25 mm thick pyrophyllite ring 1 with o.d. 3.5 mm and i.d. 2 mm. This ring is fixed with araldite cement to the face of the lower anvil. The specimen, in the form of a thin strip, is placed between two steatite discs inside the retaining ring 1. 40 to 50 μ diameter platinum current and potential leads to into the high pres-
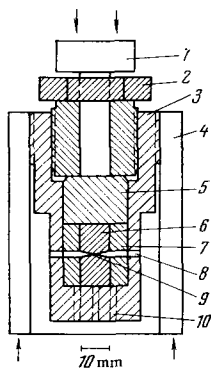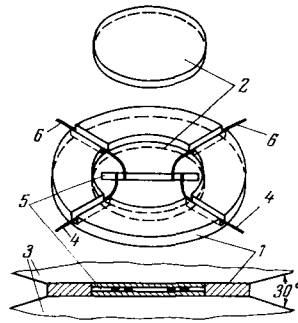
FIG. 1a   FIG. 1b

FIG. 1a. Schematic drawing of apparatus. 1 — piston; 2 — locking nut; 3 — case; 4 — yoke; 5 — pressure transmitting cylinder; 6 — upper anvil; 7 — support ring; 8 — hole for leads; 9 — high-pressure chamber; 10 — additional holes for mounting.

FIG. 1b. High-pressure chamber.[8] 1 — pyrophylite ring with grooves for electrodes; 2 — upper and lower steatite discs; 3 — transverse section through chamber; 4 — current electrodes; 5 — specimen; 6 — potential electrodes.

sure chamber through slits in the ring. The steatite which surrounds the specimen is much more plastic than pyrophyllite and thus produces sufficient uniformity in the pressure generated, while automatically becoming stronger when the outer support is compressed, preventing the steatite from flowing out at the side. The apparatus is calibrated at room temperature at the fixed points for the phase transitions Ta II–Ta III (37 kbar), Bi III–Bi V (82 kbar), Sn II–Sn III (113 kbar), Pb I–Pb II (160 kbar) so that pressures at the center of the chamber can be determined. An interesting feature of this method of obtaining the pressure is the 'intensification' effect by which the pressure at the center of the chamber is considerably greater than the mean value, calculated from the applied load and the anvil area. This 'intensification' results from the strong radial non-uniformity of the pressure between the anvil surfaces. In chamber 8, the intensification factor is 2.5 within 20%. An x-ray study[4] also shows the large factor in a similar type of apparatus, where the pressure at the center of Bridgman anvils was generally 2.5 to 3 times greater than the calculated value. Pressures of about 160 kbar were obtained at liquid helium temperatures in the apparatus described.

This method was further developed by Brandt and Berman,[10,11] who used a separate small intensifier[12] with a high-pressure chamber of design similar to Wittig's.[8] One of the advantages of using an intensifier is that the force arising between the anvils can be fixed by the freezing of water. When the pressure is fixed by mechanical means there is an undesirable pressure reduction when the press force is taken off. The intensifier is placed either in an apparatus for obtaining very low temperatures[6], so that the temperature range can be extended down to 0.1 K, or in a cryostat for measurements over a wide temperature range above the helium boiling point. The high-pressure chamber of o.d. 1.3 and i.d. 0.5 mm is made up of two 10–15 μ thick discs 2, pressed out of fine Fe_2O_3 powder, two retaining rings 3 pressed out of a Fe_2O_3 and steatite mixture and two
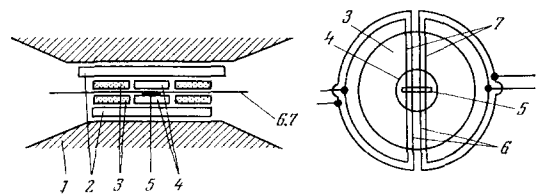

FIG. 2. High-pressure chamber [11]. 1 — VK-3 alloy Bridgman anvils; 2 — Fe_2O_3 discs; 3 — support rings; 4 — steatite washers; 5 — specimen; 6 and 7 — electrodes.

steatite washers 4 pressed out of steatite powder (Fig. 2). The electrodes are four 5 μ thick platinum strips. The pressure conditions in a chamber of this design are such that the intensification coefficient is close to unity for pressures up to ~100 kbar and then gradually increases to about 2. As a result of this, the pressure distribution in the anvils prevents their bursting and ensures reliable operation of the chamber up to ~300 kbar.

Lyon, McWhan and Stevens[13] have recently designed a cryostat for producing pressures up to 100 kbar from room to liquid helium temperatures. The pressure is attained with a 300 ton press. It takes 10 l. of liquid helium to cool the cryostat from 70 to 4.2 K, after which the evaporation rate is 1.2 l./hr.

Smith and Gardner[14] have used a calorimeter for studying the heat capacity of superconductors under pressures up to 10 kbar, which is an interesting experimental achievement. Pressure in the calorimeter is applied by compressing the specimens in a silver chloride medium. An advantage of the method is the possibility of determining accurately the volume of the superconducting phase in the specimen. It must be pointed out, however, that this method can only be used for studying superconductors with heat capacities comparable with that of the calorimeter.

We will now discuss results obtained from examining superconductivity at high pressures.

3. NON-TRANSITION METALS

It is a general feature of all superconductors of the non-transition group that their superconducting transition temperature is reduced by hydrostatic compression. The only exception is thallium, whose critical temperature increases for pressures up to 2 kbar; with a further increase in pressure the transition temperature of thallium decreases, as for all the other non-transition group superconductors. The principal parameters characterizing the behavior of non-transition metal superconductors at low pressures (for small changes in T_c) are given, e.g., by Olsen et al.[5] and Brandt and Ginzburg.[6]

From our point of view there is special interest in work on the form of the dependence of the superconducting parameters on pressure over a wide pressure range, and also in precision studies of the effect of pressure on the critical field curves, from which we can obtain information on the nature of the changes in superconducting parameters caused by compression.

One of the main results of the BCS theory of superconductivity is the expression for the superconducting transition temperature:

$$T_c = \frac{2\Delta(0)}{3.52k} = 1.14 \langle \hbar\omega \rangle \exp\left(-\frac{1}{NV}\right) ; \qquad (1)$$

where $2\Delta(0)$ is the width of the gap in the energy spectrum at T = 0 K, $\langle\hbar\omega\rangle$ is the mean energy of the phonons by which electrons near the Fermi surface are scattered ($\langle\hbar\omega\rangle$ is of order $k\Theta_D$ where Θ_D is the Debye temperature), N is the density of states at the Fermi surface in the normal state for the metal considered, and V is an electron interaction parameter. From (1) the pressure dependence of the superconducting transition temperature is determined by the presssure dependence of Θ_D, N and V. The pressure dependence of the Debye temperature can be determined either from experiments on the temperature dependence of the electrical resistance of specimens at different pressures, or by calculation from the relation

$$\Theta_D(p) = \Theta_D(0)\left(\frac{v_0}{v_p}\right)^{\xi_g}. \tag{2}$$

This relation is obtained by integrating the expression $\xi_g = - (d \ln \Theta/d \ln v)$ on the assumption that the Grüneisen coefficient ξ_g is independent of pressure (v_0 is the specimen volume for p = 0 and v_p the volume at pressure p). The coefficient ξ_g is determined from Grüneisen's formula (see [15]). It follows from (2) that the Debye temperature must increase with increasing pressure. If the pressure dependence of N is known, then the pressure dependence of the electron-phonon interaction parameter V can be determined by (1) from data on the pressure dependence of T_c and Θ_D.

Results of measuring critical field curves at different pressures over a sufficiently wide temperature range can be used to determine the pressure dependence of N. Using the expression for the coefficient γ in the electronic contribution to the heat capacity of metals in the normal state $C_e = \gamma T$

$$\gamma = \frac{2}{3}\pi^2k^2N, \tag{3}$$

and the relation

$$\gamma = (2\pi)^{-1}a_2\frac{H_0^2}{T_c^2}, \tag{4}$$

which comes from the thermodynamics of superconductors, we obtain

$$N = \frac{3}{4\pi^3k^2}a_2\frac{H_0^2(p)}{T_c^2(p)}. \tag{5}$$

The usual approximation

$$\frac{H_c}{H_0} = 1 - a_2\left(\frac{T}{T_c}\right) - a_3\left(\frac{T}{T_c}\right)^2 - \cdots,$$

has here been made for the critical field H_c, where H_0 is the critical field at T = 0 K.

The necessary data have so far been obtained for aluminum, gallium, cadmium, indium, lead, thallium, tin and zinc.

Tin and indium

The pressure dependence of the critical temperature of tin, previously measured to 10 kbar,[4] was extended to a pressure of 160 kbar[16] (see Fig. 3) by the method described above. The Sn II–Sn III phase transition takes place at 113 kbar. T_c varies nonlinearly with pressure for Sn II. At low pressures the form of the variation agrees with the earlier data.

The effect of pressure on the critical field of tin and indium between 0.1 and 4 K was determined by Berman,
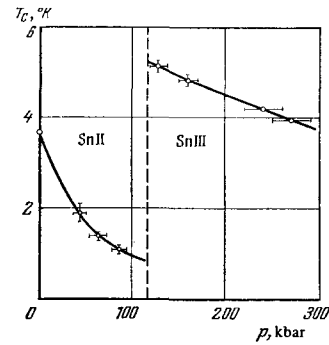

FIG. 3. Pressure dependence of critical temperature for tin; $p \leqslant$ 160 kbar [16] and $p \geqslant$ 160 kbar [10].

Brandt and Ginzburg[17] up to 32 kbar. The measurements were made in an apparatus described by Brandt and Ginzburg[6] on bulk specimens of spectroscopically pure tin and indium. The critical curves were measured down to very low temperatures so that not only the value of the critical field at T = 0 K could be determined, but the effect of pressure on the departure of the critical field curve from a parabola could be studied. It was established that the coefficient a_2 in (5), which characterizes the departure of the $H_c(T)$ curve from the parabola H = $H_0[1 - (T/T_c)^2]$, does not change for pressures up to 30 kbar, so that the pressure dependence of the density of states at the Fermi surface could be determined for tin and indium from (5) (Fig. 4). The values of ξ_e = (d ln N/d ln v), equal to 2 ± 0.3 for tin and 1.5 ± 0.3 for indium, agree with the values ξ_e = 1.7 ± 0.3 for tin and ξ_e = 1.0 ± 0.2 for indium, determined by Grenier[18] and Rohrer[19] for pressures up to 2 kbar.

It can be seen from Fig. 4 that for tin the density of states decreases linearly on compression, while for indium the rate of change of N decreases noticeably at large pressures. Such a great change in the density of states on compression is unexpected and cannot be explained on the free electron model, according to which the density of states should vary as $v^{2/3}$ (v is the volume of the specimen), i.e. $\xi = \frac{2}{3}$.

Aluminum, cadmium and zinc

The pressure dependence of T_c for aluminum was studied by Levy and Olsen[20] up to 20 kbar. Similar dependences were obtained for cadmium and zinc up to 28 kbar by Brandt and Ginzburg[21] (Fig. 5). It can be seen that $T_c(p)$ is not linear and the relative changes in T_c are ~4.5 in cadmium, ~2.7 in zinc and ~1.7 times in aluminum.

Accurate measurements of the effect of pressure on the critical field curves of aluminum between T_c = 1.1793 and 0.3 K at pressures up to 500 bar were made by Harris and Mapother[22] and up to 23 kbar by Olsen, Palmy and de Trey.[23] It was established to a high degree of accuracy that the shape of the critical field curves of aluminum and, consequently, their departures from parabolas does not change over this pressure range. Olsen et al. could thus calculate the change in the density of states at the Fermi surface on compression. It is interesting that, as for tin and cadmium, the density of states N for aluminum decreases on compression d ln N/d ln v = 6.6 ± 3. Olsen et al. found that T_c for aluminum decreased to 0.65 K at 23 kbar and H_0 to 54 gauss. Although

$N, 10^{34} \, \mathrm{erg}^{-1} \mathrm{cm}^{-3}$

$N, 10^{34} \, \mathrm{erg}^{-1} \mathrm{cm}^{-3}$
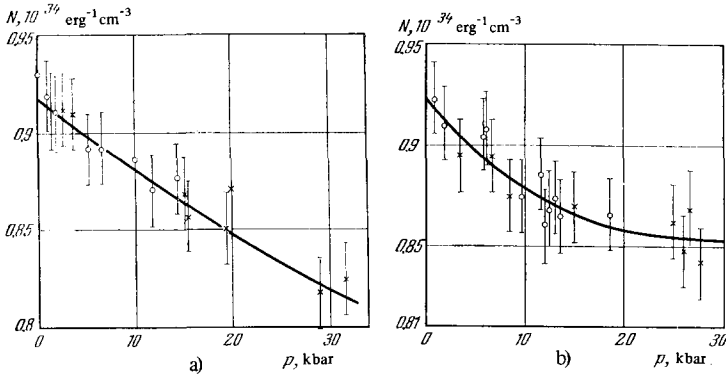
a) p, kbar

b) p, kbar

FIG. 4. Pressure dependence of the density of states N for (a) two tin specimens and (b) two indium specimens, calculated from Eq. (5) [17].
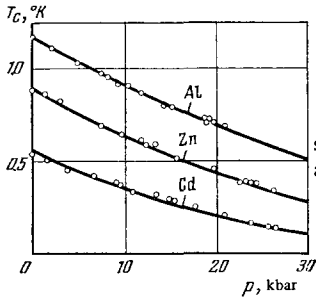
$T_C, °K$

AL

Zn

Cd

p, kbar

FIG. 5. The change of T_C with pressure for cadmium and zinc [21] and for aluminum [20].

$T_C, °K$

p, kbar

FIG. 7. The pressure dependence of T_C for two lead specimens [16].

$N, 10^{33} \, \mathrm{erg}^{-1} \mathrm{cm}^{-3}$

p, kbar

FIG. 6. The change in the density of states N for zinc (□) and cadmium (○) under hydrostatic pressure [17].

high (T_C = 7.27 K), it decreases by a factor 2, and the $T_C(p)$ curve is non-linear.

Köhnlein[24] has measured the pressure dependence of T_C for lead up to 30 kbar.

4. TRANSITION GROUP METALS

the accuracy of measuring the critical field curves of cadmium and zinc was appreciably less than Harris and Mapother achieved for aluminum, the change in the density of states could be calculated by Eq. (5) from the large relative change in T_C, on the assumption that the shape of the critical field curves for zinc and cadmium as for tin, indium and aluminum, does not change on compression. The variation of N with p for zinc and cadmium is shown in Fig. 6, and can be seen to decrease on compression. The decrease in N for zinc is 20% at p = 30 kbar and 30% for cadmium. These changes are sufficient to explain the observed reduction in T_C (see Fig. 5) on the assumption that the change in the Debye temperature Θ_D can be calculated from (2).

Lead

Figure 7 shows the temperature dependence of T_C for lead up to 160 kbar obtained by Wittig.[16] We should note that this is the first time the dependence of T_C on p has been studied for a single modification over such a wide pressure range. Although the transition temperature is
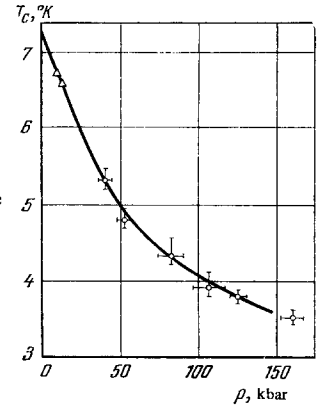
It was mentioned earlier that a characteristic feature of the behavior of superconducting non-transition metals (except for thallium at low pressures) is a decrease in the superconducting transition temperature T_C on hydrostatic compression. In contrast to non-transition metals, not only is the sign of dT_C/dp different for transition metals but the dependence of T_C on p is more complicated in a number of cases. There is another difference in behavior: for non-transition metals the value of dT_C/dp at low pressures, and the form of the T_C-p relation at high pressure found by different authors, usually agree to within the experimental accuracy, while for transition metals appreciable, or sometimes just significant, differences are observed between the results of different experiments. There would seem to be two reasons for considerable differences between results of measurements on the same metal. Firstly, transition metals cannot be obtained as pure as non-transition metals, and impurities, mainly dissolved gases, can change the superconducting properties appreciably. Secondly, T_C for transition metals generally depends on the state of the specimen and can change greatly with plastic deformation, annealing and with a change in the state of the surface layer. Results of measurements thus depend strongly on the method of applying the pressure and on its uniformity. The factors mentioned affect the results

at low pressure (near T_c) most strongly and we shall only consider data obtained recently at sufficiently high pressures.

As far as we know, titanium, vanadium, zirconium, niobium, lanthanum, tantalum, rhenium and uranium have been studied in this region. Results on zirconium and tantalum at pressures up to 28 kbar are given in the earlier review.[6]

Niobium

The effect of quasi-hydrostatic pressure up to 10 kbar on T_c for niobium has been studied by Gardner and Smith,[25] up to 25 kbar by Gey and Heyden[26] and up to 45 kbar by Köhnlein.[24] Gardner and Smith used solid cylindrical specimens, compressed by two pistons in a beryllium bronze matrix. No change in T_c was observed up to 10 kbar within an accuracy of $\pm 3 \times 10^{-6}$ K/bar. The other two sets of measurements were made by Buckel and Gey's method,[27](see also [6]). The specimens, in the form of 0.02 mm diameter wires, were compressed between two steatite washers. The results are shown in Fig. 8. Gey and Heyden found a reduction in T_c at low pressures, a flat minimum and then an increase in T_c with an ever increasing value of dT_c/dp. This form of $T_c(p)$ dependence agrees with the results obtained by Lüders[28] from a study of the shift in T_c of niobium under unidirectional extension (assuming that an extension is equivalent to a 'negative' pressure). An increase in T_c was observed on stretching 0.085 mm diameter niobium wires under loads up to 12 kbar, the change being 0.4 K at the maximum load. The rate of increase in T_c increased with the load. A little later Köhnlein[24] showed that the appearance of the minimum in the $T_c(p)$ curve results from severe strains in the initial specimens. In unstrained specimens (with T_c = 9.4 K) a monotonic increase of T_c and a decrease in dT_c/dp is observed over the whole pressure range (see Fig. 8). With plastic deformation, T_c for a specimen of niobium increases proportionally with the residual resistivity up to 10 K. On compressing a deformed specimen, a minimum appears in the $T_c(p)$ curve (see the dashed curve in Fig. 8). It can be seen that extrapolation of that part of the curve which has positive dT_c/dp, to zero pressure gives T_c close to the value of T_c for an undeformed specimen. A similar effect of deformation on T_c and on the form of the $T_c(p)$ dependence was observed earlier for zirconium and titanium by Brandt and Ginzburg.[6] It is probable that the absence of any noticeable change of T_c in Gardner and Smith's[25] experiments resulted from the cold-working of the specimens.

Vanadium

The pressure dependence of T_c for vanadium has been measured on bulk specimens to 10 kbar by Gardner and Smith[25] and to 45 kbar by Köhnlein[24] using Buckel and Gey's method.[27] An increase of T_c with pressure was observed in both sets of experiments. Gardner and Smith observed a linear increase of T_c with dT_c/dp = $(1.1 \pm 0.3) \times 10^{-5}$ K/bar. The results obtained by Köhnlein are shown in Fig. 9, where it can be seen that the $T_c(p)$ relation is non-linear. dT_c/dp at low pressures is larger than found by Gardner and Smith, being $(1.76 \pm 0.15) \times 10^{-5}$ K/bar. We should note that the form of the $T_c(p)$ relation for
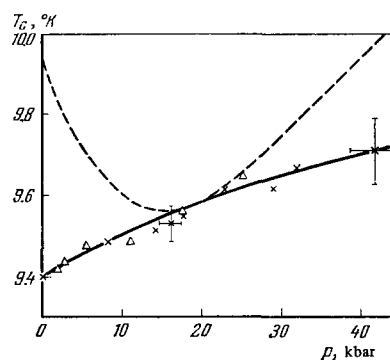
FIG. 8. The pressure dependence of T_c for undeformed ($\triangle$,X) and for heavily deformed (dashed curve) specimens of niobium [24].
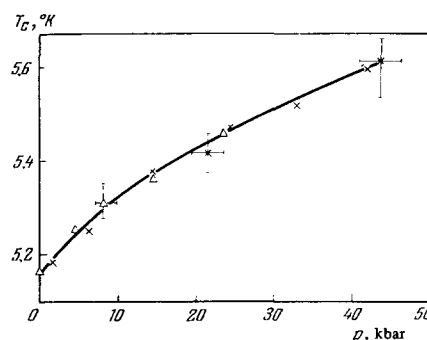
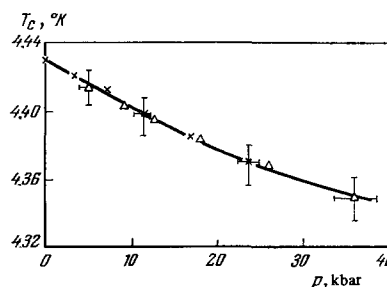FIG. 9. The change of T_c for an undeformed specimen of vanadium on compression [24].

FIG. 10. Change of T_c with compression for tantalum [24].

vanadium, as for niobium, changes greatly when there are internal strains in the specimen resulting from plastic deformation. A minimum appears in the $T_c(p)$ curve and extrapolation of that part with positive slope, to p = 0, gives a value of T_c close to T_c for originally undeformed specimens.

Tantalum

Several authors have studied the pressure dependence of T_c for tantalum.[6,21] Results of the latest work[24] are shown in Fig. 10. In contrast to the transition metals discussed above, there is good agreement between the results obtained by different methods for tantalum. This evidently results from the insensitivity of the superconducting properties of tantalum to the degree of its plastic deformation. Köhnlein showed that the maximum increase in T_c for tantalum with plastic deformation is not more

than 0.05 K, which is at least an order of magnitude less than the corresponding increase for vanadium and niobium.

Lanthanum

We will only consider results obtained by Smith and Gardner,[29] who studied the pressure dependence of T_C up to 40 kbar for two modifications of lanthanum, the hexagonal close-packed (h.c.p.) and the face-centered cubic (f.c.c.) form which occurs at room temperature at a pressure of about 23 kbar. The pressure was produced by the method of Bowen and Jones (see [4] and [6]), improved by using stronger materials and external support. In the h.c.p. phase a linear increase of T_C with hydrostatic compression was observed from 5.2 K at p = 0 to 8 K at p = 20 kbar (Fig. 11). The corresponding value of $dT_C/dp = 14 \times 10^{-5}$ K/bar is considerably greater than the derivatives for all the other superconductors discussed above. The transition to the f.c.c. modification appears as a break in the $T_C(p)$ curve, after which T_C for the f.c.c. phase also increases linearly with pressure, but with a smaller slope dT_C/dp. The data up to 10 kbar agree well with the previous results of the same authors.[30]

Uranium

Interesting results were obtained on the pressure dependence of the superconducting properties of α-uranium, using magnetic and calorimetric methods, up to 22 kbar.[31-33] It was found that contrary to existing ideas, α-uranium either has a very low transition temperature (below 0.1 K) or does not become superconducting at all. The superconductivity previously observed in α-uranium was apparently due to the presence of internal strains in the specimens. The authors came to this conclusion on the basis of calorimetric measurements from which the volume of superconducting phase in the specimen could be accurately monitored. This conclusion is confirmed by the strong pressure dependence of T_C at low pressures (Fig. 12). It can be seen that T_C increases rapidly for pressures up to 9 kbar, passes through a flat maximum and then slowly decreases. If we assume that T_C at zero pressure is really less than 0.1 K, then the observed increase of T_C to 2 K at 10 kbar is unusually great. The authors believe that the large increase in T_C (or the appearance of superconductivity) for α-uranium on compression results from a change in the density of electron states at the Fermi surface.

5. THE INFLUENCE OF IMPURITIES ON THE EFFECT OF PRESSURE ON SUPERCONDUCTORS

The study of the influence of impurities on the effect of pressure on superconductors is a relatively new direction in research on superconductivity. The first experiments on the combined effect of pressure and impurities were made on thallium to explain its anomalous behavior under pressure.[34,35] These experiments were based on the suggestion[34] that an impurity of large valency would change the Fermi energy in the same direction as pressure, while an impurity of smaller valency would change it in the opposite direction from pressure.

With a change in Fermi energy, qualitative changes can take place in the electron energy spectrum, as shown
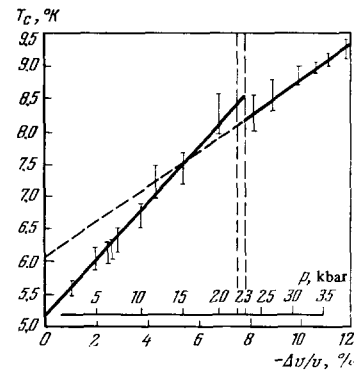

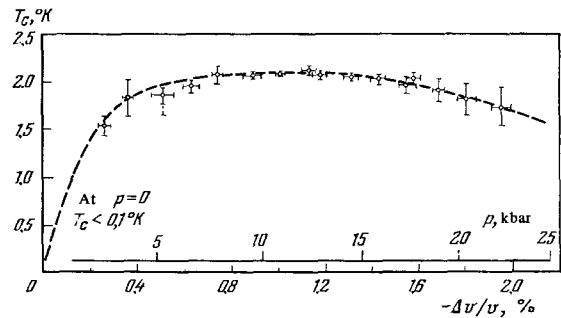FIG. 11. Change of T_C with compression for lanthanum [24].

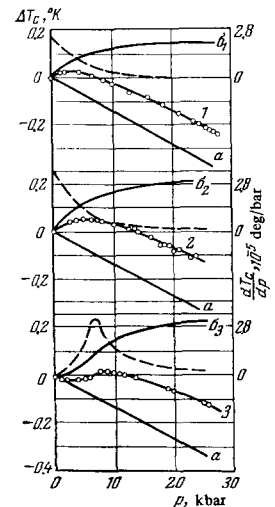FIG. 12. Superconducting transition temperature for α-uranium at different pressures [32].

FIG. 13. The change in T_C on compression for thallium and its alloys. 1— Tl; 2—Tl-Hg (0.45 at. % Hg); 3 — Tl Hg (0.9 % Hg). Curves a are the linear component, b_1, b_2, b_3 the non-linear components, and the dashed curve is dT_C/dp for the non-linear component (Brandt et al. 1965).

by Brandt et al,[35] new constant-energy surfaces can appear and the old ones can disappear. Singularities can then appear in the energy dependence of the parameter NV in the BCS formula (1), which will result in a different type of irregularity in $T_C(p, c)$ curves (c is the impurity concentration). The pressure effect in thallium was, in fact, very sensitive to the valency of the impurity atoms. For example, small concentrations of antimony and mercury change the sign of dT_C/dp at low pressures from positive to negative in thallium, and the form of the $T_C(p)$ dependence changes at the same time (Fig. 13). As a result of these experiments it was suggested that the appearance of the maximum in the $T_C(p)$ curve for thallium

is related to an irregular change in the density of states under pressure produced by an electronic phase transition.[36,37] As a result there are two components observed in the $T_c(p)$ dependence for thallium: a linear part with negative dT_c/dp and a non-linear part, rapidly saturating, with positive dT_c/dp at low pressures, which is connected with a change in the topology of the Fermi surface.

A large impurity dependence of the $T_c(p)$ relation was also found for rhenium[38] (see Fig. 14). T_c decreases in pure rhenium for pressures up to 7 kbar, passes through a minimum and then increases to a saturation value. On addition of osmium impurity the minimum in the $T_c(p)$ curve moves to lower pressures. The minimum disappears for an osmium concentration greater than 0.2 at.% and the $T_c(p)$ dependence becomes linear with dT_c/dp increasing with impurity concentration. As for thallium, these anomalies can be explained by a change in the topology of the Fermi surface of rhenium under the action of impurities and pressure. The experimental results show that the change in topology takes place at a pressure of 7 kbar or at an osmium concentration of 0.2 at.%.

The influence of impurities on the pressure effect has also been studied in indium.[39] It was found that cadmium impurity (up to 4.5 at.%) produces a positive non-linear component in the dependence of dT_c/dp on concentration. The authors associate this non-linear contribution with the breaking of the connections in the constant energy surface of the 3rd zone and the formation of a system of isolated ellipses.

Another explanation for the anomalous form of the $T_c(p)$ dependence for Tl was proposed by Gey,[40] who studied the effect of hydrostatic pressures up to 4 kbar on T_c for polycrystalline specimens of thallium with various lattice defect densities, produced by plastic deformation. It was shown that the maximum in the $T_c(p)$ curve disappears on increasing the defect density. The author deduces that the disappearance of the maximum is connected with a decrease in the anisotropy of the energy gap on deforming the lattice, since the electron mean free path is then decreased, while the appearance of the maximum for undeformed specimens is related to the increase in anisotropy of the gap with hydrostatic compression at low pressures. We should, however, point out that such a view does not explain the different effects of impurities of different valency and, in particular, the positive sign of dT_c/dp at small pressures for Tl-Hg alloys (see Fig. 13). Any impurity reducing the mean free path should decrease the gap anisotropy. Gardner and Smith[32] pointed out that the $T_c(p)$ dependence for uranium was reminiscent of the dependence for the non-linear contribution in thallium: in both cases T_c increases rapidly at low pressures and saturates, although the effect is two orders of magnitude greater in uranium than in thallium. It is thus possible that the great increase in T_c (or the appearance of superconductivity) in α-uranium at low pressures is also a consequence of an electronic transition. The possibility of such a transition receives confirmation from the observation that there is evidently an electronic transition in α-uranium at 43 K, which produces various anomalies in its properties.[41]

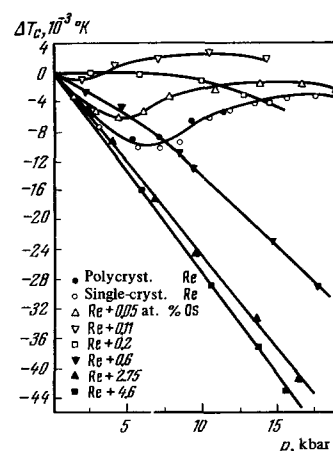The influence of paramagnetic impurities on the pressure effect was studied in solid solutions of lanthanum

FIG. 14. The influence of osmium on the pressure effect in rhenium.

with rare-earths for concentrations of the second component up to 1.3 at.% and pressures up to 10 kbar.[42] For the systems lanthanum-praseodymium, lanthanum-ytterbium and lanthanum-gadolinium there is a reduction in T_c under the influence of paramagnetic impurities, while the positive sign and magnitude of dT_c/dp is maintained. The positive sign of dT_c/dp for lanthanum changes to negative for cerium concentrations greater than 1 at.%. The general behavior of the alloys studied, except for lanthanum-cerium alloys, agrees with the theory of Abrikosov and Gor'kov[43] of the effect of paramagnetic impurities on the superconducting transition temperature. Coqblin and Retto[44] have also studied the influence of cerium and gadolinium impurities on the pressure effect in lanthanum.

6. NEW SUPERCONDUCTING MODIFICATIONS

The search for new superconducting modifications has developed in two directions: looking for superconductivity in modifications produced by high pressure in elements and compounds which are normally not superconductors, and looking for new modifications of known superconductors. Significant successes have been achieved so far in both these directions.

Group III elements

Among the elements of this group,* superconducting modifications of gallium, lanthanum and thallium have been studied.

At room temperature the Ga I–Ga II phase transition takes place at ~13 kbar. The pressure increases with decreasing temperature and evidently reaches about 30 kbar at T = 0 K. Ga I is superconducting with T_c = 1.07 K. T_c for Ga II depends on the state of the specimen, mainly on the extent of plastic deformation. However, regardless of the extent of plastic deformation, all specimens of Ga II measured had the same value of dT_c/dp = -3×10^{-5} K/bar.

It was mentioned earlier that lanthanum undergoes a polymorphic transition at about 23 kbar, when the hex-

---

*Most recently Wittig [102] has discovered superconductivity in a crystalline modification of cerium (at p > 50 kbar) with $T_c \approx 1.7°$K.

agonal (h.c.p.) lattice changes to face centered cubic (f.c.d.). It is interesting to note that this transition (see Fig. 11) is accompanied by a small (~0.4 K) reduction in the superconducting transition temperature, and an extrapolation of the $T_C(p)$ dependence for the f.c.c. phase to p = 0 gives $T_C \simeq 6$ K, which is close to the value T_C = 6.06 K[45] for the f.c.c. phase at p = 0. (Specimens of lanthanum are, in general, mixtures of these two phases.)

Gey[46] has obtained interesting results on the Tl II modification at pressures up to 50 kbar. The pressure was generated in a low temperature clamp[27] (see also [61]) in which the pressure could be changed directly at low temperatures. At the Tl I–Tl II phase transition the h.c.p. lattice changes to f.c.c. and at 2 K this starts at 35 kbar accompanied by a reduction in T_C (Fig. 15). At 35 kbar, T_C for Tl I is 1.95 K while it is 1.45 K at the same pressure for Tl II. In Tl II, dT_C/dp increases monotonically from -0.85×10^{-5} K/bar (at p = 50 kbar).
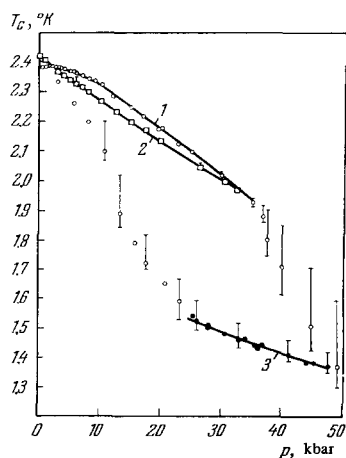

FIG. 15. The change in T_C for thallium under pressure. Curves 1 and 2 – undeformed and deformed specimens of Tl I; 3 – Tl II [10].

A characteristic feature of the Tl I–Tl II transition is the decrease in Debye temperature, although at the transition the volume decrease by 0.68%. For Tl I, Θ_D = 99 K at 35 kbar, and Θ_D = 88 K for Tl II. Comparison of the changes in the Debye temperature (−11%) and in T_C (−25%) at the Tl I–Tl II transition indicates a reduction in the product NV in the BCS formula (1) at the phase transition.

Group IV elements

Since the discovery of superconductivity in crystalline modifications of silicon and germanium[47] (see also [8]), all group IV elements, except carbon, have become superconductive. According to Bundy[48] the semiconductors silicon and germanium go over to the metallic state at room temperature at pressures of ~120 and ~115 kbar respectively. According to Jamieson's x-ray investigation[49] the metallic modifications of silicon and germanium have a body-centered tetragonal lattice of the white tin structure. The metallic phase of silicon becomes superconducting with T_C = 6.7 ± 0.1 K under a pressure of 120 kbar, with apparently a very small negative dT_C/dp.

Table I

Metal	T_c, °K	Θ_D, °K	Θ_D/T_c
Si	6.70±0.1	376	56
Ge	5.35±0.1	275	51.5
Sn	3.72	196	52.5

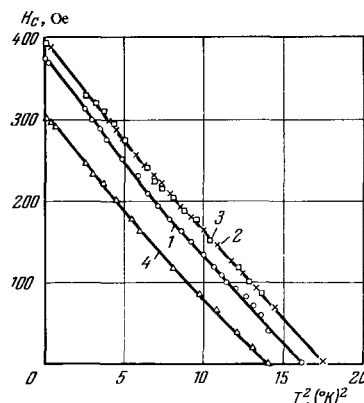

FIG. 16. Critical field curves for Sn III; 1 – p ~ 270 kbar; 2 and 3 – p ~ 240 kbar; 4 – p = 0 (Sn I).

This phase in germanium has T_C = 5.35 ± 0.1 K at a pressure of ~115 kbar with dT_C/dp = (2.1 ± 0.5) × 10^{-5} K/bar. Three elements of group IV of the periodic table thus have isomorphous lattices: the high-pressure phases of silicon and germanium, and white tin, which has T_C = 3.72 K and $dT_C/dp = -4.96 \times 10^{-5}$ K/bar. In comparing the superconducting properties of these elements, Wittig[8] pointed out the remarkable proportionality of their values of T_C and Debye temperature Θ_D determined from the temperature dependence of electrical resistivity (see Table I). The constancy of the ratio Θ_D/T_C indicates the closeness of the product NV in formula (1) for these elements.

The superconducting properties of the crystal modification of tin, Sn III, which is produced at room temperature at a pressure of 113 kbar[50] were studied up to 160 kbar by Wittig[16] and up to 270 kbar by Brandt and Berman.[10] The $T_C(p)$ relation derived from both these experiments is shown in Fig. 3. At 113 kbar, Sn III has T_C = 5.3 ± 0.1 K. With increasing pressure T_C decreases at a rate $dT_C/dp = -(1.0 \pm 0.2) \times 10^{-5}$ K/bar. Figure 16 shows the critical field curves measured at 270 ± 20 and 240 ± 20 kbar at temperatures between 0.1 and 4.2 K.[10] Similar curves for white tin at zero pressure are also shown for comparison. We note that these modifications are soft superconductors with similar critical field curves which have negative departures from parabolas. Brandt and Berman[51] have recently obtained results on the superconducting properties of the crystalline modification, Pb II, of lead, which occurs at 160 kbar. A feature of the phase transition is the absence of any noticeable change in critical temperature T_C and in the density of states at the Fermi surface.

As far as we know, the superconductivity of the modifications of zirconium and titanium, which occur at pressures of 60 and 80 kbar, have not been studied.

Group V elements

The largest number of new superconducting modifications has been found among the group V elements: for bismuth, Bi II, Bi III, Bi V; for antimony, Sb II; for phosphorus P III and apparently P V.

The modification Bi II exists over a narrow range of pressure and temperature. At room temperature, Bi II is formed at a pressure of ~ 25 kbar and goes over to Bi III at ~ 27 kbar. The pressure range over which Bi II exists narrows as the temperature decreases and below 150 K this form can only be obtained in the metastable state (see [6]). Bi II is a soft superconductor with dT_C/dp = -3.2×10^{-5} K/bar and a critical field curve similar to that of white tin. The modification Bi III becomes superconducting at $T_C \sim 7.1$ K and has a very small negative dT_C/dp.[50,6] The critical field curve of Bi III[6,52] shows that it is a hard superconductor with the largest value dH_C/dT = 2000 Oe/K for superconducting elements. Bi V is formed at pressures above 80 kbar and its superconductivity was discovered recently.[16] Bi V becomes superconducting at 80 kbar at a temperature $T_C \simeq 8.3 \pm 0.2$ K. T_C decreases with increasing pressure, reaching ~ 7.4 K and 6 K at 140 kbar[16] and 250 kbar[51] respectively. Unlike Bi III, Bi V is a soft superconductor with a critical field curve similar to that of lead. At 250 kbar H_0 = 760 Oe.

McDonald et al.[52] discovered superconductivity in the modification of antimony, Sb III, which at room temperature is stable at pressures above ~ 85 kbar. The transition temperature of this form is between 2.6 and 2.7 K, with a critical field H_{c2} = 4400 Oe at T = 1.55 K. X-ray examination by these authors showed that Sb II (at 90 kbar) is isomorphous with the modification Bi III (at 35 kbar).

Quite recently[51] superconductivity was found in the crystalline forms of phosphorus which occur at pressures above 160 kbar. One of the modifications which occurs for pressures between ~ 160 and 200 kbar becomes superconducting with T_C = 5.8 K (at ~ 180 kbar) and dH_C/dT = 1100 Oe/K. A new modification is formed above ~ 200 kbar with T_C = 5.4 K (at p $\cong$ 230 kbar) and dH_C/dT = 2400 Oe/K. Unfortunately, as far as we know, the p-T phase diagram for phosphorus has not been investigated in this pressure region, so that we cannot identify these superconducting modifications with results of crystallographic studies. At almost the same time Wittig and Matthias[54] reported the discovery of superconductivity in a modification of red phosphorus which occurs for pressures above 100 kbar. The transition temperature depended on the applied pressure and transitions were found at ~ 4.7 K, ~ 5.3 K and ~ 6.1 K.

It is natural to expect that arsenic, which lies between phosphorus and antimony in group V, will also have superconducting crystal modifications at high pressure.

Group VI elements

Among the group VI elements, superconducting modifications have been found in tellurium[55] and selenium[56] which are semiconductors under normal conditions. In tellurium, superconductivity was found in the Te II modi-

fication which is formed at pressures above 45 kbar (at room temperature). This form becomes superconducting at ~ 3.3 K (under a pressure of ~ 56 kbar) and appears to be a soft superconductor with H_0 = 250 $\pm$ 50 Oe. This data should be regarded as preliminary since the pressure in the specimens was not uniform.

The metallic modification of selenium, Se II, which is stable above 130 kbar, becomes superconducting between 6.8 and 6.9 K. Its superconducting properties have not been studied in detail.

Compounds

New results have recently been obtained on the superconductivity of crystal modifications of InSb[57-59], GaSb, [60] BiSn[61] and AlSb.[62]

Apart from the superconducting form, InSb II, with T_C = 2.0 $\pm$ 0.1 K, previously studied,[6] the existence of new modifications of InSb has been found. The absence of a p-T phase diagram makes it difficult to give a unique interpretation of the results obtained by different authors. It seems that one can assume that there are at least two crystal modifications of InSb different from InSb II: modifications of orthorhombic structure and transition temperature varying between 3.3 and 5 K, depending on the pressure (from 30 to 150 kbar) at which this phase is formed and the modification InSb III with T_C = 4.1 $\pm$ 0.1 K. The conditions of formation of these structures differ in the rate at which the pressure is applied, the magnitude of the pressure and the temperature at which it is found. It is interesting to note that the critical temperature of InSb increases greatly with the addition of small concentrations of β-Sn[63] which has the same lattice structure. At a concentration of 2.5 at. % of β-Sn, T_C has increased from 2.1 K to ~ 4.2 K.

The superconducting modification of GaSb, which is formed at pressures above 70 kbar, has T_C between 4.2 and 6 K depending on the previous heat treatment of the specimen.

The K-phase of BiSn, which is formed at pressures above 25 kbar and temperatures above room temperature, becomes superconducting at T_C = 7.88 K.

The semiconducting compound AlSb becomes metallic with the white tin structure at a pressure of about 125 kbar (at room temperature).[64,65] This modification has T_C = 2.8 $\pm$ 0.2 K (at p $\sim$ 125 kbar) and seems to have positive dT_C/dp.

7. ON THE POSSIBILITY OF OBTAINING MODIFICATIONS IN A METASTABLE STATE

Polymorphic transitions at high pressures, which lead to the formation of new modifications, are reversible at room temperature and above. The high-pressure modification can therefore only exist in this temperature range under hydrostatic compression. However, comparison of the superconducting properties of bismuth films, obtained by deposition on a substrate cooled to liquid helium temperature, with the properties of the Bi III modification led to the idea that at low temperatures the high-pressure modifications can be preserved in a metastable state without external pressure, if sufficiently strong internal strains are previously produced in them.[12] (Large internal strains arise in amorphous films obtained at low temperatures, and strained, fine-grained crystal struc-

tures form when they are mildly annealed). Bi III was chosen for the first study, since its continued existence at low temperatures can be monitored conveniently by the retention of its superconducting properties. It was found that a single crystal of bismuth, which had been turned into the superconducting Bi III modification by quasi-hydrostatic pressure (~ 27 kbar) and cooled to liquid helium temperature, changed discontinuously to the usual Bi I at $p \sim 21$ kbar when the pressure was slowly lowered. However, after several cycles of compression, when internal microstresses were formed in the specimen as a result of plastic deformation (due to an increase in the number of dislocations, a greater degree of polycrystallinity, etc.), the Bi III modification is preserved at helium temperatures at zero pressure, and has a superconducting transition temperature $T_c \sim 7.4$ K (we note that for Bi III at $p = 30$ kbar, $T_c \sim 7.1$ K). It is natural to assume that the amount of strain in the specimen, which enables Bi III to exist without external pressure, must be equivalent to a pressure of 21 kbar. The low temperature region in which such strains can exist without external pressure is the region of metastable existence of Bi III. On heating the specimen (at $p = 0$) the amount of internal stress decreases as a result of annealing, and the Bi III → Bi I transition takes place at $T = 20$ to 30 K.

It has now been established that modifications, which are normally stable only at high pressures, can be obtained in the metastable state at atmospheric pressure, and at low temperatures by a similar method for Ga,[27] InSb,[57-59] GaSb,[60] BiSn,[61] and Sb.[53] At pressures above 13 kbar gallium (as discussed earlier) exists at room temperature as the modification Ga II with $T_c \simeq 7$ K (at $p \sim 13$ kbar). The form Ga II continues to exist when the external pressure is reduced to zero at liquid helium temperatures. The value of T_c then increases to ~ 7.4 K.

The high-pressure metallic modifications of InSb and GaSb can easily be obtained in the metastable state by reducing the pressure to zero at liquid nitrogen temperature (77 K), and appears to continue to exist at temperatures below 120 to 130 K. The K-phase of BiSn stays in the metastable state at temperatures below 170 K.

The most remarkable phenomenon is the existence at liquid nitrogen temperature of the superconducting modification Sb II, which at room temperature is stable at pressures above ~ 85 kbar. The Sb II modification is maintained at temperatures below ~ 80 K. McDonald et al.[53] made an interesting attempt at a direct x-ray study of the crystal structure of Sb II (at 90 kbar) and the superconducting modification of Sb in the metastable state at atmospheric pressure. Unfortunately this study did not yield an unambiguous conclusion about the identity or otherwise of these phases, because apart from identical lines in the x-ray patterns there were some others whose origin is unexplained.

It is noticeable that all the modifications considered, except for Bi III, were obtained in the metastable state immediately after the first compression cycle. This must result from the details of the methods, which lead to great plastic deformation of the specimens on compression (for example, Bridgman anvils for the study of Sb). If this is really so, then it would be extremely interesting to repeat these measurements using a method which would produce appreciably less plastic deformation in the specimens when the pressure is being applied. Results obtained in a study of the low temperature stability of the Tl II modification of thallium[46] can to some extent be considered as confirmation of this hypothesis. It was found that if a specimen of thallium is compressed between Bridgman anvils at 2 K up to ~ 50 kbar, which exceeds the Tl I → Tl II phase transition pressure (35 kbar), and the specimen is then annealed at 220 K without taking off the pressure and cooled again to liquid helium temperature, then on decreasing the pressure a continuous strong broadening of the Tl II → Tl I transition is observed for $p \gtrsim 25$ kbar. Unfortunately the stability of strongly deformed (unannealed) specimens of thallium was not examined.

The possibility of obtaining the high-pressure modifications Bi III and Ga II in the metastable state, and the similarity of their properties to those of films of these metals obtained by low temperature deposition, indicates a similarity (or identity) of structure. We can, thus, presume that crystal structures which at high temperatures are only stable at high pressures can be produced by low temperature condensation.

8. THE EFFECT OF PRESSURE ON THE SUPERCONDUCTING TRANSITION TEMPERATURE OF ALLOYS

Studies of the effect of pressure on alloys are of interest because there is more variety in the physical and superconducting properties of alloys than of the elements. Table 2 shows new data obtained on alloys.

9. THE PRESSURE EFFECT AND THE MICROSCOPIC THEORY OF SUPERCONDUCTIVITY

Mechanisms for the effect of pressure on superconductivity

As was mentioned earlier, experimentally measured

Table II

Alloy	T, °K	dT_c/dp, deg/bar	Pressure range (kbar)
Mo$_{90}$Re$_{10}$	2.92	$5 \cdot 10^{-6}$	20—28 [66]
Nb$_{75}$Mo$_{25}$	3.47	$-0.4 \cdot 10^{-5}$	0—28 [66]
Nb$_3$Al	17.5	> 0	0—2 [67]
Nb—Al—Ge		> 0	0—2 [67]
Nb$_3$Sn	17.5	$-2.1 \cdot 10^{-4}$	0—2 [68]
Nb$_3$Sn	17.5	$-0.6 \cdot 10^{-4}$	25—30 [68]
Nb—Zr (up to 45 at. % Zr)	~ 10	< 0	25—75 [69]
Nb—Mo (up to 30 at. % Mo)	from 9 to 2	> 0	25—75 [69]
V$_3$Ga	16.5	> 0	0—18 [70]
V$_3$Si	17.1	> 0	0—18 [70]
LaAg	0.9	$3.1 \cdot 10^{-5}$	0—9.5 [71]
SrTiO$_3$	0.25	$-8 \cdot 10^{-5}$	0—1.5 [72]

quantities can be expressed in terms of certain micro-
scopic properties of a metal through the microscopic
theory of superconductivity.[3] The BCS expression (1)
for the superconducting transition temperature is espe-
cially important in this respect. In the original BCS
theory V was not evaluated, the parameter $\langle \hbar\omega \rangle$ was
taken roughly equal to $k\Theta_D$ and N was calculated on the
free electron model.

When using Eq. (1) to analyze actual experimental re-
sults, it must be remembered that the expression is,
firstly, not exact (it is derived from a simplified model
of a metal) and, secondly, its applicability is limited to
superconductors with weak interaction, that is super-
conductors for which T_C/Θ_D is sufficiently small.

The further developments of the BCS theory were both
in the direction of exact expressions for $\langle \hbar\omega \rangle$ and V or
NV, by considering the interactions between electrons in
a metal in more detail[73-75] without changing the general
form of Eq. (1), and also in the direction of generalizing
Eq. (1) to the case of strong electron-phonon interaction.
[76] Without going into details of the analysis, we will only
consider the expressions for T_C obtained by McMillan[74]
and by Hulm et al.[75] taking account of the screened Cou-
lomb potential, and also the relation between T_C and Δ
derived from the strong-interaction theory in [78].

The expression for T_C takes the form[74,75]

$$T_c = \frac{\Theta_D}{1.45} \exp \left\{ -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right\} ,   (6)$$

where λ and μ^* are constants describing the electron-
phonon attraction and the Coulomb repulsion, respectively.

The relation between T_C and Δ becomes more involved:

$$\frac{2\Delta(0)}{kT_c} = 3.52 \left[1 + 5.3 \frac{T_c^2}{\omega_0^2} \ln \left(\frac{\omega_0}{T_c} \right) \right] ;   (7)$$

where ω_0 is the limiting frequency of phonons (longitudi-
nal or transverse) which interact with the most important
electrons.

We can follow different routes when comparing the ex-
perimental results on the pressure dependence of proper-
ties of superconductors with the theory. The experimental
data can be compared directly with the BCS expression (1),
giving a definite meaning to the value of $1.14 \langle \hbar\omega \rangle$, for ex-
ample by substituting $\Theta_D/1.45$ for it (see Eq. (6)), and
considering N and V as parameters to be determined ex-
perimentally. It is then assumed that Eq. (1) remains
valid for any dispersion law for the electrons in the
metal. The dependence of NV on pressure can then be
determined directly if the pressure dependences of T_C
and Θ_D are known. If we are to find how N and V sepa-
rately change on compression, we must know how one
of them varies with pressure. We can only derive this
for N from experimental data. On the other hand, from
a theoretical calculation of $\langle \hbar\omega \rangle$, N and V in Eq. (1), the
magnitude and sign of dT_C/dp can be derived and com-

pared with experimental data. Such a comparison pro-
vides an additional possibility for verifying the various
theoretical models on the basis of which the BCS theory
has been extended (in particular, Eq. (7)). We will con-
sider what can be deduced from a comparison of the
presently known experimental data with the theory.

We will first analyze the experimental results by using
Eq. (1) in the manner discussed above. For determining
the form of the change in the density of states, N, on com-
pression, we will use both the results on the change in crit-
ical field curves at different pressures (see Eq. (5)) and
also results on the temperature dependence of the expan-
sion coefficients, α, of metals in the normal state.[77,78]

At low temperatures

$$\alpha = \alpha_e + \alpha_g = AT + BT^3,   (8)$$

where α_e and α_g are the electronic and lattice contribu-
tions to the thermal expansion. The coefficient α_e is

$$\alpha_e = \frac{1}{v} T \frac{d\gamma}{dp} ,   (9)$$

from which $d \ln N/d \ln v$ (or $d \ln N/dp$) can easily be de-
rived (using well-known relations and Eq. (3)). There are
other independent ways of determining $d \ln N/d \ln v$; for
example, from the volume change of specimens on going
into the superconducting state. However, the results ob-
tained in this way are neither sufficiently complete, nor
sufficiently accurate. Values of $d \ln N/d \ln v$ for tin, in-
dium, cadmium, zinc and aluminum, derived in the ways
described, are shown in Table III.

It can be seen that the values of $d \ln N/d \ln v$ cal-
culated from Eq. (5) are appreciably larger than the
values calculated from Eqs. (8) and (9). The large dis-
crepancy makes a unique conclusion about the form of
the change of V with pressure impossible. If we use
the results on the pressure dependence of N derived
from Eq. (5), then it appears that in tin, aluminum,
cadmium, zinc and to a lesser extent in indium, the
main cause of the change in T_C on compression is
the decrease in the density of states at the Fermi sur-
face, and that to a first approximation the parameter V
does not change with pressure in these metals.

However, if we substitute in Eq. (1) the values of
$d \ln N/d \ln v$ determined from α_e, then we are led to
the conclusion that V also decreases under the action
of pressure.

We must also realize that another uncertainty arises
from calculating the change in the Debye temperature
from Eq. (2), although the values of $\Theta_D(p)$ for tin calcu-
lated from Eq. (2) agree with the experimentally deter-
mined values at 88 kbar.[16]

Studies of the pressure effect on normal metal-
dielectric-superconductor tunnelling provide very in-
teresting information on the nature of the changes in a
number of microscopic parameters. The pressure de-
pendence of the energy gap in a superconductor can be

Table III

Metal $\quad$ $d \ln N/d \ln v$	Al	Cd	Zn	In	Sn	Pb
From (5)	6.6 ± 0.3 [22]	5.2 [17]	4.1 [17]	2.1 ± 0.3 [17]	2.1 ± 0.3 [17]	
From (8) and (9)	1.8 ± 0.1 [78]	0.7 ± 1.5 [80]	7 ± 4 [82]	1.0 ± 0.2 [79]	1.7 ± 0.3 [81]	1.7 ± 0.5 [80]

determined directly, as can the form of the change in the function $\alpha^2(\omega)\, F(\omega)$[83,84] with compression, where $\alpha^2(\omega)$ is the energy dependence of the electron-phonon interaction, and $F(\omega)$ is the phonon density of states. From the form of the change of $\alpha^2(\omega)\, F(\omega)$, the magnitudes of the shift in the maxima $F(\omega_\perp)$ and $F(\omega_{||})$ in the phonon density of states appropriate to transverse and longitudinal lattice waves can be deduced directly, and also the shift in the limiting upper energy (ω_K) for the density of states.[85] Also, knowledge of the function $\alpha^2(\omega)\, F(\omega)$ gives directly the mean electron-photon interaction:

$$\langle a^2 \rangle = \frac{\int \alpha^2(\omega)\, F(\omega)}{\int F(\omega)\, d\omega}, \tag{10}$$

the constant λ, characterizing the attraction between electrons:

$$\lambda = 2 \int \frac{\alpha^2(\omega)\, F(\omega)}{\omega}\, d\omega, \tag{11}$$

and the normalizing constant:

$$z = 1 - \lambda, \tag{12}$$

this relates the parameter N in Eq. (1) with the density of states N_{bs} calculated from the free electron model $(N = N_{bs}Z)$.

The effect of hydrostatic pressure on tunnelling in lead has been studied by Franck and Keeler[86,87] and by Franck, Keeler and Wu[88] (at $p \sim 3.4$ kbar) and by Zavaritskii, Itskevich and Voronovskii[89] (for p up to 16 kbar). The Grüneisen constants for lead,[88] $\xi_{g\omega}$ = d ln ω/d ln v, determined from the shift in the maxima of the function $\alpha^2(\omega)\, F(\omega)$ for different branches of the phonon spectra, are very different from one another ($\xi_{g\omega\perp}$ = 4.95, $\xi_{g\omega||}$ = 3.45), and their absolute values differ from the value ξ_ω = 2.7 calculated from the magnitudes of the expansion coefficient and heat capacity of lead at low temperatures. In addition, the Grüneisen constant for the electrons obtained by Garfinkel and Mapother,[90] ξ_e = 3.7, is about twice as great as the value of 1.7 ± 0.5 given in Table III. The value of d ln γ/dp = $- 18.8 \times 10^{-6}$ bar^{-1}, found by Franck, Keeler and Wu, is in turn considerably greater than the value which is required to explain the observed decrease in T_c for lead according to Eq. (6).

We can, therefore, state that the present data relevant to the mechanism for the effect of pressure on T_c for non-transition metals are conflicting. This is partly due to insufficient accuracy in the experimental determination of the parameters used (especially the derivatives), and partly to the approximate nature of Eqs. (1) and (6), in which only some averaged properties of the metals are used, whereas it is possible that only one of the

branches of the phonon spectrum is important in the electron interaction. In addition, the strong effect of anisotropy in a number of superconductors[91] is not taken into account at all. The need for refining Eq. (1) in the BCS theory and for a more detailed approach in the description of the properties of superconductors is also indicated by the empirical dependence of the ratio $2\Delta(0)/kT$ on T_c/Θ_D[92,93] (in the initial BCS theory $2\Delta(0)$ = 3.52 kT_c). This relation is explained by the strong-interaction theory of superconductivity (Eq. (7)).

Equation (7) has been confirmed for lead by Franck and Keeler,[87,88] Franck, Keeler and Wu,[89] and Zavaritskii, Itskevich and Voronovskii.[89] The value of $(2\Delta(0)/kT_c)_{\omega_\perp}$ = 4.26 calculated from Eq. (7) agrees extremely well with the experimental value $2\Delta(0)/kT_c$ = 4.3. Even more convincing confirmation of Eq. (7) was obtained from observation of tunnelling under pressure.[89] It was shown that the values of $\Delta(0)$ for lead measured at different pressures lie on a straight line, with the slope $d\Delta(0)/dp$ as calculated from Eq. (7) with independently determined values of dT_c/dp, $\omega_\perp$ and $d\omega_\perp/dp$, bearing in mind that transverse phonons make the main contribution to the electron interaction in lead.[94]

From what has been said above, we would expect that attempts to calculate the value of dT_c/dp from Eq. (1), with NV and $\langle \hbar\omega \rangle$ related to averaged properties of metals, would not give satisfactory qualitative agreement with experiment. Bar'yakhtar and Makarov[95] made such an attempt.

Olsen, Andres and Geballe[96] used Eq. (1) in the form

$$T_c = \Theta_D e^{-\frac{1}{NV}}. \tag{13}$$

On the assumption that the Coulomb repulsion is small (see Eq. (6))

$$NV = \frac{\lambda}{1+\lambda}, \tag{14}$$

where $\lambda = C/m\Theta_D^2$ is the electron-phonon interaction constant. For superconductors with strong interaction, C is a constant practically independent of pressure,[74] so that the derivative can be considered zero. Hence

$$T_c = \frac{\Theta_D}{2.7}\, e^{-\frac{1}{\lambda}} \tag{15}$$

and

$$\varphi = \frac{d\ln(NV)}{\partial \ln v} = \frac{2\xi_g}{1+\lambda}. \tag{16}$$

We note that λ should decrease with pressure because of the increase in Θ_D. Table IV shows the calculated and experimental values of φ.

We see that there is an appreciable difference between the experimental and calculated values for most of the

Table IV

Metal	Al	Cd	Zn	In	Sn	Pb	Hg α	Tl	Ga
$2\xi_g$	4.4	4.6	4.1	5 0	4.5	5.7	6.0	4.5	2.9
φ exp	3 4	2.9	2.0	2.3	2.3	2.1	1.7	3.7*)	1.8
φ calc	3.2	3.3	2.9	2.8	2.4	2.7	2.4	2.6	2.1

*) For $10 < p < 30$ kbar

metals in Table IV. The data obtained in this way thus only indirectly reflect the mechanism for the effect of pressure on T_c, and do not allow weights to be assigned separately to different interactions.

We now consider transition metals and their alloys. The characteristic difference between them and non-transition metals is the existence of two signs for the change of T_c on compression. The values of dT_c/dp and φ calculated from Eq. (6) do not agree at all with experiment for transition metals.

A feature of transition metals and alloys is the large value of the electron density of states at the Fermi surface, resulting from the overlap of the inner (d and f) bands and the conduction band. The existence of sharp maxima in the density of states in the d and f bands leads to a strong dependence of N on the position of the Fermi level; while depending on whether the Fermi lies on the left or right of the maximum, the same change in Fermi energy can lead either to an increase or to a decrease in N. As a result, there is a complicated relation between N and the effective number of valence electrons, n_V, in transition metals.[97]

Brandt and Ginzburg[6,66] suggested that the pressure dependence of N for transition metals and alloys is determined by curves analogous to the dependence of N on n_V, derived from data on electronic heat capacity. The sign of dT_c/dp must then be determined by the position of the superconductor on these curves. T_c must increase on compression for superconductors with $dN/dn_V > 0$ and fall for superconductors with $dN/dn_V < 0$. We would expect this rule to hold only for superconductors with the same band structure, and then only to a first approximation, because in transition metals the density of states at the Fermi surface does not entirely determine the magnitude of T_c.

It is possible that we should also consider the value of the effective mass for d-electrons as well as the value of N, since too large a value can lead to the disappearance of superconductivity.[98] Also, we cannot completely ignore the possibility that the parameter V changes with compression in transition metals. Nevertheless Brandt and Ginzburg's hypothesis is satisfied for a number of metals and alloys studied.[6,66]

Gey and Köhnlein[69] have recently measured the electronic heat capacity of the effect of pressures up to 75 kbar in Zr-Nb-Mo alloys to verify the relation between the sign and magnitude of dT_c/dp, and the corresponding dependence of N (or γ) on n_V. The results (Fig. 17) agree with the hypothesis not only qualitatively but quantitatively.

Can superconductivity be destroyed by pressure?

The answer to this question is related directly to other questions: Why does the superconducting transition temperature decrease with pressure? What part do various mechanisms, which determine the value of T_c for the given superconductor, play in the process? It would seem that this question merges with the problem discussed above, which is still, unfortunately, unsolved. Although one must have reliable data on the change with pressure of specific parameters of the spectrum which determine T_c, and know how they are related to T_c in order to explain the mechanism of the pressure effect on superconductivity,
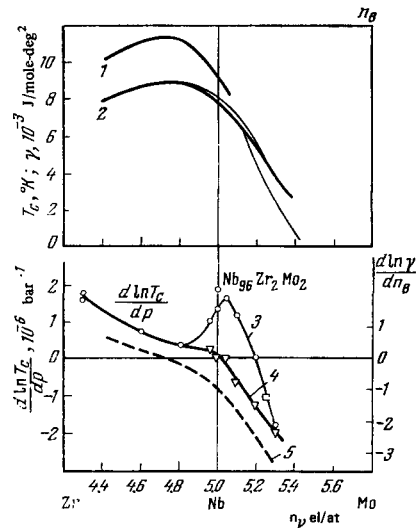

FIG. 17. Changes in T_c, γ d ln T_c/dp and d ln γ/dn_V for Zr-Nb-Mo alloys [69]. 1 — $T_c(n_V)$; 2 — $\gamma(n_V)$; 3 — d ln T_c/dp at p < 20 kbar; 4 — d ln T_c/dp at p > 25 kbar; 5 — d ln γ/dn_V.

this detail is not required to say whether superconductivity can disappear under pressure (for a single crystal modification) as this question depends on qualitative changes in the metal's properties. We can, therefore, use averaged values of the parameters of the electron and phonon spectra to determine whether, in principle, superconductivity can disappear with decreasing volume, within the framework of the BCS theory.

On the other hand, a direct experimental demonstration of the possibility of superconductivity disappearing on compression, and the determination of the law according to which T_c goes to zero, would be of major significance in testing the correctness of present ideas on the mechanism of superconductivity and in determining the conditions essential for its appearance.

From the BCS point of view (Eq. (1)), T_c going to zero at some critical value of the pressure p_c (or volume v_c) means that for $p = p_c$ (or $v = v_c$) the product NV becomes zero. N cannot become zero at any finite pressure while the metallic state is maintained. Superconductivity can only disappear if the parameter V becomes zero. We note that if we ignore the Coulomb repulsion μ^*, as was done by Olsen, Andres and Geballe,[96] then NV = $C/m\Theta_D^2$ and T_c can never become zero (we remember that C depends very little on p). Superconductivity can thus only disappear on compression for compensation (on the BCS theory) of the electron-phonon attractive and Coulomb repulsive forces, that is, under the condition (Eq. (6))

$$\mu^* = \frac{\lambda}{1 + 0.62\lambda} \cdot \tag{17}$$

In general λ is a function of electron concentration, n, and Debye temperature Θ_D.

If we use the results of Hulm et al.,[75] then for Eq. (17) to be satisfied, μ^* must at least double with the pressure. We must emphasize that the product NV can only become zero as a result of a monotonic change in the parameters μ^* and λ with pressure. The value of p_c (or v_c) at which this would happen is no special singularity for the functions $\mu^*(p)$ and $\lambda(p)$. We can therefore assume that near
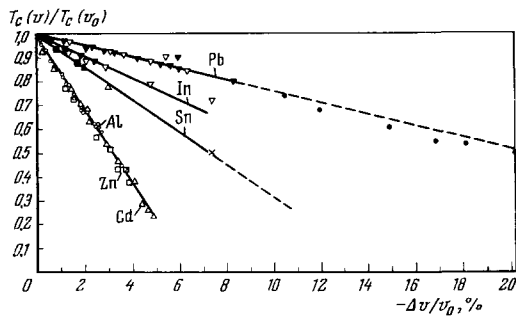
FIG. 18. Relative changes in T_C as a function of relative volume changes in specimens on compression. $\circ$ — Al [20]; $\triangle$ — Cd [21]; $\square$ — Zn (ibid); Sn ($\blacksquare$ — [4], $\blacktriangle$ — [101], $\times$ — [16]); In ($\blacktriangledown$ — [4], $\triangledown$ — [27]); Pb ($\triangledown$ — [100], $\blacktriangledown$ — [24], $\bullet$ — [16]).

Table V

Metal	100		21		20	
	p_c, kbar	$\frac{\Delta v}{v_0}$, %	p_c, kbar	$\frac{\Delta v}{v_0}$, %	p_c, kbar	$\frac{\Delta v}{v_0}$, %
Al	67	6.3	220	~16.3	>500	>26
Cd	38	6.3	120	~13.9		
Zn	41	6.3	160	~14.2		
In	163	21.8				
Sn	110	14.8				
Pb	>1000	~40				

p_c, to a first approximation, NV will vary linearly with the pressure difference $(p_c - p)$ or volume difference $(v - v_c)$. On this assumption [6,99] we would expect the dependence of T_C on p to be of the form

$$T_c(p) = 0.7\Theta_D e^{-\frac{a}{p_K - p}}, \qquad (18)$$

where a is a constant for a given metal. Brandt and Ginzburg [21] showed that the pressure dependence of T_c for cadmium, zinc and aluminum around 30 kbar is satisfactorily described by Eq. (18).

Smith and Chu [100] found an unexpected result on expressing the known relations between T_c and p by the coordinates $T_c(v)/T_c(v_0)$ and $\Delta v/v_0$

$$\frac{T_c(v)}{T_c(v_0)} \quad \text{and} \quad -\frac{\Delta v}{v_0}$$

(see Fig. 18). In these coordinates the relative change in T_c for cadmium, zinc, aluminum, tin and indium turned out to be linear functions of the relative volume changes of the specimens on compression. The values of v_c (and p_c) for these metals obtained by extrapolating these straight lines to $T_c = 0$ are given in Table V.

For comparison, the values of p_c and v_c obtained by extrapolation according to Eq. (18) are given. We notice the very low values of p_c determined by Smith and Chu. [100] In order to reconcile the linear dependence of ΔT_c on Δv with the BCS expression, Smith and Chu [100] had to assume that the parameter V changes slowly for small changes in v but then falls extremely rapidly to zero as Δv approaches Δv_c. We rather doubt such a behavior for V on the basis of the considerations put forward above ($v = v_c$ is not a singularity in the V(v) function). It is possible that the linear dependence observed is just an approximation in the range of Δv where experimental data are available, and it would become exponential for large changes Δv. Accurate experimental data on the change in T_c for cadmium, zinc and aluminum at pres-

sures above 30 kbar are required for a definite answer to the problem.

[1] G. J. Sizoo and K. H. Onnes, Proc. Amsterdam Acad. **34**, 606 (1925); G. J. Sizoo, W. J. de Haas, and K. H. Onnes, Leisen Commun. 180c (1925); W. H. Keesom, Leiden Comm. 184b (1926).

[2] B. G. Lazarev and L. S. Kan, Zh. Eksp. Teor. Fiz. **14**, 439 (1944).

[3] J. Bardeen, L. Cooper, and J. Schriffer, Phys. Rev. **106**, 162 (1957).

[4] C. Swenson, Solid State Physics **11**, 41 (1960).

[5] J. L. Olsen, E. Bucher, M. Levy, J. Muller, E. Conenzwith, and T. Geballe, Rev. Mod. Phys. **36**, 168 (1964).

[6] N. B. Brandt and N. I. Ginzburg, Usp. Fiz. Nauk **85**, 485 (1965) [Sov. Phys.-Usp. **8**, 202 (1965)].

[7] M. Levy and J. L. Olsen, Physics of High Pressures and the Condensed Phase, chap. 13, North-Holland Publishing House, Amsterdam, 1964.

[8] Jörg Wittig, Zs. Phys. **195**, 215 (1966).

[9] D. B. McWhan and M. Marezio, J. Chem. Phys. **45**, 2508 (1966).

[10] N. B. Brandt and I. V. Berman, ZhETF Pis. Rev. **7**, 198 (1968) [JETP Lett. **7**, 152 (1968)].

[11] N. B. Brandt and I. V. Berman, ibid. **7**, 412 (1968) [**7**, 323 (1968)].

[12] N. B. Brandt and N. I. Ginzburg, Fiz. Tverd. Tela **3**, 3461 (1961) [Sov. Phys. Solid State **3**, 2510 (1962)].

[13] D. N. Lyon, D. B. McWhan, and A. L. Stevens, Rev. Sci. Instrum. **38**, 1234 (1967).

[14] T. F. Smith and W. E. Gardner, Phys. Rev. **140** (5A), 1620 (1965).

[15] Yu. N. Ryabinin, K. P. Rodionov, and E. S. Alekseev, Zh. Tekh. Fiz. **34**, 1913 (1964) [Sov. Phys. Tech. Phys. **9**, 1477 (1965)].

[16] Jörg Wittig, Zs. Phys. **195**, 228 (1966).

[17] I. V. Berman, N. B. Brandt, and N. I. Ginzburg, Zh. Eksp. Teor. Fiz. **53**, 124 (1967) [Sov. Phys.-JETP **26**, 86 (1968)].

[18] C. Grenier, Compt. rend. **240**, 2302 (1955).

[19] H. Rohrer, Phil. Mag. **4**, 1207 (1959).

[20] M. Levy and J. L. Olsen, Solid State Comm. **2**, 137 (1964).

[21] N. B. Brandt and N. I. Ginzburg, Zh. Eksp. Teor. Fiz. **50**, 1260 (1966) [Sov. Phys.-JETP **23**, 838 (1966)].

[22] E. P. Harris and D. E. Mapother, Phys. Rev. **165** (2), 522 (1968).

[23] J. L. Palmy and C. and De P. Trey, Proc. XI Inst. Conf. on Low Temp. Phys. St. Andrews, Vol. 2, p. 977 (1968).

[24] D. Köhnlein, Zs. Phys. **208**, 142 (1968).

[25] W. E. Gardner and T. F. Smith, Phys. Rev. **144**, (1), 233 (1966).

[26] W. Gey and G. V. Heyden, Zs. Phys. **193**, 65 (1966).

[27] W. Buckel and W. Gey, Zs. Phys. **176**, 336 (1963).

[28] K. Lüders, Zs. Phys. **193**, 73 (1966).

[29] T. F. Smith and W. E. Gardner, Phys. Rev. **146**, 291 (1966).

[30] W. E. Gardner and T. F. Smith, Phys. Rev. **138A**, 484 (1965).

[31] T. F. Smith and W. E. Gardner, Phys. Rev. **140A**, 1620 (1965).

[32] W. E. Gardner and T. F. Smith, Phys. Rev. 154, 309 (1967).

[33] N. E. Phillips, J. C. Ho, and T. F. Smith, Proc. X Int. Conf. on Low Temp. Phys. Moscow, Fol. 2B, p. 189 (1967).

[34] B. G. Lazarev, L. S. Lazareva, V. I. Markarov, and T. A. Ignat'eva, Zh. Eksp. Teor. Fiz. 48, 1065 (1965) [Sov. Phys. JETP 21, 711 (1965).

[35] N. B. Brandt, N. I. Ginzburg, T. A. Ignat'eva, B. G. Lazarev, L. S. Lazareva, and V. I. Makarov, ibid. 49, 85 (1965) [22, 61 (1966)].

[36] I. M. Lifshitz, ibid. 38, 1569 (1960) [11, 1130 (1960)].

[37] V. I. Makarov and V. G. Bar'yakhtar, ibid. 48, 1717 (1965) [21, 1151 (1965)].

[38] C. W. Chu, T. F. Smith, and W. E. Gardner, Phys. Rev. Lett. 20, 198 (1968).

[39] V. I. Mararov and I. Ya. Volynskiĭ, ZhETF Pis. Red. 4, 369 (1966) [JETP Lett. 4, 249 (1966)].

[39a] V. I. Makarov and I. Ya. Volynskiĭ, FMM 25, 1122 (1968).

[40] W. Gey, Phys. Rev. 153, 422 (1967).

[41] E. S. Fisher and H. J. McSkimin, Phys. Rev. 124, 67 (1961).

[42] T. F. Smith, Phys. Rev. Lett. 17, 386 (1966).

[43] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 1781 (1960) [Sov. Phys.-JETP 12, 1243 (1961)].

[44] B. Coqblin and C. F. Rotto, XI Intern. Conf. on Low Temp. Phys., vol. 2, Saint Andrews, 1968, p. 1052.

[45] T. Mamiya, T. Fukuroi, and S. Tamuna, J. Phys. Soc. Japan 20, 1559 (1965).

[46] W. Gey, Solid State Comm. 4, 403 (1966).

[47] W. Buchel and J. Wittig, Phys. Lett. 17, 187 (1965).

[48] F. P. Bundy, J. Chem. Phys. 41, 3809 (1964).

[49] J. C. Jamieson, Science 139, 762 (1963).

[50] H. D. Stromberg and D. R. Stephens, Phys. Chem. Sol. 25, 1015 (1964).

[51] N. B. Brandt and I. V. Berman, Proc. XI Int. Conf. on Low Temp. Phys. St. Andrews, Vol. 2, p. 973 (1968).

[52] E. M. Compy, Phys. Lett. 18, 228 (1965).

[53] T. R. McDonald, E. Gregory, G. S. Barberich, D. B. McWhan, T. H. Geballe, and G. W. Hull, Phys. Lett. 14, 16 (1965).

[54] J. Wittig and B. T. Matthias, Science 160, 994 (1968).

[55] B. T. Matthias and J. L. Olsen, Phys. Lett. 13, 202 (1964).

[56] J. Wittig, Phys. Rev. Lett. 15, 159 (1965).

[57] S. Minomura, B. Okai, H. Nagasaki, and S. Tanuma, Phys. Lett. 21, 272 (1966).

[58] D. B. McWhan and M. Marezio, J. Chem. Phys. 45, 2508 (1966).

[59] M. D. Banus and M. C. Lavine, J. Appl. Phys. 38, 2042 (1967).

[60] D. B. McWhan, G. W. Hull, Jr., T. R. McDonald, and E. Gregory, Science 147, 1411 (1965).

[61] E. G. Ponyatovskiĭ and A. G. Ryabinin, ZhETF Pis. Red. 6, 471 (1967) [JETP Lett. 6, 10 (1967)].

[62] J. Wittig, Science 155 (No. 3763), 685 (1967).

[63] D. N. Susan, D. B. Mario, and C. C. Harry, J. Appl. Phys. 35, 1361 (1964).

[64] S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids 23, 451 (1962).

[65] J. C. Jamieson, Science 139, 845 (1963).

[66] N. B. Brandt and N. I. Ginzburg, Zh. Eksp. Teor. Fiz. 51, 59 (1966) [Sov. Phys.-JETP 24, 40 (1967)].

[67] N. E. Alekseevskiĭ, N. V. Ageev, and V. F. Shamran, Bull. Acad. Sci. U.S.S.R. Inorganic Materials, II, 2156 (1966).

[68] W. Buckel, W. Gey, and J. Wittig, Phys. Lett. 11, 98 (1964).

[69] W. Gey and D. Kohnlein, Proc. XI Int. Conf. on Low Temp. Phys. St. Andrews, Vol. 2, p. 1049 (1968).

[70] H. Neubaer and E. Saur, Proc. XI Conf. on Low Temp. Phys. St. Andrews, Vol. 2, p. 977 (1968).

[71] C. C. Chao, H. L. Luo, and T. F. Smith, J. Phys. Chem. Solids 27, 1555 (1966).

[72] E. R. Pfeffer and J. F. Schooley, Phys. Rev. Lett. 19, 783 (1967).

[73] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[74] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[75] J. K. Hulm, C. K. Jones, D. W. Deis, H. A. Fairbank, and P. A. Lawles, Phys. Rev. 169, 388 (1968).

[76] B. T. Geĭlikman and V. Kresin, Fiz. Tverd. Tela 7, 3294 (1965) [Sov. Phys.-Solid State 7, 2659 (1966)].

[77] G. K. White, Cryogenics 3, 292 (1962).

[78] G. K. White, Phil. Mag. 7, 271 (1962).

[79] H. Rohrer, Phil. Mag. 4, 1207 (1959).

[80] K. Andres, Phys. Kondens, Matherie 2, 294 (1964).

[81] C. Grenier, Compt. rend. 240, 2302 (1955).

[82] D. Gross and J. L. Olsen, Cryogenics 1, 91 (1960).

[83] W. L. McMillan and J. M. Rowell, Phys. Rev. Lett. 14, 108 (1965).

[84] J. G. Adler, B. S. Chandrasekhar, W. L. Jacksen, and T. M. W. McMillan, Preprint, 1968.

[85] P. J. Scalapino and P. W. Anderson, Phys. Rev. 133A, 921 (1964).

[86] J. P. Franck and W. J. Keeler, Phys. Lett. 25A, 624 (1967).

[87] J. P. Franck and W. J. Keeler, Phys. Rev. Lett. 20, 370 (1968).

[88] J. P. Franck, W. J. Keeler, and T. M. Wu, Preprint, 1968.

[89] N. V. Zavaritskiĭ, E. S. Itskevich, and A. N. Voronovskiĭ, ZhETF Pis. Red. 7, 271 (1968) [JETP Lett. 7, 211 (1968)].

[90] M. Garfunkel and D. E. Mapother, Phys. Rev. 122, 459 (1961).

[91] J. L. Olsen and H. Rohrer, Helv. Phys. Acta 33, 873 (1960).

[92] B. B. Goodman, Compt. rend. 244, 2899 (1957).

[93] N. V. Zavaritskiĭ, Zh. Eksp. Teor. Fiz. 34, 1116 (1958) [Sov. Phys.-JETP 7, 773 (1958)].

[94] W. L. McMillan and J. M. Rowell, Phys. Rev. Lett. 17, 1259 (1966).

[95] V. G. Bar'yakhtar and V. I. Makarov, Zh. Eksp. Teor. Fiz. 49, 1934 (1965) [Sov. Phys.-JETP 22, 1320 (1966)].

[96] J. L. Olsen, K. Andres, and T. H. Geballe, Phys. Lett. 26A, 239 (1968).

[97] F. J. Morin and J. P. Maita, Phys. Rev. 29, 1115 (1963).

[98] B. R. Coles, Rev. Mod. Phys. 36, 139 (1964).

[99] V. L. Ginzburg, Zh. Eksp. Teor. Fiz. 44, 2104 (1963) [Sov. Phys.-JETP 17, 1415 (1963)].

[100] T. F. Smith and C. W. Chu, Phys. Rev. 159, 353 (1967).

[101] P. F. Chester and J. O. Jones, Phil. Mag. 44, 1281 (1953).

[102] J. Wittig, Phys. Rev. Lett. 21, 1250 (1968).

Translated by R. Berman