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EFFECT OF HIGH PRESSURE ON THE SUPERCONDUCTING PROPERTIES OF METALS

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AN investigation of the influence of hydrostatic compression on many physical properties of metals at low temperatures, for example on quantum oscillation effects, galvanomagnetic phenomena, resonance effects, polymorphic transformations and superconductivity, is of great interest. Such investigations make it possible to determine the character of the variation of the energy spectrum of metals when the parameters of their crystal lattice change. Since the energy spectrum is one of the main characteristics determining the electric and magnetic properties of metals, and since the foregoing methods of investigating the energy spectrum require as an essential condition the application of low temperatures, the problem of obtaining high and uniform pressures at low temperatures has been attracting attention for a long time.

The main difficulty in obtaining high and uniform pressures at low temperatures lies in the fact that the plasticity of all substances usually employed to transmit the pressure greatly decreases with decreasing temperature. On the other hand, the use of liquefied gases for this purpose is confined to the region of rather low pressures (for helium up to 140 atm at $T = 4.2^\circ\text{K}$), above which the gases solidify. However, recently it became possible to obtain sufficiently uniform pressures, reaching 30,000 atm, in the region of helium and infralow temperatures.

In connection with the development of experimental methods for obtaining high pressures at low temperatures, interest has grown even more in the investigation of the influence of high pressure on different physical properties of elements, primarily the superconducting properties of metals. This increased interest has been due to a considerable degree to the appearance of the microscopic theory of superconductivity.

In this review we shall discuss essentially papers on the investigation of superconducting properties of elements at high pressures, published during the last 3-4 years, and also some earlier investigations performed in recent years and not included in Swenson's review of 1960.*

*A translation of the review of C. Swenson^[1], edited by L. F. Vereshchagin, was published with some additions in 1963.

II. METHODS OF OBTAINING HIGH PRESSURES AT LOW TEMPERATURES

All the methods proposed to date for obtaining high pressures at low temperatures can be divided into two principal groups:

1. Methods of "conservation" or "freezing" of the pressure, in which the pressure is produced at high temperature, after which the installation is cooled to the temperature of liquid helium.

The advantage of this group of methods is, in particular, the possibility of investigating at low temperatures new crystalline modifications in the supercooled state in those cases when the magnitude of the phase-transition pressure increases strongly with decreasing temperature, and also when the rate of the polymorphic transformations at low temperatures is very small.

It is obvious that in this case the plasticity of the medium transmitting the compression does not play an appreciable role at low temperatures, since the pressure is produced at a temperature when the plasticity of the medium is high. If the initial pressure is sufficiently uniform, then if the medium is isotropic and the sample is isotropic, the "frozen" pressure also remains uniform, although its magnitude can change as a result of thermal contraction of the high-pressure chamber and of the sample. It must be borne in mind, however, that cooling of an anisotropic sample compressed by a low-plasticity isotropic medium can give rise to a unilateral deformation the magnitude of which is determined essentially by the degree of anisotropy of the sample.

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

The main advantage of this group of methods is the possibility of changing the pressure directly at the temperature of the experiment. The nonuniformity of the pressure is determined in this case by the conditions under which the compression was realized, or by the plasticity of the medium transmitting the pressure.

In both groups of methods, devices are used in which the pressure is transmitted directly to the sample, as well as devices in which an intermediate medium surrounding the sample is used for pressure transmission.

Let us stop to discuss briefly the main features and parameters of devices of various types.

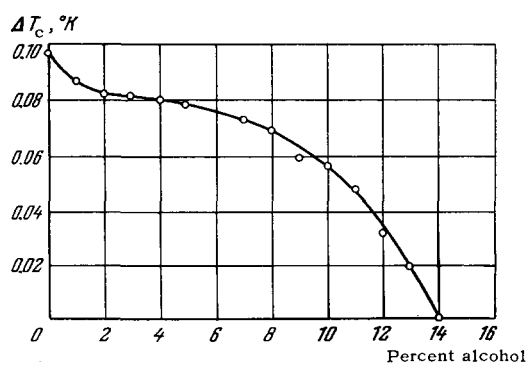


FIG. 1. Dependence of the pressure in a bomb of constant volume at liquid-helium temperature on the concentration of the raw alcohol in an alcohol-water solution. The ordinate represents the change in temperature of the superconducting transition of tin $\Delta T_c = (T_c)_{p=0} - T_c(p)$; $\Delta T_c = -4.5 \times 10^{-5} p$ (where p is in atmospheres), so that $\Delta T_c = 0.1^\circ\text{K}$ corresponds to $p \approx 2000$ atm.

1. Production of "Frozen" Pressures Using an Intermediate Medium

Among such methods one should mention first of all the ice bomb of Lazarev and Kan^[2] (see also^[1]), in which the pressure is produced by the anomalous change in the volume of water as it is frozen in a bomb of constant volume.

In investigations of samples of small dimensions (compared with the internal volume of the bomb) and of suitably chosen shape, this method makes it possible to obtain sufficiently uniform pressures. It must be kept in mind, however, that when an anisotropic sample surrounded by isotropic ice is cooled, nonuniform stresses may arise in the sample. In addition, during the process of freezing the water and heating the bomb, plastic deformation can arise as a result of possible displacements of the produced ice, which has very low plasticity. This is connected with the fact that the freezing of the water occurs in a non-equilibrium fashion, and the degree of compression in the regions that freeze earlier does not correspond to the pressure which is produced after complete freezing of the water. It is possible to obtain in this manner a fixed pressure the magnitude of which at the temperature of liquid helium is usually 1800–2000 atm. The use of aqueous solutions of raw alcohol in place of water^[3] increases the uniformity of the pressure, owing to the sharp increase in the plasticity of the medium, and also makes it possible to obtain intermediate pressures between 0 and 2000 atm (Fig. 1).

It must be noted that such a sharp increase in plasticity of the medium can lead, in the case of prolonged conservation of the pressure, to a continuous decrease of pressure in the bomb even at temperatures close to 100°K, as a result of the phase transition of "ice II" into "ice I" in the frozen solution of alcohol in water. We note that this effect, which is not observed in pure

ice, is stimulated by a small increase in temperature after cooling. Account must be taken of the influence of the rate and conditions of cooling on the magnitude of the pressure which is conserved at low temperatures. Reproducible results can apparently be obtained only when working with one and the same device in an identical cooling mode.

The influence of pressure near 1600 atm on the superconducting properties of cadmium was investigated at low temperatures for the first time in^[4] with the aid of an ice bomb.

Very uniform pressures, close to hydrostatic, were obtained in^[5]. The medium transmitting the pressure at "high" temperature was gaseous helium. The compression was effected at a temperature close to the boiling temperature of liquid hydrogen (20.4°K), after which the apparatus was cooled to helium temperatures. The initial pressure (approximately 3000 atm) was chosen in such a way that the drop in pressure in the bomb upon freezing of the helium could be neglected. Owing to the smallness of the thermal contraction in this temperature range, and also owing to the large plasticity of solid helium, the uniformity of the pressure remained practically unchanged as the apparatus was cooled.

If higher pressures are produced by this method, the result will apparently be an increase in the inhomogeneity of the pressure, owing to the change in density as the helium solidifies.

Considerably higher pressures can be obtained by using silver chloride as the medium. To obtain high pressures at low temperatures, silver chloride was first used in^[6] in an investigation of the dependence of the critical temperature on the pressure in tantalum at pressures up to 22,000 atm.

A sample of cylindrical form, approximately 5 mm in diameter, pressed in a pellet of silver chloride, was compressed between two pistons made of tungsten carbide in a matrix of beryllium bronze. The pressure was produced at room temperature with the aid of a hydraulic press, after which the device was cooled in a cryostat. The correction for the change of pressure upon cooling was determined by a tension gauge. The total error in the determination of the pressure did not exceed 10%.

Silver chloride was also used as a pressure-transmitting medium in investigations of the influence of pressure on the electric conductivity of bismuth.^[7,8] This procedure can be used successfully to investigate the influence of pressure on the critical currents of superconductors. The use of silver chloride unavoidably leads to small plastic deformation of the samples, and is convenient therefore only in investigations of superconducting properties of polycrystalline samples, when such a deformation is insignificant.

Very uniform pressures at low temperatures were obtained using a mixture of oil with dehydrated kero-

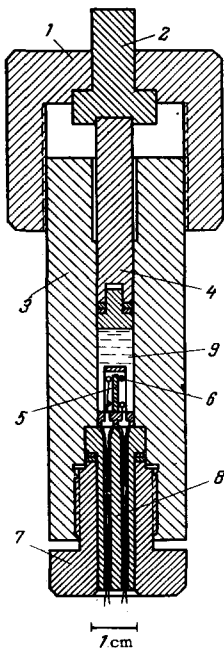


FIG. 2. High-pressure bomb. 1. Nut; 2 — rod transmitting the force from the press; 3 — housing of bomb; 4 — working piston with "mushroom" packing; 5 — investigated sample; 6 — sample holder; 7 — support nut of obturator; 8 — obturator; 9 — medium transmitting the pressure.

sene in approximately equal volumes.^[9] A high-pressure bomb using a kerosene-oil mixture is shown in Fig. 2. The pressure is produced in channel 9 at room temperature by means of a hydraulic press, and is fixed by the nut 1. The diameter of the working chamber is 8 mm, and the height at maximum pressure is approximately 20 mm, the outer diameter of the housing being 30 mm. In the obturator 8 are placed four conical electric leads with insulation made of organic glass.^[10] Sample 5 is mounted in holder 6 on obturator 8. All parts of the bomb were made of heat treated beryllium bronze. The bomb withstood at room temperature pressures up to 12,000 atm without plastic deformation. Upon cooling the bomb, the pressure decreased. The dependence of the "frozen" pressure in the bomb on the initial pressure is shown in Fig. 3. We see that a decrease in pressure upon cooling occurs only above 77°K; below this temperature, the pressure remains practically constant. The decrease in pressure resulting from the cooling is approximately 4000 atm.

The calibration shown in Fig. 3 is correct if the volume of the sample is small compared with the volume of the high-pressure chamber.

Recently oil-kerosene solutions were used at liquid-helium temperature to produce pressures up to 20,000 atm with sufficiently high degree of uniformity.^[8]

2. Production of "Frozen-in" Pressures Without the Use of a Transmitting Medium

The first investigation carried out by this method was reported in ^[11], where the pressure was produced by compressing at room temperature thin discs (approximately 50 μ thick) between two agate plungers,

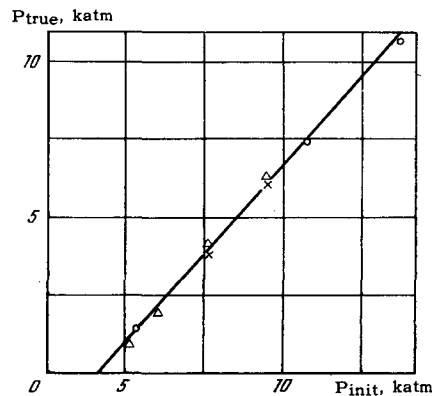


FIG. 3. Dependence of the pressure in the bomb at temperatures below 77°K on the pressure at room temperature. \times — 20.4°K; Δ — 77°K (beryllium-bronze bomb); o — 77°K (steel bomb):

followed by cooling of the apparatus to liquid-helium temperature. This method was used to investigate the effect of pressure on the temperature of the superconducting transitions of lead, tin, thallium, and to disclose the superconductivity of the crystalline modification of bismuth Bi III. In spite of the fact that the maximum pressure obtained with the aid of this method is approximately 45,000 atm, the pressure itself turned out to be quite nonuniform, varying practically from 0 on the periphery of the sample to a maximum value at the center. The great nonuniformity of the pressure greatly limits the possibility of employing this method, being apparently the main reason why it has not found extensive use.

This method was subsequently improved.^[12] Retaining the basic idea of the method, the authors have changed over to investigations of bulky cylindrical samples with diameter of approximately 5 mm and length 4 mm, compressed in a cylindrical channel of a matrix by two pistons. Liners of neoprene rubber, used as packing, were placed between the pistons and the sample. The transition of the metals to the superconducting state was manifest in the change of the mutual induction between coils and detected by a radio-engineering method. The pressure was determined at room temperature from the load on the pistons. The change in pressure upon cooling of the apparatus was corrected for with the aid of a calibrated tension gauge. The degree of uniformity of the pressure was sufficiently high, but the maximum attainable pressure did not exceed 10,000 atm.

Higher pressures with a higher degree of uniformity were attained in ^[13-15]. The pressure was produced with the aid of a multiplier, shown in Fig. 4. The cylindrical sample, with diameter of approximately 2.5–3 mm and length 3–4 mm, surrounded by a thin layer of graphite lubricant (approximately 50 μ), was compressed by means of a piston in the lower channel of a frame 2. The graphite lubricant was a layer of

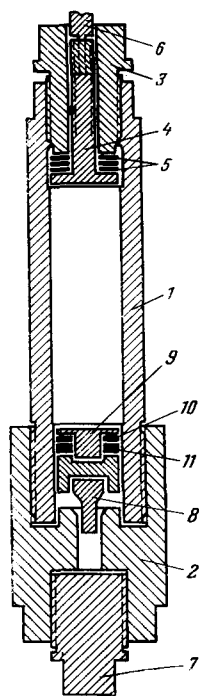


FIG. 4. Multiplier. 1, 2 – Housing; 3 – upper stopper; 4 – “mushroom”; 5 – gaskets; 6 – holders; 7 – lower stopper; 8 – piston; 9 – piston cap; 10, 11 – lead and copper linings.

thin cigaret paper, impregnated with pure graphite powder. All the parts of the multiplier were made of heat-treated beryllium bronze containing 3% beryllium. The internal walls of the channel of the frame 2 were packed by pre-compression at pressures on the order of 35,000–40,000 atm. The pressure of the upper channel of the multiplier was produced by freezing water^[2] or aqueous solutions of raw alcohol,^[3] having an anomalous coefficient of volume expansion upon freezing. The use of alcohol-water solutions makes it possible to obtain in the upper channel a prescribed pressure (ranging from 1 to 2,000 atm) and ensures the transmission of the compression through pistons 8 and 9 to the sample, owing to the sufficiently high plasticity which the alcohol solutions retained in the solid phase approximately down to -80 and -100°C .

At a multiplication coefficient of approximately 17, it is possible to obtain in the lower channel, with good reproducibility, a pressure up to 30,000 atm. The pressure was determined with the aid of a tin manometer placed alongside the sample. The superconducting transitions of the samples and of the manometer were registered by an induction method. The maximum value of the nonuniformity of the pressure, estimated from the width of the superconducting transition of the lead, did not exceed 2–3% (Fig. 5). This procedure was used to observe the superconductivity of the modification Bi II, and to investigate the superconducting properties of the modifications Bi II and Bi III.^[14–16]

The use of the multiplier has made it possible to develop a procedure for the investigation of the influence of high pressure on the superconducting properties of metals at low temperatures.^[17–19] A diagram

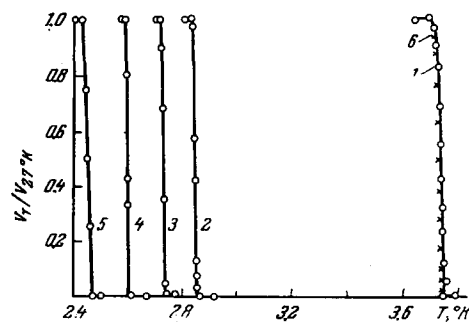


FIG. 5. Curves of superconducting transition of a tin manometer at different pressures. p (atmospheres): 1 – 0, 2 – 19,750; 3 – 22,000; 4 – 25,000; 5 – 28,400; 6 – pressure removed. The ordinates represent the relative change in the signal at the output of the radio apparatus.

of the apparatus is shown in Fig. 6. The multiplier 1 was connected with the aid of a cold duct 2, 3 mm in diameter and approximately 200 mm long, to a pellet of iron-ammonia alum 4. The multiplier was suspended on a stabrite wire 5 with 0.2 mm diameter inside a glass ampoule 6, connected with the aid of valve 13 to a carbon pump 14. The ampoule was insulated against radiation by means of a removable copper screen 16, to which measuring coils 17–18 (used to

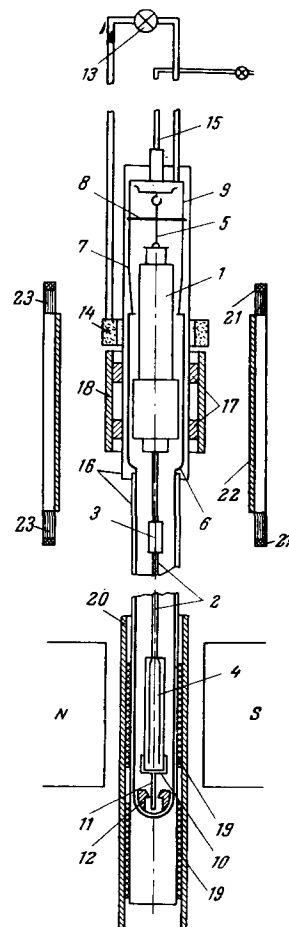


FIG. 6. Diagram of instrument for the investigation of superconducting properties of metals at high pressures at infralow temperatures. 1 – Multiplier; 2 – cold duct; 3 – connecting sleeve; 4 – salt pellet; 5 – stabrite suspension; 6 – 9 – ampoule with cover; 10, 11 – plexiglas cap with tube; 12 – diaphragm; 13 – valve of carbon pump; 14 – carbon pump; 15 – tube; 16 – copper screen; 17 – 20 – measuring coils; 21 – 23 – Helmholtz coils.

register the superconducting transition), as well as coils 19–20 (used to determine the temperature of the salt) were rigidly secured. The salt was heated from 0.08 to 0.6°K in a time 8–10 hours, making it possible to carry out the measurements at practically constant temperature. The temperature was determined from the value of the magnetic susceptibility of the salt by a ballistic method. Inasmuch as the pistons were made from cemented tungsten carbide VK-3 and acquired a weak constant ferromagnetic moment after demagnetization, the influence of the latter on the sample was reduced by placing between the piston and the sample, in the channel of the multiplier, and in a graphite lubricant, an insert made of brass or copper, 8–10 mm long. This method was used to investigate the influence of pressure up to 27,000 atm on the superconducting properties of cadmium, zirconium, and titanium.

3. Production of Pressures Directly at Low Temperatures Using an Intermediate Medium

Installations operating on this principle consist usually of a cylindrical high-pressure chamber located in a cryostat, and a mechanical system which transmits the force to the chamber from an external hydraulic press. The chamber is filled with liquefied gas through a capillary tube soldered into its upper part. When the pressure is produced, the piston moves downward, covers the opening, compresses the liquid, and solidifies it. As was shown in [20–23], the pressure-transmitting medium can be solid hydrogen or solid helium. The first experiment on the investigation of the influence of pressure on superconductivity, using solid hydrogen at pressures up to 5000 atm, was reported in [24,25]. A similar procedure was used in [26] to investigate the influence of pressures up to 10,000 atm on the superconducting properties of thallium, tin, indium, tantalum, and mercury. Data on the use of solid helium as a pressure-transmitting medium are found in [27], where attainment of a pressure of 20,000 atm was reported. However, all the investigations in these experiments were limited to measurements of the compressibility of solid gases.

In experiments using solidified hydrogen and helium, the pressure was usually calculated from the magnitude of the applied force and from the cross-section area of the high-pressure cylinder. The degree of uniformity of the resultant pressure depends to a considerable degree on the rate of compression and on the magnitude of the pressure. Unfortunately, there are no data at present on the possible use of these methods for investigations of the physical properties in the region of pressures above 10,000 atm.

Technical details regarding the use of solid hydrogen and helium as a transmitting medium are described in [1,28].

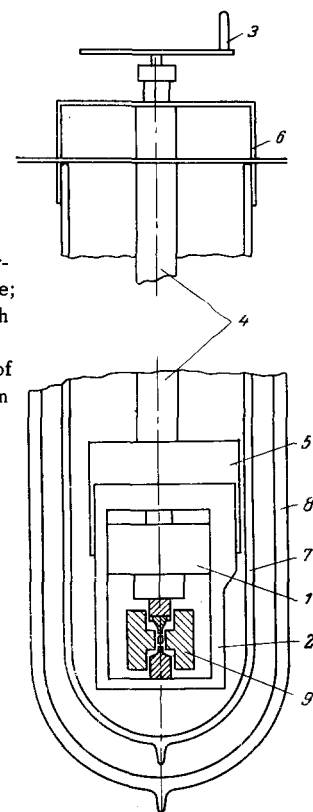


FIG. 7. Diagram of low temperature press. 1 – piston; 2 – frame; 3 – handle; 4 – stabrite tube with rod to transmit the rotation; 5 – reduction mechanism; 6 – cover of Dewar; 7, 8 – nitrogen and helium Dewars; 9 – holder with sample.

4. Production of Pressures Directly at Low Temperatures Without an Intermediate Medium

The first construction of apparatus intended for the investigation of the influence of plastic deformation on superconductivity and making it possible to produce the pressure directly at liquid-helium temperature was described in [29] (see also [30]). The apparatus comprised a low-temperature press, in which the pressure was produced with the aid of a reduction mechanism between two movable vertical steel planes. The maximum force in the press was approximately 4 tons. Later on a press of somewhat modified construction was used to obtain high quasi-hydrostatic pressures at low temperatures. [14,15] A diagram of the press is shown in Fig. 7. The pressure is produced in the press by moving piston 1 in frame 2 with the aid of reduction mechanism 5, controlled by handle 3, located on the cover 6 of the Dewar 7. The parts of the press were made of aluminum bronze, phosphor bronze, and heat treated beryllium bronze. The maximum force developed by the press was 2.5–3 tons. The lubricant for the press was powdered graphite. The pressure was produced in the internal channel of the matrix 9 with the aid of two pistons made of cemented tungsten carbide containing 3% cobalt. The matrix 9 was made of heat treated beryllium bronze. The internal channel of the matrix was self-set at a pressure of approximately 35,000 atm and then pol-

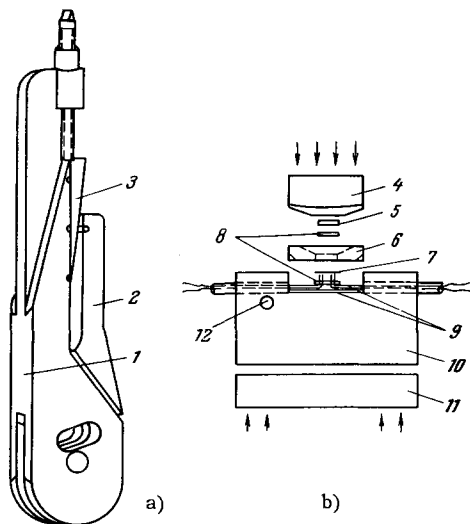


FIG. 8. a) Adjustable low-temperature clamp: 1 – housing; 2 – movable lever; 3 – wedge; b) high-pressure chamber: 4 – piston; 5 – bronze liner; 6 – sample holder; 7 – sample; 8 – upper and lower steatite washers; 9 – mica liners; 10, 11 – support liner; 12 – carbon thermometer.

ished. The sample investigated was cylindrical in form, 2.5–3 mm in diameter and 3–4 mm long; it was covered by a thin layer of graphite lubricant and placed in the center of the internal channel of the matrix. The pressure nonuniformity produced with such a method of compression was governed by the degree of deviation of the lubricant from ideal, which leads to the appearance of tangential components of pressure between the samples and the walls of the matrix channel. To determine the pressure, a tin sample is placed in the channel of the matrix, and the magnitude of the pressure is determined from the shift in the temperature of the superconducting transition of the tin.

In all the experiments in which the tin manometer was used, the pressure was determined in accordance with an arbitrary “tin” pressure scale. It was assumed that the formula for tin

$$T_c(p) = 3.733 - 4.95 \cdot 10^{-5} p + 3.9 \cdot 10^{-10} p^2, \quad (1)$$

obtained in [26] for pressures up to 10,000 atmospheres, holds true at pressures up to 30,000 atm. Some evidence in favor of the admissibility of such an extrapolation is the good agreement between the shift of T_c , determined by formula (1), and the experimental data [11] which unfortunately are not sufficiently accurate.

Another method of determining the pressure was to measure the deformation of the frame of the press 2 or of the matrix 9 (see Fig. 7) with the aid of tension pickups, calibrated at low temperatures against the value of the shift T_c for tin, and calibrated at high pressures against reference points of the phase transitions of cerium and bismuth.

The transition of the sample into the superconducting state [14, 15] was detected by a radio method [31] in-

volving the measurement of the mutual induction of two coils at a frequency of 20 cps.

Another low-temperature press construction is described in [32]. The apparatus was intended for the measurement of the electric resistivity of metals at pressures up to 35,000 atm at low temperatures. An over-all view of the instrument is shown in Fig. 8.

Samples of thickness 0.03, width 0.2, and length 2 mm were compressed between two steatite washers with the aid of a special device, the operation of which is clear from the figure. Displacement of the wedge makes it possible to change the force in a range up to 2000 kg directly at the temperature of the experiment. Details of the mounting of the sample are shown in Fig. 8b. The electrodes made of platinum strips 0.03–0.05 mm² in area were inserted through openings 0.15 mm in diameter in the lower steatite washer, and insulated with the aid of mica liners. The parts of the clamp were made of austenitic weakly-magnetic steel, while the parts of the high-pressure chamber were made of heat-treated beryllium bronze containing 2–4% beryllium. The beryllium bronze withstood a pressure up to 24,000 atm without noticeable plastic deformation at room temperature, and up to 35,000 atm at the temperature of liquid helium. The piston 4 was made of a hard alloy. The pressure was measured with the aid of tension gauges glued on the lever 2. The tension gauges were calibrated at low temperatures against the known pressure dependence of the temperature of the superconducting transition of indium. The accuracy with which the pressure was determined is, in the opinion of the authors, approximately 10% in the pressure region up to 10,000 atm, and about 20% at higher pressures, although an investigation of the dependence of the critical temperature of indium on the pressure points to a higher accuracy.

Inasmuch as the superconducting transition was detected by noting the change in the electric resistivity, the width of the superconducting-transition curve cannot be used to estimate the nonuniformity of the pressure.

To produce high pressure at low temperatures, apparatus was also used in which the pressure from a hydraulic compressor, located outside the cryostat, was transmitted to the low-temperature part of the apparatus with the aid of pole rods supporting a base plate, and a broad hollow cylinder [33] (see also [1, 28]). The construction of the press was such that a force up to 10 tons could be transmitted through the cryostat.

In comparing the methods for producing pressure directly at low temperatures with the methods of “conserving” the pressure, the following must be noted. The state of the sample compressed directly at low temperatures differs from the state of a sample which is at the same pressure produced by conservation methods. This difference is connected, on the one hand, with the decreased plasticity of the sample upon cooling and, on the other hand, with the change in the con-

Table I

Super-conductor	T_c , °K	H_0 , o	θ , °K	$\frac{\partial T_c}{\partial p} \cdot 10^5$, °K/atm	$\left(\frac{\partial H_c}{\partial p}\right)_{T=T_c} \cdot 10^3$, Oe/atm	$\left(\frac{\partial H_c}{\partial p}\right)_{T=0} \cdot 10^3$, Oe/atm	$\frac{\partial \ln(T_c/\theta)}{\partial \ln v}$	$\frac{1}{\theta} \left(\frac{\partial \theta}{\partial p}\right)_{p=0} \cdot 10^6$, atm ⁻¹	$\frac{1}{v} \frac{\partial v}{\partial p} \cdot 10^6$, atm ⁻¹	$\gamma \cdot 10^4$, cal/deg ² mole
Non-transition metals										
Al	1.19	99	418		-4.8±0.4	-3.0±0.4	20	3.55	1.34	2.59
Bi II	3.916	~320		-3.21 ¹⁶	-4.51 ¹⁶					
Bi III	7			~0 ¹⁶	0 ¹⁶					
Ga	1.09	51	240	-1.8±0.3			10.3			0.8-1.5
Ga II	6.38		200	-3.0 ³²						
In	3.407	283	109	-4.36±0.1	-6.8±0.3	-3.6±0.2	8.0	6.0	2.55	3.5-3.6
Pb	7.19	803	105	-4.5±0.5	-9.33±0.15	-7.9±0.21 ⁶⁹	5.3	6.15	2.37	7.1
Hg α	4.153	411	69	-3.6 ²⁶	-5.7±0.5	-7.2±0.3 ³⁷	5	8.8	4.0	3.75-4.5
Hg β	3.95	340	93	-4.4 ²⁶	-8.7±0.3	-7.0±0.3 ³⁷	7.5			
Tl	3.39	162	100	1.5±0.4	3.1±0.15	2.7±0.5	0	7.56	2.77	2.8-3.4
Sn	3.733	306	195	-4.4±0.3	-6.48±0.14	-5.0±1.0	9.1	4.0	1.87	3.45-3.95
Zn	0.91	53	235		-1.8±0.5	-1.4±0.2	12	3.4	1.7	1.36
Cd	0.54	28	188	-1.8±0.11 ⁷	-2.34±0.4 ⁷⁸	-1.0±0.11 ¹⁷	19	4.82	2.2	1.7
Transition metals										
La β	5.95	1600	142		-1.8±2.5	-5.5±0.5	6.7	2.81	3.51	15.2 ⁸²
Nb	9.22	1944	252		-1.2±0.3	-1.2±0.16 ⁷	1.5			19.6 ⁷⁹
Rb	1.70	201	417	-0.17±0.09	0.4±0.2		5.8			6.0 ⁷⁹
Ru	0.49	66	400		0.8±0.4		-16			7.6 ⁷⁹
Ta	4.46	830	255	-0.26	0.9±0.3 ⁸⁶	1.05±0.3 ⁸⁶	3	0.865	0.48	12.2 ⁷⁹
Th	1.33	—	142	-1.7±0.2			8.3	1.82	1.82	7.1 ⁸¹
Ti	0.40	100	429	0.55 ¹⁹	1.4* ¹⁹				1.08	8 ⁸⁰
V	5.30	1310	400		2.0±0.2	1.3±0.16 ⁷	-0.6	0.79	0.88	22.3 ⁸⁰
Zr	0.56	47	270	0.9; 1.4** ¹⁸	2.6; 2.9** ¹⁸			1.09	1.04	6.9 ⁷⁹
Mo	0.95		425	0.1±0.1			4	0.36	0.36	5.0 ⁷⁹

*Values determined in the region of high pressures (see Fig. 28).

**Values are presented for non-annealed and annealed samples, determined in the region of high pressures (see Fig. 27).

ditions on the boundary of the sample and of the high-pressure chamber. In practice this causes at pressures above ~15,000 atm the uniformity of the pressure to be much higher in the "conservation" method than the uniformity of the pressure obtained at low temperatures.

III. EFFECT OF PRESSURE ON THE PROPERTIES OF SUPERCONDUCTORS

In most work devoted to the influence of pressure on superconductivity published to date, no appreciable relative changes in temperature of the superconducting transition under the influence of pressure were attained. The purpose of the greater part of the investigations was principally to determine the sign and the magnitude of the derivatives $\partial T_c/\partial p$ and $\partial H_c/\partial p$ (T_c — critical temperature, H_c — critical field) in the region of low pressures. The parameters obtained in these investigations for pure metals are listed in Table I, while analogous data for alloys are given in Table II.*

*The values of T_c and H_0 were taken from [77]. The values of θ , $(\partial T_c/\partial p)_{T_c}$, $\partial H_c/\partial p$, and $\partial \ln(T_c/\theta)/\partial \ln v$, in the case when there is no reference, have been taken from the reviews [42, 56, 71]. The derivatives $\partial \theta/\partial p$ were calculated by the Gruneisen formula (3). The values of γ for nontransition metals were borrowed from [80], and the values of the compressibilities $(1/v)(dv/dp)$ were taken from [66].

A characteristic feature of the data presented is that the temperature of the superconducting transition decreases in most elements upon compression. An increase in the critical temperature is observed in zirconium, titanium, and a small number of binary alloys: Bi_2K , Bi_4Rh , Bi_3Ni , and $\text{Nb}_{75}\text{Zr}_{25}$, and also for thallium in the initial section of the $T_c(p)$ curve.

Particular interest is attached at the present time to investigations of the functional dependence of the critical temperature on the pressure, to which principal attention is paid in the present review.

Such data were obtained for tin, indium, thallium, cadmium, tantalum, aluminum, zirconium, titanium, α and β mercury, and a few alloys.

Table II

Alloy	T_c , °K	$\frac{\partial T_c}{\partial p} \cdot 10^5$, °K/atm	$\gamma \times 10^{-4}$ cal-deg ⁻² mole ⁻¹
Bi_2K	3.58	5.1 ³¹	
Au_2Bi	1.75	-3 ³¹	
BiLi	2.47	-3.5 ³¹	
Bi_3Ni	4.06	5.4 ³¹	
Bi_4Rh	2.9; 3.4	2.7 ³¹	
Nb_3Sn	18.3	-14 ⁴⁴	150 ⁷³
$\text{Nb}_{75}\text{Zr}_{25}$	11.1	2.2 ⁴³	~30 ⁷³
V_3Ga	14.6	-2.4 ⁴⁴	244 ⁷³
V_3Si	14.6	-2.1 ⁴⁴	186 ⁷³
InSb II	1.88	-0.01 ⁵³	
$\alpha\text{-Bi}_2\text{Pd}$	1.70	-2.5 ⁷⁶	
$\beta\text{-Bi}_2\text{Pd}$	4.25	-5.6 ⁷⁶	

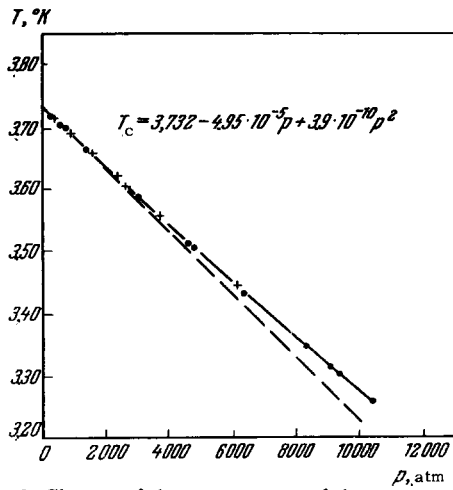


FIG. 9. Change of the temperature of the superconducting transition of tin upon compression. The solid curve is a plot of formula (1), while the dashed curve represents only its first linear term.

Tin and Indium

The first investigation in which the nonlinear character of the dependence of the critical temperature of tin on the pressure was observed was [11]. However, owing to the large nonuniformity of the resultant pressure and to inaccuracy in the determination of the magnitudes of the pressure, these results are qualitative in character. The most exact data for tin in the pressure region up to 10,000 atm, obtained in [26], are given in Fig. 9. As indicated there, extrapolation of curve 1 in accordance with formula (1) in the region of large pressures is in satisfactory agreement with the results of [11]. Analogous data for indium are given in Fig. 10. Measurements of the critical fields in compressed samples of tin are limited in [12] to a small temperature interval (3.73–2.6°K), as a result of which these data cannot be used to determine the value

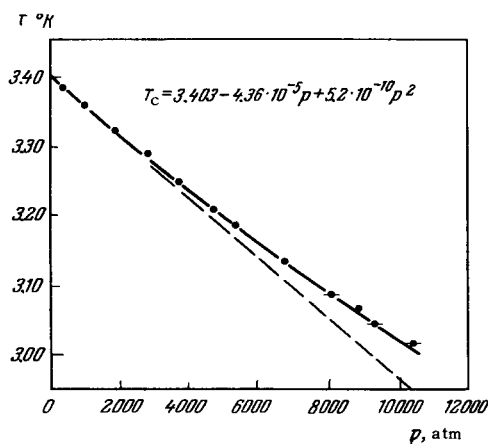


FIG. 10. Change of the temperature of the superconducting transition of indium upon compression. The solid curve is a plot of the formula given in the figure, while the dashed curve is a plot of only the first linear term.

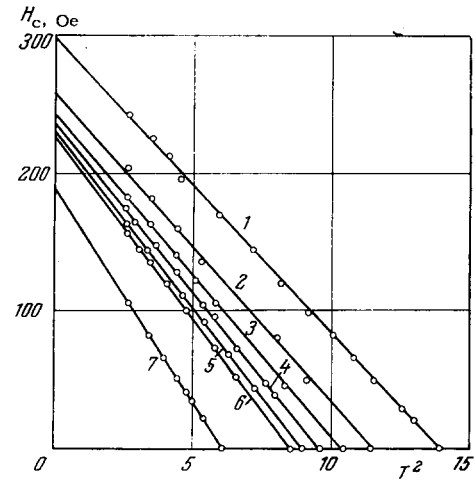


FIG. 11. Curves of critical fields for tin at different pressures. p (atmospheres); 1 - 0; 2 - 7850; 3 - 11,400; 4 - 14,350; 5 - 16,100; 6 - 17,200; 7 - 27,500.

of H_0 (critical field H_C at $T = 0$) with a sufficient degree of accuracy. Investigations of the curves of the critical field of tin and indium in a wider temperature and pressure interval were made in [34]. Figure 11 and 12 show the plots of the critical fields for different samples of tin and indium at various pressures, plotted in coordinates H_C and T^2 . The nearly linear character of this dependence enables us to determine in first approximation the pressure dependence of the critical fields H_0 .

The dependence of the critical field on the pressure for tin and indium is shown in Figs. 13 and 14. It must be noted that in the region of low pressures one observes for tin [35] an irregular $T_C(p)$ dependence (Fig. 15), which can explain the discrepancies in the values of $\partial T_C / \partial p$ obtained by different authors for

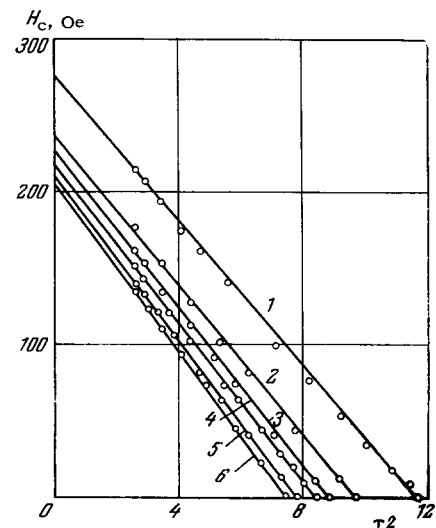


FIG. 12. Curves of critical fields for indium at different pressures. p (atmospheres); 1 - 0; 2 - 7850; 3 - 11,400; 4 - 14,350; 5 - 16,100; 6 - 17,200.

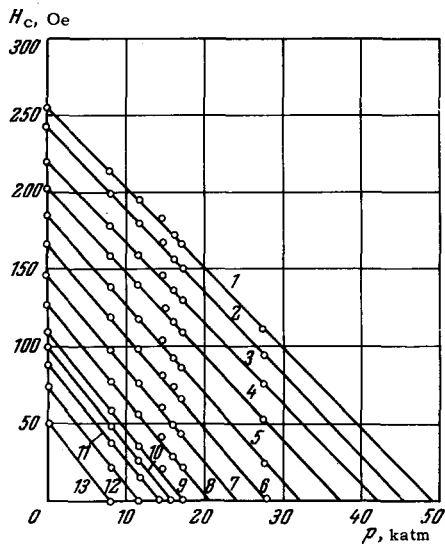


FIG. 13. Dependence of the critical field of tin on the pressure.

1 — 1.5° K; 2 — 1.7° K; 3 — 1.9° K; 4 — 2.1° K; 5 — 2.3° K;
 6 — 2.46° K; 7 — 2.65° K; 8 — 2.8° K; 9 — 2.95° K;
 10 — 3.01° K; 11 — 3.1° K; 12 — 3.22° K; 13 — 3.38° K.

different pressures. Inasmuch as the anomaly in the $T_C(p)$ dependence for tin is not the consequence of a polymorphic transformation, it possibly reflects changes which occur in the energy spectrum of tin upon compression.

Tantalum

The dependence of the critical temperature of tantalum on the pressure was investigated in the region of pressures up to 22,000 atm^[6]. The measurements were made with a sample made of tantalum 99.9% pure with a critical temperature 4.410°K. The decrease in T_C with pressure was linear, with $\partial T_C / \partial p = -(2.4 \pm 0.5) \times 10^{-6}$ °K/atm. The value of the irreversible shift of T_C , which is apparently connected with the plastic deformation of the sample, was about 0.007°K. More accurate measurements in the range

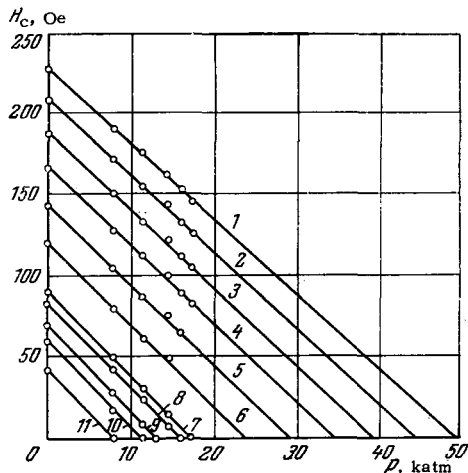


FIG. 14. Dependence of the critical field of indium on the pressure.

1 — 1.5° K; 2 — 1.7° K; 3 — 1.9° K; 4 — 2.1° K; 5 — 2.3° K;
 6 — 2.5° K; 7 — 2.74° K; 8 — 2.79° K; 9 — 2.9° K; 10 — 2.96° K;
 11 — 3.1° K.

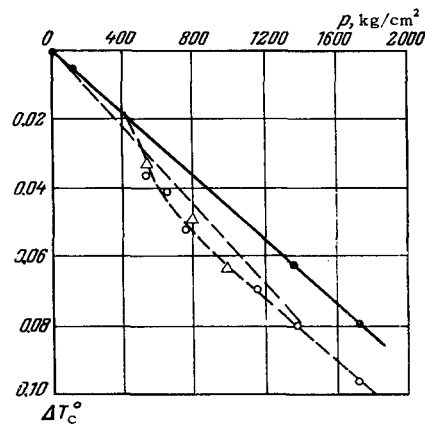


FIG. 15. Dependence of ΔT_C on p for indium (solid curve) and tin (dashed curve) Δ and O — different samples of tin.

of pressures up to 10,000 atm were reported in^[26]. In spite of the fact that the investigated tantalum was of higher purity (99.98%, $T_C = 4.384^\circ\text{K}$), and the measurements were made by a different method, the data obtained were in splendid agreement with the results of^[6]. The measurements were repeated somewhat later by the same method using a sample of tantalum of very high purity, prepared by electronic melting in a vacuum exceeding 10^{-9} mm Hg.^[36] The temperature of the superconducting transition of the tantalum sample was 4.482°K. The pressure dependence of the critical temperature is shown in Fig. 16. The value of $\partial T_C / \partial p$ as obtained in^[26,36] is $-(2.6 \pm 0.1) \times 10^{-6}$ °K/atm. All the investigations point to the independence of $\partial T_C / \partial p$ in tantalum of the degree of purity of the samples. In^[36] there was also investigated the influence of a pressure up to 2000 atm on the curves of the critical fields of tantalum. The temperature dependence of $\partial H_C / \partial p$ in this region of pressures, for different tantalum samples, is shown in Fig. 17.

Mercury

The dependence of the temperature of the superconducting transition on the pressure for two modifica-

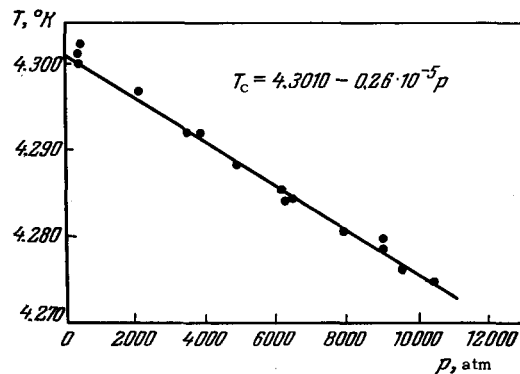


FIG. 16. Dependence of the temperature of the superconducting transition on the pressure for a tantalum sample annealed at 2300°C.

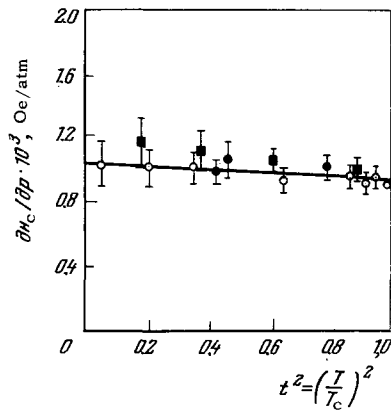


FIG. 17. Dependence of $\partial T_c / \partial p$ on the reduced temperature for different tantalum samples. O, ■, ● – different tantalum samples.

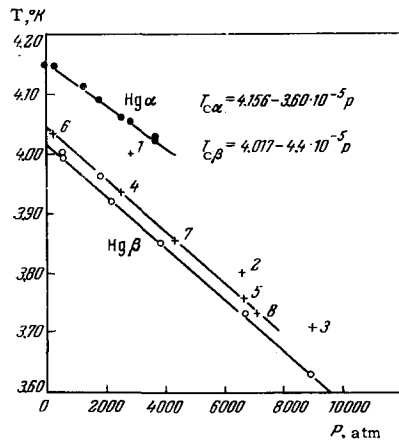


FIG. 18. Dependence of the critical temperature on the pressure for two modifications of mercury. ● – Hg α ; + and ○ – two samples of Hg β .

tions of mercury was investigated in [26]. This dependence is shown in Fig. 18.

The effect of pressure on the critical field of the modifications of mercury in the range of pressures up to 3000 atm was investigated in [37]. Samples of β mercury were obtained at 77°K by extrusion through an opening 0.4 mm in diameter at a pressure of 7000

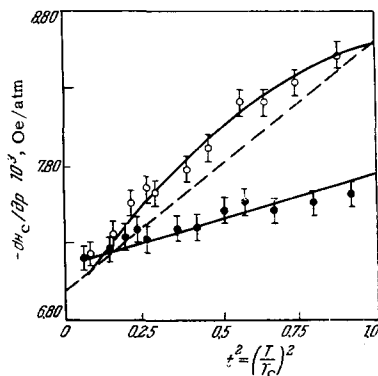


FIG. 19. Dependence of $\partial T_c / \partial p$ on the reduced temperature for the α and β modifications of mercury.

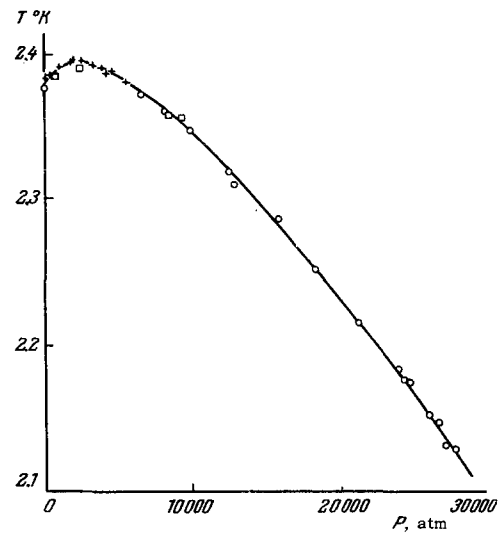


FIG. 20. Dependence of the temperature of the superconducting transition on the pressure according to data by various authors. Data of: ● – [26]; ○ – [34]; □ – [42].

atm. The temperature dependence for the α and β modifications of mercury is shown in Fig. 19.

Thallium

Thallium displays an unusual dependence of the critical temperature on the pressure. The critical temperature of thallium increases at low pressures, passes through a maximum, and then decreases. The maximum increase in T_c amounts to 0.8%. Data by different workers who measured the change of the superconducting-transition temperature of thallium under the influence of pressure are shown in Fig. 20. At pressures exceeding 2000 atm, the critical temperature decreases, with $\partial T_c / \partial p$ increasing with rising pressure. In the range of pressures from 20,000 to 28,000 atm, the value of $\partial T_c / \partial p$ of thallium is -1.4×10^{-5} °K/atm. It was observed recently that the $T_c(p)$ dependence of thallium has an irregular character [38] in the pressure range up to 2000 atm (Fig. 21), and that small admixtures of mercury strongly influence the magnitude and the sign of $\partial T_c / \partial p$. [39] It was observed in [40] and [41] that the change in length of single-crystal thallium during the superconducting transition has different signs in directions parallel and perpendicular to the hexagonal axis. Inasmuch as the

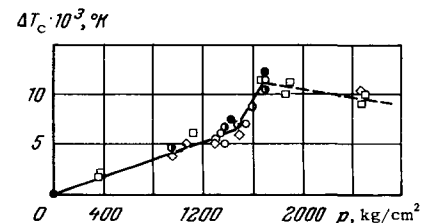


FIG. 21. Dependence of the shift of the superconducting-transition temperature on the pressure for thallium. Data of: □ – [26]; ◇ – [42]; ○, ● – [38].

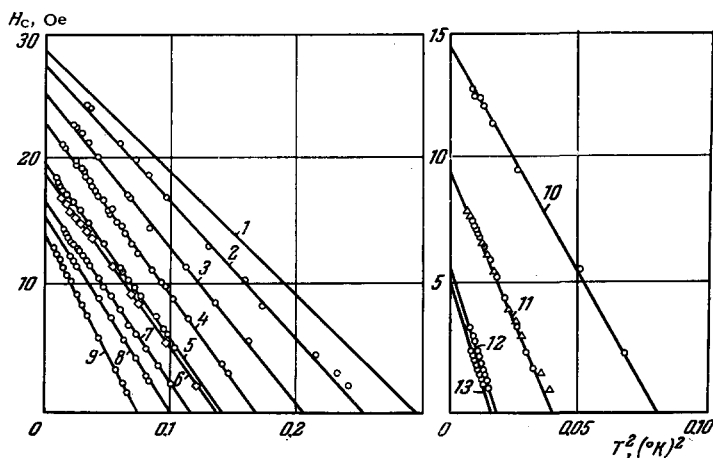


FIG. 22. Dependence of critical field of cadmium on the temperature. Curves: 1 - $p = 1$ atm, 2 - $p = 1500$ atm, 3 - $p = 3700$ atm, 4 - $p = 6600$ atm, 5 - $p = 9000$ atm, 6 - $p = 9340$ atm, 7 - $p = 12\ 050$ atm, 8 - $p = 13\ 400$ atm, 9 - $p = 15\ 300$ atm, 10 - $p = 14\ 800$ atm, 11 \circ - $p = 20\ 800$ atm, Δ - $p = 20\ 900$ atm, 12 - $p = 25\ 800$ atm, 13 - $p = 26\ 400$ atm.

sign of $\partial T_C / \partial p$ is determined by the sign of $\Delta L / L$, it was suggested^[1] that the occurrence of a maximum on the $T_C(p)$ curve of thallium is the consequence of the difference in the signs of the shift of T_C under unilateral compression in different crystallographic directions. To check this assumption, it would be of interest to determine the sign of $\Delta L / L$ in the superconducting transition of thallium alloys. If this assumption is valid, then the change in the magnitude and sign of $\Delta L / L$ in the superconducting transition of thallium alloys should correlate with the character and with the change of the critical temperature with pressure.

The dependence of H_C on the temperature in cadmium is well described, in the entire range of pressures, by the formula

$$H_c = H_0 \left[1 - \left(\frac{T}{T_C} \right)^2 \right],$$

which makes it possible to determine T_C and H_0 in the first approximation. The dependence of the superconducting-transition temperature on the pressure is shown in Fig. 23. This is not a linear dependence. The value of $\partial T_C / \partial p$ decreases with increasing pressure, from $-1.8 \times 10^{-5} \text{ }^\circ\text{K/atm}$ at $p = 0$ to $-1.25 \times 10^{-5} \text{ }^\circ\text{K/atm}$ in the range of pressures near 22,000 atm. At the maximum attained pressure of 26,400 atm, the superconducting-transition temperature decreases by a factor of 4.4 (from a value 0.543°K), and becomes equal to 0.124°K .

Figure 24 shows a plot of the critical field against pressure for different temperatures. Curve 1, ob-

Cadmium

Of special interest are the researches in the region of infralow temperatures, which make it possible to obtain large relative changes of T_C by using readily attainable pressures.

The influence of pressure on the critical field and on the temperature of the superconducting transition of spectrally pure cadmium was investigated in^[17] in the range of pressures up to 27,000 atm at temperatures $0.08-0.5^\circ\text{K}$. Figure 22 shows the dependence of the critical field on the square of the temperature for different cadmium samples at different pressures.

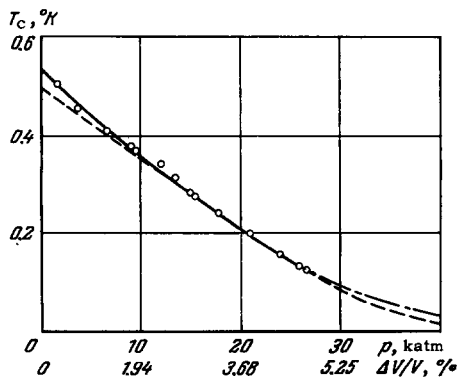


FIG. 23. Dependence of the temperature of the superconducting transition of cadmium on the pressure and on the relative change in volume.

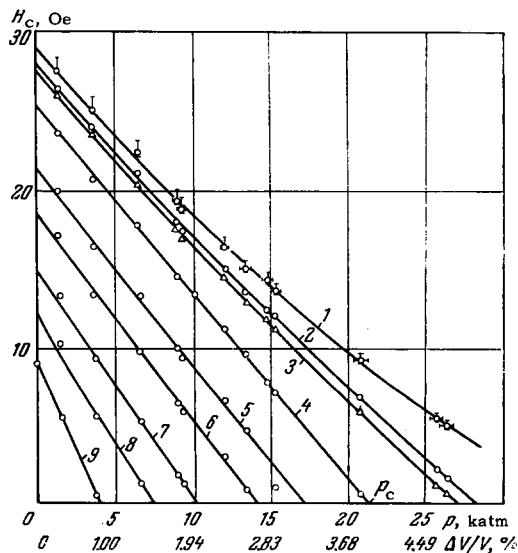


FIG. 24. Dependence of the critical field of cadmium on the pressure and on the relative change in volume. Curves: 1 - $T = 0^\circ\text{K}$; 2 - $T = 0.1^\circ\text{K}$; 3 - $T = 0.14^\circ\text{K}$; 4 - $T = 0.19^\circ\text{K}$; 5 - $T = 0.265^\circ\text{K}$; 6 - $T = 0.31^\circ\text{K}$; 7 - $T = 0.36^\circ\text{K}$; 8 - $T = 0.4^\circ\text{K}$; 9 - $T = 0.45^\circ\text{K}$.

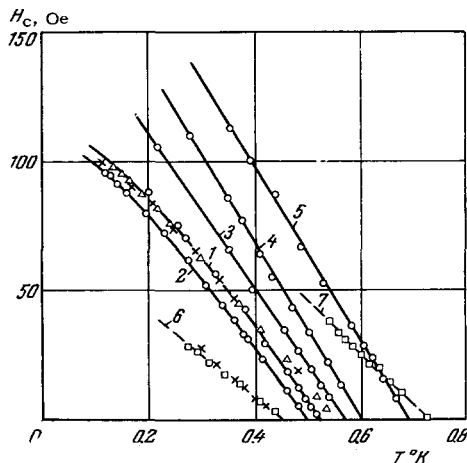


FIG. 25. Curves of critical field of zirconium in unannealed (continuous curves) and annealed samples (dashed). Curve 1 – without pressure; \circ – initial sample, \times – after fifth and Δ – after eighth cycle of compression (sample No. 1); curve 2 – $p = 3700$ atm (sample No. 2); curves: 3 – $p = 8800$ atm (sample No. 2); 4 – $p = 16,300$ atm (sample No. 3); 5 – $p = 23,600$ atm (sample No. 1); 6 – without pressure; \square – initial samples; \times – after second cycle of compression; curve 7 – $p = 18,000$ atm.

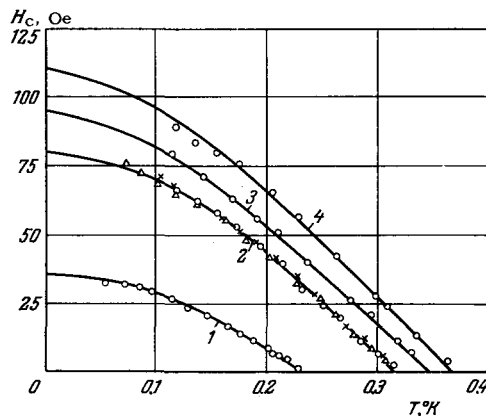
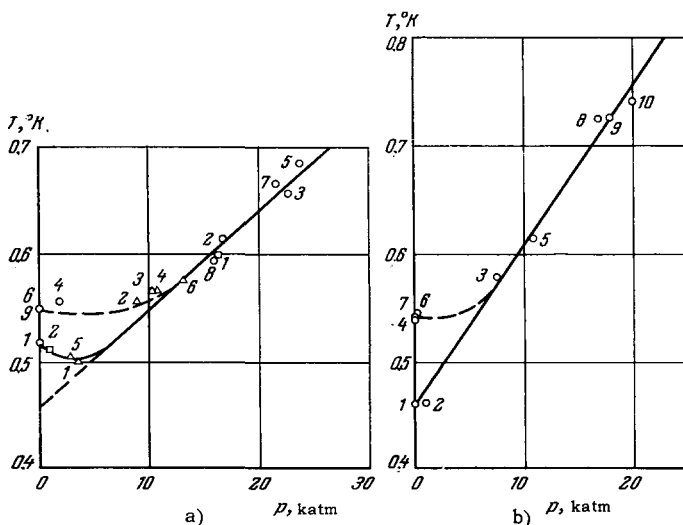


FIG. 26. Curves of critical fields of titanium. Curves: 1 – $p = 1$ atm; 2 – \circ – $p = 15,500$ atm, \times – 900 atm, Δ – 9200 atm; 3 – $p = 18,400$ atm; 4 – $p = 24,400$ atm.



tained by extrapolation, shows the pressure dependence of the critical field H_0 . With decreasing temperature, the nonlinearity in the dependence $H_C(p)$ increases. At 0.45°K the average value of $\partial H_C/\partial p$ in the interval from 0 to 4000 atm amounts to $\approx 2.2 \times 10^{-3}$ Oe/atm. At $T = 0^\circ\text{K}$ and at low pressures $\partial H_C/\partial p \approx 1 \times 10^{-3}$ Oe/atm, whereas in the region of pressures of 22,000 atm $\partial H_C/\partial p \approx 0.8 \times 10^{-3}$ Oe/atm.

Aluminum

Most recently a report was published on an investigation of the influence of pressures up to 20,000 atm on the superconducting-transition temperature of aluminum.^[42] The critical temperature of aluminum decreased upon compression from a value $T_C = 1.19^\circ\text{K}$ to a value $T_C = 0.71^\circ\text{K}$ at 20,000 atm. The derivative $\partial T_C/\partial p$ decreased with increasing pressure.

Zirconium and Titanium

Unexpected results were obtained in the investigation of zirconium and titanium^[18,19]. The samples investigated were made of zirconium iodide and titanium of purity 99.99%.

Figures 25 and 26 show some curves of critical fields for the investigated samples of zirconium and titanium. In both cases hydrostatic compression causes a considerable increase in T_C , accompanied by an increase in $(\partial H_C/\partial T)T_C$. The increase in $\partial H_C/\partial T$ remains approximately constant for different compression cycles and on the average amounts to 20–25% for both annealed and unannealed samples as the pressure changes from 0 to 25,000 atm. The dependence of the temperature of the superconducting transition on the pressure for annealed and unannealed samples of zirconium is shown in Fig. 27.

The critical temperature of unannealed zirconium samples first decreases, passes through a minimum at approximately 3000 atm, and then increases. This variation of T_C is satisfactorily reproducible in the region of pressures up to 10,000 atm for repeated

FIG. 27. Dependence of the superconducting-transition temperature on the pressure. a) For annealed samples of zirconium (\circ – sample No. 1; Δ – sample No. 2; \square – sample No. 3); b) for annealed samples of zirconium. The numbers at the points denote the sequence of the compression cycles.

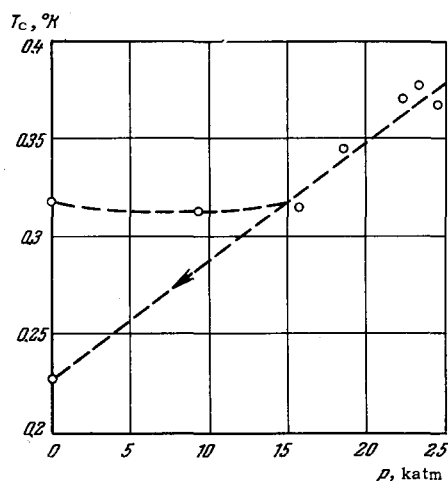


FIG. 28. Dependence of the superconducting-transition temperature of titanium on the pressure.

cycles of compression. When the pressure exceeds 10–12 thousand atm, hysteresis sets in, in which the critical temperature increases after removal of pressure from 0.52 to 0.55°K. In annealed samples, a stronger increase of T_C upon compression is observed. The dependence of T_C on the pressure is close to linear in the entire region of investigated pressures. After removal of the pressure, T_C rises irreversibly from a value 0.46°K (for the annealed sample) to 0.55°K (the value of T_C for a cold-hardened unannealed sample). Extrapolation of the linear section on the $T_C(p)$ curve of Fig. 27a to zero pressure yields a value of T_C which practically coincides with that of unannealed samples. Apparently the nonlinear character of the dependence of $T_C(p)$ of unannealed samples of zirconium and the appearance of hysteresis in annealed samples is a consequence of the quasi-hydrostatic nature of the pressures, which leads to plastic deformation of the samples. It is to be expected that purely hydrostatic pressure in the region up to 25,000 atm should cause a nearly-linear increase in the critical temperature. An analogous dependence $T_C(p)$ holds for titanium^[19] (Fig. 28).

Thus, a characteristic feature of zirconium and titanium, unlike the superconducting elements considered above, is the appreciable increase in critical temperature T_C under the influence of pressure.

Alloys

Data were published recently on the pressure dependence of the superconducting-transition temperature for Nb_3Sn , $Nb_{75}Zr_{25}^{43}$, V_3Ga , and V_3Si ⁴⁴. In the case of Nb_3Sn , in the pressure region up to 11,000 atm, a quadratic dependence was observed for the quantity $\Delta T_C = T_C(p) - T_C(0)$ on the pressure. In the pressure interval 2500–11,000 atm, this dependence is satisfactorily described by the formula $\Delta T_C = -(0.0019p^2 + 0.02)^\circ K$, where p is the pressure in thousands of atmospheres.

It must be noted that in the region of low pressures, the value obtained for $\partial T_C/\partial p$ is lower than the value $\partial T_C/\partial p = -2.6 \times 10^{-5}^\circ K/atm$, obtained for Nb_3Sn in [45], and approximately one-tenth as large as the value $\partial T_C/\partial p$ determined for Nb_3Sn in [44]. In [44] a linear dependence of T_C on the pressure was observed in the pressure interval from 0 to 1750 atm, with $\partial T_C/\partial p = 14 \times 10^{-5}^\circ K/atm$. The reason for such a large discrepancy is still unclear. We can only assume that it is connected with the character of the investigated samples.

In the $Nb_{75}Zr_{25}$ alloy at pressures up to 4000 atm, an increase in the critical temperature was observed, the magnitude of which varied strongly during different compression cycles. In the alloys V_3Ga and V_3Si , the temperature of the superconducting transition decreased linearly with increasing pressure up to 1750 atm.

Superconductivity of Crystalline Modifications

An investigation of the superconductivity of crystalline modifications of different substances, arising at high pressures, is of great interest. The change in the superconducting properties of superconductors under polymorphic transformations, and also the occurrence of superconductivity in crystalline modifications of substances which do not under ordinary conditions (at $p = 0$) exhibit superconductivity are very important for the explanation of the causes of superconducting properties. The production of superconducting modifications is also one of the ways of investigating new superconductors. In spite of the fact that a large number of elements and alloys have one or several new crystalline modifications, which are stable at high pressures, only a small number of these was investigated in the pressure region up to $\sim 40,000$ atm.

Superconductivity was observed in crystalline modifications of bismuth Bi II and Bi III, the crystalline modification of gallium Ga II, and the crystalline modification of the alloy InSb.

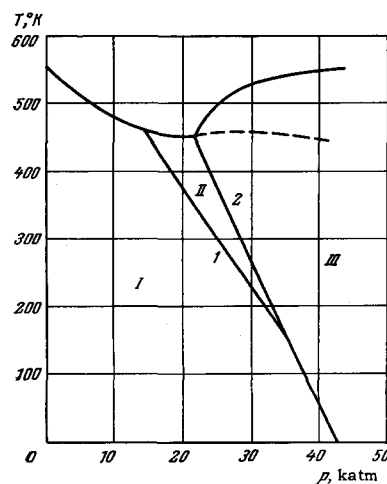


FIG. 29. Phase diagram of bismuth.

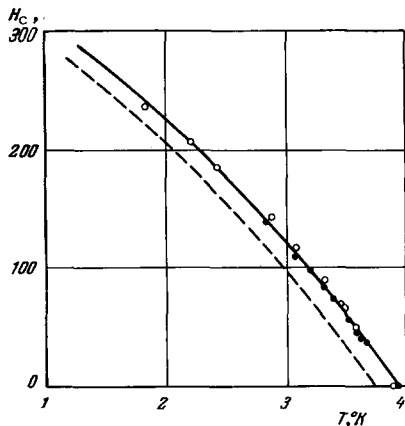


FIG. 30. Critical fields of Bi II. \circ — $p = 26,400$ atm; \bullet — experiment without tin manometer. The dashed line shows the critical-field curve for tin.

a) **Bismuth modifications Bi II and Bi III.** It follows from the phase diagram of bismuth (Fig. 29) that in the pressure region up to 40,000 atm, there exist three bismuth modifications—Bi I, Bi II, and Bi III. The region of existence of the modification Bi II, bounded by the curves 1 and 2 which cross at a temperature of approximately 100°K, is designated on the diagram by the wedge^[46,47].

Bi I is a poor metal and does not display superconductivity down to $\sim 0.005^\circ\text{K}$.^[48] As shown in^[14,15], the modification Bi II can be obtained at the temperatures of liquid helium in the supercooled form. It was established that Bi II is a superconductor with a superconducting-transition temperature 3.916°K at 25,000 atm. The value of $\partial T_c/\partial p$ in the pressure region from 25,000 to 26,000 atm is -3.2×10^{-5} deg/atm. The curves for the critical fields of Bi II are shown in Fig. 30. Bi II is a “soft” superconductor with a value $\partial H_c/\partial T$ very close to the value of $\partial H_c/\partial T$ for tin.^[16]

The superconductivity of the modification Bi III, the superconductivity of which was reported in^[11], was investigated in detail in^[14-16]. According to the data

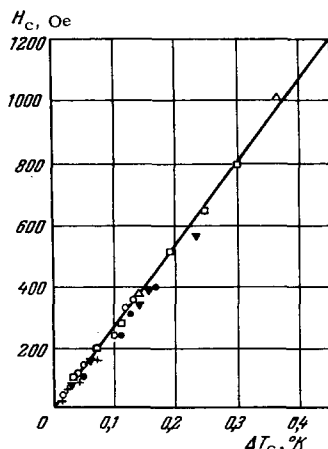


FIG. 31. Critical fields of Bi III at the following pressures: \circ , Δ , \square — 30,000 atm; ∇ , \bullet — 28,000 atm, $+$ — 30,500 atm.

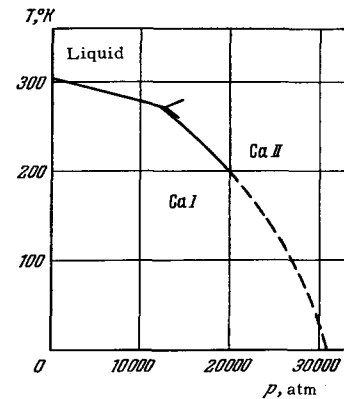


FIG. 32. Phase diagram of gallium.

of^[16], Bi III is a “hard” superconductor with a superconducting-transition temperature $\sim 7^\circ\text{K}$. The value of the critical field of Bi III near T_c is illustrated in Fig. 31. The value of $(\partial H_c/\partial T)_{T_c}$ is ~ 2600 Oe/deg. Thus, Bi III is one of the hardest superconducting elements. It must be noted that $(\partial H_c/\partial p)_{T_c}$, like $\partial T_c/\partial p$, is practically independent of the pressure in the region 28,000–30,500 atm.

The abrupt character of the superconducting transitions in Bi II and Bi III offers evidence of the homogeneous structure of the samples.

b) **The modification Ga II.** Superconductivity was recently discovered in the crystalline modification of gallium Ga II^[32], stable at a temperature 0°C at pressures above 13,000 atm (Fig. 32). The modification Ga I is a superconductor with a superconducting-transition temperature 1.07°K. The critical temperature of the modification Ga II at a pressure near 35,000 atm is 6.38°K. The average value of $\partial T_c/\partial p$ of Ga II amounts to -3×10^{-5} °K/atm. The Debye temperature of Ga II, estimated from the temperature dependence of the electric resistivity, is 200°K.

c) **The modification of InSb.** The p - T phase diagram for InSb is shown in Fig. 33. At a pressure of

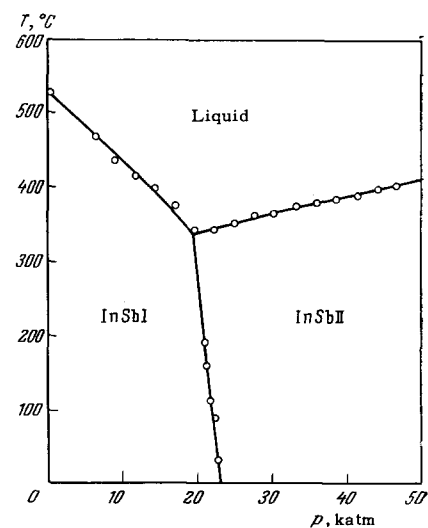


FIG. 33. Phase diagram of InSb.

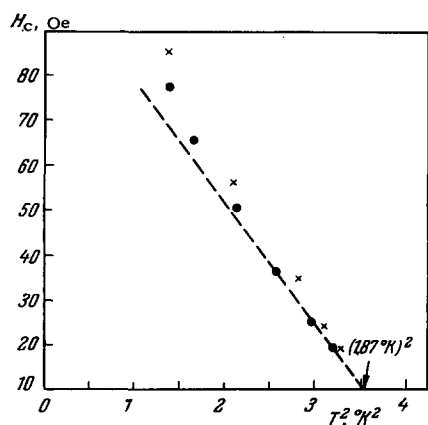


FIG. 34. Critical fields of InSb II (x and ● - different samples of InSb (I and II)).

~ 23,000 atm and at room temperature, the semiconducting compounds InSb go over into the metallic modification InSb II. This transition was investigated in detail in [49]. The slow rate of the phase transition of InSb makes it possible to obtain the metallic phase at sufficiently low temperatures in the supercooled state by gradually decreasing the pressure. Such a method of obtaining the crystalline modification of InSb was used to investigate its superconducting properties [50-52]. The metallic phase of InSb was obtained at room temperature, and was then cooled down to the temperature of liquid nitrogen, where the pressure was removed and the sample investigated at zero pressure. Measurements of the electric resistivity [51,52] have shown that InSb II is a superconductor with a superconducting-transition temperature below 2.1°K. Measurements of the critical field down to 0.4°K point to a value $H_0 \sim 1.1$ kOe. [50] Magnetic measurements of bulky samples of InSb II were made in [53]. Polycrystalline samples were investigated, with diameter approximately 5 mm and length approximately 6 mm. The critical-field curve of InSb II, shown in Fig. 34, is satisfactorily described by a parabolic $H_c(T)$ relation with a value $T_C = 1.88 \pm 0.01^\circ\text{K}$ and $H_0 \approx 100$ Oe. The value obtained for $(dH_c/dT)_{T_C}$ is $-(103 \pm 0.5)$ Oe/°K. The deviations from the parabolic relation at low temperatures are, in the opinion of the authors, the result of internal strain of the samples.

Investigation of the Stability of Superconducting Modifications

The physical considerations which have stimulated the investigation of the stability of crystalline modifications at low temperatures are the following.

It was established earlier that films of bismuth [54,55] and gallium [56], sputtered on a substrate cooled to the temperature of liquid helium, display superconductivity. Films produced by isothermal condensation at liquid-helium temperature have an amorphous structure. The crystalline structure of films appears when

the temperature is increased. These bismuth films are superconducting with $T_C \approx 6^\circ\text{K}$; when the films are heated above 15–20°K the superconductivity vanishes, apparently because of the appearance of the crystalline structure of the nonsuperconducting modification Bi I. Comparing the data for bismuth films with the data for the superconducting modification of bismuth Bi III, we can assume the following:

a) Upon condensation on a strongly cooled substrate, the bismuth crystallizes not in its usual modification Bi I, but in the denser modification Bi III, which is stable under ordinary conditions only at high pressures.

b) There exists some new modification [15], different from Bi III, which is superconducting and stable at temperatures below 20°K even at atmospheric pressure.

To check this assumption, it was considered of interest to determine whether the superconducting modification Bi III can be retained at low temperatures as the pressure is reduced to zero.

In the experiments on the investigation of the stability of the modification Bi III at liquid-helium temperature, the pressure was produced at room temperature or at liquid-nitrogen temperature, after which the apparatus was cooled to the temperature of liquid helium. At 2.2°K, the pressure was gradually reduced to zero, after which the temperature was slowly increased to approximately 10°K. It was established that the modification Bi III, obtained as a result of the compression of a single-crystal sample of bismuth, is conserved with decreasing pressure at liquid-helium temperature, up to 21,000 atm. When a pressure of 21,000 atm is reached, the entire volume of the modification Bi III goes over jumpwise into the nonsuperconducting modification Bi I. However, after repeated cycles of compression, a fraction of the volume of the sample is obtained in which the modification Bi III is retained with the pressure decreasing to zero; this fraction of the volume increases from experiment to experiment. After several cycles of compression, the modification Bi III is conserved, even if the pressure is completely removed in the entire volume of the sample. The superconducting transition of the modification Bi III is more smeared out at atmospheric pressure (compared with the transition of the modification Bi III at pressures exceeding 27,000 atm) and is shifted towards higher temperatures. The temperature of this superconducting transition is $\sim 7.6^\circ\text{K}$.

An analogous situation is observed for gallium. [32] Films of gallium with amorphous structure exhibit superconductivity with $T_C = 8.4^\circ\text{K}$. When the films are heated to 20–70°K the crystallization results in a superconducting modification with $T_C = 6.5^\circ\text{K}$. Above 70°K, the stable modification Ga I is produced with $T_C = 1.07^\circ\text{K}$.

The critical temperature of the superconducting modification Ga II is equal to 6.38°K. The modification

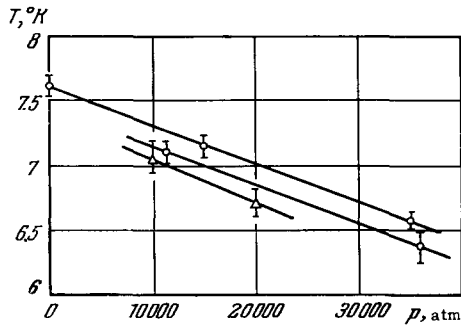


FIG. 35. Dependence of the superconducting transition temperature of Ga II on the pressure.

Samples: $\frac{R_{10^\circ\text{K}}}{R_{300^\circ\text{K}}} = 1.25 \cdot 10^{-2}$ (O); $1.43 \cdot 10^{-2}$ (□); $2.0 \cdot 10^{-2}$ (Δ).

Ga II is conserved at helium temperatures when the pressure is reduced to atmospheric, with the temperature of its superconducting transition rising to 7.5°K. The dependence of the critical temperature of Ga II on the pressure is shown in Fig. 35.

Most striking is the fact that the behavior of the superconducting modifications Bi III and Ga II is perfectly identical. The small difference in the experimental results lies in the fact that the Ga II modification, which is stable at atmospheric pressure, was produced immediately after the first compression cycle. This is apparently due to peculiarities of the method, which leads to strong plastic deformation of the sample upon compression.

It is natural to assume that the conservation of the modifications Bi III and Ga II with reduction to atmospheric pressure is due to the occurrence of internal stresses (dislocations, etc) in the samples. After repeated cycles of compression, the number of dislocations in the sample increases, and consequently the volume of the stable part of the sample increases.

The nearly equal values of the critical temperatures of the superconducting films of bismuth and gallium and of the plastically deformed phases Bi III and Ga II, as well as the possibility of the existence of the modifications Bi III and Ga II at atmospheric pressure in the region of low temperatures, give grounds for assuming that the superconducting films have the same crystalline structure as the modifications Bi III and Ga II. It becomes necessary to assume here that in freshly-condensed films internal stresses are produced. For bismuth, the magnitude of these stresses amounts to approximately 21,000 kg/cm². The vanishing of the superconductivity of the films, and also of the superconductivity of the modifications Bi III and Ga II with increasing temperature is apparently the consequence of the decrease in the internal stresses as a result of annealing.

As noted earlier, the modification InSb II is also stable at low temperatures and atmospheric pressure. The modification remains stable up to ~220°K. The inverse transition to the nonmetallic phase occurs with a volume increase of ~18.5%, and is accompanied by

destruction of the sample.

On the basis of the foregoing we can expect that InSb films obtained by sputtering at low temperatures will be superconducting.

IV. EFFECT OF PRESSURE AND MICROSCOPIC THEORY OF SUPERCONDUCTIVITY

The microscopic theory of superconductivity, developed in 1957,^[57] makes it possible to express the experimentally measured quantities in terms of certain microscopic characteristics of the metal. Of particular importance in this case is the formula for the temperature T_c of the superconducting transition

$$T_c = \frac{\Delta(0)}{3.52k} = 0.85 \theta e^{-\frac{1}{NV}}, \quad (2)$$

where $\Delta(0)$ is the width of the gap in the energy spectrum at $T = 0^\circ\text{K}$, θ is the Debye temperature, N is the density of states on the Fermi surface of the metal in question in the normal state*, and V is a parameter characterizing the interelectron interaction. We note that the coefficient 0.85 in formula (2) is tentative in character, and we retain it only to maintain correspondence with other reviews (see [42,58]).

V is not calculated within the framework of the theory in [57], and the parameters N and θ are calculated from the data obtained for the metal in the normal state using the free-electron model, etc. True, there is a whole series of attempts^[59-64] to proceed further and to calculate the parameter V or NV on the basis of a more detailed interaction between the electrons in the metal. All these attempts, however, are considerably less convincing and promising than the microscopic theory of superconductivity itself^[57] and formula (2) for T_c resulting from it.

In this connection, special interest attaches to an exhaustive comparison of theory with experiment, precisely for the purpose of analyzing the dependence of T_c on different factors, primarily the pressure.

If we base ourselves on formula (2), for which there are ample reasons, the dependence of T_c on p is obviously determined by the pressure dependence of the quantities θ , N , and V . The dependence of the Debye temperature θ on the pressure can be obtained approximately from the Grüneisen formulas for the coefficient of volume thermal expansion (see [33,65])

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \xi \chi \frac{C_v}{v}, \quad (3)$$

where

$$\xi = - \frac{d \ln \theta}{d \ln v}, \quad \chi = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T$$

*Usually one uses in place of N the symbol $N(0)$, thereby explicitly emphasizing the fact that the density of states N is taken on the Fermi surface. We shall, however, use below the symbol $N(p)$, where p is the pressure, it being implied that $N(p)$ pertains to the limiting value of the Fermi energy for all the considered values of p .

is the isothermal compressibility, C_V the specific heat of a substance with volume v , measured at constant volume. From (3) it follows that

$$\frac{d \ln \theta}{dp} = \frac{av}{C_v}, \quad (4)$$

that is, the Debye temperature should increase upon compression. The increase of θ upon compression, which satisfactorily explains the decrease in the electric resistivity under the influence of pressure in most metals in the normal state^[66], should lead in turn to an increase in the temperature of the superconducting transition [see formula (2)]. The values of $d \ln \theta/dp$, calculated with the aid of (4), are listed in Table I.

It must be borne in mind, however, that the determination of the quantity $d \ln \theta/dp$ from formula (4) is tentative in character and is valid only for metals which do not have appreciable anisotropy. Comparing the values

$$\frac{d \ln \theta}{dp} = \frac{1}{\theta} \frac{\partial \theta}{\partial p} \quad \text{and} \quad \frac{1}{T_c} \frac{\partial T_c}{\partial p},$$

we see that in most cases the sign of $\partial T_c/\partial p$ does not coincide with the sign of $\partial \theta/\partial p$, and the relative change in θ upon compression is as a rule much smaller than the corresponding change in the critical temperature.

Thus, the change in the Debye temperature is not a factor which determines the dependence of the critical temperature on the pressure.

As is well known, the electronic part of the specific heat of metals in the normal state, calculated per unit volume, is

$$c_{en} = \gamma T = \frac{2}{3} \pi^2 k^2 N T. \quad (5)$$

It follows, therefore, that by measuring the electronic part of the specific heat one can determine the density of states N . For superconducting metals it is possible to determine γ , and consequently also N , not only by calorimetric measurement, but also from the critical-field curves. The latter method is particularly convenient if the problem is to determine the dependence of N on the pressure, since measurement of the critical fields for superconductors under high-pressure conditions is an incomparably simpler problem than calorimetric measurements at low temperatures and high pressures.

On the basis of the thermodynamic equation for superconductors^[77]

$$G_n(0) - G_s(0) = \frac{v H_c^2}{8\pi} \quad (6)$$

(G_n and G_s are the free energies in the normal and in the superconducting states, and v is the volume) it follows that the difference in the specific heats of the electrons in the superconducting and normal states is

$$C_{es} - C_{en} = \frac{vT}{4\pi} \left[H_c \left(\frac{d^2 H_c}{dT^2} \right)_p + \left(\frac{dH_c}{dT} \right)_p \right]. \quad (7)$$

The dependence of H_c on T can in the general case

be written with sufficient accuracy in the polynomial form

$$\frac{H_c(T)}{H_0} = h(t) = 1 - \sum_{n=2}^N a_n t^n, \quad (8)$$

where $t = T/T_c$ and $\sum_{n=2}^N a_n = 1$.

Substituting (8) in (7) we get

$$\frac{c_{es}}{T} - \frac{c_{en}}{T} = \frac{1}{4\pi} \frac{H_0^2}{T_c^2} \{ (1 - a_2 t^2 - \dots)(2a_2) + (-2a_2 t - \dots) \}. \quad (9)$$

Inasmuch as under the most general assumptions $c_{es}/T \rightarrow 0$ as $T \rightarrow 0$, the coefficient $\gamma = c_{en}/T$ is equal to

$$\gamma = \frac{1}{2\pi} a_2 \frac{H_0^2}{T_c^2}. \quad (10)$$

This is an exact formula and makes it possible to calculate γ if the values of a_2 , H_0 and T_c are known. For a parabolic temperature dependence of H_c , formula (10) becomes simpler, since $a_2 = 1$. In the general case $a_2 \neq 1$ in (10), and the difference $1 - a_2$ is characterized by the degree of deviation of the curve $H_c(T)$ from a parabola. The value of a_2 can be determined by investigating the deviation of the experimental dependence $H_c(T)$ from parabolic. Thus, precision measurements of the dependence $H_c(T, p)$ over a wide range of temperatures make it possible to determine, besides the dependence $T_c(p)$, the dependence of the density of states on the pressure.

To determine the derivative $d\gamma/dp$, one can also use data obtained by measuring the thermal expansion at low temperatures. As shown in many papers (see, for example, ^[67, 68]), the coefficient of thermal expansion α of metals in the normal state at low temperatures is described sufficiently well by the formula

$$\alpha = \alpha_e + \alpha_g = AT + BT^3, \quad (11)$$

where α_e and α_g are the contributions made to the thermal expansion by the electrons and by the lattice, respectively. The value of the coefficient α_e is determined by the dependence of the electronic part of the entropy on the pressure:

$$\alpha_e = -\frac{1}{v} T \left(\frac{\partial \gamma}{\partial p} \right)_T. \quad (12)$$

Unlike the method considered above for determining the pressure dependence of N , formula (12) enables us to determine the magnitude and the sign of the derivative $\partial \gamma/\partial p$ only for $p = 0$, since the determination of α_e in compressed samples, especially at high pressures, is connected with almost insurmountable difficulties. We note that in the general case, especially in regions of high pressure, the function $N(p)$ is not linear and can be irregular.

The available experimental material, which can be processed in accordance with the scheme in question in a sufficiently broad region of pressures, is quite limited, and therefore at present there are no data on

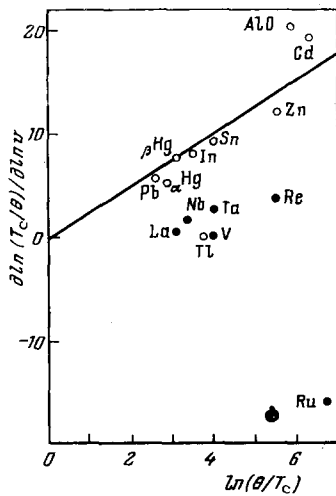


FIG. 36. Values of $\partial \ln(T_c/\theta)/\partial \ln v$ as a function of $\ln(\theta/T_c)$ for different superconductors. \circ – nontransition metals; \bullet – transition metals.

the pressure dependence of N . In most published papers (see, for example, [58,69]), the quantity $\partial \gamma/\partial p$ is determined at low pressures p from the $H_C(T)$ curves under the assumption that a_2 does not change with pressure, and also using formula (12).

The parameter V [see formula (2)], can, under sufficiently general assumptions, [59] be represented by the difference of two terms, characterizing respectively the attraction of the electrons as a result of the electron-phonon interaction, and the screened Coulomb repulsion.

The superconductivity criterion [57] consists in the fact that V must be positive, thus signifying predominance of the electron-phonon attraction over the Coulomb repulsion.

At the present time, it is impossible to determine experimentally directly the dependence of the parameter V on the pressure. However, this dependence can be obtained from formula (2) if the functions $\theta(p)$ and $N(p)$ are determined by the method described above.

In considering the approximate model constituting a system of electrons and ions interacting with the aid of a screened Coulomb field, it was found in [59] that the increase in the average interelectronic distance r_e and the valence of the ions Z contribute to the appearance of superconductivity. From this point of view, hydrostatic compression, which leads to a decrease in r_e , should cause a decrease in the critical temperature, and at a certain critical pressure it should lead to the vanishing of superconductivity. The latter corresponds to the vanishing of the parameter V . Unfortunately, it is still impossible to state that the possibility of the vanishing of the parameter V at finite pressure has been theoretically rigorously proved.

Recently a series of papers was published [60-62] in which the Coulomb and the electron-phonon inter-

actions in metals were considered in greater detail. However, attention was chiefly paid in these papers to the isotopic effect, and the pressure dependence of T_C is not discussed.

Under such conditions it becomes, obviously, necessary to seek some empirical laws, and also to process the experimental data on the basis of certain supplementary assumptions. One of the main questions which is now attracting attention is the clarification of the character of the $T_C(p)$ dependence.

On the basis of the experimental data, a linear connection was established in [58,70,71] between $d \ln(T_C/\theta)/d \ln v$ and $\ln(\theta/T_C)$ for nontransition metals, with the exception of thallium (Fig. 36). This means that for these metals we can write

$$\frac{d \ln(T_C/\theta)}{d \ln v} = \varphi_v \ln \frac{0.85\theta}{T_C} + C_1, \quad (13)$$

where φ_v and C_1 do not depend on the volume v . For lead, α and β mercury, tin, indium, gallium, zinc, and cadmium [58]

$$\varphi_v = 2.5 \pm 0.6. \quad (14)$$

Using (2), we have $\ln(T_C/\theta) = -NV + \ln 0.85$ and consequently, taking (13) into account, we get

$$\frac{d \ln(T_C/\theta)}{d \ln v} = -\frac{dNV}{d \ln v} = \varphi_v NV + C_1.$$

From Fig. 36 we can conclude that the constant C_1 is small. If we put $C_1 = 0$ and neglect $\ln 0.85$ compared with $\ln(\theta/T_C)$, then, in agreement with [42], we obtain from (13)

$$\ln\left(\frac{T_C}{\theta}\right) = C_2 v^{-\varphi_v}; \quad (15)$$

the constant $C_2 < 0$.

According to (15), the temperature T_C tends to zero with increasing pressure (that is, with decreasing volume v) only as $v \rightarrow 0$.

It must be noted, however, that we do not know any theoretical reasons for assuming the validity of formulas (13) or (15), both in general, and in particular in some broad pressure interval. Evidence that formula (15) cannot be used at high pressures is gathered from data on cadmium. Namely, cadmium (see Fig. 23) displays a stronger decrease in the critical temperature upon compression than would follow from (15). At pressures of approximately 26,000 atm, the change of T_C of cadmium, calculated from formula (15), is approximately one-third the experimentally observed value.

For transition metals, the quantity φ_v is in general not a constant (see Fig. 36).

In [58] a certain correlation is noted between φ_v and the parameter in the formula for the isotopic effect

$$T_c \sim M^{-0.5(1-\zeta)} \quad (16)$$

(M is the isotope mass). The connection between φ_v and ζ for nontransition and transition metals is illustrated by Fig. 37. On the basis of these data, the au-

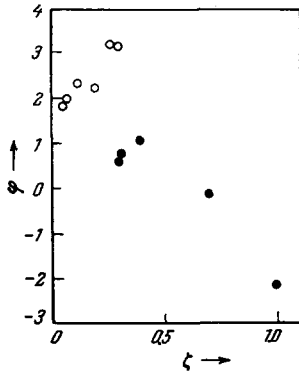


FIG. 37. Experimental values of $\varphi_v = \partial \ln NV / \partial \ln v$ as a function of ζ . ● — transition metals, ○ — nontransition metals.

thors of [58] believe that the increase in ζ of transition metals is the main cause of the deviation of φ_v from a constant value. The connection between the parameter ζ and the structure of the electronic energy spectrum of metals is considered in [60-62]. In particular, in [61] the values of ζ are calculated for a large number of transition and nontransition metals. However, no theoretical justification for a functional dependence of φ_v on ζ is contained in these papers.

In [17-19] it was assumed, in agreement with [59], that in nontransition metals the decrease in T_c with pressure is principally the consequence of the decrease in the parameter V at approximately constant N [formula (2)], and that at a certain critical pressure p_{c0} the parameter V can vanish, which should lead to the disappearance of superconductivity. Within the framework of the same assumption, the question of allowance for the influence of pressure in the theory of second-order phase transitions as applied to the superconducting transition was considered in [72]. It follows from this paper that near the critical pressure p_{c0} we can expect the pressure dependence of T_c to be expressed by the formula

$$T_c(p) = A \exp\left(-\frac{a}{p_{c0}-p}\right), \quad (17)$$

where A , a , and p_{c0} are constants. It is obvious that at a pressure $p = p_{c0}$ the temperature T_c vanishes.

To compare the experimental data with (17), it is necessary to obtain data in a wide interval of pressures in the region of temperatures close to 0°K, the only region in which the application of formula (17) can be valid. Of all the presently known data, such a comparison can be made only for cadmium [17], and with insufficient accuracy at that. If we assume that formula (17) is applicable in this case in the entire interval of pressures (Fig. 23), then we obtain values $A \approx 5.6$, $a \approx 16,500$, and $p_{c0} \approx 70,000$ atm. The extent to which these values are accurate can be seen from the results of another processing of the data. Namely, we make use of the values of $T_c(p)$ at pressures in the interval $15,000 \leq p \leq 26,000$ atm [one might think that formula (17) is the more accurate, the closer p is to p_{c0}].

Then $A \approx 2.4$, $a \approx 90,600$, and $p_{c0} \approx 57,000$ atm. Therefore the most probable value of the critical pressure, at which the gap in the energy spectrum of the superconducting cadmium closes down and the cadmium becomes nonsuperconducting, is a pressure in the region $57,000 \lesssim p_{c0} \lesssim 70,000$ atm.

At $T \neq 0^\circ\text{K}$ the width of the gap $\Delta(T)$ is smaller than $\Delta(0)$, and the "closing" of the gap should occur even at positive V . It was shown in [72] that for $T \neq 0$

$$\Delta(T, p) \propto \sqrt{p_c - p}, \quad H_c \propto (p_c - p), \quad (18)$$

where $p_c(T)$ is the pressure at which the superconducting transition occurs at a specified temperature T . Formula (18) is in good agreement with the experimental data. Figures 13, 14, and 24 show the pressure dependence of H_c for cadmium [17], tin [31], and indium [34]. We see that when $T \neq 0$ the dependence of H_c on p (for pressures close to p_c) is actually linear. We note that the ideas proposed relative to the mechanism whereby the pressure affects the value of T_c of nontransition metals does not contradict relation (14) which assumes at $C_1 = 0$ the form

$$\varphi_v = -\frac{\partial(NV)}{\partial v} \frac{v}{NV} = 2.5 \pm 0.6.$$

When $N \approx \text{const}$, this relation signifies that in nontransition metals at low pressures the relative changes in the parameter V upon compression are close to each other.

It is easy to see that when the pressure increases, φ_v should increase because of the decrease in V . $\varphi_v \rightarrow \infty$ as $V \rightarrow 0$, for it is very little likely that the derivative $\partial V / \partial v$ vanishes when $V = 0$.

In transition metals, which include zirconium, tantalum, titanium, and others, an especially important role may be played by the change in the density of the states on the Fermi surface upon compression. Data obtained in [73] in investigations of the connection between the electronic specific heat γ and T_c for a large number of superconducting transition metals and their alloys point to a very weak dependence of the parameter V of transition metals and their alloys on the effective number n_v of valence electrons. According to [73], the critical temperatures of transition metals and their alloys are determined essentially by the density of the d -electrons. From this point of view, the increase of T_c in zirconium and titanium under the influence of pressure should be the result of an increase in N . An increase in N upon compression of zirconium and titanium is also indicated by the change in the slope of the critical-field curves (Figs. 25 and 26). The average reversible increase of $(\partial H_c / \partial T)_{T_c}$ of zirconium and titanium as the pressure changes from 0 to 20,000 atm amounts to 20-25%. This is perfectly enough to explain the necessary increase in T_c upon compression. Such an interpretation of the results of [18, 19] is also in good agreement with [74], in which, from measurements of the elec-

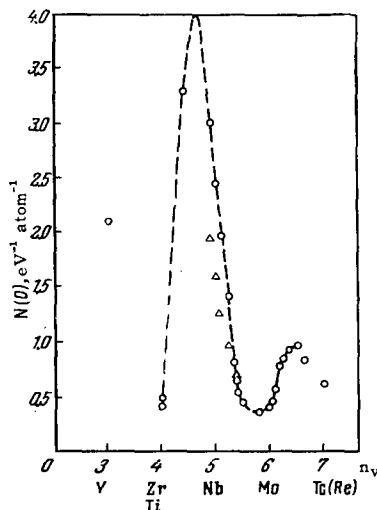


FIG. 38. Dependence of the density of the states $N(0)$ on the number of valence electrons. Δ , \circ — data of [73] and [74].

tronic specific heat, the density of states of the d-electrons of the transition metals is found as a function of the number n_v of valence electrons per atom. In the region close to zirconium and titanium, N increases with increasing number of valence electrons (Fig. 38). It can therefore be expected that N of these metals increases also upon compression. If it is assumed that the dependence of N on p is determined by curves similar to those shown in Fig. 38, then the sign of the derivative $\partial T_C / \partial p$ should be determined by the position of the considered superconductor on these curves. In superconductors with $\partial N / \partial n_v > 0$ the temperature of the superconducting transition should increase upon compression, while in superconductors with $\partial N / \partial n_v < 0$ it should decrease. This rule is well satisfied for all the investigated transition metals and their alloys. Namely, the temperature of the superconducting transition of zirconium, titanium, ruthenium, $Nb_{75}Zr_{25}$ increases upon compression, while for tantalum, Nb_3Sn , V_3Ga , and V_3Si it decreases. For molybdenum [42] $\partial T_C / \partial p$ is very small. Favoring the point of view considered above [18, 19] is also the good agreement of the data of Fig. 38 with the experimental dependence of T_C on the number of valence electrons, obtained in article [75], although it should be kept in mind that this dependence is satisfied only for metals with fixed band structure. [62] On the basis of the data on the dependence of γ on n_v [73] a positive sign of $\partial T_C / \partial p$ should be observed for $Zr_{60}Nb_{40}$ ($T_C = 8.8^\circ K$), $Mo_{95}Re_5$ ($T_C = 1.5^\circ K$), $Mo_{90}Re_{10}$ ($T_C = 2.9^\circ K$), $Mo_{80}Re_{20}$ ($T_C = 8.5^\circ K$), $Mo_{75}Re_{25}$ ($T_C = 10.5^\circ K$), $Mo_{70}Re_{30}$ ($T_C = 10.8^\circ K$). For Mo ($T_C = 0.95^\circ K$) and for the alloys $Nb_{20}Mo_{80}$ and $Mo_{80}Re_{40}$, the values of $\partial T_C / \partial p$ in the region of small pressures should be very small. In the remaining alloys investigated in [73], the usual negative sign of $\partial T_C / \partial p$ should be observed. From analogous considerations, we can also expect an increase in the criti-

cal temperature for the alloys $NbRe$ within the limits of the concentrations of the components $Nb_{38}Re_{62}$ — $Nb_{20}Re_{80}$. For these alloys, according to the data of [62], $\partial N / \partial n_v > 0$.

Unfortunately, there are no data on the electronic specific heat of the alloys Bi_3Ni and Bi_4Rh , the sign of $\partial T_C / \partial p$ of which is also positive.

An exception to the scheme described above is the behavior of the intermetallic compound Bi_2K , for which $\partial T_C / \partial p$ is positive and which is not a transition metal, and also the behavior of thallium in the region of low pressures. Unlike thallium, in which the anomalous dependence $T_C(p)$ may be connected with a sharply pronounced anisotropy, the compound Bi_2K has a cubic lattice. It is possible that in this case the parameter V increases upon compression.

When using the experimental data for transition metals and their alloys, it must be borne in mind that these data, obtained at low pressures, depend strongly on the state of the samples, and can be very inaccurate and fail to reflect the true behavior of these metals in the region of high pressures. Indeed, as can be seen from Figs. 27 and 28, the form of the curve $T_C(p)$ of transition metals in the region of low pressures depends strongly on the state of the sample (internal stresses, number of dislocations, etc), and therefore does not characterize its properties. In particular, for a hardened sample of zirconium, in which $\partial T_C / \partial p < 0$ and $\partial H_C / \partial p < 0$ in the region of low pressures, and $\partial T_C / \partial p > 0$ and $\partial H_C / \partial p > 0$ at high pressures, on the basis of the thermodynamic relation

$$\frac{v_n - v_s}{v_s} = \frac{H_C}{4\pi} \left(\frac{\partial H_C}{\partial p} \right)$$

the change in volume $v_n - v_s$ following the superconducting transition (at $p = 0$) should be negative.

Compatible data can be obtained only by investigating unstrained single-crystal samples of transition metals. This should be remembered when the value of $(\partial H_C / \partial p)_{T_C}$ is determined from data on the change in the volume v of an uncompressed sample during the superconducting transition of transition metals and their alloys.

V. SOME REMARKS ON PROSPECTS OF FURTHER RESEARCH

1. Of great importance to the clarification of the true picture of the influence of pressure on the superconducting properties of metals are precise investigations of the critical-field curves in a wide range of pressures and temperatures, including infralow temperatures. As a result it will be possible to clarify the pressure dependence of the density of states N on the Fermi surface. The experimental results in this field are very limited, and therefore further research in this direction is very promising.

2. Of very great importance is the question of the character of the dependence of T_C on p at large rela-

tive changes of the critical temperature. It is especially important to ascertain whether it is possible, by using pressure, to bring a superconductor (within the framework of a single crystalline modification) into the nonsuperconducting state. In spite of the fact that data on cadmium point to the possible disappearance of superconductivity upon compression of the metal, this question must still be regarded as open.

3. To answer these questions, it becomes necessary to develop new methods of obtaining sufficiently uniform high pressures at low and infralow temperatures. The presently attainable pressures, satisfying such requirements, do not exceed 30,000 atm, which is patently insufficient. For an unambiguous solution of the unclear question it is necessary to broaden the interval of attainable pressures to 80,000–100,000 atm.

4. In connection with the need for expanding the range of attainable pressures, particular significance is acquired by work on low-temperature barometry—the development of effective methods for measuring pressures directly at low temperatures. A very convenient tool of this type is the superconducting manometer, the use of which greatly simplifies the problem. However, the use of superconducting manometers calls for a knowledge of the dependence of the critical temperature of the barometric substance on the pressure. Unfortunately, there are at present no accurate data on the dependence of T_c on p in the region of pressures exceeding 10,000 atm, for any of the superconductors. A very promising way of carrying out calibration measurements is apparently offered by methods in which solid gases, helium and hydrogen, are used. Further development of these methods is highly desirable.

5. An interesting trend of further research is the search for new superconducting modifications, which are stable under high pressures, and a study of their properties. With broadening region of attainable pressures, more and more possibilities for carrying out researches of this type will appear.

6. In the region of already attained pressures, it is of interest to investigate the properties of superconducting alloys with variable composition, made up of transition and nontransition metals, principally for the purpose of determining the sign of $\partial T_c / \partial p$ and for comparing these data with data on the dependence of $\gamma = c_{en} / T$ on the effective concentration of the valence electrons n_v , which can be obtained by thermal measurements at low temperatures.

A study of the influence of pressure on the superconducting properties of metals is an important and effective method of research and will undoubtedly attract more and more attention.

¹ C. A. Swenson, High-pressure Physics (Russ. Transl.) IL, 1963.

² B. G. Lazarev and L. S. Kan, JETP 14, 439, 461 (1944).

³ N. B. Brandt and A. K. Tomashik, PTÉ No. 2, 113 (1958).

⁴ N. E. Alekseevskii and Yu. P. Gaïdukov, JETP 29, 898 (1955), Soviet Phys. JETP 2, 762 (1956).

⁵ J. S. Dugdale and J. A. Hulbert, Canad. J. Phys. 35, 72 (1957).

⁶ D. H. Bowen, Proc. 6th Intern. Conf. on Low Temp. Phys. and Chem., Madison, 1958, p. 337.

⁷ N. B. Brandt and D. Balla, PTÉ No. 6, 135 (1962); Cryogenics 3, 213 (1963).

⁸ D. Balla and N. B. Brandt, JETP 47, 1653 (1964), Soviet Phys. JETP 20, 1111 (1965).

⁹ E. S. Itskevich, PTÉ No. 4, 148 (1962).

¹⁰ L. F. Vereshchagin and A. I. Likhter, Dokl. Akad. Nauk SSSR 103, 191 (1955).

¹¹ P. F. Chester and G. O. Jones, Phil. Mag. 44, 1281 (1953).

¹² D. H. Bowen and G. O. Jones, Proc. Roy. Soc. A254 (No. 1279), 522 (1960).

¹³ N. B. Brandt, PTÉ No. 2, 131 (1960).

¹⁴ N. B. Brandt and N. I. Ginzburg, JETP 39, 1554 (1960), Soviet Phys. JETP 12, 1082 (1961).

¹⁵ N. B. Brandt and N. I. Ginzburg, FTT 3, 3461 (1961), Soviet Phys. Solid State 3, 2510 (1962).

¹⁶ N. B. Brandt and N. I. Ginzburg, JETP 44, 478 (1963), Soviet Phys. JETP 17, 326 (1963).

¹⁷ N. B. Brandt and N. I. Ginzburg, JETP 44, 1876 (1963), Soviet Phys. JETP 17, 1262 (1963).

¹⁸ N. B. Brandt and N. I. Ginzburg, JETP 46, 1216 (1964), Soviet Phys. JETP 19, 823 (1964).

¹⁹ N. B. Brandt and N. I. Ginzburg, JETP (in press).

²⁰ J. W. Stewart, Phys. Rev. 97, 578 (1955).

²¹ C. A. Swenson, Phys. Rev. 100, 1607 (1955).

²² R. Stevenson, J. Chem. Phys. 27, 1656 (1957).

²³ J. W. Stewart and C. A. Swenson, Phys. Rev. 94, 1096 (1954).

²⁴ J. Hatton, Phys. Rev. 100, 681 (1955).

²⁵ J. Hatton, Phys. Rev. 103, 1167 (1956).

²⁶ L. D. Jennings and C. A. Swenson, Phys. Rev. 112, 31 (1958).

²⁷ J. Stewart, Phys. Chem. Solids 1, 146 (1956).

²⁸ Sovremennaya tekhnika vysokikh davlenii (Contemporary High-pressure Techniques), Moscow, "Mir" Press, 1964.

²⁹ V. I. Khotkevich, Doctoral dissertation, Institute for Physics Problems, Acad. Sci. USSR, 1952.

³⁰ Khotkevich, Pervakov, and Genkin, PTÉ No. 5, 201 (1961); Cryogenics 2, 281 (1962).

³¹ Alekseevskii, Brandt, and Kostina, Izv. Akad. Nauk SSSR, ser. fiz. 16, 233 (1952).

³² W. Buckel and W. Gey, Z. Phys. 176(4), 336 (1963).

³³ R. I. Beecroft and C. A. Swenson, J. Phys. Chem. 18, 329 (1961).

³⁴ N. B. Brandt and N. I. Ginzburg, Trans. Ninth All-union Conference on Low-temperature Physics, Minsk, 1964.

³⁵ Kan, Lazarev, and Makarov, JETP 40, 457 (1961), Soviet Phys. JETP 13, 317 (1961).

- ³⁶ C. H. Hinrichs and C. A. Swenson, *Phys. Rev.* **123**, 1106 (1961).
- ³⁷ J. E. Schirber and C. A. Swenson, *Phys. Rev.* **123**, 1115 (1961).
- ³⁸ Lazarev, Lazareva, and Makarov, *JETP* **44**, 481 (1963), *Soviet Phys. JETP* **17**, 328 (1963).
- ³⁹ Lazarev, Lazareva, and Makarov, *Trans. Tenth All-union Conference on Low-temperature Physics, Moscow, 1963*.
- ⁴⁰ J. L. Olsen and H. Rohrer, *Helv. Phys. Acta* **30**, 49 (1957).
- ⁴¹ G. D. Cody, *Phys. Rev.* **111**, 1078 (1957).
- ⁴² Olsen, Bucher, Zevy, Muller, Corenzwit, and Geballe, *Rev. Modern Phys.* **36**(1), 168 (1964).
- ⁴³ Itskevich, Il'ina, and Sukhoparov, *JETP* **45**, 1378 (1963), *Soviet Phys. JETP* **18**, 949 (1964).
- ⁴⁴ C. B. Müller and E. J. Saur, *Rev. Modern Phys.* **36**(1), 103 (1964).
- ⁴⁵ Lazarev, Lazareva, Ovcharenko, and Matsakova, *JETP* **43**, 2309 (1962), *Soviet Phys. JETP* **16**, 1630 (1963).
- ⁴⁶ N. B. Brandt and N. I. Ginzburg, *PTÉ No. 5*, 161 (1962).
- ⁴⁷ E. P. Bundy, *Phys. Rev.* **110**, 315 (1958).
- ⁴⁸ N. Kürti and F. Simon, *Proc. Roy. Soc.* **151**, 6 (1935).
- ⁴⁹ Jayaraman, Newton, and Kennedy, *Nature* **191**, 1288 (1961).
- ⁵⁰ A. J. Darnell and W. F. Libby, *Science* **139**, 1301 (1963).
- ⁵¹ Geller, McWhan, and Hull, *Science* **140**, 62 (1963).
- ⁵² Bömmel, Darnell, Libby, and Tittman, *Science* **139**, 1301 (1963).
- ⁵³ T. T. Stromberg and C. A. Swenson, *Phys. Rev.* **134**, A21 (1964).
- ⁵⁴ R. Hilsch, *Rec. Intern. Conf. on Low Temp. Phys. Oxford, 1951*, p. 119.
- ⁵⁵ N. V. Zavaritskiĭ, *Dokl. Akad. Nauk SSSR* **86**, 687 (1952).
- ⁵⁶ W. Buckel and R. Hilsch, *Z. Phys.* **138**, 109 (1954).
- ⁵⁷ Bardeen, Cooper, and Schrieffer, *Phys. Rev.* **106**, 162 (1957); J. Bardeen and J. Schrieffer, *Recent Developments in Superconductivity, North-Holland, 1963*.
- ⁵⁸ Olsen, Andres, Meier, and de Salaberry, *Zs. Naturforsch.* **18a**, 125 (1963).
- ⁵⁹ D. Pines, *Phys. Rev.* **109**, 280 (1958).
- ⁶⁰ P. Morel and P. W. Anderson, *Phys. Rev.* **125**, 1263 (1962).
- ⁶¹ J. W. Garland and W. Janus, *Phys. Rev.* **11**, 114 (1963).
- ⁶² Bücher, Heiniger, and Müller, *Phys. Cond. Mat.* **2**(3), 210 (1964).
- ⁶³ J. Peretti, *Phys. Letts.* **2**, 275 (1962).
- ⁶⁴ J. Condo, *Progr. Theor. Phys. (Kyoto)* **29**, 1 (1963).
- ⁶⁵ Ryabinin, Rodionov, and Alekseev, *ZhTF* **34**, 1913 (1964), *Soviet Phys. Tech. Phys.* **14**, 77 (1965).
- ⁶⁶ P. W. Bridgman, *The Physics of High Pressure*, London, 1949.
- ⁶⁷ G. K. White, *Cryogenics* **3**, 292 (1962).
- ⁶⁸ G. K. White, *Phil. Mag.* **7**, 271 (1962).
- ⁶⁹ M. Garfunkel and D. E. Mapother, *Phys. Rev.* **122**, 459 (1961).
- ⁷⁰ H. Rohrer, *Helv. Phys. Acta* **33**, 675 (1960).
- ⁷¹ J. L. Olsen and H. Rohrer, *Helv. Phys. Acta* **33**, 872 (1960).
- ⁷² V. L. Ginzburg, *JETP* **44**, 2104 (1963), *Soviet Phys. JETP* **17**, 1415 (1963).
- ⁷³ F. J. Morin and J. P. Maita, *Phys. Rev.* **129**, 1115 (1963).
- ⁷⁴ J. Daunt, *Coll. Progr. in Low Temp. Phys. vol. 1, Amsterdam, 1955*, p. 202.
- ⁷⁵ B. Matthias, *Coll. Progr. in Low. Temp. Phys., vol. 2, Amsterdam, 1957*.
- ⁷⁶ N. E. Alekseevskii and I. I. Lifanov, *JETP* **30**, 405 (1956), *Soviet Phys. JETP* **3**, 294 (1956).
- ⁷⁷ E. A. Lynton, *Superconductivity, (Russ. Transl.)*, Mir 1964, p. 13, [Methuen, 1962].
- ⁷⁸ D. Gross and J. L. Olsen, *Cryogenics* **1**, 91 (1960).
- ⁷⁹ B. R. Coles, *Rev. Modern Phys.* **36**, 139 (1964).
- ⁸⁰ J. K. Hulm and R. D. Blaugher, *Phys. Rev.* **123**, 1569 (1961).
- ⁸¹ J. G. Daunt, *Phys. Rev.* **80**, 911 (1960).
- ⁸² Parkinson, Simon, and Spedding, *Proc. Roy. Soc.* **A207**, 137 (1951).

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