INVESTIGATION OF THE EFFECT OF HIGH PRESSURE ON THE SUPERCONDUCTING PROPERTIES OF CADMIUM

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Submitted to JETP editor February 13, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) 44, 1876-1883 (June, 1963)

A study was made of the effect of pressure up to 27,000 atm on the critical field curves and on the temperature T_C of the superconducting transition in cadmium in the 0.08–0.5°K temperature range. A large relative change in T_C , amounting to about 80% at 26,400 atm, was obtained. The possibility of destroying the superconductivity of cadmium without changing its crystal modification is discussed.

INTRODUCTION

N work published so far on the effect of pressure on superconductivity, it has not been possible, to the authors' knowledge, to reach a large relative change of the superconducting transition temperature T_c as a result of pressure. The largest relative change of T_c on compression did not exceed 13% (an exception is the work of Chester and Jones, ^[1] in which the pressure was produced by compressing thin ($\approx 50 \mu$) disks between two pistons and the pressure was strongly nonuniform).

Some of the published data for the highest pressures achieved are listed in the table.

Obviously the results listed are insufficient for finding the nature of the dependence of T_C on p at large relative changes $\Delta T_C/T_C$. In principle it is possible to obtain large values of $\Delta T_C/T_C$ in studies of superconductors having relatively high T_C at very high pressures (of the order of 100,000 atm) or in studies of superconductors with low values of T_C in the region of pressures which can be reached easily.^[7-9]

Alekseevskiĭ and Gaĭdukov^[5] investigated the effect of a pressure of about 1500 atm on the critical field curve of cadmium and found that the quantity $\partial T_C / \partial p$ is negative for cadmium and its absolute magnitude is close to the $\partial T_C / \partial p$ of superconductors such as tin, indium, etc. In connection

with this it was considered to be of interest to investigate the dependence of the critical temperature and critical field of cadmium (as well as of other superconductors with low values of T_c) in a wide range of pressures.

PROCEDURE

The apparatus in which measurements were carried out is shown schematically in Fig. 1. Pressure was produced by a booster 1, the construction of which has been described in detail earlier.^[7,8] At pressures up to 16,000 atm a piston of heat-treated beryllium bronze, containing 2.7% Be, was employed. To produce higher pressures we used pistons of cemented tungsten carbide, containing 3% Co (VK-3).

As pistons made of VK-3 acquire a weak permanent ferromagnetic moment after adiabatic demagnetization, an insert of beryllium bronze 10-12mm long was placed between the piston and the sample in the pressure-booster channel in order to reduce the influence of this magnetic moment. The booster was connected by a cooling duct 2, of 3 mm diameter and about 200 mm length, and a coupling 3 to a pellet of iron-ammonium alum 4, of 13 mm diameter and 70 mm length. The booster was suspended by a Staybrite wire 5 of 0.2 mm diameter and ≈ 50 mm length inside a glass ampoule

Metal	p _{max} , atm	ΔT _c , deg	ΔT _c /T _c , %	Metal	<i>p_{max},</i> atm	∆T _C , deg	Δτ _c /τ _c , %
Sn [¹] Sn [²] Tl [²] Pl [²]	17500 9400 9500 9400	$\begin{array}{c} -0.8 \\ -0.432 \\ -0.018 \\ -0.47 \end{array}$	21 11 0.8 6.5	Sn [³] A1 [⁴] Cd [⁵] Sn [⁶]	10000 2000 1600 2530	$-0.48 \\ -0.04 \\ 0.05 \\ 0.1$	13 3 9 3

1262



6, which was joined by a copper-glass seal to a copper tube 7. The tube was soldered by the use of Wood's alloy to a cover 9 along a seam 8. The salt pellet with a thin-walled Plexiglas cap 10 was centered in the ampoule by means of a glass tube 11 and a diaphragm 12.

A tap 13, above the cover of the Dewar flask, made it possible to connect the ampoule 6 to a charcoal pump 14. Pumping of the ampoule and filling it with helium for the purpose of heat exchange ($p \approx 10$ mm at $T \approx 300^{\circ}$ K) was done through a tube 15. Radiation was prevented from reaching the ampoule by a demountable copper screen 16, made of insulated cemented copper strips, to which measuring coils were rigidly attached: 17, 18 — for recording the superconducting transition, and 19, 20 — for determining the temperature of the salt.

The pressure was found from the shift of the superconducting transition temperature of a tin manometer in the form of a disk of 0.5 mm thickness, placed in the pressure-booster channel between the sample and a standard, and was calculated from the formula^[3]

$$T_{\rm c} = 3.733 - 4.95 \cdot 10^{-5} p + 3.9 \cdot 10^{-10} p^2$$

The samples were made of spectroscopically pure cadmium and were in the form of cylinders of 2-3 mm diameter and 2.5-3.4 mm length. In the present work we studied only polycrystals. The geomagnetic field and the residual field of the magnet at the point where the sample was located were compensated by a system of Helmholtz coils 21, 22 to within 0.06 Oe. The superconductivity was destroyed with the coils 23, which produced a magnetic field of 90 Oe for a current of 1 A. To eliminate the small residual magnetic field produced by the piston, measurements were carried out employing commutation of the measuring magnetic field.

The transition of the sample and the manometer from their normal to their superconducting states and conversely was recorded using the change of the mutual inductance of the coils 18 and 19, measured by an electronic method at a frequency of 22 cps. The amplitude of the alternating magnetic field did not exceed 0.05 Oe.

Adiabatic demagnetization of the salt was carried out at T = 1.6°K from a magnetic field of 14,000 Oe; during the demagnetization process the pressure booster was inside a magnetic screen. After the demagnetization the whole device was raised above the magnet by means of a lifting mechanism.

The time for the establishment of thermal equilibrium between the salt and the sample was determined in each experiment: it did not exceed 10 min at $T \approx 0.1^{\circ}$ K and 5 min at higher temperatures. Heating of the salt from 0.08 to 0.5°K took 8–10 hours, which made it possible to carry out measurements at a practically constant temperature. The temperature was determined from the magnitude of the magnetic susceptibility of the salt, using the ballistic method (coils 19, 20).

In each experiment, simultaneously with calibration of the salt, the superconducting transition curve of the tin manometer was recorded on cooling by pumping liquid helium vapor, and the pressure in the booster channel was determined. Then adiabatic demagnetization of the salt was carried out. Measurements were begun 15-20 min after the demagnetization (this was necessary for the establishment of thermal equilibrium), and they consisted of recording the dependence of the signal W at the output of the electronic apparatus on the magnetic field H produced by the Helmholtz coil 23.

RESULTS OF MEASUREMENTS

Investigation of the effect of pressure on the critical field and the superconducting transition temperature of cadmium was carried out on several samples in the pressure region up to 27,000 atm at temperatures from 0.08 to 0.5°K.

Figure 2 shows some curves of the destruction of the superconductivity in cadmium samples at various temperatures and pressures. The critical field H_c was determined from the intersection of the rectilinear part of the transition with a horizontal line corresponding to a constant value of the signal after complete destruction of the superconductivity.

Figure 3 gives the curves of the dependence of the critical fields on the temperature squared for



various samples of cadmium at various pressures. It can be seen that the dependence of H_C on temperature for cadmium is described satisfactorily over the whole region of the test pressures by the formula $H_C = H_0 [1 - (T/T_C)^2]$, which makes it possible to determine quite accurately both T_C and H_0 . It is worth noting that some of the curves exhibit a small negative deviation from the quadratic law, which is particularly pronounced at low pressures.

The pressure dependence of the superconducting transition temperature T_c is given in Fig. 4. This dependence is not linear and the quantity dT_c/dp decreases on increase of pressure from a value of -1.8×10^{-5} deg/atm at p = 0 to a value of -1.25×10^{-5} deg/atm in the pressure region 18,000-27,000 atm. At the maximum pressure reached in these tests (26,400 atm) the superconducting transition temperature decreased by a factor of 4.4 and became $0.124^{\circ}K$.

Figure 5 gives the pressure dependence of the critical field at various temperatures. The curve on the right, obtained by extrapolation, shows the pressure dependence of the critical field H_0 at

FIG. 2. Curves of the destruction of superconductivity in cadmium by a magnetic field: $\Box - p = 9000$ atm; $X - p = 20\ 800$ atm; $O - p = 25\ 800$ atm. The numbers by the curves give T in °K.



FIG. 3. Dependence of H_c on T^2 : 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) O - p = 20 800 atm; 11) $\Delta - p = 20$ 900 atm; 12) p = 25 800 atm; 13) p = 26 400 atm.



FIG. 4. Dependence of T_c on the pressure and relative change of volume. The chain and dashed curves are plotted according to Eq. (3) for, respectively, the values A = 5.65, a = 165 000, $p_{c0} = 70\ 000$ atm, and A = 2.42, a = 90 600 and $p_{c0} = 57\ 000$ atm.



FIG. 5. Dependence of H_c on the pressure and the relative change of volume: 1) $T = 0^{\circ}K$; 2) $T = 0.1^{\circ}K$; 3) $T = 0.14^{\circ}$ K; 4) $T = 0.19^{\circ}K$; 5) $T = 2.65^{\circ}K$; 6) $T = 0.31^{\circ}K$; 7) $T = 0.36^{\circ}$ K; 8) $T = 0.4^{\circ}K$; 9) $T = 0.45^{\circ}K$.

T=0. On reduction of temperature the nonlinearity of the dependence $H_{C}(p)$ increases. At T = 0.45°K the average value of dH_{C}/dp in the range 0–4000 atm is $\approx 2.2 \times 10^{-3}$ Oe/atm. At T = 0°K in the region of low pressures dH_{C}/dp $\approx 1 \times 10^{-2}$ Oe/atm and in the pressure region 1500–26,000 atm it becomes $dH_{C}/dp \approx 0.8 \times 10^{-3}$ Oe/atm.

Let us consider the accuracy of the results obtained. In determining the pressure acting on the sample it is necessary to allow for the pressure gradient along the booster channel which appears on cooling the booster below temperatures of -50 to -70° C. Special experiments, carried out with two tin manometers placed one on each side of the cadmium sample, showed that at pressures of up to 16,000 atm the pressure drop in the booster did not exceed 3% and at pressures above 16,000 atm, when a rod separating the piston and the sample was used, this drop did not exceed 6%. The lower part of the sample was always at a lower pressure than the upper part. Since the critical fields are determined from the end of the superconducting transition, their values represent a transition in the lower part of the sample, in which the pressure is practically identical with the pressure determined by means of the tin manometer lying immediately below the sample. In view of this we estimate the error in the pressure determination as not greater than $\pm 3\%$.

The error in determining the magnetic field is governed by the precision of the compensation for the geomagnetic field and the leakage field of the magnet ($\pm 0.06\%$) and the degree to which the external field H₀ represents the field H* in the sample:

$$H^* = H_0 + \Delta H_1 + \Delta H_2 + \Delta H_3$$

The quantity ΔH_1 is the average value of the constant field, produced by the weak ferromagnetic moment of the piston and the casing of the pressure booster, and by the possible "frozen in" magnetic moment in the tin manometer. The length of the cylinder separating the piston and the sample was selected so that $\Delta H_1 < 0.2$ Oe, and commutation of the field H_0 eliminated this error completely. The field ΔH_2 , which is dependent on H_0 , is due to the non-zero demagnetization factor of the tin manometer; ΔH_2 increases the field H_0 and, therefore, the error introduced by ΔH_2 may depress the values of H_C by about 3%. The magnitude of the field ΔH_3 , due to the magnetization of the piston by the field H_0 , was estimated from the magnitude of the unbalance of the recording system on introducing a field parallel to the longitudinal axis of the pressure booster; the field ΔH_3 in no case exceeded 0.05 Oe. The accuracy of the graphical determination of H_c amounted to ± 0.15 Oe. Thus the total error in determinating the field did not exceed $0.03 H_0 \pm 0.2 \text{ Oe.}$

The error in the determination of temperature, connected with the calibration inaccuracies, amounts to $\pm 2\%$. Moreover, an error is possible due to the difference between the temperature of the separate parts of the salt (which was in poor thermal contact with the cooling duct) and the sample temperature. One would expect that this error would decrease with increasing temperature,

but it was difficult to determine it. Because of this, tests were carried out using different areas of contact with the cooling duct. The small scatter in the value of the slope of the critical fields (Fig. 3) is related mainly to this circumstance.

DISCUSSION OF RESULTS

Cadmium belongs to the second group of the periodic system and has a hexagonal close-packed lattice with parameters a = 2.973 Å and c = 5.606 Å

At pressures of about 5000 atm cadmium (according to Bridgman^[ϑ]) exhibits a phase transition which is not accompanied by a marked change of volume. This transition occurs only in single crystals and obviously does not take place on compression of polycrystalline samples. This is confirmed by the monotonic nature of the variation of T_C and H_C under hydrostatic compression (Figs. 4 and 5). Apart from this transition no other phase transitions have been found in cadmium at pressures up to 100,000 atm.^[10]

The most interesting result of the present work is obviously an indication that it may actually be possible to destroy the superconductivity in cadmium by hydrostatic compression while retaining the same crystal modification. According to the BCS theory of superconductivity^[11] the superconducting transition temperature is given by

$$kT_{c} = \Delta(0)/3.52 = 1.14 (\hbar\omega)_{av} \exp[-1/N(0)V],$$
 (1)

where $\Delta(0)$ is the width of the energy gap at T = 0; $(\hbar\omega)_{aV}$ is the average energy of phonons which scatter electrons near the Fermi surface, N(0) is the density of energy states on the Fermi surface, and V is a parameter representing the average value of the interaction of electrons in the immediate vicinity of the Fermi surface. The superconductivity criterion requires that V should be positive, which implies that the electron-phonon attraction is stronger than the Coulomb repulsion. From this point of view the destruction of superconductivity means that N(0)V vanishes and the gap $\Delta(0)$ closes up.

At $T \neq 0$ the gap width $\Delta(T)$ is less than $\Delta(0)$ and the gap is also closed up when V has a positive value. V. L. Ginzburg^[12] has shown that at $T \neq 0$

$$\Delta(T, p) \sim \sqrt{p_{\rm c} - p}, \qquad H_{\rm c} \sim (p_{\rm c} - p), \qquad (2)$$

where $p_C(T)$ is the pressure at which the superconducting transition occurs at a given temperature. The dependence $p_C(T)$ is given in Fig. 4. The linear nature of the dependence of H_C on p near p_C agrees well with the experimental data (Fig. 5). The dependence of T_c on p is related to the fact that the parameters in square brackets in Eq. (1) depend on pressure and the most important is probably the pressure dependence of the interaction energy, V(p). If a formula of type Eq. (1) may also be used for $V \rightarrow 0$, then to a first approximation we may expect^[12] that the following formula is valid

$$T_{\mathbf{c}}(p) = A \exp\left(-\frac{a}{p - p_{\mathbf{c0}}}\right), \qquad (3)$$

where A, a, and p_{C0} are constants (obviously p_{C0} is the pressure at which $T_c = 0$). Using our data for $T_{C}(p)$ (Fig. 4) it is difficult to determine with any accuracy the parameters A, a, and p_{C0} in Eq. (3), even if it is assumed that the same formula is applicable over the whole range of pressures. If this assumption is made, then we obtain the values A \approx 5.65, a \approx 165,000 and p_{C0} \approx 70,000 atm. How inaccurate these values are can be seen from another analysis of the data. Let us determine A, a, and p_{C0} using only the values of $T_{C}(p)$ at pressures in the range $15,000 \le p \le 26,000$ atm [one would expect that the closer p is to p_0 the more accurate formula (3) would become]; then A $\approx 2.42,~a\approx 90,600$ and $p_{C0}\approx 57,000$ atm. Thus probably 57,000 $\leq p_{C0} \leq$ 70,000 atm.

At the pressure p = 26,400 atm attained in this study the volume changes by 4.7% (cf. ^[13]) and the average interelectron distance r_S changes by 1.6%. At the same time the temperature T_C changes by a factor of 4.4 in the range $0 \le p \le 26,400$ atm. This can be understood by taking into account the exponential nature of the dependence in Eq. (1). At p = 0 we have for cadmium exp[-1/N(0)V]= exp(-5.1) (cf. ^[14]), thus a change of T_c by a factor of 4.4 represents a change of N(0)V by about 30%. Moreover, the relative change of N(0)V may be greater by a factor of several times or even by one order of magnitude than the change of r_S (this is clear from Pines' analysis; [14] unfortunately it is not possible to use Eq. (21) from [14] for divalent metals such as cadmium). It should also be noted that on allowing for the anisotropy of the Fermi surface the dependence of T_C on r_S (or p) may be even stronger than in the isotropic model.^[11,14]

Concluding, we take this opportunity of thanking V. L. Ginzburg for discussing the results and A. I. Shal'nikov for his interest.

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Translated by A. Tybulewicz 299