EFFECT OF HIGH PRESSURE ON THE SUPERCONDUCTING PROPERTIES OF ZIRCONIUM

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The effect of pressure up to 24,000 atm on the critical field and on the superconducting transition temperature T_c of zirconium was investigated in the temperature range 0.08—0.8° K. It was found that T_c increased with pressure, the increase reaching 70% at a pressure of about 24,000 atm.

In an investigation of the influence of hydrostatic compression on the superconducting properties of cadmium[1], we detected a large relative drop of the critical temperature T_c, which reached 80% at a pressure of about 27,000 atm. It was of interest to investigate the effect of pressure on other superconductors with low values of T_c. In the present work, we report the results obtained in an investigation of zirconium.

Measurements were carried out by the method described earlier.[1] Cylindrical zirconium samples, 2.5 mm in diameter and 2—4 mm long, were prepared from 99.99% pure zirconium iodide melted in an arc furnace and then drawn. Some of the samples were annealed for 4 hours at a temperature of ≈ 700° C in an atmosphere of pure helium.

Some of the superconducting transition curves, recorded in a transverse magnetic field at various pressures and temperatures, are shown in Fig. 1. The value of the critical field H_c was determined from the point of intersection of the rectilinear part of the transition curve with the horizontal line representing the constant output signal W of the electronic apparatus after the complete destruction of the superconductivity.

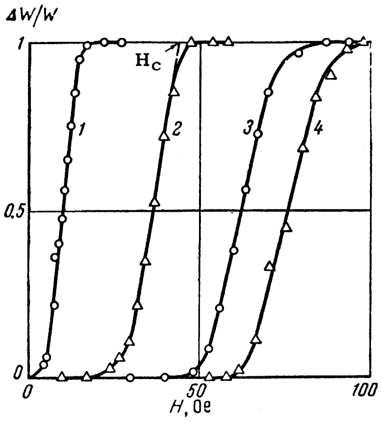

FIG. 1. Superconducting transition curves of zirconium: 1) T = 0.145°K; 2) T = 0.47°K; 3) T = 0.242°K; 4) T = 0.35°K; o—without pressure; Δ—p = 16 300 atm.

Figure 2 shows, as an example, some critical field curves for the investigated samples of zirconium. In the case of unannealed samples not subjected to pressure, $T_c \approx 0.52°$ K and $(dH_c/dT)_{T_c} \approx 280$ Oe/deg. Annealing lowered T_c to ≈ 0.46° K and $(dH_c/dT)_{T_c}$ to ≈ 160 Oe/deg.

Figure 2 demonstrates that hydrostatic compression raises the value of T_c considerably, and this is accompanied by an increase in the value of $(dH_c/dT)_{T_c}$. The rise of dH_c/dT remains approximately constant during the various compression cycles and amounts, on the average, to 20—25% for a pressure rise from 0 to 20,000 atm, for both annealed and unannealed samples.

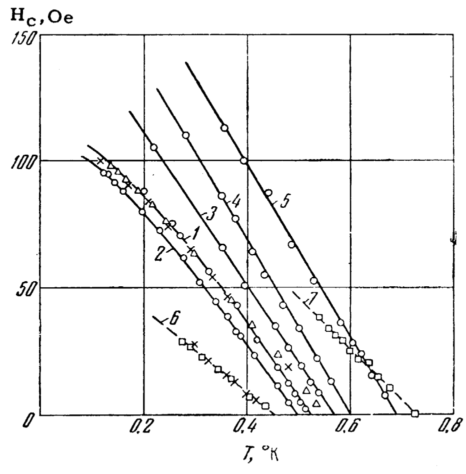

FIG. 2. Critical field curves of unannealed (continuous curves) and annealed (dashed curves) zirconium samples. 1) Without pressure: o—initial sample, ×—after fifth and Δ—after eighth compression cycle (cf. Fig. 3a, sample No. 1); 2) p = 3700 atm (sample No. 2); 3) p = 8800 atm (sample No. 2); 4) p = 16 300 atm (sample No. 3); 5) p = 23 600 atm (sample No. 1); 6) without pressure: □—initial sample, ×—after second compression cycle (Fig. 3b); 7) p = 18 000 atm.

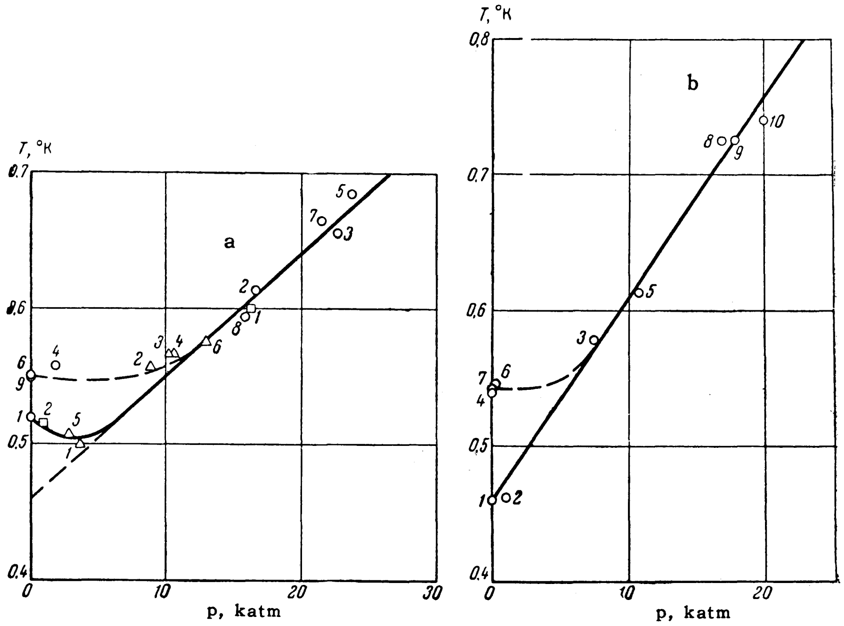

FIG. 3. Dependence of T_c on pressure: a) unannealed zirconium samples (o—sample No. 1, △—sample No. 2, □—sample No. 3); b) annealed zinc samples. Numbers at the points denote the sequence of compression cycles.

The dependence of the superconducting transition temperature on pressure for unannealed and annealed samples of zirconium is shown in Fig. 3. In the case of unannealed samples (Fig. 3a), the critical temperature first decreased with increase of pressure, then passed through a minimum at a pressure of about 3000 atm, and finally increased linearly with pressure. This nature of the variation of T_c in the pressure range up to 10,000 atm was satisfactorily reproduced in subsequent compression cycles. When the pressure exceeded 10,000—12,000 atm, a hysteresis appeared which caused the critical temperature to rise from 0.52 to 0.55° K after the removal of pressure. The value of dT_c/dp for unannealed samples amounted to about $+0.9 \times 10^{-5}$ deg/atm.

A stronger rise of the critical temperature was observed on compressing annealed samples (Fig. 3b). The pressure dependence of T_c was close to linear over the whole range of test pressures. After the removal of pressure, T_c increased irreversibly from 0.46 to ≈ 0.55° K. We note that the extrapolation of the linear portion of the $T_c(p)$ curve in Fig. 3a to zero pressure gives a value of T_c which is practically identical with the values of T_c of the samples immediately after annealing.

In interpreting the results obtained, we must bear in mind that the method used by us to apply the pressure may cause plastic deformation of the sample, as a result of which internal stresses may appear. The fall of T_c on annealing, as well as the rise of T_c after several compression cycles, are obviously a consequence of the relief and generation of internal stresses. It is possible also that a small drop of T_c in the case of unannealed samples is related to a redistribution of stresses at low pressures. Thus the nonlinear nature of the pressure dependence of T_c in the case of unannealed zirconium samples is most probably due to the presence of internal stresses in the samples, the limiting values of which should be of the order of 10,000 atm. It is natural to assume, therefore, that in annealed zirconium samples hydrostatic pressure in the region up to 25,000 atm would raise nearly linearly the critical temperature. It should be noted, however, that the reason for the different values of dT_c/dp for the annealed and unannealed samples of zirconium remains obscure. It is evident from Figs. 3a and 3b that the value of T_c of annealed samples increases by about 70% under a pressure of 20,000 atm and that of unannealed samples increases by 30% under a pressure of 24,000 atm.

Up to now, the only metal known to exhibit a rise of the critical temperature has been thallium.[2] The maximum rise of the critical temperature of thallium in the region from zero to 2000 atm amounts to 0.15%. On further increase of pressure, the quantity dT_c/dp of thallium changes its sign (cf., for example, [3]). It should also be noted that a positive value of dT_c/dp has been observed in several alloys, for example, Bi_3Ni, Bi_4Rh and Bi_2K.[4-6]

According to the microtheory of superconductivity

$$T_c \sim \exp\{-1/N(0)V\}, \tag{1}$$

where N(0) is the density of the electron states on the Fermi surface and V is a parameter which represents the electron—phonon interaction. According to Eq. (1), the main reason for the change in T_c under uniform compression is the change in the parameter N(0)V.

It follows from the semiqualitative theory[7] that for non-transition metals the product N(0)V should decrease with increase of the electron density, which does occur under uniform compression in cadmium.[1] In that case, the reduction of N(0)V is mainly due to a change in the parameter V.

The semiqualitative theory[7] is inapplicable to transition metals, which include zirconium. In these metals, a change in the density of states on the Fermi surface occuring under compression may play a very important role. The data obtained by Morin and Maita[8] indicate a very weak pressure dependence of the parameter V of transition metals and their alloys. The critical temperatures of the transition metals and their alloys investigated by Morin and Maita[8] have been found to be governed mainly by the density of d-electron states. From this point of view, the rise of T_c of zirconium under pressure should be due to an increase of N(0). The increase of N(0) due to the compression of zirconium is supported also by the change in the slope of the critical field curves (cf. Fig. 2).

As is known, the coefficient γ in the specific-heat law $C = \gamma T$ is proportional to N(0) and, according to thermodynamic reasoning, γ is proportional to the quantity $[(dH_c/dT)_{T_c}]^2$. We mentioned above that the value of $(dH_c/dT)_{T_c}$ of zirconium increases with increase of pressure. The average reversible increase of $(dH_c/dT)_{T_c}$ of zirconium amounts to 20—25% on increase of pressure from 0 to 20,000 atm. This is quite sufficient to explain the observed rise of T_c on compression. Such an interpretation of the results is also in good agreement with the work of Daunt[9] who used electronic specific-heat measurements to find the dependence of the density of d-electron states of transition metals on the number of valence electrons per atom. In the region close to zirconium, N(0) increases with increase in the number of valence electrons. Therefore, we may assume that N(0) of zirconium also increases on compression.

A similar effect should occur also in titanium, since this metal lies in the same region of the dependence of N(0) on the number of valence electrons as zirconium. We may expect the critical temperature of titanium to increase under pressure.

Finally, we take this opportunity to thank V. L. Ginzburg for discussing the results and N. N. Mikhaĭlov for kindly supplying pure zirconium.

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