



zirconium.  $\alpha$  phase: dotted line—first compression cycles (after pressure had exceeded 4.2 K.  $\omega$  phase: triangles. Inset: Comparison of the Zr-samples (10 to 90% of residual resistance) determined by the transition width of the lead nanometer

that this behaviour is a consequence of the technique, measurements were also made up to about 13 kbar. The results are in good agreement (circles). Since in the liquid cell pressures were used, the samples showed the same  $T_c(p)$  dependence as the solid cell on their first compression cycle. The differences between the two techniques were: the transition widths of the lead samples, which were practically constant with the liquid cell they increased slightly with pressure. The transition widths of the lead samples, which were practically constant with the liquid cell of  $\pm 0.3$  kbar at any

the described behaviour of the samples was observed. It is supposed that the samples

are in a perturbed lattice state, induced by the cold rolling. As in transition metals such a lattice perturbation is often accompanied by an increase in  $T_c$ , this would explain the relatively high  $T_c(0)$  of 0.66 K. The results seem to indicate, that high homogeneous pressures favour the annealing of these defects. Then the value  $dT_c/dp = 3.5 \times 10^{-6}$  K/bar will come closest to that of an unperturbed specimen. Another possible explanation would be the existence of another—probably metastable—phase. As will be pointed out below, the only other known high pressure phase,  $\omega$ -Zr, shows quite a different behaviour. Thus, the explanation in terms of phases would require the existence of a third phase.

In order to show the strong influence of lattice defects, they were deliberately produced in another experiment by altering the pressure at 4.2 K. The resulting  $dT_c/dp$  increased near 14 kbar to  $\sim 15.6 \times 10^{-6}$  K/bar (crosses). In addition, we observed a large irreversible shift in  $T_c$ : Upon releasing the pressure from 40 kbar at 4.2 K, we measured  $T_c(0) = 1.03$  K. While decreasing the pressure at 4.2 K a  $dT_c/dp$  of  $3.6 \times 10^{-6}$  K/bar was found, which equals the value determined by "tender" pressurizing at room temperature. If it is supposed that no further lattice defects are produced during removal of pressure, this result should be expected. Most important is the fact that the irreversible shift of  $T_c$  has disappeared after an annealing period of 24 h at room temperature. We may assume that the lattice defects which were generated at 4.2 K, and which are of influence on  $T_c$ , have disappeared during this time.

It remains to explain the bend in the  $T_c(p)$  dependence (crosses) near 14 kbar. This pressure corresponds approximately to the yield strength of Zr at low temperatures\*; above this pressure deformation is predominantly plastic, and lattice defects are produced at a higher rate. Another possibility is the existence of a phase transition at this pressure and 4.2 K, either into the already known  $\omega$ -Zr or into an as yet unknown phase. However, as will be shown in the next section,  $\omega$ -Zr, once formed, will not reconvert, even at room temperature, and so give rise to an irreversible change in  $T_c$ , which is stable against warming up to 300 K. Thus, the possible existence of a new low temperature—high pressure phase cannot be excluded.

Comparison of our results with those of Brandt and Ginzburg<sup>5</sup> shows that their value of  $dT_c/dp$  is about the same as in our cold work

\* Heavily deformed Zr has a 0.2%—yield strength of about 6 kbar at room temperature; at 4 K it is about twice as much<sup>14</sup>.

14 Gmelin's Handbuch der anorgan. Chemie, System Nr. 42, 8. Aufl. Weinheim: Verlag Chemie GmbH 1958.