

ing transition temperatures  $T_c(0)$  for zirconium from different authors

Crystal Samples condition and history  
Structure

Zr metal and paramagnetic salt mixed and pressed into a pill

Unannealed }  
Annealed } pressed into salt pill

Unannealed  
Heat treated at 970 K in He atmosphere  
After release of pressure from  $p > 10$  kbar

Machined from the as-cast sample after release of pressure from 45 kbar heat treated at 570 K;  
pressure  $5 \times 10^{-6}$  Torr

Retransformed from  $\omega$ -Zr at 570 K, pressure  $5 \times 10^{-6}$  Torr  
Retransformed from  $\omega$ -Zr at 1270 K, pressure  $5 \times 10^{-6}$  Torr

All sample surfaces coloured after heat treatment

After release of pressure from 65 kbar

Degassed and heat treated

Cut and cold rolled at 300 K after release of pressure from  $\geq 40$  kbar after release of pressure from  $\geq 50$  kbar Cold worked at 4.2 K up to  $\sim 40$  kbar

Cut and cold rolled at 300 K after heat treatment at 1070 K and  $10^{-10}$  Torr

Thin films evaporated at 370 K and  $5 \times 10^{-8}$  Torr

been performed.  
be compared with bulk transition temperatures, influence of lattice distortions on  $T_c$ .

le phase, and admixtures of other crystalline phases extending from 0.46 to 0.73 K can be found because of the complex behaviour involved, no

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satisfactory explanation can be given for the  $T_c(0)$  values found in the present investigation. Extended and painstaking metallurgical analyses will be necessary to solve this problem properly.

Of greater importance for our investigations is the influence of the above mentioned defects on the pressure dependence. The small amounts of impurities in our samples will presumably not alter the variation of  $T_c$  with pressure. However, lattice defects will affect the  $T_c(p)$  relationship quite drastically, as has been shown by the cold work experiments. Fortunately the residual resistance ratio as well as the transition width to the superconducting state provide means to control the grade of distortion of the samples. These same criteria also indicate the existence of a phase mixture. In our special case,  $\alpha$ - and  $\omega$ -Zr can be distinguished by their different  $T_c$  on  $p$  dependences. If in the low pressure region ( $\lesssim 45$  kbar)  $\omega$ -Zr were present in addition to  $\alpha$ -Zr, one would find  $T_c$  values corresponding to the extrapolated straight line of the  $\omega$  phase, since in electrical resistance measurements the higher of two transition temperatures will be detected.

#### Concluding Remarks

It has been shown that the earlier reported strong variation of  $T_c$  with pressure in zirconium<sup>5</sup> is drastically lowered when the production of lattice distortions during application of pressure is reduced. The complex  $T_c(0)$  and  $dT_c/dp$  behaviour is considered either a consequence of this sensitivity to lattice distortions or an indication of the existence of new high pressure phases other than  $\omega$ -Zr.

The positive slope  $dT_c/dp$  in elemental zirconium is expected, if one starts from the rigid band model and a former knowledge of the pressure effect in Zr-Nb alloys. The value of  $dT_c/dp$  determined in the present investigation agrees rather well with the results of Gey and Köhnlein<sup>4</sup>, when their data are extrapolated to  $n=4$ . As was supposed in these papers, a decrease in volume should have the same influence on  $T_c$  as adding electrons to the rigid conduction band. Since in Zr the Fermi energy is near a minimum of the density of states,  $N$  will increase rapidly on filling the conduction band<sup>23</sup>. Then it follows from the BCS-formula ( $T_c \propto \exp -1/NV$ ) that  $T_c$  will rise\*. A discussion in terms of the theory of McMillan<sup>1</sup> will fail at the time, because the pressure dependence of the important parameters  $\lambda$  and  $\mu^*$  is not well-known.

\* It is assumed that  $V$  is approximately constant and that in these metals the band structure is not strongly affected by the different crystal structures<sup>24</sup>.

23 Eastman, D. E.: Solid State Commun. 7, 1697 (1969).—Loucks, T. L.: Phys. Rev. 159, 544 (1967).

24 Merz, H., Ulmer, K.: Z. Physik 212, 435 (1968).