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ch nicht ermittelt werden. Weitere
em Ziel, die Bandenstrukturen besser
der Lichtentstehung aufzuklären.

. **89**, 1202 (1953). — Krisch, H.: Z. Physik

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Superconductivity
in α- and ω-Zirconium Under High Pressure

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The pressure dependence of the superconducting transition temperature $T_c(p)$ of α-Zr has been investigated in both solid and liquid pressure transmitting media. Up to about 45 kbar dT_c/dp was measured to be $+3.5 \times 10^{-6}$ K/bar. Cold working at 4.2 K produced a strong irreversible effect on T_c.

The superconductivity of the high pressure phase, ω-Zr, has been studied in its region of stability, i.e. above 60 kbar. For ω-Zr, $dT_c/dp = +7.7 \times 10^{-6}$ K/bar, and $T_c(0) = 0.72$ K (by extrapolation).

Introduction

The pressure dependence of the superconducting transition temperature T_c in non-transition metals can satisfactorily be explained within the framework of McMillan's theory[1] by the shift in phonon frequencies with pressure[2]. For transition metals, such a comprehensive description has not yet been found. It has been suggested[3] that dT_c/dp is governed by the shape of the d-band, expressed by the quantity dN/dn (N = electron density of states at the Fermi surface; n = number of valence electrons per atom). On this assumption the different signs of dT_c/dp in transition metals are easily understood. The connection between $T_c(p)$ and the shape of the d-band has been supported experimentally by measurements in the alloy series Zr-Nb-Mo[4], where the rigid band model is valid. It was suggested that application of pressure, i.e. reduction of volume, effects T_c in the same way as filling the conduction band by adding atoms of higher valency.

Since the investigations of Zr-Nb-Mo binary alloys were confined to the cubic (bcc) part of the series, the question remained whether the hexagonal part also exhibited some correlation between the effects of pressure and valence number. The investigation into the hcp region was begun with measurements on pure zirconium in order to compare

1 McMillan, W. L.: Phys. Rev. **167**, 331 (1968).
2 Olsen, J. L., Andres, K., Geballe, T. H.: Phys. Letters **26**A, 239 (1968).
3 Brandt, N. B., Ginzburg, N. I.: Soviet Phys.-Usp. **8**, 202 (1965).
4 Gey, W., Köhnlein, D.: Phys. Letters **29**A, 450 (1969). — Gey, W.: Z. Physik **229**, 85 (1969).

existing literature values[5] of $T_c(p)$ with values obtained using the same pressure technique as employed in the bcc alloy experiments. One great advantage of this technique is that pressure can be deliberately changed at any temperature between 300 K and 4.2 K. This permits the study of cold work effects, which will be shown to have a strong influence on T_c.

Experimental Techniques

Cryostat

Because of the low transition temperature of Zr at zero pressure[6] a He[3] cryostat was constructed. This cryostat, though conventional in principle, was adapted to meet the special requirements of the pressure apparatus used—in our case a pair of tongs[7]. A mechanism had to be provided, by which the tongs could be operated without being removed from the He[3] cryostat, so that the pressure could also be varied at helium temperatures. This was done by means of a stainless steel tube, which could be connected to the driving screw of the tongs like a socket wrench and disconnected after use in order to reduce the heat influx. Nevertheless, the heat transport was relatively high along the mechanically strong mounting support of the tongs, thus limiting the minimum temperature to about 0.4 K. Since the tongs were clamped mechanically to the He[3] bath, they could be replaced by any other pressure apparatus of the same dimensions.

Pressure Apparatus

Three different high pressure cells have been employed: a piston-cylinder cell with a solid pressure transmitting medium, another piston-cylinder cell with a liquid medium, and a Bridgman opposed anvil cell. The forces were generated by a pair of tongs[7] on the first type of cell and by a hydraulic ram in conjunction with a clamp technique[8,9] on the other cells. Although the pressure cells have been described in detail elsewhere, they shall be compared briefly.

In the so-called "teflon cell", a piston-cylinder cell containing a 1:1 fluid mixture of n-pentane and isoamyl alcohol[10], pressures will come closest to hydrostatic conditions (even though this liquid will freeze when cooled to helium temperatures). This fact is expressed

5 Brandt, N. B., Ginzburg, N. I.: Soviet Phys. JETP **19**, 823 (1964).
6 Roberts, B. W.: NBS Technical Note 408. Washington, D. C.: U.S. Government Printing Office 1966.
7 Buckel, W., Gey, W.: Z. Physik **176**, 336 (1963).
8 Chester, P. F., Jones, G. O.: Phil. Mag. 44, 1281 (1953).
9 Wittig, J.: Z. Physik **195**, 215 (1966).
10 Kim, K. S.: Rev. Sci. Instr. **41**, 1102 (1970).

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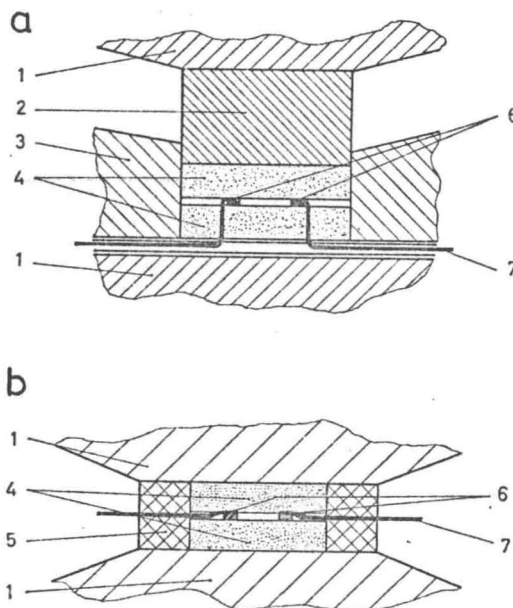ag. 44, 1281 (1953).

(1970).

Fig. 1. Pressure cells: *a*) piston-cylinder cell, *b*) Bridgman opposed anvil cell. *1* tungsten carbide anvils, *2* steel piston, *3* steel cylinder, *4* steatite discs, *5* pyrophyllite ring, *6* samples, *7* electrical leads (in type *a* isolated between mica sheets). The picture is schematical and not to scale

by the relatively narrow superconducting transition width, which is the same as at zero pressure. However, this cell is not as easy to handle as a solid cell and can present difficulties, especially if the samples have to be connected to potential and current leads for electrical resistance measurements. In our investigations it was only used to ensure that the results were not dependent on the pressure technique.

The cell used in the pressure tongs is constructed similarly[7]. It consists of a cylinder containing the pressure medium and of a piston, which will be pressed into the cylinder (Fig. 1a). Generally, this type of cell can be filled with liquid transmitting media. In our case, the dimensions of the cell surroundings, fitting into the tongs, only permit the use of solid media. If steatite is used, as is our common practice, the pressures may be regarded as "quasihydrostatic", because of the plasticity of steatite at high pressures, and also homogeneous, since the surrounding cylinder prevents the pressure medium from creeping away.

The opposed anvil cell (Fig. 1b) consists of two discs of steatite surrounded by a ring of pyrophyllite[9]. This cell is squeezed between

two parallel anvils of tungsten carbide, the lateral tightness coming
only from the friction of the pyrophyllite ring. Obviously the pressures
generated in this cell are neither ideally homogeneous nor hydrostatic.
This is reflected by the broad transitions to the superconducting state
observed with this cell. The advantage of this type of cell is the high
pressure ($\gtrsim$150 kbar) attainable, whereas the piston-cylinder arrangement
with tongs produces a maximum pressure between 50 and 60 kbar.

Samples and Procedures

The Zr samples were cut from a crystal bar of purity better than
99.9% (Koch-Light Labs.) and rolled at room temperature to 20 μm
thickness. For comparison, measurements on zone refined material
(Marz grade 99.97%, Materials Research Corporation) have been
performed*.

Temperatures in all experiments were monitored by carbon resistors,
which were mounted as close to the pressure cell as possible.

The transitions of the samples to the superconducting state were
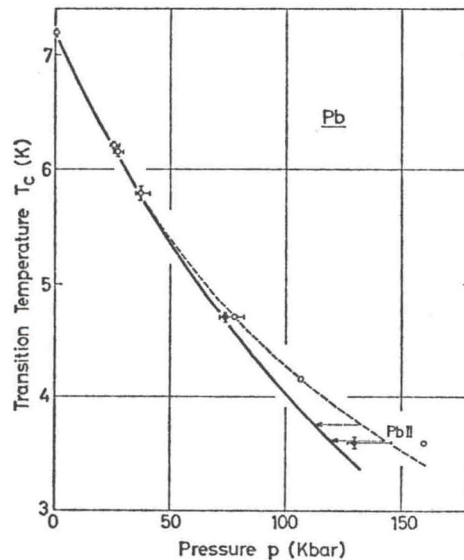detected by electrical resistance measurement.

Fig. 2. $T_c(p)$ dependence of lead, taking into account a recent correction of the high
pressure scale[12] (full line). This is not believed to represent a final recalibration of
the data of Ref.[11] (dotted line), but to show the trend of calibration change
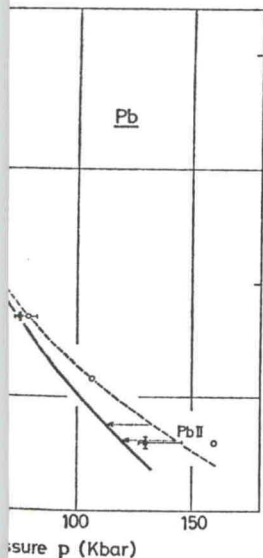
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The determination of pressure has been described earlier[11]: a lead sample serves as an internal manometer. The transition temperature of the lead sample defines the pressure, whereas the width of the transition indicates the inhomogeneity of pressure. The accepted pressure scale of phase transitions, which had been used in the calibration of the lead manometer[11], has been revised recently[12]. This gives rise to a shift of the $T_c(p)$ curve of Pb as shown in Fig. 2. The shift is not significant at pressures below 50 kbar. Our experimental points at higher pressures, however, have been derived from the revised $T_c(p)$ curve.

With the exception of the cold work experiments, pressures have always been varied at room temperature. It is known that, depending on the purity of the material, up to 70% of the change in residual resistance produced by cold work may disappear in an annealing period of 5 min at room temperature[13]. Hence we waited about 24 h before cooling down. This period is supposed to be sufficient for the annealing of lattice defects which had been produced during pressurizing.

Results and Discussion

The discussion of the results, collected in Fig. 3, will be divided into two parts, corresponding to the phase diagram of zirconium. At normal pressure, Zr is hexagonal (hcp). The transition temperatures of this α phase are less than 1.2 K over the entire pressure range of its stability. Between 50 and 60 kbar at room temperature, Zr undergoes a phase transition to the ω phase, the properties of which will be discussed in greater detail below.

α-Zirconium

T_c depends linearly on p in the whole pressure region investigated. There is, however, a distinct influence of sample history. Samples measured immediately after preparation ($T_c(0) = 0.66$ K) show a reversible pressure dependence of T_c up to approximately 40 kbar with $dT_c/dp = 5.4 \times 10^{-6}$ K/bar (dotted line), and a residual resistance ratio $\Gamma = R(300\ \text{K})/R(4.2\ \text{K}) = 17$. As soon as the pressure exceeded about 40 kbar, Γ increased to 25 and T_c was markedly lowered. After the pressure had been removed, Γ remained above 20. Moreover a new $T_c(0)$ is observed, lower by 0.02 K than the original value. In a second compression cycle a slope $dT_c/dp = 3.5 \times 10^{-6}$ K/bar is measured. The enlarged residual resistance ratio increases again slightly near 40 kbar, but $T_c(0)$ and dT_c/dp are uneffected by further cycling.

11 Eichler, A., Wittig, J.: Z. Angew. Phys. 25, 319 (1968).
12 Drickamer, H. G.: Rev. Sci. Instr. 41, 1667 (1970).
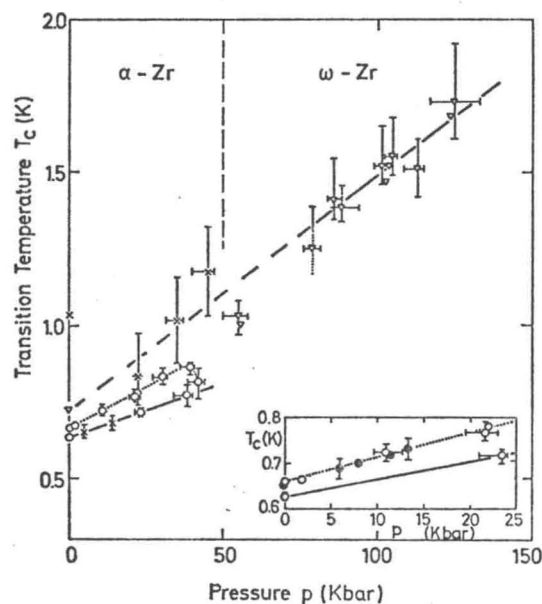13 Swanson, M. L.: Can. J. Phys. 44, 3241 (1966).

Fig. 3. Pressure dependence of T_c in zirconium. α phase: dotted line—first compression run, full line—further compression cycles (after pressure had exceeded ~40 kbar), crosses-cold work run at 4.2 K. ω phase: triangles. Inset: Comparison of data obtained with liquid cell (full circles) and steatite cell (open circles). The error bars indicate the transition widths of the Zr-samples (10 to 90% of residual resistance) and the uncertainty of pressure determined by the transition width of the lead manometer

Since it could be suspected that this behaviour is a consequence of our solid medium pressure technique, measurements were also performed with a liquid cell up to about 13 kbar. The results are included in Fig. 3 (Inset, full circles). Since in the liquid cell pressures near 40 kbar could not be attained, the samples showed the same $T_c(p)$ dependence as the samples in the solid cell on their first compression run. The only differences observed between the two techniques were: 1. the scatter in the experimental points was less with the liquid cell, 2. the transition widths of the samples were practically constant with the liquid cell, whereas with the solid cell they increased slightly with increasing pressure. From the transition widths of the lead samples, we deduced a pressure uncertainty in the liquid cell of ± 0.3 kbar at any pressure.

From this we infer that the described behaviour of the samples is an intrinsic property of the material. It is supposed that the samples

ω - Zr

0.8
$T_c(K)$
0.7
0.6
0   5   10   15   20   25
              p (Kbar)

50   100   150

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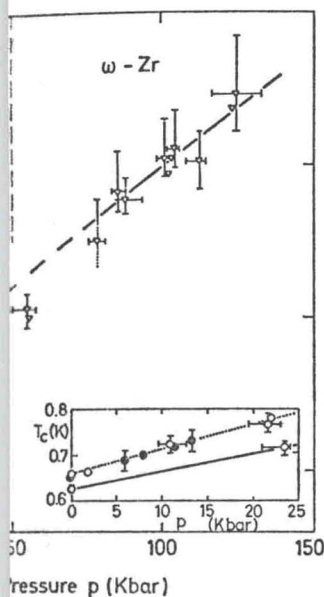
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4.2 K. ω phase: triangles. Inset: Comparison
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are in a perturbed lattice state, induced by the cold rolling. As in transi-
tion metals such a lattice perturbation is often accompanied by an
increase 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, ω-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 3.6×10^{-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 dis-
appeared 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 ω-Zr or into an as
yet unknown phase. However, as will be shown in the next section,
ω-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 temper-
ature—high pressure phase cannot be excluded.

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

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* Heavily deformed Zr has a 0.2%—yield strength of about 6 kbar at room tem-
perature; at 4 K it is about twice as much[14].
14 Gmelin's Handbuch der anorgan. Chemie, System Nr. 42, 8. Aufl. Weinheim:
Verlag Chemie GmbH 1958.

experiment*. Presumably, this is a consequence of their pressure technique. In their so-called ice bomb technique pressures are only generated on cooling down, which prevents the simultaneously grown lattice defects from healing up. It is worth noting that these authors also observed a bend in the $T_c(p)$ curve near the yield strength.

ω-Zirconium

ω-Zr is a hexagonal phase with three atoms per unit cell[15,16]. Because of its crystallographic similarity it is supposed that its formation from the high temperature phase β-Zr (bcc) is diffusionless. It is not yet clear, if it forms in this way from the α phase, too[17]. The transition from α to ω-Zr occurs at a pressure between 50 and 60 kbar at room temperature. The electrical resistance, which increases with pressure in α-Zr, is reported to decrease sharply at the transition by about 18%, but in some of these experiments no such drop is observed at all[17]. Of the superconducting properties of ω-Zr only T_c in the metastable state at zero pressure had been measured before[18].

We have investigated the pressure dependence of T_c of the ω phase mainly to determine its possible influence on the low pressure behaviour, described above. As the transition pressure is comparable to the maximum pressure of the piston-cylinder cell in the tongs, most of the attempts to reach the transition by this technique failed because the cells fractured. There were only two successful experiments, in which the pressure came close to the transition pressure. In none of them any drop in resistance could be observed. But both samples showed a strongly reduced residual resistance ratio as well as an enhanced $T_c(p)$, lying distinctly above the extrapolated $T_c(p)$ curve for the α phase. After release of pressure and subsequent annealing at room temperature $T_c(0)$ of one of the samples was 0.72 K. The other sample was damaged on removal of pressure.

To generate pressures above the α to ω transition, the opposed anvil cell was used. The corresponding clamp apparatus did not fit into the He^3 cryostat and could thus only be cooled in a He^4 dewar. Therefore, T_c values near the phase transition could not be determined. It is unfortunate that the available experimental equipment leaves a gap, both with respect to pressure and temperature, just in the inter-

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* They report a $dT_c/dp = 9 \times 10^{-6}$ K/bar for unannealed and $dT_c/dp = 15 \times 10^{-6}$ K/bar for heat treated samples[5].

15 Jamieson, J. C.: Science 140, 72 (1963).
16 Hatt, B. A., Roberts, J. A.: Acta Met. 8, 575 (1960).
17 Jayaraman, A., Klement, W., Jr., Kennedy, G. C.: Phys. Rev. 131, 644 (1963).
18 Tittmann, B., Hamilton, D., Jayaraman, A.: J. Appl. Phys. 35, 732 (1964).

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Kennedy, G. C.: Phys. Rev. **131**, 644 (1963).

man, A.: J. Appl. Phys. **35**, 732 (1964).

esting transition region. The observed dependence of the electrical
resistance on the pressure was as follows: In a first compression run R
increased until the transition was reached, whereupon it decreased.
This drop, however, was in none of the cases as great as could be ex-
pected. With further increase of pressure R decreased slightly. Any
sample, once compressed above 55 kbar, showed a monotonic decrease
of R from $p=0$ up to the highest attainable pressures in each following
experiment and a corresponding increase of R upon lowering of pressure.
This behaviour corroborates the observation, that the transformation
from ω-Zr to α-Zr is strongly retarded.

The experimental points for $T_c(p)$ of the ω phase can be approxi-
mated by a straight line, determined by a least squares fit, with the slope
$dT_c/dp=7.7\times10^{-6}$ K/bar. The broad superconducting transitions as
well as a small residual resistance ratio of about 8 indicate a highly
disturbed state of the samples, but annealing at room temperature is
of no influence on T_c. If the straight line is extrapolated to zero pressure,
$T_c(0)=0.72$ K is found. Although the agreement with the value gained
by the piston-cylinder technique* is good, it should not be overestimated
because of the uncertainties of such an extrapolation. It should be noted
that our value disagrees with that of Tittmann et al.[18] for metastable
ω-Zr ($T_c(0)=0.65$ K).

Measurements with zirconium from another stock have been performed. This
sample showed an unusually high $T_c(0)=0.8$ K, but a dT_c/dp comparable with that
of the Koch-Light Zr in the pressure range below 50 kbar. On the other hand, for
ω-Zr $dT_c/dp=11.3\times10^{-6}$ K/bar, which is distinctly greater than the corresponding
value for Koch-Light material. We have no explanation for this at present.

Induced by the high $T_c(0)$-values, efforts were made to anneal cold rolled and
trimmed samples in an ultrahigh vacuum of 10^{-10} Torr at about 1070 K, a few
degrees below the transition temperature into the cubic, high temperature β phase**.
If the high $T_c(0)$ were caused by lattice defects, this procedure should result in a
lowering of these values. This was the case ($T_c(0)=0.5$ K for MRC-Zr after heat
treatment), but at the same time the residual resistance ratio was as low as 4, so that
a contamination of the samples had to be supposed. This can be understood by the
well known gettering properties of zirconium. The slope dT_c/dp after heat treatment
was about twice the previous value of 3.5×10^{-6} K/bar. The lowering of T_c and raise
of dT_c/dp agrees with the behaviour observed by Brandt and Ginzburg[5] after heat
treatment and might suggest that their annealed samples had also been contaminated.
Unfortunately, these authors do not report data of their residual resistance ratio.

The correct value of $T_c(0)$ for Zr is as yet an open question, even though the
value 0.55 K is commonly accepted. T_c is influenced by such phenomena as im-

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* It cannot be stated unequivocally that the sample referred to had totally trans-
formed into ω.

** We want to thank Dr. P. Flécher and Mr. R. Vincon, Institut für Experimentelle
Kernphysik, Universität Karlsruhe, for the performance of this annealing treat-
ment.

A. Eichler and W. Gey:

Table 1. Comparison of superconducting transition temperatures $T_c(0)$ for zirconium as obtained from different authors

Refer-ence	Purity of stock material	$T_c(0)$ [K]	Crystal struc-ture[a]	Samples condition and history
19	—	0.70	—	Zr metal and paramagnetic salt mixed and pressed into a pill
20	99.9%	0.565 0.546	— —	Unannealed Annealed } pressed into salt pill
5	99.99%	0.52	—	Unannealed
		0.46	—	Heat treated at 970 K in He atmosphere
		0.55	—	After release of pressure from $p > 10$ kbar
18	99.95%	0.73	α	Machined from the as-cast sample
		0.70	α	after release of pressure from 45 kbar
		0.61	α	heat treated at 570 K; pressure 5×10^{-6} Torr
		0.60	α	Retransformed from ω-Zr at 570 K, pressure 5×10^{-6} Torr
		0.55	α	Retransformed from ω-Zr at 1270 K, pressure 5×10^{-6} Torr. All sample surfaces coloured after heat treatment
		0.65	ω	After release of pressure from 65 kbar
21	isotopes	0.49	—	Degassed and heat treated
This work	99.9% Koch-Light Labs.	0.66 0.63_5 0.72 1.03	— — — —	Cut and cold rolled at 300 K after release of pressure from $\gtrsim 40$ kbar after release of pressure from $\gtrsim 50$ kbar Cold worked at 4.2 K up to ~ 40 kbar
	99.97% MRC	0.8 0.5	— —	Cut and cold rolled at 300 K after heat treatment at 1070 K and 10^{-10} Torr
22	99.95%	1.3[b]	α	Thin films evaporated at 370 K and 5×10^{-8} Torr

[a] Included only, if X-ray analysis had been performed.
[b] This T_c value should actually not be compared with bulk transition temperatures, but it does illustrate the strong influence of lattice distortions on T_c.

purities, lattice defects within a single phase, and admixtures of other crystalline phases. As a consequence, α phase values extending from 0.46 to 0.73 K can be found for T_c in the literature (Table 1). Because of the complex behaviour involved, no

19 Kürti, N., Simon, F.: Proc. Roy. Soc. (London), Ser. A 151, 610 (1935).
20 Smith, T. S., Daunt, J. G.: Phys. Rev. 88, 1172 (1952).
21 Bucher, E., Müller, J., Olsen, J. L., Palmy, C.: Phys. Letters 15, 303 (1965).
22 Friebertshauser, P. E., McCamont, J. W.: J. Vacuum Sci. Technol. 6, 184 (1969).

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

rystal ruc- re[a]	Samples condition and history
	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 5×10^{-6} Torr Retransformed from ω-Zr at 570 K, pressure 5×10^{-6} Torr Retransformed from ω-Zr at 1270 K, pressure 5×10^{-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 $\gtrsim 40$ kbar after release of pressure from $\gtrsim 50$ kbar Cold worked at 4.2 K up to ~ 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 5×10^{-8} Torr

been performed.
e compared with bulk transition temperatures,
uence of lattice distortions on T_c.

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

oc. (London), Ser. A **151**, 610 (1935).
ev. **88**, 1172 (1952).
Palmy, C.: Phys. Letters **15**, 303 (1965).
J. W.: J. Vacuum Sci. Technol. **6**, 184 (1969).

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, α- and ω-Zr can be distinguished by their different T_c on p dependences. If in the low pressure region ($\lesssim 45$ kbar) ω-Zr were present in addition to α-Zr, one would find T_c values corresponding to the extrapolated straight line of the ω 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[5] 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 ω-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[4], 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[23]. 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[1] will fail at the time, because the pressure dependence of the important parameters λ and μ^* is not well-known.

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* 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[24].

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).

More definite conclusions have to be postponed until high pressure measurements on Zr-rich Zr-Nb alloys have been performed.

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