$\perp H_0, \hat{H} /\!/ H_0$) and
ch showed that α and π are
fying the magnetic dipole
ions. The sideband 58.5
ry little with polarization
ed indicate that α and σ
an electric dipole charac-

on is suggested as a mag-
$_1 \rightarrow {}^4T_1$ transition, in a
interpretation of the 56
blue [1,2]. The peak at
vever, is less than the
rgy of 72 cm^{-1} found by
This discrepancy is
bations of the magnon fre-
o the presence of the near-
n.

Geschwind, D. D. Sell and
pful discussions. The ex-
of M. B. Graifman is grate-

ev. 152 (1966) 531.
. Popkov, V. P. Novikov and
sp. i Teor. Fiz. 52 (1967) 454.
s. Chem. Solids 7 (1958) 201.
e and R. M. White, Phys. Rev.

eiser and R. W. H. Stevenson,
(1962) 212.
ce, Phys. Rev. 150 (1966) 377.
V. H. Stevenson, Proc. Phys.

$\partial T_c/\partial P$ FOR TECHNETIUM AND A COMMENT ON ITS SIGN IN RELATION TO THE OTHER TRANSITION METAL SUPERCONDUCTORS

C. W. CHU *
Institute for Pure and Applied Physical Sciences
and Department of Physics, University of California, San Diego, La Jolla, California, USA

W. E. GARDNER and T. F. SMITH
Solid State Physics Division, Atomic Energy Research Establishment, Harwell, Didcot, Berkshire, UK

Received 3 April 1968

The pressure dependence of the superconducting transition temperature of technetium has been measured up to a pressure of 15 kbar and found to be $-1.25 \pm 0.05 \times 10^{-5}$ °K/bar.

Measurements have been made of the pressure dependence of the superconducting transition temperature, T_c, of technetium up to a pressure of 15 kbars. Two samples ‡ (Tc1 and Tc2) of 99% nominal purity technetium (obtained from the Oak Ridge National Laboratory) were examined and zero pressure values for T_c of 8.00 ± 0.01°K and 7.924 ± 0.01°K respectively were determined. The pressure measurements on Tc1 were made using a pressure transmitting medium of powdered teflon. The superconducting transitions observed after the application of pressure, exhibited a broadening of the onset of superconductivity. A slight shift to higher temperatures of the zero pressure transition upon the removal of the pressure was also noted. This behaviour is similar to that observed for rhenium [2], but, in the case of technetium, does not present so serious a problem in the determination of the pressure dependence since the irreversible change of T_c is small relative to the reversible pressure-induced change. Nevertheless, an attempt was made to improve the reversibility of the measurements for Tc2 by using the more hydrostatic environment provided by a 1:1 mixture of n-pentane and isoamyl alcohol which proved so successful for the measurements on rhenium. Although this did produce an appreciable improvement in the reversibility of the zero pressure transition, little reduction of the pressure induced broadening of the transition was achieved. The change of T_c with pressure for both samples is shown in fig. 1 and from this plot a value of $\partial T_c/\partial P = -1.25 \pm 0.05 \times 10^{-5}$ °K/bar is obtained.

It has been noted for some time that the magnitude of T_c for the transition metals and their alloys follows the same periodic variation as the coefficient γ of the electronic specific heat (which is a measure of the density of electron states $N(0)$ at the Fermi surface in the normal state) between group IVB and Group VIIB [3,4] †. With this observation in mind and on the basis of pressure measurements on Ti, Zr and the alloys $Mo_{90}Re_{10}$ and $Nb_{75}Mo_{25}$, Brandt and Ginzburg [6] have proposed that the sign of $\partial N(0)\partial P$ and hence that of $\partial T_c/\partial P$ is the same as that for $\partial N(0)/\partial n_v$ where n_v is the total number of valence electrons. Although the present measurements indicate that this correlation holds for technetium, measurements for V [7,8], V + Cr [7] alloys, Nb [7-9] and Mo [10] do not follow this proposal and thus the correlation suggested by Brandt and Ginzburg would not appear to hold generally. Indeed there is no obvious reason to suppose that the effects on the density of states of applying pressure and the addition of extra electrons

‡ Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR grant number AF-AFOSR-631-67.
‡ We are indebted to Dr. G. R. Love for the loan of Tc2. This sample has a resistance ratio of 60-90, and a purity similar to that reported by Sekula et al. [1] for thei samples of Tc.

† It has recently been shown that T_c does not follow the same variation as γ in the Re-Os, Ru-Os systems [5].

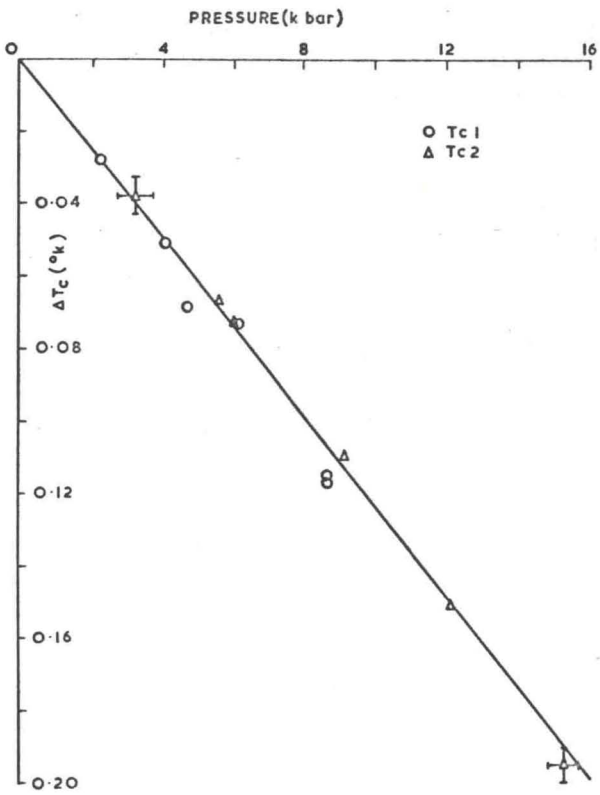

Fig. 1. Variation of superconducting transition temperature as a function of pressure for technetium.

should be equivalent. Furthermore, from general considerations we would expect the density of electron states at the Fermi surface to decrease with the application of pressure, and the available thermal expansion measurements [11] on transition metal elements, including Ti, V and Nb support this conclusion.

It is evident from the present measurement for Tc, combined with the previous measurements for Ta [8,12] Mo [10], Re [2] and Os [13] all of which have negative pressure dependences and Ru [13], which has a zero pressure dependence, that positive values of the pressure dependence of T_c only occur among the early 3d and 4d members of the transition series. Thus if, as suggested [7], this possible pressure dependence is associated with a decrease in the repulsive Coulomb interaction then the effect on T_c of such a decrease for the later transition elements must be more than compensated for by other changes (most probably by a decrease in the density of states).

References

1. S. T. Sekula, R. H. Kernohan and G. R. Love, Phys. Rev. 155 (1967) 364.
2. C. W. Chu, T. F. Smith and W. E. Gardner, Phys. Rev. Letters 20 (1968) 198.
3. B. T. Matthias, Phys. Rev. 97 (1955) 74.
4. B. R. Coles, Solid State Comm. 1 (1963) 5.
5. C. W. Chu, H. L. Luo, T. F. Smith and W. E. Gardner, A. P. S. Bulletin 13 (1968) 401.
6. N. B. Brandt and N. I. Ginzburg, Zh. Eksp. i Teor. Fiz. 46 (1964) 1216: 49 (1965) 1706: 51 (1966) 59. Soviet Physics JETP 19 (1964) 823: 22 (1966) 1167 24 (1966) 40.
7. W. E. Gardner and T. F. Smith, Phys. Rev. 144 (1966) 233:
C. W. Chu and T. F. Smith, unpublished.
8. W. Gey and G. Van Heyden, Z. Physik 193 (1966) 6
9. D. Köhlein, Z. Physik 208 (1968) 142.
10. J. L. Olsen, E. Bucher, M. Levy, J. Muller, E. Corenzwit and T. H. Geballe, Rev. Mod. Phys. 36 (1964) 168:
C. Palmy, private communication.
11. G. K. White, Cryogenics 2 (1962) 292:
K. Andres, Phys. Kond. Mat. 2 (1964) 294.
12. L. D. Jennings and C. A. Swenson, Phys. Rev. 112 (1958) 31.
13. E. Bucher, J. Müller, J. L. Olsen and C. Palmy, Cryogenics 5 (1965) 283.

* * * * *