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Effect of Pressure on Superconductivity in Transition Metal Alloys*

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Measurements on twelve alloys of the series Zr-Nb-Mo show a close correlation of dT_c/dp with the d-band structure of these alloys and suggest that the d-band is virtually rigid with respect to pressure. The results are not compatible with an empirical observation of McMillan that T_c is governed only by a phonon factor $M\omega^2$.

Introduction

The reaction of superconductivity of transition metals and their alloys to volume changes caused by the application of hydrostatic pressure is complex. Positive and negative signs of dT_c/dp and nonlinearities in $T_c(p)$ have been observed for the various superconductors of this group[1]. Attempts to correlate this behaviour with irregularities in the isotope effect of these metals are made increasingly difficult by a growing body of experimental facts[2]. Also, a correlation of dT_c/dp with the band structure could only be seen for a few selected metals and alloys[3,4].

In contrast, the situation is much simpler in superconducting non transition metals, in which the transition temperatures decrease nearly

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1 For a compilation of relevant data see: Brandt, N. B., Ginzburg, N. I.: Soviet Phys. Usp. **8**, 202 (1965). — More recent work on transition metals: Gardner, W. E., Smith, T. F.: Phys. Rev. **138**, A484 (1965); ibid. **140**, A1620 (1965); ibid. **144**, 233 (1966); ibid. **146**, 291 (1966). — Bucher, E., Müller, J., Olsen, J. L., Palmy, C.: Cryogenics **5**, 283 (1965). — Gey, W., Heyden, G. v.: Z. Physik **193**, 65 (1966). — Köhnlein, D.: Z. Physik **208**, 142 (1968). — Andres, K.: Phys. Rev. **168**, 708 (1968). — Chu, C. W., Smith, T. F., Gardner, W. E.: Phys. Rev. Letters **20**, 198 (1968). — Chu, C. W., Gardner, W. E., Smith, T. F.: Phys. Letters **26**A, 627 (1968).

2 Bucher, E., Müller, J., Olsen, J. L., Palmy, C.: Cryogenics **5**, 283 (1965).

3 Brandt, N. B., Ginzburg, N. I.: Soviet Phys. Usp. **8**, 202 (1965).

4 Brandt, N. B., Ginzburg, N. I.: Soviet Phys. JETP **24**, 40 (1967).

linearly with pressure[1,5]. An empirical rule has been established for these metals[6] which more recently has received semiquantitative justification[7,8] by use of a simplification of McMillan's theoretical formula for T_c[9]. Although not yet fully satisfactory, because use of the full expression for T_c makes the agreement worse[8], this approach certainly indicates the direction in which the solution for the simple metals is to be found.

In an attempt to detect similarly a unifying principle for the divergent behaviour of transition metals under pressure, the alloy series Zr-Nb-Mo was chosen on the following grounds:

1. The series is homologous in structure (bcc) from $Zr_{80}Nb_{20}$ to molybdenum[10]. 2. Only 4-d elements are involved. The rigid-band-model has been shown to be valid[11]. 3. Data on the electronic specific heat coefficient γ and on the Debye characteristic temperature θ exist for almost the whole composition range[12]. 4. Data on dT_c/dp for Zr, Nb, and $Nb_{75}Mo_{25}$ were already available. Those on Nb from different authors were not in complete accord[13,14]. 5. Presumably no effects of electron-magnon interactions obscure the situation[15]. Our main result is that for all alloys the variation of T_c with pressure is governed by the shape of the d-band.

Experiment

Pressure

The apparatus used for generation of high pressure has been described earlier[16]. The linear dimensions of the pressure tongs have been increased by a factor of approximately 1.5 which permits the use of a piston-

5 At first sight Tl appears to be an exception since in this case T_c passes through a flat maximum. It seems to be confirmed, however, that this maximum is due to a superposition of two monotonic functions. After subtraction of the one, which stems from a pressure dependent gap anisotropy, Tl also shows a nearly linear decrease of T_c with p. Gey, W.: Phys. Rev. **153**, 422 (1967).

6 Rohrer, H.: Helv. Phys. Acta **33**, 675 (1960).
7 Olsen, J. L., Andres, K., Geballe, T. H.: Phys. Letters **26**A, 239 (1968).
8 Gey, W.: Unpublished.
9 McMillan, W. L.: Phys. Rev. **167**, 331 (1968).
10 Berghout, C. W.: Phys. Letters **1**, 292 (1962).
11 Merz, H., Ulmer, K.: Z. Physik **210**, 92 (1968).
12 Heiniger, F., Bucher, E., Muller, J.: Phys. kondens. Materie **5**, 243 (1966).
13 Brandt, N. B., Ginzburg, N. I.: Soviet Physics JETP **19**, 823 (1964); ibid. **24**, 40 (1967).
14 Gardner, W. E., Smith, T. F.: Phys. Rev. **144**, 233 (1966). In this paper the slope dT_c/dp for niobium was reported to be zero, in contrast to the findings of Ref. [17]. More recently Smith has also obtained a positive value (private communication).
15 Jensen, M. A., Maita, J. P.: Phys. Rev. **149**, 409 (1966).
16 Buckel, W., Gey, W.: Z. Physik **176**, 336 (1963).
17 Gey, W., Heyden, G. v.: Z. Physik **193**, 65 (1966). — Köhnlein, D.: Z. Physik **208**, 142 (1968).

cylinder type cell of 3.0 mm diameter. This slight increase in cell dimensions facilitates the mounting of an additional lead sample which is used as a manometer by recording its superconducting transition temperature[17]. Calibration in the pressure range up to 10 kbar is done by comparison with the data of Jennings and Swenson on Sn and In[18], which were considered to be the most reliable. Above 10 kbar direct pressure reference points are hard to attain. Solid-solid phase transitions which prove to be useful at room temperature must be used with care because of the temperature dependence of the transformation pressure and of pressure changes during cooling. In the pressure regime up to 40 kbar we therefore rely primarily on the linearity of our strain gauge – bent beam combination. We have checked this instrument with the phase transformation in thallium whose temperature dependence, measured between 300 and 90 °K, was found to be linear and was extrapolated to 0 °K. The value of 34.5 kbar so obtained is in good agreement with the extrapolated strain gauge data (35.0 kbar). In this regime we estimate the accuracy of the pressure measurement to be $\pm 1.5\%$. For pressures between 40 and 80 kbar we use the calibration data obtained in this laboratory[19]. In this region the uncertainty rises with pressure up to an estimated value of $\pm 4\%$.

The gain in maximum pressure (80 kbar as compared with 50 kbar in the earlier equipment) is mainly due to a hard steel ring of 6.0 mm o.d. which is pressed into the softer main cylinder. This ring usually suffers fine cracks when a pressure of 50–60 kbar is reached, but still distributes the force and reduces it at its circumference.

Alloys

Nine binary alloys from $Nb_{40}Zr_{60}$ to $Nb_{73}Mo_{27}$ were made from starting materials specified as follows: Nb 99.9% rod, Koch-Light Labs.; Mo 99.95% rod, Johnson-Matthey; Zr 99.5% sponge, W. C. Heraeus. All metals were outgassed before alloying by melting in an electron beam furnace in vacuum of $10^{-5}-5\cdot 10^{-5}$ Torr. The same vacuum conditions were maintained during preparation of the alloys which was performed by casting four times. Maximum weight loss was 4.5% which probably did not affect the composition. The buttons were cut on a diamond saw and cold rolled to ribbons of 0.05 mm thickness from which the rectangular samples ($2.5\times 0.1\times 0.05$ mm) were prepared. The transition temperatures of the Zr-rich niobium alloys were higher than

18 Jennings, L. D., Swenson, C. A.: Phys. Rev. **112**, 31 (1958).

19 Eichler, A., Wittig, J.: Z. angew. Phys. **25**, 319 (1968).

those reported by Hulm and Blaugher[20] by 0.1 to 0.5 °K. For this reason the transition to superconductivity was studied for some of these alloys by an induction method in addition to the usual resistive method. Rods were used as well as ribbons; the latter were mounted in different ways (straight along the axis of the induction coil and rolled around this axis). The maximum scatter of the measured T_c amounted to only ± 0.08 °K. Further support for the homogeneity of the alloys is derived from the sharpness of the transition observed in specific heat measurements[21].

Special efforts were made to purify niobium. This was achieved by electric heating of $0.03 \times 4\ mm^2$ ribbons in ultra-high vacuum (better than 10^{-10} Torr) for five hours, gradually approaching the melting point. For this purpose that part of the glass vacuum apparatus which contained the ribbon was immersed in liquid nitrogen, thus acting as an additional cryopump. The residual resistance ratio $\Gamma = R_{10\,°K}/R_{300\,°K}$ was lowered in this way from 1/20 to 1/2100.

Measurements of Γ (ribbons) and Vickers hardness HV (buttons) for all alloys are plotted in Fig. 1 versus number n of valence electrons per atom at zero pressure*. Except for the sharp singularity for pure niobium, both quantities show no peculiarities, which is indicative of having a single phase in each of the two binary alloy series, Nb-Zr and Nb-Mo. This is corroborated by X-ray diffraction data which show, in accordance with[10], pure β-phase (bcc) for the complete alloy series. Values of the lattice constant a obey Vegard's law[22] with change in slope at $n=5$ (Fig. 1).

Two ternary alloys $Nb_{96}Zr_2Mo_2$ and $Nb_{63}Zr_{14}Mo_{23}$ with $n=5.0$ and 5.09, respectively, were also made. As expected, both hardness and resistance ratio differ from those for pure niobium and a Nb-Mo alloy of same n. It is interesting, however, that the lattice constant for $Nb_{63}Zr_{14}Mo_{23}$ falls off a Vegard's line by an amount far outside experimental error. In all relevant diagrams the data points of the ternary alloys are printed as triangles.

For niobium it had been noticed that the variation of T_c with pressure is very sensitive to lattice defects generated when pressure is applied at temperatures of liquid helium[17]. This is now found to be true also for the niobium-rich alloys $Nb_{96}Zr_4$, $Nb_{96}Mo_4$, and for the ternary alloy $Nb_{96}Zr_2Mo_2$. Irreversibilities due to the above effect were avoided in these cases by application of pressure at temperatures near 300 °K,

* n is thus defined by the chemical composition. It is not to be confused with the actual electron concentration which may be pressure dependent.

20 Hulm, J. K., Blaugher, R. D.: Phys. Rev. **123**, 1569 (1961).
21 Dummer, G.: Unpublished.
22 Vegard, L.: Z. Physik **5**, 17 (1921).

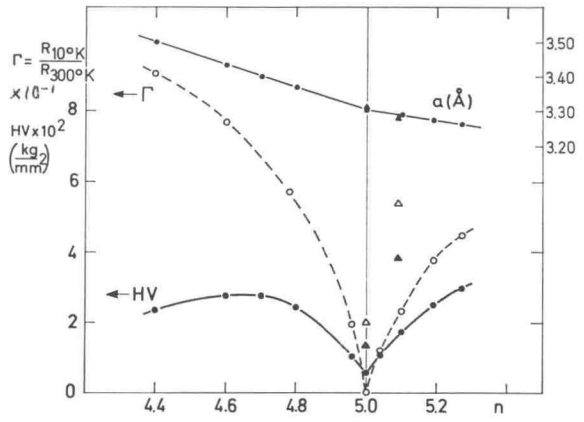

Fig. 1. Plotted versus number n of valence electrons per atom are: Lattice constant a, residual resistivity ratio Γ, and Vickers hardness HV. Data on ternary alloys are marked by triangles

which makes the experiment rather helium- and time-consuming, since every single data point $T_c(p)$ requires warming up and cooling of the apparatus. Fortunately it was no longer necessary for alloys with $n \leqq 4.8$ and $n \geqq 5.1$.

Results and Discussion

The measured variation of T_c with pressure is typical of transition metals in its complexity, as is shown in Fig. 2. For niobium and the niobium-rich alloys a pronounced kink occurs in the otherwise linear $T_c(p)$ behaviour. For example, in niobium T_c increases linearly with pressure from $p=0$ to 21 kbar by 0.23 °K, but does not change within 25 mdeg in the range of 24 to 73 kbar. For Nb-Zr alloys with 20, 40, and 60 at% Zr and for $Nb_{73}Mo_{27}$ no kink is observed; $T_c(p)$ is nearly linear for all pressures. In order not to obscure the diagram, data points are printed only for $Nb_{90}Mo_{10}$ and $Nb_{81}Mo_{19}$. Transition widths (10 to 90% of full resistivity) are indicated by bars at several points. Both scatter of the data points and transition widths are representative of those for all other alloys.

The jungle of information contained in Fig. 2 is easily unraveled by plotting versus n the slopes $d\ln T_c/dp$ for $p<20$ kbar and $p>25$ kbar (Fig. 3). The occurence of the kink in $T_c(p)$ for the niobium-rich alloys is represented by splitting of $d\ln T_c/dp$ into two branches. We discuss first the results for $p>25$ kbar where the slope $d\ln T_c/dp$ decreases monotonically with increasing number n of valence electrons per atom at zero pressure. Included in Fig. 3 are other relevant parameters. One

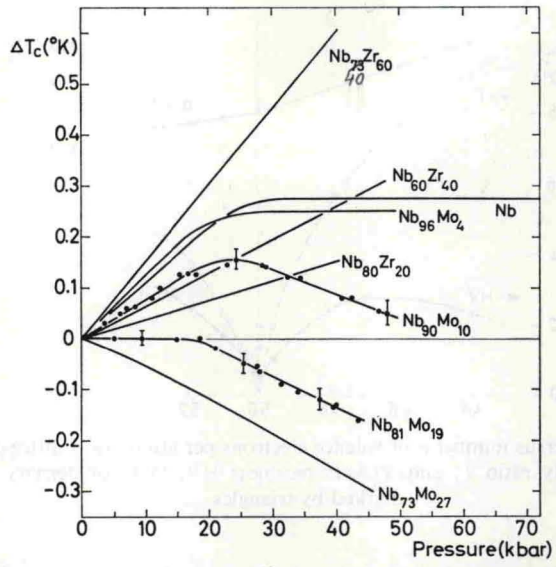

Fig. 2. Variation of transition temperature T_c with pressure p for a number of alloys investigated

notes that $d\ln T_c/dp$ changes sign at a concentration near that at which $T_c(n)$ has a maximum. Since in these alloys $T_c(n)$ is closely related to the d-band structure, this suggests that $T_c(p)$ is likewise connected with the d-band. Analyzing the data in this light, it is found that amongst several possibilities for the connection between $d\ln T_c/dp$ and the electronic structure of the alloys, i.e. with either $d\ln N/dn$, or $d\ln NV/dn$, or $d\ln T_c/dn$, or finally $d\ln T_c/dn - d\ln\theta/dn$, the last provides a linear data fit with the least scatter. This is shown in Fig. 4, from which we obtain the simple relation

$$\partial \ln T_c/\partial p = a(\partial \ln T_c/\partial n - \partial \ln \theta/\partial n) + b \qquad (1)$$

with $a = 0.40 \cdot 10^{-6}$ bar^{-1} and $b = 0.62 \cdot 10^{-6}$ bar^{-1}, θ = Debye characteristic temperature. Substitution of the BCS-expression for T_c in (1) yields

$$\partial \ln \theta/\partial p + (NV)^{-1}\,\partial \ln NV/\partial p = a \cdot (NV)^{-1}\,\partial \ln NV/\partial n + b \qquad (2)$$

$V = V_{BCS}$. For niobium $\partial\ln\theta/\partial p = \gamma_G \cdot \kappa$ can be calculated from the experimental data on γ_G (Grüneisen parameter)[23] and κ (compressi-

23 Collins, J. G., White, G. K.: Progr. Low Temp. Phys., Vol. 4, p. 450. Amsterdam: North Holland Publishing Company 1964.

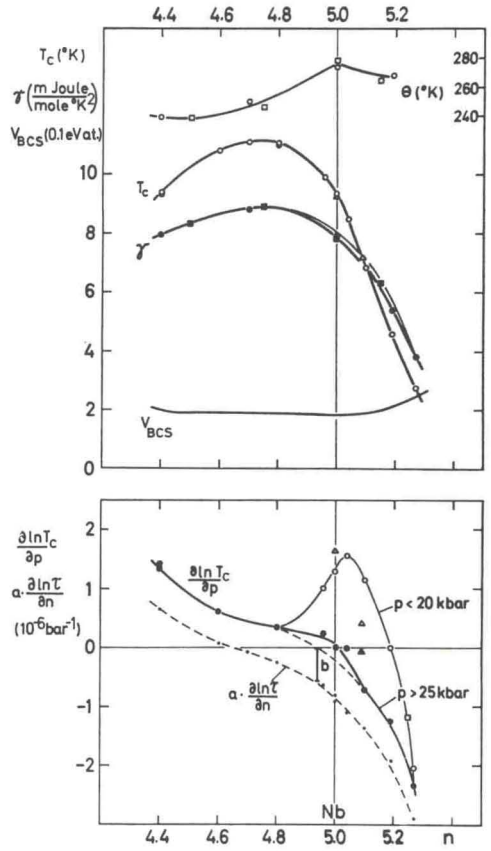

Fig. 3. Lower part: measured slopes $\partial \ln T_c/\partial p$. Due to the smallness of the pressure effect on T_c the error in writing $\partial \ln T_c/\partial p$ for $1/T_{c0} \cdot \partial T_c/\partial p$ is negligible. For $p > 25$ kbar comparison is made with $a \cdot \partial \ln \tau/\partial n \equiv a(\partial \ln T_c/\partial n - \partial \ln \theta/\partial n)$ (Eq. (1) in the text). Relevant parameters are plotted in the upper part in the usual nomenclature. Data for θ and $\gamma \propto N$ were taken from Ref. [12] (squares) and [21] (circles). Data points for ternary alloys are marked by triangles

bility)[24]. The value of $\partial \ln \theta/\partial p$ becomes $0.65 \cdot 10^{-6}$ bar^{-1} which equals our experimental term b within experimental error. Under the reasonable assumption that $\partial \ln \theta/\partial p$ does not change much with composition, Eq. (2) thus reduces to

$$\partial NV/\partial p = a \cdot \partial NV/\partial n \tag{3}$$

with the solution

$$NV = f(a\,p + n)\,. \tag{4}$$

24 Bridgman, P. W.: The physics of high pressure, p. 160. London: G. Bell & Sons, Ltd. 1958.

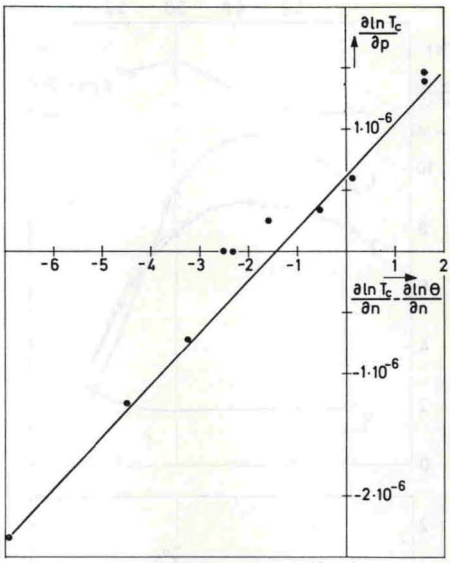

Fig. 4. Plot of $(\partial \ln T_c/\partial n - \partial \ln \theta/\partial n)$ as obtained from the upper part of Fig. 3, versus $\partial \ln T_c/\partial p$. The linear data fit is expressed in Eq. (1)

Thus we arrive at the result that for $p > 25$ kbar the shape of the function $NV(n)$ remains unaffected by pressure, i.e. is rigid with respect to pressure; within the composition range investigated NV can be changed by the same amount by either adding Δn electrons per atom or applying a pressure $\Delta p = \Delta n/a$.

Since in this alloy system V is a slowly varying function of n, the shape of $NV(n)$ is mainly determined by N. One is led to assume that this is also true for $NV(p)$, and to conclude from Eq. (4) that the effect of the application of pressure is primarily a filling of the d-band. A simple mechanism which would provide this can be seen in a pressure-induced shifting of the broad s-band relative to the narrow d-band.

We have used here the original BCS approach. The limited accuracy of the experimental information was thought to inhibit a discussion in terms of more advanced theoretical expressions for T_c which account for a more realistic model for the Coulomb interaction and the effect of electron-phonon interaction on the electronic properties[9,15,25,26]. Nevertheless, some comments are to be made:

25 Morel, P., Anderson, P. W.: Phys. Rev. **125**, 1263 (1962).
26 Garland, Jr., J. W.: Phys. Rev. Letters **11**, 111 (1963).

The improved formulas are similar in structure with the original BCS-formula, i.e.

$$T_c \propto \theta \exp(-1/g). \tag{5}$$

Modifications concern first of all the quantity g, which in the case of BCS is simply

$$g_{BCS} = N V_{BCS} = N(V_{Ph} - V_C). \tag{6}$$

V_{Ph} is the attractive electron-phonon interaction and V_C the repulsive Coulomb interaction. We have used this expression above, with $N = 3/2\pi^{-2} k_B^{-2} \gamma$, i.e. with the "dressed" density of states.

Jensen and Maita[15] obtain

$$g_{JM} = \frac{N_0(V_{Ph} - U_C)}{1 + N_0 V_{Ph}} \tag{7}$$

where N_0 is the "bare" density of states given by

$$N = N_0(1 + N_0 V_{Ph}) \tag{8}$$

and U_C is a modified Coulomb interaction parameter. Jensen and Maita find good agreement with experiment for alloys with $4 \leqq n \leqq 6$ when both interactions V_{Ph} and U_C are assumed to be very nearly constant, with $V_{Ph} \sim 0.85$ eV atom and $U_C \sim 0.27$ eV atom, respectively. Since our alloys fall in this region we have investigated our data in this respect and find indeed a much better constancy of $V_{Ph} - U_C$ than previously for V_{BCS}, V_{Ph} and U_C being 0.90 eV atom and 0.27 eV atom, respectively. With the assumption that V_{Ph} and U_C are also independent of pressure, which seems now even more justified than for V_{BCS}, we obtain, proceeding in the above manner

$$N_0 = f(a\,p + n) \tag{9}$$

which implies that the "bare" d-band would be rigid with respect to pressure.

As stated above, we do not feel that the experimental accuracy permits any preference for either equation (4) or (9) at present. We merely wish to show that with a more elaborate expression for T_c a reasonably simple interpretation for the effect of pressure on T_c in transition metals can also be made.

An analogous use of McMillan's[9] expression for T_c which had proved to be helpful in the case of non-transition metals appears to be less favourable for the alloy system investigated here. Although McMillan's formula

$$g_{MM} = \frac{\lambda - \mu(1 + 0.62\lambda)}{1.04(1 + \lambda)} \tag{10}$$

very closely resembles equation (7) of Jensen and Maita (λ corresponding to $N_0 V_{Ph}$ and $\mu(1+0.62\,\lambda)$ to $N_0 U_C$), the empirical observation which McMillan has made for λ by analyzing the data of five transition metals (V, Nb, Ta, Mo, W) is not in accord with the detailed dependence of T_c and θ on both the number n of valence electrons and on pressure. McMillan obtains empirically

$$\lambda=\frac{c}{M\theta^2} \tag{11}$$

c=constant "for a given class (bcc) of transition metals", M=ionic mass. Using (10) and (11) and assuming $d\mu=0$, one has by differentiation

$$d\ln T_c \sim d\ln\theta\left\{1-\frac{2.18\,\lambda}{(\lambda-0.62\,\lambda\mu-\mu)^2}\right\}. \tag{12}$$

Insertion of the appropriate values for niobium, $\lambda=0.82$ and $\mu=0.13$, yields

$$d\ln T_c=-3.7\,d\ln\theta. \tag{13}$$

Inspection of the shapes of both $T_c(n)$ and $\theta(n)$ near $n=5$ show that Eq. (13) is not satisfied; thus the validity of Eq. (11) is put into doubt from this point of view. The pressure data likewise suggest that McMillan's additional condition $\lambda=c/M\theta^2$ is not applicable to our metals: For $n<5.0$ the measured slopes $d\ln T_c/dp$ are definitely positive and $\lambda\sim 0.9$. Unless the constant c is assumed to be strongly pressure dependent, Eq. (12) requires the slope $d\ln\theta/dp=\gamma_G\cdot\kappa$ to be negative, which has never been observed for any material. Thus we conclude that c indeed depends on pressure and that presumably the moderate constancy of this quantity for the five bcc transition metals is accidental. We note that McMillan was able to give a theoretical proof of Eq. (11) only for the simple metals; i.e., the non-transition metals, for which, as mentioned above, the pressure effect on T_c can be semiquantitatively calculated when Eq. (11) is accepted.

The anomalous pressure dependence of T_c for the niobium-rich alloys at pressures below 20 kbar cannot be explained unambigously at present. The supposition that a small deformation of the d-band arises under pressure up to 20 kbar (as indicated by the thin line on the γ curve) is very hard to check. Alternatively it might be possible that the pressure is not fully hydrostatic and that small shear stresses σ via large shear coefficients $dT_c/d\sigma$ might increase T_c up to the yield stress, i.e., the kink. However, shear should only contribute second order effects[27], whereas the initial parts of our curves seem to be linear. There is also a

27 Pippard, A. B.: Phil. Mag. **46**, 1115 (1955).

possibility that this anomalously strong but reversible increase of T_c at low pressures is related with the peculiarities which niobium[17] and niobium-rich alloys exhibit when lattice defects are introduced by application of pressure at liquid helium temperatures. In contrast to the decrease in T_c, commonly observed when lattice disorder is generated by other means (neutron diffraction[28], thin film sputtering[29]), such pressure induced lattice defects increase T_c as well. As mentioned above, however, this occurs for $4.96 \leqq n \leqq 5.04$, i.e. in a concentration range which is narrower than that for the anomaly in question ($4.9 < n < 5.25$).

The anomaly still occurs to its full extent in the ternary alloy $Nb_{96}Zr_2Mo_2$, which is isoelectronic with pure niobium, but, due to its enhanced lattice disorder, has markedly different mechanical and electronic properties, as indicated by the difference in hardness and residual resistivity ratio (Fig. 1). We therefore argue that the anomaly is not related to the singularities which these properties show near $n=5.0$. (We note that the transition temperature at zero pressure is lower by 0.16 °K than for pure niobium.) The other ternary alloy $Nb_{73}Zr_9Mo_{18}$ made by us has a resulting $n=5.09$ which agrees with the n-value for which, for the binary alloys, the splitting of $d\ln T_c/dp$ assumes its maximum value. It can be thought as being composed of equal parts of two binary alloys $Nb_{82}Zr_{18}$ ($n=4.82$) and $Nb_{64}Mo_{36}$ ($n=5.36$), each of which alone would show no splitting of $d\ln T_c/dp$. Mixed together, they exhibit considerable splitting. This strongly suggests that the anomaly is inherently connected with the number n of valence electrons per atom.

It is interesting to note that the transition temperature of this ternary alloy at $p=0$ is practically identical with that of a binary alloy of same n. This justifies nicely the use of n as a means of classifying the alloys investigated.

Conclusion

A reasonable interpretation can be made for the effect of pressure on T_c for transition metal alloys with approximately half filled d-bands. It appears that for pressures in excess of 25 kbar this band preserves its overall shape when the volume is changed, very much as it does when the band is filled with electrons by alloying. It would be desirable to check this statement in other cases. Preliminary measurements on the series Ti-V-Cr confirm it for $n<5$, but modifications seem to be necessary for the V-Cr alloys. This does not seem surprising, because

28 Lautz, G., Metasch, H.: Atomkernenergie **11**, 295 (1966). — Sernetz, F., Berndt, H., Kartascheff, N., Wenzl, H.: Verhandl. DPG (VI) **4**, 117 (1969).

29 Fowler, P.: J. Appl. Phys. **34**, 3538 (1963). — Frerichs, R., Kircher, C. J.: ibid. **34**, 3541 (1963). — Neugebauer, C. A., Ekvall, R. A.: ibid. **35**, 547 (1964).

pure chromium is antiferromagnetic. It may be expected that detailed studies of the pressure effect on T_c of alloys of both the early transition metals (those with less than half filled d-shells) and those from the filled end of the transition series, will contribute to the understanding of superconductivity in these metals.

It is a pleasure to thank Professor Buckel for stimulating the author's interest in this problem and discussing it in all stages. Cooperation with Dr. D. Köhnlein during the work was essential and is gratefully acknowledged. The author wishes to thank Dr. G. Dummer for specific heat measurements on some of the samples, Dr. H. Wühl for preparing most of the samples, and G. Schulze for discussions.

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