Z. Physik 255, 308—314 (1972)

Superconductivity of Hf-Ta and Ta-W Alloys under Pressure

W. Gey and D. Köhnlein
Physikalisches Institut der Universität Karlsruhe

Received July 21, 1972

Measurements on ten binary alloys of the body-centered cubic part of the $5d$-alloy series Hf-Ta and Ta-W yield a linear relationship between the derivatives of the quantity g both with respect to pressure and to valence electron concentration, where g is defined by $T_c \propto \theta \exp(-1/g)$. This result agrees with observations on alloys of the $4d$-series, Zr-Nb and Nb-Mo. It is concluded that for these alloys composed from the central part of the $4d$ and $5d$ transition series, the interaction responsible for superconductivity is less subject to complications than for other transition metals and is probably governed by the electronic density of states. Data on the variation of the transition temperature with concentration in Hf-Ta alloys are included.

Introduction

Improvements in establishing expressions for the superconducting transition temperature T_c, including strong coupling effects[1], and attempts to evaluate the mean electron-phonon interaction parameter from first principles[2,3], have raised doubts about the originally assumed dominating influence of the d-band density of states on T_c in transition metals. Modifications primarily concern the parameter g, defined by the general expression for the transition temperature, $T_c \propto \langle\omega\rangle \exp(-1/g)$. It has become apparent that the simple BCS expression $g_{BCS} = NV_{BCS}$ is to be replaced by $g = f(\lambda, \mu^*) \approx \lambda$, where the electron-phonon coupling constant λ is determined by $\lambda = N\langle J^2\rangle/(M\langle\omega^2\rangle)$ (N = electronic density of states at the Fermi surface, $\langle J^2\rangle$ = average squared coupling matrix element, M = ionic mass, $\langle\omega^2\rangle$ = mean squared phonon frequency)[1].

Empirically it was found for a number of *elemental* metals[1] that $N\langle J^2\rangle$ is almost constant, i.e. λ does not inherently depend on the electronic density of states N. The apparent proportionality between N and λ which is often observed in binary transition metall *alloys* (e.g., Fig. 9 of Ref.[1]) is then to be ascribed to a correlation of N with the phonon spectrum, represented by $M\langle\omega^2\rangle$, which becomes the governing

1 McMillan, W. L.: Phys. Rev. **167**, 331 (1968).
2 Hopfield, J. J.: Phys. Rev. **186**, 443 (1969).
3 Barišic, S., Labbé, J., Friedel, J.: Phys. Rev. Letters **25**, 919 (1970).

quantity. Theoretical approaches support the approximate constancy of $N\langle J^2\rangle$[2,3]. For certain binary transition metal alloys (commonly composed from the central part of the same transition period, but also for Ti-Zr or Nb-Ta, whose constituents belong to the same group of the periodic table) the above concept is in fair agreement with experiment when the value of $N\langle J^2\rangle$ is interpolated linearly between the value for each constituent, according to their concentration[2]. However, this scheme is reported to fail for the V-Nb and V-Ta alloy systems[4].

One notes that the present understanding of superconductivity in transition metals is far from being perfect. It is unlikely to be improved by the usual practice of relying on current knowledge of such complicated parameters as $\langle J^2\rangle$ or $\langle\omega^2\rangle$. Furthermore, nothing is known of what happens to these quantities when different elements combine to form an alloy, even if the lattice type remains the same (*bcc*). It thus appears more realistic to consider the electronic density of states again as the dominate parameter affecting T_c. Alloying alone does not provide adequate information. Further knowledge can be obtained by varying the volume by application of high pressure. This is regarded as a relatively simple external agent, especially in crystals with cubic symmetry and one infers that the superconductor's response can be easily interpreted[5].

In two earlier papers[6,7] high pressure studies had been reported on the *bcc* part of the 4*d*-alloy systems Zr-Nb and Nb-Mo. From these data a simple empirical relation was established for pressures in excess of 20 kbar:

$$\frac{\partial g}{\partial p} = a \frac{\partial g}{\partial n} \tag{1}$$

where p is the pressure, n is the number of valence electrons per atom as derived from the composition, and a is a constant. It follows from Eq. (1) that over the whole range of composition ($4.4 < n < 5.27$) the quantity g can be changed by the same amount by either applying a pressure Δp or adding $\Delta n = a \cdot \Delta p$ electrons per atom.

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4 Ishikawa, M., Toth, L. M.: Phys. Rev. B**3**, 1856 (1971). — Corsan, J. M., Cook, A. J.: Phys. stat. sol. **40**, 657 (1970).

5 In the case of *non* transition elements a rather conclusive argument for the governing role of the phonon term on the transition temperature is derived from systematic pressure studies. (Olsen, J. L., Andres, K., Geballe, T. H.: Phys. Lett. **26**A, 239 (1968). — Gey, W.: Vorträge zur Sommerschule über Supraleitung. Steibis, 1969).

6 Gey, W., Köhnlein, D.: Phys. Lett. **29**A, 450 (1969).

7 Gey, W.: Z. Physik **229**, 85 (1969). — Essentially identical results for dT_C/dp of Zr-Nb-Mo-alloys have later been reported by Smith, T. F.: AIP Conf. Proc./4, Amer. Institute of Physics, editor D. H. Douglass, p. 293. New York 1972.

To determine whether the simple correlation given in Eq. (1) is of a more general validity, we have extended investigations of the effect of pressure on T_c to the *bcc* alloys of the 5-*d* transition series Hf-Ta and Ta-W. We find Eq. (1) obeyed.

Experimental

Experimental procedure and sample preparation were the same as reported in Ref.[7]. The starting materials were: Ta, 99.9% sheet, Koch-light Labs; W, 99.9% powder, Koch-Light Labs; Hf, 99.8% powder, Leyless Metal and Chemical Corp. Since Hf and W dissolve rather slowly in Ta, the ingots were remelted 12 to 15 times and turned over in the copper hearth of the electron beam furnace until homogeneity was obtained, as checked by *x*-ray diffraction. Due to this preparation excessive weight losses of up to 9% occured for some of the Hf-Ta samples. Deviations from the nominal composition were accounted for by measuring the lattice constants and interpolating linearly between samples with no weight loss and pure tantalum, respectively. The maximum error in determining n this way was $\pm 0.4\%$. X-ray data showed no traces of phases other than the β-phase (*bcc*).

Results

To our knowledge no information on $T_c(n)$ exists in the literature for Hf-Ta alloys, except for $n=4.7$ [8]. Also data on Ta-W alloys are scarce [8].

Table 1

Alloy	n	T_c(K)	a (Å)	$\partial \ln T_c/\partial p_{p>10\ \mathrm{kbar}}$ (10^{-6} bar^{-1})
$Hf_{61}Ta_{39}$	4.39	5.71		+0.88
$Hf_{52}Ta_{48}$	4.48	6.61		+0.78
$Hf_{40}Ta_{60}$	4.60	6.85	3.591	+0.57
($Hf_{30}Ta_{70}$	4.70	6.8	3.573)[8]	—
$Hf_{20}Ta_{80}$	4.80	6.90	3.341	+0.36
$Hf_{10}Ta_{90}$	4.90	5.60		−0.27
Ta	5.00	4.21	3.298	−0.62
$Ta_{96}W_4$	5.04	3.30		−0.57
$Ta_{91}W_9$	5.09	2.78		−0.80
$Ta_{84}W_{16}$	5.16	1.86		−1.10
$Ta_{78}W_{22}$	5.22	1.36		−1.2

Lattice constants a are only given for those Hf-Ta alloys which were not subject to weight losses during preparation. The approximate error for T_c is $\pm 1\%$, for $\partial \ln T_c/\partial p$ it varies from 3 to 5%.

8 Bucher, E. F., Heiniger, F., Muller, J.: Proc. LT9, p. 1059. New York: Plenum Press, Inc., 1965.

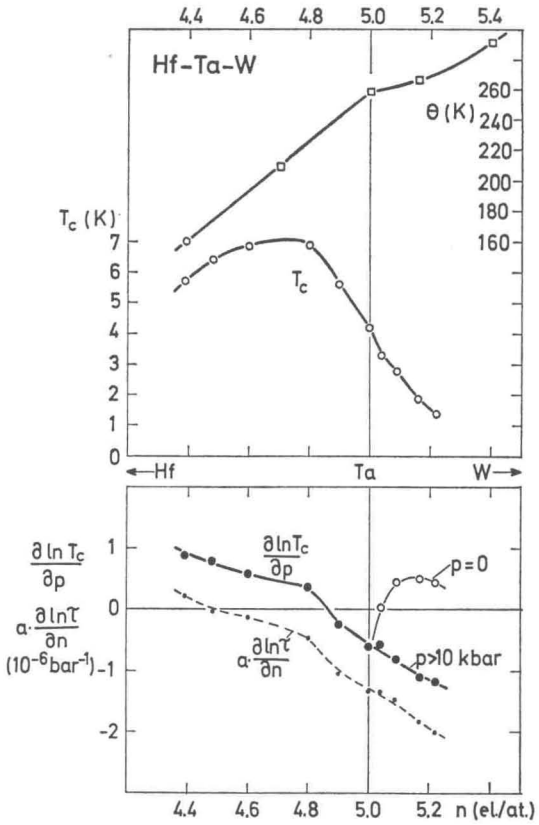

Fig. 1. Lower part: measured slopes $\partial \ln T_c/\partial p$. For $p > 10$ kbar comparison is made with $\partial \ln \tau/\partial n$. Relevant parameters are plotted in the upper part

In the Table 1 we list the relevant new data. We note that T_c of our Ta is rather low.

The data on the effect of *pressure* on these alloys are shown in Fig. 1, including values for T_c and the Debye characteristic temperature θ, if known [8, 9]. For pressures in excess of 10 kbar, the slope $1/T_{c0} \cdot \partial T_c/\partial p \approx \partial \ln T_c/\partial p$ decreases monotonically with increasing number n of valence electrons per atom. Proceeding as for the Zr-Nb-Mo alloys, we have plotted the quantity $a \cdot \partial \ln \tau/\partial n \equiv a(\partial \ln T_c/\partial n - \partial \ln \theta/\partial n)$.

9 We wish to thank G. Dammer and K. Mulder of this Laboratory for permitting us to use their unpublished data for Hf_{61} Ta_{39}.

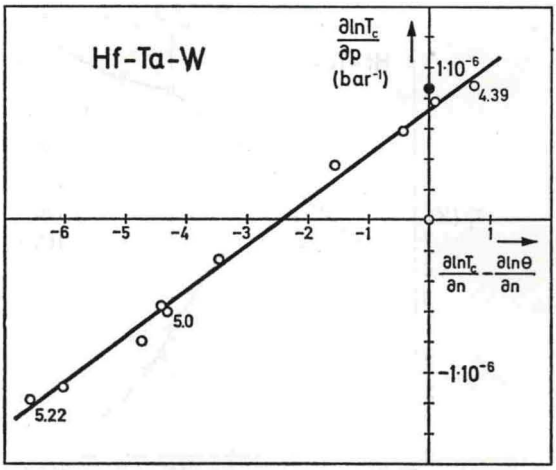

Fig. 2. Plot showing the linear relation between $\partial \ln T_c/\partial p$ and $\partial \ln \tau/\partial n$ for all alloys. The full circle represents $\partial \ln \theta/\partial p$ for Ta

One notes that for Hf-Ta-W-alloys it is also linearly related with $\partial \ln T_c/\partial p$, according to

$$\partial \ln T_c/\partial p = a(\partial \ln T_c/\partial n - \partial \ln \theta/\partial n) + b. \tag{2}$$

This is also shown in Fig. 2, from which the values of the constants $a = 0.30 \cdot 10^{-6}$ bar^{-1} and $b = 0.74 \cdot 10^{-6}$ bar^{-1} are readily obtained.

Inserting $T_c \propto \theta \exp(-1/g)$ in Eq. (2) yields

$$g^{-2} \cdot \partial g/\partial p + \partial \ln \theta/\partial p = g^{-2} \cdot a \cdot \partial g/\partial n + b. \tag{3}$$

For Ta the literature value of $\partial \ln \theta/\partial p = \gamma_G \cdot \kappa = 1.82 \cdot 0.48 \cdot 10^{-6}$ bar^{-1} = $0.87 \cdot 10^{-6}$ bar^{-1} [10] is close to the value of our term $b = 0.74 \cdot 10^{-6}$ bar^{-1} (γ_G = Grüneisen parameter, κ = compressibility). Thus, under the reasonable assumption that $\partial \ln \theta/\partial p$ does not change much with composition, Eq. (3) reduces to Eq. (1), with $a = (0.30 \pm 0.02) \cdot 10^{-6}$ bar^{-1}.

For Ta-W alloys kinks in the otherwise linear $T_c(p)$-dependence are observed near $p = 10$ kbar, as indicated by the splitting of $\partial \ln T_c/\partial p$ in Fig. 1. A similar behaviour was observed in the Zr-Nb-Mo system. However, Nb_{96} Zr_4 and Nb were also involved and the changes in slope occured near 20 kbar. We will refer to this effect in another paper.

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10 Gschneidner, K. A.: In: Solid State Physics **16**, 275 (1964), edited by F. Seitz and D. Turnbull. London-New York: Academic Press.

Discussion

We note a striking similarily in the dependence of the interaction term g on pressure and electron concentration in the binary Zr-Nb-Mo and Hf-Ta-W alloy systems. In both cases the relation

$$\Delta n = a \cdot \Delta p \tag{4}$$

is obeyed, the constant a being $0.40 \cdot 10^{-6}$ bar^{-1} and $0.30 \cdot 10^{-6}$ bar^{-1}, respectively. In our paper on Zr-Nb-Mo the apparent equivalency of application of pressure and adding electrons to the conduction band, represented by $\Delta n = a \Delta p$, was interpreted as being due to a shift of the narrow d-band with respect to other broader (s and p) bands with pressure, leaving the shape of the d-band unchanged, i.e. rigid. We adopt the same picture for Hf-Ta-W alloys. It is then interesting to compare the experimental results with band calculations which have been performed for Nb and Ta by Mattheiss in a consistent manner[11]. From these calculations it can be deduced that, within the composition ranges of our experiments, the variation of n with energy is very nearly linear, i.e.

$$\Delta n = c \cdot \Delta E \tag{5}$$

with $c \approx 30$ Rydberg^{-1} for Nb and $c \approx 24$ Rydberg^{-1} for Ta. In the rigid band description this can be combined with $\Delta n = a \cdot \Delta p$ to yield

$$\Delta E_F = \frac{a}{c} \cdot \Delta p. \tag{6}$$

Inserting the appropriate numbers of a and c for both alloy systems one obtains $a/c = 1.33 \cdot 10^{-8}$ Rydberg bar^{-1} for Zr-Nb-Mo and $a/c = 1.25 \cdot 10^{-8}$ Rydberg bar^{-1} for Hf-Ta-W. Thus, within the error of this simple calculation, the variation of the fermi energy E_F with pressure is the same for both the $4d$ Zr-Nb-Mo and the $5d$ Hf-Ta-W alloys. If, as was implied above, the broader bands show negligible variation of density of states with energy, this is equivalent to saying that pressure will shift the narrow d-band energetically by the same amount in both $4d$ and $5d$ alloys.

Conclusion

The high pressure experiments uncover not only a intimate correlation between the pressure and electron concentration dependence of the interaction term g in each of the $4d$ and $5d$ alloy series; these series seem to be related also on the basis of electronic band calculations. This

11 Mattheiss, L. F.: Phys. Rev. B**1**, 373 (1970).

suggests that for these metals of the central part of the transition series the interaction responsible for superconductivity is governed by the electronic density of states. Obviously disturbances due to paramagnon effects or other complications affecting the transition temperature are here negligible.

The authors wish to thank Prof. W. Buckel and Dr. H. Winter for useful discussions.

Dozent Dr. Wolfgang Gey
Dr. Dieter Köhnlein
Physikalisches Institut der Universität
D-7500 Karlsruhe, Engesserstr. 7
Federal Republic of Germany