A PHENOMENOLOGICAL APPROACH TO HIGH TRANSITION TEMPERATURE SUPERCONDUCTING ALLOYS

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ABSTRACT

Correlations between the observed maximum superconducting transition temperature T_c for a given binary alloy system and the alloy melting temperature T_m are pointed out. The stability of alloy phases favorable for high temperature superconductivity is discussed in terms of alloy phase diagrams. A comparison with the microscopic theory shows that the correlation between T_c and T_m can be interpreted in terms of the d-electron contribution to the cohesive energy of transition metal alloys as proposed by Barišić, Labbé, and Friedel. The prospects for obtaining high T_c 's are discussed in view of these results, and new alloy systems are suggested.

I. INTRODUCTION

Several attempts have been made to elucidate and explain the empirical trends of superconductivity in metals and alloys. Matthias¹ has pointed out optimum e/a values for different superconducting crystal structures. Hopfield² and Pines³ suggested how the empirical systematics of superconductivity in the periodic table might be derived from the BCS theory.⁴ Recently, Gomersall and Gyorffy⁵ explained the variation of superconducting transition temperature T_c with e/a values in transition metals and alloys in relation to the stability of the bcc phase. McMillan⁶ calculated T_c as a function of the Debye temperature θ_D , the electron-phonon coupling constant λ , and Coulomb pseudopotential μ^* based on the strong-coupling theory.⁷ Maximum T_c 's were predicted for several classes of materials. Experimentally, it is not clear that the maximum T_c 's predicted are ever realized. In this paper, an empirical scheme is suggested for predicting the limiting value of T_c in binary alloy systems based on a survey of known superconducting alloys, and observed correlations between T_c and other physical properties of alloys. Using the microscopic theory of superconductivity, it is shown that the cohesive energy of a metal alloy may play the major role in determining the limiting value of T_c in metal alloys.

In section II, alloys containing only transition metals are discussed. A direct correlation between alloy melting temperature T_m and the observed maximum T_c for a given binary alloy is pointed out. The features of the binary alloy phase diagrams which relate to stability and formation of intermediate alloy phases favorable for high tempera-

ture superconductivity (for example the A-15 phase) are discussed. A comparison with the microscopic theory reveals systematic trends in the electron-phonon coupling strength. Using a model of electron-phonon coupling for d-electrons proposed by Barišić, Labbé and Friedel⁸, it is shown that correlation between T_m and T_c can be interpreted in terms of the d-electron contribution to the cohesive energy of transition metal alloys. In section III, an attempt is made to generalize the ideas developed in section II for transition metal alloys to the general case of alloys containing both transition metals and non-transition metals. The prospects for obtaining higher T_c 's are discussed for both transition metal alloys and for the general case. Several suggestions are made concerning which alloy systems will be most favorable.

II. TRANSITION METAL ALLOYS

A. Observed Correlations With T_m .

For a binary transition metal alloy, several factors are observed to influence the superconducting transition temperature. The crystal structure (s) of phases present, the metallurgical condition of the alloy, and the average valence electron concentration (e/a) are all important. Any attempt to show systematic behavior of T_c must at the outset take into consideration these factors. Some simplification of the problem is required if any meaningful systematics are to be obtained. Matthias had previously pointed out that the phenomena of melting and superconductivity may be related. He correlated the superconductivity of rare-earth and transition metals to melting point anomalies.⁹ To this end, only those phases which have the maximum

T_c in each binary alloy system will be considered and used to characterize the binary alloy. With this simplification, it is possible to organize a large amount of data using the melting temperature T_m (in $^{\circ}\text{K}$) of each alloy as a parameter. Table I contains compiled data on a large number of superconducting binary transition metal alloys. In particular, the crystal structure, maximum T_c , composition, melting temperature T_m , and chemical designation of the atomic orbitals for the valence electrons of each constituent are given. The melting temperature has been defined using the phase diagram^{10, 11, 12} as the solidus temperature at the specified composition. In the majority of cases, this differs little from the liquidus temperature and thus its use in defining T_m is not unreasonable. Data on T_c and crystal structure are obtained from B. W. Roberts' compilations¹³ and other references as given in Table I. In Figure 1, a plot of T_c as a function of melting temperature is shown. The points in this plot are distinguished according to which period of the periodic table the constituents of the alloy belong.

A number of significant features can be observed in Figure I. First, for a restricted class of alloys such as the 4d-5d alloys, the maximum T_c 's are found to vary linearly with T_m . A dashed line in the figure indicates this correlation which can be expressed as $T_c \leq 0.0055 T_m$. For Mo-Re, Mo-Os, Nb-Ir, Nb-Au, Nb-Pt and Ta-Rh alloys, the maximum T_c is that of an A-15 or σ -related topologically closed packed (TCP) cubic phase occurring at an average valence electron concentration (e/a) of 6.5 to 6.7 electrons per atom. The composition of these phases varies from the ideal 3 to 1 stoichiometry of A-15 phase in Nb_3Au and Nb_3Pt to an approximate 2 to 3 atomic

Table I. Summary of data for transtion metal alloys as mentioned in section II (A).

Alloys	$T_m(^{\circ}\text{K})$	$T_c(^{\circ}\text{K})$	e/a	Structure	Ref.
3d-4d					
V_2Zr	1570	8.8	4.67	C15	13
$\text{Tc}_{0.93}\text{V}_{0.7}$	2285	11.3	6.87	A3	14
3d-5d					
HfV_2	1750	9.6	4.67	C15	13
4d-4d					
$\text{Pd}_{0.1}\text{Zr}_{0.9}$	1300	7.5	4.6	A3	13
RhZr_2	1500	11.7	5.65	C16	15, 16
$(\text{PdRu})_{0.1}\text{Zr}_{0.9}$	$\sim 1780^*$	9.0	4.5	A3	13
$\text{Nb}_{57}\text{Rh}_{40}\text{C}_3$	1830	10.1	6.68	E93	17
$\text{Nb}_{60}\text{Zr}_{40}$	2250	11.5	4.6	A2	18
$\text{Mo}_{25}\text{Tc}_{75}$	$\sim 2250^{**}$	16	6.75	A15	19, 20

(continued)

Table I. (continued)

Alloys	T_m (°K)	T_c (°K)	c/a	Structure	Ref.
4d-5d					
IrZr_2	$\sim 1500^{**}$	8.0	5.65	C16	15, 16
$\text{Rh}_{43}\text{Ta}_{54}\text{C}_3$	2000	10.1	6.76	A15	17
$\text{Nb}_{55}\text{Ir}_{40}\text{O}_5$	2225	11.7	6.65	A15	17
$(\text{Au}_{0.7}\text{Pt}_{0.3})\text{Nb}_3$	$\sim 2280^*$	12.5	6.43	A15	13
$\text{Mo}_{75}\text{Os}_{25}$	2700	11.8	6.5	A15	13
$\text{Mo}_{42}\text{Re}_{58}$	2775	15.0	6.58	cubic	21
5d-5d					
$\text{Ir}_{42}\text{Ta}_{58}$	2300	6.6-8.0	6.68	cubic	17
$\text{Hf}_{55}\text{Ta}_{45}$	2450	6.5	4.55	A2	13
Re_3Ta	3050	6.8	6.5	A12	13
$\text{Re}_{55}\text{W}_{45}$	3300	11.4	6.45	A15	22

* interpolated from binary phase diagrams.

** estimated from related phase diagrams.

Fig. 1. Maximum observed T_c as a function of T_m for alloys containing only transition metals. Alloys are distinguished in terms of periods of the periodic table.

composition in $\text{Mo}_{42}\text{Re}_{58}$. The only other alloy which appears to reach the boundary is Zr_2Ir which has the C-16 structure. For 5d-5d alloys, the maximum T_c 's are lower. Experimental work on these alloys has been much less detailed and thus less data are available compared with the 4d-5d alloys. However, for the available data, the maximum T_c does appear to increase with T_m . A dashed line containing the Ta-Ir and W-Re alloys both having an A-15 like structure and an average e/a value of 6.6 electrons per atom is shown. The case of 4d-4d alloys is still less clear. The absence of detailed work on technetium alloys, and the lack of intermediate A-15 phases with $e/a \sim 6.6$ electrons per atom among the 4d-4d binary systems make it difficult to establish any trend. However, the characteristic T_c 's are apparently higher as evidenced by comparing Zr_2Rh with $T_c = 11.4^\circ\text{K}$ to the isoelectronic phase Zr_2Ir with $T_c = 8^\circ\text{K}$ both having the C-16 structure. Also, for Mo-Tc alloys, the maximum observed T_c of 16°K is higher than that of Mo-Re although the melting temperature of the former is lower. From these facts, it appears that the maximum T_c 's of 4d-4d alloys are characteristically higher. The dashed line indicates a rough trend. Finally, several alloys containing vanadium, a 3-d metal are shown again indicating a tendency towards increasing T_c with increasing T_m . It should be emphasized that Figure 1 is a to date summary of all available data on transition metal alloys; those alloys not represented on the plot have lower values of T_c for a given range of T_m values.

B. Phase Stability Near Optimal e/a Values.

In addition to the limiting relation $T_c \leq 0.0055 T_m$, several other

factors may be isolated which when taken separately are necessary for obtaining the limiting value of T_c in a given binary system, but when taken together may yield a set of sufficient conditions for obtaining this limiting T_c . In this section, a guideline for obtaining new high T_c phases is proposed and the maximum obtainable T_c for each of such phases is predicted. Attention is given primarily to 4d-5d alloys since the available data for these are most complete.

It has been pointed out that with the exception of Zr_2Ir , all 4d-5d alloys with T_c near the observed limit have either the A-15 or a cubic σ -related structure. It is of interest to examine some representative phase diagrams of the alloys. The equilibrium phase diagrams of Nb-Ir and Mo-Re systems are shown in Figure 2(a) and (b). In both cases, the phase having the maximum T_c is metastable and occurs where $e/a \sim 6.6$ electrons per atom which corresponds to compositions in the stable σ -phase field. The maximum transition temperature $T_c = 11.7^\circ K$ for Nb-Ir alloys is obtained by inducing a phase transformation near the Ir rich side of the σ -phase field. This is accomplished metallurgically by adding a small amount of oxygen and results in an A-15 type phase having the optimal e/a value of 6.6.¹⁷ Using the sputtering technique, Testardi showed that a similar phase transformation can be induced near the eutectoidal decomposition temperature in the σ -phase field of the Mo-Re system.²¹ The new phase is σ -related but has no tetragonality. A survey of other 4d-5d phase diagrams based on Mo, Nb, (also Ta and W) reveals the following. The sequence of topologically closed packed (TCP) phases in each binary system follows the pattern $A-15 \rightarrow \sigma \rightarrow \chi$ with increasing e/a values²³ where one or more of these phases may be "missing" in a

Fig. 2. Phase diagrams of (a) Nb-Ir, (b) Mo-Re, and (c) Nb-Ru binary alloy systems. Compositions of the alloys with their corresponding e/a (electrons per atom) values are shown.

given system. For Mo-Os, Nb-Au and Nb-Pt systems, the optimal e/a value of 6.6 is achieved near the stable A-15 phase field with a 3 to 1 stoichiometry. For Mo-Re, Nb-Ir and Ta-Rh systems, the same optimal e/a value is attained in the σ -phase field. Available evidence suggests that whenever a phase transformation from the σ -phase to an A-15 (or related cubic phase) is induced for an alloy where $e/a \sim 6.5 - 6.7$ electrons per atom, the result is an increase in T_c to the value predicted by the relation $T_c = 0.0055 T_m$. Stoichiometry appears to be of little importance in determining the T_c of such transformed phases. It is interesting that the resulting increase in T_c referred to as ΔT_c due to this phase transformation is consistently observed to be $\sim 6^\circ K$ as shown in Table II. Simply put, if an A-15 phase or a cubic σ -related phase can be obtained with the optimal e/a value for a 4d-5d alloy, then its transition temperature is just given by $T_c = 0.0055 T_m$.

Assuming the validity of the preceding ideas, the next question to ask is whether an A-15 or other favorable crystal structures can be obtained at compositions corresponding to optimum e/a values. The phase diagrams again provide useful information. Experimental studies suggest that the free energy ($F = E - TS$) of the σ and A-15 phases are closely related.²⁴ The existence of a stable σ -phase in a given compositional range of a binary alloy appears to indicate that the free energy of an A-15 phase at the same composition is only slightly greater. The introduction of small quantities of a third constituent, sputtering techniques, or liquid quenching techniques frequently can alter the free energy relationships and kinetics of crystal growth of both phases sufficiently to make the A-15 phase the

Table II. Increase in T_c resulting from $\sigma \rightarrow A15$ (or σ -related cubic) phase transformation in 4d and 5d transition metal alloys. T_c data for σ phases are taken from reference 13.

Composition of A-15 phase	Composition of σ -phase	$T_c(^{\circ}K)$ (A-15)	$T_c(^{\circ}K)$ (σ)	$\Delta T_c(^{\circ}K)$
$Nb_{55}Ir_{40}O_5$	$Nb_{62}Ir_{38}$	11.7	~ 4	7.7
$Nb_{75}Pt_{25}$	$Nb_{62}Pt_{38}$	10.9	4.0	6.9
$Nb_{57}Rh_{40}C_3^{\dagger}$	$Nb_{58}Rh_{42}$	10.3	4.1	6.2
$Mo_{40}Tc_{60}$	$Mo_{30}Tc_{70}$	16.0	12.0	4.0
$Mo_{75}Ir_{25}$	$Mo_{75}Ir_{25}$	9.6	6.8	2.8
$Mo_{75}Os_{25}$	$Mo_{62}Os_{38}$	11.8	5.7	6.1
$Mo_{42}Re_{58}^*$	$Mo_{42}Re_{58}$	15.0	8.4	6.6
$W_{45}Re_{55}$	$W_{60}Re_{40}$	11.4	5.0	6.4
$Ta_{54}Rh_{43}C_3$	$Ta_{56}Rh_{44}$	10.0	2.4	7.6
$Ta_{58}Ir_{42}^*$	$Ta_{58}Ir_{42}$	6.6-8.0	**	$\sim 6-8$

$\dagger$ Metastable cubic phase not having A-15 structure

* Metastable cubic phase with uncertain structure

** No reported superconductivity

more competitive. Examples of this are the Mo-Re, Nb-Ir and Ta-Rh systems mentioned earlier. On the other hand, the existence of a stable χ -phase field is observed to be unfavorable for the formation of the A-15 phase at the same composition. In such binary systems as Nb-Os and Nb-Re, the stable χ -phase field occurs at compositions for which the optimal e/a value is realized. Thus far, efforts to obtain a high T_c phase by inducing a phase transformation within the χ -phase field have been unsuccessful.¹⁷

Finally, it should be pointed out that both the A-15 and σ -phase fields are "missing" in some binary systems. The Nb-Ru phase diagram shown in Figure 2(c) is an example. In such cases, the free energy of the A-15 phase is high and it is probably very difficult to synthesize the phase. The A-15 phase is absent in most 4d-4d binary alloys, being present only in the Mo-Tc and Nb-Rh systems. In Mo-Tc, the A-15 phase occurs near the composition $\text{Mo}_{40}\text{Tc}_{60}$ ($e/a = 6.6$) and has a maximum observed T_c of 16°K .¹⁹ For Nb-Rh, the A-15 structure forms peritectically at the composition Nb_3Rh with $e/a = 6.0$ and is not a good superconductor. However, a phase transformation from σ to a cubic phase is induced by the addition of a small amount of carbon to alloys on the Rh rich side of the σ -phase field ($\text{Nb}_{60}\text{Rh}_{40}$) with $e/a \sim 6.6$. This new phase though cubic is not of the A-15 type. It is a good superconductor with $T_c = 10.3^\circ\text{K}$.¹⁷ The A-15 phase is apparently much less competitive with other related phases in the 4d-4d alloys. This suggests that obtaining superconducting phases with the maximum T_c near the upper dashed line in Figure 1 in 4d-4d alloys will be quite difficult.

For alloys containing a 3d constituent (V_2Zr , V_2Hf), the highest

observed T_c 's follow closely those observed for 4d-5d materials. Since the atomic radii, chemical bonding strengths, and melting temperatures of 3d metals are quite different from those of 4d and 5d metals, one expects significant differences in the superconducting properties. The case of transition metal alloys based on a 3d metal will be discussed in more detail in section II (D).

C. Suggestions For New High T_c Alloys.

The implication of Figure 1 is that if favorable phases, in particular the A-15 type phase can be obtained at the optimal e/a value among the 4d-4d alloys, then the expected T_c values should be quite high. Table III contains a list of all Nb base and Mo base 4d-4d and 4d-5d alloys, comments concerning the favorability of A-15 formation at the optimal e/a value, and a prediction for the maximum T_c which may be obtained in each system. The maximum T_c is estimated from Figure 1 based on the known T_m of an alloy at the composition for which $e/a \sim 6.6$ electrons per atom. It is implicitly assumed that the limiting T_c would be obtained for the A-15 phases; however, the possibility that other metastable phases (for example, the C-16 phases Zr_2Ir and Zr_2Rh , or cubic phases such as that found in the Nb-Rh system) may also form cannot be ruled out. Thus far experimental results indicate that these phases respect the same limiting T_c relation $T_c \leq \alpha T_m$ (where α is a numerical constant depending on the particular class of alloys considered) as the A-15 type phases. The optimal e/a value for C-16 phases is $\sim 5.7^{15}$ in contrast to 6.5 - 6.7 for the A-15 type phases. The C-16 structure itself is quite different from that of the A-15 structure, being a

Table III. Favorability for formation of A15 phases in Nb and Mo based alloys and their predicted maximum T_c .

Alloy System	Equilibrium TCP phases	Favorability for A15 formation	$T_c^{\max} (^{\circ}\text{K})$
Nb-Ru	none	p	
Nb-Rh	A15, σ^*	g	14
Nb-Pd	σ^*	f	15
Nb-Re	σ, χ^*	p	
Nb-Os	A15, σ, χ^*	p	
Mo-Tc	A15, σ^*, σ^*	g	18-20
Mo-Ru	σ^*	f	18
Mo-Rh	none	p	
Mo-Pd	none	p	
Mo-Os	A15, σ^*	g	15
Mo-Ir	A15, σ^*, σ^*	g	13
Mo-Pt	none	p	

* phases where $e/a \sim 6.5-6.7$.

g - good

f - fair

p - poor

quasi-two-dimensional structure. It is interesting that the same correlation between maximum observed T_c and T_m is experimentally observed for both Zr_2Ir alloy and the A-15 type phases. This suggests that this correlation may not depend explicitly on crystal structure but is rather an expression of a more fundamental property of metallic alloys. The problem of high temperature superconductivity is closely related to the problem of lattice stability.^{25, 26} Since the melting temperature T_m of a crystal is closely related to the cohesive energy of the structure, it should therefore not be surprising that it may also be related to superconductivity. This is discussed in terms of the microscopic theory of superconductivity in the next section.

D. Implications Of The Microscopic Theory.

In order to put the empirical scheme of predicting maximum T_c 's developed from sections II (A) to II (C) on a firmer basis, it is necessary to investigate the observed trends of superconductivity using the microscopic theory. The systematic variation of T_c with T_m in transition metal alloys suggests the possibility of revealing similar trends for the microscopic parameters which determine T_c . By extending the BCS formulation to strong-coupled treatments, McMillan⁶ obtained a formula for T_c as a function of the electron-phonon and electron-electron coupling constants which is shown to be applicable to transition metal alloys. Using this formula, the electron-phonon coupling constant λ can be expressed as

$$\lambda = \frac{1.04 + \mu^* \ln(\theta_D / 1.45 T_c)}{[1 - 0.62 \mu^*] \ln(\theta_D / 1.45 T_c) - 1.04} \quad (1)$$

where θ_D is the Debye temperature, and μ^* is the Coulomb "pseudopotential" of Morel and Anderson. This equation is the result of a numerical solution of the gap equation using the phonon density of states of bcc niobium.

Values of λ for the twelve alloys having T_c near the limiting values given approximately by the three linear relations $T_c \lesssim \alpha T_m$ in Figure 1 were evaluated using equation (1). It was assumed that $\mu^* = 0.13$.

Values of θ_D were obtained from results of specific heat measurements for nine alloys. For the three newly found Nb-Ir, Nb-Rh and Ta-Rh alloys, θ_D was determined using the Lindemann relation²⁷ $\theta_D = CM^{-\frac{1}{2}}V^{-\frac{1}{3}}T_m^{\frac{1}{2}}$ where C is constant for a particular class of alloys, M and V are the average atomic mass and average atomic volume of an alloy respectively. The value of C can be determined from known values of θ_D and T_m of $Nb_3(Au_{0.3}Pt_{0.7})$ alloys having the A-15 structure. This procedure was checked for consistency by using the value of C determined to generate θ_D for Mo-Re alloys. Table IV contains summary of values for λ calculated for these alloys. McMillan also evaluated λ explicitly in the form

$$\lambda = \frac{N(0) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (2)$$

where $N(0)$ is the electronic density of states at the Fermi surface, $\langle I^2 \rangle$ is the mean square over the Fermi surface of the electronic matrix element of the change in the crystal potential, and $\langle \omega^2 \rangle$ is the mean square phonon frequency. Although $N(0) \langle I^2 \rangle$ was assumed to be nearly constant for transition metals and alloys, it is apparent that the $T_c^{\max}$ values derived by McMillan are dependent on this product.

Table IV. Data for θ_D , λ and $N(0)\langle I^2 \rangle / q_0^2$ (taking $\mu^* = 0.13$) of transition metal alloys. Values of T_c can be found in Table I.

Alloys	$\theta_D(^{\circ}\text{K})$	λ	$N(0)\langle I^2 \rangle / q_0^2$ (eV/atom)	Ref.
V_2Hf	190	0.81	1.88	28
V_2Zr	212	0.74	1.48	28
$\beta\text{-La}$	142	0.91	1.76	29
Zr_2Rh	188	1.1	2.60	15
Zr_2Ir	200	0.92	3.17	15
$\text{Nb}_{57}\text{Rh}_{40}\text{C}_3$	300	0.83	4.97	17, 27
$\text{Ta}_{54}\text{Rh}_{43}\text{C}_3$	260	0.89	5.89	17, 27
$\text{Mo}_{25}\text{Tc}_{75}$	300	1.1	6.62	30
$\text{Ir}_{40}\text{Nb}_{55}\text{O}_5$	279	0.92	6.65	17, 27
$\text{Nb}_3\text{Au}_{0.3}\text{Pt}_{0.7}$	300	0.92	6.78	31
$\text{Mo}_{42}\text{Re}_{58}$	300*	1.05	9.75	30
$\text{Re}_{55}\text{W}_{45}$	340**	0.82	12.03	32

* extrapolated from reference 30.

** extrapolated from reference 32.

Thus it is interesting to determine whether $N(0) \langle I^2 \rangle$ varies systematically with the melting temperature T_m . We evaluated the quantity $\frac{N(0) \langle I^2 \rangle}{q_0^2}$ for the twelve alloys listed in Table IV. The parameter q_0 ($\sim 1 \text{ \AA}^{-1}$) is the Slater coefficient describing the exponential $e^{-q_0 r}$ for the electronic d-state function and the reason for introducing it here will be discussed later. Using equation (2), $N(0) \langle I^2 \rangle / q_0^2$ can be equated to $\lambda M \langle \omega^2 \rangle / q_0^2$. The quantity $\langle \omega^2 \rangle$ which was defined by McMillan as $\int d\omega \omega F(\omega) / \int \frac{d\omega F(\omega)}{\omega}$ where $F(\omega)$ is the phonon density of states, is taken to be $\sim \theta_D^2 / 2$. This approximation will introduce some uncertainty in the determination of $N(0) \langle I^2 \rangle / q_0^2$. But since similar crystal structures have similar phonon spectra, therefore a systematic error is expected for this quantity calculated for the twelve alloys all having cubic TCP structures. The value of q_0 is taken to be $0.9 \text{ \AA}^{-1}$ throughout the calculation and thus amounts to a scaling factor for the $N(0) \langle I^2 \rangle$ values.

In Figure 3, the results for $N(0) \langle I^2 \rangle / q_0^2$ are plotted versus T_m . A simple linear relation is found with the 4d-4d, 4d-5d and 5d-5d alloys obeying the same functional dependence. The only assumption made in arriving at this result was that alloys considered must have T_c near αT_m , the limiting value of T_c for each class of alloy. This assumption generally restricts attention to the TCP cubic phases with optimum e/a values. Thus Figure 3 exhibits a systematic dependence of $N(0) \langle I^2 \rangle / q_0^2$ on T_m for this class of materials. Notice that alloys based on a 3d constituent ($V_2\text{Hf}$ and $V_2\text{Zr}$) have lower values of $N(0) \langle I^2 \rangle / q_0^2$ than the 4d or 5d alloys having the same T_m .

Barišić, Labbé and Friedel have suggested that the quantity

Fig. 3. Values of $N(0) \langle I^2 \rangle$ as a function of T_m for 4d and 5d alloys. Alloys V_2Hf and V_2Zr which contain a 3d constituent are also included.

$N(0) \langle I^2 \rangle$ can be directly related to the d electron contribution to the cohesive energy of a transition metal.⁸ Using a simple model with six fold atomic coordination, and the tight-binding approximation, they demonstrated that $N(0) \langle I^2 \rangle$ can be expressed as

$$N(0) \langle I^2 \rangle = -q_0^2 \int_0^{E_F} N(\epsilon) \epsilon d\epsilon = q_0^2 E_c \quad (3)$$

where ϵ is the electronic energy measured from the middle of the band and q_0 is the Slater coefficient describing the exponential attenuation of the d-electron wave functions, and E_c represents the contribution of the d-electrons to the total cohesive energy of the metal. Values of q_0 are found to vary slightly from one period of the transition metal series to the other. In particular, values of $q_0 = 0.93$, 0.91 and $0.87 \text{ \AA}^{-1}$ are estimated in reference 8. For convenience, q_0 is taken to be $0.90 \text{ \AA}^{-1}$ in the present case; the small error introduced is not significant. This value was used to convert values of $N(0) \langle I^2 \rangle$ in Figure 3 to a characteristic energy per atom. The implication of Figure 3 is then clear. Following reference 8, we identify $N(0) \langle I^2 \rangle / q_0^2$ with the d-electron contribution to cohesive energy which is then observed to scale with alloy melting temperature T_m . Indeed, the calculated values ranging from ~ 3 -12 eV/atom are of the order of observed cohesive energies for pure transition metals.³³ However, due to systematic errors introduced in approximating $\langle w^2 \rangle^{\frac{1}{2}}$, it should not be expected that the actual values are exact. Instead, the systematic behavior of $N(0) \langle I^2 \rangle / q_0^2$ as a function of T_m is most important. This suggests a simple explanation of the systematics already observed. Values of $N(0) \langle I^2 \rangle$ scale with the d-electron contribution to

the cohesive energy of the metal alloy, and thus with T_m . In turn, the maximum superconducting transition temperature for a given class of materials (e.g. 4d-4d, 4d-5d and 5d-5d TCP phases) is limited by this cohesive energy, and thus by the melting temperature. It is interesting that when $N(0) \langle I^2 \rangle / q_0^2$ is extrapolated to zero in Figure 3, one finds $T_m \sim 900^\circ\text{K}$. This suggests that removal of the d-electron contribution to the cohesive energy from these phases would lower the melting temperature to this value. This number provides an interesting measure of the s-electron cohesive energy. In fact, the measured melting temperatures of the pre-transition metals Ba and Sr are of the order of 1000°K as would be expected if this idea is correct. The alloys based on 3d constituents have lower values of $N(0) \langle I^2 \rangle / q_0^2$. It is a known fact that 3d metals have characteristically lower melting temperatures and lower cohesive energies. This is consistent with the above interpretation.

Finally, one can return to the problem of predicting maximum T_c 's for transition metal alloys. The maximum T_c for each class of alloys (i.e. 3d, 4d and 5d) can be understood based on the preceding analysis. We return to the expression for λ given by equation (2). McMillan obtained an expression for maximum T_c in a class of materials by varying $\langle \omega^2 \rangle$ keeping $N(0) \langle I^2 \rangle$ constant. The maximum T_c is obtained for $\lambda = 2$. Experimentally, $\langle \omega^2 \rangle$ is not observed to decrease arbitrary to give this optimal value of λ . The degree of phonon mode softening for a particular crystal structure is limited by its relative stability compared with competing structures. It is observed in the present study that $\langle \omega^2 \rangle \sim \theta_D^2$ is nearly constant for 4d and 5d alloys having T_c near the limiting value ($\theta_D \sim 300^\circ\text{K}$). We have found

$N(0) \langle I^2 \rangle$ to be the same linear function of T_m for both series. As a result, the difference in the limiting T_c values for a given T_m observed in Figure 1 can now be seen to result from the difference in the mean atomic mass M through λ . The M value is roughly twice as large for 5d alloys as for 4d alloys while values of $N(0) \langle I^2 \rangle$ are nearly the same; this leads to a reduced λ and thus lower limiting values for T_c in the 5d alloys. For 3d alloys, the value of M is about half that of the 4d alloys. However, the cohesive energy term $N(0) \langle I^2 \rangle / q_0^2$ is also reduced by a factor of two. Since $\langle \omega^2 \rangle$ is somewhat larger for 3d metals, the net result is a slight decrease in λ . The maximum T_c for each class of materials is thus determined mainly by $N(0) \langle I^2 \rangle$ and M . Summarizing, the highest transition temperature should be found in the 4d-4d alloys, and the 5d-5d alloys are most unfavorable for superconductivity among transition metal alloys.

III. EXTENSION TO THE GENERAL CASE

In order to extend the preceding discussion to the general case of an arbitrary superconducting alloy, data for melting temperature T_m , and maximum T_c were compiled for alloys containing non-transition metals. This information, along with crystal structure data, has been compiled in Table V. The data was obtained from B. W. Roberts' compilations mentioned previously, and other sources listed in the table. Relatively recent results for $(Pd_{1-x}Cu_x)H$, $LiTi_2O_4$ and $Mo_3S_4Sn_{0.5}$ are included. For $(Pd_{1-x}Cu_x)H$, the melting temperature is taken to be that of the non-hydrogenated $Pd_{1-x}Cu_x$ alloy since the melting temperature of the hydride cannot be measured. Following the

Table V. Summary of data for general alloys as mentioned in section III.

Alloy	$T_m(^{\circ}\text{K})$	$T_c(^{\circ}\text{K})$	Structure	Ref.
Hg	235	4.16	A10	13
Ga	300	8.0	γ -phase	13
BiIn ₂	360	5.7	β -phase	13
In _x Sn _{1-x}	~ 400	7.3		13
Bi _{0.26} Pb _{0.74}	460	8.3	A1	13
Ge ₃₀ Sn ₇₀	500	6.5	A5	34
AsPb	550	8.4		13
Al ₇₀ Si ₃₀	850	7.5	A1	34
InLa ₃	~ 1100*	10.4	L1 ₂	13
Be ₆₀ Si ₄₀	1360	9.0		34
LiO ₄ Ti ₂	1380	14.0	H1 ₂	35
Mo ₃ S ₄ Sn _{0.5}	~ 1400**	15.0	rhombohedral	36

(continued)

Table V. (continued)

$H(Cu_{0.25}Pd_{0.75})$	1600	17.0	B1	37
GaV_3	1800	16.8	A15	13
$GeNb_3$	2200	~ 23.0	A15	38, 39
$GaNb_3$	2200	20.8	A15	40
$AlNb_3$	2230	19.0	A15	13
Nb_3Sn	2300	18.0	A15	13
NNb	2640	17.3	B1	13
$Mo_{0.42}Re_{0.58}$	2775	15.0		21
NTa	2940	14.0	B1	13
NZr	3050	9.8	B1	13
CNb	3860	14.0	B1	13
CTa	4070	11.0	B1	13
$C(Hf_{0.1}Ta_{0.9})$	4323	9.0	B1	13

* Estimated based on solidus of La-Sn system

** Estimated based on T_m for MoS_2

approach of section II, an attempt to correlate maximum T_c to T_m is made. The ratio T_c/T_m is plotted versus T_m in Figure 4. The limiting values of T_c/T_m follow a definite trend as a function of T_m . The behavior can be divided into three regions. The first region, designated s-p alloys, consists of alloys containing only group A elements. For these "soft metal" alloys, T_m is rather low ranging from ~ 250 - 1300°K . Maximum values of T_c for these alloys are nearly independent of T_m . For example, $\gamma\text{-Ga}$ with $T_m = 300^\circ\text{K}$, $\text{Pb}_{0.74}\text{Bi}_{0.26}$ with $T_m = 460^\circ\text{K}$, and $\text{Be}_{60}\text{Si}_{40}$ with $T_m = 1360^\circ\text{K}$ all have $T_c \cong 9^\circ\text{K}$. This is the observed limiting value of T_c for soft metal alloys. Thus the ratio T_c/T_m is bounded by a relation $T_c/T_m \lesssim 9/T_m$. The second region consists of alloys containing both a transition metal and a non-transition metal and includes such alloys as $\text{Mo}_3\text{S}_4\text{Sn}_{0.5}$, LiTi_2O_4 , and Nb_3X where X is a group A element in an A-15 phase. These alloys are designated s-p-d alloys since the chemical bonding in these materials involve all three types of atomic orbitals. The melting temperature of these materials ranges from ~ 1500 to $\sim 2300^\circ\text{K}$. The ratio T_c/T_m is found to be nearly independent of T_m . This situation is very similar to that previously observed for transition metal alloys over a comparable range of T_m values. For these materials, the maximum T_c scales with T_m . The third region consists of materials with $\sim 2500^\circ\text{K} < T_m < 4000^\circ\text{K}$. This group includes transition metal borides, carbides, and nitrides. These materials have the NaCl type structure and are characterized by low atomic coordination (six-fold) and a strong tendency towards covalent bonding. Within this class of materials, the ratio T_c/T_m is observed to decrease with increasing

Fig. 4. Maximum observed T_c/T_m ratios as a function of T_m for general alloys. Alloys are designated by the nature of the valence electron orbitals of the constituents.

melting temperature.

The behavior of T_c in soft metal alloys suggests that a rather different description of the behavior of the coupling constant λ is required than that given in section II (D) for transition metal alloys. For the s-p-d materials in the second region, in particular for the A-15 materials V_3X and Nb_3X with X in group A, some of the ideas presented in section II (D) may be applicable. If the measured values of θ_D and T_c are used, then values of λ may be calculated for these A-15 phases. Assuming that the Nb and V atoms are of major importance in the superconductivity as discussed in the linear chain model⁴¹ and thus using their atomic masses to characterize the alloys, one can calculate the value of $N(0) \langle I^2 \rangle / q_0^2$ as was done in section II(D). The results are shown in Table VI. For the Nb_3X alloys, values of $N(0) \langle I^2 \rangle / q_0^2$ agree with those obtained for 4d and 5d alloys containing only transition metals shown in Figure 3. For the V_3X alloys, values agree well with those obtained for vanadium based transition metal alloys. This suggests that the cohesive energy of these alloys is again the major limiting factor for T_c . This accounts for the relatively lower T_c observed in V_3X compounds compared with that for Nb_3X compounds.

On the basis of Figure 4 and the preceding discussion, one can estimate the maximum value of T_c for the Nb_3X alloys. The T_c of Nb_3Ga and Nb_3Ge should be optimized near $25^\circ K$. For Nb_3Si with $T_m \sim 2300^\circ K$, an A-15 phase with T_c higher than $10^\circ K$ ⁴⁴ has not yet been obtained. The Nb-Si phase diagram suggests that the free energy of the A-15 phase is comparatively larger than that of competing phases and thus it should be difficult to obtain. If a stoichiometric

Table VI. Data for θ_D , λ and $N(0) \langle I^2 \rangle / q_0^2$ (taking $\mu^* = 0.13$ and masses of Nb and V componets only) of Nb_3X and V_3X A15 alloys. Values of T_c can be found in Table V.

Alloys	$\theta_D(^{\circ}K)$	λ	$N(0) \langle I^2 \rangle / q_0^2$	Ref.
Nb_3Al	290	1.18	6.47	42
Nb_3Ga	$\sim 300^*$	1.20	7.27	
Nb_3Ge	$\sim 300^*$	1.25	7.26	
Nb_3Sn	290	1.14	5.95	30
V_3Ga	310	1.06	3.50	30
V_3Si	330	1.02	3.90	30, 43

* estimations based on known θ_D values of Nb_3X A15 alloys.

A-15 phase can be obtained however; then the T_c should be near 26°K as implied by Figure 4. In summary, there is little ground for optimism in obtaining higher T_c 's among known alloy phases. The present study suggests that superconducting transition temperatures are probably limited to $\lesssim 30^\circ\text{K}$.

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