TREND OF SUPERCONDUCTIVITY IN AMORPHOUS SUPERCONDUCTING TRANSITION METAL AND THEIR ALLOYS

S. J. Poon

DECEMBER 1975

MASTER

A REPORT ON RESEARCH CONDUCTED
UNDER CONTRACT FOR THE
U.S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION

THERE IS NO OBJECTION FROM THE PATENT
STANDPOINT TO THE PUBLICATION OR
DISSEMINATION OF THIS DOCUMENT:

CALIFORNIA PATENT GROUP, ERDA

By: *Janet H. Ley*

Date: *January 23, 1976*

W. M. KECK LABORATORY OF
ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RECEIVED
JAN 15 1976
CALIF. PATENT GROUP

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

California Institute of Technology
W. M. Keck Laboratory of Engineering Materials

TREND OF SUPERCONDUCTIVITY IN AMORPHOUS SUPERCONDUCTING
TRANSITION METALS AND THEIR ALLOYS

by

S. J. Poon

—NOTICE—

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Energy Research and Development Agency Report No. 70, under
Contract No. AT(04-3)-822.

Professor Pol Duwez, principal investigator.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

December 1975

47

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

ABSTRACT

A plausible interpretation for the trend of superconducting transition temperature T_c in amorphous transition metal TM alloys is presented from a chemical point of view. We show that the T_c behavior is not a reflection of the dependence of the atomic parameter η on the number of electrons per atom, but rather due to two other effects. One is the changes in the density of states due to the mixing of antibonding and bonding states in the b.c.c. amorphous metals. The other is an increase in the number of valence d electrons participating in the phonon-induced d-d coupling towards the mid series.

It is well known that the dependence of superconducting transition temperature T_c on the number of valence electrons per atom (z) for crystalline transition metal (TM) alloys exhibits two distinct peaks at $z \approx 4.7$ and 6.5 . Collver and Hammond¹ observed in amorphous TM alloys a triangular peak for T_c versus z around $z \approx 7$ for both 4d and 5d transition metal series. The difference in the trends of T_c in the amorphous and crystalline states presents an interesting problem. That is, the relative importance of atomic parameters on the superconductivity in a solid of particular atomic configurations. In this paper, we first discuss the validity of the different theories in the past on the trends of T_c in amorphous TM alloys. Then, we present a new explanation from a chemical (or atomic) point of view.

The first explanation² for the T_c behavior in amorphous TM alloys conjectured the observed trend in T_c as the manifestation of a similar dependence of the atomic parameter η (or $N(o) \langle I^2 \rangle$) as introduced by McMillan³ on z around the mid series. Later, Kerker et al⁴ came to the same conclusion by presenting the first calculation of T_c for amorphous TM elements. Their calculation was based on the assumption that the atomic volume in the amorphous state increases by ΔV which is comparable to the change in atomic volume ΔV_m observed upon melting. They concluded that the changes in Coulomb pseudopotential μ^* , density of states $N(o)$, and phonon frequency moment $\langle \omega^2 \rangle$ due to lattice disorder tend to equalize T_c ; and it is the dependence of η on z which reflects T_c . However, it is doubtful from the experimental point of view that the assumption made on ΔV is realistic. Chen et al⁵ observed in amorphous transition metals that the fractional increase in volume $\frac{\Delta V}{V}$ is of the order of two percent, while $\frac{\Delta V_m}{V}$

is of the order of ten percent. Thus, a significant error can be introduced when one evaluates the changes in $\langle \omega^2 \rangle$ using the Grüneisen constant γ_G (≈ 2 in TM elements) in the formula $\frac{\Delta \langle \omega^2 \rangle}{\langle \omega^2 \rangle} \approx 1 - (1 + \frac{\Delta V}{V})^{2\gamma_G}$.

We⁶ also found that the interpretation of the T_c behavior in terms of the existence of a triangular peak in η rather problematic. For the following discussion, we will assume the same value of η for the TM amorphous state and the crystalline state as will be made clear later. The values of η obtained by Allen et al⁷ for the TM pairs Nb, Mo and Ta, W do not show any tendency towards forming such a peak. So far, the numerical results of Allen et al are considered most accurate since they were obtained from self-consistent numerical solutions of the Eliashberg equations using tunneling data. One can also use the Barisić's relation⁸ $\eta \approx q_0^2 E_d$ (E_d is the d-electron contribution to the cohesive energy, q_0 is the Slater coefficient measuring the decay of the d-electron wavefunction) to investigate the behavior of η by knowing E_d . Since E_d remains essentially the same in both the crystalline and amorphous state as evident by comparing the heats of fusion and heats of sublimation in the TM series, it is reasonable to use the same η for both states. The values of E_d are estimated by applying Brewer's technique⁹ of decomposing the total cohesive energy E_c into E_d and the sp-electron contribution to E_c . In Figures 1 and 2, we plot both the values of η and E_d obtained from references 7 and 9 respectively. The value of η for Re is quoted from Evans et al.¹⁰ For those points where reliable values of η are missing, we just plot the values of $q_0^2 E_d$. One can conclude from these plots that no distinct peak for either η or E_d around $z \approx 7$ can be observed. In view of the above arguments, a new

Fig. 1. Superconducting transition temperature T_c and atomic parameter η in the 4d transition metal series. Solid curve traces the experimental data in reference 1. Calculations of T_c for alloy systems are only performed in the Mo-Tc and Ru-Tc alloys.

Fig. 2. Same plots as in Figure 1 for the 5d series. Calculations of T_c for alloy systems are only performed in the Os-Re and Ir-Os alloys.

approach to understand the trend of superconductivity in amorphous transition metal alloys is in need.

We propose in this paper a plausible explanation for the trend of superconductivity in amorphous TM superconductors using a chemical approach. We first discuss the important assumptions on the parameters involved in the theory. Our theory is based on the detailed interplay of the four parameters μ^* , $N(o)$, $\frac{E_d}{E_b}$ (where E_b is the bonding enthalpy), and ω_d (the effective d-band width) which yields the observed T_c dependence as can be seen later. We assume that d-band superconductivity accounts for the magnitude of T_c in TM elements and alloys as can be justified either from our previous plots in Figures 1 and 2, or from reference 6. We also assume that the minimum in the electron density of states of the b.c.c. structure is less pronounced due to the mixing of antibonding and bonding orbitals in the amorphous state.¹¹ The above assumptions when taken together suggest that the product $2N(o)\omega_d$, ($N(o)$ in spin states per eV atom) should give approximately the number of valence d electrons z_d in the amorphous state. Thus, the problem is equivalent to knowing the values of μ^* , z_d , and $\frac{E_d}{E_b}$. The last parameter which is approximately given by the crystalline value measures the fraction of bond energy available for strong electron-phonon coupling. However, our theory cannot predict the actual values of T_c since they involve a detail knowledge of the electron-phonon interaction spectrum $\alpha^2 F(\omega)$, but it demonstrates a triangular peak dependence of T_c on z once the T_c of an amorphous TM is known.

We will first calculate the values of T_c in TM elements using McMillan's T_c equation, then will extend our calculation to alloys using a dense-random-packed (DRP) model for amorphous solids.¹²

According to the solution of the Eliashberg gap equations given in reference 3

$$T_c = \frac{\theta_D}{1.45} \exp \left\{ - \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right\} \quad (1)$$

where θ_D is the Debye temperature, λ is given by $\frac{N(o) \langle I^2 \rangle}{M \langle \omega^2 \rangle}$ with M the ionic mass. Since we will be dealing with superconductors where $\lambda \lesssim 1$, the accuracy of the solutions to equation (1) should be satisfactory as proved in reference 7. The Coulomb pseudopotential μ^* in the amorphous state is given by

$$\mu^* = \frac{N(o)V_c}{1 + N(o)V_c \ln\left(\frac{\omega_d}{\theta_D}\right)} \quad (2)$$

assuming the same value for the Fermi surface averaged Coulomb repulsion V_c in both the crystalline and amorphous states, and $\ln\left(\frac{\omega_d}{\theta_D}\right) \approx 5$. For small changes in $N(o)$, equation (2) reduces to

$$\mu^* \approx \frac{(1 + \frac{\Delta N}{N_o}) \mu_o^*}{1 + \frac{\Delta N}{N_o} \mu_o^* \ln\left(\frac{\omega_d}{\theta_D}\right)}, \text{ where the subscript 'o' refers to the}$$

crystalline values. The remaining discussion involves the evaluation of λ and θ_D for equation (1).

The only unknown parameter in calculating λ is the moment $\langle \omega^2 \rangle$ since the values of η are known a priori from references 6 and 7. To calculate $\langle \omega^2 \rangle$, we adopt the first-principles theory due to Gomersall

and Gyorffy.¹³ By including only the first bubble diagram in the series expansion for the dressed phonon frequency ω_{qv} in the lattice dynamical equations and averaging over the spectrum $\propto F(\omega)$, they obtained

$$\langle \omega^2 \rangle \approx \langle \Omega^2 \rangle - \frac{4}{5} \epsilon_d' N(o) M^{-1} [N(o) \langle I^2 \rangle] \quad (3)$$

The second term on the right hand side of equation (3) represents the d-electron-phonon screening physically. Here, we ignore the sp-electron contribution to the electron-phonon interaction as discussed earlier.

Equation (3) has been proved applicable to TM elements in reference 13.

Here ϵ_d is the d-band Fermi energy, and Ω_{qv} 's are the so called band structure independent phonon frequency which are the results of direct interactions between ions. Now, we propose two further approxima-

tions from a chemical point of view. First, it is obvious that $\langle \Omega^2 \rangle$ depends on the bonding strength of the valence electrons including the screened sp contributions. We suggest a Lindemann type relation for $\langle \Omega^2 \rangle$ in the form $\langle \Omega^2 \rangle \approx \frac{CE_b}{MV^{2/3}}$ where C is a crystal structure (or

short range order in the amorphous state) dependent constant and E_b is the bonding enthalpy per atom. Second, we set $\epsilon_d \approx \omega_d$ by supposing that it is mainly the electrons in the valence d state participating in the conduction process. The number of valence d electrons

$z_d \approx 2N(o)\omega_d$ discussed earlier can be determined from the Engel-Brewer rule.⁹ The latter expresses the valence state in the form $d^{n-x-y} s^x p^y$

which is determined from both empiricism and microscopic analysis of the electronic energy levels in TM elements. We assume that the value of n-x-y remains unchanged in the amorphous state. This is reasonable because the valence d electrons have very little to do with long range

ordering as shown in reference 9. Putting equation (3) into the definition of λ together with the above suggestions, we obtain

$$\lambda \approx \left[\left(\frac{E_b}{N(o) \langle I^2 \rangle} \right) \frac{C}{V^{2/3}} - \frac{2}{5} z_d \right]^{-1} \quad (4)$$

The values of θ_D can thus be obtained from $\theta_D \approx \theta_{D0} \left(\frac{\lambda_0}{\lambda} \right)^{1/2}$.

In calculating μ^* , we assume that $N(o)$ in the amorphous b.c.c. phase varies from ~ 0.6 spin states/eV atom on the two subbands to ~ 0.4 spin states/eV atom at the central minimum instead of using a uniform value of 0.5 as in reference 4. This assumption also allows for the conservation of the number of electrons in the conduction band. In Table I, the Engel-Brewer valence state configurations for TM elements together with the values of μ^* and λ in the crystalline and amorphous states are given. The corresponding values of T_c are plotted in Figures 1 and 2 for the 4d and 5d series respectively. We emphasize again that the calculation of exact T_c 's are impossible without a knowledge of $\alpha^2 F(\omega)$. At the present time, we can only assume that the T_c 's for b.c.c. Nb and h.c.p. Ru are known a priori in order to determine the structural factor C in (4) throughout the 4d series. In the 5d series, we use the known T_c of b.c.c. Ta to generate other values of T_c . The value of $C_{h.c.p.}$ for the 5d series is determined from $\left(\frac{C_{Ru}}{C_{Nb}} \right) C_{Ta}$.

There is generally good agreement between our calculated results for T_c and the experimental ones as can be seen in Figures 1 and 2. The fundamental concepts in our theory involve the changes in the density of states due to the mixing of antibonding and bonding orbitals in the amorphous state; and an increase in the number of valence

TABLE I. The Engel-Brewer valence state configurations for transition metals together with values of μ^* and λ^a . Asterisks denote elements where the experimental values of T_c are taken to determine the structural factor C. Subscript 'o' denotes crystalline values.

Metal	Valence Configuration	μ_o^*	μ^*	λ_o	λ
Y	dsp	0.15	0.15	0.35	0.37
Zr	d ² sp	0.17	0.17	0.49	0.53
Nb*	d ⁴ s	0.17	0.14	0.93	0.69
Mo	d ⁵ s	0.10	0.12	0.40	0.71
Tc	d ⁵ sp	0.13	0.13	0.72	0.67
Ru*	d ^{3.7} sp ^{0.7}	0.16	0.18	0.46	0.57
Hf	d ² sp	0.14	0.15	0.38	0.49
Ta*	d ^{3.5} sp ^{0.5}	0.15	0.14	0.72	0.52
W	d ⁵ s	0.06	0.10	0.20	0.56
Re	d ⁵ sp	0.11	0.14	0.47	0.74
Os	d ⁴ sp	0.14	0.15	0.43	0.59
Ir	d ³ sp	0.20	0.20	0.49	0.46

^aValues of μ_o^* and λ_o are taken from K. H. Bennemann and J. W. Garland; Theory, d-Band Metals; in 'Superconductivity in d- and f-band Metals', ed. D. H. Douglas (AIP, New York, 1972).

d electrons participating in the electron-phonon coupling towards the half filled d-shell. The latter effect is manifested in the amorphous state due to the smearing out of the fine structures in the d subbands. The result is an increase in λ towards the mid series where the electron valence state configuration is $d^5 sp$. The values of μ^* decreases towards the mid series due to the presence of a local minimum in the density of states of the b.c.c. phase. These two effects add to yield the observed triangular peak. Another basis in support of our theory is that it can explain the relative shift in the locations of the triangular T_c peaks in the 4d and 5d series. This is obvious from Figure 3 where we plot z_d versus the 4d and 5d TM elements. It is just due to the differences between the Engel-Brewer values of z_d in the corresponding series. Using the value of C_{Nb} , we predict the transition temperature of amorphous vanadium to be $\sim 0.1^\circ K$ in contrast to the value of $\sim 9^\circ K$ given in reference 4. Recently, Kuz'menko et al¹⁴ observed a T_c of $\sim 1^\circ K$ in thin films of amorphous vanadium which is significantly lower than the corresponding crystalline value.

To calculate the values of T_c for amorphous alloys of the form $A_x B_{1-x}$, we assume a two-sphere DRP model constructed with the use of local atomic configurations of the one-sphere DRP structure extended to two types of spheres. The values of θ_D^2 can thus be given by $x\theta_A^2 + (1-x)\theta_B^2$ using a classical model of the force constants. The calculation of λ_{AB} involves a knowledge of z_{AB} which can be represented by $xz_A + (1-x)z_B$ using the coherent potential approximations (CPA) for x close to unity or zero.¹⁵ The values of μ_{AB}^* can also be approximated in the same form by CPA. However, the form for

Fig. 3. Number of valence d electrons per atom for 4d and 5d transition metals. Straight lines show an approximate trend in the corresponding alloys.

$\left(\frac{E_b}{N(o) \langle I^2 \rangle}\right) \frac{C}{V}^{2/3}$ in the alloy case is rather uncertain at the present

time. Thus we are only able to perform calculations of T_c for alloys where those values for the corresponding elements are about the same.

In summary, we see no evidence that the T_c behavior in amorphous transition metal superconductors is a reflection of η on z . We have demonstrated a plausible interpretation for the trend of T_c in amorphous TM superconductors from a chemical point of view. The main idea involves the changes in the density of states due to the mixing of antibonding and bonding states in the b.c.c. amorphous TM elements, and an increase in the number of valence d electrons participating in the phonon-induced d-d coupling towards the mid series. The latter effect is only manifested in the amorphous state when the fine structures in the d subbands are smeared out by strong lattice disorder.

ACKNOWLEDGMENTS - The author wishes to thank Professor Pol Duwez for support throughout this work. He also thanks Professor T. C. McGill for critical reading of the manuscript.

REFERENCES

*Work supported by the Energy Research and Development Agency.

Contract No. AT(04-3)-822

1. M. M. Collver and R. H. Hammond, Phys. Rev. Lett. 30, 92 (1973).
2. R. H. Hammond and M. M. Collver, in Low Temperature Physics-LT13. K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel eds. (Plenum Press, New York - London) Vol. 3, p. 532.
3. W. L. McMillan, Phys. Rev. 167, 331 (1968).
4. G. Kerker and K. H. Bennemann, Z. Physik 264, 15 (1973).
5. H. S. Chen and B. K. Park, Acta Met. 21, 395 (1973).
6. S. J. Poon, to be published.
7. P. B. Allen and R. C. Dynes, Phys. Rev. 12, 905 (1975).
8. S. Barišić, J. Labbé, and J. Friedel, Phys. Rev. Lett. 25, 919 (1970).
9. N. Engel, Trans. Quart. of the American Society for Metals 57, 610 (1964). L. Brewer, in Phase Stability in Metals and Alloys. P. Rudman, J. Stringer, and R. I. Jaffee eds. (McGraw-Hill, New York 1967) p. 39-61.
10. R. Evans, G. Gaspari, and B. L. Gyorffy, J. Phys. F3, 39 (1973).
11. J. Friedel, 1967 Proc. Int. School of Physics 'Enrico Fermi' W. Marshall ed. (New York, Academic Press). p.283.

12. J. D. Bernal, Proc. R. Soc. A 280, 299 (1964).
13. I. R. Gomersall and B. L. Gyorffy, Phys. Rev. Lett. 33, 1286 (1974).
14. V. M. Kuz'menko, V. G. Lazarev, V. I. Mel'nikov, and A. I. Sudovtsov, Z. Eksperim. noi i Theoret. Fiziki 67, 801 (1974)
[Sov. Phys. - JETP 40, 396 (1975)].
15. B. Velicky, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).