METASTABLE SUPERCONDUCTING ALLOYS

W. L. Johnson

JULY 1978

*A REPORT ON RESEARCH CONDUCTED
UNDER CONTRACT FOR THE
DEPARTMENT OF ENERGY*

W. M. KECK LABORATORY OF
ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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

METASTABLE SUPERCONDUCTING ALLOYS

by

W. L. Johnson

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, 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.

Department of Energy Report No. 92, under Contract No. EY-76-C-03-0822.

Professor W. L. Johnson, principal investigator.

JULY 1978

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

24

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, 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

The study of metastable metals and alloys has become one of the principal activities of specialists working in the field of superconducting materials. Metastable crystalline superconductors such as the Al₅-type materials have been given much attention. Non-crystalline superconductors were first studied over twenty years ago by Buckel and Hilsch using the technique of thin film evaporation on a cryogenic substrate. More recently, melt-quenching, sputtering, and ion implantation techniques have been employed to produce a variety of amorphous superconductors. The present article presents a brief review of experimental results and a survey of current work on these materials. The systematics of superconductivity in non-crystalline metals and alloys are described along with an analysis of the microscopic parameters which underlie the observed trends. The unique properties of these superconductors which arise from the high degree of structural disorder in the amorphous state are emphasized.

I. INTRODUCTION

A metal or alloy in which the characteristic atomic arrangement does not correspond to a thermodynamic equilibrium state is said to be metastable. Extended metallic solid solutions, non-equilibrium intermetallic crystalline phases, and non-crystalline alloys are examples of metastable materials. The study of superconducting metals and alloys has led many investigators to consider a variety of metastable materials. Experience has shown that significantly altered superconducting properties are often observed when a material is prepared in a metastable state as compared with its equilibrium form. Notable examples of this are A-15 type materials such as Nb_3Ge . In equilibrium, the A-15 Nb-Ge phase is stable only for off-stoichiometric compositions between 14 and 17 at.% Ge.¹ By sputtering an Nb_3Ge target material onto a substrate at elevated temperature, Gavaler² found that a metastable near stoichiometric phase could be produced. Whereas a T_c of 7 K is observed for the equilibrium material, a T_c of ~ 23 K was found for the metastable material. Over twenty years ago, Buckel and Hilsch^{3,4} prepared non-crystalline thin films of Bi, Pb, and other simple metals by quenching the metallic vapors onto a cryogenic substrate. Non-crystalline Bi films were found to be metallic and superconducting with $T_c = 6$ K in contrast to bulk crystalline Bi which is semimetallic and non-superconducting. The instability of these films was evident in the fact that an increase in substrate temperature to ~ 25 K resulted in crystallization of the film and the subsequent disappearance of superconductivity. Since this early work, considerable effort has been devoted to studying superconductivity and other fundamental properties of non-crystalline thin films of simple metals. Results

published by numerous investigators have been comprehensively reviewed by Bergmann.⁵ Of particular interest is a systematic study of vapor-quenched non-crystalline transition metal films by Collver and Hammond.⁶ Recently, superconductivity has been observed in bulk metallic glasses^{7,8} prepared by rapid cooling of a liquid alloy. Owing to the large sample quantities made available by this technique and the comparative stability of such glasses with respect to crystallization, it has become possible to carry out several new types of studies.

The present article presents a short review of experimental work dealing with the properties of non-crystalline superconducting alloys as well as a survey of current research in this field. Metastable crystalline alloys will be mentioned only briefly as both topics cannot be adequately covered within the scope of this article. Emphasis will be placed on current topics and new results.

In section II, the occurrence and systematics of superconductivity in amorphous metals and alloys is discussed. Simple (nearly free electron) metals and transition (d-band) metals are surveyed separately. Experimental evidence suggests that a unifying conceptual scheme can be devised to account for the observed systematics of superconductivity in both of the above alloy types. This evidence is summarized in section III and a simple analysis is presented. The unique properties of amorphous superconductors which arise from a high degree of structural disorder are covered in section IV. The topics include a discussion of the upper and lower critical fields, the critical current density, flux pinning, and fluctuation phenomena.

II. SYSTEMATICS OF SUPERCONDUCTIVITY IN AMORPHOUS ALLOYS

A. Simple Metals (Non-Transition Metals)

Amorphous simple metals have generally been prepared by the method of vapor quenching onto a cryogenically cooled substrate.^{3,4,5} It has been observed that these materials crystallize on heating to room temperature. Studies of superconductivity have been carried out on numerous thin films obtained by this technique; Table I gives a summary of typical experimental data obtained. Included are film composition, superconducting transition temperature T_c , the energy gap in the low temperature limit Δ_0 , and the electron-phonon coupling constant λ . The latter two quantities are taken from superconductive tunneling data.⁵ Bergmann has emphasized that amorphous simple metals tend to be strong-coupling superconductors ($\lambda \gtrsim 1$). One consequence of this fact is that the ratio $[2\Delta_0/K_B T_c]$ referred to as the gap coefficient, is typically larger than the value 3.52 predicted by the BCS weak coupling theory.⁵ For the tunneling data in the table, this ratio is between 4 and 5 with the exception of $\text{Cd}_{.9}\text{Ge}_{.1}$ amorphous Be, and the $\text{Be}_{1-x}\text{Al}_x$ alloys.⁹ Other consequences of the large λ include a modified temperature dependence of the energy gap and critical field as compared with BCS theory. The experimental evidence for such strong coupling effects is summarized in ref. 5.

It is noteworthy that the T_c of most amorphous simple metals is comparable to or higher than that of the corresponding crystalline material. In some cases T_c is, nevertheless, rather low. Amorphous $\text{Cd}_{.9}\text{Ge}_{.1}$ films have $T_c = 1.6 \text{ K}$ ⁹ for example. Tunneling measurements on this material as well as cryoquenched films of the divalent metal Zn indicate a gap ratio

TABLE I. Superconducting properties of some amorphous simple metals. Included are chemical composition, average valence, transition temperature, energy gap at $T = 0$, and coupling constant. The latter quantities are only available for cases where tunneling studies have been carried out.

Metal (Alloy)	Average Valence	T_c (K)	$2\Delta_0$ (meV)	λ	Ref.
Bi	5	6.1	2.42	2.2-2.5	5
Pb _{.9} Cu _{.1}	3.7	6.5	2.66	2.0	5
Sn _{.9} Cu _{.1}	3.7	6.76	2.60	1.84	5
11 _{.9} 1e _{.1}	3.3	4.2	1.67	1.70	5
Ga	3.0	8.4	3.32	1.94-2.25	5
Be _{.7} Al _{.3}	2.3	6.1	1.87	----	9(b)
Cd _{.9} Ge _{.1}	2.3	1.6	0.37-0.42	----	9(a)
Be _{.9} Al _{.1}	2.1	7.2	----	----	9(c)
Mg _{.7} Zn _{.3} [*]	2.0	< 1.4	----	----	10,11
Be	2.0	9.95 ^{**}	3.00	0.5 [†]	9(c)
Au _{.84} Si _{.16} [*]	1.48	< 1.4	----	----	12,13

* prepared as bulk metallic glass by melt-quenching

** extrapolated to infinite thickness

† estimate base on tunneling data - amorphous Be is difficult to prepare in single phase form - the addition of Al stabilizes the amorphous phase

$[2\Delta_0/k_B T_c]$ close to or somewhat less than the BCS value of 3.52. Giessen and coworkers¹⁰ have shown that an alloy of two divalent simple metals $Mg_{70}Zn_{30}$ can be obtained in bulk form by melt-quenching. This amorphous alloy is stable at room temperature, but no superconductivity is observed down to $T = 1.4$ K.¹¹ An alloy of the composition $Au_{84}Si_{16}$ ¹² which is essentially an amorphous noble metal is not superconducting down to $T = 1.4$ K.¹³ From these observations, it would seem that amorphous alloys based on simple metals having low valence (one or two) tend to have low T_c while those involving high valence metals (three, four, or five) tend to have higher T_c . Only Be (and alloys containing a large amount of Be) have a high T_c among the amorphous divalent metals. This fact is related to the unusually high Debye temperature, $\theta_D \sim 1300$ K, of Be as pointed out below. The electron-phonon coupling constant λ should correspondingly be lower for amorphous monovalent and divalent metals as it is related to the ratio $[k_B T_c / \hbar \langle \omega \rangle]$ where $\langle \omega \rangle$ is a suitably averaged phonon frequency of the material. In view of these observations, one can infer that amorphous simple metals are not always strong-coupling superconductors. It does seem that λ is generally larger for an amorphous material than for the corresponding crystalline material. The coupling constant increases with disorder, but not necessarily to a value characteristic of strong-coupling.

The apparent relationship between valency and T_c suggested above is quite systematic as illustrated by the plot shown in Fig. 1. The figure shows the ratio $[k_B T_c / \hbar \Omega_p]$, where Ω_p is an ionic plasma frequency for ions of valency and density equal to those of the corresponding metals, plotted as a function of valence. The quantity Ω_p is a natural frequency scale

Fig. 1. Variation with valence of the superconducting transition temperature of simple amorphous metals. The values of T_C are normalized to the characteristic bare phonon temperature $[\hbar\Omega_p/K_B]$ of each material

for phonons in simple metals so that $[K_B T_C / \hbar \Omega_p]$ is the ratio of T_C to a characteristic phonon temperature ($\hbar \Omega_p / K_B$). In section III, a simplified physical picture which accounts for the observed correlation is presented.

B. Transition Metals

The first systematic study of amorphous transition metals was carried out by Collver and Hammond⁶ who again employed the technique of thin film evaporation on a cryogenic substrate. Metals and alloys of neighboring metals of the 4d and 5d transition series were systematically studied. The variation of T_C with valency in crystalline transition metals is characterized by two sharp maxima occurring at electron/atom ratios $[e/a]$ of 4.5 and 6.5.¹⁴ Here, all of the electrons outside of the filled inert gas core shell are considered as valence electrons. In contrast, amorphous cryoquenched transition metals exhibit a T_C which varies slowly with $[e/a]$ having a single broad maximum near $[e/a] = 6.5$. Both the amorphous and crystalline variation is illustrated in Fig. 2.

Since this initial survey by Collver and Hammond on thin films, work on transition metals has been extended to include a variety of alloys prepared by the method of rapid quenching from the melt.^{7,8} Bulk amorphous alloys which are stable with respect to crystallization well above room temperature are obtained using this method. Table II lists several representative examples of such melt-quenched alloys. The composition, transition temperature, and the upper and lower critical field gradients are given in the table. The latter quantities will be discussed in section III. All of these melt quenched alloys contain two or more transition

TABLE II. Examples of melt-quenched metallic glasses which exhibit superconductivity. The alloy composition, T_c , and critical field gradients $[dH_{c1}/dT]_{T_c}$ and $[dH_{c2}/dT]_{T_c}$ are listed in the table.

Alloy	T_c (K)	$\left[\frac{dH_{c1}}{dT}\right]_{T_c} \left(\frac{Oe}{K}\right)$	$\left[\frac{dH_{c2}}{dT}\right]_{T_c} (kOe)$	Ref.
La ₇₆ Au ₂₄	3.3	----	24.0	7
La ₈₀ Ga ₂₀	3.8	----	22.5	46
Zr ₇₅ Rh ₂₅	4.55	6.5-8.0	26-28	8,16
Zr ₇₀ Be ₃₀	2.8	----	23.8	17
Nb ₅₈ Rh ₄₂	4.7	----	31.0	7
Mo ₈₀ P ₁₀ B ₁₀	9.0	4.2	17.6	15,16
(Mo _{.6} Ru _{.4}) ₈₀ P ₂₀	6.18	6.5	25.5	15,16
(Mo _{.8} Re _{.2}) ₈₀ P ₁₀ B ₁₀	8.71	----	24.2	15,16
(W _{.6} Ru _{.4}) ₈₀ P ₂₀	4.25	----	----	*
(Mo _{.6} Ru _{.4}) ₈₀ B ₂₀	5.78	----	28	*

* unpublished results

Fig. 2. The variation of T_c for crystalline transition metals and alloys of neighboring metals (after Matthias) compared with the corresponding amorphous cryoquenched films.

metals. If the T_c 's are plotted as a function of the average $[e/a]$ of the transition metal components as shown in Fig. 3, it is seen that the melt-quenched alloys lie near or below an envelope defined by the Collver-Hammond curve. When the transition metal components are widely separated in $[e/a]$, the T_c tends to fall below that obtained by Collver-Hammond for metals and alloys of neighboring metals. This suggests that T_c is related to the number of occupied atomic-like d-orbitals on the individual atomic sites as will be discussed below.

Finally, it should be pointed out that ion implantation experiments have been carried out which produce results similar to those described above.^{18,19} Crystalline films of various transition metals were cooled to 4.2 K and implanted with a variety of high energy (~ 300 kV) atomic species. Those implanted species which fell within a certain range of atomic diameter and Pauling electronegativity produced a change in T_c very similar to that observed by Collver-Hammond when transforming from amorphous to crystalline films of the same metals. The results are indicated in Fig. 3. The data suggest that an amorphous phase is obtained as a result of implantation.

III. ELECTRONIC STRUCTURE AND MICROSCOPIC PROPERTIES

A. Simple Metals

In order to understand the observed systematics of superconductivity in the amorphous state, it is necessary to examine available experimental evidence regarding the electronic structure, lattice vibrations, and electron-lattice interaction in these materials. The nearly-free electron

Fig. 3. Comparison of T_c for cryoquenched films, melt quenched glasses, and ion implanted transition metals as a function of $[e/a]$. The horizontal arrows indicate the components of each melt quenched alloy.

picture is a common starting point for an analysis of simple metals. Ignoring the lack of spatial periodicity and subsequent loss of crystal momentum as a conserved quantity, one can model the electronic structure of amorphous simple metals using plane waves as a basis set. Assuming the amorphous metal to be an isotropic and spatially homogeneous medium to lowest order, one introduces the atomic potential (a pseudopotential model can be used) as a weak perturbation which induces scattering among plane wave states. The implications of such a model have been worked out in detail by Ziman²⁰ for liquid metals and applied to amorphous simple metals by several investigators.^{21,22,23} As a basic check, this model can be used to calculate various transport parameters such as electrical conductivity, the Hall coefficient, etc. For free electrons, the Hall coefficient is simply $R_H = (-1/ne)$. Measurements of R_H for amorphous simple metals generally agree well with this prediction.^{24,25} Measurements of the optical surface resistance of amorphous simple metals can also be accounted for by a nearly-free electron picture.^{26,27}

For the theory of superconductivity, the important electronic parameters are the bare density of states at the Fermi level $D(0)$, and the effective atomic potential $V_a(r)$ experienced by electrons. Unfortunately, little data exists which gives a direct measure of $D(0)$ in amorphous simple metals. The small sample quantities obtained in thin films make accurate specific heat data difficult to obtain. Magnetic susceptibility measurements which could also be used to obtain $D(0)$ are again precluded by the small sample quantity. An estimate of $D(0)$ has been obtained by Rainer and Bergman^{5,28} indirectly by measuring the upper critical field gradient in the superconducting state. This quantity is theoretically related to $D(0)$ by²⁸

$$[dH_{c2}/dT]_{T_c} = \eta(4K_B e/\pi) D^*(0) \rho \quad (1)$$

where

$$D^*(0) = (1 + \lambda) D(0)$$

is the electron-phonon dressed density of states, ρ the electrical resistivity in the normal state, and η a numerical constant of order 1. With λ taken from tunneling data, values of $D(0)$ for several cases were obtained which agree quite well with values calculated from a free electron model.

As mentioned in the last section, superconductive tunneling experiments directly measure the Eliashberg function $\alpha^2(\omega)F(\omega)$.^{5,29} From this function, the properties of a superconductor can in principle be computed. The strong coupling behavior found in several amorphous simple metals has been explained in terms of the measured $\alpha^2(\omega)F(\omega)$.^{5,30,31} When transforming from a crystalline metal to an amorphous metal, a general smearing of the features along with an enhanced low frequency contribution are observed for this function. One result of such changes is an increase in λ which is defined by

$$\lambda = 2 \int \alpha^2(\omega) (d\omega/\omega). \quad (2)$$

Measurements of the Debye-Waller factor using the Mössbauer technique³², and a study of the relative heat capacity³³ of an amorphous sample and its crystalline counterpart (at low temperature), both suggest that these changes are not simply a result of an altered phonon density of states $F(\omega)$. The Mössbauer experiment measures $\int F(\omega)(d\omega/\omega)$. Based on data

such as that of Happel et al.³⁴, Bergmann⁵ has argued that $\alpha^2(\omega)$, a weighted average of the electron-phonon matrix element, is significantly modified in the amorphous state owing to the loss of long range order.

Besides the above considerations of strong coupling effects, one can inquire as to the origin of the T_c variation shown in Fig. 1. McMillan³⁵ has derived an approximate solution to the Eliashberg equations from which T_c can be expressed as

$$[T_c / \langle \omega \rangle] = 0.69 e^{-\left[\frac{1.04 (1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right]} \quad (3)$$

where $\langle \omega \rangle$ is an average phonon frequency and μ^* an effective Coulomb potential. Despite the fact that this formula was derived using a phonon density of states for niobium, it can still be used to parameterize the general dependence of T_c on microscopic parameters. For simple metals, McMillan expresses λ

$$\lambda = \frac{D(0) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (4)$$

where $\langle I^2 \rangle$ is an average squared electron-phonon matrix element and M is the average ionic mass. For nearly free electrons this reduces to³⁵

$$\lambda = \frac{\pi}{2} \frac{E_F}{K_F e^2} \frac{\langle V_a^2(q) \rangle}{[\langle \omega^2 \rangle / \Omega_p^2]} \quad (5)$$

where $\langle V_a^2(q) \rangle$ is a form factor of the atomic potential, $\langle \omega^2 \rangle$ a suitable mean squared phonon frequency, and Ω_p^2 the square of the ionic plasma frequency previously introduced. Again for nearly free electron metals one

finds $(E_F/K_F) \sim Z^{1/3}$ and $\langle V^2(q) \rangle \sim Z^2$. The ratio $[\langle \omega^2 \rangle / \Omega_p^2]^{-1}$ should also be an increasing function of Z since $\langle \omega^2 \rangle \sim \Omega_p^2 / \epsilon(q,0)$ is the static dielectric function of the electron system. For free electrons in the Hartree approximation, $\epsilon(q,0)$ scales with $D(0)$ which in turn should increase with Z . Summarizing the above observations, one expects that λ will increase rapidly with increasing valency. The ratio $T_c / \langle \omega \rangle$ can be approximated as $\frac{T_c \epsilon^{1/2}(q,0)}{\Omega_p}$. Since $\epsilon^{1/2}(q,0)$ varies only slowly with Z , it is reasonable to expect that T_c / Ω_p should increase systematically with λ as predicted by equation (3). Finally, one expects that T_c / Ω_p should be a rapidly increasing function of Z . This is in agreement with experimental observation as illustrated in Fig. 1. The above discussion does not take strong coupling effects into account. The McMillan formula (eqn. (3)) may break down in the large λ limit where the Eliashberg equation must be evaluated for the particular phonon spectrum of interest. This will modify the detailed dependence of T_c on λ but should not effect the general conclusions concerning the variation of T_c with valence.

B. Transition Metals

The electronic structure of transition metals is complicated by the existence of a partially filled d-band in addition to nearly free s and p electrons. It is known for example, that the dominant contribution to the cohesive energy of transition metals arises from the splitting of atomic-like d-orbitals into essentially bonding and antibonding states which make up the low energy and high energy portions of the d-band structure.^{36,37,38} For the bcc, hcp, and fcc transition metals, the electronic band structures

have been theoretically computed using both the tight binding method^{39,40} and the augmented plane wave (APW) technique.^{41,42} The narrow d-bands give rise to sharp peaks in the electronic density of states function $D(\epsilon)$ as shown in Fig. 4 which illustrates the results of an APW calculation for bcc W.⁴¹ For W, (Mo) ϵ_F falls near a minimum in $D(\epsilon)$. For the other bcc metals, (β Hf(Zr), Ta(Nb) and W) and alloys of neighboring metals (Hf-Ta, Ta-W, and W-Re) a rigid band picture predicts that $D(\epsilon)$ remains the same while ϵ_F changes with d-band occupation. Results of specific heat measurements^{35,43} which give the electronic contribution to c_v in terms of γ (the coefficient of the linear term in c_v at low temperature) can be used to estimate $D(0) = D(\epsilon_F)$ and give support to the rigid band picture. Typical data are shown in Fig. 4 and compared with the rigid band $D(0)$ predicted from the calculation for W. The agreement is remarkably good.

It is fairly well established that superconductivity in transition metals is governed mainly by d-electrons.^{37,38} A comparison of the variation of T_c (Fig.2) in crystalline transition metals and alloys with the variation of $D(0)$ (Fig. 4) indicates a close relationship between these quantities. This relationship has been recently explained in terms of a tight-binding approximation (TBA) for the electron-lattice system by Varma and Dynes³⁸ and by Gomersall and Gyorffy.⁴⁴ The essential feature of their description is a self consistent analysis of the parameters which determines λ as given in eqn. (4). A self consistent treatment of $\langle I^2 \rangle$, $D(0)$, and $\langle \omega^2 \rangle$ indicates that the ratio $\left[\frac{\langle I^2 \rangle}{\langle \omega^2 \rangle} \right]$ remains constant for a given class of materials (e.g. bcc transition metals and alloys) when the dominant contributions to $D(0)$ arise from a particular type of quasi-atomic (e.g. d-like) orbital. This constancy physically arises from the fact that d-electron screening affects both $\langle I^2 \rangle$ and $\langle \omega^2 \rangle$ in the

Fig. 4. The electronic density of states as a function of energy (bottom) and group number (top) for bcc transition metals and amorphous transition metals. Closed circles give results of specific heat measurements for bcc metals; open circles give data for amorphous $(\text{Mo}_{1-x}\text{Ru}_x)_{80}\text{P}_{20}$ samples from magnetic susceptibility; solid lines are theoretical results obtained by Mattheiss.

same manner. The degree of screening is related to $D(0)$, the d-band density of states at the Fermi level. Thus it is found that $\lambda = D(0) \langle I^2 \rangle / M \langle \omega^2 \rangle$, and consequently T_c , are determined mainly by $D_d(0)$.

It is natural to apply the same analysis to amorphous transition metals. Experimentally, little information on the variation of $D(0)$ in amorphous transition metals is available. Low temperature specific heat measurements have recently been carried out by Schull et al for La-base metallic glasses.^{44,45} These measurements indicate a density of states far larger than that predicted by a free-electron model. Analysis of the electron and phonon contributions to the heat capacity and the use of McMillan's equations³⁵ give $\lambda \sim 0.8$ for these superconducting glasses suggesting the absence of the strong-coupling effects found in many simple metals. The author and colleagues have measured the temperature dependent normal state magnetic susceptibility $\chi(T)$ of a series of metallic glasses $(\text{Mo}_{1-x}\text{Ru}_x)_{80}\text{P}_{20}$ where T_c was observed to decrease from 9.0 K to 3.4 K with increasing x .¹⁵ A well defined temperature independent contribution, χ_0 , was found for the alloys of this series. A typical set of data are shown in Fig. 5. A simple analysis of this data indicates the Pauli paramagnetic contribution to χ_0 to be the dominant one so that a reasonable estimate of $D(0)$ can be made. The results are shown in Fig. 6. It is seen that $D(0)$ decreases monotonically with increasing x from 0.93 states/eV-atom to 0.37 states/eV-atom (one spin state). These data were shown¹⁵ to be in agreement with the Varma-Dynes model³⁸ in which T_c is governed mainly by $D_d(0)$. A comparison with $D(0)$ for the highly disordered crystalline σ -phase alloy $\text{Mo}_{61}\text{Ru}_{39}$ ⁴⁷ (obtained from specific heat data) is also shown in the figure. The T_c of the σ -phase alloy is nearly identical to that of the amorphous $(\text{Mo}_{.6}\text{Ru}_{.4})_{80}\text{P}_{20}$ alloy as are the values of $D(0)$ obtained for each.

Fig. 5. An example of magnetization data as a function of applied field at several fixed temperatures for an amorphous $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{80}\text{P}_{20}$ alloy. (upper)

Fig. 6. The temperature independent contribution to the magnetic susceptibility of amorphous $(\text{Mo}_{1-x}\text{Ru}_x)_{80}\text{P}_{20}$ alloys vs. average group number of the transition metal component. (upper) Effective density of states derived from susceptibility vs. average group number. Data for crystalline σ -phase alloys (taken from specific heat) is shown for comparison. (lower)

The values of $D(0)$ for amorphous alloys can also be compared with those of crystalline bcc alloys again using a rigid band model. This is illustrated in Fig. 4. One can conclude that the upper half of the d-band density of states $D_d(\epsilon)$ in amorphous transition metal alloys is best described by a featureless bell-shaped curve having a peak near an energy corresponding to a half filled d-band. This is in sharp contrast to the crystalline density of states function which exhibits much more structure. Further evidence to support this picture has been obtained using the technique of ultraviolet photoemission spectroscopy.⁴⁸ A comparison of the photoemission spectra of a bcc Mo film and that of an amorphous film stabilized by nitrogen impurities⁴⁹ is shown in Fig. 7. The three peaked structure of $N(0)$ (the effective density of states for photoemission) below ϵ_F is well described by the theoretical bcc band structure shown at the top of the figure. It is noteworthy that ϵ_F falls near a minimum in $N(0)$ for the bcc film as predicted by theory and confirmed by specific heat data on bulk Mo. On the other hand a broad featureless structure in $N(0)$ is observed for the amorphous Mo film suggesting a peak in $D(\epsilon)$ near the Fermi energy of amorphous Mo. These features are in good agreement with results based on magnetic susceptibility measurements discussed above and lend support to the proposed model of $D(\epsilon)$ in amorphous metals.

Returning to the Collver-Hammond curve (Fig. 2), one can now account for the observed variation in T_c with progressive filling of the d-band in amorphous transition metals. The principle microscopic parameter which governs this variation is $D(0)$. The function $D(\epsilon)$ is relatively slowly varying with d-band occupation and has a broad maximum. From the above considerations, one concludes that it will probably be difficult to obtain amorphous transition metal alloys with T_c significantly higher than that

Fig. 7. Ultraviolet photoemission spectrum of an amorphous $\text{Mo}_{80}\text{N}_{20}$ film compared with that of a crystalline bcc Mo film and a theoretical band structure calculation. Data from ref. 48.

observed for Mo-base alloys. It is of considerable interest to further substantiate the above description by carrying out low temperature specific heat measurements on metallic glasses.

As a final comment on the microscopic theory of amorphous transition metals, it should be mentioned that tunneling studies of amorphous transition metal alloys prepared by sputtering and vapor deposition have been carried out.⁵⁰ In contrast with simple metals, no evidence for strong coupling effects was found. The gap coefficient $\left[\frac{2\Delta_0}{k_B T_c} \right]$ was in all cases found to be less than 4 and typically in very good agreement with the BCS value of 3.52. Typical data are listed in Table III. The strong coupling effects which modify the BCS theory in the case of amorphous simple metals are apparently absent for amorphous transition metals. It can be concluded that strong-coupling effects are not solely a result of the disordered amorphous structure.

IV. THE ROLE OF STRUCTURAL DISORDER

The high degree of structural disorder observed in amorphous alloys has important consequences for superconductivity. In addition to the loss of detailed structure in the density of state function $D(\epsilon)$ (and subsequent changes in the variation of T_c), the basic nature of the electronic wavefunctions is altered. Bloch's theorem no longer provides an adequate starting point for discussing electron and phonon wavefunctions. In theory, one takes this into account by introducing a finite electron mean free path, ℓ_e . When ℓ_e is smaller than the BCS (clean limit) coherence length $\xi_0(T) = \frac{\hbar v_F}{\pi \Delta(T)}$ ⁵¹, a superconductor is said to be "dirty".

TABLE III. Tunneling results for amorphous transition metal alloys prepared by sputtering and evaporation from ref. 50. The T_c , energy gap Δ_0 , and gap coefficient ($2\Delta_0/k_B T_c$) are given along with the preparation method.

Alloy	T_c (K)	Δ_0 (meV)	$2\Delta_0/k_B T_c$	Method of Preparation
Nb_3Si	3.9	0.61	3.6 ± 0.1	sputtering and evaporation
Nb_3Ge	3.6	0.55	3.5 ± 0.1	sputtering and evaporation
$Mo_{\sim 80}N_{\sim 20}$	8.3	1.30	3.6 ± 0.1	reactive evaporation
$Mo_{68}Si_{32}$	6.7	0.98	3.4 ± 0.1	coevaporation

Now $\xi_0(0)$ is roughly 500-1000Å for superconductors with T_c in the range of interest while λ_e is of the order of interatomic distances for amorphous metals. Thus $\lambda_e \ll \xi_0(0)$ and amorphous superconductors are properly described by the extreme "dirty limit" of the microscopic theory.

A. The Critical Fields $H_0(T)$, $H_{c1}(T)$, and $H_{c2}(T)$.

The BCS theory⁵¹ gives ΔF_{ns} the superconducting condensation energy as

$$\Delta F_{ns} = D(0) \Delta^2(T) = H_0^2(T)/8\pi \quad (6)$$

To the extent that strong-coupling effects can be ignored, this expression remains valid for amorphous superconductors. In order to describe the behavior of $H_{c1}(T)$ and $H_{c2}(T)$ one must use the GLAG (Ginzburg-Landau, Abrikosov-Gorkov) theory of type II superconductivity. In the "dirty limit", the effective coherence length becomes⁵²

$$\xi_d(T) = 0.85 [\xi_0(0) \lambda_e]^{1/2} \left[\frac{T_c}{T_c - T} \right]^{1/2} \quad (7)$$

The penetration depth which measures the characteristic distance for spatial variation of the microscopic magnetic field is given by⁵²

$$\lambda_d(T) = 0.615 \lambda_L(0) \left[\frac{\xi_0(0)}{\lambda_e} \right]^{1/2} \left[\frac{T_c}{T_c - T} \right]^{1/2} \quad (8)$$

where $\lambda_L(0)$ is the London penetration depth. The ratio of these two lengths, called the Ginzburg-Landau parameter, is

$$\kappa(T) = \frac{\lambda(T)}{\xi(T)} = 0.725 \cdot \frac{\lambda_L(0)}{\xi_e} \quad (9)$$

In amorphous superconductors, the small value of ξ_e yields a very large $\kappa \sim 50-100$. The coherence length is small, $\xi_d(0) \sim 40-100 \text{ \AA}$, and $\lambda_d(0) \sim 2000-5000 \text{ \AA}$. Amorphous superconductors are thus extreme type II (high κ) materials. Werthamer⁵³, Maki⁵⁴, and others have computed the behavior of $H_{c1}(T)$ and $H_{c2}(T)$ in this limit. Their results for H_{c1} are compared with some typical experimental data¹⁶ in Fig. 8. A family of H_{c2} curves for a series of $(\text{Mo}_{1-x}\text{Ru}_x)$ -base alloys are shown in Fig. 9. The curves are linear with temperature over the range of the data. These data were compared with the theory of Maki in ref. 16 where it was shown that the data lie above the theoretical curves. Including spin-orbit and paramagnetic limiting corrections to the theory does not suffice to explain the observed behavior.

It should be pointed out that $H_0(T)$, and $H_{c2}(T)$ are related through the following equations^{53,55}

$$H_{c2} = \sqrt{2} \kappa H_0(T)$$

and

$$H_{c1} = \frac{1}{\sqrt{2} \kappa} (\log \kappa + 0.08) H_0(T) \quad (10)$$

in the simplest GL theory. The large characteristic κ values for amorphous superconductors thus lead to a large H_{c2} and a small H_{c1} by comparison with H_0 as Table II illustrates for various materials studied.

Fig. 8. Lower critical field $H_{C1}(T)$ for two amorphous $Zr_{75}Rh_{25}$ specimens. The data are compared with the theory of Maki.

Fig. 9. The upper critical field $H_{c2}(T)$ for a series of $(\text{Mo}_{1-x}\text{Ru}_x)$ -type alloys. The solid lines represent a linear extrapolation.

B. Fluctuation Phenomena

The width of the superconducting transition ΔT_c is extremely small for a pure crystalline bulk metal. The effects of superconducting fluctuations above T_c are restricted to a temperature interval of the order of 10^{-6} K except for the case of ultrathin films.^{56,57} For amorphous superconductors, the small coherence length leads to a dramatic increase in the width of the critical region. The effects of fluctuations can easily be observed in a bulk sample and are measureable at temperatures well above T_c .^{58,59} This provides an ideal opportunity to study critical phenomena in bulk superconductors. As an example, the resistive transition of an amorphous $Zr_{75}Rh_{25}$ sample measured in zero and several non-zero applied magnetic fields is shown in Fig. 10. The rounding of the transition above T_c was shown to arise from fluctuation phenomena and has been analyzed in terms of the three dimensional theory.^{57,60} Of fundamental significance is the fact that such fluctuation phenomena establish a minimum width ΔT_c for the transition to the superconducting state in amorphous metals. The extended temperature range over which the effects of fluctuations are measurable has motivated an extension of the theory.^{61,62}

C. Homogeneity and the Critical Current Density

For a strictly homogeneous type II superconductor, no flux pinning interactions can occur. When an externally applied current flows in the presence of a field, flux is driven by a Lorentz force and flows viscously. In order to sustain a finite supercurrent, the flux lattice must be "pinned". In a crystalline material, dislocations, grain boundaries, and other defects

Fig. 10. Detailed illustration of the resistive transition to the superconducting state for amorphous $Zr_{75}Rh_{25}$ in various applied fields. The rounding was shown to be due to fluctuation phenomena in ref. 59.

which destroy the microscopic homogeneity of the material can serve as pinning centers. In an amorphous superconductor structural disorder occurs on the atomic scale. If one were to sample the amorphous matrix by comparing the average microscopic properties of various regions having characteristic dimension $\xi \sim 50\text{-}100 \text{ \AA}$, one would find that the average properties of regions look more or less alike. Specifically, the chemical composition, density of atoms, and average internal stress field of various sampling volumes would be more or less identical. Simply put, an amorphous metal is quite homogeneous on the scale of ξ . For this reason, flux pinning interactions are very weak if they exist at all. The critical current density for $H > H_{c1}$ should be small. This is experimentally found to be the case.^{7,63,64} Typically, $J_c(H,T)$ falls from a value of order 10^5 A/cm^2 for $H = 0$, to values of order $10\text{-}100 \text{ A/cm}^2$ for fields less than but comparable in magnitude to H_{c2} . An example of this behavior is shown in Fig. 11 for an amorphous $(\text{Mo}_{.6}\text{Ru}_{.4})_{80}\text{P}_{10}\text{B}_{10}$ alloy. This severely limits the usefulness of amorphous superconductors.

The introduction of a spatial inhomogeneity into an amorphous matrix can result in flux-pinning interactions. One method of accomplishing this is to arrange for precipitation of crystalline phase particles in the matrix.⁶⁴ Interest in this phenomena is more than academic since one may ultimately be able to develop a ductile high field superconductor for practical applications based on amorphous metals. Such a material would be expected to exhibit superior tolerance to degradation by irradiation. Progress toward achieving an enhanced critical current at high field has already been made.⁶⁴ It is hoped that this work will result in a better understanding of the basic flux pinning mechanisms. Amorphous superconductors offer the possibility of fabricating a variety of metastable

Fig. 11. Critical current as a function of applied field for amorphous
(Mo_{0.6}Ru_{0.4})₈₀P₁₀B₁₀.

crystalline superconductors which occur as intermediate steps in the crystallization process. This area of research is rather new, and many novel developments can be expected.

REFERENCES

1. B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys., 35, 1 (1963).
2. J. R. Gavaler, Appl. Phys. Lett., 23, 480 (1973).
3. W. Buckel and R. Hilsch, Z. Phys., 138, 109 (1954).
4. W. Buckel and R. Hilsch, Z. Phys., 146, 27 (1956).
5. G. Bergmann, Phys. Reports, 27C, 161, (1976).
6. M. M. Collver and R. H. Hammond, Phys. Rev. Lett., 30, 92 (1973).
7. W. L. Johnson, S. J. Poon, and P. Duwez, Phys. Rev. B, 11, 150 (1975);
W. L. Johnson and S. J. Poon, J. of Appl. Phys., 46, 1787 (1975).
8. K. Togano and K. Tachikawa, Phys. Lett., 54A, 205 (1975).
- 9.(a) C. G. Granqvist and T. Claeson, J. Low Temp. Phys., 10, 735 (1973);
(b) Z. Phys., 20, 241 (1975); (c) Z. Phys., B20, 13 (1975).
10. A. Calka, M. Madhava, D. E. Polk, B. C. Giessen, H. Matyja, and
J. Vander Sande, Scr. Metall., 11, 65 (1977).
11. C. C. Tsuei and W. L. Johnson (unpublished results).
12. W. Klement, R. H. Willens, and P. Duwez, Nature, 187, 869 (1960).
13. P. Duwez, private communication.
14. B. T. Matthias, Progress in Low Temperature Physics (Interscience,
New York, Vol. 2, p. 138).

15. W. L. Johnson, S. J. Poon, J. Durand, and P. Duwez, Phys. Rev. B, 18, July 1, (1978).
16. E. R. Domb and W. L. Johnson, (to be published in J. Low Temp. Phys.)
17. R. Hasegawa and L. E. Tanner, Phys. Rev. B, 16, 3925 (1977); J. Appl. Phys., 49, (1978).
18. O. Meyer, New Uses of Ion Accelerators, Ed. by J. F. Ziegler (Plenum Press, New York, 1975) Ch. 6, p. 323.
19. O. Meyer, H. Mann, and E. Phrilingos, Applications of Ion Beams to Metals, Ed. by S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum Press, New York, 1974) p. 15.
20. J. M. Ziman, Phil. Mag., 6, 1013 (1961); C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag., 7 865 (1962).
21. J. E. Enderby, Liquid Metals, Ed. by S. Z. Beer (Marcell Dekker Inc., New York, 1972) Ch. 14.
22. J. M. Ziman, Adv. Phys., 16, 551 (1967).
23. W. A. Harrison, Pseudopotentials in the Theory of Metals, (Benjamin, New York, 1966).
24. J. Fortman and W. Buckel, Z. Phys., 162, 93 (1961).
25. A. Comberg, S. Ewert, and G. Bergmann, Z. Phys., 271, 317 (1974).
26. J. Hasse, Z. Phys., 157, 166 (1959).
27. O. Hunderi and R. Ryberg, J. Phys. F: Metal Phys., 4, 2096 (1974).

28. D. Rainer and G. Bergmann, J. Low Temp. Phys., 14, 501 (1974).
29. G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz., 38, 966 (1960).
30. N. V. Zavaritski, JETP Lett., 5, 352 (1967).
31. J. T. Chen, T. T. Chen, J. D. Leslie, and H. J. T. Smith, Phys. Lett. 25A, 679 (1967).
32. J. Bolz and F. Pobell, Z. Phys. B, 20, 95 (1975).
33. W. Buckel and Ch. Ohlerich, Proc. 13th Intern. Conf. on Low Temp. Phys., 1972, Vol. 4 (Plenum Press, New York, 1972) p. 437.
34. H. Happel, K. Knorr, and N. Barth, Z. Phys., 249, 185 (1971).
35. W. L. McMillan, Phys. Rev., 167, 331 (1968).
36. J. Friedel, Physics of Metals, Ed. by J. M. Ziman (Cambridge Press, Cambridge, 1969) p. 340.
37. S. Barasić, J. Labbé, and J. Friedel, Phys. Rev. Lett., 25, 919 (1970).
38. C. M. Varma and R. C. Dynes, Superconductivity in d-and f-band Metals, Ed. by D. H. Douglass (Plenum Press, New York and London, 1976).
39. J. Friedel, J. Phys. 16, 829, 342 (1955); 23, 501, 342 (1962).
40. F. Cyrot, Adv. Phys., 16, 393 (1967).
41. L. F. Mattheiss, Phys. Rev. B1, 373 (1970); Phys. Rev., 139, A1893 (1965).
42. L. F. Mattheiss, Phys. Rev., 151, 450 (1966).

43. E. F. Bucher, F. Heiniger, and J. Müller, Proceedings of the Ninth Intern. Conf. on Low Temp. Phys., Ed. by J. Daunt et al. (Plenum Press, New York, 1965) p. 1059.
44. I. R. Gomersall and B. L. Gyorffy, Phys. Rev. Lett., 33, 1286 (1974).
45. W. H. Schull and D. G. Naugle, Phys. Rev. Lett., 39, 1580 (1977).
46. W. H. Schull, D. G. Naugle, S. J. Poon, and W. L. Johnson, (to be published in Phys. Rev. B).
47. F. Heiniger, E. Bucher, and J. Müller, Phys. Kondens., Materie, 5, 243 (1966).
48. B. Schroeder, W. Grobman, W. L. Johnson, C. C. Tsuei, and P. Chaudhari, Proc. IV Intern. Conf. on the Phys. of Noncryst. Solids, Ed. by G. H. Frishchat (Trans Tech Publication, Switzerland, 1977) p. 190.
49. B. Schroeder, W. L. Johnson, C. C. Tsuei, and P. Chaudhari, Structure and Excitations in Amorphous Solids, AIP Conf. Proc. No. 31 (1976) p. 353.
50. C. C. Tsuei, W. L. Johnson, R. L. Laibowitz, and J. M. Viggiano, Solid State Comm., 24, 615 (1977).
51. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev., 108, 1175 (1957).
52. D. Saint-James, G. Sarma, and E. J. Thomas, Type II Superconductivity (Permagon Press, Oxford and London, 1969) Ch. 2 and Ch. 5.

53. N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966).
54. K. Maki, Phys. Rev., 148, 362 (1966).
55. M. Tinkham, Introduction to Superconductivity, (McGraw-Hill, New York, (1975).
56. R. E. Glover III, Phys. Lett., 25A, 542 (1967).
57. L. G. Aslamasov and A. I. Larkin, Phys. Lett., 26A, 238 (1968).
58. W. L. Johnson and C. C. Tsuei, Phys. Rev. B, 13, 4827 (1976).
59. W. L. Johnson, C. C. Tsuei, and P. Chaudhari, Phys. Rev. B, 17, 2884 (1978).
60. K. Maki, Prog. Theor. Phys. 39, 897 (1968).
61. S. Ami and K. Maki (to be published).
62. B. R. Patton, Bull. of the American Phys. Society, 23, 415 (1978).
63. W. L. Johnson and S. J. Poon, IEEE Trans. on Magnetics, Vol. Mag-11, 189 (1975).
64. W. L. Johnson and J. Bennett (to be published).