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Superconductivity in Ternary Molybdenum Sulfides

Final Report

NASA Grant NSG 3101

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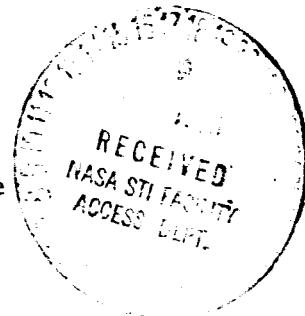
During the period of April 1, 1976 to September 30, 1978, the superconducting materials research program in the Department of Applied Physics & Information Science at the University of California, San Diego was supported by the National Aeronautics and Space Administration under the project "Superconductivity in Ternary Molybdenum Sulfides". Due to some unusual circumstances, a no-cost extension of six months was requested and granted. During the entire period of study, this program was under the monitoring of Dr. John A. Woollam of the NASA Lewis Research Center. Dr. Woollam was also an active participant in various aspects of the project. Dr. S. A. Alterovitz of Tel Aviv University was also an active participant of this work. At the time, Dr. Alterovitz was visiting the Lewis Research Center as a Senior Research Associate of the National Research Council.

Our research work can be divided into two categories.

I.   The preparation, characterization and systematic investigation of ternary molybdenum sulfides.

II. Preliminary studies of other materials related to superconductivity.

The first category embraces the major effort in our investigation. At present, the superconductor with the highest critical field belongs to the ternary molybdenum sulfide group. Prepared with conventional techniques, the ternary sulfides are always in the form of irregular porous lumps. We were the first to succeed in preparing them in coherent films with the sputtering technique.

Because of their high critical fields, the potential of applications for the ternary molybdenum sulfides exists. The preparation of this material in coherent films has made it possible to study their fundamental physical properties. At the moment, this investigation is very much an ongoing effort. The National Science Foundation has agreed to provide continual support for the study.

The second category involves mostly amorphous materials. "Amorphous" phase is still a frontier in the study of materials. Using sputtering or other vapor condensation techniques for preparation, the end product is often amorphous. For the same substance, the characteristics of the amorphous and the corresponding crystalline phases are drastically different. This motivated our investigation. We have made considerable progress in both categories of studies. The progress was documented in a series of articles published in widely circulated professional journals. The following is a list:

1. S. A. Alterovitz, J. A. Woollam, L. Kammerdiner and H. L. Luo, "Critical current in sputtered copper molybdenum sulfides," Appl. Phys. Letters <u>31</u>, 233 (1977). Also Abstract, Bull. Amer. Phys. Soc. <u>22</u>, 402 (1977).

2. S. A. Alterovitz, J. A. Woollam, L. Kammerdiner and H. L. Luo, "Critical current and scaling laws in sputtered copper molybdenum sulfides," J. Low Temp. Phys. <u>30</u>, 797 (1978). Also Abstract, Bull. Amer. Phys. Soc. <u>22</u>, 402 (1977).

3. S. A. Alterovitz, J. A. Woollam, L. Kammerdiner and H. L. Luo, "Critical current in sputtered $PbMo_6S_8$," Appl. Phys. Letters <u>33</u>, 264 (1978). Also Abstract, Bull. Amer. Phys. Soc. <u>23</u>, 383 (1978).

4. S. A. Alterovitz and J. A. Woollam, "Upper critical field of copper molybdenum sulfides," Solid State Commun. <u>25</u>, 141 (1978).

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11. B. Stritzker and H. L. Luo, "Superconductivity in Pd-Si-H(D) alloys," Solid State Commun. (in press 1979).

12. H. L. Luo and H. F. Eno, "Low-temperature specific heat of amorphous Pd-Si alloys," J. Non-Cryst. Solids, (submitted).

In the above list, the first nine publications have already been published and copies are in file with the monitoring scientist. Publications #10, #11 and #12 are in press; preprint copies are attached.

We wish to express our gratitude for the support that NASA provided. In particular, we hope to continue the beneficial working relationship with Dr. J. A. Woollam developed during the course of this investigation.

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J. Less-Common-Metals
(1979)

SUPERCONDUCTIVITY IN Th–Zr ALLOYS

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Summary

Using a fast-quenching technique, a wide range (40 - 80 at.% Zr) of the body-centred cubic phase is retained for the Th–Zr system. The superconducting transition temperatures of this phase are higher than those of the close-packed Th-rich or Zr-rich solid solutions.

1. Introduction

A common feature of the Group IV transition elements Ti, Zr, Hf and Th is that their crystal structures are all of the close-packed form but transform to a body-centred cubic (b.c.c.) modification at high temperature. They are all superconducting with rather low transition temperatures T_c [1]. In our initial investigation of the Th–Zr alloys, we detected value of T_c as high as 6 K in the as-cast state. Recently, Peterson *et al.* reported that a T_c of 5 - 6 K was associated with the high temperature b.c.c. phase, although their data indicate that they encountered difficulty in retaining the high temperature phase by quenching [2]. This investigation aims to study specifically the b.c.c. phase retained using the technique of quenching from the molten state.

2. Experimental

The samples were prepared from metals of at least 99.95% purity: "iodide" Th (Ventron Corp.) and Marz grade Zr (Materials Research Corp.). For each alloy appropriate amounts of the elements were first arc melted thoroughly in a pure helium atmosphere drawn directly from the boil-off of a liquid helium Dewar in order to minimize gaseous contamination during melting. The alloy buttons were then sliced with a carborundum wheel into

2

pieces suitable for our fast-quenching operation. This arrangement, adapted to
an arc furnace, has been described elsewhere [3]. Since weight losses during
melting were negligible, all compositions reported here are nominal.

The quenched specimens were in the form of irregular thin flakes, up to
several millimeters in dimensions. X-ray diffraction patterns were obtained
with a Debye–Scherrer camera 114.6 mm in diameter using nickel-filtered
Cu K radiation. Systematic errors in the lattice spacings were corrected by
extrapolating against the Nelson–Riley function.

Superconducting transitions were detected using an inductive technique.
The measurements monitored the reactive off-balance of an a.c. Wheatstone
bridge which compared the self-inductances of two identical coils, one
containing a specimen, the other empty. All T_c measurements were made in
an He^4 cryostat except that for pure Zr which required a dilution refrigerator.
Between 4.2 and 1.2 K, He^4 vapor pressure served as a thermometer; above
and below this temperature range, calibrated germanium and carbon resistors,
respectively, were used.

3. Results

Fast-quenched alloys in the Th–Zr system exhibit three single-phase
regions: face-centred cubic (f.c.c.), 0 - 15 at.% Zr; b.c.c., 40 - 80 at.% Zr;
and hexagonal close-packed (h.c.p.), 90 - 100 at.% Zr. The range and the
lattice parameters of the h.c.p. phase are essentially the same as those
reported by Peterson et al. [2]. The f.c.c. solid solubility is slightly greater
than that of earlier reports [4]. The most significant feature of the present
investigation is the retention by rapid quenching of a wide range of the high
temperature b.c.c. phase. The lattice parameters and the atomic volumes of

TABLE 1

Lattice parameters and atomic volumes of cubic phases in the Th-Zr alloy system

| Phase	Zr(at.%)	Lattice parameter (Å)	Atomic volume (Å^3)
f.c.c.	Th	5.0870 ± 0.0005	32.91
f.c.c.	5.0	5.0605 ± 0.0005	32.40
f.c.c.	10.0	5.035 ± 0.003	31.91
f.c.c.	15.0	5.015 ± 0.005	31.53
b.c.c.	40.1	3.867 ± 0.005	28.91
b.c.c.	50.2	3.821 ± 0.005	27.89
b.c.c.	59.7	3.774 ± 0.002	26.88
b.c.c.	66.6	3.743 ± 0.001	26.22
b.c.c.	70.0	3.7272 ± 0.0005	25.89
b.c.c.	75.0	3.704 ± 0.001	25.41
b.c.c.	80.2	3.680 ± 0.002	24.92
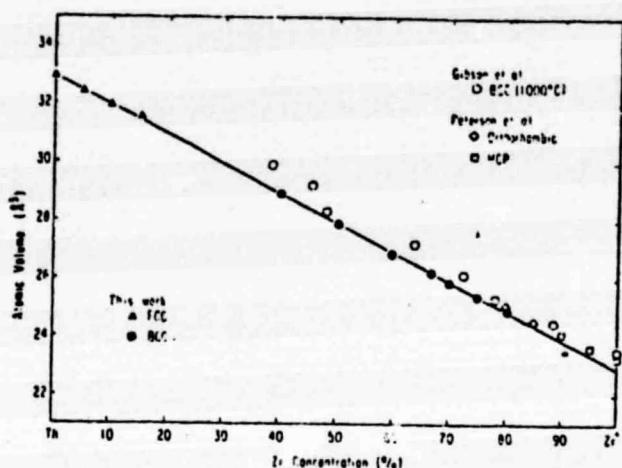
Fig. 1. Atomic volumes of various phases in the Th–Zr system.
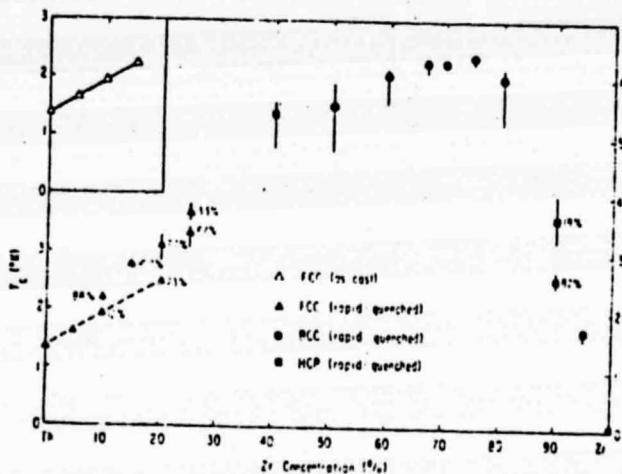
Fig. 2. Superconducting transition temperatures of rapidly quenched Th-Zr alloys. The inset shows the T_c values for as-cast Th-rich f.c.c. alloys; the observed linearity with Zr composition (solid line) is shown as a broken line.

the cubic phases are listed in Table 1. We have also plotted in Fig. 1 these atomic volumes together with other appropriate data reported in the literature.

The T_c results of all specimens whose superconducting transitions were well defined are shown in Fig. 2. As indicated by our experimental data, all these specimens were single-phase or nearly so. In the figure, the symbols mark the midpoints of the transitions and the vertical bars indicate the width between 10% and 90% of the detected signals. For some f.c.c. and h.c.p. specimens two distinct transitions were seen; the percentages of the total signals corresponding to each such transition are quoted on the figure.

4. Discussion

Previous studies of the superconductivity of Th–Zr alloys have dealt with the Th-rich and Zr-rich ends of the phase diagram [2, 5]. These studies showed that all phases superconduct and that the T_c value of the close-packed phases increase with increasing solute content. Our measurements confirm these observations; significantly, we find that the T_c value of the b.c.c. phase are uniformly elevated, having onsets between 5.6 and 6.4 K over the span from 40 to 80 at.% Zr. Since Th and Zr belong to the same transition metal group in the periodic table, such a small variation with composition is anticipated. It is, in fact, the rapid variation of T_c in the f.c.c. and h.c.p. phases that seems surprising. Future heat capacity measurements might provide an explanation for the present result. Concerning the T_c of pure Zr, Jensen has shown that this depends strongly on sample preparation [6]; thus the broad T_c beginning below 0.2 K, while unusually low, is not alarming. When arc melted only, the same Zr had a sharper T_c starting just above 0.3 K. The foregoing complications aside, it is the overall picture that is noteworthy. The Th–Zr system provides a unique demonstration that, independent of any influence of the valence electron to atom ratio, the b.c.c. structure is clearly more favorable for high T_c values than either of the close-packed structures.

Peterson *et al.* reported an additional orthorhombic phase at the composition 80 - 85 at.% Zr [2]. This phase must be related to the instability of the b.c.c. phase and can therefore be considered as an intermediate stage of the transformation from the b.c.c. to the h.c.p. structure; no trace of it was detected in the present investigation, owing to the much faster quenching rate. However, according to the reported lattice parameters and the corresponding atomic volumes, the occurrence of such an orthorhombic phase is nearly identical to the case of the Ag–Cd system [7]. The parallel between the Th–Zr and Ag–Cd alloys may not be totally surprising if we accept the view that the Th–Zr alloy would behave like some simple metal alloys because Th and Zr are isoelectronic and hence the nature of valence electrons would not change drastically across the system.

The wide range of single-phase b.c.c. solid solution retained by the present fast-quenching operation provides some very interesting observations. In this range, the lattice parameters show a strictly linear dependence on the alloy composition. The extrapolated lattice spacings for b.c.c. Zr and Th at room temperature are 3.584 Å and 4.062 Å, respectively. The Zr value agrees reasonably well with the number extrapolated from data on fast-quenched Zr–Mo and Zr–W alloys [8]. Additionally, using the early high temperature data [9], the linear thermal expansion coefficient for the b.c.c. phase is estimated to be about $9.0 \times 10^{-6}\ °C^{-1}$.

Acknowledgements

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SUPERCONDUCTIVITY IN Pd-Si-H(D) ALLOYS

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Superconductivity is reported for Pd-Si-H(D) alloys in the regions
of solid solution and the amorphous phase. The isotope effect for the
former has the inverse sign but that of the latter is normal. The
results are discussed in connection with existing theories.

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(1977)

1. Introduction

Since the discovery of superconductivity in the Pd-H system,[1] the subject has been an active area of research.[2] In particular, the enhancement of superconducting transition temperatures (T_c) in the Pd-H-noble metal alloys[3] and the observation of inverse isotope effect[4,5] have aroused great interest in the subject. A number of theories have been proposed to explain the experimental results. The mechanism of the quenching of spin-fluctuations[6] is plausible but can only be viewed as one of the necessary conditions for the occurrence of superconductivity in these systems. Another important ingredient is the enhanced electron-phonon interaction due to the strong pseudopotential of H(D).[7] The contribution to such interaction due to the optic photons was particularly suggested[8,9] and was subsequently confirmed through tunneling experiments.[10,11,12]

On the other hand, the most widely investigated metallic amorphous material is the Pd-Si alloy in the range of 17 ~ 20 at. % Si. The magnetic susceptibility data[13] indicate that the spin fluctuations are completely suppressed in the amorphous Pd-Si alloy. The electronic specific heat of amorphous Pd-Si alloys[14] (~ 1.0 mJ/mole-K^2) is equivalent to that of a 50 at. % Ag, Pd alloy[15] which would become superconducting after hydrogenation with an estimated T_c of $\lesssim$ 1K.[3]

Considering the amorphous Pd-Si phase as compatible with the Pd-noble metal alloys, it is thus of interest to investigate the possible superconductivity of the former after optimal hydrogenation. In particular, since all superconducting hydrogenated Pd-alloys reported so far have the same face-centered cubic (fcc) structure, it is pertinent to examine if the crystal symmetry is important for the occurrence of superconductivity in these systems. Reported here are the results.

2. Experimental Procedures

For most specimens, the Si was of ultra-high purity (electronics grade from DuPont) and the Pd was supplied by Johnson-Matheys with magnetic impurities < 3 ppm. In the amorphous region, a second set of specimens were also prepared using a less pure grade of Pd which contained 100 ~ 200 ppm Fe.

Appropriate amounts of the elements were

first either induction- or arc-melted thoroughly in an argon atmosphere. Alloy foils were then fabricated by quenching from the molten state using the piston-and-anvil technique.[16] The general dimensions of the foils were ~ 1.5^{cm} in diameter and 40 ~ 50 μm thick. Since the weight losses during the melting processes were insignificant, the reported compositions were all nominal.

All alloy foils were examined using x-ray diffraction techniques. Only those specimens which were of "single-phase", either fcc solid solution or amorphous, were subjected to ion-implantation and to the subsequent T_c measurements. Even so, we feel that the specimen of 7 at. % Si contained a small amount of second phase.

The implantation H(D) was carried out in two steps.[3]

(1) Precharging at 300°C under 4 bars $H_2(D_2)$ gas pressure: A final H(D)/metal ratio between 0.74 (0.66) and 0.44 (0.35) in the crystalline alloys with Si content up to 4.7 at. % was reached, whereas the amorphous alloys with ~ 20 at. % Si did not take up any measurable amount of H or D.

(2) Implantation experiments of H_2^+ or D_2^+ ions were performed with an energy of 100 kev for all Pd-Si alloys. The specimens were kept below 10°K during the entire implanting process.

3. Results

The lattice parameters of the fcc solid solution increase very slightly with increasing Si contents as listed in Table I.

Table I. Lattice Parameters of the Face-Centered Cubic Pd-Si Solid Solution.

At. % Si	Lattice Parameter (Å)
0	3.890 ± 0.001
0.7	3.890 ± 0.002
2.5	3.894 ± 0.003
3.9	3.895 ± 0.005
4.7	3.900 ± 0.005

The optimum T_c's with respect to the H(D) concentration are shown in Figure 1 as a function of alloy compositions. Starting from 8.8°K (10.7°K) in Pd-H(D) alloys, T_c passes through a maximum as

the Si content increases. The Si concentration
at which such maximum occurs is lower in the
Pd-Si-D than in the Pd-Si-H system. Throughout
the fcc region (up to 4.7 at. % Si) the inverse
isotope effect is maintained. Apparently the
isotopic mass exponent changes sign as the Si
content increases. In the amorphous region
(17.2 ~ 19.9 at. % Si), the superconducting
transitions are much sharper than those of crys-
talline material, and the corresponding isotopic
mass exponent has at least the correct sign. Its
magnitude is still much less than the commonly
accepted value of ~ 0.5. The exact composition
at which the sign change occurred could not be
determined because it was definitely located in
the two-phase region.

The optimal H(D)/metal ratios were estimated
from the precharged concentration and the actual
counting of ion charges by assuming that the dis-
tribution of the implanted atoms inside the Pd-Si
alloys was independent of the Si content. The
H(D)/metal ratios corresponding to the maximum T_c

values decrease with increasing Si content in the
fcc region from 1.0 to 0.7. In the amorphous re-
gion, the optimum H(D)/metal ratio is close to
0.5.

Under the same hydrogenation condition, the
amorphous alloys prepared from the Pd containing
100 ~ 200 ppm Fe remained normal down to 1.3°K.

4. Discussion

The T_c of the Pd-Si-H(D) alloys is plotted
in Fig. 1 to express our view: Had a "single-
phase" material been prepared throughout the com-
position range in the present investigation, we
would have expected that the isotopic-mass ex-
ponent would vary continuously and smoothly from
the inverted to the normal values with increas-
ing Si content.

This view is consistent with the general
behavior of other Pd-M-H(D) systems[2] where M is
an element which contributes to suppress the
strong spin fluctuations in pure Pd. In fact,
with all Pd-M-H(D) systems, two common features
are noteworthy:
(1) With increasing consentration of M, T_c ini-
     tially increases and passes through a maxi-
     mum value. In all known cases,[2] the $T_{c,max}$

     in the Pd-M-D system always occurs at lower

M concentration than that of the correspond-
ing Pd-M-H system.

(2) The isotopic mass exponent changes sign with
increasing M content.

At the present time, it is not possible to
offer quantitative explanations for these super-
conducting behaviors common to all Pd-M-H(D) sys-
tems, even though a number of theoretical models
have been proposed.[2] However, based on the
existing theories, a good qualitative understand-
ing can be advanced.

In view of the fact that superconductivity
is induced by hydrogenation in pure Pd metal as
well as in several Pd-M alloy systems, the den-
sity-of-states which is responsible for the super-
conductivity must be mostly of the sp-band but
admixed with some residual d-band character of Pd.
Such hybridization would vary smoothly and slowly
in such a manner that the influence of the d-band
character would gradually diminish as more and
more M-element was alloyed with Pd. In other
words the superconductivity of Pd-H(D) and
Pd-M-H(D) cannot be attributed to any sharp rise
in the density of states of the system.

Equally important for the occurrence of
superconductivity is the strong electron-phonon
coupling. The superconductivity in Pd and Pd-M
alloys after hydrogenation can be attributed to
the special role of H or D. The H(D) intersti-
tials give rise to a large electron-phonon coup-
ling due to the optic phonon modes occurring at
rather low energies within the Pd lattice[8-12]
and to the large pseudopotential of the rather un-
screened protons or deuterons.[7] Recent theories
based on detailed band structure calculations[9,17]
underline the importance of the low frequency
H(D) mode.

When a third element M is alloyed into the
Pd-H(D) system, the added conduction electrons
would provide more screening which would lead to
the reductions of both the Coulomb repulsion and
the electron-phonon coupling. The former tends
to raise T_c while the latter can lead to lower

it. These competing effects could probably ex-
plain the $T_{c,max}$ in the Pd-M-H(D) systems.

The anharmonic model proposed by Ganguly[8]
was rather attractive in explaining the inverse
isotope effect. The sign reversal of the iso-
topic mass exponent at higher M concentration can
then be understood as due to the decrease in har-
monicity. According to this model, the inverted

isotope effect in the Pd-Cu-H(D) system would have been further enhanced at higher Cu content due to the consideration of decreasing lattice constants. But experimental results showed just the opposite.[18] In this connection, a rough picture can be presented based on McMillan's theory.[19] Strong Coulomb repulsion coupled with strong electron-phonon coupling could give rise to an inverted isotope effect. Simultaneous reduction of both would lead a sign reversal in the isotopic mass exponent. For a better understanding, accurate specific heat, neutron scattering and tunneling measurements on superconducting Pd-alloys implanted with different but well-controlled amounts of H and D are necessary to reveal the relative importance of the effects due to the electronic density of states, the acoustic and optic phonons, and anharmonicity.

The present results clearly show that the occurrence of superconductivity in hydrogenated Pd alloys does not depend on a regular fcc host lattice. Presumably, a densely-packed, amorphous agglomeration of Pd, element M and H(D) atoms is sufficient to initiate superconductivity in these alloys. From this experiment, it can be inferred that neither any specific peak in the electronic density of states near the Fermi surface nor distinctive phonon distribution which usually associates with crystalline lattice is responsible for the occurrence of superconductivity in the Pd-M-H(D) alloys.

It is also interesting to note that $100 \sim 200$ ppm of Fe depressed the T_c of Pd-Si-H(D) to below 1.3°K. The large suppression of T_c is in full agreement with specific heat measurements of the Pd-H alloys.[20] Even though we cannot rule out the effect due to possible local polarization, it is very likely that Fe forms a well-defined magnetic moment in the Pd-Si-H(D) alloy matrix as in the case of Pd-H alloys.[21] In this situation, the magnetic impurities modify drastically the superconducting properties of the host matrix through the pair-breaking effect of the spin exchange interaction with conduction electrons.[22] We estimate that the initial depression of T_c is comparable with that of the Mo-Fe alloys.[23]

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Figure 1. Superconducting transition tempera-
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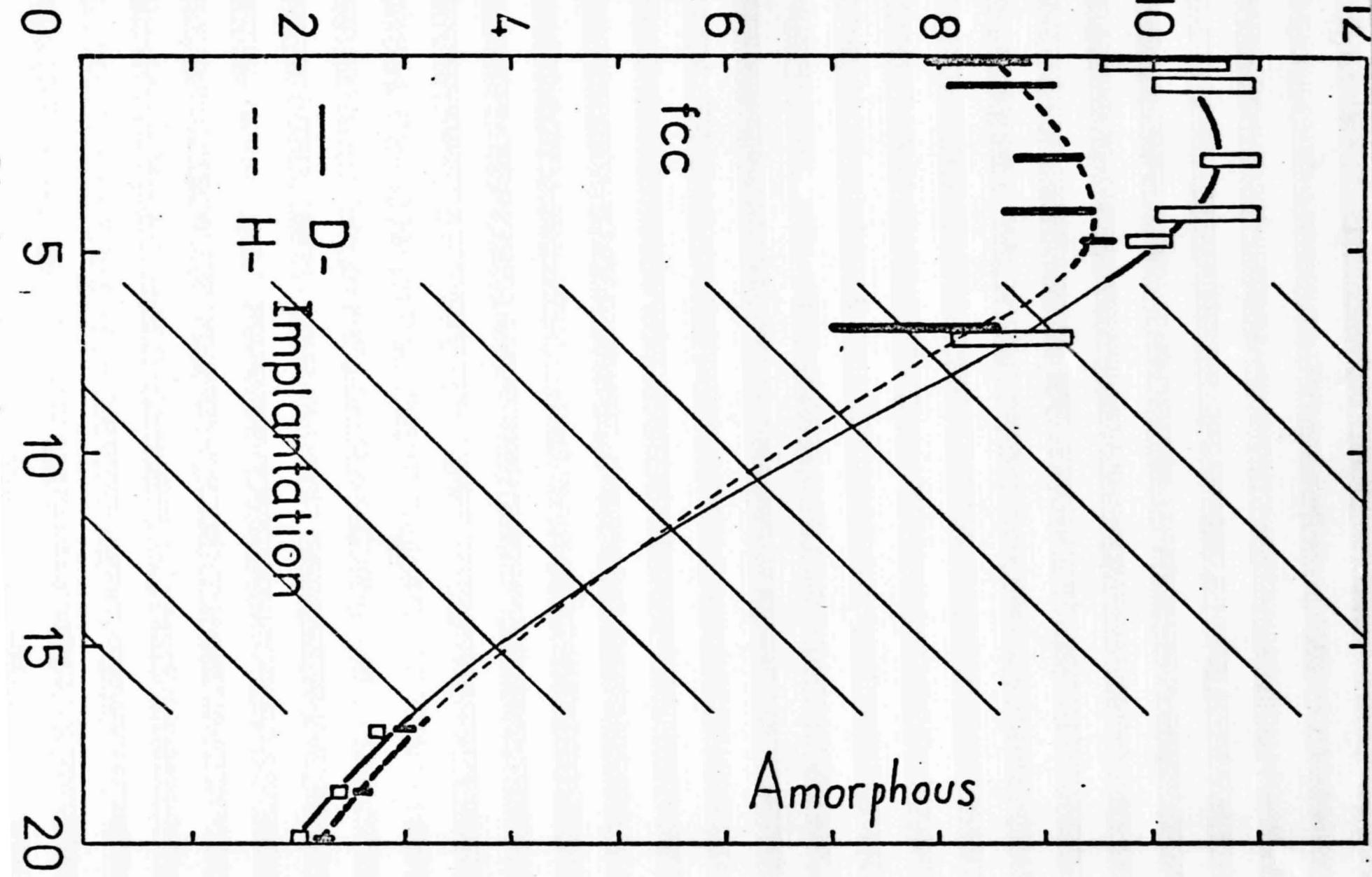
LOW-TEMPERATURE SPECIFIC HEAT OF AMORPHOUS
Pd-Si ALLOYS[*]

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Abstract

The low temperature specific heat of an amorphous $Pd_{0.818}Si_{0.182}$-alloy is measured and compared with that of amorphous $Pd_{.775}Si_{.165}Cu_{.06}$, and the corresponding crystalline phases. The electronic contribution is about the same in all cases. The lattice contribution to the specific heat is largest in the binary alloy, intermediate in the ternary alloy, and smallest in the crystalline forms. The results are discussed in terms of softening in shear resistance of the material.

Introduction.

Among metallic glasses, the amorphous phase in the Pd-Si system (containing 17 ~ 20 at. % Si), produced by rapid quenching, is the most widely known and the most extensively studied. Since it is difficult, to prepare the binary amorphous Pd-Si phase in bulk form, most of the data on properties that required bulk specimens were usually obtained from samples containing a few percent of a third element, such as Cu [1-3], which tends to stabilize the amorphous state.

Under this circumstance, it is appropriate to ask the question: Is there any difference between a binary Pd-Si alloy and its ternary variations prepared by different quenching procedures, even if they are all "amorphous"?

In an attempt to find the answer, we measured the low-temperature specific heat of binary amorphous Pd-Si alloys. Reported here are these results and their comparison with published data on a ternary alloy.

Experimental Procedures.

A master alloy of the composition 18.2 at.% Si; Pd was prepared by induction-melting the appropriate amounts of the pure elements in an argon atmosphere. There was no detectable weight change due to the melting process. Small slices (0.2 ~ 0.3 gm) of the master alloy were quenched into thin foils, using the anvil-and-piston arrangement [4]. The dimensions of quenched foils were ~ 2^{cm} in diameter and 40 ~ 50 μm thick.

Prior to specific heat measurements, all specimens were screened by x-ray diffraction. In the as-quenched state, all foils were amorphous. Crystalline specimens were obtained by annealing the quenched foils in vacuum at ~ 400°C for a few hours.

Specific heat experiments were conducted in two temperature ranges: 2° to 20° K and 60°C to 500°C. In the low temperature range, the

1

Sullivan-Seidel AC technique [5] was used, while the upper range employed a Perkin-Elmer differential scanning calorimeter at 20°C/min. Both of these techniques are extensively covered in the literature. In each case, a sample of $\sim$ 50 mg, cut from the quenched foil, was used.

Results and Discussion

The results of the differential scanning calorimetry from several runs were quite consistent. The onset temperature of crystallization at 390°C and the heat of crystallization of 950 ± 5 cal./gm formula wt. agree closely with the literature data [6]. However, the glass transition temperature, expected at $\sim$ 380°C could not be convincingly delineated.

The low-temperature specific heat (C) is plotted as a function of temperature (T) in the usual $\frac{C}{T}$ vs T^2 manner, shown in Fig. 1, together with the published data of an alloy $Pd_{0.775}Cu_{0.06}Si_{0.165}$ [1,2]. The specific heats in the crystalline states in all cases are quite compatible. The well-known features of the low-temperature excess specific heat of the amorphous states are evident. Of particular interest is the observation that the excess specific heat of the amorphous $Pd_{81.8}Si_{18.2}$ alloy is larger than that of the amorphous $Pd_{0.775}Cu_{0.06}Si_{0.165}$ alloy. Such variation points to a fundamental difference in structures of the two cases. In order to make direct comparison, we fitted all data with the same expression

$$C = \gamma T + \beta T^3,$$

without higher-order terms, where γ is the electronic specific heat, and β is a function of the Debye temperature (Θ_D). Since the excess specific heat increases rapidly with increasing T above 5°K, only the data below 3°K were used for the fitting procedures. The values of γ and Θ_D are listed in Table I.

The decrease of Θ_D and the excess low-termperature specific heat can be

2

considered of the same structure-related origin. Comparing the crystalline and amorphous states of the alloy $Pd_{0.775}Cu_{0.06}Si_{0.165}$, the shear modulus ($C_{44}$) of the latter is much lower, which corresponds directly to a lower Θ_D[1]. The present results indicate that the C_{44} of the binary amorphous Pd-Si phase is lower than the ternary amorphous alloy quenched in bulk form.

So far, there is no direct measurement on C_{44} of any binary amorphous Pd-Si alloy. But such C_{44} values can be reliably estimated from the data on Young's modulus (E) and bulk modulus (B) which are more convenient to measure.

For an isotropic material, the three elastic moduli C_{11}, C_{12}, and C_{44} are not independent but are related by the expression $C_{44} = \frac{1}{2}(C_{11} - C_{12})$. Since it is known that the bulk modulus of a metallic glass differs from its crystalline counterpart by just a few percent and is given by $B = \frac{1}{3}(C_{11} + 2C_{12})$, the Young's modulus, given by

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{C_{11} + C_{12}}$$

is expected to be roughly proportional to C_{44}. Therefore calculating C_{44} from E for any given metallic glass is equivalent to extrapolating the linear relationship between C_{44} and E. This is plotted in Fig. 2 using published data [7,8]. Using $E = 7.8 \times 10^{11}$ dynes/cm^2 for a $Pd_{0.82}Si_{0.18}$ alloy [9], the C_{44} is estimated to be 2.77×10^{11} dynes/cm^2.

The densities of the binary $Pd_{0.818}Si_{0.182}$ and the ternary $Pd_{0.775}Cu_{0.06}Si_{0.165}$ are nearly identical. The difference in Θ_D can therefore be attributed entirely to the variations in C_{44}. Indeed the Θ_D and C_{44} values listed in Table I satisfy the relation $\Theta_D \propto C_{44}^{1/2}$.

3

Thus the low Θ_D - value of an amorphous phase derived from low-temperature specific heat data provides a good indicator of its structure-related properties.

The "amorphous" state is a poorly defined term. The case of arsenic is a good example. Amorphous states of As prepared by different processes demonstrate drastically different structure-related behaviors [10]. The present results also indicate that there are important structure differences between amorphous states for Pd-Si and related alloys by different preparation processes.

Recently a set of low-temperature specific heat data in amorphous Pd-Si alloys and the ternary variations produced by a spinning wheel technique was reported [11]. These values fall in between that of the present investigation and those reported in Ref. [1] and [2], further illustrating that the structure of an amorphous phase is very dependent on the quenching rate or on the specimen preparation procedures in general. On the other hand, the difference between an amorphous phase and its derivatives obtained from substituting just a few percent of its constituents with other components may be minor, as indicated in Ref. [11]. Conventional diffraction techniques, however, may not be sensitive enough to detect the small structure differences due to different preparation conditions. The analysis based on energy dispersive x-ray diffraction [12] may prove to be more useful.

Another interesting observation concerns the stability of an amorphous phase. We suggest that one of the reasons that, in some systems, amorphous phases only exist over certain limited composition ranges is due to their softness in the shear resistance. For this to be true, there must exist a composition within the range of stability for amorphous phases for which E or Θ_D reaches a maximum value. On either side of the maximum the E or Θ_D

4

value will then necessarily decline. The compositional limits of the amorphous phase thus corresponds to the points at which the amorphous phase become unstable against shear. Admittedly this model has not taken other important crystallization factors into consideration. However, a survey of known metallic glasses with limited composition ranges indicates that a number of such examples indeed exist, eg. Zr-Cu, Nb-Ni [13], Pd-Ni-P [8], and La-Ga [14]. When the specific heat data of Pd-Si alloys in Ref [11] are analyzed, the Θ_D-values also satisfy this criterion.

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Figure Captions

Figure 1. Specific Heats of Pd-Si Alloys. (Open symbols: amorphous state;
           solid symbols: corresponding crystalline state).

Figure 2. Relationship between Young's Modulus and Shear Modulus of Metallic
           Glasses. All data were taken from Ref. 7 and 8.

Table I. A Comparison of Properties of Pd-Si Alloys

Pd-Si Alloys

	$\rho(gm/cm^3)$	$\gamma(mj/mole\text{-}K^2)$	$\Theta_D(°K)$	$C_{44}(10^{12} dynes/cm^2)$
$Pd_{0.775}Cu_{0.06}Si_{0.165}$	10.52[a]	1.2	235	0.348[a]
$Pd_{0.818}Si_{0.182}$	10.53	1.3	210	0.277
Crystalline	10.69[a]	1.1	280	0.469[a]

(a) From Reference (1)

8