

## General Disclaimer

### One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

**Superconductivity in Ternary Molybdenum Sulfides**



UNIVERSITY OF CALIFORNIA, SAN DIEGO

SANTA BARBARA • SANTA CRUZ  
BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO

**Final Report**

**NASA Grant NSG 3101**

1-CR-158345) SUPERCONDUCTIVITY IN  
TERNARY MOLYBDENUM SULFIDES Final Report  
(University of California, San Diego, La Jolla.)  
HC A03/NE A01

N79-22933

CSCI 201

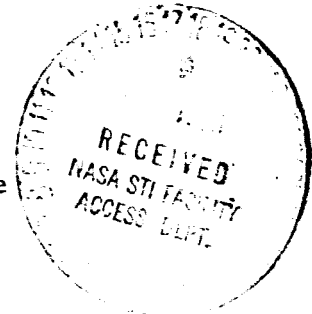
G3/76

Unclas  
25098

H. L. Luo

Applied Physics & Information Science  
University of California, San Diego

La Jolla, CA 92093



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 31, 233 (1977). Also Abstract, Bull. Amer. Phys. Soc. 22, 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. 30, 797 (1978). Also Abstract, Bull. Amer. Phys. Soc. 22, 402 (1977).
3. S. A. Alterovitz, J. A. Woollam, L. Kammerdiner and H. L. Luo, "Critical current in sputtered  $\text{PbMo}_6\text{S}_8$ ," Appl. Phys. Letters 33, 264 (1978). Also Abstract, Bull. Amer. Phys. Soc. 23, 383 (1978).
4. S. A. Alterovitz and J. A. Woollam, "Upper critical field of copper molybdenum sulfides," Solid State Commun. 25, 141 (1978).
5. J. A. Woollam and S. A. Alterovitz, "Normal state properties of the ternary molybdenum sulfides," 27, 669 (1978).
6. J. A. Woollam, S. A. Alterovitz and E. J. Haugland, "Hall effect and magnetoresistivity in the ternary molybdenum sulfides," Phys. Letters 68A, 122 (1978).

7. J. A. Woollam and S. A. Alterovitz, "Indirect measurements of Fermi surface parameters of some Cherrel phase materials," J. Mag. Mag. Materials, in press (1978).
8. J. A. Woollam and S. A. Alterovitz, "Low temperature normal state resistance of ternary molybdenum sulfides," Solid State Commun. 27, 571 (1978).
9. J. S. Lannin, H. F. Eno and H. L. Luo, "The specific heat of bulk amorphous arsenic," Solid State Commun. 25, 81 (1978).
10. H. L. Luo and J. G. Huber, "Superconductivity in Th-Zr alloys," J. Less-Common Metals (in press 1979).
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.

AUTHOR	<input checked="" type="checkbox"/> EDITOR	MASTERCOPY	5 pages	LCM	3268
QUERIES*	<input type="checkbox"/> CORRECTION	Vol. No.	pp.		

Only typographical correction will be accepted at this stage. \*Please see request for keywords, on last page.

*Journal of the Less-Common Metals*,  
© Elsevier Sequoia S.A., Lausanne — Printed in the Netherlands

To be published in  
*J. Less-Common-Metals*  
(1979)

## SUPERCONDUCTIVITY IN Th-Zr ALLOYS

H. L. LUO

*Department of Applied Physics and Information Science, University of California, San Diego, La Jolla, Calif. 92093 (U.S.A.)*

JOHN G. HUBER

*Department of Physics, Tufts University, Medford, Mass. 02155 (U.S.A.)*

(Received September 11, 1978)

ORIGINAL PAGE IS  
OF POOR QUALITY

### 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

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<sup>4</sup> cryostat except that for pure Zr which required a dilution refrigerator. Between 4.2 and 1.2 K, He<sup>4</sup> 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 <sup>3</sup> )
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

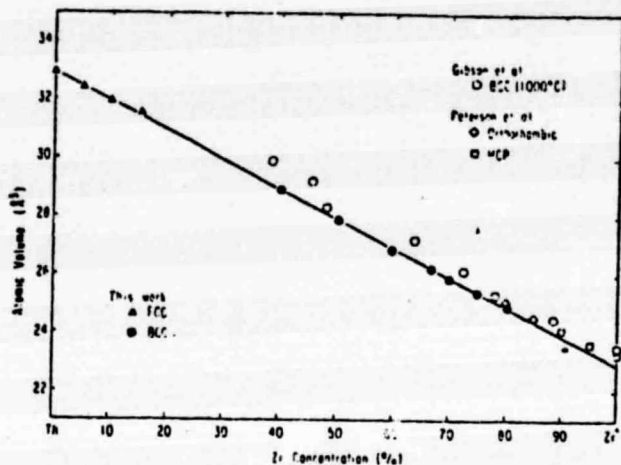


Fig. 1. Atomic volumes of various phases in the Th-Zr system.

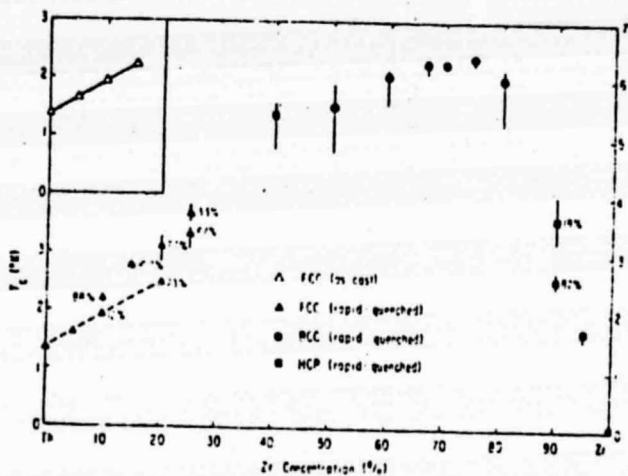


Fig. 2. Superconducting transition temperatures of rapidly quenched Th-Zr alloys. The inset shows the  $T_c$  values for as-cast Th-rich f.c.c. alloys; the observed linearity with Zr composition (solid line) is shown as a broken line.

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  $9.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .

### Acknowledgements

We are indebted to Mr. Ben Ricks for his assistance in the preparation of the specimens. We also wish to thank Professor B. T. Matthias for his encouragement during the course of this work.

This work was supported by NASA Grant NSG 3103 (to H. L. L.) and USAF/F44620-72-C-0017 and NSF Contract DMR 78-18066 (to J. G. H.).

### References

- 1 B. W. Roberts, *J. Phys. Chem. Ref. Data*, 5 (1976) 581.
- 2 W. A. Taylor and D. T. Peterson, *Bull. Am. Phys. Soc.*, 22 (1977) 403.  
D. T. Peterson, J. E. Ostenson and W. A. Taylor, to be published in *J. Less-Common Met.*
- 3 H. L. Luo, *J. Less-Common Met.*, 15 (1968) 299.
- 4 R. H. Johnson and R. W. K. Honeycombe, *J. Nucl. Mater.*, 4 (1961) 59.  
D. S. Evans and G. V. Raynor, *J. Nucl. Mater.*, 4 (1961) 66.
- 5 J. G. Huber and M. B. Maple, in K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel (eds.), *Low Temperature Physics - LT13*, Vol. 2, Plenum Press, New York, 1974.
- 6 M. A. Jensen, Ph. D. Thesis, University of California, San Diego, 1965.
- 7 D. B. Masson and C. S. Barrett, *Trans. Metall. Soc. AIME*, 212 (1958) 260.  
D. B. Masson, *Trans. Metall. Soc. AIME*, 216 (1960) 94.
- 8 O. Rapp, *J. Less-Common Met.*, 21 (1970) 27.
- 9 E. D. Gibson, B. A. Loomis and O. N. Carlson, *Trans. Am. Soc. Met.*, 50 (1958) 348.

ORIGINAL PAGE IS  
OF POOR QUALITY

SUPERCONDUCTIVITY IN Pd-Si-H(D) ALLOYS

B. Stritzker

Institut für Festkörperforschung, KFA Jülich, D-5170 Jülich, W. Germany

and H. L. Luo\*

Department of Applied Physics & Information Science, University of California, San Diego,  
La Jolla, CA 92093

---

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.

PRECEDING PAGE BLANK NOT FILMED

To be published in  
Solid State Communications  
(1979)

## 1. Introduction

Since the discovery of superconductivity in the Pd-H system,<sup>1</sup> the subject has been an active area of research.<sup>2</sup> In particular, the enhancement of superconducting transition temperatures ( $T_c$ ) in the Pd-H-noble metal alloys<sup>3</sup> and the observation of inverse isotope effect<sup>4,5</sup> 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<sup>6</sup> 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).<sup>7</sup> The contribution to such interaction due to the optic photons was particularly suggested<sup>8,9</sup> and was subsequently confirmed through tunneling experiments.<sup>10,11,12</sup>

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<sup>13</sup> indicate that the spin fluctuations are completely suppressed in the amorphous Pd-Si alloy. The electronic specific heat of amorphous Pd-Si alloys<sup>14</sup> (~ 1.0 mJ/mole-K<sup>2</sup>) is equivalent to that of a 50 at. % Ag, Pd alloy<sup>15</sup> which would become superconducting after hydrogenation with an estimated  $T_c$  of  $\lesssim 1$ K.<sup>3</sup>

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

ORIGINAL PAGE IS  
OF POOR QUALITY

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.<sup>16</sup> The general dimensions of the foils were  $\sim 1.5$  cm in diameter and  $40 \sim 50$   $\mu$ m 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.<sup>3</sup>

- (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  $\sim 20$  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	$3.890 \pm 0.001$
0.7	$3.890 \pm 0.002$
2.5	$3.894 \pm 0.003$
3.9	$3.895 \pm 0.005$
4.7	$3.900 \pm 0.005$

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 crystalline 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  $\sim 0.5$ . 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 distribution 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 region, 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 composition range in the present investigation, we would have expected that the isotopic-mass exponent would vary continuously and smoothly from the inverted to the normal values with increasing Si content.

This view is consistent with the general behavior of other Pd-M-H(D) systems<sup>2</sup> 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 concentration of M,  $T_c$  initially increases and passes through a  $T_{c,max}$  maximum value. In all known cases,<sup>2</sup> the  $T_{c,max}$  in the Pd-M-D system always occurs at lower

M concentration than that of the corresponding 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 superconducting behaviors common to all Pd-M-H(D) systems, even though a number of theoretical models have been proposed.<sup>2</sup> However, based on the existing theories, a good qualitative understanding 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 density-of-states which is responsible for the superconductivity 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) interstitials give rise to a large electron-phonon coupling due to the optic phonon modes occurring at rather low energies within the Pd lattice<sup>8-12</sup> and to the large pseudopotential of the rather unscreened protons or deuterons.<sup>7</sup> Recent theories based on detailed band structure calculations<sup>9,17</sup> 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 explain the  $T_{c,max}$  in the Pd-M-H(D) systems.

The anharmonic model proposed by Ganguly<sup>8</sup> was rather attractive in explaining the inverse isotope effect. The sign reversal of the isotopic mass exponent at higher M concentration can then be understood as due to the decrease in harmonicity. 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.<sup>18</sup> In this connection, a rough picture can be presented based on McMillan's theory.<sup>19</sup> 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 ~ 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.<sup>20</sup> 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.<sup>21</sup> 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.<sup>22</sup> We estimate that the initial depression of  $T_c$  is comparable with that of the Mo-Fe alloys.<sup>23</sup>

Acknowledgement--This work was initiated during a 12-month stay (of HLL) in Germany sponsored by the Alexander von Humboldt Stiftung. We are grateful to Professor P. Duwez for allowing us to use his laboratory facilities in preparing all the specimens.



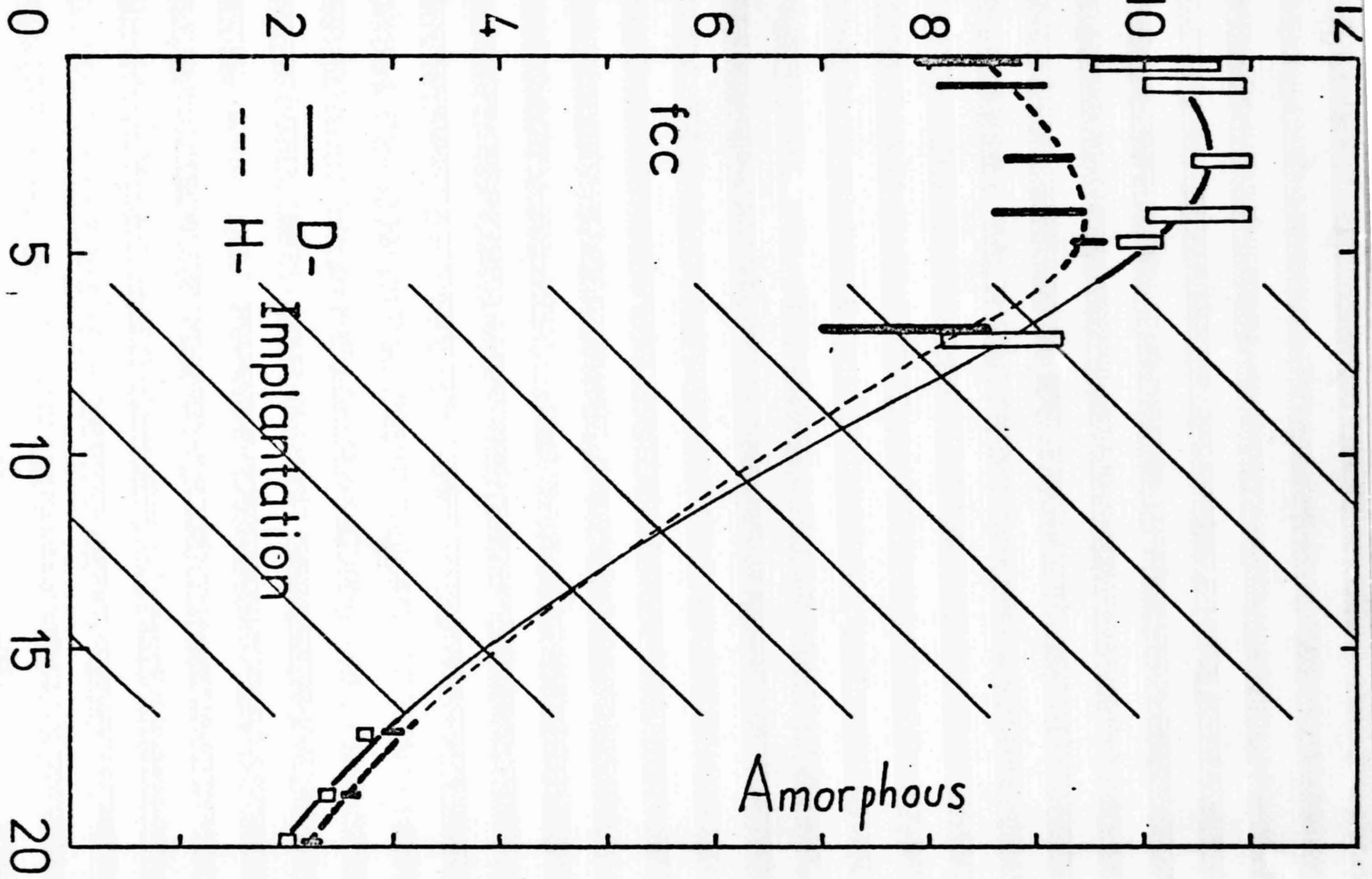
## References

- \* Supported by U.S. NASA Grant 3103.
1. T. SKOSKIEWICZ, *Physica Status Solidi A* 11, K123(1972); B59, 329(1973).
  2. For recent reviews, see A. C. SWITENDICK: "Change in Electronic Properties on Hydrogen Alloying and Hydride Formation;" and B. STRITZKER and H. WÜHL: "Superconductivity in Metal-Hydrogen Systems;" in *Topics in Applied Physics*, Vols. 28 and 29, eds. G. ALEFELD and J. VOLK, Springer Verlag, 1978.
  3. B. STRITZKER, *Zeitschrift für Physik*, 268, 261(1974).
  4. B. STRITZKER and W. BUCKEL, *Zeitschrift für Physik* 257, 1(1972).
  5. R. J. MILLER and C. B. SATTERTHWAITTE, *Physical Review Letters* 34, 144(1975).
  6. K. H. BENNEMANN and J. W. GARLAND, *Zeitschrift für Physik* 260, 367(1973).
  7. B. STRITZKER and J. BECKER, *Physics Letters* 51A, 147(1975).
  8. B. N. GANGULY, *Zeitschrift für Physik* 265, 433(1973); B22, 127(1975).
  9. D. A. PAPACONSTANTOPOULOS, B. M. KLEIN, E. N. ECONOMOU and L. L. BOYER, *Physical Review* B17, 141(1978).
  10. A. EICHLER, H. WÜHL and B. STRITZKER, *Solid State Communications* 17, 213(1975).
  11. R. C. DYNES and J. P. GARNO, *Bulletin of the American Physical Society* 20, 422(1975).
  12. P. NÉDELLEC, L. DUMOULIN, C. ARZOUMANIAN and J. P. BURGER, *Journal de Physique*, C6-432(1978).
  13. C. C. TSUEI, Private Communication.
  14. H. F. ENO and H. L. LUO, to be published.
  15. G. M. STOCK, R. W. WILLIAMS and J. S. FAULKNER, *Journal of Physics F: Metal Physics* 3, 1688 (1973).
  16. P. PIETROKOWSKY, *Journal of Scientific Instruments* 34, 445(1962).
  17. D. A. PAPACONSTANTOPOULOS, E. N. ECONOMOU, B. M. KLEIN and L. L. BOYER, *Journal de Physique* C6-435(1978).
  18. B. STRITZKER, *Journal of Nuclear Materials* 72, 256(1978).
  19. W. L. McMILLAN, *Physical Review* 167, 331(1968).
  20. C. A. MACKLIET, D. J. GILLESPIE and A. I. SCHINDLER, *Journal of Physics and Chemistry of Solids* 37, 379(1976).
  21. J. A. MYDOSH, *Physical Review Letters* 33, 1562(1974).
  22. For a review of paramagnetic effect in superconductors, see M. B. MAPLE in "Magnetism" (G. T. RADO and H. SUHL, eds.) vol. V, pp. 289-325, Academic Press, New York, 1973.
  23. S. TAKAYANAGI, M. TAKANO, Y. KIMURA and T. SUGAWARA, *Journal of Low Temperature Physics* 16, 519(1974).

**Figure Caption**

**Figure 1. Superconducting transition temperatures of the Pd-Si-H(D) alloys.**

Transition Temperature / K



LOW-TEMPERATURE SPECIFIC HEAT OF AMORPHOUS  
Pd-Si ALLOYS\*

Submitted to  
*J. of Non-Crystalline  
Solids for publication.*

H. L. LUO and H. F. ENO<sup>†</sup>

Department of Applied Physics & Information Science, University of California,  
San Diego, La Jolla, California 92093, USA

Abstract

The low temperature specific heat of an amorphous  $\text{Pd}_{0.818}\text{Si}_{0.182}$ -alloy is measured and compared with that of amorphous  $\text{Pd}_{.775}\text{Si}_{.165}\text{Cu}_{.06}$ , 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.

PRECEDING PAGE BLANK NOT FILMED

\* Supported by NASA Grant NSG 3103

† Deceased 1978. This manuscript was written posthumously.

## 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<sup>cm</sup> in diameter and 40 ~ 50  $\mu$ m 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

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 ~ 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  $950 \pm 5$  cal./gm formula wt. agree closely with the literature data [6]. However, the glass transition temperature, expected at ~ 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  $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$  [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  $\text{Pd}_{81.8}\text{Si}_{18.2}$  alloy is larger than that of the amorphous  $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$  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  $\gamma$  is the electronic specific heat, and  $\beta$  is a function of the Debye temperature ( $\Theta_D$ ). 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  $\gamma$  and  $\Theta_D$  are listed in Table I.

The decrease of  $\Theta_D$  and the excess low-temperature specific heat can be

considered of the same structure-related origin. Comparing the crystalline and amorphous states of the alloy  $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$ , the shear modulus ( $C_{44}$ ) of the latter is much lower, which corresponds directly to a lower  $\Theta_D$  [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<sup>2</sup> for a  $\text{Pd}_{0.82}\text{Si}_{0.18}$  alloy [9], the  $C_{44}$  is estimated to be  $2.77 \times 10^{11}$  dynes/cm<sup>2</sup>.

The densities of the binary  $\text{Pd}_{0.818}\text{Si}_{0.182}$  and the ternary  $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$  are nearly identical. The difference in  $\Theta_D$  can therefore be attributed entirely to the variations in  $C_{44}$ . Indeed the  $\Theta_D$  and  $C_{44}$  values listed in Table I satisfy the relation  $\Theta_D \propto C_{44}^{\frac{1}{2}}$ .

Thus the low  $\Theta_D$  - 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  $\Theta_D$  reaches a maximum value. On either side of the maximum the  $E$  or  $\Theta_D$



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  $\Theta_D$ -values also satisfy this criterion.

**Acknowledgement:** We are indebted to Professor P. Duwez for allowing us to use the fast-quenching facilities in his laboratory.

## References

- [1] B. Golding, B.G. Bagley and F.S.L. Hsu, *Phys. Rev. Letters* 29 (1972) 68.
- [2] H.S. Chen and W.H. Haemmerle, *J. Non-Cryst. Solids* 11 (1972) 161.
- [2] G. Bellessa and O. Bethoux, *Phys. Letters* 62A (1977) 125.
- [4] P. Pietrokowsky, *J. Sci. Instr.* 34 (1962) 445.
- [5] P.F. Sullivan and G. Seidel, *Phys. Rev.* 173 (1968) 679.
- [6] H.S. Chen and D. Turnbull, *Acta Met.* 17 (1969) 1021.
- [7] M. Dutoit and H.S. Chen, *Appl. Phys. Letters* 23 (1973) 357.
- [8] H.S. Chen, J.T. Krause and E. Coleman, *J. Non-Cryst. Solids* 18 (1975) 157.
- [9] B.S. Berry and W.C. Pritchett, *J. Appl. Phys.* 44 (1973) 3122.
- [10] C.T. Wu and H.L. Luo, *J. Non-Cryst. Solids* 13 (1973) 437; J.S. Lannin, H.F. Eno and H.L. Luo, *Solid State Commun.* 25 (1978) 81.
- [11] T.B. Massalski, U. Mizntani, K.T. Hartung and R.W. Hopper, *Proc. 3<sup>rd</sup> Internat. Conf. Rapidly Quenched Metals* (Ed. B. Cantor), Vol. 2, p. 81. The Metal Society, London (1978).
- [12] T. Egami, *J. Mat. Sci.* 13 (1978) 2587.
- [13] H.S. Chen and J.T. Krause, *Script. Met.* 11 (1977) 761.
- [14] W.H. Shull, D.G. Nagle, S.J. Poon and W.L. Johnsen, *Phys. Rev.* B18 (1978) 3263.

## 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 <sup>3</sup> )	$\gamma$ (mj/mole-K <sup>2</sup> )	$\Theta_D$ (°K)	$C_{44}$ (10 <sup>12</sup> dynes/cm <sup>2</sup> )
$\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$	10.52 <sup>(a)</sup>	1.2	235	0.348 <sup>(a)</sup>
$\text{Pd}_{0.818}\text{Si}_{0.182}$	10.53	1.3	210	0.277
Crystalline	10.69 <sup>(a)</sup>	1.1	280	0.469 <sup>(a)</sup>

(a) From Reference (1)

