TECHNICAL REPORT ARLCB-TR-81045

SUPERCONDUCTIVITY IN HYDROGEN-CHARGED
COPPER-IMPLANTED PALLADIUM

A. Leiberich
W. Scholz
W. J. Standish
C. G. Homan

December 1981

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER WEAPON SYSTEMS LABORATORY
BENÉT WEAPONS LABORATORY
WATERVLIET, N. Y. 12189

DISCLAIMER

The findings in this report are not to be construed as an official
Department of the Army position unless so designated by other author-
ized documents.

The use of trade name(s) and/or manufacture(s) does not consti-
tute an official indorsement or approval.

DISPOSITION

Destroy this report when it is no longer needed. Do not return it
to the originator.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARLCB -TR-81045	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* SUPERCONDUCTIVITY IN HYDROGEN-CHARGED COPPER-IMPLANTED PALLADIUM		5. TYPE OF REPORT & PERIOD COVERED FINAL
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) A. Leiberich, W. Scholz, W. J. Standish, and C. G. Homan (CONT'D ON REVERSE)		8. CONTRACT OR GRANT NUMBER(s) AMCMS NO.611102H600011 PRON No.1A1283121A1A
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army Armament Research & Development Command Benet Weapons Laboratory, DRDAR-LCB-TL Watervliet, NY 12189		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Armament Research & Development Command Large Caliber Weapon Systems Laboratory Dover, NJ 07801		12. REPORT DATE December 1981
		13. NUMBER OF PAGES 10
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Superconductivity
Ion Implantation
Palladium-Copper Hydride

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A superconducting transition temperature, T_c, of 124. K has been observed in palladium implanted with copper ions and electrolytically charged with hydrogen at dry ice temperature. A step-wise warmup procedure between 77 K and 273 K produces considerable variations in T_c. Annealing the copper implanted palladium before electrolysis does not change T_c to a substantial degree.

DD FORM 1473 1 JAN 73   EDITION OF 1 NOV 65 IS OBSOLETE   UNCLASSIFIED

7. AUTHOR(S)

A. Leiberich, W. Scholz, and W. J. Standish
Department of Physics
State University of New York at Albany
Albany, NY

C. G. Homan
US Army Armament Research & Development Command
Large Caliber Weapon Systems Laboratory
Benet Weapons Laboratory

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

INTRODUCTION

The palladium-hydrogen system has been studied extensively, but superconductivity in this system was not discovered until 1972 when Skoskiewicz[1] found a maximum transition temperature $T_{c,max}$ = 6.6 K for an atom ratio H/Pd = 0.94. Since then superconductivity has also been reported[2] in the Pd-D and the Pd-M-H(D) system where M is one of the noble metals copper, silver, or gold. The highest transition temperature $T_{c,max}$ = 16.6 K was observed by Strikzker[3] for an alloy with the composition $H/Pd_{55}Cu_{45} \simeq 0.7$.

EXPERIMENTAL METHODS

A number of methods have been used to achieve the high H-concentration required for superconductivity in Pd and its alloys.[2] For PdH_x, these include (a) electrolytic charging at room and dry ice temperature,[4-6] (b) high pressure charging using several kbar,[7] (c) precharging to H/Pd $\simeq$ 0.7 at 4 bar and 300°C with additional implantation of H at liquid helium temperature,[8] (d) H implantation only at 4 K into thin evaporated Pd films,[9] and (e) codeposition of H and Pd at 4 K.[10] Of these, electrolysis at dry ice temperature appears to be most widely used for PdH_x because of its relative ease for reaching H/Pd $\simeq$ 1.0 with the attendant $T_{c,max} \simeq$ 9 K. The higher transition temperatures for the Pd alloys, on the other hand, have only been achieved with the precharging-implantation method.[3] Of the other methods, only high pressure charging has been reported for the Pd alloys.[11] However, the high pressure experiments fail to reproduce the higher transition temperatures achieved with the implantation method.

---

*References are listed at the end of this report.

Hydrogen solubility in Pd[12] and Pd-Ag alloys[13] has been studied in some detail. PdH_x forms an isotropically expanded fcc host lattice of Pd in which the H atoms occupy a fraction of the octahedral sites. Below the critical point at T_{cr} = 565 K, PdH_x exists in the form of a mixture of low H concentration α phase and high H concentration β phase separated by a miscibility gap. At room temperature the maximum concentration of the α phase and the minimum concentration of the β phase are α_{max} = 0.008 and β_{min} = 6.07, respectively.[12] For Pd-Ag alloys, on the other hand, T_{cr} and β_{min} become progressively smaller with increasing Ag concentration, and the miscibility gap narrows.[13] The decreased H solubility in Pd-Ag alloys,[13] and probably other Pd alloys as well, may be a contributing factor for the lack of success in achieving high transition temperatures in uniform alloys using high pressure charging.[11]

In this report we discuss a new method for producing superconducting Pd-Cu alloys which requires only electrolytic charging at dry ice temperature. Singly charged Cu ions were implanted at 100 keV into 38 μm thick Pd foil (nominal purity 99.99%, Fe content ≤ 10 ppm) to a dose of 8 x 10^{16} at./cm^2. The range and range straggling of 100 keV Cu ions in Pd are expected to be $\langle x \rangle$ = 0.023 μm and σ = 0.013 μm, respectively.[14] Because of sputtering[15] the surface will recede during the implantation by several Cu ion ranges and the implant profile will be given approximately by a complementary error function $erfc[(x-\langle x \rangle)/\sqrt{2}\sigma]$, where x is the depth into the sample. The relative fraction of Cu atoms at the surface under such steady-state conditions is given by the inverse of the Cu self-sputtering yield S_{Cu}. For S_{Cu} = 4.3 ± 0.8,[16] a maximum Cu concentration (atom fraction) of 0.23 ± 0.04 is obtained

2

at the surface corresponding to a Cu atom density of $(1.6 \pm 0.3) \times 10^{22}$ at./cm^3 since Cu can be assumed to be substitutional.[17] The total remaining Cu implant dose calculated from S_{Cu} and the range parameters is $(3.7 \pm 0.7) \times 10^{16}$ at./cm^2. An independent determination of the implant dose using Rutherford backscattering (RBS) yielded $(2.5 \pm 0.5) \times 10^{16}$ at./cm^2, a reasonably close value in view of the uncertainities of the experiments, the sputtering yield, and the range parameters. The Cu-implanted foils were epoxied onto a hollow plexiglas tube which held the thermocouple and other needed connections with the implant facing out. Charging with H was performed in an electrolytic bath at dry ice temperature using using the method of van Dongen and Mydosh.[6] Samples charged in this way to H/Pd $\simeq$ 1 were immediately placed in liquid nitrogen upon removal from the electrolyte. During the subsequent transfer to liquid helium the temperature of the samples never exceeded 77 K.

Four probe dc resistance measurements were made with currents[18] varying from 40 mA to 2 A. Temperature control to about 0.5 K was accomplished by means of a thermal link to the liquid helium bath. Stable temperatures were measured with a thermocouple calibrated at 4.2 K and at the superconducting transitions of Nb, Pb, and V. T_c was defined as the average of the temperataures at 10 and 90 percent of the normal state resistance.

RESULTS

After electrolysis and transfer to the liquid helium bath, the superconducting transition curve was measured. Following this initial measurement the sample was warmed up to increasingly higher temperatures and the transition curves were remeasured. The warming procedure involved withdrawing the sample from the liquid helium bath until it reached a given temperature, then quickly returning it. Figure 1 shows results obtained on a sample following this procedure. Starting with an initial value of 11.1 K, T_c increases to 12.4 K after the sample is warmed to 113 K. Subsequent warmup steps reduce T_c until, after warming to 193 K, T_c begins to increase again, from 10.9 K to 12.4 K. The remaining warmup steps above 203 K all produce a decrease in T_c. The normal state resistance of the sample above the critical temperature remains fairly constant for warmup steps up to 213 K indicating a small loss of H from bulk up to this point.[1,11] Above 213 K, H is released from bulk as indicated by the increase in normal state resistance.[19] After warmup to 273 K the onset of the superconducting transition is just visible at 4.2 K.

In pure PdH_x, the maximum observed transition temperature is about 9 K for $H/Pd \simeq 1.0$.[2] Indeed, pure Pd samples studied by us under experimental conditions identical to those for the Cu implanted samples did not exceed $T_c \simeq$ 9 K. Thus, the elevated T_c values observed in our experiment must be due to the Cu-implanted region. The changes in T_c above 9 K induced by warming up the sample must then be caused changes in H concentration in the implant region since no other atomic species is sufficiently mobile below 273 K.

4
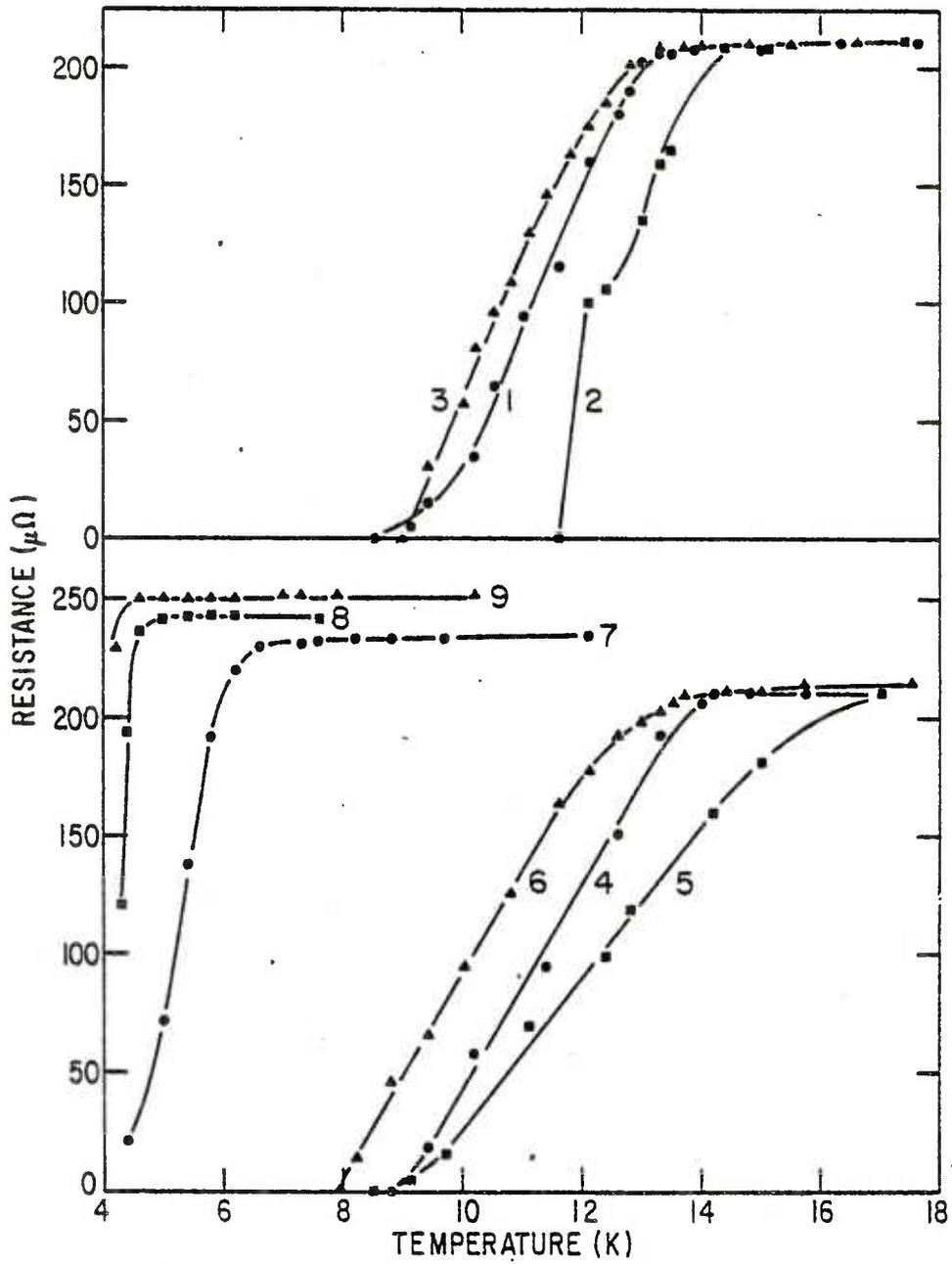
Figure 1. Superconducting transitions measured on a Cu implanted Pd sample immediately after electrolysis at dry ice temperature and transfer to the liquid helium bath (1). Transition curves measured after letting the sample warm up to 113 and 143 K and quickly cooling it again are labeled (2) and (3), respectively. Transition curves measured after warmup to 193, 203, 213, 253, 263, and 273 K are labeled (4) through (9), respectively.

Measurements of the H concentration and depth distribution by nuclear reaction analysis[20] in similar samples following the same warmup procedure reveal a strong correlation between H concentration in the implant region and T_c. The fact that both the H and Cu distributions are depth dependent may account for the broadness in some of the higher T_c transition curves.

Our theoretical analysis of the Cu concentration in the implant region suggests an alloy with a maximum concentration of ~ 23 at. percent Cu in Pd occurring at the surface. For a bulk alloy of similar composition, Stritzker[3] reports $T_{c,max} \simeq 13$ K, in good agreement with our value. However, our transition curves are broader than his, having onset temperatures as high as ~ 16 K. This is a value which in bulk alloys is reached only for concentrations of ~ 40 at. percent Cu. It is unlikely that our concentration is higher than ~ 23 at. percent Cu since the sputtering yield chosen in our analysis[16] is already at the low range of reported values.[15] Furthermore, our RBS data also indicate lower concentrations. A more complete characterization of the samples from both our and Stritzker's[3] experiment is clearly desirable.

It has been reported that Pd films condensed onto a cool substrate can be made superconducting by irradiation with He^{+} ions at low temperature without H implantation.[21] Other authors have not succeeded in confirming these results[22] but rather have found that the defects produced during irradiation tend to increase the H concentration required for a given value of T_c.[9] In order to investigate whether damage resulting from the Cu implantation had an effect on T_c, an implanted sample was annealed at 773 K in Ar gas flow for one hour. Using Pd-Cu interdiffusion coefficients extrapolated from the temperature range 1104 - 1334 K,[23] the diffusion length is estimated to be

~ 10 Å , sufficient to anneal defects but not so large as to modify substantially the implanted Cu profile. $T_{c,max} \simeq 11.6$ K was observed for this sample with an onset of the transition curve at ~ 15 K. Subsequent warmup steps eventually decreased T_c to below 4.2 K. Thus, it would seem that defects produced during Cu implantation have no significant effect on the observed T_c.

As an additional check, another Cu implanted sample was annealed at 973 K for one hour. Since Cu and Pd will interdiffuse by ~ 0.1 μ under these conditions, the maximum Cu concentration in the implant profile will be reduced to less than five percent. Indeed, the maximum transition temperature observed on this sample was 8.8 K, reflecting superconductivity in essentially pure PdH_x.[3]

CONCLUSIONS

The results reported here indicate that the high transition temperatures in the Pd-noble metal system can be achieved with considerably simpler means than used previously.[3] It appears that the pure Pd backing behind the Cu-implanted surface can act as a high concentration H reservoir for the low H solubility Pd-Cu alloy region. This opens up exciting new possibilities for the study and modification of this important system. It will be of interest to extend these measurements to higher Cu concentrations as well as to other implant species. Samples prepared as described in this report are particularly suited for H profiling using nuclear reaction analysis.[20] Measurements of the H concentration and distribution in superconducting Pd-noble metal-H systems should be extremely helpful in advancing our understanding of these systems.

REFERENCES

1. T. Skoskiewicz, Phys. Stat. Sol. (a) $\underline{11}$, K123 (1972), and Phys. Stat. Sol. (b) $\underline{59}$, 329 (1973).

2. For a recent review, see B. Stritzker and H. Wühl, in Hydrogen in Metals, edited by G. Alefeld and J. Vökl (Springer-Verlag, Berlin-Heidelberg-New York, 1978), p. 243.

3. W. Buckel and B. Stritzker, Phys. Lett., $\underline{43A}$, 403 (1973); B. Stritzker, Z. Physik $\underline{268}$, 261 (1974).

4. J. M. E. Harper, Phys. Lett., $\underline{47A}$, 69 (1974).

5. R. J. Miller and C. B. Satterthwaite, Phys. Rev. Letters $\underline{34}$, 144 (1975).

6. J. C. M. van Dongen and J. A. Mydosh, Z. Phys. Chem. N. F. $\underline{116}$, 149 (1979).

7. T. Skoskiewicz, A. W. Szafranski, W. Bujnowski, and B. Baranowski, J. Phys. C$\underline{7}$, 2670 (1974).

8. B. Stritzker and W. Buckel, Z. Physik $\underline{257}$, 1 (1973).

9. H. Bernas, A. Traverse, L. Brossard, J. Chaumont, F. Lalu, and L. Dumoulin, in Ion Beam Modification of Materials, edited by R. E. Benenson, E. N. Daufmann, G. L. Miller, and W. W. Scholz, Nucl. Instr. and Meth. $\underline{182/183}$, 1033 (1981).

10. L. Sansores and R. E. Glover, Bull. Am. Phys. Soc. $\underline{19}$, 437 (1974); P. I. Silverman and C. V. Briscoe, Phys. Lett. $\underline{53A}$, 221 (1975).

11. T. Skoskiewicz, A. W. Szafranski and B. Baranowski, Phys. Stat. Sol. (b) $\underline{59}$, K135 (1973); B. Baranowski and T. Skoskiewicz, in High Pressure and Low Temperature Physics, edited by C. W. Chu and J. A. Wollan (Plenum Press, New York and London 1978), p. 43; A. W. Szafranski, T. Skoskiewicz,

and B. Baranowski, Phys. Stat. Sol. (a) $\underline{37}$, K163 (1976).

12. E. Wicke and H. Brodowsky in Hydrogen in Metals, edited by G. Alefeld and J. Völkl (Springer Verlag, Berlin-Heidelberg-New York, 1978) p. 73.

13. H. Brodowsky and E. Poeschel, Z. Phys. Chem. N.F. $\underline{44}$, 143 (1965).

14. Ion Implantation, Vol. 8 of Defects in Crystalline Solids, G. Dearnaley, J. H. Freeman, R. S. Nelson, and J. Stephen (North-Holland, Amsterdam, 1973), p. 766.

15. H. H. Andersen and H. L. Bay, in Sputtering by Ion Bombardment, edited by R. Behrisch, (Springer Verlag, Berlin-Heidelberg-New York, in press).

16. G. W. Reynolds, A. R. Knudson and C. R. Gossett, in Ion Beam Modification of Materials, edited by R. E. Benenson, E. N. Kaufman, G. L. Miller, and W. W. Scholz, Nucl. Instr. and Methods, $\underline{182/183}$, 179 (1981); R. G. Allas, A. R. Knudson, J. M. Lambert, P. A. Treado, and G. W. Reynolds, to be published in Proceedings of the 9th International Conference on Atomic Collisions in Solids, held in Lyon, France, July 6-10, 1981.

17. M. Hansen, Constitution of Binary Alloys, 2nd Ed. (McGraw-Hill, New York, 1958).

18. A current of 2 A was passed through the samples while they remained in the superconducting state above 9 K. This result suggests critical currents on the order of 10^6 A/cm^2 in the implant region of our samples.

19. Because of the way the sample is mounted, there are two narrow strips along the sample edge which are not exposed to the electrolyte. Thus, as distinct from References 1 and 11, normal-state resistance is only useful as a qualitative measure for H concentration.

20. W. J. Standish, A. Leiberich, W. Scholz, and C. G. Homan, to be published.

21. B. Stritzker, J. Phys. (Paris) Lett. <u>39</u>, L397 (1978), and Phys. Rev. Lett. <u>42</u>, 1769 (1979).

22. H. Bernas and P. Nedellec, in Ion Beam Modification of Materials, edited by R. E. Benenson, E. N. Kaufman, G. 1. Miller, and W. W. Scholz, Nucl. Instr. and Meth. <u>182/183</u>, 845 (1981).

23. M. Badia in Diffusion Data <u>4</u>, 28 (1970).

TECHNICAL REPORT INTERNAL DISTRIBUTION LIST

	NO. OF COPIES
COMMANDER	1
CHIEF, DEVELOPMENT ENGINEERING BRANCH	1
ATTN: DRDAR-LCB-DA	1
-DM	1
-DP	1
-DR	1
-DS	1
-DC	1
CHIEF, ENGINEERING SUPPORT BRANCH	1
ATTN: DRDAR-LCB-SE	1
-SA	1
CHIEF, RESEARCH BRANCH	2
ATTN: DRDAR-LCB-RA	1
-RC	1
-RM	1
-RP	1
CHIEF, LWC MORTAR SYS. OFC.	1
ATTN: DRDAR-LCM	1
CHIEF, IMP. 81MM MORTAR OFC.	1
ATTN: DRDAR-LCB-I	1
TECHNICAL LIBRARY	5
ATTN: DRDAR-LCB-TL	
TECHNICAL PUBLICATIONS & EDITING UNIT	2
ATTN: DRDAR-LCB-TL	
DIRECTOR, OPERATIONS DIRECTORATE	1
DIRECTOR, PROCUREMENT DIRECTORATE	1
DIRECTOR, PRODUCE ASSURANCE DIRECTORATE	1

NOTE: PLEASE NOTIFY ASSOC. DIRECTOR, BENET WEAPONS LABORATORY, ATTN:
DRDAR-LCB-TL, OF ANY REQUIRED CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST

	NO. OF COPIES		NO. OF COPIES
ASST SEC OF THE ARMY RESEARCH & DEVELOPMENT ATTN: DEP FOR SCI & TECH THE PENTAGON WASHINGTON, D.C. 20315	1	COMMANDER US ARMY TANK-AUTMV R&D COMD ATTN: TECH LIB - DRDTA-UL MAT LAB - DRDTA-RK WARREN, MICHIGAN 48090	1 1
COMMANDER US ARMY MAT DEV & READ. COMD ATTN: DRCDE 5001 EISENHOWER AVE ALEXANDRIA, VA 22333	1	COMMANDER US MILITARY ACADEMY ATTN: CHMN, MECH ENGR DEPT WEST POINT, NY 10996	1
COMMANDER US ARMY ARRADCOM ATTN: DRDAR-LC -LCA (PLASTICS TECH EVAL CEN) -LCE -LCM -LCS -LCW -TSS (STINFO) DOVER, NJ 0780I	1 1 1 1 1 1 2	US ARMY MISSILE COMD REDSTONE SCIENTIFIC INFO CEN ATTN: DOCUMENTS SECT, BLDG 4484 REDSTONE ARSENAL, AL 35898 COMMANDER REDSTONE ARSENAL ATTN: DRSMI-RRS -RSM ALABAMA 35809	2 1 1
COMMANDER US ARMY ARRCOM ATTN: DRSAR-LEP-L ROCK ISLAND ARSENAL ROCK ISLAND, IL 61299	1	COMMANDER ROCK ISLAND ARSENAL ATTN: SARRI-ENM (MAT SCI DIV) ROCK ISLAND, IL 61202	1
DIRECTOR US ARMY BALLISTIC RESEARCH LABORATORY ATTN: DRDAR-TSB-S (STINFO) ABERDEEN PROVING GROUND, MD 21005	1	COMMANDER HQ, US ARMY AVN SCH ATTN: OFC OF THE LIBRARIAN FT RUCKER, ALABAMA 36362	1
COMMANDER US ARMY ELECTRONICS COMD ATTN: TECH LIB FT MONMOUTH, NJ 07703	1	COMMANDER US ARMY FGN SCIENCE & TECH CEN ATTN: DRXST-SD 220 7TH STREET, N.E. CHARLOTTESVILLE, VA 22901	1
COMMANDER US ARMY MOBILITY EQUIP R&D COMD ATTN: TECH LIB FT BELVOIR, VA 22060	1	COMMANDER US ARMY MATERIALS & MECHANICS RESEARCH CENTER ATTN: TECH LIB - DRXMR-PL WATERTOWN, MASS 02172	2

NOTE: PLEASE NOTIFY COMMANDER, ARRADCOM, ATTN: BENET WEAPONS LABORATORY,
DRDAR-LCB-TL, WATERVLIET ARSENAL, WATERVLIET, N.Y. 12189, OF ANY
REQUIRED CHANGES.

	NO. OF COPIES		NO. OF COPIES
COMMANDER US ARMY RESEARCH OFFICE. P.O. BOX 12211 RESEARCH TRIANGLE PARK, NC 27709	1	COMMANDER DEFENSE TECHNICAL INFO CENTER ATTN: DTIA-TCA CAMERON STATION ALEXANDRIA, VA 22314	12
COMMANDER US ARMY HARRY DIAMOND LAB ATTN: TECH LIB 2800 POWDER MILL ROAD ADELPHIA, ME 20783	1	METALS & CERAMICS INFO CEN BATTELLE COLUMBUS LAB 505 KING AVE COLUMBUS, OHIO 43201	1
DIRECTOR US ARMY INDUSTRIAL BASE ENG ACT ATTN: DRXPE-MT ROCK ISLAND, IL 61201	1	MECHANICAL PROPERTIES DATA CTR BATTELLE COLUMBUS LAB 505 KING AVE COLUMBUS, OHIO 43201	1
CHIEF, MATERIALS BRANCH US ARMY R&S GROUP, EUR BOX 65, FPO N.Y. 09510	1	MATERIEL SYSTEMS ANALYSIS ACTV ATTN: DRXSY-MP ABERDEEN PROVING GROUND MARYLAND 21005	1
COMMANDER NAVAL SURFACE WEAPONS CEN ATTN: CHIEF, MAT SCIENCE DIV DAHLGREN, VA 22448	1		
DIRECTOR US NAVAL RESEARCH LAB ATTN: DIR, MECH DIV CODE 26-27 (DOC LIB) WASHINGTON, D. C. 20375	1 1		
NASA SCIENTIFIC & TECH INFO FAC. P. O. BOX S757, ATTN: ACQ BR BALTIMORE/WASHINGTON INTL AIRPORT MARYLAND 21240	1		

NOTE: PLEASE NOTIFY COMMANDER, ARRADCOM, ATTN: BENET WEAPONS LABORATORY, DRDAR-LCB-TL, WATERVLIET ARSENAL, WATERVLIET, N.Y. 12189, OF ANY REQUIRED CHANGES.