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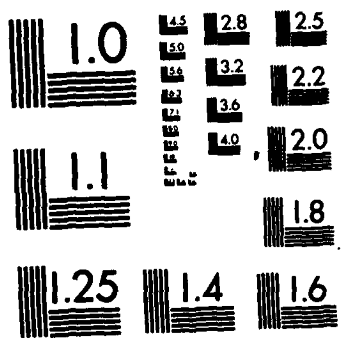

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TECHNICAL REPORT ARLCB-TR-83026

SUPERCONDUCTIVITY IN HYDROGEN-CHARGED ION-BEAM MIXED PALLADIUM COPPER ALLOY

W. SCHOLZ

A. LEIBERICH

W. J. STANDISH

C. G. HOMAN

JUNE 1983

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND

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Superconducting $Pd_xCu_{1-x}(H)$ has been made by ion-beam mixing and low-temperature electrolysis. A multi-layered sample consisting of alternate layers of Cu and Pd, sputter-deposited onto a Pd foil substrate, was bombarded with 125 KeV Xe^+ ions. Analysis by Rutherford backscattering (RBS) showed the formation of a $Pd_{.6}Cu_{.4}$ alloy region approximately 38 $\mu g/cm^2$ thick. After electrolytic charging with H at dry ice temperature, superconductivity was

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7. AUTHOR(S) (CONT'D)

*W. Scholz, A. Leiberich, and W. J. Standish
State University of New York at Albany
Albany, NY 12222

20. ABSTRACT (CONT'D)

observed, with a transition temperature, T_c, of 11.4 K in the alloy region. The effects of increased currents and changes in the H distribution due to annealing between 77 K and 85°C on the transition curves have been investigated. Transition curves produced in this fashion are broad with an onset of the superconducting transition as high as 14 K. The sample remains partially superconducting even after overnight anneal at room temperature. Electrolysis at room temperature also produces superconducting transitions with onsets as high as 17 K.

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INTRODUCTION

Superconductivity in homogeneous $Pd_xCu_{1-x}(H)$ has been observed by Stritzker[1] and by Baranowski and Skoskiewicz.[2] The two experiments differ in their method of hydrogen (H) insertion into the alloy and lead to results for the transition temperature (T_c) which are at variance with each other. In Stritzker's[1] experiment, H is implanted at liquid helium (He) temperatures into the alloy. T_c for the optimum H concentration first increases with increasing Cu concentration from the value of ~9 K for Pd-H[3] and reaches a maximum, $T_{c,max}$ = 16.6 K, for an alloy with the composition $Pd_{.55}Cu_{.45}(H)$. Further addition of Cu lowers T_c. Baranowski and Skoskiewicz[2] use high-pressure charging at 13 kbar with subsequent cooling to He temperatures without releasing pressure. Except for the lowest Cu concentrations their results show a monotonic decrease of T_c with increasing Cu content. $T_c \approx$ 0.6 K for $Pd_{.64}Cu_{.36}(H)$, the alloy with the maximum Cu concentration investigated. The discrepancy between the two experiments has been interpreted as being due to a decrease in H solubility in Pd-Cu alloys.[2] This is in line with the observation that the high H concentrations and the attendant high T_c's produced by implantation of H at liquid He temperatures are not stable in these alloys even at and below 77 K.[1]

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[1] Stritzker, B., "High Superconducting Transition Temperatures in the Palladium-Noble Metal-Hydrogen System," Z. Physik, 268 (1974), p. 261.

[2] Baranowski, B. and Skoskiewicz, T., High-Pressure and Low-Temperature Physics, (Chu, C. W. and Wollan, J. A., Eds.), Plenum Press, New York, 1978, p. 43.

[3] For a recent review, see Stritzker, B. and Wühl, H., Hydrogen in Metals, (Alefeld, G. and Völkl, J., Eds.), Springer, Berlin, 1978, p. 243.

In a recent experiment, Leiberich et al[4] have observed substantially increased T_c values as compared with pure Pd-H for an inhomogeneous Pd-Cu alloy formed by ion implantation of Cu into a Pd substrate and subsequent electrolytic charging at dry ice temperature. Superconductivity in such samples can be maintained for extended periods by keeping them at LN_2 temperature. Warming the samples above 77 K produces changes in T_c and the transition curves which can be correlated with changes in the H concentration in the Cu-implanted layer.[5]

In this report, we describe T_c measurements on an inhomogeneous Pd-Cu alloy formed by ion-beam mixing of alternating layers of Cu and Pd on a Pd substrate. The sample was charged with H by electrolysis at dry ice as well as at room temperature. The effects of annealing above 77 K and of high current densities have been studied.

EXPERIMENTAL METHOD

A multi-layered sample was prepared by sputtering of four alternate layers of Cu and Pd, each approximately 125 Å thick, onto a 38 μm thick Pd foil. Mixing of the layers was achieved by bombarding with 125 KeV Xe^+ ions to a dose of 1.6×10^{16} at./cm^2. The sample was analyzed before and after mixing by Rutherford backscattering (RBS) (Figure 1). The two spectra are

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[4]Leiberich, A., Scholz, W., Standish, W. J., and Homan, C. G., "Superconductivity in H-Charged Cu-Implanted Pd," Phys. Lett. 87A, 1981, p. 57.

[5]Standish, W. J., Leiberich, A., Scholz, W., and Homan, C. G., "Superconductivity and Hydrogen Depth Profiles in Electrolytically Charged Cu-Implanted Pd," International Symposium on the Electronic Structure and Properties of Hydrogen in Metals, 4-6 March 1982, Richmond, VA, in press.

lined up at the Pd edge. The detector resolution is insufficient to separate the two unmixed layers of Pd (channel 780-810) and Cu (channel 690-720) in curve a. The break near channel 835 in curve b is taken as the signature of the mixed layer. The RBS analysis indicated the formation of a $Pd_{.6}Cu_{.4}$ alloy region of approximately 38 $\mu g/cm^2$ thickness on top of the Pd substrate. The reduced thickness of the mixed alloy layer, compared with the total thickness of the alternating Cu and Pd layers as deposited, is due to sputtering by the Xe^+ ions. The sample was mounted with epoxy on a hollow plexiglas tube containing the thermocouple and the necessary electrical connections, and electrolytically charged with H at dry ice temperature as described previously.[4] The mixed region was facing away from the electrolyte. After completion of the T_c measurements, H was expelled from the sample by warming it up to 80°C. The identical sample was reelectrolyzed at room temperature in an aqueous solution of H_2SO_4 following which T_c measurements were performed again.

Superconducting transitions were measured using the four-probe dc resistance technique. Temperature control to about 0.5 K was achieved by means of a thermal link to the liquid He bath. The thermocouple mounted on the sample was calibrated at the superconducting transitions of Nb, Pb, and V. T_c for complete and partial superconducting transition is defined by the midpoint of the transition.

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[4]Leiberich, A., Scholz, W., Standish, W. J., and Homan, C. G., "Superconductivity in H-Charged Cu-Implanted Pd," Phys. Lett. 87A, 1981, p. 57.

RESULTS

Electrolysis at Dry Ice Temperature

Figure 2 shows transition temperature curves obtained following electrolysis at dry ice temperature. In curve 1 of Figure 2(a) the square and round symbols represent, respectively, measurements taken immediately after electrolysis and after overnight storage at 77 K. The measured T_c is 11.4 K with an onset of 14 K. Since in pure Pd(H) the maximum observed T_c is about 9 K, the elevated transition temperatures above 9 K must be due to the ion-beam mixed region. Thus, these data show that, as distinct from bulk alloys,[1] the elevated T_c's can be maintained at LN_2 temperatures for $Pd_xCu_{1-x}(H)$ layers formed on top of Pd(H).

Figure 2(a) shows the effect of increasing the sample current on the transition curves. Curves 1, 2, and 3 have been measured, respectively, with currents of 0.2, 0.5, and 1.0 A. There is a significant lowering of T_c with increasing current with an even more substantial change in onset temperature leading to a sharpening of the transition curves. The data imply considerable sample inhomogeneities. The highest T_c components appear to sustain the lowest total critical currents. The sharpening of the curves with increasing current would seem to indicate that the regions corresponding to the high T_c components are embedded in regions with lower T_c and occupy only a small region of the actual sample volume. Thus, critical current densities carried by these high T_c regions may be substantially higher than can be estimated

[1] Stritzker, B., "High Superconducting Transition Temperatures in the Palladium-Noble Metal-Hydrogen System," Z. Physik, 268 (1974), p. 261.

using the cross-section of the actual sample region that can be superconducting above 9 K, i.e., approximately 1 cm wide by 350 Å thick.

Figure 2(b) shows transition curves measured after letting the sample warm up to increasingly higher temperatures. The warm-up procedure involves removing the sample from contact with the liquid He bath until it reaches a specified temperature and quickly quenching it again to the He temperature range. Curves 4, 5, and 6 have been measured following warm-up to 113 K, 203 K, and room temperature, respectively. There is a decrease in T_c with each warm-up step but, as distinct from our previous experiment with a Cu-implanted Pd sample, this sample remains partially superconducting after warm-up to room temperature.

Figure 2(c) shows the transition temperature curve measured after overnight annealing of the sample at room temperature (curve 7). The partial superconducting transition temperature is still present. In fact, a slight increase in the onset temperature of the transition, from 8.3 to 9.5 K has taken place during the overnight annealing. Further warming the sample to 80°C to expel the H finally destroys superconductivity completely (curve 8). The loss of H is also reflected in the drop of normal state resistance between curves 7 and 8. The partial nature of the transition in curves 6 and 7 is believed to be caused by relatively large scale inhomogeneities of the sample. A nearly complete superconduction transition could be observed by selecting another pair of contacts, located at a different position on the sample, to perform the voltage reading.

Electrolysis at Room Temperature

After some additional experimentation and prior to this experiment, the sample was warmed up to 85°C. Figure 3(a) shows the resulting resistance curve indicating an initially non-superconducting sample. Following electrolysis at room temperature as described above, the transition curves shown in Figures 3(b) and (c) were measured using, respectively, currents of 70 mA and 500 mA. A partial superconducting transition is observed with an onset at about 15 K. Similarly, as shown in Figure 2(a), the onset temperature decreases with increasing current, again indicating sample inhomogeneities. Further electrolysis at room temperature actually leads to a decrease in the transition-temperature onset (Figure 3(d)). Finally, after overnight annealing at room temperature, a partial superconducting transition with an onset at about 17 K is observed.

Measurements of the sample resistance at room temperature during electrolysis indicate no change in bulk H concentration between Figures 3(c) and (d). The changes in normal state resistance observed at liquid He temperature for Figures 3(b) through (e) are believed to be due to H gradually reaching portions of the sample which are covered by epoxy and not in direct communication with the electrolyte. H-free portions of the sample can, because of their comparatively low resistivity at liquid He temperatures, effectively short the sample and thus substantially affect the measured normal state resistance. The resistance measurements also indicate that bulk H concentrations in the Pd substrate may not be useful in correlating and predicting the superconducting properties of such compound layered samples as the one described herein. More microscopic methods such as H-depth profiling may be required to arrive at a better understanding of such systems.[5]

DISCUSSION OF RESULTS AND CONCLUSIONS

The results presented here indicate that high T_c superconductivity in $Pd_xCu_{1-x}(H)$ can also be achieved by electrolytic charging of samples prepared by ion-beam mixing of alternating Pd and Cu layers on a Pd substrate. Unlike the case of ion implantation,[4] where the maximum Cu concentration obtainable is restricted due to sputtering, the full range of Cu concentrations is accessible by ion-beam mixing. The compound samples described here and in a previous letter,[4] wherein a Pd-Cu alloy layer is in contact with a stabilizing, H-bearing pure Pd region, exhibit high T_c superconductivity which can be maintained for extended periods at 77 K. In addition, in the present experiment, portions of the sample have been found to remain superconducting even after having been annealed at room temperature for several hours. Neither would be possible with the high T_c superconductors prepared by H implantation at liquid He temperatures into bulk Pd-Cu alloys. H will diffuse out from the narrow implant profile at 77 K and even below,[1] resulting in H concentrations which are too low for superconductivity.

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[1]Stritzker, B., "High Superconducting Transition Temperatures in the Palladium-Noble Metal-Hydrogen System," Z. Physik, 268 (1974), p. 261.

[4]Leiberich, A., Scholz, W., Standish, W. J., and Homan, C. G., "Superconductivity in H-Charged Cu-Implanted Pd," Phys. Lett. 87A, 1981, p. 57.

[5]Standish, W. J., Leiberich, A., Scholz, W., and Homan, C. G., "Superconductivity and Hydrogen Depth Profiles in Electrolytically Charged Cu-Implanted Pd," International Symposium on the Electronic Structure and Properties of Hydrogen in Metals, 4-6 March 1982, Richmond, VA, in press.

The transition curves observed in the present $Pd_xCu_{1-x}(H)$ on Pd(H) compound samples are typically rather broad, presumably reflecting uncontrolled inhomogeneities in the Cu as well as in the H-distribution. The superconducting properties are strongly affected by H mobility and cannot be easily correlated with bulk H concentrations in the Pd substrate as determined by methods such as resistivity measurements. More microscopic characterizations of these samples are desirable for the high T_c regions found here.

REFERENCES

1. Stritzker, B., "High Superconducting Transition Temperatures in the Palladium-Noble Metal-Hydrogen System," Z. Phy ik, 268 (1974), p. 261.

2. Baranowski, B. and Skoskiewicz, T., High-Pressure and Low-Temperature Physics, (Chu, C. W. and Wollan, J. A., Eds.), Plenum Press, New York, 1978, p. 43.

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5. Standish, W. J., Leiberich, A., Scholz, and Homan, C. G., "Superconductivity and Hydrogen Depth Profiles in Electrolytically Charged Cu-Implanted Pd," International Symposium on the Electronic Structure and Properties of Hydrogen in Metals, 4-6 March 1982, Richmond, VA, in press.

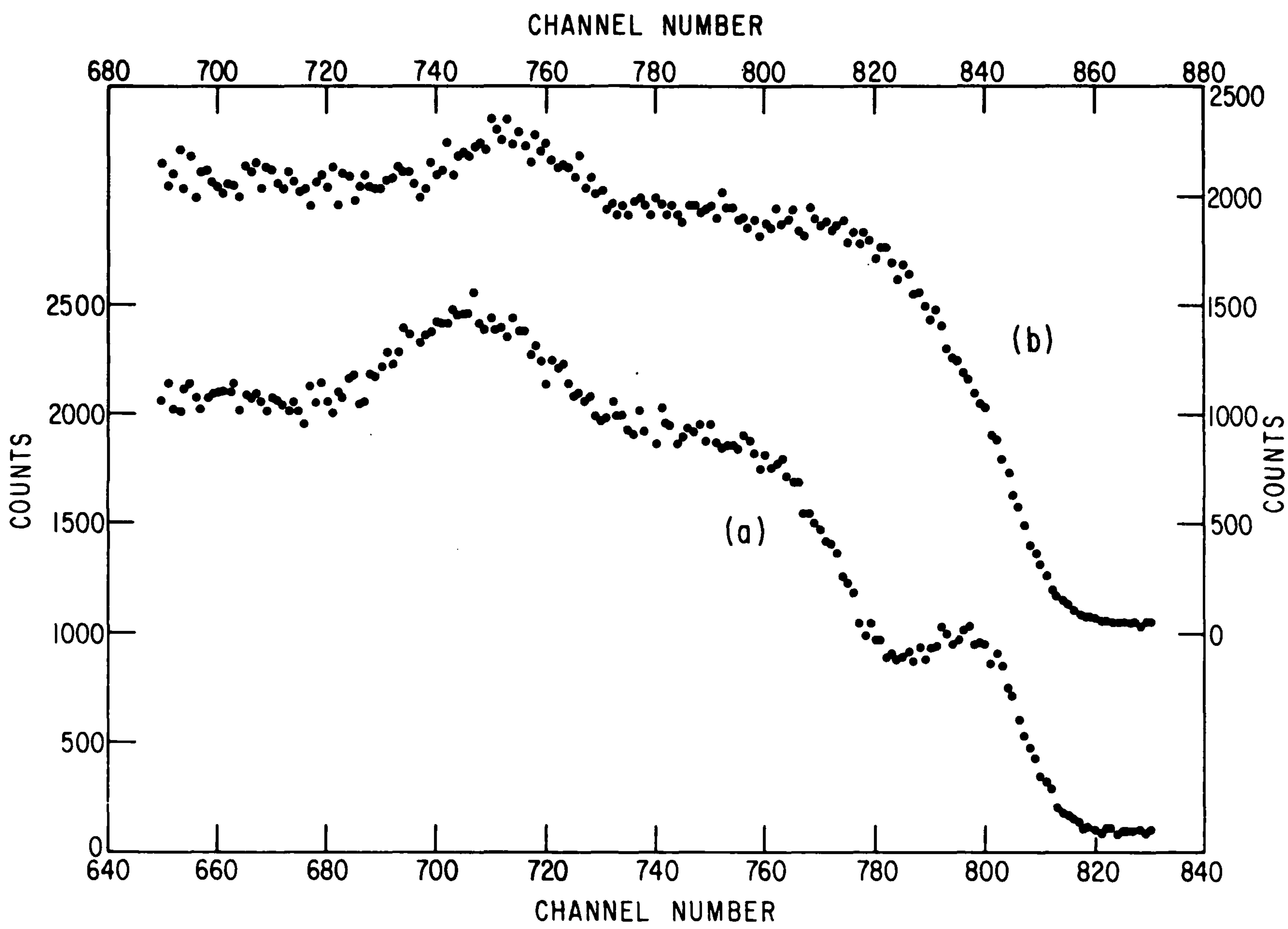

Fig. 1 Backscattering spectra of 2 MeV He^+ ions incident on a layered Pd and Cu sample on a Pd substrate before (a) and after (b) ion beam mixing with Xe^+ ions.

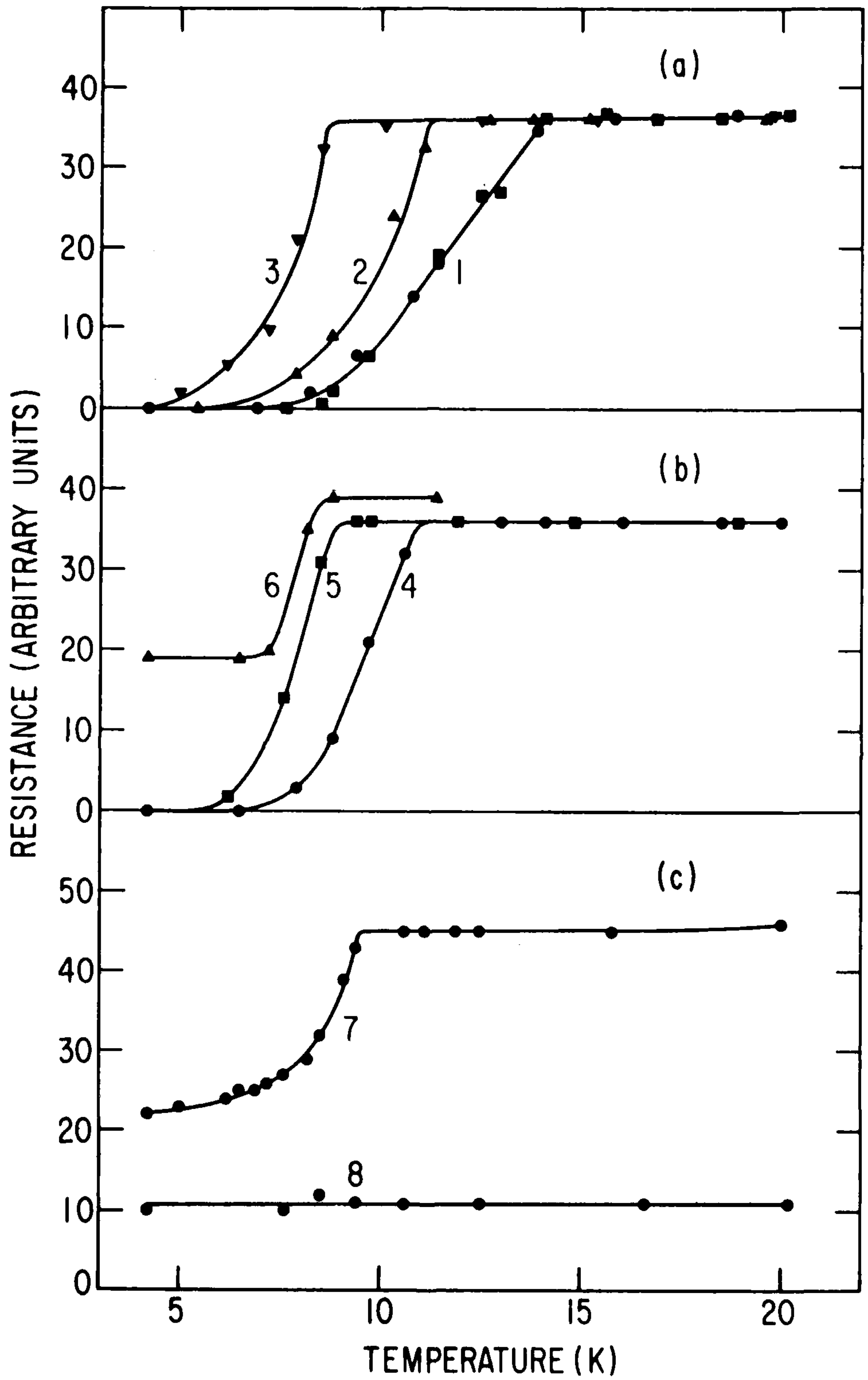

Fig. 2 Superconducting transition curves measured on a $Pd_{.6}Cu_{.4}$ ion beam mixed sample after electrolysis at dry ice temperature.

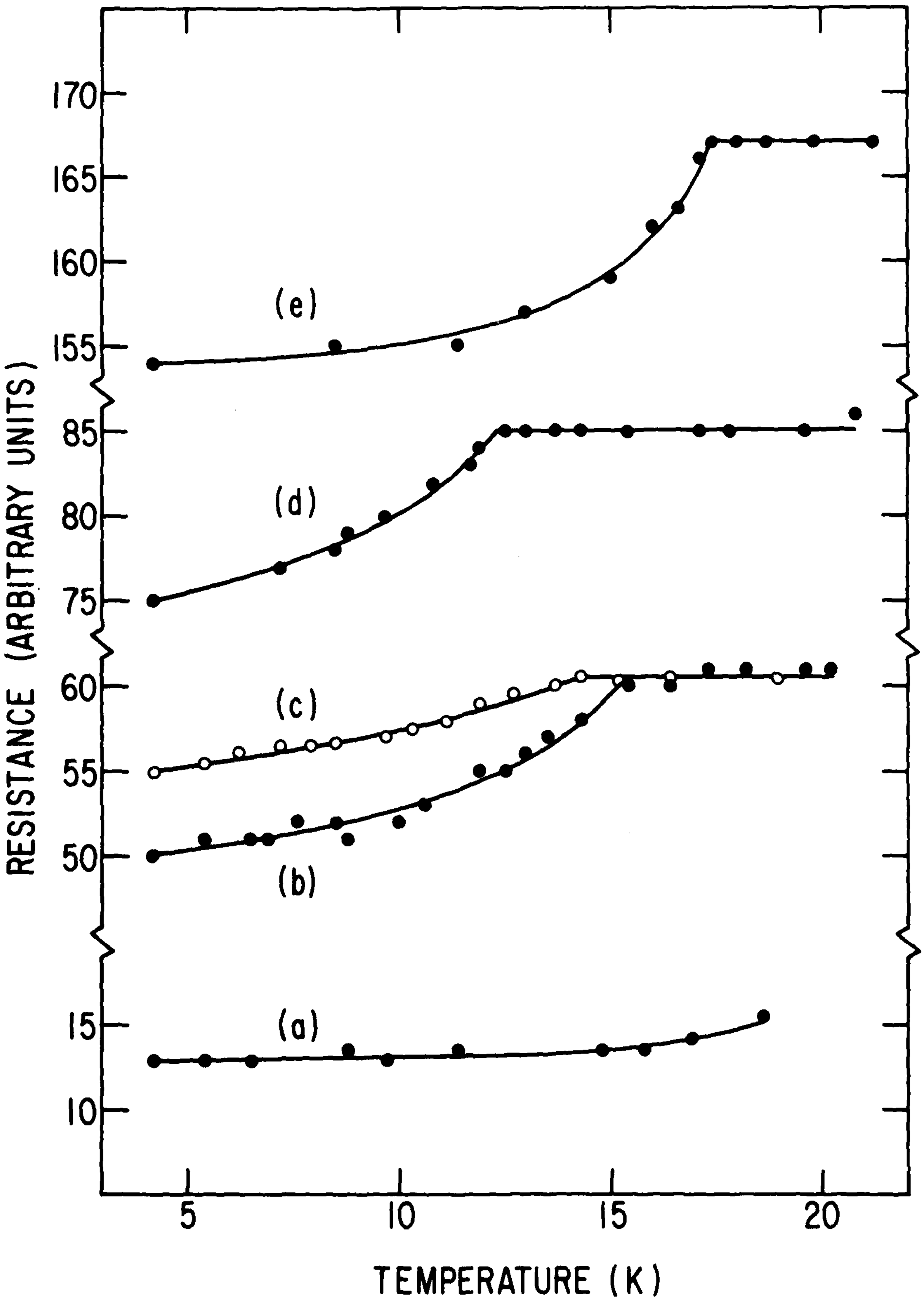

Fig. 3 Resistance curve (a) indicates an initial non-superconducting sample and superconducting transition curves (b) through (e) measured following room temperature electrolysis for the sample in Figure 2.

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