

Concentration dependence of the superconducting transition temperature in PdH_x and PdD_x[†]

J. E. Schirber and C. J. M. Northrup, Jr.

Sandia Laboratories, Albuquerque, New Mexico 87115

(Received 19 June 1974)

We have verified the existence of an inverse isotope effect between homogeneous bulk PdH_x and PdD_x. Maximum *x* values achieved by high-pressure charging were 0.99 and 0.97 for the hydride and deuteride, respectively. Our extrapolated values for the superconducting transition temperatures of PdH and PdD are 8 and 10 K, respectively.

There has been a great deal of interest recently in the superconductivity of the hydrides and deuterides of Pd and its alloys. An unexpected inverse isotope reported by Buckel and Stritzker¹ for hydrides and deuterides of Pd formed by ion implantation has been of particular concern. These investigators reported a maximum superconducting transition temperature *T_c* for PdH of ~ 9 K while an ~ 11-K transition was achieved for PdH under similar conditions.

There have been several attempts to explain this inverse isotope effect. Bennemann and Garland,² in explaining the isotope effect, discuss quenching of spin fluctuations by volume effects which predict a positive pressure derivative for *T_c*. Recent measurements^{3,4} have shown that *d*ln*T_c*/*dP* is negative for both PdH and PdD. Several groups^{5,6} have attempted to explain this isotope effect by softening of lattice modes, and Auluck⁷ has treated the Pd hydrides as alloys of metallic hydrogen.

Somewhat overlooked have been the following important questions with reference to the ion-implanted materials: (i) Is damage an important factor? (ii) Since the highly concentrated region is narrow, are thin-film-like effects important? (iii) Since it is not possible to directly measure the implantation levels in the sample, are the maximum *T_c* values at the same concentrations in PdD_x and PdH_x? In an effort to answer these questions, we have developed a high-pressure hydrogen system so that bulk samples of the hydrides and deuterides can be formed⁸ which are sufficiently large and homogeneous that accurate volumetric measurements of the hydrogen isotope concentration can be made.⁹ During the course of this investigation, several groups initiated studies on cathodically charged samples, which also help shed light on the above questions. These results will be compared with ours in our discussion.

The samples were nominal 99.999% Pd in the form of less than 425 mesh powder.¹⁰ No annealing or heat treatment was performed on the materials before hydriding.

The pressure system is similar to that described earlier¹¹ with the important distinction that all components in contact with the hydrogen are either Be-Cu or 316 stainless steel. This was accomplished by duplicating the valve stems in Be-Cu and lining the gas-oil separator with a ½-in. -wall Be-Cu sleeve. The hydriding procedure consisted of admitting H₂ or D₂ gas to the Be-Cu pressure vessel containing the Pd powder and increasing the pressure to the desired level of ≤ 5 kbar usually at room temperature. The sample was then cooled slowly (over the course of an hour) to 77 K by lowering it into a liquid-N₂ bath. For low-concentration samples (hydrogen pressures below 0.2 kbar) the samples were quenched to liquid-nitrogen temperatures. The pressure was then released and the H₂ or D₂ pumped out of the dead volume of the system (~ 0.5 cm³). The system was then sealed by closing a high-pressure valve at the top of the probe and maintained at liquid-nitrogen temperatures or below until measurements of the superconducting transition temperature *T_c* were completed.

The superconducting transition temperature was determined inductively using a General Radio inductance bridge. Temperatures were controlled in a heat-leak chamber and measured with a germanium-resistance thermometer. The temperature calibration was checked by measurement of *T_c* of high-purity Nb and Pb. Our *T_c* values agreed with the accepted values to within 10–20 mK.

The hydrogen concentration in the samples was determined using standard pressure-volume-temperature (*p-v-t*) techniques. The palladium hydride samples (641.8 and 779.3 mg) were dissociated by heating them to 200 °C and successively extracting aliquots of hydrogen. By adjusting the size of the calibrated gas volumes, all of the hydrogen could be removed in three to four extractions with the final overpressure being less than 2 Torr. Palladium deuteride has a higher dissociation pressure for a given temperature than the hydride and therefore it was only heated to 150 °C for a comparable extraction. The pressures were measured simultaneously with two transducers: (i) a Digigauge

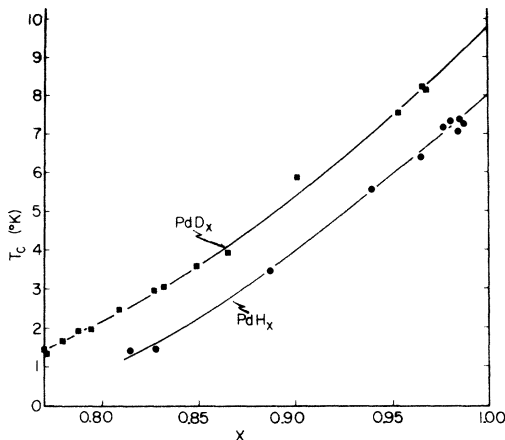


FIG. 1. Concentration dependence of T_c in PdH_x and PdD_x . We define x as the ratio of H or D to Pd.

(Ashcraft Industries; $0-2600 \pm 1.0$ Torr) and (ii) a Baratron (MKS Instruments Inc., $0-1000 \pm 0.5$ Torr). The calibrated vessel manifold contained seven vessels with volumes ranging from 3.8 liters to 25 cm^3 . The volumes of the glass vessels were determined by weighing with water. The volumes of the metal vessels and tubing were determined by expanding helium from the glass vessels. The uncertainty in the volume calibration was 0.1% or less. The calibration system was maintained in a circulating air bath and the temperature measured by four-lead platinum probes attached to the vessels. The uncertainty in the temperature was less than ± 0.1 °C. The hydrogen remaining in the sample after a normal p - v - t measurement was determined to be of the order of 2 ppm after the final run by using standard hot-gas extraction techniques. The overall uncertainty in the composition, x , is estimated to be ± 0.005 . The bulk of this uncertainty probably stems from poisoning of small amounts of the Pd because of impurities in the H_2 or D_2 picked up in the high-pressure charging process.

Our results for the concentration dependence of T_c for PdH_x and PdD_x are given in Fig. 1, where x is defined as the H or D ratio with respect to Pd. Three different Pd samples were employed. Two of them were charged alternately several times with D_2 and H_2 . The reproducibility was typically better than ± 0.03 K in T_c and ± 0.003 in x for identical charging conditions. One set of three successive deuteride runs was found to be systematically lower by over 0.02 in x . This was not repeatable and occurred after the sample had been exposed to air inadvertently. We assume that a small fraction of the Pd was not taking up hydrogen and that this condition corrected itself after a few hydriding cycles.

We see that there is a substantially higher T_c value for PdD_x than for PdH_x at a given value of x . Extrapolation of our results to $x=1$ gives a T_c value of about 10 K for PdD and 8 K for PdH. Skośkiewicz¹² has published T_c data on cathodically charged PdH_x up to values of x of about 0.92. Our results are in satisfactory agreement within his quoted uncertainty in x of ± 0.02 with the possible exception of his highest points ($T_c = 6.6$ K). His extrapolated value for T_c for PdH of 11 K is, however, considerably higher than ours.

We have defined our T_c values as the midpoint of the inductance change. Typical inductance versus temperature curves are reproduced in Fig. 2. This "average" value would seem to be most appropriate because we are measuring an average concentration. Buckel and Stritzker¹ used a point on their resistivity-versus-temperature curve very near the higher-temperature end of the transition. Since their transitions are quite wide (typically greater than 1 K), their values tend to be systematically higher. Our transitions are much narrower, ranging from 0.015 K at the high T_c values to 0.060 K in the lowest T_c region. The latter samples are formed by quenching from room temperature to liquid- N_2 temperatures. This is a region where T_c is a rapidly varying function of charging pressure, so we expect that this procedure might well result in a less homogeneous material and a broadened transition.

During the course of our investigation, studies of Pd hydrides and deuterides formed by cathodic charging at low temperatures were reported by Harper *et al.*¹³ and by Miller and Satterthwaite.¹⁴ These studies indicate, as do ours, that thin-film and radiation effects are not important factors in these materials. Based on the width of the superconducting transitions, our samples are considerably more homogeneous than those of Miller and Satterthwaite, but our results are probably in acceptable agreement as to the size of the isotope

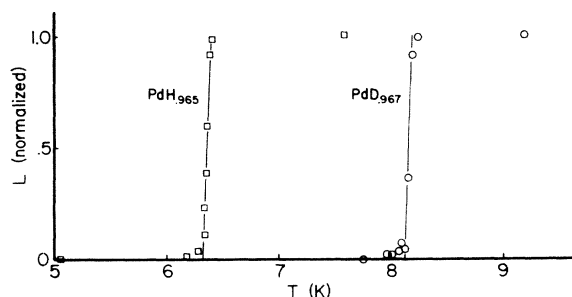


FIG. 2. Normalized susceptibility vs temperature for typical examples of PdH_x and PdD_x . The $\text{PdH}_{0.965}$ was formed and described in the text at a H_2 pressure of 44 800 lb/in.² while the $\text{PdD}_{0.967}$ required a D_2 pressure of 72 000 lb/in.²

effect in consideration of the entirely different preparation techniques and the combined experimental uncertainties involved.

We, therefore, conclude that the inverse isotope effect is indeed real in homogeneous bulk material and of the magnitude reported by Buckel and Stritzker. This indicates that damage and thin-film

effects play no important role as far as this aspect of superconductivity is concerned.

We acknowledge the expert technical assistance of R. P. Wemple and R. L. White and thank Dr. Miller and Professor Satterthwaite for discussions of their results prior to publication. We thank S. L. Erickson for the final hot-gas extraction.

†This work was supported by the U.S. Atomic Energy Commission.

¹W. Buckel and B. Stritzker, *Phys. Lett. A* **43**, 403 (1973).

²K. H. Bennemann and J. W. Garland, *Z. Phys.* **260**, 367 (1973).

³J. E. Schirber, *Phys. Lett. A* **46**, 285 (1973).

⁴W. Buckel, A. Eichler, and B. Stritzker, *Z. Phys.* **263**, 1 (1973).

⁵I. R. Gomersall and B. L. Gyorffy, *J. Phys. F* **3**, L138 (1973).

⁶B. N. Ganguly, *Z. Phys.* **265**, 433 (1973).

⁷S. Auluck, *Nuovo Cimento Lett.* **7**, 545 (1973).

⁸J. E. Schirber, *Phys. Lett. A* **45**, 141 (1973).

⁹Baranowski has reported on a system with which he can charge samples to ~ 25 kbar at room temperature [B. Baranowski, *Platinum Metals Rev.* **16**, 10 (1972)].

¹⁰Gallard Schlesinger Chemical Manufacturing Corp., Carle Place, New York.

¹¹J. E. Schirber, *Cryogenics* **10**, 418 (1970).

¹²T. Skoškiewicz, *Phys. Status Solidi* **59**, 329 (1973).

¹³J. M. E. Harper, R. Hammond, and T. H. Geballe, *Bull. Am. Phys. Soc.* **18**, 326 (1973); J. M. E. Harper, *Phys. Lett. A* **47**, 69 (1974).

¹⁴R. J. Miller and C. B. Satterthwaite, *Bull. Am. Phys. Soc.* **19**, 76 (1974), and private communication.