

# Lattice constants of $\beta$ -PdH<sub>x</sub> and $\beta$ -PdD<sub>x</sub> with $x$ near 1.0\*

J. E. Schirber and B. Morosin

Sandia Laboratories, Albuquerque, New Mexico 87115

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Lattice constants of the  $\beta$  phase of PdH<sub>x</sub> and PdD<sub>x</sub> for the concentration range  $0.8 < x < 0.98$  have been measured at 77 K using a powder x-ray diffraction technique. The lattice constant  $a_0$  of PdH<sub>x</sub> is slightly larger ( $\sim 0.1\%$ ) than that of PdD<sub>x</sub> and  $d \ln a_0 / dx = 0.044$  for both PdH<sub>x</sub> and PdD<sub>x</sub>; extrapolated  $a_0$  values for  $x = 1.0$  are 4.090 and 4.084 Å for PdH and PdD, respectively. This study shows that the inverse isotope effect in the superconducting transition temperature is not simply a result of the relative volume of PdH<sub>x</sub> and PdD<sub>x</sub>.

Recently, Schirber and Northrup<sup>1,2</sup> verified the existence of an inverse-isotope effect in the superconducting transition temperature  $T_c$  first reported by Buckel and Stritzker<sup>3</sup> for the hydrides and deuterides of Pd. They obtained homogeneous bulk samples with maximum values of  $x$  near 0.99 and 0.97 for PdH<sub>x</sub> and PdD<sub>x</sub> by high-pressure ( $\leq 5$  kbar) charging. Concentrations were determined to within an estimated uncertainty of  $\pm 0.005$  in  $x$  using standard pressure-volume-temperature techniques upon dissociation of the hydride or deuteride.

There have been a number of attempts to explain this inverse-isotope effect which are cited in Ref. 1. The experimental fact that  $T_c$  increases with volume when coupled with the reported values for the lattice constants of PdH<sub>x</sub> ( $x \sim 0.58$ ) and PdD<sub>x</sub> ( $x \sim 0.56$ ) of 4.025 and 4.027 Å, respectively, raises the possibility that the inverse-isotope effect could be explained simply on the basis of lattice spacing. (The above room-temperature lattice-parameter values are reported to be at the  $\alpha + \beta$ ,  $\beta$ -phase boundary; this phase boundary point is commonly referred to as  $\beta_{\min}$ .)

In order to investigate this possibility, we have prepared our powder x-ray specimens (standard 0.03-mm Lindemann capillaries were used) in exactly the same manner as in Ref. 1 and used the superconducting transition data to monitor the concentration both before and after the lattice-constant determination. The previous work<sup>1</sup> had shown that high- $x$ -value compositions could be quenched and retained at  $\leq 77$  K.

Liquid nitrogen was dripped directly upon the sample, contained within a paper cylinder ( $\sim 2$  mm) to ensure some retention of liquid nitrogen adjacent to the sample at all times. A horizontally mounted Norelco x-ray tube, a 118-mm powder camera, and copper  $K\alpha$  radiation ( $\lambda_{\alpha_1} = 1.54051$  Å) were employed throughout this study. All x-ray data showed considerable line broadening as reported by other investigators.<sup>4</sup> We have determined relative expansivity between room temperature and 77 K on samples stable at one or less atmosphere gas pressure; however, the precise concentration

( $x$  value) appears to be in question. Previous early x-ray measurements claimed  $\beta_{\min}$  values for the H to Pd ratio  $R_H$  as large as<sup>5</sup> 0.63 and<sup>6</sup> 0.77; however, 0.58 is the usually accepted value. More recent electrochemical measurements gave<sup>7</sup>  $R_H = 0.57$  and pressure-composition-temperature measurements gave  $R_H = 0.61$  (and<sup>8</sup>  $R_D = 0.60$ ) as the position of this phase boundary. Typically, pres-

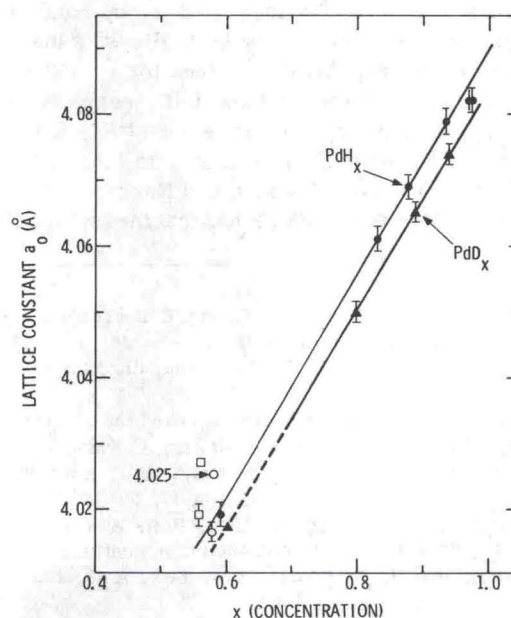


FIG. 1. Lattice constants versus concentration for  $\beta$ -PdH<sub>x</sub> and  $\beta$ -PdD<sub>x</sub> at 77 K. The upper line passes through values for  $\beta$ -PdH<sub>x</sub> while the lower line passes through those for  $\beta$ -PdD<sub>x</sub>. Previously accepted room-temperature  $\beta_{\min}$  values for PdD<sub>x</sub> and PdH<sub>x</sub> are shown as an open square and circle, respectively; the 77-K values were obtained by subtracting  $\Delta$  (see text) and are shown as an open square and circle with error limits similar to those we experienced in our measurements. Solid triangle gives our PdD<sub>x</sub> value (4.016 Å) at 77 K provided it would lie on the line extended from our higher  $x$  values. Our sample of PdH<sub>x</sub> prepared at 20-Torr pressure yielded  $a_0 = 4.028$  and 4.019 Å for room temperature and 77 K, respectively; this sample might contain at most 5% of the  $\alpha$  phase.



sure-composition isotherms at the  $\beta_{\min}$  boundary enter two-phase regions with some slope so that pressures slightly in excess of the correct one may produce one phase ( $\beta$ ) at an  $x$  value several hundredths higher than that precisely at the boundary. Furthermore, hysteresis is usually observed in such isotherms. For samples near  $\beta_{\min}$  which we report here, the preparation procedure subjected the Pd metal to an atmosphere pressure (near 620 Torr) of gas, the sample tube was then evacuated and then rehydridated at the desired pressure (all at room temperature). A 15-Torr-pressure hydrogen run produced only the  $\alpha$  lines, an 18-Torr run, which unfortunately leaked, both  $\alpha$  and  $\beta$ , and a 20-Torr run only the  $\beta$  phase. The difference  $\Delta$  between room temperature and 77 K on several samples measured near  $\beta_{\min}$  and on one preparation at 630-Torr pressure was 0.009 Å.

Our lattice-constant values are summarized in Fig. 1 together with the usually quoted  $\beta_{\min}$  values. The lattice constant  $a_0$  of  $\text{PdH}_x$  is slightly larger ( $\sim 0.1\%$ ) than that of  $\text{PdD}_x$ ; therefore, the inverse-isotope effect cannot be accounted for by relative volume considerations. For both alloys,  $d \ln a_0 / dx = 0.044$ . Extrapolated  $a_0$  values for  $x = 1.0$  are 4.090 and 4.084 Å for  $\text{PdH}$  and  $\text{PdD}$ , respectively. At the  $\beta_{\min}$  boundary, our data suggest  $R_D = 0.60$  rather than 0.56; such a value of  $x$  is in good agreement with data of Wicke and Nernst.<sup>8</sup>

Although this work establishes that the isotope effect

cannot be explained by the relative lattice constants of  $\text{PdH}_x$  and  $\text{PdD}_x$ , it is still of interest to determine how much of the increase in  $T_c$  in either of these materials is due to the increase in lattice parameter. This information will be needed in assessing any quantitative model for the superconductivity of these systems. If one assumes  $T_c$  is a function of  $x$  and  $V$  (volume) only, it is straightforward to express  $dT_c/dx$  in terms of the explicit volume and concentration contributions and  $|\partial \ln T_c / \partial \ln V|_x$ . If we assume the compressibility of these materials is near that of pure Pd,<sup>9</sup> we can, using our measured  $T_c$  versus  $x$ ,<sup>1</sup>  $d \ln T_c / dP$  versus  $x$ ,<sup>10</sup> and  $V$  versus  $x$  data, calculate the magnitude of the pure or explicit volume contribution to the variation of  $T_c$  with  $x$ . This contribution is  $\sim 13\%$  at  $x \approx 0.8$  and  $\sim 37\%$  at  $x \approx 1.0$  of the total change in  $T_c$  with  $x$ ,  $dT_c/dx$ . These  $x$  values are near the extremes of where we have data necessary to make the comparison. We have ignored slight differences in the derivatives between  $\text{PdD}_x$  and  $\text{PdH}_x$  in these considerations.

In summary, our determination of the lattice parameters of  $\text{PdH}_x$  and  $\text{PdD}_x$  as a function of  $x$  shows that the inverse-isotope effect *cannot* be explained on the basis of the relative sizes of the  $\text{PdH}_x$  and  $\text{PdD}_x$  lattices. Furthermore, we can make a quantitative estimate of the magnitude of the pure-volume contribution to the concentration dependence of  $T_c$  in  $\text{PdH}_x$  and  $\text{PdD}_x$ .

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<sup>2</sup>Several other investigators have verified the inverse-isotope effect: T. Skoskiewicz *et al.*, J. Phys. C **7**, 2670 (1974); J. M. E. Harper *et al.*, Bull. Am. Phys. Soc. **18**, 326 (1973); Phys. Lett. A **47**, 69 (1974); R. J. Miller and C. B. Satterthwaite, Bull. Am. Phys. Soc. **19**, 76 (1974); and private communication.

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<sup>4</sup>F. A. Lewis, *The Palladium Hydrogen System* (Academic, New York, 1967).

<sup>5</sup>J. O. Linde and G. Borelius, Ann. Phys. **84**, 747 (1927).

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<sup>7</sup>T. B. Flanagan and F. A. Lewis, Trans. Faraday Soc. **55**, 1409 (1959).

<sup>8</sup>E. Wicke and G. H. Nernst, Ber. Bunsenges. Phys. Chem. **68**, 224 (1964); also Ref. 4, p. 123.

<sup>9</sup>No compressibility or elastic-constant data are available for  $\text{PdH}_x$  or  $\text{PdD}_x$ , but Macklait and Schindler [Phys. Rev. **146**, 463 (1966)], find essentially the same Debye  $\Theta$  values as for pure Pd.

<sup>10</sup>J. E. Schirber, Phys. Lett. A **46**, 285 (1973).