

Debye–Waller factors of PdD_x materials by neutron powder diffraction*

A. C. Lawson, J. W. Conant, R. Robertson, R. K. Rohwer, V. A. Young
and C. L. Talcott

Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)

(Received June 27, 1991)

Abstract

We have completed a neutron powder diffraction study of four PdD_x materials: palladium metal, α-PdD_x and two samples of β-PdD_{0.6}. We measured the lattice constants and Debye–Waller factors at several temperatures between 15 and 300 K. This information was analyzed to yield thermal expansion data and atom-specific Debye temperatures for each of the samples. We were unable to locate the deuterium atoms in α-PdD_x.

1. Introduction

The palladium–hydrogen phase diagram [1, 2] is characterized by a very high solubility of hydrogen that extends out past H:Pd = 0.9. The high solubility means that palladium and its alloys are important materials for hydrogen technology. We have studied the Pd–D system, but we use the word “hydrogen” to refer generally to either protium (¹H) or deuterium (²H). Throughout this paper we denote the variable D:Pd ratio by the subscript *x*.

Like palladium metal, the solid solution has an f.c.c. structure. At temperatures below 600 K a miscibility gap develops in the system and the α- and β-PdD_x phases are distinct. The α phase is the phase of low hydrogen solubility, below *x* = 0.05 at room temperature [2]. Because of the low hydrogen concentration, the positions of the hydrogen atoms in the lattice have never been experimentally determined. The β phase is the phase of much higher hydrogen content, with 0.6 < *x* < 0.9. In this phase the hydrogen atoms randomly occupy vacant octahedral sites in the f.c.c. palladium structure. There is a phase transition in the β phase at 50 K; below this temperature there is some occupation of the vacant tetrahedral sites in the structure. However, the kinetics of this transition are very sluggish and many days are required to complete the transformation [3–5].

Very precise structural information can be obtained from neutron powder diffraction data by use of the Rietveld analysis method [6]. If the data are taken at a pulsed neutron source, reflections of very low *d*-spacing (about

*This paper is dedicated with respect and affection to Dr. Ch. J. Raub on the occasion of his 60th birthday.

0.4 Å) can be observed. Then the mean-square thermal displacements of the atoms can be measured via the Debye–Waller factors [7]. The temperature dependence of the thermal displacements can be used to determine atom-specific Debye–Waller temperatures (θ) which are in turn related to the elastic constants of the material. The symbol θ refers to essentially atomic bulk moduli (spring constants) expressed in temperature units. We undertook the present experiments to make such measurements for palladium and deuterium in β -PdD_x. Measurements on palladium metal and on α -PdD_x were also made for comparison.

2. Experimental procedure

We prepared palladium deuteride powder samples by cleaning and loading palladium powder with deuterium gas. (Deuterium was used in order to avoid the incoherent neutron-scattering characteristic of protium.) The palladium powder was of nominal purity 99.9% from Engelhard Corporation, except for one of the β samples which was prepared from Metz palladium black. Approximately 5 g of palladium powder was loaded into the vanadium diffraction sample container. It was cleaned by heating it to 150 °C in vacuum and then submitted to three deuterium flushes. Each flush consisted of bringing the sample at 150 °C to 600 Torr of deuterium followed by evacuation to less than 30 mTorr. After the flushes the sample was pumped below 10^{-6} Torr. Once the samples were clean, the α -PdD_x sample was loaded to 300 Torr of deuterium at room temperature. The β -PdD_x samples were loaded to 2100 Torr of deuterium at room temperature, giving samples completely in the β phase.

We made neutron diffraction studies using the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. We studied four samples: pure palladium metal, α -PdD_x and two samples of β -PdD_x. Of the two β samples, the one designated “Metz” was prepared from palladium black of very fine particle size. The deuterated samples were measured in sealed vanadium sample holders designed to hold the required pressure of deuterium gas at room temperature. Each sample was cooled from room temperature to 15 K during an interval of about 3 h. Measurements were made on warming at six or seven temperatures between 15 and 305 K. Approximately 2 h were spent at each temperature for the measurement and another 1 h was allowed for heating to the next temperature. Temperatures were controlled automatically to ± 1 K. However, the highest actual temperature in some of the temperature series (about 300 K) was sometimes several degrees lower than the measured temperature. This occurred because helium gas was admitted to the vacuum chamber in an ill-conceived effort to conserve beam time at the end of a series.

Lattice constants, deuterium fractions, microstrains, particle sizes [8] and thermal factors were determined at each temperature by Rietveld re-

finement using the General Structure Analysis System (GSAS) of Larson and Von Dreele [9]. Debye–Waller temperatures [7] were determined from the refined parameters using previously described procedures.

3. Results and discussion

The palladium metal, α -PdD_x and β -PdD_x phases were found as expected. We tried to locate deuterium in both the octahedral and tetrahedral positions of α -PdD_x at both 15 and 305 K. In every case the refined atom fraction was 0.001(1), indicating that the deuterium content of the α phase is below the limit of detectability of our diffraction technique. This result is in disagreement with the nominal α phase concentration of 0.05 (α_{\max}) that is usually given [2] for room temperature. Nelin [10] was able to demonstrate octahedral occupancy for the α phase, but only for samples above room temperature where the equilibrium hydrogen concentration is much higher. Further work is required on this point.

The refined deuterium occupancy of the octahedral sites of the β phase had a random variation with temperature of a few per cent. We subsequently held x constant at the values shown in Table 1 for the final refinements. We also tried to detect the presence of deuterium in the tetrahedral interstices as a test for the occurrence of the low temperature phase transition. Again the refined fraction was 0.001(1), indicating that no appreciable transition had occurred. The latter result is not surprising given the rapidity of cooling below 50 K in our experiments.

The lattice constants are shown in Figs. 1 and 2. As shown in Table 1, the overall discrepancy in lattice constants for the two β samples is associated with their different deuterium fractions. The interpolated 77 K lattice constants of these samples are in good agreement with those reported by Schirber and Morosin [11]. Also, the thermal expansion coefficients of the two β samples are in good agreement with each other except near room temperature. The lattice constants for palladium metal and α -PdD_x are nearly identical. The 250 K point for α -PdD_x is about 0.001 Å higher than that of the metal, in agreement with earlier work at room temperature. Unfortunately, our 305 K point is unreliable, as mentioned. However, the curves do appear to cross one another at 200 K, where we experienced no difficulty with temperature

TABLE 1
Refined parameters for PdD_x samples

Sample	θ_{Pd} (K)	θ_{D} (K)	Strain (%)	P (Å)
Pd metal	324(2)	—	0.57(1)	—
α -PdD _x	329(3)	—	0.48(1)	—
β -PdD _{0.66}	302(2)	849(5)	0.75(2)	—
β -PdD _{0.60} (Metz)	296(4)	861(9)	0.61(4)	99(1)

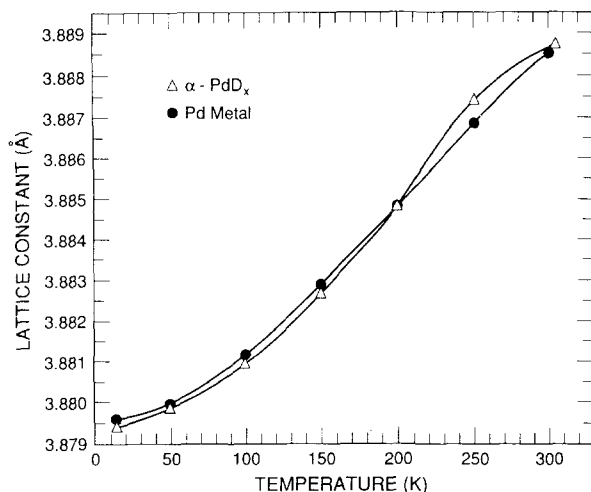


Fig. 1. Lattice constants of palladium metal and α -PdD_x vs. temperature. The errors on the measured lattice constants are smaller than the plotted points, but the highest temperature is subject to some error, as described in the text.

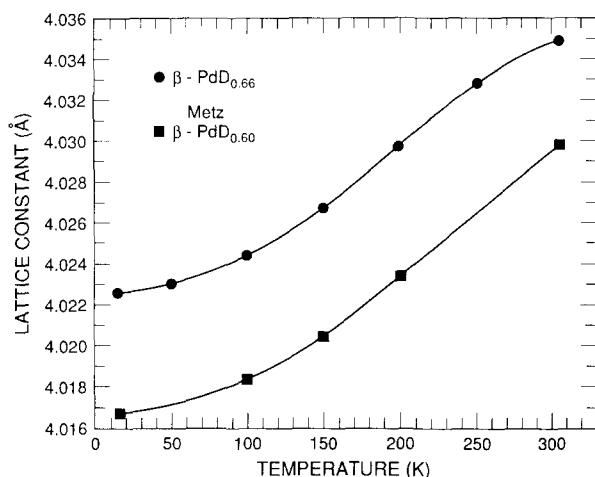


Fig. 2. Lattice constants of two samples of β -PdD_{0.60} vs. temperature. The sample designated "Metz" has a small particle size of approximately 100 Å. The errors on the measured lattice constants are smaller than the plotted points, but the highest temperature is subject to some error, as described in the text.

control. We do not know the origin of this cross-over effect, but it is what might be expected if α -PdD_x were to disproportionate below 200 K. Further work on the thermal expansion of the α phase is required.

Debye-Waller curves are shown in Figs. 3 and 4. The Debye-Waller temperatures (θ) derived from these data are shown in Table 1. Our results for palladium metal and for α -PdD_x are in close numerical agreement, just as would be expected for similar materials. The numerical value for θ is

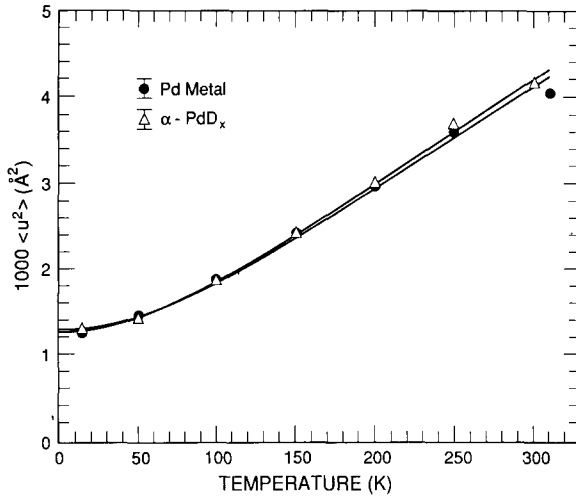


Fig. 3. Mean-square atomic displacement vs. temperature for palladium metal and α -PdD_x. The error bars are shown in the legend. The fitted curve is a simple Debye model with an additive constant term.

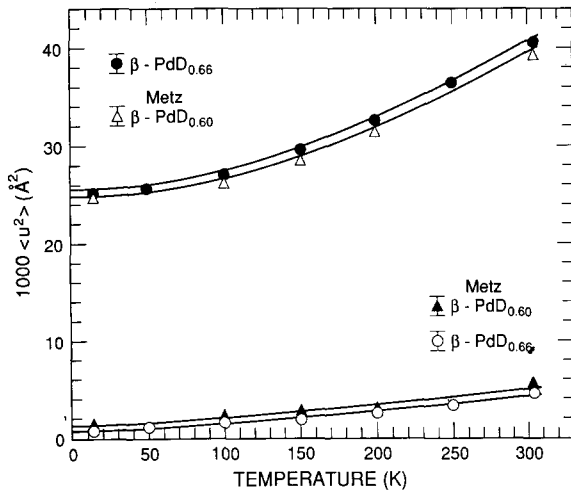


Fig. 4. Mean-square atomic displacement vs. temperature for two samples of β -PdD_{0.60}. The sample designated "Metz" has a small particle size of approximately 100 Å. The error bars are shown in the legend. The fitted curve is a simple Debye model with an additive constant term.

about 16% higher than the published heat capacity values for palladium metal [12, 13]. This is the largest discrepancy between heat capacity and Debye–Waller temperatures that we have so far observed. However, the diffraction value reported by Nelin [10] does agree with our result. The agreement between the θ values for the two β samples is also quite good, despite their distinctly different particle sizes (P) and slightly different

compositions. As expected from the different masses, θ_D is much higher than θ_{Pd} . However, the numerical ratio $\theta_D/\theta_{Pd}=2.83$ is much smaller than that expected from a simple model based on truly independent sublattices of palladium and deuterium, *i.e.* $(M_{Pd}/M_D)^{1/2}=7.29$. This is an indication that the model based on independent atoms (Einstein model) is inappropriate for β -PdD_x. Our value for θ_{Pd} is about 50% higher than the mass-average values reported for β -PdH_x by Ferguson *et al.* [5] and Nelin [10]. These were obtained by thermal analysis and neutron diffraction respectively.

4. Conclusions

Neutron diffraction experiments were performed on palladium metal and α - and β -PdD_x. We found some indication of an anomaly in the thermal expansion of α -PdD_x, but this point requires further investigation. We were unable to locate the deuterium in α -PdD_x. Debye–Waller temperatures were determined for all the materials, including atom-specific values of θ for β -PdD_x.

Acknowledgments

This work was supported under the auspices of the United States Department of Energy. The Manuel Lujan, Jr., Neutron Scattering Center is a national user facility funded by the United States Department of Energy, Office of Basic Energy Science. We are indebted to J. J. Ross and R. O. Nelson for their help with the data acquisition computer system and to J. A. Goldstone and D. E. Peterson for a careful reading of the manuscript.

References

- 1 B. Siegel and G. G. Libowitz, The covalent hydrides and hydrides of the groups V to VIII transition metals, in W. M. Mueller, J. P. Blackledge and G. G. Libowitz (eds.), *Metal Hydrides*, Academic, New York, 1968, pp. 545–674.
- 2 F. A. Lewis, *The Palladium Hydrogen System*, Academic, London, 1967.
- 3 T. E. Ellis, C. B. Satterthwaite, M. H. Mueller and T. O. Brun, *Phys. Rev. Lett.*, **42** (1979) 456.
- 4 J. S. Anderson, C. J. Carlile and D. J. Ross, *J. Phys. C: Solid State Phys.*, **11** (1978) L381.
- 5 G. A. Ferguson Jr., A. I. Schindler, T. Tanaka and T. Morita, *Phys. Rev.*, **137** (1965) A483.
- 6 R. B. Von Dreele, Neutron powder diffraction, in D. L. Bish and J. E. Post (eds.), *Reviews in Mineralogy*, Vol. 20, *Modern Powder Diffraction*, Mineralogical Society of America, Washington, DC, 1989, pp. 333–369.
- 7 A. C. Lawson, A. Williams, J. A. Goldstone, D. T. Eash, R. J. Martinez, J. I. Archuleta, D. J. Martinez, B. Cort and M. F. Stevens, *J. Less-Common Met.*, **167** (1991) 353.
- 8 A. C. Lawson, J. W. Conant, C. L. Talcott, M. A. David, J. Vaninetti, J. A. Goldstone, A. Williams, R. B. Roof, R. B. Von Dreele, R. L. Hitterman, J. W. Richardson Jr. and J. Faber Jr., Strain and particle size of palladium metal powders by time-of-flight neutron diffraction,

- in C. S. Barrett *et al.* (eds.), *Advances in X-ray Analysis*, Vol. 33, Plenum, New York, 1990, p. 403.
- 9 A. C. Larson and R. B. Von Dreele, General Structure Analysis System, *LAUR 86-748*, 1986 (Los Alamos National Laboratory).
 - 10 G. Nelin, *Phys. Status Solidi B*, 45 (1971) 527.
 - 11 J. E. Schirber and B. Morosin, *Phys. Rev. B*, 12 (1975) 117.
 - 12 K. A. Gschneidner Jr., Physical properties and interrelationships of metallic and semimetallic elements, in F. Seitz and D. Turnbull (eds.), *Solid State Physics*, Vol. 16, Academic, New York, 1964, p. 300.
 - 13 C. Kittel, *Introduction to Solid State Physics*, Wiley, New York, 4th edn., 1971, p. 219.