

Dynamics of dilute H in  $\beta$ -phase palladium deuteride: A novel mass defect

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We present a neutron scattering study of the vibrations of a light-atom defect which, in contrast with earlier studies, is both *chemically identical to* and half the mass of its heavy-atom host, namely, 3.7 at. % H in  $\beta$ -palladium deuteride. We observe a large shift in hydrogen vibration modes from those in  $\beta$ -PdH, which is in close agreement with the local-mode frequency predicted for an isolated mass defect and provides a prototype example for such a system.

It has been known for over half a century<sup>1,2</sup> that light- or heavy-atom mass defects substituted in an otherwise perfect crystal destroy the translational symmetry of the system and at the same time strongly interact with the host medium. This interaction produces either in-band or local-vibrational modes which can be shifted significantly from the lattice vibrations of the host, and greatly change the local properties, and in some cases, the bulk properties of the solid. The theory for the local vibration of an isolated light-atom mass defect in such a system predicts a frequency  $\omega_l$  of the local mode as follows:<sup>3</sup>

$$\int \frac{g(\omega)d\omega}{\omega_l^2 - \omega^2} = \frac{1}{\epsilon\omega_l^2}, \quad (1)$$

where  $g(\omega)$  is the density of states of the host crystal  $\int g(\omega)d\omega = 1$ ,  $\epsilon = M_h - M_l/M_l$ , and  $M_{l(h)}$  is the mass of the defect (host) atom.

Almost all previous studies in simple crystals,<sup>4</sup> including a variety of work in alloys, semiconductors, and inorganic crystals, have involved the substitution of impurity atoms (or ions), which are light or heavy with respect to the mass of the host. This almost always requires the insertion of chemically or electronically different atoms in the crystal, which introduces a local electronic perturbation along with the dynamical perturbation due to dissimilar masses, and thus does not allow a direct comparison with the simple theory. In a number of cases, local electronic effects have been small, and good agreement with mass-defect theory was obtained.

In this Rapid Communication we describe the first neutron scattering study of the local vibration of a light-atom defect which is both *chemically identical to* and half the mass of its heavy-atom host, namely, hydrogen in the  $\beta$  phase of palladium deuteride. The results of this study show a large change in hydrogen vibration modes from those measured in the hydride, which is in close agreement with the local-mode behavior predicted for an isolated mass defect, and, in fact, provides a prototype example for such a model system.

A mixed-phase sample of palladium and palladium deuteride was prepared by loading 300 g of Pd sheets (nominal purity 99.999%) with deuterium from the gas phase to a stoichiometry of PdD<sub>0.125</sub>. The sample was maintained at 120°C for several hours to assure that equilibrium was achieved. At 300 K, such a deuterium concentration pro-

vides a specimen in which 90% of the deuterium is presented as  $\beta$ -phase PdD<sub>0.6</sub> and 10% dissolved in the  $\alpha$ -phase Pd. At 80 K, essentially all of the deuterium is present as  $\beta$ -phase palladium deuteride. After neutron spectra were measured for the deuteride, the sample was loaded with enough hydrogen to provide a sample with 3.7 at. % H (stoichiometry PdD<sub>0.125</sub>H<sub>0.005</sub>). The sample was allowed to equilibrate overnight to assure random distribution of the hydrogen "defects" in the palladium-deuteride matrix.

Neutron spectra were measured at 80 and 295 K on the pure Pd, PdD<sub>0.125</sub>, and PdD<sub>0.125</sub>H<sub>0.005</sub> samples at the BT-4 triple-axis spectrometer at the NBS reactor, using a well-shielded Be filter as analyzer to provide spectra with a high signal and low fast-neutron background. Collimation was 40 min before and after the monochromator, providing an energy resolution between 5 and 7 meV over the energy range scanned. Difference spectra obtained by suitable subtraction of these results directly reflect the density of states of either  $\beta$ -phase PdD<sub>0.6</sub> or of the H defects randomly distributed in the  $\beta$ -phase region.

The neutron spectra measured at 80 K for the  $\beta$ -palladium deuteride and for the same deuteride sample doped with 3.7 at. % H are shown in Fig. 1. A comparison of these results shows that while the deuteride density of vibrational states is unaffected by the hydrogen defects, a strong additional peak is observed around 70 meV in the spectrum of the H-doped sample. This peak is far displaced from the density-of-states peak of  $\beta$ -PdH<sub>0.6</sub>, and is even higher in energy than that observed for dilute interstitial hydrogen in  $\alpha$ -phase palladium.<sup>5</sup> When the two spectra in Fig. 1 are subtracted to reveal the dynamics of the hydrogen defects, a single peak is obtained, as shown in Fig. 2. This peak must arise from the local vibrations of hydrogen mass defects randomly distributed among chemically identical deuterium atoms in the cubic (NaCl)  $\beta$ -palladium deuteride structure. The width of the observed peak is about twice the experimental resolution, as a result of both the fact that the H defects are not infinitely dilute (about one out of three H atoms has a hydrogen among its nearest-neighbor deuterium atoms) and anharmonicity. There is also evidence of shoulders on either side of the peak associated with multiphonon scattering. Still, the clear implication of these results is that the 71 meV peak is due to a novel mass-defect mode, displaced to an energy above the second

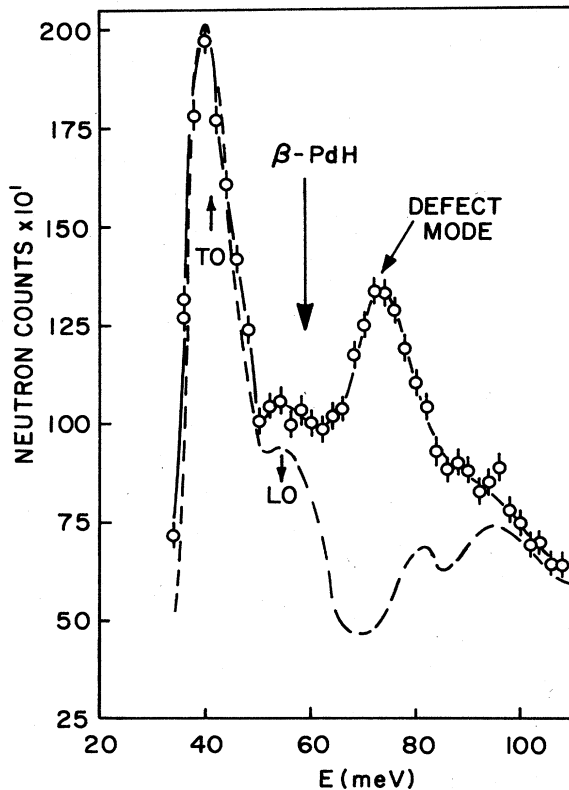


FIG. 1. Neutron-energy loss spectrum for  $\beta$ -palladium deuteride containing 3.7 at. % H. The spectrum measured for the deuteride before introducing the H defects is also shown as a dashed line. The position of the dominant density-of-states peak for  $\beta$ -PdH<sub>0.6</sub> is also indicated.

optical density-of-states peak in PdD which overlaps the normal lower-optical vibrational peak for palladium hydride (see Fig. 1).

As discussed in Refs. 1–3, the hydrogen defect cannot by symmetry vibrate with a frequency and wave vector corresponding to the longitudinal optic modes of the PdD host and therefore must be shifted beyond the edge of the associated density-of-states peaks (Fig. 1). Using the simple theory for the local vibrations of a light-atom mass defect in

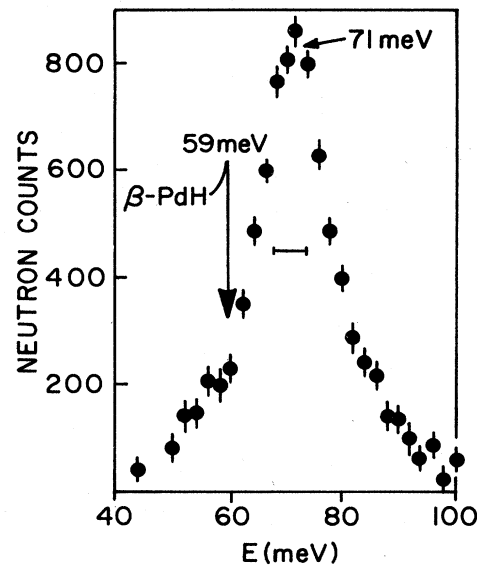


FIG. 2. Neutron spectrum for the 3.7 at. % H mass defects in palladium deuteride. The energy resolution full width at half maximum (FWHM) is also indicated.

such a system [Eq. (1)], we have calculated the energy of the expected local-mode peak, using the measured deuteride density of states shown in Fig. 2. From this expression we obtain a predicted local-mode energy of 70.5 meV, which is in excellent agreement with the measured value of 71 ( $\pm 1$ ) meV. Thus, as would be expected for an isotropic impurity, the simple mass-defect theory is sufficient to describe the present results, aside from the width of the local-mode peak which is likely a result of anharmonicity and/or the fact that the defects are not truly “isolated.”

In summary, the results on this metal-deuteride mass-defect system are a direct demonstration of the strong vibrational mode shifts resulting from a large defect-host mass ratio, without the complications associated with force constant or other chemical changes. It should be noted that the large change in vibration energies produced by defects in such a metal-hydrogen system will have a dramatic effect on thermodynamic and other properties which are directly related to the lattice dynamics.

<sup>1</sup>Lord Raleigh, *Theory of Sound* (Dover, New York, 1945), Vol. I.

<sup>2</sup>A. A. Maradudin, E. W. Montroll, and G. H. Weis, *Theory of Lattice Dynamics in the Harmonic Approximation*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Chap. V.

<sup>3</sup>R. J. Elliot and A. A. Maradudin, in *Inelastic Scattering of Neutrons*

(IAEA, Vienna, 1965), Vol. I, p. 231.

<sup>4</sup>See, e.g., D. W. Taylor, in *Dynamics of Impurities in Crystals*, edited by G. K. Horton and A. A. Maradudin (North-Holland/American Elsevier, New York, 1975), Chap. 5.

<sup>5</sup>J. J. Rush, J. M. Rowe, and D. Richter, *Z. Phys. B* 55, 283 (1984).