

## "In-Band" Modes of Vibration of PdH<sub>0.03</sub><sup>†</sup>

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The [110] transverse branch of the phonon dispersion relation in a single crystal of PdH<sub>0.03</sub> has been measured and compared to the results for pure Pd. A limited amount of data has been taken for other branches, and the mean frequency ratio (PdH<sub>0.03</sub>/Pd) observed for all measurements is 0.995. No change was observed in the shape or strength of the anomaly in the [110]T<sub>1</sub> branch.

### I. INTRODUCTION

In a recent letter,<sup>1</sup> results of a neutron scattering study of diffusion of hydrogen in a single crystal of palladium were presented. In the present work we have extended the study of this crystal to include a limited comparison of the "in-band" normal modes of the PdH<sub>0.03</sub> crystal to the modes of pure palladium. Measurements of the lattice dynamics of Pd<sup>2,3</sup> and Pt<sup>4</sup> by other authors have shown the existence of a broad anomaly in one transverse branch (called the T<sub>1</sub> branch) of the dispersion relation in the [110] direction. This anomaly has been attributed<sup>4</sup> by these authors to a large number of Kohn anomalies<sup>5</sup> arising from various portions of the Fermi surface of these metals. Recent calculations<sup>6</sup> of the effects of hydrogen on the band structure of Pd, have suggested, that, contrary to previous speculation, the rigid-band model for the effects of adding hydrogen to Pd is not a good approximation. Thus, although no calculations have been done for the present concentrations, one could expect that small amounts of hydrogen added to Pd might cause significant changes in the Fermi surface. For this reason, assuming the proposed explanation of the anomalous behavior of the [110] branch to be correct, it seemed desirable to study the PdH<sub>0.03</sub> lattice vibrations and to compare the results with those for pure Pd, with particular emphasis on the [110]T<sub>1</sub> branch.

### II. EXPERIMENTAL DETAILS

The specimen used in these measurements was the same single crystal used in the earlier diffusion studies.<sup>1</sup> After the measurements were completed, this crystal was heated in a vacuum overnight to remove the hydrogen, and this crystal was used to remeasure the pure-Pd dispersion relations. This procedure minimized systematic errors due to possible miscalibration and resolu-

tion effects of the spectrometer. The elastic incoherent scattering from the sample was measured before and after removing the hydrogen to test the reliability of the procedure used. The results indicate that virtually all of the hydrogen was removed by this process.

The measurements were performed using the triple-axis spectrometer HB4A at the HFIR reactor at Oak Ridge National Laboratory, using a fixed incident energy of approximately 8 THz ( $\approx 32$  meV). All scans were taken at "constant-Q" in a (010) plane of the reciprocal lattice. The most extensive series of measurements were

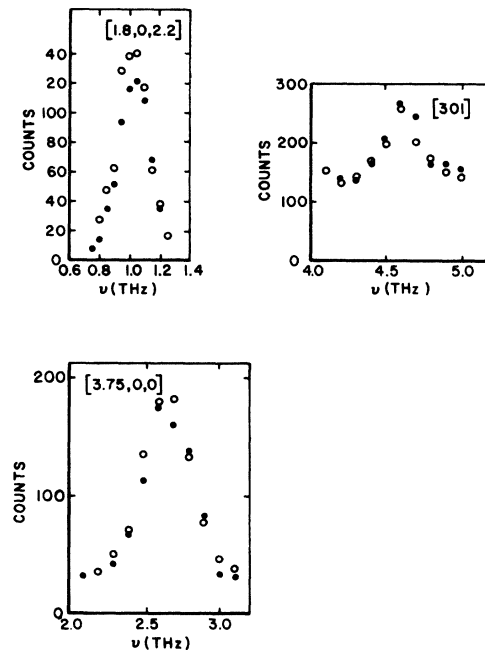


FIG. 1. Typical neutron group observed for pure palladium (●) and for PdH<sub>0.03</sub> (○).

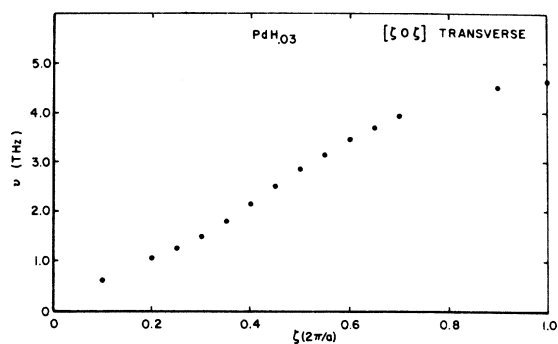


FIG. 2. Frequency vs wave-vector dispersion relation for the  $\text{PdH}_{0.03}$  transverse ( $T_1$ ) branch propagating in the  $[110]$  direction. The results for pure palladium are not shown, as they would be indistinguishable from the  $\text{PdH}_{0.03}$  result in this scale.

made along the  $[\zeta 0 \zeta]T_1$  branch, but a limited amount of data was taken for the  $[00 \zeta]L$  branch.

### III. RESULTS

Some typical examples of the data obtained are shown in Fig. 1, with the results of pure Pd and  $\text{PdH}_{0.03}$  shown on the same plots. As can be seen from the figure there is very little difference in the neutron scattering observed. The collected results for the  $[110]T_1$  branch are shown in Fig. 2. The pure-Pd results are not shown here, since the points lie so close to those for  $\text{PdH}_{0.03}$  that they could not be distinguished. The results for Pd agree with earlier measurements<sup>2,3</sup> to within the combined errors of the two experiments.

In all, a total of 24 different phonons were compared for the  $\text{PdH}_{0.03}$  and pure-Pd samples. The mean ratio of frequencies observed ( $\text{PdH}_{0.03}/\text{Pd}$ ) was 0.995, unity within the errors of the measurements. As can be seen in Fig. 1, there is a slight tendency to lower frequencies observable in the neutron groups and this tendency is also

present in the groups not shown. However, the shape of the anomaly in the  $[110]T_1$  branch does not show any change in either shape or strength in the  $\text{PdH}_{0.03}$  sample. Several explanations for this negative result are possible, e.g., the anomaly is not due to the detailed shape of the Fermi surface, or the shape of the Fermi surface is not sufficiently changed by the addition of this amount of hydrogen. Since the present concentration represents the maximum achievable at room temperature without going into the two-phase region, the latter possibility could not be checked experimentally. As pointed out in Ref. 6, a detailed calculation of the band structure of the  $\text{PdH}_{0.03}$  alloy is required to estimate the magnitude of the effect.

### IV. DISCUSSION

The present results show clearly that the addition of 3-at.% H to Pd does not significantly alter the lattice dynamics of the Pd host lattice. In particular, the anomaly in the  $[110]T_1$  branch is not changed in shape or in strength. The origin of this negative result can only be determined by a calculation of the Pd lattice dynamics from a microscopic point of view (incorporating details of the Fermi surface) and from a calculation of the band structure of  $\text{PdH}_{0.03}$ .

We are presently preparing a single crystal of the approximate composition  $\text{PdD}_{0.7}$  with which we intend to measure the complete dispersion relation, including the optical modes.

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<sup>1</sup>J. M. Rowe, J. J. Rush, L. A. de Graaf, and G. A. Ferguson, *Phys. Rev. Lett.* **29**, 1250 (1972).

<sup>2</sup>A. P. Müller and B. N. Brockhouse, *Phys. Rev. Lett.* **20**, 798 (1968).

<sup>3</sup>A. P. Müller and B. N. Brockhouse, *Can. J. Phys.* **49**, 704 (1971).

<sup>4</sup>D. H. Dutton, B. N. Brockhouse, and A. P. Müller, *Can. J. Phys.* **50**, 2915 (1972).

<sup>5</sup>W. Kohn, *Phys. Rev. Lett.* **2**, 393 (1959).

<sup>6</sup>A. C. Switendick, *Ber. Bunsenges. Phys. Chem.* **76**, 535 (1972); *Bull. Am. Phys. Soc.* **18**, 326 (1973).