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Lattice Dynamics of a Single Crystal of PdD$_{0.63}$†

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The frequency–wave-vector dispersion relations of a single crystal of PdD$_{0.63}$ have been measured by coherent neutron inelastic scattering at 78, 150, 220, and 295 K. The acoustic modes are considerably lower in frequency than the corresponding modes for pure Pd, in accord with the observed lattice expansion. The optic modes, in which D motions predominate, show considerable dispersion. In particular, the shape of the [100] LO branch shows conclusively that second–like-neighbor D-D interactions are comparable to the first–like-neighbor D-D interactions.

The physical properties of metal hydrides have been studied extensively for many years.[1] Recently there have been even more vigorous efforts in the investigation of the microscopic properties of hydrides, in part as a result of the increasing importance of metal-hydrogen systems in technological applications.[2] This has lead to renewed emphasis on the electronic structure and interatomic forces which underlie the properties of these multiphase solids, and for which the existing experimental information is often contradictory.[2] To date there have been no experimental results which could give direct information on the metal-hydrogen and hydrogen-hydrogen forces in these materials. In this Letter we present the first detailed measurements of the phonon dispersion relation in a metallic hydride—PdD$_{0.63}$. The only previous data on the dynamics of β-phase palladium hydride were derived from incoherent neutron scattering[3,4] on polycrystalline samples. The present results, derived from coherent neutron scattering on a

single-crystal sample, show in detail that the picture of the dynamics derived from the earlier measurements is in error. In particular, we find large dispersion in the longitudinal optic modes (which are dominated by deuterium motions)—a result in direct contradiction with the theoretical results recently obtained by Hertel[5] in an attempt to correlate the lattice dynamics and the superconducting properties[6,7] of nearly stoichiometric PdD and PdH. In addition we find that the frequencies of the acoustic modes are considerably changed from those in palladium, again in contradiction to existing theoretical predictions.[5] The present sample certainly has a superconducting temperature less than 1 K, so that pronounced phonon anomalies like those observed in the transition-metal carbide[8-10] are neither expected nor observed. However, the present results do show conclusively that strong interactions between deuterium atoms extend to more than nearest neighbors and that the lattice dynamics of palladium hydride can only be ex-

plained by a model which fully and correctly incorporates the detailed electronic structure of these alloys.

The sample was prepared by adding high-purity deuterium gas (H/D < 0.004) to a 12-mm-diam ×50-mm-long single crystal of palladium. The initial loading was carried out at temperatures greater than 300°C to avoid the two-phase region of the phase diagram.[11] The final concentration of deuterium was determined to be $PdD_{0.63\pm0.02}$ by measuring the weight increase of the crystal. The specimen had a large mosaic spread (2.4° full width at half-maximum), with some evidence of structure in the Bragg-peak rocking curves. This large mosaic spread led to increased widths for the neutron groups for transverse modes, and to a large number of spurious peaks in the neutron data arising from multiple Bragg scattering, but did not otherwise affect the measurements significantly. The data were collected on the HB3 triple-axis spectrometer at the high-flux isotope reactor at the Oak Ridge National Laboratory, by using the standard techniques of coherent neutron scattering. Several different scattering energies and resolutions were used to help identify and eliminate spurious peaks in the data.

Data were collected at 78, 150, 220, and 295 K, with the most detailed measurements of the acoustic branches made at 295 K, and of the optic modes at 78 and 150 K. Some typical neutron groups obtained at selected temperatures and wave vectors are shown in Fig. 1. It should be noted that deuterium is not a purely coherent scatterer, and peaks due to incoherent scattering are indicated in this figure. The groups at different temperatures were measured under identical conditions, with allowance made for the observed change in lattice parameter—$a = 4.052$ Å at 295 K; $a = 4.032$ Å at 78 K. The most important points to be noted are that the centroids of the groups do not change appreciably as a function of temperature, while the groups themselves broaden considerably as the temperature increases.

In Fig. 2, we show the dispersion relations for $PdD_{0.63}$ obtained from these measurements. Data from different temperatures have been combined in this figure. The solid lines represent the results of a least-squares fit of a fourth-nearest-neighbor Born–von Kármán model to the data. The least-squares analysis was based on the data obtained at 150 K for the LA, LO, TA, and TO branches in the [001] direction, and the LA, LO, TA_1, and TO_1 branches in the [110] direction com-
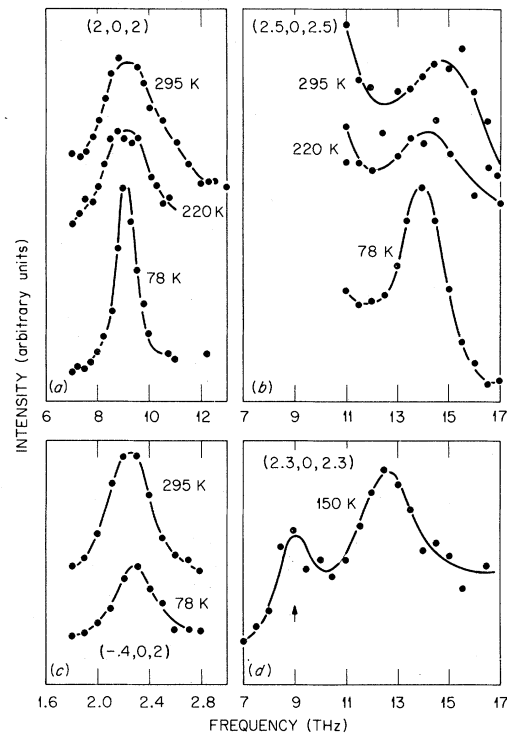

FIG. 1. Selected phonon groups at several temperatures in $PdD_{0.63}$. The arrow in (d) indicates an incoherent peak due to the flat TO modes.

bined with the LA and TA modes in the [111] direction obtained at 295 K. The crystal was treated as stoichiometric for the Born–von Kármán fit, and the third-neighbor, (111) Pd-D force constants were fixed at zero values, leaving twelve fitting parameters. A fit of similar quality can be obtained with a simple screened shell model, like that used by Weber and co-workers[10] to fit the nonsuperconducting transition-metal carbides. The dashed lines are the dispersion curves observed[12] for pure Pd at 300 K. The anomaly found[13] in the T_1 branch in the [110] direction in pure Pd and $PdH_{0.03}$ is not observed. (There are, of course, no optic modes in pure Pd.) In agreement with the results of the incoherent-scattering studies,[3,4] the frequency of the optic modes at the zone center is low in comparison with other hydrides, thus implying a weak nearest-neighbor Pd-D force constant. The observed dispersion of the longitudinal optic modes is large. Moreover, the fact that the frequency of the LO mode in the [100] direction reaches a maximum before the zone boundary implies strong second–like-neighbor D-D interactions, comparable to the first–like-neighbor D-D interactions, which are, however, much weaker than the first–like-neighbor
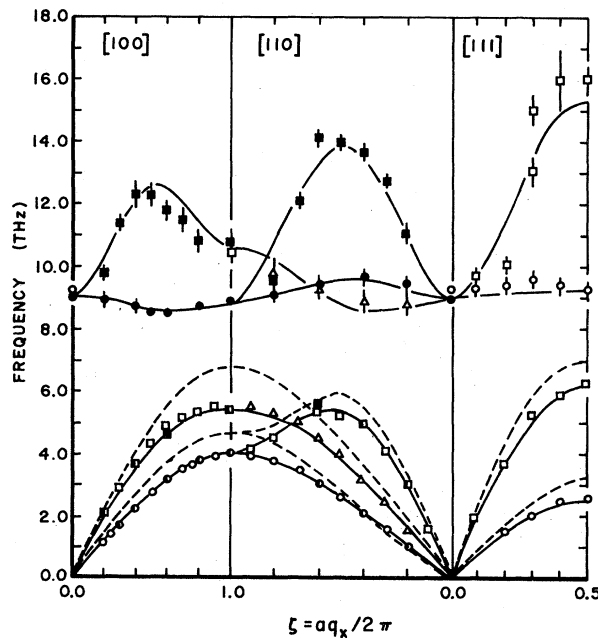
FIG. 2. Phonon dispersion curves in $PdD_{0.63}$. The solid curves are calculated based on a Born–von Kármán model with twelve parameters. The solid (open) symbols are phonon groups obtained at 150 K (295 K). The dashed curves are the dispersion curves observed for pure Pd at 300 K (Ref. 12).

Pd-Pd interaction. The existence of such inter-actions has been predicted by Switendick[14] from the results of his band-structure calculations for these alloys. The acoustic modes are 20–30% lower in frequency than the corresponding modes in pure Pd, a result quite consistent with the ob-served lattice expansion. The Born–von Kármán force constants derived from the fit to the data fully support these conclusions. These results will be presented in detail in a subsequent full length paper.

The present data are in complete disagreement with the results of a simple screened-pseudo-potential calculation by Hertel[5] for both the optic and the acoustic modes. Thus, the conclusions drawn about small ionic charges in that work are clearly invalid. We have independently verified by a similar calculation that this model will not reproduce the dispersion found in the LO modes. Thus, the use of this oversimplified model to ex-plain the superconducting properties (as was done in Ref. 5) is unwarranted. It is obvious that any theoretical calculations of the phonon dis-persion relation in palladium hydride must in-corporate the complete electronic band-structure results.[14] It is probable that this will be gener-ally true for other transition-metal hydrides.

Finally, in Fig. 3 we show frequency distribu-tions for PdD and PdH derived from the Born–

von Kármán model fitted to the experimental re-sults for $PdD_{0.63}$; the deuterium mass was re-placed by the hydrogen mass to obtain the PdH density of states. This assumes that the forces in these two systems are identical, which is not completely correct in a system with the large anharmonicity indicated by the temperature de-pendence of the neutron groups shown in Fig. 1. However, any corrections due to this effect are not expected to change significantly the shape shown in Fig. 3. These results bear little re-semblance to the incoherent-neutron-scattering results, and do not support the conclusions of
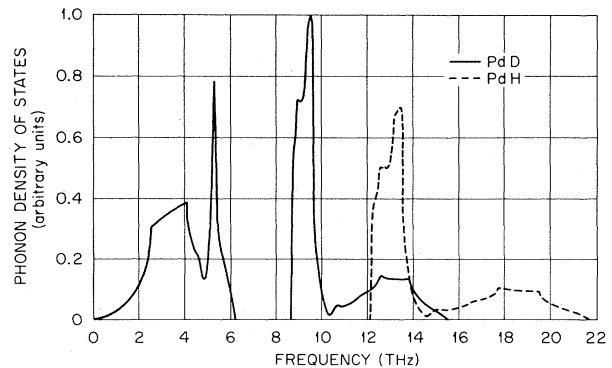

FIG. 3. Frequency distributions for PdD and PdH based on the force constants obtained from the Born–von Kármán model for $PdD_{0.63}$.

Ref. 4 concerning observed linewidths. We believe this discrepancy to be due to multiphonon effects, which are clearly present in the data shown in Fig. 1, especially at temperatures near 300 K, as the broad, intense background upon which the coherent peaks are observed. This conjecture could most readily be checked by repeating the incoherent measurements at very small values of momentum transfer; such measurements are currently in progress.

In conclusion, we have determined the phonon dispersion relations of $PdD_{0.63}$ by coherent neutron scattering. The results are in accord with the electronic band-structure calculations[14] and in complete disagreement with calculations[5] based upon the rigid-band model. The temperature dependence of the observed neutron groups shows clear evidence of strong anharmonicity, part of which may be due to the fact that the present sample is not stoichiometric. Efforts are in progress to load the crystal with higher concentrations of deuterium.

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Spin-Dependent Energy Transfer in CaF_2 :Ce, Mn

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The ground-state magnetic resonance of Mn^{2+} in CaF_2:Ce, Mn can be observed by monitoring the change in either the Mn^{2+} or Ce^{3+} luminescent intensity. This spin-dependent luminescence is evidence for an exchange-coupled energy-transfer process between the cerium sensitizer and the manganese activator.

Energy-transfer processes involving exchange interactions between magnetic ions in luminescent systems have been proposed by several workers including Leach,[1] Birgeneau,[2] and, more recently, Soules et al.[3] In particular, Soules et al. have studied Sb-to-Mn transfer in fluoro-