

Lattice dynamics of β -PdD_{0.78} at 85 K and ordering effects at 75 K

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The phonon dispersion relations of PdD_{0.78} have been measured by inelastic neutron scattering at temperatures slightly above and below the order-disorder transition. The acoustic modes are not sensitive to the ordering process and are somewhat higher in frequency than the corresponding modes in PdD_{0.63}. The optic frequencies in the disordered phase of PdD_{0.78} are equal to those of PdD_{0.63}. After ordering, a slight increase was observed in some transverse branches.

I. INTRODUCTION

Among the metal hydrides the PdH_x(D_x) system has attracted particular interest because it occupies a special position in many respects: The superconducting transition temperature T_c increases strongly with concentration up to $T_c = 11$ K for the stoichiometric compound; the isotope effect is inverse¹; the frequency of the hydrogen vibrations is very low and decreases with concentration^{2,3}; and in non-stoichiometric compounds ordering of the vacancies occurs at low temperatures.^{4,7} The first detailed information on the metal-hydrogen and hydrogen-hydrogen forces in PdD_x has been obtained from measurements of the phonon dispersion curves of Rowe *et al.*³ It turned out that the acoustic frequencies are by 20% lower than in pure Pd. The optic modes in PdD_{0.63} show a pronounced dispersion indicating a strong D-D interaction. Moreover, the frequencies of the transversal optic phonons are lower than the frequency of the local mode of the D atoms found at small concentrations.² Tunneling experiments suggest that the optical phonon frequencies further decrease linearly with the D content up to high concentrations.⁵ Optical phonon lines, especially the longitudinal ones, were found to be broad in PdD_{0.63}. Their line shapes could largely be explained by a model of Glinka *et al.*⁶ which takes the non-stoichiometry of the sample explicitly into account.

In recent experiments on PdD_x with $x = 0.76$ and 0.78 it has been found that at temperatures below 80 K superlattice reflections appear at $(\frac{4}{5}, \frac{2}{5}, 0)$.⁷ After a period of 50 h at 75 K the intensity of these reflections reaches 2% of the fundamental Bragg reflections, corresponding to a fully ordered interstitial D structure (Ni₄Mo structure) stoichiometric at 80 at. % D.

In the present work, we report on measurements of phonon dispersion curves and phonon line shapes in a crystal with much higher D content than that of Rowe *et al.*, i.e., PdD_{0.78}. The results are analyzed on the basis of a model similar to that of Glinka *et al.*⁶ In order to investigate the influence of the order-disorder transition on the lattice dynamics the phonon measurements were performed at temperatures slightly above and below the transition temperature, i.e., 85 and 75 K, respectively.

II. EXPERIMENTAL

The measurements were made on a conventional triple axis spectrometer at the FR2-reactor in Karlsruhe. Cu(111)- and pyrolytic graphite (002)-crystals were used as monochromator and analyzer, respectively. All collimators, beginning with the in-pile collimator, had a divergence of 30'.

As sample a cylindrical single crystal of PdD_{0.78} with a volume of about 1 cm³ was mounted into a cryostat. The sample was prepared by loading a Pd crystal with deuterium in the gas phase. Pressures up to 200 bars were applied at temperatures of 670 K to avoid the two phase region during loading. The measurements were started at 85 K, where the D atoms are disordered on the octahedral interstitial sites; then the sample was cooled to 75 K, and when the superlattice reflections of the interstitial Ni₄Mo structure were fully developed, the measurements were continued in the order state.

III. RESULTS

The phonon dispersion curves of disordered β -PdD_{0.78} at 85 K are shown in Fig. 1. A comparison

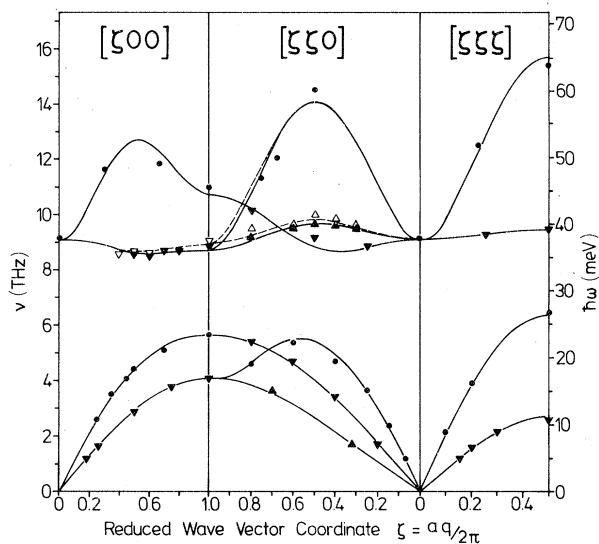


FIG. 1. Phonon dispersion curves in $\text{PdD}_{0.78}$ at 85 K (full symbols, full lines). Open symbols and dashed lines refer to changes of the dispersion curves after ordering at 75 K. All lines are calculated on the basis of a 12-parameter Born-von Karman model assuming a rocksalt structure.

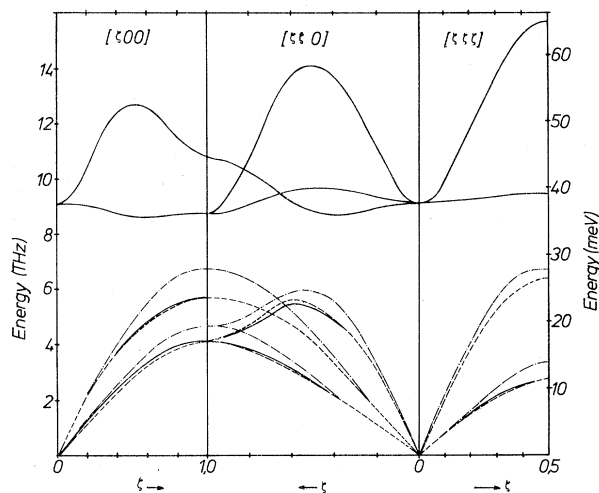


FIG. 2. Comparison of the phonon dispersion relations of $\text{PdD}_{0.78}$ (full lines) with those of pure Pd (dashed-dotted lines, after Ref. 8) and of $\text{PdD}_{0.63}$ (dashed lines, after Ref. 3).

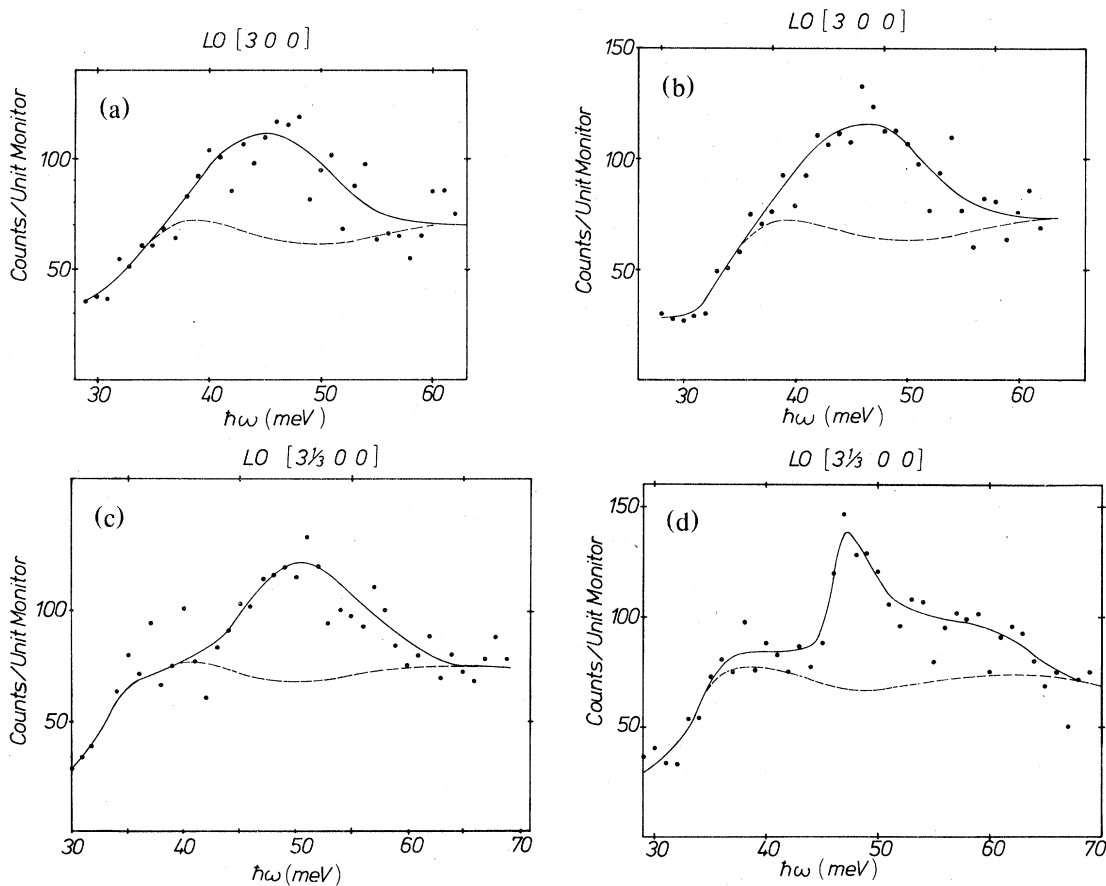


FIG. 3. Optical phonon line shapes in $\text{PdD}_{0.78}$ in the disordered phase [(a) $LO[3,0,0]$, (c) $LO[3\frac{1}{3},0,0]$] and in the ordered phase [(b) $LO[3,0,0]$, (d) $LO[3\frac{1}{3},0,0]$]. Full lines are guides to the eye. Dashed lines denote the background level.

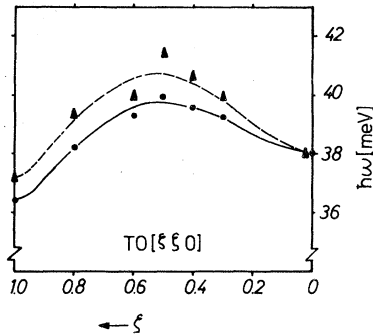


FIG. 4. Dispersion relation of the $TO[\xi\xi 0]$ branch with polarization $[\xi-\xi 0]$ in $PdD_{0.78}$ in the disordered phase at 85 K (full circles, full lines) and in the ordered phase of 75 K (triangles, dashed lines). Lines are guides to the eye.

of the present results with the dispersion relations in $PdD_{0.63}$ and in pure Pd is shown in Fig. 2.⁸ The optic frequencies in $PdD_{0.78}$ are, within the errors, the same as in $PdD_{0.63}$.³ In the acoustic region the softening of the frequencies when going from $PdD_{0.63}$ is not continued when going to $PdD_{0.78}$: Even a frequency increase of several percent is observed in some branches.

Measurements of longitudinal optic modes in disordered $PdD_{0.78}$ gave broad intensity distributions. Two of them are depicted in Figs. 3(a) and 3(c) and are very similar to the phonon groups observed in $PdD_{0.63}$ by Glinka *et al.*⁶ That means, that phonon line shapes are not very sensitive to concentration changes between $x=0.63$ and 0.78.

After ordering at 75 K, acoustic phonon frequencies were unchanged. However, significant changes were observed in the optic region (Fig. 1): Wide regions of the TO dispersion curves, in particular of the $TO_1[\xi\xi 0]$ branch (Fig. 4), showed a frequency increase upon ordering. Furthermore, the ordering process produced changes of line shapes of some, but not all longitudinal optic phonons: Sharp structures appeared which were absent for the disordered state [Figs. 3(b) and 3(d)].

Finally, some optic and acoustic phonons were measured at room temperature. The acoustic phonons at room temperature are by 3% lower, but the optic phonons by 2% higher than at 85 K indicating the important anharmonicity of the optic vibrations.

IV. MODEL CALCULATIONS

As a first step we fitted the data by using a 12-parameter fourth-nearest-neighbor Born-von Kármán model—the third-nearest-neighbor Pd-D force constants are set equal to zero—treating the crystal as stoichiometric. The same model was applied by Rowe *et al.*³ for $PdD_{0.63}$ (Fig. 1). The calculations showed that the force constants of the ordered and

disordered phase in $PdD_{0.78}$ are very similar and also very similar to those in $PdD_{0.63}$. This result is not astonishing in view of the similarity of the corresponding dispersion curves.

The application of a model assuming a rocksalt structure seems to be very inadequate for $PdD_{0.78}$ especially with respect to the ordered phase. To take the nonstoichiometry and the position of the vacancies into account we calculated the dispersion curves for a supercell containing an arrangement of D atoms and vacancies. Glinka *et al.*⁶ used this approach in $PdD_{0.63}$. For our calculations we took the elementary cell of the ordered phase of $PdD_{0.80}$ as supercell. It contains 10 Pd atoms, 8 D atoms, and 2 vacancies. The forces were taken to be axially symmetric (10 adjustable parameters). The disordered phase was simulated by averaging the results for about 30 configurations with a variable number of vacancies ranging from 0 to 4. For the ordered phase the positions of the atoms are determined by the ideal Ni_4Mo structure. Due to the 18 atoms in the elementary cell there are 54 branches for each symmetry direction in the reduced zone scheme. Comparing the observed phonons with the calculations one has to take into account that in most cases appreciable contributions from several branches are present. In the acoustic region ($h\omega < 25$ meV) their frequencies differ by a few tenths of one meV only, but in the optical region by several meV. Moreover in the ordered phase the crystal consists of three different types of domains due to the tetragonal symmetry of the Ni_4Mo structure. In many cases the calculated intensity was found to be markedly different for each domain. Therefore the comparison between calculation and experiment was based on frequency averages—it was assumed that the three domains have equal volume portion—or even on the line shapes as well for the disordered as the ordered phase. The calculations yielded longitudinal and transverse D-D force constants which are by 20% and 10% larger, respectively, than those of the stoichiometric model. The other force constants have the same value. We would like to note that the supercell calculations of Glinka *et al.*⁶ for $PdD_{0.63}$ yielded values of the D-D force constants which are by 50% larger than those of the stoichiometric model.

One goal of our analysis was to find out whether the frequency shifts upon ordering the vacancies are due to changes in the force constants or are merely caused by a different arrangement of the D atoms. It turned out that frequency averages depend mainly on the concentration but very little on the position of the vacancies. The frequency shift upon ordering is therefore due to changes in the force constants—e.g., we found that with unaltered force constants the frequency of the $TO_1[0.5,0.5,0]$ should change by no more than 0.2% upon ordering, whereas the observed change amounts to 3%.

V. DISCUSSION

The present investigations of phonon dispersion relations in $\text{PdD}_{0.78}$ show that in the high concentration region of the PdD_x system the concentration dependence of phonon frequencies is different from that assumed in the literature. The softening of the acoustic modes between Pd and $\text{PdD}_{0.63}$ cannot be extrapolated to higher D concentrations and there is even a change of sign in the concentration dependence: the phonon frequencies and the corresponding force constants are higher in $\text{PdD}_{0.78}$. We would like to note that the expansion of the lattice continues when going from $\text{PdD}_{0.63}$ to $\text{PdD}_{0.78}$.

The optic modes, which are assumed to show a linear frequency decrease with D concentration, as indicated by tunneling data (Fig. 5) of high concentrated PdD_x samples (5), show no concentration dependence between $\text{PdD}_{0.63}$ and $\text{PdD}_{0.78}$. Since the deviation of our point for $\text{PdD}_{0.78}$ from the straight line through the others implies an unphysical concentration dependence of the optic frequencies, the question arises whether it might be caused by experimental errors: both data sets, for $\text{PdD}_{0.63}$ and for $\text{PdD}_{0.78}$, are results of at least two different runs with independent instrumental calibration. Therefore we are confident that the error bars given in Fig. 5 are not underestimated. Our results, some hardening of the acoustic and no softening of the optical frequencies in $\text{PdD}_{0.78}$ compared to $\text{PdD}_{0.63}$, do not only contradict the expectations derived from other investigations of the phonon frequencies in PdD_x , but are also unexpected in view of the concentration dependence of the superconducting transition temperature T_c . However, the fact, that the mean optic frequency does not change from $\text{PdD}_{0.63}$ to $\text{PdD}_{0.78}$, does not mean that the contribution of the optic phonons to the electron-phonon coupling remains the same: It is substantially enhanced by the increase of degrees of freedom due to the larger number of atoms per unit volume. As has been observed by Standley⁹ the ordered phase of $\text{PdD}_{0.81}$ has a $T_c = 2.2$ K which is 0.2 K lower than that of the disordered phase. This

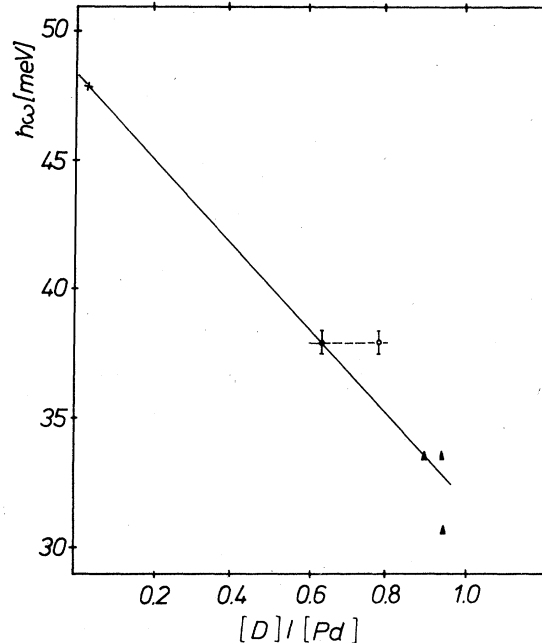


FIG. 5. Concentration dependence of the optic modes in PdD_x . The cross represents the neutron scattering results of Ref. 2, the full circle those of Ref. 3, and the open circle the results of the present work. Triangles are tunneling data of Ref. 5.

difference in T_c is connected with a difference in the electron-phonon coupling constant λ of about 1% only. An estimate of the change of λ due to the observed changes in the optical phonon spectrum after ordering on the basis of McMillan's formalism yields a value of similar size.

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