Isotope Effects in the PdH System: Lattice Dynamics of $PdT_{0.7}$

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(Received 21 July 1986)

The quasiharmonic phonon dispersion relation of $PdT_{0.7}$ has been determined by coherent neutron scattering. Calculation of the phonon terms entering the current models for superconductivity in PdH, PdD, and PdT shows conclusively that the magnitude of the measured anharmonic frequency shifts is not sufficient to explain the reverse isotope effect in these systems. The effect of the large zero-point motion of the hydrogen isotopes on both the electronic structure and the electron-phonon interaction is estimated, and shown to be necessary to explain the experimental data.

PACS numbers: 63.20.Dj, 63.20.Kr, 74.70.Dg

The existence of a reverse isotope effect in the superconducting transition temperature (T_c) in high-concentration PdH_x and PdD_x [$T_c(PdD) > T_c(PdH)$] has been known for some time.[1] Recently, T_c has also been measured for the PdT_x system,[2] with the result $T_c(PdT) > T_c(PdD)$. Although several different mechanisms were proposed to explain these unusual observations, including anharmonicity,[3] volume dependence,[4] and electronic effects[5] resulting from the large mean square displacements of the hydrogen isotopes, a series[6] of papers combining accurate band-structure calculations and neutron-scattering results for the phonon terms[7,8] seemed to show definitively that the effect was the result of anharmonicity of the phonons. In this Letter, we present new measurements of the phonon dispersion relation in a single crystal of $PdT_{0.7}$, which allows a much more accurate estimate of anharmonic effects on the phonon dispersion of different isotopes of H in Pd. These new data, along with other neutron data[9] on $PdH_{0.6}$ that were not available at the time of the calculations,[6] show that anharmonic effects are a factor of 2 smaller than was assumed in the calculations, and that the reverse isotope effect cannot be explained on this basis alone.

A single crystal of Pd (4.231 g, approximately 6-mm diameter by 12-mm-long cylinder) was loaded with tritium at the Sandia Tritium Research Laboratory following a temperature-pressure path that avoided the two-phase region of the palladium-tritium phase diagram. The crystal was placed in a BeCu pressure vessel and the temperature was raised to 673 K. The tritium pressure was gradually increased to 700 psi, then the temperature was decreased to room temperature in 50-K steps, allowing $\frac{1}{2}$ h at each temperature for equilibration. The crystal was then rapidly transferred to a thin-walled container for the neutron measurements. After the neutron studies were complete (3 weeks), the tritium was measured both calorimetrically and by pressure-temperature-concentration assay, yielding $PdT_{0.71 \pm 0.03}$. The hydrogen and deuterium concentrations present as tritium contaminants were determined to be 0.7% and 0.6%, respectively, of the total hydrogen isotope present. The ^3He concentration introduced into the Pd lattice by radioactive decay of the tritium (and strongly trapped there) was calculated to be 1100 at. ppm at the beginning of the experiments, and 2200 at. ppm at the end. This corresponds to an absorption cross section which varied from 6 to 12 b during the course of the experiment, in addition to the 8-b Pd absorption cross section.

The measurements were performed on a triple-axis spectrometer at the NBS Research Reactor, by use of variable incident energy with fixed final energies of 14.8, 28.0, and 35.0 meV. Most of the results were obtained with a Cu (220) monochromator and a pyrolitic graphite analyzer. The collimation (minutes of arc) before and after the monochromator and analyzer was 60-40-40-80 or 60-40-80-80 for most of the optic-mode measurements. A pyrolitic graphite filter was used in front of the analyzer in all cases. It should be noted that the scattering from the present sample is 25 times weaker than that from the earlier $PdD_{0.63}$ sample, as a result of the reduced scattering cross section for T, and of the small sample size dictated by the radioactivity of T and by the presence of ^3He.

As a result, we were unable to measure as many points on the phonon dispersion relation as were measured for $PdD_{0.63}$, especially for the acoustic modes, which are in any case not much shifted from their values in $PdD_{0.63}$, or to determine the line shapes for the scattering in a quantitative sense[10] as was done for $PdD_{0.63}$. Nonetheless, the results obtained at 80 K are more than adequate to determine both the Pd-T force constants and the T-T interactions at this concentration. A representative neutron group for the threefold degenerate mode at the origin (Γ), measured at the (220) reciprocal-lattice point, is shown in Fig. 1, along with the same group remeasured in the sample of $PdD_{0.63}$ that was used for the earlier experiment.[7] This latter measurement ensures that the results presented are not affected by spectrometer calibration—the present remeasurement agrees to well within the error with the earlier results. This particular mode was measured in $PdT_{0.7}$ at three different lattice points and under many different spectrometer conditions, as it is the critical measurement for determination of the Pd-T force constant. The temperature dependence of this mode is similar to that observed for $PdD_{0.63}$.

The collected results at 80 K are shown in Fig. 2, where the solid line is the result of a fit to the data by the same Born-von Kármán model as was used earlier[7,11] for $PdD_{0.63}$. Although the force constants resulting from this model cannot be claimed to have physical significance, the model does allow a comparison of the results for the two isotopes to be made on a consistent basis. For the model result shown, the Pd-Pd force constants were constrained to have the same values as for $PdD_{0.63}$ in order to compensate for the smaller number of data points available for $PdT_{0.6}$; however, relaxing this condition did not lead to significantly different results in either the goodness of fit or any calculated quantity, such as the frequency averages over the density of states. The frequency of the mode at the Γ point is determined within the model by a linear combination of the two Pd-T force constants and the reduced mass. The ratio of this linear combination in PdD to that in PdT is 1.04 ± 0.01, whether determined from the fitted force constants, or directly from the ratio of $(\mu\omega^2)_D/(\mu\omega^2)_T$, where μ is the reduced mass and ω is the measured frequency of vibration.

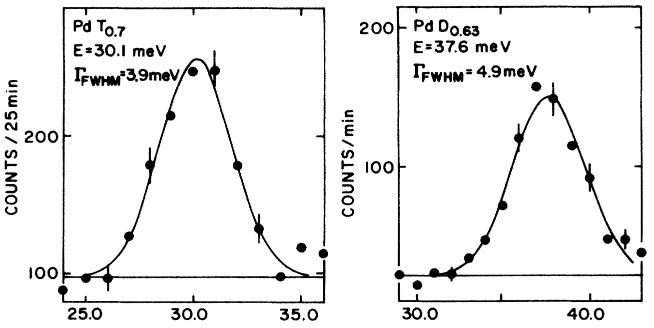

FIG. 1. Measurements of the optic mode at the Γ point, $Q = (2.0,2.0,0.0)$ in units of $2\pi/a$, where a is the lattice parameter, for $PdT_{0.7}$ and $PdD_{0.63}$ at 80 K. Solid lines are fits by Gaussian line shape and constant background. (Note different energy and counting-rate scales.)

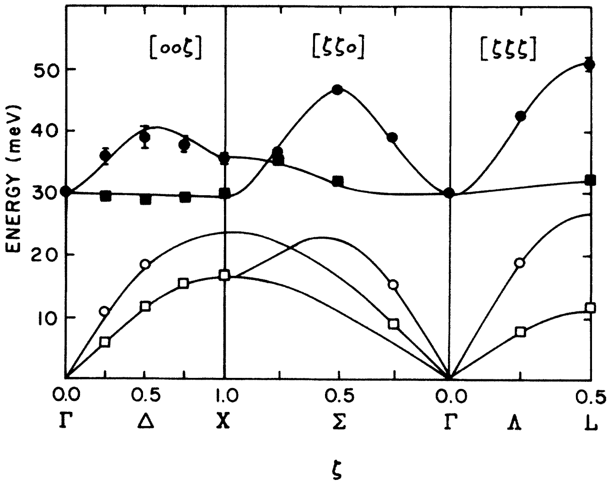

FIG. 2. Collected results for the phonon dispersion relation in $PdT_{0.7}$ at 80 K, phonon energy plotted as a function of the reduced wave vector ζ (units of $2\pi/a$, $a = 4.03$ Å). Solid lines are the result of a fit to a Born-von Kármán model.

The amplitude-weighted densities of states for $PdT_{0.7}$ and $PdD_{0.63}$ were derived from the fitted parameters of the Born-von Kármán model, and used to calculate the phonon frequency moments for the metal and hydrogen isotope separately. The resulting values, shown in Table I, can then be combined with the electronic terms given in Ref. 6 to estimate T_c. After trying many different weighting schemes for the phonon part of this theory, we conclude that the measured ratio of frequencies, and hence the anharmonicity, *cannot* explain the observed[2,12] isotope dependence of T_c for D and T in Pd. As a result of this observation, we have reanalyzed the results for the phonon moments of PdH that were used in Ref. 6. The frequency spectra for $PdH_{0.6}$ and $PdD_{0.6}$ have been remeasured[9] recently under the same experimental conditions, with the result that the ratio of frequencies in $PdH_{0.6}$ to those in $PdD_{0.6}$ were 1.49 ± 0.02, a result that was considered in satisfactory agreement with the earlier ratio of 1.54 obtained in Ref. 8. The more recent result

TABLE I. Amplitude-weighted energy moments of phonon dispersion relation.

		$\langle E \rangle$ (meV)	$(\langle E^{-1} \rangle)^{-1}$ (meV)
$PdH_{0.6}$[a]	Pd	16.5	14.4
	H	63.7	61.8
$PdD_{0.63}$[b]	Pd	16.4	14.3
	D	43.3	41.7
$PdT_{0.6}$	Pd	16.1	14.0
	T	34.4	32.8

[a] Derived from $PdD_{0.63}$ force constants (see footnote b), with the Pd-H force constants scaled by the ratio determined in Ref. 9.

[b] Derived from force constants fitted to $PdD_{0.63}$ data (Ref. 11).

TABLE II. Combined phonon, electron, and T_c data for PdH, PdD, and PdT.

	$\omega_{\log}$ (K)	λ_1[a]	λ_2[a]	$\lambda = \lambda_1 + \lambda_2$	T_c(calc.)[b] (K)	T_c(meas.)[c] (K)
PdH	517	0.143	0.417	0.560	9.5 (8.5)	8.0
PdD	377	0.145	0.454	0.599	9.2 (9.8)	10.0
PdT	312	0.151	0.477	0.628	8.7 (10.2)	12.0

[a] λ's derived from phonon data in Table I and electronic data (η's) in Ref. 6, with $\lambda_i = \eta_i/(M_i\langle\omega\rangle_i/\langle\omega_i^{-1}\rangle)$.

[b] $T_c = f_1 f_2 \omega_{\log}(1.2)^{-1}\exp\{-1.04(1+\lambda)/[\lambda - \mu^*(1+0.62\lambda)]\}$ as given in Ref. 14, with $\mu = 0.1$, and $f_1 f_2 = 1$. Values in parentheses are determined for $\mu^* = 0.085$ and incorporate estimates of the effects of the zero-point motion on the electronic structure (Ref. 15) and electron-phonon interaction (Ref. 13) as described in the text.

[c] Values taken from Refs. 2 and 12, in order to have a consistent set.

gives $(\mu\omega^2)_{\mathrm{H}}/(\mu\omega^2)_{\mathrm{D}} = 1.12 \pm 0.02$, a result significantly lower than the value of 1.2 used in Ref. 6, and in good agreement with all of the results obtained by different techniques and summarized in Table I of Griessen and deGroot.[13] We have scaled the Pd-D force constants by this ratio, keeping the H-H force constants at the values found in $\mathrm{PdD}_{0.63}$ (an *Ansatz* supported by the present $\mathrm{PdT}_{0.7}$ results), and calculated the phonon moments for $\mathrm{PdH}_{0.6}$ which are shown in Table I. The results of Table I were combined with the electronic calculations of Ref. 6 to derive the interaction parameters and T_c's shown in Table II. We observe that the reverse isotope effect is *not* reproduced for any of the series. It may be argued that the use of the experimentally determined dispersion relation in this way is unjustified; however, Ganguly[16] has shown that this is a good first approximation. It can also be argued that the use of results for hydrogen isotope concentrations of approximately 0.6 is the source of the discrepancy; however, results for $\mathrm{PdD}_{0.88}$ show[17] that there is little concentration dependence of the optic modes. We are thus led to conclude, on the basis of the most accurate data currently available, that anharmonicity alone cannot reproduce the observed reverse isotope effect in PdH, PdD, and PdT, although it does shift the T_c values in the correct direction.

Jena, Jones, and Nieminen[18] have calculated the effect of the large mean square displacements of the isotopes of hydrogen on the electronic structure of PdH within a local-density model, following the idea proposed by Miller and Satterthwaite.[5] They calculated new values of the electron-phonon matrix element η for H and D in Pd that were larger than those in Ref. 6, and found that $\eta_{\mathrm{D}}/\eta_{\mathrm{H}} \approx 1.15$. They concluded that this effect, in conjunction with a ratio of force constants for PdH/PdD of 1.1, would be adequate to explain the reverse isotope effect within the McMillan[15] formulation for T_c. However, this conclusion was based on the use of the Debye temperature as a prefactor in the McMillan equation. This formulation is incorrect for compounds, and use of a properly defined average frequency $\langle\omega\rangle$ as given in Ref. 15 destroys the agreement with experiment. Again starting from the large zero-point motion of hydrogen isotopes in Pd, Griessen and deGroot[13] have proposed that the electron-phonon matrix element in the McMillan theory should be modified by a Debye-Waller factor, $\exp(-Q^2\langle u^2\rangle)$, where Q is the momentum transfer and $\langle u^2\rangle$ is the mean square displacement of the hydrogen isotopes. This factor should appear even for harmonic forces, and is strongly isotope dependent, since $\langle u^2\rangle$ is proportional to $\langle\omega^{-1}\rangle/M$, or to $1/\sqrt{M}$ in the harmonic case. This factor is negligible for most superconductors because of the large value of M, but is quite important for hydrogen and its isotopes in Pd. Griessen and deGroot[13] showed that a value of Q corresponding to approximately 3 Å^{-1} is the dominant term in the calculation, and estimated ratios of the values of the electron-phonon interaction parameter λ for PdH and PdD by calculating $\langle u^2\rangle$ from the available neutron data. These ratios were in satisfactory agreement with the experimental data, and showed that this effect was as large as the anharmonic effects. However, we have used this formalism to modify the η given in Ref. 6 in order to calculate T_c for all three isotopes. While the reverse isotope effect is reproduced for PdH, PdD, and PdT, the magnitudes of T_c are nearly a factor of 2 too small. If we use the larger values of η obtained from the local-density calculation[16] and include the Debye-Waller factor as suggested in Ref. 13, the calculated values of T_c exhibit both the correct order of magnitude and the correct sign of the isotope effect, although some discrepancies in detail remain (see values in parentheses in Table II). Therefore, we conclude that all of the elements of a correct theory for superconductivity in the PdH system have been identified, although the present formulations remain somewhat *ad hoc*. In order to verify these effects, a comprehensive and critical reevaluation of all of the elements of the theory is required that properly takes into account the large mean square displacements characteristic of this system. The present results provide the phonon data necessary for this calculation.

We acknowledge the skillful technical assistance of D. L. Overmyer and R. M. Watson. We also thank W. Wall for the calorimetric measurement of the tritium concentration, and K. Greulich for the spectrometric

analysis of the tritium contaminants.

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