[24] R. E. Walstedt, V. Jaccarino, and N. Kaplan, J. Phys. Soc. Jpn. 21, 1843 (1966).
[25] B. Chornik, Phys. Rev. B 4, 681 (1971).
[26] See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, London, 1961), p. 310.
[27] B. I. Halperin, private communication.

Inverse Isotope Effect and the x Dependence of the Superconducting Transition Temperature in PdH_x and PdD_x

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First-principles electronic–band-structure calculations and measured phonon properties are employed in a calculation of the concentration dependence of the superconducting transition temperatures for PdH_x and PdD_x, including the inverse isotope effect. Excellent agreement with the experimental results is obtained. Our model also gives a qualitative understanding of the enhanced transition temperatures in the palladium–noble-metal hydrides.

Since the discovery[1,2] of superconductivity in PdH_x and PdD_x with $x \gtrsim 0.8$, it has been well established that the role of the hydrogen or deuterium optic-mode vibrations is fundamental in determining the superconducting properties of these systems. Ganguly[3] has emphasized the importance of the H or D "local modes" in PdH_x (PdD_x) based on purely theoretical considerations, while Papaconstantopoulos and Klein,[4,5] and Switendick[6] have done detailed calculations of the superconducting transition temperatures, T_c, which have put these theoretical ideas on a firm quantitative basis. Recent tunneling measurements[7-9] have, at least qualitatively, verified the conclusions of these works.

In this Letter we have extended the work of Refs. 4 and 5 to examine in a quantitative way the question of the inverse isotope effect[10-13] and the x dependence of T_c[10-14] in PdH_x (PdD_x). Furthermore, our analysis provides a qualitative explanation for the occurrence of even higher values of T_c in the palladium–noble-metal hydrides.[15] We have employed *ab initio* augmented–plane-wave (APW) band-structure calculations, and measured phonon densities of states (DOS) to obtain T_c for PdH_x (PdD_x); no adjusted parameters are used. The agreement between theory and experiment is remarkable, and strongly indicates that a basic understanding of superconductivity in the palladium-hydrogen (-deuterium) system is at hand. Further experimental checks of our interpretation are suggested.

The inverse isotope effect is attributed to the effective increase of the Pd-H force constant, $k_{\text{Pd-H}}$, over $k_{\text{Pd-D}}$, due to enhanced anharmonicity of the H motion, as originally proposed by Ganguly. Rahman *et al.*[16] have found, by analyzing their neutron scattering measurements on $PdH_{0.63}$, and comparing them with the $PdD_{0.63}$ data,[17] that $k_{\text{Pd-H}} \approx 1.2\, k_{\text{Pd-D}}$, which leads to a 20% increase in $\langle\omega^2\rangle_D M_D/M_H$. We show here that this increase is enough to account quantitatively for the observed inverse isotope effect.

The x dependence of T_c in PdH_x (PdD_x) is mainly due, according to the present analysis, to a rapid increase of the average electron–optic-phonon (i.e., H or D vibration) interaction, λ_{opt}, as x approaches 1. Although the total electronic DOS decreases as x increases, the H- or D-site components of the DOS (see Fig. 1) rise[6,18] in a way such that λ_{opt} increases with x. In effect, more electrons are found in the vicinity of the H or D sites with increasing H or D concentration. This effect continues for $x > 1.0$, and we argue that this is the explanation for the enhanced T_c's in the palladium–noble-metal hydrides.

Our detailed calculations of T_c are based on solutions to the linearized Eliashberg equations,[19] which have as input the quantities $\alpha^2(\omega)F(\omega)$ and μ^*. Here $F(\omega)$ is the phonon DOS; $\alpha^2(\omega)$ contains the pairing electron-phonon interaction; and μ^* is the pair-breaking Coulomb pseudopotential. We calculated T_c also using the McMillan-type[20] equation proposed by Allen and Dynes[21] with results which agree within 10% of the Eliashberg-equation solutions.

Making use of the theory of Gaspari and Gyorffy,[22] and a generalization to compounds[23,24] of

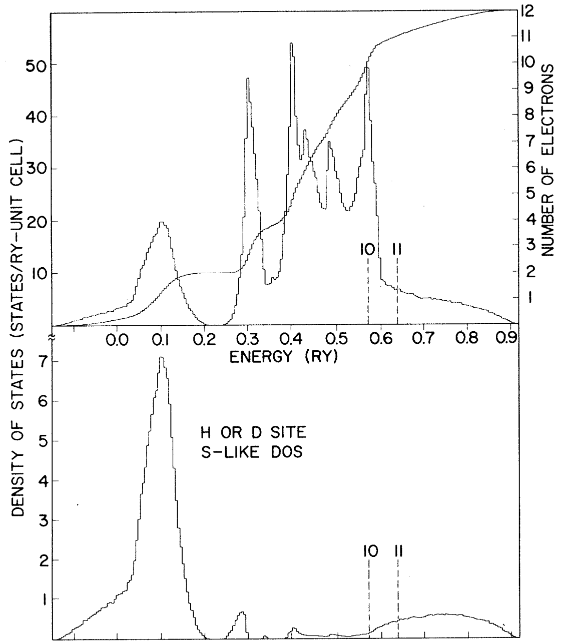

FIG. 1. Calculated electronic densities of states for PdH or PdD vs energy. The vertical dashed lines show the location of the Fermi level, E_F, for ten or eleven electrons per unit cell ($x = 0.0$ and 1.0, respectively).

McMillan's[20] "constant-α^2" approximation, one can arrive at the following expressions:

$$\alpha^2(\omega)F(\omega) = \alpha_{\rm Pd}^2 F_{\rm Pd} + x\alpha_{\rm H(D)}^2 F_{\rm H(D)}, \tag{1}$$

$$\alpha_j^2 = (\eta_j/2M_j)\langle\omega\rangle_j, \tag{2}$$

$$\eta_j = \frac{E_F}{\pi^2 N} \times \sum_{l=0}^{2} \frac{2(l+1)\sin^2(\delta_{l+1,j} - \delta_{l,j}) N_{l+1,j} N_{l,j}}{N_{l+1,j}^{(1)} N_{l,j}^{(1)}}. \tag{3}$$

The index j denotes an atom in the unit cell of atomic mass M_j; and $F_j(\omega)$ is the projected, or site-decomposed phonon DOS for atom j. The scattering phase shifts ($\delta_{l,j}$); total electronic DOS (N); the site-angular-momentum decomposed DOS ($N_{l,j}$); and the free-scatterer DOS ($N_{l,j}^{(1)}$) are all evaluated at the Fermi level, E_F.[22-24] The factor x shown in Eq. (1) arises because only occupied H or D sites make a contribution to the electron-phonon interaction. There is also an implicit x dependence contained in E_F, which we discuss below. In addition, since $M_{\rm Pd} \gg M_{\rm H(D)}$, to very good accuracy $F_{\rm Pd}(\omega)$ and $F_{\rm H(D)}(\omega)$ are the acoustic- and optic-mode parts of the phonon spectra, respectively.[4,23,24] In what follows we will refer to the H (D) contributions to α^2F as the optic-mode part, and the Pd contribution as the acoustic-mode part.

Our evaluation of η_j is based on self-consistent, relativistic (without spin-orbit splitting) APW calculations for stoichiometric PdH, ($\rm PdD_1$) in the rock-salt structure, which were reported earlier.[4] Figure 1 shows the total DOS and the H (D) site-decomposed s-like DOS for $\rm PdH_1$ ($\rm PdD_1$). Two points should be emphasized regarding these DOS: (1) These curves are considerably more accurate than those used earlier,[4] because the present results are based on a QUAD[25] fit to the energy bands using 89 APW $\vec{k}$ points in the irreducible Brillouin zone (for those bands near E_F), versus 20 APW $\vec{k}$ points used previously[26]; (2) we use the same band structure for both PdH and PdD.

In order to obtain $\eta_j(x)$ we have used the rigid-band approximation (RBA), so that the x dependence in Eq. (3) is included implicitly through E_F, which is determined by filling the DOS of $\rm PdH_1$ ($\rm PdD_1$) to $(10+x)$ electrons. The RBA seems adequate for our present purposes in view of the facts that the DOS above $E_1 \cong 0.57$ Ry (see Fig. 1) depends only weakly on x[18]; and that the integral of the DOS up to E_1 is, by direct calculation, independent of x in the two limits $x = 0.0$ and $x = 1.0$ [ten electrons for both Pd metal and $\rm PdH_1$ ($\rm PdD_1$)]. For the phonon DOS we make use of the Born–von Kármán fits obtained by Rowe *et al.*[17] to their measured dispersion curves of $\rm PdD_{0.63}$, with a small adjustment to account for the slightly larger lattice constants[27] in the stoichiometric hydrides and deuterides. This adjustment was achieved by linearly extrapolating the Pd[28] and $\rm PdD_{0.63}$[17] results for $\langle\omega\rangle_{\rm ac}$ to $\rm PdD_{1.0}$, and gave a 6% decrease in $\langle\omega\rangle_{\rm ac}$ from its $x = 0.63$ value. The correction to $F_{\rm opt}(\omega)$ was found to be negligible.

For the hydride we used the same $F_{\rm ac}(\omega)$ as in the deuteride, but the optic mode part, $F_{\rm H}(\omega)$, was adjusted to take account of the experiment of Rahman *et al.*[16] on $\rm PdH_{0.63}$. We did this by uniformly shifting the "harmonic" $F_{\rm H}(\omega)$[17] ($M_{\rm D} \to M_{\rm H}$ only) upward in frequency, so as to obtain the 20% increase in $\langle\omega^2\rangle_{\rm H}$ over the "harmonic" value,[17] thus accounting for the 20% increase in the Pd-H force constant.[16]

Having thus the phonon DOS for $x = 1.0$, we neglected in our subsequent calculations its weak x dependence. The latter is largely cancelled by the implicit x dependence of $\eta_J(x, a_0(x))$ through the lattice constant, $a_0(x)$, which is also ignored in the RBA. Based on measurements of T_c under pressure,[11,29,30] and calculations[5,6] of the shifts in the $\rm PdH_1$ ($\rm PdD_1$) band structure under pressure, we estimate that our results for T_c could

TABLE I. Calculated and measured superconducting transition temperatures, T_c (in °K); calculated electron-phonon mass enhancement factors λ; and Coulomb pseudopotentials μ^* as a function of hydrogen concentration x in PdD_x and PdH_x. Here, $\mu^*(x) = 0.26N(E_\mathrm{F};\, x)/[1+N(E_\mathrm{F};\, x)]$.

		PdD_x				PdH_x			
x	μ^*	λ_tot	T_c(calc)	T_c(expt)[a]	T_c(expt)[b]	λ_tot	T_c(calc)	T_c(expt)[a]	T_c(expt)[b]
1.00	0.085	0.62	9.6	9.8	10.3	0.54	7.9	8.0	9.1
0.96	0.087	0.56	6.6	7.8	9.1	0.49	5.2	6.3	6.6
0.92	0.091	0.52	4.9	6.4	7.1	0.46	3.6	4.8	4.8
0.89	0.093	0.49	3.5	5.0	5.1	0.43	2.5	3.5	3.1
0.85	0.093	0.44	2.1	3.7	3.3	0.39	1.4	2.2	2.1
0.81	0.097	0.41	1.4	2.5	...	0.37	0.9	1.3	...
0.77	0.101	0.36	0.6	...	...	0.33	0.3	...	...

[a] Ref. 12. [b] Ref. 13.

be affected by up to 5% as a result of these omissions.

The Coulomb pseudopotential μ^* was estimated for both PdD_x and PdH_x by using the formula of Bennemann and Garland.[31] With this formula, μ^* shows a fairly weak dependence on x, varying from 0.085 at $x = 1.0$, to 0.10 at $x = 0.77$.

The variables just described, along with the band-structure potentials, were used to determine the quantities in Eqs. (1)–(3), which were then used to obtain a solution of the Eliashberg equations for T_c. Table I shows our results for $T_c(x)$ for the hydrides and deuterides, along with the experimental results of Schirber and Northrup[12] and Miller and Satterthwaite.[13] Quite remarkably, the theory predicts the correct x dependence of T_c, including the proper magnitude of the opposite or inverse isotope effect, without any adjustment of parameters. We emphasize that our quantitative prediction for the inverse isotope effect is independent of the exact values of μ^* that we have used, provided only that μ^* is the same for both PdH_x and PdD_x.

Since the mechanism for the opposite isotope effect is included in the optic-mode contribution, this effect tends to go away as x decreases (see Table I). This is because the optic mode, or H (D) contribution to T_c decreases as x becomes smaller. This is shown in Fig. 2, where we plot the ratios of the optic (H or D) to the acoustic (Pd) contributions, $\alpha_\mathrm{opt}^2/\alpha_\mathrm{ac}^2$, and the values of $\lambda_j = \eta_j/M_j\langle\omega\rangle_j\langle\omega^{-1}\rangle_j^{-1}$, versus x for the two systems. These can be regarded as theoretical predictions to be checked by tunneling measurements done on the hydrides and deuterides.

The rapid decrease of $\alpha_\mathrm{opt}^2/\alpha_\mathrm{ac}^2$ as x decreases can, to some extent, explain the puzzling discrepancy between some of the tunneling measurements of Dynes and Garno,[7] and of Eichler, Wuhl, and Stritzker.[9] The former find that $\alpha_\mathrm{opt}^2/\alpha_\mathrm{ac}^2$ is very large (no structure was seen in the tunneling characteristics for the acoustic-mode region); while the latter find a value between 1 and 2. Although part of these differences can be explained by the experimental uncertaintites in measuring the high-frequency part of the tunneling spectrum, our theoretical results, which show a very strong composition dependence of $\alpha_\mathrm{opt}^2/\alpha_\mathrm{ac}^2$, indicates that this ratio is very sensitive to the actual H (D) concentration of the sample. Thus, tunneling measurements in well-characterized samples would be very important in further checking the present theory.

We have emphasized here that T_c rises with x

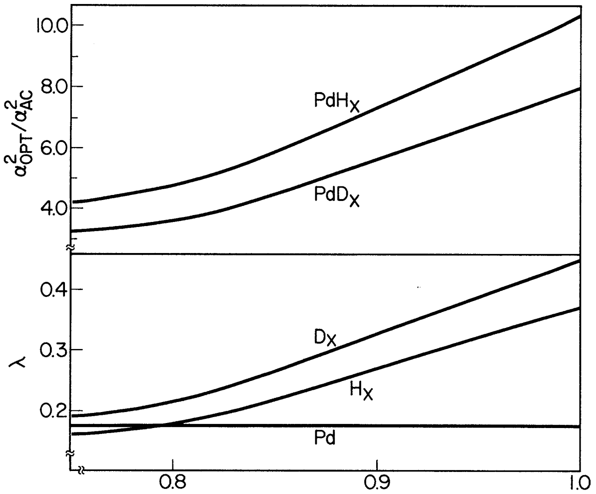

FIG. 2. Calculated ratios of the optic- to acoustic-phonon–mode contributions to the tunneling spectrum (upper panel), and values of $\lambda_j = \eta_j/M_j\langle\omega^2\rangle_j$ (lower panel) vs x in PdH_x and PdD_x.

mainly due to an increase in $\eta_{\mathrm{H(D)}}$, as a result of the H or D s-like DOS increasing with x. It can also be seen from Fig. 1, that an increase of x to values greater than 1.0 would further enhance T_c. We offer the explanation that this is the cause of the higher T_c's in the palladium-noble-metal hydrides investigated by Stritzker,[15] where it is found that T_c increases to values in excess of 10°K with the addition of Cu, Ag, or Au to Pd and the ion implantation of H or D. Alloying Pd with these noble metals allows the Fermi level to fall in a region corresponding to more than eleven valence electrons per unit cell, or $x > 1.0$ in our rigid-band model of PdH_x (PdD_x) Of course this argument is appropriate for relatively low concentrations of the noble metals, where the rigid-band model is expected to be valid.

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[1] T. Skoskiewicz, Phys. Status Solidi (a) 11, K123 (1972).

[2] B. Stritzker and W. Buckel, Z. Phys. 257, 1 (1972).

[3] B. N. Ganguly, Z. Phys. 265, 433 (1973), and B22, 127 (1975).

[4] D. A. Papaconstantopoulos and B. M. Klein, Phys. Rev. Lett. 35, 110 (1975).

[5] D. A. Papaconstantopoulos and B. M. Klein, unpublished.

[6] A. C. Switendick, Bull. Am. Phys. Soc. 20, 420 (1975).

[7] R. C. Dynes and J. P. Garno, Bull. Am. Phys. Soc. 20, 422 (1975).

[8] P. J. Silverman and C. V. Briscoe, Phys. Lett. 53A, 221 (1975).

[9] A. Eichler, H. Wuhl, and B. Stritzker, Solid State Commun. 17, 213 (1975).

[10] W. Buckel and B. Stritzker, Phys. Lett. 43A, 403 (1973).

[11] T. Skoskiewicz, A. W. Szafranski, W. Bujnowski, and B. Baranowski, J. Phys. C 7, 2670 (1974).

[12] J. E. Schirber and C. J. M. Northrup, Jr., Phys. Rev. B 10, 3818 (1974).

[13] R. J. Miller and C. B. Satterthwaite, Phys. Rev. Lett. 34, 144 (1975).

[14] J. M. E. Harper, Phys. Lett. 47A, 69 (1974).

[15] B. Stritzker, Z. Phys. 268, 261 (1974).

[16] A. Rahman, K. Sköld, C. Pelizzari, and S. K. Sinha, Phys. Rev. B 14, 3630 (1976).

[17] J. M. Rowe, J. J. Rush, H. G. Smith, M. Mostoller, and H. E. Flotow, Phys. Rev. Lett. 33, 1297 (1974).

[18] J. S. Faulkner, Phys. Rev. B 13, 2391 (1976).

[19] G. Bergmann and D. Rainer, Z. Phys. 263, 59 (1973); C. R. Leavens, Solid State Commun. 15, 1329 (1974).

[20] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[21] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).

[22] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 29, 801 (1972).

[23] B. M. Klein and D. A. Papaconstantopoulos, J. Phys. F 6, 1135 (1976).

[24] B. M. Klein, D. A. Papaconstantopoulos, and L. L. Boyer, in *Proceedings of the Second Rochester Conference on Superconductivity in d- and f-band Metals*, edited by D. H. Douglass (Plenum, New York, 1976), p. 339.

[25] F. M. Mueller, J. W. Garland, M. H. Cohen, and K. H. Bennemann, Ann. Phys. (N.Y.) 67, 19 (1971).

[26] This accounts for the differences in our present results for stoichiometric PdH (PdD) ($x = 1.0$), compared to those in Ref. 4.

[27] J. E. Schirber and B. Morosin, Phys. Rev. B 12, 117 (1975).

[28] A. P. Miller and B. N. Brockhouse, Can. J. Phys. 49, 704 (1971).

[29] W. Buckel, A. Eichler, and B. Stritzker, Z. Phys. 263, 1 (1973).

[30] J. E. Schirber, Phys. Lett. 46A, 285 (1973).

[31] K. H. Bennemann and J. W. Garland, in *Superconductivity in d- and f-band Metals*, AIP Conference Proceedings No. 4, edited by D. H. Douglass (American Institute of Physics, New York, 1972), p. 103.