lak, R. DiStefano, and D. Jepsen.

Note added.—The recently measured Si(2s) core spectra for SiO_2 exhibits only transitions to the lowest and third excited states of t_2 symmetry. From this it may be inferred that the two lowest excited states are derived from the antibonding $t_2{}^*$ and $a_1{}^*$ orbitals, and that the next or third excited state probably corresponds to the Si(3d)-derived t_2 orbital (details to be published.)

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*On leave from the Department of Applied Physics, University of Tokyo, Tokyo, Tokyo, Japan.

[1] F. C. Brown, in *Solid State Physics*, edited by F. Seitz, H. Ehrenreich, and D. Turnbull (Academic, New York, 1974), Vol. 29.

[2] R. Ludeke and L. Esaki, Phys. Rev. Lett. 33, 653 (1974), and Surface Sci. 47, 132 (1975).

[3] R. Ludeke and A. Koma, Phys. Rev. Lett. 34, 817 (1975).

[4] H. Ibach and J. E. Rowe, Phys. Rev. B 9, 1951 (1974), and 10, 710 (1974).

[5] G. Hollinger, J. Tousset, and Tran Minh Duc, in *Tetrahedrally Bonded Amorphous Semiconductors*, AIP Conference Proceedings No. 20, edited by M. H. Brodsky, S. Kirkpatrick, and D. Weaire (American Institute of Physics, New York, 1974), p. 102. See also discussions at end.

[6] J. E. Rowe, Phys. Lett. 46A, 400 (1974).

[7] F. C. Brown and O. P. Rustgi, Phys. Rev. Lett. 28, 497 (1972).

[8] R. Ludeke and A. Koma, Phys. Rev. Lett. 34, 1170 (1975).

[9] T. G. Heil and H. F. Schaefer, III, J. Chem. Phys. 56, 958 (1972).

[10] H. R. Philipp, J. Phys. Chem. Solids 32, 1935 (1971).

[11] K. Platzöder, Phys. Status Solidi 29, K63 (1968).

[12] T. H. DiStefano and D. E. Eastman, Phys. Rev. Lett. 27, 1560 (1971).

[13] G. A. D. Collins, D. W. J. Cruikshank, and A. Breeze, J. Chem. Soc., Faraday Trans. II 68, 1189 (1972).

[14] G. Wiech, in *Soft X-Ray Band Spectra*, edited by D. J. Fabian (Academic, New York, 1968), p. 59.

[15] M. H. Reilly, J. Phys. Chem. Solids 31, 1041 (1970).

[16] J. A. Tossell, D. J. Vaughan, and K. H. Johnson, Chem. Phys. Lett. 20, 329 (1973).

[17] G. Klein and H. U. Chun, Phys. Status Solidi (b) 49, 167 (1972).

[18] A. R. Ruffa, Phys. Status Solidi 29, 605 (1968).

[19] T. L. Gilbert, W. J. Stevens, H. Schrenk, M. Yoshimine, and P. S. Bagus, Phys. Rev. B 8, 5977 (1973).

[20] D. S. Urch, J. Chem. Soc. A 1969, 3026.

Superconductivity in the Palladium-Hydrogen System*

D. A. Papaconstantopoulos and B. M. Klein
George Mason University, Fairfax, Virginia 22030, and Naval Research Laboratory, Washington, D. C. 20375

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Band theory and phonon measurements are used to calculate the electron-phonon coupling constant λ for Pd and PdD. The results indicate that superconductivity is absent in Pd metal because of the large value of the Coulomb pseudopotential μ^*, and that superconductivity occurs in PdD primarily because of coupling with the optic phonons. These results are consistent with superconducting transition-temperature measurements for these systems.

The possible technological applications[1] of metal-hydrogen systems have created great interest in the study of these systems both experimentally and theoretically. In particular, Skoskiewicz[2] and Stritzker and Buckel[2] found that the superconducting transition temperature T_c of PdH increases as a function of H concentration. These measurements stimulated several theoretical investigations of this phenomenon.

Bennemann and Garland[3] attribute superconductivity in PdH to the quenching of the spin fluctuations and the decrease of the Coulomb interaction of the d electrons of Pd. Hertel[4] concludes that the optical phonons, which correspond almost entirely to hydrogen vibrations in PdH, do not play an important role. In direct contradiction to these explanations we will show in this paper that hydrogen has the major contribution to the electron-phonon interaction parameter λ which determines T_c. Our results are consistent with the neutron-scattering experiments of Rowe *et al.*,[5] and are also in agreement with the work of Ganguly[6] who concludes that the optic modes of PdH may give a significant contribution to the electron-phonon coupling.

We have approached the problem from the point of view of a generalized form of McMillan's strong-coupling theory[7-9] which approximates the electron-phonon coupling constant by the expression

$$\lambda = \frac{n(E_F)\langle I^2\rangle_{Pd}}{M_{Pd}\langle\omega^2\rangle_{Pd}} + \frac{n(E_F)\langle I^2\rangle_H}{M_H\langle\omega^2\rangle_H}, \quad (1)$$

where $n(E_F)$ is the spin density of states at the Fermi level, $\langle I^2\rangle$ is an average over the Fermi surface of the square of the electron-phonon matrix element, M is the atomic mass, and $\langle\omega^2\rangle$ is the second moment of the phonon frequencies, as defined in Ref. 7, weighted by the amplitudes of vibration at each site. We wish to stress here that Eq. (1) is valid since the ratio M_H/M_{Pd} is small (~0.01), and because of this, in a given phonon mode, essentially only one of the atoms vibrates: Pd in the acoustic modes and H in the optic modes.

We have then used the Gaspari-Gyorffy[9] (GG) theory with the same refinements made in our earlier work on transition metals and transition-metal carbides.[8] The GG theory has been criticized for invoking spherical bands to obtain the final expression for $n(E_F)\langle I^2\rangle$. John,[10] however, using a form of multiple-scattering theory developed by Gyorffy and Stott[11] and also used by Gomersall and Gyorffy,[12] rederived the GG formula and showed that it is exact for cubic crystals if it is taken within the muffin-tin spheres. The exact equation is

$$n(E_F)\langle I^2\rangle = \frac{E_F}{\pi^2 n(E_F)}\sum_{l=0}^{2} 2(l+1) \times \sin^2(\delta_{l+1}-\delta_l)\frac{n_{l+1}n_l}{n_{l+1}^{(1)}n_l^{(1)}}, \quad (2)$$

where E_F is the Fermi energy, n_l are the angular momentum components of the electronic density of states (DOS), δ_l are scattering phase shifts, and $n_l^{(1)}$, called free-scattering DOS, are given by,

$$n_l^{(1)} = (\sqrt{E_F}/\pi)\sum_l(2l+1)\int_0^{R_s} dr\, r^2 R_l^2(r,E_F), \quad (3)$$

where R_l is the radial wave function and R_s the muffin-tin radius.

In order to calculate the right-hand sides of Eqs. (2) and (3) we have performed self-consistent energy-band calculations for both Pd and stoichiometric PdH(D) using Slater's augmented-plane-wave (APW) method. Since the lattice constants[13] of PdD and PdH are almost identical, the band structures, within the APW model, will also be the same. These calculations were performed with the $X\alpha$ exchange parameters 0.702[14] for Pd and 0.777[15] for H(D), and included the mass-velocity and Darwin relativistic corrections.[16] Using perturbation theory[17] we have also calculated the spin-orbit splitting and found that it can be neglected since the values of the densities of states at the Fermi level will be shifted by less than 1%. Each iteration of the APW calculation was carried out for 32 k points in the fcc Brillouin zone. Convergence to better than 5 mRy for the energy eigenvalues was reached after five iterations. The levels corresponding to the atomic $4s$, $4p$, and $4d$ states of Pd and the $1s$ state of H were treated as bands while the inner levels of Pd were calculated "atomiclike" in each iteration. The final potential was used to calculate the energy eigenvalues and the electronic charges inside the APW spheres for 256 k points in the zone. These results were then interpolated to 48×10^5 k points by Mueller's QUAD method[18] to determine the total DOS and its angular momentum components n_l inside the APW spheres. For the n_l's we had to modify QUAD in in order to perform the integration[19]:

$$n_l = \sum_n \int_S \frac{Q_{n,l}(\vec{k})}{|\nabla E_n(\vec{k})|}\, dS, \quad (4)$$

where $Q_{n,l}(k)$ are the electronic charges inside the APW spheres as defined by Mattheiss, Wood, and Switendick.[20] Table I lists the values of the total and angular-momentum-decomposed DOS inside the APW spheres for Pd and PdH at the Fermi level. It is interesting to note that the DOS of both Pd and PdH are dominated by the d-like DOS of the Pd site. We also note from Table I that the total DOS of elemental Pd is about a factor of 3 larger than that of PdH.

We have calculated λ for Pd and PdH using Eqs. (1)–(4) with the phonon moments for Pd computed using the experimental phonon DOS of Miller and Brockhouse,[21] and for PdD, the like quantity from Rowe *et al.*[5] who did neutron-scattering experiments for $PdD_{0.63}$. Extrapolating from $PdD_{0.63}$ to stoichiometric PdD could possibly introduce some new structure into the phonon dispersion curves, but since the scale of the optic modes is mainly determined by the Pd-D nearest-neighbor interaction, our results using the phonon DOS[5] should be adequate. Calculations for superconductivity in PdH cannot be done until the phonon spectrum of this material is measured.

Our results for λ and the other quantities entering our calculation are listed in Table I. They show that the major contribution to λ in PdD comes from D and is due to the low-lying optic-

TABLE I. Quantities entering into the superconductivity calculations for Pd and PdD.

	Pd	Pd in PdD	D in PdD
Densities of states [states/(Ry unit cell spin)]			
$n(E_F)$	15.052	4.224	
n_s	0.141	0.069	0.379
n_p	0.156	0.143	0.046
n_d	14.435	3.294	0.006
n_f	0.063	0.014	0.002
Phase shifts			
δ_0	−0.223	−0.421	1.072
δ_1	−0.024	−0.115	0.037
δ_2	−0.304	−0.389	0.001
δ_3	0.002	0.003	0.000
Ratios $n_l/n_l^{(1)}$			
s	0.334	0.233	1.082
p	0.324	0.429	0.514
d	7.204	1.669	1.167
f	5.273	1.063	12.201
$n(E_F)\langle I^2\rangle$ (eV/Å^2)	3.591	1.279	0.623
$M\langle\omega^2\rangle$ (eV/Å^2)	7.546[a]	5.971[b]	0.863[b]
λ	0.47	0.21	0.72

[a] Ref. 21.
[b] Ref. 5.

mode branches in which essentially only the D atoms vibrate. It should be noted that $n\langle I^2\rangle \simeq \frac{1}{2}n \times \langle I^2\rangle_{\text{Pd}}$ and $M_{\text{D}}\langle\omega^2\rangle_{\text{D}} \simeq \frac{1}{7}M_{\text{Pd}}\langle\omega^2\rangle_{\text{Pd}}$ and their ratio gives $\lambda_{\text{D}} \simeq 3\lambda_{\text{Pd}}$ in contradiction to the prediction of Hertel[4] that $\lambda_{\text{D}} \simeq 0.2\lambda_{\text{Pd}}$. In typical binary compounds, the values of $M\langle\omega^2\rangle$ are approximately the same for both sites, while in the deuteride they differ by a factor of 7. This signals a very large mean squared displacement for D in PdD and is indicative of a large zero-point motion and anharmonicity. We are currently investigating how this anharmonicity might modify the electronic band structure and how it is related to the inverse isotope effect.[2,22] Our calculated λ from the GG theory[9] is not consistent with the value obtained from our calculated total density of states and the measurement of the electronic coefficient of the specific heat of PdH.[23] The discrepancy may be due either to the anharmonicity of the H atoms or to the fact that the experiment was done on a nonstoichiometric crystal.

For pure Pd we have calculated $\lambda = 0.47$, and therefore many-body effects, such as paramagnons,[24] suppress superconductivity. From the measurements of Choteau *et al.*,[25] we have calculated the specific heat λ to be 0.7. This value presumably includes additional contributions other than the electron-phonon interaction.[24,26] The many-body effects would manifest themselves in a large value of μ^* in a McMillan type of equation. We find that μ^* must be at least 0.28 in order to account for the fact that Pd is not superconducting.

Before discussing the calculation of T_c from these results, it is important to comment on the accuracy of our calculation of λ. Comparing our self-consistent (SC) energy-band calculations with the non-self-consistent (NSC) ones of Mueller *et al.*[26] for Pd, and of Switendick[27] for PdH, we see that the total DOS at the Fermi level differs by less than 3% in Pd but by about 25% in PdH. We also expect to have discrepancies in the values of the partial DOS n_l which depend on the electronic charges Q_l. We have checked the Q_l's for several states and found differences of about 15% for s states and 3% for d states between SC and NSC calculations. We have also noted differences in the phase-shift terms $\sin^2(\delta_{l+1} - \delta_l)$ of about 70% between SC and NSC potentials for the Pd site and about 10% for the H site. We therefore conclude that although the NSC calculations of Switendick lead to the same qualitative result,[28] namely the importance of optic modes in PdH, they should be used with caution for any quantitative evaluation of λ. Having carried our calculations to self-consistency and included relativistic effects, we find that the most serious uncertainty is in the interpolation of the Q_l's to obtain the decomposed DOS. We estimate that this could lead to an error in the calculated λ of up to 10%.

To calculate the superconducting transition temperature (T_c) of PdD, we have used Dynes's[29] modification of McMillan's equation,[7]

$$T_c = \frac{\langle\omega\rangle}{1.2}\exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right). \tag{5}$$

We have calculated $\langle\omega\rangle$ using the phonon-spectra measurements of Rowe *et al.*,[5] weighting the contributions from the acoustic and optic modes using our calculated values of λ_{Pd} and λ_{D} to estimate α^2 for each site.[7,30] In view of the large value of μ^* we have inferred for pure Pd, the value for PdD is somewhat uncertain. In Table II we show calculated T_c's for three values of μ^*. We see that our calculations of T_c show that the measured value[2] of 11°K can be reproduced for a $\mu^* = 0.22$ which is higher than the value generally ascribed to transition-metal compounds, and is likely to be related to the large value of μ^* in pure Pd. Quantitative calculations of T_c for PdH

TABLE II. Variation of T_c with μ^* for PdD.

μ^*	T_c (°K)
0.10	25.6
0.22	11.0
0.30	4.3

as well as a discussion of the inverse isotope effect[2] in PdH(D) will have to await the phonon measurements in this system.

Our prediction that the electron–optic-mode coupling is the dominant mechanism for superconductivity in the palladium-hydrogen system has been verified by the tunneling measurements of Dynes and Garno.[31]

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[1] Proceedings of the International Conference on Hydrogen in Metals, Jülich, Germany, 1972 [Ber. Bunsenges. Phys. Chem. 76, 705 (1972)].

[2] T. Skoskiewicz, Phys. Status Solidi (a) 11, K123 (1972); B. Stritzker and W. Buckel, Z. Phys. 257, 1 (1972).

[3] K. H. Bennemann and J. W. Garland, Z. Phys. 260, 367 (1973).

[4] P. Hertel, Z. Phys. 268, 111 (1974).

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

[6] B. N. Ganguly, Z. Phys. 265, 433 (1973).

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

[8] B. M. Klein and D. A. Papaconstantopoulos, Phys. Rev. Lett. 32, 1193 (1974).

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

[10] W. John, J. Phys. F: Metal Phys. 3, L231 (1973).

[11] B. L. Gyorffy and M. J. Stott, Solid State Commun. 9, 613 (1971).

[12] I. R. Gomersall and B. L. Gyorffy, J. Phys. F: Metal Phys. 4, 1204 (1974).

[13] B. Baranowski, S. Majchrazak, and T. B. Flanagan, J. Phys. F: Metal Phys. 1, 258 (1971).

[14] K. Schwarz, Theor. Chim. Acta 34, 225 (1974).

[15] J. C. Slater, Int. J. Quant. Chem. S7, 533 (1973).

[16] T. L. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967); J. O. Dimmock, Solid State Phys. 26, 103 (1971).

[17] L. L. Boyer and B. M. Klein, to be published.

[18] F. M. Mueller, J. W. Garland, M. H. Cohen, and K. H. Bennemann, Ann. Phys. (New York) 67, 19 (1971).

[19] J. W. McCaffrey and D. A. Papaconstantopoulos, Solid State Commun. 14, 1055 (1974).

[20] L. F. Mattheiss, J. H. Wood, and A. C. Switendick, *Methods in Computational Physics* (Academic, New York, 1968), Vol. 8.

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

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

[23] C. A. Mackliet, D. J. Gillespie, and A. I. Schindler, Solid State Commun. 15, 207 (1974).

[24] N. F. Berk and J. R. Schrieffer, Phys. Rev. Lett. 17, 433 (1966).

[25] G. Choteau, R. Fourneaux, K. Gobrecht, and R. Tournier, Phys. Rev. Lett. 20, 193 (1968).

[26] F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdyna, Phys. Rev. B 1, 4617 (1970).

[27] A. C. Switendick, Ber. Bunsenges. Phys. Chem. 76, 535 (1972).

[28] A. C. Switendick, Bull. Amer. Phys. Soc. 20, 420 (1972).

[29] R. C. Dynes, Solid State Commun. 10, 615 (1972).

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

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