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REVIEW OF RECENT LITERATURE ON PALLADIUM HYDRIDES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The motivation for this report is to collect my ideas, reviews of other people's articles, computations, etc. re superconductivity in the Pd-M-H systems (where M is a metal, particularly a noble metal). This is not meant to be anything close to an exhaustive review (see particularly the article by Stritzker and Wuhl in "Hydrogen in Metals II," Eds. Alefeld and Volkl, 1978, Reference 1 and A. C. Switendick, Ibid, Reference 1A). The main purpose is simply to examine and tie together a number of separate ideas and define areas of critical experimentation to test these ideas.		

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I. REVIEW OF GENERAL THEORY

This section is not meant to be a capsule history of progress in superconductivity but is rather an attempt to give some background for the theory being applied here to superconductivity in palladium hydrides.

In 1957 Bardeen, Cooper and Schrieffer² (BCS) developed a microscopic theory of superconductivity. According to BCS the transition temperature is given by

$$T_c = 1.14 \langle w \rangle \exp[-1/N(0)V] \quad (1)$$

where $\langle w \rangle$ is a typical phonon energy and $N(0)V$ is the interaction strength; $N(0)$ is the electron density of states at the Fermi surface and V is the pairing potential arising from the electron-phonon interaction.

It should be kept in mind that Eq. (1) is a weak-coupling approximation to

$$1 = N(0)V \int_0^{\langle w \rangle / 2kT_c} dx \frac{\tanh x}{x} \quad (2)$$

with $x = \epsilon / 2kT_c$. (Eq. (2) is Eq. (3,28) of Reference 2.) The asymptotic behavior if Eq. (2) is

$$T_c \rightarrow \frac{N(0)V}{2} \langle w \rangle. \quad (3)$$

Actually, since BCS theory is a weak-coupling theory, this result should not be taken too seriously.³

Since the BCS paper, much progress has been made in understanding the role of the electron-phonon interaction in normal and superconducting metals. Migdal⁴ showed that, in normal metals, the electron-phonon interaction could be treated accurately even for strong coupling to order $(m/M)^{1/2}$.

Eliashberg⁵ and Nambu⁶ extended the Migdal treatment to the superconducting state. Eliashberg Theory takes into account the retarded nature of the phonon-induced interaction and treats properly the damping of the excitations.

Based on the Eliashberg equations, McMillan⁷ made an extensive study of the relation between microscopic theory and observed superconducting transition temperature. The central result of McMillan's paper is his solution of the finite-temperature Eliashberg theory to find T_c for various cases, and the construction from this of an approximate equation relating T_c to a small number of simple parameters. (Evaluation of these parameters, however, is not at all simple.) McMillan's T_c equation is

$$T_c = (\theta_D/1.45) \exp\left(\frac{-1.64(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) \quad (4)$$

where θ_D is the Debye temperature, μ^* is an effective Coulomb repulsion reduced from the instantaneous repulsion μ by the fact that Coulomb coupling is propagated much more readily than phonon coupling, and

$$\lambda \equiv 2 \int_0^\infty \frac{dw \alpha^2(w) F(w)}{w} \quad (5)$$

with $\alpha^2 F(w)$ being the electron-phonon spectral function, $F(w)$ is the phonon density of states and $\alpha^2(w)$ represents the electron-phonon interaction, λ as defined by Eq. (6) is a dimensionless measure of the strength of $\alpha^2 F$.

Various modifications of the McMillan equation are frequently used:

Dynes⁸: The premultiplier $(\theta_D/1.45)$ is replaced by $\langle w \rangle / 1.20$.

$$\langle w^n \rangle = \frac{2}{\pi} \int_0^\infty dw \alpha^2(w) F(w) w^{n-1} \quad (6)$$

This is the "nth" moment of $g(w) = (2/\lambda w)\alpha^2 F$. (nth moment = $\int_0^\infty dw g(w)w^n$.)
This is the notation of Allen and Dynes³ and is consistent with McMillan.

Allen and Dynes³: The premultiplier is replaced by

$$\frac{F_1 F_2 w_{\log}}{112}$$

where $w_{\log} = \lim_{n \rightarrow 0} \bar{w}_n = \exp\left(\frac{2}{\lambda} \int_0^\infty \frac{dw}{w} \alpha^2 F(w) \ln w\right)$; F_1 is a function of λ and μ^* ;
 F_2 is a function of λ , μ^* , $\bar{w}_2$ and $w_{\log}$.

Roughly speaking, λ represents attraction and μ^* represents repulsion;
bigger λ leads to higher T_c ; bigger μ^* leads to lower T_c .

McMillan has shown that λ as defined by Eq. (5) can be written

$$\lambda = \frac{N(0) \langle I^2 \rangle}{M \langle w^2 \rangle} \quad (7)$$

where M is the ion mass and I is the electronic matrix element of the change
in the crystal potential U as one atom is moved

$$I(pp') = \int \psi_p^* (\epsilon_{pp'} + \nabla U) \psi_{p'} d\vec{r} \quad (8)$$

$\langle I^2 \rangle$ is the average over the Fermi surface of the square of I . While
Eq. (7) is rigorous, the relationship [Eq. (4) and modifications] between
 T_c and λ as defined by Eq. (5) - or Eq. (7) is not on such rigorous footing.
Eq. (4) and its modifications do, however, have considerable theoretical
justification (as good approximations) and considerable experimental verifi-
cation (again as good approximations).

One of the standard ways to obtain λ (by calculation) is to use the Gaspari-Gyorffy (GG) approximation.⁹ This is an approximation for the numerator (usually called η) of λ as given in Eq. (7) and expresses η in terms of scattering phase shifts and the decomposed electronic density of states (decomposed by atomic sites in real space and by angular momentum label ℓ). The central result of GG is to approximate $\eta = N(0) \langle I^2 \rangle$ by

$$\eta \approx \frac{2m}{\hbar^2} \frac{E_F}{N(E_F)} \sum_{\ell} \frac{2(\ell+1) \sin^2(\delta_{\ell+1} - \delta_{\ell}) n_{\ell} n_{\ell+1}}{n_{\ell}^{(1)} n_{\ell+1}^{(1)}} \quad (9)$$

where $N(E_F) = N(0)$, the δ_{ℓ} are the scattering phase shifts, n_{ℓ} is the density of states of angular momentum ℓ at E_F , and the $n_{\ell}^{(1)}$ are the "free scatterer" density of states. (In atomic units $\frac{2m}{\hbar^2}$ is replaced by 1.) Note: see also Evans, Gaspari, and Gyorffy, reference 10.

II. SALIENT EXPERIMENTAL POINTS IN PALLADIUM HYDRIDES

The first known enhancement of T_c due to H was Th_4H_{15} with T_c of 9°K discovered by Satterthwaite and Toepke.¹¹ (Pure thorium has $T_c = 1.37^\circ\text{K}$.)

Palladium Hydrides:

1. Pure Palladium is not superconducting down to 0.002°K (ref. 12 - this is ref. 2 of B. Stritzker, Phys. Rev. Lett. 42, 1769 (1979)).

2. In 1972, Skoskiewicz¹³ found superconductivity in $\text{PdH}_{0.87}$ with $T_c \sim 4^\circ\text{K}$. Skoskiewicz used an equilibrium technique putting the Pd in H_2 gas at pressures on the order of 10 kbar.

3. Also in 1972, Stritzker and Buckel,¹⁴ using an implantation technique achieved T_c 's of $\sim 9^\circ\text{K}$ and 11°K in PdH_x and PdD_x respectively. While x was

not known accurately, it was estimated to be about 1.0 in each case. The inverse isotope effect (T_c for PdD higher than T_c for PdH) should be noted. It appears that Pd/H ratios ≥ 0.8 are necessary to obtain superconductivity (in undamaged Pd).

Subsequent to Stritzker and Buckel, the Baranowski-Skoskiewicz group were also able to achieve T_c 's of this order in PdH_x and PdD_x .^{15,16}

4. In 1974, Stritzker¹⁷ demonstrated further increases in T_c upon addition of noble metals. Pd-Au-H, $T_{c\text{max}} = 13.6^\circ\text{K}$; Pd-Ag-H, $T_{c\text{max}} = 15.6^\circ\text{K}$; Pd-Cu-H, $T_{c\text{max}} = 17^\circ\text{K}$. The addition of Rh decreases T_c . It appears to be accepted as fact that there is a maximum T_c with respect to the noble metal concentration for each noble metal. The "optimum" Cu concentration is 45%, Ag $\approx 30\%$, Au $\sim 16\%$. Whether there is a maximum T_c with respect to H concentration is more controversial. Stritzker states that there is but it must be kept in mind that Stritzker does not have good control of his H concentration.

5. In 1979, Stritzker¹⁸ demonstrated that pure Pd, ordinarily not a superconductor, becomes superconducting by means of irradiation at low temperatures with He^+ ions with a maximum T_c of 3.2°K .

6. For Pd-Ni-H systems, Stritzker¹⁸ and also Baranowski and Skoskiewicz¹⁹ find an initial decrease of T_c as Ni concentration increases above 10%. The two groups differ for Ni concentrations above 10%. Stritzker finds very low T_c ; Skoskiewicz finds a second maximum in T_c at about 25% Ni.

7. Susceptibility: For both PdAg_x and PdH_x (or PdD_x) χ decreases (roughly linearly) with increasing x (see references 1 and 21). For PdAl_x susceptibility decreases very rapidly with x (see reference 21).

Comment: While, as Ruvalds²¹ states, this rapid decrease of χ with x makes PdAl_x a promising candidate for superconductivity, this factor is no guarantee. From Ruvalds' Figure 1, the χ vs. x curves for PdAg_x and PdH_x are quite similar; PdH_x (for high enough x) is superconducting, PdAg_x is not.

8. Density of states: The total density of states at E_F drops by a factor of about 4 to 6 on going from pure Pd to PdH. This is indicated both by experiment [specific heat, susceptibility - see references in Reference 1 (page 259 for specific heat) and in Reference 1A (page 107 for specific heat and for susceptibility)] and by calculation (Reference 1A - Switendick) and Reference 20 - Papaconstantopoulos, et al.

9. Pd-Al-H: Pd-In-H

For the H concentration giving momentum T_c for a given Al (or In) concentration, both systems show a very slight increase in T_c as Al (In) is added initially and then a drop in T_c - this drop is precipitous in Al and somewhat slower in In.²¹

III. BAND STRUCTURE EVIDENCE FROM CALCULATION

There are a large number of Pd, PdH, Pd-Ag-H, etc. band structure calculations in the literature (see references). Some earlier calculations by Switendick are very fruitful reading (see separate report by me (4/11/78) on his 1970 Solid State Commun. paper^{19A}).

Switendick^{19A} pointed out the fact that for PdH, using names like "proton" or "onion" model is much too simple - these names have connotations which just don't hold up. He also pointed out^{19B} that the H s-electrons fill three distinct types of states (1) the H-induced bonding states - well below E_F ; (2) the 0.36 hole in the d bands of Pd (near E_F); (3) The sp bands of Pd - well above E_F (see Reference 30, p. 146).

Papaconstantopoulos et al have published a series of papers on PdH(D)_x ²⁰ and Pd-Ag-H and Pd-Rh-H alloys²² (also see Miller and Satterthwaite³⁰). Two separate memos have been written on these papers (1978 - The comments on Pd-Ag-H refer to an earlier version of Reference 22). These are APW calculations. The authors use the Gaspari-Gyorffy approximation for η . The main thrust of these papers is that the s-like density of states at the hydrogen site is crucially important. The overall band structure is in reasonable agreement with Switendick's. The calculated total density of states at E_F shows the large drop on going from pure Pd to PdH as is observed experimentally.

IV. VARIOUS MODELS

The various models constructed to explain superconductivity in Pd hydrides fall into three categories: (1) Phenomenological, (2) Phenomenological but include attempts to put realistic quantitative values into a McMillan-like T_C expression or into some modification thereof, (3) Attempts to actually calculate some of the parameters that determine T_C from band structure calculation.

A. Phenomenological

1. Bennemann and Garland²³

(a) Spin-quenching: Pure Pd metal has unfilled d states. The spin fluctuations ("paramagnons") associated with these unfilled d states destroy superconductivity. In the BG view, the main function of H(D) in PdH(D) is to provide s electrons which tend to fill these d states, thus quenching the paramagnons; coupling between acoustic phonons and d electrons is then sufficient for superconductivity.

Comment: Everyone agrees that quenching of spin is necessary; the question is whether this alone is sufficient. I feel there is good reason to drop the BG model on both experimental and theoretical grounds.

Experimental: Alloying Pd with Ag also decreases the unfilled d states but doesn't lead to superconductivity (see ref. 33). Theoretical: Ganguly's 1973 paper²⁴ showed that quenching of spin alone, even under the most favorable coulomb condition ($\mu^* = 0$, i.e., complete quenching) leads to a $(\lambda^* - \mu^*)$ which is not large enough to account for the observed T_c .

(b) BG Explanation of Isotope Effect: BG explains the inverse isotope effect as a consequence of the smaller lattice for PdD than for PdH; they take the view that a smaller lattice constant is better for higher T_c .

Comment: This is contradicted by the observed²⁵⁻²⁷ negative dT_c/dP . One should note that this negative dT_c/dP does not bear on the BG suppression-of-spin idea.

2. Auluck²⁸: The point of view taken is that Pd is merely a host for "metallic" H.

Comment: This is contradicted by tunneling measurements. The sizeable contribution to $\alpha^2F(w)$ from Pd indicates that superconductivity isn't all from H. Skoskiewicz et al¹⁶ felt that the observed negative dT_c/dP contradicted Auluck's model; Rowe²⁴, however, feels that the tunneling data represent the strongest contradiction to the model. Skoskiewicz et al¹⁶ also felt that the observed inverse isotope effect contradicted the metallic hydrogen model - I suppose on grounds that some sort of interaction between Pd and H(D) is necessary to produce this inverse isotope effect.

3. Miller and Satterthwaite³⁰: The zero-point motion of H in PdH is larger than that of D in PdD. These authors postulate that this leads to differences in electronic properties. Utilizing Switendick's picture^{19B} of where the H s electrons go, MS argue that the large vibrations in the PdH case cause more overlap - thus, more H s electrons go into the PdH bonding states, leaving fewer for superconductivity.

Comment: This may be consistent with Ganguly's model (below). However, this MS model will give $\eta_D > \eta_H$. This difference, combined with a difference in $M \langle w^2 \rangle$ could well lead to a too-large inverse isotope effect. Calculations of electronic differences between PdH and PdD is beyond the present state-of-the-art of band structure calculation.

B. Phenomenological Combined with T_c Equations

1. Hertel³¹: Optical phonons don't play a role.

Comment: This idea seems pretty well contradicted by the tunneling measurements of Dynes and Garno³² for PdH and of Eichler et al³³ for PdH (see also Section 6.63 of Ref. 1). Hertel's model is also inconsistent with the calculations of Papaconstantopoulos et al.^{20,35,36} Hertel purports to show that if optic phonons influenced T_c , a regular isotope effect would result; I am not able to follow his argument.

Hertel's model is contradicted by the coherent neutron scattering measurements of Rowe et al.⁴³ For PdD_{0.63} these authors found large dispersion in the longitudinal optic modes (which are dominated by deuterium motion). They also found that the frequencies of the acoustic modes of PdD_{0.63} are considerable changed from those in pure Pd, again in contradiction to Hertel. These authors feel that a simple screened-pseudopotential calculation (such as Hertel's) is too oversimplified to explain the superconducting properties; calculation of the phonon dispersion relation in Pd hydrides must incorporate the complete electronic band structure results - their results are in accord with Switendick's^{19B} band structure calculation. (Rowe et al consider Hertel's model to be rigid-band.)

Finally, we note that Hertel has λ_H (in PdH) $\approx 0.2 \lambda_{Pd}$ (in PdH) (see his Eq. (3)); Papaconstantopoulos et al (Table II of Ref. 20) have λ_H (in PdH) $\approx 2.1 \lambda_{Pd}$ (in PdH).

2. Ganguly²⁴: (see also References 37, 38) Optic phonons play a major role.

The central point here is the addition of λ_{opt} (λ optical) to λ_{acc} (λ acoustical). Ganguly adds λ_{opt} by means of a three-square-well model

(a modification of the McMillan⁷ equation similar to that of Allender et al³⁴ for excitons) and gets values of T_c for PdH and PdD close to the observed values - including the opposite isotope effect. The opposite isotope effect is explained by the increased anharmonicity of H.

Strong support for Ganguly's model comes from the tunneling measurements³² on Al-oxide-PdH(D). These measurements showed pronounced structure in the current voltage curves at the appropriate place for H(D) optical phonons.

Eichler et al³³ consider that high energy local modes of D in PdD definitely share in the electron-phonon interaction leading to superconductivity; this conclusion is based on these modes showing up in the derivatives of the superconducting tunneling characteristic curves.

Ganguly's ideas are supported in a series of papers by Papaconstantopoulos et al.^{20,35,36}

Comment: Ganguly's model is consistent with most of the observed facts. One open question is associated with the existence of an optimum H/metal ratio for maximum T_c . Ganguly's explanation for such an optimum in Pd/noble metal/H, in terms of "preferential siting" - i.e., the H atoms preferring to sit in Pd-rich regions, remains to be tested. Also, the Ganguly model predicts that the inverse isotope effect should be accentuated in Pd/Cu/H (smaller "cage" size); this does not seem to be the case (see Reference 1 and Figure 3 of Reference 39) but this is not really clear-cut evidence against Ganguly's model.

While the views of Stritzker's group (see pp. 3 and 4 of Reference 44) are similar to Ganguly's regarding phonon modes, I believe there are some

differences. On page 246 of Reference 17, Stritzker says, "The difference in the maximum T_c values of the three Pd-noble metal-H systems can be described by the isotope effect...", Ganguly would say that force constants are involved (and not just mass as mass enters the BCS equation).

C. Actual Band Structure Calculation $\rightarrow T_c$ Parameters.

1. Papaconstantopoulos et al^{20,22,35,36} - These authors do APW calculations.

(a) PdD_x and PdH_x (primarily from Reference 20) - The band structure calculations were performed self-consistently for two choices of the exchange parameters within the $X\alpha$ scheme. Spin-independent relativistic corrections (i.e., the "scalar" corrections; mass-velocity and Darwin) were included explicitly. The rigid-band model is used for $x \neq 1.0$. From the band structure calculation they compute the density of states (decomposed by sites in real space and by angular momentum quantum number, ℓ). From the decomposed density of states they obtain η (the numerator of λ) using the Gaspari-Gyorffy approximation.⁹ A central feature of their calculation is the importance of the s-like density of states at the H(D) site. As contrasted to Miller and Satterthwaite, the present authors take the purely electronic properties of PdH and PdD to be identical, thus η_H equals η_D . $\alpha^2 F(w)$ for PdH(D) is taken as $\alpha^2_{Pd} F_{acc}(w)$ for $0 \leq w \leq w_1$ and as $\alpha^2_{H(D)} F_{opt}(w)$ for $w_2 \leq w \leq \infty$. $M\langle w^2 \rangle$ (the denominator of λ) is taken from experiment.⁴⁰ The Bennemann-Garland⁴¹ expression for μ^* is used:

$$\mu^* = \frac{0.26n(E_F)}{1 + n(E_F)} \quad (10)$$

Using these parameters, the linearized Eliashberg equations⁵ are solved following the formulation of Leavens.⁴² They have also obtained solutions for T_c using the Allen and Dynes³ equation. Their calculated results for T_c are about 1°K higher using Allen and Dynes than those using the Eliashberg equations. These T_c results are in good agreement with measured values and are consistent with Ganguly's model.

Comment: It is important to note that the ratio

$$M \langle w^2 \rangle_H = 1.2 M \langle w^2 \rangle_D \quad (11)$$

is taken from experiment.⁴⁰ With such a ratio one is well on the way to obtaining the inverse isotope effect. I feel that the major "confirmation" of Ganguly's model by these authors is that they not only get (with no adjustable parameters) an inverse isotope effect but also obtain values agreeing with the experimental values both as to individual (PdH and PdD) values of T_c and as to the relative difference in T_c .

In Reference 36, the Coherent-Potential Approximation (CPA) is used for PdH_x. The electron-phonon interaction and T_c as a function of x are in good agreement with experiment and with the rigid-band calculation.²⁰ The CPA results³⁶ for the electronic-specific-heat coefficient as a function of x are in excellent agreement with experiment while the results²⁰ of the rigid-band model are not. The CPA results are consistent with the central conclusion of Reference 20; namely, that the increase of T_c with x is mainly due to the increase of the hydrogen-site electron-phonon interaction η_H , which in turn is due to the increase with x of the s-like density of states at the H site.

(b) Pd-Ag-H (primarily Reference 22) - The band structure calculation for $\text{Pd}_{1-y}\text{Ag}_y\text{H}_x$ (and $\text{Pd}_{1-y}\text{Rh}_y\text{H}_x$) was performed using the APW method and procedures similar to that of Reference 20. The present calculations are not carried to self-consistency. The virtual crystal approximation (for y) and the rigid-band model (for x) are used. Equation (11) is used. T_c is calculated from the Allen and Dynes³ equation. The authors feel that the assumptions made are well justified within the ranges of x and y used. Results for T_c are in good agreement with experiment. One adjustable parameter μ^* , is now used. The importance of the s-like density of states at the H site is again stressed.

Comment: It is important to note that the "calculated" maximum T_c with respect to Ag concentration is not pure calculation but uses an empirical fact as input - namely, the assumption that one can't get H above a certain concentration and that this "maximum H content" decreases as the Ag concentration increases. This supports ideas of Baranowski/Skoskiewicz. Without the assumption, the values of T_c in Reference 22 would simply increase as y increases (no maximum).

We note that for $\text{Pd}_{0.7}\text{Ag}_{0.3}\text{H}_x$ n_{SH} appears to be increasing through $x = 1.0$. This does not lend any support to getting a maximum T_c with respect to H concentration. n_{total} is decreasing in this range. (n_{SH} and n_d for PdH_x behave qualitatively similarly to the $\text{Pd}_{0.7}\text{Ag}_{0.3}\text{H}_x$ case.)

Summary of models:

1. Spin quenching is necessary but not sufficient.
2. Optic phonons play a major role.

3. The increased anharmonicity of H (over D) can give an inverse isotope effect through

$$M\langle w^2 \rangle_H = cM\langle w^2 \rangle_D$$

with $c = 1.2$ (and not 1.0) and with $\eta_H = \eta_D$.

4. The calculations of Papaconstantopoulos et al are consistent with Ganguly's model.

5. Ganguly's model, while leaving some questions open, seems as good a starting point as any.

6. The Miller-Satterthwaite idea of anharmonicity contributing to an electronic difference in PdH(D) (and to $\eta_D > \eta_H$) cannot yet be ruled out.

V. PROPOSED DIRECTIONS

A. Experimental

(1) Measurement of T_c of PdH_x and PdD_x with good control on x. Just getting a good H profile would be an important step. Also try to settle the question of the existence of a maximum T_c with respect to H concentration. (The papers of Stritzker et al indicate that such a maximum exists; the Baranowski/Skoskiewicz group do not see any evidence of such a maximum - see page 332 of Reference 15, for example. For definite statements by Stritzker see page 2 of Reference 14, Reference 1, etc.)

(2) As in (1) above but for Pd_{1-y}M_yH_x (and Pd_{1-y}M_yD_x) where M is Cu, Ag or Au. (Again Stritzker et al believe that a maximum T_c with respect to x exists - see, for example page 403 of Reference 45 and page 262 of Reference 17.) The existence of a maximum T_c with respect to y seems pretty well

established. (See also Section II4 of this report.)

(3) Possible preferential occupancy of Pd-rich regions when H is added to, say, $\text{Pd}_{(1-y)}\text{Ag}_y$. This is an idea of Ganguly's³⁸ to explain the (assumed) maximum in T_c with respect to H concentration in Pd-noble metal-H systems. This question is associated with (2) above but is also of interest in its own right. (Note: If there really is no maximum T_c with respect to H concentration in these systems, this question of preferential siting becomes less important.) This, if it exists, would be one way in which increased H could lower T_c and would provide a competing mechanism to:

(a) Increased H $\rightarrow$ more optic phonon interactions $\rightarrow$ higher T_c .

(b) Increased H $\rightarrow$ larger lattice $\rightarrow$ higher T_c .

Testing this idea will require sets of phonon spectrum measurements. I suggest, in $\text{Pd}_{(1-y)}\text{Ag}_y\text{H}_x$, say, keeping x fixed (at about 0.6, say) and increasing y - see where spectrum starts to change. Ganguly's idea requires that $f_{\text{Ag-H}}$ be greater than $f_{\text{Pd-H}}$.

(4) Measurement of T_c in $\text{Pd}_{1-y}\text{Ni}_y\text{H}_x$ with good control on x (and y) one wants that x which gives maximum T_c for a given y. (See section II6 of this report.) I don't know if the Ni-H force constant is known. The Baranowski and Skoskiewicz¹⁹ curves look too smooth to indicate a phase change. Can Ni be converting some of its own s electrons into d electrons? (Auluck²⁸ suggests such an idea for PdH - addition of H inducing Pd to convert some of its s-electrons into d-electrons.)

In my opinion, while this (possible) second maximum in Pd-Ni=H is very intriguing, this is not the key to superconductivity in the Pd hydrides.

(5) Try Pd-In-H. This would check Ruvald's²¹ measurements but now with good control on the H concentration.

(6) Possibly look at radiation damage. Stritzker¹⁸ has done this for pure Pd (see Section II5 of this report). It would be interesting to start with superconducting PdH, say, and then apply radiation damage, noting the effect on T_c .

B. Theoretical/Experimental

Pursue Ganguly's idea of adding another element to "utilize the portion of the phonon spectrum between the acoustical Pd mode and optical H mode". This third element would (according to Ganguly) have to form its own sublattice - it's not sufficient to just go onto the Pd lattice substitutionally.

C. Calculation

(1) Pursue an idea of Stritzker and Luo⁴⁶ regarding the observed maximum in T_c with respect to noble metal concentration. They suggest that increasing the noble metal concentration increases the screening of the H electrons - this should cause a decrease in the electron-phonon interaction (decrease in λ) and also a decrease in the coulomb repulsion (decrease in μ). The former effect tends to decrease T_c , the latter to raise T_c . The interplay between these two effects could cause the observed maximum. I have done some very preliminary and purely numerical computations on this.⁴⁷

(2) Continuation of band structure calculation - The main computer program for band structure calculation (using the MPW method) of $\text{PdH}_{1.0}$ is "BSNACL" this program does not yet have provision for relativistic corrections. It does have the perturbation procedure for computing hydrostatic ΔE . It does not include self-consistency and is not set up to do PdH_x for $x \neq 1.0$.

To a large extent, good band structure calculations for PdH_x have already been done by Papaconstantopoulos et al. The feature we have that he does not have is the ability to compute small ΔE shifts. Those authors would circumvent this by calculating both E° (for lattice constant a_0) and E' (for lattice constant a_1). This is probably adequate for entities like total (and decomposed) density of states at E_F (the important band structure parameter for superconductivity considerations).

They probably cannot get good ΔE values for specific $E(k)$ due to their procedure having no "fixed zero" of potential (see pages 94 and 95 of Reference 47).

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