Theory of superconductivity in palladium–noble-metal hydrides

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The tight-binding coherent-potential approximation is used to calculate the electron densities of states for various concentrations of palladium–noble-metal hydrides. Our results are used to give a satisfactory explanation of the mechanism of superconductivity in these systems and to predict the variation of the phonon moments as a function of noble-metal concentration.

During the last ten years the phenomenon of superconductivity in the palladium-hydrogen system has been studied extensively.[1] It is now well accepted that the soft optic-mode phonon frequencies that are associated with local hydrogen vibrations are the primary reason for the occurrence of superconductivity in this system.[2] It has also been shown[3] that these low phonon frequencies couple in PdH, unlike other hydrides, with a relative high density of s-like hydrogen-induced states at the Fermi level (E_F). This coupling produces a strong electron-phonon interaction mainly on the hydrogen sites[3] which is responsible for the high transition temperature $T_c \approx 10$ K for PdH.

In 1974 Stritzker[4] reported even higher T_c's of 16.6, 15.6, and 13.6 K for Pd-Cu, -Ag, and -Au alloys, respectively, charged with large amounts of hydrogen by ion implantation. These measurements showed an increase of T_c to the maxima cited above and subsequent decrease to practically 0 K at high noble-metal content. Since that time there has been no quantitative calculation of T_c for these materials. One of the present authors and his co-workers attempted[5] an evaluation of the electron-phonon coupling λ and T_c in Pd-Ag-H. However, this calculation should not be considered very reliable since the virtual-crystal approximation (VCA) was made to simulate the substitutional disorder between Pd and Ag. A better calculation of the electronic structure of Pd-Ag-H was done by Temmerman and Pindor[6] using the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA), but these authors do not address the problem of superconductivity in any quantitative manner.

We have now performed state-of-the-art calculations of the electronic states of the Pd–noble-metal hydrides using a tight-binding form of the coherent-potential approximation (TB-CPA),[7] and use the results in the evaluation of the superconducting properties of these alloys. In our CPA model we have a metal sublattice in which the sites are randomly occupied by metal A or B, and a hydrogen sublattice where the sites are randomly either vacant or occupied by H. The procedure we describe below differs from the early[8] TB-CPA calculations in two respects:

(1) Our Slater-Koster (SK) Hamiltonians for the stoichiometric hydrides are much more accurate than those used by other workers.

(2) Previous[8] TB-CPA calculations freeze the s and p bands in transition metals and apply a so-called one-level TB model which ignores the coupling of t_{2g} and e_g orbitals. In our calculations we use five coupled CPA conditions corresponding to the self-energies of s, p, t_{2g}, e_g, and s_H symmetry.

Our calculations proceed as follows. We first generate scalar-relativistic and self-consistent band structures for the pure hydrides PdH, AgH, CuH, and AuH by the augmented-plane-wave (APW) method. Second, we obtain highly accurate (rms error less than 5 mRy for 7 bands) three-center orthogonal SK fits to the APW energy bands. The size of our Hamiltonian is 10×10, i.e., it contains s-, p-, and d-like orbitals on the metal site and an s-like orbital on the hydrogen site. We then use the CPA employing an effective Hamiltonian that contains five self-energies Σ_l, (where $l = s$, p, t_{2g}, e_g, and s_H) neglecting off-diagonal disorder, and approximating the off-diagonal matrix elements by an average of the pure hydride parameters weighted according to the concentration of the particular alloy. We contend that when the TB-CPA is employed with these improvements, the resulting densities of states (DOS's) are comparable to those of the KKR-CPA calculations, as shown below.

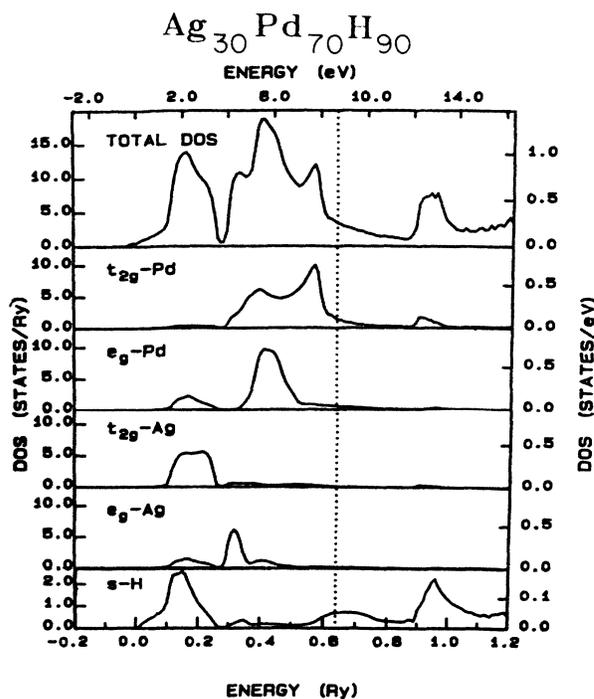In Fig. 1 we show the CPA densities of states for

FIG. 1. Densities of electronic states for $Ag_{0.30}Pd_{0.70}H_{0.90}$: total DOS, t_{2g} and e_g DOS for Pd and Ag sites, and hydrogen-site DOS.

$Pd_{0.7}Ag_{0.3}H_{0.9}$. This figure shows the total DOS of the alloy, the Pd- and Ag-site d-like DOS's separated into t_{2g} and e_g symmetries, and the H-site DOS. We note that the d states of Pd and Ag are clearly separated with the d states of Pd being nearer the Fermi level E_F. This separation of the two d bands is not seen in the VCA calculations and cannot be reproduced by any rigid-band argument; it is a true effect of alloying which is given only by the CPA theory. In addition, looking at the H-site DOS we identify the low-lying bonding states (bonding between s-H, e_g-Pd, and t_{2g}-Ag states) and above E_F the antibonding states (bonding between s-H and t_{2g}-Pd states). Table I lists the total and site-decomposed DOS's at E_F for various compositions in $Pd_{1-y}Ag_yH_x$. Where available the value of the KKR-CPA calculations of Temmerman and Pindor[6] are also included, to demonstrate the level of agreement between these two methods. Considering the different forms of CPA used and the fact that Temmerman and Pindor[6] employed non-self-consistent potentials with an $\alpha = 1$ exchange coefficient (while our calculations of the periodic structures are self-consistent and use the $X\alpha$ exchange) there is satisfactory agreement between the two calculations.

We have also performed TB-CPA calculations for $Pd_{1-y}Cu_yH_x$ and $Pd_{1-y}Au_yH_x$. In these systems the DOS's display a similar behavior with the exception that the separation of the two metal d-band complexes is less pronounced.

Our DOS values at E_F can be used to calculate the electronic specific-heat coefficient γ and the electron-phonon coupling λ. The quantity λ, which enters both in the determination of γ and of the superconducting temperature T_c, is found from[9]

$$\lambda = \sum_i \frac{\eta_i}{M_i \langle \omega_i^2 \rangle} , \qquad (1)$$

where the index i indicates the lattice sites, i.e., metal or hydrogen, η_i is the McMillan-Hopfield parameter which describes the electronic part of the electron-phonon interaction, M_i is the atomic mass, and $\langle \omega_i^2 \rangle$ is an average phonon frequency.

For a stoichiometric compound, the quantity η_i is calculated in the rigid-muffin-tin approximation (RMTA) by the theory of Gaspari and Gyorffy,[10] which we have applied for $PdH_{1.0}$, $CuH_{1.0}$, $AgH_{1.0}$, and $AuH_{1.0}$. In the case of the alloys it can be shown[11] that, neglecting vertex corrections, η
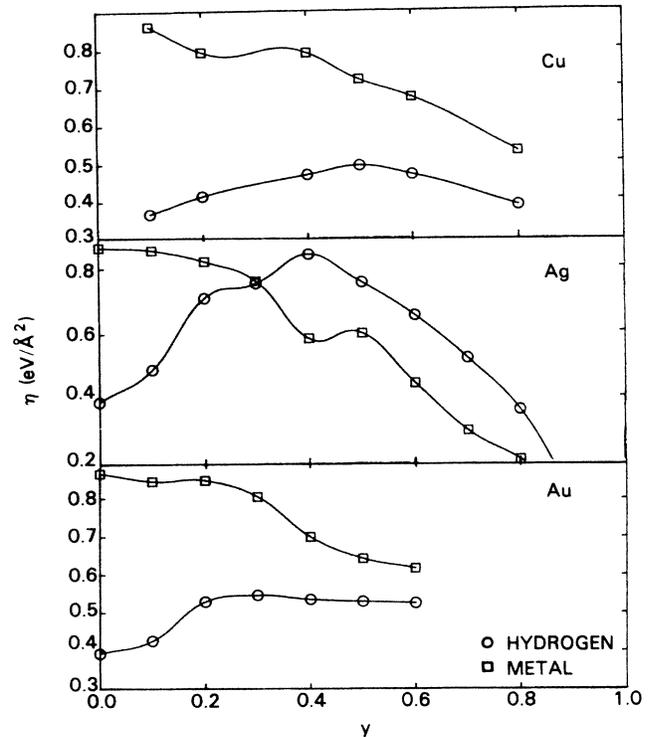
FIG. 2. McMillan-Hopfield parameter η plotted against noble-metal concentration y.

is proportional to the DOS at E_F. We have thus generalized this result for each constituent of the alloy to the expression

$$\eta_i(y) = C_i N_i(E_F, y) , \qquad (2)$$

where $N_i(E_F, y)$ is the site-decomposed DOS at E_F which we obtain from our CPA calculations for a particular noble-metal concentration y. The quantity C_i is a proportionality constant determined from our RMTA results at the fully stoichiometric ends. Our results for η_i vs y are plotted in Fig. 2 for the three different alloys that we considered. While the η of the metal sites decreases monotonically, the η_H initially increases to a maximum value and then drops to very small values at high noble-metal concentrations. This variation of η_H vs y is similar to that of T_c in Stritzker's ex-

TABLE I. Comparison of site-decomposed densities of states at the Fermi level.

	Present calculation				Temmerman and Pindor			
	n_t	n_{Pd}	n_{Ag}	n_H	n_t	n_{Pd}	n_{Ag}	n_H
PdH	3.140	2.628	· · ·	0.512	3.24	2.89	· · ·	0.36
PdH_{80}	3.096	2.836	· · ·	0.261	3.33	2.98	· · ·	0.30
$Pd_{90}Ag_{10}H_{80}$	3.419	2.874	0.162	0.383	3.48	3.03	0.08	0.33
$Pd_{80}Ag_{20}H_{80}$	3.342	2.546	0.307	0.489	3.23	2.54	0.31	0.33
$Pd_{80}Ag_{20}H_{99}$	3.689	2.704	0.305	0.680				
$Pd_{80}Ag_{20}H_{90}$	3.391	2.521	0.289	0.580				
$Pd_{80}Ag_{20}H_{80}$	3.342	2.546	0.307	0.489	3.23	2.54	0.31	0.33
$Pd_{80}Ag_{20}H_{70}$	3.352	2.674	0.271	0.406				
$Pd_{80}Ag_{20}H_{65}$	3.731	3.107	0.309	0.315				
$Pd_{80}Ag_{20}H_{60}$					3.07	2.59	0.16	0.23
$Pd_{80}Ag_{20}H_{50}$	3.944	3.51	0.230	0.199				

periments and taken together with the absence of such behavior in η_{met} (note the monotonic form of the metal component) is consistent with the notion that the optic-mode contribution is the dominant factor in the variation of T_c.

An analysis of neutron scattering data[12] for PdH has given the following estimates: $M_{Pd}\omega_{Pd}^2 = 4.951$ eV/$\mathring{A}^2$ and $M_H\omega_H^2 = 1.062$ eV/$\mathring{A}^2$. For the alloys, the metal-site (acoustic-mode) force constant has been estimated with a linear averaging of the phonon frequencies and atomic masses. The phonon frequencies of the Pd site are known,[12] and those of the noble metals are assumed to be proportional to their Debye temperatures. Thus, comparing end points, $M(\omega^2)_{M_1}/M(\omega^2)_{Pd} = 0.94$, 0.67, and 0.68 for $M_1 = $ Cu, Au, and Ag, respectively.

On the other hand, the variation with y of the hydrogen-site (optic-mode) force constant is difficult to estimate since there is not sufficient neutron scattering data for these alloys. For this reason, instead of making assumptions for the variation of $M\omega_H^2(y)$ and then estimating T_c, we invert the McMillan-Allen-Dynes[13] equation using Stritzker's measured T_c values to obtain

$$\lambda(y) = \frac{A\mu^* - 1.04}{A - 0.62A\mu^* + 1.04} , \qquad (3)$$

where

$$A = \ln(1.2T_c/\omega_{log}) .$$

We then fix ω_{log} to its value for PdH$_{1.0}$ and calculate μ^* from the Bennemann-Garland formula.[14] Now using the

expression

$$\lambda_H(y) = \lambda(y) - \lambda_{met}(y) \qquad (4)$$

and our calculated values of $\eta_{met}(y)$, $\eta_H(y)$, and $M\omega_{met}^2(y)$ we determine $M\omega_H^2(y)$.

In performing the calculation we make the additional assumption that we are dealing with a fixed large H concentration throughout the entire range of y. Stritzker makes no such claim as to his samples, but rather records the optimum T_c for a given y value obtained from testing samples of varying H concentration.

In Fig. 3 we present λ_{tot}, λ_{met}, and λ_H for Pd$_{1-y}$Cu$_y$H$_{0.90}$, Pd$_{1-y}$Ag$_y$H$_{0.99}$, and Pd$_{1-y}$Au$_y$H$_{0.99}$. It is strikingly clear from this display that the hydrogen contribution is the controlling factor in the structure of λ and hence T_c. Support for this analysis can be found by considering the ratio λ_H/λ_{met}. In Pd$_{1-y}$Ag$_y$H$_{0.99}$ we find λ_H/λ_{met} drastically reduced from ~ 2.3 at $y = 0$ to ~ 0.5 at $y = 0.9$. This is in good agreement with resistivity measurements[15] performed on deuterium-rich AgD which yielded $\lambda_H/\lambda_{met} \approx 0.8$. (We would expect the ratio to be smaller for AgH.)

In Fig. 4 we present the force constants $M\omega^2$ as a function of noble-metal concentration. The metal component, as shown above, is a slowly varying quantity which is derived from a weighted average of the constituent metal force constants. On the other hand, $M\omega_H^2(y)$ is found to have considerably different behavior. For Ag, and to a lesser extent Au, the y dependence is quite pronounced, while for Cu it is almost constant. The $M\omega_H^2(y)$ variation constitutes a primary prediction of this paper.
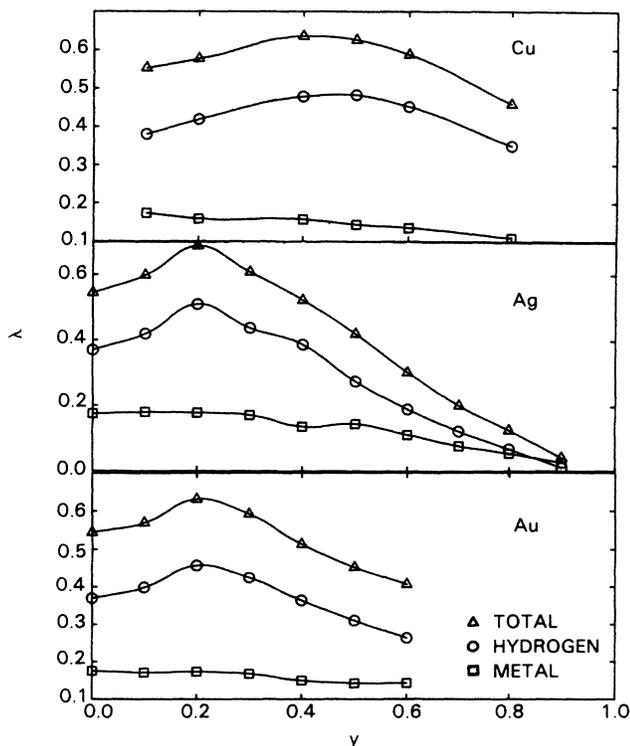
We encourage experimentalists to carry out detailed neu-

FIG. 3. Electron-phonon coupling constant λ plotted against noble-metal concentration y.
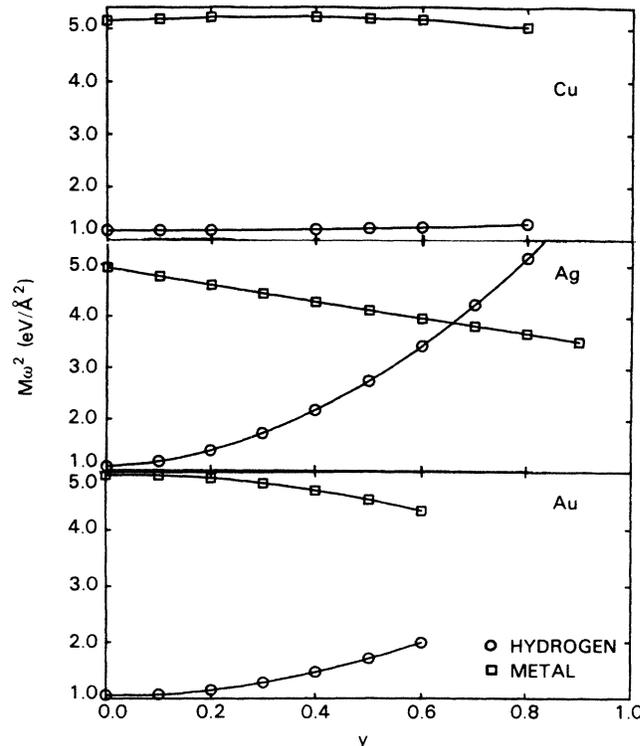

FIG. 4. Force constant $M\omega^2$ plotted against noble-metal concentration y.

tron scattering studies of these alloys in order to clarify the behavior of the phonon frequency spectrum as it depends on alloying. To date, there is only one reported neutron scattering[16] study of this type of system which finds no significant change in the local mode frequency in the palladium-silver system for silver concentrations up to 20%.

In conclusion, we have shown that the observed variation of T_c with the addition of a noble metal in PdH, is due to a similar behavior of the hydrogen-site contribution to the electron-phonon interaction.

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