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Electronic states of substoichiometric compounds and application to palladium hydride*

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A theory for the electronic states of substoichiometric compounds based on the coherent-potential approximation is described. Extensive numerical calculations have been carried out on palladium hydride. These results and the applicability of the theory to this system and other systems will be discussed.

I. INTRODUCTION

A common type of disorder that occurs in ionic crystals made of relatively heavy metal ions and light anions is substoichiometry. To a first approximation the metal-ion sublattice in such a crystal is perfectly periodic, but the anion sublattice has a number of vacant sites.

For example, palladium hydride can be made by diffusing hydrogen into palladium metal.[1,2] Throughout this process the palladium lattice remains fcc and the hydrogen fills the octahedral interstitial sites until, upon filling all these sites, stoichiometric PdH which has the NaCl structure is obtained. There is a lattice-constant change upon the formation of a hydride phase, but to a good approximation substoichiometric PdH can be viewed as a periodic fcc metal lattice with hydrogen atoms distributed randomly over some fraction of the octahedral sites.

The technique for calculating the electronic states of substoichiometric crystals given here is a rather straightforward application of the coherent-potential approximation[3] (CPA). Calculations of electronic states for binary alloys using this approximation[4,5] have shown good agreement with experiment. The only previous calculation on substoichiometric crystals[6] used the virtual-crystal approximation, which is known to be a rather low level of approximation and, indeed, led to anomalous results. Actual calculations will be shown for palladium hydride over the full range of hydrogen concentrations, and these results will be discussed in connection with the known properties of this system.

II. THEORY

The Slater-Koster interpolation scheme[7] is frequently used by band theorists to obtain more detail from calculations on periodic ionic crystals. The procedure is to write out the results of a hypothetical tight-binding calculation based on a set of atomic functions $\phi_\alpha(\vec{r}-\vec{r}_i-\vec{R}_\mu)$ which represents the αth atomic function centered on the ith atom in the μth unit cell of the crystal. The matrix elements of the Hamiltonian

$$H(i\mu,j\nu)_{\alpha\beta}=\int dV\,\phi^*_\alpha(\vec{r}-\vec{r}_i-\vec{R}_\mu)\,H\phi_\beta(\vec{r}-\vec{r}_j-\vec{R}_\nu)\ , \tag{1}$$

and the overlap integrals

$$\Delta(i\mu,j\nu)_{\alpha\beta}=\int dV\,\phi^*_\alpha(\vec{r}-\vec{r}_i-\vec{R}_\mu)\,\phi_\beta(\vec{r}-\vec{r}_j-\vec{R}_\nu)\ , \tag{2}$$

are treated as parameters which are adjusted to make the tight-binding results agree with the eigenvalues given by a first-principles band-theory calculation at some finite set of $\vec{k}$ points in the Brillouin zone. Eigenvalues for other $\vec{k}$ points can be obtained easily from the tight-binding matrices if matrix elements corresponding to interactions of atoms that are beyond the first- or second-neighbor shell are ignored. Experience has shown that the eigenvalues so obtained are in reasonable agreement with first-principles band-theory results.

It is well known that many nearest-neighbor interactions as well as atomic wave functions corresponding to excited states must be included to make a real tight-binding band-theory calculation converge. There have been speculations in the literature[8] that there should be a set of localized functions that could be used instead of atomic functions in calculations on solids which are adapted to the crystal structure in such a way that more rapid convergence would be obtained. It can be argued that the parameters obtained from a Slater-Koster interpolation fit are just the ones that would be obtained in a tight-binding calculation based on this set of optimal localization functions. We find it helpful to take this view in the derivations of the CPA equations below.

Although the CPA equations for calculating the electronic states of a random substitutional alloy for the general case of muffin-tin potentials are known,[9] the only calculations on three-dimensional systems that have been carried out use some form of the tight-binding model. It is therefore convenient that the tight-binding model is commonly used in band-theory calculations on ionic crystals.

In order to formulate tight-binding CPA equations in a form such that the interpolation parameters $H(i\mu,j\nu)_{\alpha\beta}$ and $\Delta(i\mu,j\nu)_{\alpha\beta}$ can be used directly we first introduce a set of abstract vectors $|i,\mu,\alpha\rangle$ such that

$$\langle\vec{r}|i,\mu,\alpha\rangle=\phi_\alpha(\vec{r}-\vec{r}_i-\vec{R}_\mu)\ , \tag{3}$$

and an associated set $|j,\mu,\alpha)$ such that

$$\langle i,\mu,\alpha|j,\nu,\beta)=\delta_{ij}\delta_{\mu\nu}\delta_{\alpha\beta}\ . \tag{4}$$

With this notation the Hamiltonian can be written in operator form:

$$H=\sum H(i\mu,j\nu)_{\alpha\beta}|i,\mu,\alpha)(j,\nu,\beta| \tag{5}$$

or

$$H=\sum\epsilon(i\mu)_{\alpha\beta}|i,\mu,\alpha)(i,\mu,\beta|$$
$$+\sum U(i\mu,j\nu)_{\alpha\beta}|i,\mu,\alpha)(j,\nu,\beta|\ , \tag{6}$$

where the matrix elements $H(i\mu,j\nu)_{\alpha\beta}$ are called $\epsilon(i\mu)_{\alpha\beta}$ if the atomic indices are the same and $U(i\mu,j\nu)_{\alpha\beta}$ otherwise. Unless otherwise indicated summations will be taken over all repeated indices.

We now specialize the notation to crystal structures with just two atoms per unit cell. This is sufficient for treating many substoichiometric materials, and the generalization to more complicated structures is straightforward. We recall that the metal-ion sublattice, which we call sublattice 1, is periodic; that is, $\epsilon(1\mu)_{\alpha\beta}=\epsilon^1_{\alpha\beta}$ is the same for all unit cells. There will be either an anion or a vacancy on the second site in a unit cell. For the cells that have a vacancy we set $\epsilon(2\mu)_{\alpha\beta}$ equal to infinity because this will prevent any electron from hopping onto that site. The elements $\epsilon(2\mu)_{\alpha\beta}$ take on the values $\epsilon^2_{\alpha\beta}$ if the μth cell contains an anion on the second site. The off-diagonal elements $U(i\mu,j\nu)_{\alpha\beta}$ are the same in the nonstoichiometric crystal as they are in the periodic crystal. This does not lead to any difficulties since the electron cannot hop onto a vacant site and therefore the values of the hopping integrals to that site are irrelevant. In the terminology of disordered-systems theory this means that we can ignore the problems of off-diagonal disorder for this case.[10]

Application of the CPA to this system leads to a periodic model Hamiltonian $\hat{H}$ which has the property that quantities calculated from the Green's function

$$\hat{G}(Z)=(Z-\hat{H})^{-1}\ , \tag{7}$$

such as the density of states

$$\rho(E)=-(1/\pi)\lim_{Z\to E^+}\operatorname{Im}\operatorname{Tr}\hat{G}(Z)\ , \tag{8}$$

are very good approximations to those that would be obtained using the actual nonperiodic Hamiltonian. As usual, the limit notation means that Z is equal to the energy E plus a positive imaginary quantity that is allowed to go to zero at the end. For the nonstoichiometric crystal already described,

$$\hat{H}=\sum\epsilon^1_{\alpha\beta}|1,\mu,\alpha)(1,\mu,\beta|+\sum\sigma_{\alpha\beta}|2,\mu,\alpha)(2,\mu,\beta|$$
$$+\sum U(i\mu,j\nu)_{\alpha\beta}|i,\mu,\alpha)(j,\nu,\beta|\ , \tag{9}$$

where the only unknowns are the matrix elements $\sigma_{\alpha\beta}$ that replace the $\epsilon(2\mu)_{\alpha\beta}$ on the anion sites. To obtain them from the CPA, the scattering operators that describe scattering from an anion or vacancy in the central cell of an otherwise periodic crystal with the $\sigma_{\alpha\beta}$ on the other anion sites must be found. If there are n atomic functions centered on an anion site we construct an $n\times n$ matrix $\underline{G}^2$ from the matrix elements of the Green's function with respect to these functions,

$$G^2_{\alpha\beta}(E)=\lim_{Z\to E^+}(2,0,\alpha|\hat{G}|2,0,\beta)\ , \tag{10}$$

and also $n\times n$ matrices $\underline{\epsilon}^2$ and $\underline{\sigma}$ with elements $\epsilon^2_{\alpha\beta}$ and $\sigma_{\alpha\beta}$. It can be shown that the desired scattering operators can be written in the form

$$t^x=\sum_{\alpha\beta}\tau^x_{\alpha\beta}|2,0,\alpha)(2,0,\beta|\ , \tag{11}$$

and the scattering matrix for the anion whose elements $\tau^A_{\alpha\beta}$ would be used in Eq. (11) is

$$\underline{\tau}^A=[1-(\underline{\epsilon}^2-\underline{\sigma})\underline{G}^2]^{-1}(\underline{\epsilon}^2-\underline{\sigma})\ . \tag{12}$$

The scattering matrix for the vacancy is as above but with $\underline{\epsilon}^2\to\infty$, so

$$\underline{\tau}^V=-(\underline{G}^2)^{-1}\ . \tag{13}$$

If C is the concentration of vacancies or the fraction of unfilled anion sites, the CPA equations for the $\sigma_{\alpha\beta}$ are

$$C\underline{\tau}^V+(1-C)\underline{\tau}^A=0 \tag{14}$$

or

$$\underline{\sigma}=\underline{\epsilon}^2-C(\underline{G}^2)^{-1}\ . \tag{15}$$

Since $\underline{G}^2$ is a function of $\underline{\sigma}$, this matrix equation must be solved by iteration.

The model operator $\hat{H}$ is periodic so lattice Fourier transforms can be used to find the matrix elements $G^2_{\alpha\beta}$. We define matrix elements $\hat{\epsilon}^i_{\alpha\beta}$ by $\hat{\epsilon}^i_{\alpha\beta}=\epsilon^1_{\alpha\beta}$ for $i=1$ and $\hat{\epsilon}^i_{\alpha\beta}=\sigma_{\alpha\beta}$ for $i=2$, $W^{ij}_{\alpha\beta}(\vec{k})$ by

$$W^{ij}_{\alpha\beta}(\vec{k})=e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\sum_\mu e^{i\vec{k}\cdot\vec{R}_\mu}U(i\mu,j0)_{\alpha\beta}\ , \tag{16}$$

and $\Delta^{ij}_{\alpha\beta}(\vec{k})$ by

$$\Delta^{ij}_{\alpha\beta}(\vec{k})=e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\sum_\mu e^{i\vec{k}\cdot\vec{R}_\mu}\Delta(i\mu,j0)_{\alpha\beta}\ . \tag{17}$$

If the sum of the number of atomic functions centered on the metal-ion sites and those on the anion sites is m, the $m\times m$ square matrix $\underline{H}(\vec{k})$ has elements

$$H^{ij}_{\alpha\beta}(\vec{k}) = \hat{\epsilon}^{i}_{\alpha\beta}\delta_{ij} + W^{ij}_{\alpha\beta}(\vec{k}) \ , \tag{18}$$

while the elements of the $m\times m$ matrix $\underline{\Delta}(\vec{k})$ are given in Eq. (17). The equation for an element of $\underline{G}^2$ is

$$G^2_{\alpha\beta}(E) = (1/\Omega)\lim_{Z\to E^+}\int d\vec{k}\{[Z\underline{\Delta}(\vec{k}) - \underline{H}(\vec{k})]^{-1}\}_{2,\alpha,2,\beta} , \tag{19}$$

which means that we form the $m\times m$ matrix $Z\underline{\Delta} - \underline{H}$ for each $\vec{k}$ in the Brillouin zone, take its inverse, find the element in the $2,\alpha$ row and $2,\beta$ column, and then integrate over the Brillouin zone. Of course, in practice one chooses a large but finite set of $\vec{k}$'s in the Brillouin zone and carries out a weighted sum rather than the integral in Eq. (19).

The self-energy matrix elements $\sigma_{\alpha\beta}$ are found from Eqs. (15) and (19). It is clear from Eq. (15) that they depend only on the energy, and it turns out that they are complex. It can be seen from the above that the $\vec{k}$ dependence of $\underline{H}(\vec{k})$ and $\underline{\Delta}(\vec{k})$ arises from terms that are independent of the concentration since we do not have to consider off-diagonal randomness in this problem. Partly for this reason the iterative solution of these equations turns out to be quite tractable in practice.

Since the atomic functions $\phi_\alpha(\vec{r} - \vec{r}_i - \vec{R}_\mu)$ are not orthogonal, care must be used in finding the density of states after the CPA equations have been solved. The first step, it can be shown, is to construct the matrix

$$\underline{S}(Z) = (1/\Omega)\int d\vec{k}\,\underline{\Delta}(\vec{k})[Z\underline{\Delta}(\vec{k}) - \underline{H}(\vec{k})]^{-1} , \tag{20}$$

which differs from the Green's-function matrix by the introduction of an additional $\underline{\Delta}(\vec{k})$. The density of states of the metal ion is

$$\rho_M(E) = (-1/\pi)\lim_{Z\to E^+}\mathrm{Im}\sum_{\alpha} S^{11}_{\alpha\alpha}(Z) , \tag{21}$$

and for the anion site

$$\rho_A(E) = (-1/\pi)\lim_{Z\to E^+}\mathrm{Im}\sum_{\alpha} S^{22}_{\alpha\alpha}(Z) . \tag{22}$$

This partial-density-of-states function describes the occupation of the atomic sites with electrons having energies between E and $E+dE$. The total density of states of the system is

$$\rho(E) = \rho_M(E) + \rho_A(E) . \tag{23}$$

III. CALCULATION ON PdH

The first problem that arises in applying the preceding theory to nonstoichiometric PdH is to find a set of interpolation parameters that will reproduce the energy bands of pure Pd and stoichiometric PdH. In an early stage of these calculations[11] we used our own Korringa-Kohn-Rostoker band-theory calculations on Pd and PdH as a starting point, but some more elaborate first-principles calculations on these materials have been reported by Papaconstantopoulos and Klein[12] and they are used in the present calculations. In fitting to the first-principles values we reproduce their essential features very well, but we have not striven for the kind of accuracy that is normally obtained in band-theory applications. One reason for this is that we want to keep our model Hamiltonian as simple as possible to facilitate the CPA calculations. Another reason arises from the fact that in the present stage of development of band theory there will be sizable differences in the bands obtained for a given material from calculations which use different starting assumptions, even though the various calculations are equally legitimate.

Our interpolation Hamiltonian is taken directly from the paper by Slater and Koster.[7] In this calculation we set the overlap matrix equal to a unit matrix. We treat nearest-neighbor and next-nearest-neighbor interactions in PdH and just nearest-neighbor interactions in Pd, and the two-center approximation is made. On the Pd sites we put one s function, three p functions, and five d functions, and we put one s function on the H site. In Fig. 1 we show the E-versus-$\vec{k}$ curves for Pd that we ob-

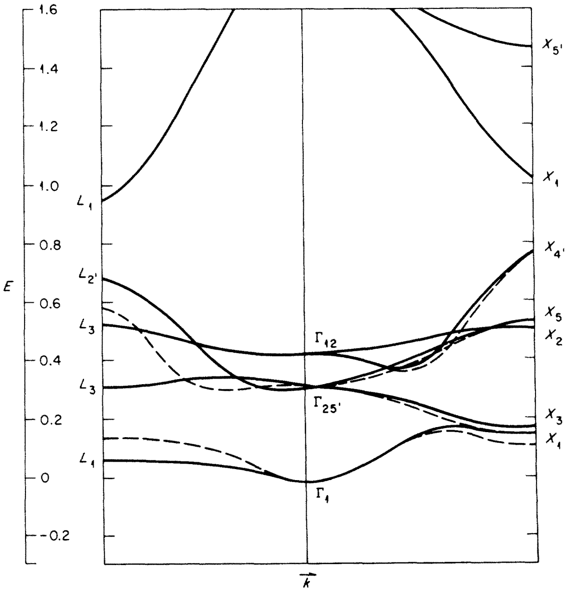

FIG. 1. E-vs-k curves along the [100] symmetry line (Γ to X) and the [111] symmetry line (Γ to L) for Pd. The heavy solid lines were obtained from our interpolation Hamiltonian and the dashed lines show the results described in Ref. 12 when they differ enough from ours to be seen.

TABLE I. Parameters for interpolation Hamiltonian in notation of Ref. 7.

Palladium-palladium	
$s_0 = 0.7000$	
$d_0 = 1.3700$	hydrogen-hydrogen
$p_0 = 0.3859$	
$(ss\sigma) = -0.0598$	$s_0 = 1.0000$
$(pp\sigma) = 0.1500$	$(ss\sigma) = 0.0$
$(pp\pi) = -0.0250$	
$(dd\sigma) = -0.0494$	hydrogen-palladium
$(dd\pi) = 0.0197$	
$(dd\delta) = -0.0018$	$(ss\sigma) = 0.0876$
$(sp\sigma) = 0.0900$	$(sp\sigma) = 0.1620$
$(pd\sigma) = 0.0$	$(sd\sigma) = 0.1200$
$(pd\pi) = 0.0$	
$(sd\sigma) = 0.0667$	

tain using the first 13 interpolation parameters in Table I. The E-versus-$\vec{k}$ curves for PdH shown in Fig. 2 is obtained by adding one more parameter which fixes the position at which the hydrogen band would appear in the absence of the palladium and three parameters that describe the interaction of the hydrogen s state with the palladium s, p, and d states. As can be seen by comparing these figures, the primary effect of adding hydrogen to palladium appears to be to convert the lowest-lying palladium conduction band to a palladium-hydrogen bonding band which has a lower energy over all. The palladium-hydrogen antibonding band appears in the neighborhood of 1.0 Ry in Fig. 2.

It can be seen from Table I that the interaction between the hydrogen s state and the palladium p states is very strong. This is not surprising when it is realized that the energy of the isolated hydrogen atom, 1.0 Ry, falls in the energy region where the palladium bands are dominated by p states. Figures 1 and 2 also illustrate the point that the agreement with the first-principles bands of Papaconstantopoulos and Klein is adequate.

The densities of states for Pd and PdH have been calculated by summing the eigenvalues from the interpolation Hamiltonians that fall between E and $E + dE$ and also by taking the trace of the Green's functions for the pure systems. It has been found that adequate detail is obtained if an integral over the Brillouin zone is replaced by a weighted sum over 408 $\vec{k}$ points in the irreducible $\frac{1}{48}$ portion of the zone. Of course, it is necessary to add a small imaginary part δ to the energy when using the Green's-function method. We obtain good agreement between the densities of states calculated by the two methods using $\delta = 0.002$. In Fig. 3 we show the densities of states of Pd and PdH calculated by the Green's-function method, since this is the method that can be carried over into alloy calculations.

Starting from this description of the pure materials, the periodic model Hamiltonian $\hat{H}$ and the Green's function for substoichiometric PdH for any concentration of vacancies, C, can be found from the CPA equations of Sec. II. Since there is only one atomic state associated with the hydrogen atom Eq. (15) becomes a scalar rather than a matrix equation. The CPA self-energy $\sigma(E)$ is just a complex function of the energy for this case, and the iterative solution of Eq. (15) is relatively easy.

We found $\sigma(E)$ for PdH with 5%, 10%, 15%, 20%, 30%, 40%, 60%, and 80% vacancies over a range of energies from -0.3 to 0.7 Ry. The densities of states were found from Eqs. (20)–(23) and the integrated densities of states were obtained by numerical integration. From these we were able to get the Fermi energy and also the total number of electrons on the palladium and hydrogen sites.

In Fig. 3 we show the densities of states and Fermi energies for Pd, PdH, and a number of substoichiometric compounds. It is clear that no rigid band model would give these results, and that the Fermi energy moves to higher energy with increasing hydrogen content. The densities of states associated with hydrogen sites is shown in Fig. 4 for PdH and two substoichiometric compounds. These results illustrate that one cannot identify just one band on the E-versus-$\vec{k}$ curves of Fig. 2 as a hydrogen band. They also show that there are changes in the distribution of states associated with these sites and not just a scaling of the magnitudes of the distributions.

The hydrogen concentration or ratio of hydrogen to palladium atoms, H/Pd $= 1 - C$, has been used to

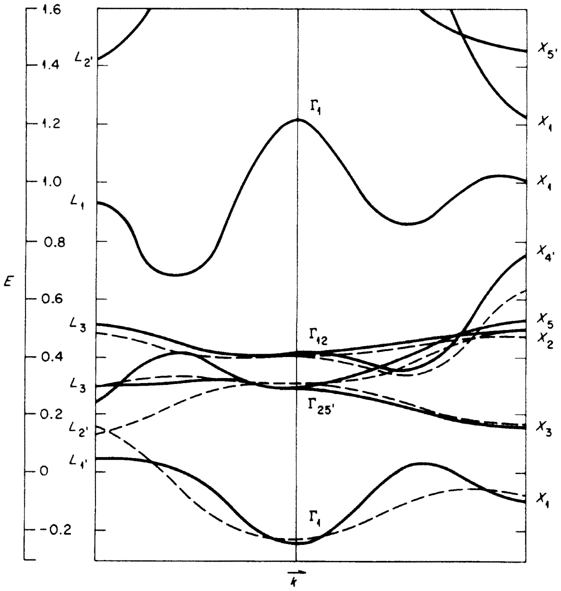

FIG. 2. E-vs-k curves for stoichiometric PdH with same conventions as Fig. 1.

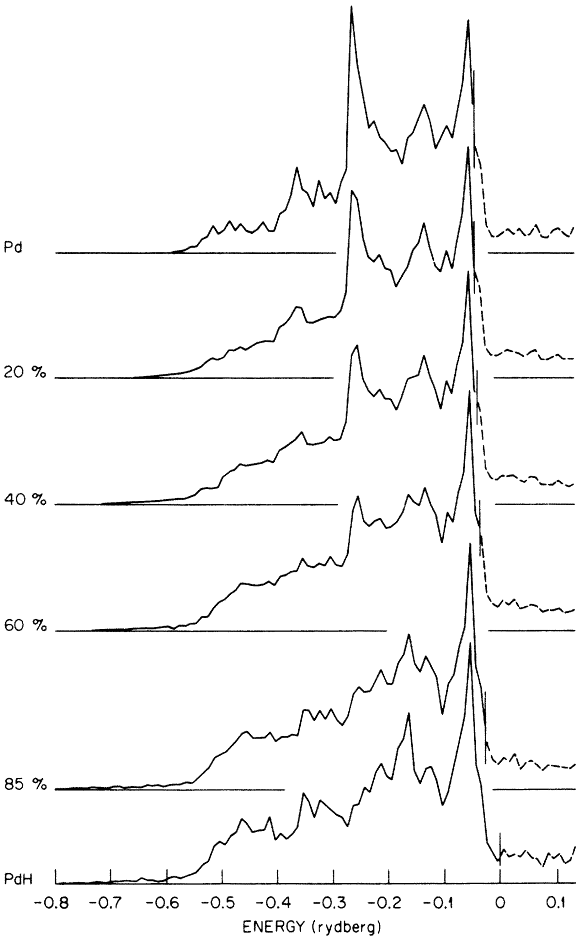

FIG. 3. Density of states vs energy of Pd and PdH and also five substoichiometric compounds. The fraction of hydrogen sites that are filled is shown on the left as a percentage. The vertical line on each curve shows the Fermi energy and the dotted portion of the curves show the regions of unfilled energy states.

label these drawings as this is a more common terminology than the concentration of vacancies, *C*.

IV. DISCUSSION

Interest in PdH has increased in recent years owing to the discovery that palladium and certain of its alloys become superconductors when they are charged with hydrogen.[13] In particular PdH becomes a superconductor when the hydrogen concentration becomes greater than 0.77 and its superconducting transition temperature T_c approaches 10 K as H/Pd approaches 1. Even higher T_c's are measured in Pd-Ag-H systems. There are also experiments on the resistivity, magnetic susceptibility, specific heat, and optical properties of PdH which are interesting.[1,2,14]

The present calculations have not been used to obtain estimates for T_c because there are a number of uncertainties in doing this for a disordered system, but they are relevant to the discussion. In Fig. 5(a) we show the density of states at the Fermi energy for PdH systems over the full range of hydrogen concentration. These results coupled with those shown in Fig. 3 indicate that the Fermi energy falls in a range of high density of states and $\rho(E_f)$ is roughly constant for hydrogen concentrations below about 0.7. For higher values of H/Pd the Fermi energy moves out of the *d* bands and $\rho(E_f)$ falls to values typical of simple metals. The exact value of H/Pd at which this transition takes place and the steepness of the drop in $\rho(E_f)$ depends sensitively on the details of the band-theory results. Specific-heat measurements of Mackliet and Schindler[14] can be interpreted as indicating that the transition is completed as H/Pd goes from

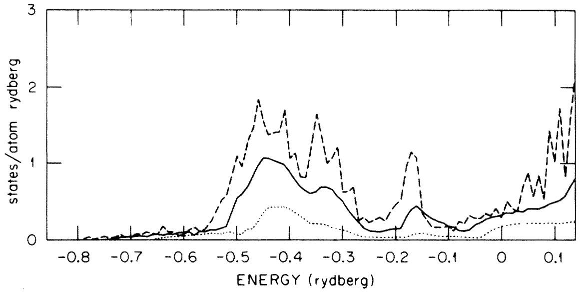

FIG. 4. Average density of states on the hydrogen site vs energy for stoichiometric PdH (dashed) and also substoichiometric compounds with a ratio of filled hydrogen sites H/Pd equal to 0.60 (solid) and 0.20 (dots).

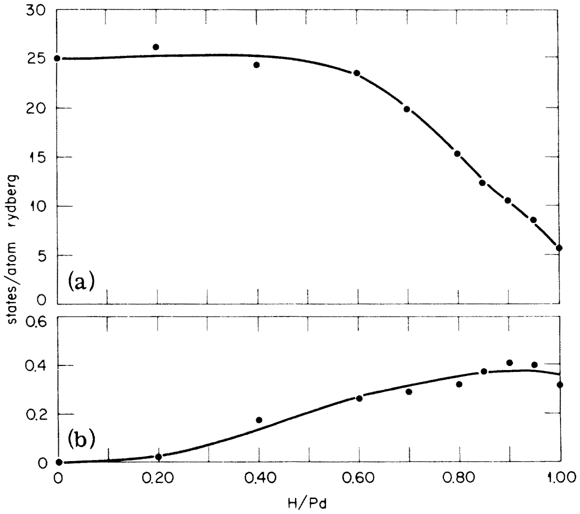

FIG. 5. Density of states at the Fermi energy of various PdH compounds versus the ratio of filled hydrogen sites expressed as a decimal fraction. The total density of states is shown in (a), while the average density of states on the hydrogen site is in (b). Note the change of scale between (a) and (b).

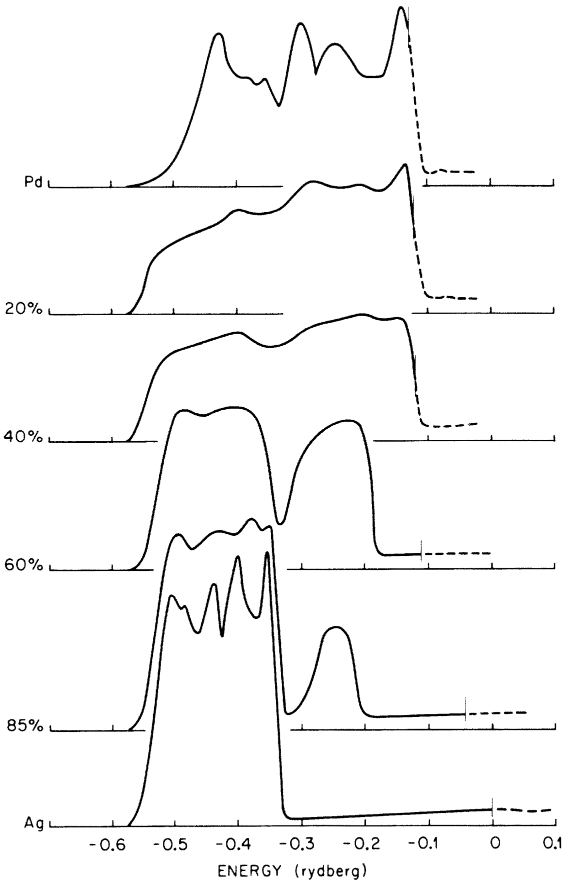

FIG. 6. Density of states of Pd, Ag, and a number of PdAg substitutive alloys. The percentage of Pd atoms replaced by Ag atoms in the alloys is shown on the left of the curves. The Fermi energy is shown with a vertical line and the unfilled states are shown as a dashed line.

0.57 to 0.07. In any case the Fermi energy should be outside the *d* bands in the range of hydrogen concentrations for which PdH is a superconductor. It can be seen from Fig. 5(b) that the density of states on the hydrogen site increases to about its maximum value for H/Pd in the superconducting range. This lends further credence to the mechanism for superconductivity in PdH discussed by Papaconstantopoulos and Klein[12] rather than the one put forward by Bennemann and Garland.[15] The former authors used band-theory results for stoichiometric PdH and came to the conclusion that the major contribution to the electron-phonon interaction parameter which determines T_c arises from the hydrogen. Our results indicate that the relative magnitudes of the densities of states that they based their arguments on remain qualitatively correct for the substoichiometric crystals which show superconductivity.

Samples of PdH containing enough hydrogen to be superconducting have the structural phase called the β phase. The assumptions used in this calculation concerning structure are quite good for this phase, which is generally described as a NaCl structure with randomly distributed vacancies at the hydrogen sites. Samples with hydrogen concentrations less than about 0.6 are in a two-phase region of the phase diagram where the β phase is in equilibrium with the α phase, which is essentially pure fcc palladium having a lattice constant about 4% smaller than that of the β phase. Our calculations are suspect for values of H/Pd in this range, but they should be at least indicative. Quite different lattice constants were used for the Pd and PdH calculations that we have taken as a basis for this work, and, as is seen in Figs. 1 and 2, the major features of the bands are not particularly sensitive to this.

The existence of the two-phase region does make the interpretation of some of the experimental data for PdH more difficult. The experiments we are aware of are consistent with the results we have obtained, however. Our calculations show that each electron that is added to the solid with the addition of a hydrogen atom is divided between the palladium and hydrogen sites in the ratio of 3 to 2, and this ratio remains quite constant over the whole range of hydrogen concentrations. This does not mean that a modified rigid band model can be used, though, because the density-of-states function for the palladium site changes with hydrogen concentration.

In some of the early discussions of the electronic structure of PdH it was thought that adding a hydrogen atom to a unit cell would have the same effect as replacing the palladium atom with a silver atom. In Fig. 6 we show a resume of results previously obtained for PdAg alloys[5] with silver concentrations equal to the H/Pd concentrations in Fig. 3. It can be seen that the way the densities of states vary is quite different for the two systems.

It would be possible to carry out more elaborate CPA calculations on PdH. This would be justified if the results of optical or other experiments which could give rather direct measurements of the electronic structure of β-phase PdH become available. The technique outlined in this paper has proved to be quite tractable, and it should be possible to use it to calculate the electronic states in other substoichiometric compounds.

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