Optical absorption in PdH

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Résumé. — Nous avons calculé la densité d'états et la contribution des transitions directes interbandes de la partie imaginaire de la constante diélectrique $\varepsilon_2^b(\omega)$ de PdH par une méthode développée antérieurement. Les densités d'états totales, partielles, et les densités d'états intégrées sont cohérentes avec les autres calculs existants. La contribution interbande de la constante diélectrique présente un seuil d'absorption de 0,07 Ry; ce seuil peut être attribué à l'absence de bandes dégénérées au niveau de Fermi. Notre calcul présente des structures bien marquées, différentes du palladium pur; nous espérons qu'elles seront confirmées bientôt par l'expérience.

Abstract. — The density of states and the direct interband contribution to the imaginary part of the dielectric function ($\varepsilon_2^b(\omega)$) of PdH are calculated. The total, partial and integrated densities of states compare favourably with other calculations. The interband dielectric function is found to have an absorption edge of $\simeq 0.07$ Ry, which is due to the absence of any degenerate band at the Fermi level. Although there is no experimental data on PdH as yet, the presence of high intensity peaks in $\varepsilon_2^b(\omega)$ should be easily observable.

1. **Introduction.** — The fact that hydrogen is very soluble in palladium [1, 2] and also that the critical temperature T_c of the superconductivity in PdH$_x$ ($x \leqslant 1$) increases as a function of hydrogen content [3-5] has evoked a great interest in metal hydrides in general and in PdH in particular. Unfortunately, as far as we know, there is no experimental data on the optical absorption in PdH, though it is evident that PdH should have some optical absorption peculiarities when compared to those of Pd.

In the following, we present the calculation of the imaginary part $\varepsilon_2(\omega)$ of the dielectric function of PdH and compare it with the previous data on Pd [6]. It will be shown that the interband contribution to $\varepsilon_2(\omega)$ has an absorption edge and at low frequencies Drude's correction has to be included. The interband absorption edge is inherent in the energy band of PdH and we shall discuss it in detail. We shall present the methods of the calculation in section 2, our

results in section 3, the discussion in section 4 and the conclusion in section 5.

2. **Methods of calculation.** — In general the calculation of the imaginary part of the dielectric function involves the following steps :

i) calculation of the band structure;
ii) calculation of the density of states and the Fermi level and finally;
iii) the calculation of $\varepsilon_2(\omega)$ itself.

For PdH we shall use the band scheme of Papaconstantopoulos *et al.* [4]. These authors have given Slater-Koster interpolation parameters [4] to their original augmented plane wave calculation of the band structure of PdH [7]. Using these parameters, we first calculate the partial and total densities of states for a precise determination of the Fermi level and compare them with those of Papaconstantopoulos *et al.* [4, 7] and also with those of Cubiotti and Ginatempo [8]. The precisely determined Fermi level is then used for the calculation of the interband contribution to $\varepsilon_2(\omega)$.

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2.1 INTEGRATION OVER THE BRILLOUIN ZONE. —
The calculation of the density of states $n(\omega)$ and of the imaginary part of the dielectric function $\varepsilon_2(\omega)$ necessitates the singular integration of one and two electrons over the Brillouin Zone (BZ). There are many numerical methods [9, 10] to perform this kind of integration but recently one of us [11] has developed a general technique for the BZ singular integration using the idea that any BZ may be partitioned into convex polytop cells. The cubes [9] and the tetrahedrons [10] are only two particular forms of the convex polytops [12]. The details of this method have been laid out in [11], so we shall just recall a few important points in this section.

The density of states is a sum of contributions over the convex polytops covering the irreducible part of the BZ :

$$n(\omega) = \sum_{\substack{\text{cells} \\ n}} \frac{S_c}{|\nabla E_{n\bar{k}}|} \qquad (1)$$

where S_c is the area of the polygon (also a convex polytop) defined by the domain enclosed by :

$$E_{n\bar{k}} = \omega \qquad (2)$$

and

$$d_i(\bar{k}) \leqslant d_i^0 \quad i = 1, 2, ..., I . \qquad (3)$$

$E_{n\bar{k}}$ is the energy of the nth band at $\bar{k}$ and it is localized within the cells. Expression (2) defines a hyperplane of constant energy ω and the expression (3) of inequalities defines the half-spaces bounding a cell, and eventually, the zone boundaries. I is the total number of inequality constraints.

In conventional methods [9, 10], analytic formulae are established for this area as a function of the orientation of the constant energy plane and its position. In the present work the vertex points of the polygon are directly determined and managed by the computer, since any point of the domain defined by (2-3) can be written as a barycentre of the vertex points, with adequate positive weight attached to each vertex. Finally, a polygon can be subdivided into triangles by choosing a point inside it, and the sum of the areas of the triangles gives the area of the polygon.

For the imaginary part of the dielectric function or any other similar quantity the domain is defined by :

$$\omega_{nn'\bar{k}} = \omega \qquad (4)$$

$$d_i(\bar{k}) \leqslant d_i^0 ; \quad i = 1, 2, ..., I \qquad (2)$$

$$E_{n\bar{k}} \leqslant E_F \qquad (5)$$

and

$$- E_{n'\bar{k}} \leqslant - E_F \qquad (6)$$

where

$$\omega_{nn'\bar{k}} = E_{n'\bar{k}} - E_{n\bar{k}} ;$$

$|n\bar{k}\rangle$ and $|n'\bar{k}\rangle$ are the initial (occupied) and final (empty) states respectively. ω is the photon energy and E_F is the Fermi level. This method of integration has been already used for the calculation of $\varepsilon_2(\omega)$ of Si and Pd [6].

2.2 IMAGINARY PART OF THE DIELECTRIC FUNCTION
$\varepsilon_2(\omega)$. — The optical absorption is proportional to the imaginary part of the dielectric function which arises from two distinct contributions.

(i) The free charge carriers or free electrons give an important effect at low energy limit which is also called Drude's term and then (ii) the interband transitions give rise to structures in the optical absorption curves

$$\varepsilon_2(\omega) = \varepsilon_2^f(\omega) + \varepsilon_2^b(\omega) \qquad (7)$$

where the free electrons part $\varepsilon_2^f(\omega)$ is [13] :

$$\varepsilon_2^f = \frac{4 \pi N_f e^2}{m^*} \frac{\tau}{\omega(1 + \omega^2 \tau^2)} \qquad (8)$$

N_f is the number of free charge carriers per unit volume. In metals it is the number of s-p conduction electrons which can be determined from band structures. m^* is the optical effective mass and this quantity may also be determined from energy bands [14]. The relaxation time τ is determined from experimental measurements. The expression (8) shows that the free electron part becomes more and more important as $\omega \to 0$, or at $\omega \simeq 0$ it is roughly a delta function.

The interband $\varepsilon_2^b(\omega)$ part is written as [6] :

$$\varepsilon_2^b(\omega) = \frac{e^2}{2 \pi m^2 \omega^2} \int_Z d^3k \sum_{nn'} |P_{nn'\bar{k}}|^2 \delta(\omega - \omega_{nn'\bar{k}}) \times$$
$$\times |f(E_{n\bar{k}}) - f(E_{n'\bar{k}})| \qquad (9)$$

where

$$\bar{P}_{nn'\bar{k}} = \langle n'\bar{k} | \bar{P} | n\bar{k} \rangle \qquad (10)$$

is the dipolar matrix element.

The difference between the two Fermi functions in (9) can be written at $T = 0$ K as

$$f(E_{n\bar{k}}) (1 - f(E_{n'\bar{k}}))$$

i.e. with the aid of two-step function θ :

$$f(E_{n\bar{k}}) (1 - f(E_{n'\bar{k}})) =$$
$$= \theta(E_F - E_{n\bar{k}}) \theta(E_{n'\bar{k}} - E_F) \qquad (11)$$

which simply means that the initial state must be occupied and the final state empty.

Finally the expression (9) can be written as (in atomic units) :

$$\varepsilon_2^b(\omega) = \frac{1}{2\,\pi\omega^2} \sum_{nn'} \int_S |P_{nn'\bar{k}}|^2 \,\theta(E_F - E_{n\bar{k}}) \times$$

$$\times\; \theta(E_{n'\bar{k}} - E_F)\,\frac{dS_k}{|\nabla_k\omega_{nn'\bar{k}}|} \qquad (12)$$

where

$$S = \{\,\bar{k},\, E_{n'\bar{k}} - E_{n\bar{k}} = \omega\,\}\,.$$

For the calculation of the interband contribution $\varepsilon_2^b(\omega)$ we are still left with the problem of determining (i) the dipolar matrix elements $P_{nn'\bar{k}}$ and (ii) the energy gradient $\nabla_k\omega_{nn'\bar{k}}$.

In a full band calculation, providing both energy eigenvalues and eigenfunction there is no special problem to compute the dipolar matrix elements at a given $\bar{k}$-point. Otherwise, we are led to the alternative of taking the matrix elements as constant, or better, to fit an interpolation tight-binding band scheme to the first principle bands and to approximate the matrix element of P by [15] :

$$P_{nn'\bar{k}} = \langle\, n\bar{k}\,|\,\nabla_k H\,|\,n'\,\bar{k}\,\rangle\,. \qquad (13)$$

H being the tight-binding Hamiltonian. For PdH we have used the two approximations i.e. $P_{nn'\bar{k}} = 1$ and $\langle\,n\bar{k}\,|\,\nabla_k H\,|\,n'\bar{k}\,\rangle$. The result of calculation will be presented in the next section.

We have used the Hellman-Feynman theorem to obtain an analytical expression for the energy gradient $\nabla_k\omega_{nn'\bar{k}} = \nabla_k E_{n'\bar{k}} - \nabla_k E_{n\bar{k}}$ in the tight-binding approximation. The details are given in [6], so here we shall content ourselves in giving only the final result i.e. :

$$\nabla_k E_{n\bar{k}} = \frac{\displaystyle\sum_{mm'} X_{n\bar{k}}^{m*}\,[(\nabla_k H)^{mm'} - E_{n\bar{k}}(\nabla_k S)^{mm'}]\,X_{n\bar{k}}^{m'}}{\displaystyle\sum_{mm'} X_{n\bar{k}}^{m*}\,S^{mm'}\,X_{n\bar{k}}^{m'}}$$

$$(14)$$

where the eigenstates $|\,n\bar{k}\,\rangle$ are expressed in terms of orbital Bloch sums $|\,m\bar{k}\,\rangle$ such that :

$$|\,n\bar{k}\,\rangle = \sum_m X_{n\bar{k}}^m\,|\,m\bar{k}\,\rangle \qquad (15)$$

and

$$|\,m\bar{k}\,\rangle = (N)^{-1/2} \sum_\lambda e^{i\bar{k}.\bar{\lambda}}\,|\,m\bar{k}\,\rangle \qquad (16)$$

with N as the number of sites and

$$\langle\,\bar{r}\,|\,m\bar{\lambda}\,\rangle = \varphi_m(\bar{r} - \bar{\lambda})\,,$$

the atomic orbital centred at the site $\bar{\lambda}$. $H^{mm'}$ and $S^{mm'}$ are the energy and overlap matrix elements.

3. Results.

The electronic band structure of the palladium-hydrogen system was made by Papaconstantopoulos [7] using the augmented plane wave method. The muffin-tin sphere radii for Pd and H were chosen to be 2.3795 a.u. and 1.4850 a.u. respectively. The exchange potential was treated by Slater's $X\alpha$ method with exchange parameters 0.702 for Pd and 0.777 for hydrogen. The exchange parameter for the interstitial region was set equal to 2/3. The calculation was done self-consistently within the muffin-tin approximation and included relativistic effects (except spin-orbit splitting). This band calculation from first principles, was later used [4] to produce a Slater-Koster interpolation scheme for PdH. In the first principles band structure [7] ten bands with some contribution of the « f » symmetry are fully presented. For the Slater-Koster fit only seven bands at nineteen high symmetry points and six energies from 8th and 9th bands having p-like character are used. The overall agreement is remarkably good around the Fermi level and the root mean square deviation is less than 0.06 Ry for the bands beyond [4]. Unfortunately, the same cannot be said about the densities of states. In their original work [7], there is an evident presence of the bonding state at the bottom of the band mostly of s-like symmetry. This state is not as pronounced in [4]. Apart from this small discrepancy, the overall interpolated density of states is fairly good around the Fermi level.
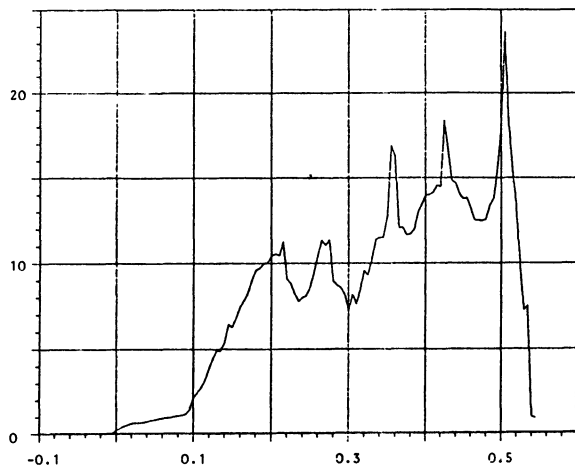
3.1 DENSITY OF STATES OF PdH.

We have calculated the total, partial and integrated density of states by a general method [6, 11] of polytops. We used $\Gamma X = 6, 8, 10$ and 12 divisions and the energy step as small as 0.0025 Ry. It was necessary, due to the flat bands arising from the interpolation scheme [4], to take a subdivision of $\Gamma X \geqslant 10$ and energy mesh size $\leqslant 0.005$ Ry in order to obtain the total number of electrons within a band up to 3 decimal points. We noticed that the position of the Fermi level also is very sensitive to the mesh sizes and stabilizes at 0.675 Ry. The value 0.642 Ry given by Papaconstantopoulos [4] somewhat smaller is, in our opinion, due to the insufficient number of points in the irreducible wedge of the BZ, for the root-sampling method they use. In figure 1a we present the total density of states (TDOS) of PdH and, for comparison, TDOS of Pd [6] is also traced in figure 1b.

Figures 2-4 show, respectively, the partial density of states (PDOS) of « d », « p » and « s » like symmetries originating from palladium in PdH. The PDOS of s symmetry of hydrogen is shown on figure 5. We must point out the presence of a bonding state (Fig. 1a) and that the Fermi level in PdH falls in the low density region. The total charge of different symmetry types emanating from Pd and H in PdH are presented in table I and they are compared with the corresponding charges in palladium. In the same table we also present these quantities calculated by Cubiotti and Ginatempo [8] by the recursion method. We shall discuss this table in more detail in the next section.

3.2 THE DIELECTRIC FUNCTION $\varepsilon_2^b(\omega)$.

In the interpolation scheme of Papaconstantopoulos et al. [4]
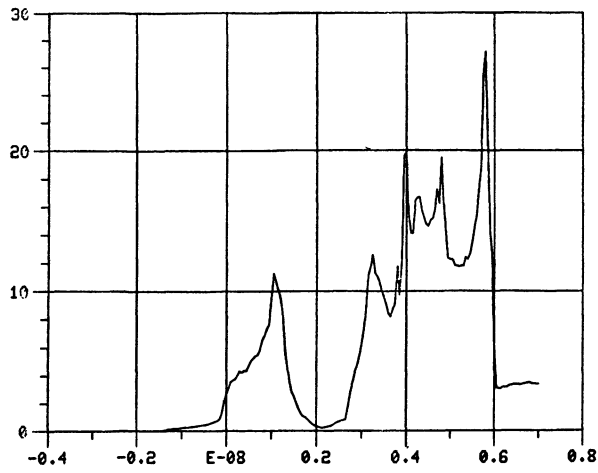
a

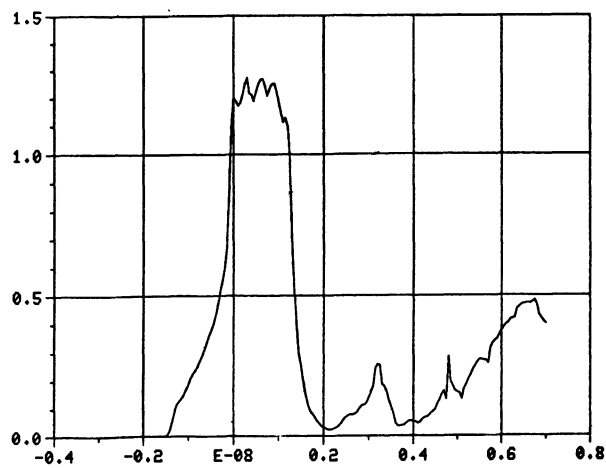
b

Fig. 1. — Total density of states of : (a) PdH; (b) Pd.

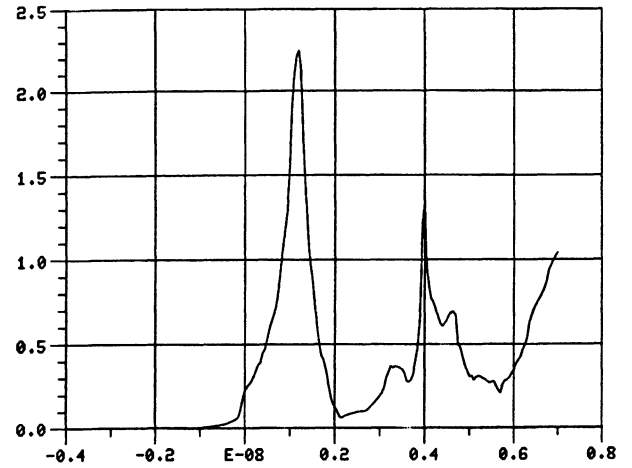Fig. 3. — Partial density of states of « p » symmetry of Pd in PdH.

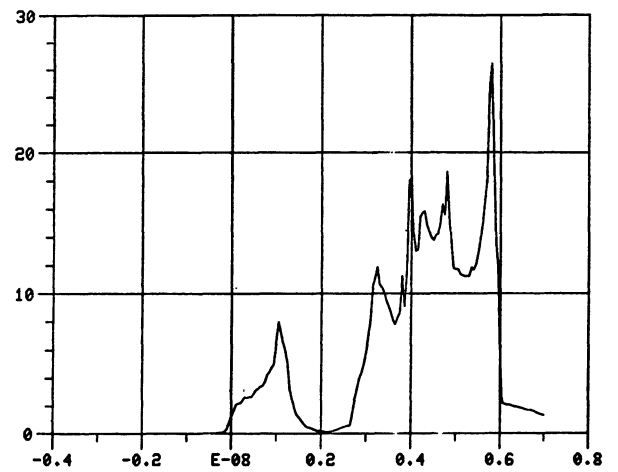Fig. 4. — Partial density of states of « d » symmetry of Pd in PdH.

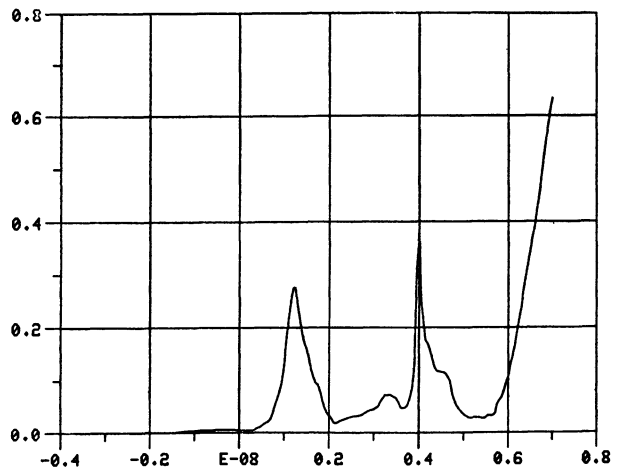Fig. 2. — Partial density of states of « s » symmetry of Pd in PdH.

Fig. 5. — Partial density of states of « s » symmetry of H in PdH.

Table I. — *Electronic charge of* s, p *and* d *symmetry types in* PdH *and* Pd. s^{Pd} *and* s^H *denote the* « s » *electrons from* Pd *and* H *respectively.*

		s^{Pd}	p	d	s^H
Present work	PdH	0.62	0.74	9.50	0.14
	Pd	0.50	0.37	0.13	—
Ref. [8]	PdH	0.80	0.54	9.38	0.28
	Pd	0.73	0.17	9.10	—

the intersite overlap integrals are zeros, so the energy gradient expression (14) simplifies to :

$$\nabla_k E_{n\bar{k}} = \sum_{mm'} X_{n\bar{k}}^{m*} (\nabla_k H)^{mm'} X_{n\bar{k}}^{m'} . \tag{17}$$

With this simple expression for the energy gradient, the computation of the $\varepsilon_2^b(\omega)$ becomes an easy task. For the dipolar matrix, we have used the constant element approximation and then we have evaluated this factor with the help of equation (13) to bring out the $\bar{k}$ dependence of the structure in the $\varepsilon_2^b(\omega)$ *versus* ω curve. In figures 6 and 7 we present these two calculations.

4. **Discussion.** — The density of states that we calculated with the SK parameters given in [4] agrees with that of Papaconstantopoulos *et al.* [4] except that our Fermi level is slightly higher than theirs. As mentioned earlier we have studied the convergence of the density of states as a function of the mesh size and the energy step and we noticed that the Fermi level E_F stabilizes at 0.675 Ry and not at 0.642 Ry as reported in [4]. We think that the number of k points in the irreducible wedge of the BZ were not sufficient in [4]. Another point to be noticed from the density of states figures (particularly Fig. 1a) is that there is a low-lying band almost completely separated from the rest of the band. Papaconstantopoulos *et al.*, in their earlier work [7] obtained a localized state in the low energy range and a transfer of charge from Pd to hydrogen, but in their later work [4] which we use here, the situation is somewhat different i.e. there is a charge transfer from hydrogen to palladium and the localized state is not as separated as in [7]. The well separated localized state that we obtain shows the superiority of the present method of integration. This state was missed to some extent in [4] due to the sampling procedure. Another similar feature is that the sharp peaks in the density of states that we obtain with the interpolation scheme [4] were levelled-off in [4]. Other authors such as Switendick [16], Faulkner [17] and Cubiotti and Ginatempo [8], all obtained a charge transfer from hydrogen to palladium in PdH. The present density of states calculations are in agreement with all the first principles band structure calculations except [7], which in itself has been modified later [4]. In table I we present some electronic charge values of different symmetry and site origin.
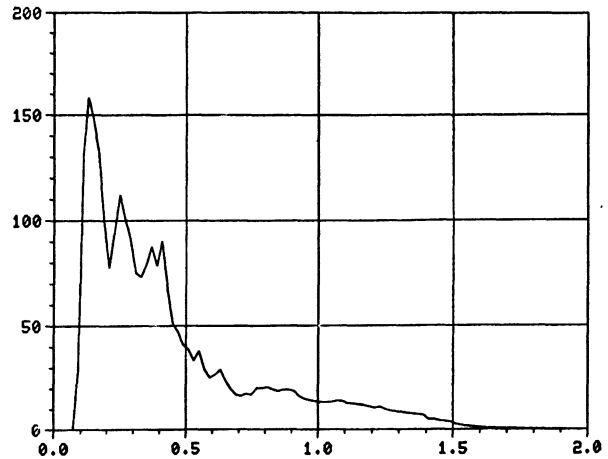

Fig. 6. — $\varepsilon_2^b(\omega)$ with dipolar matrix element $P_{nn'\bar{k}} = 1$.
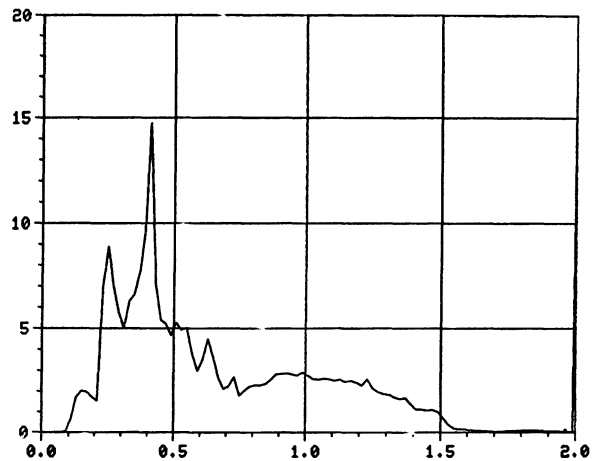

Fig. 7. — $\varepsilon_2^b(\omega)$ with dipolar matrix element =

$$\langle\, n'\, \bar{k}\, |\, \nabla_k H\, |\, n\bar{k}\, \rangle .$$

These values are compared with those given in [8]. As compared to Pd, in PdH there are less « d » holes. We obtain slightly bigger charge transfer and a higher number of « p » type electronic charge, otherwise the general trend and the magnitude of the charge transfers are the same.

In figures 6 and 7 we have presented only the interband $\varepsilon_2^b(\omega)$ contribution to the imaginary part of the dielectric function. In figure 6, we have considered $P_{nn'\bar{k}} = 1$, and the $\bar{k}$ dependence of the dipolar matrix is shown in figure 7. Both of these figures reveal an optically transparent behaviour at low energy side (below 0.07 Ry). Although we have shown the curves up to 2.0 Ry, beyond $\simeq 0.75$ Ry the structure in figures 6 and 7 are not very significant due to the limitation in the band structure scheme [4]. These two figures show a certain number of strong absorption peaks and their positions are roughly the same in the two cases. The $\bar{k}$ dependence of $P_{nn'\bar{k}}$ brings out the

importance of the oscillator strengths and hence the importance of the relative weights of the peaks.

Blount's approximation [15] that we use for the oscillator strength, even if not exact quantitatively for Bloch states, conserves their symmetry and k-dependence properties. In actual computation, contributions from various bands are not separated, so it is not possible to assign the peaks to particular band to band transitions, but the most intense peak at 0.41 Ry (Fig. 7) is most probably due to collective transitions at Z, W, Q and K high symmetry points (Fig. 1 of reference [4]). In the absence of any experimental data of optical absorption in PdH, we shall simply add that the structure due to interband transitions will be observed only when $\omega > 0.07$ Ry, a small shoulder will appear at 0.15 Ry, the first peak at 0.25 Ry and the most intense peak at 0.41 Ry. Beyond this there may be many small structures (Fig. 7).

So far we have only discussed the interband part ignoring the free electron contribution. We have noticed that considering only the interband contribution makes PdH look like a semiconductor with a small optical gap. This observation is inherent in the band structure of PdH itself. Whenever the Fermi level cuts only the non-degenerate bands, the band-to-band transition starts only after an absorption edge. The same phenomena are observed in many other similar cases like aluminium [18, 19], vanadium [20] and sodium [14] in which case the band-to-band transition does not start before 2 eV. When there are some degenerate bands present at the Fermi level, the interband optically transparent behaviour does not exist [6, 21, 22]. As the free charge carriers exist in all these cases, it is this contribution that mainly gives

the metallic nature to the class of substances where there is no degenerate band at the Fermi level.

The electron relaxation time « τ » in expression (8) is estimated from the experimental data. Since there is no such data for PdH, it is difficult to add correctly the Drude's contribution to $\varepsilon_2^b(\omega)$. Anyway, it will have a general form of $1/\omega$ at $\omega \to 0$ and $1/\omega^3$ at higher energies. This correction will give a high conductivity for ω tending to zero and a smooth, rapidly decreasing contribution for higher values of ω. This correction will not alter the peak positions nor their relative intensities as obtained by the interband transition.

5. **Conclusion.** — Using the Slater-Koster scheme of Papaconstantopoulos et al. [4] for the energy bands of PdH and a new and efficient method for singular integration [6, 11], we have calculated the density of states and the interband dielectric function. The density of states gives a charge transfer from hydrogen to palladium in agreement with many other previous calculations [8, 16, 17]. The interband dielectric function has a zero contribution below 0.07 Ry. A similar calculation for Pd [6] showed a divergence for $\varepsilon_2^b(\omega)$ at $\omega \to 0$. This difference lies in the fact that in Pd there are some degenerate bands (Δ_5 and Δ_3) at the Fermi level, whereas in PdH there are only non-degenerate bands crossing the Fermi level.

In the absence of any experimental data it is difficult to add the free electron contribution correctly, but this will not change the main feature of the absorption peaks as obtained in $\varepsilon_2^b(\omega)$ versus ω. We hope that the experimentally observed absorption spectra of PdH will be available in the near future for a meaningful comparison with the present work.

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