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Electronic structure and proton spin-lattice relaxation in PdH

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We report a detailed augmented-plane-wave energy-band study and wave-function analysis of stoichiometric PdH which shows that, even though the Fermi surface of PdH is qualitatively similar to that of silver, the simple "proton model" is not valid. Instead, the screening of the proton in PdH is found to be larger than in an isolated H atom due, in part, to the formation of a H-Pd bonding band below the bottom of the d-band complex. This result, which is in qualitative agreement with Switendick's earlier calculation, is confirmed by ultraviolet photoemission experiments. A partial density-of-states (DOS) analysis in the energy range spanned by the six valence and conduction bands reveals the quantitative details of the bonding mechanism between the Pd and H constituents. At the Fermi energy, the high Pd d to H s DOS ratio ~ 10.3 is found to be far higher than expected in silver, despite the fact that the Fermi-surface geometry is similar. The field-induced conduction-electron spin density at the proton site is evaluated from the wave functions at the Fermi energy. The calculated value of the spin-lattice relaxation rate arising from the contact term in the hyperfine interaction is found to be in good agreement with the experimental value of Wiley *et al.*

I. INTRODUCTION

The metal-hydrogen systems have received wide attention due, in part, to the large number of their technical applications.[1,2] They are also important for the tests they provide of several theories. The study of the behavior of a proton in a simple metal was started with the pioneering work of Friedel,[3] and later extended by several authors.[4] It is now well established that the screening of a proton in an electron gas is not well described by linear screening theories, because the perturbation introduced by a proton is simply too strong and nonlinear screening effects are very important.[4] These theories essentially treat the proton as an isolated impurity in an electron gas, and are based upon a self-consistent solution of the Schrödinger equation using the Hohenberg-Kohn-Sham[5] local-density-functional formalism; they are expected to give interesting results only for the so-called "simple metals" which are known to absorb an extremely small quantity of hydrogen. While electron-gas models provide useful information about variation in the screening with variation of the average interelectronic distance, their quantitative predictions must be treated with caution, as the jellium model is recognized[6] to be a quite crude representation because even the so-called simple metals show substantial departures in their Fermi-surface properties, etc., from that of an electron gas.

Since the transition metals like Pd can absorb a large amount of hydrogen, the proton cannot be treated as a dilute impurity. Thus, for these d-electron systems one would not expect to obtain meaningful results from electron-gas theories. To describe properly the electronic structure of transition-metal hydrides, alternative methods, like the augmented-plane-wave (APW) band-structure method, have been used by Switendick[7] and other authors.[8,9] Theoretical studies have also been made of nonstoichiometric compounds, using either the supercell method[7] (with an assumed rigid order of the vacancies) or the virtual-crystal approximation.[9] Recently, the electronic structure of disordered substoichiometric PdH_x compounds has been obtained using the average-t-matrix approximation,[10] and the coherent-potential approximation.[11]

Among the transition-metal hydrides, the PdH_x system is of particular interest because (i) the superconducting transition temperature[12] T_c increases with increasing values of x (for $x \geq 0.8$) and (ii) the reverse isotope effect[13] on T_c (observed when H is replaced by deuterium) is a challenging problem for both theorists and experimentalists. Miller and Satterthwaite[14] proposed a qualitative explanation of (ii) based upon changes in the electronic structure which arise from differences in the zero-point motion amplitudes of the two isotopes, leading to a stronger bonding of the hydrogen atom (compared to D) to the palladium atom. An alternative explanation, given by Ganguly,[15] proposes that the anharmonicity due to a large zero-point motion amplitude of the protons leads to a different electron-phonon coupling and to a reduction of the electron-phonon coupling constant λ when D is replaced by H. This theory assumes that the electronic properties of PdH and PdD are identical (e.g., same density of states at the Fermi energy...). The importance of anharmonic effects in the electron-phonon interaction is supported by the tunneling experiments[16]; also, recent inelastic-neutron-scattering experiments[17] indicate strong anharmonic optical phonons in $PdH_{0.6}$. A Born–von Kármán approach to the lattice dynamics of the nonstoichiometric compounds (using the supercell method with random position of the vacancies[18]) showed a pronounced stiffening of the force constants for $PdH_{0.63}$ compared to $PdD_{0.63}$.

Although Ganguly's theory[15] seems to be quite generally well accepted, some questions remain unanswered, and more experimental and theoretical information concerning both the vibrational and electronic properties is needed. Nuclear magnetic resonance (NMR) experiments, for example, can provide such an insight. Recently, Wiley *et al.*[19] measured the spin-lattice relaxation rate[20] T_1^{-1} of protons in the PdH_x system (with $0.8 \leq x \leq 1.0$) between 3 and 77 K in order to determine information concerning the wave functions of the conduction electrons at the Fermi energy. In this temperature range, the relaxation proceeds via a coupling of the nuclear spins with the conduction electrons by the magnetic hyperfine interaction (which is often viewed as a spin-flip scattering mechanism of the unpaired electrons at E_F). At higher temperatures, estimated[21] to be greater than 160 K for PdH, the diffusion of the protons in the Pd lattice becomes important and produces, via the nuclear spin-spin interaction, a strong fluctuation of the local fields. This mechanism is responsible for the well-known motional narrowing of the NMR resonance lines, and the relaxation rate increases, due to the addition of a diffusion contribution T_{1d}^{-1}, to the electronic contribution T_{1e}^{-1},

$$1/T_1 = 1/T_{1e} + 1/T_{1d}. \qquad (1)$$

A study of the frequency and temperature dependence of the diffusion term, when analyzed using simplified theories,[22] provides values of the jump rate and activation energy for the diffusion of protons in the Pd lattice. An accurate theoretical determination of the electronic term is of great interest *per se*, but is also important if one intends to separate out the diffusion term. Experimentally, the electronic contribution can be separated from the diffusion term by making use of the linear temperature dependence of the Korringa term.[20]

Theoretical estimate of the first term in Eq. (1) requires detailed knowledge of the wave functions at the Fermi energy. The purpose of this paper is (i) to provide, for the first time, a detailed analysis of the wave function character of the occupied energy bands in order to obtain more quantitative insight concerning the bonding mechanism of hydrogen in palladium, and (ii) to study the properties of the wave functions at E_F from which to infer a value of the electronic contribution to the proton spin-lattice relaxation rate. Section II discusses some features of the electronic structure of PdH (i.e., energy bands, Fermi surface geometry, density of states), compares them with previous calculations and available experimental data, and analyzes the partial density of states into its angular momentum components inside both the hydrogen and palladium muffin-tin spheres. Section III is devoted to an analysis of the contact term of the hyperfine field at the proton site and to a comparison with the experimental value of the spin-lattice relaxation rate of protons in PdH obtained by Wiley *et al.*[19] Concluding remarks are given in Sec. IV.

II. ELECTRONIC STRUCTURE OF STOICHIOMETRIC PdH

A. Energy-band structure

The energy-band structure of the rocksalt structure stoichiometric β-phase PdH was determined using a value of the lattice constant $a = 4.090$ Å obtained by Schirber and Morosin[23] from an extrapolation to $x = 1.0$ of their accurate recent x-ray diffraction experiment performed on PdH_x. As input to the augmented-plane-wave[24] (APW) calculations, a "warped muffin-tin" potential was generated using sphere radii equal to 2.4596 a.u. (Pd) and 1.3499 a.u. (H). The crystal charge density was obtained as a superposition of atomic charge densities, using 14 shells of neighbors; for Pd, the Herman-Skillman self-consistent charge density corresponding to the atomic configuration $4d^{10}5s^0$ and full Slater exchange ($\alpha = 1$) was used. For Pd metal, it has been shown[7,25] that the results of APW non-self-consistent calculations, based on either $4d^{10}5s^0$ or $4d^95s^1$ atomic configurations, lead to very similar results for the Fermi-surface properties. In the present calculation of the proton spin-lattice relaxation rate, we will be concerned also with the wave functions at the Fermi energy E_F. While we do not expect them to be very much affected by the choice of the starting atomic configuration, it is important to note that the magnetic-field-induced neutron magnetic form factor for Pd metal (derived from the wave functions at E_F with the $4d^{10}5s^0$ potential used here) was found to be in very good agreement with experiment.[25] In the one-electron Hamiltonian of the crystal, the exchange term of the potential was calculated within the Slater local exchange approximation, also with a value $\alpha = 1.0$ for the exchange parameter.

The resulting energy eigenvalues, calculated for 6 bands at 89 points in the $\frac{1}{48}$th wedge of the irreducible Brillouin zone (BZ), are plotted along several symmetry directions in Fig. 1. It is in-

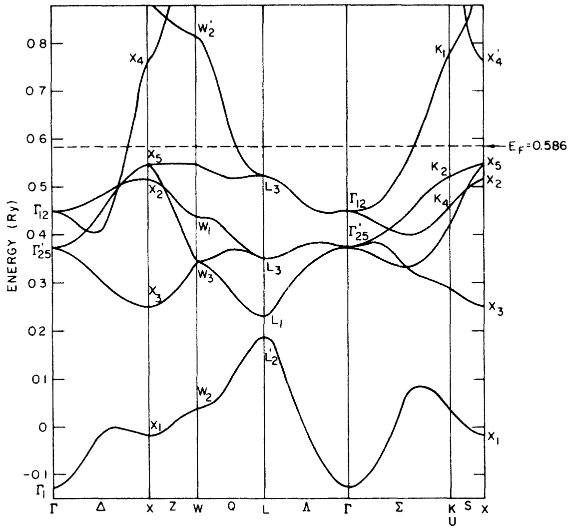

FIG. 1. Energy bands of PdH along several high-symmetry directions. Energies are in Ry.

structive to compare these results with the energy bands obtained from a calculation of similar accuracy for Pd metal. We notice several essential differences: (i) By a visual inspection of the bands and the position of the Fermi energy in PdH, one can see that the 0.36 holes at the top of the 4*d* bands in Pd appear to be filled in the hydride and some additional states above the top of the *d* bands (marked arbitrarily by the X_5 point, for example), are also occupied. If we compare the bands of PdH to those of silver,[26] at least qualitatively, the Fermi level appears to fall in the same general portion of the 5*s*-5*p* band which overlaps and hybridizes the metal 4*d* bands. Note however, that E_F is higher in Ag, falling ~4 eV above the X_5 point but only ~0.5 eV above the X_5 point in PdH. These preliminary remarks appear to favor the donation of electrons from hydrogen to the Pd *d* bands. However, even within this oversimplified picture, and considering the position of E_F in PdH compared to that in Ag, one can immediately say that certainly less than one electron has been "added" at the top of the *d* bands. Further, we shall also see that a more detailed analysis reveals that these statements only qualitatively characterize the main differences between Pd and PdH. In reality, the differences are more complex and the "proton model" is not valid, as pointed out by Switendick.[7] (ii) The most remarkable feature is the formation of a new band ~4.2 eV wide, centered ~2.7 eV below the bottom of the Pd 4*d* bands. A comparison of these bands with those of Pd shows that this low-lying band in PdH results from the lowering of states which are either occupied in pure Pd (like X_1, Γ_1) or empty (like L_2'). This drastic lowering in energy (which is larger than 5 eV for L_2') is expected to be due to a strong Pd-H interaction in the compound, as we shall see in Sec. III. In the present calculation, this low-lying band is separated from the rest of the Pd 4*d* band complex, contrary to Switendick's result[7]; this is essentially due to his use of a different atomic configuration for Pd ($4d^9 5s^1$) to generate the crystal charge density and a different value of the lattice constant ($a = 4.03$ Å).

The overall width of the Pd 4*d* band complex, ~4.35 eV from L_1 to X_5 is in agreement with the value of 4.4 eV given by Eastman *et al.*[27] from their ultraviolet photoemission spectra. The position of the Pd-H bonding band obtained in the present calculation is lower than indicated by the uv photoemission experiment. A result similar to ours has been obtained by Zbasnik and Mahnig[9] and Gelatt *et al.*[10] We notice in this connection that the experiment of Eastman *et al.*[27] seems to correspond to a different H to Pd ratio (H/Pd ~ 0.6)[14]; this could be due to the fact that the experiment was performed at room temperature, at which a full stoichiometry of hydrogen is difficult to achieve.

B. Fermi-surface geometry

As in the noble metals, the Fermi surface (FS) is determined by one band (band 6). The FS cross sections in several high-symmetry planes, (100) and (110), are plotted in Fig. 2. The geometry of this FS is qualitatively similar to that of Ag (or Cu and Au); namely, it is a multiply-connected electron surface which can be described as a deformed sphere around Γ, with "necks" along the Γ*L* directions. A cross section of the "belly" is given in Fig. 2(a); the departure from sphericity can be noted by simple visual inspection, as flat portions appear, perpendicular to the [110] direction and protuberances appear in the [100] direction. Among the three noble metals Cu, Ag, Au, the FS of Ag displays the minimum asphericity. In the case of PdH, however, the departure of the "belly" from sphericity is even larger than it is in Cu. We shall see in Sec. III that these differences in the FS geometry are accompanied by an increasing *s* character at E_F in going from PdH to Cu and Ag. Figures 2(b) and 2(c) plot, respectively, the "neck" in the Γ*L* direction, and a cross section of the "neck" formed by a hexagonal face of the BZ, this latter cross section has a circular shape, and a larger area than in the noble metals which is probably associated with the larger *d* character at E_F in PdH.

Because of the difficulty in preparing stoichiometric PdH and PdD samples with high resistivity ratio, no de Haas–van Alphen experiments have

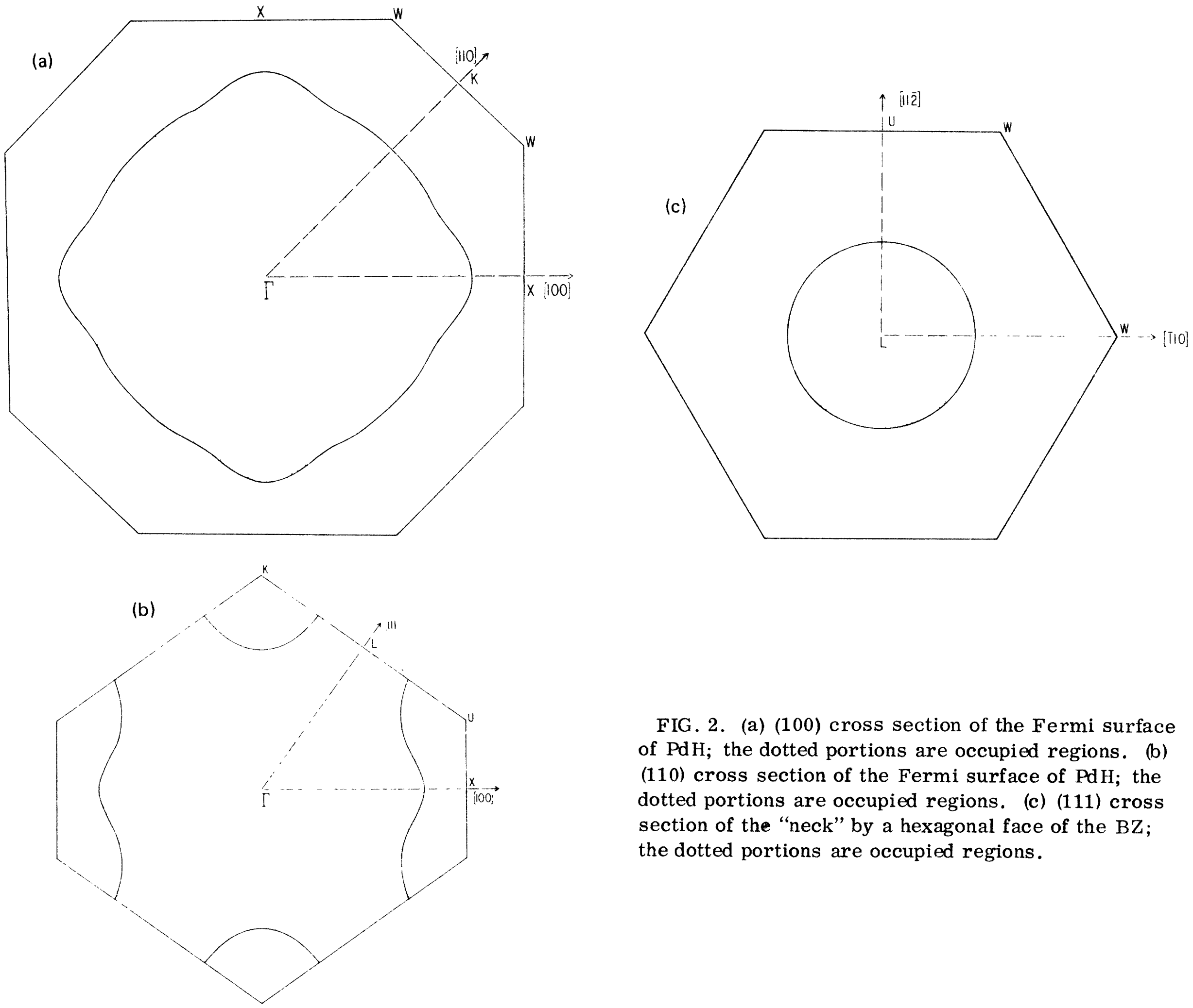

FIG. 2. (a) (100) cross section of the Fermi surface of PdH; the dotted portions are occupied regions. (b) (110) cross section of the Fermi surface of PdH; the dotted portions are occupied regions. (c) (111) cross section of the "neck" by a hexagonal face of the BZ; the dotted portions are occupied regions.

yet been reported. Such experimental information would be very instructive because it could perhaps differentiate PdD from PdH and shed some more light on the problem of the reverse isotope effect on T_c. de Haas–van Alphen data on nearly stoichiometric PdH_x ($x \leq 0.03$) have been obtained by Jacobs *et al.*[28]; no noticeable difference with the cyclotron frequencies measured for pure Pd were

TABLE I. Comparison of the neck and belly radii R (in units of free-electron sphere radii) and Fermi-surface cross sections A (in units of diametral cross section of the free-electron sphere) of PdH with other noble metals.

		R_{neck}	$R_{[100]}$	$R_{[110]}$	$R_{[100]}/R_{[110]}$	A_{neck}	$A_{(100)}$	$A_{(110)}$
PdH	Present calculation	0.350	1.024	0.889	1.15	0.129	0.866	1.076
	Morse[a]	0.167	0.979	0.958	1.02	···	···	···
Cu	Burdick[b]	0.167 ± 0.021	1.049 ± 0.021	0.965 ± 0.021	1.09	···	···	···
	Schoenberg	0.14	···	···	···	···	0.980 ± 0.003	···
Ag	Bohm and Esterling[c]	0.142	1.072	0.955	1.13	···	···	···
	Morse[a]	···	1.006	0.975	1.03	···	···	···
Au	Shoenberg[d]	···	···	···	···	0.034	···	1.087

[a] See Ref. 40.
[b] See Ref. 41.
[c] See Ref. 43.
[d] See Ref. 42.

observed, indicating that the Fermi surface of PdH_x cannot be obtained by applying a simple rigid-band model to the bands of pure Pd, and suggesting the formation of a low-lying band. The cross-section areas and dimensions of the FS of PdH obtained in the present work are summarized in Table I; in order to underline the differences, we also list in this table the corresponding experimental values for the noble metals. From the qualitative similarity of the Fermi surface geometry of PdH with that of Ag (the next-door neighbor of Pd to the right of the Periodic Table), a naive picture of the "proton model" could be inferred. Although this model is in some respects qualitatively correct as it leads to a low value of the density of states at E_F, we shall see in what follows from a study of the bonding mechanism that this model is oversimplified.

C. Density of states (DOS) and partial DOS analysis

1. Total DOS

In order to calculate the DOS, the energy eigenvalues obtained *ab initio* at 89 points in the $\frac{1}{48}$th wedge of the irreducible BZ were expanded into a linear combination of 51 symmetrized plane waves; this procedure leads to a maximum rms error of 2 mRy for the 6 bands plotted in Fig. 1. The BZ integration was then performed using the accurate linear energy tetrahedron scheme.[29] Dividing the $\frac{1}{48}$th part of the BZ into 6144 tetrahedra, and assuming a linear variation of the energy inside each microtetrahedron, the DOS was obtained on a 1 mRy mesh.

The essential features of the band structure discussed above appear in the DOS plotted in Fig. 3. The states between $E = -0.13$ Ry and $E = +0.19$ Ry correspond to the low-lying Pd-H bonding band, while the states above $E = +0.23$ Ry are expected to be essentially Pd 4*d*-like. However, if we compare the DOS of the band complex of PdH to that of pure Pd, there is no correspondence between the different peaks and structure of the DOS; this indicates that the states have been strongly modified by the presence of hydrogen in the Pd lattice, and a simpleminded rigid shift of the Fermi energy applied to the bands of pure Pd, according to the "proton model," can be seen to be in substantial error.

In PdH, the Fermi energy, $E_F = 0.586$ Ry, falls in a region of low density of states, the DOS being 3.4055 states of one spin/(Ry unit-cell) at E_F. This value is drastically lower than the value[25] of 14.45 states of one spin/(Ry unit-cell) in pure Pd. Contrary to the case of metallic Pd, the variation of the DOS around E_F (which decreases with increasing energy) in PdH is very weak. The sharp variation of the DOS at E_F in Pd has been invoked to explain the anomalous temperature dependence of the high temperature resistivity.[30] The large values of the DOS at E_F for Pd leads to a large Stoner factor, and an exchange enhanced susceptibility, the condition for a spin fluctuation being nearly satisfied; the low value of the DOS at E_F and its slow variation explains why such effects are suppressed in PdH.

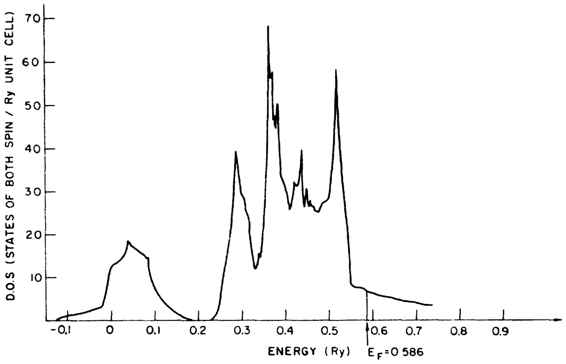

FIG. 3. Total DOS of PdH.

The value of the electronic specific heat of the stoichiometric compound is not known; however, Mackliet *et al.*[31] studied the low-temperature heat capacity of PdH_x for $0.835_7 < x < 0.874_5$; the value N of the DOS at E_F for one spin direction, in a noninteracting electron model is given by the well-known expression[32]

$$N = 3\gamma/2\pi^2 k_B^2, \tag{2}$$

where γ is the electronic specific heat and k_B the Boltzmann constant. Using the experimental value $\gamma = 1.54 \pm 0.13$ mJ mol^{-1} K^{-2} given in Ref. 31, the calculated value of N is, according to Eq. (2), $N = 0.33 \pm 0.02$ states/(eV atom). Assuming that this value remains of the same order of magnitude for a fully stoichiometric compound, the electron-phonon mass enhancement λ defined by

$$N = N(0)(1+\lambda) \tag{3}$$

is of the order of 0.25. We should, however, mention that, from their low-temperature heat capacity measurements performed on PdH_x (and PdD_x), for a broader composition range $0.78 \le x \le 0.96$, Zimmermann *et al.*[33] obtained for $x \sim 0.86$ a value of γ 4% lower than the one quoted in Ref. 31 and observed a drastic decrease of γ with increasing x. For $x = 0.96$, the measured value[33] of γ leads, with the use of Eq. (2), to a DOS smaller than the one found in the present calculation. The large difference between the theoretical value of the unenhanced DOS and the values obtained from heat capacity measurements has been observed previously.[8] It is interesting to recall here that the experiments of Zimmermann *et al.*[33] suggest a smaller value of the unenhanced DOS at E_F for PdD compared to PdH. Recently, McLachlan *et al.*[34] obtained from magnetic measurements a value of γ far lower than the one of Mackliet *et al*[31]; this value[34] of γ leads to a DOS practically equal to our unenhanced $N(0)$; however, these authors[34] report some uncertainty in their experiment, due to an inhomogeneous distribution of hydrogen in the samples, and extremely irreversible magnetization curves. The theoretical value of the DOS at E_F obtained by Papaconstantopoulos and Klein[8] is 24% larger than the one obtained in the present work and would lead to an even smaller value of λ. Our value of $N(0)$ agrees within 10% with the result obtained by Switendick using linear-combination-of-atomic orbitals (LCAO)-APW scheme,[7] although this author reports a very different value from his APW calculation. From our calculated value of the DOS at E_F for one spin direction, we can obtain the Pauli spin paramagnetic susceptibility given by

$$\chi_p = 2\mu_B^2 N, \tag{4}$$

where μ_B is the Bohr magneton. Experimentally, however, it is well known that the large paramagnetic susceptibility of Pd is drastically reduced by introducing hydrogen in the lattice and for a ratio H/Pd $\geq$ 0.63, the susceptibility becomes diamagnetic and independent of hydrogen concentration. The difference between $\chi_{\text{measured}} < 0$ and $\chi_{\text{Pauli}} = 16.2 \times 10^{-6}$ esu/mole is due to the negative contribution of the sum of the other contributions to χ, namely, $\chi_{\text{ion-core diamagn.}} + \chi_{\text{Landau diamagn.}} + \chi_{\text{orbital paramagn.}}$

2. *Partial DOS*

In order to understand the nature of the bonding mechanism in PdH, we generated the wave functions in the energy range: $-0.13 \leq E \leq 0.85$ Ry, at 89 *ab initio* $\vec{k}$ points, in the $\frac{1}{48}$th BZ. Using the angular momentum decomposition of the wave functions inside the muffin-tin Pd and H spheres, we projected the total DOS into its partial angular momentum components $l = 0, 1, 2$ inside the muffin-tin spheres. The partial DOS of the low lying PdH band (band 1), are plotted in Fig. 4(a) for the Pd sphere and in Fig. 4(b) for the H sphere. Inside the Pd sphere, the $l = 2$ component is dominant; however, some s and p character is also present. At the bottom of the band, a non-negligible Pd $l = 0$ contribution is observed, as the 5s-5p band which overlaps and hybridizes with the 4d states in pure Pd has been pulled down in energy, due to the strong interaction with H. Inside the hydrogen sphere, the $l = 0$ component dominates; the contributions from higher components ($l = 1, 2$) are very small and cannot be plotted on the same scale. The most salient feature is that the Pd $l = 2$ component is of equal importance to the H $l = 0$ contribution; this low lying band can thus be described as a strong bonding band between Pd d and H s states, with a residual Pd s and p character. The total charge associated with band 1 is $Q = 0.666664$ electrons inside the hydrogen sphere and 0.80006 electrons inside the palladium sphere. For an isolated H atom, a sphere of the same radius $[R_{\text{MT}}(H) = 1.3499$ a.u.$]$ contains only 0.494 electrons. We notice that, in the solid, electrons pile up around the proton site, leading to a well-screened proton. The large screening of an isolated proton in an electron gas was emphasized by Stott *et al.*[4] who found the existence of a bound state H$^-$. Their model is relevant to the problem of hydrogen in simple metals; the present calculation shows that in the palladium lattice, the protons are well screened also. The charge analysis concerning band 1 only already demonstrates that even though the hydrogen atom appears to "donate" electrons to Pd, which fill the

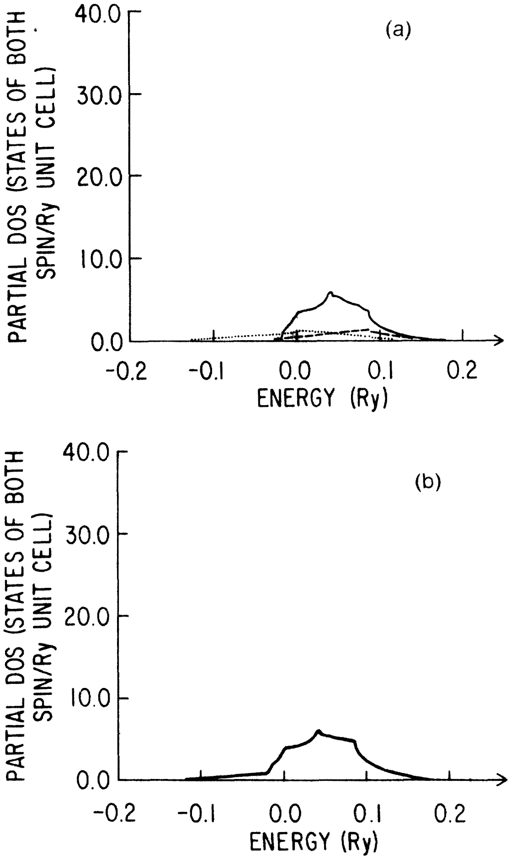

FIG. 4. (a) Partial DOS decomposition of the Pd-H low lying band inside the Pd sphere; $l = 0$ (dotted line); $l = 1$ (dashed line); $l = 2$ (full line). (b) The partial DOS analysis ($l = 0$ component) of the Pd-H low lying band inside the H sphere; other-components are negligible.

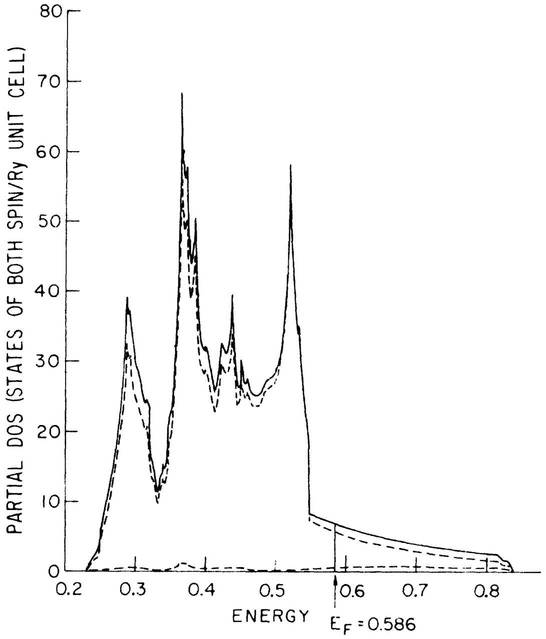

FIG. 5. Partial DOS analysis of the conduction bands, inside the muffin-tin Pd sphere (upper-dashed curve); inside the H sphere (lower-dashed curve). Solid curve shows the total DOS.

Pd 4*d* band holes, and lead to a Fermi surface geometry qualitatively similar to that of silver (a picture which favors the "proton" model); the proton is nevertheless well screened (a picture which favors the "anion model"). This simple discussion shows that none of these oversimplified anion or proton models is correct. The real situation is more complex, as all the states of Pd have been strongly perturbed by the presence of hydrogen in the lattice.

A similar partial DOS analysis has been performed for the higher bands (bands 2–6). Figure 5 plots the total DOS for $E > +0.23$ Ry (solid curve) together with the partial DOS inside the Pd muffin-tin (MT) sphere (including up to $l = 2$ component), and inside the hydrogen MT sphere (dashed curves). Thus, the small difference between the solid curve and the sum of the two dashed-line curves represents the contribution to the DOS from the interstitial region, as momentum components for $l > 2$ can be neglected inside the MT spheres. Inside the Pd sphere, the $l = 2$ component is dominant; the *s* and *p* partial waves are too small to be drawn on the same scale. It appears that the contribution to the DOS from states inside the Pd sphere is dominant in the full energy range shown in Fig. 5, and this band complex can thus be described quite accurately as a Pd 4*d* band complex. Inside the H sphere, the $l = 0$ contribution overwhelms the *p* and *d* partial waves. The hydrogen states do not play a very important role over most of the energy range analyzed in Fig. 5; however, the H *s* contribution increases from $E = 0.5$ Ry up to E_F and above. At the Fermi energy, the *H s* contribution is about $\frac{1}{10}$th of the Pd *d* contribution. For band 6, which determines the Fermi surface, the charge inside the Pd MT sphere is very large (0.9274 electrons) compared to only 0.03012 electrons inside the H sphere.

TABLE II. Partial wave DOS analysis, N_l, inside the muffin-tin Pd and H spheres at $E = E_F$. The total DOS at E_F is $N = 3.4055$, units are states/(Ry unit-cell spin).

	$N_s(l=0)$	$N_p(l=1)$	$N_d(l=2)$
Pd sphere	0.0581	0.1633	2.6177
H sphere	0.2550	0.0296	0.0016

Details of the projected DOS at E_F inside the MT Pd and H spheres are given in Table II. We also notice that the contribution to the DOS at E_F from the interstitial region, 0.2626 states/(Ry unit-cell spin), is comparable to the total contribution inside the H sphere (0.2877 in the same units). It is conceptually different, within the APW method, to study for a compound the partial DOS arising from the interstitial region, as these states cannot be assigned precisely to either Pd or H, and would give difficult angular momentum components if projected either at the Pd or at the H site. For unit cells containing only one type of atom, the analysis of the charge in the interstitial region is easier to perform. If we restrict the analysis of the DOS at E_F to the MT spheres, the Pd *d* to H *s* ratio is 10.265; if we consider the plane-wave states in the interstitial region to be essentially H *s*-like, the *d* to *s* ratio at E_F, 5.507, is still quite high. This analysis of the DOS at E_F is very instructive; naively, from the position of the Fermi energy, in the generally called 5*s*-5*p* part of the Pd bands, and from the geometry of the Fermi surface, which is so similar to the *s* type metal silver, one could have expected a larger *s* character at E_F (except maybe, in the region of the "necks"), as the major portion of the FS is a "deformed sphere." The present result however shows that PdH has retained at E_F, a substantial Pd *d* character. In a recent study of the resistivity of Pd and PdH_x for $0 < x < 1$, Burger *et al.*[35] noticed from the analysis of their data, that PdH should be considered as intermediate between Pd and Ag, for the *d* contribution at E_F. To our knowledge, no partial DOS analysis at E_F has been yet reported for Ag or Cu, but these materials have probably a larger *s*-*p* character at E_F than does PdH. With the aim of calculating the electron-phonon coupling constant λ, using the Gaspari-Gyorffy[36] formalism, in which the screening of the phonon field by the conduction electrons is neglected, Papaconstantopoulos and Klein[8] determined the partial DOS at E_F for PdH; their value of the Pd $l = 2$ to H $l = 0$ ratio at E_F, 8.69, is 15% smaller than ours. Switendick[7] did not study the wave functions of PdH; however, his calculation had the merit of pointing out for the first time that the "proton model" is misleading and that the rigid band model cannot be applied to the bands of pure Pd.

We wish to emphasize here that, besides the interesting information provided by the partial wave analysis at E_F about the conduction electrons which are directly responsible for the occurence of superconductivity, the partial DOS analysis in the full energy range spanned by the valence and conduction bands gives some indication about the shape of the x-ray absorption and emission spectra which, in the constant matrix element approximation, are governed by the dipole selection rule. Unfortunately, no experimental data are available as yet for comparison with the results presented here.

III. PROTON SPIN-LATTICE RELAXATION IN PdH

In the high "spin-temperature" approximation, when the perturbation responsible for inducing transitions in a nuclear spin system is switched off, the spin system relaxes to its ground state by transferring its excess energy to the lattice in time T_1, the spin-lattice relaxation time. In this process, the lattice acts as a "thermal reservoir"; the nuclear spin-lattice relaxation can be viewed as a spin flip scattering experiment of the conduction electrons, due to the magnetic hyperfine interaction with the nuclear spins.[20] The Hamiltonian of this interaction can be written

$$H = -\gamma_N \hbar \vec{I} \cdot \vec{H} , \tag{5}$$

where $\vec{H}$ is the effective hyperfine field operator (including the Fermi contact term, the core polarization, the spin-dipolar and the orbital contributions); $\vec{I}$ is the spin angular momentum operator of the proton, γ_N its nuclear gyromagnetic ratio. The transition probabilities to the different spin eigenstates can be calculated by applying the first-order time-dependent perturbation theory to the Hamiltonian. From the transition probabilities one obtains directly the relaxation rate at the proton site given by

$$T_1^{-1} = \frac{\pi}{\hbar} (\gamma_N \hbar)^2 \sum_{nn'} \sum_{\vec{k}\vec{k}'} \sum_{\sigma\sigma'} |\langle \psi_{n'\vec{k}'\sigma'} | H_- | \psi_{n\vec{k}\sigma} \rangle |^2 \times f_{n\vec{k}\sigma} (1 - f_{n'\vec{k}'\sigma'}) \delta(\Delta E) , \tag{6}$$

where $\vec{k}$ is the wave vector, n the band index, σ the electronic spin of the Bloch function ψ; f is the corresponding occupation number. The δ function expresses energy conservation; however, the changes in the electronic and nuclear Zeeman energies in the relaxation process will be ignored as they are negligible compared to the kinetic energy of the electrons. One then obtains

$$T_1^{-1} = \frac{\Omega^2}{(2\pi)^6} \frac{4\pi}{\hbar} (\gamma_N \hbar)^2 k_B T \times \sum_{nn'} \int_{\text{FS}} |\langle \psi_{n'\vec{k}'\uparrow} | H_- | \psi_{n\vec{k}\downarrow} \rangle |^2 \times \frac{dS_{n\vec{k}}}{|\nabla_{\vec{k}} E_{n'\vec{k}}|} \frac{dS_{n'\vec{k}}}{|\nabla_{\vec{k}} E_{n'\vec{k}}|} , \tag{7}$$

where Ω is the unit-cell volume, k_B the Boltzmann constant, $\nabla_{\vec{k}} E_{n\vec{k}}$ is the gradient of the energy of band n; dS_{nk} is a surface element on the Fermi surface, and the integration $\int_{\text{FS}}$ is carried out over the Fermi surface. Let us assume that H is dominated by the Fermi contact interaction at site $\vec{R}_\nu$,

$$H_{\text{cont.}} = \frac{8\pi}{3} \gamma_e \hbar \sum_{i=1}^{N} \sigma_i \delta(\vec{r}_i - \vec{R}_\nu) , \tag{8}$$

where γ_e is the gyromagnetic ratio of the electron and σ_i the Pauli spin operator for electron i. The contact hyperfine interaction contribution to the relaxation rate at the proton site of PdH, for which only one band determines the Fermi surface, can thus be written

$$T_1^{-1} = \frac{\Omega^2}{9\pi^3} \hbar^3 \gamma_N^2 \gamma_e^2 k_B T \left| \int_{\text{FS}} |\psi_k^s \text{ (H site)}|^2 \frac{dS_{\vec{k}}}{|\nabla_{\vec{k}} E_{\vec{k}}|} \right|^2 . \tag{9}$$

As given by Eq. (9), when the contact interaction alone is included, the expression of the relaxation rate involves essentially the spin density at the nucleus (here the H site) arising from the electronic states at the Fermi surface. It is clear that at the H site, only the s-wave part of the wavefunctions of the electrons at the FS will have a nonzero contribution. This contribution was calculated by generating the wave functions at 15000 $\vec{k}$ points at the Fermi surface; for each $\vec{k}$ point only the s-wave part of the wave function, at the proton site was retained and the $\vec{k}$ space integration at the Fermi energy was then performed as described in Sec. IIC for the DOS integration. The Knight-shift ratio[37] ξ, defined as the ratio of the contact hyperfine field in the compound (PdH) at the proton site, to its value for a free hydrogen atom is

$$\xi = \frac{\langle \psi^2_{\text{H } site \cdot in \text{ PdH}} \rangle_{\text{FS}}}{\psi^2_{\text{H } site, \ free \ atom}} = 0.18 .$$

This ratio is essentially a measure of the amount of s character at the Fermi energy. One should of course keep in mind that PdH is a compound and that the *s* character involved here is relative to the proton site only. This ratio can be compared to the calculated value $\xi = 0.43$ reported by Davis[38] for Cu. For silver, the "measured value" of ξ is 0.7 (quoted by Yafet and Jaccarino[39]). The increasing value of ξ from PdH to Cu and Ag is consistent with an increase in the *s* character at the Fermi surface, which was already predicted in Sec. II B) from the differences in the Fermi surface geometries. We note here that ξ is much more sensitive to the wave-function character than is the Fermi surface geometry.

Equation (9) is often written in the convenient factorized form

$$T_1^{-1} = 4\pi\gamma_N^2 k_B T (N_s H_{\text{hfs}})^2, \tag{10}$$

where N_s is the partial density of states of *s* type at the Fermi energy, for one spin direction.

The experimental results of Wiley *et al.*[19] between 3 and 77 K lead to a Korringa term $T_1 T = 48 \pm 2$ sec K, for the stoichiometric compound. This value corresponds to $(N_s H_{\text{hfs}})_{\text{expt.}} = (4.0 \pm 0.1) \times 10^{15}$ G. erg^{-1} compared to our theoretical value $(N_s H_{\text{hfs}})_{\text{theory}} = 4.4 \times 10^{15}$ G erg^{-1}. The agreement with experiment of this term alone appears to be quite satisfactory, since the theoretical value arising from the contact interaction lies within 7% of the experimental error bar.

Yafet and Jaccarino[39] have shown that, in cubic metals, there is no contribution to the relaxation rate arising from the interference between the contact interaction and the core polarization contributions—even when the wave functions at the Fermi surface show *s-d* hybridization—due to the fact that *s* and *d* functions belong to different irreducible representations of the cubic group. The additional terms of the hyperfine interaction (other than the direct conduction electron contact term) are difficult to evaluate from *ab initio* calculations. If they were included, they would add to the theoretical value of the relaxation rate due to the contact term, which is already higher than the experimental result. If one accepts the good agreement obtained as indicating that the dominant term is provided by the conduction electron Fermi contact interaction then the additional hyperfine interaction due to the core polarization, the spin-dipolar and the orbital contributions are expected to be small at the proton site.

The difference between theoretical and experimental estimates of the relaxation rate may be attributed to the approximation inherent in the calculation (lack of self-consistency, use of the Slater local exchange approximation, etc). However, a comparison of the present results with the values of the DOS at E_F from band calculations[7-9] corresponding to different crystal potentials, shows that other authors have obtained a larger DOS at E_F than found here. Papaconstantopoulos and Klein's[8] calculation leads to N_s/N_{total} at $E_F = 8.97\%$, compared to our value of 7.49%, and would lead, if other factors are equal, to a relaxation rate even higher than the one obtained in the present calculation, and consequently, to a larger discrepancy with the experimental data of Wiley *et al.*[19]

Wiley *et al.*[19] have also studied the spin-lattice relaxation rate of protons in nonstoichiometric compounds. For an $x = \text{H/Pd}$ ratio of $0.7 \leq x \leq 0.8$, $T_1 T = 70 \pm 3$ sec K; this increase over the value for stoichiometric PdH, corresponds, if other factors are equal, to a decrease of 21% in the value of the partial *s* DOS at E_F, for $x < 1$. Direct comparison with our calculated result is quite difficult to perform, since, as shown in Sec. II, the rigid-band model does not apply to the Pd band results because the Pd states are strongly modified by the addition of H into the lattice. For the same reasons, we do not expect the rigid-band model to apply to PdH, even in the vicinity of full stoichiometry. We notice however, that shifting the Fermi level to lower values of the energy to simulate PdH_x with $x = 0.8$ in the rigid-band model, the value of N_s decreases by 21%, as suggested by the experimental data.[19] This result, which reproduces the experimental observation, could however be fortuitous, due to the inadequacy of the rigid-band model; more accurate treatments of the nonstoichiometric compounds are needed to answer this question unambiguously.

IV. CONCLUSIONS

The present results show that the previous success of the proton model was based on the fact that several measurable properties are related to the low value of the DOS at E_F [~3.4 states/(spin Ry unit-cell)] and that E_F falls in the same general portion of the bands as in the noble metals, thereby suggesting the transfer of electrons from H to the top of the Pd bands. Quantitative results about the partial DOS decomposition and charge analysis reveal that the electronic structure of PdH is more complex than that suggested by the simple proton model, as the proton in the solid is found to be very well screened, and hydrogen states interact strongly with the Pd states, leading to a low lying H-Pd bonding band. We have also shown the details of the Fermi surface geometry, which is roughly similar to that of the noble metals but displays a larger anistropy; the FS characteristics had not been previously discussed in the literature. Surprisingly, in view of the FS geometry, the electrons at the Fermi energy, which are responsible for the occurence of superconductivity, retain a large *d* character; however, the *s* contribution is non-negligible and is found to increase as a function of energy, in the vicinity of E_F. PdH can be considered as intermediate between Pd and Ag for the amount of *d* character at the Fermi energy. The proton spin-lattice relaxation rate is well described by the Fermi contact contribution of the magnetic hyperfine interaction alone and leads to a theoretical value in satisfactory agreement with the experimental data of Wiley and collaborators.

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[1] See extensive reviews in W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, *Metal Hydrides* (Academic, New York and London, 1968); G. G. Libowitz, Ber. Bunsenges. Phys. Chem. 76, 705 (1972).

[2] G. G. Libowitz, Ber. Bunsenges. Phys. Chem. 76, 705 (1972).

[3] J. Friedel, Philos. Mag. 43, 153 (1952).

[4] A. Sjölander and M. J. Stott, Phys. Rev. B 5, 2109 (1972); Z. P. Popovic and M. J. Stott, Phys. Rev. Lett. 33, 1164 (1974); C. O. Almbladh, U. von Barth, Z. P. Popovic, and M. J. Stott, Phys. Rev. B 14, 2250 (1976).

[5] H. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1964); W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

[6] M. H. Cohen, Philos. Mag. 3, 762 (1958).

[7] A. C. Switendick, Solid State Commun. 8, 1463 (1970); A. C. Switendick, Int. J. Quantum Chem. 5, 459 (1971); A. C. Switendick, Ber. Bunsenges. Phys. Chem. 76, 535 (1972).

[8] D. A. Papaconstantopoulos and B. M. Klein, Phys. Rev. Lett. 35, 110 (1975).

[9] J. Zbasnik and M. Mahnig, Z. Phys. B 23, 15 (1976).

[10] C. D. Gelatt, Jr., J. A. Weiss, and H. Ehrenreich, Solid State Commun. 17, 663 (1975).

[11] J. S. Faulkner, Phys. Rev. B 13, 239 (1976).

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

[13] W. Buckel and B. Strizker, Phys. Lett. A 43, 403 (1973); J. E. Schirber and C. J. M. Northrup, Jr., Phys. Rev. B 10, 3818 (1974).

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

[15] B. N. Ganguly, Z. Phys. 265, 433 (1975); Phys. Rev. B 14, 3848 (1976).

[16] A. Eichler, H. Wühl, and B. Strizker, Solid State Commun. 17, 213 (1975); R. C. Dynes and J. P. Garno, Bull. Am. Phys. Soc. 20, 422 (1975); P. J. Silverman and C. V. Briscoe, Phys. Lett. A 53, 221 (1975).

[17] J. D. Jorgensen, K. Sköld, A. Rahman, C. A. Pelizzari, H. E. Flotow, R. J. Miller, R. Standley, and T. O. Brun, Proceedings of the Conference on Neutron Scattering, Gatlinburg, Tennessee, 1976, p. 535 (unpublished).

[18] A. Rahman, K. Sköld, C. Pelizzari, and S. K. Sinha, Phys. Rev. B 14, 3630 (1976).

[19] C. L. Wiley, G. Cinader, and F. Y. Fradin, Bull. Am. Phys. Soc. 21, 404 (1976).

[20] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London and New York, 1961).

[21] G. K. Schoep, N. J. Poulis, and R. R. Arons, Physica (Utr.) 75, 297 (1974).

[22] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[23] J. E. Schirber and B. Morosin, Phys. Rev. B 12, 117 (1975).

[24] J. C. Slater, Phys. Rev. 51, 846 (1937); T. L. Loucks, *The Augmented Plane Wave Method* (Benjamin, New York and Amsterdam, 1967).

[25] F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdyna, Phys. Rev. B 1, 4617 (1970); T. J. Watson-Yang; B. N. Harmon, and A. J. Freeman, J. Magn. Mag. Mater. 2, 334 (1976).

[26] B. Segall, General Electric Research Laboratory Report No. 61-RL (2785G), (1961) (unpublished); E. C. Snow, Phys. Rev. 172, 708 (1968); S. Bhatnagar, Phys. Rev. 183, 657 (1969).

[27] D. E. Eastman, J. K. Cashion, and A. C. Switendick, Phys. Rev. Lett. 27, 35 (1971).

[28] J. Jacobs, R. Griessen, F. D. Manchester, and Y. de Ribaupierre, Bull. Am. Phys. Soc. 21, 409 (1976).

[29] O. Jepsen and O. K. Andersen, Solid State Commun. 9, 1763 (1971); G. Lehman and M. Taut, Phys. Status Solidi 37, K27 (1970).

[30] F. Y. Fradin, Phys. Rev. Lett. 33, 158 (1974).

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

[32] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U.P., London, 1964).

[33] M. Zimmerman, G. Wolf, and K. Bohmhammel, Phys. Status Solidi A 31, 511 (1975); G. Wolf and M. Zimmermann, *ibid*. 37, 485 (1976).

[34] D. S. Mclachlan, T. B. Doyle, and J. P. Burger, J. Low Temp. Phys. 26, 589 (1977).

[35] J. P. Burger, S. Senoussi, and B. Soufaché, J. Less Common Metals 49, 213 (1976).

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

[37] W. D. Knight, Solid State Phys. 2, 93 (1956).

[38] H. L. Davis, Phys. Lett. A 28, 85 (1968).

[39] Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).

[40] R. W. Morse, in *The Fermi Surface of Metals*, edited by W. A. Harrison and M. B. Webb (Wiley, New York, 1960), p. 214.

[41] G. A. Burdick, Phys. Rev. Lett. 7, 156 (1961).

[42] D. Shoenberg, Philos. Mag. 5, 105 (1960); D. Shoenberg, Phil. Trans. R. Soc. Lond. A 255, 85 (1962–63).

[43] H. V. Bohm and V. J. Esterling, Phys. Rev. 128, 1021 (1962).