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Electronic structure and scattering in PdB_x from de Haas—van Alphen measurements

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The relaxation times for electron scattering (Dingle temperatures) and the concentration dependence of extremal cross-sectional areas A of the Fermi surface of dilute palladium-boron alloys (PdB_x with $0 \leq x < 0.002$) have been determined from de Haas—van Alphen measurements in fields up to 15 T and temperatures down to 0.4 K. The Fermi surface change $d \ln A/dx$ induced by boron in Pd is 1.3 for the [001] extremal cross-sectional area of the Γ-centered electron sheet and -16.5 and -14.6 for the smallest and largest cross-sectional area of the X-centered hole pocket. For the Γ-centered electron sheet $d \ln A/dx$ is approximately five times larger than in PdH_x and PdD_x, and for the X pocket eight or four times larger than in PdH_x and PdD_x, respectively. These experimental results are discussed in terms of a Thomas-Fermi—type potential and compared to band-structure calculations of Pd, PdH, and PdB and to average—t-matrix calculations for substoichiometric alloys. The Dingle temperatures are compared to electrical resistivity data and analyzed in terms of the Gupta-Benedek formula.

I. INTRODUCTION

In a recent article Gelatt *et al.*[1] presented a theory of the bonding of transition metals to nontransition elements and concluded that two dominant factors determined the electronic structure of this class of compounds. These factors are (i) the lattice expansion of the transition metal by the nontransition element and (ii) the interaction of s-p states of the nontransition element with the d states of the transition metal. Among the examples discussed in their paper PdB takes a special position since in this material the $2p$ states of boron are nearly degenerate with the palladium d band. Since the atomic $2p$ level of boron falls approximately at the center of the Pd d band there is a strong p-d hybridization which results in a p-d bonding and antibonding complex. This is clearly illustrated by the results shown in Fig. 1 (Ref. 2) for the energy levels of Pd_6, Pd_6H, and Pd_6B clusters.[3,4] One of the purposes of this work is to look for hybridization effects in the concentration dependence of the dimensions of the Fermi surface of dilute PdB_x alloys.

Another reason for our interest in these alloys is the similarity which exists between boron and hydrogen (and its isotopes) dissolved in palladium. Boron occupies, for example, the same octahedral interstitial sites[5] of the Pd lattice as hydrogen. The phase diagram of PdB_x for $x \lesssim 0.15$ has the same topology as that of PdH_x for $x \lesssim 0.7$.[6] Both H and B donate electrons which fill empty states of the Pd d band at the Fermi energy. Husemann and Brodowsky[7] concluded from magnetic susceptibility measurements that boron contributed three times more electrons to the Pd d band than H or Ag. This factor of 3 was also confirmed by the heat-capacity measurements of Mahnig and Toth[8] and somewhat more indirectly by the lattice expansion measurements of Alqasmi *et al.*[9] and

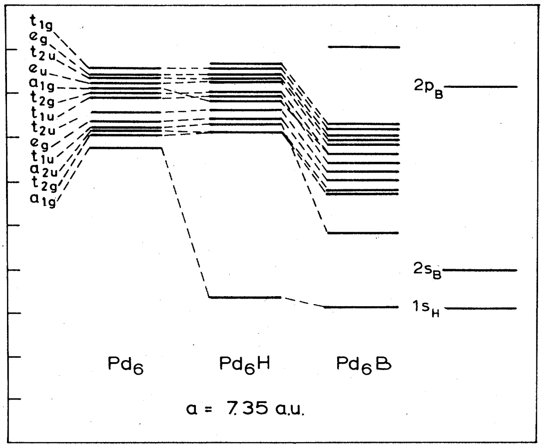

FIG. 1. Calculated energy levels for Pd_6, Pd_6H, and Pd_6B clusters (from Ref. 2). The lattice parameter is equal to 7.3512 a.u. Also indicated are the atomic levels of boron $2p$ and $2s$ states and the hydrogen $1s$ state.

Brodowsky and Schaller[10] and by H-absorption measurements of Husemann and Brodowsky.[7]

In the context of de Haas—van Alphen (dHvA) studies of interstitial alloys boron is also attractive because of its relative large mass. The analysis of the results is then not complicated by the zero-point motion of the interstitial element. (The question of the influence of zero-point motion on the electronic structure of a metal shall be discussed elsewhere on the basis of dHvA measurements on the palladium-hydrogen, -deuterium, and -tritium system.[11]) In addition to Fermi-surface changes we shall also report on relaxation-time measurements for the electron scattering by boron in palladium and compare these results with those obtained in PdH_x and PdD_x.

In Sec. II we indicate the method of preparation of the PdB_x single crystals and give a brief description of the two dHvA spectrometers used in this investigation. Experimental results for Fermi-surface area changes $d\ln A/dx$ and Dingle temperature variations dT_D/dx are presented in Sec. III and discussed in Sec. IV.

II. EXPERIMENTAL TECHNIQUE

A. Sample preparation

The palladium samples used in this work are prepared from palladium powder with a total quoted impurity content of 6 ppm with less than 2 ppm iron supplied by Johnson and Matthey. The powder is melted in a water-cooled copper boat with high-frequency induction heating to obtain a rod-shaped ingot. From this ingot a cylindrical single crystal with a diameter of ~7 mm and a length of ~80 mm is grown by means of zone melting and subsequently cut with spark erosion into rectangular bars of $0.7\times0.7\times10$ mm^3. The crystals are etched in dilute aqua regia to obtain a clean surface and annealed in air for 72 h at 1000 °C.

The palladium crystals are charged with boron at elevated temperatures (800—1000 °C) by a chemical method, the *in situ* reduction of B_2O_3 in an H_2-H_2O atmosphere:[10,12]

$$\tfrac{1}{2}B_2O_3+\tfrac{3}{2}H_2\rightleftarrows B(Pd)+\tfrac{3}{2}H_2O\ . \tag{1}$$

According to the law of mass action, the boron activity in the presence of pure B_2O_3, at the temperature T is

$$a_B=\left[\frac{P_{H_2}}{P_{H_2O}}\right]^{3/2}\exp(-\Delta G^0/RT)\ , \tag{2}$$

where ΔG^0 is the standard free energy of reaction (values from Ref. 13). A well-defined partial pressure ratio P_{H_2}/P_{H_2O} is maintained in the system by equilibration with a Fe-FeO mixture at a different temperature in the two-zone furnace:

$$H_2O+Fe\rightleftarrows FeO+H_2\ . \tag{3}$$

Since the activity coefficient f_B of boron in palladium is known for a number of temperatures[4,10,12] and can be interpolated for others, the mole fraction x_B of boron is also known (with an accuracy of about 4%):

$$x_B=a_B/f_B\ . \tag{4}$$

In order to obtain a homogeneous concentration (deviation less than 1% of the average concentration throughout the sample) the samples are kept at the loading temperature for a time longer than r^2/D_B where r is the radius of the sample and D_B is the diffusion coefficient of B in Pd given by $D_B=D_0\exp(-E_a/kT)$, where D_0 is equal to 0.003 cm^2/sec and $E_a=1.045$ eV.[14]

After loading with boron the samples are placed in boiling water to remove the B_2O_3 sticking to the surface and annealed in vacuum at 200 °C to remove the absorbed hydrogen. As a further check the concentration is additionally determined from the weight increase of a Pd foil which is loaded at the same time in the same chamber. The weight increase is measured on a foil of ~1 g because the dHvA samples are too small to detect the boron concentration accurately enough. The reproducibility of the gravimetric measurements is ~2 μg and the corresponding uncertainty in the boron atomic fraction is $\Delta x/x\sim4\%$.

B. Measurement technique

The changes of the Fermi surface as well as the variation of the conduction-electron scattering rate over the Fermi surface of palladium due to small concentrations of boron impurities are determined from dHvA measurements. The sample magnetization is measured by the standard large-amplitude low-frequency field-modulation technique[15] in dHvA spectrometers located at the Vrije Universiteit in Amsterdam and at the Argonne National Laboratory. The second harmonic of the modulation frequency is used for detecting the oscillations.

The measurements on the X-centered fourth-band hole pocket are carried out in the Amsterdam spectrometer in fields up to 11 T and temperatures down to 1.5 K. The dual dHvA spectrometer is described in detail by Bakker *et al.*[16] The data sampling of the PdB_x dHvA signal is triggered by the dHvA signal of a copper reference single crystal. In this way frequency changes of 1 part in $\sim10^5$ could be detected in the PdH_x and PdD_x alloys, where the crystals were soldered on the positioning plunger. In the present investigation the accuracy is lower (10^{-4}) because a gluing or soldering of the Pd crystal on the positioning plunger is impossible due to the high loading temperatures for B in Pd (1300 K compared to 600 K for PdH_x and PdD_x). The investigations are therefore carried out on different crystals with the same orientation from the same batch. One of these crystals is kept virgin and the others are charged with different concentrations of boron. The uncertainty in the dHvA frequencies is obtained by subsequently mounting and demounting the virgin crystal and comparing the dHvA results of the various runs with each other.

The orbits on the Γ-centered electron sheet are studied at Argonne in fields up to 15 T and at temperatures as low as 0.4 K. Due to the large scattering of the electrons at the boron impurities, dHvA signals of sufficient quality are only detectable in specimens with less than 0.05 at. % boron. The relative change of the Γ-centered electron sheet induced by boron is about ten times smaller than that of the X-centered hole sheet. In order to reach the accuracy in sample orientation and field calibration required to measure such small dHvA frequency changes, we constructed a sample holder in which the crystal can be tilted through an angle of 15° in two vertical planes perpendicular to each other.[17] The specimen is tilted until the magnetic field is lined up with the required symmetry direction as indicated by the turning points of the dHvA phase with angle in a steady field. The two tilt drives contain differential screws constructed in such a way that one revolution on the driving shaft on top of the cryostat corresponds to 0.3° in tilt of the specimen. For the alignment of the symmetry direction of the specimen with the magnetic field an accuracy of better than 0.05° is achieved. In order to avoid inaccuracies in the frequencies from irreproducibilities in the field calibration the signal of a pure palladium specimen is detected simultaneously as reference. Special care is taken to reproduce the orientation of the reference crystal with respect to the magnetic field from sample change to sample change. The reference sample is carefully aligned by means of x-ray diffraction along the [100] symmetry direction and is rigidly mounted in the immediate vicinity of the tilting mechanism. The dHvA frequency of the reference crystal

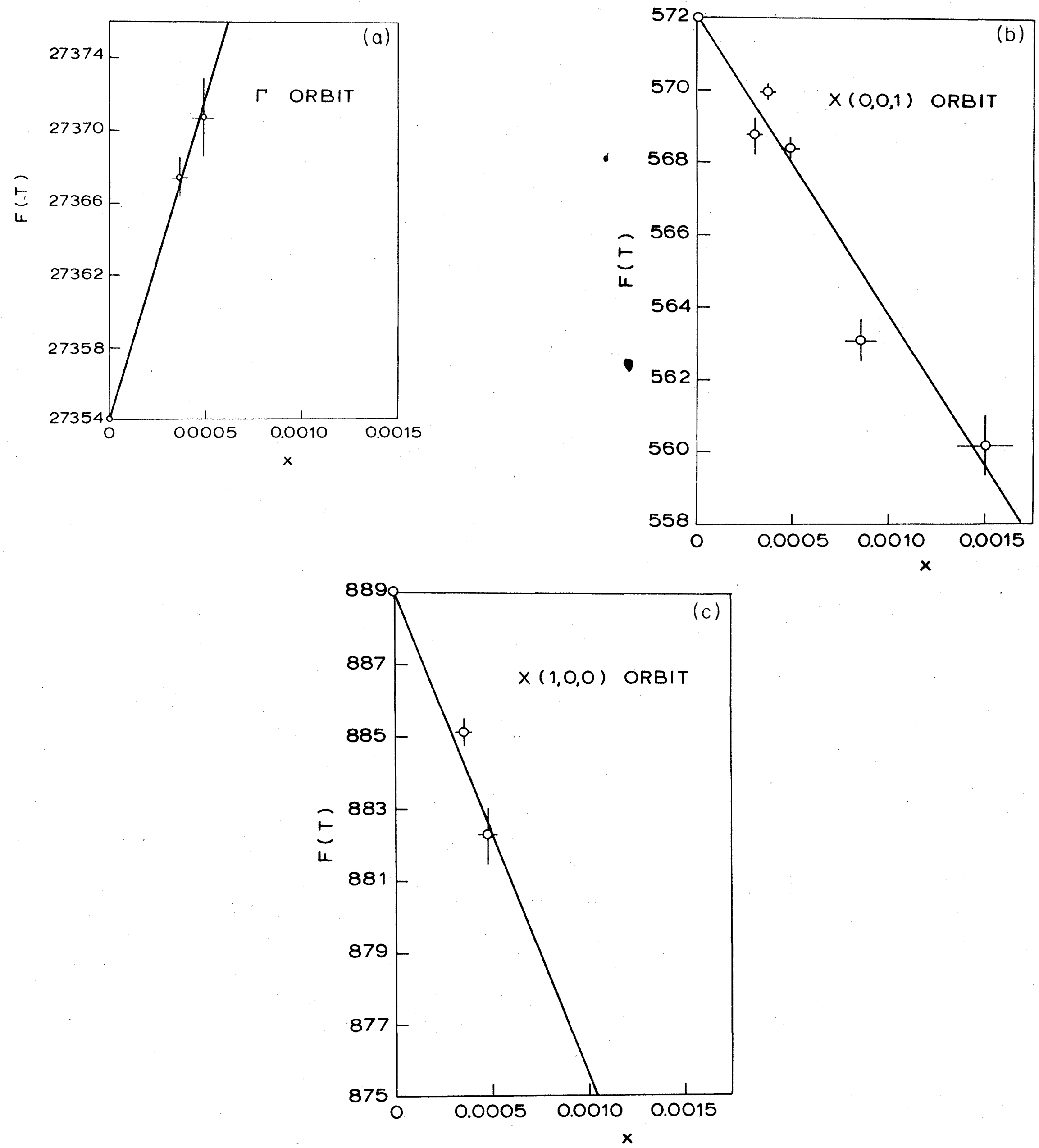

FIG. 2. Concentration dependence of the dHvA frequency of several extremal cross-sectional areas of PdB$_x$ with magnetic field along the [001] direction. (a) Γ orbit, (b) X(0,0,1) orbit, and (c) X(1,0,0) orbit.

is compared before and after the PdB_x measurements with another pure sample mounted on the tilting table by counting ~3000 oscillations over a field range of 14.7 to 5.6 T. In the PdB_x specimens with $x=0.036$ and 0.048 at. %, 2200 and 1000 oscillations are detected to determine the concentration dependence of the dHvA frequency. Samples of ~1 mm^3 are used in this part of the study. The Dingle temperatures are determined in a standard manner from the field dependence of the dHvA amplitude using Dingle plots and assuming a mass of 2.02 for the Γ orbit with the field along [001].[18]

III. RESULTS

The Fermi surface of palladium consists of a sixth-band electron sheet centered at point Γ of the Brillouin zone, three equivalent fourth-band hole ellipsoids centered at point *X*, four equivalent fifth-band hole ellipsoids centered at point *L*, and a complex structure of interconnected tubes open along the (001) directions, the so-called jungle gym (see, for instance, Dye *et al.*[19]). Until now we have succeeded in determining the concentration dependence of the dHvA frequencies associated with the Γ sheet and the *X* pockets. Even at the lowest boron concentration ($x=0.029$ at. %) the frequency of the *L* orbit could not be determined. The boron concentration dependence of the dHvA frequencies of the *X* orbits and the Γ orbit is shown in Figs. 2(a)–2(c). The values for $d\ln A/dx$ derived from the slopes of the curves in these figures are given in Table I together with the values for dT_D/dx derived from the slopes of the curves in Figs. 3(a)–3(c), where the concentration dependence of the Dingle temperature T_D is shown. The data in Figs. 2 and 3 and in Table I indicate that the concentration dependence of the frequencies associated with the *X* pockets in PdB_x is approximately eight times larger than in PdH_x and four times larger than in PdD_x.[16] The concentration dependence of the frequency of the Γ orbit is approximately five times larger than in PdH_x or in PdD_x. The concentration dependence of the Dingle temperature of the *X* orbits is approximately 14 times larger than in PdH_x and the Dingle temperature of the Γ orbit is approximately six times larger in PdB_x than in $PdH_x(D_x)$ as reported by Bakker *et al.*[20]

In order to compare the experimental results to theoretical predictions we carried out average—*t*-matrix (ATA) calculations[21] for PdB with $x=0.0$, 0.05, and 0.15. The potentials are obtained by overlapping atomic potentials[22]

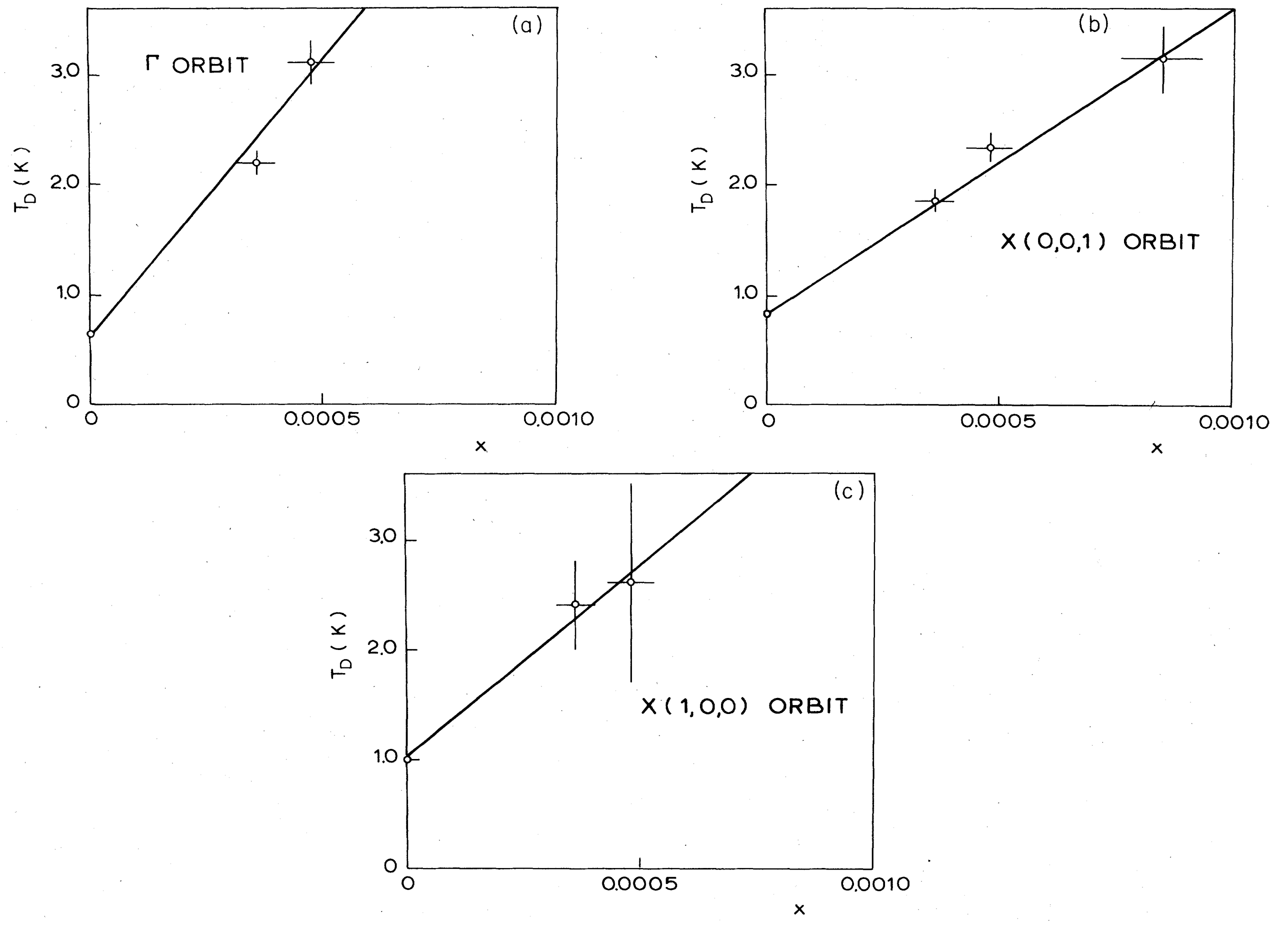

FIG. 3. Concentration dependence of the dHvA Dingle temperature T_D of several extremal cross-sectional areas of PdB_x with magnetic field along the [001] direction. (a) Γ orbit, (b) *X*(0,0,1) orbit, and (c) *X*(1,0,0) orbit.

TABLE I. Boron-concentration derivatives of the dHvA frequencies F associated with the extremal cross-sectional areas A ($F=\hbar cA/2\pi e$) and their Dingle temperatures T_D as obtained from dHvA experiments and from ATA calculations.

	Fermi-surface sheet		
	Γ-electron sheet	X-hole pocket	
Orbit center	Γ(0,0,0)	X(0,0,1)	X(1,0,0)
Field direction	[001]	[001]	[001]
F (T)	27 354	572	889
A (a.u.)	0.7312[a]	0.0153[a]	0.0238[a]
$\left.\frac{d\ln A}{dx}\right\vert_{\text{dHvA}}$	1.33±0.13	−16.5±1.2	−14.6±1.9
$\left.\frac{d\ln A}{dx}\right\vert_{\text{ATA}}$	1.3	−13.0	−14.4
$\left.\frac{dT_D}{dx}\right\vert_{\text{dHvA}}$ (K)	4600±260	3000±200	3800±1000
$\left.\frac{dT_D}{dx}\right\vert_{\text{ATA}}$ (K)	18 000	100	100

[a] Reference 19.

for each separate value of x. The calculational techniques are the same as those used previously to study the properties of hydrides,[23] where results were found that were in reasonable agreement with experiment. The only difference here is that alloy potentials are used which are obtained by overlapping atomic charge densities instead of potentials obtained from renormalized atoms.[24] The results of the calculations for $d\ln A/dx$ are shown in Table I as well as the results of the Dingle temperatures for the X and Γ orbits. The Fermi energy is obtained using ten Baldereschi points[25] for the required Brillouin-zone integrations. When $x=0.0$, the bands are undamped and the calculations using only ten such points are rather inaccurate. However, when x increases, the bands are smeared out and the use of only ten Baldereschi points is justified.

IV. DISCUSSION

A. Energy shifts

The area changes, $d\ln A/dx$, can be converted to average shifts in energy of the states on the corresponding orbits by means of the following procedure. The volume effects are first separated from purely electronic effects and the volume-corrected frequency shifts are then converted to energy shifts $\Delta E=\langle E_{\mathbf{k}}-E_F\rangle$ at constant volume Ω. The brackets $\langle\ \rangle$ indicate an average over the orbit A of an extremal cross section. The resulting energy shifts are then[16]

$$\frac{\Delta E}{x}=\frac{A}{\pi m_b}\left[\frac{d\ln A}{dx}-\frac{2}{3}\frac{1-2\nu}{1-\nu}\frac{d\ln\Omega}{dx}\frac{\partial\ln A}{\partial\ln\Omega}\right]. \tag{5}$$

In Eq. (5) it is implicitly assumed that the electron band mass is independent of the boron concentration. The Poisson ratio ν of the host metal matrix is equal to 0.435 for palladium.[26] The volume derivatives of the dHvA frequencies have been measured by Venema *et al.*[27] in Pd. We assume that they are independent of the boron concentration for small x. The energy shifts calculated by means of Eq. (5) with $d\ln\Omega/dx=0.51$ (Ref. 10) are given in Table II. For comparison we give also the energy shifts for PdH$_x$ and PdD$_x$ (Ref. 16) and the values expected on the basis of a rigid-band model (RBM) with the assumption that 1 electron per H or D and 3 electrons per B are filling empty states at the Fermi energy of the host metal.

Since the data for PdH$_x$ and PdD$_x$ indicate that the behavior of the X ellipsoids is complicated by zero-point motion effects, let us first discuss the results obtained for the Γ sheet. As discussed by Bakker *et al.*[16] and by Griessen and Huisman[28] the electronic states on that Fermi-surface sheet have a strong s character with respect to the octahedral sites occupied by H, D, or B. The electron density at these interstitial sites is approximately constant in space and consequently the amplitude of the zero-point motion has a negligible influence on the energy of these states. From the results given in Table II one finds that the ratio of the energy shifts ΔE_i^{Γ} ($i=$H, D, or B) is

TABLE II. Concentration derivatives at constant volume of average energy shifts $\Delta E/x$ (in mRy) for various orbits of the Fermi surface of PdH$_x$, PdD$_x$, and PdB$_x$. The values of the X orbits are averages over the measured orbits indicated in Table I. Also given are the values from the rigid-band model (RBM) and the values from the ATA calculation.

	$\frac{\Delta E}{x}$ (mRy) (experimental)			$\frac{\Delta E}{x}$ (mRy) (ATA)	
Orbit	PdH$_x$[a]	PdD$_x$[a]	PdB$_x$	PdH$_x$, PdD$_x$	PdB$_x$
Γ	−47±5	−43±5	−231±23	−42	−226
X	−23±2.4	−45±4	−190±25	−16	−163
L	−23±2.9	−64±2.5			
RBM	−32	−32	−96		

[a] Reference 16.

$$\frac{\Delta E_{\mathrm{B}}^{\Gamma}}{\Delta E_{\mathrm{H,D}}^{\Gamma}}=5.1 \ . \tag{6}$$

This ratio can be understood as follows. To lowest order the energy shift ΔE_i^{Γ} corresponding to a concentration x of the interstitial i is given by

$$\frac{\Delta E_i^{\Gamma}}{x}=|\varphi(0)|^2\int V_i(\mathbf{r})d^3r \ , \tag{7}$$

where $|\varphi(0)|^2$ is the electron density at the octahedral site in pure Pd. The potential V may be estimated by means of the Poisson equation $\nabla^2 V_i=-4\pi\rho_i$ from electronic charge densities $\rho(\mathbf{r})$ of neutral atoms, since Klein and Pickett[29] have shown, at least for H in Pd, that the charge density around a proton in Pd is virtually the same as that of a neutral H atom. The atomic potentials calculated using a self-consistent relativistic routine according to Desclaux[30] are given in Fig. 4. The ratio of the calculated integrals for H and B turns out to be 5.2, in remarkably good agreement with the experimental value given in Eq. (6).

The interpretation of the measured energy shifts for the X orbits is much more difficult than for the Γ orbit. For the states on these ellipsoids, which have nearly xz or yz symmetry, the resulting energy shifts can be evaluated by replacing the four lobes of the d states by δ functions 1.0 a.u. away from the Pd atom. When the strength of the hydrogen and boron potentials is compared at these positions it is seen that V_{B} is approximately eight times stronger than V_{H}. The agreement with the measured values is probably fortuitous since it would be more realistic to compare V_{B} with V_{D} because the zero-point motion amplitude for deuterium in the Pd lattice is smaller than for hydrogen in Pd. The ratio between the measured energy shifts is then only a factor of 4. The measured energy shift is in agreement with an ATA calculation as is shown in Table II.

In the remaining part of this section we show that the absence of anisotropy in $d\ln A/dx$ for the X ellipsoids gives information about the band structure of disordered alloys. To discuss this point we consider the band structures of Pd, stoichiometric PdH, and PdB as shown in Fig. 5.[31] One can make the following general observations.

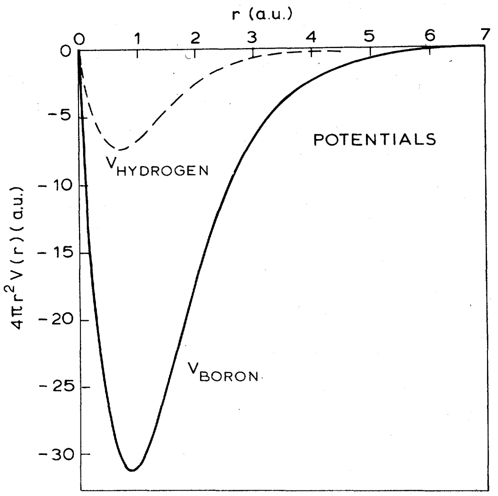

FIG. 4. Atomic potentials of hydrogen and boron calculated according to the method of Desclaux (Ref. 30).

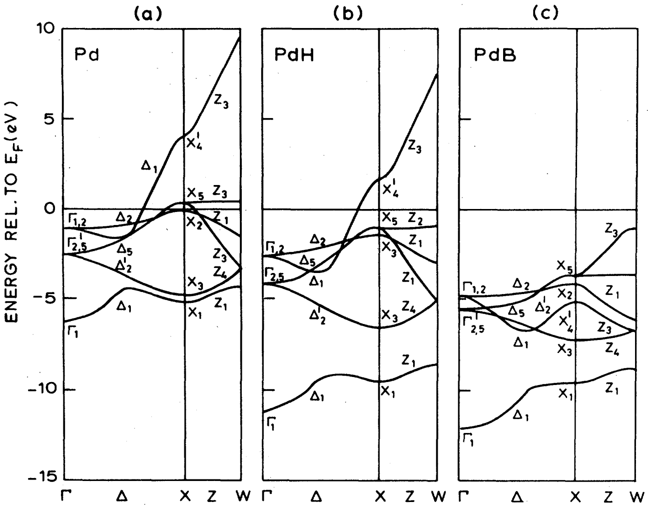

FIG. 5. (a) Energy bands for Pd in the fcc structure. The lattice constant is 7.4578 a.u. (b) Energy bands for stoichiometric PdH in the NaCl structure. The lattice constant is 7.4489 a.u. (c) Energy bands for stoichiometric PdB in the NaCl structure. The lattice constant is 8.3824 a.u. All three curves are from Gelatt (Ref. 31). (The lattice parameters in these calculations do not correspond to the measured lattice spacings.)

(i) The d-band complex in PdB is narrower than in PdH or Pd as a result of the larger lattice spacing a of PdB and an $a^{-4.04}$ dependence of the d-band width $(E_{X_5}-E_{X_3})$.

(ii) The d and the s band in PdB lie much lower in energy with respect to E_F than in Pd and PdH. The ratio of the energy shifts of the s band for PdB and PdH derived from the change in $E_{X_4'}$ with respect to the middle of the d-band complex is approximately 5, in reasonable agreement with the measured energy shifts of the Γ orbit (see Table II).

(iii) The fall of $E_{X_4'}$ below E_{X_5} in PdB leads to a marked difference in the band structures of PdB around point X of the Brillouin zone (see Fig. 6). The dotted line indicates the Fermi energy for 10 electrons per metal atom (pure Pd). The dashed lines represent schematically the Z_3 bands (marked Z_3' and Z_3'') which would be obtained by rigidly shifting the corresponding bands of pure Pd. In this case the main axes of the hole ellipsoid at X would be k_Γ and k_w. However, as the Z_3' band and the Z_3'' band belong to the same representation, they cannot cross each other. The resulting hybridization gap is so large that these bands are more and more pushed apart when going from X to W. From this one could conclude that in *dilute* PdB$_x$ alloys the Z_3'' band would *gradually* be pushed up when the boron concentration increases. k_w would then increase. Since the shape of the Δ_5 branch (and thus k_Γ) is virtually unaffected by boron, one expects

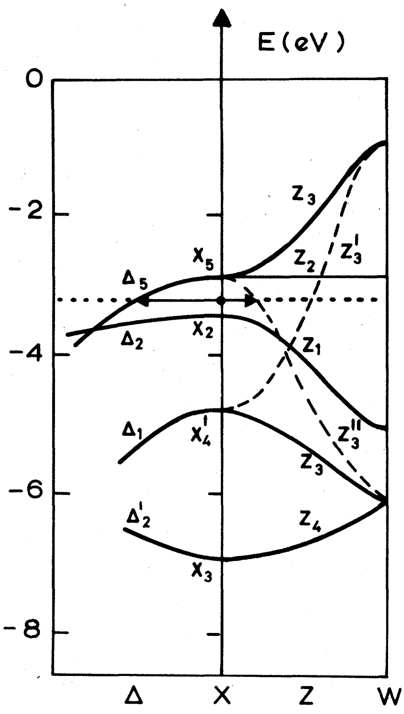

FIG. 6. Enlargement of a part of Fig. 5(c). The dotted line describes the Fermi energy of a system with 10 electrons per atom. The dashed lines labeled Z_3' and Z_3'' are the original Z_3 branches of pure Pd shifted in energy according to the calculated energies $E_{X_4'}$ and E_{X_5} in PdB. These branches are only drawn to facilitate the discussion of the boron-concentration dependence of the hole-pocket radii k_Γ and k_w in dilute PdB_x.

then a positive contribution to $d\ln A/dx$ which is two times larger for the smallest orbit (of area πk_w^2) than for the largest orbit (of area $\pi k_\Gamma k_w$) on the X pocket. The other contribution to $d\ln A/dx$ which arises from the filling of the band when the boron concentration is increased is essentially the same for both orbits and negative. From this one would conclude that the *total* derivative $d\ln A/dx$ for the smallest orbit is greater than that of the largest orbit on the X pocket. This is not substantiated by the experiment (see Table I). There is thus no gradual pushing up of the Z_3'' branch by B in Pd. It is much more plausible that although the Z_3 branches gradually lose spectral weight their shape and position are essentially unchanged by alloying with boron. A similar situation has been found by Gelatt *et al.*[23] and Bansil *et al.*[32] for the lowest bonding band in substoichiometric PdH_x alloys.

B. Electron scattering

In order to extract more information about the scattering of electrons by boron impurities a phase-shift analysis is made. In the same way as for PdH_x and PdD_x (Ref. 16) we estimate phase shifts from the Gupta-Benedek formula[33] with the help of the measured resistivity increase of B in Pd:[34]

$$\frac{\rho}{x}=\frac{3\Omega_0}{\pi e^2\hbar N_{\mathrm{tot}}(E_F)\sum_n\langle v_F^2\rangle_n N_n(E_F)}\times\sum_l(l+1)\sin^2(\varphi_{l+1}-\varphi_l)\,, \tag{8}$$

where $\langle v_F\rangle_n^2$ is the average of the squared Fermi velocity for a given sheet n and $N_n(E_F)$ is the partial density of states corresponding to that sheet. Ω_0 is the atomic volume. The Friedel phase shifts φ_l are assumed to obey the Friedel-Blatt sum rule:

$$\Delta Z-Z^{\mathrm{Pd}}\left[\frac{\Delta V}{V}\right]_{\mathrm{loc}}=\frac{2}{\pi}\sum_l(2l+1)\varphi_l\,, \tag{9}$$

where ΔZ is equal to the valence difference between host and impurity atoms. For an interstitial boron atom $\Delta Z=3$. The valence Z^{Pd} of palladium could either, in analogy with the noble metals, be taken to be equal to the number of electrons contained in the s-like Γ sheet of the Fermi surface (i.e., $Z^{\mathrm{Pd}}=0.375$) or, from a chemical point of view, be set equal to 2. For the purpose of the present analysis we shall arbitrarily set $Z^{\mathrm{Pd}}=1$. In Eq. (9) the local relative volume dilation around the impurity is given (in an elastic continuum model) by

$$\left[\frac{\Delta V}{V}\right]_{\mathrm{loc}}=\frac{1}{3}\,\frac{1+\nu}{1-\nu}\left[\frac{\Delta V}{V}\right], \tag{10}$$

where $\Delta V/V$ is the relative change in lattice volume per unit concentration.[10] With the help of Eqs. (8)—(10) a set of phase shifts can be derived from the resistivity increase $d\rho/dx=2.05\ \mu\Omega\,\mathrm{cm/at.}\,\%$.[34] Using values for the density of states and the Fermi velocity given by Joss and Crabtree,[35] we find

$$\varphi_0=0.17,\quad \varphi_1=1.28\;. \tag{11}$$

These phase shifts show that B in Pd is essentially a p scatterer in contrast to H or D which have a strong s character. The value of $d\rho/dx$ for PdB_x is ~six times larger than $d\rho/dx$ for PdH_x.[20] The fact that this same factor 6 is found for the dT_D/dx of the Γ orbit of both systems support the conclusion of Stocks and Butler[36] that more than 80% of the electrical current is carried by the Γ sheet in Pd-based alloys.

It is seen from Table II that the ATA values for the Dingle temperature increase show serious discrepancies with the experimental values. As discussed in Ref. 20 this is due to the same reasons as in PdH_x and PdD_x (for a discussion of the accuracy of ATA calculations in interstitial alloys see also Refs. 37 and 38).

V. CONCLUSION

The influence of boron on the electronic structure of palladium has been determined by means of dHvA measurements. The results can be qualitatively explained with the help of the atomic potential of boron and are in good agreement with band-structure calculations based on the average—t-matrix approximation. The influence of strong p-d hybridization is not found in the concentration dependence of the dHvA frequencies, but the large influence of boron p electrons is seen in electron scattering. The ATA values for the concentration dependence of the dHvA frequencies are in very good agreement with experiment, but the values for the Dingle temperature changes show serious discrepancies as is the case for PdH_x (PdD_x).[20]

Note added in proof. Recent calculations performed with the extended defect formalism (Refs. 37 and 38) resulted in values for dT_D/dx of 2500 for the Γ sheet and of 2500 and 2100 for the X pockets. These values are in much better agreement with experiment than the ATA results.

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