Table 1. Pressure dependence of the electronic structure of palladium

	Parameters	PDU	PDV	PDW	PDQ	PDZ	PDX	PDR
Lattice Constant (in Bohr radii)	a	7.193	7.2292	7.2665	7.2936	7.3302	7.3761	7.4036
	$do^{\dagger}$	0.3940	0.3896	0.3852	0.3815	0.3767	0.3707	0.3680
	$dd\sigma$	−0.0520	−0.0502	−0.0488	−0.0477	−0.0465	−0.0444	−0.0433
d bands	$dd\pi_1$	0.0167	0.0162	0.0156	0.0153	0.0149	0.0142	0.0138
	$dd\pi_2$	0.0190	0.0185	0.0178	0.0174	0.0169	0.0162	0.0158
	$dd\delta$	0.0003	−0.0003	−0.0003	−0.0003	−0.0003	−0.0003	−0.0003
	γ^{*}	−0.0003	−0.0003	−0.0003	−0.0003	−0.0003	−0.0003	−0.0003
	V_{000}	−0.9324	−0.9366	−0.9409	−0.9439	−0.9480	−0.9524	−0.9559
Conduction bands	V_{111}	0.0067	0.0067	0.0067	0.0067	0.0067	0.0067	0.0067
	V_{222}	0.0023	0.0023	0.0023	0.0023	0.0023	0.0023	0.0023
Orthogonality	A	1.4367	1.4325	1.4285	1.4255	1.4220	1.4168	1.4149
	$LR_0{}^{*}$	2.4010	2.4010	2.4010	2.4010	2.4010	2.4010	2.4010
Hybridization	B	1.5965	1.5775	1.5575	1.5443	1.5233	1.5035	1.4900
	$LR_1{}^{*}$	1.7340	1.7340	1.7340	1.7340	1.7340	1.7340	1.7340
Spin orbit	$E_P{}^{*}$	0.0109	0.0109	0.0109	0.0109	0.0109	0.0109	0.0109
r.m.s. error of fit	σ	0.0075	0.0071	0.0067	0.0063	0.0062	0.0062	0.0062
Fermi energy	$E_F{}^{\dagger}$	0.5263	−	−	−	−	−	−
Pressure in kbars	P	107.0	−	−	−	0.0	−	59.0
Volume of electron/ hole sheet(s)	$V_{e,h}$	0.3860	−	−	−	0.3708	−	0.3603
Total	$N(E_F)$	28.7	−	−	−	30.8	−	31.7
Density of	N_4	0.9	−	−	−	0.8	−	0.7
States per Subbands	N_5	23.6	−	−	−	25.4	−	26.5
Ry-atom	N_6	4.2	−	−	−	4.4	−	4.5

*Value derived from PDZ alone.   †Given relative to $\Gamma_1 \equiv 0$.

was treated by Slaters $\rho^{1/3}$ approximation ($\alpha = 1$). For the 'normal' lattice constant, $a_l = 7.33$ (in atomic units), the RAPW secular equation was solved for the lowest six eigenvalues at 89 independent points (a '$\pi/4a$' mesh) of the BZ. The energy levels were then fitted by a least-square-fit technique in terms of the combined interpolation scheme parameters to an r.m.s. error of 0.005 Ryd. This agreed with the results of Mueller, Freeman, Dimmock and Furdyna[7] to within the r.m.s. error of two fits even though slightly different lattice constants were used.

For the other six cases a simpler procedure was followed. Here energy levels at only five high symmetry points (Γ, X, L, W, K) were found from the RAPW and the six potentials. Using the 12 parameters from the 'normal' lattice constant as an initial choice, new parameters were derived for each of the other six cases by a simplified technique consistent with the analysis of Pettifor.[12] Only the following four 'physical' parameters were varied: (1) V_0, the position of the bottom of the plane wave bands (which follows essentially the variation of the muffin-tin constant); (2) d_0, the position of the d-band complex relative to V_0; (3) W, a multiplicative parameter common to all of the d–d overlap parameters (leading to the adjustment of the d-band width); (4) a multiplicative parameter which leads to simultaneous variation of the overlap (A) and the hybridization (B) of the d-bands with the plane wave. Based on these four parameters,

the results given in Table 1 were found by fitting the six levels at each of the five symmetry points.

Using the parameter listed in the extreme right and left hand portion of the table, energy levels were found from the CIS at 2249 independence points of the BZ. The band energies found at additional points were obtained, using a quadratic interpolation fit[15] on the above energy eigenvalue to produce the smoothed density-of-states histograms plotted in Fig. 1. The Fermi energy was chosen to include 10 electrons/atom. The most surprising result found here was that the 1 per cent of lattice constant, given in Table 1, (corresponding to approximately 100 kbars of pressure) produces a change of over 10 per cent in the density of states at the Fermi energy $N(E_F)$. Also surprising is the strong dependence of the electron volume V_e on the lattice constant. Although the charge neutrality of palladium demands that electron and hole volumes be equal, the exact value for V_e (or V_h) is only fixed through E_F. This strongly modulates the electron–electron interaction leading to a pressure dependent susceptibility and Stoner enhancement factor. In Fig. 2 we show this compensated volume change by scaling the resulting Fermi surface. If palladium were a simple metal, where the change in the Fermi radius with lattice constant was as simple as $k_F \propto a^{-1}$, then the three curves of Fig. 2 would coincide exactly. Figure 2 convincingly demonstrates that the changes in the electronic structure of palladium is not of such a simple 'hydrostatic' form. (The small spurious 5th band hole-pocket observed by Mueller *et al.* in Pd is found to be present at all the lattice constants. Thus further experiments are necessary regarding this point.) Other changes in the electronic structure (broadening and shifting of levels) are more straightforward and may be understood by examining Fig. 1 and Table 1. We point out that if we forced our energy shifts per unit volume onto a traditional deformation potential form, we find that the d-bands of transition metal are some ten times more sensitive to such effects than, say, typical semiconductors. This is also true for the energy shifts found in copper by Faulkner, Davis and Joy.[13]

In summary we conclude from our investigation that the major effects of hydrostatic pressure (a = lattice constant) can be classified as:

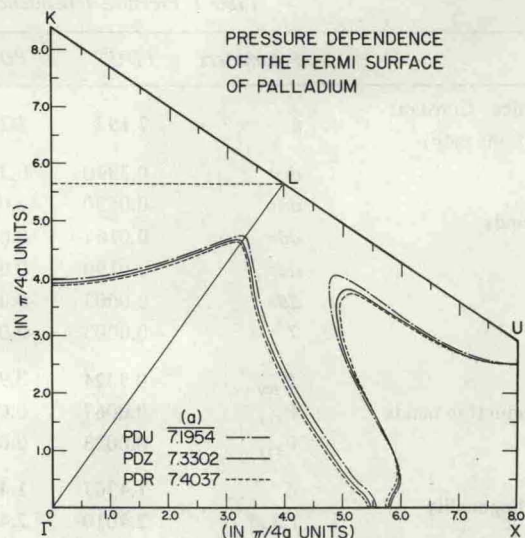(1) Broadening of the plane wave bands as a^{-2} as expected.

FIG. 2. The intersection of the Fermi surface of palladium with the 110 plane for expanded (*PDU*) normal (*PDZ*) and compressed (*PDR*) lattice of palladium. The pure hydrostatic changes in the Fermi surface due to pressure will not be seen in this figure as the scale is in units of $\pi/4a$.

(2) Broadening of the d-band complex due to greater d–d interation as $a^{-6.47}$.

(3) Increased hybridization and orthogonality of the plane waves with the d bands, but not as a simple power law which might be due to the relatively poor representation of the orthogonality and hybridization effects.[16]

(4) Net s–d shift due primarily to the systematic shift of the effective muffin-tin constant with pressure.

(5) Change of the volume of the hole (electron) surface of palladium as $a^{-4.0}$.

(6) Variation of the density of states at the Fermi energy $N(E_F)$ as $a^{+7.8}$.

We have also calculated the dHvA external cross sectional area S for palladium as a function of pressure P along the three symmetry planes. The average value of the pressure derivative $D = \partial(\ln S)/\partial P = 5.4$ $(\pm 0.6) \times 10^{-4}$ kbar^{-1} obtained during this work is in reasonable agreement with $D = 4.0 \pm (0.4) \times 10^{-4}$ kbar^{-1} inferred by Vullemin and Bryant[17] from dHvA experimental data.