PRESSURE DEPENDENCE OF THE ELECTRONIC STRUCTURE AND FERMI SURFACE OF PALLADIUM[*]

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We have considered the effects of hydrostatic pressure on the de Haas–van Alphen external cross-sectional areas of the Fermi surface of palladium. Our calculations for the density of states in palladium with extended and contracted lattice constants show that a change of 2 per cent in the lattice constant changes the density of states at Fermi energy by 10 per cent.

RECENTLY, interest in the electronic structure of pure palladium has been centered on its incipient ferromagnetic nature and the effects of spin fluctuations.[2] However, the importance of the electron–phonon interaction as compared to the electron–paramagnon interaction in the enhancement of the electronic specific heat[3] and the effective cyclotronic mass[4] is still unknown. Moreover, if the effects of spin–orbit coupling on the electronic states are included, then the electron–phonon interaction *does* couple to the exchange-enhanced RPA susceptibility.[5] Our purpose here is to stimulate further experimental interest in the effects of long-wave length phonons on the electronic properties of pure palladium so as to derive the effective electron–phonon coupling constant(s). Among the most direct experimental evidence would be those experiments involving the effects of pressure on the Fermi surface.

A priori we should anticipate that palladium would be a most favorable case on which to measure such effects since the Fermi energy falls at a place on the single-particle density of states curve where it has both large zeroth and first derivatives.[6] This is due to the presence of a saddle point in the purely *d*-like part of the 5th band just 1.89 mRy below the Fermi level and 90 per cent of the contribution to the total density of states comes from the *d*-like holes in Pd (4th and 5th band).[7] Moreover, the Fermi surface of palladium has three separate sheets, which have highly anisotropic effective masses.[4] Thus even small changes induced in the electronic structure of palladium by hydrostatic pressure would have large changes in the Fermi surface.

It has been only relatively recent that transition metal band structures have been available with sufficient
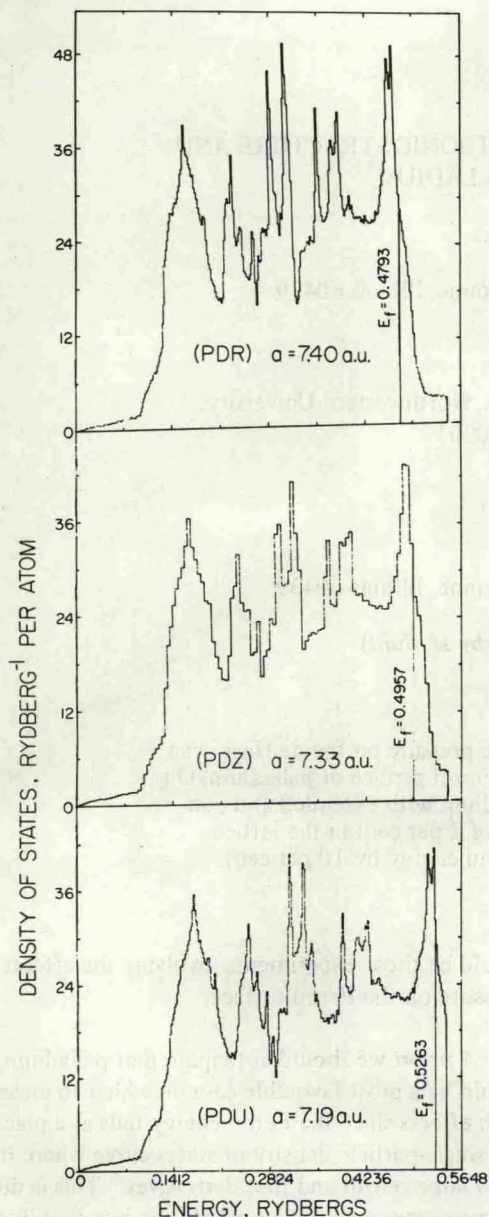
FIG. 1. The density of states for the compressed (*PDR*), normal (*PDZ*) and expanded (*PDU*) lattice of palladium. The energy scale has been shifted such that the bottom of the conduction bands are lined up. As is mentioned in the text, the density of states at the Fermi energy is a very sensitive function of the position of Fermi level because of the saddle point singularity just above the Fermi level

reliability and accuracy to make detailed comparisons with experimental results very meaningful.[6,7] A problematic feature of the early calculations was the

placement of the *d*-band complex relative to the plane wave background. Mattheiss[8] in 1965 using an approximation to self-consistency and charge neutrality gave the first systematic treatment of the first row of the transition metals. The essential feature of these calculations is: (1) the dominance of crystallographic structures in the determination of the form of the *d*-band complex; (2) the relative insensitivity of the electronic structure, other than *d*-band broadening and net shifts within a single crystal type. Based on this insight, Hodges, Ehrenreich and Lang,[9] (HEL) and simultaneously Mueller and Phillips[10] (CIS), proposed schemes which focussed on these results. The narrow *d*-bands were treated as five tight-binding states with a few disposable parameters (essentially the Slater Koster[11] Hamiltonian); the broad $s-p$ bands were treated as four orthogonalized plane waves (the main difference between HEL and CIS occurs here — HEL used a local pseudopotential approximation, where CIS uses a nonlocal pseudopotential), with further disposable parameters. Later on Pettifor[12] (and many others) derived from the first principles (starting from KKR formalism) the hybrid nearly free-electron tight-binding (H–NFE–TB) model Hamiltonian which was very similar to the one empirically derived by Mueller and Phillips and HEL. The model Hamiltonian approach is found to yield quite an accurate description of the band structure of the transition metals like palladium, platinum nickel, etc., at normal lattice constant.[7] Here we consider a more complicated case, namely, the analysis of the electronic structure of transition metal, palladium, using the model Hamiltonian approach, when the lattice constant is treated as a variable. In copper, such calculations by Faulkner, David and Joy[13] using the KKR scheme show remarkable agreement with pressure dependent de Haas–van Alphen data of O'Sullivan and Shirber.[14] This analysis which may be thought of as a form of 'Deformation Potential Theory', offers insight into electron–phonon interaction in the transition metals.

Relativistic augmented plane wave (RAPW) calculations were carried out for palladium based on the seven different lattice constants a_j listed in Table 1. The potentials used in these calculations were constructed as follows. A constant atomic configuration of $4d^{10} 5s^0$ was assumed. The muffin-tin constant was varied so as to maintain charge neutrality (via the Mattheiss scheme) for each choice of a_l. (Thus static electronic screening on these charge densities, exchange

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
	d_0†	0.3940	0.3896	0.3852	0.3815	0.3767	0.3707	0.3680
d bands	$dd\sigma$	−0.0520	−0.0502	−0.0488	−0.0477	−0.0465	−0.0444	−0.0433
	$dd\pi_1$	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
Conduction bands	V_{000}	−0.9324	−0.9366	−0.9409	−0.9439	−0.9480	−0.9524	−0.9559
	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†	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:

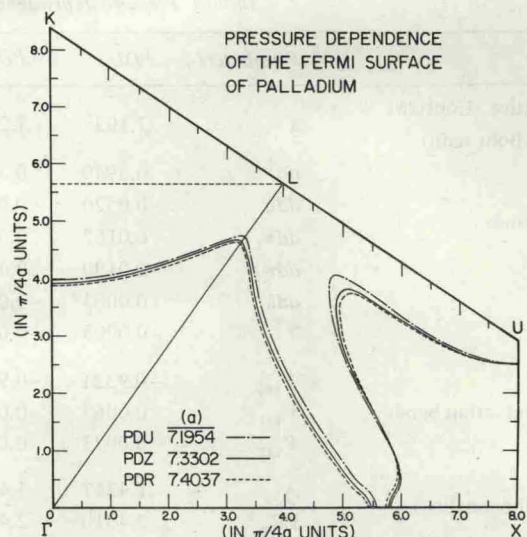(1) Broadening of the plane wave bands as a^{-2} as expected.

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 $D = \partial(\ln S)/\partial P = 5.4$ (± 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.

Finally, although for reasons of simplicity, we have restricted our attention here to changes in the Fermi surface of palladium, it is clear from Table 1 that the application of pressure should induce large changes in other experimental situations as well. For example, measurements of optical properties (piezoreflecting), spin—lattice relaxation times, and the static susceptibility under pressure would all contribute our understanding of the electron—phonon interaction in transition metals. One of us (SGD)[16] has formulated a method of studying the electron—phonon interaction in noble and transition metals. The study of such effects on palladium using the above mentioned formulation is presently underway.

REFERENCES

1. FONER S. and MCNIFF E.J., Jr., *Phys. Rev Lett.* **19**, 1438 (1967).

2. DIAMOND J.B., *J. appl. Phys.* **42**, 1621 (1971); BERK N. and SCHRIEFFER J.R., *Phys. Rev. Lett.* **17**, 433 (1966); DONIACH S. and ENGLESBERG S., *Phys. Rev Lett.* **18**, 554 (1967); SCHRIEFFER J.R., *Phys. Rev. Lett.* **19**, 642 (1968); CLOGSTON A.M., *Phys. Rev. Lett.* **19**, 583 (1967).

3. HOARE F.E. and YATES B., *Proc. R. Soc. (London)* **A240**, 42 (1957).

4. WINDMILLER L.R., KETTERSON J.B. and HORNFELDT S., *Phys. Rev.* **3**, 4213 (1971).

5. This can be seen as either a g-shift of the conduction electrons, or as a change in the density of state as the Fermi energy. Since both effects enter additively in the denominator of the large Stoner—Wohlfarth factor of palladium[6] ($D \sim 15$), the effective lifetime of the paramagnons would be strongly modulated by the electron—phonon interaction. If we assume in the RPA form for the Stoner—Wohlfarth factor $D \sim [1 - \bar{I}N(E_F)]^{-1}$ ($N(E_F)$ being the density of states at the Fermi energy) the effective exchange interaction coupling constant $\bar{I}$ is independent of pressure, then based on the values of Table 1, we would predict that palladium would be ferromagnetic at 75 kbar pressure. However, we believe that the dependence of $\bar{I}$ is even stronger than that the density of states.

6. MUELLER F.M., FREEMAN A.J., DIMMOCK J.O. and FURDYNA A., *Phys. Rev.* **B1**, 4617 (1970).

7. ANDERSON O.K. and MACKINTOSH A.R., *Solid State Commun.* **6**, 285 (1968); ANDERSON O.K., *Phys. Rev.* **B2**, 883 (1970).

8. MATTHEISS L.F., *Phys. Rev.* **139** , A1893 (1965).

9. HODGE L., EHRENREICH H. and LONG N.D., *Phys. Rev.* **152**, 505 (1966).

10. MUELLER F.M., *Phys. Rev.* **153**, 659 (1967) and PHILLIPS J.C., *Phys. Rev.* **133**, A1020 (1969).

11. SLATER J.C. and KOSTER G.F., *Phys. Rev.* **58**, 1498 (1954).

12. PETTIFOR D.G., *J. Phys. C.* **2**, 1051 (1969).

13. DAVIS H.L., FAULKNER J.S. and JOY H.W., *Phys. Rev.* **162**, 601 (1968).

14. O'SULLIVAN W.J. and SCHIRBER J.E., *Phys Rev.* **170**, 667 (1968).

15. MUELLER F.M. *et al., J. appl. Phys.* **37**, 1256 (1966).

16. DAS SHASHIKALA G., to be published;

17. VULLEMIN J.J. and BRYANT H.J., *Phys. Rev. Lett.* **23**, 914 (1969).

Der Einfluss von hydrostatischem Druck auf die De Haas-van Alphen Querschnitte der Fermifläche von Palladium wird behaudelt. Unsere Berechnungen für die Zustandsdichte in Palladium mit ausgedehnten und verkürzten Gitterkoustanten zeigen, dass 2% Äuderung der Gitterkoustanten zu einer Äuderung der Zustandsdichtenan der Fermifläche um 10% führen.