Electronic structure of palladium

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An attempt is made to obtain a good fit to the Fermi-surface data of Pd by using the interpolation scheme. The starting point was the parameters of the scheme that had been fitted to the photoemission data. Making minimal changes in the parameters, we obtain a good fit to the Fermi surface, and at the same time good agreement with the optical data is achieved.

Recently Jepsen *et al.* have demonstrated that (with the use of a linearized augmented-plane-wave method) it is not possible to obtain a good fit to both the Fermi-surface data (governed by eigenvalues near the Fermi energy E_F) and the optical data (governed by eigenvalues away from E_F) for the noble metals.[1] On the other hand, Chen and Segall have demonstrated that this is possible with the use of an empirical approach.[2] Our work on the noble metals, which employs the interpolation scheme, indicates that we can obtain a good fit to both these sets of data. In this article, we take up the case for a transition metal with a complicated Fermi surface, palladium.

The plan of the paper is as follows. In Sec. I, we present the parameters of our model and discuss the fit to the Fermi surface. In Sec. II, we discuss the fit to the optical data. In Sec. III, we conclude by summarizing our findings.

I. FERMI-SURFACE PARAMETRIZATION

We have used the interpolation scheme given originally by Hodges, Ehrenreich, and Lang[3] and modified by Smith and Mattheiss.[4] Since this has appeared a number of times in the past, we shall skip the treatment and refer the reader to the original articles.

The Fermi surface of Pd consists of four sheets. There is a large electron sheet centered at Γ, small hole pockets centered at L, hole pockets centered at X, and an open-hole surface. Accurate de Haas–van Alphen data exist for all the four sheets.

The parameters of the interpolation scheme chosen by Smith to fit the photoemission data are listed in Table I.[5] Using these parameters, we have calculated the extremal areas of 17 orbits, well distributed over the four Fermi sheets, with the magnetic field oriented along different symmetry directions. The calculated areas are listed in Table II together with the experimental data. We see that the calculated areas are in excellent agreement with the expreimental data for all the sheets except for the Γ-centered electron surface. We measure the accuracy to the Fermi-surface fit in terms of a shift ΔE_F in Fermi energy required to match the calculated area with the experimental area. This is 7.9 mRy using Smith's parameters.

We have therefore adjusted some parameters so as to fit the Fermi surface. We were motivated to make only minimal changes so that the agreement with the photoemission data is maintained. Extremal areas

TABLE I. Parameters of the combined interpolation scheme for the empirical band structure of Pd. Energies are in rydbergs.

	Smith's model (Ref. 5)	Our model
OPW		
α	0.013 29	0.013 29
V_{000}	0.043	0.038
V_{111}	0.0545	0.0225
V_{200}	0.0678	0.1125
Orthogonality and hybridization		
R	0.41	0.41
S	1.30	0.52
B_t	1.42	1.398
B_e	1.42	1.398
d bands		
E_0	0.429	0.429
A_1	0.0362	0.0356
A_2	0.0091	0.0091
A_3	0.0126	0.0114
A_4	0.0190	0.0190
A_5	0.0049	0.0049
A_6	0.0171	0.0171
Δ	0.0013	0.0013
Spin orbit		
ξ	0.015	0.015
Fermi energy		
E_F	0.557	0.555

TABLE II. Orbital areas (a.u.) in Pd.

Field direction	Experiment (Ref. 6)	Smith's model (Ref. 5)	Our model
Γ-centered electrons			
⟨100⟩	0.7312	0.697 49	0.726 58
⟨110⟩	0.8265	0.800 48	0.820 83
⟨111⟩	0.6480	0.640 13	0.650 55
X-centered holes			
⟨100⟩*XWU*	0.015 29	0.016 29	0.014 26
⟨010⟩*XW*Γ	0.023 76	0.027 14	0.024 89
⟨110⟩*XU*Γ	0.023 87	0.027 39	0.025 07
⟨110⟩	0.018 39	0.020 02	0.017 66
⟨111⟩	0.020 05	0.021 28	0.018 80
L-centered holes			
⟨100⟩	0.006 137	0.006 442	0.005 553
⟨110⟩*LK*Γ	0.008 782	0.009 176	0.008 380
⟨110⟩	0.005 806	0.012 109	0.009 946
⟨111⟩*LKW*	0.005 090	0.007 096	0.005 667
⟨111⟩	0.007 804	0.008 007	0.006 060
Open-hole surface			
⟨100⟩ϵ		1.922 45	1.946 84
⟨110⟩β		0.323 09	0.306 83
⟨111⟩β	0.2326	0.269 47	0.258 15
⟨100⟩α	0.071 90	0.075 94	0.069 29

are calculated by changing each parameter listed in Table I so as to determine their effect on the Fermi-surface fit. We then determined the set of parameters which gave the best fit to the Fermi surface as determined by ΔE_F. Owing to nonlinear variations that the change in each parameter produces, this procedure had to be repeated many times before we converged to a good model. Since the *d* bands were already in good agreement with the photoemission data, they were disturbed the least. Moreover, we were guided by making minimal changes in the parameters so that the fit to the photoemission data was least disturbed. Our new set of parameters is given in Table I, where we have changed only half the original parameters. The Fermi-surface areas calculated by using our set of parameters are given in Table II. There is a significant improvement over Smith's model. We find an extreme ΔE_F of 2.2 mRy. Obviously, this improvement has been at the cost of the agreement with the photoemission data. Our calculation, nonetheless, demonstrates that one can use the interpolation scheme to parametrize the Fermi surface of a complicated transition metal such as Pd.

Dye *et al.*[6] have recently done a Korringa-Kohn-Rostoker parametrization of the Pd Fermi surface. They were able to obtain an extreme error of 0.8 mRy. We believe Dye *et al.* obtain a better Fermi-surface fit because their fitting procedure is more systematic and because they are not constrained by the requirement of fitting optical data as well.

With a veiw toward studying the role of many-body interactions in determining the low-temperature properties of Pd, we have also calculated the band masses of the 17 orbits listed in Table II. For Smith's[5] as well as our model we find that the experimental masses are greater than the calculated masses. This is attributed to the electron-phonon and electron-paramagnon interactions. The ratio $m^*_{\text{expt}}/m_{\text{calc}} = 1+\lambda_c$, where λ_c is the enhancement factor. We find the average values of $(1+\lambda_c)$ for Smith's[5] and our model to be 1.33 and 1.34, respectively. We note that these values of $(1+\lambda_c)$ are significantly lower than the mean enhancement factors reported by other workers,[7–10] but are in agreement with the recent calculations of MacDonald[11] who obtained a value of 1.36.

II. COMPARISON WITH THE OPTICAL DATA

In this section we would like to see whether we can obtain a good fit to the optical data using the model of the previous section. Here we would like to mention that the optical data cannot be considered to be as accurate as the Fermi-surface data because of the difficulties involved in assigning structures in $\epsilon_2(\omega)$ to different $\vec{k}$ regions in the Brillouin zone.[12] Often a number of regions of $\vec{k}$ space contribute to a structure in $\epsilon_2(\omega)$. Angle-resolved-photoemission experiments of recent years have helped to resolve these difficulties to a great extent. Even then, the inherent "spread" in energy location of structure in optical data makes comparison of band-structure calculations with them less sensitive than comparison with Fermi-surface data. Nevertheless, comparison with optical data perhaps constitutes the only way to judge the correctness of a band model away from the Fermi energy.

There is a wide range of optical data for Pd (Refs. 13–17) taken by workers at different photon energy ranges. The experimental data of Weaver *et al.*[13–15] show a change of slope at 1.3 eV, a well-defined shoulder at ~4.3 eV, and a minimum at ~8.9 eV followed by a plateau region having three broad structures at about 10.0, 15.0, and 20.4 eV. Lässer and Smith[18] have done a band-to-band decomposition of $\epsilon_2(\omega)$ and have been able to identify the approximate regions in $\vec{k}$ space which give rise to these structures. We shall use the assignments given by Lässer and Smith for comparison. The assignments are given in Table III. Also given there are the values of the energy gaps obtained from Smith's[5] as

TABLE III. Locations in energy and $\vec{k}$ space of experimental and theoretical ϵ_2 structures in Pd.

Expt. (eV)	Band pair i-f	$\vec{k}$-space location	Smith's model (eV)	Present calculation (eV)	Remarks
1.3[a]	4→6	L	1.04	1.44	
~2.3[a]	3→5	L	2.63	2.45	Tentative assignments
~4.3[b],~4.8[a]	1→6	Σ	4.73	4.71	
~5.0[c]					
~10.0[c,d]	4→7	Q	10.18	8.71	
	3→7	L	9.95	8.09	
	3→7	U,X	10.33–10.66	9.41–9.33	
~15.0[c,d]	3→8	Z	17.0 –13.37	16.53–13.0	
~20.4[c,d]	3→8	L	27.44	27.38	
	2→8	L	27.82	27.75	

[a]Reference 16.
[b]Reference 13.
[c]Reference 14.
[d]Reference 15.

well as our model. Our model seems to be in better agreement with the optical data compared to Smith's model in the lower-energy region ($\hbar\omega \leq 5$ eV). Although our model gives the correct energy location for the 15-eV structure the 10-eV structure appears at a lower energy. Both the models are unable to give the high-energy structure at 20 eV. Inclusion of 16 orthogonalized plane waves (OPWs), as done by Lässer and Smith, resulted in good agreement with the 20-eV structure. In the absence of specific identification of $\vec{k}$ regions responsible for the experimental structures in $\epsilon_2(\omega)$ at ~1.3 and ~2.3 eV, we are tempted to suggest tentative assignments for these structures. These are given in Table III.

III. CONCLUSIONS

We have shown that the interpolation scheme can be used to parametrize the Fermi surface of the transition metal Pd. We have started with the parameters chosen by Smith to fit the photoemission data and made only minimal changes. As a consequence we see that the resulting band structure gives energy gaps which are in reasonably good agreement with the optical data. There seems to be a discrepancy in the higher band energies which could be remedied by increasing the number of OPWs in the matrix representation.

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