Photoemission spectra and band structures of *d*-band metals. III. Model band calculations on Rh, Pd, Ag, Ir, Pt, and Au

Neville V. Smith

Bell Laboratories, Murray Hill, New Jersey 07974 (Received 21 May 1973)

Model band structures are constructed for Rh, Pd, Ag, Ir, Pt, and Au using a combined interpolation scheme. Spin-orbit coupling and other relativistic corrections are included. The energy distributions of the joint densities of states (EDJDOS) are calculated using quadratic interpolation and a Monte Carlo sampling of k space. Extensive numerical results are presented. A strong resemblance is found between the variation of the profile of the EDJDOS with photon energy and the profile changes seen in experimental photoemission spectra. This has been used to make empirical adjustments to the widths of the d bands in some of the model band structures.

I. INTRODUCTION

In the preceding paper of this series¹ (hereafter referred to as II), experimental photoemission spectra were presented for Rh, Ir, Ni, Pd, and Pt and were compared with those on Cu, Ag, and Au. A consistent pattern of behavior was observed from metal to metal for the changes in the profile of the spectrum on varying the photon energy $\hbar\omega$. In this third paper of the series, we examine in detail the extent to which this pattern is predicted by the one-electron band theory. To this end, we have used the variant of the combined interpolation scheme described in the first paper of the series² (hereafter referred to as I).

In Sec. II, the construction of the empirical band structures for Rh, Pd, Ag, Ir, Pt, and Au is described. The starting point is the set of parameters for the scheme obtained by a nonlinear leastsquares fit to the nonrelativistic augmented-planewave (APW) calculations presented in I. To these parameters, two basic adjustments are made: the first to accommodate relativistic effects, and the second, where necessary, to bring the width of the d band into closer agreement with the experimental photoemission spectra of II.

In Sec. III we present, in the form of figures, the results of numerical calculations of the energy distribution of the joint density of states (EDJDOS) for each of the metals under consideration. It will be seen that the evolution of the profile of the EDJDOS on varying $\hbar\omega$ closely parallels that observed in the experimental spectra reported in II. Indeed, this forms the basis of the identifications used in the empirical adjustments to the bands.

We do not consider, in this paper, the 3d metals, Cu and Ni. Cu has been discussed extensively elsewhere.³ In the case of Ni, the experimental data is fragmentary. Also, the complication of ferromagnetism would take us beyond the scope of this paper. In this regard, we note that there are

indications⁴ that the photoelectric properties of Ni may not be consistent with a simple band model. We confine ourselves, therefore, to the 4d and 5dmetals Rh, Pd, Ag, Ir, Pt, and Au. Calculations of a similar nature have been reported for some of these metals by Christensen and by Janak et al.⁵

II. EMPIRICAL BAND STRUCTURES

The model band structures presented here were generated by the following systematic procedure. The starting point was the nonrelativistic-APW calculations reported in I. To these results were fitted the parameters of the combined interpolation scheme also described in I. We will use hereon the nomenclature of that paper and will refer to this starting set of parameters as the Mattheiss parameters. The scheme is a variant of the one devised originally by Hodges, Ehrenreich and Lang and by Mueller.⁶ It differs from the earlier schemes in that special attention has been given to obtaining a good reproduction of the unoccupied bands.

A. Relativistic corrections

The most conspicuous relativistic correction required in the model band structures is for spinorbit coupling. It lifts degeneracies and brings about a qualitative modification to the bands. It is readily incorporated into the model Hamiltonian by insertion of the matrices M and N given by Friedel *et al.* and Abate and Asdente.⁷ A further parameter is required, namely, the spin-orbit parameter ξ . To avoid introducing this as a disposable parameter, we simply set it equal to the atomic value taken from the tables of Herman and Skillman.⁸

The other relativistic corrections (mass-velocity and Darwin shifts) were absorbed by adjustment of the parameters of the scheme so as to fit certain eigenvalues of the relativistic-augmented-

9

plane-wave (RAPW) calculations of Andersen⁹ (Rh, Pd, Ir, and Pt) and Christensen^{10,11} (Ag and Au). It was found that, after insertion of the spinorbit coupling and adjustment of the parameter

 E_0 , the *d*-band eigenvalues obtained using the Mattheiss parameters were quite close to the first-principles RAPW results. At this stage, therefore, we have all the parameters of the *d*-*d* block, namely, E_0 , A_1 , A_2 , A_3 , A_4 , A_5 , A_6 , and Δ .

The parameters of the plane-wave and hybridization blocks were then obtained by application of the quick recipe described in Sec. III B of I to the appropriate RAPW eigenvalues. Before this could be done, however, it was necessary to remove the ambiguities in the identification of the four planewave-like levels at W. As discussed in Sec. III D of I, the four relativisitic levels, W_6 , W_7 , W_6 , and W_7 , correspond in the nonrelativistic limit to the levels W_1 , W_2 , W_3 , and W_3 , but the individual identifications are not obvious. We would like to know which levels in the relativistic case would correspond to which levels in the nonrelativistic case if spin-orbit coupling were removed but the other relativistic effects retained. In the case of Au, it was argued in I that the respective shifts of the s- and p-like levels at X and L indicate that the identification and ordering of the four planewave-like levels at W must be $E(W_{2^*}) > E(W_3)$ $> E(W_3) > E(W_1)$. Likewise, comparison of Christensen's RAPW eigenvalues for Ag¹¹ with his earlier nonrelativistic results using the same potential¹² leads one to conclude that the identification and ordering would be $E(W_{2'}) > E(W_1) > E(W_3) > E(W_3)$. In the cases of Rh, Ir, Pd, and Pt, Andersen¹³ has kindly provided the author with estimates of the identification and ordering. These are shown in Table I together with those already inferred for Ag and Au.

Having obtained the ordering of the plane-wave levels at W, we may now proceed straightforwardly with the recipe of Sec. III B of I. First of all, we set the radius parameter R equal to a constant value of 0.41, and thereby remove it from the list of disposable parameters. This maneuver is jus-

TABLE I. Identification and ordering of the four plane-wave levels at W in RAPW calculations.

	Decreasing Energy →					
Rh	W_2 ,	<i>W</i> ₁	W ₃	<i>W</i> ₃		
Pd	W_2 .	W_1	W ₃	W_3		
Ag	$m{W}_2$,	W_1	W_3	W_3		
Ir	W_2 ,	W_3	W_1	W_3		
Pt	W_2 .	W_3	W_3	W_1		
Au	W_2 .	W ₃	W ₃	W ₁		

tified by the nonlinear least-squares fitting experiments described in Sec. IV of I. There, it was shown that R deviates very little from its average value of 0.41 for all the metals considered.

The hybridization parameter B was determined by examining the hybridization shifts of the d-like levels X_1 , L_1 , $W_{2'}$, and W_3 according to the recipe. We made no distinction here between the e_g and t_{2g} subbands (i.e., we set $B_e = B_t = B$). This is also justified by the nonlinear least-squares fitting experiments in I, where it was found that the values determined for B_e and B_t were always very close.

The parameters V_{111} , V_{200} , and S were fitted to the band gaps between the plane-wave-like levels at X, L, and W. The parameters V_{000} and α were obtained by a similar straightforward application of the recipe. All that remains, at this stage, of the original Mattheiss parameters are the values for A_1 , A_2 , A_3 , A_4 , A_5 , A_6 , and Δ . All the other parameters have suffered some adjustment.

The procedure adopted in this paper differs from that in an earlier paper by Smith and Traum¹⁴ in only one respect. Here we have used, for each individual metal, the Mattheiss parameters for the *d* bands. In the earlier paper we used a uniformly stretched version of the parameters required to fit the *d*-bands of the APW calculation on Cu by Burdick.¹⁵ Our concern there was to perform an explicit test of the resonance formulation of *d*-band metals.^{16,17} The main results of the resonance formulation are embodied in the Mattheiss parameters since it can be seen, from Table IV of I, that the Fletcher-Wohlfarth A_n parameters maintain roughly constant ratios with respect to each other.

The parameters presented in this paper are believed to be superior to those used by Smith and Traum¹⁴ for two reasons. Firstly, Cu represents an extreme case since it is the metal of the group having the narrowest d bands. It may therefore be unwise to use it as the starting point of an extrapolation to other metals. Secondly, the Mattheiss parameters are more reliable since they were obtained by an elaborate nonlinear leastsquares fitting procedure at many points in the Brillouin zone (BZ). The Burdick Cu parameters, on the other hand, were obtained by fitting a few purely d-like levels (namely, Γ_{25} , Γ_{12} , X_5 , X_3 , X_2, L_3^{u}, L_3^{l} , and K_4). Incidentally, it should be pointed out that, while this latter method for fitting the d-band parameters of the scheme to firstprinciples results works reasonably well for Cu, it is not so successful for the 4d and 5d metals. The difficulty arises when one tries to determine the parameters B and R from the second-order hybridization shifts at X_1 and L_1 . The estimates of these shifts are quite sensitive to the values of

 A_1 , A_2 , etc., determined at an earlier stage. This can lead to unphysical values for the hybridization parameters. This, for example, accounts for the overly large values for R in Ag, Au, and Rh obtained in previous work by the author¹⁸ and by Pierce.¹⁹ Our present method avoids this difficulty, and the model band structures presented here supersede all others presented by the author.^{14, 18, 20}

B. Width and position of d bands

In addition to the adjustments made above, the following *empirical* adjustments were made, where necessary, in order to bring the model band structures into closer agreement with experimental photoemission spectra. Actual comparison with experiment is deferred until Sec. III E. Here we discuss only the details of the adjustment itself.

In the cases of Rh and Pd, it was found that, within the limits of accuracy of the interpolation scheme and the limit of resolution of the photoemission experiments, the agreement was as good as could be expected. No further adjustments were made to the parameters for Rh and Pd.

In the cases of Ag, Ir, Pt, and Au, the d bands were widened by 21%, 8%, 14%, and 26%, respectively. The widening was accomplished by scal-

ing the parameters A_{1-6} and Δ uniformly in proportion to the d-band width W. The hybridization coefficient B was scaled as $W^{1/2}$ in rough accordance with the requirements of the resonance formulation.¹⁷ The position of the d band, E_0 , was then given a small readjustment in order to assure reasonable agreement for the Fermi-surface topology. In the cases of Ir and Pt, the Fermi level intersects the top of the d bands and is pinned⁹ there by the requirements that the total number of occupied states be equivalent to nine and ten electrons per atom, respectively. For Ir and Pt we, therefore, arranged that any adjustment of w be accompanied by an adjustment of E_0 such that E_0 $+4A_1$ (representing, in the absence of spin-orbit splitting, the X_5 level at the top of the d bands) remain constant. In the cases of Ag and Au, it was arranged that the distance between the Fermi level and the top of the d bands $(E_F - E_0 - 4A_1)$ was in agreement with the photoemission spectra and that the separation between E_F and L_2 , gave a reasonable value for the radius of the Fermi-surface neck. All other parameters of the scheme $(\alpha, V_{000}, V_{1f1}, V_{200}, R, S, \text{ and } \xi)$ were left unchanged.

The final values of the parameters for the scheme are shown in Table II. These are to be compared

TABLE II. Parameters of the combined interpolation scheme for the empirical band structures of Rh, Pd, Ag, Ir, Pt, and Au. Energies are in Rydbergs.

	Rh	Pd	Ασ	Ir	Pt	Au
ODW						
OPW						
α	0.01419	0.01329	0.01175	0.01541	0.01436	0.01297
V_{000}	0.142	0.043	-0.107	0.029	-0.060	-0.164
<i>V</i> ₁₁₁	0.0725	0.0545	0.0236	0.0295	0.0102	-0.0133
V_{200}	0.0739	0.0678	0.0494	0.0455	0.0313	0.0090
Orthogon	ality & Hybr	ridization				
R	0.41	0.41	0.41	0.41	0.41	0.41
S	1.58	1.30	0.81	1.63	1.38	0.92
B_t	1.70	1,42	1.10	2.04	1.76	1.45
B_e	1.70	1.42	1.10	2.04	1.76	1.45
d bands						
\boldsymbol{E}_0	0.582	0.429	0.056	0.629	0.461	0.191
A_1	0.0448	0.0362	0.0254	0.0590	0.0510	0.0390
A_2	0.0112	0.0091	0.0065	0.0139	0.0122	0.0094
A_3	0.0154	0.0126	0.0090	0.0191	0.0169	0.0132
A_4	0.0238	0.0190	0.0124	0.0302	0.0258	0.0191
A_5	0.0061	0.0049	0.0035	0.0079	0.0068	0.0054
A_6	0.0231	0.0171	0.0115	0.0282	0.0242	0.0182
Δ	0.0001	0.0013	0.0050	0.0005	0.0019	0.0044
Spin orbi	t					
ξ	0.012	0.015	0.019	0.041	0.046	0.053
Fermi er	nergy					
E _F	0.715	0.557	0.450	0.790	0.645	0.530



FIG. 1. Model band structure for Rh.

with the starting parameters in Table IV of I. Apart from the changes described above, the other notable difference between the starting values and final values occurs in the values for the local pseudopotential parameters, V_{111} and V_{200} , in the 5*d* metals. These are considerably smaller in the final set than in the starting set. While this improves agreement with photoemission results (by lowering band 7 and permitting transitions to it at lower photon energies), this adjustment was not done by fitting the experimental spectra. It is actually a relativistic effect and arises naturally in the corrections of Sec. II A. Lowering V_{111} and V_{200} , while keeping S roughly the same, brings about both the relativistic shrinking of the plane-wave



FIG. 2. Model band structure for Pd.



FIG. 3. Model band structure for Ag.

gaps at L and X and also the relativistic inversion of the s- and p-like levels at W.

The model band structures obtained using the final set of parameters of Table II are displayed in Figs. 1-6. The zero of energy, in these figures, is taken at the Fermi level.

III. ENERGY DISTRIBUTIONS OF JOINT DENSITIES OF STATES

A. Photoemission and band structure

A fundamental assumption made in the interpretation presented here is that conventional oneelectron band theory is applicable. We therefore require that the optical transitions be direct; i.e., the initial and final states have the same reduced



FIG. 4. Model band structure for Ir.



FIG. 5. Model band structure for Pt.

wave vector \vec{k} and their energies are obtainable from a one-electron band calculation. As pointed out in several earlier papers, ^{14,18,20} we then expect a resemblance between the photoelectron energy spectra and the (EDJDOS) defined by the following integral over the Brillouin zone:

$$D(E, \hbar\omega) = \sum_{f,i} \int_{\mathbf{BZ}} d^3 k \,\delta(E_f - E_i - \hbar\omega) \,\delta(E - E_i) \,.$$
(1)

 $E_i(\vec{k})$ and $E_f(\vec{k})$ are, respectively, the energies at \vec{k} in an initial band, *i*, and a final band, *f*. The summation is made over all pairs (f, i) of bands which can participate. The initial state must, of course, be occupied and the final state unoccupied. It is therefore understood that $D(E, \hbar \omega)$ includes the factor $F(E_i)[1-F(E_f)]$, where *F* is the Fermi occupation function.

An important word in the preceding paragraph is "resemblance." Even within the one-electron band approach, $D(E, \hbar \omega)$ is a rather crude approximation to $N(E, \hbar \omega)$, the actual photoelectron energy spectrum. A more precise expression would be

$$N(E, \hbar\omega) = C \sum_{f,i} \int_{BZ} d^3k \left| P_{fi} \right|^2 T(E_f, \vec{k})$$
$$\times \delta(E_f - E_i - \hbar\omega) \,\delta(E - E_i) \,. \tag{2}$$

C is a normalization parameter; $|P_{fi}|^2$ is the square of a momentum matrix element representing the strength of a given optical transition; $T(E_f, \vec{k})$ is an over-all escape factor representing the probability of the excited electron reaching the surface without inelastic scattering and then escaping across it.

In this paper we offer calculations and results only for the EDJDOS $D(E, \hbar\omega)$. Our major concern is with energy locations of structure in the spectra. Relative intensities of various pieces of structure are not considered in detail since they will be affected by the weighting factors $|P_{fi}|^2$ and $T(E_f, \vec{k})$ which have not been calculated in this investigation. The effects of the latter factor can be simulated approximately by assuming that $T(E_f, \vec{k})$ is independent of \vec{k} . It may then be taken outside the integral of (2) and expressed in the form derived by Berglund and Spicer²¹ using their three-step model. The approximate $N(E, \hbar \omega)$ curve is then obtained simply by multiplying $D(E, \hbar \omega)$ by this "effective threshold" function²² T(E). Its main effect is to cause the simulated $N(E, \hbar \omega)$ to fall smoothly as E approaches the low-energy limit determined by the work function, and then to vanish below this energy. The procedure here will be to present the entire $D(E, \hbar \omega)$ curve. Insertion of the T(E) factor, if desired, is left to the interested reader.

B. k-space integrations

A practical advantage of disregarding the weighting factors discussed above, is that the EDJDOS is determined entirely by the $E(\vec{k})$ dispersion relations. In order to evaluate the EDJDOS, all that is required is a fast method of generating the energy eigenvalues at any point in the BZ. This need is amply fulfilled by the combined interpolation scheme discussed in I, and whose parameters have been presented above. The method used here for performing the k-space integration was a histogram technique involving quadratic interpolation and a Monte Carlo sampling similar in principle to the methods described by Brust²³ and Mueller *et al.*²⁴ The details are as follows.

The calculations were performed in the same $\frac{1}{48}$ th



FIG. 6. Model band structure for Au.

irreducible wedge of the BZ used in I $(k_y \ge k_z \ge k_z)$. The BZ was divided into cubes having a cube edge equal to one-tenth of the Γ to X distance (i. e. MESH = 10 in the nomenclature of Mueller $et al.^{24}$). We will refer to these cubes as the big cubes, and we considered only those big cubes necessary to enclose completely our $\frac{1}{48}$ th wedge. Each of these big cubes was then divided into 27 subcubes having one-third the cube edge. At 13 points within each big cube the energy eigenvalues were obtained by diagonalizing the model Hamiltonian. The 13 points were the center of the center subcube and the centers of the 12 subcubes disposed about the center of the center subcube in the $\langle 110 \rangle$ directions. For each band, therefore, we have 13 energy eigenvalues which are more than sufficient to determine the ten parameters of a quadratic interpolation of the form

$$E(\vec{\mathbf{k}}_0 + \delta \vec{\mathbf{k}}) = E(\vec{\mathbf{k}}_0) + \vec{\mathbf{m}} \cdot \delta \vec{\mathbf{k}} + \delta \vec{\mathbf{k}} \cdot \vec{\mathbf{q}} \cdot \delta \vec{\mathbf{k}} , \qquad (3)$$

where $\vec{k_0}$ is the center of the big cube. For MESH = 10, a total of 1625 diagonalizations are required. Precautions were taken in those big cubes which are intersected by the boundary planes of the $\frac{1}{49}$ th wedge. Some of the subcube centers may lie outside the wedge. Rather than diagonalize at such a point, we diagonalized instead at the point equivalent to it by symmetry lying inside the wedge.

Having set up the quadratic interpolation coefficients within a given big cube, we then performed a Monte Carlo sampling. In each big cube, 3000 points were generated. This corresponds to a total of 250 000 points in the $\frac{1}{48}$ th wedge or 12 000 000 in the entire BZ. In the boundary big cubes, each point was tested, and those lying outside the $\frac{1}{48}$ th wedge were rejected. At each Monte Carlo point, we deduced the initial energies and photon energies of the direct transitions and added them into the appropriate EDJDOS histogram bins. A bin width of 0.1 eV was used on both the E and $\hbar\omega$ scales. All the numerical results presented here employed 3000 Monte Carlo points in each big cube. In some of the earlier runs, where we were concerned only to construct the structure plot, a sample of 1000 points per big cube was found to be adequate.

C. Numerical results

The results obtained for the EDJDOS are shown in Figs. 7 and 8 for the 4d and 5d metals, respectively. Curves are shown for photon energies spaced at 0.3-eV intervals from $\hbar\omega = 4.5 - 11.4$ eV. Each curve is labeled by the upper limit of the corresponding 0.1-eV histogram bin; in other words, a curve labeled $\hbar\omega = 10.2$ eV corresponds to optical transitions in the 10.1 $\leq \hbar\omega \leq 10.2$ -eV interval. The curves have been smoothed by convolution with a Lorentzian broadening function of 0.3-eV full width at half-maximum. This is done primarily for clarity in presenting the figures, but it has the incidental advantage of simulating the finite experimental resolution and possible lifetime-broadening effects.

In Figs. 7 and 8 we present only the EDJDOS itself. The curves contain no information concerning the momentum matrix elements. They represent only the phase space available for optical transitions at their respective photon energies. As discussed above, no estimate has been included for attenuation of the curve by scattering or finite escape probability. Actually, omission of the effective threshold factor T(E) has the advantage of permitting the reader to inspect the low-energy end of the EDJDOS which would otherwise have been cut off. This may ultimately be of use to workers concerned with the interpretation of experimental data for ϵ_2 , the imaginary part of the dielectric constant. In a constant matrix element approximation, $\omega^2 \epsilon_2$ is proportional to the joint density of states which is given by the total area under the EDJDOS curve.¹⁸ It may be possible to trace structures in the frequency dependence of ϵ , to developments of the profile of the EDJDOS in the same frequency range. No such analysis will be attempted here. We turn, rather, to a detailed discussion of the consequences of these results with respect to photoemission spectra.

D. Discussion and identification of structure

The smoothed EDJDOS curves of Figs. 7 and 8 are quite rich in structure, and the profiles of the curves vary quite markedly with photon energy. This latter feature is a consequence of the \vec{k} -conservation selection rule. The EDJDOS is the density of states over a surface in the BZ. The surface moves through the BZ as $\hbar\omega$ is varied, so that we sample a continuously changing section of the band structure. We will concentrate here on the more prominent structures toward the higher energies; i.e., the features corresponding to electrons capable of surmounting the surface barrier and being observable in the measured photoelectron energy spectrum.

Some of the peaks in Figs. 7 and 8 have been numbered. We have adopted a uniform numbering system here in order to bring out our identifications of given pieces of structure from metal to metal. The system is the same as that used in II and is intended also to bring out our identifications of peaks in the EDJDOS with structures in the experimental photoemission spectra. We now list some of the specific changes in the EDJDOS as $\hbar\omega$ is varied.

Feature (i). At the low photon energies in Pd, Ag, Pt, and Au, a peak labeled 1' is observed. This corresponds to optical transitions from the



FIG. 7. EDJDOS for the 4*d* metals, Rb, Pd, and Ag, plotted at 0.3-eV intervals in the 4.5-11.4-eV photon energy range.

flat uppermost d-band. As $\hbar \omega$ is increased, this peak is observed to undergo a sudden increase in strength. This is seen in the curves for Pd, Ag, Pt, and Au at $\hbar \omega = 7.5$, 7.8, 6.3, and 6.0 eV, respectively. After this sudden growth the peak is given the new label 1. Proceeding to higher photon energies, peak 1 is observed to split into a doublet labeled 1*a* and 1*b*. The component 1*a* stays at the same initial energy as 1. The component 1*b* moves to lower initial energies as $\hbar \omega$ is increased. In Ir and Rh, the features listed above are not all observable. This is because the Fermi level falls lower so that the flat uppermost *d* band is largely unoccupied.

Feature (ii). At intermediate photon energies, a peak is observed which we have labeled 2'. This is to be seen in Figs. 7 and 8 at $\hbar\omega = 9.0$, 8.1, 8.4,

8.4, 7.8, and 6.9 eV for Rh, Pd, Ag, Ir, Pt, and Au, respectively. On increasing \hbar_{ω} , this peak splits into the doublet labeled 2a and 2b. The component 2a remains at roughly the same initial energy at which 2' occurs at the photon energies listed above. The component 2b appears at a somewhat lower initial energy. This splitting is quite clear in Ir, Pt, Au, Rh, and Pd. It is only barely resolved in Ag.

Feature (iii). If the same feature labeled 2' and discussed in (ii) is pursued to lower photon energies it is observed to undergo further changes in profile. Shoulders appear on the high-energy side. In Ir, Pt, and Rh, peak 2' is seen to evolve into a doublet. The lower-energy component is labeled 2c' and the upper component retains the label 2'. In the other metals, the components are not well



FIG. 8. EDJDOS for the 5d metals, Ir, Pt, and Au, plotted at 0.3-eV intervals in the 4.5-11.4-eV photon energy range.

resolved and are simply lumped together under the collective label 2'.

Feature (iv). A peak labeled 3' in the EDJDOS curves and Figs. 7 and 8 is observed to move downwards slightly in initial energy as $\hbar \omega$ is increased. At a sufficiently high photon energy, peak 3' becomes obscured by the abrupt emergence of a peak labeled 3 at a somewhat higher initial energy. This event can be seen in the curves at $\hbar \omega = 10.8, 9.6, 9.3, 10.5, 9.3, and 8.4 \text{ eV}$ for Rh, Pd, Ag, Ir, Pt, and Au, respectively.

Feature (v). A peak labeled 4' at the lower photon energies is observed for initial energies below those of peak 3'. At a sufficiently high photon energy, a peak 4 emerges abruptly. This event is seen in the curves at $\hbar\omega = 10.5$, 9.9, 10.8, and 9.9 eV for Pd, Ag, Pt, and Au, respectively. It is labeled specifically in Figs. 7 and 8 only for Ag and Au.

It will be noted from the Figs. 7 and 8 that the structures listed above tend to remain fairly stationary as $\hbar\omega$ is varied. These features therefore have "initial-state character" and are related to the occupied *d* bands. There is, however, anotable feature of the EDJDOS curves which has final-state character. For example, if we examine the curves for Pt in Fig. 8, the abrupt emergences of peaks 1, 2b, 3, and 4 at initial energies of about -0.2, -2.0, -3.2, and -4.6 eV are first observed in Fig. 8 at photon energies 6.3, 8.1, 9.3, and 10.8 eV, respectively. To within a tenth of an eV, these events occur at initial energies (*E*) given by

$$E + \hbar \omega = 6.1 \text{ eV} . \tag{4}$$

The transitions involved in these events, therefore, occur to final states roughly constant in energy located about 6.1 eV above the Fermi level. This indicates something rather special about the band structure at this energy. Appeal to Fig. 5 reveals the simple explanation that the minimum energy of band 7 occurs at about 6.0 eV. The events described above are therefore attributed to the onset of transitions to this new final-state band. Similar features in the other metals can be explained in the same way.

The curves for Rh and Ir (and, to a lesser extent, those for Pd and Pt) show large contributions to the EDJDOS at its extreme low-energy end. They are designated as "dd" in Figs. 7 and 8. These represent transitions from states within the d bands to the unoccupied d states just above the Fermi level. These features will not be observable in photoemission, since they occur below the vacuum-level cutoff; nor are they expected to influence ϵ_2 too strongly. This is because d - d transitions are forbidden in the free atom, and the momentum matrix elements in the solid are consequently expected to be small.

The structure, labeled L and indicated by a dashed line in the curves for Ag and Au in Figs. 7 and 8, respectively, is the edge of a rectangular-box shaped contribution²⁵ to the EDJDOS due to conduction-band-to-conduction-band transitions in the vicinity of $L_{2'} + L_1$.

E. Comparison with experiment

The reader will probably have noted a strong point-by-point resemblance between features (i)-(v) and the respective features observed in the experimental spectra described in Secs. III C and III D of II. This, indeed, forms the basis of our identifications and was used to make the empirical adjustments described in Sec. II B.

There are two differences in detail between the features of the EDJDOS described above and those observed experimentally. The abrupt growth of peak 1' of the EDJDOS into peak 1 has not been observed experimentally. Likewise, the emergence of peak 4 at an initial energy close to that of peak 4' has not been established experimentally. There is also a more general difference between the EDJDOS and the experimental spectra. The EDJDOS, apart from the effective threshold factor T(E), corresponds to the photoelectron energy distribution curve (EDC) denoted by $N(E, \hbar \omega)$. The features of the experimental spectra of II, however, refer to the negative of the second derivative of the EDC, $-N''(E, \hbar\omega)$. It appears, therefore, that features of the EDJDOS can be seen and identified in the experimental spectra, but they are often weak and appear to be riding on a background. The background may be an intrinsic phenomenon (as in the model developed by Doniach²⁶) or it may be a consequence of imperfect sample or surface preparation. In this regard, we note that cesiation is responsible, at least in part, for the washing out of structure in the experimental spectra.

Turning now to energy locations of structure, we show, in Figs. 9 and 10, structure plots for the 4d and 5d metals comparing the peak loci of the EDJDOS with those of structure in the experimental spectra. The full and open circles represent, respectively, the positions of peaks and shoulders in the experimental $-N''(E, \hbar\omega)$ spectra and are the same as those shown in Fig. 12 of II. The full and broken lines indicate the locations of structure in the EDJDOS. These were obtained, as in previous papers, ^{14,20} by constructing a coarse contour map of the $-D''(E, \hbar\omega)$ histogram.

It is seen in Figs. 9 and 10 that agreement between band theory and experiment is quite good. In the case of Rh and Pd, no empirical adjustment of the Mattheiss parameters for the d bands was regarded necessary. The agreement was as close as could be expected considering the experimental



FIG. 9. Structure plots comparing the predictions of band theory with the experimental results for the 4d metals Rh, Pd, and Ag. The full (open) circles represent peaks (shoulders) in the experimental derivative spectra, -N'' ($E, \ \pi\omega$). The full and broken lines represent loci of structures in the EDJDOS.



FIG. 10. Structure plots comparing the predictions of band theory with the experimental results for the 5d metals, Ir, Pt, and Au. The full (open) circles represent peaks (shoulders) in the experimental derivative spectra, $-N''(E, \hbar \omega)$. The full and broken lines represent loci of structures in the EDJDOS.

resolution and the inaccuracies inherent in the application of the interpolation scheme. In the case of the other metals, Ag, Ir, Pt, and Au, the width and position of the d bands were adjusted, as described in Sec. IIB, until the alignment between the peak loci of the EDJDOS and the experimental structure was similar to that for Rh and Pd. No elaborate fitting procedure was employed. Satisfactory alignment was judged by the eye of the author.

Events such as the emergence of peaks 2b and 3 occur at about the same photon energies in the EDJDOS as in the experimental spectra. As noted in Sec. III D, these particular events are attributed to the onset of transitions to band 7. The comparisons of Figs. 9 and 10 therefore confirm the rough locations of band 7 in Figs. 1-6. Note that there would have been significant disagreement here had the relativistic corrections described in Sec. II A had not been made.

Finally, we comment upon an interesting feature in the Ir and Rh comparisons of Figs. 9 and 10 which appears to indicate an outright breakdown of the model. In Ir, it can be seen in Fig. 10 that the leading edge of the EDJDOS falls to lower initial energies as $\hbar \omega$ is increased from 5.0 to 8.3 eV. The edge of the experimental spectra, which lies just above the uppermost row of circles, stays quite stationary in initial energy. Possible explanations have been discussed in Sec. IV B of II.

IV. CONCLUSIONS

This paper and the two preceding papers (I and II) represent an extended program of work attempting to establish the connection between the photoelectron energy spectra and the one-electron-band structures of the fcc d-band metals. A brief summary of the work of all three papers is as follows.

(a) It has been observed experimentally in II that the positions of structure in the photoelectron energy spectra, when plotted in the $E - \hbar \omega$ plane, display a consistent pattern from metal to metal. The pattern for one metal can be obtained from the next by uniform shifting and stretching operations. This is in accordance with the resonance formulation^{16, 17} of *d*-band metals, and so the experimental data has been offered¹⁴ as the first direct experimental evidence for the resonance formulation.

(b) The model calculations of this paper using the combined interpolation scheme developed in I show that the main features of the pattern are predicted by one-electron band theory and a direct transition model. The structure observed experimentally, however, is weaker than that calculated. This may indicate some smearing or a background due to effects beyond the simple direct transition model. 26

(c) Observations (a) and (b) have been exploited to construct empirical d bands¹⁴ or, as in the present paper, to make small empirical adjustments to the first-principles APW calculations of I. The model band structures which we have finally arrived at may be of use in the interpretation of other electronic properties of these metals. They are readily constructed by diagonalization of the model Hamiltonian described in I using the parameters of Table II.

ACKNOWLEDGMENTS

I am indebted to Dr. O. K. Andersen for helpful communications. I am grateful also to my colleagues L. F. Mattheiss and M. M. Traum for helpful discussions.

TABLE III. Identification of the present numbering scheme for peaks in the photoemission spectra with schemes used in previous papers. The band-to-band assignments are shown in columns 6 and 7.

Present numbering	Au (Ref. 20)	Au (Ref. 27)	Ag (Ref. 28)	Cu (Refs. 29 and 30)	Band in <i>i</i>	dices f
1 <i>a'</i>	1 <i>a</i>	• • •	•••	•••	•••	• • •
1'	(,)	(م)	(n)	(n)	5	6
1, 1 <i>a</i>	{ 1 }	{ ° }	{ B }	$\{B\}$	5	7
1 <i>b</i>	2	С	-	Н	3,4,5	7
2a '	3 a	•••	•••	• • •	•••	•••
2 c'	3 c	• • •	• • •	• • •	• • •	•••
2'	(3, 4), 3b	• • •	()		4	6
2 a	3	D	$\langle c \rangle$	{ ^c }	4	7
2b	4	Ε	()	F	4	7
3'	5 <i>a</i>	•••	D	D	3	6
3	5	F	E	G	3	7
4'	(.)	()	()	(-)	1.2	6
4	{6 }	$\{G\}$	$\left\{ H \right\}$	${E}$	3	7
L	• • •	H	A	A	6	7

APPENDIX

A major aim of the present work has been to examine trends in the behavior of the photoemission spectra as a function of position in the periodic table. As part of this survey, we have adopted a uniform numbering system for structures intended to indicate (a) the identifications of peaks from metal to metal and (b) the identifications of experimental structures with peaks in the theoretical EDJDOS. Previously, a variety of labeling schemes have been used. Table III is a Rosetta Stone which translates the present numbering scheme into the labeling schemes used by other papers, and, in particular, by the papers on the noble metals by the photoemission workers at Chalmers University, ²⁷⁻²⁹ who have performed experiments on cesiated samples very similar to those described in II.

Our present numbering scheme has the additional advantage of embodying the band-to-band assign-

¹M. M. Traum and N. V. Smith, preceding paper, Phys. Rev. B 9, 1353 (1974) (referred to as II).

- ²N. V. Smith and L. F. Matthiess, second preceding paper, Phys. Rev. B 9, 1341 (1974) (referred to as I).
- ³N. V. Smith and W. E. Spicer, Opt. Commun. <u>1</u>, 157 (1969); N. V. Smith, Phys. Rev. Lett. <u>23</u>, 1452 (1969);
 I. Lindau and L. Wallden, Solid State Commun. <u>9</u>, 209 (1971); A. R. Williams, J. F. Janak, and V. L. Moruzzi, Phys. Rev. Lett. <u>28</u>, 671 (1972).
- ⁴U. Bänninger, G. Busch, M. Campagna, and H. C. Seigmann, Phys. Rev. Lett. <u>25</u>, 585 (1970); D. T. Pierce and W. E. Spicer, Phys. Rev. Lett. <u>25</u>, 581 (1970).
- ⁵N. E. Christensen, Phys. Status Solidi <u>52</u>, 241 (1972); Phys. Status Solidi <u>55</u>, 117 (1973); J. F. Janak, D. E. Eastman, and A. R. Williams, Solid State Commun. <u>8</u>, 271 (1970).

ments discussed recently, in the case of Cu, by Moruzzi, Williams, and Janak.³⁰ Their identifications of the initial- and final-state bands contributing to various peaks in the spectra of Cu are displayed in columns 6 and 7 of Table III. Because of the similarities from metal to metal, observed in II, we expect these band-to-band assignments to apply equally well to the other metals. In the present numbering scheme, structures in the spectra have been given labels of the form N, N', Na, Nb, etc., where N is an integer. Structures which have a common value of N tend to originate from the same initial state band, given by i = 6 - N. At the lower photon energies, the labels are primed, indicating that the final states lie in band 6. At the higher photon energies, band 7 becomes available as an additional source of final states; this corresponds to the use of unprimed labels in the present numbering system.

⁶L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. <u>152</u>, 505 (1966); H. Ehrenreich and L. Hodges, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1968), Vol. 8, p. 149; F. M. Mueller, Phys. Rev. <u>153</u>, 659 (1967).

- ⁷J. Friedel, P. Lenglart, and G. Leman, J. Phys. Chem. Solids <u>25</u>, 781 (1964); E. Abate and M. Asdente, Phys. Rev. <u>140</u>, A1303 (1965).
- ⁸F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).
- ⁹O. K. Andersen, Phys. Rev. B <u>2</u>, 883 (1970).
- ¹⁰N. E. Christensen and B. O. Seraphin, Phys. Rev. B <u>4</u>, 3321 (1971).
- ¹¹N. E. Christensen, Phys. Status Solidi <u>54</u>, 551 (1972).
- ¹²N. E. Christensen, Phys. Status Solidi <u>31</u>, 635 (1969).

- ¹³O. K. Andersen (private communication); Dr. Andersen points out that, since his RAPW codes were not symmetrized and eigenvectors were not calculated, the identification of levels must be done by inspection. The W_3 levels are easily identified by switching off the spin-orbit coupling. His identification of the W_1 and W_2 , levels was based on an inspection of the logarithmic derivatives at the Wigner-Seitz sphere. This procedure works well for Pt and Ir, but for Pd and Rh, the estimate of the relative ordering of W_2 , and W_1 is more tentative.
- ¹⁴N. V. Smith and M. M. Traum, Phys. Rev. Lett. <u>29</u>, 1243 (1972).
- ¹⁵G. A. Burdick, Phys. Rev. <u>129</u>, 138 (1963).
- ¹⁶J. M. Ziman, Proc. Phys. Soc. Lond <u>86</u>, 337 (1965);
 J. Hubbard, Proc. Phys. Soc. Lond. <u>92</u>, 921 (1967).
- ¹⁷V. Heine, Phys. Rev. <u>153</u>, 673 (1967); D. G. Pettifor, Phys. Rev. B <u>2</u>, 3031 (1970).
- ¹⁸N. V. Smith, Phys. Rev. B <u>3</u>, 1862 (1971).
- ¹⁹D. T. Pierce, Ph.D. thesis (Stanford University, 1970) (unpublished).
- ²⁰N. V. Smith, Phys. Rev. B <u>5</u>, 1192 (1972).
- ²¹C. N. Berglund and W. E. Spicer, Phys. Rev. <u>136</u>, A1030 (1964).

- ²²W. F. Krolikowski and W. E. Spicer, Phys. Rev. <u>185</u>, 882 (1969).
- ²³D. Brust, Phys. Rev. <u>139</u>, A489 (1965).
- ²⁴F. M. Mueller, J. W. Garland, M. H. Cohen, and K. Benneman, Ann. Phys. (N.Y.) <u>67</u>, 19 (1971).
- ²⁵R. Y. Koyama and N. V. Smith, Phys. Rev. B <u>2</u>, 3049 (1970).
- ²⁶S. Doniach, Phys. Rev. B 2, 3898 (1970); W. E.
 Spicer, Phys. Rev. 154, 385 (1967); J. G. Endriz and
 W. E. Spicer, Phys. Rev. Lett. 27, 570 (1971); W. L.
 Schaich and N. W. Ashcroft, Phys. Rev. B 3, 2452 (1971); B. J. Waclawski and E. W. Plummer, Phys.
 Rev. Lett. 29, 783 (1972); B. Feuerbacher and B. Fitton, Phys. Rev. Lett. 29, 786 (1972).
- ²⁷P. O. Nilsson, C. Norris and L. Walldén, Solid State Commun. <u>7</u>, 1705 (1969); Phys. Kondens. Materie <u>11</u>, 220 (1970).
- ²⁸L. Walldén and T. Gustafsson, Physica Scripta, <u>6</u>, 73 (1972).
- ²⁹I. Lindau and L. Walldén, Physica Scripta, <u>3</u>, 77 (1971).
- ³⁰V. L. Moruzzi, A. R. Williams, and J. F. Janak, Phys. Rev. B <u>8</u>, 2546 (1973).