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Optical properties of Rh, Pd, Ir, and Pt

J. H. Weaver*

Physical Sciences Laboratory, University of Wisconsin–Madison, Stoughton, Wisconsin 53589

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The reflectivity and ϵ_2 spectra of the fcc metals Rh, Pd, Ir, and Pt are reviewed and discussed between about 0.1 and 30 eV. Structures in ϵ_2 are interpreted in terms of recent band calculations. Calculations of the joint density of states and ϵ_2, based on the energy distribution of the joint-density-of-states results of Smith, are presented and compared with experiment. The low-energy dielectric functions are observed to be sensitive to the bands near the symmetry point L, notably the spin-orbit-split d-like states which shift relative to the sp-like L_6^- level and affect transitions below about 2 eV. Structure near 2.8 eV in Rh is interpreted in terms of transitions between bands 3 and 5 along Q. Like the bcc and hcp transition metals, the fcc metals display minima in ϵ_2 near 10 eV and, at higher energies, characteristic structures are observed which can be understood qualitatively in terms of transitions to high-lying bands. The fcc metals, like the bcc and hcp transition metals, are shown to have two volume and two surface plasmons. In the discussion, shortcomings and uncertainties in the optical data are pointed out and appeals for further study are made.

INTRODUCTION

The last few years have seen an increasing interest in the optical properties of the transition metals,[1,2] and there has been a store of optical data accumulated in the literature. For many of the transition metals, first-generation optical studies have determined the reflectivity $R(E)$ and the dielectric functions either from analysis of $R(E)$ or by ellipsometric techniques. Second-generation thermoreflectance measurements[3,4] are beginning to appear, and ultraviolet-photoemission-spectroscopy (UPS), x-ray-photoemission-spectroscopy (XPS), and electron-spectroscopy-for-chemical-analysis (ESCA) experiments have and are being performed. Coincident with the experimental efforts have come increasingly reliable theoretical efforts to describe the d electrons, calculate high-lying bands, and consider such difficult problems as exchange and atomic configuration. Fast interpolation schemes have made energy-band calculations feasible away from high-symmetry points and make calculations of ϵ_2 for comparison to optical data possible.[5–8]

In earlier studies we have considered the bcc metals (Nb,[9] V,[10] Ta,[10] Mo,[4,10] W,[11] and[12] Cr) and have attempted to review the literature, present optical data over a wide energy range, and discuss the dielectric functions in terms of the electronic energy bands. The same has been done for several of the hcp metals (Ti,[13] Zr,[13] Hf,[13] and[14] Y). In this paper, the fcc metals Rh, Pd, Ir, and Pt are considered, but the emphasis is on interpreting structure observed in existing optical data. Calculations of ϵ_2 in a constant-matrix-element approximation are presented, based upon the results of Smith.[15] Systematics and trends are considered within the fcc group, and they are compared to the other transition metals. For Rh and for Pt it will be seen that several studies have been reported and the results are in good agreement. There appears to be greater uncertainty for Pd, and the optical properties for Ir have not been determined between 4.1 and 6.2 eV.

Since the reflectivity $R(E)$ is the most frequently measured quantity, we will briefly review the spectra for Rh, Pd, Ir, and Pt, in that order. The imaginary part of the complex dielectric function, ϵ_2, where $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$, lends itself to comparison with calculations, and figures comparing experimental ϵ_2 with calculations will be discussed. It will become clear that sizable gaps in our knowledge exist, and it is hoped that this study will serve as a stimulus for future experimental and theoretical efforts.

One of the shortcomings of most studies of the fcc metals is that they have often been limited to a relatively narrow energy range. An attempt has been made here to bring together the various data between ~ 0.1 and ~ 30 eV so that comparisons can be made and each study viewed in conjunction with others. The interpretation will start in the infrared spectral region where free-electron contributions are important, span the range of interband absorption, and extend to high energy where transitions from core states are observed. The interpretation of structure in ϵ_2 will be based largely on the calculations of Smith and Mattheiss,[8,15] Christensen,[16] Andersen,[17] and Mueller *et al.*[18] Smith and coworkers[8,15,19,20] recently considered these same metals using higher-derivative UPS[19] and XPS[20] data and a fast interpolation scheme to obtain energy bands which were in good agreement with experiment. Those bands will be reproduced here. Additional discussion will be based on the ESCA measurements of Baer *et al.*[21] (Rh, Pd, Ir, Pt)

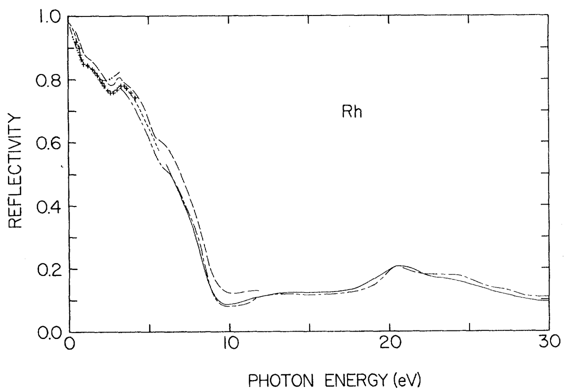

FIG. 1. Reflectivity spectra of Rh. Experimental results are as follows: dot-dot-dashed line, Ref. 26; short-dashed line, Ref. 27; crosses, Ref. 28; long-dashed line, Ref. 29; long-short-dashed line, Ref. 30; solid line, Ref. 31.

and Clarke *et al.*[22] (Pt), and the XPS studies of Shirley and co-workers[23] (Rh, Pd, Ir, Pt), Hüfner *et al.*[24] (Rh, Pd), and Dobbyn *et al.*[25] (Pt).

PRESENTATION OF EXPERIMENTAL DATA

Rhodium

The optical properties of Rh have been determined over a wide energy range, as is shown in Fig. 1. In the infrared and visible, measurements have been reported by Bolotin and Chukina[26] (11 μm to 4000 Å or ~ 0.1 to 3.1 eV). They used the method of Beattie to obtain n and k for bulk Rh samples. They reported structure near 0.2 eV, but it has not been observed by other groups. Drummeter and Hass[27] measured $R(E)$ between 20 μm and 2200 Å (0.06–5.6 eV) using vacuum-deposited films, but dielectric functions were not calculated. The data of Coulter *et al.*[28] covered part of the same wavelength range, and agreement was quite good. Coulter *et al.* did determine n and k by several techniques but at only six wavelengths. The measurements of Pierce[29] extended from 0.5 to ~ 12 eV, and his data were in good qualitative agreement with those of Hass and co-workers.[27,28]

At higher energy, the reflectivity spectra for Rh are in generally good agreement. Seignac and Robin[30] show a minimum in R near 2.7 eV, a maximum at 3.2 eV, a feature near 6 eV, and a sharp drop to a minimum near 9.8 eV. Pierce also reported the structure near 6 eV. The minimum in R near 10 eV is a feature observed for all of the transition metals studied to date. Its significance will be discussed in more detail later. In the vacuum ultraviolet (vuv), the data of Cox *et al.*[31] and Seignac and Robin are in good agreement. $R(E)$ can be seen to rise above 10 eV to a broad shelf extending to about 17 eV. A maximum appears near 20.6 eV with a shoulder at about 25 eV. At higher energy, core transitions attributed to the $N_{\mathrm{II,III}}$ levels have been reported at 46.1 eV,[31] compared with atomic values of 47.9± 0.4 eV.[32]

The reflectivity spectra of the other metals will be compared before returning to discuss the dielectric functions or comparing with photoemission results.

Palladium

Palladium has been studied more than the other metals under discussion, but the results show considerable differences. Experimentally, Pd is difficult to study in the bulk form since contamination forms readily and Pd does not electropolish easily. In the infrared, the effects of oxides and hydroxides may be small, but in the vuv they could be very strong. Vacuum deposition is relatively easy, but aging effects have been shown to be significant.

The low-energy behavior of $R(E)$ for Pd is shown in Fig. 2(a). Duisebaeva *et al.*[33] studied electropolished samples (technique not reported for electropolishing) and reported structure near 0.5 eV. Their reflectivities were the highest reported and are in marked disagreement with those of Bolotin *et al.*[34] The latter also used crystals but these were mechanically polished only. The interband

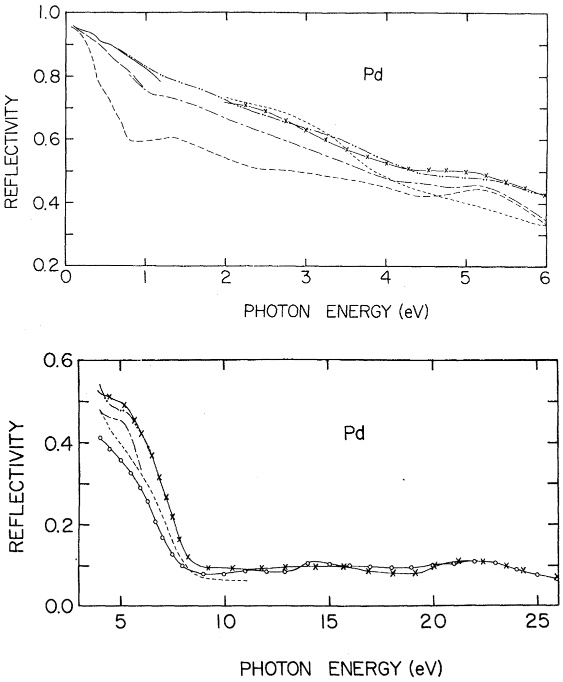

FIG. 2. Reflectivity spectra of Pd. Experimental results are as follows: solid line, Ref. 33; short-dashed line, Ref. 34, long-dashed line, Ref. 35; long-short-dashed line, Ref. 36; dot-dot-dashed line, Ref. 37; crosses, Ref. 38; very short-dashed line, Ref. 39; open circles, Ref. 40.

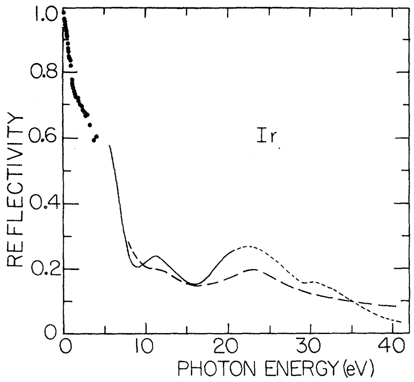

FIG. 3. Reflectivity spectra of Ir. Experimental results are as follows: solid circles, Ref. 41; solid line, Ref. 42; long-dashed line, Ref. 43; short-dashed line, Ref. 44.

conductivity was reported by Dold and Mecke[35] and the results were in reasonable agreement with those of Duisebaeva *et al.* Near 1.1 eV, Lostis[36] reported structure in R (measured in air with films evaporated at 10^{-6} Torr, 100 °C substrates of Si, annealed *in situ*) and the results of Johnson and Christy[37] (10^{-6} Torr, measured in N_2) suggest a change in slope at 1.4 eV. The latter also showed a minimum in R near 2.4 eV and a more pronounced minimum at 4.5 eV. Vehse *et al.*[38] reported a minimum near 4 eV (films evaporated at 10^{-8} Torr, measured *in situ* within one hour of evaporation). Their results suggest that a change in slope exists beyond the limit of their data (2 eV) in order to bring R to unity at zero frequency. Yu and Spicer[39] also studied films (10^{-8} Torr) and, like Vehse *et al.*, indicated that surface contamination was a severe problem for Pd. Their data extended from 2 to 11.6 eV and revealed shoulders in R near 3 and 6 eV.

In the vuv, the characteristic minimum in R is reported near 9 eV [Fig. 2(b)]. At higher energy, Vehse *et al.* reported structure at 15.5 and 22 eV. Robin[40] measured R at several angles of incidence using films evaporated at 10^{-6} Torr and also reported features near 14 and 22 eV, but in addition observed a dip in R at 12.5 eV.

Iridium

Ir is the least studied of the group under consideration. Kirillova *et al.*[41] measured n and k between 0.08 and 4.08 eV at 77 and 295 K. Hass *et al.*[42] and Samson[43] reported vuv reflectivities, but only the former performed an analysis to determine $\tilde{\epsilon}$. Their results are shown in Fig. 3 together with the high-energy $R(E)$ of Hunter.[44] A minimum in R was reported near 16 eV with a second near 9 (Hass *et al.*) or 11 eV (Samson). Maxima appeared at 11.5 and roughly 23 eV.

Platinum

Since Pt is highly reflecting and chemically stable, its reflectivity has been measured with an eye toward mirrors and grating coatings. Drummeter and Hass[27] (20 μm to 2200 Å; 0.06–5.6 eV), Kirillova *et al.*[45] (0.17–4.65 eV), Hass and Hunter[46] (2000 to 150 Å; 6.2–8.5 eV), Jacobus *et al.*[47] (2200 to 500 Å; 5.6–24.8 eV), and Linton[48] (2000 to 400 Å; 6.2–24.8 eV) have reported such $R(E)$ measurements. Yu, Spicer, and Hass[49] determined $R(E)$ at several angles of incidence to determine the dielectric functions at 14 wavelengths in the vuv, but these were not interpreted in any detail. Seignac and Robin[50] measured $R(E)$ at 20° and 60° between 4000 and 250 Å (3.1–50 eV) and determined $\tilde{\epsilon}$ (E) from data. Their reflectivity at 20° is shown in Fig. 4 together with the results of some of the other workers. At low energy (2.5–50 μm or 0.5–0.025 eV), Jones *et al.*[51] measured the absorptivity $(1-R)$ at several temperatures and compared with anomalous-skin-effect calculations. Finally, the author measured the absorptivity of a large (~1×5×8 mm) polycrystal of Pt at near-normal incidence and at 4.2 K as described in Ref. 9. The sample was spark cut from an electron-beam-melted ingot, and was annealed, mechanically polished, and etched

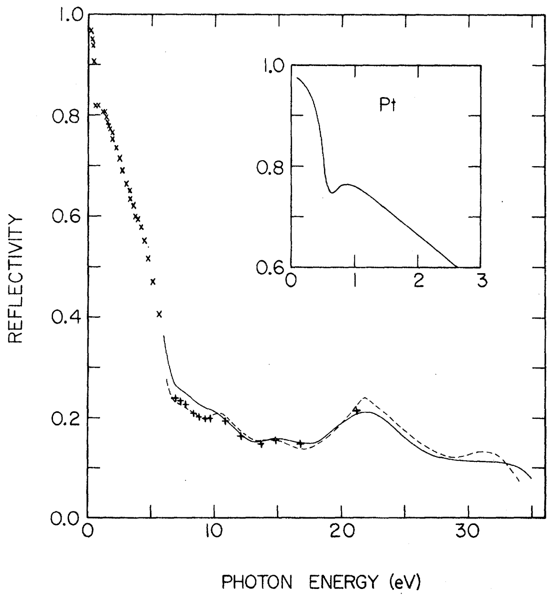

FIG. 4. Reflectivity spectra of Pt. Experimental results are as follows: crosses, Ref. 27; dashed line, Ref. 46; pluses, Ref. 49; solid line, Ref. 50. The insert shows the low-energy region with $R(E)$ as taken calorimetrically at 4.2 K, near-normal incidence by the author.

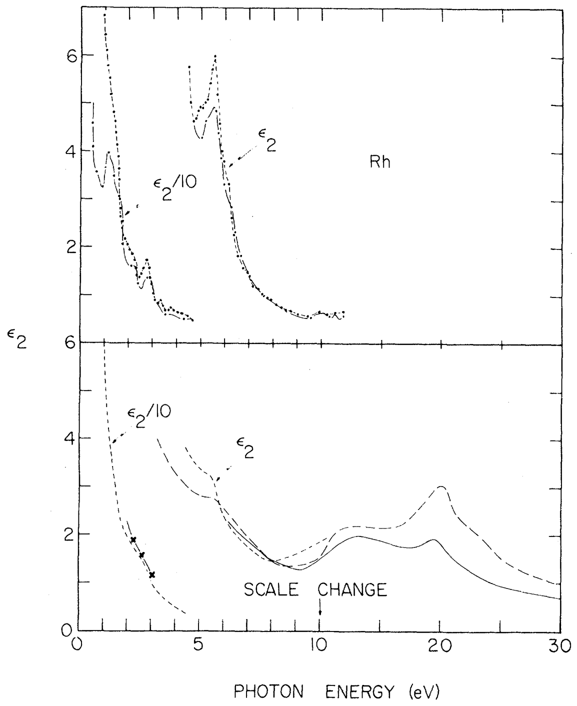

FIG. 5. ϵ_2 spectra of Rh. The upper section shows the calculated results of Christensen (dot-dashed line, Ref. 16) and those obtained using Smith's results as discussed in the text (solid circles). The experimental spectra are as follows: crosses, Ref. 28; short-dashed line, Ref. 29; long-dashed line, Ref. 30; solid line, Ref. 31.

in boiling aqua regia. The resulting reflectivity is shown in Fig. 4.

Rhodium

The imaginary part of the dielectric function, ϵ_2, for Rh is shown in Fig. 5. The first interband structure appears as a weak shoulder at about 1.2 eV (shown more clearly in plots of ϵ_2/λ[16,29]). The contribution of the free-electron gas to ϵ_2 is difficult to quantitatively assess since at the lowest energy (0.06 eV), the reflectivity is steadily dropping (Fig. 1). If $\omega\tau \gg 1$, such behavior would be typical of the interband region rather than the intraband region in which $R(E)$ would be large and constant. At higher energy, structure can be seen at about 3.8 and 5.5 eV, both structures lying on large backgrounds of steadily decreasing ϵ_2. The minimum in ϵ_2 occurs near 9 eV with additional absorption bands evident at higher energy (maxima about 13 and 19.8 eV). The upper part of Fig. 5 will be discussed shortly.

Palladium

The imaginary part of $\tilde{\epsilon}$ for Pd is shown in Fig. 6. In light of the uncertainty at low energy, ϵ_2 is shown only above 1 eV, and even there not all of the literature data are shown. From those shown, however, a factor of 2 uncertainty is apparent. In addition, the energy position of structure is not unambiguous: Johnson and Christy[37] report structure in ϵ_2/λ at about 2.3 and 4.8 eV; Vehse *et al.*[38] and Yu and Spicer[39] report a shoulder in ϵ_2 near 4 eV. At higher energy, ϵ_2 has a minimum near 8 eV with three additional features at higher energy, but below the onset of core transitions at about 50 eV.

Iridium

The optical properties of Ir have been reported only by Kirillova *et al.*[41] and Hass *et al.*[42] As shown in Fig. 7, maxima are evident in ϵ_2 at 6.4, 10.5, and 18.8 eV. Low-energy structure is better shown in the conductivity,[41] where structure has been reported near 0.4, 1.0, 1.6, 2.1, and 3 eV. The strong feature at 1 eV is visible in Fig. 7.

Platinum

The dielectric functions of Pt have been determined by Linton,[48] Yu *et al.*,[49] and Seignac and Robin[50] above about 4 eV. At lower energy, ϵ_2 has been reported only by Kirillova *et al.*[45] To determine ϵ_2, continuously, a Kramers-Kronig analysis was performed using the author's $R(E)$ data with an extrapolation in the infrared chosen to give a Drude-like behavior. The data of Hass and Hunter[46] and the absorption-coefficient results of Haensel *et al.*[52]

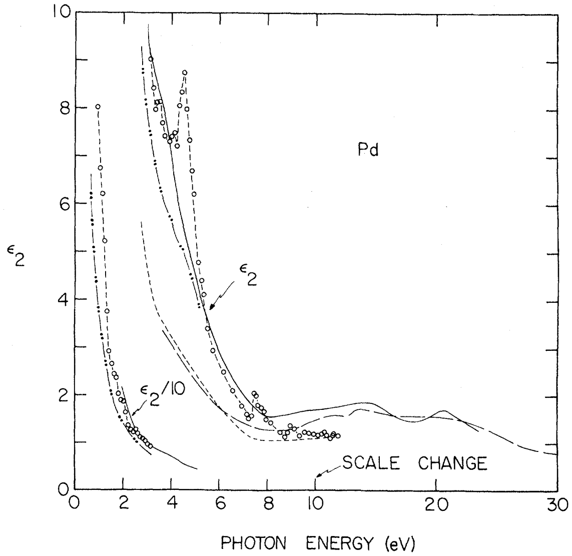

FIG. 6. ϵ_2 spectra of Pd. The scales have been expanded for clarity. The open-circles curve represents the calculated ϵ_2. Experimental results are as follows: dot-dot-dashed line, Ref. 37; solid line, Ref. 38; short-dashed line, Ref. 39; long-dashed line, Ref. 40.

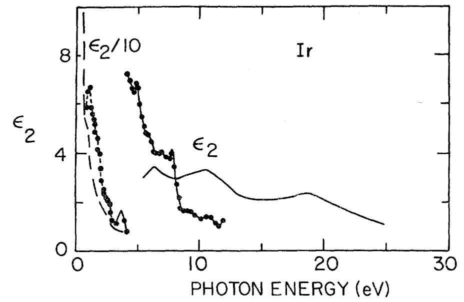

FIG. 7. ϵ_2 spectra of Ir comparing the calculated results with experimental results of Ref. 41 (dashed line) and Ref. 42 (solid line).

were used to extend the high-energy extrapolation to 600 eV. The resulting ϵ_2 spectrum is in good agreement with those of Yu *et al.*, and Seignac and Robin as shown in Fig. 8. Structure is evident at 7.4, 9.8, and 19.9 eV. Like the other transition metals, Pt possesses the characteristic minimum in ϵ_2 (near 13 eV) with additional structure at higher energy.

INTERPRETATION AND DISCUSSION

The approach often taken when comparing structure observed in an experimental ϵ_2 to energy bands is to search for allowed transitions between reasonably parallel bands [high joint density of states (JDOS)] which occur at roughly the right energy. This has its pitfalls particularly since it depends on calculated bands which often have been fit to experimental results only at E_F and which have been calculated only along high-symmetry lines in $\vec{k}$ space. Comparison can be made more reliable by EDJDOS (energy distribution of the joint density of states) or JDOS calculations even in the constant-matrix-element approximation. Direct comparison can be made by calculating ϵ_2 from

$$\omega^2\epsilon_2=\frac{e^2\hbar^2}{3\pi m^2}\sum_{if}\int d^3k\,|\vec{p}_{if}|^2\delta(E_f(\vec{k})-E_i(\vec{k})-\hbar\omega), \qquad (1)$$

which requires wave functions and the matrix elements p_{if} for transitions between an occupied initial state and an unoccupied state above E_F. This is a very difficult task. The constant-matrix-element assumption is usually made so that

$$\omega^2\epsilon_2\propto\sum_{if}\int d^3k\,\delta(E_f(\vec{k})-E_i(\vec{k})-\hbar\omega). \qquad (2)$$

A useful quantity to determine is the EDJDOS

$$D(E,\hbar\omega)=(2\pi)^{-3}\sum_{if}\int d^3k\,\delta(E_F(\vec{k})-E_i(\vec{k})-\hbar\omega)$$
$$\times\delta(E-E_i(\vec{k}))\ , \qquad (3)$$

which, when integrated over energy E, gives the JDOS as defined by the quantity on the right of Eq. (2). In the EDJDOS, only transitions occurring at energy $\hbar\omega$ are considered when the initial state lies at E_i. If the EDJDOS is known, it is possible to show the development of structure which ultimately contributes to the JDOS. The JDOS characterizes the energy bands, is a purely geometric quantity, and carries no information concerning the wave functions, matrix elements, or selection rules. Nevertheless, it is useful for obtaining qualitative agreement between theory and experiment provided the assumption is made that matrix elements do not introduce new structure but may reduce or distort what has been predicted by the JDOS.

It is not necessary at this point to review the difficulties encountered in determining reliable energy bands. The nature of the d electrons, the choice of exchange parameters, and atomic configuration have been discussed elsewhere. The problems continue to be fundamental, but are made more tractable by reliable experimental ϵ_2 over a wide range of energy, by modulation data, and by photoemission data.

The energy bands of Rh, Pd, Pt, and Ir are shown in Figs. 9–12 as calculated by Smith.[15] Andersen[17] systematically studied the d-like L_3 ($L_4^+L_5^+$, L_6^+) states and their relationship to the p-like L_2' (L_6^-) states. He showed that the d bandwidth increases on going from Pd to Rh to Pt to Ir and that this increase is accompanied by a movement of the sp band deeper into the d bands. For Pd and Rh, L_6^- lies above $L_4^+L_5^+$ and L_6^+ but for Pt it falls between the split d states. For Ir, both d-like states are

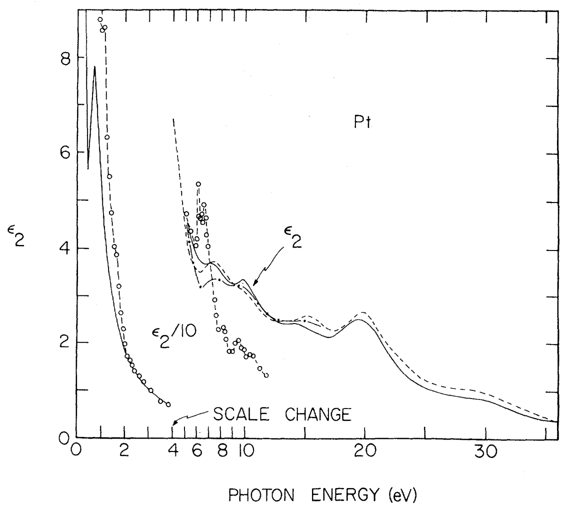

FIG. 8. ϵ_2 spectra of Pt. The calculated results are shown as open circles. The solid line represents the results obtained using the author's $R(E)$ data plus the high-energy $R(E)$ of Ref. 46. Experimental results are as follows: solid circles, Ref. 49; dashed line, Ref. 50. The energy scale is linear, but the scale doubles at 4 eV.

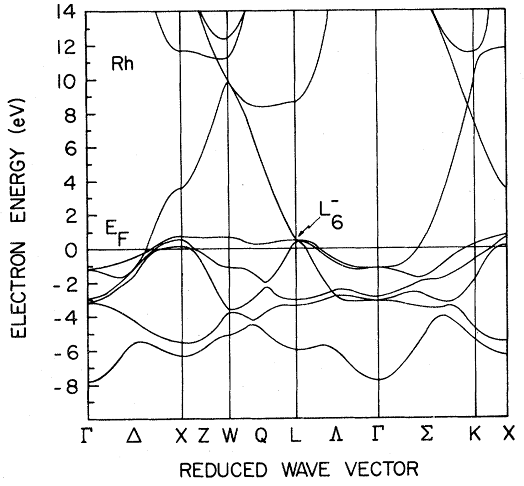

FIG. 9. Energy bands of Rh as calculated by Smith (Ref. 15).

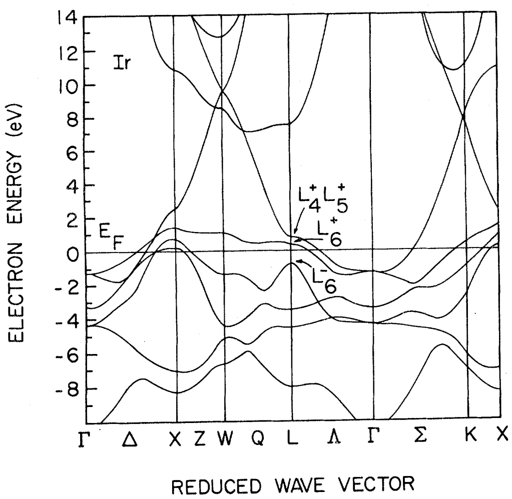

FIG. 11. Energy bands of Ir as calculated by Smith.

higher than L_6^- and lie above E_F. To account for the strong absorption in Pt at 0.7 eV, one can identify transitions occurring between the p-like L_6^- band and the d-like $L_4^+L_5^+$ band above E_F and nearby regions of k space. Possible contributions might also come from the region of X, but at X the states are almost purely d-like and the X_6^+ and X_7^+ states are degenerate in the absence of spin-orbit effects (X_5).

The bands at L can also be expected to give rise to structure observed at low energy in Rh (near 1.2 eV), except that the states involved are removed from L, probably in all directions around L. The purely d-like or p-like character is mixed by hybridization so the reduction in strength is not surprising. (The hybridized character of the Rh Fermi surface has been pointed out by Andersen.) For Pd, the appearance of low-energy interband structure would not be surprising in light of the nature of the bands at L. Now L_6^- lies higher than the d-like states and one might expect the structure to be weaker than in Pt, the transitions being largely d- to p-like. Further experimental effort is suggested to clarify the low-energy structure in Pd. (In addition to structure reported by Duisebaeva *et al.*[33] near 0.5 eV, Vehse *et al.*[38] saw evidence for strong structure in the conductivity at 1.3 eV; this should be treated cautiously, however, since it would be strongly influenced by their infrared Kramers-Kronig extrapolation. Their low-energy data extended to 2 eV.) For Ir, structure

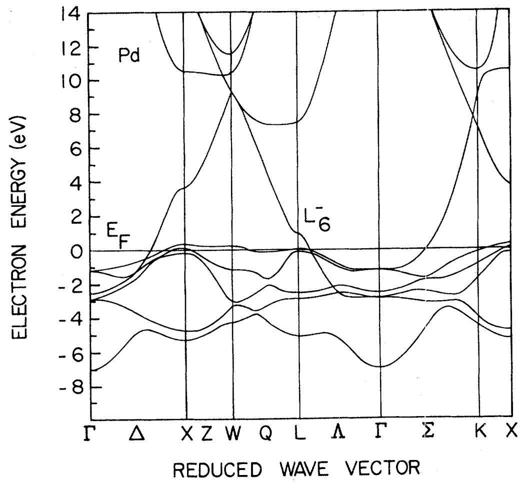

FIG. 10. Energy bands of Pd as calculated by Smith.

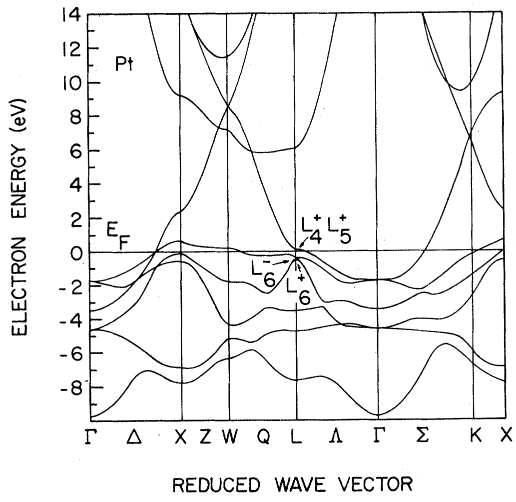

FIG. 12. Energy bands of Pt as calculated by Smith.

has been observed[41] at ~ 1 eV and 1.6 eV. Since both d-like states lie above E_F,[53] and since they are split by several tenths of an eV, it seems reasonable to assign $L_6^- \rightarrow L_6^+$, $L_4^+ L_5^+$ transitions (and transitions in nearby regions of $\vec{k}$ space) to the experimental structures.

The width of the d bands in the transition metals is a subject of considerable interest. Recent UPS measurements[19,54] have supported the resonance formulation of the d bands and have provided qualitative confirmation of the trend revealed by Andersen's calculations. ESCA studies by Baer *et al.*[21] have shown that the d bands do increase in width on going from Pd to Rh to Pt to Ir. XPS measurements by Fadley and Shirley[23] also show the pattern. The recent work by Clarke *et al.*[22] (ESCA) and Kowalczyk *et al.*[23] (high-resolution XPS) for Pt are in good agreement giving 7.1 (Kowalczyk *et al.*) and 7.3 eV for the (111) surface and 7.5 eV for the (100) surface (Clarke *et al.*). XPS measurements by Dobbyn *et al.*[25] agree rather well with these latter Pt studies. The results of Kowalczyk *et al.* for Ir indicate a bandwidth of 7.4 eV, while the results of Baer *et al.* give 7.1 eV. Eastman's[55] results for Pd give a bandwidth of 4.6 eV while Pollak *et al.*[23] reported 4.7 eV. Baer *et al.* reported 4.5 eV for Pd and 5.2 eV for Rh. Comparisons of UPS and XPS data with band calculations for the four fcc metals under consideration have been reported by Smith *et al.*[20]

Fong[56] has recently performed calculations to determine the optical properties of Pd. Using a pseudopotential formalism, he calculated an interband ϵ_2, combined that with a free-carrier contribution, then used a Kramers-Kronig analysis to determine ϵ_1. Finally, he calculated the reflectivity and compared his results with experimental spectra. The agreement was not unreasonable, particularly when account is taken of the uncertainty in the experimental reflectivity [Figs. 2(a) and 2(b)]. An important outcome of the calculations was that structure in ϵ_2 arises from extended regions of $\vec{k}$ space. It is hoped that further calculations of this sort will be performed.

In order to better compare the experimental ϵ_2 with the bands of Figs. 9–12, the JDOS was calculated for each metal using the EDJDOS results of Smith. Those results were available for energies greater than about 1 eV making comparison at higher energy possible, but precluding comparison with the lower-energy transitions at L. Christensen[16] has performed similar ϵ_2 calculations for Rh and his results are also shown in Fig. 5. He shows good agreement with the first structure near 1.2 eV (better seen in his comparison of ϵ_2/λ), though the simple JDOS calculation appears to overestimate the strength of the transition. At higher energy, the two calculations are in excellent agreement.

Structure in ϵ_2 has been observed in Rh near 2.8 eV, for which there is no counterpart in Pd or Pt. This can be understood in terms of transitions along Q from the third to the fifth band ($Q3$ to $Q5$ in our notation). The EDJDOS results show these transitions to be particularly strong for E_i near 2.4 eV and E_f just above E_F. As shown in Fig. 9, structure originating from transitions between $W4$ and $W5$ would be predicted by JDOS considerations, but when account is taken of their predominant d-like nature, their contribution to the experimental spectrum would be suppressed.

While transitions from $Q3$ to $Q5$ are not possible for Pd and Pt (the final states lie below E_F), the fifth band of Ir is seen to be similar to that of Rh. One might expect structure to be found in ϵ_2 near 3.5 eV which can be related to $Q3$-$Q5$ transitions. Kirillova *et al.*[41] assigned a weak feature in the conductivity at 2.9 eV to the part of the Brillouin zone near W.

It has been shown that the d band grows wider on moving from Pd to Rh to Pt to Ir. With this, there is a shift of the center of d-band resonance relative to the bottom of the conduction band. This trend can be observed in the optical properties of the fcc metals by identifying the structure in ϵ_2 at about 4 (Pd), 5.5 (Rh), and 7.4 eV (Pt) as originating from transitions from the first band along Σ and along Δ with the final states near the Fermi level. For Au, structure at 7 eV in ϵ_2[57] and a strong thermoreflectance signal[58,59] at that energy has made the Fermi-surface-involving transition from Σ_1 to Σ_6 rather secure.[60] For Au, the d bands lie entirely below E_F, but for Rh, Pd, Pt, and Ir, the position of E_F within the bands makes other final states possible. The identification of the structure as originating from the Σ and Δ bands must be made rather cautiously at this point. The development of structure in the EDJDOS at those energies does place strong structure as originating well below E_F, but to separate contributions from Σ from those of Δ would require an interpolation scheme which selectively samples regions of $\vec{k}$ space rather than initial energies.

For Pd and Pt, structure can be seen in the calculated ϵ_2 near 7.5 and 6.5 eV, respectively. For Pt, this falls on the low-energy side of the calculated structure identified as corresponding to transitions along Σ and Δ. These structures can be related to the high JDOS between the d-like states at $L(E_F)$ and the seventh band at L and between $Q5$ and $Q7$. These structures do not correspond to experimental ϵ_2 structure and will not be considered further.

An experimental structure has been observed for Pt at 9.8 eV which has no counterpart for the other metals under consideration. This can be related to the calculated ϵ_2 peak at 9.5 eV which is much stronger than for Rh (10.8 eV), Pd (9.6 eV) or Ir (9.3 eV). These features can be identified as direct transitions from the $Q3$ band to the nearly flat $Q7$ band, but identification of this structure with the experimental feature for Pt must be done with caution.

It is characteristic of these metals and the hcp and bcc metals that low-energy structure appears in ϵ_2 which can be related to transitions within the *sp*, *d*, and hybridized bands cut by E_F. Above the top of the *d* bands, a region of low density of states appears before the lowest of the high bands is reached–the seventh band minimum. A characteristic minimum in ϵ_2 is observed which corresponds to the dearth of absorption before the onset of transitions to the high bands. This onset appears at about 8–10 eV and continues for another 10–15 eV with typically two or three broad features observed in ϵ_2. These can be seen in Figs. 5–8. The structure can be described only qualitatively in terms of the density-of-states profiles.

Andersen and Jepsen[61] have recently examined the bands of Pd and have included the high-lying 5*s* and 5*p* states. They have shown that considerable structure persists in the density of states to more than ~20 eV above E_F. At lower energy, their results agree with previous calculations.[62] Although the contributions of the *f*-like states were not included in the work of Andersen and Jepsen, Christensen[63] has taken their bands and has calculated the total joint density of states and partial, band to band, joint density of states. From his results, it appears reasonable to make the identification that the structure above ~10 eV is due to transitions to the high-lying states. While these were the first calculations that extended to such high energy, it is hoped that further efforts will soon follow.

At higher energies (above about 30 eV) the additional structure in ϵ_2 can be related to transitions from the core states. Such effects have been seen in Rh near 46.1 eV.

It has been shown that photoemission experiments for these metals are particularly sensitive to the region of *k* space along Q. This has been observed for Pd and has been discussed at length elsewhere.[64] This behavior led Smith to place the seventh band minimum as shown in Figs. 9–12. Except for Rh and perhaps for Ir, optical measurements have been rather insensitive to that part of the zone, but have provided information about transitions at L and along Σ and Δ.

Once the dielectric functions are known, it is possible to calculate the surface and volume loss functions $\mathrm{Im}\,[-1/(\tilde{\epsilon}+1)]$ and $\mathrm{Im}\,(-1/\tilde{\epsilon})$, respectively. Peaks in these functions occur at energies which correspond to the energies a fast electron would lose in exciting volume or surface plasmons. When the spectra of ϵ_1 and ϵ_2 are known, the contributions from such collective effects can be separated from single-particle (interband) structure. The plasmon peaks generally occur where ϵ_2 is small and structureless, $d\epsilon_2/dE < 0$, ϵ_1 is small, and $d\epsilon_1/dE > 0$. It has been shown[9–13] that the bcc and hcp metals possess two volume and two surface plasmons and that none of these bear the $\sqrt{2}$ relationship of volume to surface-plasmon energy which might be expected for a free-electron gas. For Rh, there is agreement that a volume plasmon appears near 8.7 eV[29–31] with a nearby surface plasmon at about 7.9 eV. At higher energy, the volume plasmon falls near 32.5 eV.[31] A calculation of treating all *s*, *p*, and *d* electrons as free gives 30.0 eV. The results of Cox *et al.*[31] show a broad structure in the surface loss function at about 22 eV. For Pd, the lower-energy volume plasmon appears near 7.6 eV[38–40]; Vehse *et al.*[38] report a surface plasmon nearby at 7.1 eV. At higher energy, the volume plasmon probably appears near 26 eV,[40] but the case is less clear. The calculated plasma energy is 30.6 eV. Robin[40] reports structure nearby in the loss function at 31.7 eV, but she also saw structure in ϵ_2 at about that energy. For Ir, only the lower-energy pair have been observed in optical studies. Hass *et al.*[42] report a peak in the volume loss function at 8 eV with a corresponding peak at 7.5 eV in the surface loss function. For Pt, the high-energy pair occurs near 33.7 (volume) and 23.3 eV (surface).[30]

Energy-loss measurements using fast electrons reflected or transmitted through samples of these metals have been reported, but a detailed comparison is beyond the scope of this paper. While the occurrence of two volume and two surface plasmons appears a characteristic trait of the transition metals, there has been no adequate theoretical description of them.

SUMMARY

It has been shown that the fcc metals display considerable similarities with regard to their optical properties and that these are of value in assessing the electronic energy bands. It has been shown that below ~2 eV, the transitions at L are very important. The calculations of the EDJDOS and JDOS have been of considerable value in interpreting the observed structure, even when account is taken of the relatively crude manner in which the bands were fit to UPS data. Finally, at high energy, the characteristic absorption spectra and loss-function spectra of the bcc and hcp transition metals have been observed in the fcc metals.

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