Optical investigation of the electronic structure of bulk Rh and Ir

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Optical-reflectivity data are presented for Rh and Ir for a photon energy range between 0.2 and 40 eV. Strong interband structures are observed in the calculated dielectric functions and optical conductivities, and these are discussed in terms of recent energy-band calculations. The dielectric functions are used to calculate the electron-energy-loss functions. Both metals are shown to possess the characteristic double pair of surface and volume plasmons, though the higher-energy pair is strongly distorted by interband absorption occurring near $\hbar\omega_p$.

The electronic structures of Rh, Pd, Ir, and Pt have been discussed in detail in a recent paper by one of the authors.[1] At that time, it was pointed out that optical studies of Ir were few, and that the results were incomplete and not without ambiguity. We take this opportunity to present our new measurements of crystalline Ir as well as its 4*d* transition-metal counterpart Rh. This study should be viewed as a continuation of our efforts to understand the complex electronic structure of the transition metals. Much of the discussion presented here will draw upon that of Ref. 1.

The reflectivity R, or the absorptivity $A = 1 - R$, has been measured between 0.2 and 50 eV using techniques which have been described in detail elsewhere.[2,3] Large polycrystalline samples were cut from a crystal rod of Ir or an electron-beam-melted button of Rh. The samples were mechanically polished to obtain specular surfaces, boiled in aqua regia, and ultimately heated *in vacuo* of 10^{-7} Torr to produce clean, strain-free surfaces for the optical measurements. The samples were then transferred to the ion-pumped experimental chambers, and the absorptivity (near-normal incidence, 4.2 K sample temperature, 0.2–4.4 eV photon energy range, estimated uncertainty of 1% of the measured quantity) or the reflectivity (10° angle of incidence, 300 K temperature, 3.0–40 eV photon energy range with synchrotron radiation, estimated uncertainty of 5% of the measured quantity) was measured. Reproducibility from one run to the next was excellent, as was the agreement in the region of overlap of the two sets of data.

The results of the measurements are shown in Figs. 1 and 2. The reflectivity spectra shown there extend from the infrared, through the visible and vacuum ultraviolet, and into the soft-x-ray energy range — terminating just short of the onset of the 4*p* and 5*p* core absorption structures.[4,5] Numerous structures are apparent, the energy locations of which are indicated in the figures.

While the measured quantity was the absorptivity or the reflectivity, it is the imaginary part of the dielectric function ϵ_2, or the optical conductivity $\sigma = \epsilon_2 E/4\pi\hbar$, which is the caliper of the interband transition strength and which is most readily evaluated from wave-function/band-structure calculations. In order to determine $\tilde{\epsilon}$ and σ, Kramers-Kronig analyses were performed with the spectra of Fig. 1 together with Drude infrared extrapolations, high-energy absorption coefficient data to 250 eV (Rh)[4] or 600 eV (Ir)[5], and, ultimately, a power-law decay of R given by $R = R_0 E^{-3.5}$ extending

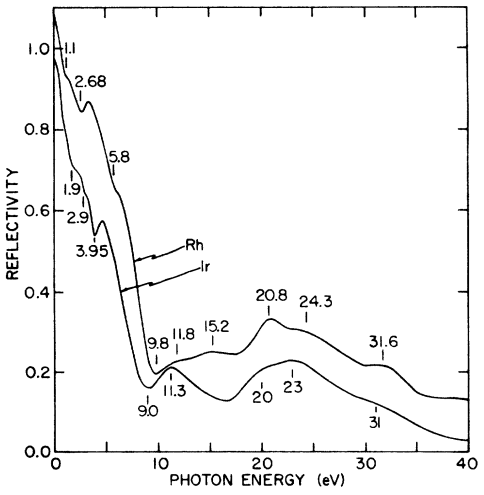

FIG. 1. Reflectivity of bulk crystals of Rh and Ir. The Ir spectrum is referenced to the left-hand scale while that of Rh is shifted by 0.1 for clarity.

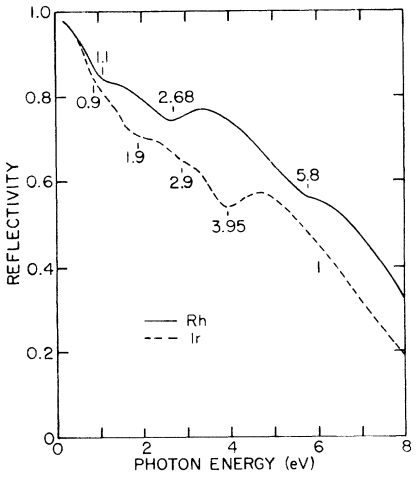

FIG. 2. Reflectivity spectra of Rh and Ir between 0.2 and 8 eV showing the low-energy features. The tic mark at 6 eV indicates a subtle inflection in the reflectivity of iridium.

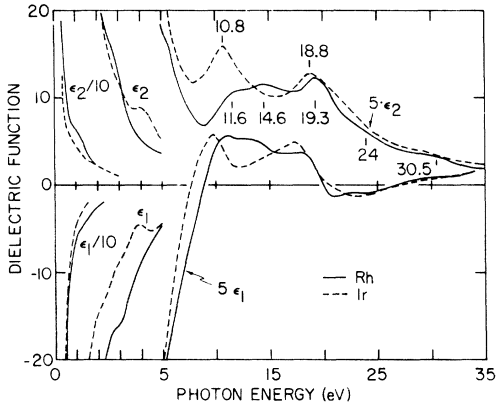

FIG. 3. Dielectric functions for Rh and Ir. The energy scale is linear, but changes at 5 eV. The low-energy structure is shown better in a plot of the conductivity (see Fig. 4).

to 10^5 eV. The results of those calculations are shown in Figs. 3 (dielectric function) and 4 (conductivity). Again, the energy locations of structures are indicated in the figures.

For Rh, the agreement with existing work is very good. Comparison with the results of Coulter *et al.*,[6] Drummeter and Hass,[7] Pierce and Spicer,[8] Cox *et al.*,[9] and Seignac and Robin[10] shows gratifying agreement — a situation which is not always encountered in optical measurements. For Ir, only Kirillova *et al.*[11] have reported low energy results. The reflectivities calculated from their tabulation of n and k are close to ours in magnitude, but showed considerable spread with some ambiguity as to how to connect the points. Hunter[12] reported reflectivity data for Ir films above 6 eV, but did not determine the dielectric functions; Samson *et al.*[13] measured R at several points in the vacuum ultraviolet. Our reflectivities are in good agreement with the latter two, show the low-energy absorption features without ambiguity, and are the only existing data between 3 and 6 eV.

There have been no new band calculations or comparisons between theory and experiment for Rh and Ir of the sort recently completed for Pd by Christensen.[14] Hence, the interpretation of our results for Ir and Rh parallels that of Refs. 1 and 15. There, we showed that, for the fcc transition metals, low-energy optical structures were observed which could be related to transitions involving the bands near L in the Brillouin zone. Those are the p-like L_6^- and the spin-orbit split d-like L_6^+ and $L_4^+L_5^+$ bands at L which are hybridized in nearby regions of k space. We suggest that the structure observed in the conductivity of Fig. 4 for Rh at 1.05 eV arises from transitions from the fourth to the fifth and sixth bands in an appreciable volume of k space near (but removed from) L and involving Fermi-surface transitions. (The fourth band at L is above E_F, but dips below E_F in the Q and Λ directions.) Analogous transitions would be observed in Ir where the L_6^- state falls below E_F and the d-like bands are strongly split by relativistic considerations. Hence, we suggest that the two features in the conductivity of Ir at 1.05 and 1.9 eV (Fig. 4) arise from transitions close to and at L with final states being the spin-orbit-split d-like bands.

In our earlier examination of these metals, we

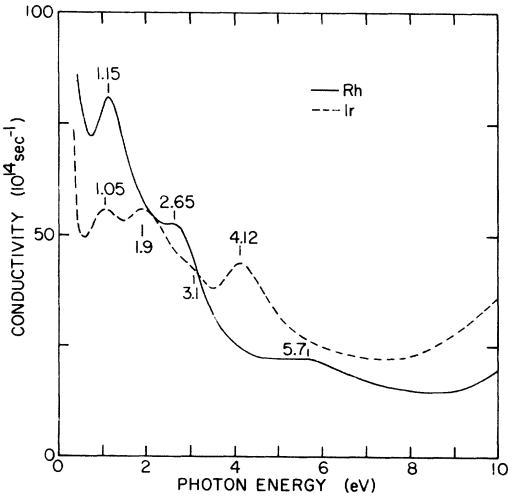

FIG. 4. Optical conductivity of Rh and Ir.

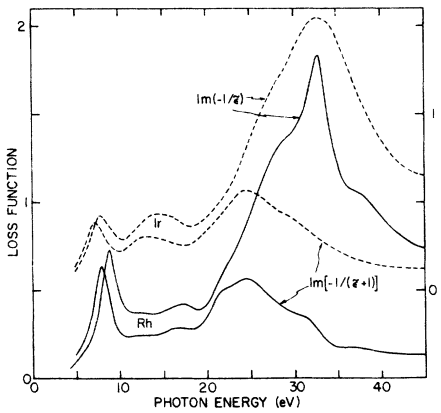

FIG. 5. Energy-loss functions for Rh and Ir. The results for Ir (dashed line) are referenced to the right-hand scale.

suggested that the structure observed previously in the conductivity Rh near 2.65 eV was related to transitions between the third and fifth bands along Q. Since the energy separation of those bands is thought to be greater in Ir than in Rh,[16] a similar feature might be expected in Ir at roughly 3.5 eV (band structure of Smith[16]) or 3.7 eV (band structure of Andersen[17]). From Fig. 4, we see a weak feature in the conductivity near 3.1 eV and a much stronger one at 4.15 eV. We suggest that the latter structure should be compared with the feature in Rh, although it requires that the band eigenvalues be shifted by several tenths of an electron volt or that appreciable volumes of k space near Q are involved.

In Ref. 1, we argued that the structure observed in the conductivity of Rh at about 5.7 eV arose from transitions from the first to the sixth bands along Σ and Δ, basing the argument on systematics with the fcc metals and thermoreflectance work with Au.[18] Analogous structure should appear in Ir near 8 eV. That no such structure is seen in Fig. 1 does not necessarily obviate the interpretation since the magnitude of the absorption is increasing near 8 eV due to transitions involving the seventh and high-lying bands. The Σ and Δ transitions may simply be contributing to the large broad structure which ultimately crests near 11 eV. Alternatively, the absorption in Ir might be quite weak, the inflection seen in R in Fig. 2 being the only clue of its existence. Thermoreflectance measurements should be able to resolve the question since the transitions are Fermi-surface involving.

Broad, strong, structured features are observed in the dielectric function (Fig. 3) and the reflectivity above 8–10 eV. We qualitatively interpret those as arising from complex absorption involving final states which lie many electron volts above the Fermi level. Those structures will be discussed and compared in detail to similar features observed in the other $4d$ and $5d$ transition metals in a subsequent paper.

From the calculated dielectric function, it is possible to examine surface and volume plasmons through the quantities Im $(-1/\tilde{\epsilon}+1)$ and Im $(-1/\tilde{\epsilon})$, respectively. These are shown in Fig. 5. At low energy, each metal has a set of strong, sharp structures which compare well to those observed in the other transition metals. We identify the maxima at 8.8 eV (Rh) and 7.8 eV (Ir) as volume plasmons and at 9.0 eV (Rh) and 7.2 eV (Ir) as surface plasmons. The higher-energy plasmon is more difficult to delineate since strong interband absorption is occurring near the free-electron plasma energy of 30.0 eV (Rh) and 29.6 eV (Ir), as is shown particularly well in Fig. 1. Hence, we interpret the large maxima in the volume loss functions at 33 eV as being largely interband-like while the plasmon itself occurs closer to 29 eV.

Comparison of the spectra of Fig. 5 with those obtained from energy-loss measurements[19,20] shows quite good qualitative agreement. For both Rh and Ir, the latter measurements show low-energy losses near 8 eV and broad losses near 30 eV; in these measurements, however, there is no separation between volume and surface plasmons.

Since it is difficult to extract meaningful numbers from the journal-sized figures, tables of our results can be obtained from the authors.

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