PHYSICAL REVIEW B VOLUME 14, NUMBER 8 15 OCTOBER 1976

Optical absorption in the 4d transition metals from 20 to 250 eV

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(Received 7 May 1976)

The optical absorption of Y, Zr, Nb, Mo, Rh, Pd, Hf, and W has been measured between 20 and 250 eV using synchrotron radiation from the Tantalus I electron storage ring. The samples were thin, self-supporting films, and transmission measurements were performed at normal incidence. The results were compared with our results from previous reflectivity measurements in the range of overlap (20–40 eV), as well as with electron-energy-loss measurements where available. The data were interpreted in terms of largely atomiclike transitions of the 4p-to-4d type. Arguments were presented to support this interpretation, and analogies were drawn to the higher-energy 4d-4f transitions in the rare earths. Structures were observed on the low-energy side of the onset which were interpreted in terms of the spin-orbit splitting of the initial $4p_{1/2}$ and $4p_{3/2}$ states. The broadening of the p-d structure was interpreted qualitatively in terms of multiplet splitting and autoionization processes. At higher energy, structures related to 3d transitions were observed.

INTRODUCTION

The electronic properties of many of the transition metals have been studied in the low-energy range[1] ($h\nu \lesssim 30$ eV), where band-structure effects predominate, and the 3d and 5d transition metals have been investigated[2] above about 30 eV, where atomic phenomena appear to be dominant, but there have been few studies in the transition or intermediate range, where both atomic and band features are contributing to optical absorption.[3] In part, this is because the intermediate range falls in a technologically difficult region of the spectrum. Synchrotron radiation sources are very well suited for measurements in this range, but a changeover in monochromator systems and a change from reflectivity to absorption techniques often results in experimental ambiguity. Because of the theoretical complexity of treating either band or atomic aspects separately, there have been very few studies which have tried to include both simultaneously. Many fine contributions do exist, but a cohesive picture which bridges the mixed-character region is lacking. To aid in the formulation of that picture, we have embarked on a series of experimental studies which we hope will clarify the problem. In this paper, we report on our optical measurements of the 4d metals Y, Zr, Nb, Mo, Rh, and Pd, and the 5d metals Hf and W. We will make comparisons, where possible, with existing data.

Optical measurements at low energy reveal features of the band structure since both initial and final states are bandlike and lie within a few electron volts of the Fermi level. Such measurements are very important in revealing the electronic properties. The interpretation of experimental data, at least in metals, follows a reasonably well established pattern, and the mechanisms involved are rather well understood, if difficult to quantify.

At high energy, the quantity generally determined in optical studies is the absorption coefficient, and the data reflect the largely atomic character of the electrons. In many cases, it is possible to describe the absorption phenomena accurately in terms of atomic wave functions and interactions—the influence of the nearest neighbors is generally very small (at least until the extended x-ray absorption fine structure region is reached), and solid state effects can be almost ignored. While the physics of the interactions is often very complicated, it is nevertheless simplified by being free of mixed solid state and atomic contributions.

In the intermediate energy range, it is no longer possible to ignore solid state (bandlike) effects. The definition of what we mean by "intermediate energy range" is vague since it varies for different materials and *a priori* may have little meaning. An individual investigation of each group of materials is necessary to assess the interplay of the two pictures though a general upper limit of the intermediate range might be 200 eV.

The rare-earth metals form a group of metals which have been studied both experimentally[4] (optical absorption) and theoretically.[5] The calculations gave excellent agreement with experiment. Of particular interest to us here is the treatment of the dipole transitions $4d^{10}4f^{N}$-$4d^{9}4f^{N+1}$ followed by the interaction of the discrete state with the continuum $4d^{9}4f^{N+1}$-$4d^{9}4f^{N}\epsilon f$. Since our interpretation of the observed 4p-4d structure in the

$4d$ metals will be similar in many respects to the analogous $4d$-$4f$ transitions of the rare earths, we will, after a brief discussion of the experimental technique, review some of the critical points of the rare-earth analysis.

EXPERIMENTAL TECHNIQUE AND RESULTS

Synchrotron radiation sources have played a critical role in most measurements of the sort reported here since they alone offer the intense continuum radiation necessary to study optical absorption over a wide photon energy range. Unfortunately, though the sources are ideally suited for the measurements, a changeover in experimental techniques has generally occurred near 30 eV. At lower energies, reflectivity measurements have been performed which extend into that region, but the reflectivity is generally very small and normal incidence monochromators are quite inefficient. At higher energies, transmission measurements with thin films are often done with grazing incidence monochromators, but scattered light and higher order problems are often severe. Hence, there is a dearth of data around 30–40 eV.

In the present set of measurements, we have measured the absorption coefficient using a single technique but two different experimental systems. The technique has involved the measurement of the photon flux transmitted by a suitable substrate with and without a sample over it. The ratio gave the transmission, which could be converted to the absorption coefficient if the thickness of the sample was known.

The samples were thin films of the metal deposited by electron beam evaporation techniques onto microscope slides with *vacuo* of the order of 10^{-8}–10^{-6} Torr, depending on the metal. The microscope slides were coated with a parting agent and were maintained at room temperature. After deposition, the films were floated off in distilled water, picked up and supported by a 60% transmitting Ni mesh, and allowed to dry in the air. They were then attached to a sample holder in one of two sample chambers.

For the measurements between 20 and 70 eV, a Seya-Namioka monochromator built at the Synchrotron Radiation Center was used with a very short-wavelength blazed grating. Second-order and scattered-light problems were reduced by using Al and Formvar filters. The detector was an electron multiplier. In these measurements, the synchrotron radiation beam was first dispersed and filtered, then passed through the sample to the detector.

In the second set of measurements, a Hilger-Watts grazing incidence monochromator was used. In this case, the sample was positioned in the direct beam [which had first passed through a filter chamber containing Al, Formvar, polypropylene $(CH_2)_x$, Si, and Au filters which were used in the appropriate energy ranges to reduce scattered and higher-order light]. The radiation then entered the monochromator and was dispersed and detected by a channeltron detector. The energy range of these measurements extended from 40 to 250 eV.

The absorption coefficient (μ) for the metals studied is shown in Figs. 1 and 2 with the scales

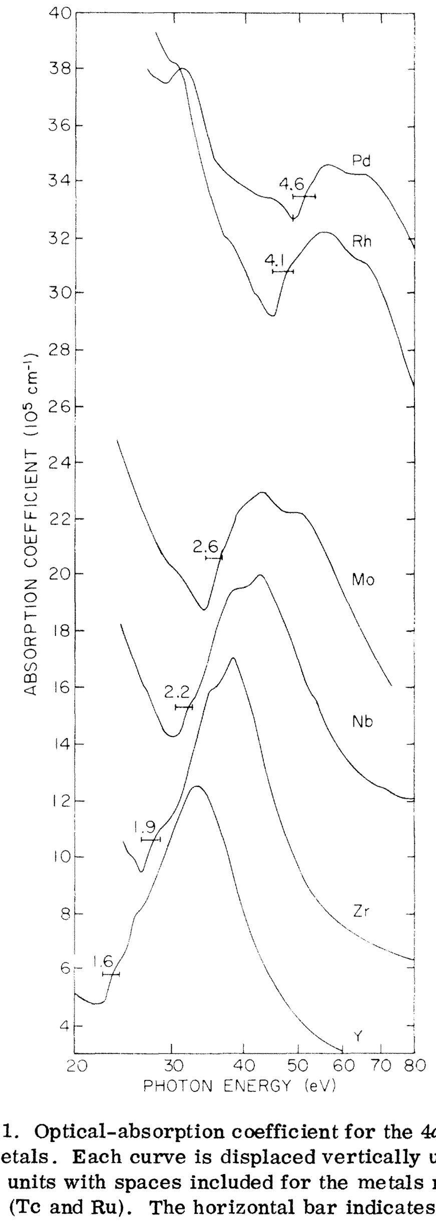

FIG. 1. Optical-absorption coefficient for the $4d$ transition metals. Each curve is displaced vertically upward by four units with spaces included for the metals not studied (Tc and Ru). The horizontal bar indicates the spin-orbit splitting for these metals from Scofield (Ref. 14), positioned on the energy scale to correspond to the experimental onset of the $4p$ transitions.

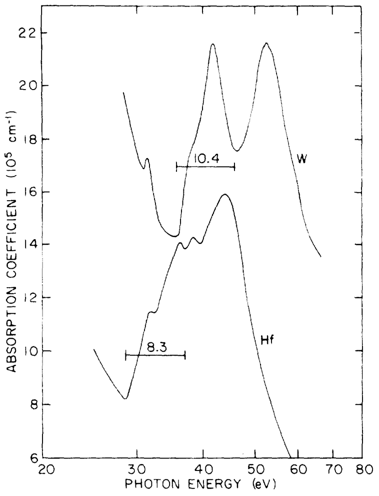

FIG. 2. Optical absorption coefficient for Hf and W. The W curve is displaced vertically upward by six units. The horizontal bar indicates the calculated spin-orbit splitting (Ref. 14), positioned on the energy scale to correspond to the experimental onset of the $5p$ transitions.

shifted for clarity. Characteristically, the magnitude of μ is dropping at 20 eV, rises above the onset of the np core transitions, and shows a broad, structured absorption feature extending over 10–20 eV. Above that structure, μ falls smoothly or with weak structure until the onset of the nd core structure is reached. Electron-energy-loss measurements and synchrotron radiation absorption or partial yield measurements have shown that the $3d$ and the $5d$ transition metals exhibit similar behavior.[2] Comparison of our data with existing data on[2] W and[6] Pd shows excellent agreement, though we have greater sensitivity for small structure in the 20–50-eV range because of our freedom from second order and stray light in that energy range.

DISCUSSION

In a rare-earth atom, the $4f$ electrons are highly localized near the nucleus and are shielded from interatomic forces by the $5s^2 5p^6$ electrons. As a result, the $4f$ electrons in either a metal or an oxide can be described very well by free-ion wave functions.[5] (They have no direct involvement in band-structure features though they do shield the outer electrons from the nucleus.[7]) Similarly, the rare-earth $4d$ levels lie ~100 eV below the Fermi level and are well described by atomic wave functions. In the atom (for $Z \geqslant 57$), the $4d$ and $4f$ orbits have appreciable overlap, and a strong exchange interaction between the d-state hole and the f-states results from that overlap. The exchange interaction then splits the many final-state terms and pushes some of the energy levels with $4d^9 4f^{N+1}$ configuration high enough in energy that they can interact with the continuum and autoionize. Sum rules indicate that the $4d$ oscillator strength decreases with increasing Z, and the total strength is proportional to the number of vacancies in the $4f$ subshell. Finally, because of the effective potential energy barrier (the so-called centrifugal barrier), the decay into the continuum is delayed several eV above threshold. The observed spectrum then shows discrete lines corresponding to transitions to the various levels of $4d^9 4f^{N+1}$ configuration, weighted according to transition strengths and distributed across an energy range which reflects the exchange interaction. At higher energies it has a strong feature which corresponds to transitions to discrete $4d^9 4f^{N+1}$ states which autoionize and are shifted in energy and broadened through the interaction of the discrete states with the continua channels.

In the transition metals, the initial states are the p states and they lie ~30 eV below the Fermi level. The final states, unlike the highly localized f states of the rare earths, are d states, and, at first glance, one might think they should be best described by wave functions which are far from atomic. Calculations have shown, however, that the $5s$ electrons shield the region of space occupied by the $4d$'s, and that the d-like region of the atom falls within 2 atomic units of the nucleus. In a renormalized atom calculation, Hodges *et al.*[8] showed that most of the total charge of the d states lies within the Wigner-Seitz sphere, and that the d states can be described within the sphere by atomic wave functions. (In Ag, for example, ~98% of the d charge lies within the Wigner-Seitz sphere, assuming a $4d^n 5s^1$ configuration.)

Two somewhat different approaches can be taken in calculations of the optical absorption spectrum. In one, the calculation might proceed along the lines established by the rare earth work: the assumption that the one-electron wave functions of initial (np) and final (nd) states are atomic in character; the determination of the multiplet terms in the excited configuration; the calculation of the exchange interaction and the distribution of final states; a calculation of the weighting of the transitions to each of the allowed final states; and finally a consideration of the multilevel, multichannel autoionization problem. To improve the calculations, solid-state effects must be considered since the d electrons do have some itinerant character, do form bands, and do hybridize with the sp bands. Such effects will be difficult to include, however, since the formation of a deep hole has the effect of distorting the local environment and raising complex questions regarding the validity of a band model.

Calculations of the sort indicated have been performed for the $3d$ metals by Combet-Farnoux and coworkers.[9] She has determined, in an intermediate-coupling scheme, the energy-level structure of Sc, Ti, V, and Co, and has calculated oscillator strengths for the various transitions. Though there have been no calculations of the effects of autoionization, the results look promising.

A second approach has been applied to the $3d$ transition metals. It also is an atomic model and includes a term which deals with an interference of two atomic absorption and decay processes. One of these is the excitation of the initial state p electron into a final d state followed by a super Coster-Kronig decay[10] ($3p^63d^N \rightarrow 3p^53d^{N+1} \rightarrow 3p^63d^{N-1}\epsilon f$), and the other is the direct transition of the form $3p^63d^N \rightarrow 3p^63d^{N-1}\epsilon f$. The model was suggested by Dietz *et al.*[11] to describe the behavior of the energy loss spectra of Ni, and has been extended by Davis and Feldkamp[12] to treat the other $3d$ metals. In the latter work, the splitting of the multiplets of the $3p^53d^{N+1}$ configuration was included, as was the interaction of the many discrete states with the many continua channels. Solid-state effects were heuristically included. The model describes the systematics of the $3d$ spectra, but it has not yet been applied to the $4d$ or $5d$ metals.

In the transition metals, the experimental data of Figs. 1 and 2 and Ref. 2 do not reveal sharp lines below the threshold, but do show a strong, broad absorption feature resembling that seen in the rare earths. The absence of the discrete lines might be a result of either solid state broadening effects of the relative weakness of the lines which do not overlap with the continuum. Comparison of the structures shown in Fig. 1 for the $4d$ metals with the corresponding spectra for the $3d$ metals (Refs. 2 and 6) and $5d$ metals (Fig. 2 and Ref. 2) shows considerable similarity, as should be expected. In each case, p and d electrons are involved, though the principal quantum number changes.

From Fig. 1, the progression of the center of gravity of the absorption feature toward higher energy with increasing Z is seen to be slower toward the second half of the $4d$ period than at the beginning though the onset of the p absorption moves linearly with Z, as shown in Fig. 3. Any attempt at this point to interpret the systematics would be speculative and should probably await the completion of detailed calculations.

In Fig. 1, we note that the onset of the structure for the lighter metals, in particular, shows a feature on the low-energy side of the maximum. Though the feature might be related to an atomic multiplet, we suggest that its origin is in the spin-orbit splitting of the initial state. Estimates of the $p_{1/2}, p_{3/2}$ splitting can be obtained from Herman and Skillman[13] or from Schofield[14]; we show those values as horizontal lines in Figs. 1 and 2. A shifting of the onset of the $p_{1/2}$ transitions to correspond to the onset in the experimental structure places the onset for the $p_{3/2}$ states at about the right place to account for the inflection in the absorption spectrum. We have not tried to deconvolute the spectra or fit the line shape with weighted 2:1 transition strengths since the other effects are strong.

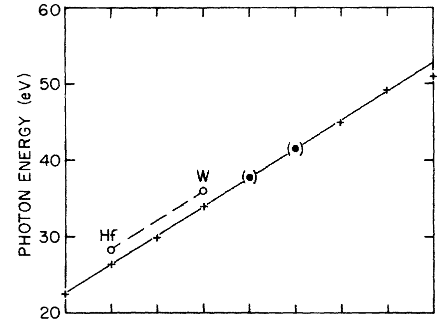

FIG. 3. Plot showing the movement of the $4p$ absorption edge toward higher energy with increasing atomic number. The $5p$ onsets are shown for Hf and W.

Above the $p \rightarrow d$ transitions, the absorption coefficient decreases monotonically until the energies of the $3d$ electrons are reached. The onset of the $3d$ transitions can be seen for Y and Zr, but the onset for the heavier metals is less obvious as seen in Fig. 4.

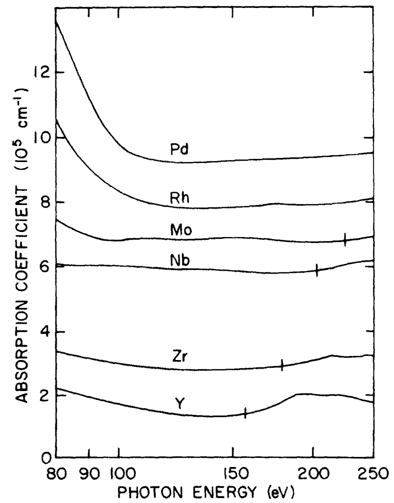

FIG. 4. Optical absorption of the $4d$ transition metals from 80 to 250 eV. Each curve was displaced one unit upward for visual clarity. The tic mark indicates the onset of the $3d$ absorption according to Bearden and Burr (Ref. 16).

So far we have indicated that our data for the 4*d* metals and Hf and W are consistent with existing optical absorption and reliable energy-loss measurements of the 3*d* and 5*d* metals. Indeed, a comparison of our data with the Deutsches Elektronen-Synchrotron (DESY) results for tungsten[2] shows excellent agreement, both in magnitude and topology, though, with our greater sensitivity below ~70 eV, we report slightly more structure near the onset. Comparison of our Pd data with electron energy-loss measurements[6] can be made, and again the agreement is excellent.

An interesting problem arises when the present absorption spectra are compared with results from existing reflectivity studies. The agreement can only be described as fair for Y,[15] Zr,[1] and Hf,[1] although it is quite good for[1] Nb and the other metals studied.[1] In principle, a reflectivity measurement followed by a Kramers-Kronig calculation of the absorption coefficient should yield the same shape of the absorption coefficient curve (magnitudes may be different because of the extrapolation uncertainties) as that determined directly from transmission measurements. We believe that the discrepancies for the reactive hcp metals Y, Zr, and Hf result from the additive nature of interband and atomic absorption processes. In our crystalline studies, we observed that band features were strong and structured between 25 and 35 eV. These were interpreted according to transitions from near E_F to high-lying final states. In Y, Zr, and Hf, these are strong and overwhelm the atomic or *p*-to-*d* transitions in reflectivity measurements with ordered crystals. In the other metals, the background interband absorption was structureless so that, fortuitously, the reflectivity measurements revealed the core structures, and there is excellent agreement between the absorption and reflectivity results. In the absorption measurements of the reactive hcp metals, the evaporated samples exhibited gettering tendencies and undoubtedly contained appreciable impurities so that band features were weaker and localized atomic features were emphasized. What is clear from these sets of measurements is that both atomic and interband absorption are occurring in the "intermediate" energy range, and further efforts, such as those now underway in our group, are needed before a cohesive picture can be drawn.

ACKNOWLEDGMENTS

We are grateful for the continued support of E. M. Rowe, the Director of the Synchrotron Radiation Center, and stimulating discussions with D. W. Lynch and R. E. Dietz. Results of work prior to publication were generously supplied by C. Wehenkel and B. Gauthé. The Synchrotron Radiation Center is supported under NSF Grant No. DMR-74-15089.

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*Supported under NSF Grant No. DMR-74-15089.

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