PHYSICAL REVIEW B VOLUME 15, NUMBER 10 15 MAY 1977

Interband structure and the role of the 5*f* electronic states of thorium: An optical investigation

J. H. Weaver
Synchrotron Radiation Center, University of Wisconsin, Stoughton, Wisconsin 53589*

C. G. Olson
Ames Laboratory, U.S. Energy Research and Development Administration, Ames, Iowa 50011

(Received 9 December 1976)

The optical properties of crystalline thorium have been determined between 0.2 and 8 eV. The reflectivity and interband conductivity are seen to be rich in structures, some of which can be identified as arising from *d*-to-*d* interband transitions and others which must involve hybridized 5*f* final states. Strong structure previously reported near 4 eV is shown to be an artifact. Comparisons are made with existing band calculations, and tentative interpretations are suggested.

INTRODUCTION

The actinide metals and actinide compounds display a wide range of interesting phenomena and these are being examined with increasing intensity.[1] In many respects, the lighter actinide metals display electronic structures which are analogous to those of the lighter transition metals, while the structure of the heavier actinides is such that they more closely resemble the rare-earth metals.[2-4] The feature which is of principal concern in most investigations is the character of the 5*f* electrons. A considerable controversy over how best to describe the 5*f*'s has existed, and considerable discussion continues. Recent efforts[1-4] suggest that the 5*f* states in the lighter actinide metals are itinerant or bandlike, lie within the $7s^2 6d^n$ band manifold, and hybridize strongly with the *sp*-*d* states. According to this itinerant model, the degree of 5*f* localization in Th is roughly intermediate between that of the 3*d* electrons in the first transition-metal series and the 4*f* electrons in the rare-earth metals.[2,3] To describe the 5*f*'s in the lighter actinides, a one-electron formalism is then satisfactory, and calculations show that in Th the *f*-derived states lie close to, but above, the Fermi level. On the other hand, in the heavier actinides, where the 5*f* states are occupied, the width of the *f* bands is markedly narrower, reflecting much greater localization. With such actinides as Cf, for example, a one-electron formalism is no longer valid to treat the 5*f* states. A complete and consistent description of the electronic structure of the actinide metals thus offers many interesting challenges, and some of those are being addressed now.[1-5]

Several experimental studies of the electronic structure of the actinides are presently underway or have recently been completed. Most investigations of the metals have involved the lighter actinides Th and α-phase U, but a considerably larger literature exists for the actinide oxides and compounds. For thorium, in addition to the earlier de Haas–van Alphen results,[6] there are now studies of the pressure dependence of the Fermi surface.[7] X-ray photoelectron spectroscopy,[8,9] appearance potential spectroscopy,[10,11] low-energy-electron diffraction,[12] and soft-x-ray absorption[13] measurements have been reported. Optical studies of thorium have been limited to a single investigation[14] and, as will be shown here, a crucial feature of that study is in error.

A series of calculations of the electronic structures of the actinides[15] has been closely linked with the experimental investigations. Th has again received the most attention since it has an fcc crystal structure and is more tractable to calculation than orthorhombic α-U. The most recent studies[16] of the electronic behavior of Th are focusing on sophisticated comparisons between experiment and (itinerant-model) calculations including the consideration of matrix-element effects in optical absorption.

In this paper, we present the results of an optical study of Th and emphasize the photon energy range between 0.2 and 8 eV. A discussion of the higher-energy interband absorption, 6*p* absorption, and absorption due to the deeper 5*d* core levels will be postponed until subsequent papers. Qualitative comparisons between the present data and existing calculations will be made now, and the groundwork prepared for more elaborate comparisons in the near future.

EXPERIMENTAL TECHNIQUES AND RESULTS

The sample used in these measurements was a large high-purity crystal generously provided by Peterson of the Ames Laboratory, U. S. ERDA.[17] The techniques employed in measuring the optical

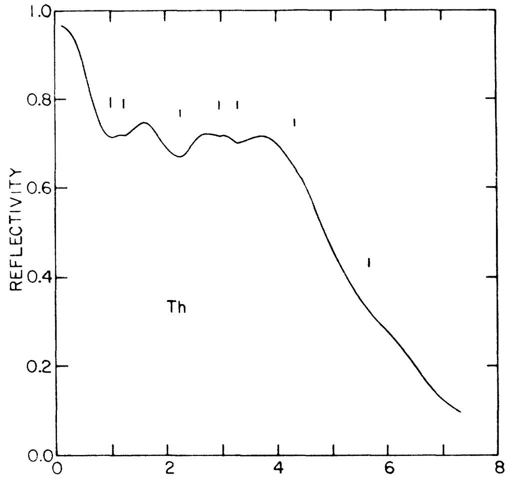

FIG. 1. Optical reflectivity of crystalline thorium from 0.2 to 8 eV.

reflectivity R, or the absorptivity $A = 1 - R$, have been discussed in considerable detail elsewhere[18] and have been used extensively in studies of the transition metals and rare-earth metals. Briefly, the absorptivity was determined at near-normal incidence by a calorimetric technique which lends itself particularly well to low-energy measurements, where A is small (R large)—as is generally the case for metals in the near infrared and visible. The sample temperature was 4.2 K, and the data were taken between 0.2 and 4.4 eV. They are estimated to be accurate to better than 1% (e.g., at 1 eV, $A = 0.286 \pm 0.003$) and showed excellent reproducibility from one run to another. Between 2.5 and 35 eV, the reflectivity was determined at room temperature and near-normal incidence with an uncertainty in R of less than 5% of the magnitude of R—again with excellent reproducibility. For the reflectivity measurements, the intense, highly polarized, continuum radiation from the Tantalus I electron storage ring[19] was used. (Tantalus I is operated under the auspices of the Synchrotron Radiation Center, University of Wisconsin–Madison and is supported by the NSF.) In the region of overlap, the agreement was very good. For each set of measurements, the sample was electropolished[20] and quickly transferred to the nitrogen-purged ion-pumped experimental chamber. Since exposure to the atmosphere was unavoidable, the influence of a thin oxide layer has been assessed. ThO_2 is transparent in the photon energy range under discussion,[21] and a thin layer introduced no significant changes in the measured spectrum.

The results of our measurements are shown in Fig. 1. The reflectivity spectrum is rich in structure. Strong structures in the form of reflectivity minima are evident at 1.02, 1.22, 2.25, and 3.3 eV, with a weaker feature at 2.96 eV and inflections at 4.3 and 5.7 eV.

A comparison between theory and experiment is made best through the imaginary part of the dielectric function ϵ_2 or the optical conductivity $\sigma = \epsilon_2 E / 4\pi\hbar$, since it is these functions which are most readily calculated and are a measure of the interband absorption strength. A Kramers-Kronig analysis was used to determine σ from the reflectivity spectrum of Fig. 1. A Drude extrapolation was assumed for the Kramers-Kronig analysis below 0.2 eV, and a power law of the form $R = R_0 E^{-3.5}$ was assumed in the high-energy range to the upper limit of $E = 10^5$ eV. The results of that analysis are shown in Fig. 2, and, in addition to the total conductivity, an interband conductivity obtained by subtracting the assumed Drude contribution is also shown in Fig. 2. For that subtraction and the infrared Kramers-Kronig extrapolation, Drude parameters of $\sigma_0 = 3.7 \times 10^{16}$ sec^{-1} and $\tau/\hbar = 10.1$ eV^{-1} were used, but these should not be taken too seriously. To determine reliable Drude parameters, the low-energy data must extend sufficiently far into the infrared that only intraband absorption was being measured. Ours did not, and we could not uniquely determine the intraband absorption. Nevertheless, the assumption of a reasonable Drude contribution proved to be useful to accent interband features.

Strong features in the interband conductivity are visible in Fig. 2 at 1.08, 1.28, and 2.32 eV with additional weaker structures at 2.92, 3.34, 4.2, and 5.88 eV. These latter weak features correspond to the reflectivity features marked in Fig. 1.

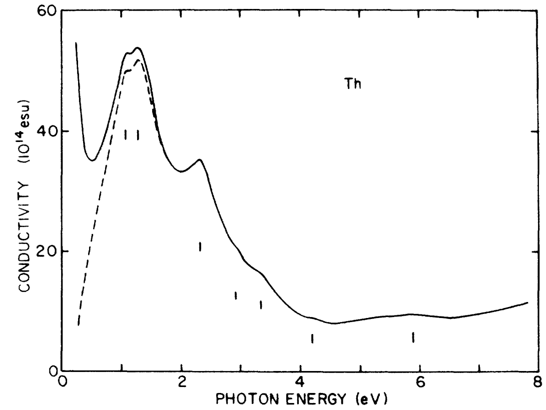

FIG. 2. Optical conductivity of crystalline thorium obtained after Kramers-Kronig analysis of the data of Fig. 1. The dashed line represents the interband conductivity as determined through subtraction of a Drude contribution from the total conductivity.

The low-energy optical spectrum of Th is clearly rich in structure, and these provide us with valuable information about the electronic states removed in energy from E_F. They provide an excellent and compelling test of any band calculation, as well as any assumptions made concerning matrix-element effects.

A comparison of the results shown in Figs. 1 and 2 with those of Veal *et al.*[14] shows only very rough agreement. Below ~4 eV, the two sets of data have some resemblance, though the present results show the structures far more clearly. The more striking discrepancy occurs above 4 eV. In that region, Veal *et al.* reported a minimum in R while we show a gradual, structured decrease toward a minimum in R not shown in Fig. 1. It is now felt[22] that the structure previously reported results from surface-roughness-induced coupling of the photon to surface plasmons. (The surface roughness came as a result of the rather severe etching from the glow discharge sputtering of the surface.) While such an effect is interesting, it provides no information regarding $5f$ final states.

DISCUSSION

The electronic structure of Th is particularly intriguing. Not only does Th possess bandlike $5f$ states (itinerant model), but it also possesses a partially filled d band which is analogous to what is found in the $5d$ (fcc) transition metals. Comparison of the bands of Th with those of, say, Au reveals several interesting features. In Au, the $5d$ bands are completely occupied, the interband edge at $h\nu \simeq 2.5$ eV involves the p-like states, and subsequent strong absorption arises from the predominantly d-like initial states. The f-like states at Γ with symmetry 7^-, 8^-, and 6^- lie $\gtrsim 18$ eV above E_F,[23] and have been of considerable interest because of their possible involvement in high-energy interband transitions.[24-26] The band structure of Th is qualitatively similar, but now the $5f$ levels lie *within* the d bands, the width of the d bands is very large (~12 eV), and the p-like X_6^- and L_6^- states are deep within the d bands. In addition, the Fermi level lies far lower in the d bands than in any of the fcc transition metals.

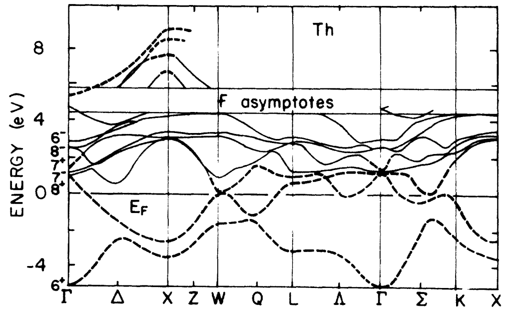

FIG. 3. Energy bands of Th determined by Ref. 29 using a symmetrized relativistic augmented-plane-wave (RAPW) technique, d^2s^2 configuration, $\alpha = \frac{2}{3}$. The dashed bands are (sp-d)-like and have little or no hybridized f character.

The energy band structure of Th, as calculated by Koelling and Freeman,[27] is shown in Fig. 3. It should be noted that these bands are now being refined,[16] but they are sufficient for the qualitative interpretations suggested here. Comparison of the bands of Fig. 3 with those of an fcc transition metal, or the tabulated sp-d eigenvalues for Th (Ref. 2, p. 73), shows that the first two bands are entirely sp-d like without any hybridization with the nearby, but empty, $5f$ states. Hybridization begins with the third band. In particular, the third band near X is derived from the f levels, but at Γ, L, and W it is nearly all d-like. Subsequent higher bands are strongly f-like. Above the seven f bands and the region labeled f asymptotes, the d character is again dominant.

Two points should be made before attempts are made to compare the experimental results of Figs. 1 and 2 with the energy bands of Fig. 3. First, any comparison is at best qualitative and can be made quantitative only after detailed matrix element calculations are completed. Existing calculations indicate that the constant matrix element assumption is too rough an approximation. Second, our work with the transition metals[28] has shown that large volumes of k space are often involved in a particular experimental structure, and, further, that volumes of k space which are removed from lines of high symmetry (and hence not shown in band calculations) can be responsible for experimental features. As a result, the identifications which we can make at this point are subject to verification or vilification as the calculations improve.

Strong structures are seen in the conductivity (Fig. 2) at 1.08 and 1.28 eV. Interband absorption continues to lower energy, but its strength is impossible to assess at this point because of the uncertainty in the Drude contribution to the total conductivity. Certain candidates can be found from the bands of Fig. 3 to account for the strong absorption below ~2 eV. In particular, transitions between bands 2 and 3 along Σ appear to have an energy separation of approximately the right magnitude. All bands along Σ have Σ_5 symmetry and hence the transitions are allowed, d to d transitions. Additional absorption may arise from the bands along Λ.

The interpretation of the strong feature at 2.32 eV is difficult since a large number of possible states might be involved. Of these, few are d to d

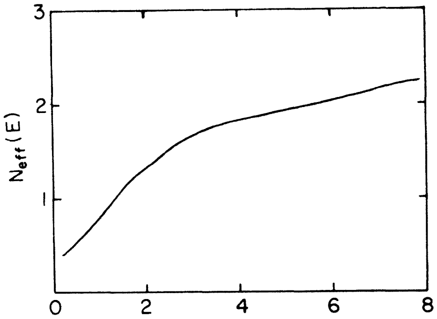

FIG. 4. $N_{eff}(E)$ sum rule for thorium using the data of Fig. 2. The magnitude of $N_{eff}(E)$ reaches four electrons per atom near 16 eV.

transitions. Only between bands 1 and 3 near W and between bands 2 and 3 along Q are d band transitions possible. Other possible volumes of k space involve d-like initial states and hybridized f-like final states. Among these, transitions between bands 2 and 5 in the Δ and Σ directions are possible. From a joint density of states argument, bands 2 and 4 along Q may also be important. Bands 2 and 4 along Λ (energy separation 1.6 eV and f-like final state) have a hard-to-estimate influence. What should be clear at this point is that the lower-energy features in thorium present a great many experimental features, that several parts of k space may be involved, but that is not yet possible to sort out the contributions of each.

It is interesting to consider the sum rule defined by

$$N_{eff}(E) = \frac{2}{\pi} \frac{1}{(\hbar\omega p)^2} \int_{E_1}^{E_2} \epsilon_2 E \, dE ,$$

and representing the number of electrons which have been involved in absorption between energies E_1 and E_2. $\hbar\omega p$ is the plasma frequency and is calculated to be 12.94 eV. $N_{eff}(E)$ has been calculated with the results of Fig. 2 and is shown in Fig. 4 for the energy range between 0.1 and 8 eV. It is clear that below 8 eV, the oscillator strength is quite low. Only by continuing the integration to 16 eV (using our unpublished vacuum-ultraviolet data) does N_{eff} reach the four electrons per atom magnitude expected. Above 16 eV, the contributions of the $6p_{1/2}$ and $6p_{3/2}$ core levels are evident, as will be discussed at a later time. What is clear is that all of the oscillator strength is not bunched into relatively narrow energy range corresponding to transitions to f-like final states.

ACKNOWLEDGMENTS

The authors are grateful to D. T. Peterson for providing the sample and generously assisting us in our understanding of it. The continued strong support of E. M. Rowe is appreciated. Discussions with D. W. Lynch, D. D. Koelling, B. N. Harmon, and B. W. Veal are gratefully acknowledged.

---

*The Synchrotron Radiation Center is operated under NSF Grant No. DMR-7415089.

[1] For an excellent review of the actinides, see *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. R. Darby, Jr. (Academic, New York, 1974).

[2] A. J. Freeman and D. D. Koelling, Ref. 1, Chap. 2.

[3] D. D. Koelling and A. J. Freeman, Phys. Rev. B 12, 5622 (1975); E. A. Kmetko and H. H. Hill, Nucl. Met. 17, 233 (1970); J. F. Herbst, R. E. Watson, and I. Lindgren, Phys. Rev. B 14, 3265 (1976).

[4] B. Johansson, Phys. Rev. B 11, 2740 (1975); B. Johansson and A. Rosengren, *ibid.* 11, 1367 (1975); A. Rosengren, I. Ebbsjö, and B. Johansson, *ibid.* 12, 1337 (1975).

[5] R. Jullien, E. Galleani d'Agliano, and B. Coqblin, Phys. Rev. B 6, 2139 (1972).

[6] A. C. Thorsen, A. S. Joseph, and L. E. Valby, Phys. Rev. 162, 574 (1967); and D. J. Boyle and A. V. Gold, Phys. Rev. Lett. 22, 461 (1969).

[7] J. E. Schirber (private communication).

[8] B. W. Veal and D. J. Lam, Phys. Rev. B 10, 4902 (1974).

[9] J. C. Fuggle, A. F. Burr, L. M. Watson, D. J. Fabian, and W. Lang, J. Phys. F 4, 335 (1974).

[10] P. A. Redhead and G. W. Richardson, J. Appl. Phys. 43, 2970 (1972).

[11] M. S. Murphy and P. A. Redhead, J. Vac. Sci. Technol. 11, 837 (1974).

[12] T. N. Taylor, C. A. Colmenares, R. L. Smith, and G. A. Somorjai, Surf. Sci. 54, 317 (1976).

[13] J. H. Weaver and C. G. Olson (unpublished data for $5d \rightarrow 5f$ absorption in Th, $ThCl_4$, and U).

[14] B. W. Veal, D. D. Koelling, and A. J. Freeman, Phys. Rev. Lett. 30, 1061 (1973).

[15] See Ref. 2 for a good review of the literature concerning the band structures of the actinide metals.

[16] D. D. Koelling (private communication).

[17] The sample measured ~ 10×15×1 mm, had been cold rolled, then annealed *in vacuo* at 800 °C to promote recrystallization. The crystallites were small with an estimated 3000 grains per mm^3. The resistivity ratio was ~ 40. Purity analysis showed the following impurities (in parts per million): C:6; oxygen:86 (mostly as diffuse, dispersed ThO_2 since the solubility of oxygen is ~ 15–20 ppm); N:14; Al and Ca: ~ 20 each; Fe, Cr, Ni, Mn, Mg all less than 20 ppm (lower limit of sensitivity); W:8; Ta:70. For further details of the handling of Th metal, see D. T. Peterson, W. E. Krupp, and F. A. Schmidt, J. Less Common Met. 7, 288 (1967).

[18] For a discussion of the basic calorimetric technique, see L. W. Bos and D. W. Lynch, Phys. Rev. B 2, 4567 (1970). The vacuum-ultraviolet technique is best described in C. G. Olson and D. W. Lynch, Phys. Rev.

B 9, 3159 (1974).

[19] E. M. Rowe and F. E. Mills, Particle Accel. 4, 211 (1973); and Synchrotron Radiation Center Users Handbook, edited by J. H. Weaver (unpublished) (available upon request of the author).

[20] Electropolished in a 6% by volume solution of perchloric acid in methanol cooled to ~ 200 K. The authors gratefully acknowledge the assistance of H. H. Baker in this aspect of the work.

[21] The optical reflectivity of ThO_2 has been reported by J. Naegele, L. Manes, and H. Winkelman (private communication).

[22] B. W. Veal (private communication).

[23] N. E. Christensen, Phys. Rev. B 13, 2698 (1976).

[24] C. G. Olson, M. Piacentini, and D. W. Lynch, Phys. Rev. Lett. 33, 644 (1974).

[25] J. Hermanson, J. Anderson, and G. J. Lapeyre, Phys. Rev. B 12, 5410 (1975).

[26] J. H. Weaver and C. G. Olson (unpublished).

[27] D. D. Koelling and A. J. Freeman, Solid State Commun. 9, 1369 (1971).

[28] See for example, J. H. Weaver, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 1293 (1975); 14, 459 (1976), and references therein to our other transition-metal work and that of others.