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Thermoreflectance investigation of Th band structure

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Thermoreflectance measurements have been carried out on thorium bulk samples at about 140 K in the (0.5—5)-eV photon energy range. The data are interpreted within the framework of existing energy-band calculations. Several critical-point transitions and a Fermi-surface transition have been clearly identified and located in the Brillouin zone.

I. INTRODUCTION

The most interesting physical problem posed by the investigation of the electronic structure of thorium and, in general, of the actinides, is the nature of the $5f$ electrons.[1] Considerable controversy has arisen in recent years on how best to describe the character of the $5f$'s for the different elements since they lie on the borderline where neither a localized nor an itinerant picture seems appropriate. It has been shown,[2–5] however, that the $5f$ shell electrons in the actinide metals do form bands which overlap and hybridize with the $6d$ and $7s$ bands. This greatly complicates the resulting band structure, but it seems well established that the $5f$ must be considered itinerant electrons and not, as in the $4f$ case, localized electron states.

Thorium is at the beginning of the actinide series and it has empty $5f$ states just above the Fermi level. Since it has a simple (fcc) crystal structure, it has been often taken as a test case for energy-band calculations of the actinides.

From an experimental point of view, quite a substantial amount of new information has become available on Th in recent times. Valence and empty conduction-band levels have been probed by photoemission[6–8] and bremsstrahlung isochromat spectroscopy,[8] and detailed Fermi-surface calipers have been determined by de Haas—van Alphen measurements.[9,10]. Also several optical studies[5,11,12] exist which, however, have been limited so far to the more conventional "static" techniques.

Among optical techniques, modulation spectroscopies play a very important role[13,14] since the resulting spectra show better resolved structures then static measurements. The line shape of these structures is often a clear fingerprint of particular features (critical points) in the electron band structure.

Thermomodulation has been proven particularly suitable for studying metals[15] and alloys[16] since, in addition, it shows the characteristic line shapes of the optical transitions which involve the Fermi surface.[17]

In the following we report thermoreflectance measurements on Th in the (0.5—5)-eV photon energy range. We identify several critical point transitions and we give clear evidence of a Fermi-surface transition. The location of these features in $\vec{k}$ space is a considerable progress towards a more extensive test of Th band-structure calculation.

II. EXPERIMENTAL

The thermoreflectance spectra $\Delta R/R$ (i.e., the relative temperature-induced changes in the reflectance) were measured with a Perkin-Elmer 99 prism monochromator in the (0.5—5)-eV photon energy range at about 140 K. The details of the experimental technique and of the optical layout can be found elsewhere.[18,19] The heating system is the now standard high efficiency system successfully used in a number of thermoreflectance studies. A complete discussion of the thermal behavior of the thermomodulation setup (sample plus heater) will be published elsewhere.[20]

A high-purity Th bulk sample was made available by the Ames Laboratories and it was cut with a low-speed diamond saw into the form of thin platelets of about $2\times3\times0.2$ mm^3. These were polished to a mirror finish and electropolished in a

solution of 6 vol % of perchloric acid in methanol cooled to 200 K, to remove the cold worked layers from the mechanically polished surface. Exposure to the atmosphere was unavoidable; however, ThO_2 is transparent[6] in the photon energy range of our measurements and a thin layer of oxide does not introduce any significant changes in the measured spectrum.

III. RESULTS

The results of our measurements are shown in Fig. 1. As usual, the spectrum is much richer in structures than the static reflectivity curve.[12] Most of the features, however, occur in agreement with the static determinations.

A comparison between theory and experiment is best made through $\Delta\epsilon_1+i\Delta\epsilon_2$ spectra. The variation of the imaginary part of the dielectric function $\Delta\epsilon_2$ is directly correlated to the change of absorption induced by the temperature modulation. Furthermore, the correlation of structures in $\Delta\epsilon_1$ and $\Delta\epsilon_2$ gives further insight on the origin of optical transitions in $\vec{k}$ space.[14] Accordingly, we have determined $\Delta\epsilon_1$ and $\Delta\epsilon_2$ spectra through the Kramers-Kronig (KK) analysis of $\Delta R/R$. The analysis requires an extrapolation of the $\Delta R/R$ data outside the measurements range, but for derivative spectra, the results are not very sensitive from the details of the extrapolation. It has been demonstrated that it introduces negligible errors on the energy position of optical structures.[21] The static optical constants needed in the KK inversion were taken from Ref. 12. The results are shown in Fig. 2. In the infrared, below about 0.8 eV, $\Delta\epsilon_1$ and $\Delta\epsilon_2$ show a rapid rise with decreasing energy which reflects the temperature modulation of the free-electron part of the dielectric function, mainly through the temperature dependence of the free-electron relaxation time. At higher photon energies, modulation of interband features dominate. By inspection of the line shapes in Fig. 2, the contributions of an M_2 critical point at about 2.3 eV and of an M_0 at 3.7 eV are clearly recognizable. The insets in the same figure show their theoretical line shapes.[14] It is well known that the theory[14] of optical absorption at critical points takes into account only the topology of the initial and final bands involved in direct transitions. The dependence of the dipole matrix element from the wave vector $\vec{K}$ can introduce modifications to theoretical line shapes. The overall agreement between experimental and calculated behavior for the proposed critical points is in this case quite good.

Identifications of critical points are unambiguous and straightforward when well recognizable line shapes in both $\Delta\epsilon_1$ and $\Delta\epsilon_2$ occur. In more complicated cases, more insight into the origin of structures in the spectra can be obtained by writing

$$\frac{\Delta R}{R}=\alpha(\epsilon_1,\epsilon_2)\Delta\epsilon_1+\beta(\epsilon_1,\epsilon_2)\Delta\epsilon_2 \tag{1}$$

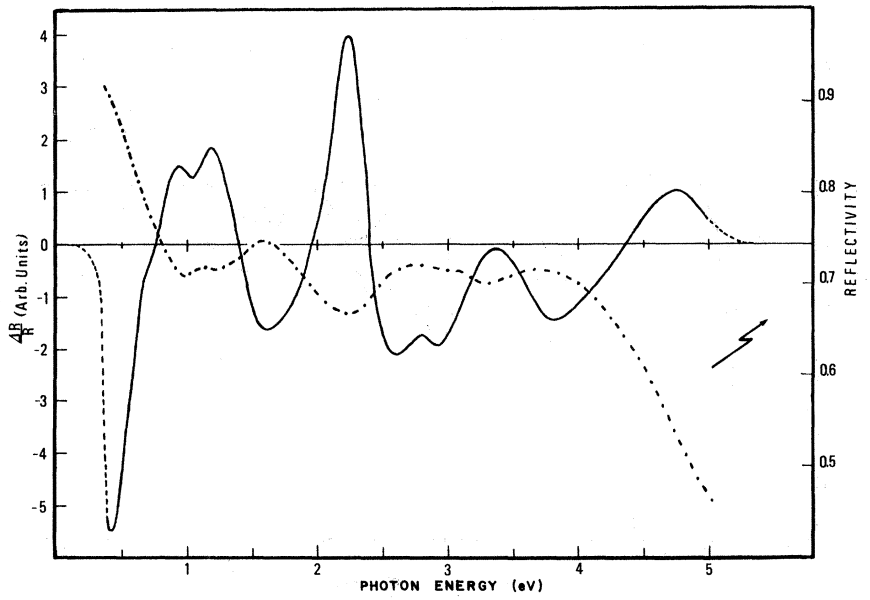

FIG. 1. Thermoreflectance spectrum of Th taken at 140 K. The extrapolations used for the KK analysis are shown as dashed lines. The reflectivity spectrum of Th taken from Ref. 12 is also shown (dashed-dotted line).

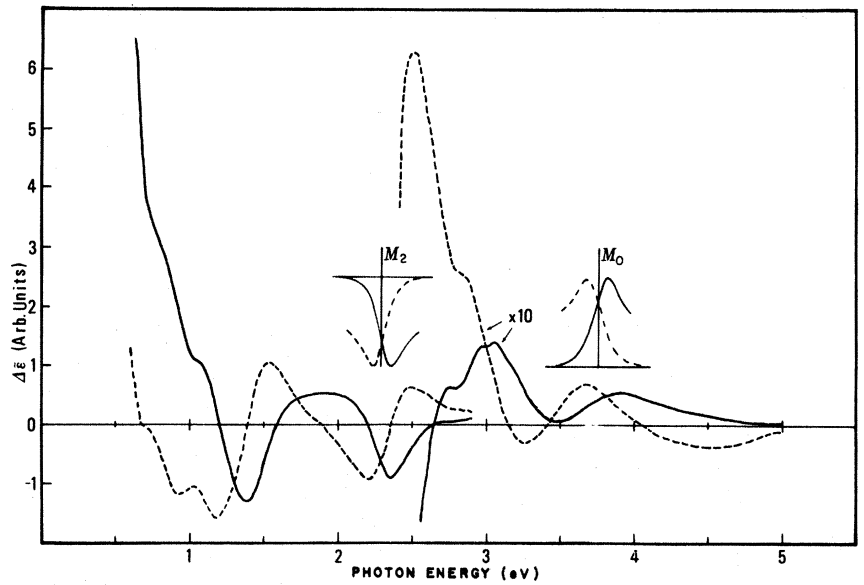

FIG. 2. Temperature-induced variation of the dielectric function; solid curve, $\Delta\epsilon_2$; dashed curve, $\Delta\epsilon_1$.

and plotting separately the two contributions to $\Delta R/R$. These are shown in Fig. 3. Both the $\alpha(\epsilon_1,\epsilon_2)$ and $\beta(\epsilon_1,\epsilon_2)$ coefficients, as calculated from Weaver and Olson's optical constants,[12] are almost structureless. $\alpha(\epsilon_1\epsilon_2)$ is negative over our experimental energy range and is predominant with respect to $\beta(\epsilon_1,\epsilon_2)$. As a result, the $\Delta R/R$ spectrum is $\Delta\epsilon_1$-like (but with reversed sign) and "fingerprints" of $\Delta\epsilon_1$ critical-point line shapes show up clearly in it. Bearing this in mind, the

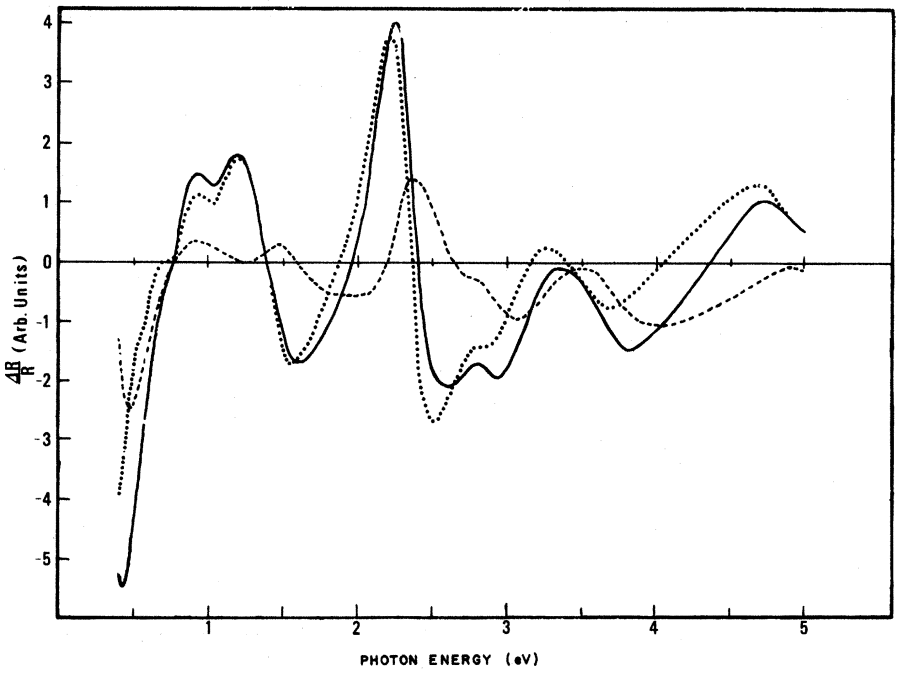

FIG. 3. Contributions to the $\Delta R/R$ spectrum; solid line, total $\Delta R/R$; dashed line, $\Delta\epsilon_2$ contribution; dotted line, $\Delta\epsilon_1$ contribution.

comparison of $\Delta R/R$ with its contributions allows one to delimit much better each structure and recognize and discard from consideration any feature due to the superposition of adjacent structures.

The M_2 critical point at 2.3 eV gives rise to a strong positive peak in $\Delta R/R$ (see Fig. 3) and its contributions extend roughly from 2 to 2.4 eV. The origin of the minimum at about 2.6 eV must be due to a different critical point which we identify as an Mo critical point located at about 2.7 eV. This identification is substantiated by the similar behavior the $\beta\Delta\epsilon_1$ function shows around 2.7 and 3.7 eV. By analogy, the structure in $\Delta R/R$ around 3 eV is assigned to another M_0 critical-point absorption.

The line shapes in the low-energy range (1—2 eV) are more difficult to recognize. We find that most likely the origin is a superposition of contributions from a Fermi-surface transition at ~ 1.2 eV and an M_3 critical point at ~ 1.5 eV as shown schematically in Fig. 4. Indeed, $\Delta\epsilon_1$ shows a strong minimum just where $\Delta\epsilon_2$ has a flex and crosses the zero line supporting a Fermi-surface contribution.[17] Moreover, the $\Delta\epsilon_1$ positive lobe around 1.5 eV occurs together with negative values of $\Delta\epsilon_2$ confirming the M_3 critical-point identification.[13,14]

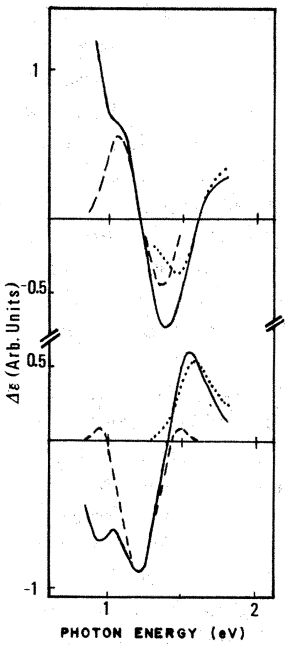

FIG. 4. Low-energy contributions to $\Delta\epsilon_2$ (upper curve) and $\Delta\epsilon_1$ (lower curve): Fermi-surface transition (dashed line); M_3 critical-point transition (dotted lines).

Although the line shapes of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ at this energy range (1.1—1.6 eV) appear similar to those around 2.3 eV, we rule out the occurrence of an M_2 critical-point contribution. This would give rise to the positive peak in $\Delta R/R$ at 1.2 eV but could never produce the negative minimum at 1.6 eV.

In order to substantiate our attributions on the relative weight of the different contributions and obtain more quantitative insight, we have set up a $\Delta R/R$ model using a standard theory.[14] The variation of the dielectric function $\tilde{\epsilon}$ with respect[22] to the interband energy E_0 near the critical point M_r ($r=0,1,2,3$) is:

$$\Delta\tilde{\epsilon}_r = -(i)^{(r+1)} J_r \frac{|\vec{P}|^2}{(\hbar\omega)^2} \Gamma^{-1/2} \times [F(x) - iF(-x)]\Delta E_0 , \tag{2}$$

where

$$F(x) = [(x^2+1)^{1/2}+x]^{1/2}/(x^2+1)^{1/2}$$

with $x = (\hbar\omega - E_0)/\Gamma$ and J_r a topological factor, depending on the effective masses of the two bands involved in the optical transitions. $\vec{P}$ is the dipole matrix element and Γ the Lorentzian broadening parameter. From these formulas, a theoretical $\Delta R/R$ curve can be computed by using Eq. 1.

The results obtained with the parameters of Table I are shown in Fig. 5. They reproduce quite well the overall line shape of the $\Delta R/R$ curve giving strong support to our attributions. A more detailed fit of the experimental curve with our model has not been attempted. Indeed, the effort of further improving the agreement is not warranted because several approximations are included in the model (chiefly the constant matrix element approximation). The same model has been already used

TABLE I. Parameters used for the model shown in Fig. 5. E_0 and Γ are the energy and the broadening parameter of the critical point. W is the weight of each contribution to the $\Delta R/R$ spectrum.

Critical point	E_0 (eV)	Γ (eV)	W (eV^2)
M_3	1.53	0.10	0.730
M_2	2.29	0.12	0.900
M_0	2.60	0.15	0.450
M_0	2.92	0.11	0.185
M_0	3.76	0.16	0.130

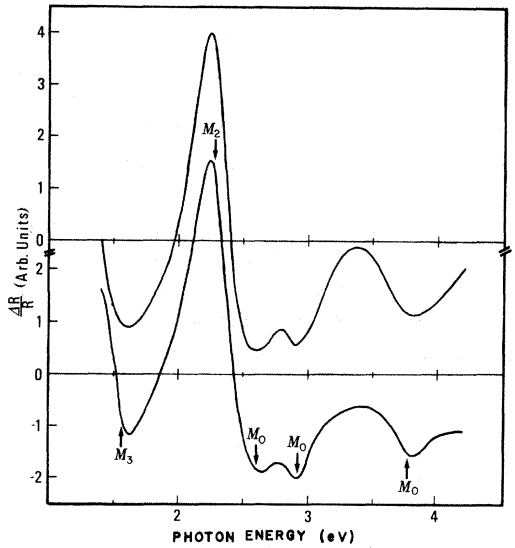

FIG. 5. Comparison between the $\Delta R/R$ experimental spectrum (upper curve) and the spectrum (lower curve) obtained using the standard theory.

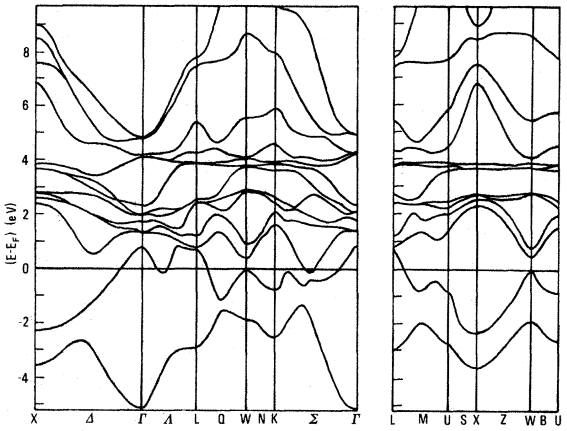

FIG. 6. Thorium band structure (Ref. 4).

to single out an M_3 critical-point contribution in Nb.[16] To our knowledge, however, this is the first time that such a large range of a thermomodulation spectrum is quantitatively interpreted. This procedure appears to be very promising for a quantitative and unambiguous interpretation of modulation spectra.

The energy location of the critical points is considered reliable within ± 0.01 eV and the broadening parameters within $\pm 5\%$. Not too much physical significance should be attached, however, to the weight parameter W, which depends on many factors (dipole matrix element of the transition, deformation potential of the bands involved, etc.).

IV. DISCUSSION

The electronic structure of Th is particularly intriguing and complicated, since Th not only has $5f$ states just above the Fermi surface, but it also has a partially filled d band. Figure 6 shows self-consistent energy bands as calculated by Skriver and Jan.[4] This is the most recent and detailed band-structure calculation of Th. The agreement with de Haas–van Alphen measurements[9,10] (including the pressure dependence of Fermi-surface calipers) is very good so that it should be a good starting point for understanding the optical properties of Th. Below the Fermi level the l-character of electronic levels is entirely $7s$,$6d$-like without any hybridization, with p-like levels which, instead, lie well above E_F. Starting from E_F, the f-states increasingly influence the electronic levels through d-f hybridization. Their contribution to the total density of states at E_F is about 30%. A relatively narrow band (width $\sim$ 3, 4 eV) of mainly $5f$-like states has its lower edge at about 0.9 eV above E_F. The f-partial density of states shows strong peaks at $\sim$ 2.7 eV and $\sim$ 3.6 eV, which are expected to influence the optical properties of Th.

We locate the Fermi-surface transition (at 1.2 eV in our spectra) along the Λ symmetry direction, between bands 2 and 3. Also the M_3 critical point transition at 1.53 can be located along Λ between bands 2 and 4. Faldt and Nilsson[5] also attribute the low-energy structure in their static optical spectra to transitions along Λ in agreement with our more detailed assignments.

The M_2 critical point at 2.29 eV is more difficult to locate. Possible candidates are transitions between bands 2 and 3 at U and K. A definite assignment would need an expansion of the bands near U and K and a detailed matrix element calculation.

The last three M_0 critical points at 2.60, 2.92, and 3.76 eV can all be located at W (band $1\rightarrow 4$; $2\rightarrow 5$, 6, and $2\rightarrow 7$, 8 transitions). Detailed matrix element calculations would be helpful also in this case for supporting our attributions. However, the joint density of states for transitions between bands 2 and 5–6 as well as 2 and 7–8, just above the critical point, should be particularly high (owing to the flatness of the f-like final states). Besides, these transitions are highly allowed $d\rightarrow f$ transitions, so that our attribution seems to rest on solid ground.

Interestingly, if these attributions are correct, the energy difference of these two transitions directly gives the separation between the f final states, in very good agreement with the band calculations. Moreover, since the second band at W is generally located very close to the Fermi surface, our determinations also give the absolute energy positions of the flat $5f$ final states. Our assignment excludes the presence of a hole pocket in band 2 near W, otherwise we should observe Fermi-surface transitions in our spectra and not M_0 critical-point line shapes.

Our "$\Delta R/R$ model" uses negative values of the temperature-induced shifts of energy gaps. Thus, the identified transitions occur between bands approaching each other by increasing the temperature. Skriver and Jan's calculations[4] on pressure dependence of electronic states of Th give support to our assignments. The bands involved in the observed optical absorptions are d and f-like and their relative energy distance is expected[4] to change with pressure and to decrease by increasing the lattice parameter.

In principle, it would be possible to determine with our method also the magnitude of the energy shifts induced by the temperature. This has been done in simple cases[23,24] and involves a direct evaluation of the oscillator strength of each contribution to ϵ_2. Unfortunately, when too many different absorptions occur in the same energy range, this evaluation cannot be done.

The identifications made in the present paper show that the procedure of comparing $\Delta R/R$, $\Delta\tilde{\epsilon}$, and its contributions to $\Delta R/R$, is very fruitful. This method, together with the use of a "theoretical" $\Delta R/R$ model, allows us to put the interpretation of thermoreflectance spectra on much firmer grounds.

Our results and the above discussion demonstrate the possibility of analyzing the optical thermomodulated properties of thorium in terms of the usual concepts such as Fermi-surface transitions and interband critical points. These concepts are suitable even when f-like final states are involved, giving clear evidence of their bandlike itinerant character in agreement with most recent views. The general agreement between experimentally determined band separations and their theoretical counterparts is very good. This shows that modern methods of band-structure calculations are highly reliable, even when difficult problems such as the investigation of highly relativistic metals and the determination of the position of $5f$-derived levels are involved.

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