# Optical properties of thorium in the range 0.5–25 eV

Åke Fäldt and P. O. Nilsson
*Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden*
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The optical properties of evaporated films of thorium have been studied in the range 0.5–25 eV. The data have been analyzed in terms of direct transitions in a band structure, thus assuming that the 5*f* electrons have an itinerant nature for excitations in the optical region.

## I. INTRODUCTION

One central problem concerning the electronic structure of the actinides is the degree of localization of the 5*f* levels for the different elements and in various situations. One prototype to study is thorium, which has no occupied 5*f* states. Accordingly the problem of exchange interaction need not be considered in this case. Moreover, thorium is favorable from an experimental point of view: It is obtainable in sufficient quantities, it is not active, and it is possible to evaporate and keep clean in UHV. Some optical data exist for low energies ($\lesssim 6$ eV); however, these show some variations. We have found it worthwhile to reexamine this energy region carefully and also to extend the data to higher energies. Detailed analysis of the data was carried out, using a model with direct transitions in a recently published band structure.

## II. EXPERIMENTAL

### A. Ellipsometric measurements (0.5-4.5 eV)

The specimens were prepared by evaporation *in situ* from a tungsten spiral onto a smooth sapphire substrate. Owing to the fact that Th has a relatively high melting point and a low vapor pressure the tungsten wire had to be rather thick, about 0.6 mm, in order not to break during the evaporation. The thorium, of 99.9% purity, was originally in the form of a rod which was cut into pieces and placed in the evaporation source. The source was carefully outgassed prior to the evaporation. As we annealed our films we also had to outgas the substrate holder before the evaporation. This was done by heating the substrate to about 250 °C for several hours. The base pressure in the chamber was in the $5\times10^{-10}$-torr region. During the evaporation the pressure rose to the $10^{-8}$ torr region but immediately after depositing the metal, the pressure went back into the $10^{-10}$-torr region. Owing to the high melting point of Th one could suspect that the samples could contain tungsten from the evaporation source. However, characteristic x-ray fluorescence analysis showed that the content of tungsten was below 0.1 at.%.

Normally the thickness of our samples is measured by means of a quartz crystal monitor placed close to the substrate. In the present case, however, the evaporation process produces so much heat that it was impossible to use that method. Instead we covered the samples with an Al film after having completed all the measurements and determined the thickness with interference microscopy. The thicknesses of the films studied were between 1000 and 2000 Å.

The ellipsometer used in this work has been described previously by Liljenvall *et al.*[1] The angle of incidence was 75.5° in all our measurements and the incident light was polarized at 45° relative to the plane of incidence. We evaporated onto a substrate that was at room temperature and a set of data was immediately taken after alignment of the ellipsometer.

Each run, consisting of about 75 points between 0.5 and 4.5 eV, took about two hours to perform. After we measured the optical constants on the film at room temperature, the sample was cooled to liquid-nitrogen temperature where another set of data was taken. Thereafter the temperature was raised to around 200 °C and the sample was annealed for 30 min, cooled down to liquid-nitrogen temperature, and remeasured. During the annealing process the pressure in the chamber stayed in the low $10^{-9}$-torr region. As the experimental system was equipped with a He cryostat, we could decrease the temperature down to about 10 K and measure at this temperature. After having done the measurement at He temperature, we allowed the sample to go up to room temperature again where it was remeasured.

### B. Normal-incidence reflectance measurements (3-25 eV)

The specimens were prepared in the same way as in the ellipsometer system. However, we did not have the opportunity to make our measurements at different temperatures or to anneal the films. Accordingly, all data were taken at room temperature. The base pressure in this UHV system was in the $10^{-10}$-torr region. During the evaporation

 

the pressure rose to the $10^{-8}$-torr region but was back in the $10^{-10}$-torr region soon again. As a light source we used synchrotron radiation from the 1.2-GeV synchrotron LUSY at the University of Lund. The light was monochromatized by a 1-m normal-incidence Hilger spectrometer. The light then passed into a vacuum chamber containing a toroidal mirror which focused the light beam onto the sample in the experimental UHV chamber. The reflectance was measured with a near-normal-incidence reflectometer described elsewhere.[2]

## III. RESULTS

The result for the dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, at low temperatures (~10 K), obtained by the ellipsometric method, is shown in Fig. 1 for photon energies between 0.5 and 4.2 eV. The frequency dependence is dominated by a strong Drude-type behavior, which is characteristic of a metal with a high density of states around the Fermi level. Superimposed on this behavior are two oscillators, which occur as two distinct absorption peaks in the optical-conductivity data, $\sigma(\omega) = \epsilon_2(\omega)\omega/4\pi$, in Fig. 2. The peaks occur at 1.05 and 2.25 eV, respectively. The room-temperature data are quite similar, differing only by having peaks which are slightly more smeared. The effect of annealing was also found negligible.

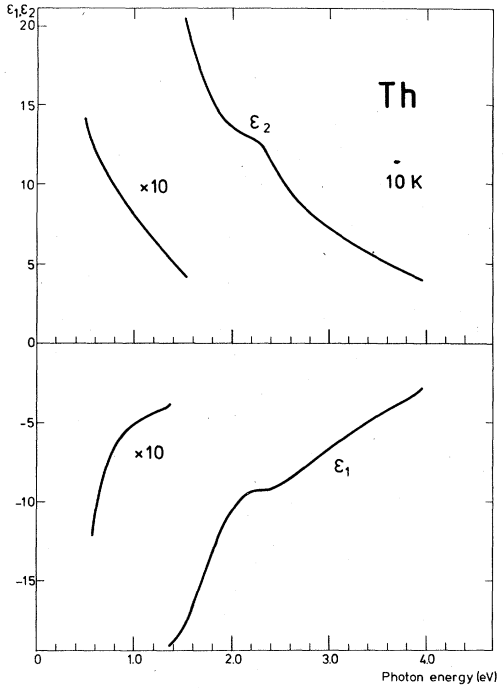


FIG. 1. The real and imaginary part of the dielectric function of Th at 10 K obtained with ellipsometric technique.

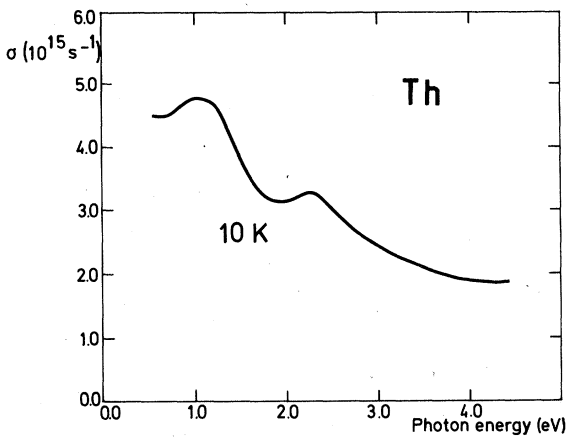


FIG. 2. The optical conductivity of Th at 10 K obtained with ellipsometric technique.

The high-energy synchrotron radiation data start at 3 eV and extend up to about 25 eV. In the region overlapping the ellipsometric data, 3.5 to 4.8 eV, there is a small difference in the absolute magnitude of the reflectance as compared to that calculated from the ellipsometric data. This discrepancy is assumed to be due to a slight misalignment of the near-normal-incidence reflectometer. Accordingly, the reflectance was corrected with a multiplication factor throughout the whole measured region, resulting in excellent agreement in the whole overlap region. The synchrotron data were further corrected by subtraction of a back-

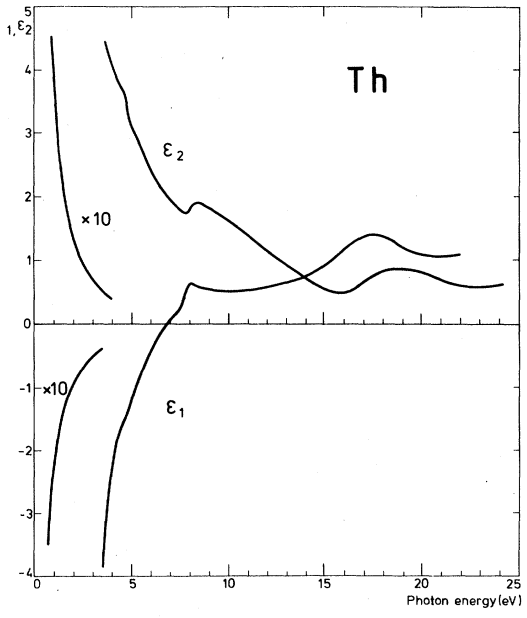


FIG. 3. The real and imaginary part of the dielectric function of Th at room temperature obtained from dispersion analysis of normal reflectance data.

ground (~2% absolute reflectance) due to scattered light. On the so-combined and corrected reflectance a Kramers-Kronig (KK) analysis was performed. The unknown reflectance above 25 eV was taken into account by including an approximation to the phase-shift contribution from that region.[3] The approximation includes one parameter which was determined by requiring that the analysis give the directly measured optical constants for a chosen photon energy $\hbar\omega_0$ in the low-energy region (Fig. 1). The result was found to be quite independent of the choice of $\hbar\omega_0$, which strongly indicates a high accuracy in the analysis. The dielectric function is shown in Fig. 3. Owing to the above-mentioned approximations in the KK analysis the functions become slightly distorted close to the lower and upper frequency limits. For this reason we have used the ellipsometric data below 3 eV in Fig. 4, where the optical conductivity is displayed.

It seems[4] that no optical data on Th exist prior to 1970. Veal *et al.*[5] reported optical-conductivity measurements up to 6 eV in 1973. New and modified data were more recently published by Weaver and Olson[6] up to 8 eV. These results are shown together with our results in Fig. 5. During the course of the present work Alvani and Neagle[7] have reported a considerable dependence of the low-energy (~4 eV) optical data on the surface smoothness. The best results were obtained for electropolished samples, the corresponding optical conductivity of which is also reproduced in Fig. 5.

Comparing all these results we can conclude the following: Th shows two optical-absorption peaks at 1.2 and 2.3 eV. Further, all data show a breaking point (or minimum) in the optical conductivity around 4 eV, but of varying strength.

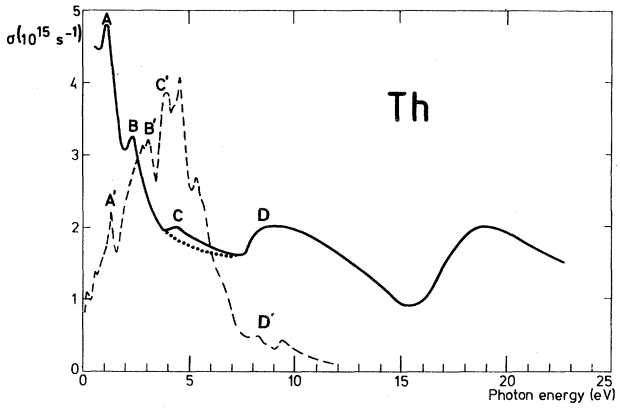


FIG. 4. The optical conductivity of Th obtained from a combination of the data in Figs. 2 and 3. The dotted curve around 4 eV is a possible correction of the data due to surface roughness. The hatched curve is a calculation of the joint density of states (see text).

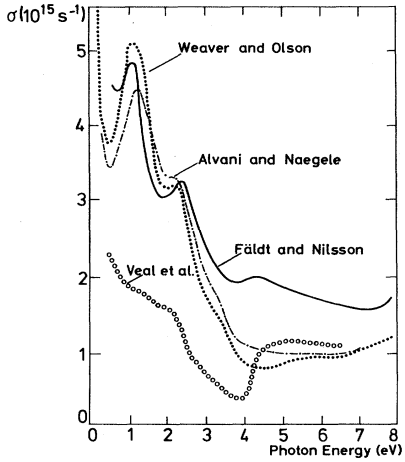


FIG. 5. The optical conductivity of Th below 7 eV as obtained by different authors.

The phenomenon seems to be correlated[7] with surface roughness (excitation of a surface plasmon). The question of a residual, minor absorption peak in this region is difficult to resolve at this stage. At high energies our data show an absorption threshold at 7.5 eV. There seems to be an indication of the onset of this absorption also in the data of Weaver and Olson.[6] Finally at 16 eV a strong and broad peak starts.

## IV. INTERPRETATION AND DISCUSSION

The interpretation of optical-absorption spectra when a band-structure description is justified has been discussed in Ref. 2. In general one finds that the contribution arises from direct (i.e. $k$-conserving) transitions on an optical surface extending over large areas of the Brillouin zone. Using a band structure along symmetry lines only for the interpretation can thus be highly misleading, as also will be discussed below.

The band structure of Th has been calculated by several authors. Gupta and Loucks[8] assumed localized 5$f$ state (like the 4$f$'s in the lanthanides) while Koelling and Freeman[9] argued for an itinerant band description. In an attempt to distinguish between these two models Veal *et al.*[5,10] compared the experimental optical conductivity with two theoretical conductivities, one with the 5$f$'s (itinerant model) and one without the 5$f$'s (localized model). A strong dip in the conductivity at 4 eV was taken as a proof for the validity of the itinerant (band) model. The present new optical-absorption data, together with other spectroscopic results[7,11] and new band calculations (12), makes it worthwhile to reexamine the problem.

We first recall the fact that the 4-eV optical-absorption peak is strongly dependent on the sur-

face smoothness. In Fig. 4 we have indicated a possible removal of this piece of structure, leaving a smooth curve with a possible slope change in the 4-eV region. In the same figure we show the joint density of states (JDOS) which we have calculated from the band structure by Skriver and Jan[12] using a Monte Carlo technique with Lagrange interpolation. The result is quite similar to that in Ref. 5. Because the matrix elements have been omitted we can expect large discrepancies in amplitudes. However, we find two low-energy peaks ($A'$ and $B'$) at 1.4 and 3.2 eV in the JDOS, which quite nicely reproduce the experimental peaks ($A$ and $B$) at 1.1 and 2.3 eV. The calculated, strong peak ($C$) at 4.3 eV is not observed, or possibly is very faintly observed experimentally as discussed above. The experimental threshold at 7.5 eV can be traced in the theoretical spectrum, but is not as strong as observed experimentally. The high-energy peak around 18 eV is not expected in theory for reasons to be discussed below.

We have identified the origin of these peaks. The 1.1-eV peak ($A'$) is almost entirely due to transitions from the second-lowest band into the next-higher band. We denote such transitions $2\rightarrow3$ and use the convention of numbering the bands from low to high energies at each $k$ point. This means that a renumbering occurs for crossing bands. In Fig. 6 we show the optical surface for $2\rightarrow3$, 4 transitions. As seen there is a contribution over a very large area of the Brillouin zone. An analysis shows that all initial energies of the occupied band number 2 contribute. We have denoted some of the transitions occurring on symmetry lines with small letters ($a,b,c$). These transitions can be found in the band structure, Fig. 7. The bands displayed here are from the Skriver and Jan calculation[12] including spin-orbit interaction, while we used results without this interaction for the calculations. The difference is, however, very small.

The 3.2-eV peak ($B'$) is composed of many band-to-band contributions but is dominated by $2\rightarrow5$, 6, 7. An optical surface is shown in Fig. 6 and

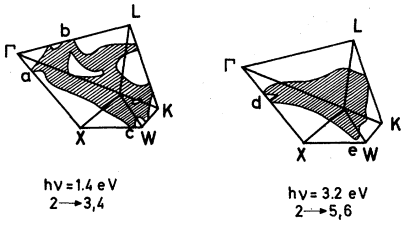


FIG. 6. The optical surfaces associated with the transitions making most of the contributions to calculated peak $A$ ($h\nu=1.4$ eV) and $B$ ($h\nu=3.2$). The small letters refer to specific transitions, marked in Fig. 7.

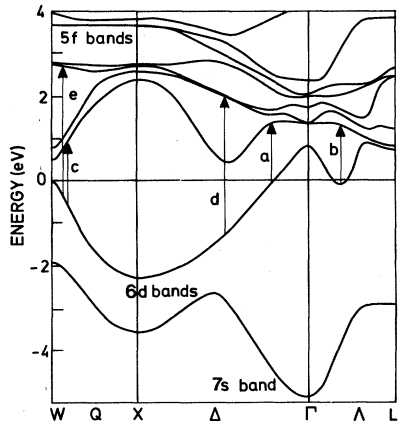


FIG. 7. Reproduction of part of the band structure of Th calculated by Skriver and Jan (Ref. 12).

some of the transitions in Fig. 7. The final state is dominated by the lower component of the $5f$ band, which is illustrated by the $e$ transition along the $WX$ direction in Fig. 7.

The $C'$ peak in the JDOS is associated with transitions to the high-energy $5f$ band. In Fig. 7 we find this, e.g., along the $Q$ line between 3 and 4 eV above the Fermi level. In the experimental spectrum the transitions are not or are only very weakly observed (feature $C$).

To investigate whether the $5f$ states are expected to be observed at all (e.g., Gupta and Loucks[8] did not include the $5f$ states) we have estimated the dipole matrix elements using atomic, nonrelativistic wave functions (Herman-Skillman). The $6d\rightarrow5f$ transitions were compared with the distinctly observed $6p_{3/2}\rightarrow6d$, $7s$ core transition around 18 eV. The result is that these two transition strengths are of the same order of magnitude. Accordingly, excitations into $5f$ states should be easily observable in this approximation. Thus if the $B$ peak is associated with transitions into the lower $5f$ subband, there remains the need to explain why transitions into the upper band are so weak. We cannot, for the moment, without resorting to more extensive calculations, explain this effect. A group theoretical analysis, for example, gives no hint here. We note, however, that the same phenomenon seems to occur in optical reflectance for gold.[13] Here strong $6d\rightarrow5f(\Gamma_6^-)$ transitions are observed around 20 eV photon energy while the higher component ($\Gamma_8^-$), expected around 23 eV, is missing (but observed in thermoreflectance[13]).

The calculated structure for energies above the peak $C'$ originates from many different transitions. One reason why this is not strongly observed is that many of the transitions originate from the

lowest, $s$-type band. As there is a low partial density of states (PDOS) in the final state these transitions are expected to be weak. The absorption threshold at 7.5 eV is interpreted as transitions from band 2 into flat bands at the top of the $6d$-band complex. An analysis shows that most of the contribution comes from transitions into band No. 12.

Finally, the threshold at about 16 eV, as mentioned above, is associated with the $6p_{3/2}$ core level. As this level was not included in the band calculation, and accordingly not in the JDOS calculation, it also does not appear in the theoretical spectrum of Fig. 4. When the absorption threshold for the core-level width is corrected, good agreement is obtained with x-ray-photoemission-spectroscopy data[14] which places the level at 16.8 eV. The shape of the absorption peak should be a replica of the $6d$ PDOS (with possibly some contribution from $7s$). The $d$ band has a width of about 8 eV (Ref. 12) which is roughly compatible with the peak width in Fig. 5.

In conclusion, the optical-absorption spectrum of Th seems to be consistent with direct transitions in the band structure calculated by Skriver and Jan.[12] However, a calculation of the optical conductivity including matrix elements, which is quite feasible, should be performed for a more detailed analysis. This is of special interest because it remains to be seen to what extent many-body effects are involved in the optical-absorption process. We know that the $5f$ band is localized in the ground state for actinides with high $Z$ (but not for low-$Z$ elements like Th) (Ref. 15). For core spectra the $5f$: $s$ localize even in Th due to the attractive potential of the hole. This phenomenon gives rise to strong many-body effects[16] as established earlier for rare earths.[17] A similar effect could, in principle, also occur in the optical spectrum if the subbands of the $6d$ complex are flat enough to produce a strong overlap with the final state in the $6d \rightarrow 5f$ transition. If this effect really is strong, then the 1- and 2-eV peaks in the optical spectrum could be interpreted as shifted $5f$ levels. However, having yet no support for such an effect, we favor the conventional band-picture interpretation.

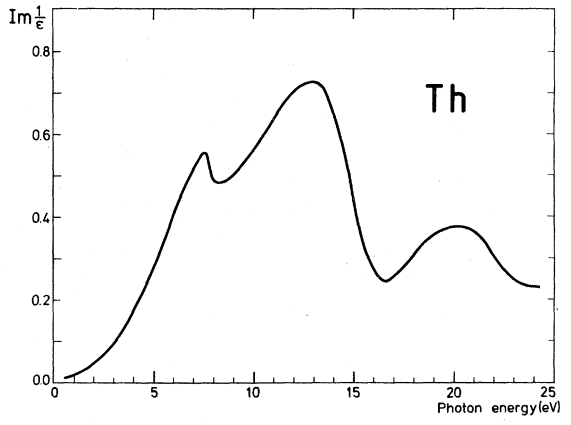


FIG. 8. The energy-loss function Im $(1/\epsilon)$ calculated from the data in Fig. 1.

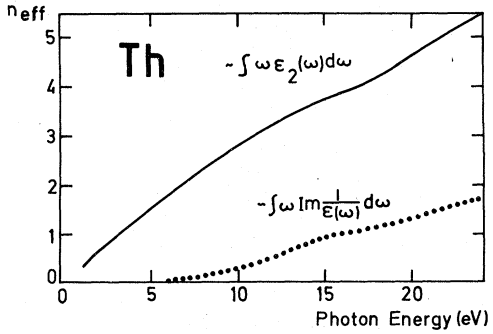


FIG. 9. The "effective number" of electrons contributing to the absorption and electron energy loss as a function of maximum photon energy.

The energy-loss spectrum has been calculated from the dielectric function and is displayed in Fig. 8. The high-energy peak corresponds to excitation of the $6p_{3/2}$ core level as discussed above. At lower energies two peaks are observed at 7.5 and 13.0 eV which are both associated with modified hybridized plasma oscillations. The calculated free-electron value for four effective electrons is 13.0 eV, which accidently coincides with the observed value. Note, however, that the resonance is not completely free-electronlike because $\epsilon_1(\omega)$ does not pass through zero. For the lower peak, $\epsilon_1(\omega)$ is forced through zero because of the absorption peak at 7.5 eV. The situation with two plasmons is therefore analogous to the case of calcium.[2]

In Fig. 9 we have plotted "the effective number" of electrons contributing to the optical absorption. We observe that this function exceeds the value 4, the number of valence electrons, at about 17 eV, approximately where the $6p_{3/2}$ core absorption starts. This does not mean, however, that all the oscillator strength of the valence-band absorption is completely exhausted at this energy. The sum rule is only strictly valid for integration up to infinity, where it gives the total number of electrons per atom. In our limited energy range the contribution from the valence electrons will be enhanced because the exclusion of negative oscillator strengths down to the $6p_{3/2}$ core level. The $n_{\mathrm{eff}}$ curve is, however, strong indication of the correctness of our data.

## V. CONCLUSION

The optical properties of Th have been studied in the energy range 0.5–25 eV. The data agrees fairly well with recent data below 6 eV, while new information is obtained above this energy. The optical conductivity is interpreted in terms of direct transitions in a band structure, which means that itinerant 5*f* states are involved. More detailed calculations would be valuable in investigating transition probabilities and possible contributions of many-body effects.

## ACKNOWLEDGMENTS

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[1]H. G. Liljenvall, A. G. Mathewson, and H. P. Myers, Philos. Mag. 22, 243 (1970).
[2]P. O. Nilsson and G. Forssell, Phys. Rev. B 16, 3352 (1977).
[3]P. O. Nilsson and L. Munkby, Phys. Kondens. Mater. 10, 290 (1969).
[4]P. O. Nilsson, *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1974), Vol. 29, p. 139.
[5]B. W. Veal, D. D. Koelling, and A. J. Freeman, Phys. Rev. Lett. 30, 1061 (1973).
[6]J. H. Weaver and C. G. Olson, Phys. Rev. B 15, 4602 (1977).
[7]C. Alvani and J. Naegle, J. Phys. (Paris) 40, C4-131 (1979).
[8]R. P. Gupta and T. L. Loucks, Phys. Rev. Lett. 22, 458 (1969); Phys. Rev. B 3, 1834 (1971).
[9]D. D. Koelling and A. J. Freeman, Solid State Commun. 9, 1369 (1971).
[10]B. W. Veal, in *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974), Vol. 1, p. 73.
[11]Y. Baer and J. K. Lang (unpublished).
[12]H. L. Skriver and J. P. Jan (unpublished).
[13]J. Hermanson, J. Anderson, and G. Lapeyre, Phys. Rev. B 12, 5410 (1975).
[14]J. C. Fuggle, A. F. Burr, L. M. Watson, D. J. Fabian, and W. Lang, J. Phys. F 4, 335 (1974).
[15]B. Johansson, Phys. Rev. B 11, 2740 (1975).
[16]T. K. Sham and G. Wendin (unpublished).
[17]G. Wendin, in *Photoionization and Other Probes of Many-Electron Interactions*, edited by J. Wuilleumier (Plenum, New York, 1976), p. 61.