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The band structure of gold for energies far above the Fermi level has been calculated using the relativistic augmented-plane-wave method. The calculated f-band edge (Γ_6^-) lies 15.6 eV above the Fermi level is agreement with recent photoemission work. The band model is applied to interpret temperature-modulated reflectance data covering photon energies up to 35 eV.

Although the electronic energy-band structure of gold has been subject of many theoretical and experimental investigations, it is only recently that the energy range far above the Fermi level has been included in detailed examinations. The growing interest in the high-lying bands (f bands) is connected to the new experimental possibilities offered by synchrotron radiation facilities. In order to support the interpretation of optical experiments on gold where high photon energies are applied we present a relativistic augmented plane wave (RAPW) calculation that covers the high-energy regime. It is emphasized that the band calculation is based on the same potential as was used in previous studies[1-3] of the bands in the neighborhood of the Fermi level, and therefore the actual position of the highly excited levels may not fit the experiments without adjustment. Although this reservation must be taken, it appears that the f-band edge is in agreement with experiments,[4] and it will be demonstrated that it is possible from the present band structure to interpret the thermoreflectance data by Olson, Piacentini, and Lynch.[5] These experiments cover photon energies up to 35 eV.

The energy bands have been calculated by means of the RAPW method as described earlier.[1-3] Up to 1.7 Ry above the muffin-tin zero they are therefore almost identical to those used previously. In the extended calculation it has been necessary to use a dense k mesh corresponding to 64 intervals on the Γ-X line. The band structure at the main symmetry lines is shown[6] in Fig. 1. The energies are given in rydbergs and measured from the muffin-tin zero. The Fermi level is $E_F = 0.530$ Ry on this scale.

Modulation spectroscopy experiments are well suited[1] for comparison to band structure calculations since they emphasize critical-point transitions over the large noncritical background appearing in the static reflection traces. We shall here attempt an interpretation of the thermoreflectance data obtained by Olson, Piacentini, and Lynch.[5] It will be assumed that the observed elements of structure can be related to Fermi-level transi-

tions and transitions at critical points. Further, it is assumed that the most important critical points are to be found along the symmetry lines. Thus, only the part of the band structure which is shown in Fig. 1 will be considered.

The experimental values for spectral positions of critical-point thresholds were determined[5] as the energies corresponding to the negative peaks[7] in $\Delta R/R$. The first column of Table I gives the experimental[5] edges for photon energies above 9 eV. The second column contains critical-point energy separations as obtained in the present band-structure calculation without any shifts. In many cases several critical-point transitions contribute to an element of structure, and only a detailed calculation of transition matrix elements can select those of most importance. The assignment presented here involves all the elements of structure in the experimental trace,[5] whereas only nine were discussed by Olson, Piacentini, and Lynch. They related the observed spectral positions of structure elements to the band structure calculation by Connolly and Johnson.[8] It was, however, necessary to introduce[5] shifts in the computed bands of up to 1.3 eV.

If the assignment suggested in Table I is correct, then it follows that the experiment and the band calculation agree within ~ 0.1 eV, as far as band separations are concerned.[9] Further, it can be seen that our assignment differs somewhat from the one given in Ref. 5. The 10.0-eV transition is here assumed to take place at W between band 3 and 6 (10.05 eV in the present calculation). The transition $3 \rightarrow 7$ at K which was considered responsible in Ref. 5 is not a critical-point transition, and thus it is ruled out. The structure at 10.6 eV appears to have contributions from the transition $4 \rightarrow 8$ near K, but instead of $1 \rightarrow 7$ at[5] Q we suggest that the $4 \rightarrow 8$ transition at W contributes. Concerning the structure at 13.2 eV we agree with Ref. 5 that transitions from band 2 to 8 at W can be responsible, but in addition the present band structure contains a critical point at the Σ line ($2 \rightarrow 8$). It cannot be expected that $2 \rightarrow 8$ transitions[5] at K play any important role since there is no such
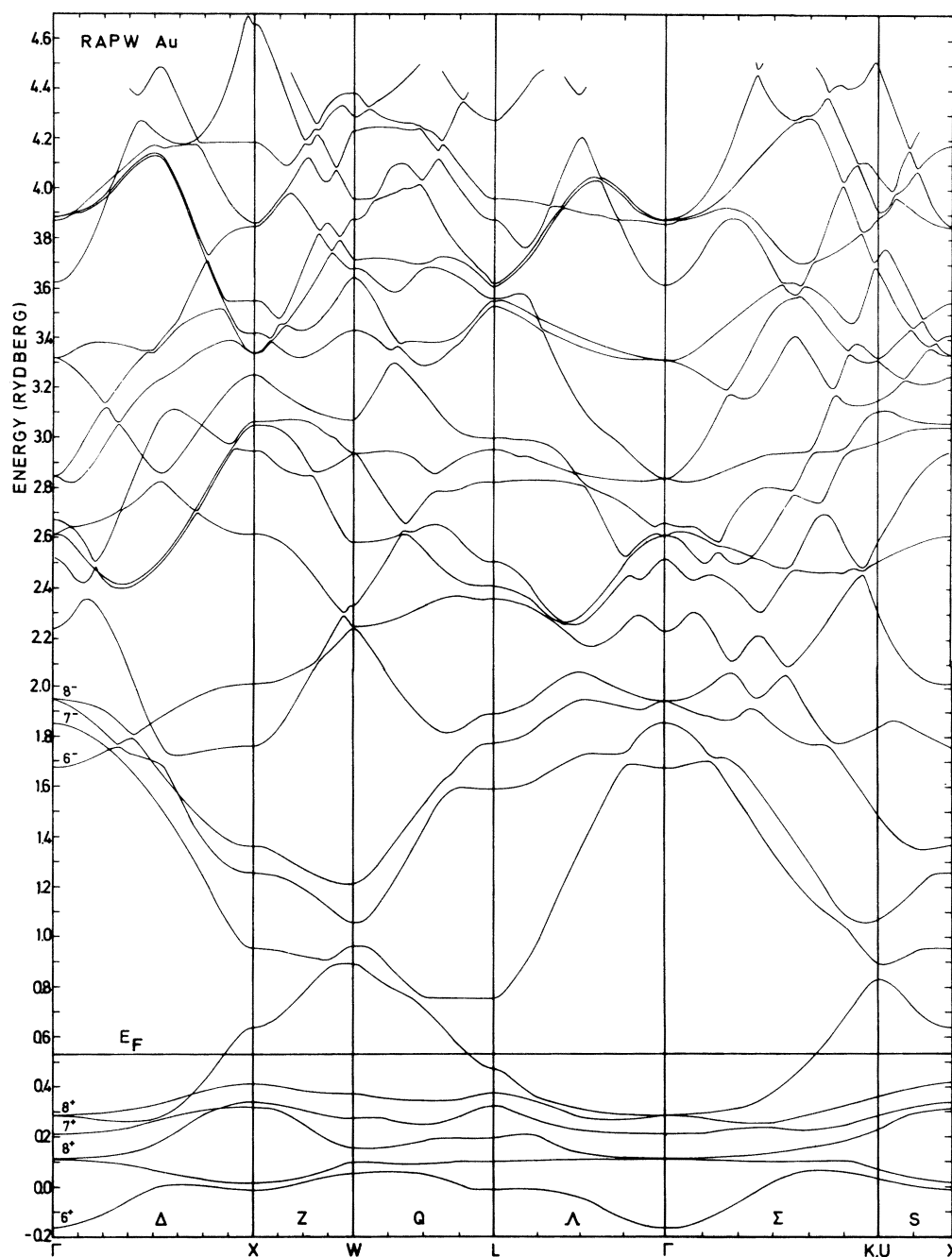
FIG. 1. Electronic energy bands for gold as calculated by the relativistic augmented plane wave method.

critical point (the considered bands are not parallel). The assignment of the element at 14.7 eV represents the poorest agreement between the calculation and experiment. Tentatively it is suggested that transitions from the Fermi-level to band 8, possibly in an extended region of k space, contribute. The energy gap for such transitions (6 → 8) is 14.54 eV at Q. Olson, Piacentini, and Lynch did not assign any particular transitions to the 17.3-eV structure. Here it appears that two transitions both having band 8 as final state are involved, 1 → 8 at X and 4 → 8 at L. Owing to the forbidden character of the X transition it is expected that the L transition dominates. The interpretation of the structure element at 19.9 eV given in Table I differs essentially from the one by Olson *et al.*, who ascribe it to a $\Gamma_8^+ \to \Gamma_7^-$ transition. It should be noted that this, in fact, must be re-

TABLE I. Structure in the thermoreflectance spectrum of gold (Ref. 5) and the assignments to critical-point transitions in the calculated (RAPW) band structure (Fig. 1). The initial- and final-state band numbers are given in the parentheses. The levels are at each point numbered in order of increasing energy.

Experiment (Ref. 5) (eV)	Calculated energy gap (eV)	Assignment
9.0	9.00	$Q(2 \to 7)$
10.0	10.05	$W(3 \to 6)$
10.6	10.71	$W(4 \to 8)$
	10.71	$K(4 \to 8)$
11.7	11.70	$W(2 \to 7)$
13.2	13.10	$W(2 \to 8)$
	13.13	$\Sigma(2 \to 8)$
14.7	[14.41	$W(3 \to 9)]$
	14.54	$E_F(6) \to 8$
17.3	17.31	$X(1 \to 8)$
	17.26	$L(4 \to 8)$
19.9	19.92	$\Gamma(4 \to 7)$
	19.84	$\Sigma(5 \to 10)$
	19.81	$L(4 \to 9)$
21.2	21.33	$\Gamma[(5,6) \to 8]$
	21.23	$\Gamma[(2,3) \to 7]$
21.8	21.65	$X(5 \to 11)$
	21.80	$L(1 \to 8)$
22.7	22.63	$\Gamma[(5,6) \to (9,10)]$
	22.75	$\Sigma(2 \to 9)$
	22.74	$X(4 \to 11)$
	22.79	$L(2 \to 9)$
24.4	24.20	$\Sigma[(2,3) \to 9]$
	24.32	$L(1 \to 9)$
	24.43	$L(2 \to 10)$
27.7	27.55	$X(1 \to 11)$
	27.47	$\Gamma(4 \to 11)$
	27.64	$L(4 \to 11)$
28.6	28.77	$\Gamma[(2,3) \to 11]$
	28.71	$\Sigma(2 \to 11)$
	28.71	$\Sigma(5 \to 12)$
29.1	29.10	$W(2 \to 10)$
	29.18	$W(2 \to 11)$
	29.00	$W(5 \to 13)$
	29.10	$W(5 \to 14)$
31.0	30.90	$X(4 \to 12)$
	(31.35)	$[\Gamma(4 \to 12)]$
32.0	32.18	$L(1 \to 11)$
	31.90	$L(6 \to 14)$
	32.10	$L(6 \to 15)$

vised to $\Gamma_8^+ \to \Gamma_6^-$ since the f-band edge at Γ is band 7, which is a Γ_6^- level. The labeling used by Connolly and Johnson[8] can not be correct at this point since Γ_7^- results from a spin-orbit splitting

of the threefold degenerate level Γ'_{15} (single group notation). It follows from Table I that three critical points have the correct energy gap. The transition at $\Gamma(4 \to 7)$ occurs between the Γ_7^- and Γ_6^- levels, and the initial-state energy (Γ_7^-) is 4.34 eV below the Fermi level. This value and the position of Γ_6^- (15.58 eV above E_F) are both in excellent agreement with photoemission results obtained by Hermanson Anderson, and Lapeyre,[4] who synchronously varied the photon energy and the kinetic energy of the analyzed electrons to obtain "constant initial-state-energy spectra." It follows from the discussion above that also for the assignments given in Ref. 5 to the structure elements at 21.2 and 22.7 eV alternative suggestions must be considered. The 21.2-eV element is here related to $\Gamma_8^+ \to \Gamma_7^-$ (in our labeling) and $\Gamma_8^+ \to \Gamma_6^-$, whereas the 22.7-eV structure may have four contributions, one being $\Gamma_8^+ \to \Gamma_8^-$. Hermanson, Anderson and Lapeyre[4] suggest that Γ_8^- [band (9, 10) at Γ] should be moved downwards[6] by 0.8 eV (from 19.32 to 18.55 eV above E_F). This would not be consistent with the present interpretation of the thermoreflectance results, and further this would also imply that Γ_7^- (band 8 at Γ) should be displaced by the same amount since the separation of the levels Γ_8^-, Γ_7^- is determined by the spin-orbit splitting. As in usual full-angle photoemission measurements on polycrystalline samples it cannot in general be expected that the peaks originate in localized regions in k space.[2] There are several bandpairs with 24.2-eV separation and having the initial-state energy -5.65 eV. The band diagram in Fig. 1 contains at least two such regions, $(2,3) \to 9$ at Λ and $(2,3) \to 9$ at Σ, both in the neighborhood of Γ. In addition, the latter contains, in fact, a critical point. The negative peak in $\Delta R/R$ at 32 eV has been related[5] to the plasmon at 32.6 eV. The present calculation shows that in addition critical point transitions may contribute.

The present work demonstrates that it is possible to extend the band-structure calculation for gold far above the Fermi level and use the results in what seems to be a consistent interpretation of thermoreflectance experiments up to 35 eV. It is realized, however, that other band models may apply as well with other assignments. Therefore, only a careful calculation of transition probabilities and a line-shape analysis of the experimental trace can lend a more firm basis to the assignments. Apart from the comparison to the thermoreflectance experiment, we have presented a band calculation in the high-energy regime that may serve as a guideline for interpretations of future experiments using the synchrotron radiation. The necessity of such a calculation follows from observation[5] that the optical spectra contain very sharp elements

of structure even in this high-energy regime. This demonstrates the existence of well-defined energy bands far above the Fermi level, at least up to 33 eV; the plasmon energy referred to above.

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[1]N. E. Christensen and B. O. Seraphin, Phys. Rev. B 4, 3321 (1971).

[2]N. E. Christensen, Phys. Status Solidi B 52, 241 (1972).

[3]N. E. Christensen, Solid State Commun. 9, 749 (1971).

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

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

[6]The present calculation revealed that a plotting error appeared in the previous graphs (Refs. 1 and 2) at Δ for energies between 1.7 and 2.0 Ry since a Γ_7^- level erroneously was ascribed Γ_8^- symmetry.

[7]R. Rosei and D. W. Lynch, Phys. Rev. B 5, 3883 (1972).

[8]J. W. D. Connolly and K. H. Johnson, Massachusetts Institute of Solid State and Molecular Theory Group Report No. 72, 1970, p. 19 (unpublished).

[9]The comparison between calculated energies of individual levels should be done with some caution, since the RAPW calculation was performed using the He-temperature lattice constant (Ref. 1), whereas most optical experiments are carried out at room temperature. We have performed RAPW calculations over the entire Brillouin zone for three different lattice constants, showing that, the majority of the levels are shifted downwards by 0.15–0.22 eV relative to E_F, if the 300-K lattice constant is used instead of the 4.2-K value. This implies that the comparison in Table I is not affected since the thermoreflectance experiment was carried out at 200 K.