



Photoemission from Au{111} and {110}. Temperature effects

Christensen, Niels Egede

Published in:
Physical Review B

Link to article, DOI:
[10.1103/PhysRevB.20.3205](https://doi.org/10.1103/PhysRevB.20.3205)

Publication date:
1979

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Christensen, N. E. (1979). Photoemission from Au{111} and {110}. Temperature effects. *Physical Review B*, 20(8), 3205-3209. <https://doi.org/10.1103/PhysRevB.20.3205>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Photoemission from Au {111} and {110}. Temperature effects

N. E. Christensen

Physics Laboratory I, The Technical University of Denmark, DK-2800 Lyngby, Denmark

(Received 9 April 1979)

Full zone band structures of gold have been calculated for three lattice constants by means of the relativistic augmented-plane-wave method. The results are used in an analysis of recent high-resolution symmetry-oriented normal photoemission data (Heiman and Neddermeyer). For those elements of structure which can be interpreted as bulk direct contributions we find temperature *shifts* in the spectral positions in agreement with the experiment. Comparison of absolute spectral positions suggests that the *d*-band complex in the calculation should be downshifted by 0.38 eV relative to the Fermi level in order to provide a match to the experiment. Such a shift does not seem compatible with the analysis of optical data. The features in the photoemission data which are classified as being due to "surface emission" differ from the bulk calculation with respect to spectral position as well as temperature coefficient.

I. INTRODUCTION

The noble metals, Cu, Ag, and Au, are among those materials for which the band structure has been studied most thoroughly experimentally by means of optical and spectroscopic methods. The high resolution achieved lately in these experiments has served to identify specific states and determine very accurately their energies. In particular, modulated-reflectance experiments proved very useful for this task.¹⁻³ From the analysis of such experimental results it is now clear that the "*L* gap" ($L_2' \rightarrow L_1$, single-group notation) is systematically attributed a value that is too small when the band structure is calculated by using a local *ad hoc* potential of the "standard type" (see Ref. 4) with full Slater exchange. This is due to an underestimate of the hybridization between the states near the Fermi level and the states at the bottom of the *d* band. For the same reason, the same theoretical models yield Fermi surfaces which are too little anisotropic when compared⁵ to experiments, this anisotropy being measured by the ratio between the Fermi-surface dimensions in the [100] and [110] directions. This observation is common to all three noble metals (for further discussion, see Ref. 6). In spite of these discrepancies, it follows from a comparison with the optical data that the spectral position of the *top of the d band* in gold⁴ (and silver⁵) with respect to the Fermi level is given very accurately by the calculations. The calculated optical interband edge in Au is 2.38 eV, which agrees with the experimental values, 2.35 to 2.45 eV. Thus, we believe, and this is important for the subsequent discussion, that the relativistic augmented-plane-wave (RAPW) calculation for gold^{4,7} predicts a spectral position of the *d* top (in the \bar{k} -space region⁴ where the edge transitions occur) which at least is accurate to within ± 0.1 eV.

II. PHOTOEMISSION

The recent symmetry-oriented normal photoemission experiments by Neddermeyer *et al.*⁸⁻¹¹ are characterized by a very excellent energy resolution, i.e., the instrumental line broadening is very small. This has enabled, not only accurate determination of spectral positions of peaks, but also a study¹¹ of line widths, and their dependence on temperature. It was found¹¹ that peaks in the spectra related to *bulk direct transitions* show a broadening which increases with temperature, whereas such broadening is absent for those features which are interpreted in terms of *surface photoemission*. We shall not discuss here this broadening, but just quote the result, which may serve as an additional criterion for distinguishing between the two types of emission. Rather, we will here consider the spectral positions of the peaks in the {111} and {110} spectra.¹¹ The two main peaks (*A* and *B*) in the {111} spectra were interpreted¹¹ as being due to bulk direct transitions between the band pairs (6,7) and (5,7). Two difficulties are encountered, however, when the experiment is compared to the band-structure calculation.^{4,7} First, for all photoemission data on Au it appeared necessary to shift the theoretical *d*-bands *downwards* in energy by ≈ 0.35 eV to achieve good agreement with the experiment. Such a shift would not be "acceptable", as follows from the introductory remarks. Second, the experimental peaks move towards higher energies when the temperature is increased.¹¹ This may, at the first sight, seem to be in contrast to the calculation which shows that "the majority of the energy levels move downwards with increasing lattice constant". This statement (from a footnote in Ref. 7) is correct for many levels (but not all) at symmetry points. A comparison to the experiment of Ref. 11 requires a more detailed analysis. This can be performed by

means of the RAPW calculations for three¹² different lattice constants $a = 7.6220$ a.u., $a = 7.6813$ a.u. ($T \approx 0$ K), and $a = 7.7820$ a.u. The results for the $\langle 111 \rangle$ and $\langle 110 \rangle$ symmetry lines are shown in Figs. 1–3. The dashed curves are the relevant final-state bands shifted downwards by 16.85 eV, the photon energy applied in the experiment.¹¹ Energetically possible transitions are determined by the points of crossing between the dashed curves and the band curves drawn with a full line. In the case of normal emission from a $\{111\}$ plane we would expect the direct transition contributions to be related to the one-dimensional energy distribution of joint density of states along the symmetry line. The transitions labeled *a*, *b*, and *c* in Figs. 1–3 are particularly important in relation to the work of Ref. 11. The main peaks (*A* and *B*, Ref. 11) were interpreted as being due to the transitions *b* and *c*. The temperature dependence, which may be derived from the calculation, Figs. 1–3, is not in disagreement with exper-

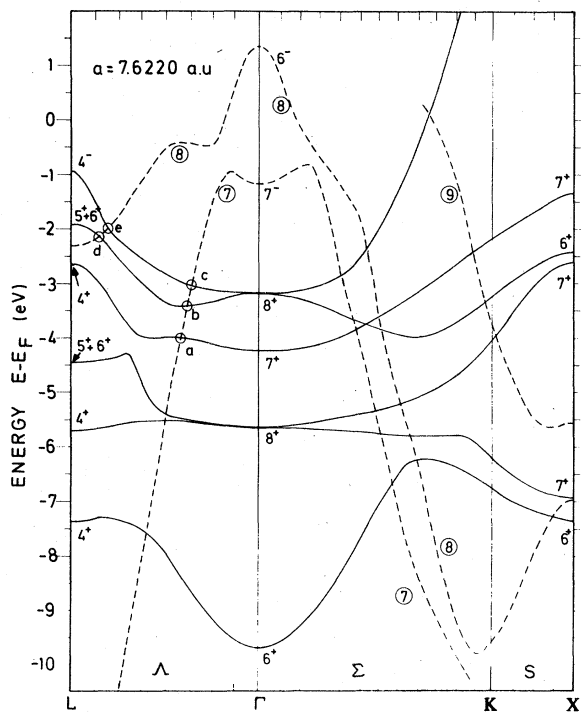


FIG. 1. RAPW band structure of gold along the $\langle 111 \rangle$ and $\langle 110 \rangle$ symmetry lines. The lattice is compressed relative to the normal volume (0 K). The lattice constant $a = 7.6220$ a.u. $= 4.0444$ Å. The curves shown with a full line represent the unmodified band structure, whereas the dashed curves are final-state bands which are down shifted by $\hbar\omega = 16.85$ eV, the photon energy applied in the experiment (Ref. 11). The important direct transitions at the Λ line are labeled *a*, *b*, and *c*. The transitions *e* and *d* do not show up in the experiment, the reasons being given in Ref. 9. (E_F is the Fermi level.)

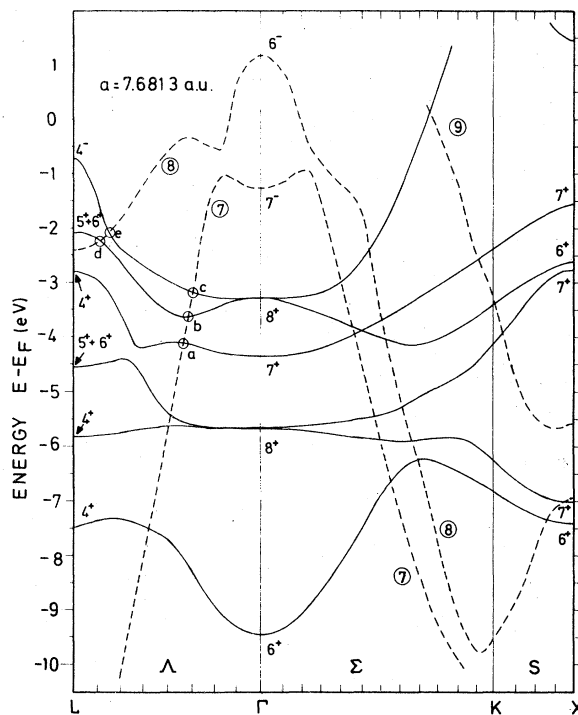


FIG. 2. RAPW band structure of gold (Refs. 2, 3, and 5) for $a = 7.6813$ a.u. $= 4.0646$ Å ($T \approx 0$ K), the "normal volume lattice".

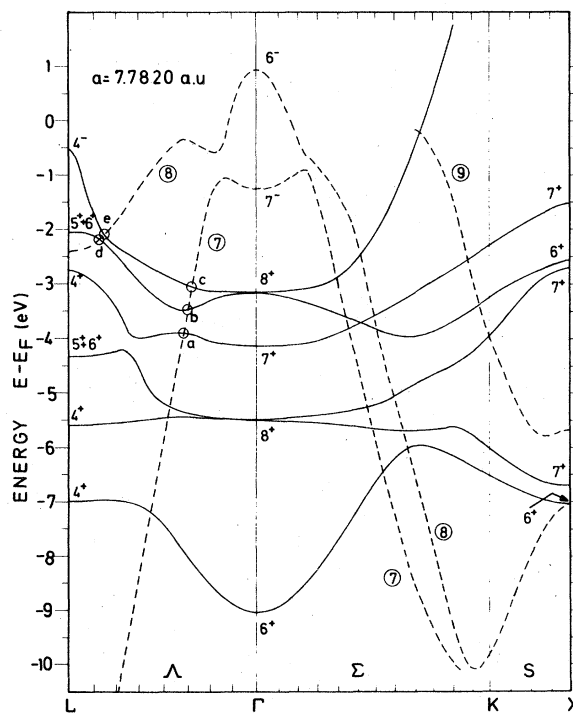


FIG. 3. Dilated-lattice band structure of gold, $a = 7.7820$ a.u. $= 4.1179$ Å.

ment. It is seen that for small values of the lattice constant (i.e., below the zero-temperature value) all three spectral positions, a , b , and c , will move towards *lower* energies when the lattice is expanded. The situation changes, however, when the lattice constant is increased beyond the 0-K value. For $T \geq 0$ K we see that the three spectral positions move towards *higher* energies when the lattice is expanded. In a linear approximation we find for $T \geq 0$ K, the following temperature coefficients: for a : 0.25 meV/K, b : 0.35 meV/K, and c : 0.32 meV/K. The experimental temperature¹¹ coefficients for A and B are 0.28 meV/K and 0.24 meV/K, respectively; i.e., values that agree with those of a , b , and c in *sign* as well as order of magnitude. The variation of a , b , and c with lattice constant is shown in Fig. 4. In the same figure we have also shown the $5 \rightarrow 8$ and $6 \rightarrow 8$ direct transitions (d and e in Figs. 1-3). It follows that there is good agreement between theory and experiment if A and B are related to a , b , and/or c if the temperature shifts are considered. There appears, however, to be a marked

difference between the experimental and theoretical spectral positions. At $T=0$ K the experimental values for A and B are -3.98 and -3.43 eV, respectively. The calculated energies of a , b , and c are ($T=0$ K) -4.10 , -3.60 , and -3.20 eV, respectively. The experimental peak A is assigned to the transition b and B to c . The transition a may also be identified in the experimental trace⁹ (not shown here). This interpretation can only be quantitatively justified in terms of the band model if the theoretically calculated spectral positions of a , b , and c are down shifted by ≈ 0.38 eV. Such a shift should be accounted for entirely by shifting the d bands down since in particular b is located where the initial band is flat. The discrepancy therefore cannot be totally ascribed to errors in the calculated final-state band (band 7). It follows from the discussion in Sec. I that a down shift of the d bands by 0.38 eV cannot be justified by the analysis of optical experiments since the spectral position of the main interband edge (transitions from the d -band top to the Fermi level⁴) is accurately predicted by the theoretical model. It

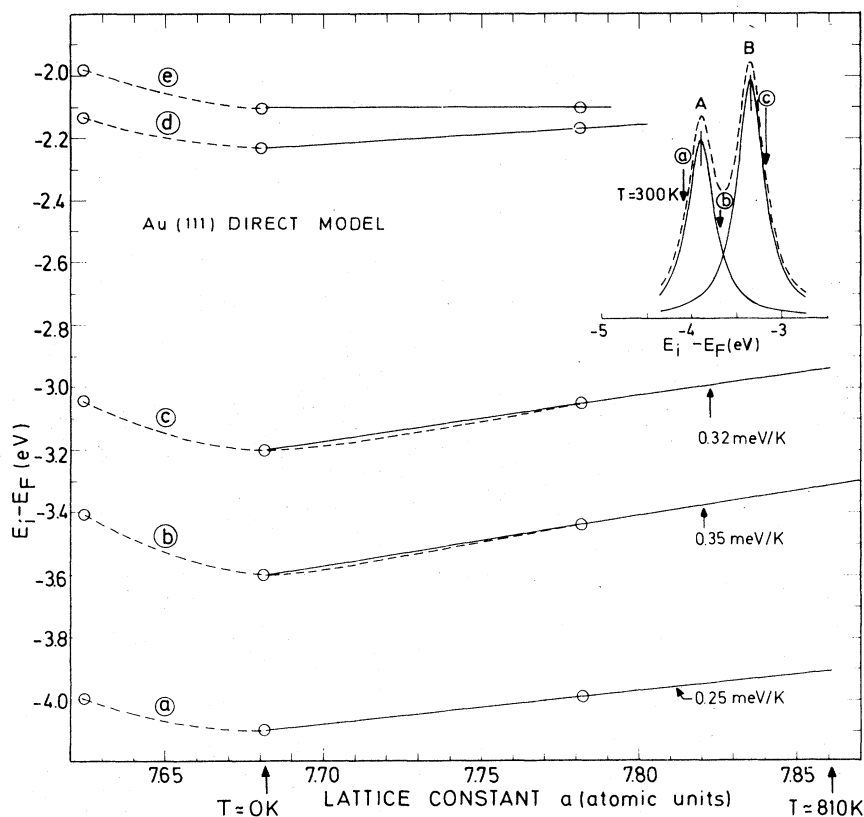


FIG. 4. Spectral positions (dashed curves) (initial state energies) of the direct transitions a , b , c , d , and e at the symmetry line Λ as a function of lattice parameter, a . The temperature coefficients are obtained from a linear approximation (solid lines) using the 0-K-lattice calculation and the expanded-lattice calculation, i.e., they have been derived from only two calculations. The inset shows a part of the experimental spectrum (Ref. 11, $T=300$ K) and its decomposition in two Lorentzians with peaks A and B . The calculated positions of a , b , and c are also indicated on the inset.

may be suggested that the initial states of the optical excitation are in principle different in the case of photoemission ("large" photon energy) from those observed in the optical absorption measurement ("small" photon energy); i.e., the apparent inconsistency is not related to systematical errors in the band model, but reflects rather that there are quite large many-body corrections (localization effects), and that these are different at "large" and "small" photon energies.

The angle-resolved photoemission spectra⁹⁻¹¹ for the {110} faces have been interpreted in terms of *surface photoemission*.¹³ This means that the EDC's (energy distribution curves) for Au {110} reflect essentially structure in the one-dimensional density-of-states function along the Γ - K - X line. For example, the peak C in Ref. 11 is related to the d -band top (X_7^+) at X . The spectral position of this peak is -1.93 eV at $T=0$ K according to the experiment and it has a temperature coefficient of 0.13 meV/K. The results obtained from the *bulk band structures* are -1.54 eV and ≈ 0.06 meV/K. Thus the band model values differ from the experiment with respect to spectral position as well as temperature coefficient in this case. The fact that the observed position of the d -band top in the case of surface photoemission is lower than the bulk value is consistent with the observations for tungsten.^{13,14} It is indeed expected that the d band is narrower at the surface than in the bulk due to the reduced, effective d - d overlap in the surface region.

A very crude estimate (as in Ref. 14) based on the tight-binding model suggests that, in the absence of surface relaxation, one should expect the d band at the surface to be $\approx 18\%$ narrower than the bulk d band. Assuming the d -band center to be essentially unchanged, this implies that this crude model predicts an X_7^+ (d -top) level which is ≈ 0.5 eV below the bulk level. The experiment shows that the X_7^+ level is 0.4 eV below the calculated bulk value, and consequently this may be taken as evidence for band narrowing at the surface. The order of magnitude of this narrowing agrees extremely well with the results of the crude model referred to above.

So far we have in the theoretical model assumed that temperature shifts are predominantly due to thermal lattice expansion effects. However, the potential smear out due to lattice vibrations⁴ may also influence the temperature coefficients. This contribution may be particularly important in the case of "surface emission" since the vibration amplitudes are considerably larger at the surface than in the bulk.

III. DISCUSSION: OTHER EXPERIMENTS

The model for calculation of the band narrowing is indeed crude, and surface relaxation is ignored. In the case of silver, it has been argued¹⁵ that no band

narrowing is observed. However, the narrowing may in this case be *compensated by a negative surface relaxation*¹⁶; experiments¹⁷ indicate that the lattice constant normal to the Ag {110} faces are smaller than in the bulk. It is not known whether such effects appear in gold as well. Further, as mentioned in Ref. 9, a down shift of the valence-band complex which also lowers the L_4^- level from -0.72 to -1.01 eV appears to be consistent with the piezo-optical results by Chen and Segall.¹⁸ This is, on the other hand, not in agreement with the tunneling results by Jacklevic and Lambe,¹⁹ who find $E(L_4^-) \approx -0.7$ eV ($T=77$ K). Also the interpretation of the optical data²⁰⁻²² should be analyzed carefully. As stated in the introduction, the main interband edge, $\hbar\omega_i = 2.38$ eV (transitions from the d -band top to E_F near L) differs from experiments by at most 0.1 eV. This does not necessarily imply, that the X_7^+ level simultaneously is correctly predicted. It was found⁴ that there is a tail in $\epsilon_2(\omega)$ due to interband transitions near X below the main edge. The calculated⁴ value of the onset of these transitions (0-K lattice) is $\hbar\omega_x = 1.88$ eV. The value obtained experimentally is^{20,21} $\hbar\omega_x = 1.94$ eV at $T=295$ K and $\hbar\omega_x = 2.04$ eV at $T=90$ K, i.e., results which suggest that the d -band top near X should be lowered by ≈ 0.2 eV. Our calculated X_7^+ level (0 K lattice) is $\hbar\omega_{X_7^+} = 1.53$ eV below E_F . The energy of this level was obtained in Ref. 20 as a *fitting parameter* in a procedure of adjusting a theoretical expression for $\epsilon_2(\omega)$ to the experiments.^{20,22} We believe that the results of these fits are quite informative. The value of $\hbar\omega_{X_7^+}$ which produced a good fit to the experiment²⁰ was $\hbar\omega_{X_7^+} = 1.77$ eV ($T=295$ K), i.e., 0.24 eV larger than the calculated value. The best fit to the experiment by Théye²² was obtained with a *smaller* value, 1.65 eV. Guerrisi *et al.*²⁰ performed similar line-shape fits for the transitions near L (i.e., near the main edge), but in this case the same gap parameters applied equally well to the experiments of Refs. 20 and 22. The reason for this is probably that the experiments of Refs. 20 (and 21) used a bulk sample whereas Théye²² used thin-film samples. This means that the subtracted Drude term will be quite different in the two cases. This subtraction will influence the shape of the tail strongly, but has only little effect near the "main edge". Simultaneously, it follows that the significance of the fitting parameter $\hbar\omega_{X_7^+}$ depends on how accurately the intraband contributions can be subtracted. For this reason, and also because the fitting procedure^{20,21} applied parameters [masses and $E(X_6^-)$] from the calculation⁴ in regions (band 6) where we *know* that the band model disagrees with experiments, we hesitate to consider the values^{20,21} of $\hbar\omega_{X_7^+}$ as supporting strongly a down shift of the calculated d bands⁴ relative to the Fermi level. We believe, at the present, that a band model

for gold which is improved over that of Ref. 4 should essentially have the same d -band position with respect to the Fermi level, but band 6 should be deformed to reproduce the Fermi surface better, and the L gap increased by 0.6 eV by raising L_{4+} . It is suggested that the necessity⁸⁻¹¹ of down shifting the d bands by 0.35 eV in the band model in order to establish agreement with the photoemission results is not taken as evidence for inaccuracies in the band structure but rather as an indication of initial-state

shifts characteristic to the actual photoexcitation process itself. In general, it appears that the large number of recent high-resolution angle-resolved photoemission experiments, in particular for the noble metals, require a careful theoretical reexamination of which initial and final states actually are seen in photoemission. The agreement with one-electron band models which appeared convincing five years ago are not so obvious when very recent angle-resolved data are analyzed.²³

-
- ¹W. J. Scouler, Phys. Rev. Lett. **18**, 445 (1967).
²M. Garfinkel, J. J. Tieman, and W. E. Engeler, Phys. Rev. **148**, 695 (1965).
³P. Szczepanek, thesis (University of Maryland, 1973) (unpublished).
⁴N. E. Christensen and B. O. Seraphin, Phys. Rev. B **4**, 3321 (1971); Solid State Commun. **8**, 1221 (1970).
⁵N. E. Christensen, Phys. Status Solidi B **54**, 551 (1972).
⁶A. R. Mackintosh and O. K. Andersen, in *Electrons at the Fermi Surface: a Festschrift for David Shoenberg*, edited by M. Springfield (1979).
⁷N. E. Christensen, Phys. Rev. B **13**, 2698 (1976).
⁸H. Neddermeyer, P. Heiman, and H. F. Roloff, J. Phys. E **9**, 756 (1976).
⁹P. Heiman and H. Neddermeyer, J. Phys. F **7**, L37 (1977).
¹⁰P. Heiman, H. Neddermeyer, and H. F. Roloff, J. Phys. C **10**, L17 (1977).
¹¹P. Heiman and H. Neddermeyer, Solid State Commun. **26**, 279 (1978).
¹²Tables of energy eigenvalues throughout the zone may be obtained from the author.
¹³B. Feuerbacher and N. E. Christensen, Phys. Rev. B **10**, 2373 (1974).
¹⁴N. E. Christensen and B. Feuerbacher, Phys. Rev. B **10**, 2349 (1974).
¹⁵P. Heiman, H. Neddermeyer, and H. F. Roloff, Phys. Rev. Lett. **37**, 775 (1976); and in *Proceedings of the International Symposium on Photoemission, Noordwijk, Holland, 1976*, edited by R. F. Willis *et al.* (European Space Agency, Noordwijk, Holland, 1976).
¹⁶N. E. Christensen, in *Proceedings of the International Symposium on Photoemission Noordwijk, Holland, 1976*, edited by R. F. Willis *et al.* (European Space Agency, Noordwijk, Holland, 1976).
¹⁷E. Zanazzi, F. Jona, D. W. Jepsen, and P. M. Marcus, J. Phys. C **10**, 375 (1977).
¹⁸A. B. Chen and B. Segal, Solid State Commun. **18**, 149 (1976).
¹⁹R. C. Jacklevic and J. Lambe, Surf. Sci. **37**, 022 (1973).
²⁰M. Guerrisi, R. Rosei, and P. Winsemius, Phys. Rev. B **12**, 557 (1975).
²¹P. Winsemius, M. Guerrisi, and R. Rosei, Phys. Rev. B **12**, 4570 (1975).
²²M. L. Théye, Phys. Rev. B **2**, 3060 (1970).
²³See for example P. Heiman, H. Miosga, and H. Neddermeyer, Solid State Commun. **29**, 463 (1979).