Angle-resolved photoemission study of the Ag band structure along the ΓΔX line

1989 J. Phys.: Condens. Matter 1 4795

(http://iopscience.iop.org/0953-8984/1/29/006)

J. Phys.: Condens. Matter 1 (1989) 4795–4804. Printed in the UK

Angle-resolved photoemission study of the Ag band structure along the ΓΔX line

S C Wu†, C K C Lok‡, J Sokolov‡§, J Quinn‡, Y S Li‡, D Tian‡ and F Jona‡

† Physics Department, Peking University, Beijing, People's Republic of China
‡ College of Engineering and Applied Science, State University of New York, Stony Brook, NY 11794, USA

Received 31 January 1989, in final form 3 April 1989

Abstract. Angle-resolved photoemission experiments have been carried out on Ag{001} in the photon-energy range from 13 to 105 eV with both s- and s–p-polarised synchrotron radiation. The valence-band structure has been determined along the high-symmetry Δ line. For photon energies smaller than 30 eV the photoemission peaks could be interpreted as results of direct transitions between initial and final energy bands in the relativistic self-consistent band structure calculated by Eckardt, Fritsche and Noffke. For photon energies larger than 30 eV the final band was obtained by extrapolation from the calculated Δ_6 band to the 2ΓX point of a free-electron band with inner potential −5.2 eV. Measured critical points for bands numbered with decreasing energy are: $\Gamma_{8+} = -4.8$ eV, $\Gamma_{7+} = -5.50$ eV and $\Gamma_{8+} = -5.95$ eV, in good agreement, within 0.13 eV, with the theoretical values. A surface resonance is also reported 4.1 eV below the Fermi level at the centre of the surface Brillouin zone $\bar{\Gamma}$ which has the same origin as the surface resonances that have been observed on Cu{001} and Pd{001}.

1. Introduction

We report here the results of an extensive study of the photoemission from an Ag{001} surface which made it possible to determine experimentally the band structure of Ag along the ΓΔX line. An important factor in this kind of studies, which are based on the interpretation of angle-resolved photoemission spectra, is the choice of the final electron states. In previous studies [1, 2], final states consisting of single plane waves have often been employed in order to calculate the angular dependence of photoemission spectra. However, there are indications that the plane-wave final-state model is inadequate for Ag at low final-state energies [3–5]. Roloff and Neddermeyer [4] reported that the energy-distribution curves of photoelectrons emitted with noble-gas resonance lamps in the direction normal to the {001} and {111} surfaces of Ag can indeed be well explained by direct transitions in the band structure calculated by Christensen [6], but those measured on Ag{110} cannot. Courths, Bachelier and Hüfner [5] attempted to map the band structure of Ag from off-normal emission spectra obtained with noble-gas resonance lamps, and found that the final states deviate from those calculated by Christensen [6] and from the free-electron parabolas with the bottom at the muffin-tin

§ Present address: Physics Department, Queens College, New York, USA.

0953-8984/89/294795+10$02.50

zero of Christensen. In the case of normal emission from a {111} surface of Ag Nelson *et al* [7] found that a single band, band 7 in the calculations of Christensen [6] and of Eckardt, Fritsche and Noffke [8], is the only energetically accessible final state for photon energies up to 25 eV.

The present work, carried out with s- and s–p-polarised synchrotron radiation, produces good agreement between experiment and theory for photon energies smaller than 30 eV, but indicates that for larger photon energies, up to 45 eV, a free-electron-like final state gives better agreement than calculated final bands. We give experimental details in §2 and we present the experimental band structure of Ag along ΓΔX in §3. In §4 we discuss experimental evidence for a surface resonance on Ag{001} originating from the Δ_7 band, and in §5 we summarise the conclusions of this work.

2. Experimental procedure

The photoemission experiments were carried out at beam line U7 of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory. A plane-grating monochromator was used to disperse the synchrotron light, and the experiments were carried out in the range of photon energies from 13 eV to 105 eV. The electron energies were analysed with an angle-resolved double-pass cylindrical mirror analyser with an angular resolution of 2°. The sample was mounted on a manipulator that allowed rotations around three mutually perpendicular axes, so that measurements could be done with either pure s- or 25%-p-polarised radiation.

A clean Ag{001} surface was prepared by sequences of argon-ion bombardment and annealing cycles. The cleaning process was continued until Auger electron spectroscopy spectra of the surface showed no C, O or S signals, although the C line was somewhat obscured by an Ag peak near 260 eV. The crystallinity of the surface was checked by low-energy electron diffraction.

3. Experimental determination of band structure: results and discussion

Figure 1 depicts both the theoretical and the experimental results pertinent to the electron band structure of Ag along the ΓΔX line of the Brillouin zone. The full curves were calculated by Eckardt, Fritsche and Noffke (EFN) [8] and the broken curves by Christensen [6]. The full triangles are experimental results obtained with photon energies varied between 13 and 25 eV. The initial states were determined by subtracting the value of the photon energy from the measured final-state energy E_{kin} and by determining the perpendicular momentum $k_\perp$ along the ΓΔX line with the final Δ_6 band as calculated by EFN. The pertinent experimental curves will be presented and discussed below (figure 2).

The open and full circles in figure 1 are results obtained from experiments with photon energies between 26 and 45 eV as presented and discussed below (figures 3 and 4). Electronic transitions with final-state bands in the range between 25 and 30 eV could not be assigned to the final bands calculated by EFN, but could be satisfactorily explained by the assumption of a free-electron-like final state. This final state was extrapolated from the EFN final band at about 24 eV to the 2ΓX point calculated for a free-electron-like band with inner potential $V_0 = -5.2$ eV. (In Christensen's calculation [6] the Fermi level lies 0.444 Ryd above the muffin-tin zero, i.e., $V_0 = -6$ eV. We

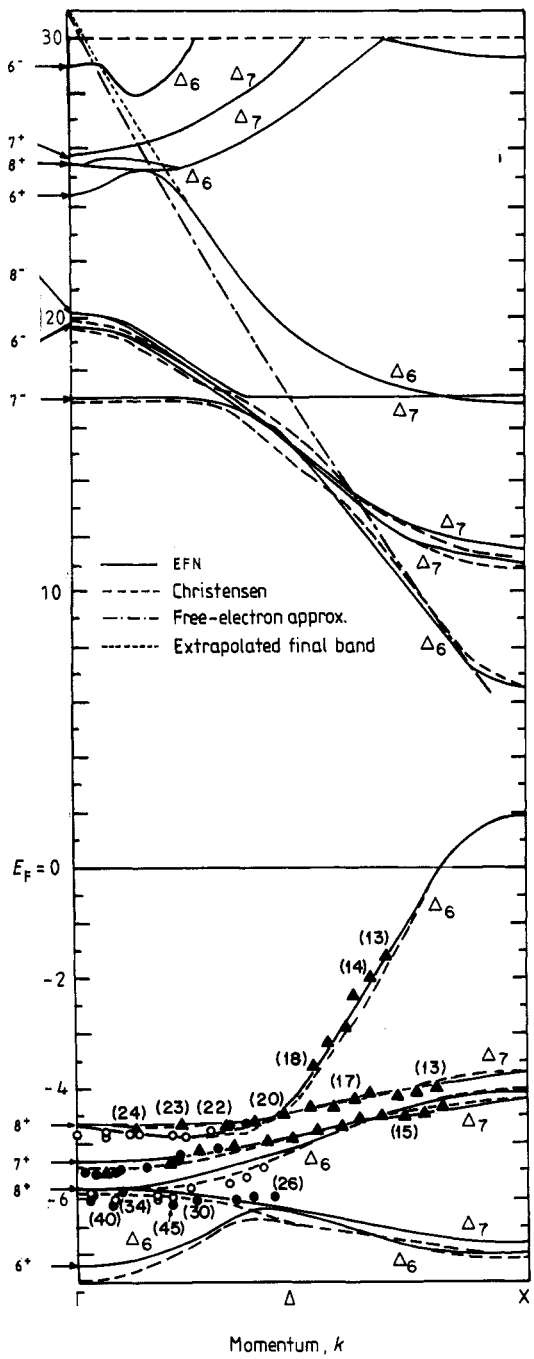

Figure 1. Band structure of Ag along ΓΔX. Full and broken curves were calculated by Eckardt, Fritsche and Noffke (EFN) [8] and by Christensen [6], respectively. Full triangles correspond to features A and B in figure 2 ($h\nu \leq 25$ eV) and were evaluated with the curves calculated by EFN. Open and full circles correspond to features in the difference curves of the two sets of EDCs depicted in figure 3 ($25 \leq h\nu \leq 45$ eV), an example being given in figure 4. The numbers in parentheses give the photon energy in eV.

choose $V_0 = -5.2$ eV to achieve best fit with the theoretical bands and to match the dependence on photon energy of the surface-sensitive peak discussed in connection with figure 5.) The free-electron band is depicted in figure 1 with a chain curve, and the extrapolated band is shown with a dotted curve. The experimental initial-band positions presented in figure 1 are generally in satisfactory agreement to within 0.3 eV with EFN's calculations, demonstrating that the free-electron-like extrapolation used here works well up to photon energies of 45 eV. The experimental values of critical points for bands numbered with decreasing energy are: $\Gamma_{8+} = -4.8$ eV, $\Gamma_{7+} = -5.50$ eV and $\Gamma_{8+} = -5.95$ eV, to be compared with EFN's calculations: $\Gamma_{8+} = -4.69$ eV, $\Gamma_{7+} = -5.37$ eV and $\Gamma_{8+} = -5.82$ eV.

In the following, we discuss the experimental data which have led us to the band structure shown in figure 1. Figure 2 depicts angle-resolved electron-distribution curves (EDCs) from Ag{001} as measured for normal emission with photon energies $h\nu$ between 13 and 24 eV, the full curves with pure s- and the broken curves with 25%-p-polarised radiation. We note the following features.

(i) The main peak, denoted by A in figure 2, disperses from −4.35 eV at $h\nu = 13$ eV to −5.40 eV at $h\nu = 24$ eV. This peak is due to electronic transitions from the second Δ_7 band below the Fermi level E_F (initial bands are numbered sequentially with increasing binding energy).

(ii) On the low binding-energy side of peak A there is a weak shoulder in each curve, marked B in figure 2, which becomes clearly resolved at about $h\nu = 24$ eV and disperses from −4.0 eV at $h\nu = 13$ eV to −4.8 eV at $h\nu = 24$ eV. This peak arises from transitions starting from the first Δ_7 band below E_F. Its intensity is large around 24 eV because at this photon energy both the initial and the final states are near the centre of the Brillouin zone (see figure 1), where the the dispersions are smallest and the densities of states are largest.

(iii) A step-like feature, marked C, is visible in figure 2 at small values of $h\nu$. This feature corresponds to constant final energy ($\simeq 6.9$ eV) for all values of $h\nu$ and marks the bottom of the free-electron-like Δ_6 final band [9].

(iv) A small peak, marked D, is observed to disperse from −1.6 eV at $h\nu = 13$ eV to −3.5 eV at $h\nu = 18$ eV and is due to transitions from the s–p band with Δ_6 symmetry (see figure 1). This transitions are sensitive to p-polarised light, hence the corresponding peaks are visible in figure 2 in the EDCs measured with 25%-p-polarised light and do not appear in the EDCs measured with pure s-polarised radiation.

(v) Apart from peak D, in figure 2 the EDCs measured with 25%-p-polarised light do not differ much from those measured with pure s-polarised radiation. This result suggests that in the photon energy range between 13 and 24 eV the contribution of transitions from the Δ_6 band is smaller than that of transitions from the Δ_7 band.

At higher photon energies the relative contributions from different bands change. Figure 3 shows normal-emission EDCs measured with $h\nu$ values between 25 and 45 eV—the full curves are for pure s- and the broken curves are for 25%-p-polarised light. The full curves exhibit more features than those in figure 2. It appears that in this energy range the contribution of transitions from the Δ_6 band is larger than at smaller $h\nu$ values: the relativistic selection rules do not forbid transitions from the Δ_6 band at normal emission with p-polarised light [10], but dictate that transitions from the Δ_7 band can only be excited by the s component of the incident radiation.

An efficient way to distinguish the contributions of either band from one another and to identify the symmetries of the wave functions involved is to examine difference

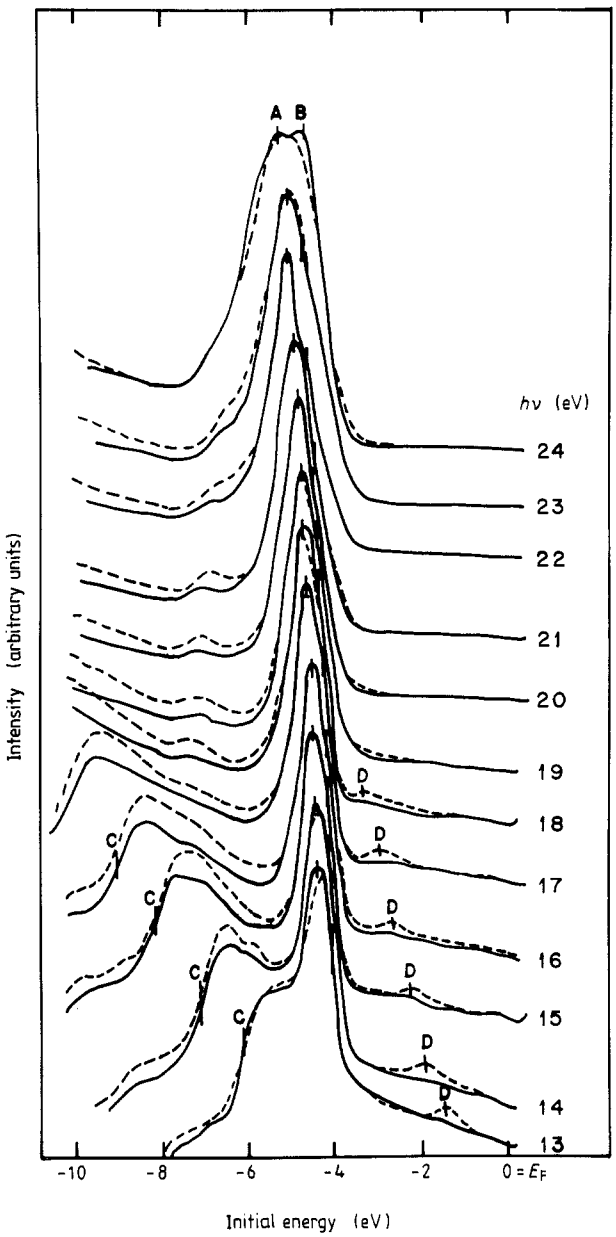

Figure 2. Angle-resolved electron distribution curves for normal emission from Ag{001} measured with photon energies between 13 and 24 eV with s- (full) and s–p- (broken) polarised light.

curves. An example is given in figure 4 for $h\nu = 28$ eV. The full curve (marked A) is the EDC obtained with pure s-polarised light, the broken curve (marked B) is the EDC measured with 25%-p-polarised light, while the chain curve (marked C) represents the difference B—A. The two peaks in the difference curve located at 4.75 and 5.70 eV

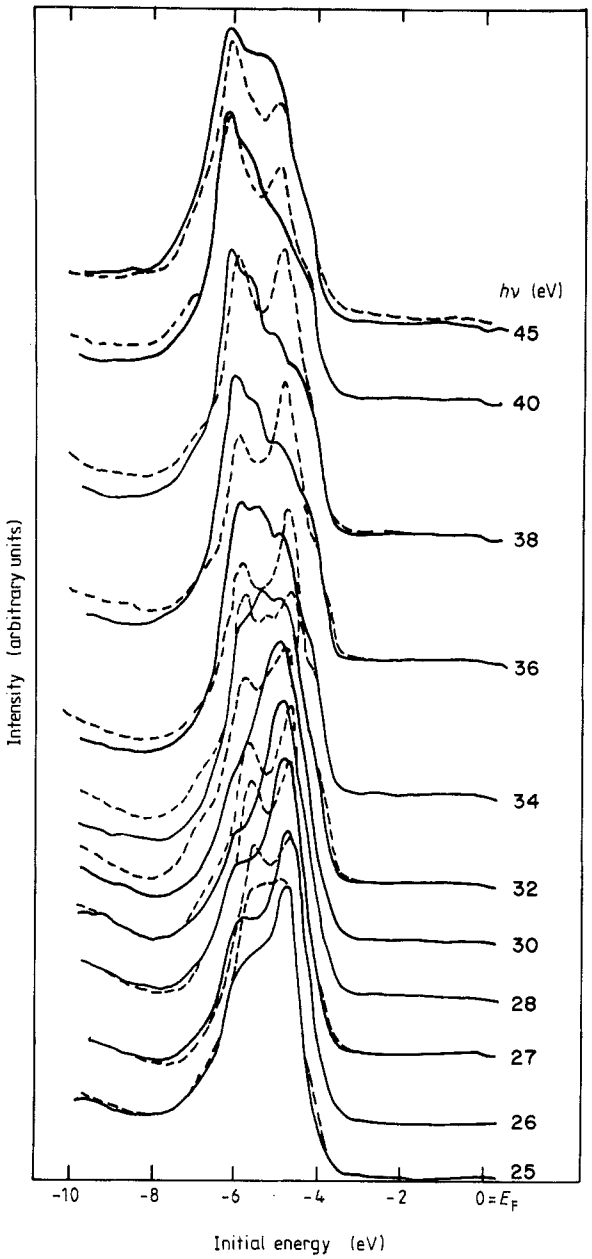

Figure 3. Angle-resolved electron distribution curves for normal emission from Ag{001} measured with photon energies between 25 and 45 eV with s- (full) and s–p- (broken) polarised light.

below E_F mark the positions of the Δ_6 initial state, because the contribution from this state increases with increasing p component of the light. The two valleys located at 5.10 and 6.10 eV below E_F in the difference curve mark the position of the Δ_7 initial

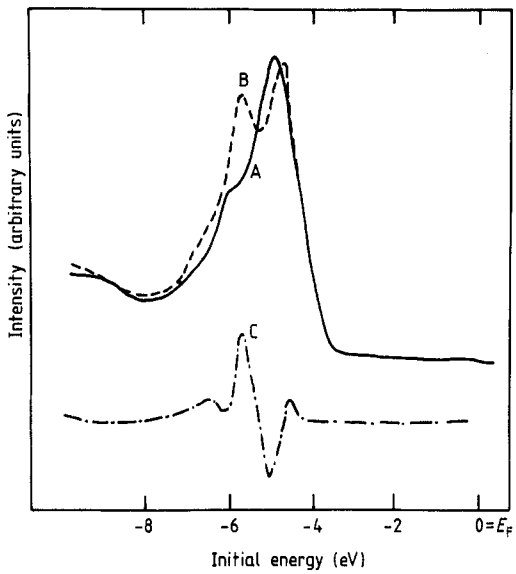

Figure 4. Angle-resolved electron distribution curves for normal emission from Ag{001} measured with photon energy 28 eV and s-polarised light (curve A, full) or s–p-polarised light (curve B, broken). Curve C is the difference B–A.

state, because they are sensitive to the s component of the incident light.

4. Surface resonance

Figure 5 depicts normal-emission EDCs from Ag{001} as measured with s-polarised light and photon energies between 75 and 105 eV. Each EDC exhibits a strong peak at about 4.1 eV below E_F which has many attributes characteristic of surface states or surface resonances.

(i) The energy at which the peak appears is independent of the photon energy. Since the EDCs were taken at normal emission this fact indicates that the peak position is independent of $k_\perp$.

(ii) The intensity of this peak relative to that of nearby (bulk) peaks is a function of the photon energy and reaches a maximum for $h\nu$ values between 80 and 85 V. This general behaviour is characteristic of surface states, as was originally demonstrated by Louie *et al* [12] and later discussed by others [12, 13]. The theory states that the peak intensity of a surface state that is derived from a single band is periodic in $k_{f\perp}$ (the perpendicular component of the final-state momentum) and, in particular, has a maximum at photon energies corresponding to the $k_{f\perp}$-value at which the energy of the bulk band is closest to the surface-state energy. In the free-electron approximation the final-state momentum at normal emission is given by the formula $k_{f\perp} = 0.512(h\nu - E_b + |V_0|)^{1/2}$, where E_b and V_0 are the binding energy of the surface state and the inner potential, both in eV, respectively. Assuming the validity of the free-electron approximation and choosing $V_0 = -5.2$ V, we find, with $E_b = 4.1$ V and $h\nu$ between 80 and 85 V, that $k_{f\perp}$ is about 3ΓX, where ΓX is the distance between the Γ and the X point of the bulk Brillouin zone (for $h\nu = 83$ eV, $k_{f\perp} = 3.05$ΓX with

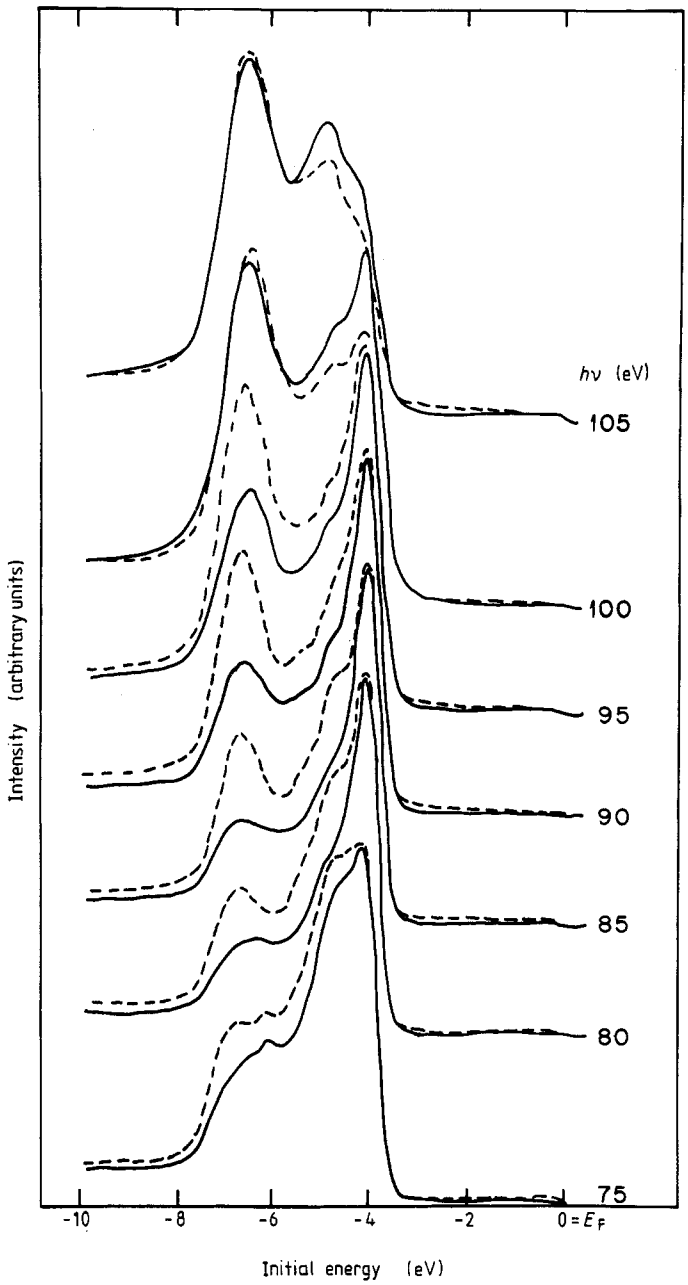

Figure 5. Angle-resolved electron distribution curves measured for normal emission with pure s-polarised light from Ag{001} (full) and from Ag{001} + 600 L of oxygen (broken).

$\Gamma X = 1.54$ Å^{-1}). Thus, it appears that the peak at 4.1 eV originates from a state that has the properties of surface states as predicted by the theory of Louie *et al* [11].

(iii) Exposure of the clean Ag{001} surface to 600 L of oxygen gas markedly decreases the intensity of the peak at 4.1 eV relative to the intensity of the nearby

bulk peaks (see the broken curves in figure 5). This sensitivity of the peak intensity to the presence of impurities on the surface is another indication of the surface-state character of the initial 4.1 eV state. However, since there is no energy gap in this energy range, the state is more properly called a surface resonance rather than a surface state.

Information about the symmetry and the origin of this surface resonance can be obtained from the dependence of the corresponding peak intensity upon the polarisation of the light. Our experiments indicate that the intensity of the 4.1 eV peak is largest with s-polarised radiation and decreases when the p component of the light increases (not shown here). Thus, the corresponding wave function has Δ_7-like symmetry and the state is just a little above the critical point X_{7+} (−4.25 eV in EFN's calculation), originating from the second Δ_7 band (Δ_5 band in the non-relativistic limit). This assignment is consistent with the expectation that, in noble metals, the surface valence band is shifted toward lower binding energies with respect to the bulk [14]. Furthermore, both energy position and wavefunction symmetry are in good agreement with the calculations of Smith *et al* [15] (see figure 9 of [15]). We suggest that this surface resonance on Ag{001} has the same origin as the surface resonance states observed on Cu{001} [16] and Pd{001} [17].

5. Conclusion

Angle-resolved photoemission experiments on clean Ag{001} with s- and s–p-polarised synchrotron radiation have made possible an experimental determination of the band structure of Ag along the $\Gamma\Delta X$ line. For photon energies smaller than 30 eV the photoemission spectra could be succesfully interpreted in terms of direct transitions between initial and final bands in the band structure calculated relativistically and self-consistently by Eckardt, Fritsche and Noffke (EFN) [8]. For photon energies larger than 30 eV the final state was obtained by extrapolation from EFN's Δ_6 final band to the position of the free-electron band in the centre of the Brillouin zone. This procedure appears to be successful up to photon energies of 45 eV. The physical significance of this procedure has been discussed by Ilver and Nilsson [18] and by Dietz and Himpsel [19], and is based on the recognition that within conduction band gaps evanescent states play an important role. The width of an energy gap is usually determined by means of calculations that do not take into account the damping of the electrons. However, inclusion of electron damping causes narrowing and eventually closing of the energy gap, and consequently the band dispersion approaches that of a free electron. In Ag, the photoelectrons produced by photons with energies between 30 and 45 eV have very short mean free paths (i.e., large damping), so that the photoemission peaks are dominated by transitions into evanescent states.

A surface resonance was detected at 4.1 eV below the Fermi level which is believed to have the same origin as the surface resonances that have been observed on Cu{001} and on Pd{001}.

Acknowledgments

We gratefully acknowledge partial support of this work by the Department of Energy with Grant No DE-FG0286ER45239. One of us (SCW) is also indebted to the Science

and Technology Commission of the People's Republic of China for partial support through Grant No 9187002.

References

[1] Gadzuk J W 1974 *Phys. Rev.* B **10** 5030
[2] Stöhr J, Apai G, Wehner P S, McFeely F R, Williams R S and Shirley D A 1976 *Phys. Rev.* B **14** 4431
[3] Shevchik N J and Liebowitz D 1977 *Phys. Rev.* B **16** 2395
[4] Roloff H F and Neddermeyer H *Solid State Commun.* **21** 561
[5] Courths R, Bachelier V and Hüfner S 1981 *Solid State Commun.* **38** 887
[6] Christensen N E 1972 *Phys. Status Solidi* b **54** 551
[7] Nelson J G, Kim S, Gignac W J, Williams R S, Tobin J G, Robey S W and Shirley D A 1985 *Phys. Rev.* B **32** 3465
[8] Eckardt H, Fritsche L and Noffke J 1984 *J. Phys. F: Metal Phys.* **14** 97
[9] Himpsel F J and Eastman D E 1978 *Phys. Rev.* B **18** 5236
[10] Borstel G, Neumann M and Wöhlecke M 1981 *Phys. Rev.* B **23** 3121
[11] Louie S G, Thiry P, Pinchaux R, Petroff Y, Chandesris D and Lecante J 1980 *Phys. Rev. Lett.* **44** 549
[12] Kevan S D, Stoffel N G and Smith N V 1985 *Phys. Rev.* B **31** 3384
[13] Kevan S D and Gaylord R H 1987 *Phys. Rev.* B **36** 5809
[14] Citrin P H and Wertheim G K 1983 *Phys. Rev.* B **27** 3176
[15] Smith J R, Arlinghaus F J and Gay J G 1980 *Phys. Rev.* B **22** 4757
[16] Wu S C, Lok C K C, Sokolov J, Quinn J, Li Y S, Tian D and Jona F 1989 *Phys. Rev.* B at press
[17] Wu S C, Lok C K C, Sokolov J, Quinn J, Li Y S, Tian D and Jona F unpublished
[18] Ilver L and Nilsson P O 1976 *Solid State Commun.* **18** 677
[19] Dietz E and Himpsel F J 1979 *Solid State Commun.* **30** 235