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Photoemission study of the final band in Ag(111)

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Abstract. For direct transitions in angle-resolved photoemission from a single crystal, the final electronic states inside the crystal can be approximately described by a free-electron-like band for energies higher than ≈ 30 eV above the Fermi level. We report a determination of the dispersion relation for this band in Ag along the [111] direction over a wide photon energy range (40–180 eV), from which the inner potential (average electrostatic potential in the solid within the Hartree approximation) and the energy-dependent electron effective mass are deduced. The effective mass is found to increase from approximately $1.00 m$ at 54 eV to $1.08 m$ at 149 eV above the Fermi level (m is the free electron mass). This result is compared with existing many-body model calculations. The present study is also relevant to the problem of surface state resonance in this system discussed previously.

1. Introduction

Angle-resolved photoemission has been successfully applied to the mapping of band dispersion relations of many materials [1]. Perhaps the most straightforward approach is to employ high photon energies (>30 eV) and a normal emission geometry. Under these conditions, the final states involved in the photoexcitation process can be approximately described by a free-electron-like band [1–3]; within the extended-zone scheme, the dispersion relation is given by

$$E_i(k) = \hbar^2 k^2 / 2m^* - U \quad (1)$$

where k is the wave vector pointing along the surface-normal direction, m^* is the electron effective mass, and U is the inner potential referred to the Fermi level. Using equation (1) and the conditions of conservation of energy and momentum, the wave vector along the surface normal for the initial state can be determined to yield the initial-band dispersion. This approach has been described in detail elsewhere [1–3]. We will adopt here the interpretation that the inner potential U in equation (1) is the average electrostatic potential within the crystal, which is typically 5–10 eV relative to the Fermi level based on the simple jellium model or other calculations. All many-body effects beyond the average electrostatic interaction (Hartree approximation) are modelled by an energy-dependent effective mass m^* which, however, is not expected to deviate much from the free electron mass [4, 5]. Most previous photoemission measurements covered a relatively limited range of energies, and these two parameters were justifiably treated as energy-independent fitting parameters to provide the best description of the data. The main objective of the present study is to investigate the final-band dispersion relation

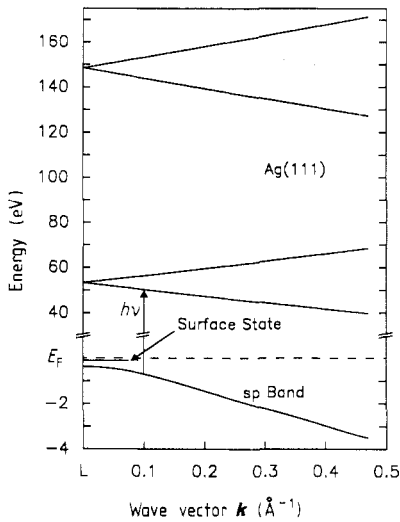


Figure 1. Schematic energy band diagram for Ag. The horizontal axis is the wave vector k along the [111] direction; the origin is chosen at the L point in the Brillouin zone. The vertical energy axis uses two different linear scales above and below the Fermi level E_F to show details. The surface state is indicated with a short horizontal line. A typical direct transition is shown by the vertical arrow.

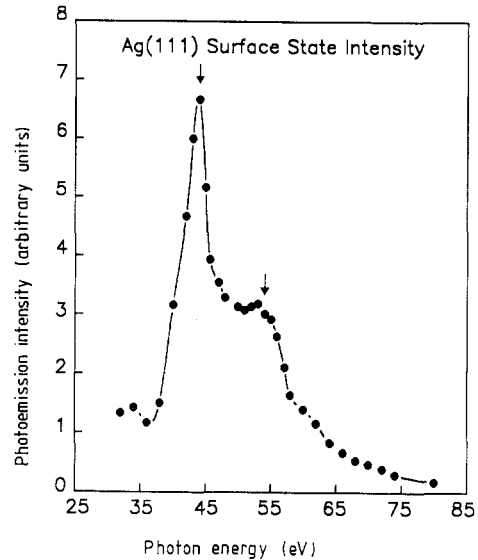


Figure 2. The Ag(111) surface state intensity as a function of photon energy. The circles are the data points, and the curve is just a guide to the eye. The two arrows at 44 and 54 eV indicate the locations of resonances.

over a wide energy range. We examine the energy dependence of the effective mass, which is of fundamental interest in solid state physics [4, 5]. The present result will also provide some general understanding of the accuracy and limitations involved in band mapping with the above-described technique.

Specifically, this study concerns the final band for transitions originating from the sp valence band and the surface state near the sp band edge in Ag(111). The relevant portion of the band diagram in the reduced-zone scheme is shown in figure 1. The top of the sp valence band is located at the L point in the Brillouin zone, and its energy is -0.33 eV relative to the Fermi level [6, 7]. The d valence bands, not shown in the figure, are below -4 eV. The surface state just below the Fermi level has a single-particle wave function fairly similar to that of the bulk sp valence state at the band edge; the main difference is that the wave vector of the surface state has a small imaginary part which causes the surface state wave function to decay away from the surface [8, 9]. If the surface state wave function is spectrally resolved in terms of the real wave vector, the imaginary part of the wave vector is equivalent to a broadening. Thus, the spectral distribution will be finite and centred about the L point. The final-band dispersion for this system has been uncertain [8, 9]. The portion of the final-band dispersion near 54 eV shown in figure 1 is taken from [9]. The point at which the final band crosses the L point corresponds to $k = 3 k_{\Gamma L}$ in the extended zone, where $k_{\Gamma L}$ is the distance between the Γ and L points in the first Brillouin zone. Due to lifetime broadening and crystal-field effects, the final band actually has an effective energy width. Also illustrated in figure 1 is a typical direct transition indicated by the vertical arrow; this particular transition occurs at photon energy $h\nu = 50$ eV. Clearly, increasing the photon energy from this

point will cause the transition to move toward the left in the figure, and at 54 eV the transition will be at the L point. For even higher energies, the vertical transition will move away from the L point to the right in the figure. Since the surface state has a spectral distribution centred about the L point, the direct transition from the surface state to the final band will be centred about $h\nu = 54$ eV, the same energy at which the sp valence band is being probed at the L point. Thus, the photoemission intensity of the surface state is expected to show a maximum at $h\nu = 54$ eV [8, 9]. A related system, Cu(111), has been investigated previously; a similar resonance at 70 eV was predicted and observed [3, 10].

Figure 2 shows the measured surface state intensity of Ag(111) as a function of photon energy. The present set of data reproduce the line shapes described in two previous reports [8, 9], apart from some minor differences. The differences are mainly due to different methods of background estimation; in the present analysis, we followed that employed in [3]. The main point here is that all measurements so far indicated the presence of two peaks, a large peak at 44 eV and a small peak at 54 eV, while the model described above suggests only one peak in this energy range corresponding to the L point transition. In one previous report [9], the small peak at 54 eV was assigned to be the L point transition, and the large peak at 44 eV was ascribed to an atomic-type resonance. The final-band dispersion around 54 eV shown in figure 1 is based upon this assignment. In the other previous report [8], the large peak was assigned to be the L point transition, and the small peak was thought to be due to an Umklapp process. The above two descriptions yield final-band dispersion relations differing by 10 eV at the L point. This has resulted in a correspondingly large uncertainty in the inner potential or the electron effective mass. An independent measurement of the final-band dispersion relation will be useful for clarifying this question.

In this experiment, we determine the final-band dispersion relation by investigating the direct transitions originating from the sp valence band as described above. These transitions escaped our attention or detection in an earlier related study because of the very low peak intensities and large widths [9]. The present results show that the L point transition corresponding to $k = 3 k_{\text{FL}}$ occurs at 54 eV. In addition, the measurement has been carried out to higher energies to probe the next point at which the final band crosses the L point, $k = 5k_{\text{FL}}$ in the extended zone. This occurs at 149 eV as indicated in figure 1. With the energies of the two L point transitions determined, the energy dependence of the effective mass of the photoexcited electron can then be deduced.

2. Experimental details

The photoemission measurements were performed at the Synchrotron Radiation Centre of the University of Wisconsin–Madison at Stoughton, Wisconsin. A 6 m toroidal-grating monochromator and the ‘Extended-Range-Grasshopper’ monochromator of the University of Illinois beam line were used during separate runs. The photoelectrons emitted along the sample surface normal were collected and detected by a hemispherical analyser having a full acceptance angle of 3° . The measured Fermi edge of a polycrystalline gold foil in electrical contact with the sample was used as the energy reference. The width of the edge also provided a measure of the overall energy resolution. The energy resolution was about 0.1 eV at photon energy $h\nu = 35$ eV, and increased to about 0.4 eV at $h\nu = 150$ eV.

The Ag(111) sample was aligned with Laue diffraction to within 0.5° , cut by electrodischarge machining, and then mechanically polished on a cloth pad loaded with

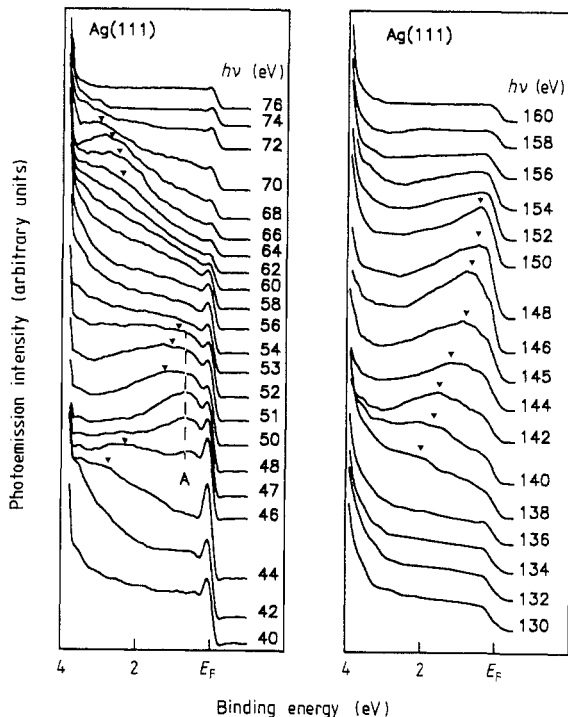


Figure 3. Normal emission spectra of Ag(111) taken with various photon energies. The triangles indicate peak positions for direct transitions from the sp valence band. A peak near the Fermi level in the left-hand panel is indicated by the vertical broken line and labelled A.

alumina slurry. Immediately prior to insertion into the vacuum chamber the sample was chemically polished in a dilute KCN solution. The sample was then prepared by repeated cycles of Ar ion sputtering and annealing. The surface quality was checked by electron diffraction and Auger spectroscopy.

3. Results and discussion

3.1. Transitions from the sp valence band near $k = 3k_{TL}$

Figure 3 shows some of the normal-emission spectra. The sharp peak just below the Fermi level seen in some of the spectra is the L gap surface state [8, 9]. The portions of the spectra for binding energies larger than 4 eV are dominated by d-band emission, and therefore not shown here. For increasing photon energies in the range of 40–80 eV where transitions from the sp valence band are expected to appear in the spectra, a broad dispersive peak, indicated by the triangles, can be seen to move toward, and then turn away from the Fermi level. This corresponds to the expected behaviour of the transitions from the sp valence band. There is another peak in the spectra, labelled A, whose origin is not clear (see below). It appears to be dispersionless, and its intensity varies as a function of photon energy. The energy position of the dispersive peak cannot be determined for many of the spectra because of the rather large width and low intensity and its (partial) overlap with peak A. For the three spectra taken with $h\nu = 50, 51,$ and 52 eV shown in figure 3, the triangles indicating peak positions should be taken as the 'best guess'. These tentative assignments could be eliminated from the analysis to be presented below, without affecting the conclusions. The situation here is fairly similar to that for Cu(111) in which direct transitions from the sp valence band cannot be observed clearly at binding energies close to the sp band edge at the L point [3].

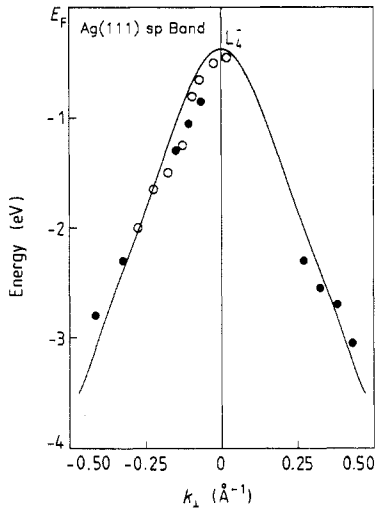


Figure 4. The dispersion relation of the sp valence band of Ag. The horizontal axis is the wave vector along the sample surface normal, the [111] direction; the origin is chosen at the L point in the Brillouin zone. The vertical energy axis is relative to the Fermi level E_F . The full and open circles are data points obtained for k near $3k_{\Gamma L}$ and $5k_{\Gamma L}$, respectively, in the extended zone. The curve represents previous experimental results taken from [6, 7].

Based on the peak positions indicated in the left-hand panel of figure 3, we have found that the best description for the relevant portion of the final band is given by $m^* = m$ (the free electron mass), and $U = 6.7$ eV; these values are the same as those reported in [9]. The initial-band dispersion is obtained by combining equation (1) with the requirement of conservation of energy and momentum [2]

$$E_i(k) + h\nu = E_f(k). \quad (2)$$

Figure 4 shows the resulting initial-band dispersion relation (full circles). The three somewhat questionable triangles in figure 3 correspond to the topmost three full circles in figure 4. The full curve in figure 4 shows a previously determined band dispersion relation; the part of the curve for binding energies less than 1.5 eV is taken from [7] (a quantum well measurement), and the rest of the curve is taken from [6] (a low energy photoemission measurement). The good agreement between the full circles and the curve in figure 4 justifies our choices of the parameters for the final-band dispersion relation. To maintain a reasonably good agreement, the above choice of U can be varied by at most ± 1 eV, and the value of m^* will have to be adjusted correspondingly by about $\pm 2\%$. In any case, the final band has an energy of about 54 eV at $k = 3k_{\Gamma L}$, not 44 eV.

3.2. Surface state intensity resonance

The above result suggests that the smaller peak in figure 2 at 54 eV corresponds to the resonance at the L point. The larger peak at 44 eV has been ascribed to an atomic-type resonance in a previous report [9]. Briefly, the transition matrix element between the initial and final states contains two factors. One factor is an integral over the periodic lattice, which gives rise to resonances at k -values equal to odd multiples of $k_{\Gamma L}$. The other factor is an integral within a unit cell, which resembles that for the free atom at high energies except that the relevant wave functions are modified by the solid state environment. Since the atomic cross section for the Ag 5s state shows a maximum at about 40 eV, it seems reasonable to ascribe the peak at 44 eV in figure 2 to this effect. This explanation has not been verified by realistic calculations. Note that narrow resonances in photoemission cross section have been observed in other systems and attributed to atomic effects [11]. In general, it is much easier to explain the photoemission

peak positions than the cross-section variations. A closely related example is the direct transition from the sp band in Cu(111), which shows an intensity variation unexplainable in terms of single-particle models, although the peak position can be easily understood [3, 10].

While the Ag(111) data show a double-peak resonance, the corresponding data for Au(111) and Cu(111) show just one peak in each case [8]. This may suggest that the Ag(111) case is an anomalous one. On the other hand, the Au(111) and Cu(111) resonances seem to show some asymmetry with higher intensity on the side with higher photon energy. This could be a problem arising from the intensity normalisation employed to correct for the monochromator efficiency, or it could arise from the same effect as the small peak seen in Ag(111), only not resolved in the Cu(111) and Au(111) cases [8]. Intuitively, one would expect that all three noble metals should show similar effects.

Clearly, the peculiar profile of the Ag(111) surface state resonance remains an open question. This issue can probably be resolved more readily by theoretical calculations than experimental work.

3.3. *The unknown feature A*

Feature A in figure 3 shows an intensity maximum of around 50 eV. A possible explanation is the resonant enhancement of the emission of a density of states feature near the sp valence band edge by the same mechanism as discussed above for the resonant enhancement of the surface state intensity. The wave functions of the sp valence states near the band edge and the wave function of the surface state are similar (but not the same) [8, 9, 12]; this could explain why the resonances in the two cases occur at similar energies.

This feature has also been observed by S D Kevan [13]. He noticed that it seems to minimise in intensity as the surface state maximises; the behaviour is similar to that of the dispersive valence band peak observed in Cu(111) [3]. He proposed a possible interpretation where the density-of-states feature transfers all of its intensity to the surface state at resonance [13, 14], but he also noted that this interpretation does not quite match the bulk dispersion shown in figure 1.

3.4. *Transitions from the sp valence band near $k = 5k_{\Gamma T}$*

If the final band with the parameters used above ($m^* = m$, and $U = 6.7$ eV) is extended to $k = 5k_{\Gamma L}$, an energy of 162 eV is obtained. This provides only a crude estimate for the energy of the L point transition, because a 10% change in the effective mass, for example, could cause this energy to change by about 15 eV. We have searched for this transition for both the sp valence band and the surface state up to $h\nu = 180$ eV. Only one dispersive peak is observed in this energy range, which is indicated in the right-hand panel in figure 3 with triangles. It moves to near the Fermi level at about 150 eV for increasing photon energies, implying that the L-point transition should be at about 150 eV. The peak presumably is also present in the spectra for $h\nu > 150$ eV, but it is too broad and weak for a determination of its position. Some of the spectra in figure 3 also show a small bump or shoulder just below the Fermi level due to the surface state emission. The resolution of the monochromator used in this range of energy is about 0.4 eV, not suitable for a detailed examination of this surface state which has a width less than 52 meV [15].

To reconcile the data in figure 3 with the band dispersion shown in figure 4, we are led to $m^* = 1.08 m$ with the value of U fixed at 6.7 eV for the final band. This choice of

m^* yields an energy of 149 eV for the final band at $k = 5k_{\text{TL}}$. The resulting dispersion relation for the sp valence band is indicated in figure 4 with open circles. These data agree fairly well with those mentioned above (full circles) and earlier experimental results (curve). Changing the effective mass to either $1.07 m$ or $1.09 m$ would noticeably upset the agreement.

3.5. Energy dependence of the effective mass

The above results indicate that the effective mass of the photoexcited electron increases by 8% as its energy is increased from 54 to 149 eV above the Fermi level. Within this energy range, the effective mass remains fairly close to the free electron mass in agreement with available theoretical models [4, 5]. Various authors have derived general expressions for the self-energy of a hot electron in a solid [4, 5]. The actual numerical computation is, however, rather involved, and has been carried out only for 'free-electron-like' or 'jellium-like' materials within various approximations and limits. These results generally indicate that the effective mass should decrease for increasing energies, which is opposite to the trend observed here. This is not a serious cause for concern, since Ag is not a free-electron-like material as pointed out in one of the calculations [4]. Furthermore, band-structure effects are most likely still significant at 54 eV above the Fermi level. Even some atomic-type effects might be present; for example, it has been pointed out that f-wave resonances could be important at $\approx 16\text{--}20$ eV above the Fermi level for Ag and Au [8, 16–19]. Although our measurement of the final band involves energies higher than 40 eV above the Fermi level, the residual effects from the f-wave resonances might still have some influence at the low end of our measurement. As far as we know, there exists no numerical calculation for Ag in this energy range with the above-mentioned effects taken into account.

In previous studies of near-edge x-ray absorption in several metals, discrepancies were found between theory and experiment. In order to reconcile the theory and experiment, it was necessary to introduce (without justification) a scale factor for the energy above the edge [20]. Specifically, this scale factor for the K-absorption edge of Pd was determined to be ≈ 1.06 . The introduction of a scale factor for the energy has a similar effect to that of the effective mass adjustment mentioned above. The similarity between these observations suggest a possible relationship or a common explanation.

4. Summary

We have observed direct transitions in photoemission originating from the sp valence band in Ag. The results are analysed in terms of a free-electron-like final-band dispersion. The electron effective mass is found to increase from about $1.00 m$ at 54 eV to $1.08 m$ at 149 eV above the Fermi level. The observed increase is opposite to predictions of available many-body calculations based on a jellium model; thus, this discrepancy points to the importance of solid state effects and possibly atomic effects in this system. The inner potential has also been determined. These results should stimulate further theoretical studies in this area of research. The measured final-band dispersion relation is also relevant to the issue concerning the peculiar profile of the intensity resonance of the L gap surface state. Although the present experiment does not provide a solution to this issue, it does show that existing models are inadequate and more sophisticated calculations are needed.

Acknowledgments

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