Direct transitions, indirect transitions, and surface photoemission in the prototypical system Ag(111)

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Received 8 July 1996; accepted for publication 20 November 1996

Abstract

The sp band of Ag(111) is nearly free-electron like near the Fermi level. Photoemission from this band in the surface-normal direction gives rise to a direct-transition peak which disperses with varying photon energies. Contrary to predictions of the standard three-step model, the line shape is significantly asymmetric. The lower binding-energy side of this peak has a higher intensity, and is joined by a broad indirect-transition plateau extending to a rounded cut-off at the sp band edge. This study is an analysis of the asymmetry of the direct-transition peak and the intensity and line shape of the indirect-transition region. The optical transition-matrix element consists of two terms. One is the usual momentum-matrix element dominated by the direct band-to-band transitions in the bulk, with a small contribution from the surface due to the finite mean-free path. The other is a V·A term, which dominates the surface contribution and gives rise to indirect transitions involving all valence states without any restrictions on the crystal momentum. Interference between the bulk and surface contributions results in an asymmetric line shape for the direct-transition peak. The contribution from V·A is shown to be well correlated with the difference in dielectric function between Ag and vacuum.

The effects discussed in this paper are fairly general in nature, and should be taken into account in high-resolution photoemission work. © 1997 Elsevier Science B.V. All rights reserved

Keywords: Angle resolved photoemission; Electron density, excitation spectra calculations; Low index single crystal surfaces; Photoelectron emission; Semi-empirical models and model calculations; Silver; Surface electronic phenomena; Synchrotron radiation photoelectron spectroscopy;

1. Introduction

Spectral features including peak positions, emission intensities, and line shapes, as observed by angle-resolved photoemission from single crystals, are determined by the electronic properties and response functions of the system under study. Most of the studies to date have focused on the peak positions, which are generally associated with the band structure. Indeed, angle-resolved photoemission is the only general tool for mapping valence-band dispersions. Less frequently studied are the relative peak intensities, which can be related to the transition-matrix elements and the surface boundary conditions (escape probability for the photoexcited electron, surface diffraction effects, etc.). Perhaps the most difficult to analyze, and the
least frequently studied, are the line shapes. Strange-looking spectra involving asymmetric peaks and very broad features of unknown origin are, however, not uncommon, even for simple systems, but these are typically left unexplained or attributed to some unspecified higher-order processes or "background" emission. With the advent of new instrumentation and synchrotron sources, high-resolution angle-resolved photoemission measurements are increasingly being applied to studies of complex materials, including, for example, (high-temperature) oxide superconductors [1], fullerides [2], f-electron compounds [3], magnetic systems [4], etc., where minute details in the spectra are often related to key physical properties of the system under study. Clearly, the lack of a good understanding of the basic line shape can be a significant problem for the photoemission technique as a probe of the electronic properties of materials.

This paper is an investigation of the angle-resolved photoemission line shape from the $sp$ band of Ag(111) [5]. This is one of the simplest systems, and has been studied before [6—9]. Ag and Cu, with similar band structures, have served as prototypical systems in the early days of the development of the photoemission technique. The $sp$ band of Ag(111) is nearly free-electron like near the Fermi level, and a simple symmetric peak is expected for the direct band-to-band transition based on standard models [10]. Yet the experimentally observed line shape is significantly asymmetric. This fact has been known for almost twenty years, but remains unexplained. Furthermore, there is a broad emission below the $sp$ band edge, which has been attributed to indirect transitions. The indirect transition is defined as any optical transition which does not conserve the crystal momentum. The mechanism for it has been vaguely attributed to scattering by the surface (which breaks the translational symmetry along the surface normal or the $z$-direction, resulting in a loss of crystal momentum conservation along this direction), scattering by phonons and defects (which can break the translational symmetry in all three dimensions), etc. This indirect transition in Ag(111) is observed to be bounded by a rounded cut-off at the band edge, and the emission near this onset is referred to as a "density-of-states feature". Such density-of-state features, defined as non-dispersive spectral features with binding energies near critical points of the band structure or points of high state densities, have been seen in many systems. The problem for Ag(111) is that the theoretical density of states for the $sp$ band, whether based on a one- or three-dimensional model, involves a singularity at the band edge and does not look like the experimental line shape at all.

The present study offers a simple explanation. The indirect transition and the density-of-states feature are caused by the surface. The dominant mechanism for surface photoemission in the present case is a surface response to the photon field. The vast majority of photoemission papers assume that the incident photon beam is somehow unaffected by the surface. As pointed out in several publications, this is not necessarily a good approximation [10—12]. The $\nabla \cdot A$ term in the matrix element, negligible for a homogeneous medium and usually ignored, can have a significant contribution near a surface due to rapid changes in the dielectric response function. A prediction of our model is that this surface contribution will be closely related to $(-1)$, i.e. the difference between the substrate and vacuum dielectric functions. This correlation is verified in the present study. Another important result from our modeling is that the surface and bulk contributions remain phase-correlated (as opposed to defect scattering, which causes phase incoherence). This phase relationship suggests that the bulk and surface contributions can interfere with each other. This is indeed observed, and is reflected in the asymmetric line shape of the direct-transition peak. The density of states is included in our modeling, but the divergent singularity at the band edge is quenched by a vanishing matrix element, resulting in a rounded cut-off as seen in experiments [13]. This vanishing of the matrix element at the band edge is again caused by the surface, and the detailed mechanism is concerned with the surface boundary condition imposed on the electronic wave function.

A similar interference effect between bulk and surface photoemission has been reported by Shung and Mahan [14] to explain the unusual line shape in Na observed by Jensen and Plummer [15]. The
mechanism for surface photoemission proposed in that work is different from the $V \cdot A$ contribution mentioned above. The relationship between the Na work and the present work on Ag(111) will be discussed.

2. Experimental details

Our experiment was performed at the Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin. A small hemispherical analyzer with a $\pm 1.5^\circ$ acceptance cone was used to collect the data. The synchrotron beam was $p$-polarized and had an angle of incidence of $45^\circ$. A normal-emission geometry was used. The Ag(111) substrates were prepared by sputtering and annealing in the usual manner, and the final surfaces showed a very sharp $(1 \times 1)$ reflection high-energy electron diffraction pattern. Each sample was kept at room temperature during the photoemission measurements. Several sets of data were taken on different beamlines using several samples prepared at different times, and the line shapes were verified to be reproducible.

3. Overview of the results

Fig. 1 shows five normal-emission spectra taken with photon energies of $h\nu = 6-10$ eV in 1 eV steps. The major spectral features are labeled in the figure. The energy reference is the Fermi level. The narrow intense peak just below the Fermi level is derived from a Shockley surface state located within the $sp$ band gap at the $L$-point in the Brillouin zone $[6-9,16]$. At higher binding energies is a broad plateau of emission, which is derived from indirect transitions from the $sp$ band $[6-9]$. This indirect-transition plateau shows an onset at the $sp$ band edge as labeled in Fig. 1. This emission onset (or cut-off) has been referred to as a density-of-states feature in the literature. Adjoining the indirect-transition plateau is a peak which disperses as a function of photon energy $h\nu$. This peak is derived from the direct band-to-band transition $[6-9,16]$. At even higher binding energies, the spectra for $h\nu = 9$ and 10 eV show a tail derived from emission from the Ag 4d states. This Ag 4d emission is not observed for the other three spectra due to cut-off at the vacuum level.

Fig. 2 shows the band structure of Ag along the $[111]$ direction, which is the direction probed by the normal-emission geometry. The nearly free-electron-like $sp$ band has a crystal-potential induced band gap at the Brillouin-zone boundary. The Shockley surface state mentioned above is located near the bottom of this band gap. The vacuum level, indicated in Fig. 2 by a horizontal dashed line, is very close to the bottom of the upper $sp$ branch. The top of the Ag 4$d$ bands is at about 4 eV binding energy. The vertical arrows indicate the direct band-to-band transitions for $h\nu = 6-10$ eV. As $h\nu$ increases, the transition moves to the left in Fig. 2, resulting in a change in binding energy of the direct-transition peak as seen in
Fig. 2. Band structure of Ag along the [111] direction. The horizontal axis is the wave vector normalized to the distance between the zone center and the zone boundary. Direct transitions for photon energies of 6, 7, 8, 9 and 10 eV are indicated by vertical arrows. The dashed horizontal line shows the position of the vacuum level.

Fig. 1. This peak movement as a function of $h\nu$ has been used to deduce the $sp$ band dispersion [6,7,9]. The dashed horizontal lines in Fig. 1 indicate the zero-intensity level for each spectrum. It is clear that the direct-transition peak is asymmetric, with the emission intensity on the lower binding-energy side being significantly higher. Each spectrum should also contain a background caused by inelastic scattering of the photoelectrons. The inelastic scattering, being a cascading process with more secondary electrons generated at higher binding energies, is characterized by a monotonically increasing function for increasing binding energy. The asymmetry of the direct-transition peak as well as the indirect transition on the lower binding-energy side cannot be explained by an inelastic background function.

The standard three-step model of photoemission suggests that the direct-transition peak should be a Lorentzian with a width determined by the electron and hole lifetimes [10]. The asymmetric line shape seen in Fig. 1 shows that this model is inadequate. The same three-step model offers no explanations for the indirect-transition plateau and the density-of-states feature. A better model is needed. This will be presented in Section 4.

4. Modeling

We have performed a model calculation, incorporating all of the essential physics which is known to apply for the present system. The model begins with a two-band fit to the nearly free-electron like Ag $sp$ band dispersions [17]. An excellent fit is obtained; the parameters include a pseudopotential $V_{111}$, which is related to the size of the gap, and two effective electron masses, one each for the two $sp$ branches separated by the $L$ gap. These effective masses are needed to account for higher-order hybridization effects [17], and are adjusted separately to fit the curvature of each of the two $sp$ branches. The corresponding Bloch wave functions are then constructed, and at each energy the initial wave function is formed by a linear combination of two Bloch states, one traveling toward $+z$ (pointing into vacuum) and the other traveling toward $-z$. For the Ag–vacuum interface, we assume a step potential corresponding to the work function of Ag. The position of this potential step at $z = z_0 > 0$ does not quite coincide with the classical surface at $z=0$ due to electrons spilling over into the vacuum side. The value of $z_0$ is determined in our calculation by fitting to the known energy of the Shockley surface state.

The final state of photoemission is one in which a photoelectron is captured by the detector. It is much easier to think in terms of its time-reversed state. Upon time reversal, the photoelectron is sent from the detector to the surface, and the result is the same as a low-energy electron diffraction (LEED) experiment [18]. The electron is partially transmitted and partially reflected. The transmitted beam becomes a Bloch state in the substrate traveling toward $-z$, and is gradually attenuated by inelastic scattering. This attenuation of the Bloch wave function is modeled by an exponential decaying envelope function with a decay length of $2\xi$, where $\xi$ is the mean-free path. This effectively leads
to a complex wave vector for the final Bloch wave function, or a complex energy (the imaginary part corresponds to a lifetime broadening). Reversing this LEED state in time yields the photoemission final state. This formalism is known as the one-step model for photoemission [10,18], and is adopted in our calculation.

The optical transition-matrix element consists of two terms

\[ \langle \psi_f | A \cdot \nabla \pm (\nabla \cdot A)/2 | \psi_i \rangle \equiv M_b + M_s, \]  

(1)

where \( A \) is the vector potential. Inserting this transition-matrix element and the initial and final density of states into Fermi's golden rule formula yields a photoemission spectrum. The first term \( M_b \) in Eq. (1), in the limit of an infinitely long mean-free path, is proportional to the usual momentum-matrix element seen in the standard calculations of bulk optical properties. It gives rise to the direct band-to-band transitions in photoemission [10]. Due to a finite mean-free path, the presence of the surface does have an influence on this term, but this effect is small for the present case (see below). The second term in Eq. (1) is zero for a homogeneous medium and is usually ignored in such calculations. If we ignore this second term for the moment and carry out the calculation, what we obtain is a fairly symmetric direct-transition peak in good agreement with the three-step model. This is not surprising, as previous theoretical studies have shown that the three-step model is an excellent approximation for the one-step model at low photon energies where the photoelectron mean-free path is long [19].

Since the first term alone in Eq. (1) does not lead to the observed line shapes, we need to examine the second term \( M_s \). This term is important near a surface [10–12]. Classically, there is a discontinuity in the dielectric function at the surface, which, upon differentiation, leads to a term proportional to \( \delta(z-z_0) \) for \( \partial A_z / \partial z \). This delta function is somewhat broadened, phase-shifted, and otherwise modified (Friedel-like oscillations) when the quantum-mechanical response function of the system is taken into account. This is a computationally challenging problem, and has been worked out only for fairly simple model systems [11]. In the present study, we will not attempt to calculate this surface term accurately. Rather, we will make an estimate, and show that this effect can indeed lead to the observed line shapes. Furthermore, we can predict the dependence of the line shape on \( h\nu \), which can be verified by experiment.

The surface contribution \( M_s \) has a very short range, of the order of the atomic layer thickness \( d \) (the length scale over which the electrons can effectively screen out an external perturbation). We therefore have

\[ M_s \approx C \psi_f(z_0) \psi_i(z_0), \]

(2)

where the surface photoelectric coefficient \( C \) is of the order of

\[ \frac{\partial A_z}{\partial z} \bigg|_{z_0} d. \]

This derivative of \( A_z \) is of the order of \( k \Delta A_z \), where \( \Delta A_z = (-1)A_z \) is the difference between the internal and external fields, and \( k = \pi/d \) is the wave vector at the Brillouin-zone boundary. Combining these relations and assuming that the field is normalized such that \( A_z = 1 \), we obtain

\[ C \approx \pi (-1). \]

(3)

What we have done so far is to express a complicated quantum-mechanical quantity \( C \) in terms of a macroscopic quantity \( \delta \), which is easily measured by optical means and available from the literature. The photoemission spectra calculated using this approximate form of \( M_s \) show a great deal of resemblance to the data, including an asymmetric direct-transition peak, an indirect-transition plateau, and a rounded cut-off of the indirect-transition plateau at the band edge. A good match is neither expected nor observed, because Eq. (3) is derived from a very rough estimate.

The small circles in Fig. 3 represent the 8 eV spectrum. The curve overlapping these data points is a fit to the data with the surface photoelectric coefficient \( C \) treated as an adjustable (complex) parameter. The value of \( C \) from this fit is \(-3.0 + 3.5i\), which is of the same order of magnitude as \( \pi (-1) = -1.8 + 4.3i \) from the known optical constant of Ag [20–24]. Similar fits have been
obtained for the other spectra in Fig. 1. In constructing the fitting function, several other parameters are needed. These include the known full width at half maximum of 75 meV for the surface state peak [25], and an instrumental resolution of 55 meV. The intensity of the surface-state peak is treated as an adjustable parameter in our model; its physical significance has been discussed before by a different group [26], and we will not elaborate on it here. The width of the direct-transition peak is determined mostly by the damping of the time-reversed LEED state through the mean-free path $\xi$, and to a lesser extent by the broadening of the hole state. The latter quantity is 100 meV from our fits to all five spectra, and is somewhat larger than the surface state broadening of 75 meV as expected. These additional parameters have nothing to do with the asymmetry of the direct-transition peak, which is entirely determined by $C$.

The absolute square of the matrix element described above is multiplied by the initial and final density of states and a Fermi–Dirac distribution function at room temperature to yield the elastic spectrum. We still need a parameter to describe the inelastic background function. Here we employ the so-called Shirley function [27], which is just an integral of the elastic spectrum covering the entire lower binding-energy side up to the energy of interest. This provides a measure of the total number of elastic electrons which are capable of yielding secondary electrons at the energy of interest. The Shirley function times a proportional constant as a fitting parameter is added to the elastic spectrum to yield the final fitting function. The dotted curve below the spectrum in Fig. 3 is the background function from the fit.

5. Major results from the modeling

An important prediction of our model is Eq. (3); namely, $C$ is proportional to the difference in dielectric function between Ag and vacuum. The proportional constant may in fact depend on energy, but this dependence should be relatively unimportant over a small range. The real and imaginary parts of $C$ obtained from our fits to the five spectra in Fig. 1 are plotted in Fig. 4 as a function of $h \nu$. To guide the eye, a linear regression curve for the real part and a quadratic regression curve for the imaginary part are shown. Also shown for comparison are the real and imaginary parts of $2\pi(\epsilon - 1)$ and their corresponding regression curves.
curve for the imaginary part are shown. Also shown in Fig. 4 are the real and imaginary parts of $2\pi(-1)$ and their corresponding regression curves for comparison. The extra factor 2 inserted here is arbitrary, but remember that Eq. (3) is just a rough estimate. With this extra factor of 2, the real parts match pretty well. The imaginary parts also match pretty well in the overall shape of the curve, but there is a constant offset. This offset should not be a big concern. It turns out that different determinations of the dielectric function often differ by a constant offset, even though the variations are very well reproduced [20–24]. The difference seen in Fig. 4 could be due to this uncertainty, but could also be due to any extra energy dependence which is not included in our simple estimate. In any case there is clearly a good correlation between $C$ and $(-1)$ in that the overall slope and curvature are similar. This result lends strong support to our model.

Fig. 5 shows the mean-free path from our fits to the five spectra. Strictly speaking, our determination of the mean-free path is slightly in error. What we have done is to fit each spectrum in Fig. 1 assuming a constant mean-free path for the particular spectrum. The error is small, however. Since all of the bulk features except the direct-transition peak are very broad, they are not appreciably affected by this broadening mechanism. In other words, this parameter is predominately determined by the width of the direct-transition peak. The mean-free path shown in Fig. 5 should be understood as the mean-free path for a direct-transition photoelectron traveling along the [111] direction. It is about 20 Å for $h\nu=10$ eV, and increases to about 50 Å at $h\nu=6$ eV, when the photoelectron is just about the vacuum level. This increase is expected. As the photoelectron energy decreases, so does the phase space available for electron-electron scattering, and therefore the mean-free path increases. The corresponding reduction in the overall width of the direct-transition peak is visibly evident in Fig. 1.

6. Discussion

The fit for the 8 eV spectrum shown in Fig. 3 is excellent. This fitting curve, with the inelastic background and the surface-state peak ignored, is shown as the top curve in Fig. 6. It is interesting to note that the elastic emission intensity diminishes to practically zero on the left end of the spectrum. The matrix element for this spectrum consists of three separate integrals. The term $M_b$ in Eq. (1) is made up of two integrals, one for $z<z_0$ and the other for $z>z_0$; these will be referred to as the bulk integral and the vacuum integral, respectively. The term $M_s$ in Eq. (1) will be referred to as the $V\cdot A$ integral. The three middle curves in Fig. 6 show the results of the same calculation but with only one of the three integrals retained in the calculation. These are referred to as the bulk, the vacuum, and the $V\cdot A$ spectrum, respectively.

The bulk spectrum in Fig. 6 shows a symmetric peak, in agreement with the prediction of the three-step model. The peaked behavior has to do with crystal-momentum conservation. The vacuum spectrum has a relatively low intensity because it involves just the exponential tail of the initial wave function for $z>z_0$. The $V\cdot A$ spectrum shows a broad distribution covering the entire valence-band region, because crystal momentum is not conserved and all states contribute. These three integrals are complex functions, and when they
are added and absolute-squared, the resulting spectrum depends very much on the relative phases. On the lower binding-energy side of the direct-transition peak, these contributions are mostly in-phase, resulting in an enhancement of the intensity by constructive interference. This gives rise to the indirect-transition plateau. On the higher binding-energy side, destructive interference causes the intensity to become very small. This changeover from constructive interference to destructive interference across the direct-transition peak is the reason for the asymmetric line shape, and is mainly caused by a phase change of \( \pi \) of the bulk integral. Perhaps the easiest way to understand this phenomenon is to consider the bulk integral from perturbation theory. The dominant term in the bulk integral is proportional to \( 1/(E_b - E_{sp}) \), where \( E_b \) is the binding energy and \( E_{sp} \) is the direct-transition energy (with an imaginary part to represent broadening). This energy denominator changes sign when \( E_b \) sweeps through \( E_{sp} \), leading to a phase change of \( \pi \). This type of phenomenon, in which a discrete transition interferes with a broad continuum to form an asymmetric line shape, is well known in atomic physics (Fano resonances). A comparison of the various curves in Fig. 6 shows the importance of the surface contribution, which is dominated by the \( \mathbf{V} \cdot \mathbf{A} \) term in the present case.

A photoemission calculation based on the one-step model, but without the \( \mathbf{V} \cdot \mathbf{A} \) term, still contains a surface contribution due to the finite mean-free path. In the above treatment, one could identify the vacuum integral as a surface contribution. It is approximately proportional to \( \psi_f^\dagger(z_0)\psi_i(z_0) \); in other words, its energy dependence is similar to that of the \( \mathbf{V} \cdot \mathbf{A} \) term. This is the mechanism proposed by Shung and Mahan [14] to explain the unusual line shape in Na observed by Jensen and Plummer [15]. Even though the matrix element used by Shung and Mahan has a different form, it is equivalent to our \( M_b \) by a simple transformation. The \( M_s \) term is ignored in their calculation, but this is justified for the case of the Na experiment. Unlike the Ag case, the dielectric function of Na is very close to unity [20], and consequently the \( M_s \) term, being proportional to \( (-1) \), is negligible. The net surface contribution is nevertheless quite large in the Na experiment because of the short mean-free path at higher photon energies. Our finding is thus consistent with the work of Shung and Mahan.

The final density of states included in our calculation is a smooth function. Its effect on the line shape is minimal. The initial density of states, shown as the bottom curve in Fig. 6, has a divergent singularity at the band edge. Even though the initial density of states is a multiplicative factor for the model function, this singularity does not appear in the calculated spectrum. The reason for this is that the matrix element diminishes near the band edge. Fig. 7 shows the initial wave function for initial energies 0.01, 0.1 and 1.0 eV below the band edge. These wave functions are characterized by a rapid oscillation with a wave vector near the zone boundary modulated by an envelope function with a longer wavelength. This envelope function is caused by beating of the Bloch waves traveling in
7. Implications

Except for some simple systems where $\epsilon \approx 1$, the $\mathbf{V} \cdot \mathbf{A}$ contribution will be significant and can be the dominant source for indirect transition or surface photoemission. The analysis discussed in this paper should be generally applicable to a variety of systems. As mentioned earlier, asymmetric line shapes are not uncommon. As an example, a recent high-resolution study of Ag(100) shows an $sp$ direct-transition peak which is asymmetric in a way which is very similar to the Ag(111) case [28]. This is evident by examining the spectra in Figs. 2 and 4 in Ref. [28]. A study of Cu(100) for the same transition also shows a similar result [29,30]. These asymmetric peaks are probably caused by the surface effect discussed above.

High-temperature superconductors have received much interest in recent years, and there have been a number of high-resolution photoemission studies of such materials [1]. Much of the attention has been focused on the line width and its connection to the question of the applicability of the Fermi-liquid theory [31]. Since indirect transitions are necessarily present, which can interfere with the direct transitions, it is important to consider this effect in analyzing the data.

The mean-free path in the present study is fairly long. It can become much shorter at higher photon energies. Surface photoemission by the $\mathbf{V} \cdot \mathbf{A}$ term as well as the vacuum term will become correspondingly more important relative to the bulk contribution. A breakdown of the three-step model can happen near the minimum of the mean free path ($h\nu \approx 50$ eV), where the amplitude of the surface contribution can become of the same order as the bulk contribution. This might be the reason for the unusual results seen in Ag at higher energies [32]. At even higher photon energies, the mean-free path increases, and the dielectric function for most materials begins to converge to unity value. This surface effect is expected to diminish.

Any surface effect with a short-range potential can give rise to indirect transitions. The mathematics involved is fairly similar to the calculation of the $M_0$ term (see Eq. (2)). A significant surface reconstruction or relaxation can be associated with a surface potential, which can induce surface photoemission. Although this effect has been conjectured to be important for some systems, a detailed numerical treatment has not been attempted as far as we know. Likewise, a thin overlayer deposited on a surface can modify the surface potential and the surface dielectric response, resulting in a significant modification to the surface photoemission process. It will be interesting to find a model system to test this idea.

Surface photoemission is also important for quantum-well systems. As an example, Ag films grown epitaxially on Au exhibit discrete quantum-
well peaks within the Au band gap due to electron confinement [33]. As the Ag film thickness increases, these quantum-well peaks become more numerous, and eventually merge into the indirect-transition plateau. Most quantum-well studies to date have focused on the peak positions only. A quantitative understanding of the intensities of these peaks [34] will have to take into account the V·A term.

8. Summary and conclusions

This paper is a study of the photoemission line shape observed in Ag(111), a simple prototypical system with a spectrum dominated by a single direct-transition peak in the sp region. The line shape of this peak has for a long time been known to be asymmetric. The physical origins for this asymmetry and the indirect-transition plateau are clarified. It is shown that these are caused by surface photoemission, and the asymmetric line shape is caused by interference between the bulk and surface contributions. This surface contribution is dominated by the V·A term in the transition-matrix element, and its dependence on hv is shown to be related to (−1) based on a simple argument. A numerically accurate calculation for this surface photoemission process will require a self-consistent treatment involving both the electrons and the electromagnetic waves as a coupled system – a challenging task. We hope that the present work will stimulate sufficient interest for theorists to solve this problem. The phenomena and effects discussed in this paper are fairly general in nature, and are likely to be important for other systems. Photoemission spectroscopy is an important tool for materials studies. A detailed understanding of the basic line shape is essential for an accurate interpretation of the results.

Acknowledgements

This material is based upon work supported by the US National Science Foundation under Grant No. DMR-92-23546. An acknowledgement is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the US Department of Energy, Division of Materials Sciences (Grant No. DEFG02-91ER45439) for partial support of the synchrotron beamline operation and for support of the central facilities of the Seitz Materials Research Laboratory. The Synchrotron Radiation Center of the University of Wisconsin is supported by the National Science Foundation under Grant No. DMR-95-31009.

References


[11] P.J. Feibelman, Phys. Rev. B 12 (1975) 1319. This is a self-consistent calculation of the surface optical response of a jellium, which is an approximate representation of simple metals. Similar and more refined calculations have been performed later by other authors. See, for example, A. Liebsch and W.L. Schaich, Phys. Rev. B 52 (1995) 14219. The model employed in this calculation is a better approximation for the noble metals, because the polarizability of the filled d-states, in addition to the jellium response, was taken into account.


