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THEORY OF PHOTOEMISSION

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Résumé. — La discussion porte sur une théorie de la photoémission comprenant les processus de la diffusion multiple, les effets de surfaces et la durée de vie des trous. On discute les conséquences importantes des durées de vie des trous et on présente des calculs pour trois catégories de matériaux représentées par le cuivre, le nickel et l'aluminium.

Abstract. — We discuss a theory of photoemission which includes multiple scattering processes, surface effects and hole-lifetimes. The important consequences of hole-lifetimes are discussed and calculations presented for three classes of materials represented by copper, nickel and aluminium.

1. **Outline of the theory.** — Photoemission experiments are almost the only check we have on bands deep below the Fermi level, yet until recently much of the information contained in these experiments has not been exploited because relatively crude interpretation has been made of these experiments. For example, angle integrated photoemission experiments are usually compared with a density of states calculation and only rarely are refinements such as matrix elements included, still less corrections for surface effects, etc. This is perhaps surprising, because the relevant pieces of theory have been available separately for some time. Only the drawing together of these pieces into one coherent calculation is required. So the time has come for a detailed theory of photoemission which enables us to interpret experimental data with the best possible resolution that current theories allow.

The photon field gives rise to photoemission *via* a perturbing term in the Hamiltonian

$$A = \frac{1}{2c} (\mathbf{P} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{P})$$

where

$$\mathbf{A} = \mathbf{a} \cos(\mathbf{q} \cdot \mathbf{r} - \omega t). \quad (1)$$

The photon energy is typically in the 10 eV-200 eV range. The \mathbf{A} -vector should have dielectric corrections made to it which in principle may be quite complicated, but we have found by experience that it is often satisfactory only to calculate the classical refraction at the surface changing the direction of the incident light beam, though as we shall mention later in the paper, there are some reservations about this simple approximation. With the assumption that the dielectric constant produces only a straight-

forward refraction at the surface, we can transform equation (1) to give the form which we use for calculation. The positive frequency component has amplitude

$$A = \frac{\mathbf{a} \cdot \nabla V}{2\omega c} \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (2)$$

Throughout this paper formulae are expressed in a.u. in which $\hbar = m = e = 1$, and the velocity of light $c = 137$.

Because photoemission involves several different theories being mixed together, the details of calculations are quite involved, but in spite of this the underlying theory is not very complex, and to show this we start from a simple *golden rule* expression for the photocurrent

$$I(\mathbf{k}_{\parallel}, E + \omega) = \sum_j \frac{L}{k_z^+} |\langle \mathbf{k}_{\parallel}, E + \omega | A | j, E \rangle|^2 \quad (3)$$

The final state which carries the photoelectrons out of the crystal is simply the time reversal of a LEED state, and can be calculated using LEED theory. Its direction is specified by \mathbf{k}_{\parallel} , momentum parallel to the surface. The initial state is a linear combination of Bloch waves of the crystal adjusted so as to meet the boundary conditions at the crystal surface. It can be calculated by conventional band theory techniques such as have been applied to investigation of surface states. Although techniques are available for evaluating equation (3) they are not very convenient computationally, and in any case we shall need to make an important extension of the *golden rule* theory which will not be possible within the framework of equation (3).

The philosophy of the *golden rule* is that the occupied states have been sitting in the crystal for an infinite length of time. They are stationary states of the crystal, and when the photon field arrives it couples them to other stationary states at higher energies which can couple to the detector. This is a static picture of the photoemission process, and in contrast we shall develop a dynamic method of calculating in which we do not calculate the stationary states, but instead we evaluate the matrix element by making use of scattering theory. To this end we re-write equation (3)

$$I(\mathbf{k}_{\parallel}, E + \omega) = \sum_j \frac{L}{k_z^+} \langle \mathbf{k}_{\parallel}, E + \omega | \Delta | j, E \rangle \times \langle j, E | \Delta^\dagger | \mathbf{k}_{\parallel}, E + \omega \rangle. \quad (4)$$

Next we make two substitutions. Firstly, the final state is re-written in terms of a source term on which the Green's function at high energies $G_2^+(E + \omega)$ acts. The second substitution recognises that the sum over occupied states can also be written in terms of a Green's function $G_1^+(E)$:

$$\langle \mathbf{r} | \mathbf{k}_{\parallel}, E + \omega \rangle = (\langle \mathbf{r} | G_2^+ | \varphi^* \rangle)^* = \langle \mathbf{r} | G_2^- | \varphi \rangle \quad (5)$$

where

$$\langle \mathbf{r} | \varphi \rangle = \frac{1}{L} \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}) \delta(z - Z), \quad (6)$$

$$\sum_j |j, E\rangle \langle j, E| = -\frac{1}{\pi} \text{Im} G_1^+(E) \quad (7)$$

L is the length of a large box confining the experiment, Z is the plane of observation. Substituting both these expressions back into equation (4) we regain a new expression for the photocurrent.

$$I(\mathbf{k}_{\parallel}, E + \omega) = -\pi^{-1} \text{Im} \langle \varphi | G_2^+ \Delta G_1^+ \Delta^\dagger G_2^- | \varphi \rangle \quad (8)$$

This expression is the same as the one derived by Caroli [1]. We can go on to re-interpret the Green's function, not as an expansion over stationary states, but in its alternative guise as a propagator which sums over all scattering paths within the crystal [2].

Let us give a step-by-step account of the calculation. We begin with a plane wave headed towards the crystal (we shall time-reverse this part of the calculation by complex conjugation eventually) and using LEED theory we can calculate the function $\langle \mathbf{r} | G_2^+ | \varphi \rangle$ by summing all scattering paths between layers of atoms and within layers of atoms. In particular,

the amplitudes of this state, the time reversal of the outgoing wave, near the centres of the atoms is

$$\frac{1}{L} \sum_{lm} A_{2lm}(s) \psi_{2l}(|\mathbf{r} - \mathbf{R}_j|) Y_{lm}(\mathbf{r} - \mathbf{R}_j) \exp(i\delta_{2l}) \quad (9)$$

where ψ_{2l} is the solution of the radial Schrödinger equation and δ_{2l} is the phase shift for angular momentum l . Subscript «s» refers to the layer in which the atom finds itself and \mathbf{R}_j is the position of the atom relative to the origin in that layer. \mathbf{k}_{\parallel} is the crystal momentum parallel to the surface which is conserved in the calculation, since we assume a perfectly periodic surface. Next we take the photon field which can be expressed as

$$\Delta^\dagger = \frac{|\mathbf{a}|}{2\omega c} \frac{dV}{dr} \frac{4\pi}{3} \sum_{m'=-1}^{+1} Y_{1m'}^*(\mathbf{a}) Y_{1m'}(\mathbf{r} - \mathbf{R}_j) \times \exp(-i\mathbf{q} \cdot \mathbf{R}_j) \quad (10)$$

and we assume that any necessary corrections to the \mathbf{A} -vector have been made. Tracing through the next step in formula (8) the photon field, acting on the incident wave, acts as a source of holes in the crystal. The waves radiating from the j th atom, as yet uncorrected for multiple scattering, are

$$\frac{1}{L} \sum_{lm} B_{1lm}^{(0)} \psi_{1l}^+(|\mathbf{r}' - \mathbf{R}_j|) Y_{lm}(\mathbf{r}' - \mathbf{R}_j) \exp(-i\delta_{1l}) \quad (11)$$

where

$$B_{1lm}^{(0)} = \frac{-i\kappa_1 4\pi |\mathbf{a}| \exp(-i\mathbf{q} \cdot \mathbf{R}_j)}{6\omega c} \times \sum_{l'm'} A_{2l'm'}^* Y_{1m'+m}^*(\mathbf{a}) \exp(i\delta_{1l} - i\delta_{2l'}) \times \int_0^\infty r^2 \psi_{1l}(r) \frac{dV}{dr} \psi_{2l'}(r) dr \times \int Y_{lm} Y_{1m+m'} Y_{l'm'}^* d\Omega \quad (12)$$

κ_1 is the wave-vector of the hole wavefunction, and δ_{1l} the phase shift, ψ_{1l} the regular solution and ψ_{1l}^+ the outgoing wave solution for the hole in the l th angular momentum channel. Each atom radiates an outgoing hole-wave. The calculation must let these waves interfere with one another, scatter off all layers of atoms, scatter off the surface barrier and finally evaluate the total wavefield accumulating at every atom centre. Let us suppose this has been done and that the total hole wavefield is given by

$$\frac{1}{L} \sum_{lm} C_{1lm} \psi_{1l} Y_{lm} \exp(i\delta_{1l}) + B_{1lm}^{(0)} \psi_{1l}^+ Y_{lm} \exp(-i\delta_{1l}). \quad (13)$$

All that remains to be done is to complete the matrix element by taking a scalar product with the original incident wavefield. The summation is over the contribution of each atom within the crystal to the photocurrent. This may be positive or negative, because of interference of contributions from different atoms, but of course the total current must remain positive. Though we have not mentioned it specifically in our account, the gradient of the potential of the surface barrier also acts as a source of holes, and takes part in the photoemission process. We shall see in a subsequent section that this can be a large contribution to the photocurrent in some materials.

2. Hole-lifetimes. — So far we have merely reformulated the *golden rule*, but we now wish to introduce an element to our calculation that is not present within the *golden rule* formulation: the lifetime of the hole left behind in the crystal. It is evident that this lifetime must affect spectra because the uncertainty principle dictates that the shorter the lifetime the less detail will be apparent in the photocurrent. The *golden rule* has no knowledge of the lifetime of the hole state and implicitly assumes that this state is infinitely long-lived, because it works in terms of static states. However, our formula though derived from the *golden rule* in the first instance, is capable of generalisation to include the hole lifetime. This is because the philosophy of interpretation of equation (8) is quite different. The photon operates on the ground state of the crystal to produce an electron and a hole. G_1^+ is the Green's function for the hole state, not for the occupied electronic states. Since the hole only appears on the scene at the moment of its creation, it is now sensible to talk of giving this state a finite lifetime.

The lifetimes arise principally by Auger decay processes and vary a great deal from one material to another. They can be calculated by Green's function techniques derived for calculation of the self-energy of propagators [3] and are therefore many body corrections to the photoemission process. In formal language our propagator acquires an imaginary part to its self energy and the waves radiated from the atoms in our photoemission calculation decay as the distance from the source increases. The point we make is not simply a philosophical one, it actually changes the mathematics of the calculation. By way of example, we should consider lifetimes for the photoemission of a single atom. Let us consider calculation of the photocurrent in an emitted wave

$$A\psi_{2l}^+(\kappa_2 r) Y_{lm}(\mathbf{r}) \quad (14)$$

caused by a photon field

$$\Delta = \frac{|a|}{2\omega c} \frac{dV}{dr} \frac{4\pi}{3} \sum_{m''=-1}^{+1} Y_{1m''}^*(\mathbf{a}) Y_{1m''}(\mathbf{r}). \quad (15)$$

The Green's function G_1^+ for a free atom is given by

$$G_1^{(0)+}(\mathbf{r}\mathbf{r}') = -ik_1 \sum_{l'm'} \psi_{1l}(r_<) \psi_{1l'}^+(r_>) Y_{l'm'}^*(\mathbf{r}) Y_{l'm'}(\mathbf{r}') \quad (16)$$

and we can combine these formulae to give an expression for the photocurrent emitted from a free atom.

$$I \propto \text{Im } i \sum_{l'm'} \iint r^2 dr r'^2 dr' \psi_{2l}(r') \psi_{1l'}(r_<) \times \psi_{1l'}^+(r_>) \psi_{2l}^*(r) \frac{dV}{dr} \times \left| \sum_{m''} Y_{1m''}^*(\mathbf{a}) \int Y_{lm} Y_{1m''} Y_{l'm'}^* d\Omega \right|^2 \quad (17)$$

On the real axis this formula can be transformed to give the traditional *golden rule* expression, i.e. we can reverse our steps taken in section 1. To do this we simply note that

$$\text{Im } i\psi_{1l'}^+ = \psi_{1l'} \quad (18)$$

and hence we regain the *golden rule* formula

$$I \propto \sum_{l'm'} \left| \int r^2 dr \psi_{2l}(r) \psi_{1l'}(r) \frac{dV}{dr} \right|^2 \times \left| \sum_{m''} Y_{1m''}^*(\mathbf{a}) \int Y_{lm} Y_{1m''} Y_{l'm'}^* d\Omega \right|^2. \quad (19)$$

Equation (19) is only valid when the hole is infinitely long-lived, and therefore the energy of the wavefunctions in equation (18) is on the real axis, otherwise we cannot reverse our steps. So we see that the *golden rule* does not take account of hole-lifetimes.

The importance of using equation (8) which is the correct formula if one wishes to put in hole-lifetimes, is particularly great when the atoms of the crystal have tightly bound states such as d-bands. The resonant d-state gives rise to a pole in the scattering amplitude above the real axis, and if the resonance is a sharp one, as d-resonances are, this pole can be very close to the real axis. The implication is that we do not have to decrease the hole-lifetime very much before the line along which we are calculating in the complex energy plane crosses to the other side of this pole and completely changes the nature of the wavefunctions in the vicinity of the pole. To illustrate this point we consider the phase shifts for an atom with a d-resonance. If we do not correct the calculation for the lifetime of the hole state the phase shifts take a resonant form shown schematically in figure 1a. The phase shift begins near zero at low energies, climbs sharply through $\pi/2$ at the resonance and attains a value close to π above the resonance. Now let us make the correction for the hole-lifetime. The phase shift becomes complex, of course, with a positive imaginary part representing the fact that

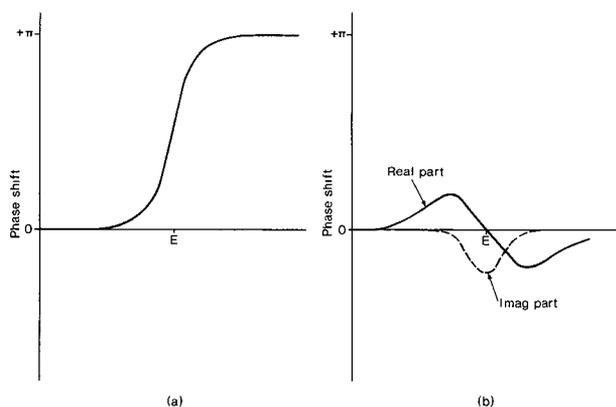


FIG. 1. — Qualitative behaviour of the d-phase shift in the presence of a resonance *a*) when the particle lifetime is infinite ($\Sigma_1 = 0$) *b*) when the lifetime is short ($|\Sigma_1| \gg$ resonance width).

part of the amplitude decays during the scattering process. If the lifetime as measured by the imaginary part of the self energy, Σ_1 , is large enough to push the line along which we calculate beyond the singularity, the phase shift now appears as in figure 1*b*, which clearly gives qualitatively different scattering from the phase shift shown in figure 1*a*.

We have dwelt at some length on the corrections for the hole-lifetime, because in almost all materials it is an essential ingredient of the calculation, and in some materials can be the dominant ingredient.

3. Calculations. — We shall present calculations for three materials : copper, nickel and aluminium, each typical of its own class of material, and different effects will come to the fore in each of these materials.

We consider first copper. This metal had d-bands which result in a rich electronic structure, and we have learnt from the photoemission spectra that copper has a very long lifetime for holes created in the d-band. This is due to the low density of states in the vicinity of the Fermi level which restricts the phase space for Auger decay of the hole. The presence of d-bands implies that the effective potential of the atom is very strong and therefore if we compare the contributions to equation (2) of the potential in the ion core region, and the potential in the region of the surface barrier, the ion cores are seen to dominate the photoemission matrix elements. Therefore copper gives rise to photoemission spectra with well-defined detailed structure. To illustrate this point we compare in figure 2*a* calculation for the (111) surface of copper with experiments by Ilver and Nilsson [4]. The comparison is typical for copper. All the general features are present with the correct widths and relevant intensities, but there are discrepancies in the energies at which these features appear. This is due to the fact that our calculation is based on the Chowdorow [5] potential, which is misplacing the bands by anything up to 0.5 eV.

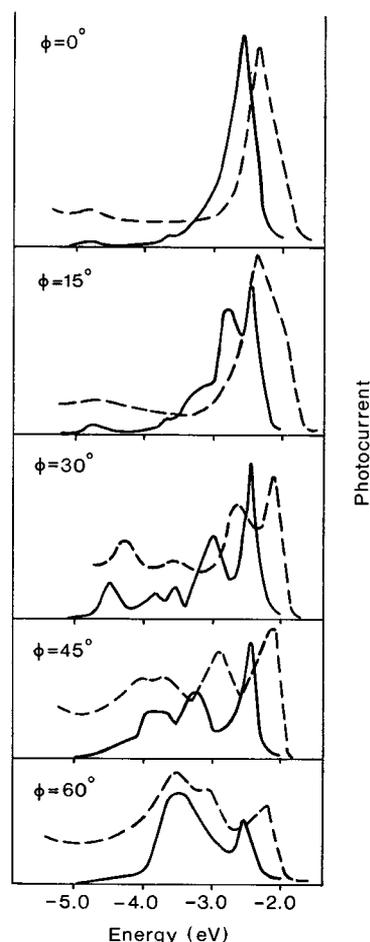


FIG. 2. — Photoemission spectra for a copper (111) surface. Unpolarized radiation, $\hbar\omega = 16.8$ eV is incident normally on the surface and the electrons are emitted at $\theta = 45^\circ$ to the normal. The angle ϕ is measured relative to the $(\bar{2}11)$ azimuth (---) theory, (---) experiment. The energy is measured relative to E_F and the imaginary part of the hole self energy is given by $\Sigma_1 = -0.054$ eV.

In this calculation the imaginary part of the self energy for copper was set equally to -0.054 eV and to show how sensitive spectra are to this parameter, we have increased the value of Σ_1 successively in figure 3. Note the dramatic broadening of spectra with decreasing lifetime, until finally no details are observable, only a single hump. It is quite easy to fix the order of magnitude of Σ_1 from these photoemission experiments, though very careful comparison of a wide range of spectra is required to get a really accurate fix on Σ_1 .

The structure found in the spectra has a complicated origin. Much of it is due to interband transitions conserving momentum normal to the surface. Other parts of it may be due to density of states effects and occasionally some feature may be due to the presence of a surface state. Structure due to surface states in copper tends to be swamped by a rich mass of structure coming from the bulk bands, and only occasionally do we see prominent features which are attributable to surface states.

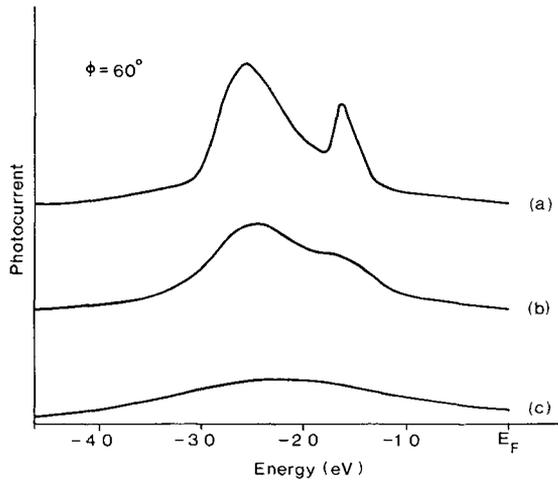


FIG. 3. — Calculations made for the copper (111) surface as above, except that the imaginary part of the hole self energy is varied $\Sigma_1 = a) - 0.054$ eV, $b) - 0.27$ eV, $c) - 1.0$ eV.

The next material we consider is nickel, which also possesses d-bands. Superficially, the theory of electronic structure in nickel is similar to copper. Certainly band structure calculations reveal bands which are very similar indeed, but they omit a key ingredient to the photoemission spectra; that is to say, the hole-lifetime. Spectra for nickel all show a similar trend at energies deeper in the d-band: structure gets broader and less prominent until, more than 2 eV below the top of the d-band, sharp structure is almost never observed. The reason seems to be that Σ_1 for nickel is a strong function of $E - E_F$. The Fermi level in nickel occurs almost at the top of the d-band thus increasing the phase space available for Auger decay as compared with copper. In addition the energy of the hole modifies strongly the phase space for decay, approximately as $(E - E_F)^2$. If we assume a parametrized form for

$$\Sigma_1 = -\alpha(E - E_F)^2, \quad (20)$$

$$\alpha = 0.102 \text{ (eV)}^{-1}, \quad (21)$$

shown plotted in figure 4, we can get good agreement with experiment shown in figure 5. Also shown in this figure is the calculation assuming a much longer lifetime of -0.014 eV for the hole states and it will be seen that the detailed structure deep in the d-band predicted by the long lifetime model is in clear disagreement with the experiments [6].

The spectra for nickel are dominated by the short hole-lifetimes. So short has this lifetime become at the bottom of the d-band that a hole with energy near the bottom of the d-band created on an atom will decay by Auger processes before it has a chance to hop to another atom. The structure in Σ_1 is also of importance. We have seen how a quadratic variation with $(E - E_F)$ seems to fit the particular spectrum shown in figure 5, but there are other spectra which provide evidence that Σ_1 in nickel is also a function

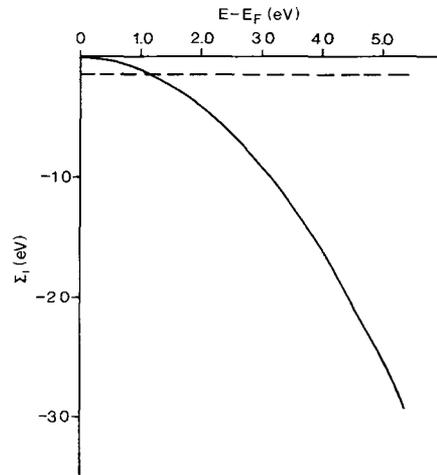


FIG. 4. — The imaginary part of the self energy for holes in the d-band of nickel, (—) as postulated in the present paper (theory 2). The dashed curve shows the small value used to calculate « theory 1 » in figure 5 for contrast with « theory 2 ».

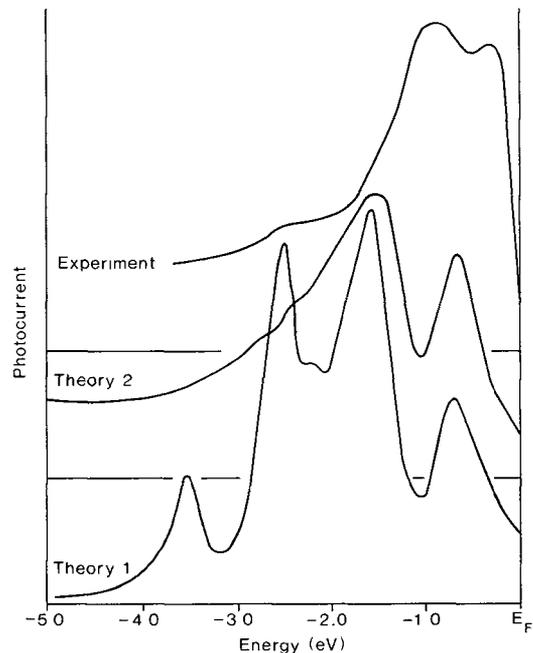


FIG. 5. — Photoemission spectra for a nickel (001) surface. Unpolarized radiation, $\hbar\omega = 16.8$ eV, is incident normally on the surface and the electrons are emitted at $\theta = 48^\circ$ in the (010) azimuth. Two calculations are shown differing in the imaginary part of the self energy used for the hole, defined in figure 4.

of position in the crystal, which is not too surprising since the Auger decay takes place *via* excitation out of the d-band, and the d-band tends to be localized near the atom centres.

The third material is aluminium, which is a nearly-free-electron material, and therefore the effective potential of the ion cores is weak. Photoemission spectra for aluminium tend to be dominated by emission from the surface barrier contribution to equation (2), with an incident photon beam that has

a p polarised component. Hence we expect interband transitions not to play any substantial role in spectra for aluminium. Also calculations for free-electron-like materials [7] revealed that the hole-lifetime is quite short in aluminium, Σ_1 being of the order of ~ 0.5 eV. Therefore we expect rather broad structure in the spectra of aluminium and we also expect, because of the absence of other structure from interband transitions, that surface states will play a more prominent role in spectra. In figure 6 we show some data taken by Gartland and Slagsvold [8] which we compare with our calculations. The spectra show

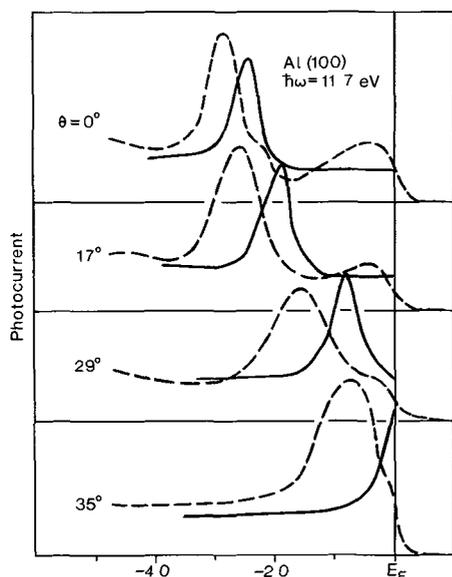


FIG. 6. — Photoemission spectra for an aluminium (001) surface. Unpolarized radiation, $\hbar\omega = 11.7$ eV, is incident at 45° to the normal in the (110) azimuth and the electrons are emitted at various polar angles, θ , in the (110) azimuth. (—) theory, (---) experiment. $\Sigma_1 = -0.27$ eV.

a single large peak which moves with angle of emission but not with photon energy. This behaviour is characteristic of a surface state which theory shows to be the cause of the peak. For smaller values of θ the surface state has a width dictated by the value of Σ_1 we have chosen in our calculation, but at higher angles the surface state becomes a surface resonance rather than a true bound state at the surface, and there is an additional broadening due to decay of the surface state into waves propagating away from the surface. In figure 7 we also show the dispersion of the surface state plotted against $|k_{\parallel}|$, the momentum parallel to the surface, and we see that in both theory and experiment it is parabolic, as it should be for a nearly-free-electron material.

At smaller values of θ in figure 6 a shoulder will be seen on the main peak. Gartland and Slagsvold interpret this as a peak in the density of states due

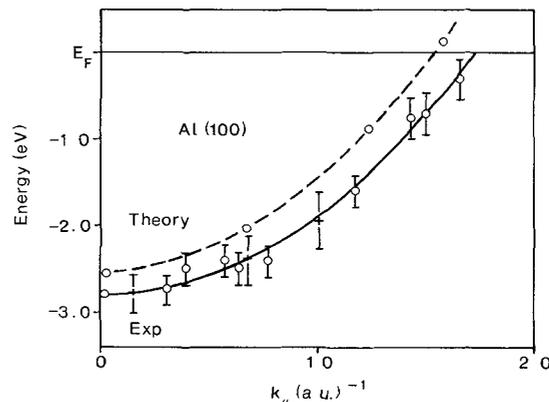


FIG. 7. — Experimental and theoretical dispersion of the surface state peak in an aluminium (001) surface.

to the band edges, and though our theory does not show it, they are probably correct in this interpretation. We believe the reason our calculations do not reproduce this shoulder is that the theory contains no contribution from the terms due to the $\text{div } \mathbf{A}$ being non-zero within the first few layers of atoms. Only contributions from the ion cores, which are very weak, and from the surface barrier are included. The surface barrier lies at the edge of the crystal where the bulk band edge singularities round off and are no longer visible as peaks, whereas the $\text{div } \mathbf{A}$ contribution operates within the first few layers of atoms and therefore will be capable of giving some contribution from the band edges.

4. Conclusions. — Our model of photoemission works for a range of materials and the important elements in obtaining agreement with experiment are the use of an accurate crystal potential and inclusion of finite lifetimes for the hole. There seems to be room for improvement of several of the parameters. For example, the potential seems to be accurate only to within ± 0.5 eV, and it will be desirable to improve calculations to give much better accuracy than this. Also the lifetimes of holes as at present gauged from photoemission are accurate only within, say, a factor of 2, and this ought to improve with more detailed studies. Finally, it will be useful in the case of the free-electron materials to have a more accurate calculation of the surface photoemission terms (such as the $\text{div } \mathbf{A}$ contributions) in order to bring the aluminium spectra into better agreement with experiment.

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