

A Review of (e,2e) Studies in Thin Films and Some Recent Results*

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Abstract

The form of the (e,2e) cross section applicable to high energy symmetric transmission measurements in thin films is given in the plane wave impulse approximation. The difference expected for single crystal, non-single crystal and amorphous films is discussed. For certain kinematics, the measured (e,2e) coincidence intensity can be related directly to the energy-momentum distribution of the target electron and a map of the occupied electron states can be obtained in principle. Recent experimental work in the authors' laboratory using about 100 Å thin films of aluminium/aluminium oxide is discussed. Two peaks in the valence binding energy are seen at 13 and 31 eV whose angular correlations indicate that both are dispersionless and resemble P and S type atomic orbitals of oxygen. Neither peak resembles the free electron structure of aluminium. Improving the electron energy resolution from 4.5 to 1.5 eV while maintaining the momentum resolution constant at about 0.9 Å^{-1} did not significantly change the data which indicates the dominant effects of multiple scattering.

1. Introduction

The direct ionisation process described by the equation $e+A \rightarrow A^++2e$ is referred to as an (e,2e) process. An incoming electron of known momentum ejects a bound electron, and the two outgoing electrons are then detected in time coincidence with defined momenta, which ensures that they originated from the same scattering event. The kinematics, except for reaction spin, are then well defined as indicated in Fig. 1. The observed scattering probabilities can be related to the quantum mechanical configuration before scattering of the ejected electron. For certain kinematics, the measured intensity can be related directly to the energy-momentum distribution of the target electron. A map of the occupied electron states as a function of their binding momentum and energy can in principle be obtained.

There are many experimental methods that provide either information on the energy or integrated momentum distributions of solid-state electrons but none of these allow the direct measurement of the spectral momentum map. The most successful of these approaches is angular resolved photoelectron spectroscopy (ARUPS), reviewed by Courths and Hufner (1984) and Marchland

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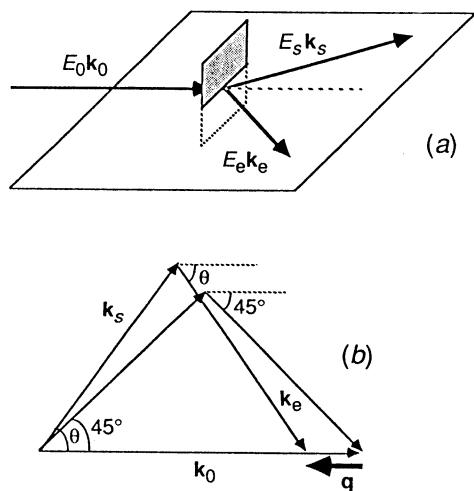


Fig. 1. Scattering kinematics for the coplanar symmetric (e, 2e) experiment: (a) The incident, scattered and ejected electrons have energies E_0 , E_s and E_e and momenta $\mathbf{k}_0$, $\mathbf{k}_s$ and $\mathbf{k}_e$ respectively. From the momentum conservation diagram (b), the sampled binding momentum $\mathbf{q}$ is parallel to the incident beam direction when the polar angles θ are changed equally and symmetrically.

et al. (1984). This technique has been widely used to examine valence and conduction band dispersion by detecting the energy-selected photoelectrons at specific polar angles. The photoelectron's momentum component parallel to the crystal surface is conserved. The data are well resolved in energy and the structures can be mapped accurately in momentum. In order to associate identifiable peaks with particular transitions, a band map has to be presupposed. The technique does not provide direct information about the momentum density.

Other methods such as Compton profiling give an integrated momentum density of the valence region (e.g. Holt 1986). This approach has problems close to zero momentum and it only provides a density value averaged over all valence states. Similar information is derived from the observations of angular correlations of the two photons produced from positron annihilation by a bound electron (Berko *et al.* 1977) for which precise directional momentum information is found for the solid near the Fermi surface, the intensity being a summation over valence energies. Also X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) provide density-of-state information for a solid through, for example a self-deconvolution procedure of core-valence-valence Auger transitions. These methods give no direct information about the energy or momentum distribution of individual bands which is the aim of (e, 2e) structure studies.

2. The (e, 2e) Theory for Solid Targets

Levin *et al.* (1972) outlined the (e, 2e) reaction theory on solids and showed that in the plane wave impulse approximation (PWIA) the (e, 2e) differential cross section was proportional to the spectral momentum density, i.e. the probability of finding a bound electron at a particular energy and momentum in the valence band of a solid. The measured kinematics of the (e, 2e) process, precisely determines the energy and momentum of the sampled bound electron population.

The theory begun by Levin *et al.* (1972) was followed up by D'Andrea and Del Sole (1978) who examined the reflection (e, 2e) geometry. The primary beam strikes the crystal surface at a grazing angle and the scattered and ejected electrons are then detected in coincidence at small angles in reflection. This technique is expected to be extremely surface sensitive with a penetration depth of between 5 to 10 Å for grazing angles of 3° at typical keV beam energies. The theory examines the (111) surface of silicon, where reconstruction and dangling bond effects are expected in the form factor. Of special interest to this paper, however, is the transmission mode (e, 2e) reaction, where the scattered and ejected electrons are detected on the opposite side of the foil to the incident electron.

The differential cross section for the (e, 2e) knockout reaction in the coplanar symmetric geometry can be derived from the PWIA for high incoming and outgoing electron energies. First, consider the (e, 2e) differential cross section for an ideal oriented single crystal and where diffraction effects of the incoming and outgoing electrons are assumed small. By analogy to atomic theory, the electron-electron scattering term f_{ee} is unchanged. The form factor $F_{ks}(\mathbf{q})$ defines the scattering amplitude of an electron with quasi-momentum k being ejected from the s th band. The form factor can be written as the Fourier transform of the single independent particle wavefunction (Levin *et al.* 1972)

$$F_{ks}(\mathbf{q}) = (2\pi)^{-3/2} \int \exp(i\mathbf{q} \cdot \mathbf{r}) \Psi_{ks}(\mathbf{r}) d\mathbf{r}. \quad (1)$$

Using the fact that the electron in the crystal must satisfy the Bloch relation

$$\Psi_{ks}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \Psi_{ks}(\mathbf{r}),$$

where $\mathbf{R}$ is an arbitrary lattice vector, the squared modulus of (1) becomes

$$|F_{ks}(\mathbf{q})|^2 = \sum_{\mathbf{B}, s'} \delta_{\mathbf{q}, \mathbf{k} + \mathbf{B}} |\Psi_{ks'}(\mathbf{k} + \mathbf{B})|^2. \quad (2)$$

The summation is carried out over all reciprocal lattice vectors $\mathbf{B}$ and s' bands not resolved in energy. For a non-zero differential cross section, the measured binding momentum must satisfy $\mathbf{q} = \mathbf{k} + \mathbf{B}$ and the measured binding energy be equal to the s' band energy, $\epsilon = \epsilon_{s'}(\mathbf{q}) = \epsilon_{s'}(\mathbf{k} + \mathbf{B}) = \epsilon_{s'}(\mathbf{k})$. The coincidence conservation equations can be rewritten as

$$\mathbf{k}_s + \mathbf{k}_e = \mathbf{k}_0 - \mathbf{q}, \quad E_s + E_e + \epsilon_{s'}(\mathbf{k}) = E_0, \quad \mathbf{q} = \mathbf{k} + \mathbf{B}. \quad (3)$$

These relations are the same as in the repeated zone scheme, where the structure is repeated in momentum space by the reciprocal lattice vector. The (e, 2e) coincidence experiment is then able to map the band structure directly with the intensity being modulated by the momentum density $|\Psi_{ks'}(\mathbf{q})|^2$.

To illustrate the information being derived from the experiment we shall consider the two simplifying cases where the electronic structure is described by either the tight-binding or the complementary free electron model. The tight-binding approximation treats materials where the overlap between atomic wavefunctions on a periodic lattice is small, e.g. insulators and the deeper bands of a larger set of materials. The single electron wavefunction is

constructed out of the atomic orbital $\phi_s(\mathbf{r})$ that satisfies the periodic boundary conditions through

$$\Psi_{\mathbf{k}s}(\mathbf{r}) = N^{-1/2} \sum_{\mathbf{R}} \exp(i \mathbf{k} \cdot \mathbf{R}) \phi_s(\mathbf{r} - \mathbf{R}),$$

where N is the number of atoms in the crystal. Substituting the wavefunction into (1) gives the form factor

$$F_{\mathbf{k}s}(\mathbf{q}) = N^{1/2} (2\pi)^{-3/2} \phi_s(\mathbf{q}) \delta_{\mathbf{q}, \mathbf{k} + \mathbf{B}}. \quad (4)$$

Thus, as with the atomic studies, the form factor becomes directly proportional to the Fourier transform of the atomic orbital. More generally, the wavefunction would be made up of a linear combination of atomic orbitals, with the result that (4) is the Fourier transform of this characteristic orbital. The differential cross section is then (Neudatchin *et al.* 1969)

$$\frac{d^3\sigma}{dW_s dW_e dE_s} = n \frac{k_s k_e}{k_0} |\phi_s(\mathbf{q})|^2 f_{ee} \left(1 - \frac{\mathbf{k}_e \Delta_k e_s(\mathbf{k})}{2E_e} \right)^{-1} \delta_{\mathbf{q}, \mathbf{k} + \mathbf{B}}, \quad (5)$$

where n is the number of valence electrons per unit volume. The term in parentheses arises from the state being selected by energy conservation which for a solid depends on momentum. This term, typically varies by less than 2% for free-electron-like valence bands and is close to one for atomic-like bands at high beam energies of the order of 10 keV.

The free electron model of a solid considers the other extreme where the electrons are completely delocalised. The wavefunction for the independent single electron state is then a plane wave $V^{-1/2} \exp(i \mathbf{k} \cdot \mathbf{r})$, where V is the crystal volume. Through (1), the form factor is simply

$$F_{\mathbf{k}}(\mathbf{q}) = V^{-1/2} (2\pi)^{-3/2} \delta_{\mathbf{q}, \mathbf{k}}. \quad (6)$$

The form factor for the free electron is of constant height from the centre of the Brillouin zone out to the Fermi momentum k_f , where it drops to zero. In the case of materials like aluminium, the orthogonalised plane wave model only makes minor corrections to the free electron model. At the zone boundaries, a mixing of counter propagating wavefunctions, $|\Psi\rangle = 2^{-1/2}(|\mathbf{k}\rangle \pm |-\mathbf{k}\rangle)$ occurs, which removes the degeneracy at these points. The calculated form factor, then depending only on one component of the quasi-momentum, drops to half its value at these boundary points.

For more complex systems such as copper (Levin *et al.* 1972), the form factors for the individual bands are a mixture of the nearly free s -bands and the tight-binding approximated s - d interactions. In general, the mixture results in smoothly varying, norm squared form factors that still exhibit symmetry characteristics of atomic states.

Within the frozen orbital assumption, the (e,2e) experiment measures the binding energy and momentum of the target state before the collision. As mentioned for gases, however, configurations of the residual electron system can produce satellite peaks in binding energy spectra. The reorganisation processes in solids for the weakly correlated s and p bands are thought to be small, while for the more strongly correlated d and f bands the frozen orbital

assumption may no longer be correct. Because of the high electron density the hole may also couple the plasma to produce satellite states, which will be discussed in more detail later.

The theory described above has ignored the potential contribution of the high energy electrons travelling in the periodic crystal potential. In single channel studies, the extended energy loss fine structure (EXELFS) observed in the ejected electron energy distribution can be related to diffraction from the local atomic structure. Maslen and Rossouw (1983, 1984) theoretically described the K-shell knock-out reaction using (e, 2e) scattering kinematics in the dynamical diffraction model. The fast electrons before and after the ionisation were represented by a summation of Bloch waves. The theoretical framework has recently been extended by Allen *et al.* (1990; present issue p. 453). The theory indicates that the scattering probability becomes site dependent, which is opposed to the plane wave view discussed earlier. For a high energy electron the coherent superposition of the elastically scattered waves gives a varying probability density within the crystal unit cell. The (e, 2e) cross section which is proportional to the product of the three independent probability densities (belonging respectively to incoming and two outgoing electrons) may also depend on the ionisation site. At present the (e, 2e) theory has not been sufficiently developed to predict where diffraction effects are likely to be significant or under what conditions they can be minimised, except for the high energy limit.

3. Non-single Crystal Target Theory

The targets prepared as thin solid films can be divided into three categories, crystalline, polycrystalline and amorphous. As discussed above, the information derived from a single crystal is sampled along one of its lattice directions. For polycrystalline samples, the band structure is expected to remain intact, and $|F(q)|^2$ is averaged over all crystal orientations. Its value at the centre of the zone and near the origin is unchanged. The sharp dips in the form factor at the zone boundaries will average out and disappear. The net result is that $|F(q)|_{av}^2$ remains constant inside the closest distance to the Fermi surface and then smoothly decreases to zero at the maximum Fermi surface distance. The band map similarly will reveal this averaging with the measured bandwidths depending on the isotropy of the crystal. For aluminium, the dispersion in all directions is similar, so the averaged map $e_s(q)_{av}$ will follow the free electron like parabola, except that the measured bands will broaden as q moves away from the zone centre. At the zone centre, the binding energies should remain unchanged. For a more anisotropic material, where the effective mass tensor depends strongly on direction, the information will blur closer to the zone centre. The $|F_s(q)|_{av}^2$ factor will become a more smoothly varying function which, however, still portrays the global characteristics of the band.

Amorphous solids are possibly of more interest since as electron systems they are not well understood and hold the promise of application to high-efficiency low cost solar cells, thin-film transistors and photoconductors for use in electrophotography. In that case, the crystal order is completely broken down. With the framework of a periodic lattice no longer applicable, the quasi-momentum k is not a good quantum number. The current theoretical understanding of electronic structure depends on the real space atomic

configurations and its statistical nature. Short-range order is generally studied for this reason by extended X-ray fine structure (EXAFS) and Raman vibrational spectroscopy (Lucovsky and Hayes 1985; Lannin 1988). The probing of the 'band' structure of these solids has mainly occurred through XPS and photoabsorption experiments which allow some measurement of the density of states and indirect determination of the band gaps.

The short-range order in the amorphous state is similar to the crystalline state, which leads to some of the basic features of the electronic structure being conserved. In the tight-binding approximation, the atomic wavefunctions are only perturbed by nearest neighbour interactions. General modifications, however, have been suggested to account for the translational disorder, mainly in reference to the transport properties of the amorphous semiconductors. Two major models indicate the presence of localised states at the band extremities which are respectively called Cohen-Fritzsche-Ovinsky (CFO) and Davis-Mott (DM) models. Fluctuations from an average distance cause variations in the potential acting on the electrons which, in turn, adjusts the energy of the electron state about the band centre. The states feeling the deepest potential variation make-up the extremities. The conduction valence band edges then tail into the band gap, with the tail states being localised in space. In the CFO model these tails extend smoothly from each side of the band gap and overlap at the centre. In the DM model, the tail only slightly broadens the bands with a single narrow band of levels lying near midgap, which are associated with dangling bonds. These localised states are thought to determine the electronic properties of technologically important amorphous solids. With a direct (e, 2e) measurement it should be possible to map the occupied states in the band gap and determine their binding momentum characteristics, which will depend on the degree of localisation.

It would also be informative to examine the 'band' structure of amorphous materials. For instance, carbon deposited amorphously will have bonds that resemble its two crystal forms—diamond (tetrahedral) and graphitic (hexagonal). From the overall character of the band map it may be possible to select between bonding models (Ritter *et al.* 1984). The theoretical qualitative prediction by Ziman (1971) is that the band map should resemble the crystalline solid close to the Brillouin zone centre, with the bands broadening for momentum values near the crystalline boundaries. Thus, k is still a fairly good quantum number in this description. The idea follows from the zone centre representing long wavelength states, whose phase is unaffected by local characteristics. It would be experimentally interesting to measure the band properties of an amorphous solid directly, as attempted by Ritter *et al.* (1984).

4. Other Solid State Influences

Apart from the binary collision theory other solid state contributions have been suggested in the literature. The first is, and perhaps most importantly, multiple scattering which occurs in the dense solid. With the effective increase in the electron density by approximately 10^6 over gaseous targets, the probability of the incoming and/or outgoing electrons suffering a single channel scattering, before or after the (e, 2e) reaction, is many times greater in the solid. The term single channel is meant to imply uncorrelated (extrinsic)

scattering of the individual (e, 2e) electrons. For a solid target typically 100 Å thick being probed with a high energy electron beam, the mean free paths (mfps) are of the order of the target thickness. The result is a reduction in the total coincidence signal and the appearance of satellite structures in the experimental spectral momentum density. Methods have been suggested (Jones and Ritter 1986; Hayes *et al.* 1988) to remove this structure by considering in detail the elastic and inelastic scattering contributions along each trajectory. The creation of collective oscillations, plasmons, in the solid state electron gas is found to be the major inelastic mechanism. Plasmons have also been suggested to couple intrinsically with the sudden hole created by the (e, 2e) reaction and give rise to a 'plasmaron' state. This coupling falls under the general heading of Mahan-Nozieres-de Dominicis X-ray edge structure, since it was largely developed for XPS studies. The appearance of a hole causes the electronic system to respond in a screening fashion. The fastest way to achieve this is by the coherent superposition of plasmons (about 10^{-16} s) and valence electron-hole pairs (about 10^{-15} s). Lundqvist (1967, 1968, 1969) predicted the appearance of a plasmaron branch, located one to two times the plasmon excitation energy below the free electron band, with a momentum density sharply peaked at zero. The theory was formalised with respect to the (e, 2e) experiment by Neudatchin and Zhivopistseva (1974) and Zhivopistseva and Comas (1979, 1980), though the hole state in each case was considered deep, that is, strongly localised.

5. Experimental (e, 2e) Studies of Solids

Before reviewing (e, 2e) measurements of energy-momentum distributions of bound solid-state electrons, two other studies that employ a similar reaction mechanism should be mentioned. Secondary electron emission from thin carbon films was investigated by Voreades (1976) using electron coincidence techniques. A high energy beam of between 15 and 25 keV was scattered from the solid target with the transmitted energy-discriminated electrons detected in coincidence with the reflected secondary electrons. The resulting spectra, normalised to the scattered electron count rate, indicated that plasmon decay gave rise to the secondary electron population (Goryni and Markarova 1979), though interband transitions could not be ruled out.

Another class of experiments by Haak and Sawatsky (1978) used Auger photoelectron coincidence spectroscopy to separate features in the Auger spectra of copper. They showed that the $L_{23}M_{45}M_{45}$ Auger peak recorded in the usual single channel manner for copper can be decomposed into components created from the $2p_{1/2}$ and $2p_{3/2}$ photoelectrons, uniquely identified by the coincidence mode. This allows a background-free measurement of the relative contributions of the two Auger transitions and the clear identification of the Coster-Kronig transition.

Electron momentum coincidence measurements using solid targets were initiated by Amaldi *et al.* (1969) using a 14.7 keV primary beam transmitted through a thin polyvinyl-formal film, 200 Å in the symmetric coplanar mode. The K and L shells of carbon were well resolved. A small peak in the binding energy spectrum was attributed to the K shell of oxygen. The first angular correlation, i.e. coincident intensity versus detector angles at fixed

binding energy, was performed on essentially the same apparatus by Camilloni *et al.* (1972). The carbon core states were again studied, but with a thin carbon film (250 Å) as the target and a primary beam energy of 9 keV. The momentum distribution of the 1s state was shown to correspond, within experimental error, to the Roothan-Hartree-Fock wavefunction in the PWIA. The L shell, however, was not resolved at an energy resolution of about 130 eV. The data were confirmed under similar conditions by Krasil'nikova *et al.* (1975) also in the coplanar symmetric mode. For a primary beam energy of 10 keV and an energy resolution of 140 eV, the K-shell carbon angular correlations obtained from carbon and collodion [an incomplete polymer with basic structure $C_6H_7O_2(ONO_2)_3$] films agreed within the experimental accuracy, and again corresponded with the Hartree-Fock wavefunctions in the PWIA. In addition, the angular correlation of the oxygen K shell was determined. The valence region of aluminium was studied later by the same group at 10 keV primary beam energy (Persiantseva *et al.* 1979) using the improved calculated energy resolution of 15 eV fwhm. The data however were not sufficient to separate contributions from individual states. From formvar (Dey *et al.* 1987), with an energy resolution of 14 eV for a 6 keV incident energy beam, several states could be identified in the spectrum but the complex character of the foil did not allow a unique understanding of the angular correlation data. Aluminium (Dey *et al.* 1987), at the same beam energy and with a resolution of 19 eV, revealed a similar distribution to that found by Persiantseva, with the binding energies corresponding to deep losses with energies greater than 60 eV, clearly showing the effects of multiple scattering.

The first (e,2e) experiment to deliver information about the spectral momentum density in the valence band from a solid was performed by Ritter *et al.* (1984). With the significantly higher beam energy of 25 keV and an energy resolution of about 6 eV, two bands became visible from a thin (about 100 Å) amorphous carbon foil. The structure is generally consistent with what would be expected from graphitically bonded carbon. The lower band had an S-like character with a peak at $q = 0 \text{ Å}^{-1}$ allowing for an experimental momentum offset, and it showed dispersion in energy from 23 to 9 eV, from the centre of the Brillouin zone to $q = -3 \text{ Å}^{-1}$. It was similar to the s band of graphite or diamond. The upper band, at about 9 eV, was harder to assign to a single crystal band because of its dispersionless nature. As Ritter *et al.* showed from its positioning and nature, it does not conform to either diamond or graphite structures. The momentum density revealed a P-like character with a local minimum at $q = 0 \text{ Å}^{-1}$. The upper band appeared to be related to the amorphous nature of the foil, possibly blending together the upper and s bands of crystalline states. Subsequently Gao *et al.* (1988) used a 25 keV incident beam to probe a semi-oriented graphite sample with its c-axis parallel to the beam direction. Data were collected in the coplanar and noncoplanar symmetric modes to probe the binding momenta, perpendicular and parallel to the crystal's basal plane. The valence band was probed from 4.4 eV above the Fermi energy to 27.6 eV below, in a binding momentum range of about 0 to 2 Å^{-1} , with an energy resolution of 8.6 eV and an estimated momentum resolution of 0.47 and 0.73 Å^{-1} , parallel and perpendicular to the c-axis respectively. Two bands were again revealed and shown to have different

dispersion characteristics along the orthogonal crystal directions. Graphite is a particularly interesting sample in this regard, with a free electron band structure (parabolic energy-momentum dependence) in the plane and atomic-like nature perpendicular to the plane. The results generally agreed with calculated band maps and momentum densities, with discrepancies possibly being accounted for by the statistical nature of the data collected over a four-month period.

The amount of information that potentially could be obtained from coincidence studies of solids is matched by its technical difficulties. There have only been a handful of (e, 2e) measurements on solids since the coincidence signal, as will be shown later, is seriously degraded by multiple scattering even in 100 Å thick foils. For energy and momentum resolutions 4 eV and 0.9 Å^{-1} respectively, the real coincidence count rate per channel is of order 0.02 Hz in the valence band at $q=0 \text{ Å}^{-1}$ compared with typical gas coincidence signals at similar resolutions of order 1 Hz. The contrast is further magnified when the information required from each target is considered. For a gas target the coincidence intensity can be mapped out for a fixed binding energy to find the momentum density of that state. The solid target however requires a complete binding energy spectrum to be collected at each momentum value, with the interest directed at the energy dispersion and the changing character of the band map at higher momentum. This effectively multiplies the data collection time by about 30 (1 eV binding energy steps over 30 eV). Other technical problems arise out of the high beam energies needed in the solid measurement, where the total energy stabilisation (of order 50 ppm) and momentum stabilisation (of order 0.1° alignment precision) must be maintained over the experimental period. These factors usually result in an experimental compromise between resolution and acquisition time.

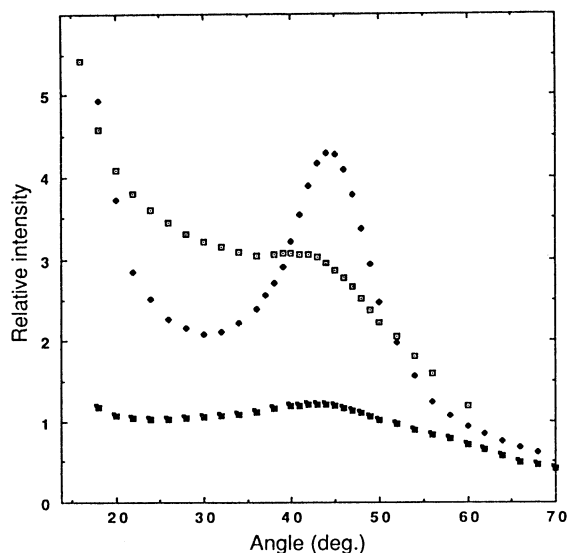


Fig. 2. Quasi-elastic spectra are shown for evaporated free standing films of 100 Å carbon (diamonds) and 120 Å aluminium (open squares) and cleaved 170 Å graphite (solid squares, lowest data set). The incident electron energy is 7.5 keV and each graph is normalised to a second analyser count rate at 70° .

Finally, mention should be made of the usefulness of 'quasi-elastic' or simple binary scattering as a qualitative method of evaluating the ability of a film to give a coincidence signal. Fig. 2 shows the angular distribution of scattered electrons with energy equal to half the incident energy. It was found that the relative coincidence count rates from each of these films is similar to that of the relative quasi-elastic count rates for these conditions. However, by fixing the electron scattering angle at 45° the energy distribution around the quasi-elastic peak is seen to be flat for carbon, graphite and aluminium but formvar (polyvinyl-formal) shows a significant peak. The prominence of that peak is also a good guide to the size of the coincidence peak from a film.

6. Coplanar Symmetric Coincidence Data for Aluminium

Recent studies in our laboratory (Hayes *et al.* 1988) have used a parallel detection method which has increased the efficiency of the (e,2e) experiment by about 100. A pair of microchannel plate position sensitive detectors are positioned at the energy dispersed outputs of two 180 hemispherical analysers. Coupled together through position and time computing electronics, coincidence events have been effectively collected in parallel over a definable binding energy interval. The increased efficiency has allowed a significant improvement of energy resolution and data reliability in the (e,2e) study of thin solid targets in the valence region.

The disadvantage of coplanar symmetric kinematics is that the binding momentum can only be sampled in the beam direction. For unoriented amorphous/polycrystalline foils such as evaporated carbon and aluminium, this one-dimensional momentum map represents an 'averaged' spectral momentum density. The data were typically acquired at a primary beam energy of 7.5 keV, with momentum and energy resolutions of $0.9\text{--}1.1 \text{ \AA}^{-1}$ (fwhm) and 4.5 eV (fwhm) respectively. At this beam energy, the major origin of error is the misalignment of the analysing system, either mechanical or operator related. Small angular deflections at this energy result in substantial changes in the analysed momentum. The positioning of the primary beam, in particular, affects both the momentum and the analysed energy, through the analyser's optical relation to the position sensitive detector. The coincidence interaction region defined by the incoming electron beam and the solid foil can be located to within 0.3 mm, which corresponds to an angular deflection of about 0.25° or a binding momentum error of $\pm 0.2 \text{ \AA}^{-1}$. Alignment of the analysers, by eye and with laser, has an estimated tolerance of $\pm 0.2^\circ$ or an associated momentum of $\pm 0.1 \text{ \AA}^{-1}$. These small systematic errors have the effect of distorting the binding momentum spectrum according to the direction of the error momentum. Through resolving the error momentum, the experimentally measured momentum q_m is derived from the expected momentum q by

$$q_m = \{(q-p_{\parallel})^2 + p_{\perp}^2\}^{0.5}, \quad (7)$$

where $(p_{\parallel}, p_{\perp})$ are the error components parallel and perpendicular to the ideal beam direction. The parallel component has the effect of shifting the measured binding zero momentum while the perpendicular component narrows the momentum distribution (since $q_m > q$), eliminating the zero momentum arrangement. The minimum measured momentum is thus $0.66 \text{ \AA}^{-1}$. The

energy scales were made absolute by calibrating to the $3p$ argon ion state at 15.76 eV. For solid targets, however, the contact potential between the target and the system is not compensated by this method.

Apart from determining parameters such as the momentum resolution, it is interesting to note the effect of the Mott electron scattering term on the symmetry of the angular correlation. As the scattering angle increases, this term decreases smoothly, distorting the angular distribution through weighting the forward binding momenta data upwards relative to the backward momenta. The effect is obvious in the argon $3p$ state data, while the slight change in symmetry of S-type function is less discernible. As we shall see next, this valence structure is mirrored in the s - p nature solid-state electrons in the low Z materials considered.

Thin aluminium targets used in all (e, 2e) coincidence studies to date have been prepared external to the (e, 2e) system. Aluminium, because of its high chemical reactivity, is known to oxidise readily at its surfaces to stable depths of 15 to 30 Å. For the evaporated foils used here, of order 100 Å, the oxide represents about half the foil thickness. The foils are considered as a two component system, evenly divided between the amorphous oxide and the polycrystalline aluminium. The band structure is expected to be a complex mixture of the two states. The aluminium/aluminium oxide data have revealed states that were more consistent with the oxide component of the foil. There was the advantage, however, of being able to study an oxide insulator, which, in free-standing conditions, would charge under a probing electron beam. There is considerable interest in aluminium oxidation, because of its similarities to SiO_2 and their potential in MOS gate technology, which have been reviewed by Batra and Klenman (1984).

The oxidation process of aluminium has been widely studied as functions of time and evolving gas exposure using UHV techniques such as low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and extended X-ray fine structure (EXAFS) (see Batra and Klienman 1984). From the data, oxidation appears to proceed on the low index faces of pure aluminium in a disordered over/under layer, with the exception of the densely packed (111) face. As the exposure is increased the oxygen is driven to deeper subsurface sites until it becomes stable to further doses. The amorphous alumina surface has been shown through XPS (Balzerotti and Biaconi 1976) to have similar electronic properties to its crystalline forms $\alpha\text{-Al}_2\text{O}_3$ (corundum) and $\gamma\text{-Al}_2\text{O}_3$. There is, however, limited data about the details of this valence band. It is accepted that the valence region can be divided into two bands though there is no general agreement as to widths or the separation, theoretically or experimentally. With the Fermi energy lying in the conduction-valence band gap (i.e. no obvious energy normalisation) and the appearance of low energy structures in the excitation spectra assigned to exciton absorption (Balzerotti and Biaconi 1976; Olivier and Poirer 1981), the unambiguous interpretation of results has been frustrated.

The bulk aluminium of the target seen from electron diffraction experiments shows only distinct fringes corresponding to the low order Bragg angles of face centred cubic aluminium. The diffraction rings reveal only slight evidence of any preferred crystallite orientation. The specimen was considered to be a polycrystalline sample with no specific orientation. From directional isotropy

it was expected that the measured spectral momentum density would reach a value averaged over all crystal orientations, and depend only on the magnitude of the sampled binding momentum. Aluminium's band structure resembles that of the ideal free electron in a weak periodic potential (Ashcroft and Mermin 1976). In the first Brillouin zone the band map is approximately rotationally symmetric about $q=0 \text{ \AA}^{-1}$ (G point), so that the parabolic free electron dispersion relation should still be visible in the coincidence signal. The momentum density (Levin *et al.* 1972) in the ideal free electron case is nearly constant across the Brillouin zone until the the Fermi surface is reached where it drops rapidly to zero. This simple band structure should be clearly visible in the (e,2e) spectrum at the resolutions used here if the sample is pure.

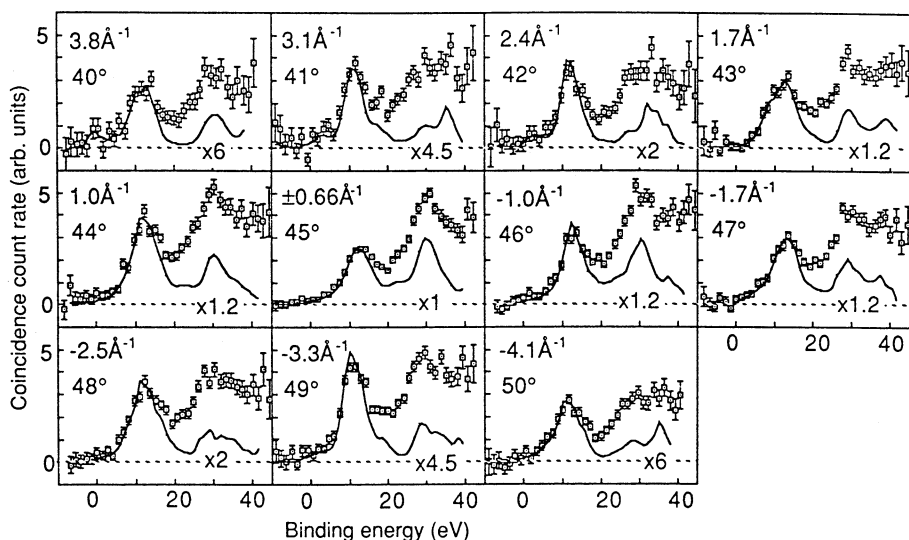


Fig. 3. Coincidence count rate as a function of electron binding energy at selected binding momenta. The full lines are the results of deconvoluting the theoretical single channel energy losses from the data.

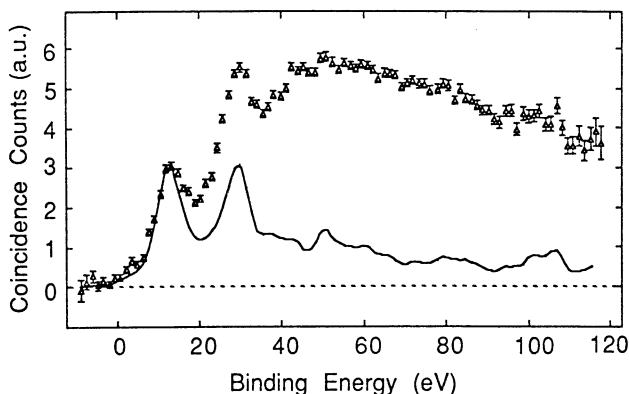


Fig. 4. Extended binding energy spectrum from a 130 Å aluminium film. The full line is the result of deconvoluting the single channel energy losses.

The results presented here have sufficient resolution to partially resolve valence band details of thin aluminium/aluminium oxide foils (Hayes *et al.* 1988). Previous experiments (Dey *et al.* 1987) and Persiantseva *et al.* (1979) using beam energies of 6 keV and 10 keV respectively could not employ binding energy resolutions better than 16 eV because of the poor coincidence count rates, which were mainly due to the reduction of signal through multiple scattering. The recorded momentum distributions do not allow a unique identification due to the complexity of the target, however, they reveal the need for at least two states in the valence band, separated by approximately about 20 eV.

The data in Figs 3 and 4 were recorded from one aluminium foil (130 ± 20 Å thick), and have been checked using other aluminium foils of equivalent thickness. The primary beam energy was 7.5 keV with the analysing system set at energy and momentum resolutions 4.5 eV fwhm and 1.1 Å^{-1} fwhm respectively.

The raw spectral momentum map shown in Fig. 3 was acquired in about one week by cyclically stepping through the binding momenta, periodically checking the $q = 0.66 \text{ Å}^{-1}$ spectrum for any time dependent behaviour. Two clear valence peaks appear in the binding energy spectra for $q = 0.66 \text{ Å}^{-1}$ at 13 and 31 eV. Again, single channel multiple scattering is visible in spectra with the second peak sitting on the rising satellite counts of the earlier binding energy state. This is more obvious in the extended binding energy loss spectrum of Fig. 3. For aluminium metal we would expect the bottom of the valence band to be located at about 12 eV, with no other state between it and the L shell states. By assuming that the first peak (13 eV) is from aluminium metal, the second maxima could be assigned to a sharp plasmon satellite. The short mfps for plasmon interaction makes this a real possibility (110 Å at 3.75 keV). The energy difference is close to the volume plasmon loss energy of 15.2 eV. From the raw data of angular correlations of the two peaks, we see that the first peak is dispersionless, within 1 eV over the momentum range, with a momentum distribution that has a local minima at $q = 0 \text{ Å}^{-1}$, i.e. P-like. The second band's momentum distribution, if it were a satellite, should have a momentum distribution that mirrors the first band. The second state does also appear to be dispersionless, however its S-like density distribution with a peak at $q = 0.66 \text{ Å}^{-1}$ and rapid decline for increasing q , discounts the possibility that this peak arises solely due to the plasmon interaction.

From the experimental spectral momentum density, the two states appear to correspond to the oxide component of the foil. The valence band for aluminium oxide, as mentioned earlier, divides into two bands with an overall oxygen-like character. From Ciraci and Batra (1983) and Balzerotti and Biaconi (1976), the upper band (lowest binding energy) is dominated by the influence of O $2p$ and, similarly, the lower band by the O $2s$ orbitals. The nearest neighbour coordination of amorphous alumina is strongly biased towards the rhombohedral structure of α -alumina (Balzerotti and Biaconi 1976). It is expected that the amorphous data presented would at least parallel this structure close to $q = 0 \text{ Å}^{-1}$. The theoretical details from the band calculations for α -alumina vary considerably (Kowalsky *et al.* 1977; Batra and Klienman 1984). Fig. 5 shows the theoretical band structure from Ciraci and Batra for α -alumina. The upper valence band is composed of a series of closely spaced bands which are relatively dispersionless. It splits into contributions from

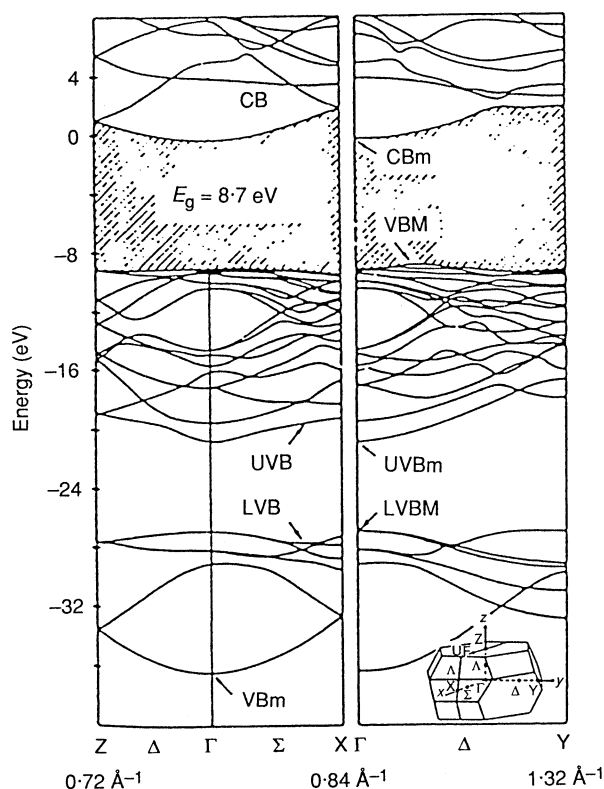


Fig. 5. Energy band map of α -alumina along high symmetry crystal directions from Ciraci and Batra (1983). The Brillouin zone is shown in the inset.

the O 2*p* lone pair orbitals (0 to 2 eV relative to the valence band maximum) and the hybridisation of the oxygen-aluminium orbitals (−2 to −6 eV), with the major component being the O 2*p* orbitals. There is a gap to the lower valence band, that again is composed of several relatively dispersionless bands from −16 to −19 eV. The lower valence band arises from the O 2*s* and Al 3*s* and O 2*s* bonding combinations. Studies such as XPS and XES (Kowalsky *et al.* 1977), put the centre to centre band separation at about 16 to 17 eV, which corresponds closely to the energy separation for this study.

The proximity of the satellite plasmon loss peak to the second band probably influences the measured magnitude of this state. To find its true intensity, the single channel energy losses have to be removed from the binding energy spectrum. First, a typical coincidence energy loss distribution was found through Monte Carlo simulation, then this distribution was deconvoluted from the data using the iterative van Cittert method. Typical single channel energy loss measurements are shown in Fig. 6. A check was performed on the lower energy parameters by simulating the energy loss spectrum at 0° and comparing it with the experimental spectrum. Fig. 7 shows reasonable agreement, with a slight discrepancy at zero energy loss, which is probably due to electrons leaking through the stress cracks around the edge of the foil or possibly a slight angular misalignment of the analyser.

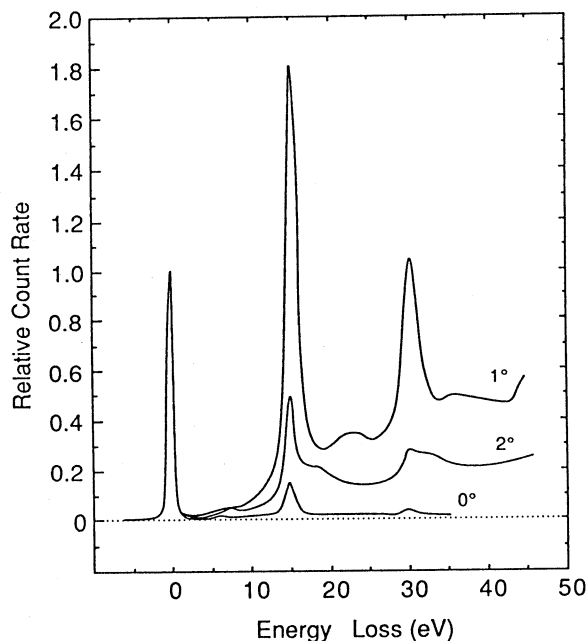


Fig. 6. Single channel energy loss spectra from a 120 Å aluminium film at scattering angles of 0°, 1° and 2° for an incident electron energy of 7.5 keV. All plots are normalised to the elastic peak intensity for a 0.8 eV fwhm. Relative to 0° the elastic peak intensity was 1.1×10^{-2} and 8.4×10^{-3} for 1° and 2° respectively.

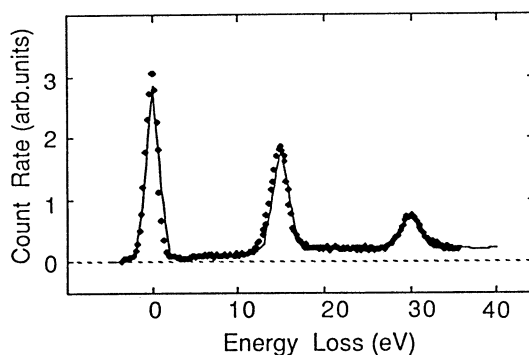


Fig. 7. Single channel energy loss spectrum for 3750 eV electrons transmitted at 0° through a 130 Å film. The line represents a Monte Carlo simulation of the loss processes within the film.

The full curve in Fig. 4 earlier is the result of deconvoluting the simulated background from the raw data. The two peaks are now of similar magnitude and located at 13 and 30 eV. The background, however, does not tend towards zero but slowly declines with increasing binding energies. The most likely reason for the nonzero background is an overestimate of the mfp values

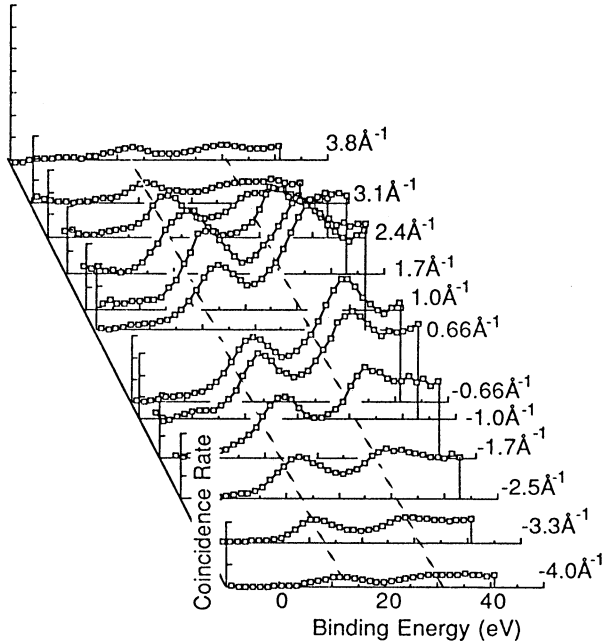


Fig. 8. Smoothed experimental spectral momentum data. The dashed lines indicate the 13 and 31 eV binding energies.

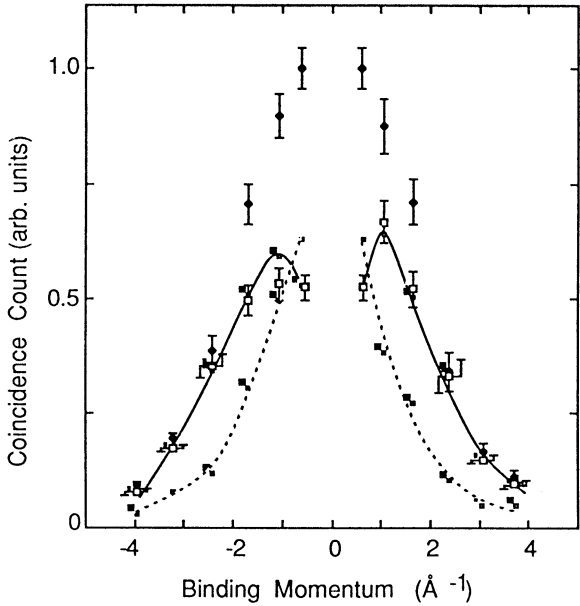


Fig. 9. Coincidence count rate as a function of binding momentum at 13 eV (open squares) and 31 eV (solid circles) binding energies. The 31 eV data after correction for the background, given in Fig. 4, are shown as diamonds. The amplitudes for the deconvoluted data are shown by the full and dashed lines respectively.

used in the simulation; in particular those of the oxide plasmon. The surface sensitivity of detected coincidence events tends to magnify the importance of the broad oxide plasmon at the exit side of the foil. By approximately halving the oxide plasmon mfps, the binding energy distribution becomes zero away from the valence band. The second peak's amplitude decreases by about 15%. The relative angular correlation of the lower band remains largely unaffected. The upper band intensity is not altered at all using adjusted mfps. There is minimal evidence, in either case, of the $L_{2,3}$ state in aluminium/aluminium oxide at 82 eV (Citrin *et al.* 1976).

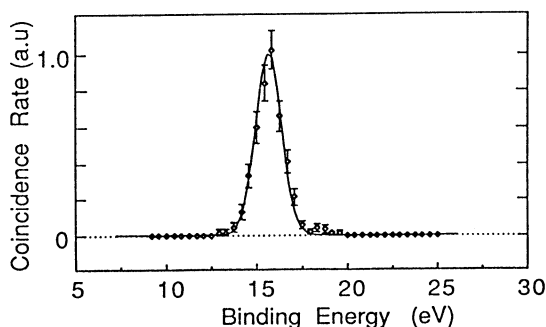


Fig. 10. Binding energy spectrum for the 3p argon ion state at 15.73 eV showing the instrumental energy resolution of 1.5 eV fwhm.

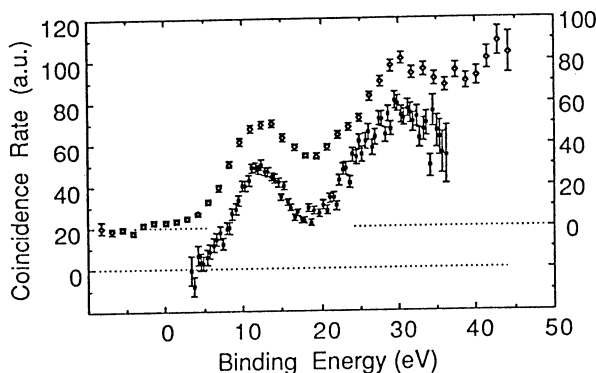


Fig. 11. Binding energy spectrum for a 130 Å film at a binding momentum of 0 Å^{-1} at energy resolutions of 1.5 eV (squares) and 4.5 eV (diamonds).

From the spectral momentum map of Fig. 3 the deconvoluted spectra show the same form as the raw data. The collected data have been redrawn in Fig. 8 for a comparison between different binding momenta. Fig. 9 is the amplitude plot of the two dispersionless bands as a function of binding momentum, to more clearly reveal the relative differences. The first, with a local minimum at $q = 0 \text{ Å}^{-1}$, appears to represent a P-like wavefunction which is consistent with this band being dominated by the O 2p, while the S-like behaviour of the

second agrees with this band being associated with the O 2s orbital. Neither of these peaks are consistent with the nature of the free electron structure of aluminium. The contribution to the spectra from aluminium metal, which is expected to be from about 4 to 12 eV, appears to be totally obscured by the strong oxide signal. The peak widths from the deconvoluted spectra are about 10 and 8 eV (fwhm) for the first and second bands respectively near $q = 0 \text{ \AA}^{-1}$.

To try and resolve further structure, a coincidence experiment was performed at the better binding energy resolution of 1.5 eV fwhm near $q = 0 \text{ \AA}^{-1}$, verified by the argon 3p state in the coincidence mode (Fig. 10). The momentum resolution was not altered. The aluminium result shown in Fig. 11 was, disappointingly, very similar to the poorer resolution data taken from the same foil, with the only notable difference being the minima at the centre of the two peaks declining to a slightly lower value. As mentioned earlier, the α -alumina upper valence band can be subdivided into two populations, approximately separated by 4 eV, that depend on different bonding characteristics. The first peak does not reveal this structure, which could be the result of several causes. The amorphous nature of the solid will mix several bands in the valence region. The variety of bonding schemes and potential defect states occurring near the surface may in addition be significantly altering the band structure (Batra and Klienman 1984). Aluminium metal coincidence events will also be detected in this region. The poor momentum resolution hinders this measurement by effectively averaging over the dimensions equivalent to the first Brillouin zone of α -alumina. Contamination of the foil, other than the oxide component, may be adding structure to this region.

In summary, the data obtained from the (e,2e) coincidence study of thin aluminium/aluminium oxide foils for the first time reveal two dispersionless bands at 13 and 30 eV. The lack of dispersion and the P-like and S-like momentum densities more closely correspond to the atomic-like behaviour of the oxide component of the prepared foil. Work is progressing in the direction of using higher incident electron energies to decrease the effects of multiple scattering and using better energy and momentum resolutions to better define the observed states.

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