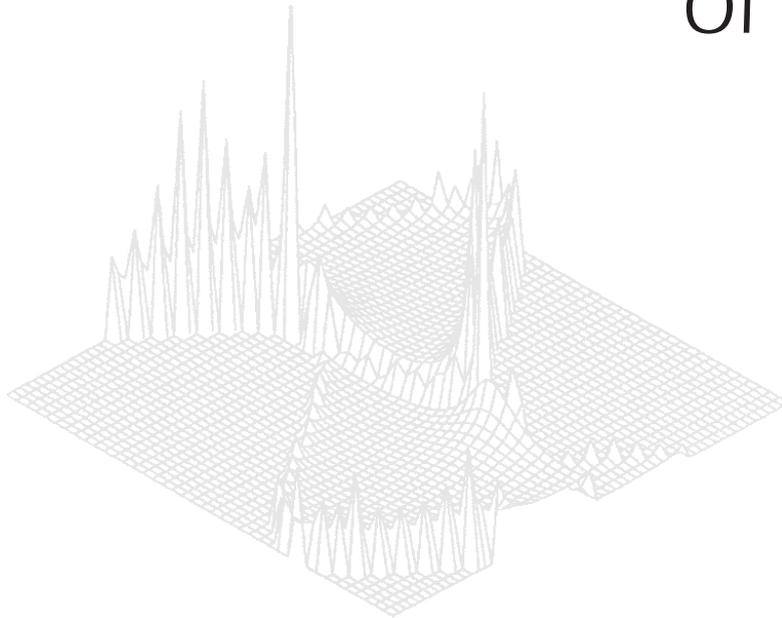

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Recent Developments in Electron Momentum Spectroscopy of Solids*

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Abstract

With the advent of two-dimensional electron detection, electron momentum spectroscopy of solids evolved from a spectroscopy in its infancy to a new, viable technique, looking for its place in solid state physics. Here I give an overview of the first sets of experiments, the evolution of the interpretation of these experiments and possible future directions.

1. Introduction, the Early Years

Electron momentum spectroscopy [EMS, also called (e, 2e) spectroscopy] is an electron scattering approach to the determination of the electronic structure of matter. Its principles are simple. An energetic incoming electron collides with a target electron and transfers a large fraction of its energy and momentum to this electron. This target electron becomes a free electron as well, and is detected in coincidence with the scattered electron. Both detected electrons are analysed for energy and momentum. From these results one infers the binding energy and momentum of the ejected target electron before the collision.

The first (e, 2e) experiments were done in Italy more than 25 years ago (Amaldi *et al.* 1969; Camilloni *et al.* 1972). A few things were clear from these early measurements. First the major experimental challenge is to obtain a useful count rate. High energies are necessary to assure that a significant fraction of the incoming beam has only one interaction [the (e, 2e) event] with the target. This in turn means small cross sections for the (e, 2e) event, and thus low count rates. The second fact that became obvious is that the experimental results are very rewarding, and provide direct information on the electronic structure of matter. In this first experiment the momentum distribution of the carbon 1s electrons was found to agree well with the calculations of an atomic C 1s level, and to be different from that measured for the valence electrons.

After this first experiment on solids, the EMS technique was applied to gas phase targets (Weigold *et al.* 1973). Here the density of the gas could be controlled easily and even for low energies multiple scattering was no serious problem. This led to a successful series of experiments on gases. Interpretation

* Dedicated to Professor Erich Weigold on the occasion of his sixtieth birthday.

of the experiment was developed, including many-body effects (McCarthy and Weigold 1991).

The success of the technique in the field of atoms and molecules made its application to solids again an important goal. In solid state physics the valence band region is of most interest, as its nature is thought to determine most properties of solids. Thus, in order to become a useful tool in solid state physics, the energy resolution had to be improved so one cannot only resolve the valence band from the core levels, but the structure of the valence band itself as well. This increase in energy resolution should not be at the expense of momentum resolution and/or measurement time, or at the energies of the particles involved,

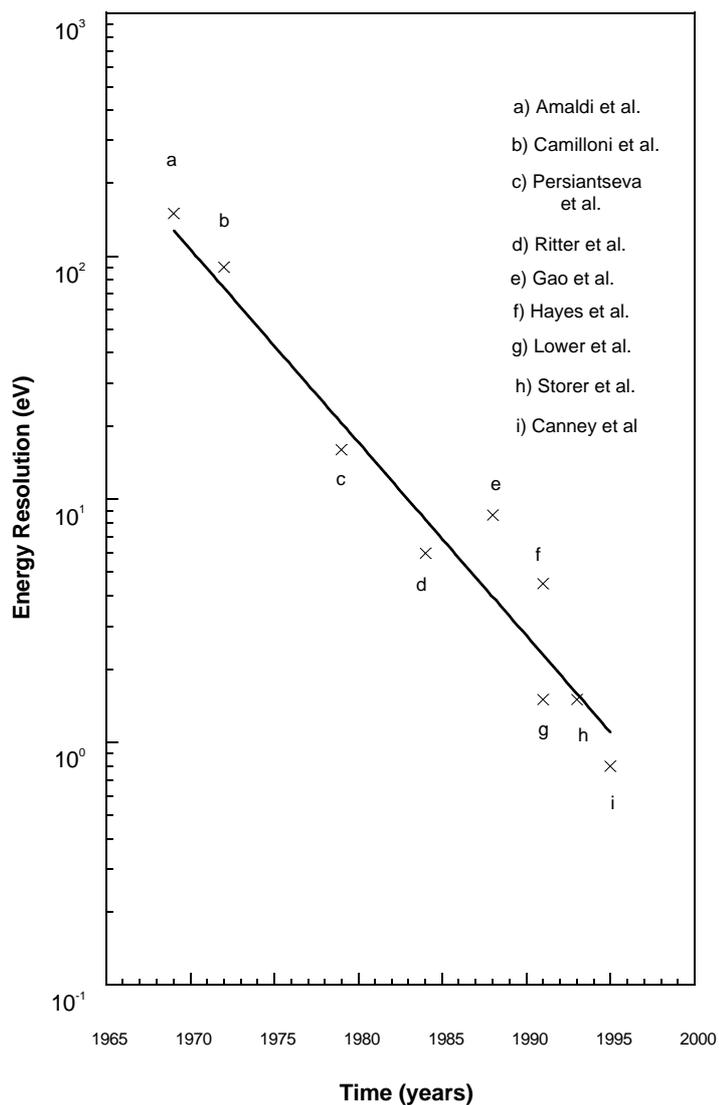


Fig. 1. The development of the energy resolution in solid state transmission EMS experiments with time.

which would increase multiple scattering. In Fig. 1 the evolution of the energy resolution with time is indicated. It is clear that quite a few groups contributed to the evolution of the spectroscopy. With the advent of two-dimensional detection at the Flinders University of South Australia (each of the two electron detectors measures a range of energies and momenta) energy resolution could be improved to about 1 eV (Canney *et al.* 1997c). Moreover, the data-collection time was reduced to typically 'just' two days.

At this point the nature of the field changed somewhat. The main emphasis shifted from spectrometer development to the measurement of different targets, and the interpretation of these measurements. The technique had to fulfil its promises, and show that indeed it could contribute to the understanding of the properties of solids. It is this part of the development that I want to describe here in some detail. More general introductions to this technique as applied to solids are given by Vos and McCarthy (1995, 1997).

2. Sample Preparation and Characterisation

The main hurdle in each EMS experiment on solids is sample preparation. The requirements are severe. The fabrication of a thin sample of thickness of around 100–200 Å, freestanding over an area of at least 0.3 mm diameter, with well known composition is no small feat. Moreover one surface has to be clean

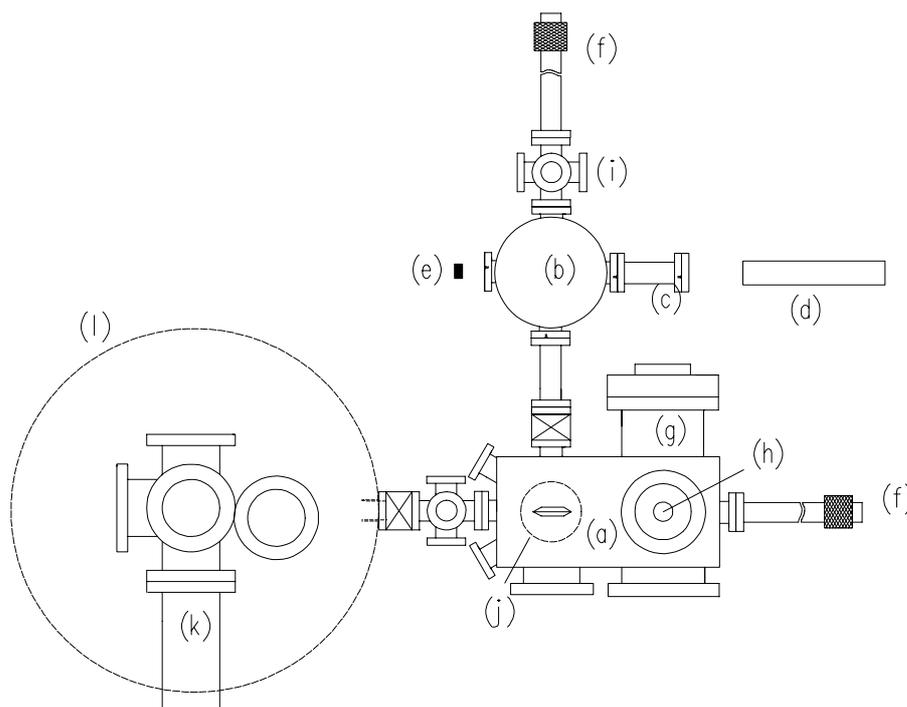


Fig. 2. Schematic top view of the sample preparation facility: (a) UHV preparation chamber, (b) (reactive) ion etching chamber, (c) ion gun, (d) laser, (e) photon detector, (f) transfer arms, (g) Auger system, (h) sample manipulator plus annealing facility, (i) sample viewing via optical microscope and load lock, (j) evaporator (from below), (k) transmission diffraction set-up, and (l) (dashed) circumference main spectrometer.

as, due to the a symmetric nature of the spectrometer, it is mainly sensitive to one side of the sample. Countless hours are spent in refining the sample preparation techniques.

In Fig. 2 we show a schematic representation of the facilities developed. It includes an (inert and reactive) ion beam etching facility with coaxial laser interferometer for simultaneous thickness determination, an Auger system for sample surface composition determination, a sample annealing set-up, an evaporation facility, and on top of the main spectrometer a transmission electron diffraction facility. On the main sample manipulator there is the possibility of rotating the sample around the surface normal of the sample, so it can be aligned using the diffraction set-up and transferred to the measurement stage in this alignment. In this way momentum densities can be determined along different crystallographic directions. The samples are inserted using a load-lock system, so one can maintain ultra-high vacuum (UHV) conditions in the preparation chambers. Sample transfer under UHV conditions from one chamber to the other is possible as well.

These facilities are necessary for the production of a range of high-quality targets. Samples successfully fabricated at Flinders include graphite and silicon single crystals, free standing films of copper, aluminum oxide and silicon/silicon oxide.

The only short-cut that sometimes works is evaporation. Due to the surface sensitive nature of the spectrometer a thin layer of evaporated material (on a thin carbon film) can dominate completely the EMS spectrum. However, the evaporated film should not form islands or react with the carbon film. Films fabricated in this way include Al, amorphous Si and C₆₀ films. For more information about sample preparation see Utteridge (1996) and Fang *et al.* (1997).

3. Understanding and Explaining the Results

Within a single-particle framework the understanding of an EMS experiment is in principle simple. An electronic structure calculation provides wave functions, usually in coordinate space, each with a certain binding energy. A Fourier transform results in a wave function in momentum space. The modulus square of the momentum wave function determines how much it contributes at a certain momentum value to the EMS spectrum. This all applies to atoms, molecules as well as solids. Indeed this uniform framework is one of the appealing aspects of the technique. The interpretation of the first single-crystal EMS results by Gao *et al.* (1988) were done along these lines, and (within a single particle model) there are no real doubts of its validity.

In Fig. 3 we show an example of how the momentum density of a molecule (H₂) evolves in a (linear) solid in computer calculations of hypothetical linear chains of hydrogen atoms. The interatomic distance in the chain is equal to that in a hydrogen molecule. The momentum density plotted is for the momentum in the direction along the axis of the molecule. Clearly, discrete levels become more and more closely spaced, with increasing chain length. At the same time the momentum density becomes more and more peaked around a particular value. The transition into a continuous band-like structure for a chain of infinite length is obvious from this model (Vos and McCarthy 1995).

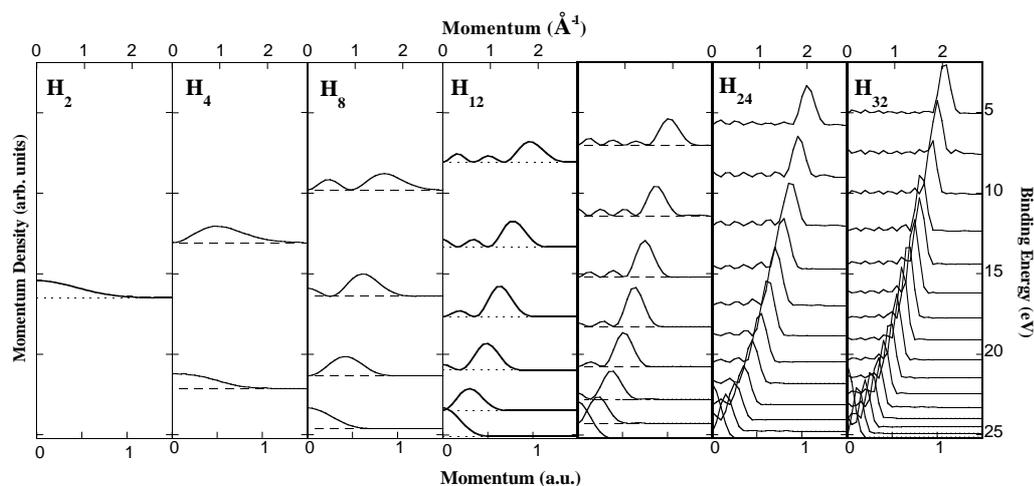


Fig. 3. A model calculation of the momentum densities for a linear chain of hydrogen atoms. The different orbitals are shifted vertically by an amount proportional to their binding energy (right axis). With increasing chain length the momentum distributions of the different orbitals change from that typical for molecules to a band-like picture typical for solids.

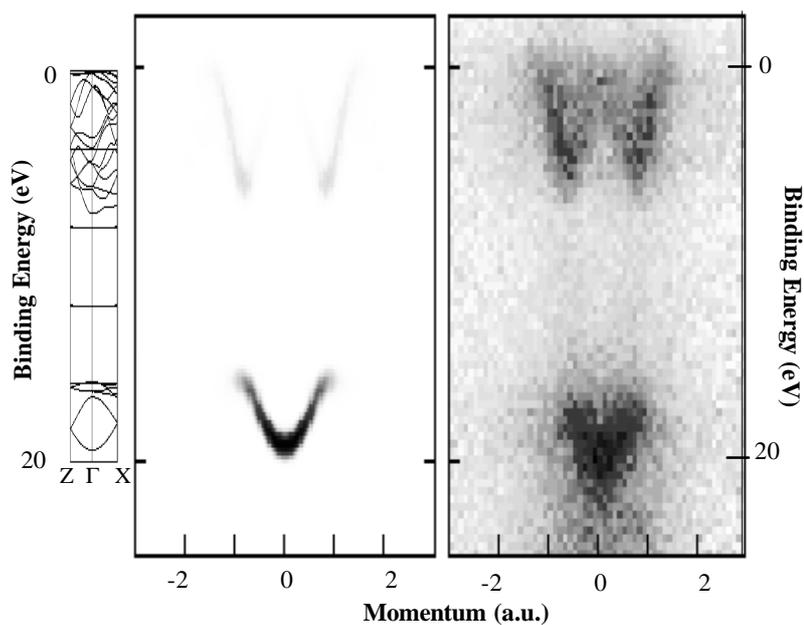


Fig. 4. Calculated and measured electronic structure of Al_2O_3 . In the left-hand panel the band structure is presented in the reduced zone scheme along two major symmetry directions. The centre panel shows the calculated spectral momentum density averaged over all crystallographic directions. The right-hand panel shows the measured intensity for an oxidised aluminum film. All binding energies are relative to the valence band maximum. All three plots have the same energy and momentum scale.

The main ‘problem’ is that until now most information of the electronic structure is obtained using photons (e.g. angle resolved photoelectron spectroscopy, see for example Hüfner 1995). These techniques determine the relation between binding energy and crystal momentum (dispersion). It is in this way as well that almost all electronic structure calculations are presented, and indeed crystal momentum is a good quantum number for a periodic solid.

The EMS technique measures real momentum. Is there any advantage in this? Let us as an example look at the data obtained by Guo *et al.* (1996) for an Al_2O_3 film (Fig. 4). Alumina is known to exist in various crystal forms, the most well known is $\alpha\text{-Al}_2\text{O}_3$. It has, compared to most pure elements, a relatively large unit cell (10 atoms) and low (trigonal) symmetry. Hence the Brillouin zone is rather small (from Γ to the critical points at the Brillouin zone boundary is of the order of 0.5 a.u.) and the band structure, as plotted in the reduced zone scheme, is rather complicated. There is intensity in two binding energy regions (upper and lower valence band) with up to 18 different bands contributing to the upper valence band.

As our samples were at best polycrystalline (and probably not pure $\alpha\text{-Al}_2\text{O}_3$) we calculated the spectral momentum density averaged out over all different directions of the unit cell. In spite of the polycrystalline averaging and the complicated band structure in the reduced zone scheme, the calculated spectral momentum density is of surprising simplicity. There are of course still two regions of intensity. The lower valence band has its maximum intensity at zero momentum, whereas the upper valence band has a minimum in its intensity here. This shows at once the different origin of the two levels. The lower valence band is mainly derived from the oxygen 2s level and the upper valence band from the oxygen 2p level. The intensity distribution as a function of momentum is still characteristic of that for the atomic 2s and 2p levels. The relation between the observed binding energy and momentum is typical for an s- and a p-derived tight-binding band (Vos and McCarthy 1997).

The experimentally observed intensities are plotted as well in Fig. 4. These are obtained from evaporated aluminum films exposed to oxygen in between evaporations. Although the contrast is less than in the calculations the similarity in shape and intensity between experiment and calculations is quite good. The decrease in contrast is due to multiple scattering, to be discussed later.

It is thus clear that the electronic structure appears more simple if plotted as a spectral momentum density, rather than as a traditional band structure, in the reduced zone scheme. In the case of the spectral momentum density the physical interpretation is more apparent as well. Of course the spherical averaging is not a necessary part of this procedure, it was just done because the sample was not available as an ultra-thin single-crystal form.

In the case of graphite, samples were available in a single-crystal form. Graphite is a layered material with a completely different bonding between the atoms in the plane and in between the planes

In the plane there is strong covalent bonding between atoms corresponding to the σ band. Perpendicular to the plane (i.e. along the c -axis) a carbon 2p atomic orbital (oriented along the c -axis) forms weak (van der Waals) bonding in between the planes. The corresponding band is usually referred to as π band. This orbital changes sign below and above the carbon plane, and hence has zero

intensity in the plane. In momentum space this translates to different signs of the wave function along the positive and negative p_c axis, and hence zero intensity for momenta with $p_c = 0$.

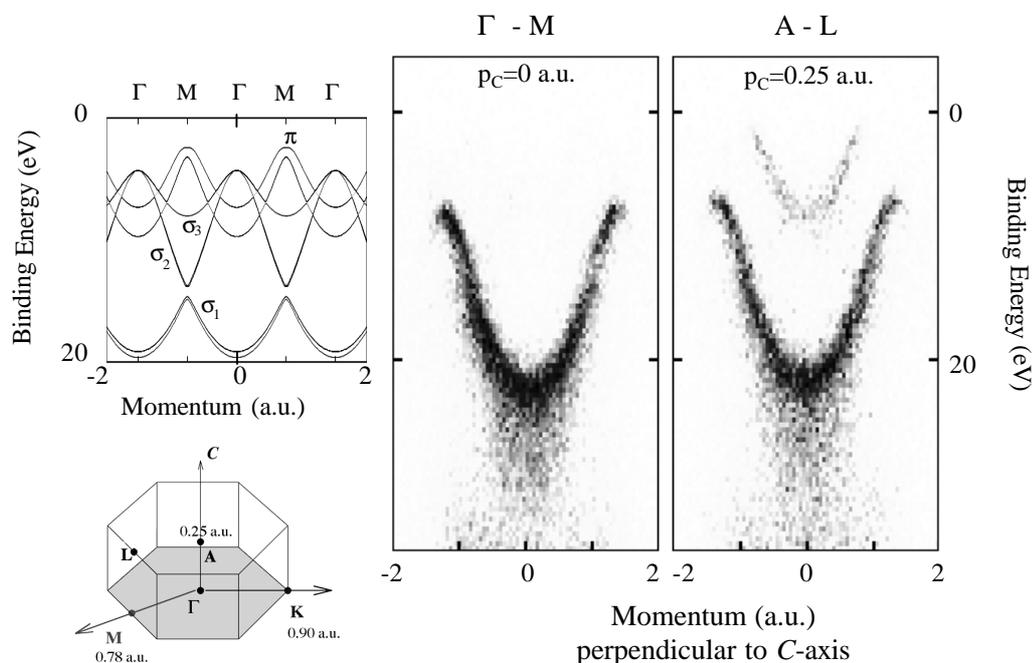


Fig. 5. Two different measurements of graphite single crystals. One measurement is from Γ to M , thus corresponding to electrons with momentum perpendicular to the c axis. The other measurement has a (fixed) component of the momentum of 0.25 a.u. along the c axis. It corresponds to the part of the band structure along a line from A to L . Also shown are the band structure in the repeated zone scheme, with the energy and momentum axis on the same scale as the experimental graphs, and in the top half of the first Brillouin zone.

In Fig. 5 we show the band structure along the $\Gamma - M$ direction in the repeated zone scheme. In the experimental measurement for this direction only a few of these bands contribute. From zero momentum (Γ) to 0.78 [M at the boundary of the (first) Brillouin zone] the σ_1 band contributes. From 0.78 to 1.56 a.u. (again a Γ point but one reciprocal lattice vector away from the origin) the dominating contributions are from the σ_2 band. There is no trace of either the σ_3 or π band in the measured intensity. Indeed it can be shown that these bands, assuming perfect alignment and infinite momentum resolution, should not contribute at all. If we change the scattering parameters of the experiment (in this case the energy of the incoming and scattered electron, as well as the angle of the slow electron detector), we can access the densities with 0.25 a.u. of momentum perpendicular to the graphite plane, i.e. we measure along the $A - L$ direction. This is shown in Fig. 5 as well (right panel). As the dispersion along the c -axis is minimal the shape of the σ_1, σ_2 structure does not change noticeably. However, now the π band becomes visible as well in the first Brillouin zone, as expected for measurements away from $p_c = 0$.

By rotation of the crystal we can compare more different crystallographic directions. Vos *et al.* (1997) showed that the differences in dispersion of the sigma bands along the ($\Gamma - M$ and $\Gamma - K$) directions agree well with the theoretically predicted ones.

Thus the spectral momentum density, both as calculated and as measured, contains information about which band has non-vanishing momentum densities in which Brillouin zone. Electron momentum spectroscopy is currently the only spectroscopy that can access this information.

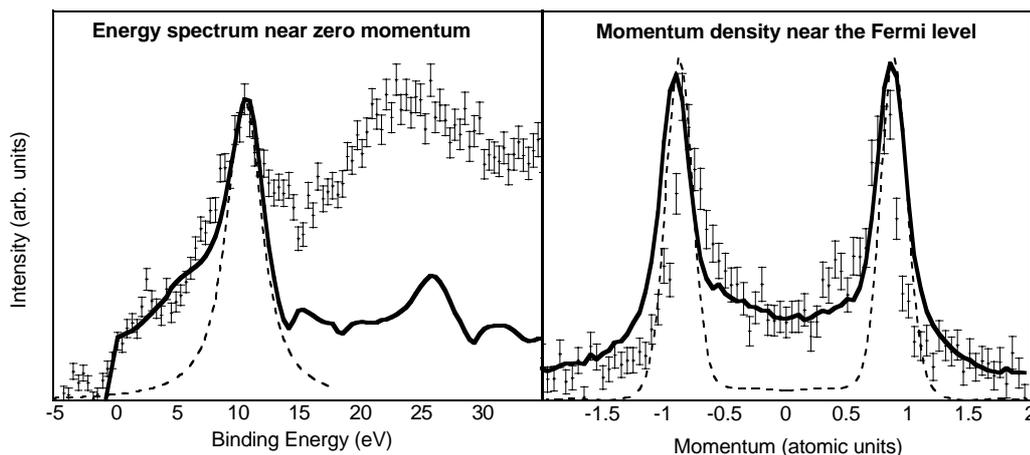


Fig. 6. Measured momentum density near the Fermi level, and a measured spectrum for an aluminum film at zero momentum. Error bars correspond to the experiment, dotted curves to the LMTO calculations, and full curves to LMTO calculations plus an estimate of the multiple scattering contributions using Monte Carlo procedures.

4. Multiple Scattering

In all cases presented above the calculations show more contrast than the experimentally obtained results. This is attributed to multiple scattering. By this we mean that in addition to the ($e, 2e$) collision, at least one of the electrons involved suffered additional scattering. If the additional scattering event was elastic (i.e. only a change in direction of propagation), the intensity will appear at a different momentum value and hence decrease the contrast. In the same way inelastic scattering (mainly plasmon creation) causes intensity to shift to lower binding energies. All these processes are well known and for energetic particles can be modelled quite accurately (Vos and Bottema 1996). This was done for the case of an aluminum metal film (Canney *et al.* 1997a). Results are shown in Fig. 6. The raw data show agreement with the band structure calculations as far as the peak positions are concerned. However, there is a lot of intensity in the experiment where the calculations predict zero intensity. This changes if we include the effect of multiple scattering experiments by doing Monte Carlo simulations. The band structure is used as input data to these calculations. If multiple scattering occurs in these simulations the contribution of the spectral momentum density is shifted along the momentum axis by the momentum transfer involved and along the energy axis by the energy losses involved. Simulating a

large number of trajectories we obtain the results shown as solid curves in Fig. 6. Agreement is very good near the Fermi edge, but at larger binding energies the measured intensity is still substantially higher than the calculated one. This could be due to the presence of an extremely thin oxide layer, that could form, even under UHV conditions, during the measurement. However, a systematic investigation of the oxidation of aluminum shows that the major oxygen-related features are not in this binding energy range (Canney *et al.* 1997b).

It is clear from these plots that multiple scattering is a very substantial effect. In principle it can be reduced by increasing the energy of the incoming and outgoing electrons. Efforts along this line are under way at the Australian National University. However, even in the present results the difference at large binding energies between the simulated and measured intensity is unlikely to be due to incomplete understanding of these scattering processes, and could be a failure of the one-particle theory of the electronic structure. Indeed theories that go beyond a single particle description predict substantial additional intensities at higher binding energy (Lundqvist 1968; Aryasetiawan *et al.* 1996).

5. Discussion and Outlook

Electron momentum spectroscopy would measure the spectral momentum density directly, if multiple scattering did not occur. However, multiple scattering can be modelled quite accurately, so its contribution to the measured intensity can be identified. The spectral momentum density is a very complete description of the electronic structure of a solid, and contains much information that is not contained in the traditional band structure plot. At the same time it appears more simple.

Near the Fermi level the energy resolution of EMS is still the limiting factor, but at larger binding energy the amount of detail that can be resolved is determined by the lifetime broadening of the energy levels that are a property of the solid. This is a consequence of the electron–electron correlation. The same electron–electron correlation is the origin of the excess intensity observed at high binding energy. In the theory these effects can be included by calculation of the spectral function (the imaginary part of the one particle Green function), rather than the one-particle band-structure calculations which include the electron–electron interaction only in an average way. It is expected that, especially if we can minimise multiple scattering further, these experiments can contribute to further development of theories in this area, in a way similar to developments in atomic and molecular physics in the past (McCarthy and Weigold 1991).

Acknowledgments

This paper summarises a few of the results of the Electronic Structure of Materials Centre which was funded by the Australian Research Council as a special research centre from 1988 to 1996. It could only be written because of the contributions of all people involved in this centre. On a longer time scale it is one of the fruits of research using electron coincidence techniques as pursued by Erich Weigold since the early seventies.

References

- Amaldi, U., Jr, Egidi, A., Marconero, R., and Pizzella, G. (1969). *Rev. Sci. Instrum.* **40**, 1001.
- Aryasetiawan, F., Hedin, L., and Karlsson, K. (1996). *Phys. Rev. Lett.* **77**, 2268.
- Camilloni, R., Giardini Guidoni, A., Tiribelli, R., and Stefani, G. (1972). *Phys. Rev. Lett.* **29**, 618.
- Canney, S. A., Brunger, M. J., McCarthy, I. E., Storer, P. J., Utteridge, S., Vos, M., and Weigold, E. (1997c). *J. Elect. Spect. Rel. Phenom.* **83**, 65.
- Canney, S. A., Vos, M., Kheifets, A. S., Clisby, N., McCarthy, I. E., and Weigold, E. (1997a). *J. Phys. C* **9**, 1931.
- Canney, S. A., Vos, M., Kheifets, A. S., Guo, X., McCarthy, I. E., and Weigold, E. (1997b). *Surf. Sci.* **382**, 241.
- Fang, Z., Guo, X., Utteridge, S., Canney, S. A., McCarthy, I. E., Vos, M., and Weigold, E. (1997). *Rev. Sci. Instrum.* **68**, 4396.
- Gao, C., Ritter, A. L., Dennison, J. R., and Holzwarth, N. A. W. (1988). *Phys. Rev. B* **37**, 3914.
- Guo, X., Canney, S., Kheifets, A. S., Vos, M., Fang, Z., Utteridge, S., McCarthy, I. E., and Weigold, E. (1996). *Phys. Rev. B* **54**, 17943.
- Hayes, P., Williams, J. F., and Flexman, A. (1991). *Phys. Rev. B* **43**, 1928.
- Hüfner, S. (1995). 'Photoelectron Spectroscopy: Principles and Applications' (Springer: Berlin).
- Lower, J., Bharathi, S. M., Chen, Y., Nygaard, K. J., and Weigold, E. (1991). *Surf. Sci.* **251/52**, 213.
- Lundqvist, B. I. (1968). *Phys. Kondens. Materie* **7**, 117.
- McCarthy, I. E., and Weigold, E. (1991). *Rep. Prog. Phys.* **54**, 789.
- Persiantseva, N. M., Krasil'nikova, N. A., and Neudachin, V. G. (1979). *Sov. Phys. JETP* **49**, 530.
- Ritter, A. L., Dennison, J. R., and Jones, R. (1984). *Phys. Rev. Lett.* **53**, 2054.
- Storer, P. J., Caprari, R. S., Clark, S. A. C., Vos, M., and Weigold, E. (1994). *Rev. Sci. Instrum.* **65**, 2214.
- Utteridge, S. J. (1996). PhD thesis, Flinders University, Adelaide (unpublished).
- Vos, M., and Bottema, M. (1996). *Phys. Rev. B* **54**, 5946.
- Vos, M., and McCarthy, I. E. (1995). *Rev. Mod. Phys.* **67**, 713.
- Vos, M., and McCarthy, I. E. (1997). *Am. J. Phys.* **65**, 544.
- Vos, M., Fang, Z., Canney, S., Kheifets, A., McCarthy, I. E., and Weigold, E. (1997). *Phys. Rev. B* **56**, 963.
- Weigold, E., Hood, S. T., and Teubner, P. J. O. (1973). *Phys. Rev. Lett.* **30**, 475.