

Elastic electron scattering at high momentum transfer: A possible new analytic tool

M. Vos*, M.R. Went

*Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering,
The Australian National University, Canberra 0200, Australia*

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Abstract

Recently it has become clear that for large-angle elastic scattering of keV electrons, the energy of the scattered electrons is reduced. This energy loss depends on the mass of the atom it scattered from, as well as its momentum. Hence, we can study the atomic composition of samples as well as their vibrational properties in momentum space. Here we present some examples of spectra obtained by this technique and discuss possible applications in the field of scanning electron microscopy.

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1. Introduction

Scattering of keV electrons (or photons) over large angles has long been used to study the electronic structure of materials, see e.g. [1]. Under these conditions the electron–electron collision becomes a binary collision and these collisions can be used to study electron momentum densities by measuring the energy loss of the scattered electron (so called Compton scattering experiments). When applying coincidence techniques these collisions form the basis of electron momentum spectroscopy, allowing for measurement of the complete spectral function. The power of these techniques is that they are based on the most elemental of physics: the laws of momentum conservation and energy conservation.

The subject of electrons scattering from nuclei over large angles has received much less attention (with pioneering work by Boersch et al. as a noticeable exception [2]). Again at large momentum transfer one has a binary collision between an electron and a single nucleus. Generally, it is (tacitly) assumed that the mass of the nucleus is infinitely large compared to that of an electron. Hence, it would follow that the scattered electron has the same energy before and after the collision. Of course the mass of the nuclei is finite and, as we will see, the small

energy loss of an electron scattering from a nucleus can be readily resolved, especially for the lighter elements. This realization has made a new class of experiments possible. We will give here a few examples that have emerged over the last few years. The aim of this paper is not to give an in-depth description of the underlying physics, but sketch the range of phenomena that can be studied in this new field. The application of this type of scattering to gas-phase molecules is described in a different contribution to this issue [3].

As the incoming and scattered electrons have (within a few eV) the same energy, the magnitude of their momenta is virtually unchanged, but the direction is not. The momentum transferred to the scattering atom is called q . Its magnitude is given by: $q = 2k_0 \sin \theta/2$ with k_0 the momentum of the incoming electron and θ the scattering angle. If the atom was stationary before the collision then the energy transfer is just $q^2/2M$ with M the mass of the atom. Some examples of calculated energy transfers are given in Table 1. In our spectrometer there is a small ambiguity in the zero point of the energy scale. Thus the exact energy loss in a collision is hard to determine, but one can determine very well the difference in energy loss for scattering from atoms with different masses. For convenience the spectra shown in this paper are aligned in such a way that the main peak coincides with the corresponding value of $q^2/2M$.

Generally, the atoms are not stationary. The momentum of the atoms in molecules and solids is generally not well described by classical thermal physics ($(1/2)kT$ energy per degree of

* Corresponding author. Tel.: +61 2 6125 4985.

E-mail address: Maarten.Vos@anu.edu.au (M. Vos).

freedom) but has to be described using quantum physics. For example in the case of protons bonded to carbon, one calculates the wave function of the particle in its potential using the Born–Oppenheimer approximation. The modulus-square of the Fourier transform of this wave function would be proportional to the momentum density of this proton. In the case of a crystalline solid with N atoms there are $\simeq 3N$ phonon modes. In the low temperature limit all phonons are in the ground state with energy $(1/2)\hbar\omega$. Half of this would be kinetic energy from which a corresponding momentum distribution can be obtained.

For scattering of an electron from an atom with momentum p one obtains the energy transfer:

$$E_r = \frac{(\mathbf{q} + \mathbf{p})^2}{2M} - \frac{p^2}{2M} = \frac{q^2}{2M} + \frac{\mathbf{q} \cdot \mathbf{p}}{M} \quad (1)$$

The first term is a shift, the second term is Doppler broadening due to the vibrations of the nuclei. In these studies the following questions arise:

- Can we separate the signal of two nuclei with different mass? and if so: is the energy separation as predicted by Eq. (1), and do we understand the ratio of the intensity of the signals?
- Can we resolve the Doppler broadening, and if so, do we understand the amount of Doppler broadening?
- Is the naive picture, sketched above, in which we assume that the collision between electron and nucleus can be described as the collision between a free electron and a free nucleus correct?

Rather than discuss any of these questions in detail, we illustrate our current experimental capabilities and understanding by presenting some examples. References to more detailed discussions are given, where available.

2. Examples

The first example we want to give here is the separation of carbon and hydrogen. As is clear from Table 1 this experiment requires only limited energy resolution. Our first observation of a separate hydrogen peak was done in a transmission experiment [4]. Varga et al. showed that these experiments can be done as well in a reflection mode at 2 keV [5]. Here we show data for polyethylene $(-\text{CH}_2-)_n$ (using ordinary household low density polyethylene wrap), taken at higher energies, again in

Table 1
The energy loss (eV) of electrons scattered elastically from some common elements, given for two scattering angles and incoming energies

	45°		120°	
	15 keV (48.4 Å ⁻¹)	40 keV (79.9 Å ⁻¹)	15 keV (109.5 Å ⁻¹)	40 keV (180.9 Å ⁻¹)
H	4.89	13.3	25.0	68.4
C	0.41	1.11	2.08	5.70
Si	0.17	0.48	0.89	2.44
Ar	0.12	0.33	0.52	1.71
Cu	0.08	0.21	0.39	1.05
Au	0.02	0.07	0.13	0.35

q -values are given in parenthesis.

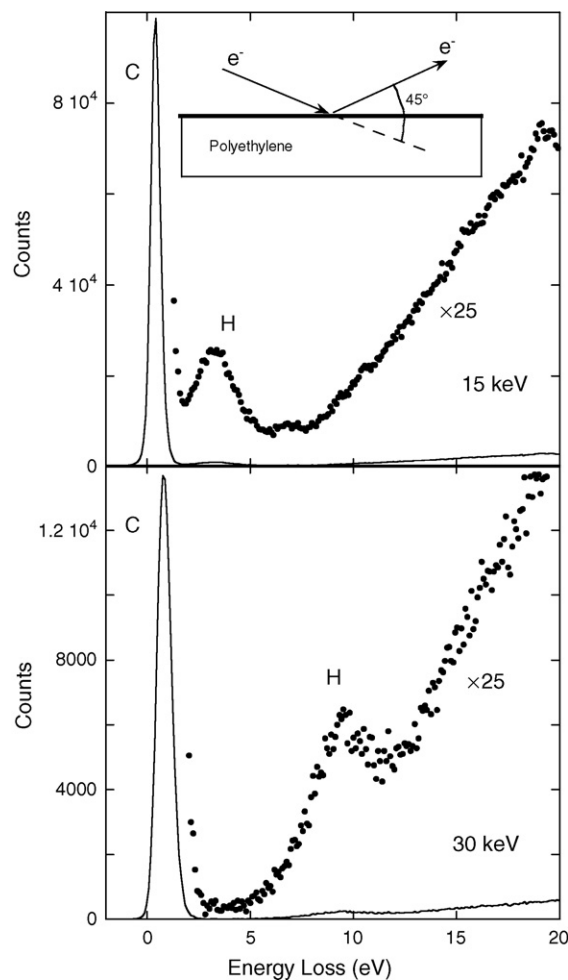


Fig. 1. Spectra obtained at 15 keV and 30 keV from a polyethylene film.

reflection mode (Fig. 1). Clearly there are two peaks visible. The main peak, near 0 eV, attributed to carbon, and a much smaller peak, at larger energy loss values (3 eV for 15 keV, 8 eV for 30 keV measurement). This peak is attributed to hydrogen. The separation is much larger at 30 keV compared to 15 keV. This would not be the case if the second peak was due to inelastic excitations (e.g. plasmon excitation). These inelastic excitations do occur and give rise to the background under the hydrogen peak. The shape of this background is in first approximation independent of the energy of the scattered particle.

In contrast to the transmission measurements using thin films, the separation of the hydrogen and carbon peak is, especially for the 15 keV case, significantly smaller than the separation calculated from Eq. (1). This is attributed to charging of the polyethylene caused by the impinging beam. Hence the electrons are decelerated approaching the film, scatter at an energy smaller than 15 (30) keV and accelerated again leaving the film. Thus, the charging does not affect the resolution, but changes the separation. Indeed measurements using smaller beam currents showed an increase in the separation of the carbon and hydrogen peak.

Hydrogen is more easily detected at 15 keV compared to 30 keV. The hydrogen peak is broader at 30 keV due to the larger Doppler broadening. Also at 30 keV the hydrogen signal is at energies where there exist significant intensity from electrons

that have scattered elastically from carbon, and have lost some energy due to inelastic multiple scattering (electron hole pair creation, plasmon excitations, etc.). As we will see the fact that better results are obtained at lower scattering energies is quite specific for hydrogen. In most other cases the analysis of sample composition is best done in experiments with the highest attainable momentum transfer.

The strong Z dependence of the elastic cross-section implies that the hydrogen signal will be much weaker than the carbon signal. Classically, extremely large momentum transfer collisions correspond to small impact parameter collisions. For sufficiently small impact parameters screening of the nuclear charge by the atoms own electrons becomes insignificant and the cross-section approaches the Rutherford one, i.e. it is proportional to Z^2 . The same behavior is obtained from a proper quantum treatment of the scattering (see e.g. [6]). Thus, as there are two hydrogens per carbon in polyethylene we expect the hydrogen signal to be $6^2/2 = 18\times$ weaker than the carbon signal. In reality, it is even weaker. Quantitative analysis was not done for these house-hold quality polyethylene films. For details in the case of transmission experiments see extensive discussions elsewhere [7,8].

If we want to study systems with heavier elements then it is clear from Table 1 that this is best done at higher energies (or, even better, larger scattering angles). First we discuss two 40 keV transmission experiments at 45° scattering angle using thin, free-standing carbon films. Now we use the Z dependence of the cross-section to our advantage, to detect a relatively small number of high Z atoms on the carbon film. One 100 Å thick C film was sputter-thinned using 600 eV Ar^+ ions. Both sides of the free standing film were bombarded with Ar^+ ions for approximately 5 min. On another similar film we evaporated a thin (nominally 1 Å thick) Au layer. Both samples showed clearly that the elastic peak was composed of two different components; a broad peak at 1 eV and a sharper peak at smaller energy loss. For the case of the sputtered carbon film, the sharp peak at small energy loss is attributed to Ar implanted in the thin film. Similar data were obtained by the Debrecen group for Kr implanted in C [9]. In the Au case the separation of the two peaks is 0.9 eV, slightly smaller than expected according to Eq. (1). This discrepancy seems to be quite reproducible. In a series of experiment using films of different thicknesses and measurement geometries we always obtain values of the separation of C and Au that are 0.05–0.1 eV too small [10]. This discrepancy should be understood if one wants to use peak separation as a mean to identify the scatterer. The Ar–C separation is somewhat smaller than the Au–C separation, in line with the fact that Ar is lighter. Indeed it is in good agreement with the expectations based on Eq. (1).

It is also obvious from Fig. 2 that the width of the carbon component is larger than the width of the Au and Ar components. Thus the Doppler broadening is well resolved for carbon. We explored this fact for graphite in more detail [10]. In highly oriented pyrolytic graphite (HOPG) the graphite sheets are all aligned. The atoms are bonded strongly within the sheet, whereas the interaction between atoms in different sheets is much weaker. Due to the strong bonding of the carbon atoms in the sheet they are well localized in coordinate space. As a

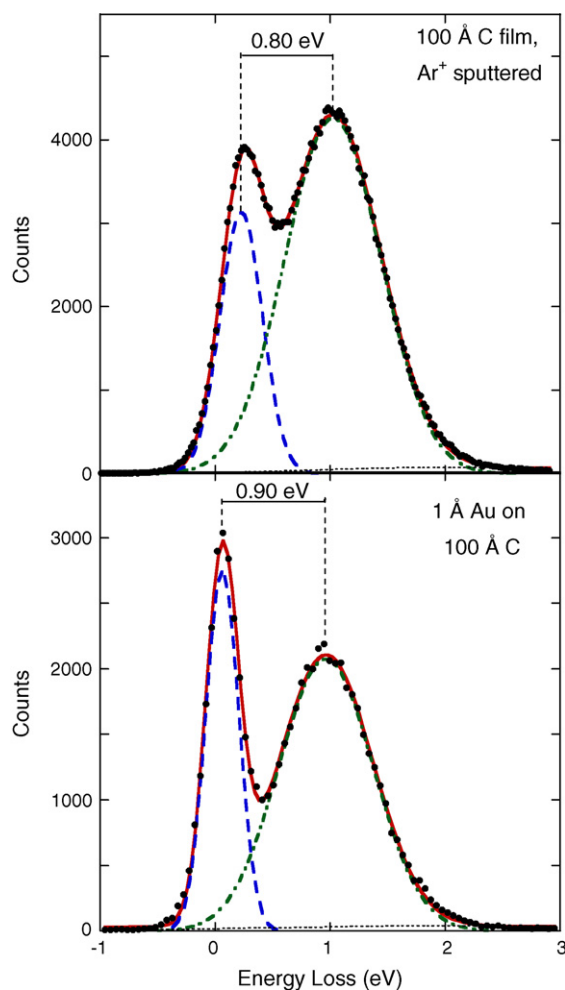


Fig. 2. Spectra obtained for 40 keV electrons scattered over 45° from a 100 Å thick carbon film after ion bombardment (top) and after deposition of 1 Å of Au. In both cases the elastic peak consists of two components.

consequence (Heisenberg uncertainty principle) the wave function in momentum space is delocalized, and a broad peak is expected if \mathbf{q} is directed along the sheets. Perpendicular to the sheets the potential well is broader causing delocalization in coordinate space, and hence a narrower distribution in momentum space. The elastic peak is thus expected to be relatively narrow if \mathbf{q} is perpendicular to the graphite sheets. This comparison can be done by inspecting a transmission spectrum and a reflection spectrum, as shown in Fig. 3. Indeed a clear difference in width is obtained. Studies of amorphous carbon films of different thicknesses show a much smaller dependence of peak width on sample thickness and measurement geometry. Thus the observed difference cannot be explained by different degrees of multiple scattering in both geometries. Indeed the observed widths for HOPG are basically consistent with those obtained from calculated phonon spectra and neutron Compton measurements [11]. Careful inspection of these spectra, especially of the transmission case with \mathbf{q} along the graphite planes, reveal an asymmetry. The spectra are sharper at the low energy loss side. Such effects are known, again from neutron Compton scattering, and are due to failure of the impulse approximation [12]. Here the fact reveals itself that the carbon atom is bonded to its

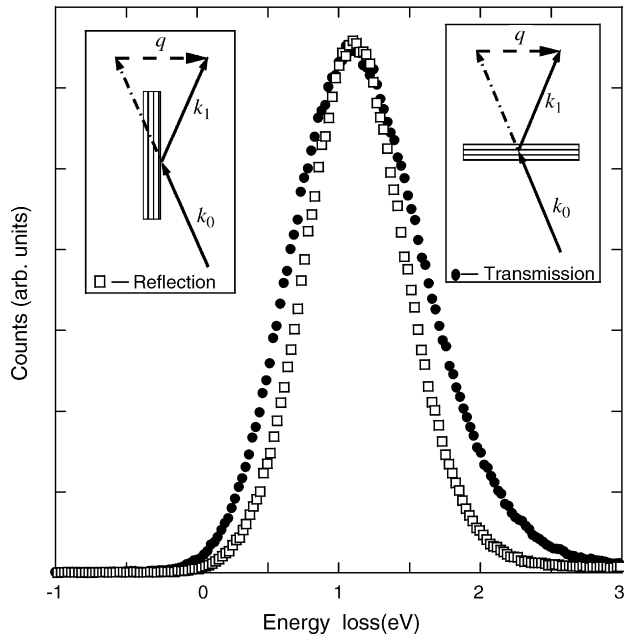


Fig. 3. Spectra obtained at 40 keV for a HOPG film in different orientations, as indicated in the insets. The peak observed with q along the graphite sheets is much broader than the peak observed with q perpendicular to the sheets. This reflects the anisotropy of the momentum distribution of carbon atoms in this layered material.

neighbors, and the limitations of the model treating the collision as a collision between free particles (impulse approximation) become evident. A similar asymmetry is found in low energy X-ray Compton scattering from electrons (the so called Compton defect, see e.g. [13]) and this asymmetry is also attributed to a failure of the impulse approximation (here the electron, from which the photon scattered, does not quite act as a free particle). This is a nice illustration that similar physics applies to completely different scattering experiments.

Finally we want to show the dramatic effect of changing the scattering angle. Very recently another electron gun was added to our spectrometer, and now experiments can be done at a scattering angle of 120° . Fig. 4 shows the very first result, at 40 keV, obtained with this gun. Again the target system is 1 Å thick Au layer deposited on C. The C and Au peaks are now completely separated, and the energy splitting is 5.43 eV, in good agreement with the value of 5.35 eV calculated using Eq. (1). Clear indications of two separate peaks is obtained, at a few nA beam current, in seconds. We think therefore that this technique has great potential for compositional thin film analysis in a scanning electron microscope. To illustrate the analytical potential we moved the electron beam from the carbon film to its supporting stainless steel shim, resulting in the spectrum shown as an inset. A Au signal (as of course Au was evaporated at the shim as well) is still clearly visible as a shoulder next to the main signal of the shim.

For a quantitative interpretation, one has to understand what determines the relative strength of the signals that make up the spectrum. The Au signal is determined by its differential elastic cross-section. The same is of course true for carbon, but for car-

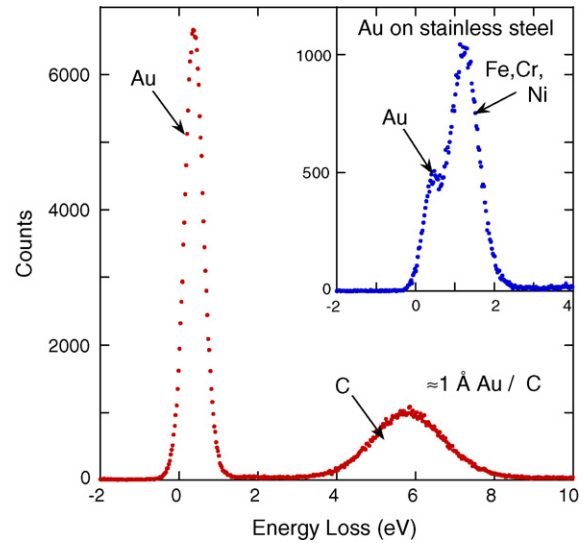


Fig. 4. Spectrum of a 1 Å Au layer on a thick carbon (main plot), as well as Au deposited on stainless steel (inset). The beam energy was 40 keV and the scattering angle 120° .

bon atoms located at a significant depth the contribution to the elastic peak is decreased by the probability that inelastic scattering occurred along the incoming or outgoing trajectory. Thus the depth that contributes to the carbon signal is roughly of the order of the inelastic mean free path (about 400 Å at 40 keV electrons in C). In a scanning electron microscope there are currently two techniques used for obtaining sample composition: scanning Auger microscopy (SAM) and EPMA (electron probe microanalysis), detecting emerging X-rays from a sample. The first technique detects low energy Auger electrons (typically a few 100 eV) and is hence very surface sensitive (probing depth ≈ 10 Å). EPMA detects the X-rays that are generated along a large fraction of the trajectory of the incoming electron. This limits its spatial and depth resolution to about 1000 Å. The lateral resolution of the current elastic scattering technique is determined by the probe size. The depth resolution is determined by the geometry and energy used, but will generally be in between that of EPMA and SAM. Thus it is quite possible that this technique can be developed in a thin-film analytical technique, helpful in analyzing sample composition at a depth scale of about 100 Å.

3. Conclusion

Scattering of electrons with keV energy over large angles has long been used to study the electronic structure. Now, due to improved resolution, it becomes clear that electron scattering can be used as well to study properties of atoms that are part of a solid or even just part of a molecule. In both the electron and atom case, interpretation is simple at high energies due to the plane-wave impulse approximation: the collision appears to be between two free particles. Scattering of electrons from atoms, as sketched in this paper, is still in its infancy. However, elastic scattering is a relative strong signal (even at these large scattering angles), and possible applications in, for example, scanning electron microscopy appear a realistic possibility.

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