

1982

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Jouffrey, Bernard (1982) "Electron Scattering and Energy Losses as a Function of the Incident Energy: Application to Chemical Analysis," *Scanning Electron Microscopy*: Vol. 1982 : No. 1 , Article 20.

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ELECTRON SCATTERING AND ENERGY LOSSES AS A FUNCTION OF THE INCIDENT ENERGY: APPLICATION TO CHEMICAL ANALYSIS

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Abstract

This paper gives a rapid overview on the use of the energy losses suffered by an incident electron beam. General approximations are remembered. Then some recent results on inner shell excitations as a function of energy (in high voltage electron microscopy) are given, and the problem of thick samples is rapidly discussed.

The problem of the observation of sensitive materials in electron microscopy is discussed. A simple model is proposed to determine some orders of magnitude on the inelastic mean free path and the elementary volume of defects created during the irradiation with electrons of different energies. This model can be used to have an idea of the evolution, as a function of time, of the number of characteristic electrons which have suffered a loss corresponding to an inner shell excitation. So it seems possible, when the cross section corresponding has been determined, to know an approximate variation of the characteristic electrons of the unperturbed structure of the sensitive samples.

Introduction

The idea of using energy losses in a purpose of chemical analysis is rather old since it was proposed by Ruthemann (1942, 1948) and Hillier and Baker (1944). Later on Watanabe observed the Beryllium K edge (1966). After the independent works of Wittry et al. (1969) on carbon in the 1970's, and Colliex and Jouffrey (1970, 1972) on Li, C, Al, Mg, Si, Cu and condensed rare gases (Jouffrey, 1975), it appeared that these characteristic losses could be practically used for chemical analysis. Isaacson (1972) performed experiments with a scanning transmission electron microscope (STEM) and Isaacson and Johnson (1975) published a review on this method. More recently, Egerton (1975), Jouffrey and Sèvely (1976), Colliex et al. (1976), Joy and Maher (1977, 1981) and others have published many results showing the interest and the difficulties of this type of chemical analysis.

In this field, many questions have been discussed. One of them is the problem of increasing the energy of incident electrons. For that purpose, we have essentially used our 1.2 MeV microscope. We have also been constructing, for a few years, a high voltage STEM (1.6 MeV) with field emission gun. Until now only a few experiments have been performed on energy losses with our 3 MeV microscope.

The first idea of using high energy incident electrons was based on the fact that the increasing of the observable thickness would be of interest, the other that the collection of characteristic electrons would be easier.

We shall give a few results obtained in this field. We shall discuss also, very briefly, the general treatment of cross sections before giving some results on the problem of sensitive materials.

Spectrometers

We have used, until now, three kinds of spectrometers: a) The Castaing-Henry filter up to 100 keV (Castaing and Henry, 1962); b) A magnetic $\pi/2$ spectrometer type on our 1.2 MeV (Sèvely et al., 1973; Perez et al., 1975) (Fig. 1) and 3 MeV microscopes (Fig. 2) (Jouffrey, 1978; Sèvely et al., 1982). The 3 MeV spectrometer is followed by two lenses to magnify the spectrum; c) An Ω filter on the 1.2 MeV microscope (Fig. 3) (Zanchi et al., 1975, 1977; Sèvely et al., 1977; Jouffrey, 1978; Zanchi, 1978).

KEY WORDS: Electron scattering, High voltage, Chemical analysis, Inner shell excitations.

List of Symbols

A	: Amplitude of the diffracted wave	$\Delta \vec{r}_z$: Displacement of the "cells" in the z direction
a_0	: Bohr radius	$\overline{\Delta r_{xp}^2}$: Square average displacement in the x direction (p is for perturbed and np for nonperturbed)
c	: Velocity of light	S	: Irradiated surface of the sample
D_{cr}	: Critical dose	\vec{S}	: Excitation error (vector defining the diffraction conditions)
E_0	: Fundamental energy level	T_a	: Absolute temperature
E_1	: Kinetic energy of the valence electrons	T	: $(\hbar^2 q^2)/2m$
E_i	: Incident energy	U	: Activation energy
E_n	: Energy of the n^{th} atomic level	v	: Speed of the electrons
ΔE_B	: Energy loss corresponding to the background before the edge	v_0	: Elementary damaged volume
ΔE_e	: Elementary energy loss	v'	: Speed of the electron after the collision
ΔE_I	: Mean ionization energy	Z	: Atomic number
ΔE_i	: Mean energy loss corresponding to the mean free path λ_i	z_1	: Thickness of the sample
ΔE_K	: Energy loss corresponding to the excitation of a K electron	z_0	: Initial thickness of the sample
ΔE_{on}	: $E_n - E_0$	β	: v/c
e_1	: Charge of the incident electron	γ	: $1/\sqrt{1 - \beta^2}$
e_2	: Charge of the knocked on particle	ϕ_0	: Incident flux of electrons
$F_{on}(\vec{q})$: Oscillator strength	λ_{el}	: Mean free path corresponding to the elementary loss
f_{on}	: Generalized oscillator strength	λ_e	: Elastic mean free path
$f_x(\vec{q})$: Form factor	λ_i	: Inelastic mean free path
\vec{g}	: Diffraction vector	λ_K	: Mean free path corresponding to the K excitation
I	: Intensity corresponding to the scattered wave	ν_0	: Characteristic frequency
I_0	: Incident intensity	σ_i	: Inelastic cross-section
I_0'	: $I_0(z_0/\lambda_e)$	σ_{on}	: Inelastic cross-section corresponding to the excitation $0 \rightarrow n$
\vec{k}	: Wave vector	θ	: Scattering angle
m	: Rest mass of the electron	θ_0	: Screening angle
m_r	: Reduced mass	θ_B	: Bragg angle
N	: Number of intact elementary volumes	θ_E	: Characteristic angle corresponding to the mean ionization energy
N_s	: Number of scattering centers by unit volume	θ_G	: Mean scattering angle
N_0	: Number of small elementary volumes per unit volume	θ_i	: Single deviation corresponding to a given excitation
P	: Probability of rearrangement	θ_K	: Single deviation corresponding to a K excitation
$P_B(n)$: Probability of n excitations corresponding to the background	θ_{on}	: Characteristic angle corresponding to the excitation $0 \rightarrow n$
$P_K(1)$: Probability of the event of one K excitation	ψ_0	: Wave representing the initial state of the atom
\vec{q}	: Scattering vector	ψ_n	: Wave representing the final state of the atom
\vec{r}	: Position of cells		
\vec{r}_i	: Position of the i^{th} electron		
\vec{r}_j	: Position of the j^{th} electron		
$\Delta \vec{r}_x$: Displacement of the "cells" in the x direction		

Energy Losses as a Function of the Incident Energy

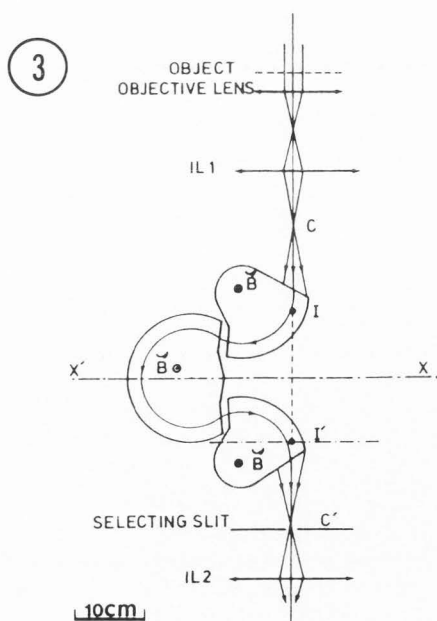
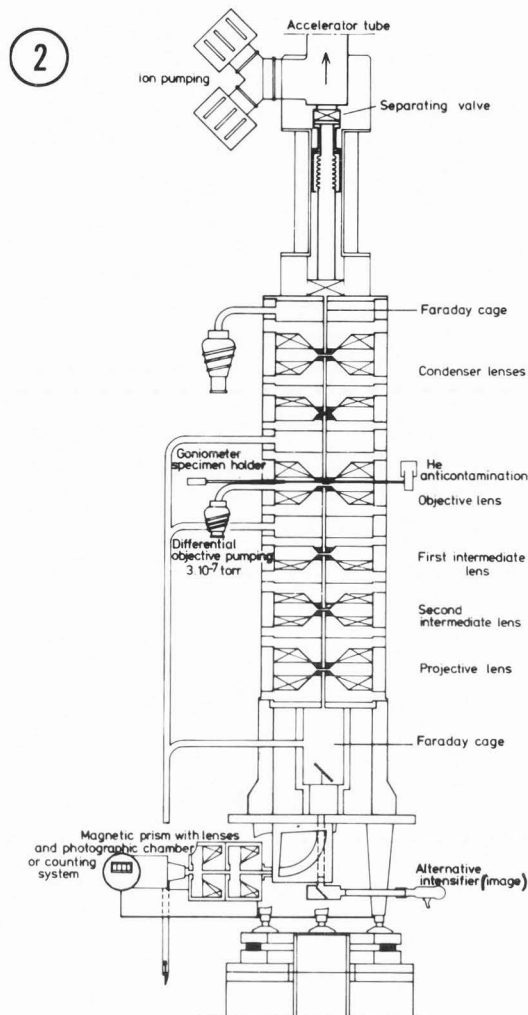
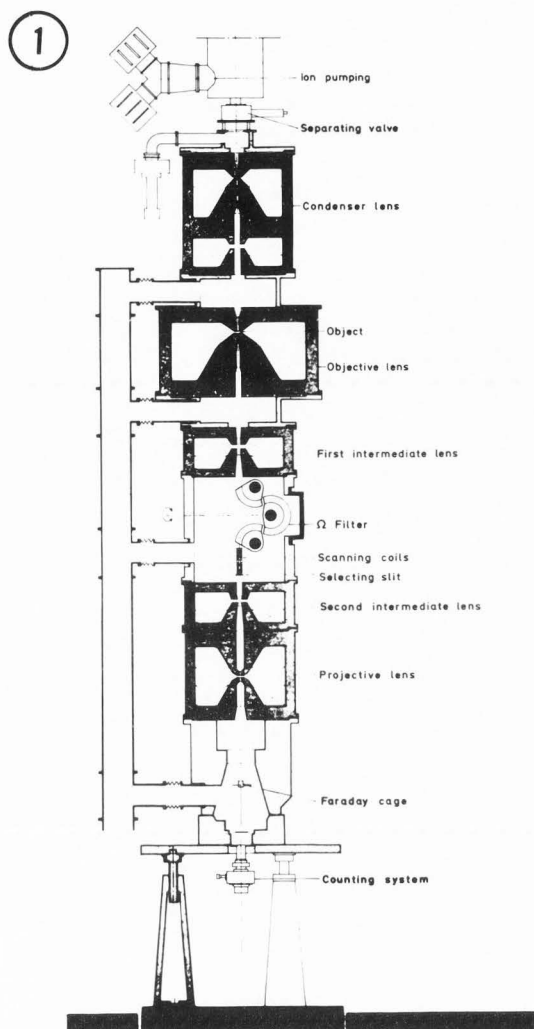


Fig. 1. 1.2 MV electron microscope with filtering device.

Fig. 2. 3.5 MV electron microscope with a $\pi/2$ spectrometer.

Fig. 3. Drawing of the Ω system. C, C' and I, I' are pairs of conjugate points. The system is stigmatic. Moreover the point I' is achromatic. B represents the magnetic fields. The intermediate lens IL1 transports with the help of the objective the crossover in C and the image in I. The spectrum is at the level of C'. Taking I' as object, for the second intermediate lens IL2, and choosing the loss by the selecting slit enables one to get a filtered image.

This type of attachment will before long be adapted on a 100 kV instrument (Sévely et al., 1977). The idea of the Ω filter was inspired by work of Senoussi (Senoussi, 1971; Senoussi et al., 1972).

We refer to previous publications for the description of these attachments. In Fig. 4 is shown a spectrum obtained at 1 MeV for different thicknesses of aluminium. In Fig. 5 is a carbon K spectrum at 2.5 MeV (Jouffrey, 1980).

The counting system we use is a Si(Li) doped diode. The interest is to be able to separate the pulses due to electrons or to photons. This problem is in fact important to get reliable results (Kihn et al., 1980). The dynamic range is of the order of 10^4 to $2 \cdot 10^4$ counts per second.

Elementary Excitations

We have been principally involved with two types of inelastic collisions: inner shell excitations and collective oscillations (plasmons).

Inner Shell Excitations

The starting equation of the Bethe model to be used for obtaining cross sections for comparison with experiment is (Bethe, 1933):

$$d\sigma_{on} = \frac{4m_e^2 e_1^2 e_2^2}{\hbar^4} \frac{v'}{v} \frac{1}{q^4} |F_{on}|^2 d\Omega \quad (1)$$

where:

$$|F_{on}|^2 = \left| \int \sum_i e^{-i\vec{q} \cdot \vec{r}_i} \psi_n^*(\vec{r}_i) \psi_0(\vec{r}_i) d^3r_i \right|^2 \quad (2)$$

\vec{q} is the scattering vector defining the direction $\vec{k}' = \vec{k} + \vec{q}$ (Fig. 6) in which the electrons are studied. ψ_0 and ψ_n represent the initial and final states of the atom. \vec{v} and \vec{v}' are the velocities of the electron before and after the collision. m_r is the reduced mass, e_1 and e_2 are the charges of the incident particle and the particle which is knocked down. For electron interacting with one atom, we can write:

$$d\sigma_{on} = \frac{2\pi e^4}{m v^2} \frac{dT}{T^2} |F_{on}|^2 \quad (3)$$

where $T = (\hbar^2 q^2)/2m$, m being the rest mass of the electron.

As was done by Bethe (1933), the quantity:

$$\frac{1}{q^2} \frac{2m}{\hbar^2} (E_n - E_0) |F_{on}(\vec{q})|^2 = \frac{\Delta E_{on}}{T} |F_{on}(\vec{q})|^2 = f_{on}(\vec{q})$$

is introduced. It gives:

$$d\sigma_{on} = \frac{2\pi e^4}{m v^2} \frac{1}{\Delta E_{on}} f_{on}(\vec{q}) d(\text{Log } T)$$

This expression can be integrated to be compared to measurements in electron microscopy from T_{min} to T corresponding to the maximum q , corresponding to the maximum scattering angle which is used (the solid angle is $\int_0^\theta 2\pi \sin \theta d\theta$). Using the dipole approximation valid at a small scattering angle, it gives:

$$\sigma_{on}(0 \rightarrow \theta) = \frac{2\pi e^4}{m c^2} \frac{1}{\beta^2 \Delta E_{on}} f_{on} \text{Log} \frac{\theta_{on}^2 + \theta^2}{\theta_{on}^2} \quad (4)$$

In this expression the change of the energy of the incident electron is dependent on β^2 and

$$\theta_{on} = \frac{\Delta E_{on} \gamma}{m c^2 (\gamma^2 - 1)} \quad (5)$$

β and γ are the classical relativistic terms. $\gamma = 1/(1 - \beta^2)^{1/2}$ with $\beta = v/c$, v and c being respectively the speed of electrons and the velocity of light.

It is related to T_{min} through $q_{min} = k\theta_{on} (\Delta E_{on} m\gamma)/(\hbar^2 k)$.

This last expression is easy to derive by writing $\Delta E_{on} = (\gamma - \gamma') m c^2$ which is the change in kinetic energy of the incident electron, γ' being the value of the relativistic parameter γ following the loss.

In electron microscopy, this formula may be tested at low or high voltages. That is what we have done at low energy (60 keV) for the L_{2-3} edges of Al, Mg, Si, (Colliex and Jouffrey, 1970, 1972; Kihn et al., 1976) and at 60 keV to 1.2 MeV in detail for K excitations in C and Al (Jouffrey et al., 1978). Some calculated values of $\sigma_{on}(0 \rightarrow \theta)$ are given in Jouffrey et al., 1977.

For details about the oscillator strength problem see the papers of Inokuti (Inokuti, 1971; Inokuti and Manson, 1983) and Powell (1970).

Now equation (4) is not fully correct from the relativistic point of view. The study of this problem has been carried out in detail by Fano (1956) following the work of Möller (1932) and Bethe (1932). The expression which is obtained is:

$$\sigma_{on}(0 \rightarrow \theta) = \frac{2\pi e^4}{m c^2 \beta^2} \frac{f_{on}}{\Delta E_{on}} \left\{ \log \frac{\theta^2}{\theta_{on}^2} + \log \frac{1}{1 - \beta^2} - \beta^2 \right\} \quad (6)$$

θ_{on} is given by equation (5) with ΔE_{on} replaced by ΔE_{on} taken as $3/2(\Delta E_{on})$ due to the variation of f with ΔE_{on} beyond the edge such as $dF/dE \sim E^{-p}$, p being of the order of 3. In this relation ΔE_{on} is nearly varying as Z^2 . So it is rather favourable for light materials. The corresponding mean free path is given by $\lambda_{on} = 1/(N_s \sigma_{on})$ where N_s is the number of scattering centers (K electrons for instance) per unit volume.

The relativistic correction can be seen as essentially one part due to the longitudinal correction ($\sim (1 - \beta^2)$) and the other due to the perpendicular correction ($\sim \log(1/(1 - \beta^2)) - 1$). These two different corrections appear for bound electrons (Bohr, 1915; Jouffrey, 1983). The other correction is due to the minimum transmitted momentum $k\theta_{on}$. That can explain the different behaviour of volume plasmons (longitudinal excitations) in comparison with other excitations as a function of the energy.

Experimentally we have tried to compare our results with these expressions, essentially in the case of carbon and aluminium as we said before (Sévely et al., 1976; Jouffrey et al., 1980). It was difficult to find a noticeable difference between the two models even though it seemed that a slight maximum for λ_k was observed (Sévely et al., 1975; Jouffrey and Sévely, 1976). This shows nevertheless that the global agreement between theory and experiment is good.

Plasmon Mean Free Path

The experiments on the plasmon determination of mean free paths show a variation in β^2 without any maximum as is explained by the Pines expres-

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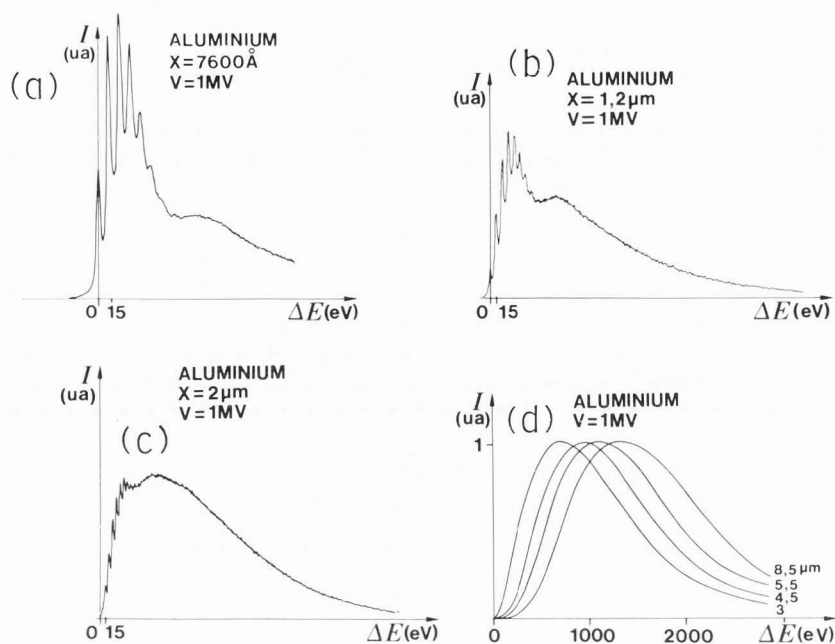


Fig. 4. Spectrums for different thicknesses of aluminium. The incident energy is 1.2 MeV. a) 7,600 Å, b) 1.2 μm , c) 2 μm , d) 3, 4.5, 5.5, 8.5 μm .

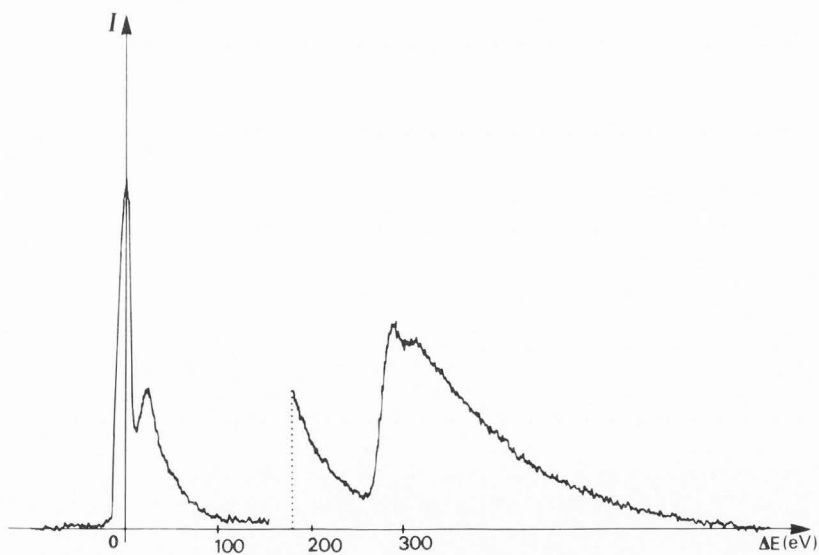


Fig. 5. Carbon K edge; the incident energy is 2.5 MeV.

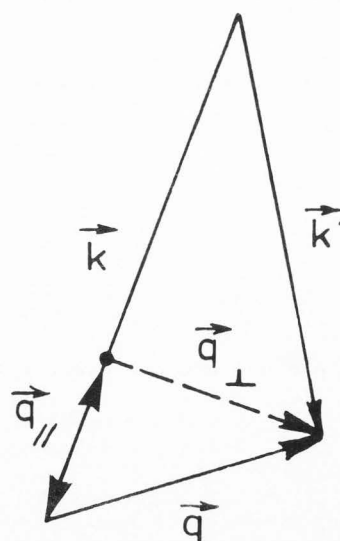


Fig. 6. Momentum conservation.

sion (Pines, 1956) or the Ashley and Ritchie treatment (Ashley and Ritchie, 1970). Recent experiments (Sévely et al., 1982) up to 2.5 MeV have confirmed that the β^2 curve is correct.

Global Treatment

Starting from equation (1), it is easy to show that:

$$\sum_n \frac{d\sigma_{on}}{d\Omega} = \frac{d\sigma_i}{d\Omega} = 4 \left(\frac{\gamma}{a_0} \right)^2 \frac{k'}{k} \frac{1}{q^4} [Z - f_x(\vec{q}) + \sum_{i \neq j} e^{i\vec{q}(\vec{r}_i - \vec{r}_j)}] \quad (7)$$

a_0 is the Bohr radius, $f_x(\vec{q})$ the form factor. \vec{r}_i and \vec{r}_j define the positions of electrons i and j .

The Raman Compton simplification is to write that the electron scattering factor is the same for each electron i or j and that it is taken as real. Therefore:

$$\begin{aligned} Z + \sum_{i \neq j} e^{i\vec{q}(\vec{r}_i - \vec{r}_j)} &= Z + \sum_{i \neq j} f_i(\vec{q}) f_j(\vec{q}) \\ &= Z(Z - 1) \frac{f_x^2(\vec{q})}{Z^2} \end{aligned}$$

$$\text{so: } \frac{d\sigma_i}{d\Omega} = 4 \left(\frac{\gamma}{a_0} \right)^2 \frac{k'}{k} \frac{1}{q^4} [Z - \frac{f_x^2(q)}{Z^2}] \quad (8)$$

Using the Wentzel-Yukawa potential it is found for instance,

$$\frac{d\sigma_i}{d\Omega} = 4 \left(\frac{\gamma}{a_0} \right)^2 \frac{Z}{k^4} \frac{\theta^2 + \theta_E^2 + 2\theta_0^2}{(\theta^2 + \theta_E^2)(\theta^2 + \theta_E^2 + \theta_0^2)}$$

where $\theta_0 = \frac{1}{ka}$

and θ_E is corresponding to the expression (5) obtained with ΔE_I , the mean ionization energy. We see for instance $\theta_E \sim 1.2 \cdot 10^{-4}$ rad $< \theta_0 \sim 6 \cdot 10^{-3}$ rad at 1 MeV for Al. At a large angle we find, from equations 7 or 8, the expression:

$$\frac{d\sigma_i}{d\Omega(\text{large } q)} \approx 4 \left(\frac{\gamma}{a_0} \right)^2 \frac{Z}{q^4} \quad (9)$$

As we see the relativistic correction is done only through simple terms. Experimentally, this type of cross section is available for global experiments on transmission or backscattering coefficients studies (Balladore et al., 1983; Soum et al., 1979, 1981, 1983). On the other hand, it is more difficult to get the stopping power through this model. As a first approximation we can use an average loss corresponding to $\lambda_i = 1/(n\sigma_i)$. So, $dE/dx = (\Delta E_i)/\lambda_i$ where λ_i is the inelastic mean free path and $\Delta E_i \approx \Delta E_i$.

Chemical Analysis

The first K loss image, which was published by Colliex and Jouffrey (1970), had shown that, by using the electrons corresponding to the K loss to get an image, only the thin part of the graphite sample was bright due to the single scattering of a K excitation. The selection of electrons having suffered energy losses just before the edge to get

an image allows the observation of the thick part of the sample. That means the background before the edge is due to multiple scattering and, in the thin part, the probability of exciting a K loss is higher than the probability of exciting n small losses, where n is such that $n \Delta E_e = \Delta E_B$, the subscript e being for elementary and B for background at the level of the edge, if there is only one type of loss for the background. In fact, in a general case, we would have to write $\Delta E_K = n_1 \Delta E_e^{(1)} + n_2 \Delta E_e^{(2)} + \dots$ if we consider the background is due to several processes (collective, individual excitations, tail of inner shell excitations ...), n_i can be one for a given process. The height and the shape of the background depend obviously on the probability of every event and on the nature of the sample and on the value of the edges.

As was calculated by Egerton (1975), in the case of carbon, using the Gryzinski model, the most probable part of the peak for the background would be around 40 mrad at 80 keV ($\theta_B^2 = (\Delta E_B - E_1)/E_i$, where ΔE_B is the energy before the edge, say 200-250 eV, E_1 the kinetic energy of the valence electrons and E_i the incident energy). This point has to be confirmed to establish whether the weight of valence band individual electrons is important or not. In fact, the point is to know what kinds of excitation give the background.

Very simply it can be said that when increasing the energy, the most probable angle for the K loss diminishes as $\gamma/(\gamma^2 - 1)$. If we consider that the background is due only to a given type of excitation, we have a probability which can be roughly considered as a Gaussian around θ_G such that:

$$\overline{\theta_G^2} = \sum_i \frac{n}{i} \overline{\theta_i^2} = n \overline{\theta_i^2}$$

for one type of excitation. θ_i varies as equation (5) and n is independent of the energy of the incident electrons. So the ratio between θ_G and θ_K is of the order of $\sqrt{n} \theta_i/\theta_K$. It does not vary as a first approximation with E . In fact, it depends on the aperture which is used. Now we look to the probability of a K loss for a sample of thickness z :

$$P_K(1) = \frac{z}{\lambda_K} \exp - \frac{z}{\lambda_K} \exp - \frac{z}{\lambda_{e1}}$$

For the background we have:

$$P_B(n) = \frac{1}{n!} \left(\frac{z}{\lambda_{e1}} \right)^n \exp - \frac{z}{\lambda_{e1}} \exp - \frac{z}{\lambda_K}$$

$$\begin{aligned} \text{So the ratio } \frac{P_K(1)}{P_B(n)} &= \frac{1}{z^{n-1}} n! \frac{\lambda_{e1}^n}{\lambda_K} \\ &= n! \frac{C}{z^{n-1}} \beta^2(n-1) \end{aligned} \quad (10)$$

where λ_{e1} is the mean free path corresponding to the elementary loss at the origin of the background (we can obviously have several) and C a constant to calculate from the expressions of the elementary interactions. Obviously these expressions are not fully correct because we would have to include the convolution due to the angular scattering problem and the elastic scattering and other excitations but the tendency is to give an advantage to high

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voltage because of the multiple scattering between other points.

A way to treat this problem of convolution was described by Zanchi et al. (1981).

Fig. 7 shows experimental results which confirm again the gain in high voltage electron microscopy (HVEM) (Jouffrey, 1982). We must add that, because of the small scattering angle in high voltage, the collection efficiency is much better in HVEM (Jouffrey, 1977). On the other hand, the angle dependence studies are obviously more difficult to do.

So the interest of HVEM will be increased for "thick" samples when we have plural scattering. At the opposite, for very thin samples, it was not possible to detect any definitive advantage except for detecting very large losses (a few thousand eV).

So we have to remember here that it is easier in increasing the energy of the incident electrons to collect electrons corresponding to very large losses. The larger the loss, the easier it is compared to lower energy incident electrons; Fig. 7 shows this point (the background is lower at large losses when increasing the voltage). We succeeded a few years ago (Jouffrey and Sevely, 1976) in detecting the Germanium K loss ($\sim 11,500$ eV).

Therefore it is a good way to do chemical analysis to use high energy electrons. The available thickness is generally around 2,000 - 3,000 Å; it means nearly five-ten times the thickness available at low voltage. We can notice that the energy resolution is equal to 2-4 eV at 1.2 MeV. So it is possible to have a better resolution at lower voltage. We show here four examples. One is in biology with Be in a lung section. We see that the mapping of Be clusters is well in evidence (Fig. 8) in using the α filter system. The size of the clusters is 100 Å or slightly less. Another one is in mineralogy (Fig. 9) where it has been possible to detect lithium in triphylite and amblygonite. It has in this domain also been possible to do relative quantitative analysis between Mn and Zn in a natural sulphide (Sèvely et al., 1981).

We show another example (Fig. 10) in very pure iron in which were however detected some thin precipitates (Fourdeux (private communication)). We had to use HVEM to study them; we were able to detect easily the rare platelets which could be found. Finally Al and N were easily detected at 1 MeV. The precipitates were recognized as an aluminium nitride.

The last is a ceramics Si Al ON sample (Fig. 11). It appears also on the same area that in this ceramic the S/B is better when increasing the voltage (S defines the height of the peak and B the background just before the K edge).

Many other applications have been successfully done by our group using HVEM.

Thick Samples

As we discussed in Pérez et al., 1977, and is shown in Fig. 12, the energy loss distribution is varying as z/v^2 , where z is the thickness of the sample.

This behaviour can be observed when looking at the most probable energy losses at the full width at half maximum. That corresponds to the general behaviour of the energy losses as can be seen from the simplest models of interaction. The comparison

with some spectra obtained at 100 keV (Jouffrey, 1975) is interesting from that point of view. We observe in that figure that background at the level of the aluminium K loss will be less important when increasing the voltage as was said previously.

We compared the Bethe stopping power and the Landau distribution. Our experiments agree rather well with the Landau calculations with some corrections explained by Pérez et al. (1977).

This behaviour is interesting because it explains, for instance, the interest of using HVEM to observe thick samples. It shows also when introducing the chromatic aberrations that, for a given thickness, the resolution in HVEM will be much better (Dupouy, 1968; Jouffrey, 1975).

Sensitive Materials

The interest of using HVEM for the study of sensitive materials has been claimed and demonstrated for a long time even if there are some controversies about this point. The arguments were based on the global behaviour of σ_j as a function of energy.

In fact, the sensitive materials have a lifetime which increases with the energy of the incident electron, roughly as β^2 . For a survey on this problem see Dupouy (1974), Reimer and Spruth (1978), Boudet (1981), Locatelli-Lapeyre (1981), Jouffrey (1975) and Jouffrey et al. (1979). It has been said that there is no gain because cut films or plates to record the image need in the same time an increase in exposure time proportional to β^2 . This point is true if the lifetime of the sample is of the same order or less than the one of the plate at low voltage. However, if the lifetime is more by a factor of say 10 or 100 or more, the gain will be quite decisive for applications. As we know from the work of Dietrich et al. (1983), it would be still better to combine the observation with cooling the sample down to about 4.2 K.

The study of sensitive materials becomes more and more interesting. Outside the biological sample, organic conductors and semiconductors will become more and more important. Resist for microlithography is also of interest. Therefore there is an interest to study the sensitive materials' behaviour under the beam.

We know that, if we observe a crystalline organic sample, the diffraction pattern disappears more or less rapidly. The outside spots disappear first (Kobayashi and Ohara, 1966). This effect has been explained by introducing a Debye-Waller factor (see Reimer and Spruth, 1978 for a review). It is possible to introduce it easily through the kinematical theory of the contrast (see below).

Another point is to look in more detail at a general law of disappearance of the diffraction pattern. This problem is very complicated. However, the use of a very simple model enables one to understand several points and also to raise some questions. About the chemistry involved in the change under irradiations see Pacansky (1983).

The expression for the wave is:

$$\sum_{\text{cells}} \exp - i (\vec{S} + \vec{g}) \cdot \vec{r}$$

with \vec{g} the diffraction vector, \vec{S} the vector meaning

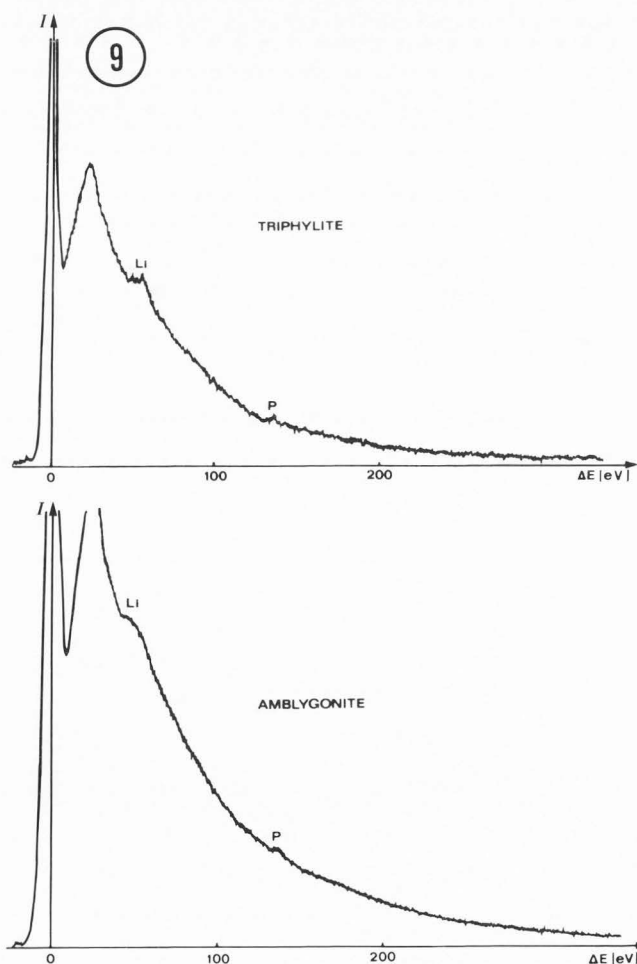
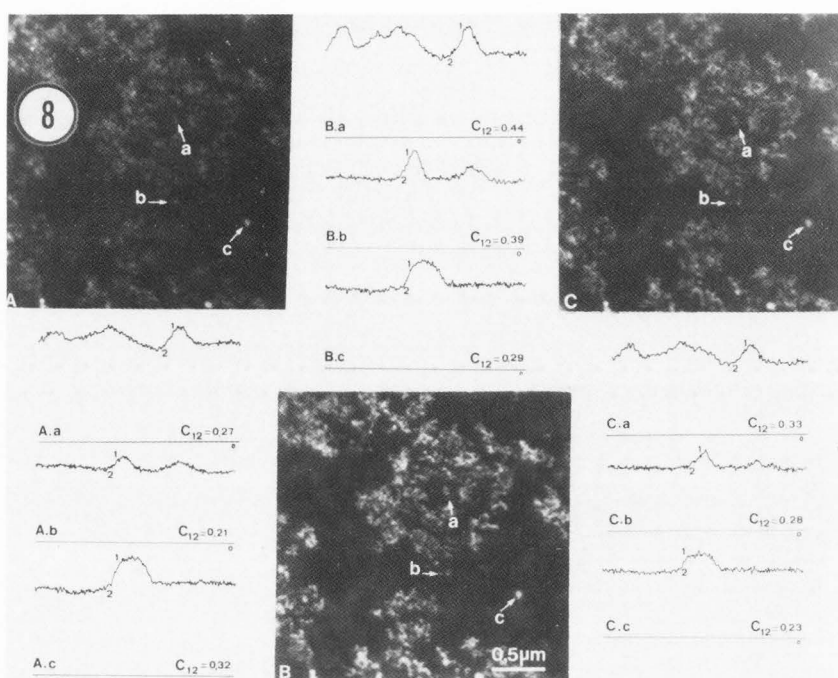
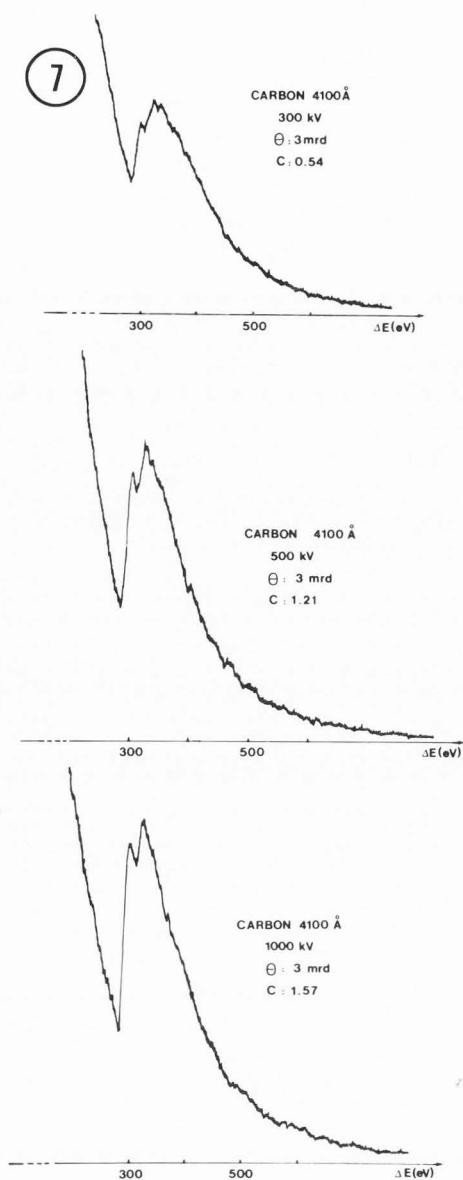


Fig. 7. This figure shows the K loss spectrum feature in the case of a given carbon film (4,100 Å thick). Changing the energy gives a modification of the visibility of the K signal. So these experiments confirm again the gain in HVEM (Zanchi et al., 1981). C is the contrast $(I_{\max} - I_{\min})/I_{\min}$ of the K peak.

Fig. 8. Pathological lung section. Mapping obtained by selections energy losses on both sides of the beryllium K edge. A is taken before the edge, B on the edge and C beyond the edge. The accelerating voltage is 1 MeV. The selected window is ± 5 eV. (Same magnification for the three micrographs).

Fig. 9. Detection of lithium K edge at 55 eV in thin mineralogical specimens amblygonite and triphylite (1 MeV).

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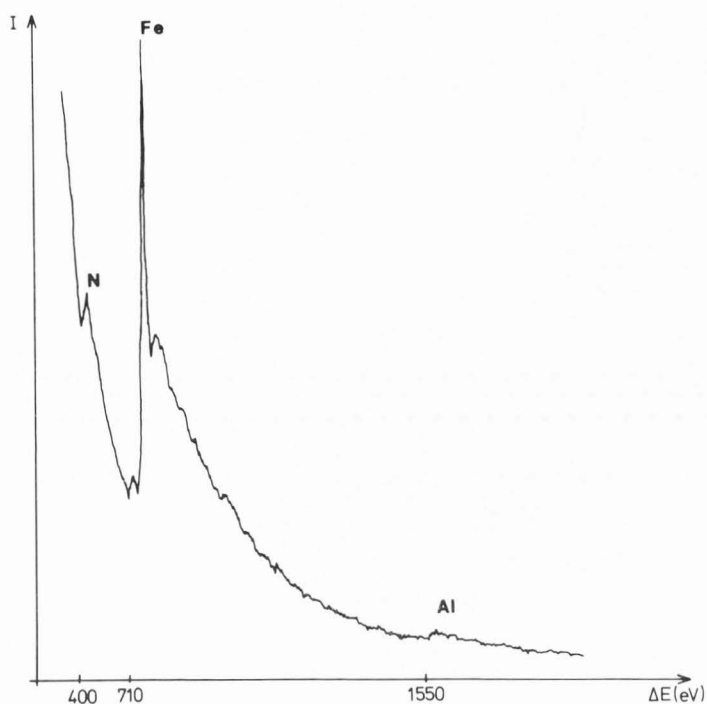


Fig. 10. Precipitate of an aluminium nitride in iron.

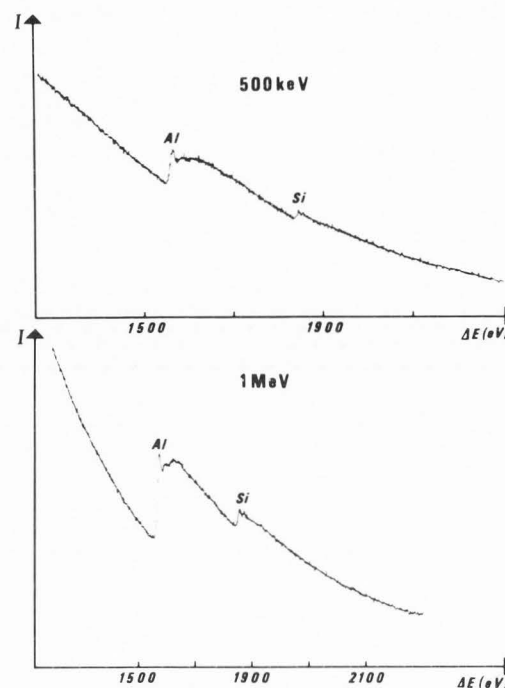


Fig. 11. Comparison of the same area of a SiALON ceramic sample.

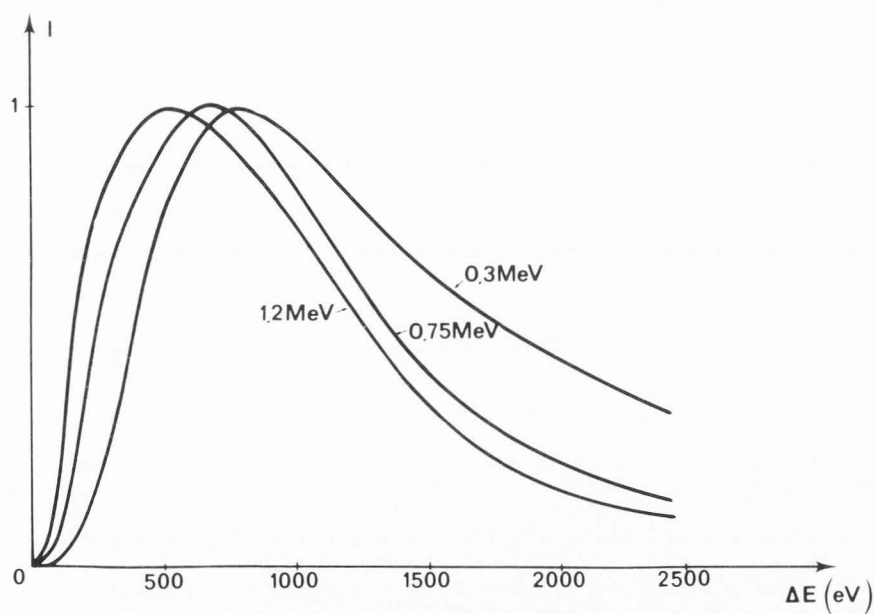


Fig. 12. Energy loss distribution as a function of accelerating voltage for a same 3 μm thick aluminium sample. The most probable energy loss, the full width half height and the mean loss are less important as the electron incident energy increases.

the deviation from the Bragg condition and \vec{r} the coordinate vector for the cells of the sample ($\vec{g} \cdot \vec{r}$ is an integer). As it is well known in the Debye-Waller model it can be written:

$$\sum_{\text{cells}} \exp - i (\vec{s} + \vec{g})(\vec{r} + \Delta\vec{r})$$

That is equal to:

$$\sum_{\text{cells}} \exp [- i(\vec{s} \cdot \vec{r})] \exp - i(\vec{s} \Delta\vec{r}_z + \vec{g} \Delta\vec{r}_x)$$

where the component z is roughly the direction of \vec{s} and $\Delta\vec{r}_x$ is the component of the displacement of the cells in the direction \vec{g} . $\Delta\vec{r}$ being small, it is possible to expand the exponential. When doing the average on $\Delta\vec{r}$, the first order term in the expression is zero. The second order term has a finite value (see for instance Guinier, 1956). So we have:

$$\begin{aligned} \langle \sum \exp - i(\vec{s} + \vec{g})(\vec{r} + \Delta\vec{r}) \rangle_{\Delta\vec{r}} &= \int dz (\exp - i sz) \\ \exp - \frac{1}{2} [s^2 \cdot \overline{\Delta r_z^2} + g^2 \cdot \overline{\Delta r_x^2}] &\sim \int_0^z dz \exp - i sz \\ \exp - \frac{1}{2} (g^2 \cdot \overline{\Delta r_x^2}). \end{aligned} \quad (11)$$

We imagine that for the perturbed molecules $\overline{\Delta r_{xp}^2}$ will be more important than for the nonperturbed one $\overline{\Delta r_{x,np}^2}$. So we find if we consider from $0 \rightarrow z$, the term $\overline{\Delta r_{np}^2}$ and from $z_1 \rightarrow z_2$ the term $\overline{\Delta r_p^2}$ with obvious notations that the amplitude is:

$$\begin{aligned} A &= \frac{1}{is} \{ (\exp - \frac{1}{2} g^2 \cdot \overline{\Delta r_{np}^2}) [(\exp - i s z_1) - 1] + \\ &(\exp - \frac{1}{2} g^2 \cdot \overline{\Delta r_p^2}) [(\exp - i s z_2) - (\exp - i s z_1)] \} \end{aligned} \quad (12)$$

The second term is negligible since the Debye-Waller factor is very small. Only the first term remains. It shows that we have, adding to the fact that the atomic scattering factor is small at a large angle, an attenuation due to the Debye-Waller factor. The disappearance occurs with the diminution of z_1 . In fact this model considers that the cells which are perturbed give an equivalence to a diminution of thickness (we shall see this point again later on). It would be more correct to consider that the cells are localized at random. So an average has to be done to get the good amplitude A . That can be done, at least partly, from the phase amplitude diagram which gives a simple problem of locus to solve.

Now the problem is to describe z_1 as a function of time. The simplest way to do so is to consider that the number of defects is proportional to the inelastic cross-section to be determined and to the time. So $z_1 = N_0 S z_0 (1 - \sigma_i \phi_0 t)$ where σ_i is the corresponding inelastic cross-section, ϕ_0 the incident flux and N_0 the number of small basic volumes which corresponds to one defect (v_0 is the elementary damaged volume, S the irradiated area). The critical dose is therefore $1/(\sigma_i \phi_0)$, which gives only a rough appreciation. However, this model shows that in some cases the intensity $I = AA^*$ can first increase before decreasing.

We can remark also that $\overline{\Delta r_{np}^2}$ and $\overline{\Delta r_p^2}$ are a

function of temperature but not exactly in the same way. If they vary as a function of temperature through the well known treatment of Debye-Waller, $\overline{\Delta r_p^2}$ at a given temperature has to be multiplied in a rough approximation by a term e^{-Pt} where $P = v_0 \exp - U/(kT_a)$, which takes into account the rearrangement of the damaged cells. v_0 is a characteristic frequency, U the "activation energy" of the process and T_a the absolute temperature. More particularly it means at low temperature that $\overline{\Delta r_p^2}$ is a function of the local rearrangement which is a function of time (Kohl et al., 1981). In any case, after rearrangement, only the first term of equation 12 remains. At room temperature, this rearrangement can be considered in many cases as practically instantaneous. So only the first term of (12) remains.

Another way to try to understand what is occurring is to remark that in the preceding model we don't get a disappearance with time which becomes slower and slower. This last effect makes difficult the determination of the critical dose $(\phi_0 t)_{cr} = D_{cr}$.

The reason for this slowing down is easy to understand. The probability of creating defects can be written $(1 - \exp - (z/\lambda_i))$ where λ_i is related to σ_i by $\sigma_i = 1/(N_0 \lambda_i)$; $1/N_0$ is the basic perturbed volume. When an interaction has taken place in a given volume, it becomes noncrystalline and therefore doesn't contribute any more to the diffraction pattern. It gives diffuse scattering which increases the background. It means that if another inelastic event takes place in the same volume it doesn't affect the diffraction pattern further and therefore is not any more involved with our problem. Only in this model a new damaged volume will give a diminution of the diffracted intensity. So the probability of perturbing new elementary volumes becomes smaller and so needs an increase of electron dose above a pure proportionality. This type of situation can be described, as an average, by the type of equation $dN/dt = - N \sigma_i \phi_0$ where N is the number of intact volumes, or $(S/v_0)(dz/dt) = - (S/v_0) z \sigma_i \phi_0$, that is written $dz/dt = - z \sigma_i \phi_0$, which has the obvious solution $z_1 = z_0 \exp - \sigma_i \phi_0 t$ where z_0 is the initial thickness of the sample.

That can be treated by using, instead of the mean distribution, the Poisson probability. So we get:

$$(1 - \exp - \frac{z_1}{\lambda_i}) \phi_0 S dt = - \frac{\Delta z S}{v_0}$$

Δz being the change in thickness corresponding to the creation of one defect. ($\Delta z S = v_0$).

$$\text{So: } (1 - \exp - \frac{z_1}{\lambda_i}) \phi_0 S dt = - N_0 \Delta z S$$

We remark that if z_1/λ_i is small we have:

$$\frac{z_1}{\lambda_i} \phi_0 S dt \sim - N_0 \Delta z S \text{ or } N_0 z_1 \sigma_i \phi_0 S dt = - N_0 \Delta z S$$

which is equivalent to the equation:

$$\frac{dz_1}{dt} = - (1 - \exp - \frac{z_1}{\lambda_i}) \frac{\phi_0}{N_0}$$

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The integration gives:

$$z_1 = \lambda_i \log \left[1 + (e^{z_0/\lambda_i} - 1) e^{-\frac{\phi_0}{N_0 \lambda_i} t} \right] \quad (13)$$

So we get a very simple variation of z as a function of time with correct boundary conditions (Fig. 13).

We can introduce this value in the kinematical equation (12). So we can find oscillations in the disappearance of the diffraction pattern.

More simply if we use a Poisson distribution we can say as a rough approximation that the intensity of a "spot" is given by an expression of the form:

$$I = I_0 \left\{ 1 - \exp - \frac{\lambda_i}{\lambda_e} \log \left[1 + (e^{z_0/\lambda_i} - 1) e^{-\frac{\phi_0}{N_0 \lambda_i} t} \right] \right\} \quad (14)$$

For small t and small z_0 we find: $\lambda_i \sim \frac{I_0}{I_0' - I}$

$\frac{\phi_0}{N_0} t$ which is a good order of magnitude. $I_0' = I_0 \frac{z_0}{\lambda_0}$ where I_0 is the incident intensity. To get λ_i it seems possible to use, not the critical dose, but the first beginning of the damage. It is also possible to calculate the inflexion point and to determine the slope at this level but detailed experiments have to be performed. However, the comparison of these expressions has been made with experimental values given by Boudet (1981) for polyethylene (Figs. 14 and 15). If we take a critical dose $(\phi_0 t)_{cr}$ at 100 keV equal to $4.69 \cdot 10^{16}$ e/cm² corresponding to an intensity of $I = 10^{-3} I_0$, we get λ_i . The point is that $1/N_0$, the elementary volume which is damaged in an "interaction," can also be adjusted. For instance, $\lambda_i = 730$ Å with $N_0 = 1.4 \cdot 10^{21}/\text{cm}^3$ fits quite well with the expressions ($\lambda_e = 3,660$ Å). The comparison with the calculated stopping power (we calculated $5.4 \cdot 10^6$ eV/cm at 100 keV) would show that $\Delta E_I \sim 40$ eV is in good agreement. In fact, by adjustment, it seems better values are $\lambda_i = 1,000$ Å, $\Delta E_I \sim 55$ eV, and $N_0 = 1.46 \cdot 10^{21}/\text{cm}^3$ ($v_0 \sim 680$ Å³). No information is obtained on the anisotropy. That damage is due to the global combination between the direct collision effect and the secondary electrons (the effect would be different close to the free surfaces but the equations could also take into account, in an analogous way, the mass loss; see above).

At higher voltages (2.5 MeV in the case of polyethylene), the agreement between experiment and the above expressions can be obtained. However, with $N_0 = 1.46 \cdot 10^{21}/\text{cm}^3$, we had determined before, we get $\lambda_i = 7,400$ Å ($\lambda_e = 11,860$ Å). This value seems rather large. If we take a shorter mean free path λ_i , in agreement with the Bethe law as a function of the electron incident energy (in that case $\lambda_i \sim 2,600$ Å), we would find: $N_0 = 4.15 \cdot 10^{21}/\text{cm}^3$ which corresponds to an elementary damaged volume of about 240 Å³. The damaged volume at high energy would be less important compared to lower voltages. In fact, it is very difficult to say definitive things because: a) the model is sen-

sitive to the thickness which is not well known; b) in polyethylene at high voltage, channeling effects seem important (Boudet, 1981); c) we need more detailed experimental curves with other materials as well. Nevertheless, it is possible to have a mean curve which can be matched with experiments. From the rate of variation of z , it can be deduced, by using expressions given by Crewe and Groves (1974) and Zanchi et al. (1980), if, for instance, it is possible to record a "K loss" or to record a dark field image under given conditions. It would be possible to take into account the orientation effects and to determine also the spatial resolution as a function of time.

In fact it seems possible with this model to determine more directly the cross section $\sigma_i = 1/(N_0 \lambda_i)$ and $1/N_0$ (Jouffrey, to be published).

The damage is due to a direct effect due to the incident electron but also to the secondary electrons. The global effect as we have seen can be characterized by a mean free path λ_i . In this model, the effect of diminishing the temperature is to increase λ_i phenomenologically. That means this quantity has to be multiplied by a term which is a function of time (for rearrangement) and temperature in a way analogous to the one used by Kohl et al. (1981).

When it is required to count electrons corresponding to a "K" edge, the number of characteristic electrons recorded after a time t will be of the order of:

$$N_C = \phi_0 S t \frac{\lambda_i}{\lambda_K} \log \left[1 + (e^{z_0/\lambda_i} - 1) e^{-\frac{\phi_0}{N_0 \lambda_i} t} \right] \exp - \frac{\lambda_i}{\lambda_K} \log \left[1 + (e^{z_0/\lambda_i} - 1) e^{-\frac{\phi_0}{N_0 \lambda_i} t} \right] \quad (15)$$

Conclusion

One principal limitation in the possibility of doing chemical analysis in transmission electron microscopy in the case of "sensitive materials" by using either characteristic energy losses or x rays is damage formation. The material evolves during the irradiation and so it is interesting to know what is the part of the specimen which has changed during the counting. Therefore, when λ_i is determined, it is possible to know if a given experiment is possible.

The interest of energy losses for doing chemical analysis is now well established. In many applications the use of high energy incident electrons can be quite interesting if the necessary resolution in energy on the spectrums is above 2.5 eV about and the thickness of the specimens can be much higher than the one used at lower voltages (~ 100 keV). The use of 300 keV microscopes could be an intermediate way of doing chemical analysis.

Acknowledgements

The author thanks people who have worked with him, for stimulating discussions and results of experiments: Drs. Sèvely, Zanchi, Pérez and Kihn for energy losses studies, Dr. Boudet about sensitive materials, and Drs. Rühle, Fourdeux, Mignon-Conte and Gout for proposing samples.

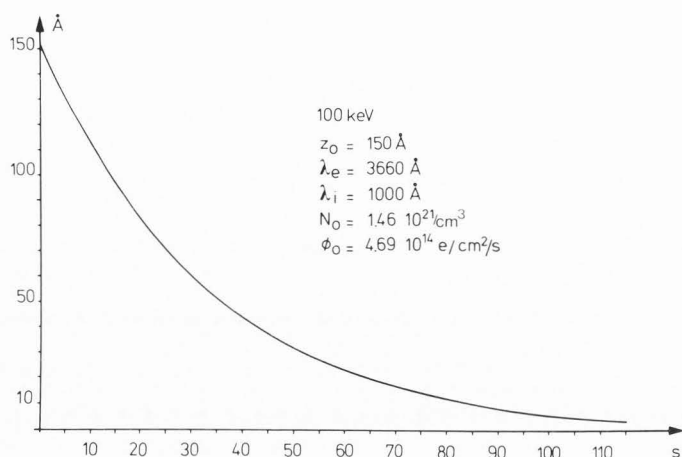


Fig. 13. Diffracting thickness as a function of irradiation time or dose (100 keV) in a case of polyethylene.

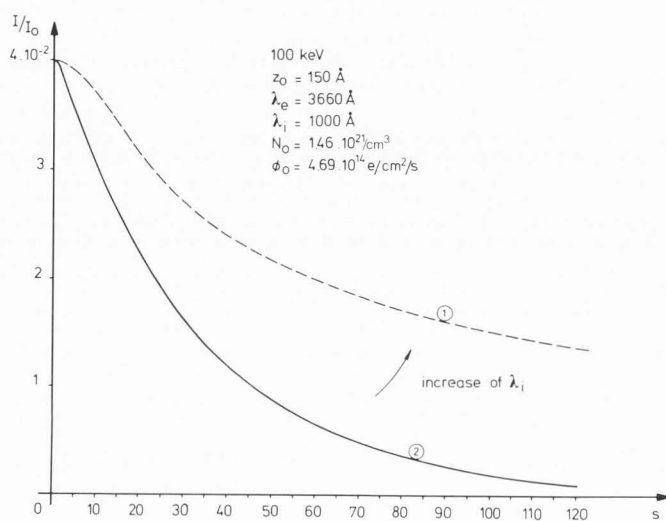


Fig. 14. Decrease in intensity corresponding to Fig. 13 when using Poisson statistics; 100 keV.

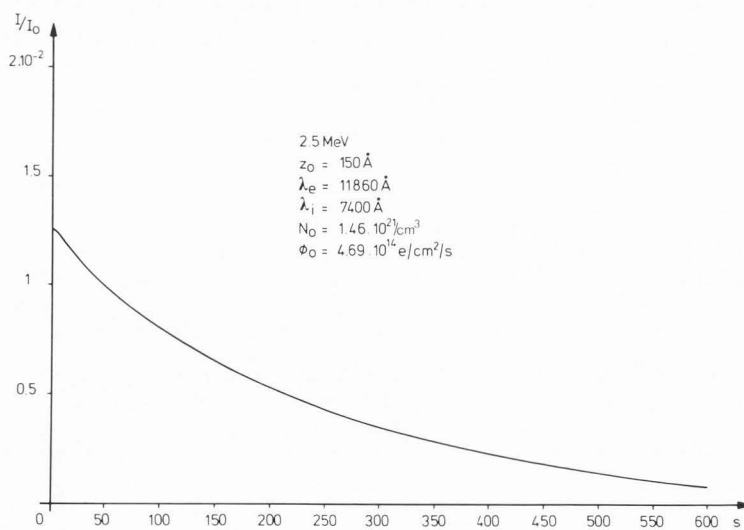


Fig. 15. Decrease in intensity as treated in Fig. 14; 2.5 MeV.

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