Elastic Scattering

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CHAPTER PREVIEW

Elastically scattered electrons are the major source of contrast in TEM images and they also create the intensity distributions in diffraction patterns, so we need to understand what controls this process. We'll consider elastic scattering first from single isolated atoms and then from many atoms together in the specimen. To comprehend elastic scattering we need to invoke both particle and wave aspects of the character of the electron.

Scattering from isolated atoms can occur either as a result of electrons interacting with the negatively charged electron cloud and scattered through small angles of a few degrees, or attracted to the positive nucleus and scattered through large angles up to 180°. The scattering from the nucleus can be interpreted in terms of simple particle–particle collisions, cross sections, and mean free paths that we introduced in the previous chapter. We'll introduce the Rutherford differential cross section, which explains the strong dependence of high-angle elastic scattering on the atomic number (Z) of the atom. Later, we'll use this Z dependence in different ways to form images that reflect the chemistry of the specimen. We can also treat the electrons as waves, in which case their *coherency* becomes important. The coherency of the scattered electrons is related to their *semi-angle* of scattering (θ). As the scattering angle becomes larger, the degree of coherency becomes less and Rutherford-scattered electrons are incoherent.

In contrast to Rutherford high-angle scattering, electrons which are elastically scattered through less than ~3° are coherent. The intensity of this low-angle scattering is strongly affected by the arrangement of atoms within the specimen. Such collective scattering by the atoms is referred to as *diffraction* and can only be

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understood if we treat the electron as a wave and ignore particle concepts such as cross sections. Diffraction is controlled mainly by the angle of incidence of the electron beam to the atomic planes in the specimen and the spacing of atoms or planes of atoms. So this low-angle scattering is invaluable in characterizing the crystallography of the specimen and is undoubtedly the most significant scattering phenomenon in the TEM.

When we think about the scattering of electrons, we often imagine a beam of particles which hits a target and is deflected to emerge as a beam in another direction, termed the scattered beam, much as we might imagine a beam of light being a group of photons. However, the scattering of light does not always follow the rules of geometric optics because light has a wave character. Similar considerations apply to the diffraction of electrons and this is one of the fundamental concepts of TEM. So you will find the wave-particle duality being used simultaneously, because of both lines of thought.

Elastic Scattering

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3.1. PARTICLES AND WAVES

We have two different ways of looking at how an electron beam interacts with our specimen in the TEM. We can consider the beam as a succession of particles or as a number of waves. What we want to do is understand the relationship between the two approaches. We can summarize the two viewpoints:

Electrons are *particles* so they have the following properties, which we introduced in Chapter 2.

- They have a scattering cross section and differential scattering cross section.
- They can be scattered through particular angles.
- The electrons interact with the nucleus through Coulomb forces.
- We can relate this process to scattering of other particles, such as α particles, so lots of analysis can carry over from other systems.

When we discuss *X-ray* and *electron spectrometry* you'll see that we have to use a particle description.

Electrons have a *wave* nature and the electron beam is almost a *plane wave*, hence:

- Waves are diffracted by atoms or "scattering centers."
- How strongly a wave is scattered by an atom is determined by the atomic scattering amplitude.
- We can relate the process to the scattering of X-rays, so lots of analysis already exists.

When we discuss *imaging, HRTEM,* and *diffraction patterns* you'll see that we use a wave description.

The terminology is sometimes confusing if you look at it closely. A clear definition of diffraction is given by Taylor (1987):

An interaction between a wave of any kind and an object of any kind.

Collins dictionary defines *diffraction* as "a deviation in the direction of a wave at the edge of an obstacle in its path" while *scattering* is defined as "the process in which particles, atoms, etc., are deflected as a result of collision." The word scatter can also be a noun denoting the act of scattering. So scattering might best apply to particles and diffraction to waves; both terms thus apply to electrons! You should also note that the term diffraction is not limited to Bragg diffraction; it refers to any interaction involving a wave.

3.2. MECHANISMS OF ELASTIC SCATTERING

In the previous chapter we simply stated that electrons going through a thin specimen are either scattered or not scattered, and either lose energy or don't lose energy. It's now time to describe the ways in which this scattering occurs and in this chapter we'll confine our attention to elastic events.

It's convenient to divide elastic scattering mechanisms into two principal forms: electron scattering from isolated single atoms and collective scattering from many atoms together within the specimen. We'll start in the same way as we did in the previous chapter by looking first at the interaction of a single electron with an isolated atom. In this situation, elastic scattering can occur in one of two ways, both of which involve Coulomb forces. As shown in Figure 3.1, the electron may interact with the electron

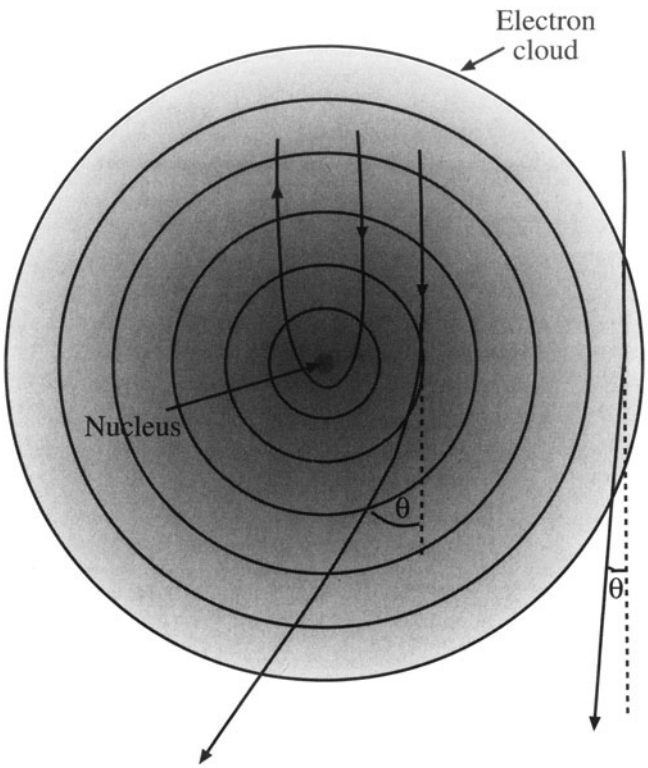

Figure 3.1. Two mechanisms by which a high-energy electron is scattered by an isolated atom. Coulombic interaction within the electron cloud results in low-angle (θ) scatter while Coulombic attraction by the nucleus causes high θ scatter and perhaps complete backscatter. The potential within the electron cloud is always positive.

cloud, resulting in a small angular deviation. Alternatively, if an electron penetrates the electron cloud and approaches the nucleus, it will be strongly attracted and may be scattered through a larger angle that in rare cases in the TEM can approach 180° (complete backscattering).

> You should be aware that either of these two interactions may not be truly elastic, so our separation of scattering into elastic and inelastic is a bit of a simplification.

In fact many electron–electron interactions are inelastic, as we'll see in the next chapter. We'll also see, for example, that the nuclear interaction may result in the generation of a bremsstrahlung X-ray, or may even result in the displacement of the atom from its site in the crystal, both of which involve some energy loss for the electron. Indeed, the higher the angle of scattering of an electron emerging from the specimen, the greater the chance that it will have undergone an inelastic event at some time during its passage through the specimen. Despite all this, we'll ignore any inelastic effects in this chapter.

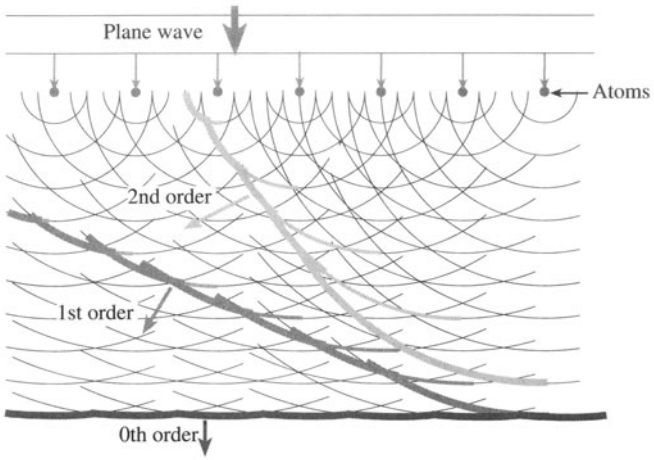

Figure 3.2. A plane coherent electron wave generates secondary wavelets from a row of scattering centers (e.g., atoms in the specimen). The secondary wavelets interfere, resulting in a strong direct (zero-order) beam and several orders of coherent beams scattered (diffracted) at specific angles.

The second principal form of elastic scattering occurs when the electron wave interacts with the specimen as a whole. We've already mentioned the best known form of this interaction, namely diffraction, which is particularly important at low angles. Understanding diffraction involves treating the electron beam as a wave, rather than as a particle as we did in Figure 3.1. Following the original approach of Huygens for the diffraction of visible light, we imagine each atom in the specimen acting as a source of "secondary" spherical wavelets as illustrated in Figure 3.2. These wavelets reinforce one another in certain angular directions and cancel in others. Thus the low-angle elastic scattering distribution is modified by the crystal structure of the specimen, and intense diffracted beams emerge at certain specific angles; we'll discuss these higher-order effects in Chapters 11 and 12. We'll now go on to examine these two forms of elastic scattering in more detail, starting with the simplest concept which is sometimes referred to as the billiard-ball model. We will briefly describe the scattering of a wave to show how it relates to this particle-scattering treatment and use this as the basis later for a full analysis of diffraction.

3.3. SCATTER FROM ISOLATED ATOMS

Consider the two paths for an electron passing close to an atomic nucleus shown in Figure 3.1. In either case, the di-

rection traveled by the electron changes; the electron is scattered through an angle θ.

Elastic electron–electron interactions usually result in a relatively low scattering angle, while electron–nucleus interactions cause higher-angle scattering.

If we just consider an electron, charge e, scattering from an isolated atom, the electron–electron and electron–nucleus scattering cross sections can be easily expressed by two very simple equations (Hall 1953)

$$\sigma_{\text{electron}} = \pi r_e^2 = \pi\left(\frac{e}{V\theta}\right)^2 \qquad [3.1]$$

$$\sigma_{\text{nucleus}} = \pi r_n^2 = \pi\left(\frac{Ze}{V\theta}\right)^2 \qquad [3.2]$$

Remember that we are using a billiard-ball model where r_e and r_n are the radii of the electron cloud and the nucleus, respectively. Hopefully no one will ask you to prove these simple expressions.

You can see that the atomic number Z of the atom controls the elastic interaction with the nucleus, but the electron–electron scattering is more a function of the incident beam energy (V in volts). We'll see later in Chapter 22 that the strong effect of Z becomes important when we need to enhance scattering in low-Z materials, such as polymers and biological tissue, in order to get better TEM image contrast. Notice that when the electron passes close to the nucleus (r_n is small) the angle θ will be large. We'll see in Chapter 22 that this dependence on θ directly relates to TEM-image contrast. The electron beam energy can also control the image contrast to some extent. For the time being, we'll ignore the low-angle electron cloud scattering and concentrate only on scattering by the nucleus.

3.4. THE RUTHERFORD CROSS SECTION

The high-angle electron–nucleus interaction is analogous to the backscattering of α particles from a thin metal foil. The first observation of such backscattering in 1911 by H. Geiger (of *counter* fame) and a Manchester University *undergraduate*, E. Marsden, enabled their professor, Rutherford, to deduce the existence of the nucleus (never overlook undergraduate research results!). Rutherford (1911), describing backscattering as "the most incredible event that has ever happened to me," derived the following expression for the differential cross section for this kind of scattering

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{e^4 Z^2}{16(E_0)^2 \sin^4\frac{\theta}{2}} \qquad [3.3]$$

All the terms in this equation were defined in Chapter 2. The expression assumes that the incident electron does not lose significant energy through inelastic processes, so that the energy of the electrons, E_0 (in keV), is fixed. This is generally a good assumption in the TEM. We can substitute appropriate values for the various constants and integrate the differential cross section from 0 to π to obtain the total elastic nuclear cross section (in scattering events per electron per atom per m^2) in a more accurate form than that given in equation 3.2

$$\sigma_{\text{nucleus}} = 1.62 \times 10^{-24}\left(\frac{Z}{E_0}\right)^2 \cot^2\frac{\theta}{2} \qquad [3.4]$$

Again we see that the beam energy (E_0), the angle of scattering (θ), and the atomic number (Z) all affect the probability that an electron will be scattered by the nucleus. As in Chapter 2, we can modify this expression for a single isolated atom to take into account the scattering from atoms in a TEM specimen of thickness t

$$\begin{aligned} Q_{\text{nucleus}}\, t &= \left(N_0 \frac{\rho}{A} t\right)\sigma \\ &= 1.62\, x\, 10^{-24} \left(N_0 \frac{\rho}{A} t\right)\left(\frac{Z}{E_0}\right)^2 \cot^2\left(\frac{\theta}{2}\right) \end{aligned} \qquad [3.5]$$

Notice that we still have the mass-thickness dependence, ρt, but that the strong dependence on Z is now obvious (compare to equation 2.5). See Joy *et al.* (1986) for further discussion of these calculations.

3.5. MODIFICATIONS TO THE RUTHERFORD CROSS SECTION

You'll often see the Rutherford differential cross section (equation 3.3) in different, but mathematically similar, forms. The expression given here neglects the screening effect of the surrounding electron cloud, which acts to reduce the differential cross section, thus lowering the amount of scattering. In other words, when the electron does not pass close to the nucleus, the scattering angle will be small (say < 5°) because screening is important. If we wish to account for screening, we replace the $\sin^2(\theta/2)$ term with $[\sin^2(\theta/2) + (\theta_0/2)^2]$, where θ_0 is called the screening parameter given by

$$\theta_0 = \frac{0.117\, Z^{1/3}}{E_0^{1/2}} \qquad [3.6]$$

(Here E_0 is in keV.) What we are saying is that the screening parameter can be described by a particular scattering angle, θ_0. When the scattering angle is greater than θ_0, we can neglect electron–electron interactions and the nuclear interaction is dominant. The value of θ_0 at 100 keV is only ~ 2° for Cu and less for lighter elements, so above this angle all scattering can be approximated to Rutherford-type high-angle scattering.

You should note that equation 3.3 is nonrelativistic, which is unfortunate since relativistic effects are significant for electrons with energies greater than 100 keV, as in the TEM. However, we can correct for relativity to give a more accurate differential cross section which is expressed using λ_R, the relativistically corrected wavelength (see equation 1.7), and a_0, the Bohr radius of the scattering atom

$$a_0 = \frac{h^2 \varepsilon_0}{\pi m_0 e^2} \qquad [3.7]$$

where ε_0 is the dielectric constant. Using the other constants listed in Table 1.1 we find a_0 is 0.0529 nm (remember this as 0.5 Å). The result is

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{\lambda_R^{\,4} Z^2}{64\pi^4 (a_0)^2 \left(\sin^2 \frac{\theta}{2} + \left(\frac{\theta_0}{2} \right)^2 \right)^2} \qquad [3.8]$$

This is called the screened relativistic Rutherford cross section.

This cross section is the one most widely used for TEM calculations, although it has particular limitations at the highest TEM voltages (300–400 kV) and for the heavier elements (Z>30), which cause large scattering angles. Under these circumstances you should use another cross section, such as that of Mott, for which you should consult the text by Mott and Massey (Chapter 2).

The best way to summarize the characteristics of cross sections is to present some data. Figure 3.3 shows the variation of the screened Rutherford cross section with scattering angle for three different elements and two different electron-beam energies. As you can see, the cross section decreases by several orders of magnitude from ~10^6 barns to about 10 barns as the scattering angle increases from 0–180°; so, as expected, scattering is most likely to occur in the forward (θ close to 0°) direction. Doubling the electron-beam energy can lower the cross section by a factor of two or three, which confirms that higher-energy electrons are less likely to be scattered, all else being equal. Figure 3.4 plots the related mean free paths for elastic scattering. From this graph you can see that very few high-angle elastic scattering events will occur if you keep your specimen below 100-nm thickness and you can then approach the ideal of single scattering that we'll assume many times throughout this text.

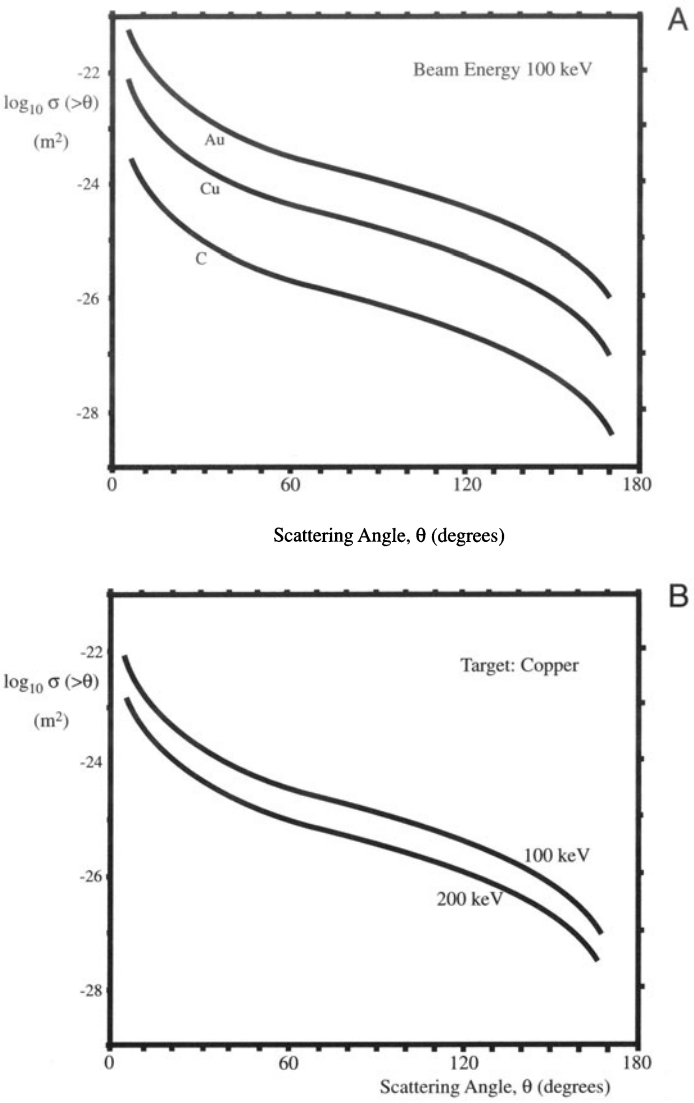

Figure 3.3. The variation of the logarithm of the screened relativistic Rutherford cross section with scattering angle: (A) for different elements at 100 keV and (B) for Cu at different TEM voltages.

3.6. COHERENCY OF THE RUTHERFORD-SCATTERED ELECTRONS

Up to now we've treated the electron as a particle, but there is useful insight to be gained if we examine the wave nature of the scattered electron. The coherency of the scattered electron wave is a distinguishing characteristic. High-angle

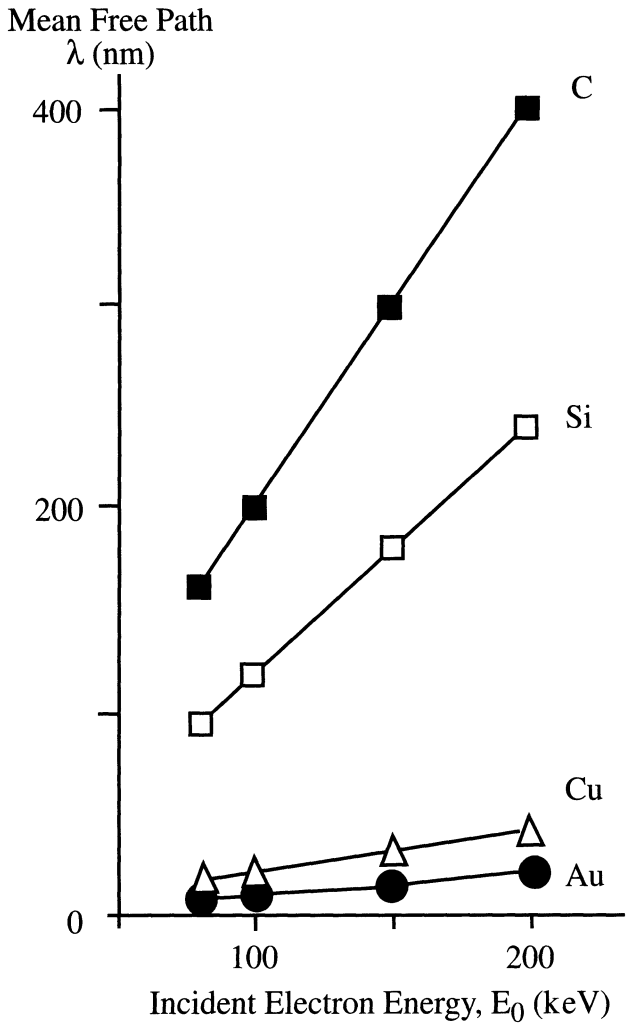

Figure 3.4. The variation of the mean free paths of elastic scatter for four different elements as a function of the beam energy, calculated assuming a screened, relativistic Rutherford cross section.

Rutherford-scattered electrons are *incoherent:* the phases of the electron waves are not in step. Such incoherent scattering is important in two respects. First, the high-angle forward scattering can be used to form exceptionally high-resolution images of a crystalline specimen in which the image contrast is due to the value of *Z*, not the orientation of the specimen, as we'll see is the case for low-angle coherent scattering. Such *Z-contrast images,* as we'll see in Chapter 22, provide qualitative atomic resolution microanalysis in addition to showing atomic resolution detail at interfaces between regions of different *Z*. This is a relatively new imaging technique which may revolutionize our understanding of materials. Second, the high-angle backscattered electrons can be used to form images of the beam entrance surface of the specimen in which the contrast is not only due to differences in *Z*, but also to changes in surface topography of the specimen. Backscattered electron images are rarely used in the TEM because the backscattered signal is small. If you go back and look at the Monte Carlo simulation in Figure 2.4, you'll see that out of 10^3 incident electrons in Cu only about three (0.3%) were backscattered, and only one of these escaped from the foil. Therefore, the quality of the signal is very poor and the images are noisy. This contrasts with bulk specimens in an SEM in which many electrons are backscattered (about 30% in Cu).

3.7. THE ATOMIC SCATTERING FACTOR

The classical Rutherford differential cross section cannot be used to calculate the cross section exactly, because it ignores the wave nature of the electron beam. A full treatment involves wave mechanics and is well beyond the scope of this text.

Perhaps the most familiar aspect of the wave approach to a cross section is the concept of the atomic scattering factor $f(\theta)$. The atomic scattering factor is related to the differential elastic scattering cross section, thus

$$|f(\theta)|^2 = \frac{d\sigma(\theta)}{d\Omega} \qquad [3.9]$$

What we will do is to highlight some of the important features that lead to this result by outlining the arguments.

- $f(\theta)$ is a measure of the amplitude of an electron wave scattered from an isolated atom.
- $|f(\theta)|^2$ is proportional to the scattered intensity.

From these two statements you can appreciate why $f(\theta)$ is such an important parameter.

The scattering-factor approach is complementary to the Rutherford differential cross section, because it is most useful for describing the low-angle elastic scattering where the Rutherford model is inappropriate. Usually, the atomic scattering factor is defined in the following manner

$$f(\theta) = \frac{\left(1 + \frac{E_0}{m_0 c^2}\right)}{8\pi^2 a_0}\left(\frac{\lambda}{\sin\frac{\theta}{2}}\right)^2 (Z - f_x) \qquad [3.10]$$

where all the terms have been previously defined. If you need a more detailed approach you could consult the text by Reimer (1993). The wavelength is λ and f_x is the scattering factor for X-rays, which is well known. The best source of electron scattering factors is that due to Doyle and Turner

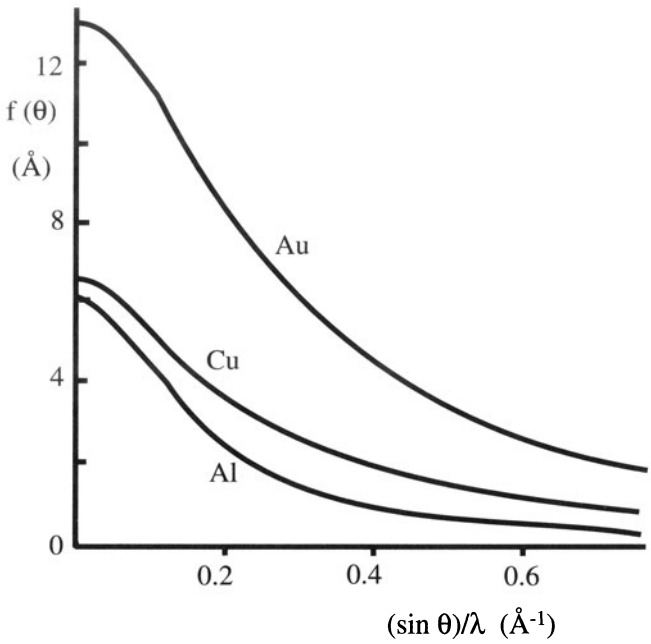

Figure 3.5. Change in the atomic scattering factor $f(\theta)$ with scattering angle θ (calculated from equation 3.10) showing that elastic scattering decreases with angle away from the incident beam direction ($\theta = 0°$) and increases with Z.

(1968), and you can also find values in the NCEMSS software (Section 1.5). The appearance of f_x in this formula is a reminder that $f(\theta)$ is a fundamental result of the wave nature of the electron.

$f(\theta)$ depends on λ, θ, and Z.

We can plot this angular variation for a single isolated atom. Figure 3.5 summarizes graphically what we already know about elastic scattering:

- It decreases as θ increases ($\theta = 0°$ for the incident beam direction).
- It decreases as λ decreases (i.e., as the accelerating voltage increases).
- It increases with Z for any value of θ.

The important point to remember is that both the differential cross section and the scattering factor are simply a measure of how the electron scattering intensity varies with θ.

This expression (equation 3.10) for $f(\theta)$ contains components of both elastic nuclear scattering (the Z term) and elastic electron-cloud scattering (the f_x term). We'll see later in the chapters on diffraction that the $f(\theta)$ approach is used exclusively, and if we neglect the f_x term then it can be shown that $|f(\theta)|^2$ is mathematically equivalent to the high-angle Rutherford differential cross section.

3.8. THE ORIGIN OF $f(\theta)$

Since $f(\theta)$ relates to the amplitude of a scattered wave, we will briefly consider how it arises. The following analysis is not intended to be completely rigorous, but only to give the fundamental ideas behind the meaning of $f(\theta)$ and its relation to the differential scattering cross section. You can safely delay studying this topic until curiosity wins.

To find the total elastic scattering cross section, we have to integrate $d\sigma/d\Omega$. We note that this is a particle model, but we should note how the wave nature of the electrons is brought in. We can consider the wave nature by looking at Figure 3.6.

The incident beam can described as a wave of amplitude ψ and phase $2\pi kr$

$$\psi = \psi_0 e^{2\pi i kr} \qquad [3.11]$$

In this definition of phase, k is the magnitude of the wave vector and r is the distance that the wave has propagated, as we'll discuss in detail in Chapter 11. When it is scattered

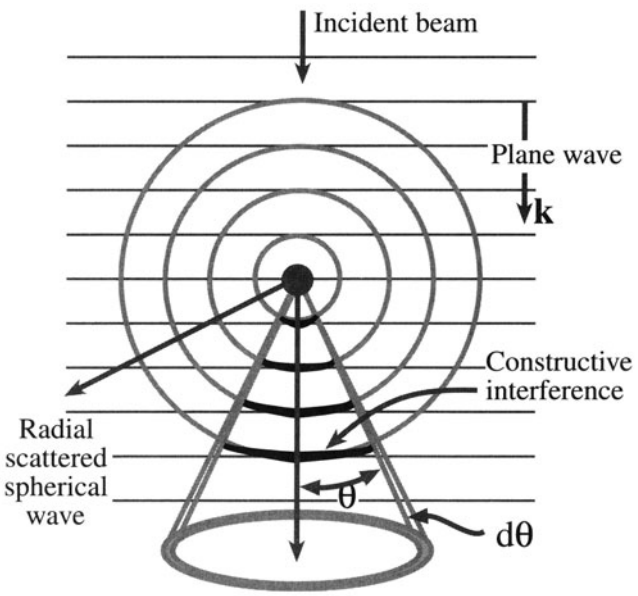

Figure 3.6. The generation of a scattered wave by the interaction of a plane wave (horizontal lines) with a point charge. The circles represent the scattered spherical wavefronts which are in phase (same λ). The in-phase constructive interference between the plane and spherical waves is shown by the dark arcs. The angles θ and $d\theta$ are the same as in Figure 2.3.

by the point charge, a spherical scattered wave is created which has amplitude ψ_{sc} but the same phase

$$\psi_{sc} = \psi_0 f(\theta) \frac{e^{2\pi i k r}}{r} \qquad [3.12]$$

In this equation, $f(\theta)$ is the amplitude we would have if $\psi_0 = 1$, i.e., it is the *atomic scattering amplitude.*

Now we need to know the atomic scattering amplitude. Up to this point, our treatment has been quite rigorous. So we need a model for $f(\theta)$ to make the problem manageable. Ideally, the model would distinguish between a neutral atom in a metal, a covalently bonded atom, and an ion. In practice, we usually use a simple approximation.

The quantity $f(\theta)$ can always, in principle, be calculated from the Schrödinger equation. If we write down the expression for the scattering process shown in Figure 3.6, then we have

$$\psi_{sc} = \psi_0 \left[e^{2\pi i \mathbf{k}_1 \cdot \mathbf{r}} + i f(\theta) \frac{e^{2\pi i k r}}{r} \right] \qquad [3.13]$$

Note that, as usual for Huygens wavelets, there is a 90° phase shift (shown by the inclusion of i in the second term) between the incident and scattered beams, and second, that $f(\theta)$ can be expressed as

$$f(\theta) = |f(\theta)| e^{i\eta(\theta)} = |f(\theta)| \left(\cos\eta(\theta) + i \sin\eta(\theta) \right) \qquad [3.14]$$

which means that the phase, $\eta(\theta)$, of $f(\theta)$ also depends on θ.

First aside: In writing equation 3.13, we have introduced two wave propagation parameters: the vector $\mathbf{k}_1$ for the incident plane wave and the scalar k for the spherical scattered wavelet. By writing the 2π factor separately as part of the phase term, we have implicitly defined k to be $1/\lambda$. Many physics textbooks include the 2π in k, so they have k given by $2\pi/\lambda$. Just be careful when you compare similar formulas in two textbooks.

Second aside: The 90° phase change for the scattered wave component in equation 3.14 can be easily understood by considering the following. If the amplitude of the wave is initially $\psi_0 \sin(2\pi k r)$, then after it has passed through the specimen it will be ψ_{tot}; after scattering, the phase is increased by ϕ. We can express the new ψ_{tot} as

$$\psi_{tot} = \psi_0 \sin(2\pi k z + \phi) = \psi_0 \sin(2\pi k z)\cos\phi + \psi_0 \cos(2\pi k z)\sin\phi \qquad [3.15]$$

If ϕ is small, then $\cos\phi \approx 1$ and $\sin\phi \approx \phi$; $\cos\theta$ is always the same as $\sin(\theta + \pi/2)$, hence

$$\psi_{tot} = \psi_0 \sin(2\pi k z) + \psi_0 \phi \sin\left(2\pi k z + \frac{\pi}{2}\right) \qquad [3.16]$$

As Reimer notes, the $\pi/2$ would arise if we used the exponential rather than the sine to denote the phase, so we can then write equation 3.16 as

$$\psi_{tot} = \psi + i\psi_{sc} \qquad [3.17]$$

which we see then has the form given in equation 3.13.

3.9. THE STRUCTURE FACTOR $F(\theta)$

The next introductory step in discussing electron scattering is to take the idea of individual atoms scattering electrons (the atomic scattering factor), which we've just discussed in some detail, and consider what happens when the atoms are stacked together in crystals. We will deal with this point in great detail in Chapter 13, but for now we can introduce the structure factor $F(\theta)$, which is a measure of the amplitude scattered by a unit cell of a crystal structure. Because it is an amplitude like $f(\theta)$ it also has dimensions of length. We can define $F(\theta)$ in terms of the sum of the atomic scattering factors from all the i atoms in the unit cell (with atomic coordinates x_i, y_i, z_i) multiplied by the phase factor that takes account of the difference in phase between waves scattered from atoms on different planes with Miller indices $(hk\ell)$. The scattering angle θ is the angle between the incident and scattered electron beams. So we can write

$$F(\theta) = \sum_i f_i e^{i\varphi_i} = \sum_i f_i e^{2\pi i (hx_i + ky_i + \ell z_i)} \qquad [3.18]$$

All this means is that the amplitude (and hence the intensity) of scatter is influenced by the type of atom ($f(\theta)$), the position of the atom in the cell (x,y,z), and the specific atomic planes $(hk\ell)$ that make up the crystal structure. None of this is very surprising, but it turns out that this equation predicts that in certain circumstances the amplitude of scatter is zero, which is often a very useful diagnostic test when determining crystal structures in the TEM. We'll return to this in Chapter 13 in much more detail.

3.10. SIMPLE DIFFRACTION CONCEPTS

As we mentioned earlier, electron diffraction is by far the most important scattering phenomenon in the TEM. The importance arises because, as we'll show you in Chapters 11 and 12, we can use diffraction to determine the spacing of planes in crystals. The interplanar spacings in different crystal structures are characteristic of that structure. As a result we can distinguish between different crystal structures by observing and measuring diffraction patterns. We'll see that the *positions* of the diffracted beams of electrons are determined by the size and shape of the unit cell, and the *intensities* of the diffracted beams are governed by the distribution, number, and types of atoms in the specimen. We'll also show you how the diffraction process leads to contrast in TEM images which is related to the orientation of a crystalline specimen.

The combination of the diffraction pattern and the image is a most powerful tool for characterizing crystals and their defects.

It's easy to see, in a qualitative manner, how diffraction modifies the distribution of the low-angle scattering, described by $f(\theta)$, and shown for a single atom in Figure 3.5. When we consider the effect of the arrangement of atoms in the specimen, then Figure 3.5 has to be modified. For an amorphous specimen, the atoms are almost (but not quite) randomly arranged. A random arrangement would result in a similar plot as for Figure 3.5, but there are certain interatomic spacings that tend to occur in an amorphous structure (e.g., first- and second-nearest neighbor spacings are usually relatively well defined). As a result, the amplitude (and hence the intensity) of diffraction is stronger at some angles than at others, which we see as rings of intensity shown in Figure 3.7A, and in the diffraction pattern in Figure 2.11a. If the specimen is crystalline, then the intensity of the diffracted beams is a maximum at specific angles because the interplanar spacings are fixed (Figure 3.7B). The variation of $f(\theta)$ with θ in Figures 3.7A and B is equivalent to the intensity variation across the diffraction patterns in Figures 2.11a and b/c, respectively, and thus emphasizes the strong relationship between $f(\theta)$ and diffracted intensity. We'll describe this important relationship mathematically in Section 3.10.B below.

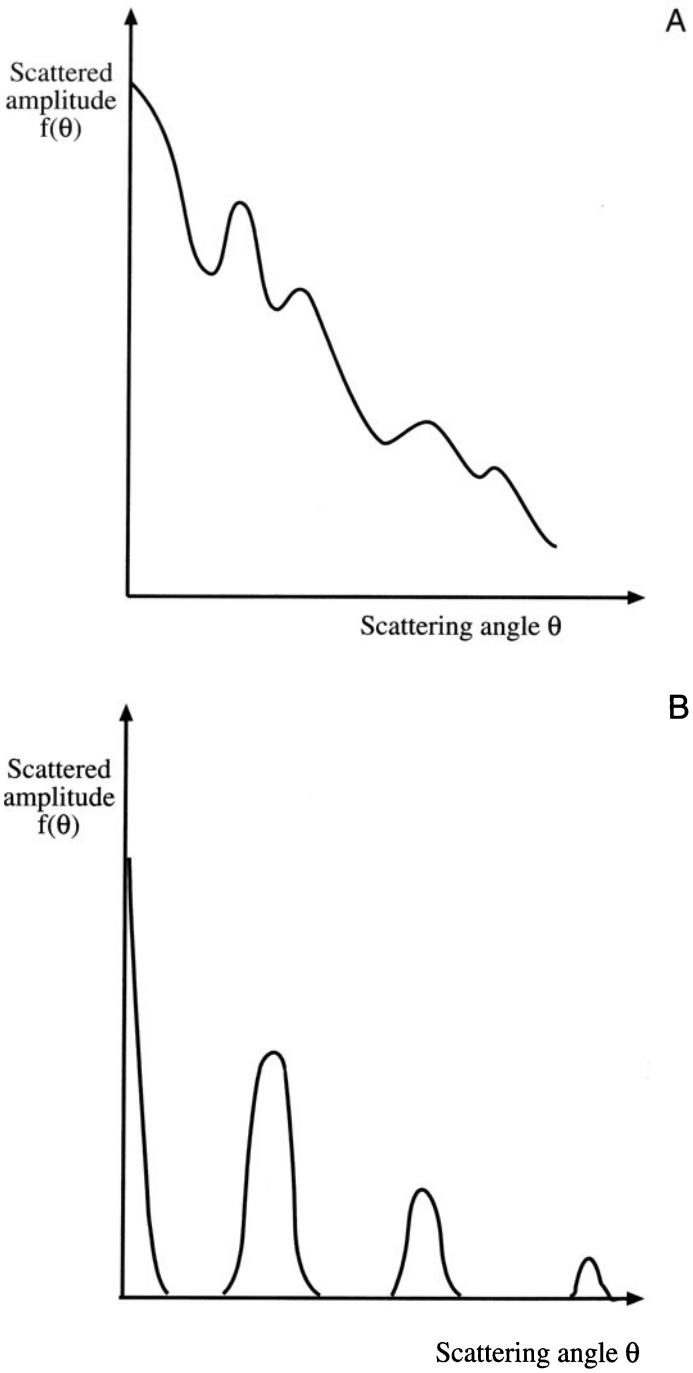

Figure 3.7. Change in $f(\theta)$ with θ (A) for an amorphous specimen and (B) for a crystalline specimen. The amplitude (and therefore the intensity) of scatter generally decreases with increasing θ, but the smooth decrease is modified at certain scattering angles (compare with the intensity variation along a line from the middle of the diffraction patterns in Figures 2.11a and b).

3.10.A. Interference of Electron Waves

To interpret this low-angle elastic scattering (which is primarily from the electron cloud) it is best to think in terms of electron waves and not in terms of particle interactions that characterize high-angle scattering. If you go back and look at Figure 3.2, you see a periodic one-dimensional array of scattering centers (slits); a monochromatic wave (fixed λ) is advancing toward the centers. Each slit acts as a new source of a wave of the same λ. Thus many new

waves are created and, when more than one wave is present, the waves can interfere with one another. This process happens from even the thinnest specimens, and is entirely a wave phenomenon that doesn't need concepts such as cross section, which we apply when we think of the electron as a particle.

A rule of wave theory is that waves reinforce one another (this is constructive interference) when they are in phase, i.e., when they are coherent. Waves also cancel one another (destructive interference) when they are out of phase. What you see in Figure 3.2 is that the diffracted waves are in phase with one another only in certain directions. There is invariably a *zero-order wave* which proceeds in the same direction as the incident wave, which in the TEM we'll refer to as the direct beam of electrons. There are also *higher-order waves* which propagate in directions that are at some fixed angle to the incident wave and we'll call these the diffracted beams.

So diffraction creates many electron beams traveling at specific angles relative to a single monochromatic incident beam. In the chapters on diffraction, we'll find ways to measure these angles and relate them to the spacing of the scattering planes.

3.10.B. Diffraction Equations

Here we'll introduce the mathematical relationships that describe the diffraction process. The idea of using diffraction to probe the atomic structure of materials was accredited to von Laue in Germany in 1912, although others such as Ewald were working on similar ideas at the same time. At von Laue's suggestion, his colleagues Friedrich and Knipping irradiated a copper sulfate crystal and became the first to observe diffraction from crystal planes. In fact, it was a remarkable stroke of luck that the $CuSO_4$ diffracted the X-rays at all because of the strict equations which govern diffraction.

Von Laue used the well-known light-optics approach to argue that the diffracted waves are in phase if the path difference between waves scattered by adjacent scattering centers is a whole number of wavelengths, $h\lambda$, and h is an integer. Thus, as shown in Figure 3.8, if the scattering centers (B and C) are spaced some distance a apart and the incident beam (wavelength λ) makes an angle θ_1 with the line connecting the scattering centers, and is diffracted at an angle θ_2, then the path difference (AB – CD) is then

$$a(\cos\theta_1 - \cos\theta_2) = h\lambda \qquad [3.19]$$

Now in three dimensions, two more Laue equations can be written for two more distances, b and c, and appropriate angles θ_n

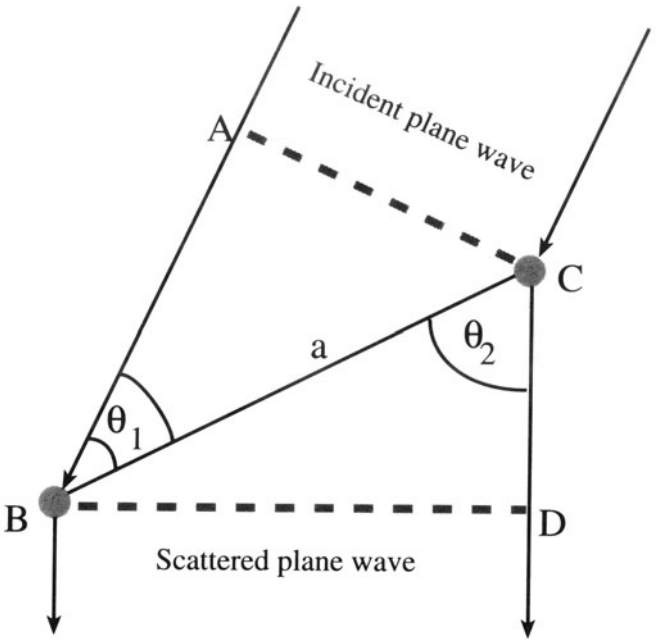

Figure 3.8. The approach used by von Laue to calculate the path difference for a wave (wavelength λ). In this one-dimensional figure the wave is incident at angle θ_1 and scattered at angle θ_2 from two atoms (B and C) spaced distance a apart. The path difference between scattered waves is AB – CD.

$$b(\cos\theta_3 - \cos\theta_4) = k\lambda \qquad [3.20]$$

$$c(\cos\theta_5 - \cos\theta_6) = \ell\lambda \qquad [3.21]$$

These three simultaneous equations bear von Laue's name, and for this work he received the Nobel Prize. If, in a TEM specimen, all three Laue equations are satisfied simultaneously, we will show in Chapter 11 that a diffracted beam is produced. We'll also show you in Chapters 11 and 12 that the letters $hk\ell$ are the indices of the diffracted beam and are equivalent to the Miller indices $(hk\ell)$ of a crystal plane, or some multiple thereof.

Usually in TEM, we use a simpler approach to describe diffraction. Von Laue's approach was simplified by Bragg (the elder) in England who argued that the waves behaved as if they were reflected off atomic planes as shown in Figure 3.9. Bragg showed that waves reflected off adjacent scattering centers must have a path difference equal to an integral number of wavelengths if they are to remain in phase. So, in the TEM, the path difference between electron waves reflected from the upper and lower planes in Figure 3.9 is (AB + BC). Thus, if the "reflecting" $hk\ell$ planes are spaced a distance d apart and the wave is incident and reflected at an angle θ_B, both AB and BC are

equal to $d \sin \theta_B$ and the total path difference is $2d \sin \theta_B$. Then we have Bragg's law

$$n\lambda = 2d \sin \theta_B \qquad [3.22]$$

We'll reserve θ_B for the Bragg angle, which is the most important scattering angle in TEM and you'll come across it many more times in this text. Bragg also received a Nobel Prize for this one equation, even though the idea of reflected electrons, while mathematically correct, is physically wrong! We'll continue to use the term "Bragg reflection" to describe diffraction because everyone does so, even though it's inaccurate. We will demonstrate, in a rigorous fashion, the equivalence of the Bragg and Laue approaches in Chapter 12.

It is simple to see from the Bragg equation that atomic planes which are closer together give rise to larger angles of scatter. This reciprocal relationship (d is proportional to $1/\theta$; see Chapter 12) is very important in diffraction pattern interpretation. So, if we know λ for the incident electron and we can measure θ experimentally, we can work out the interplanar spacings in the crystal. It is this crystallographic information that makes diffraction such an important aspect of the TEM.

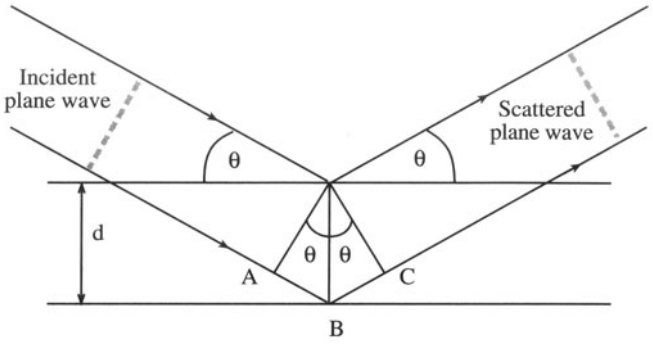

Figure 3.9. The Bragg description of diffraction in terms of the reflection of a plane wave (wavelength λ) incident at an angle θ to atomic planes of spacing d. The path difference between reflected waves is AB + BC.

CHAPTER SUMMARY

What should you remember from this chapter? Until you have time to study this material very carefully you may find it difficult, so here are a few suggestions:

- Know the words! In particular, we can describe the scattering process by three parameters:

$\sigma(\theta)$	the scattering cross section
$\frac{d\sigma(\theta)}{d\Omega}$	the differential scattering cross section
$f(\theta)$	the atomic scattering amplitude

In particular, don't be put off because "differential scattering cross section" sounds difficult. All three terms are *very* important in different parts of TEM.

- The relationships between $f(\theta)$ and $\sigma(\theta)$ are very important.
- The relationships between $f(\theta)$ and the intensity in a diffraction pattern are very important.

Remember that although we often write $\sigma(\theta)$ as σ, there is an angle involved in any σ.

- The fact that the electron is a charged particle is critical to the whole scattering process.

Yes, a really rigorous treatment of scattering would take into account the wave nature of the electron (wave mechanics), relativity, and the electron charge at the same time. We won't do this! Fortunately we can do very well using compiled tables.

- The strength of the scattering, $f(\theta)$, depends inversely on the scattering angle, θ.
- $F(\theta)$ is a measure of the amplitude scattered by a unit cell.

A final point to think about: remember that $f(\theta)$ is the property of a "scattering center." We usually think of this center as being an atom. What happens if the scattering center is an ion (i.e., if it is charged)? Is the scattering process affected by how this atom is bonded to its neighbors? What changes if the atom is covalently bonded? We'll answer these questions as we go on.

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