3

Elastic Scattering

CHAPTER PREVIEW

Elastically scattered electrons are the major source of contrast in TEM images. They also create much of the intensity in DPs, so we need to understand what controls this process. First we'll consider elastic scattering 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 characteristics of electrons.

Scattering from isolated atoms can occur either as a result of electrons interacting with the negatively charged electron cloud, which results in angular deviations of only a few degrees, or by attraction toward the positive nucleus which scatters the electrons through much larger angles, up to 180°. Such scattering can often be interpreted in terms of billiard-ball type, 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 in the book, we'll show how to use this Z dependence to form images that reflect the chemistry of the specimen. When we treat the electrons as waves, their *coherency* becomes important. The coherency of the scattered electrons is related to their *angle* of scattering (θ). As this angle becomes larger, the degree of coherency becomes less and electrons that are Rutherford-scattered out to high angles are incoherent.

In contrast to Rutherford scattering, electrons that are scattered elastically through small angles (which we'll define as $<3°$) are coherent. The intensity of this low-angle scattering is strongly affected by the arrangement of atoms within the specimen. As we introduced in the previous chapter, such collective scattering by the atoms is referred to as *diffraction* and can only be understood if we treat the electron as a wave. Diffraction is controlled mainly by the angle of incidence of the electron beam to the atomic planes in the specimen, the spacing between these planes, and interatomic distances within the planes. So this small-angle, coherent scattering is invaluable for characterizing the crystallography of the specimen and is undoubtedly *the* most significant scattering phenomenon in the TEM.

So as we discuss elastic scattering, you'll see that we often use the wave-particle duality simultaneously, because both lines of thought are necessary for a full understanding.

3.1 PARTICLES AND WAVES

We have two different ways of looking at how an electron beam interacts with our TEM specimens. 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 and we can summarize the two viewpoints thus:

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

- They have a scattering cross section and a differential scattering cross section.
- They can be scattered through particular angles (remember our angles are semi-angles).
- The electrons interact with the nucleus and the electron cloud 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.

PARTICLES AND WAVES

When we discuss X-ray and electron spectrometry you'll see that we have to use a particle description. When we discuss imaging, HRTEM, and DPs you'll see that we use a wave 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.
- When we gather atoms together into a solid, the diffraction process gets much more complicated but it is central to TEM.
- We can relate the process to the diffraction of X-rays, so lots of analysis already exists.

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, saving inelastic scattering for Chapter 4.

It’s convenient to divide elastic-scattering mechanisms into two principal forms: electron scattering from single, isolated atoms and collective scattering from many atoms together within the specimen. We’ll start in the same way 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 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° (i.e., complete backscattering).

ELASTIC?

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 continue to ignore any inelastic effects in this chapter.

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-scattering 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 that interacts with the incident plane wave acts as a source of secondary spherical wavelets, as illustrated in Figure 3.2.

INTERFERENCE

These wavelets reinforce one another in certain angular directions and cancel in other directions: both reinforcement and cancellation are extremely useful phenomena.

Thus, the low-angle, elastic scattering distribution is modified by the crystal structure of the specimen, and strong diffracted beams emerge at specific angles. The

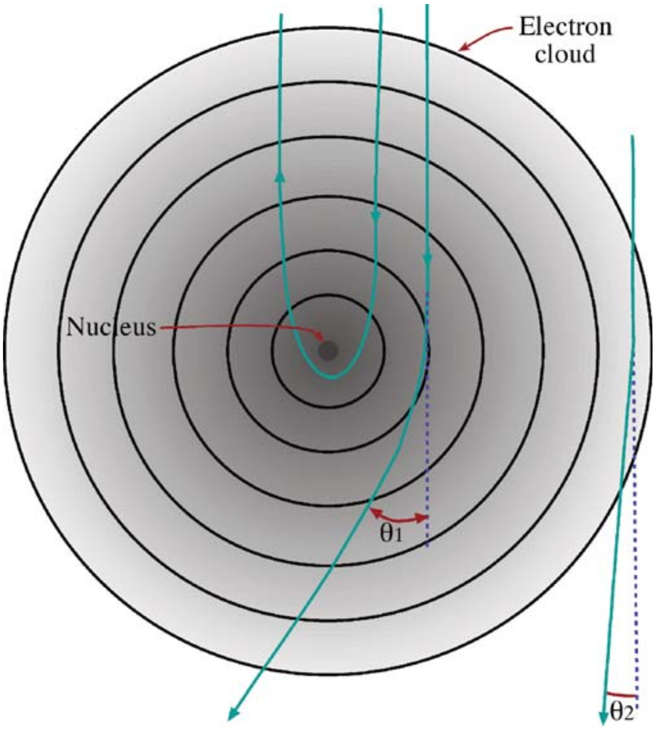

FIGURE 3.1. An isolated atom can scatter a high-energy electron by two mechanisms. Coulombic interaction within the electron cloud results in low-angle scattering; Coulombic attraction by the nucleus causes higher-angle scattering (and perhaps complete backscatter when θ > 90°). The potential within the electron cloud is always positive.

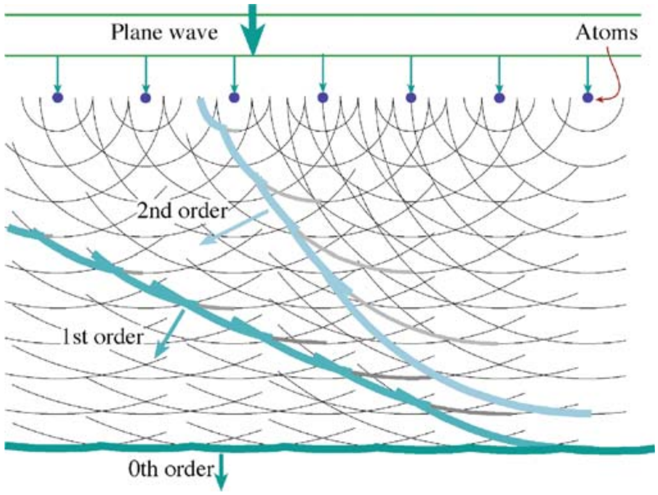

FIGURE 3.2. A plane, coherent electron wave generates secondary wavelets from a row of scattering centers (e.g., atoms in the specimen). The secondary wavelets interfere, resulting in a strong direct (zero-order) beam and several (higher order) coherent beams scattered (diffracted) at specific angles.

diffracted beam scattered through the smallest angle is called the first-order beam and we'll discuss these and higher-order effects in depth in Chapters 11 and 12. We'll now go on to examine these two forms of elastic scattering in more detail, starting with the billiard-ball approach. Then we will briefly describe the scattering of a wave to show how it relates to this particle-based treatment and later we'll use the wave approach as the basis for a full analysis of diffraction.

3.3 ELASTIC SCATTERING FROM ISOLATED ATOMS

So let's look at two possible paths for a beam electron interacting with an isolated atom as shown in Figure 3.1. Whether it interacts more strongly with the nucleus or the electrons, the electron is scattered through an angle θ.

SCATTERING ANGLE

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, accelerated through a voltage V before being scattered from an isolated atom, the electron-electron and electron-nucleus scattering paths are hyperbolic and can be given by two simple equations (Hall 1953) which are useful because they summarize the principal factors that control elastic scattering

$$r_{\mathrm{e}} = \mathrm{e}/V\theta \tag{3.1}$$

$$r_{\mathrm{n}} = Z\mathrm{e}/V\theta \tag{3.2}$$

where r is the radius of the scattering field of the nucleus and the electron. The different cross sections for scattering through angles $> \theta$ are given by πr_{n}^2 for the nucleus and $Z\pi r_{\mathrm{e}}^2$ for the scattering by Z electrons in the cloud. If we sum the two components and (just as back in equation 2.8) multiply by $N_0\rho t/A$ we'll get a sense of the total elastic scattering through a film of thickness t.

This approach is "defective in many respects" as Hall says but gives you a good qualitative sense of the various parameters that affect elastic scattering. 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 (which has to be in esu if the dimensions of these equations are to be correct). 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. So Z, V, and θ all affect image contrast and are the three major reasons why you cannot avoid having to study the physics of electron scattering.

3.4 THE RUTHERFORD CROSS SECTION

For the next three sections, we'll ignore the low-angle, electron-electron scattering and concentrate only on scattering by the nucleus. 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, Ernest Rutherford, to deduce the existence of the nucleus (never overlook undergraduate research results!). Rutherford (1911) described backscattering as "the most incredible event that has ever happened to me" (even though he'd already won the Nobel Prize for Chemistry in 1908), and he derived the following expression for the differential cross section for this high-angle scattering by the nucleus alone

$$\sigma_{\mathrm{R}}(\theta) = \frac{\mathrm{e}^4 Z^2}{16(4\pi\varepsilon_0 E_0)^2} \frac{d\Omega}{\sin^4 \frac{\theta}{2}} \tag{3.3}$$

All the terms in this equation were defined back in Chapter 2. The expression ignores relativistic effects and 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. As we've already noted, although strictly inaccurate, these assumptions can be tolerated in the TEM (at least at 100 keV or below).

3.5 MODIFICATIONS TO THE RUTHERFORD CROSS SECTION

You'll often see the Rutherford differential cross section in different, but mathematically similar, forms. For example, equation 3.3 neglects the so-called screening effect of the electron cloud. Screening can be thought of as making the nucleus appear somewhat less positive to the incident electron (although the overall charge within the electron cloud is *always* positive). So the differential cross section is effectively reduced and the amount of scattering is lowered. Screening is only important when the beam electron passes far from the nucleus and under these circumstances the scattering angle will be small (say $<\sim 3^\circ$). 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

$$\theta_0 = \frac{0.117 Z^{1/3}}{E_0^{\ 1/2}} \tag{3.4}$$

(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 electron-nucleus interaction is dominant. The value of θ_0 at 100 keV is only $\sim 2^\circ$ for Cu and less for lighter elements, so above a few degrees, all scattering can be approximated to Rutherford high-angle scattering.

As we've noted, so far all our equations are non-relativistic, which is unfortunate since relativistic effects are significant for electrons with energies $>\sim 100$ keV (which is the case for most materials investigations in the TEM). Fortunately, we can easily correct for relativity to give a more accurate cross section by using λ_R, the relativistically corrected electron wavelength (see equation 1.7), and a_0, the Bohr radius of the scattering atom

$$a_0 = \frac{h^2 \varepsilon_0}{\pi m_0 e^2} \tag{3.5}$$

where ε_0 is the dielectric constant. Using the other constants listed in Table 1.1 we find a_0 is 0.0529 nm (if you're old enough you can easily remember this as 0.5 Å). The net result of adding screening and relativity corrections is that

$$\sigma_R(\theta) = \frac{Z^2 \lambda_R^4}{64 \pi^4 a_0^2} \frac{d\Omega}{\left[\sin^2\left(\frac{\theta}{2}\right) + \frac{\theta_0^2}{4}\right]^2} \tag{3.6}$$

This expression describes the screened, relativistic, differential Rutherford cross section. One very important effect of incorporating screening into these equations is that the cross section does not go to infinity as the scattering angle goes to zero which is an important limitation of all the simpler equations that we used initially.

The screened Rutherford cross section is the one most widely used for TEM calculations, although it has particular limitations at the highest operating voltages (300–400 kV) and for heavier elements ($Z>30$) which scatter electrons through large 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 (which we referred to in Chapter 2) or Newbury (1986).

So, as we did for the basic cross section back in Chapter 2, we can integrate this expression to obtain the total cross section over specific angular ranges. We can substitute appropriate values for the various constants and integrate the differential cross section from θ to π to obtain the total nuclear cross section (in scattering events/electron/atom/m^2) for electrons elastically scattered into angles $> \theta$

$$\sigma_{\text{nucleus}} = 1.62 \times 10^{-24} \left(\frac{Z}{E_0}\right)^2 \cot^2 \frac{\theta}{2} \tag{3.7}$$

(From what we told you in Chapter 2 you ought to be able to work out the integration necessary to determine the probability of electrons being scattered into angles $<\theta$.) 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 nuclei of atoms in the specimen. If you simplify this last expression by assuming that θ is small you should be able to see some parallels with Hall's less accurate equation 3.2 for nuclear scattering. However, there's much more to this whole scattering process than we have covered here and you should read Newbury (1986) and Jones (1992) for further discussion of these calculations once you really appreciate their significance.

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 in equation 3.7 with scattering angle for (a) three different elements and (b) two different beam energies. As you can see for Cu, the cross section decreases by several orders of magnitude from $\sim 10^{-22}$ to $\sim 10^{-28}$ m^2 as the scattering angle increases from 0 to 180°; so, as we've already told you, scattering is most likely to occur in the forward ($\theta \sim 0^\circ$) direction and drops off rapidly

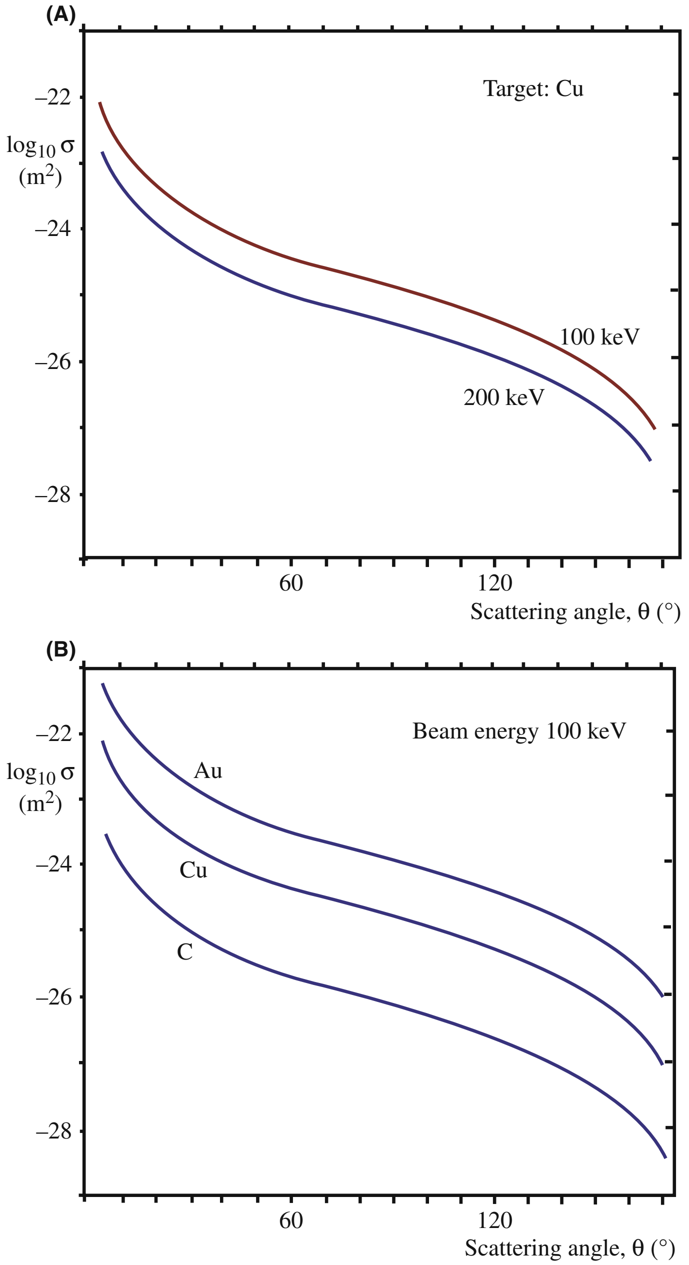

FIGURE 3.3. The variation of the logarithm of the screened relativistic Rutherford cross section with scattering angle from equation 3.7, describing the change in cross section for electrons scattered at angles $> \theta$ (A) for different elements at 100 keV and (B) for scattering from Cu at different accelerating voltages.

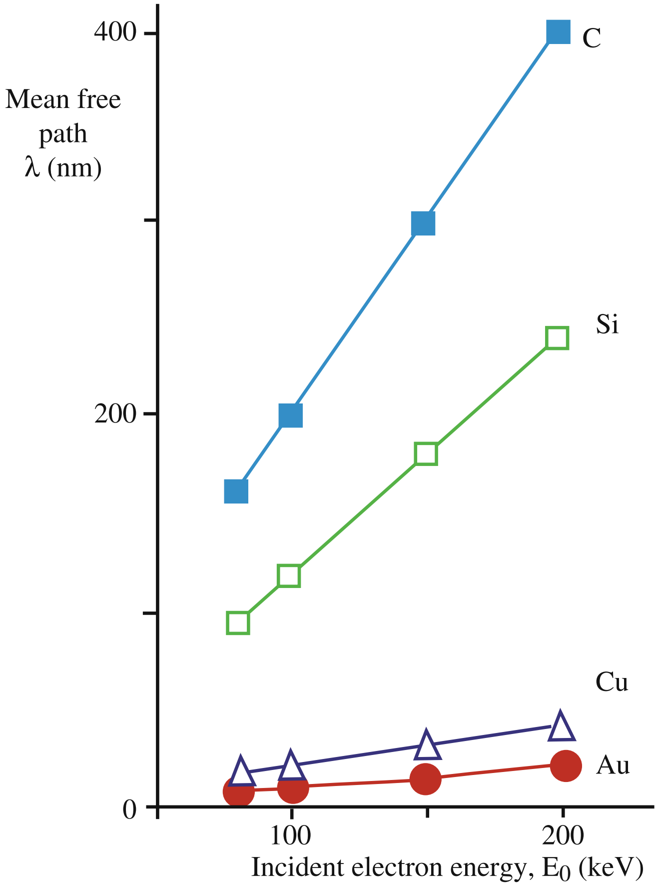

FIGURE 3.4. The variation of the mean free paths of elastic scattering for four different elements as a function of the beam energy, calculated assuming a screened, relativistic Rutherford cross section.

above a few degrees. Increasing Z from carbon to gold can increase the cross section by a factor of $\sim$100, which is why you need proportionately thinner TEM specimens if you want to 'see' through higher-Z materials. Doubling the electron-beam energy can lower the cross section by a factor of two or three, which is why higher-energy electrons are less likely to be scattered by your specimen than lower-energy electrons, 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 can make your specimen < 100 nm in thickness. Within such specimens, most electrons either undergo a single-scattering event or are not scattered and we'll assume that this simplification is a viable approximation to what's actually going on in the microscope many times throughout this text. This approximation is the main reason why, as we've already noted that in almost all TEM studies, the 'thinner is better' criterion applies.

3.6 COHERENCY OF THE RUTHERFORD-SCATTERED ELECTRONS

Up to now, in this chapter, 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. High-angle Rutherford-scattered electrons are *incoherent*: i.e., there is no phase relationship between them. This is a tricky concept because we are scattering particles. 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 solely to the value of Z, not the orientation of the specimen (as is the case for low-angle coherent diffraction). Such *Z-contrast images,* as we'll see in Chapter 22, provide qualitative atomic-resolution elemental analysis, in addition to showing atomic-resolution detail at interfaces between regions of different Z. Compared to other image-contrast mechanisms, Z-contrast imaging is a relatively new technique for most microscopists but, particularly since the availability of C_s-correctors, it has consistently held the record for the highest-resolution images and analysis in the TEM (e.g., Varela et al. 2005) and is already beginning to revolutionize our understanding of the atomic-level structure and chemistry of crystal defects.

COHERENCY

Coherency of the scattered electron is a wave property. If the scattered electron waves have a phase relationship they must be coherent.

Second (but much less important), the high-angle backscattered electrons (BSEs) 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. BSE images are rarely used in the TEM because the BSE 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. Therefore, the quality of this signal is very poor, the images are noisy, and the contrast is low. The contrast is much better for bulk specimens in an SEM in which many more electrons are backscattered (e.g., about 30% in Cu) and BSEs provide a stable, high-contrast imaging technique in SEMs in which you can discriminate between the signals from adjacent elements in the periodic table. In principle, Z-contrast should be able to do the same in the TEM.

3.7 THE ATOMIC-SCATTERING FACTOR

The classic 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 cross sections is the concept of the atomic-scattering factor $f(\theta)$, which is related to the differential elastic cross section by a simple equation (more on this in Section 3.8)

$$|f(\theta)|^2 = \frac{d\sigma(\theta)}{d\Omega} \qquad (3.8)$$

What we will now do is to highlight some of the important features that lead to this result by outlining the basic 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 and given the importance of scattered-electron intensity in images and DPs, you can appreciate why $f(\theta)$ is such an important parameter in TEM.

The scattering-factor approach is complementary to the Rutherford differential cross section analysis, because it is most useful for describing the low-angle (i.e., $<\sim 3^\circ$) elastic scattering where the Rutherford model is inappropriate. Usually, $f(\theta)$ is defined in the following manner

$$f(\theta) = \frac{\left(1 + \frac{E_0}{m_0c^2}\right)}{8\pi^2 a_0}\left(\frac{\lambda}{\sin\frac{\theta}{2}}\right)^2 (Z - f_x) \qquad (3.9)$$

All the terms have been previously defined (note that we've dropped the screening term, so remember what this implies). If you need a more detailed approach you could consult the physics-based text by Reimer. Because we're now thinking in terms of waves, we need the wavelength λ (controlled of course by the beam energy E_0), and f_x is the scattering factor for X-rays, which is well known. The most widely referenced source of electron-scattering factors for TEM was usually the classic work of Doyle and Turner (1968), but you can now find values in software packages (see Section 1.6) and you can even do your own calculations using the free software on the NIST database (also in Section 1.6 and URL #1). The appearance of f_x in equation 3.9 is a reminder that $f(\theta)$ is a fundamental result of the wave nature of the electron.

***f*(θ)**

The atomic-scattering factor $f(\theta)$ 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 the magnitude of elastic scattering (see equations 3.1 and 3.2)

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

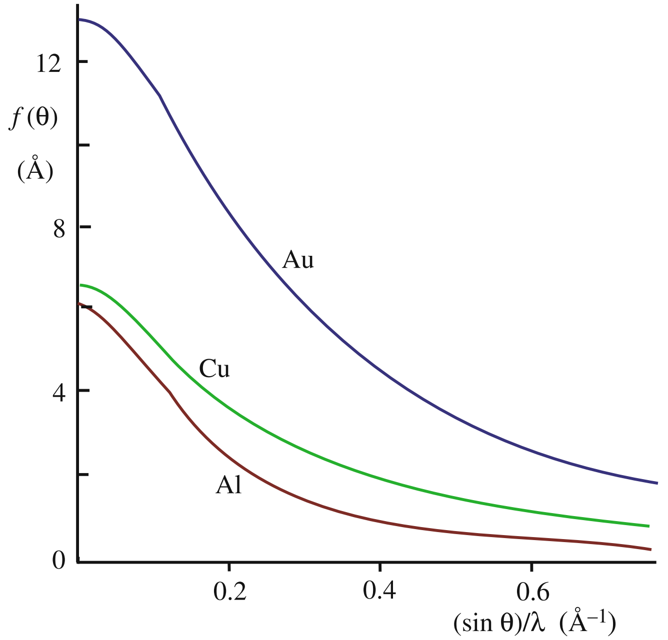

FIGURE 3.5. Change in the atomic scattering factor $f(\theta)$ with scattering angle θ (calculated from equation 3.9) showing that elastic scattering decreases with angle away from the incident beam direction ($\theta = 0°$) and increases with Z.

This expression (equation 3.9) 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 in Part 2 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, as we defined it in equation 3.6. So now we've tied together the particle and wave approaches to elastic scattering.

ANGLE VARIATION

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

3.8 THE ORIGIN OF *f*(θ)

Since $f(\theta)$ relates to the amplitude of a scattered wave, we'll consider briefly 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, then you can go and read the really thick physics textbooks.

To find the total elastic-scattering cross section, we have to integrate $d\sigma/d\Omega$. Note that this is a particle model, but you should also be aware of how the wave nature of the electrons is brought in. We can consider the wave nature by looking at Figure 3.6 (which you should realize is closely related to Figures 2.3 and 2.12).

We can describe the incident beam as a wave of amplitude ψ_0 and phase $2\pi kr$

$$\psi = \psi_0 e^{2\pi i k r} \tag{3.10}$$

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 later in Chapter 11. When the incident plane wave is scattered by a point charge, a spherical scattered wave is created which has a different amplitude ψ_{sc} but keeps the same phase apart from a $\pi/2$ addition which we return to in a moment

$$\psi_{sc} = \psi_0 f(\theta) \frac{e^{2\pi i k r}}{r} \tag{3.11}$$

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

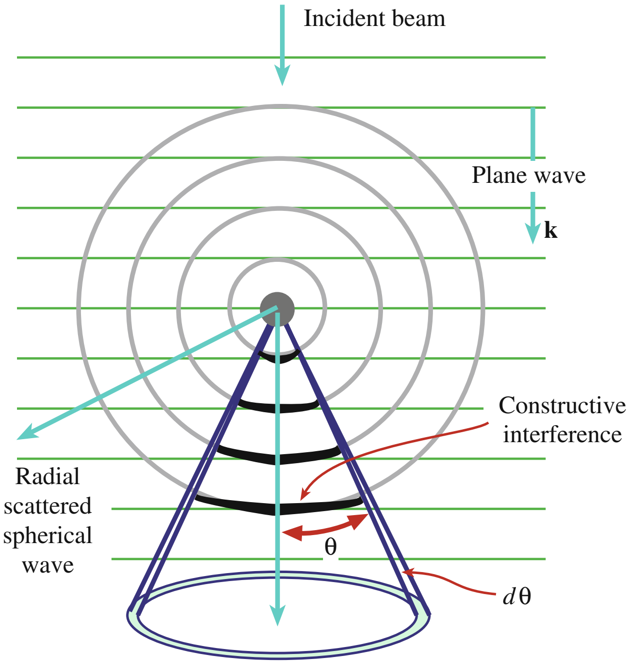

FIGURE 3.6. Generating a scattered wave by the interaction of a plane wave (horizontal line, wavelength λ) with a point charge. The circles represent the scattered spherical wavefronts which are in phase and retain the original λ. The in-phase, constructive interference between the plane and spherical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

So obviously we need to know $f(\theta)$ and an acceptable model is essential to make the problem manageable. Up to this point, our treatment has been quite rigorous and ideally, the model would distinguish between a neutral atom in a metal, a covalently bonded atom, and an ion. If you're desperate, the quantity $f(\theta)$ can always, in principle, be calculated from the Schrödinger equation. In practice, however, we usually use a simple approximation which we'll now describe.

If we write down the expression for the scattering process shown in Figure 3.6, then we have

$$\psi_{sc} = \psi_0 \left[e^{2\pi i \mathbf{k}_I \cdot \mathbf{r}} + i f(\theta) \frac{e^{2\pi i k r}}{r} \right] \tag{3.12}$$

You should note first of all 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 secondly, that $f(\theta)$ can be expressed as

$$f(\theta) = |f(\theta)| e^{i\eta(\theta)} = |f(\theta)| (\cos \eta(\theta) + i \sin \eta(\theta)) \tag{3.13}$$

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

> *First aside*: In writing equation 3.12, we have introduced two wave-propagation parameters: the vector $\mathbf{k}_I$ 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.

1/λ AND 2π/λ

Sometimes $k = 1/\lambda$ and sometimes $k = 2\pi/\lambda$ and it's sometimes difficult to find out which definition is being used.

> *Second aside*: The 90° phase change for the scattered-wave component in equation 3.13 can be easily understood if you consider 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, so we can express the new ψ_{tot} as
>
> $$\begin{aligned} \psi_{tot} = \psi_0 \sin(2\pi k z + \phi) &= \psi_0 \sin(2\pi k z) \cos \phi \\ &\quad + \psi_0 \cos(2\pi k z) \sin \phi \end{aligned} \tag{3.14}$$
>
> Now 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
>
> $$\psi_{tot} = \psi_0 \sin(2\pi k z) + \psi_0 \phi \sin\left(2\pi k z + \frac{\pi}{2}\right) \tag{3.15}$$
>
> The $\pi/2$ term would arise if we used the exponential rather than the sine to denote phase, so we can now write equation 3.15 as
>
> $$\psi_{tot} = \psi + i\psi_{sc} \tag{3.16}$$
>
> This equation has the same form as that given in equation 3.12.

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 (i.e., $f(\theta)$), which we've just discussed in some detail, and consider what happens when the atoms are stacked together regularly in a crystal structure. (We can, in principle, also do this for an amorphous solid but we'll stick to crystals for simplicity.) We will deal with this approach 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 $F(\theta)$ is an amplitude like $f(\theta)$, it also has dimensions of length. We can define $F(\theta)$ as the sum of the $f(\theta)$ terms from all the i atoms in the unit cell (with atomic coordinates $x_i\, y_i\, z_i$) multiplied by a phase factor. The phase factor takes account of the difference in phase between waves scattered from atoms on different but parallel atomic planes with the same Miller indices (hkl). The scattering angle θ is the angle between the incident and scattered electron beams. So we can write

$$F(\theta) = \sum_{i}^{\infty} f_i e^{2\pi i (h x_i + k y_i + l z_i)} \tag{3.17}$$

The amplitude (and hence its square, the intensity) of scattering 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* (hkl) 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 scattering is zero. This behavior is intrinsic to the scattering process, is implicit back in Figure 3.2, and is often a very useful diagnostic test when determining crystal structures in the TEM.

ZERO SCATTERING

Under specific conditions, electrons scattering in a crystal may result in ZERO scattered intensity. Why might this occur?

We'll return to this point 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 reason for this importance, as we'll show you in Chapters 11 and 12, is that we can use diffraction to determine the spacing of planes in crystals and, as you'll see later in Chapters 20, 21, and in the companion text, there is a whole field termed *electron crystallography* which gives an unprecedented amount of crystallographic information from space-group symmetry data right down to the dimensions of single unit cells. At the most basic level, the interplanar spacings in different crystal structures are characteristic of that structure.

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 in Part 3 how diffraction leads to contrast in TEM images which is controlled by the orientation of a crystal with respect to the electron beam and which you can control simply by tilting your specimen.

DP PLUS IMAGE

We can distinguish different crystal structures by observing and measuring DPs. The combination of the DP and the electron image(s) is a most powerful tool for characterizing crystals and particularly 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 plot similar to 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, so we see diffuse, bright rings on the TEM screen. If the specimen is crystalline, then the intensity of the diffracted beams is a maximum at specific angles because the interplanar spacings are very well defined. The variation of $f(\theta)$ with θ plotted in Figure 3.7A and B is equivalent to the radial intensity variation across the DPs in Figure 2.13A and 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.

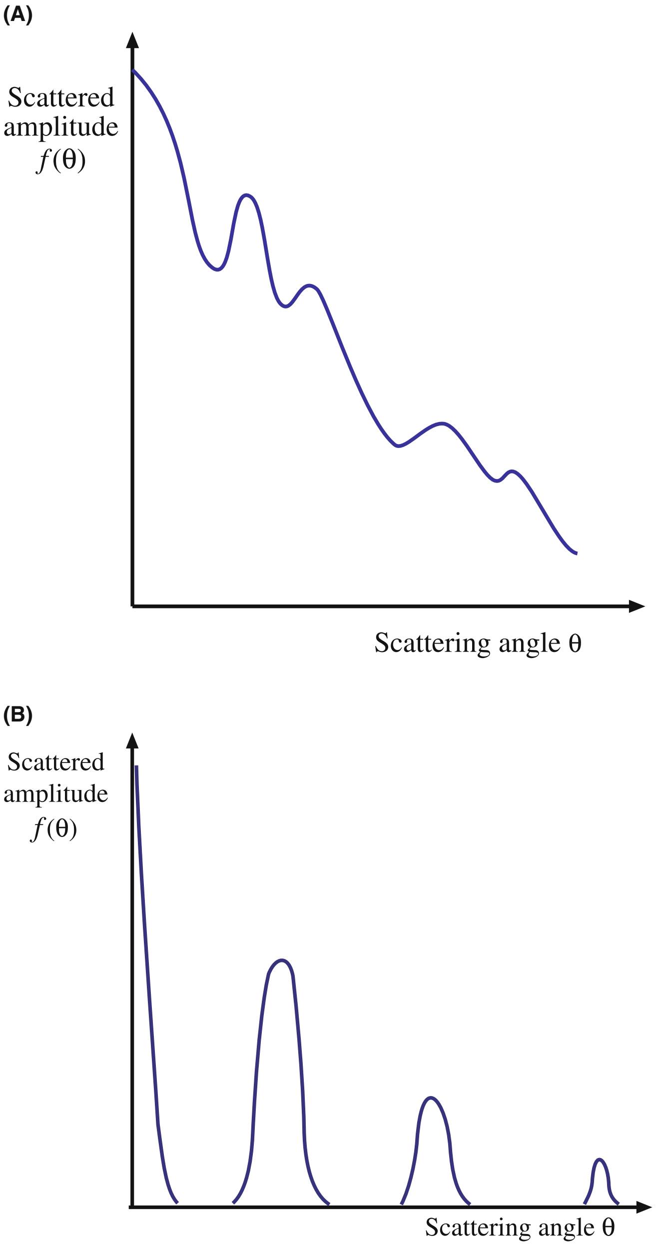

FIGURE 3.7. Change in $f(\theta)$ with θ for (A) an amorphous specimen and (B) a crystalline specimen. The amplitude (and therefore the intensity) of scattering generally decreases with increasing θ but the smooth decrease is modified at certain scattering angles (compare these curves with the intensity variation along a radius of the DPs in Figure 2.13A and C, respectively).

3.10.A Interference of Electron Waves; Creation of the Direct and Diffracted Beams

To interpret 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-particle interactions that characterize high-angle Rutherford scattering. If you go back and look at Figure 3.2 you see a periodic one-dimensional array of scattering centers (slits), and a monochromatic wave (i.e., fixed λ) is advancing toward these centers. Each center 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. 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* that proceeds in the same direction as the incident wave, which in the TEM we'll refer to as the direct beam of electrons, as we defined at the start of Chapter 2. There are also *higher-order waves* that propagate in forward directions that are at some fixed (but very small) 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 in Part 2, we'll find ways to measure these angles and relate them to the spacing of the scattering planes.

DIRECT AND DIFFRACTED

The direct beam consists of electron, scattered in the same direction as the incident beam. Often in TEM terminology these electrons are called the transmitted beam but this term is ambiguous since, in fact, all forward-scattered beams are 'transmitted' through the specimen.

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 credited to von Laue (1913) in Germany, although others such as Ewald were working on similar ideas at the same time. Von Laue's crucial idea was that much shorter electromagnetic rays than light would cause diffraction or interference phenomena in a crystal. Although his colleague Sommerfeld, with whom he discussed the idea while skiing, disagreed, Friedrich, one of Sommerfeld's assistants, and Knipping tested the idea experimentally by irradiating 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 that 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, $h\lambda$ (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

$$a(\cos\theta_1 - \cos\theta_2) = h\lambda \qquad (3.18)$$

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

$$b(\cos\theta_3 - \cos\theta_4) = k\lambda \qquad (3.19)$$

$$c(\cos\theta_5 - \cos\theta_6) = l\lambda \qquad (3.20)$$

These three simultaneous equations bear von Laue's name and for his original suggestion and the analysis of the experiments of Sommerfeld's students, he received the Nobel Prize in Physics in 1914 (nice work: three equations). We'll show in Chapter 11 that

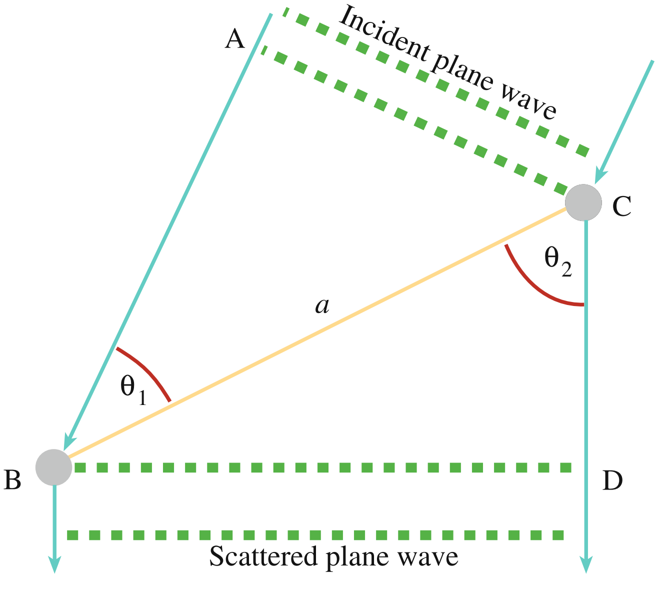

FIGURE 3.8. The approach used by von Laue to calculate the path difference for a wave (wavelength λ). In this one-dimensional figure the wave is incident at an angle θ_1 and scattered at an angle θ_2 from two atoms (B and C) spaced distance a apart. The path difference between scattered waves is AB –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

in a TEM specimen, when all three Laue equations are satisfied simultaneously a diffracted beam is produced. We'll also show you in Chapters 11 and 12 that the letters *hkl* are the indices of the diffracted beam and are equivalent to the Miller indices (*hkl*) of the diffracting crystal plane (or some multiple thereof).

Usually in TEM, we use a simpler approach to describe diffraction. Von Laue's approach was simplified by the family team of Sir William H. (obviously the dad) and Mr. W. Lawrence Bragg (the son) in England who proposed (Bragg and Bragg 1913) that the waves behaved as if they were reflected off atomic planes as shown in Figure 3.9.

In parallel with von Laue's optical approach, the Braggs argued 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*l 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 $2d \sin \theta_B$. So we can write what is known as Bragg's (although grammatically and historically it should be Braggs') law

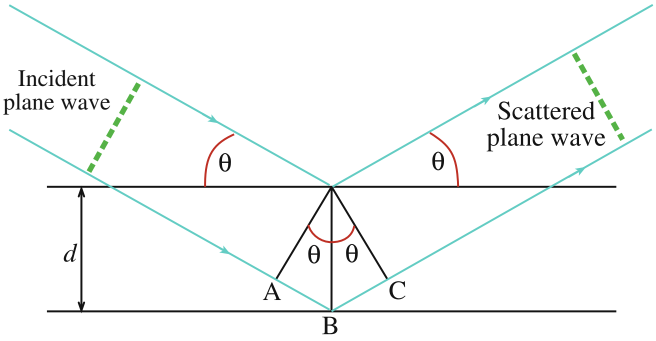

FIGURE 3.9. The Bragg description of diffraction in terms of the reflection of a plane wave (wavelength λ) incident at an angle θ to atomic planes of spacing *d*. The path difference between reflected waves is AB + BC.

$$n\lambda = 2d \sin \theta_B \qquad (3.21)$$

We'll reserve θ_B for the Bragg angle, which is *the* most important scattering angle (remember we really mean *semi*-angle) in TEM and you'll come across it many more times in this text. The Braggs also received a Nobel Prize in Physics a year after von Laue but this time for only one equation (even nicer work!) and despite the fact that the idea of reflected electrons, while mathematically correct, is physically wrong. We'll continue to use the term Bragg reflection to describe diffraction in the TEM because everyone does so, even though it's inaccurate, and because it is extremely useful. However, we'll demonstrate to you, in a rigorous fashion, the mathematical equivalence of the Bragg and von 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 you know λ for the incident electron (which you control by choosing the accelerating voltage) and you can measure θ experimentally, you can work out the interplanar spacings in your specimen. It is this crystallographic information that makes diffraction such an important aspect of the TEM.

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 (as a principle, but not much used in practice).

- The relationship between $f(\theta)$ and the intensity in a DP is 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.
- The strength of the scattering, $f(\theta)$, depends inversely on the scattering angle, θ.

Yes, a really rigorous treatment of scattering would take into account the wave nature of the electron (wave mechanics), relativity, and the electron charge, all at the same time. Because we're good guys we won't inflict this on you or ourselves. Fortunately, if required, we can do very well using compiled tables of cross sections and scattering data, which are available on the web (e.g., URL #1).

We can describe the effect of the crystal structure on the electron scattering by one more parameter, the structure factor $F(\theta)$

- $F(\theta)$ is a measure of the amplitude scattered by a unit cell and $|F(\theta)|^2$ is proportional to the scattered intensity.

The diffraction process from a TEM specimen is usually described by the Bragg equation which tells us the important reciprocal relationship between atomic-plane spacings and scattering angles.

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 has a covalent rather than a metallic bond? These are important questions (otherwise we wouldn't ask them) and we'll teach you the answers as we go on.

DIFFRACTION AND SCATTERING

Andrews, KW, Dyson, DJ and Keown, SR 1967 *Electron Diffraction Patterns* The Institute of Physics Bristol UK. The original text focused on diffraction in the TEM.

Bragg, WH and Bragg, WL 1913 *The Reflection of X-rays by Crystals* Proc. Roy. Soc. Lond. **A88** 428–438. The paper that led to the Nobel Prize.

Doyle, PA and Turner, PS 1968 *Relativistic Hartree-Fock X-ray and Electron Scattering Factors* Acta Crystallogr. **A24** 390–397.

Mott, NF and Massey, HSW 1965 *The Theory of Atomic Collisions* Oxford University Press New York.

Reimer, L 1997 *Transmission Electron Microscopy; Physics of Image Formation and Microanalysis* 4th Ed. Springer New York. Rigorous thorough treatment of the scattering process, especially as used in Section 3.8.

Rutherford, E 1911 *The Scattering of α and β Particles by Matter and the Structure of the Atom* Phil. Mag. **21** 669–688. His scattering.

von Laue, M 1913 *Kritische Bemerkungen zu den Deutungen der Photoframme von Friedrich und Knipping* Phys. Z. **14** 421–423. Paper that led to the Nobel Prize.

Wang, ZL 1995 *Elastic and Inelastic Scattering in Electron Diffraction and Imaging* Plenum Press New York. Much more detailed than the approach used here.

SCATTERING APPLIED TO EM

Hall, CE 1953 *Introduction to Electron Microscopy* p 229 McGraw-Hill New York.

Jones, IP 1992. *Chemical Microanalysis Using Electron Beams* Institute of Materials London.

Newbury, DE 1986 *Electron Beam-Specimen Interactions in the Analytical Electron Microscope* in *Principles of Analytical Electron Microscopy* p 1 Eds. DC Joy, AD Romig Jr and JI Goldstein Plenum Press New York.

Varela, M, Lupini, AR, van Benthem, K, Borisevich, AY, Chisholm, MF, Shibata, N, Abe, E and Pennycook, SJ 2005 *Materials Characterization in the Aberration-Corrected Scanning Transmission Electron Microscope* Annu. Rev. Mat. Sci. **35** 539–569. Review of Z-contrast imaging.

URLs

(1) www.nist.gov/srd/nist64.htm NIST Standard reference database #64 provides values of the differential elastic-scattering cross sections, total elastic-scattering cross sections, phase shifts, and transport cross sections for elements with $Z = 1$ to 96 and for beam energies from 50 eV to 300 keV (in steps of 1 eV).

SELF-ASSESSMENT QUESTIONS

Q3.1 What are the primary causes of elastic scattering?

Q3.2 What do we mean by the term 'wave-particle duality'?

Q3.3 What forces act on an electron as it interacts with atoms?

Q3.4 What term describes the strength of the scattering process?

Q3.5 What factors control the interference between waves?

Q3.6 How is the scattering amplitude related to the intensity of the scattered beams that we see in the microscope?

Q3.7 What are the two principal forms of elastic scatter?

Q3.8 Relate the general form of the Rutherford differential cross section (equation 3.3) to the equation describing the cross section for nucleus scattering proposed by Hall (equation 3.2).

Q3.9 What is a screening parameter and why do we need to incorporate it in the equations that describe scattering?

Q3.10 Why is it important to include a screening parameter in the Rutherford cross section?

Q3.11 Why do elastic electron-electron interactions usually result in a relatively low scattering angle, while elastic electron-nucleus interactions cause higher-angle scattering?

Q3.12 From your answer to the previous question describe the different information that might be contained in low-angle and high-angle scattered electrons and how you might obtain that information

Q3.13 How thin should your specimen be so that scattering within it approaches the ideal of a single event per electron?

Q3.14 What is the relationship between the atomic scattering factor $f(\theta)$ and the structure factor $F(\theta)$?

Q3.15 Why do crystalline and amorphous specimens give rise to different scattering distributions?

Q3.16 What are the fundamental differences between the von Laue and Bragg approaches to diffraction and what are the similarities?

Q3.17 Put some reasonable values for d and λ into equation 3.21 and calculate a typical Bragg angle in a TEM.

Q3.18 Why is the Bragg approach fundamentally incorrect?

Q3.19 What do we mean by the term 'scattering center'?

Q3.20 What is the relationship between the spacing of the lattice planes and the angle of scatter?

TEXT-SPECIFIC QUESTIONS

T3.1 In Figure 3.1, why are the electrons interacting with both the nucleus and the electron cloud shown to deviate in the same directions (i.e., both are bent through an angle θ) when the nucleus and the electron clouds in fact have opposite electrical charges?

T3.2 Why do we show the electron close to the nucleus in Figure 3.1 as being turned around rather than being pulled directly into the (highly positively charged) nucleus?

T3.3 Look again at Figure 3.1 and explain why elastic electron-electron interactions usually result in a relatively low scattering angle, while elastic electron-nucleus interactions cause higher-angle scattering.

T3.4 In Figure 3.2 why don't we see a third-order scattered beam?

T3.5 Relate Figure 3.3 to equations 3.1 and 3.2.

T3.6 Can you show that the data in Figures 3.3 and 3.4 are consistent? (Hint: assume that θ is small (i.e., $\sim 0°$) for elastic scatter.)

T3.7 Relate Figure 3.5 to equations 3.1 and 3.2.

T3.8 Is Figure 3.5 plotted for a screened or unscreened atomic potential? Explain your answer.

T3.9 In Figure 3.6 why don't we show constructive interference of waves going back in the direction of the incident beam?

T3.10 Figures 3.3, 3.5, and 3.7 all have the same general form. Why is this?

T3.11 Discuss the advantages and disadvantages of the Rutherford cross section for elastic scattering. Put in some values into equation 3.7 and determine the value of the cross section.

T3.12 Write down concise definitions of coherent, incoherent, elastic, and inelastic as we use them. (Hint: first take a look at Webster's.)

T3.13 Explain in a paragraph the relationship between scattering cross section and atomic scattering factor mentioning the important factors that influence them.

T3.14 In Figure 3.6, if this process were Bragg diffraction, how would the Bragg angle relate to θ?

T3.15 Use equation 3.21 to determine the value of θ if $n = 1$ and $d = 2$ for each of the wavelengths in Table 1.2. Thus, discuss whether or not relativistic corrections are important.

T3.16 Copy Figure 3.8 and draw on it where other atoms in the diffracting planes might be positioned. (Hint: look at Figure 3.9.)

T3.17 Explain why we talk about the Bragg angle in Figure 3.9 as being a semi-angle of scattering.