Diffraction from Crystals

16

CHAPTER PREVIEW

Since our emphasis is on crystalline materials, we will first discuss how the details of the crystal symmetry affect the DPs we expect to see. What we're doing here is taking the concepts of the reciprocal lattice and applying it to particular examples. There are two basic lessons:

- You must learn some of the rules that we will derive for particular crystal structures; one example will be to determine which reflections are allowed for an fcc crystal.
- The other lesson is more general and is really concerned with why we have these rules. Why are certain reflections absent or weak and how can you use this information to learn more about your material?

We can deduce some selection rules for different crystal structures that tell you which reflections are allowed. We suggest you learn the most common ones by heart. Throughout this chapter, we'll assume that the crystal is perfect and infinite, which it never is. In Chapter 17, we will examine what happens when we include defects or allow the diffracting crystal to become relatively small. In Chapter 18, we'll go through the process of indexing experimental DPs.

D. B. Williams et al., *Transmission Electron Microscopy*

Diffraction from Crystals

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16.1. REVIEW OF DIFFRACTION FROM A PRIMITIVE LATTICE

In Chapters 11 to 15, we examined diffraction from a regular array of lattice points. We will now define such an array as a primitive lattice where there is only one lattice point in the unit cell. Actually, we did begin to consider the present topic when we discussed the meaning of n in the Bragg equation $2d \sin \theta_B = n\lambda$ in Sections 11.5 and 12.4. We showed that the diffraction from the (200) planes would give rise to a 200 reflection even when there were only atoms on the (100) planes.

By combining equations 13.3 and 13.4, we can see that the amplitude of the diffracted beam is given by

$$\phi_g = \frac{ai\lambda F_g}{V_c \cos \Theta} \sum_n e^{-2\pi i \mathbf{K} \cdot \mathbf{r}_n} e^{2\pi i \mathbf{k}_D \cdot \mathbf{r}} \qquad [16.1]$$

where F_g is the structure factor for the material. Since the same type of atom was at each lattice point, we only needed to consider one atomic scattering factor f in Chapter 13. Now we are going to include different types of atoms as we build up real crystal unit cells. From Section 3.7 we know that f varies with the scattering angle. However, in this chapter we are going to restrict ourselves to small values of θ (excluding zero) and will assume that we have fixed values of f; you can easily extend this analysis to other scattering angles. For convenience, we've summarized some useful values of f in Table 16.1.

If you study the original paper of Ibers (1957), from which these data were taken, you will appreciate that these numbers are not really well known. This is unfortunate since much of our analysis depends on the values of f. Furthermore, we have an additional reason for choosing θ not to be zero in Table 16.1 because these values are even less reliable. Fortunately, what saves us is that we are only interested in the details of the intensities in some special cases and then the effects are really insensitive to the precise value of f.

We are just going to take these numbers and move on, but you may want to investigate a little further. Some points you should consider are:

- Why are these numbers not better known? We discussed this topic in Chapters 2 and 3. The atomic scattering factor is related to the differential scattering cross section (Section 3.7)

$$|f(\theta)|^2 = \frac{d\sigma(\theta)}{d\Omega} \qquad [16.2]$$

  and the cross section is not well known at typical TEM voltages.
- If the crystal is ionic, do we use $f(\theta)$ for the atom or for the ion?
- If the material is covalently bonded, how can we incorporate the bonds into our scattering model?

How we calculate $f(\theta)$ depends on the model we use to describe the atom. You can find more details in the references at the end of the chapter, but beware, this is not an easy topic.

The simplest method is just to ignore any ionic character! If you look at Table 16.1, you'll see that if the atomic number is large enough, then the change in f caused by removing an electron may not be great. In ionic materials, we form ions by removing or adding outer electrons so the interaction of the electron beam with the nucleus is not significantly affected. However, you should remember that this argument applies only to f. We'll see in Part IV that we can detect differences between differently bonded atoms using EELS.

The overall effect of the covalent, i.e., directional, component of the bonding is usually ignored. However, as you realize, all the bonds in Si, for example, are aligned

Table 16.1. Selected Values of $f(\theta)$, the Atomic Scattering Amplitude at $\theta = \theta_B$[a]

Element	$f(\theta)$(Å)	Element	$f(\theta)$(Å)
H	0.31	Ca	3.40
Li	0.75	Cr	3.56
Be	1.16	Mn	3.55
B	1.37	Fe	3.54
C	1.43	Co	3.51
N	1.44	Ni	3.48
O	1.42		
		Cu	3.44
Na	1.59	Zn	3.39
Mg	1.95	Ga	3.64
Al	2.30	As	4.07
P	2.59	Ag	5.58
		W	7.43

[a]These are values given by Edington (1976) using a self-consistent field theory ($\sin\theta/\lambda = 0.2$Å^{-1}) and are based on the rest mass. The $f(\theta)$ value must be multiplied by $(1 - (v/c)^2)^{-1/2}$ for electrons with velocity v.

along one particular type of crystallographic direction, so you may indeed be able to detect some special features in the DPs.

16.2. STRUCTURE FACTORS: THE IDEA

In this section, we are building on Chapter 12. To keep things simple, we will illustrate the concept of the structure factor for cubic crystals. If we have a simple-cubic crystal, then all possible values of **g** can give a reflection in the DP. Each reciprocal lattice point will then correspond to a possible beam. The next step will be to add the basis (i.e., the group of atoms associated with each lattice point) to the primitive lattice. Since we still have the primitive lattice, all of these points will still exist in the reciprocal lattice but the reflections will be weighted. You will find that there are three different ways to look at the situation, which in fact are all equivalent:

- *Selection rules:* This is perhaps closest to physics. The structure of the crystal imposes certain selection rules which determine which beams are allowed.
- *Weights* (or *weighting factors*): We can assign a weight (which may be zero) to each of the points in the reciprocal lattice. This is the terminology used by Ewald. The nice feature about weighting factors is that they are analogous to scattering factors.
- *Structure factors* (F): These are the unit-cell equivalents of the atomic scattering amplitude, $f(\theta)$; they can be thought of as unit-cell scattering amplitudes. This is the terminology favored in materials science.

There are two ways to address this topic:

- We can examine the physical idea of interference as we did in Chapters 2 and 3. This approach can give some useful guidelines to you, the experimentalist. For example, we'll see that the 200 reflection in Si should usually be absent; it should always be present, though weak, in GaAs. Similarly, in Ni_3Al, the 100 reflection is weak but in Ni it is absent.
- Some materials have a special lattice in real space, for example, fcc or bcc lattices. In these cases, we can describe a corresponding special lattice in reciprocal space. What this means is that certain reflections are always forbidden for these particular structures; these are known as "kinematically forbidden" reflections. (We'll see, however, that they can be present due to dynamical scattering events, and structure factors do not take any account of dynamical scattering.) The reciprocal lattice (of allowed reflections) of an fcc crystal is bcc, and vice versa.

In equation 13.1 we described the scattering from the unit cell by the expression

$$A_{\text{cell}} = \frac{e^{2\pi ikr}}{r} \sum_i f_i(\theta) e^{2\pi i \mathbf{K}\cdot\mathbf{r}_i} \qquad [16.3]$$

What this equation says is that the atoms within the unit cell all scatter with a phase difference given by $2\pi i\mathbf{K}\cdot\mathbf{r}_i$, where $\mathbf{r}_i$ is a vector which defines the location of each atom within the unit cell

$$\mathbf{r}_i = x_i\,\mathbf{a} + y_i\,\mathbf{b} + z_i\,\mathbf{c} \qquad [16.4]$$

We'll start by considering only the case where $\mathbf{K} = \mathbf{g}$ since this is an infinite, perfect crystal

$$\mathbf{K} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + \ell\,\mathbf{c}^* \qquad [16.5]$$

So we can write

$$F_{hk\ell} = \sum_i f_i e^{2\pi i\left(hx_i + ky_i + \ell z_i\right)} \qquad [16.6]$$

This is our key equation; it is completely general.

This equation applies whether there is one atom or one hundred atoms in the unit cell, no matter where they are located, and it applies to all crystal lattices. What we do

next is simply insert the atomic coordinates into equation 16.6 and calculate $F_{hk\ell}$.

16.3. SOME IMPORTANT STRUCTURES: bcc, fcc, AND hcp

We will now calculate the structure factor for bcc and fcc crystals, because they illustrate the points we just made in Section 16.2 and because, as a materials scientist, you must know these results. You can regard the reciprocal lattice in two ways:

- The reciprocal lattices for bcc and fcc are themselves special lattices.
- All reciprocal lattices of cubic materials are simple cubic, but some of the lattice points have a zero structure factor.

Body-centered cubic: The bcc structure is particularly easy. If we set the origin on one lattice point at (0, 0, 0), the other lattice point is at (1/2,1/2,1/2) and we substitute these values of (x, y, z) into equation 16.6; then

$$F = f\left\{1 + e^{\pi i(h+k+\ell)}\right\} \qquad [16.7]$$

Now, since h, k, ℓ are all integers, if we define the sum $h + k + \ell = N$, then the exponential can take two values: +1, for N even; and -1, for N odd.

Thus, we can say that:

- $F = 2f$ if $h + k + \ell$ is even,
- $F = 0$ if $h + k + \ell$ is odd.

There are **no** other possibilities. The resulting bcc reciprocal lattice is shown in Figure 16.1. This lattice of allowed reflections is face-centered cubic. The reason it may not look like the familiar fcc lattice in real space is that the indices in reciprocal space must all be integers.

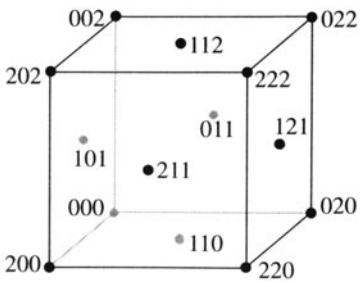

Figure 16.1. The reciprocal lattice for the bcc crystal structure. The lattice points that correspond to systematic absences have been removed, so the actual arrangement of points is an fcc lattice.

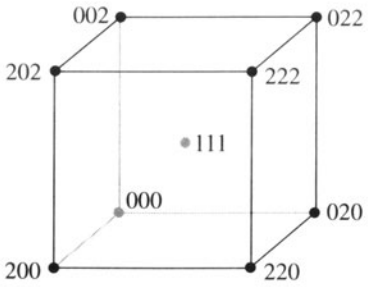

Figure 16.2. The reciprocal lattice for the fcc crystal structure. The lattice points that correspond to systematic absences have been removed, so the actual arrangement of points is a bcc lattice.

Face-centered cubic: If we take the same approach for the fcc structure, we now have to include four atoms in the unit cell. We can view this cell as simple cubic with a four-atom basis. The coordinates of the atoms are

$$(\mathbf{x}, \mathbf{y}, \mathbf{z}) = (0, 0, 0), (\tfrac{1}{2}, \tfrac{1}{2}, 0), (\tfrac{1}{2}, 0, \tfrac{1}{2}), (0, \tfrac{1}{2}, \tfrac{1}{2}) \qquad [16.8]$$

Substituting these values for $\mathbf{r}_i$ into equation 16.6 gives

$$F = f\left\{1 + e^{\pi i(h+k)} + e^{\pi i(h+\ell)} + e^{\pi i(k+\ell)}\right\} \qquad [16.9]$$

Again, we consider the possible values of the integers h, k, ℓ. If all three are either odd or even, then all of the exponential terms are $e^{2n\pi i}$. Therefore, all the phases of the diffracted waves are multiples of 2π and are in phase. However, if one of $h, k,$ or ℓ is odd but the other two are even, or vice versa, then two of the three phase factors will be odd multiples of π, giving two terms of -1 in equation 16.9. Therefore:

- $F = 4f$ if h, k, ℓ are all even or all odd,
- $F = 0$ if h, k, ℓ are mixed even and odd.

The resulting lattice is shown in Figure 16.2. This time the reciprocal lattice of allowed reflections is bcc with all the indices being integers.

Hexagonal close-packed: Generally DPs from hcp crystals are more difficult to index for three reasons.

- Except for (0001), the patterns can be different for every material because the *c/a* ratio is different.
- We use the three-index notation to derive the structure-factor rules.
- We use the four-index Miller–Bravais notation to index the lattice planes and thus the DPs.

For the hcp structure, we only have to include two atoms in the unit cell. We can view this cell as a simple

rhombohedral cell with a two-atom basis. The coordinates of the atoms are

$$(x, y, z) = (0, 0, 0), (\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{2}) \qquad [16.10]$$

Substituting these values for $\mathbf{r}_i$ into equation 16.6 gives

$$F = f\left\{1 + e^{2\pi i\left(\frac{h}{3} + \frac{2k}{3} + \frac{\ell}{2}\right)}\right\} \qquad [16.11]$$

We simplify the notation by setting $h/3 + 2k/3 + \ell/2 = X$; the complication is simply that X may be a fraction. The analysis is quite straightforward if we consider $|F|^2$, which is what we need in the expression for intensities. Then we can rearrange as follows

$$|F|^2 = f^2\left(1 + e^{2\pi iX}\right)\left(1 + e^{-2\pi iX}\right) = f^2\left(2 + e^{2\pi iX} + e^{-2\pi iX}\right) \qquad [16.12]$$

$$|F|^2 = f^2\left(2 + 2\cos 2\pi X\right) = f^2\left(4\cos^2 \pi X\right) \qquad [16.13]$$

Now we can write down the rules for hcp which depend mainly on whether or not $h + 2k$ is a multiple of 3:

- $|F|^2 = 0$ if $h + 2k = 3m$ and ℓ is odd,
- $|F|^2 = 4f^2$ if $h + 2k = 3m$ and ℓ is even,
- $|F|^2 = 3f^2$ if $h + 2k = 3m + 1$ and ℓ is odd,
- $|F|^2 = f^2$ if $h + 2k = 3m + 1$ and ℓ is even.

Thus the $11\bar{2}0$ and $11\bar{2}6$ reflections will be strong but the $11\bar{2}3$ reflection will be absent. Likewise, $10\bar{1}0$ and $20\bar{2}0$ are weak but $30\bar{3}0$ is strong. Most importantly, 0001 is absent. You can see that the four-index Miller–Bravais notation takes some time to master. The third index is only included to emphasize the symmetry; if the third index were not included, you might not realize that, e.g., the (110) and $(1\bar{2}0)$ are crystallographically equivalent.

You need to know a few other expressions for this system. If you are working with hcp materials, you *must* have a copy of Frank's 1965 paper on indexing this system.

If the direction $[uvtw]$ lies in the plane $(hki\ell)$, then we can show that

$$uh + vk + ti + w\ell = 0 \qquad [16.14]$$

The normal to the plane (h,k,i,ℓ) is actually the Cartesian vector $[h,k,i,\ell/\lambda]$, and likewise the crystallographic direction $[u,v,t,w]$ is actually the vector $[u,v,t,\lambda w]$ in the Cartesian system. So using the four-index Cartesian vector notation, equation 16.14 can be written as

$$[u,v,t,\lambda w]\cdot[h,k,i,\ell/\lambda] = 0 \qquad [16.15]$$

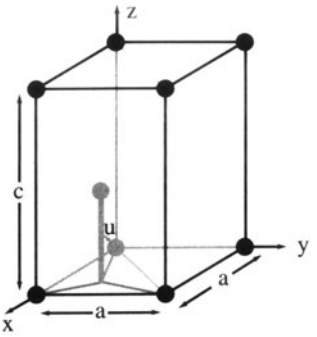

Figure 16.3. The hcp unit cell showing the four axes used in the Miller–Bravais indexing system. The three axes in the basal plane, *x*, *y*, and *u*, are all crystallographically equivalent and the *z*-axis is normal to the basal plane.

In cubic crystals, the direction $[hk\ell]$ is always normal to the plane $(hk\ell)$, but this is not the case for hcp crystals. You can show using some simple geometry that

$$\lambda^2 = \left(\frac{2}{3}\right)\left(\frac{c}{a}\right)^2 \qquad [16.16]$$

Thus the Cartesian vector $[HKIL]$, which is normal to the plane $(hki\ell)$, is the vector

$$\left(h, k, i, \frac{3}{2}\left(\frac{a}{c}\right)^2\ell\right) \qquad [16.17]$$

So, $[11\bar{2}0]$ is normal to the $(11\bar{2}0)$ plane because ℓ is zero but $[01\bar{1}2]$ is not normal to the $(01\bar{1}2)$ plane.

We can now write down an expression for the angle, ϕ, between two planes $(hki\ell)$ and $(defg)$. We use equation 16.17 to deduce the normals to the planes, then take the dot product of these two four-index vectors to deduce $\cos\phi$ in the form

$$\cos\phi = \frac{hd + ke + \frac{1}{2}(he + kd) + \frac{3}{4}\ell g\left(\frac{a}{c}\right)^2}{\left\{h^2 + k^2 + hk + \frac{3}{4}\ell^2\left(\frac{a}{c}\right)^2\right\}^{\frac{1}{2}}\left\{d^2 + e^2 + de^2 + \frac{3}{4}g^2\left(\frac{a}{c}\right)^2\right\}^{\frac{1}{2}}} \qquad [16.18]$$

The hcp unit cell is shown in Figure 16.3. Remember that there are three crystallographically equivalent axes, *x*, *y*, and *u*, and that the indices of any plane can be written as $(uviw)$ where $i = -(u + v)$. We'll come across simpler expressions in the cubic system in Chapter 18.

16.4. EXTENDING fcc AND hcp TO INCLUDE A BASIS

What we did in the previous section was to calculate the reciprocal lattice of a simple-cubic crystal with a basis of

four atoms in fcc and two atoms in bcc. We can take this analysis one step further by starting with fcc and adding a basis. This extension both illustrates the technique and deduces structure-factor rules for three important materials.

NaCl, GaAs, and Si: Each of these three crystal structures is an fcc lattice with a basis. In other words, we can separate out the atoms lying on the fcc lattice and those which make up the basis.

NaCl: Let's locate each of the Na atoms on an fcc site; although NaCl is ionic, we'll refer to the ions as atoms since we generally do not take account of the charge on the ion.

We usually say that for every Na atom, there is a Cl atom related to it by the vector [1/2, 0, 0]. However, to emphasize the cubic symmetry, we can choose the alternative basis vector [1/2, 1/2, 1/2]. The phase factor for the Cl atom will be the same as for the Na atom, but with an additional phase of $\pi i(h + k + \ell)$. Of course, the atomic scattering amplitudes, f, are also different for the two atoms. We can write this expression for F as

$$F = \left\{f_{Na} + f_{Cl}\, e^{\pi i(h+k+\ell)}\right\}\left\{1 + e^{\pi i(h+k)} + e^{\pi i(h+\ell)} + e^{\pi i(k+\ell)}\right\} \qquad [16.19]$$

This again gives rise to some rules:

- $F = 4(f_{Na} + f_{Cl})$ if h, k, ℓ are all even,
- $F = 4(f_{Na} - f_{Cl})$ if h, k, ℓ are all odd,
- $F = 0$ if h, k, ℓ are mixed.

Clearly, the third condition is the same as for any fcc structure because the factor with four terms is then zero, exactly as we deduced for fcc. You can check this if you imagine that f_{Cl} is zero. Whether the sign in $(f_{Na} \pm f_{Cl})$ is positive or negative is the new feature. What this means in practice is that reflections with h, k, ℓ all even will appear much more intense in the DP than those with h, k, ℓ all odd. Look at the values given for f in Table 16.1. LiF, KCl, MgO, NiO, FeO, and ErAs all have the NaCl structure. Since they have different pairs of atomic scattering amplitudes, the term corresponding to $4(f_{Na} - f_{Cl})$ will be different in each case. Reflections with h, k, and ℓ all odd are thus sensitive to the chemistry of the compound and we call them "chemically sensitive reflections." We will see further examples in Chapter 31 of how this sensitivity can be used in imaging.

GaAs: You should repeat the above exercise with the Ga located on the fcc lattice and the As related to it by the basis vector [1/4, 1/4, 1/4]. (Crystallographers will immediately note that this puts the As atom in the tetrahedron instead of the octahedron, as found in NaCl.) Now the expression for F becomes (see equation 16.9 for F_{fcc})

$$F = \left\{f_{Ga} + f_{As}\, e^{\frac{\pi}{2} i(h+k+\ell)}\right\} F_{fcc} \qquad [16.20]$$

So the rules are slightly more complicated:

- $F = 0$ if h, k, ℓ are mixed as always for fcc,
- $F = 4\,(f_{Ga} \pm i f_{As})$ if h, k, ℓ are all odd,
- $F = 4\,(f_{Ga} - f_{As})$ if h, k, ℓ are all even and $h + k + \ell = 2N$ where N is odd (e.g., the 200 reflection),
- $F = 4\,(f_{Ga} + f_{As})$ if h, k, ℓ are all even and $h + k + \ell = 2N$ where N is even (e.g., the 400 reflection).

You can appreciate the difference between the 200 reflection and the 400 reflection by drawing a projection onto the (001) plane and applying the physical ideas we discussed in Chapter 11. The case where all three indices are odd is interesting. However, remember that we only see intensities (i.e., $|F|^2$ not F), so $|F|^2$ is $16(f_{Ga}^2 + f_{As}^2)$ and is independent of the sign initially present. Of course, the structure factor is still different than the others derived here.

Si: Now we can easily extend this analysis to Si, Ge, or diamond. Just replace f_{Ga} and f_{As} in our results with f_{Si}. The major change is that F is zero when $h + k + \ell = 2N$ and N is odd. The best known example of this is again the 200 reflection. For Si it has $F = 0$, but F is finite for GaAs.

Wurtzite: The wurtzite structure is to hcp what GaAs (or zinc blende) is to fcc! It is an important structure because it includes BeO, ZnO, and AlN, all of which have been widely studied. We can think of it as adding a second hcp lattice displaced by [1/3, 1/3, 1/8] or [0, 0, 3/8] relative to the first. The problem is that we now have a four-atom basis because the second atom in the hcp cell does not lie at a lattice site. This is a good exercise for Section 16.8, if you look ahead.

16.5. APPLYING THE bcc AND fcc ANALYSIS TO SIMPLE CUBIC

Extending bcc to NiAl ($L1_0$): For this material, we can easily modify the original treatment of the bcc structure, since now the centering atom is different. If we choose to place

the Ni atom at (0, 0, 0) and the Al atoms at [1/2, 1/2, 1/2], then

$$F = \{f_{Ni} + f_{Al}\, e^{\pi i(h+k+\ell)}\} \qquad [16.21]$$

This leads to two values for F, *neither* of which is zero:

- $F = f_{Ni} + f_{Al}$ if $h + k + \ell$ is even,
- $F = f_{Ni} - f_{Al}$ if $h + k + \ell$ is odd.

This would, of course, be the bcc result if f_{Ni} and f_{Al} were the same. The result of this difference is that all of the reflections for a simple-cubic lattice will be present in a DP because F is never zero. This result is of course exactly what we would expect, because NiAl really *is* simple cubic. Other materials with this structure are CsCl, CoGa, FeAl, and CuZn. Reflections like (100) are chemically sensitive for NiAl.

The Cu_3Au ($L1_2$) structure: There are many important ordered intermetallics with this structure such as Al_3Li and Fe_3Al. The most important is Ni_3Al (because of its role in Ni-base superalloys.) We can treat Ni_3Al in a similar manner to NiAl. Here, the Al atom sits on the (0, 0, 0) site and the three Ni atoms center the faces. The expression for F now becomes

$$F = f_{Al} + f_{Ni}\{e^{\pi i(h+k)} + e^{\pi i(h+\ell)} + e^{\pi i(k+\ell)}\} \qquad [16.22]$$

The rules for Ni_3Al are:

- $F = (f_{Al} + 3f_{Ni})$ if h, k, ℓ are all even or all odd,
- $F = (f_{Al} - f_{Ni})$ if h, k, ℓ are mixed.

Again, all of the possible reciprocal lattice points of the simple-cubic lattice will give rise to Bragg reflections because the structure is really simple cubic. The mixed $hk\ell$ reflections are now the chemically sensitive reflections. This material is particularly interesting, since it can be heat-treated to randomize the distribution of the two elements; then each site will be occupied by 75% Ni, 25% Al, and F for mixed $hk\ell$ will be zero. For this reason, reflections with mixed $hk\ell$ are referred to as superlattice reflections (see Section 16.7).

16.6. EXTENDING hcp TO TiAl

The TiAl structure is not as well known as the previous two cases, but illustrates a similar class of materials. We noted in Section 16.4 that the two atoms in the hcp structure are not equivalent. In TiAl, we actually make them chemically distinct, too. This means that the rules for hcp will be modified again. Using equation 16.11, we find that

$$F = f_{Ti} + f_{Al}\, e^{2\pi i\left(\frac{h}{3} + \frac{2k}{3} + \frac{\ell}{2}\right)} \qquad [16.23]$$

The most important result is that the (0001) reflection is now allowed since $F = f_{Ti} - f_{Al}$. TiAl really does have a primitive hexagonal unit cell.

16.7. SUPERLATTICE REFLECTIONS AND IMAGING

The reciprocal lattices for Ni_3Al and NiAl are shown in Figure 16.4; the small circles indicate the chemically sensitive reciprocal lattice points. The terminology which has developed calls the chemically sensitive reflections *superlattice reflections*; the idea is that the fcc lattice is viewed as the lattice and the chemically sensitive reflections then lie on a lattice with a finer scale in reciprocal space. The

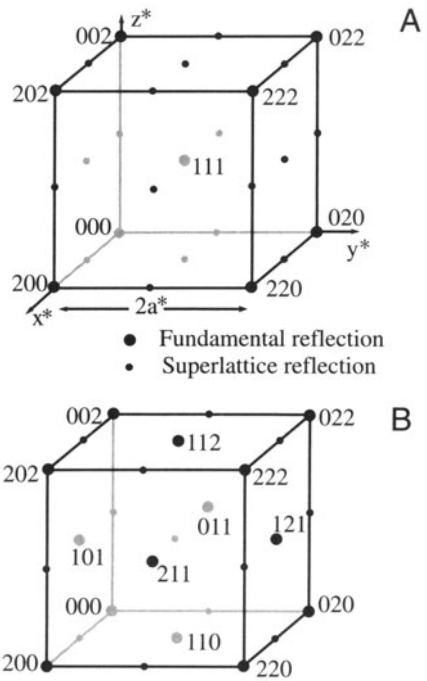

Figure 16.4. The reciprocal lattices for (A) the Ni_3Al and (B) the NiAl structures. In (A) Ni_3Al is fcc, so the fcc forbidden reflections (h, k, ℓ mixed even and odd) are allowed and become chemically sensitive (superlattice) reflections. In (B) NiAl is bcc, so the bcc forbidden reflections (if $h + k + \ell$ odd) are now allowed superlattice reflections.

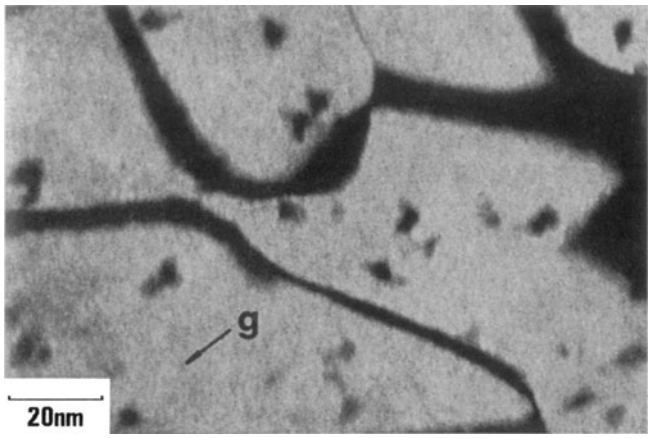

Figure 16.5. DF image from a chemically sensitive 110 reflection showing bright ordered domains in Cu_3Au. The dark areas in the bright domains are regions of local disorder induced by ion beam damage.

chemically sensitive superlattice reflections are all forbidden in the disordered fcc structure.

> Superlattice reflections are those present because the material is ordered such that the actual real-space unit cell is larger and thus the reciprocal-space cell is smaller.

For many years, these superlattice reflections were regarded as a special feature in some unusual materials. However, ordered materials, particularly the ordered intermetallics which we mentioned in Section 16.4, are finding increased uses. We will illustrate the wide variety of superlattice effects by selecting some examples.

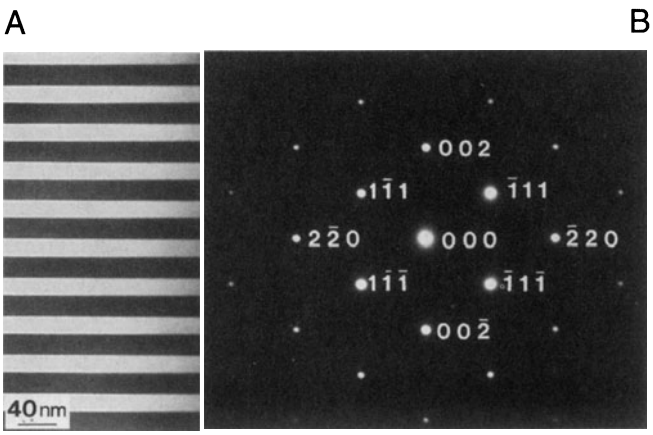

Figure 16.6. (A) DF image from a 002 superlattice reflection in GaAs. The $Al_xGa_{1-x}As$ is the lighter region because Al has replaced Ga in the GaAs (darker regions). (B) Diffraction pattern showing the less intense 002 and other superlattice reflections.

Figure 16.5 shows an image from Cu_3Au, the archetypal A_3B ordered fcc structure. The crystal has been irradiated with ions so that small regions known as cascades have been damaged just enough that the Cu and Au have been mixed up, i.e., the ordering has been destroyed locally (Jenkins *et al.* 1976). The DF image has been formed using the 110 reflection, which we know is a superlattice reflection. By destroying the ordering, we "destroy" the superlattice reflection for the disordered region, so the disordered region appears black when the ordered matrix appears bright. Thus, we can "see" the disordered region, measure its size, etc., even though it is not diffracting electrons. The dark bands between the domains are inclined anti-phase domain boundaries (APBs), a specific kind of planar defect which we'll examine in more detail in Section 24.6.

Figure 16.6A and B show a 002 DF image and the corresponding DP from a GaAs/$Al_xGa_{1-x}As$ quantum well structure. The $Al_xGa_{1-x}As$ appears lighter than the GaAs because the 002 reflection is a superlattice reflection; remember, it would be forbidden for GaAs if f_{Ga} and f_{As} were equal. The reason the $Al_xGa_{1-x}As$ appears lighter is that we have replaced a fraction x of the Ga atoms with the lighter Al atoms, thus increasing the difference $f_{III} - f_V$. Clearly, this is a classic example of chemically sensitive reflections. At this point we should remind you about intensities in images and DPs. The discussion we have just gone through assumes that we have a thin specimen, so that we are within the first thickness zone (i.e., the specimen is thinner than one extinction distance). In other words, be wary of trying to be quantitative about these intensities since superlattice beams are also dynamically diffracted.

Our third example is from a ceramic, vanadium carbide. The structure of VC is the same as for NaCl so we already have the rules. However, this carbide is usually non-stoichiometric, having the composition V_xC_y, where $x > y$. The two images and DPs shown in Figure 16.7 were taken from well-ordered V_6C_5 and V_8C_7, where 1/6 and 1/8 of the carbon sites are not occupied by C: we say these sites are occupied by vacancies and the vacancies have formed ordered arrays. Clearly, since we only have four atoms of each element in the unit cell, the vacancies must be distributed over more than one cell so the new lattice parameter must be greater than the lattice parameter (a) of the VC fcc lattice. So, we expect to see extra spots which are closer to the origin than (001). This is the case in both patterns shown here. The ordering actually destroys the cubic symmetry, so we have several orientations of the ordered carbides which are related to one another by the way they break the symmetry. By forming DF images, we can identify which region of the specimen corresponds to which variant (Dodsworth *et al.* 1983).

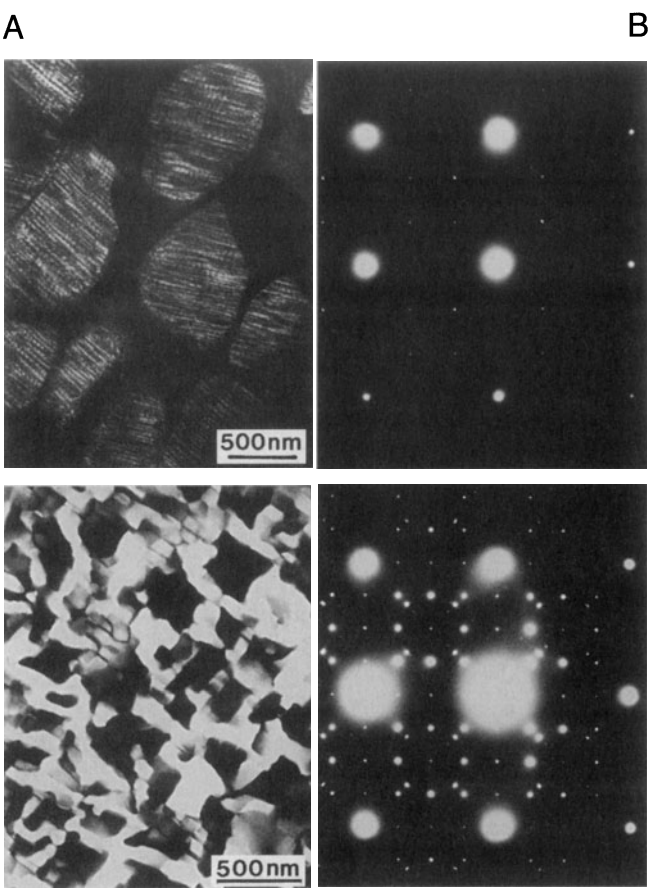

Figure 16.7. (A) DF image of ordered V_6C_5 and (B) accompanying diffraction pattern. (C) DF image of V_8C_7 and (D) diffraction pattern. In both carbides the ordering is due to vacancies on the C sublattice.

16.8. DIFFRACTION FROM LONG-PERIOD SUPERLATTICES

In the previous section, the atoms or vacancies in the different structures essentially arranged themselves to increase the lattice parameter and therefore give rise to superlattice reflections. In this section, we will discuss several examples where either we (or nature) have arranged the materials to give much larger superlattices. We will begin by considering the image and DP shown in Figure 16.8, which are from an artificial GaAs/Al_xGa_{1-x}As superlattice. The superlattice is created chemically by changing from four layers of GaAs to four of (Al_xGa_{1-x})As. So we see a series of three closely spaced extra spots in the DP which correspond to the new long lattice parameter in real space.

Another example is shown in Figure 16.9. This is a very long period (~10 nm) artificial superlattice of alternating layers of Si and Mo. The extra reflections are very close

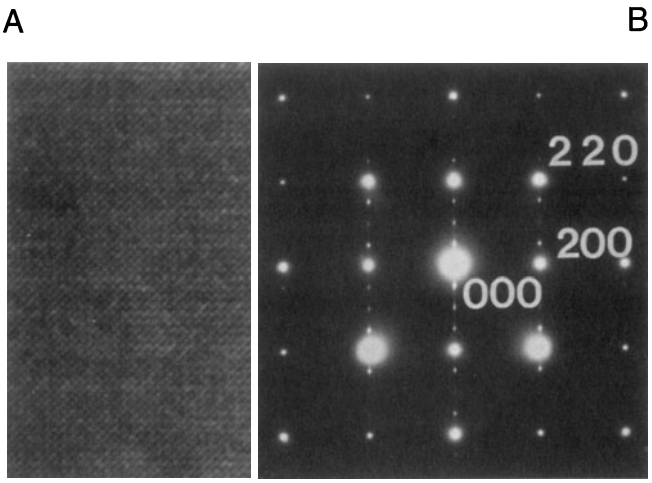

Figure 16.8. (A) Artificial GaAs/Al_xGa_{1-x}As structure in which order is created by alternating four layers of GaAs and four of (Al_xGa_{1-x})As. (B) DP showing three superlattice spots between the fundamental reflections in the 020 direction.

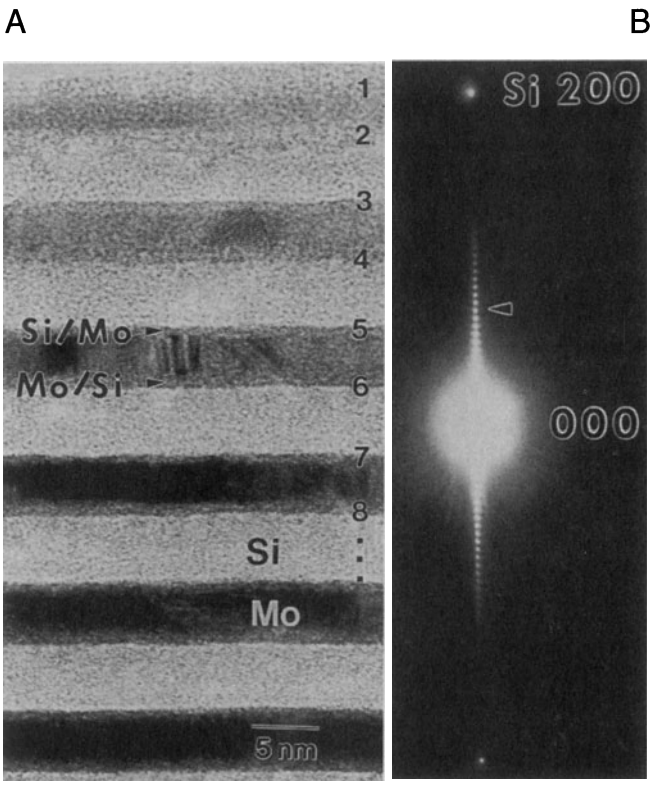

Figure 16.9. (A) Artificial superlattice of Si and Mo layers ~5 nm thick (B) Expanded DP around 000 showing many superlattice spots (arrowed). The large spacing of the superlattice in real space results in very small spacing of the superlattice reflections in the DP in reciprocal space. Compare with Figure 16.8.

and are not as useful as they were in Figure 16.6, but they do allow us to check the periodicity of the real-space structure very easily and quickly and without needing to use HRTEM (Chapter 28). This can be useful, particularly for artificially grown superlattices, since the superlattice periodicity is "internally calibrated" in the DP by the lattice spacing of the material. (Remember that the magnification of a TEM image is usually subject to a ±10% uncertainty.)

16.9. FORBIDDEN REFLECTIONS

We mentioned in Section 16.2 that certain reflections are always forbidden for some structures because they have $F = 0$. They are known as kinematically forbidden reflections, because such reflections can sometimes actually be present due to dynamical scattering events. This process is illustrated in Figure 16.10. The diffraction pattern is the [011] in Si so that the 200 reflection should be absent, according to Section 16.4. The reason it is actually present is that, since we are oriented at the zone axis, the 111 beam, which has $F \neq 0$, acts like a new incident beam and is rediffracted by the (111) plane. The result is that we appear to excite the 200 reflection since

$$(11\bar{1}) + (1\bar{1}1) = (200) \qquad [16.24]$$

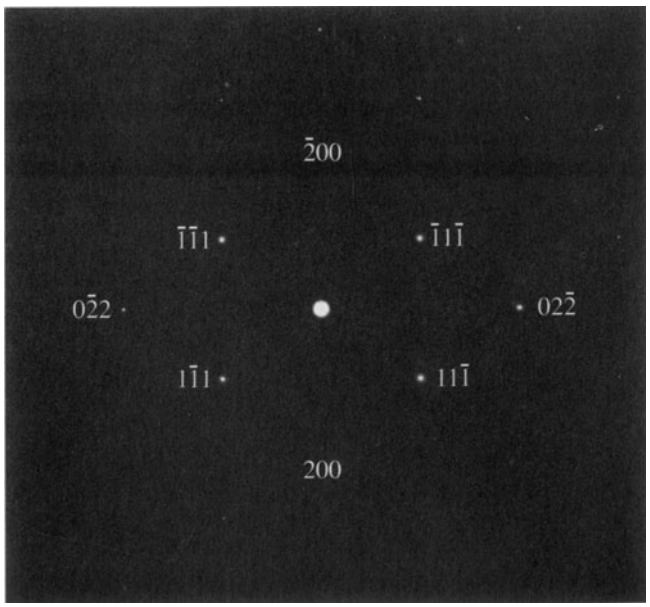

Figure 16.10. The [011] diffraction pattern from Si. The 200 reflection is forbidden, but it is present because the allowed $11\bar{1}$ diffracted beam acts like a new incident beam and is rediffracted by the $(1\bar{1}1)$ plane. The sum of the two allowed reflections, $(11\bar{1}) + (1\bar{1}1)$, results in a 200 reflection, which is so weak you may not see it.

From this example, you can appreciate the use of the phrase "kinematically forbidden."

16.10. USING THE INTERNATIONAL TABLES

As long as you work with fcc or bcc metals or the other special structures listed here, you can use the simple rules derived in this chapter. Once you venture further, you should quickly become familiar with the International Tables for Crystallography (Hahn 1988), in particular with the introductory booklet. You must know the crystal structure of your material; if not, you will, in principle, be able to determine it after studying Chapter 21. If, for example, you were working with α-Al_2O_3, you would know that the space group is $R\bar{3}c$ or No. 167. Looking this up in the International Tables, you would find the information shown in Figure 16.11A. In this case, you'd have to decide whether you want to use rhombohedral axes or hexagonal axes; you'll notice that there are three times as many atoms in the hexagonal cell. The tables in Figure 16.11B tell you which reflections are allowed, although you will

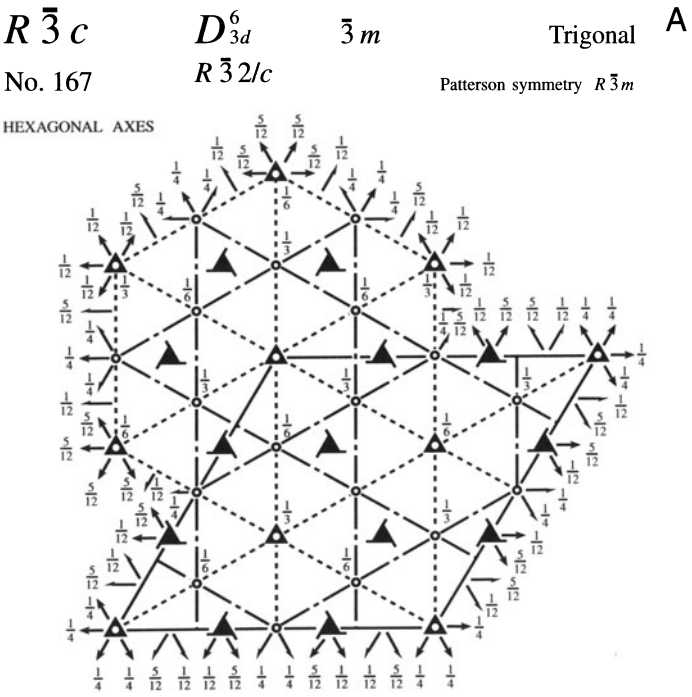

Figure 16.11. (A) Symmetry information, as given in the International Tables for trigonal α-Al_2O_3, with space group $R\bar{3}c$, showing the two possible unit cells based on the rhombohedral and hexagonal cells. The symmetry elements at specific lattice points are also indicated. (B) The atomic positions for the two choices of unit cells in (A).

B Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
			(0,0,0)+	$(\frac{2}{3},\frac{1}{3},\frac{1}{3})$+	$(\frac{1}{3},\frac{2}{3},\frac{2}{3})$+	
						General:
36	f	1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$	$hkil$: $-h+k+l=3n$
			(4) $y,x,\bar{z}+\frac{1}{2}$	(5) $x-y,\bar{y},\bar{z}+\frac{1}{2}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{1}{2}$	$hki0$: $-h+k=3n$
			(7) $\bar{x},\bar{y},\bar{z}$	(8) $y,\bar{x}+y,\bar{z}$	(9) $x-y,x,\bar{z}$	$hh\bar{2}hl$: $l=3n$
			(10) $\bar{y},\bar{x},z+\frac{1}{2}$	(11) $\bar{x}+y,y,z+\frac{1}{2}$	(12) $x,x-y,z+\frac{1}{2}$	$h\bar{h}0l$: $h+l=3n$, $l=2n$
						$000l$: $l=6n$
						$h\bar{h}00$: $h=3n$
						Special: as above, plus
18	e	.2	$x,0,\frac{1}{4}$	$0,x,\frac{1}{4}$	$\bar{x},\bar{x},\frac{1}{4}$	$\bar{x},0,\frac{3}{4}$ $0,\bar{x},\frac{3}{4}$ $x,x,\frac{3}{4}$
						no extra conditions
18	d	$\bar{1}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$ $\frac{1}{2},0,\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
						$hkil$: $l=2n$
12	c	3.	$0,0,z$	$0,0,\bar{z}+\frac{1}{2}$	$0,0,\bar{z}$	$0,0,z+\frac{1}{2}$
						$hkil$: $l=2n$
6	b	$\bar{3}$.	$0,0,0$	$0,0,\frac{1}{2}$		
						$hkil$: $l=2n$
6	a	32	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$		
						$hkil$: $l=2n$

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
						General:
36	f	1	(1) x,y,z	(2) z,x,y	(3) y,z,x	hhl : $l=2n$
			(4) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$	(5) $\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2}$	(6) $\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2}$	hhh : $h=2n$
			(7) $\bar{x},\bar{y},\bar{z}$	(8) $\bar{z},\bar{x},\bar{y}$	(9) $\bar{y},\bar{z},\bar{x}$	
			(10) $y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$	(11) $x+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2}$	(12) $z+\frac{1}{2},y+\frac{1}{2},x+\frac{1}{2}$	
						Special: as above, plus
6	e	.2	$x,\bar{x}+\frac{1}{2},\frac{1}{4}$	$\frac{1}{4},x,\bar{x}+\frac{1}{2}$	$\bar{x}+\frac{1}{2},\frac{1}{4},x$	
			$\bar{x},x+\frac{1}{2},\frac{3}{4}$	$\frac{3}{4},\bar{x},x+\frac{1}{2}$	$x+\frac{1}{2},\frac{3}{4},\bar{x}$	no extra conditions
6	d	$\bar{1}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$ $0,\frac{1}{2},\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},0$
						hkl : $h+k+l=2n$
4	c	3.	x,x,x	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2}$	$\bar{x},\bar{x},\bar{x}$	$x+\frac{1}{2},x+\frac{1}{2},x+\frac{1}{2}$
						hkl : $h+k+l=2n$
2	b	$\bar{3}$.	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
						hkl : $h+k+l=2n$
2	a	32	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{3}{4},\frac{3}{4},\frac{3}{4}$		
						hkl : $h+k+l=2n$

Figure 16.11. (Continued)

can work out the values of F if you want them. You know the chemical formula of your material, but you still need to know which sites are occupied. Look up the positions from X-ray diffraction data. The paper by Lee and Lagerlof (1985) summarizes the analysis for this particular example.

That was the traditional approach. Now, you should have access to Desktop Microscopist or Crystal Kit. Alternatively, use EMS over the WWW (Section 1.5). In all these software packages you can just type in your space group or pull down a menu to find the structure-factor information.

Table 16.2. Examples of Selection Rules for Several Crystal Structures Where *F* is the Structure Factor

Crystal type	Reflection present for	F	Lattice points per cell
Primitive	Any h, k, ℓ	f	1
Body centered cubic	$(h + k + \ell) = 2n$	$2f$	2
Face centered cubic including GaAs and NaCl	$h, k,$ and ℓ all odd or all even	$4f$	4
Diamond cubic	As fcc but if all even and $h + k + \ell \neq 4N$ then absent, anyway.		
Base centered	h, k and ℓ all odd or all even	$2f$	2
			Example
Hexagonal close-packed	$h + 2k = 3n$ with ℓ odd	0	0001
	$h + 2k = 3n$ with ℓ even	$2f$	0002
	$h + 2k = 3n \pm 1$ with ℓ odd	$f\sqrt{3}$	$01\bar{1}1$
	$h + 2k = 3n \pm 1$ with ℓ even	f	$01\bar{1}0$

CHAPTER SUMMARY

When we introduced the primitive lattice at the beginning of this chapter, we only considered the lattice sites which actually define the unit cell. If there are other lattice points, these would give us the Bravais lattices. We will conclude by summarizing some of the selection rules for the different structures in Table 16.2.

In practice, it will become important that you simply *know* some of the DPs for your material. You can, however, look up schematic indexed patterns in some of the textbooks listed in Chapter 1, but the best sources are Andrews *et al.* (1971) and Edington (1976) and we reproduce some of them in Figures 18.17–18.19. Alternatively, software (e.g., EMS) available on the WWW (Section 1.5) will print out standard spot patterns of most important crystal structures. When you're sitting at the TEM, you don't have time to index a pattern from first principles and then decide whether or not you are at a pole which contains the reflection you want to use. To do this you'll have to be able to index the diffraction patterns and determine the beam direction, which we'll describe in detail in Chapter 18.

REFERENCES

General References

Andrews, K.W., Dyson, D.J., and Keown, S.R. (1971) *Interpretation of Electron Diffraction Patterns,* 2nd edition, Plenum Press, New York. Stereographic projections, angles, spacings, and much more.

Cullity, B.D. (1978) *Elements of X-ray Diffraction,* 2nd edition, Addison-Wesley, Reading, Massachusetts.

Massalski, T., Okamoto, H., Subramanian, P.R., and Kacprzak, L., Eds. (1990) *Binary Alloy Phase Diagrams,* 2nd edition, ASM International, Materials Park, Ohio. Appendix A1 gives a complete list of the Pearson Symbols ($L1_2$, etc.) with their space group and Strukturbericht designation.

Misell, D.L. and Brown, E.B. (1987) *Electron Diffraction: An Introduction for Biologists,* Volume 12 of the series *Practical Methods in Electron Microscopy* (Ed. A.M. Glauert), Elsevier, New York. Materials science students should not be put off by the title: this is an invaluable practical guide to indexing diffraction patterns and more.

Specific References

Crystal Kit, see Section 1.5.

Desktop Microscopist, see Section 1.5.

Dodsworth, J., Kohlstedt, D.L., and Carter, C.B. (1983) *Adv. Ceram.* **6**, 102.

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