

Lecture 7 — Defects in Crystals.

1 Introduction

In this lecture, we will explicitly consider crystal "imperfections" of different kinds, starting from the simplest form of translational symmetry breaking (the effects arising from the finite size of the crystals) and considering in turn other, more complex types of defects: "point" defects, correlated defects and "line" or "plane" defects (dislocations or stacking faults). As we shall see, all these defects give rise to particular kinds of scattering, most often away from the Bragg peaks.

1.1 Space and time scales: coherence

When dealing with crystal imperfections, one of the first questions one should ask is whether they will contribute *coherently* (i.e., amplitudes are summed) or *incoherently* (i.e., intensities are summed) to the diffraction patterns. The answer is: it depends on the lengthscale of the imperfections as compared with the **coherence lengths** for X-rays, neutrons, electrons etc. Small-scale deviations for a perfect crystal will contribute *coherently*; large-scale, *incoherently*. The intrinsic λ very similar argument may be construed for *timescales*. If the positions of the atoms in the crystal "fluctuate", e.g., due to phonons, do the different configurations occurring at different times contribute coherently or incoherently to the diffraction pattern? If the timescale of the fluctuations is slow, the latter will be true, but, as the timescale of the fluctuations is reduced, this will no longer be the case. What is the typical **coherence time** of the different probes?

- One distinguishes between **transverse** and **longitudinal** coherence lengths, perpendicular and parallel, respectively, to the direction of the beam.
- For a quasi-parallel beam geometry (as it is typical of a diffraction instrument), the **transverse coherence length** ξ_t is proportional to the wavelength and inversely proportional to the beam divergence α ($\xi_t = \lambda/\alpha$). Here, the beam divergence is defined as *the angle subtended by the source as seen from the sample*. The derivation is analogous to that of the double-slit experiment. Highly coherent X-ray beams (several tens of μm) are employed for special studies (lensless imaging, "speckle" patterns), revealing the shape and internal structure of large crystal domains. Neutron beams have comparatively relaxed divergences, and typical coherence lengths are 1000-2000 Å.
- For geometries employing focussing, (e.g., electron diffraction) it is possible to manipulate the coherence domain by varying the focal plane where the diffraction pattern is formed (see below).

- The **longitudinal coherence length** is inversely proportional to the relative wavelength spread of the beam: $\xi_l = \frac{1}{2}\lambda/(\Delta\lambda/\lambda)$. High-resolution monochromators at synchrotron sources typically yield $\Delta\lambda/\lambda \sim 0.5 - 1 \times 10^{-4}$, so at 1 Å ξ_l is about 1 μm. The wavelength spread of neutron and electron beams is typically 10 times and 100 times larger, respectively.
- The **coherence time** can be calculated using the uncertainty principle as $\tau = \hbar/\Delta E$ or from the relation $\tau = \xi_l/v$, yielding the same result apart for a factor of the order 1. Adopting the first approach, we obtain

$$\begin{aligned}\tau &= \frac{1}{\pi^2} \frac{m\lambda^2}{\hbar} \left(\frac{\Delta\lambda}{\lambda}\right)^{-1} \text{ for particles with mass} \\ \tau &= \frac{1}{2\pi} \frac{\lambda}{c} \left(\frac{\Delta\lambda}{\lambda}\right)^{-1} \text{ for photons}\end{aligned}\quad (1)$$

The prefactor is 1.6×10^{-14} [secÅ⁻²] for neutrons, 0.9×10^{-17} [secÅ⁻²] for electrons and 5×10^{-20} [secÅ⁻¹] for photons. Using the wavelengths and monochromaticity values mentioned above, we find that coherence times for neutrons, photons and 100 Kev electrons are in the picosecond, femtosecond and tens of attosecond ranges, respectively.

2 Finite size effects

Up to this point, we have consider the crystal lattice to be of infinite extent. As we have seen, the cross section becomes then a series of delta functions, centered on the RL nodes. We can relax our approximation by starting form eq. 6 in Lecture 6 (the cross section) and solve explicitly for the finite summations. in fact, we need not make any particular approximation other than the fact that the crystal should be composed of N_1, N_2 and N_3 unit cell in the $\mathbf{a}_1, \mathbf{a}_2$ and \mathbf{a}_3 directions, respectively. Remembering that

$$\sum_{n=-N}^N e^{-inx} = \frac{\sin\left((2N+1)\frac{x}{2}\right)}{\sin\frac{x}{2}} \quad (2)$$

after some straightforward math (in each direction, $x = \mathbf{q} \cdot \mathbf{a}_i$) we obtain

$$\boxed{\frac{d\sigma}{d\Omega} = \left[\prod_i \frac{\sin^2(N_i \frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i)}{\sin^2(\frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i)} \right] |F(\mathbf{q})|^2 [\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}']^2} \quad (3)$$

The diffraction pattern from a small single crystal taken with *coherent* radiation, i.e., radiation with *coherence length* (=wavepacket length/width) larger than the crystal, will display **3-dimensional fringes**, as typical of the function $\sin^2(Nx)/\sin^2 x$. However, for typical experiments with incoherent radiation, the number of unit cells is set by the coherence length of each photon rather than by the crystal size, and the oscillations will be smeared out. In this case, we can replace the oscillatory functions with a *Gaussian* function with the same maximum and same area:

$$\frac{\sin^2 Nx}{\sin^2 x} \rightarrow N^2 e^{-(Nx)^2/\pi} \quad (4)$$

Observing that $\prod_i N_i = N_c$, the total number of unit cell in the crystal, we obtain

$$\boxed{\frac{d\sigma}{d\Omega} = N_c^2 \left[\prod_i e^{-(N_i \frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i)^2/\pi} \right] |F(\mathbf{q})|^2 [\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}']^2} \quad (5)$$

where the Gaussian functions have variance and FWHM

$$\begin{aligned} \sigma_i^2 &= \frac{2\pi}{N_i^2 a_i^2} \\ FWHM &= \frac{4\sqrt{\pi \ln 2}}{N_i a_i} \end{aligned} \quad (6)$$

We can therefore conclude that:

- The **cross section at a given \mathbf{q}** is proportional to N_c^2 .
- The **width** in \mathbf{q} is *inversely proportional to the number of unit cells along that direction*.
- The **integrated cross section** in three dimensions (remember the Gaussian integral $\sqrt{2\pi\sigma^2}$) is therefore proportional to N_c , which reproduces the result we obtained for the infinite crystal (eq. 8, lecture 6).

3 Beyond the perfect-crystal approximation: diffuse scattering

Finite-size effects only generate scattering in the vicinity of the "ideal" Bragg positions, leaving the integrated intensity of the reflection unaltered. In this section, we will demonstrate that

additional scattering is generated whenever either the atomic scattering factors or the positions of individual atoms deviate from the average values and/or the “ideal” lattice sites. In general, this additional scattering is present throughout reciprocal space, and is therefore known as **diffuse scattering**. In the remainder of this section, we will consider the deviations from perfect periodicity as **static**. In other words, we will imagine that the scattering process occurs coherently from a **frozen snapshot** of the crystal. To estimate the full scattered intensity, at the end, we will undertake a time/thermal averaging process on the scattered intensities. This is a very good approximation in the case of X-rays (and electrons), since the coherence times are *much shorter than phonon frequencies*. For neutrons, where this is clearly not the case, a more complex treatment is required, but qualitatively similar considerations (with some caveats) can be applied.

3.1 Classification of disorder in crystals

We will here consider two types of disorder:

- **Substitutional disorder** is typical of alloys and, more generally, of solid solutions. It occurs when more than one atomic species can reside on the same crystallographic site, and gives rise to a fluctuation of the atomic scattering factor around an “average” value, the latter reflecting the average composition of the alloy. For example, in a 67%Cu-33%Au “random” alloy, Cu and Au occupy the same crystallographic sites of the FCC structure. To calculate the Bragg scattering from such an alloy, one should use the *average* atomic scattering factor ($f_{ave}(0) = 45.7$). However, *locally*, the scattering factor varies between that of Cu ($f_{Cu}(0) = 29$) and Au ($f_{Au}(0) = 79$). This local fluctuation, as we shall see, gives rise to diffuse scattering. Substitutional disorder is almost always **static**, since atoms in alloys do not usually move from one site to the next, but counter-examples do exist (e.g., in the case of fast ion conductors).
- **Dynamic displacive disorder** is present in all materials even at zero temperatures, due to phonons and zero-point motion. In addition to scattering contrast fluctuations, substitutional disorder can itself produce *static* displacive disorder, since different species have in general different atomic radii.

3.2 Simple diffuse scattering calculations

We shall now calculate the *full* scattering cross section for an (infinite) crystal in the presence of both substitutional and displacive disorder. To simplify the formalism, we will perform this calculation in the case of a crystal with one atom per unit cell, but the extension to more complex

structures is completely straightforward. Let us therefore re-write the cross section in eq. 6, Lecture 6 in this case.

$$\frac{d\sigma}{d\Omega} = r_0^2 \mathcal{P}(\gamma) \left(\sum_j \sum_i e^{-i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \right) f_i(\mathbf{q}) f_j^*(\mathbf{q}) \quad (7)$$

In eq. 7, \mathbf{r}_i represent the *actual* positions of the atoms, while we indicate with \mathbf{R}_i the position of the lattice nodes. Moreover, we will write

$$\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i \quad (8)$$

where the \mathbf{u}_i are the *displacements* away from the lattice nodes and are “small” (see below). With the additional notation $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ and $\mathbf{u}_{ij} = \mathbf{u}_i - \mathbf{u}_j$ we can write:

$$\frac{d\sigma}{d\Omega} = r_0^2 \mathcal{P}(\gamma) \sum_{\mathbf{R}_{ij}} e^{-i\mathbf{q}\cdot\mathbf{R}_{ij}} \sum_{\text{Pairs with } \mathbf{R}_{ij}} [f_i(\mathbf{q}) f_j^*(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{u}_{ij}}] \quad (9)$$

In eq. 9, we have rearranged the double summation, so that the rightmost sum runs over all pairs of unit cells joined by a given vector \mathbf{R}_{ij} , whereas the leftmost sum runs over these vectors. Using, for example, periodic boundary conditions, we find that for each \mathbf{R}_{ij} , there are exactly N pairs of sites joined by it (N being the total number of atoms in the crystal). We can therefore re-write eq. 9 as:

$$\frac{d\sigma}{d\Omega} = N r_0^2 \mathcal{P}(\gamma) \sum_{\mathbf{R}_{ij}} e^{-i\mathbf{q}\cdot\mathbf{R}_{ij}} \langle f_i(\mathbf{q}) f_j^*(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{u}_{ij}} \rangle_{\mathbf{R}_{ij}} \quad (10)$$

We can subtract from eq. 10 the Bragg scattering cross section to obtain the expression for the non-Bragg or **diffuse scattering** (we stress, once again, that the *average* atomic scattering factor is used to calculate the Bragg scattering):

$$\left(\frac{d\sigma}{d\Omega} \right)_{diff} = N r_0^2 \mathcal{P}(\gamma) \sum_{\mathbf{R}_{ij}} e^{-i\mathbf{q}\cdot\mathbf{R}_{ij}} \langle f_i(\mathbf{q}) f_j^*(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{u}_{ij}} - |f_{ave}(\mathbf{q})|^2 e^{-2W} \rangle_{\mathbf{R}_{ij}} \quad (11)$$

where the sign $\langle \rangle_{\mathbf{R}_{ij}}$ indicates the *average* of the quantity within it over all the pairs in the coherence domain joint by the vector \mathbf{R}_{ij} .

3.2.1 Diffuse scattering from uncorrelated substitutional disorder

Here, we will make the slightly unrealistic assumption that the atoms are not displaced at all from their ideal lattice sites, and consider the diffuse scattering arising from purely substitutional disorder ($\mathbf{u}_{ij} = 0$). We can write

$$\left(\frac{d\sigma}{d\Omega}\right)_{diff} = Nr_0^2 \mathcal{P}(\gamma) \sum_{\mathbf{R}_{ij}} e^{-i\mathbf{q}\cdot\mathbf{R}_{ij}} \langle f_i(\mathbf{q}) f_j^*(\mathbf{q}) - |f_{ave}(\mathbf{q})|^2 \rangle_{\mathbf{R}_{ij}} \quad (12)$$

If the sites have random occupancy, for $i \neq j$ the average is identically zero for all \mathbf{R}_{ij} , so only the autocorrelation term $i = j$ survives, yielding

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{diff} = Nr_0^2 \mathcal{P}(\gamma) [(|f(\mathbf{q})|^2)_{ave} - |f_{ave}(\mathbf{q})|^2]} \quad (13)$$

For example, for a binary alloy with species A and B and concentrations C_A and $1 - C_A$, we obtain

$$\left(\frac{d\sigma}{d\Omega}\right)_{diff} = Nr_0^2 \mathcal{P}(\gamma) C_A (1 - C_A) |f_A(\mathbf{q}) - f_B(\mathbf{q})|^2 \quad (14)$$

As we can see, these cross sections are slowly varying in q , since they are only modulated by the atomic scattering factors, and have their maximum near $q = 0$.

3.2.2 Diffuse scattering from uncorrelated displacements

Let us now assume that we have a single atomic species ($f_i = f_j = f_{ave}$) and that the displacements of atoms i and j are not correlated with each other. If $i \neq j$,

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_{ij}} \rangle = \langle e^{-i\mathbf{q}\cdot\mathbf{u}_i} \rangle \langle e^{-i\mathbf{q}\cdot\mathbf{u}_j} \rangle = e^{-2W} \quad (15)$$

so \mathbf{R}_{ij} vectors joining different atoms do not give any contributions to the diffuse scattering. The only surviving term is the autocorrelation term, for which $\mathbf{u}_{ij} = 0$. Therefore,

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{diff} = Nr_0^2 \mathcal{P}(\gamma) |f(\mathbf{q})|^2 (1 - e^{-2W})} \quad (16)$$

As we can see from eq. 16, the diffuse scattering from uncorrelated displacements is a slowly varying function of \mathbf{q} ; it is zero near the origin of the reciprocal space and *increases* with q (it is in the first approximation proportional to q^2), only to decay again with the decay of the atomic scattering factors.

3.3 General treatment of displacive disorder and thermal diffuse scattering

In the two simple examples we proposed above, we have treated the deviations from the average structure as completely uncorrelated from site to site. The result, in both cases, is a form of diffuse scattering that has very little structure in reciprocal space. In the extreme case of *neutron* studies of substitutional disorder, the atomic form factor is a constant, and the resulting diffuse scattering is completely flat.

In realistic cases, correlations are almost always present: even in disordered alloys, a given species may have a “preference” to be surrounded by atoms of the same kind or, quite frequently, of a different kind, so near-neighbour probabilities are generally different from the average. These correlations are lost after a few unit cells, and they are referred to as **short-range order**. In this case, beside the autocorrelation term, additional terms in the summation (eq. 12) will be non-zero, giving rise to a more structured diffuse scattering pattern. Note that each \mathbf{R}_{ij} pair that corresponds to a definite correlation will contribute with a Fourier component $\exp(\mathbf{R} \cdot \mathbf{R}_{ij})$ (or $\cos \mathbf{R} \cdot \mathbf{R}_{ij}$ in the centrosymmetric case) to the diffuse scattering.

The **correlated displacements** due to thermal vibrations are of even longer range: an ideal plane-wave phonon involves all sites of the crystal, and therefore involves all terms in the summation (eq. 11). The correlation terms \mathbf{u}_{ij} will typically involve sums and differences of sines and cosines, and since they appear in the exponential, the summation over an infinite number of pairs cannot be performed analytically. The typical approach is to expand the exponential in Taylor series. This is done as follows: for simplicity, let us rewrite eq. 11 in the case of pure displacive disorder (no substitutional disorder):

$$\left(\frac{d\sigma}{d\Omega}\right)_{diff} = Nr_0^2 \mathcal{P}(\gamma) \sum_{\mathbf{R}_{ij}} e^{-i\mathbf{q} \cdot \mathbf{R}_{ij}} |f(\mathbf{q})|^2 \left[\langle e^{-i\mathbf{q} \cdot \mathbf{u}_{ij}} \rangle_{\mathbf{R}_{ij}} - e^{-2W} \right] \quad (17)$$

Next, we will use again eq. 13, Lecture 6, which is valid for small displacements or harmonic displacements:

$$\langle e^{-i\mathbf{q} \cdot \mathbf{u}_{ij}} \rangle = e^{-\frac{1}{2} \langle [\mathbf{q} \cdot \mathbf{u}_{ij}]^2 \rangle} \quad (18)$$

Finally, we expand the exponential in eq. 18 in Taylor series:

$$\begin{aligned}
\left(\frac{d\sigma}{d\Omega}\right)_{diff} &= Nr_0^2 \mathcal{P}(\gamma) \sum_{\mathbf{R}_{ij}} e^{-i\mathbf{q}\cdot\mathbf{R}_{ij}} |f(\mathbf{q})|^2 \left\{ \left[-\frac{1}{2} \langle [\mathbf{q} \cdot \mathbf{u}_{ij}]^2 \rangle + 2W \right] \right. \\
&\quad \left. + \left[\frac{1}{8} \langle [\mathbf{q} \cdot \mathbf{u}_{ij}]^2 \rangle^2 - 2W^2 \right] + \dots \right\} \\
&= I_1 + I_2 + \dots
\end{aligned} \tag{19}$$

The different terms in eq. 19 are known as first-order, second-order etc., diffuse scattering.

3.3.1 First-order thermal diffuse scattering

In well-ordered crystals, the most important contribution to the diffuse scattering is that from the displacement patterns due to phonons. This type of diffuse scattering is known as Thermal Diffuse Scattering or TDS. The first-order term in eq. 19 is often the dominant contribution, particularly at moderate temperatures. The calculation of diffuse scattering for monoatomic solid is not inaccessible at the present level, but it is rather lengthy. Here, we summarise the main steps and present the final result, so that its structure can be analysed.

- Only phonons with the same wavevector \mathbf{k} and the same branch index contribute coherently to first-order TDS. The scattering from one such phonon is not difficult to calculate: it generate *satellite peaks* at $\pm\mathbf{k}$ around any given Bragg peaks.
- One needs to sum the *scattered intensity* of phonons with different wavevectors, taking into account the fact that their amplitude is related to the thermal population.
- The final result is:

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{1^{st}TDS} = Nr_0^2 \mathcal{P}(\gamma) \frac{\hbar}{2M} \sum_j \frac{1}{\omega_j(\mathbf{q})} \coth\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_B T}\right) |F_j(\mathbf{q})|^2} \tag{20}$$

where the sum is over the different phonon branches and

$$F_j(\mathbf{q}) = f(\mathbf{q}) e^{-W} [\mathbf{q} \cdot \mathbf{e}_j(\mathbf{q})] \tag{21}$$

is the so-called **one-phonon structure factor** and $\mathbf{e}_j(\mathbf{q})$ is the polarisation vector of phonon branch j at the wavevector \mathbf{q} . In order to evaluate the quantities $\mathbf{e}_j(\mathbf{q})$ and $\omega_j(\mathbf{q})$, one needs to reduce \mathbf{q} to the first Brillouin zone in the usual way.

- The function $\frac{1}{\omega_j(\mathbf{q})} \coth\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_B T}\right)$ **decreases rapidly** with increasing frequency. Therefore **low-energy, acoustic phonons provide the largest contribution to first-order TDS**. For the same reason, the TDS diverges at the Bragg peak positions and is minimum between the Bragg peaks.
- When the same reduced wavevector is considered in different Brillouin zones, one finds that the cross section is proportional to q^2 , similar to the diffuse scattering due to uncorrelated displacements (eq. 21).

4 Scattering from non-crystalline solids and liquids

Our discussion of the scattering cross sections for "defective" crystal would not be complete without a mention of the most extreme form of defects — the complete loss of crystalline order, as in the case of non-crystalline solids (glasses) or liquids. In this case, it is no longer possible to define a crystal lattice; nevertheless, the formalism to calculate the scattering cross section is very similar to the one we have already encountered (eq. 9). The main difference is that, for obvious reasons, decomposing position vectors in \mathbf{R}_{ij} and \mathbf{u}_{ij} will no longer make sense, and we will therefore employ the original notation \mathbf{r}_{ij}

$$\frac{d\sigma}{d\Omega} = r_0^2 \mathcal{P}(\gamma) \sum_{m=1}^N \sum_{\mathbf{r}_{ij}} f_i(\mathbf{q}) f_j^*(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} \quad (22)$$

where the first sum runs over all the atoms in the sample. For simplicity, we will proceed from here assuming that all the atoms in the sample are the same, as appropriate, for example, for a monoatomic liquid like mercury. The extension to polyatomic liquids or glasses is rather straightforward but requires a heavier notation. With our assumption, we can extract $N|f(\mathbf{q})|^2$ from all the summations and replace the sums with averages; we will also isolate the autocorrelation term ($\mathbf{r}_{ij} = 0$) which yields 1:

$$\frac{d\sigma}{d\Omega} = N r_0^2 \mathcal{P}(\gamma) |f(\mathbf{q})|^2 \left[1 + \sum_{\mathbf{r}_{ij} \neq 0} \langle e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} \rangle \right] \quad (23)$$

We now want to take advantage of the fact that, in a disordered sample, if a vector \mathbf{r}_{ij} connecting two atoms is present, then all other vectors with the same modulus r_{ij} will also be present with equal probability somewhere in the sample. This will enable us average over the angular variables and replace the summation in eq. 23 with a sum over r_{ij} . In doing so, we have to account for the

fact that any given atom may be surrounded by more than one atom at the same distance r_{ij} , and we will do so by introducing the **average coordination number** $n(r_{ij})$.

$$\frac{d\sigma}{d\Omega} = Nr_0^2 \mathcal{P}(\gamma) |f(\mathbf{q})|^2 \left[1 + \sum_{r_{ij} \neq 0} n(r_{ij}) \frac{1}{4\pi} \int_0^\pi e^{-iqr_{ij} \cos \theta} \sin \theta d\theta d\phi \right] \quad (24)$$

The integral is straightforward and yields $4\pi \sin qr_{ij}/qr_{ij}$.

$$\boxed{\frac{d\sigma}{d\Omega} = Nr_0^2 \mathcal{P}(\gamma) |f(\mathbf{q})|^2 \left[1 + \sum_{r_{ij} \neq 0} n(r_{ij}) \frac{\sin qr_{ij}}{qr_{ij}} \right]} \quad (25)$$

The structure of eq. 25 clearly illustrates the main feature of the scattering from non-crystalline materials: the cross section only depends on q , so the scattering will occur as **uniform spheres in reciprocal space**. Analysis of the scattering will provide information about the **average coordination number** at every distance r_{ij} around a given atom. More details about this, with particular reference to the Pair Distribution Function analysis method, are provided in the extended version of the notes (see also [2]).

5 Other defects in crystals: point defects, dislocations and planar defects

In this section, we will be concerned with a few additional modes of departures from perfect crystal ordering, known as **point defects**, **dislocations** and **planar defects**. These defects are associated with points, lines or planes in the crystal, and move slowly or not at all, so they can generally be considered as static, as far as diffraction is concerned.

5.1 Point defects

A point defect occurs when the crystal periodicity is primarily broken at one lattice site or at a few adjacent sites, although its influence can propagate far away into the crystal (see below). The simplest examples of a point defect are **substitutions** **vacancies** and **interstitials**, in which, respectively, atoms on a given site are replaced by a different species, are absent altogether or occupy a position that is usually unoccupied. **Substitutional disorder in alloys** can be thought as an extreme example of a high density of point defects. Point defects often occurs in pairs up to

maintain stoichiometry or charge neutrality, as in the case of Frenkel defects (a vacancy and an interstitial) or Schottky defects (vacancy of ions with opposite charge). In the case of **extended defects**, the coordination environment around the defect site is modified to approximate the preferred environment of the new species. For example, if a cation with a preference for tetrahedral coordination is substituted on an octahedral site, the six surrounding anions can be distorted and one or two can be missing altogether, forming an extended defect.

If present in sufficient concentration, point defects can give rise to diffuse scattering, in complete analogy to substitutional disorder. Another form of diffuse scattering associated with point defects is **Huang scattering**: this arises from the static displacement field due to the elastic deformation of the lattice around the defect, and its treatment is analogous to that of first-order TDS.

5.2 Dislocations

Dislocations are linear defects that commonly form in metals as a result of the application of stresses, e.g. due to repeated bending. They play an important role in both the strength and the failure of materials: **work hardening** (such as beating a red-hot piece of metal on an anvil) has been used for centuries by blacksmiths to introduce dislocations into materials, increasing their yield strengths. On the other hand, the infamous **metal fatigue fracture** (responsible, for example, for the De Havilland Comet disasters) are initiated by dislocations, which eventually form persistent slip bands that nucleate short cracks

Two main types of dislocations are identified: **edge dislocations** and **screw dislocation**, although most real dislocation are intermediate between these types. They are characterised by two direction vectors: the **dislocation direction** — the direction of the linear structure in question, and the **Burgers vector** — the principal direction of the strain (displacement) field near the dislocation. Burgers vectors are essential elements of the theory behind imaging defects by electron microscopy — see, for example, [1].

5.2.1 Burgers vectors for edge and screw dislocations

The classic definition of the Burgers vector is the following (see fig. 1 and 2): Let us consider a part of the crystal that is *free* from any defect, and let us define a closed loop of atoms. Let us now insert the dislocation so that the dislocation line is *inside* and *perpendicular* to the loop. The strain (displacement) field generated by the defect will displace the existing atoms, so that the rectangle will be deformed, whilst, by definition, remaining a closed loop. If the rectangle is deformed into a trapezium, the Burgers vector will be *perpendicular* to the dislocation line (**edge dislocation**, fig. 1). If the rectangle is deformed into a 3-dimensional shape, the Burgers vector

will be *parallel* to the dislocation line (**screw dislocation**, fig. 2).

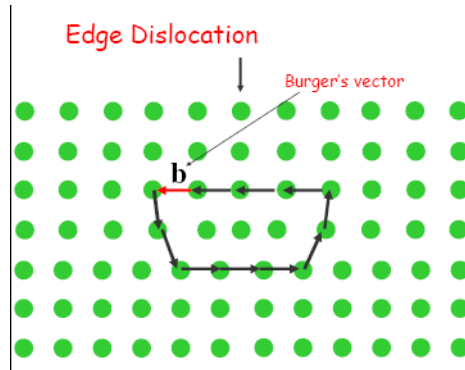


Figure 1: An edge dislocation and its associated Burgers vector. An edge dislocation arises when a plane of atoms is abruptly terminated within the crystal. The displacement field around the edge dislocation is defined by its Burgers vector, and, is **perpendicular to the dislocation line**.

Screw dislocation

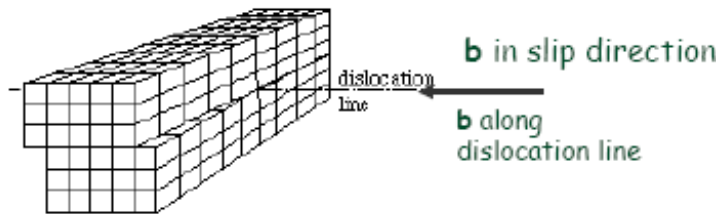


Figure 2: A screw dislocation and its associated Burgers vector. We can imagine that a screw dislocation is generated by “slicing” a plane through the crystal up to a certain line, and by displacing the atoms on one side of the plane by one unit cell along the direction of the line. The displacement field around the edge dislocation is defined by its Burgers vector, and is **perpendicular to the dislocation line**.

5.3 Stacking faults

The last family of crystal defects we will consider in this lecture are the *planar defects*. As the word implies, the defect originated at a planar locus in the crystal, although the strain field can propagate some way away from the plane. Although other types of planar defects exist (for example, the **twin planes**), here we will only consider the **stacking faults**.

Stacking faults are defects in the “stacking” of atomic layers — most commonly a fault in the stacking sequence of the layers, a missing layer or an added layer, either of the same type or of

a different type with respect to the bulk layers. Unsurprisingly, **stacking faults are common in layered structures**, but are also encountered in isotropic structures: in fact, perhaps the best known type of stacking fault occurs in FCC metals, and is a fault of the ...ABCABCABC... stacking sequence of the (111) layers, as, for example, in ...ABCABABCABC... Stacking faults of this type can be described as a **displacement (slip)** of an entire plane of atoms **perpendicular** to the fault plane, so that the fault is described by two vectors: the **stacking vector** (perpendicular to the fault plane) and the **slip vector**, describing the displacement direction of the plane of atoms. The slip vector plays a similar role to the Burgers vectors in the imaging of stacking faults by TEM (see below). In this case of the (111) faults in FCC metals, the **slip vector** is along the $(\bar{2}11)$ direction or its equivalents (fig. 3).

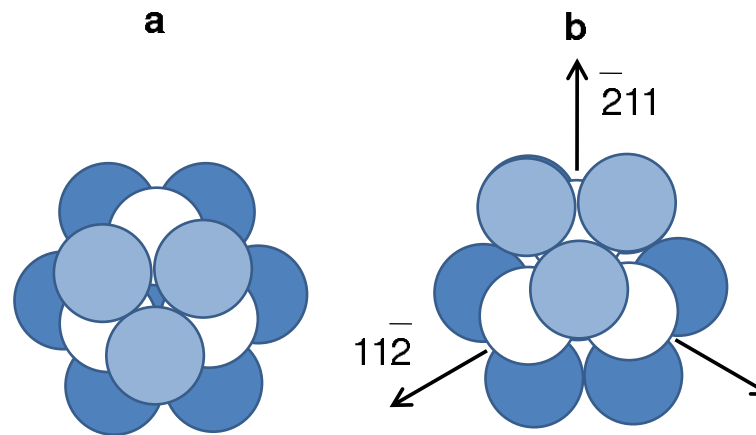


Figure 3: **A**: a portion of the unfaulted FCC structure, with stacking sequence ...ABCABCABC...**B** A stacking fault, in which the “A” layer is inserted instead of a “C”, and the corresponding possible slip vectors.

6 Bibliography

P.J. Grundy & G.A. Jones [1] A handy booklet on electron microscopy, a bit old but still useful to understand how dislocations can be imaged.

S.J.L. Billinge & M.F. Thorpe [2] A good collection of articles on diffuse scattering and scattering from disordered materials.

References

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- [2] S.J.L. Billinge and M.F. Thorpe eds., “Local structure from diffraction”, Kluwer Academic Publishers New York, Boston, Dordrecht, London, Moscow, 2002.