

X-ray scattering:

Measuring crystal structures by coherent elastic scattering requires wavelengths less than the spacing of lattice planes. Aside from x-rays (photon energy = keV's), which have wavelengths appropriate for typical crystals, other methods include neutron and electron scattering. Neutron scattering requires a centralized facility, and there are currently about 10 such facilities in the US, for example Oak Ridge and NIST have high-profile centers. Neutron scattering as we will see later is also a sensitive probe typically used for phonons (vibrational excitations). The smaller penetration depth in electron scattering lends itself to surface studies, such as in Low Energy Electron Diffraction (LEED), which measures 2D surface structure and is often used in semiconductor deposition chambers. LEED is the analog of the Davisson-Germer experiment. Electron diffraction for 3D crystal studies typically takes place in transmission-electron microscopes (TEM's). In a high-resolution TEM the beam may be focused upon individual nano-scale crystallites and particles, and the measurements are thus particularly important for nanoscience and materials science research. On the other hand because of the penetration depth is is somewhat more difficult to obtain extremely high resolution in measuring lattice-plane spacings than the other methods. X-ray scattering may also be carried out at centralized synchrotron radiation facilities for extreme resolution, such as at the Advanced Light Source at Lawrence Berkeley Lab, and National Synchrotron Light Source at Brookhaven. Spectrometers using traditional x-ray tubes are used for more routine crystal studies (although still with impressively high resolution). There are probably several 10's of such spectrometers in various laboratories at Texas A&M.

As an example see Figure 1 from a publication from my laboratory. The main part of the top figure is an x-ray powder spectrum, for the material shown in the inset. The relative intensity of the peaks can be fitted to the positions and identities of the basis atoms—the lowest curve (blue in the original) is the difference between the data and the fit that was carried out using a standard software package. The lower 3 panels show electron diffraction images taken from small crystallites by using a TEM.

Scattering from crystals: The Bragg scattering law is:

$$n\lambda = 2d \sin \theta. \quad [1]$$

Note that since the sin cannot exceed 1, clearly λ must be smaller than $2d$ in order to observe any scattering. Recall that d is the spacing of Bragg planes, constructed from the Bravais lattice, without considering the basis. Thus the observed angles are determined by the primitive cell dimensions only, not the positions of atoms inside the cell. (The atom positions and identities determine the structure factor, as shown below, which gives the relative *intensities* of the observed lines.)

Laue scattering and structure factor: Consider the incoming and outgoing wavevectors to be \vec{k} and \vec{k}' . The scattering angle, θ , is 1/2 the angle between \vec{k} and \vec{k}' . We consider each atom to scatter the plane wave elastically into an outgoing spherical-type wave, of amplitude,

$$f_i(\theta) \exp(ik'r) / r, \quad [2]$$

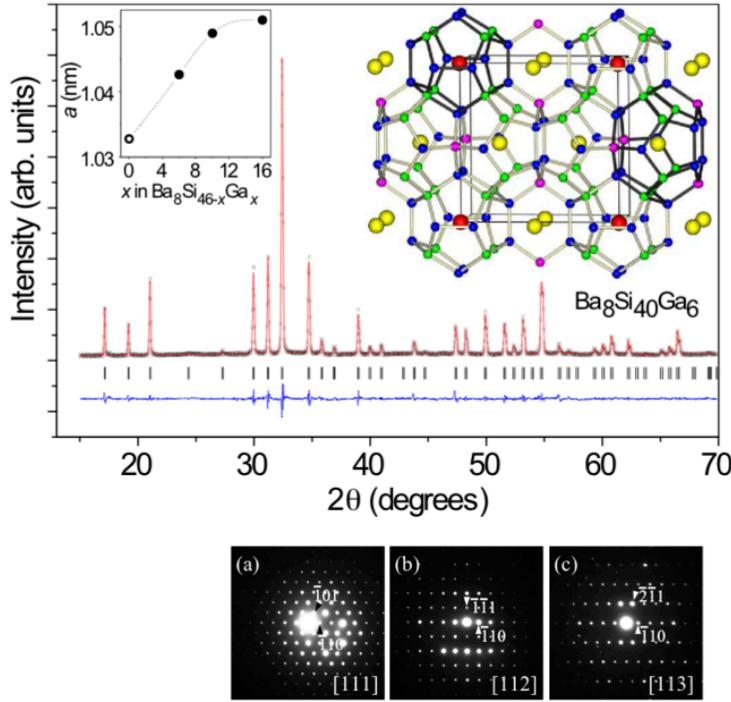
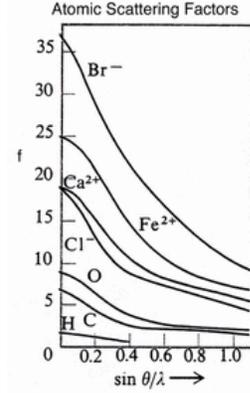


Figure 1. Upper figure at left: Powder x-ray diffraction spectrum, with fitted spectrum after structural refinement, for $\text{Ba}_8\text{Si}_{40}\text{Ga}_6$ (crystal in inset). Lower left: Three electron diffraction scans for crystallites of the same material, orientations indicated. Ref: Y. Li *et al.*, Phys. Rev. B **75**, 054513 (2007).

Below: Form factors for several ions. [Xray0.Princeton.edu]



where in the exponent the product is magnitudes, and the prefactor is the *atomic form factor* f_i containing all the physics of atomic scattering. In general the magnitude of $f_i(\theta)$ features a slow decay with increasing angle. [Note that the form factor also typically includes a small imaginary part. Also similar to Rayleigh scattering from molecules, there is in addition a $(1 + \cos^2\theta)$ factor that should multiply the results in equation [2], at least for unpolarized incoming radiation -- this is the typical situation for x-ray tubes, while for polarized synchrotron radiation the factor is somewhat different -- in any case here we will ignore this detail.]

The detector (whose position we label \vec{r}) measures a superposition of scattered waves, emanating from positions $\vec{R}_n + \vec{d}_j$ (Bravais lattice + basis position). The far-field detected waves are essentially parallel, and each has a relative phase

$$\phi = \vec{k} \cdot (\vec{R}_n + \vec{d}_i) + \vec{k}' \cdot (\vec{r} - \vec{R}_n - \vec{d}_i) \equiv \vec{k}' \cdot \vec{r} - \vec{q} \cdot (\vec{R}_n + \vec{d}_i), \quad [3]$$

where $\vec{q} = \vec{k}' - \vec{k}$. In the middle expression the first term is the phase of the incoming wave as it reaches the atom, and the second is the further phase picked up along the path to the detector.

The term $\vec{k}' \cdot \vec{r}$ on the right is a phase factor that is the same for all atoms and can be dropped. That leaves the last term, containing the wave-vector difference defined as $\vec{q} = \vec{k}' - \vec{k}$.

The amplitude in the detector is the sum [2] over all atoms, with each term multiplied by the appropriate phase factor using [3]. With n for the Bravais lattice and j counting the basis atoms this gives,

$$A(2\theta) \propto \sum_n \sum_j f_j(2\theta) \exp(-i\vec{q} \cdot (\vec{R}_n + \vec{d}_j)). \quad [4]$$

One way to view this is that the x-ray scattering amplitude A is the **Fourier transform of the electron density of the crystal corresponding to wave-vector q** . This is because the form factor is essentially the corresponding integral of the electron density of each atom; see the very last section of chapter 2 in Kittel.

In far field θ is the same for all atoms, so the sum over n can be separated as:

$$\sum_n \exp(-i\vec{q} \cdot \vec{R}_n), \quad [5]$$

multiplied by the sum over j , which is independent of n . [5] is proportional to $\delta(\vec{q} - \vec{G})$ in the infinite crystal limit, with \vec{G} a reciprocal lattice vector. This leads to the **Laue condition**,

$$\vec{q} = \vec{k}' - \vec{k} = \vec{G}. \quad [6]$$

This result shows that elastic scattering occurs only for wave-vectors corresponding to the reciprocal lattice, in delta-function-like peaks at angles θ where $\vec{k}' - \vec{k} = \vec{G}$. (Note also the homework problem from the Kittel text addressing the more general situation of a finite sized crystal: in practical situations where crystallite sizes are on the order of nanometers, the delta-function becomes significantly broadened, and in fact this is used as a tool for nano-crystallography.)

Putting everything together, we have the amplitude for each scattering peak satisfying [6],

$$A \propto S_{\vec{G}} \equiv \sum_j f_j(2\theta) \exp(-i\vec{G} \cdot \vec{d}_j). \quad [7]$$

In [7], $S_{\vec{G}}$ is called the **structure factor**, which gives the peak amplitude for each \vec{G} -vector, as a sum over the basis atoms. The intensity, which is what is measured experimentally, is proportional to the square of [7]. The symmetries of the crystal determine the structure factor and can lead, for example, to systematic zeroes. These can therefore allow the more specific structure of the crystal to be identified (these are for example the 230 total space groups I mentioned in class).

Regarding measurement techniques, note that the Laue condition (or equivalently the Bragg law) gives the possibility that there could be scattering at a given angle, but this also implicitly requires that the crystal has a very specific orientation relative to the incoming beam. As I will discuss more in class, this leads to somewhat different measurement techniques depending upon whether a powder or a single crystal is used for measurements.

Figure 2 shows a sketch of some of the Bragg planes for the three cubic Bravais lattices. Note for example that for both BCC and FCC the (100) planes, would not be included. In both cases it is easy to demonstrate that the set of (100) planes will not intersect all of the lattice sites. This leads to “missing peaks” in the corresponding scattering spectra, as shown in Figure 3.

The structure factor [7] is another way to arrive at the same conclusion, as will be shown in class. For example for the FCC lattice, viewed as a simple cubic lattice with a basis of four identical atoms, it is easy to show that $S_{\vec{k}}$ consists of $f(2\theta)$ multiplied by a factor equal to either 4 or 0. The zeros correspond to indices 100, 110, 210, etc., identical to the missing reflections shown in Fig. 3.

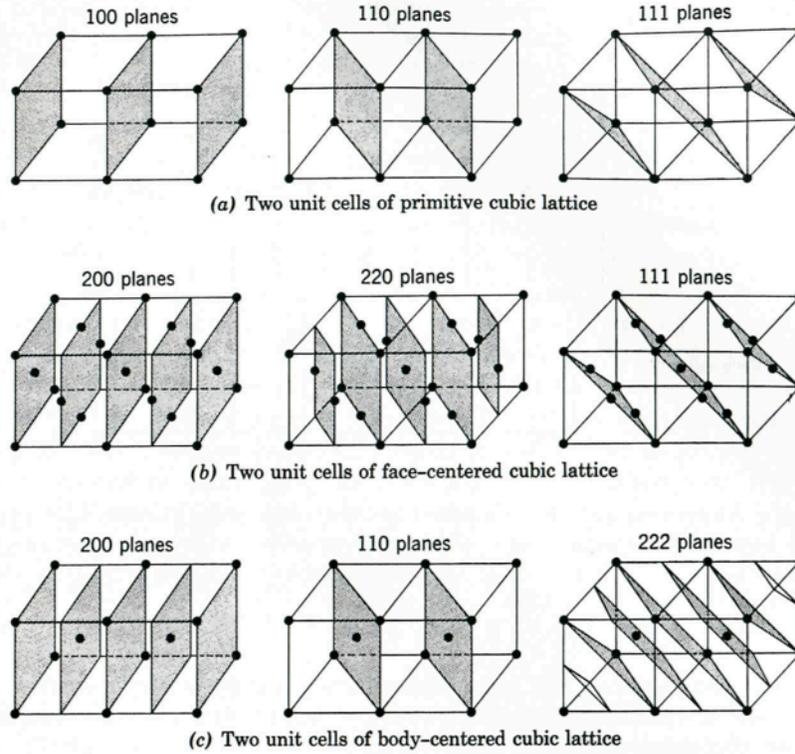


Fig. 19.9 Planes through cubic lattices.

Figure 2

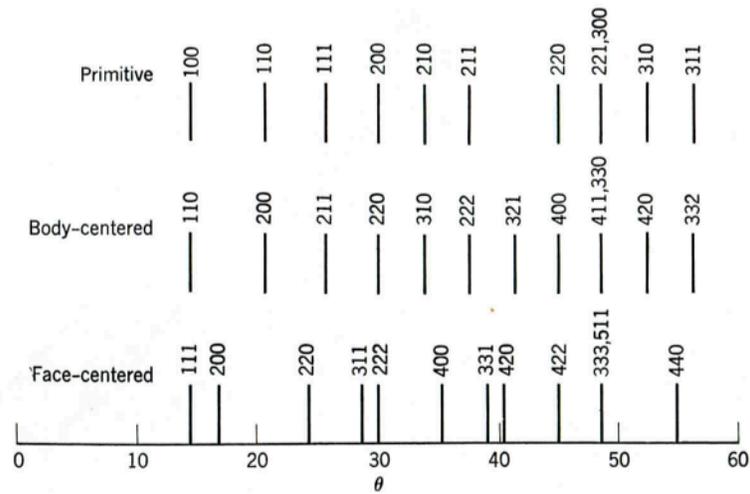


Fig. 19.10 Angles of incidence θ and reflection indices from cubic crystals. The values of λ/a have been chosen arbitrarily to cause the first reflection to fall at the same angle for each type of crystal. For primitive cubic, $\lambda/a = 0.500$; for body-centered cubic, $\lambda/a = 0.353$; for face-centered cubic, $\lambda/a = 0.289$.

Figure 3

Figures 2 and 3 from "Physical Chemistry" [Daniels and Alberty, 1975].