**Scattering**

**Photon Scattering**

We could talk about photon scattering processes. Typically, we’d be doing this in the context of shining a laser into a crystal and looking to see what light we got back out. Normally we look at a process whereby a single phonon is created or destroyed. These would be described by conservation of momentum/energy equations (q ~ phonon, k ~ photon):

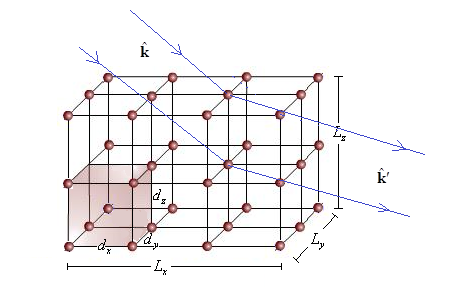
respectively. Or if we allow Umklapp processes, then,

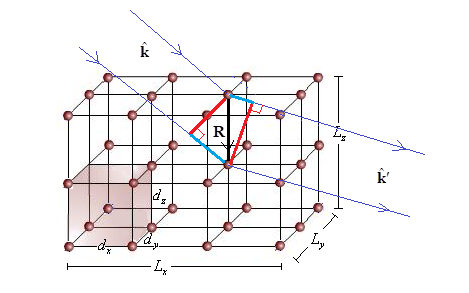
If we’re at low T’s, then both q and ωq will be small. Energy conservation then requires ωk ~ ωk´. But this means k ~ k´, and so momentum conservation means we shouldn’t have any solutions with non-zero **G**. Thus at low T’s, Umklapp processes are frozen out.

**Neutron Scattering and Crystal Structure**

One can determine the RLV’s (and from these the BLV’s) from scattering experiments. Consider sending radiation into a crystal. The radiation source (typically neutrons, as these would have wavelengths around a lattice spacing and can interact with neutral objects) is presumed far enough away that the incident beam is in phase and headed along direction , and presume that each molecule specularly reflects the radiation – equally in all directions (perhaps we must assume that the incoming radiation is close to a resonant frequency?). Let’s consider one particular direction ´.



Let’s work out the condition for constructive interference of these waves when they hit the detector. To do so, we must isolate the path length difference,



The difference(s) (highlighted in bold blue) is:



And they’ll be in phase if:



In order to make a distinctive bright spot on the detector we need more than just two coherent waves. Preferably all waves scattering off the atoms/molecules would be in phase. This would require:



for all **R** ∈ LV, though with presumably different n’s. It suffices to make this true for all primitive cell basis vectors, as all others are linear combinations of such, and so would consequently automatically satisfy our condition. Exponentiating this expression we have:



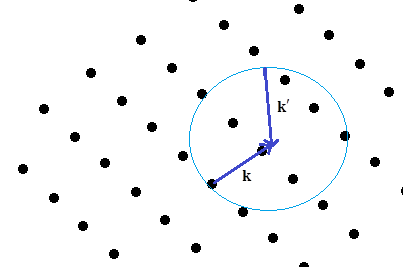
Of course it is the reciprocal lattice vectors that satisfy this equation. So we must have:



Note how this just expresses crystal momentum conservation presuming our neutron didn’t excite any phonons, and we could’ve just started from here. For elastic scattering, as we’re presuming, **k** and **k**´ must have the same magnitude. So for a given **k**, we’ll only get constructive interference at a **k**´ if it happens that **k** - **k**´ (where **k**´ has same magnitude as **k**) is a RLV.

**Ewald Construction**

I guess the easiest way to get them is by the Ewald construction. In reciprocal lattice vector space, starting at a RLV point,



you start with your **k** (it looks like the tip of **k** is lying on a RLV point, but it’s not meant to be per se´), you draw a **k**´ of equal length tip to tip, and then rotate the **k**´ base around the tip of **k**. If **k**´ touches a lattice point, then that **k**´ is a constructive reflection. So it’s clearly not a given that there will be constructive interference reflections for a given **k**. In fact, for arbitrary fixed k, it seems quite unlikely. Incidentally, this method gives us a good way to experimentally determine the RL. We can start with a small **k**, and then rotate our detector to pick up all, if any, **k**´. Then you increase **k** a little and do it again. With the **k**´, you have **k**-**k**´, and so the **G**’s.Then you can work out the **G**primitive’s, and thence, **R**primitives. On another note, we can see from this construction that if k << 2π/a (a being typical atomic spacing), then there will be no solutions to that geometrical Ewald equation. If k >> 2π/a, then there will probably be many solutions. This shows that if we have λ >> a then there should be practically no scattering, while if λ << a, then there should be a lot (too much).

**Von Laue Condition**

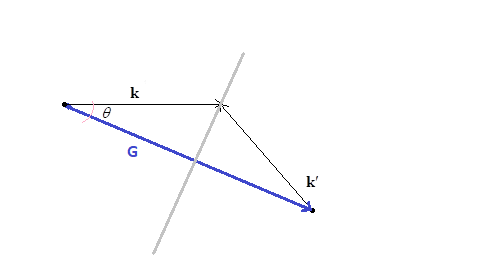
We can write this another way, which tells us which incident **k** vectors will give us constructive interference scattering. For some **G**, we have **k** - **k**´ = **G**. Now **k** and **k**´ have the same magnitude, since the scattering is elastic, so:



which is:



this is the Von Laue condition. Geometrically, our equation looks like this:



It says that we start with our **k**, and then compare it against all the **G**’s. We only get constructive interference scattering for **G**’s such that when **k** is projected against **G** we get G/2. In other words, only **G**’s for which **k** lies on its perpendicular bisector of **G**. And the scattered vector, **k**´, will be the vector reflected about **G** (in other words, draw the perpendicular bisector of **G**, pretend it’s a mirror, and reflect **k** off of it to get **k´**)**.** Looking at the Ewald construction, we’ll observe that we don’t actually have to try an unlimited number of G’s; we can’t have G > 2k.

**Von Laue Gmin Condition**

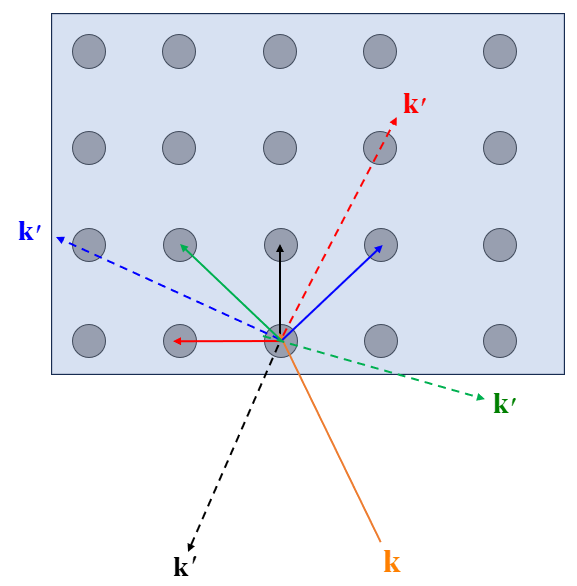
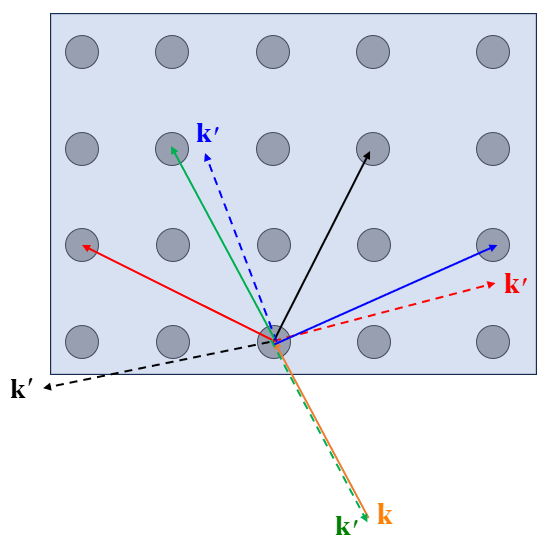
Now let’s write this another way, and get the Bragg condition, well eventually. So consider that angle θ up above. We have:



where **G**min is the smallest RLV parallel to **G** (see Electron-Crystal Interaction file apropos Lattice Planes and Miller Indices). So we have:



It says that we start with our **k**, and then compare it against all the **G**min’s. Gmin will be of the form **G**min = h**b**1 + k**b**2 + ℓ**b**3, the hkℓ of which, as we discussed in the Electron-Crystal Interaction file, will be such as to have no common factors. Choosing **G**min automatically fixes θ. We only get constructive interference scattering for **G**min if there is an n that satisfies that equation. Looking at the Ewald construction, or indeed at our equation above, we’ll observe that we needn’t check any Gmin > 2k. We can form some **G**min vectors, and then **k**´ will be the reflection of **k** about the plane perpendicular to **G**min. I drew a couple **G**min RLV’s in black, green, red and blue. I drew the incident **k** wave in orange, and a possible reflected wave **k**´ about the RLV as a dotted arrow in the same color as the RLV. Note that on the left, RLV’s are, using Miller Indices for our 2D lattice: black = (0,1), red = (-1,0), green = (-1,1), blue = (1,1). And on the right, we have: black = (1,2), red = (-2,1), green = (-1,2), and blue = (2,1). The **k**´ drawn isn’t *guaranteed* to be an actual reflection though; we’d have to check whether the condition is satisfied, i.e., whether 2kcosθ = nGmin for that **k**, **k**´, and some/any n, or, equivalently, whether that **k**∙ = nGmin/2.

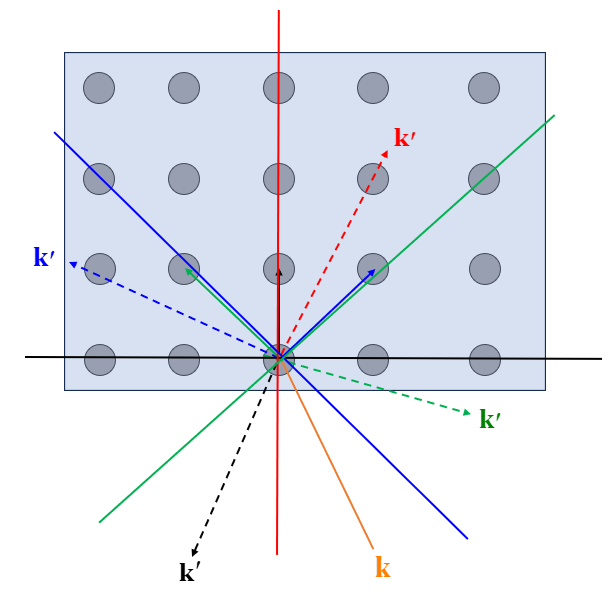
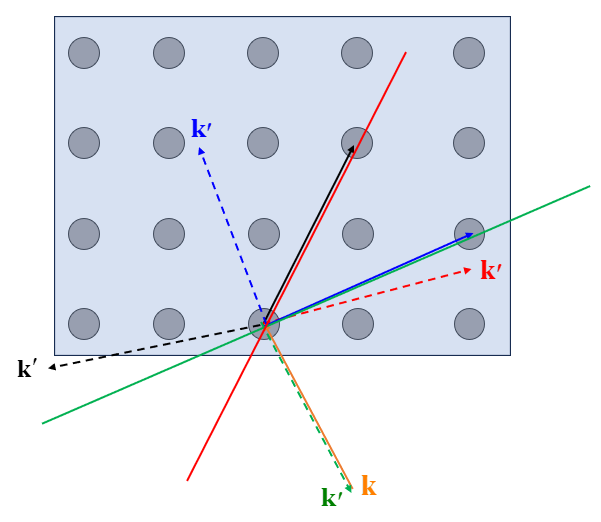
Now if, say, the incident ray happens to be at a magic angle for one of those RLV’s so that we get Bragg reflection, it isn’t likely that it would also be at a magic incident angle w/r to any of the others, to also get Bragg reflection from one of them. So I’d think we’d be getting Bragg reflection from basically one **G**min at a time? Or just a few? Another thing is, if we are likely to get Bragg reflection from the first set of {**G**min} (the ones on the left), we are less and less likely to get Bragg reflection from the larger {**G**min} (the ones on the right, and others even larger, not displayed).

**Bragg Condition**

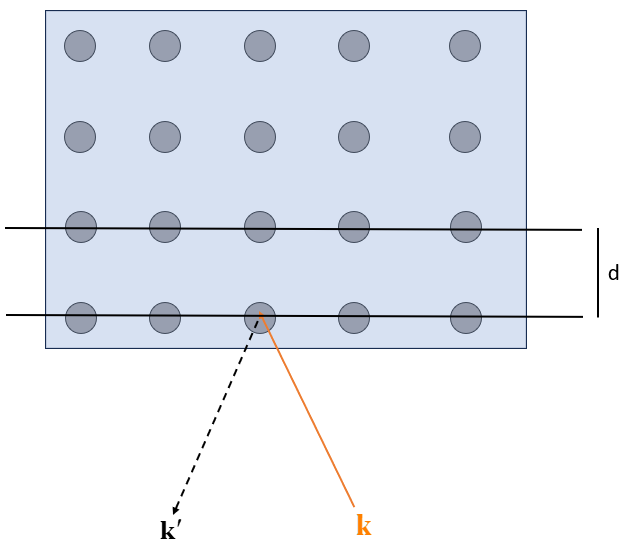
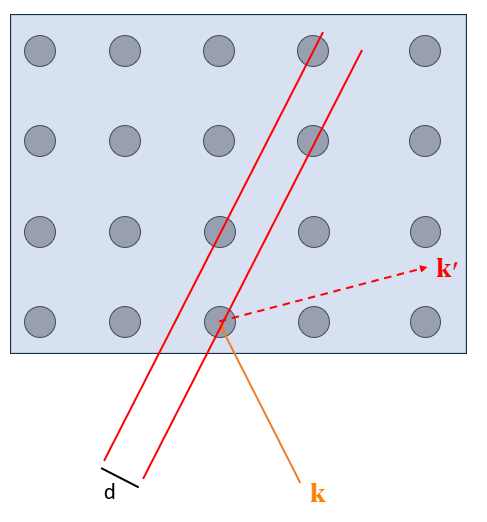
Now let’s get the Bragg condition a couple different ways. As we discussed in the Electron-Crystal Interaction, each **G**min can be written as **G**min = (2π/d), where d is smallest distance between lattice planes perpendicular to ). So let’s write this, and also let k = 2π/λ. Then we can write:



This is the Bragg scattering condition. It says that we start with our given **λ**, and then compare it against all lattice planes. With λ, fixing a lattice plane will fix d and θ. We only get reflection off of that lattice plane if the equation has a solution for some n. We can see that for a given **λ** and set of lattice planes with spacings, d, and angle θ, it is unlikely that there is an n to make the equation work. So most of the time, we should get no constructive reflections, again, for arbitrary fixed λ. Looking at the Ewald construction, or indeed at our equation above, we’ll observe that we *needn’t* check any Gmin > 2k 🡪 2π/d > 4π/λ 🡪 d < λ/2. These smaller d’s will come from lattice planes connecting more and more remote neighbors.

Here’s the lattice planes explicitly shown for two cases. Can see that the lattice planes get thinner as they connect more remote neighbors.

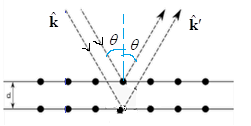
 

Last thing. If we take the Bragg condition and solve for θ, we’d have:



This formula tells us that if λ << d, then there would be lots of angles at which we’d get constructive interference – too many to resolve if λ << d in the extreme. On the other hand, if λ >> d, then we may fail to get any angles – because nλ/2d > 1 for all n, and so we’d get no angles with constructive interference. This is the same as we concluded from the Ewald construction, and illustrates the fact that we need to use λ ~ d if we are to practically probe the structure of the crystal.

Let us have two incident plane waves, making angle θ with the RL plane. And suppose they exit at the same angle, reflecting, so to speak, off of the two planes (angle θ is the angle w/r to the normal, not the more typical angle w/r to the plane).



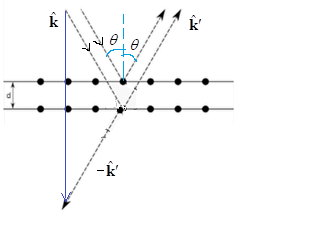
Then of course the path length difference between them must be equal to nλ in order to get constructive interference, as we asserted above. And equivalently, we require:



The difference of the two vectors lies in the direction perpendicular to the planes. The reciprocal lattice basis vector in this direction is (2π/d)(letting the normal vector point along the z-direction). And so we must have:



The difference of the two vectors is illustrated below:



Using law of cosines, say, to get the magnitude of the difference, we have:



and this reduces to:



just as the Bragg condition says it must.

**Example**

Say we had an orthorhombic lattice.

Chart, line chart

Description automatically generated

Starting at the origin, as labelled, we can posit the primitive basis vectors displayed above (there are others, many others).



What is the reciprocal lattice? Well, we have:



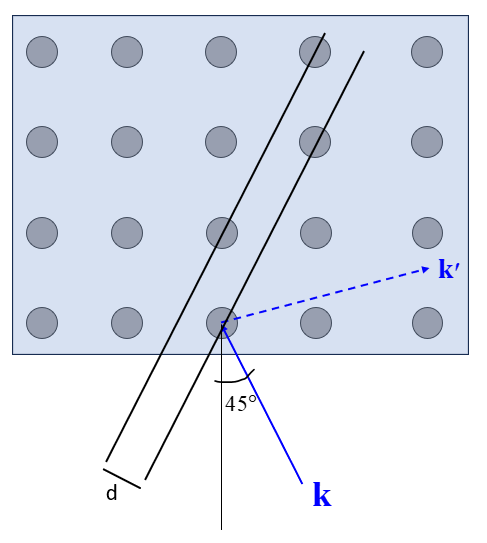
The set of **G**min would be given by **G**min = {h**b**1 + k**b**2 + ℓ**b**3} where h, k, ℓ have no common indices. Now say we send a given beam characterized by **k** into the crystal. What angles will it reflect at? This is given by the Bragg condition:



where θ is angle between **k** and **G**min.

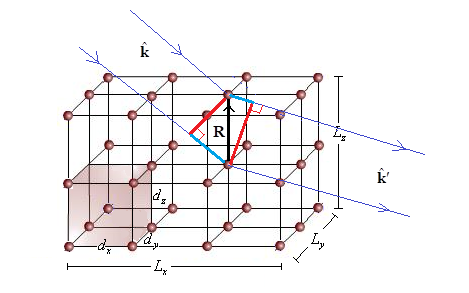
**Example**

Say we have a square lattice with lattice length *a*. Say we send an (orange) wave with wavelength λ = *a* at an angle of 45o w/r to the face of the crystal. At what angles will we get constructive interference.



**Scattering in a Lattice with a Basis**

In order to add in a basis, it’s easiest to go back to the beginning and look at it a different way. So we revisit our lattice and look at the two incoming and exiting waves.



Now let’s write down an expression for the scattered electric field of these two waves. This would be something like,



The phase difference φR of the top wave is basically the amount of phase that it has/or doesn’t have, relative to the bottom wave. We can see this is φR = **k**∙**R**. (Another way to see it is to write write **E** = **E**0ei**k**´∙**r**-iωt + **E**0ei**k**´∙**r**-iωt + φ, and observe that φ = **k**∙**R** - **k**´∙**R** = bottom thick blue segment – top thick blue segment) So we can write,



Now let’s put all the waves, coming from all the atoms, together,



This guy in parentheses is called the structure factor (well, sometimes |S(q)|2 = S(q)S(-q) is called the structure factor instead),



So we can write,



For most **q** = **k**´ - **k**, S(q) will wash out to zero. But we will get constructive interference when we have:



in which case S(q) = N. And this will happen if,



for all **R**, which would happen if,



as we found before. And so we have recovered our earlier result, and all that follows from it. Now if we have a basis, we would amend our result for **E**, to include as well, a sum over all position vectors within the basis, **d**j (**R** + **d**j is the position of the jth atom in the basis at position **R**). But not only this. Each different atom in the basis will reradiate the field with a different amplitude. We have to account for this by putting in a so-called form factor *f(j), which depends on the identity of the atom, but not the atom’s location.*



Defining the structure factor again, now accounting for the extra atoms in the basis,



we have, again:



Considering SR(q) by itself for the moment, we can say that we’ll recover all of our old results for **k** and **k**´. Adding Sd(q) back into the mix, we see that if the pair **k** and **k**´ is such as to make Sd(**k**-**k**´) = 0, then that pair will be disallowed. How can we tell if a pair that we solve for from the Bragg condition will be one for which Sd = 0? Well, we will know **G**smallest = h**b**1 + k**b**2 + ℓ**b**3 by presumption. And **G** will just be **G** = n**G**smallest. And **k** - **k**´ = **G**. So basically, the nth order result is eliminated if Sd(n**G**smallest) = 0.

**Example**

Consider a crystal of CsCl with a simple cubic lattice that has a unit cell of a = 4.12A˚ .  
A beam of electrons of energy E=128 eV is incident on the crystal. At what angles will there be Bragg reflection, perpendicular to the planes **G**smallest = (0,1,1)? Assume for the sake of discussion that the form factors of the two atoms are identical, so f(Cs) = f(Cl) = 1.

CsCl is a simple cubic lattice, with a basis. The Cesium atom sits in the middle of the cube. If the basis vectors are,



then since **G**smallest = (0,1,1), we have:



which points at a 45o angle in the y-z plane. This gives us an effective d of a/√2. So now the Bragg condition yields,



Let’s get λ,



So, for n = 1, 2, 3, 4, 5, we have:



Now not all of these will be allowed, possibly. So we have to work out Sd(q). So the basis consists of a Choride atom at the origin, and a Cesium atom in the middle of the cube. So Sd is:



Now gotta work out,



Since this doesn’t equal 0 for any n, none of the reflections we found are disallowed.

**Intensity of Radiation**

The radiation intensity is proportional to the structure factor squared,



Filling in our result for S,



So,



**Example**

Barium Titanate, BaTiO3, crystalizes in a simple cubic Bravais lattice structure. The basis consists of one Ba atom at (0,0,0), one Ti atom at (1,1,1)a/2, and three O atoms at (1,0,1)a/2, (0,1,1)a/2, and (1,1,0)a/2, where a is the lattice constant. Given that the form factors of the atoms are fBa = 7fO, and fTi = 3fO, determine the intensity relationship between the first four Bragg reflections, I(200): I(111): I(110): I(100).

Well we’ll recall:



Constructive interference will give us that SR(k´-k) = N (since e-i(**k**´-**k**)∙**R** = 1). So,



What is Sd(q)?



Okay, so:



and,



and,



and finally,



So the ratio of intensities is:

