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C12T (Solid State Physics)

Topic – Crystal Structure (Part – 3)

We have already discussed part 2 of this e-report.

Now let us continue part 3 of it.

Wave Diffraction by Crystals: Reciprocal Lattice:

As we already know, the most common experimental technique employed to investigate crystal structures is the *X-ray diffraction* (or *XRD*) method. The crystal photograph as recorded on the X-ray film represents the diffraction pattern of the crystal in which each of the spots corresponds to the diffraction maximum of a different family of parallel planes, with a certain orientation and common spacing (shown in Fig. 1). The derivation of the actual crystal structure from this photographic pattern in terms of atomic positions and orientation of planes in the usual three-dimensional space is not straightforward. This is done by having various geometrical constructions in the recorded photograph the details of which can be found in any resource on crystallography.

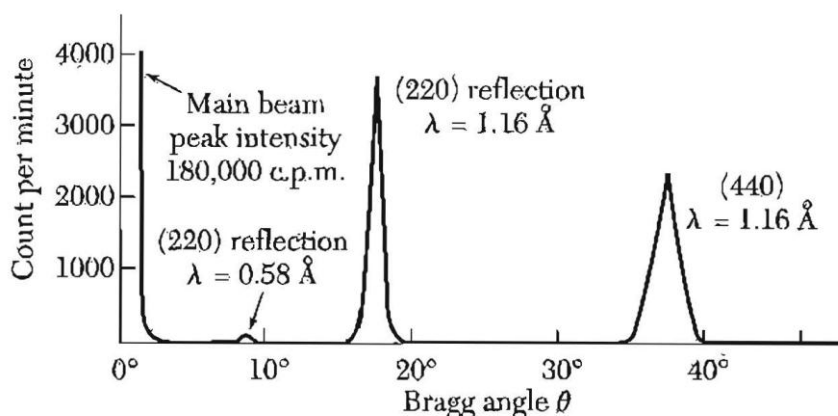


Fig. 1

Nevertheless, it is important to find some correlation between the structure of a crystal and its planar X-ray pattern. A family of parallel planes may as well be

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represented by their common normal. It is much easier to visualize the motion of a normal (equivalent to a rod) than that of a plane which is a two-dimensional figure. If a length in some proportion of the common spacing be chosen and signified by a point along the normal, the point acts as a perfect representative of the family of planes under consideration. The relevant theory will show that the X-rays diffracted from the family of planes produce the maximum intensity at this point. Further, the analysis shows that the distance of the point from an origin fixed at an arbitrary lattice point on the normal is proportional to the reciprocal of the interplanar spacing. The dimension of the representative position vector is thus the reciprocal of length. It is due to this reason that each of such points is called a *reciprocal lattice point*. These points happen to be arranged in a regular pattern forming a space lattice which is referred to as the *reciprocal lattice*.

Bragg's Law:

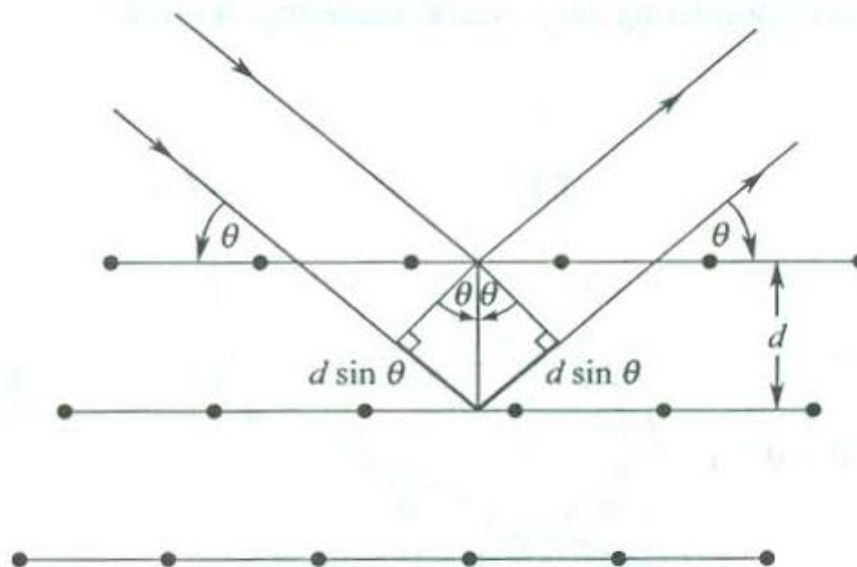


Fig. 2

Bragg put forward a simple explanation of the diffracted beams from a crystal. The simplified derivation method is convincing only because it reproduces the correct result. Suppose that the incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane reflecting only a very



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small fraction of the radiation, like a lightly silvered mirror. In specular (mirror like) reflection the angle of incidence is equal to the angle of reflection. The diffracted beams are found when the reflections from parallel planes of atoms interfere constructively, as in Fig. 2. We treat elastic scattering, in which the energy of the X-ray beam is not changed on reflection.

Let us consider parallel lattice planes spaced d apart. The X-ray radiation is incident on the plane with an angle θ . Bragg's Law states that, *constructive interference of the radiation from successive planes occurs when*

$$2d \sin \theta = n\lambda$$

where n is any positive integer and λ is the wavelength of the radiation. The angle θ is popularly called as *Bragg Angle*.

The basic derivation is very simple. The X-ray diffraction peak will occur only when two parallel beams interfere constructively. For, that the phase difference between those two need to be an integral multiple of 2π (equivalently the path difference between them to be an integral multiple of wavelength λ). According to the Fig. 2, the path difference (Δ) for rays reflected from adjacent planes (d apart) is $d \sin \theta + d \sin \theta = 2d \sin \theta$. Therefore, the condition for constructive interference should be $\Delta = 2d \sin \theta = n\lambda$, which establishes Bragg's Law.

We, also observe that since $\sin \theta \leq 1$, we obtain $\lambda \leq \frac{2d}{n} \sim d \sim 1$ nm for a typical crystal. This clearly explains why Bragg diffraction cannot occur with visible light having $\lambda \sim 300 - 700$ nm.

Reciprocal Lattice Vector:

We already have seen that for a given lattice there is an associated reciprocal lattice, which is obtained by the Fourier Transform of the lattice in real space. We, therefore construct the axis vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ of the reciprocal lattice by using the following set of formula (from axis vectors \vec{a}_1, \vec{a}_2 and \vec{a}_3 of the given lattice in real space)



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$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}$$

If \vec{a}_1 , \vec{a}_2 and \vec{a}_3 are the primitive vectors of the real crystal lattice, then \vec{b}_1 , \vec{b}_2 and \vec{b}_3 are the primitive vectors of the reciprocal lattice. Each vector defined by the previous formula is orthogonal to two axis vectors of the crystal lattice. Thus \vec{b}_1 , \vec{b}_2 and \vec{b}_3 will follow the property $\vec{b}_i \cdot \vec{a}_j = \vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$.

Now, lattice points in the reciprocal lattice are mapped by the set of vectors given by $\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$, with m_1 , m_2 and m_3 as positive or negative integers. A vector \vec{G} of this form is called a *reciprocal lattice vector*.

Fourier Analysis of the Crystal. We have seen that a crystal is invariant under any translation of the form $\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, where n_1 , n_2 and n_3 are integers and \vec{a}_1 , \vec{a}_2 and \vec{a}_3 are the crystal axes. Any local physical property of the crystal, such as the charge concentration, electron number density or magnetic moment density is invariant under \vec{T} . Here the most important parameter to us is the electron number density $n(\vec{r})$, which is a periodic function of \vec{r} , with periods a_1 , a_2 , a_3 in the directions of the three crystal axes, respectively, so $n(\vec{r} + \vec{T}) = n(\vec{r})$. Such periodicity creates an ideal situation for Fourier expansion.

According to Fourier Analysis, a periodic function $f(x)$ in one dimension with period a in the direction x can be expanded as

$$f(x) = \sum_p f_p e^{i2\pi px/a}$$

where all the f_p s are called as the Fourier Coefficient of the function $f(x)$.



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Similarly the extension of the Fourier Analysis to the periodic function $n(\vec{r})$ in three dimensions is straightforward. We must find a set of vectors \vec{G} such that

$$n(\vec{r}) = \sum_G n_G e^{i\vec{G} \cdot \vec{r}}$$

and in this way, $n(\vec{r})$ is invariant under all crystal translations \vec{T} that leave the crystal invariant. Here \vec{G} is the reciprocal lattice vector defined before. The derivation of the invariance of $n(\vec{r})$ is straight forward. According to the previous expansion, we write $n(\vec{r} + \vec{T}) = \sum_G n_G e^{i\vec{G} \cdot (\vec{r} + \vec{T})} = \sum_G n_G e^{i\vec{G} \cdot \vec{r}} e^{i\vec{G} \cdot \vec{T}}$. Now, $\vec{G} \cdot \vec{T}$ can be calculated as

$$\begin{aligned} \vec{G} \cdot \vec{T} &= (m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3) \cdot (n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3) \\ &= 2\pi(m_1 n_1 + m_2 n_2 + m_3 n_3) = 2\pi p \end{aligned}$$

Here p is an integer, and therefore, $e^{i\vec{G} \cdot \vec{T}} = e^{i2\pi p} = 1$.

So, we finally get $n(\vec{r} + \vec{T}) = \sum_G n_G e^{i\vec{G} \cdot \vec{r}} = n(\vec{r})$, as expected.

Vectors in the real (or direct) lattice have the dimensions of [length], but vectors in the reciprocal lattice have the dimensions of [1/length]. The reciprocal lattice is a lattice in the Fourier space associated with the crystal.

Diffraction Condition from Laue Interpretation:

According to Laue Interpretation, the set of reciprocal lattice vectors \vec{G} determines the possible X-ray reflections. As shown in Fig. 3, we have a crystal specimen. The incoming plane wave beam is given as $e^{i\vec{k} \cdot \vec{r}}$ and the diffracted beam is written as $e^{i\vec{k}' \cdot \vec{r}}$, where \vec{k} and \vec{k}' are the corresponding wave vectors. The difference in path length of the incident wave at the origin and \vec{r} is $r \sin \phi$ and the phase angle is $\frac{2\pi}{\lambda} r \sin \phi = |\vec{k}| r \sin \phi = \vec{k} \cdot \vec{r}$. Similarly it can be shown that the phase angle for the diffracted wave is $-\vec{k}' \cdot \vec{r}$. The total difference in phase angle is $(\vec{k} - \vec{k}') \cdot \vec{r}$, and the wave scattered from scattering element dV at \vec{r} has the phase factor $e^{i(\vec{k} - \vec{k}') \cdot \vec{r}}$ relative to the wave scattered from a volume

element at the origin. Therefore, the total amplitude of the scattered wave in the direction of \vec{k}' is proportional to the integral over the crystal of $n(\vec{r})dV$ times the phase factor. We therefore write the scattering amplitude F as

$$F = \int dV n(\vec{r}) e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} = \int dV n(\vec{r}) e^{-i\Delta\vec{k} \cdot \vec{r}}$$

where $\Delta\vec{k} = \vec{k}' - \vec{k}$ is the change in wave vector and is called the *scattering vector*.

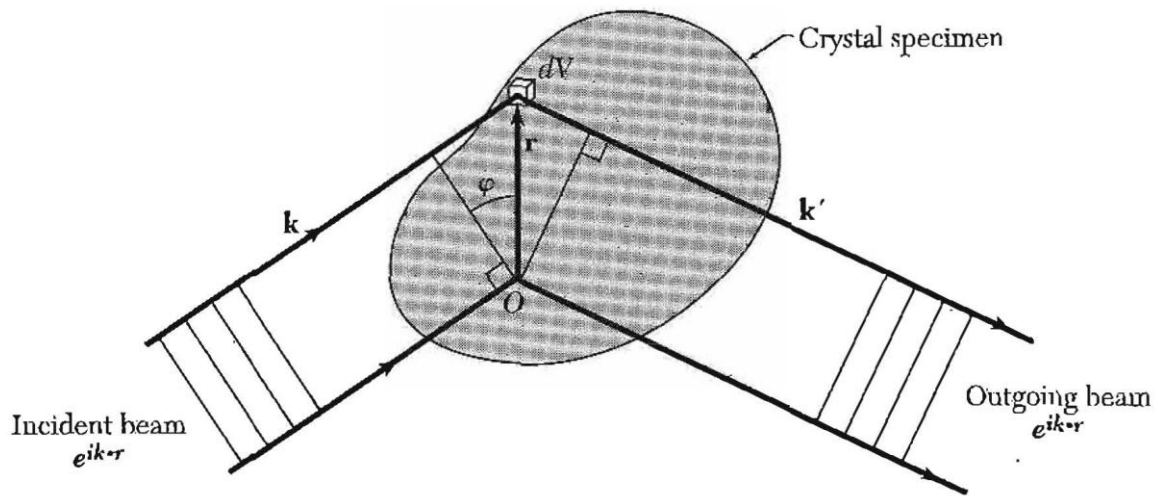


Fig. 3

Now, we introduce the Fourier components of $n(\vec{r})$ into the previous equation to obtain for the scattering amplitude as

$$F = \sum_G \int dV n_G e^{i(\vec{G} - \Delta\vec{k}) \cdot \vec{r}}$$

It can be shown that F is negligibly small when $\Delta\vec{k}$ differs significantly from any \vec{G} . Therefore, the condition for the maximum of F is $\Delta\vec{k} = \vec{G}$ or $\vec{k}' - \vec{k} = \vec{G}$ or $\vec{k}' = \vec{k} + \vec{G}$. In elastic scattering of a photon its energy is conserved, so that the frequency $\omega = ck$ of the emergent beam is equal to the frequency of the incident beam. Thus the magnitudes k and k' are equal (as shown in Fig. 4). We can write

$$|\vec{k}'|^2 = |\vec{k} + \vec{G}|^2 \text{ or } k^2 = k^2 + G^2 + 2\vec{k} \cdot \vec{G} \text{ or}$$



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$$2\vec{k} \cdot \vec{G} + G^2 = 0$$

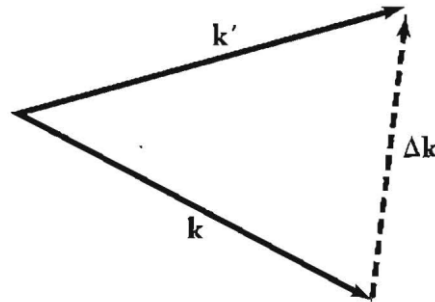


Fig. 4

If \vec{G} is a reciprocal lattice vector, so is $-\vec{G}$, and therefore we can substitute $-\vec{G}$ in place of \vec{G} in the previous equation to obtain

$$2\vec{k} \cdot \vec{G} = G^2$$

This particular expression is called as *Laue Condition for diffraction*.

Equivalence of Laue Condition and Bragg's Law. It is very trivial to show that the previous condition is another statement of Bragg's Law. We will use an important result that the spacing d_{hkl} between parallel lattice planes which are normal to the reciprocal vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$, can be written as $\frac{2\pi}{G}$. So, we get $G = \frac{2\pi}{d_{hkl}}$.

Therefore the result $2\vec{k} \cdot \vec{G} = G^2$ can be written as $2 \frac{2\pi}{\lambda} \sin \theta = \frac{2\pi}{d_{hkl}}$ or $2d_{hkl} \sin \theta = \lambda$. θ is the angle between the incident beam and the crystal plane.

The integers h, k, l that define \vec{G} are not necessarily identical with the indices of an actual crystal plane, because the h, k, l may contain a common factor n , whereas in the definition of the indices the common factor has been eliminated. We thus obtain the Bragg result



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$$2d \sin \theta = n\lambda$$

where d is the spacing between adjacent parallel planes with indices h/n , k/n , l/n .

This concludes part 3 of this e-report.

The discussion will be continuing in the part 4 of this e-report.

Reference(s):

Introduction to Solid State Physics, Charles Kittel, Wiley

Elements of Solid State Physics, J.P. Srivastava, PHI Learning

(All the figures have been collected from the above mentioned references)