

# 8.231 Physics of Solids I — Fall 2017

## Recitation 4

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October 6, 2017

What is the significance of reciprocal lattice? In this recitation, we will see the reciprocal lattice is important because they

- (Mathematically) Constitute all possible Fourier components;
- (Geometrically) Specify all lattice planes;
- (Physically) Specify all possible X-ray diffractions through conservation of crystal momentum.

## 1 Reciprocal Lattice

### 1.1 Reciprocal Lattice as Fourier Components

Consider the periodic electronic potential in the lattice  $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$ ,  $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$  is any lattice vector. Here  $n_i$  are any integers and  $\mathbf{a}_i$  are the primitive lattice vectors.

Mathematically, a periodic function can be expanded by Fourier series:  $V(\mathbf{r}) = \sum_{\mathbf{G}} V(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}$ , where

$$V(\mathbf{G}) = \frac{1}{V} \int_V d\mathbf{r} V(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} \quad (1)$$

$$= \frac{1}{V} \int_V d\mathbf{r} V(\mathbf{r} + \mathbf{R}) e^{-i\mathbf{G}\cdot\mathbf{r}} \quad (2)$$

$$= \frac{1}{V} \int_V d\mathbf{r} V(\mathbf{r}) e^{-i\mathbf{G}\cdot(\mathbf{r}-\mathbf{R})} \quad (3)$$

$$= \frac{1}{V} e^{i\mathbf{G}\cdot\mathbf{R}} \int_V d\mathbf{r} V(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}. \quad (4)$$

Compare Eq. (1) and (4), we must have

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1 \quad \Leftrightarrow \quad \mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3, \quad (5)$$

where  $\mathbf{b}_i$  are the basis for the reciprocal lattice, satisfying  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ .

**Interlude** Two useful identities:

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$$\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = N \sum_{\mathbf{G}} \delta(\mathbf{k} - \mathbf{G}). \quad (6)$$

where the summation is over all lattice vectors  $\mathbf{R}$  and all the reciprocal lattice  $\mathbf{G}$ .

*Proof* Let  $\mathbf{R}_0$  be any reciprocal lattice vector:

$$\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{R}_0)} \quad (7)$$

$$\Rightarrow (1 - e^{i\mathbf{k}\cdot\mathbf{R}_0}) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = 0. \quad (8)$$

If  $e^{i\mathbf{k}\cdot\mathbf{R}_0} \neq 1$ , i.e.,  $\mathbf{k}$  is not any reciprocal lattice vector, then  $\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = 0$ . If  $e^{i\mathbf{k}\cdot\mathbf{R}_0} = 1$ , then the summation is just  $\sum_{\mathbf{R}} 1$ , which is the number of the lattice sites  $N$ .

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$$\int_{\Omega} d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} = V_{\Omega} \delta(\mathbf{k}), \quad (9)$$

where  $\Omega$  is the integral over the unit cell and  $V_{\Omega}$  is the volume of the unit cell.

*Proof* Let  $\mathbf{d}$  be any vector,

$$\int_{\Omega} d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} = \int_{\Omega} d\mathbf{r} e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{d})} \quad (10)$$

$$\Rightarrow (1 - e^{i\mathbf{k}\cdot\mathbf{d}}) \int_{\Omega} d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} = 0. \quad (11)$$

The first identity is due to the fact the choice of the unit cell is arbitrary. Then the identity can be proved similar to the first identity.

Notice this identity can also be generalized to the integral of the whole space.

## 1.2 Reciprocal Lattice Specifies Lattice Plane

There is a one to one correspondence between the direction of the reciprocal vector and the lattice plane.

For each integer  $m$ , the identity  $\mathbf{G} \cdot \mathbf{r} = 2\pi m$  specifies a family of lattice planes, the lattice points on which is constituted by  $\mathbf{r}$ . To see that, decompose  $\mathbf{r} = \mathbf{r}_{\perp} + \mathbf{r}_{\parallel}$ , where  $\perp$  and  $\parallel$  are with respect to  $\mathbf{G}$ . Note that every lattice points is a member of one of those planes since  $e^{i\mathbf{G}\cdot\mathbf{r}} = 1$ .

Denote  $\mathbf{G}_{\min}$  as the minimum length reciprocal lattice vector that is parallel to  $\mathbf{G}$ . The plane spacing are given by  $\mathbf{G}_{\min} \cdot (\mathbf{r}_2 - \mathbf{r}_1) = |\mathbf{G}_{\min}|d = 2\pi$  because  $\mathbf{r}_2 - \mathbf{r}_1$  is parallel to  $\mathbf{G}_{\min}$ . Hence

$$d = \frac{2\pi}{|\mathbf{G}_{\min}|}. \quad (12)$$

For a general  $\mathbf{G} = n\mathbf{G}_{\min}$ , the lattice spacing may not be the smallest one. The result becomes

$$|\mathbf{G}| = \frac{2\pi n}{d}. \quad (13)$$

## 2 X-ray Diffraction

### 2.1 Scattering Condition

Suppose the light are plane waves. The incident light is  $|\mathbf{k}\rangle$  and the scattered light is  $|\mathbf{k}'\rangle$ , where  $\mathbf{k}$  and  $\mathbf{k}'$  are wavevectors. The transition probability can be computed from time-dependent perturbation theory. The so-called Fermi's Golden rule is

$$\Gamma(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'}). \quad (14)$$

The last term is conservation of energy. Let us compute the transition matrix element  $\langle \mathbf{k}' | V | \mathbf{k} \rangle$ . Notice  $|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$ , we have

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \frac{1}{V} \int d\mathbf{r} V(\mathbf{r}) e^{-i(\mathbf{k}' - \mathbf{k})\cdot\mathbf{r}} \quad (15)$$

$$= \frac{1}{V} \sum_{\mathbf{R}} \int_{\Omega} d\mathbf{r} V(\mathbf{r} + \mathbf{R}) e^{-i(\mathbf{k}' - \mathbf{k})\cdot(\mathbf{r} + \mathbf{R})} \quad (16)$$

$$= \frac{1}{V} \sum_{\mathbf{R}} e^{-i\Delta\mathbf{k}\cdot\mathbf{R}} \int_{\Omega} d\mathbf{r} V(\mathbf{r}) e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}. \quad (17)$$

Recall identity Eq. (6). The factor  $\sum_{\mathbf{R}} e^{-i\Delta\mathbf{k}\cdot\mathbf{R}}$  does not vanish only

$$\Delta\mathbf{k} = \mathbf{G}, \quad (18)$$

where  $\mathbf{G}$  is any reciprocal lattice vector. Eq. (18) is called the Laue condition. In this way, the reciprocal lattice specifies all possible X-ray scattering.

In fact, Laue condition is a manifestation of conservation of crystal momentum. We know from Noether's theorem that symmetry implies conservation law. The continuous translational symmetry implies the conservation of momentum. In the lattice, there is only discrete translational symmetry. The new conserved quantity is actually the crystal momentum implied in Bloch's theorem, and the crystal momentum is conserved modulo any reciprocal lattice vector  $\mathbf{G}$ .

Here are some typical diffraction patterns:

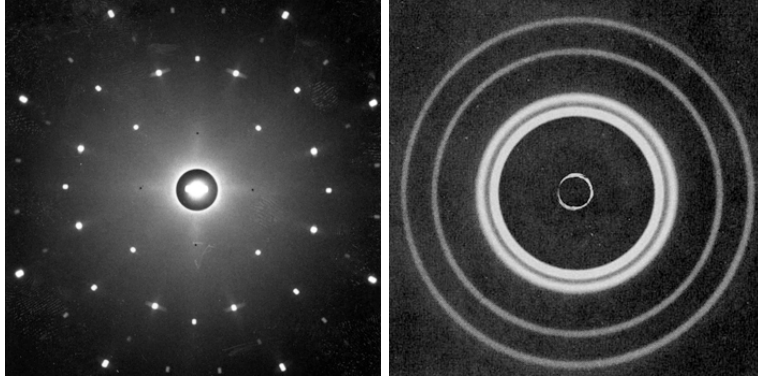


Figure 1: X-ray diffraction pattern for a single crystal (left) and powders (right). In the left one can clearly see the reciprocal lattice. The right can be seen as resulting from a rotating superposition of the left.

**Elastic Scattering** Let us consider the special case of elastic scattering where  $|\mathbf{k}| = |\mathbf{k}'|$ . Eliminate  $\mathbf{k}'$  from

$$\begin{cases} \mathbf{k}' - \mathbf{k} = \mathbf{G}, \\ |\mathbf{k}| = |\mathbf{k}'|, \end{cases} \quad (19)$$

we get

$$2\mathbf{k} \cdot \mathbf{G} = |\mathbf{G}|^2. \quad (20)$$

Insert Eq. (13), we have

$$2d \sin \theta = n\lambda, \quad (21)$$

where  $\lambda = 2\pi/k$  and  $\theta$  is the angle between the incident wave and the lattice plane. (See Fig. 2. ) This is called the Bragg condition.

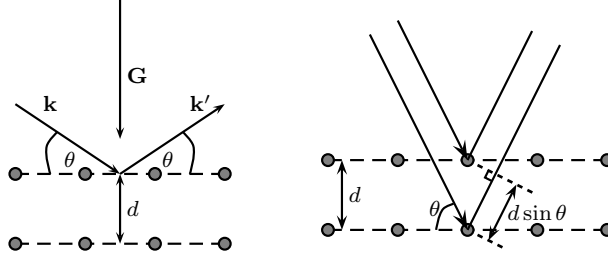


Figure 2: Schematics of elastic scattering. Left: Geometry of the scattering; Right: Diffraction understanding of Bragg condition.

Bragg condition can also be understood from the diffraction point of view. As shown in the right of Fig. 2, the extra distance traveled by the wave striking the lower diffraction plane is  $2d \sin \theta$ . In order for the interference to be constructive, the extra distance must satisfy Bragg condition Eq. (21).

Finally, let us rewrite Eq. (20) as

$$\mathbf{k} \cdot \frac{\mathbf{G}}{2} = \left| \frac{\mathbf{G}}{2} \right|^2. \quad (22)$$

The geometric implication is that all the possible  $\mathbf{k}$  lies on the perpendicular bisector of  $\mathbf{G}$ , which is exactly the boundary of the Brillouin zone (Wigner-Seitz unit cell).

## 2.2 Structure Factor and Form Factor

Previously we have been focusing on the first factor in the matrix element Eq. (17), which says the momentum transfer in the scattering must be a reciprocal lattice vector  $\Delta \mathbf{k} = \mathbf{G}$ . For all these possible  $\Delta \mathbf{k}$ , the relative magnitudes of the scattering strength are not necessarily the same. This is reflected by the second factor in Eq. (17), which is called the “structure factor”:

$$S(\mathbf{G}) \equiv \int_{\Omega} d\mathbf{r} V(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}. \quad (23)$$

Suppose there are  $j$  atoms in the unit cell, whose position is given by  $\mathbf{r}_j$  and its electronic potential is  $V_j(\mathbf{r})$ . In this way,

$$S(\mathbf{G}) = \int_{\Omega} d\mathbf{r} \sum_j V_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G} \cdot \mathbf{r}} \quad (24)$$

$$= \int_{\Omega} d\mathbf{r} \sum_j V_j(\mathbf{r}) e^{-i\mathbf{G} \cdot (\mathbf{r} + \mathbf{r}_j)} \quad (25)$$

$$= \sum_j e^{-i\mathbf{G} \cdot \mathbf{r}_j} f_j(\mathbf{G}), \quad (26)$$

where

$$f_j(\mathbf{G}) \equiv \int_{\Omega} V_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}, \quad (27)$$

is called the (atomic) form factor. Note in Eq. (25) we have used the fact that the choice of unit cell is arbitrary again.

**Example** Cs is of bcc structure. There are two Cs atoms per unit cell, located at  $\mathbf{r}_1 = (0, 0, 0)$  and  $\mathbf{r}_2 = (1, 1, 1)a/2$ , where  $a$  is the unit cell spacing. The structure factor for  $\mathbf{G}_{hkl}$  is

$$S(\mathbf{G}) = f_{\text{Cs}}(hkl) [1 + (-1)^{h+k+l}]. \quad (28)$$

It vanishes when  $h + k + l$  is odd. This is called systematic absence. Although such  $\mathbf{G}$  is allowed by the Laue condition, the organization of atoms in the unit cell requires such diffraction peak to vanish. In fact, one can determine the crystal structure from the systematic absence.