PHYS 342/555 Condensed Matter in a Nutshell

Instructor: Dr. Pengcheng Dai Professor of Physics The University of Tennessee (Room 407A, Nielsen, 974-1509) (Office hours: TR 1:10PM-2:00 PM) Lecture 2, room 314 Nielsen Chapter 2: Crystal Structures Lecture in pdf format will be available at: http://www.phys.utk.edu **Periodic Lattice in a solid.**



For any given Bravais lattice, the set of primitive vectors is not unique. There are many nonequivalent choices.



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Primitive lattice cell :

The vectors \vec{a}_i appearing in definition of a Bravais lattice are called primitive vectors and are said to generate or span lattice.

Primitive cell is a minimum-volume cell:

A volume of space that, when translated through all the vectors in a Bravais lattice, just fills all of space without either overlapping itself or leaving voids is called a primitive cell or primitive unit cell. There is no unique way of choosing a primitive cell for a given Bravias lattice.

The volume of a primitive cell is independent of the choice of cell: $V_c = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|,$

A primitive cell must contain precisely one lattice point.

Primitive unit cell:

Given any two primitive cells of arbitrary shape, it is possible to cut the first up into pieces, which, when translated through appropriate lattice vectors, can be reassembled to give the second.



Bravais Lattice:

(a) A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, for whichever of the points the array is viewed.

(b) A (3D) Briavais lattice consists of all points with position vectors \vec{R} of the form: $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, where $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are any

three vectors not all in the same plane, and n_1 , n_2 , n_3 are all integeral values. Thus the point $\sum n_i \vec{a}_i$ is reached by moving n_i steps of \vec{a}_i length in the direction of \vec{a}_i for i = 1, 2, 3...



Definition of reciprocal lattice:

Consider a set of point \vec{R} constituting a Bravais lattice, and a plane wave, $e^{i\vec{k}\cdot\vec{r}}$. For general \vec{k} , such a plane wave will not have the periodicity of the Bravais lattice, but for certain special choices of wave vectors it will. The set of all wave vectors \vec{k} that yield plane waves with the periodicity of a given Bravais lattice is known as it reciprocal lattice.

 \vec{k} belongs to the reciprocal lattice of a Bravais lattice of points \vec{R} , provided that $e^{i\vec{k}\cdot(\vec{R}+\vec{r})} = e^{i\vec{k}\cdot\vec{r}}$ holds for any \vec{r} , and for all \vec{R} in the Bravais lattice. The reciprocal lattice is a set of wave vectors \vec{k} satisfying $e^{i\vec{k}\cdot\vec{R}} = 1$. Reciprocal lattice is a Bravais lattice:

Let \vec{a}_1 , \vec{a}_2 , and \vec{a}_3 be a set of primitive vectors for the direct lattice. Then the reciprocal lattice

 $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}.$ Note $\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$, if $i \neq j$, $\delta_{ij} = 0$; if i = j, $\delta_{ij} = 1$. For any vector \vec{k} in reciprocal space, $\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3$. For any vector \vec{R} in reciprocal space, $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$. $\vec{k} \cdot \vec{R} = 2\pi (k_1 m_1 + k_2 m_2 + k_3 m_3).$

Since $\vec{k} \cdot \vec{R}$ must be times an integer for any choices of integers n_i . This requires the coefficients k_i to be integers.

The reciprocal of the reciprocal space is the real space. Examples of reciprocal lattice units.

Reciprocal lattice units in simple cubic case:

Let $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, and $\vec{a}_3 = a\hat{z}$ $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{a} \hat{x}$, $\vec{b}_2 = \frac{2\pi}{a} \hat{y}$, $\vec{b}_3 = \frac{2\pi}{a} \hat{z}$.

Prove that the reciprocal lattice primitive vectors satisfy

$$\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}.$$

Note vector identity: $(\vec{c} \times \vec{a}) \times (\vec{a} \times \vec{b}) = (\vec{c} \cdot \vec{a} \times \vec{b})\vec{a}$

Reciprocal lattice units in fcc case: Primitive vectors

$$\vec{a}_{1} = \frac{a}{2}(\hat{y} + \hat{z}), \vec{a}_{2} = \frac{a}{2}(\hat{z} + \hat{x}), \vec{a}_{3} = \frac{a}{2}(\hat{x} + \hat{y}).$$
$$\vec{b}_{1} = \frac{2\pi}{a}(\hat{y} + \hat{z} - \hat{x}), \vec{b}_{2} = \frac{2\pi}{a}(\hat{z} + \hat{x} - \hat{y}), \vec{b}_{3} = \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z}).$$



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Reciprocal lattice units in bcc case: Primitive vectors

$$\vec{a}_{1} = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \vec{a}_{2} = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \vec{a}_{3} = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}).$$
$$\vec{b}_{1} = \frac{2\pi}{a}(\hat{y} + \hat{z}), \vec{b}_{2} = \frac{2\pi}{a}(\hat{z} + \hat{x}), \vec{b}_{3} = \frac{2\pi}{a}(\hat{x} + \hat{y}).$$



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First Brillouin zone

The Wigner-Seitz primitive cell of the reciprocal lattice is known as the first Brillouin zone. (Wigner-Seitz is real space concept while Brillouin zone is a reciprocal space idea).



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Two dimensional real and reciprocal space





FIGURE 2.4. Two-dimensional plane triangular lattice.



Solve a problem

The primitive translation vectors of the hexagonal space lattice may be taken as

$$\vec{a}_{1} = (3^{1/2}a/2)\hat{x} + (a/2)\hat{y};$$

$$\vec{a}_{2} = -(3^{1/2}a/2)\hat{x} + (a/2)\hat{y};$$

$$\vec{a}_{3} = c\hat{z}.$$

(a) Show that the volume of the primitive cell is $(3^{1/2}a/2)a^2c$.

(b) Show that the primitive translations of the reciprocal lattice are

$$\vec{b}_{1} = (2\pi/3^{1/2}a)\hat{x} + (2\pi/a)\hat{y};$$

$$\vec{b}_{2} = -(2\pi/3^{1/2}a)\hat{x} + (2\pi/a)\hat{y};$$

$$\vec{b}_{3} = (2\pi/c)\hat{z},$$

so that the lattice is its own reciprocal, but with a rotation of axes.

(c) describe and sketch the first Brillouin zone of the hexagonal space lattice.

Lattice planes

A lattice plane is defined to be any plane containing at least three noncollinear Bravais lattice points. A family of lattice planes is a set of parallel, equally spaced lattice planes, with together contain all the points of the 3D Bravais lattice.

For any family of lattice planes separated by a distance *d*, there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length of $2\pi/d$. Conversely, for any reciprocal lattice vector *K*, there is a family of lattice planes normal to *K* and separated by a distance *d*, where $2\pi/d$ is the length of the shortest reciprocal lattice vector parallel to *K*.



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Index of the plane 1. Find the intercepts on the axes in terms of lattice constants. 2. Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. (*hkl*)-plane



Miller indices:

The Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vectors normal to that plane, with respect to a specified set of primitive reciprocal lattice vectors.

A plane with Miller indices *h*, *k*, *l*, is normal to the reciprocal lattice vector: $h\vec{b}_1 + h\vec{b}_2 + h\vec{b}_3$.

the Miller indices are integers, can have no common factors, and depend on the particular choice of primitive vectors.

Conventions for specifying directions:

Lattice planes are usually specified by giving their Miller indices in parentheses (h, k, l). When specifying directions in the direct lattice, we use the notation $[n_1, n_2, n_3]$ from the origin. Since the (100), (010), and (001) planes are all equivalent in a cubic crystal. One denotes these planes as $\{100\}$ planes. Similarly, the [100], [010], [001], [100], [010], and [001] in a cubic crystal are equivalent, and referred to collectively as the $\langle 100 \rangle$ direction.

Bragg Law: $2d \sin \theta = n\lambda$, $\lambda \approx 10^{-8}$ cm. The crystal is made out of parallel planes of ions, spaced *d* apart. (1) the x-rays are specularly reflected by the ions in any one plane. (2) the reflected rays from successive planes should interfere constructively.



Thin films: gasoline on water



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Constructive and destructive interference

Cases (a) & (b): constructive interference

 $d\sin\theta = m\lambda$ $m = 0, \pm 1, \pm 2..$

Case (c): destructive interference

 $d\sin\theta = (m+1/2)\lambda$ $m = 0, \pm 1, \pm 2, ...$





Diffraction gratings



Diffraction maxima $d\sin\theta = m\lambda$ (m=0, ±1, ±2..) m=order of diffraction First minimum

 $\sin\theta = \frac{\lambda}{Nd}$ (N:total number of slits covered by wave) There are N-2 secondary maxima between two primary maxima

Von Laue formulation of x-ray diffraction

If one regards the crystal as composed of idential atoms at sites \vec{R} of a Bravais lattice, each of which can reradiate incident beam in all directions. Sharp peaks will be observed only in directions and at wavelengths for which the rays scattered from all lattice points interfere constructively.

Incident beam wavevector $\vec{k} = 2\pi \hat{n} / \lambda$

Scattered beam wavevector $\vec{k}' = 2\pi \hat{n}'/\lambda$

Constructive interference:

 $d\cos\theta + d\cos\theta' = \vec{d} \cdot (\hat{n} - \hat{n}') = m\lambda \quad (m=0, \pm 1, \pm 2..)$ This can also be written as $\vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m$



Since the lattice sites are displaced from one another by the Bravais lattice vector \vec{R} , the condition that all scattered rays interfere constructively means that $\vec{d} = \vec{R}$ or $\vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi m$ or $e^{i\vec{R} \cdot (\vec{k} - \vec{k}')} = 1$, for all Bravais lattice vector \vec{R} . Constructive interference will occur if the change in wavevector, $\vec{K} = \vec{k} - \vec{k}'$, is a vector of the reciprocal lattice. Dai/PHYS 342/555 Spring 2012 Chapter 2-26

Constructive and destructive interference







The geometrical structure factor

If the crystal structure has *n*-atoms per unit cell, monatomic, then the contents of each primitive cell can be further analyzed into a set of identical scatters at $d_1, ..., d_n$. The phase differences between the rays scattered at $\vec{d_i}$ and $\vec{d_j}$ will be $\vec{K} \cdot (\vec{d_i} - \vec{d_j})$. The phases of the rays at $\vec{d_i}$ are in ratio $e^{i\vec{K}\cdot\vec{d_i}}$. The net ray scattered by the entire primitive cell is the sum of the individual rays, and will therefore have an amplitude containing the factor, called the geometrical structure factor

$$S_{K} = \sum_{i=1}^{n} e^{i\vec{K}\cdot\vec{d}i}$$

Bragg peak intensity is proportional to $|S\kappa|^2$

BCC considered as simple cubic with a basis



Primitive vectors $a\hat{x}, a\hat{y}, \text{ and } a\hat{z},$ with a two-point basis of d = 0and $d_2 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$ $S_K = 1 + \exp[i\vec{K} \cdot \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})]$ $\vec{K} = \frac{2\pi}{2}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$ $S_K = 1 + (-1)^{(n_1+n_2+n_3)} = \begin{cases} 2, n_1 + n_2 + n_3 \text{ even} \\ 0, n_1 + n_2 + n_3 \text{ odd} \end{cases}$

FCC considered as simple cubic with a basis



Primitive vectors
$$a\hat{x}, a\hat{y}, \text{ and } a\hat{z},$$

with four atoms per unit cell at
 $(000), (0\frac{1}{2}\frac{1}{2}), (\frac{1}{2}0\frac{1}{2}), (\frac{1}{2}\frac{1}{2}0)$
 $S\kappa = 1 + \sum_{i=1}^{4} \exp[i\vec{K}\cdot\vec{d_i}]$
 $\vec{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$
 $S\kappa = 1 + (-1)^{(n_1+n_2)} + (-1)^{(n_2+n_3)} + (-1)^{(n_3+n_1)}$
 $= \begin{cases} 4, n_1, n_2, n_3 \text{ are even or odd} \\ 0, n_1, n_2, n_3 \text{ mixed even/odd} \end{cases}$

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Atomic form factor for x-rays

$$S_{K} = \sum_{j=1}^{n} f_{j}(\vec{K}) e^{i\vec{K}\cdot\vec{d}_{j}}$$

where $f_i(\vec{K})$ is the atomic form factor, and is determined by the internal structure of the ion that occupies position $\vec{d_j}$ in the basis. The atomic form factor at \vec{K} is taken to be proportional to the Fourier transform of the electron charge distribution of the corresponding ion:

 $f_j(\vec{K}) = \int dV n_j(\vec{r}) \exp(-i\vec{K} \cdot \vec{r})$

Here $n_j(\vec{r})$ is electron density concentration.

X-ray diffraction by a small crystal

Structure factor F of the system is then

$$F = \sum_{j=1}^{n} f e^{i\vec{K}\cdot\vec{R}_{j}} = f \sum_{j=0}^{N_{1,2,3}-1} e^{i\vec{K}\cdot(n_{1}\vec{a}_{1}+n_{2}\vec{a}_{2}+n_{3}\vec{a}_{3})}$$
$$= f \frac{e^{i\vec{K}\cdot N_{1}\vec{a}_{1}} - 1}{e^{i\vec{K}\cdot N_{2}\vec{a}_{2}} - 1} \frac{e^{i\vec{K}\cdot N_{3}\vec{a}_{3}} - 1}{e^{i\vec{K}\cdot\vec{a}_{3}} - 1}$$

where f_n is the structural factor of the unit cell. The total scattered intensity then $I = F \cdot F^*$ We suppose that in a linear crystal there are identical point scattering centers at every lattice point $\vec{\rho}_m = m\vec{a}$, where *m* is an integer. Show that the scattering intensity is proportional to $|F|^2$

a)
$$I = F \cdot F^* = \frac{\sin^2 M(a \cdot \Delta k)/2}{\sin^2(a \cdot \Delta k)/2}$$

b) We know that a diffraction maximum appears when $a \cdot \Delta k = 2\pi h$, where h is an integer. We change Δk slightly and define ε in $a \cdot \Delta k = 2\pi h + \varepsilon$ such that ε gives the position of the first zero in $\sin^2 M(a \cdot \Delta k)/2$. Show that $\varepsilon = 2\pi/M$, so that the width of the diffraction maximum is proportional to 1/M and can be extremely narrow for macroscopic values of M.