project:

X ray Scattering at UCD

Fadley group (Advanced Light Source) LBL : synchrotron

esp layered materials

also xray in, e^- out "photoemission"

Savrasov group – theoretical calculation of phonons (lattice vibrations)
probed by inelastic x ray scattering

$|\vec{k}| \neq |\vec{k}'|$ $E_k \neq E_{k'}$

$E_{k'} - E_k \rightarrow$ phonons

Pickett group / LLNL DAC group $CaLi_2$ under pressure

superconductor under pressure

xray diffraction at APS at ANL

another synchrotron

Where do x rays come from?

Accelerated e^- hitting anode (Röntgen 1895)
Nobel Prize 1901

project: FT1D

FOURIER TRANSFORM AND RECIPROCAL LATTICE — One dimensional example

$X_n = na \qquad n = 0, 1, 2, 3, 4, \ldots$

$f_k = \sum_n e^{ikx_n}$ Wave number k has units $1/\text{Length}$

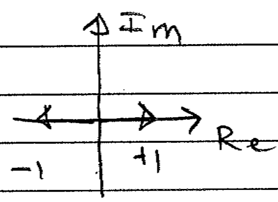
$k = \pi/a \qquad e^{ikx_n} = e^{i(\pi/a)na} = e^{i\pi n} = (-1)^n$

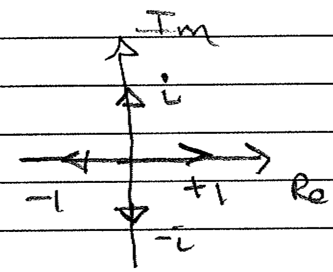
$f_{\frac{\pi}{a}} = \sum_n (-1)^n = 1 - 1 + 1 - 1 + 1 - 1 \ldots \rightarrow \phi$

$k = \pi/2a \qquad e^{ikx_n} = i^n = 1, i, -1, -i, 1, i, \ldots$

again $f_{\pi/2a} \rightarrow \phi$

Pictorially





Cancellation will occur $\forall k$ except $k = 2\pi/a \, \ell$

(Do really not need to consider k outside $[0, 2\pi/a]$ because

$$e^{i(k + 2\pi/a)x_n} = e^{ikx_n}$$

"Brillouin Zone")

$k = 2\pi/a \, \ell$ ← "Reciprical lattice vector"

$e^{ikx_n} = 1 \quad \forall x_n$ in lattice

more appropriate when we consider $d > 1$

project: R-1

In $d=1$ we considered k which give $e^{ikr} = e^{ikna} = 1$

$k = \frac{2\pi}{a}$

Reciprocal Lattice

We have discussed lattices of atoms which have property that if you move to a new location $\vec{r} \to \vec{r} + \vec{R}$ your environment looks the same.

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

It turns out to be very useful to ask which $\vec{k}$ vectors generate plane waves which obey this same periodicity

$$e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot(\vec{r}+\vec{R})} \implies e^{i\vec{k}\cdot\vec{R}} = 1$$

The answer is $\vec{K} = k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3$ (k_i integers)

where
$$\vec{b}_1 = \frac{2\pi}{V_c}\,\vec{a}_2 \times \vec{a}_3$$

$$\vec{b}_2 = \frac{2\pi}{V_c}\,\vec{a}_3 \times \vec{a}_1$$

$V_c = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

volume of unit cell

$$\vec{b}_3 = \frac{2\pi}{V_c}\,\vec{a}_1 \times \vec{a}_2$$

proof $\vec{b}_i \cdot \vec{a}_j = 2\pi\,\delta_{ij}$

eg $\vec{b}_1 \cdot \vec{a}_1 = 2\pi$ obviously

likewise $\vec{b}_1 \cdot \vec{a}_2 = 0$ also obvious $\vec{a}_2 \perp \vec{a}_2 \times \vec{a}_3$

So $\vec{K}\cdot\vec{R} = (\underbrace{k_1 n_1 + k_2 n_2 + k_3 n_3}_{\text{integer}})\,2\pi \implies e^{i\vec{K}\cdot\vec{R}} = 1$

DiVOGA

project:

R-2

The reciprocal of the reciprocal lattice is the original lattice.

Almost obvious interchange roles of $\vec{k}$ and $\vec{R}$.

But calc also prove

$$\vec{c}_1 = \frac{2\pi}{V_c'} \vec{b}_2 \times \vec{b}_3 = \frac{2\pi}{V_c'}\left(\frac{2\pi}{V_c}\right)^2 (\vec{a}_3 \times \vec{a}_1) \times (\vec{a}_1 \times \vec{a}_2)$$

$$\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A}\cdot\vec{C}) - \vec{C}(\vec{A}\cdot\vec{B}) \qquad \text{"BAC-CAB"}$$

$$\sim \quad \vec{a}_1 \underbrace{\left[(\vec{a}_3 \times \vec{a}_1)\cdot a_2\right]}_{V_c} - \vec{a}_2 \underbrace{\left[(\vec{a}_3 \times \vec{a}_1)\cdot \vec{a}_1\right]}_{0}$$

$$= \frac{2\pi}{V_c'}\left(\frac{2\pi}{V_c}\right)^2 V_c \, \vec{a}_1$$

$$V_c' = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)$$

$$= \left(\frac{2\pi}{V_c}\right)^3 (\vec{a}_2 \times \vec{a}_3) \cdot \underbrace{\left[(\vec{a}_3 \times \vec{a}_1) \times (\vec{a}_1 \times \vec{a}_2)\right]}_{V_c \vec{a}_1} \qquad \text{from above}$$

$$= \left(\frac{2\pi}{V_c}\right)^3 V_c^2 = \frac{(2\pi)^3}{V_c}$$

Finally $\quad \vec{c}_1 = 2\pi \underbrace{\frac{V_c}{(2\pi)^3}}_{1/V_c'} \left(\frac{2\pi}{V_c}\right)^2 V_c \, \vec{a}_1 = \vec{a}_1$

whew!

project:
R-3

SC $\vec{a}_1 = a\hat{x}$ $\vec{a}_2 = a\hat{y}$ $\vec{a}_3 = a\hat{z}$

$\vec{b}_1 = \frac{2\pi}{a}\hat{x}$ $\vec{b}_2 = \frac{2\pi}{a}\hat{y}$ $\vec{b}_3 = \frac{2\pi}{a}\hat{z}$ $\rightarrow$ also SC

Can easily show

FCC reciprocal lattice is BCC
BCC " " " FCC

follows also from page R-2

Wigner Seitz cell of Reciprocal lattice $\leftrightarrow$ "First Brillouin Zone"

Miller Indices

We specified positions of unit cells via

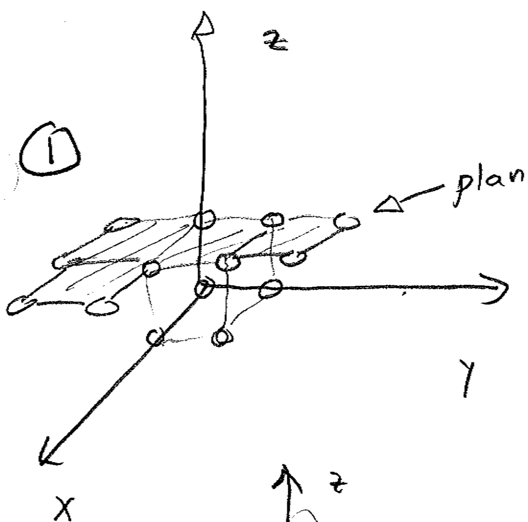
$$\vec{r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

Another way to describe regular crystal structure is via set of parallel planes which contain ∞ #s of atoms

Eg simple cubic : xy planes (normal is $\hat{z}$)

$z = \ldots, -2a, -a, 0, a, 2a, \ldots$

(1)

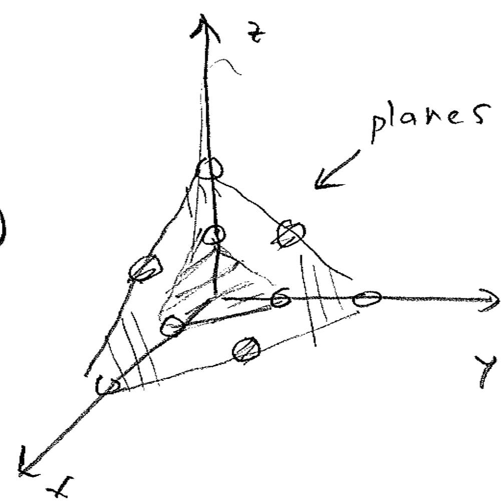


But many possibilities even besides $x = -2a, -a, 0, a, 2a \ldots$

$y = -2a, -a, 0, a, 2a, \ldots$

eg

(2)



$x + y + z = a$
$x + y + z = 2a$

Thm: Given a family of planes separated by d there are reciprocal lattice vectors $\perp$ to planes the shortest of which has length $\frac{2\pi}{d}$,

The Miller indices $(k_1\, k_2\, k_3)$ are the $k_1\, k_2\, k_3$ which give the smallest $|\vec{q}|$,

$\boxed{\text{Eqn of Plane}}$

WLOG normalize eqn so $a^2+b^2+c^2=1$

$$ax + by + cz = d$$

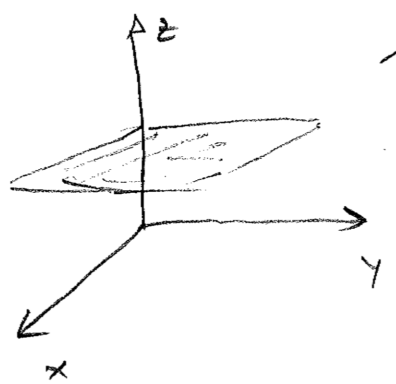
$$(a,b,c)\cdot(x,y,z) = d$$

geometrical significance

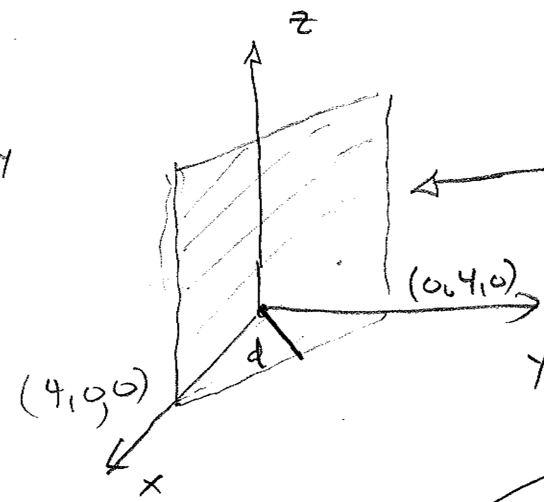
shortest distance of plane to origin

$(a,b,c) \Rightarrow$ normal to plane

Examples



$z = 3$ $\quad (a,b,c) = (0,0,1) \Rightarrow \hat{z}$



$x + y = 4$

$(a,b,c) = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$

$\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)\cdot(x\ y\ z)$

$= \frac{4}{\sqrt{2}}$

clearly this is $\hat{n}$ to plane

clearly this is distance d to origin

proof (See page P1)

planes are defined by Eqn $\hat{n} \cdot \vec{r} = d$

normal to plane $(|\hat{n}| = 1)$

distance from origin to plane

If we choose $\vec{G} = \frac{2\pi}{d} \hat{n}\,(\text{integer})$

$$e^{i\vec{G}\cdot\vec{r}} = e^{i\frac{2\pi}{d}(\text{integer})\,\hat{n}\cdot\vec{r}} = e^{i2\pi(\text{integer})} = 1$$

Such a $\vec{G}$ is a reciprocal lattice vector since it obeys the defining eqn $e^{i\vec{G}\cdot\vec{r}} = 1$ of a RLV,

Miller indices of planes on page M1

(1) $z = -2a, -a, 0, a, 2a, \ldots$

$\vec{a}_1 = a\hat{x}$ $\quad \vec{b}_1 = 2\pi/a\ \hat{x}$

$\vec{a}_2 = a\hat{y}$ $\quad \vec{b}_2 = 2\pi/a\ \hat{y}$

$\vec{a}_3 = a\hat{z}$ $\quad \vec{b}_3 = 2\pi/a\ \hat{z}$

vectors $\vec{G} = k_3 \vec{b}_3$ are normal to planes, Shortest is $\frac{2\pi}{a}$

M-3

② Planes $x+y+z=a$

$x+y+z=2a$

$x+y+z=3a$

normal is clearly $\propto (1,1,1)$

to get this from $k_1\vec{b}_1+k_2\vec{b}_2+k_3\vec{b}_3$ need $k_1=k_2=k_3$

so $\vec{G} = \frac{2\pi}{a}k(\hat{x}+\hat{y}+\hat{z})$

Shortest length is $k=1$ $\frac{2\pi}{a}\sqrt{3}$

Meanwhile distance between planes is $a/\sqrt{3}$

(consider points $\left(\frac{a}{3},\frac{a}{3},\frac{a}{3}\right)$ on $x+y+z=a$

$\left(\frac{2a}{3},\frac{2a}{3},\frac{2a}{3}\right)$ on $x+y+z=2a$

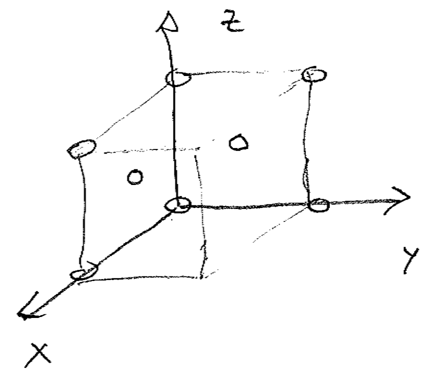
separation is $\sqrt{3(a/3)^2} = a/\sqrt{3}$

Theorem says shortest $|G| = \frac{2\pi}{a} = 2\pi/(a/\sqrt{3}) = \frac{2\pi}{a}\sqrt{3}$ W

Another Example fcc

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})$$
$$\vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{z})$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y}+\hat{z}-\hat{x})$$
$$\vec{b}_2 = \frac{2\pi}{a}(\hat{x}+\hat{z}-\hat{y})$$
$$\vec{b}_3 = \frac{2\pi}{a}(\hat{y}+\hat{x}-\hat{z})$$



One set of planes is $z = -a, -\frac{a}{2}, 0, \frac{a}{2}, a, \ldots$

separation $d = a/2$

Theorem says there are $\vec{G}$ normal to planes, ie $\vec{G} = \#\hat{z}$

the shortest of which is length $\frac{2\pi}{(a/2)} = \frac{4\pi}{a}$

$$k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3 = \#\hat{z}$$

$$\frac{2\pi}{a}(-k_1+k_3+k_2)\hat{x} + \frac{2\pi}{a}(k_1+k_3-k_2)\hat{y} + \frac{2\pi}{a}(k_1+k_2-k_3)\hat{z} = \#\hat{z}$$

$$\begin{aligned} -k+k_3+k_2 &= 0 \\ k_1+k_3-k_2 &= 0 \end{aligned} \Rightarrow \begin{aligned} k_3 &= 0 \\ k_1 &= k_2 \end{aligned}$$

$$\frac{2\pi}{a}2k_1\hat{z}$$

$$\frac{4\pi}{a}k_1\hat{z}$$

integer

shortest length $\frac{4\pi}{a}$ ✓

project: SKIP

Another view of Miller indices

$$k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3 = \vec{G}$$

is $\perp$ to plane of atoms

$$n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 = \vec{R} \quad \Rightarrow \quad \vec{G}\cdot\vec{R} = A$$

This plane hits $\vec{a}_1$ axis at $x_1\vec{a}_1$

$$\vec{G}\cdot x_1\vec{a}_1 = 2\pi k_1 x_1 = A \qquad x_1 = A/2\pi k_1$$

$$\vec{G}\cdot x_2\vec{a}_2 = 2\pi k_2 x_2 = A \qquad x_2 = A/2\pi k_2$$

$$\vec{G}\cdot x_3\vec{a}_3 = 2\pi k_3 x_3 = A \qquad x_3 = A/2\pi k_3$$

So in the coordinate system $\vec{a}_1, \vec{a}_2, \vec{a}_3$

the intercepts with axes are inversely proportional to

Miller indices