PHYS 460 LECTURE 6

LAST WEEK, WE WERE DISCUSSING PERIODIC ARRAYS OF ATOMS, AND HOW BEST TO DESCRIBE THESE MATHEMATICALLY. WE INTRODUCED TWO EQUIVALENT STRUCTURES:

(1) THE "DIRECT LATTICE", WHERE ONE NOTES THE POSITION OF A REPEATING UNIT IN REAL SPACE USING

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

WHERE $n_i \in \mathbb{Z}$

$\{\vec{a}_i\}$ ANY 3 VECTORS

PERHAPS WITH BASIS

AND

(2) THE "RECIPROCAL LATTICE"

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

WHERE $m_i \in \mathbb{Z}$

AND

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

BOTH OF THESE STRUCTURES ARE "BRAVAIS LATTICES" AND ARE COMPLETELY EQUIVALENT. I ARGUED THE LATTER TO OFTEN BE MORE USEFUL, HOWEVER, AND IT CAN BE INTERPRETED MANY WAYS:

(A) AS THE COMPLETE LIST OF ALL WAVEVECTORS SUPPORTED BY LATTICE $\vec{R}$

(B) AS THE FOURIER TRANSFORM OF THE LATTICE $\vec{R}$

TODAY, I AM GOING TO INTRODUCE ONE LAST INTERPRETATION OF THE RECIPROCAL LATTICE:

(c) A COMPETE LIST OF ALL FAMILIES OF REPEATING PLANES INSIDE A CRYSTAL STRUCTURE,

THIS INTERPRETATION STARTS WITH THE OBSERVATION THAT

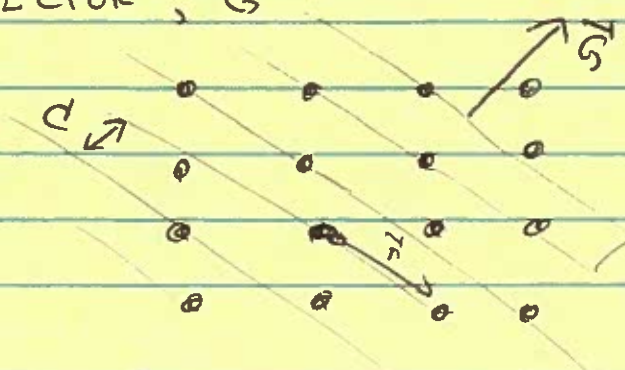
$$\vec{G} \cdot \vec{r} = 2\pi m \qquad m \in \mathbb{Z}$$

FOR ALL $\vec{r} \in \vec{R}$

SO, SINCE THERE AN INFINITE NUMBER OF $\vec{r} \in \vec{R}$ WHICH SATISFY THIS RELATIONSHIP, WE CAN JUST CHOOSE ONE, $\vec{r}_0$, AS A REFERENCE. THEN, ALL OTHER $\vec{r}$, SUCH THAT $\vec{G} \cdot \vec{r} = 2\pi m = \vec{G} \cdot \vec{r}_0$

$$\Rightarrow \boxed{\vec{G} \cdot (\vec{r} - \vec{r}_0) = 0}$$

WHICH IS THE DEFINITION OF A PLANE PERPENDICULAR TO $\vec{G}$. SINCE THE TOP RELATION IS TRUE FOR ALL $\vec{r} \in \vec{R}$, BY DEFINITION, WE CAN SAY ALL POSITION VECTORS IN THE DIRECT LATTICE ARE PART OF A PLANE PERPENDICULAR TO ANY GIVEN ~~EA~~ RECIPROCAL LATTICE VECTOR, $\vec{G}$



$\vec{G} \cdot \vec{r} = 2\pi m$

PLANE DETERMINED BY INTEGER m

MOREOVER, CONSIDER TWO VECTORS FROM ADJACENT PLANES

$$\vec{G} \cdot \vec{r}_1 = 2\pi m$$

AND $$\vec{G} \cdot \vec{r}_2 = 2\pi(m+1)$$

$$\Rightarrow \vec{G} \cdot (\vec{r}_2 - \vec{r}_1) = 2\pi$$

EACH OF THESE VECTORS CAN BE SEPARATED INTO PARTS PARALLEL AND PERPENDICULAR TO $\vec{G}$

$$\Rightarrow \vec{G} \cdot (\vec{r}_{2,\parallel} - \vec{r}_{1,\parallel} + \vec{r}_{2,\perp} - \vec{r}_{1,\perp}) = 2\pi$$

$$\Rightarrow \vec{G} \cdot (\vec{r}_{2,\perp} - \vec{r}_{1,\perp}) = 2\pi$$

$$|\vec{G}|\, d = 2\pi$$ WHERE d IS PLANE SEPERATION

$$\boxed{d = \frac{2\pi}{|\vec{G}|}}$$

∴ NOT ONLY DOES $\vec{G}$ INDEX ALL THE PLANES, BUT ALSO QUANTIFIES THE SPACING BETWEEN ADJACENT PLANES!

IT IS THUS VERY COMMON TO REFER TO A FAMILY OF PLANES BY THEIR "MILLER INDICES" ⟶ THE INTEGER COEFFICIENTS OF THE RECIPROCAL LATTICE PRIMITIVE VECTORS

MILLER INDICES

$$\vec{G}_{(h,k,l)} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

WHERE $\vec{G}_{(h,k,l)}$ IS THE SMALL R.L. VECTOR PERPENDICULAR TO THE PLANES OF INTEREST.

NOTES: (1) THOUGH WE PRESENTED THIS DISCUSSION IN THE CONTEXT OF ATOMS, IT IS REALLY JUST A STATEMENT OF GEOMETRY. MILLER WAS A MINERALOGIST AND CAME UP WITH THIS DESCRIPTION TO EXPLAIN CLEAVAGE PLANES IN GEMS.

WILLIAM HALLOWES MILLER (1801–1880)

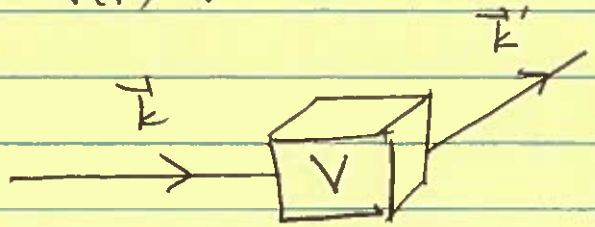
(2) MILLER INDICES ARE RELATED TO THE DIRECT LATTICE METHOD FOR DESCRIBING PLANES, IN TERMS OF FINDING INTERCEPTS x_1, x_2, x_3:

$$\frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} = h : k : l$$

(3) SINCE $\vec{G}$ GIVES PLANES AND DISTANCES, WE CAN IMMEDIATELY SEE THAT IT WILL BE RELEVANT FOR DESCRIBING X-RAY DIFFRACTION

INTRODUCTION TO SCATTERING

X-RAY DIFFRACTION IS A SPECIAL CASE OF A MORE GENERAL QUANTUM MECHANICAL CALCULATION. BEYOND JUST IN THE CONTEXT OF PHOTONS, ONE CAN ASK: WHAT IS THE PROBABILITY THAT A WAVE WITH WAVEVECTOR $\vec{k}$ IS SCATTERED INTO A STATE WITH WAVEVECTOR $\vec{k}'$ BY A POTENTIAL $V(\vec{r})$?



WITHOUT GOING INTO DETAILS, THE ANSWER IS GIVEN BY "FERMI'S GOLDEN RULE"

FROM PERTURBATION THEORY →

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

WHERE THE δ FUNCTION ENSURES CONSERVATION OF ENERGY AND THE MATRIX ELEMENT

$$\langle \vec{k}' | V | \vec{k} \rangle = \int d\vec{r} \, \frac{e^{-i\vec{k}'\cdot\vec{r}}}{\sqrt{L^3}} V(\vec{r}) \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{L^3}}$$

$$= \frac{1}{L^3} \int d\vec{r} \, e^{-i(\vec{k}'-\vec{k})\cdot\vec{r}} V(\vec{r})$$

$$\equiv V(\vec{k}' - \vec{k})$$

IS JUST THE FOURIER TRANSFORM OF THE POTENTIAL!

BUT WE'VE DEALT WITH FOURIER TRANSFORMS BEFORE! LET'S USE WHAT WE LEARNED. ASSUME THAT $V(\vec{r})$ HAS THE SAME PERIODICITY AS OUR LATTICE, $\vec{R}$, AND LET $\vec{r} = \vec{R} + \vec{x}$

THEN

$$\langle \vec{k}' | V | \vec{k} \rangle = \frac{1}{L^3} \sum_{\vec{R}} \int_{\text{UNIT CELL}} d\vec{x}\; e^{-i(\vec{k}'-\vec{k})\cdot(\vec{x}+\vec{R})} V(\vec{x}+\vec{R})$$

$$= \frac{1}{L^3} \left[\sum_{\vec{R}} e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}} \right] \left[\int_{\text{UNIT CELL}} d\vec{x}\; e^{-i(\vec{k}'-\vec{k})\cdot\vec{x}} V(\vec{x}) \right]$$

WHERE IN THE LAST STEP WE USED $V(\vec{x}+\vec{R}) = V(\vec{x})$.

WE SAW AT THE END OF LAST LECTURE THAT FIRST SUM IS ZERO UNLESS

$$\vec{k}' - \vec{k} = \vec{G} \qquad \text{(POISSON SUMMATION FORMULA)}$$

$$\Rightarrow \quad \langle \vec{k}' | V | \vec{k} \rangle = \left(\frac{2\pi}{L}\right)^3 \delta(\vec{k}'-\vec{k}-\vec{G})\, S(\vec{k}'-\vec{k})$$

WHERE $S(\vec{k}'-\vec{k}) \equiv \int_{\text{UNIT CELL}} d\vec{x}\; e^{-i(\vec{k}'-\vec{k})\cdot\vec{x}} V(\vec{x})$

IS A FUNCTION WE CALL THE "STRUCTURE FACTOR"

∴ FOR ANY INCOMING WAVES, $\vec{k}$, THE INTENSITY OF OUTGOING WAVES

$$I(\vec{k}'-\vec{k}) \propto \delta(\vec{k}'-\vec{k}-\vec{G})\, |S(\vec{k}'-\vec{k})|^2$$

✱ IS JUST AN IMAGE OF THE RECIPROCAL LATTICE, $\vec{G}$!

SPECIFICALLY, WE JUST DERIVED A CONDITION FOR WHEN SHOULD SEE A SPOT IN A DIFFRACTION EXPERIMENT (A "BRAGG REFLECTION")

$$\boxed{\Delta\vec{k} \equiv \vec{k}' - \vec{k} = \vec{G}}$$

Laue Condition

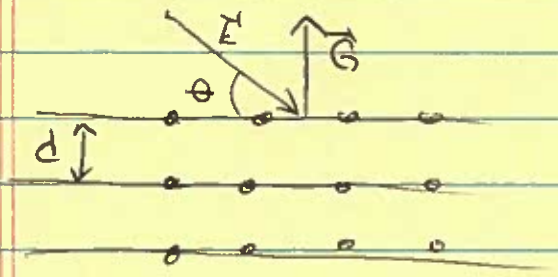
USING THE FACT THAT $|\vec{k}'| = |\vec{k}|$, ENSURED BY THE δ-FUNCTION IN FERMI'S GOLDEN RULE, ONE CAN FIND A EQUIVALENT FORM:

$$(\vec{k}')^2 = (\vec{k} + \vec{G})^2$$

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

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

THIS MAY NOT BE OBVIOUS AT FIRST GLANCE, BUT IT IS EASY TO SHOW THAT THE ABOVE CONDITION IS JUST BRAGG'S LAW:



$$2\vec{k}\cdot\vec{G} = 2|\vec{k}||\vec{G}|\sin\theta = |\vec{G}|^2$$

$$2 \times \frac{2\pi}{\lambda}\sin\theta = |G|$$

$$= \frac{2\pi}{d}$$

$$\boxed{2d\sin\theta = \lambda}$$

BRAGG'S LAW

THESE CONDITIONS GIVE THE LOCATION (SCATTERING ANGLE) OF BRAGG REFLECTIONS. INFORMATION ABOUT SCATTERING INTENSITY IS CONTAINED IN THE STRUCTURE FACTOR.

$$S(\vec{G}) = \int_{\text{UNIT CELL}} d\vec{x}\; e^{i\vec{G}\cdot\vec{x}}\, V(\vec{x})$$

WHERE WE ARE NOW MAKING USE OF THE FACT THAT $\vec{k}' - \vec{k} = \vec{G}$ AT BRAGG LOCATIONS.

IN ORDER TO CALCULATE THIS FUNCTION, IT IS COMMON TO MAKE THE ASSUMPTION THAT THE SCATTERING FROM THE LATTICE IS JUST THE SUM OF THE SCATTERING FROM INDIVIDUAL ATOMS (WHICH IS USUALLY VERY CLOSE TO BEING CORRECT):

$$V(\vec{x}) = \sum_{\text{ATOMS } j} V_j(\vec{x} - \vec{x}_j)$$

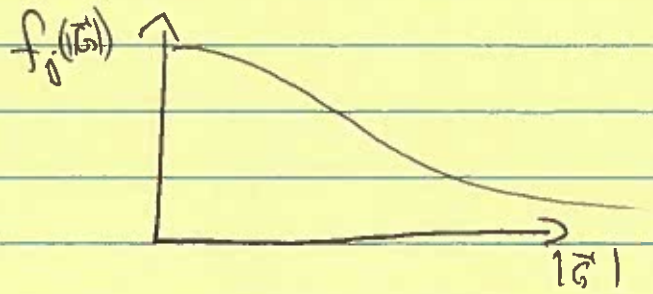
WHERE $\vec{x}_j$ IS THE POSITION OF THE j^{th} ATOM IN THE UNIT CELL.

FOR WAVES WHOSE INTERACTIONS ARE SUFFICIENTLY SHORT-RANGED (E.G. X-RAYS OR NEUTRONS) THIS CONDITION REDUCES THE STRUCTURE FACTOR TO

$$S(\vec{G}) = \sum_j f_j(\vec{G})\, e^{i\vec{G}\cdot\vec{x}_j}$$

WHERE THE QUANTITIES f_j ARE ELEMENT SPECIFIC "FORM FACTORS". FOR NEUTRONS, f_j'S ARE JUST CONSTANTS KNOWN AS

(COHERENT) NEUTRON SCATTERING LENGTHS, b_j, AND ARE TABULATED. FOR X-RAY SCATTERING, $f_j \propto Z_j$ (ATOMIC NUMBER) AND REPRESENT THE FOURIER TRANSFORM OF THE ELECTRON DENSITY ABOUT ATOM j. THIS GIVES THE SCATTERING INTENSITY A NATURAL "DECAY" WITH INCREASING $|\vec{G}|$



EXAMPLE: THE BCC LATTICE WITH SINGLE ATOM TYPE (e.g. Cs)

USING CONVENTIONAL CUBIC CELL, THE BASIS HAS TWO ATOMS

(1) $\vec{x}_1 = 0\hat{x} + 0\hat{y} + 0\hat{z}$

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

WHERE a - LATTICE PARAM

THE PRIMITIVE VECTORS FOR THE RECIPROCAL LATTICE ARE $\vec{b}_j = \frac{2\pi}{a}\hat{r}_j$ WHERE $\hat{r}_j = \{\hat{x}, \hat{y}, \hat{z}\}$.

THUS, $\vec{G} = \frac{2\pi}{a}(h\hat{x} + k\hat{y} + l\hat{z})$

$$S_{(hkl)} = f e^{i(h\hat{x}+k\hat{y}+l\hat{z})\cdot\vec{0}} + f e^{i\frac{2\pi}{a}(h\hat{x}+k\hat{y}+l\hat{z})\cdot(\frac{a}{2}\hat{x}+\frac{a}{2}\hat{y}+\frac{a}{2}\hat{z})}$$

$$= f\left(1 + (-1)^{h+k+l}\right)$$

THUS, THE STRUCTURE FACTOR FOR BCC PREDICTS THE "SELECTION RULE" $h+k+l = 2n \quad n \in \mathbb{Z}$

EXAMPLE: THE FCC LATTICE

AGAIN, CHOOSE CONVENTIONAL CUBIC CELL, NOW WITH FOUR ATOM BASIS

$$\vec{x}_1 = 0\hat{x} + 0\hat{y} + 0\hat{z}$$
$$\vec{x}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$
$$\vec{x}_3 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$
$$\vec{x}_4 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

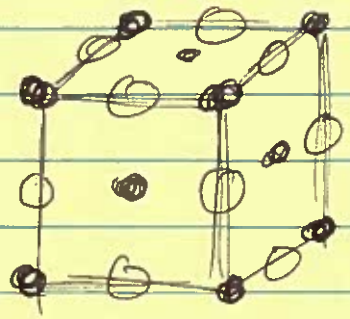
$$\Rightarrow S_{(hkl)} = f\left(1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right)$$

$$= f\left(1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}\right)$$

$$= \begin{cases} 4f & h,k,l \text{ ALL EVEN} \\ 4f & h,k,l \text{ ALL ODD} \\ 0 & \text{OTHERWISE} \end{cases}$$

NOTE THAT, IN BOTH OF THESE CASES, THE STRUCTURE FACTOR PREDICTS THE EXISTENCE OF "SYSTEMATIC ABSENCES". THAT IS, CERTAIN BRAGG PEAKS ARE NEGATED. THIS IS BECAUSE THE CUBIC CELL ISN'T A PRIMITIVE CELL FOR THESE STRUCTURES. IF WE USED REAL PRIMITIVES $\vec{a}_i$ FOR THESE BRAVAIS LATTICES, EVERY RECIPROCAL LATTICE VECTOR WOULD CORRESPOND TO A BRAGG POSITION

EXAMPLE: $NaCl$ - FOR MULTI ATOM BASIS, YOU SIMPLY INSERT THE ~~APPROPRIATE~~ APPROPRIATE FORM FACTOR f_j FOR THE ATOM.



$\vec{x}_{Na1} = 0$ $\quad \vec{x}_{Cl1} = \frac{a}{2}(0,0,1)$

$\vec{x}_{Na2} = \frac{a}{2}(1,1,0)$ $\quad \vec{x}_{Cl2} = \frac{a}{2}(1,0,0)$

$\vec{x}_{Na3} = \frac{a}{2}(1,0,1)$ $\quad \vec{x}_{Cl3} = \frac{a}{2}(0,1,0)$

$\vec{x}_{Na4} = \frac{a}{2}(0,1,1)$ $\quad \vec{x}_{Cl4} = \frac{a}{2}(1,1,1)$

$$S_{(hkl)} = f_{Na}\left[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}\right]$$

$$+ f_{Cl}\, e^{i\pi l}\left[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}\right]$$

$$= \left[f_{Na} + e^{i\pi l} f_{Cl}\right] \times S_{FCC}$$

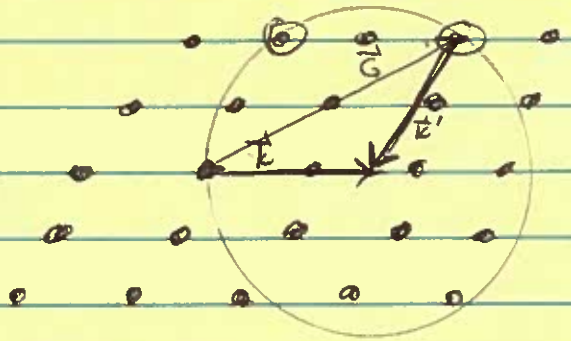
USING SIMILAR ANALYSIS, ONE CAN MAKE PREDICTIONS FOR THE DIFFRACTION PATTERN OF ANY ATOMIC LATTICE (OR CONVERSELY MAKE EDUCATED GUESSES ABOUT THE ATOMIC STRUCTURE BY MISAPORING THE DIFFRACTION PATTERN)

THE EWALD CONSTRUCTION

THE LAUE CONDITION ALLOWS ONE TO VERIFY WHEN BRAGG SCATTERING SHOULD OCCUR, BUT IT IS OFTEN MUCH MORE DIFFICULT TO PREDICT WHICH BRAGG PEAKS WILL BE SEEN (IF ANY) FOR A GIVEN INCIDENT WAVEVECTOR $\vec{k}$. FOR THIS, PHYSICISTS OFTEN TURN TO THE EWALD CONSTRUCTION (OR EWALD SPHERE), WHICH IS SIMPLY A GRAPHICAL APPLICATION OF THE LAUE CONDITION

$$\vec{k}' - \vec{k} = \vec{G}$$

, ALONG WITH $|\vec{k}'| = |\vec{k}|$



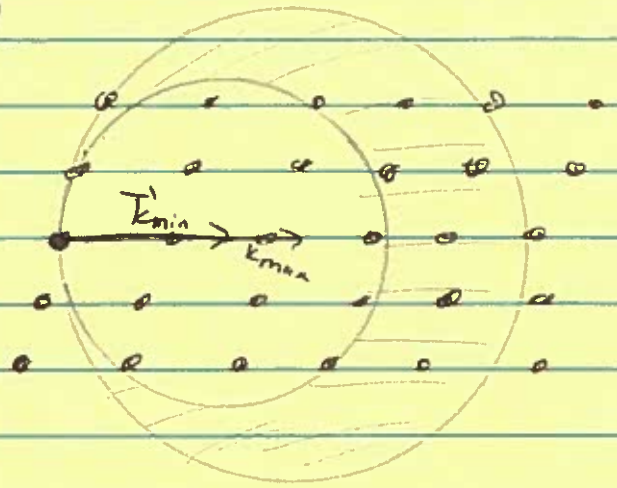
(1) DRAW AN ARROW OF LENGTH $|\vec{k}| = \frac{2\pi}{\lambda}$ WITH TAIL ON ONE R.L POINT

(2) DRAW A SPHERE OF RADIUS $|\vec{k}'| = |\vec{k}|$ ABOUT TIP OF FIRST ARROW.

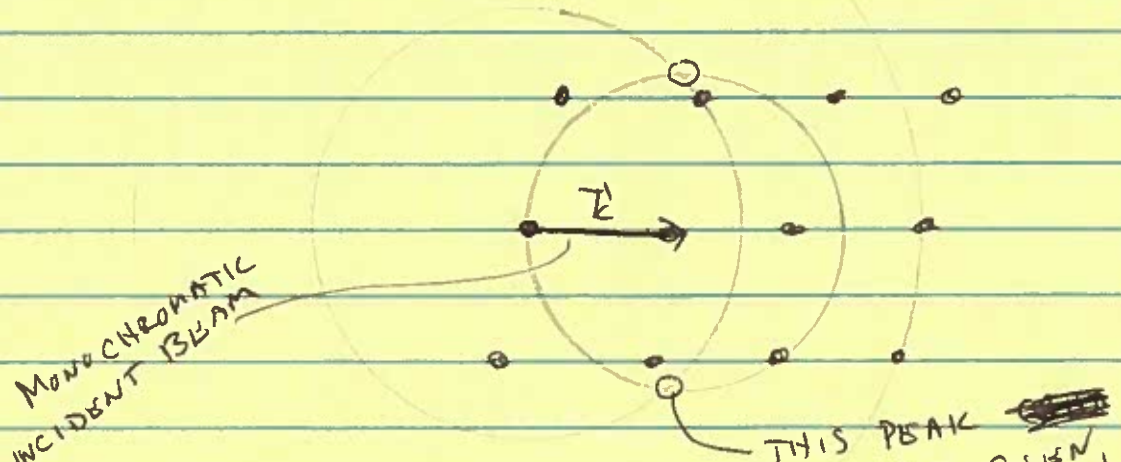
(3) IF THE SPHERE INTERSECTS ON OTHER R.L POINT → BRAGG PEAK!

THOUGH COMPUTERS ARE MORE FREQUENTLY USED THAN GRAPH PAPER IN MODERN TIMES, THE EWALD CONSTRUCTION IS VERY USEFUL FOR VISUALIZED SEVERAL STANDARD METHODS (AND THEIR MOTIVATION)

(1) LAUE METHOD - THIS METHOD INCREASES THE NUMBER OF R.L POINTS INTERSECTED BY THE EWALD SPHERE BY USING A RANGE OF X-RAY (OR NEUTRON) WAVELENGTHS (COMMONLY REFERRED TO AS A "WHITE BEAM")

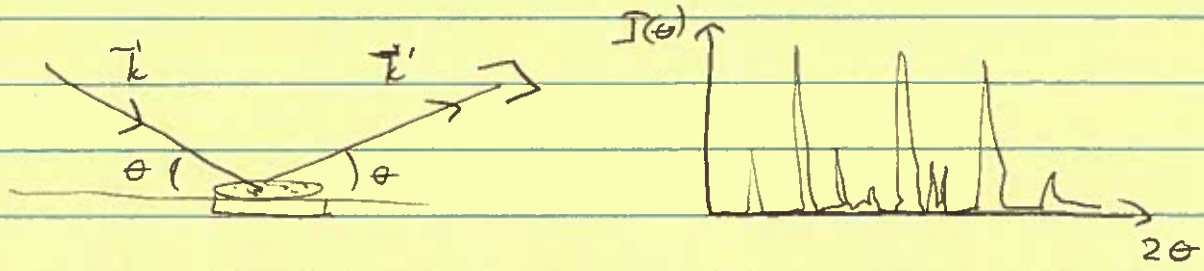


(2) ROTATING SAMPLE METHOD - THIS METHOD ROTATES THE SAMPLE (RECIPROCAL LATTICE) AROUND SOME AXIS, BRINGING MORE POINTS IN CONTACT WITH THE (STATIONARY) EWALD SPHERE



(3) THE POWDER METHOD (DEBYE-SCHERRER)

THE ULTIMATE ROTATING CRYSTAL EXPERIMENT. THE ORIENTATIONAL PART OF THE BRAGG CONDITION IS SATISFIED AUTOMATICALLY. THUS, ONE JUST VARIES THE SCATTERING ANGLE SYSTEMATICALLY, AND ONE WILL SEE A PEAK IN SCATTERING INTENSITY WHENEVER $\sin\theta = \lambda \frac{|\vec{G}|}{4\pi}$



BY FAR THE MOST COMMON METHOD, BUT REQUIRES CAREFUL MODELLING AND COMPLICATED NON-LINEAR FITS OF DATA.

SEE SIMON 14.3.2 FOR A FULLY WORKED EXAMPLE