

DESCRIPTION AND DETERMINATION OF ATOMIC POSITIONS IN CRYSTALLINE SOLIDS

IN THE LAST SEVERAL CLASSES WE HAVE DISCUSSED THE ARRANGEMENT OF IONS IN IONIC SOLIDS - HOW TO PREDICT COORDINATION NUMBERS FROM IONIC "RADII", THE ORIGIN AND LIMITATIONS OF SETS OF SELF-CONSISTANT RADII, THE INTERPRETATION OF STRUCTURES IN TERMS OF COORDINATION POLYHEDRA AND THEIR LINKAGE, AND PAULING'S FIVE GUIDELINES FOR REASONABLE STRUCTURES. IT WORTH POINTING OUT AGAIN THAT NOT ALL SOLID MATERIALS ARE CRYSTALLINE! AMORPHOUS SOLIDS ARE ALSO POSSIBLE AND IMPORTANT. (WE WILL RETURN TO NON-CRYSTALLINE SOLIDS AGAIN) WE SHOULD ALSO RECALL THAT MATERIALS IN WHICH THE COHESIVE FORCE ARISES FROM ELECTRON INTERACTIONS - COVALENT BONDING AND METALLIC BONDING BEHAVE VERY DIFFERENTLY AND SUCH INTERACTIONS ARE GOVERNED BY PRINCIPLES MUCH MORE COMPLEX THAN COULOMB'S LAW! (SUCH INTERACTIONS WILL BE TREATED IN THE SECOND HALF OF THIS SEMESTER.)

WE WOULD LIKE TO TURN NOW TO TWO OTHER ASPECTS OF THE CRYSTALLINE STATE

(1) WHAT SORT OF LANGUAGE CAN ONE DEVELOPE TO DESCRIBE ATOMIC ARRANGEMENTS? CLEARLY DESCRIPTIONS SUCH AS "THE BLACK BALLS ARE AT THE CORNERS OF THE CUBE, THE RED BALLS ARE AT THE CENTERS OF THE EDGES, AND THE CHARTREUSE BALL ARE --- WELL, TUCKED UP IN THE CORNERS, A LITTLE CLOSER TO TWO FACES THAN THE OTHER ---" ARE GOING TO HAVE LIMITED MILEAGE FOR ANY BUT THE SIMPLEST ATOMIC ARRANGEMENTS!

THIS LANGUAGE IS CRYSTALLOGRAPHY (OR "GEOMETRICAL CRYSTALLOGRAPHY"), LITERALLY WRITING OR SPECIFICATION OF AN OBJECT (-"GRAPHY"), THAT OBJECT BEING A CRYSTAL. IT IS

LANGUAGE THAT IS FUSSY BUT UNAMBIGUOUS. IT IS THE LANGUAGE IN WHICH ATOMIC ARRANGEMENTS ARE REPORTED IN THE LITERATURE (MEANING THAT ONE MUST BE PREPARED TO GRACK THIS CODE IF ONE WISHES TO USE THIS INFORMATION) MOREOVER, SYMMETRY THEORY (GEOMETRICAL CRYSTALLOGRAPHY) CAN PREDICT IMPORTANT FEATURE OF THE PROPERTIES OF A CRYSTAL THAT ARE VERY NON-INTUITIVE (FOR EXAMPLE, THAT SOME PROPERTIES SUCH AS PIEZOELECTRICITY OR PYROELECTRICITY ARE IMPOSSIBLE FOR CERTAIN CRYSTALLOGRAPHIC SYMMETRIES)

(2) WHAT ARE THE EXPERIMENTAL METHODS FOR THE EXPERIMENTAL MEASUREMENT OF LATTICE DIMENSIONS AND ATOMIC COORDINATES? THIS IS TYPICALLY DONE WITH THE AID OF DIFFRACTION METHODS. THAT ASPECT OF DIFFRACTION THAT DEALS WITH CRYSTAL GEOMETRY AND ITS DETERMINATION IS OFTEN REFERRED TO AS "X-RAY CRYSTALLOGRAPHY" (NO MATTER THAT, TODAY, ONE MIGHT AS OFTEN AS NOT USE ELECTRONS OR NEUTRONS FOR THIS PURPOSE !!) AS OPPOSED TO PHENOMENA CONCERNED WITH DIFFUSE SCATTERING THAT ARE MORE DEEPLY ROOTED IN PHYSICS.

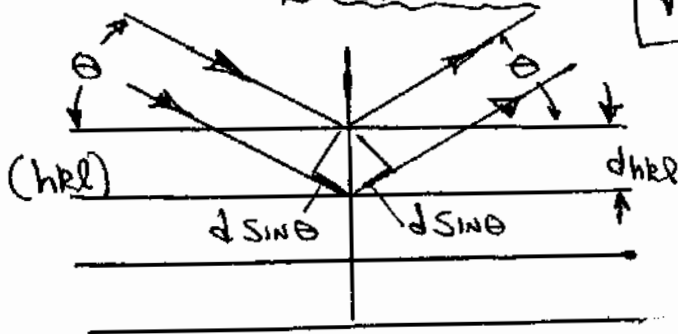
DIFFRACTION AND BRAGG'S LAW

MANY PROBES EXIST FOR THE STUDY OF THE STRUCTURE OF MATERIALS ON AN ATOMIC SCALE — BOTH CRYSTALLINE OR NON-CRYSTALLINE. ORDERED, CRYSTALLINE MATERIALS ARE ESPECIALLY AMENABLE TO ANALYSIS BY MEANS OF DIFFRACTION.

ALTHOUGH SUCH METHODS WERE A HIGH-RISK ADVENTURE UNTIL THE MID 1960'S, IN THEORY COMBINED WITH THE ADVENT OF COMPUTERS WITH HIGH SPEED AND LARGE STORAGE CAPACITY HAVE MADE THE DETERMINATION OF ATOMIC POSITIONS (TO 1 PART IN 10^9 OF A CELL EDGE) AND LATTICE DIMENSIONS (TO ONE PART IN 10^5) FAIRLY ROUTINE FOR MOST (BUT NOT ALL!) CRYSTALLINE MATERIALS. IT IS WORTH EMPHASIZING, HOWEVER, THAT THE INFORMATION OBTAINED IS FOR AN AVERAGE CELL — BOTH A TIME AND POSITION AVERAGE.

ONE OF THE BASIC RELATIONS FOR DIFFRACTION, EXPRESSING THE RELATION BETWEEN INTER-PLANAR SPACINGS IN A LATTICE AND THE ANGLES, θ , AT WHICH CONSTRUCTIVE INTERFERENCE OF SCATTERED BEAMS OF WAVE LENGTH, λ , OCCURS IS THE EQUATION KNOWN AS BRAGG'S LAW.

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



A BEAM OF RADIATION INCIDENT ON LATTICE PLANES (HRL) AT ANGLE θ AND SCATTERED AT ANGLE θ WILL DESTRUCTIVELY INTERFERE UNLESS THE PATH

DIFFERENCE BETWEEN NEIGHBORING

LATTICE PLANES IN THE CRYSTAL, $2d \sin\theta$ IS AN INTEGRAL NUMBER OF WAVE LENGTHS $n\lambda$. AND, d_{hkl} THE INTERPLANAR SPACING DEPENDS ON THE MILLER-BRAVAIS INDICES OF THIS RATIONAL STACK OF PLANES AND THE DIMENSIONS OF THE LATTICE. (THIS IS A VERY TIGHT CONSTRAINT! ONE MIGHT WONDER WHAT DIFFERENCE A MILLIONTH OF A WAVELENGTH MIGHT MAKE. ISN'T THAT CLOSE ENOUGH??)

THE ANSWER IS THAT "CLOSE" WINS NO CIGAR! THE PATH DIFFERENCE BETWEEN ADJACENT LATTICE PLANES INCREASES LINEARLY WITH PROGRESSIVE PLANES IN THE STACK — THAT IS, IF THE PATH DIFFERENCE BETWEEN THE FIRST AND SECOND LATTICE PLANE IS $n\lambda$, THE PATH DIFFERENCE BETWEEN THE FIRST AND THIRD WILL BE $2n\lambda$, $3n\lambda$ WITH THE FOURTH, AND SO ON. FOR EVEN A MILLIONTH OF A WAVELENGTH DIFFERENCE FROM $n\lambda$, THEREFORE, THE PLANE THAT IS $500,000^{\text{th}}$ BELOW THE FIRST WILL SCATTER EXACTLY OUT OF PHASE WITH THE FIRST AND WIPE IT OUT. THE SPACING BETWEEN LATTICE PLANES — ON THE ORDER OF \AA — IS SO SMALL THAT THE NUMBER OF LATTICE PLANES WITHIN A CRYSTAL SO SMALL AS TO BE INVISIBLE TO THE UNAIDED EYE ($\approx 0.1 \text{ mm}$ SAY) WILL STILL CONTAIN A STACK OF 10^6 LATTICE PLANES. BUT WHAT IF THE CRYSTAL IS SMALLER THAN THIS? OR IS IMPERFECT SO THAT EVERY LATTICE PLANE DOES NOT SCATTER EXACTLY THE SAME INTENSITY? IN SUCH CASES THE SCATTERING CONDITION BECOMES MORE "FUZZY" AND THE RANGE OF ANGLES, θ , AT WHICH MEASURABLE INTENSITY MAY BE DETECTED BECOMES BROADER. TURNING THIS AROUND, MEASUREMENT OF THE ANGULAR WIDTH OF THE DIFFRACTION MAXIMUM MAY BE USED TO MEASURE CRYSTALLITE SIZE AND PERFECTION.

BUT, HOLD ON BEFORE WE GET CARRIED AWAY!! LATTICE POINTS ARE A GEOMETRIC FICTION AND PLANES PASSED BETWEEN ARE EVEN MORE SO! ATOMS SCATTER ELECTROMAGNETIC RADIATION WITH WAVELENGTHS CLOSE TO THE INTERATOMIC DISTANCE AND NOT SHIMMERING, IMAGINARY LATTICE PLANES! THE SAME OBJECTION HOLD FOR DIFFRACTION OF PARTICLES, SUCH AS NEUTRONS OR ELECTRONS THAT, WITH MOMENTUM $p = \text{mass} \times \text{velocity}$ HAVE AN ASSOCIATED DE BROGLIE WAVE OF $\lambda = h/p$ WHERE h IS PLANCK'S CONSTANT. WHERE, THEREFORE, ARE THE ATOMISTICS OF BRAGG'S LAW??? AND WHY SHOULD THE ANGLE OF INCIDENCE BE EQUAL TO THE ANGLE OF REFLECTION FROM THIS "PLANE"? ATOMS SCATTER RADIATION IN ALL DIRECTIONS.

Clearly, there must be some merit to Bragg's Law if only because everybody uses it (and it was worth a Nobel Prize in 1915!) Equally clearly, something has been left out and the derivation given above has left something out.

A proper beginning from first principles may be based on Huygen's construction. (Christiaan Huygens, 1629-1695, was a Dutch physicist and astronomer. He hit upon an improved way to grind telescope lenses, built an improved telescope 23 feet in length, and used this in important discoveries such as the Orion Nebula, the rings of Saturn and the markings on the surface of Mars. In physics he challenged Newton on the theory of light claiming that waves, rather than particles, could be used to explain reflection and refraction.)

Waves are scattered when they encounter an obstruction. If the scatterers are arranged in a periodic fashion three types of behavior may be noted, depending on the value of the wavelength, λ , relative to the spacing, a , of the scatterers.

- If $\lambda \gg a$ the wave passes by hardly noticing the scatterers. This behavior is well illustrated by water waves passing by a set of pilings under a dock. A long period ground swell passes by unperturbed.

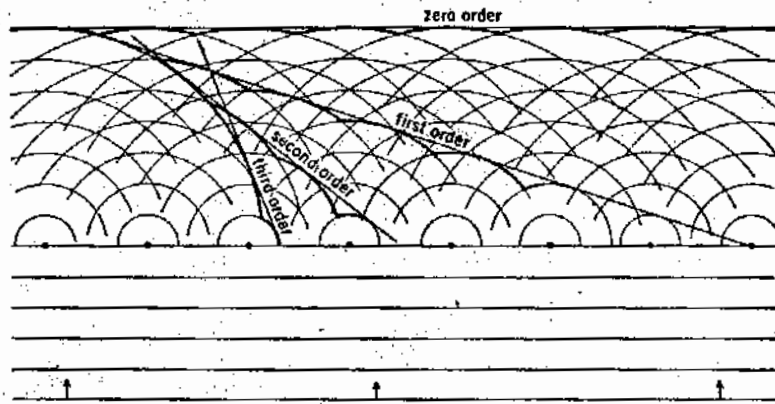
- If $\lambda \ll a$ the scatterers cast shadows. This behavior may be noted for water waves and pilings, but is also illustrated by light passing through Venetian blinds.

- If $\lambda \approx a$ things get interesting! A very complex pattern of interferences occurs close to the scattering centers (referred to as Fresnel Diffraction). As the wave fronts spread out and their radius increases they increasingly approach a plane wave. Plane waves of significant amplitude may be observed only in discrete directions (Fraunhofer Diffraction Region).

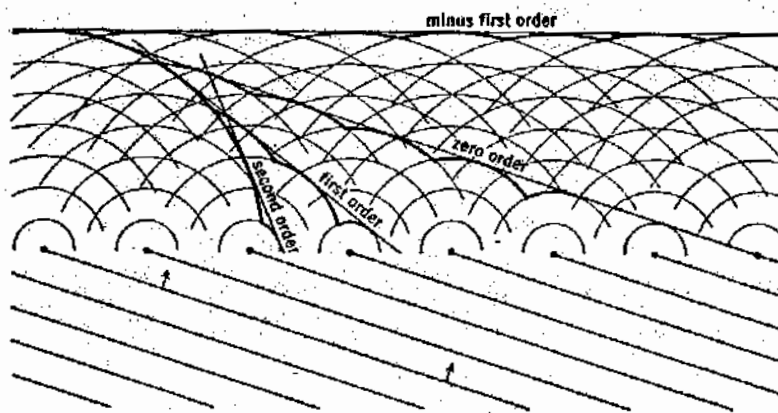
WE WILL START WITH HUYGENS' CONSTRUCTION APPLIED TO A ONE-DIMENSIONAL ROW OF A SINGLE KIND OF SCATTERER - AN ATOM. NEXT WE WILL EXAMINE A TWO-DIMENSIONAL CRYSTAL WITH ONE ATOM PER LATTICE POINT, AND THEN A THREE-DIMENSIONAL ARRAY. FINALLY, WE WILL CONSIDER THE SCATTERING WHEN AN ARBITRARY NUMBER OF DIFFERENT ATOMS ARE "HUNG" AT EACH LATTICE POINT.

HUYGENS' CONSTRUCTION FOR A PLANE WAVE INCIDENT ON A ROW OF POINT SCATTERERS

(1) NORMAL INCIDENCE



(2) OBLIQUE INCIDENCE



If — ON A SCALE MUCH LARGER THAN THE SPACING BETWEEN ATOMS — WE WERE TO POINT A DETECTOR AT THE CRYSTAL WE WOULD DETECT ZERO INTENSITY: THE PHASE DIFFERENCE OF THE WAVES SCATTERED FROM NEIGHBORING ATOMS WOULD BE RANDOM AND THE RAYS SCATTERED FROM INDIVIDUAL ATOMS WOULD CANCEL. WE WOULD MEASURE A DIFFRACTED INTENSITY ONLY WHEN THE RAYS SCATTERED BY INDIVIDUAL ATOMS ARE EXACTLY IN PHASE.

HUYGENS' CONSTRUCTION SHOWS US HOW TO FIND THESE DIRECTIONS: LET'S LOOK AT WAVE FRONTS SCATTERED BY THE ATOMS THAT ARE EXACTLY IN PHASE, DIFFER IN PHASE BY ONE WAVELENGTH, BY TWO WAVELENGTHS AND SO ON. THIS IS DONE IN THE DIAGRAMS ON THE PRECEDING PAGE FOR A PLANE WAVE NORMALLY INCIDENT ON THE LATTICE ROW AND FOR A PLANE WAVE INCLINED TO THE ROW. FOR EACH OF THESE COLLECTIONS OF SPHERICAL WAVE FRONTS WE CONSTRUCT A COMMON TANGENT. THE SURFACE OF THE SPHERICAL WAVES IS HIGHLY CRENNELLATED IN CLOSE TO THE SCATTERING CENTERS BUT HAVE ALMOST FLATTENED OUT TO A PLANE WAVE AT ONLY SEVEN WAVELENGTHS DISTANCE. THE NORMAL TO THIS WAVEFRONT IS THE DIRECTION OF PROPAGATION

SCATTERING BY REAL ATOMS

WE WILL CONSIDER ONLY X-RAY AND NEUTRON SCATTERING.

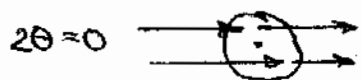
X-RAYS ARE SCATTERED BY THE FACT THAT THE PERIODIC ELECTRIC FIELD \vec{E} IN THE X-RAY BEAM EXERTS A FORCE ON THE POSITIVELY CHARGED NUCLEUS AND THE NEGATIVELY CHARGED ELECTRONS THAT SURROUND THE NUCLEUS. FOR FREQUENCIES THAT CORRESPOND TO



WAVELENGTHS OF USE FOR DIFFRACTION THE PERIOD IS JUST TOO SHORT FOR THE NUCLEUS TO RESPOND BECAUSE OF

ITS MASS. THE LIGHT ELECTRONS ARE SWEEPED BACK AND FORTH WITH THE PERIODICITY OF THE INCIDENT X-RAY BEAM. MAXWELL'S EQUATIONS SAY THAT AN ACCELERATED CHARGE SHOULD RADIATE

A spherical wave front is radiated about each oscillating atom. The amplitude of the scattered wave depends on the number of electrons on the atom. If we define 2θ the angle between the incident beam and a scattered ray, the intensity of the scattered beam will be proportional to Z , the number of electrons on the atom or ion, as every electron scatters in phase when



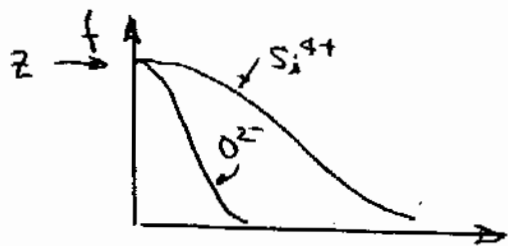
$2\theta = 0$. For $2\theta \neq 0$ there will be a



path difference between electrons scattering from different positions on the atom. A phase difference $\Delta\phi = \Delta x / \lambda \cdot 2\pi$, where Δx is the

path difference, will cause partial destructive interference.

The larger the distribution of electrons, the greater the amount of the possible phase difference. The scattering power of the atom, f , will decrease with the increasing size of the atom (the Δx term in $\Delta\phi$) and will decrease with increasing 2θ (again, the Δx term in $\Delta\phi$) if we change λ the value of f will decrease in proportion to λ^{-1} .



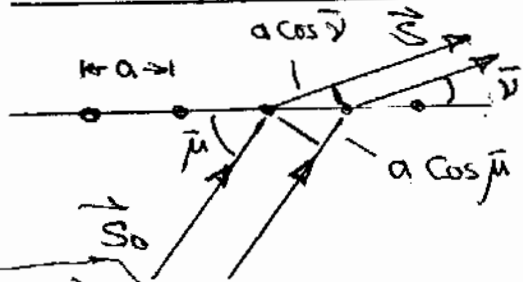
This behavior is nicely illustrated

by the series of isoelectronic ions

	O^{2-}	Mg^{2+}	Al^{3+}	Si^{4+}
Z	8	12	13	14
No. of electrons	10	10	10	10
Ionic radius	1.40	0.65	0.50	0.41

values of f are tabulated in International Tables for Crystallography. — As a function of increments of values for $\sin\theta/\lambda$ or as a polynomial in powers of $(\sin\theta/\lambda)$ as a variable. Where do these numbers come from? They are purely theoretical, calculated from wave functions for an isolated atom.

SCATTERING FROM A ONE-DIMENSIONAL CRYSTAL WITH ONE KIND OF ATOM



PATH DIFFERENCE = $a \cos \nu - a \cos \mu$

CONSTRUCTIVE INTERFERENCE WILL OCCUR

WHEN

$$a \cos \nu - a \cos \mu = m\lambda$$

WHERE m IS AN INTEGER. WE CAN SELECT μ FOR

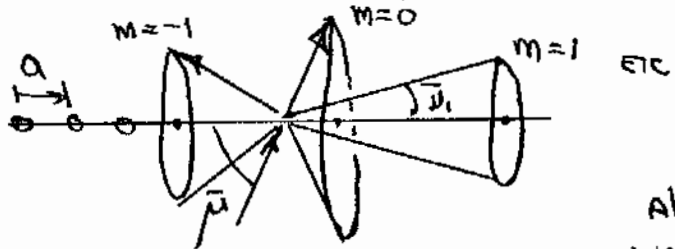
OUR EXPERIMENT. DIFFRACTION THEN OCCURS AT

$$\cos \nu = \frac{m\lambda}{a} + \cos \mu$$

\vec{S} AND \vec{S}_0 ARE UNIT VECTORS ALONG THE DIFFRACTED AND INCIDENT BEAMS

m CAN TAKE ON ALL VALUES FOR WHICH $-1 < \cos \nu < +1$

FOR A "REAL" ONE-DIMENSIONAL CRYSTAL IN A THREE DIMENSIONAL SPACE



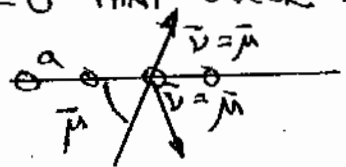
DIFFRACTION OCCURS FOR ANY VALUE OF μ

DIFFRACTED BEAMS OCCUR ALONG CONES OF HALF-ANGULAR OPENING ν THAT ARE CONCENTRIC

WITH THE LATTICE VECTOR \vec{a}

THIS DOESN'T SEEM TO HAVE MUCH TO DO WITH THE PROCESS OF "REFLECTION" AKA BRAGG'S LAW, DOES IT?? WELL --- LET'S LOOK AT THE

BEAMS FOR $m=0$ THAT OCCUR IN A PLANE DEFINED BY \vec{S}_0 AND \vec{a} .



FOR $m=0$

$$\cos \nu = \cos \mu$$

$$\text{AND } \mu = \pm \nu$$

THE GENERATORS OF THE DIFFRACTION

CONE LOOK LIKE A CONTINUATION OF

THE DIRECT BEAM $\vec{S} = \vec{S}_0$ AND A "REFLECTED" BEAM!!

WE CAN PUT THIS EQUATION IN A NEAT VECTOR FORM USING \vec{S} AND \vec{S}_0 AND THE FACT

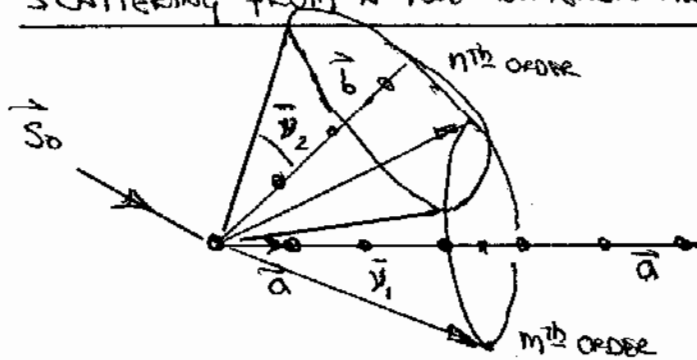
$$\left. \begin{aligned} \vec{S} \cdot \vec{a} &= |\vec{S}| |\vec{a}| \cos \nu \\ \vec{S}_0 \cdot \vec{a} &= |\vec{S}_0| |\vec{a}| \cos \mu \end{aligned} \right\}$$

$$\therefore \begin{aligned} a \cos \nu &= \vec{S} \cdot \vec{a} \\ a \cos \mu &= \vec{S}_0 \cdot \vec{a} \end{aligned}$$

AND $\vec{S} \cdot \vec{a} - \vec{S}_0 \cdot \vec{a} = m\lambda$

$$\boxed{(\vec{S} - \vec{S}_0) \cdot \vec{a} = m\lambda}$$

SCATTERING FROM A TWO-DIMENSIONAL CRYSTAL WITH ONE KIND OF ATOM



THE ATOMS IN THE ROW SPECIFIED BY THE PERIODICITY \vec{a} WILL SCATTER IN PHASE IN THE m^{th} ORDER WHEN

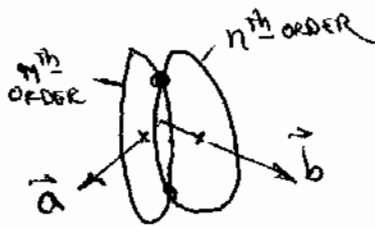
$$\cos \bar{\nu}_1 = \cos \bar{\mu}_1 + \frac{m\lambda}{a}$$

ANY PAIR OF ATOMS SEPARATED BY \vec{a} THIS SCATTER WITH A PATH-LENGTH DIFFERENCE OF $m\lambda$ OR A PHASE DIFFERENCE OF 2π

SIMILARLY ATOMS IN THE ROW SPECIFIED BY THE PERIODICITY \vec{b} SCATTER IN THE n^{th} ORDER WHEN

$$\cos \bar{\nu}_2 = \cos \bar{\mu}_2 + \frac{n\lambda}{b}$$

UNLESS BOTH EQUATIONS ARE SATISFIED THERE IS NO RESULTING CONSTRUCTIVE INTERFERENCE. THE DIRECTION OF THE DIFFRACTED BEAMS FOR WHICH THIS OCCURS MUST LIE ALONG THE INTERSECTION OF THE TWO DIFFRACTION CONES



THEREFORE ONLY TWO BEAMS ARE GENERATED AND THESE OCCUR SYMMETRICALLY ABOVE AND BELOW THE PLANE DEFINED BY \vec{a} AND \vec{b}

IN THREE DIMENSIONS, WHERE WE HAVE A THIRD TRANSLATIONAL PERIODICITY \vec{c} , WE MUST HAVE A THIRD CONDITION.

$$\cos \bar{\nu}_3 = \cos \bar{\mu}_3 + p \frac{\lambda}{c}$$

OR ELSE A ROW OF ATOMS SEPARATED BY \vec{c} WOULD NOT SCATTER IN PHASE WITH THE SHEETS DEFINED BY \vec{a} AND \vec{b}

THUS, TO OBTAIN A DIFFRACTED BEAM FROM A THREE-DIMENSIONAL CRYSTAL, THE THREE EQUATIONS

$$\begin{cases} \cos \bar{\nu}_1 = \cos \bar{\mu}_1 + \frac{m\lambda}{a} \\ \cos \bar{\nu}_2 = \cos \bar{\mu}_2 + \frac{n\lambda}{b} \\ \cos \bar{\nu}_3 = \cos \bar{\mu}_3 + \frac{p\lambda}{c} \end{cases}$$

THESE ARE KNOWN AS THE VON LAUE EQUATIONS AND WERE THE ORIGINAL DESCRIPTION OF DIFFRACTION BY A CRYSTAL

OR, IN VECTOR FORM

$$\begin{cases} (\vec{S} - \vec{S}_0) \cdot \vec{a} = m\lambda \\ (\vec{S} - \vec{S}_0) \cdot \vec{b} = n\lambda \\ (\vec{S} - \vec{S}_0) \cdot \vec{c} = p\lambda \end{cases}$$

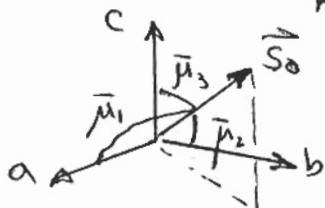
HOW MANY DEGREES OF FREEDOM ARE AT OUR DISPOSAL?

WELL, WE CAN SELECT THE WAVELENGTH λ THAT WE CHOOSE TO USE IN OUR EXPERIMENT BUT, ONCE WE PICK IT, THE VALUE IS FIXED.

THE CRYSTAL THAT WE SELECT FOR STUDY PROVIDES \vec{a} , \vec{b} & \vec{c} ACCORDINGLY, THESE ARE NOT VARIABLES UNLESS WE THROW OUT THE CRYSTAL AND WORK ON A DIFFERENT MATERIAL

THE VARIABLES, THEN, ARE $\bar{\mu}_1$, $\bar{\mu}_2$, $\bar{\mu}_3$ AND $\bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_3$

TWO MORE EQUATIONS RELATE THESE ANGLES



IF \vec{a} , \vec{b} AND \vec{c} ARE MUTUALLY PERPENDICULAR

$$\cos^2 \bar{\mu}_1 + \cos^2 \bar{\mu}_2 + \cos^2 \bar{\mu}_3 = 1$$

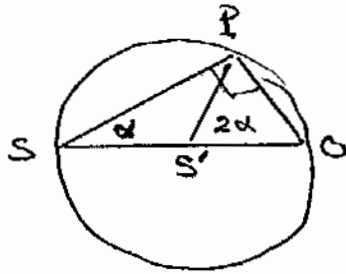
AND SIMILARLY WE MUST HAVE

$$\cos^2 \bar{\nu}_1 + \cos^2 \bar{\nu}_2 + \cos^2 \bar{\nu}_3 = 1$$

THERE IS THUS ONLY ONE DEGREE OF FREEDOM IN SATISFYING THE DIFFRACTION CONDITION!

THE EWALD CONSTRUCTION

A SPHERE HAS SOME PECULIAR GEOMETRIC PROPERTIES



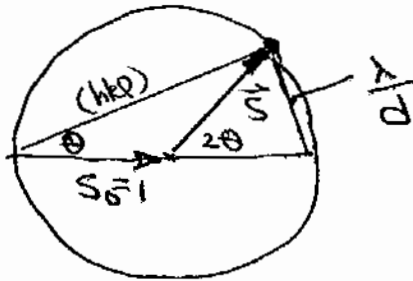
IF WE DRAW A DIAMETER OF THE SPHERE AND A POINT P ON THE SURFACE OF THE SPHERE THEN

- THE ANGLE SPO IS ALWAYS 90° !
- THE ANGLE OS'P IS ALWAYS TWICE ANGLE OSP!

WE CAN PLACE SOME LABELS ON THE CONSTRUCTION TO PROVIDE A NIFTY GEOMETRY REPRESENTATION OF BRAGG'S LAW. LET SS' OR S'O BE THE DIRECTION OF THE INCIDENT BEAM \vec{S}_0

LET S'P BE THE DIRECTION OF THE DIFFRACTED BEAM \vec{S}

THEN IF $\alpha \equiv \theta$ AND $2\alpha \equiv 2\theta$



THEN BRAGG'S LAW RESULTS

$$\sin \theta = \frac{\lambda/d}{2}$$

IF WE LABEL THE REMAINING LEG OF THE TRIANGLE AS λ/d

WE HAVE SHOWN THAT WHEN ATOMS SEPARATED BY A FIRST TRANSLATION, \vec{a} , SCATTER IN PHASE WITH A PATH DIFFERENCE BETWEEN RAYS SCATTERED BY NEIGHBORING ATOMS EQUAL TO $n\lambda$ (PHASE DIFFERENCE $2\pi n$) AND, SIMILARLY, WHEN ATOMS RELATED BY \vec{b} AND \vec{c} SCATTER IN PHASE WITH PHASE DIFFERENCES OF $2\pi m$ AND $2\pi p$, RESPECTIVELY, THEN THE LAUE EQUATIONS PROVIDE

$$\begin{cases} m\lambda = a \cos \bar{\nu}_1 - a \cos \bar{\mu}_1 = (\vec{S} - \vec{S}_0) \cdot \vec{a} \\ n\lambda = b \cos \bar{\nu}_2 - b \cos \bar{\mu}_2 = (\vec{S} - \vec{S}_0) \cdot \vec{b} \\ p\lambda = c \cos \bar{\nu}_3 - c \cos \bar{\mu}_3 = (\vec{S} - \vec{S}_0) \cdot \vec{c} \end{cases}$$

WHERE $\bar{\nu}_i$ IS THE ANGLE BETWEEN THE DIFFRACTED BEAM AND THE TRANSLATION \vec{a}_i , AND $\bar{\mu}_i$ IS THE ANGLE BETWEEN THE DIFFRACTED BEAM AND THE TRANSLATION \vec{a}_i

COSINES OF THE SET OF ANGLES $\bar{\nu}_1, \bar{\nu}_2$ AND $\bar{\nu}_3$ REPRESENT THE DIRECTION COSINES OF THE DIFFRACTED BEAM RELATIVE TO THE (GENERALLY) OBLIQUE AXES \vec{a}, \vec{b} AND \vec{c} . AS THE DIRECTION COSINES MAY BE REGARDED AS THE COMPONENTS OF A UNIT VECTOR \vec{u} ALONG THE DIFFRACTED BEAM, $\cos^2 \bar{\nu}_1 + \cos^2 \bar{\nu}_2 + \cos^2 \bar{\nu}_3 = 1$ WHEN \vec{a}, \vec{b} AND \vec{c} ARE MUTUALLY ORTHOGONAL. IF NOT, THE DIRECTION COSINES ARE STILL RELATED, BUT BY A MORE COMPLEX EQUATION THAT INVOLVES a, b, c AND THE INTER-AXIAL ANGLES α, β AND γ .

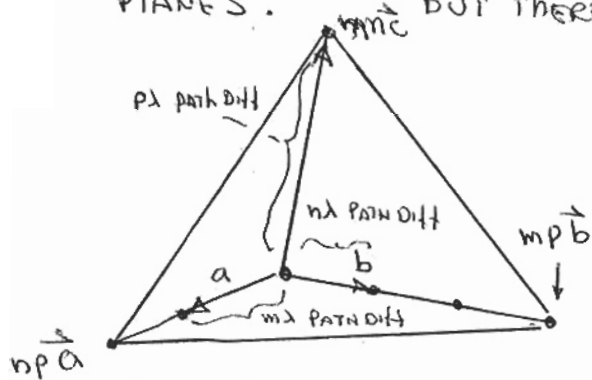
A SIMILAR EQUATION RELATES THE COSINES OF THE ANGLES BETWEEN THE INCIDENT BEAM \vec{S}_0 AND THE AXES \vec{a} , \vec{b} AND \vec{c} :

$\cos^2 \bar{\mu}_1 + \cos^2 \bar{\mu}_2 + \cos^2 \bar{\mu}_3 = 1$ IF THE TRANSLATIONS ARE ORTHOGONAL.

THERE ARE, ACCORDINGLY, FIVE EQUATIONS THAT RELATE THE SIX DIFFRACTION ANGLES $\bar{\nu}_i$ AND $\bar{\mu}_i$ TO λ , \vec{a} , \vec{b} AND \vec{c} PLUS THE "ORDER" OF THE DIFFRACTION MAXIMUM (THAT IS, THE VALUES OF THE INTEGERS mnp). THEREFORE ONCE WE SELECT A MATERIAL (WHICH THEN FIXES \vec{a} , \vec{b} , \vec{c} , α , β , γ BY THE LATTICE THAT IT HAS), PICK A VALUE FOR λ AND DECIDE TO PRODUCE A DIFFRACTED BEAM WITH ORDERS m n AND p (WHICH MIGHT PROVE IMPOSSIBLE) ONLY ONE DEGREE OF FREEDOM EXISTS IN SATISFYING THE LAUE EQUATION.

RELATION BETWEEN THE LAUE EQUATIONS AND "REFLECTION" OF X-RAYS

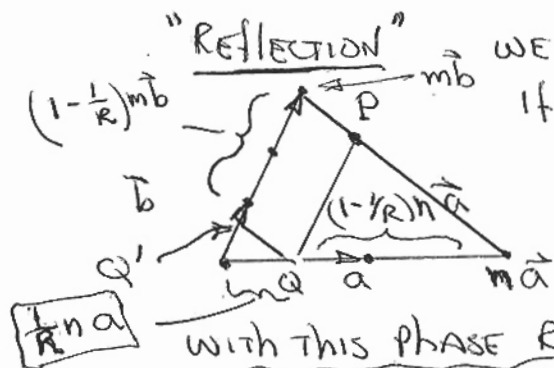
THERE WOULD APPEAR TO BE LITTLE CONNECTION BETWEEN THE SCATTERING OF RADIATION BY ATOMS ACCORDING TO THE LAUE EQUATIONS AND REFLECTION OF X-RAYS OR OTHER RADIATION FROM RATIONAL LATTICE PLANES. BUT THERE IS!!



LET US CONSIDER AN ARRANGEMENT OF THE INCIDENT BEAM \vec{S}_0 AND THE DIFFRACTED BEAM \vec{S} THAT CORRESPONDS TO LATTICE ROW \vec{a} SCATTERING IN THE m^{th} ORDER, LATTICE ROW \vec{b} IN THE n^{th} ORDER AND \vec{c} IN THE p^{th} ORDER.

LET US NOW LOCATE THE LATTICE POINT OUT ALONG \vec{a} BY np TRANSLATIONS. THE ATOM AT THIS LOCATION THEREFORE SCATTERS WITH PATH DIFFERENCE $mp (m\lambda)$ RELATIVE TO THE ORIGIN. SIMILARLY, LET'S MOVE $mp\vec{b}$ TO DEFINE AN ATOM THAT SCATTERS WITH PATH DIFFERENCE $mp (n\lambda)$ RELATIVE TO THE ORIGIN AND $mn\vec{c}$ THAT SCATTERS WITH PATH DIFFERENCE $mn (p\lambda)$

ALL THREE OF THE ABOVE ATOMS, THEREFORE, SCATTER ^{RAIS} WITH THE SAME PATH DIFFERENCE $(mnp)\lambda$ RELATIVE TO THE SCATTERING FROM THE ORIGIN ATOM. ("BIG DEAL", YOU YAWN, "YOU MADE IT COME OUT THAT WAY!"). THESE THREE LOCATIONS $mp\vec{a}$, $mp\vec{b}$ AND $mn\vec{c}$ ARE LATTICE POINTS. WE CAN, THEREFORE, PASS A RATIONAL LATTICE PLANE THROUGH THEM AS IS DONE IN THE ABOVE DIAGRAM

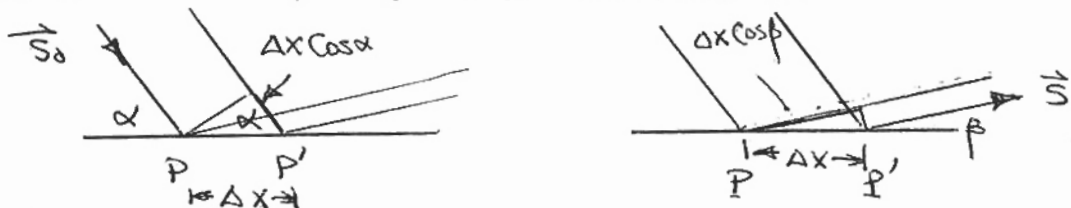


WE WILL NOW SHOW THAT, RATHER ASTOUNDINGLY, IF THE THREE POINTS USED TO DEFINE THE LATTICE PLANE ALL SCATTER WITH THE SAME PHASE AS THE ATOM AT THE ORIGIN, THEN ANY POINT ON THIS PLANE SCATTERS

WITH THIS PHASE RELATIVE TO THE ORIGIN ATOM !! LET POINT P BE AN ARBITRARY POINT ON THE PLANE - MAYBE AT AN ATOM, MAYBE NOT. DRAW A LINE PARALLEL TO \vec{b} UNTIL IT INTERSECTS \vec{a} AT POINT Q . DRAW A LINE PARALLEL TO THE LATTICE PLANE UNTIL IT INTERSECTS \vec{b} AT Q' . SUPPOSE POINT Q IS SOME FRACTION, $1/r$, OF THE WAY OUT TO THE LATTICE PLANE. THIS POINT WOULD THUS SCATTER WITH PHASE $1/r$ TIMES THE PHASE $n(m\vec{a})$ OF THE POINT AT $n\vec{a}$ (WE WOULD PICK UP THE REMAINING PHASE DIFFERENCE $(1-1/r)mn \cdot 2\pi$ IN MOVING FROM Q TO THE TERMINUS ATOM AT $n\vec{a}$)

SIMILARLY, WE WOULD ACCUMULATE $1/r$ OF THE TOTAL PHASE DIFFERENCE $mn \cdot 2\pi$ IN MOVING FROM THE ORIGIN TO Q' AND AN ADDITIONAL PHASE DIFFERENCE $(1-1/r)mn \cdot 2\pi$ IN MOVING FROM Q' TO THE ATOM AT THE TERMINUS $m\vec{b}$. BUT PATH DIFFERENCE FROM Q' TO THIS POINT IS IN THE SAME DIRECTION AND BY THE SAME DISTANCE AS THE PATH FROM Q TO P . IN TOTAL, THEN, THE PHASE OF THE RAY THAT WOULD BE SCATTERED FROM P IS $1/r nm + (1-1/r nm) = nm$ THEREFORE THE ARBITRARILY-SELECTED POINT P SCATTERS WITH THE SAME PHASE RELATIVE TO THE ORIGIN AS THE ATOM AT $n\vec{a}$ AND $m\vec{b}$ AND ANY POINT ON THIS PLANE SCATTERS EXACTLY IN PHASE!

AS THE FINAL STEP IN THIS SET OF CONSIDERATIONS, LET'S EXAMINE THE CONSTRAINTS IMPOSED ON THE RELATIVE ORIENTATIONS OF THE INCIDENT BEAM \vec{S}_0 AND THE DIFFRACTED BEAM \vec{S} IF ALL POINTS ON THE RATIONAL LATTICE PLANE MUST SCATTER EXACTLY IN PHASE



CONSIDER TWO POINTS ON THE LATTICE PLANE, P AND P', THAT ARE SEPARATED BY ΔX . THE INCIDENT BEAM \vec{S}_0 TRAVELS AN EXTRA DISTANCE $\Delta X \cos \alpha$ WHERE α IS THE ANGLE OF INCIDENCE OF \vec{S}_0 ON THE LATTICE PLANE. AFTER DIFFRACTION THE BEAM SCATTERED FROM P TRAVELS AN EXTRA DISTANCE $\Delta X \cos \beta$. THE PATH DIFFERENCE BETWEEN THE TWO BEAMS IS NOT ZERO BUT IS

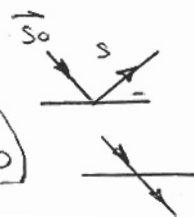
$$\Delta X \cos \alpha - \Delta X \cos \beta = \Delta X (\cos \alpha - \cos \beta)$$

THE PATH DIFFERENCE AND PHASE DIFFERENCE IS SUPPOSED TO BE ZERO FOR THESE TWO RAYS. THIS CAN BE TRUE ONLY IF $\Delta X = 0$ (WHICH DOESN'T HELP - THE PHASE DIFFERENCE MUST BE ZERO FOR ALL POINTS!) THIS LEAVES THE ONLY POSSIBILITY, THAT $\cos \alpha - \cos \beta = 0$

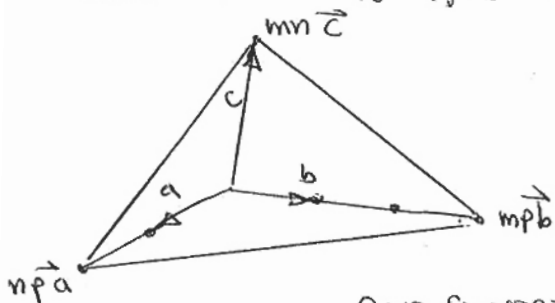
$$\therefore \cos \alpha = \cos \beta$$

AND THE ONLY SOLUTIONS ARE

$\alpha = \beta$	SPECULAR REFLECTION
$\alpha = -\beta$	TRANSMISSION WITHOUT BEING SCATTERED



FINALLY, THE PLANE THAT WE HAVE CONSTRUCTED IS A RATIONAL LATTICE PLANE WITH INTERCEPTS np ON \vec{a} mp ON \vec{b} mn ON \vec{c}



WE CAN FIND THE MILLER-BRAVAIS INDICES OF THIS PLANE BY TAKING THE RECIPROALS OF THE INTERCEPTS (IN UNITS OF THE TRANSLATION IN THAT DIRECTION)

$$hkl \propto \frac{1}{np} \quad \frac{1}{mp} \quad \frac{1}{mn}$$

AND CONVERTING TO INTEGERS BY MULTIPLYING THROUGH BY THE

INTEGER mnp

$$\therefore (hkl) = (mnp) !!$$

what we have thus shown, then, is that when the conditions expressed by the Laue equations are satisfied for diffraction by \vec{a} in the m^{th} order, diffraction by \vec{b} in the n^{th} order and diffraction by \vec{c} in the p^{th} order, the relative arrangement of the incident beam \vec{S}_0 and the diffracted beam \vec{S} is such that they look like they have undergone specular reflection from the rational lattice plane (mnp) .

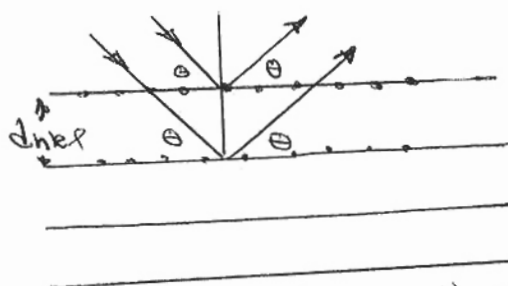
\rightarrow (angle of incidence = angle of reflection)

This being the case, we can rewrite the Laue equations in terms of the Miller indices of the lattice plane that is "reflecting" them:

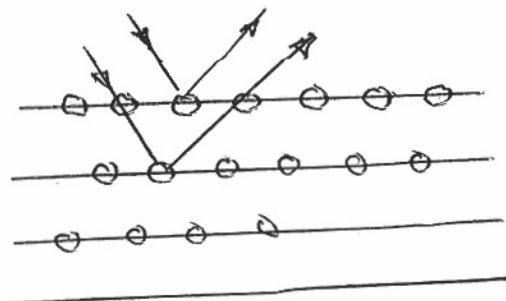
$$\begin{aligned}
 (\vec{S} - \vec{S}_0) \cdot \vec{a} &= h\lambda = a \cos \bar{\nu}_1 - a \cos \bar{\mu}_1 \\
 (\vec{S} - \vec{S}_0) \cdot \vec{b} &= k\lambda = b \cos \bar{\nu}_2 - b \cos \bar{\mu}_2 \\
 (\vec{S} - \vec{S}_0) \cdot \vec{c} &= l\lambda = c \cos \bar{\nu}_3 - c \cos \bar{\mu}_3
 \end{aligned}$$

REHABILITATION OF PROFESSOR BRAGG

BRAGG'S FAMOUS LAW IS USUALLY PRESENTED IN TERMS OF "LATTICE PLANES". WE HAVE DEALT WITH HIS EQUATION RATHER HARSHLY, CLAIMING THAT LATTICE PLANES ARE FICTIONAL CONSTRUCTS — LATTICE PLANES DON'T SCATTER, ATOMS DO! THUS FAR WE HAVE DEALT WITH STRUCTURES THAT HAVE ONLY ONE ATOM PER LATTICE POINT. THERE IS NO UNIQUE ORIGIN TO THE LATTICE POINT SO WE ARE FREE TO PLACE IT RIGHT AT THE ATOM IF WE SO CHOOSE



REFLECTING LATTICE PLANES

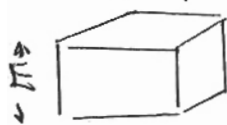


SCATTERING ATOMS

THE RELATION $n\lambda = 2d_{hkl} \sin \theta$ HAS TO HOLD TRUE FOR BOTH ^{SHEETS OF} SCATTERING ATOMS AND STACKS OF CONSTRUCTED LATTICE PLANES IF ATOMS ON SUBSEQUENT LAYERS ARE TO SCATTER IN PHASE. SO FAR SO GOOD. WHAT IS OMITTED FROM BRAGG'S LAW, AS IT IS USUALLY PRESENTED, IS THE DEMONSTRATION THAT, IN ORDER FOR ALL THE ATOMS IN THE SAME LAYER TO SCATTER IN PHASE, IT IS NECESSARY FOR THE ANGLE OF INCIDENCE TO BE EQUAL TO THE ANGLE OF REFLECTION: OR, SPECULAR SCATTERING!

A PLEA FOR WELL-CRAFTED CRYSTALLOGRAPHIC GRAMMAR. IN THE

IN THE ABOVE DIAGRAMS WE HAVE IDENTIFIED INTERPLANAR SPACINGS, d_{hkl} . THIS IS AN ACCEPTABLE STATEMENT! PEOPLE CONSTANTLY REFER TO SUCH SPACINGS IN A CRYSTAL AS "... THE d -SPACINGS". YUK!



HERE IS A CUBE. THE LENGTH OF ITS EDGE IS E . WOULD ONE SUBSEQUENTLY REFER TO "E-EDGES"

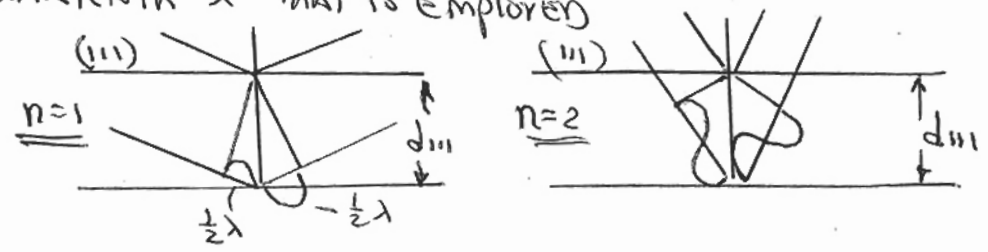
OR "L-LENGTHS" OR "TEA-TIMES" ??! NO!

SO NO "... d -SPACINGS, IF YOU PLEASE!"

ON THE MESSY FACTOR OF n

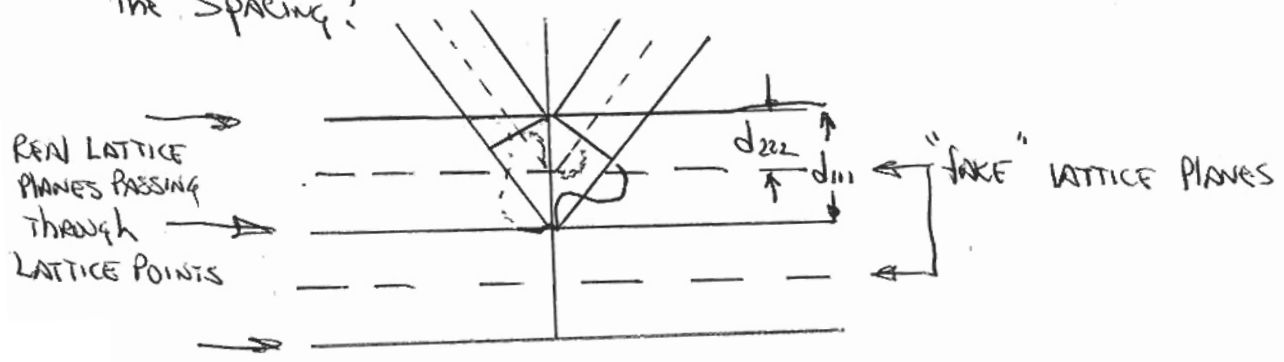
IN DIFFRACTION FROM A GIVEN SET OF PLANES - (111) SAY - ONE PRODUCES A SUBSTANTIAL NUMBER OF ORDERS OF INTERFERENCE THAT IS LIMITED ONLY BY THE VALUE OF THE WAVELENGTH λ THAT IS EMPLOYED

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



IT IS GOING TO BE INCONVENIENT TO BE FORCED TO REFER TO THE "FIRST ORDER REFLECTION FROM (111)" AND -- "THE SECOND ORDER REFLECTION FROM (111)" -- AND SO ON. IT WOULD BE NICE IF EVERYTHING WERE FIRST ORDER THEN WE COULD IDENTIFY THE INDICES OF THE DIFFRACTING PLANE SIMPLY BY hkl !

SINCE hkl ARE DEFINED BY INTERCEPTS ON AXES WE CAN DO THIS BY DESCRIBING THE SECOND-ORDER DIFFRACTION MAXIMUM FROM (111) BY DEFINING THIS AS THE (222) MAXIMUM. A "(222)" PLANE DOES NOT EXIST! BUT IF WE WOULD ATTEMPT TO DRAW IT, A FAKE PLANE WOULD BE INSERTED IN THE STACK AS DOUBLING THE INDICES WOULD HALVE THE SPACING!



IT IS THUS CONVENIENT TO DENOTE THE n^{th} ORDER DIFFRACTION FROM (hkl) AS THE ($nh nk nl$) MAXIMUM. ONE THEN NO LONGER HAS TO KEEP TRACK OF "ORDER"