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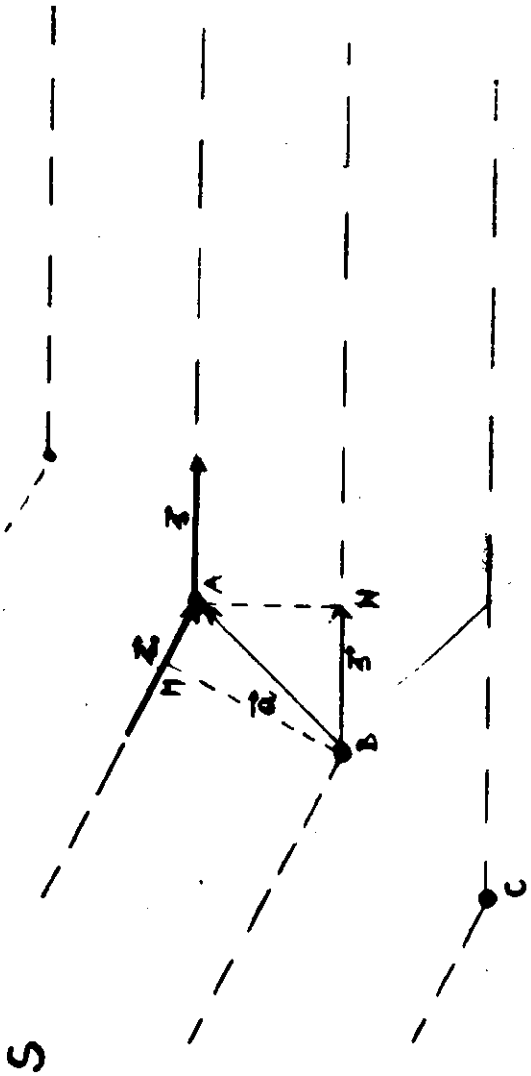
SMR/348 - 10

EXPERIMENTAL WORKSHOP ON
HIGH TEMPERATURE SUPERCONDUCTORS
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INTRODUCTION TO X-RAY DIFFRACTION ACTIVITY

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These are preliminary lecture notes, intended only for distribution to participants.



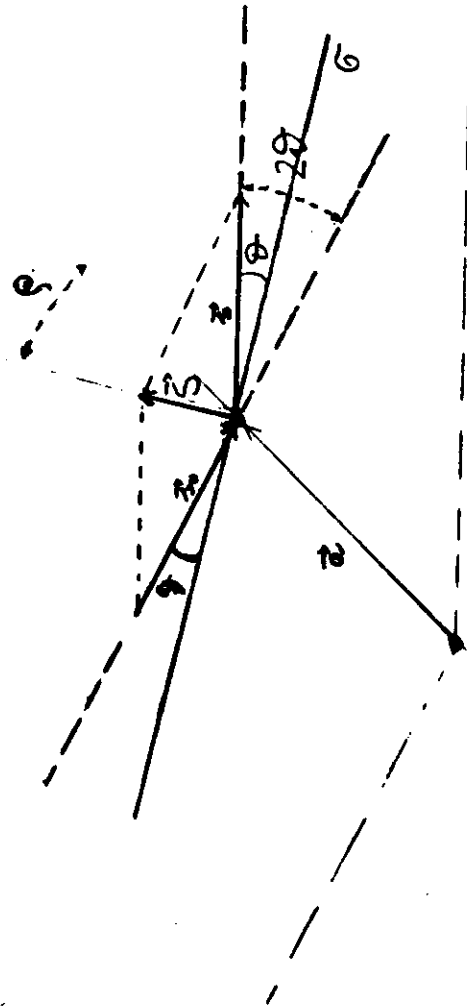
Q

$$|\vec{S}| = |\vec{S}_0| = \frac{1}{\lambda}$$

$$\Delta = \overline{BN} - \overline{AH} = \vec{a} \cdot (\vec{S} - \vec{S}_0)$$

$$\Delta = \vec{a} \cdot \vec{S}$$

$$|\vec{S}| = \frac{2 \sin \theta}{\lambda}$$



1

Line of identical scattering points

$$A_A = \frac{A^0}{R} e^{i\omega t}$$

$$A_B = \frac{A^0}{R} e^{i\omega t + 2\pi \vec{a} \cdot \vec{S}}$$

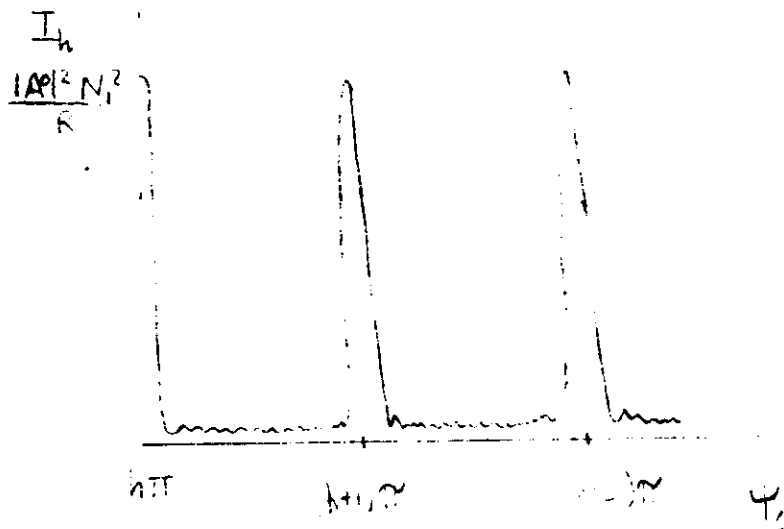
$$A = \frac{A^0}{R} e^{i\omega t} \sum_{u=0}^{N_1-1} e^{i2\pi u (\vec{a} \cdot \vec{S})}$$

$$I = A \cdot A^* = \frac{|A^0|^2}{R^2} \frac{\sin^2(N_1 \psi_1)}{\sin^2 \psi_1} \quad \text{where } \psi_1 = \frac{1}{2} \pi (\vec{a} \cdot \vec{S})$$

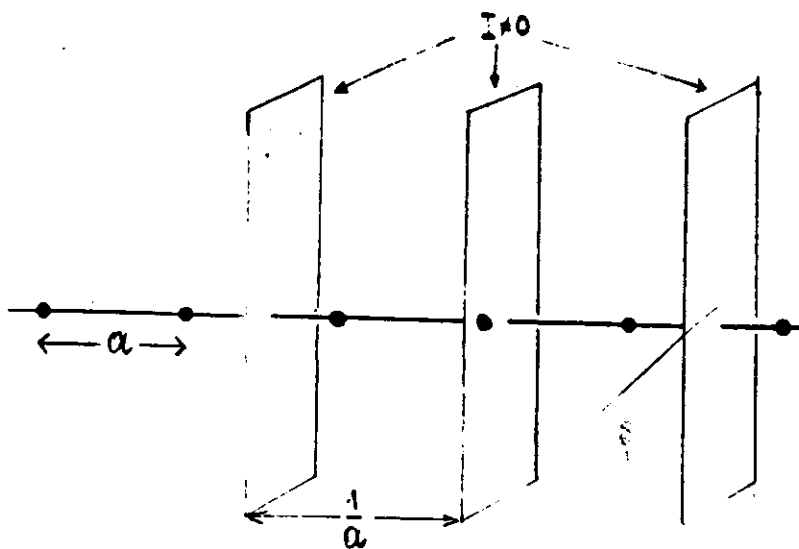
$$\text{if } N_1 \rightarrow \infty$$

$$I_h = \frac{|A^0|^2}{R^2} N_1^2 \quad \text{when } \pi (\vec{a} \cdot \vec{S}) = h\pi \quad \text{with } h \text{ integer}$$

$$\vec{S} \cdot \vec{a} = h$$

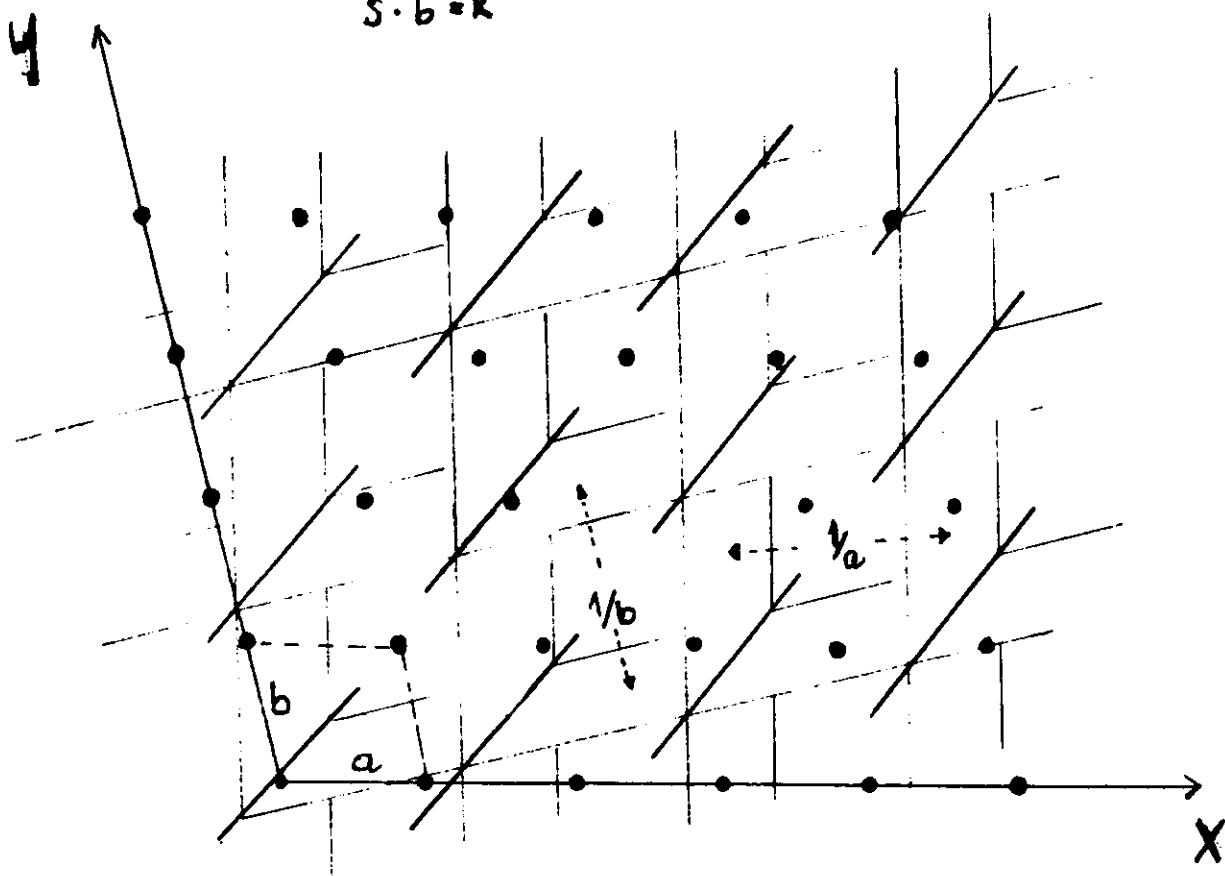


(2)



$$\vec{S} \cdot \vec{a} = h$$

$$\begin{aligned} \vec{S} \cdot \vec{a} &= h \\ \vec{S} \cdot \vec{b} &= k \end{aligned}$$



Space-lattice of identical scattering points

$$A = \frac{A^0}{R} e^{i\omega t} \sum_u^{N_1-1} \sum_v^{N_2-1} \sum_w^{N_3-1} e^{i2\pi(u\vec{a} + v\vec{b} + w\vec{c}) \cdot \vec{S}}$$

$$\left\{ \begin{array}{l} I_{hkl} = \frac{|A^0|^2}{R^2} N_1^2 N_2^2 N_3^2 \quad (N_1, N_2, N_3 \rightarrow \infty) \\ \vec{S} \cdot \vec{a} = h \\ \vec{S} \cdot \vec{b} = k \\ \vec{S} \cdot \vec{c} = l \end{array} \right. \quad (h, k, l \text{ integer})$$

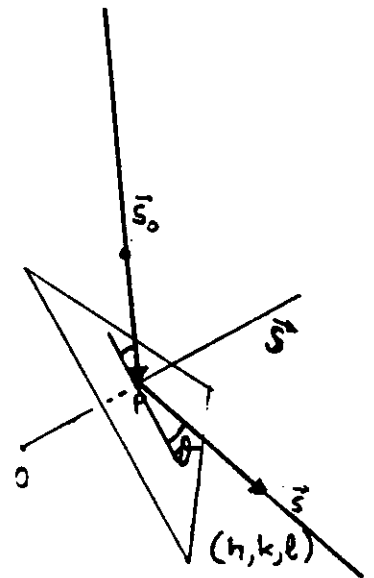
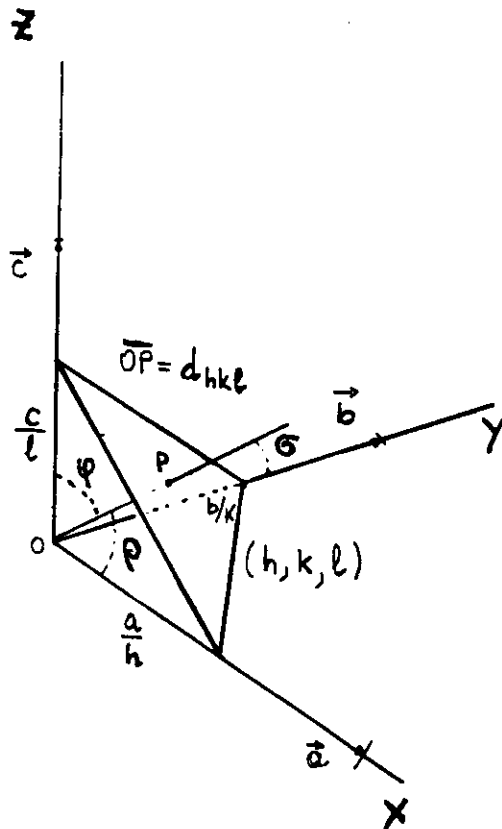
Lane equations

$$\begin{aligned}
 \vec{S} \cdot \vec{a} &= h & ; & \quad 2 \sin \theta \cdot a \cdot \cos \rho = h \lambda \\
 \vec{S} \cdot \vec{b} &= k & ; & \quad 2 \sin \theta \cdot b \cdot \cos \sigma = k \lambda \\
 \vec{S} \cdot \vec{c} &= l & ; & \quad 2 \sin \theta \cdot c \cdot \cos \varphi = l \lambda
 \end{aligned}
 \quad (1) \quad h, k, l \text{ integers}$$

$$d_{hkl} = \frac{a}{h} \cos \rho = \frac{b}{k} \cos \sigma = \frac{c}{l} \cos \varphi \quad (2)$$

Bragg equation $\underline{2 d_{hkl} \sin \theta = \lambda}$; $\vec{OP} = \vec{S}$

$$d_{hkl} = \frac{1}{|\vec{S}|_{hkl}}$$

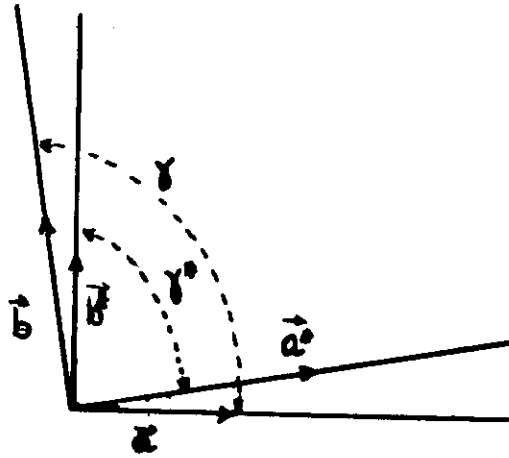


Reciprocal lattice

$$\vec{S}_{hke} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$\vec{a}^* \cdot \vec{b} = \vec{a}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{c} = \vec{b}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{a} = \vec{c}^* \cdot \vec{b} = 0$$

$$\vec{a}^* \cdot \vec{a} = \vec{b}^* \cdot \vec{b} = \vec{c}^* \cdot \vec{c} = 1$$



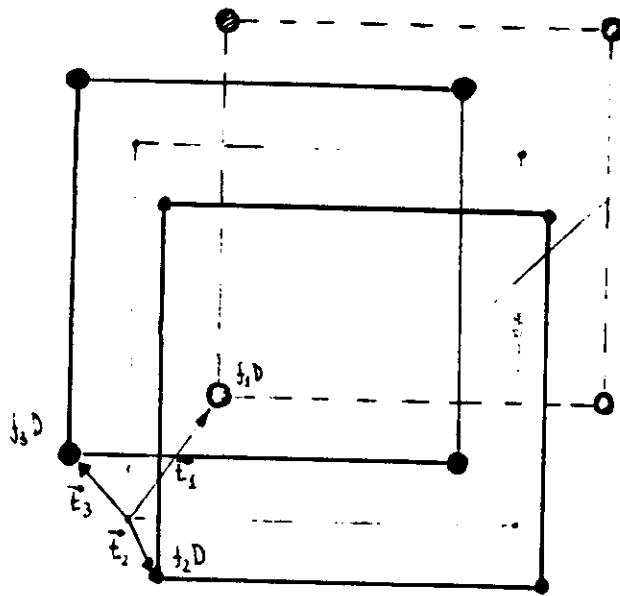
$$d_{hke} = \frac{1}{|\vec{S}_{hke}|} \quad \text{where}$$

$$|\vec{S}_{hke}|^2 = |h\vec{a}^* + k\vec{b}^* + l\vec{c}^*|^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hk a^* b^* \cos \gamma^* + 2kl b^* c^* \cos \alpha^* + 2lh a^* c^* \cos \beta^*$$

for cubic unit cells:

$$d_{hke} = \frac{1}{a^3 (h^2 + k^2 + l^2)^{1/2}} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

Crystal



$$\vec{r}_i = x_i \vec{a} + y_i \vec{b} + z_i \vec{c}$$

$$A_i = \frac{A_i^0}{R} e^{i\omega t} \sum_u \sum_v \sum_w e^{i2\pi [u\vec{a} + v\vec{b} + w\vec{c}] \cdot \vec{r}_i} \cdot \vec{S} = \frac{e^{i\omega t}}{R} A_i^0 \vec{r}_i \cdot \vec{S} \sum_u \sum_v \sum_w e^{i2\pi \vec{r}_i \cdot \vec{S}}$$

$$A = A_1 + A_2 + \dots + A_p = \frac{e^{i\omega t}}{R} \left(A_1^0 e^{i2\pi \vec{r}_1 \cdot \vec{S}} + \dots + A_p^0 e^{i2\pi \vec{r}_p \cdot \vec{S}} \right) \sum_u \sum_v \sum_w e^{i2\pi \vec{r}_i \cdot \vec{S}}$$

$$A = \frac{e^{i\omega t}}{R} \left(\sum_i^p A_i^0 e^{i2\pi \vec{r}_i \cdot \vec{S}} \right) \sum_u \sum_v \sum_w e^{i2\pi \vec{r}_i \cdot \vec{S}}$$

when $N_1, N_2, N_3 \rightarrow \infty$

$$A_{hke} = \frac{e^{i\omega t}}{R} (N_1 N_2 N_3) \sum_i^p A_i^0 e^{i2\pi \vec{S} \cdot \vec{r}_i}$$

since $\vec{S} \cdot \vec{r}_i = (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) (x_i \vec{a} + y_i \vec{b} + z_i \vec{c}) = hx_i + ky_i + lz_i$

$$A_{hke} = \frac{1}{R} \sum_i^p A_i^0 e^{i2\pi (hx_i + ky_i + lz_i)}$$

if $A_i^0 = f_i D$

$$F_{hke} = \sum_i^p f_i e^{i2\pi (hx_i + ky_i + lz_i)}$$

Structure factor

$$\rho(x, y, z) = \frac{1}{V_{\text{cell}}} \sum_h \sum_k \sum_{l=-\infty}^{+\infty} F_{hkl} e^{-2\pi i (hx + ky + lz)}$$

$$\rho(x, y, z) = \frac{2}{V_{\text{cell}}} \sum_h \sum_k \sum_{l=0}^{\infty} |F_{hkl}| \cos \left\{ 2\pi (hx + ky + lz + \frac{\phi}{2\pi}) \right\}$$

phase

PHASE PROBLEM

Collection of the XR pattern

Powder methods

1. Determination of the unit cell
2. Refinement of "simple" crystal structures (Rietveld method)
3. Crystallite size, etc.

Intensity is collected as function of θ . Thus diffracted beams with equal or very close θ overlap.

Single crystal methods

1. Determination of the unit cell
2. Solution of the crystal structure
3. Refinement of the crystal structure

Intensity of each diffracted beam is measured without overlap.

REFERENCES

1. THE CRYSTALLINE STATE Vol. II ed. L. Bragg "The optical Principles of the Diffraction of X-Rays" by R.W. James
C. Bell & Sons, London, 1967
2. THE CRYSTAL STRUCTURE OF SOLIDS by P.J. Brown,
J.B. Forsyth ; Edward Arnold. Ltd., London, 1973

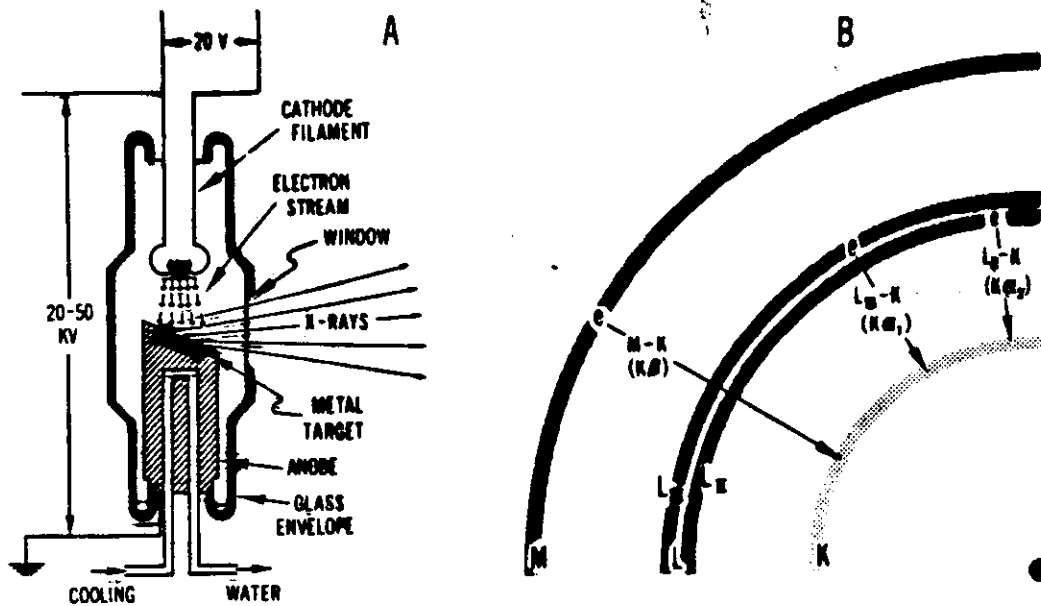


FIGURE 13-1

(A) Generalized cross section through an X-ray tube. High-energy electrons from the cathode strike the metal target on the anode, exciting the metal atoms by "knocking" electrons out of their *K* shells.

(B) Schematic energy-level diagram illustrating how the excited *K* shell captures electrons from outer shells, the *M-K* transition producing *K β* X-rays, the *L-K* transitions producing *K α_1* and *K α_2* X-rays.

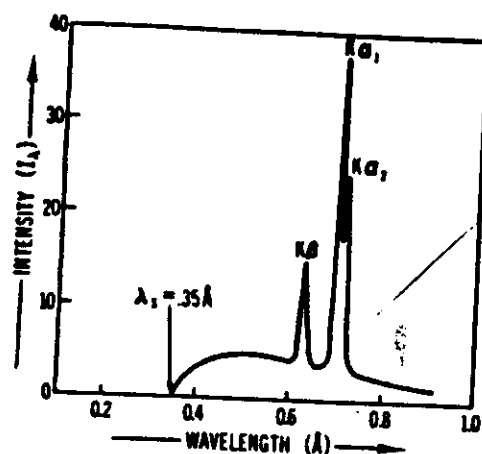


FIGURE 13-2

Relative intensities I_λ for the various wavelengths of X-rays emitted by an X-ray tube with a molybdenum target operated at 35 kV.

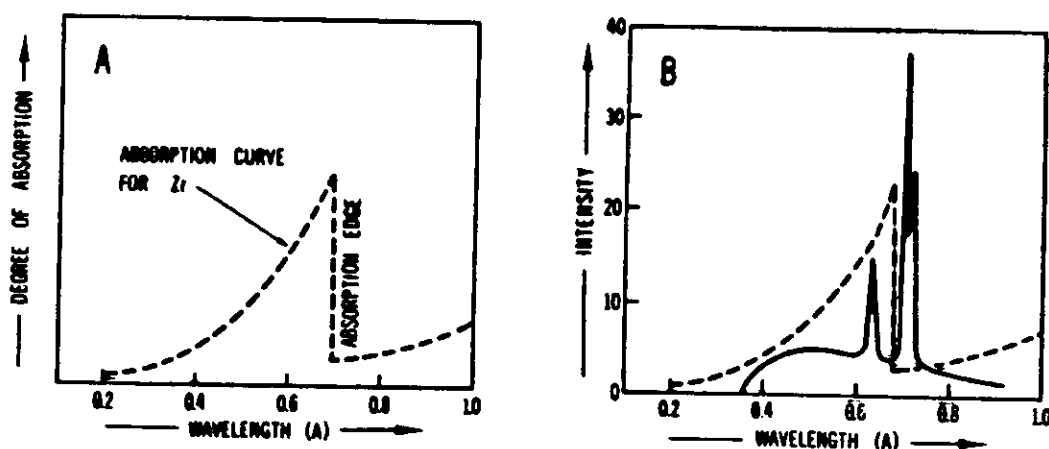


FIGURE 13-3

(A) Absorption curve for zirconium foil for X-rays of wavelengths between 0.2 and 1.0 Å. The abrupt decrease in ability to absorb at $\lambda = 0.687$ Å marks zirconium's *absorption edge*.

(B) Curve showing the intensities of X-rays emitted by a molybdenum tube operated at 35 kV on which is superimposed the absorption curve for zirconium foil. The absorption edge for zirconium (atomic number, 40) falls between the $K\beta$ and $K\alpha$ peaks for molybdenum (atomic number, 42). This permits zirconium foil to filter out the $MoK\beta$ radiation from the X-rays emitted by a molybdenum tube.

contains many thousands of small, randomly oriented crystals, and consequently many grains are expected to be in the proper position at all times to permit diffraction from all the permissible lattice planes.

Figure 1a illustrates a single grain in a powder sample which has a lattice layer oriented perpendicular to the page of the book and is inclined to the incident x-ray beam at the appropriate diffraction angle θ . The diffracted beam, still in the plane of the paper, is inclined to the lattice layer by the same angle θ and to the direct beam by angle 2θ . Since there are many thousands of grains in the powder sample, several of them will be in a position such that they have the same lattice layer inclined to the

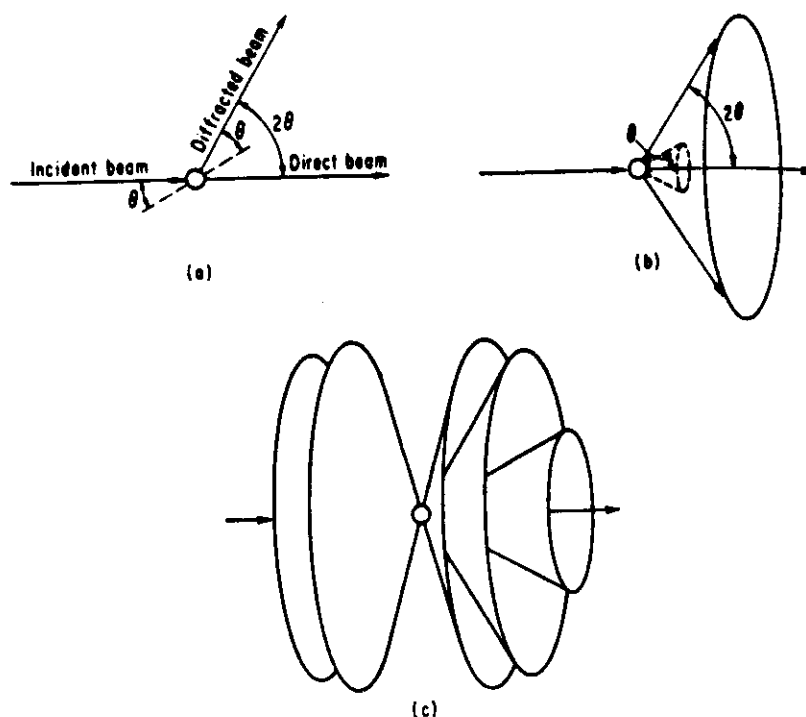


FIG. 1. Illustration of the diffraction of x-rays (a) by a lattice layer of a single grain. (b) by identical lattice layers from many grains, and (c) by different lattice layers of many grains.

incident beam by the same angle θ of Fig. 1a, and since the Bragg equation defines the inclination of the lattice plane in one dimension only, there will be identical lattice layers in the proper diffraction position oriented tangentially along the surface of a cone whose inclination with the direct beam will be θ . Similarly there will be a cone of diffracted beams inclined to the direct beam by an angle of 2θ (see Fig. 1b). Simultaneously, other lattice layers with different interplanar spacing and, consequently, with different θ inclination will be in diffracting position, thus giving rise to various diffraction cones. Several diffraction cones are illustrated in Fig. 1c.

All the powder cameras are designed to record these diffraction cones; however, many of them differ in the geometry and construction of the design. There are three major types of powder cameras: (1) the Debye-Scherrer camera, (2) the focusing cameras, and (3) the flat-film cameras. These three cameras select different ranges of the diffraction spectrum, record the diffraction cones in different ways, and emphasize

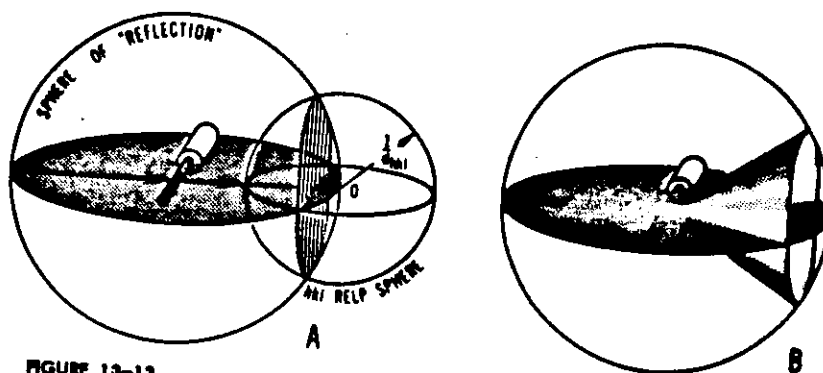


FIGURE 13-13

(A) Where a powder rod is struck by the direct beam, we locate the center of the imaginary sphere of reflection (radius, $1/\lambda$). The origin of the reciprocal lattice for each of the variously oriented grains in the powder rod is at O , the point where the direct beam emerges from this sphere of reflection. If the same hkl relp were plotted, for example, relp 213, for each of these variously oriented grains, a relp sphere would result of radius $1/d_{hkl}$, that is, of radius $1/d_{213}$ for our specific example. This relp sphere intersects the sphere of reflection in the dotted circle (vertically ruled). (B) From the powder rod, diffracted rays travel toward those relps located on the dotted circle to form the cone shown. Numerous other relp spheres, each with a different radius, for example, $1/d_{100}$, $1/d_{111}$, $1/d_{221}$, could be drawn centered at O and would similarly intersect the sphere of reflection in circles to which cones of diffracted rays would proceed from the powder rod.

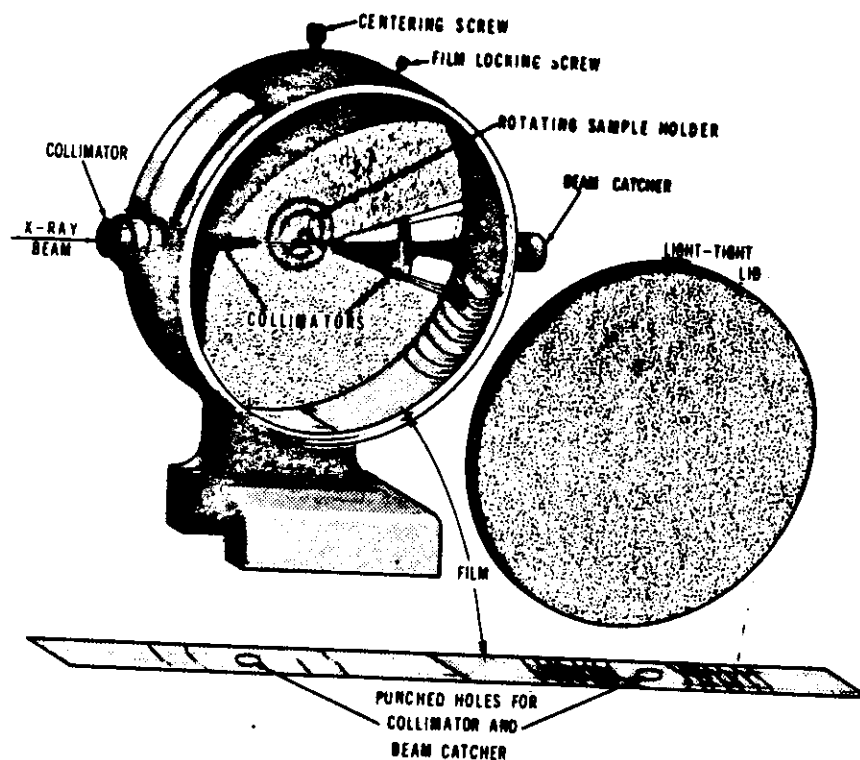


FIGURE 13-12

Schematic view of a powder camera with its light-tight lid removed. Its collimator is placed against the exit port of the X-ray tube and blocks out all X-rays except a fine beam that impinges on the powder rod. This powder rod is rotated about its axis by a small motor which is not shown. For reasons to be discussed in Figure 13-13, cones of diffracted X-rays emanate from the powder rod where it is struck by the direct beam, these cones exposing the film in a series of arcs which, after the film is developed, might appear as shown here.

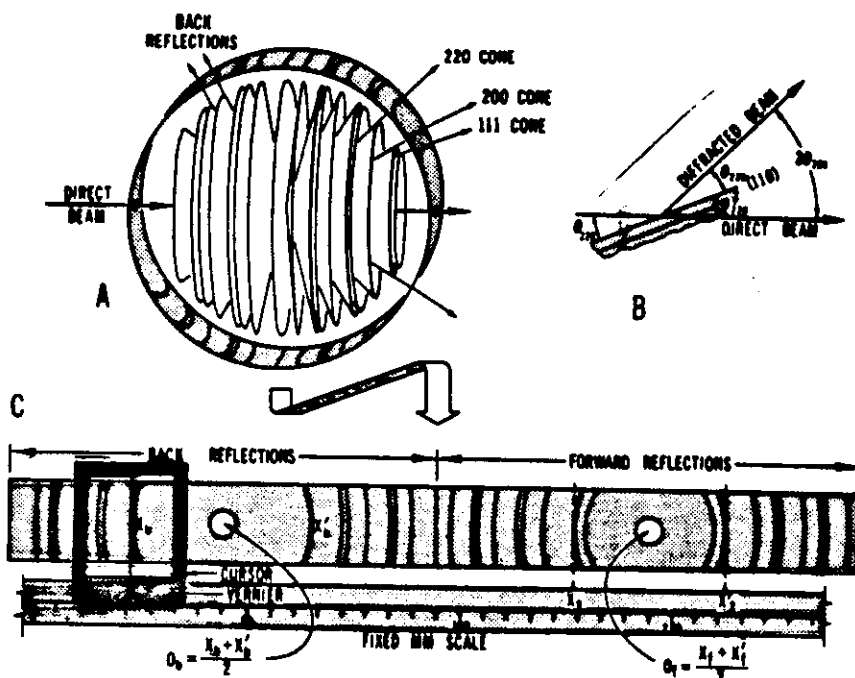


FIGURE 13-14

(A) The numerous cones of diffracted rays that emanate from a powder rod (hidden by the cones) expose the film strip in a powder camera to produce a series of arcs. The powder camera itself is not shown. The powder rod would be rotating on its axis, which is also the axis of the squat cylinder formed by the film strip. (B) Cross section (enlarged 100,000,000X) of a grain whose diffracted beam lies along the arrow on the 220 cone in (A). As this cross section is rotated 360° around the direct beam as an axis, it successively represents the cross section of each grain in the rod that produces a diffracted ray lying in the 220 cone. If we compare this cross section with itself after a 180° rotation around the direct beam, we see that 4θ represents the cone angle, that is, the angle between the two most divergent rays in the same diffraction cone.

(C) Enlarged drawing of the film in (A) after its processing and mounting onto a device for measuring the distance between arcs on a powder film. For example, the cursor now indicates the midpoint of arc x_1 to be above 40.6 on the fixed millimeter scale (whose finer divisions have been largely omitted). The cursor could next be slid to coincide with the midpoint of x_1' . The distance in millimeters between x_1 and x_1' , corrected for film shrinkage, equals 4θ for the cone which produced these arcs, if a powder camera was used whose circumference equals 360 mm. Similarly, we could determine 4θ for arcs resultant from forward reflections, for example, the distance between x_1 and x_1' . Note that O_0 , the arithmetic average of two arcs from the same back-reflected diffraction cone [$\frac{1}{2}(x_1 + x_1')$] marks the point where the direct beam enters the film in (A). Similarly O_1 , the arithmetic average of two arcs from the same forward-reflected cone, is the coordinate of the point where the direct beam leaves the powder camera (through a hole punched in the film). The intensities of the back reflections are greatly exaggerated.

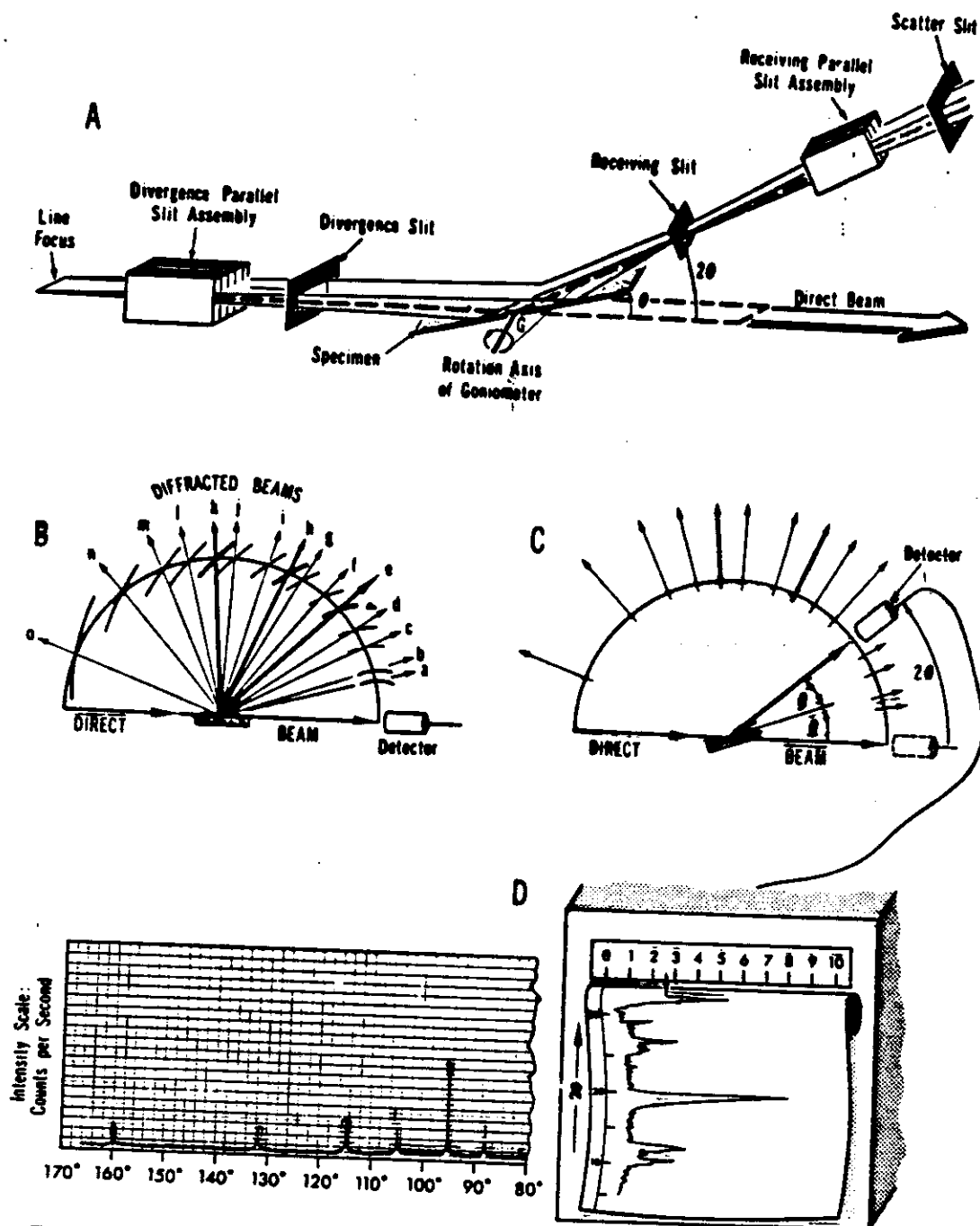


FIGURE 13-21

- (A) Schematic drawing of the principal parts of an x-ray diffractometer. X-rays from the tube's line focus are collimated by passage through a parallel slit assembly (Soller slit) and a divergence slit before striking the powder (stippled) on a glass slide or sample holder. While the slide (length exaggerated) rotates about axis G so as to be at an angle θ to the direct beam, a detector (stripped of its housing to reveal its receiving, Soller, and scatter slits) scans through the angle 2θ .
- (B) Segments of rhp spheres $a, b, \dots m, n, o$ for the crystalline powder intersect the sphere of reflection (semicircle) to produce diffracted rays $a, b, \dots m, n, o$.
- (C) While the sample rotates through an angle θ about the axis G , which is now

$$d_{hkl}^2 = \frac{a^2}{(h^2 + k^2 + l^2)}$$

$$\left(\frac{d_1}{d_{hkl}}\right)^2 = \frac{h^2 + k^2 + l^2}{h_1^2 + k_1^2 + l_1^2}$$

$$\begin{array}{l} N \\ \left. \begin{array}{l} 100 \\ 010 \\ 001 \end{array} \right\} 1 \\ \left. \begin{array}{l} 110 \\ 011 \\ 101 \end{array} \right\} 2 \\ 111 \quad 3 \end{array}$$

TABLE 13-5

Observed 2θ and Calculated d_1^2/d^2 Values for a Powder Film of Synthetic Spinel, $MgAl_2O_4$

$2\theta_{obs}$	d_{hkl}	d_{hkl}^2	d_1^2/d^2	hkl	N^a	d_{calc}^b
19.02 α	4.6658	21.7697	1	111	3	8.0814
31.30 α	2.8577	8.1664	2.666	220	8	8.0828
36.894 α	2.4365	5.9365	3.667	311	11	8.0810
44.84 α	2.0212	4.0852	5.329	400	16	8.0848
55.702 α	1.6501	2.7232	7.994	422	24	8.0838
59.427 α	1.5553	2.4190	8.999	511/333	27	8.0816
65.287 α	1.4291	2.0423	10.659	440	32	8.0842
68.736 α	1.3656	1.8649	11.673	531	35	8.0790
74.19 α	1.2781	1.6335	13.327	620	40	8.0834
77.388 α	1.2331	1.5205	14.317	533	43	8.0860
82.691 α	1.1670	1.3619	15.984	444	48	8.0852
85.78 α	1.1327	1.2830	16.968	711/551	51	8.0891
94.171 α_1	1.0517	1.1063	19.678	731/553	59	8.0783
94.451 α_2	1.0520					8.0806
99.37 α_1	1.0102					8.0816
99.72 α_2	1.0101					8.0808
107.92 α_1	0.95257	0.90729	23.994	822/660	72	8.0828
108.327 α_2	0.95248					8.0821
111.26 α_1	0.93318					8.0816
111.656 α_2	0.93330	0.87094	24.995	751/555	75	8.0826
116.944 α_1	0.90365	0.81640	26.665	840	80	8.0825
117.45 α_2	0.90345					8.0807
120.50 α_1	0.88719	0.78582	27.667	911/753	83	8.0827
121.074 α_2	0.88686					8.0797
130.744 α_1	0.84733	0.71797	30.321	931	91	8.0836
131.366 α_2	0.84734					8.0831
138.028 α_1	0.82497					8.0830
138.785 α_2	0.82495	0.68056	31.987	844	96	8.0828

$$^a N = h^2 + k^2 + l^2$$

$$^b a = d\sqrt{N}$$

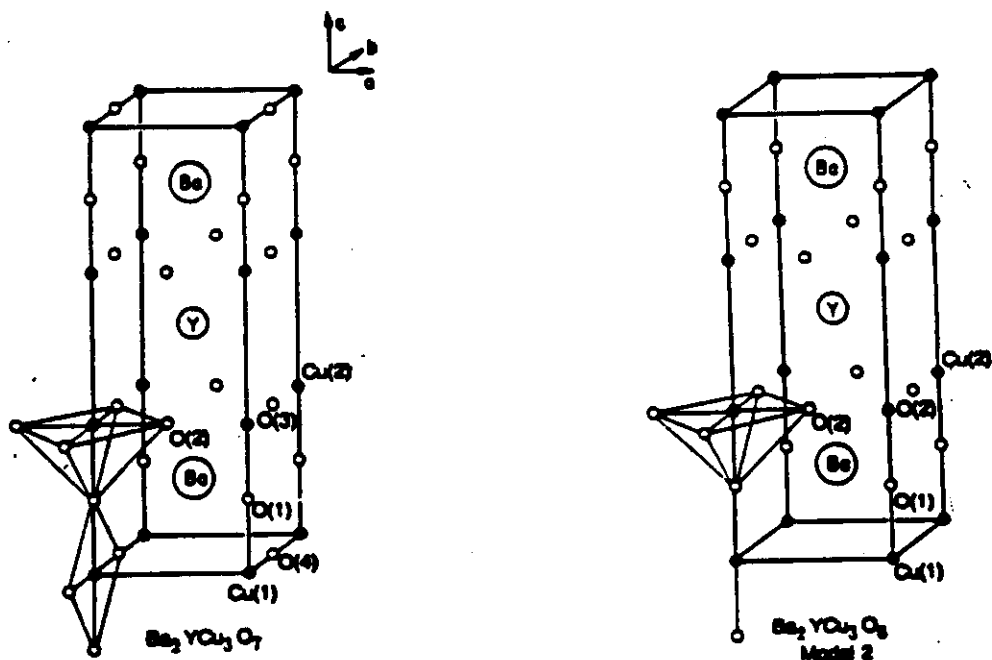
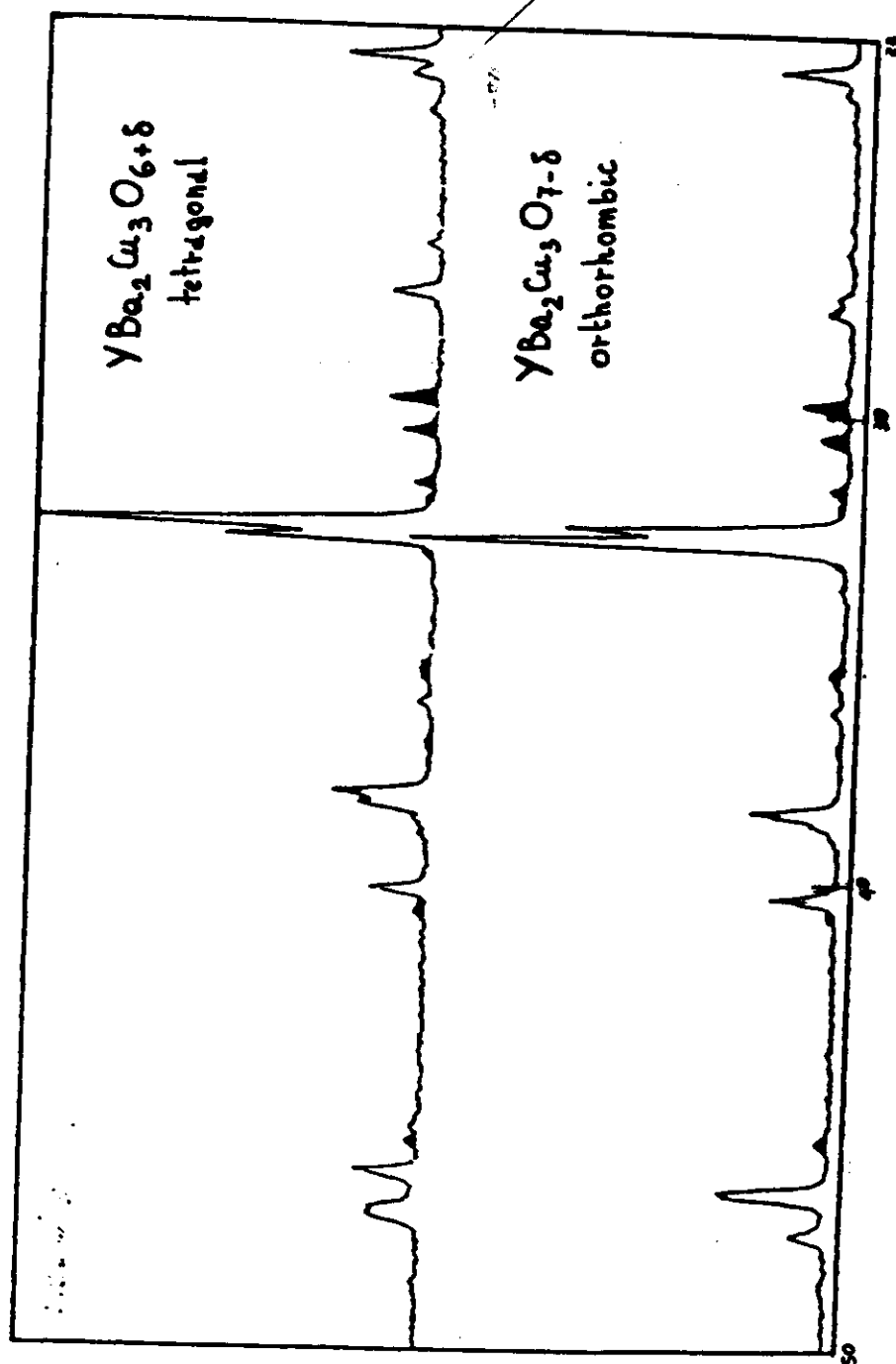


Fig. 1
Schematic unit cells for $\text{Ba}_2\text{YCu}_3\text{O}_x$.

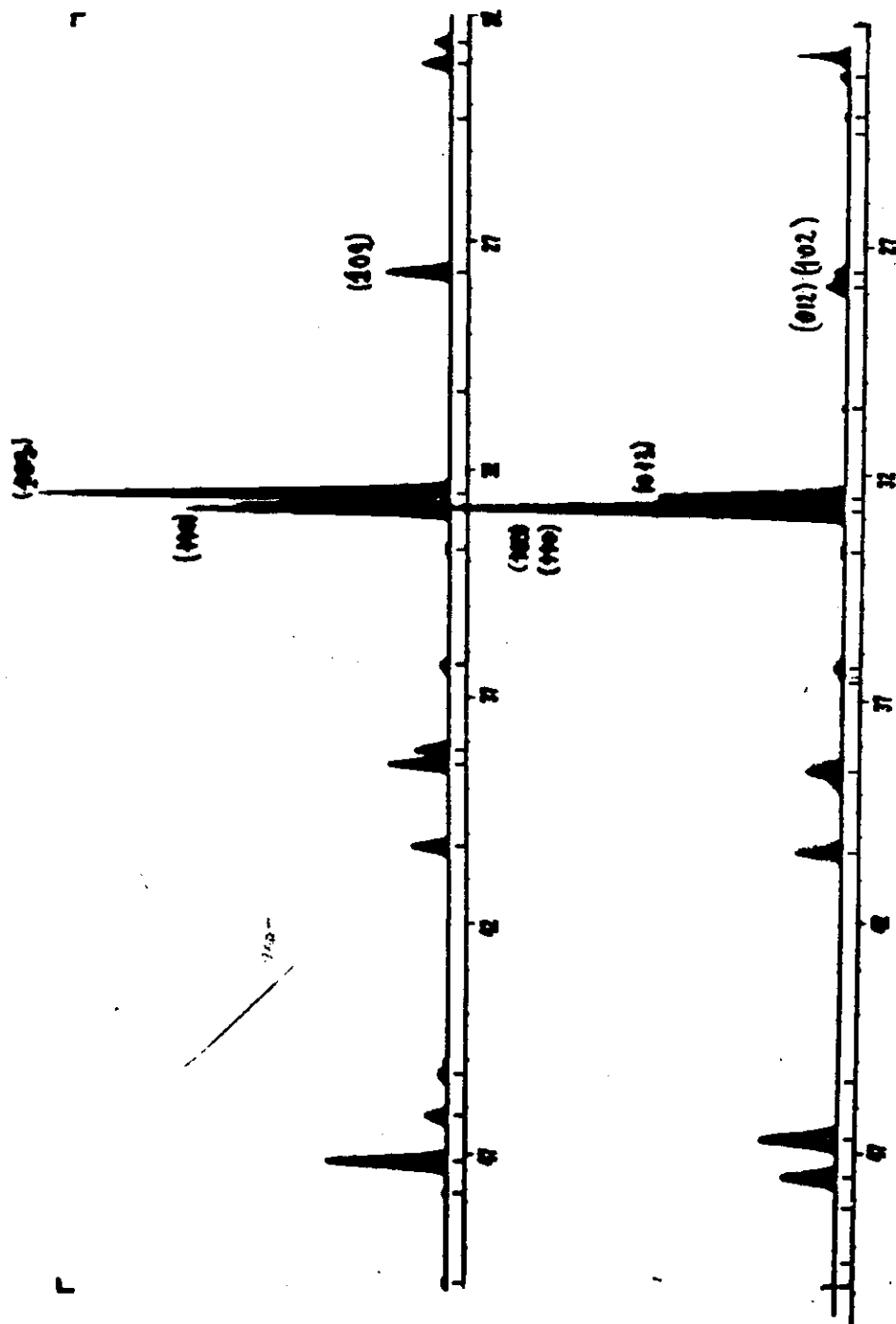
$$a = b = a_p$$

$$c = 3a_p$$



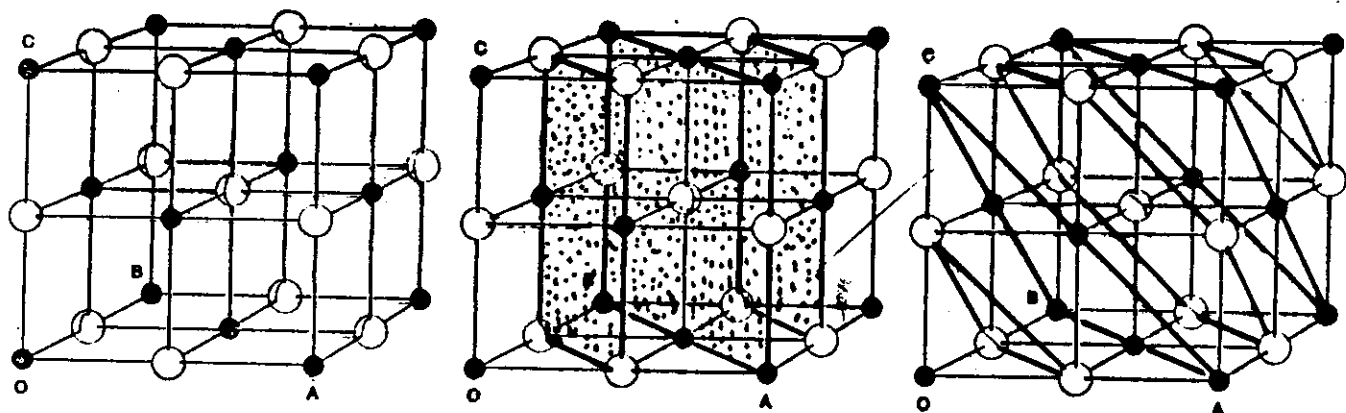
$a=b=3.86 \text{ \AA}$
 $c=11.80 \text{ \AA}$

$a=3.82 \text{ \AA}$
 $b=3.88 \text{ \AA}$
 $c=11.68 \text{ \AA}$



20

29



Questa figura mostra tre possibili disposizioni degli strati di atomi riflettenti in un cristallo di cloruro di sodio (rappresentate mediante piani colorati). Gli assi di questo semplice cristallo cubico sono indicati con OA , OB e OC . Nello schema a sinistra viene assegnato alla prima riflessione da parte di piani perpendicolari all'asse OA l'ordine (200), poiché vi è una differenza di percorso di due lunghezze d'onda tra O e A per piani riflettenti paralleli agli assi OB e OC ; (in que-

sto caso $h = 2$, $k = 0$ e $l = 0$). In modo analogo la riflessione iniziale da parte dei piani mostrati nello schema centrale viene designata con (220), mentre per lo schema a destra è (111) rispetto ai piani di cloro. In genere gli ordini con indici pari si riferiscono a strati identici, e hanno perciò come risultato riflessioni intense e in fase, mentre gli ordini con indici dispari provengono da strati occupati in modo alternato, e hanno perciò come risultato riflessioni deboli e sfasate.

Faremo qui un'analisi abbastanza dettagliata poiché, pur essendo questo particolare caso estremamente semplice, può esemplificare il procedimento generale. Uno sguardo ai diagrammi di struttura del cloruro di sodio mostra come i piani rappresentati siano di due tipi. Le riflessioni, o ordini, indicate con (200), (400), (600) ecc. e quelle indicate con (220), (440), (660) e così via hanno origine da strati atomici identici, ciascuno dei quali contiene un numero uguale di atomi di sodio e di cloro. Ci si aspetterebbe che la sequenza degli ordini successivi diminuisca regolarmente come intensità. Come mostra il disegno a destra della figura in alto, le riflessioni (111) provengono invece da un insieme di piani più complessi, in quanto gli strati sono alternativamente occupati da atomi di sodio e di cloro. Poiché per le riflessioni (111) vi è una differenza di percorso di una lunghezza d'onda rispetto ai piani intensamente riflettenti formati dagli atomi di cloro, le onde riflesse dai piani intermedi formati dagli atomi di sodio più debolmente riflettenti avranno fase opposta. L'ordine (111) sarà perciò debole, poiché il contributo del sodio annulla in parte quello del cloro; per l'ordine (222), invece, i contributi saranno in fase e quest'ordine sarà intenso.

In questo tipo di « reticolo spaziale », come viene chiamato, vi sono punti identici nel centro delle facce e nei vertici del cubo, il che implica che gli indici debbano essere o tutti dispari o tutti pari. Si possono generalizzare queste osservazioni dicendo che gli ordini con indici pari, come (200), (220) e

vrebbero essere relativamente deboli.

In effetti, questo è proprio ciò che si osserva. La figura a pag. 41 mostra uno dei primi gruppi di misure relative al cloruro di sodio e al cloruro di potassio fatte con lo spettrometro a ionizzazione, un apparato inventato da mio padre, W. H. Bragg, nel 1913. In ascisse sono riportate le misure dell'angolo di radenza, in ordinate le intensità della riflessione. I due picchi che si vedono in ciascun ordine sono le « righe » K_α e K_β dello spettro del palladio dell'anticatodo, la più intensa delle quali è la K_α . Gli ordini sono riflessi dalle facce del cristallo di indici cristallografici (100), (110) e (111). Come mostrano le curve, l'ordine (111) relativo al cloruro di sodio è piccolo in modo anormale, mentre l'ordine (222) entra nella stessa sequenza degli ordini (200) e (220). Per il cloruro di potassio invece la capacità di diffusione degli atomi di potassio e di cloro è all'incirca identica, per cui l'ordine (111) è troppo debole per essere osservabile. È stato proprio sulla base di questi dati che venne confermata la disposizione strutturale di entrambi questi alcalogenuri alcalini. Anche se l'analisi precedente è alquanto semplificata, essa rappresenta un esempio tipico del metodo usato nelle prime determinazioni della struttura dei cristalli. Venivano misurati un certo numero di ordini di onde difratte, con lo spettrometro a ionizzazione o con lastre fotografiche, e si cercava poi di trovare una disposizione atomica che rendesse conto delle intensità dei vari ordini.

sua determinazione è lo scopo finale di tutti i metodi sperimentali. Questa quantità è una misura, per ogni ordine (hkl), dell'intensità del fascio diffuso da una unità strutturale completa, espressa rispetto alla quantità diffusa da un singolo elettrone assunta come unità. Per esempio, la quantità $F(000)$ è diffusa in avanti con angolo zero, cosicché non vi è differenza di percorso che possa causare interferenze; $F(000)$ è perciò il numero totale di elettroni per unità strutturale. Per ordini più alti vi è una diminuzione d'intensità da attribuirsi all'interferenza.

È importante notare che $F(hkl)$ è un rapporto adimensionale, caratteristico soltanto della struttura cristallina e indipendente dalla lunghezza d'onda dei raggi X impiegati. Se si usa una lunghezza d'onda più breve, gli ordini compaiono ad angoli più piccoli e le differenze di percorso sono ridotte, ma le differenze di fase rimangono le stesse. Cioè $F(hkl)$ dipende soltanto dalla distribuzione della materia diffradente nella cella unitaria, il che è proprio l'obiettivo dell'analisi a raggi X.

Le basi teoriche per misurare i valori di $F(hkl)$ vennero formulate da C. G. Darwin in due brillanti articoli comparsi poco dopo la scoperta della diffrazione dei raggi X. A quei tempi le osservazioni sperimentali erano troppo approssimative per costituire un test per la sua teoria, e passò un certo numero di anni prima che si potesse applicarla.

Nei suoi primi calcoli Darwin fece l'ipotesi di un cristallo « idealmente perfetto ». I primi test approssimativi indagarono però che l'efficienza di rifles-