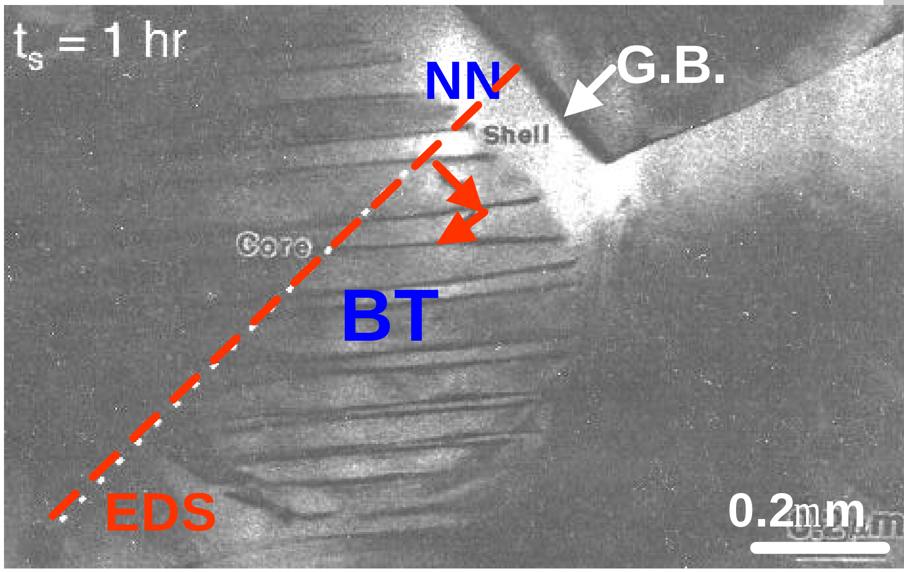
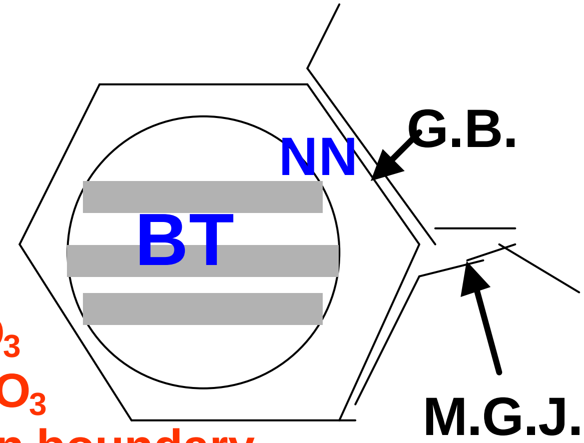
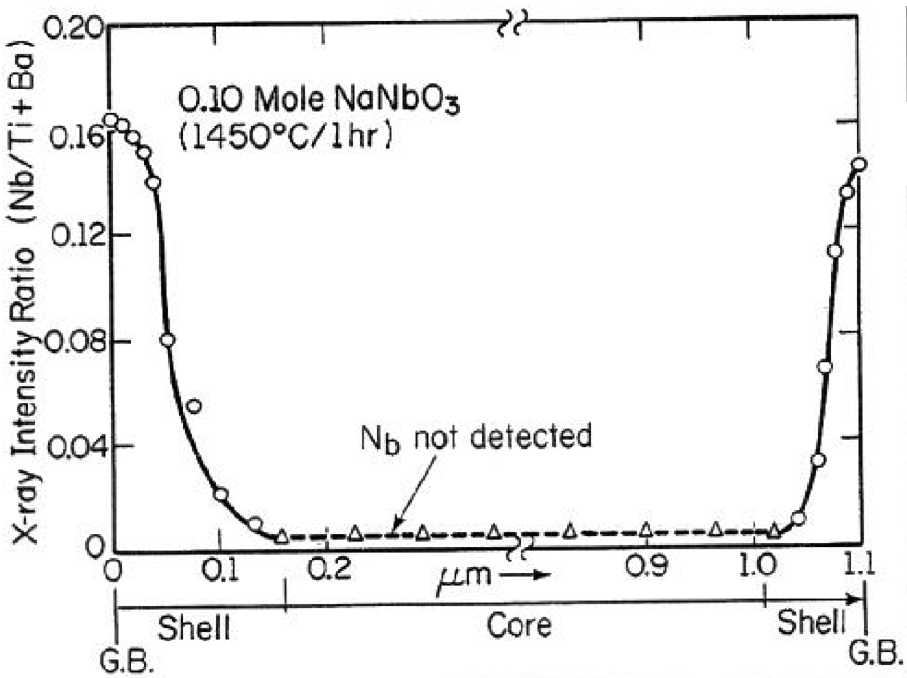
Limits of OM, XRD and SEM





BT-$BaTiO_3$
NN-$NaNbO_3$
G.B.-Grain boundary
M.G.J.-multiple grain junction



¬ **NN/BT**

- **Lateral resolution: ~mm**
- **Details of microstructure: e.g., domain structure, chemical inhomogeneity phase distribution, grain boundaries, interfaces, precipitates, dislocations, etc.**

2-D Reciprocal Lattices

Real space:

Unit cell vectors: **a**,**b**

d-spacing direction

a d_{10} [10]

b d_{01} [01]

Reciprocal space:

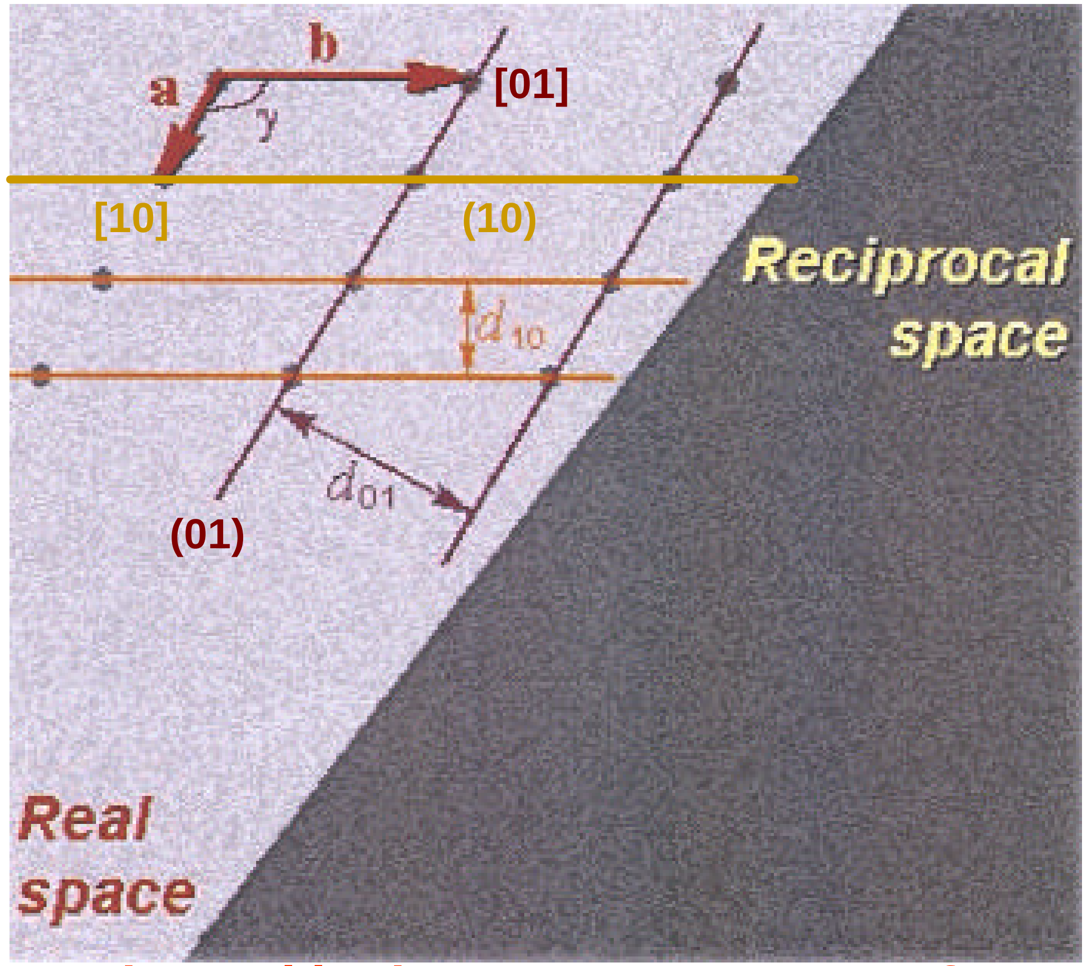
Unit cell vectors: **a***,**b***

magnitude direction

a* $1/d_{10}$ ^ **b**

b* $1/d_{01}$ ^ **a**

A reciprocal lattice can be built using reciprocal vectors.



Note: each point in the reciprocal lattice represents a set of planes.

3-D Reciprocal Lattice

Real space:

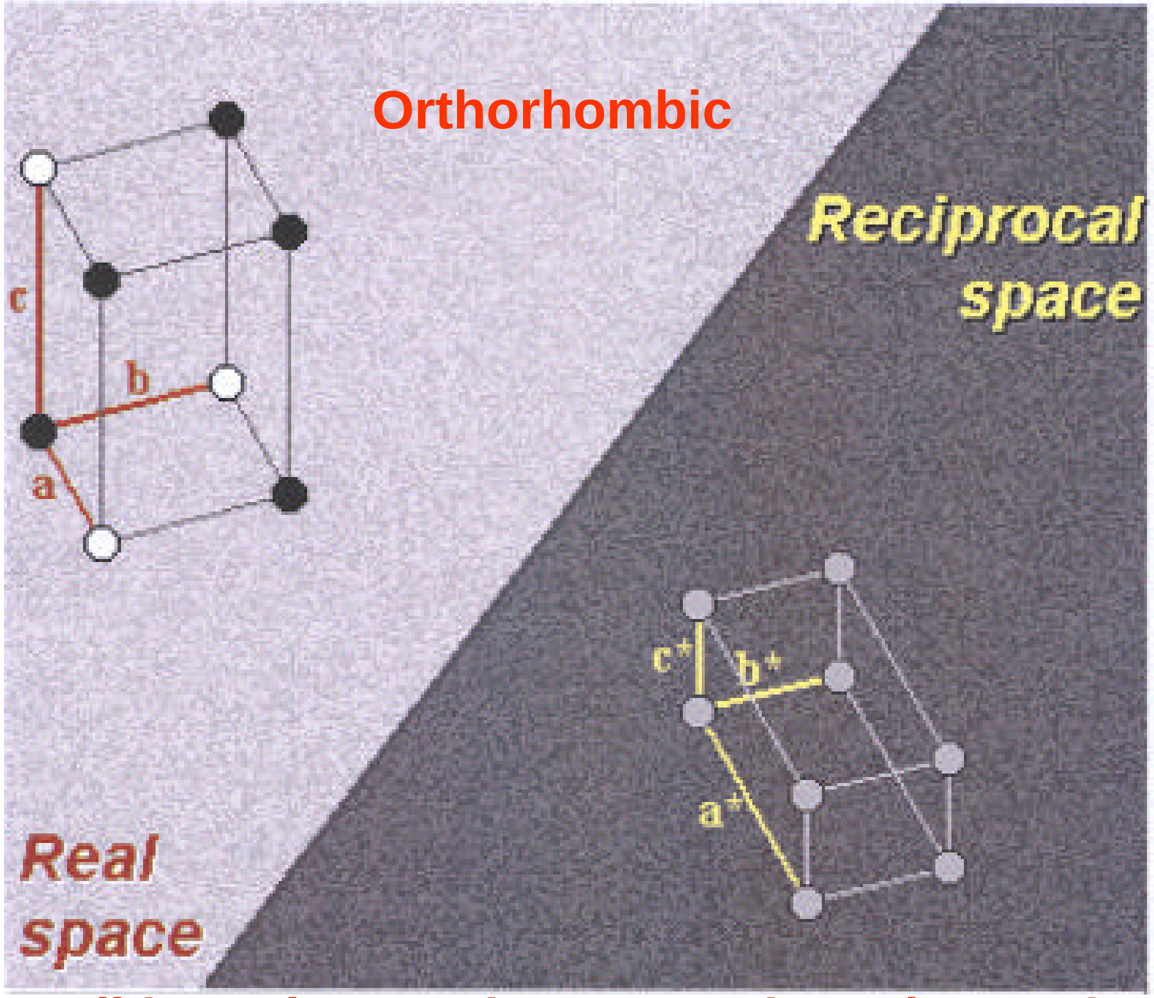
Unit cell vectors: **a**,**b**,**c**

	magnitude	direction
a	d_{100}	[100]
b	d_{010}	[010]
c	d_{001}	[001]

Reciprocal space:

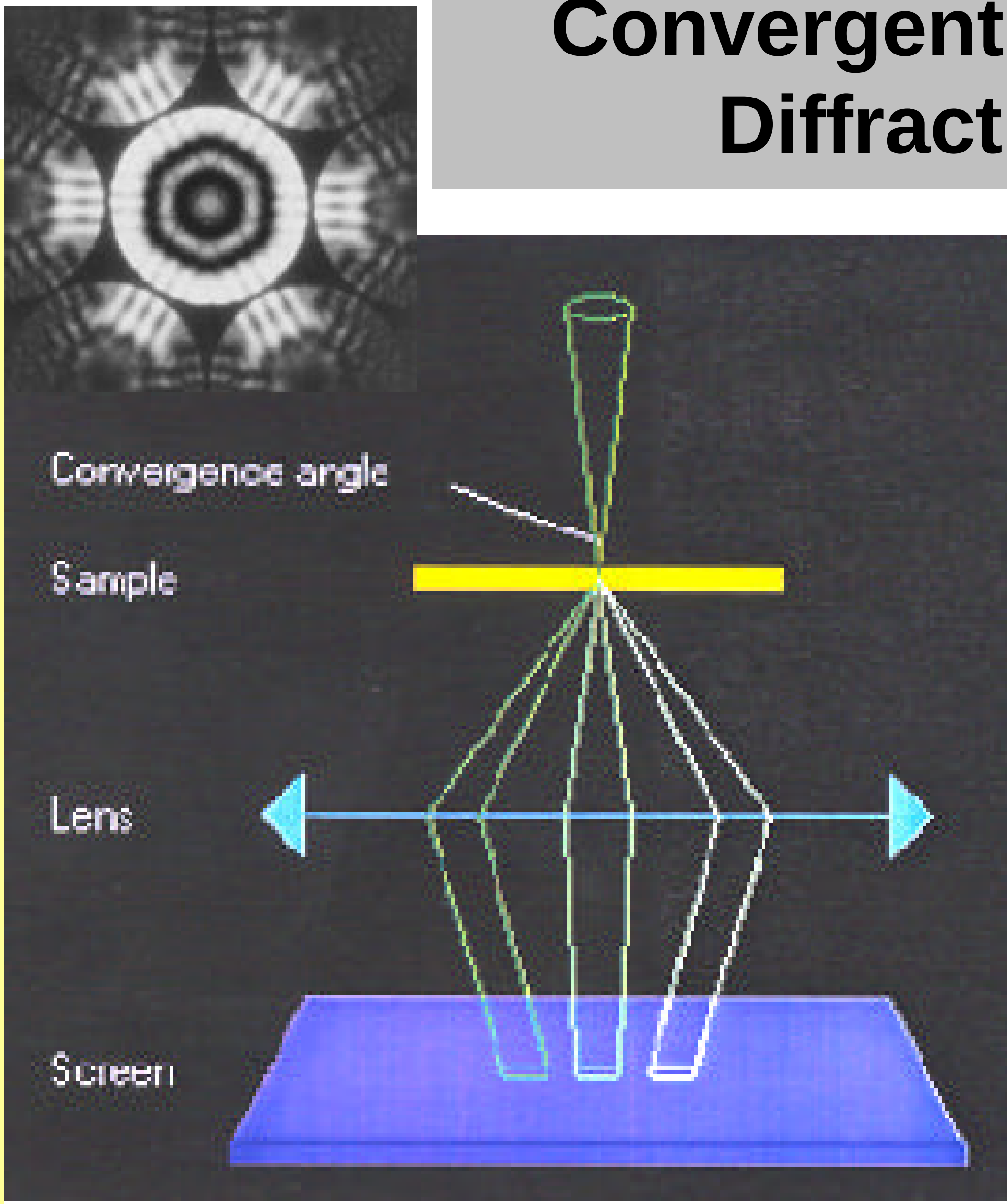
Unit cell vectors: **a***,**b***

	magnitude	direction
a*	$1/d_{100}$	^ **b** and **c**
b*	$1/d_{010}$	^ **a** and **c**
c*	$1/d_{001}$	^ **a** and **b**



Note: **as volume of unit cell in real space increases the volume of unit cell in reciprocal space decreases, and vice versa.** **a***,**b*** and **c*** **are parallel to corresponding** **a**,**b** and **c**, **and this is only true for the unit cells of cubic, tetragonal and orthorhmbic crystal systems.**

Convergent Beam Electron Diffraction (CBED)



CBED uses a convergent beam of electrons to limit area of specimen which contributes to diffraction pattern.
Each spot in SAED then becomes a disc within which variations in intensity can be seen.
CBED patterns contain a wealth of information about symmetry and thickness of specimen.
Big advantage of CBED is that the information is generated from small regions beyond reach of other techniques.

Why CBED?

Why CBED? Why not SAD?

Limits of Conventional SAD

Conventional SAD uses an aperture to define the area from which the pattern is to be recorded. The aperture is placed in the image plane of the objective lens to create a virtual aperture in the specimen plane (Le Poole 1947). The spatial resolution in SAD is limited by both spherical aberration and the ability of the operator to focus the aperture of the and the image in the same plane. The error in area selection U is given by:

$$U = C_s(2q_B)^3 + D2q_B$$

where: C_s= spherical aberration coefficient

q_B= Bragg angle

D= minimum focus step.

The result is that the theoretical lower limit of area selection is ~0.5µm (in practice governed by aperture size).

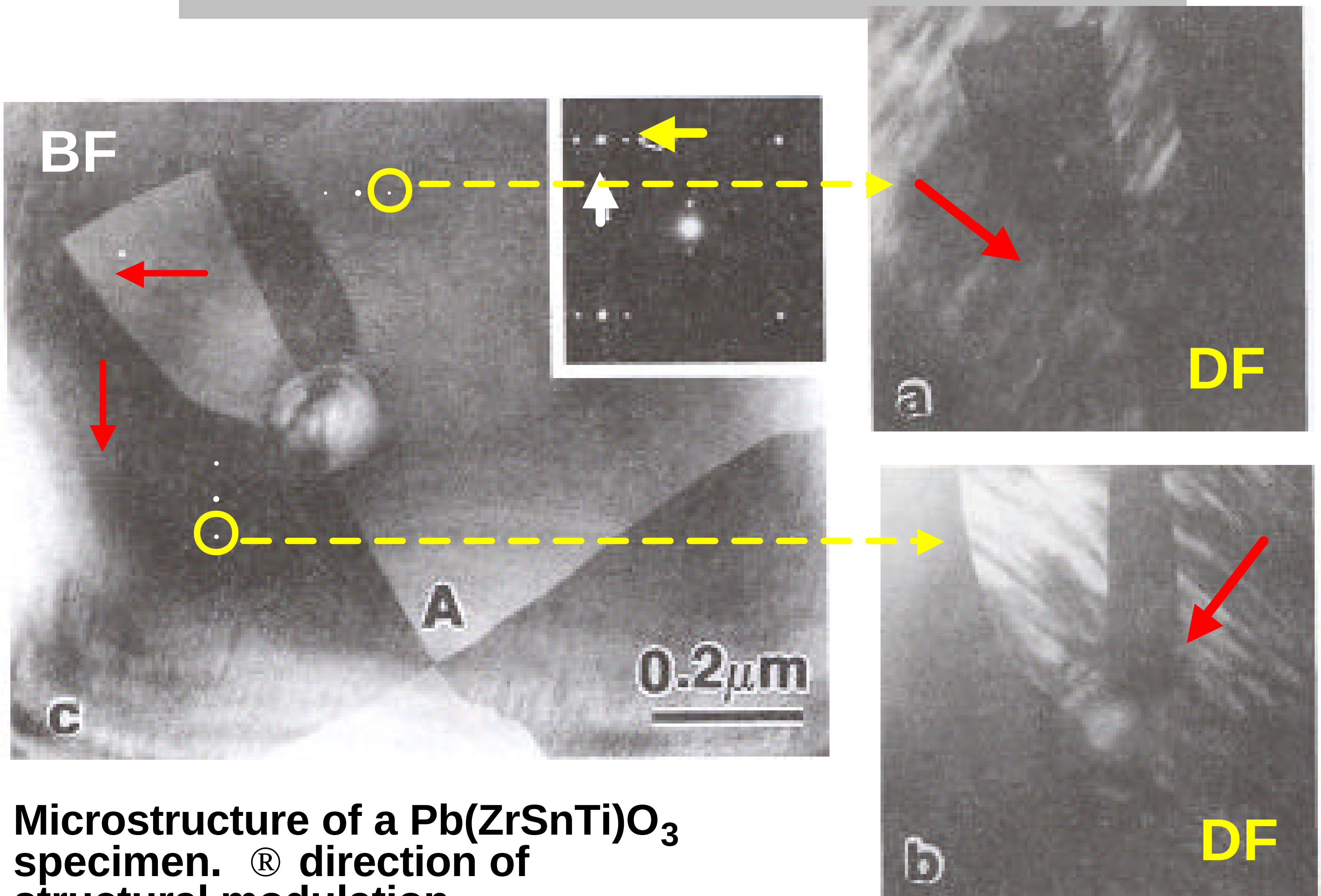
J.B. Le Poole, Philips Tech. Rundsch 9 (1947) 33.

Symmetry Deviations

Possible reasons for Symmetry to deviate from that which is expected

- Crystal Defects - Point defects, dislocations, stacking faults
- Element not in mid-plane
- Glide or Screw out of surface
- Probe smaller than unit cell
- Heavily tilted sample

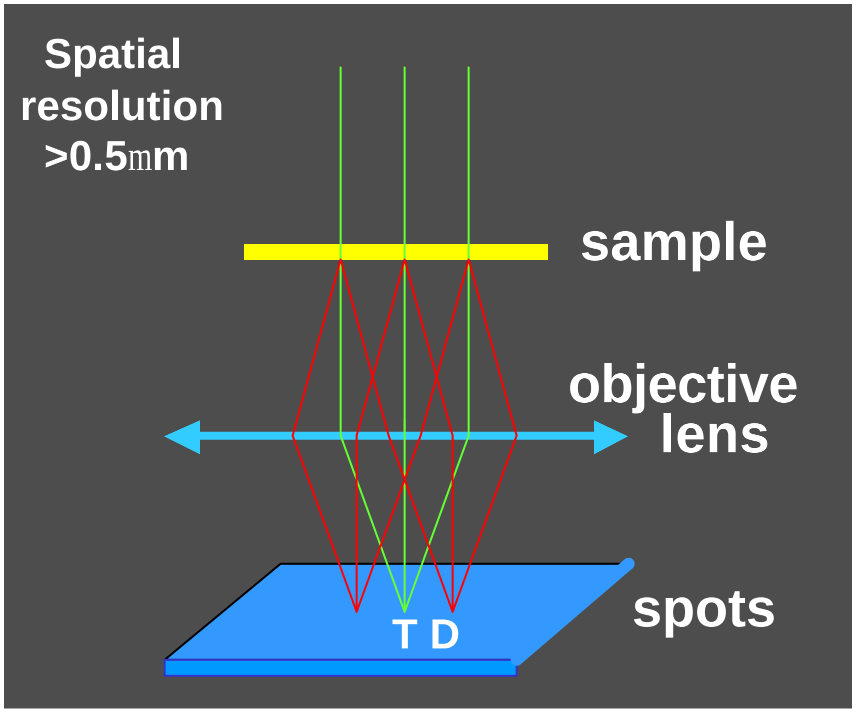
Bright and Dark Field Imaging

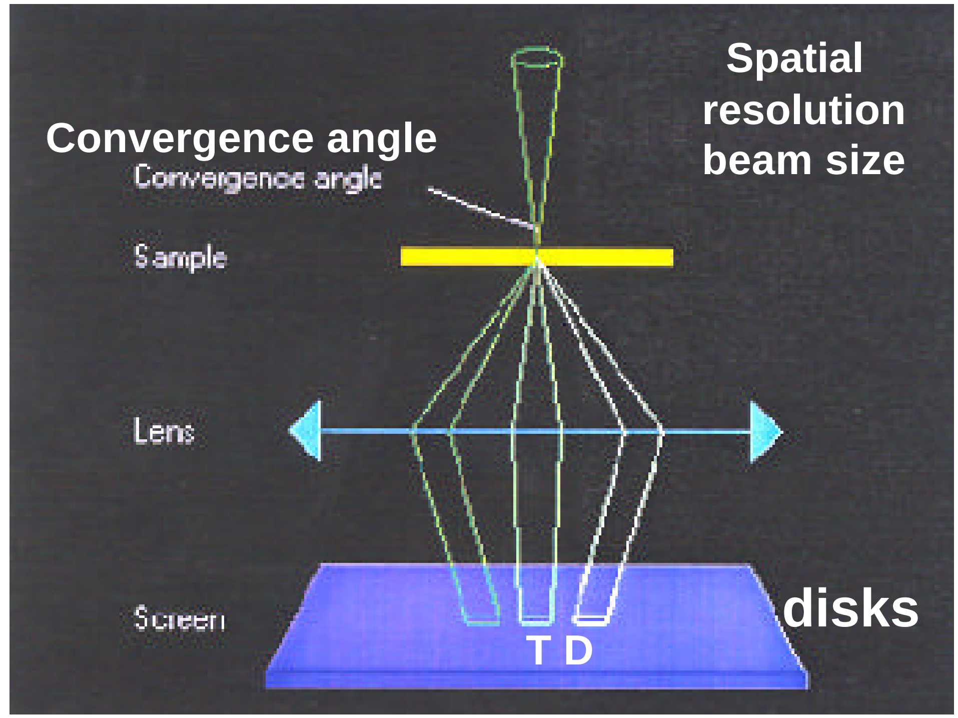


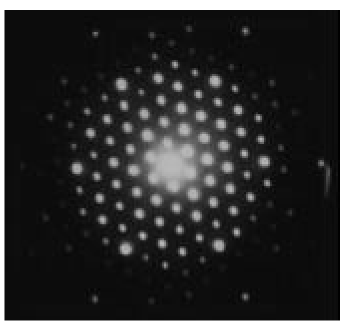
Microstructure of a Pb(ZrSnTi)O_3 specimen. ® direction of structural modulation.

SAED vs CBED

Parallel beam **Convergent beam**

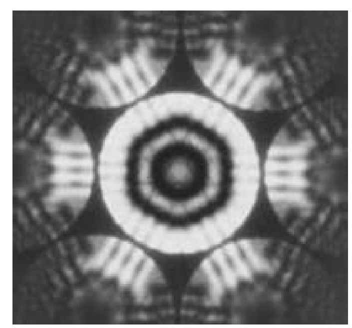






SAED

CBED

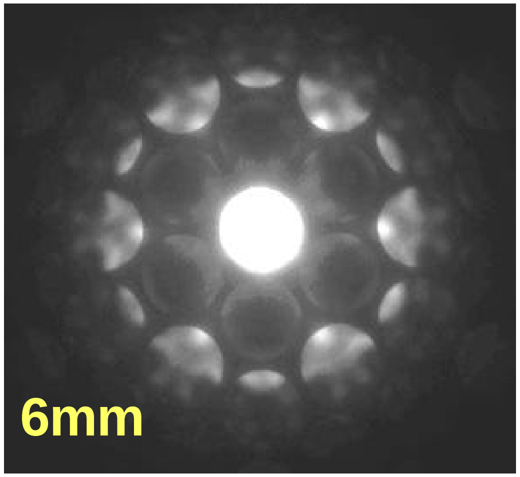


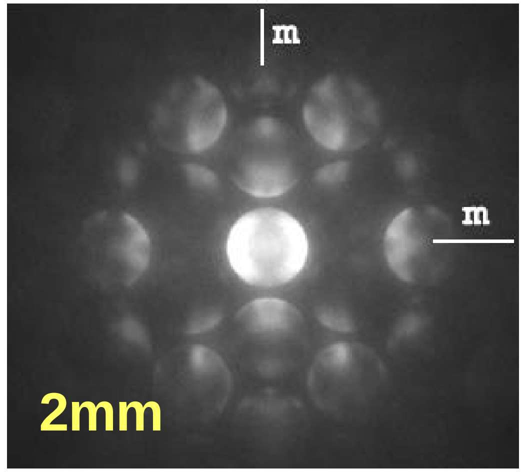
Applications of CBED

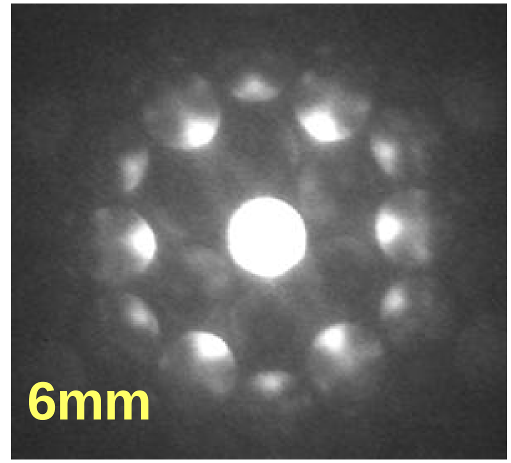
- Phase identification
- Symmetry determination-point and space group
- Phase fingerprinting
- Thickness measurement
- Strain and lattice parameter measurement
- Structure factor determination

Phase Identification in $BaAl_2Si_2O_8$

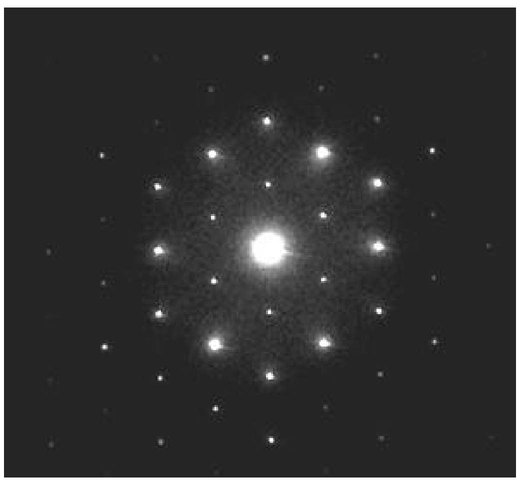
Hexagonal | Orthorhombic | Hexagonal

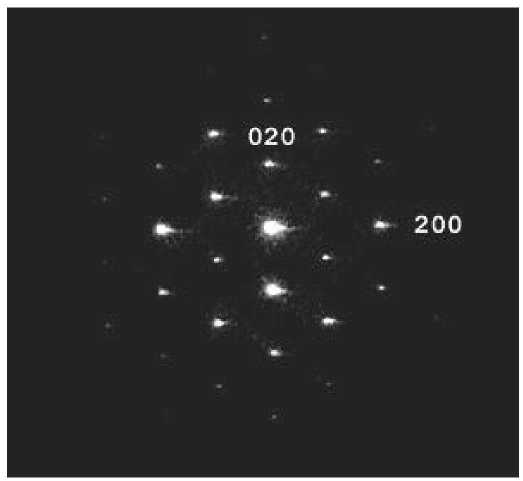


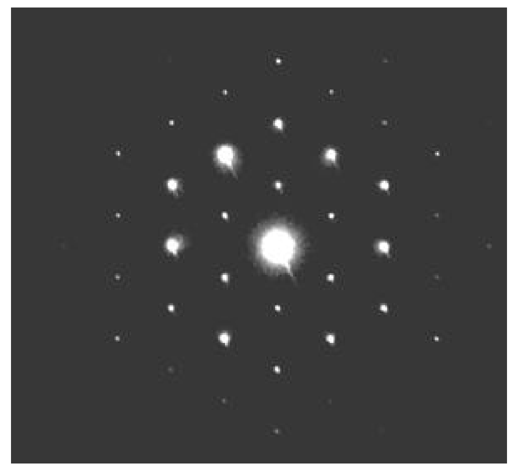




200°C | 400°C | 800°C





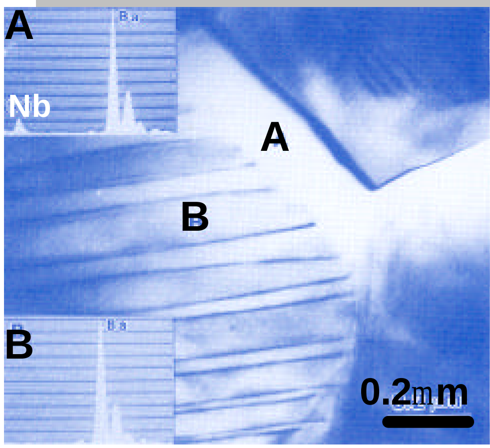


<0001>

CBED

Symmetry and Lattice Parameter Determination

EDS

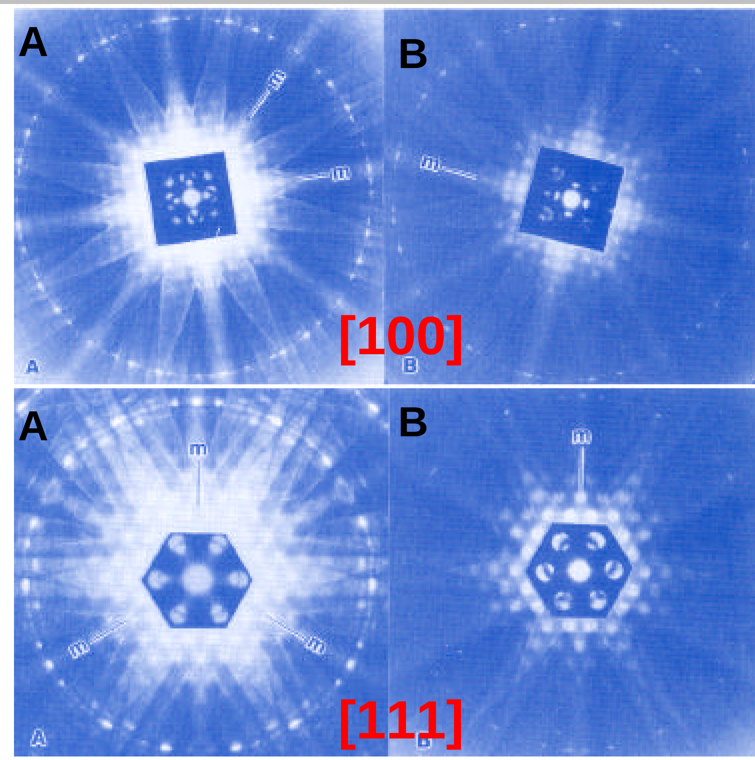


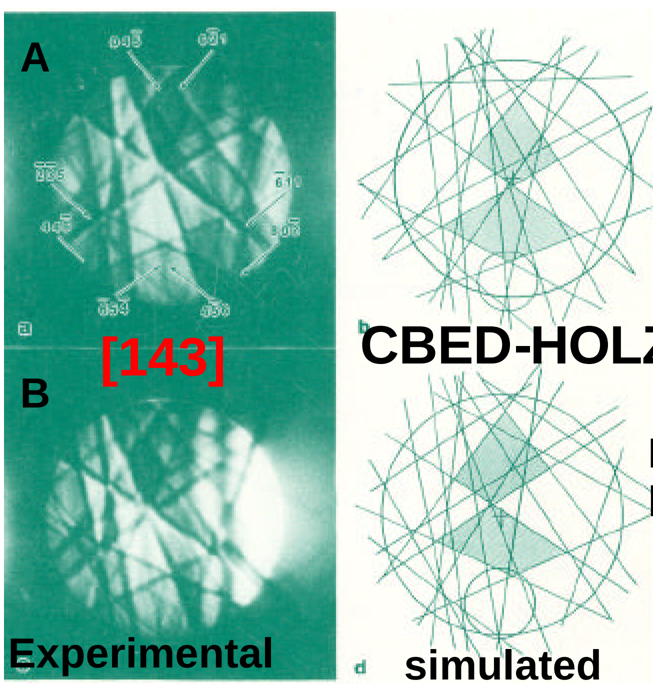
BF

010

SAED

CBED





CBED-HOLZ → Lattice parameters

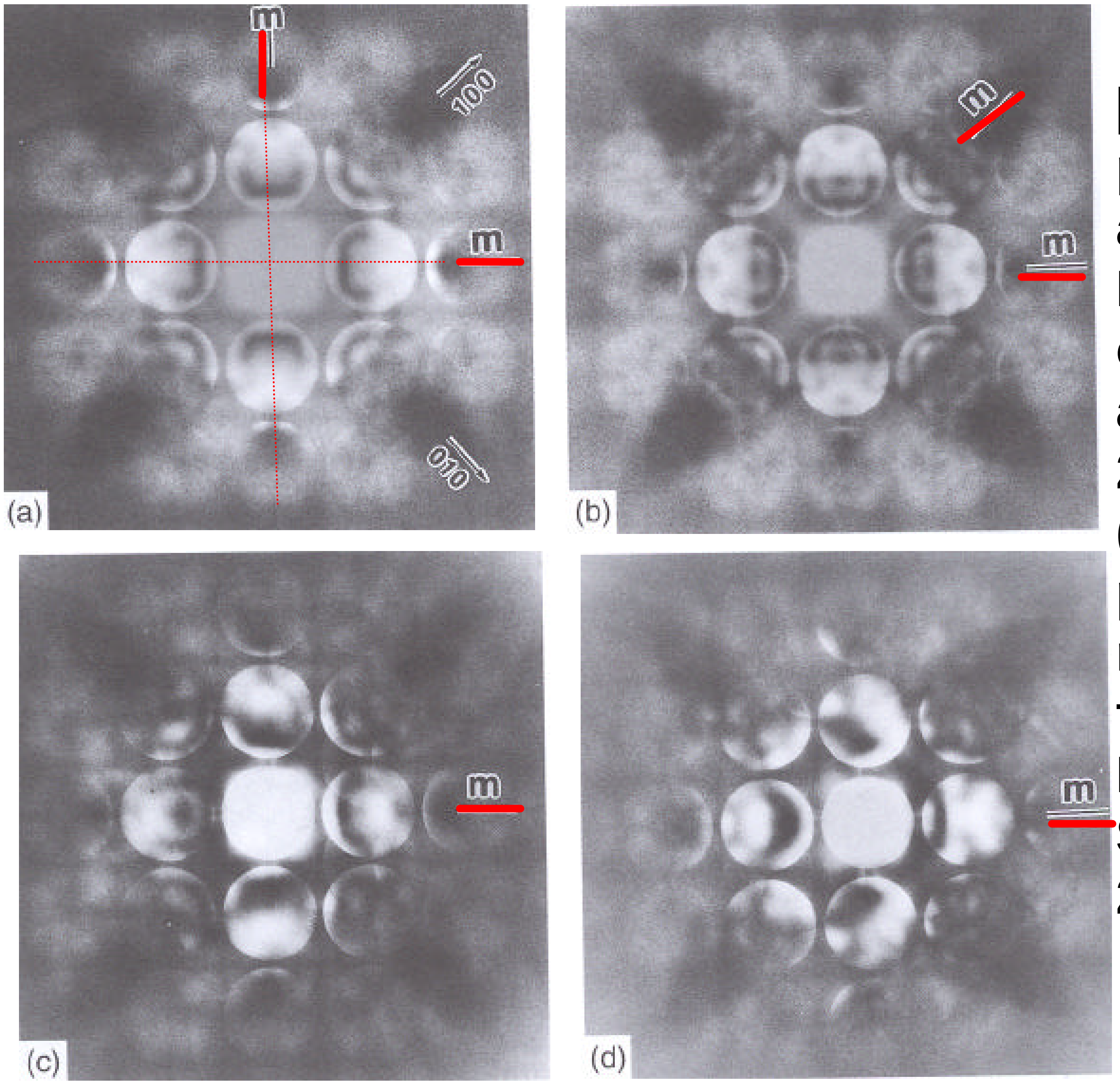
Table 1 Relation Between Point Group and Whole Pattern Symmetry

Crystal Structure	Point Group	Zone Axis	Whole Pattern Symmetry
Tetragonal	4mm	[100]	m
		[111]	m
Cubic	m3m	[100]	4mm
		[111]	3m

CBED

Phase Fingerprinting

Orthorhombic AFE | Cubic PE



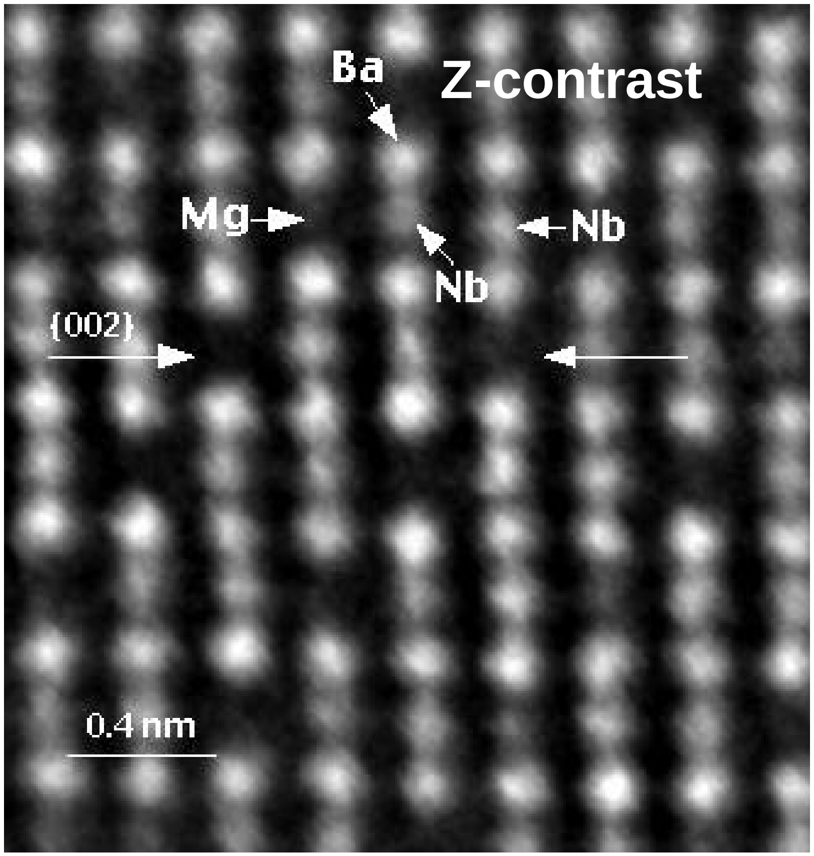
Rhombohedral FE | Rhombohedral FE

[001] CBED patterns of an antiferroelectric $PbZrO_3$ single crystal specimen at (a) 20^{o}C, (b) 280^{o}C, (c)220^{o}C. (d) [001] CBED pattern of a rhombohedral ferroelectric $Pb(ZrTi)O_3$ Specimen at 20^{o}C.

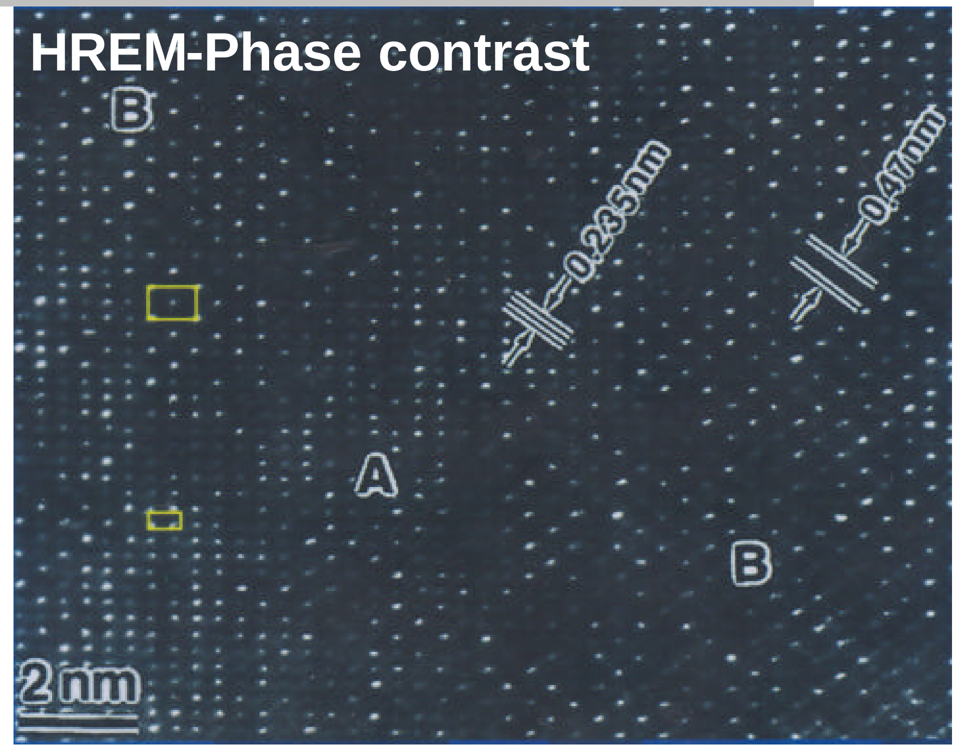
CBED

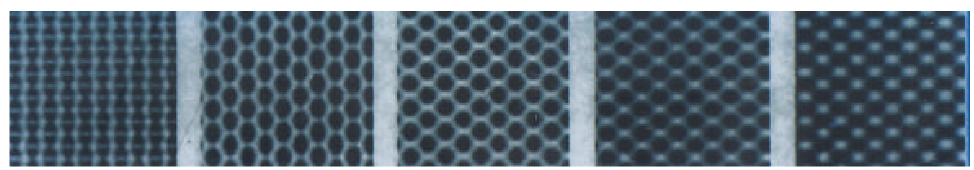
High Resolution Z-contrast Imaging
Atomic Ordering in $Ba(Mg_{1/3}Nb_{2/3})O_3$

$I \propto Z^2$



(STEM)

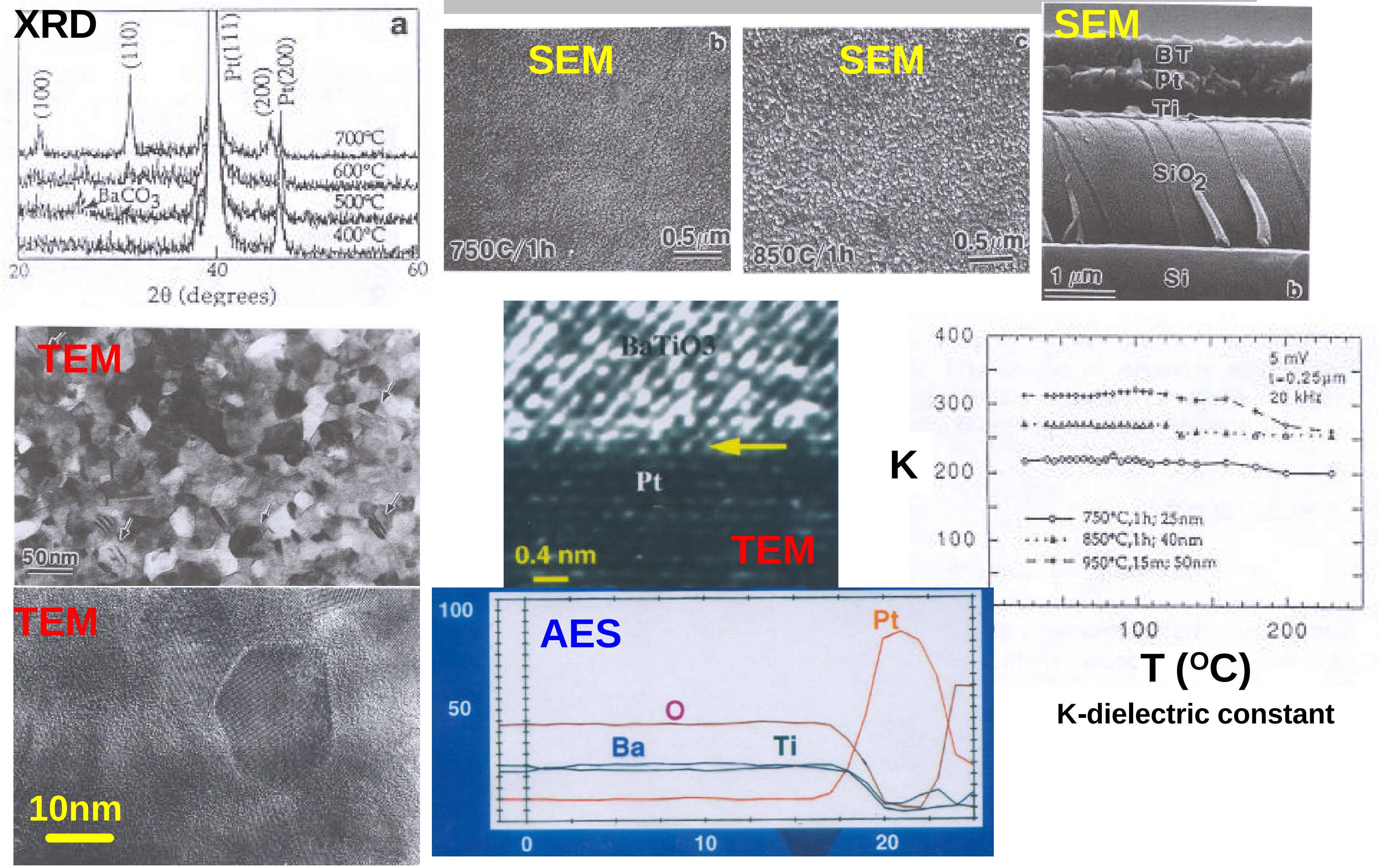




Δf: -52 -64 -76 -88 -100nm

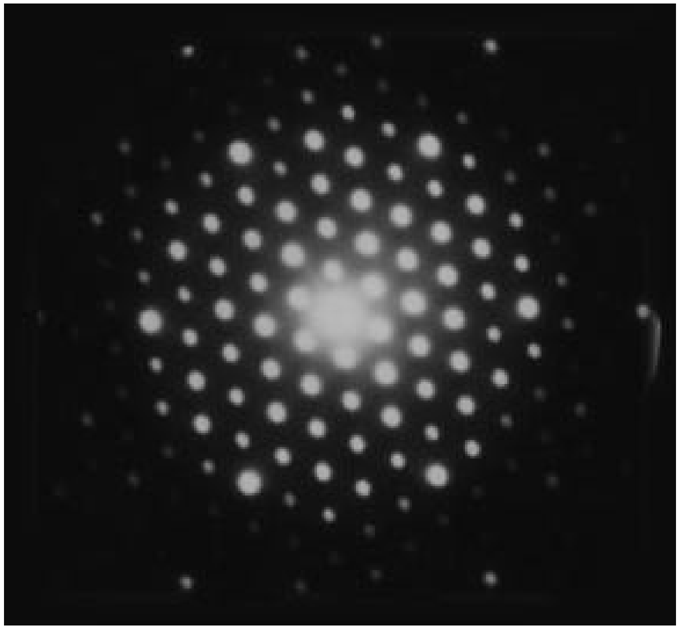
A: disordered B: ordered region

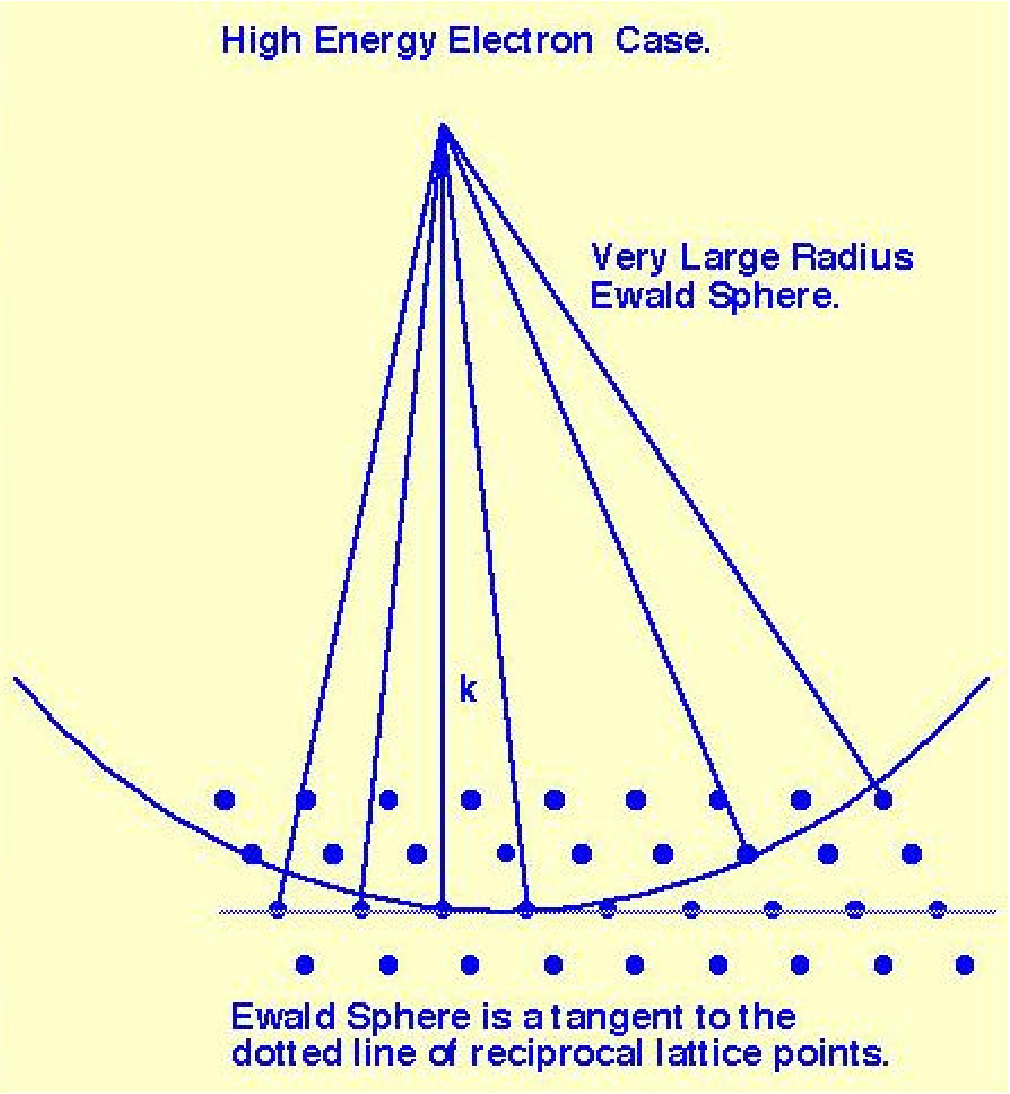
XRD, SEM and TEM Studies of Nanocrystalline $BaTiO_3$ Thin Film



K-dielectric constant

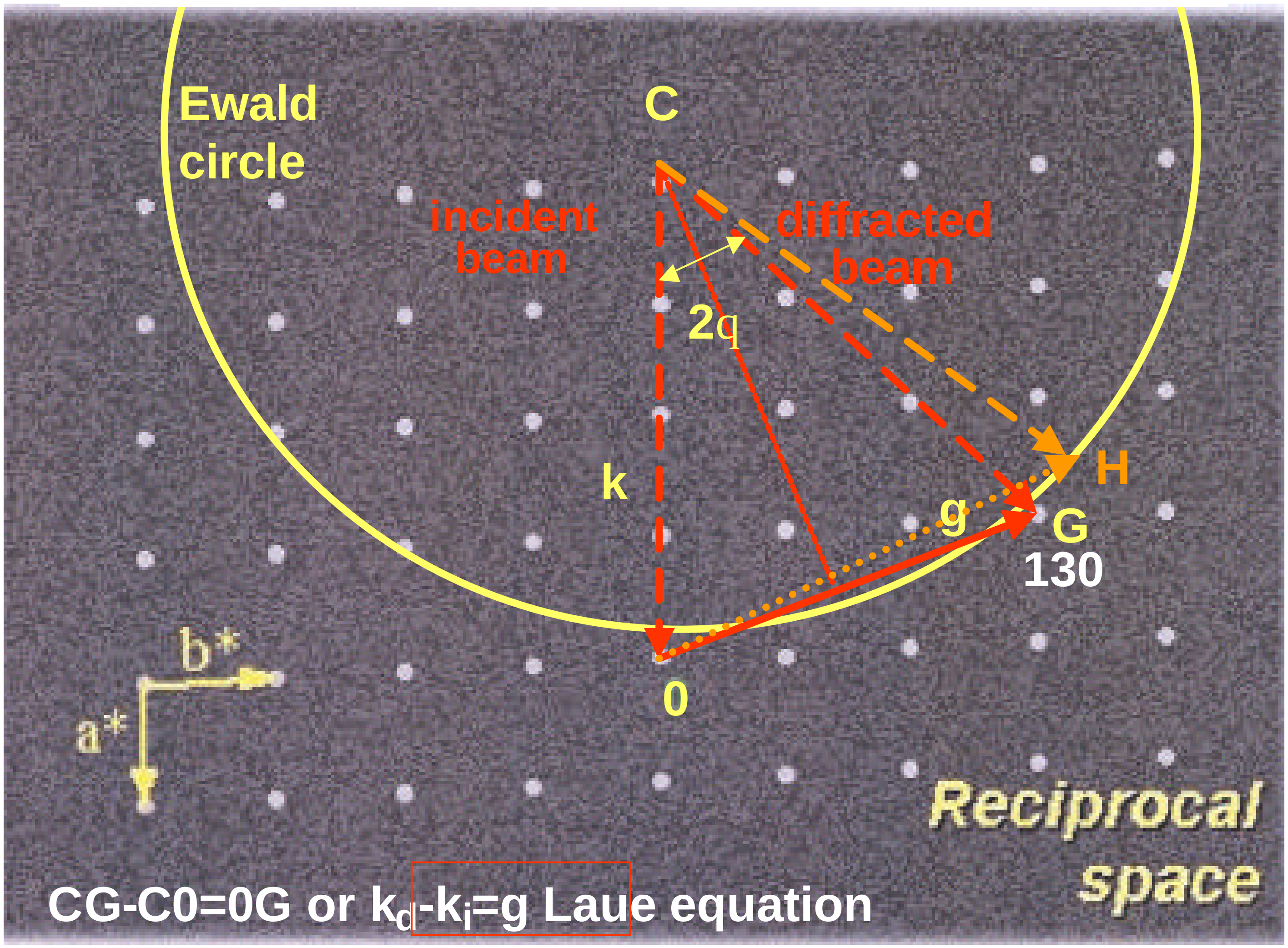
Why are there so many spots?
The Ewald Sphere





Ewald's Sphere

Ewald's sphere is built for interpreting diffraction



At G, diffraction occurs, at H no diffraction

Construction of Ewald's Sphere

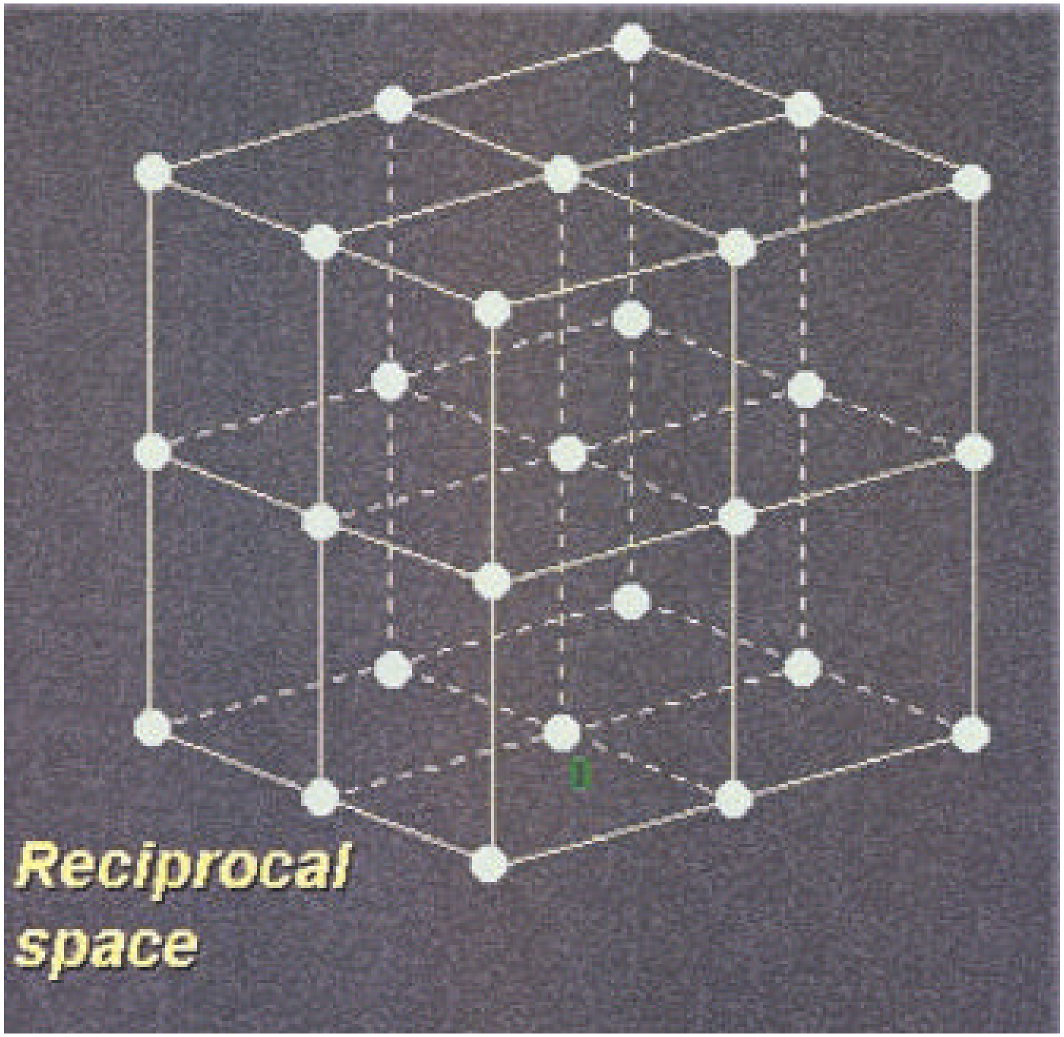
Ewald's sphere is built for interpreting diffraction patterns and it shows which sets of planes are at (or close to) their Bragg angle for diffraction to occur.

- **Incident wave is represented by a reciprocal vector k ($|k|=1/\lambda$ and points in the direction of wave).**
- **Construct a circle with radius $1/\lambda$ (i.e., k), which passes through origin of reciprocal lattice, 0.**
- **Wherever a reciprocal point touches the circle, Bragg's law is obeyed and a diffracted beam will occur.**
- **C0–incident beam and CG–diffracted beam. The angle between C0 and CG must be 2θ.**
- **0G is the reciprocal vector g_{130} and has magnitude of $1/d_{130}$.**

$$0G/2=|k|\sin\theta, \rightarrow 0G=2/\lambda \sin\theta, \rightarrow 1/d_{130}=2/\lambda \sin\theta_{130}$$

$$\rightarrow \lambda=2d_{130}\sin\theta_{130}$$

Ewald’s Sphere Construction in 3D



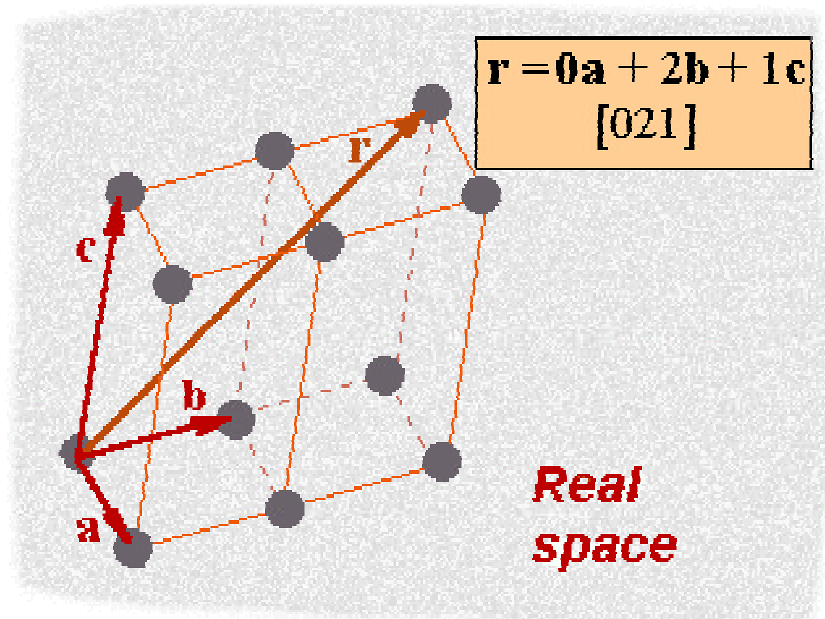
In a single crystal only a few sets of planes are oriented at their Bragg angle at any one time.

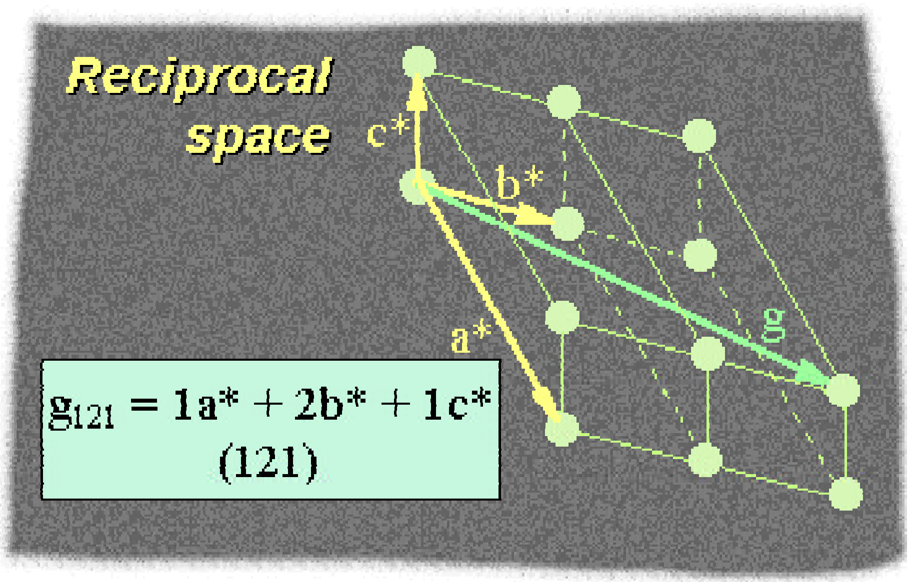
Lattice Vectors

Real space lattice vector corresponds to directions in crystal and it can be defined as:

r=ua+vb+wc

a,b and c are unit cell vectors, u,v and w are components of the direction index [uvw].



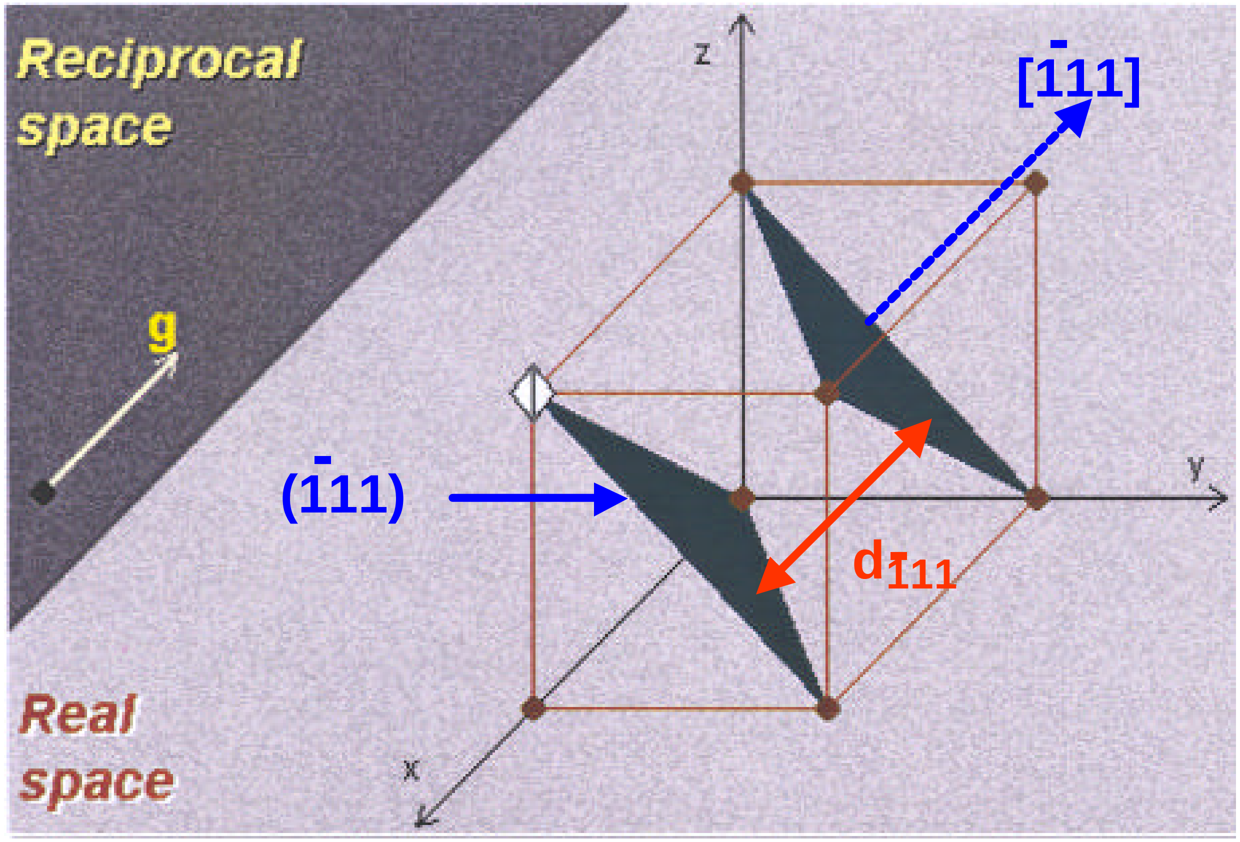


A reciprocal lattice vector can be written as:

g*=ha*+kb*+lc*

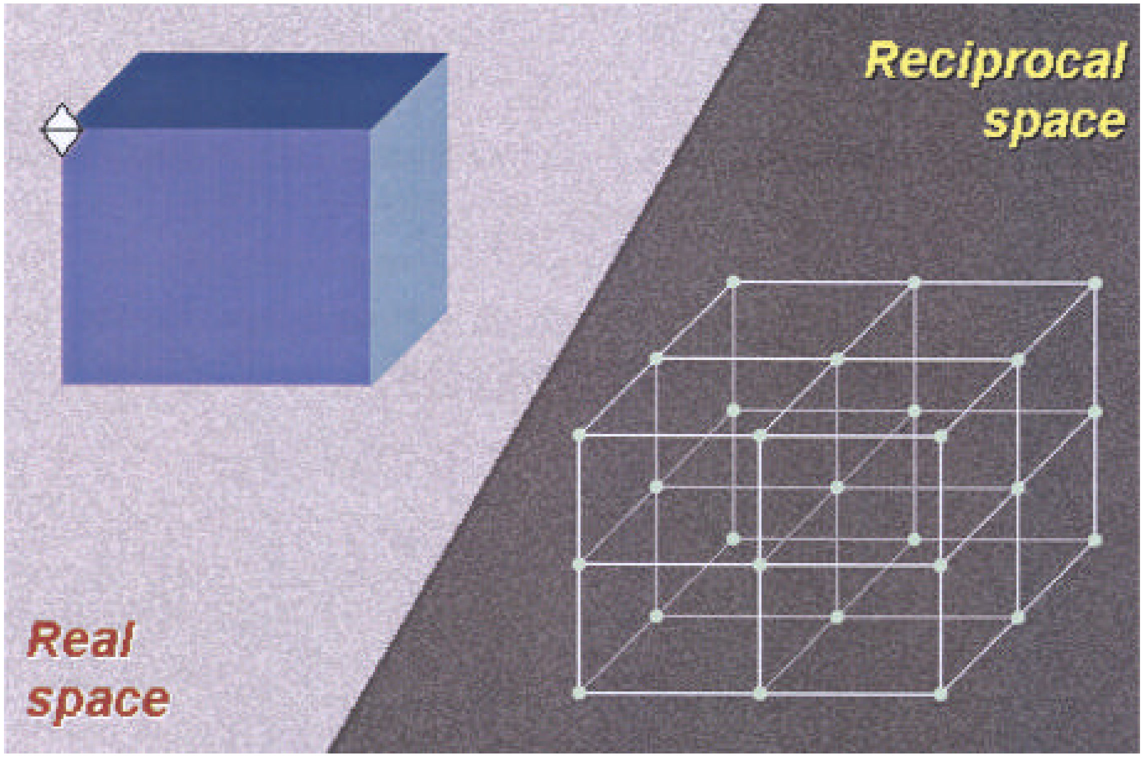
a*,b* and c* are reciprocal unit vectors, and h,k and l are the Miller indices of the plane (hkl).

Effect of Spacing of planes in Real Space on Length of Reciprocal Vector, g



In a crystal of any structure, g_{hkl} is normal to the (hkl) plane and has a length inversely proportional to the interplanar spacing of the planes.

Streaking Reciprocal Lattice Points



Bragg's law predicts diffraction at only precise Bragg angles for an infinite crystal. In TEM experiments, specimens are thin in at least one dimension (thickness).

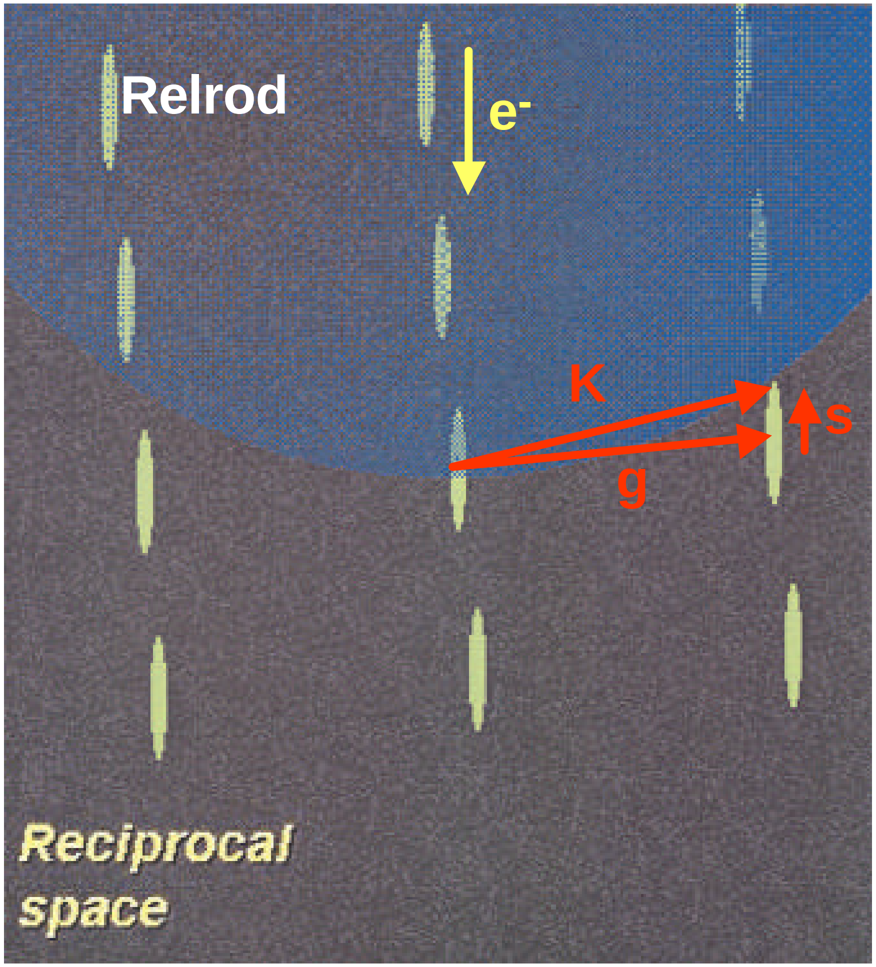
Effect of small dimensions is to allow diffraction over a range of angles close to Bragg angle, or as if reciprocal lattice points are stretched out in the thickness direction. The stretched reciprocal lattice points are called relrods.

Deviation Parameter, s

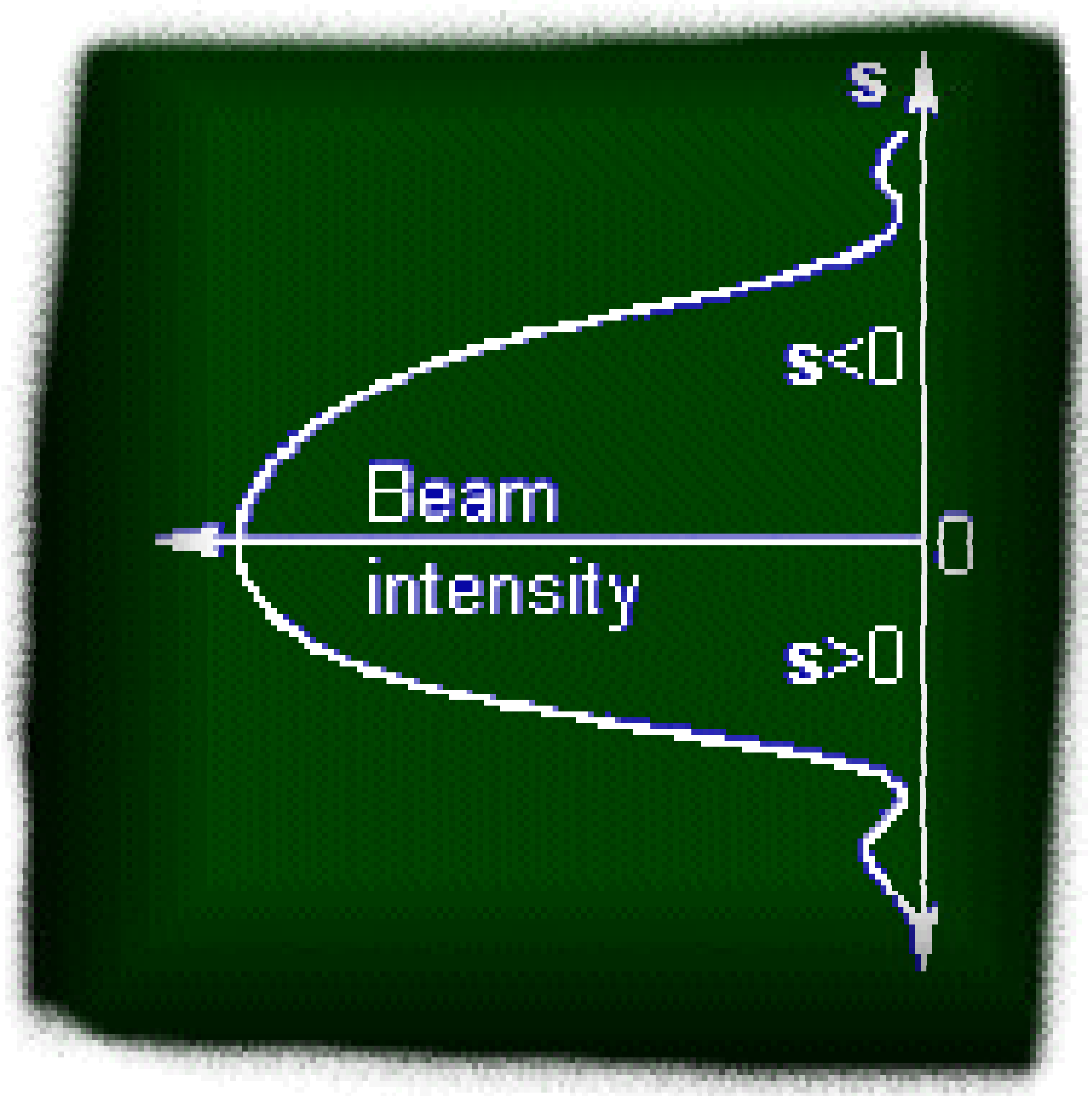
Ewald sphere can intersect with a relrod even when it misses the actual reciprocal lattice point. Diffraction, at reduced intensity, can still occur. Deviation parameter, s, defines how close a relrod Is to the Ewald sphere and Diffraction vector K is given:

K=g+s

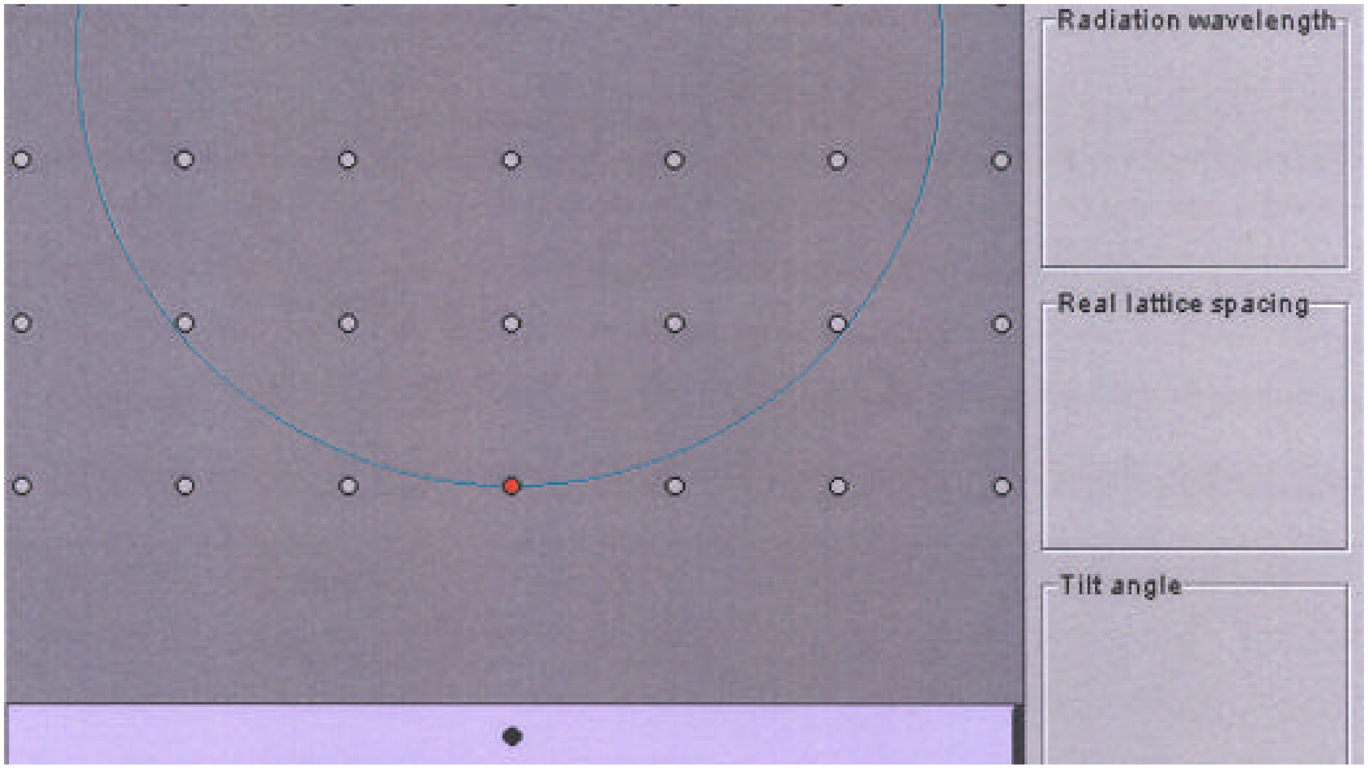
The s is defined to be positive In the direction of the beam And negative if it points Upwards (as here).



Beam Intensity vs Deviation, s



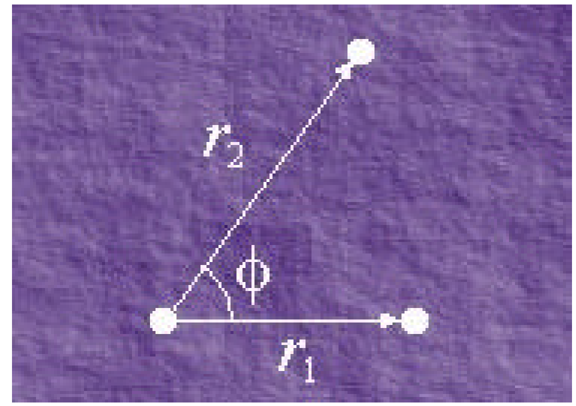
Ewald's Sphere and Diffraction Patterns



The curvature of the circle with respect to the reciprocal lattice, depends on the relative values of the wavelength λ, and the spacing of the lattice planes in the crystal, d.

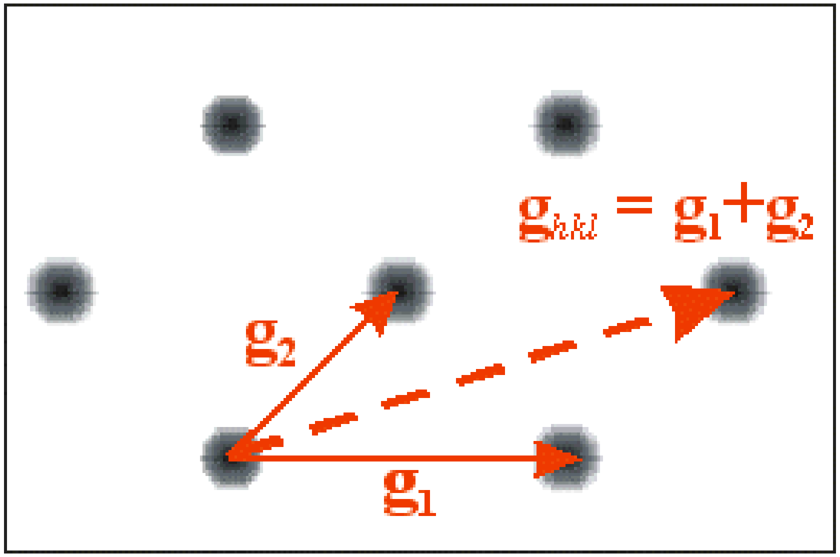
Indexing Diffraction Pattern-ratio Technique

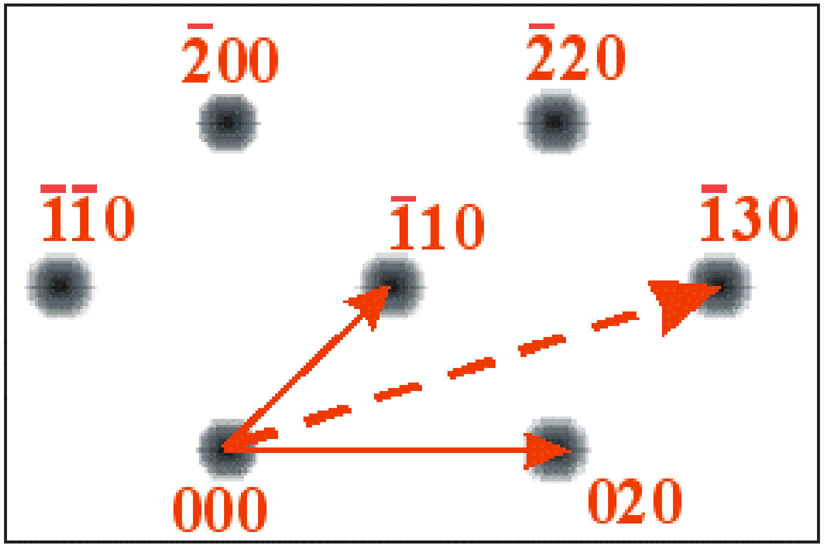
Any 2-D section of a reciprocal lattice can be defined by two vectors so only need to index 2 spots.



1. **Choose one spot to be the origin and measure r_1**
2. **measure the spacing of a second spot r_2**
3. **measure the angle, f**
4. **prepare a table giving the ratios of the spacings of permitted diffraction planes in the known structure**
5. **take measured ratio r_1/r_2 and locate a value close to this in the table**
6. **assign more widely-spaced plane (lower indices) to the shorter r value**
7. **calculate angle between pair of planes of the type you have indexed**
8. **if measured f agrees with one of possible value, accept indexing. if not, revisit the table and select another possible pair of planes**
9. **finish indexing the pattern by vector addition.**

Indexing Electron Diffraction Patterns





If we know the index for two diffraction spots It is possible to index the rest of the spots by Using vector addition as shown. Every spots Can be reached by a combination of these two Vectors.

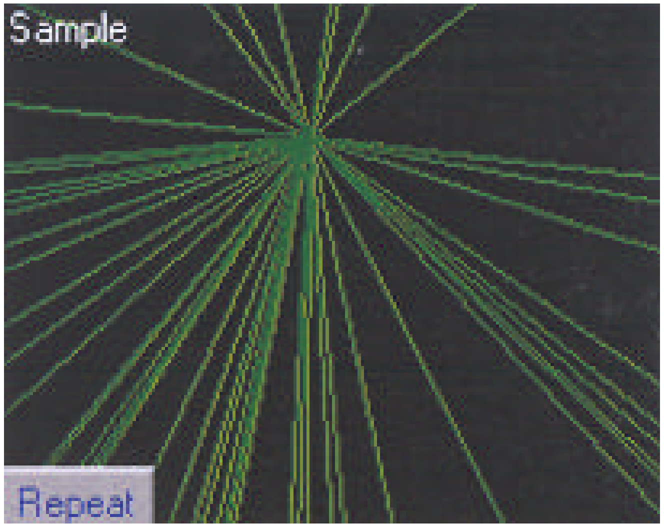
Kikuchi Lines-1

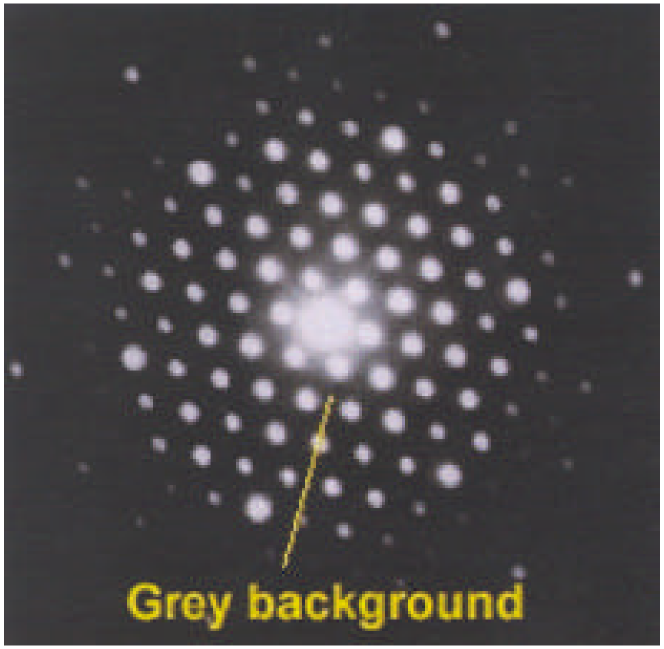
e^-

In a thick enough specimen, inelastic scattering (in 3-D) also take place.

Inelastically scattered e^-s travel in all directions but their distribution peaks in a forward direction.

More are scattered forward Than sideways. This contri-butes a grey background around the central spot of the diffraction pattern, as shown.

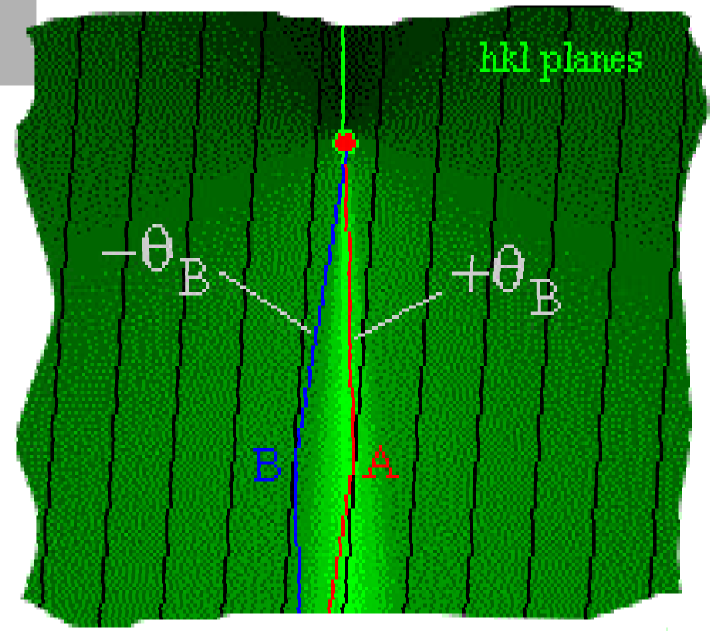


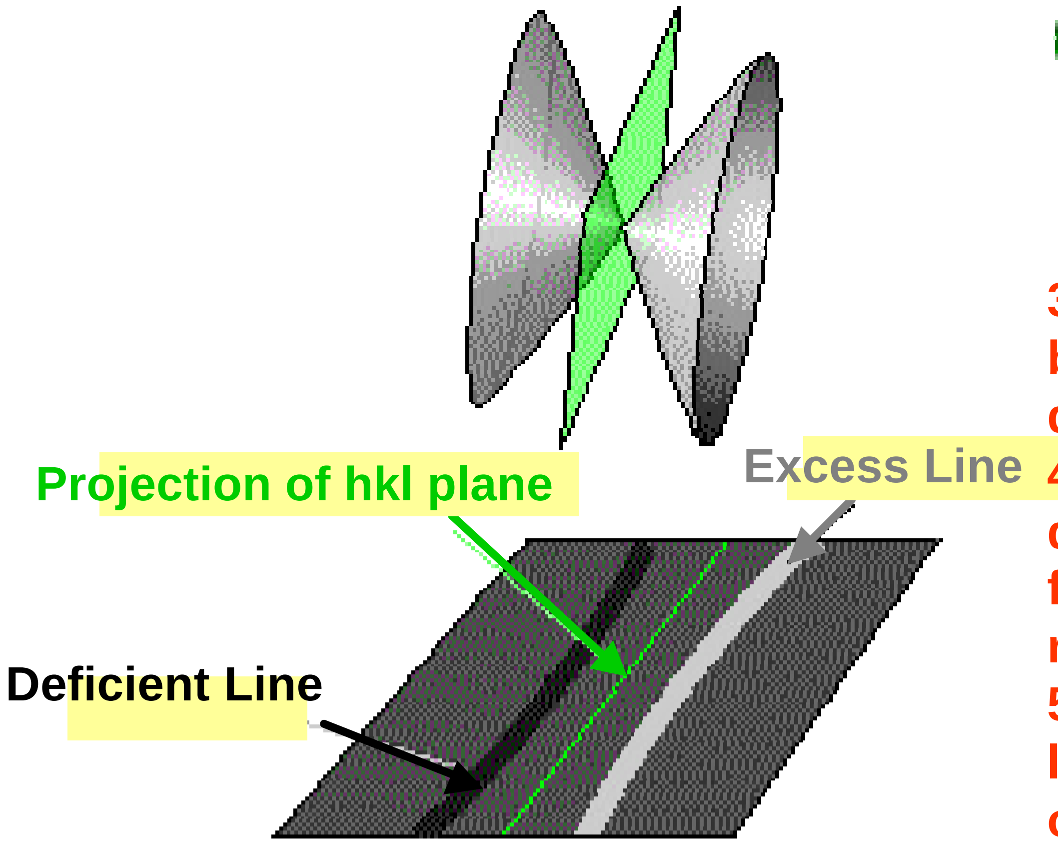


Kikuchi Lines-2

1.**Inelastically** scattered e^-s can be **diffracted** only if they are traveling at **Bragg angle,**q_B to a set of planes.

2.Two sets of e^-s will be able to do this - those at $+q_B$ and those at $-q_B$.



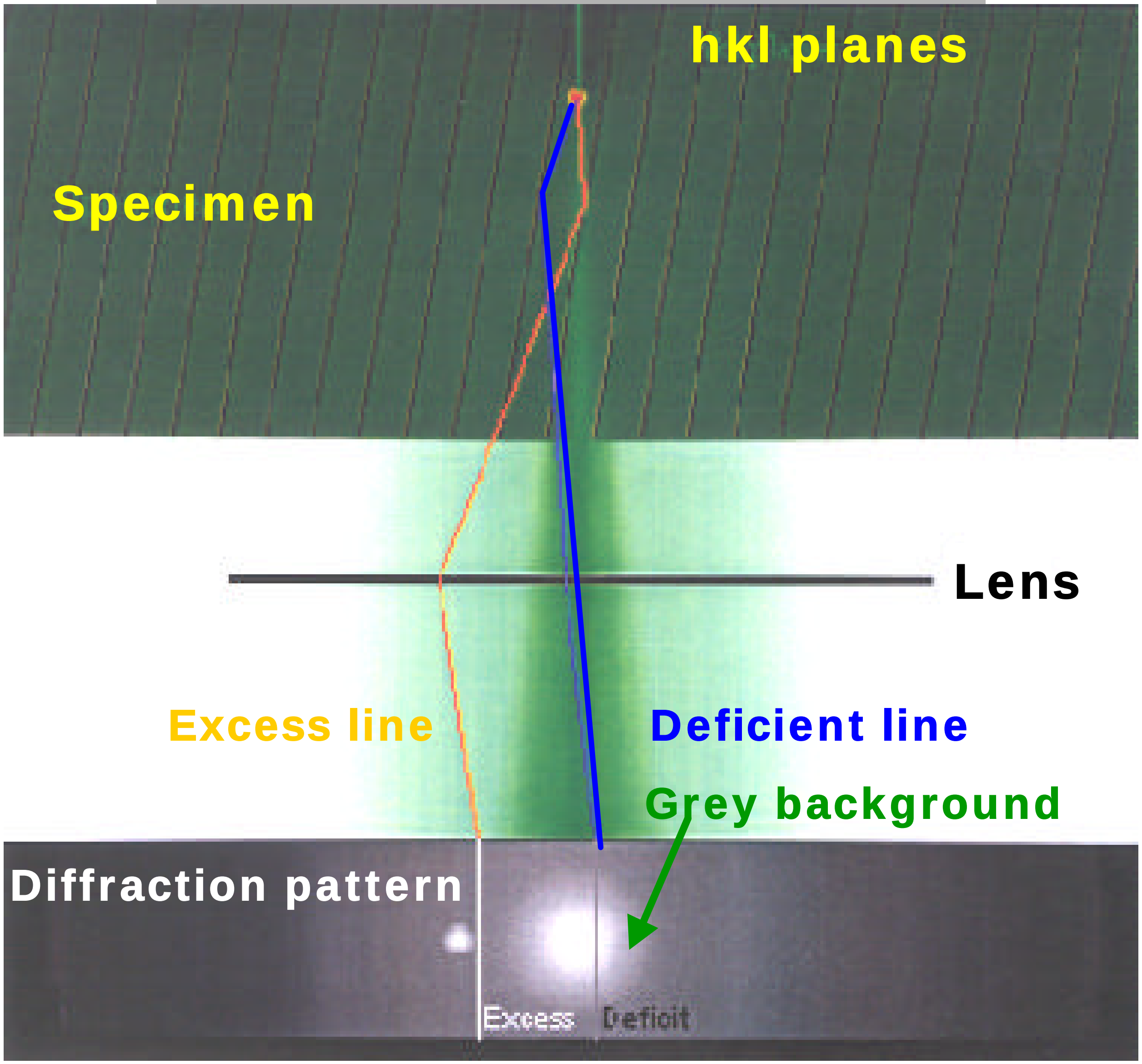


3.More e^-s at A than B, one bright (excess) line and one dark (deficient) line result.

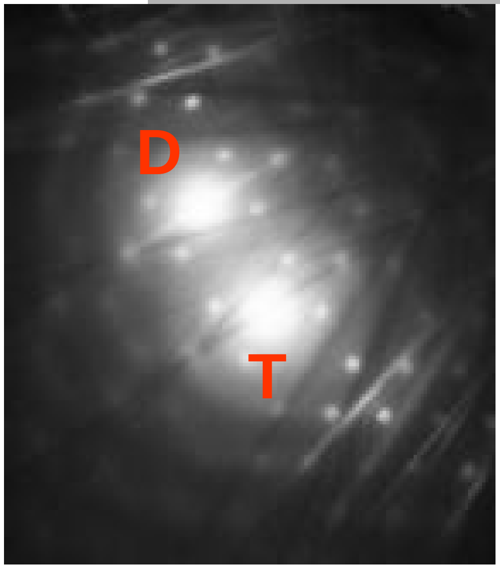
4. e^-s are scattered in all directions, diffracted e^-s form a cone, not a beam resulted in Kikuchi lines.

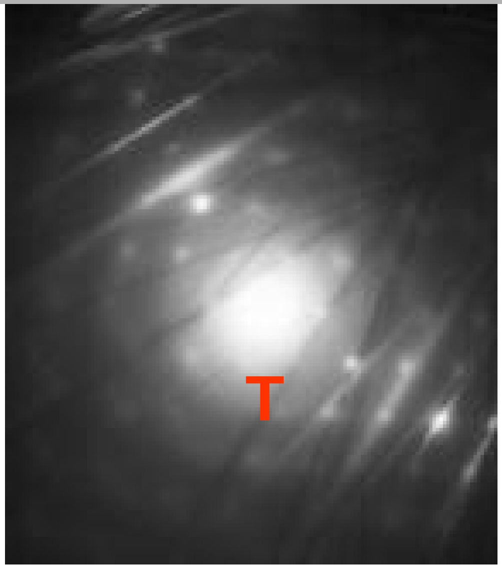
5.Spacing of pair of Kikuchi lines is the same as spacing of diffracted spots from the same plane.

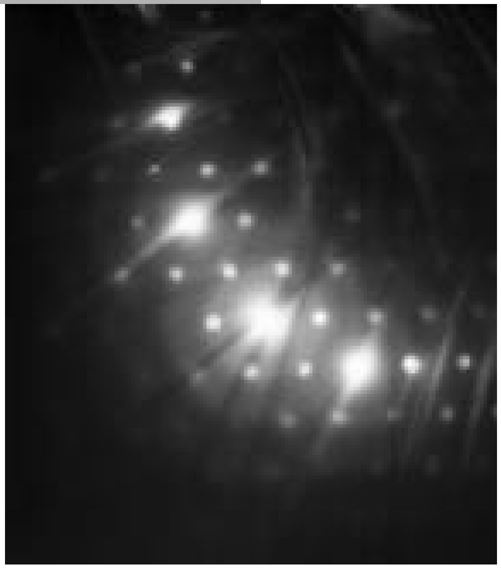
Kikuchi Lines-3



Kikuchi Line Patterns for Si







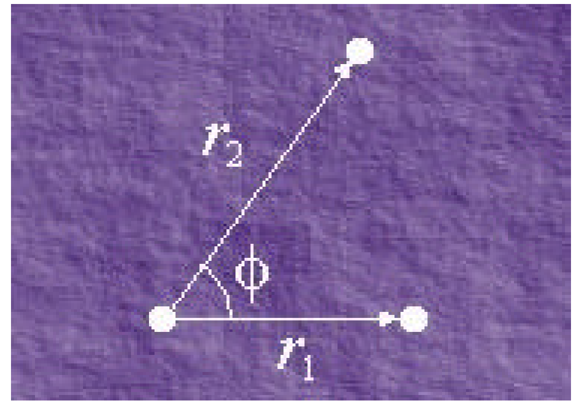
Kikuchi lines pass straight through transmitted and diffracted spots. Diffracting planes are tilted at exactly the Bragg angle to optic axis.

Crystal has been titled slightly away from Bragg angle, so that Kikuchi lines no longer pass through trans-mitted and diffracted spots.

Here the crystal is tilted so that more that one set of planes are diffracting. Each set of diffracting planes has its own pair of Kikuchi lines.

Indexing Diffraction Pattern-ratio technique

Any 2-D section of a reciprocal lattice can be defined by two vectors so only need to index 2 spots.



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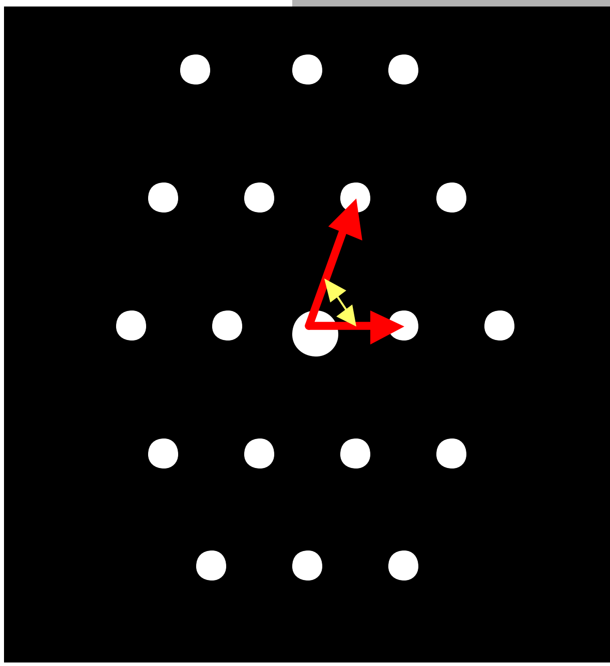
8. **if measured f agrees with one of possible value, accept indexing. if not, revisit the table and select another possible pair of planes**
9. **finish indexing the pattern by vector addition.**

Indexing - Example

[01$\bar{3}$]



1. Choose T as the origin, r_1-7.75mm
2. r_2-12.87mm
3. $\phi \sim 72^o$
4. Get a table giving relative reciprocal lattice spacings
5. $r_2 / r_1 = 1.66$ gives several possible pair of planes in the table
6. From the table of interplanar angle in cubic, $\phi \sim 72^o$ gives only one matched pair of planes, {100} (or {200}) and {311} for a face-centered lattice. {100} diffraction is not allowed in a face-centered structure.
7. Calculating interplanar angles leads to (131) or (113) and (200) angle between (311) and (200) is 25.2^o.
8. Zone axis of pattern: $r_1 \times r_2$ = [013] for (131) and (200) pair

Formation of HOLZ Lines