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Title: Phase Identification and Twinning

Author(s): Field, Robert D.

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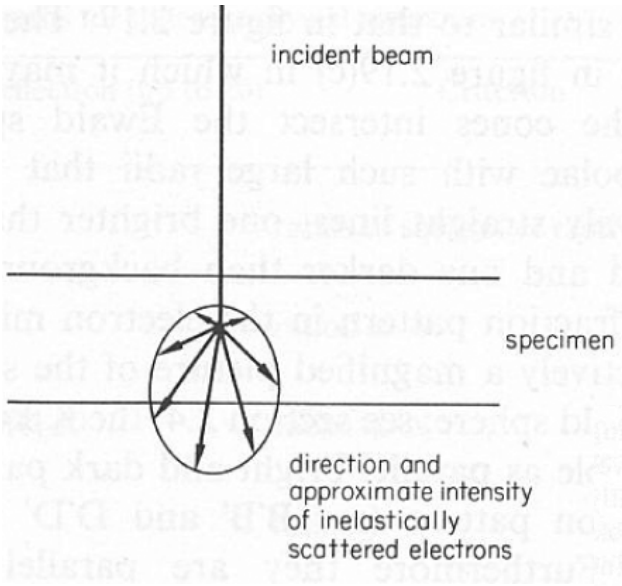
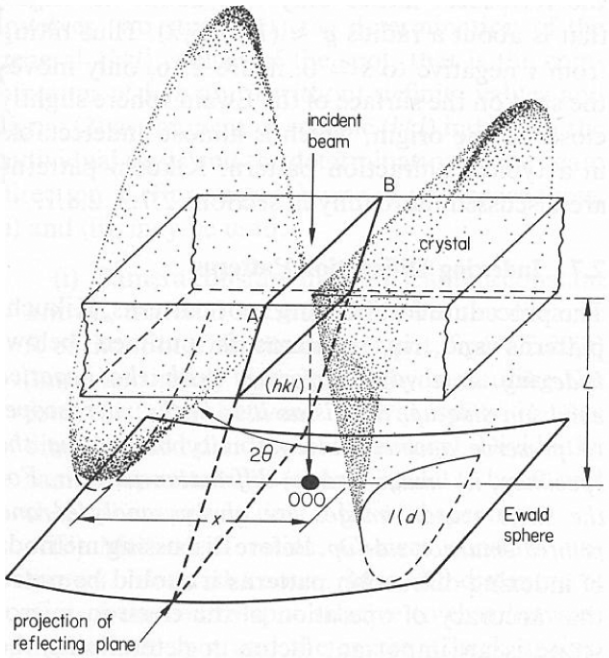
Phase Identification and Twinning

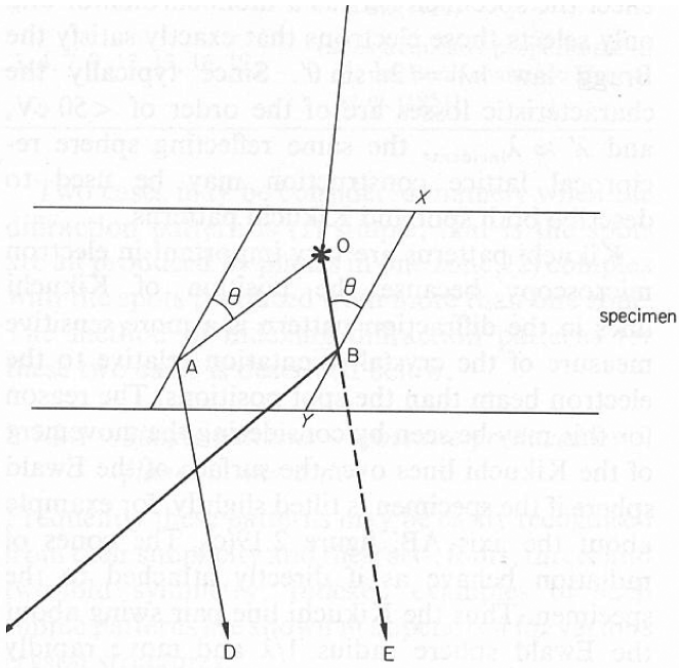
R.D. Field, Los Alamos National Laboratory

- Tilting in the TEM
  - Kikuchi lines: your map to reciprocal space
  - Tips for tilting
- Diffraction patterns and indexing
  - A little crystallography
  - Tips for indexing
- Orientation relationships and variants
  - Single variant
  - Multiple variant
  - Twins
- Miscellaneous examples

Kikuchi Lines: Road Maps of Reciprocal Space

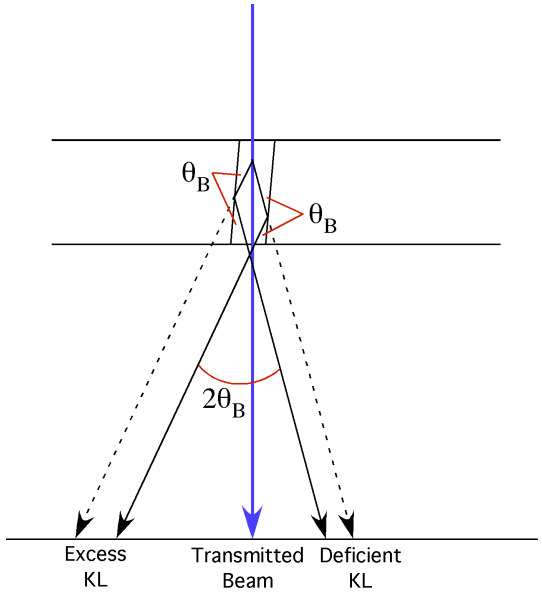


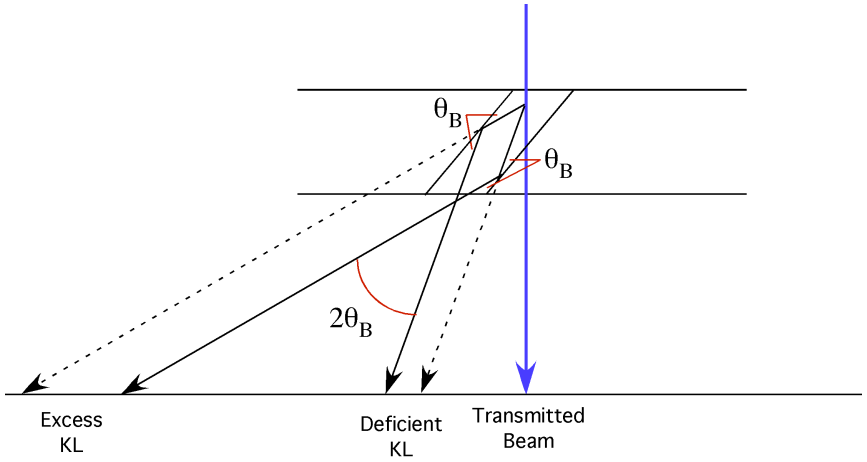


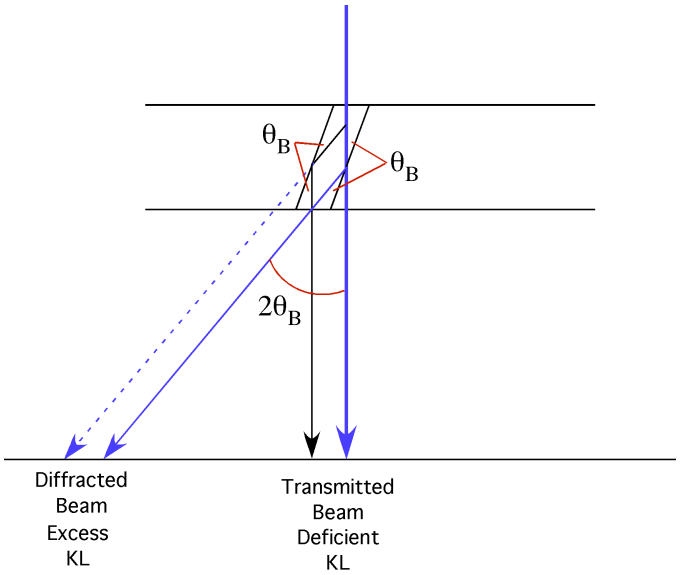


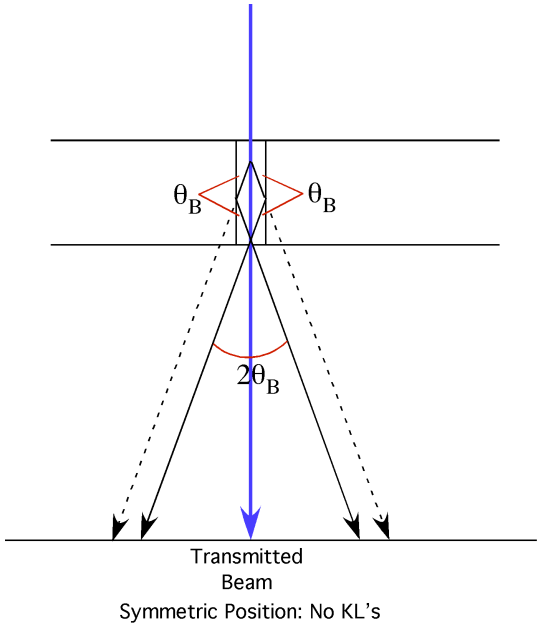
(Figures from Edington, "Practical Electron Microscopy in Materials Science")

Kikuchi Line Formation









Experimental Kikuchi Patterns

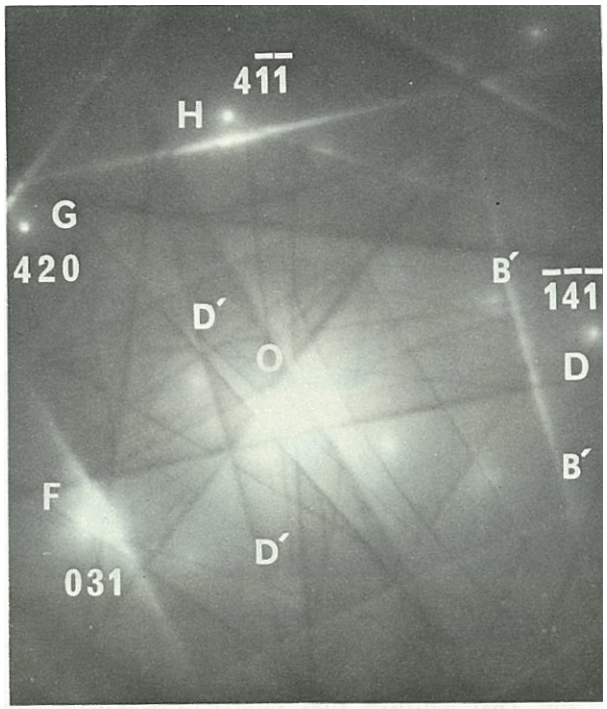


Figure 2.22 A combined spot and Kikuchi line pattern from fully annealed α-iron showing two zones of spots [Courtesy of C. A. Shell]

Kikuchi lines

(Figure from Loretto and Smallman, "Defect Analysis in Electron Microscopy")

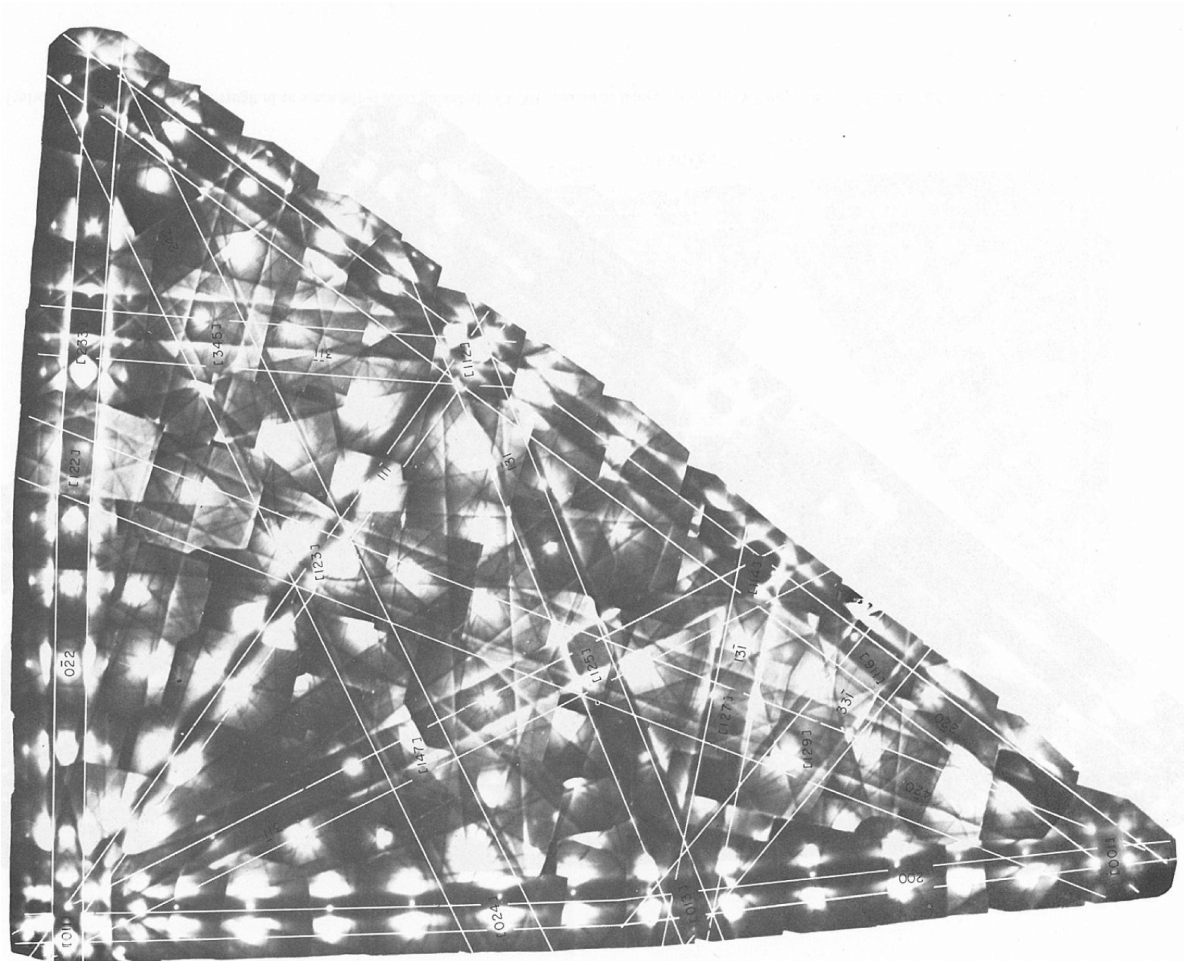


Figure A5.1 An indexed Kikuchi map for the f.c.c. crystal structure; 100 kV. The indices in square brackets are those of the beam direction **B** for the particular Kikuchi line pattern. The unbracketed indices are those for the Kikuchi line pair [Courtesy of A. Samuelson]

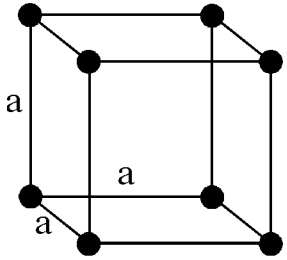
Kikuchi map of fcc (montage)

(Figure from Edington, "Practical Electron Microscopy in Materials Science")

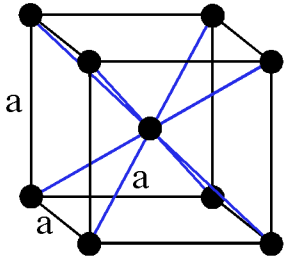
Tilting Tips

- Tilt in CBED mode
  - defocus condenser lens to see image in discs
- Follow short g-vectors and mirror planes
- Follow more than one g-vector
  - “turn a corner”
- Record tilts between zone axes
  – one more thing to fit to phase information

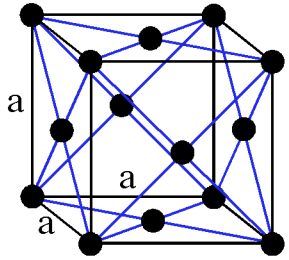
Major Symmetry Operations



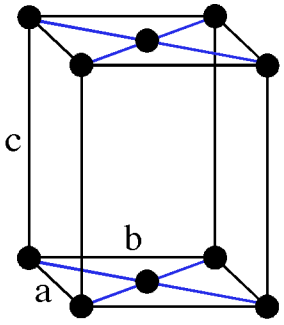
Simple (Primitive) Cubic (P)



Body-Centered Cubic (I)



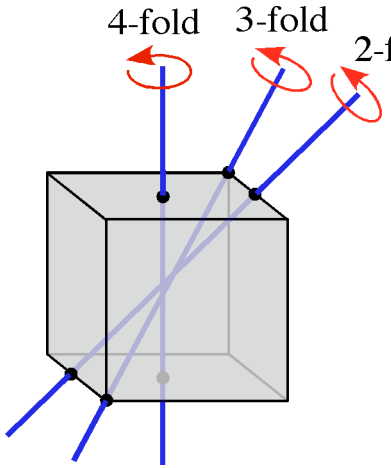
Face-Centered Cubic (F)



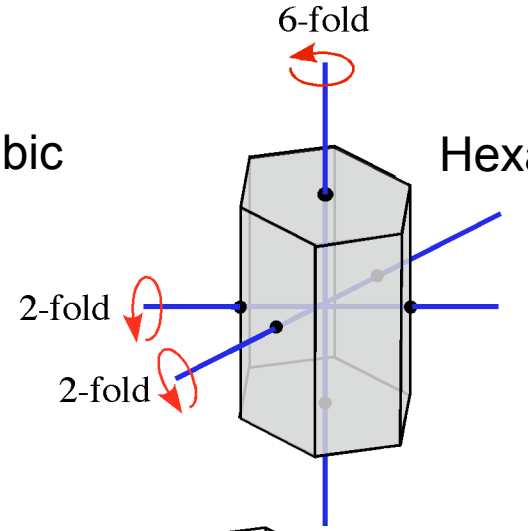
Base-Centered Orthorhombic (C)

Cell Centering
(P,I,F,C,R†)

† Rhombohedral

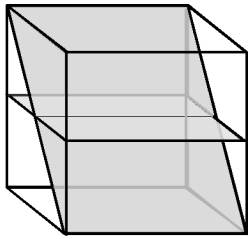


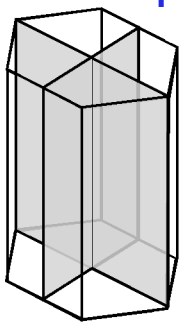
Cubic



Hexagonal

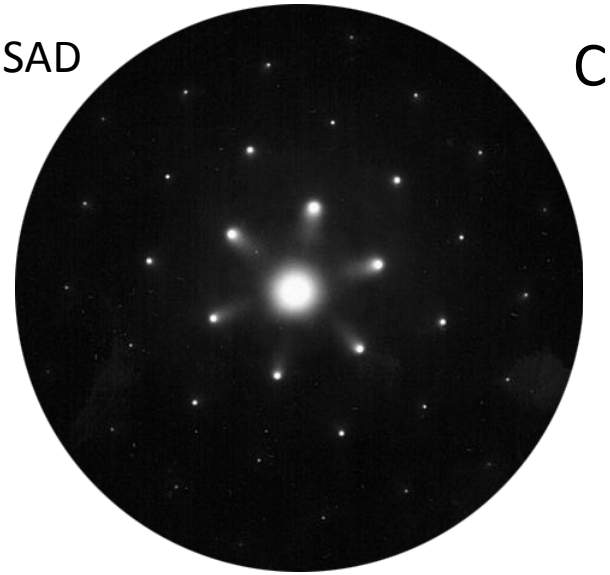
Rotation Axes
(2,3,4,6)
or
Screw Axes
(e.g. 2_1,3_1,4_1,6_3)


Cubic

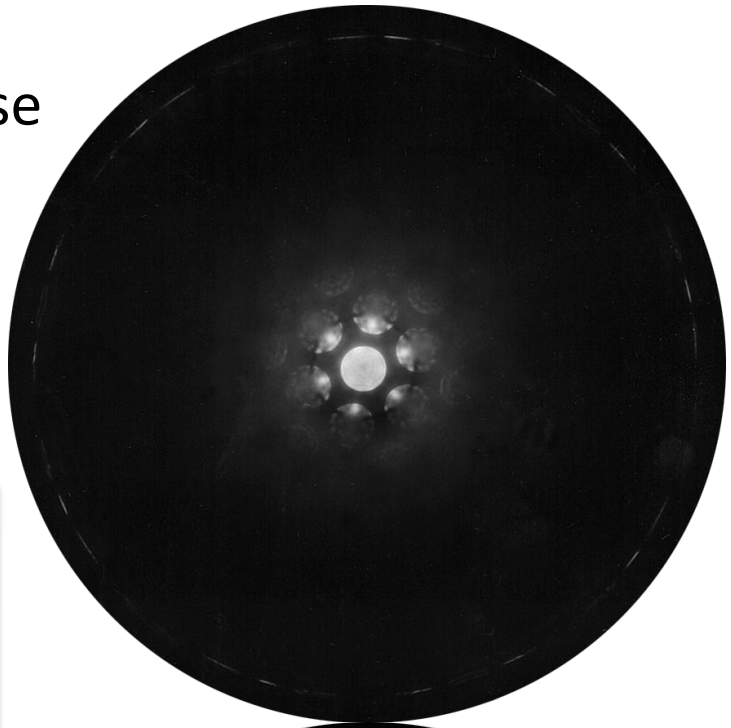

Hexagonal

Mirror Planes (m)
or
Glide Planes
(a,c,n,d)

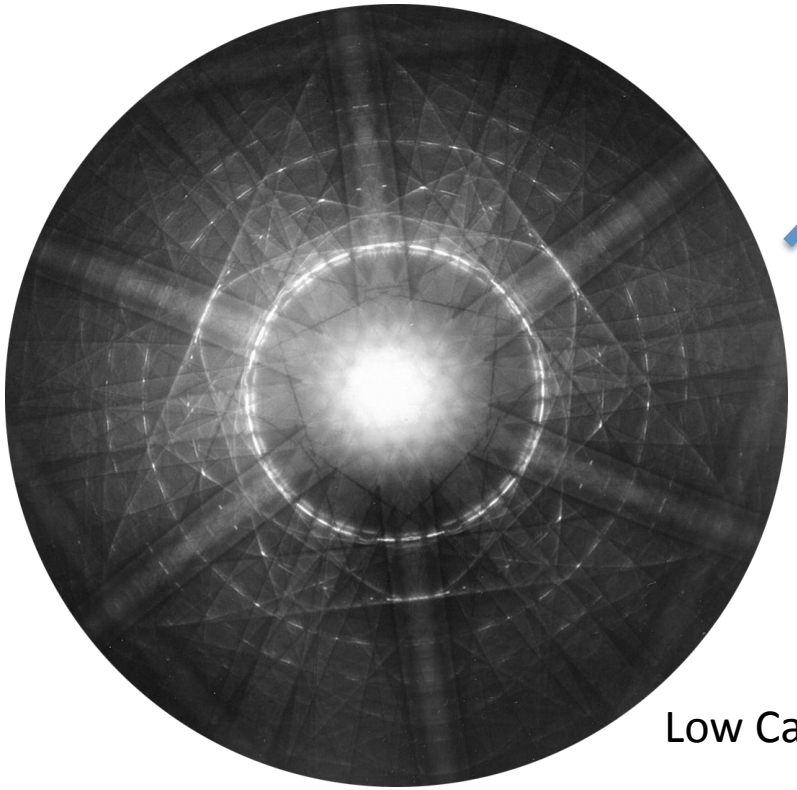
SAD



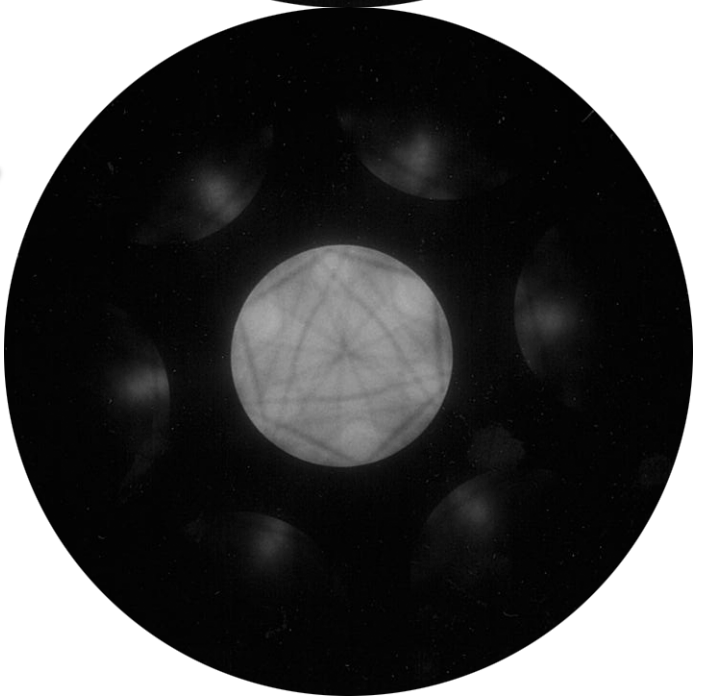
CBED of Fd-3m Phase (Diamond Cubic)



Higher Camera Lengths



Low Camera Length



Indexing Diffraction Patterns

- Measure d-spacings from reflections (SAD)
  - calibrated instrument
  - note that precision is in the ±0.1Å range (SAD)
  - generally 2 g-vectors is sufficient per zone axis

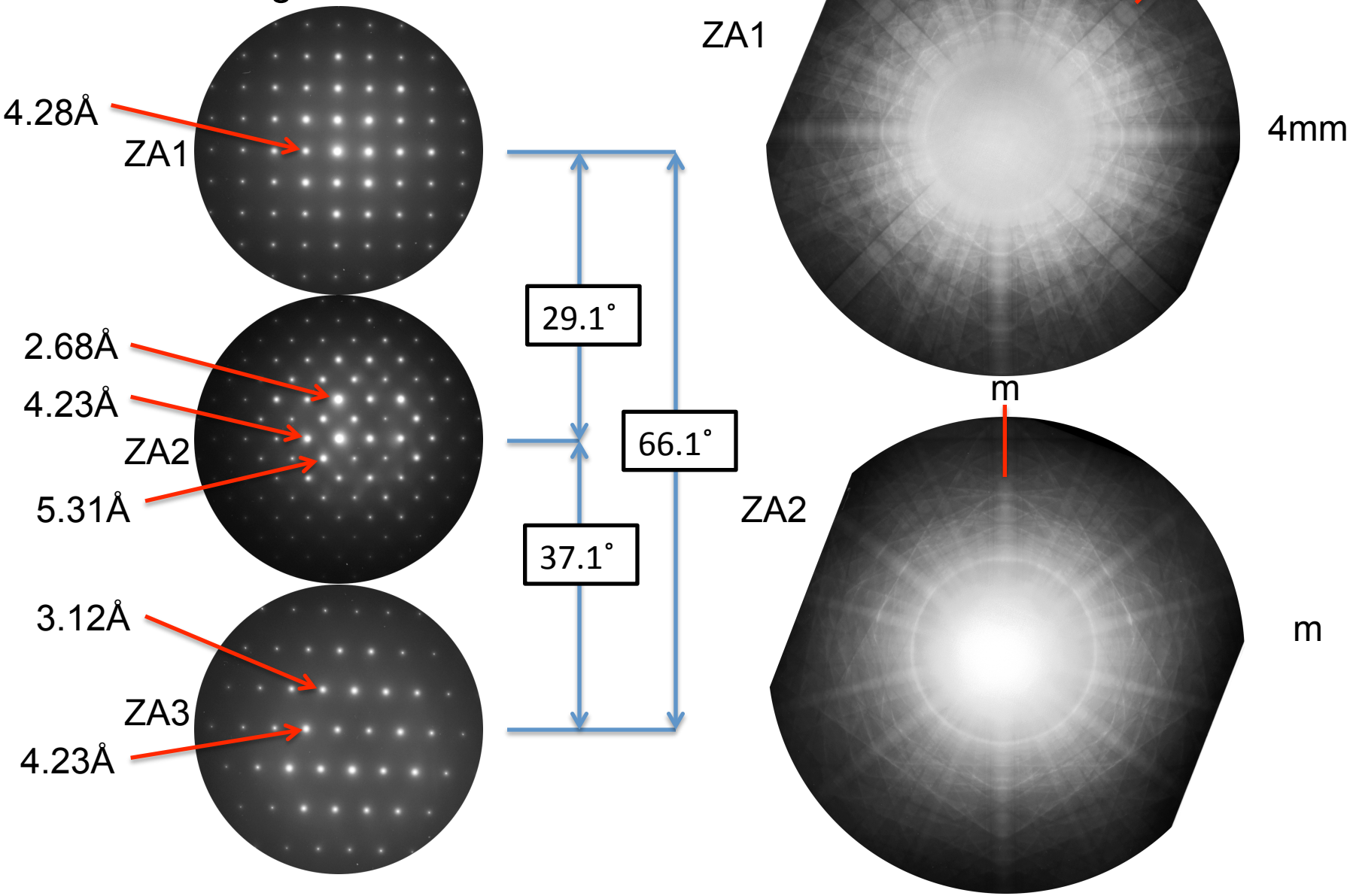
- Angles between reflections can be useful
  - for low symmetry zone axes

- Note symmetry (CBED)
  - will limit which planes to consider

- Compare to known/proposed phase data
  - d-spacing
  - symmetry considerations
  - extinctions

Indexing Example: Mo_5SiB_2

Accumulating the Data



Indexing Example: Mo_5SiB_2†

Fitting the Data

D-spacing measurements

d-meas.	ZA	plane	d-calc.	Allowed/ Double Diffr.	Extinction Rule††
4.28/4.23	1,2,3	1-10	4.24	Allowed	NA
5.31	1	10-1	5.27	DD	hkl: h+k+l = 2n
3.35	2	11-2	3.36	Allowed	NA
3.12	3	10-3	3.13	DD	0kl: k,l = 2n

Angles between zone axes

ZA-uvw	ZA	1	2	3
001	1	-	29.1˚	66.1˚
111	2	29.0˚	-	37.1˚
331	3	66.6˚	37.6˚	-

Measured

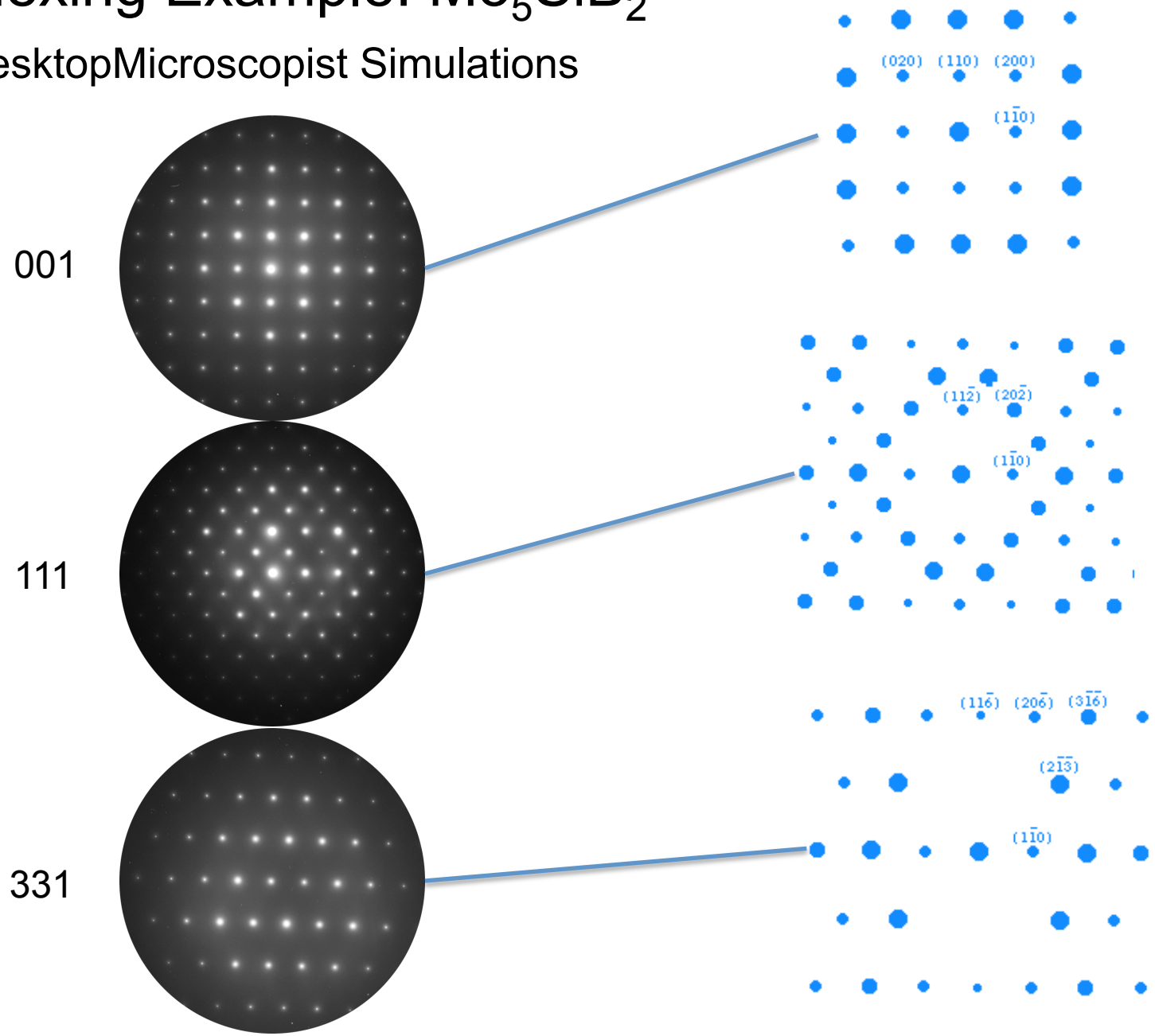
Calculated

† tI32, I4/mcm, a=6.00Å, c=11.03Å

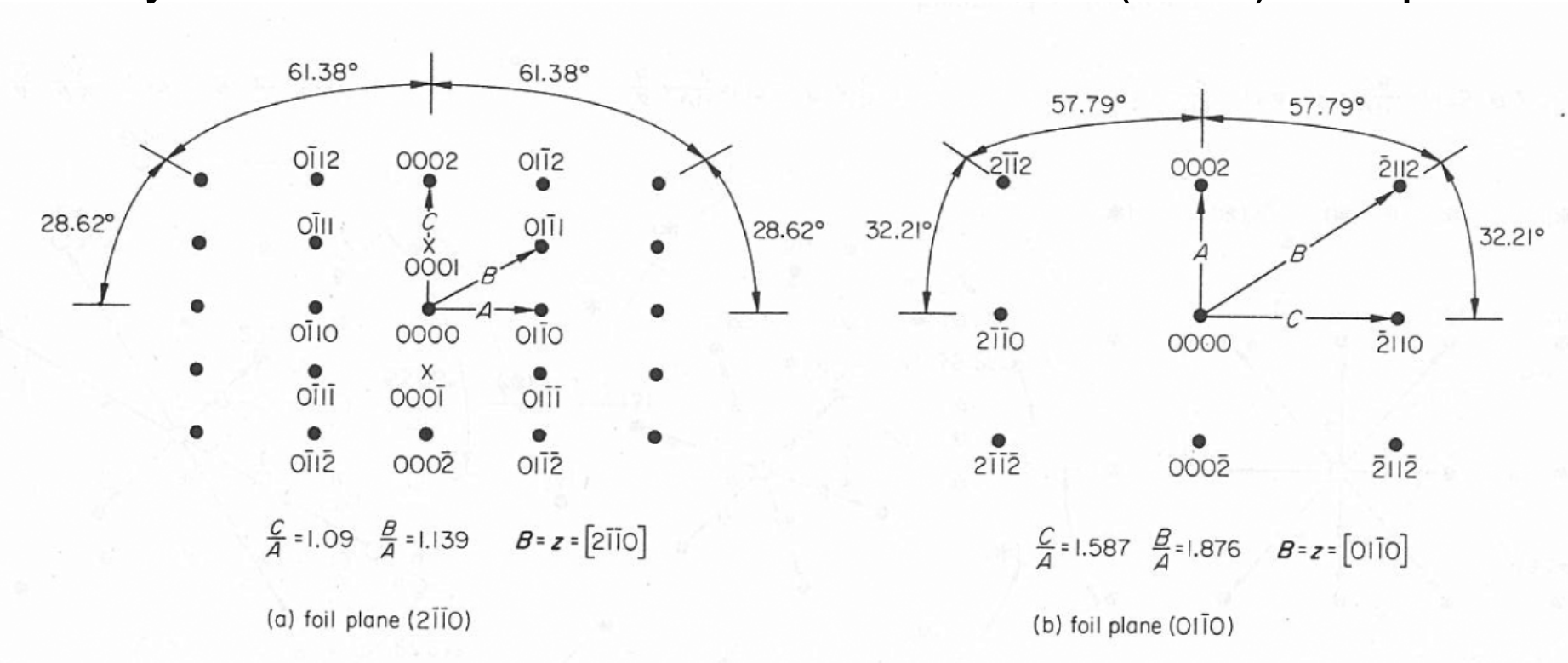
†† Extinction rules from International Tables of Crystallography, Vol. A

Indexing Example: Mo_5SiB_2

DesktopMicroscopist Simulations



Dynamic Diffraction: Double Diffraction of (0001) in hcp



Tips:

- Reflection may appear in one ZA, but not another
- Tilt off ZA to systematic row
- Extinction conditions in CBED

(Figure from Edington, "Practical Electron Microscopy in Materials Science")

Precipitates: Orientation Relationship with Single Variant

- Crystallographic orientation relationship (OR) between matrix and precipitate
- Generally designated as direction and plane aligned in M/P:

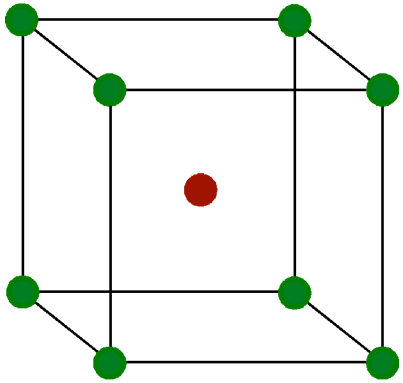
$$[uvw]_P \parallel [uvw]_M$$
$$(hkl)_P \parallel (hkl)_M$$

- Simplest example is “cube-on-cube” (single variant):

$$[001]_P \parallel [001]_M$$
$$(100)_P \parallel (100)_M$$

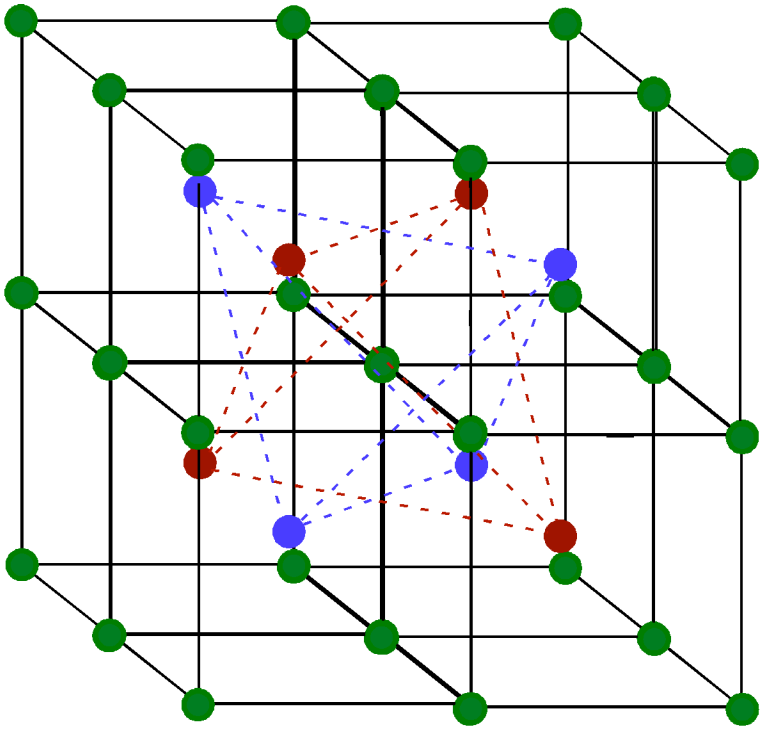
- Tilt on matrix and record diffraction patterns along matrix zone axes

B2 vs. L21: Ordering on Al/Ti Sublattice



NiAl (CsCl-B2)
$Pm\bar{3}m$, cP2

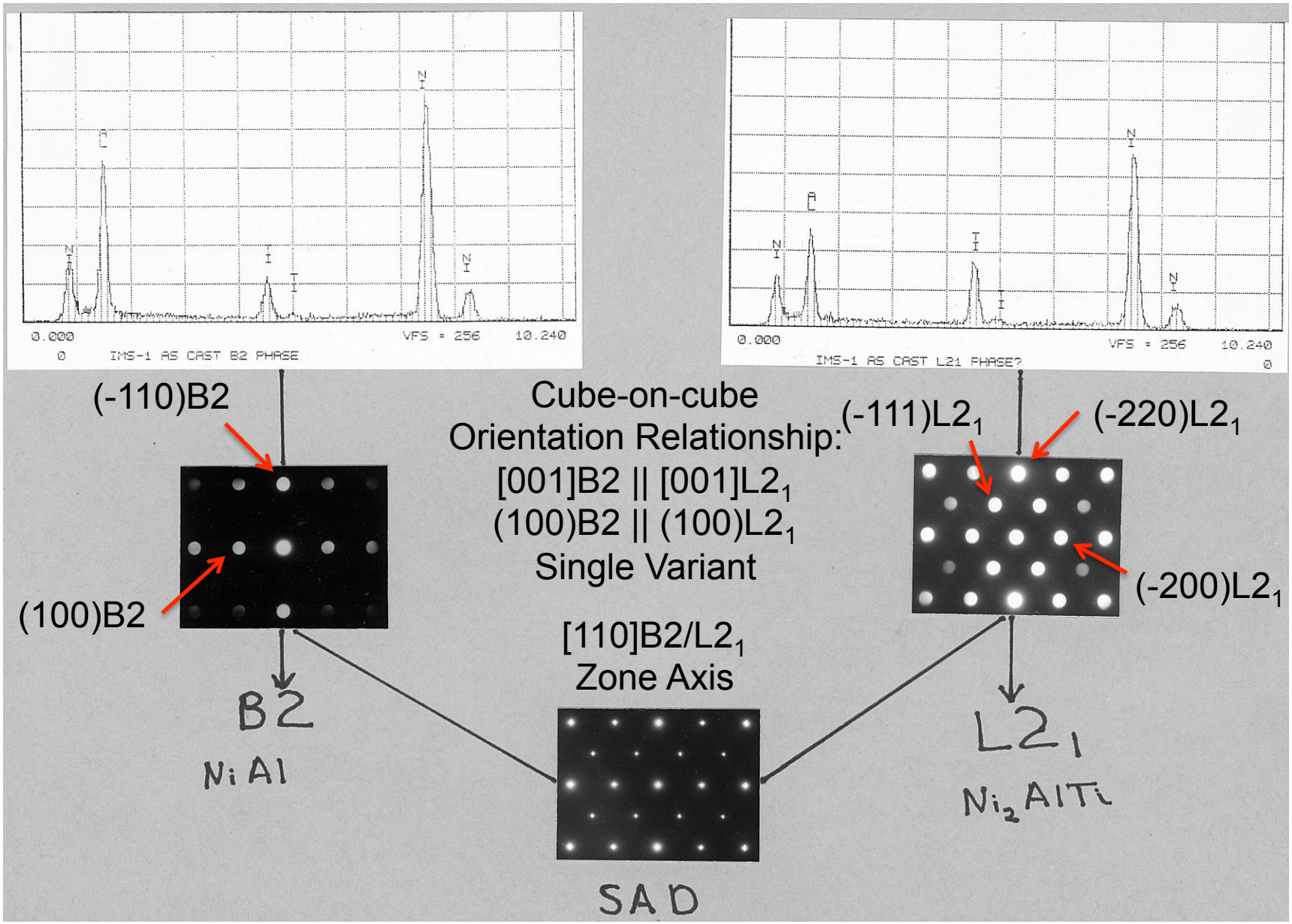
Ni Al/Ti



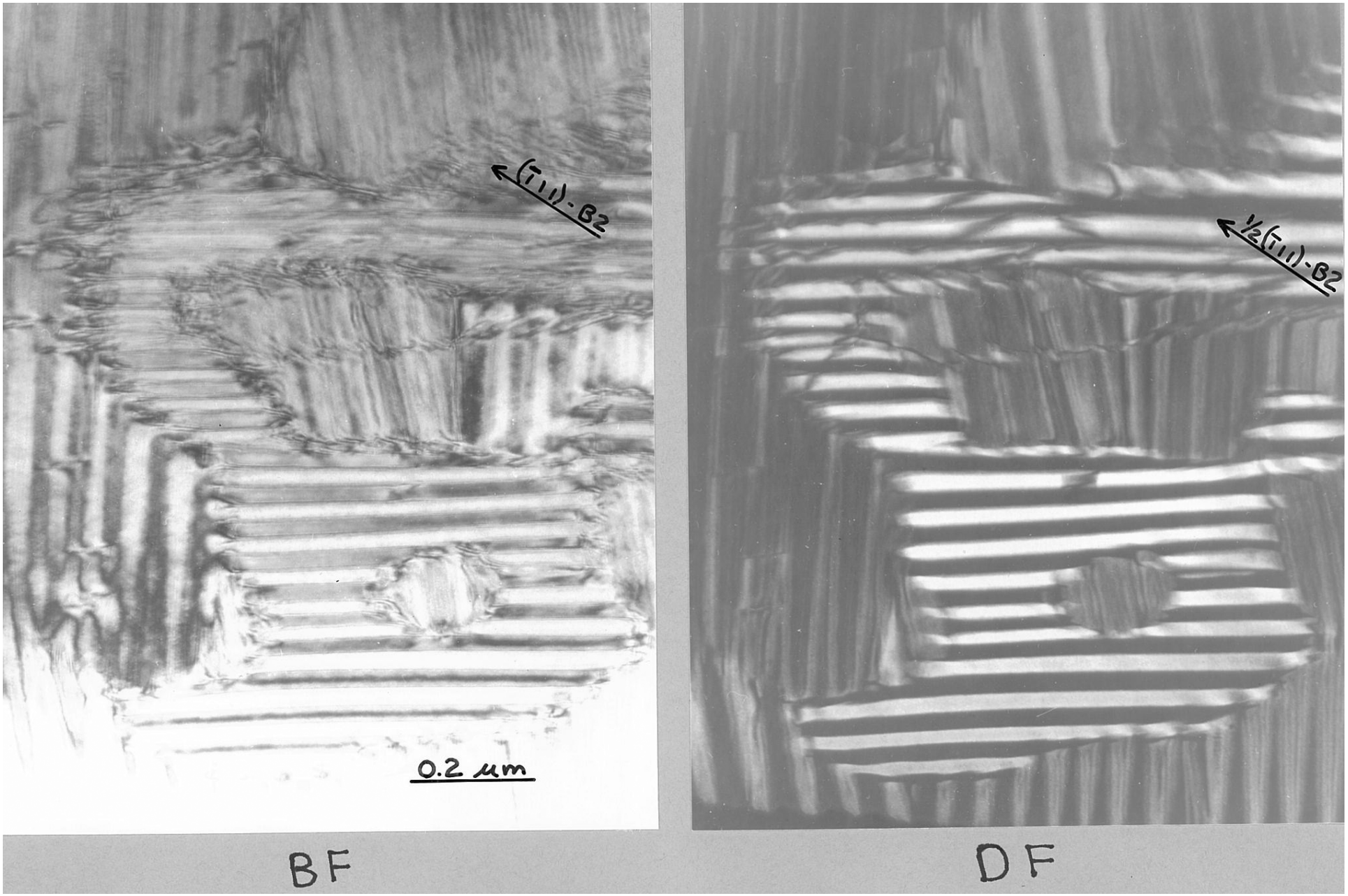
Ni_2AlTi (BiF_3-$L2_1$)
Heusler phase
$Fm\bar{3}m$, cF16

Ni Al Ti

$B2/L2_1$ Conditional Spinodal Ordering

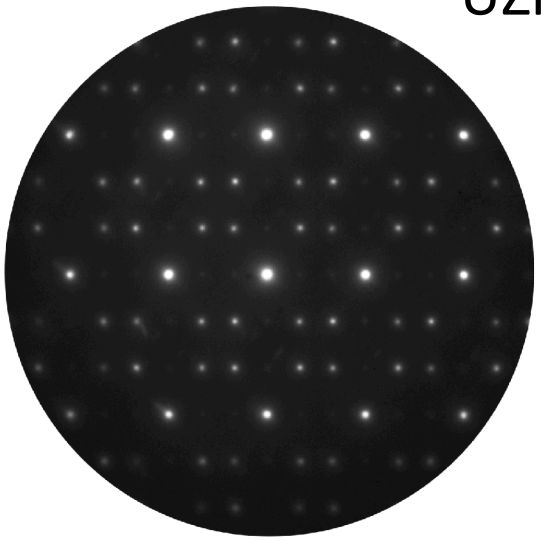


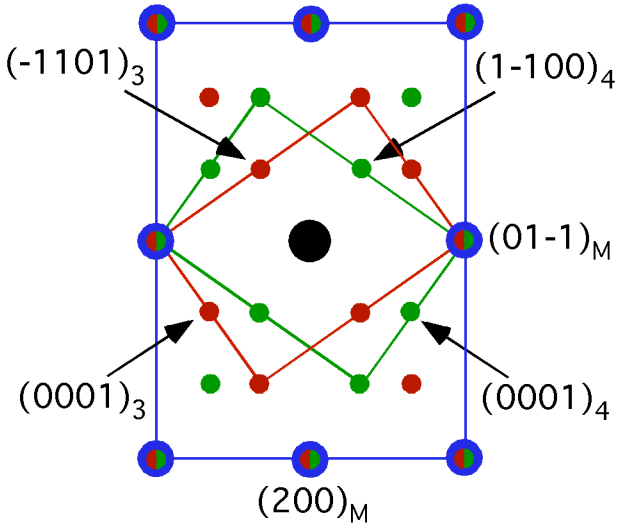
B2/$L2_1$ Conditional Spinodal Ordering – Dark Field



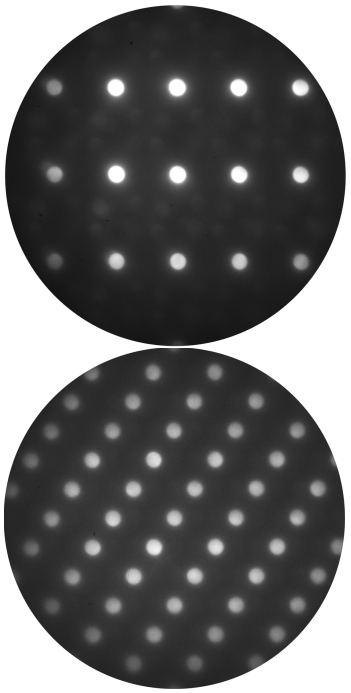
Precipitates: Orientation Relationship with Multiple Variants

UZr_2 Precipitates in γ-U (bcc) Matrix





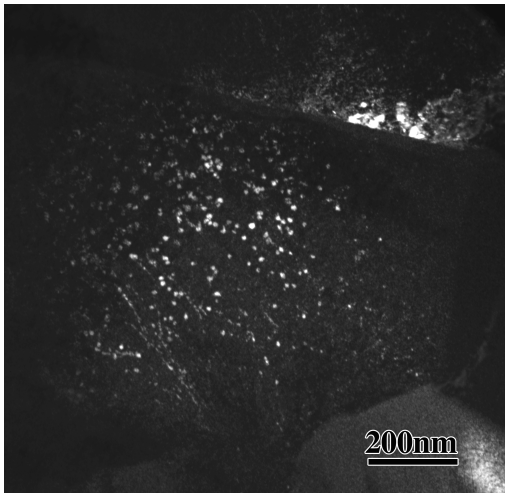
$[011]_M \parallel [11\text{-}20]_3 \parallel [11\text{-}20]_4$

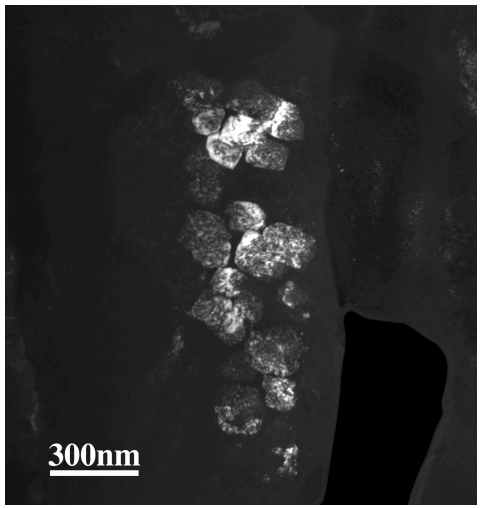


Microdiffraction

Orientation Relationships

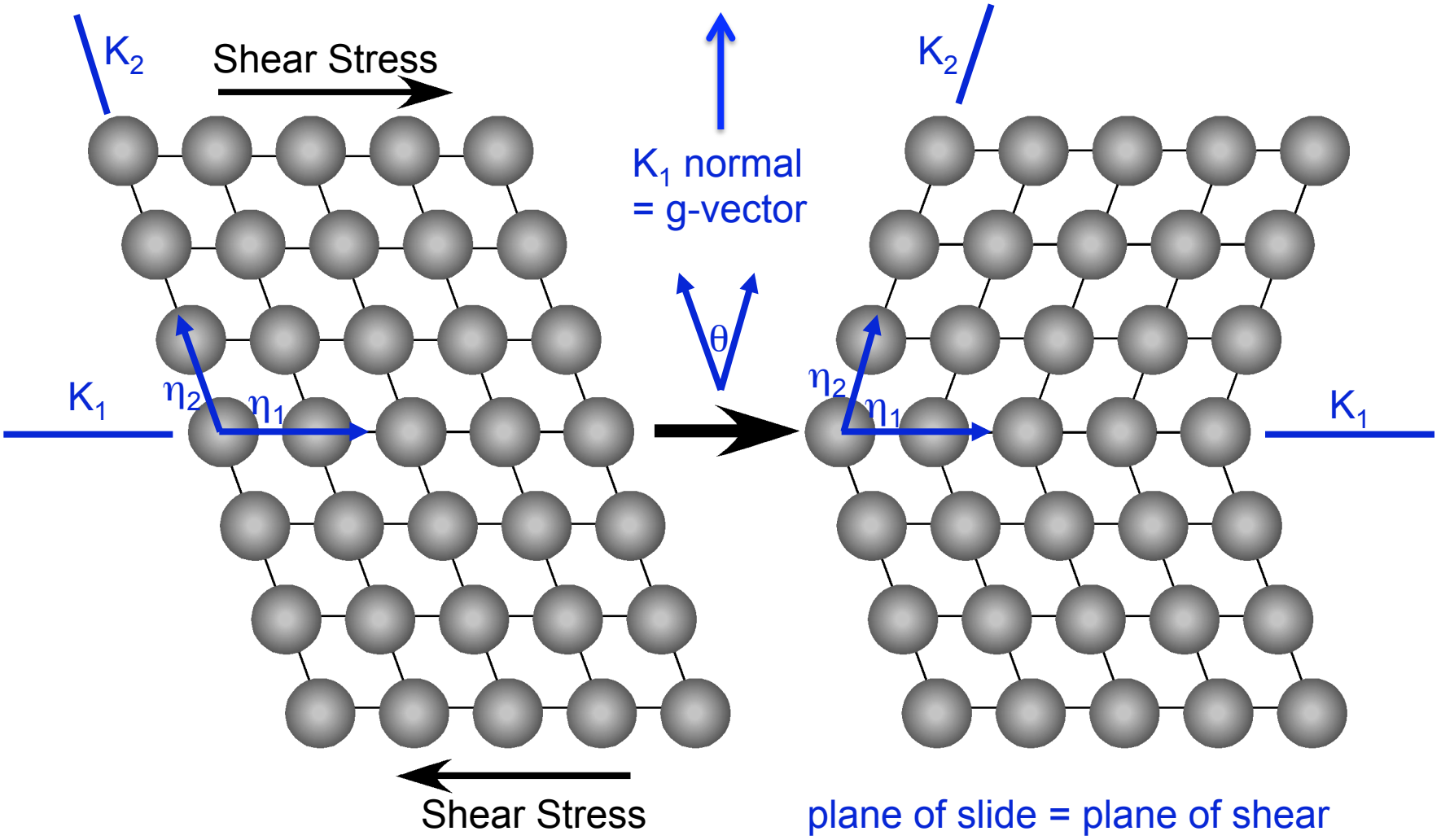
Variant 1	$[111]\gamma$	$\parallel [0001]UZr_2$
	$(01\text{-}1)\gamma$	$\parallel (11\text{-}20)\ UZr_2$
Variant 2	$[\text{-}111]\gamma$	$\parallel [0001]UZr_2$
	$(01\text{-}1)\gamma$	$\parallel (11\text{-}20)\ UZr_2$
Variant 3	$[1\text{-}11]\gamma$	$\parallel [0001]UZr_2$
	$(011)\gamma$	$\parallel (11\text{-}20)\ UZr_2$
Variant 4	$[11\text{-}1]\gamma$	$\parallel [0001]UZr_2$
	$(011)\gamma$	$\parallel (11\text{-}20)\ UZr_2$



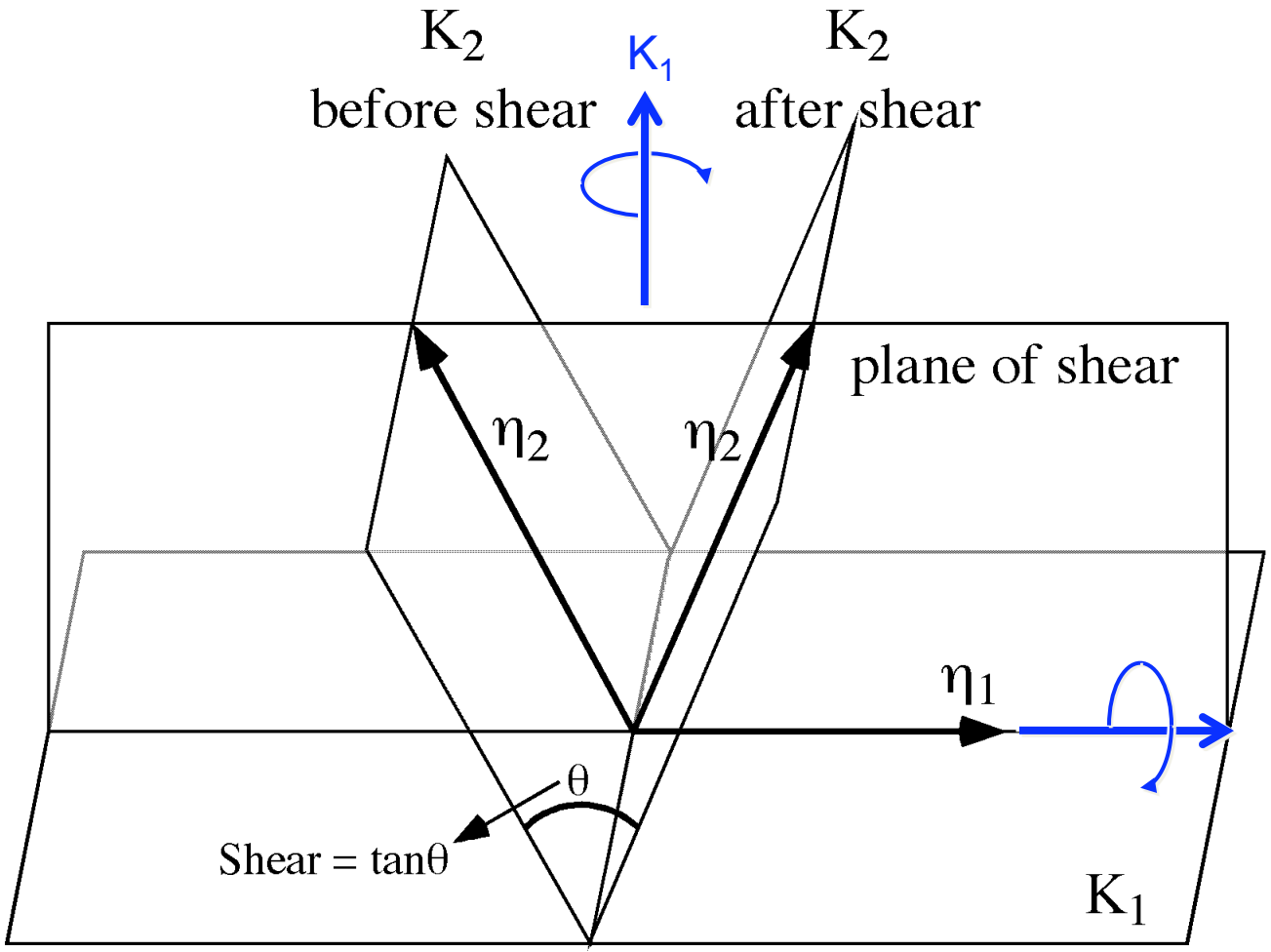


Dark Field Micrographs – doesn't show all variants

Basic Elements of Twinning - Atomistic View



Basic Elements of Twinning



Type I:
- K_1&η_2 rational
- K_2&η_1 irrational

Type II:
- K_2&η_1 rational
- K_1&η_2 irrational

Compound:
- All elements rational

Reciprocal Twins:
- K_1 <-> K_2
- η_1 <-> η_2

Diffraction Patterns from Twins

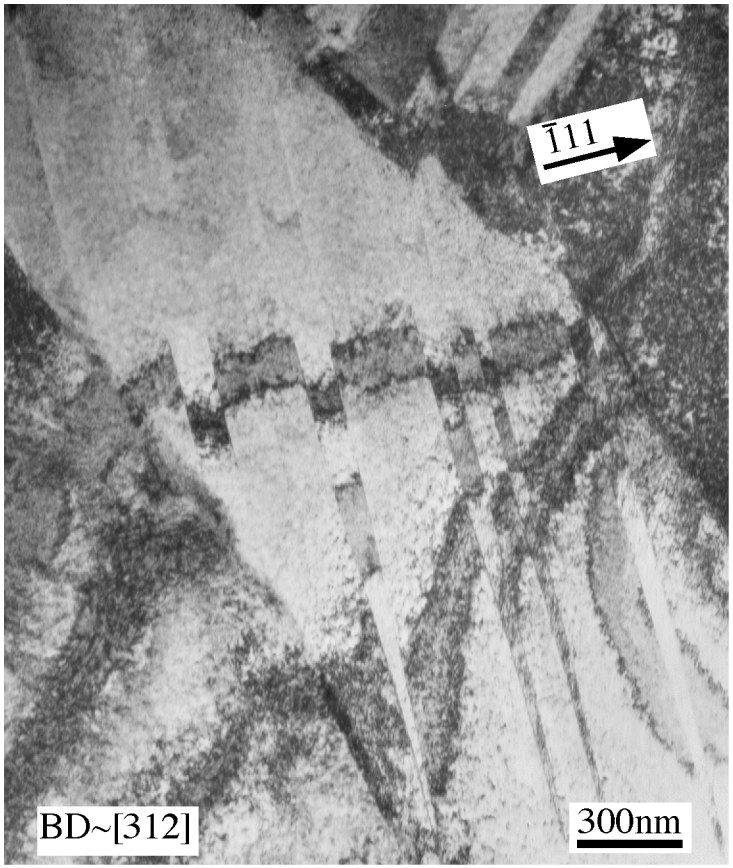
- Same phase, different orientation
  - similar to second phase

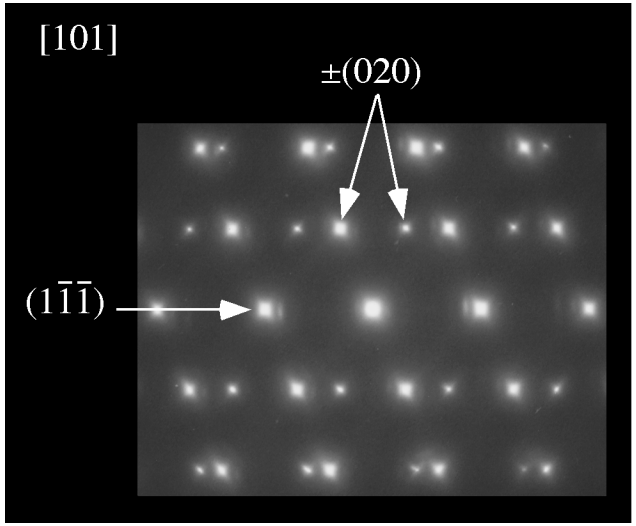
- Most twins will display diffraction pattern mirrored about K_1 plane

- Tilting hints:
  1) Tilt about axis ~perpendicular to K_1 normal
     - tilt until beam direction is contained within K_1
       - matrix and twin will go dark together when g-vector = K_1
  2) Tilt along K_1 to zone axis

Diffraction from Type I or Compound Twin

Twin orientation relationship: 180˚ rotation about K_1

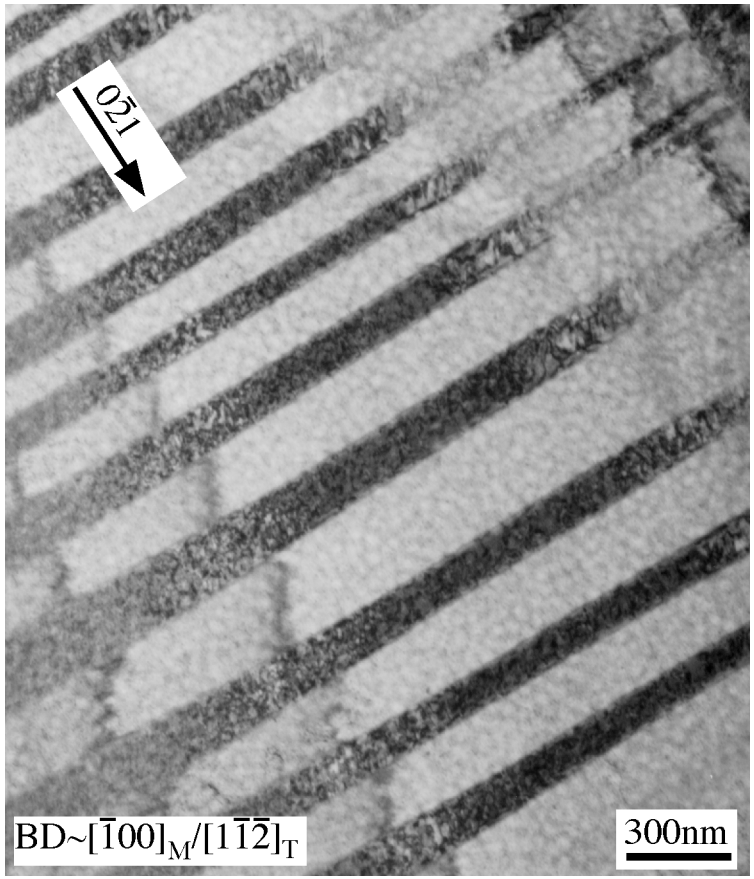


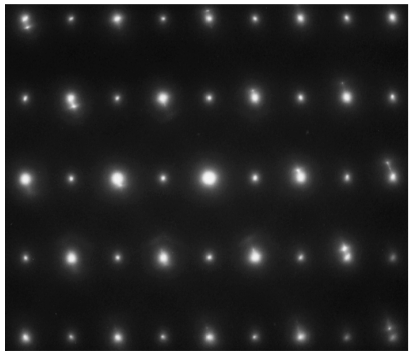


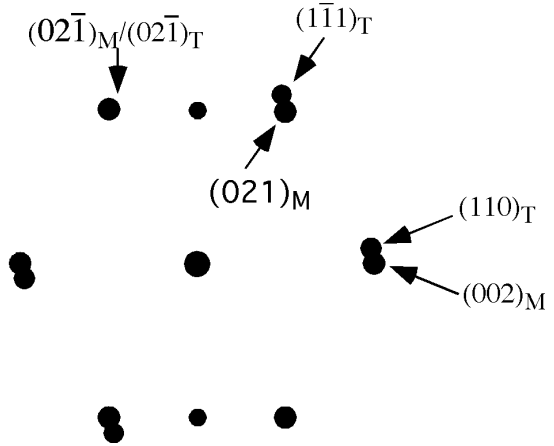
Diffraction pattern from ZA containing twin plane: mirror about twin plane

Diffraction from Type II Twin

Twin orientation relationship: 180˚ rotation about η_1







Diffraction patterns from twins no longer show mirror symmetry with matrix

A Few More Examples

- Precise lattice parameter measurements with HOLZ lines (High Order Laue Zones)
- Friedel's Law and electron diffraction
- Streaking and spiking
- Amorphous/fine grain polycrystalline patterns

Using HOLZ lines to measure γ/γ' lattice mismatch in a Ni-Base Superalloy

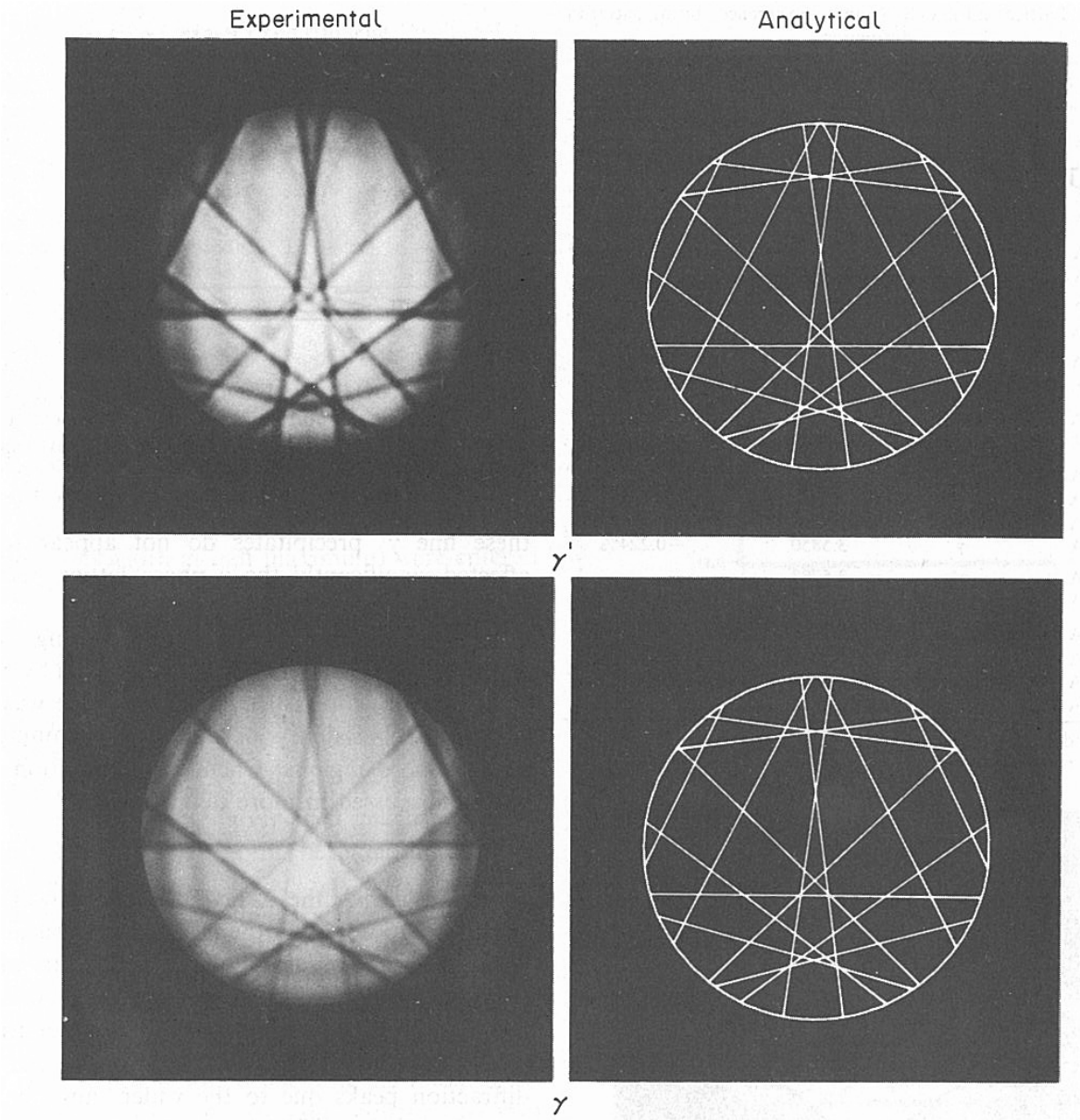
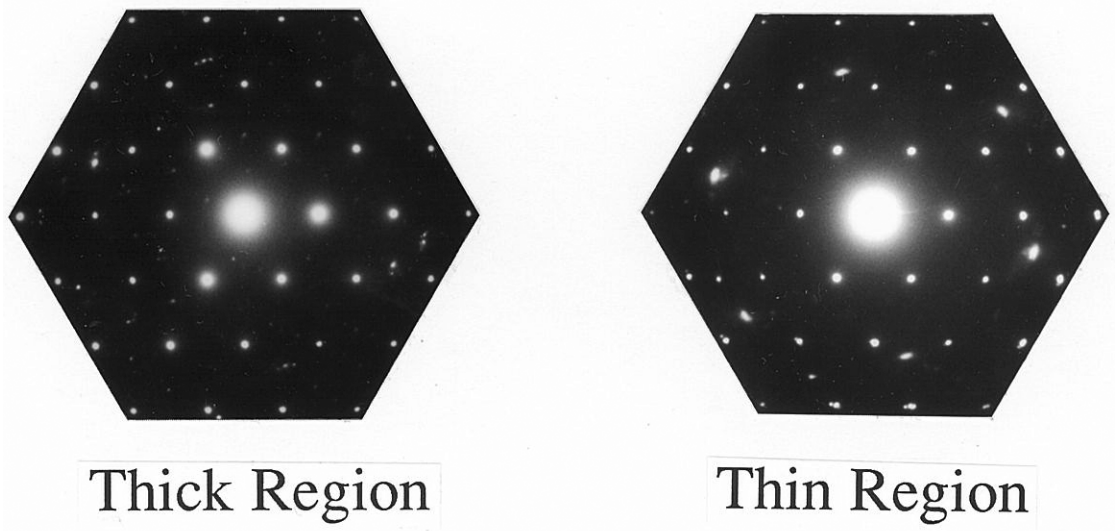


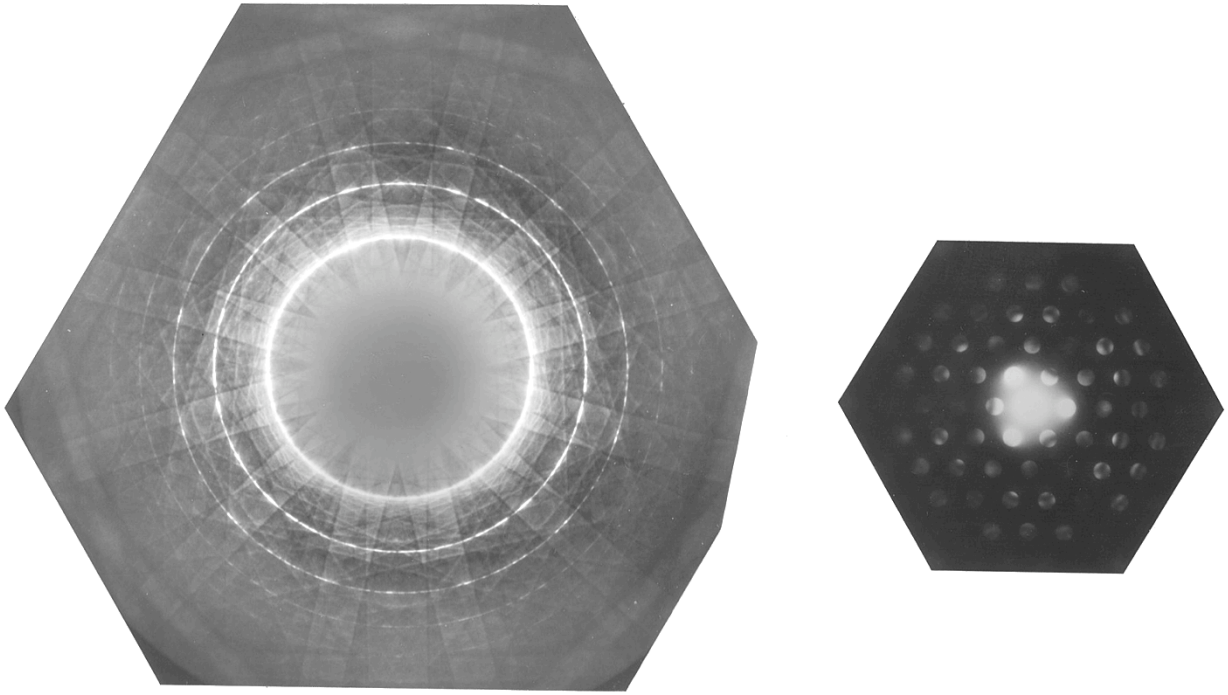
Fig. 7. Experimental and analytical FOLZ line patterns from the [114] zone axis for the alloy in the over-age condition. The lattice parameter of each phase is: $\gamma = 3.5840$ Å, $\gamma' = 3.5765$ Å. The lattice mismatch for this pair is -0.21%.

Structure Lacking Center of Symmetry (Friedel's Law)

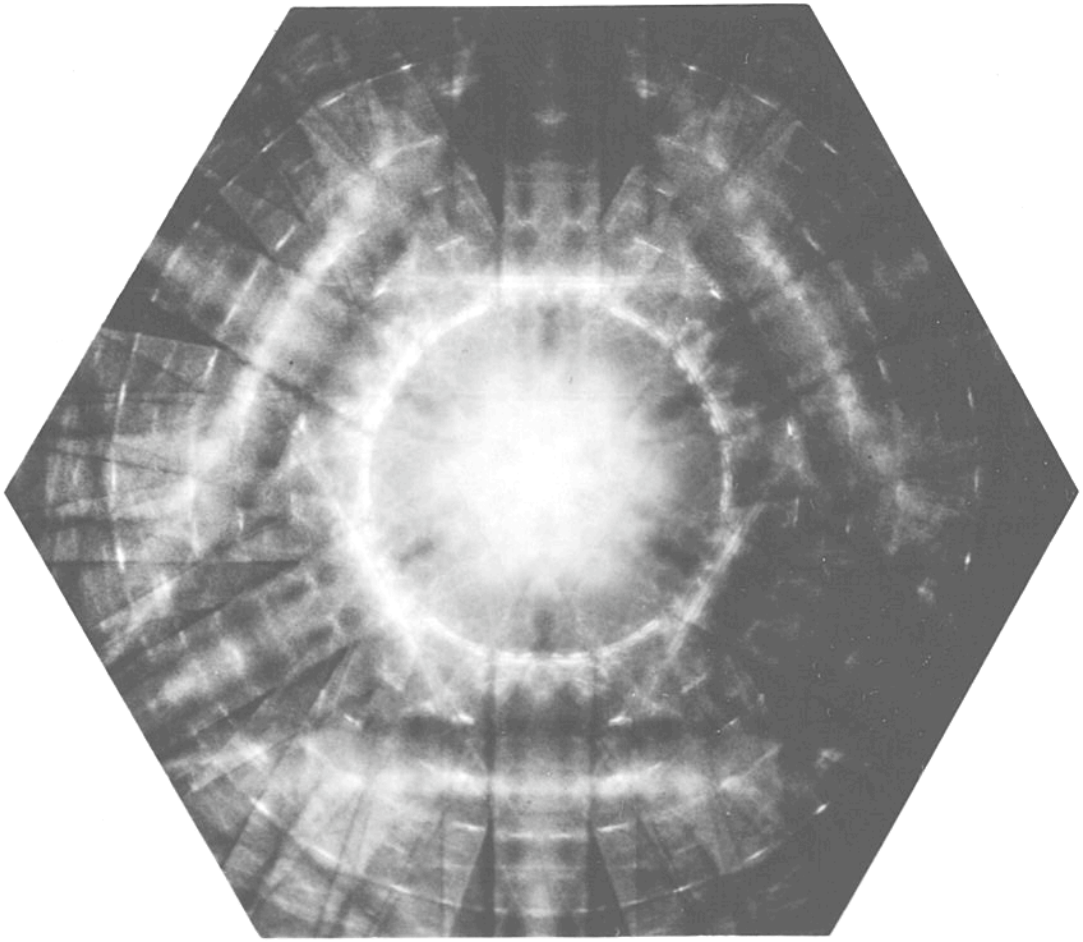
SAD: Thin region is more Kinematic
Thick region is more Dynamical

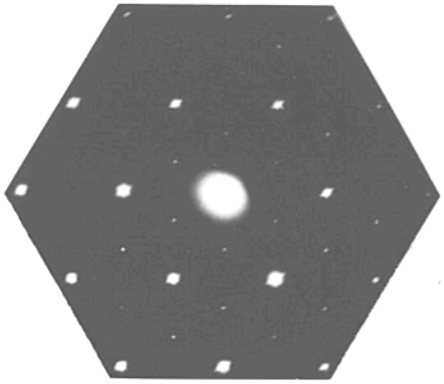


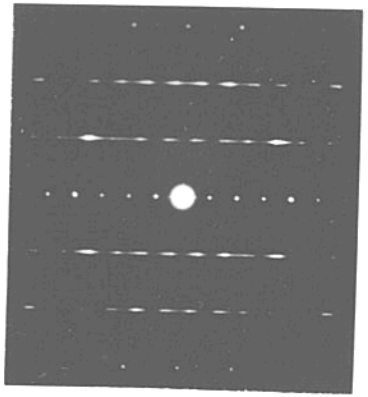
Convergent Beam

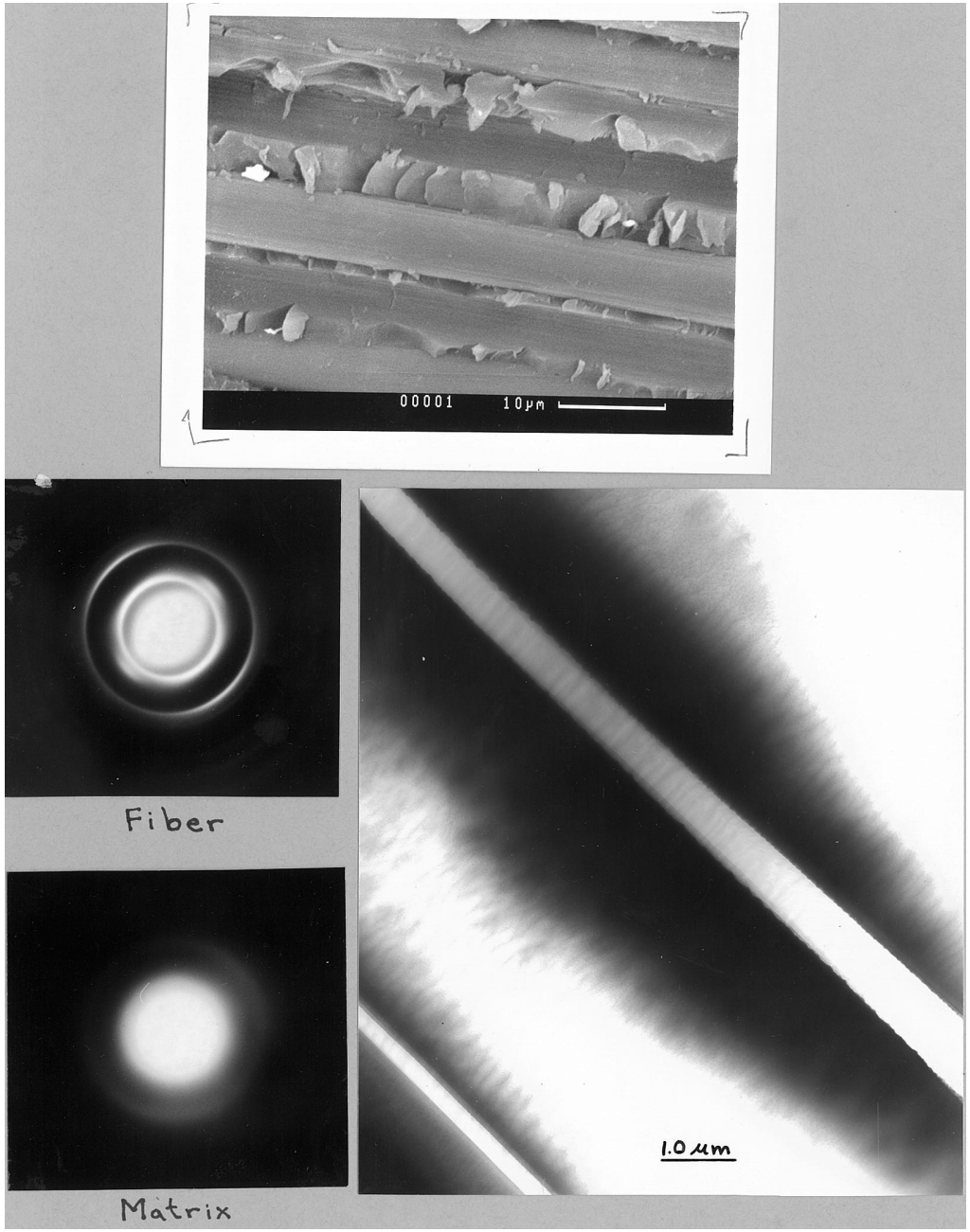


Mu Phase in Ni Base Superalloy: Streaking/Spiking of RL Points









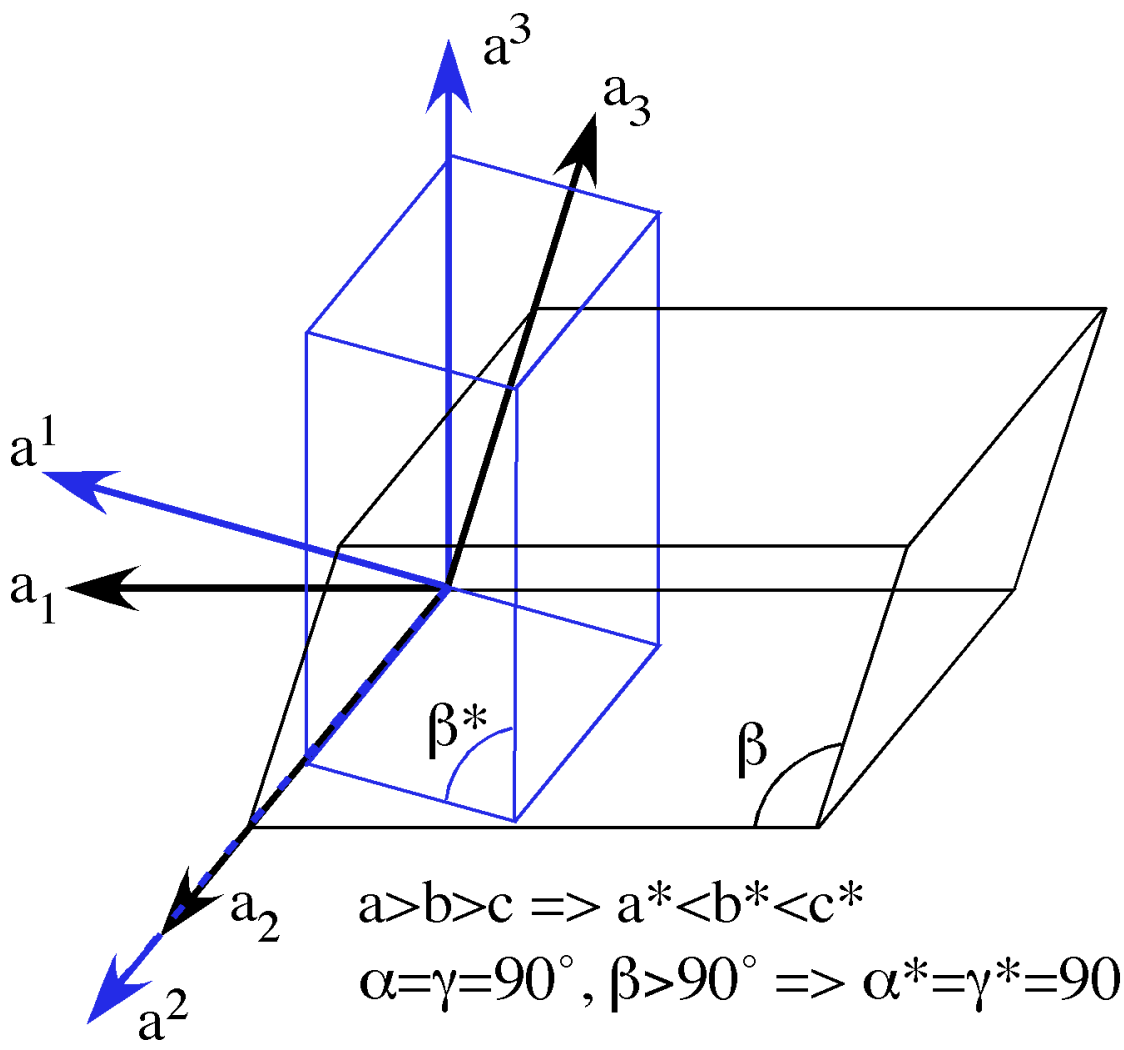
Carbon-Carbon Composite

Amorphous Matrix

Fine-grained textured fibers

Questions?

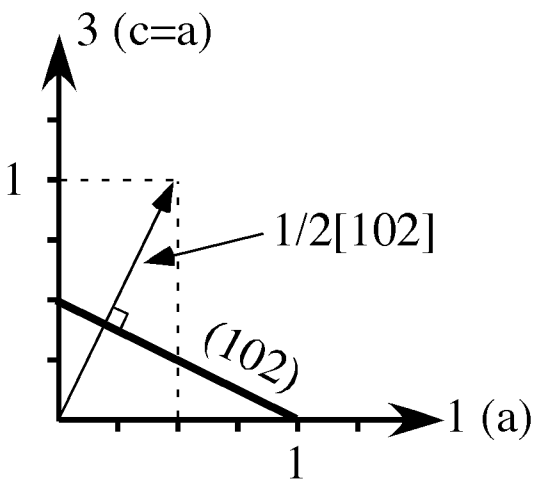
Real vs. Reciprocal Space Unit Cells



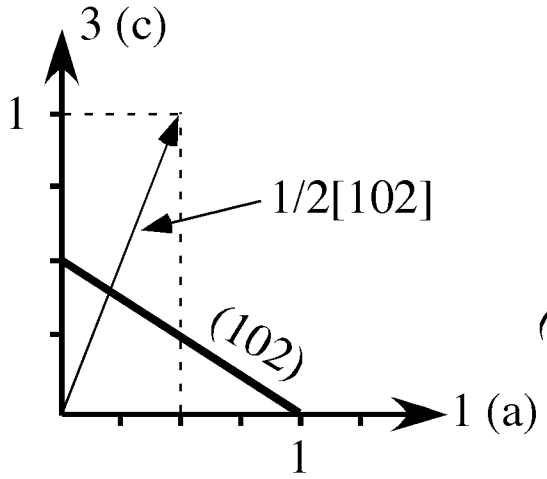
$a>b>c \Rightarrow a^*<b^*<c^*$

$\alpha=\gamma=90^\circ, \beta>90^\circ \Rightarrow \alpha^*=\gamma^*=90^\circ, \beta^*<90^\circ$

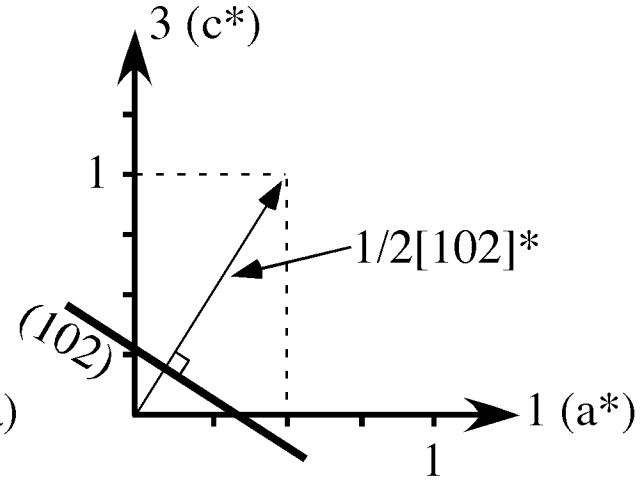
Directions vs. Poles (plane normals)
Real vs. Reciprocal Space



Real Space:
Cubic



Real Space:
Tetragonal



Reciprocal Space:
Tetragonal

Directions in reciprocal space (poles) are always normal
to planes in real space with same indices (and vice-versa)