Lesson 14

- Growing Crystals
- Collecting Data

Use Systematic Absences

- By using the systematic absences we can assign the possible space groups.
- Frequently more than one possible space group is possible.
- Use table 3.1.4 in volume A of the International Tables for Crystallography
- Look at space groups.

Program XPREP

- This is the program for working with completed data
- It will check for centering
- It will look at equivalent reflections to determine a Laue Group
- It will look at systematic absences to determine possible space groups
- It will transform the space group into the standard setting.

What is Crystallization

- Crystallization is the process of trying to arrange a collection of molecules or ions to maximize the attractive forces and minimize the repulsive ones.
- This is best accomplished at equilibrium where the crystal components are free to enter and leave the lattice.
- This means it must be done slowly.

The Energetics of Crystal Growth

- For a process to occur spontaneously we know that ΔG must be negative
- $\Delta G=\Delta H-T\Delta S$ where G is the Gibb's Free Energy; H is the energy difference between the initial and final states and S is the entropy
- Since crystals are very ordered forming a crystal always results in a negative change in the entropy! $T\Delta S < 0$
- Therefore the energy crystallization must be large enough to offset this.

Sources for Energy Gain

- Ionic Interactions
- Dipole-dipole interactions
  - If a molecule has a dipole than one end is + and the other -
  - Results in a head to tail interaction or inversion center
- Hydrogen bonding
- Π-Π interactions
- Van der Waals interactions

Relations between cell constants and crystal faces.

- Many, though not all crystals, crystallize on primary faces (1,0,0) (0,1,0) (0,0,1)
- In general the shorter the axis the stronger the interaction along it. Therefore it pays to have as many short axis repeats in the crystal
- Therefore a crystal with one short and two long axes will grow as needles.
- Crystals with two short and one long one will grow as plates.
- Changing crystallization conditions will not alter this

Crystallization involving solvents

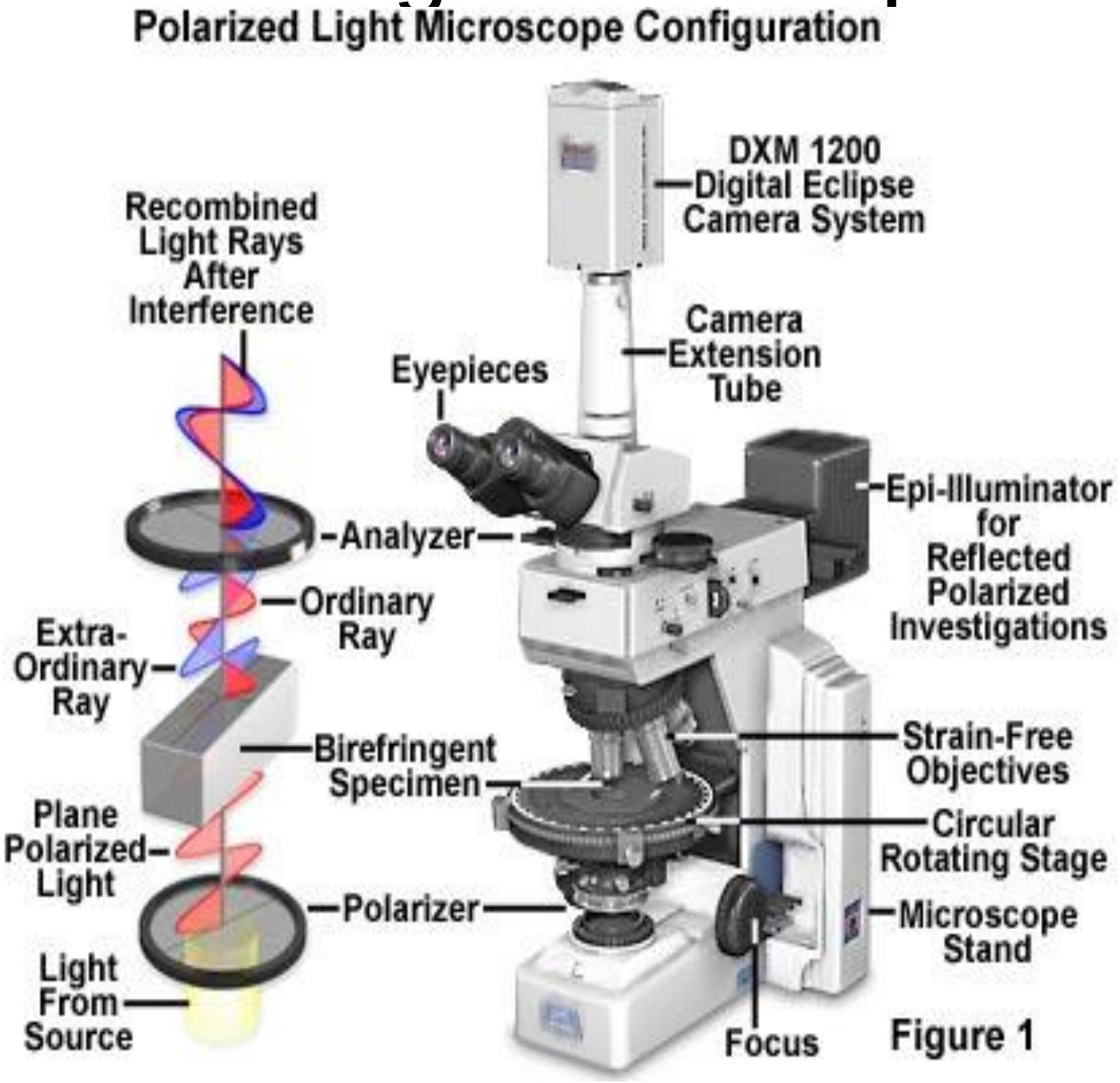
- Choose a solvent in which the compound is moderately soluble. If it is too soluble the crystallization will occur rapidly as the last bit of solvent evaporates.
- If possible try to avoid solvents that hydrogen bond. The less stable the solution the bigger the difference in energy between the solution and the crystal. However lessens entropy
- Avoid low boiling solvents especially diethyl ether in inorganics.
- Chose an appropriate container

Look at some methods

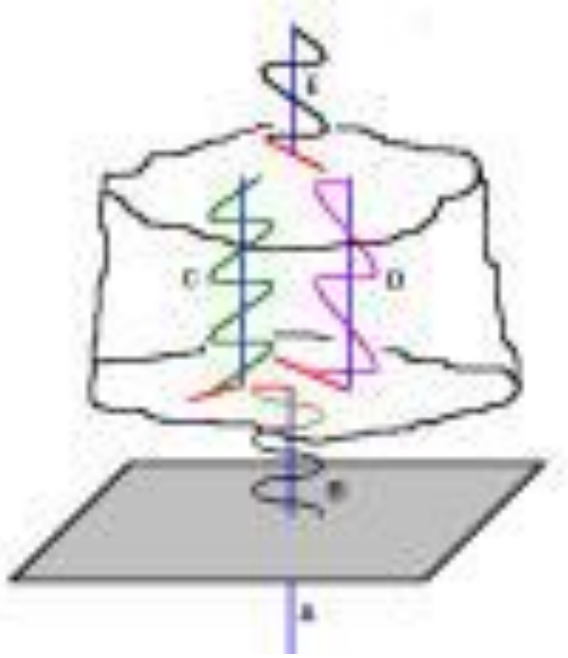
Selecting Crystals

- Crystals should have well defined faces.
- They should have smooth faces without imperfections.
- Should not be larger than 0.5mm in the long direction. Can usually cut crystals. For the Rigaku diffractometer no bigger than 0.2mm.
- If light goes through them they should be examined under a polarizing microscope.
- Obviously must make accommodations for the real world.

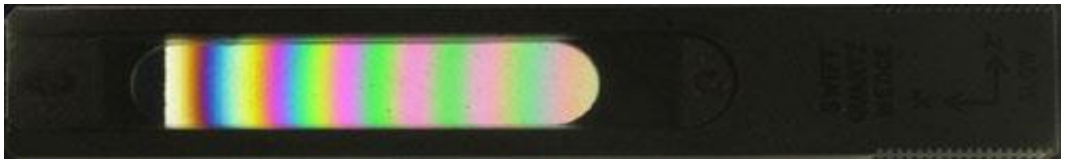
Polarizing Microscope



General Position



Interference Colors



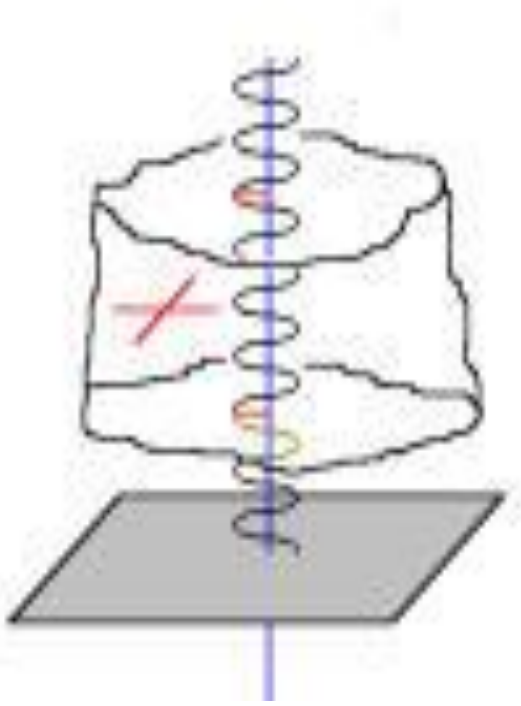
A function of the thickness of the crystal and the difference in the refractive indices in the two directions.

As crystals get thicker these colors disappear.

The more light that comes through the better the crystal

Layered crystals will not be bright because of internal reflection between the layers.

Extinction



Some Comments on Extinction

- Cubic crystals are isotropic and hence always dark between crossed polarizers!
- Hexagonal, trigonal and tetragonal crystal have an isotropic axis (c). When looked at down that axis the crystals will always be dark.
- In triclinic and most faces in monoclinic crystals the extinction directions may be a function of wavelength. Instead of going black they will get dark blue then go dark red or vice versa. This is ok
- Some crystals change colors under one polarizer—dichroism.

Selecting a Crystal

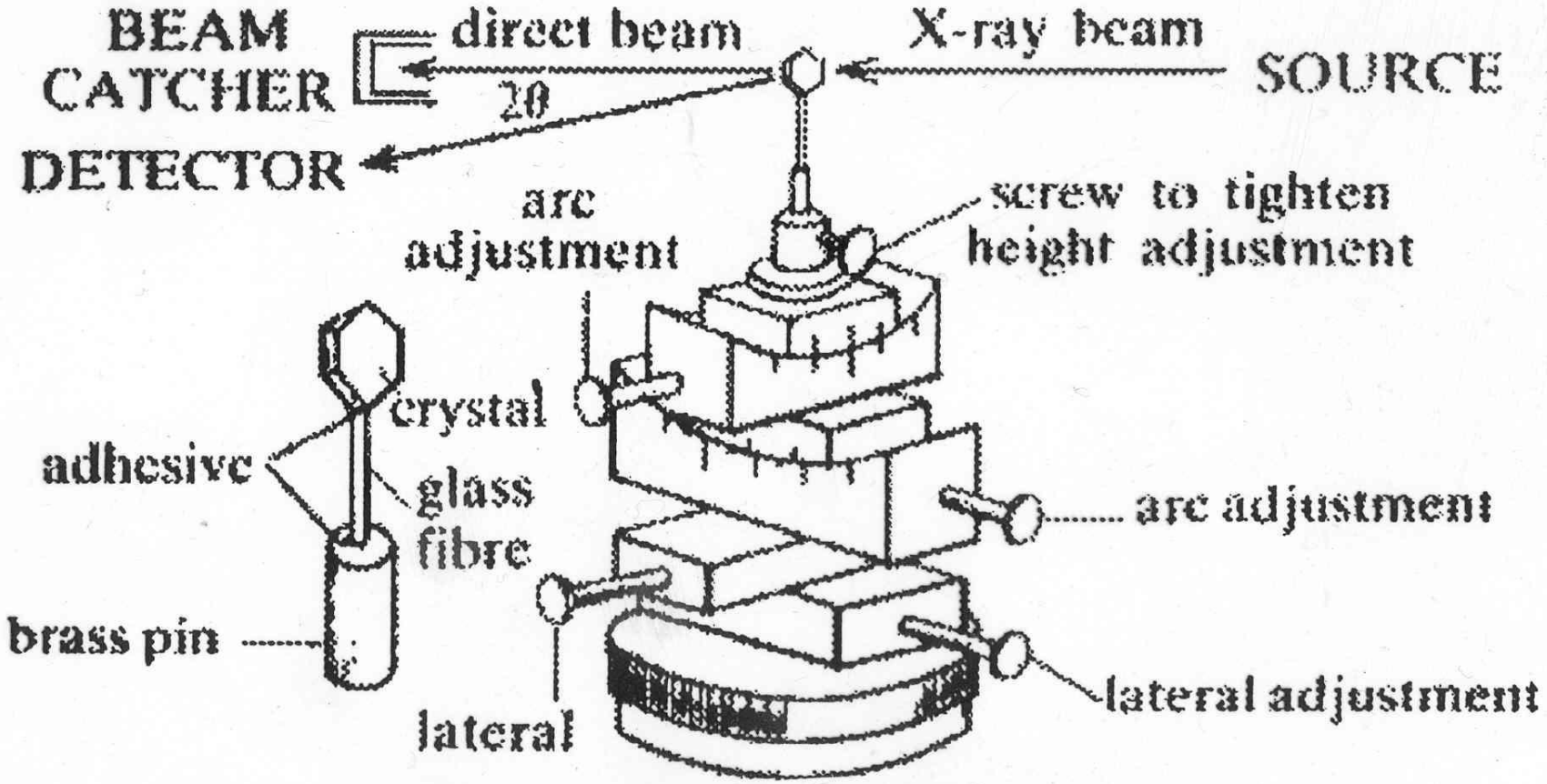
- It is worth spending some time with the microscope to get the best crystal.
- Make sure the crystal is representative of the batch.
- Size is not as important as quality
- Remember—The quality of the final structure depends almost entirely on the quality of the crystal studied!

Crystal Mounting

- Crystals were typically mounted on a glass or quartz fiber. Since these materials are not crystalline they do not diffract but they can scatter the beam.
- Lately using nylon loop mounts from Mitegen
- Crystals can be glued to the fiber with epoxy, super glue, or thermal glue for room temperature work.
- For low temperature work or using loops grease (Apeazon H) can be used.

Goniometer Head

Figure 23



Magnetic Caps

Fiber is glued into copper tube.
A magnet on the goniometer head holds the cap in place
Can easily and quickly be removed from diffractometer

Mitegen Nylon Mounts

Film Methods

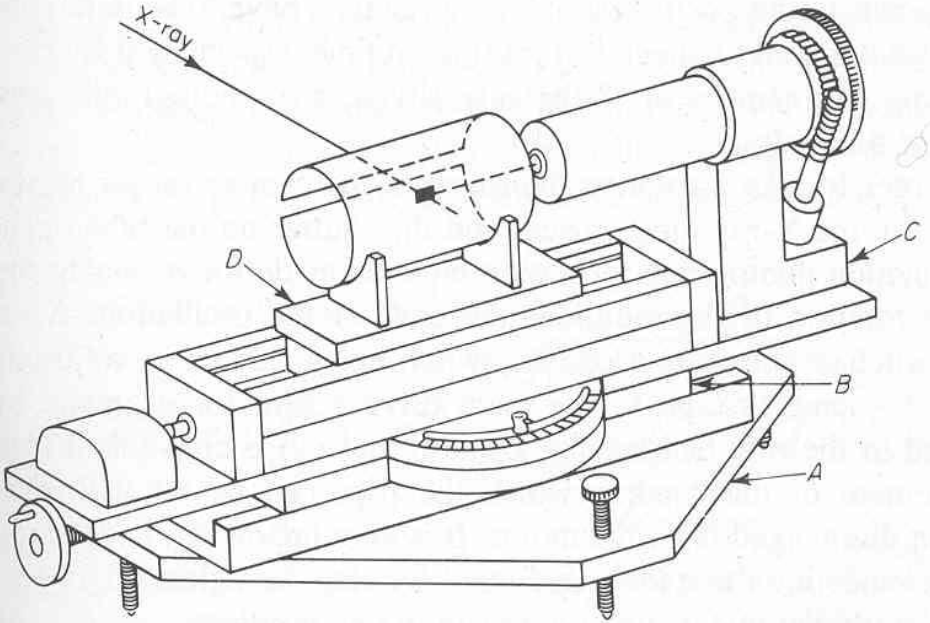


Figure 5.11. Schematic view of a Weissenberg camera.

Rotation Photograph

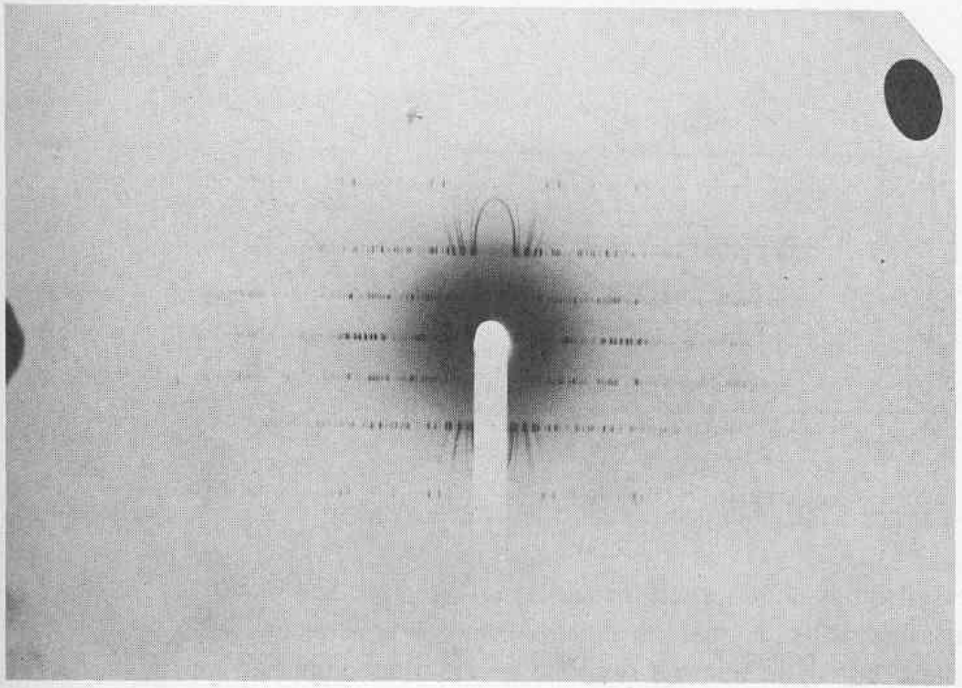


Figure 5.8. Rotation photograph.

Weissenberg Photos

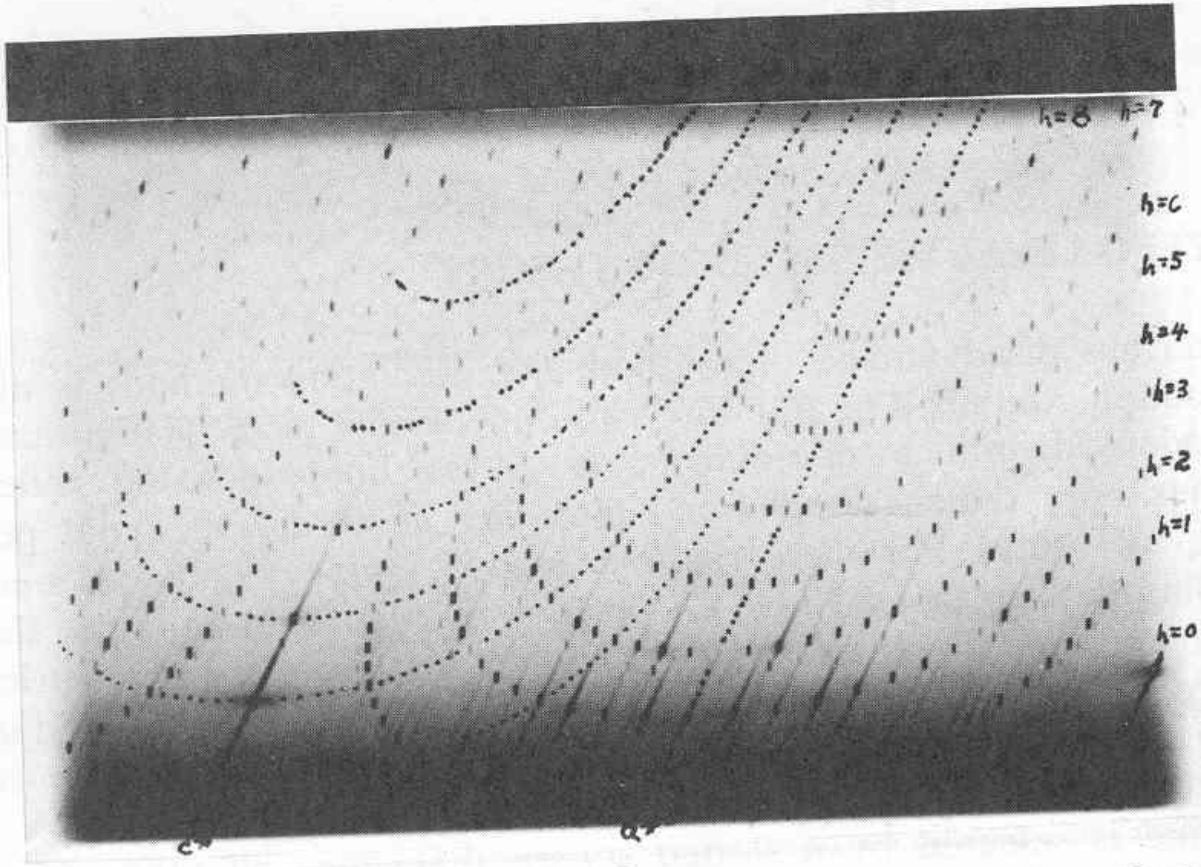
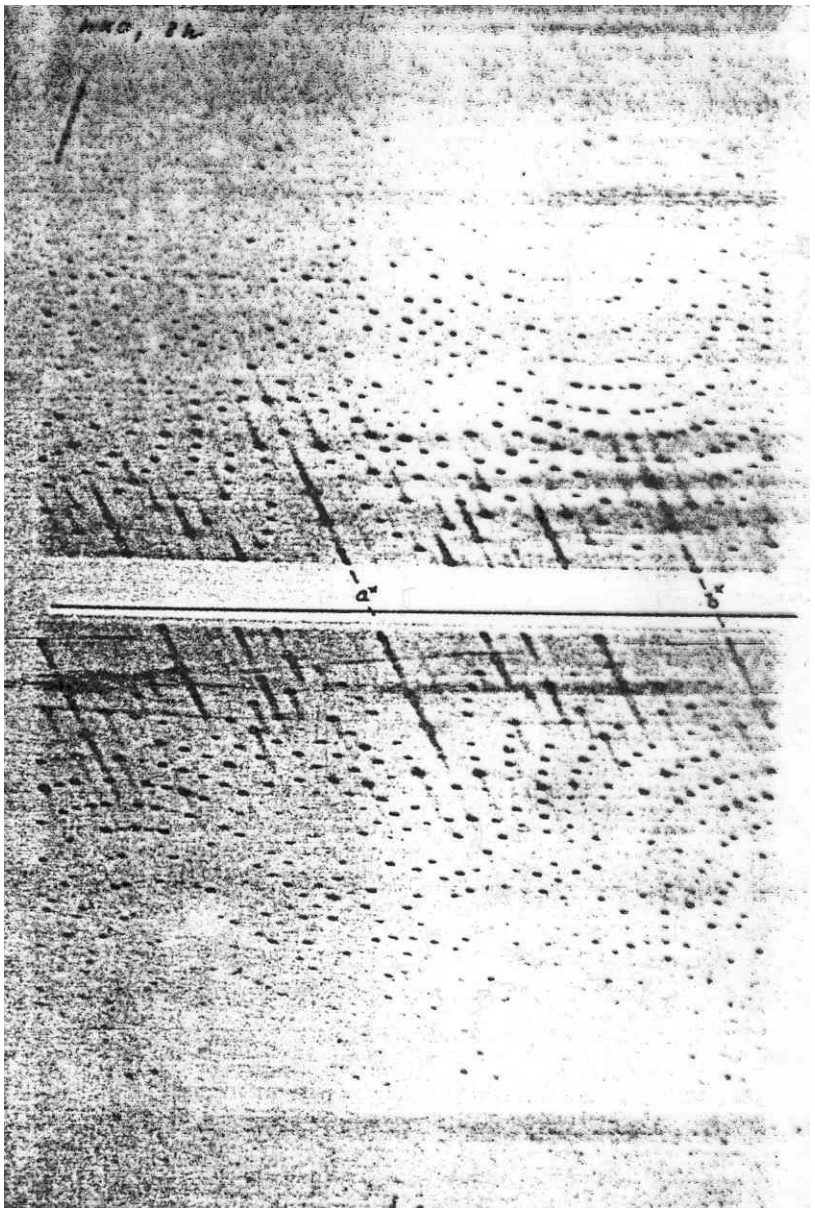


Figure 5.20. Half a Weissenberg photograph showing indexed r.l. lines. Dotted lines added for $l = 0, 4, 8, 12, 16, 20, 24$.


a''
b''

Problems

- Must align about a real axis
- Alignment is fairly fast.
- Exposure takes days.
- Picture is hard to read.
- Film is curved so Polaroid cannot be used

How to get data?

- Must determine the intensity of the spots.
- To do this must compare the intensities to some scale.
- To expand the cell the camera holds six films. The front one is used for weak reflections while the last one is used for strong reflections
- The six films are scaled by common spots.
- How do you determine standard uncertainty?
- Very tedious and inexact.

Using Film

- Very low background –can take very long exposures
- Fairly sensitive to radiation
- Covers a wide area.
- Obviously slow to expose and very tedious to measure the intensities off of.
- No one uses film any more—in fact it is impossible to find good quality film.

Next Time

- Diffractometers and area detectors
- Start to look at how the instruments are used at Purdue.