

# Diffraction Techniques for Crystal Structure Analysis

- Diffraction - The constructive interference, or reinforcement, of a beam of x-rays or electrons interacting with a material. The diffracted beam provides useful information concerning the structure of the material.
- Bragg's law - The relationship describing the angle  $\theta$  at which a beam of x-rays of a particular wavelength diffracts from crystallographic planes of a given interplanar spacing.
- In a diffractometer a moving x-ray detector records the  $2\theta$  angles at which the beam is diffracted, giving a characteristic diffraction pattern

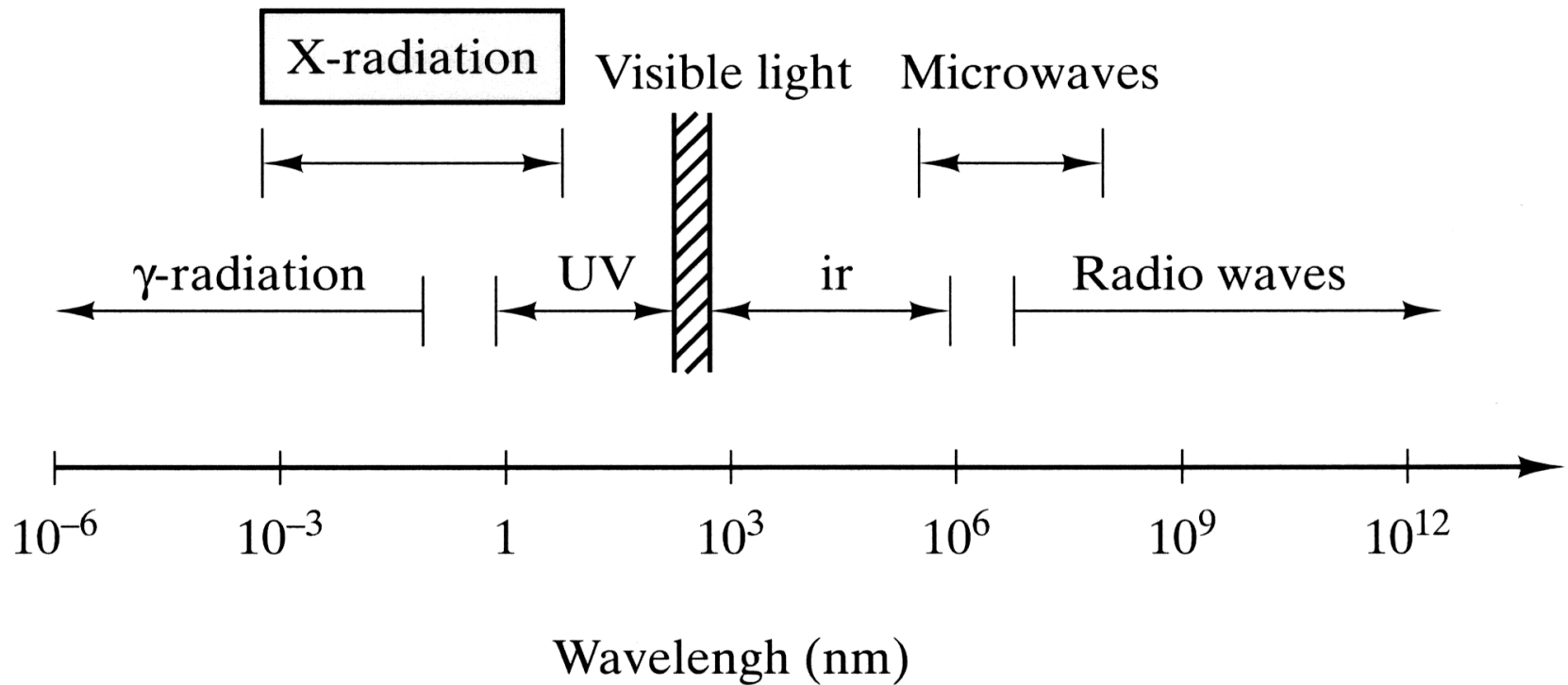


Figure 3-34 *Electromagnetic radiation spectrum. X-radiation represents that portion with wavelengths around 0.1 nm.*

**Lattice constants range from about 0.1 nm to some 50 - 100 nm. Most crystals' lattice constants are in the 1-5 nm range, since crystals are periodic, they are the ideal diffraction grating for X-rays,** Max von Laue's 1914 Nobel prize that proved both, crystals are periodic 3D arrangements of atoms and X-rays are waves (well wave-particles actually)

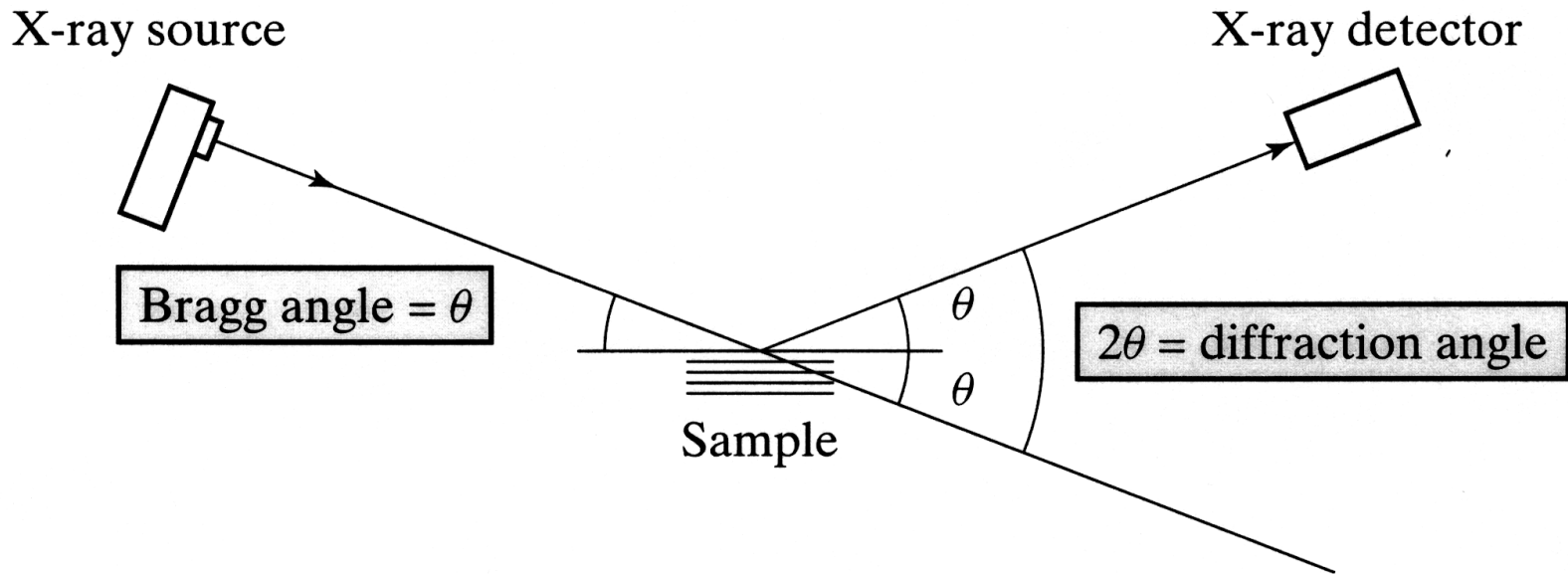
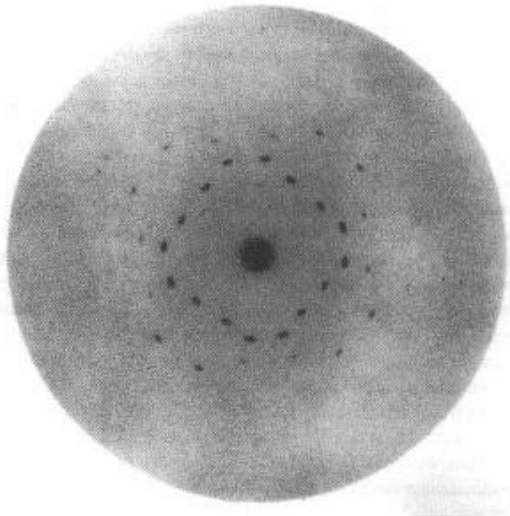


Figure 3-36 *Relationship of the Bragg angle ( $\theta$ ) and the experimentally measured diffraction angle ( $2\theta$ ).*

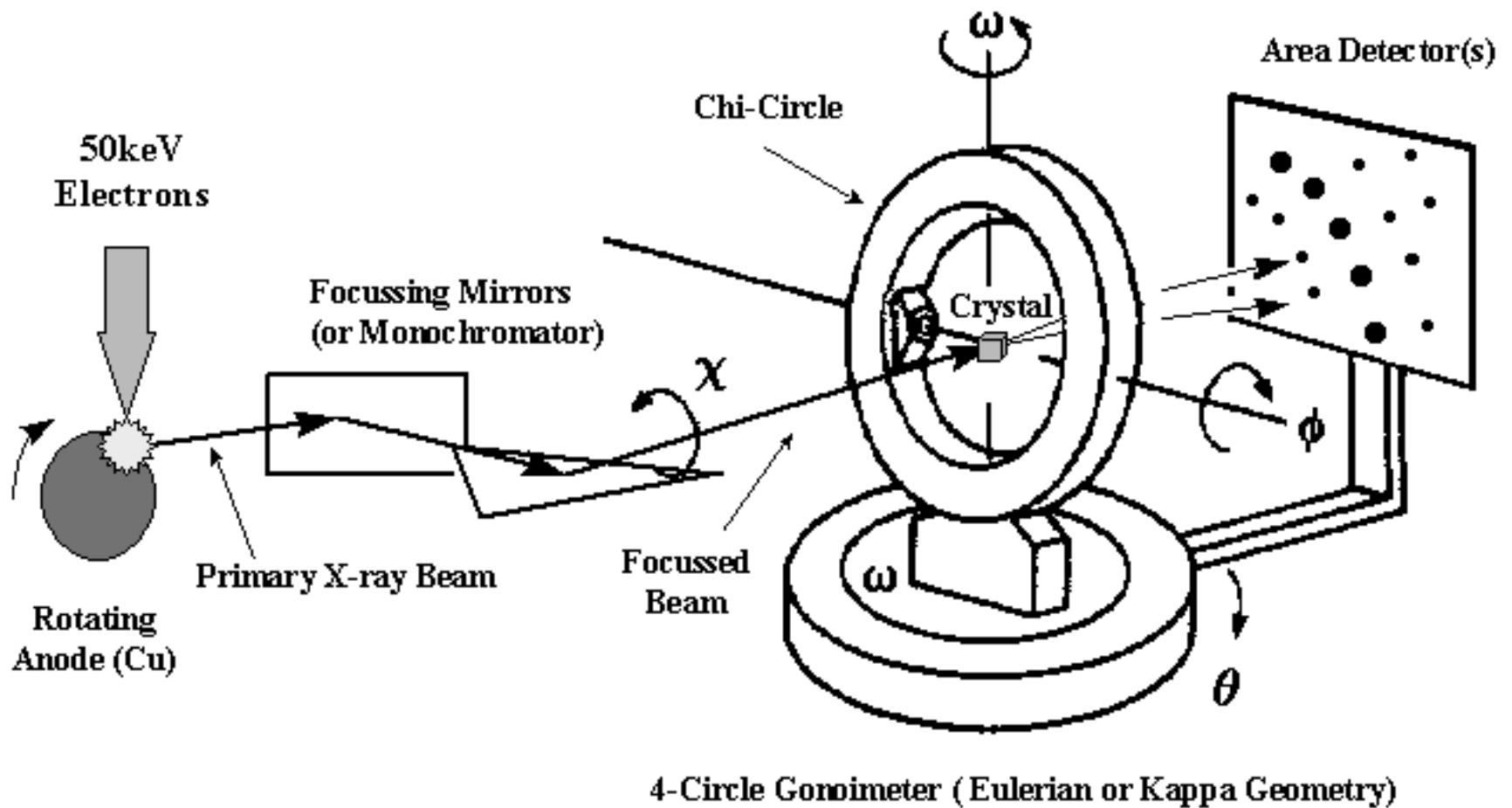


**The diffraction angle is always  $2\theta$ ?**

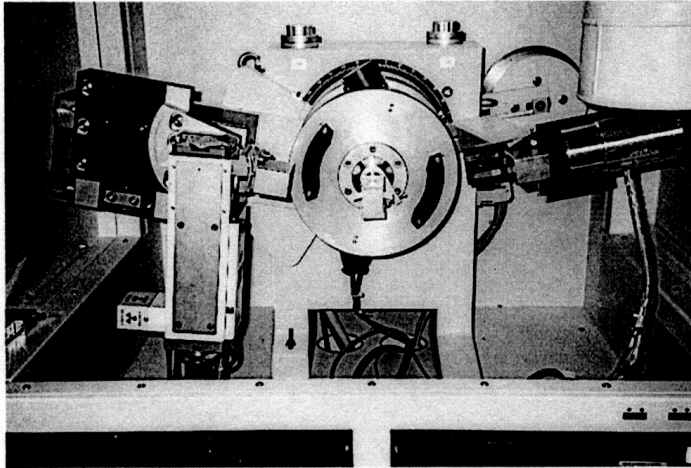
**Bragg's law:  $n \lambda = 2 d_{hkl} \sin \theta$  ?**

**$n$  – the order of reflection can be dropped by allowing indices for  $hkl$  that are not smallest integers, i.e.**

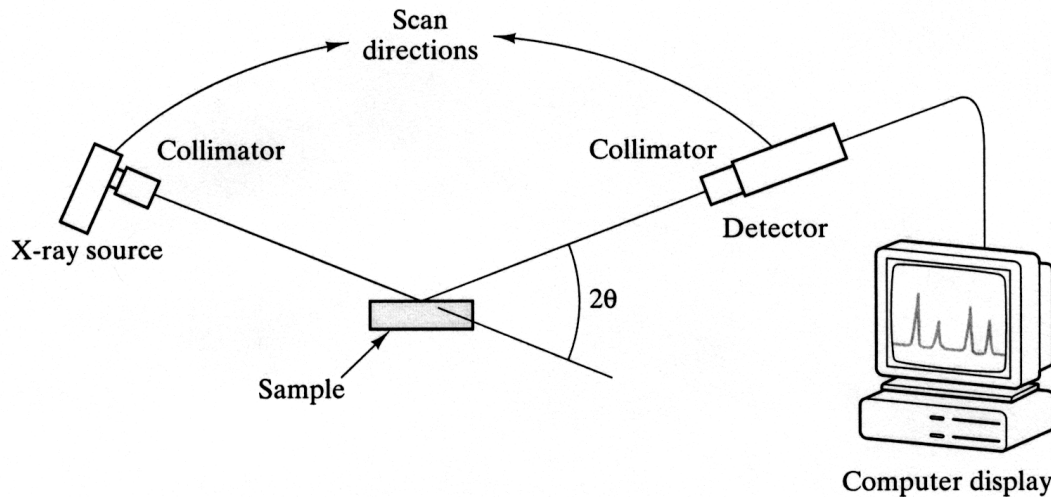
**HKL**



Single crystal diffractometers are more sophisticated



(a)

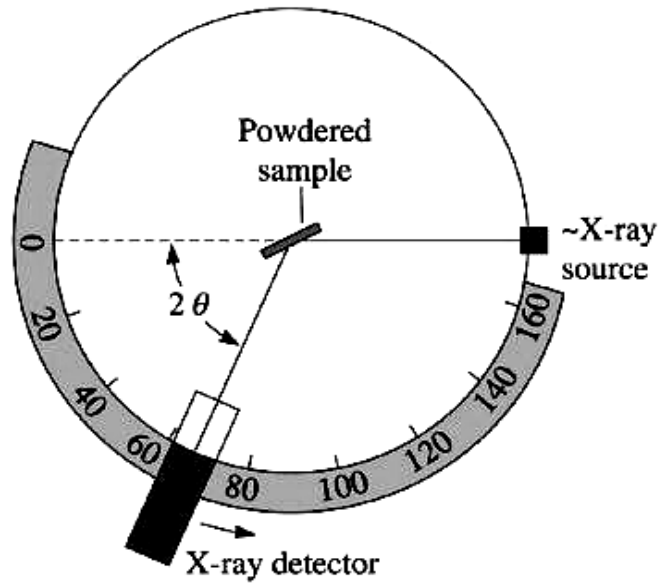


(b)

Powder diffractometers (for polycrystalline powder)

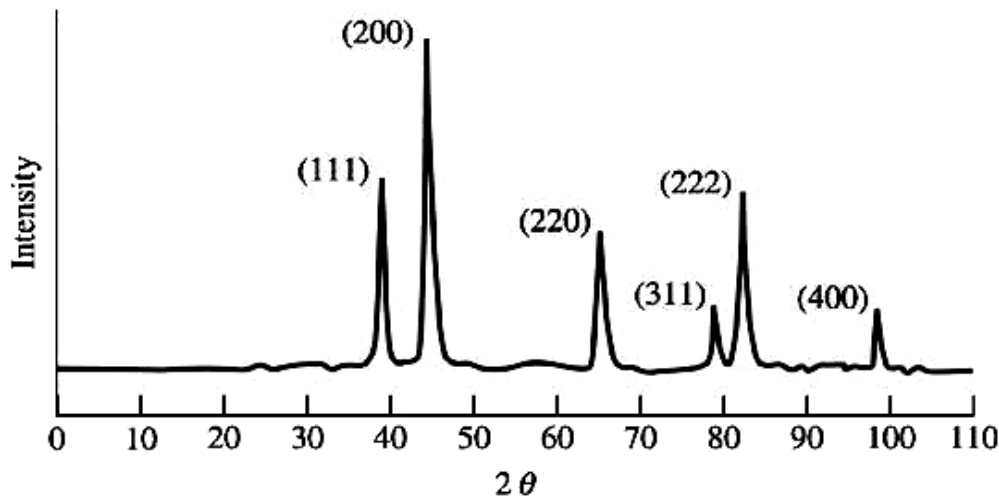
are less sophisticated and can be found in many places

Figure 3-40 (a) An x-ray diffractometer. (Courtesy of Scintag, Inc.) (b) A schematic of the experiment.



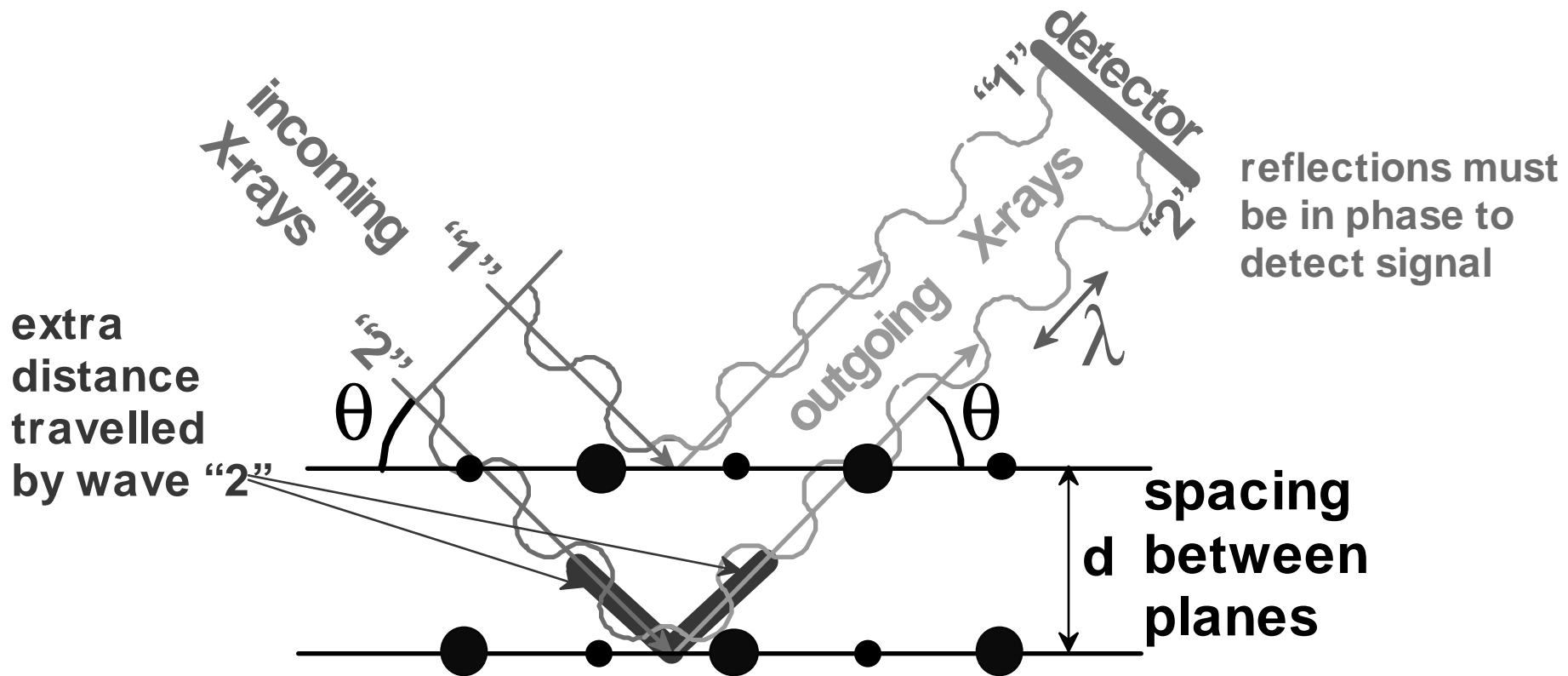
(a)

(a) sketch of a diffractometer viewed from above, showing powder sample, incident and diffracted beams.

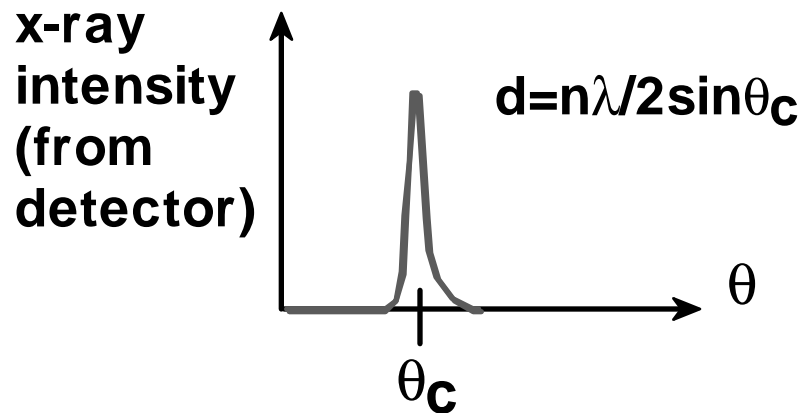


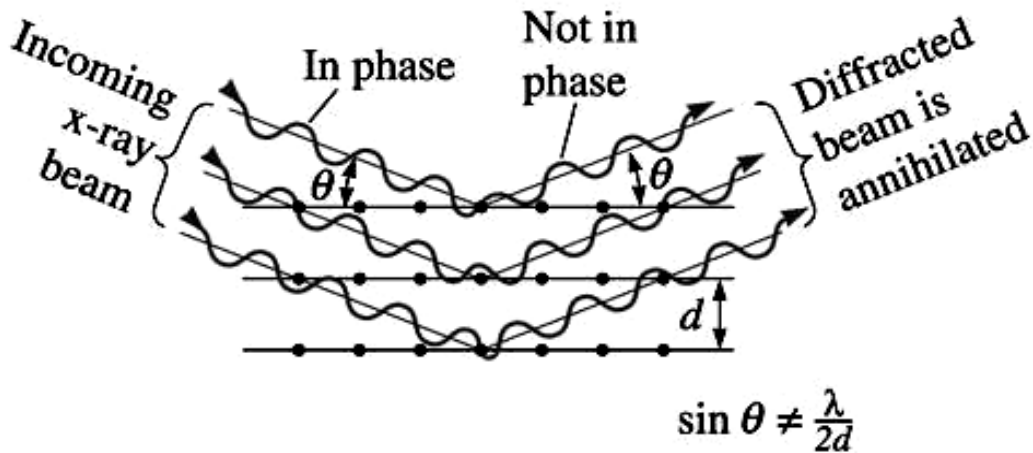
(b)

(b) diffraction pattern obtained from a sample of gold powder, notice the Miller indices of the diffracting crystal planes

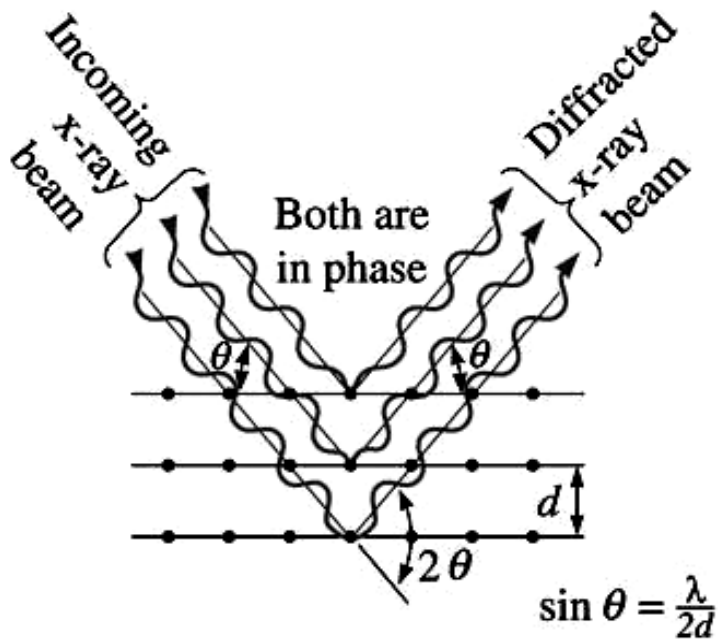


- **Measurement of:** "reflection" angles (Bragg angles),  $\theta$ , for X-rays provide atomic spacing,  $d$ .





(a)



(b)

(a) Destructive and (b) reinforcing (constructive) interference between x-rays "reflected" on a set of planes. Reinforcement occurs only at angles that satisfy Bragg's law.

$$l = 2 d_{HKL} \sin \theta$$

No other X-ray diffraction peaks occur



# X-ray Diffraction for an forensic examination

The results of a x-ray diffraction experiment on some metal powder found at a crime scene using characteristic x-rays with  $\lambda = 0.7107 \text{ \AA}$  (a radiation obtained from molybdenum (Mo) target) show that diffracted peaks occur at the following  $2\theta$  angles:

Peak	$2\theta$	Peak	$2\theta$
1	20.20	5	46.19
2	28.72	6	50.90
3	35.36	7	55.28
4	41.07	8	59.42

Determine the indices of the plane producing each peak, and from that the lattice parameter of the material and from that identify the material (you know it is some metal so it is a good guess to assume the crystals in the powder are cubic)

## SOLUTION

$$\lambda = 2 d_{HKL} \sin \theta \quad \left( \frac{\lambda}{2d_{HKL}} \right)^2 = \sin^2 \theta$$

$$d_{HKL} = \frac{1}{\sqrt{H^2 + K^2 + L^2}} = (Ha^* + Kb^* + Lc^*)^{-1} = (d_{HKL}^*)^{-1} = \vec{g}$$

We first determine the  $\sin^2 \theta$  value for each peak, then divide through by the lowest denominator, 0.0308, "guess" the indices

Peak	$2\theta$	$\sin^2 \theta$	$\sin^2 \theta / 0.0308$	$h^2 + k^2 + l^2$	(hkl)
1	20.20	0.0308	1	2	(110)
2	28.72	0.0615	2	4	(200)
3	35.36	0.0922	3	6	(211)
4	41.07	0.1230	4	8	(220)
5	46.19	0.1539	5	10	(310)
6	50.90	0.1847	6	12	(222)
7	55.28	0.2152	7	14	(321)
8	59.42	0.2456	8	16	(400)

## SOLUTION (Continued)

We could then use  $2\theta$  values for any of the peaks to calculate the interplanar spacing and thus the lattice parameter. Picking peak 8:

$$2\theta = 59.42 \text{ or } \theta = 29.71$$

$$d_{400} = \frac{a_0}{2 \sin \theta} = \frac{0.7107}{2 \sin(29.71)} = 0.71699 \text{ \AA}$$

$$a_0 = d_{400} \sqrt{h^2 + k^2 + l^2} = (0.71699)(4) = 2.868 \text{ \AA}$$

This is the lattice parameter for body-centered cubic iron.

**So the gardener did steal the cookies –  
only kidding**

**Since out of all metals only Po has the simple cubic structure, and we do know our material was not radioactive and difficult to obtain, we didn't check for an indexing scheme for a simple cubic lattice, it would have gotten us nowhere anyway**

# There are certain systematic absences of reflections

You may have noticed that there are no  $(hkl)$  triplets with  $h+k+l = \text{odd}$ .

Laue's kinematical theory of X-ray diffraction (1912) explains why,

different structures have forbidden reflections, i.e. reflections that do not show up in diffraction but these planes do of course exist in the crystals, it is just that diffraction on them is destructive

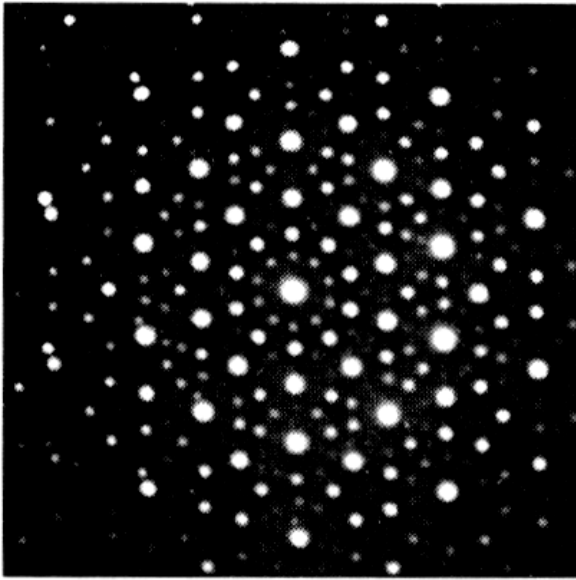
Simple cubic crystals have no forbidden reflections

## Rules for Determining the Diffracting $\{hkl\}$ Planes in Cubic Crystals

Bravais lattice	Reflections present	Reflections absent
BCC	$(h + k + l) = \text{even}$	$(h + k + l) = \text{odd}$
FCC	$(h, k, l)$ all odd or all even	$(h, k, l)$ not all odd or all even

## Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes $\{hkl\}$	$h^2 + k^2 + l^2$	Sum $\Sigma(h^2 + k^2 + l^2)$	Cubic diffracting planes $\{hkl\}$	
			FCC	BCC
{100}	$1^2 + 0^2 + 0^2$	1		
{110}	$1^2 + 1^2 + 0^2$	2	...	110
{111}	$1^2 + 1^2 + 1^2$	3	111	
{200}	$2^2 + 0^2 + 0^2$	4	200	200
{210}	$2^2 + 1^2 + 0^2$	5		
{211}	$2^2 + 1^2 + 1^2$	6	...	211
...		7		
{220}	$2^2 + 2^2 + 0^2$	8	220	220
{221}	$2^2 + 2^2 + 1^2$	9		
{310}	$3^2 + 1^2 + 0^2$	10	...	310

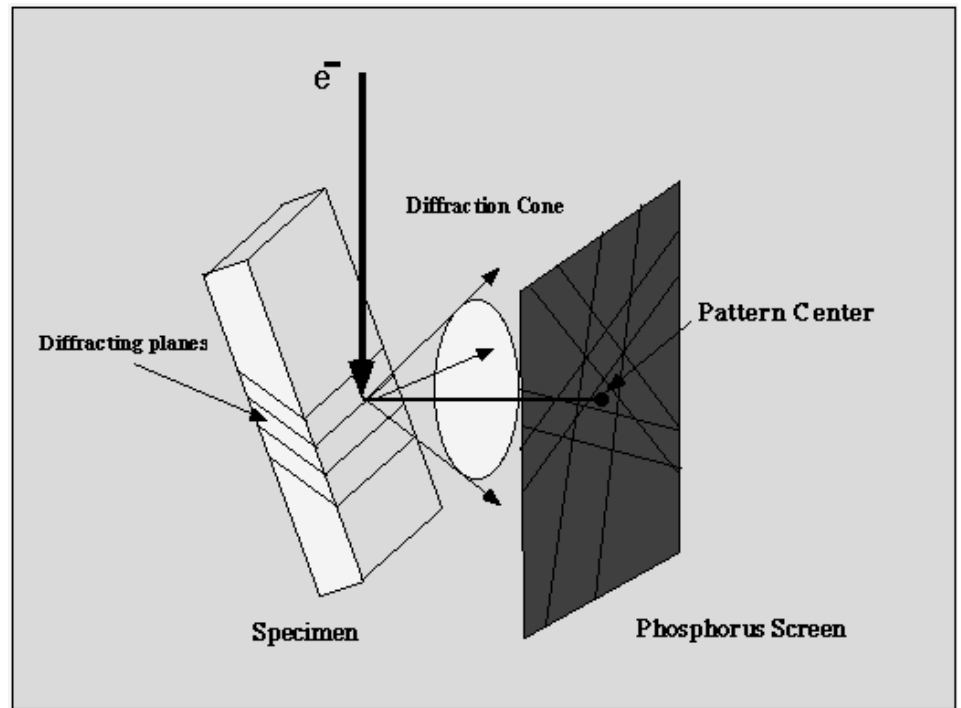


## *Wow, what is that?*

It can't be a crystal as it obviously has a five fold symmetry, it is not amorphous either as it clearly has a diffraction pattern?

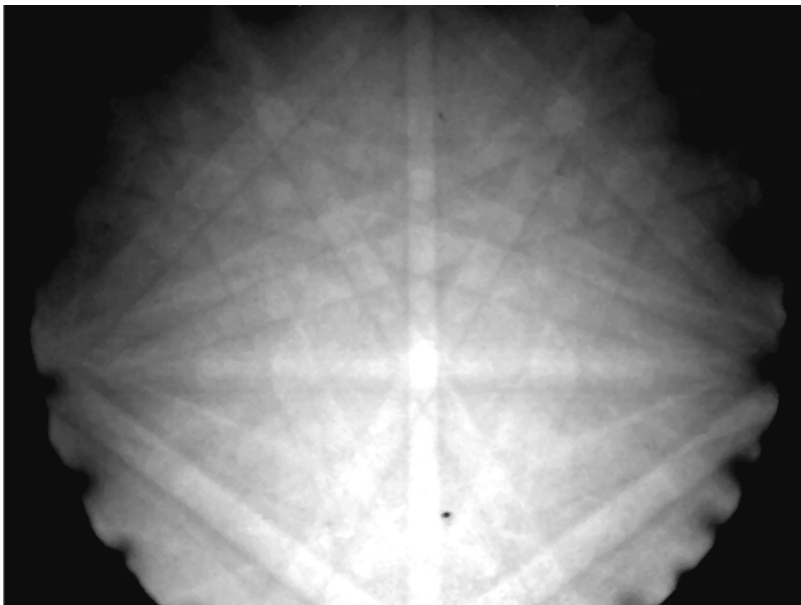
It's a **quasi-crystal**, i.e. an entity with short range order (as amorphous and crystalline materials) and long range order (as a crystal), the crucial difference is, the long range order is **non periodic**

Figure 4-27 *Electron diffraction pattern of a rapidly cooled  $Al_6Mn$  alloy showing fivefold symmetry; that is, the pattern is identical with each rotation of  $360^\circ/5$ , or  $72^\circ$ , about its center. Such symmetry is impossible in traditional crystallography. [After D. Schechtman et al., Phys. Rev. Letters 53, 1951 (1984).]*



**Crystallographic work  
can also be done in  
modern SEMs !**

Electron backscatter  
(Kikuchi) diffraction  
(EBSD), here of a Si  
crystal



# scanning probe microscopy, STM, AFM, ...

**Atoms can be arranged and imaged!**

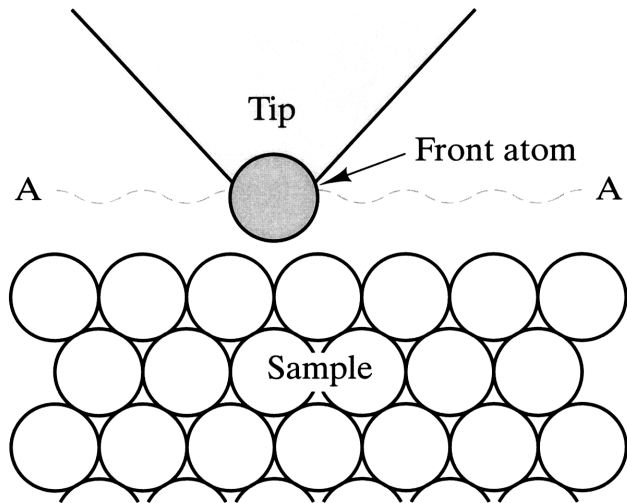
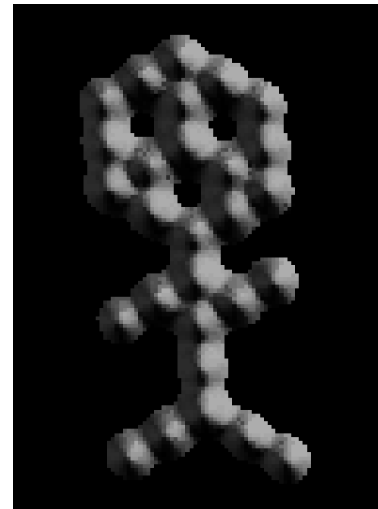
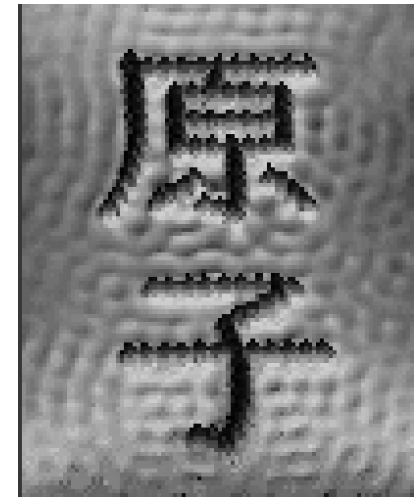


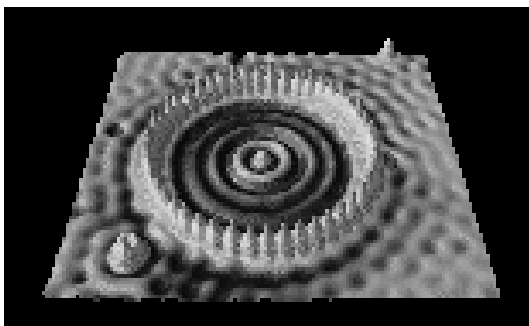
Figure 4-41 *Schematic of the principle by which the probe tip of either a scanning tunneling microscope (STM) or an atomic force microscope (AFM) operates. The sharp tip follows the contour A-A as it maintains either a constant tunneling current (in the STM) or a constant force (in the AFM). The STM requires a conductive sample while the AFM can also inspect insulators.*



**Carbon monoxide molecules arranged on a platinum (111) surface.**



**Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word "atom".**



**Something more useful, the square of the quantum mechanical wave function of an electron that is trapped in a "cage" of Cu atoms**