奈米量測技術 (III)
XRD (X-ray Diffraction)(部分)

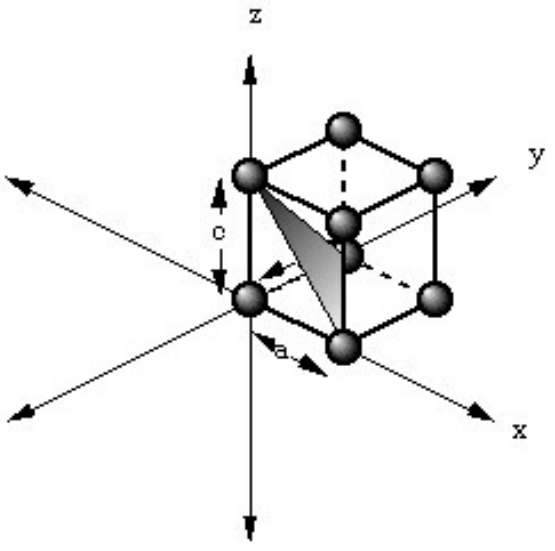
連興隆

X-ray Diffraction

- Miller indices
- 布拉格定律(Bragg's Law)
- Scherrer's Formula
- Data Analysis Examples

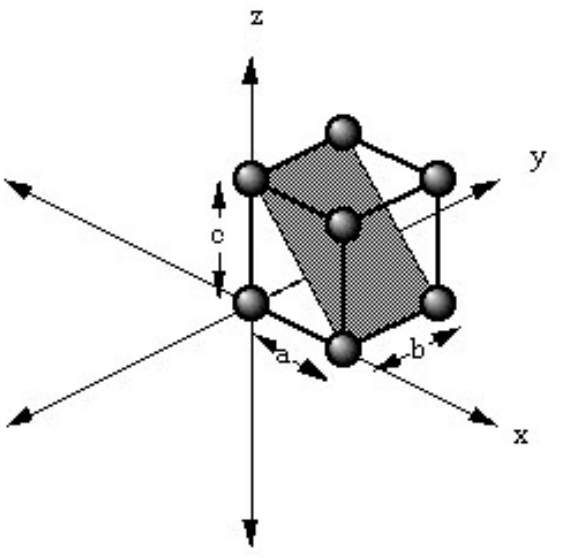
Miller Indices

- **Miller Indices** are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.
- (*hkl*) = parenthesis designate a **crystal face** or a **family of planes** throughout a crystal lattice.



	a	b	c
intercept length	1	1	1
reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
cleared fraction	1	1	1

Miller indice (111)



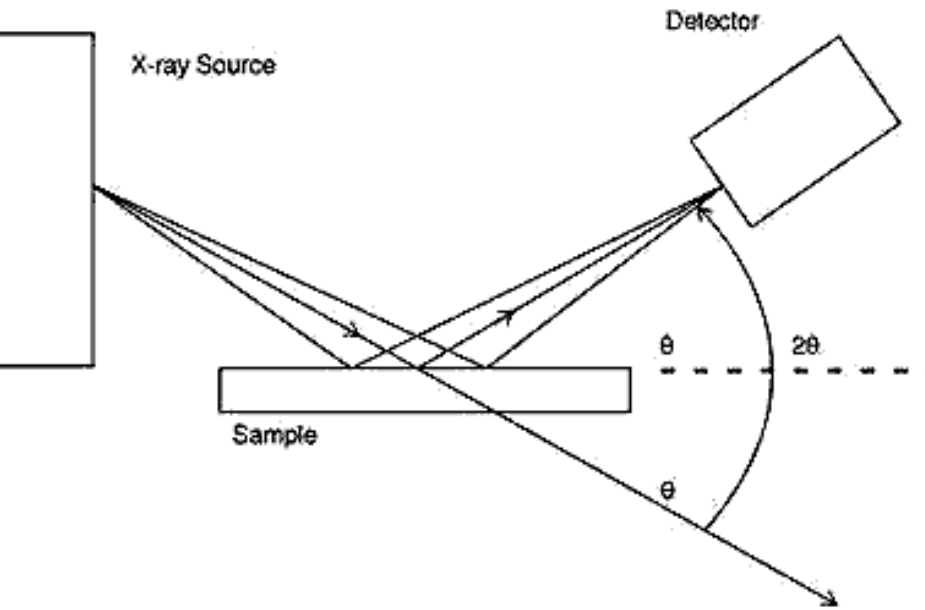
	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1

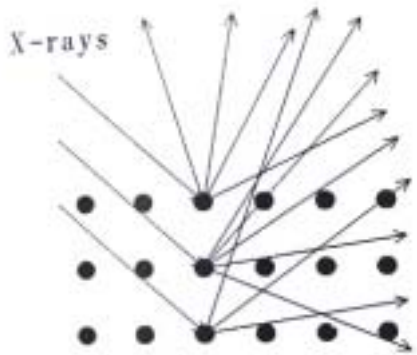
Miller indice (101)

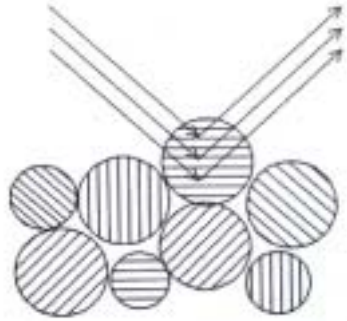
XRD

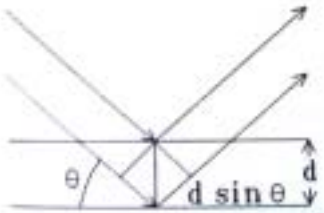
Energy source: X-Ray
Cu Kα 8.04 keV, λ = 0.154 nm

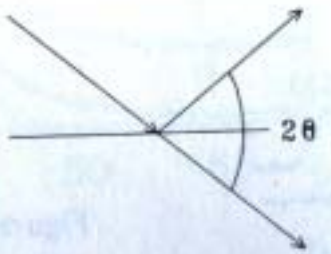
當X-ray透過具晶格結構之材料時, 產生建設性干涉(constructive interference)







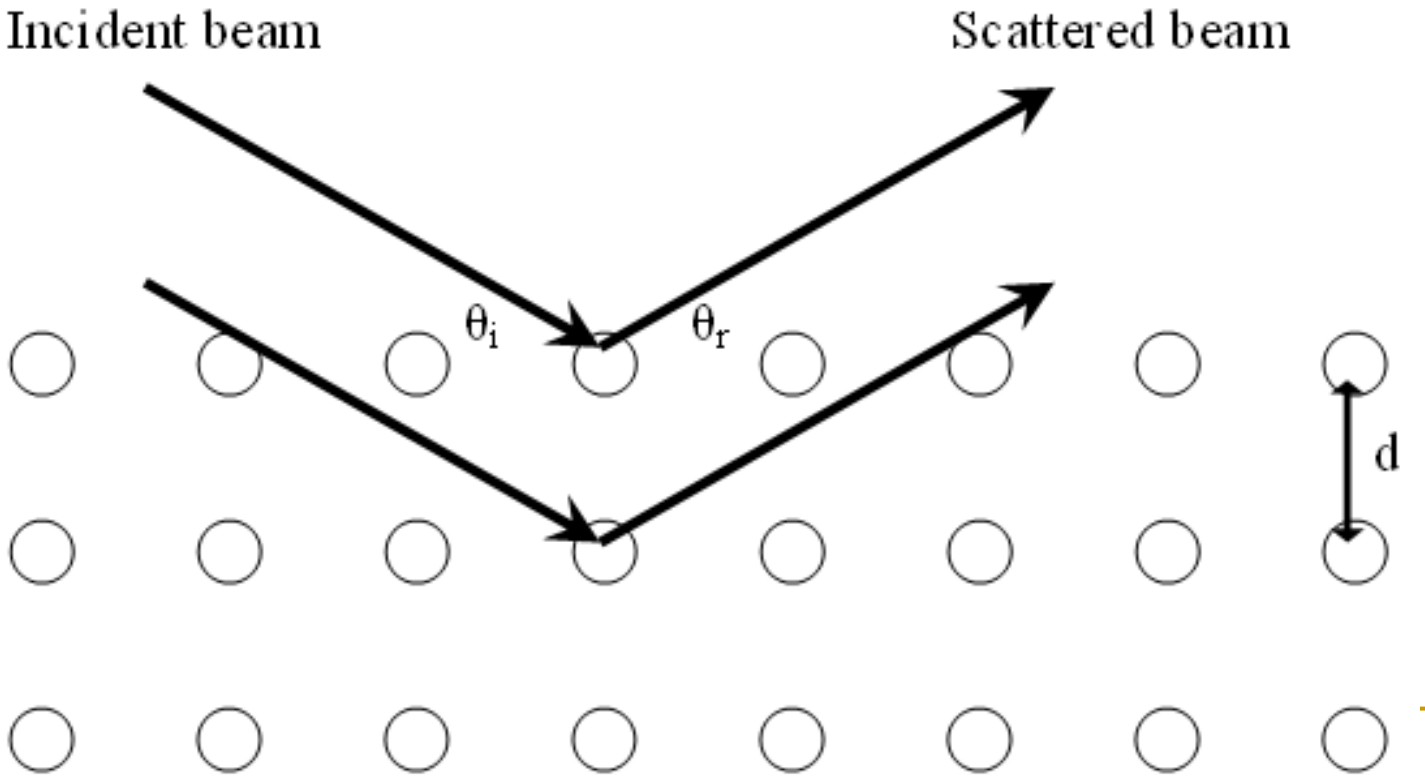




Bragg's Law

$$n\lambda = 2d\sin\theta$$

- Constructive interference only occurs for certain θ's correlating to a (*hkl*) plane, specifically when the path difference is equal to n wavelengths.



Summary of Bragg & Laue

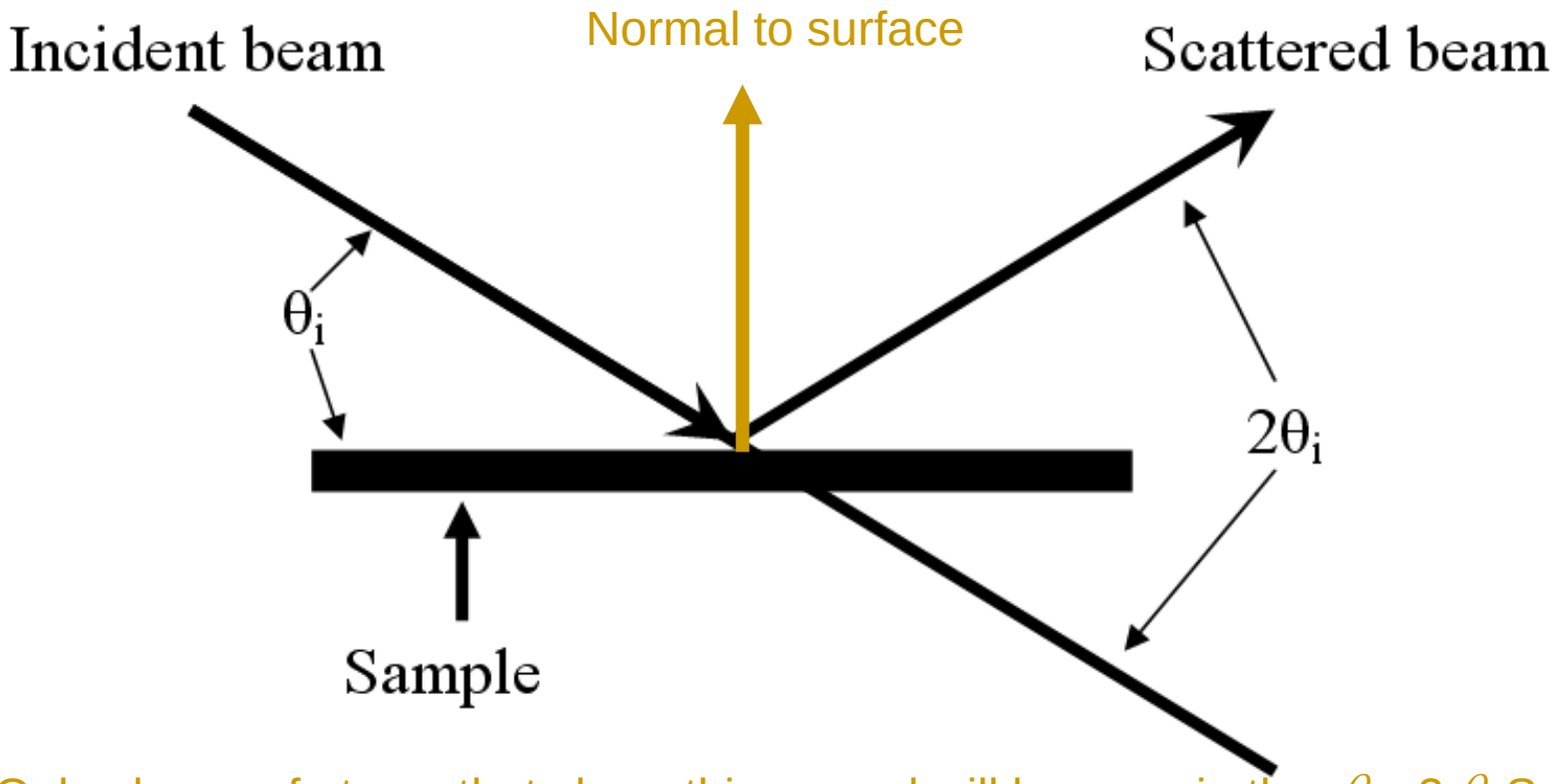
- When a diffraction condition is met there can be a reflected X-ray
  - Extra atoms in the basis can suppress reflections
- Three variables λ, θ, and *d*
  - λ is known
  - θ is measured in the experiment (2 θ)
  - d is calculated
- From the planes (*hkl*)
  - *a* is calculated

$$d = \frac{n\lambda}{2\sin\theta}$$

$$a = d\sqrt{h^2 + k^2 + l^2}$$

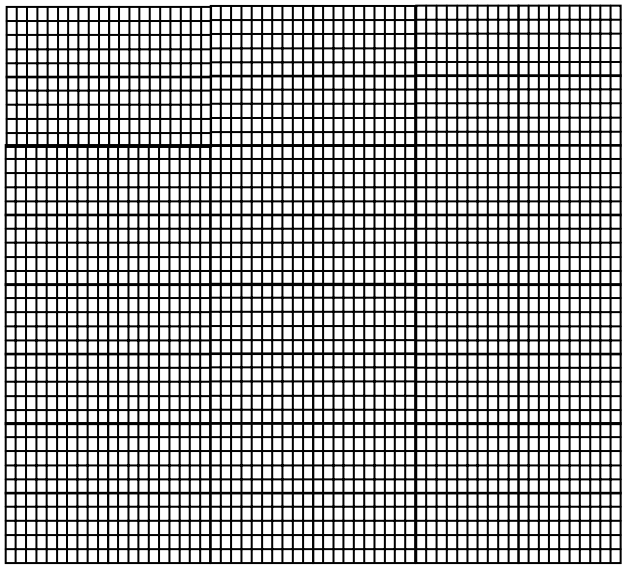
θ - 2 θ Scan

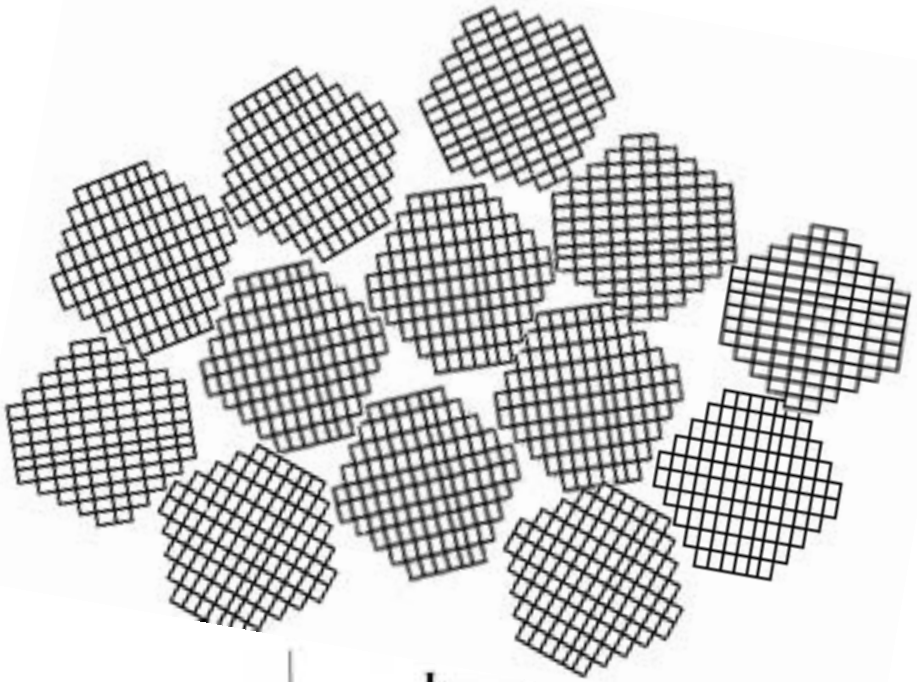
The θ - 2 θ scan maintains these angles with the sample, detector and X-ray source

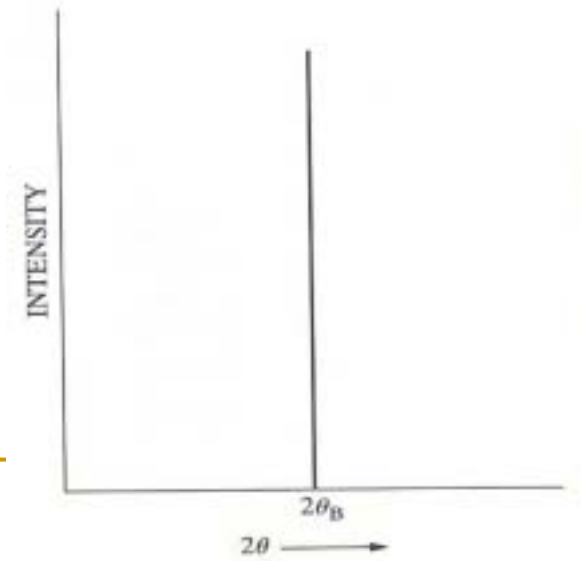


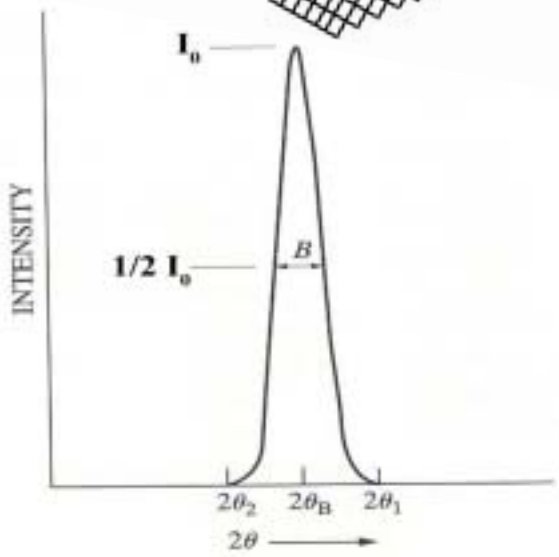
Only planes of atoms that share this normal will be seen in the θ - 2 θ Scan

Smaller Crystals Produce Broader XRD Peaks









Scherrer's Formula

$$t = \frac{K * \lambda}{B * \cos\theta_B}$$

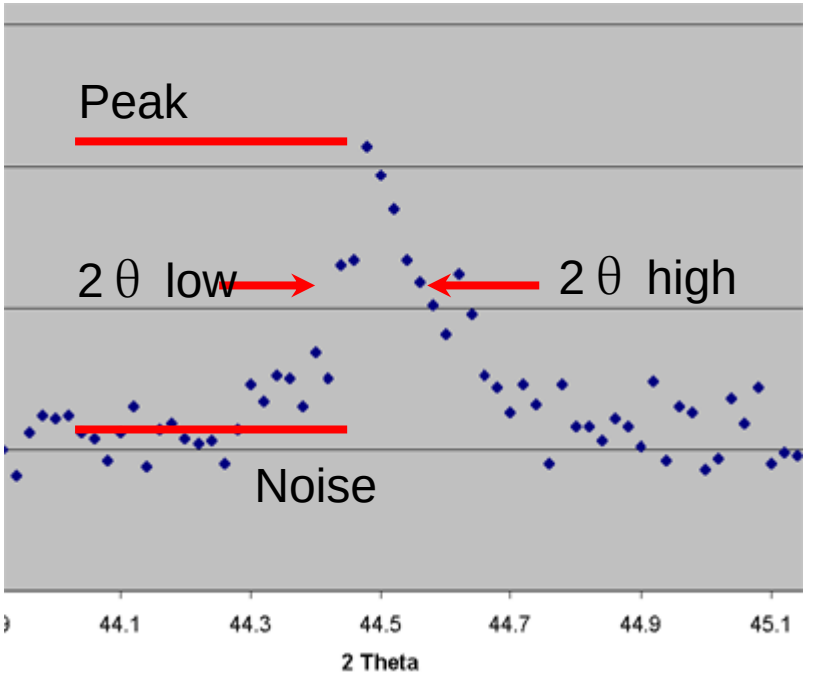
t = thickness of crystallite
K = constant dependent on crystallite shape (1-0.89)
λ = x-ray wavelength
B = FWHM (full width at half max) or integral breadth
θ_B = Bragg Angle

Scherrer's Formula

What is *B*?

B = (2 θ High) – (2 θ Low)

B is the difference in angles at half max



When to Use Scherrer's Formula

- Crystallite size <1000 Å
- Peak broadening by other factors
  - Causes of broadening
    - Size
    - Strain
    - Instrument
  - If breadth consistent for each peak then assured broadening due to crystallite size
- K depends on definition of t and *B*
- Within 20%-30% accuracy at best

Sherrer's Formula References

Corman, D. Scherrer's Formula: Using XRD to Determine Average Diameter of Nanocrystals.

Data Analysis

- Plot the data (2 θ vs. Counts)
- Determine the Bragg Angles for the peaks
- Identification of samples
  - International Centre for Diffraction Data (ICDD)- Joint Committee on Powder Diffraction Standards (JCPDS). (資料庫,很貴)
  - X Ray Spacing (http://webmineral.com/X-Ray.shtml)免費,但.
  - 查文獻
- Calculate *d* and *a* for each peak
- Apply Scherrer's Formula to the peaks

Sample: A:1206-3
Data file: B:1206-3.RAW

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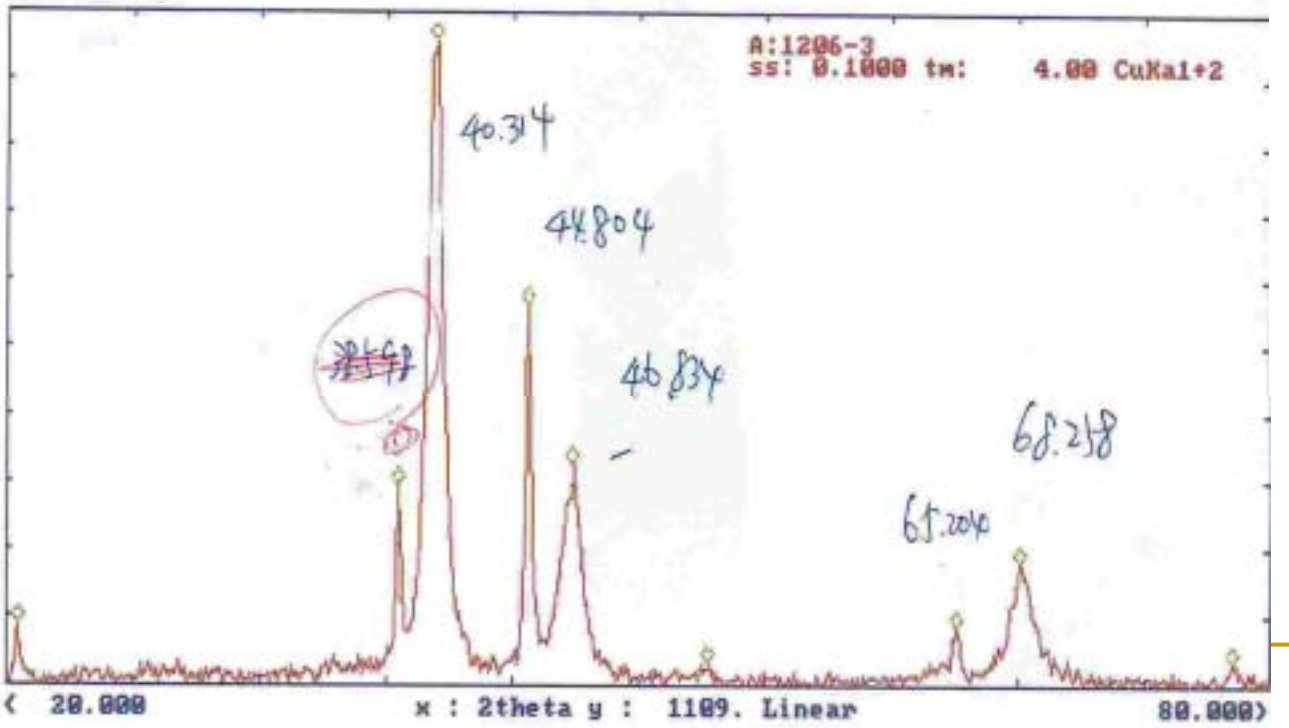
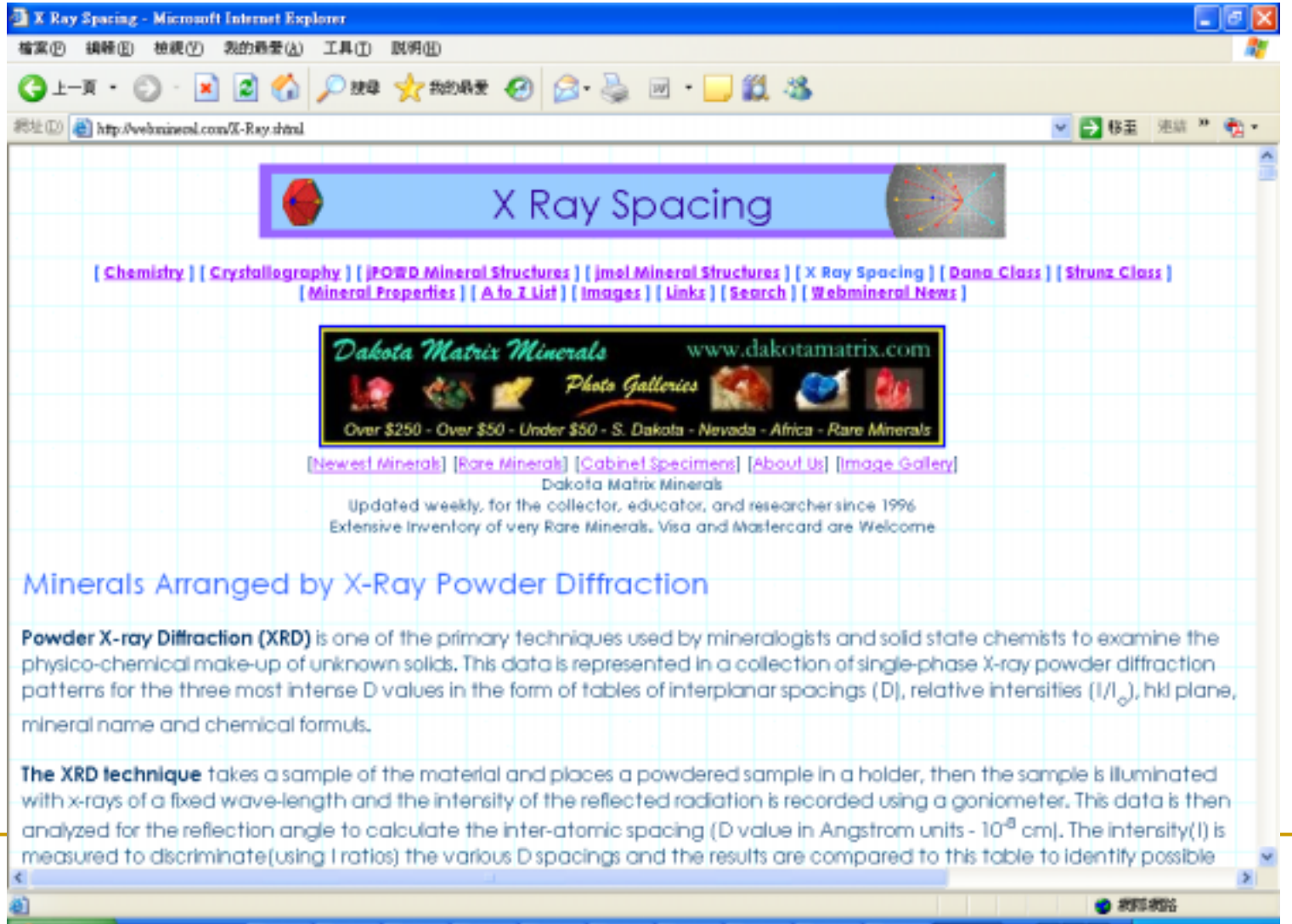
Seq	2theta	d	rel. I		Seq	2theta	d	rel. I	
1	20.442	4.3419	8.99		3	40.314	2.2358	100.00	
2	38.598	2.3312	30.77		4	44.804	2.0216	58.64	
3	40.314	2.2358	100.00		5	46.834	1.9386	34.01	
4	44.804	2.0216	58.64		2	38.598	2.3312	30.77	
5	46.834	1.9386	34.01		8	68.258	1.3732	18.61	
6	53.300	1.7177	3.52	?	1	20.442	4.3419	8.99	
7	65.204	1.4299	8.83		7	65.204	1.4299	8.83	
8	68.258	1.3732	18.61		6	53.300	1.7177	3.52	?
9	78.341	1.2198	3.30		9	78.341	1.2198	3.30	



http://webmineral.com/X-Ray.shtml



X Ray Spacing

D1(Io)(hkl)	D2(I/Io)(hkl)	D3(I/Io)(hkl)	Mineral Name	Chemical Formula
0.7768(1)	0.7877(1)	3(1)	Bowieite	(Rh,Ir,Pt)1.77S3
0.779(1)	2.18(1)	0.8237(0.9)	Sudburyite	(Pd,Ni)Sb
0.7874(1)	0.8623(0.8)	0.8847(0.7)	Rhodium	(Rh,Pt)
0.8666(1)	2.122(1)(110)	0.8021(0.7)(321)	Skaergaardite	! CuPd
1.019(1)	1.081(0.75)	1.887(0.63)	Nowackiite	Cu6Zn3As4S12
1.019(1)	1.757(1)	1.91(0.8)	Kalininite	ZnCr2S4
2.246(1)	1.945(0.42)	1.376(0.25)	Palladium	Pd,Pt

回家作業(II)

1.決定是何物質?
2.計算粒徑大小