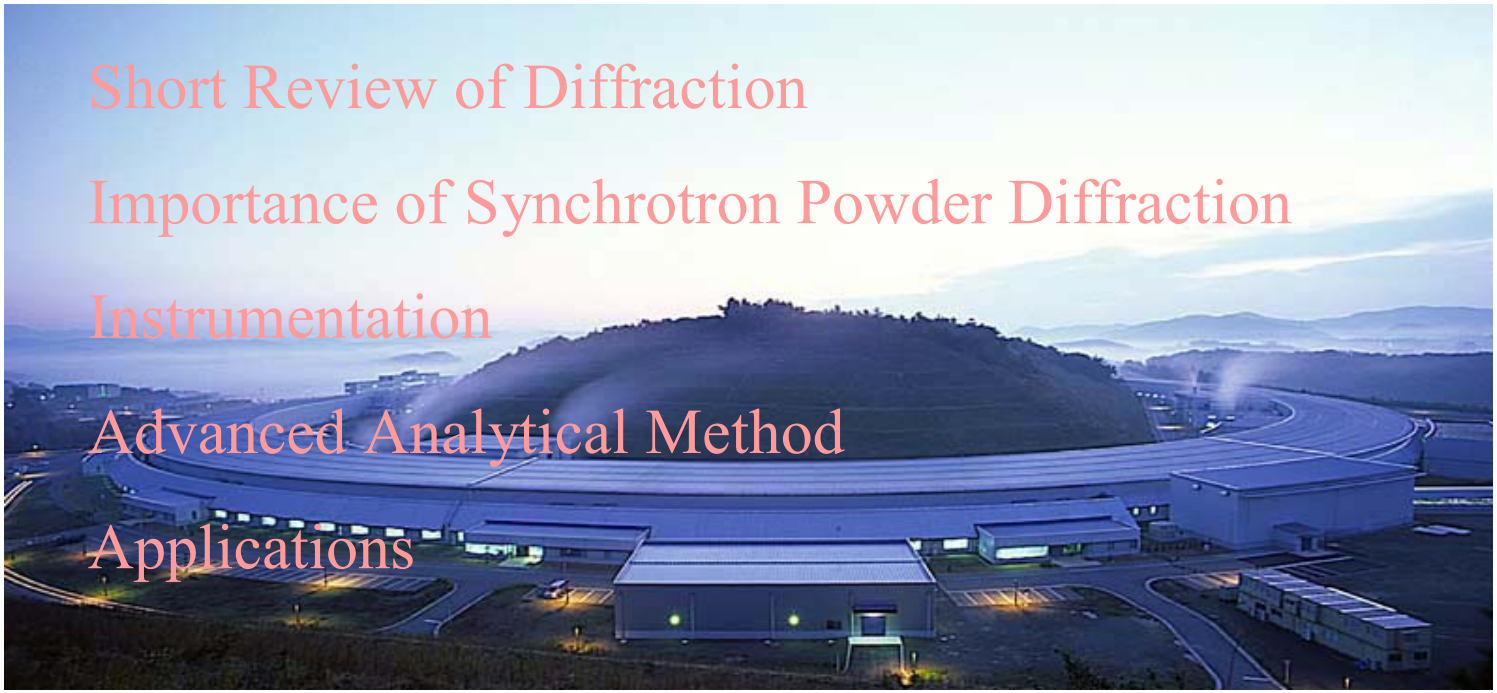
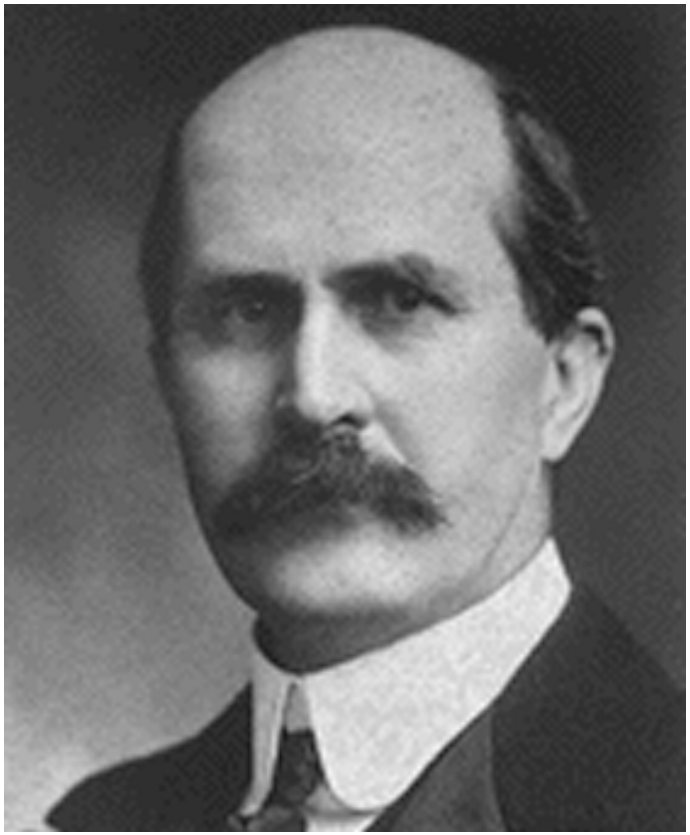
JSPS Asian Science Seminar Synchrotron Science Seminar

Diffraction for Materials Science

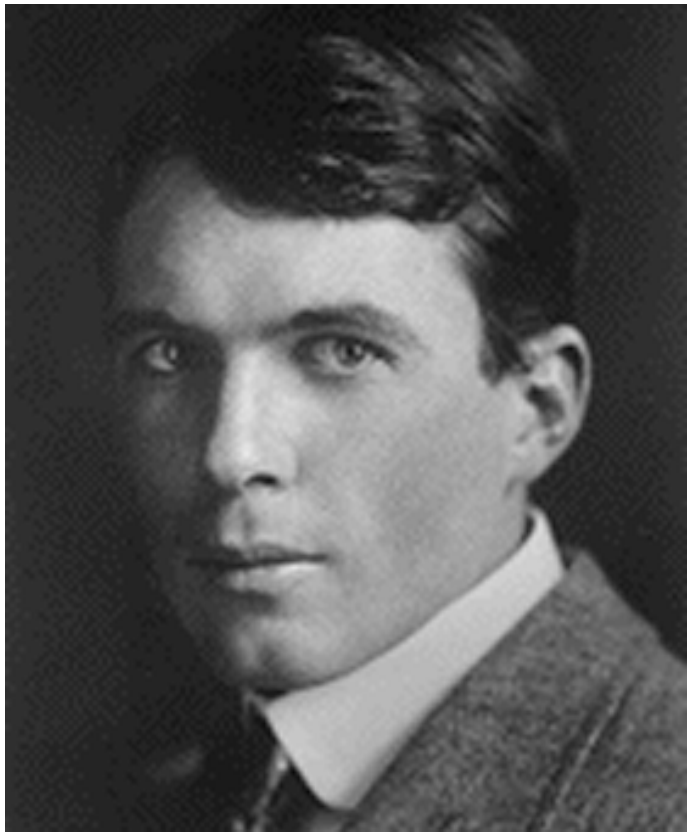
Makoto SAKATA (Nagoya University, JAPAN)



Very Short Review of Diffraction



Prof.W.H.Bragg



Sir W.L.Bragg

Bragg's Equation

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

d : Lattice Spacing

λ : Wavelength of X-ray

θ : Bragg Angle

Calculation of *d* spacing from Lattice constants

$$d_{hkl}=\frac{\sin\beta}{\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}\sin^2\beta+\frac{l^2}{c^2}-\frac{2hl}{ac}\cos\beta\right)^{1/2}}$$

$$d_{hkl}=\frac{1}{\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{1/2}}$$

$$d_{hkl}=\frac{a}{\left\{h^2+k^2+\left(\frac{a}{c}\right)^2 l^2\right\}^{1/2}}$$

Cubic: $$d_{hkl}=\frac{a}{(h^2+k^2+l^2)^{1/2}}$$

$$d_{hkl}=\frac{a}{\left\{\frac{4}{3}(h^2+hk+k^2)+\left(\frac{a}{c}\right)^2 l^2\right\}^{1/2}}$$

Fundamental Equation of X-ray Diffraction

Structure Factor

$$F(h) = \int_{UnitCell} \rho(r)\, e^{2\pi i h\cdot r}\, dv$$

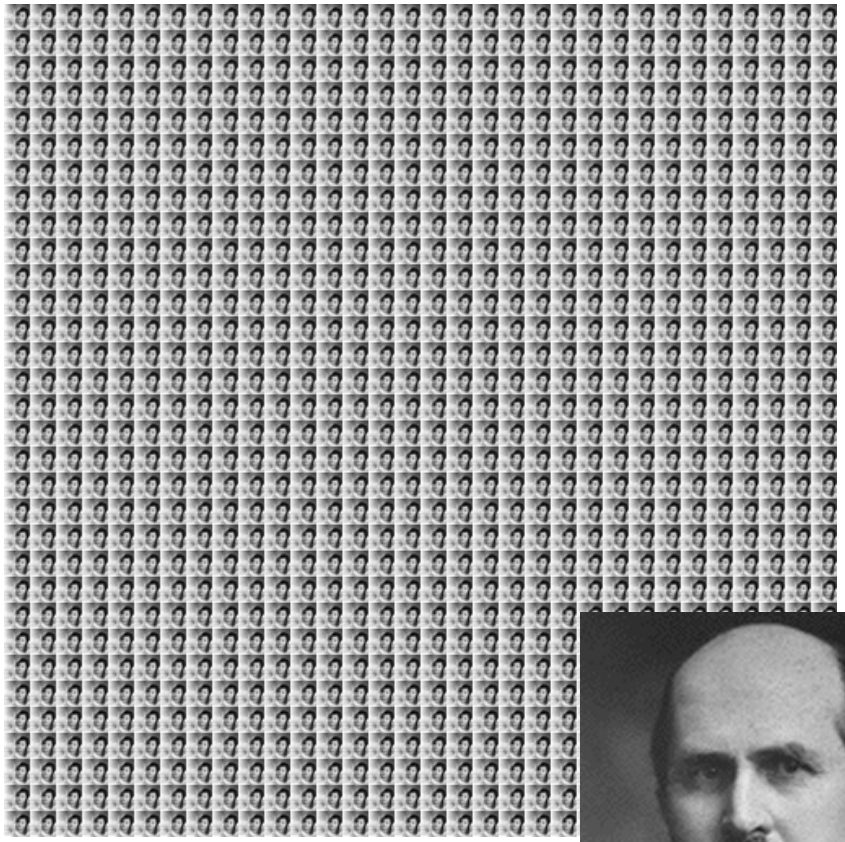
Charge Density ρ(r)

$$\rho(r) = \int F(h) e^{-2\pi i h\cdot r}\, dh$$

$$= \frac{1}{v_c} \sum_{h} F(h) e^{-2\pi i h\cdot r}$$

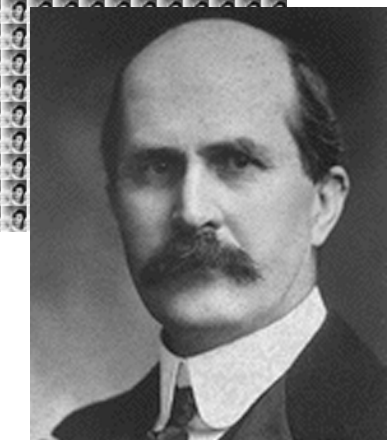
Fourier Transform of Crystal

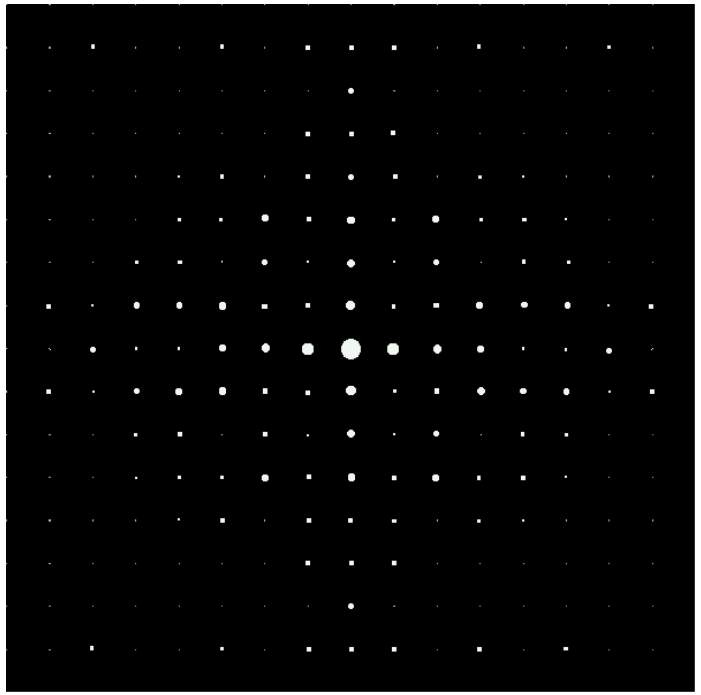
$$I \propto |F|^2$$



Real Space

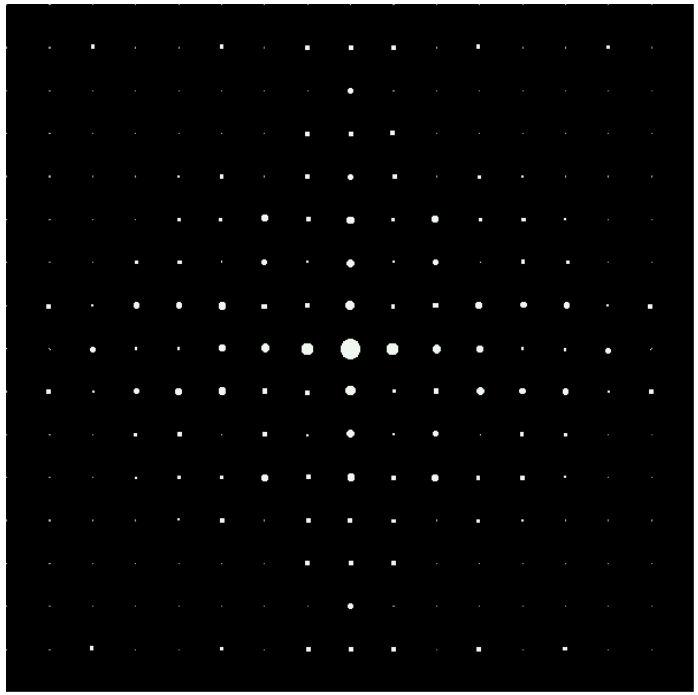
F



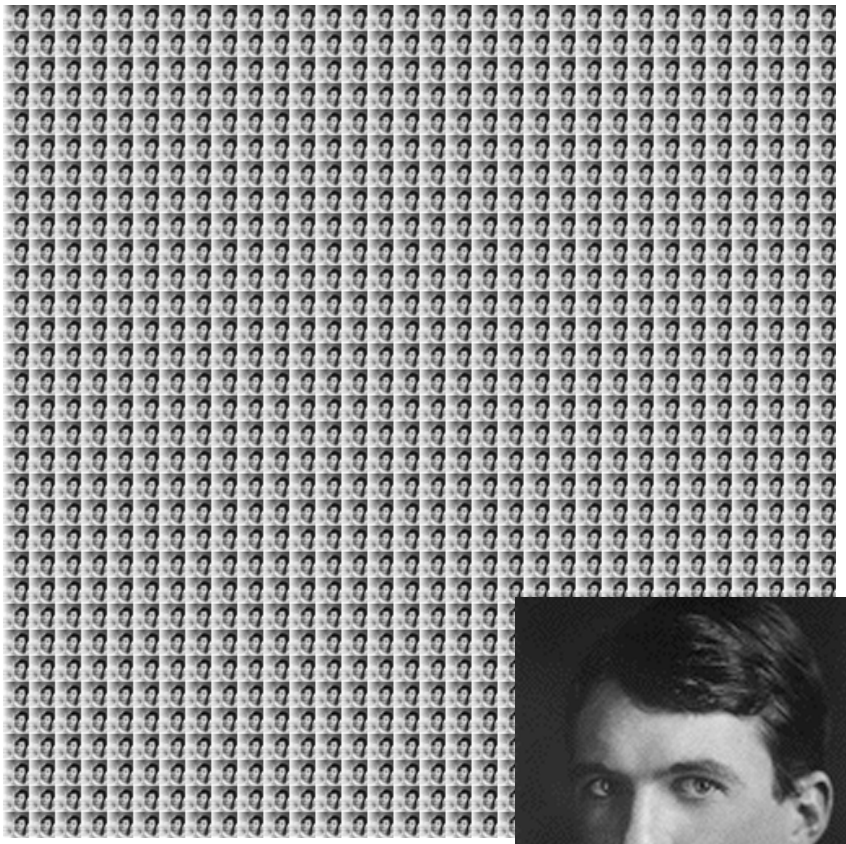


Reciprocal Space

Crystal Structure Determination

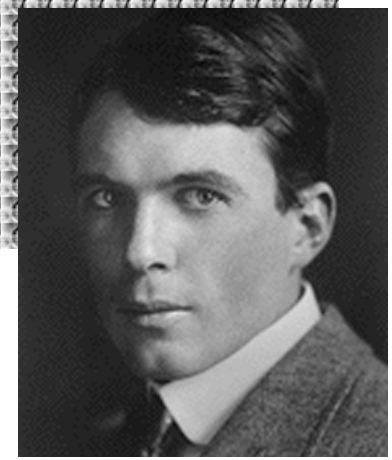


F^{-1}

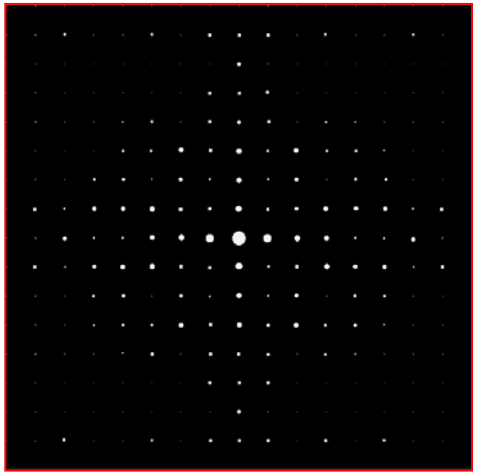


Reciprocal Space

Real Space



Crystal structure and Bragg Intensities



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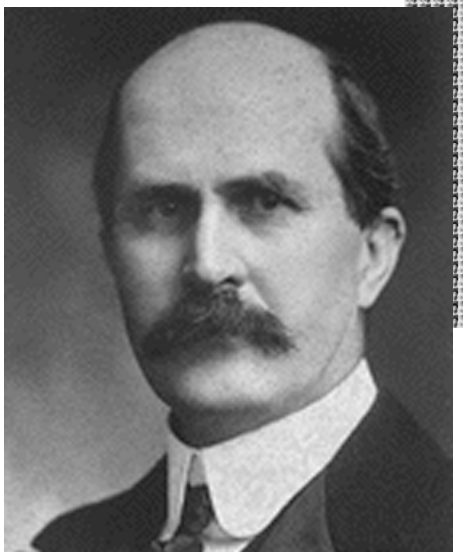
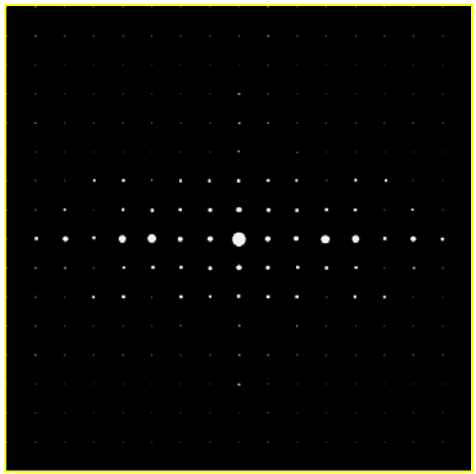


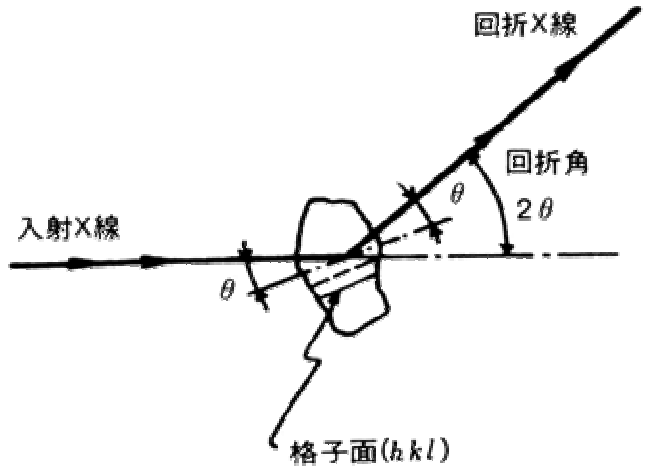


F^{-1}

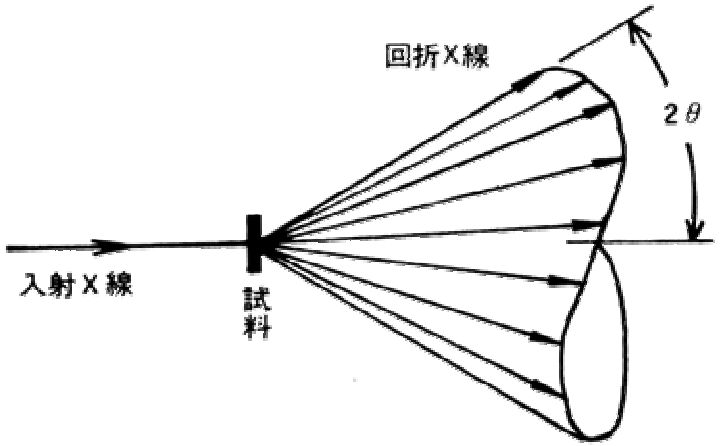
Synchrotron Powder Diffraction

- Powder Diffraction by Lab. Source
- Instrumentation of Synchrotron Powder Diffraction
- Importance of Synchrotron Powder Diffraction in Materials Science

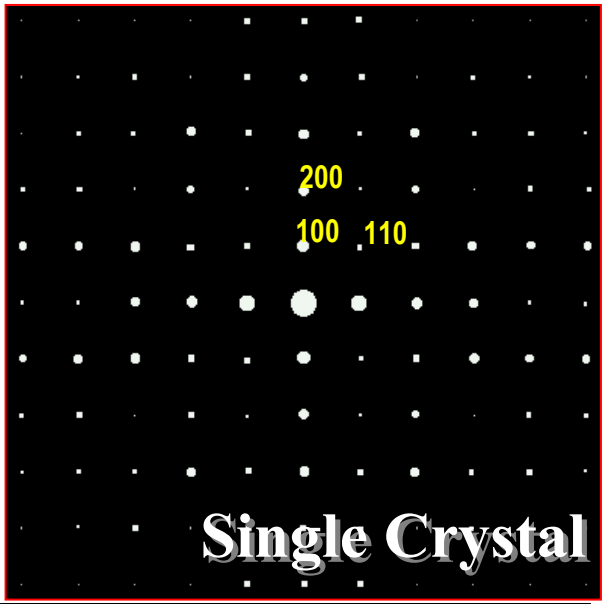
Principle of Powder Diffraction

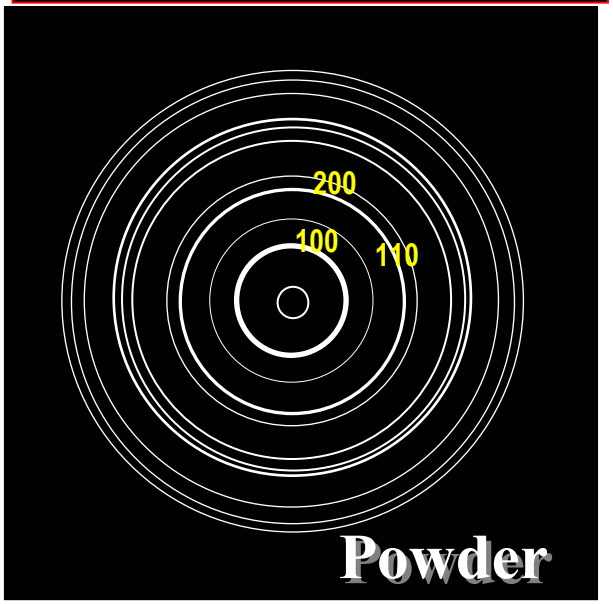


（a）１つの結晶による回折



（b）粉末による回折





Powder Diffraction By Bebye-Sherrer Camera

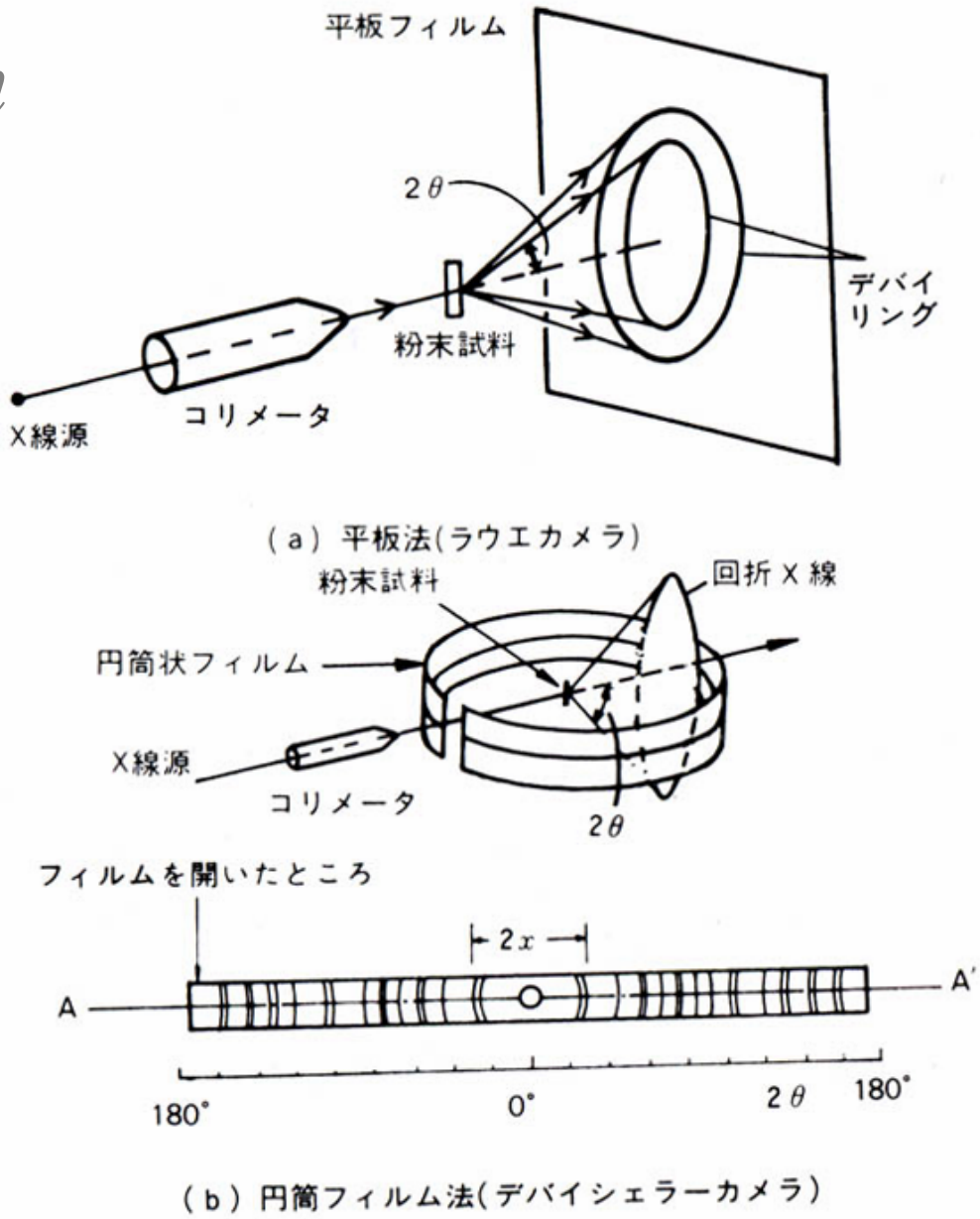
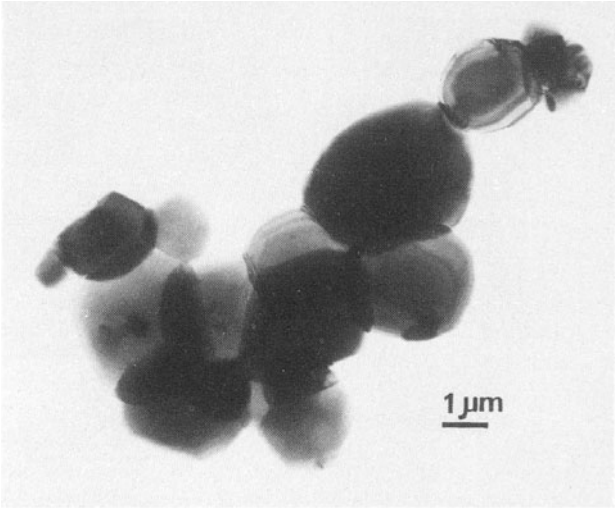
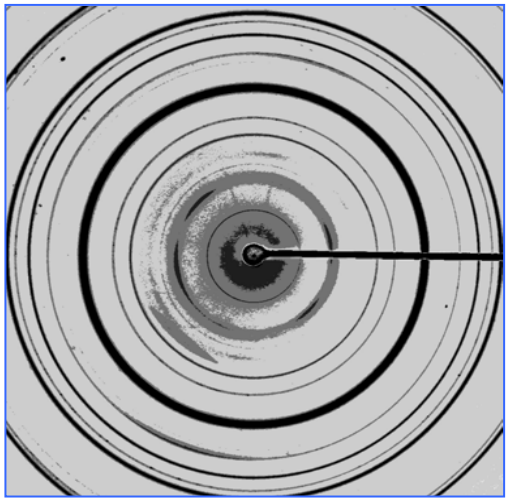
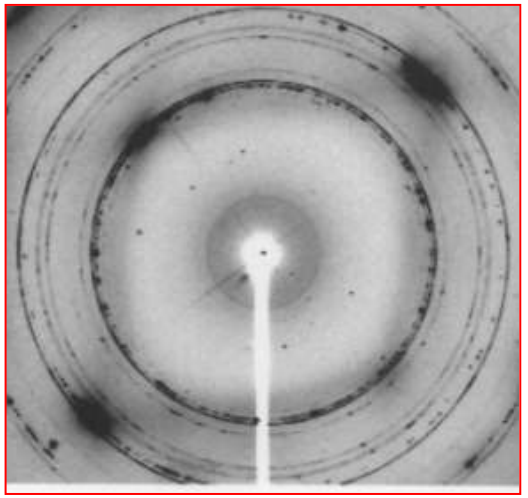


図1.12.2　粉末法の原理

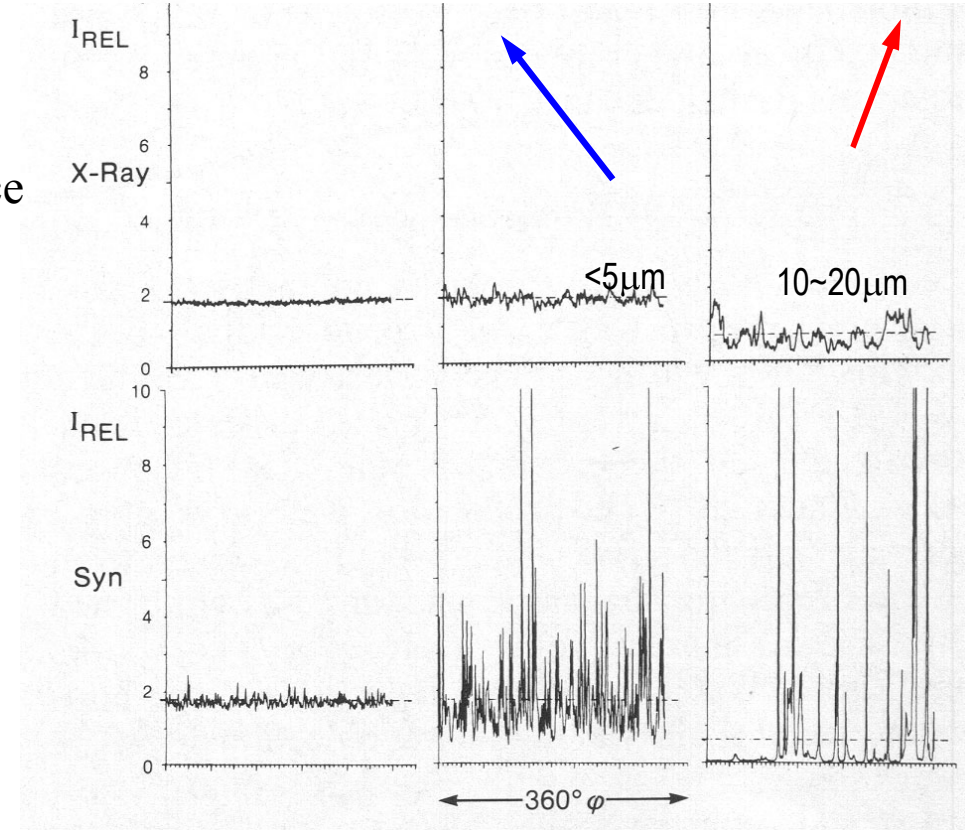






Lab. source

SR



Powder Diffraction

by Diffractometer

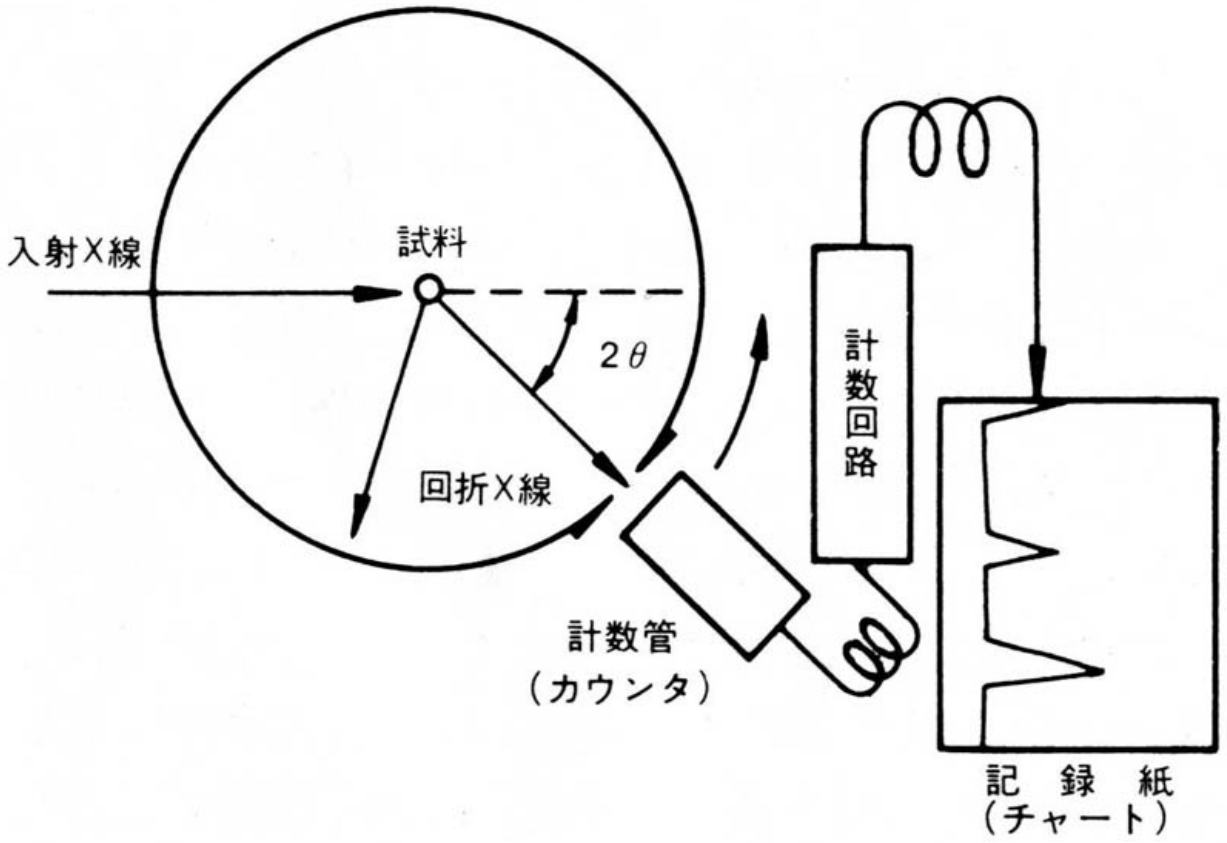
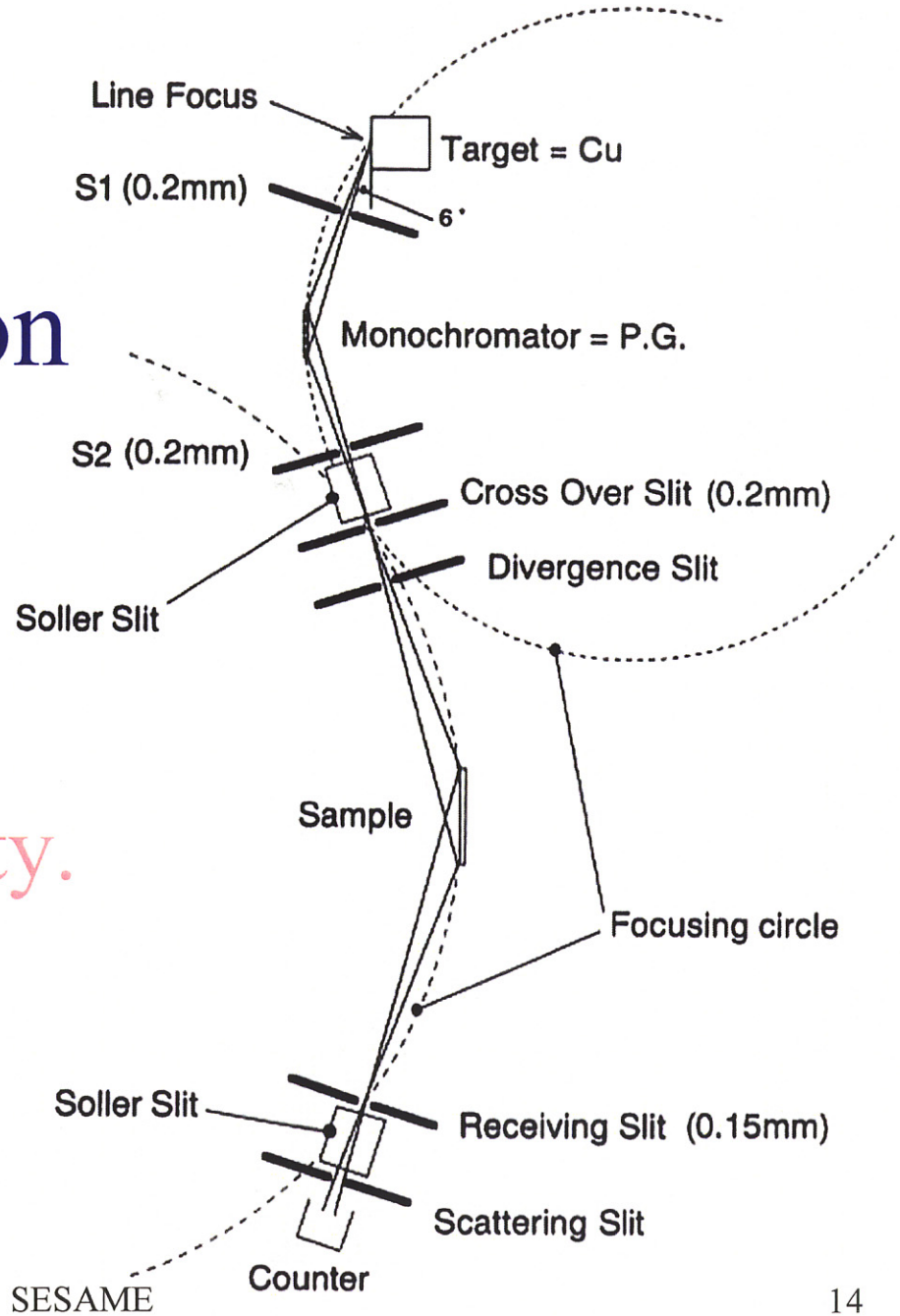


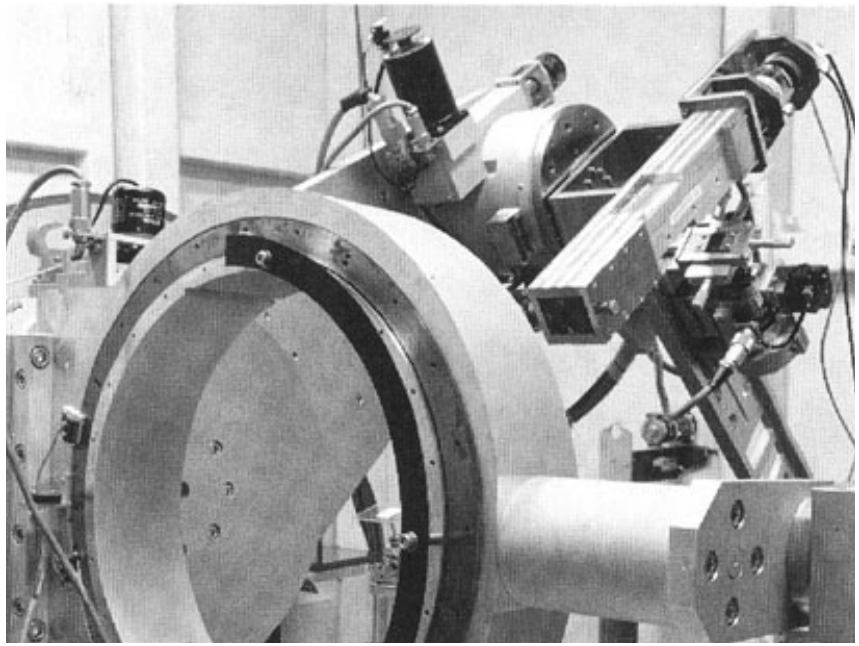
図1.12.3　ディフラクトメータの基本原理

PowderDiffraction by Lab. Source

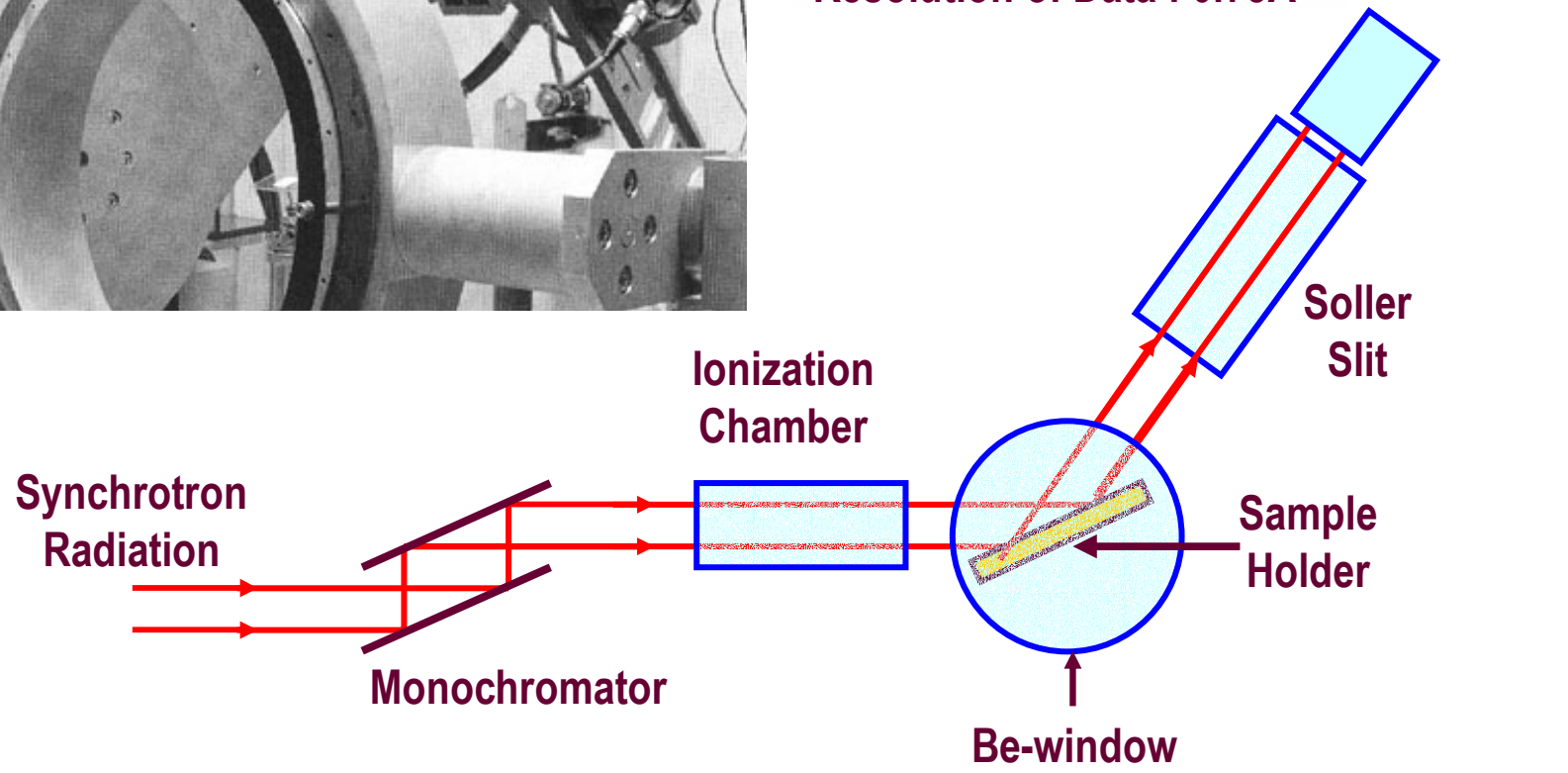
Focusing is necessity.



Synchrotron Powder Diffraction (Photon Factory BL-3A Case)



Sample : $NdSr_2Mn_2O_7$
Temperature : R.T. & 19K
Wave Length : 1.0Å
Step in 2θ : 0.01°
Collection Time : 20s
Resolution of Data : 0.78Å



Solar Slit

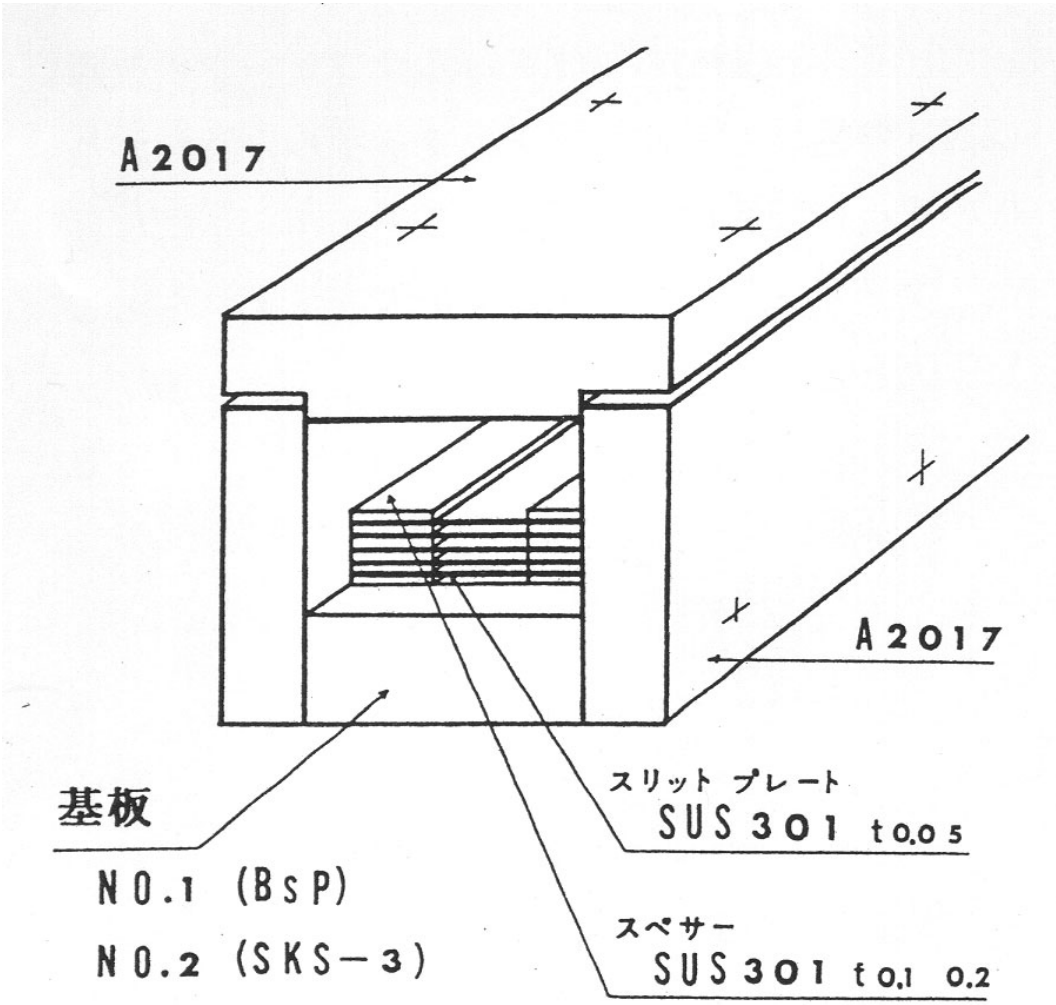
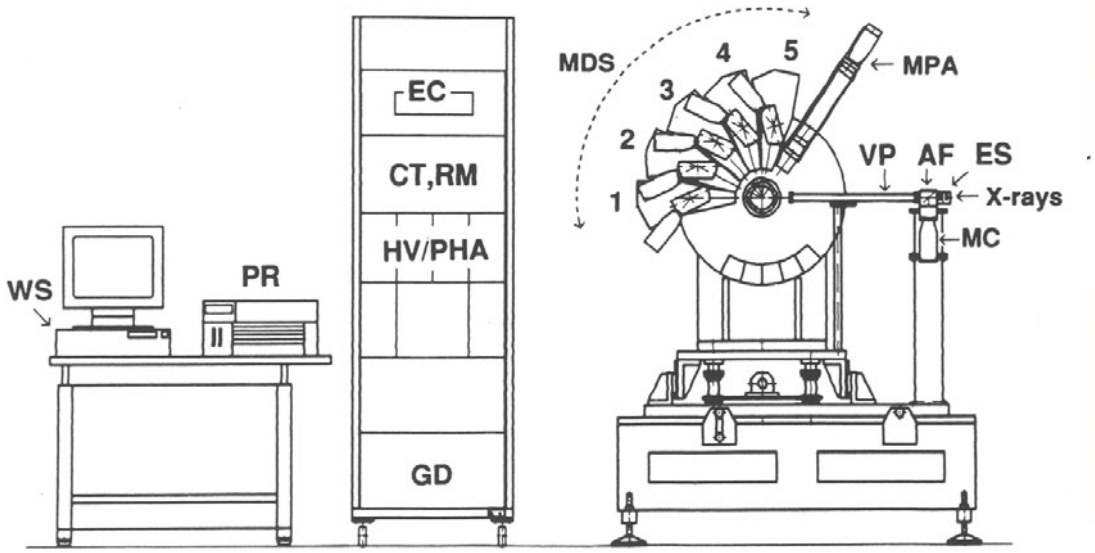


Fig.2 Solar slit with piling up the plates.

Multi-counter Powder Diffratometer BL-4B(PF)



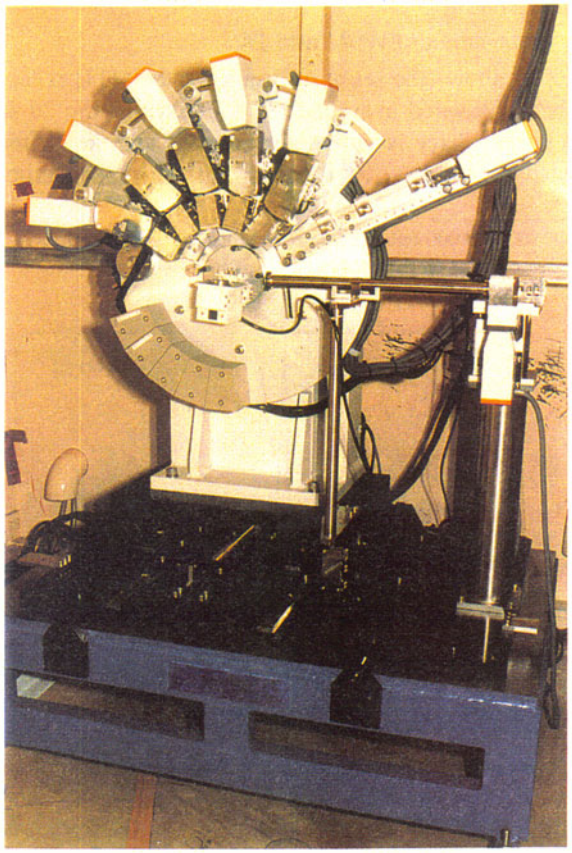
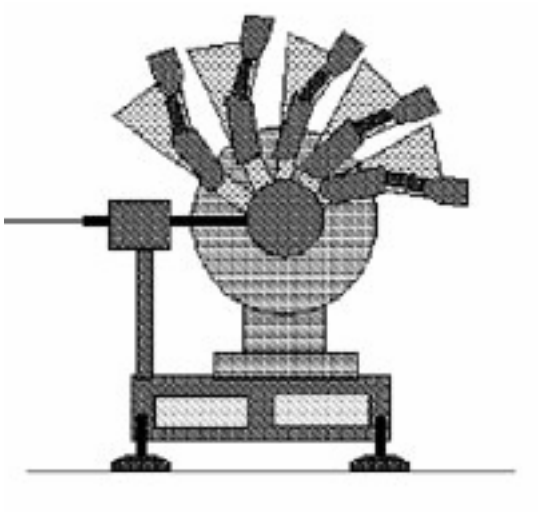
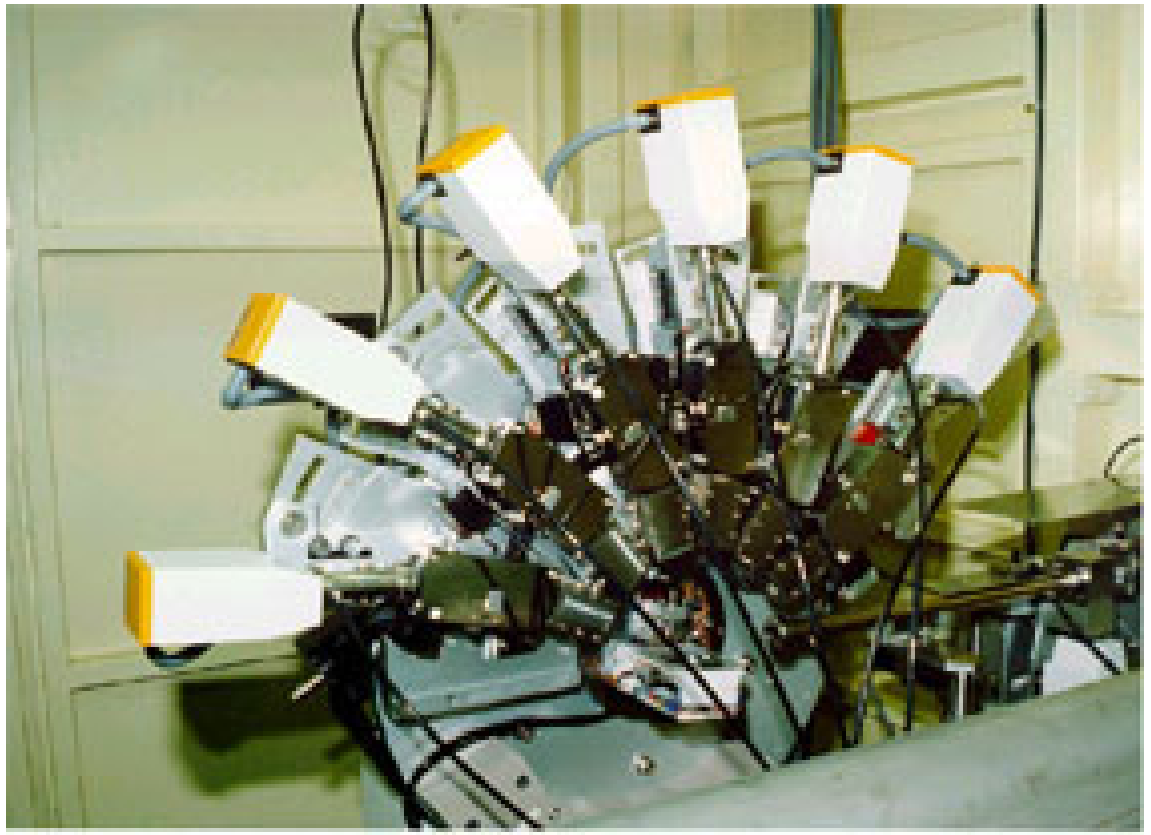


Figure 2
The diffractometer inside the hutch of the BL-4B experimental station at the Photon Factory.

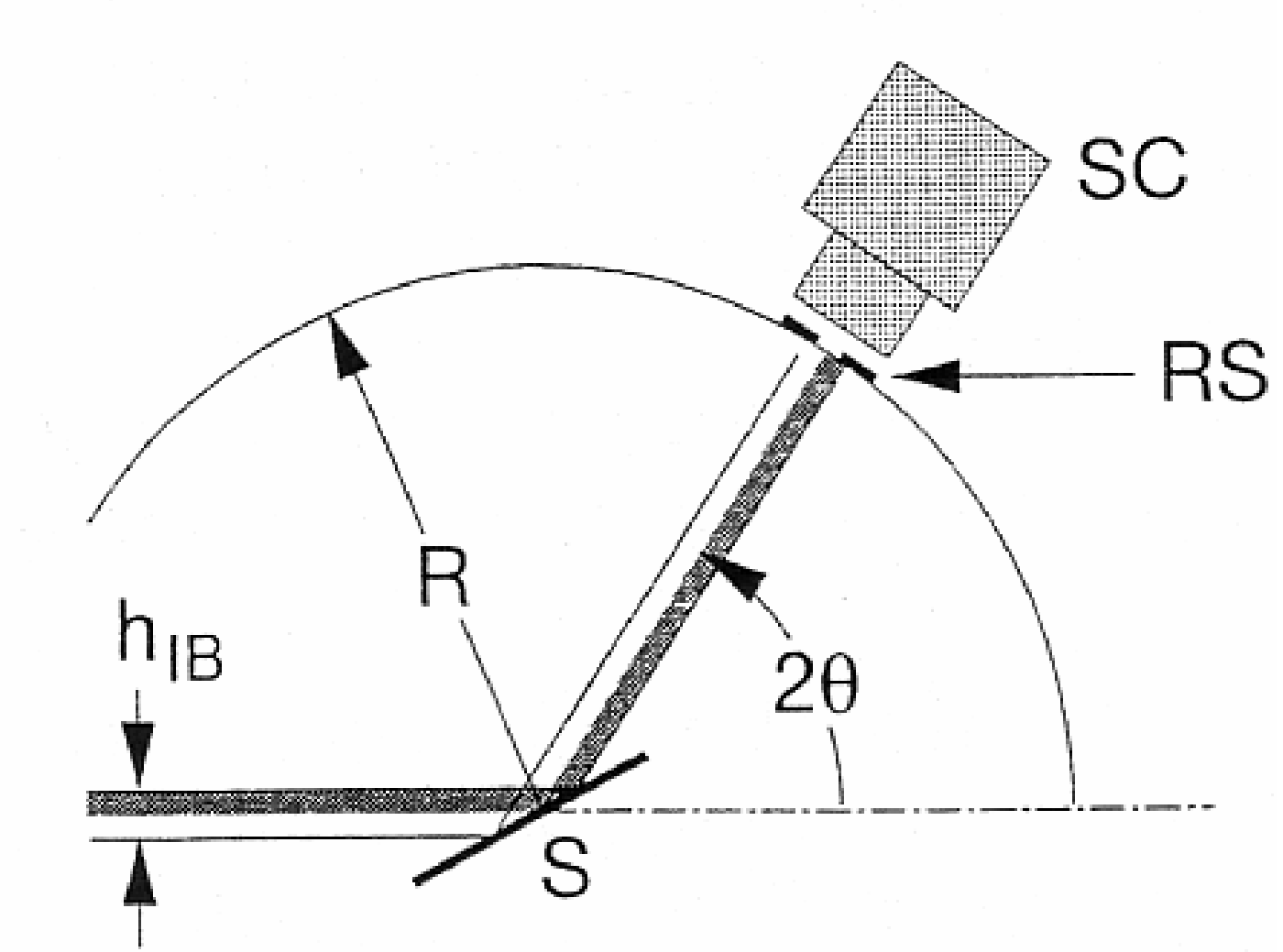
Synchrotron Powder Diffractometer with multicounters



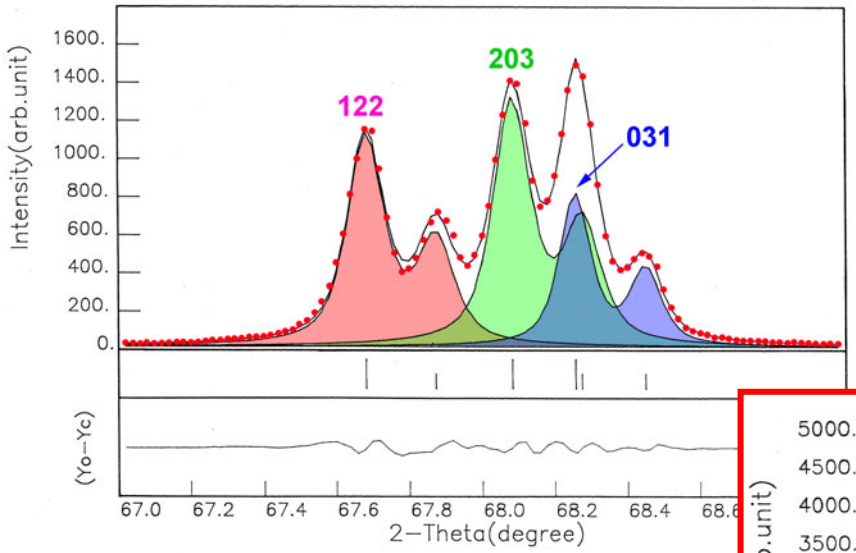


PF BL4B2

Parallel Beam Diffraction by SR



Difference between Synchrotron and Lab. Data



Lab. Source

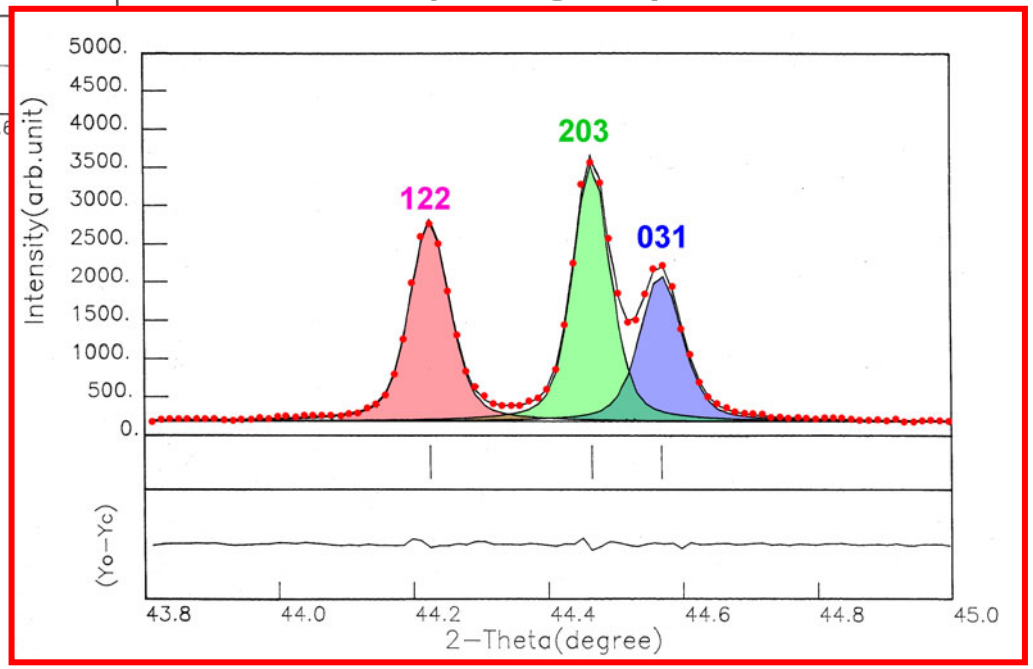
SiO_2

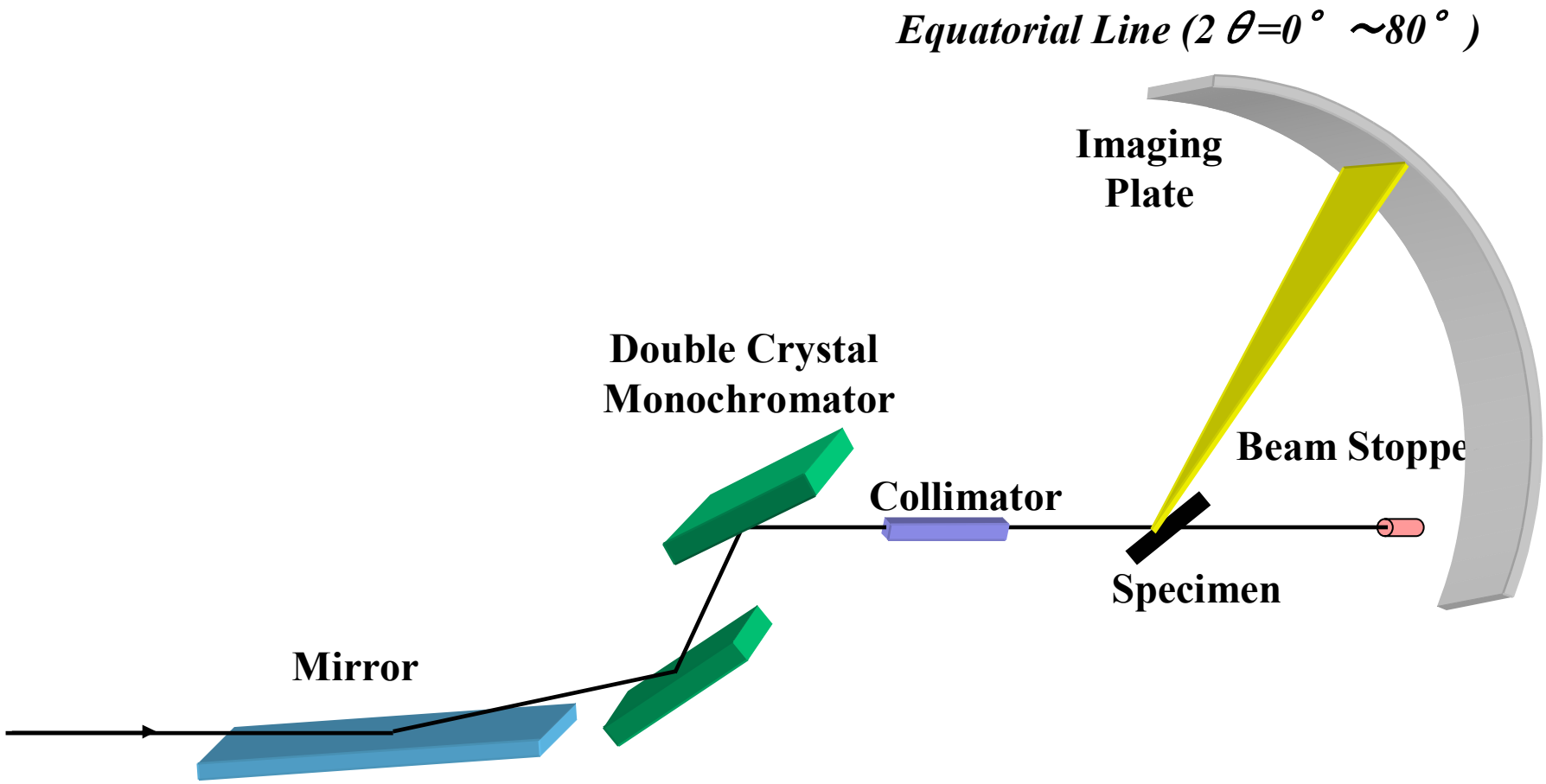
(5fingers)

Synchrotron

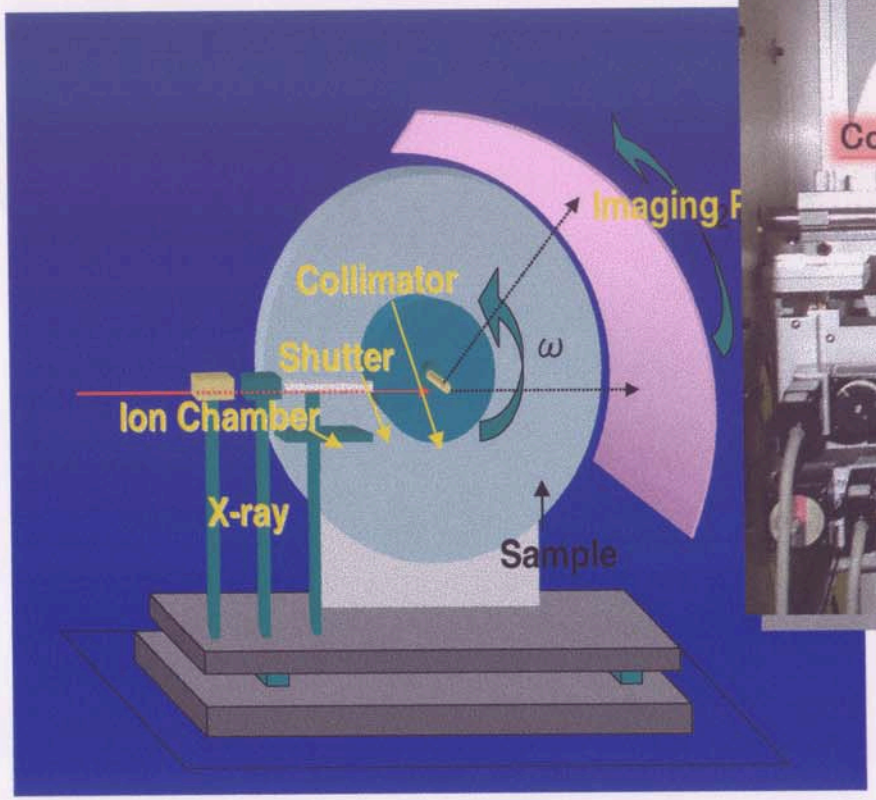
SiO_2

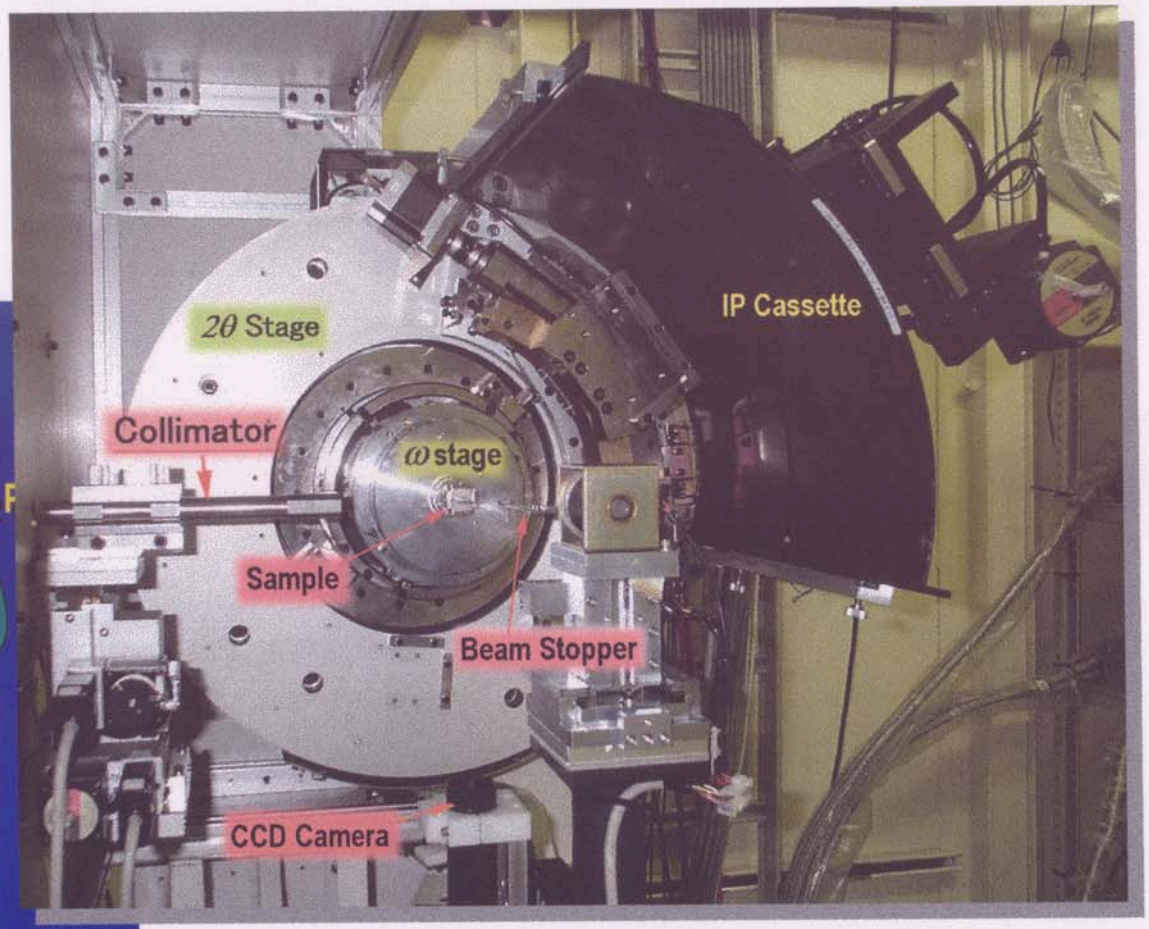
(3fingers)




Equatorial Line (2θ=0° ～80°)
Imaging
Plate
Double Crystal
Monochromator
Beam Stoppe
Collimator
Specimen
Mirror

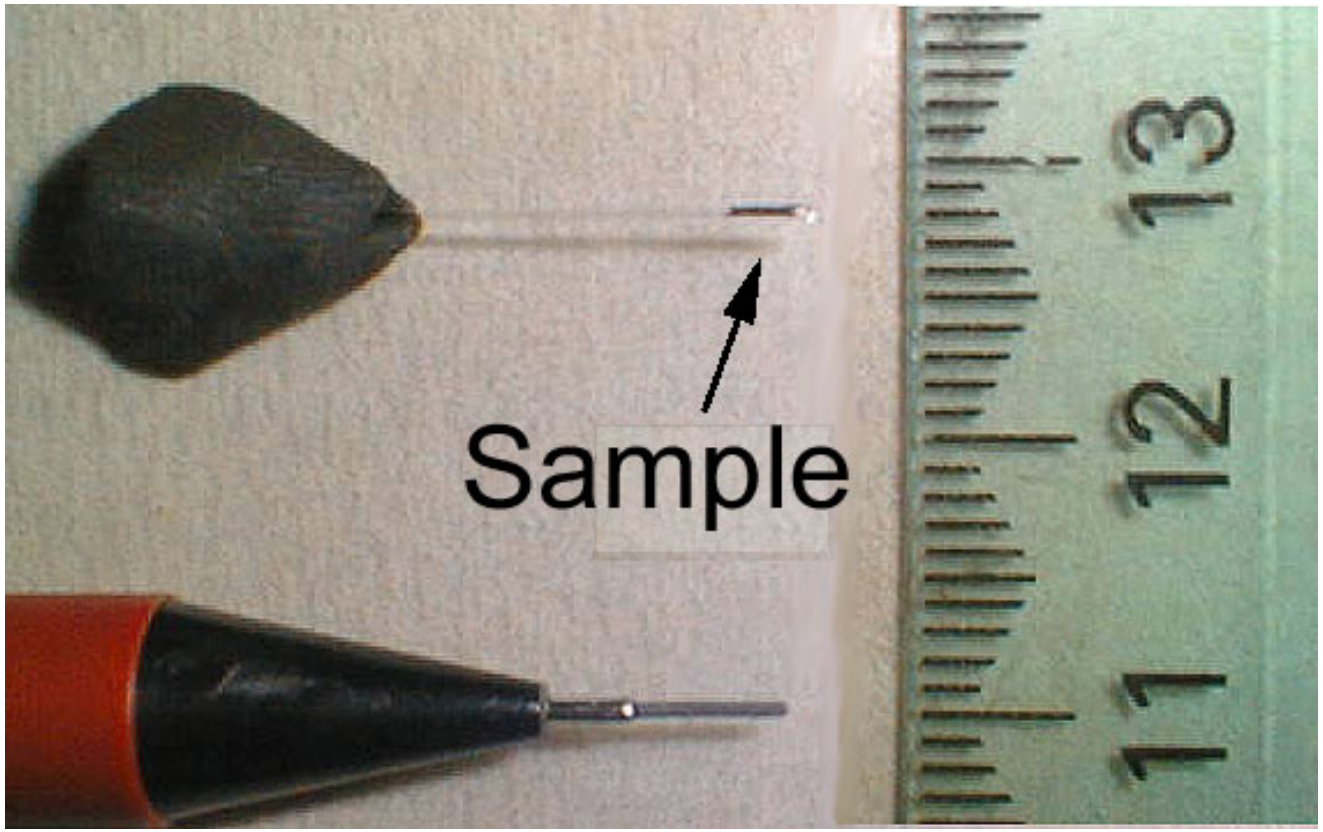
The Large Debye-Scherrer Camera at SPring-8 BL02B2





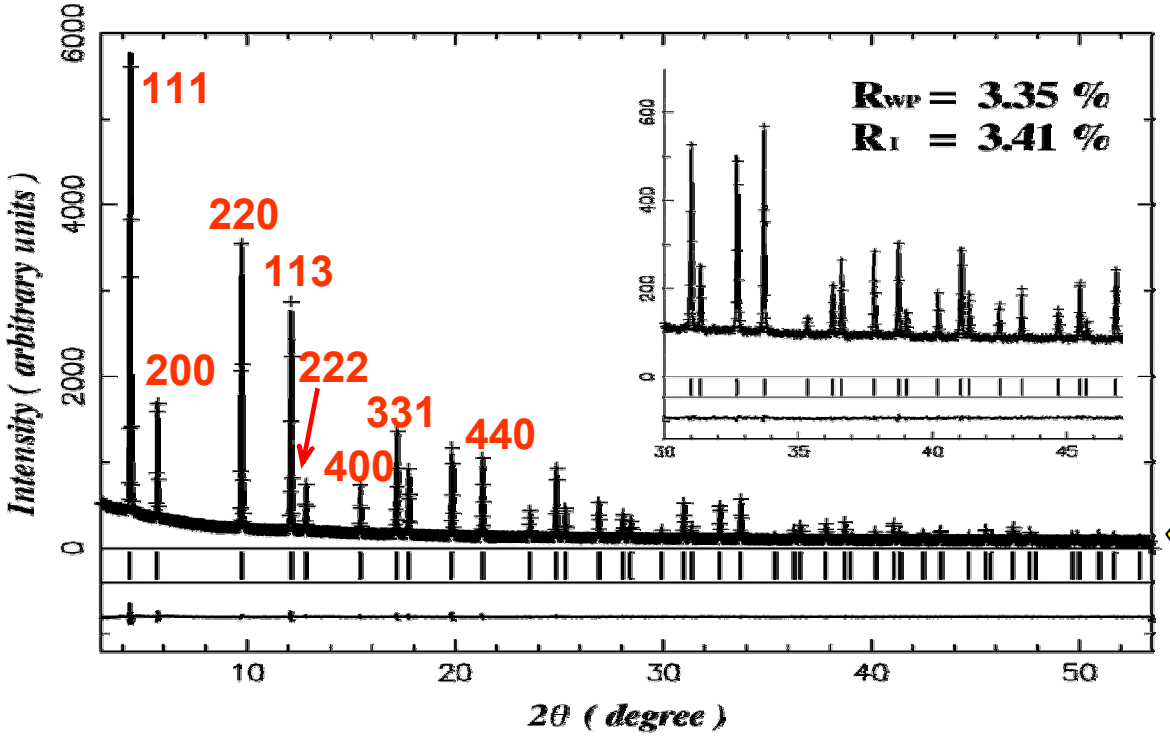
Powder Sample Sealed in Silica Glass Capillary

(0.2mm int. diam.)

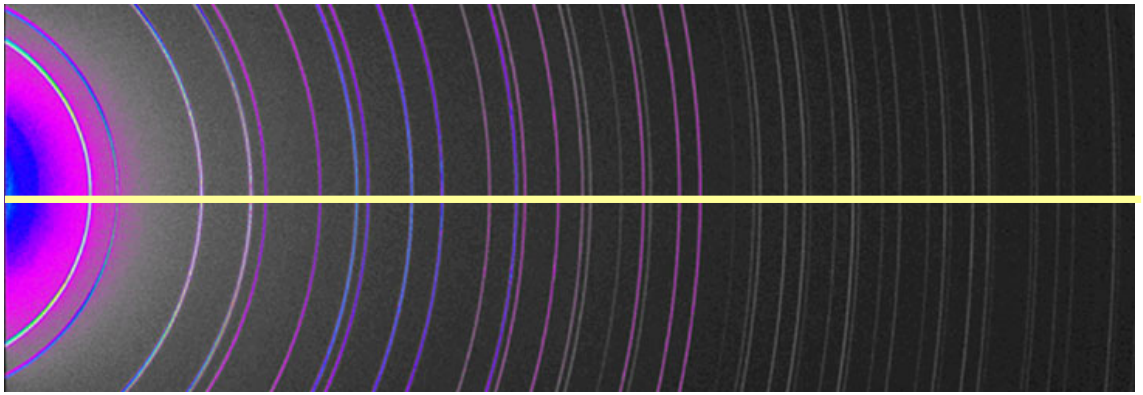


Synchrotron Powder Data of CeO_2

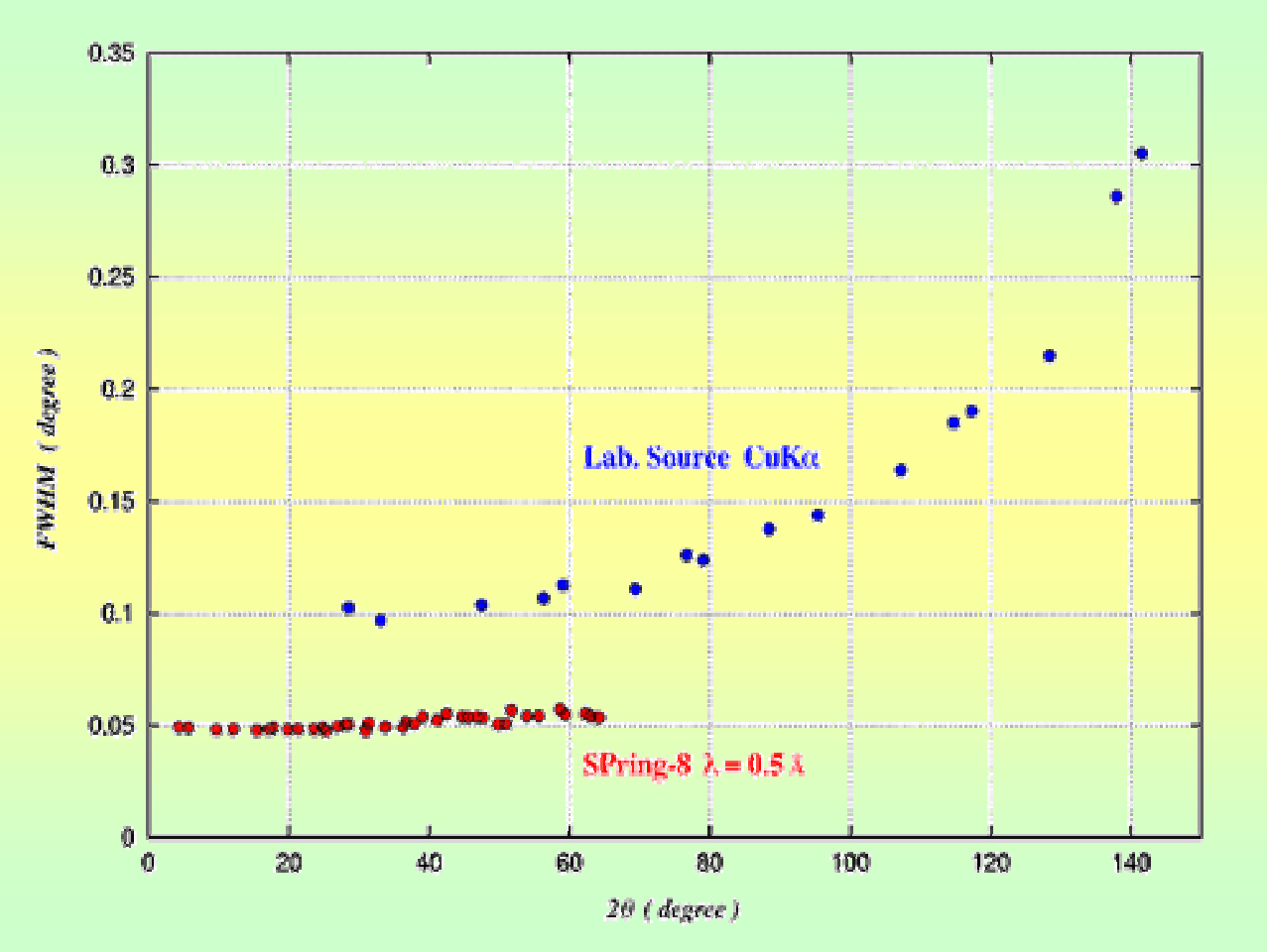
Whole Pattern



2D Pattern

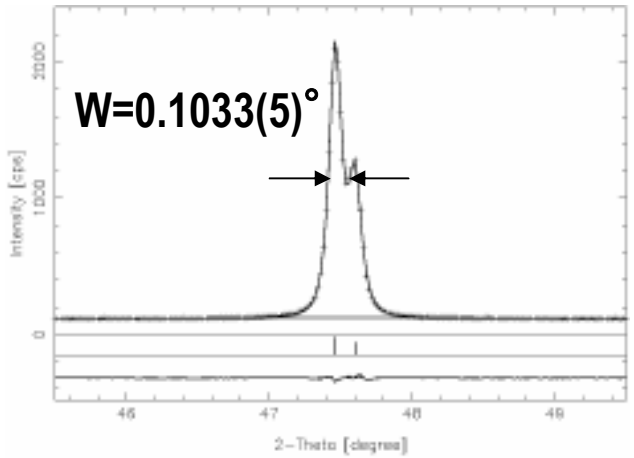


Variations of FWHM of CeO_2 with 2θ for SPring-8 & Lab. Source

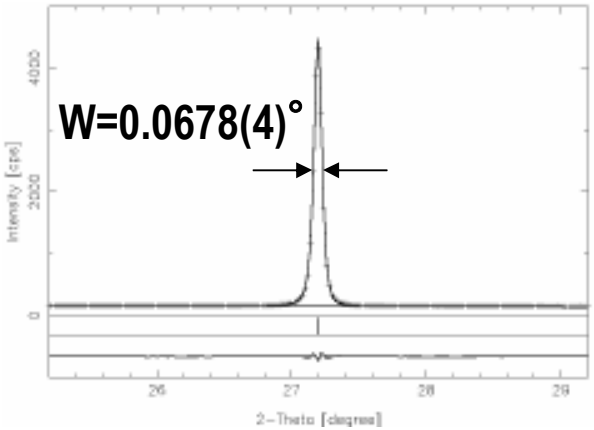


Powder profiles of CeO_2(220)

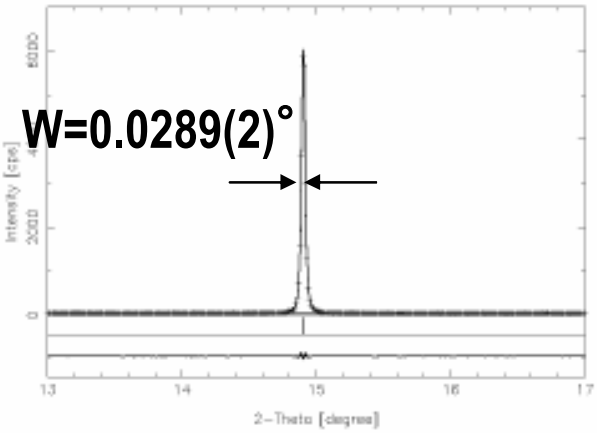
Lab. Source CuK_α



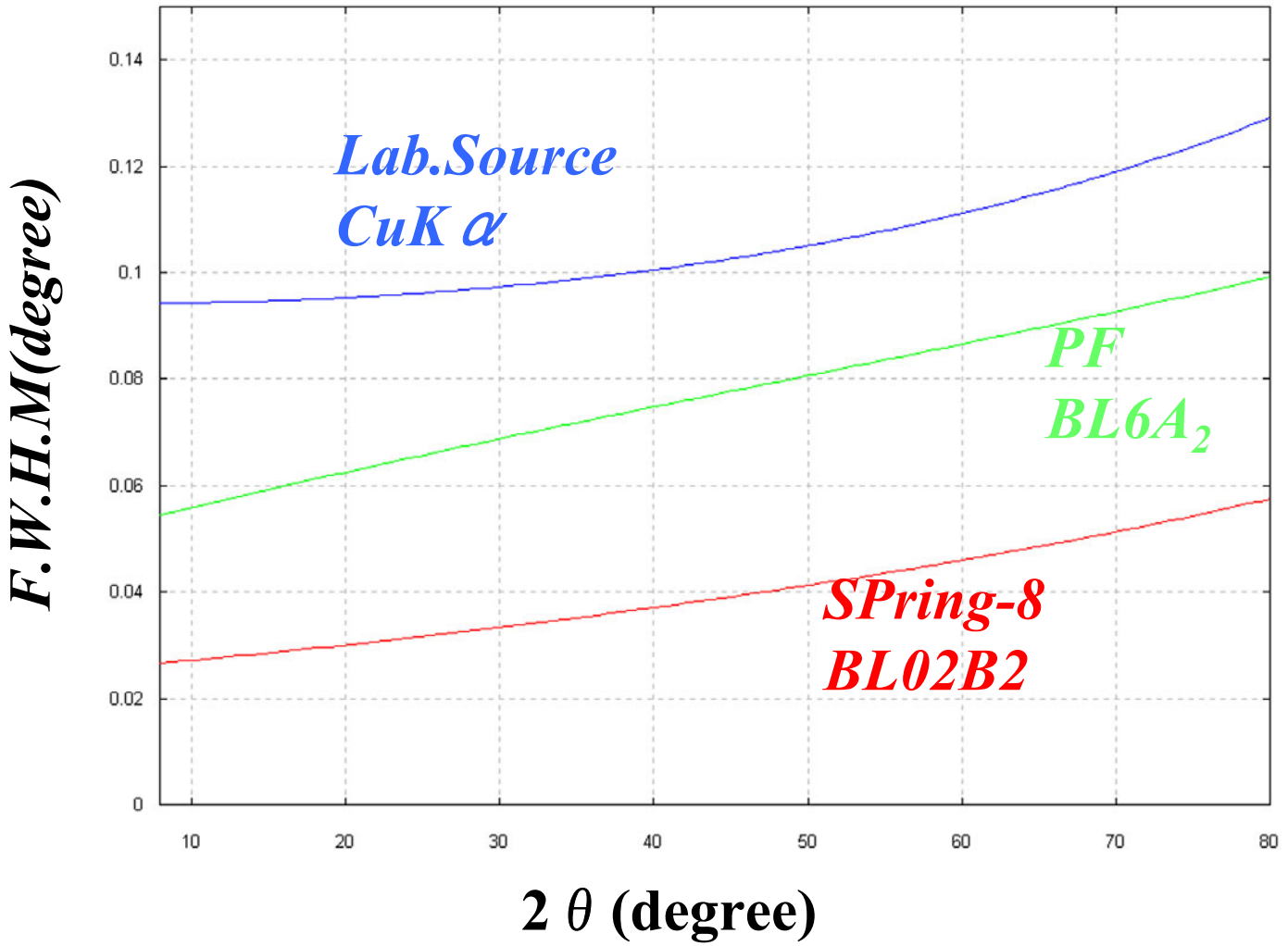
PF BL-6A$_2$ λ =0.9 Å



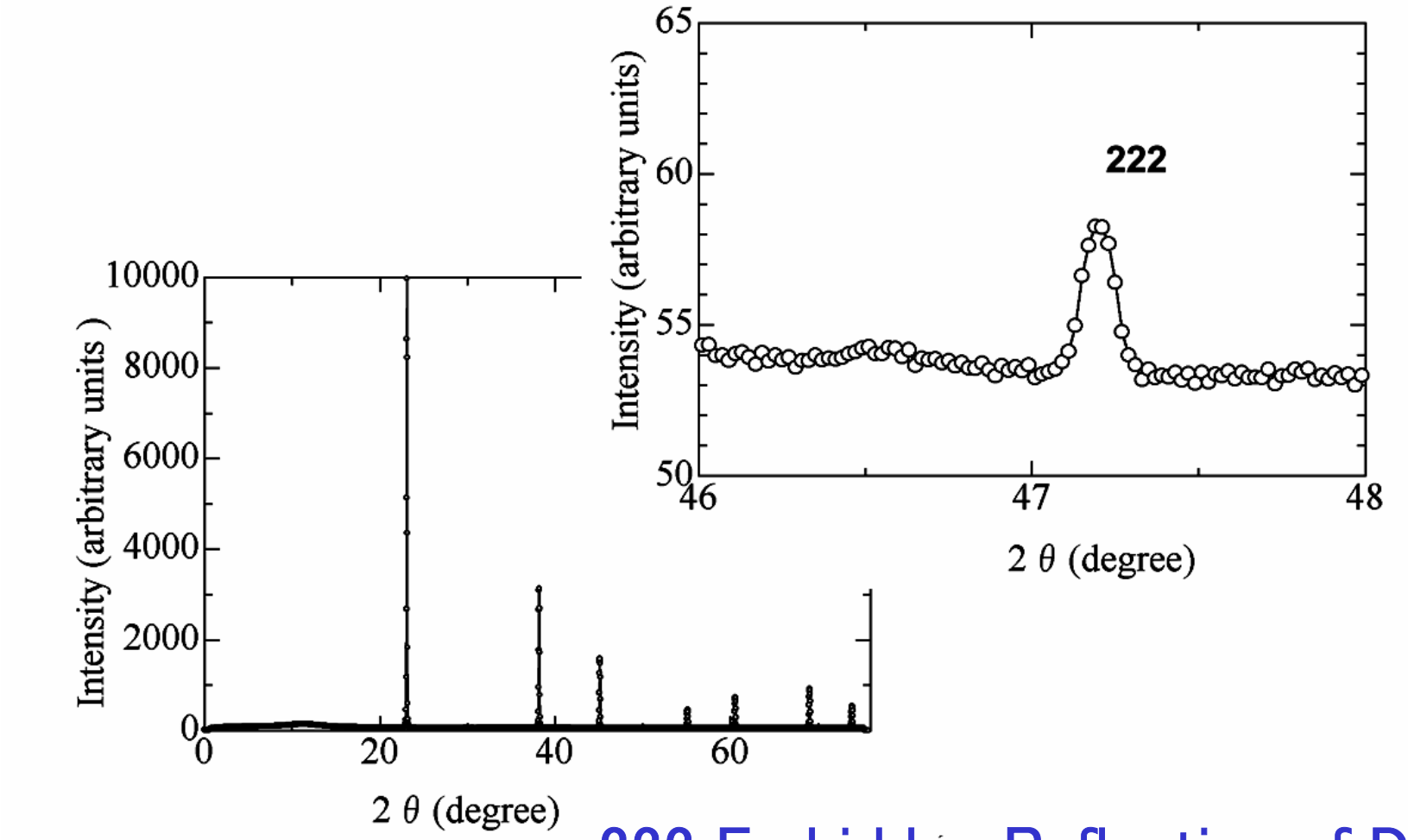
SPring-8 BL02B2 λ =0.5 Å



Full Width at Half Maximum



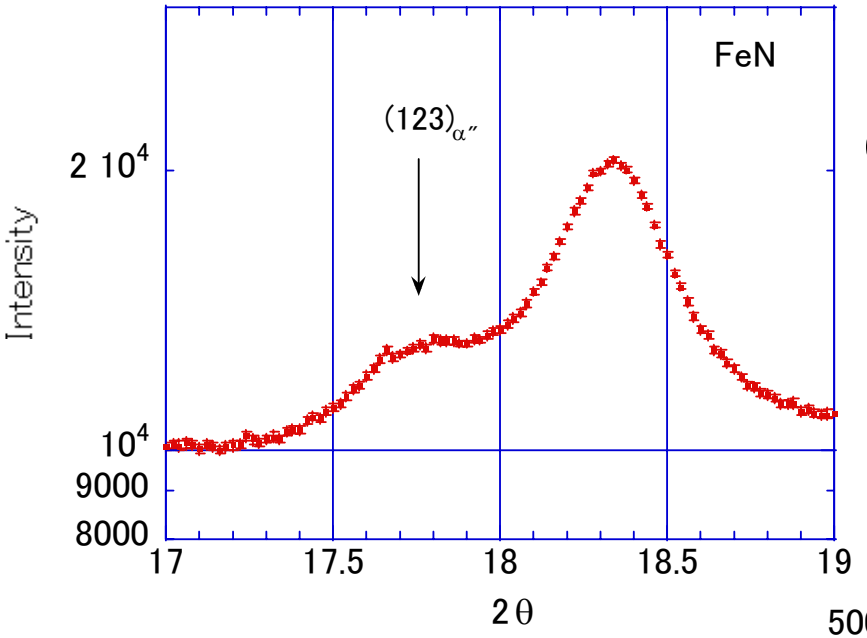
Measurement of Weak Reflection by SR



222 Forbidden Reflection of Diamond

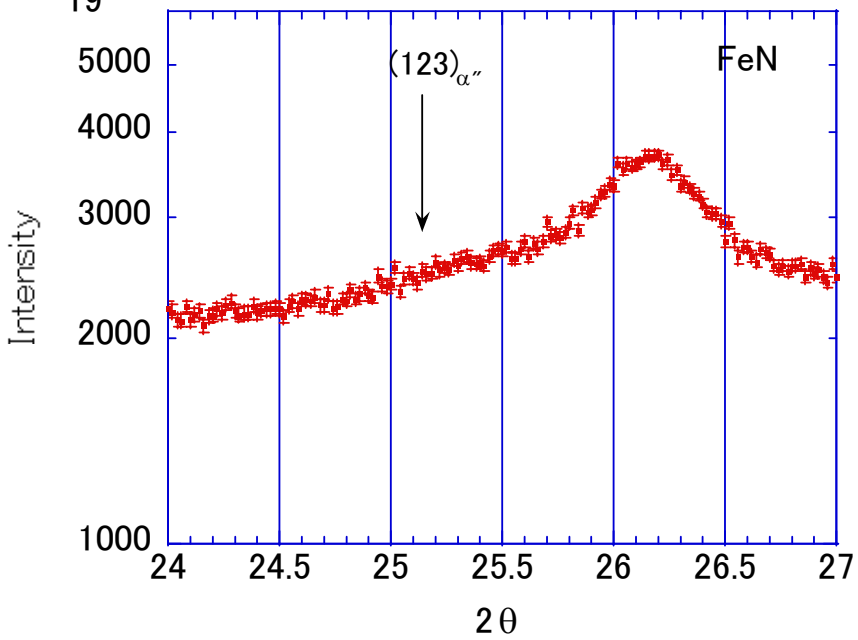
An Example

By Y.Koyano & T.Ohba

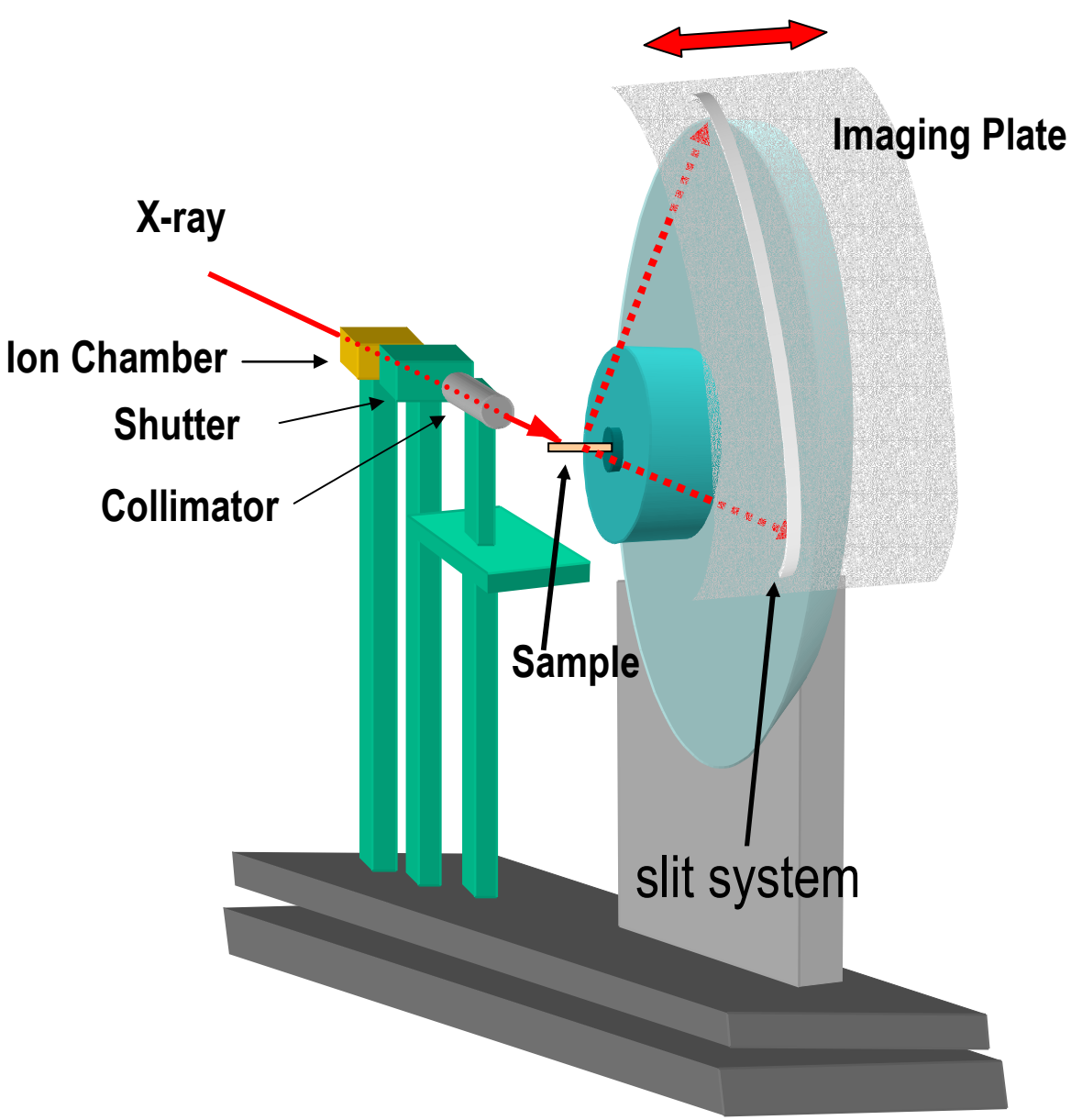


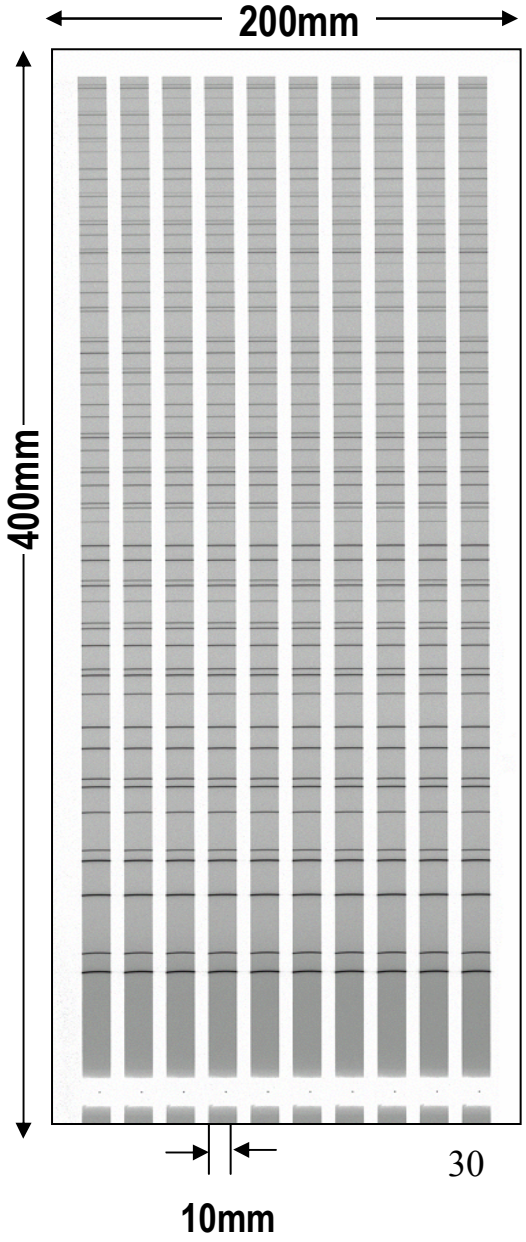
@ SPring-8 BL02B2
40min.

@ Lab. Source
18kW
One week measurement



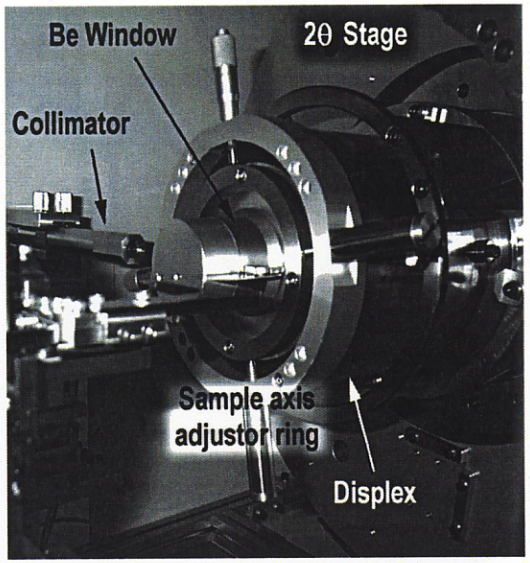
Multi Pattern Recording System

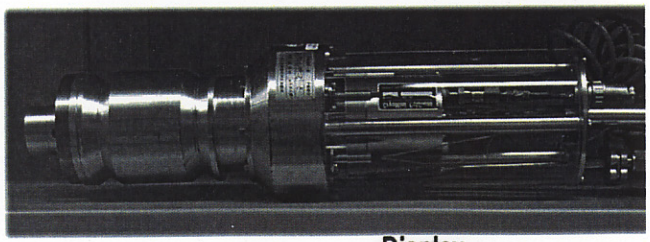




Low and High Temperature Powder Diffraction

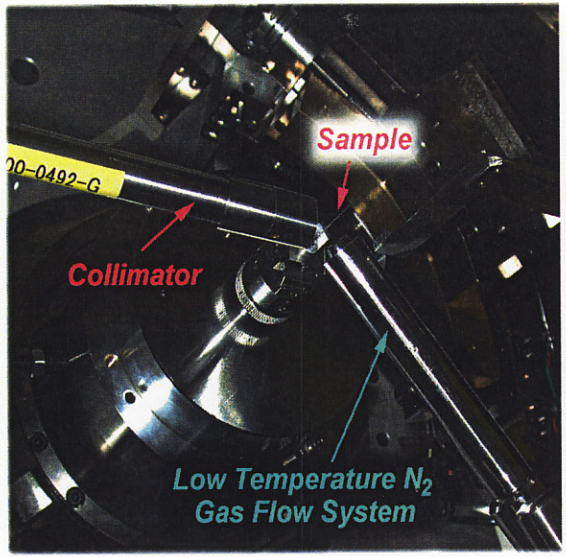
15K～300K
Displex System



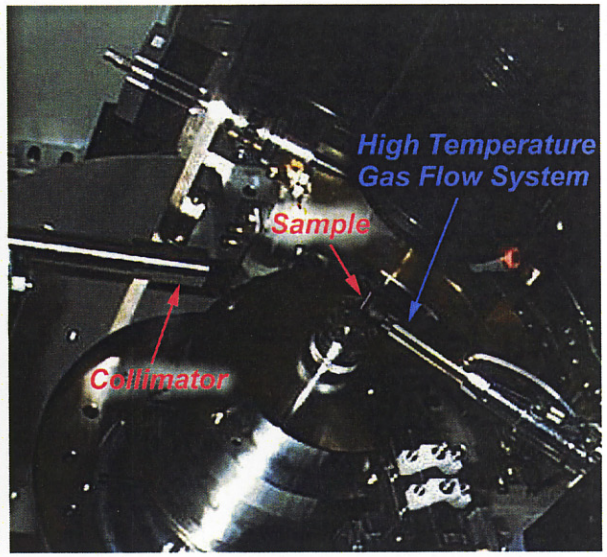


Displex

80K～300K
Dry N_2 Gas Flow System



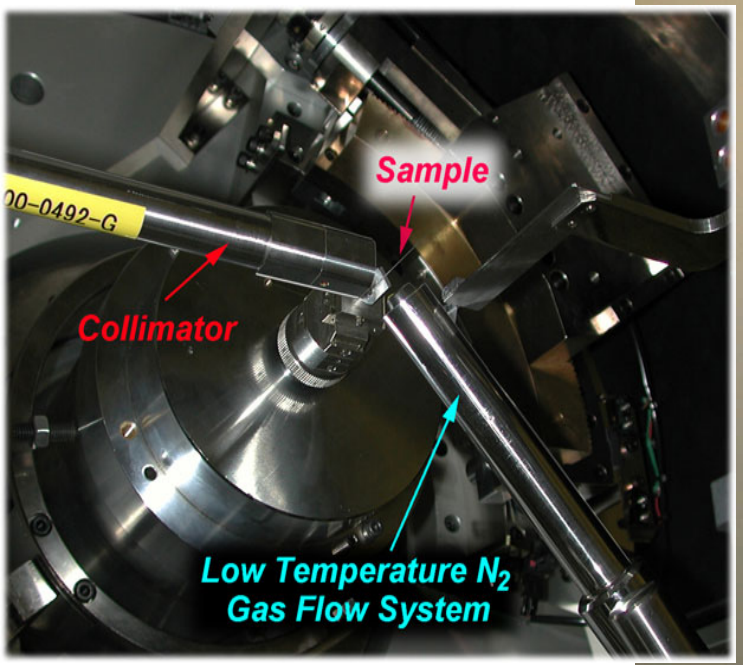
300K～1000K
Dry N_2 Gas Flow System

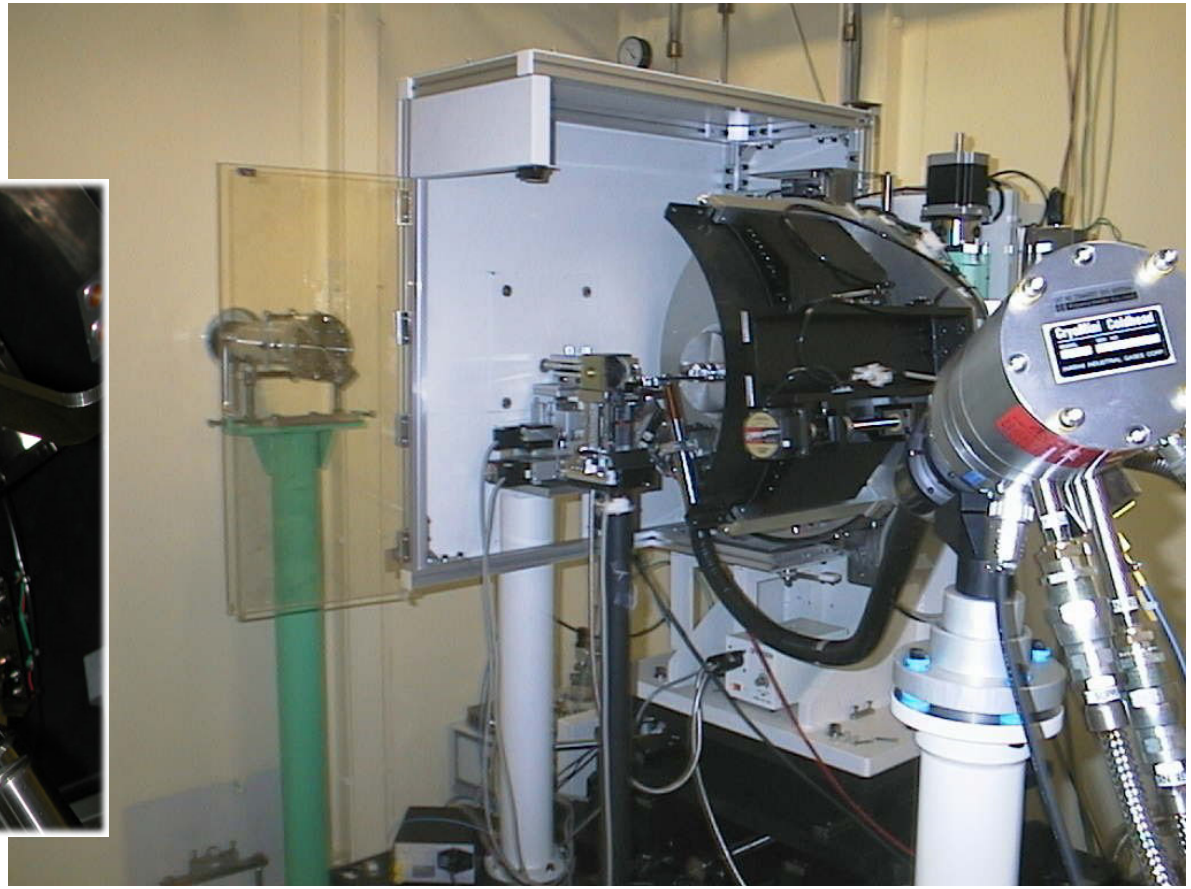


Low Temperature N_2 Gas Flow System

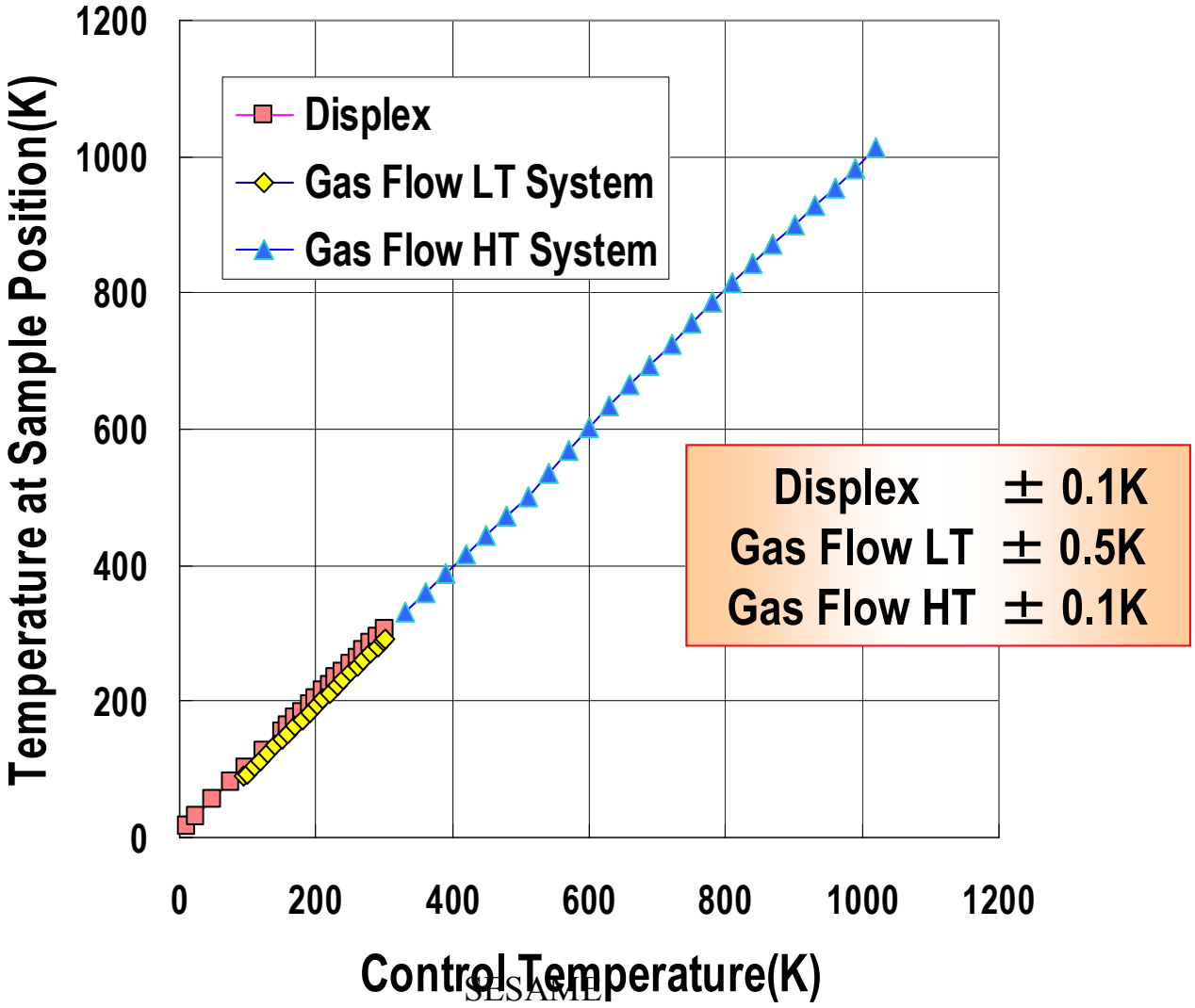
Temperature Range : 80K～300K

Gas : N_2

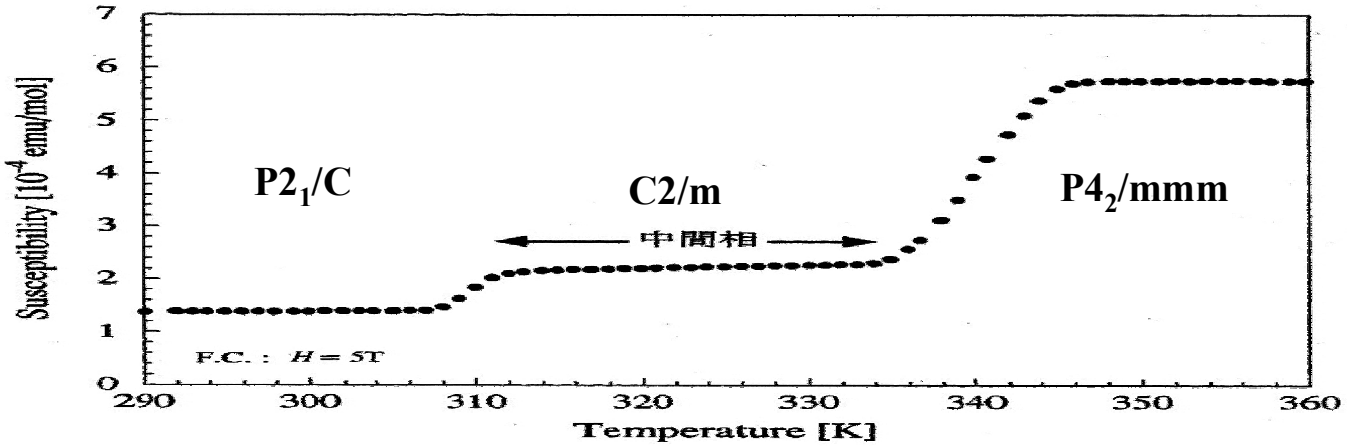


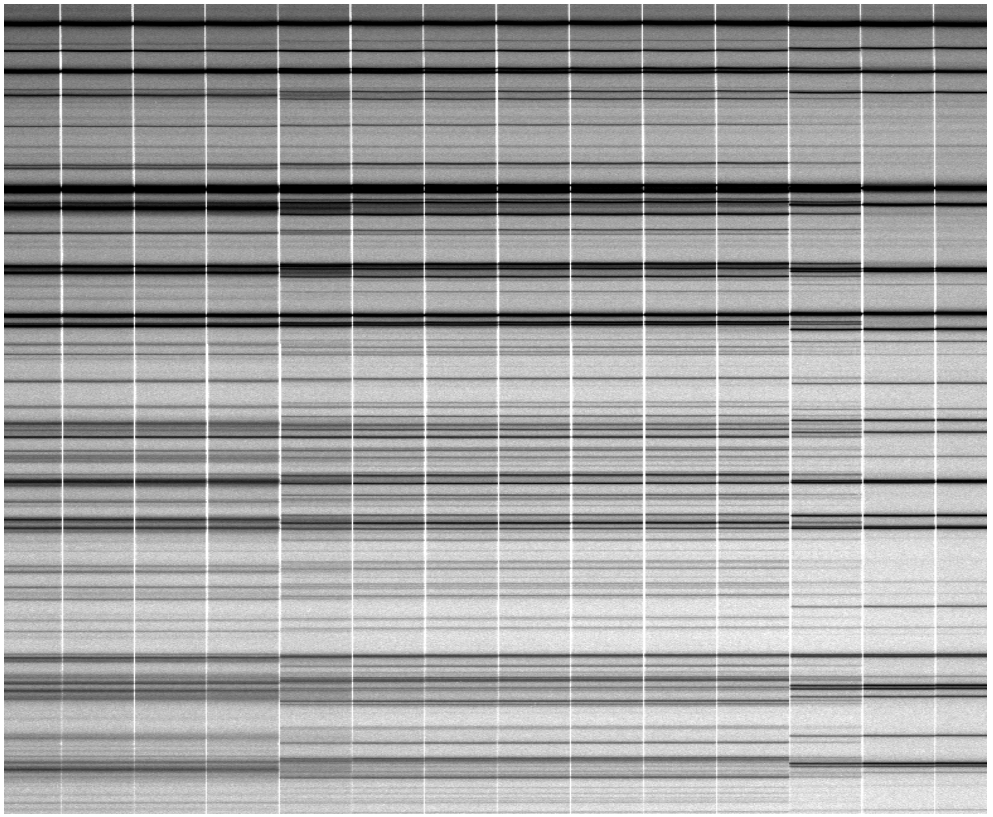


Stability of Temperature Control



Metal Insulator Phase transition of $V_xTi_{1-x}O_2$





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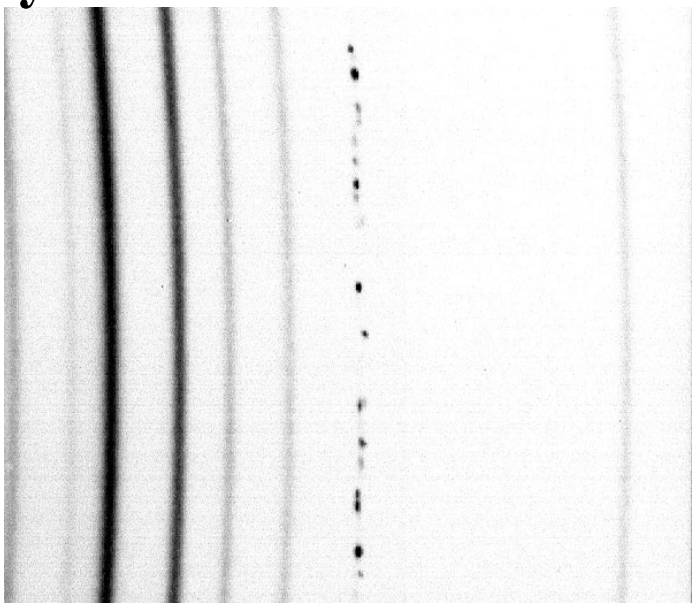
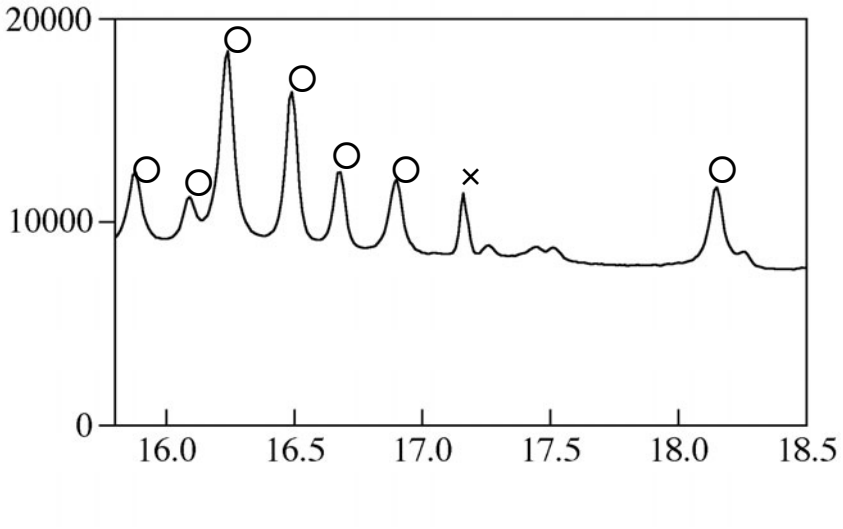
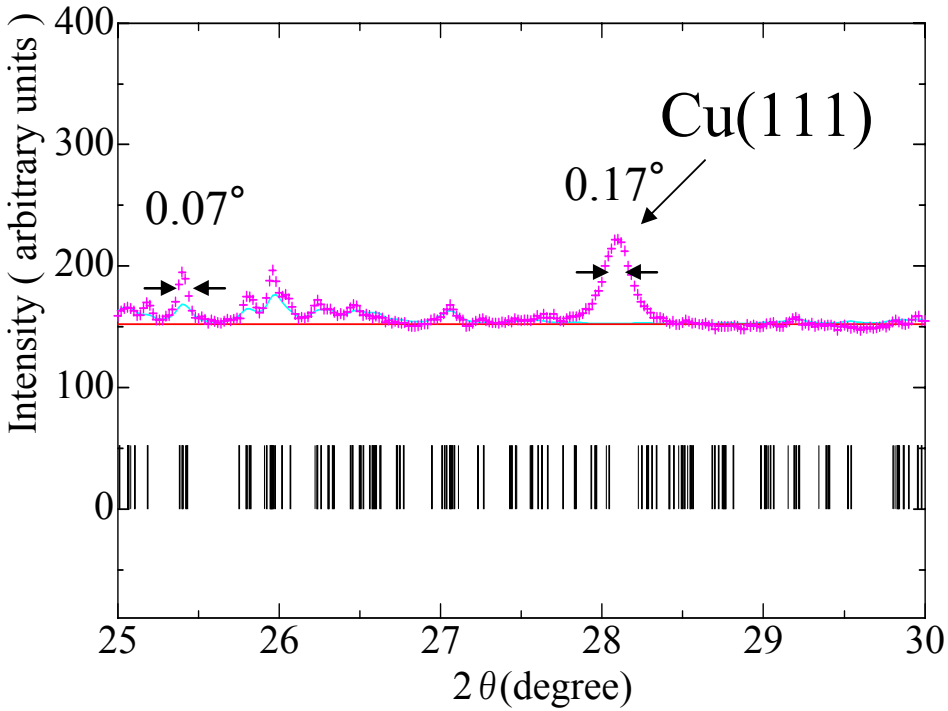
@BL02B2

Identification of Impurity Peak

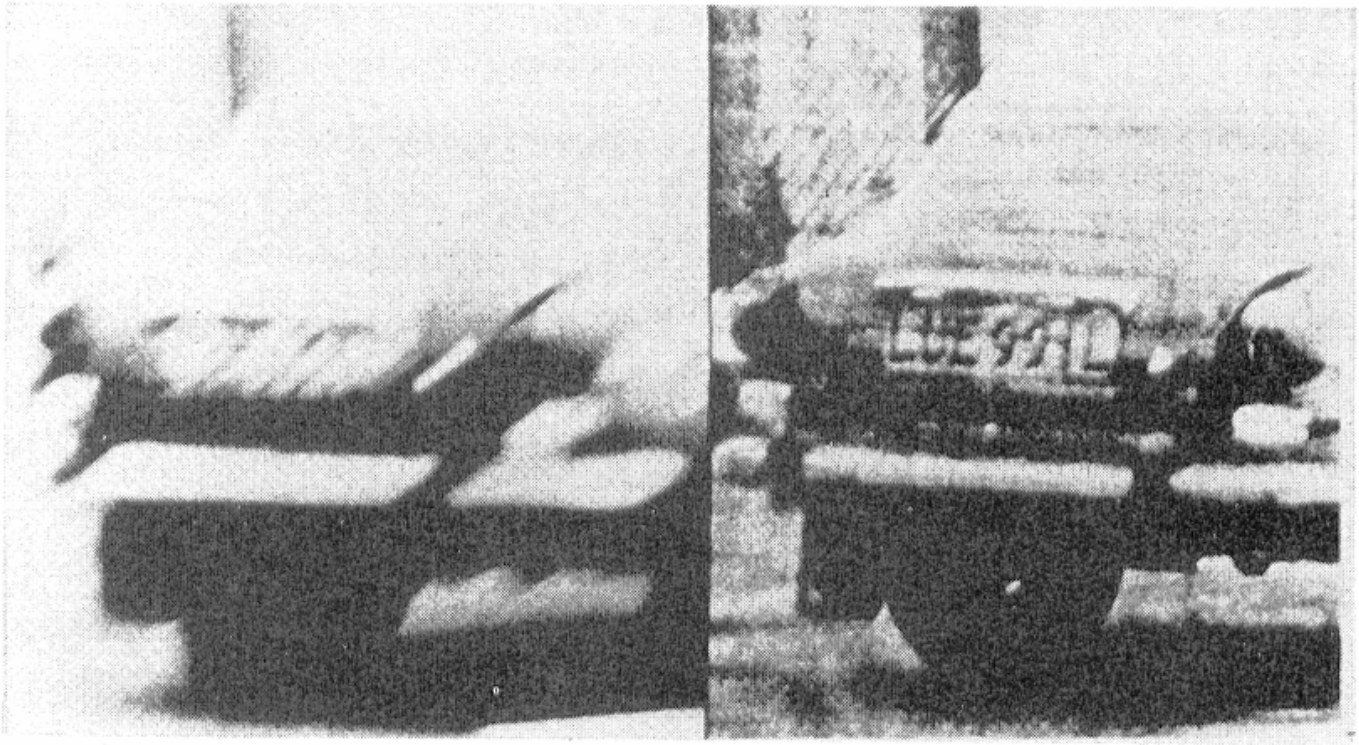
Debye Scherrer Pattern on IP







Reconstruction by MEM



Data Reconstruction

Fig. 1 The picture of a running car and the deconvoluted one by the Maximum Entropy Method. (quated from Silver et al.(1990)[8])

Fundamental Equation of X-ray Diffraction

Structure Factor

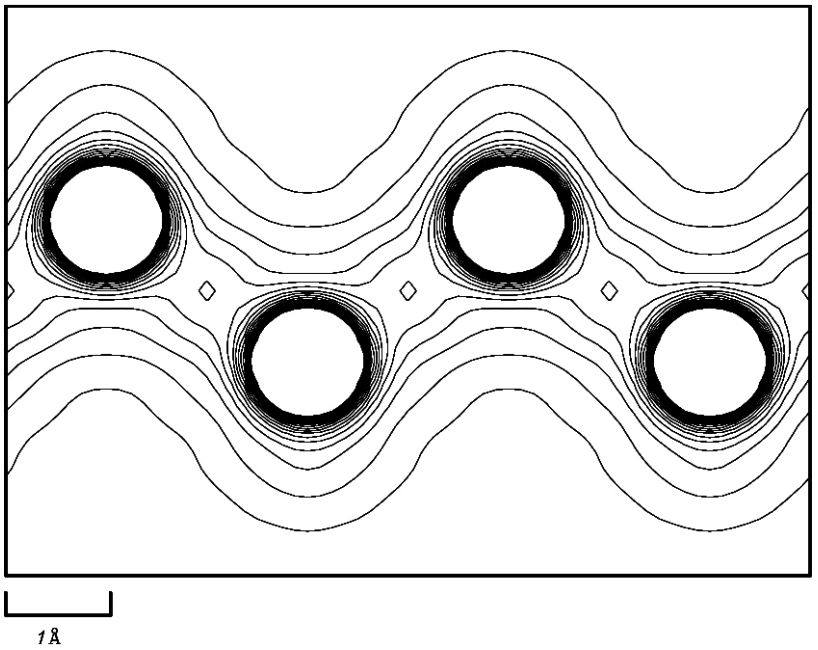
$$F(h) = \int_{UnitCell} \rho(r)\, e^{2\pi i h\cdot r}\, dv$$

Charge Density ρ(r)

$$\rho(r) = \int F(h) e^{-2\pi i h\cdot r}\, dh$$

$$= \frac{1}{v_c} \sum_{h} F(h) e^{-2\pi i h\cdot r}$$

Charge Densities of Silicon (110) Plane



MEM

Fourier synthesis

-2.0 ～2.0,0.1[e/Å^3] step

MEM Charge Density Analysis

X-ray Diffraction Data

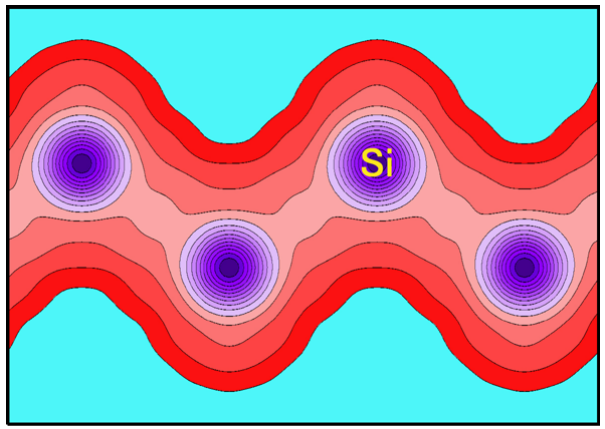
$h\ k\ l$	F_{obs}
0 0 0	112.000
1 1 1	-60.131(2)
2 2 0	-67.343(3)
1 1 3	-43.634(1)
4 0 0	-56.234(2)
...	...
6 6 4	19.126(1)

MEM

$$S = -\rho(r) \ln \frac{\rho(r)}{\tau(r)} - \lambda(C-1)$$

$$C = \frac{1}{N} \sum_{n} \frac{\left| F_{cal}(k) - F_{obs}(k) \right|^2}{\sigma^2(k)}$$

Charge Density



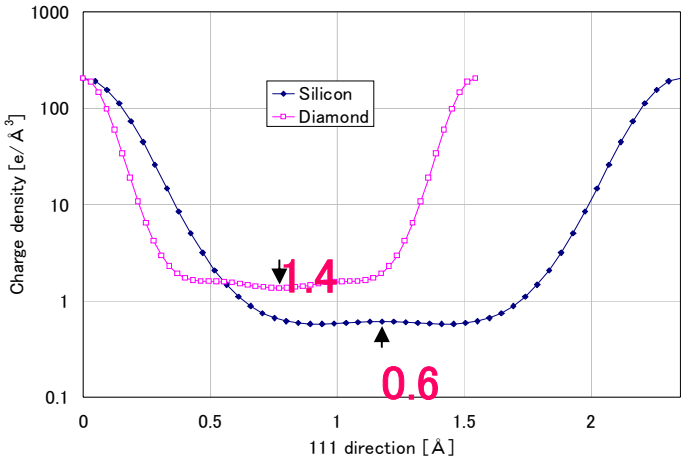
$$F_{cal}(k) = \sum_{r} \rho(r) \exp[2\pi i k r]$$

$$\rho(r) = \sum_{k} F(k) \exp[-2\pi i k r]$$

Electron densities at bond midpoint

Si

Reference	Density[e/Å^3]
Spackman (1986)	0.617(6)
Yang & Coppens (1974)	0.69
Yin & Cohen (1983)	0.565
Yin & Cohen (1982)	0.59
Wang & Klein (1981)	0.58
Kenton & Ribarsky (1981)	0.50
Zunger (1980)	0.60
Hamann (1979)	0.55
Chelikowsky & Cohen (1974)	0.65
MEM density (R.T.)	**0.6**



Diamond

Reference	Density[e/Å^3]
Spackman (1991)	1.57(6)
Orlando, et al. (1990)	1.96
Rodriguez, et al. (1987)	1.61
van Camp, et al. (1986)	1.53
Denteneer & van Haeringen (1985)	1.54
Jones & Lewis (1984)	1.54
MEM density (R.T.)	**1.4**

Applications

Orbital Order of Manganites

A-type: $NdSr_2Mn_2O_7$

CE-type: $Nd_{0.5}Sr_{0.5}MnO_3$

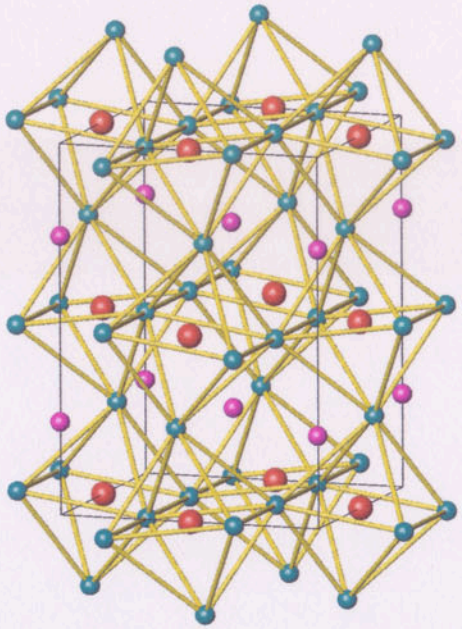
C-type: $Nd_{0.35}Sr_{0.65}MnO_3$

If time is allowed,

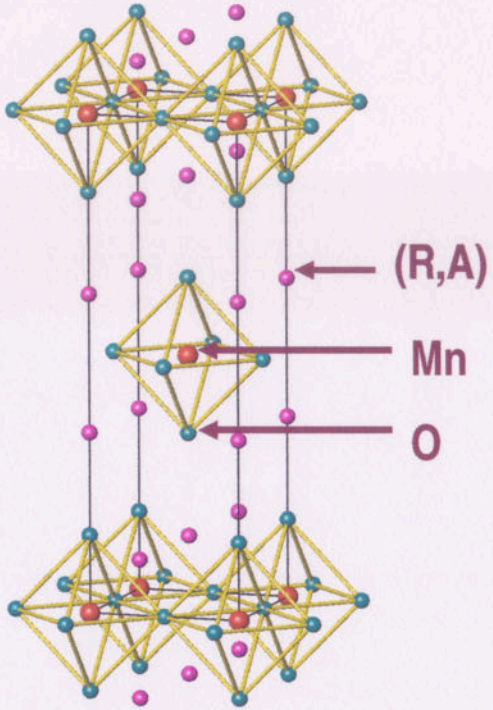
- Fullerene compounds
- VO_2 system

Perovskite-type Manganite : $(R,A)_{1+n}Mn_nO_{3n+1}$

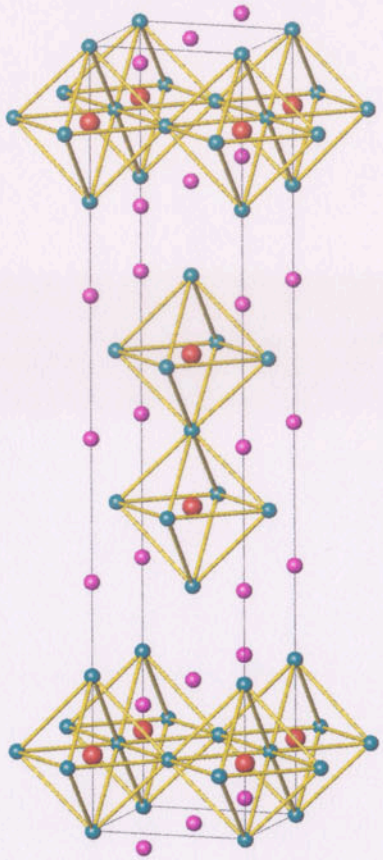
n=∞



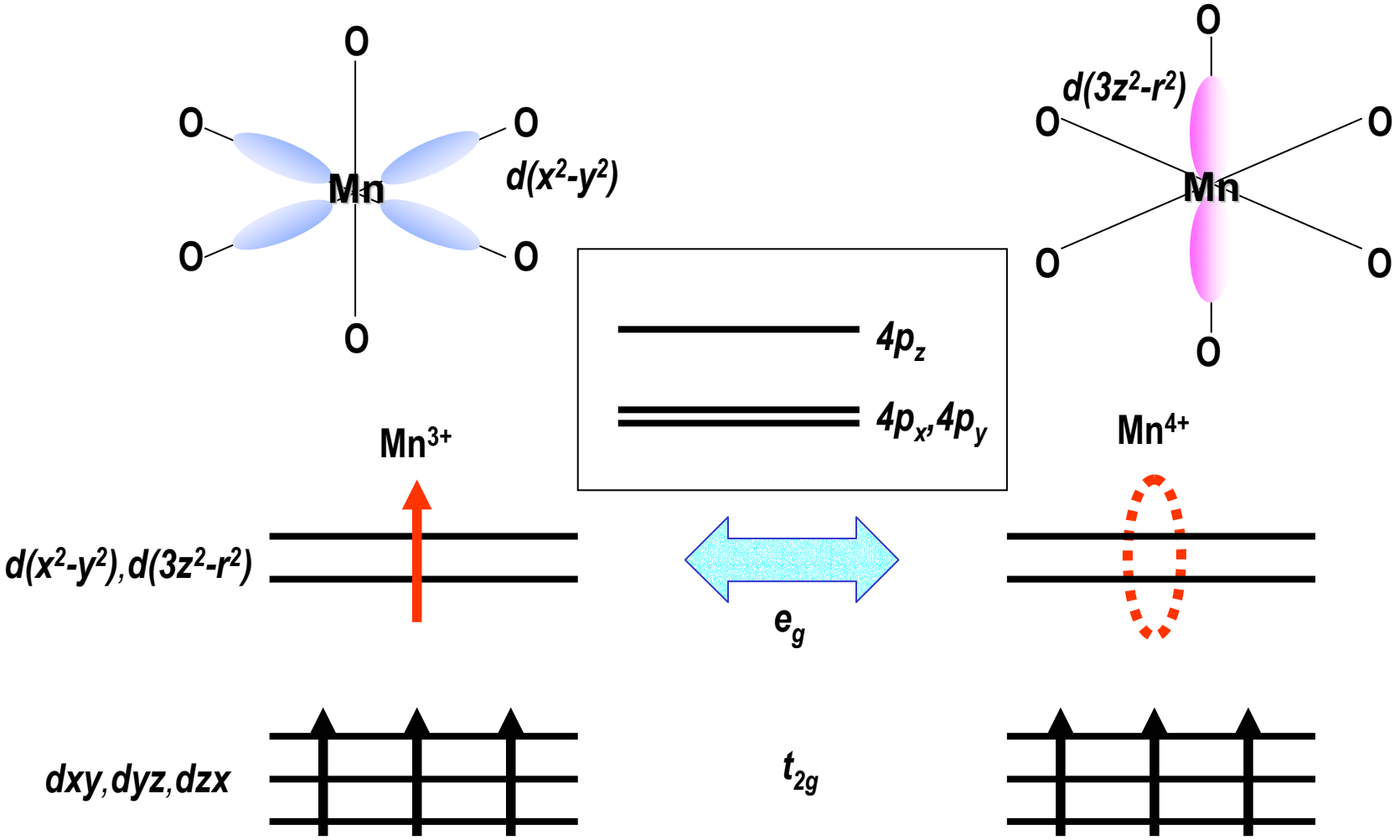
n=1



n=2

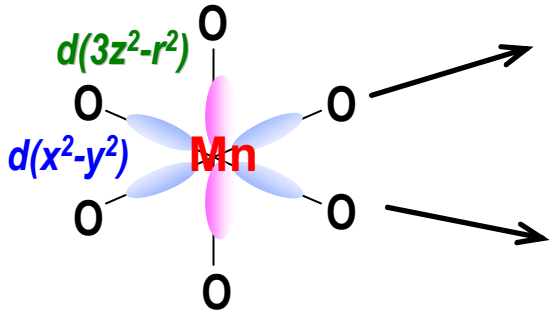


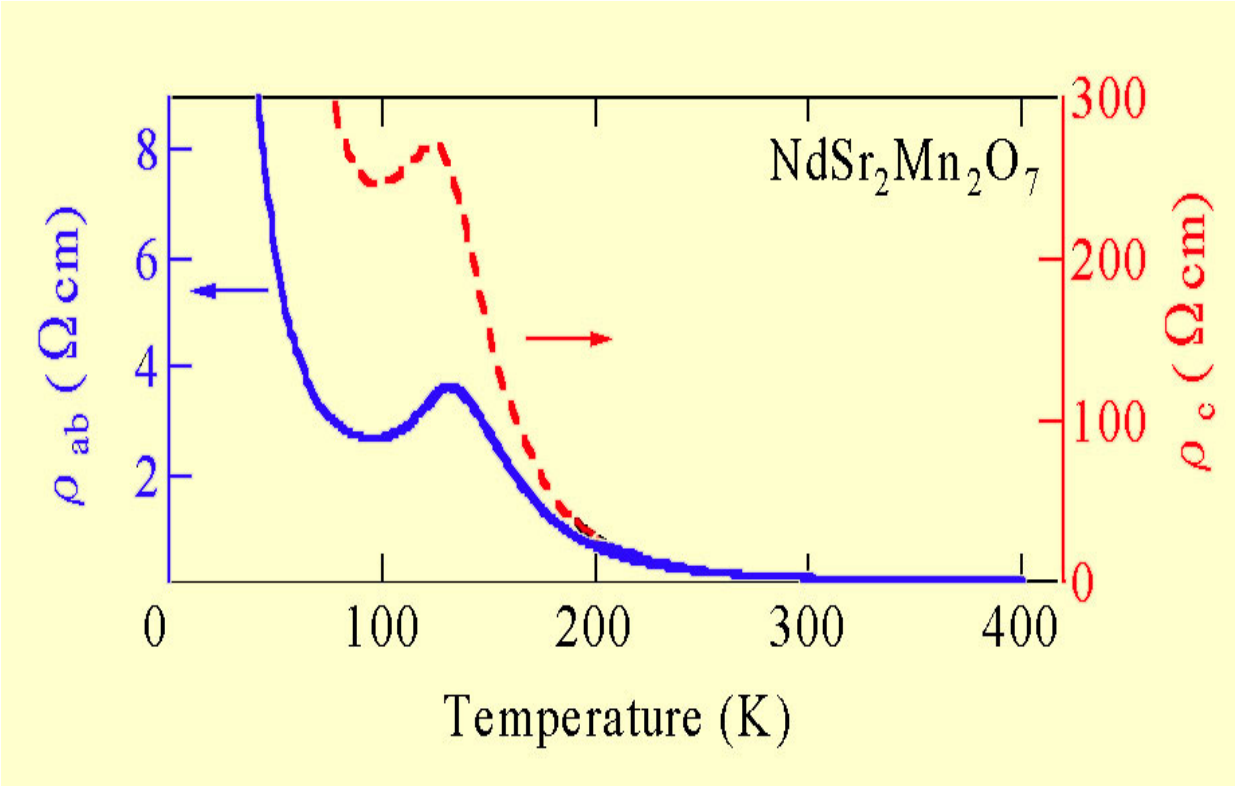
The Double Exchange Model



Direct Observation of Orbital Order of Manganites

To reveal a structure-property relationship





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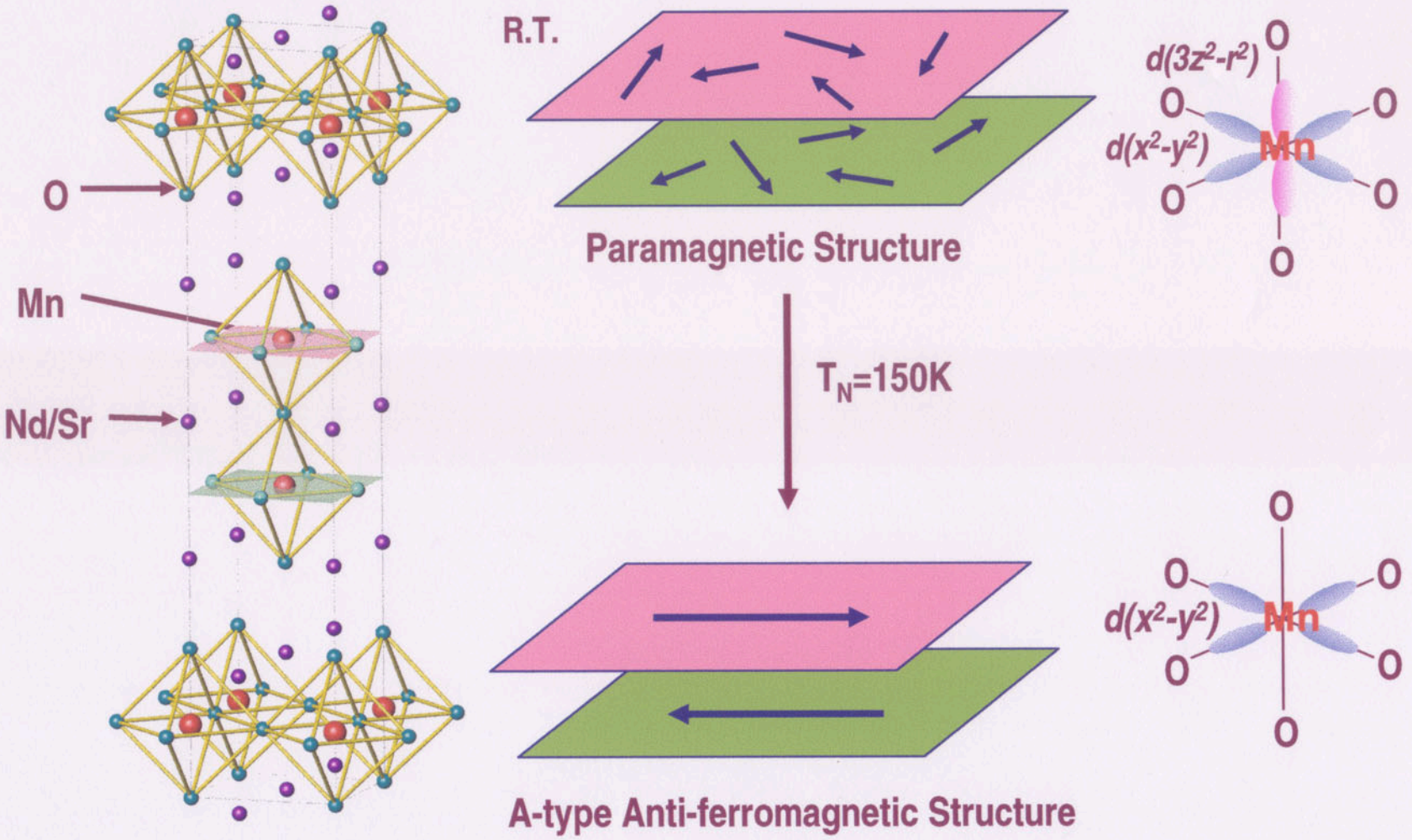
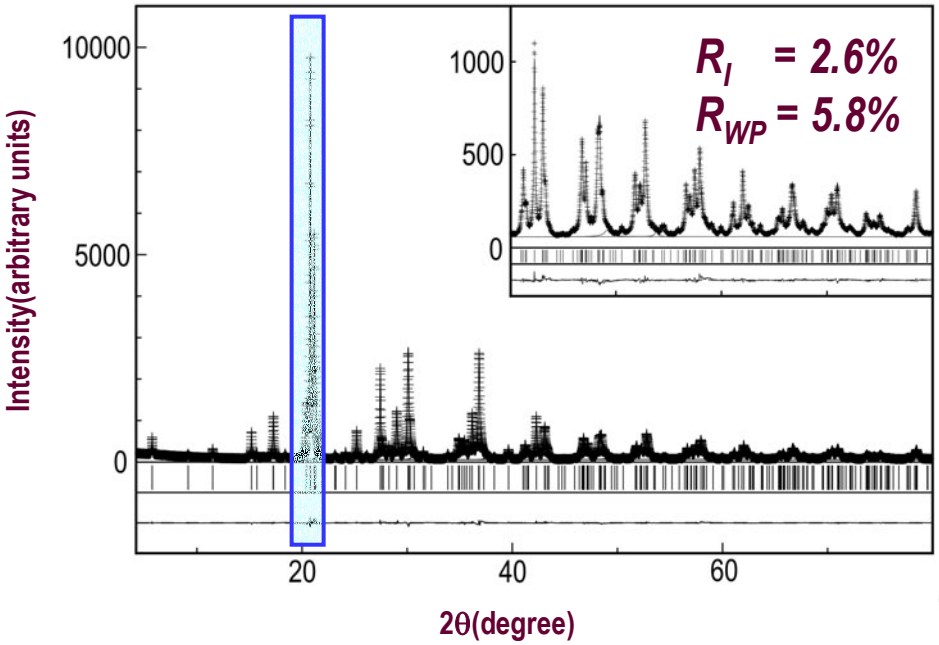
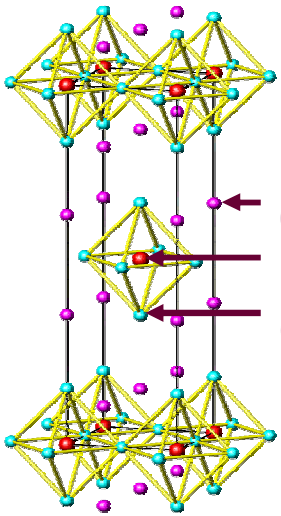
The Crystal and Magnetic Structure of $NdSr_2Mn_2O_7$

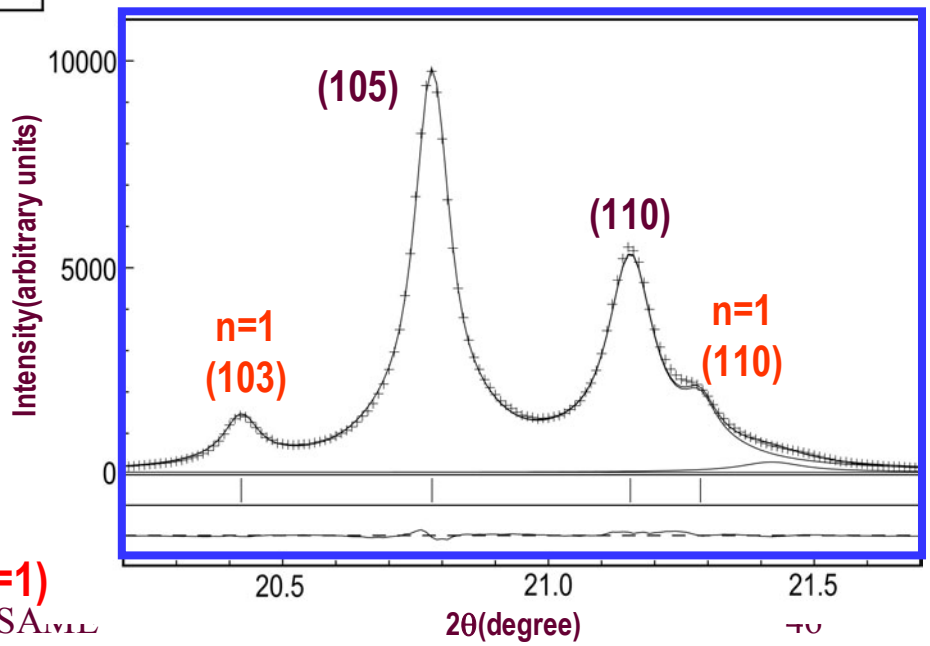


The Rietveld Fitting Result of $NdSr_2Mn_2O_7$ at R.T.

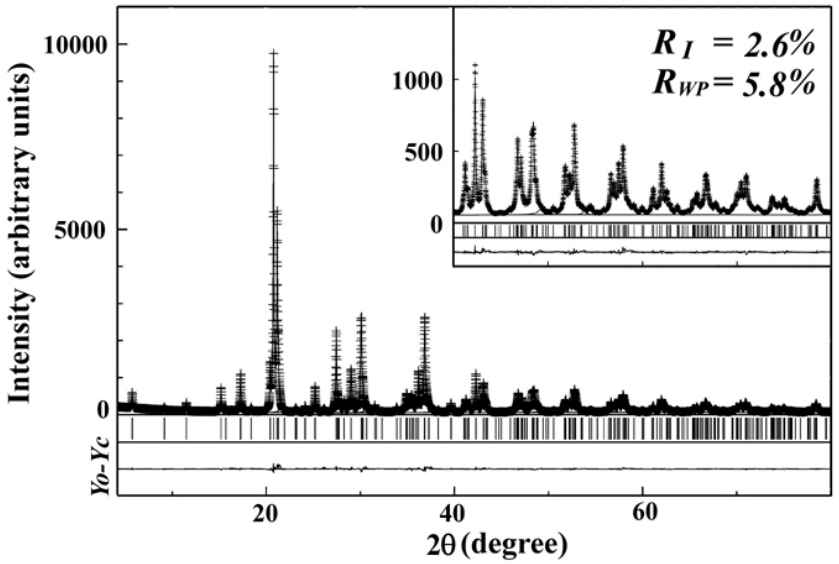




$NdSrMnO_4$(n=1)

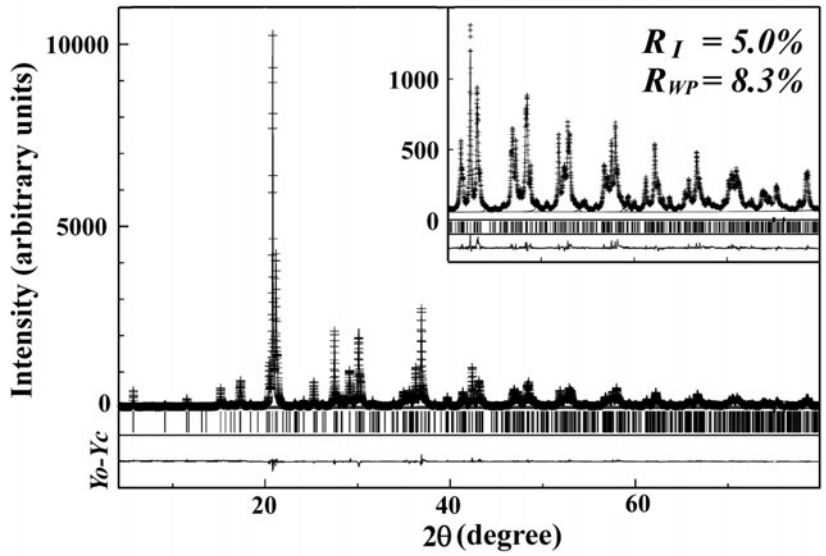


The Rietveld Fitting Result of $NdSr_2Mn_2O_7$



R.T.

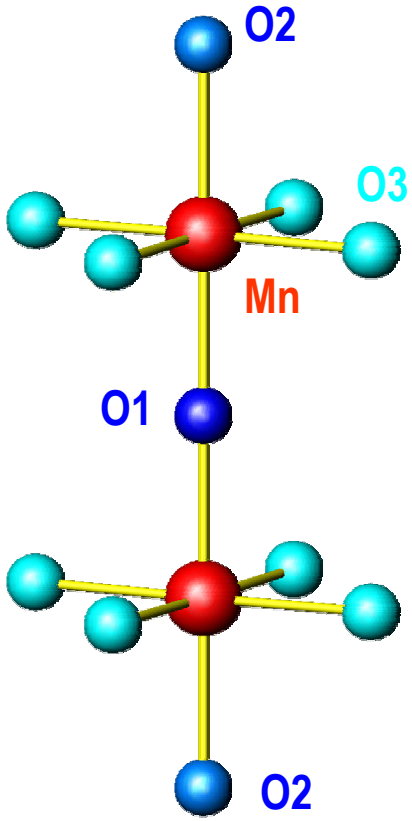
19K



SES

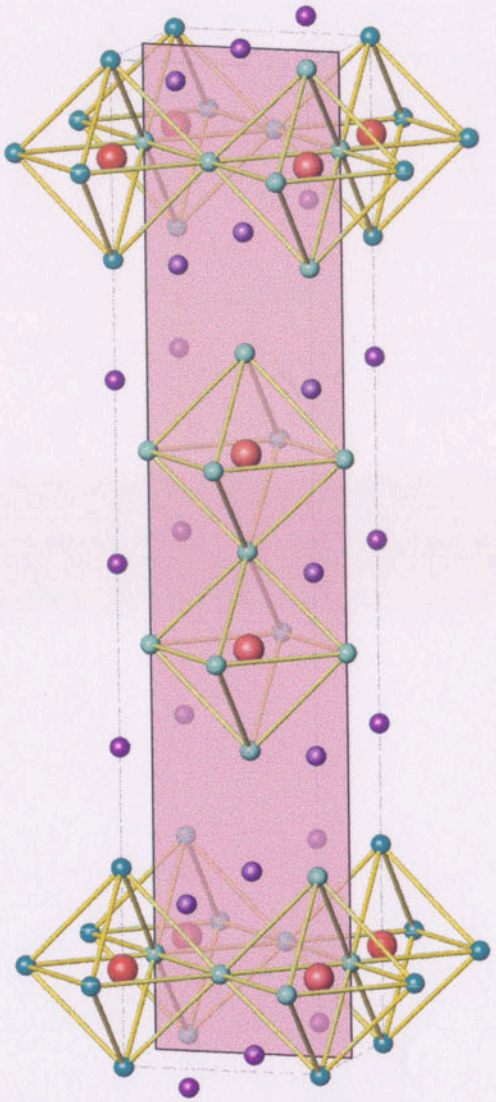
Structure Parameters of $NdSr_2Mn_2O_7$ from Rietveld Analysis

I4/mmm		*R.T.*	*19K*
Lattice Parameters(Å)	*a*	3.85029(6)	3.85015(7)
	c	19.9540(3)	19.8867(4)
Bond Lengths(Å)	*Mn-O1*	1.934(1)	1.928(1)
	Mn-O2	2.009(4)	1.968(4)
	Mn-O3	1.925181(7)	1.925086(5)

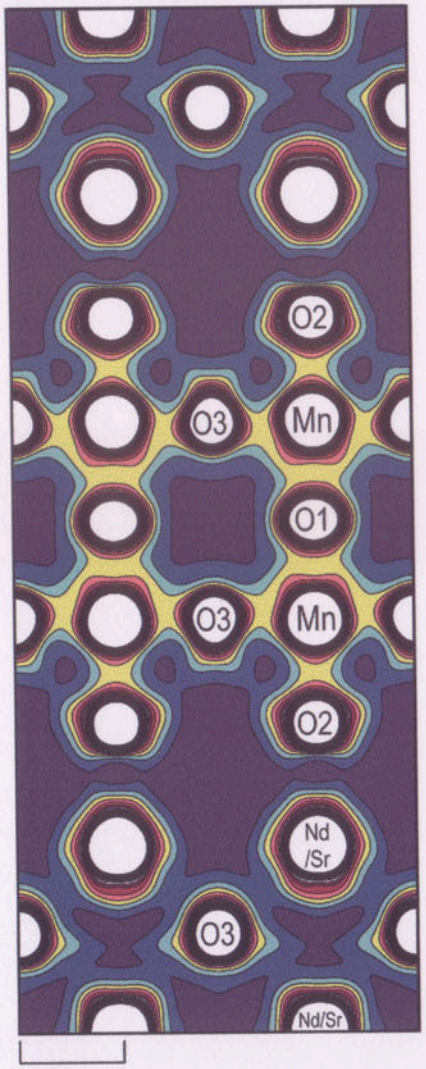


The MEM Charge Densities of $NdSr_2Mn_2O_7$ for (200) Plane

0.0~4.0[e Å^{-3}],step:0.2 [e Å^{-3}]

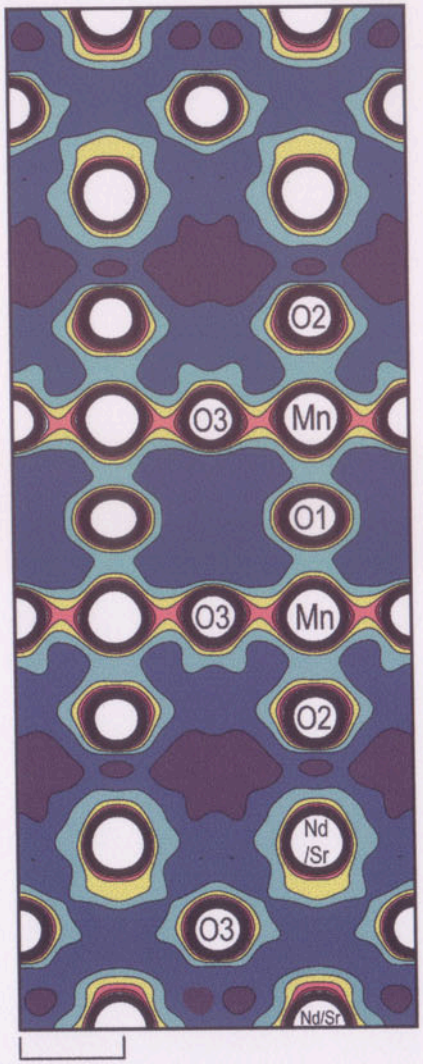


[R.T.]



[001]Axis

[19K]

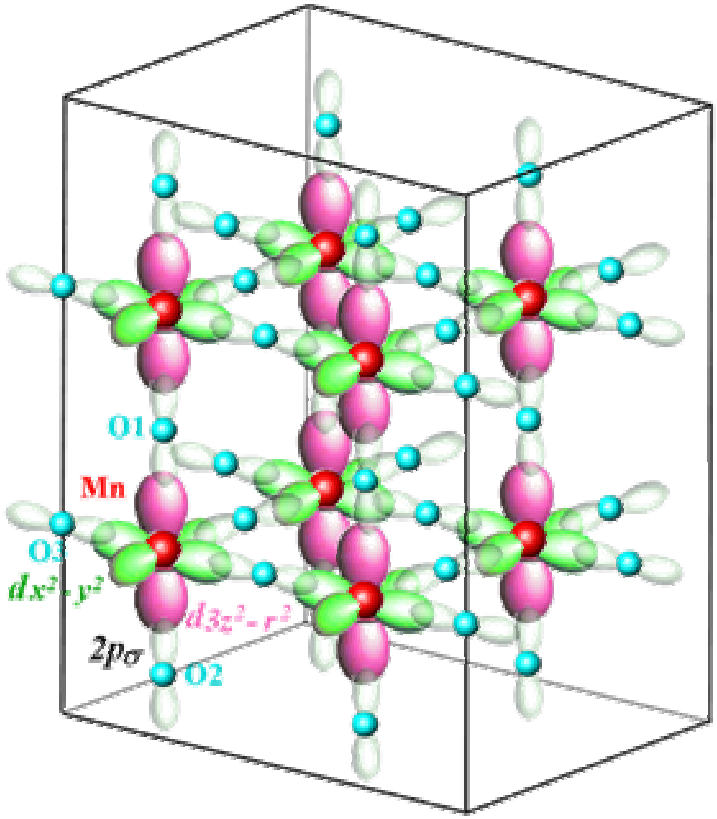


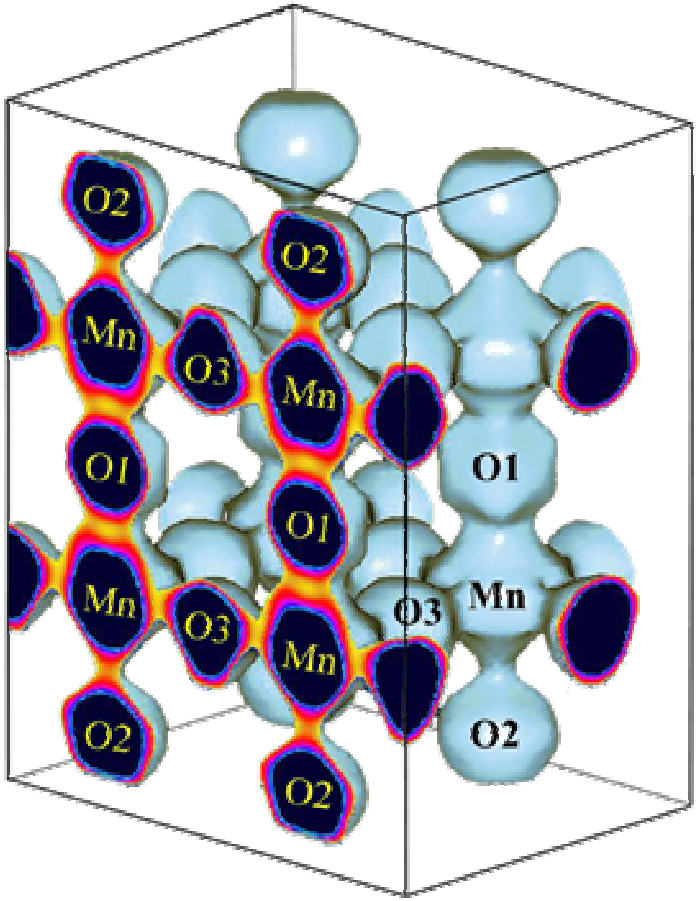
2Å

SESAME

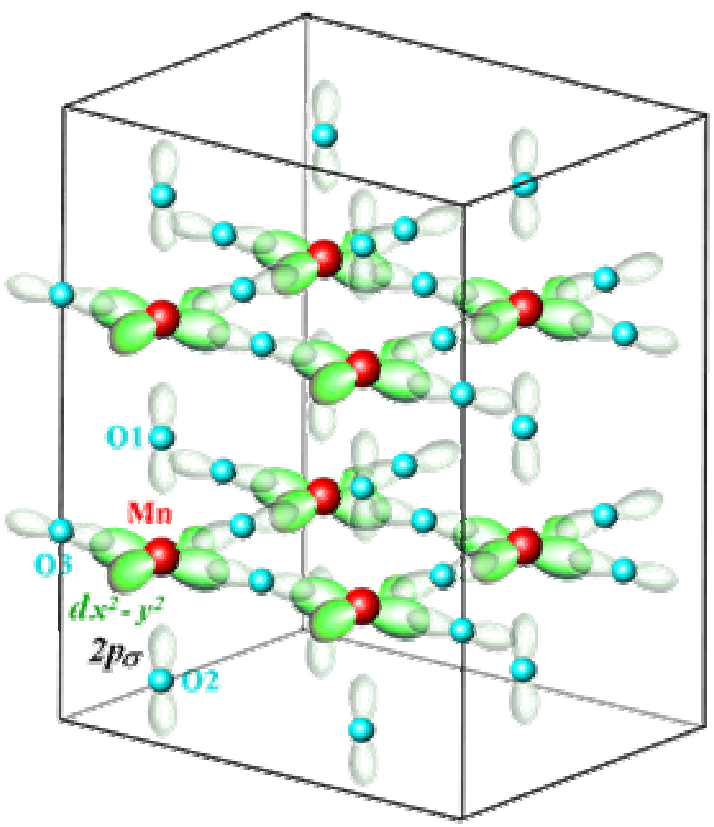
2Å

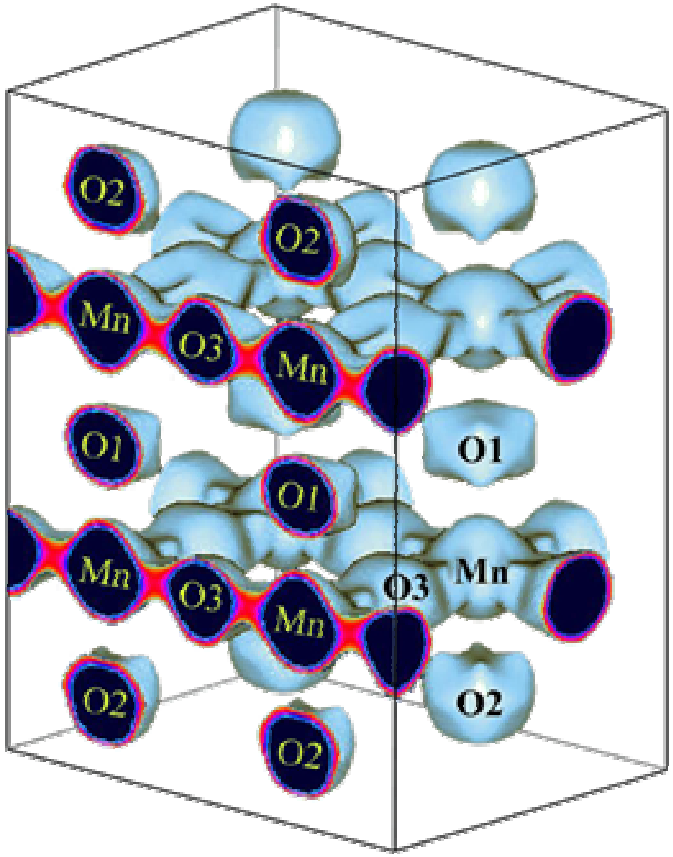
The Equi-contour(*0.6eÅ^{-3}*) Density Map of the MEM Charge Densities of $NdSr_2Mn_2O_7$ at R.T.





The Equi-contour(*0.6e Å*$^{-3}$) Density Map of the MEM Charge Densities of $NdSr_2Mn_2O_7$ at 19K





Direct Observation of Orbital Ordering

Synchrotron Radiation Powder Data

MEM / Rietveld