Early Development of Dispersive X-Ray Absorption Spectrometer and Recent Extension of Dispersive Optics to Quick X-ray Reflectometery

T. Matsushita, Photon Factory – KEK

Tsukuba, Ibaraki, Japan

outline

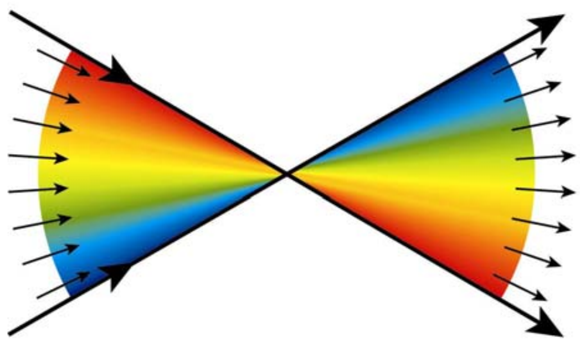
- ○ laboratory dispersive XAS using a Laue-case flat crystal polychromator
  (1978 – 1979)
- ○ dispersive XAS on a synchrotron beamline at Stanford (1980)
  X-ray film (1980 - 1982)
  photodiode array (1981-1982)
- ○ stopped-flow experiment at the Photon Factory (1983 -1986)

- ○ X-ray Reflectometry in dispersive geometry (2006 – present)
  curved crystal polychromator
  laterally graded multilayer on an elliptic substrate

The first idea of the dispersive geometry

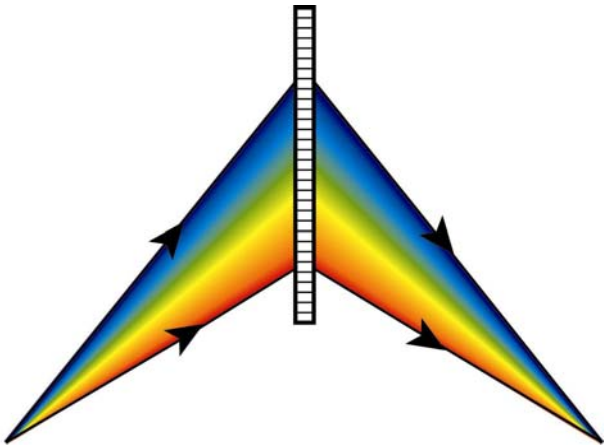
In 1978, a small workshop was held in Osaka on an EXAFS spectrometer to be constructed at the Photon Factory which started construction at that time. A professor of Tohoku university commented about the necessity of a quick EXAFS spectrometer for time-resolved study of reacting objects.

Immediately in the conference room



No mechanical movement during the measurement

On the train back to Tokyo



Focalization by a Laue-case single crystal

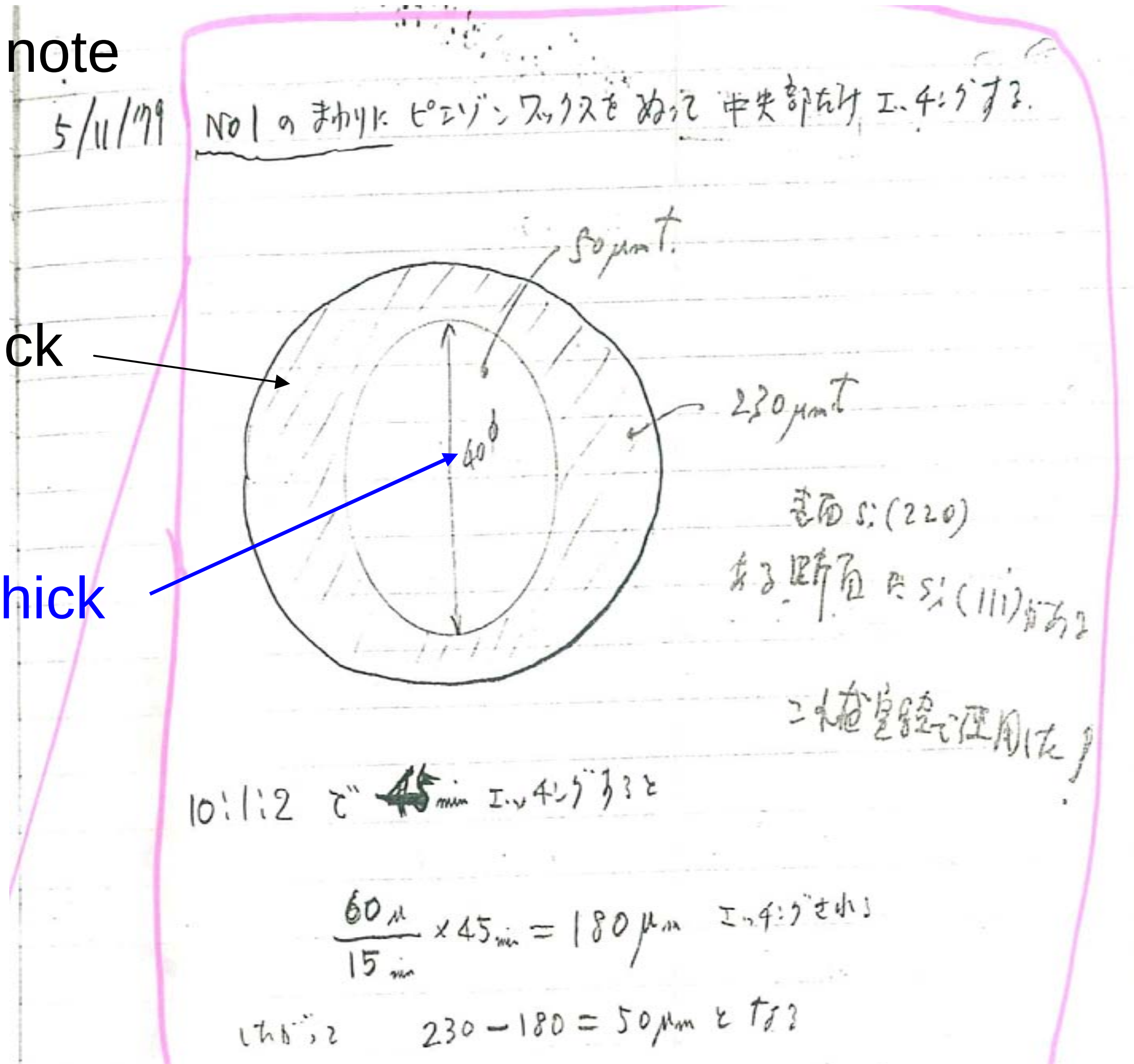
Preparation of a thin crystal

From Kaminaga's note

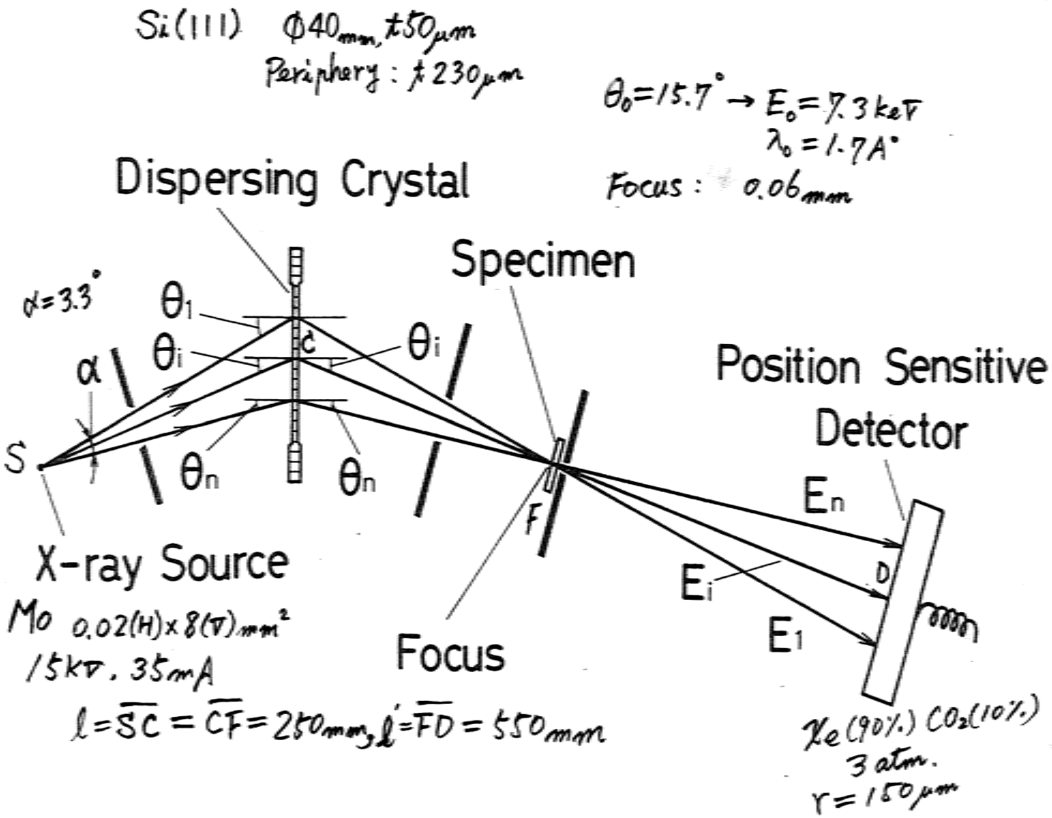
May 11, 1979

230 μm thick

50 μm thick



Dispersive X-ray absorption spectrometer - Laue-case single crystal polychromator and Laboratory X-ray source -



Energy range

$$E_n - E_1 = E_0 \alpha \cot\theta_{B0} = 1.5\ \mathrm{keV}$$

$$\left(\begin{array}{l} E_0 = 7.3\ \mathrm{keV} \\ \alpha = 3.3^\circ \\ \theta_{B0} = 15.7^\circ \end{array} \right)$$

Energy resolution

$$\frac{\Delta E}{E_0} = \sqrt{\left(\frac{S}{l}\right)^2 + \left(\frac{W}{l}\right)^2 + \left(\frac{r}{l'}\right)^2 + \omega^2 + \frac{\phi^4}{4}\tan^2\theta_{B0}} \cdot \cot\theta_{B0}$$

$$\left(\begin{array}{ll} S \equiv 0.03\ \mathrm{mm} & \theta_{B0} = 15.7^\circ \\ l = 250\ \mathrm{mm} & r = 0.150\ \mathrm{mm} \\ l' = 550\ \mathrm{mm} & E_0 = 7.3\ \mathrm{keV} \\ t = 0.05\ \mathrm{mm} & W = 2t\sin\theta_{B0} \\ \omega = 7'' & \\ \phi = 0.72^\circ & \end{array} \right)$$

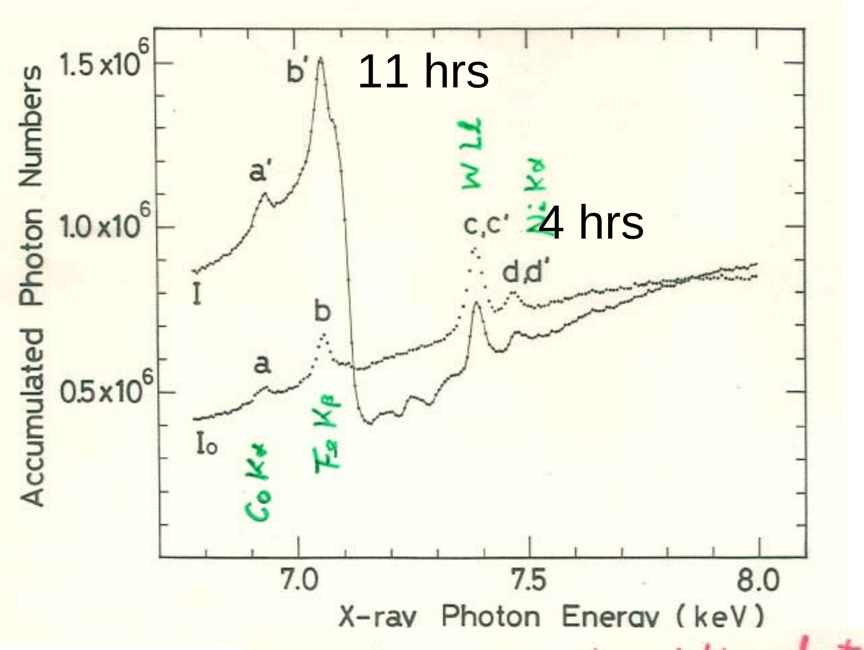
$$\frac{\Delta E}{E_0} = 1.14 \times 10^{-3} \rightarrow \Delta E = 8.3\ \mathrm{eV}$$

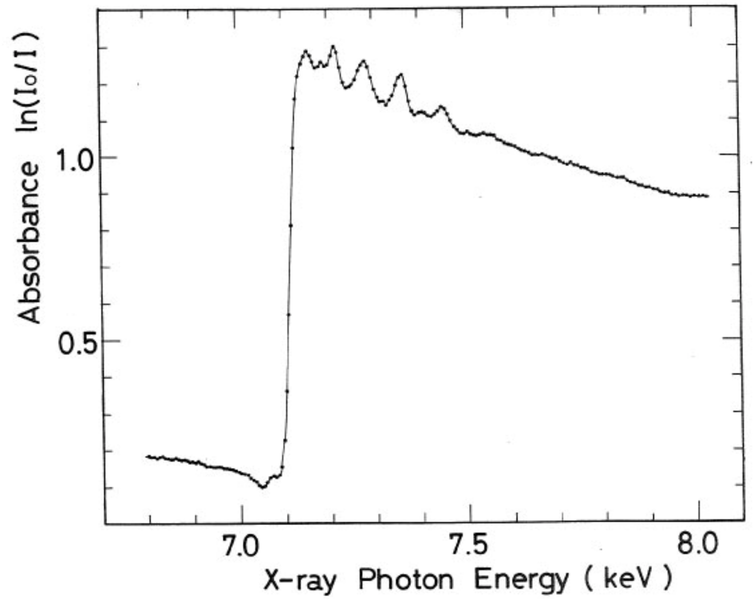
Energy vs position

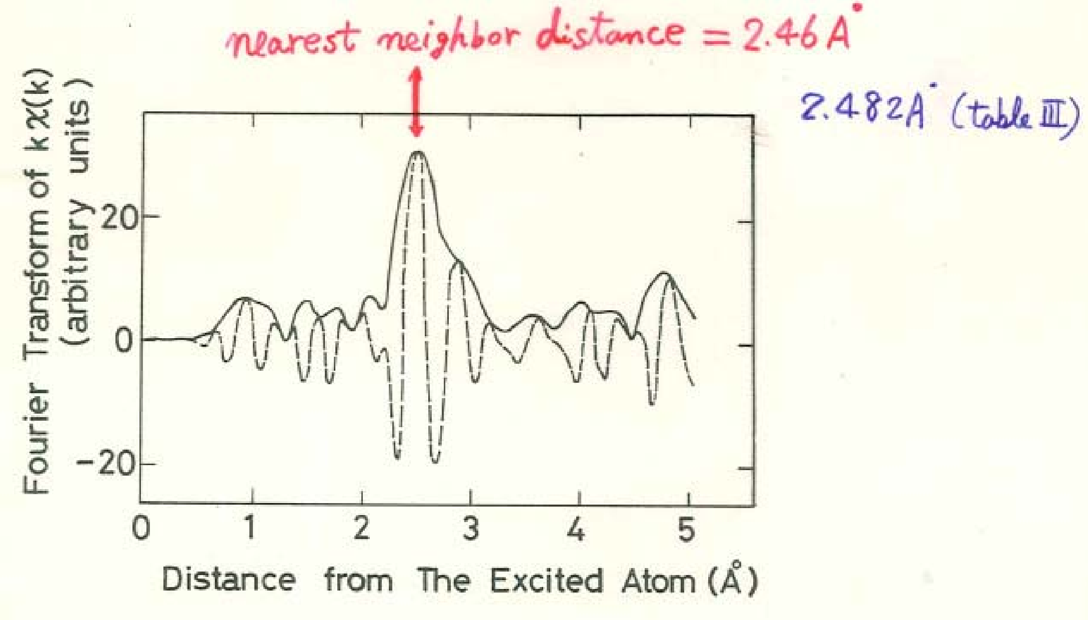
$$x - x_0 = l' \tan(\theta - \theta_{B0})$$

$$\therefore E = \frac{\lambda}{2d\sin\{\theta_{B0} + \tan^{-1}(\frac{x - x_0}{l'})\}}$$

Fe foil K edge and EXAFS





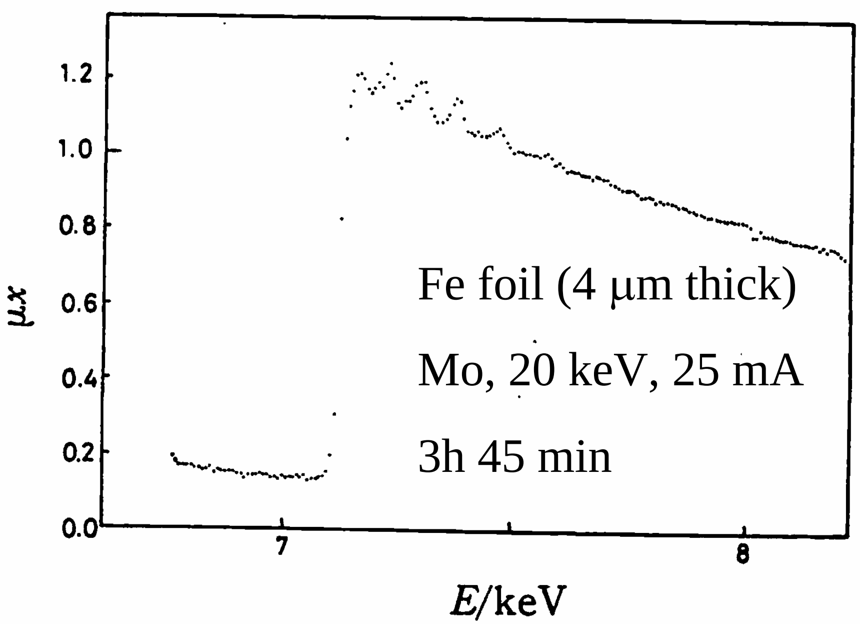


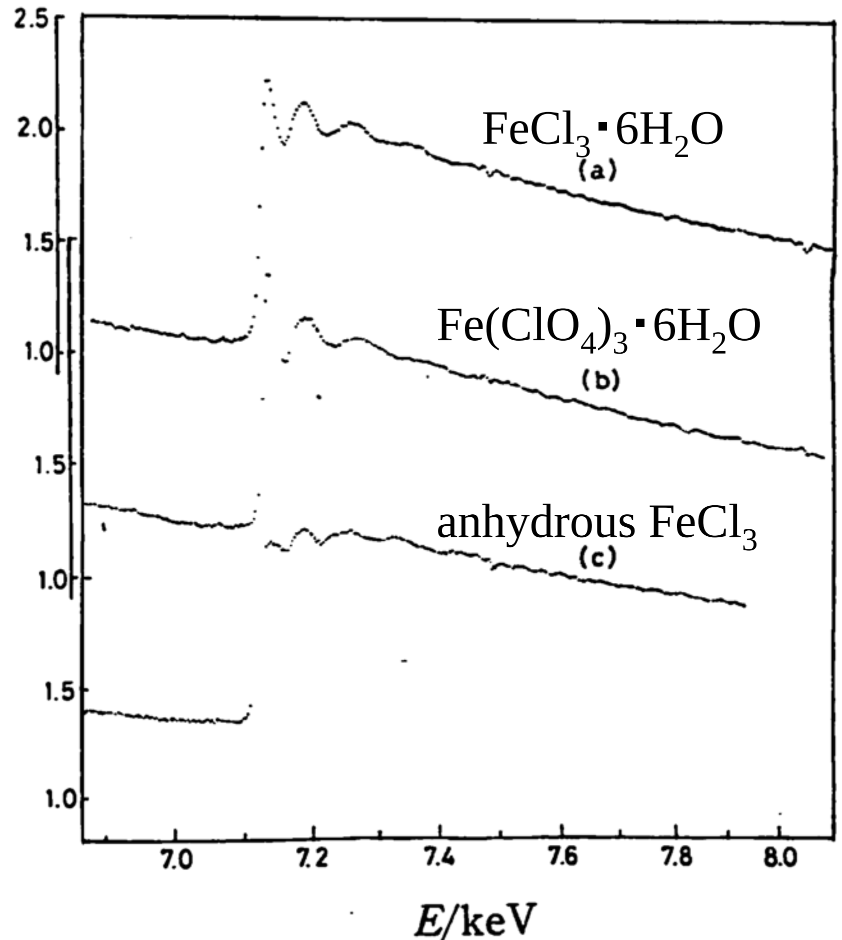
Application to the study of some Iron(III) compounds

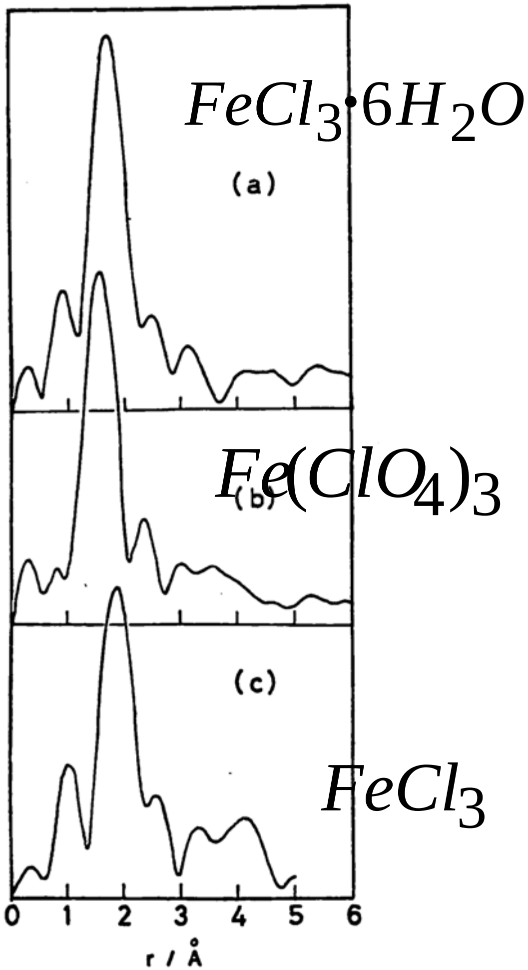
M. Nomura et. al., Bull. Chem. Soc. Jpn., **55**, 3911-3914 (1982)

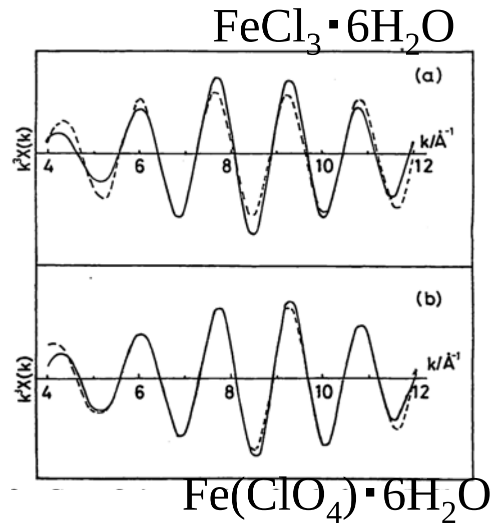
$FeCl_3 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$, anhydrous $FeCl_3$

system improvement









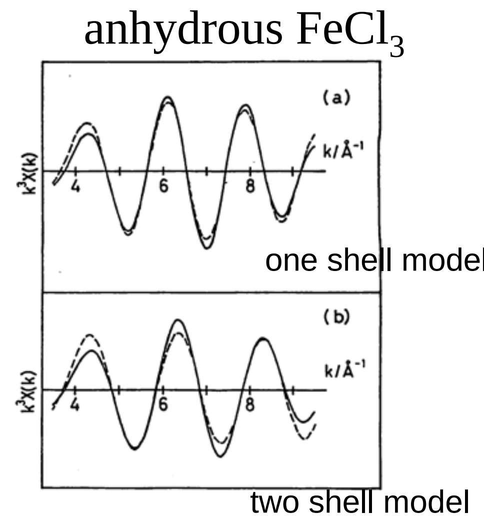


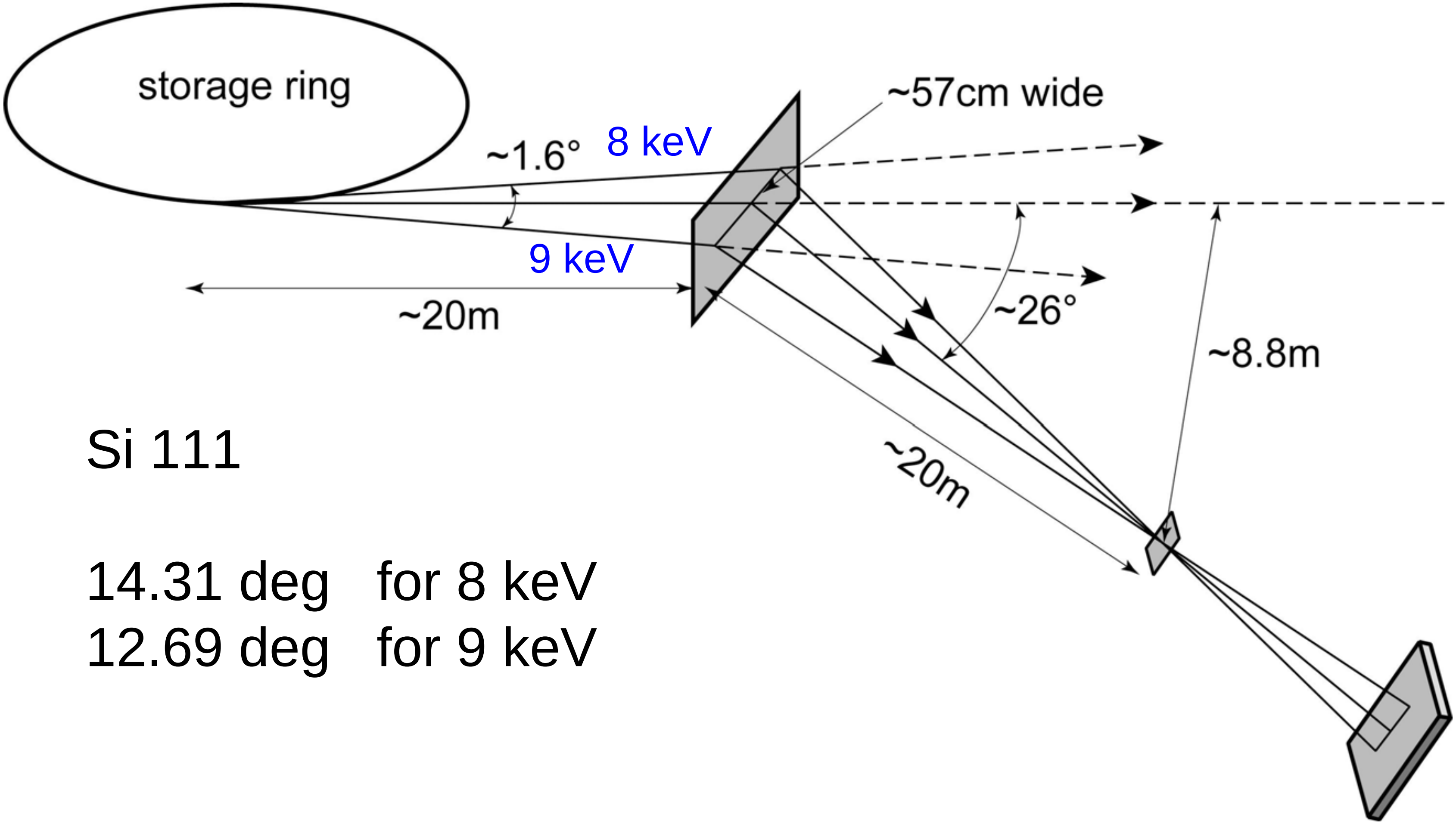
TABLE 1. BOND DISTANCES OBTAINED BY THE ANALYSES OF EXAFS DATA OF Fe(III) COMPOUNDS

The coordination numbers assumed in the analyses are given in parentheses.

Sample		Bond	Bond length d/Å (EXAFS)	(diffraction)
$FeCl_3 \cdot 6H_2O$		Fe–Cl(2)	2.28	2.30[a]
		Fe–O(4)	2.03	2.07[a]
$Fe(ClO_4)_3 \cdot 6H_2O$		Fe–O(6)	2.00	—
$(Fe(NO_3)_3 \cdot 9H_2O$		Fe–O	—	1.99[b]
$FeCl_3$	(Model 1)[d]	Fe–Cl(6)	2.25	2.48[c]
	(Model 2)[e]	Fe–Cl(3)	2.24	
		Fe–Cl(3)	2.59	

a) From Ref. 15. b) Average of six Fe–O bond lengths, from Ref. 16. c) From Ref. 17b. d) Octahedrally coordinated model (BiI_3-like structure). e) AsI_3-like structure.

From July, 1979 to June, 1980 Matsushita stayed at SSRL. He first simply wanted to extend the Laue-case flat crystal system on synchrotron beamline. But , it was practically impossible.



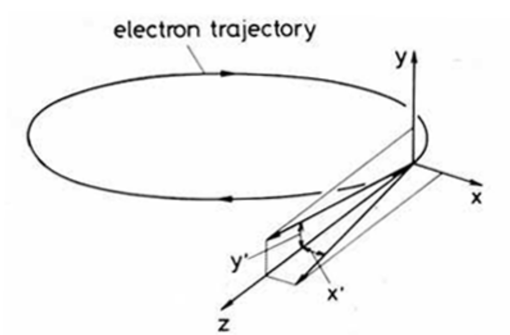
Si 111

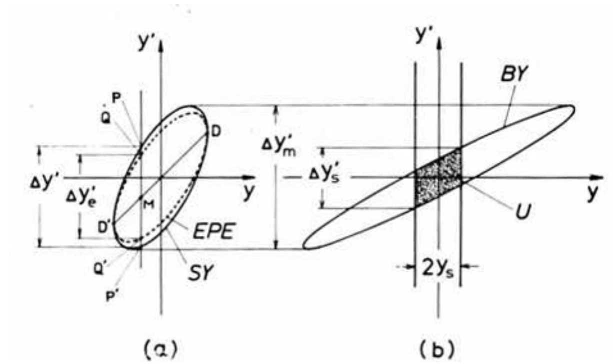
14.31 deg for 8 keV
12.69 deg for 9 keV

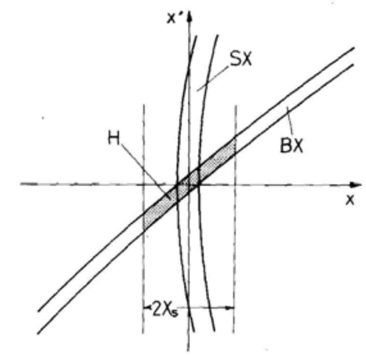
Graphical method for describing X-ray optics

Phase space optics

- crystal monochromator in the position-angle space -



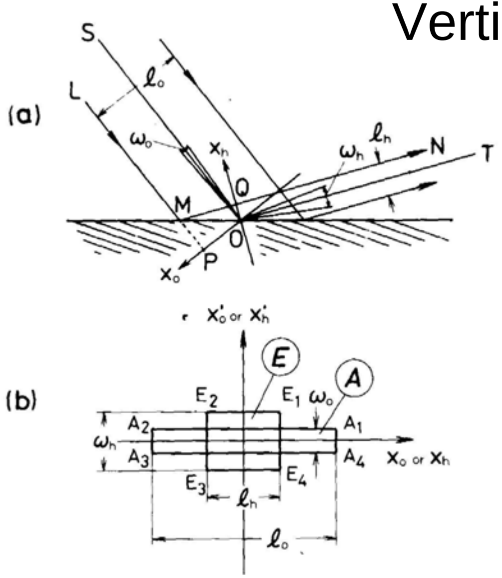




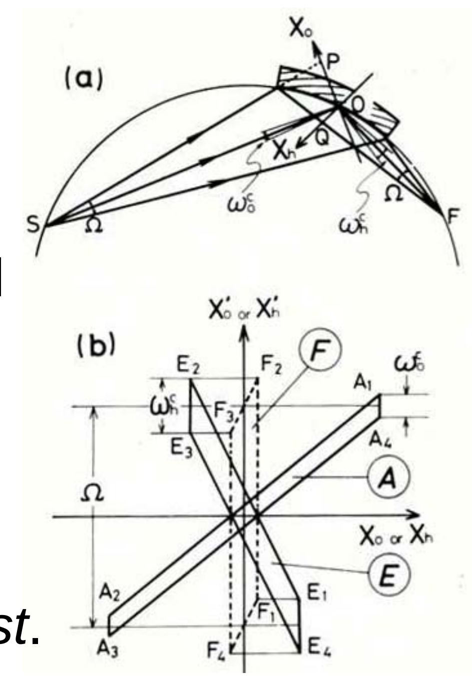
Horizontal plane

Vertical plane

Flat crystal



Curved crystal



T. Matsushita and U. Kaminaga, *J. Appl. Cryst*. 13 465-471 (1980), *ibid* 13, 472-478 (1980).

Graphical method of describing X-ray optics

Combining the phase space picture with the DuMond diagram

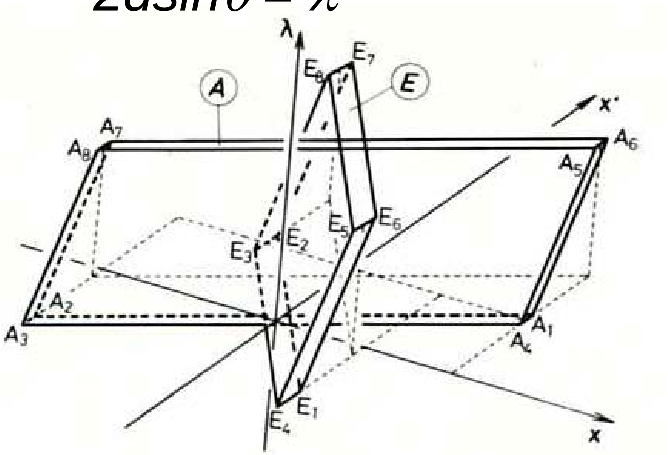
Phase space:

position-angle space

DuMond diagram:

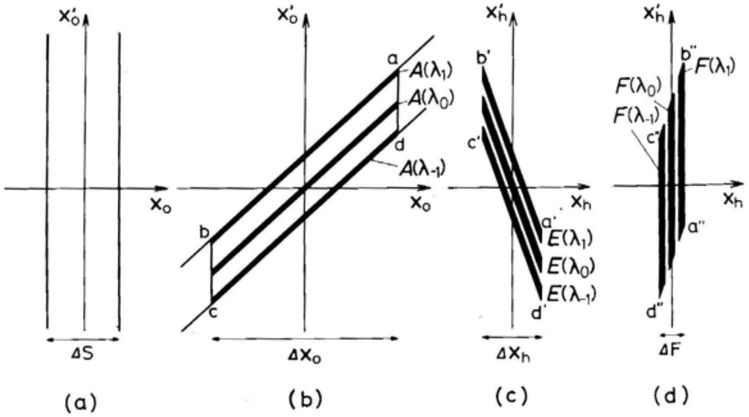
angle-wavelength space

$2d\sin\theta = \lambda$

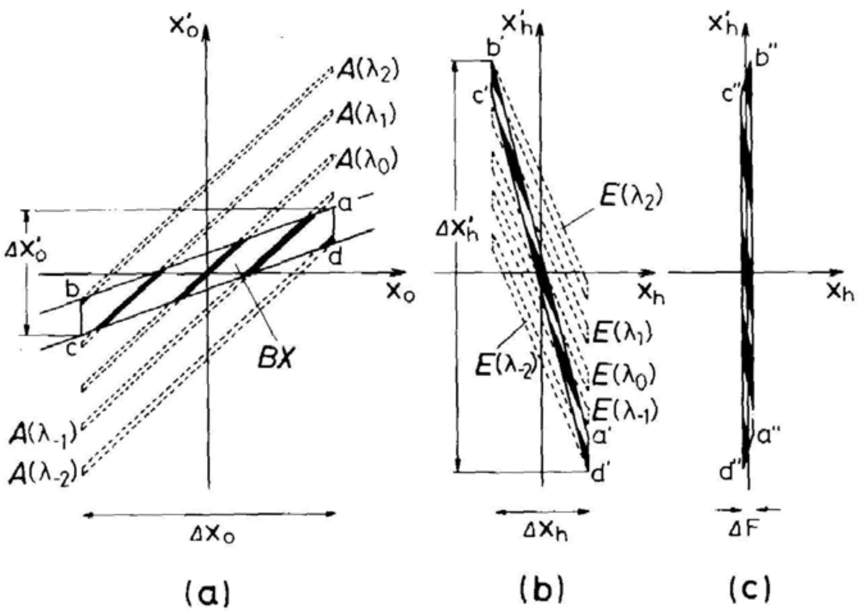


position-angle-wavelength space

source on the Rowland circle



source outside the Rowland circle

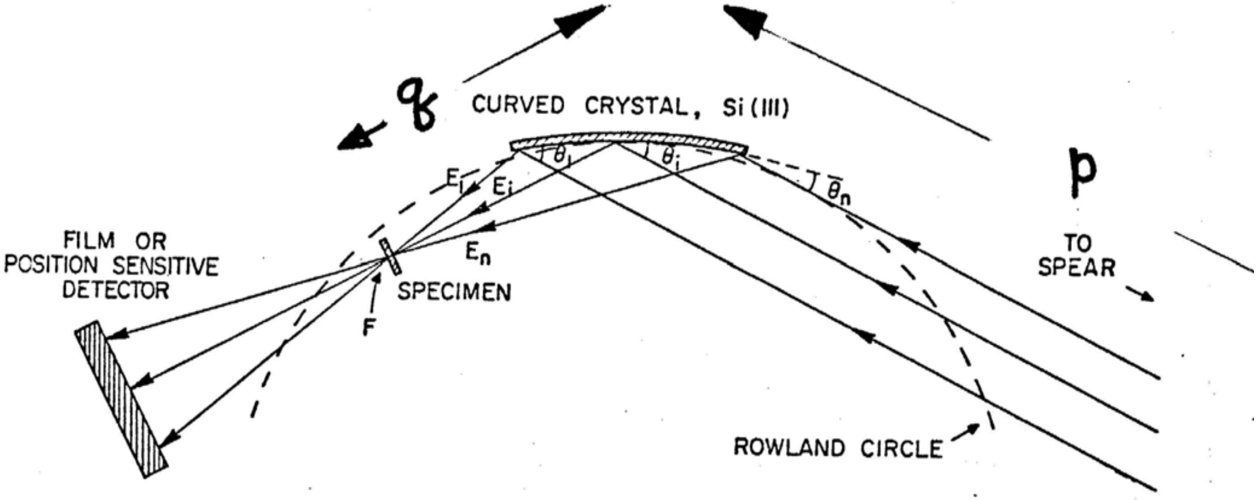


at the entrance of the crystal

At the exit of the crystal

at the focus

Curved crystal optics on SR beamline : energy range to be covered and the position-energy relation

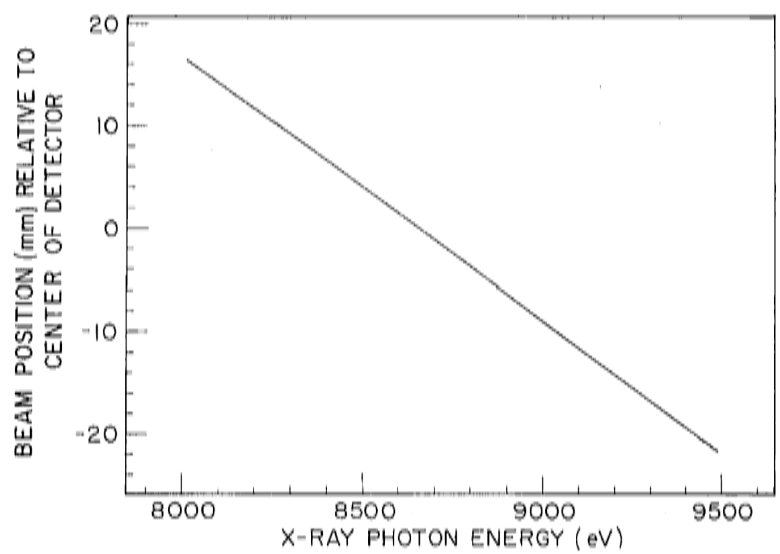


$$\frac{1}{p}+\frac{1}{q}=\frac{2}{R\sin\theta_B}$$

$$\frac{\Delta E}{E_o}=\ell\left(\frac{1}{R}-\frac{\sin\theta_B}{p}\right)\cot\theta_B$$

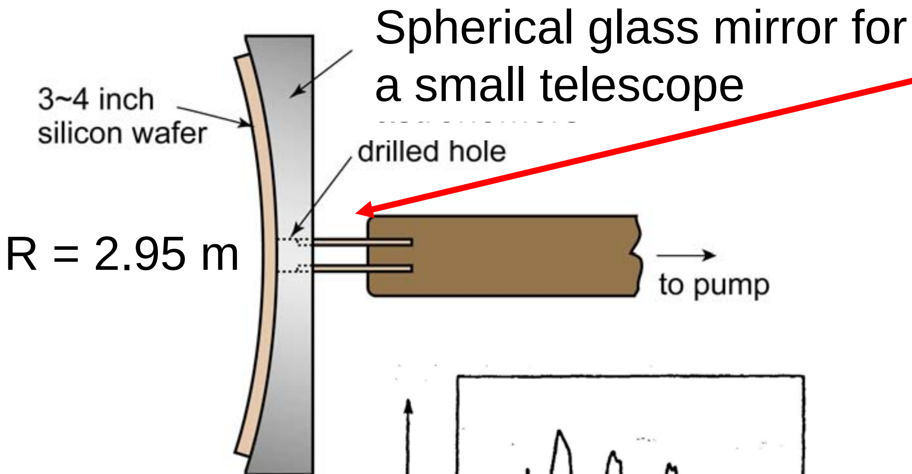
10 cm long Si 111 crystal

R(m)		X-ray Energy (KeV)						
		4	5	6	7	8	9	10
2.5	ΔE(eV)				911	1209	1547	19
	q(mm)				361	315	279	25
2.0	ΔE(eV)			826	1149	1523	1947	
	q(mm)			336	287	251	223	
1.5	ΔE(eV)		747	1113	1545	2045		
	q(mm)		302	251	215	187		
1.0	ΔE(eV)	683	1134	1686	2338			
	q(mm)	251	200	166	142			

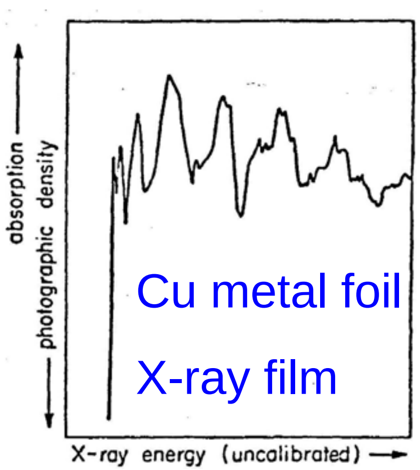


BL-II-4 (topography hutch) at SSRL

Any other person was using the topography hutch.



A total of ~ 50 U.S. dollars



From 1980 SSRL report

also, reported in “the workshop for laboratory EXAFS facilities” held in Seattle (1980)

Fe K-edge recorded on a Polaroid film

February 11, 1980

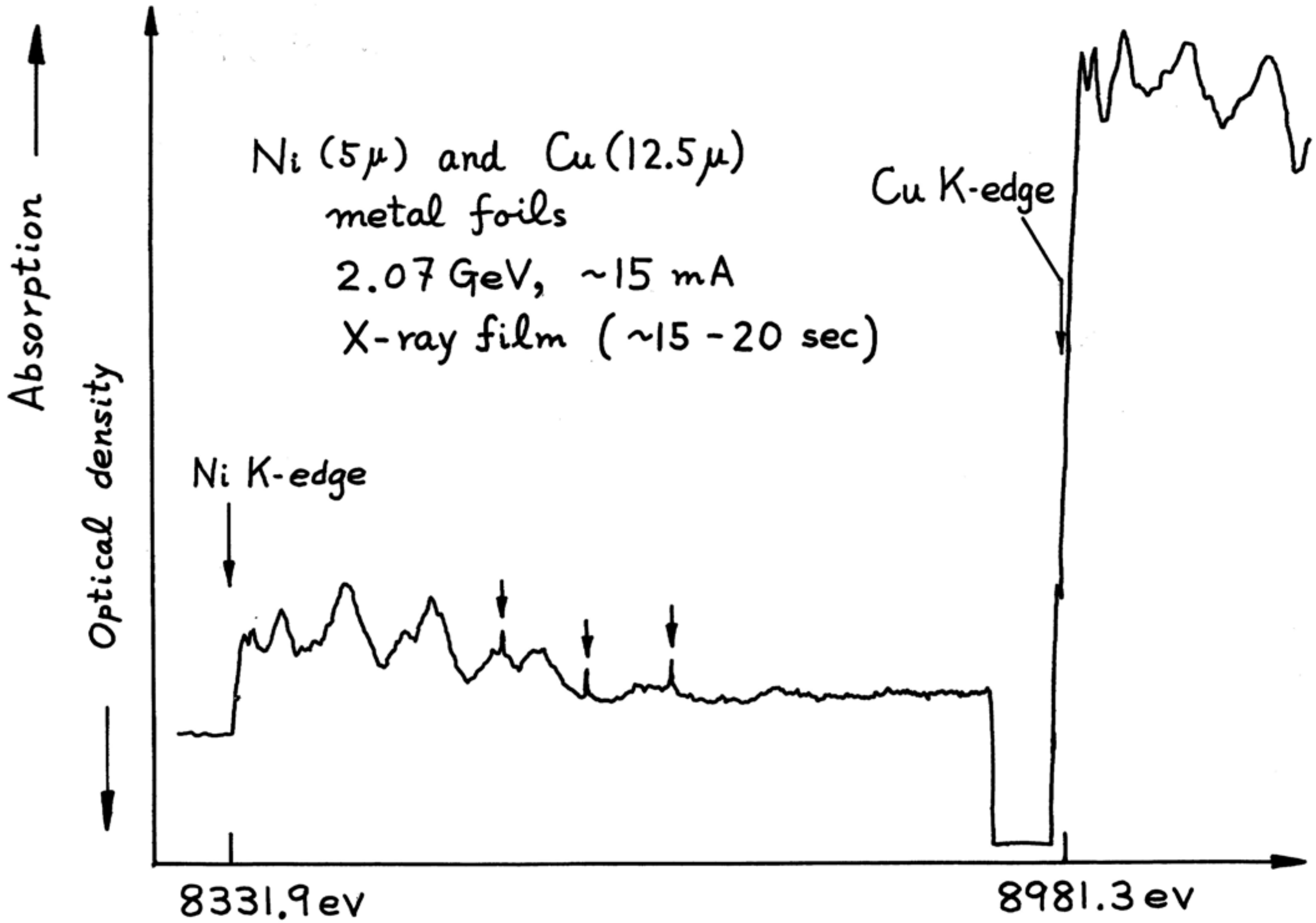
3 GeV, 50 mA , ~1 s exposure

Cu K-edge and oscillation on a Polaroid film

2.07 GeV, ~ 12 mA, ~ 1 min. exposure

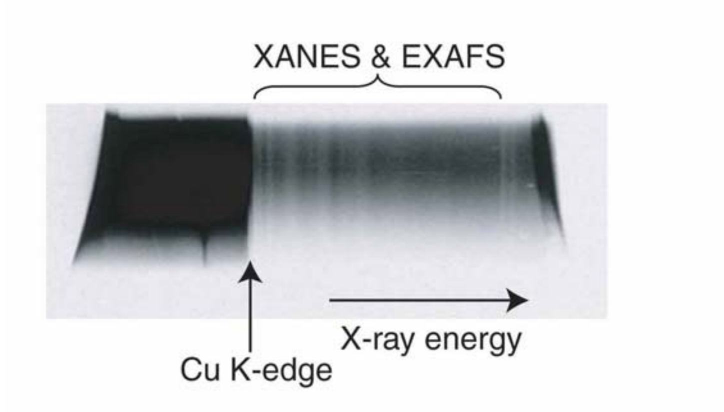
March 29, 1980

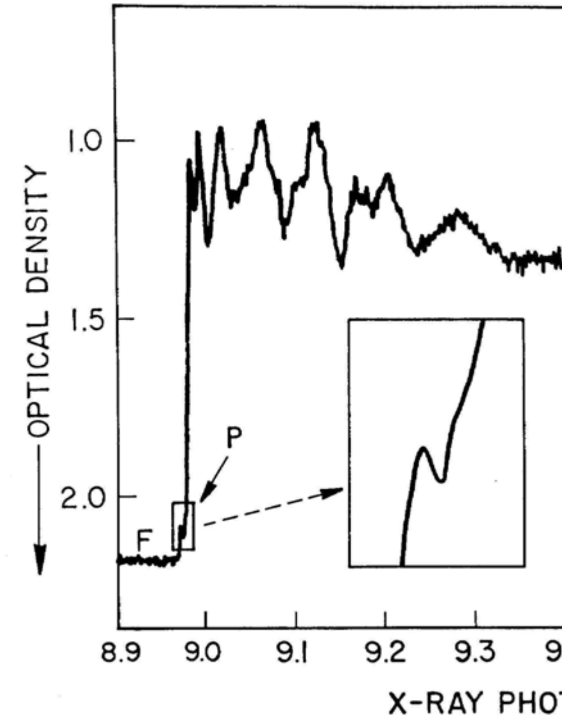
Calibration of the position-energy relation

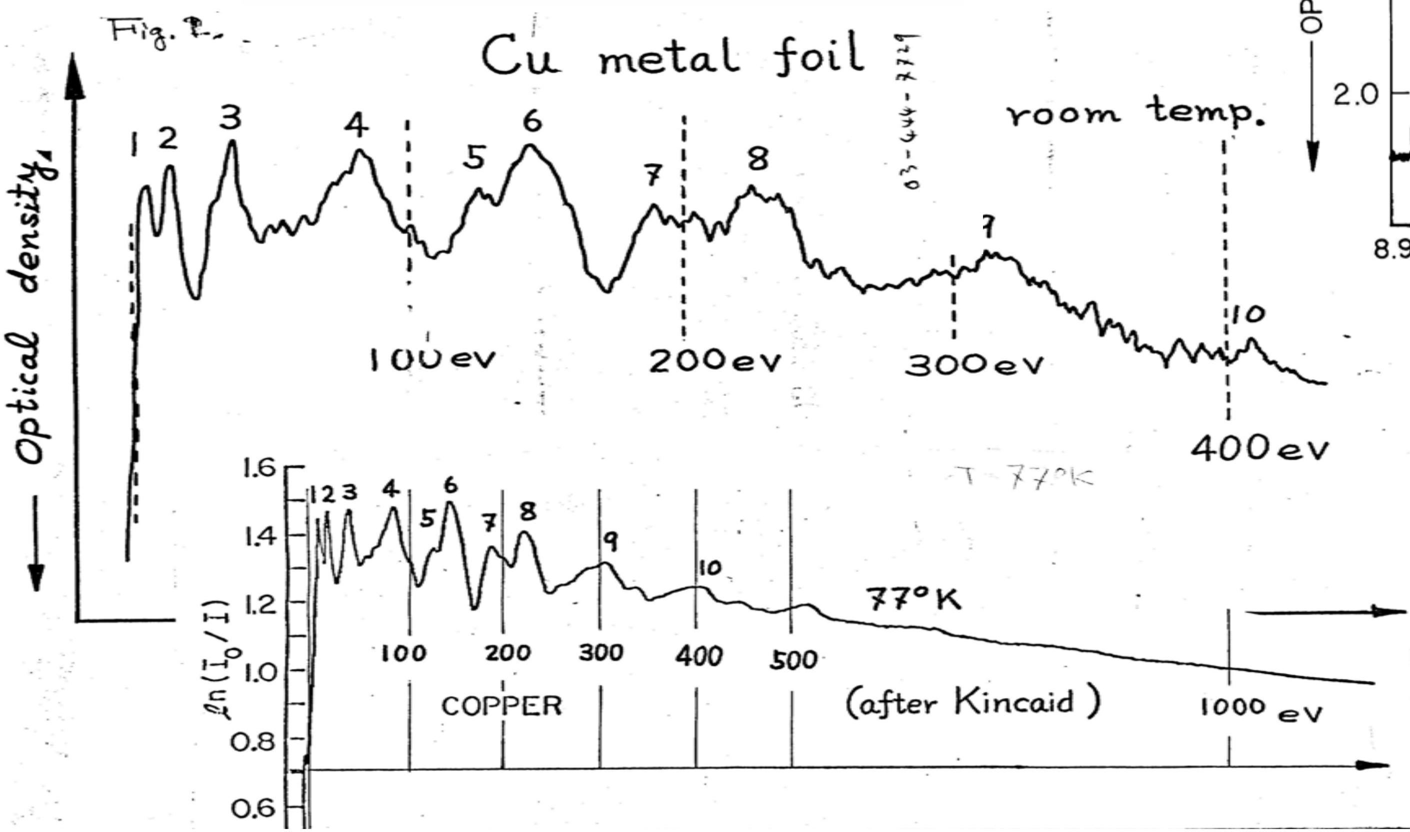


Cu metal foil

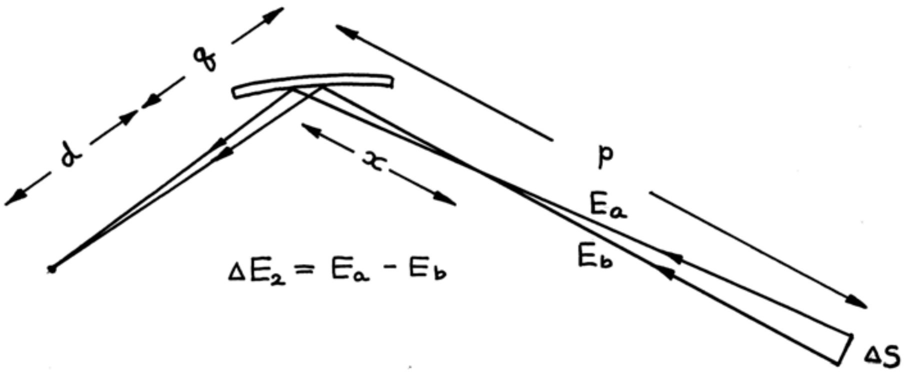
1980







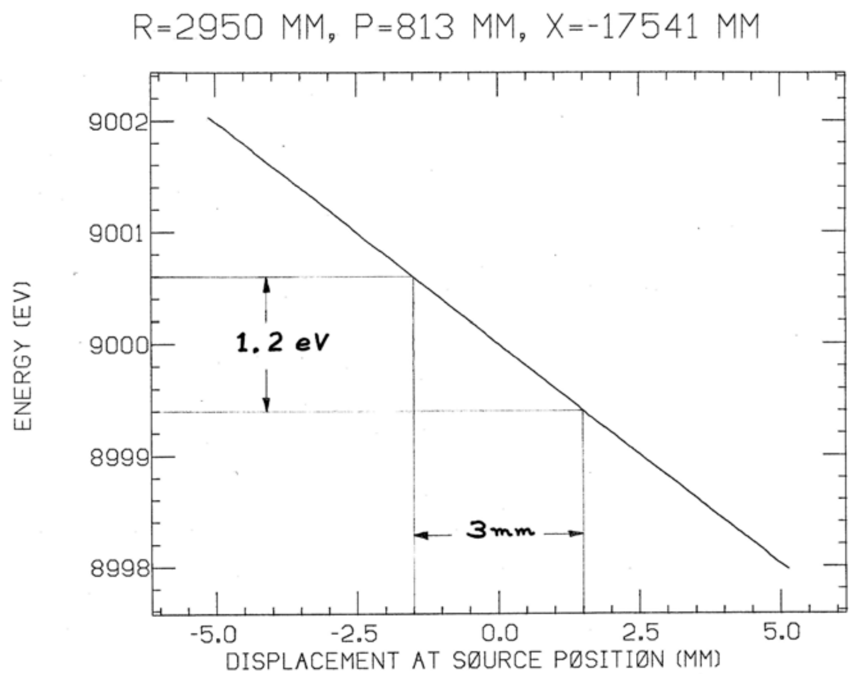
Contribution from the source size



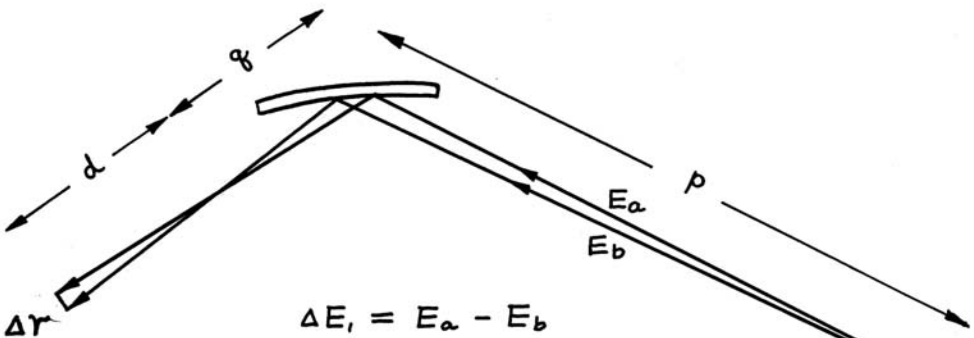
$$\Delta E_2 = E_0 \left(\frac{1}{R \sin\theta_B} - \frac{1}{x} \right) \frac{x}{p - x} \Delta S \cot\theta_B$$

where $$x = \frac{1}{\frac{2}{R \sin\theta_B} - \frac{1}{q + d}}$$

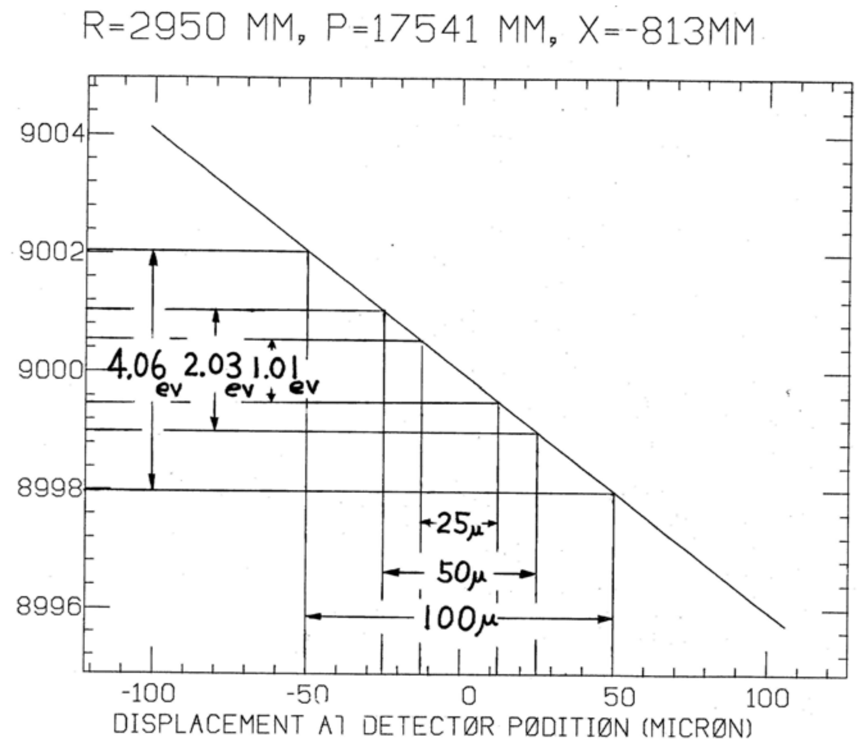
if $q + d = R \sin\theta_B \rightarrow x = R \sin\theta_B \rightarrow \Delta E_2 = 0$



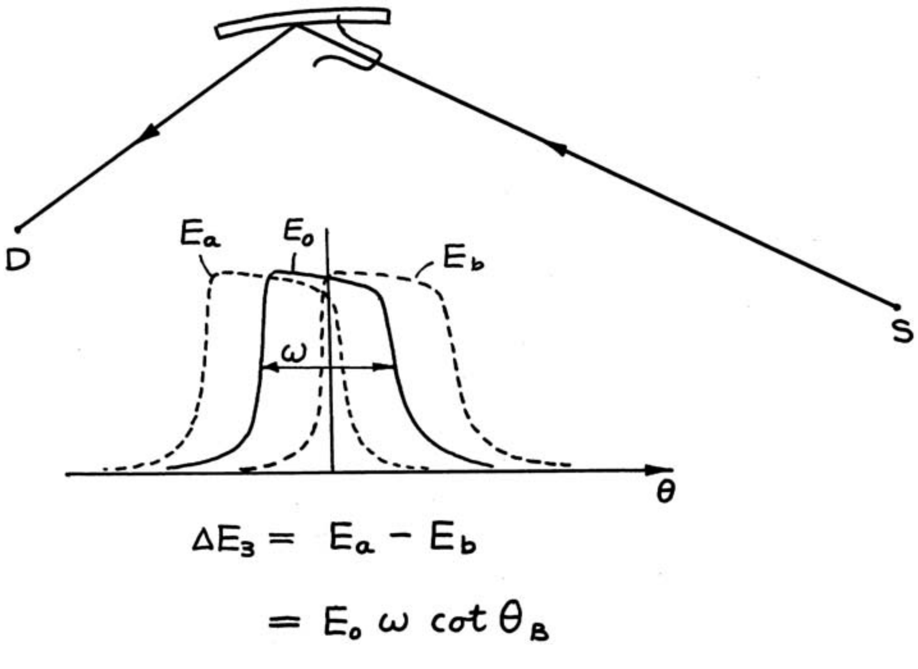
Contribution from the spatial resolution of the detector



$$\Delta E_1 = E_0 \frac{\Delta r}{d} \frac{\left(\frac{1}{R} - \frac{\sin\theta_B}{p}\right)}{\left(\frac{2}{R} - \frac{\sin\theta_B}{p}\right)} \cot\theta_B$$



Contribution from the angular width of diffraction



Overall resolution

$$\delta E = (\delta E_1{}^2 + \delta E_2{}^2 + \delta E_3{}^2)^{1/2}$$

p = 17.5 m (source-to-crystal)

q + d = 0.81 m (crystal-to-detector)

R = 2.95 m

Si 111 reflection, E = 9 keV

δE_1 = 1.01 eV

δE_2 = 1.20 eV

δE_3= 1.26 eV

δE = 2.0 eV

Japanese Journal of Applied Physics
Vol. 20, No. 11, November, 1981 pp. 2223–2228

A Fast X-Ray Absorption Spectrometer for Use with Synchrotron Radiation

Tadashi Matsushita* and R. Paul Phizackerley

Stanford Synchrotron Radiation Laboratory, Stanford University, SLAC, P.O. Box 4349, Bin 69, Stanford, California 94305, USA

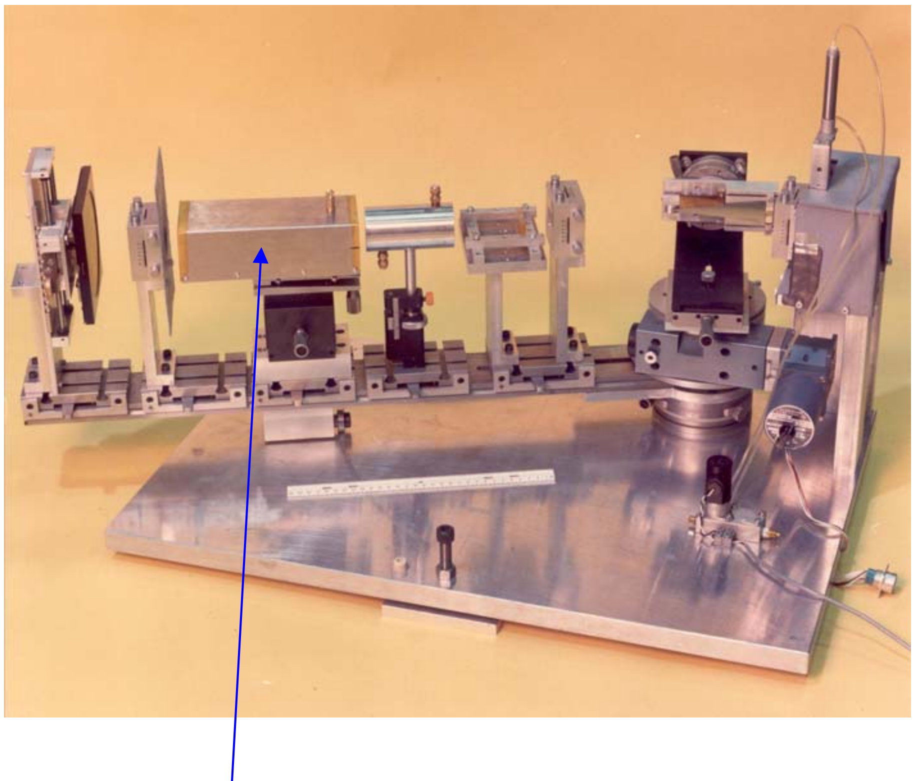
(Received July 6, 1981; accepted for publication August 22, 1981)

A quasi-parallel and polychromatic beam of synchrotron radiation is focused and dispersed by a curved crystal, so that the energy of each ray of the focused beam varies as a function of convergence angle through the focus. The specimen is placed at the focus. By measuring the X-ray intensity distribution across the beam behind the focus, in the presence and absence of the specimen, the absorption spectra of Cu and Ni metal foils were obtained. Using an X-ray film as the detector, a spectrum from a Cu foil was obtained in 0.1 seconds when the SPEAR storage ring at Stanford was operated at 3.1 GeV and 80 mA. The energy resolution is approximately 2.0 eV and the energy range of the spectrum is approximately 1 keV.

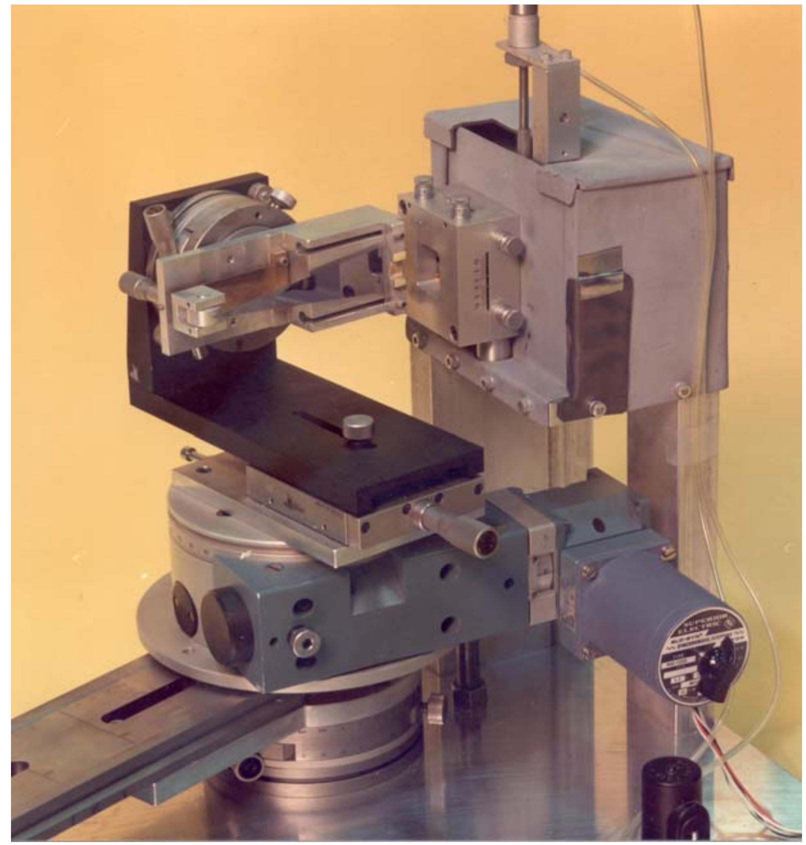
Jpn. J. Appl. Phys. **20**, 2223 – 2228, (1981)

R. P. Phizackerly, Z. U. Rek, G. B. Stephenson,
S. D. Conradson, K. O. Hodgson, T. Matsushita and H. Oyanagi,
J. Appl. Cryst. **16**, 220-232 (1983)

under US-Japan collaboration (1981 – 1982)

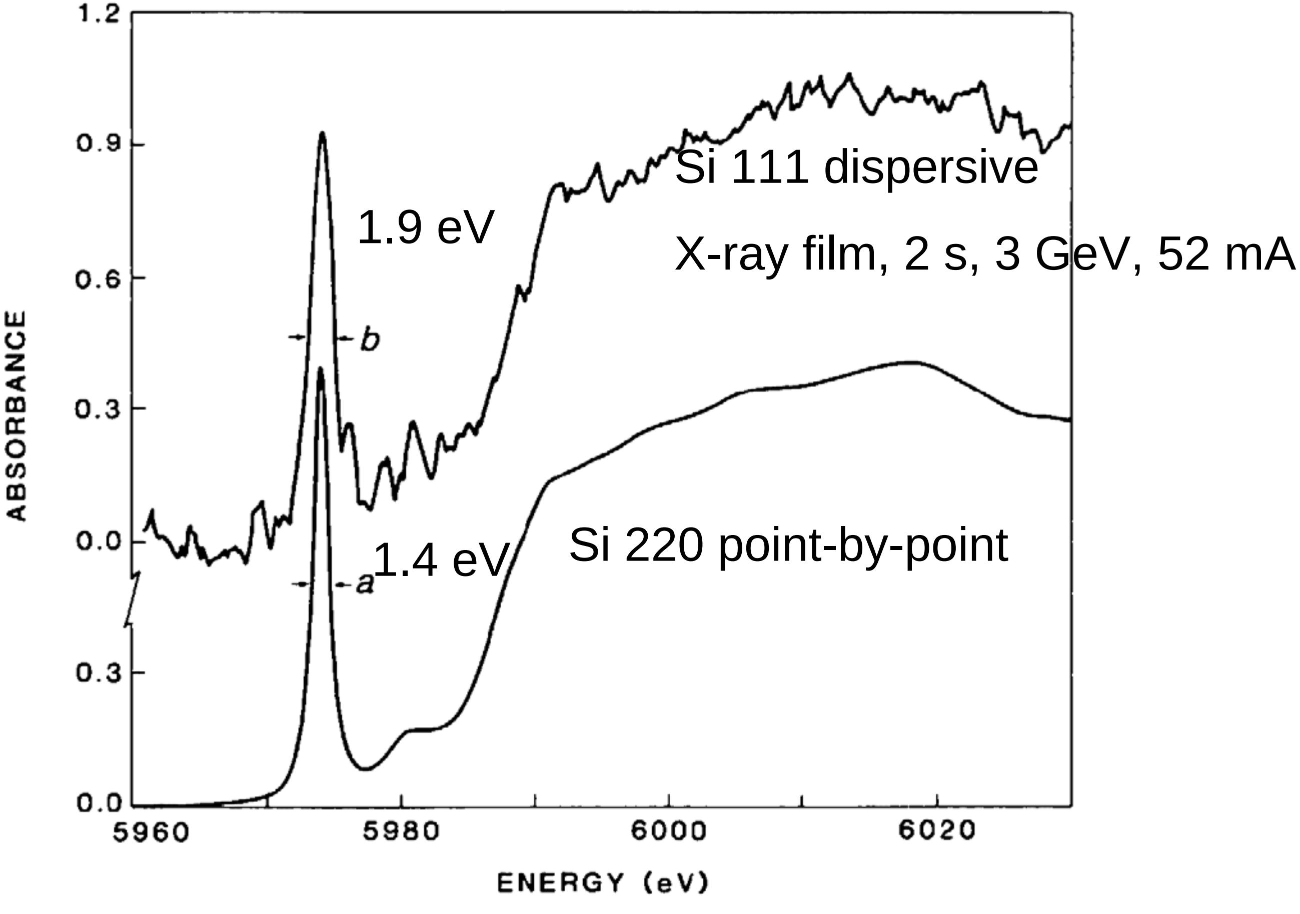


total reflection mirror



Crystal and crystal bender

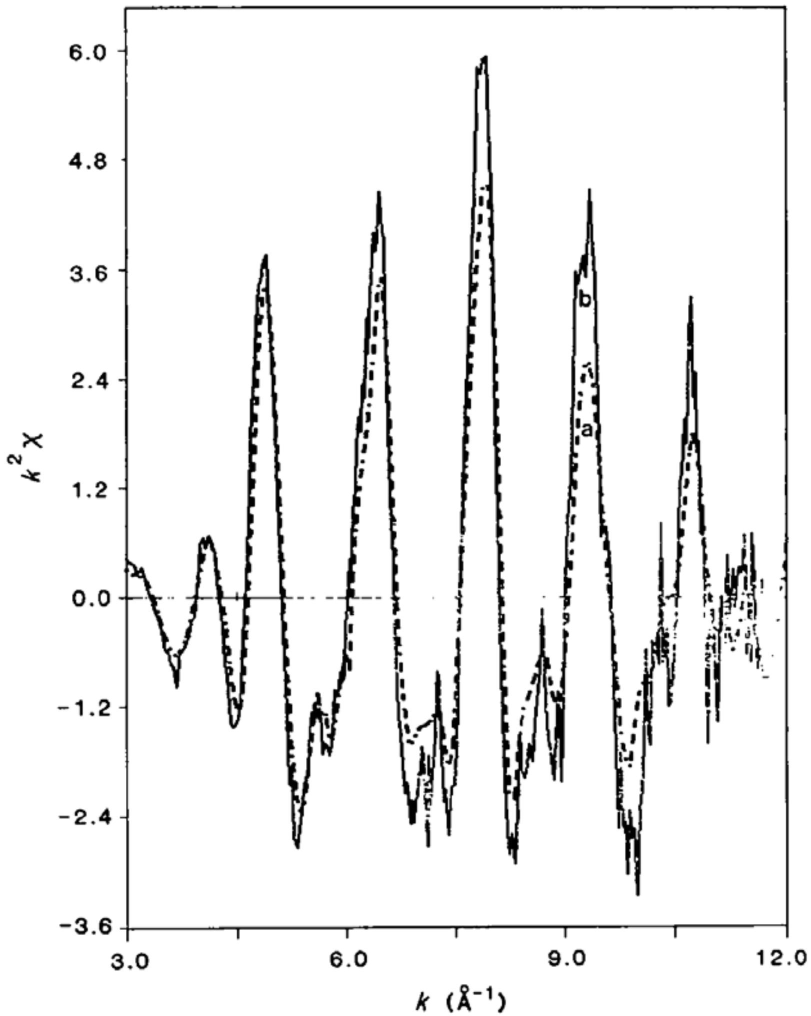
K_2CrO_4 solution

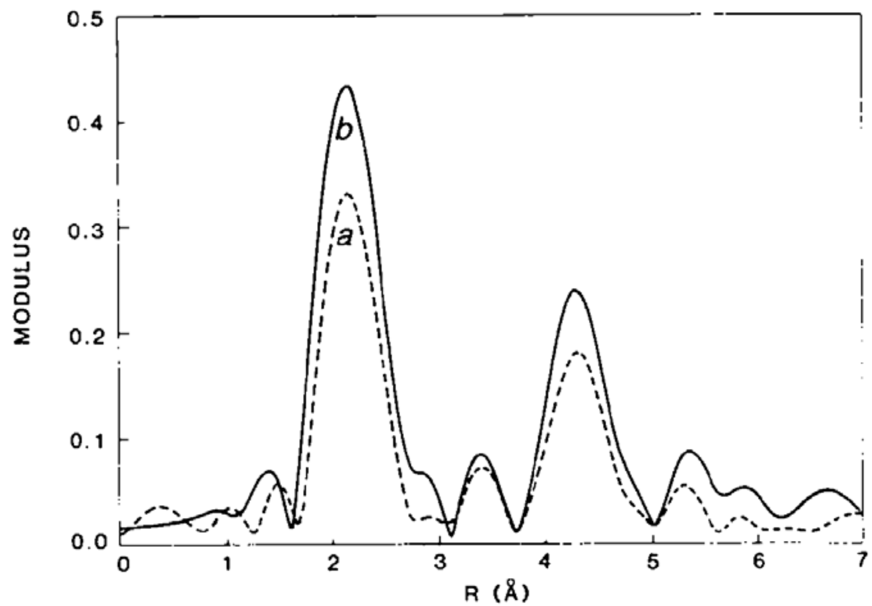


Fe metal foil, K-edge EXAFS

a: conventional point-by-point method

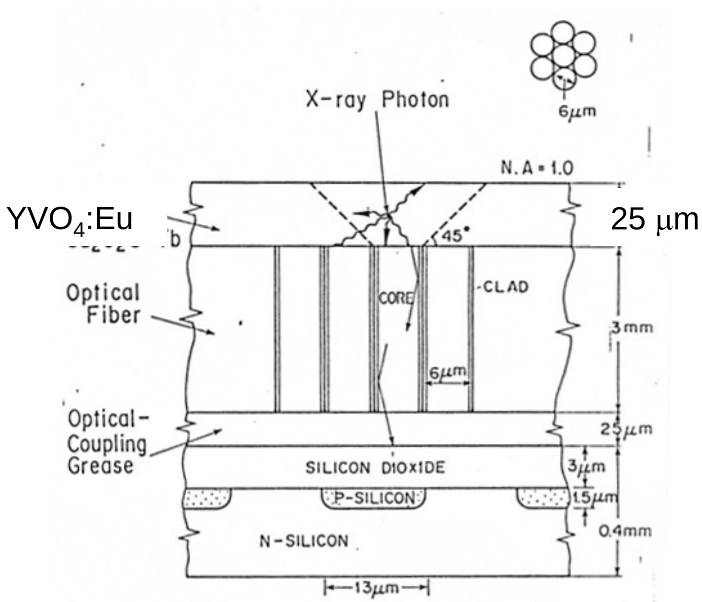
b: dispersive method (X-ray film)

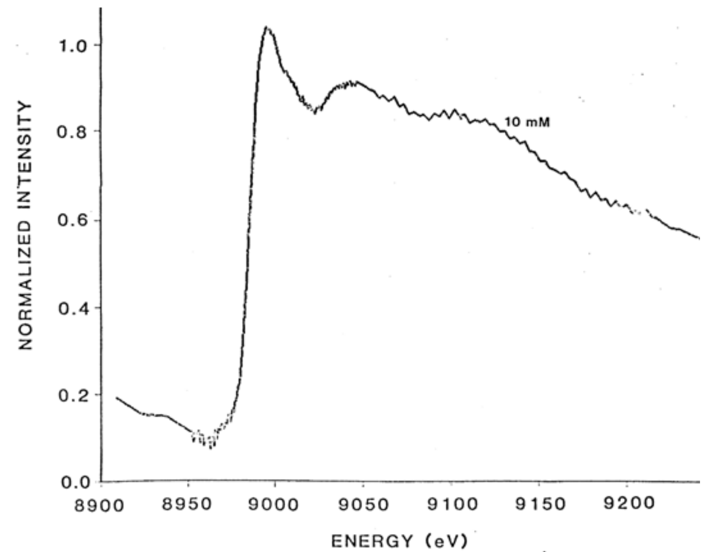


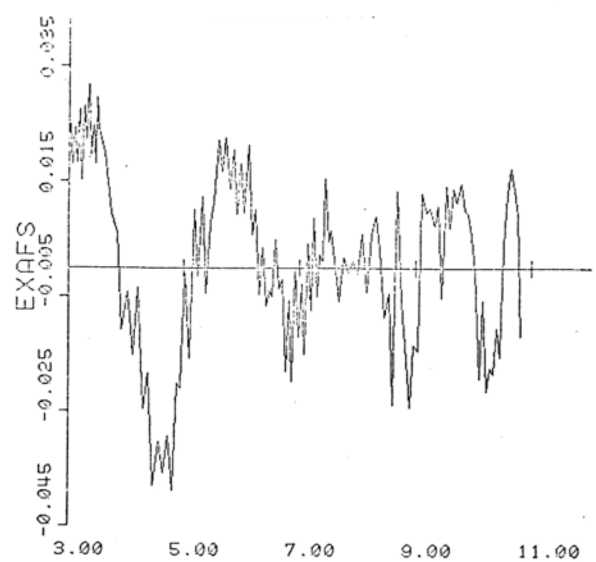


photodiode array
(EG&G Reticon RL 1024SF)

10 mmol dm^{-3} aqueous Cu^{2+} solution



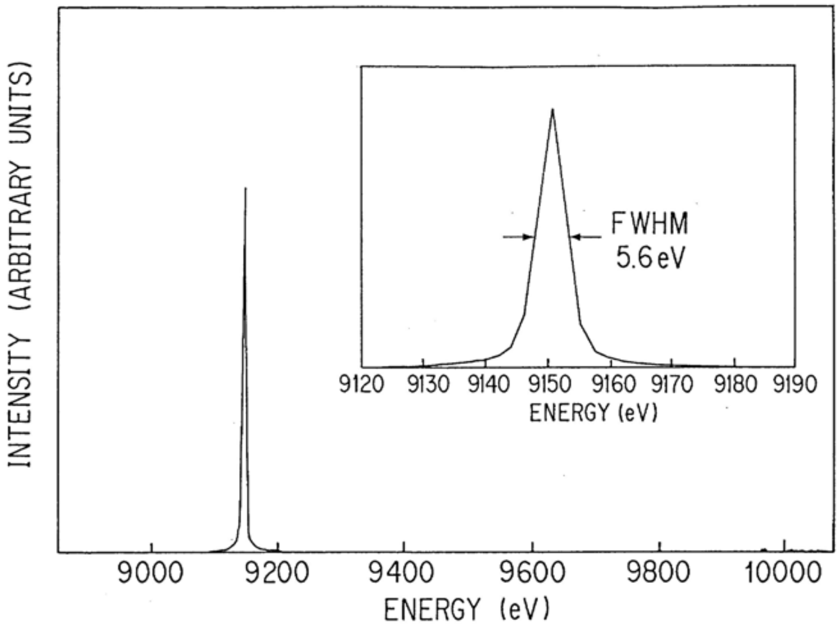


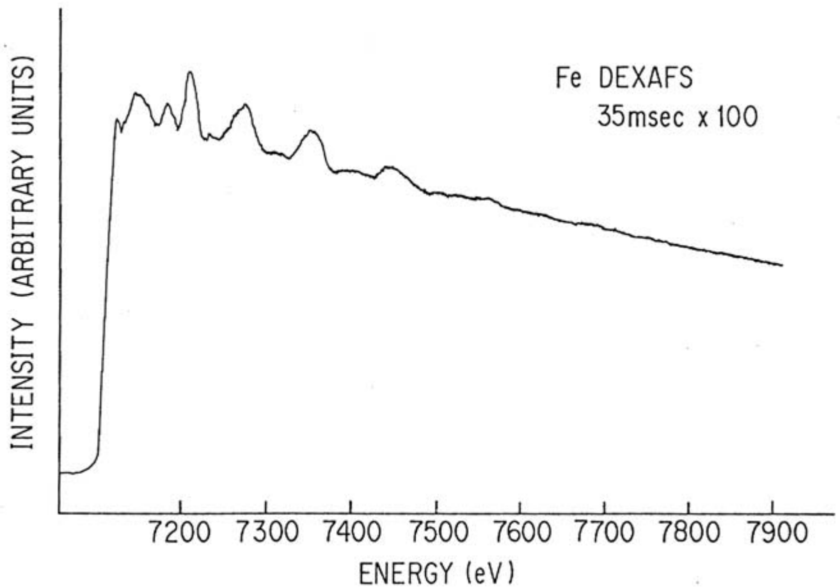


DXAS at the Photon Factory (1983-1986)
with H. Oyanagi, S. Saigo, M. Yoshida

EG&G Reticon detector (RL 1024 SF)

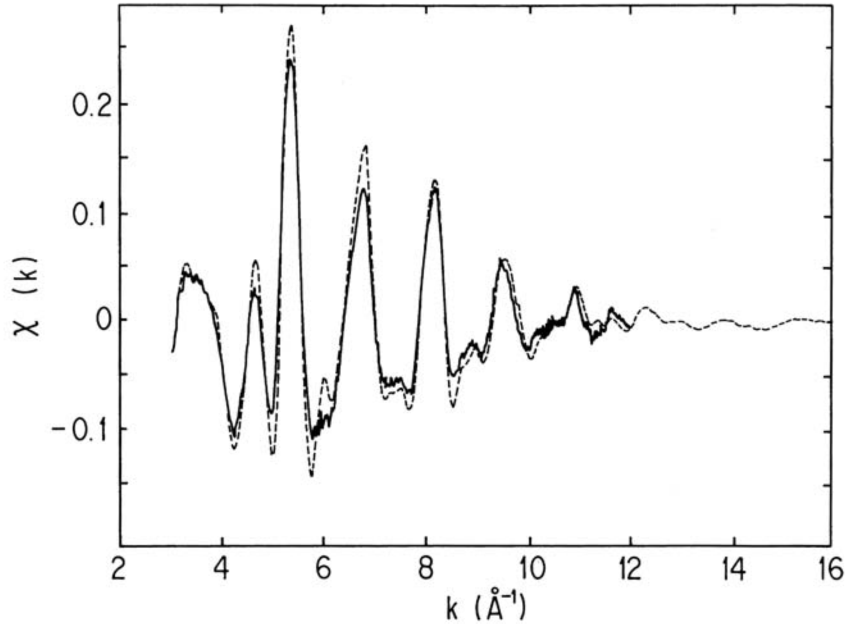
Gd_2O_2S:Tb phosphor, 50 μm thick

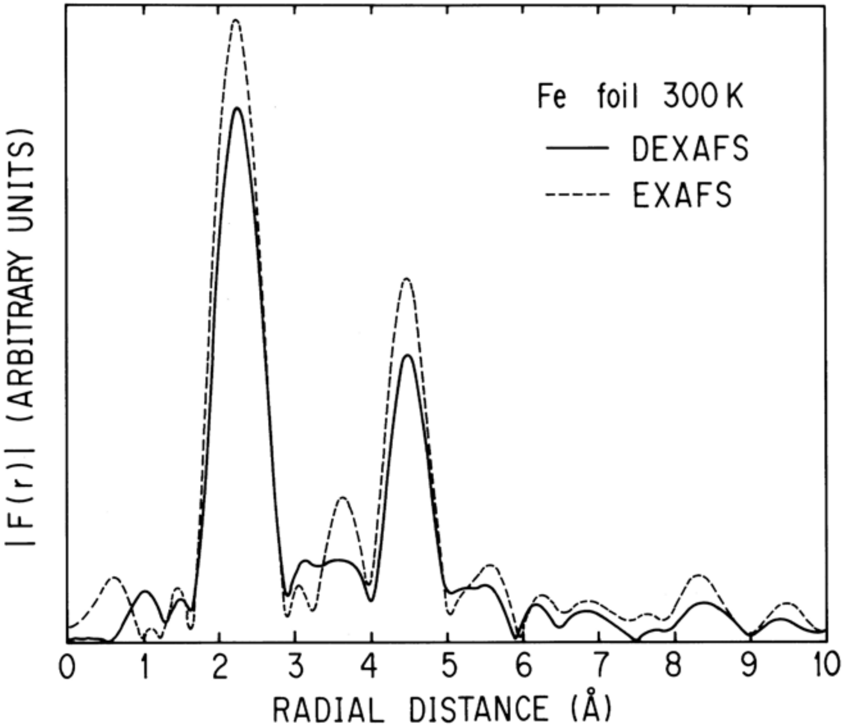




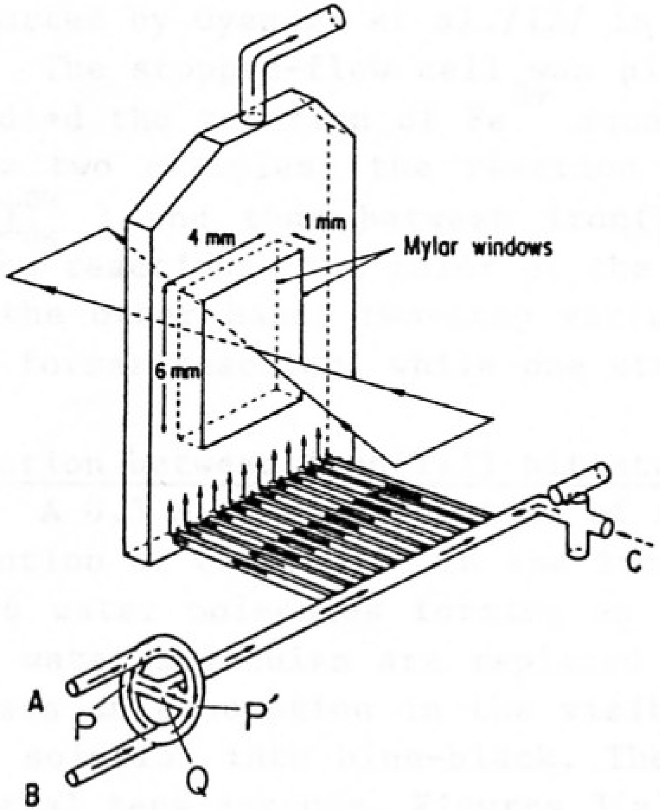
Fe metal foil EXAS

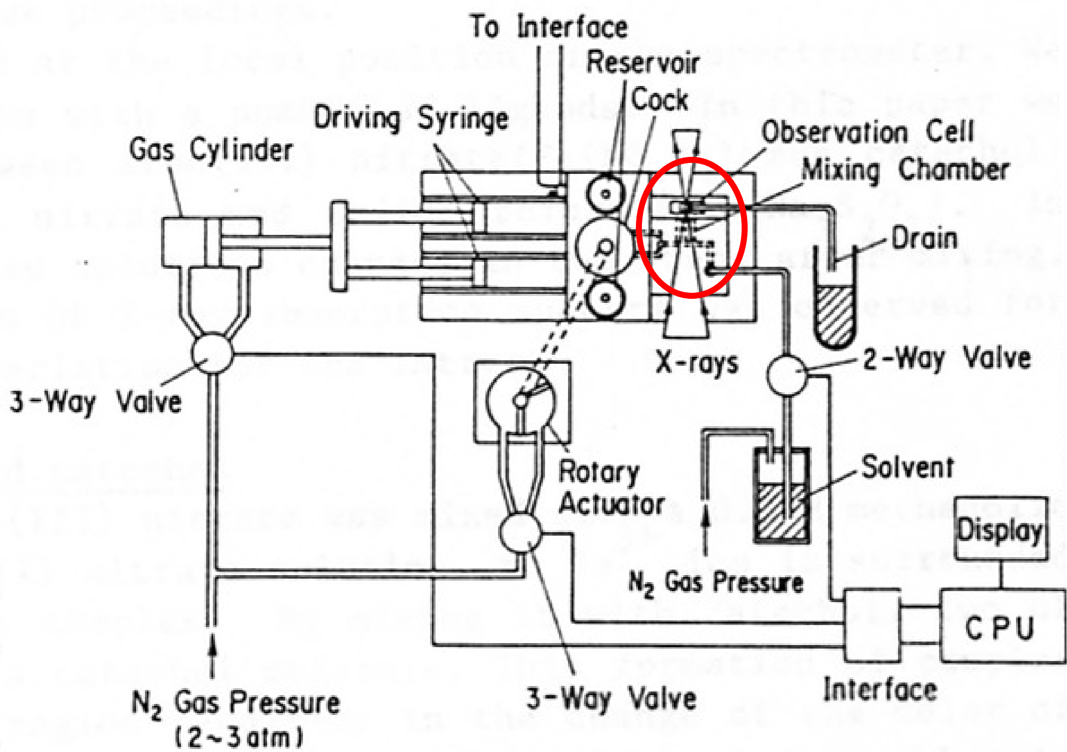
conventional step by step method (Si 311)
dispersive method (Si 111, photodiode array)





Stopped-flow experiments



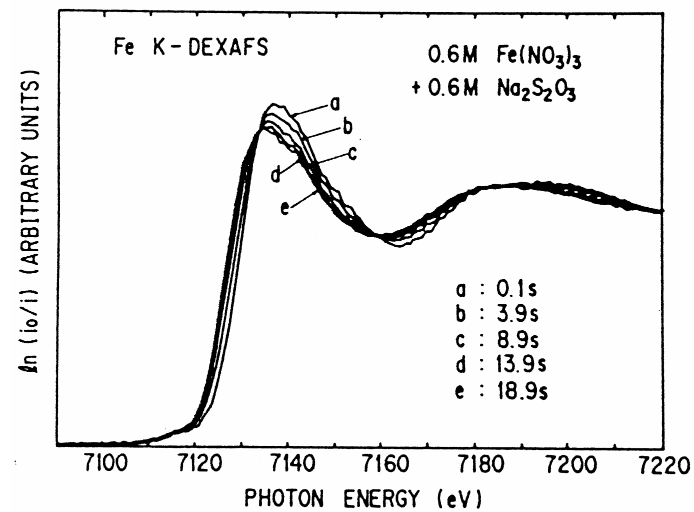


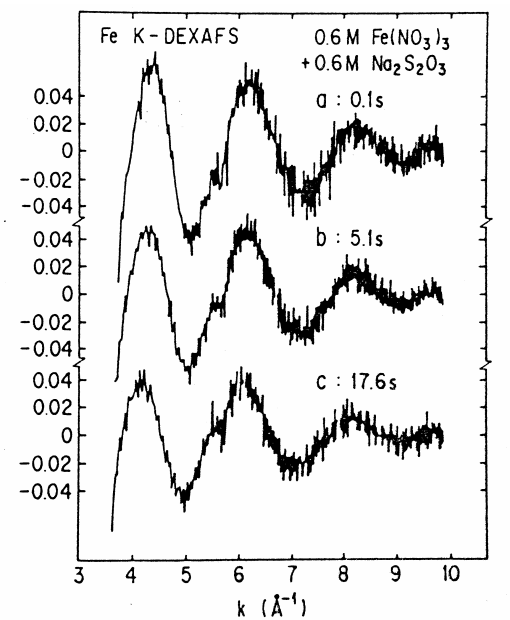
S. Saigo, H. Oyanagi, T. Matsushita, H. Hashimoto, N. Yoshida, M. Fujimoto and T. Nagamura, J. de Phys. 47, C8-555-561 (1986).

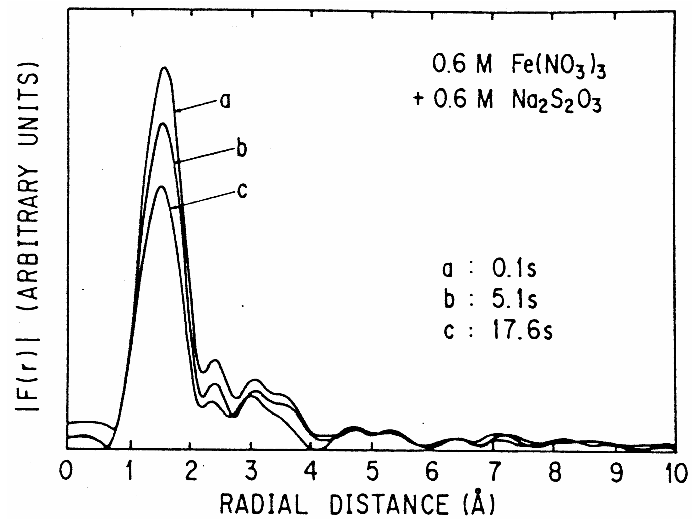
Reaction between sodium thiosalfate and iron(III) nitrate

$Fe^{3+} + 2S_2O_3^{-} \longrightarrow Fe(S_2O_3)^{2-}$ (1)

$Fe(S_2O_3)^{2-} + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$ (2)

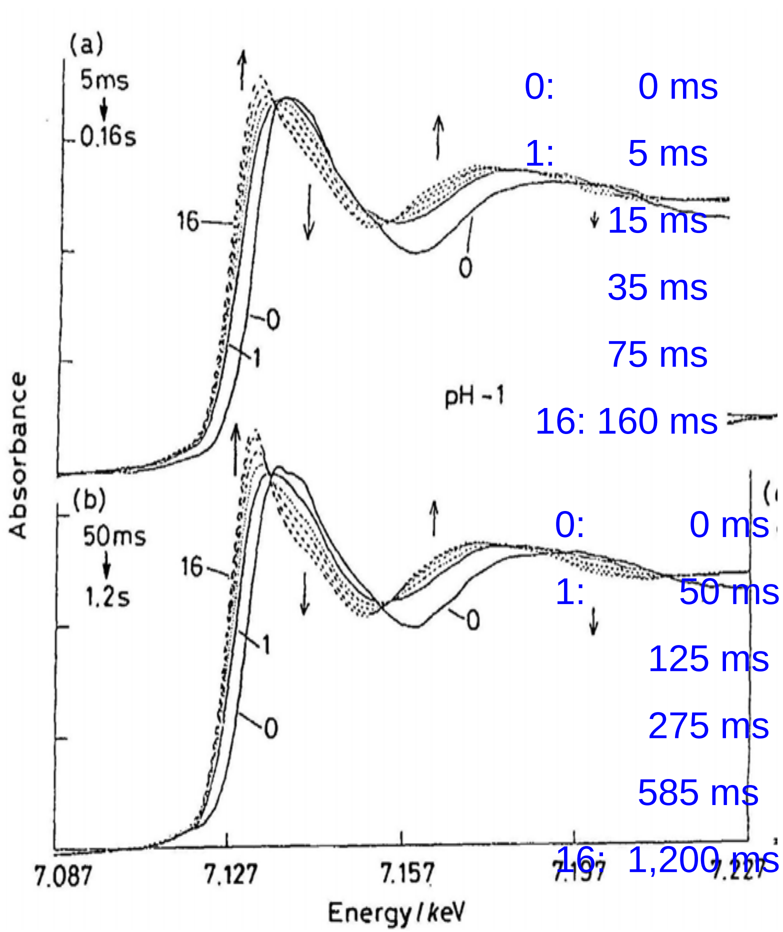


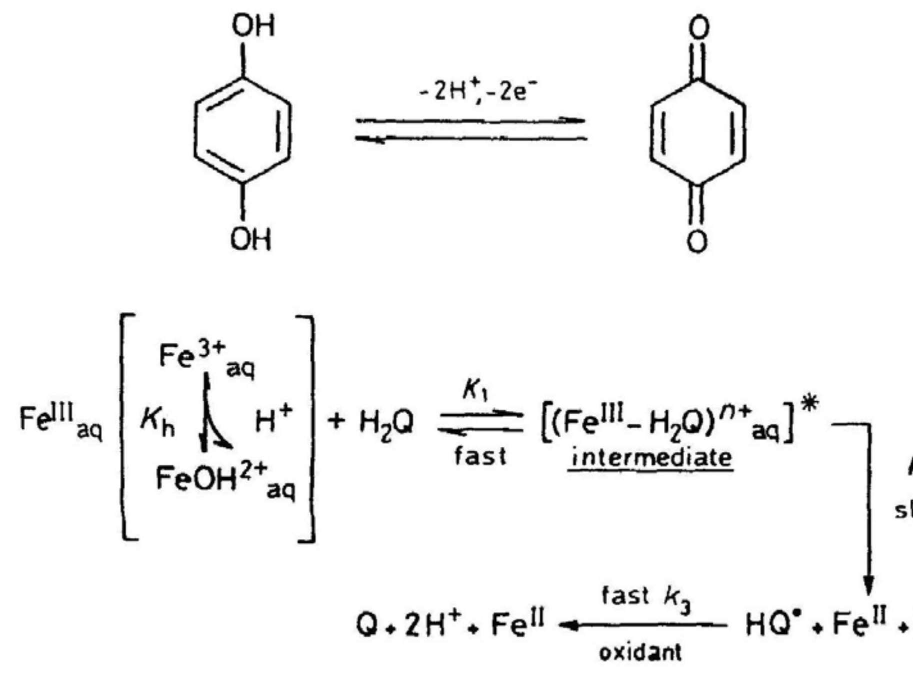




Reaction between Iron(III) Nitrate and Hydroquinone

16 spectra successively collected





Scheme 1

N.Yoshiba, T. Matsushita, S. Saigo, H. Oyanagi, H. Hashimoto, and M. Fujiimoto,

J. Chem. Soc.,Chem. Comm.4, 354-356 (1990)

Quick X-Ray Reflectometory in Dispersive Mode Utilizing a Curved Crystal Polychromator (2006 – present)

$$Q = 4\pi \sin(\alpha)/\lambda$$

$$\sim E \sin(\alpha)$$

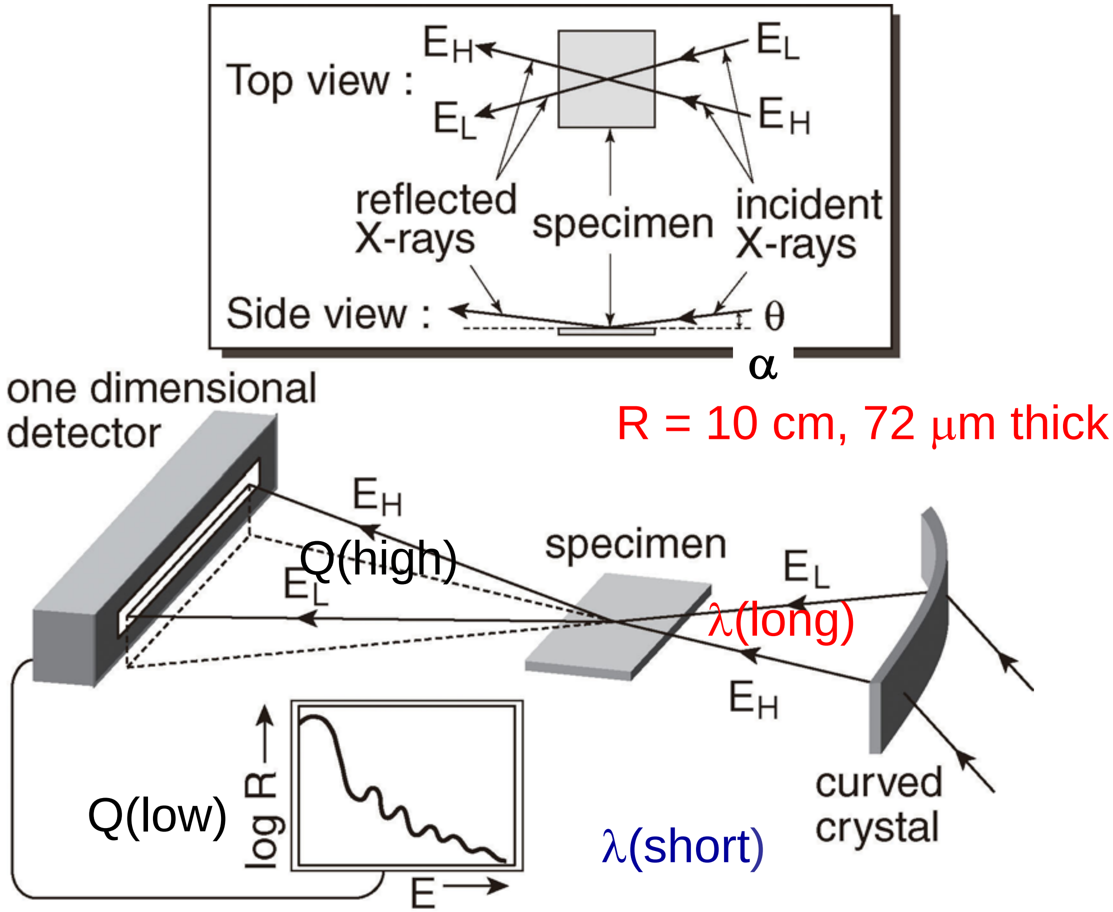
if Q: 0.08~0.8 $Å^{-1}$

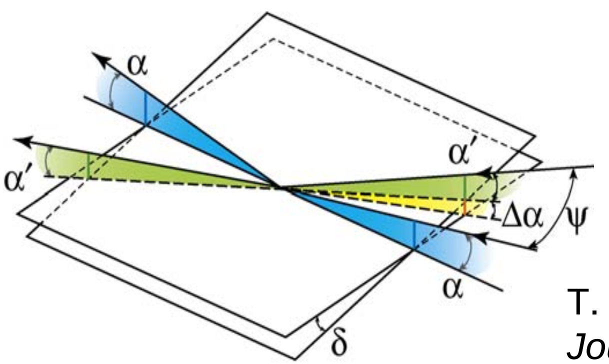
Q_{max}/Q_{min}=10

E_{max}/E_{min} =10

R = 10~30 cm

E_H - E_L = 30 ~ 50 keV

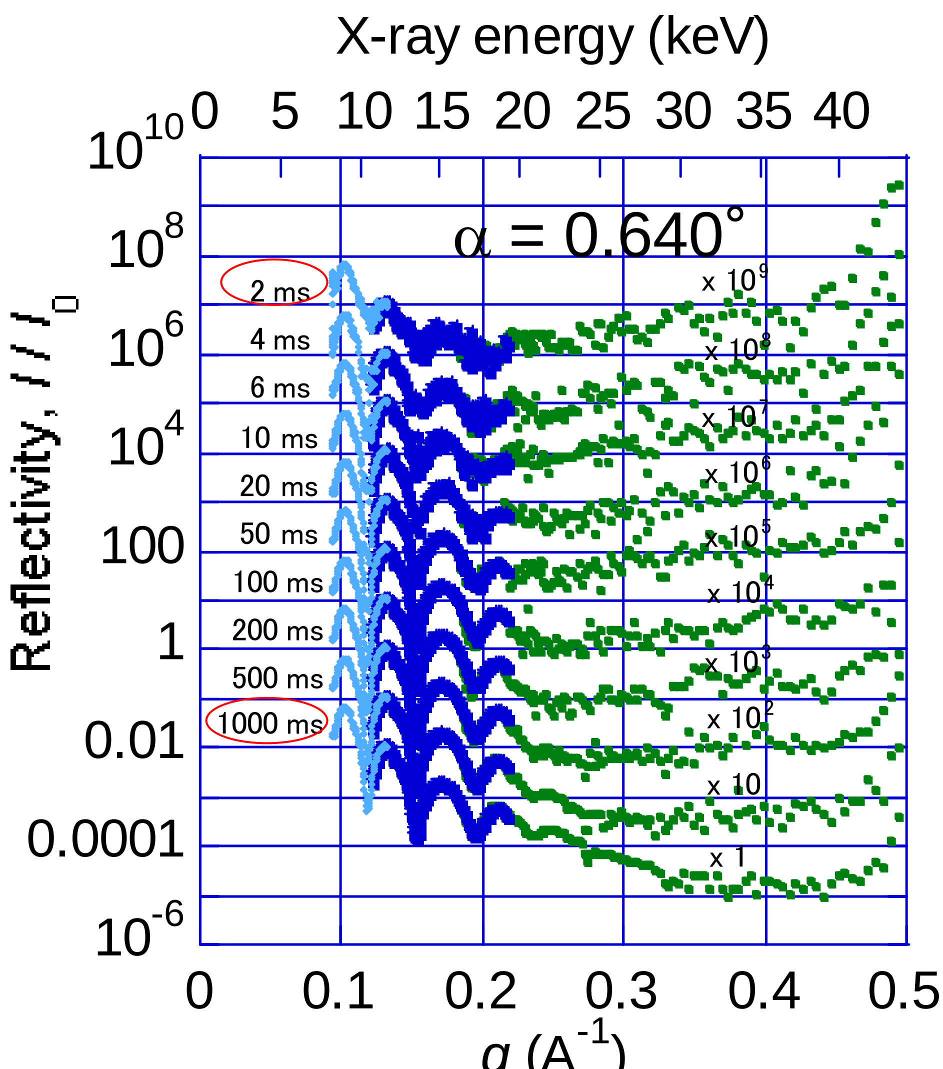




T. Matsushita, Y. Inada, Y. Niwa, M. Ishii, K. Sakurai, and M. Nomura, *Journal of Physics: Conference Series* **83**, 012021 (2007)
T. Matsushita, Y. Niwa, Y. Inada, M. Nomura, M. Ishii, K. Sakurai, and E. Arakawa, *Appl. Phys. Lett.* **92**, 024103 (2008)

Gold film（14.3 nm thick）on silicon substrate

Static measurement



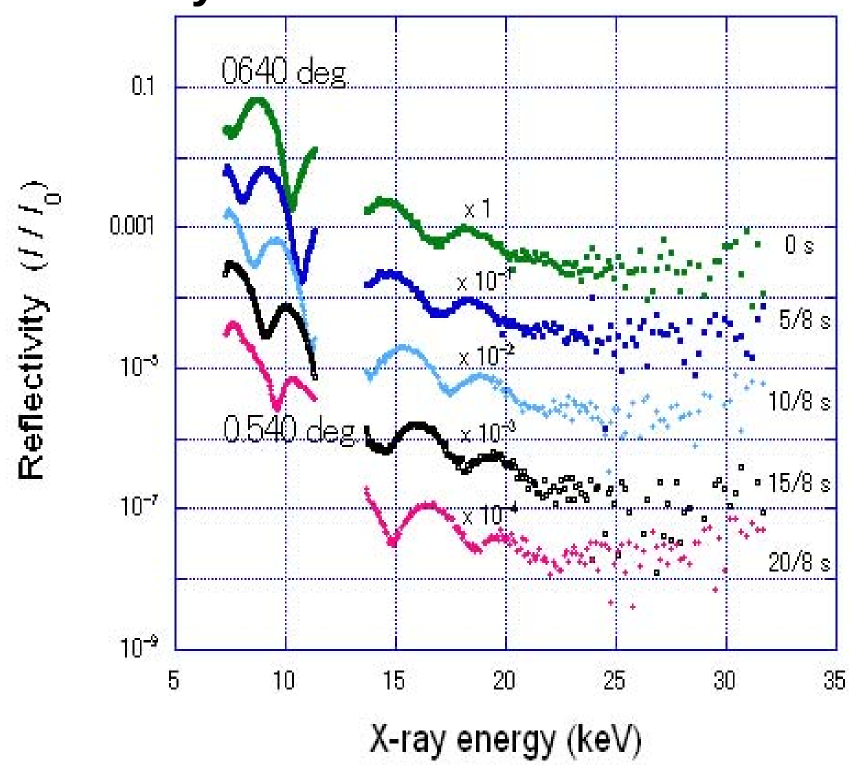
Dynamic measurement

Successive measurement while the specimen is rotated.

2-D X-ray CCD

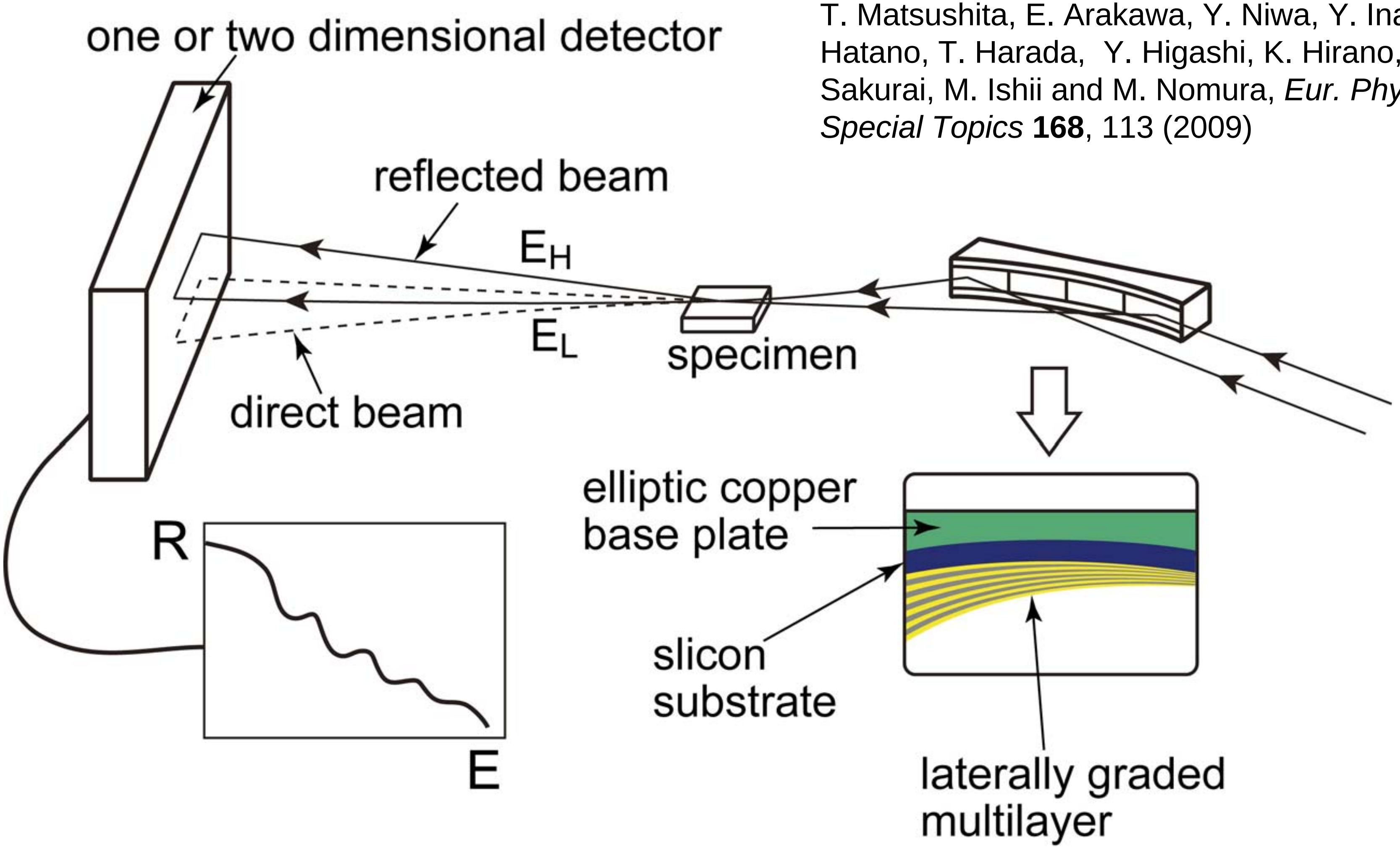
20 ms exposure

Every 5/8 seconds



Simultaneous Multiwavelength Dispersive X-Ray Reflectometer Utilizing a Laterally Graded Multilayer

T. Matsushita, E. Arakawa, Y. Niwa, Y. Inada, T. Hatano, T. Harada, Y. Higashi, K. Hirano, K. Sakurai, M. Ishii and M. Nomura, *Eur. Phys. J. Special Topics* **168**, 113 (2009)



Laterally d-graded multilayer on elliptic surface:

first trial (June, 2008): preliminary results

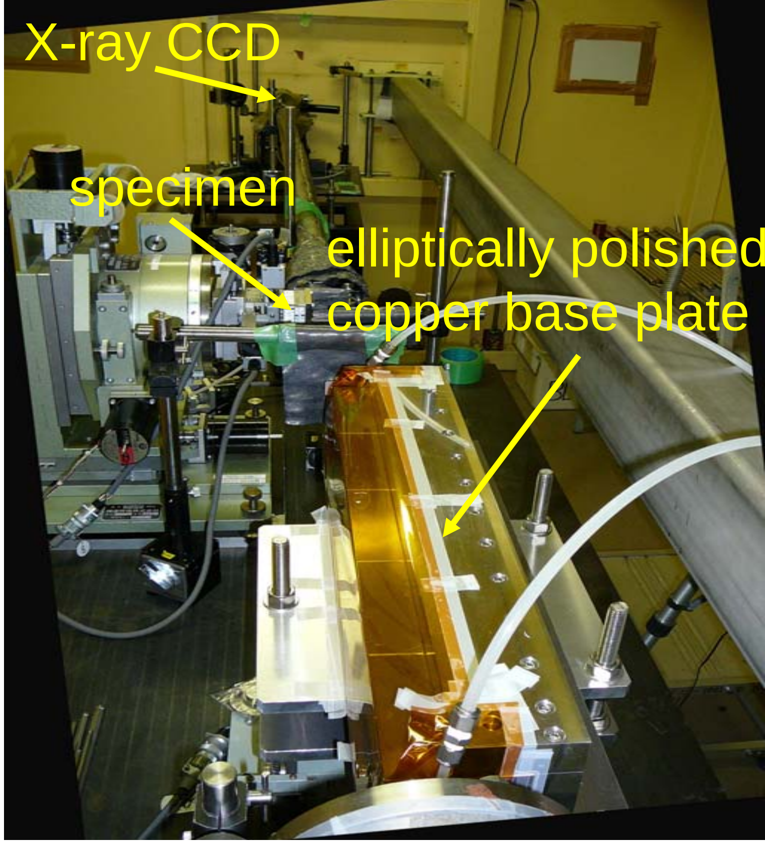
Photon Factory bending magnet BL

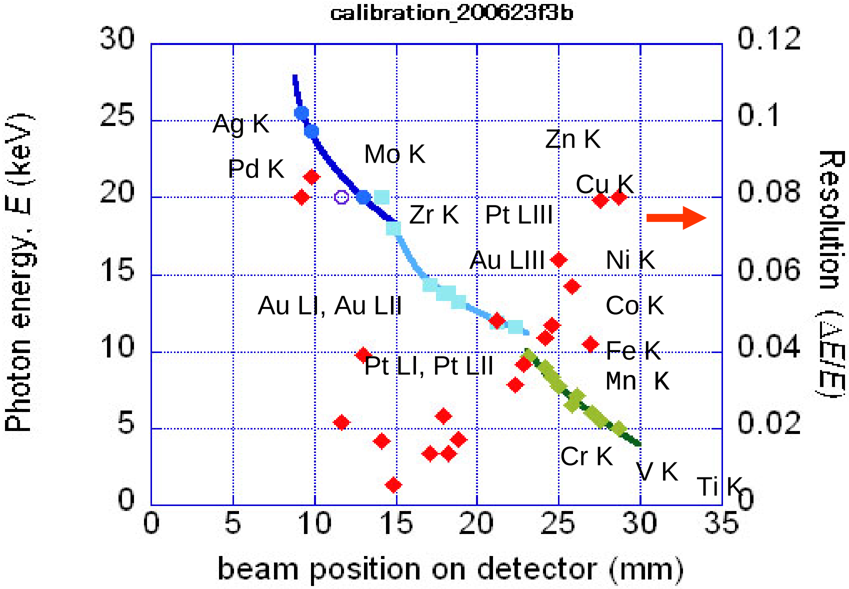
2.5 GeV, 450mA, ε = 36 nm rad

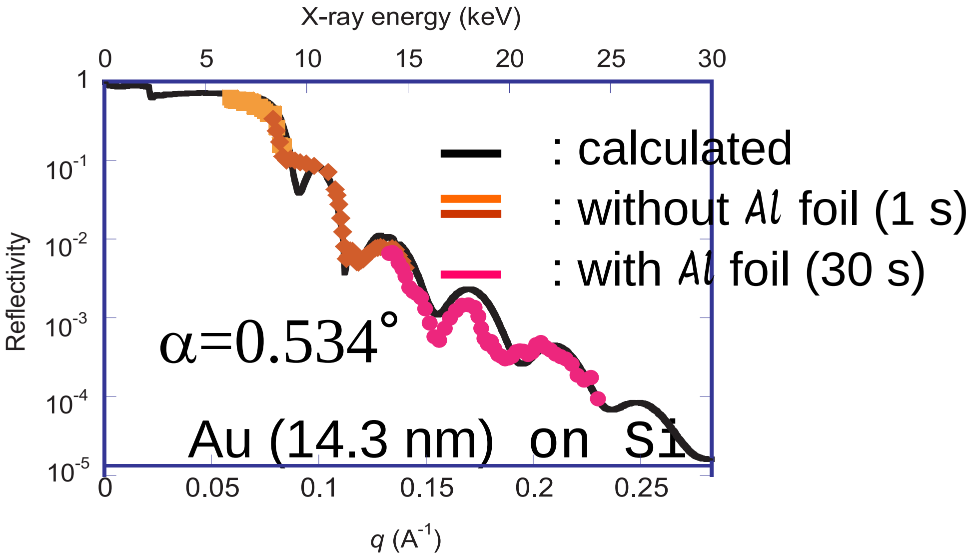
Source size: 0.56 mm, detector resolution: ~50 μm

Elliptically polished copper base plate

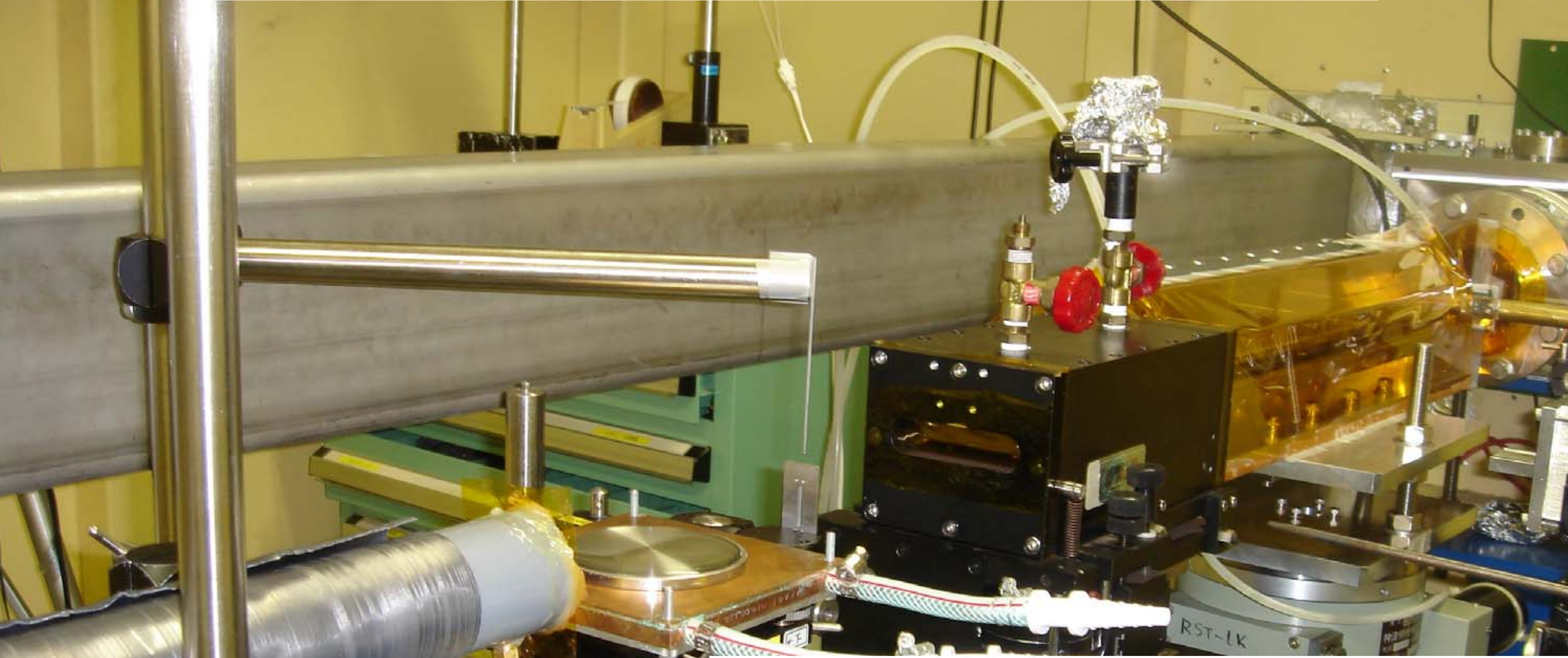
Four laterally graded SiC/C or V/C multilayers deposited on 4 of 15 cm long silicon wafers

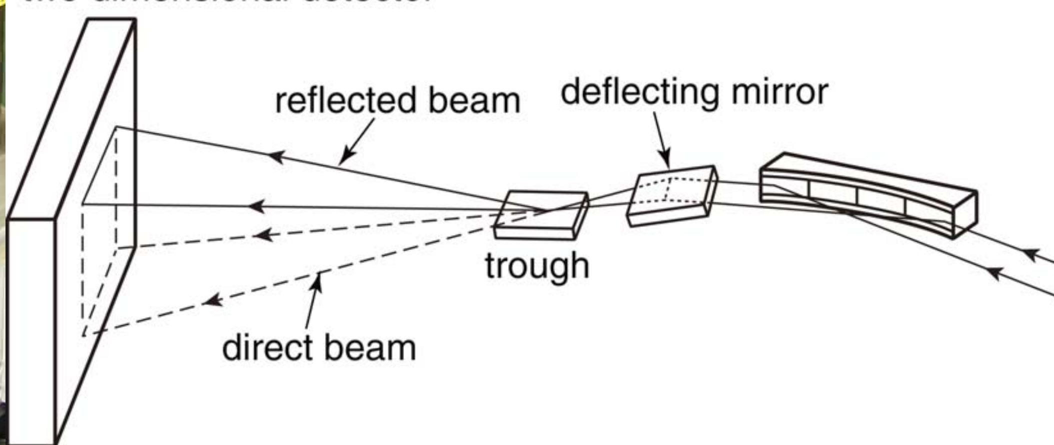






X-ray reflection from liquid surface





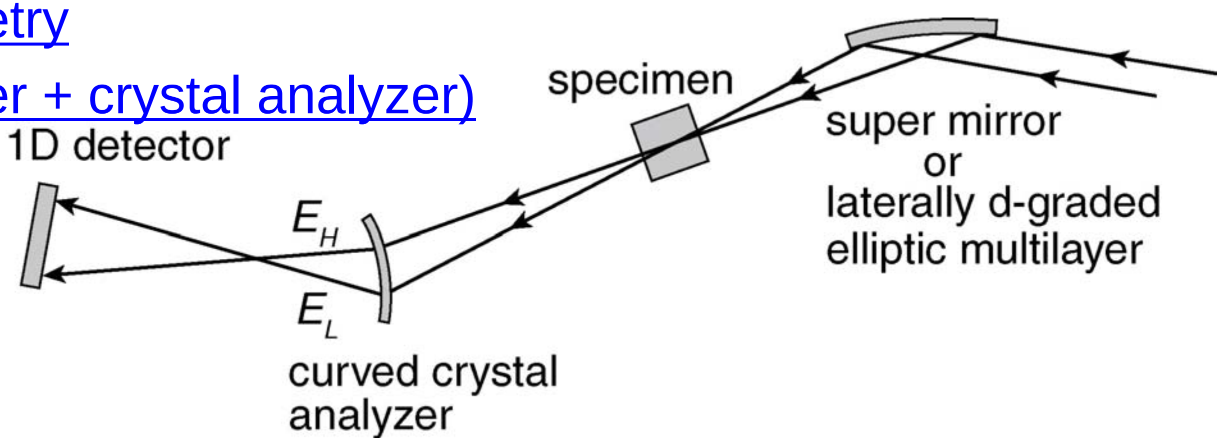
The results look encouraging. But, further improvements are necessary.

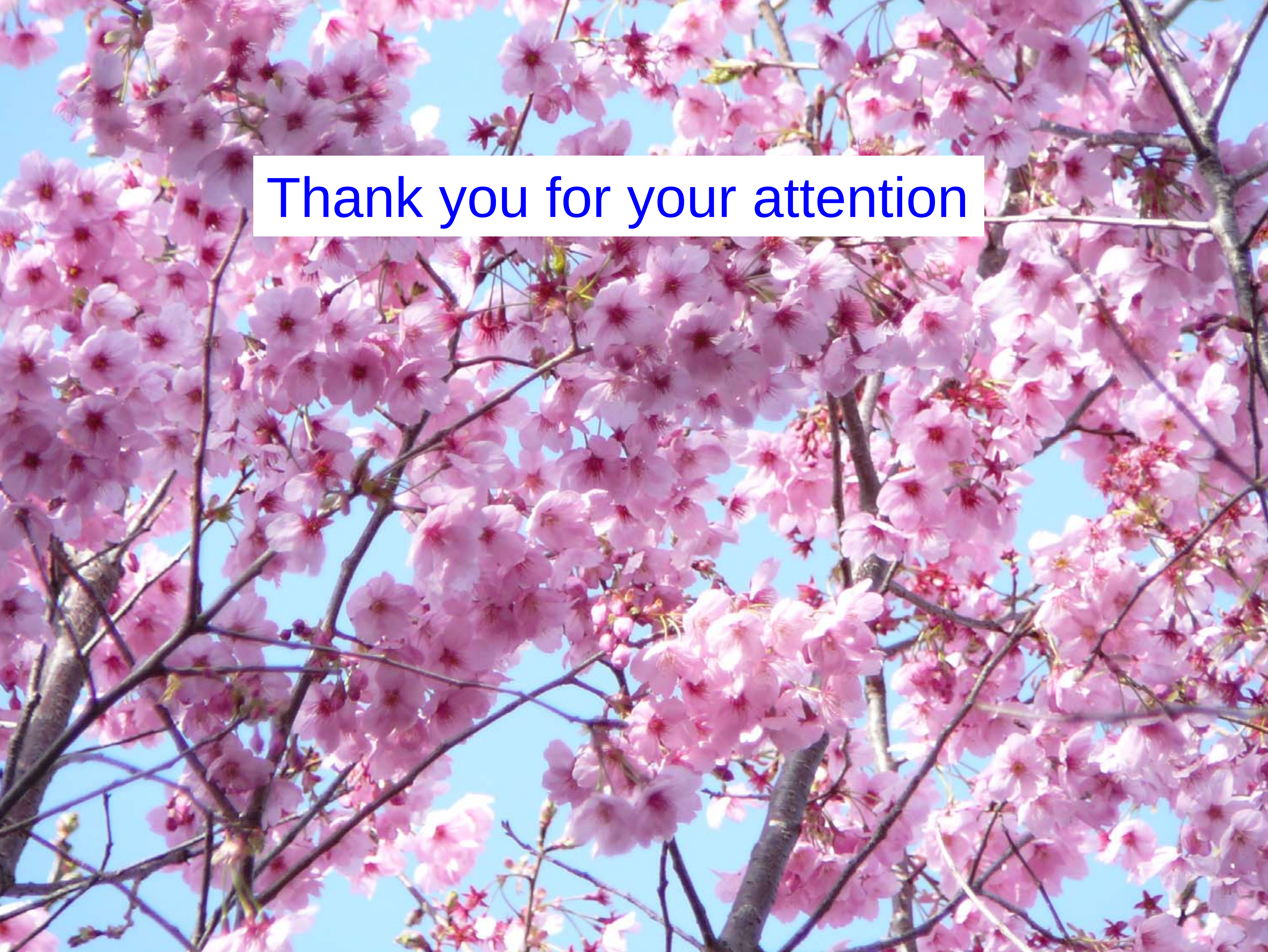
- Wide energy range (~5 keV - ~30 keV) covered.
- Relatively small focus (~0.2 mm) achieved.
- Reflectivity down to 10^{-4} recorded.
- Reflectivity from a liquid surface measured.

- Have to correct the very non-uniform intensity distribution of the X-ray beam on the detector surface.
- More smooth energy scale curve necessary – better control of surface d-variation of multilayers.
- Rejection of low energy specular reflection from multilayers.
- have to improve resolution (2-3 times better).
- One- or Two–dimensional detector with independent energy window for each pixel will drastically improve the data quality.
- Development of a super mirror is necessary to deflect the X-ray beam downward for the study of liquid surface.

combined geometry

(graded multilayer + crystal analyzer)




Thank you for your attention