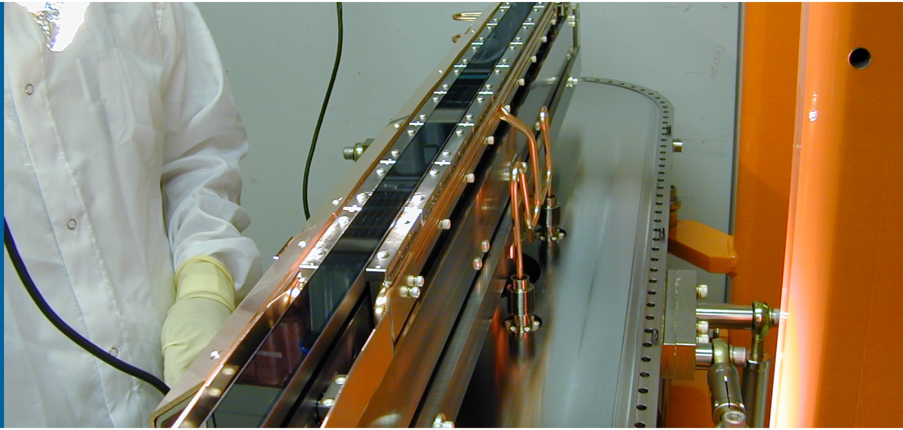
25th Annual NXSchool

OPTICAL COMPONENTS FOR HARD X-RAY SYNCHROTRON RADIATION SOURCES



DENNIS MILLS
Deputy Associate Laboratory Director
Advanced Photon Source

National School for Neutron and X-ray Scattering
August 2023

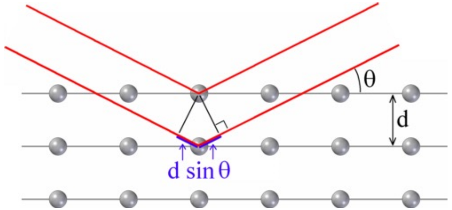
Outline of Presentation

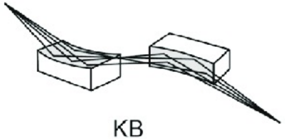
1. Historical Perspectives
2. Why Do We Need Optics?
3. X-ray Mirrors (Reflective Optics)
4. X-ray Lenses (Refractive Optics)
5. Single Crystal, Multilayers & Zone Plates (Diffractive Optics)
6. High Heat Load Optics (monochromators)

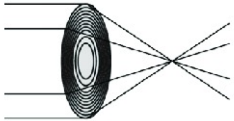
I will not be discussion gratings as they are used in the soft x-ray region of the spectrum and the focus of this talk will be hard x-ray optics.

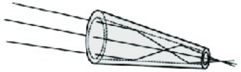
X-RAY PHYSICS AND X-RAY OPTICS

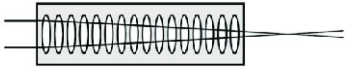
- The first time the term “X-ray Optics” was used (that I could find in the literature) was in Compton’s 1927 Nobel Prize lecture: *“X-rays as a Branch of Optics”*
  - *One of the most fascinating aspects of recent physics research has been the gradual extension of familiar laws of optics to the very high frequencies of X-rays, until at the present there is hardly a phenomenon in the realm of light whose parallel is not found in the realm of X-rays. Reflection, refraction, diffuse scattering, polarization, diffraction, emission and absorption spectra, photoelectric effect, all of the essential characteristics of light have been found also to be characteristic of X-rays….*
  - *It has not always been recognized that X-rays is a branch of optics. As a result of the early studies of Röntgen and his followers it was concluded that X-rays could not be reflected or refracted, that they were not polarized on traversing crystals, and that they showed no signs of diffraction on passing through narrow slits. In fact, about the only property which they were found to possess in common with light was that of propagation in straight lines.*

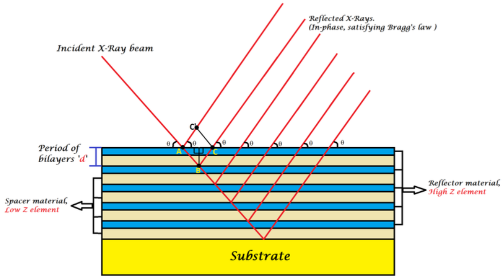



KB


FZP


Capillaries


CRL

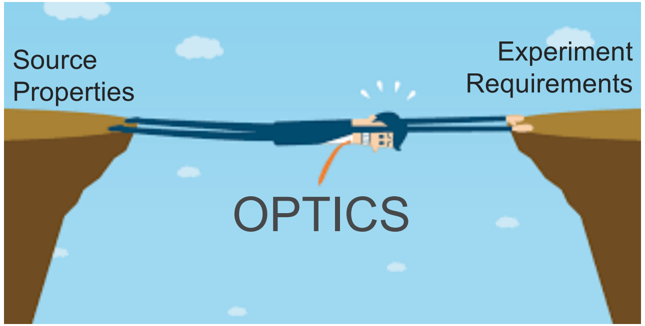


Argonne NATIONAL LABORATORY

OPTICS BRIDGE THE SOURCE AND EXPERIMENT

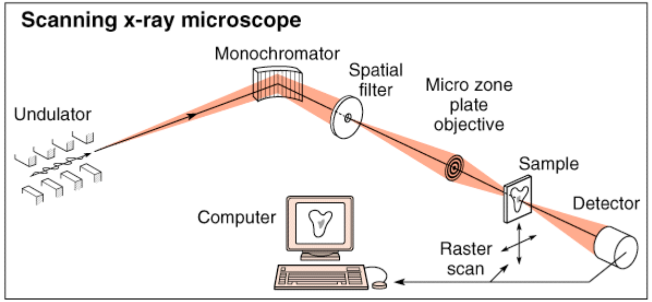
Source Properties

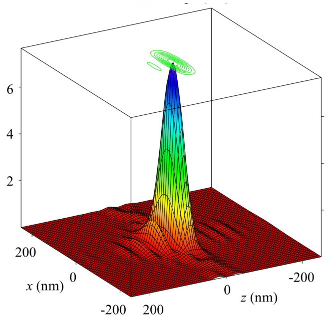
- x-ray energy ranges from BMs and IDs
- x-ray intensity
- emittance of the source
- degree of coherence
- polarization*

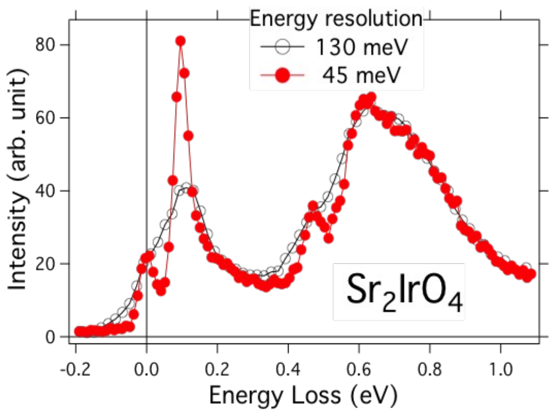


Experiment Requirements

- photons/sec on sample
- beam size
- collimation
- energy resolution (ΔE/E)
- coherence
- polarization*



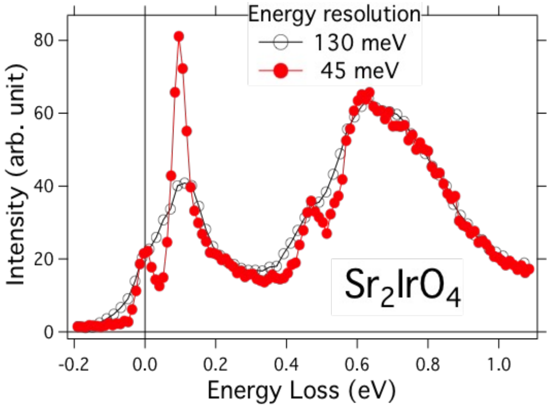




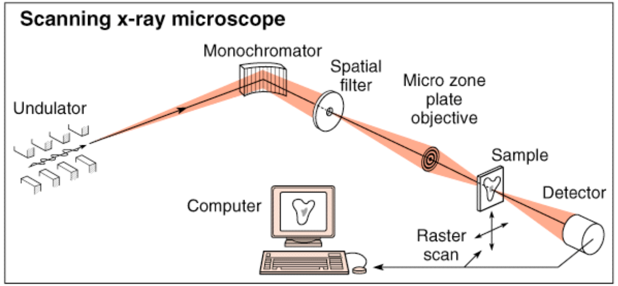
*Production of polarized (linear, circular, etc) beams is often accomplished by using specialized insertion devices and will not be covered in this talk.

WHY X-RAY OPTICS?

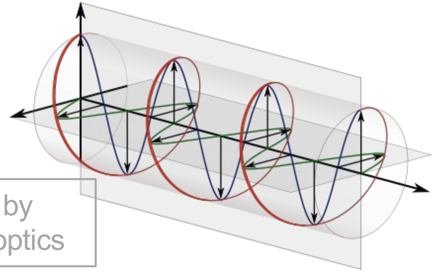
- Control the energy (E) and bandwidth (ΔE) of the beam.
  - **ΔE = 1-2 keV** @ 10 keV; $\Delta E/E = 10^{-1}$ (wide bandpass to increased flux for time-resolved studies – lectures latter this week)
  - **ΔE = 1-2 eV** @ 10 keV; $\Delta E/E = 10^{-4}$ (typical diffraction exp.)
  - **ΔE = a few milli-eV** @ 10 keV; $\Delta E/E = 10^{-7}$ (inelastic scattering – lecture on Monday)



- Control the size/divergence of the beam (often related).
  - Micro- or nano-beams (spot sizes microns to 10's of nanometers)
  - Highly collimated beams



- Control the polarization of the beam.
  - Linear
  - Circular (magnetic x-ray scattering or spectroscopy)



Now typically done by the ID and not the optics

REFLECTIVE OPTICS:
X-RAY MIRRORS

INDEX OF REFRACTION FOR X-RAYS: N < 1

- This expression for the (real part) of the index of refraction, n, is:

$$n = [1 - (n_e(e^2/mc^2)\,\lambda^2/\pi)]^{1/2} \approx 1 - (n_e r_e/2\pi)\lambda^2$$

is usually written as:

$$n = 1 - \delta, \quad \text{where} \quad \delta = (n_e r_e/2\pi)\lambda^2.$$

varies as the density and the square of the wavelength.

and $r_e = (e^2/mc^2)$ is the classical radius of the electron (2.82×10^{-13} cm), n_e is the electron density, and λ is the wavelength of the x-ray.

- When you plug in the numbers for the real part of the index of refraction you find:

$$\boldsymbol{\delta = 10^{-5} \text{ to } 10^{-6}}$$

- So you have:
  - **an index of refraction less than one**
  - **differing from unity by only a few ppm**

This simple treatment did not include any absorption. A more detailed calculation would result in an expression:

$$n = 1 - \delta - i\beta$$

Where $\beta = \lambda\mu/4\pi$, with μ the linear absorption coefficient ($I = I_o e^{-\mu t}$).

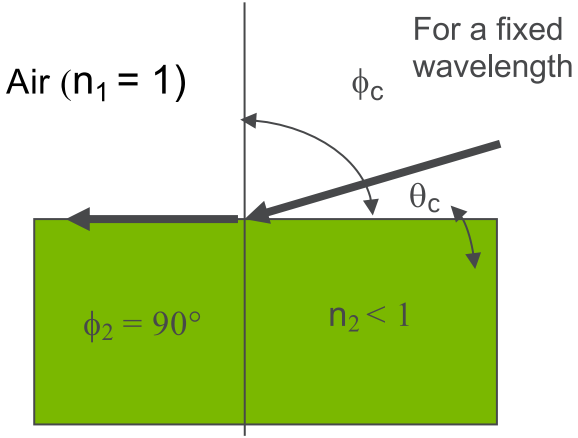
CRITICAL ANGLE FOR TOTAL EXTERNAL REFLECTION

- Let an x-ray (in vacuum, where $n_1 = 1$) impinge on a material with index of refraction n_2. From Snell's Law (when $\phi_2 = 90°$), we have:

$$n_1 \sin(\phi_c) = n_2 \sin(90°);$$

$$\cos(\theta_c) = n_2 \cos(0) \quad (\theta = 90° - \phi)$$

$$\cos(\theta_c) = n_2$$



Because the n <1, the refracted x-rays bends away from the surface normal. For visible light where n>1, the rays bend toward the normal.

- Expanding the cosine of a small angle and substituting for n_2 in the above equation gives:

$$\mathbf{1 - \tfrac{1}{2}(\theta_c)^2 = 1 - \delta}$$

$$\boldsymbol{\theta_c = (2\delta)^{1/2}}$$

Recall that the typical values for δ at 1 Å is 10^{-5} to 10^{-6} and so the critical angle is going to be about 10^{-3} or a few milliradians

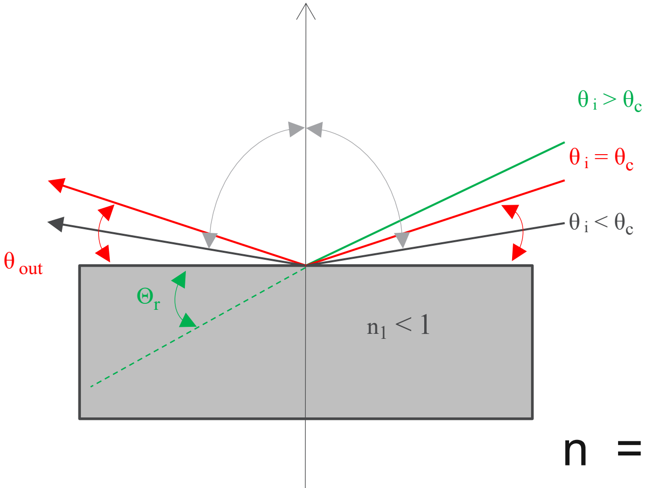
θ_c is the so-called **critical angle**, the angle at which there is **total external reflection** and the material behaves like a mirror.

X-RAY REFLECTIVITY

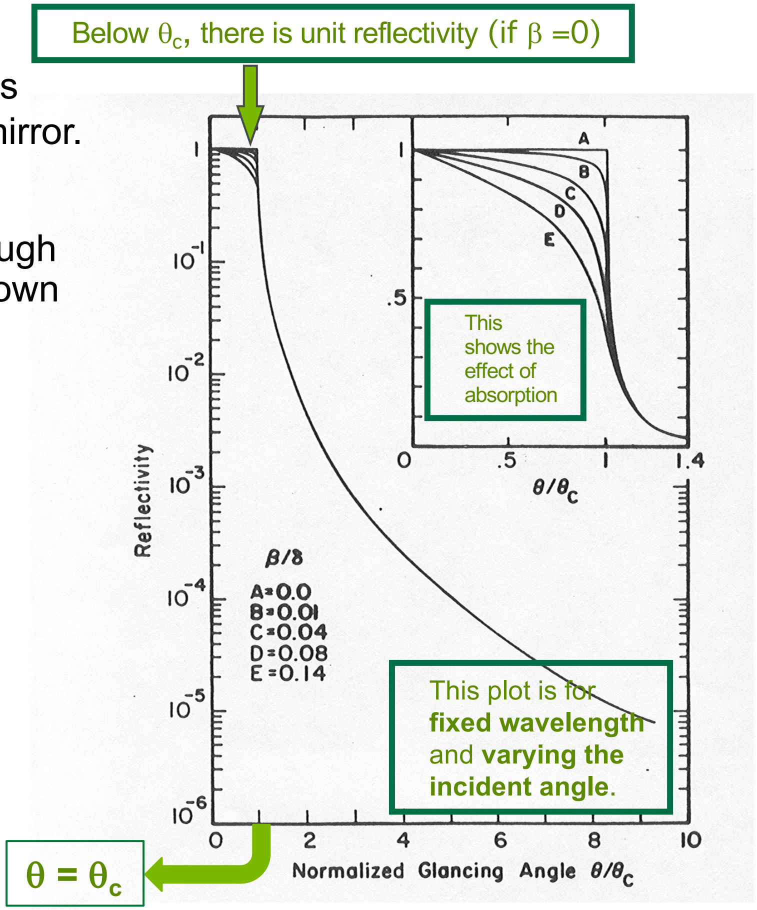
- θ_c is the so-called **critical angle**, the angle at which there is **total external reflection** and the material behaves like a mirror.

$$\theta_c = (2\delta)^{1/2}$$

- The amplitude of the reflected wave can be determined through the Fresnel equations. Sparing you the details, it can be shown that:
  - **Below θ_c, there is unit reflectivity** (when β, the absorption, equals 0)
  - **Above θ_c, the reflectivity falls rapidly**



$$n = 1 - \delta - i\beta$$



PHYSICAL REVIEW VOLUME 95, NUMBER 2 JULY 15, 1954

Surface Studies of Solids by Total Reflection of X-Rays*

L. G. Parratt
Cornell University, Ithaca, New York

(Received March 22, 1954)

ENERGY CUTOFF FOR A FIXED ANGLE-OF-INCIDENCE MIRROR

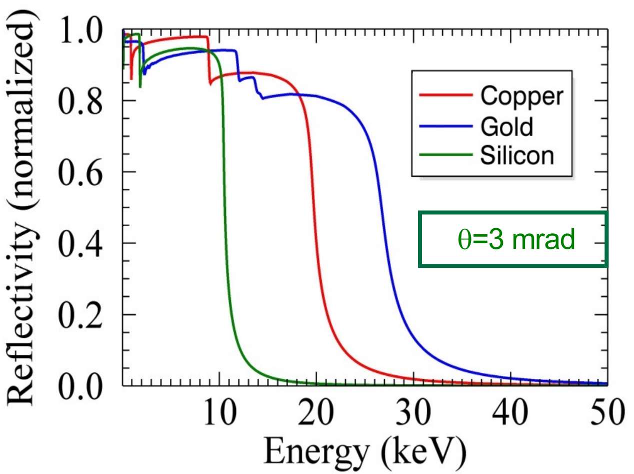
- Often mirrors are used as first optical components. This means a **polychromatic incident beam strikes the mirror at some fixed angle.**

- The relationship for the critical angle and wavelength can be re-written, for a **fixed angle of incidence** θ, in terms of a cut-off wavelength, $\lambda_{cut\ off}$, where wavelengths above $\lambda_{cut\ off}$ are reflected and those below $\lambda_{cut\ off}$ are not. Since $E = hc/\lambda$, I can re-write this and get a relationship for a **fixed incident angle, θ, and determine the maximum, or cut-off energy, $E_{cut\ off}$, that will be totally reflected by the mirror.**

$$\theta_c = (2\delta)^{1/2} = \lambda(n_e r_e/\pi)^{1/2}$$

$$E_{cut\ off} = hc/\lambda_{cut\ off} = (hc/\theta)(n_e r_e/\pi)^{1/2}$$

Cut-off energy, $E_{cut\ off}$ for fixed angle θ



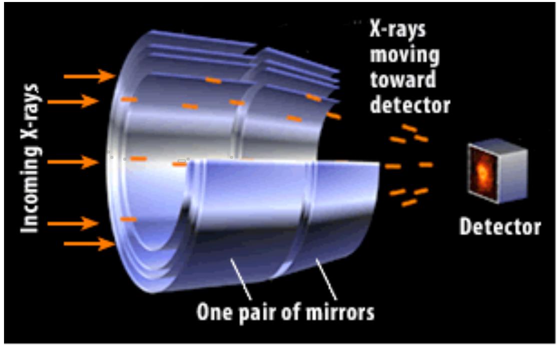
For a fixed angle of incidence, you can vary the cut-off energy by coating the mirror with materials of different electron densities, n_e.

GRAZING INCIDENCE X-RAY MIRRORS

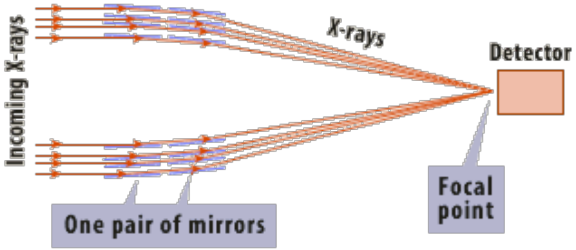
- Because the incidence angle are small (a few milliradians) to capture the full extent of the beam (about 1 mm or so), x-ray mirrors tend to be very long (sometimes over a meter).

- Low-pass filters
  - mirrors can be used to effectively suppress high energies
  - mirrors are designed so that the cutoff energy, $E_{cut\ off}$, can be varied by having several different coatings deposited on the mirror substrate

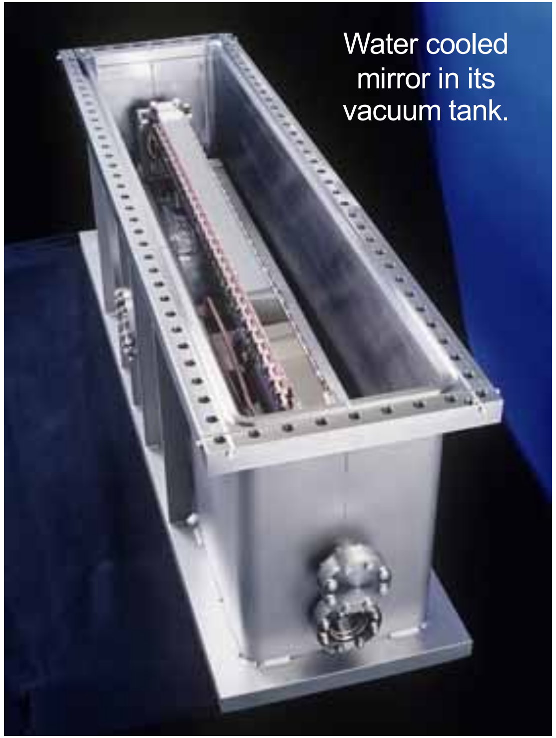
- Mirrors can effectively remove a considerable amount of the heat from the incident (polychromatic) beam and reduce the thermal loading on downstream optics.



Courtesy Chandra mission website: http://chandra.harvard.edu



Chandra's mirrors are positioned so they're almost parallel to the entering X-rays. The mirrors look like open cylinders, or barrels. The X-rays skip across the mirrors much like stones skip across the surface of a pond.

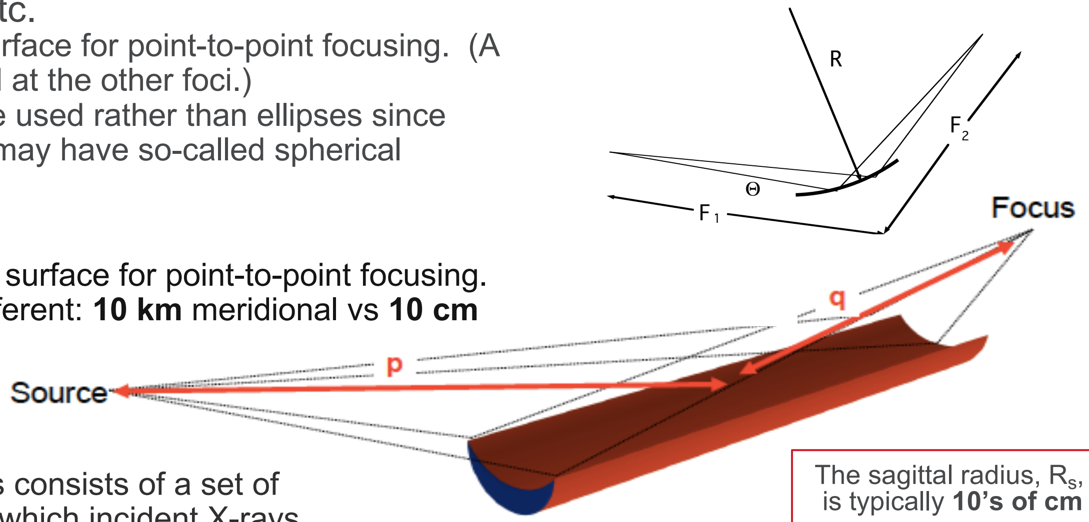


Most mirrors are made from silicon coated with one or multiple stripes of high-Z material after polishing.

Argonne NATIONAL LABORATORY

MIRRORS AS FOCUSING ELEMENTS

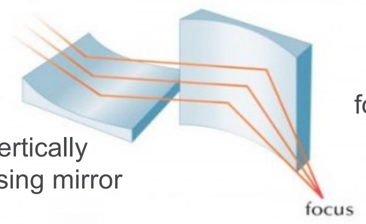
Typical meridional radius, R, is around **10’s of kilometers.**



- **One-dimensional focusing**, collimating, etc.
  - An ellipse is the ideal shape for a reflecting surface for point-to-point focusing. (A source at one foci of the ellipse will be imaged at the other foci.)
  - In many cases cylindrically shaped mirrors are used rather than ellipses since they are considerably easier to fabricate (but may have so-called spherical aberrations).
- **Two -dimensional focusing**
  - An ellipsoid is the ideal shape for a reflecting surface for point-to-point focusing.
  - However, the radii of curvature are widely different: **10 km** meridional vs **10 cm** sagittal
  - Very difficult to fab a mirror like this

The sagittal radius, R_s, is typically **10’s of cm**

- **Kirkpatrick – Baez (KB) geometry**
  - Another system that focuses in two dimensions consists of a set of **two orthogonal singly focusing mirrors**, off which incident X-rays reflect successively, as first proposed in 1948 by Kirkpatrick and Baez (KB).
  - This system allows for easier fabrication of the mirrors and is used frequently at synchrotron sources.



Horizontally focusing mirror

Vertically focusing mirror

Mirrors are achromatic, i.e. the focal length is independent of x-ray wavelength.

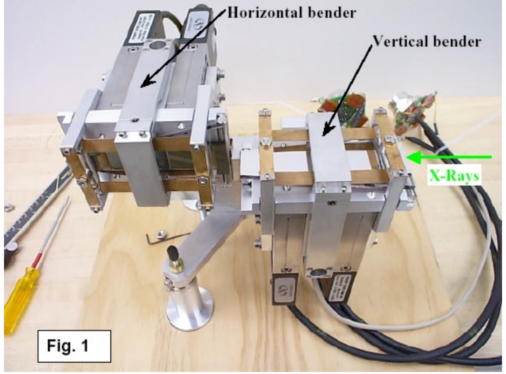
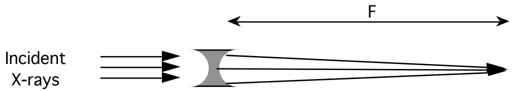


Fig. 1

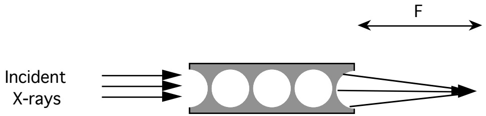
Argonne NATIONAL LABORATORY

REFRACTIVE OPTICS:
X-RAY LENSES

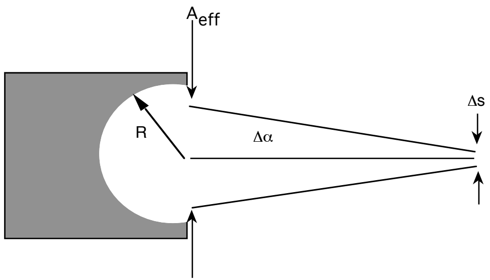
COMPOUND REFRACTIVE LENSES



Single Refractive Lens



Compound Refractive Lens



These are chromatic, i.e. the focal length is dependent on x-ray wavelength since δ is a function of λ.

- The Lens Maker's Equation for x-rays still applies:

$$1/F = \delta\,(1/R_1 + 1/R_2 + \text{etc.})$$

- For a single lens:

$$1/F = \delta(1/R + 1/R) \quad \text{or} \quad F = R / 2\delta$$

this is for a lens with 2 curved surfaces

- If we have N surfaces, all with radius R:

$$F = R/2N\delta$$

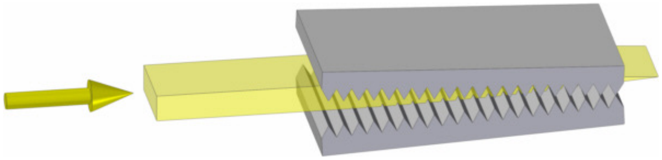
- Using the same numbers as before but with 50 lenses, i.e.:

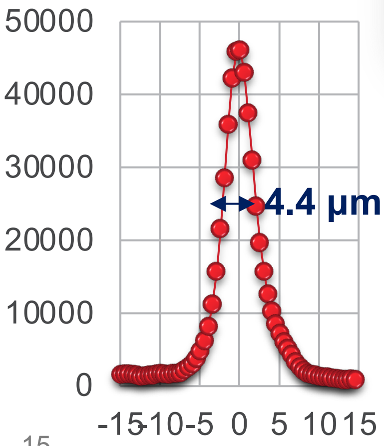
$$R = 1\text{ mm} \quad \delta \approx 10^{-5} \quad N = 50$$

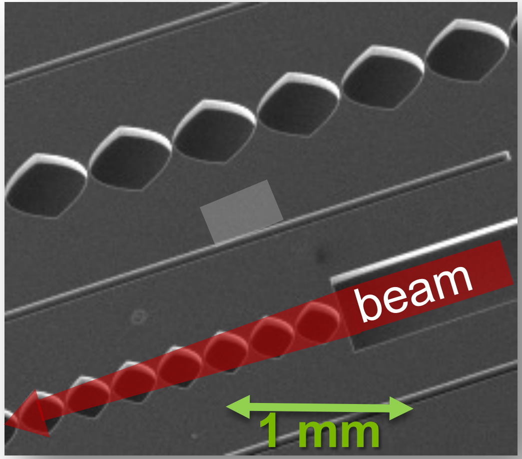
- Then the focal length, F, would be at 1 m.
- These lenses focus at rather larger distances and are well adapted to the scale of synchrotron radiation beamlines.

FOCUSING IN ONE DIMENSIONS WITH REFRACTIVE LENSES

- Planar technologies
  - Leverage planar technologies from micro-electronics industry
  - Fabricate compound lens systems in a small space
  - Small radius means moderate focal spots with a single lens or nano-focusing with a moderate number of lenses





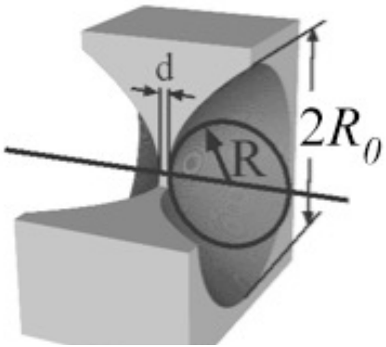


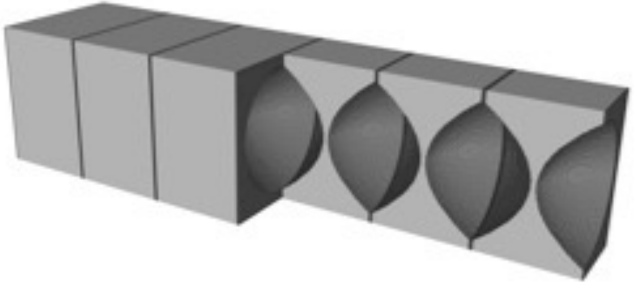
Parabolic lenses etched 400 µm deep into Si wafer made at CNM and tested at APS. The gray shaded area is one lens. At left is focusing performance at 87 keV.

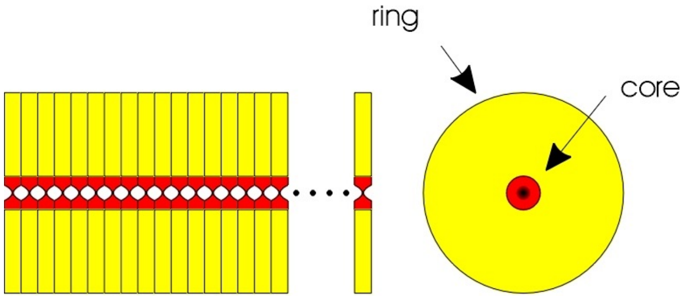
- Sawtooth lenses
  - The amount of lens material projected on the lateral plane is a (nearly) parabolic profile.
  - By varying angle between the plates one can keep focal length fixed as energy is changed or to vary the focal length.

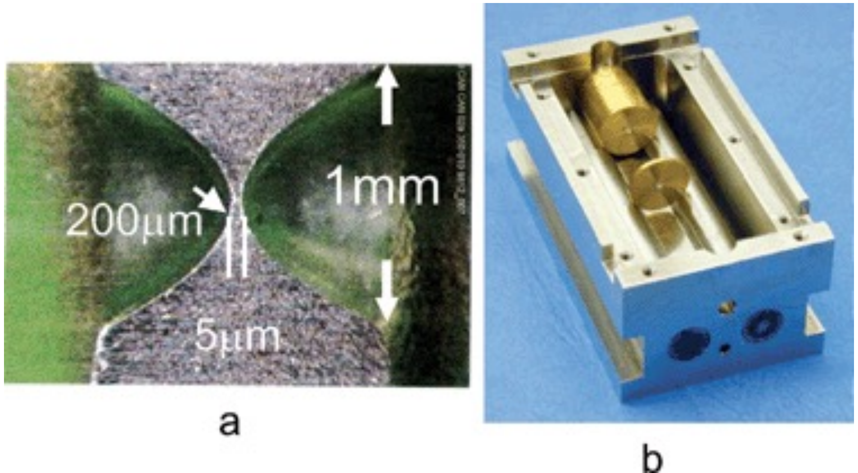
FOCUSING IN TWO DIMENSIONS WITH REFRACTIVE LENSES

- 2-D lenses typically “embossed” and made from Be, Al or Ni
- Spherical lenses are easy to make but suffer from spherical aberrations.
- Paraboloids eliminate spherical aberrations.





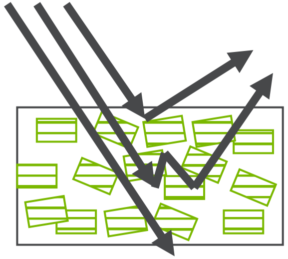




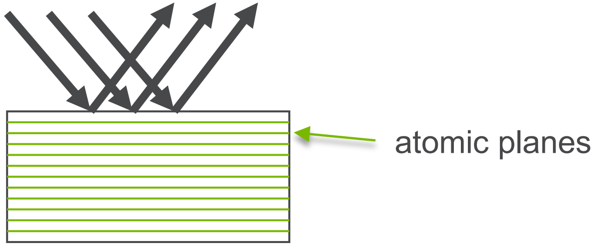
DIFFRACTIVE OPTICS: SINGLE CRYSTALS, MULTILAYERS & ZONE PLATES

DIFFRACTION FROM PERFECT CRYSTALS

- The theory that describes diffraction from perfect crystals is called **dynamical diffraction theory** (as compared with kinematical theory, which describes diffraction from imperfect or mosaic crystals) first proposed in 1914 by C. G. Darwin in two seminal papers.



Mosaic crystal model



Perfect crystal model

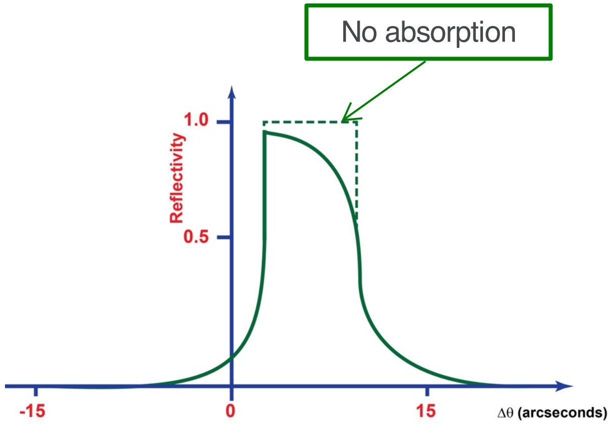
http://www.eoht.info/page/C.G.+Darwin

- In the case of a strong reflection from a perfect crystal of a monochromatic x-ray beam, the penetration of the x-rays into the crystal is not limited by the (photoelectric) absorption, but the beam is attenuated due to the reflecting power of the atomic planes. (This type of attenuation is called "extinction".) *" if the crystal is perfect all the radiation that can be reflected is so, long before the depth at which the rays at a different angle are appreciably absorbed."*

Aside: C. G. Darwin was the first to calculate the index of refraction for x-rays. Charles G. Darwin was the grandson of the "more famous" Charles Darwin of evolution fame.

TWO CONSEQUENCES OF LIMITED PENETRATION IN DIFFRACTION FROM PERFECT CRYSTALS

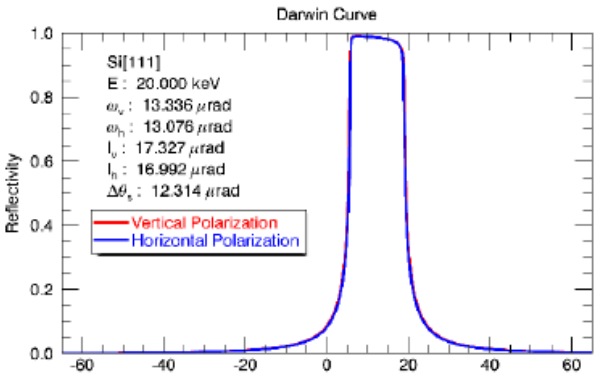
- The limited penetration due to extinction (reflection by the atomic planes) means at the Bragg condition, the x-ray beam is limited in the number of atomic planes it "experiences".
- Consequence #1:
  - There is a finite angular width over which the diffraction occurs. This is is often called the ***Darwin width***, ω_D
  - Depends on the strength of the reflection, F(hkl), and square of the wavelength, λ^2.
- Consequence #2:
  - The reflectivity over this narrow angular width is nearly unity, even in crystals with a finite absorption.

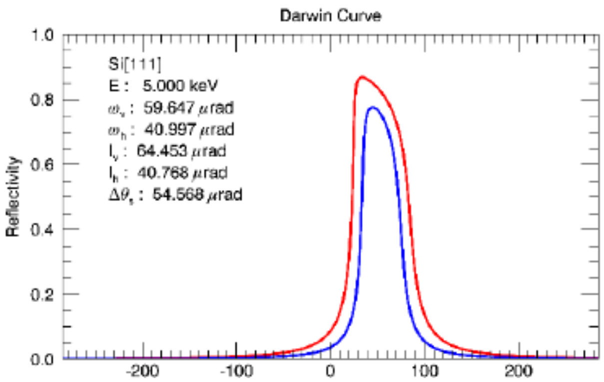


Using modern notation, Darwin width, ω_D, can be written as:

$$\omega_D = 2r_eF(hkl)\lambda^2/\pi V\sin(2\theta)$$

F(hkl) = structure factor and
V = volume of unit cell





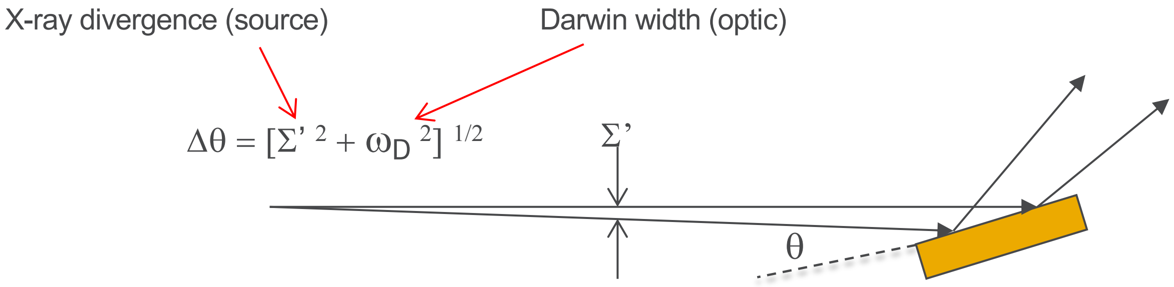
PERFECT CRYSTAL X-RAY MONOCHROMATORS

- Simply use Bragg's Law to select a particular wavelength (or energy)

$$\lambda = 2d \sin(\theta).$$

- If we differentiate Bragg's Law ($\Delta\lambda = \cos(\theta)\ \Delta\theta$), divide this by the original equation and recall that $\Delta\lambda / \lambda = \Delta E/E$ for small deltas, then we can determine the energy resolution of the monochromator.

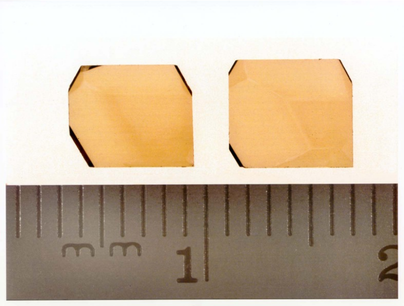
$$\Delta\lambda / \lambda = \Delta E/E = \cot(\theta)\ \Delta\theta$$



$$\Delta\theta = [\Sigma'^{\,2} + \omega_D^{\,2}]^{1/2}$$

- At 8 keV (1.5Å) for Si(111) $\omega_D \approx 40$ microradians. Recall that, for an APS undulator, the opening angle is about 5-10 microradians.
- In this case the energy resolution of the mono is determined by the crystal. Plugging in the values you get **$\Delta E/E = 10^{-4}$.** So for at 8 keV x-ray the bandwidth (or ΔE) would be about 0.8 eV.

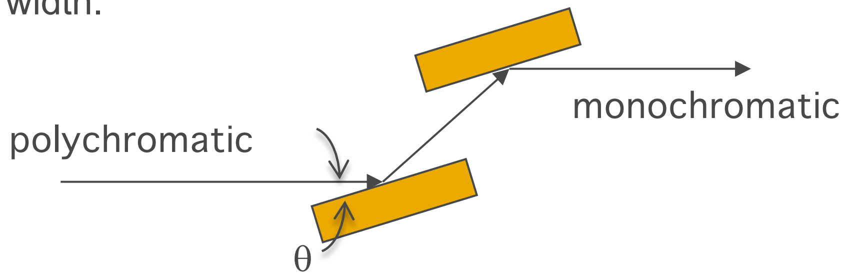
Silicon is used for monochromtor crystals as as it can be easily obtained and has good thermo-mechanical properties for cooling.



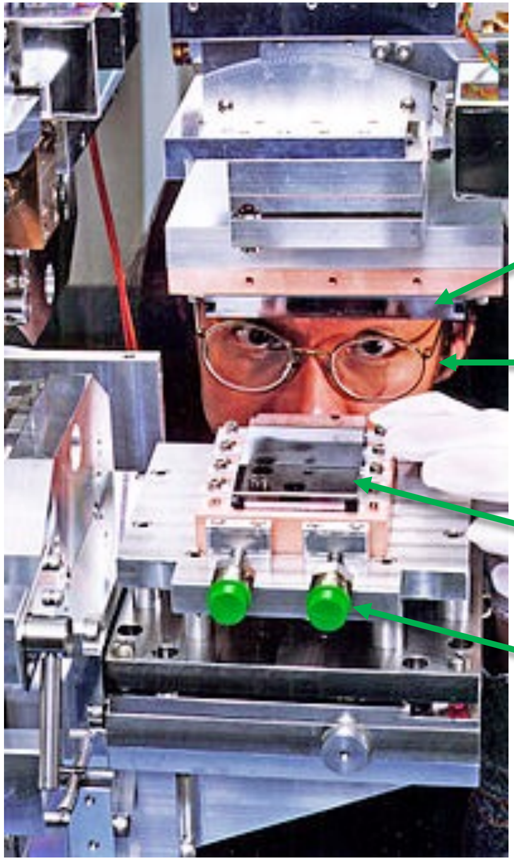
Synthetic diamonds are also a good choice but much harder to find with the required quality

DOUBLE CRYSTAL MONOCHROMATORS

- The most common arrangement for a monochromator is the double-crystal monochromator (DCM). It:
  - is **non-dispersive**, that is all rays that diffract from the first crystal simultaneously diffract from the second crystal (if same crystals with same hkl's are used)
  - **keeps the beam parallel to the incident beam** as the energy is changed (by changing the Bragg angle, θ).
- There is little loss in the throughput using two crystals because the reflectivity is near unity over the Darwin width.



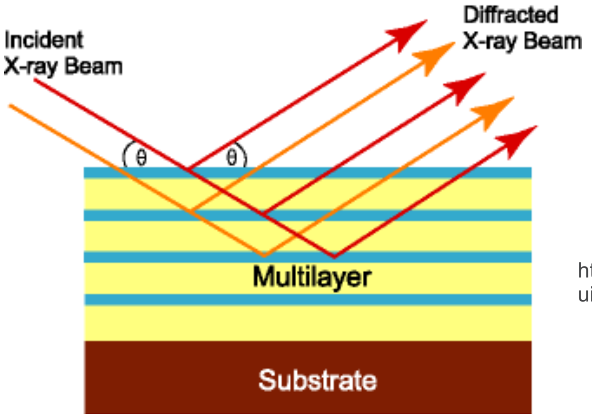
- Monochromators need to be cooled to maintain the desired properties.
  - Silicon monos are often liquid N_2 cooled to enhance thermal properties (higher conductivity and coefficient of thermal expansion goes through a zero at about 120° K) so that distortion from the high-power x-ray beams from undulators is minimized.



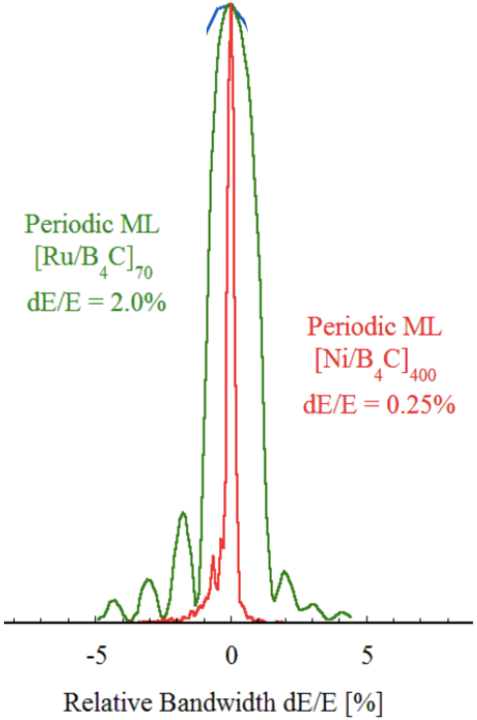
polychromatic beam going into the slide

HARD X-RAY MULTILAYER OPTICS

- A “periodic multilayer” coating is a film stack comprising a number of identical repetitions of two or more optically dissimilar component layers.
  - Wide energy band-pass
  - Focusing : θ_B multilayer >> θ_c mirror so multilayer length << mirror length
  - Increased numerical aperture
- The energy is selected using Bragg’s Law.
- The energy bandwidth is determined by the number of layers N; $\Delta E/E \approx 1/N$.



http://xray0.princeton.edu/~phil/Facility/Guides/XrayDataCollection.html



Calculated bandwidth from 2 different multilayers:

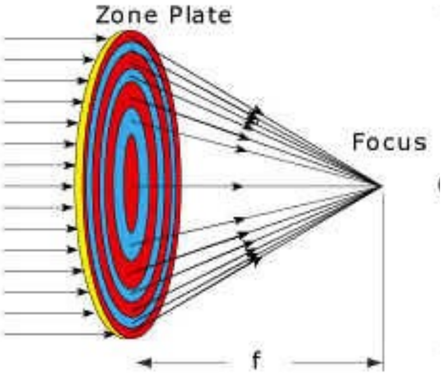
- Green: 70 layers of Ru/B_4C; $\Delta E/E = 2\%$
- Red: 400 layers of Ni/B_4C; $\Delta E/E = 0.25\%$

Argonne NATIONAL LABORATORY

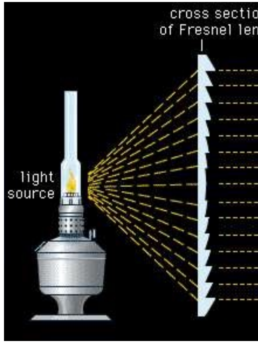
FRESNEL ZONE PLATES

- The focusing capability is based on constructive interference of the wavefront modified by passage through the zone plate. The wave that emerges from the zone plate is the superposition of spherical waves, one from each of the zones.
- In general, the size of the **focal spot from the zone plate, Δs**, is determined by the width of the outermost ring, Δr_n , and is given by:

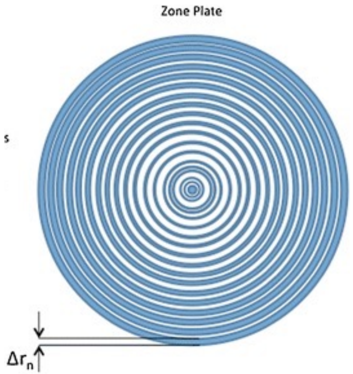
$$\Delta s = 1.22\ \Delta r_n$$

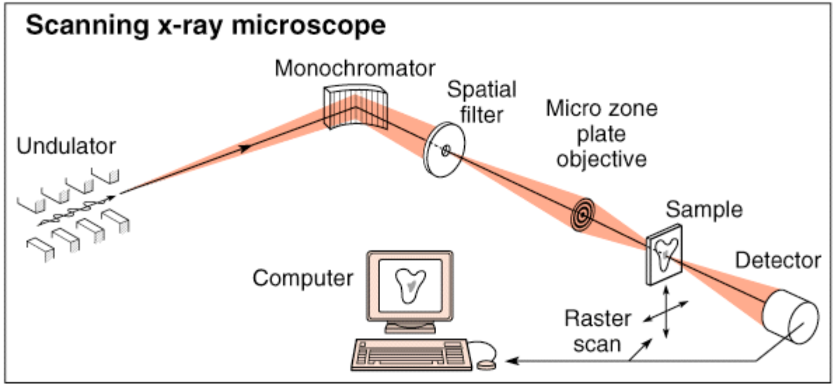


Zone plates satisfy the condition that the pathlength varies by $\lambda/2$ for each ring. They are composed of alternating concentric zones of two materials with different (complex) refractive indices.



Zone plates are chromatic, i.e. the focal length is dependent on x-ray wavelength.

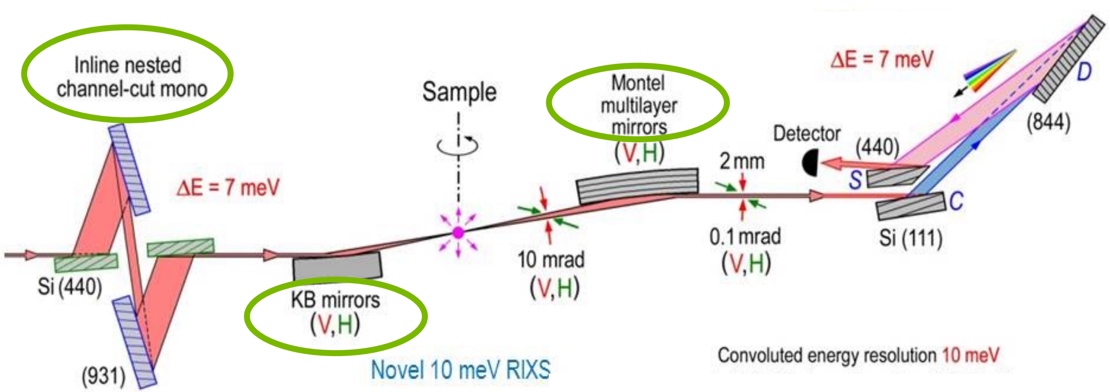




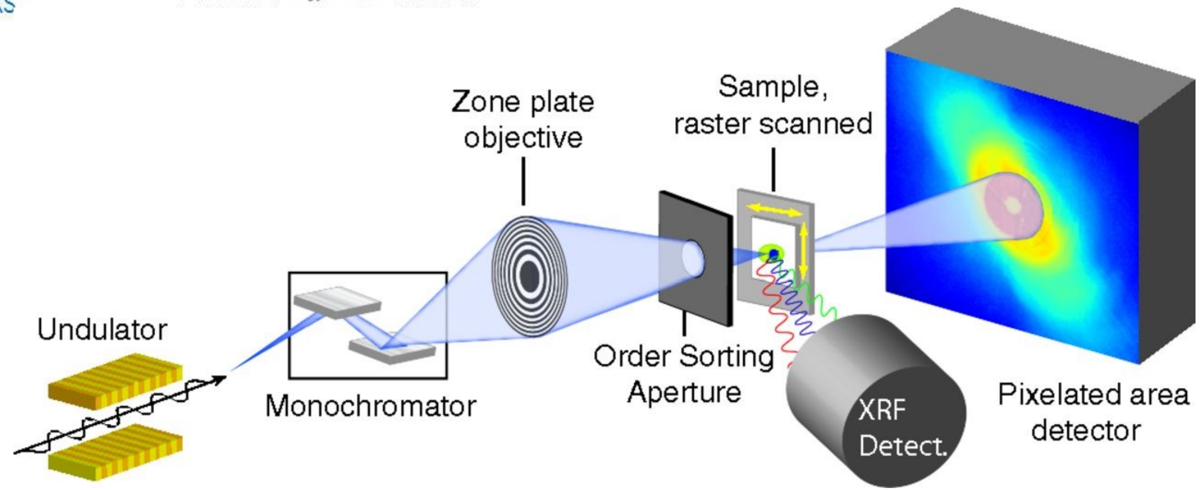
Cape Meares Lighthouse (Oregon); first-order Fresnel lens

The challenge in making zone plates for hard x-rays is making Δr_n small while maintaining a high thickness for efficiency, i.e. you need to have a high aspect ratio – very challenging!!!!

VARIOUS OPTICAL COMPONENTS ARE OFTEN FOUND IN A SINGLE BEAMLINE



Design of an ultrahigh-resolution crystal monochromator and analyzer (from sub-10 meV to sub-meV) for inelastic x-ray scattering.



Schematic layout of a scanning x-ray microscope (Bio-nanoprobe) at the APS.

HIGH HEAT LOAD X-RAY OPTICS

THERMAL LOADING ON OPTICAL COMPONENTS

- Along with the enormous increase in x-ray beam brilliance from insertion devices comes unprecedented powers and power densities that must be effectively handled so that thermal distortions in optical components are minimized and the full beam brilliance can be delivered to the sample.

Process	Approx. Heat Flux (W/mm^2)
Interior of rocket nozzle	10
Commercial plasma jet	20
Fusion reactor components	0.05 to 80
Meteor entry into atmosphere	100 to 500
APS Undulator @ 30m (on-axis 2.4 m 100 mA)	10 to 160

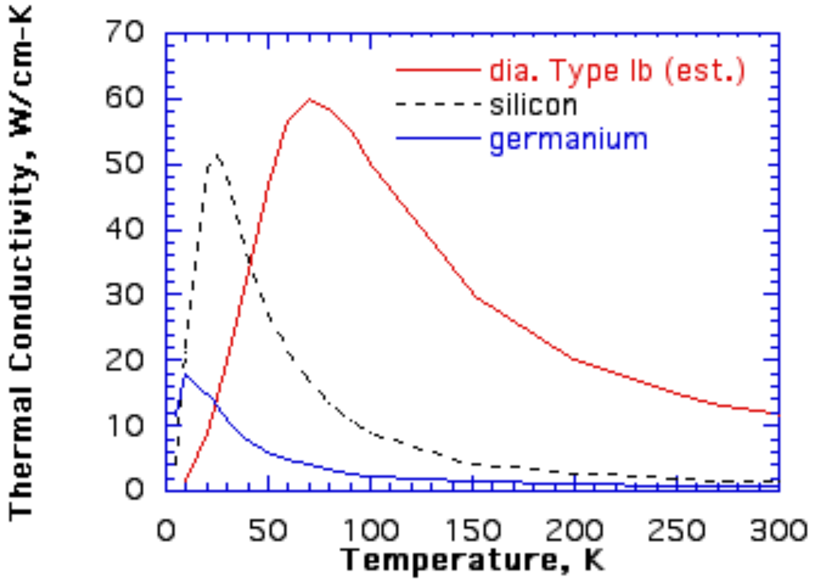
In order to maintain the beam intensity and collimation (i.e., brightness) through the optics, special attention must be paid to the issue of thermal management for those first optical components.

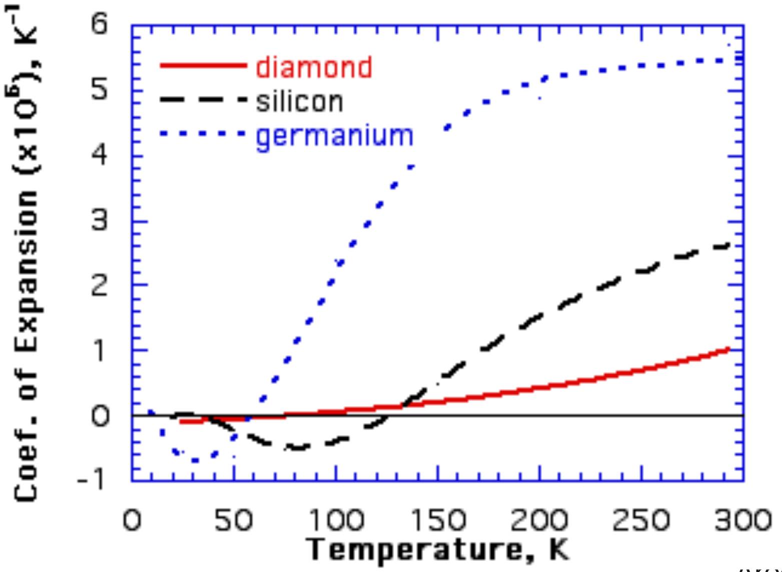
PROPERTIES OF SI, GE, AND C(DIAMOND)

Thermal gradients, ΔT, and coefficient of thermal expansion, α, contribute to crystal distortions:

$$\alpha \Delta T = \Delta d/d$$

We therefore need to look for materials that have a very low coefficient of thermal expansion, α, and/or have a very high thermal conductivity, k, so that the material cannot support large ΔT's.





MINIMIZING DISTORTION OF OPTICAL COMPONENTS – THERMAL MANAGEMENT

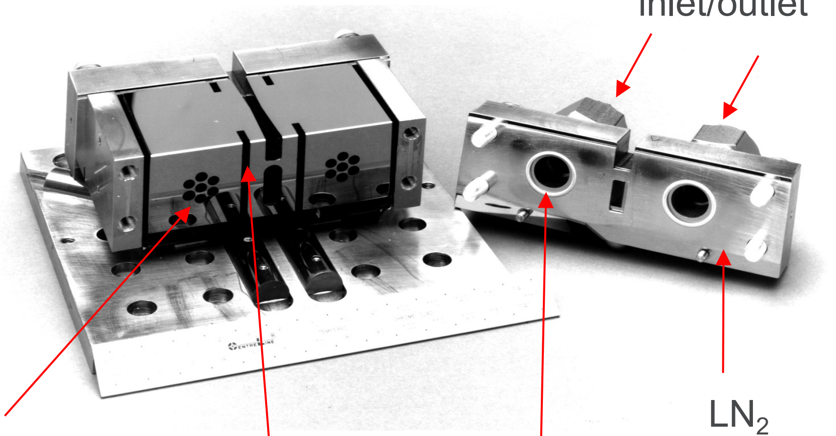
FOM of Typical Monochromator Materials

Material and Temperature	Thermal Conductivity (k)	Coef. Thermal Expansion (α)	Figure of Merit FOM (k/α)
Si (300K)	1.2 W/cm-K	2.3×10^{-6} /K	0.5
Si (78K)	14 W/cm-K	-0.5×10^{-6} /K	28
Dia. (300K)	20 W/cm-K	0.8×10^{-6} /K	25

These properties motivate us to use cryogenically cooled silicon or room temperature diamond as high heat load monochromators.

LN_2 COOLED Si MONOCHROMATORS

Cryogenically (LN_2) Cooled Si Mono

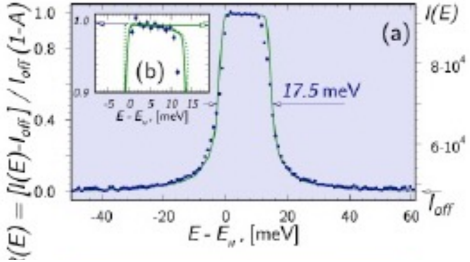


The historical development of cryogenically cooled monochromators for third-generation synchrotron radiation sources, Bilderback, Freund, Knapp, and Mills, J. Synch. Rad. **7**, 2000.

Liquid nitrogen pump

SUMMARY

- X-ray optics is an active area of research at both universities and national laboratories.
- High-brightness sources provide new opportunities but ever higher demands on the quality of optics to ensure beam coherence is preserved through the optics.
- Metrology is key to making good optics – **" You Can't Improve What You Can't Measure"**



LETTERS
PUBLISHED ONLINE: 17 JANUARY 2010 | DOI: 10.1038/NPHYS1506
nature physics

High-reflectivity high-resolution X-ray crystal optics with diamonds

Yuri V. Shvyd'ko[1]★, Stanislav Stoupin[1], Alessandro Cunsolo[1,2], Ayman H. Said[1] and Xianrong Huang[2]

LETTERS
PUBLISHED ONLINE: 22 NOVEMBER 2009 | DOI: 10.1038/NPHYS1457
nature physics

Breaking the 10 nm barrier in hard-X-ray focusing

Hidekazu Mimura[1]★, Soichiro Handa[1], Takashi Kimura[1], Hirokatsu Yumoto[2], Daisuke Yamakawa[1], Hikaru Yokoyama[1], Satoshi Matsuyama[1], Kouji Inagaki[1], Kazuya Yamamura[3], Yasuhisa Sano[1], Kenji Tamasaku[4], Yoshinori Nishino[4], Makina Yabashi[4], Tetsuya Ishikawa[4] and Kazuto Yamauchi[1,3]

SCIENTIFIC REPORTS
OPEN

Interlaced zone plate optics for hard X-ray imaging in the 10 nm range

Received: 18 August 2016

Journal of Applied Physics

Proposal for entangled x-ray beams

Cite as: J. Appl. Phys. **131**, 224401 (2022); doi: 10.1063/5.0091947
Submitted: 18 March 2022 · Accepted: 16 May 2022 · Published Online: 13 June 2022

Stephen M. Durbin[a)]

AFFILIATIONS

Department of Physics & Astronomy, Purdue University, West Lafayette Indiana 47907, USA

Physics Reports 974 (2022) 1–40

Contents lists available at ScienceDirect

Physics Reports

journal homepage: www.elsevier.com/locate/physrep

ELSEVIER

Wavefront preserving X-ray optics for Synchrotron and Free Electron Laser photon beam transport systems

D. Cocco[a,*], G. Cutler[a], M. Sanchez del Rio[b], L. Rebuffi[c], X. Shi[c], K. Yamauchi[d]

[a] Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, 94720, CA, USA
[b] ESRF, 71 Avenue des Martyrs, Grenoble, 38000, France
[c] Argonne National Laboratory, 9700 S. Cass Avenue, Lemont, 60439, IL, USA
[d] Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Osaka, 565-0871, Suita, Japan

REFERENCES

Classics

- *The Optical Principles of the Diffraction of X-rays*, R. W. James, Cornell University Press (1965)
- *X-ray Optics*, H. J. Queisser, Editor, Springer-Verlag (1977)

Hard X-ray Optics

- *Elements of Modern X-ray Physics*, Jens Als-Nielsen and Des McMorrow, John Wiley and Sons (2001).
- *Third Generation Hard X-ray Synchrotron Radiation Sources*, Dennis Mills, Editor, John Wiley and Sons (2002).
- *Dynamical Theory of X-ray Diffraction*, Andre Authier, IUCr Oxford Science Publications (2001).
- *Report of the Basic Energy Sciences Workshop on X-ray Optics for BES Light Source Facilities*, Dennis Mills and Howard Padmore, Co-Chairs, March 27-29, 2013 (http://science.energy.gov/~/media/bes/pdf/reports/files/BES_XRay_Optics_rpt.pdf)

Soft X-ray Optics

- *Soft X-ray Optics*, Eberhard Spiller, SPIE Optical Engineering Press (1994)

QUESTIONS