IFUSP

Physical Solution of the *'Phase Problem'* in X-ray Crystallography

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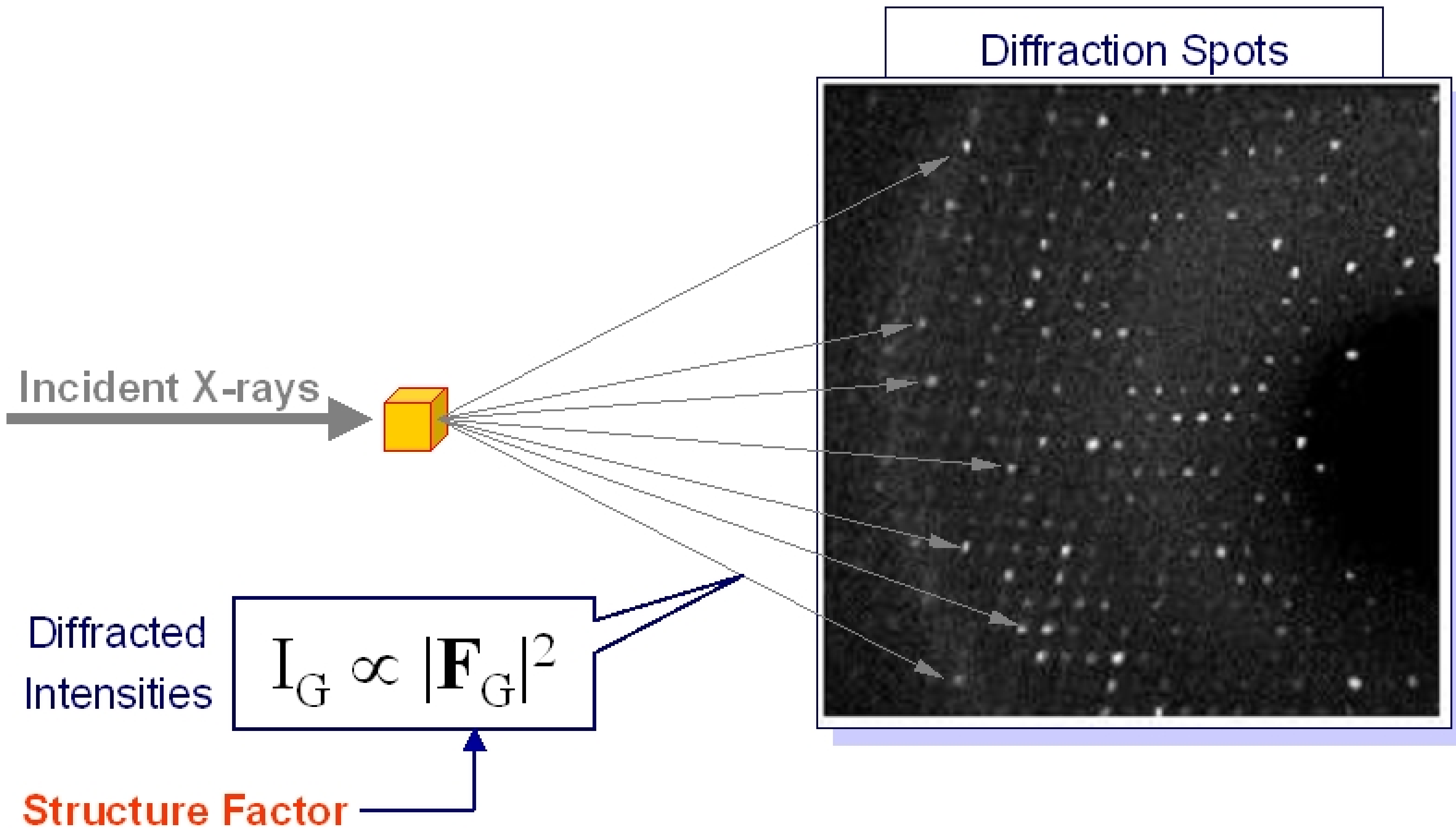
X-ray Crystallography

In 1912 Max von Laue reported the diffraction of X rays by a crystal
(Nobel Prize in physics in 1914)

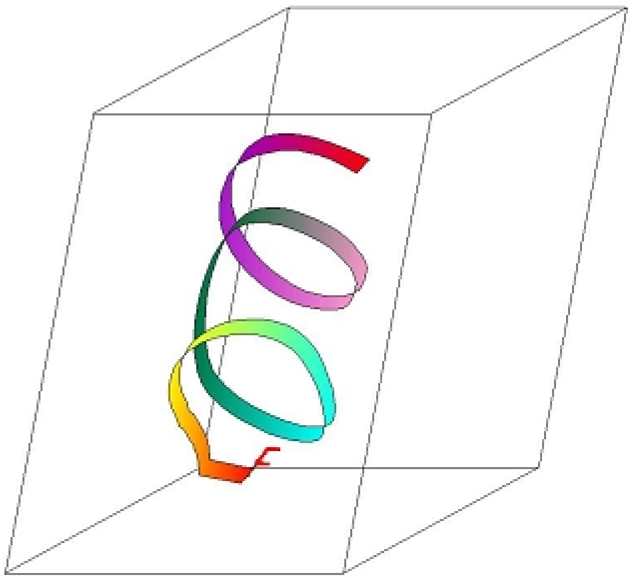
W. Henry Bragg & W. Lawrence Bragg seminal roles in X-ray crystallography
(Nobel Prize in physics in 1915)



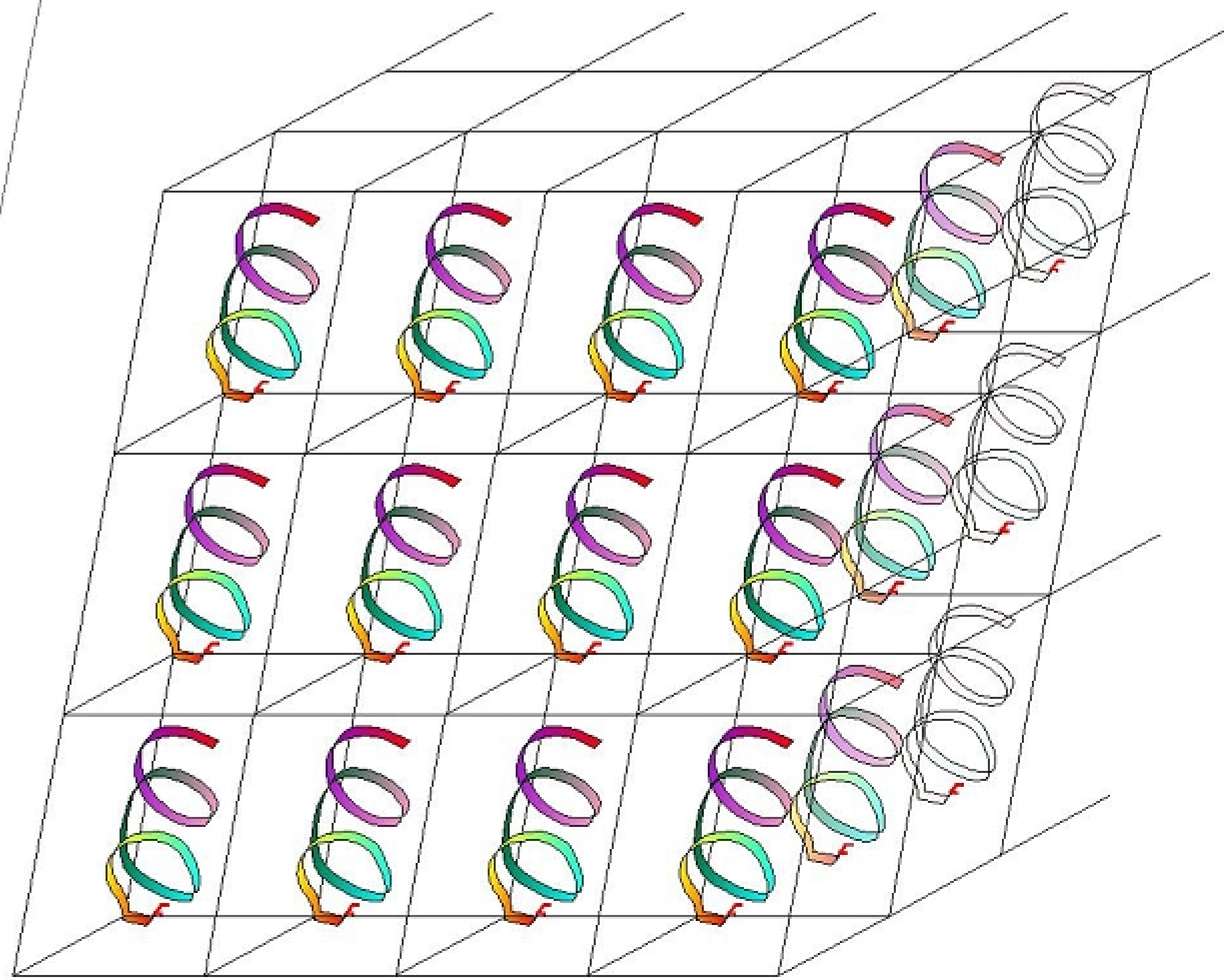
Crystal Lattice

Dimensions ⇒ Diffraction spots

Electron density ⇒ Structure Factor (F_G)



Unit Cell



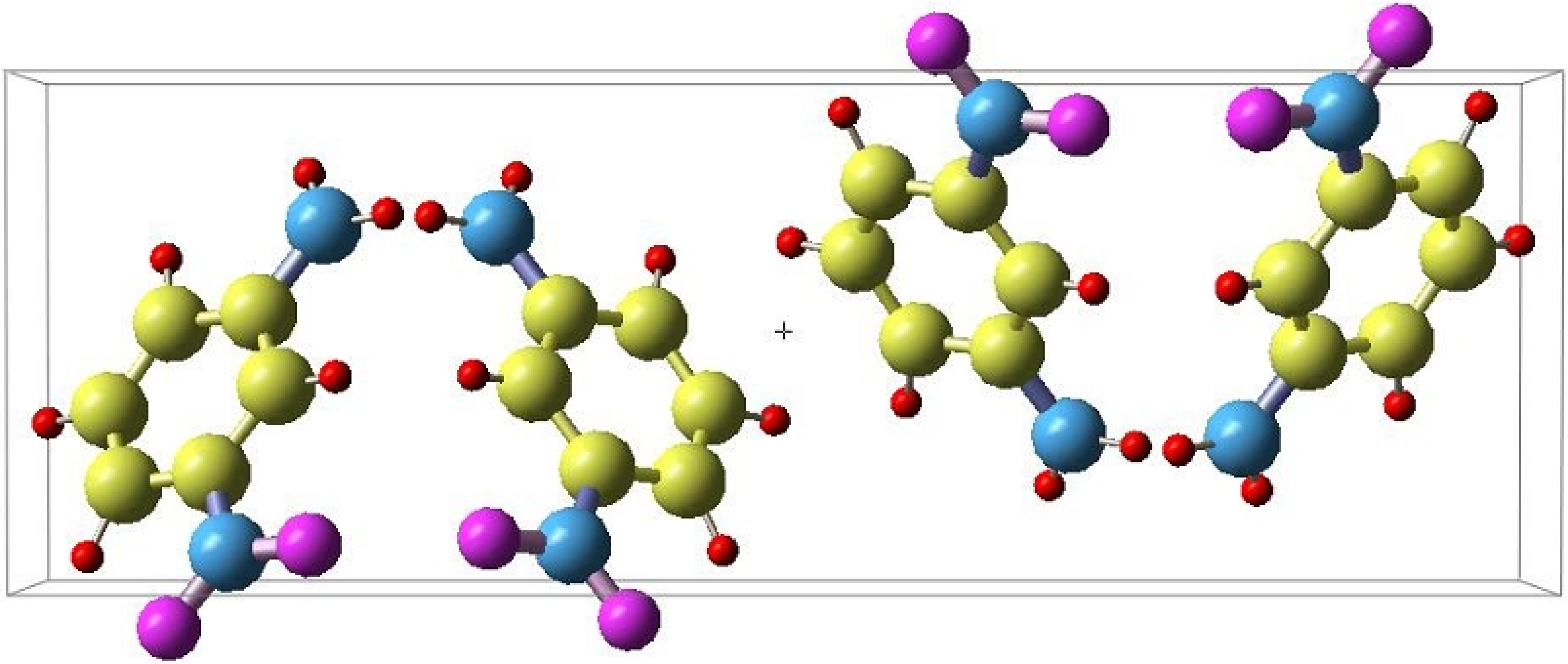
Structure Factor

Diffraction vector → $\vec{G}$; Atomic position → $\vec{R}_a$

$$\mathbf{F}_G = \sum_a f_a e^{2\pi i \vec{G}\cdot\vec{R}_a} = |\mathbf{F}_G| e^{i\delta}$$

f_a: Atomic scattering factor

δ: **PHASE**



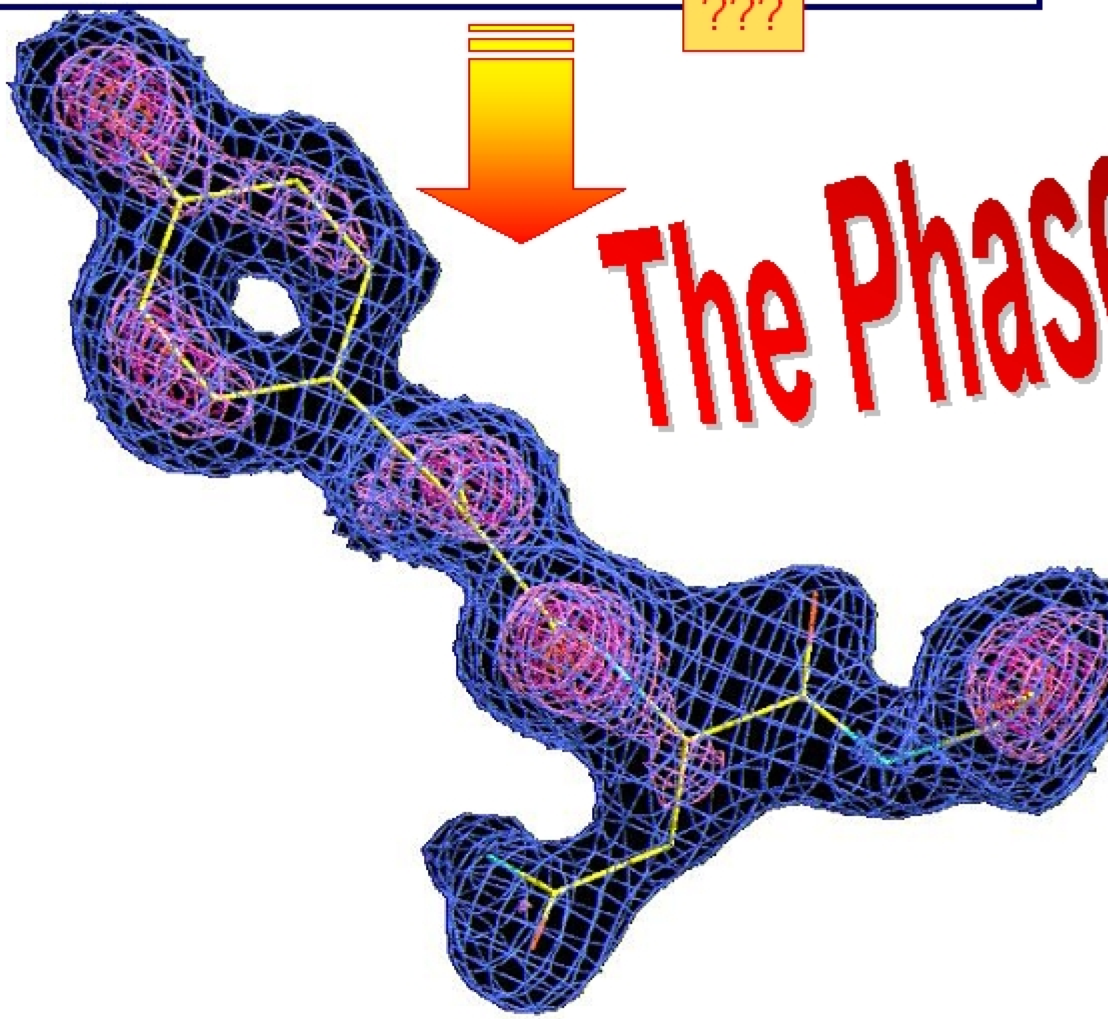
Structure Determination

Experiments: $I_G \propto |F_G|^2$

$$\rho_{u.c.}(\vec{r}) = \frac{1}{V}\sum_{G} \left|\mathbf{F}_G\right| e^{i\delta}\, e^{-2\pi i \vec{G}\cdot\vec{r}}$$

???

The Phase Problem

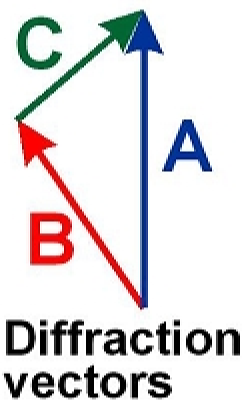


Electron density of the molecules

Approaches to the '*phase problem*'

Direct Methods: *Intrinsic relationship among the phase values*

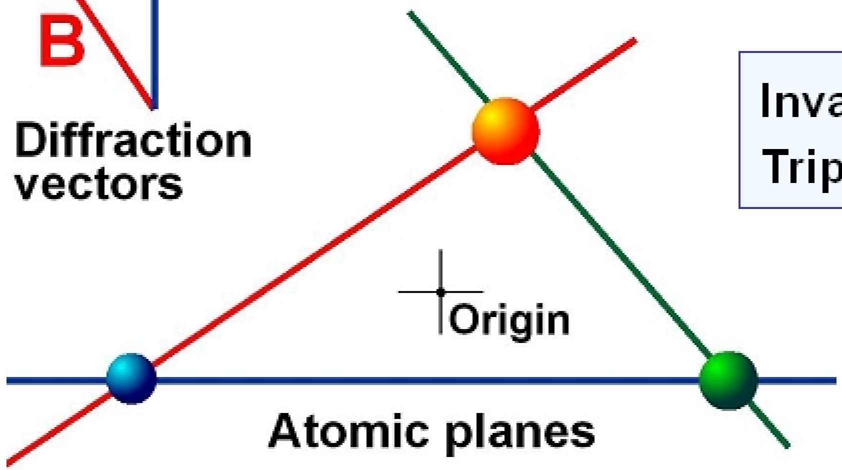
H. Kaufman & J. Karl Nobel Prize in Chemistry 1985

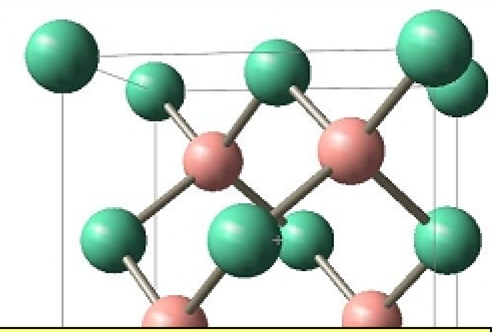


$$\frac{F_B F_C}{F_A} = \frac{|F_B||F_C|}{|F_A|} e^{i(\delta_B + \delta_C - \delta_A)} e^{2\pi i(\vec{B} + \vec{C} - \vec{A})\cdot\Delta\vec{R}}$$

Invariant Triplet Phase : δ_T

Choice of position for the Unit Cell origin





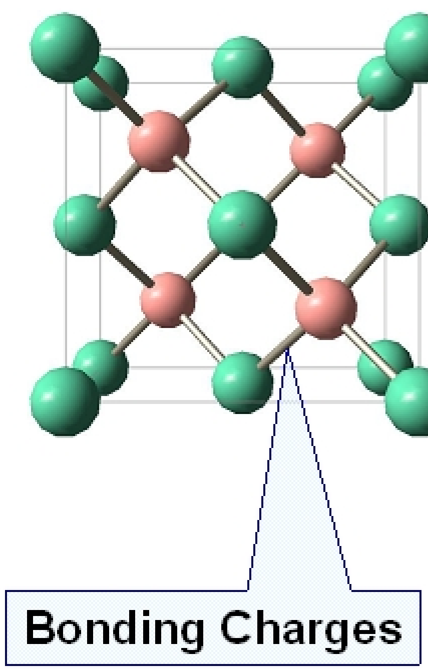
Complex Molecules

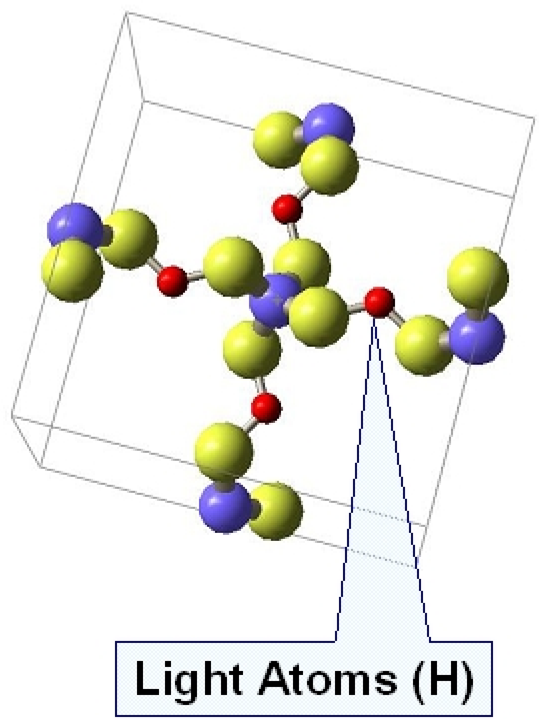
- MIR – *Multiple Isomorphous Replacement*
- MAD – *Multiple Anomalous Dispersion*

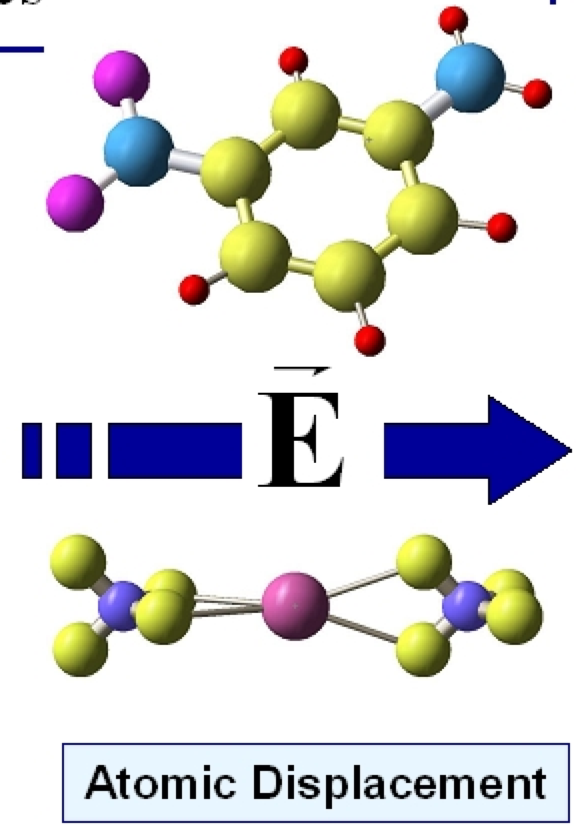
Accurate Phase Determination

$$\sum_{a} (f_a + \Delta f_a) e^{2\pi i \vec{G} \cdot (\vec{R}_a + \Delta \vec{R}_a)} \cong |\mathbf{F}_G| e^{i(\delta + \Delta\delta)}$$

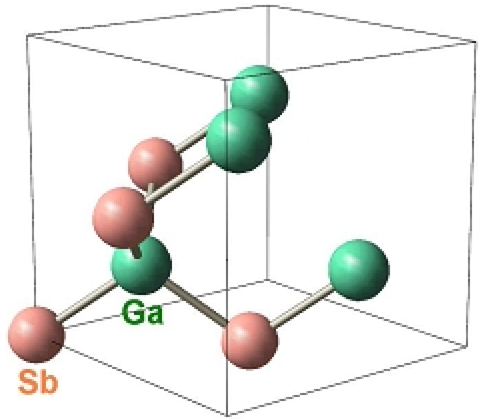
The phase is very sensitivy to small features (Δf_a, $\Delta \mathbf{R}_a$) of crystalline structures

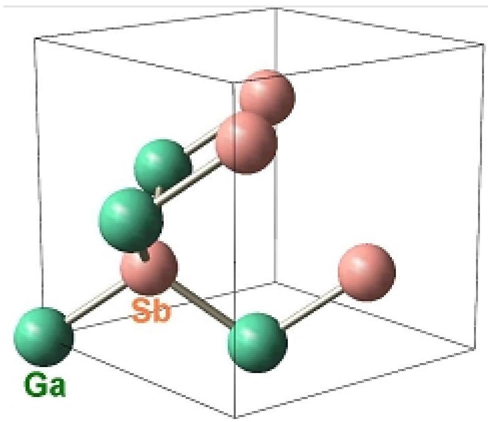






Chemical Bonds and Anomalous Dispersion





CORRECTION	δ_T	
None:	-62.0°	62.0°
Dispersion:	-59.0°	52.0°
Covalent bonds:	-66.1°	66.1°
Dispersion + bonds:	-65.9°	53.4°
$\Delta\delta_T$:	4.1°	8.6°

Anomalous Dispersion
E = 9560 eV

Ga:
$f' = -2.19$
$f'' = 0.52$

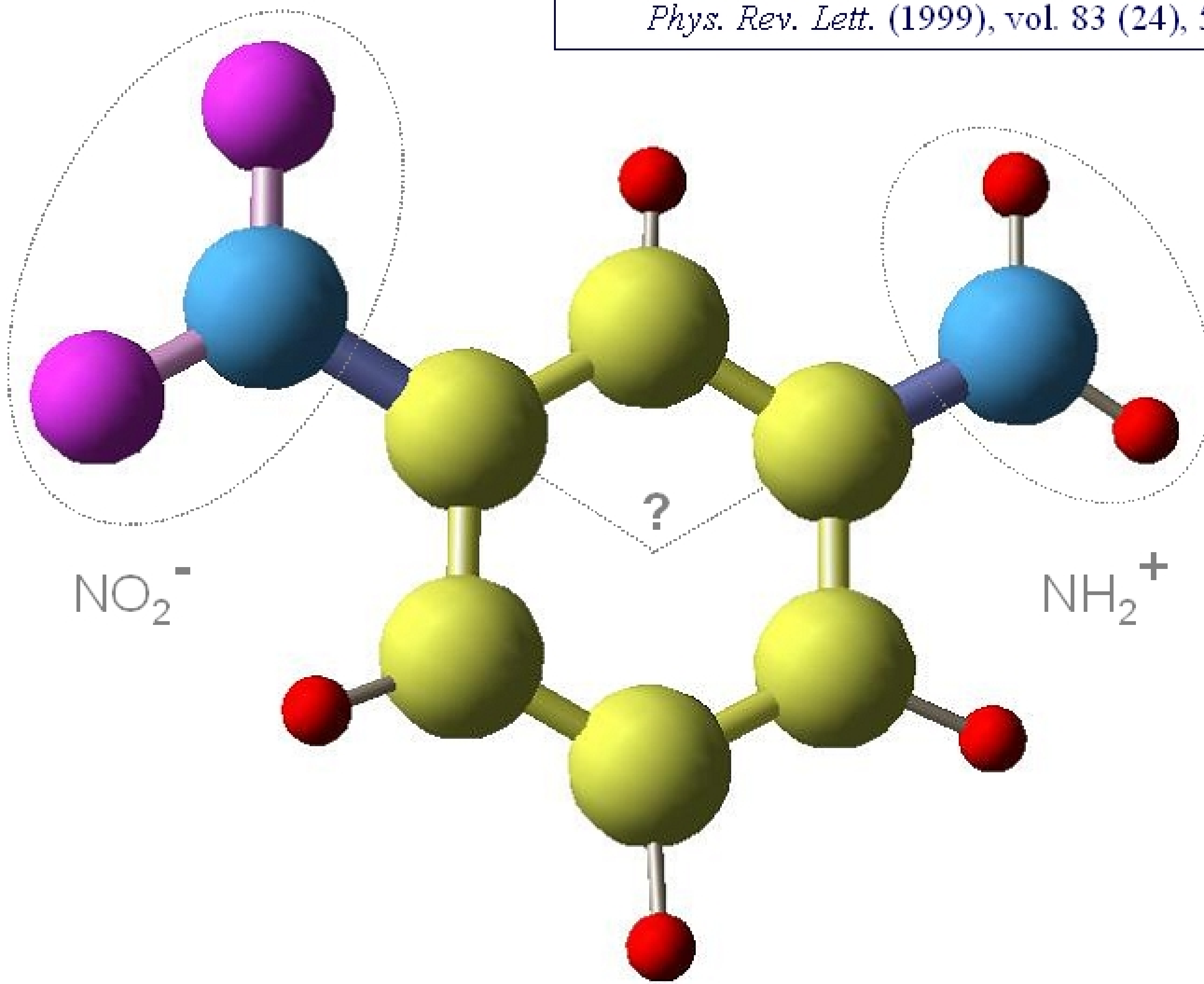
Sb:
$f' = 0.07$
$f'' = 4.38$

Covalent bonds

$f_{Ga} \rightarrow f_{Ga} + 1$
$f_{Sb} \rightarrow f_{Sb} - 1$

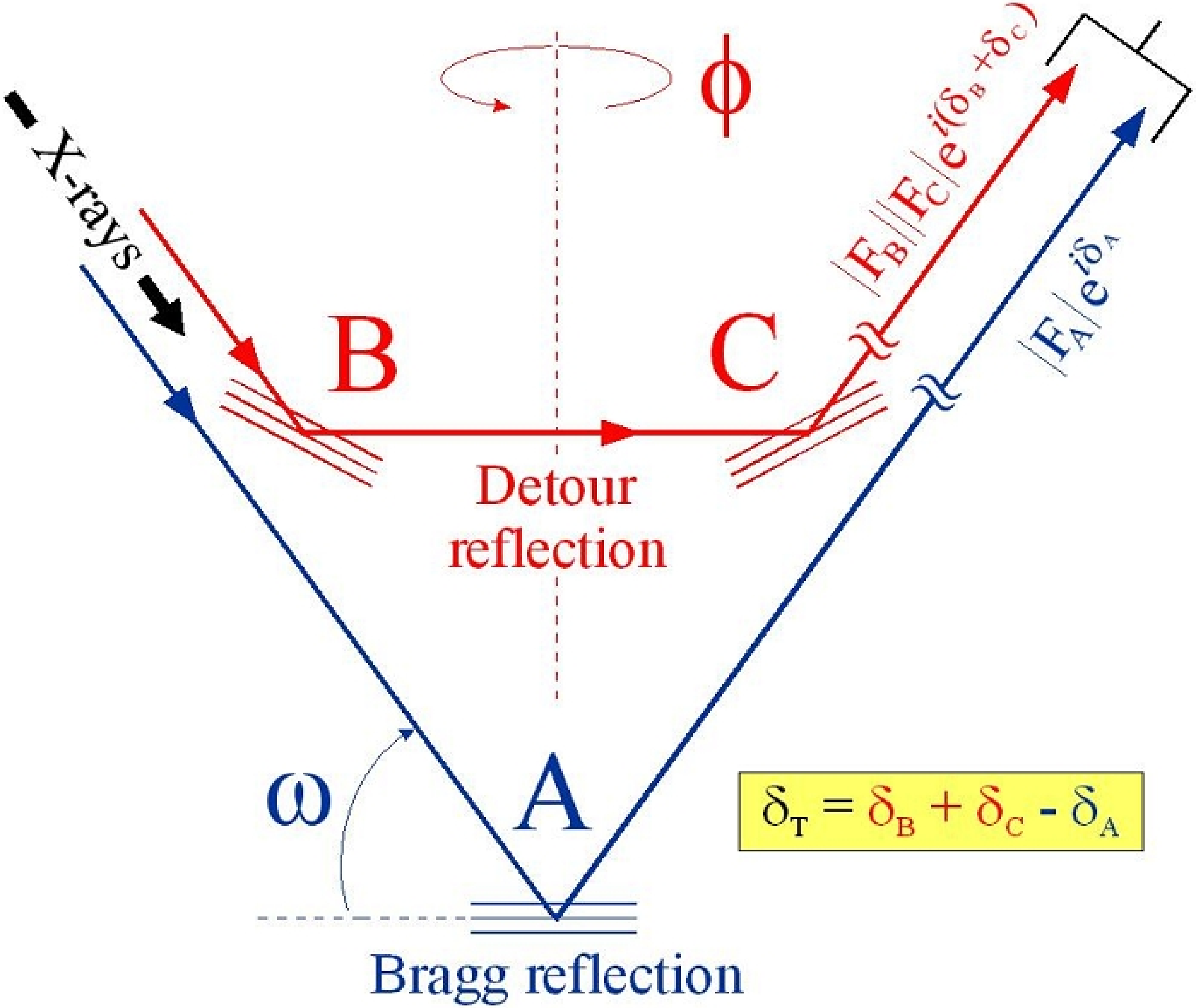
Structure Refinement of Molecules

Hysteresislike Behavior in Meta-Nitroaniline Crystals
Avanci, L.H. *et. al.*,
Phys. Rev. Lett. (1999), vol. 83 (24), 5146-5148

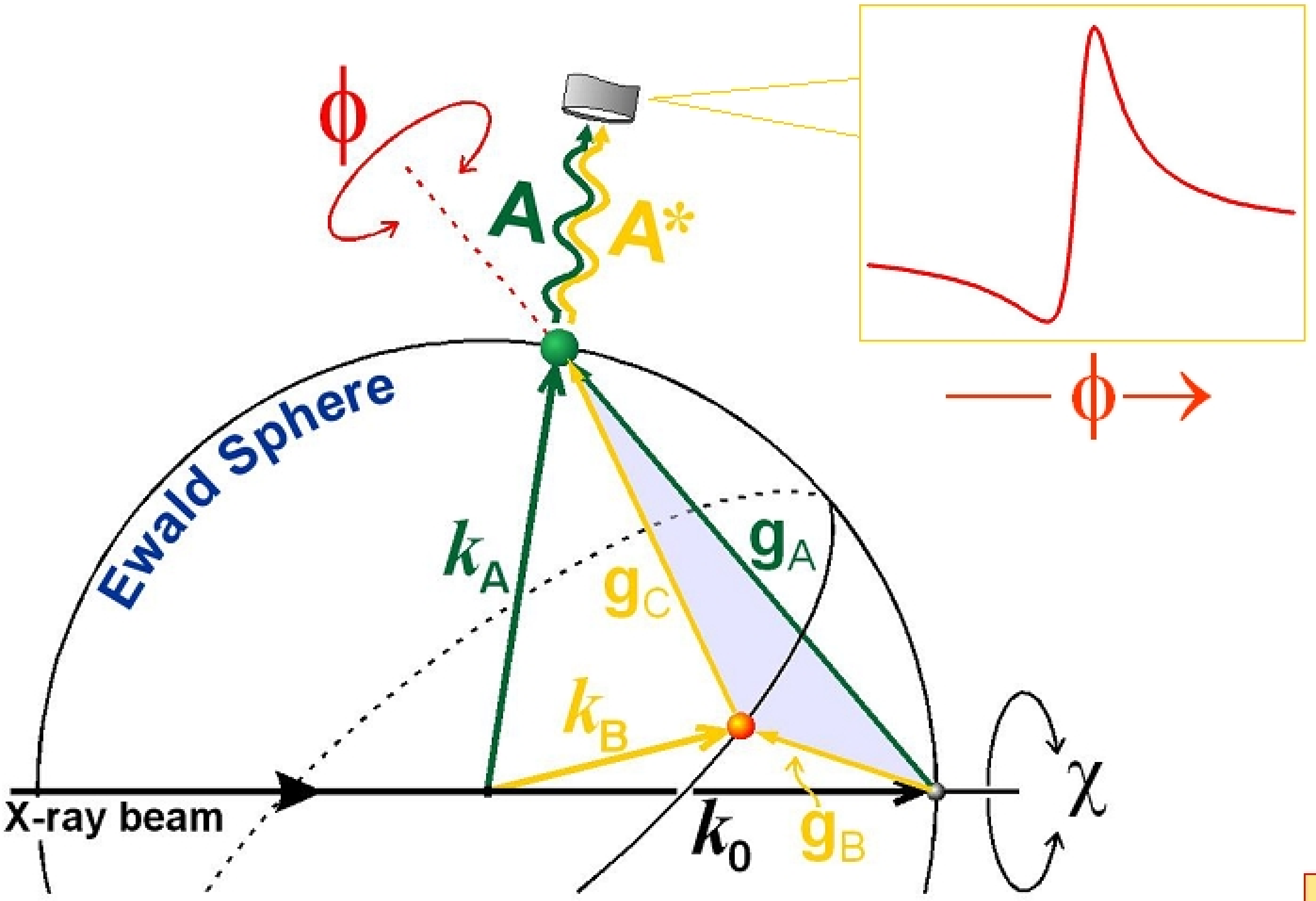


1% variation in the NO_2^- — NH_2^+ distance $\Rightarrow \Delta\delta_T \approx 3.5°$

Three-beam Diffraction



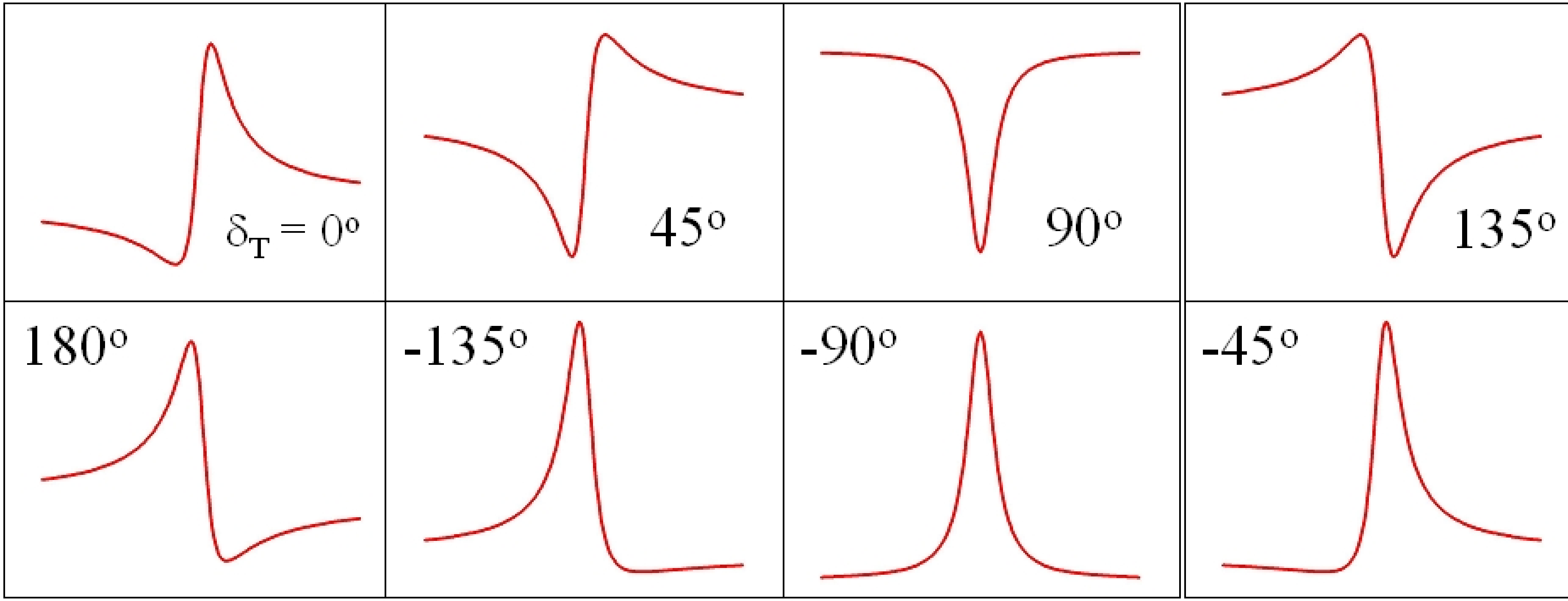
Three-beam Diffraction (reciprocal space)



Triplet phase

$$I(\phi) = |\mathbf{A}|^2 + |\mathbf{A}^*(\phi)|^2 + 2|\mathbf{A}||\mathbf{A}^*(\phi)|\cos(\Omega + \delta_T)$$

Azimuthal (ϕ) Scan x δ_T



$$I(\phi) = 1 + R^2(\phi) + 2R(\phi)\cos(\Omega + \delta_T)$$

$$R(\phi) = \left|A^*(\phi)\right| / \left|A\right|$$

Maximum sensitivity

$$R_{max} = R(\phi_0) \approx |F_B||F_C| / |F_A| \approx 1$$

Azimuthal (ϕ) Scan x δ_T

M. Hart and A.R. Lang, Phys. Rev. Lett. **7**, 120 (1961).

B. Post, Phys. Rev. Lett. **39**, 760 (1977).

L.D. Chapman, D.R. Yoder, and R. Colella, Phys. Rev. Lett. **46**, 1578 (1981).

S.L. Chang, Phys. Rev. Lett. **48**, 163 (1982).

H.J. Juretschke, Phys. Rev. Lett. **48**, 1487 (1982).

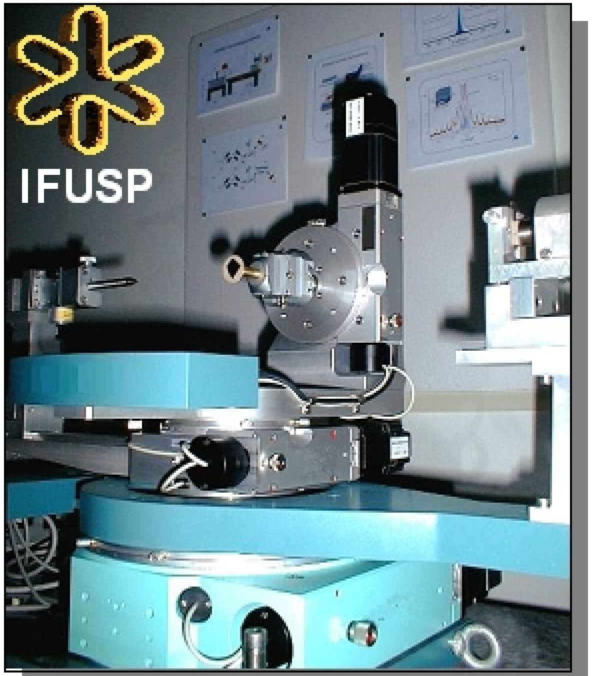
Q. Shen and R. Colella, Nature (London) **329**, 232 (1987).

Q. Shen and K.D. Finkelstein, Phys. Rev. Lett. **65**, 3337 (1990).

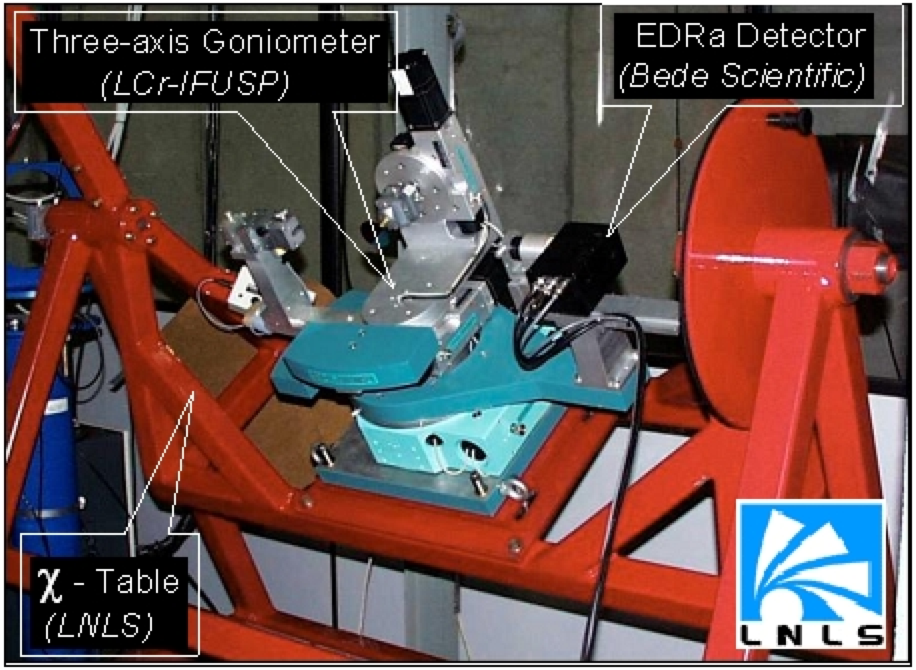
Q. Shen, Phys. Rev. Lett. **80**, 3268 (1998).

Experimental Set up

Laboratório Nacional de Luz Síncrotron - LNLS



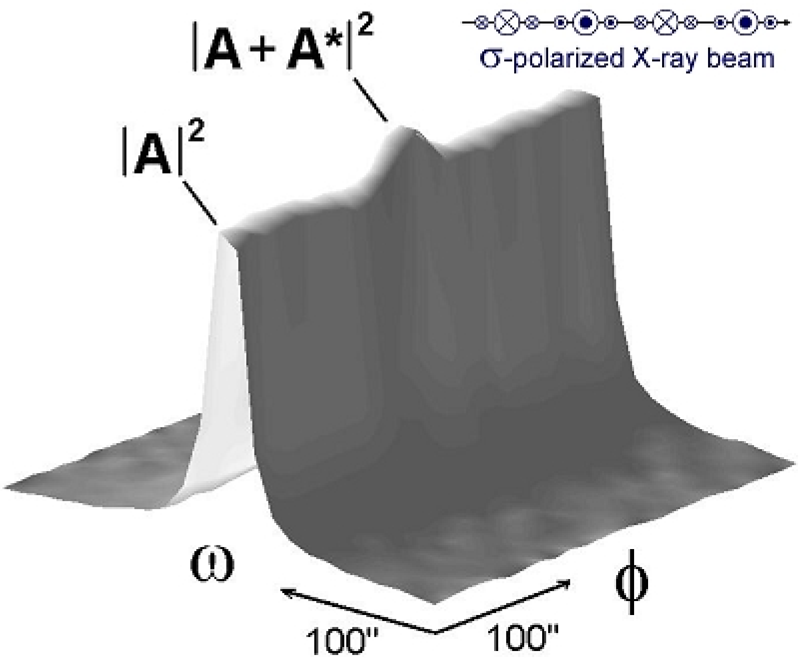
FAPESP
project # 97/13757-8

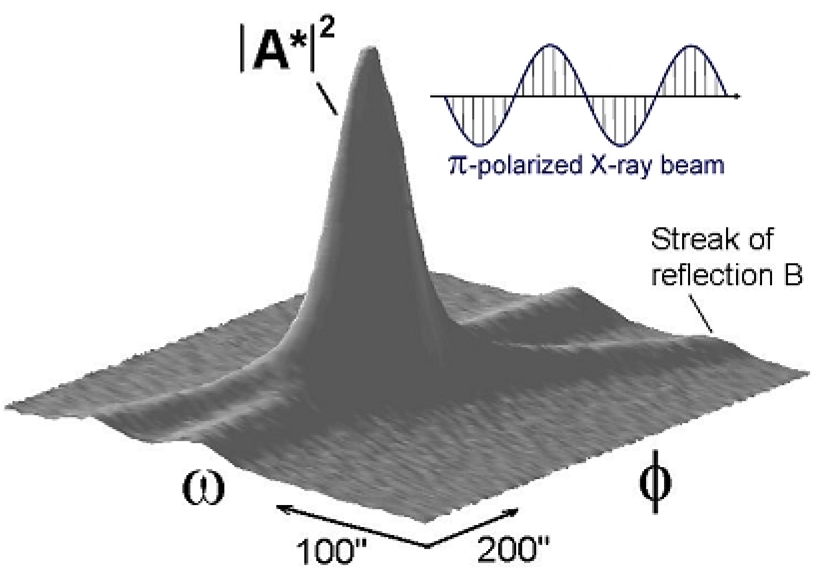


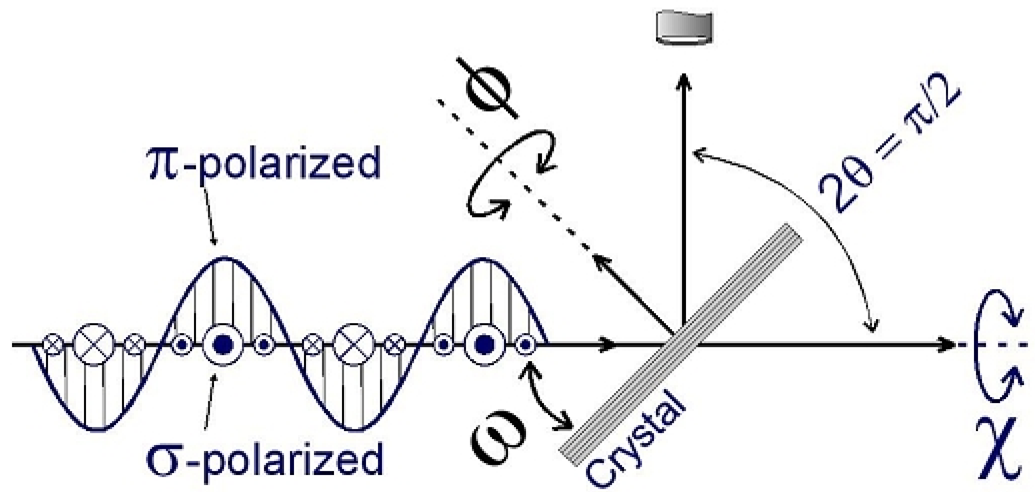
Fully Automated version is now Available (XRD-1)

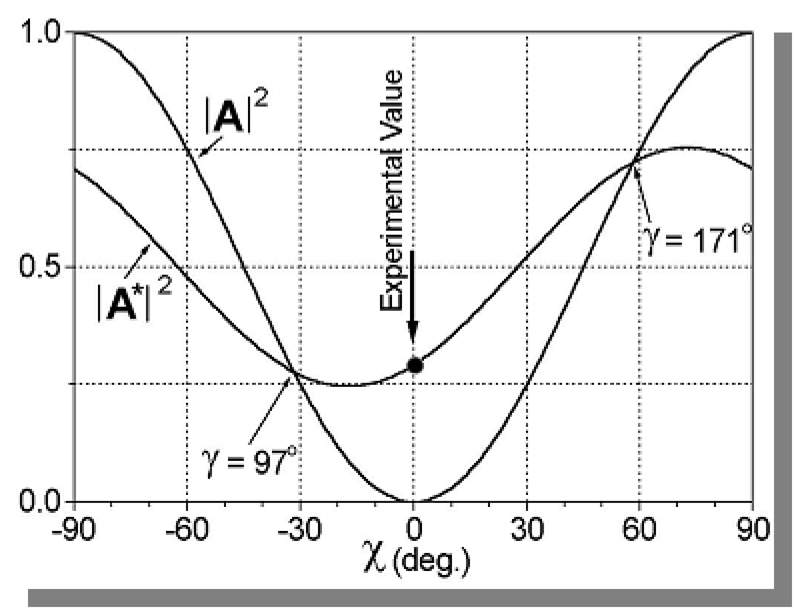
An X-ray Diffractometer for Accurate Structural Invariant Phase Determination
Journal of Synchrotron Radiation (2003), **10**, 236-241

Polarization Forbidden Primary Reflection





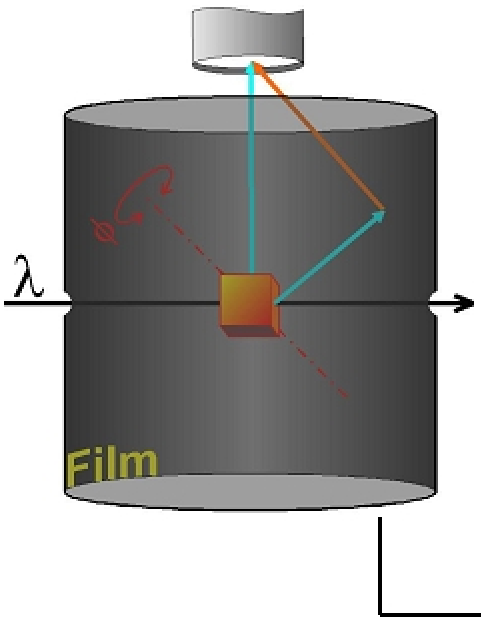


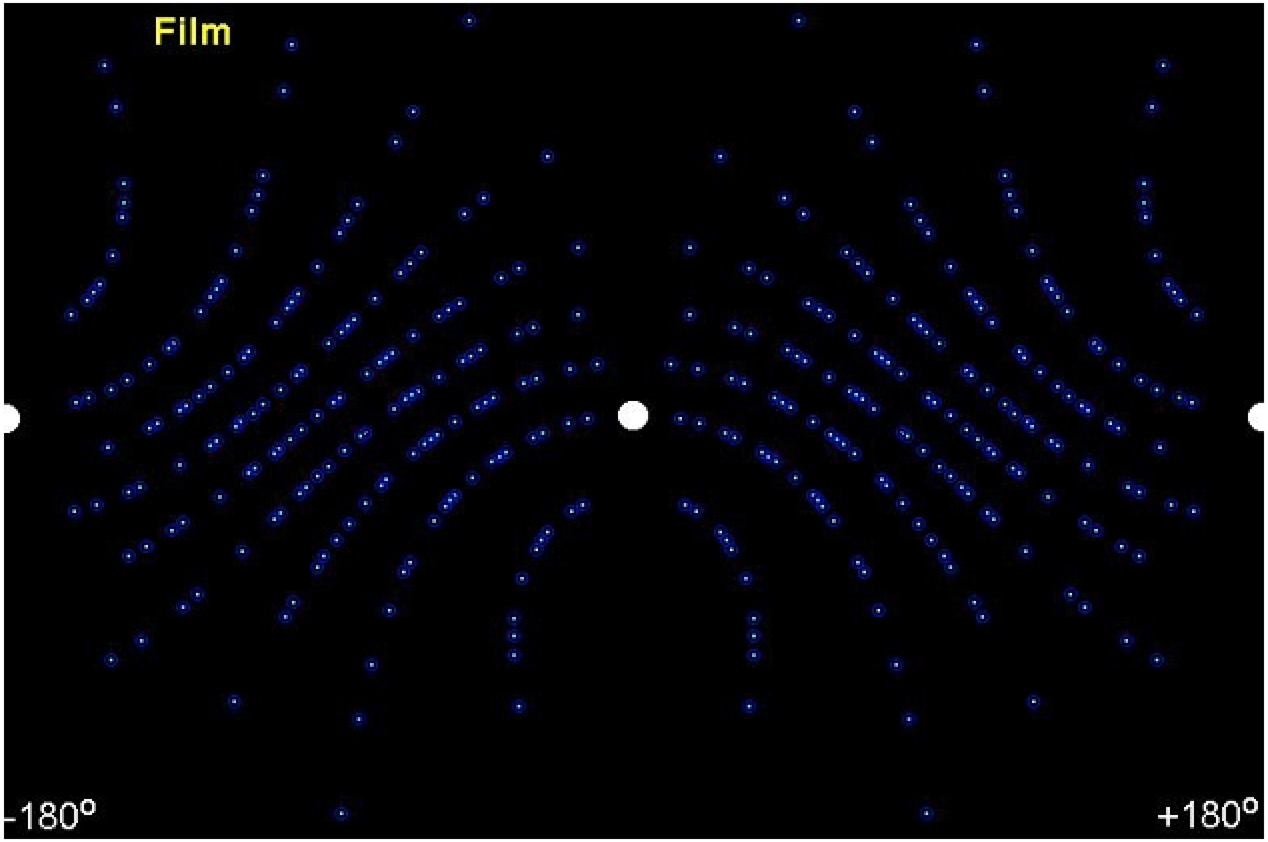


Strength Tuning of Multiple Waves in Crystals

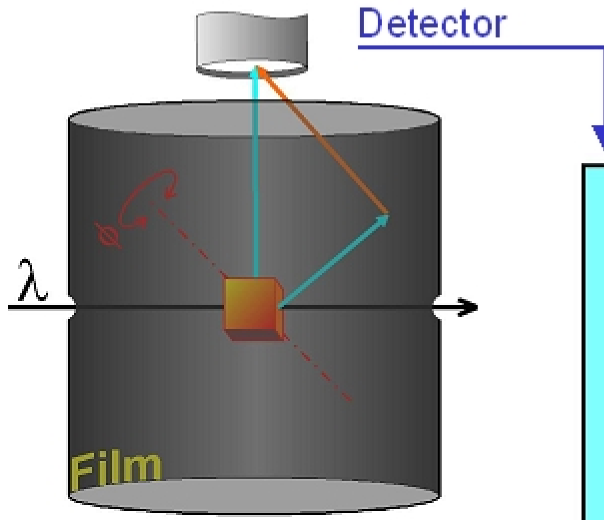
Acta Cryst. A57, 192-196 (2001)

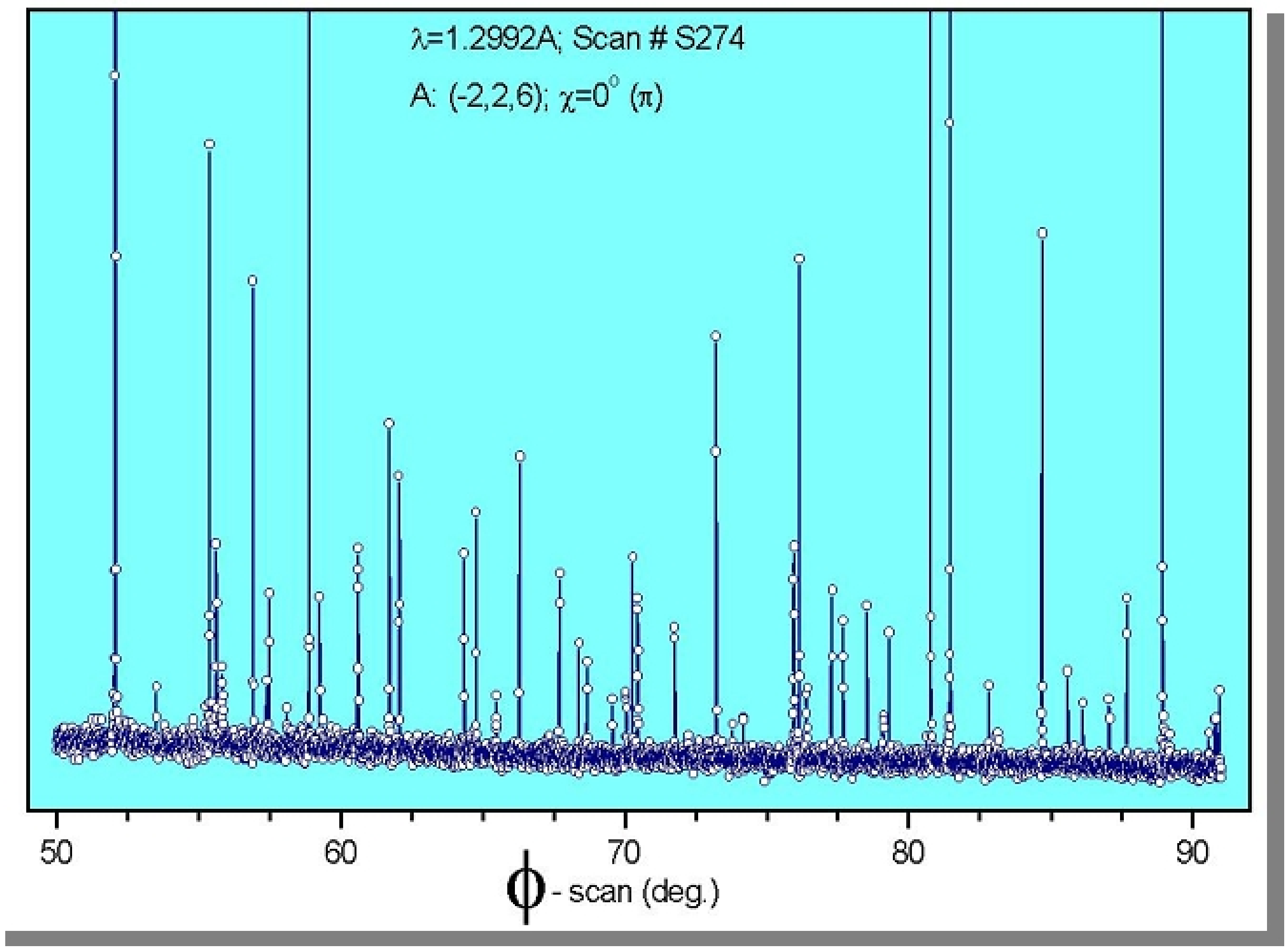
Data Collection Procedure



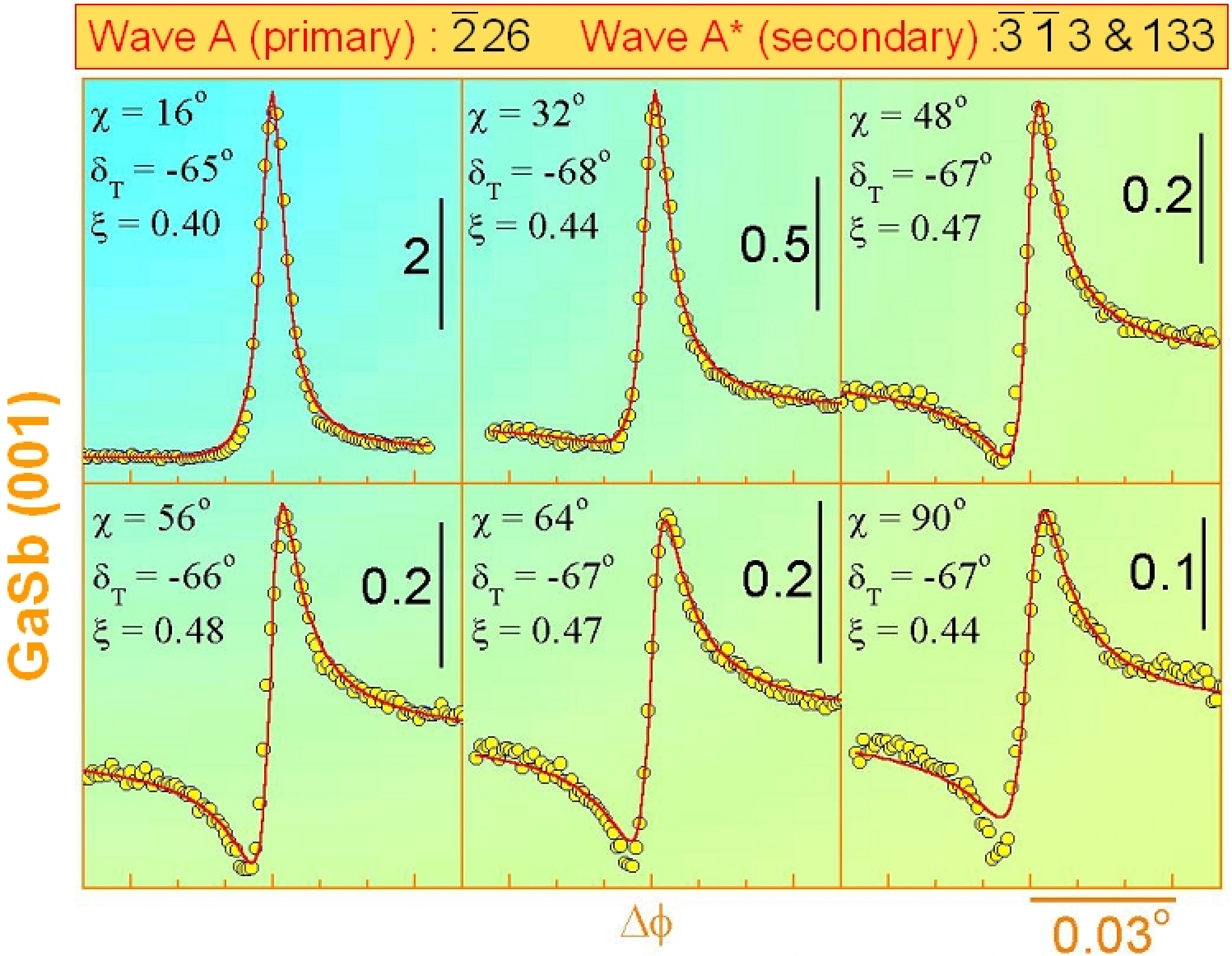


Data Collection Procedure



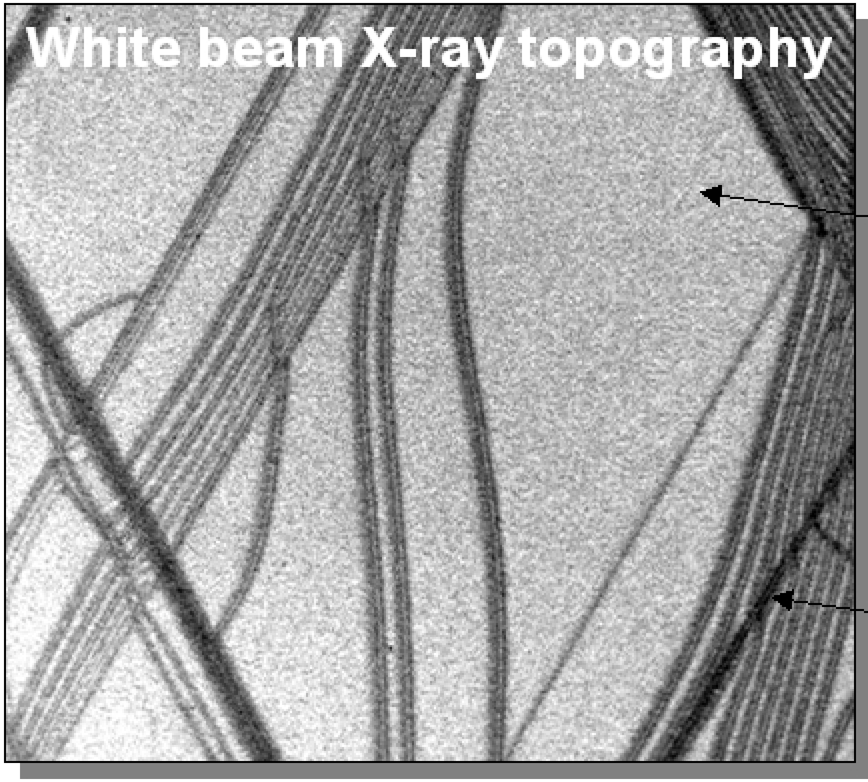


Azimuthal (φ) Scan x polarization angle χ



Enhanced X-ray Phase Determination by Three-beam Diffraction
Physical Review Letters (2002), **89**(1), 015501

Kinematical x Dynamical Diffraction



Dislocations in dendritic web silicon,
J. Cryst. Growth 213 (3-4), 288 (2000)

Detector reading : **I**

Coherent diffracted intensity
(Dynamical diffraction)

$$\mathbf{I}_{dyn} = (1-\alpha)\,\mathbf{I}$$

Lost of coherence
(Kinematical diffraction)

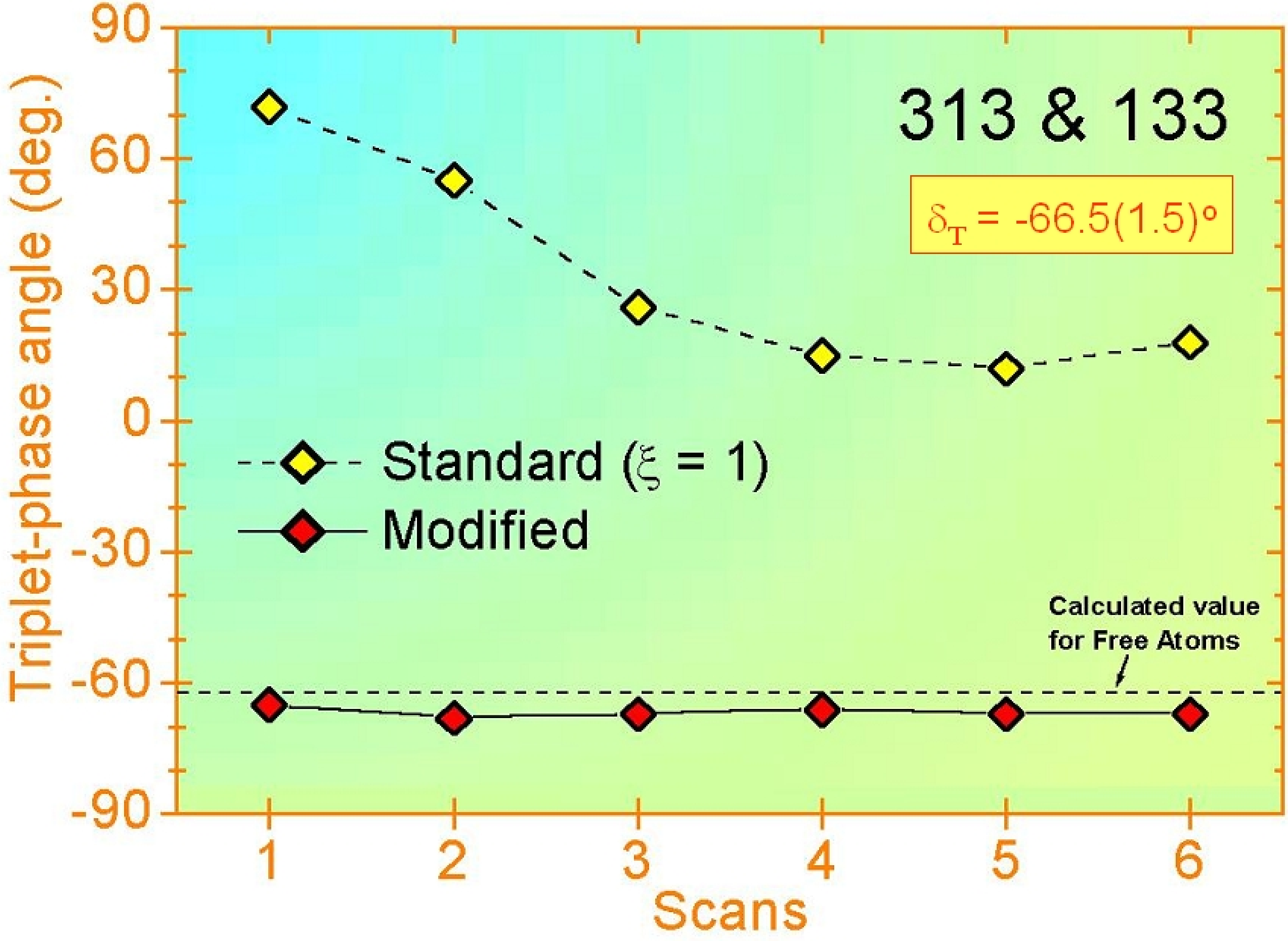
$$\mathbf{I}_{kin} = \alpha\,\mathbf{I}$$

$$0 \le \xi \le 1$$

$$I(\phi) = 1 + R^2(\phi) + 2\sqrt{1-\alpha}\sqrt{1-\alpha^*}\,R(\phi)\cos(\Omega + \delta_T)$$

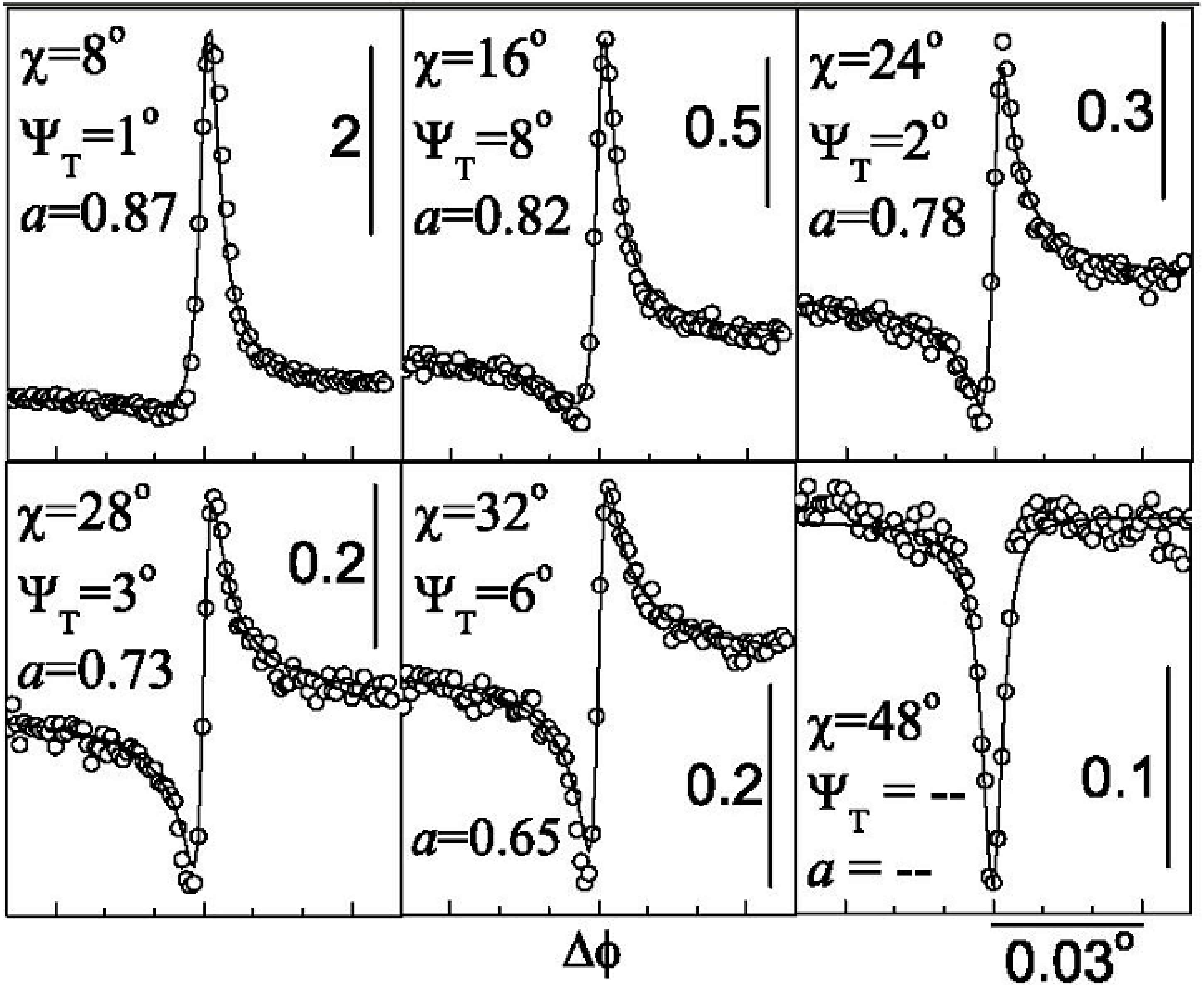
Accurate triplet phase determination in non-perfect crystals - a general phasing procedure
Acta Crystallographica Section A (2003), **59**, 470-480

Comparison Standard × Modified Approach



Aufhellung

Wave A (primary) : $\bar{2}26$ Wave A* (secondary) : 226 & $\bar{4}00$



General Intensity Profile Function

$$\mathrm{I}(\phi) = v_P^2(1 - b|\mathrm{f}(\phi)|^2) + R^2|\mathrm{f}(\phi)|^2 v_S^2 + 2\xi R|\mathrm{f}(\phi)|\vec{v}_P \cdot \vec{v}_S \cos(\Omega + \delta_T)$$

A $= \vec{v}_P$ (primary wave); **A** $^*(\phi) = R\,\mathrm{f}(\phi)\,e^{i\delta_T}\,\vec{v}_S$ (secondary wave);

$\mathrm{f}(\phi) = |\mathrm{f}(\phi)|\,e^{i\Omega}$ (excitation function for **A***)

I(ϕ) is a 4-parameter (R, b, ξ, δ_T) adjustable equation !!!

R : amplitude reflectivity ratio
This parameter can not be estimated. It must be measured.

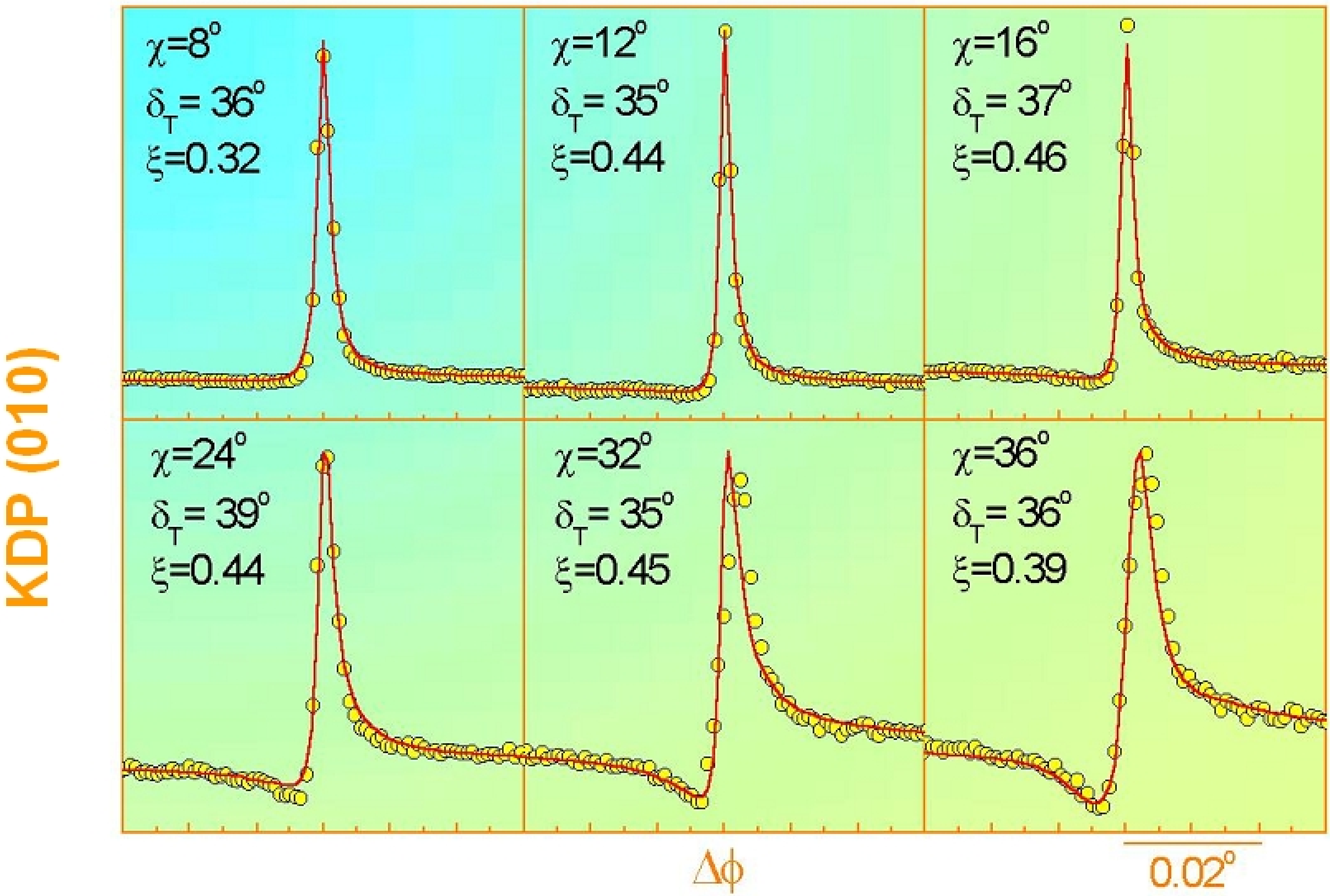
b : '*Aufhellung*' effect
This parameter represents the amount of energy taken by the wave **B**.

δ_T : invariant phase triplet
This parameter contains real structure phase information.

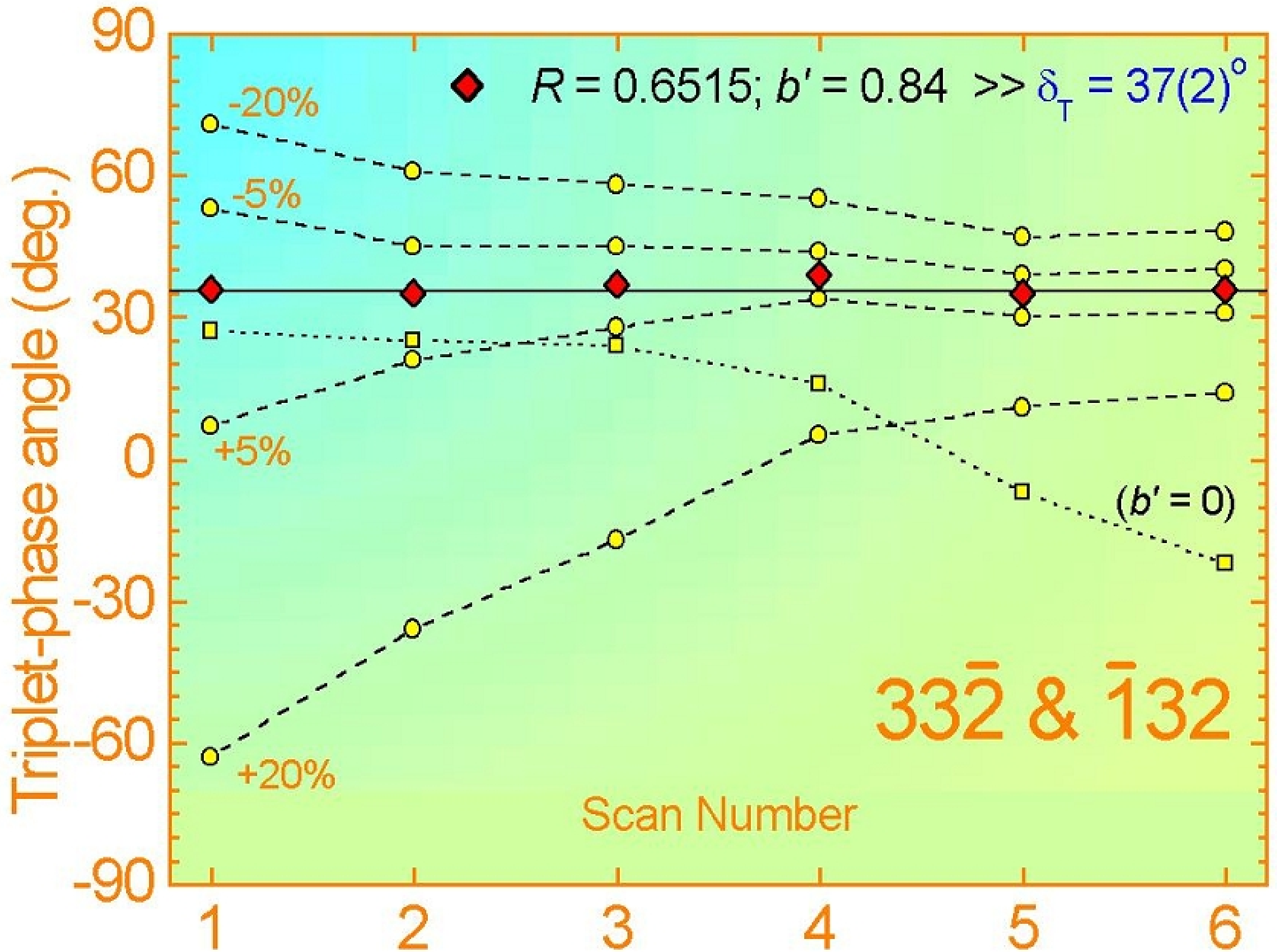
ξ : coherence coefficient
This is a new parameter that states the capability of the waves **A** *and* **A*** *to interfere.*

Azimuthal (ϕ) Scan x polarization angle χ

Wave A (primary) : 260 Wave A* (secondary) : $33\bar{2}$ & $\bar{1}32$



Comparison $\delta_T \times R$



Algorithm for Phase Determination

ERROR FUNCTION

$$E(\boldsymbol{p}) = \frac{1}{N-1}\sum_{n=1}^{N}\left|I(\phi_n, \boldsymbol{p}) - I_{EXP}(\phi_n)\right|$$

Parameter vector

$\boldsymbol{p} = [\phi_0, w, w_G, R, b, \xi, \delta_T]$

δ_T : global variable (same value for all ϕ-scans)

$\phi_0, w, w_G, R, b, \xi$: local variables

(adjusted for each ϕ-scan)

Collaborators

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