Strain Effects in Thin Films and Progress in Reference-Beam Phasing

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Direct measurements of a large number of Bragg reflection phases in protein crystallography experiment

- Intro to reference beam diffraction
- Experimental setup & procedures
- Strategies on using measured phases
- Summary

Interplay between strain & physical properties in thin films
=> semiconductor band gap
=> exchange striction
=> magnetic anisotropy

- Ave. strain & strain gradients
- Magnetic thin-film Fe/GaAs
- Conclusions
Typical Crystallography

Expression → Crystallization → Data collection → |F(H)| → Phasing

- SeMet substitution
- heavy-atom buffer
- heavy-atom soak

Incorporating heavy atoms into protein structures

|F(H)| = |F(H)|e^{-iα(H)}

α(H) = ??

anomalous signal from heavy-atoms

Structure
Phasing Proteins w/o Heavy Atoms?

Expression ➔ Crystallization ➔ Data collection ➔ $|F(H)| \& \alpha(H)$

⇒ Reference-beam diffraction ➔ Structure
(a) Conventional oscillation method

Reference Beam Diffraction Technique

$$\delta = \alpha_{H-G} + \alpha_{G} - \alpha_{H}$$

→ Triplet Phase

(b) Reference-beam diffraction
Reference-Beam Data Collection

RBD data set: \( I(hkl) \) vs. \( \theta - \theta_G \)

Analogy to MAD data set: \( I(hkl) \) vs. \( \lambda \)
Conventional 3-Beam Diffraction


- Tetragonal lysozyme
- Time-consuming: ~10 min per profile
- Difficult for protein crystallography
Special Kappa Diffractometer

- Compact 50° κ-design
- G-reflection alignment with κ-φ
- Oscillation axis ψ with DC motor control
- Easy incorporation into oscillation setup
Phase-Sensitive XRD Theory

**Kinematic theory**
- single scattering
- commonly used
- no phase sensitivity

**Approximate theories**
- double scattering
- triplet-phase sensitive
- easy for curve-fitting

**Dynamical theory**
- all scattering terms
- phase-sensitive
- only numerical calc.

**Second-order Born Approximation (2nd BA):**  

\[
D = D^{(0)} + D^{(1)} + D^{(2)} + \ldots
\]

\[
I_H(\theta) = 1 + 2 \frac{F_{H-G}}{F_H} \sqrt{R_G(\theta) \cos[\delta + \nu_G(\theta)]}
\]

with \( R_G(\theta) = \text{reflectivity} \) and \( \nu_G(\theta) = \text{phase shift of } G \).

**Expanded Distorted-Wave Approach (EDWA):**  
Shen (1999) PRL; Shen (2000) PRB.

\[
I_H(\eta_G) = 1 - \tau \sin \delta \frac{\sin^2 (A \eta_G)}{A \eta_G^2} + \frac{\tau}{\eta_G} \left( \cos \delta + \frac{\tau}{2 \eta_G} \right) \left( 1 - \frac{\sin(2A \eta_G)}{2A \eta_G} \right)
\]

with \( \tau = |F_{H-G}/F_H|, A = \pi \Gamma |F_G| t/(\lambda \cos \theta_G) \) and \( A \eta_G = \pi (\theta - \theta_G) t/d \).

\( \Rightarrow \) takes into account phase-independent effect accurately.
Automatic Curve Fitting

\( \Rightarrow \) Distorted-wave approximation (EDWA) is very accurate for biological crystals

\( \Rightarrow \) Curve-fit to experimental data using EDWA, with 4 parameters

**Comparison of EDWA with dynamical theory**

- \( \delta = 90^\circ \)
- \( \delta = 0^\circ \)
- \( \delta = 180^\circ \)
- \( \delta = +90^\circ \)

\( A = 0.12 \)

\( \eta_G \)

Normalized Intensity

Phase \( \delta \)

Base \( I_0 \)

Amplitude \( p \)

Center \( \theta_0 \)

\( \Rightarrow \) So far PC-based program ORIGIN is used for automatic curve-fitting to obtain triplet-phase \( \delta \).
Experiment Example

**Tetragonal lysozyme P4$_3$2$_1$2**

- Room temperature measurements
- Reference reflection $G = (1,1,1)$
- Typical exposure ~15 sec for $\Delta \psi = 2^\circ$.
- Number of $\theta$-steps 15 to 21
- Typical $\theta$ range ~ 0.05$^\circ$ to 0.1$^\circ$
- 90$^\circ$ rotation $\Rightarrow$ 86% completeness
- Diffraction resolution to ~2.5 Å

- 14914 RBD profiles
- Total time ~ 12 hrs

$\Rightarrow$ 14914 triplet phases
MOSFLM Indexing and Integration

- Indexing
- Integration
- Scale \((\text{no merge})\)
- Sort \(\Rightarrow I_H(\theta)\)
Typical Interference Profiles

P4₃2₁₂ lysozyme

All profiles shown from same oscillation series
Results: triplet-phase data set

- Error histogram for measured triplet-phase data set

  - Whole data set:
    - 14914 phases, $\Delta \delta_m = 61^\circ$
  
  - With rejection criteria based on goodness-of-fits parameters ($\sigma$, $\chi^2$, $F_{hg}$):
    - 7360 phases, $\Delta \delta_m = 45^\circ$
Strategies on Using Measured Phases

RBD experiments ➔ measured triplet-phases: \( \delta = \alpha_{H-G} + \alpha_G - \alpha_H \)

⇒ How to deduce individual structure-factor phases: \( \alpha_H = ?? \)

- **Direct methods:**
  replace guesses based on probability with measured triplet phases


- **Other methods??**
Unique Recurrence Pattern in RBD

⇾ RBD geometry leads to a systematic recurrence pattern of individual phases:
  a) all triplets contain a common $\alpha_G$
  b) $\alpha_H$ appears in exactly 2 triplets
  c) the two $\alpha_H$-triplets are adjacent

⇾ Different from conventional 3-beam measurements

Conventional 3-beam:
\[
\begin{align*}
\delta_1 &= \alpha_{G1} + \alpha_{H1-G1} - \alpha_{H1} \\
\delta_2 &= \alpha_{G2} + \alpha_{H2-G2} - \alpha_{H2} \\
\delta_3 &= \alpha_{G3} + \alpha_{H3-G3} - \alpha_{H3} \\
\end{align*}
\]

$N$ equations
~$3N$ unknowns

Reference-beam method:
\[
\begin{align*}
\delta_0 &= \alpha_G + \alpha_{H-G} - \alpha_H \\
\delta_1 &= \alpha_G + \alpha_H - \alpha_{H+G} \\
\delta_2 &= \alpha_G + \alpha_{H+G} - \alpha_{H+2G} \\
\end{align*}
\]

$N$ equations
$N+2$ unknowns
Recursive RBD Phasing Algorithm

Program: RBD_Phasing
RBD_phasing Using Measured Phases

- 191 unique (hk0) phases plus G=(111) phase from PDB 193L as starting phases
- using measured data set of 7360 triplet phases with median phase error 45°
- obtained 1085 individual phases with mean phase error 66°
- calculated electron density map (z=0) of tetragonal lysozyme

Based on 7360 measured triplet-phases

Based on calculated triplet-phases
Reducing Number of Initial Phases

- Low-resolution phases from molecular envelope?
- Measurements of three RBD datasets with non-coplanar G's
- Use of symmetry equivalent indexing to effectively have three RBD datasets?
- In principle, only 4 initial phases are needed to solve a structure

\[ H = n_1G_1 + n_2G_2 + n_3G_3 + H_0 \]
Inverse Beam Measurements

Reference-beam coupled Friedel pairs:

\[ \text{H} / \text{G} / \text{H} \rightarrow \overline{\text{H}} / \overline{\text{G}} / \text{G} - \text{H} \]


(a) \((3,-2,4)/(2,3,0)\)
\[ \delta_{\text{fit}} = -116^\circ \]

(b) \((-3,2,-4)/(-2,-3,0)\)
\[ \delta_{\text{fit}} = 77^\circ \]
Summary on reference-beam phasing


Where we are now:

⇒ Experimental:
  • demonstrated RBD technique for practical triplet-phase measurements
  • dedicated \( \kappa \)-diffractometer
  • modified oscillation camera setup

⇒ Theoretical:
  • phase-sensitive diffraction theory
  • automatic fits to obtain \( \delta \)

⇒ Data reduction & usage:
  • tested existing crystallogr. software
  • developed automatic fitting routine
  • started new phasing algorithm

Where we are going:

⇒ Further developments:
  • automated alignment control
  • rejection criteria to select reliable measurements
  • dealing with simultaneous beams and mosaic spread

⇒ Strategies for using phases:
  • use with direct methods
  • recursive individual phases
  • \( \Delta I_{\pm H} \Rightarrow \) analogy to SAD?

⇒ Goal:
  • solve new protein structures
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Thin Films & Nanostructures

Nanostructures: 1-100 nm
- semiconductors
- magnetic
- organic polymers

Basic information:
- size
- shape -- morphology
- strain -- internal structure

Physical properties:
- semiconductor band gap
- growth kinetics
- phase transitions
- magnetization
- …..
Example: band gap in semiconductors

InGaAs QWR: $t = 10\text{nm}$

Reed, Tentarelli, Eastman et al. (1995)
Intrinsic and External Strain

Elastic Strain: \[ \{\sigma\} = \{C\} \{\varepsilon\} \] Hook’s Law

⇒ External: external pressure
lattice mismatch

⇒ Intrinsic: microscopic nature
exchange striction

In general, strain information is not easily available from many surface probe (AFM, SEM, STM) measurements
Structural Characterization

Experimental Methods: TEM, XRD

Technical challenges:
- Signal to background?
- Particle size broadening?
- Strain variation?
Basic Concepts in XRD

**Size Effect:**
- Real space
- Reciprocal space
  \[ \Delta Q \sim \frac{1}{L} \]
  \[ \Delta Q = \text{independent of } |Q| \]

**Strain Effect:**
- \[ \Delta Q = -|Q| \frac{\Delta a}{a} \]
- \[ \Delta Q = |Q| \Delta \theta \]
- \[ \Delta Q \propto |Q| \]
Advanced XRD Techniques

⇒ Reciprocal space mapping
⇒ Grazing-incidence diffraction
⇒ Coherent Grating diffraction
⇒ Crystal truncation rod (CTR)
Examples of Grating Diffraction

InGaAs QWR
/ GaAs (001)

Si (001) needles
Average Strain

Sample: ~0.5mm$^2$ multiple regions w/ different QWRs
Strain Effects on Band Gap

Size-dependent strain in QWRs

Deformation potentials:

\[ a = -9.016 \text{ eV} \]
\[ b = -1.96 \text{ eV} \]

Band-gap change w.r.t. quantum well:

\[ \Delta E = a(\varepsilon_{xx} + \varepsilon_{zz}) + b(\varepsilon_{zz} - \varepsilon_{xx}/2) \]

Shen et al. (1996) PRB 54, 16381.
Average Strain vs. Strain Gradient

(a) Without strain relaxation

(b) With uniform strain relaxation

(c) With lateral strain gradient
Strain Gradient Example

Shen & Kycia (1997)
PRB 55, 15791.
Longitudinal vs. Transverse Gradients

Longitudinal wave

Longitudinal Gradient :
\[ \frac{\partial a_x}{\partial x} \]

Transverse wave

Transverse Gradient :
\[ \frac{\partial a_z}{\partial x} \]

Shen & Kycia (1997)
PRB 55, 15791.
Transverse Strain Gradients
Simulations Compared with Experiments
Information that can be obtained from crystal gratings

=> Size and shape information:
   width, height, period,
   side-wall slope, ...

=> Imperfections:
   inhomogeneities, defects, ...

=> Time-resolved changes
   e.g. during oxidation, ...

=> Superlattice registry
   w.r.t. substrate lattice

=> Strain in nanostructures:
   average strain
   strain variation (gradient)
   => longitudinal $\partial a_x/\partial x$
   => transverse $\partial a_z/\partial x$
Anti-ferromagnetic Thin Film
\( \text{Zn}_{0.07}\text{Mn}_{0.93}\text{Te} / \text{ZnTe} \)

1 \( \mu \text{m} \)

\( \text{ZnMnTe: fcc} \)

\( \text{ZnTe} \)
Three Orthorhombic Domains

3. Same as Problem 2. At low temperatures (<60 K) the Zn_{0.07}Mn_{0.93}Te becomes antiferromagnetic, and the crystal lattice transforms into orthorhombic, resulting in 3 types of domains that co-exist in the sample. The orthorhombic distortion in each type of domains can be expressed by: \( \varepsilon = 7 \times 10^{-4} \)

\[
\begin{align*}
    a &\rightarrow a(1-\varepsilon), & b &\rightarrow b(1-\varepsilon), & c &\rightarrow c(1+\varepsilon), \\
    a &\rightarrow a(1-\varepsilon), & b &\rightarrow b(1+2.75\varepsilon), & c &\rightarrow c(1-2.75\varepsilon), \\
    a &\rightarrow a(1+2.75\varepsilon), & b &\rightarrow b(1-\varepsilon), & c &\rightarrow c(1-2.75\varepsilon),
\end{align*}
\]

for c-type, for b-type, for a-type.

(a) Repeat (d) in Problem 2. (Ignore the ZnTe).

Interfacial stress \( \Rightarrow \) Preferred c-type domain population 3:1:1
The exchange striction is the result of an energy balance between the magnetoelastic energy involving spatial derivative $\nabla J(r)$ of the exchange interaction [11,18]

$$U_m = -2 \sum_{i>j} \varepsilon_{\alpha\beta} x_{\alpha} \partial J(r_{ij})/\partial x_{\beta} (S_i \cdot S_j),$$

and the elastic energy of the crystal [1]

$$U_e = \frac{1}{2} C_{11} (\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2)$$

$$+ C_{12} (\varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{yy} \varepsilon_{zz} + \varepsilon_{zz} \varepsilon_{xx}),$$

Fe Thin Film on GaAs (001)

Misfit = -1.4%
\( a_{\text{GaAs}} = 0.56537 \text{ nm} \)
\( a_{\text{Fe}} = 0.28664 \text{ nm} \)
Cube on cube epitaxy

Olivier Thomas
U. Marceille

In-plane uniaxial magnetic anisotropy below 5 nm

J. Krebs, B. Jonker, G. Prinz,
JAP 61 (1987) 2596

\( t_f = 1.7 \text{ nm: } [110] \text{ easy} \)
\( t_f = 80 \text{ nm: } <100> \text{ easy} \)
Magnetic Anisotropy

- Domain shape anisotropy
- Magnetoelastic coupling
- Magnetocrystalline anisotropy
- Interface-induced effect
Fe / GaAs (001) Samples

MBE: GaAs 500 nm buffer
As rich (2x4) surface
1.5 \times 10^{-10} \text{Torr}
Fe: 1 nm/min at RT
3 nm Al capping layer

Fe thickness
from 1.5 to 13 nm

[110]: defined as unit-cell doubling direction
X-ray Diffraction Study

CHESS F3: 8 keV

⇒ Out-of-plane reflections:
   (004) and (224)
   film thickness
   out-of-plane lattice const.
   separate Fe and GaAs peaks

⇒ In-plane reflections:
   (220), (400), ...
   in-plane lattice strain
   in-plane domain size & shape
   in-plane correlations
Out of Plane Scans

Data: s389_J
Model: Lor2AsymSinc
Equation: \( y = y_0 + \frac{A_0}{1 + \left(\frac{x-x_0}{w_0}\right)^2} \cdot \left(1 + \left(\frac{x-x_0}{w_0}\right)^2\right) + A_c \cdot \exp\left(-\left(\frac{x-x_c}{w_2}\right)^3 - \left(\frac{x-x_c}{w_1}\right)^2\right) \cdot \left(\frac{x-x_c}{w_c}\right)^2 \)

- \( y_0 \): 3 ± --
- \( A_0 \): 600000 ± --
- \( x_0 \): 3.9988 ± --
- \( w_0 \): 0.0065 ± --
- \( A_c \): 12000 ± --
- \( x_c \): 3.8885 ± --
- \( w_c \): 0.047 ± --
- \( w_1 \): 0.36 ± --
- \( w_2 \): 0.37 ± --

Intensity (cts/1.5sec)

Thomas, Shen, et al. (2002).

1.5 nm Fe on GaAs (001)

3.9 nm Fe on GaAs (001)
In-plane Map for $t = 1.5$ nm

MBE95: 1.5 nm
Fe/GaAs (001)
In-plane Map for $t = 13$ nm

MBE241: 13 nm
Fe/GaAs (001)
In-plane 4-scans

(220)
In-plane $\theta$-2$\theta$ scans

$t = 1.5$ nm  $t = 3.9$ nm  $t = 13$ nm
Anisotropic Domain & Strain Relaxation

- Strain Relaxation $\Delta a/a$
  - $[110]$
  - $[110]$

- Domain Size (Å)
  - $L[-110]$
  - $L[110]$

Fe Film Thickness (Å)

Graphs showing the relationship between Fe film thickness and strain relaxation, as well as domain size for different crystallographic orientations.
Magnetic free energy density:

\[ f_m = \frac{K_1}{4} \sin^2 2\phi + \frac{K_u}{t} \sin^2 \left( \phi - \frac{\pi}{4} \right) + \frac{B_2}{2} \varepsilon_6 \sin 2\phi \]

\( \phi \) = angle between magnetization and [100]

\( K_1 = 48 \text{ kJ m}^{-3} \) is the cubic anisotropy energy of Fe

\( B_2 = 7620 \text{ kJ m}^{-3} \) is the magneto-elastic coupling coefficient of Fe

\( \varepsilon_6 \) = shear strain measured in x-ray diffraction experiment

\( \Rightarrow \) additional \( K_u/t \) term that favors [110] easy: \( K_u = 1 \times 10^{-4} \text{ J m}^{-2} \)
Comparison with MOKE

(MOKE data from André Guivarch, Université de Rennes)

\[ t = 1.5 \text{ nm} \]
\[ t = 3.9 \text{ nm} \]
\[ t = 13 \text{ nm} \]
Conclusions on Fe / GaAs

⇒ Considerable strain and shape anisotropies do exist in these Fe thin films

⇒ The interfacial effect, $K_u / t$ term, is the principal contributor to the observed UMA for thin Fe films

⇒ The strain anisotropy is the main factor responsible for the reversal of UMA at thicker Fe films
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