ε-Machine Spectral Reconstruction Theory Applied to Discovering Planar Disorder in Close-Packed Stuctures

Dowman P Varn

dpv@complexmatter.org

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Readings for this lecture:

BTFM1 and BTFM2 articles in *CMR* and *Lecture Notes*

Phenomenology of Polytypism

- Definition: Polytypism is the phenomenon of a substance that can assume two or more layer-like structures each having the same stoichiometry but differing in the manner of the stacking of layers. (Called Modular Layers)

- One-Dimensional: The *intra*-layer bonding is much sronger than the *inter*-layer bonding, creating effectively one-dimensional materials.

- Wide Spread: Occurs in SiC, ZnS, CdI_2; micas such as muscovite and mangarite; III-VI compounds like GaS, GaSe and InSe; metals and alloys like Co, Li and $ZrCr_2$; oxides like $Ba_5Nb_4O_{15}$ and $BaRuO_3$; sulfides like $BaTaS_3$.

- Variety of Materials: Many have widely varying properties: metals & insulators, covalent & ionic bonding.

- Plethora of Structures: In some compounds, there can be 100's of different crystalline structures.

- Long Range Order: Some of these structures can exist over 100 modular layers.

- Disordered: Many of these structures have considerable planar disorder.

Stacking Faults in SiC
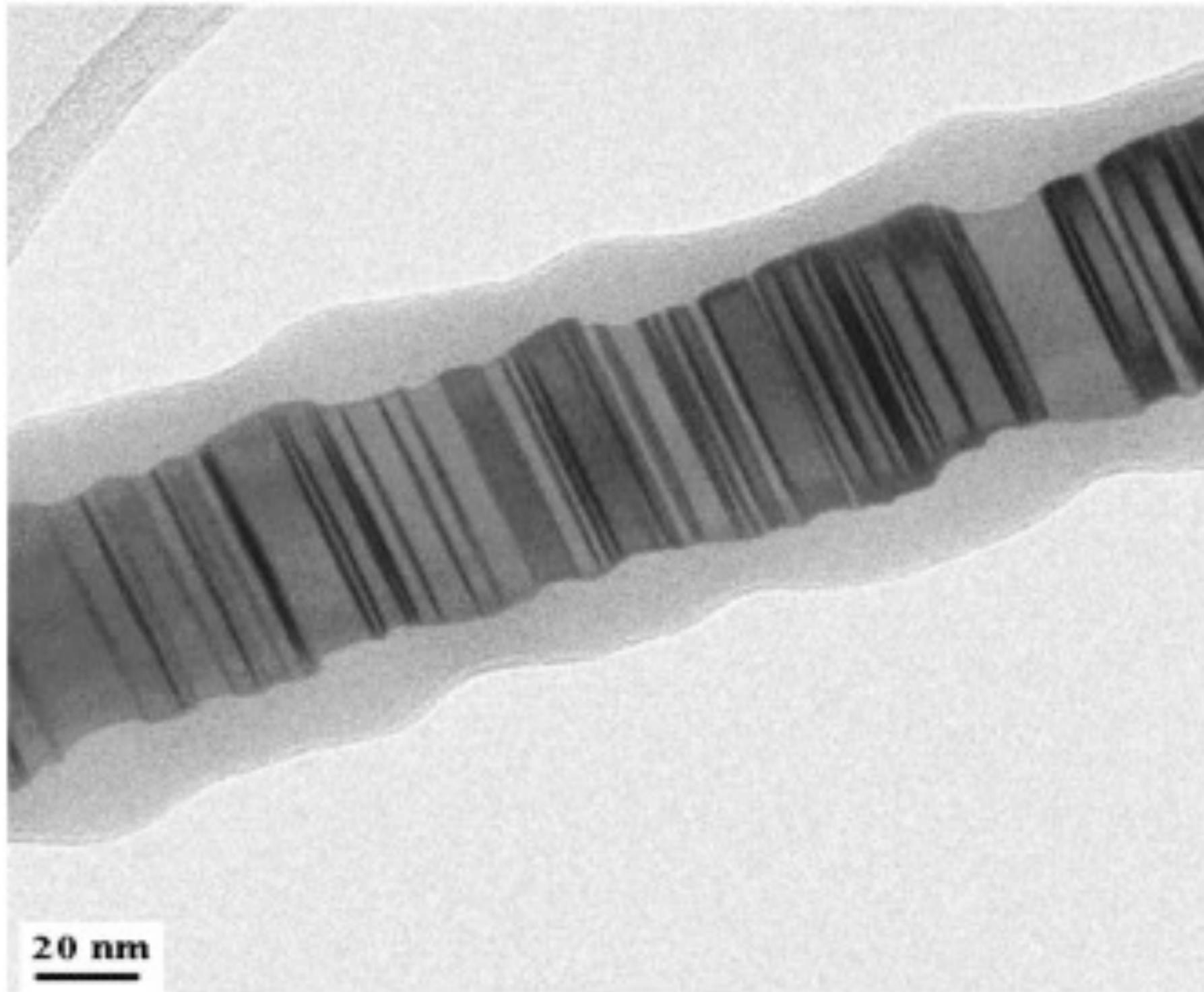
"TEM image of stacking faults present in pyrolyzed–oxidized sample of SiC." From Shivani B. Mishra, Ajay K. Mishra, Bhekie B. Mamba & Michael J. Witcomb, *Materials Letters* 65 (2011) 2245–2247

Previous Descriptions of Planar Disorder

- Jagodzinski's Disorder Theory (Jagodzinski, 1949)

- The Fault Model (Sebastian & Krishna, 1980 and many others)

- Reverse Monte Carlo (McGreevy & Pusztai, 1988)

Close-Packed Structures
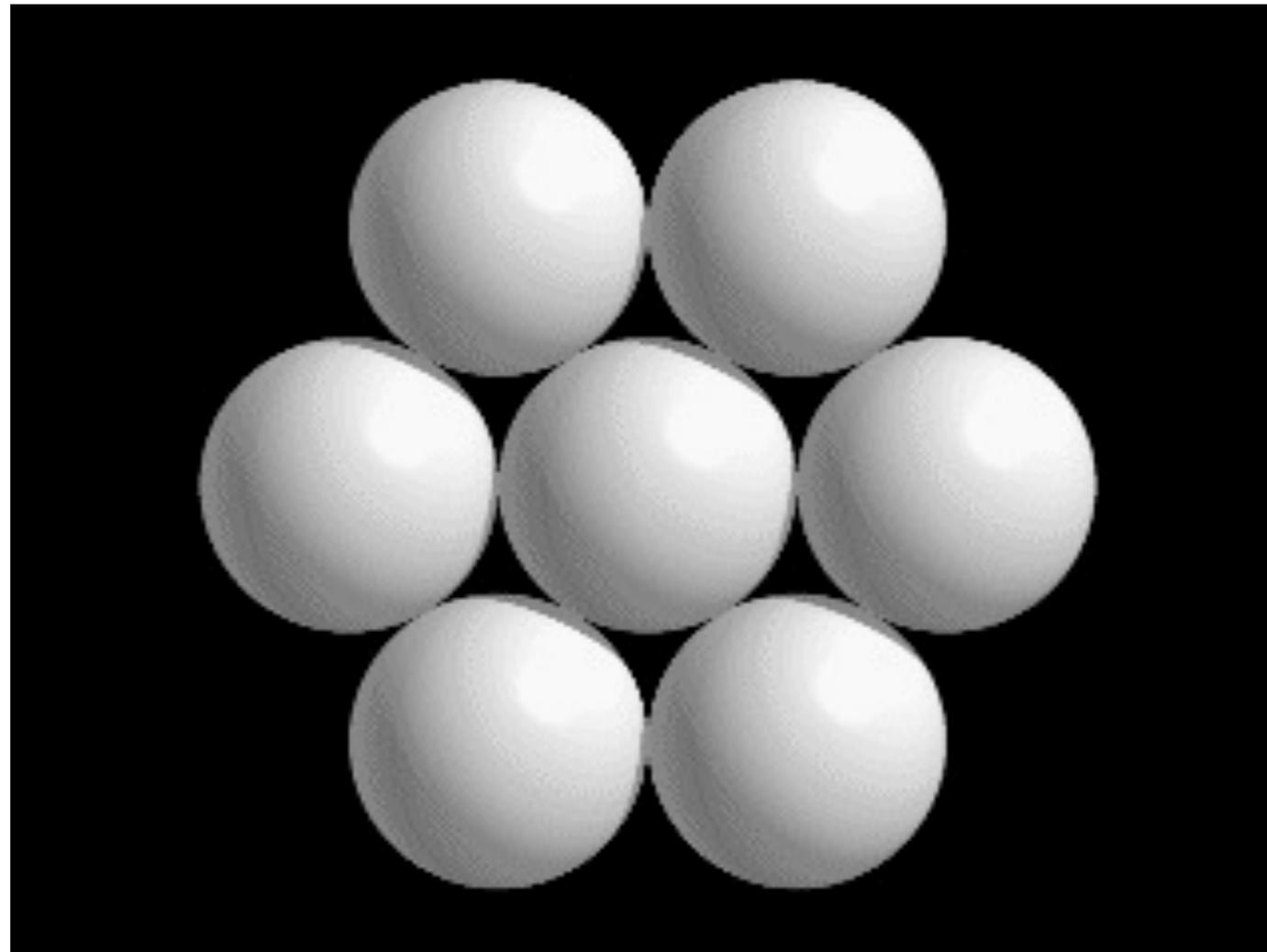
Hexagonal Close-Packed Structures (2H)
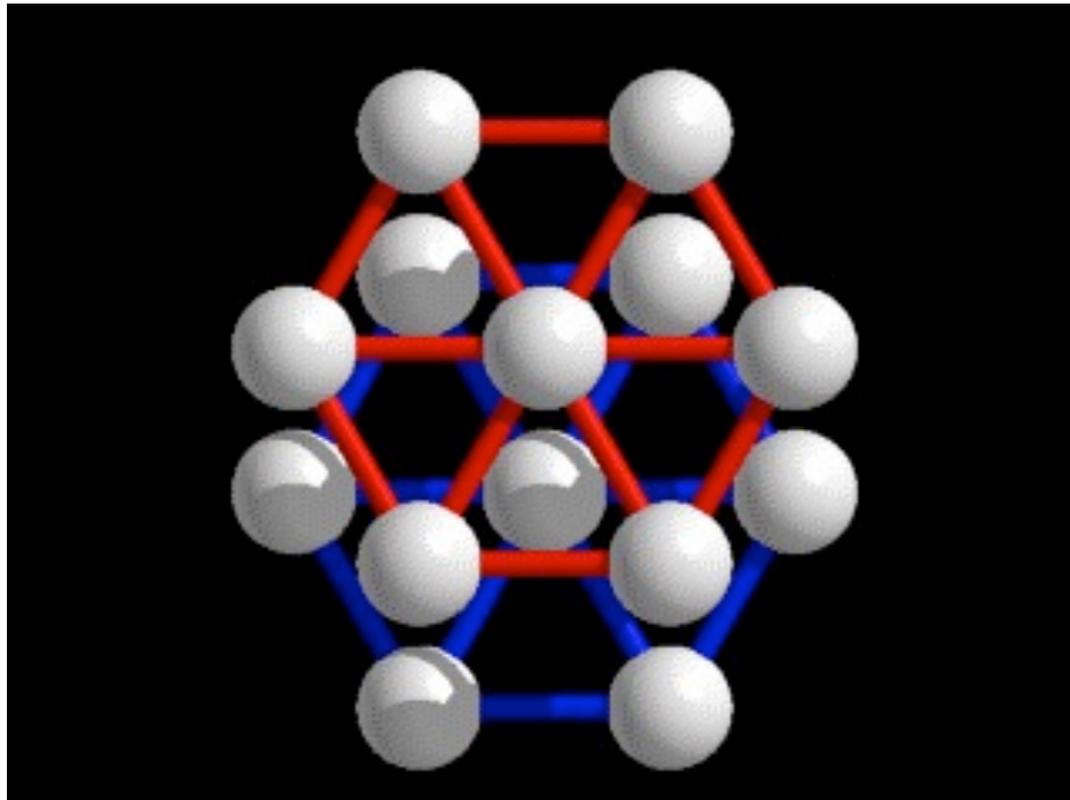
Hexagonal Close-Packed Structure
as seen from above
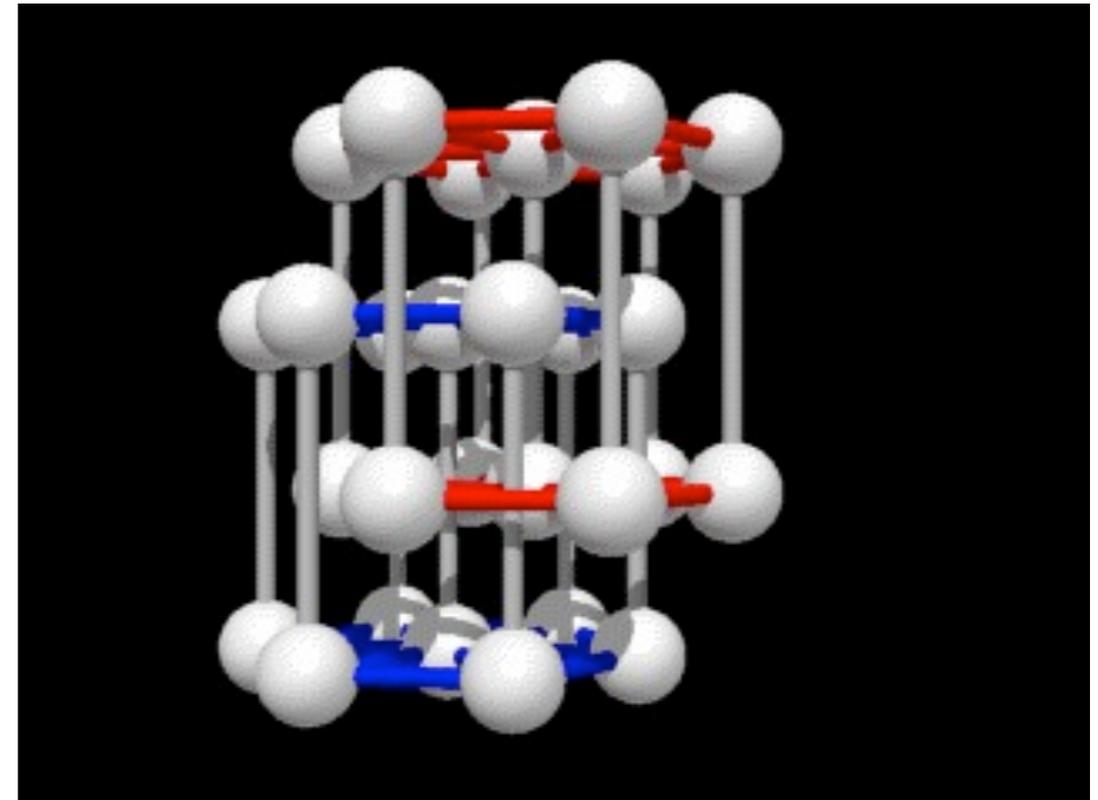
Hexagonal Close-Packed Structure
as seen from the side

Cubic Close-Packed Structures (3C)
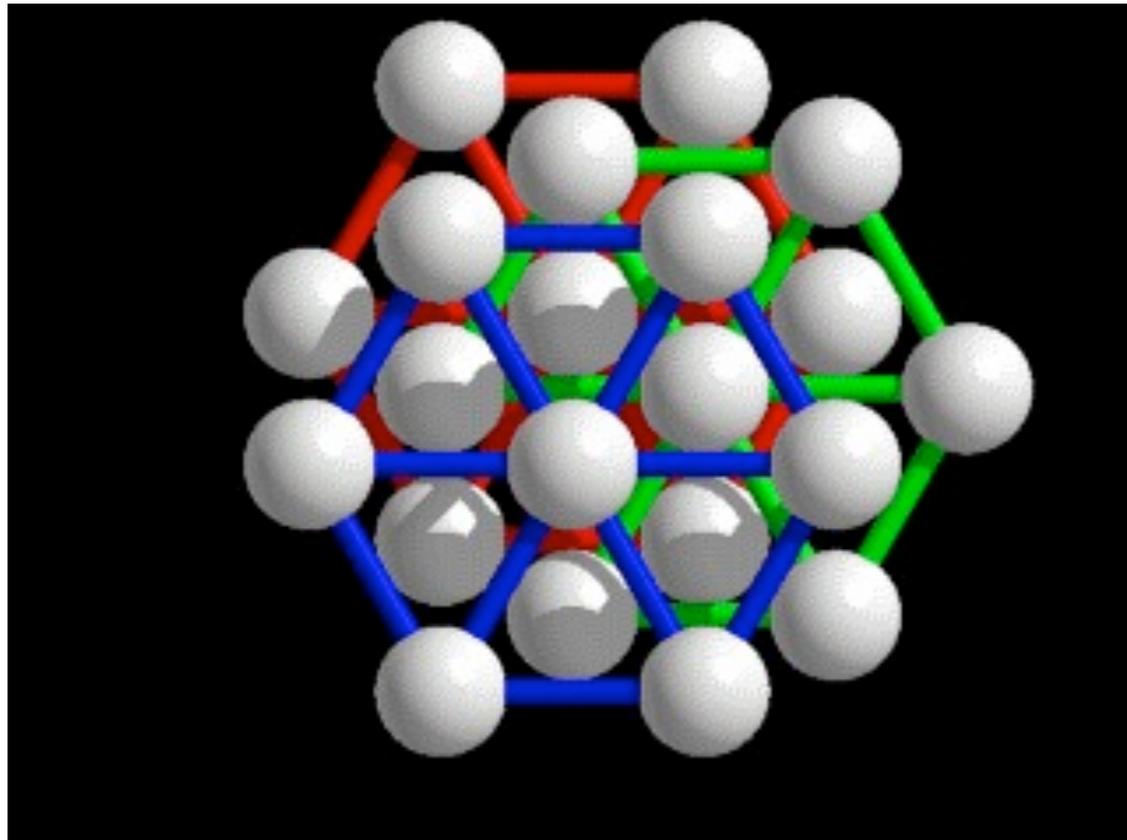
Cubic Close-Packed Structure
as seen from above
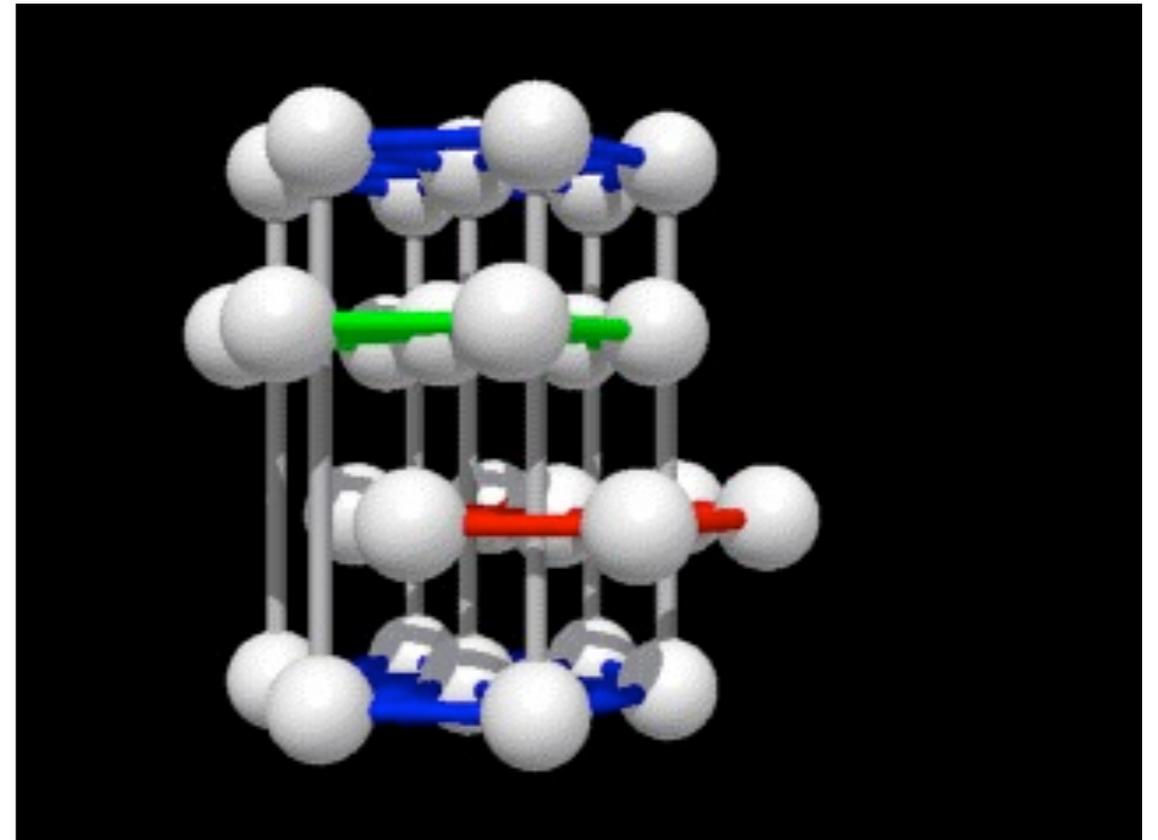
Cubic Close-Packed Structure
as seen from the side

The Structure of Zinc Sulphide

• Consider the 'basic unit' to be a zinc-sulphur pair stacked vertically. (A green-brown pair in the figure to the left.)

• Then, Modular Layers are formed from a hexagonal net of these units.

• It turns out that there are only three possible orientations any modular layer can occupy. Call them **A**, **B**, and **C**.

• A sample is specified by giving the sequence of modular layers.

• The stacking constraints can be expressed as no two adjacent layers can have the same orientation.

• We can take advantage of this by using an alternate labeling scheme:

$$\mathbf{A} \to \mathbf{B} \to \mathbf{C} \to \mathbf{A} \ : \ \text{'1'}$$

$$\mathbf{A} \to \mathbf{C} \to \mathbf{B} \to \mathbf{A} \ : \ \text{'0'}$$

• So the sequence to left (reading from bottom to top) would be **ABABCA** which could be written in as **10111**.
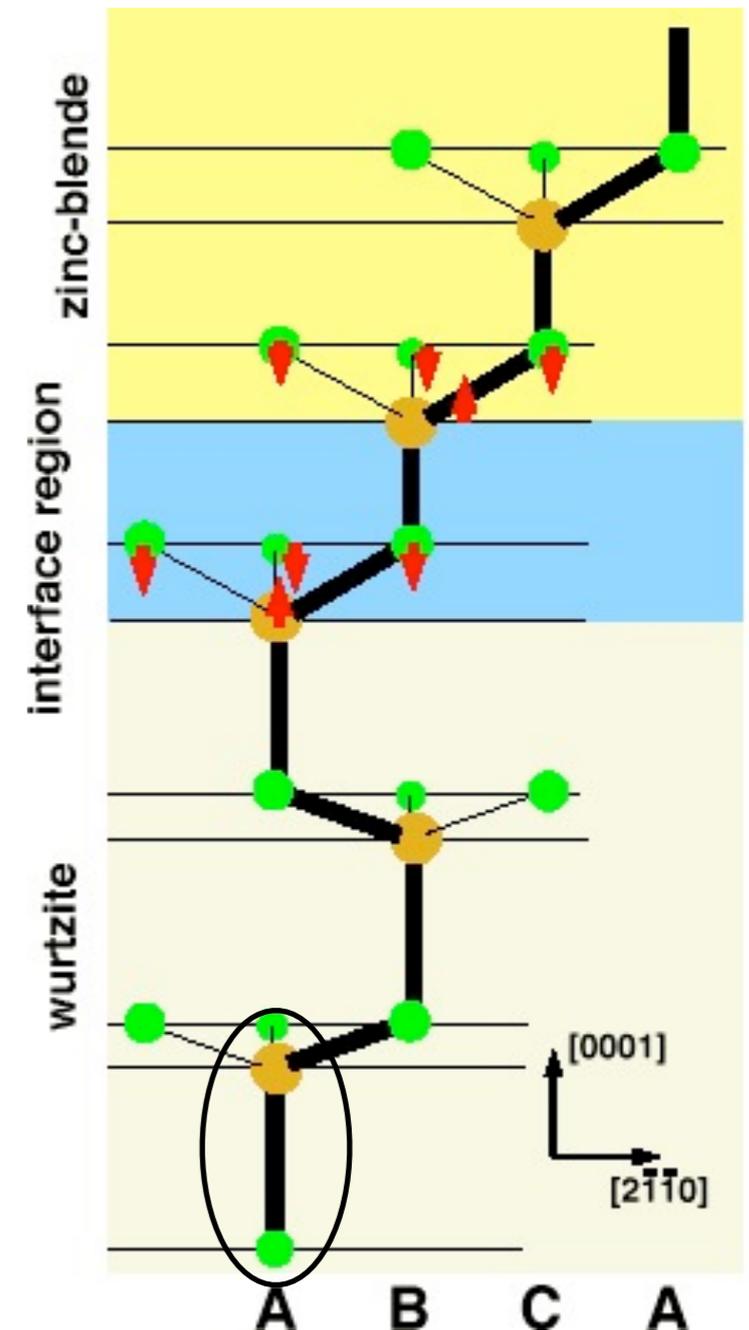
Thus, a crystal is completely specified by a sequence of **1**'s and **0**'s

Some Common Stacking Structures in CPSs
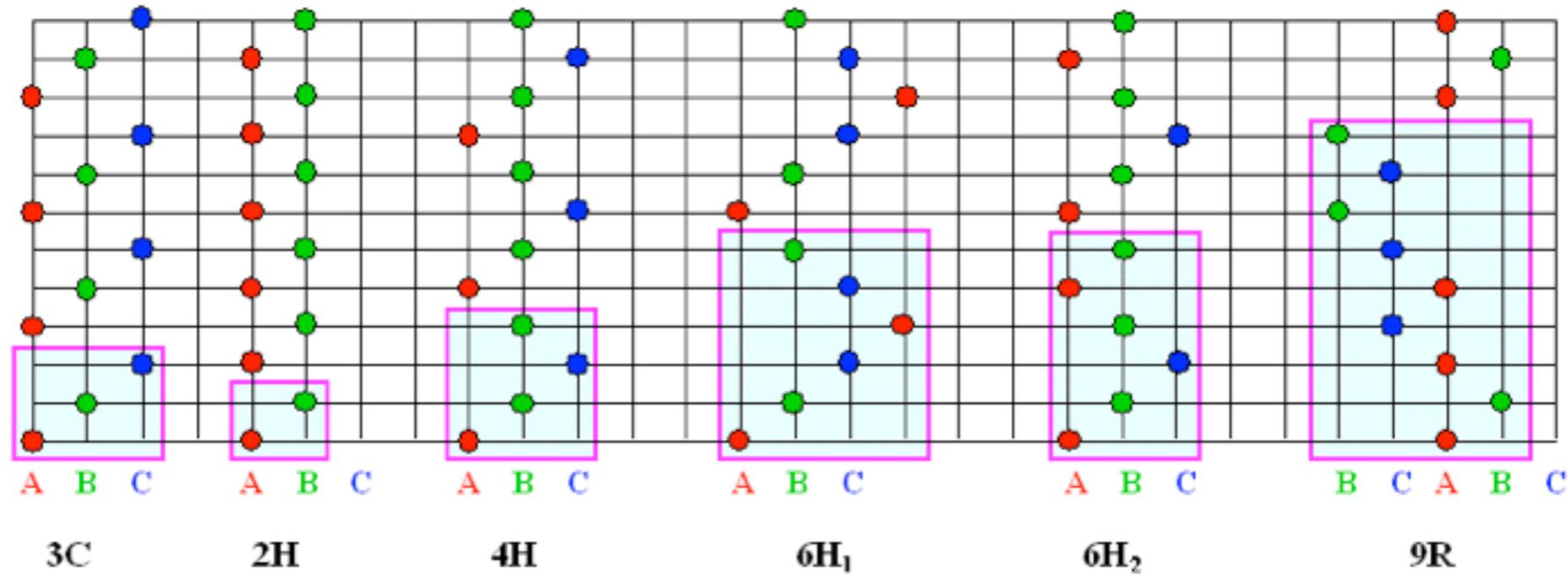
3C$^+$: ...ABCABCABCABC... or ...111111111111... or (1)*

3C$^-$: ....ACBACBACBACB... or ...00000000000... or (0)* (Not shown)

2H: .....ABABABABABAB... or ...1010101010101... or (01)*

4H: .....ABCBABCBABCB... or ...110011001110... or (1100)*

6H$_1$: ...ABCACBABCACB... or ...111000111100... or (111000)*

6H$_2$: ...ABCBABABCBAB... or ...110010110010... or (110010)*

9R$^+$: ...ACABABCBCACA... or ...011011011101... or (011)* (Not shown)

9R$^-$: ....ABACACBCBABA... or ...10010010010... or (100)*

Notice that the period in the two notations *need not be the same!*

Stacking Faults in ZnS
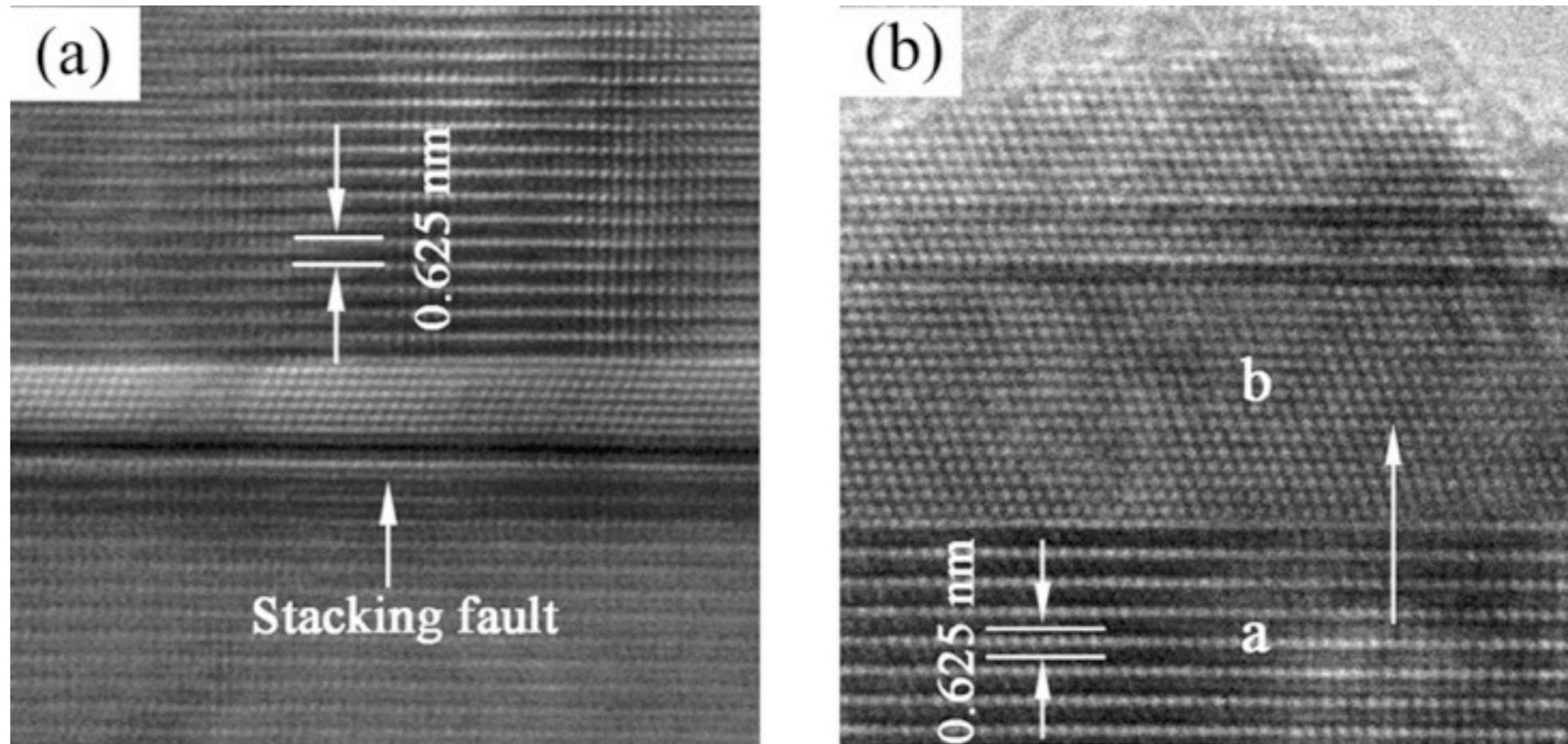
"Figure 9a illustrates the stacking fault existed in a single nanobelt, which is parallel to the axis and runs through out the nanobelt. Figure 9b shows two types of structure zone existed in a leg of tetrapod ZnS. One consists of the wurtzite structure (hcp, hexagonal close-packed) in zone a and the other is sphalerite structure (fcc, face centered cubic) in zone b, and the two different structures were formed by changing the stacking sequence of the closed-packed planes of the ZnS crystal and resulted from the crystallogenesis of ZnS. It should be noted that some properties, such as the photoluminescence, gas sensing property of obtained products are closely related to the intrinsic defects in crystals (Jiang et al., 2003)."

Polytypes in Bulk $Zn_{1-x}Mg_xSe$ crystals
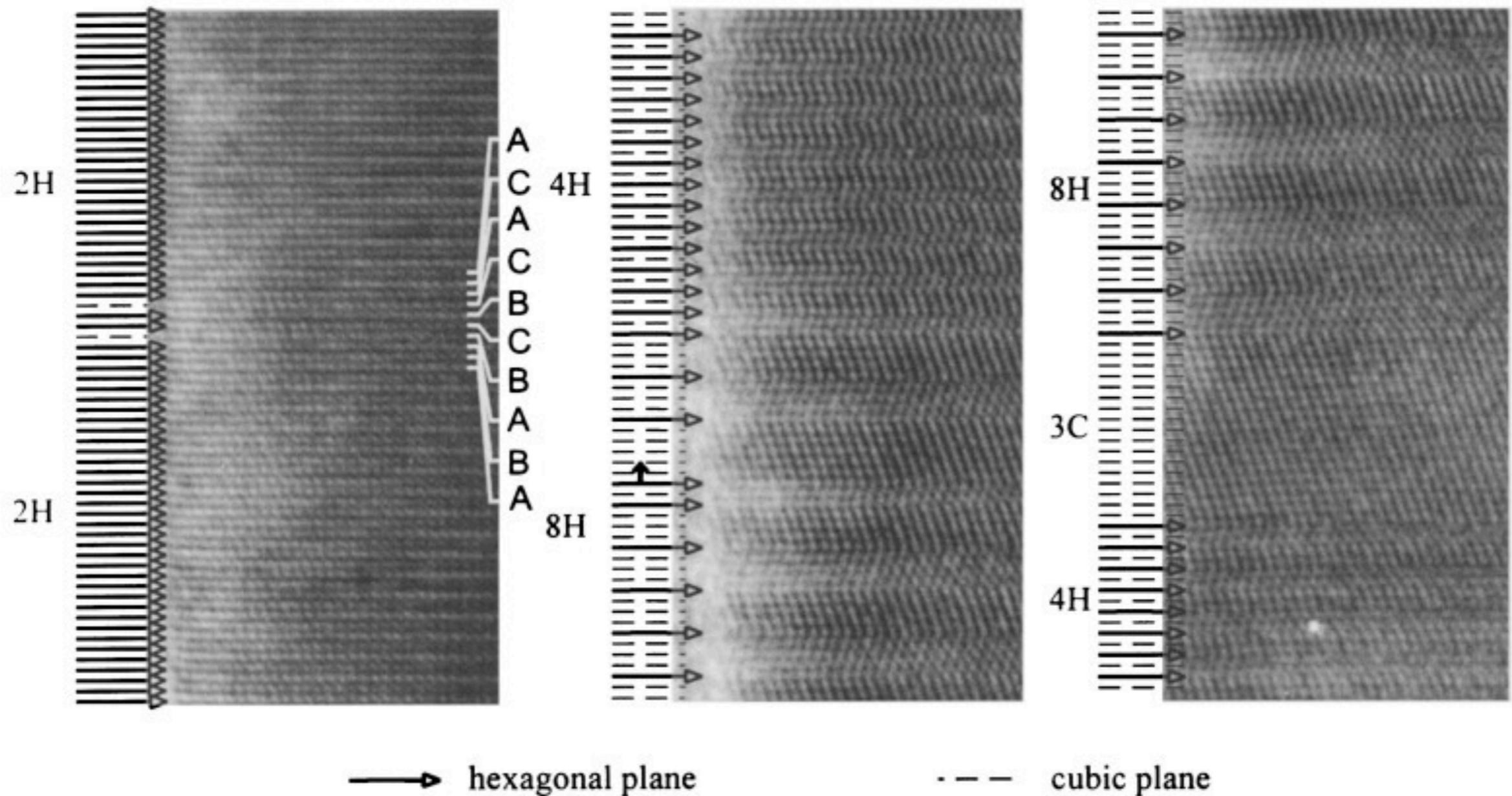
"HRTEM images of plate B5: (a) 2H domain with a defect consisting of additional planes with cubic stacking indicated by the dashed lines. On the right side of the picture the stacking sequence is explained. (b) Direct 8H/4H interface; a stacking fault in 8H domain is indicated by the vertical arrow, (c) An 8H/4H interface; at the interface, a strip built of 17 planes stacked according to the 3C structure is observed." From: W Paszkowicz, P Dluewski and ZM Spolnik and F Firszt and H Meczynska (1999) Journal of Alloys and Compounds 286, pp. 224-235.

Experimental Details

Experiment measures the intensity **I** scattered into an angle θ. Sometimes, though, the intensity is reported as a function of the component of the reciprocal lattice vector perpendicular to the modular layers (l). Without going through the kinematics, it is sufficient to know that l indexes the angle θ. Thus, instead of **I**(θ) we often have **I**(l).
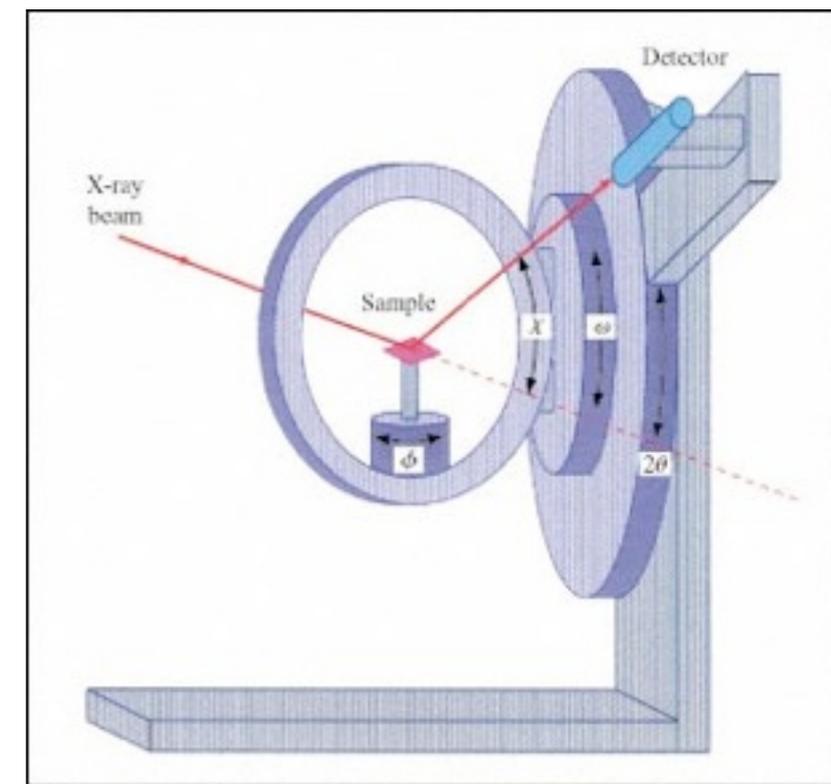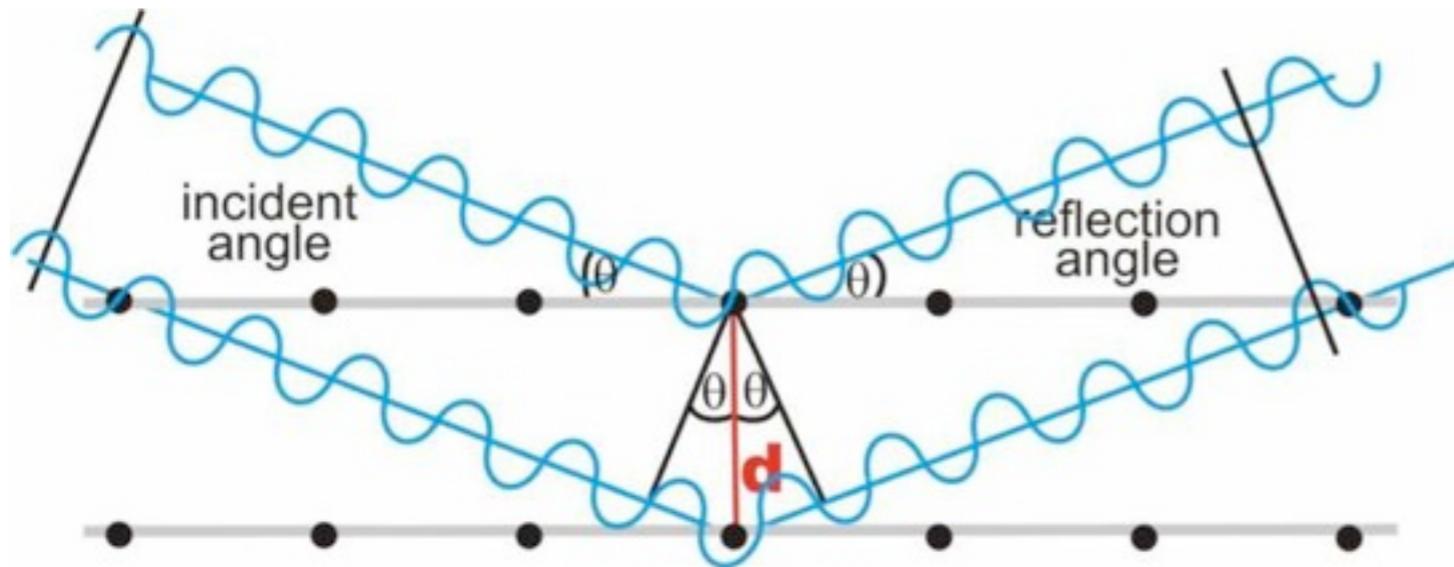
Schematic of a Four-Circle Diffractometer

Four Circle Diffractometer

From: http://en.wikipedia.org/wiki/File:Kappa_goniometer_animation.ogg

Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield

Four Circle Diffractometer
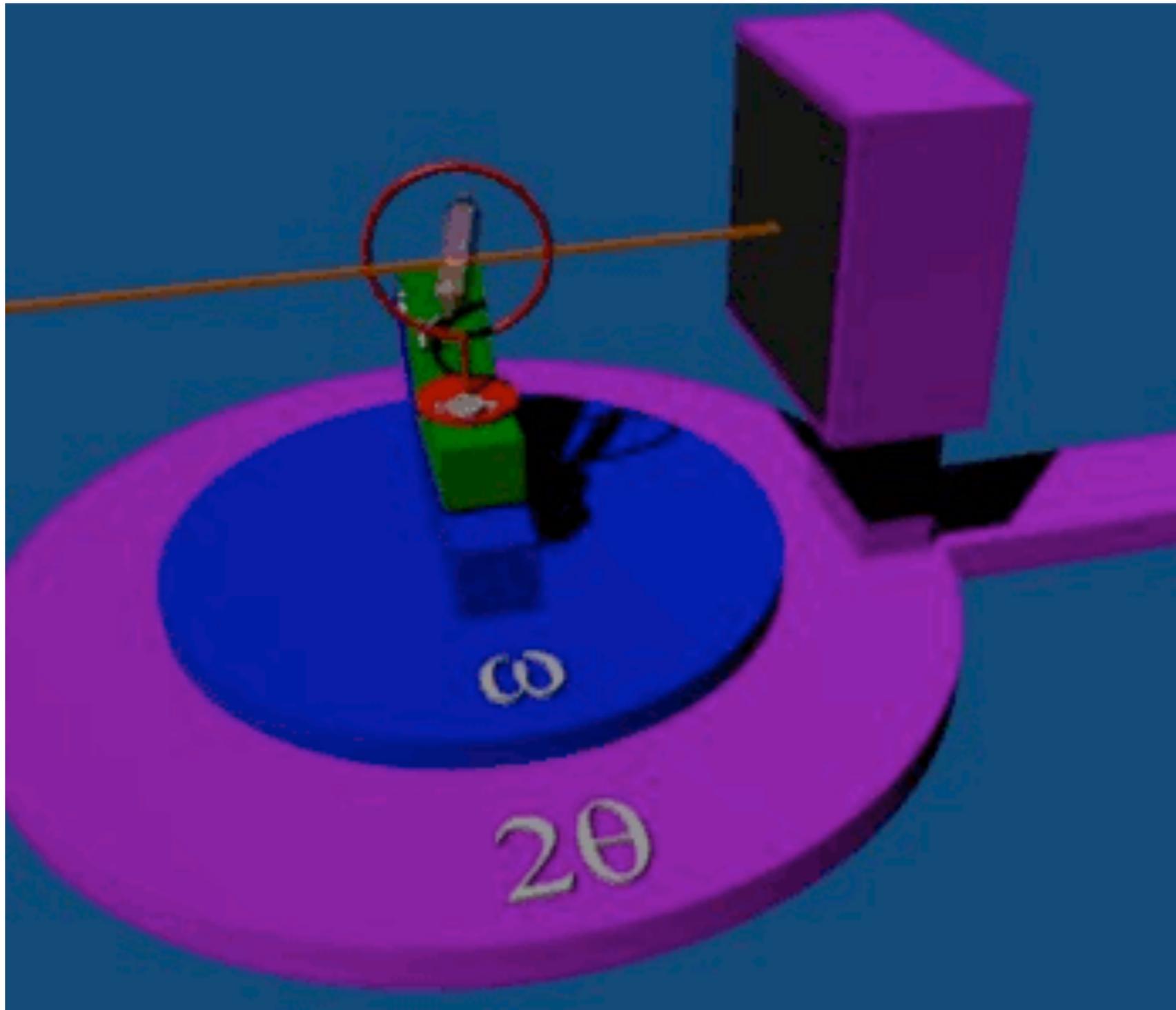
From: http://en.wikipedia.org/wiki/File:Kappa_goniometer_animation.ogg

Diffraction Spectra from Close-Packed Structures

$$I(l) = \psi^2(l)\left(\frac{\sin^2(\pi N l)}{\sin^2(\pi l)} - 2\sqrt{3}\sum_{n=1}^{N}\left\{(N-n)\left[Q_c(n)\cos(2\pi nl + \frac{\pi}{6}) + Q_a(n)\cos(2\pi nl - \frac{\pi}{6})\right]\right\}\right),$$

- *I(l)* is the diffracted intensity along the direction perpendicular to the stacking,
- *l* indexes the magnitude of the perpendicular component of the diffracted wave,
- *ψ²(l)* accounts for scattering factors,
- *N* is the number of modular layers,
- *$Q_c(n)$* and *$Q_a(n)$* are the Correlation Functions, i.e., the probability any two modular layers at separation cyclically or anti-cyclically related. *$Q_s(n)$* is probability that two layers at separation *n* have the same orientation. Note that *$Q_c(n) + Q_a(n) + Q_s(n) = 1$*.

We can expand the cosine terms and integrate over a unit interval and find,

$$X(n) = \oint I(l)\cos(2\pi nl)\,dl \qquad \text{and} \qquad Y(n) = \oint I(l)\sin(2\pi nl)\,dl$$

Thus the correlation functions can be written as:

$$Q_c(n) = \frac{1}{3} - \frac{1}{3}\left[X(n) - \sqrt{3}Y(n)\right] \qquad \text{and} \qquad Q_a(n) = \frac{1}{3} - \frac{1}{3}\left[X(n) + \sqrt{3}Y(n)\right]$$

Thus, the correlation functions can found by Fourier Analysis of the Diffraction Spectrum

Figures-of-Merit for Diffraction Spectra

It can be shown that the diffraction spectrum must obey two equalities when integrated over a unit interval in l. We can use this to evaluate the quality of data over candidate unit intervals.

$$\gamma = \oint \mathsf{I}(l) \cos(2\pi l) \, dl = -1/2$$

$$\beta = 2Q_c(1) + Q_c(2) - Q_a(2) = 1$$

Quick Derivations:

$$Q_c(1) + Q_a(1) = 1$$

$$\mathsf{X}(1) = -1/2$$

$$\gamma = \oint \mathsf{I}(l) \cos(2\pi l) \, dl$$

$$\gamma = -1/2$$

$$\Pr(00) + 2\Pr(01) + \Pr(11) = 1$$

$$\Pr(01) = \Pr(1) - \Pr(11)$$

$$\Pr(00) + 2\Pr(1) - \Pr(11) = 1$$

$$2Q_c(1) + Q_c(2) - Q_a(2) = 1$$

$$\beta = 2Q_c(1) + Q_c(2) - Q_a(2)$$

$$\beta = 1$$

Some Diffraction Spectra for Periodic CPSs

Diffraction Pattern for a FCC Lattice

3C⁺

(1)*

Diffraction Pattern for a HCP Lattice

2H

(01)*
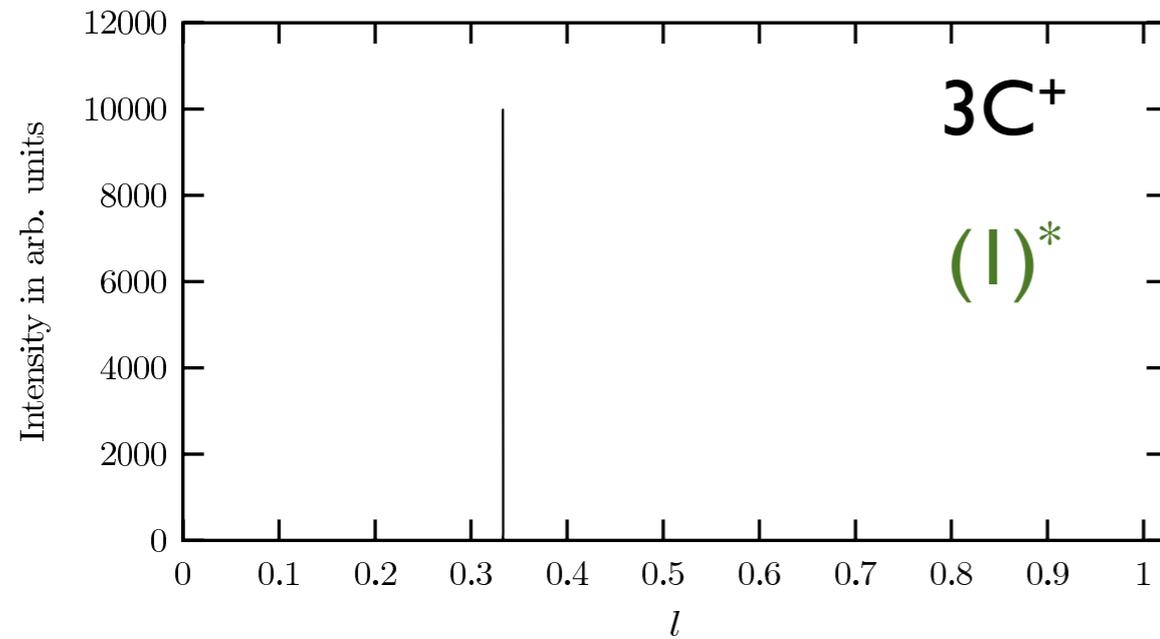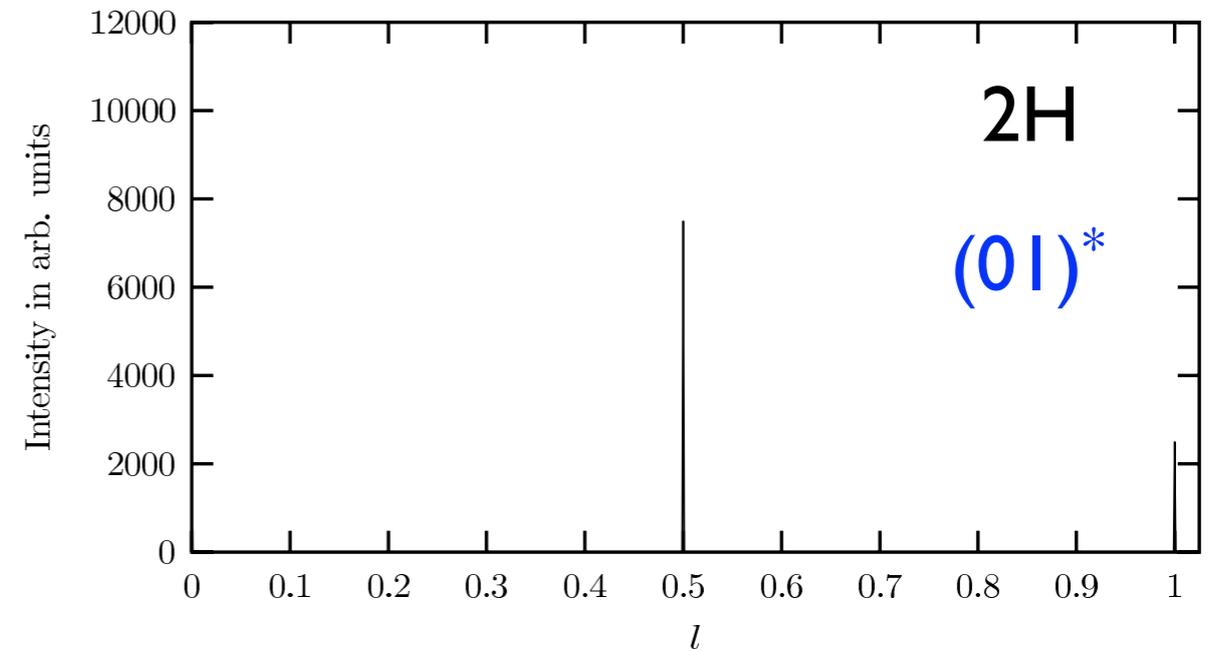
Diffraction Pattern for the 4H Process

4H

(1100)*

Diffraction Pattern for the 6H Process

6H₁
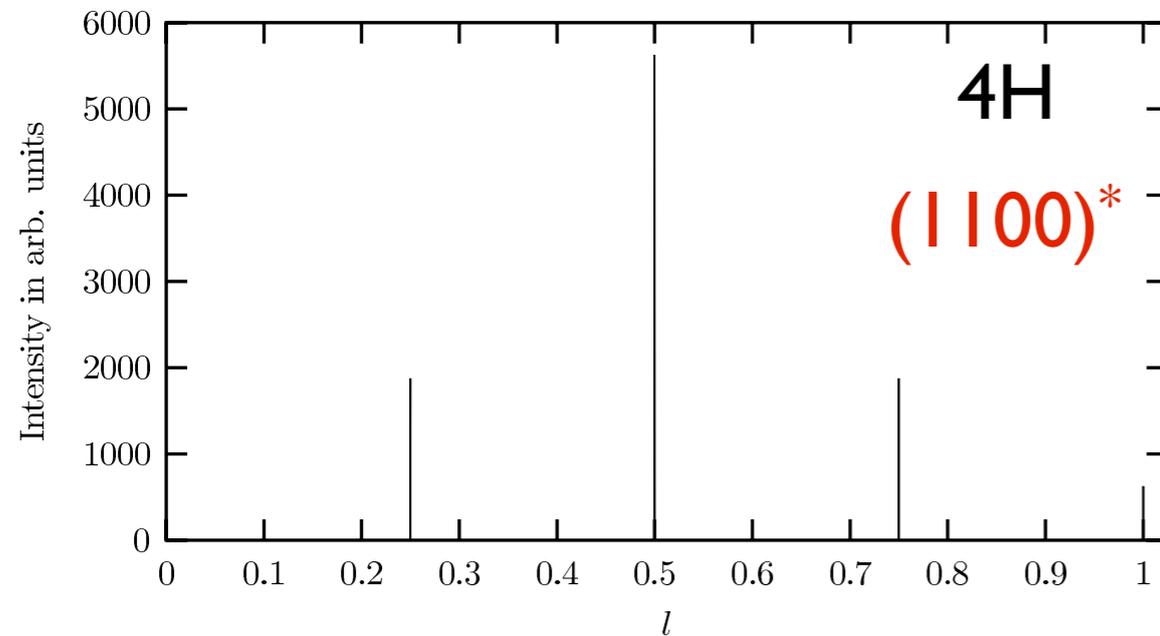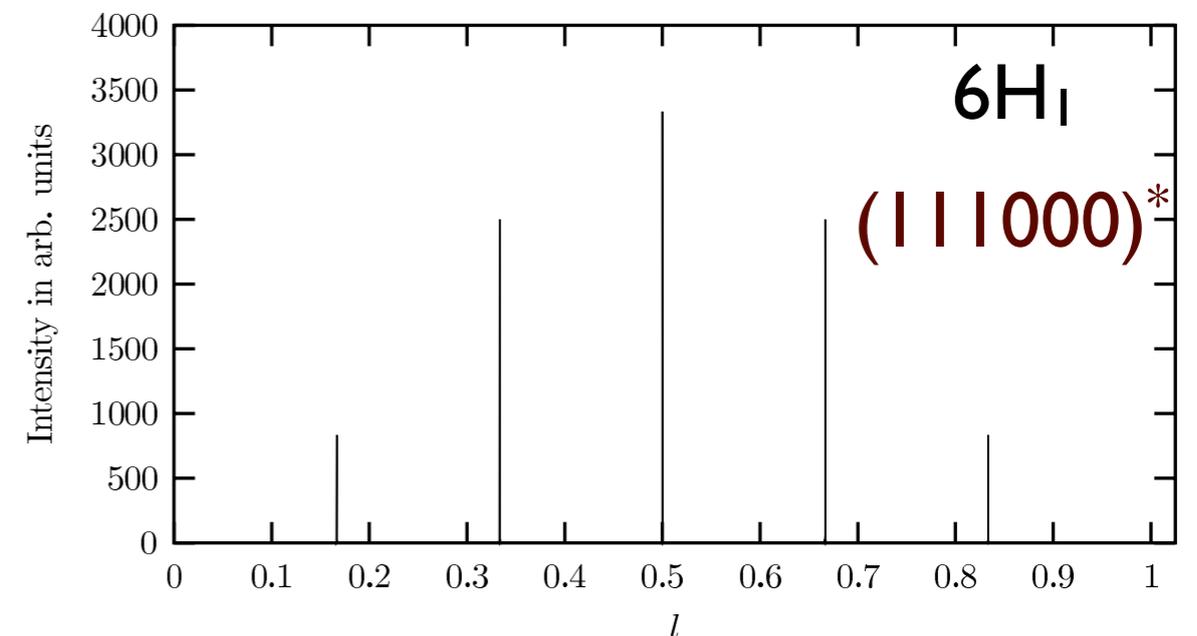
(111000)*

The $r = 3$ Spectral Equations for CPSs

$$\Pr(0000) + \Pr(0001) + \Pr(0010) + \Pr(0011) + \Pr(0100)\,\Pr(0101) + \Pr(0110) + \Pr(0111) + \Pr(1000) + \Pr(1001$$

$$\Pr(1010) + \Pr(1011) + \Pr(1100) + \Pr(1101) + \Pr(1110)\,\Pr(1111) = 1$$

$$
\begin{aligned}
Q_c(2) &= \Pr(0000) + \Pr(0001) + \Pr(0010) + \Pr(0011) \,, \\
Q_r(2) &= \Pr(1100) + \Pr(1101) + \Pr(1110) + \Pr(1111) \,, \\
Q_c(3) &= \Pr(0110) + \Pr(0111) + \Pr(1010) + \Pr(1011) \\
&\quad + \Pr(1100) + \Pr(1101) \,, \\
Q_r(3) &= \Pr(0010) + \Pr(0011) + \Pr(0100) + \Pr(0101) \\
&\quad + \Pr(1000) + \Pr(1001) \,, \\
Q_c(4) &= \Pr(1111) + \Pr(1000) + \Pr(0100) + \Pr(0010) \\
&\quad + \Pr(0001) \,, \\
Q_r(4) &= \Pr(0000) + \Pr(0111) + \Pr(1011) + \Pr(1101) \\
&\quad + \Pr(1110) \,,
\end{aligned}
$$

$$
\begin{aligned}
\Pr(0111) &= \Pr(1110) \,, \\
\Pr(0001) &= \Pr(1000) \,, \\
\Pr(0011) + \Pr(1011) &= \Pr(0111) + \Pr(0110) \,, \\
\Pr(0101) + \Pr(1101) &= \Pr(1011) + \Pr(1010) \,, \\
\Pr(0010) + \Pr(1010) &= \Pr(0101) + \Pr(0100) \,, \\
\Pr(0001) + \Pr(1001) &= \Pr(0011) + \Pr(0010) \,, \\
\Pr(0100) + \Pr(1100) &= \Pr(1001) + \Pr(1000) \,.
\end{aligned}
$$

$$
\begin{aligned}
Q_c(5) = {}& \frac{\Pr^2(0000)}{\Pr(0000) + \Pr(0001)} + \frac{\Pr(0011)\,\Pr(0111)}{\Pr(0111) + \Pr(0110)} + \frac{\Pr(0101)\,\Pr(1011)}{\Pr(1011) + \Pr(1010)} + \frac{\Pr(0110)\,\Pr(1101)}{\Pr(1101) + \Pr(1100)} \\
&+ \frac{\Pr(0111)\,\Pr(1110)}{\Pr(1110) + \Pr(1111)} + \frac{\Pr(1001)\,\Pr(0011)}{\Pr(0011) + \Pr(0010)} + \frac{\Pr(1010)\,\Pr(0101)}{\Pr(0101) + \Pr(0100)} + \frac{\Pr(1011)\,\Pr(0110)}{\Pr(110) + \Pr(0111)} \\
&+ \frac{\Pr(1100)\,\Pr(1001)}{\Pr(1001) + \Pr(1000)} + \frac{\Pr(1101)\,\Pr(1010)}{\Pr(1010) + \Pr(1011)} + \frac{\Pr(1110)\,\Pr(1100)}{\Pr(1100) + \Pr(1101)} \,,
\end{aligned}
$$

$$
\begin{aligned}
Q_r(5) = {}& \frac{\Pr^2(1111)}{\Pr(1111) + \Pr(1110)} + \frac{\Pr(1100)\,\Pr(1000)}{\Pr(1000) + \Pr(1001)} + \frac{\Pr(1010)\,\Pr(0100)}{\Pr(0100) + \Pr(0101)} + \frac{\Pr(1001)\,\Pr(0010)}{\Pr(0010) + \Pr(0011)} \\
&+ \frac{\Pr(1000)\,\Pr(0001)}{\Pr(0001) + \Pr(0000)} + \frac{\Pr(0110)\,\Pr(1100)}{\Pr(1100) + \Pr(1101)} + \frac{\Pr(0101)\,\Pr(1010)}{\Pr(1010) + \Pr(1011)} + \frac{\Pr(0100)\,\Pr(1001)}{\Pr(1001) + \Pr(1000)} \\
&+ \frac{\Pr(0011)\,\Pr(0110)}{\Pr(0110) + \Pr(0111)} + \frac{\Pr(0010)\,\Pr(0101)}{\Pr(0101) + \Pr(0100)} + \frac{\Pr(0001)\,\Pr(0011)}{\Pr(0011) + \Pr(0010)}
\end{aligned}
$$

All of the equations are linear except for the last two. We solve them for sequence probabilities $\Pr(s_1 s_2 s_3 s_4)$ given the correlation functions.

The εMSR Algorithm[1]

Experimental Diffraction Pattern → Experimental Correlation Functions

Compare Experimental and Theory Diffraction Patterns — Bad Agreement: $r \rightarrow r + 1$ → Solve the Spectral Eqs for $P(\omega^r)$

Good Agreement → Quit

Solve the Spectral Eqs for $P(\omega^r)$ → Construct the candidate ε-M → Calculate Theoretical Correlation Functions → Calculate Theoretical Diffraction Pattern → Compare Experimental and Theory Diffraction Patterns

[1]DP Varn, GS Canright, & JP Crutchfield, "ε-Machine spectral reconstruction theory: A direct method for inferring planar disorder and structure from X-ray diffraction studies," Submitted to: *Acta Crystallographica A*.

The Most General $r = 3$ ε-Machine
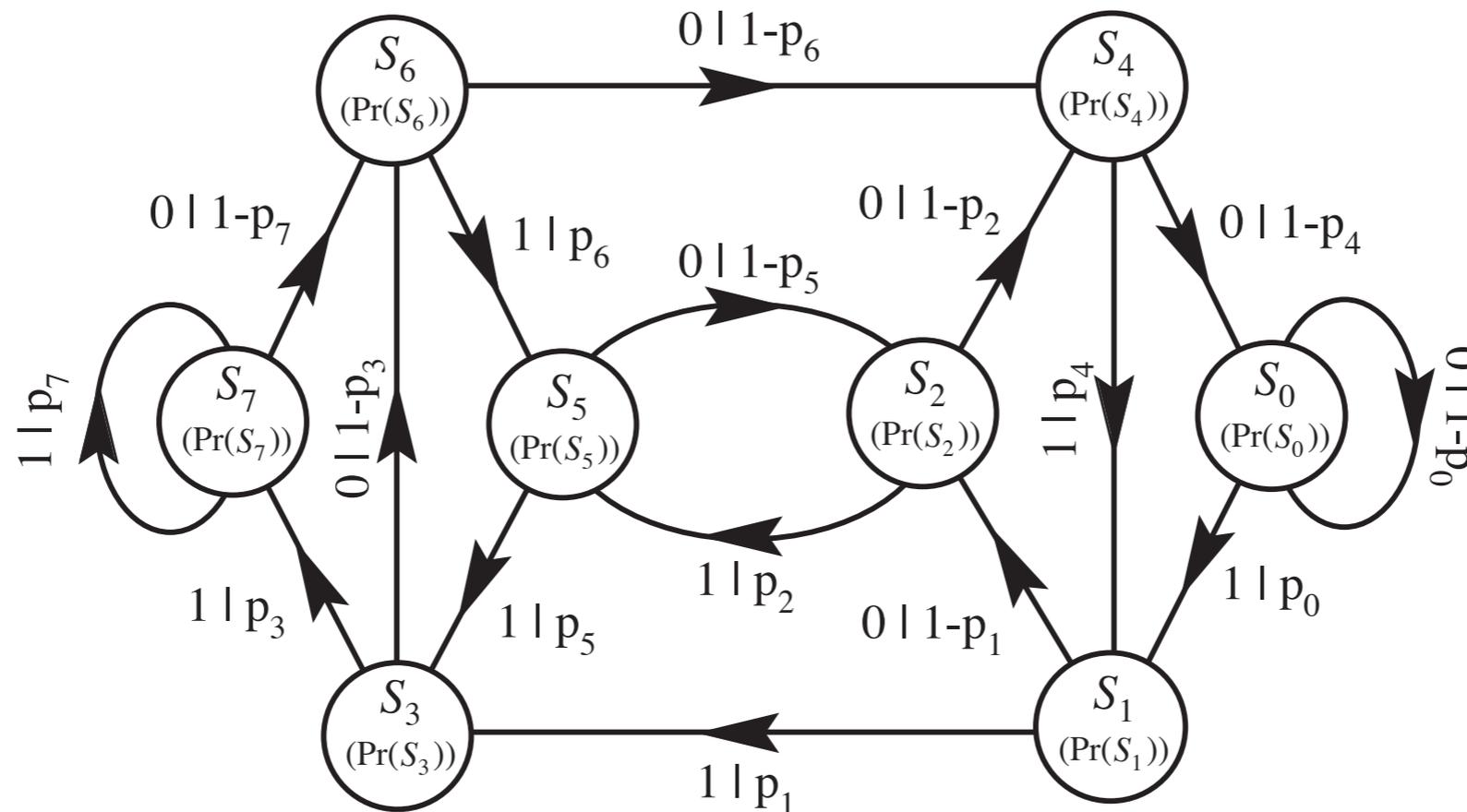
The most general $r=3$ ε-machine. We show only the recurrent portion of the ε-machine as the transient part is not physically relevant. The causal states are labeled by the last three spins seen, i.e, S_5 means that 101 were the last three spins seen. The edge label $s|p$ indicates a transition on spin s with probability p. By 'most general' we mean that all pasts at $r=3$ are distinguished, and all possible transitions between causal states exist. This is a 3rd order Markov Process.

Definition: Causal State Cycles

Causal State Cycle: A non-self intersecting, closed, symbol-specific path on an ε-machine.

3C+ & 3C- Crystal Structure on an *r = 3* ε-Machine

(...| | | | | ...)

Diffraction Pattern for a FCC Lattice

3C+
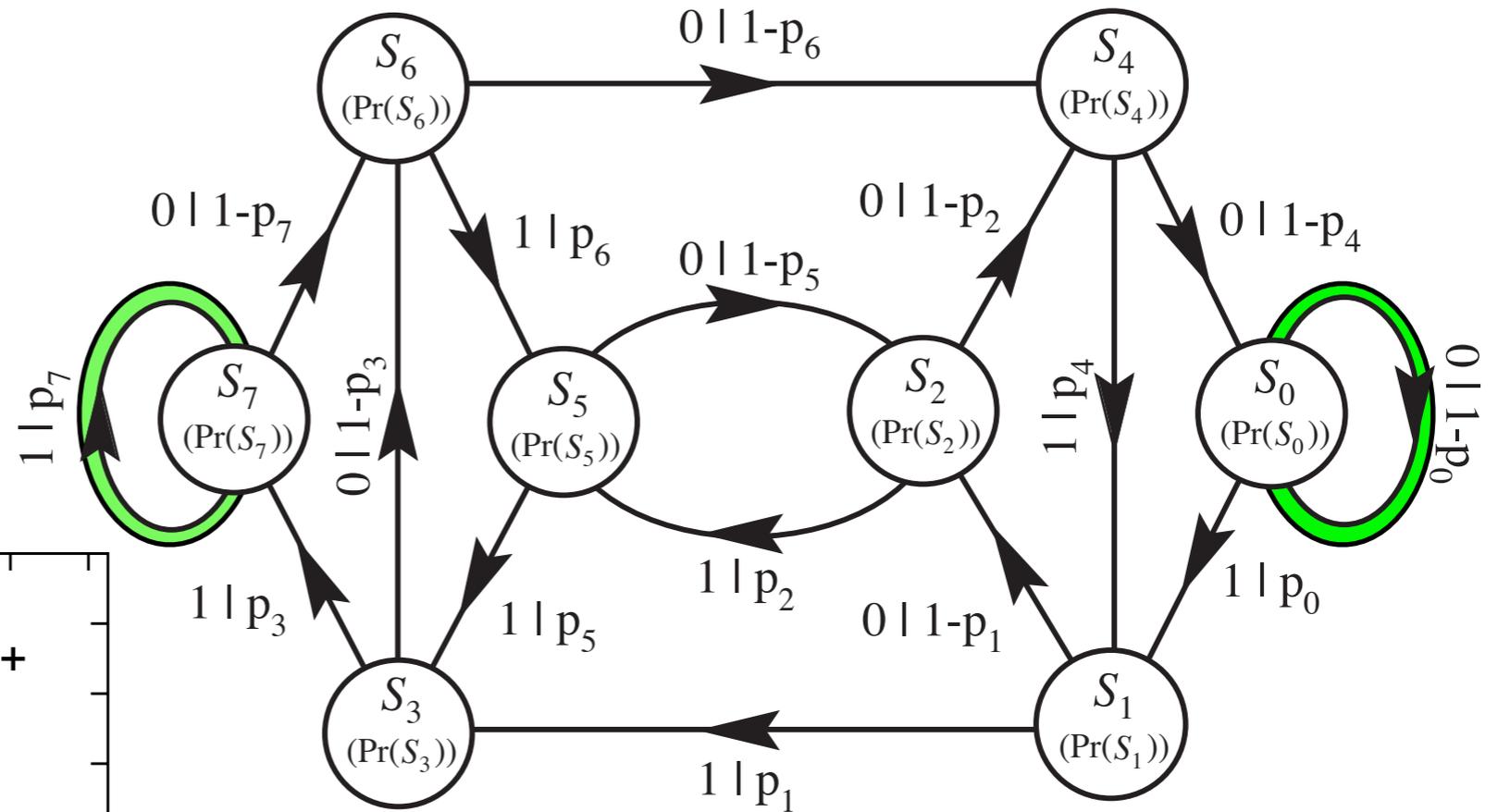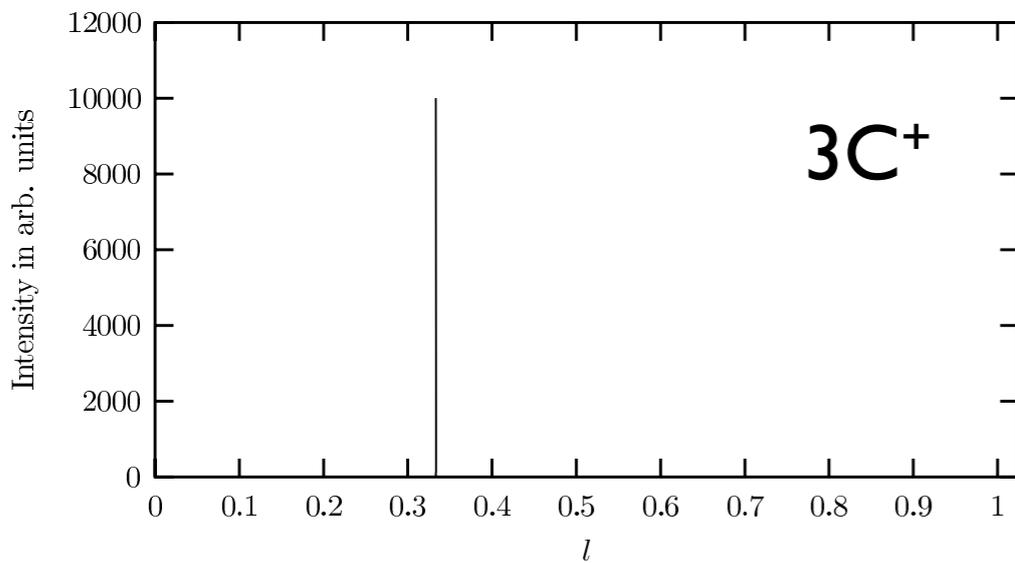
The causal state cycles that correspond to the 3C structure on an *r=3* ε-machine. Recall, 3C+ is just ...11111111..., and 3C- is just ...0000000....

2H Crystal Structure on an *r = 3* ε-Machine

Diffraction Pattern for a HCP Lattice

2H
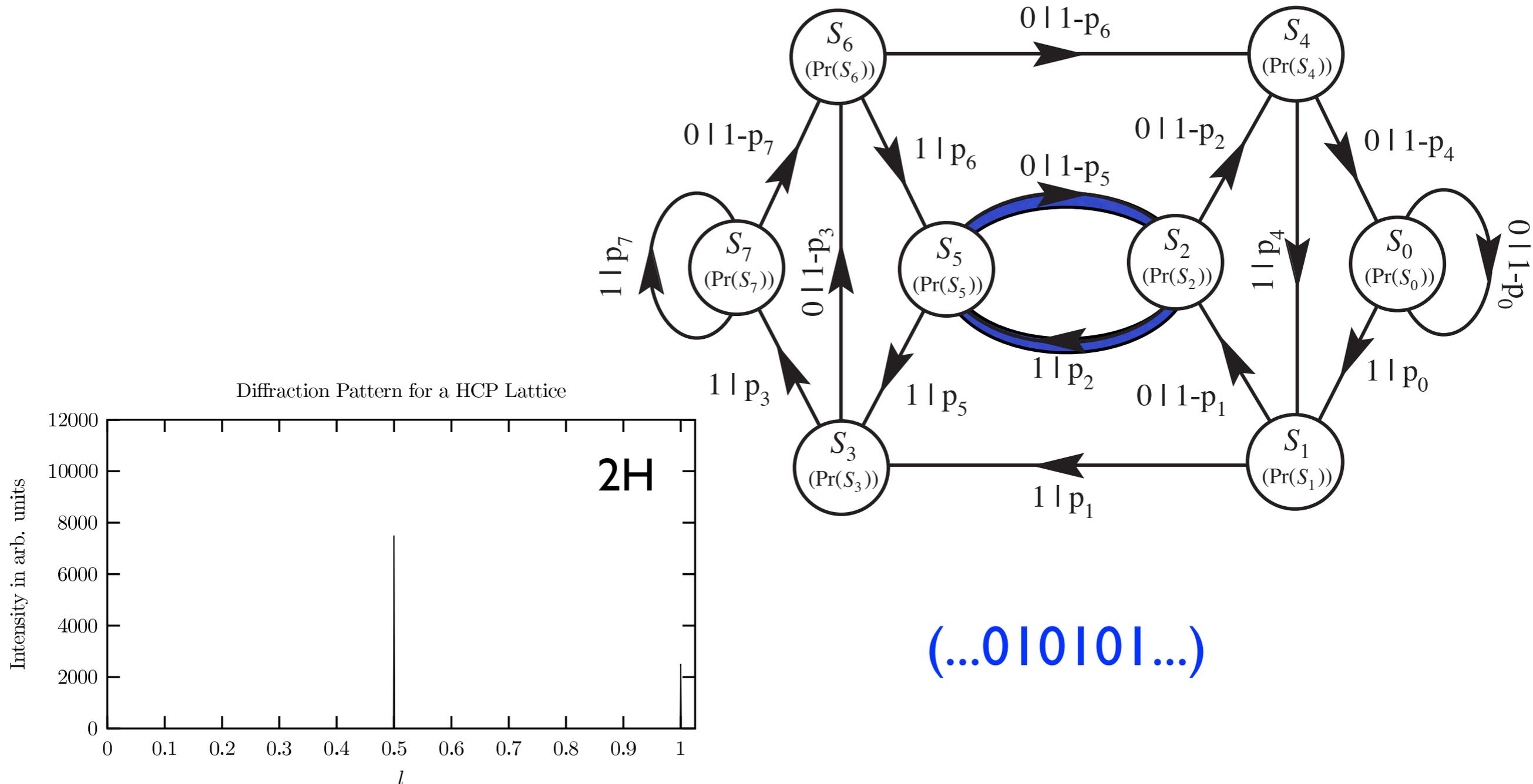
(...010101...)

The causal state cycle that correspond to the 2H structure on an *r=3* ε-machine. Recall, 2H is just ...1010101....

4H Crystal Structure on an *r = 3* ε-Machine
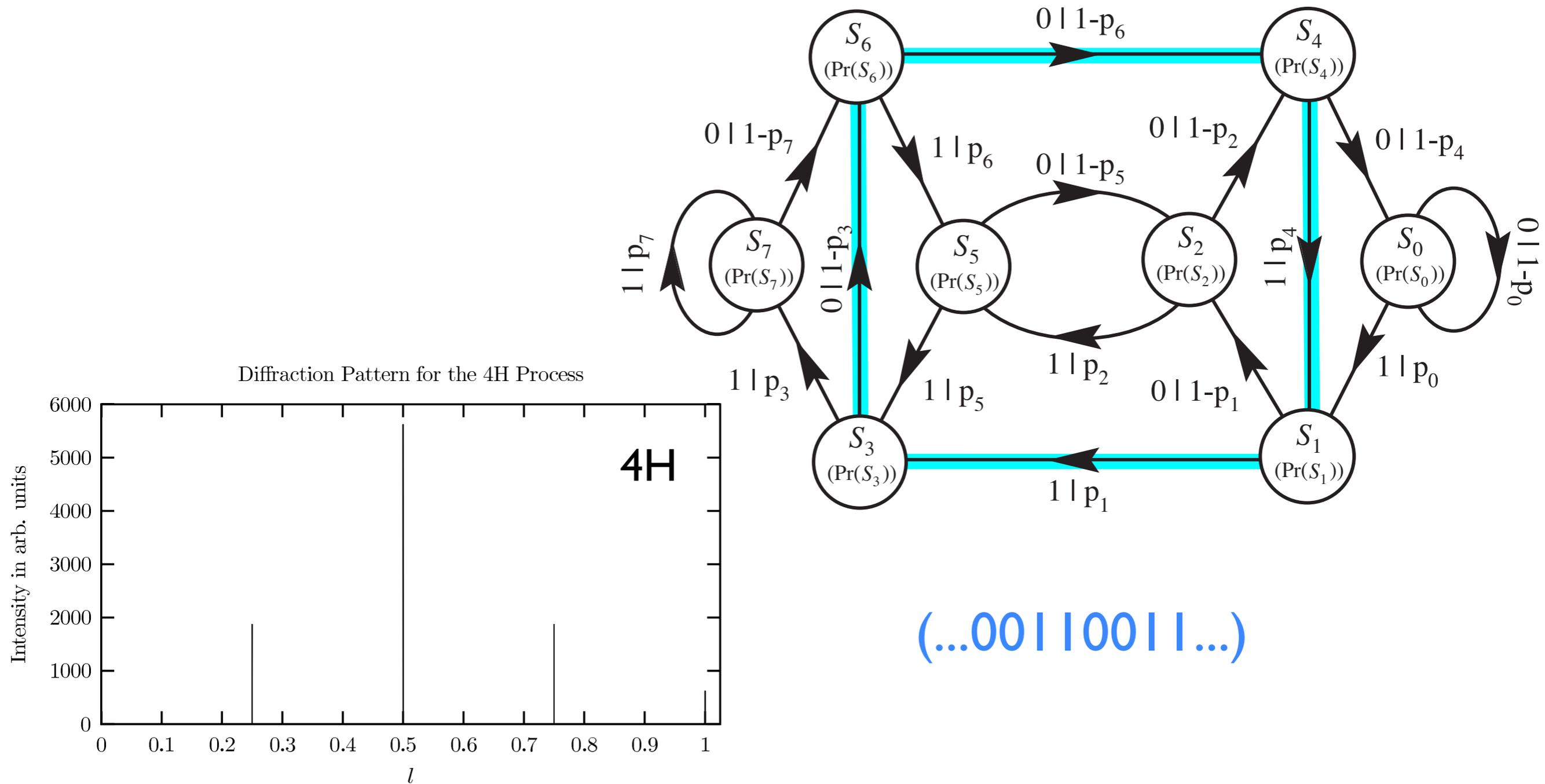
(...00110011...)

The causal state cycle that correspond to the 4H structure on an *r=3* ε-machine. Recall, 4H is just ...11001100....

6H Crystal Structure on an *r = 3* ε-Machine
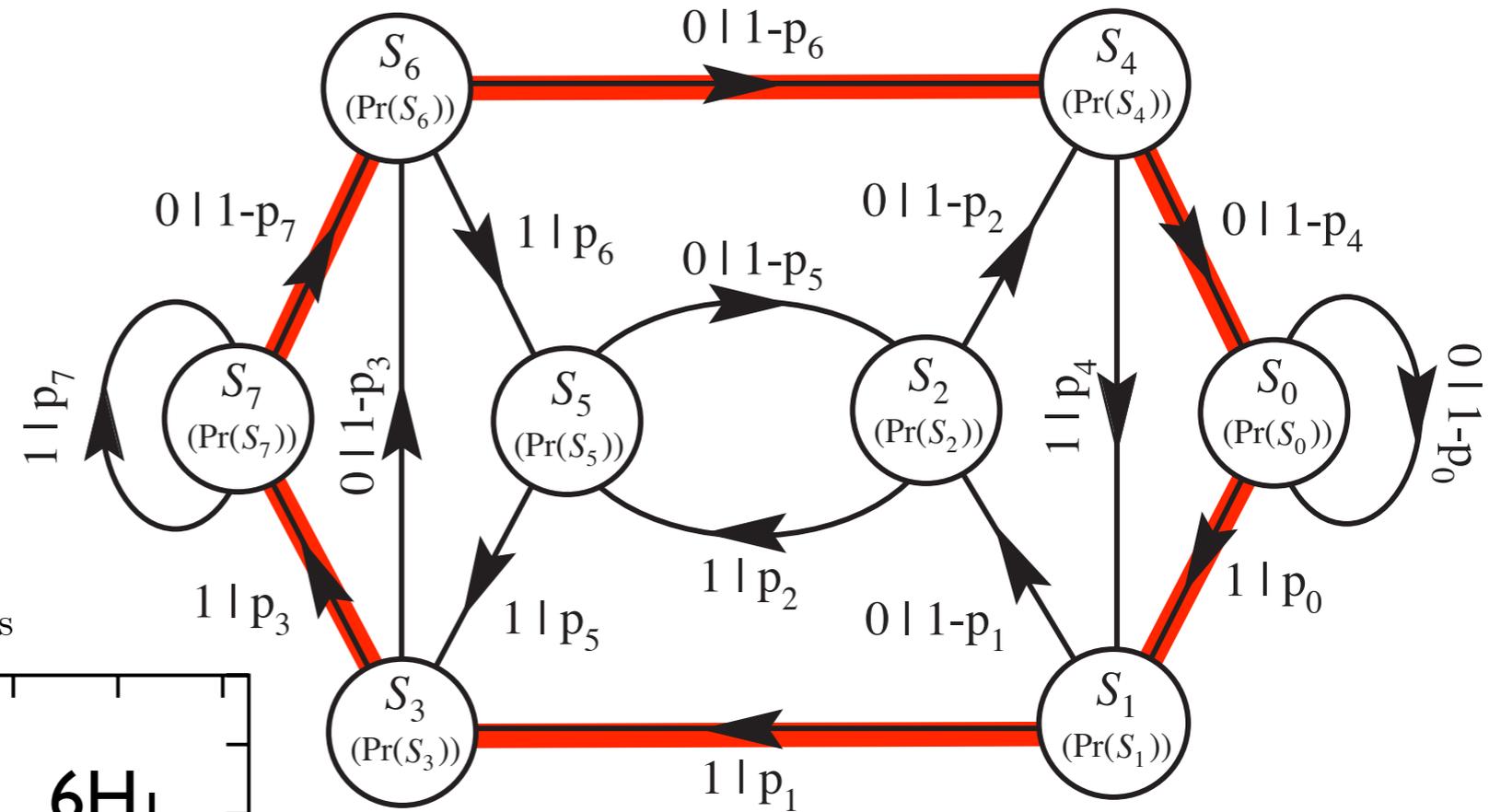
Diffraction Pattern for the 6H Process

6H₁

(...000111000111...)
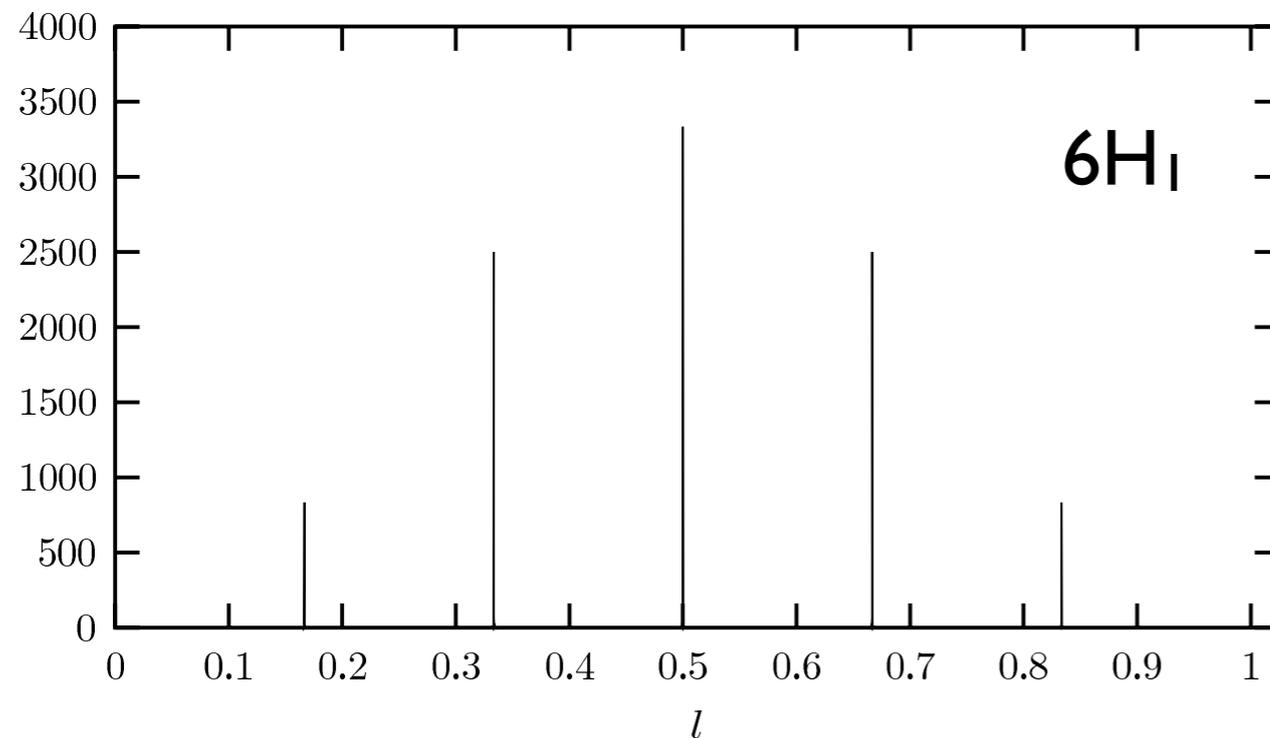
The causal state cycle that correspond to the 6H structure on an *r=3* ε-machine. Recall, 6H is just ...111000111000....

Completely Random Stacking of Layers

Diffraction Pattern for a RNG
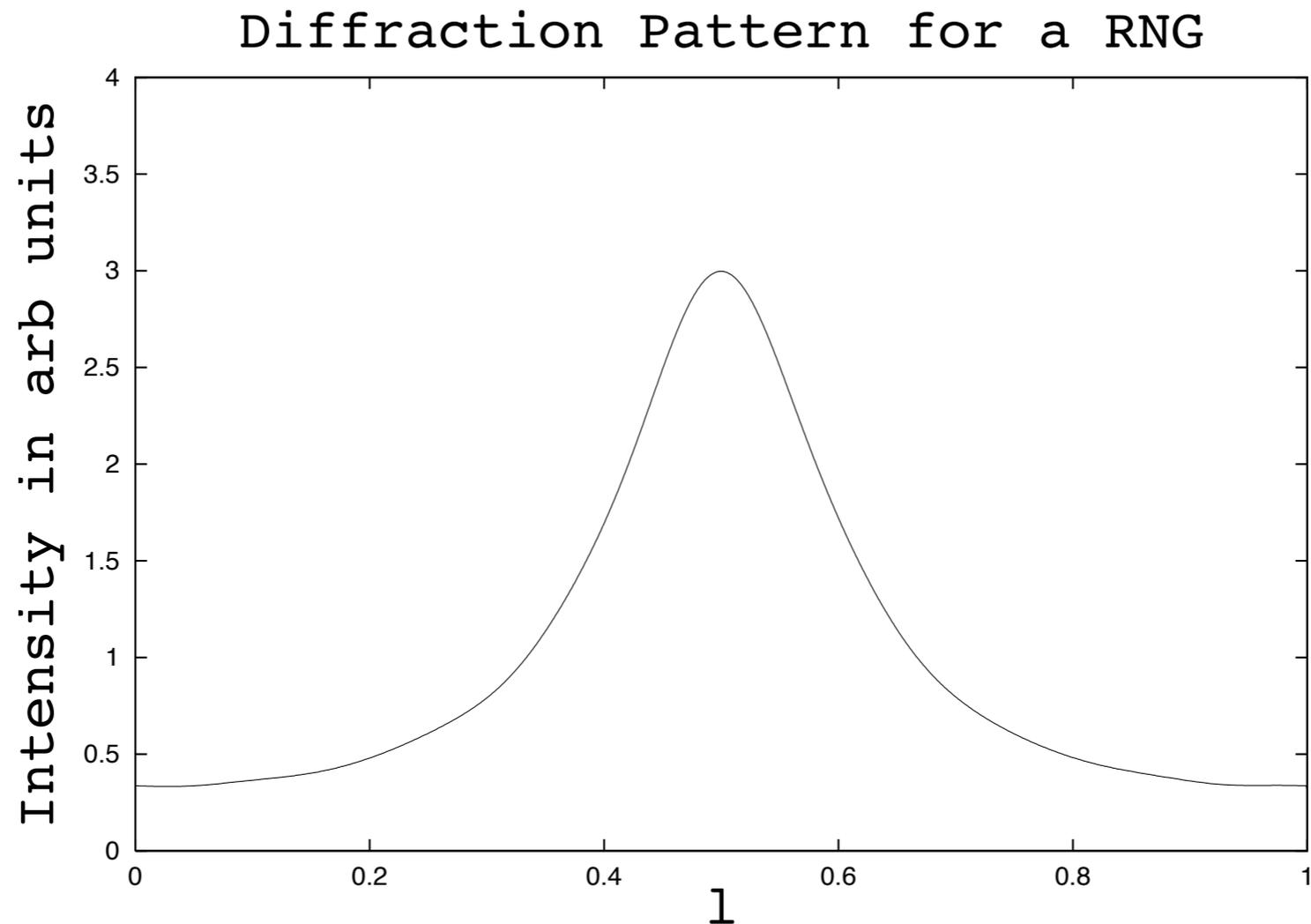
For contrast, here is the diffraction spectrum for a completely random stacking structure. The spectrum is entirely diffuse.

Causal State Cycles on an $r = 3$ ε-Machine
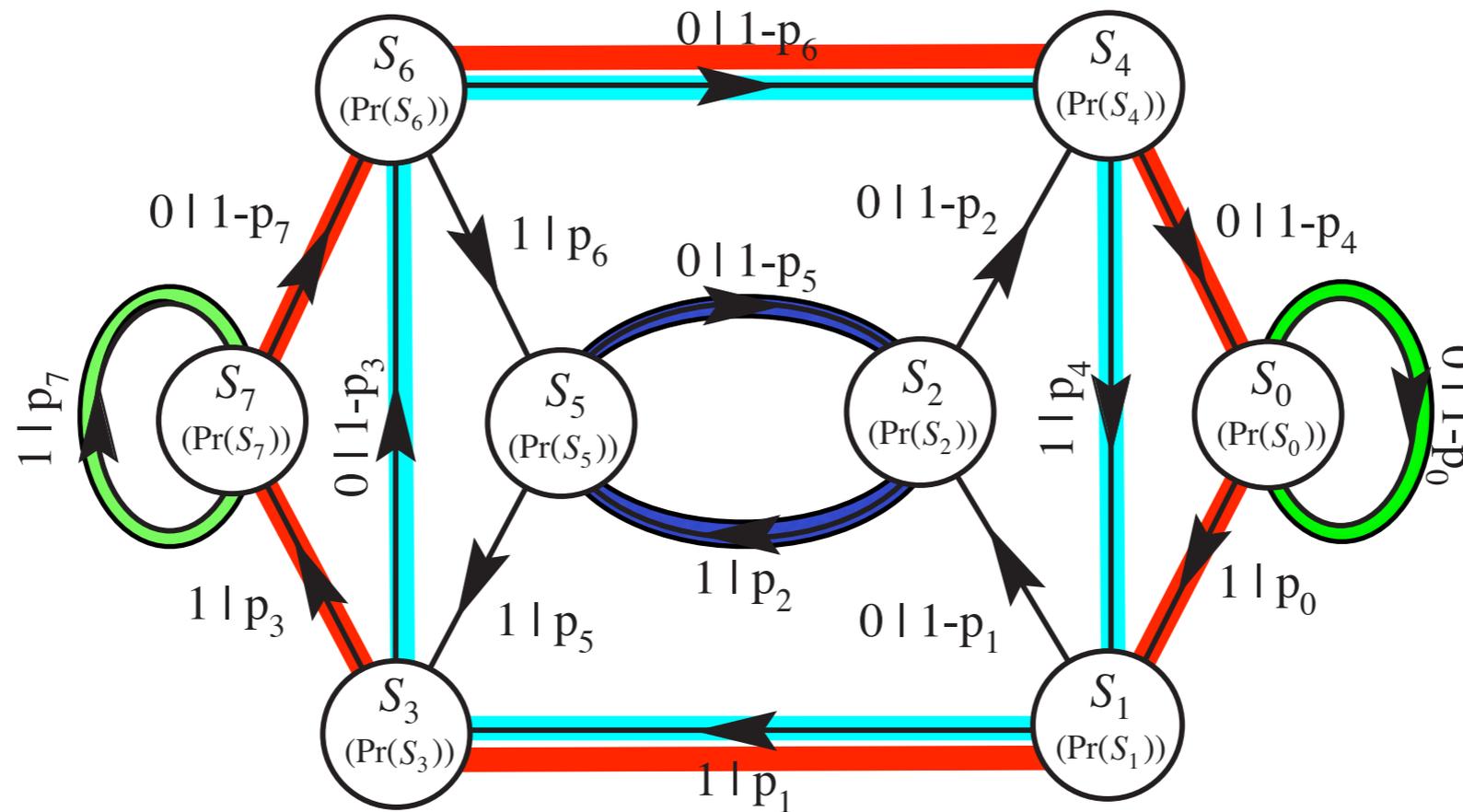
Causal State Cycles: A non-self intersecting, closed, symbol specific path on an ε-machine. They can lead to crystal structures: 3C (green), 2H (blue), 6H (red), and 4H (cyan). These are four of the possible 19 causal state cycles on an $r=3$ ε-machine. They can also lead to faulting structures, as seen on the next slide.

Faulting Structures for 3C

Growth Fault

Layer Displacement Fault

Deformation Fault

Growth Fault: The stacking rule is broken for a layer, such that the next layer added isn't different from the previous two. This leads to twinned crystal:

$$...000000000... \rightarrow ...0000|1111...$$

Deformation Fault: A spin is flipped. This can't lead to a twinned crystal:

$$...111111111... \rightarrow ...1110 1111...$$

Layer Displacement Fault: Two adjacent layers switch orientation. This is equivalent to flipping three adjacent spins. This can't lead to a twinned crystal:

$$...111111111... \rightarrow ...11000 11111...$$

Faulting Structures for 2H

Growth Fault
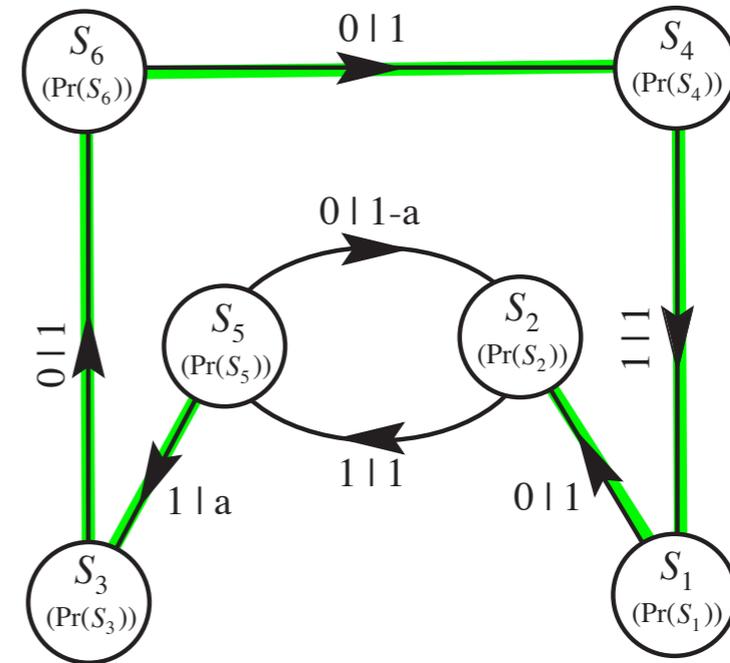
Layer Displacement Fault
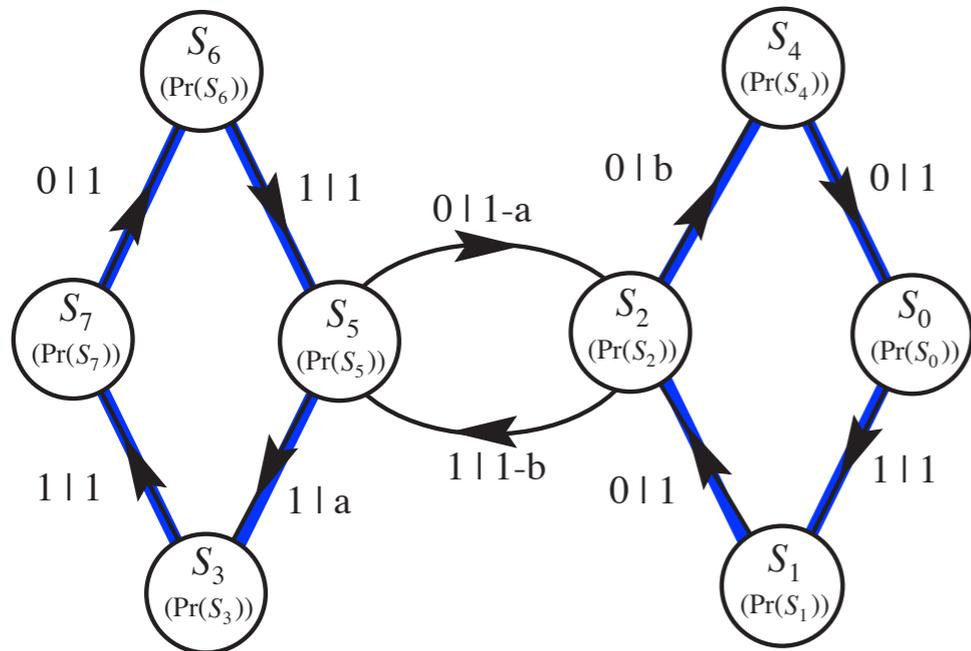
Deformation Fault

Growth Fault: Insertion of spin: ...101010... ➔ ...1010010...

Deformation Fault: Flip a spin: ...010101... ➔ ...011101...

Layer Displacement Fault: Exchange adjacent spins:
...010101... ➔ ...011001...

Polytypism in Zinc Sulphide

- Discovered by Frondel and Palache in 1948.

- Over 185 observed crystalline structures that can be formed and co-exist *under virtually identical thermodynamic conditions*.

- Longest period observed is 114 modular layers.

- Many disordered structures exist.

- Found in both mineral and synthetic ZnS crystals.

- Only two *stable* structures in ZnS are thought to exist: The hexagonal close-packed (HCP, aka 2H and wurtzite) above 1024 C, and the face-centered cubic (FCC, aka cubic close-packed, 3C and zinc-blende) below 1024 C. All others are believed to be meta-stable.

- ZnS can undergo solid-state transformations upon annealing.

Experimental Spectrum SK134
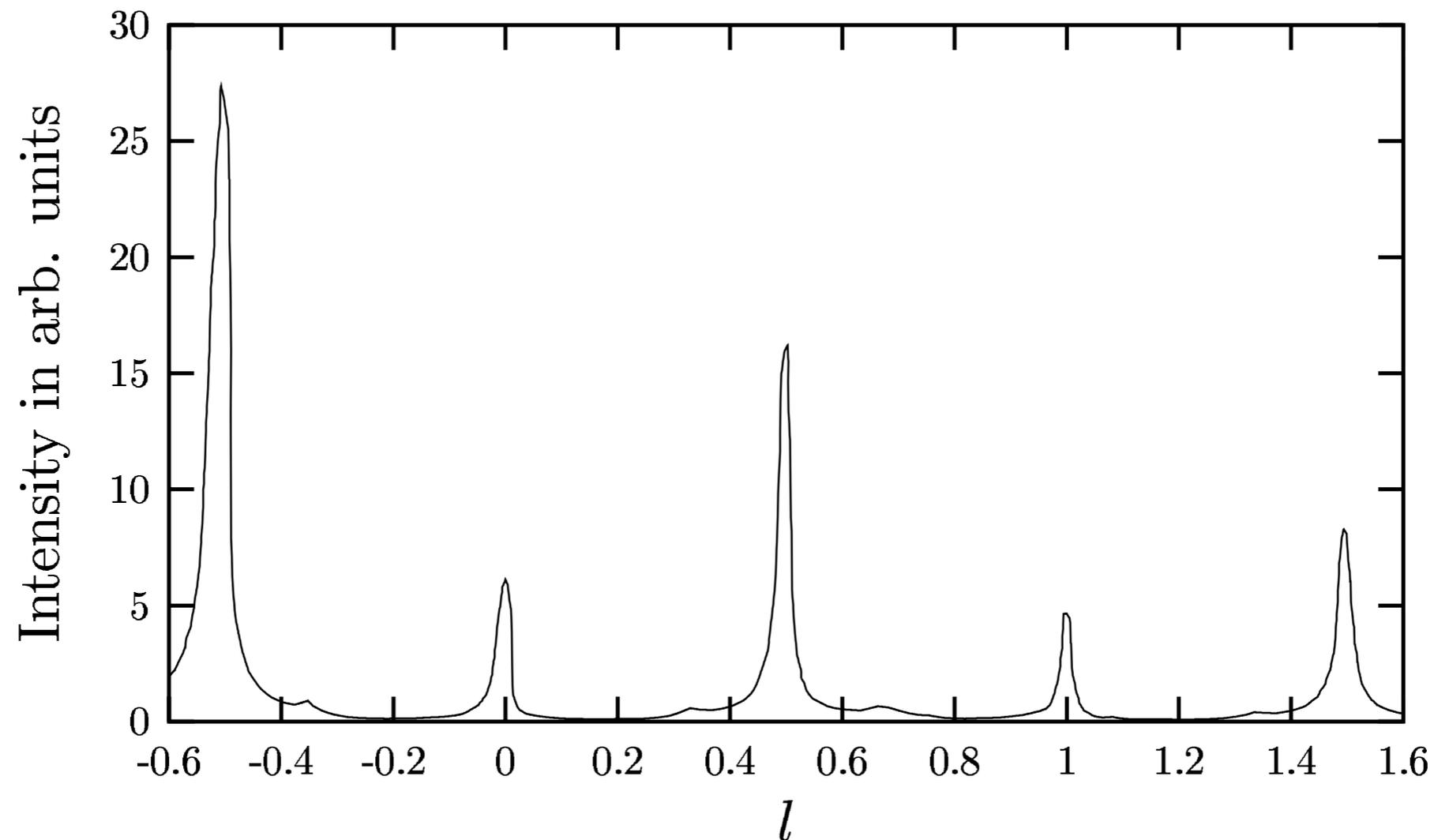
The experimental spectrum for zinc sulphide. This spectrum should be periodic in l with period one but clearly it is not. This illustrates the need to choose a unit interval in l that is relatively error free.

Experimental Spectrum SK134
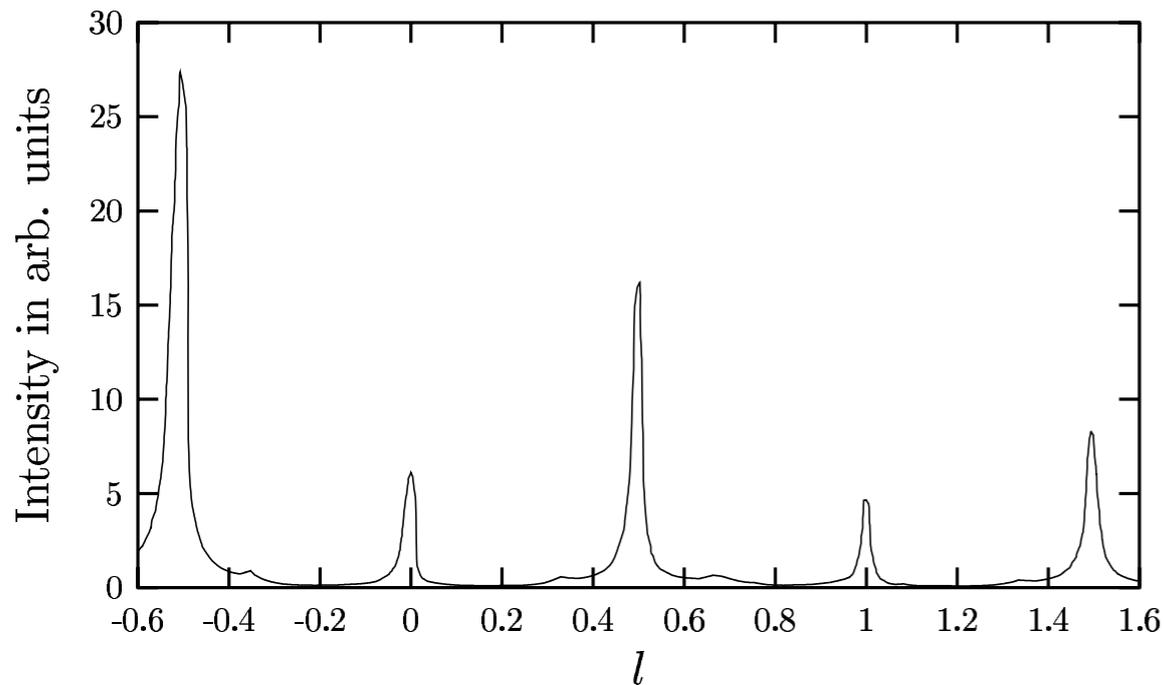
The experimental spectrum for zinc sulphide. This spectrum should be periodic in l with period one but clearly it is not. This illustrates the need to choose a unit interval in l that is relatively error free.
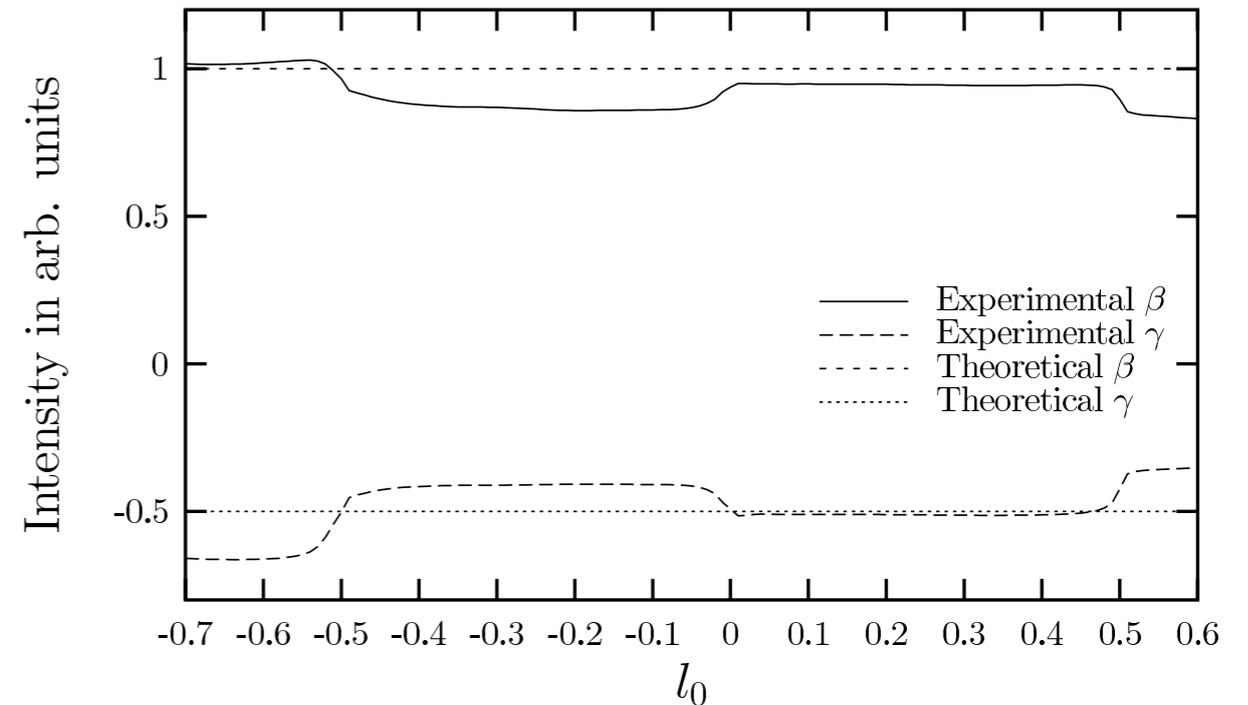
The figures-of-merit calculated over various intervals l_0 to $l_0 + 1$. We see that near $l_0 = 0$, the figures-of-merit are roughly near their theoretical values.

Experimental Spectrum SK134 (▲)
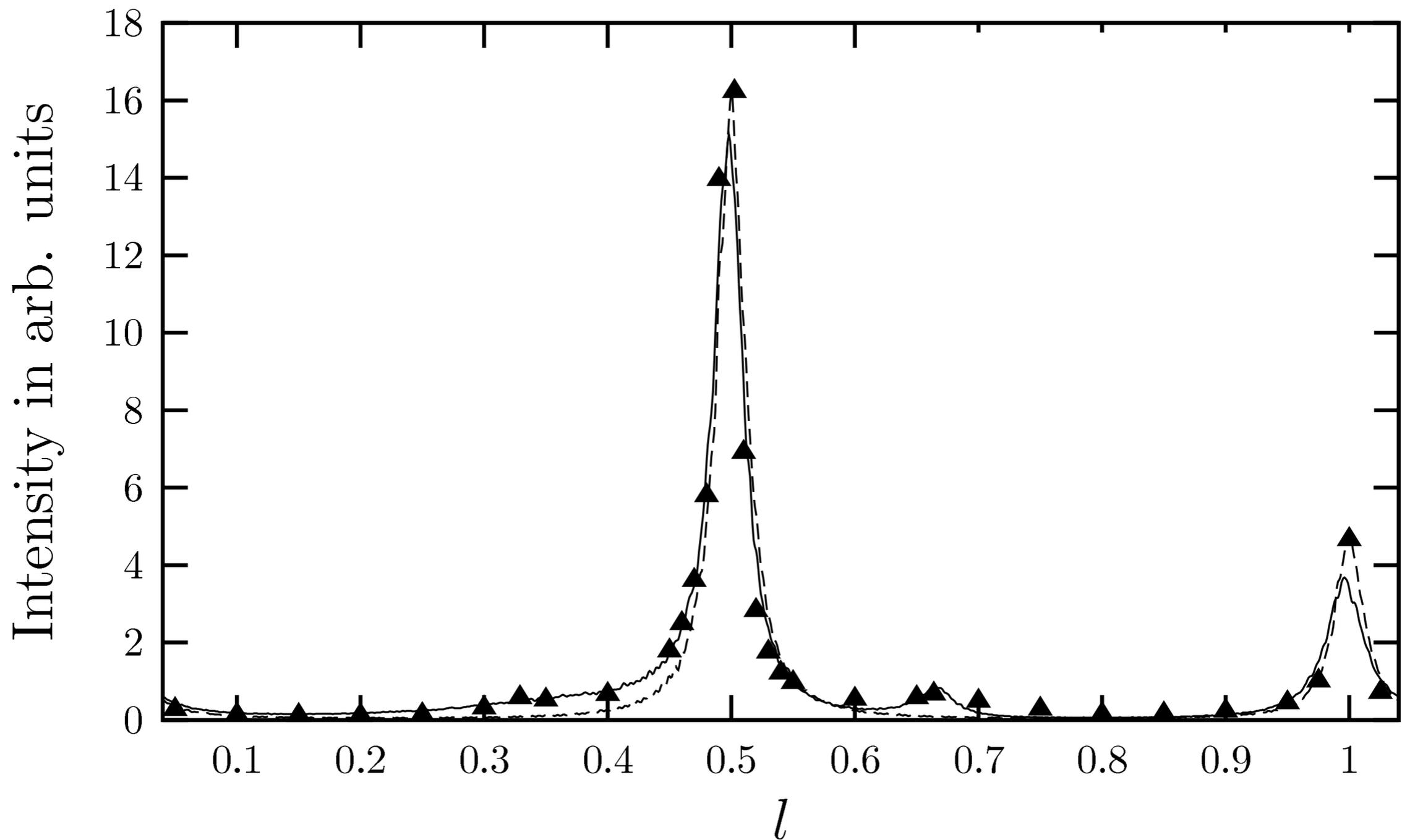
The $r = 3$ Reconstructed ε-Machine for SK134
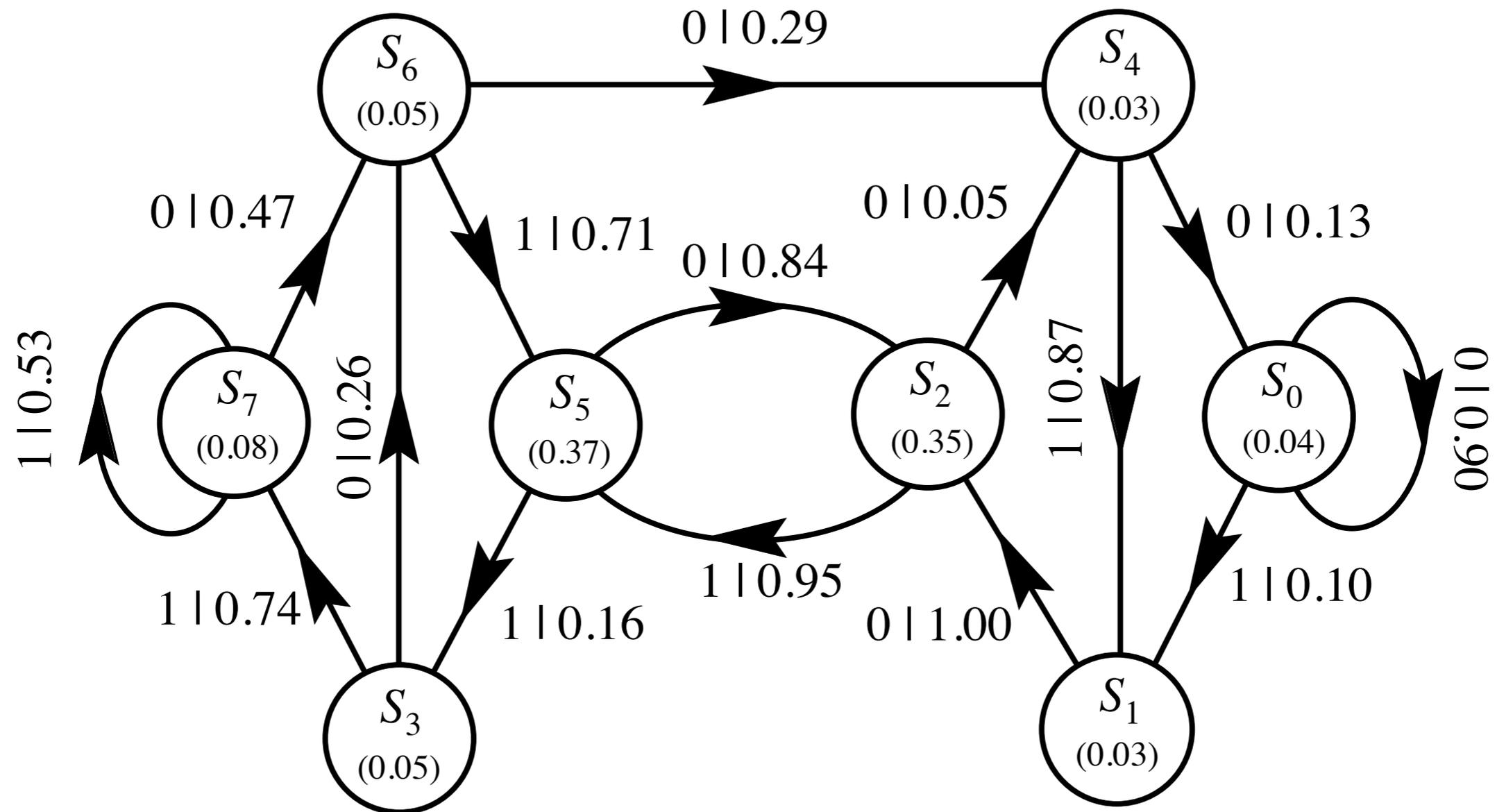
Experimental Spectrum SK134
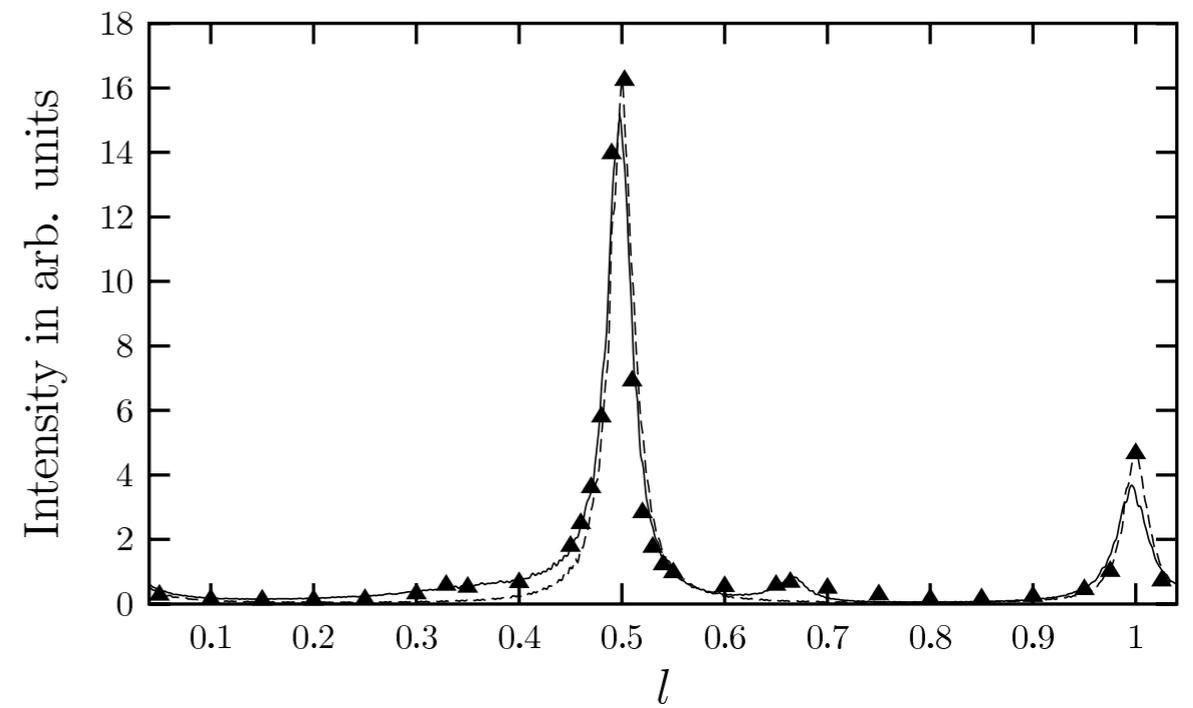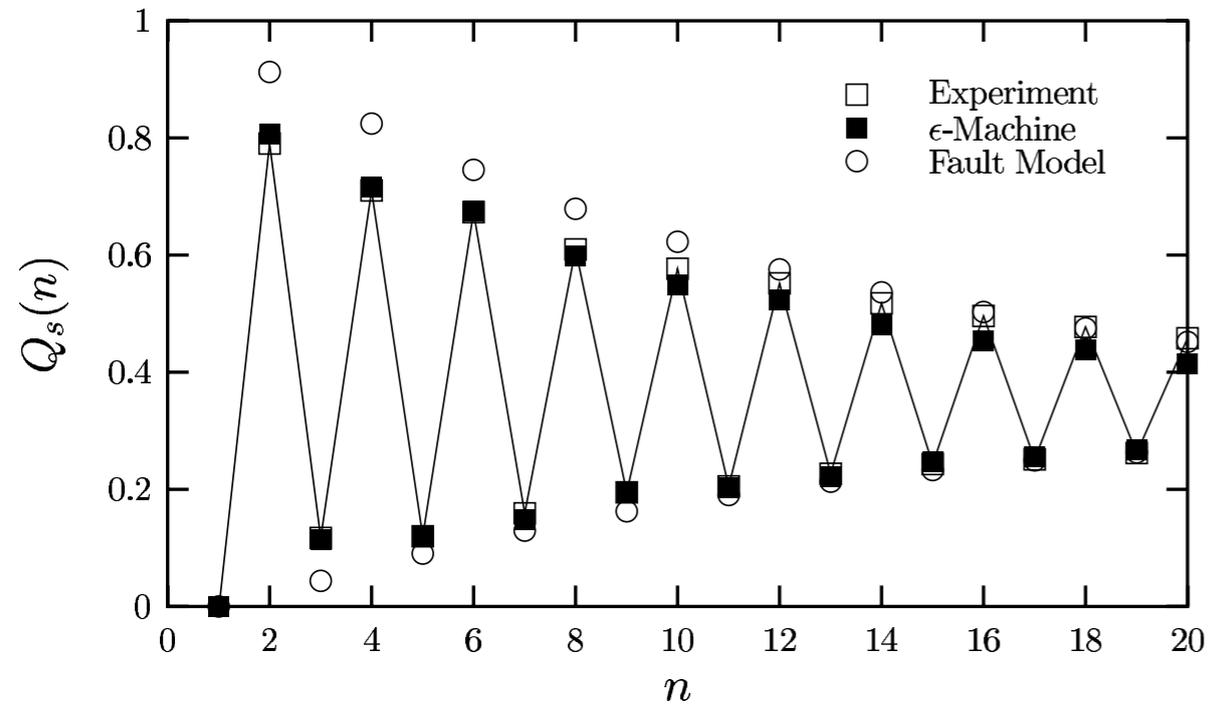
Experimental Spectrum SK134
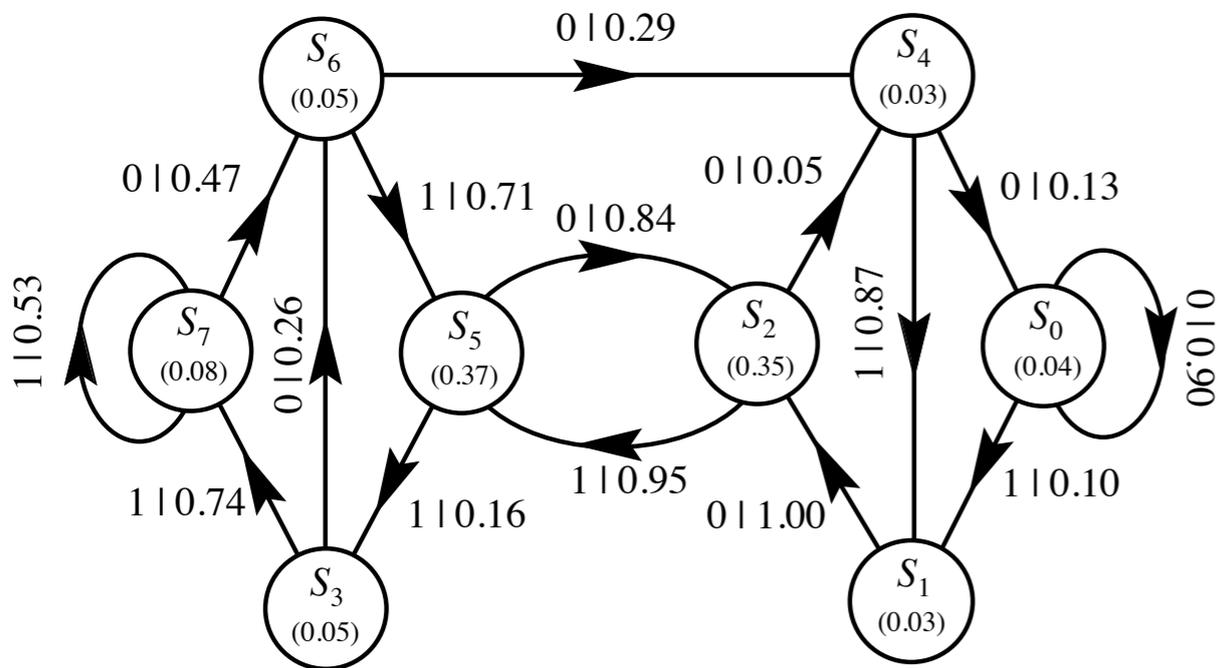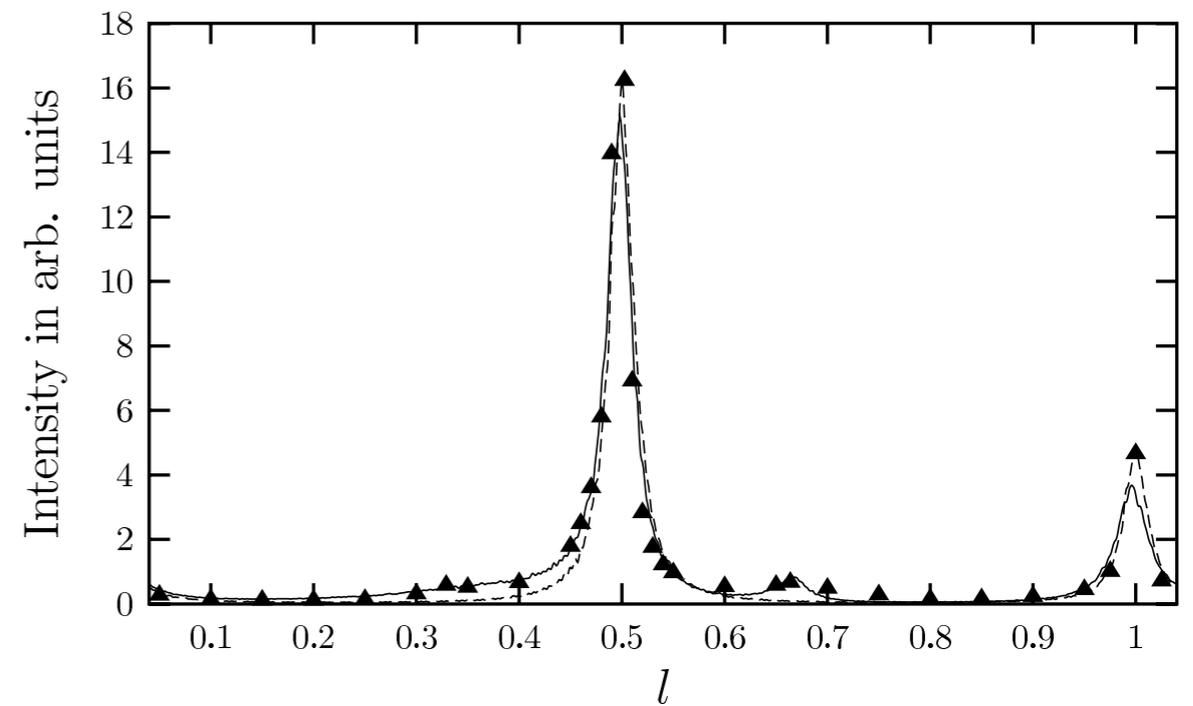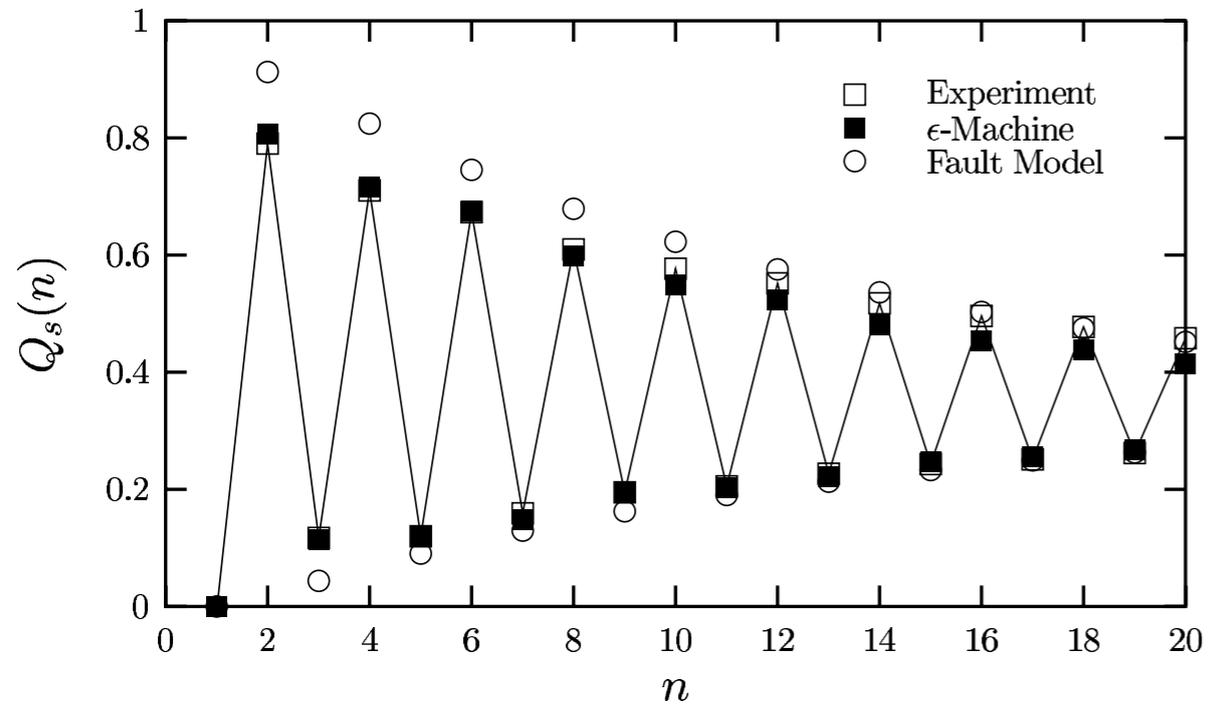
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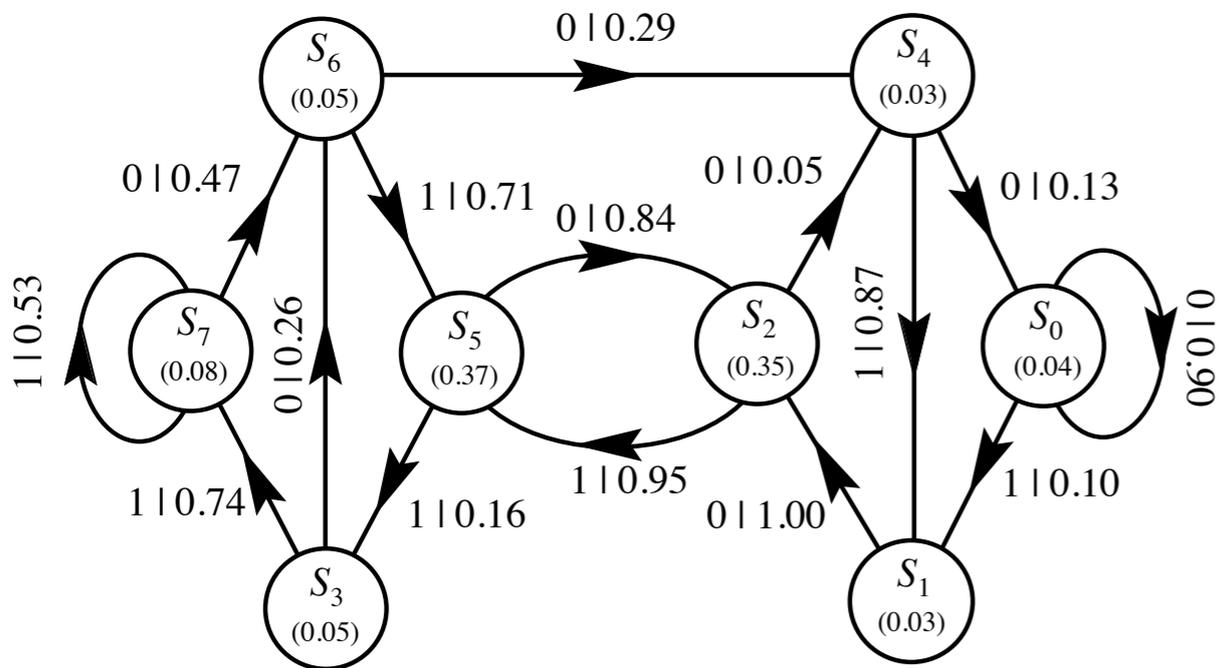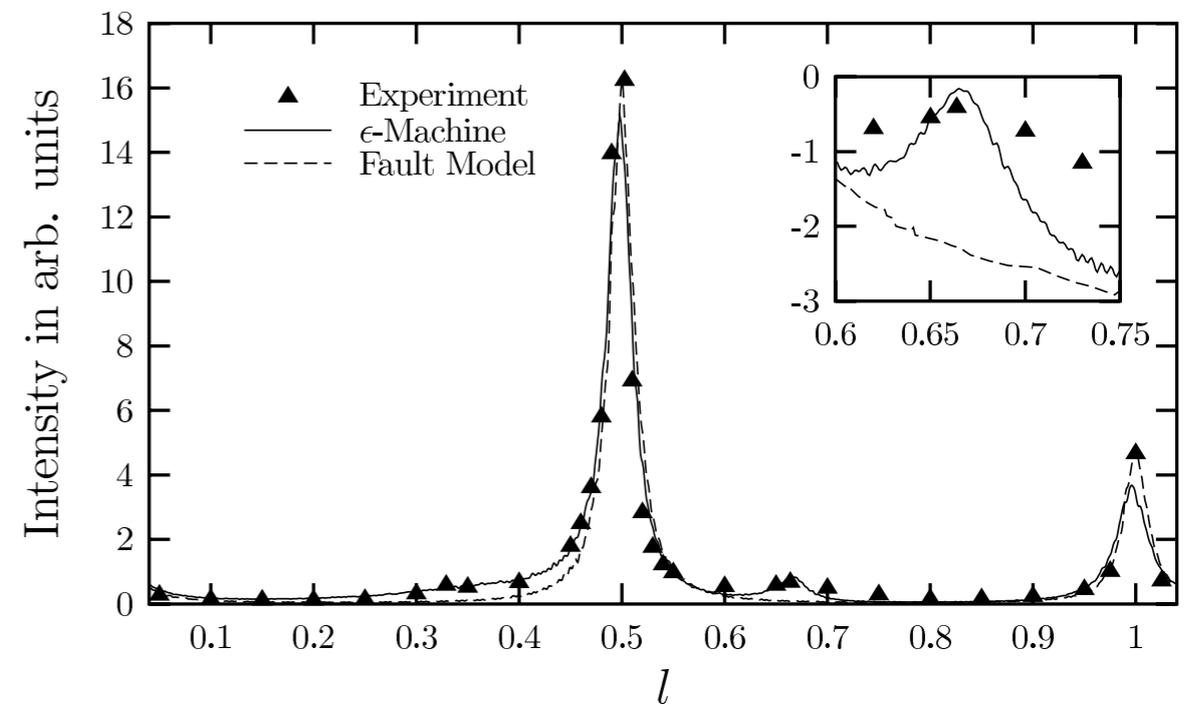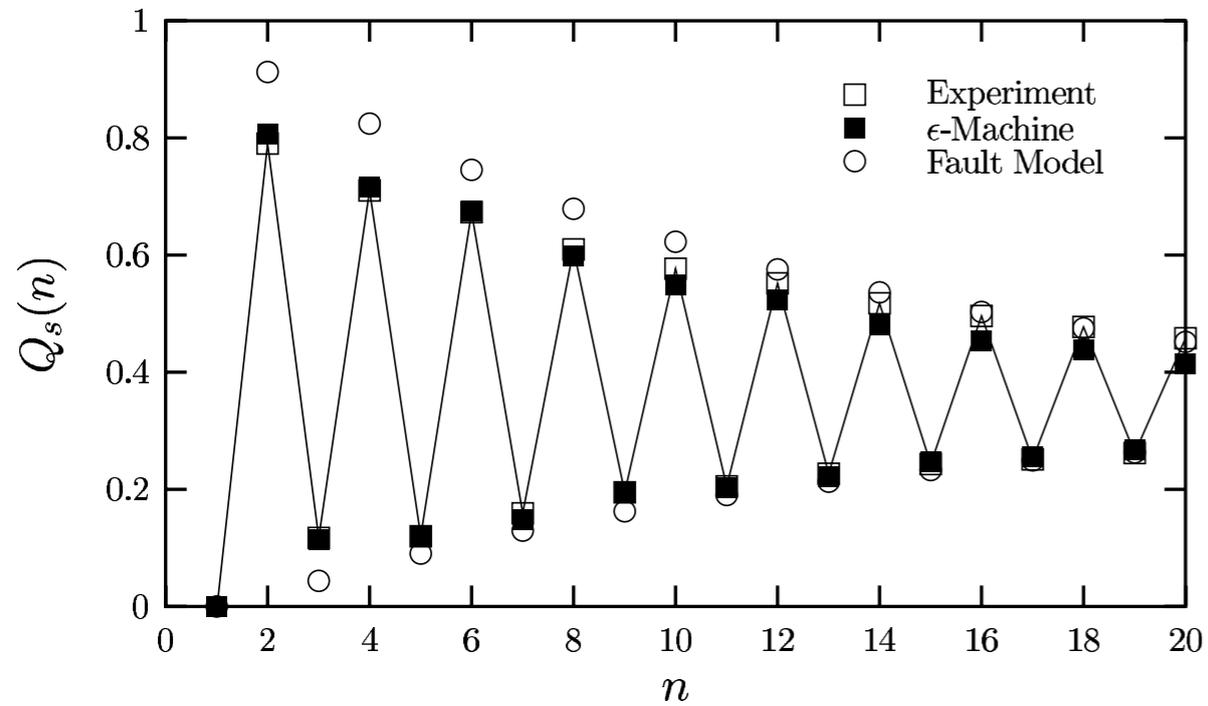
Structure	ε-M	FM
2H	64%	83%
3C	8%	0%
Deformation	16%	17%
Growth	6%	0%
Layer - Displacement	6%	0%

Experimental Spectrum SK135 (▲)
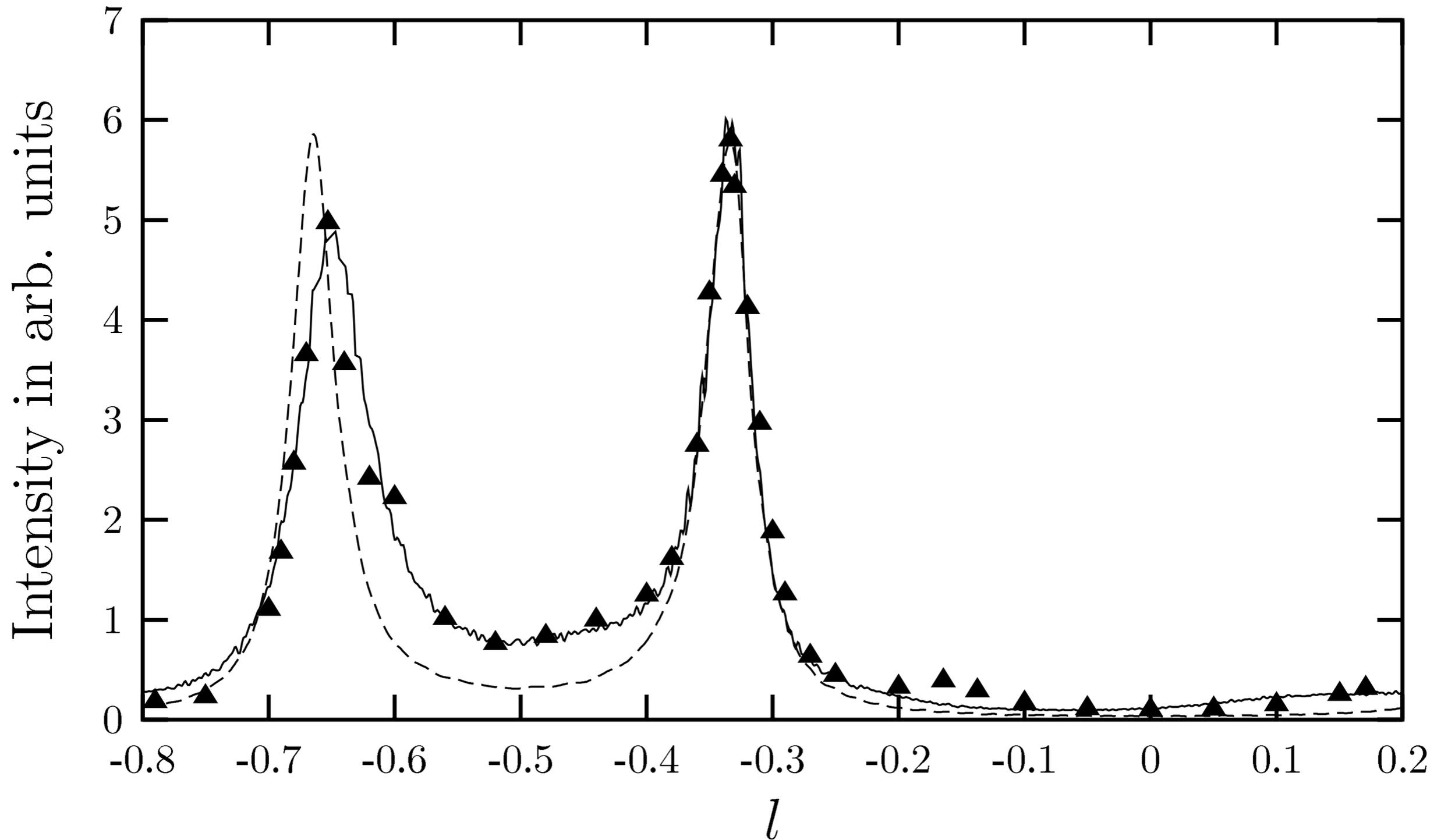
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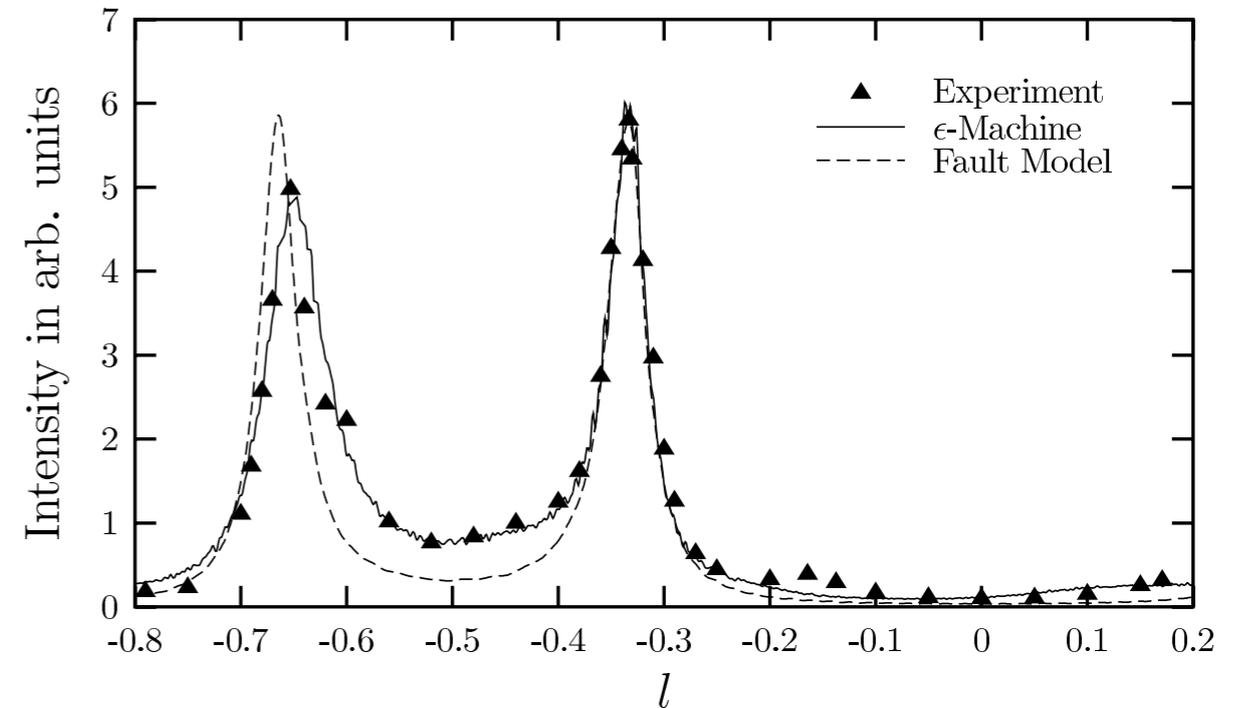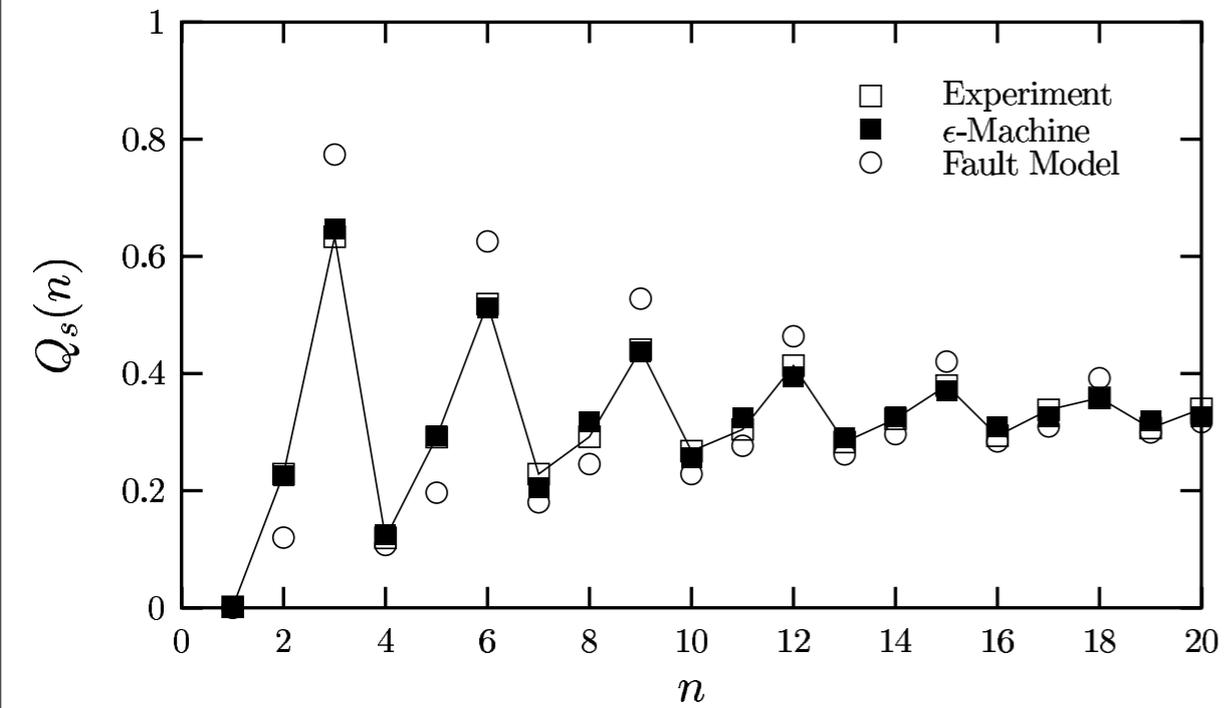
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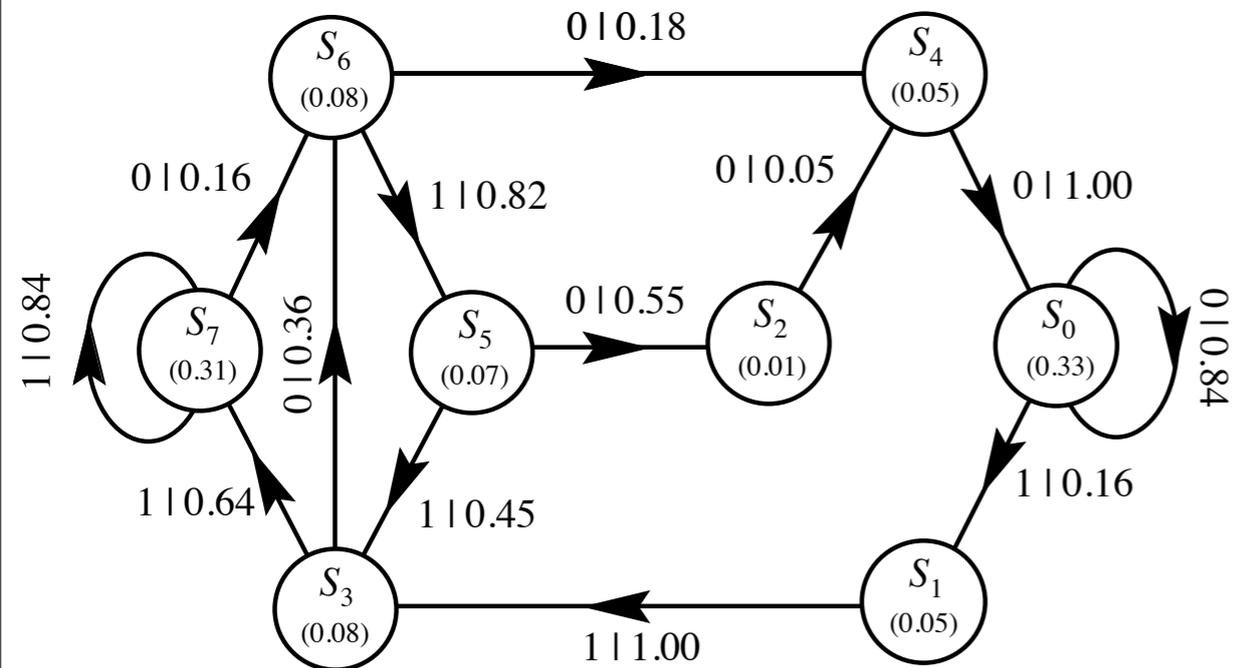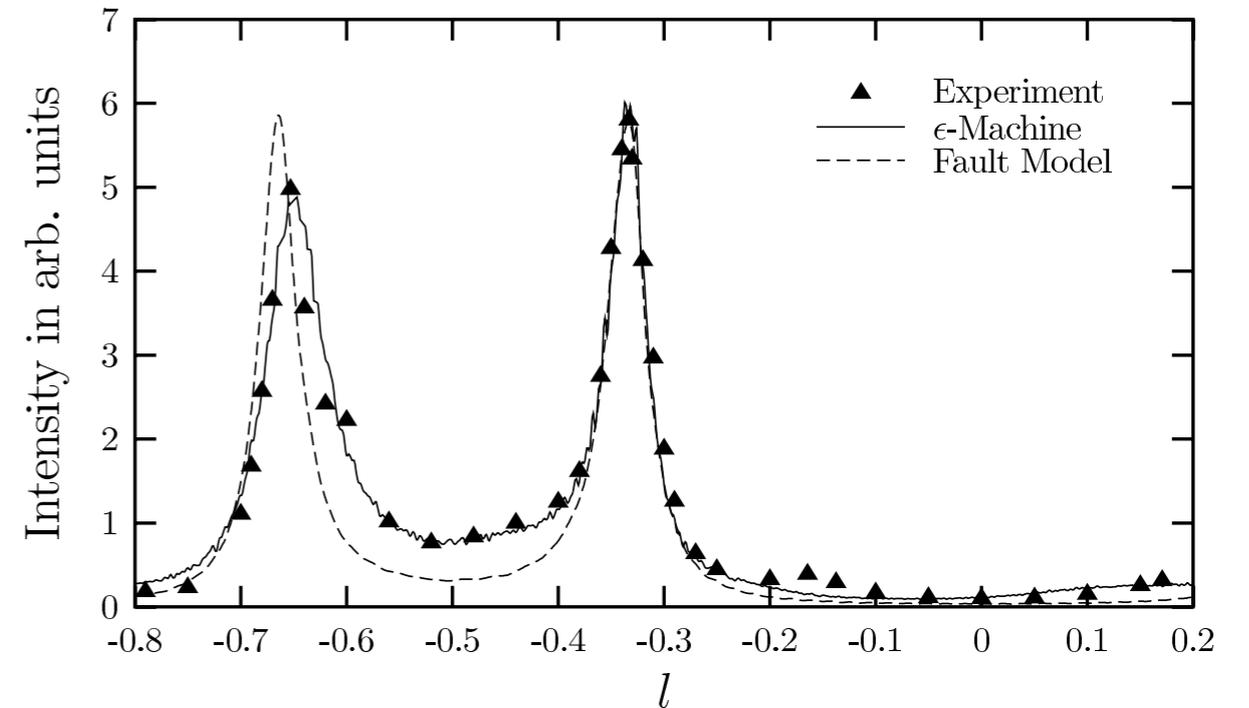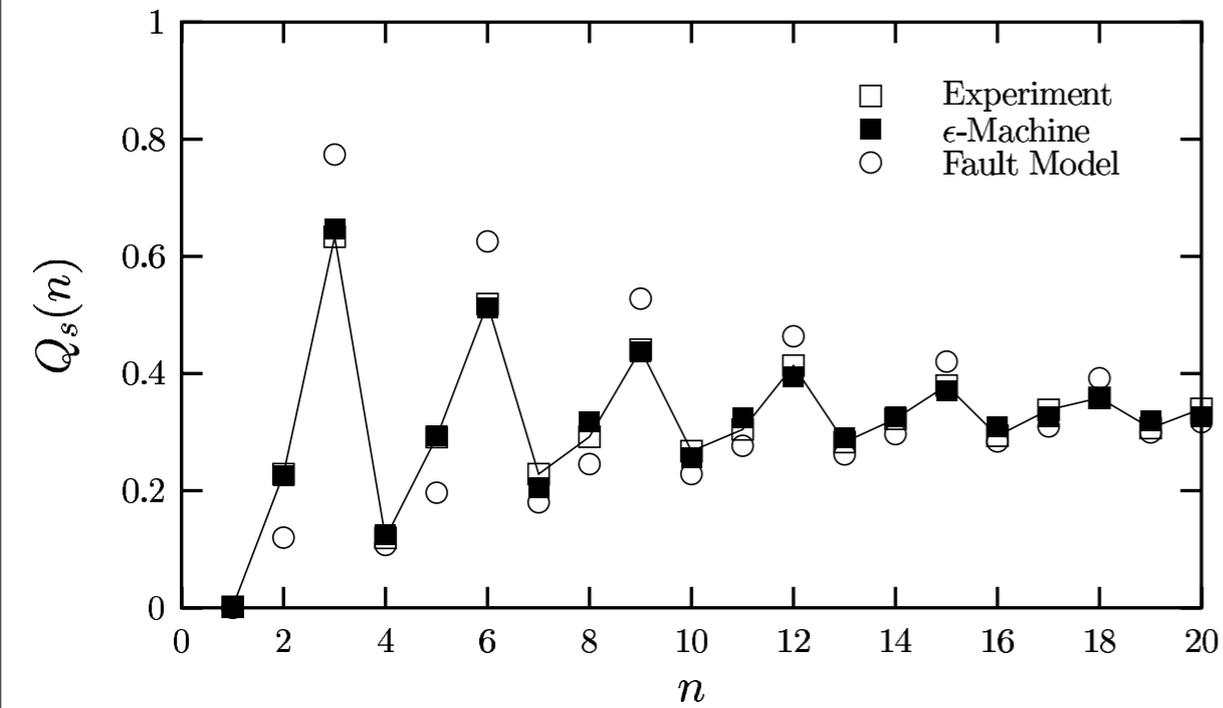
Experimental Spectrum SK135
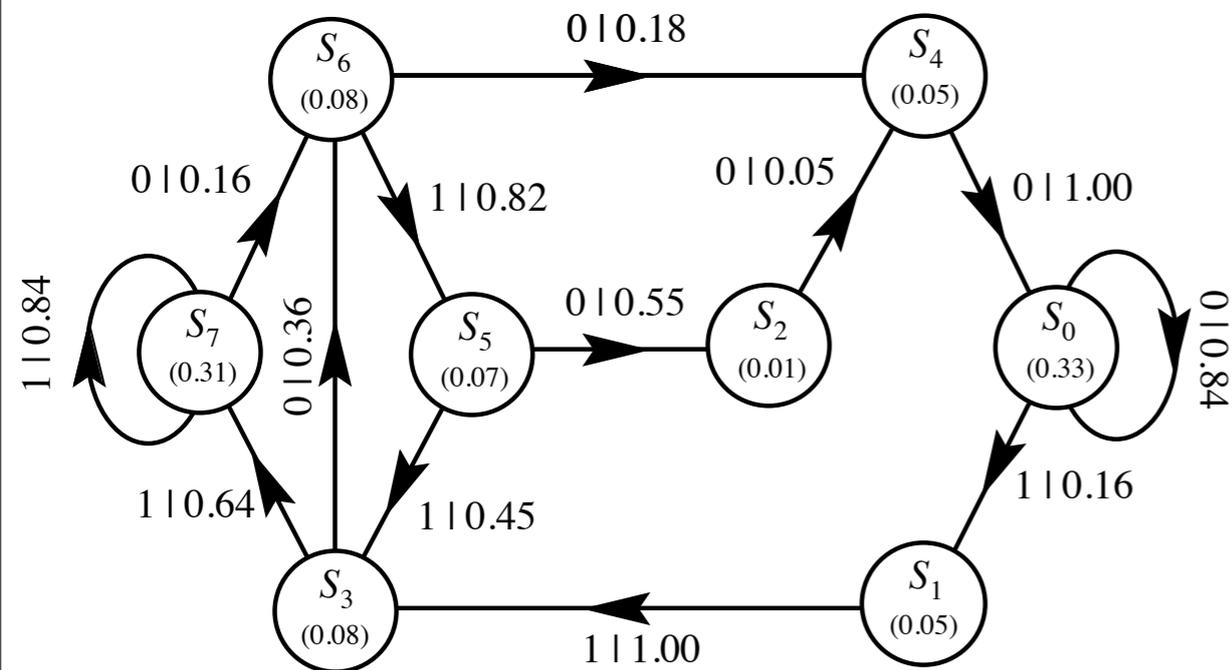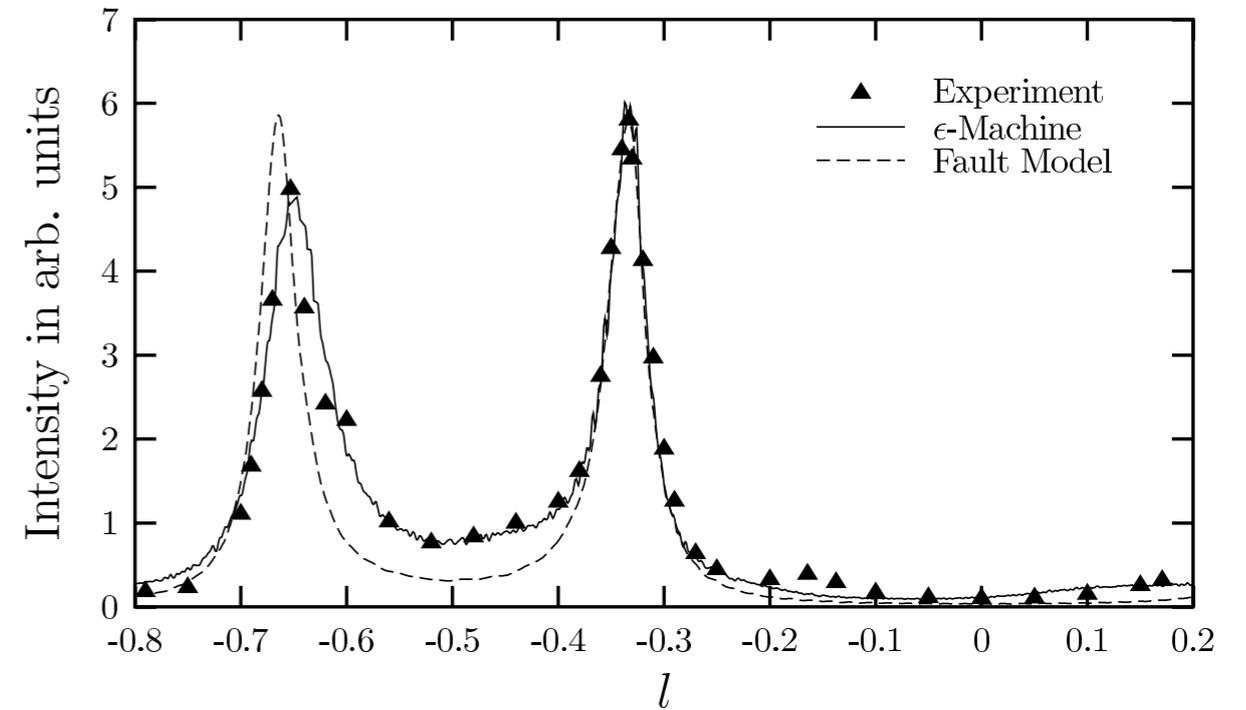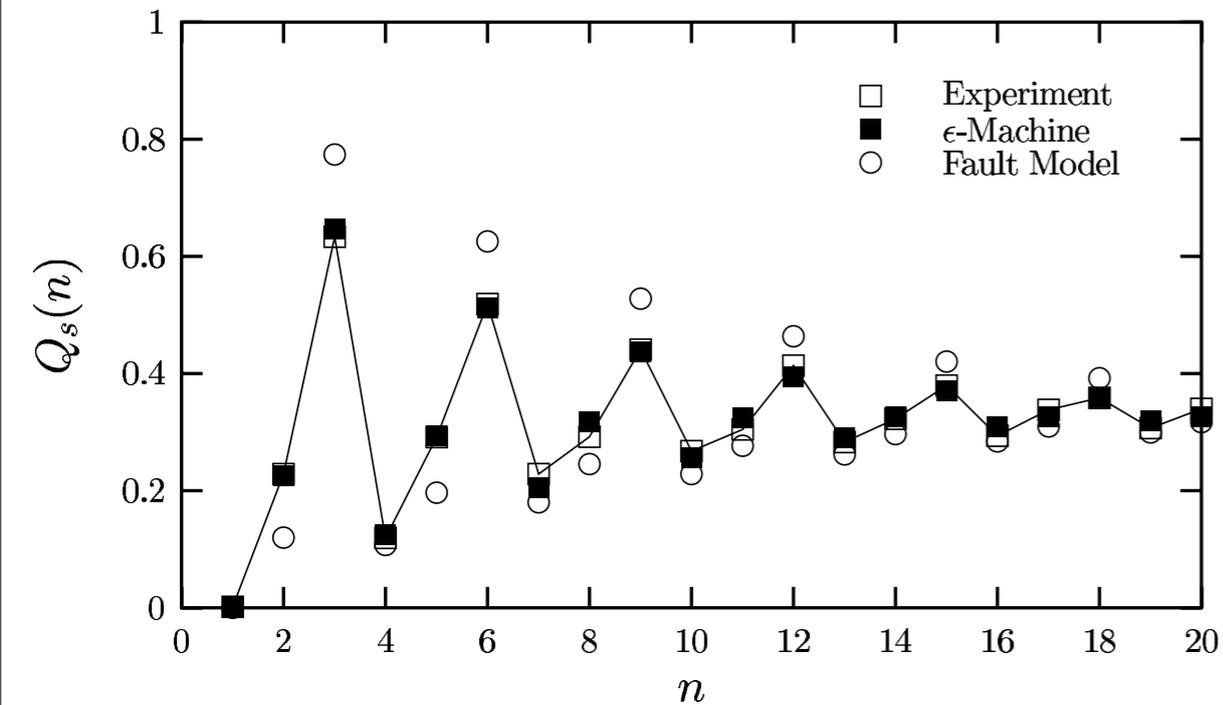
No sensible fault model analysis is possible here.

Computational, Informational, and Physical Quantities

System	P	r_l	$h_\mu(bits/ML)$	$C_\mu(bits)$	$E\ (meV)$	α
2H	2	1	0	1.0	1.95	1.00
3C	1	0	0	0.0	-1.79	0.00
6H	6	3	0	2.6	-0.65	0.33
SK134	4.8	3	0.50	2.3	1.13	0.80
SK135	5.6	3	0.59	2.5	-1.02	0.24

Computational, informational, and physical quantities calculated for the two samples, as well as the three crystalline structures we considered. E is configurational energy per Zn-S pair associated with the stacking. α is the hexagonality of each sample. (The hexagonality is defined as that fraction of modular layers which are hexagonally related to their neighbors.)

Advantages over Other Methods

Table 1: A comparison between ϵ-machine spectral reconstruction (ϵMSR), the fault model (FM) and Jagodzinski's disorder model (JDM). We see that ϵMSR has many advantages over previous analyses.

	ϵMSR	FM	JDM	RMC
1. Description of Disorder	ϵ-Machine	Fault Probabilities	Conditional Probabilities	Stacking Sequence
2. Method of Analysis	Fourier Analysis	Peak Analysis	Fit Diffraction Spectrum	Fit Diffraction Spectrum or Correlation Functions
3. Treats any amount of Disorder?	yes	no	yes(?)	yes
4. Unique Description?	yes	no	yes	no
5. Assumes a Markov Process?	yes, $r = 3$ (can go higher)	yes, $r = 3$	yes, $r = 2$	yes(?)
6. Simultaneously Allows more than one Crystal Structure ?	yes	no	yes (limited)	yes
7. Treats Crystal/Fault Structure the Same ?	yes	no	no	yes
8. Uses all the Information in the Diffraction Pattern?	yes	no	no	yes
9. Allows Calculation of Physical Parameters	yes	no	no	yes

So, Summing Up:

• εMSR provides the most general description possible of disorder in one dimension.

• No assumption about the crystal structure or fault structure need be made.

• *Any kind or amount* of planar disorder can be be treated.

• There may be more than one crystal structure present.

• Treats fault and crystal structure on an equal footing.

• All the information in the spectrum---both Bragg like and and diffuse scattering---is used to generate the model.

• Parameters of physical interest are amenable to calculation from the ε-machine.

• εMSR can evaluate the quality of experimental data before beginning reconstruction.

Open Research Questions

1. Impose symmetry conditions on the sequence probabilities, and develop symmetric ε-machine spectral reconstruction theory (SεMSR).
2. Extend εMSR and SεMSR to the *r = 4* case.
3. Use Reverse Monte Carlo Modeling to find sample, disordered crystals, and then use standard reconstruction techniques to find the ε-machine.
4. Simulate layer displacement faulting to model the 2H to 3C transformation, and both deformation and layer displacement faulting to simulate the 3C to 2H transformation.
5. Examine other close-packed structures, like SiC or perhaps graphene. Or more complicated polytypes for that matter.
6. Consider the implications of various kinds of disorder on various phenomena in condensed matter systems, such as Anderson Localization.
7. Consider the interpretations/applications of new computational measures in the polytype setting.
8. Suppose that one had some phase information, how could one incorporate that into the Spectral Equations?
9. It is claimed that from the analysis of peak profiles one can extract correlation information--$Q_s(n)$--from powder diffraction data, assuming spin inversion symmetry. When one combines this with SεMSR, how good is the reconstructed ε-machine?
10. Explore how εMSR handles noisy diffraction spectra.
11. Two Dimensions, Anyone?

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