Materials Discovery for Fuel Cells

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New Opportunities at the Intersection of Constraint Reasoning and Learning

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Motivation

Cornell Fuel Cell Institute

Mission: develop **new materials** for **fuel cells**.

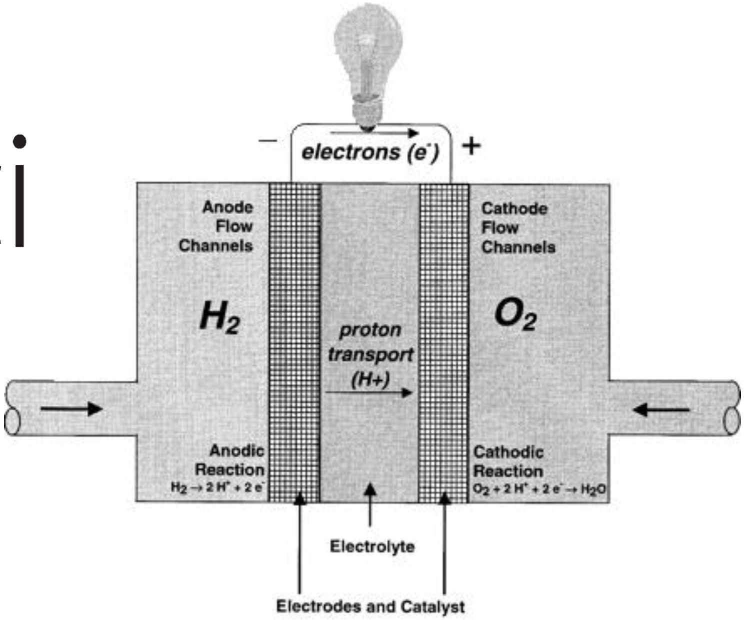


Figure 1. Fuel cell schematic.
Source: Annual Reveiws of Energy and the Environment. http://energy.annualreviews.org/cgi/content/full/24/1/281

An **Electrocatalyst** must:

1) Be electronically **conducting**
2) **Facilitate** both reactions

Platinum is the best known metal to fulfill that role, but:

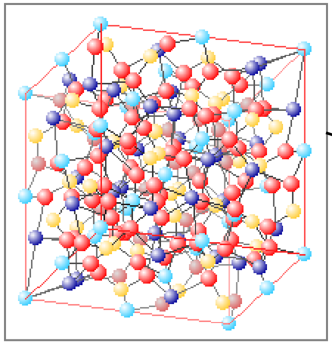
1) The reaction rate is still considered slow (causing **energy loss**)
2) Platinum is fairly **costly**, **intolerant** to fuel **contaminants**, and has a **short lifetime**.

Goal: Find an **intermetallic compound** that is a better catalyst than Pt.

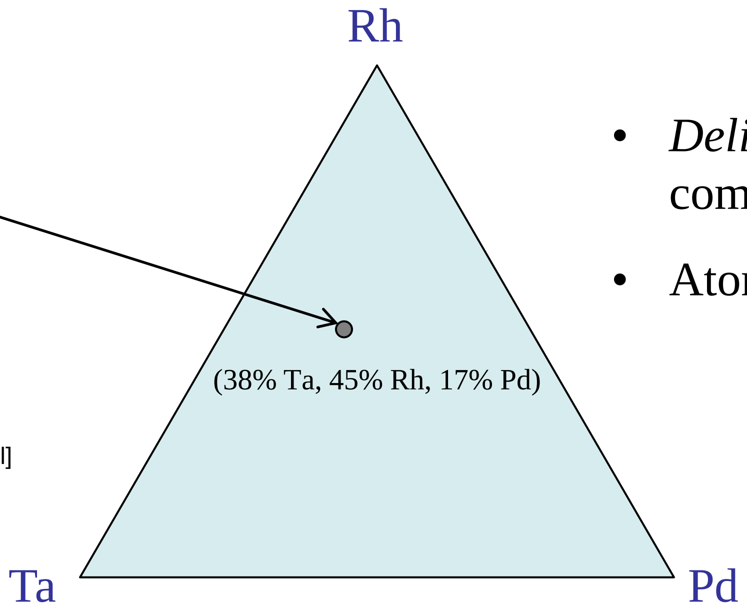
Motivation

Recipe for finding alternatives to Platinum

1) *In a vacuum chamber, place a silicon wafer.*
2) *Add three metals.*
3) *Mix until smooth, using three sputter guns.*
4) *Bake for 2 hours at 650ºC*



[Source: *Pyrotope*, Sebastien Merkel]

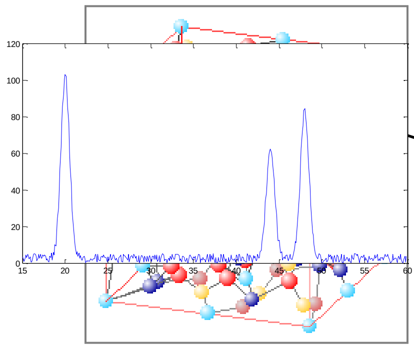


- *Deliberately* inhomogeneous composition on Si wafer
- Atoms are intimately mixed

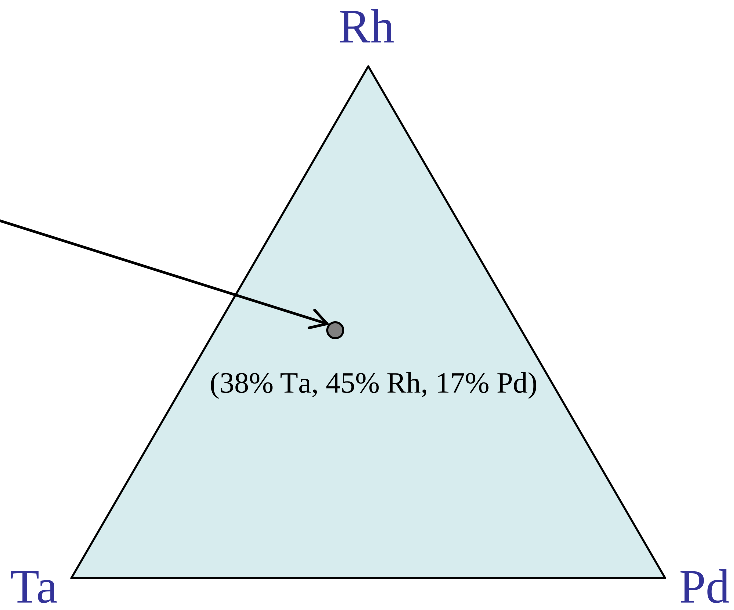
Motivation

Identifying crystal structure using **X-Ray Diffraction** at CHESS

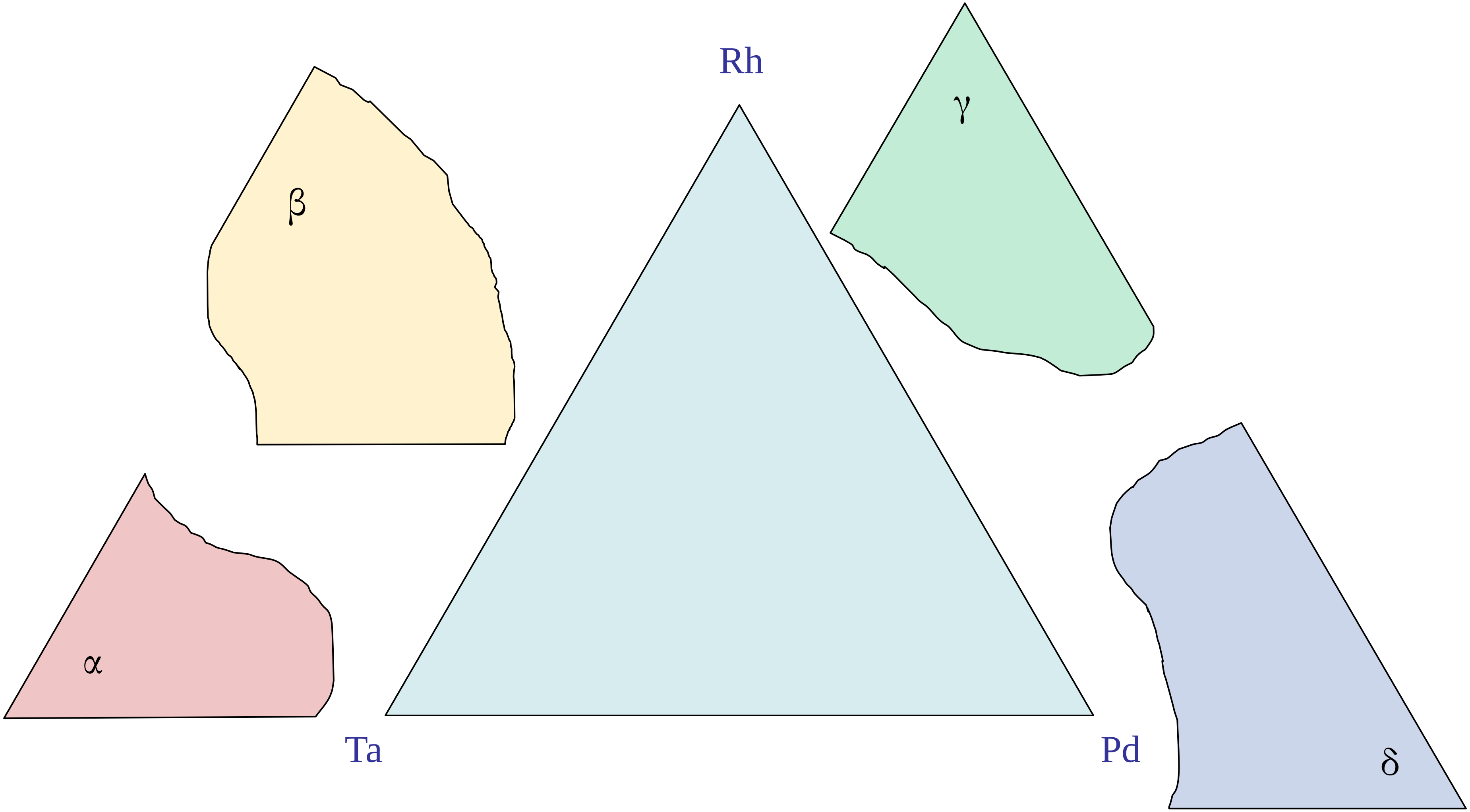
- XRD pattern **characterizes** the underlying **crystal** fairly well
- **Expensive** experimentations: Bruce van Dover’s research team has access to the facility **one week every year**.



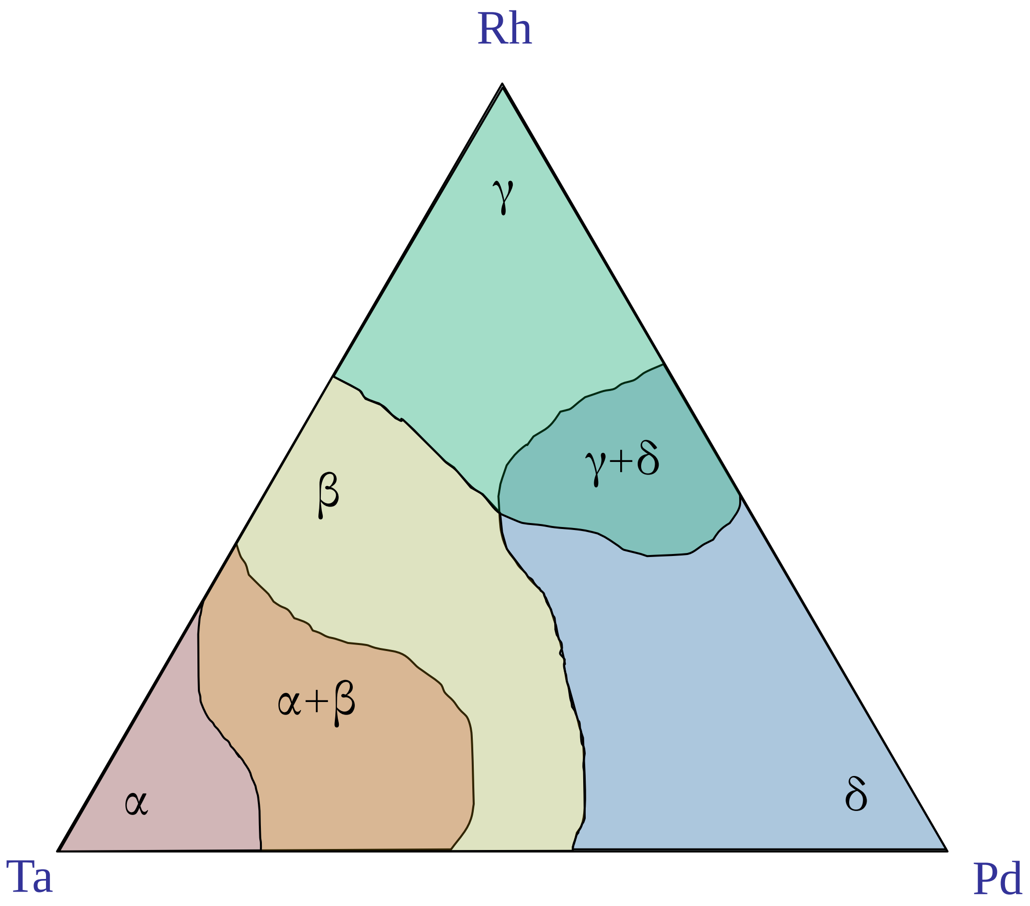
[Source: *Pyrotope*, Sebastien Merkel]



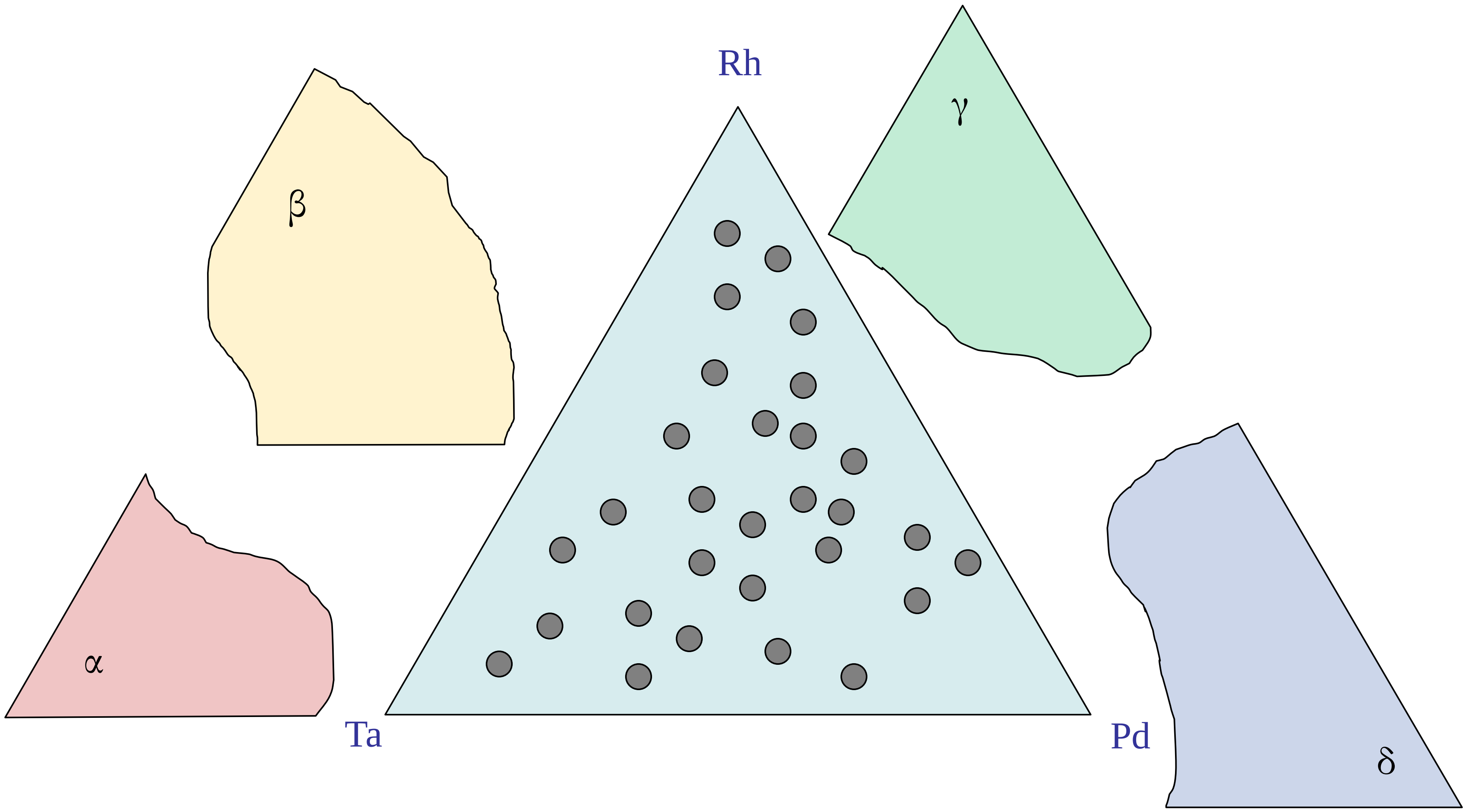
Motivation



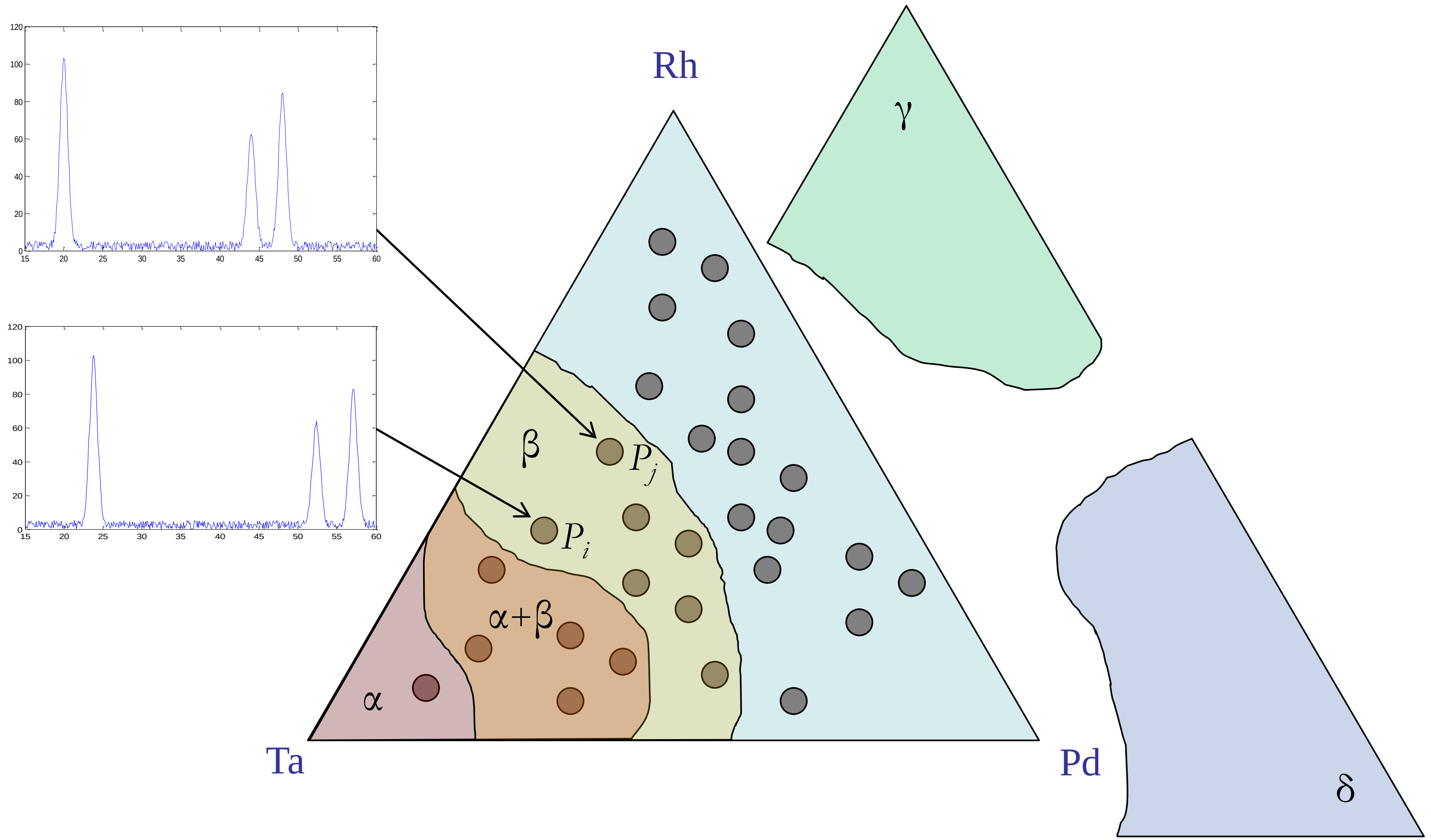
Motivation



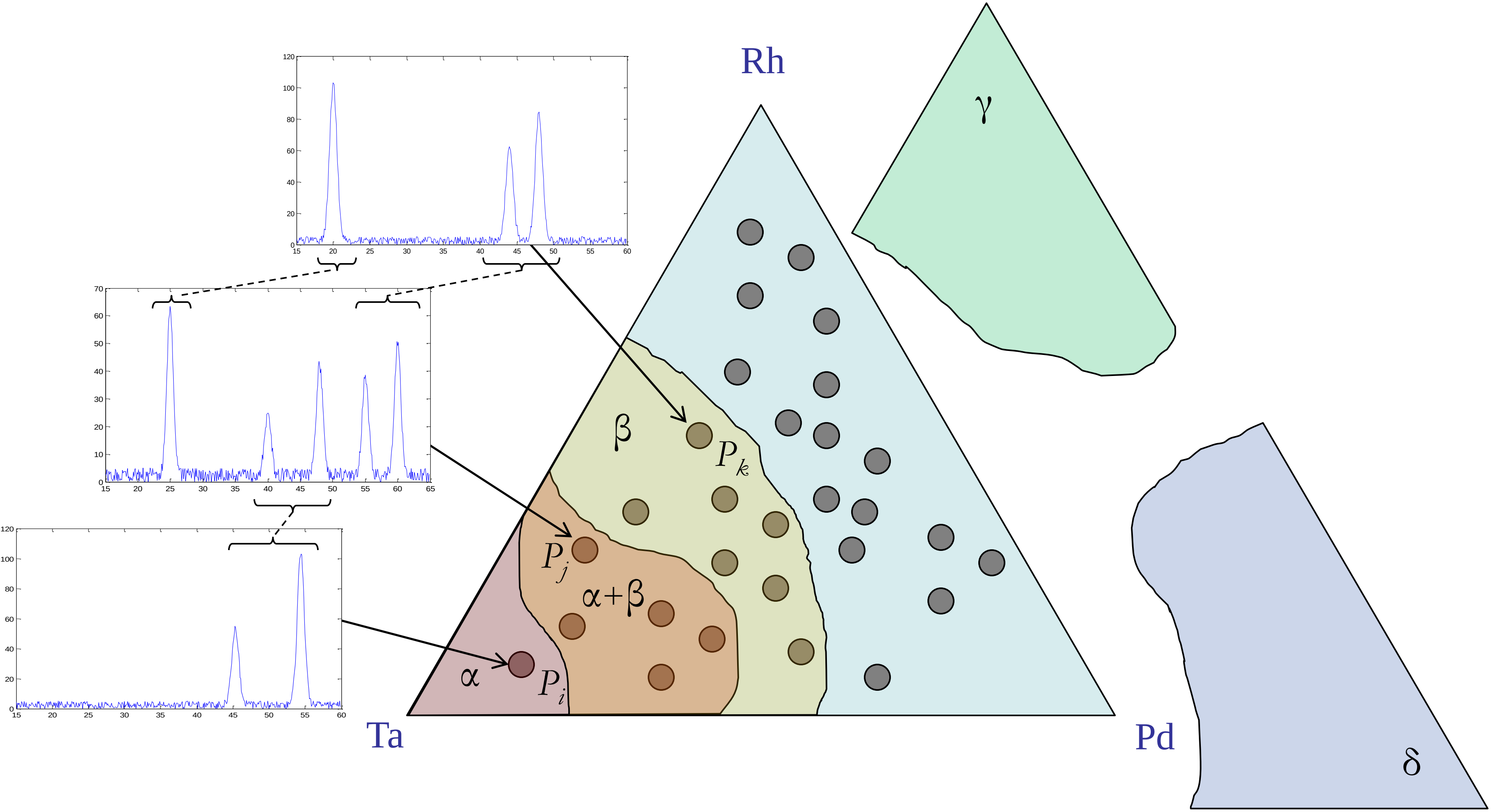
Motivation



Motivation

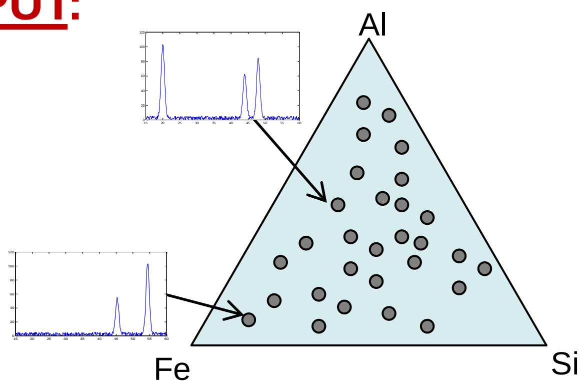


Motivation



Motivation

INPUT:

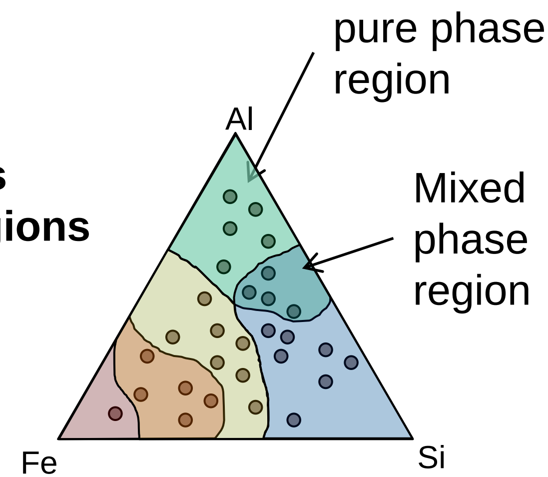


OUTPUT:

***m* phase regions**

- ***k* pure regions**
- ***m-k* mixed regions**

XRD pattern characterizing pure phases



Additional Physical characteristics:

- Phase Connectivity
- Mixtures of ≤ 3 pure phases
- Peaks shift by ≤ 15% within a region
  - Continuous and Monotonic
- Noisy detection

Motivation

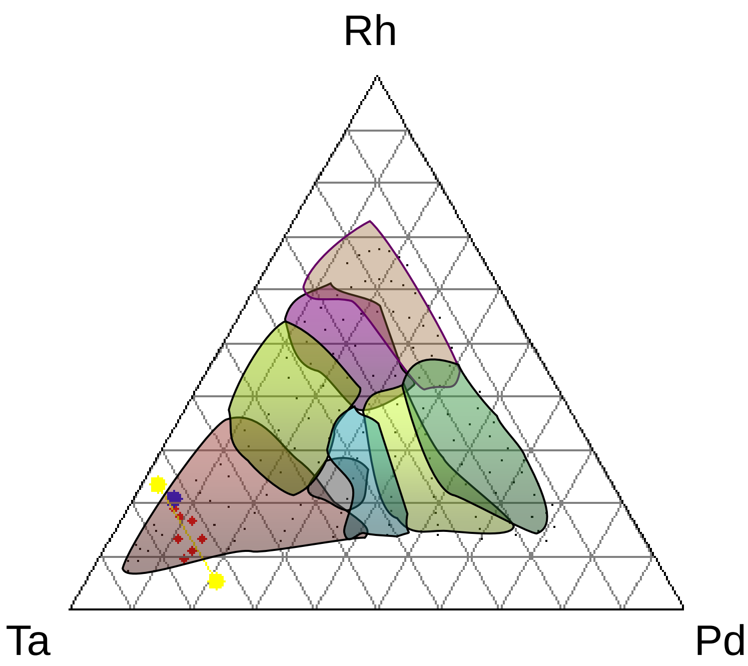


Figure 1: Phase regions of Ta-Rh-Pd

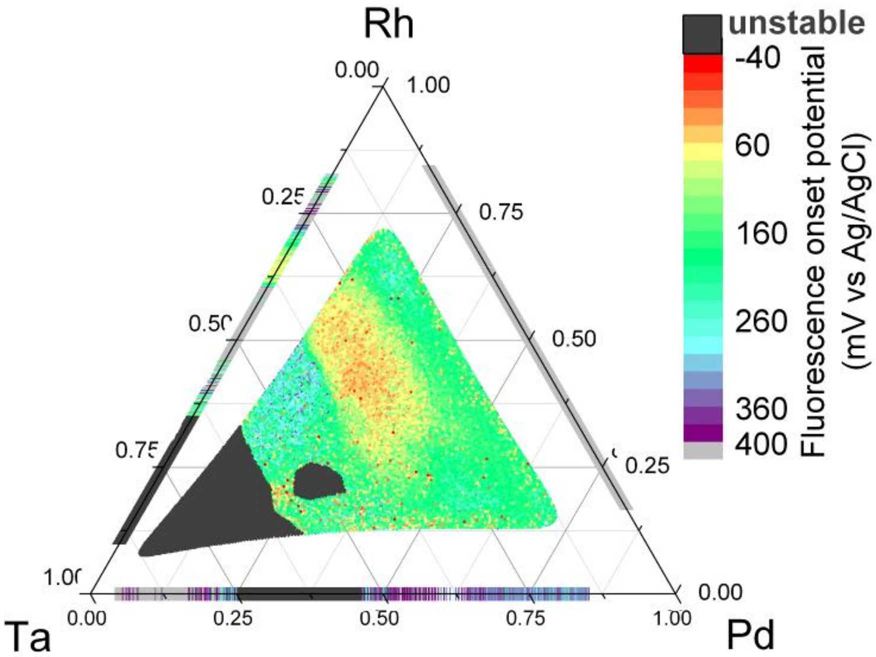


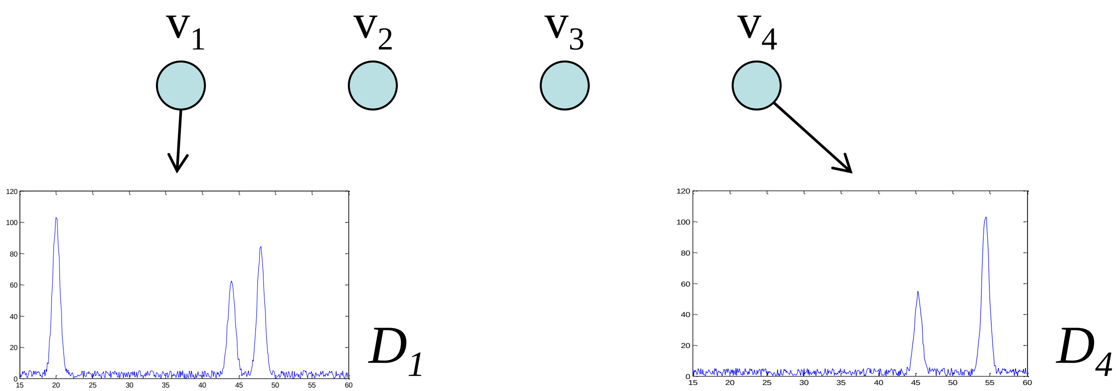
Figure 2: Fluorescence activity of Ta-Rh-Pd

Outline

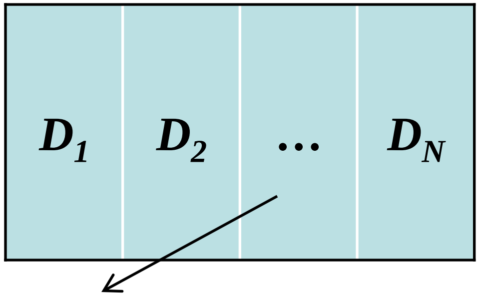
- Motivation
- Problem Definition (Part I)
- Previous Work: Non-negative Matrix Factorization
- Problem Definition (Part II)
- Our Work: Satisfiability Modulo Theories Approach
- Conclusion and Future work

Problem Definition (Part I)

- **Input:**
  - A list of points on the silicon wafer



  - A real vector $\boldsymbol{D_i}$ per vertex v_i (diffraction patterns)
  - K = user specified number of pure phases
- **Goal**: a basis of K vectors for



$$\boldsymbol{D_i} = a_{i1}\boldsymbol{B_1} + \ldots + a_{iK}\boldsymbol{B_K}$$

Problem Definition (Part I)

- There is **experimental noise**

Minimize norm instead

$$\boldsymbol{D_i} = a_{i1}\boldsymbol{B_1} + \ldots + a_{iK}\boldsymbol{B_K} \quad \Rightarrow \quad \boldsymbol{min}\ \|\boldsymbol{D_i} - (a_{i1}\boldsymbol{B_1} + \ldots + a_{iK}\boldsymbol{B_K})\|$$

- **Non-negative** basis vectors and coefficients

$$\boldsymbol{B_i} \geq \boldsymbol{0},\ a_{ij} \geq 0$$

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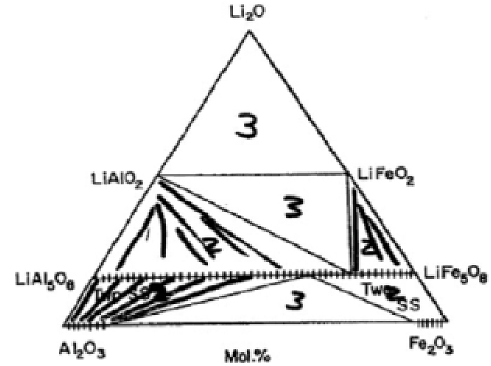
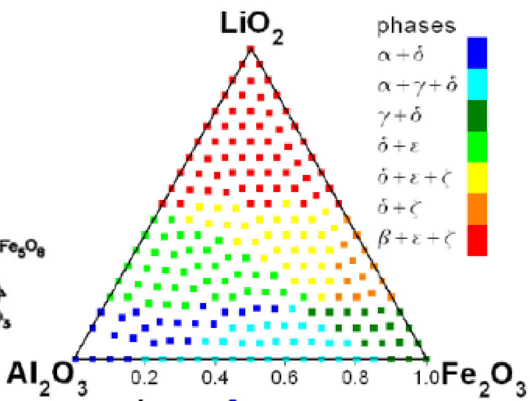
Non-negative Matrix Factorization [Long et al., 2009]

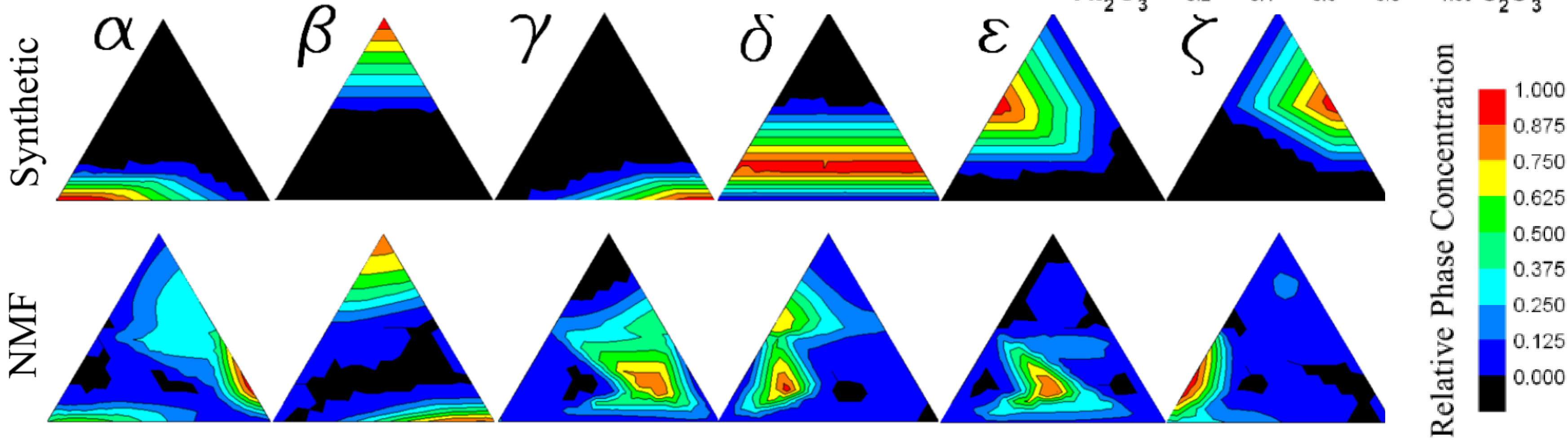
Advantages: scales up very well, accurately solves simple systems

Drawbacks: overlooks critical physical behavior, making the results physically meaningless for more complex systems.

Illustration on synthetic instances from the *Al-Li-Fe* ternary system







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Problem Definition (Part II)

- There is **experimental noise**

$$\boldsymbol{D_i} = a_{i1}\boldsymbol{B_1} + \ldots + a_{iK}\boldsymbol{B_K} \quad \Rightarrow \quad \boldsymbol{min}\ \|\boldsymbol{D_i} - (a_{i1}\boldsymbol{B_1} + \ldots + a_{iK}\boldsymbol{B_K})\|$$

Minimize norm instead

- **Non-negative** basis vectors and coefficients

$$\boldsymbol{B_i} \geq \boldsymbol{0},\ a_{ij} \geq 0$$

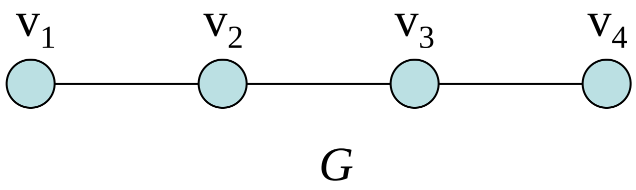
- **At most M (=3) non-zero coefficients** per point

$$|\{j \mid a_{ij} > 0\}| \leq M$$

- Basis patterns appear in **contiguous** locations on silicon wafer

Build a graph G of the points on the silicon wafer

The subgraph induced by $|\{i \mid a_{ij} > 0\}|$ is connected



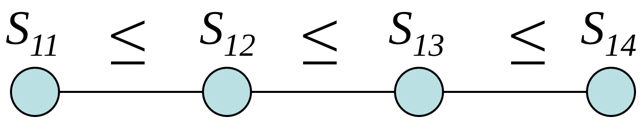
Problem Definition (Part II)

- Basis vector can be **shifted**

Shift operator → S; Shift coefficients → s_{iK}

$$\boldsymbol{min} \ || \ \boldsymbol{D_i} - (a_{i1} S(\boldsymbol{B_1}, s_{i1}) + \ldots + a_{iK} S(\boldsymbol{B_K}, s_{iK})) \ ||$$

- Shifts coefficients are **bounded**, **continuous** and **monotonic**



$$|S_{12} - S_{11}| \leq c$$

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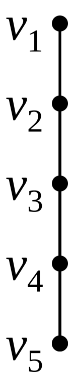
Satisfiability Modulo Theories Approach

- Initial graph G and number K of basis patterns

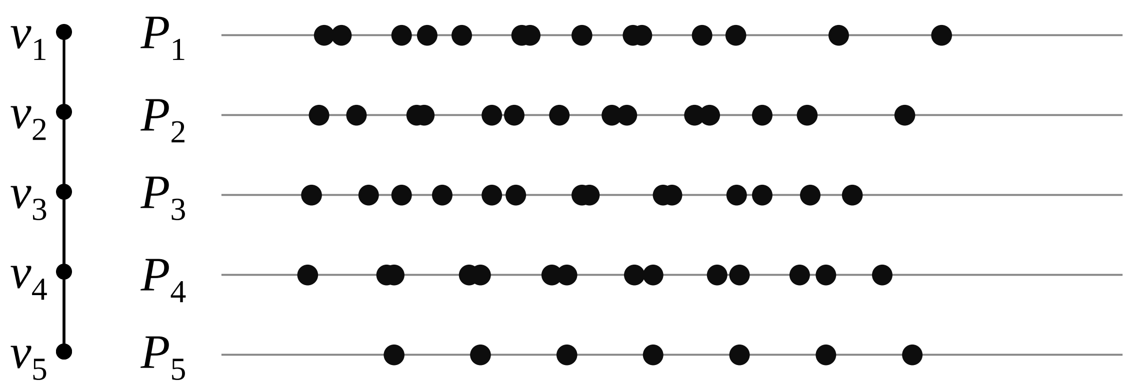
K=2
basis
patterns



Satisfiability Modulo Theories Approach

- Initial graph *G* and number *K* of basis patterns
- *Peak detection* to extract a set of peaks P_i for each diffraction pattern $\boldsymbol{D_i}$

K=2 basis patterns



Satisfiability Modulo Theories Approach

- Initial graph *G* and number *K* of basis patterns
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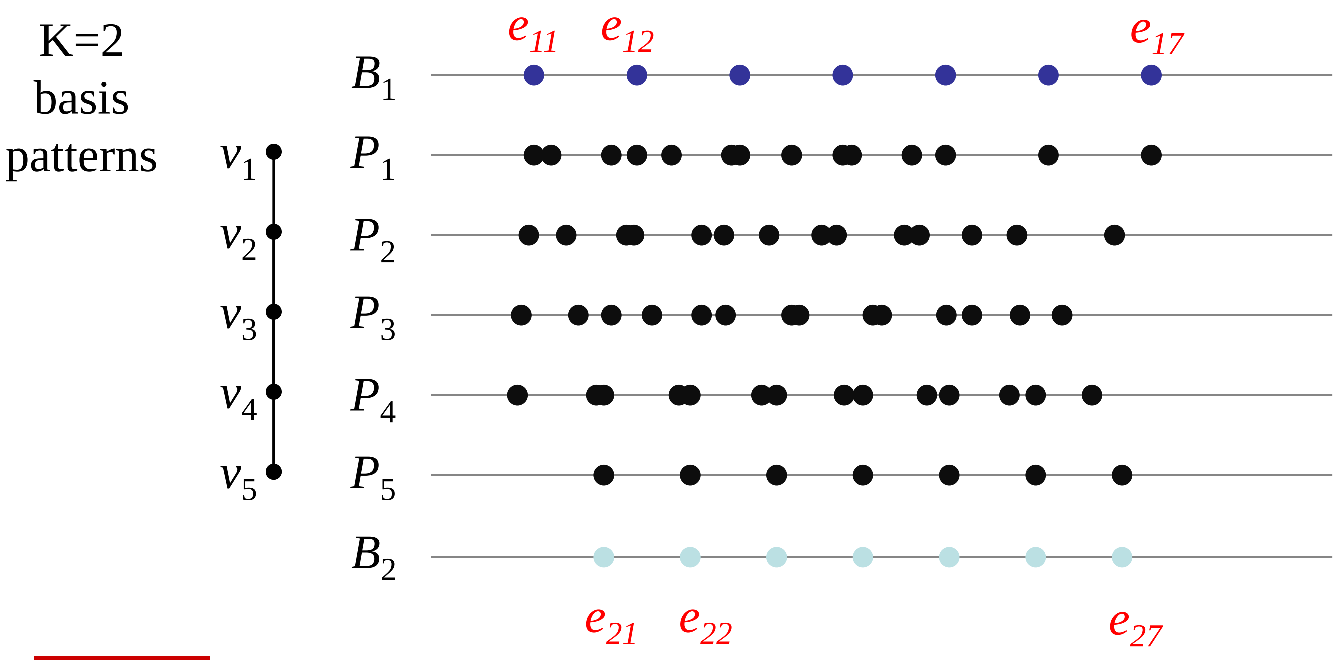
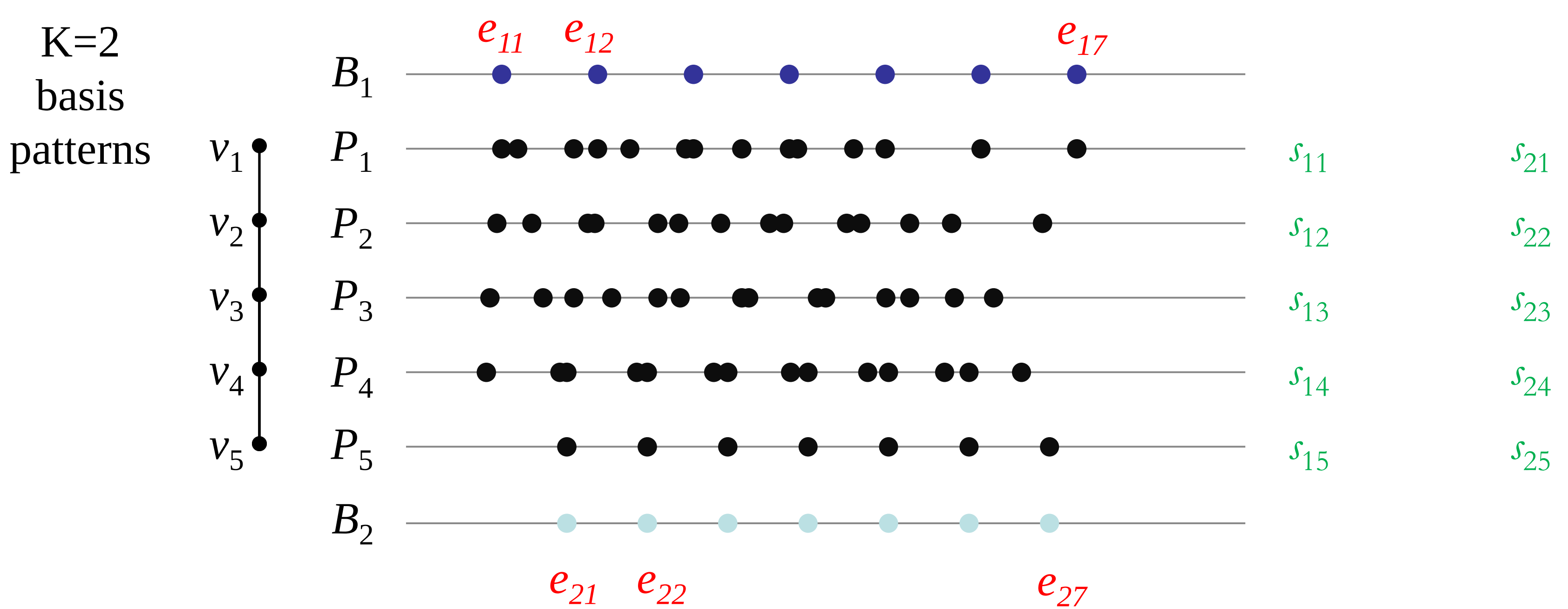
- Real variable e_{jk} for the **location of peak** *k* in basis B_j



Satisfiability Modulo Theories Approach

- Initial graph G and number K of basis patterns
- *Peak detection* to extract a set of peaks P_i for each diffraction pattern $\boldsymbol{D_i}$
- Real variable e_{jk} for the **location of peak** k in basis B_j
- Real variable s_{ij} for the **shift** coefficient of basis B_j in point P_i



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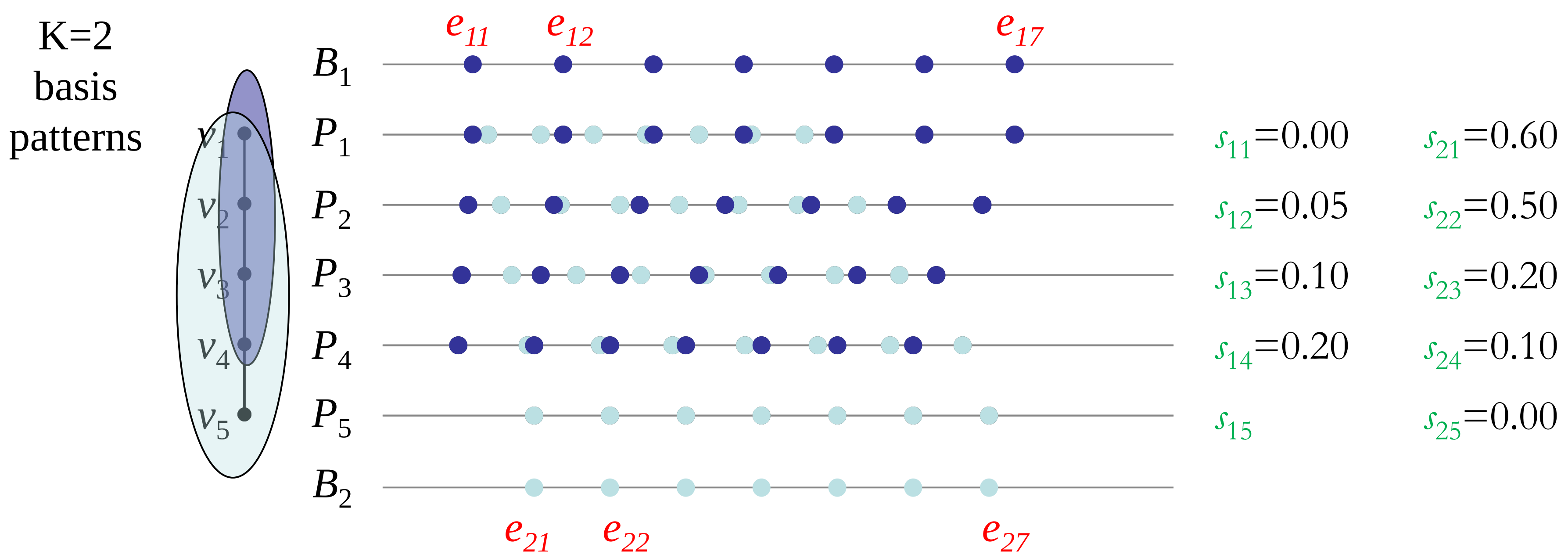
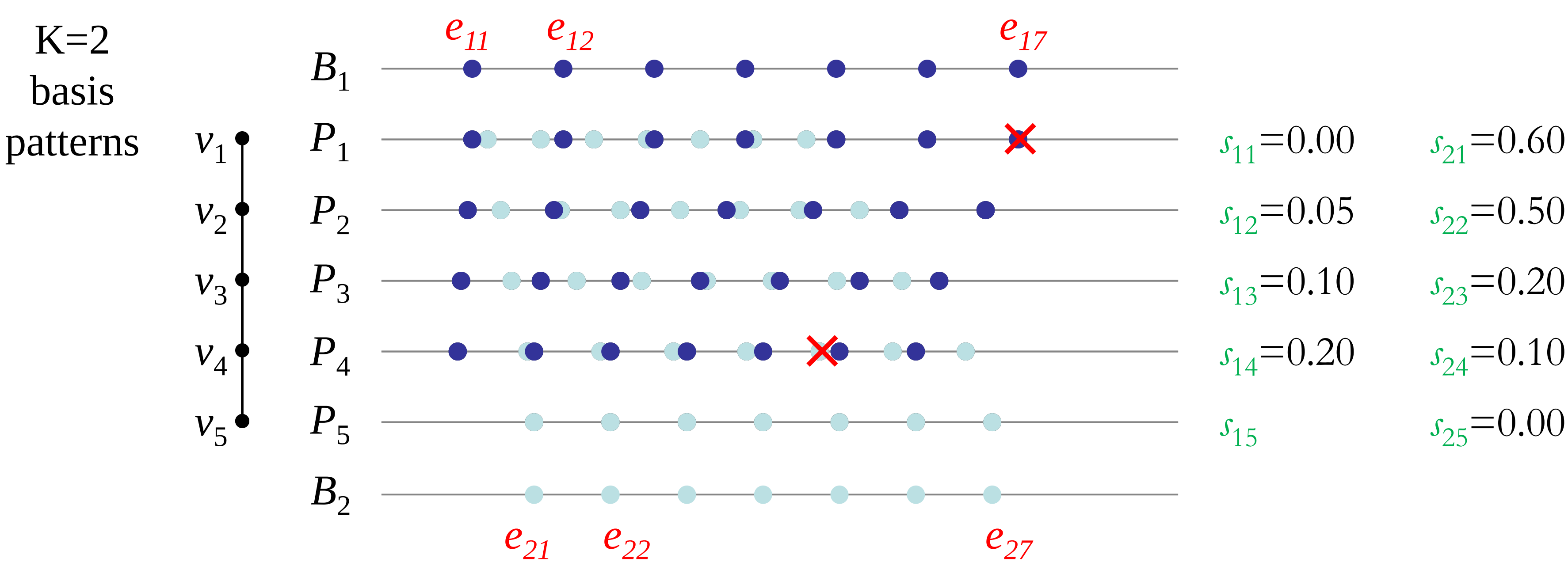
Satisfiability Modulo Theories Approach

- An observed peak p is "*explained*" if there exists s_{ij}, e_{jk} s.t. $|p-(s_{ij} + e_{jk})| \leq \varepsilon$
- Every observed peak must be *explained*



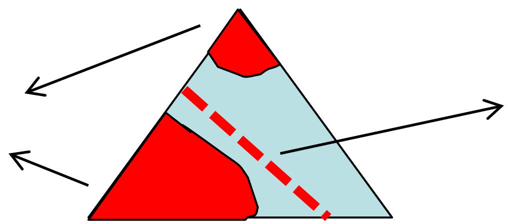
Satisfiability Modulo Theories Approach

- An observed peak p is "*explained*" if there exists s_{ij} ,e_{jk} s.t. $|p-(s_{ij} + e_{jk})| \leq \varepsilon$
- Every observed peak must be *explained*
- Some peaks might be missing (unobserved)
- Bound the number of missing peaks $\leq T$
- Minimization by (binary) search on T



Satisfiability Modulo Theories Approach

- Linear phase usage constraints (up to *M* basis patterns per point)
- Linear constraints for shift monotonicity and continuity ($s_{ij} \leq s_{lm}$)
- **Lazy connectivity**: add a cut if current solution is not connected



- **Symmetry breaking**:
  - Renaming of pure phases
  - Ordering of the peak locations e_{jk} (per basis pattern)

Quantifier-free linear arithmetic

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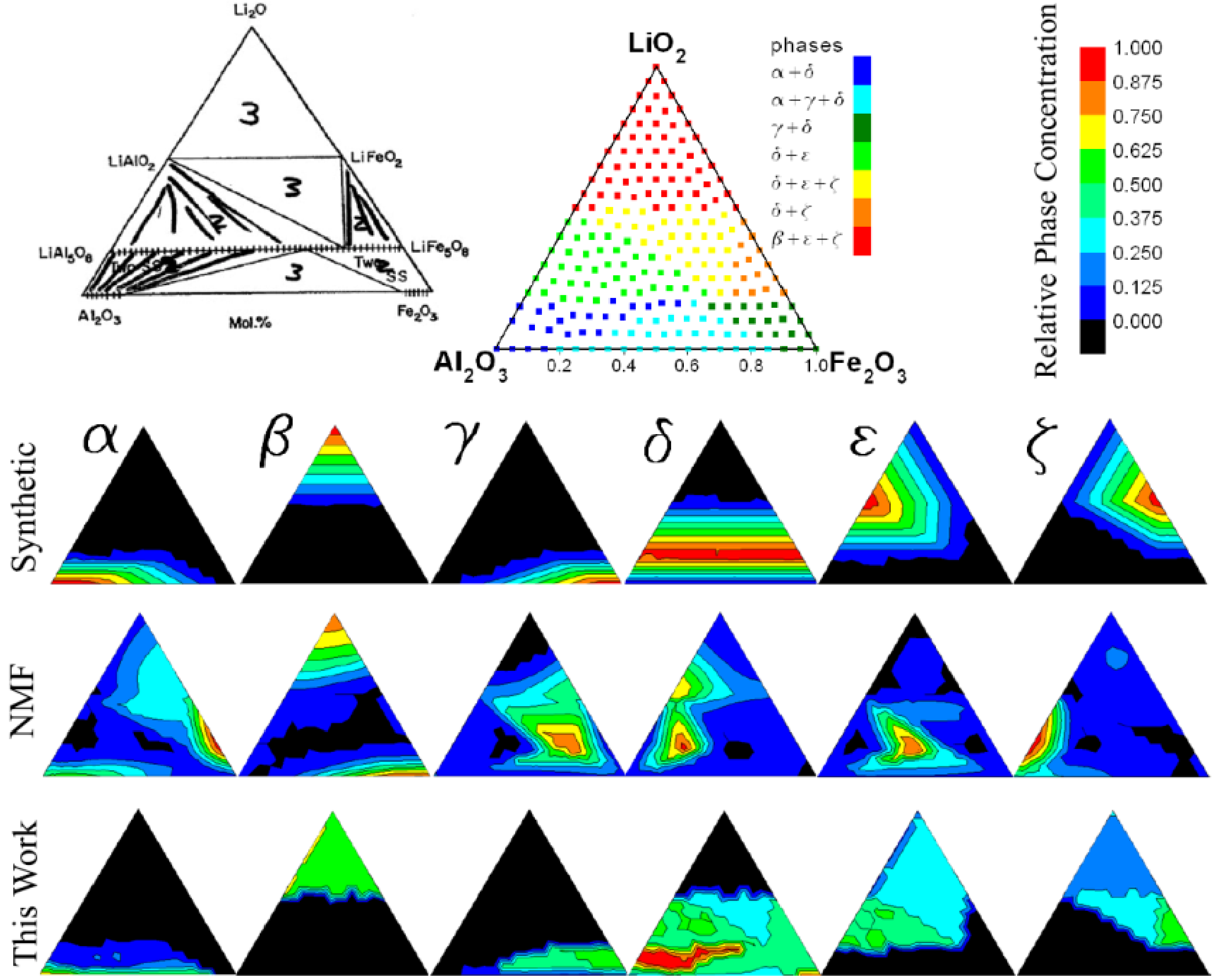
Experimental Results

•Illustration on Al-Li-Fe system



Conclusion and Future work

- Novel **SMT** encoding for Materials Discovery
- Good performance on synthetic data:
  - Scales to **realistic sized problems** (~50 points)
  - Provides **physically-meaningful** solutions
  - **Good accuracy** (>90% precision and recall)
  - Outperforms both Constraint Programming and Mixed Integer Programming direct translations of the SMT model
- **Future work**: online adaptive sampling during data collection
- Exciting results analyzing and explaining **real-world data**

THANK YOU!

Extra slides

Runtime

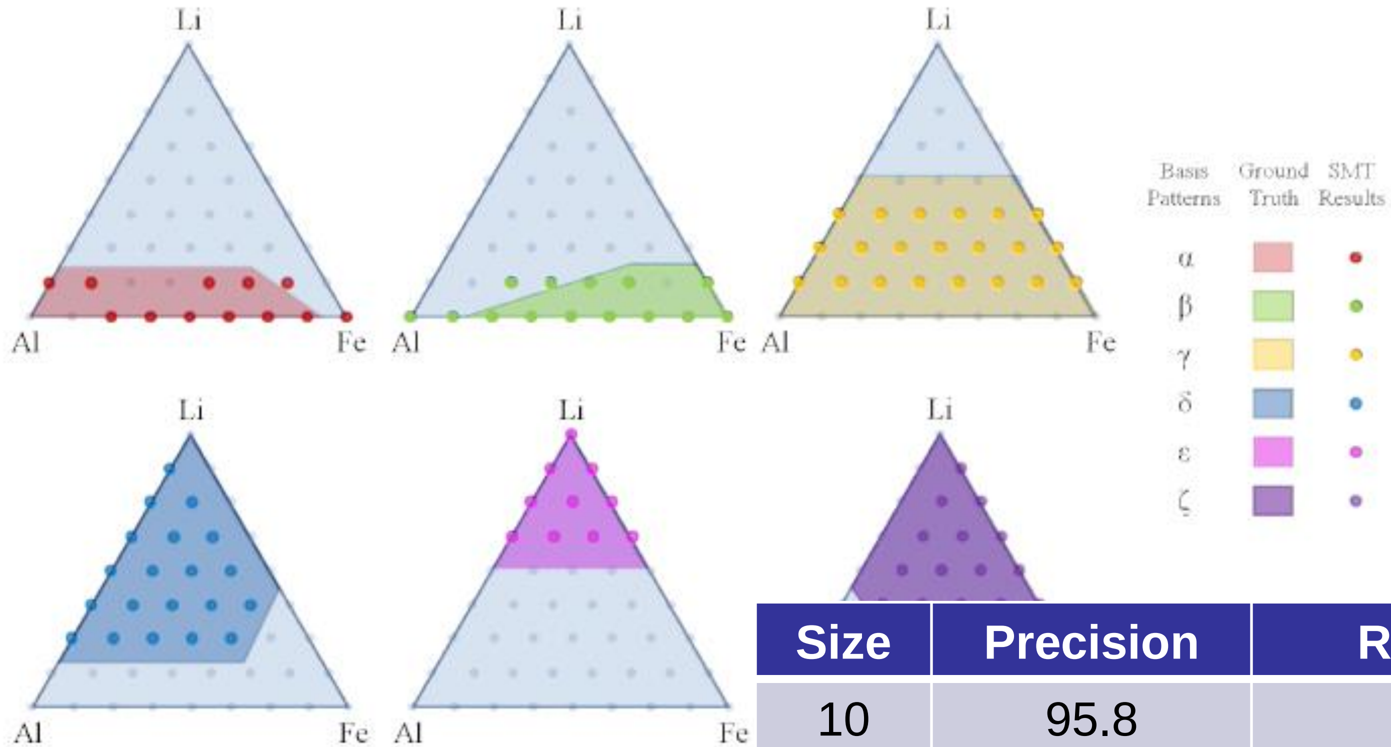
# Points	Unknown Phases	Arithmetic + Z3 (s)	Set-based + CPLEX (s)
10	3	8	**0.5**
	6	**12**	Timeout
15	3	13	**0.5**
	6	**20**	Timeout
18	3	**29**	384.8
	6	**125**	Timeout
29	3	**78**	276
	6	**186**	Timeout
45	6	**518**	Timeout

Z3 scales to realistic sized problems!

Arithmetic encoding translated to CP and MIP:

- MIP is appealing because it can optimize the objective
- They don't scale → SMT solving strategy

Precision/Recall



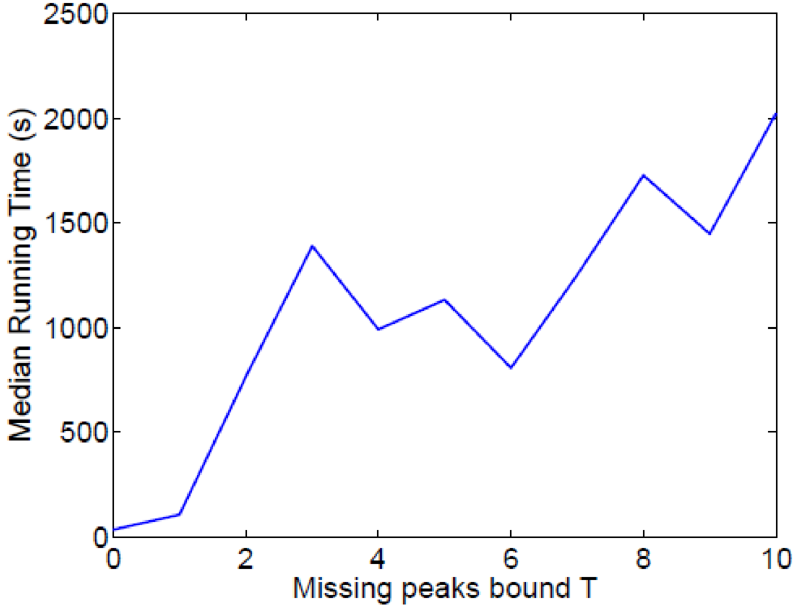
Recovers ground truth

Size	Precision	Recall
10	95.8	100
15	96.6	100
18	97.2	96.6
29	96.1	92.8
45	95.8	91.6

Robustness

- Remove some peaks to simulate experimental noise
- Size = 15 points

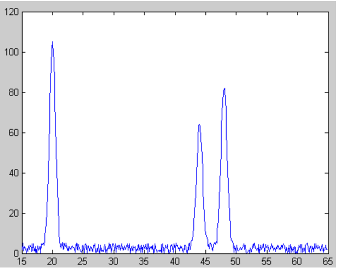
Missing Peaks	Precision	Recall
1	96.1	99.6
2	96.3	99.3
3	96.7	99.5
4	95.3	98.9
5	94.8	99.7



Solutions are still **accurate**. Runtime increases approx **linearly**.

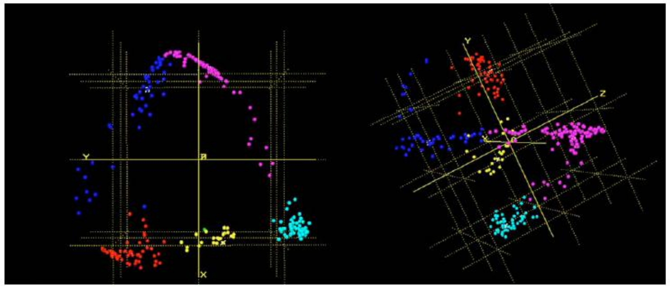
Previous Work 1: Cluster Analysis [Long et al., 2007]

$x_i =$

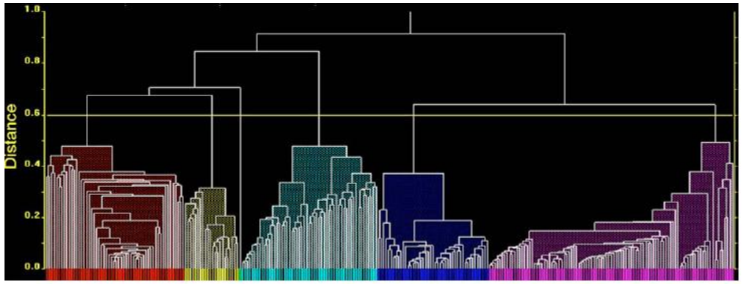


$$C_{xy} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\left[\sum_{i=1}^{n} (x_i - \bar{x})^2 \sum_{i=1}^{n} (y_i - \bar{y})^2 \right]^{1/2}} \longrightarrow D = (1 - C)/2.$$

Feature vector *Pearson correlation coefficients* *Distance matrix*



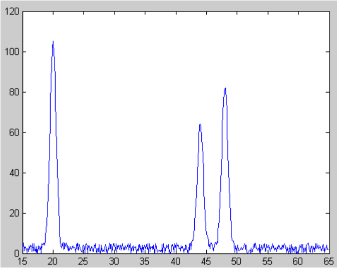
PCA – 3 dimensional approx



Hierarchical Agglomerative Clustering

Drawback: Requires sampling of pure phases, detects phase regions (not phases), overlooks peak shifts, may violate physical constraints (phase continuity, etc.).

Previous Work 2: NMF [Long et al., 2009]

$x_i =$ 

$\longrightarrow$ $X = A.S + E$ $\longrightarrow$ $Min\ \|E\|$

Feature vector

Linear positive combination (A) of basis patterns (S)

Minimizing squared Frobenius norm

Drawback: Overlooks peak shifts (linear combination only), may violate physical constraints (phase continuity, etc.).

SMT formulation

- **Parameters**
  - Number of pure phases *K*, tolerance *ε*
- Key components
  - Variables peak positions per base
  - Shifts per point
  - Point *p* is explained by base *k*

SMT formulation

- New arithmetic-based encoding:
  - Real variables e_{ij} for the peak locations in each B_i
  - Real variables for the shift coefficients s_{ij} (per base, per point)
  - An observed peak p is explained if $|p-s_{ij} - e_{ij}| \leq \varepsilon$ (Match the height of the peaks)
  - Bound the number of missing peaks $\leq T$