Modeling Complex Diffusion Mechanisms in $L1_2$-Structured Compounds

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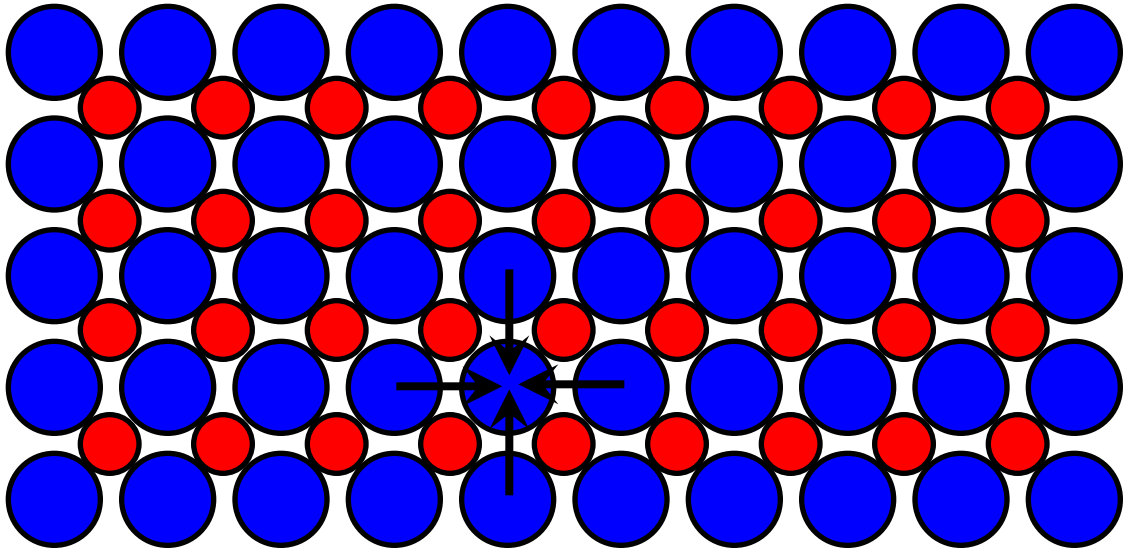
Modeling Complex Diffusion Mechanisms in $L1_2$-Structured Compounds

Overall goal: To determine when PAC and other hyperfine methods can be used to identify diffusion mechanisms

1. Diffusion mechanisms in intermetallic compounds
2. Recent PAC findings in $L1_2$-structured compounds
3. Stochastic models of complex mechanisms
4. Simulations for $L1_2$ compounds

Diffusion in intermetallic compounds

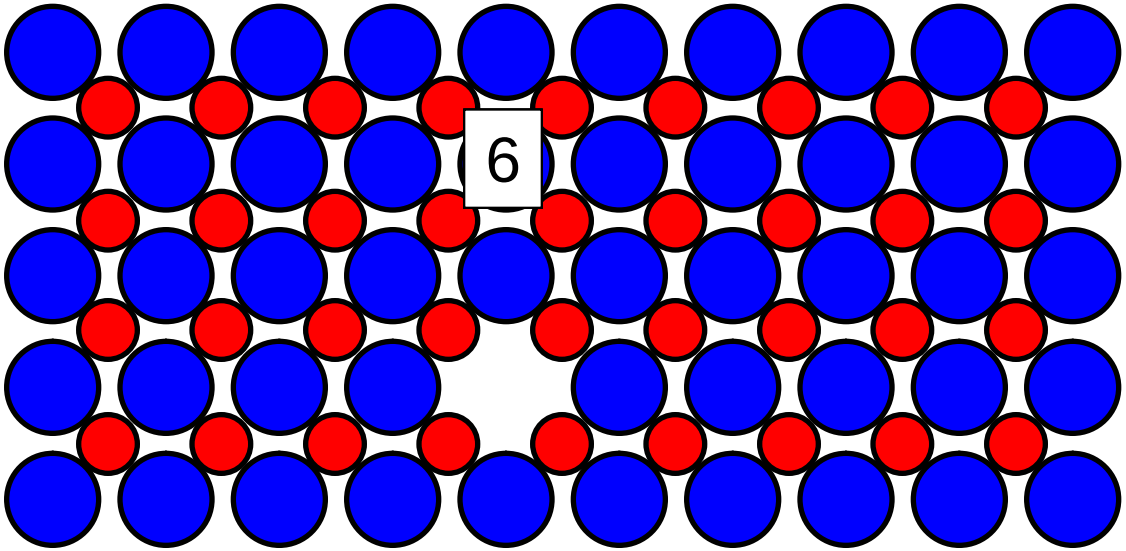
example: simple vacancy diffusion



Diffusion in intermetallic compounds

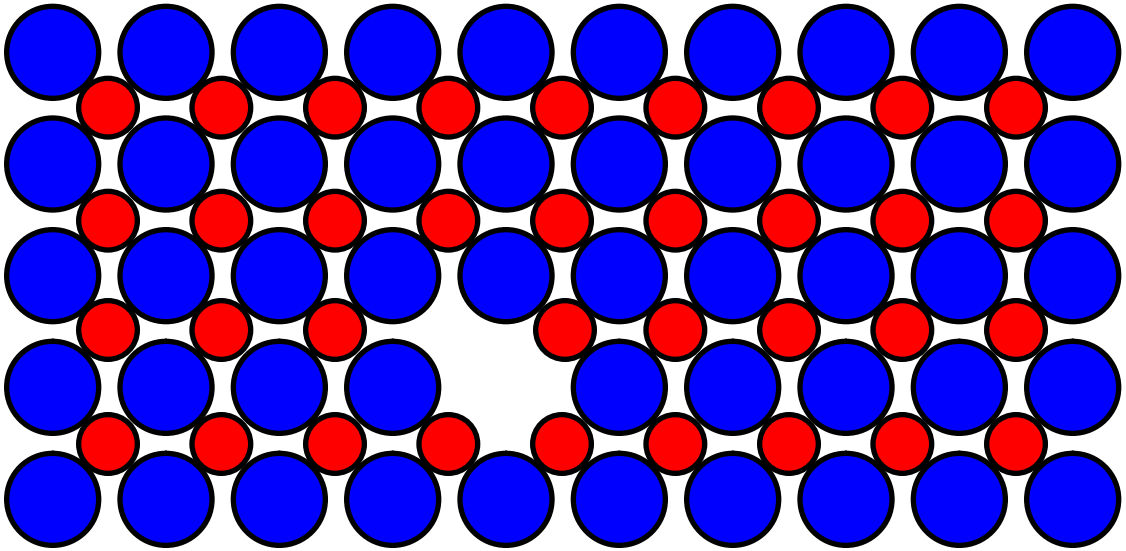
Only first-neighbor jumps allowed

example: 6-jump cycle



Diffusion in intermetallic compounds

Possible alternative: divacancy



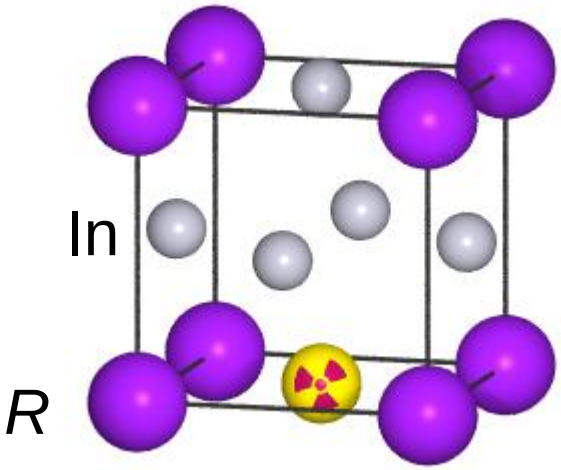
Diffusion in intermetallic compounds

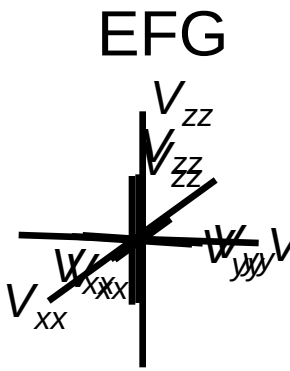
- How to distinguish diffusion mechanisms in alloys (elements *A* and *B*) experimentally?
- Conventional radiotracer sectioning methods
  - Measure diffusion coefficients of each element, D_A and D_B and compare ratios.
  - *E.g.* in A_3B ($L1_2$)*
    - $0.11 < D_A/D_B < 0.85$ for 6-jump cycle
    - $0.07 < D_A/D_B < 3$ for divacancy
- Perturbed angular correlation spectroscopy?

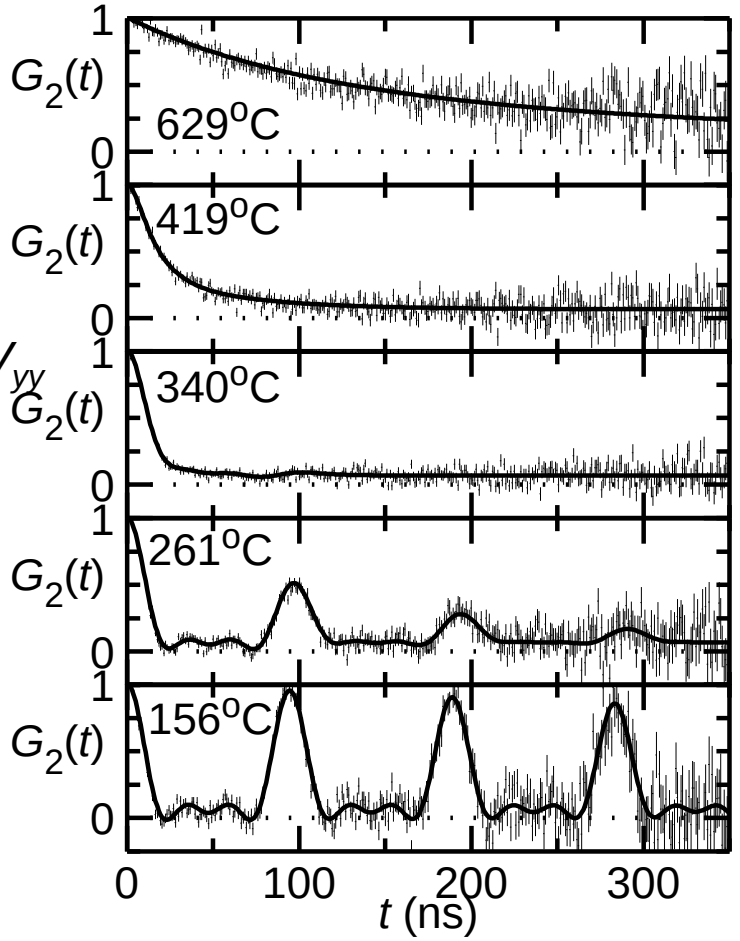
*Koiwa, Numakura, Ishioka, *Def. & Diff. Forum* **143-147**, 209 (1997)

PAC measurements of Cd jump rates in $L1_2$ structured compounds*

- $R\text{In}_3$, $R\text{Ga}_3$, $R\text{Sn}_3$ with R=rare earth
- $L1_2$ structure:







*Collins, Jiang, Bevington, Selim, Zacate, *PRL* **102**, 155901 (2009) and refs. therein; Jiang, Zacate, Collins, *Def. & Diff. Forum* **289-292**, 725 (2009);

PAC measurements of Cd jump rates in $L1_2$ structured compounds

- $R\text{In}_3$, $R\text{Ga}_3$, $R\text{Sn}_3$ with R=rare earth
- Jump rates at phase boundaries:

jump rate larger for R-poorer boundary	jump rate larger for R-rich boundary
LaIn_3, CeIn_3, PrIn_3	LuIn_3, TmIn_3, ErIn_3, HoIn_3, DyIn_3, TbIn_3, GdIn_3 LaSn_3, CeSn_3, SmSn_3, GdSn_3

divacancy or 6-jump mechanism

Simple vacancy mechanism

Collins, Jiang, Bevington, Selim, Zacate, *PRL* **102**, 155901 (2009)

PAC measurements of Cd jump rates in $L1_2$ structured compounds

- $R\mathrm{In}_3$, $R\mathrm{Ga}_3$, $R\mathrm{Sn}_3$ with R=rare earth
- Jump rates at phase boundaries indicate complex diffusion mechanism in light rare earth tri-indides
- No defects observed in spectra

- Is it possible to observe direct evidence?

436 different binary compounds with $L1_2$ structure

Method of simulating PAC spectra

Stochastic model of Winkler and Gerdau:

$$G_2(t) = \sum_q G_q \exp\left[-(\lambda_q + i\omega_q)t\right]$$

where

$$G_q = \sum_{m_1 m_2 P} (-1)^{2I+m_1+m_2} \begin{pmatrix} I & I & k \\ m_1' & -m_1 & P \end{pmatrix} \begin{pmatrix} I & I & k \\ m_2' & -m_2 & P \end{pmatrix} \sum_{abr} p_a \langle bm_2 m_2' | N_q^r \rangle \langle M_q^r | am_1 m_1' \rangle$$

The $(\lambda_q + i\omega_q)$ and $|N_q\rangle$ are eigenvalues and eigenvectors of the Blume matrix

Z. Phys. 262, 363-376 (1973)

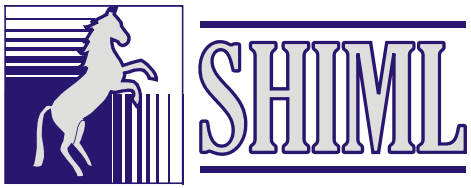
Method of simulating PAC spectra

Blume matrix $\hat{B} = -iH^{\times}_{st} / \hbar + \hat{R}$

Hamiltonians of all accessible EFGs

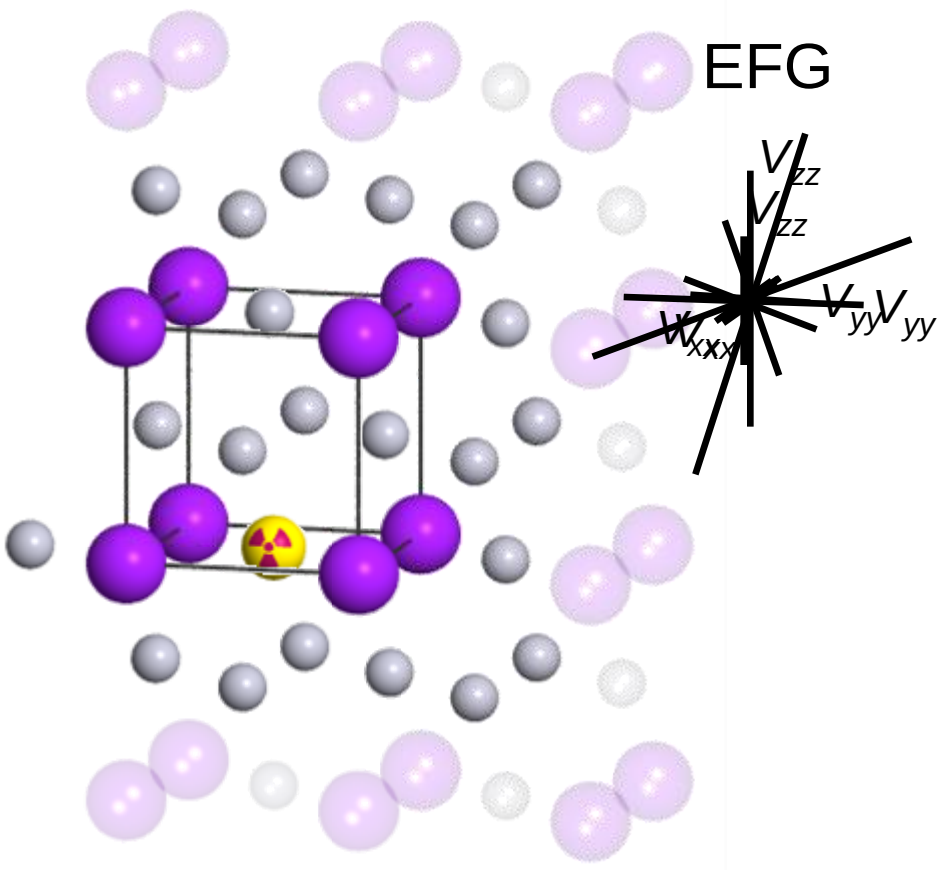
transition rates among EFGs

- Model completely specified by
  1. List of Hamiltonians for all accessible states
  2. Transition rates among the states
  3. Initial occupations of accessible states
- Use *Stochastic Hyperfine Interactions Modeling Library* (SHIML) to calculate spectra



Simple vacancy diffusion in $L1_2$ compounds

Review of the simple vacancy model*



15 different EFGs

4 transition rates

in the near-neighbor approximation

*Muhammed, Zacate, Evenson, *Hyperfine Interact.* **177**, 45 (2007)

Simple vacancy diffusion in $L1_2$ compounds

Review of the simple vacancy model*

transition rates

adjacent: $r_a = w_1$

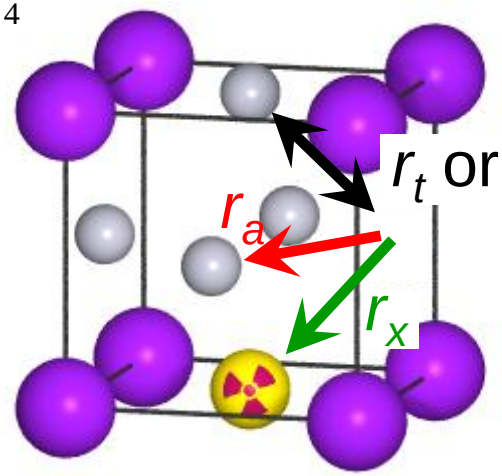
exchange: $r_x = w_2$

detrap: $r_d = 5[V]w_3$

trap: $r_t = 10[V]w_4$

[V] = vacancy concentration

w_1-w_4 are from the 5-frequency model



15 different EFGs

4 transition rates

r_x – exchange

r_a – adjacent

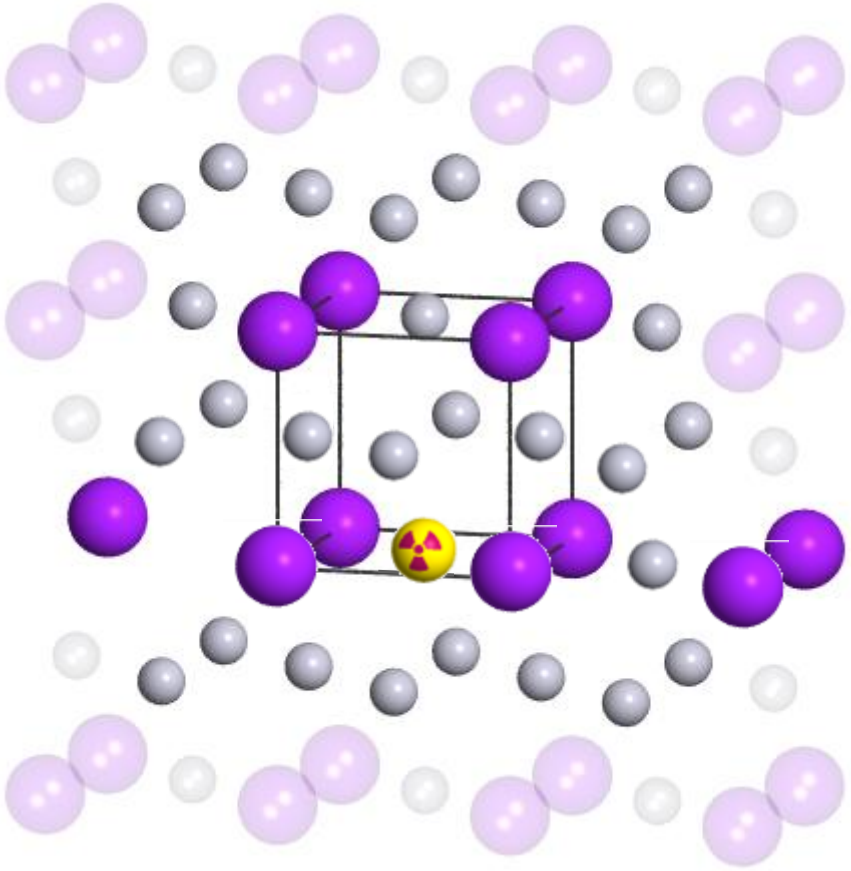
r_d – detrap

r_t – trap

*Muhammed, Zacate, Evenson, *Hyperfine Interact.* **177**, 45 (2007)

Complex Diffusion in $L1_2$ compounds

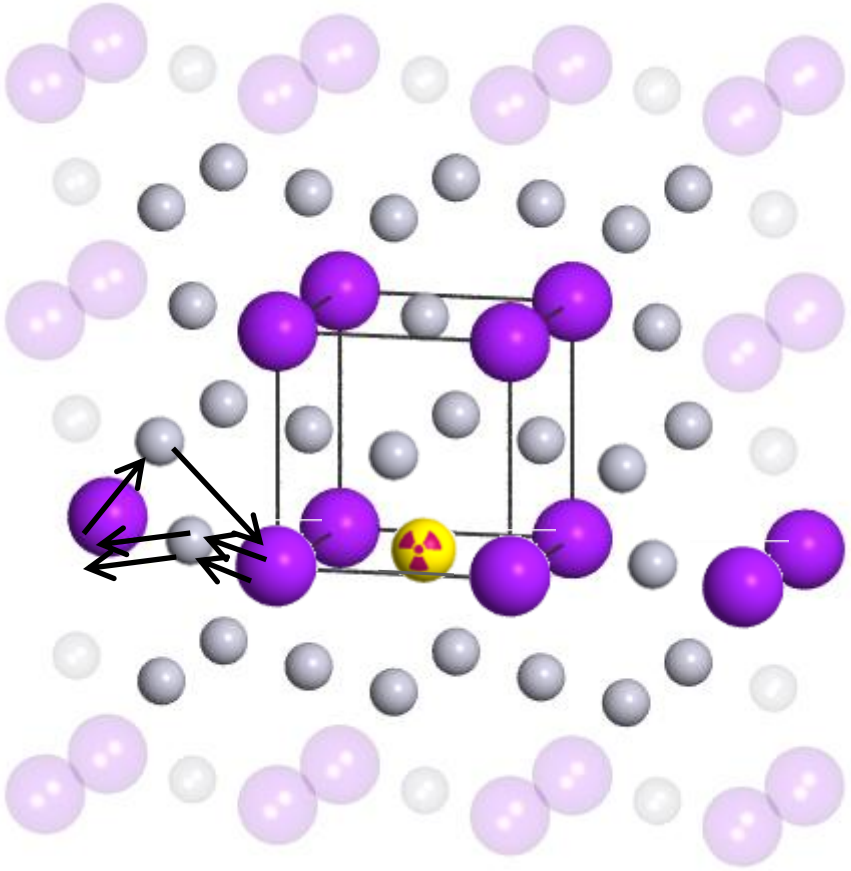
Divacancy in A_3B



45 EFGs in the near neighbor approximation

Simulating Simple Vacancy Diffusion in Cu_3Au-Structured Compounds…

6-jump cycle A_3B



588 EFGs (!)
in the near neighbor approximation

Deriving stochastic models linked to defect jump rates

Developed a nearly automated 3 step process

1. Determine all possible configurations of defects near the probe and atomic jumps among them
2. Determine unique EFGs to a cutoff distance from the probe and rates of transition
3. Correct rates for transitions out of defect-free EFGs

Deriving stochastic models linked to defect jump rates

- Step 1
  - Types of defect jumps identified and assigned rates $w_{k'}$
- Step 2
  - Determine unique EFGs: $k(q, j)$
  - Determine reorientation rate from EFG q to EFG r:

index of j^{th} degenerate configuration with EFG q

$$R_{rq} = \sum_{ij} p_k(q,j)\, W_{k'}(r,i \mid q,j)$$

0 or a rate $w_{k'}$

$$p_k(q,i) = P_k(q,i) / \sum_j P_k(q,j)$$

probabilities of defect configurations, *i.e.* defect concentrations

Deriving stochastic models linked to defect jump rates

- Step 2
  - Determine unique EFGs: $k(q, j)$

index of j^{th} degenerate configuration with EFG q

  - Determine reorientation rate from EFG q to EFG r:

$$R_{rq} = \sum_{ij} p_k(q,j)\, W_k(r,i \mid q,j)$$

$p_k(q,j)$

$W_k(r,i \mid q,j)$ = 0 or a rate $w_{k'}$

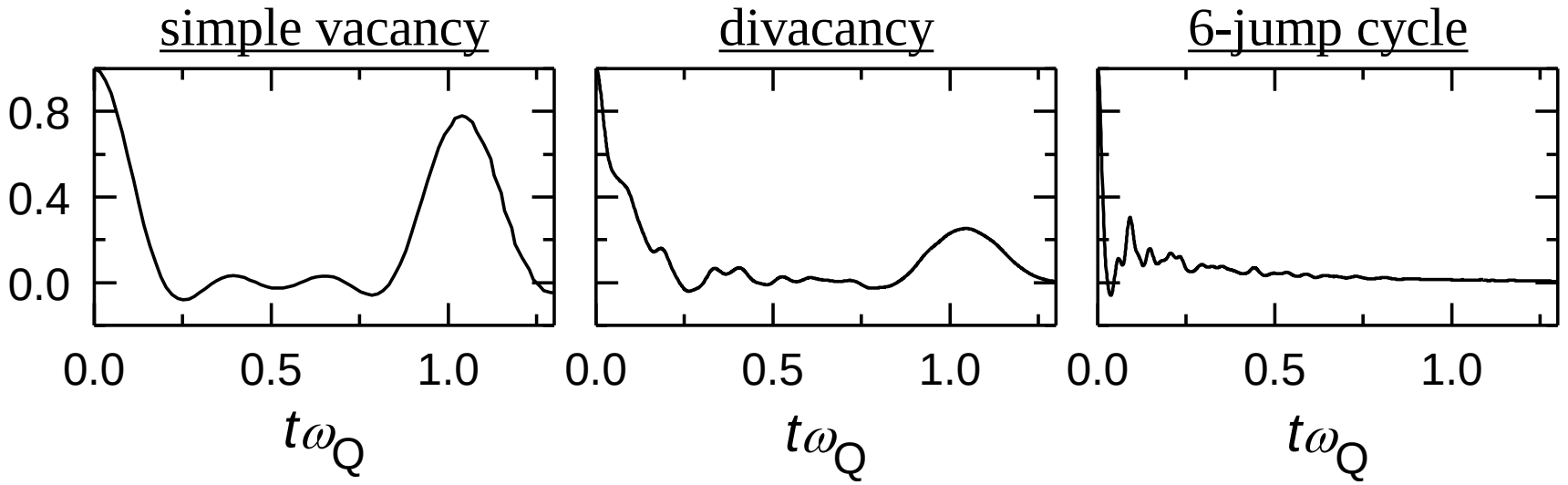
$$p_k(q,i) = P_k(q,i) / \sum_j P_k(q,j)$$

- Step 3
  - For q indexing a defect free EFG, $\sum_j P_k(q,j) \to \infty$ so that $R_{rq} = N_{rq}$ defect w

number of jump paths

a rate $w_{k'}$

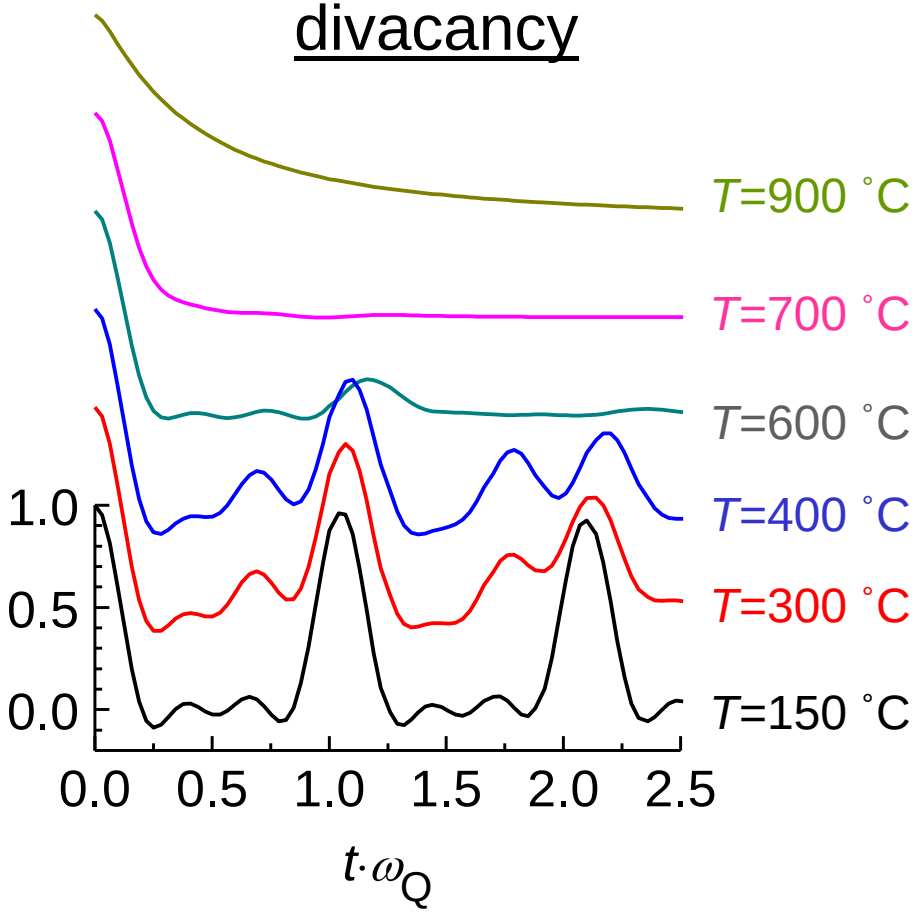
Comparison of diffusion models in $L1_2$



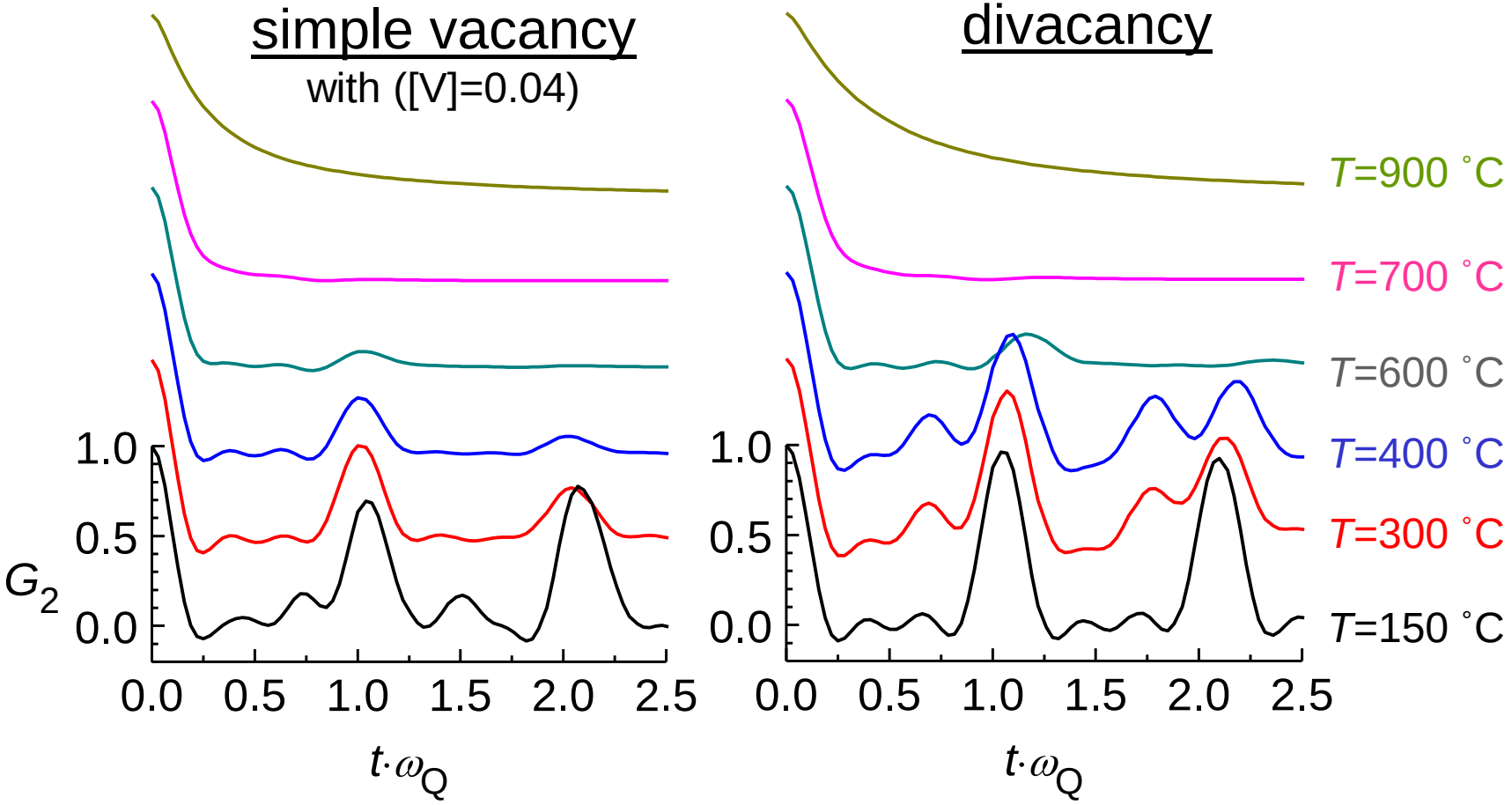
- Defect charges chosen so that contribution of each defect to the EFG is $5.66|V_0|$ where $|V_0|$ is the strength of the lattice EFG.
- All jump rates = ω_Q
- All [defect] = 0.01

Comparison of diffusion models – part 2

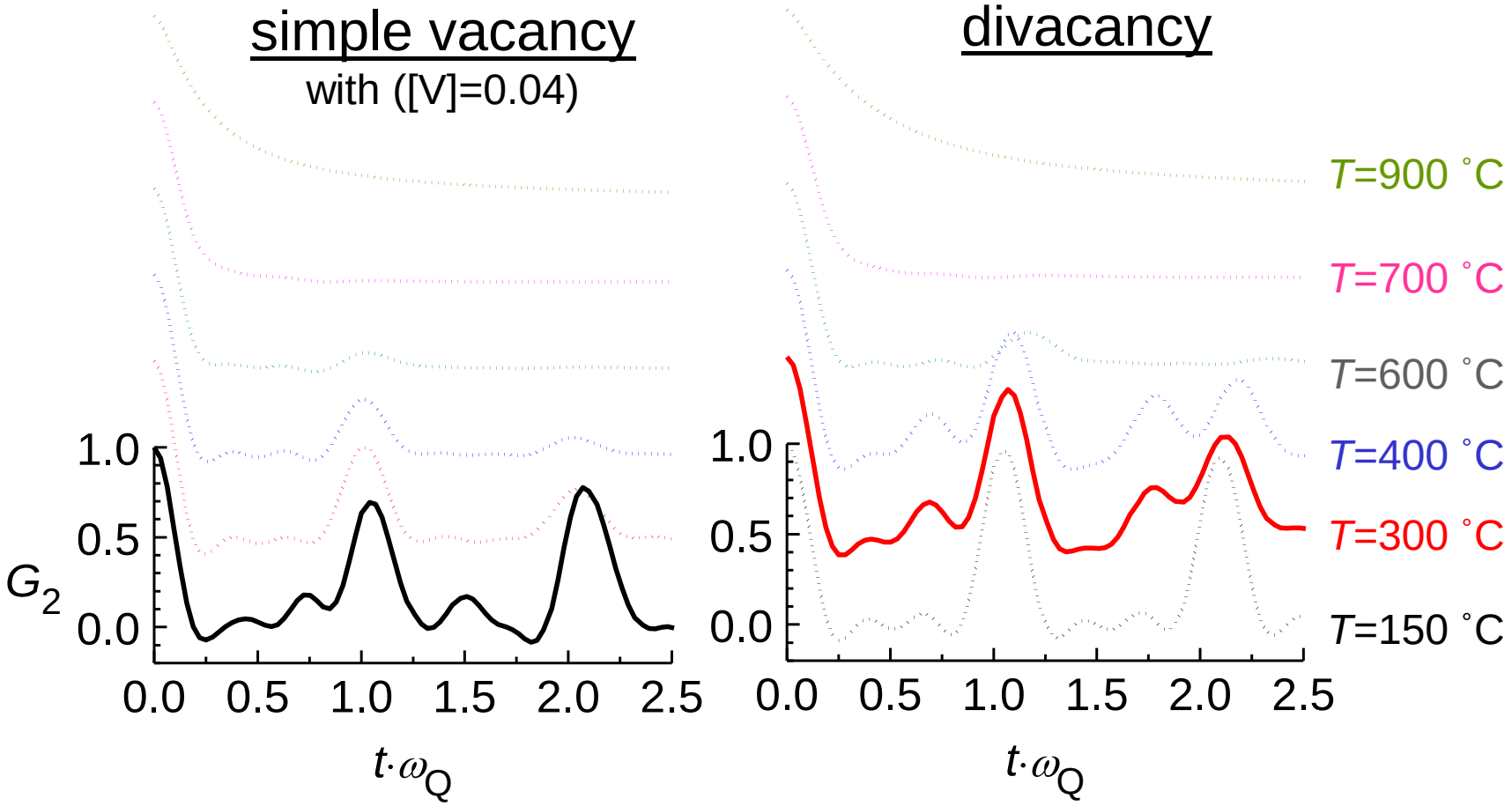
- point charge parameters for $LaIn_3$
- thermal vacancies with
  [V] = exp(1.4) exp(-(0.36 eV)/k_BT)
- vacancy jump rates:
  $w_A = 1.3 \cdot 10^5 \omega_Q$ exp(-(0.4 eV)/k_BT)
  $w_B = 1.3 \cdot 10^5 \omega_Q$ exp(-(0.5 eV)/k_BT)



Comparison of diffusion models – part 2



Comparison of diffusion models – part 2



Summary: Modeling Complex Diffusion Mechanisms…

1. Developed a 3 step process to develop a stochastic model of fluctuating hyperfine interactions for diffusion mechanisms – applicable to any structure
2. Demonstrated that simulations of PAC spectra for simple vacancy, divacancy, and 6-jump cycle diffusion mechanisms can look different
3. Showed for a physically reasonable set of parameters that one can obtain a signal due to defects in the divacancy mechanism

Work continues to determine conditions under which one can unambiguously identify diffusion mechanisms