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Diffusion in Intermetallic Compounds Studied Using Short-Lived Radioisotopes

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Diffusion

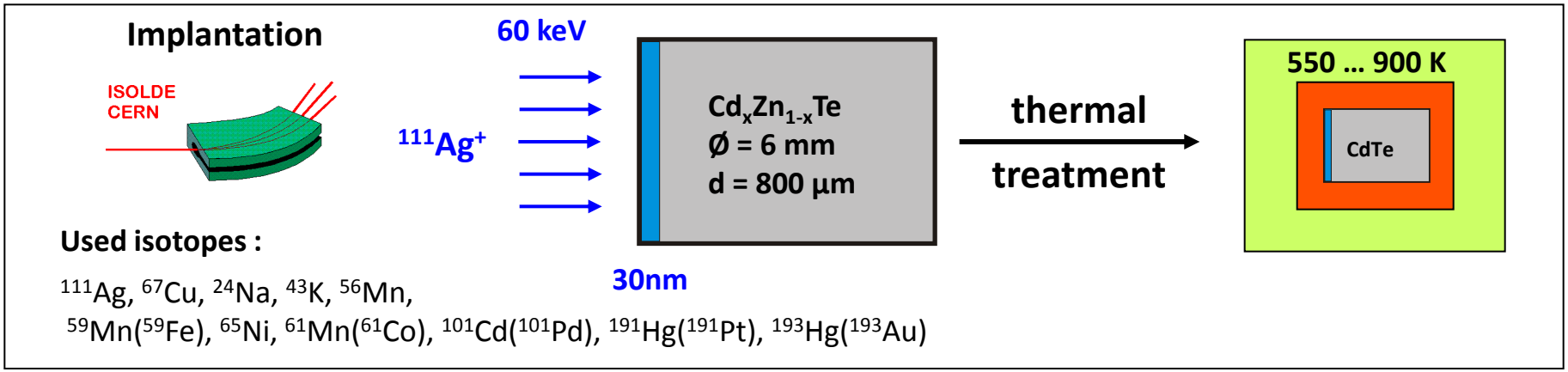
Study of diffusion important for the understanding and controlling of impurities in materials

- Control of useful/problematical impurities
- Activation energies
- Study of fundamental diffusion properties.

Already considerable programme of diffusion studies underway at ISOLDE: IS489.

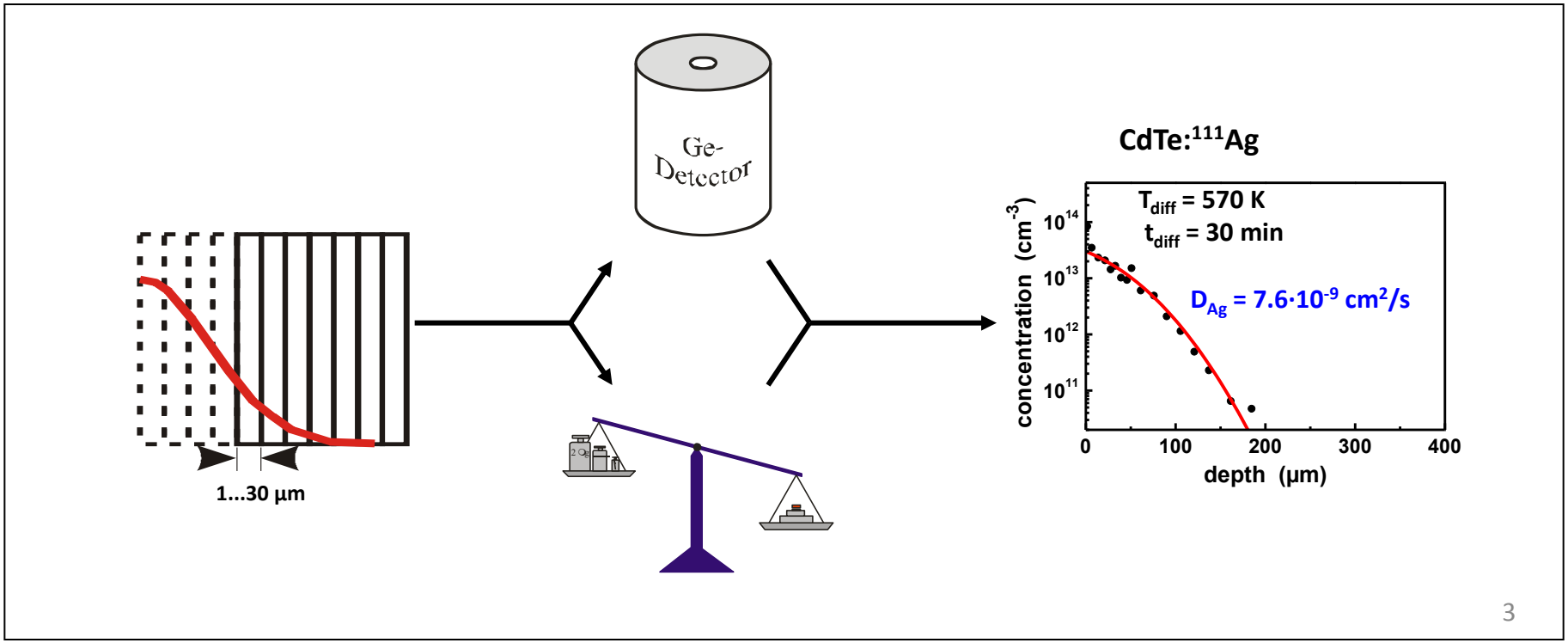
Use of radiotracers using short and long-lived isotopes.

Radiotracer Technique (IS489)



Used isotopes :

^{111}Ag, ^{67}Cu, ^{24}Na, ^{43}K, ^{56}Mn,
^{59}Mn(^{59}Fe), ^{65}Ni, ^{61}Mn(^{61}Co), ^{101}Cd(^{101}Pd), ^{191}Hg(^{191}Pt), ^{193}Hg(^{193}Au)



What's different about this work

Use of PAC (perturbed angular correlation) to examine the atomic nature of diffusion processes.

PAC very versatile technique (as evidenced by other proposals in this session)….but not usually used to study diffusion.

Study of intermetallic compounds:

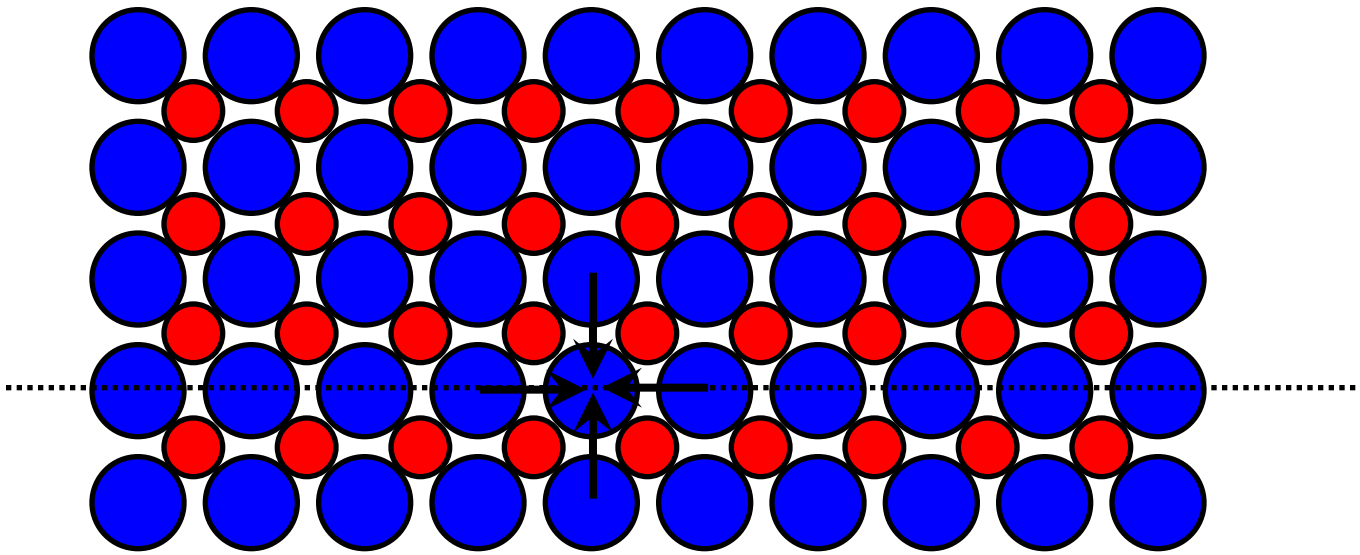
- $L1_2$ compounds: RIn_3, RGa_3, RSn_3
- Gd_3P_7

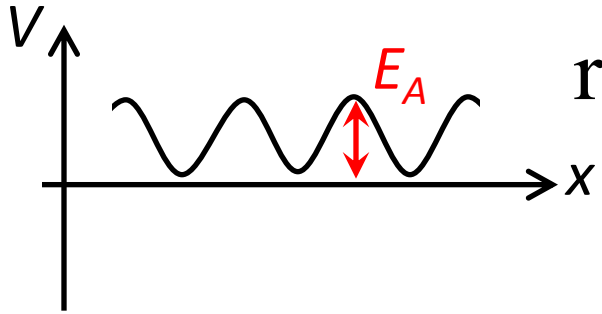
Examine on a local scale some of the unusual diffusion behaviour associated with these compounds.

Tests last year during the Ag beamtime were encouraging.

Diffusion in solids

example: simple vacancy diffusion



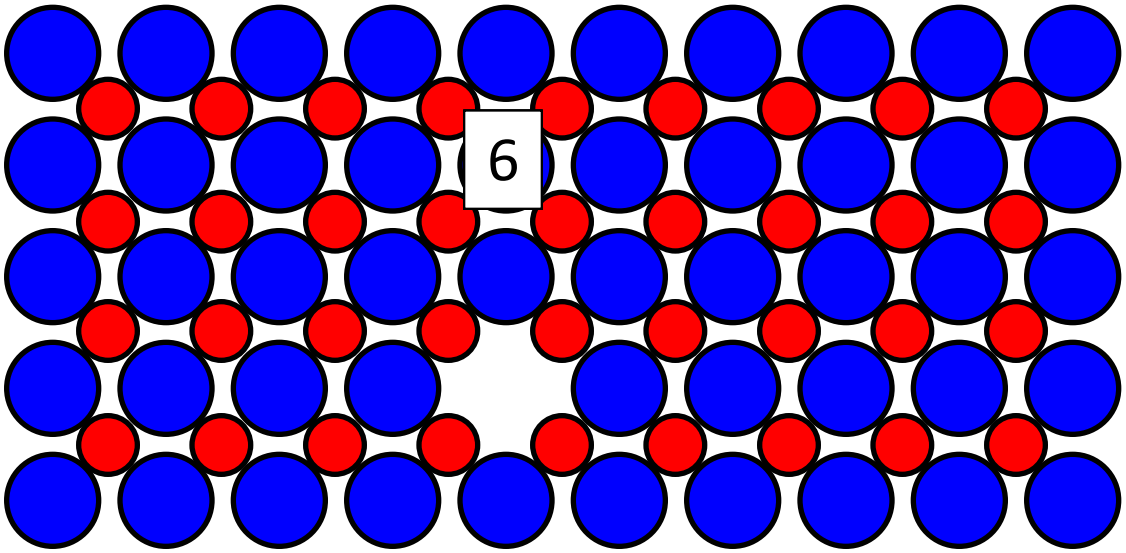


$$\text{rate} \propto \exp\left(-E_A / k_B T\right)$$

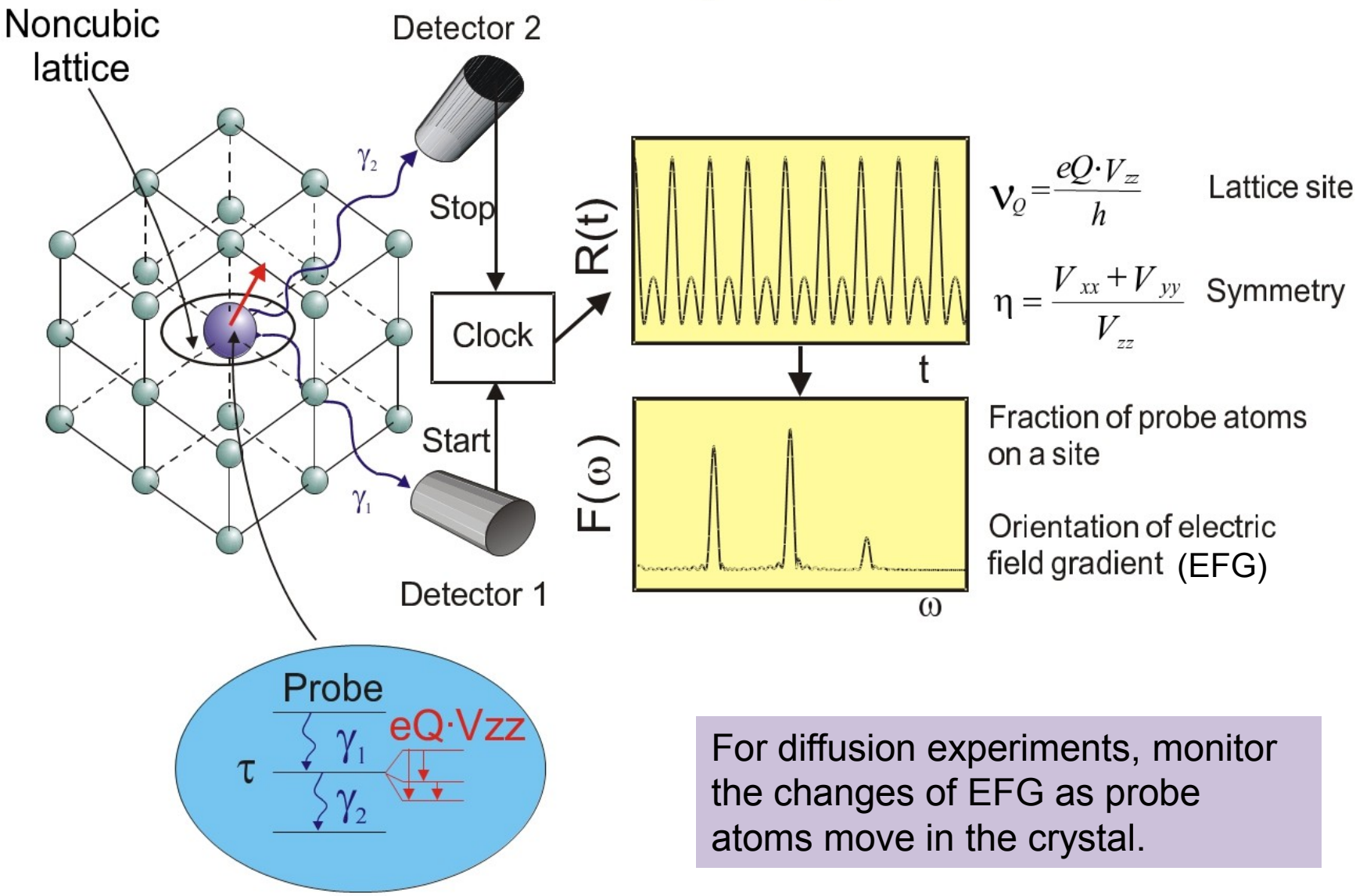
Diffusion in intermetallic compounds

Only first-neighbor jumps allowed (?)

example: 6-jump cycle



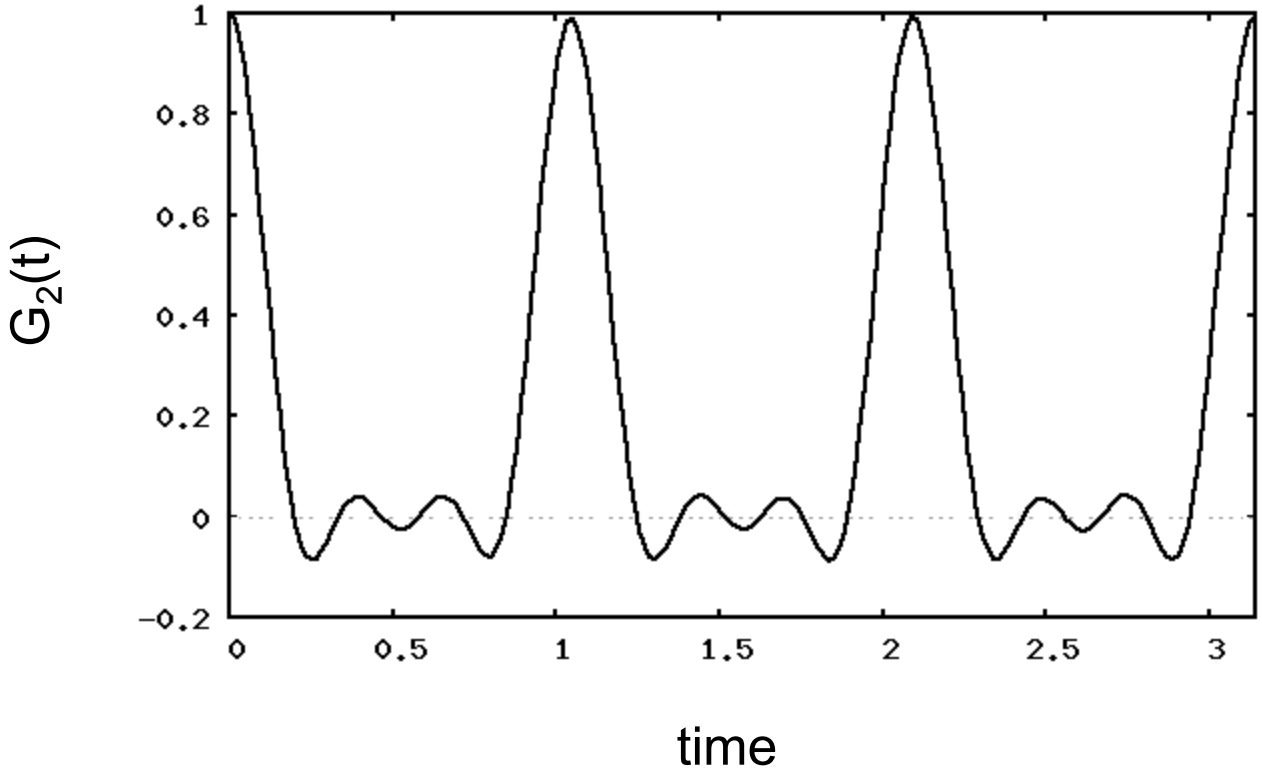
Perturbed γγ Angular Correlation (PAC)



For diffusion experiments, monitor the changes of EFG as probe atoms move in the crystal.

Observing diffusion by PAC: Reorientation of EFG tensor

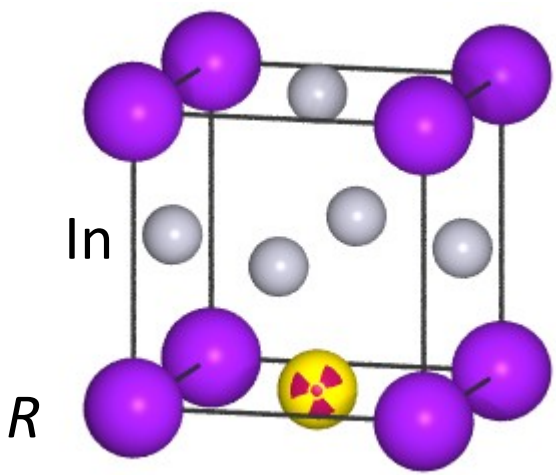
Heating increases jump frequency...

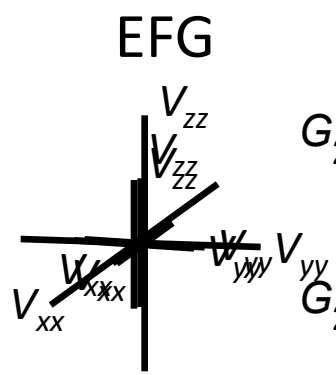


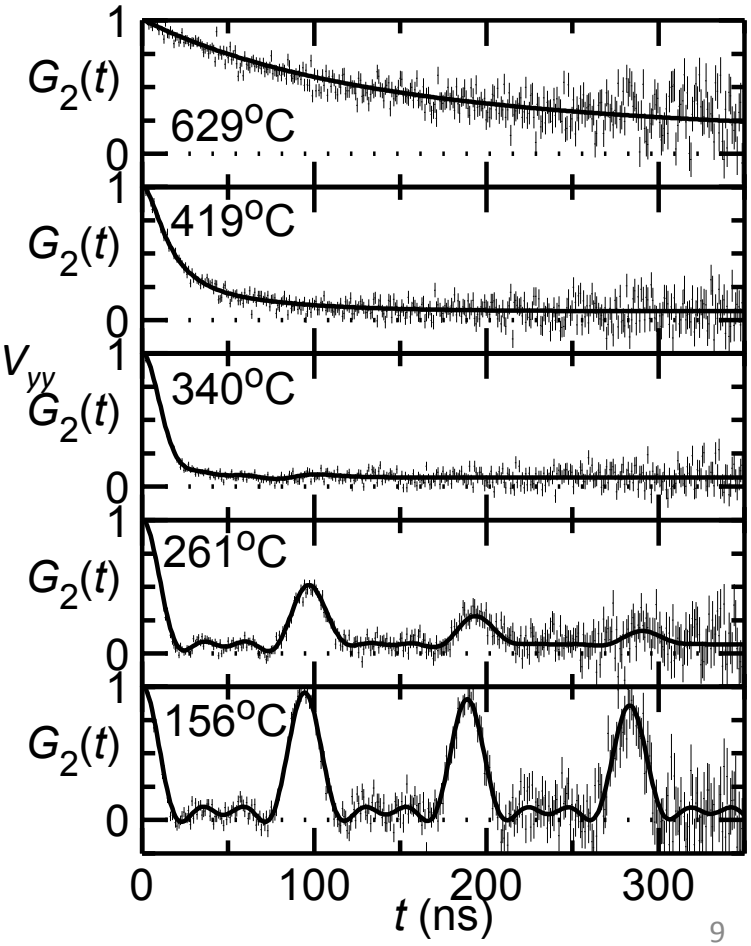
...first increases, then reduces relaxation.

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
- $L1_2$ 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*

- RIn$_3$, RGa$_3$, RSn$_3$ 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$_3$ **divacancy or 6-jump mechanism**	LuIn$_3$, TmIn$_3$, ErIn$_3$, HoIn$_3$, DyIn$_3$, TbIn$_3$, GdIn$_3$ LaSn$_3$, CeSn$_3$, SmSn$_3$, GdSn$_3$

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

- Possible explanation: constitutional defects differ in light and heavy R compounds

Light R	Heavy R
V_R and R_{In}	V_{In} and In_R

Aim of proposed experiments is to detect which defects are present across the $R\mathrm{In}_3$ series using ^{111m}Cd

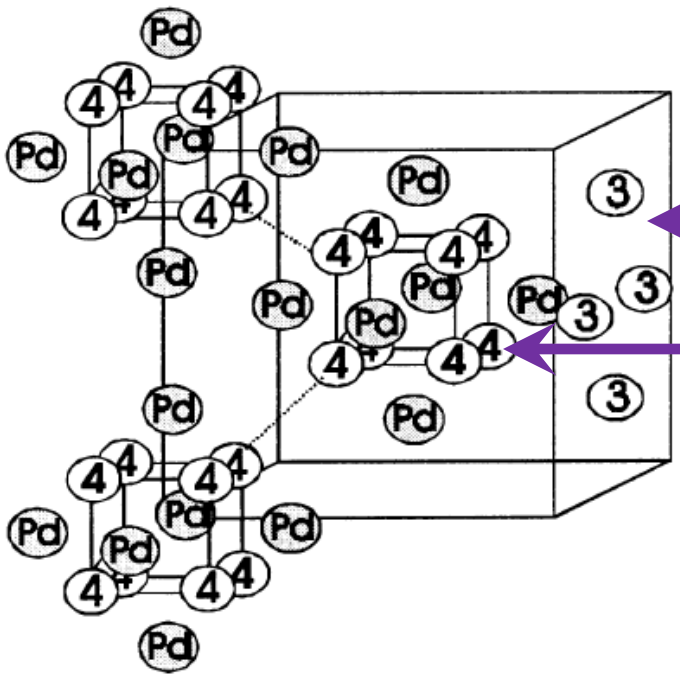
PAC measurements of Cd jump rates in $L1_2$ structured compounds*

Why ^{111m}Cd?

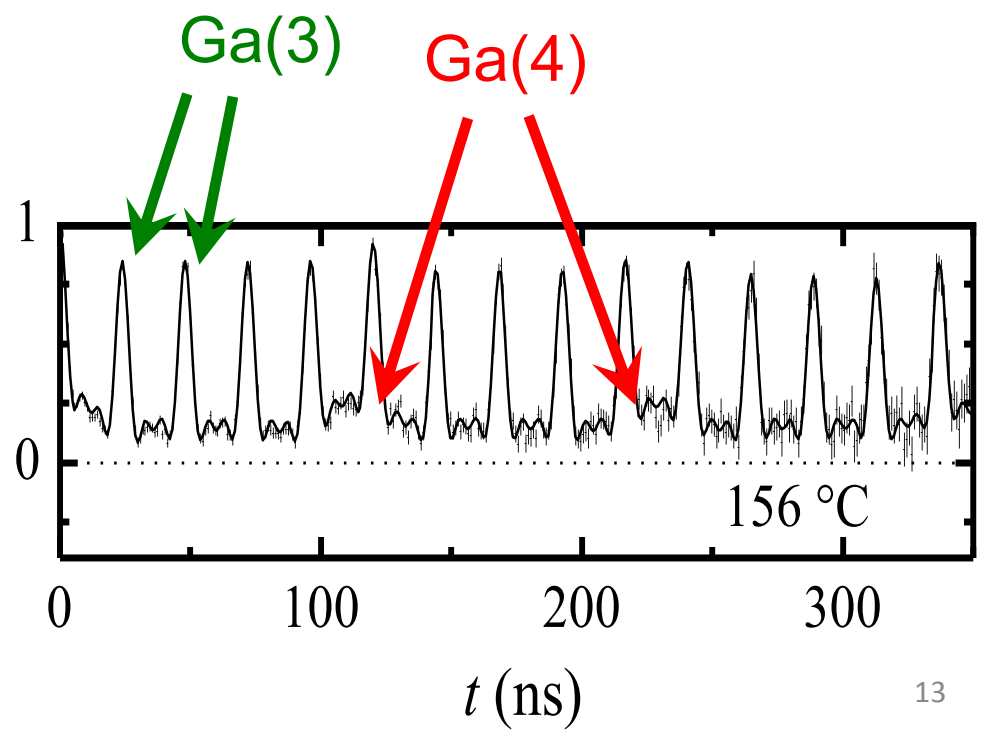
- Too few defects to be observed using ^{111}In
- ^{111m}Cd is an **impurity** so that association between defects and Cd could enhance site fractions enough to determine defect configurations

Aim of proposed experiments is to detect which defects are present across the RIn$_3$ series using ^{111m}Cd

Ga_7Pd_3



- One Pd site
- Two inequivalent Ga sites (3 & 4)

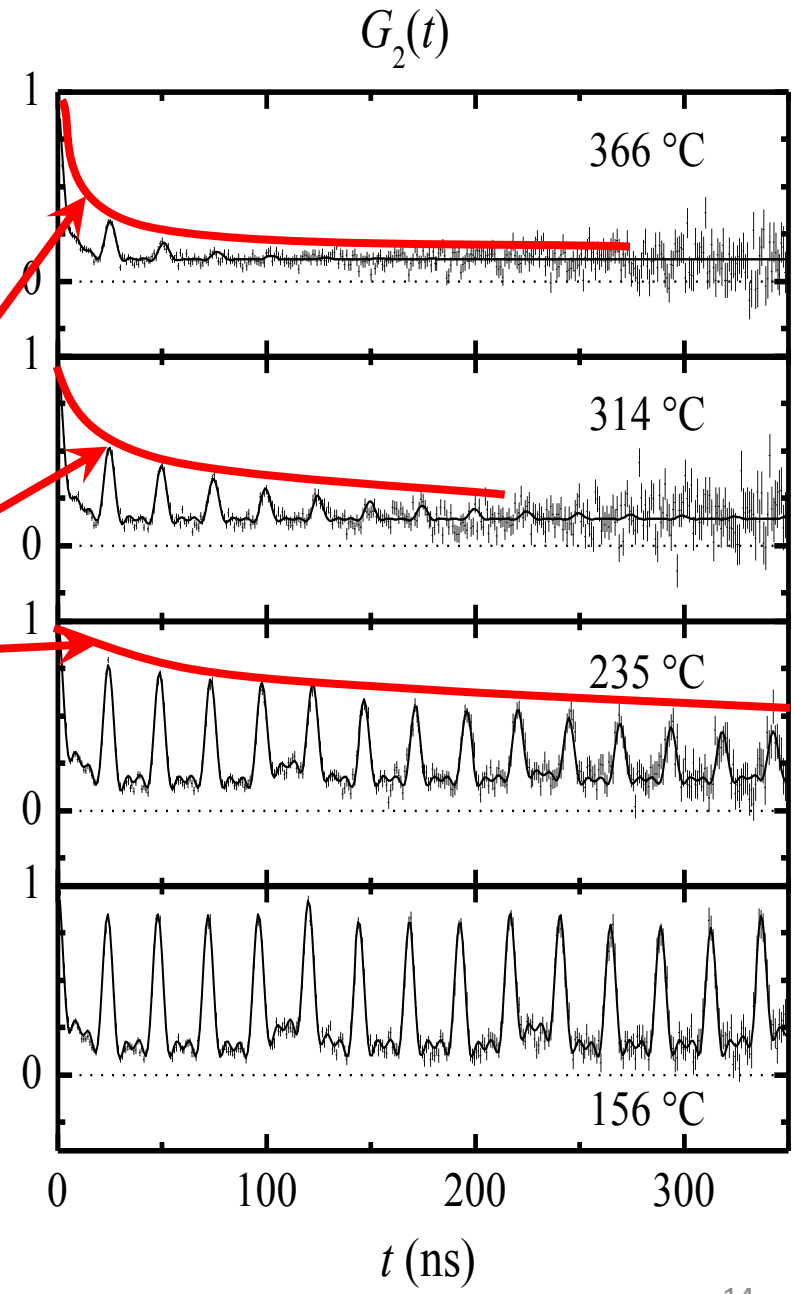


^{111}In/Cd in Ga_7Pd_3

- In/Cd only on Ga sites
- No defects observed

^{111}In/Cd in Pd_3Ga_7 (high temperature)

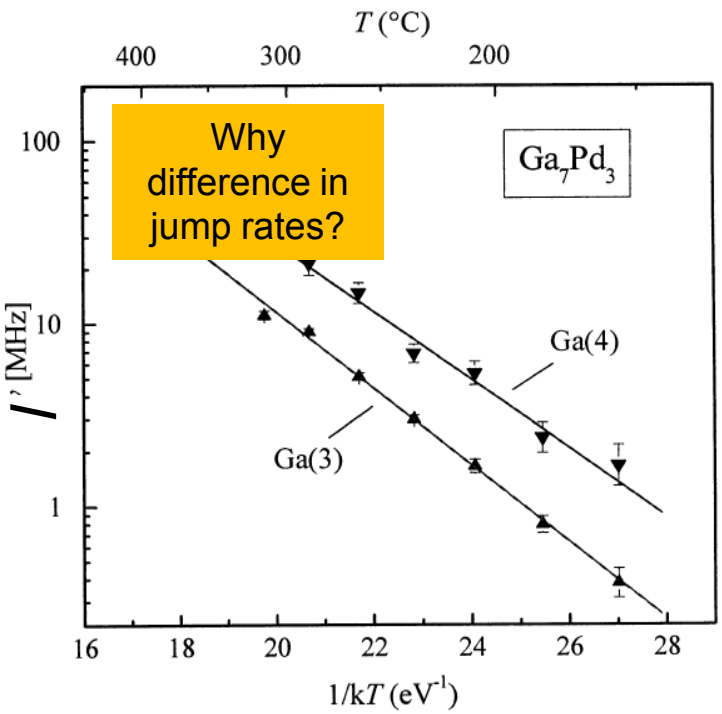
Damping of signal is due to loss in coherence among spin states as tracers jump



Diffusion and Defect Data **264**, 27-32 (2007)

Cd jump rates in Ga_7Pd_3 – empirical analysis

$$G_2(t) \cong \exp(-\lambda t) G_{2,\text{static}}(t)$$



Why difference in jump rates?

$$\lambda \propto \tau^{-1}$$

Diffusion and Defect Data **264**, 27-32 (2007)

Stochastic Model

Seven distinct EFGs

- Three EFGs for Ga(3) site parameterized by quadrupole interaction frequency $w_Q(3)$
- Four EFGs for Ga(4) site parameterized by quadrupole interaction frequency $w_Q(4)$

Four EFG transition rates: $r_{3\to3}$, $r_{4\to4}$, $r_{3\to4}$, and $r_{4\to3}$

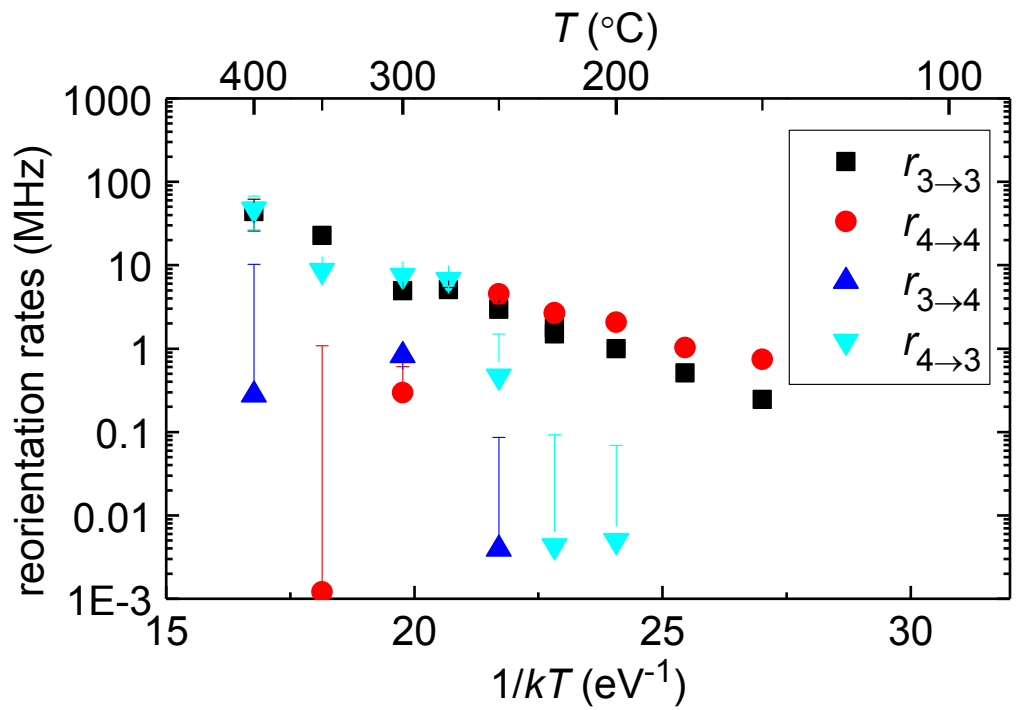
Initial fraction of probes on Ga(3) sites: f_3

Spectra calculated using SHIML (*Comput. Phys. Commun.* **182**, 1061 (2011)) following the method of Winkler and Gerdau (*Z. Phys.* **262**, 363 (1973))

Cd jump rates in Ga_7Pd_3

- Scatter in the fits using stochastic model.

- Need to understand this better; Could perform DFT calculations, but experimental solution is more direct



- Proposal: repeat experiments using the ^{111m}Cd probe and analyze using the stochastic model.

- Use of ^{111m}Cd allows elimination of f_3 in the model because of the principle of detailed balance:

$$f_3 \cdot 4r_{3\to4} = \left(1 - f_3\right) \cdot 3r_{4\to3}$$

- This offers a unique opportunity to measure separately inter- and intra-sublattice jump rates.

Beam request

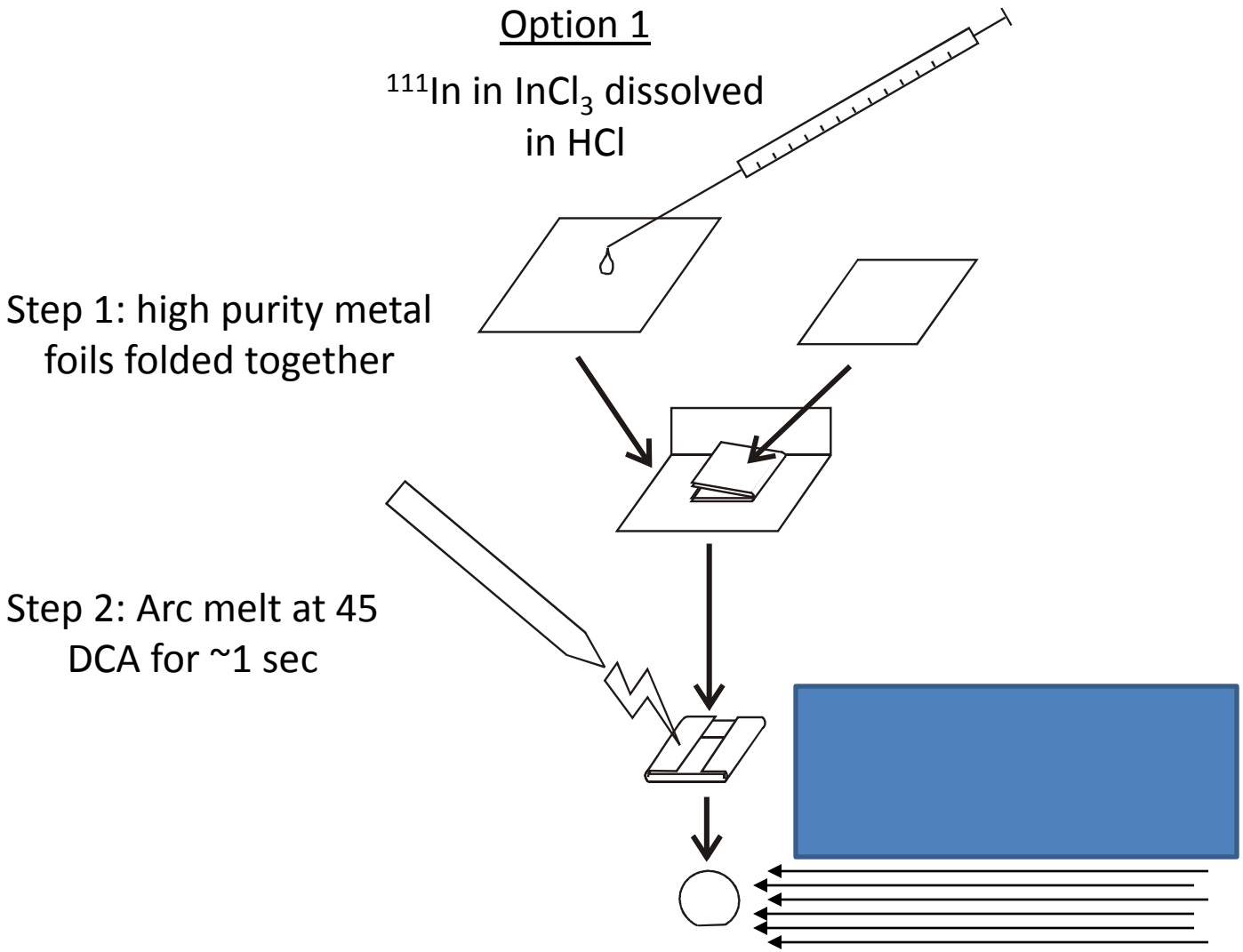
Isotope	$T_{1/2}$	Target	Yield (ions/μC)	Ion source	Shipping?
^{111m}Cd	48 min	Sn	2×10^8	HP (VADIS)	No

- 10 shifts split over 2-3 years.
- Collections of ~ 15 mins allow many experiments to be performed over 3-4 day beamtime.
- Easy to accommodate other groups.

Work involved:

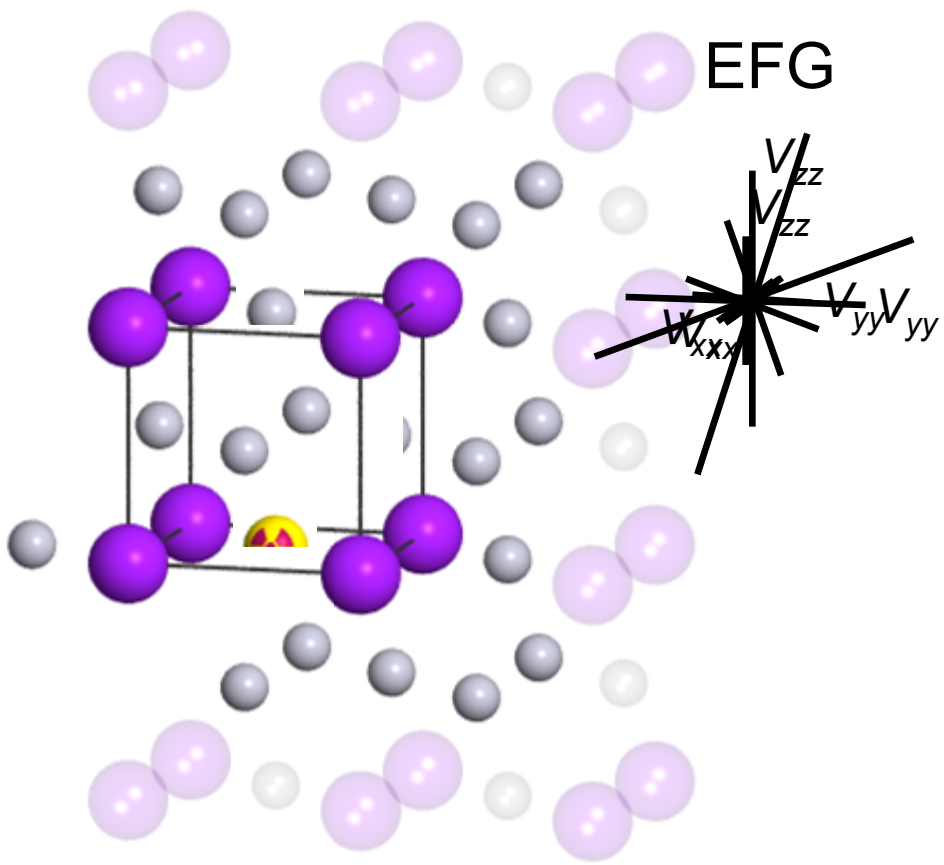
- Need to determine "good" annealing temperatures for the compounds following implantation.
- Ga_7Pd_3 more focused, priority for 2011.
- Large variety of $L1_2$ compounds to be examined, great flexibility.

Sample preparation



Simple vacancy diffusion in $L1_2$ compounds

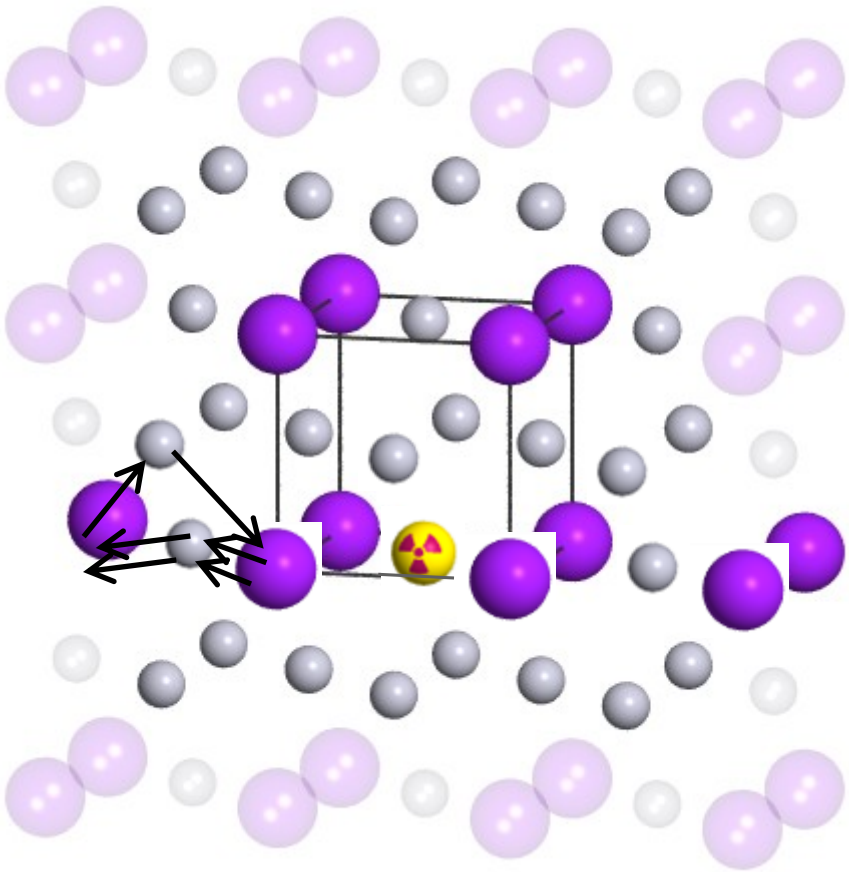
Simple vacancy jumps in $L1_2$



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

Simulating Simple Vacancy Diffusion in $L1_2$-Structured Compounds…

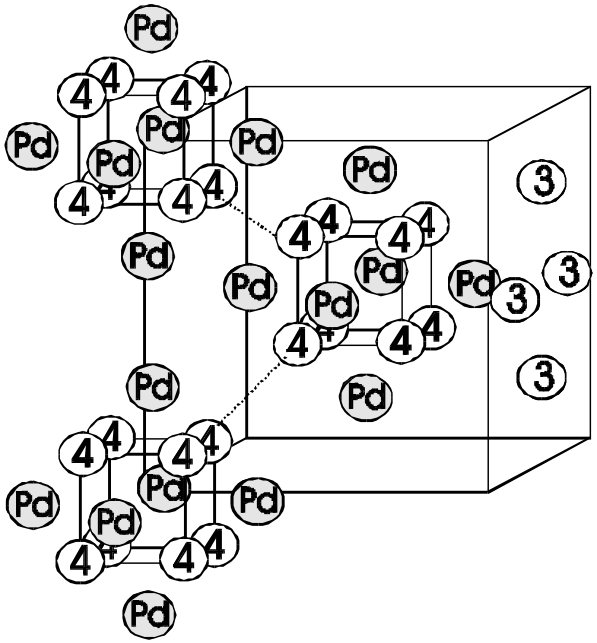
6-jump cycle $L1_2$

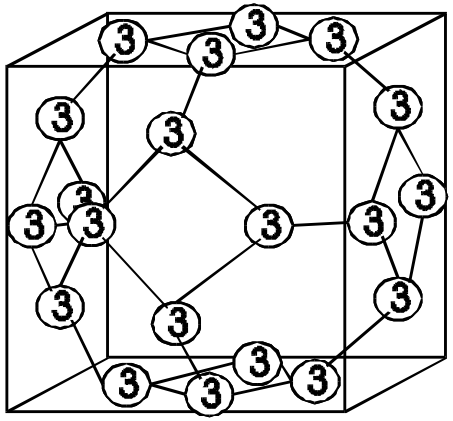


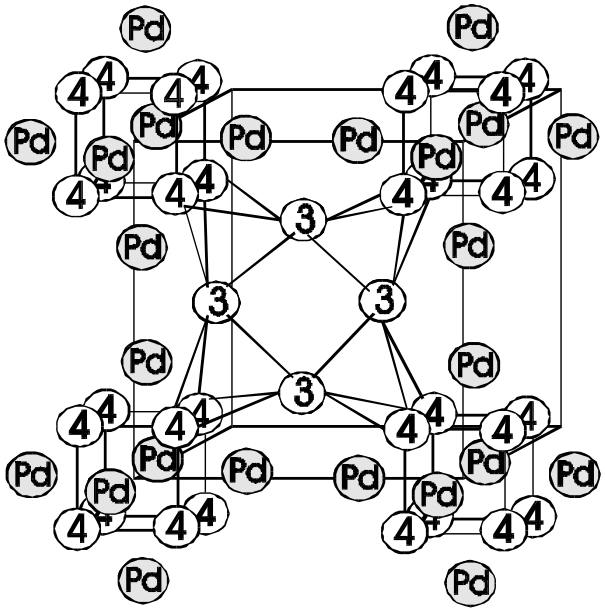
Ga sites in Ga_7Pd_3

Tracer jumps that lead to a change in EFG:

Ga(4) → Ga(4) Ga(3) → Ga(3) Ga(3) ↔ Ga(4)







Jump distances: Ga(4)-Ga(4): 0.280 nm (×3) and 0.273 nm

Ga(3)-Ga(3): 0.310 nm (×4)

Ga(3)-Ga(4): 0.338 nm (×4)