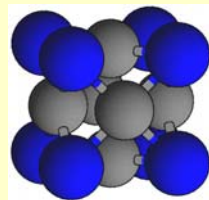


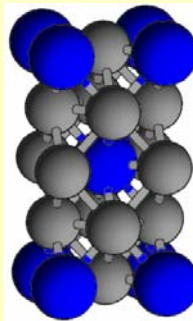
# Site preferences of indium impurity atoms in intermetallics having $Al_3Ti$ and $Al_3Zr$ crystal structures

John P. Bevington, Farida Selim and Gary S. Collins

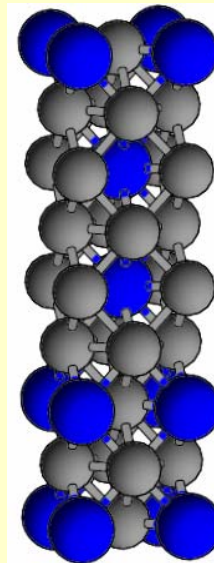
Department of Physics, Washington State University, Pullman, WA, USA



$L1_2$   
 $Cu_3Au$



$DO_{22}$   
 $Al_3Ti$



$DO_{23}$   
 $Al_3Zr$

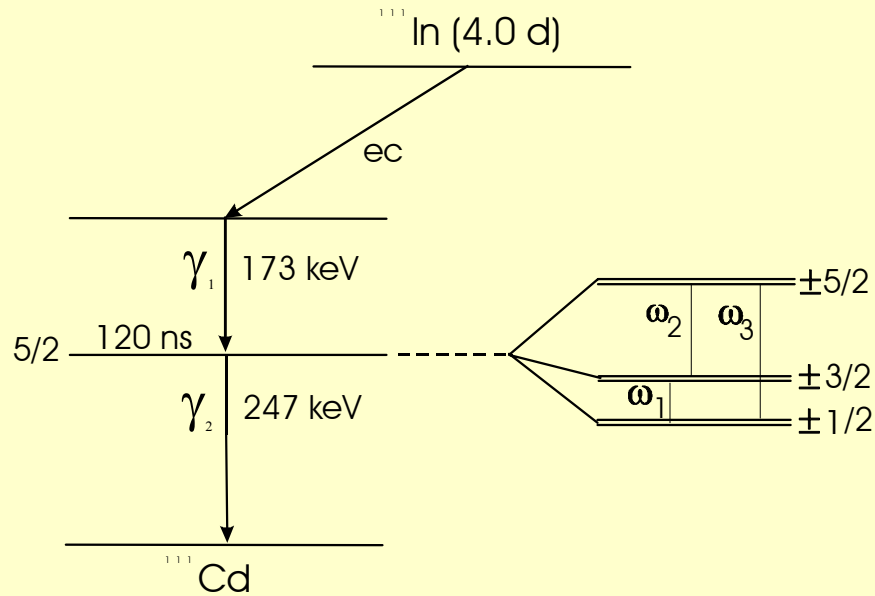


Supported in part by the National Science Foundation under grant DMR 05-04843 (Metals Program) and Praveen Sinha Fund for Physics Research.

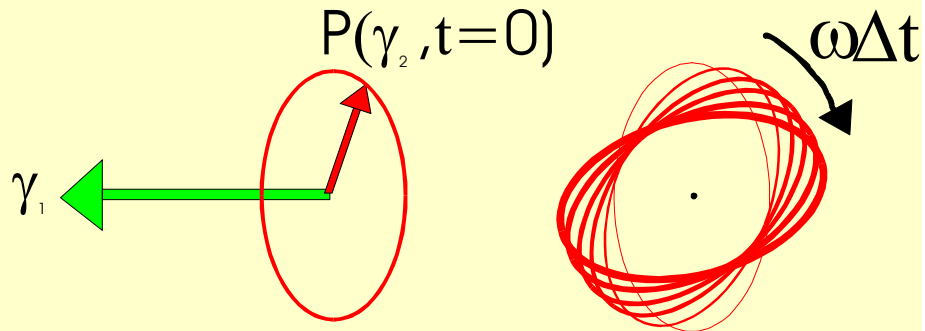
## Outline

- Indium was doped in samples of  $\text{Al}_3\text{V}$  and  $\text{Al}_3\text{Ti}$  ( $\text{Al}_3\text{Ti}$  structure) and  $\text{Al}_3\text{Zr}$  ( $\text{Al}_3\text{Zr}$  structure) by arc-melting; doping at 10 ppb level.
- Inequivalent Al-sites occupied by indium solutes were identified by measuring nuclear quadrupole interactions using PAC.
- Differences between vibrational entropies and enthalpies of solutes at different sites are obtained from temperature dependences of ratios of site fractions.
- Enthalpy differences appear to be explained by volume mismatch between transition-metal and aluminum atoms.

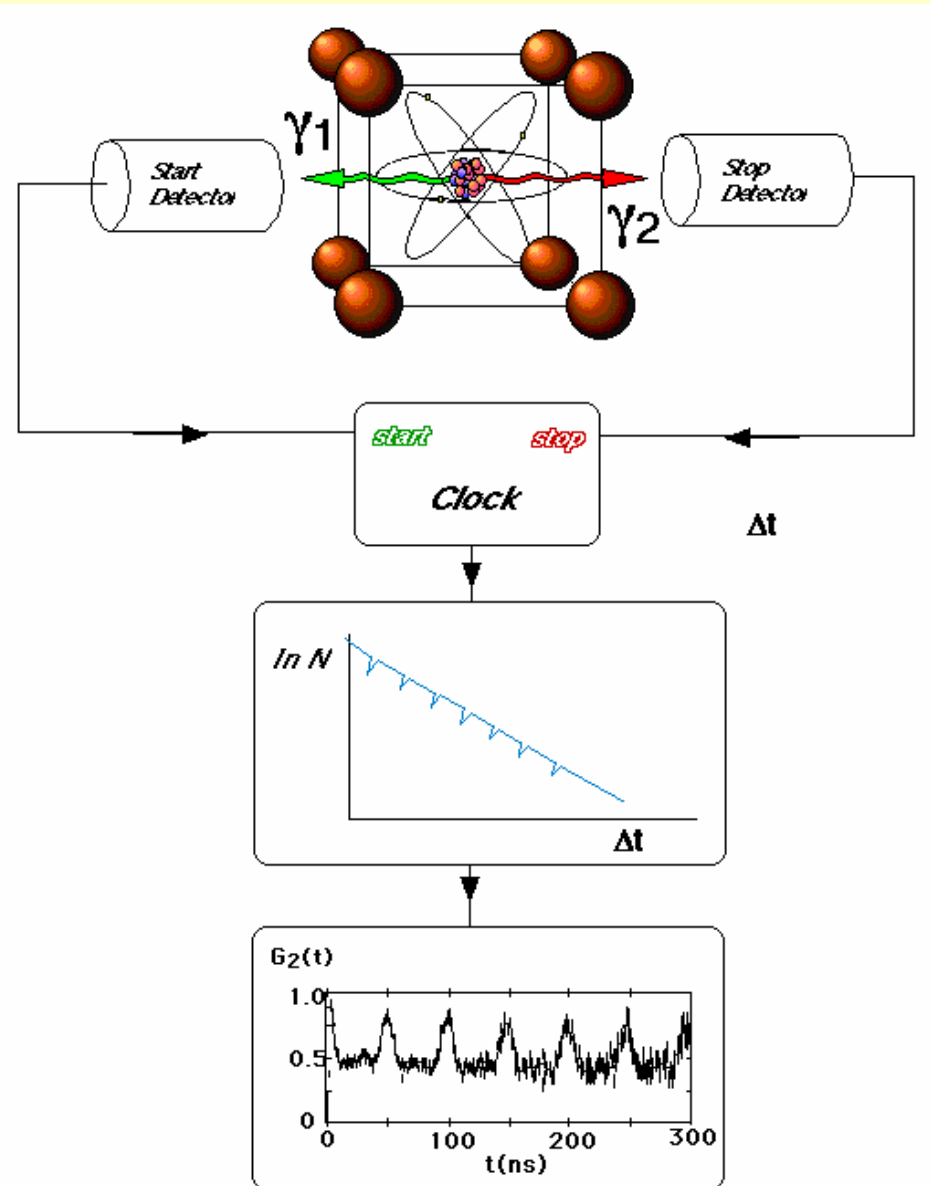
# Perturbed angular correlation of gamma rays (PAC)



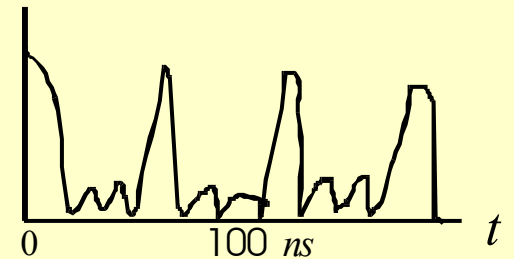
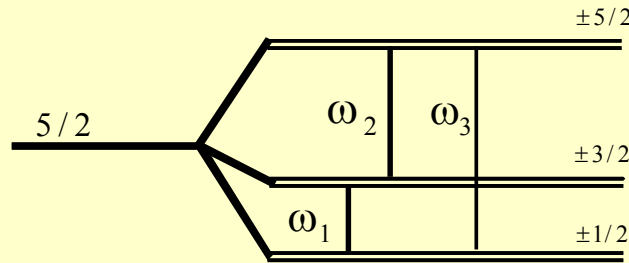
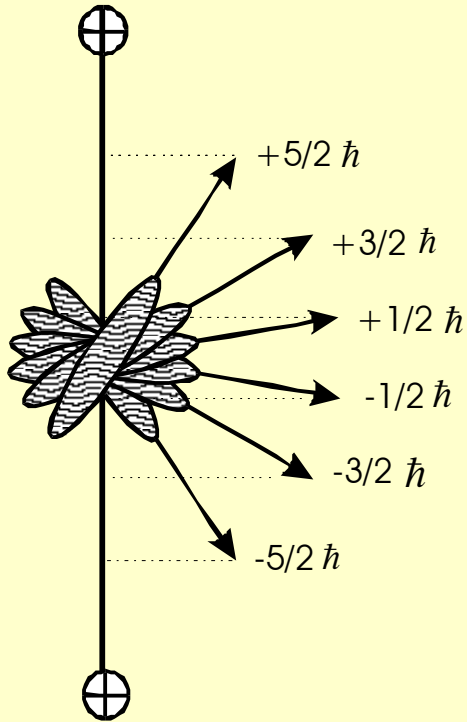
Long-lived intermediate state



Anisotropy in emission of 2<sup>nd</sup>  $\gamma$ -ray



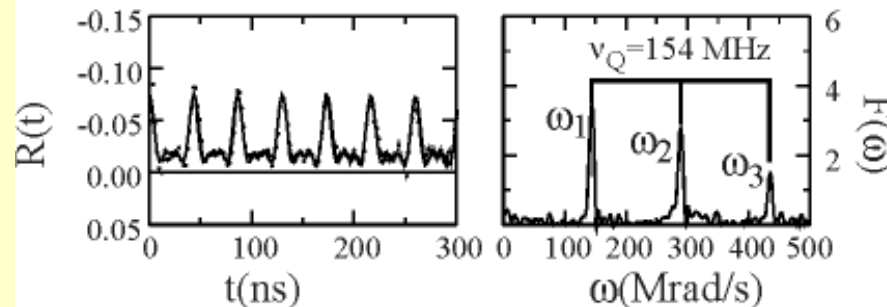
# Quadrupole interaction in PAC (spin 5/2)



Spin precessions detected in time domain

Static PAC perturbation function for axial symmetry

$$G_2(t) = \frac{1}{5} + \frac{13}{35} \cos \omega_0 t + \frac{10}{35} \cos 2\omega_0 t + \frac{5}{35} \cos 3\omega_0 t$$



**13:10:5**  
ratio of  
amplitudes  
applies for  
random  
polycrystal  
line texture

$\omega_0=0$  for cubic symmetry

Spin 5/2 nucleus,  
US football shape, in  
electric field gradient

# Related previous work: Indium in $\text{Al}_2\text{Gd}$

Laves phase: C15 ( $\text{Cu}_2\text{Mg}$ ), cubic, 2 sites

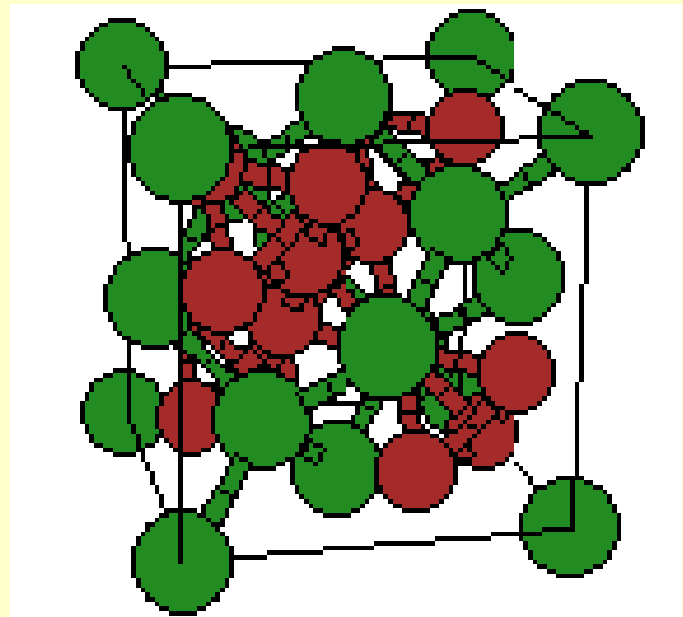
Gd-site (green): cubic point symmetry ( $\omega = 0$ )

Al-site (brown): three-fold symmetry ( $\omega \neq 0$ )

A model system:

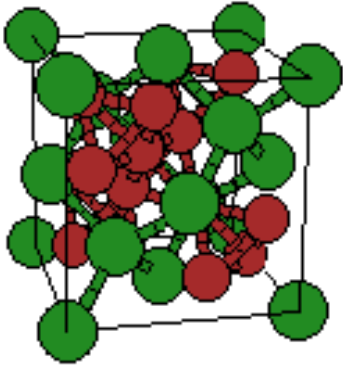
Al, In, Gd are all trivalent

$V(\text{Al}) < V(\text{In}) < V(\text{Gd})$



Easy to identify signals with sites...

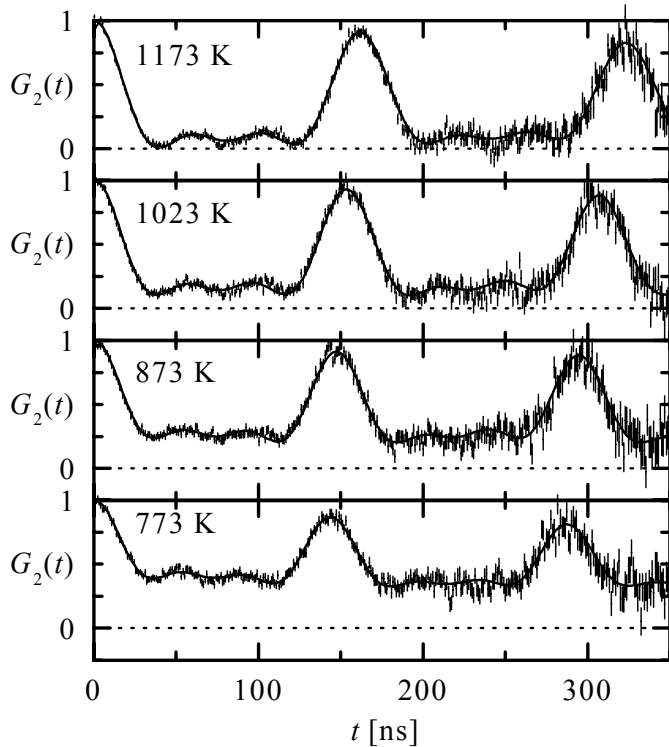
*So, where does indium go??*



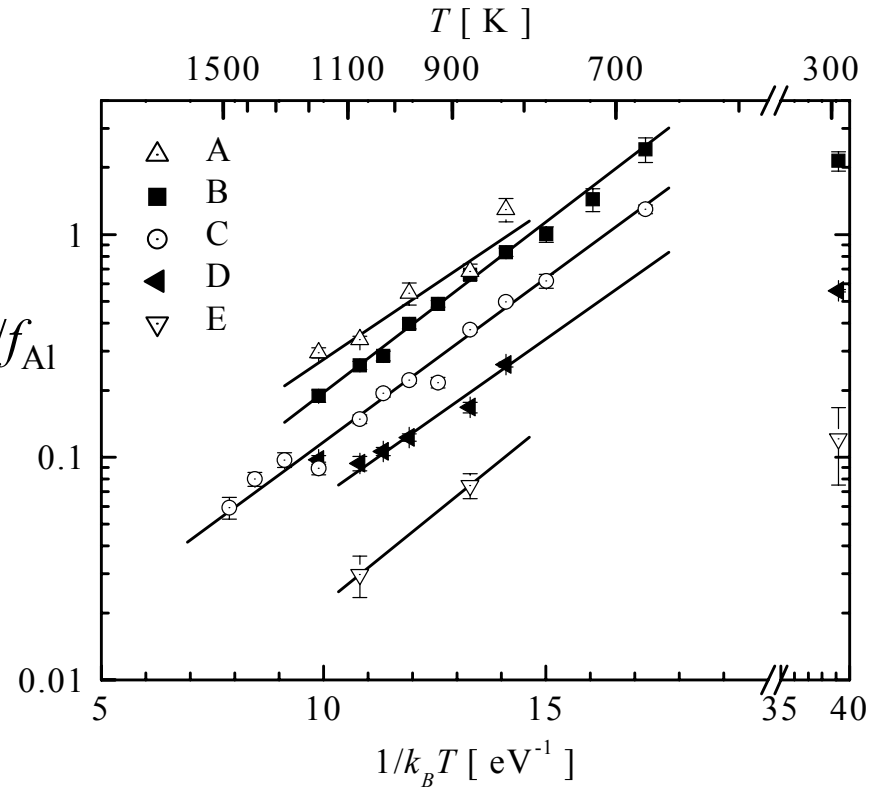
Indium goes to either site, depending on composition and temperature !

1. Five samples: A (more-Al-rich) ..to.. E (less Al-rich)
2. Different temperatures

Sample B

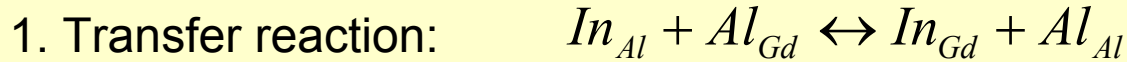


$$f_{\text{Gd}}/f_{\text{Al}}$$



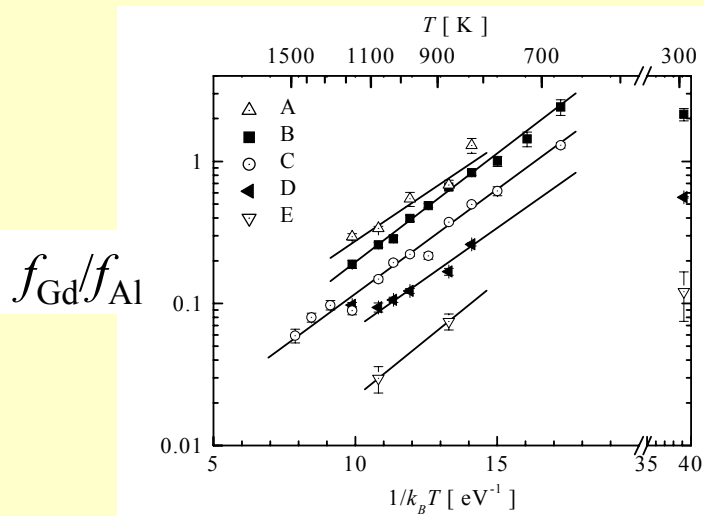
***Thermally activated:  
Transfer enthalpy= 0.343(2) eV***

## What the ratio of site fractions means:



2. Law of mass action:  $\frac{[In_{Gd}][Al_{Al}]}{[In_{Al}][Al_{Gd}]} = \exp(-G_{tr} / k_B T) = \exp(S_{tr} / k_B) \cdot \exp(-H_{tr} / k_B T)$   
 [ ]  $\equiv$  mole fraction  
 on sublattice

3. Ratio of site fractions:  $\frac{f_{Gd}}{f_{Al}} = \frac{[In_{Gd}]}{2[In_{Al}]} = [Al_{Gd}] \exp(-G_{tr} / k_B T)$



## What about $[Al_{Gd}]$ ??

1. A strong function of composition. It may be a constitutional defect if composition is not stoichiometric (constitutional defect).
2. It might be thermally activated itself; e.g.,  $0 \rightarrow Al_{Gd} + Gd_{Al}$

*Need additional information to interpret activation enthalpy...*

# This work: Indium in $\text{Al}_3\text{V}$ , $\text{Al}_3\text{Ti}$ , $\text{Al}_3\text{Zr}$

## Tetragonal structures

### Three or four sites:

one TM site, 2 or 3 inequivalent Al-sites

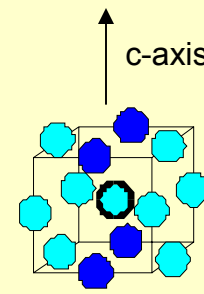
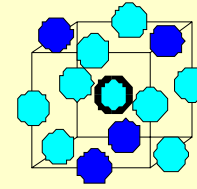
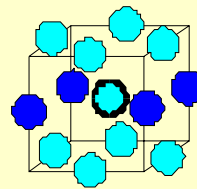
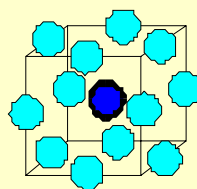
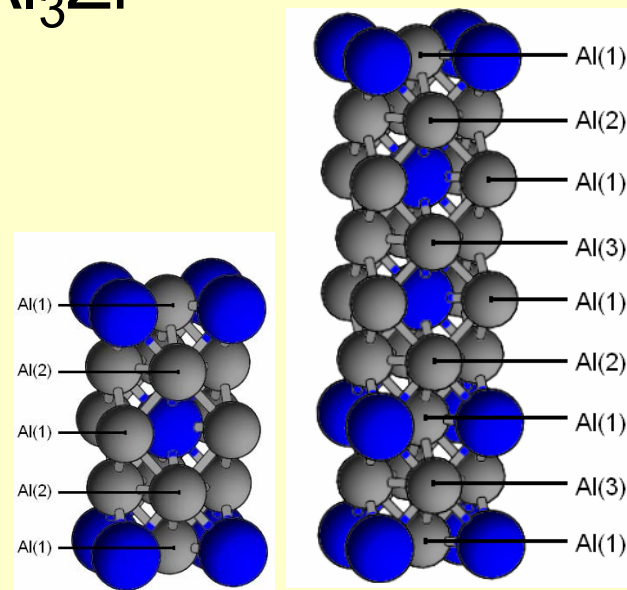
### Local environments:

TM site has 12 Al near-neighbors (nn)

Al(1) has 4 TM nn in square

Al(2) has 4 TM nn in tetrahedron

Al(3) has 4 TM nn in square ( $\text{Al}_3\text{Zr}$  only)

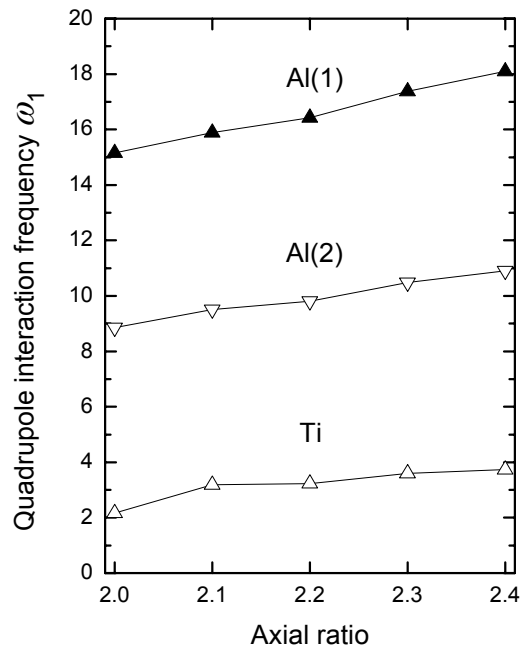


Sites:

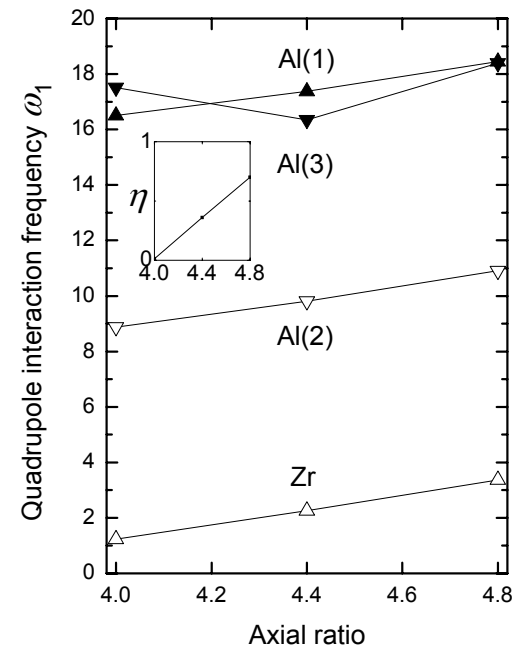
	TM	Al(1)	Al(2)	Al(3)
EFG symmetry:	axial	axial	axial	non-axial
EFG axis:	c (tetragonal)	c	c	a (transverse)

Identifying sites: EFG calculations in point-charge approximation  
guide identification of sites

$\text{Al}_3\text{Ti}$  structure



$\text{Al}_3\text{Zr}$  structure



- No indium on TM site:
- TM site surrounded by 12 nn Al-atoms, as in Al-metal.
  - Indium insoluble in Al, ruling out preference for Tm site.

# This work: Indium in $\text{Al}_3\text{V}$ , $\text{Al}_3\text{Ti}$ , $\text{Al}_3\text{Zr}$

## Tetragonal structures

### Three or four sites:

one TM site, 2 or 3 inequivalent Al-sites

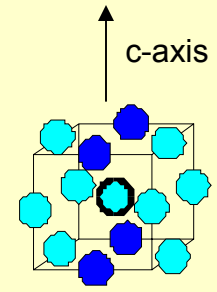
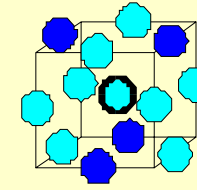
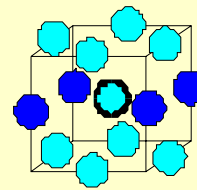
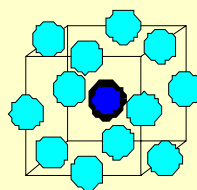
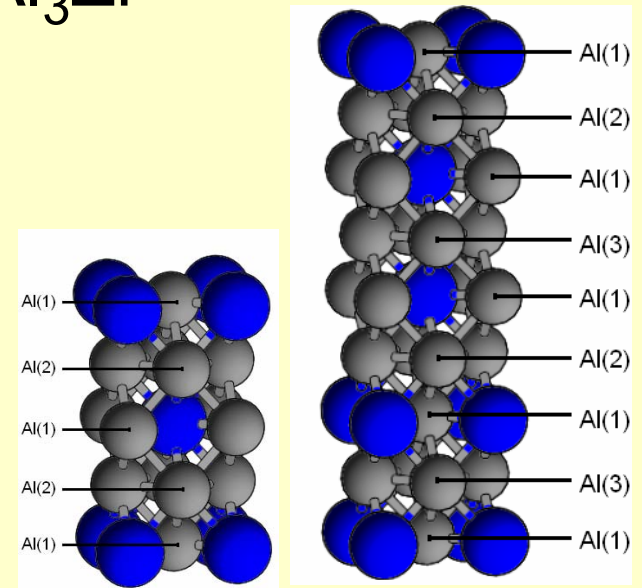
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TM site has 12 Al-near-neighbors (nn)

Al(1) has 4 TM nn in square

Al(2) has 4 TM nn in tetrahedron

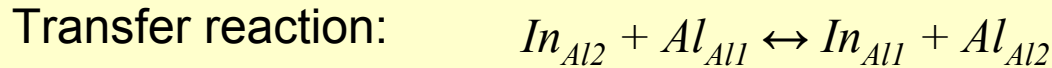
Al(3) has 4 TM nn in square ( $\text{Al}_3\text{Zr}$  only)



Sites:

	TM	Al(1)	Al(2)	Al(3)
EFG symmetry:	axial	axial	axial	non-axial
EFG axis:	c (tetragonal)	c	c	a (transverse)
EFG magnitudes:	very low	high	intermediate	high

## Transfer of solutes between inequivalent sites of one element:



Law of mass action:  $\frac{[In_{Al2}][Al_{Al1}]}{[In_{Al1}][Al_{Al2}]} = \frac{[In_{Al2}]}{[In_{Al1}]} = \exp(-G_{tr} / k_B T)$   
[ ]  $\equiv$  mole fraction

Ratio of site fractions:  $\frac{f_{Al2}}{f_{Al1}} = \frac{2[In_{Al2}]}{[In_{Al1}]} = 2 \exp(-G_{tr} / k_B T)$  (factor of 2 for Al<sub>3</sub>Ti)

### Much simpler result !

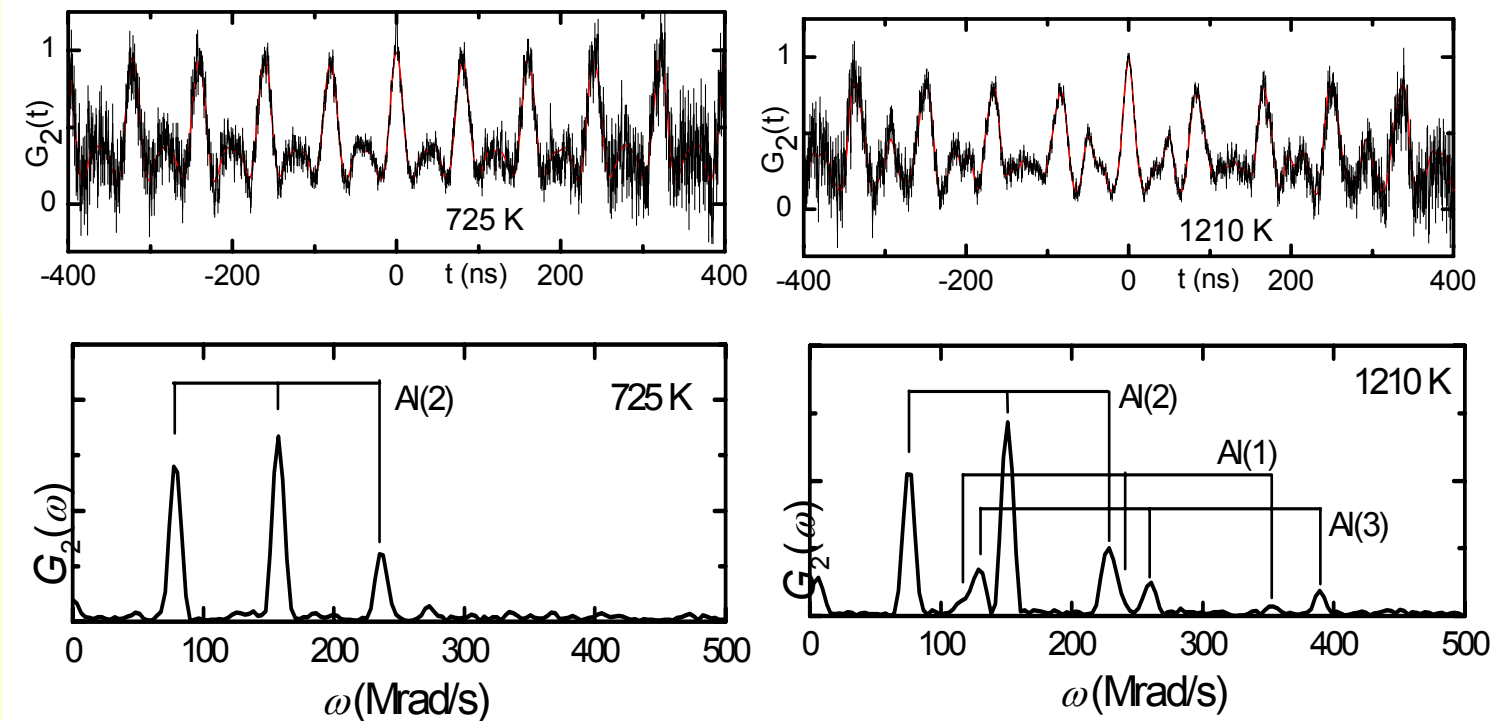
1. independent of composition
2. directly gives differences of vibrational entropies and enthalpies of solute on the two sites:

$$\frac{f_{Al2}}{2f_{Al1}} = \frac{[In_{Al2}]}{[In_{Al1}]} = \exp(-G_{tr} / k_B T) = \exp((S_2 - S_1) / k_B) \cdot \exp(-(H_2 - H_1) / k_B T)$$

$S_2 - S_1$  = difference of vibrational entropies of solute

$H_2 - H_1$  = difference of enthalpies of solute in the two sites

## Measurements: $\text{Al}_3\text{Zr}$ (3 Al-sites) measured at 725 K and 1210 K



725K: Single signal dominates;  
attributed to Al(2) due to low frequency.  
Non-random polycrystalline texture.

1210K: Two new signals. Neither has  
detectable EFG asymmetry, but one signal  
has non-random amplitudes just like Al(2);  
attribute to Al(1). Remaining signal  
attributed to Al(3).

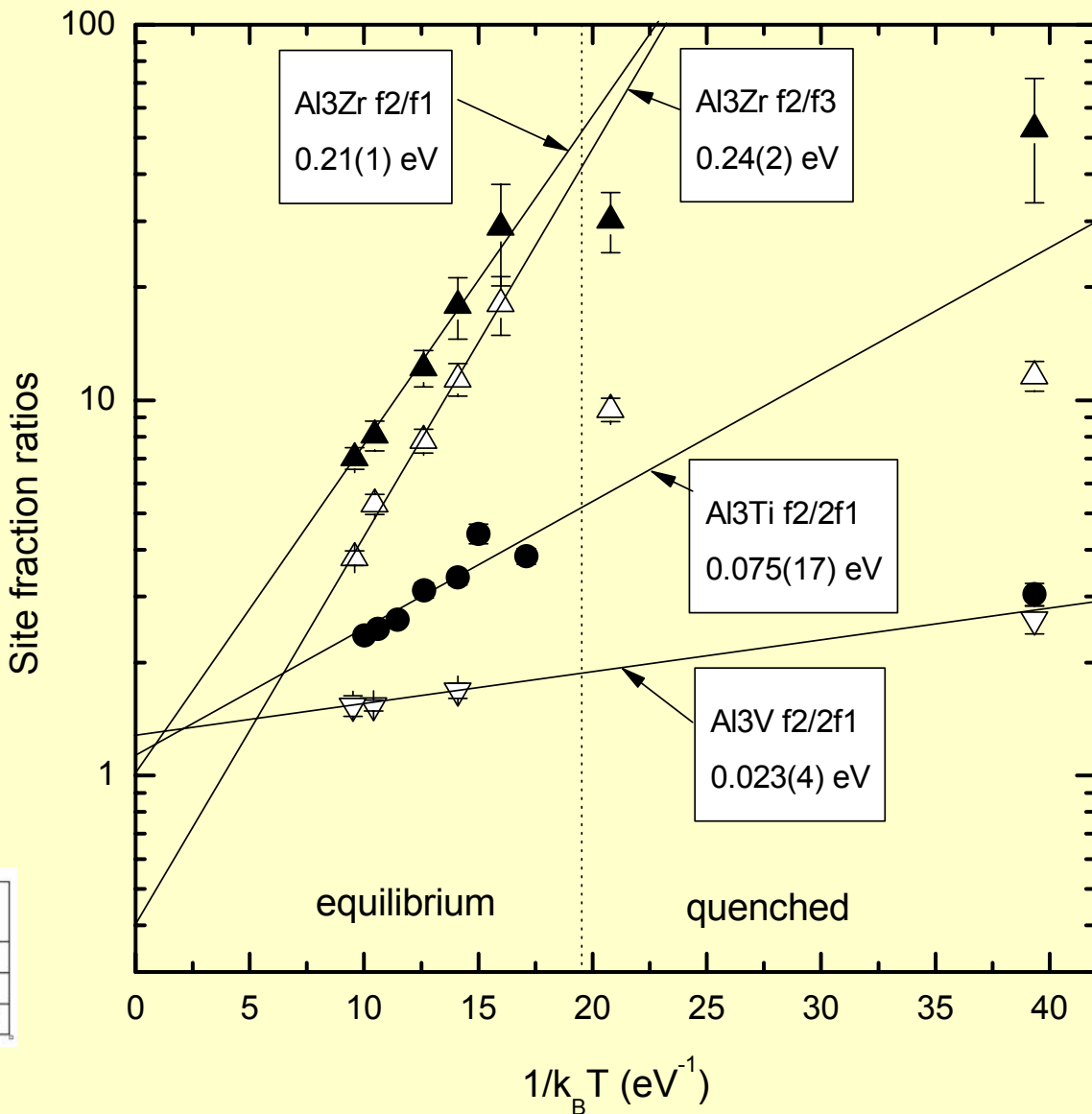
All measurements in thermal equilibrium (changes in site fractions reversible)

# Results: Arrhenius plot of ratios of site fractions

Equilibrium above  $\sim 300$  C

Fitted enthalpy differences  
given in figure

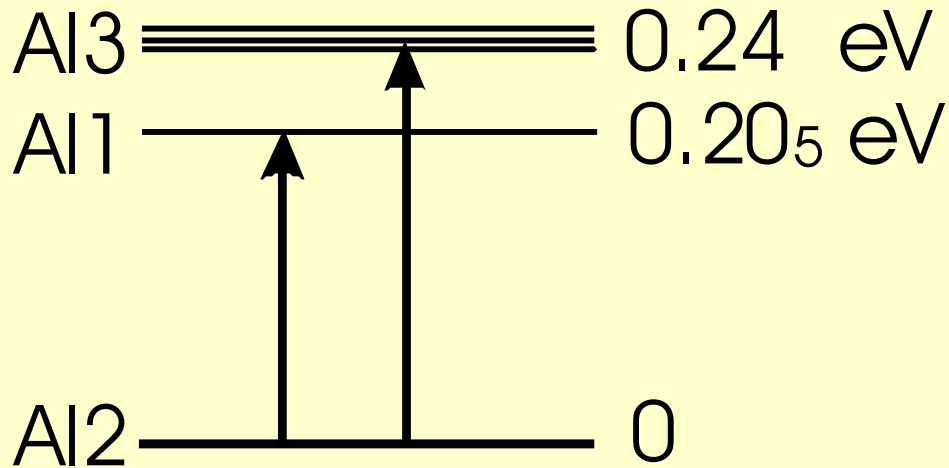
Intercepts at  $T = \infty$  give  
 $\exp((S_2 - S_1)/k_B)$



Phase	H1-H2 (eV)	S1-S2 (kB)	H3-H2 (eV)	S3-S2 (kB)
Al <sub>3</sub> V	+0.023(4)	-0.30		
Al <sub>3</sub> Ti	+0.075(17)	-0.18		
Al <sub>3</sub> Zr	+0.205(12)	0.0	+0.24(2)	+0.92(19)

# Interpretation of site preferences in Al<sub>3</sub>Zr:

## Three-level quantum system



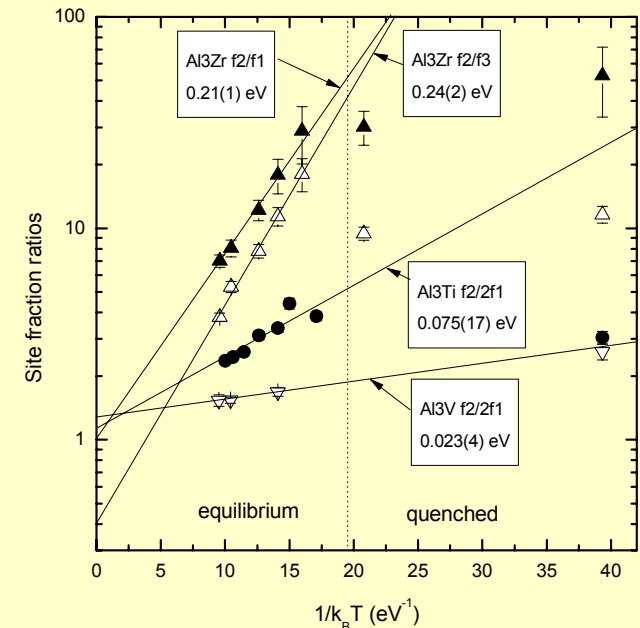
Large degeneracy of site Al(3) attributed to low frequency vibrational modes; enhanced population of Al(3) sites at low temperature.

Higher entropy of site Al(3) “wins out” at high temperature.

Degeneracies:

$$\exp((S_3 - S_2) / k_B) \cong 2.5$$

$$\exp((S_1 - S_2) / k_B) \cong 1$$



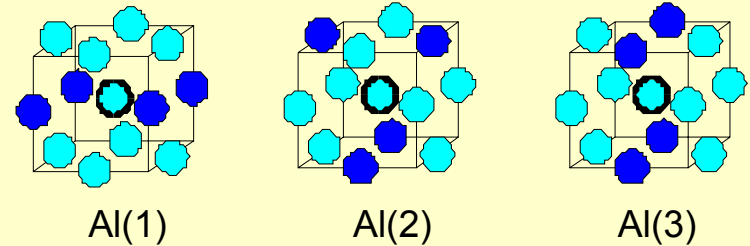
# $\Delta H$ correlated with volume mismatch of TM and Al-atoms

In-solute is oversized.

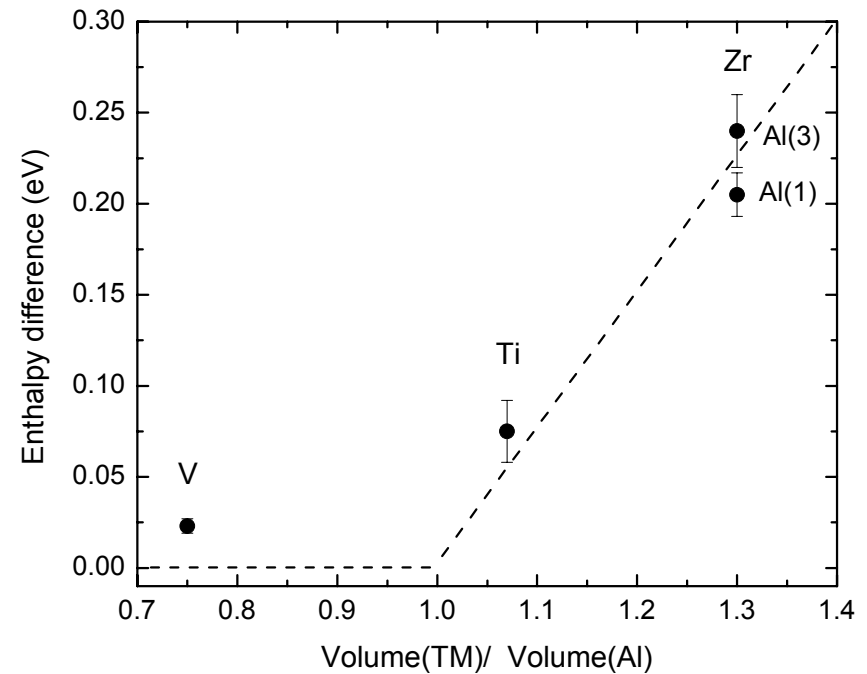
Oversized TM atoms create additional lattice strain.

Strain more anisotropic for “square” configurations, greater strain energy.

$\Delta H \approx 0$  if TM atom is undersized.



Atom	Relative volume
V	0.75
Al	1.00
Ti	1.07
Zr	1.30
In	1.46



# Summary

Site fractions of indium solutes on inequivalent Al-sites in intermetallic compounds were measured using PAC.

Temperature dependences of ratios of site fractions were observed to be thermally activated. Activation enthalpies and prefactors are interpreted in terms of differences in enthalpies and vibrational entropies of solutes on different sites using a thermodynamic model.

The magnitude of site-enthalpy differences was shown to be correlated with atomic volume mismatches.

These appear to be the first measurements of differences of entropies and enthalpies of solutes on inequivalent sites of one element.

*THANK YOU*