

*Assessment of Diffusion Mobilities in  
the  $\gamma'$  ( $L1_2$ -Ni<sub>3</sub>Al) and B2 (NiAl)  
Structures*

C. E. Campbell

February 7, 2006

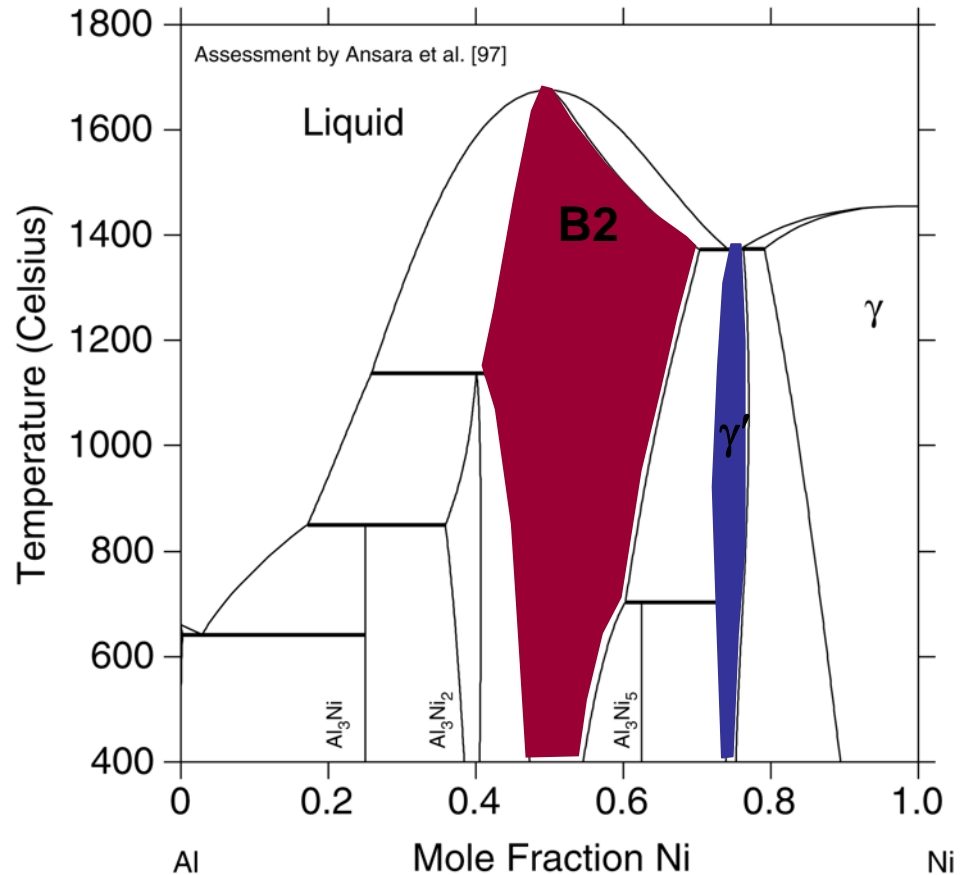
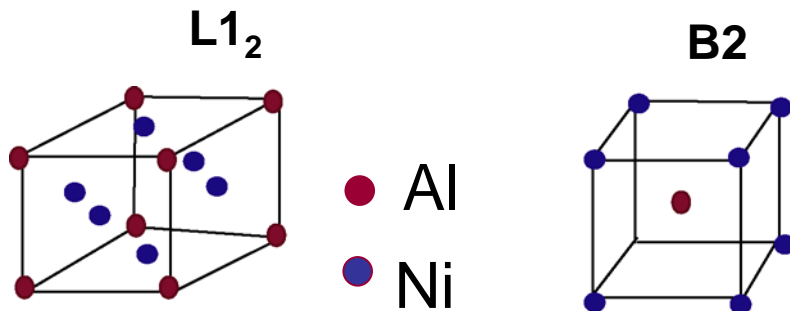
# Ordered Phase in Ni-base Superalloys

B2: CsCl structure

$\gamma'$  : L1<sub>2</sub> base

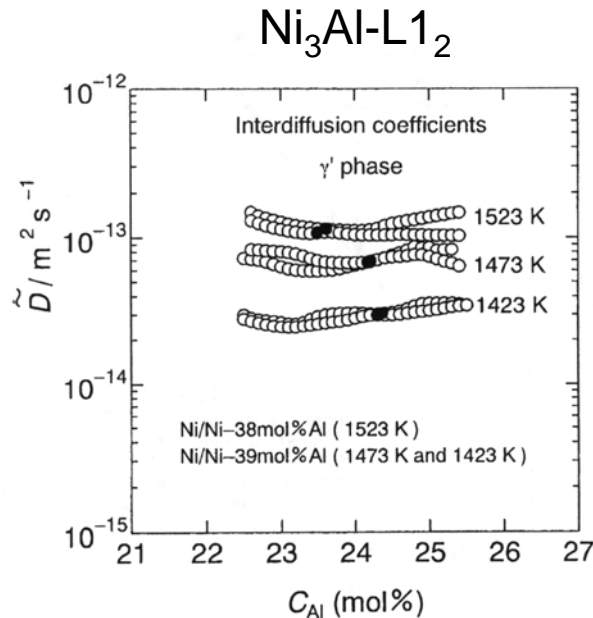
B2: Wide homogeneity range (~36 to 57 at.% Al)

Atomic mechanism: consists of several consecutive jumps

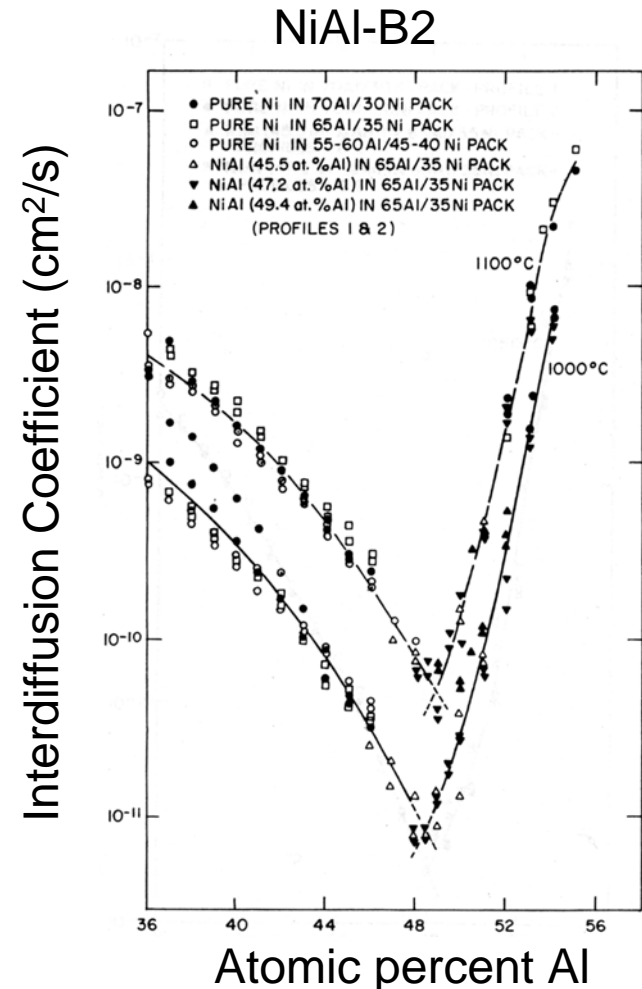


# Why add ordering to diffusion model

- Strongly composition dependent diffusion coefficients (B2-NiAl)
- Phase fractions are significant; should not ignore diffusion



From Fujiwara and Horita, *Acta Mater.*, **50** (2002) 1571.)



From Shankar and Seigle, *Metall. Trans.* **9A**, (1978) 1476.

# *Defects in Intermetallics*

- 4-type of defects in  $A_aB_b$  intermetallics
  - Vacancies on both sublattices:  $V_A$  and  $V_B$
  - Atoms on unlike sublattices  $A_B$  and  $B_A$
  - Structural defects: defects that are present in thermal equilibrium
  - Thermal defects
- Effect of crystal structure on the self-diffusion properties of  $Ni_3Al-L1_2$  and  $NiAl-B2$ 
  - $Ni_3Al$ : metal sublattice contains a connected network for nearest neighbor jumps for vacancies
  - $NiAl$ : metal sublattice requires jumps between different sublattices.

# Diffusion Database Development: *Inputs*

- Thermodynamics (CALPHAD approach)
- Diffusion experiments (unary, binary, ternary systems)
  - Tracer diffusivity,
  - Intrinsic diffusivity
  - Interdiffusion coefficients
- Define Mobility Functions
  - Composition and temperature dependent

$$M_i = \frac{M_i^\circ}{RT} \exp\left(\frac{-\Delta Q_i^*}{RT}\right) \text{ where } \Delta Q_i^* = f(c_i, T)$$

$$\Delta Q_i^* = \sum_{p=1}^n x_p Q_i^p + \sum_p \sum_{q>p}^n x_p x_q \left[ \sum_{r=0}^m A_i^{pq} (x_p - x_q)^r \right] + \sum_p \sum_{q>p} \sum_{v>q} x_p x_q x_v \left[ v_{pqv}^s B_i^{pqv} \right]$$

is exponentially dependent on composition  $M_i = \frac{1}{RT} \exp\left(\frac{\Delta Q_i}{RT}\right)$

$$\Delta Q_i = \Delta Q_i^* - RT\Theta_i \text{ and } M_i^0 = \exp(\Theta_i)$$

# Effect of chemical ordering on diffusion

$$M_i = \frac{M_i^\circ}{RT} \exp\left(\frac{-\Delta Q_i}{RT}\right) \text{ where } \Delta Q_i = f(c_i, T) \text{ and } M_i^\circ = f(c_i, T)$$

- Based on Bragg-Williams approach by Girifalco for a binary system

(*J. Phys. Chem. Solids*, 1964, **24**, 323.)

$$\Delta Q_k = \Delta Q_k^{dis} \left[ 1 + \alpha_k (S^{ord})^2 \right] \quad S^{ord} = p_A^\alpha - p_A^\beta = \text{long-range order parameter}$$

$p_A^\alpha$  is the probability of finding A atom on an  $\alpha$  site

- Expansion to Multicomponent systems Helander and Ågren, (*Acta Mater.*, 1999, **47**, 1141.)

$$\Delta Q = \Delta Q^{dis} + \Delta Q^{ord}$$

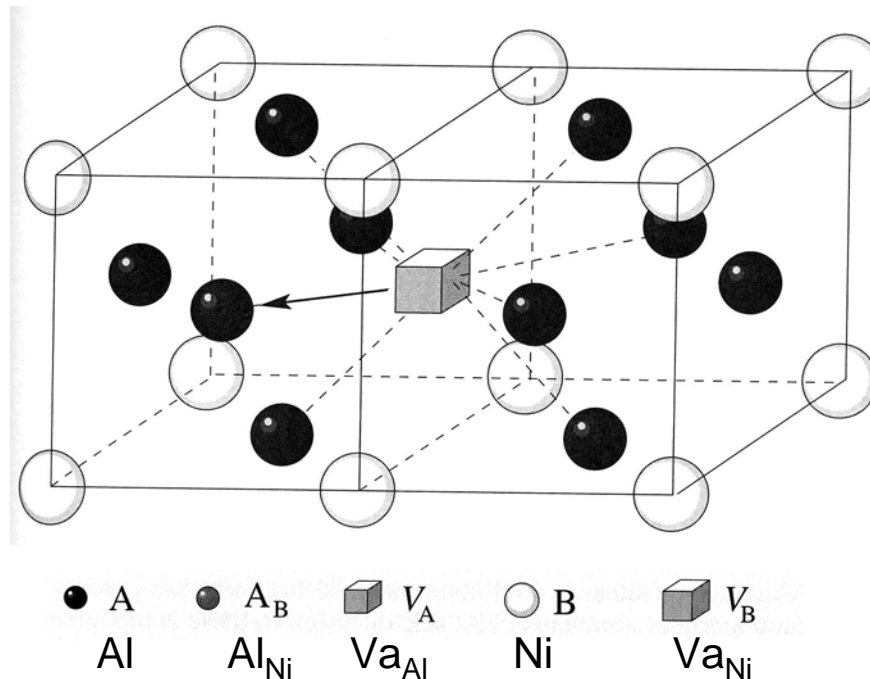
$\Delta Q_{ij}^{ord}$  = contribution to activation energy for component  $k$  as a result of the ordering of  $i$ - $j$  atoms

$$\begin{aligned} \Delta Q_i^{ord} = & \sum_i \sum_j \Delta Q_{i:j}^{ord} [y_i^\alpha y_j^\beta - x_i x_j] \\ & + \sum_i \sum_j \sum_k \Delta Q_{ij:k}^{ord} [y_i^\alpha y_j^\alpha y_k^\beta - x_i x_j x_k] \\ & + \sum_i \sum_j \sum_k \Delta Q_{k:ij}^{ord} [y_i^\beta y_j^\beta y_k^\alpha - x_i x_j x_k] \end{aligned}$$

$$y_i^\alpha = \frac{N_i^\alpha}{N_{tot}^\alpha} = p_i^\alpha$$

# *Ni<sub>3</sub>Al: Diffusion Mechanism*

- Sublattice diffusion mechanism
  - Random jumps of a vacancy on a sublattice do not affect the order in the compound.
  - Diffusivities of the two components are not coupled
    - Ni diffusion is expected to be faster than Al diffusion



# *Experimental observations*

- Self-Diffusion

- Ni Diffusion

- Temperature dependence

- $T > 1100$  K: Arrhenius temperature on temperature

- $T < 1100$  K: Some experimental results show a deviation from the linear Arrhenius dependence on temperature.

- » Frank et al. showed this deviation is due to short-circuit diffusion in polycrystalline samples

- Composition dependence

- Experiments indicate some minimum in  $D^* \sim 76\%$  at. Ni; however, this may be due short-circuit diffusion or grain boundary diffusion effects.

- Monte Carlo studies found a minimum at the stoichiometric composition due to the existence of Al and Ni antistructure atoms in Ni and Al rich alloys.

- Marginal composition dependence

- Al diffusion (limited experimental data)

- Small composition dependence

- $D_{Al}^*/D^* \approx 0.3$  (Ikeda 1998)

- Interdiffusion

- Marginal composition dependence



# Assessment of diffusion mobilities in $Ni_3Al$

- $L1_2$  ( $Ni_3Al$ ) ( $Ni, Al: Ni, Al$ )
- Disorder description fixed

$$M_i = \frac{M_i^\circ}{RT} \exp\left(\frac{-\Delta Q_i^*}{RT}\right) \text{ where } \Delta Q_i^* = f(c_i, T)$$

$$\Delta Q_{Ni}^* = x_{Ni} Q_{Ni}^{Ni} + x_{Al} Q_{Al}^{Ni}$$

$$\Delta Q_{Al}^* = x_{Ni} Q_{Ni}^{Al} + x_{Al} Q_{Al}^{Al} + x_{Al} x_{Ni} Q_{Al, Ni}^{Al}$$

- Order description

$$\Delta Q_{Ni}^{ord} = \Delta Q_{Al: Ni}^{ord} [y_{Al}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni}] + \Delta Q_{Ni: Al}^{ord} [y_{Ni}^{Ni} y_{Al}^{Al} - x_{Al} x_{Ni}]$$

$$+ \Delta Q_{Al: Al}^{ord} [y_{Al}^{Ni} y_{Al}^{Al} - x_{Al} x_{Al}] + \Delta Q_{Ni: Ni}^{ord} [y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Ni} x_{Ni}]$$

$$\Delta Q_{Al}^{ord} = \Delta Q_{Al: Ni}^{ord} [y_{Al}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni}] + \Delta Q_{Ni: Al}^{ord} [y_{Ni}^{Ni} y_{Al}^{Al} - x_{Al} x_{Ni}]$$

$$+ \Delta Q_{Al: Al}^{ord} [y_{Al}^{Ni} y_{Al}^{Al} - x_{Al} x_{Al}] + \Delta Q_{Ni: Ni}^{ord} [y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Ni} x_{Ni}]$$

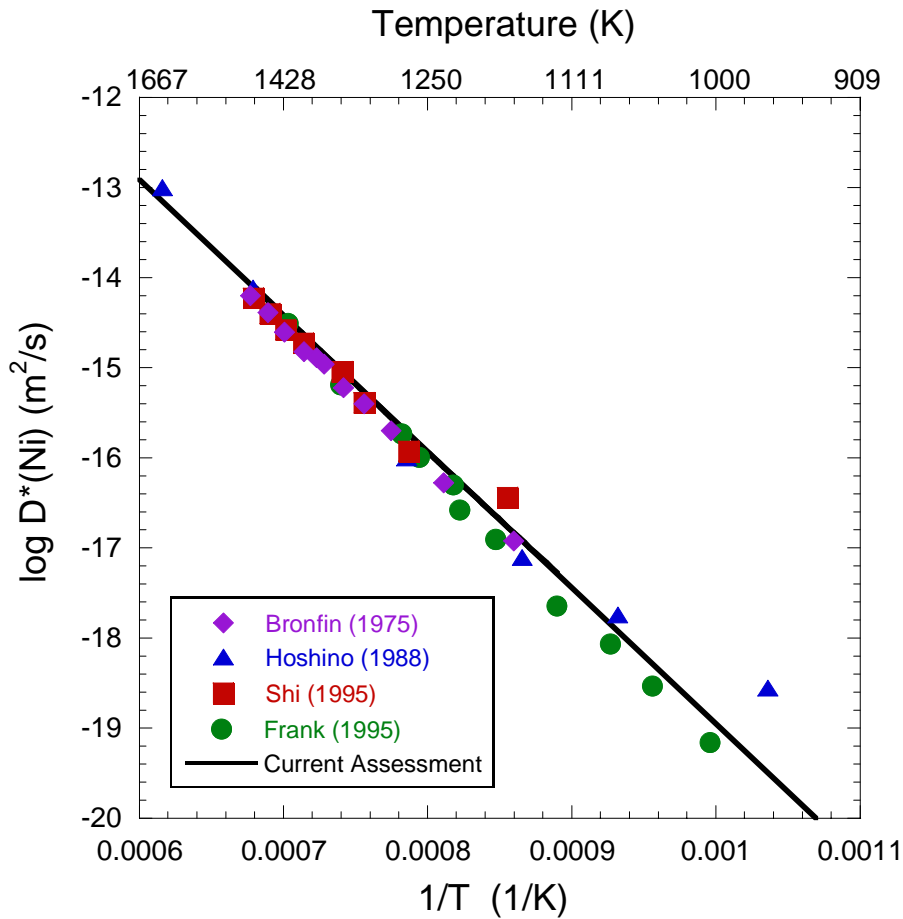
$$+ \Delta Q_{Al, Ni: Al}^{ord} [y_{Al}^{Ni} y_{Ni}^{Ni} y_{Al}^{Al} - x_{Al} x_{Ni} x_{Al}]$$

$$+ \Delta Q_{Al, Ni: Ni}^{ord} [y_{Al}^{Ni} y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni} x_{Ni}]$$

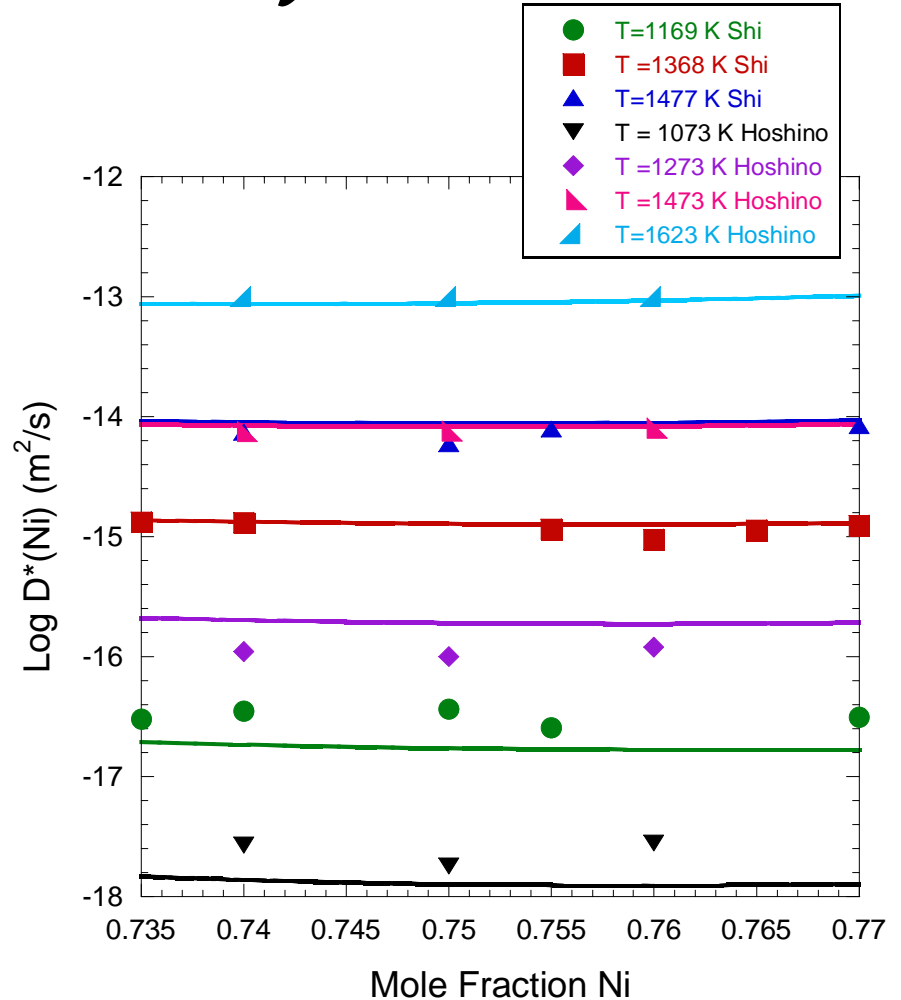
# *Assessed Mobility Parameters*

Mobility Parameters	Value
Ni	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al}$	-87723-58.15*T
$\Delta Q_{Al:Al}$	57853
$\Delta Q_{Ni:Ni}^{ord}$	-889101
Al	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al}$	2255-20.22*T
$\Delta Q_{Al:Al}$	-268884
$\Delta Q_{Ni:Ni}^{ord}$	84356
$\Delta Q_{Al,Ni:Al}^{ord} = \Delta Q_{Al,Ni:Ni}^{ord}$	2333274

# Self Diffusion of Ni



Arrhenius temperature dependence

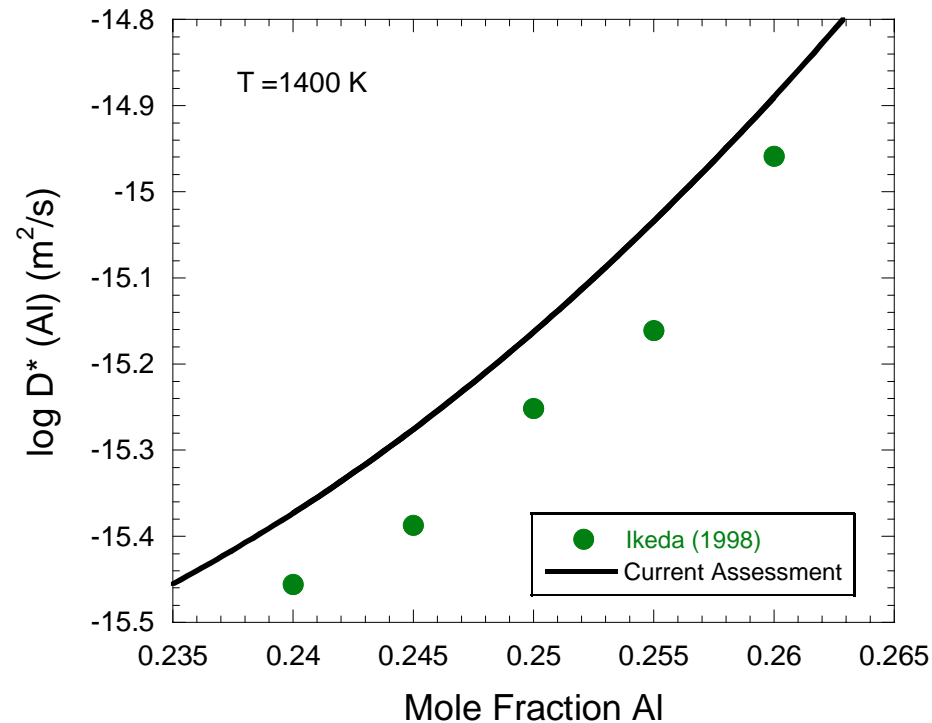
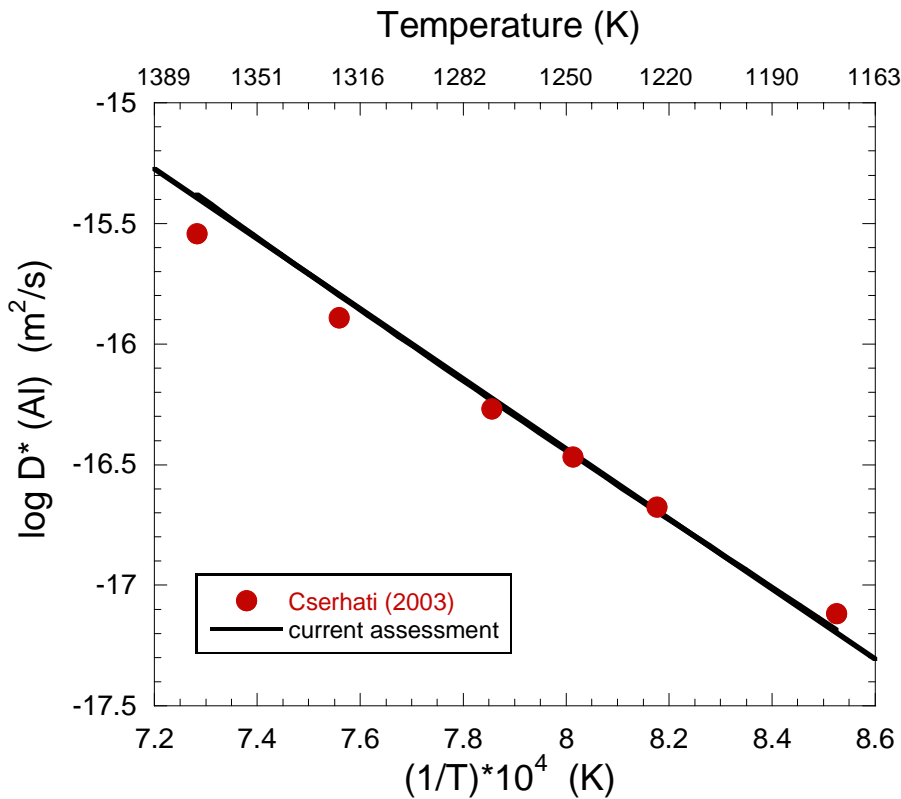


Small Composition dependence

# Self-Diffusion of Al

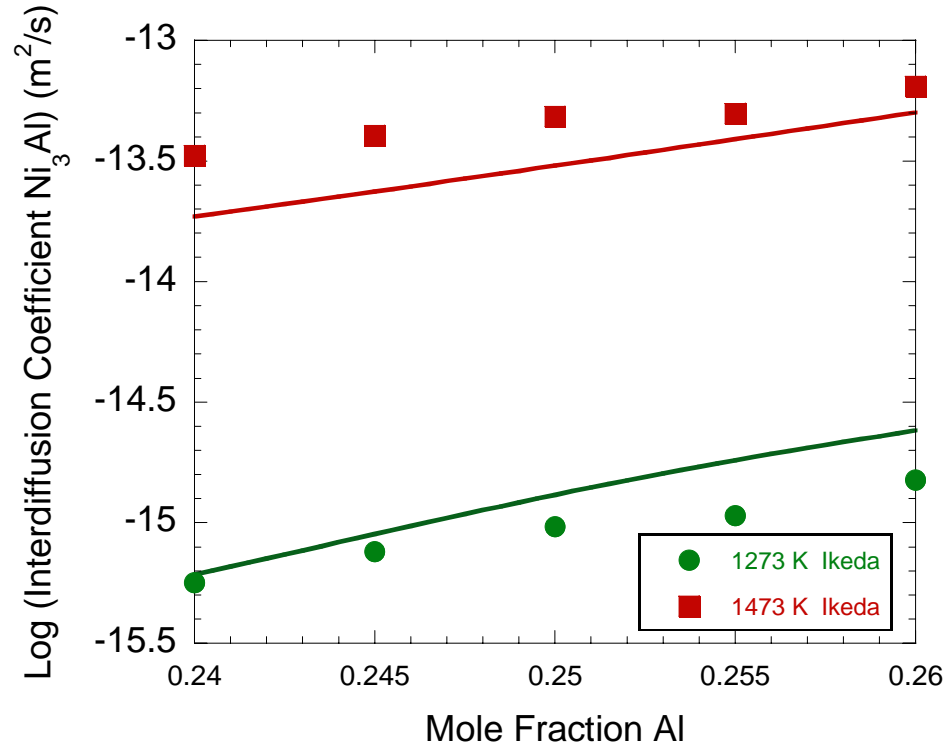
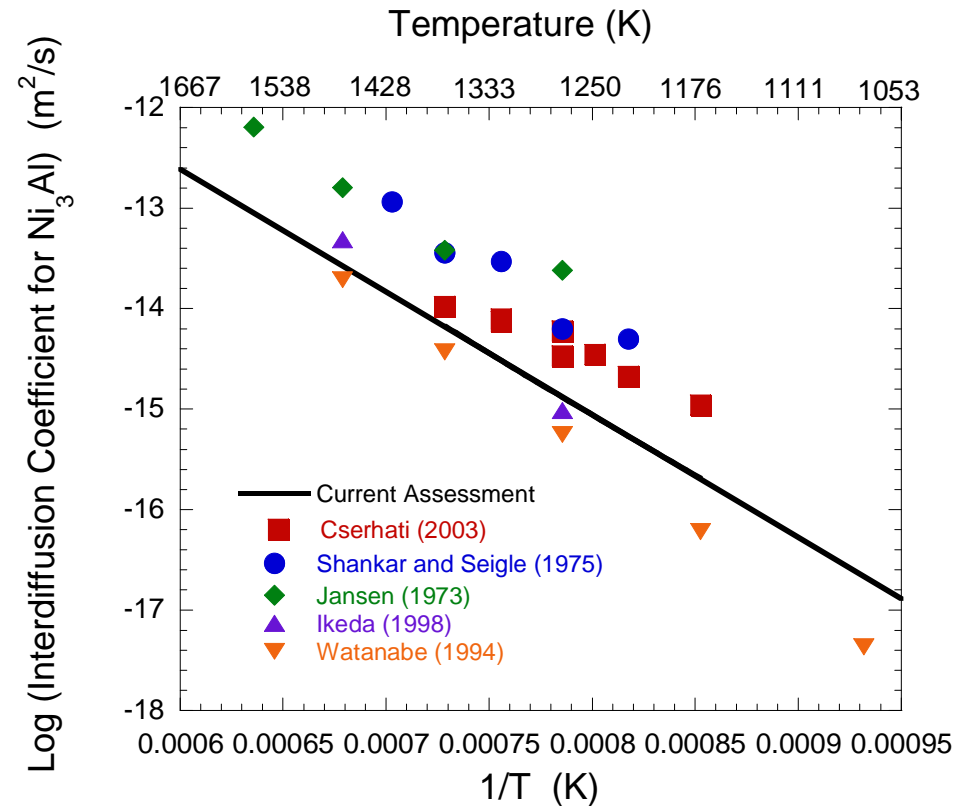
Experimental  $D_{Al}^*$  is determined from  $\tilde{D}_{Ni_3Al}$  using the Darken-Manning eqn.

$$\tilde{D} = (x_{Al}D_{Ni}^* + x_{Ni}D_{Al}^*) \cdot \Phi \cdot S$$

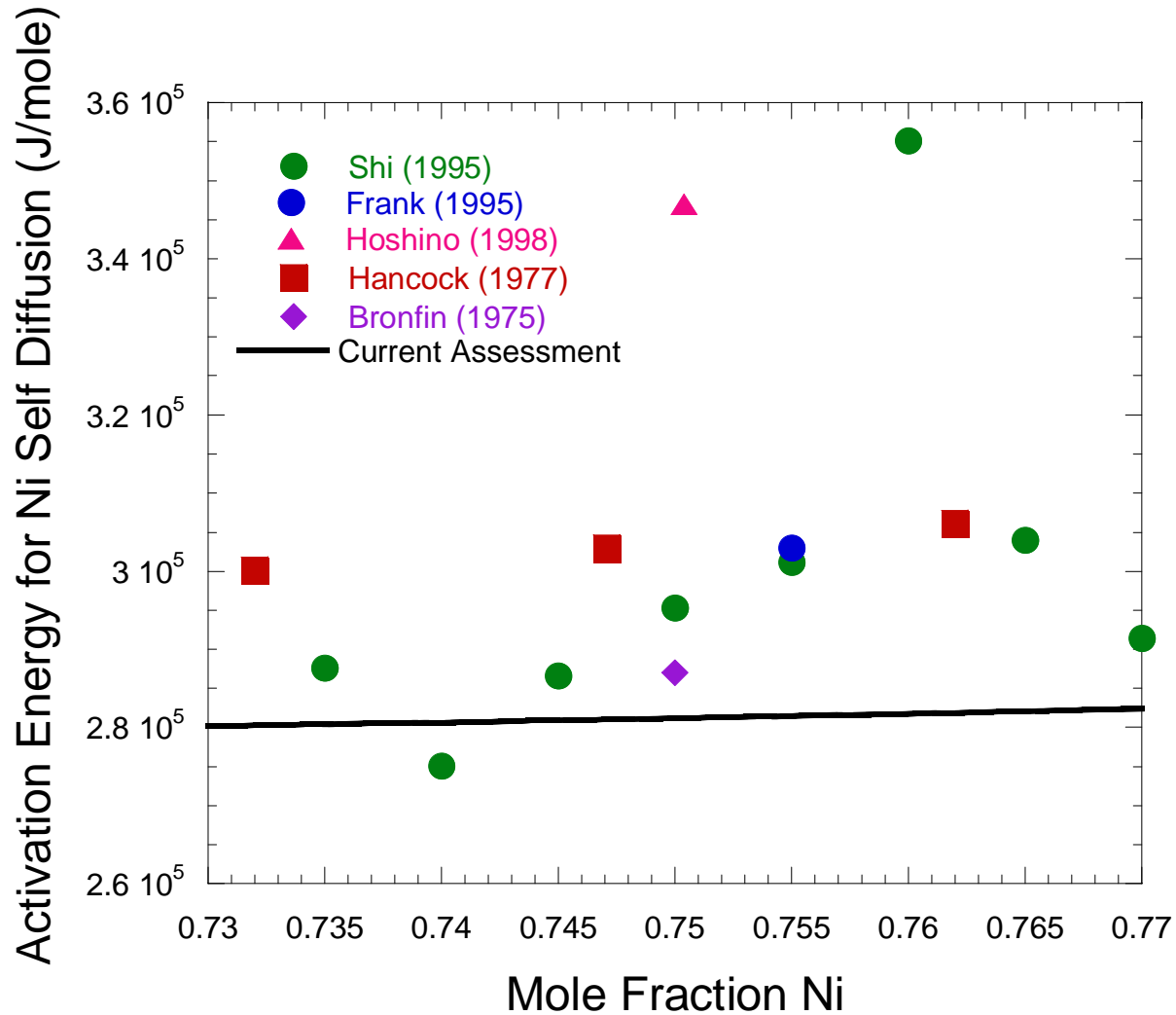


$D_{Al}^*$  increases by a factor of 3  
for a 3 percent change in Al

# Interdiffusion Data



# Activation Energy



# *NiAl-B2 Crystal Structure*

- 2 penetrating simple cubic lattices
  - Al atoms occupy the corners of one sublattice
  - Ni atoms occupy the corners of the other sublattice.
- Different defect structures on either side of the stoichiometric composition
  - Al-rich side: excess Ni atoms occupy Al lattice sites  
→ anti-structure defects and structural Ni vacancies
  - Ni-rich side: structural vacancies

# *Experimental Observations*

- **Ni-Self Diffusion**

- Temperature dependence:  $T > 1500$  K upward deviation from Arrhenius dependence.
- Composition dependence:
  - On Al-rich side, structural Ni-vacancies do not increase diffusivity (Frank et. al. 2001)
  - Ni-rich side: increasing diffusivity
- Activation energy
  - Constant from 46.5 to 53 at.% Ni
  - Decreasing for Ni>53 at.%

- **Al-Self Diffusion**

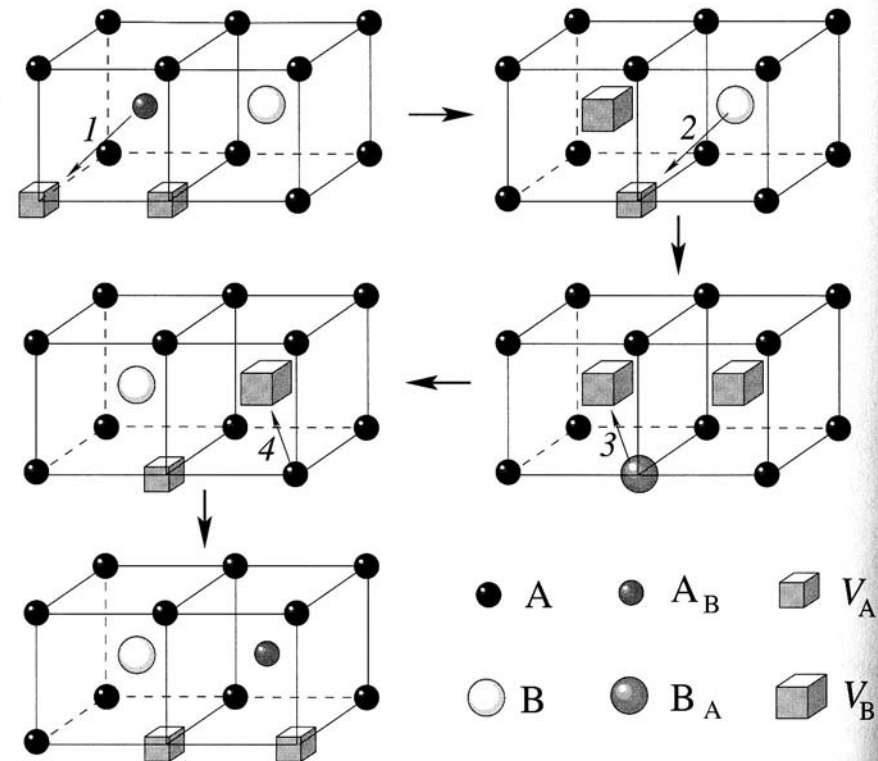
- No direct measurements
- Significant composition dependence deduced from interdiffusion coefficient measurements (deep minimum at stoichiometric composition)
- Dependent on presence of  $V_{Ni}$



# Diffusion Mechanisms in NiAl-B2

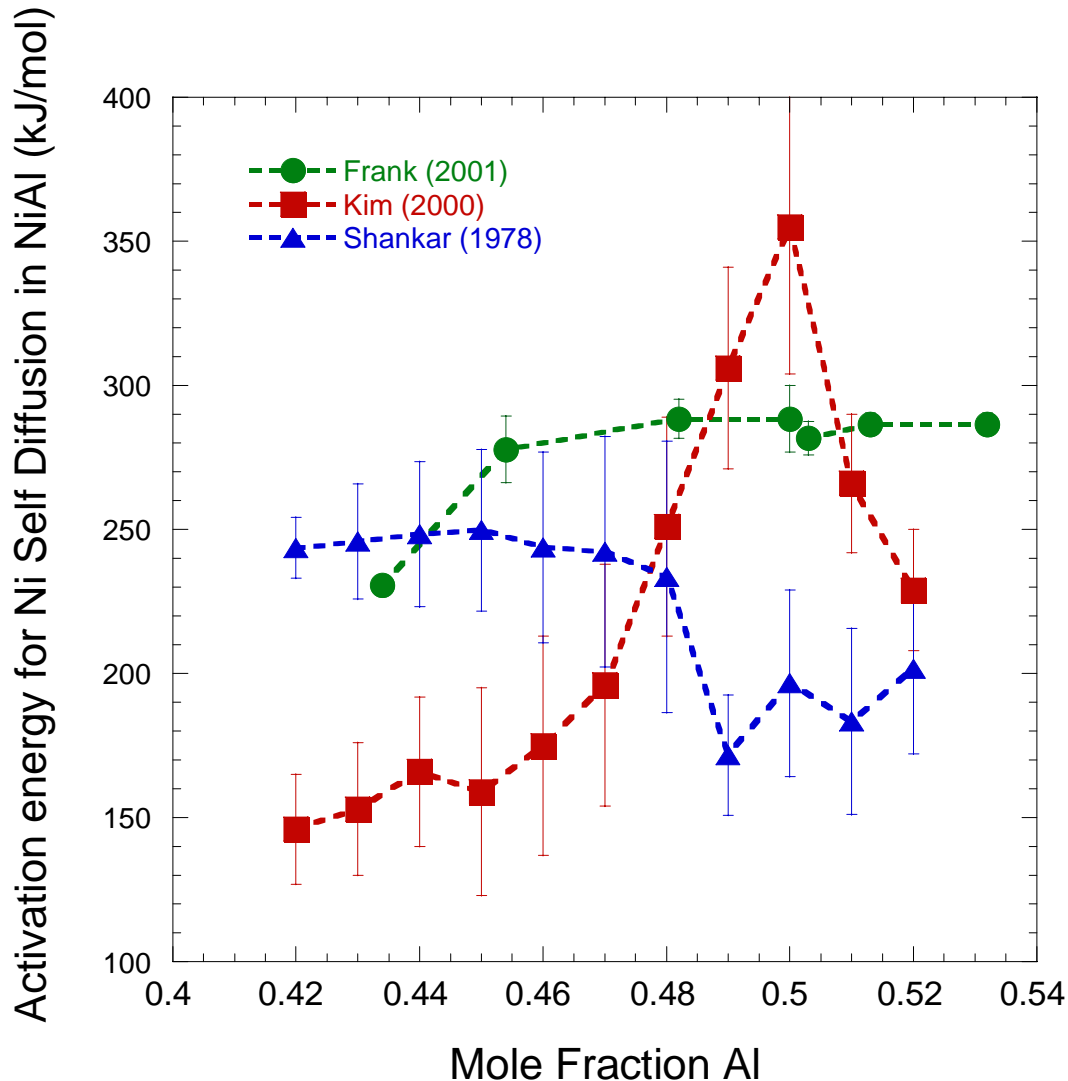
- All nearest neighbor jumps are jumps between different sublattices
- Ni vacancies on the Al-rich side significantly affect the Ni self-diffusion
- Active diffusion mechanisms:
  - Triple-defect mechanism ( $2 V_{\text{Ni}} \text{Ni}_{\text{Al}}$ )
    - Composition independent activation energy ( $\sim 300 \text{ kJ/mol}$ )
  - Anti-structure Bridge Mechanism (ASB)
    - Percolation effect (threshold  $> 55.5 \text{ at.\% Ni}$ )
  - Next nearest neighbor jumps of Ni atoms
    - Lower temperatures in Al-rich compositions

## Triple Defect Mechanism in a NiAl-B2 Structure



From Frank et al. Acta Mater. 2001

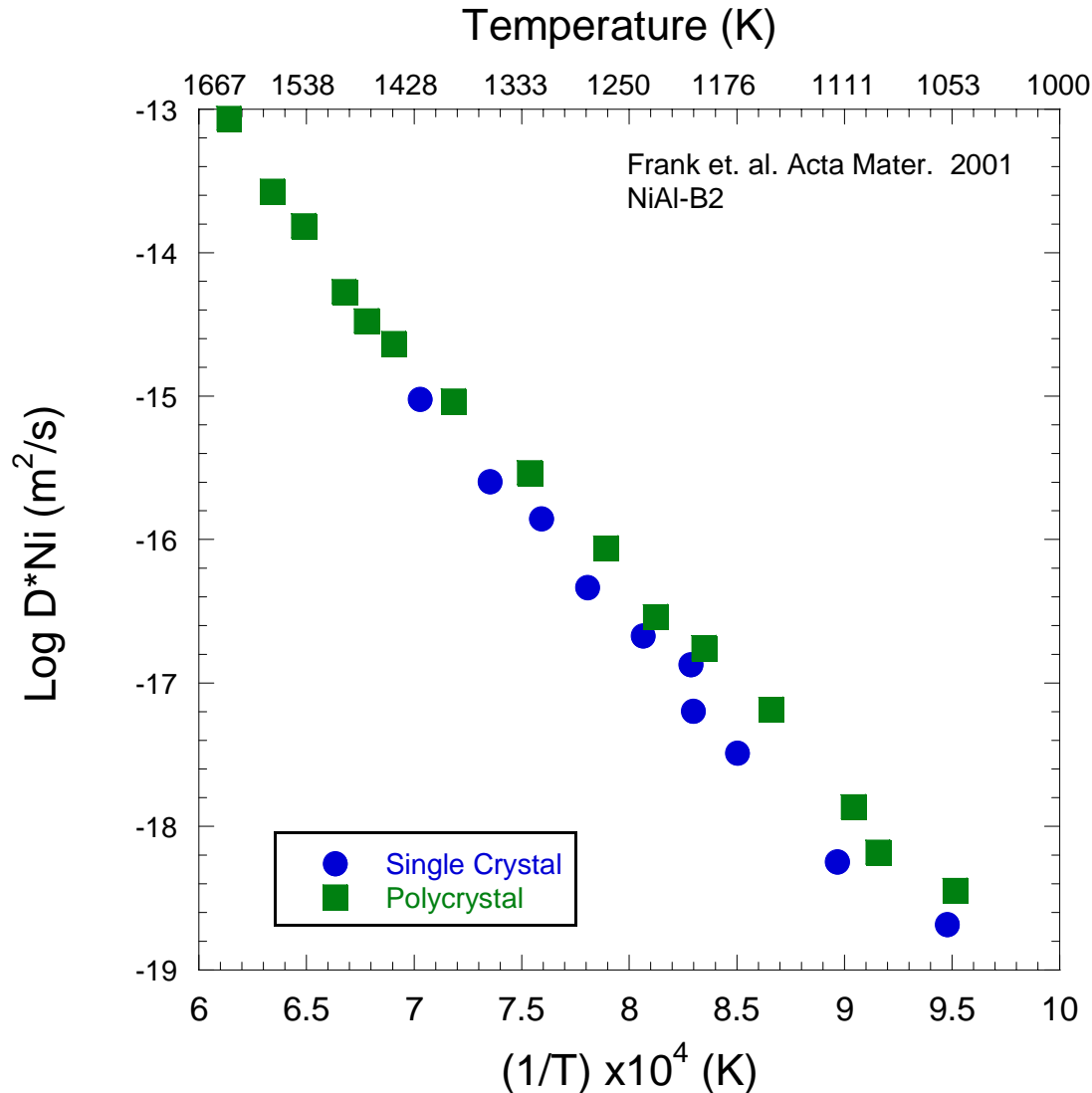
# Activation Energy



Why so much disagreement?

- Grain boundary diffusion
- Annealing treatment: high temperatures may result in quenched vacancies that are not in thermodynamic equilibrium
- Kim and Chang used lattice-mole fraction

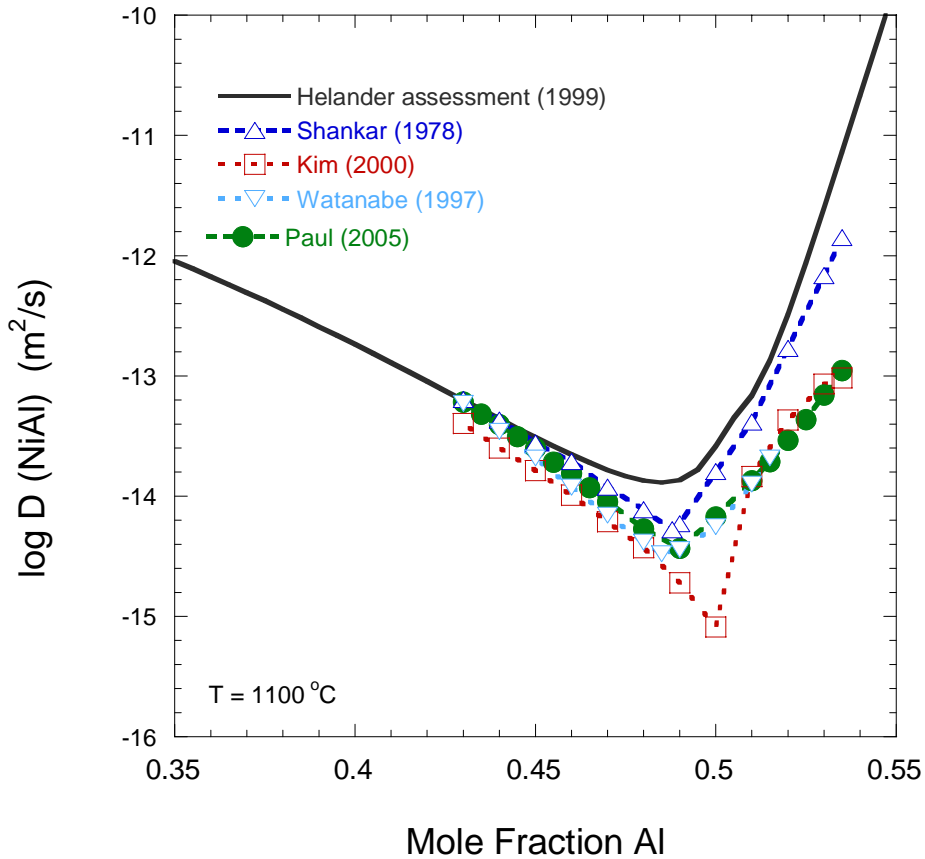
# Temperature Dependence of Ni Self-Diffusion in NiAl



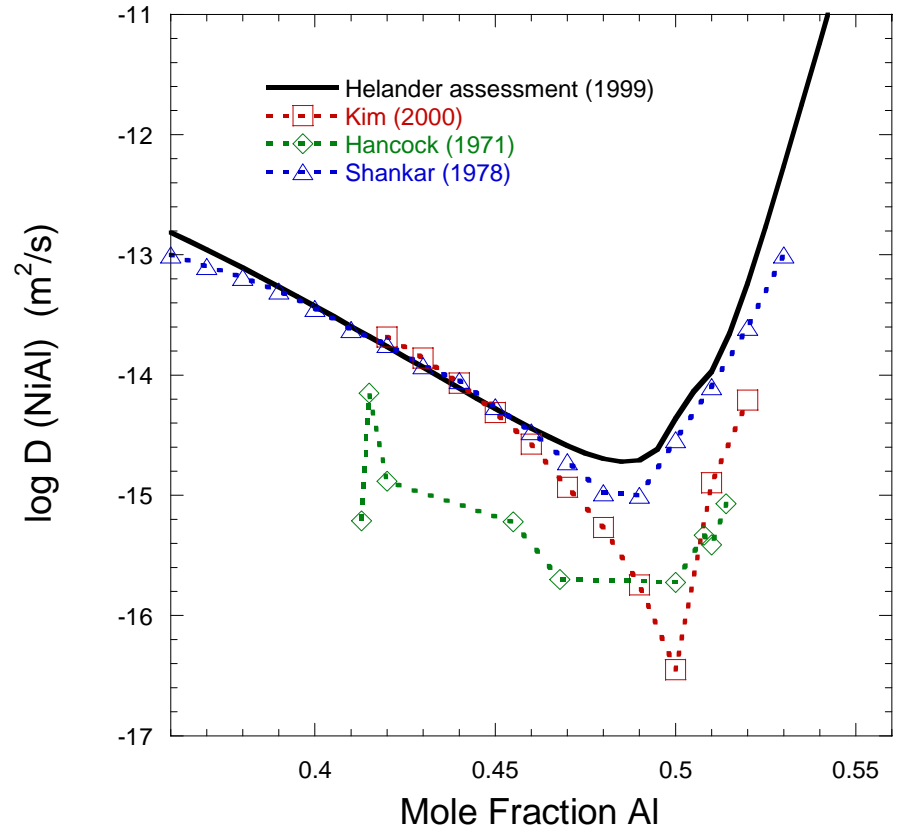
Similar results on  
the Ni-rich and Al-  
rich compositions

# Diffusion in B2-NiAl

NiAl (B2) at 1100 °C



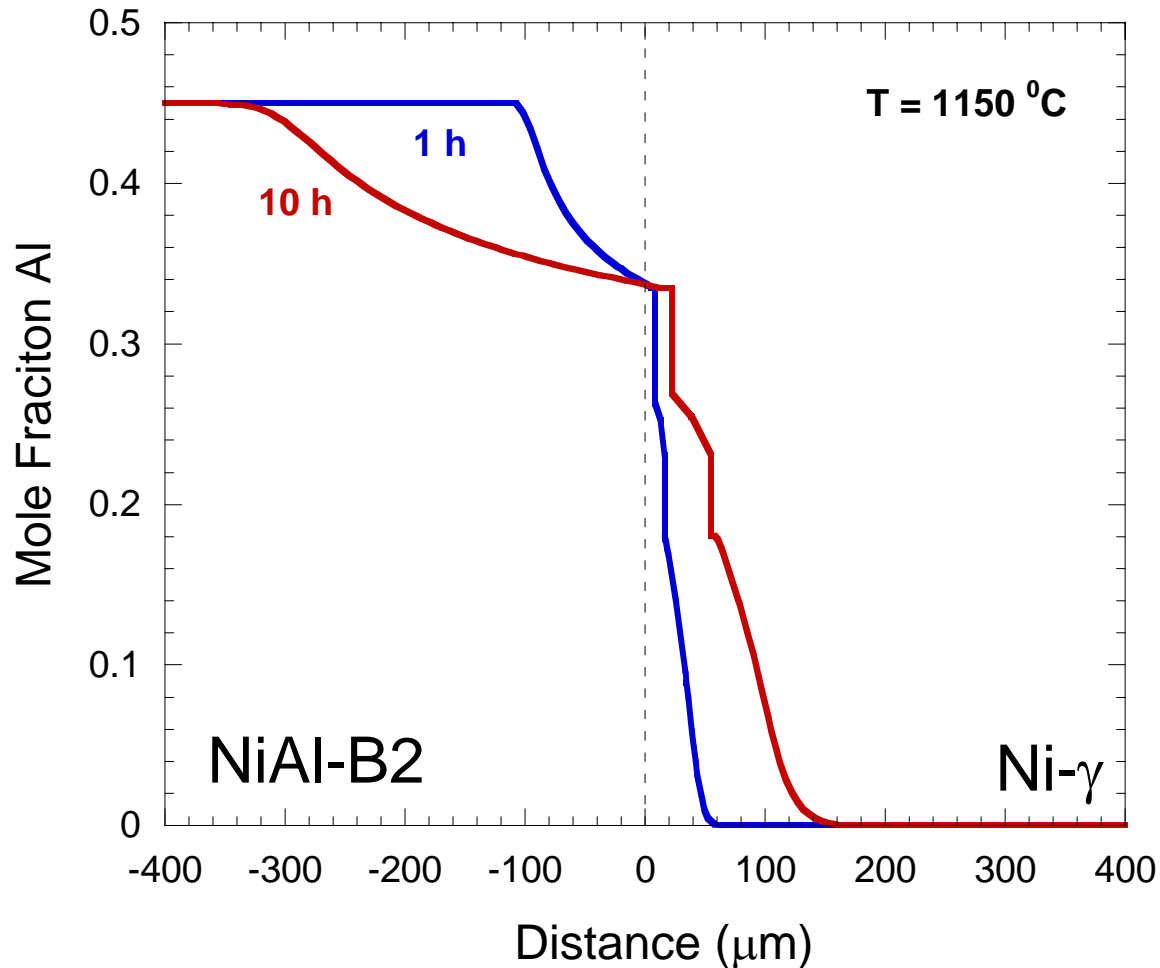
NiAl (B2) at 1000 °C



# *Features the B2 model must reproduce*

- Activation energy
  - Does not depend on composition in the range  $0.46 < x_{\text{Ni}} < 0.53$ : constant  $\approx 290$  kJ/mol
  - Decreases with increasing Ni for  $x_{\text{Ni}} > 0.53$
- Ni self diffusion
  - Ni-rich side ( $0.5 < x_{\text{Ni}} < 0.53$ ): increases with increasing Ni composition
  - Al-rich side ( $0.46 < x_{\text{Ni}} < 0.50$ ): remains constant with increasing Ni composition

# *Example: NiAl/Ni at 1150 °C*



# *Summary*

- Order diffusion model developed by Helandar and Agren successfully applied to Ni<sub>3</sub>Al.
- Order diffusion modeling of NiAl-B2 is a greater challenge
  - Need to incorporate vacancies on sublattice model
  - *Does the Darken-Manning eq hold?*