Development of a Diffusion Mobility Database for Cu-In-Se

C. E. Campbell
NIST/Metallurgy Division

Collaborators: T. Anderson (U. Florida), W.K. Kim (Institute of Energy Conversion, U. Delaware) and J.Y. Shen (General Research Institute for Non-ferrous Metals of Beijing, China)

NIST Diffusion Workshop

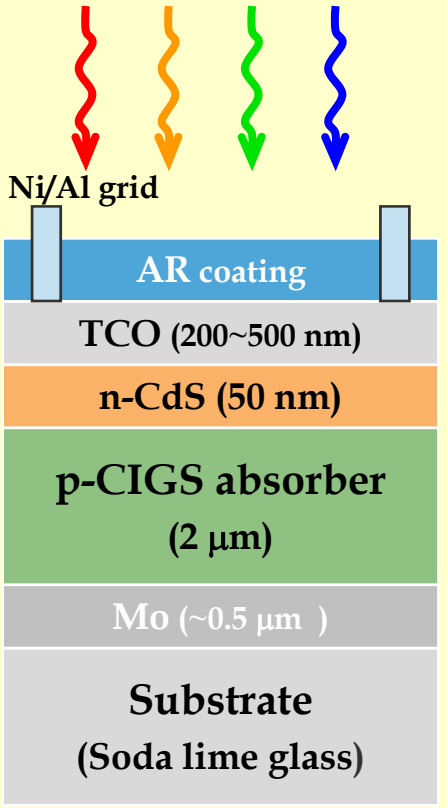
March 25, 2009

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

CIGS Solar Cell

Chalcopyrite α-Cu(InGa)Se_2

- A bilayer Ni/Al grid is used as a front contact material
- Anti-reflection (AR) coating (e.g., MgF2)
- Transparent conducting oxide film: ZnO
- CdS buffer layer (n-type)
- **Polycrystalline CIGS layer**
  - acts as a p-type light absorber
  - forms a p-n junction with CdS
- Back contact electrode: Mo
- Substrate:
  - typically soda lime glass
  - flexible substrates: polymer and metal foils

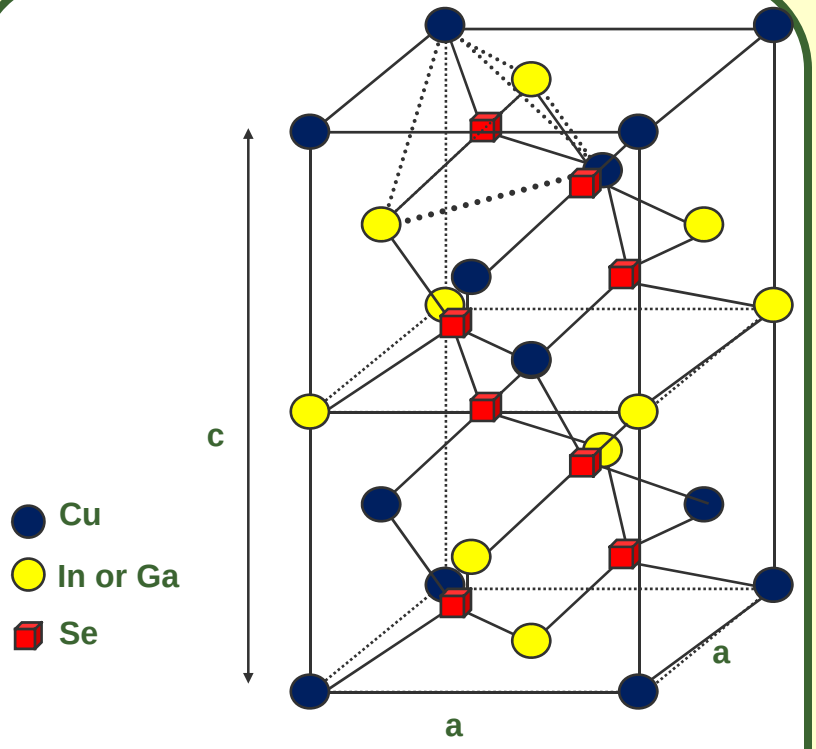


Typical device structure

W. K. Kim , U. Florida, PhD Thesis, 2006.

Chalcopyrite α-$Cu(InGa)Se_2$

- Similar to Zinc-blende structure
- Cu and In are each surrounded by 4 anions (Se)
- Se is surround by 2 Cu and 2 In
- Se deficiency occurs as Cu occupies an interstitial position
- Lattice parameter ratio c/a ≈ 2



Chalcopyrite CIGS structure

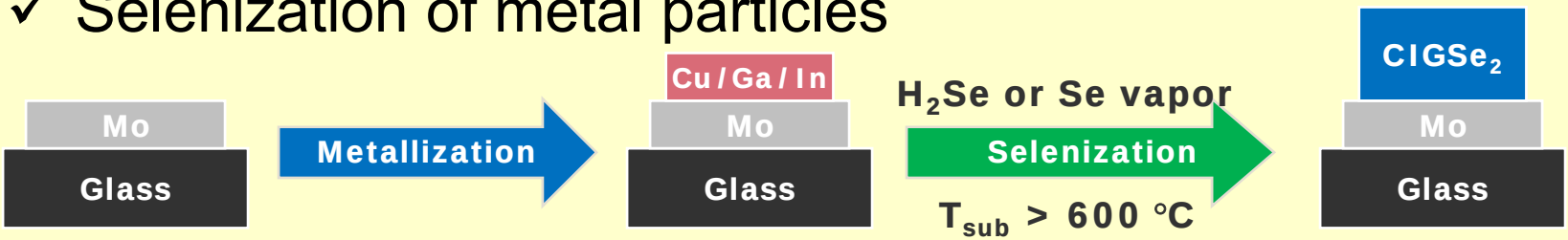
W. K. Kim , U. Florida, PhD Thesis, 2006.

CIGS Processing Routes

- ✓ Co-Deposition of Elements (PVD, MBE etc)
  - High efficiency achieved with this method.

- ✓ Rapid thermal processing of stacked elemental layers

- ✓ Selenization of metal particles



W. K. Kim, NIST Diffusion Workshop, May 2008.

GOAL

- **Need to make CIGS cost-effective need to reduce processing time from ~ 30 min to < 3 min.**

- **Need to develop methodology to predict processing pathways to achieve order magnitude decreases in processing time**

Develop diffusion mobility database for Cu-In-Ga-Se

CALPHAD Approach

Phase Equilibria & Thermodynamics

Experiments
DTA, Metallography,
X-ray Diffraction,
Calorimetry, EMF,
Vapor Pressure

Physics-based
Model Functions
with *Adjustable Parameters*

Theory
Quantum Mechanics,
Statstical Thermodynamics

Parameter
Optimization
for *Thermodynamic Description*

Thermodynamic Database

Diffusion

Experiments
Tracer, Intrinsic,
Chemical (Interdiffusion)

Theory
Atomistic
Calculations

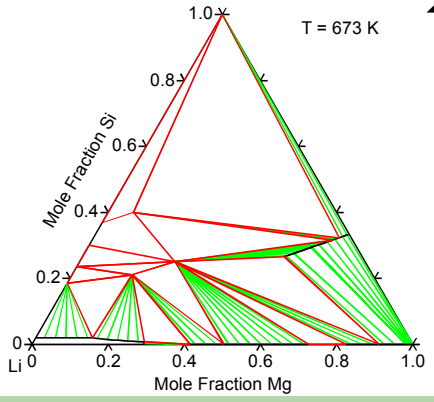
Parameter
Optimization
for *Diffusion Mobility Description*

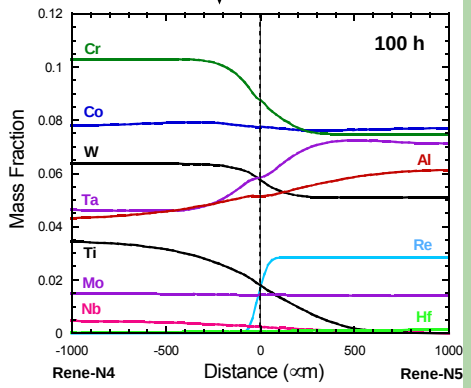
Diffusion Mobility Database

Thermodynamic Factor

Thermodynamic Factor

Applications
Solidification,
Phase Transormation Kinetics,
...





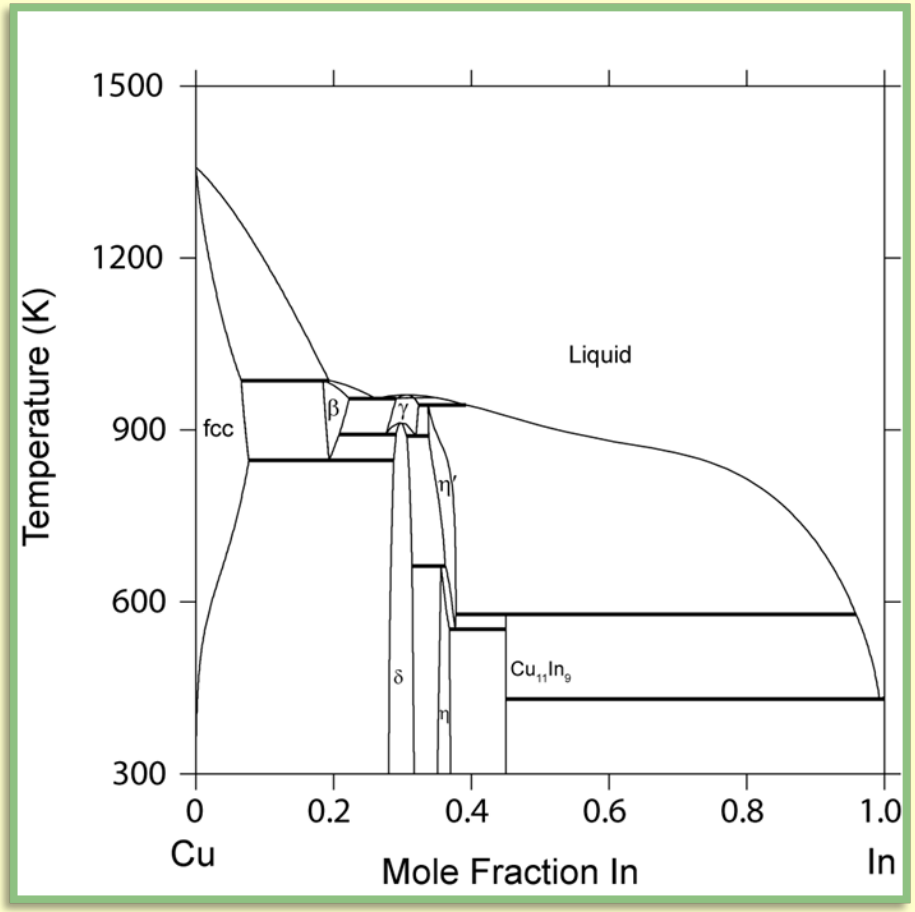
Published thermodynamic assessments

System	Reference
Cu-Ga	Li JB, Ji LN, Liang JK, Zhang Y, Luo J, Li CR, Rao GH. A thermodynamic assessment of the copper-gallium system. Calphad 2008;32:447.
Cu-In	Liu HS, Liu XJ, Cui Y, Wang CP, Ohnuma I, Kainuma ZP, Ishida K. Thermodynamic Assessment of the Cu-In Binary System. Journal of Phase Equilibria 2002;23:409.
Cu-In	Kao CR, Chen S-L, Chen SW, Chang YA. Phase Equilibria of the Cu-In System: II Thermodynamic Assessment and Calculation of Phase Diagram. Journal of Phase Equilibria 1993;14:22.
Cu-In	Hertz J, Aissaoui KE, Bouirden L. A Thermodynamic Optimization of the Cu-In System. Journal of Phase Equilibria 2002;23:473.
Cu-Se	Kim WK. STUDY OF REACTION PATHWAYS AND KINETICS IN $Cu(In_xGa_{1-x})Se_2$ THIN FILM GROWTH. vol. PhD. Gainesville, Fl: University of Florida, 2006.
Ga-Se	Zheng F, Shen JY, Liu YQ, Kim WK, Chu MY, Ider M, Bao XH, Anderson TJ. Thermodynamic optimization of Ga-Se system. Calphad 2008;32:432.
In-Se	Li J-B, Record M-C, Tedanac J-C. A thermodynamic assessment of the In-Se system. ZEITSCHRIFT FUR METALLKUNDE 2003;94:381.
Cu-In-Se	Shen J, Kim WK, Shang S, Chu M, Cao S, Anderson TJ. Thermodynamic description of the ternary compounds in the Cu-In-Se system. Rare metals 2006;25:481.

Cu-In Thermodynamics

- **3 solution phases:**
  - liquid, fcc(Cu) and β (bcc)
- **2 ordered phases:**
  - γ $(Cu)_{0.654}(Cu,In)_{0.115}(In)_{0.231}$
  - η $(Cu)_{0.545}(Cu,In)_{0.122}(In)_{0.333}$
- **3 stoichiometric phases:**
  - δ $(Cu_{0.7}In_{0.3})$,
  - η $(Cu_{0.64}In_{0.36})$
  - $Cu_{11}In_9$

Thermodynamics by Shen and Kim 2006



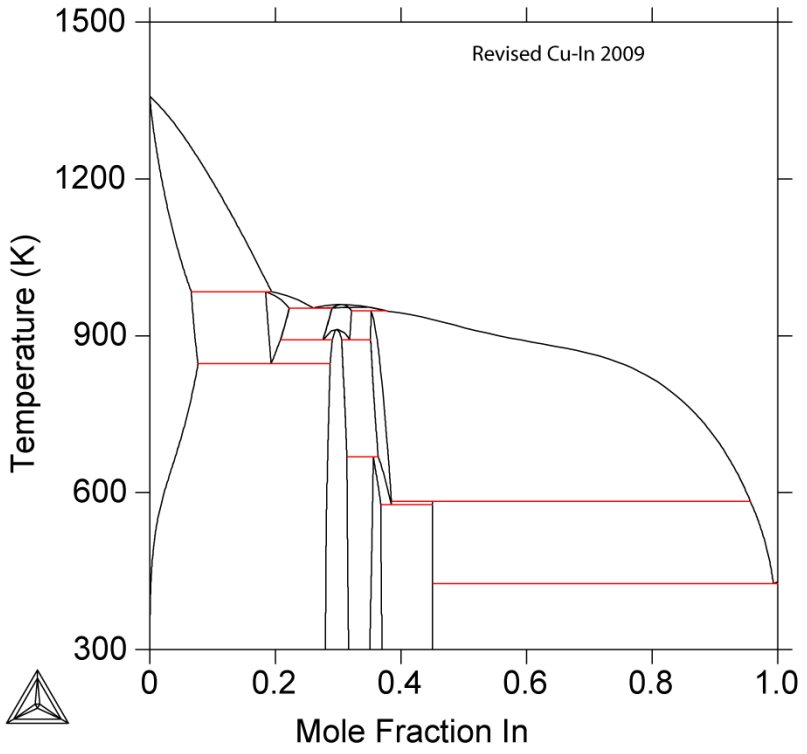
η phase modified for diffusion modeling and did not extended to ternary system → η (Cu,Va) (Cu) (In)

Cu-In Thermodynamics

Revised Description

- **3 solution phases:**
  - liquid, fcc(Cu) and β (bcc)
- **2 ordered phases:**
  - γ $(Cu)_{0.654}(Cu,In)_{0.115}(In)_{0.231}$
  - η $(Cu)_{0.545}(Cu,In)_{0.122}(In)_{0.333}$
- **3 stoichiometric phases:**
  - δ $(Cu_{0.7}In_{0.3})$,
  - η $(Cu_{0.64}In_{0.36})$
  - $Cu_{11}In_9$

Thermodynamics by Shen and Kim 2006

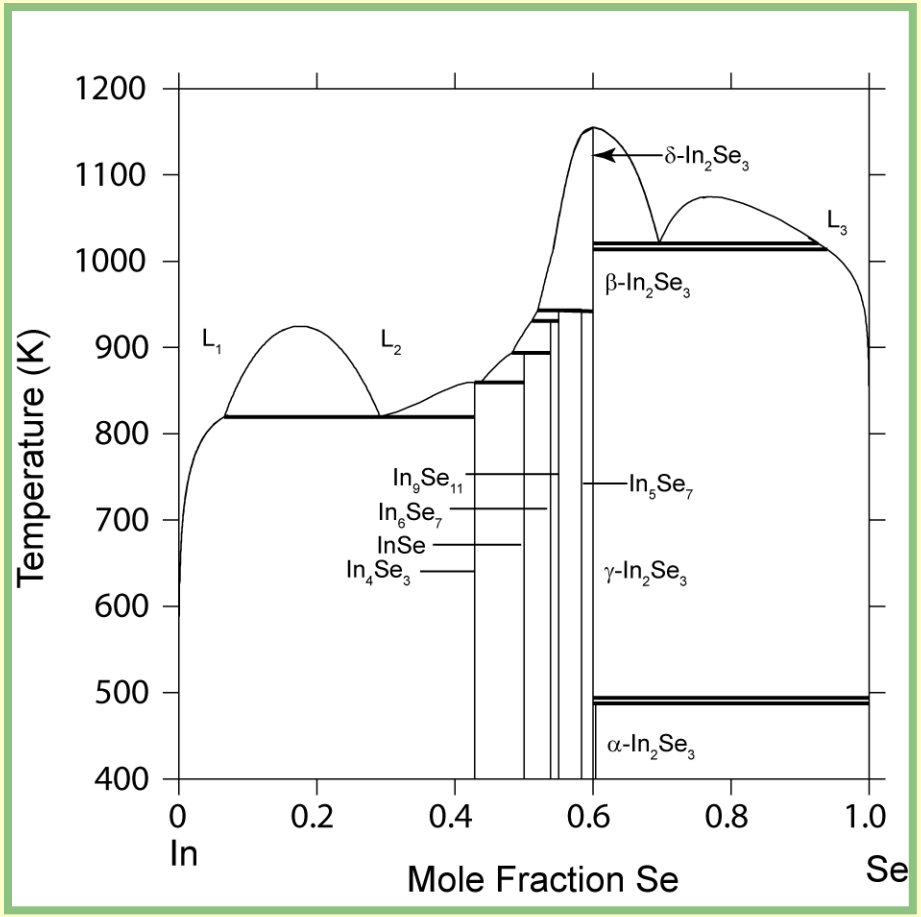


η phase modified for diffusion modeling and did not extended to ternary system → η (Cu,Va) (Cu) (In)

In-SeThermodynamics

2 solution phases (Se and In)

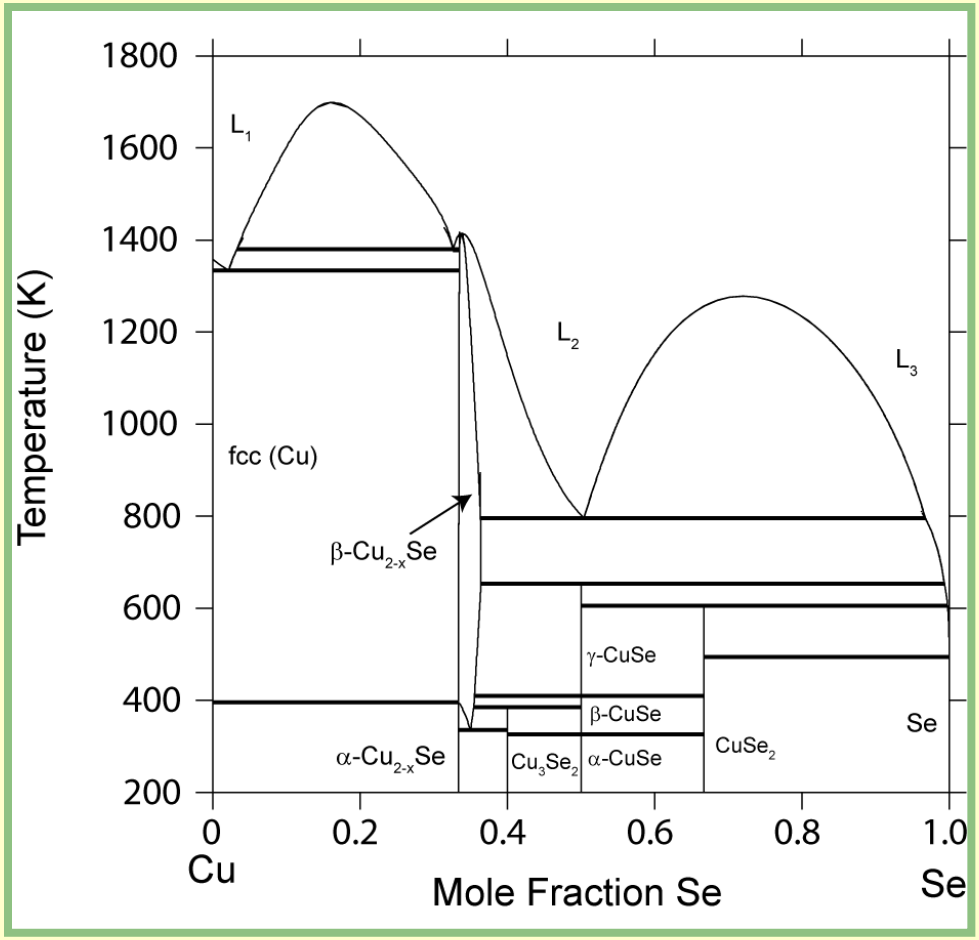
- 1 ionic liquid
- 6 stoichiometric phases
  - In_4Se_3,
  - InSe,
  - In_6Se_7,
  - In_9Se_{11},
  - In_5Se_7
  - polymorphic In_2Se_3 (α, β, γ, and δ)



Thermodynamics by Shen and Kim 2006

Cu-Se Thermodynamics

- 2 solution phases:
  - fcc(Cu) and Se
- 1 ionic liquid
- 1 ordered phases:
  - Cu_2Se with 2 polymorphs (α and β)
- 3 stoichiometric phases:
  - Cu_3Se_2
  - CuSe (α, β, γ)
  - $CuSe_2$

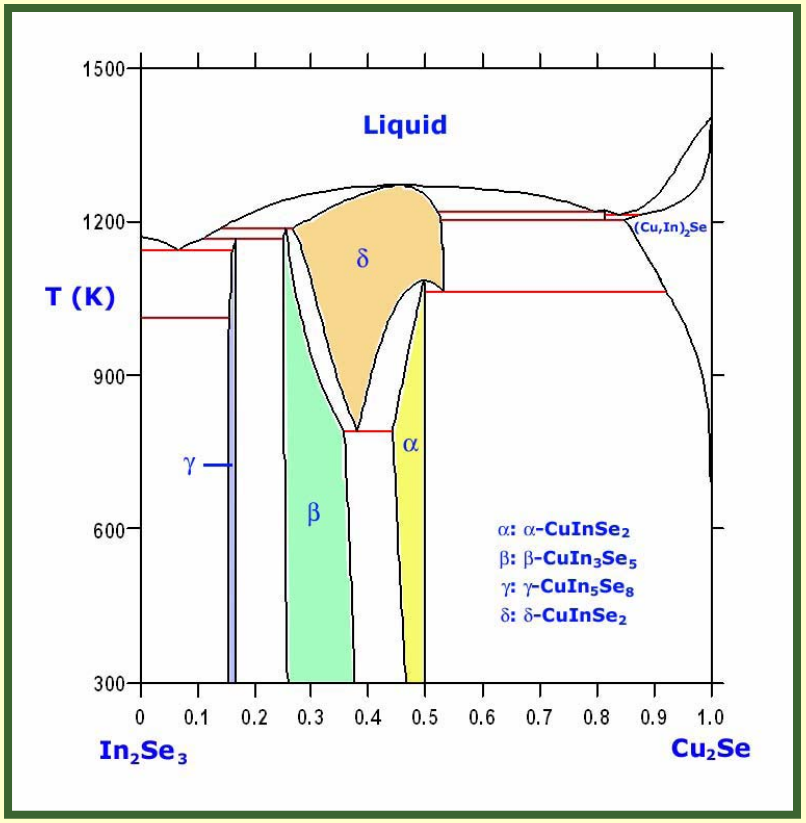


Thermodynamics by Shen and Kim 2006

Cu-In-Se

Ternary Phases

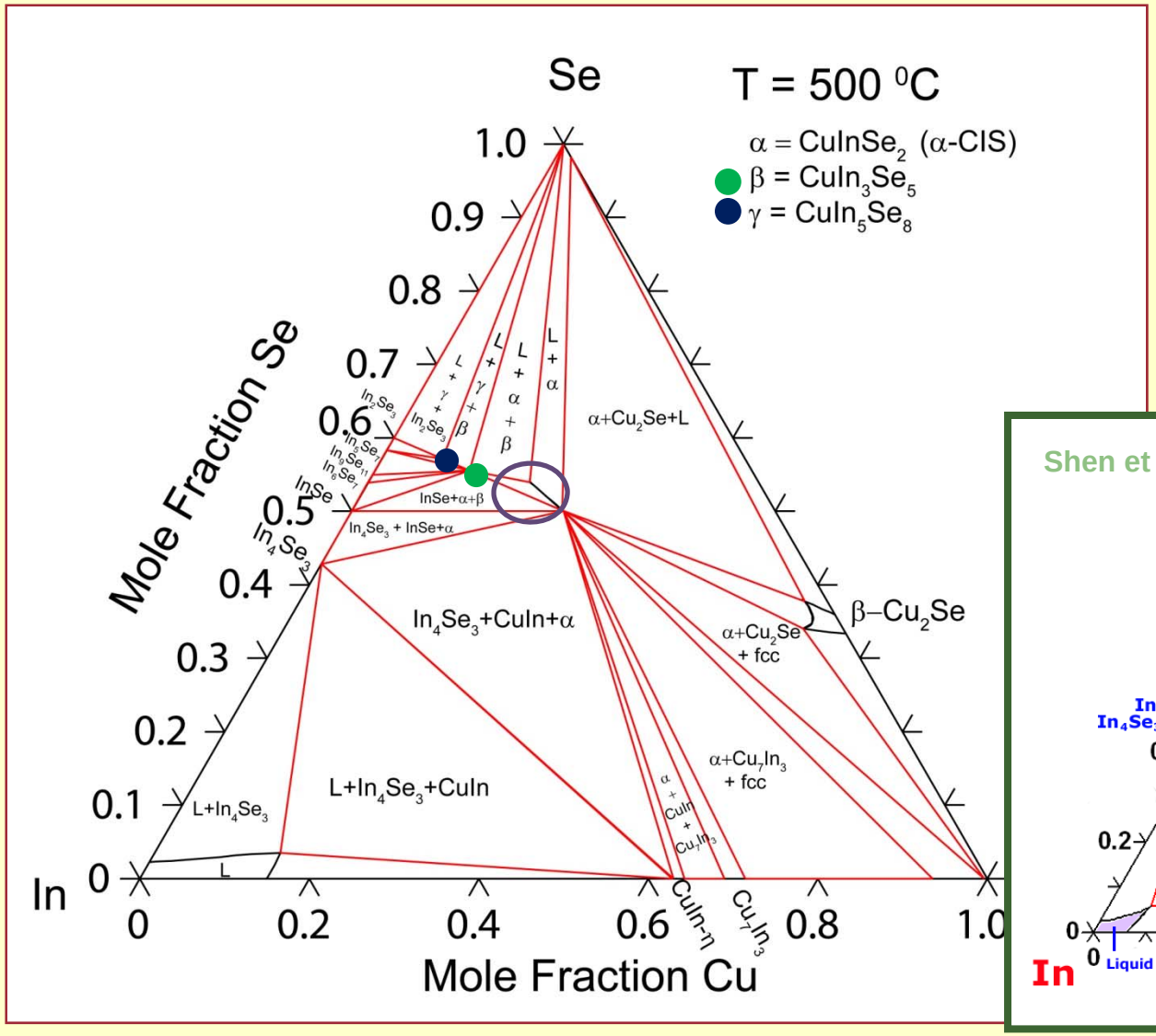
- 1 Ionic Liquid (Cu+1, In+3) (Se-2, Va, Se)
- α $CuInSe_2$ (Cu%,In,Va)(Cu,In%,Va)Se_2 (Chalcopyrite)
- δ $CuInSe_2$ $(Cu\%,In,Va)_2$ Se $(Se,Va)_2$ (Sphalerite)
- β $CuIn_3Se_5$ (Cu%,In,Va) $(Cu,In,Va)_3Se_5$ (Defect Chalcopyrite)
- γ $CuIn_5Se_8$ (Cu%,In,Va) $(Cu,In\%,Va)_5$ Se_8
- β Cu_2Se (Cu,Va) Se (Cu,In)

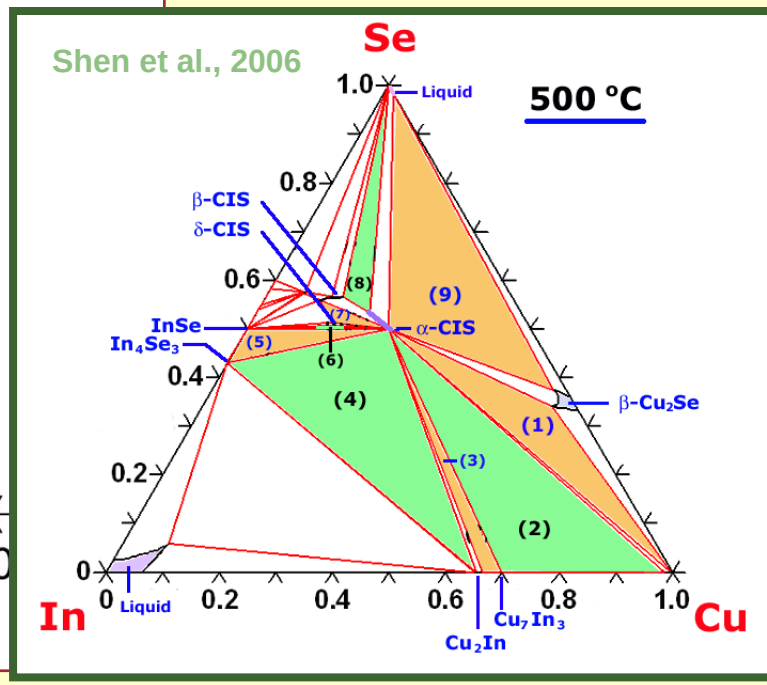


β and γ phases are treated as stoichiometric phases for the initial diffusion modeling

Thermodynamics by Shen and Kim 2006

Cu-In-Se Thermodynamics





Diffusion Mobility Descriptions

- **Inputs:**
  - **Thermodynamics (CALPHAD approach)**
  - **Diffusion experiments (unary, binary, ternary systems)**
    - **Tracer diffusivity,**
    - **Intrinsic diffusivity,**
    - **Interdiffusion coefficients/Marker motion**
- **Optimize value of mobilities, M_i, for all binaries consistent with available data**
  - **Composition and Temperature-dependent**
  - **Consistent with estimates of Metastable end members e.g., FCC W**
  - **Optimized using code, DICTRA (Parrot)**

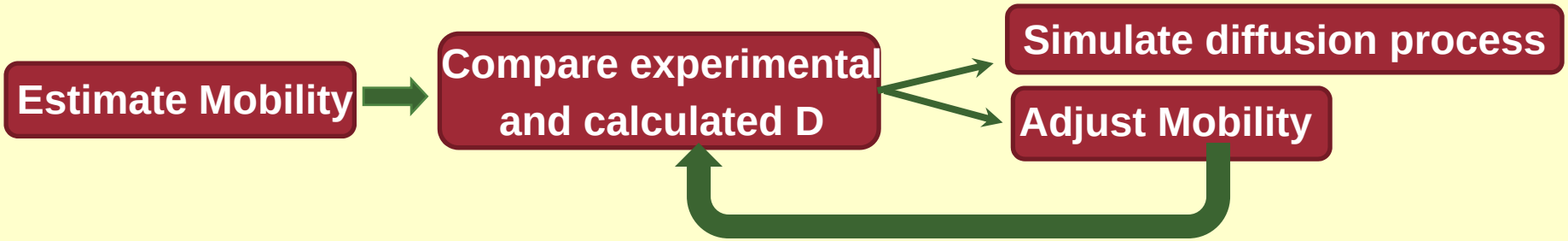
$$M_i = \frac{M_i^{\circ}}{RT}\exp\left(\frac{-\Delta Q_i^*}{RT}\right) \text{ where } \Delta Q_i^* = f(c_i, T)$$

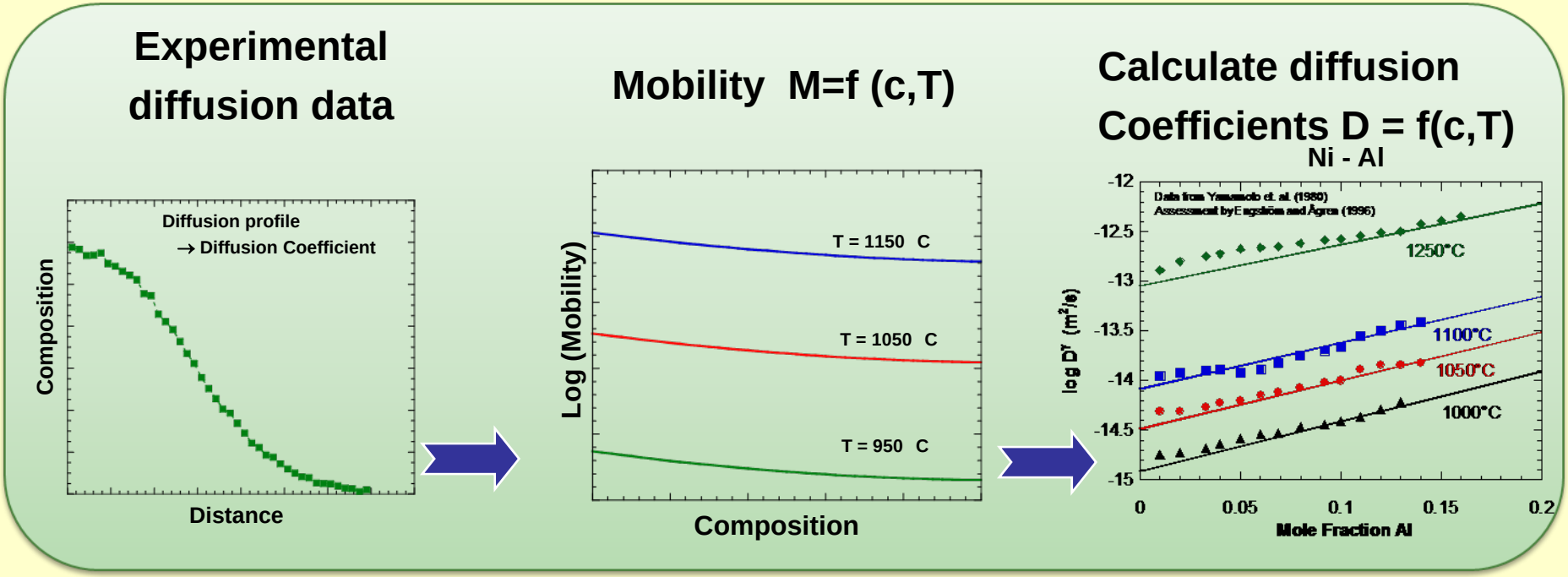
M_i^0 **is exponentially dependent on composition** $M_i = \frac{1}{RT}\exp\left(\frac{\Delta Q_i^*}{RT}\right)$

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

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

Assessment of Diffusion Mobilities





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

For a binary: $Q_i^{\phi} = c_i Q_i^i + c_j Q_i^j + c_i c_j \left(A_i^{i,j} + (c_i - c_j) B_i^{i,j} + (c_i - c_j)^2 C_i^{i,j} + \ldots\right)$

Diffusion Modeling Challenges

- Stoichiometric compounds
- Ternary intermetallic phases
- Anisotropic crystal structures

- Lots of missing data

- Many reactions are promoted by epitaxy: vacancy-driven diffusion is not the dominate diffusion mechanism.

- $D_{eff} = D_{bulk} + D_{stress} + D_{gb} + D_{ele}$

Disordered Phases: FCC

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

- **Cu self diffusion and fcc-In self diffusion taken from previous assessment work.**
- **Cu-In parameter evaluated based on experimental work.**
- **Self diffusion for fcc Se based on diffusion correlations of Brown and Ashby (after calculating a metastable fcc melting temperature for Se)**

$$\Delta^{fcc}Q_{Cu}^* = x_{Cu}Q_{Cu}^{Cu} + x_{In}Q_{Cu}^{In} + x_{Se}Q_{Cu}^{Se} + x_{Cu}x_{In}Q_{Cu}^{Cu,In}$$
$$\Delta^{fcc}Q_{In}^* = x_{Cu}Q_{In}^{Cu} + x_{In}Q_{In}^{In} + x_{Se}Q_{In}^{Se} + x_{Cu}x_{In}Q_{In}^{Cu,In}$$
$$\Delta^{fcc}Q_{Se}^* = x_{Cu}Q_{Se}^{Cu} + x_{In}Q_{Se}^{In} + x_{Se}Q_{Se}^{Se}$$

Both Se and In have anisotropic crystal structures.

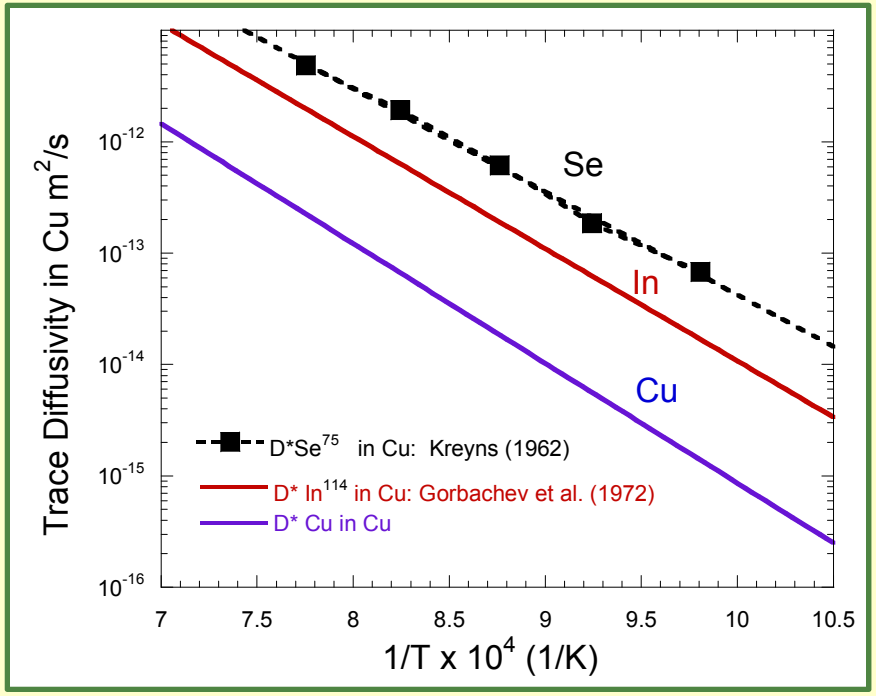
- **Use average values or value for the fastest diffusion directions.**

Disordered Parameters

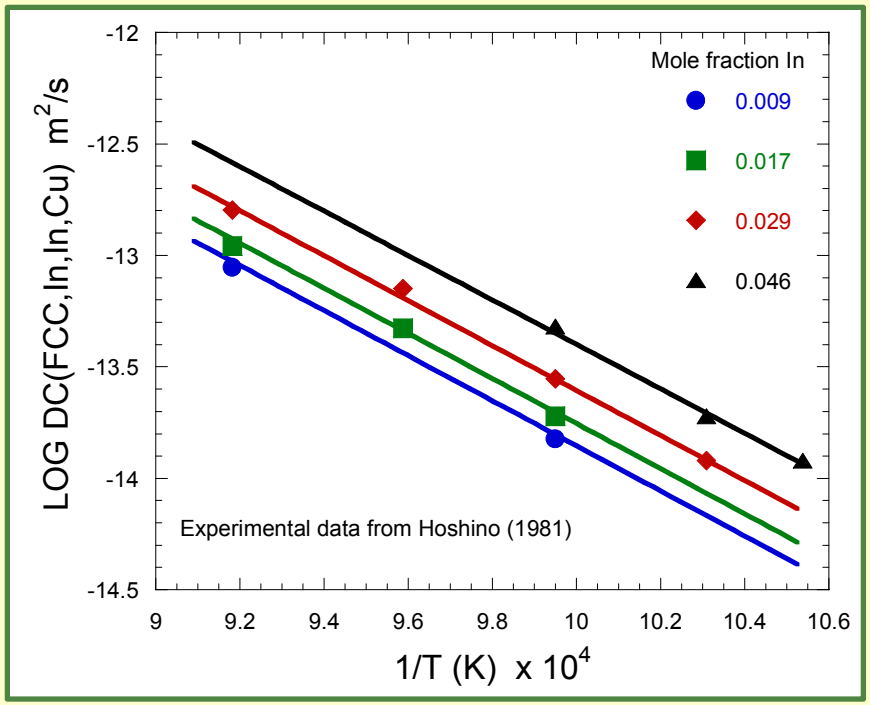
Parameter	Value	Reference
${}^{fcc}Q_{Cu}^{Cu}$	-205872+R*T*LN(4.889e-5)	[Ghosh, 2001]
${}^{fcc}Q_{Cu}^{In}$	-120904+R*T*LN(8.3e-5)	This work
${}^{fcc}Q_{Cu}^{Se}$	-120904+R*T*LN(8.3e-5)	This work (treat like In)
${}^{fcc}Q_{Cu}^{Cu,In}$	+691337-346*T	This work
${}^{fcc}Q_{In}^{Cu}$	-193000+R*T*LN(1.3e-4)	This work (based on [Hoshino K, 1981,1982])
${}^{fcc}Q_{In}^{In}$	-111000+R*T*LN(4.47e-4)	[Ghosh, 1998]
${}^{fcc}Q_{In}^{Se}$	-193000+R*T*LN(1.3e-4)	This work (treat like Cu in fcc-In)
${}^{fcc}Q_{In}^{Cu,In}$	+100405	This work
${}^{fcc}Q_{Se}^{Cu}$	-177187+R*T*(7.6e-5)	This work (based on [Kreyns, 1962])
${}^{fcc}Q_{Se}^{In}$	-177187+R*T*(7.6e-5)	This work Treat like Se in fcc-Cu
${}^{fcc}Q_{Se}^{Se}$	-47566 +R*T*LN(1.0e-5)	This work (Brown Ashby correlation)
${}^{In-bct}Q_{In}^{In}$	-78240+R*T*LN(3.2e-4)	This work (based on [Dickey, 1959])
${}^{tri}Q_{Se}^{Se}$	-115822+R*T*LN(8.2e-7)	This work (based on [Günther, 1985])
${}^{tri}Q_{In}^{Se}$	-7400+R*T*LN(5.6e-10)	[Akhundov, 1958]

Diffusion in FCC

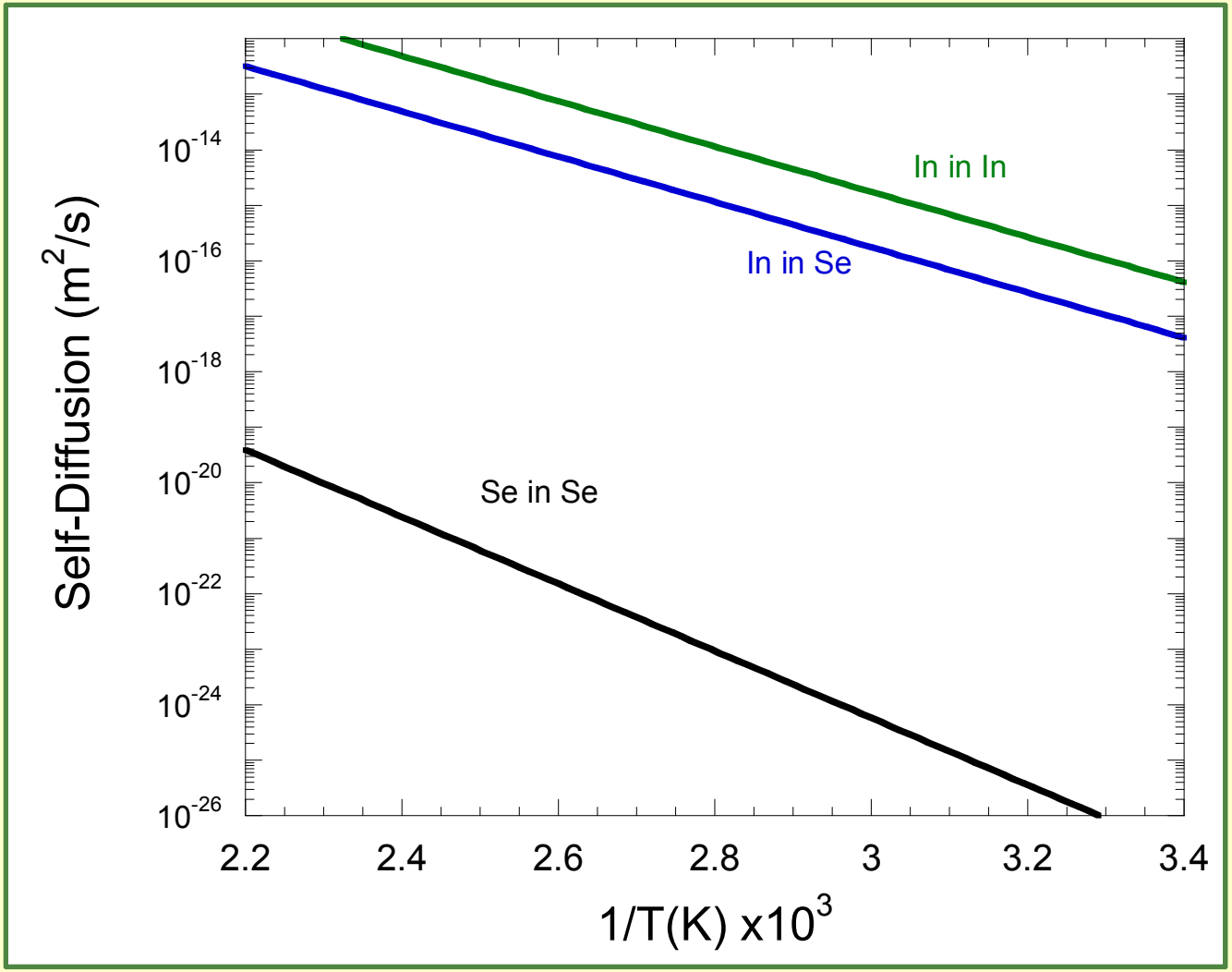
Tracer Diffusivity



Interdiffusion



In and Se tracer diffusivity



Modeling of Stoichiometric Intermetallic Phases

- Generally only a single interdiffusion coefficient available.
- Model with no composition dependence; all the parameters are set equal.
- Using "GENERAL" diffusion model in DICTRA
  - Mobilities on the individual sublattices are summed.
  - Example: $(A,B)(A,B)_2$
    - $M(PHASE, A\#1) = \left(y'_A y''^{\,A}_B M'_{A:B} + y'_B y''^{\,A}_A M'_{B:A}\right)\frac{y'_A}{RT}$
    - M(Phase,A)=M(PHASE,A#1)+M(PHASE,A#2)

$$D^*_A = \left(y'_A M'_A + y'_A M''_A\right)\frac{RT}{u(A)}$$

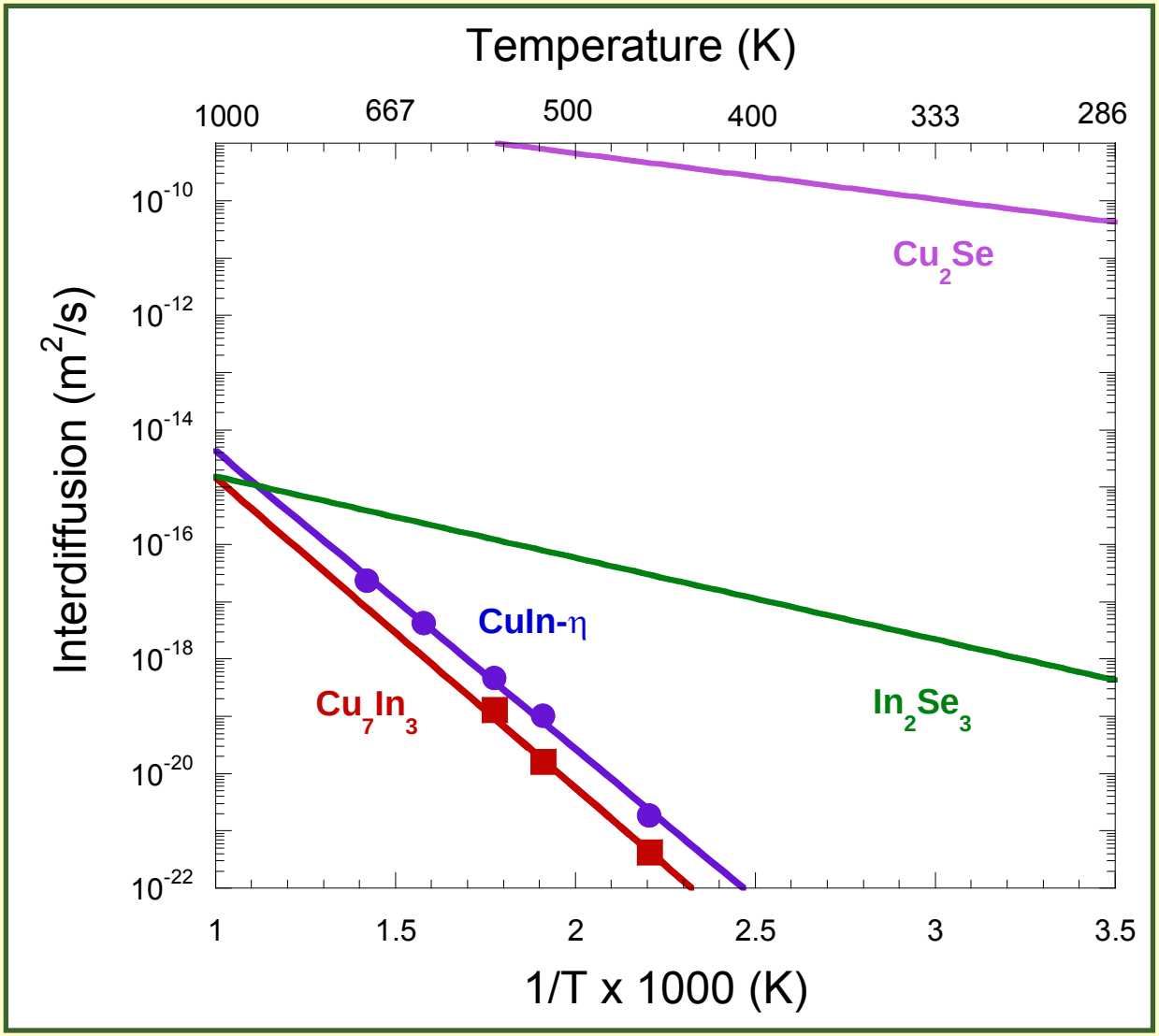
- where *u(A)*= total number of atoms of A.

Applied to Cu-In: δ ($Cu_{0.7}In_{0.3}$), η (CuIn) and $Cu_{11}In_9$

In-Se: In_4Se_3, InSe, In_6Se_7, In_9Se_{11}, In_5Se_7 and the polymorphic In_2Se_3

Cu-Se: Cu_3Se_2 CuSe (α, β, γ) Cu_2Se

Comparison of Interdiffusion in Various Intermetallics in Cu-In-Se



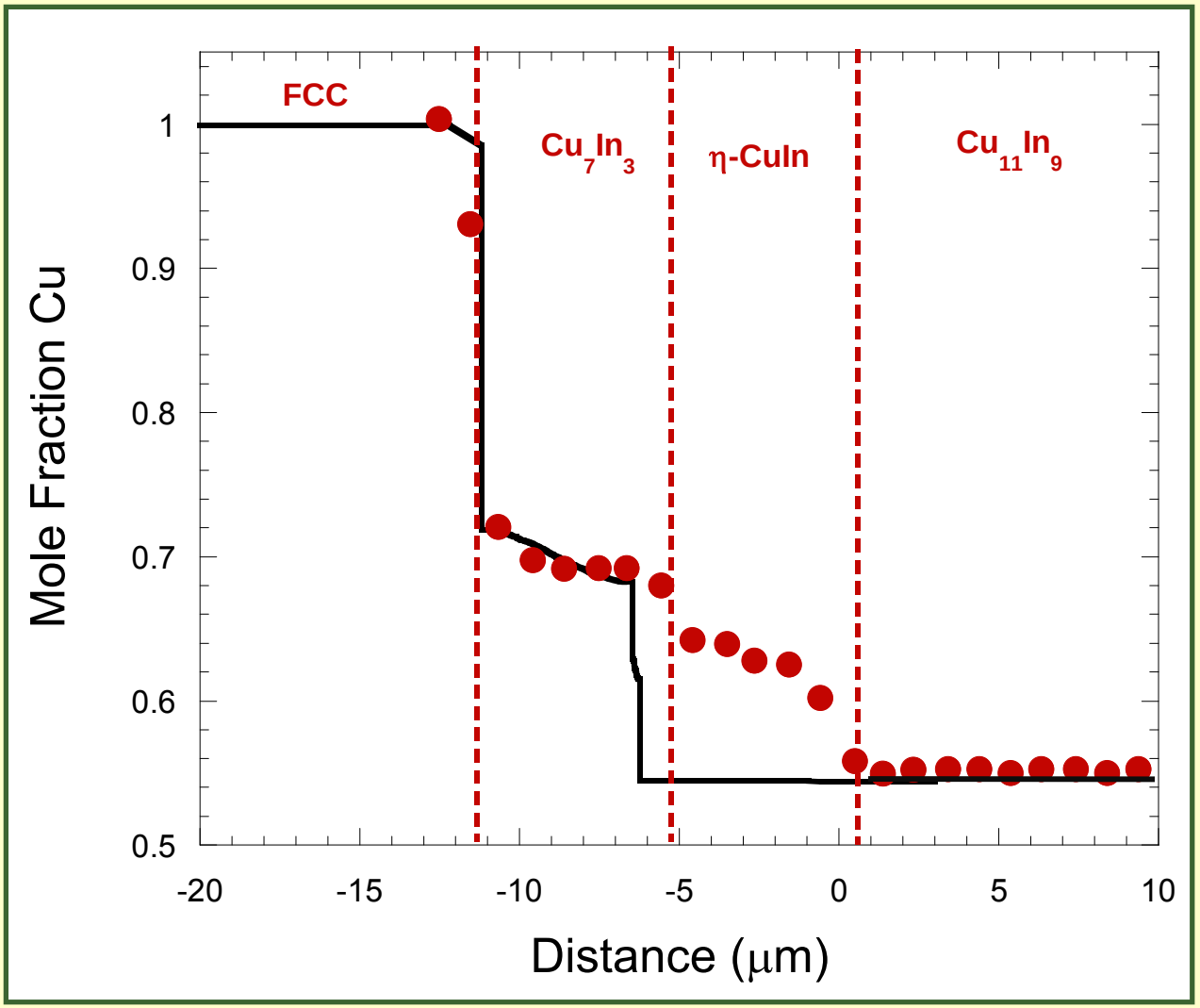
$MQ(Cu_7In_3)$=
-105000+R*T*LN(1.0e-9)

MQ(CuIn-η)=
-108700+R*T*LN(2.0e-10)

$MQ(In_2Se_3)$=
-27245+R*T*LN(4.1e-14)

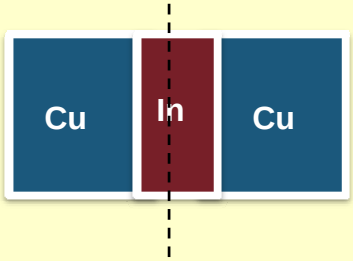
$MQ(Cu_2Se)$=
-15359+R*T*LN(2.7e-08)

Cu/In/Cu Solder Joints at 290 °C for 16 days



● Sommadossi, et al. 2003

Time = 0 s



Note : Diffusion in $Cu_{11}In_9$ must be adjusted.

Diffusion Model for Ternary Intermetallics

α-$CuInSe_2$: (Cu%,In,Va)(Cu,In%,Va)Se_2

- **Diffusion via Cu vacancies dominates. (Dagen 1992)**

$$D_{Cu}^{*} = \frac{RT}{u_{Cu}}\left(y'_{Cu}M'_{Cu} + y''_{Cu}M''_{Cu}\right)$$

$$D_{In}^{*} = \frac{RT}{u_{Cu}}\left(y'_{In}M'_{In} + y''_{In}M''_{In}\right)$$

$$D_{Se}^{*} = \frac{RT}{u_{Se}}\left(M'''_{Se}\right)$$

Similar approach applied to:

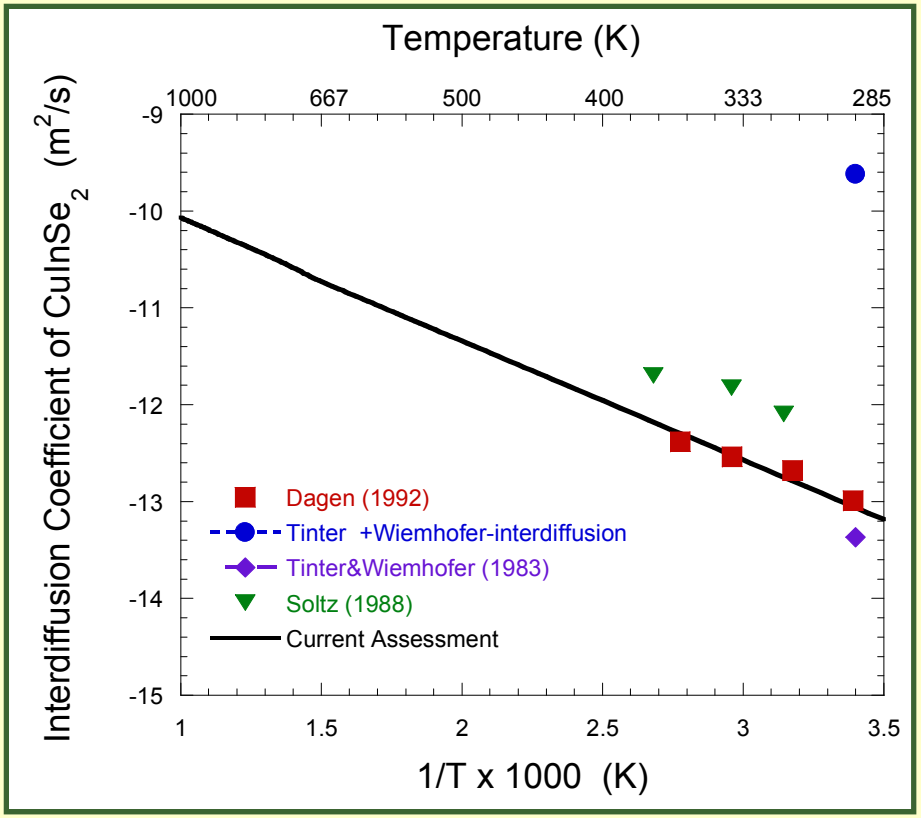
$\delta CuInSe_2$ $(Cu\%,In,Va)_2$ Se $(Se,Va)_2$

β $CuIn_3Se_5$ $(Cu\%,In,Va)(Cu,In,Va)_3Se_5$

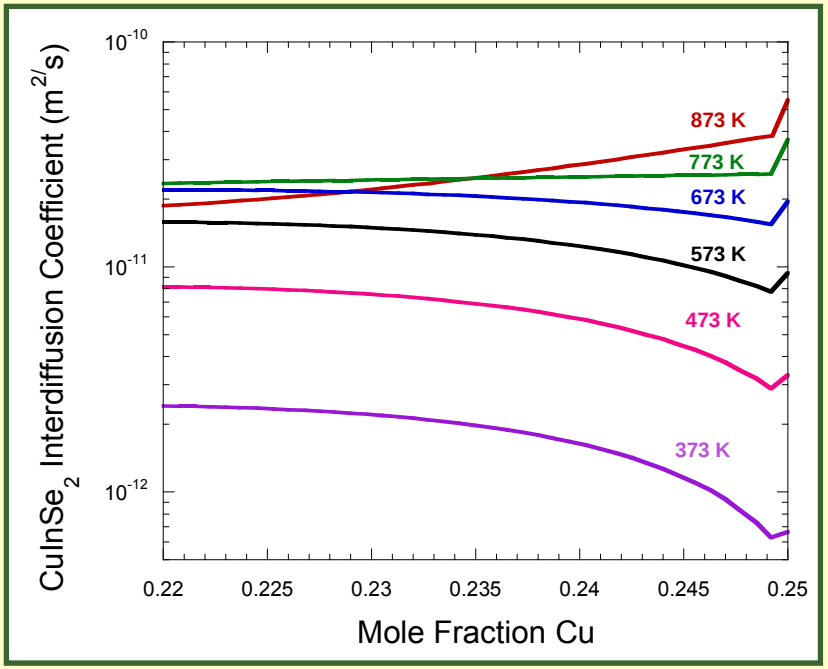
γ $CuIn_5Se_8$ $(Cu\%,In,Va)$ $(Cu,In\%,Va)_5$ Se_8

Interdiffusion Coefficients in α-$CuInSe_2$

Measured and Calculated Temperature Dependence



Predicted Composition Dependence



α-$CuInSe_2$ diffusion mobilities modeled using general model

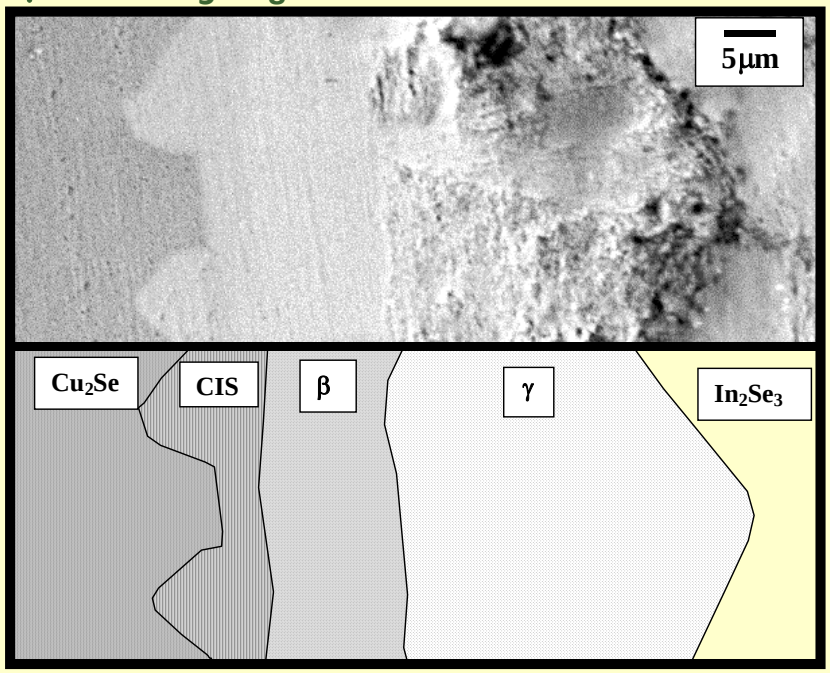
Q = -25050 J/mole; M_0 = 9.975e-10 m^2/s

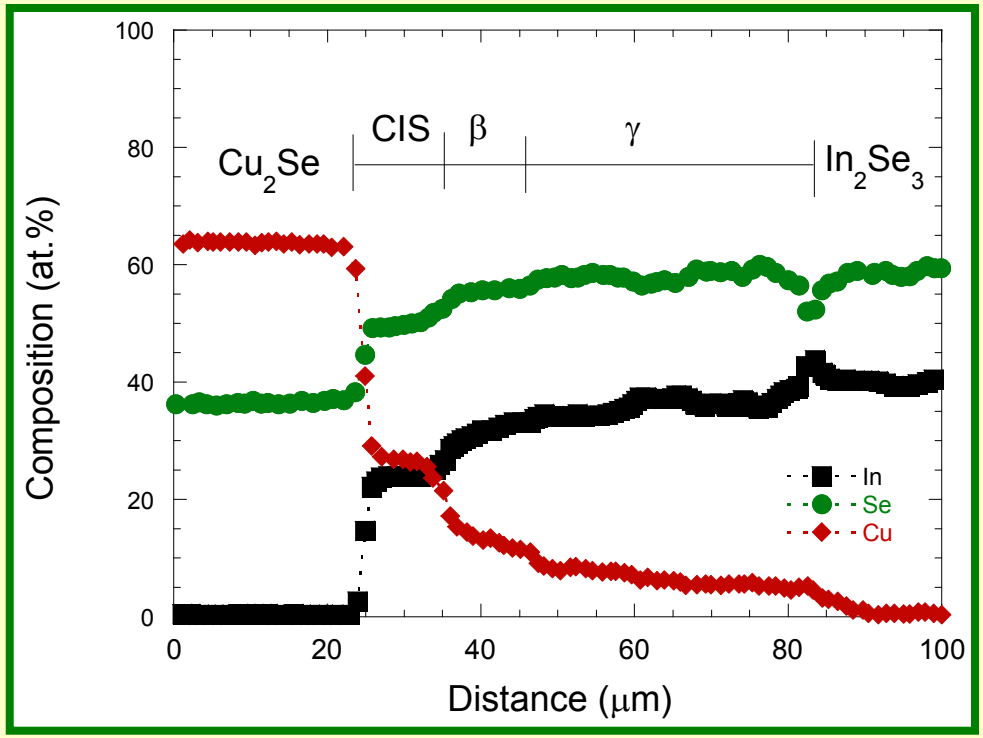
Cu_2Se/In_2Se_3 Diffusion Couple at 550 °C for 1.5 h

CIS = $CuInSe_2$

β= defect chacopyrite ($CuIn_3Se_5$)

γ = $CuIn_5Se_8$





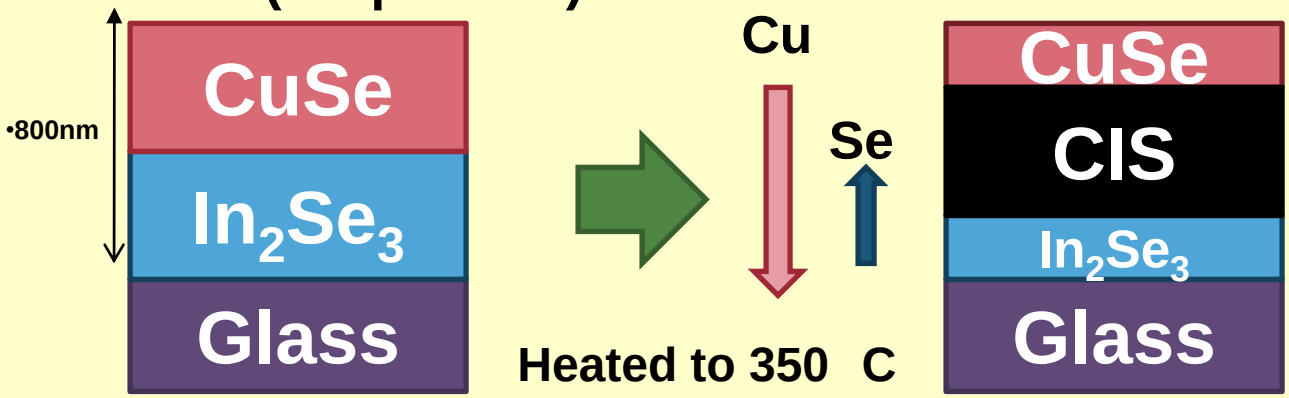
- Estimate of In diffusion in Cu_2Se =4.2x10^{-10} m^2/s
- Defect structure leads to rapid diffusion.
- In diffuses via an ionic lattice diffusion through the Cu vacancy sites on Cu_2Se

Park et. al. , J. Appl. Phys. 87 (2000) 3683.

Type of Reactions to Simulate

Kim et. al., *J. Phys. Chem. Solids*, 2005. : CuSe/In_2Se_3 precursor

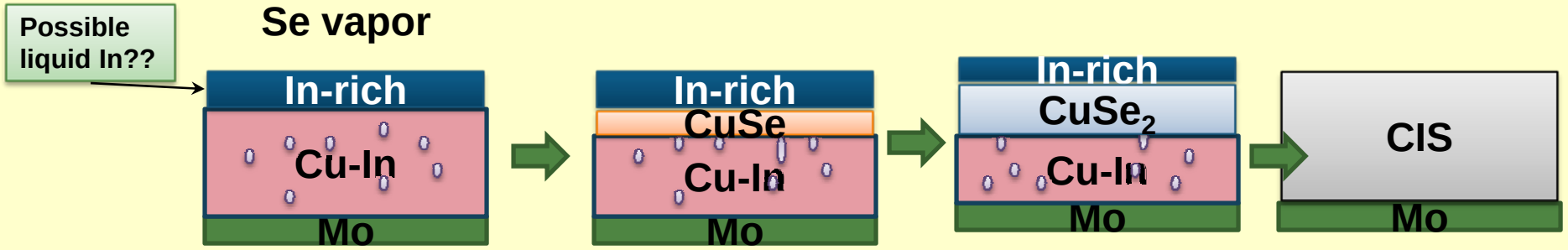
CIS + Se (evaporated)



Activation energy 162 +/- 5 KJ/mol (parabolic model)

J. Crystal Growth , 2005. : Cu/In selenization

CuSe +In + *n*Se (vapor) → CuSe2 +In +*n*Se (vapor) → CIS



Activation energy 124 +/- 19 kJ/mol (Avrami model); 100 +/- 14 kJ/mol parabolic

Conclusions

- **Significant challenges**
  - ✓ **Lack of data**
    - Use diffusion correlations
    - Extract activation energies
    - Estimate from bulk diffusion couples
  - ✓ **Anisotropic crystal structures**
    - Treat average diffusion (assume polycrystalline)
  - ✓ **Diffusion models**
    - Models have developed and are in the process of being implemented
  - ✓ **Enhanced diffusion due to coherency relations**
    - Mechanisms available to adjust thermodynamics and diffusion activation energies

These challenges can be overcome