Challenges in Creating a Pure Element Tracer Diffusion Database

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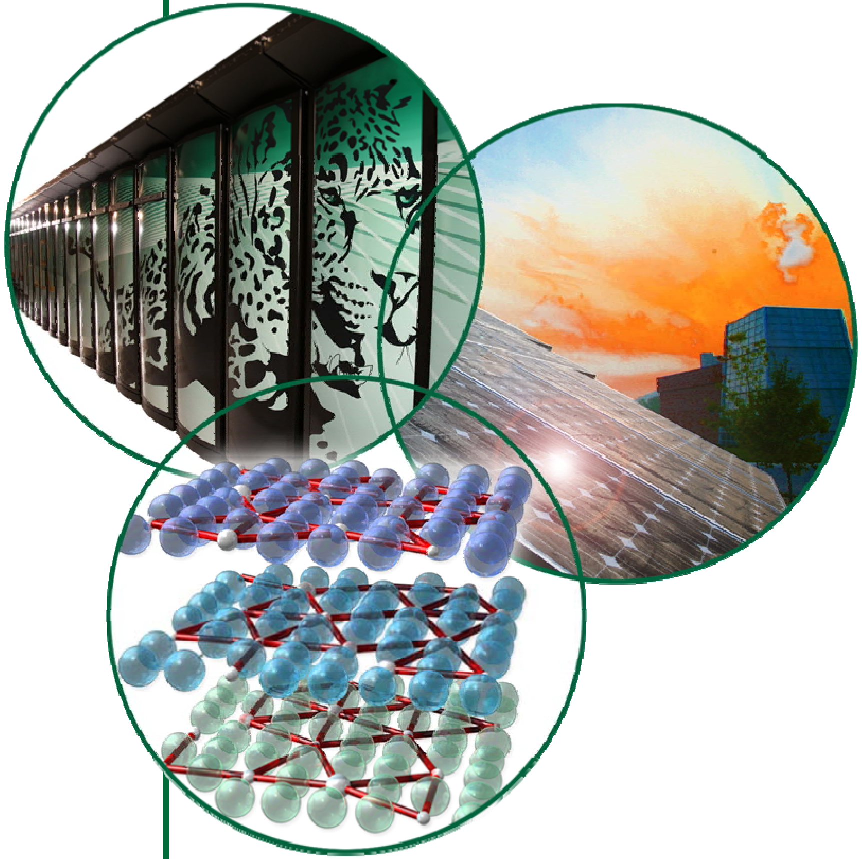

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U.S. DEPARTMENT OF ENERGY

THE UNIVERSITY of TENNESSEE UT

OAK RIDGE NATIONAL LABORATORY
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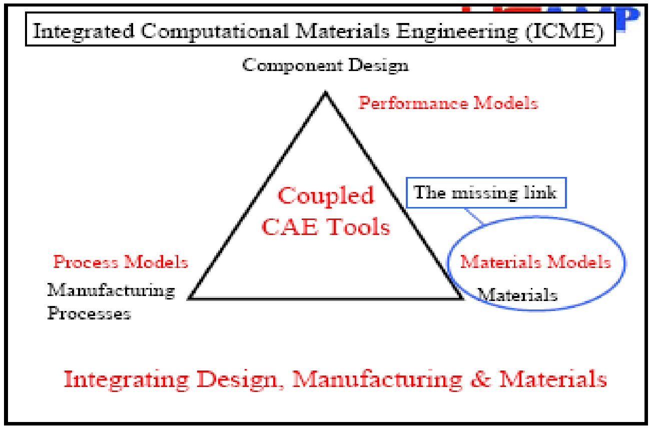
Outline

- Diffusion Databases: Key questions
- Technical issues
  - Formalisms: Many!
  - Data for databases: Many!
  - Content of database: Types of diffusion data
  - Approach for constructing db's: Calphad only?
  - Modeling/software: long, exciting road ahead
- Tracer diffusion databases
  - Past Concerns, Current Approach
  - DOE Isotope Program
  - SIMS Instrumentation challenges
  - Experimental challenges, current efforts

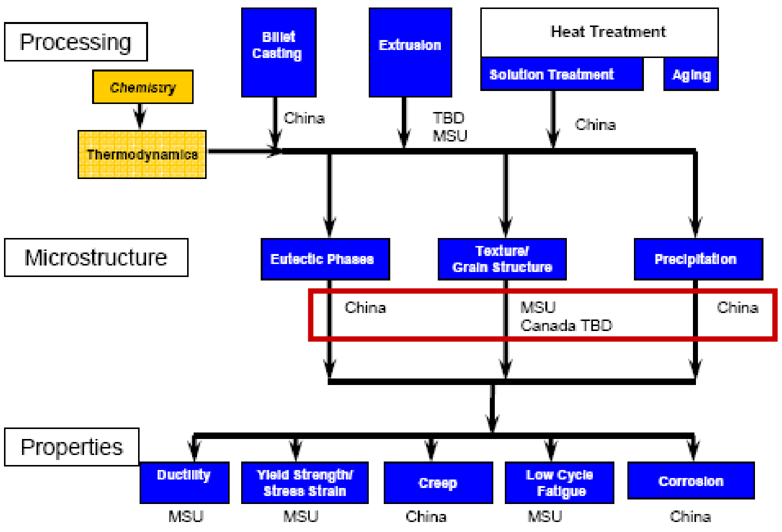
Diffusion databases: Key Questions

- Why do we need these?
  - How is this information used for something useful?
- Who needs these?
  - Industrial applications and partners
  - Basic R&D efforts at universities, labs, etc.
- Who will support the work?
  - Offices within the federal government
    - Commerce (NIST), Energy (ORNL, Argonne, etc.), NSF, Homeland Security, NIH, Transportation, Defense (DARPA, Army, Air Force, etc.)
  - Industry partners
  - Industry/University/Government collaborations
    - Sematech, SRC, Focus Centers, professional organizations, etc.
  - International organizations, multinational partnerships



DOE/US-AMP Mg-ICME program requires thermo & diffusion databases

Extrusion Processing-Structure-Property Diagram



Diffusion Formalisms for Databases

- Mobility
- Phenomenological
- Others
  - Interdiffusion (effective), Jump frequencies, ...

A: “Mobility” Formalism/Database: DICTRA

Lawrence Darken

- Intrinsic flux expression that ignores cross-terms

$$J_k = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial x} = -L_{kk} \frac{\partial \mu_k}{\partial x} = -c_k M_k \frac{\partial \mu_k}{\partial x} \qquad (L_{ki} = 0,\, k \neq i)$$

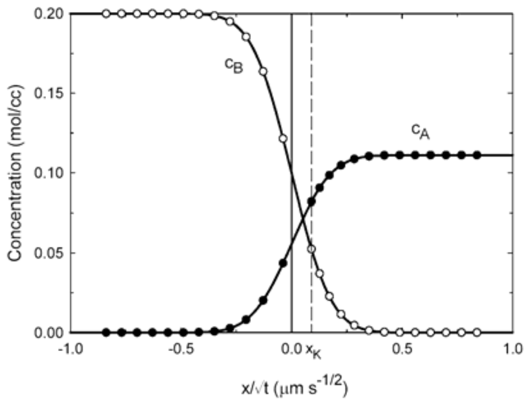
- M_k is known as the “mobility” [Darken 1948]:
  - One unique mobility for each component in a multicomponent system with above assumption
  - Vacancy wind effects included (perhaps artificially) in diagonal terms since off-diagonal phenomenological coefficients ignored

- Multicomponent Darken theory connects mobilities with tracer diffusion coefficients
  - Diffusion coefficients in other frames (e.g., lab frame for interdiffusion) can be obtained from mobilities (or Lkk’s) and thermodynamic information by suitable transformations

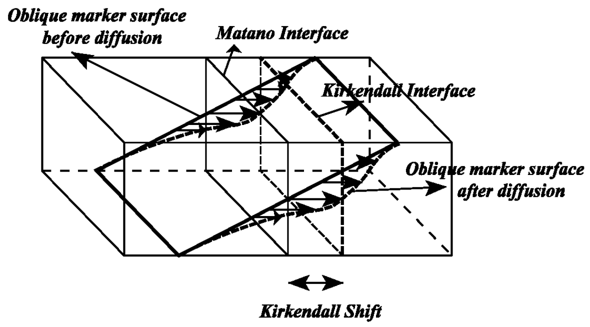
$$L_{kk} = c_k M_k = \frac{c_k D_k^*}{R\,T}$$

Input for Mobility Databases: Diffusion data + thermodynamics

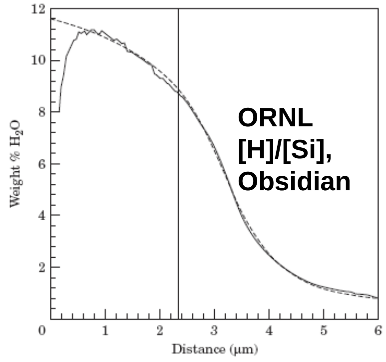
- Interdiffusion Data: Convert to mobilities with thermo
  - Steep concentration gradients, molar volume changes, grain boundary effects, can introduce errors in measurements and subsequent analysis: still manageable
  - Very long annealing times may be needed for improved accuracy i kinetics are slow
    - Very difficult in *compounds* unless solubility range is extended



- Intrinsic Diffusion Data: Convert to mobilities with thermo
  - Require suitable "inert" markers throughout diffusion zone
    - Multiple markers rarely employed except at original "Kirkendall Interface" due to experimental difficulties
  - Vacancy super-saturation (porosity) or under-saturation can caus errors in both analysis



- Tracer Diffusion Data: Directly obtain mobilities
  - Most reliable but use of radioactive tracers is time-consuming and expensive
  - Tracer data using non-radioactive (stable) isotopes not established



B: Phenomenological Formalism: Tracer Database

- Intrinsic fluxes defined in the lattice or Kirkendall frame where driving forces are chemical potential gradients

$$J_k = -\sum_{i=1}^{n-1} L_{ki}^{n}\, grad\, \mu_i \qquad (k = 1, 2, \ldots, n) \qquad\qquad \sum_{k=1}^{n} J_k = -J_v$$

- L_{ki}'s obtained from tracer diffusion database using Manning, Moleko *et al*., or latest theories

$$L_{11} = \frac{X_1}{V} \cdot \frac{Dt_1}{R \cdot T} \cdot \left[1 + \frac{2 \cdot X_1 \cdot Dt_1}{M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)} \right]$$

$$L_{12} = \frac{2 \cdot X_1 \cdot Dt_1 \cdot X_2 \cdot Dt_2}{V \cdot R \cdot T \cdot M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)}$$

- Chemical potentials from Calphad databases

➢ *Tracer diffusion database is independent of thermodynamic database*

➢ *No assumptions other than the usual phenomenological assumption*

Other Formalisms for Databases?

- Interdiffusion
  - Multicomponent version (extension of Fick's Law) with concentration gradients as driving forces

$$J_k = -\sum_{j=1}^{n-1} D_{kj}^{n}\, grad\, c_j$$

    - Using "square-root diffusivity" approach interdiffusion coefficients can always be measured (sufficient solid solubility) (Morral et al.)
  - Effective integrated interdiffusivities (Dayananda et al.)
    - Amenable to databases?

- Jump Frequencies
  - Multicomponent intrinsic flux composed of biased and unbiased fluxes (DeHoff et al.)

$$J_k = 2\alpha_{k+}\lambda c_k \Gamma_k - \frac{1}{6}\lambda^2 \frac{d c_k \Gamma_k}{dx}$$

  - Γ_k are tracer jump frequencies

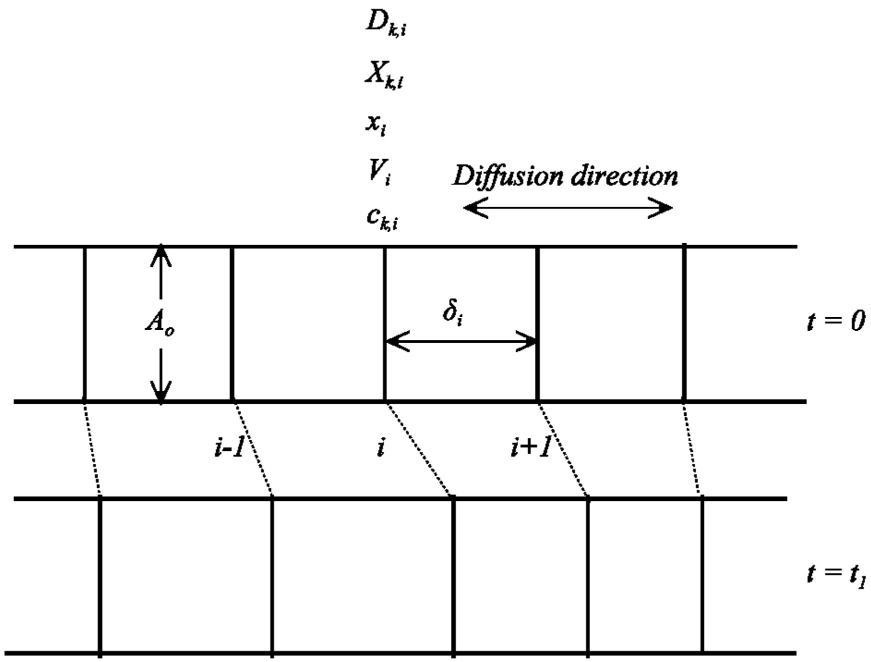
Which Formalism to Use?

- Mobility or Phenomenological Formalism or Others?

Intrinsic Diffusion Simulation for Assessing Diffusion Formalisms

C. Iswaran, Ph.D. Thesis, Univ. of Florida,1993
Kulkarni & DeHoff, Acta Mat 2005

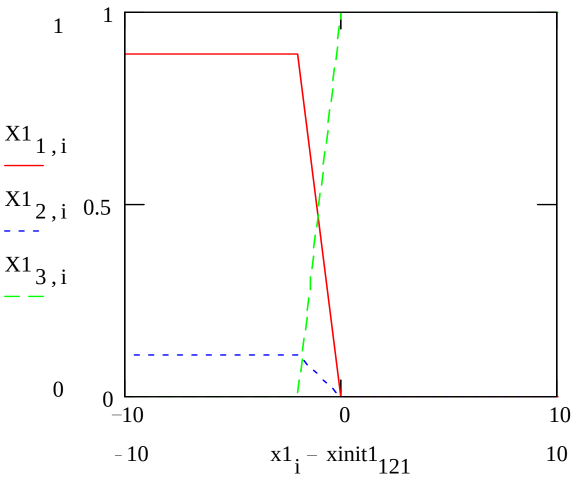
1. Initial concentration distribution for each component
2. Depending upon the formalism, kinetic descriptors as a function of composition, temperature or other variables
3. Thermodynamics of phase, if needed
4. Molar volume as a function of composition



Finite difference method for semi-infinite couples

- **Simple yet effective algorithm**
- **Handles variable molar volumes**
- **Developed in MathCad – user-friendly**
- **Efficient – practical output for a single diffusion couple in less than a minute**
- **Versatile – adaptable to various formalisms**

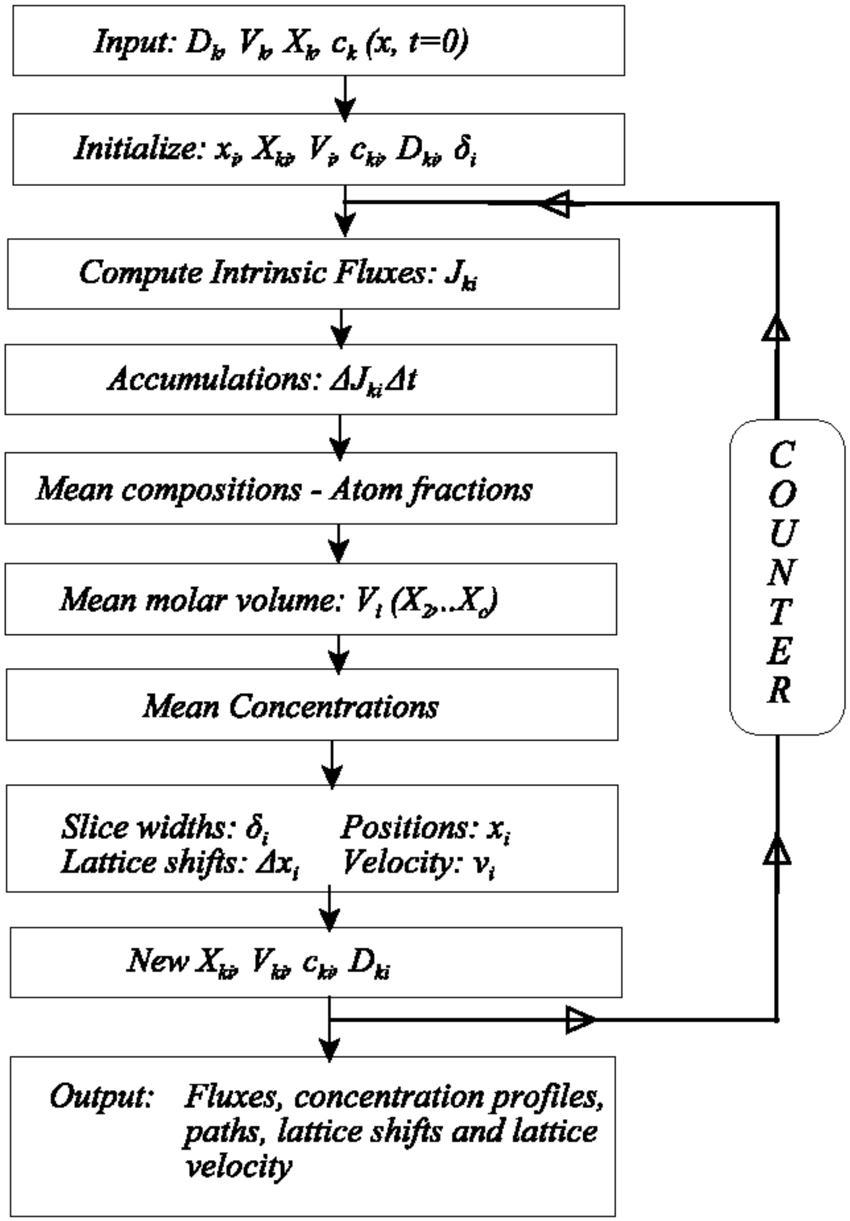
Simulation Algorithm



Initial concentrations ($c_{k,i} = X_{k,i} / V$)

$$J^K_{k,i} = -D^K_{k,i} \frac{c_{k,i+1} - c_{k,i-1}}{x_{k,i+1} - x_{k,i-1}}$$

Fluxes computed using finite difference form



Input: D_k, V_k, X_k, c_k (x, t=0)

Initialize: x_i, X_{ki}, V_i, c_{ki}, D_{ki}, δ_i

Compute Intrinsic Fluxes: J_{ki}

Accumulations: $\Delta J_{ki}\Delta t$

Mean compositions - Atom fractions

Mean molar volume: V_i (X_2,..X_o)

Mean Concentrations

Slice widths: δ_i Positions: x_i
Lattice shifts: Δx_i Velocity: v_i

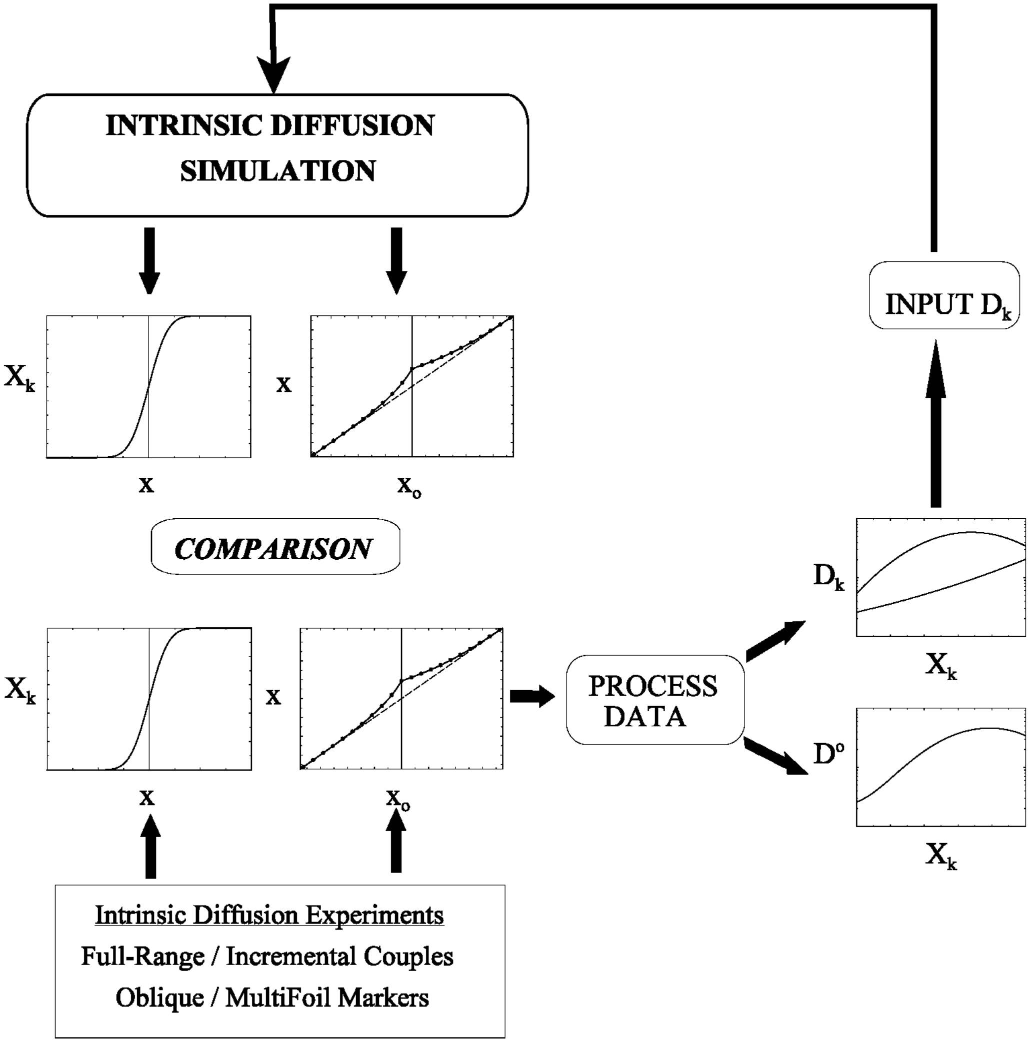
New X_{ki}, V_{ki}, c_{ki}, D_{ki}

Output: Fluxes, concentration profiles, paths, lattice shifts and lattice velocity

COUNTER

Procedure for Assessing Darken (Mobility) and Manning (Phenom.)

A. Establishing consistency of experimental measurements and procedures



INTRINSIC DIFFUSION SIMULATION

COMPARISON

PROCESS DATA

INPUT D_k

<u>Intrinsic Diffusion Experiments</u>
Full-Range / Incremental Couples
Oblique / MultiFoil Markers

B. Procedure for testing the D-M relations with aid of the simulation

$$D_A = D_A^*\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right) = D_A^*\Phi$$

$$D_B = D_B^*\left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}\right) = D_B^*\Phi$$

$$D^o = (X_B D_A^* + X_A D_B^*)\Phi$$

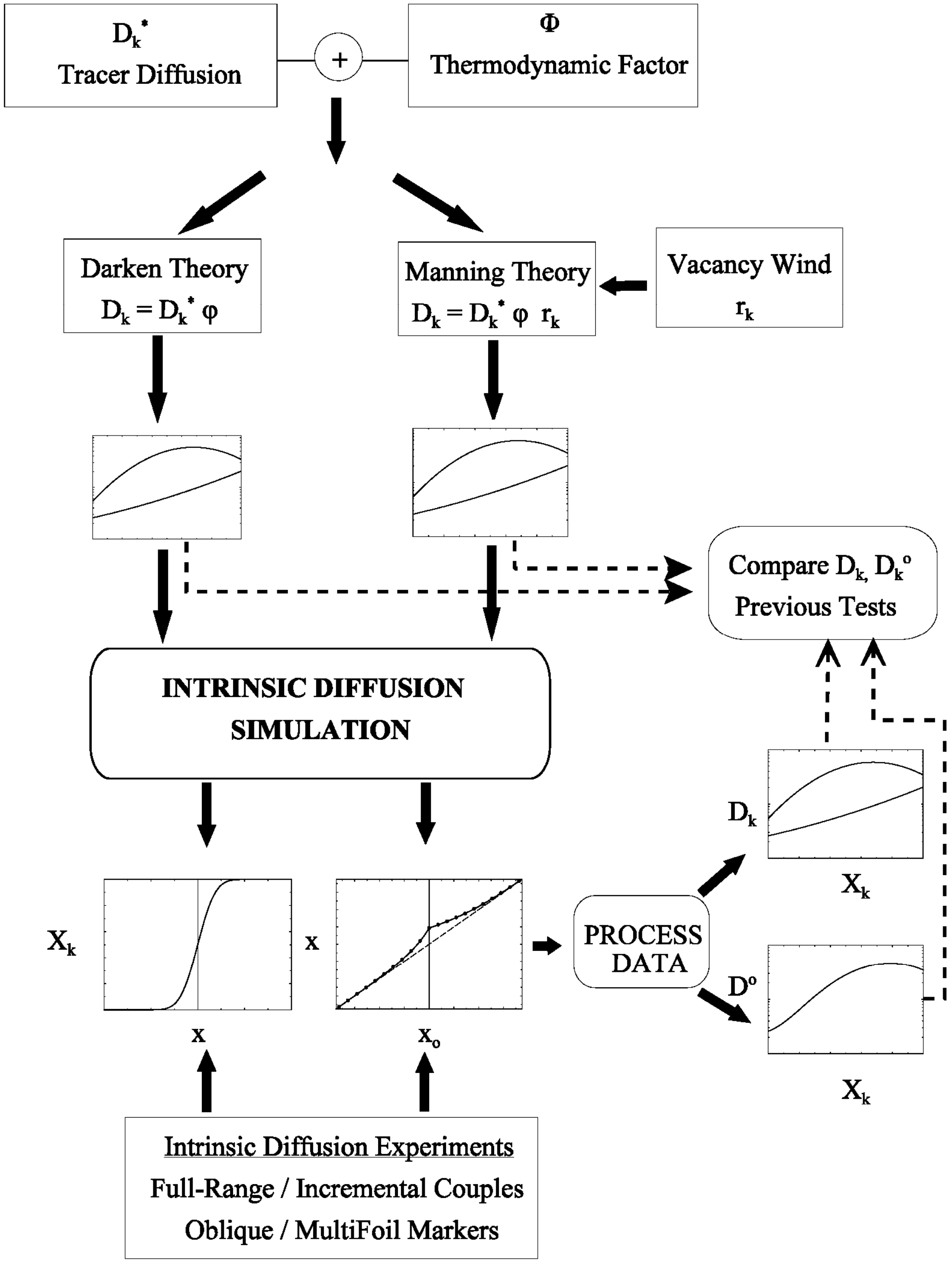
Darken relations

$$D_A = D_A^*\Phi(1 + V_A)$$

$$D_B = D_B^*\Phi(1 - V_B)$$

$$D^o = (X_B D_A^* + X_A D_B^*)\Phi S$$

Manning relations



D_k^* Tracer Diffusion

+

Φ Thermodynamic Factor

Darken Theory $D_k = D_k^*\ \varphi$

Manning Theory $D_k = D_k^*\ \varphi\ r_k$

Vacancy Wind r_k

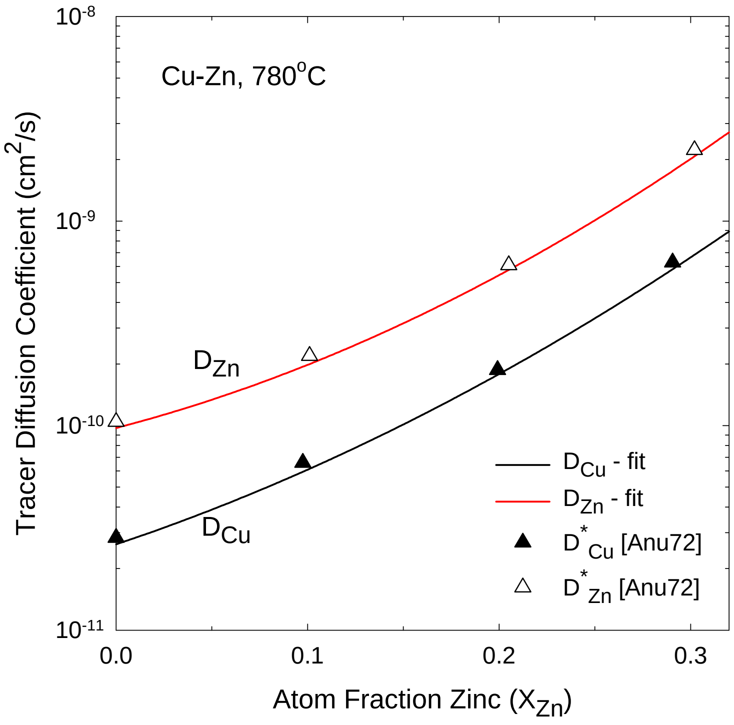
Compare D_k, D_k^o Previous Tests

INTRINSIC DIFFUSION SIMULATION

PROCESS DATA

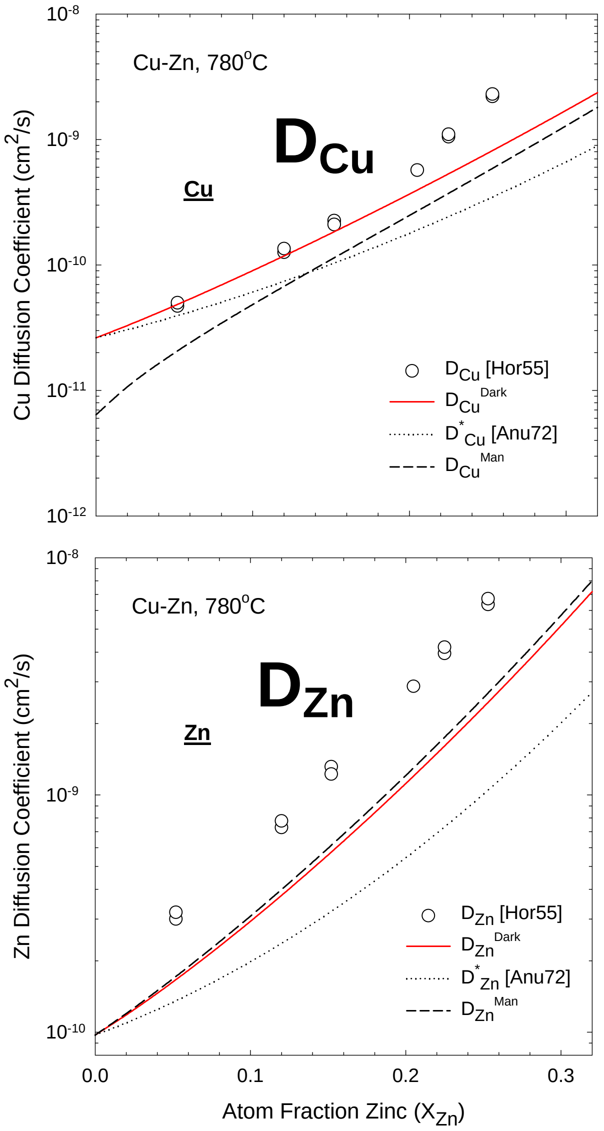
Intrinsic Diffusion Experiments
Full-Range / Incremental Couples
Oblique / MultiFoil Markers

Assessing D-M Relations for Cu-Zn



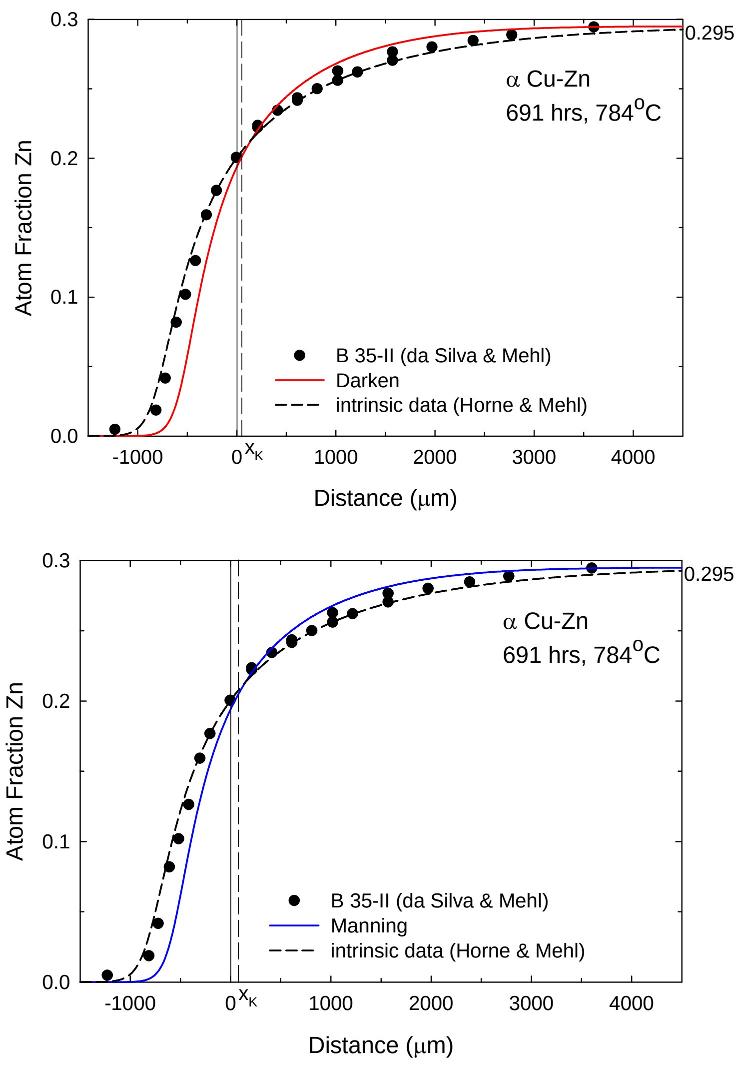
Tracer diffusion data

[Anusavice et al., Met. Trans., 1972]



- **Problem with predicted intrinsic coefficients at high Zn compositions**

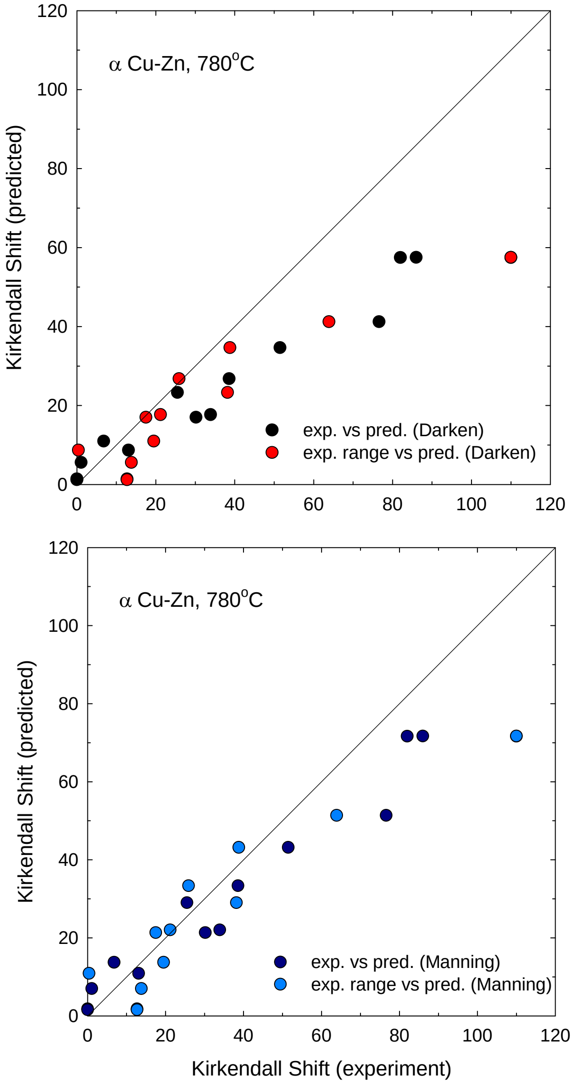
D-M Relations for Cu-Zn contd.



Concentration profiles

Darken

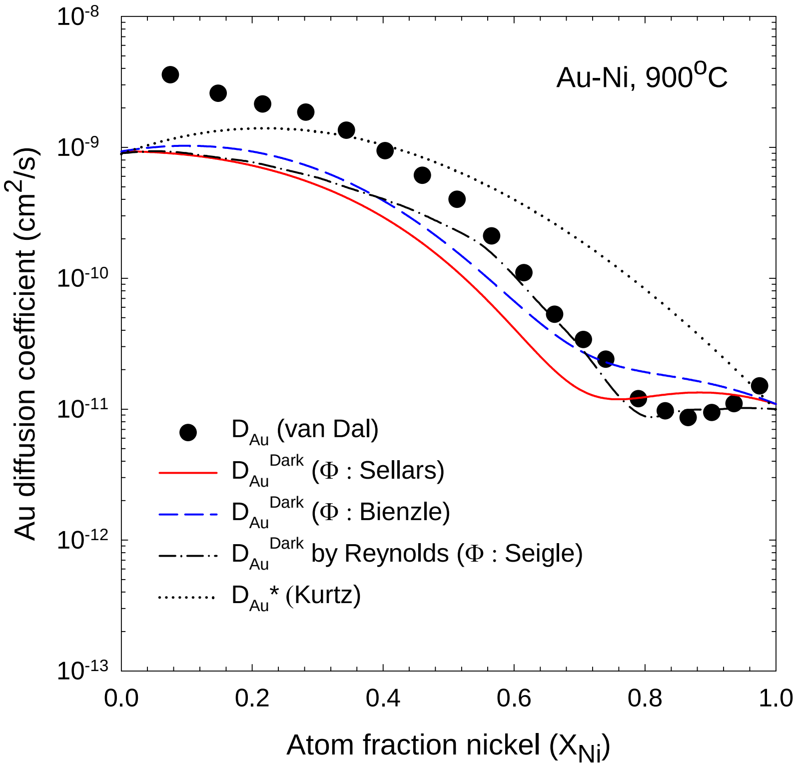
Manning



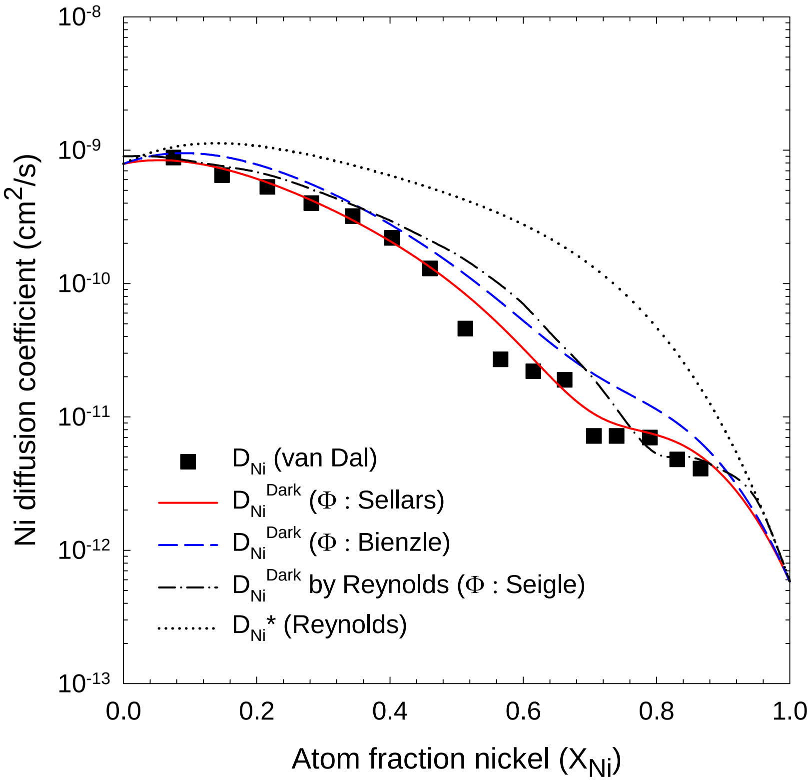
Kirkendall shifts

- **Minor differences between Darken (mobility approach) and Manning**

Darken Relations for Au-Ni: Predicted Intrinsic Diffusion Coefficients



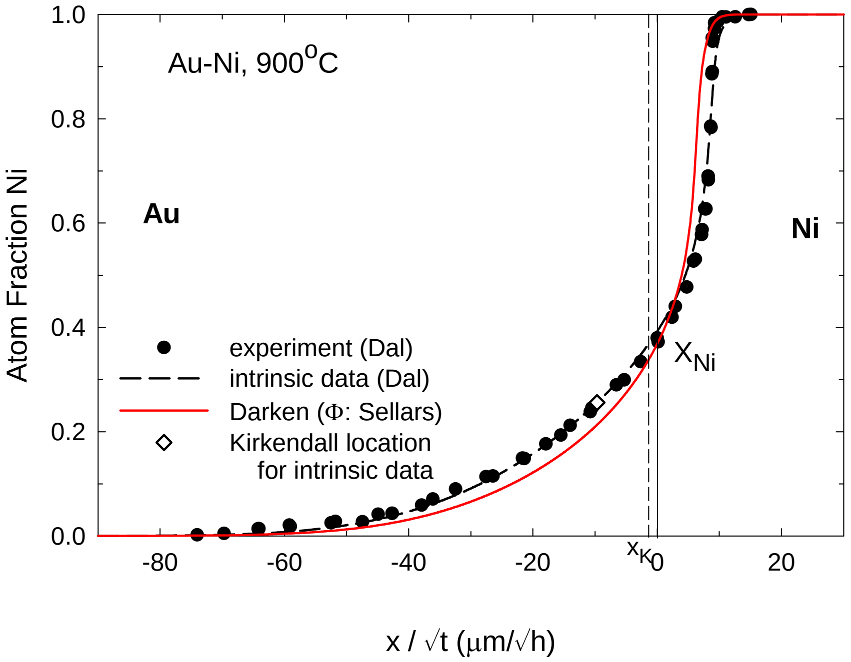
Darken: D_{Au}

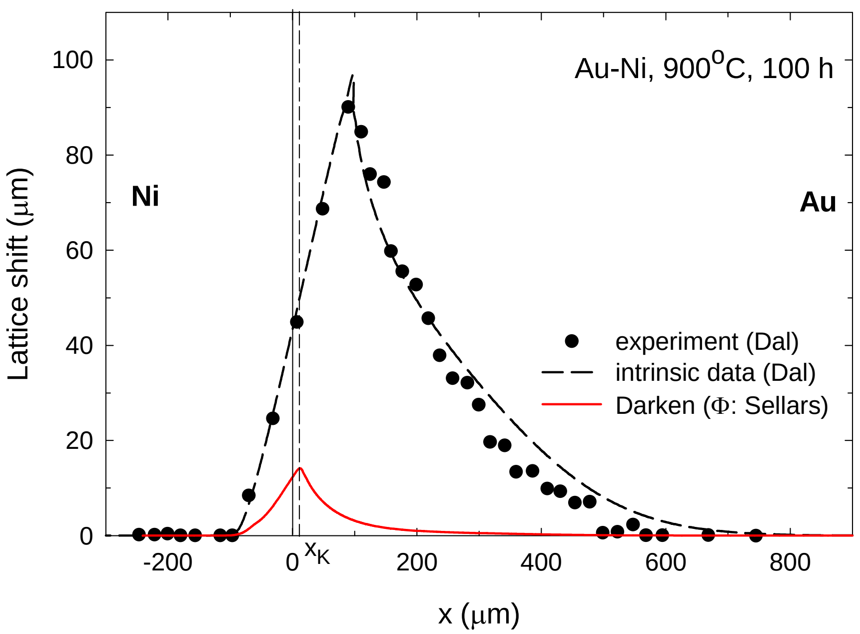


Darken: D_{Ni}

- **Problem with predicted Au intrinsic diffusion coefficient**

Assessing Darken Relations for Au-Ni with Simulation





Lattice shift profile

- **Differences between predicted and experimental D_{Au} results in large differences in lattice shift profiles**
- **Manning correction outside limits (need to check Moleko et al. formalism)**

Mobility Formalism: Cu-Ni-Zn

$$\log\left(Dt_{Cu}\right) = -3.53 \cdot X_{Ni}^{1.16} + 3.6 \cdot X_{Zn}^{1.02} - 9.46$$

$$\log\left(Dt_{Ni}\right) = -4.05 \cdot X_{Ni}^{1.3} + 3.28 \cdot X_{Zn}^{1.07} - 9.96$$

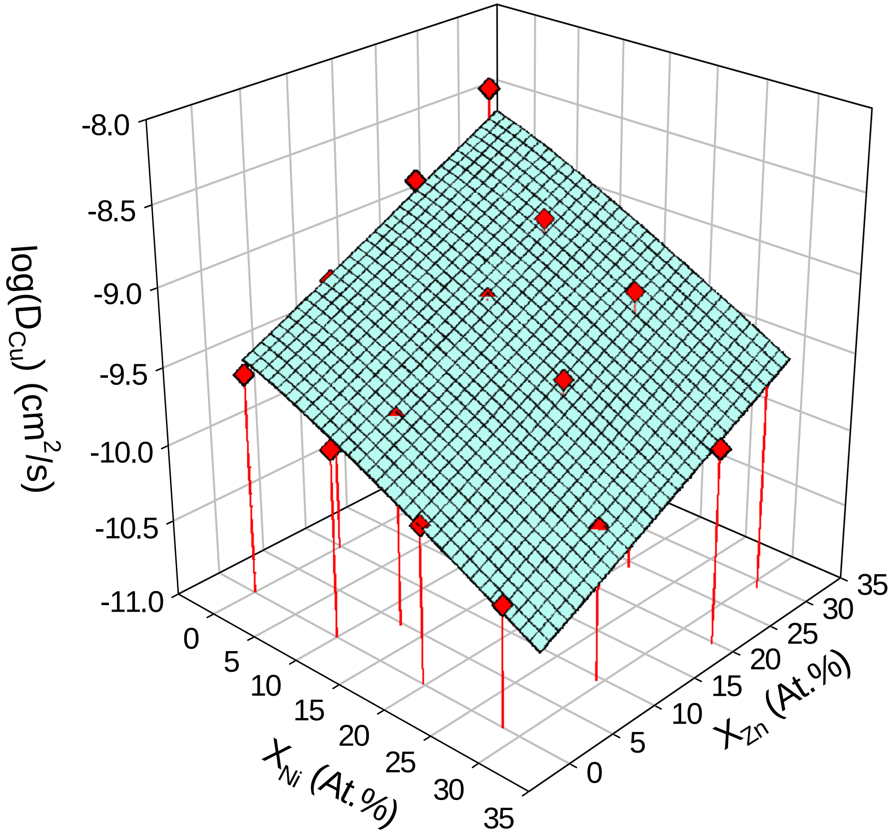
$$\log\left(Dt_{Zn}\right) = -3.2 \cdot X_{Ni} + 5.21 \cdot X_{Zn}^{1.25} - 9$$

$$D^*_{Zn} > D^*_{Cu} > D^*_{Ni}$$

Similar composition dependence

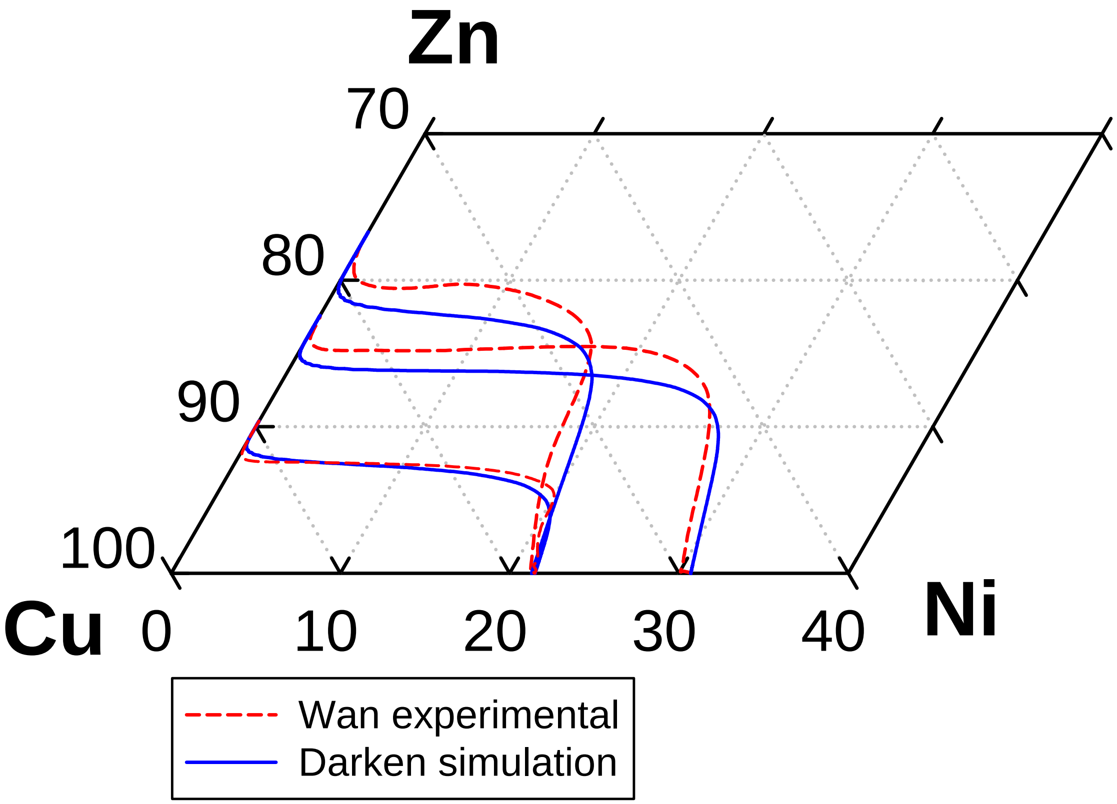
Thermodynamics from Jiang, Ishida *et al.*, *J. Phys. Chem. Sol.*, 2004.

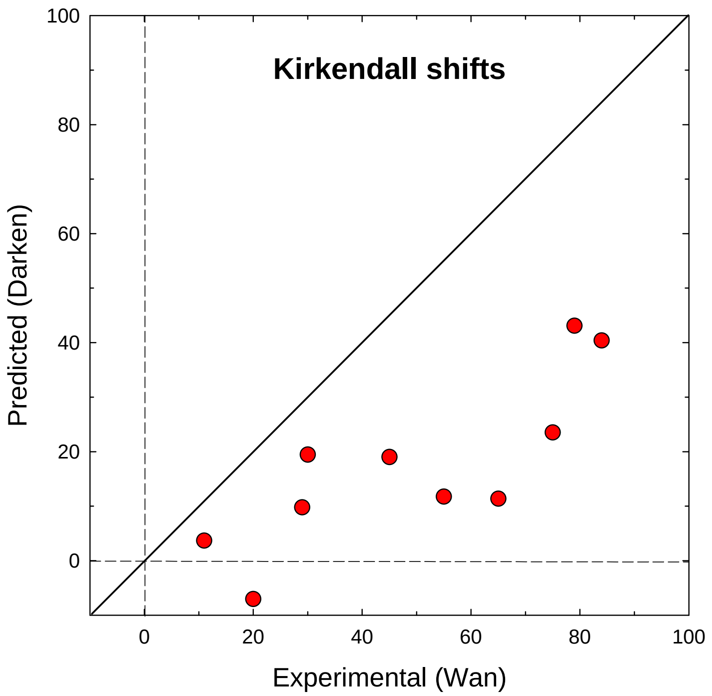
Tracer diffusion coefficients



Anusavice & DeHoff, *Met. Trans. A., 1972*

Mobility Formalism: Cu-Ni-Zn contd.





- **Mobility formalism provides reasonable composition paths**
- **Underestimates Kirkendall shifts**

Manning Relations in Cu-Ni-Zn: Fluxes

$$J_i = -L_{ii}\cdot\frac{d}{dx}\mu_i - \sum_j L_{ij}\cdot\frac{d}{dx}\mu_j$$

$$J_1 = R\cdot T\cdot\left[-L_{11}\cdot\left(\frac{\Phi_{11}}{X_1}\cdot\frac{d}{dx}X_1+\frac{\Phi_{12}}{X_2}\cdot\frac{d}{dx}X_2\right)-L_{12}\left(\frac{\Phi_{22}}{X_2}\cdot\frac{d}{dx}X_2+\frac{\Phi_{21}}{X_1}\cdot\frac{d}{dx}X_1\right)-\frac{L_{13}}{X_3}\cdot(-1)\cdot\left[X_1\cdot\left(\frac{\Phi_{11}}{X_1}\cdot\frac{d}{dx}X_1+\frac{\Phi_{12}}{X_2}\cdot\frac{d}{dx}X_2\right)+X_2\cdot\left(\frac{\Phi_{22}}{X_2}\cdot\frac{d}{dx}X_2+\frac{\Phi_{21}}{X_1}\cdot\frac{d}{dx}X_1\right)\right]\right]$$

$$J_2 = R\cdot T\cdot\left[-L_{21}\cdot\left(\frac{\Phi_{11}}{X_1}\cdot\frac{d}{dx}X_1+\frac{\Phi_{12}}{X_2}\cdot\frac{d}{dx}X_2\right)-L_{22}\left(\frac{\Phi_{22}}{X_2}\cdot\frac{d}{dx}X_2+\frac{\Phi_{21}}{X_1}\cdot\frac{d}{dx}X_1\right)-\frac{L_{23}}{X_3}\cdot(-1)\cdot\left[X_1\cdot\left(\frac{\Phi_{11}}{X_1}\cdot\frac{d}{dx}X_1+\frac{\Phi_{12}}{X_2}\cdot\frac{d}{dx}X_2\right)+X_2\cdot\left(\frac{\Phi_{22}}{X_2}\cdot\frac{d}{dx}X_2+\frac{\Phi_{21}}{X_1}\cdot\frac{d}{dx}X_1\right)\right]\right]$$

$$J_3 = R\cdot T\cdot\left[-L_{31}\cdot\left(\frac{\Phi_{11}}{X_1}\cdot\frac{d}{dx}X_1+\frac{\Phi_{12}}{X_2}\cdot\frac{d}{dx}X_2\right)-L_{32}\left(\frac{\Phi_{22}}{X_2}\cdot\frac{d}{dx}X_2+\frac{\Phi_{21}}{X_1}\cdot\frac{d}{dx}X_1\right)-\frac{L_{33}}{X_3}\cdot(-1)\cdot\left[X_1\cdot\left(\frac{\Phi_{11}}{X_1}\cdot\frac{d}{dx}X_1+\frac{\Phi_{12}}{X_2}\cdot\frac{d}{dx}X_2\right)+X_2\cdot\left(\frac{\Phi_{22}}{X_2}\cdot\frac{d}{dx}X_2+\frac{\Phi_{21}}{X_1}\cdot\frac{d}{dx}X_1\right)\right]\right]$$

Manning Relations in Cu-Ni-Zn: Lij’s

$$L_{11} = \frac{X_1}{V} \cdot \frac{Dt_1}{R \cdot T} \cdot \left[1 + \frac{2 \cdot X_1 \cdot Dt_1}{M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)} \right]$$

$$L_{12} = \frac{2 \cdot X_1 \cdot Dt_1 \cdot X_2 \cdot Dt_2}{V \cdot R \cdot T \cdot M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)}$$

$$L_{13} = \frac{2 \cdot X_1 \cdot Dt_1 \cdot X_3 \cdot Dt_3}{V \cdot R \cdot T \cdot M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)}$$

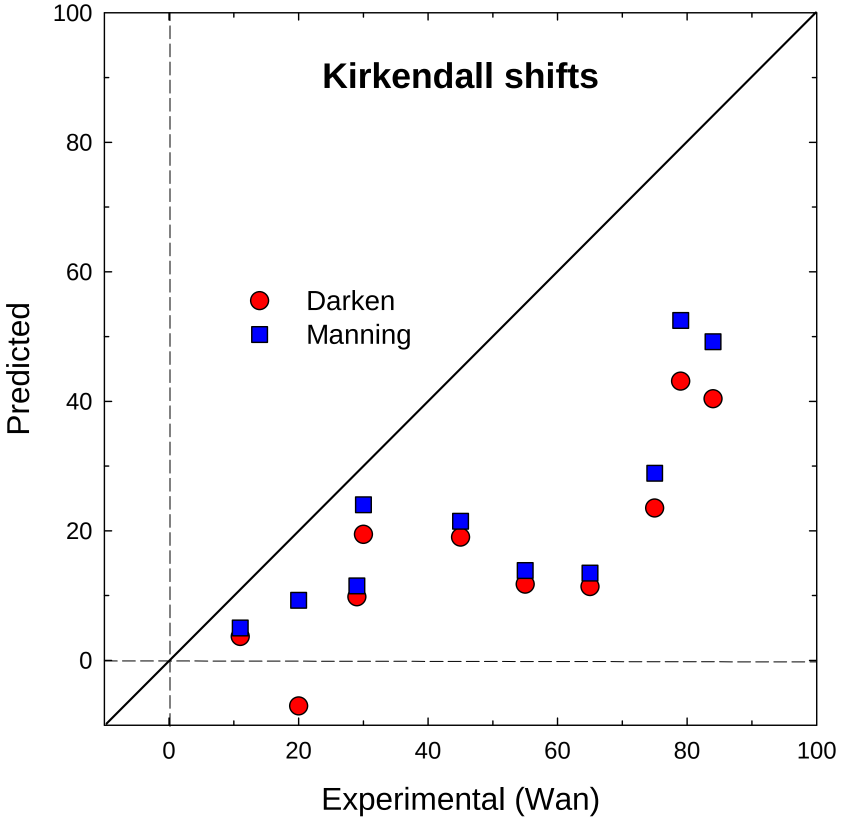
$$L_{22} = \frac{X_2}{V} \cdot \frac{Dt_2}{R \cdot T} \cdot \left[1 + \frac{2 \cdot X_2 \cdot Dt_2}{M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)} \right]$$

$$L_{23} = \frac{2 \cdot X_2 \cdot Dt_2 \cdot X_3 \cdot Dt_3}{V \cdot R \cdot T \cdot M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)}$$

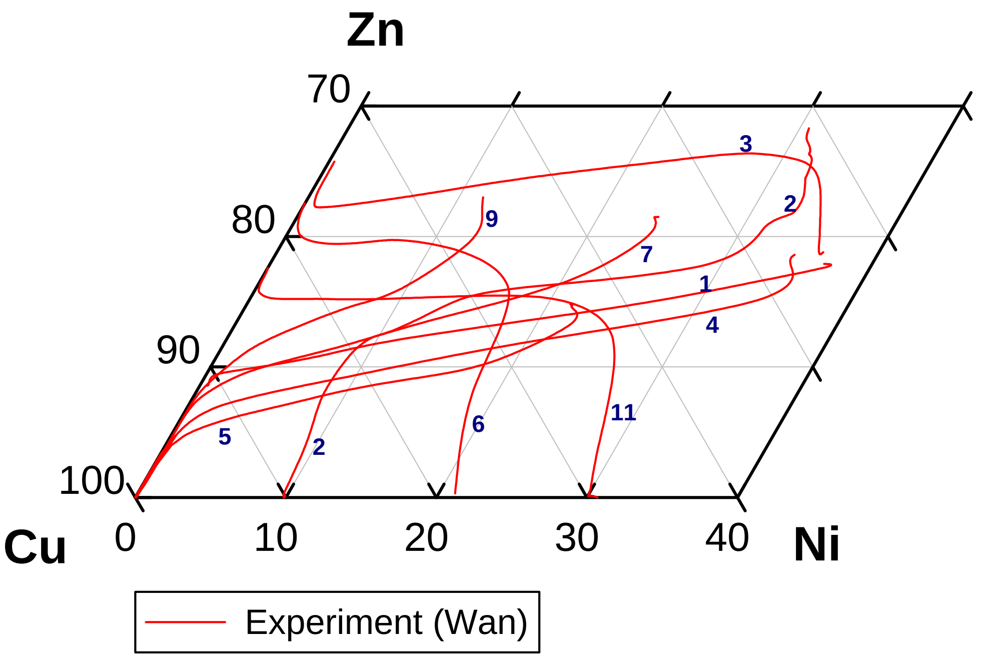
$$L_{ij} = L_{ji}$$

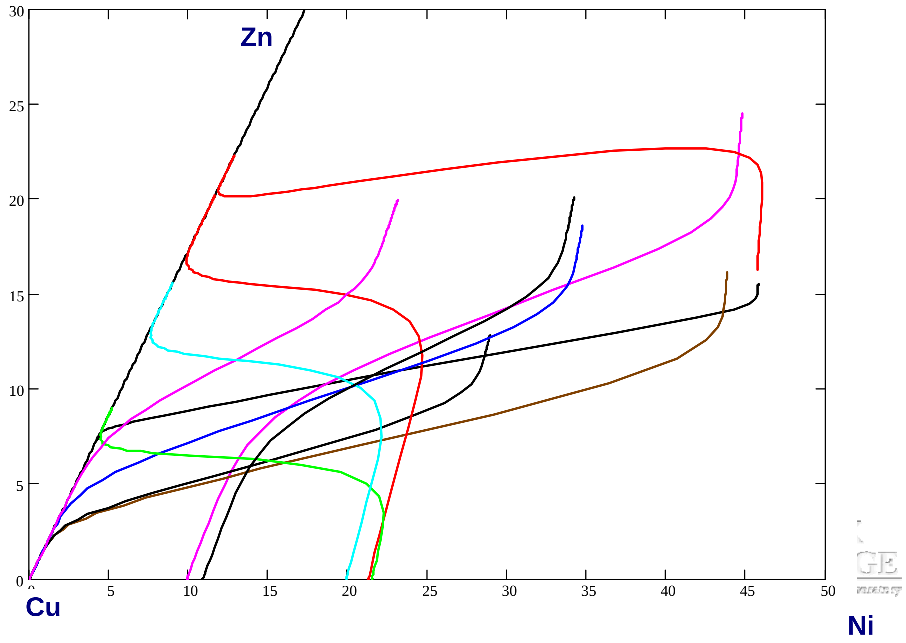
$$L_{33} = \frac{X_3}{V} \cdot \frac{Dt_3}{R \cdot T} \cdot \left[1 + \frac{2 \cdot X_3 \cdot Dt_3}{M_o \cdot \left(X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3 \right)} \right]$$

Manning: Cu-Ni-Zn



Diffusion Composition Paths in Cu-Ni-Zn at 900^{o}C





- **Manning formalism slightly better for Kirkendall shifts**

So Which Formalism to Use?

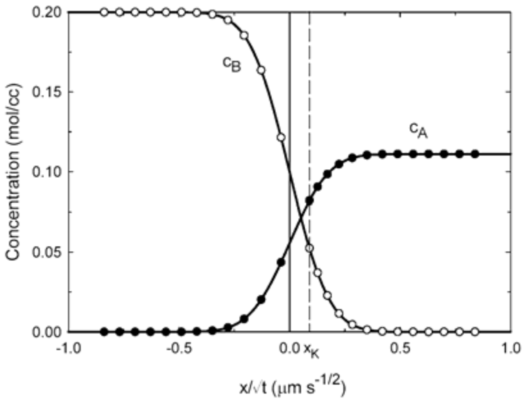
- Mobility or Phenomenological Formalism or Others?
  - Phenomenological formalism slightly better for systems studied, so far…
    - Fewer assumptions
  - Better to have software capable of handling different formalisms, e.g., Phenomenological can handle Mobility formalism as a limiting case but not vice versa.
  - Better to keep diffusion database independent of thermodynamic database.
  - Tracer diffusion database that feeds into Lij's has diffusivity *units of cm^2/s* that provides more physical meaning to user.

➢ **Ultimately, choice of the individual user!**

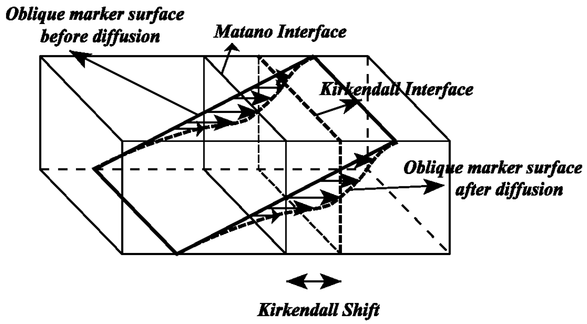
Data for Diffusion Databases

Experimental data

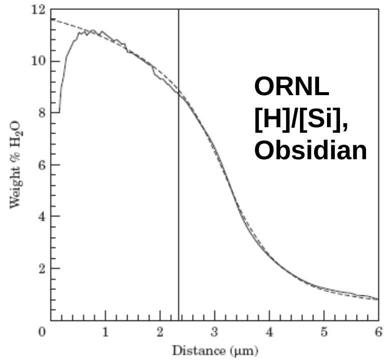
- Interdiffusion Data
  - Steep concentration gradients, molar volume changes, grain boundary effects, can introduce errors in measurements and subsequent analysis: still manageable
  - Very long annealing times may be needed for improved accuracy if kinetics are slow
    - Very difficult in *compounds* unless solubility range is extended



- Intrinsic Diffusion Data
  - Require suitable "inert" markers throughout diffusion zone
    - Multiple markers rarely employed except at original "Kirkendall Interface" due to experimental difficulties
  - Vacancy super-saturation (porosity) or under-saturation can cause errors in both analysis



- Tracer Diffusion Data
  - Most reliable but use of radioactive tracers is time-consuming and expensive
  - *Tracer data using non-radioactive (stable) isotopes not established but promising*



Data for Databases contd.

First-principles data

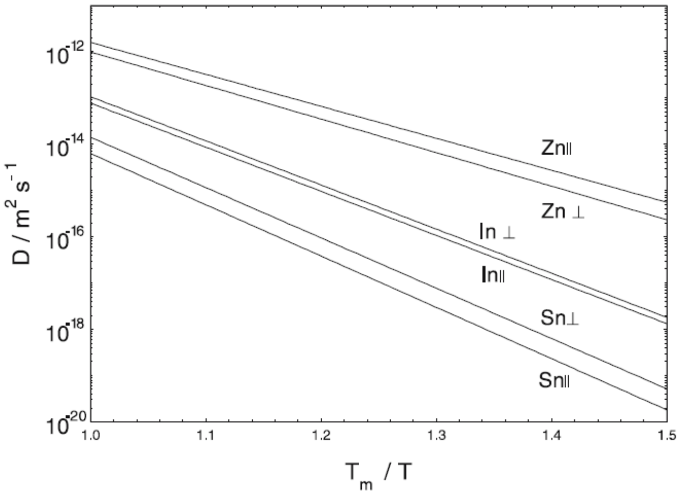
- Mg data/mechanisms (Z.K. Liu., Wolverton et al.)
- NiAl intermetallic data/mechanisms (A. Van der Ven, …
- Other pure and compound systems
- Oxides (Ågren et al.), Nitrides, ?

Empirical data

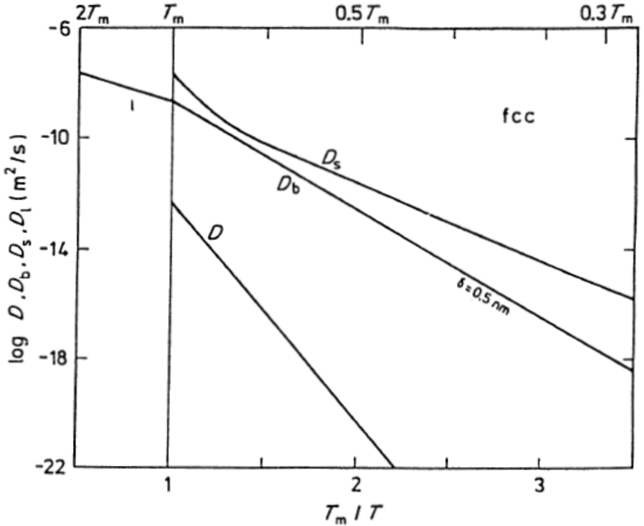
- CIGS system: Empirical approach by Ashby & Brown
  - Utilized by Campbell, et al. for reference pure element diffusivities
- Interdiffusivities: Birchenall & Mehl, others

Diffusion Databases: What should they contain?

- Volume diffusivities
  - Mostly
- Orientation dependent diffusivities
  - Important for non-isotropic elements (Mg, Zn) and compounds
- Grain boundary diffusivities: No systematic experimental effort (?)
  - Bicrystals, tricrystals
  - Modeling (Mishin et al.)
  - Directly using EBSD + SIMS integrated system (the future…)
- Surface/Interface diffusivities
  - Cu/SiN interfacial diffusion dominates electromigration flux in damascene interconnects



Self-diffusion in single crystals of Zn (hex.), In and Sn (tetrag.) parallel and perpendicular to their unique axis (Mehrer, Diffusion in Solids)



Self-diffusion in fcc metals in lattice (D), along grain boundaries (D_g), on surface (D_s) and liquid phase (Herzig and Mishin).

Approach for Constructing Diffusion Databases

Calphad Approach (Volume diffusivities)

- Based on constructing models for multicomponent systems using assessed models from relevant binary systems
- Need pure element reference tracer diffusivities
  - Use first principles or empirical approaches if data not available
  - Conduct difficult experiments (CVD, high pressure, creative experiments
- Optimization of various types of data (tracer, interdiffusion, intrinsic diffusion, first principles, etc.) from various sources
  - Employ desired weighting
- Composition dependence using Redlich-Kister type polynomial functions
- Temperature dependence using Arrhenius expressions

Approach for Diffusion Dbs. Contd.

However ...

- Calphad approach is convenient but …
  - Diffusivities are absolute quantities and not relative like Gibbs energies that require reference state values.
    - Hence standard element reference diffusivities need not be used if not available, e.g., Al hcp, Mg fcc.
    - Because kinetic coefficients may vary by several orders in magnitude, small errors in non-measurable reference element values may cause large errors in unknown coefficients
  - Some may prefer to keep diffusion database independent of thermodynamic database.
    - Use only tracer diffusion or first principles data
      - Hence, optimization efforts may be simplified
  - Impurity diffusion, other diffusion mechanisms (aided with first principles analysis) may require more than a single polynomial model or non-polynomial models (?).

Tracer Data Fit for Cu-Ni-Zn

$$\log\left(Dt_{Cu}\right) = -3.53\cdot X_{Ni}^{1.16} + 3.6\cdot X_{Zn}^{1.02} - 9.46$$

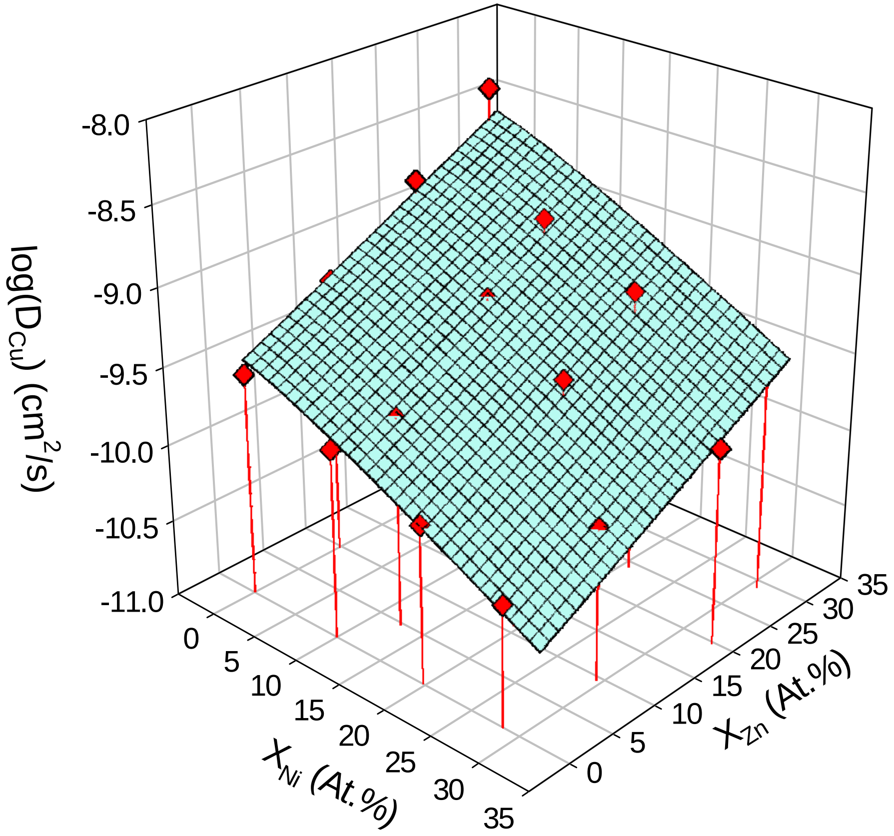
$$\log\left(Dt_{Ni}\right) = -4.05\cdot X_{Ni}^{1.3} + 3.28\cdot X_{Zn}^{1.07} - 9.96$$

$$\log\left(Dt_{Zn}\right) = -3.2\cdot X_{Ni} + 5.21\cdot X_{Zn}^{1.25} - 9$$

$$D^*_{Zn} > D^*_{Cu} > D^*_{Ni}$$

Similar composition dependence

Tracer diffusion coefficients



Anusavice & DeHoff, *Met. Trans. A., 1972*

Diffusion Modeling Software

- Type of diffusion database
  - Integrated with thermodynamic db
  - Independent of thermodynamic db
- 1D vs 3D
- Thin film vs Bulk
  - Grain boundary, orientation, nucleation, texture, stress, etc.
- Phase Field / Crystal Phase Field
  - Special cases only?
- Input information
  - Molar volume, temperature, composition, crystal structure, different boundary conditions, etc.
- Ease of interface with other software and db's
  - Properties

Tracer Diffusion Database

Radioactive Isotopes

- Tracer diffusion coefficient in a homogeneous single-phase system from the thin film solution

Tracer flux

$$J_k^{U,Fick} = -D_k^* \frac{\partial c_k}{\partial x}$$

Thin film solution for D_k^*

$$c^*(x,t) = \frac{S}{2\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right)$$

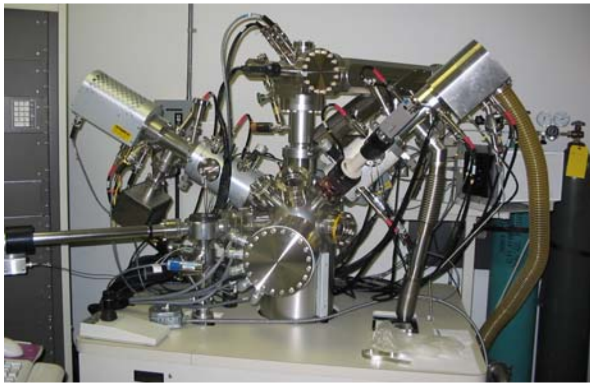
  - Measure D^*_k at each composition for samples annealed for different times; Repeat procedure at different temperatures; Plot D*k vs 1/T to obtain Arrhenius parameters for each sample composition within various phases; Fit tracer diffusivities in a phase as a function of temperature and composition for binaries using polynomial functions for composition dependence.
- Tracer is an isotope of one of the elements in the homogeneous alloy that is present in extremely dilute amounts (ppm) so that
  - Thin film solution for diffusion coefficient is valid and
  - Initial composition of the alloy is unchanged
- Previously, only with a radioactive isotope could trace amounts of the isotope (tracer) be detected due to the high intensity of radiation (beta, gamma):
  - Time, Money and Safety Issues

Tracer Diffusion Database

Stable Isotopes and SIMS

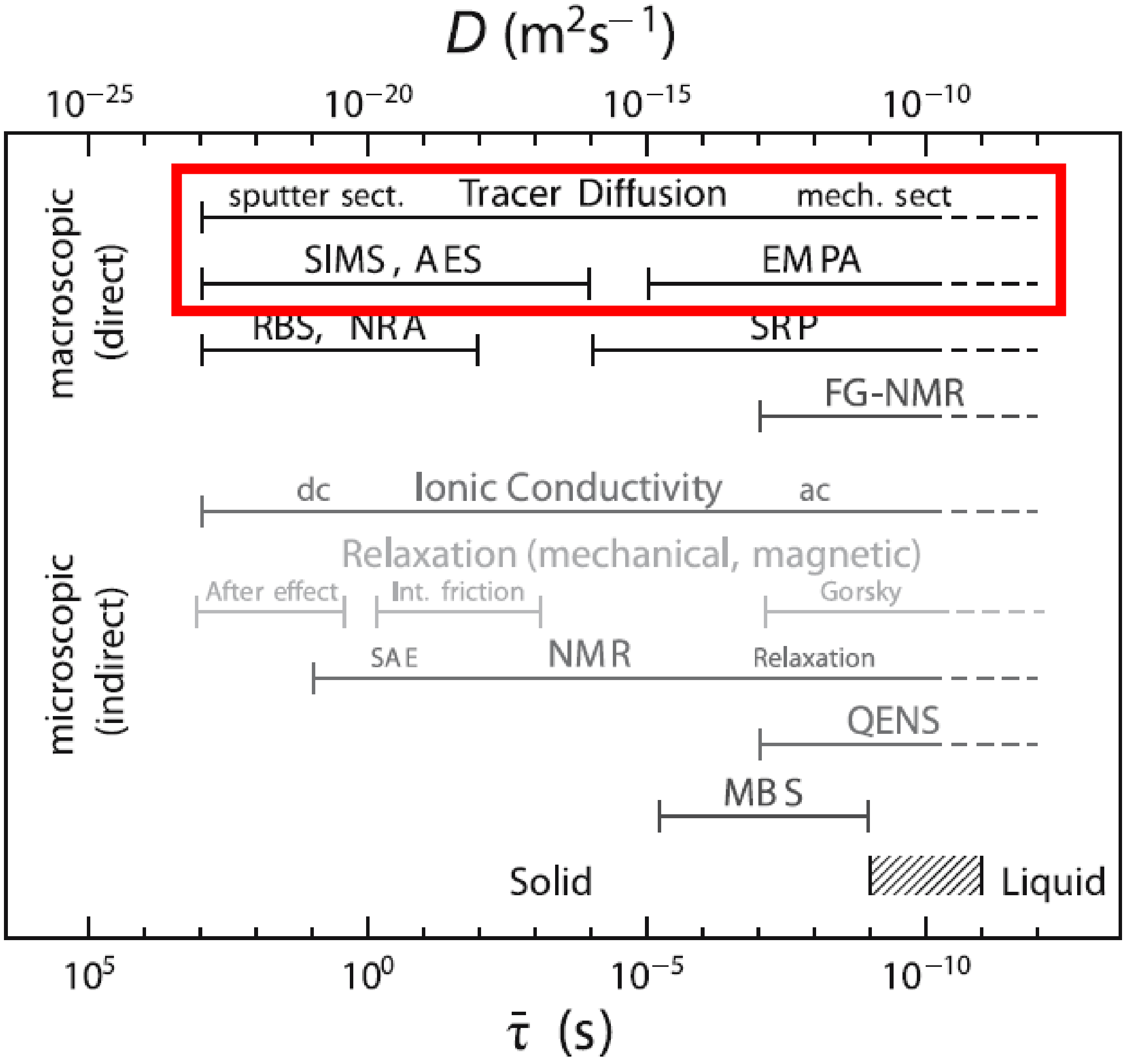
- Use of stable isotopes has a dramatic effect on safety and reduced costs.
- Advancements in Secondary Ion Mass Spectrometry (SIMS) for the accurate detection of trace amounts of stable isotopes permits thin film solution to be utilized, i.e., essentially the same-simple analytical treatment as before.
- SIMS systems at ORNL and UCF measure isotopic ratio of concentrations as a function of depth or at any point in sample
- We can map elements, isotopes over an area of about 1 cm^2, and with a lateral resolution of about 1-2 μm, and depth resolution of about 10 nm.
- Future nano-SIMS integration with EBSD capability may enable measurement of:
  - *Diffusivities as a function of orientation in micro/nano grained materials*
  - *Grain boundary diffusivities*

Cameca IMS 4F at ORNL



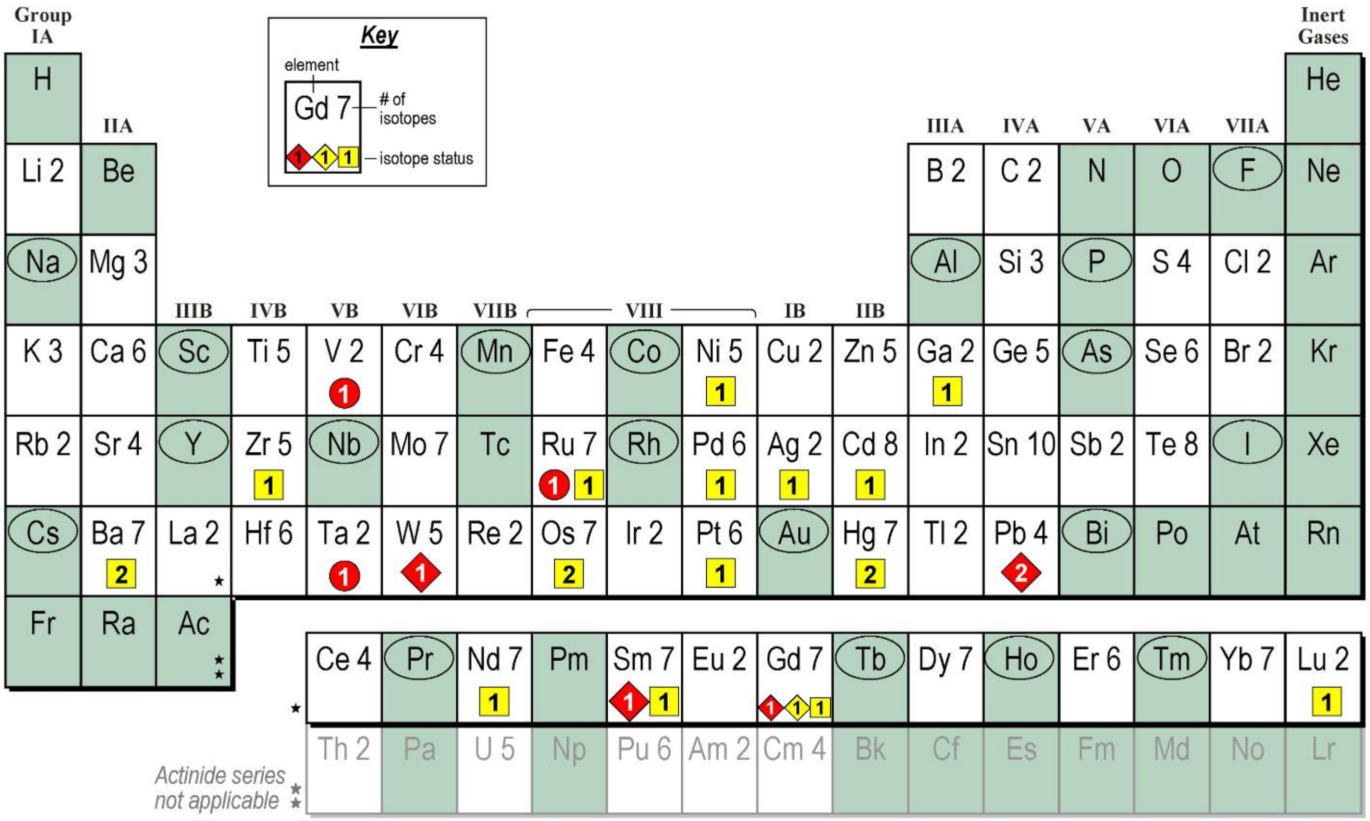
Cameca IMS 3F at UCF

Tracer Diffusion contd.



Typical ranges of diffusivity (Mehrer, Diffusion in Solids)

ORNL Isotopes Enriched by the Calutrons



Key

element

Gd 7 — # of isotopes

♦1 ◇1 🟨1 — isotope status

Group IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Inert Gases
H																	He
Li 2	Be											B 2	C 2	N	O	F	Ne
Na	Mg 3											Al	Si 3	P	S 4	Cl 2	Ar
K 3	Ca 6	Sc	Ti 5	V 2 🔴1	Cr 4	Mn	Fe 4	Co	Ni 5 🟨1	Cu 2	Zn 5	Ga 2 🟨1	Ge 5	As	Se 6	Br 2	Kr
Rb 2	Sr 4	Y	Zr 5 🟨1	Nb	Mo 7	Tc	Ru 7 🔴1 🟨1	Rh	Pd 6 🟨1	Ag 2 🟨1	Cd 8 🟨1	In 2	Sn 10	Sb 2	Te 8	I	Xe
Cs	Ba 7 🟨2	La 2 ★	Hf 6	Ta 2 🔴1	W 5 ♦1	Re 2	Os 7 🟨2	Ir 2	Pt 6 🟨1	Au	Hg 7 🟨2	Tl 2	Pb 4 ♦2	Bi	Po	At	Rn
Fr	Ra	Ac ★★															

★	Ce 4	Pr	Nd 7 🟨1	Pm	Sm 7 ♦1 🟨1	Eu 2	Gd 7 ♦1 ◇1 🟨1	Tb	Dy 7	Ho	Er 6	Tm	Yb 7	Lu 2 🟨1
Actinide series not applicable ★★	Th 2	Pa	U 5	Np	Pu 6	Am 2	Cm 4	Bk	Cf	Es	Fm	Md	No	Lr

☐ Elements separated in Calutrons and number of isotopes collected

🟩 Elements not separated in Calutrons

◯ Stable elements with no naturally occurring stable isotopes

🔴 Number of isotopes currently sold-out

♦ Number of isotopes sold-out, second pass high enrichment

🟨 Number of isotopes with <20 year supply

◇ Number of isotopes with <20 year supply, second pass high enrichment

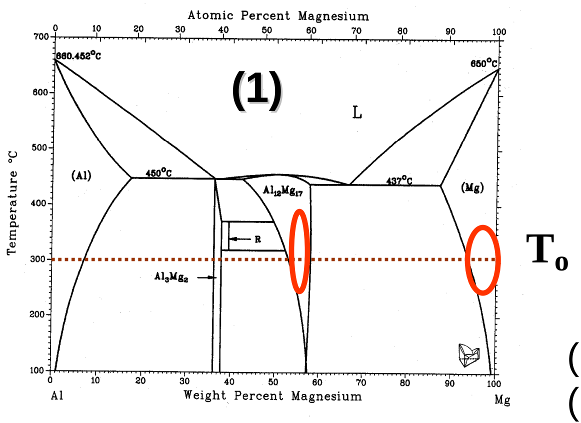
- Cannot avoid working with radioactive isotopes in some cases, e.g., Al, Mn, etc., but can still use SIMS

Inventory ORNL Isotopes

$360M*
Worth of
Stable
Isotopes

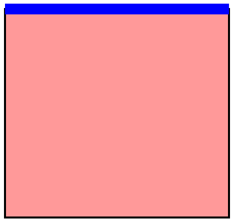
(* list price)

Procedure for Tracer Diffusion Measurements (Review by Rothman)



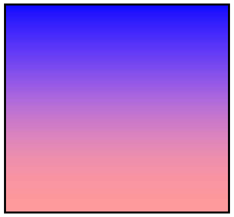
(1) Prepare single phase alloy sample (e.g., Mg-5%Al) at T_o

(2)

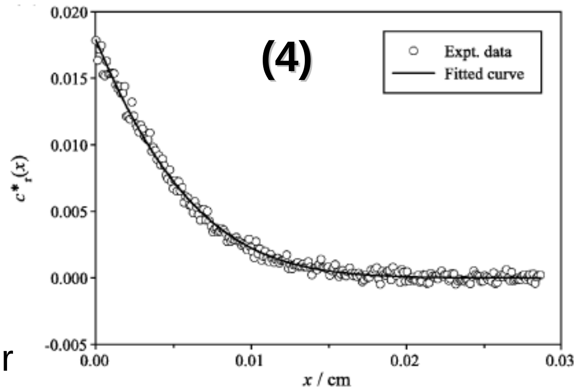


(2) Deposit thin film (100 nm) of stable isotope of an alloy element (e.g., Mg^{26}) on sample surface

(3)



(3) Anneal at T_o for desired times (mins to hrs) to cause isotope to diffuse inwards

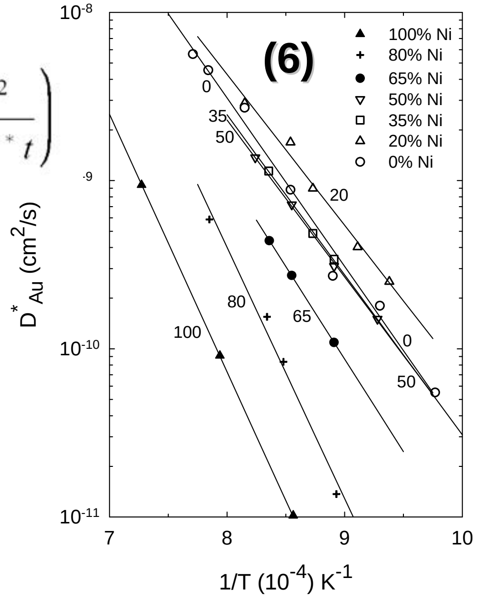


(4) Measure depth profile of isotope or isotope ratio with SIMS (e.g., O^{18} with Time of Flight technique, *De Souza et al., Sol. State Ionics '05)*

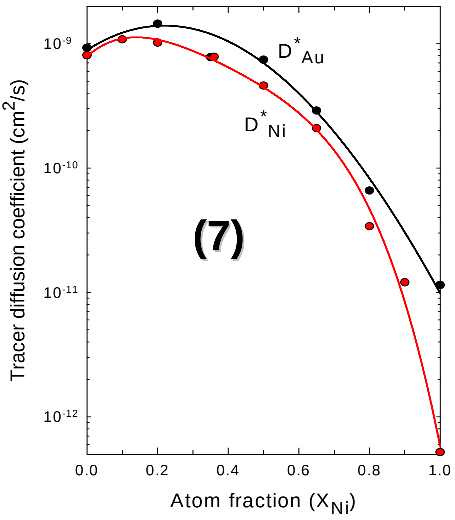
(5)

$$c^*(x,t) = \frac{S}{2\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right)$$

(5) Fit depth profile data for isotope in (4) with above thin film solution to extract tracer diffusivity D*.



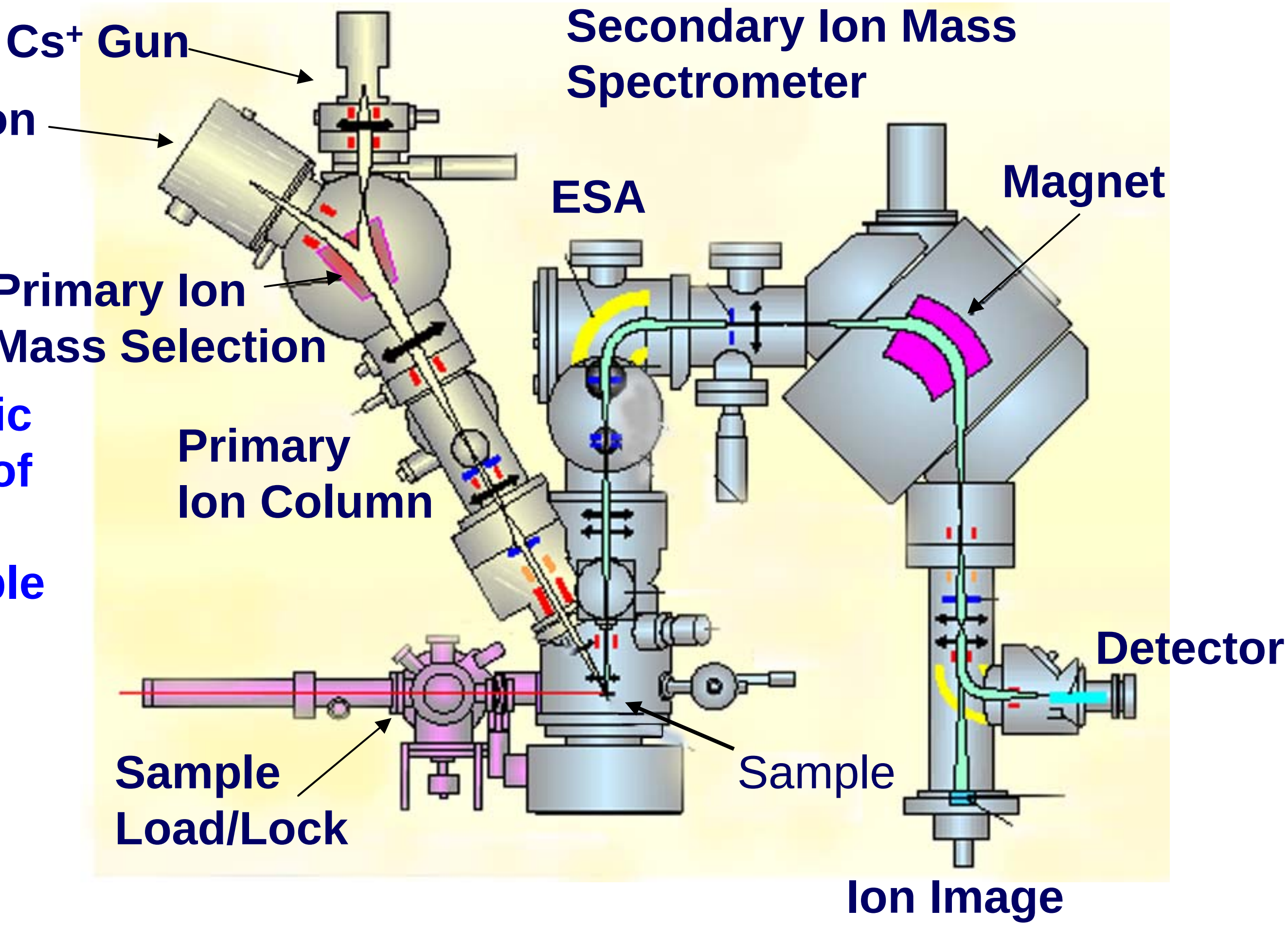
(6) Repeat for different temperatures and compositions to check for Arrhenius fits (e.g. Au in Au-Ni alloys, *Kurtz et al., Acta Met.'55*)



(7) Fit using suitable polynomials for functional form of isotopic diffusivity $D_k^*(X_1, X_2, \ldots, T)$ (e.g. Au-Ni tracer diffusion at 900°C, *Reynolds et al. Acta Met. '57*)

SIMS: ORNL (CAMECA IMS-4F) & UCF (IMS-3F) $2-3M

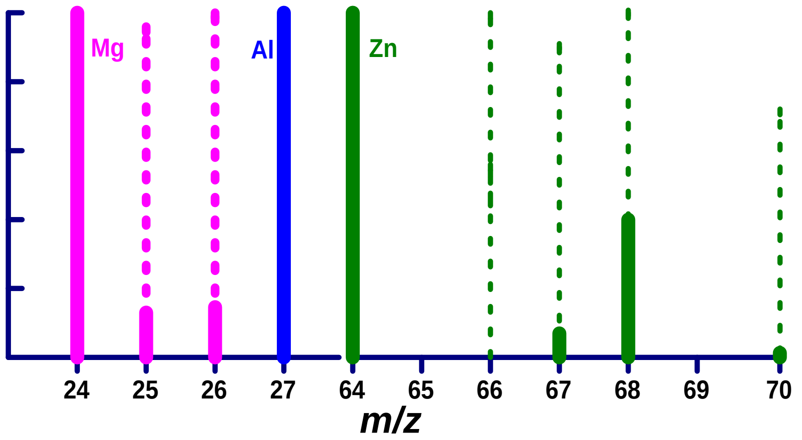
Cameca ims-4f Ideally Suited for Isotope Ratio Depth Profiles
High Spatial Resolution (1μm), High Mass Resolution, High Sensitivity



- ✓ Can measure isotopic ratios as a function of depth.
- ✓ Can measure multiple beams at a time.
- ✓ Has imaging capability.
- ✓ System can be automated for high throughput measurements of samples on a wafer.

Our Modifications – Increase Flexibility, Compatibility with SEM, Optical Microscopes, Reliability

Stable Isotopes Available
[Not Radioactive]



Isotopically Labeled Alloy

Δ Isotope Ratio Measured

Headroom

Ratios, e.g. $[^{26}\text{Mg}]/[^{24}\text{Mg}]$ =14.04%

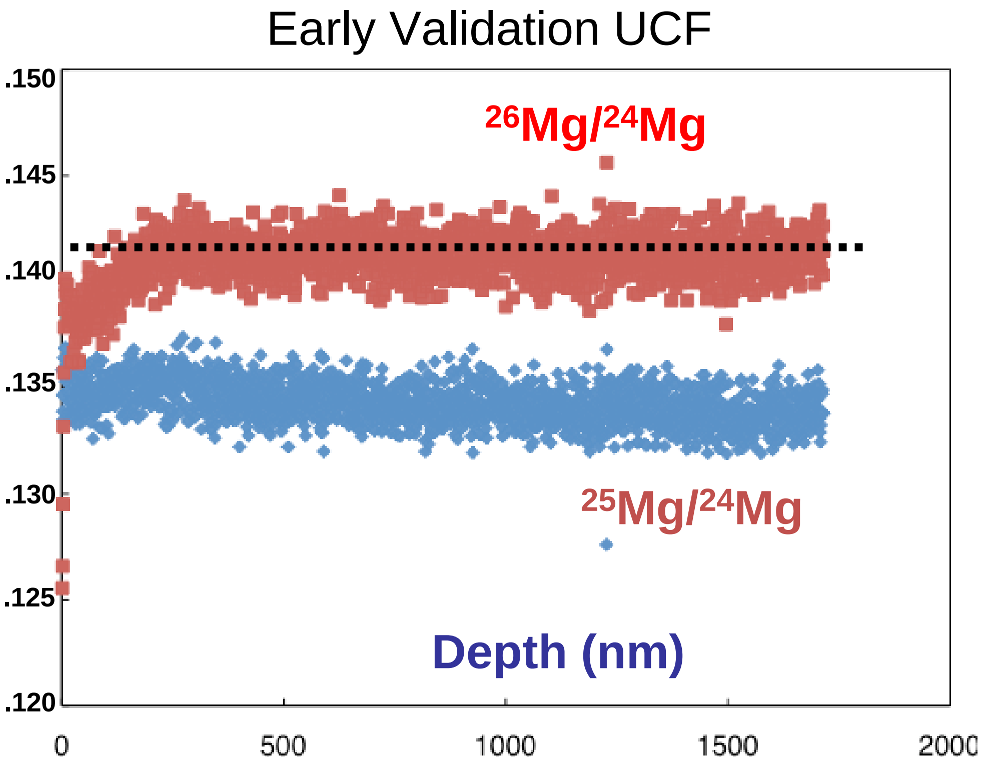
Nat. Ab., e.g., $[^{25}\text{Mg}]/[^{24}\text{Mg}]$ =13.90%

…1% difference readily detected.

100% Available: ca. 10^4 Headroom

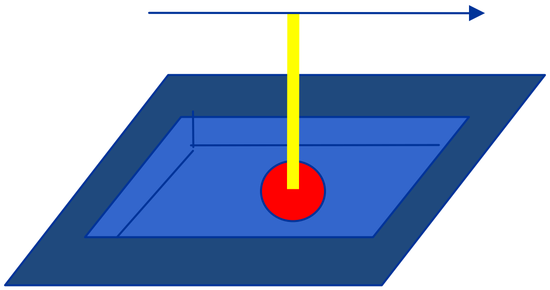
Isotope Ratios Readily Measured…

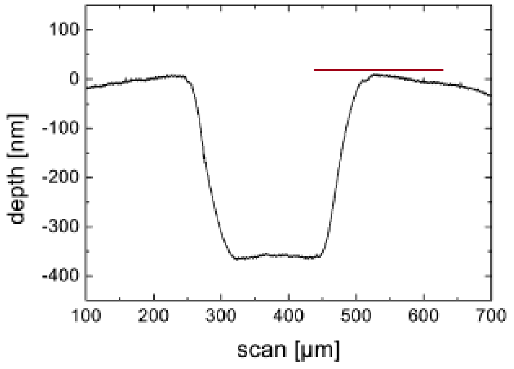
Cameca 3F UCF	$^{25}Mg/^{24}Mg$ (RSD)	$^{26}Mg/^{24}Mg$ (RSD)
Reference value	**0.127**	**0.139**
Mg	**0.129 (<0.001)**	**0.138 (<0.001)**
Mg-Al-Zn	**0.130 (<0.001)**	**0.139 (<0.001)**
AZ31B-2	**0.129 (<0.001)**	**0.138 (<0.001)**
AM60B-2	**0.130 (<0.001)**	**0.139 (<0.001)**



Measurements independent of depth within 1% Relative Standard Deviation

Sputtering Depth: Precisely Measured





Profilometer
Resolution: < 0.1 nm
Accuracy: Surface

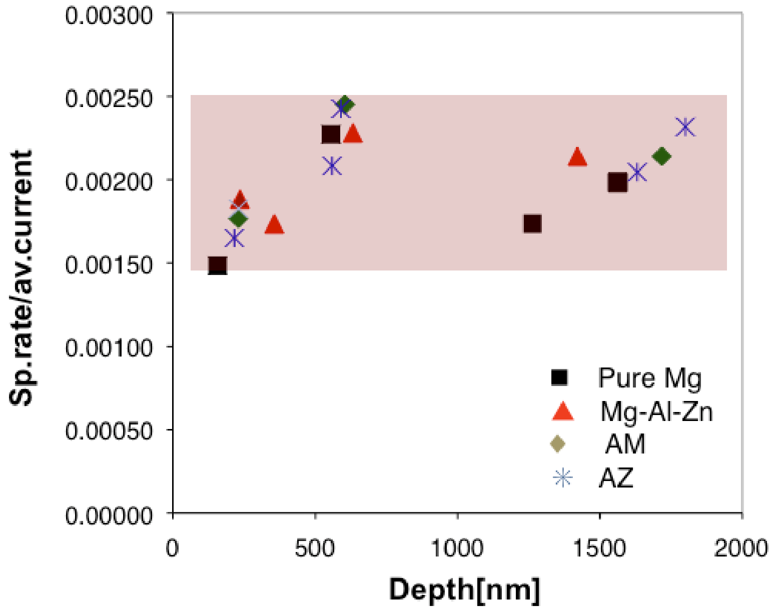
- **Sputtering Rate Uncertainty (uncertainty Primary Ion Current)**
- **Measure depth of each crater**
- **Sputter Rate Only for Scoping**

Assumption
For any Given Crater, given primary ion current, Sputtering Rate Constant … if Not Known Precisely

Standard: Si Sputtering

Primary Ion Current:
ca. 10-100 nA
Spot Size: 1-10 µm

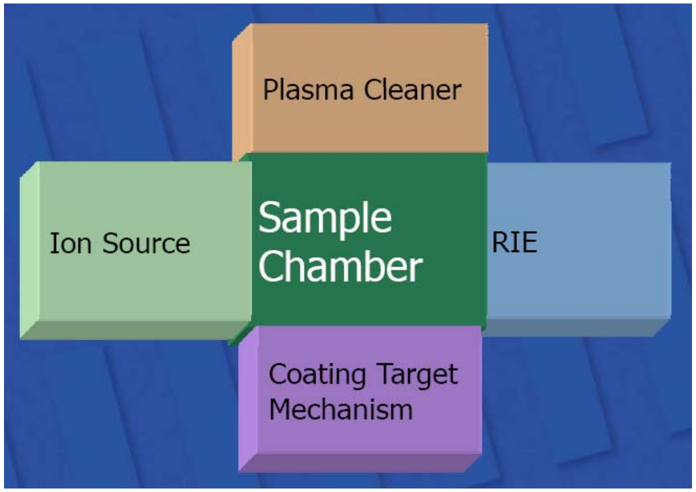
Real Data



Sputter Rate vs. Depth

Vapor Deposition of Stable Isotopes – Automated Sample Preparation System (ASAP)

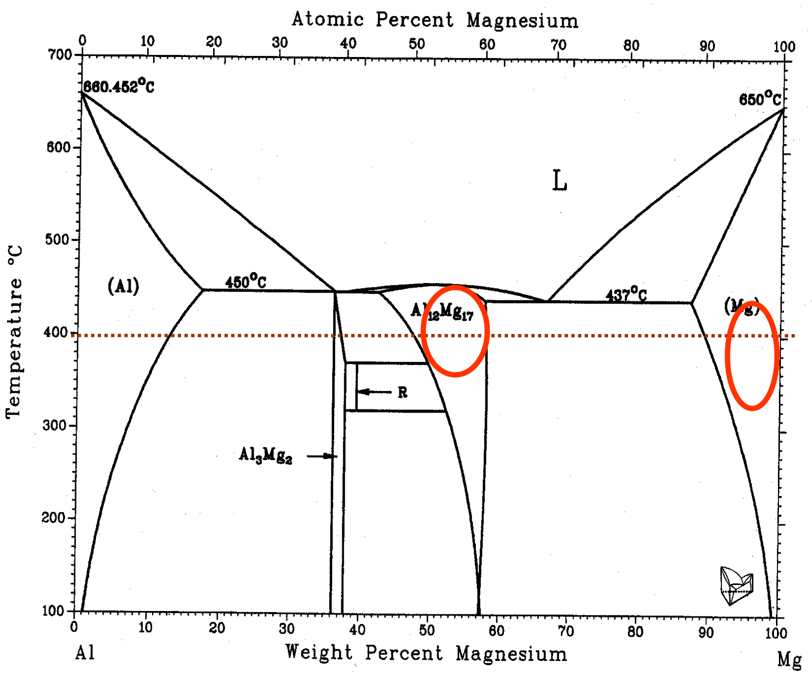
- Clean, planarize sample surface prior to sputter deposition
  - Plasma Clean (PC)
  - Ion Beam Etching (IBE)
  - Reactive Ion Etching (RIE)
  - Ion Beam Sputter Coating (IBSC)
- Pure atmosphere (Ar) during ion beam sputter deposition
  - Attempts to increase deposition rate (Xe?)
  - Metal getter system, in-situ gettering being explored
- Load lock – multiple sample capability
- Controlled thickness, automation



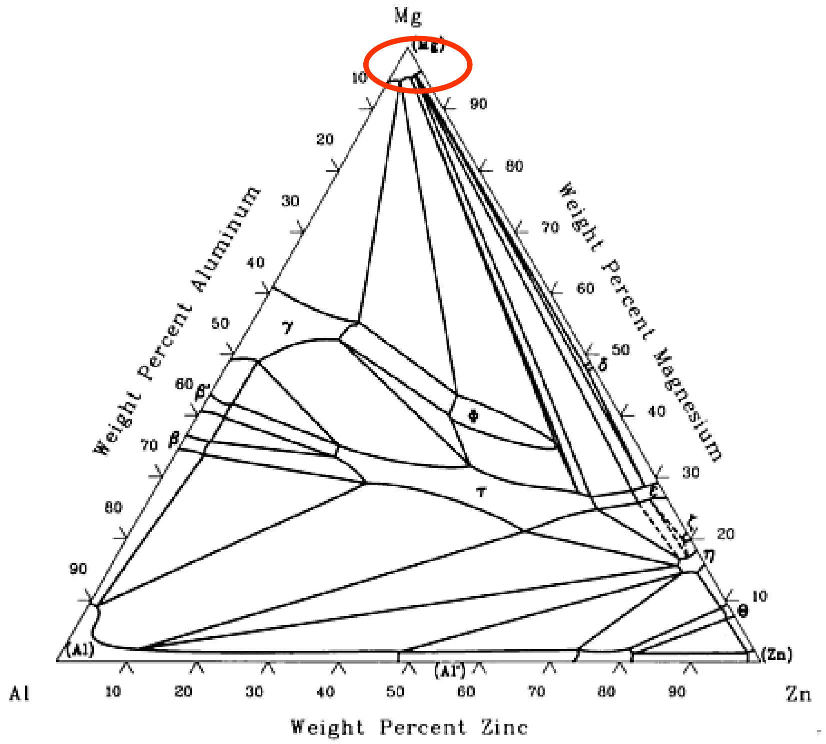
Top view

Current Work in Mg-Al-Zn (Mg rich phase)

- Impurity diffusion (Al, Zn) studies in Mg.
- Improvements in current ion beam sputter tool to minimize oxygen levels in Mg isotope film.
- Future years: Mg-Al-Mn and Mg-Al-Zn-Mn



T_o



Summary

- Justification for effort
  - Clarity and specificity
- Address technical issues
  - Volume databases alone may not be sufficient
    - Grain boundary, orientation effects
  - 1D Software for bulk diffusion may not be enough
    - Thin films, non-planar interfaces, varied boundary conditions
- Tracer diffusion databases
  - Stable isotopes to the rescue but not always (Al, Pb, Mn, etc.)
  - Free of major assumptions
  - Independent of thermodynamics
  - Can assess newer/improved formalisms as they develop
  - Amenable to a variety of driving forces
  - Necessary for line compounds, grain boundary measurements, …
  - Instrumentation/experimentation challenges & costs are significant
    - National Labs/Centers can play a major role

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Oak Ridge National Laboratory