NIST 2010 Diffusion Workshop

Atomic mobility and diffusivity in Al alloys

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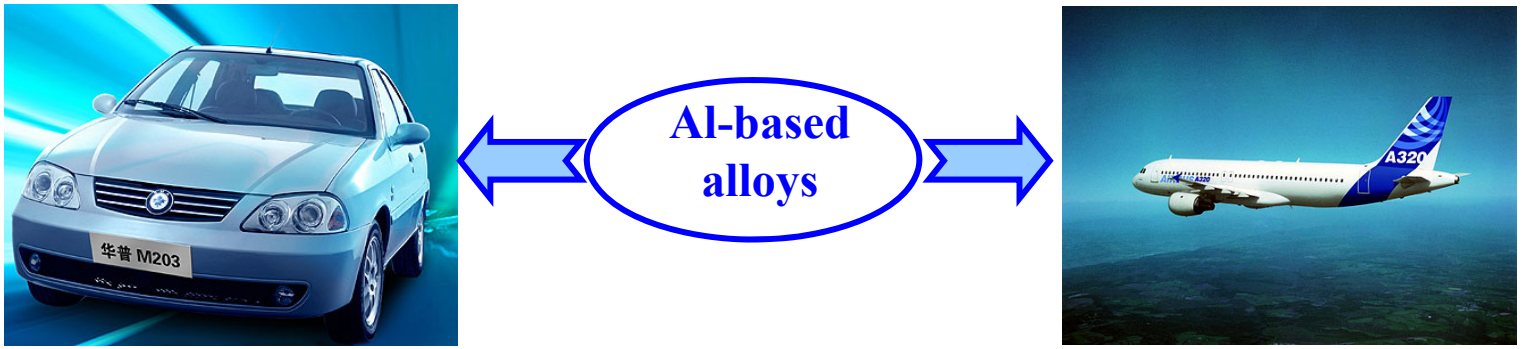
Atomic mobility and diffusivity in Al alloys

1. Motivation
2. Computational and experimental methods
   - 2.1 Diffusion couple with EPMA technique
   - 2.2 Empirical approaches
   - 2.3 First-principles method
   - 2.4 DICTRA approach
3. Atomic mobility and diffusivity in binary Al alloys
4. Atomic mobility and diffusivity in ternary Al alloys
5. Summary

1. Motivation

- Al-based alloys are widely used as aeronautic and civil materials



- (I) Al-based thermodynamic database is reasonably established.

(II) Lack of reliable kinetic databases for Al alloys!

- Our work: To establish an atomic mobility database for Al alloys via a combination of experiments, empirical approach, first-principles method and DICTRA approach.

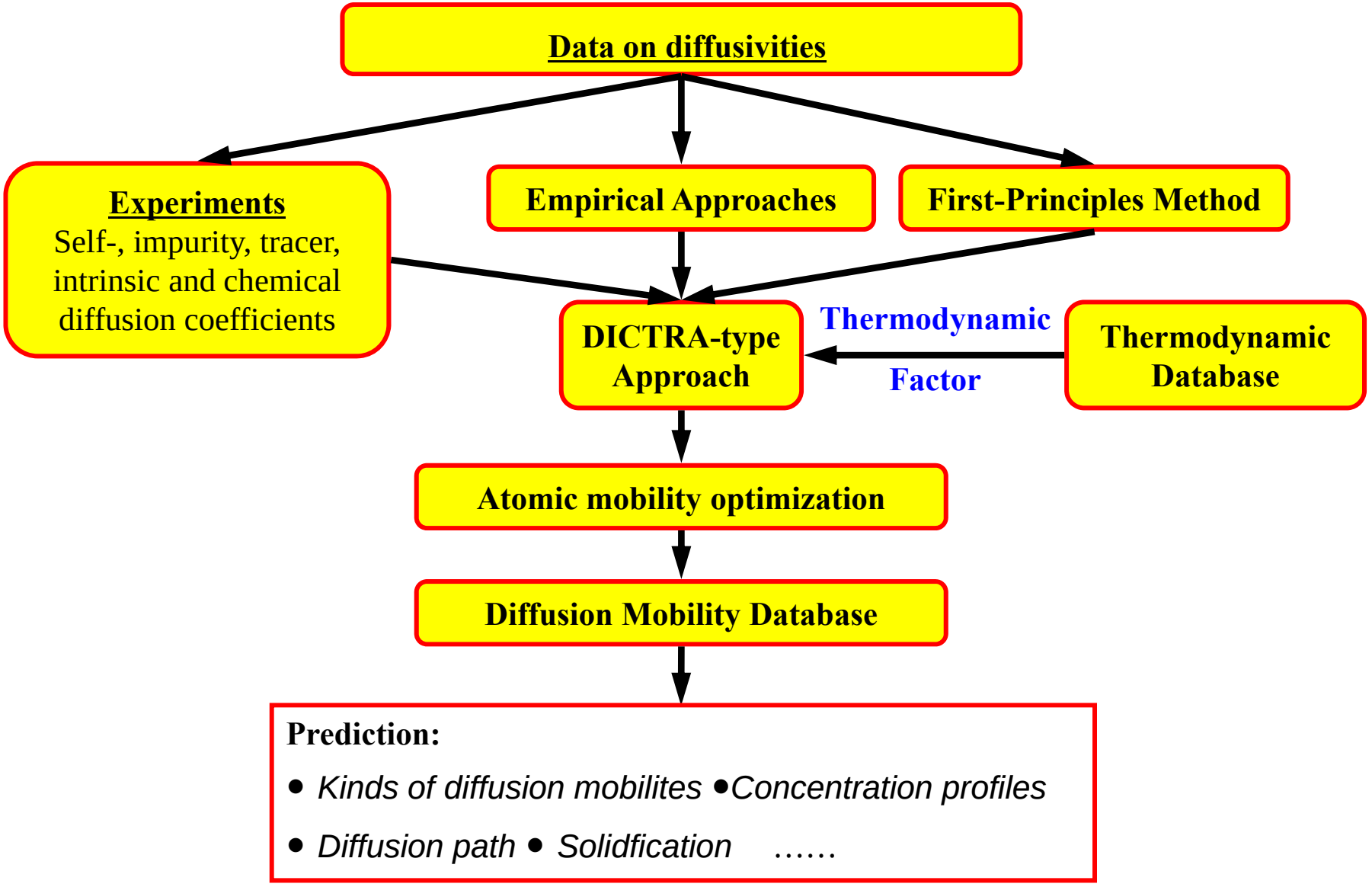


Fig.1 Our strategy to establish an atomic mobility database in Al alloys

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2. Computational and experimental methods

2.1 Diffusion couple with EPMA technique

2.2 Empirical approaches

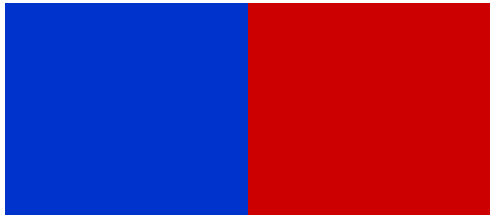
2.3 First-principles method

2.4 DICTRA approach

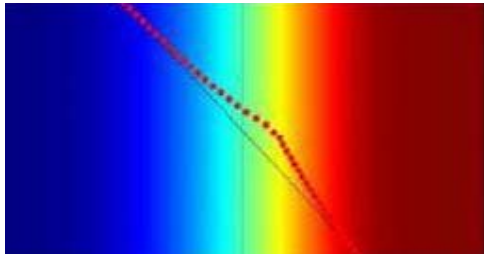
2.1 Diffusion couple with EPMA technique

Diffusion Couples → **EPMA Technique** → **Diffusion Coefficient**

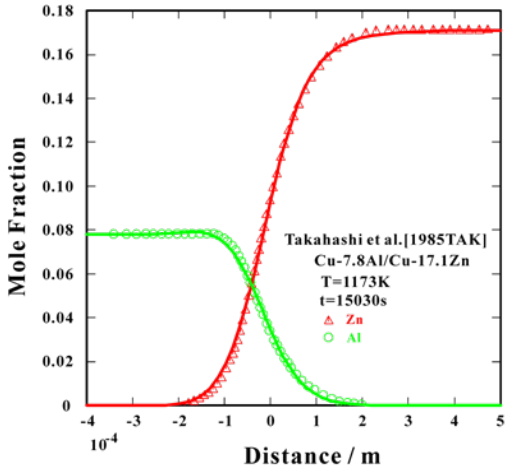
◆**Prepare diffusion couples**



◆ **annealed**
at certain temperature
for certain time

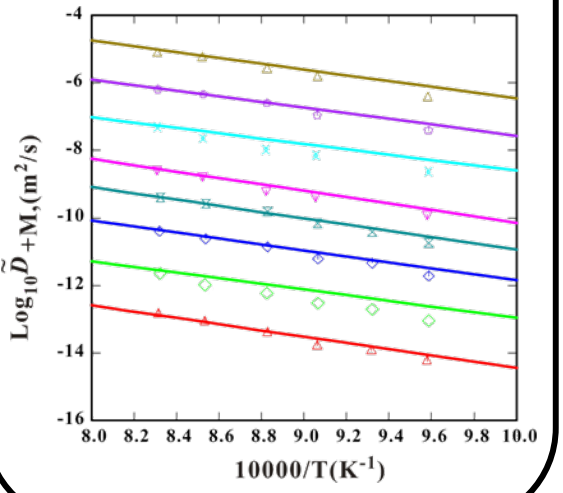


◆**Measurement of the concentration profiles via Electron Probe Microanalysis (EPMA)**



◆**Calculate the diffusion coefficient**

$$\tilde{D}(C^*) = -\frac{1}{2t}\frac{\int_{C_L}^{C^*} x dC}{(dC/dx)_{C^*}}$$



2.1 Diffusion couple with EPMA technique

Experimental procedure

Al-Cu-Zn (fcc in Al-rich side)

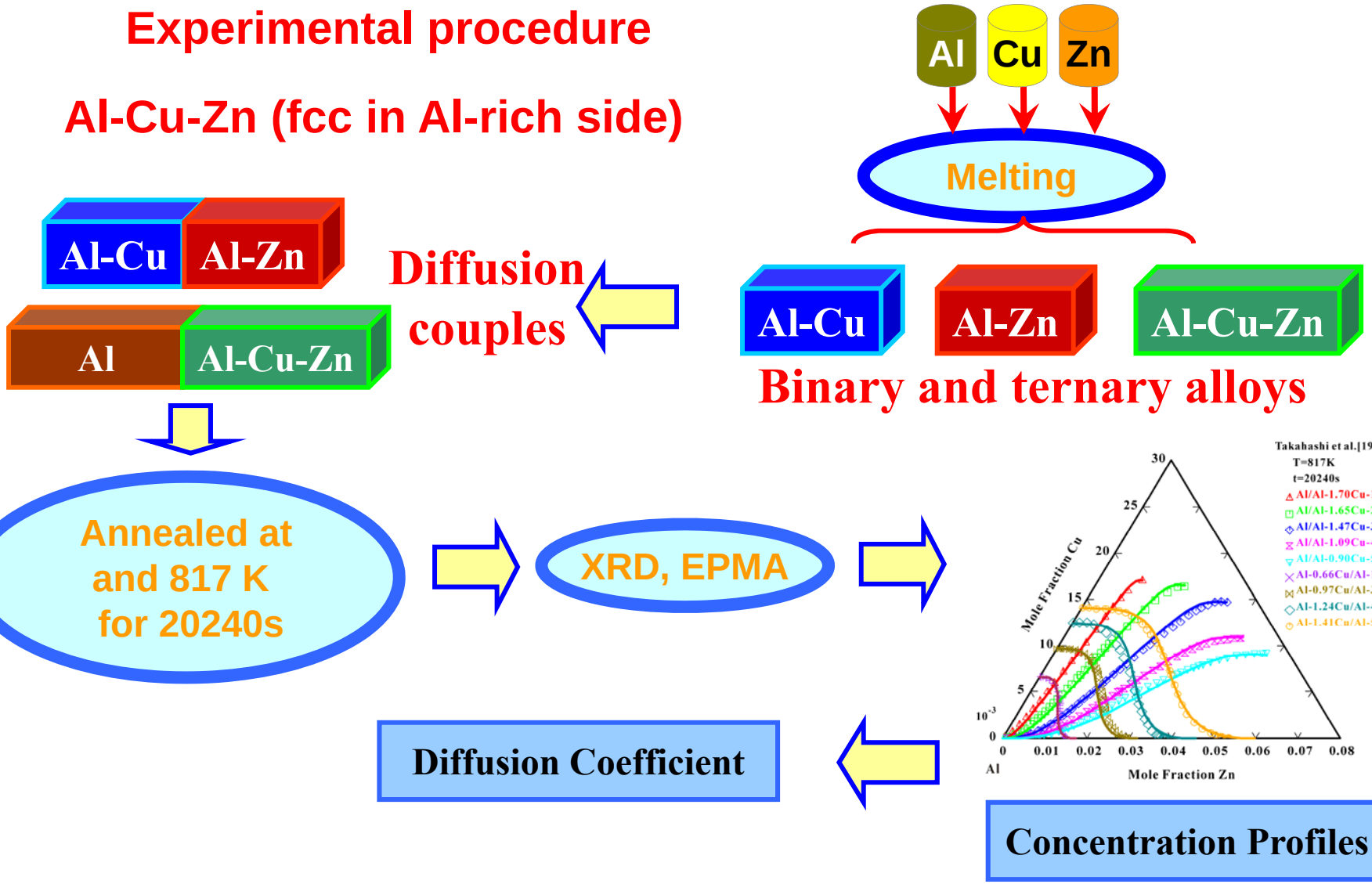


Fig. 2. Experimental procedure to Measure the Diffusion Coefficient of the Al-Cu-Zn system

2. Computational and experimental methods

2.1 Diffusion couple with EPMA technique

2.2 Empirical approaches

2.3 First-principles method

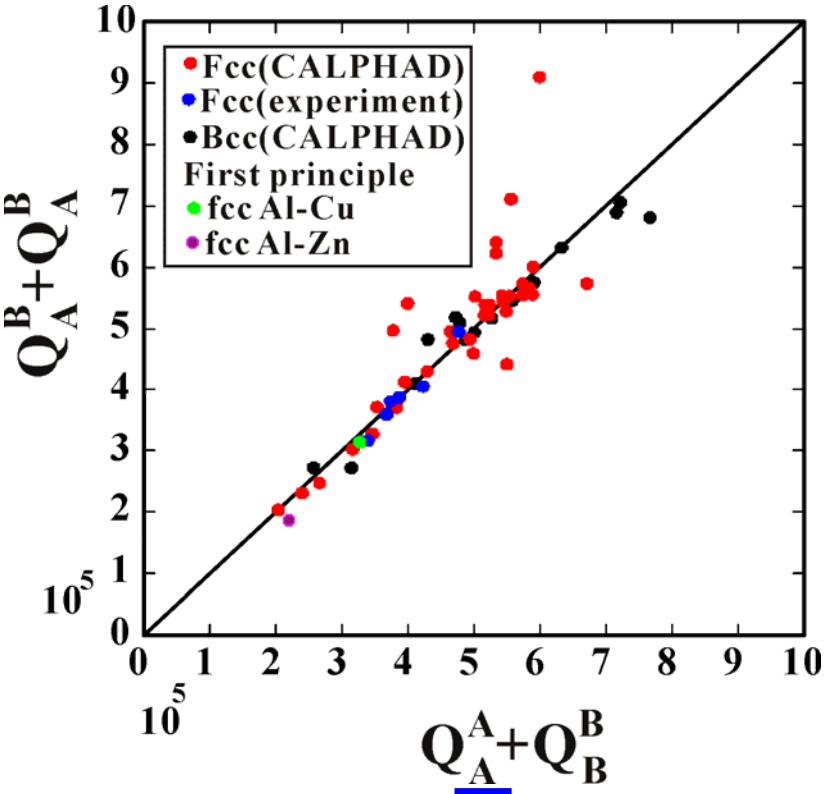
2.4 DICTRA approach

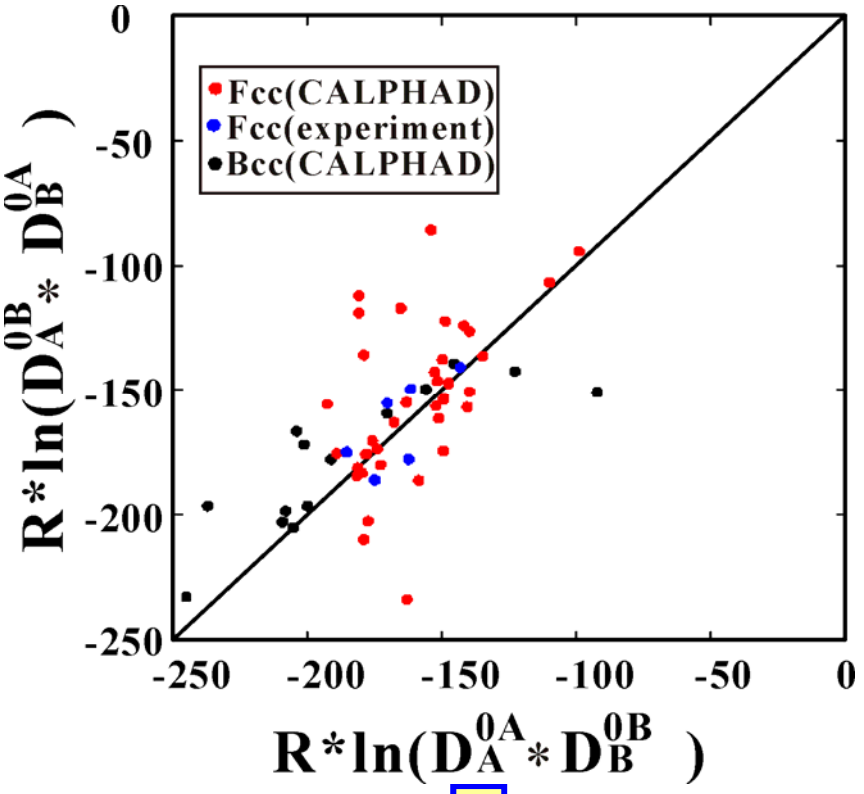
2.2 Empirical approaches

Summary of empirical approaches to estimate self-diffusivity and impurity diffusivity

values	relation	reference
Q_{self}	$Q = ATm$, (Tm is melting point; A=38 cal/mol for fcc; A=32.5 for bcc) $Q = 16.5\ Lf$,(Lf is latent heat of fusion, in kcal/mole) $Q = 0.65\ Ls$, (Ls is latent heat of sublimation, in kcal/mole)	J. Askill, IFI/Plenum, pp. 19-26 (1971)
	$Q=B/\chi$, (χ is compressibility)	G.B. Gibbs, C.E.G.B. Report RD/B/n/355, Nov.1964
	$Q = 700/\alpha$, (α is coefficient of linear expansion at RT, in ppm/^{0}C)	G. Askill, phys. Stat. Soli.,11:K49(1965)
	$Q=KE_0a^3$, (K is a proportionality constant depending only on the crystal structure, E_0 is an appropriate constant, a is the lattice parameter)	S. Dushman and I. Langmuir, Phys. Rev., 20:113(1922)
	$Q = (Ko+V)RTm$, (Ko is a crystal structure factor: 14 for bcc; 17 for fcc and Hcp; 21 for diamond structure. V = valence of the metal.)	O.D. Sherby and M.T. Simnad, Trans. ASM, 54, 227-40(1961)
	$Q=RTm(K+1.5V)$, (K=13 for bcc, 15.5 for fcc and cph, 20 for diamond)	A.D. Leclaire, Phil. Mag. , 7 (13) :141(1962)
D_0^{self}	$D_0=a^2 \cdot v \cdot \exp(\lambda \cdot \beta \cdot Q/RTm)$, (a = lattice parameter; v = vibrational frequency; λ = constant (0.6 for bcc, and 0.8 for fcc); β = 0.5)	C. Zener, Acta Cryst., 3, 346 (1950)
	$D_0 = 1.04 \cdot 10\text{-}3\ Q\ a^2$	J. Askill, IFI/Plenum, pp. 19-26 (1971)
D_{self}	$D=3.4\times10^{-5}Tm \cdot a^2\exp(-17.0Tm/T)$cm^2/sec, (T, Tm is temperature (K), a is lattice parameter(10^{-10}).)	J. Askill, IFI/Plenum, pp. 19-26 (1971)
D_{AA}^{B}	$D = (D_{A\text{ in }B})x_B\ (D_{B\text{ in }A})x_A\ \exp(-16\ \Delta TS/(RT)F$, (Δ TS is the difference between solidus temperature of the alloy and the temperature obtained by letting the solidus temperature vary linearly with the composition, $D_{A\text{ in }B}$ and $D_{B\text{ in }A}$ are impurity diffusivities.)	A. Vignes and G.E. Birchenall, Acta Metal.,16, 1117-25(1968)

2.2 One new empirical approach (our work)





$$Q_A^A + Q_B^B = Q_A^B + Q_B^A$$

$$\ln(D_A^{0A} * D_B^{0B}) = \ln(D_B^{0A} * D_A^{0B})$$

Our proposed equation could predict one of the four atomic mobilities .

S.L. Cui, Y.Du et al., J.Phase Equilibria and Diffusion, in review, 2010

2.2 One new empirical approach (our work)

$$\ln(D_A^{0A} * D_B^{0B}) = \ln(D_B^{0A} * D_A^{0B})$$

$$Q_A^A + Q_B^B = Q_A^B + Q_B^A$$

(1) Partial molar volume of solute ≅ molar volume of solvent
(2) Vegard rule holds for volume

Our proposed empirical approach could work for disordered substitution phase.

2.2 Empirical approach (our work)

Al-Zn (fcc phase)

The four end-members for **Al-Zn** *system are*

√ Φ^{Al}_{Al} ⟶ **From Zhang and Du(2009)** $\quad \Phi^{Al}_{Al} = -123111.6 - 97.34 * T$

√ Φ^{Zn}_{Zn} ⟶ **Empirical approach by Askill** $\quad \Phi^{Zn}_{Zn} = -76569 \quad -86.21 * T$

fcc Zn phase is metastable.

FP (-80.57)

Q=RTm(K+1.5V) ⟶ **-76.6KJ/mol**

$D_0 = 1.04 \times 10^{-3}$ Q a^2 ⟶ **0.314cm²/s**

√ Φ^{Al}_{Zn} ⟶ **From Du et al. (2003)** $\quad \Phi^{Al}_{Zn} = -116100 - 94.28 * T$

Φ^{Zn}_{Al} ⟶ **Our proposed approach** $\quad \Phi^{Zn}_{Al} = -83580.6 - 89.27 * T$

2. Computational and experimental methods

2.1 Diffusion couple with EPMA technique

2.2 Empirical approaches

2.3 First-principles method

2.4 DICTRA approach

2.3 First-principles method

Self-diffusion: **M.Mantina,Y.Wang, R.Arryave, L.Q.Chen,Z.K.Liu, PRL, 100,215901(2008)**

Self-diffusion coefficient is calculated by the following equation:

Self-diffusion coefficient

Correction factor (for fcc-system, 0.7815)

Lattice constant

$$D = fa^2Cw$$

Jump Frequency

Vacancy concentration

$$C_{eq} = \exp(\frac{\Delta S_f^v}{k_B})\exp(-\frac{\Delta H_f}{k_B T})$$

$$w = \left[\prod_{i=1}^{3N-3} v_i^{vac} \Big/ \prod_{i=1}^{3N-4} v_i^{sad}\right] \times \exp(-\Delta H_v^{mig} / k_B T)$$

ΔS^v_f = entropy of vacancy formation

ΔH_f= enthalpy of vacancy formation

ΔH_v^{mig} = vacancy migration enthalpy (energy barrier to be overcome for an atom to jump into the vacancy)

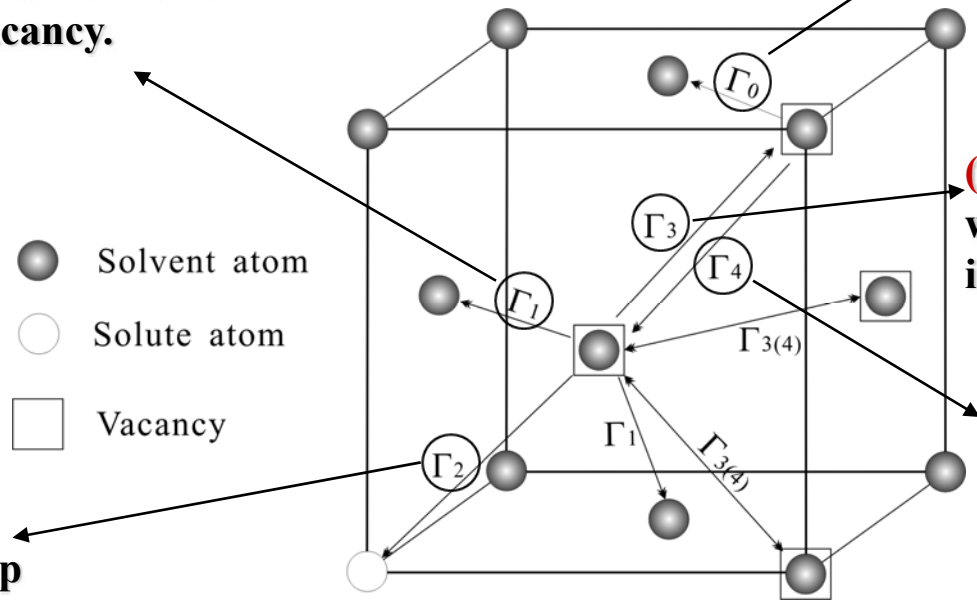
ν_i^{vac} and ν_i^{sad} = Phonon frequencies in normal and saddle-point configurations

2.3 First-principles method

Impurity-diffusion:

(1) a host atom (nearest neighbor to an impurity) jump which does not "dissociate" the impurity from the vacancy.

(5) host atom jump in the absence of an impurity.



(3) a host atom jump which "dissociates" the impurity and vacancy

(4) Reverse of jump Γ_3

(2) impurity atom jump

Fig .3. Five frequency model illustration for the case of an fcc system with a dilute impurity concentration. The arrows indicate the direction of the vacancy jump.

A.D. LeClaire and A.B. Lidiard, Phil. Mag., 47, 518 (1970)

2.3 First-principles method

Impurity-diffusion:

f_2= correction factor for impurity diffusion

f_0 =self-diffusion correction factor

According to the five jump frequency model, we have:

$$\frac{D_2}{D_0} = \frac{f_2}{f_0}\frac{w_4}{w_0}\frac{w_1}{w_3}\frac{w_2}{w_1}$$

we can obtain:

$$D_2 = f_2 w_2 a^2 \exp\left(-\frac{\Delta G_f^0 - \Delta G_b}{k_B T}\right)$$

Since jump frequency of the solute atom is:

$$w_2 = v^* \exp\left(-\frac{\Delta H_m}{k_B T}\right)$$

Substitute

So we can get the expression for impurity diffusion coefficient:

$$D_2 = f_2 v^* a^2 \exp\left(\frac{\Delta S_f}{k_B}\right)\exp\left(-\frac{\Delta H_m + \Delta H_f - \Delta G_B}{k_B T}\right)$$

***E*nthalpy of vacancy formation**

Solute-vacancy binding energy

Energy barrier for the exchange of the solute impurity with a nearest-neighbor vacancy.

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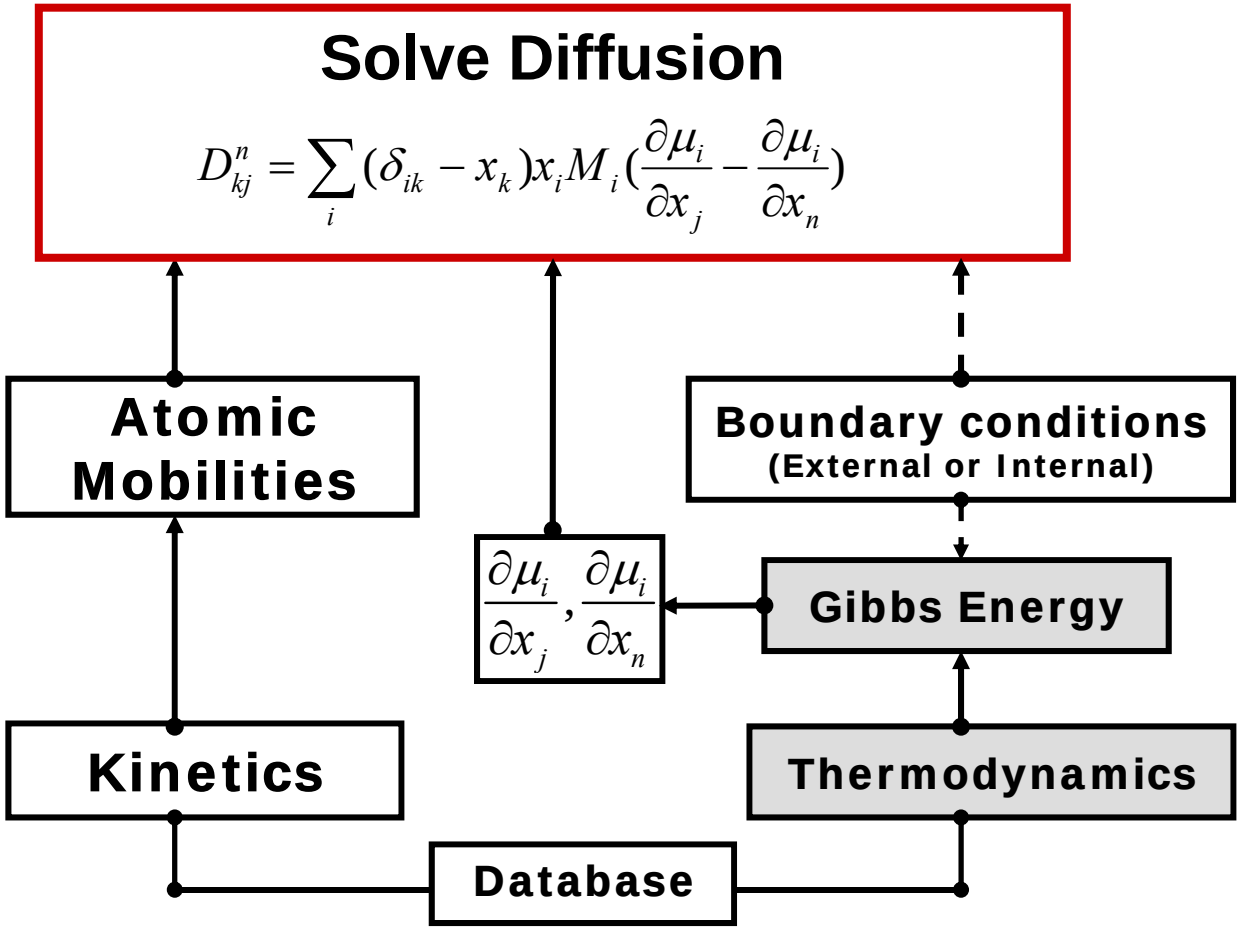
DICTRA (**DI**ffusion **C**ontrolled **TRA**nsformations):

a full coupling of thermodynamics and kinetics



2.4 DICTRA approach

According to Andersson and Ågren, the atomic mobility for an element B can be expressed by an equation of the form:

$$M_B = \exp\left(\frac{RT \ln M_B^0}{RT}\right)\exp\left(\frac{-Q_B}{RT}\right)\frac{1}{RT}{}^{mg}\Omega$$

M_B	*Mobility for element B*
M_B^0	*frequency factor*
Q_B	*activation energy*
${}^{mg}\Omega$	*Ferromagnetic contribution*

Composition dependency of atomic mobility is represented with a linear combination of the values at each endpoint of the composition space:

$$\Phi_B = \sum_i x_i \Phi_B^i + \sum_i \sum_{j>i} x_i x_j \left[\sum_{r=0}^{m} {}^r\Phi_B^{i,j}\left(x_i - x_j\right)^r\right]$$

$$+ \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \left[\sum_s v_{ijk}^s {}^s\Phi_B^{i,j,k}\right]; \qquad (s = i, j, k)$$

$$v_{ijk}^s = x_s + \left(1 - x_i - x_j - x_k\right)/3$$

where Φ_B represents $RT \ln M_B^0 - Q_B$.

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4. Atomic mobility and diffusivity in ternary Al alloys
5. Summary

The Al-Cu binary system (fcc phase)

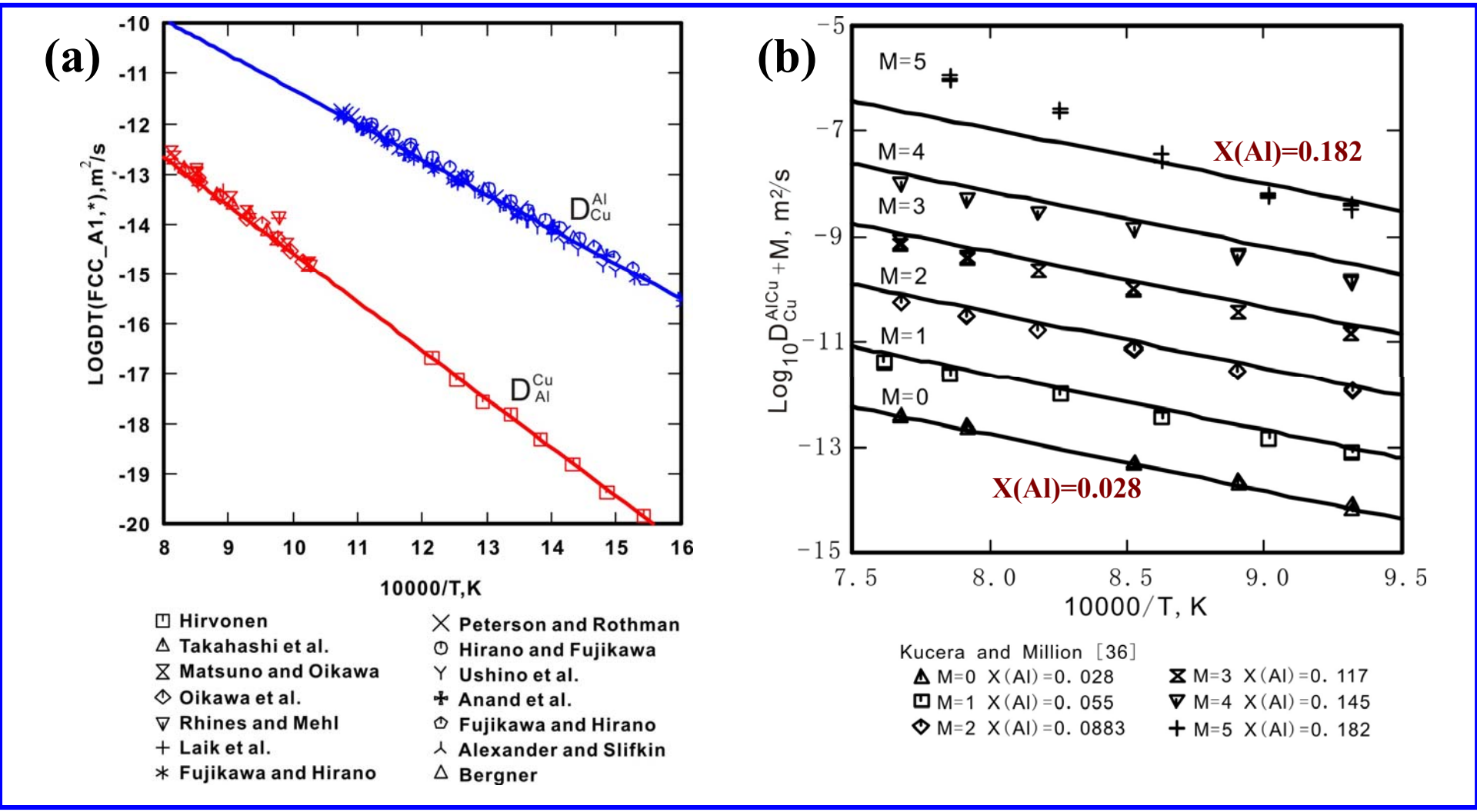

Fig. 4. Comparison between the calculated and measured coefficients of
(a) impurity diffusion Al in pure Cu and Cu in pure Al
(b) tracer diffusion of Cu in different fcc Al-Cu alloys

The Al-Mg binary system (fcc phase)

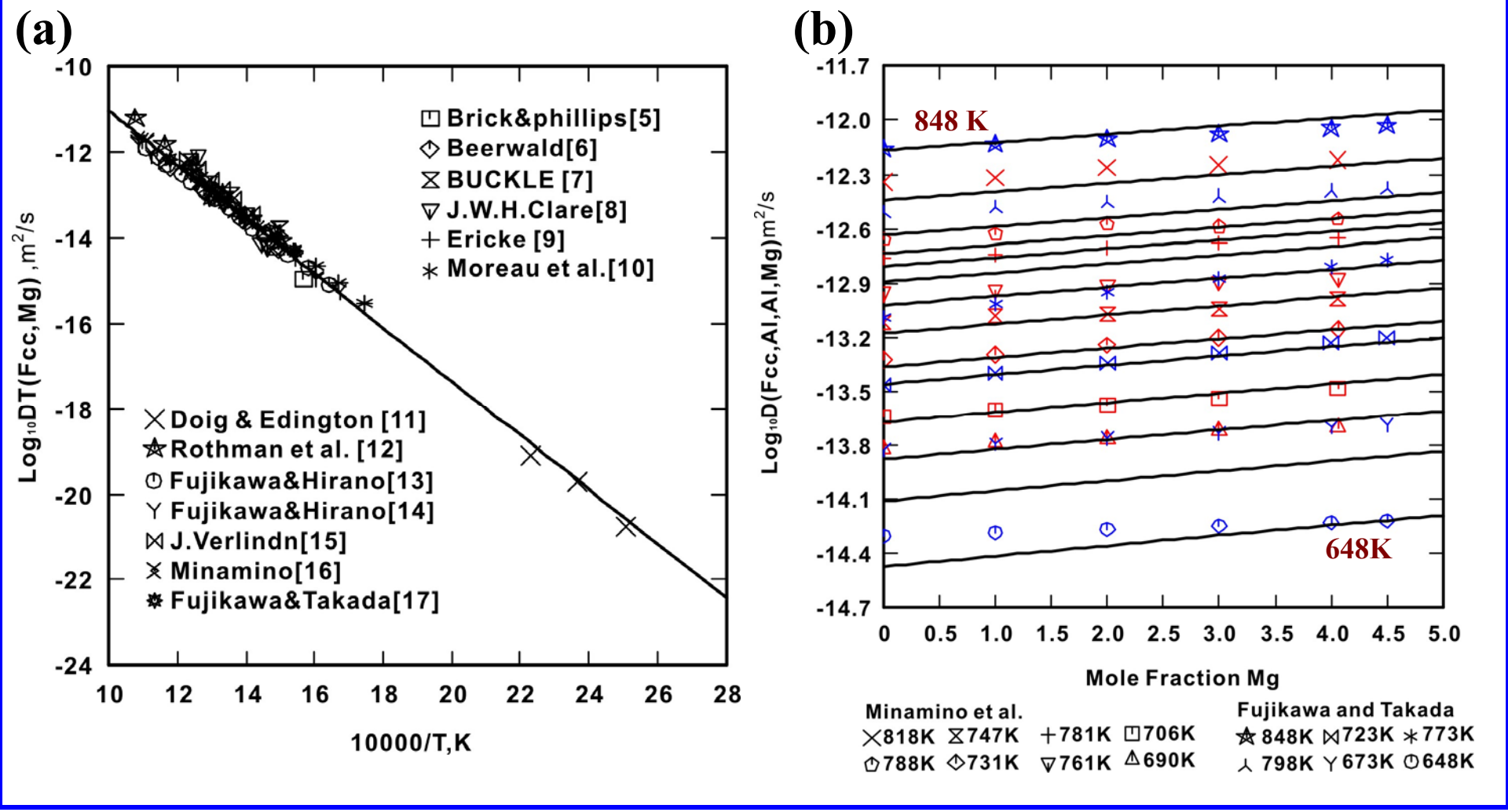

Fig. 5. Comparison between calculated and measured coefficients of
(a) impurity diffusion Mg in pure Al
(b) interdiffusion on Al-rich side of Al-Mg alloys .

The Al-Zn binary system (fcc phase)

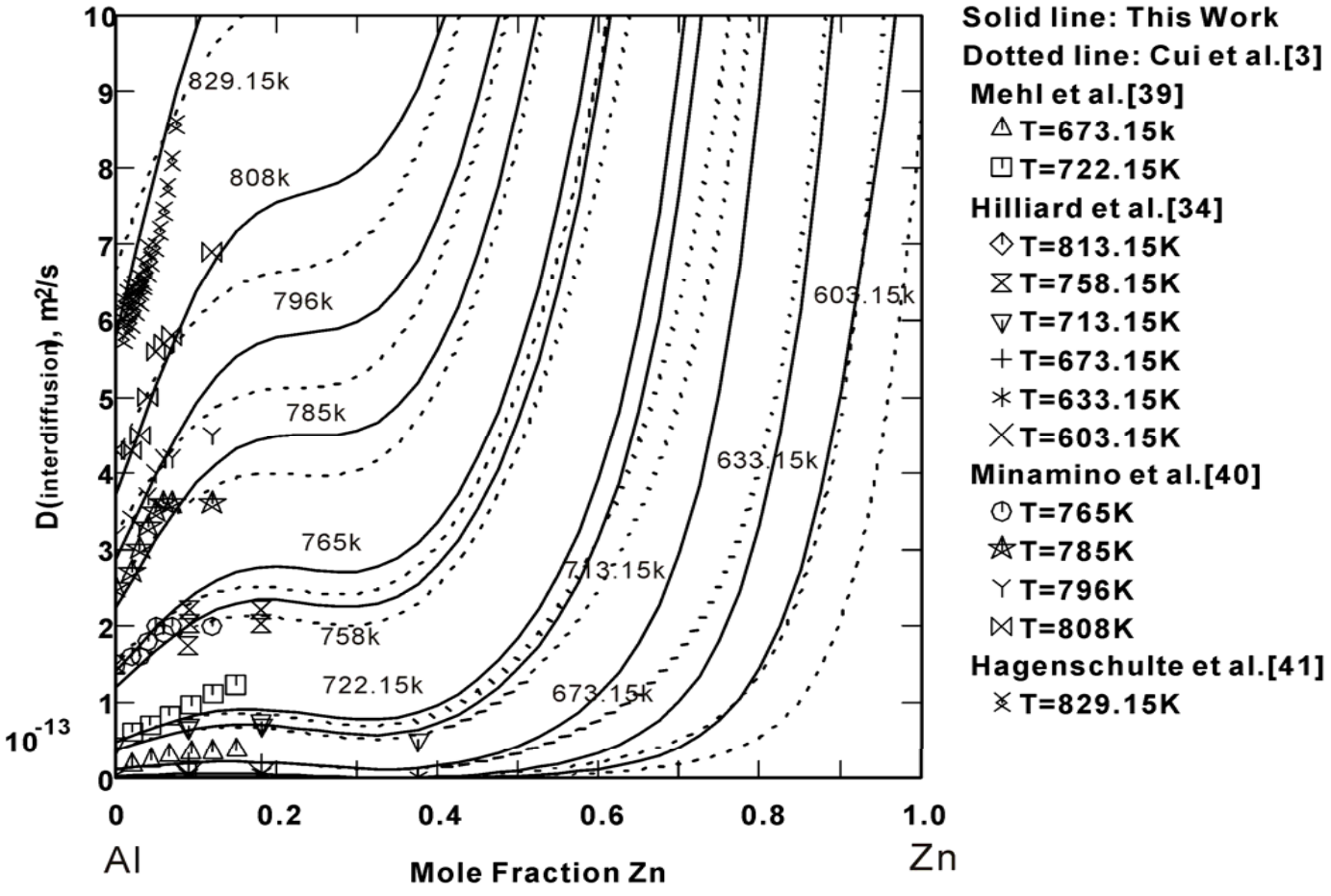

Fig. 6. Comparison between calculated and measured interdiffusion coefficients of Al-Zn alloys.

The Al-Zn binary system (fcc phase)

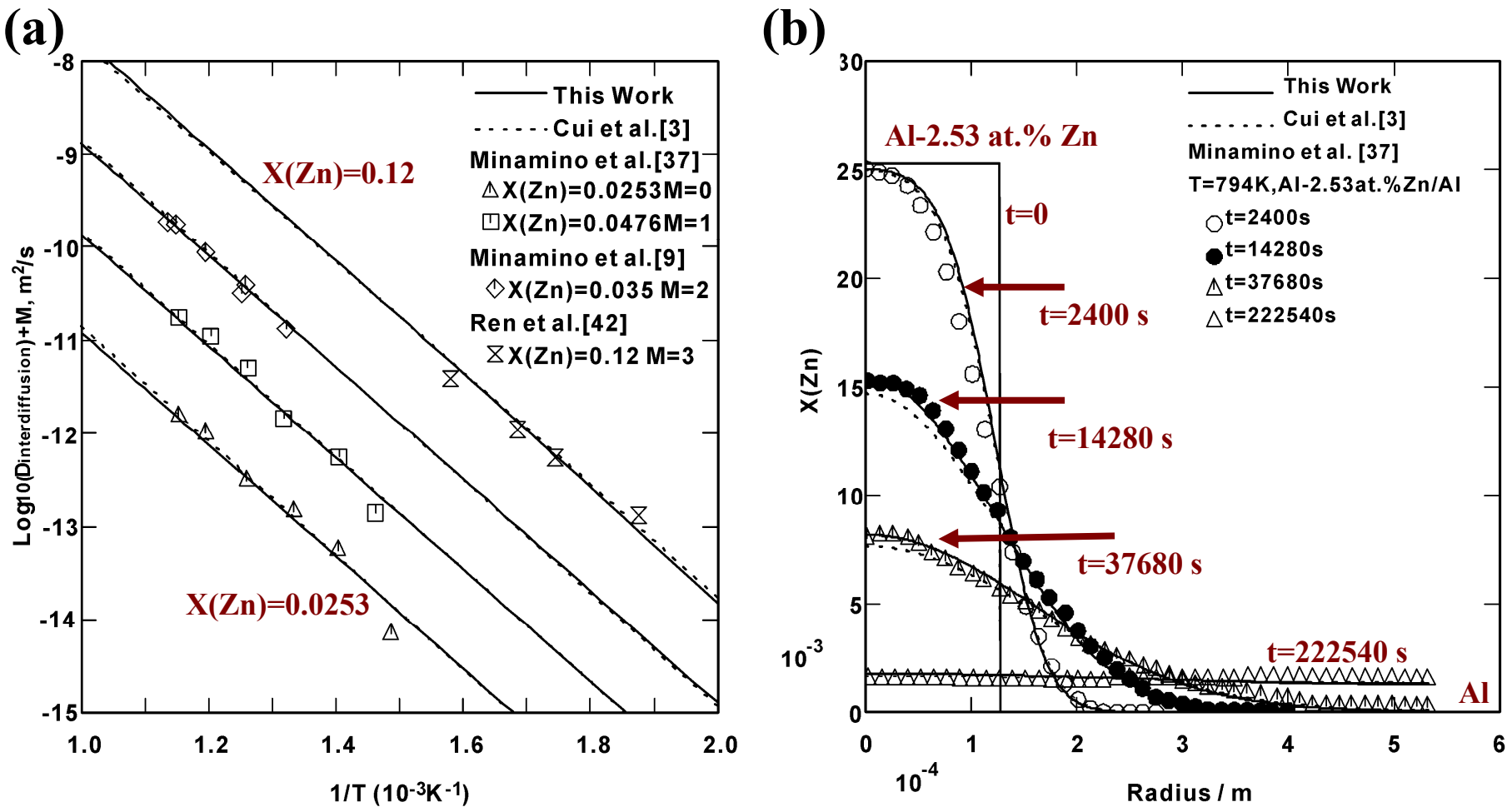

Fig. 7. Comparison between calculated and measured coefficients of
(a) Interdiffusion on Al-Zn alloys
(b) Predicted concentration profiles of Al-2.53at.%Zn/Al diffusion couple

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The Al-Cu-Zn ternary system (fcc phase)

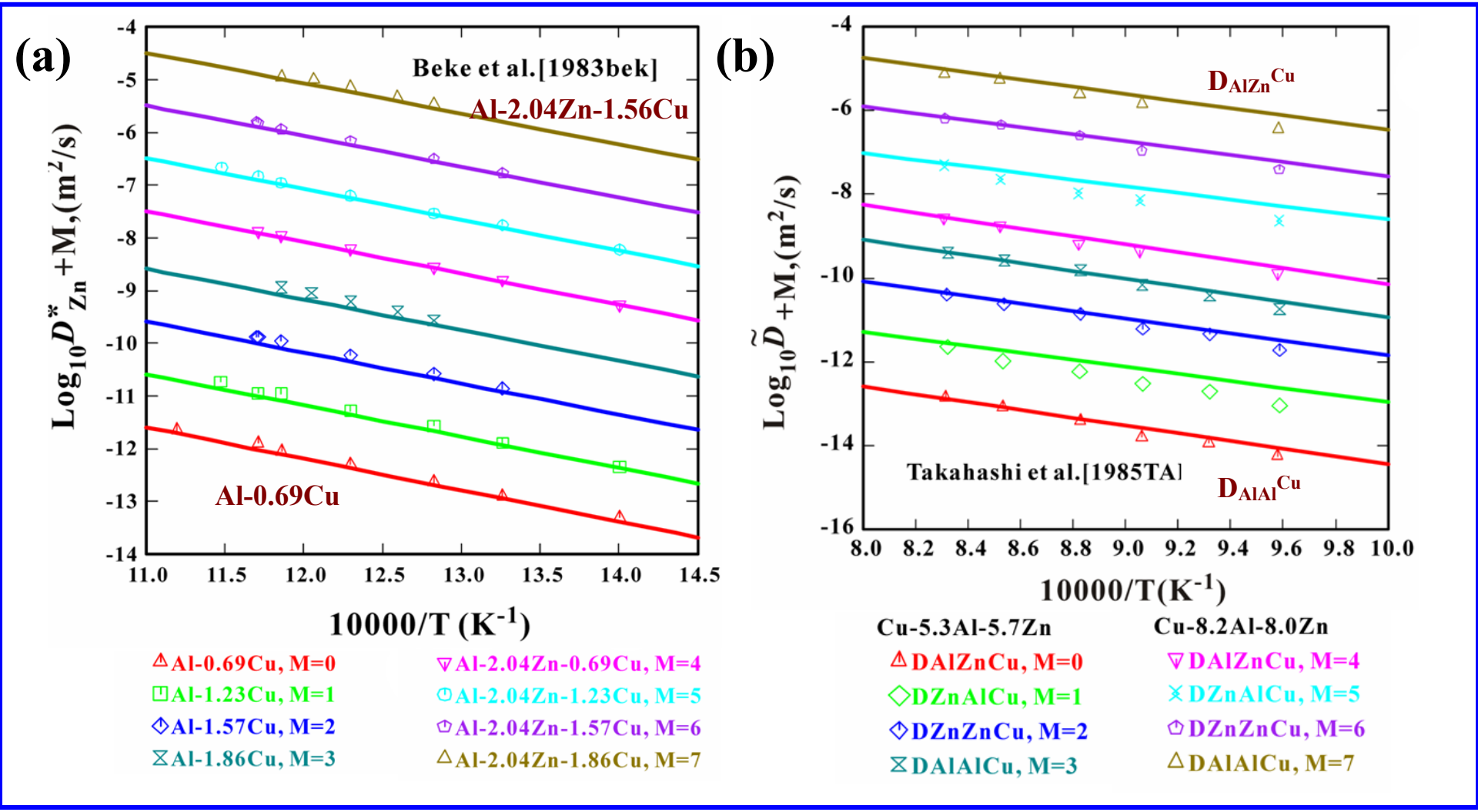


Fig. 8. Comparison between calculated and measured coefficients of
(a) tracer diffusion coefficients of Zn in Al-Cu and Al-Cu-Zn alloys
(b) interdiffusion coefficients in the Al-Cu-Zn alloy

The Al-Cu-Zn ternary system (fcc phase)

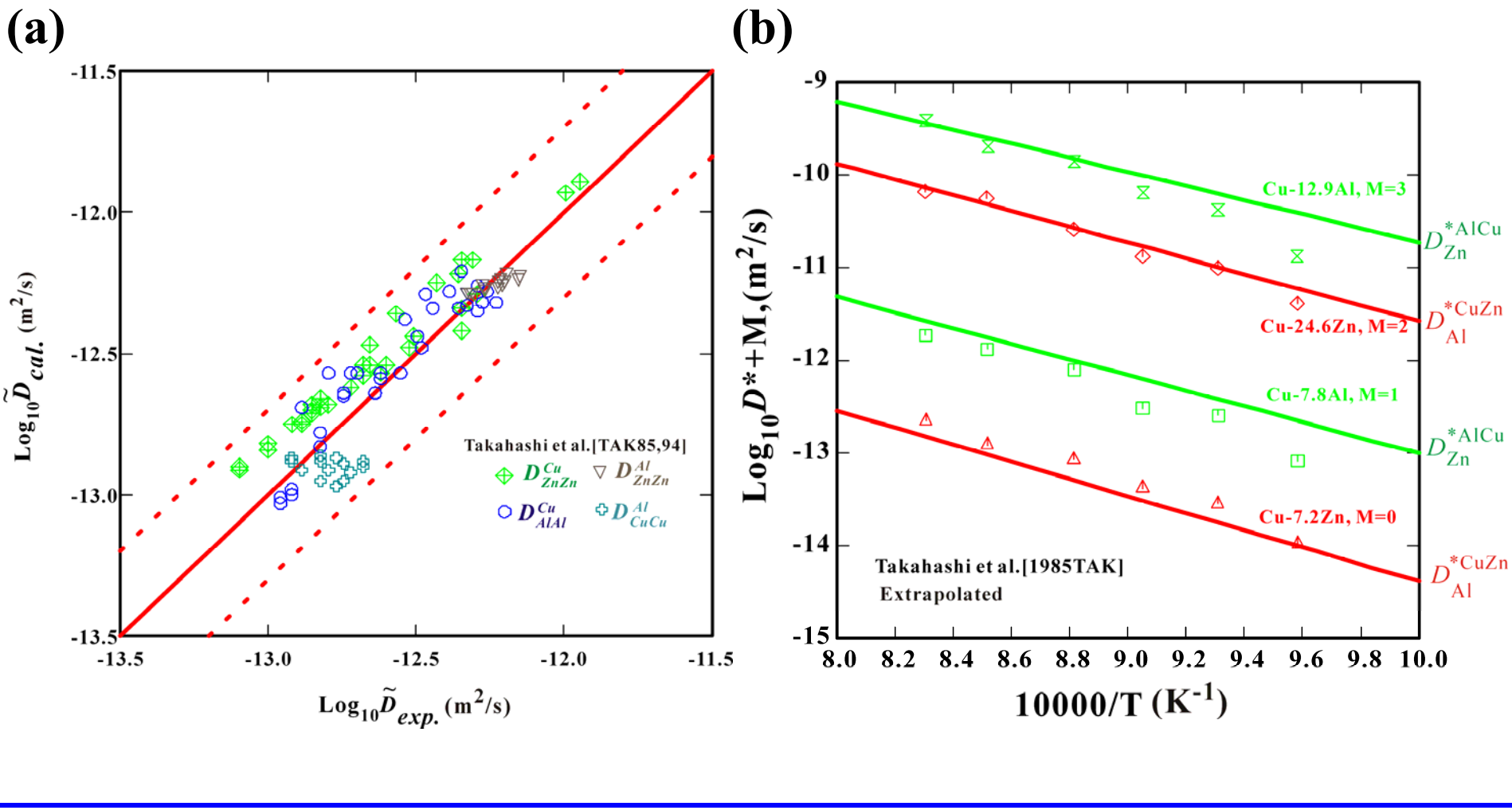
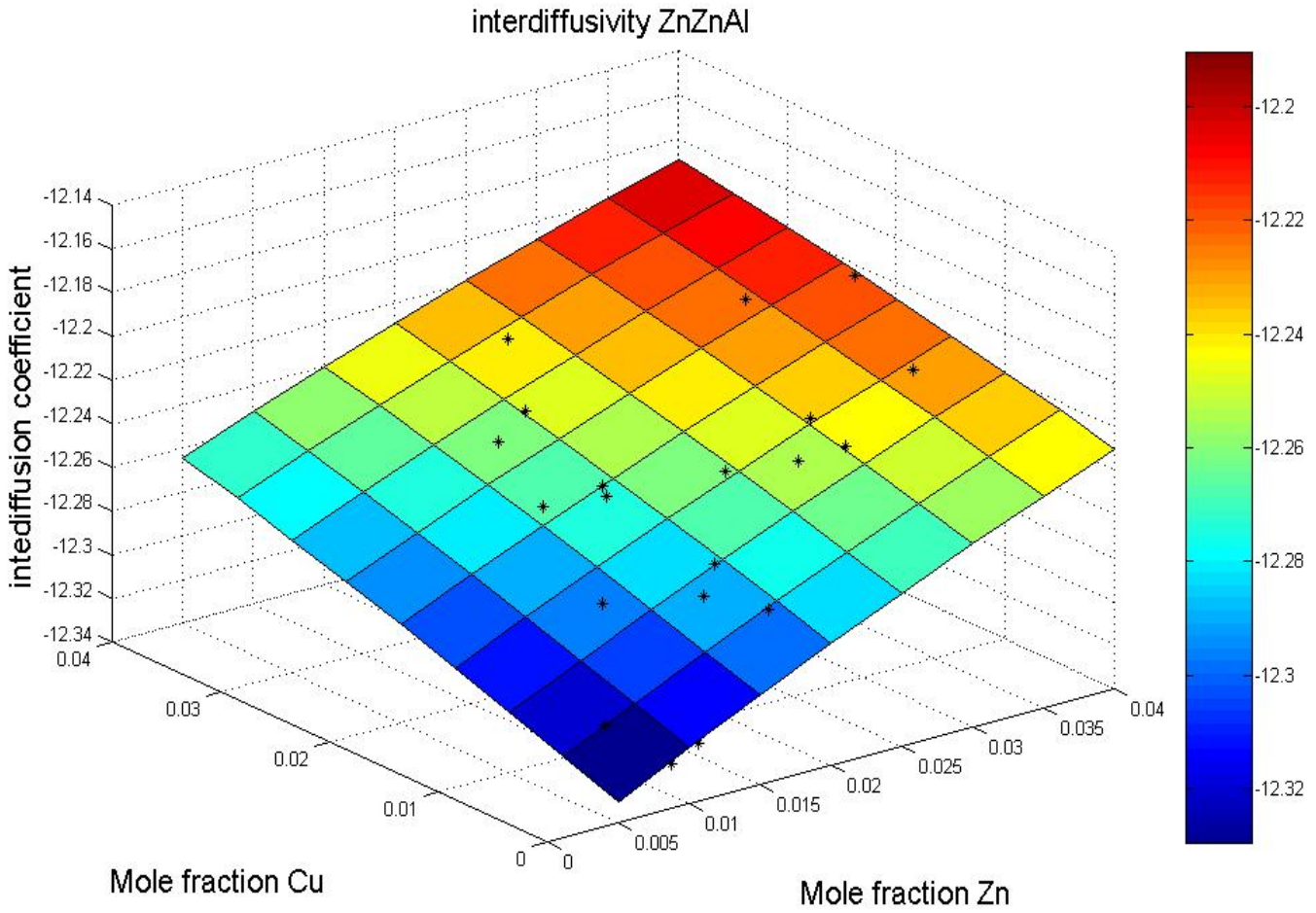


Fig. 9. Comparison between calculated and measured coefficients of
(a) main diffusion coefficients in Al-Cu-Zn alloys
(b) tracer diffusion coefficients: Zn in Al-Cu alloy, Al in Cu-Zn alloy.

The Al-Cu-Zn ternary system (fcc phase)



Close up on Fig. 9 (a). Comparison between calculated and measured main diffusion coefficients in Al-Cu-Zn alloys

The Al-Cu-Zn ternary system (fcc phase)

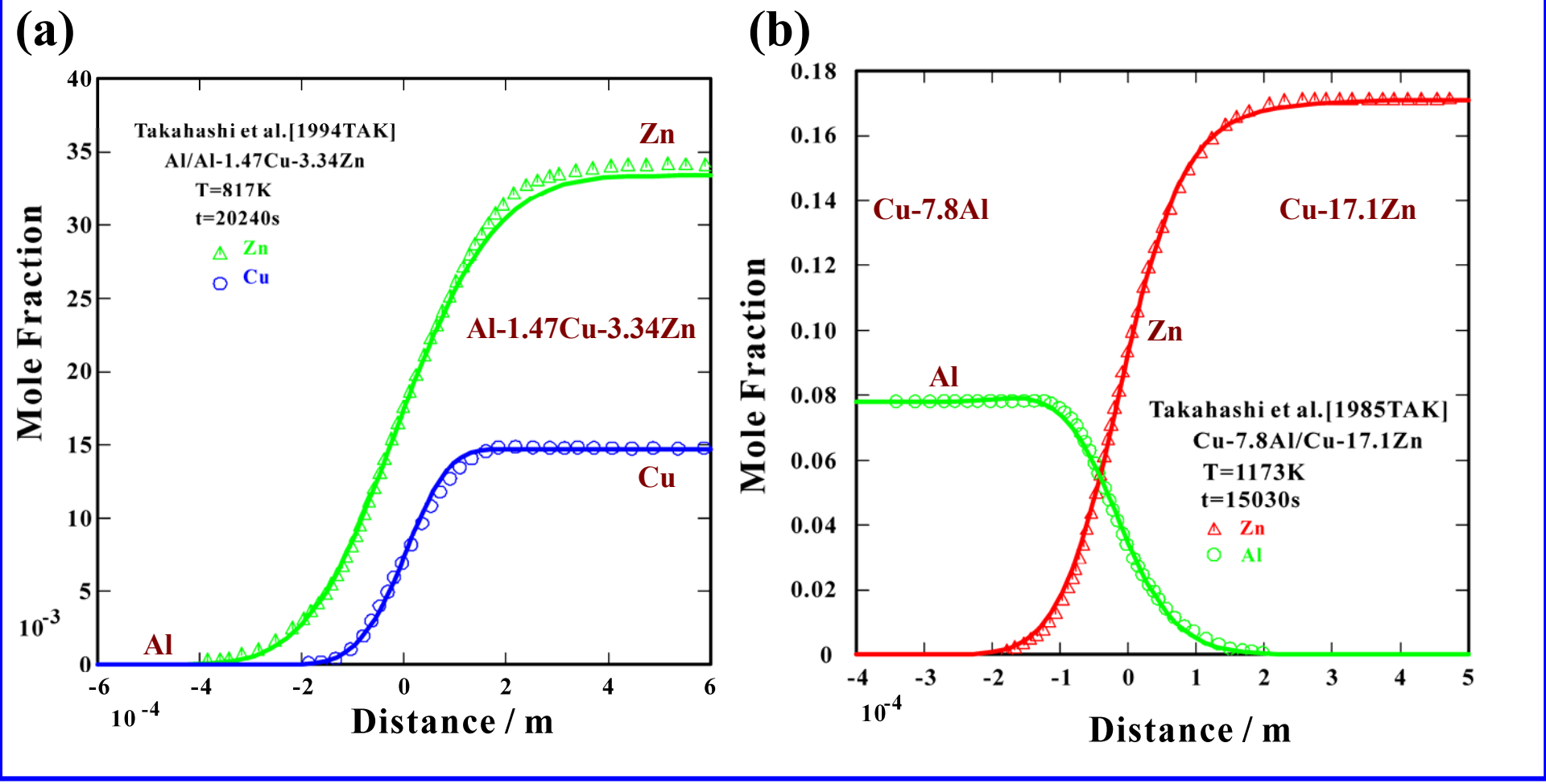


Fig. 10. Comparison between calculated and measured coefficients of
(a) Predicted concentration profiles of Al/Al-1.47 at.% Cu-3.34 at.% Zn diffusion couple
(b) Predicted concentration profiles of Cu-7.8 at.%Al /Cu-17.1 at.%Zn diffusion couple

The Al-Cu-Zn ternary system (fcc phase)

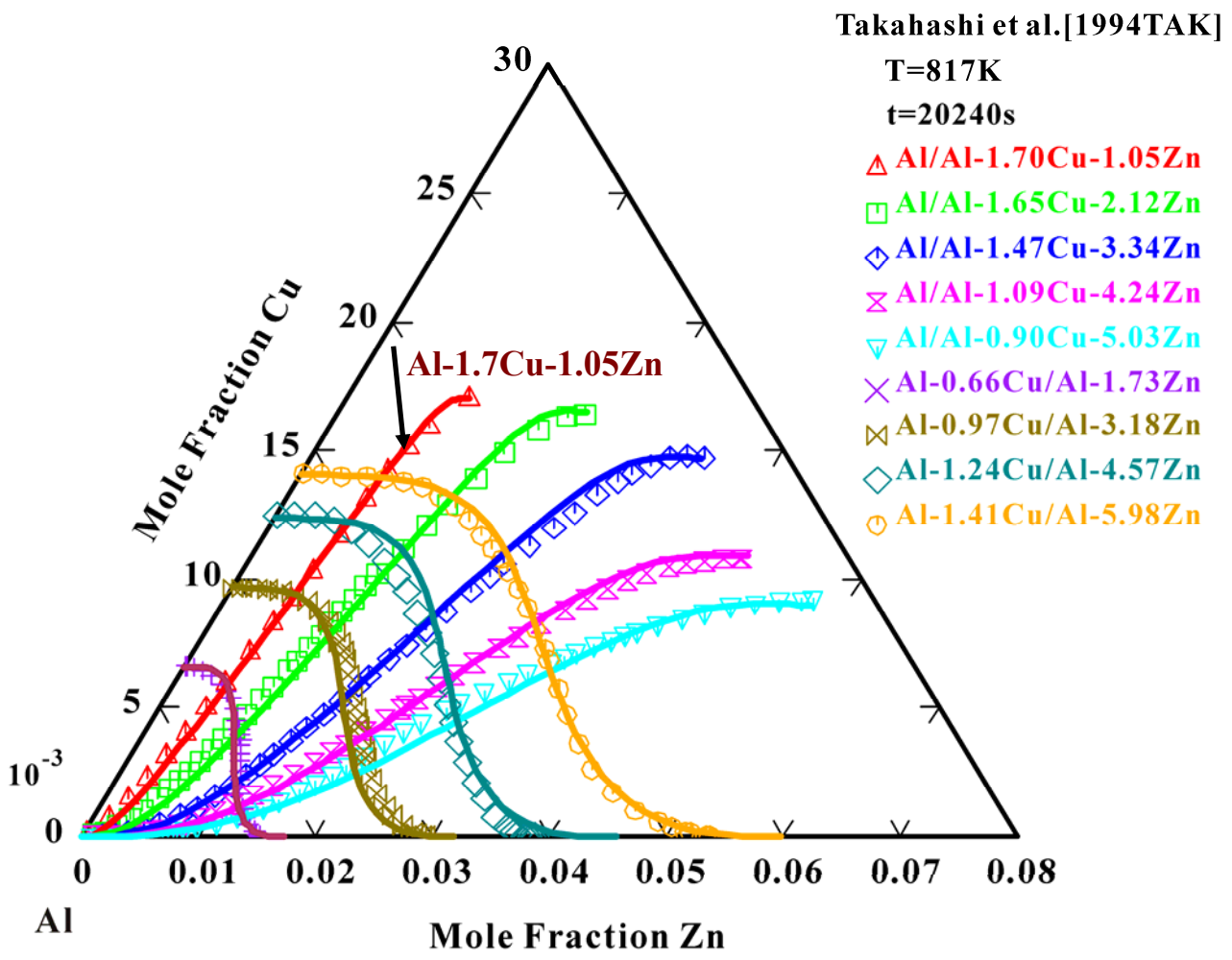


Fig. 11. Calculated diffusion path for ternary diffusion couples annealed at 817K for 20240s

The Al-Cu-Mg ternary system (fcc phase)

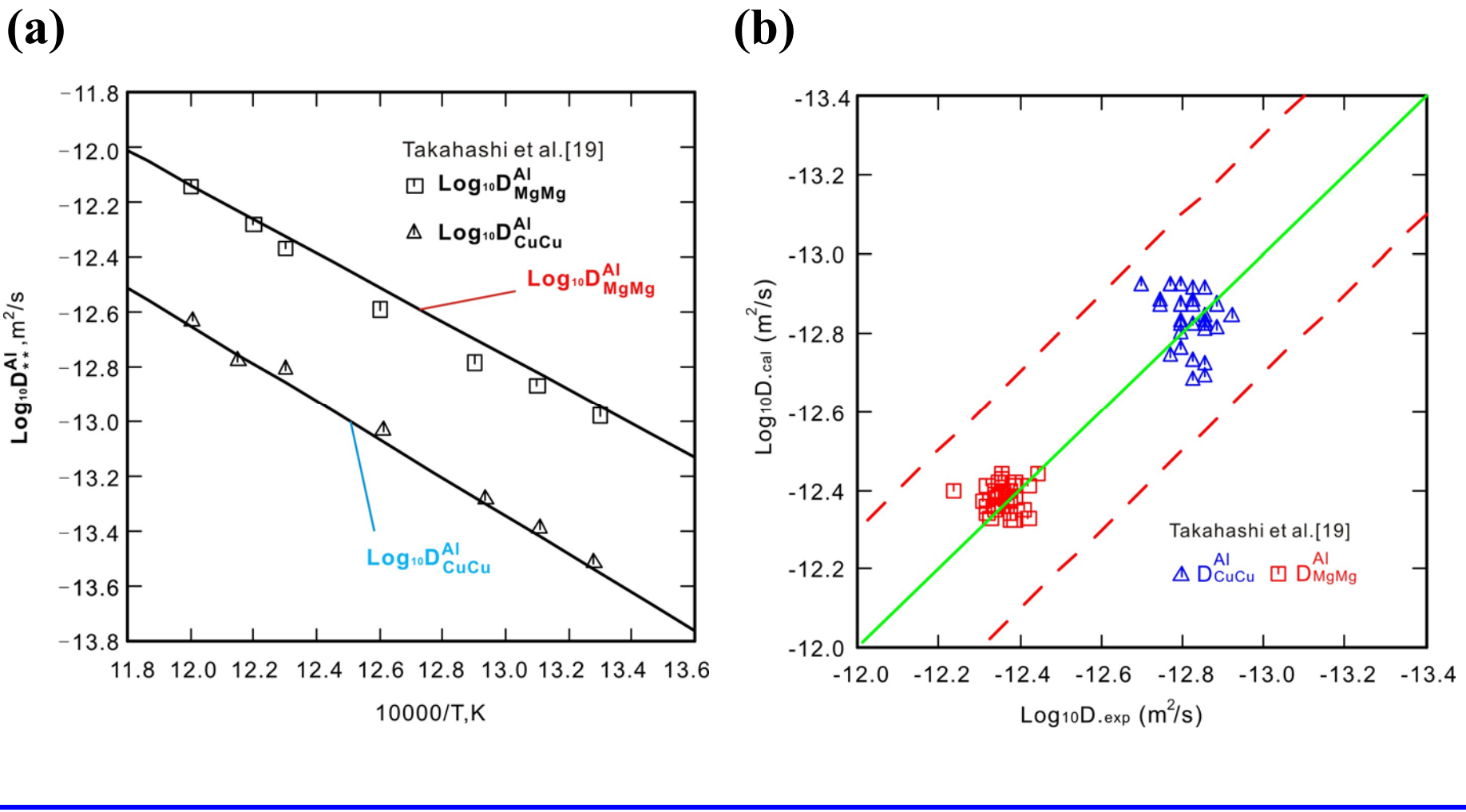


Fig. 12. Comparison between calculated and measured coefficients of
(a) main diffusion coefficients in Al-1at.%Cu-1at.%Mg
(b) main diffusion coefficients in Al-Cu-Mg alloy at 813K

The Al-Cu-Mg ternary system (fcc phase)

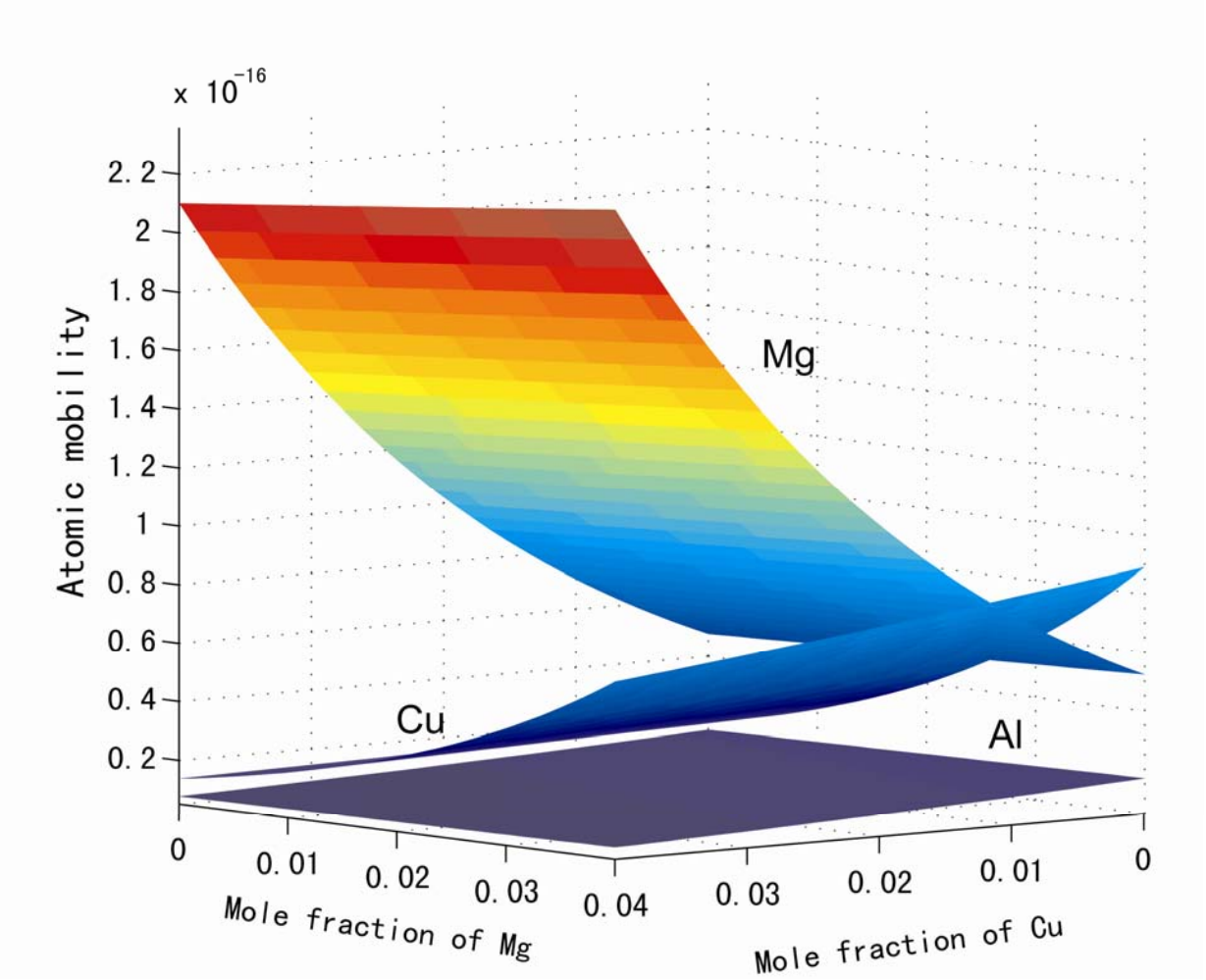


Fig. 13. 3D view of atomic mobility surfaces for Al,Cu and Mg at the Al-rich side at 813K

The Al-Cu-Mg ternary system (fcc phase)

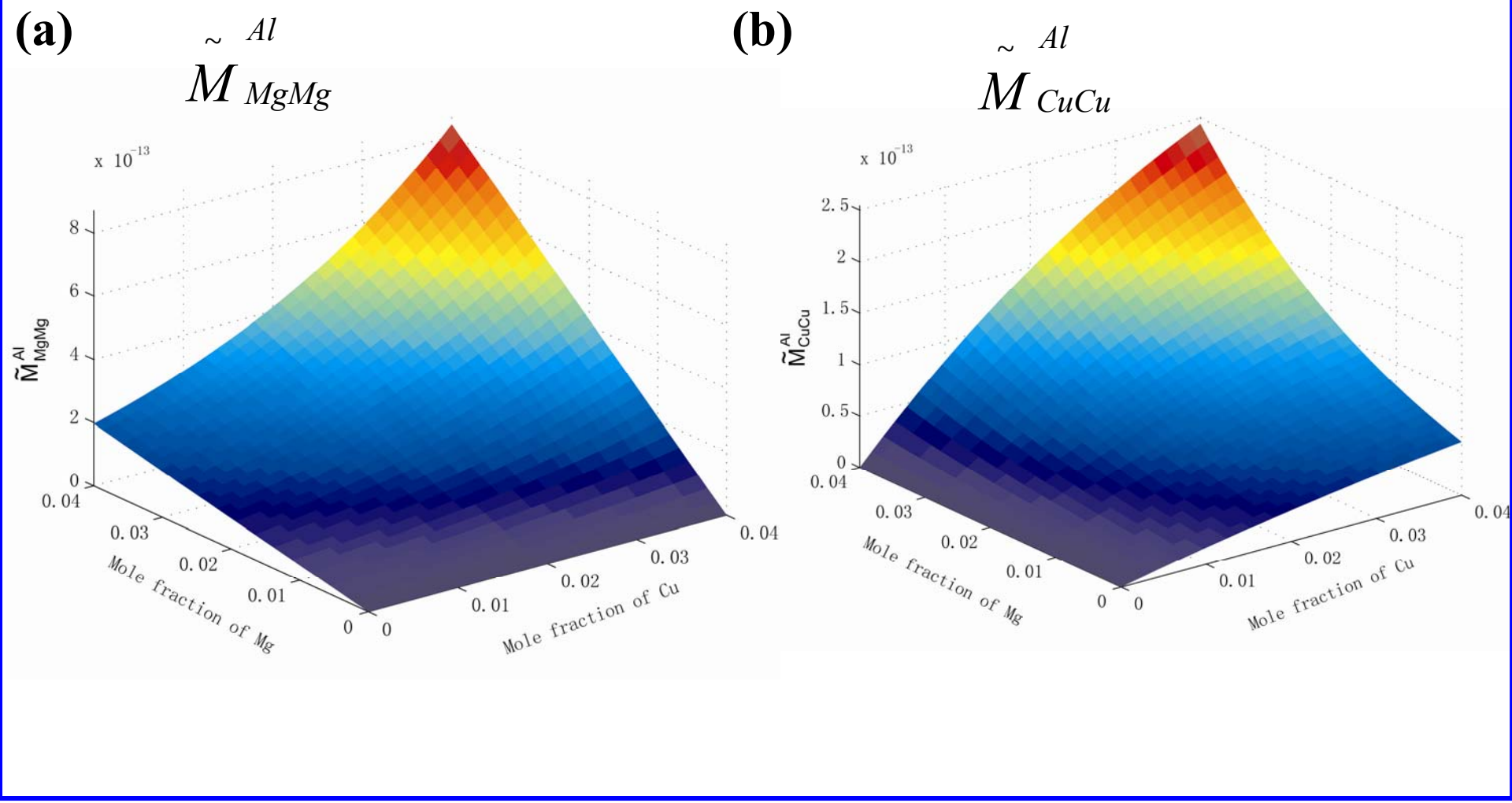


Fig.14. Chemical mobilities of ternary Al-Cu-Mg alloys at 813K, (a) $\tilde{M}^{Al}_{MgMg}$ **(b)** $\tilde{M}^{Al}_{CuCu}$

The Al-Cu-Mg ternary system (fcc phase)

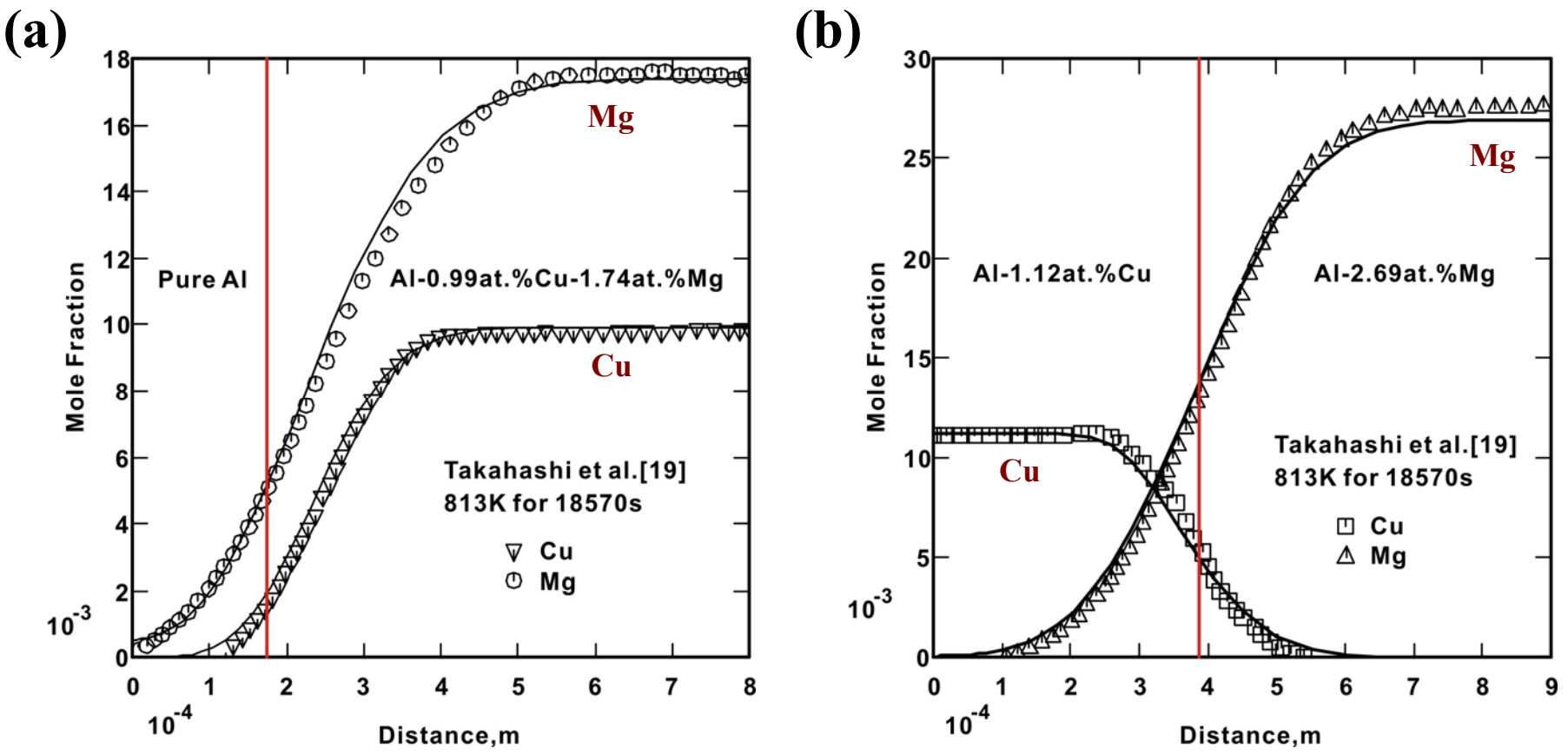


Fig. 15. Comparison between calculated and measured coefficients of
(a) Predicted concentration profile of Al/Al-0.99 at.% Cu-1.74 at.% Mg diffusion couple
(b) Predicted concentration profile of Al-1.12at.% Cu /Al-2.69 at.% Mg diffusion couple

The Al-Cu-Mg ternary system (fcc phase)

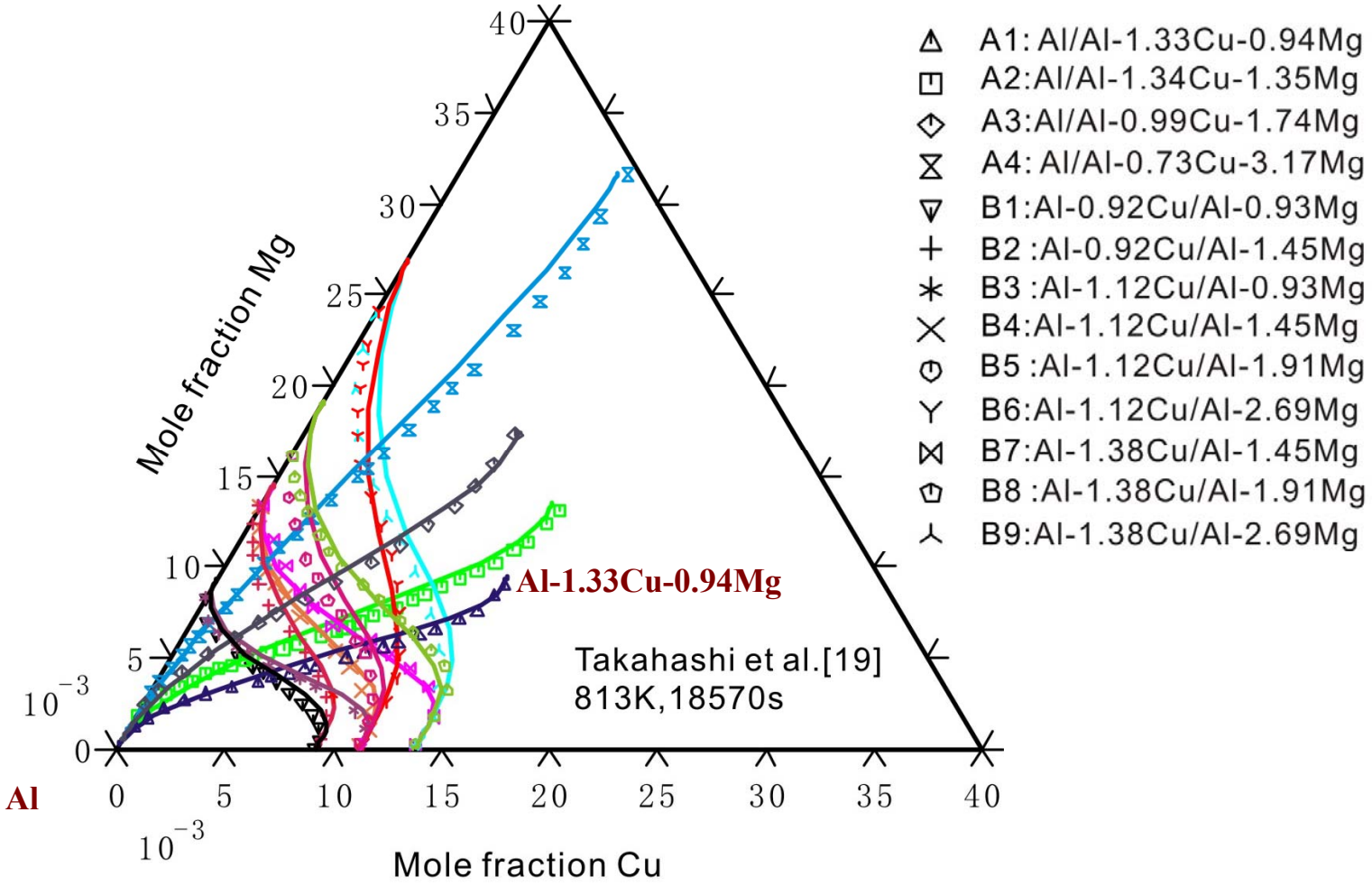


Fig. 16. Calculated diffusion path for ternary diffusion couples annealed at 813K for 18570s

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- A hybrid approach combing key experiments, empirical methods, first-principles calculations and DICTRA method is used to establish the atomic mobility database in Al alloys.

- The current progress in the binary and ternary systems were reported, and some typical results were presented.

- The established atomic mobility can be used to predict various kinds of diffusion coefficients, concentration profiles, diffusion path and even solidfication in Al alloys.

Two representative papers:

1,Lijun Zhang, Yong Du, *et al.,* "Atomic mobilities, diffusivities, and simulation of diffusion growths in the Co-Si system", *Acta Mater.,* 56, 3940-3950 (2008).
2, Lijun Zhang, Yong Du, *et al.,* "Diffusivities of the Al-Fe-Ni melt and their effects on the microstructure during solidification", *Acta Mater*., in press (2010).

Thank you for your attention!

Welcome to

Changsha **Zhangjiajie**

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