Westfälische Wilhelms-Universität Münster

Augmented tracer-interdiffusion couple method

A high-throughput approach for consistent measurements of the tracer diffusion coefficients

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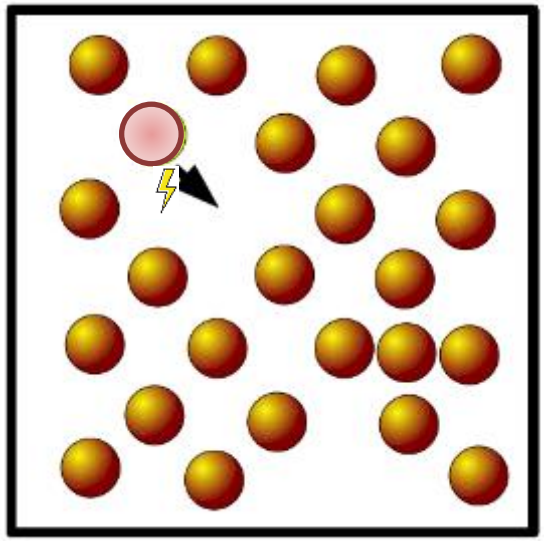
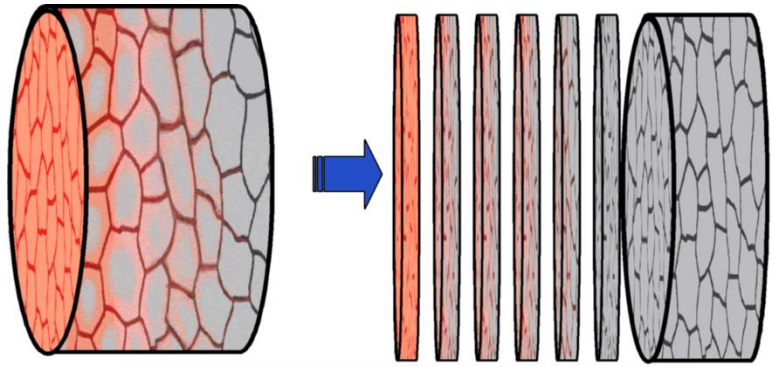
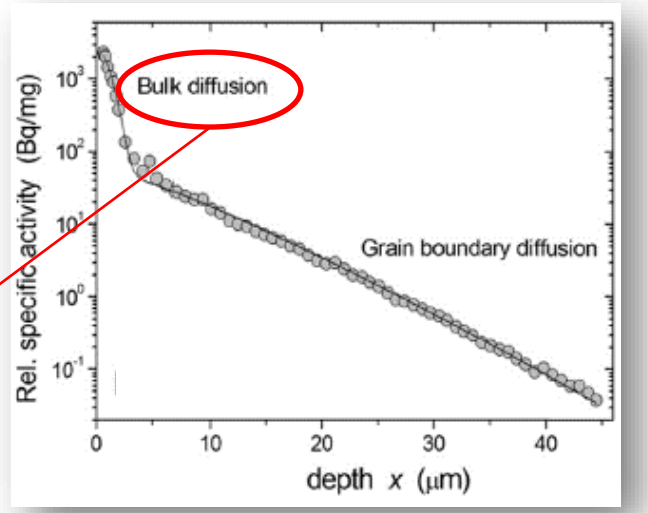
wissen.leben
WWU Münster

How to measure diffusion?

Tracer diffusion

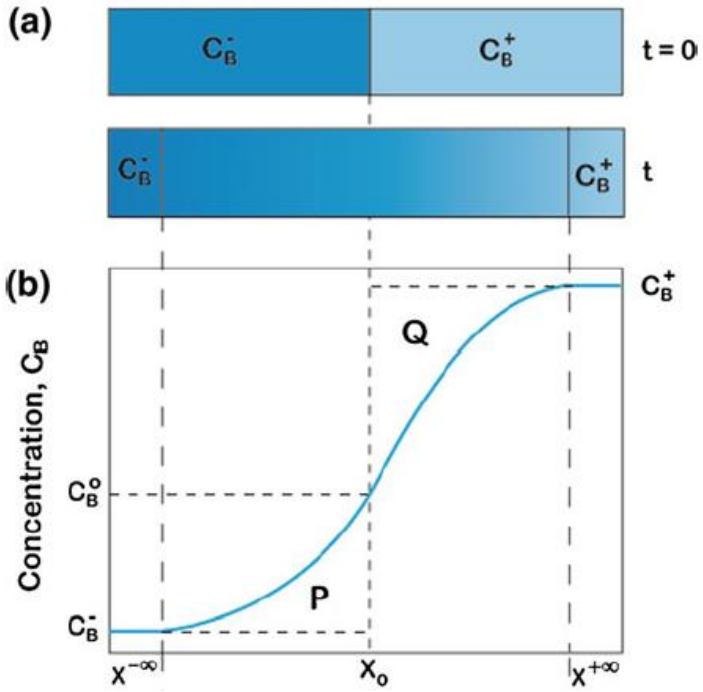






D_A^*

Chemical (inter-) diffusion



$\tilde{D}_{AB}$

→ Different (but related) quantities are measured!

Diffusion in multi-component alloys

Common knowledge

Tracer measurements

- D_{XYZ}^{A*}
- Homogeneous alloys
- Available tracers
- Single compositions
- Accounting for volume and short-circuit (GB, dislocation, etc.) diffusion

Inter-diffusion measurements

- Binary AB alloys ($\widetilde{D}$, D_A, D_B)
- Ternary ABC alloys (D_{ij}^{k})
- Multi-component (*n*>3) alloys – no solution $\Rightarrow$ numerical methods (CALPHAD-type) *the uniqueness of the solution is not proven*!!
- GB diffusion can interfere the results (e.g. Nb_3Sn)

Recent developments

- Tracer diffusion in chemical gradient: **augmented tracer-interdiffusion couple method**
  (D. Gaertner et al., 2019; M. Muralikrishna et al. 2021)
- Concentration-dependent D_{XYZ}^{A*}
- Available tracers
- Accounting for volume and short-circuit (GB, dislocation, etc.) diffusion

- **Pseudo-binary and pseudo-ternary methods**
  (A. Paul et al., 2013-2025)
- Body-diagonal method
  (J. Morral, 2018; K. Kulkarni et al. 2020)
- New numerical schemes
  (L. Zhang et al, 2015-2022; J. Dabrowa, M. Danielewski, et al. 2020; S. Bhattacharyya et al 2021; Y. Sohn et al. 2020; A. Paul, Saswata, et al. 2021-2025)

Tracer-interdiffusion couple approach

PHYSICAL REVIEW VOLUME 116, NUMBER 1 OCTOBER 1, 1959

Tracer Diffusion in a Chemical Concentration Gradient in Silver-Cadmium*†

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PHYSICAL REVIEW VOLUME 149, NUMBER 2 16 SEPTEMBER 1966

Activity Coefficient and Vacancy-Flow Effects on Diffusion in Silver-Gold Alloys*

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Philosophical Magazine, 2014
Vol. 94, No. 31, 3560–3573, http://dx.doi.org

Simultaneous tracer diffusion configuration to provide the diffus

I.V. Belova[a]*, N.S. Kull

[a]*Centre for Mass and Thermal Transport Callaghan, NSW 2308, Australia;* [b]*Knox and Analysis Center and Department of M Florid*

(Received 10 February

In this paper, a new formalis
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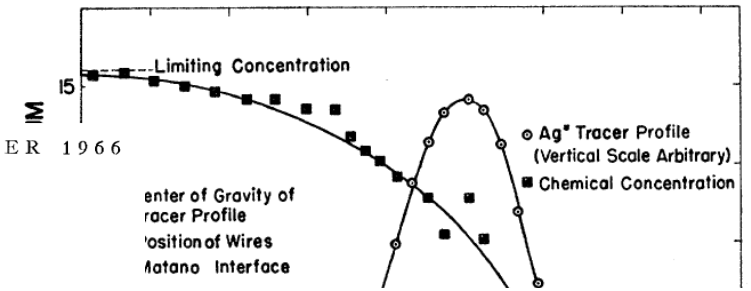

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Full length article

Concentration-dependent atomic mobilities in FCC CoCrFeMnNi high-entropy alloys

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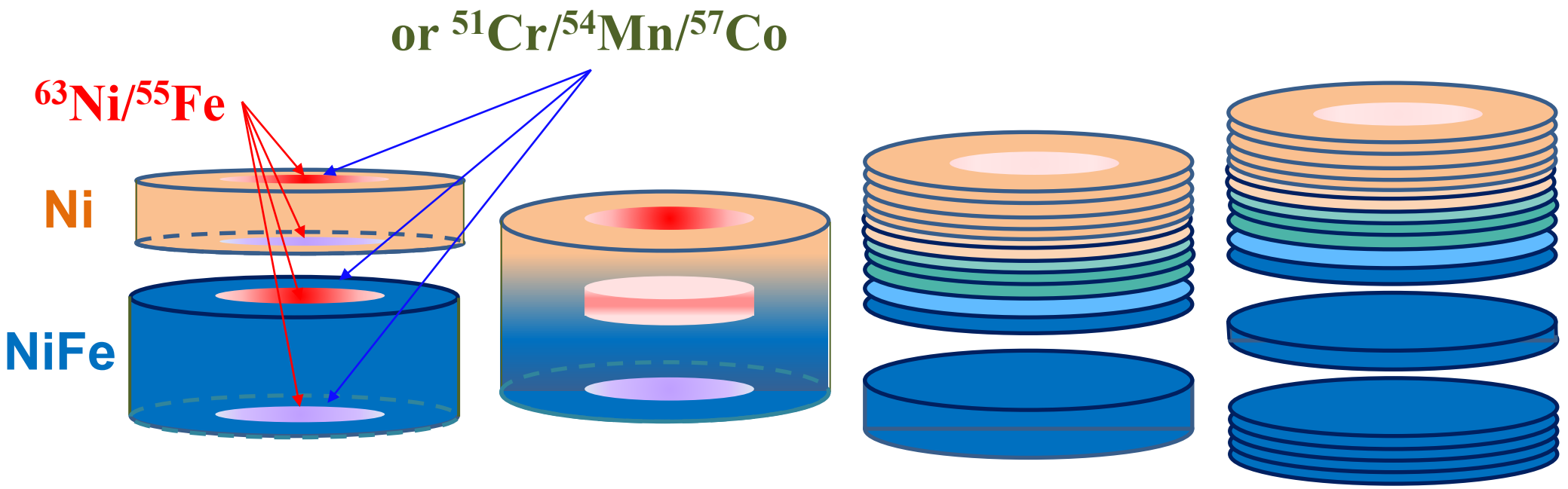
Pair-wise diffusion model
CALPHAD databases

ABSTRACT

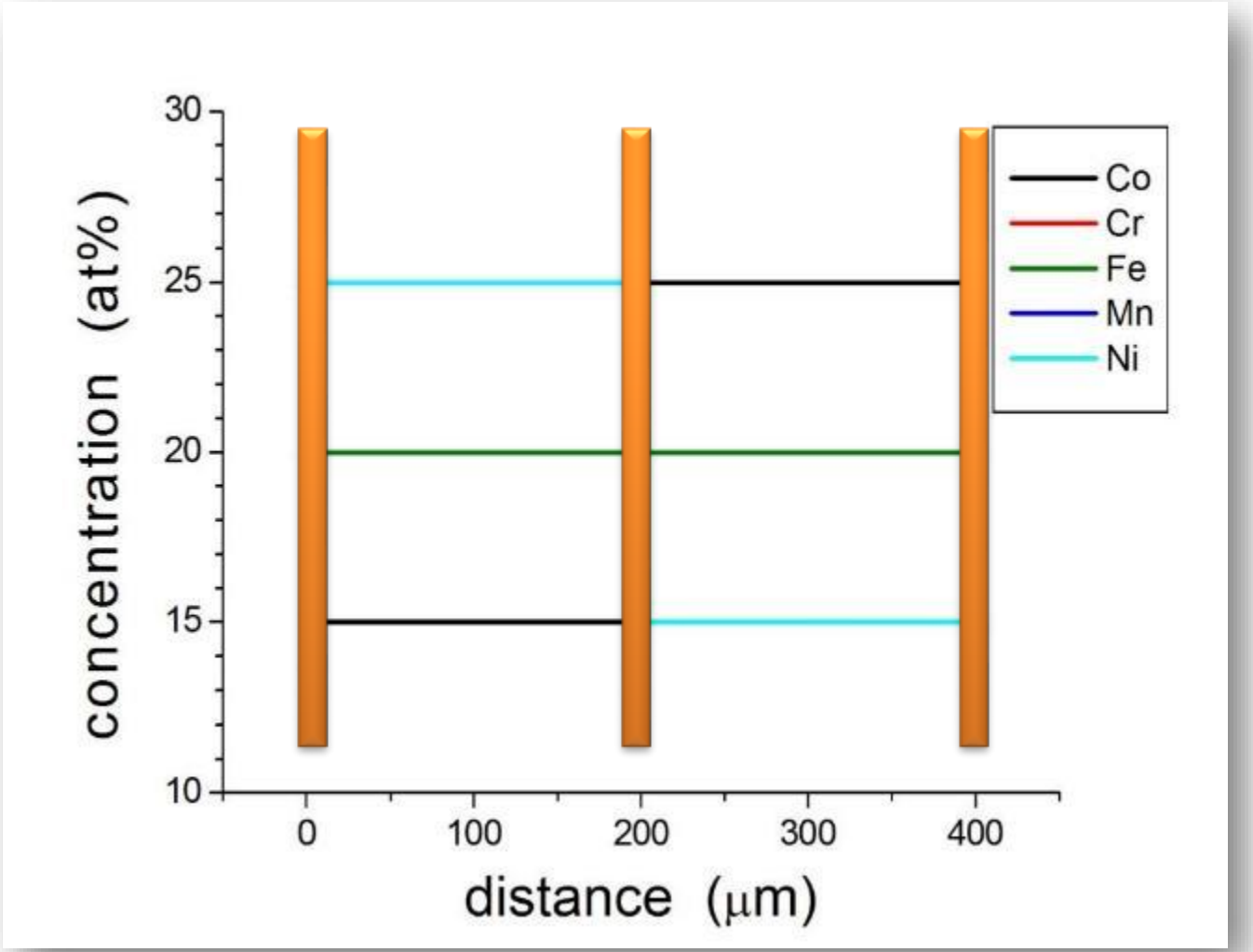
The diffusion kinetics in a CoCrFeMnNi high entropy alloy is investigated by a combined radiotracer–interdiffusion experiment applied to a pseudo-binary $Co_{15}Cr_{20}Fe_{20}Mn_{20}Ni_{25}/Co_{25}Cr_{20}Fe_{20}Mn_{20}Ni_{15}$ couple. As a result, the composition-dependent tracer diffusion coefficients of Co, Cr, Fe and Mn are determined. The elements are characterized by significantly different diffusion rates, with Mn being the fastest element and Co being the slowest one. The elements having originally equiatomic concentration through the diffusion couple are found to reveal up-hill diffusion, especially Cr and Mn. The atomic mobility of Co seems to follow a S-shaped concentration dependence along the diffusion path. The experimentally measured kinetic data are checked against the existing CALPHAD-type databases.

In order to ensure a consistent treatment of tracer and chemical diffusion a generalized symmetrized continuum approach for multi-component interdiffusion is proposed. Both, tracer and chemical diffusion concentration profiles are simulated and compared to the measurements. By using the measured tracer diffusion coefficients the chemical profiles can be described, almost perfectly, including up-hill diffusion.

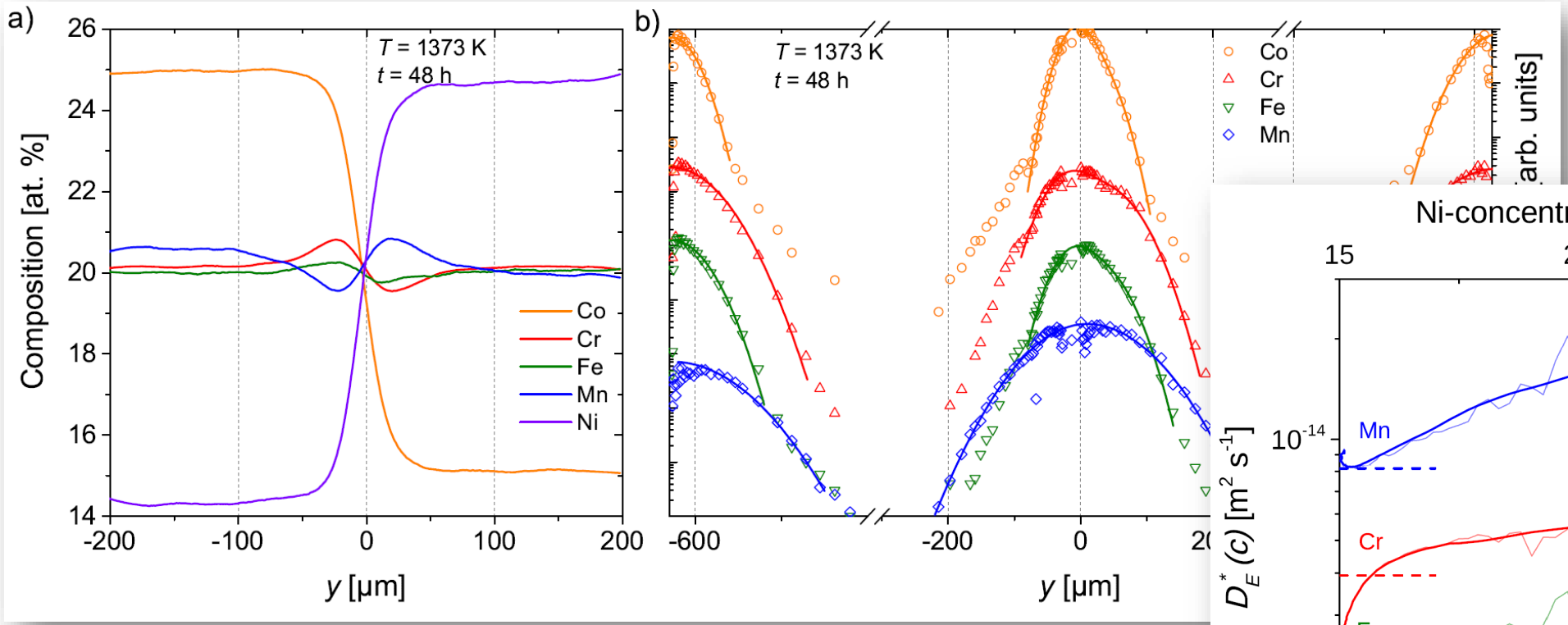
Composition dependent atomic mobilities: combination of tracer and chemical diffusion measurements

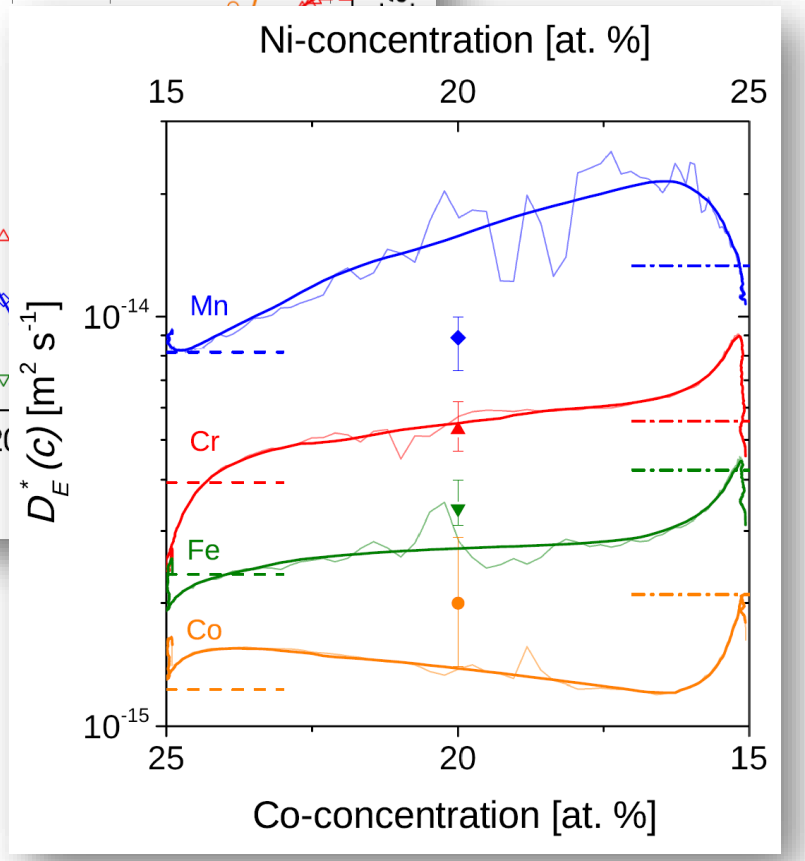


Augmented tracer-interdiffusion couple method: HEA



Interdiffusion and tracer diffusion in CoCrFeMnNi HEA



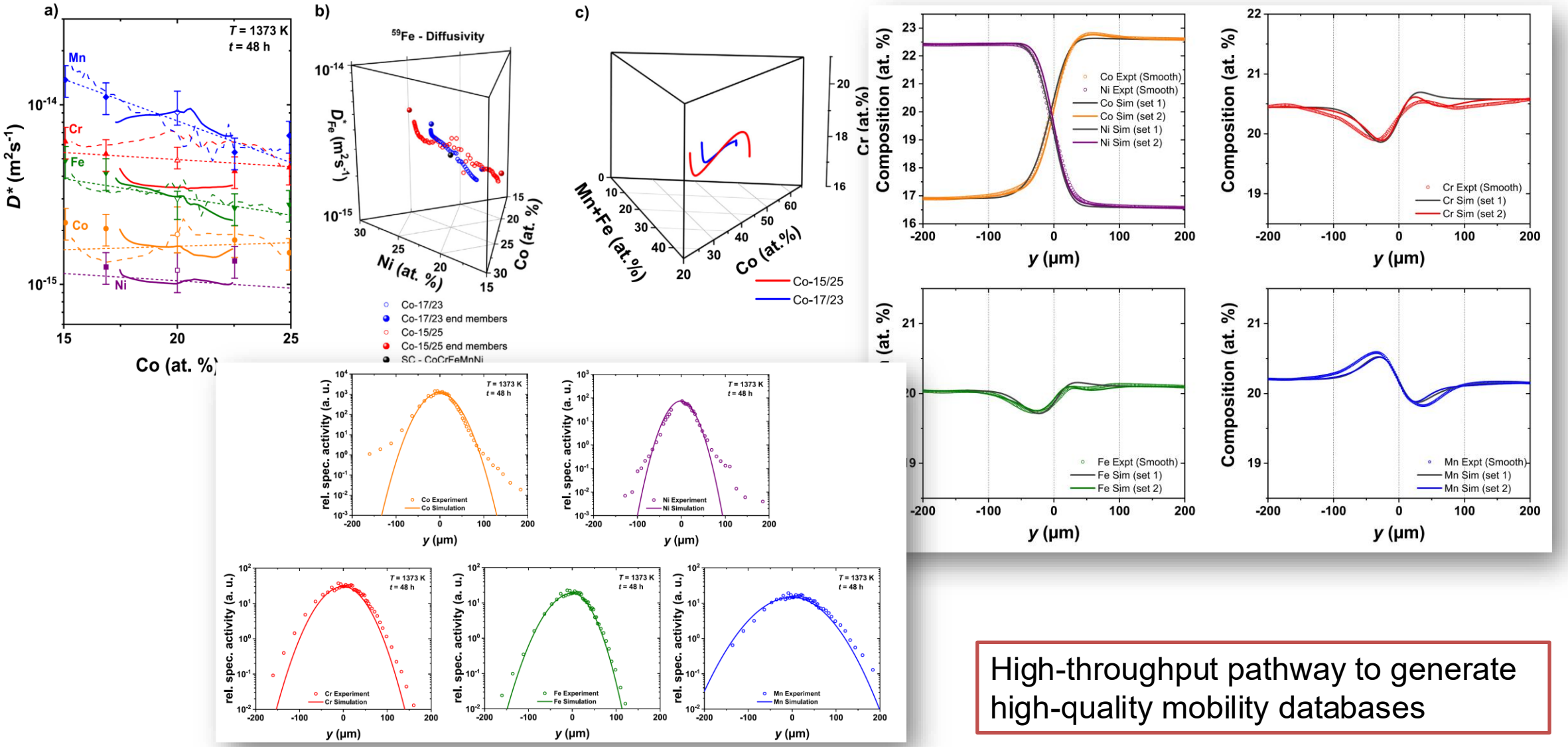


Belova & Murch (2013-2015)

$$D_i^* = -\left(\frac{(x+a)}{2t} + \frac{\tilde{J}_i V_m}{N_i}\right) \Big/ \left(\frac{\partial \ln C_i^*}{\partial x} - \frac{\partial \ln C_i}{\partial x}\right)$$

D. Gaertner et al. Acta Materialia (2019)

Interdiffusion and tracer diffusion in CoCrFeMnNi HEA



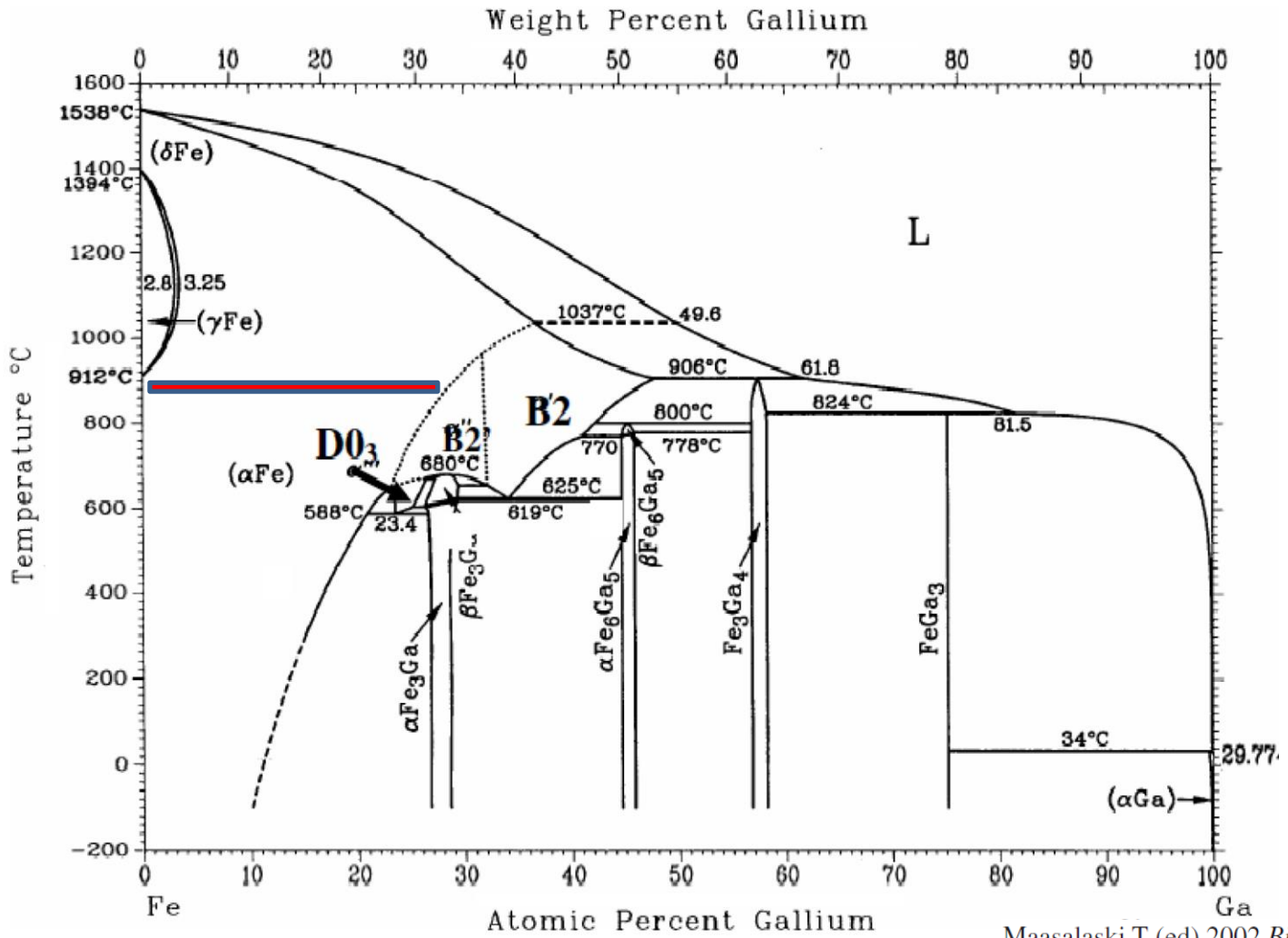
High-throughput pathway to generate high-quality mobility databases

D. Gaertner et al. JALCOM (2023)

Extensive tests of the augmented tracer-interdiffusion couple method…

Augmented tracer-interdiffusion couple method: FeGa

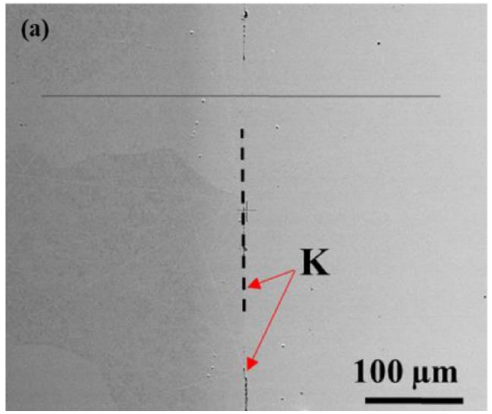
the case of strong composition-dependent diffusivities

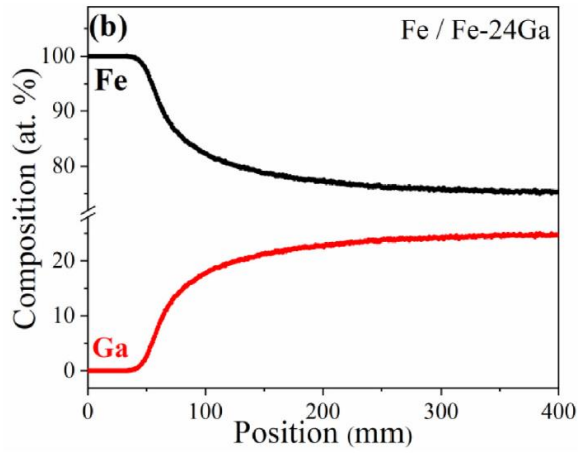


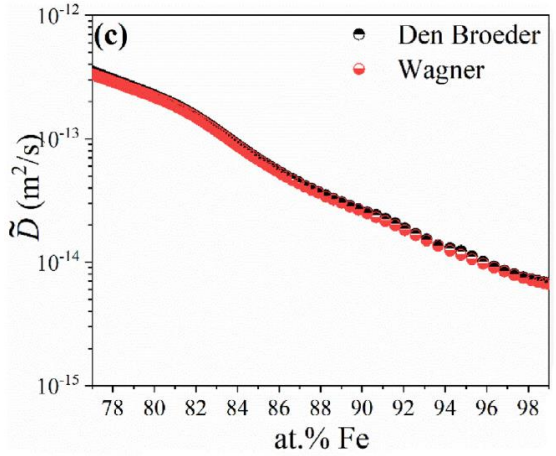
Maasalaski T (ed) 2002 *Binary Alloy Phase Diagrams* 2nd edn (Materials Park, OH: ASM International)

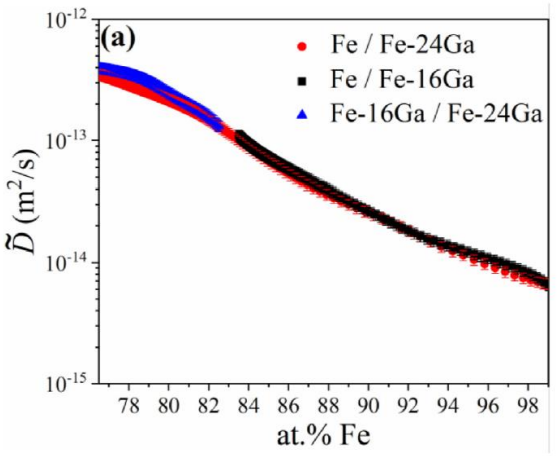
M.G. Muralikrishna et al. Acta Materialia (2021)

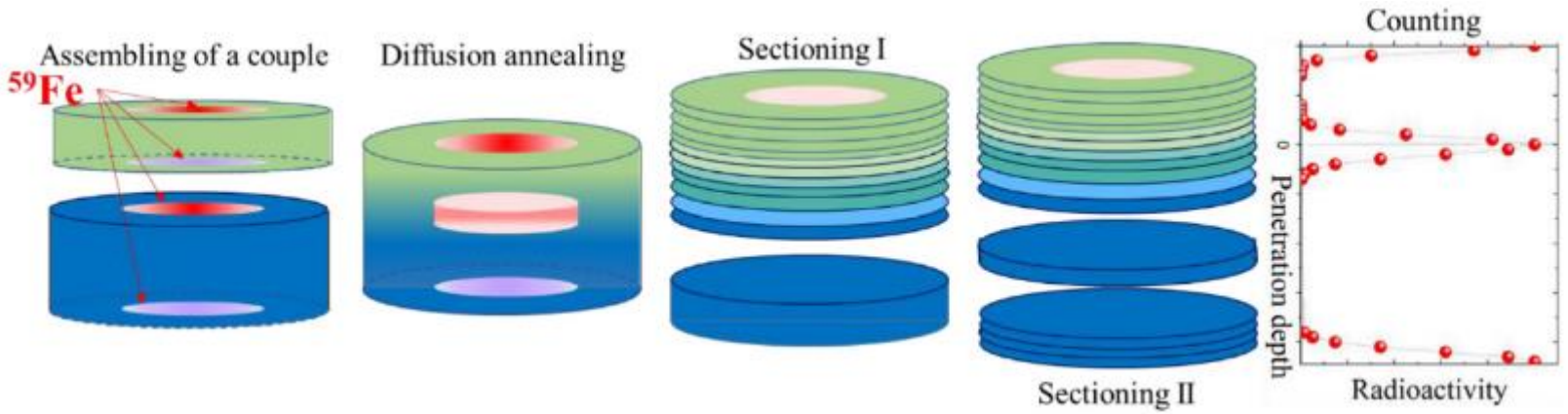
Augmented tracer-interdiffusion couple method: FeGa





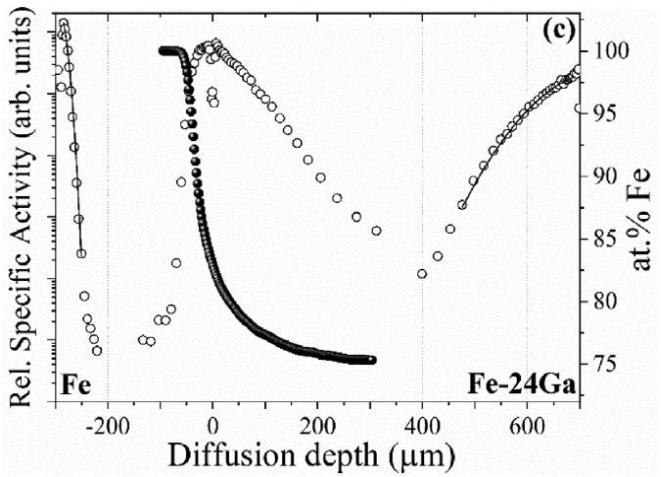


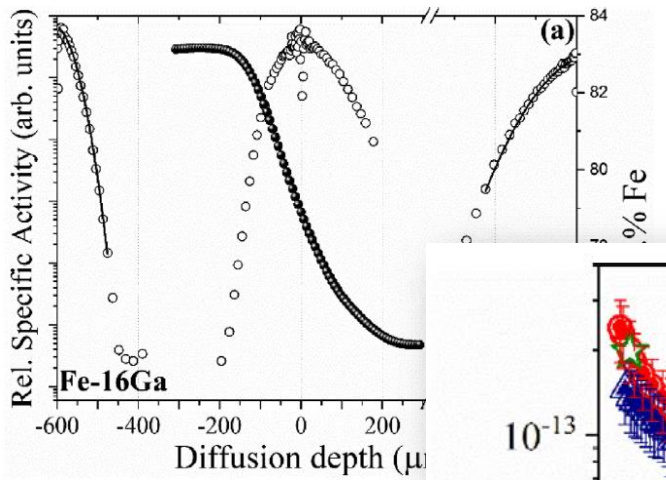


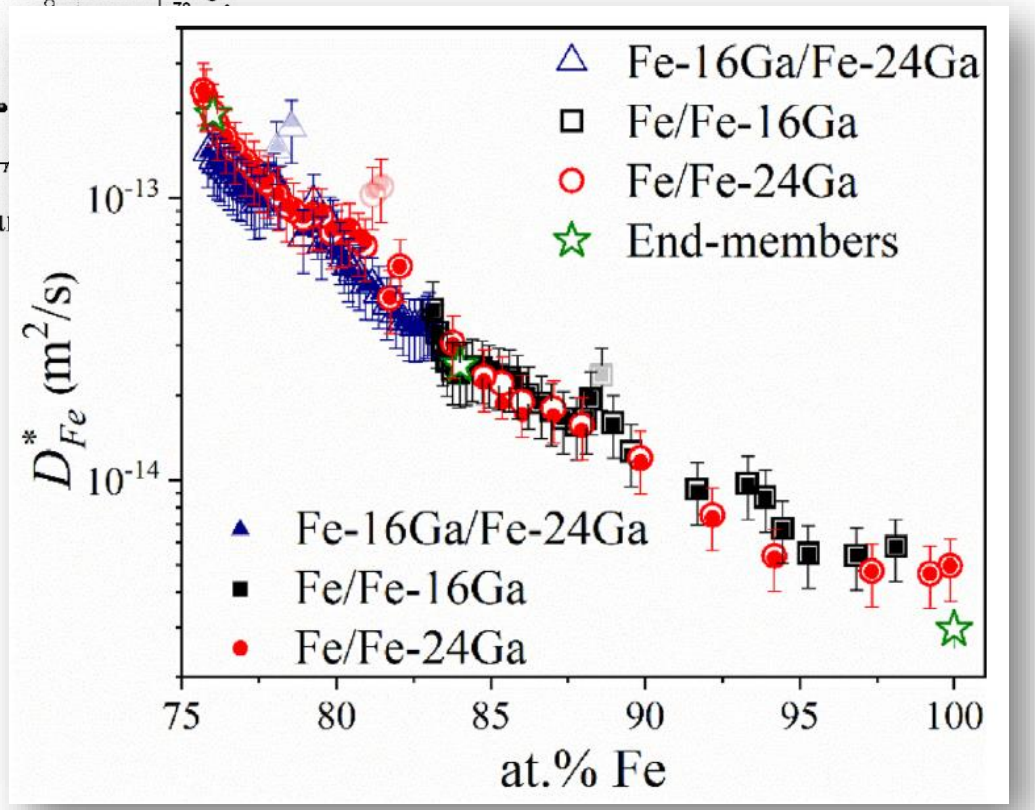


M.G. Muralikrishna et al. Acta Materialia (2021)

Augmented tracer-interdiffusion couple method: FeGa







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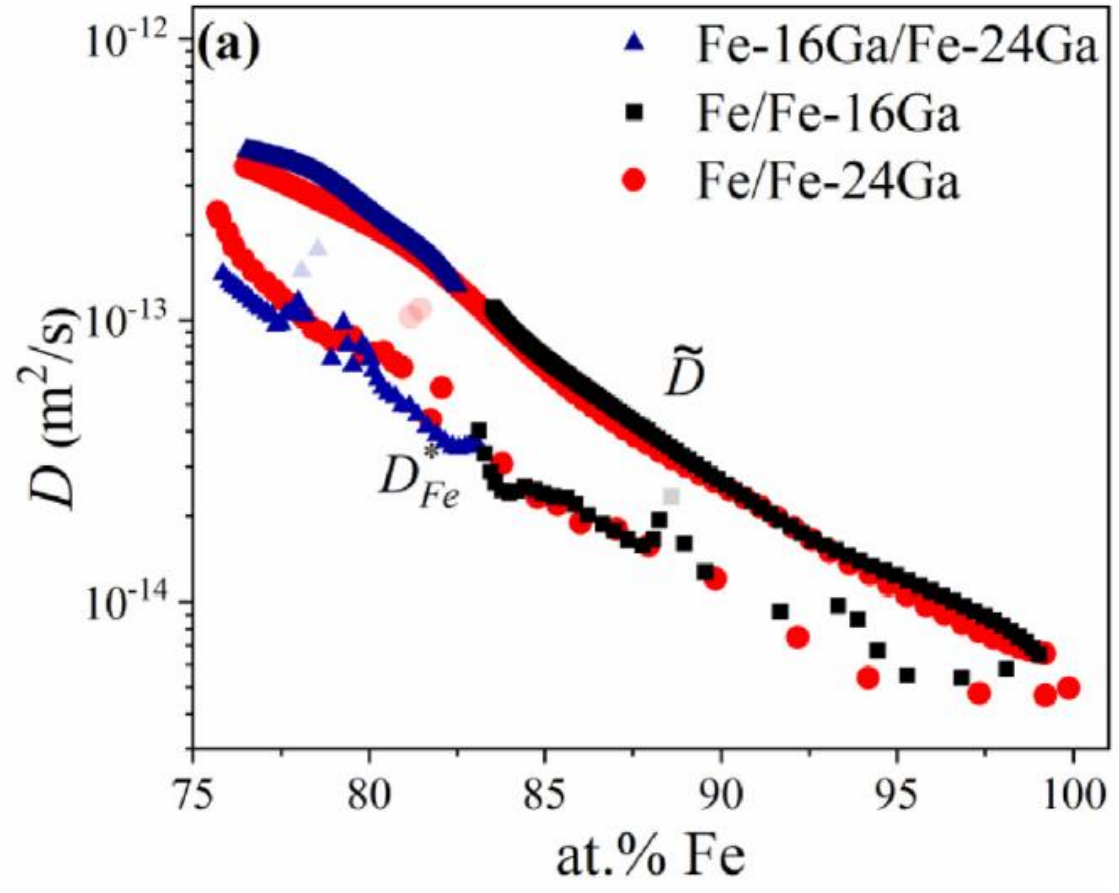
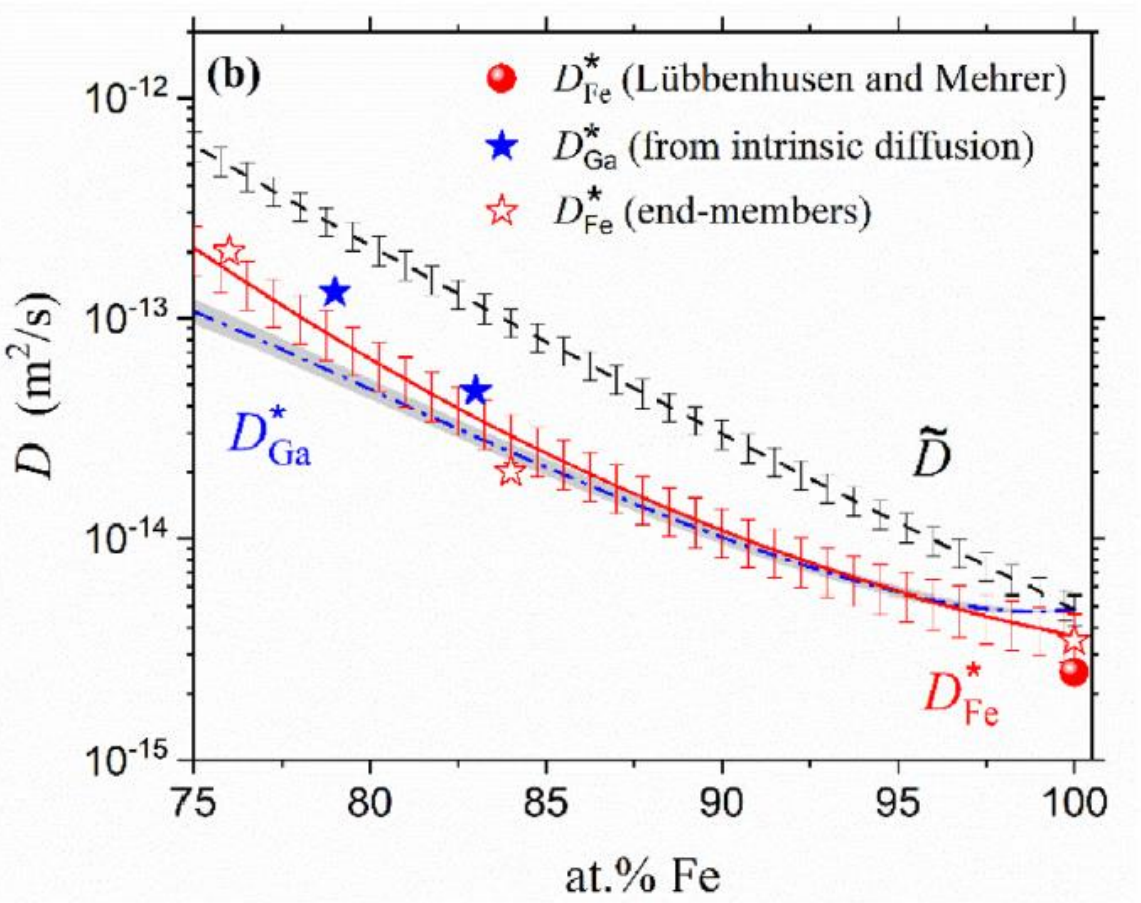
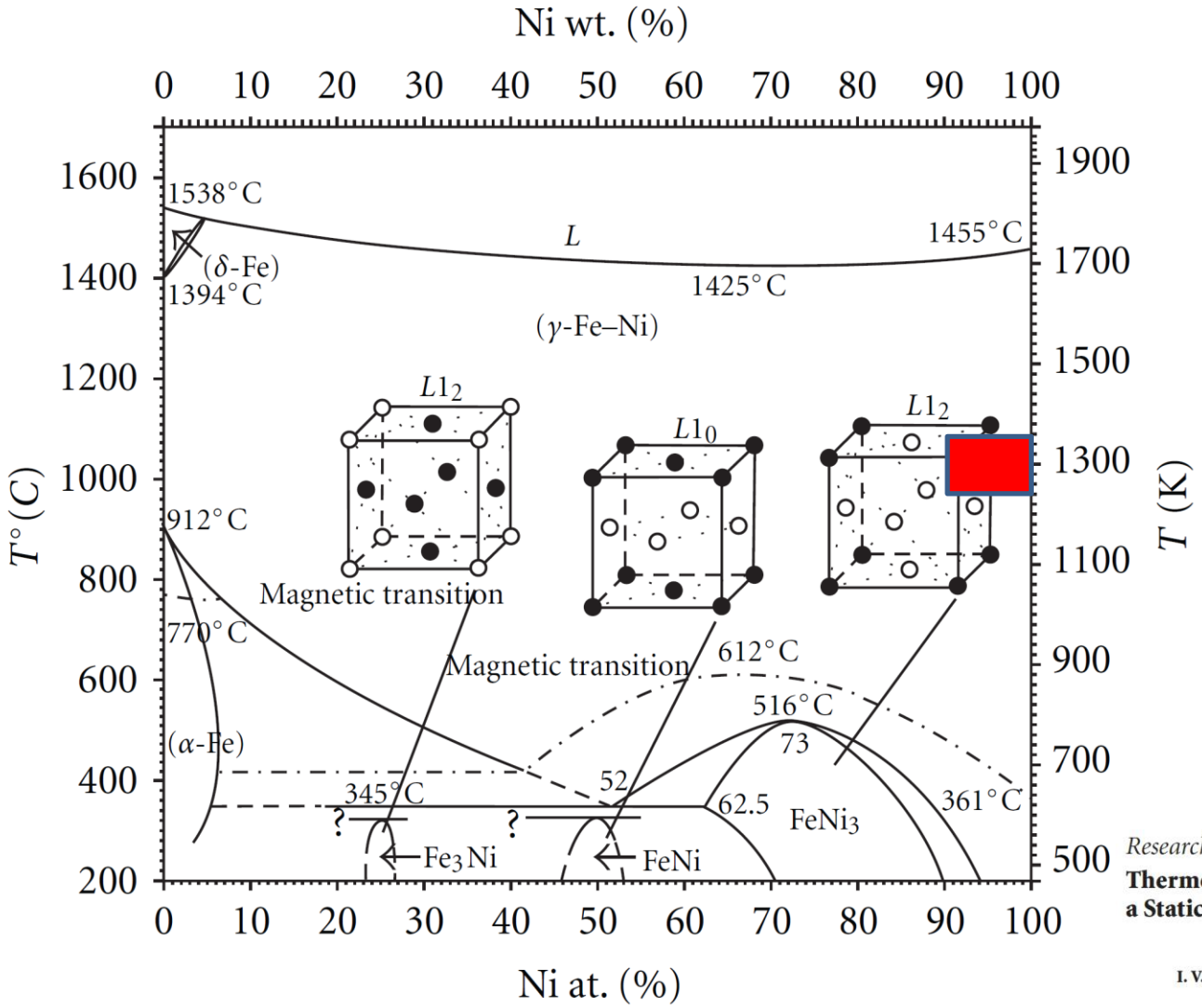




M.G. Muralikrishna et al. Acta Materialia (2021)

Augmented tracer-interdiffusion couple method: NiFe alloy

the case of well-known thermodynamics



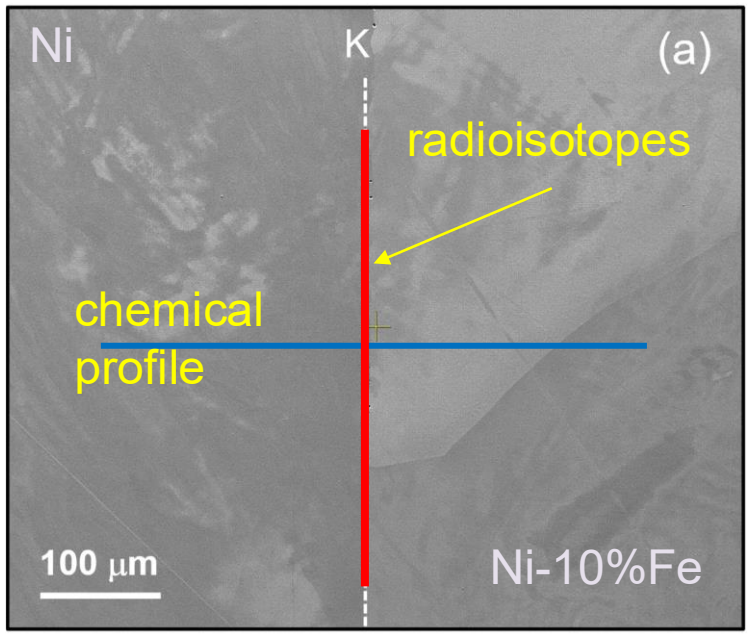
Research Article

Thermodynamics of f.c.c.-Ni–Fe Alloys in a Static Applied Magnetic Field

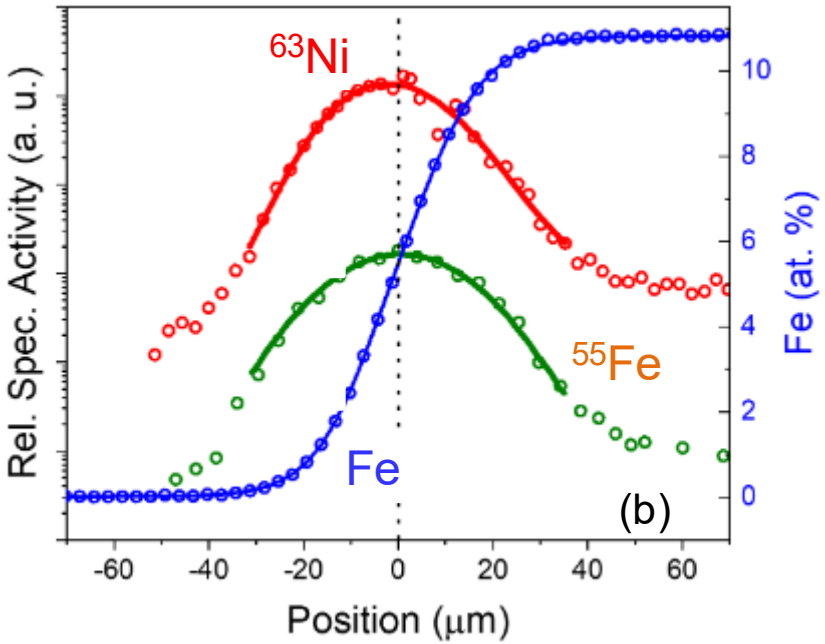
I. V. Vernyhora,[1,2] V. A. Tatarenko,[2] and S. M. Bokoch[3,4]

N. Esakkiraja et al. Acta Materialia (2025)

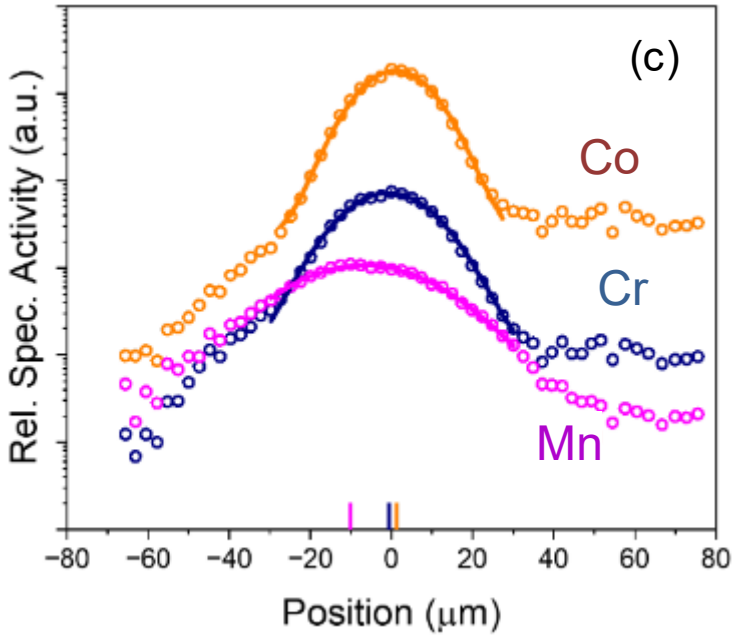
Augmented tracer-interdiffusion couple method: NiFe alloy



self-diffusion

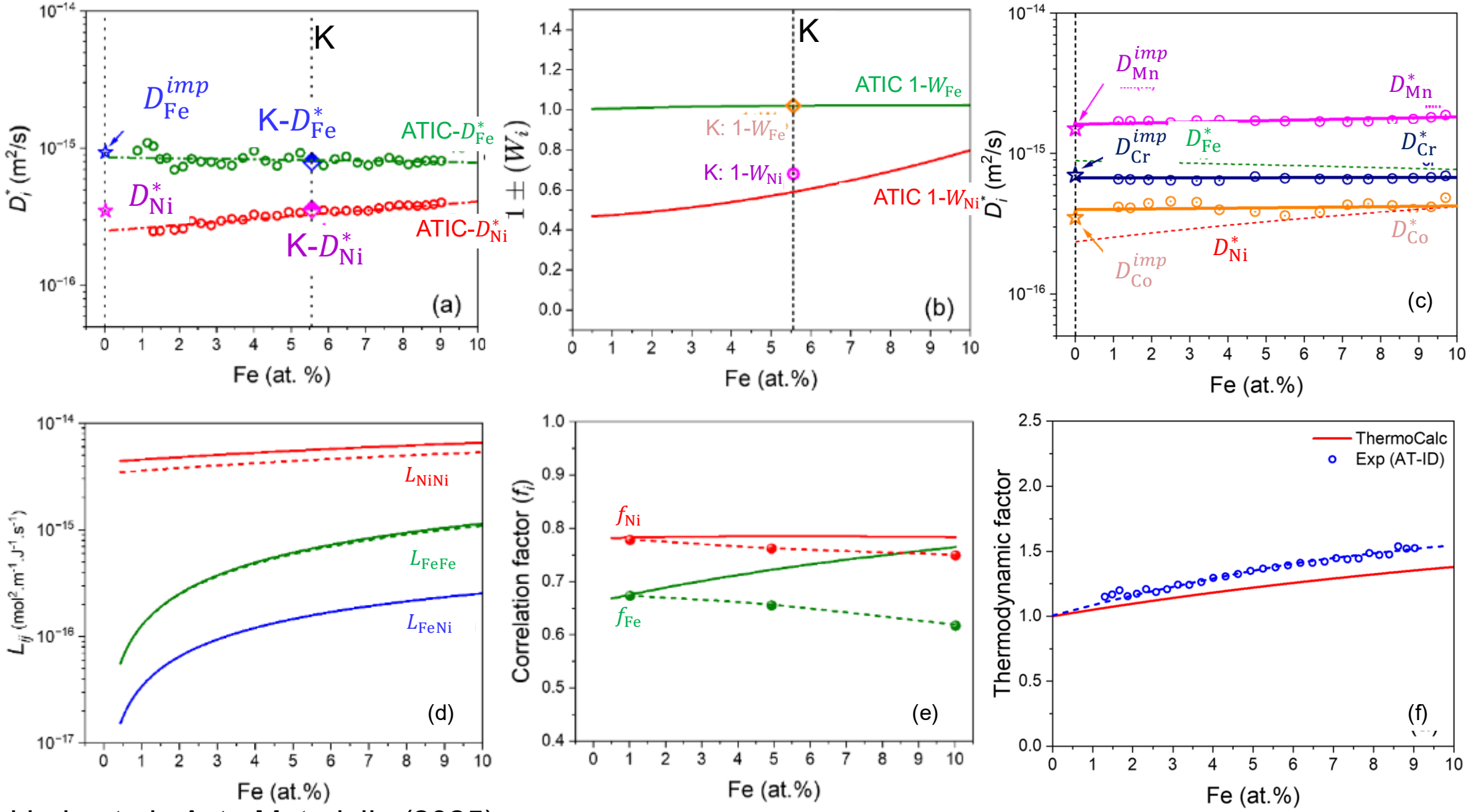


impurity diffusion



N. Esakkiraja et al. Acta Materialia (2025)

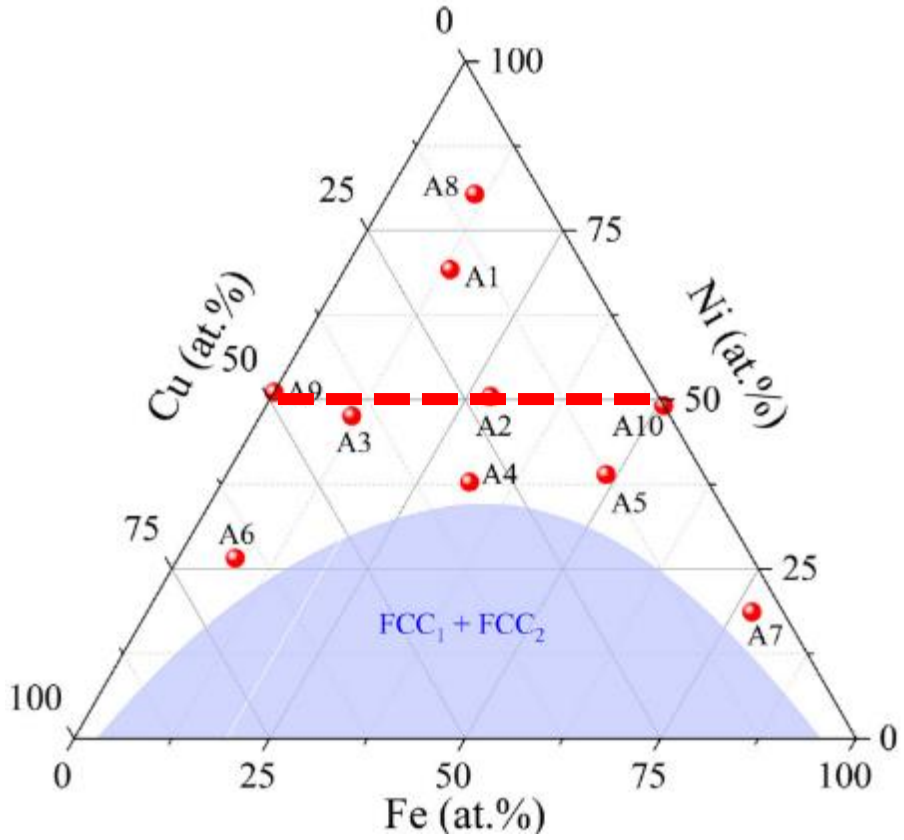
Augmented tracer-interdiffusion couple method: NiFe alloy

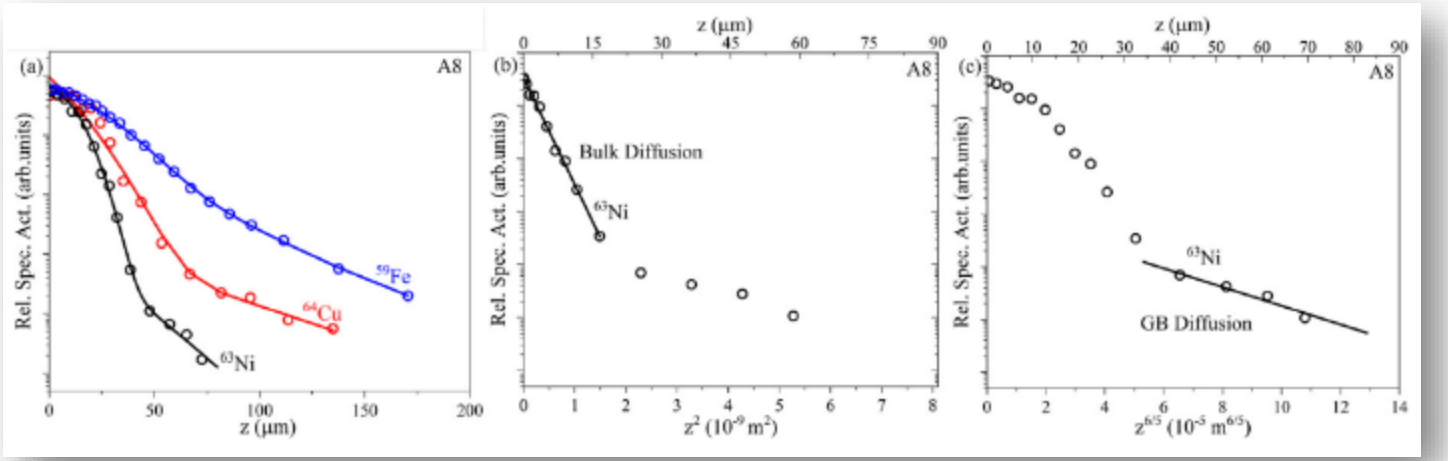


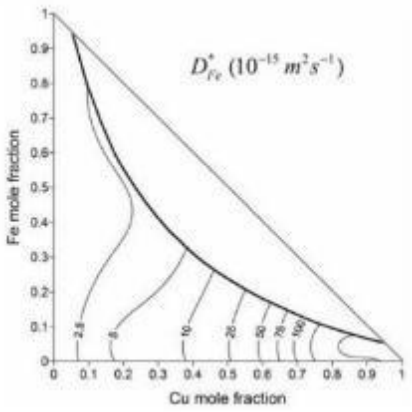
N. Esakkiraja et al. Acta Materialia (2025)

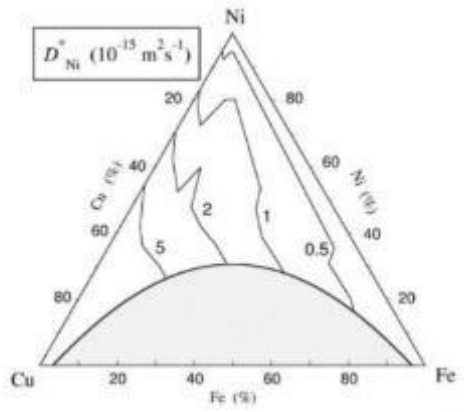
Augmented tracer-interdiffusion couple method: CuFeNi

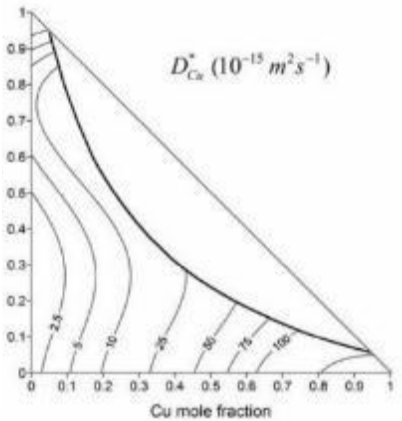
the case of strong composition-dependent diffusivities and well-assessed thermodynamics











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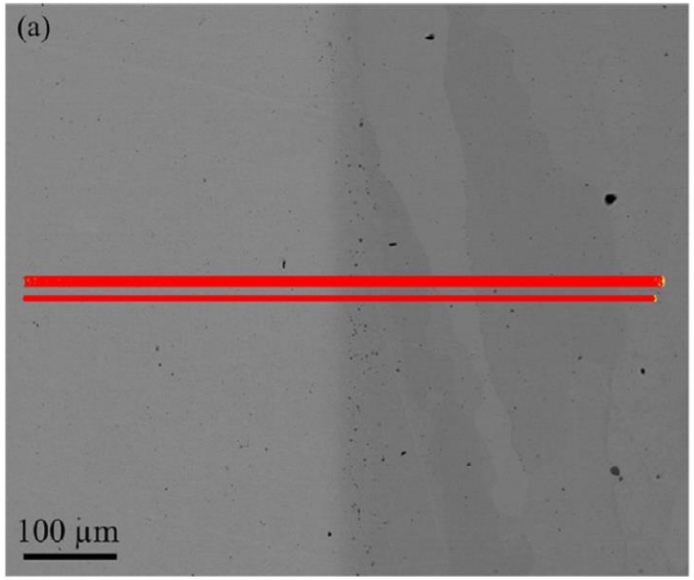
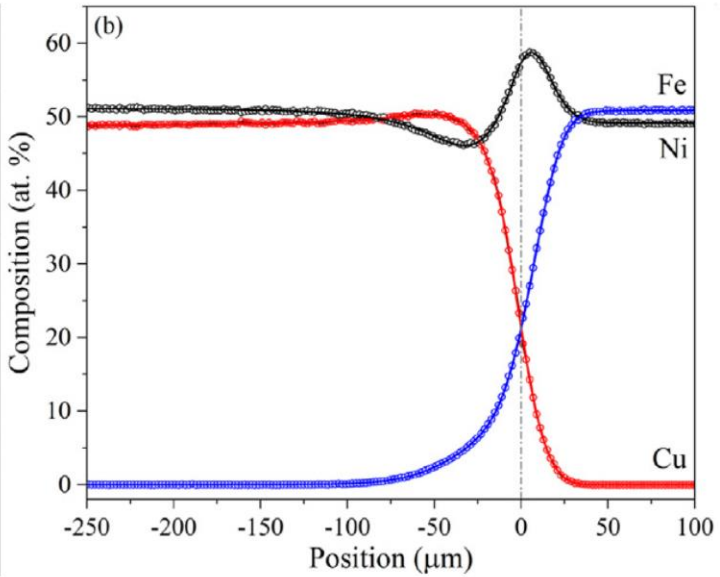
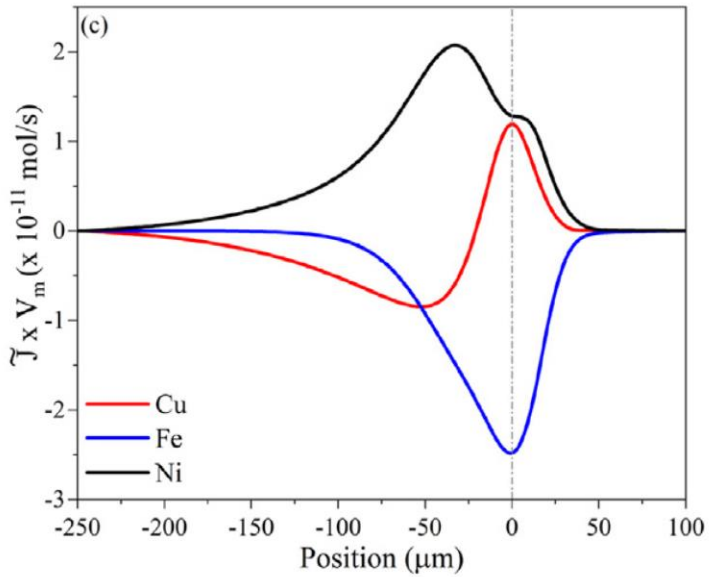
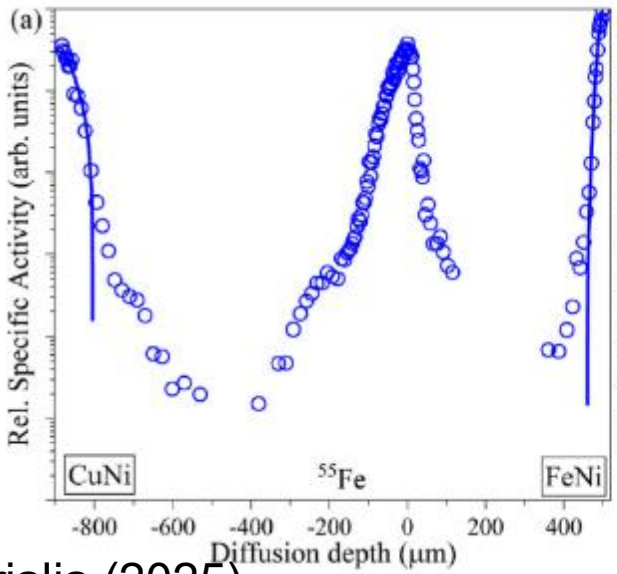
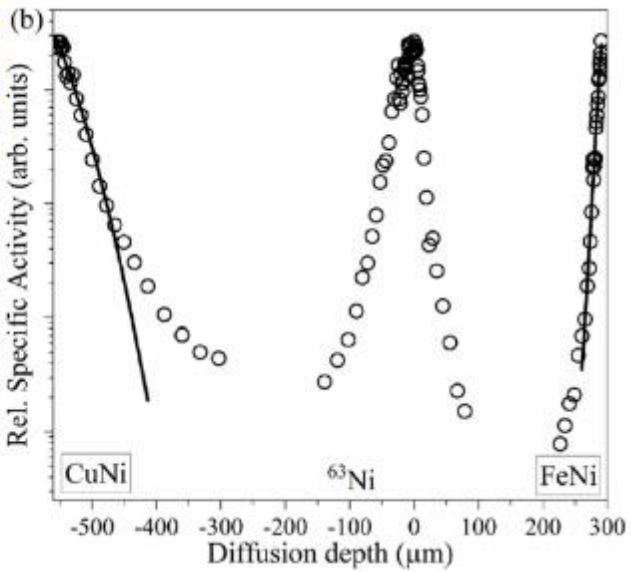
Augmented tracer-interdiffusion couple method: CuFeNi





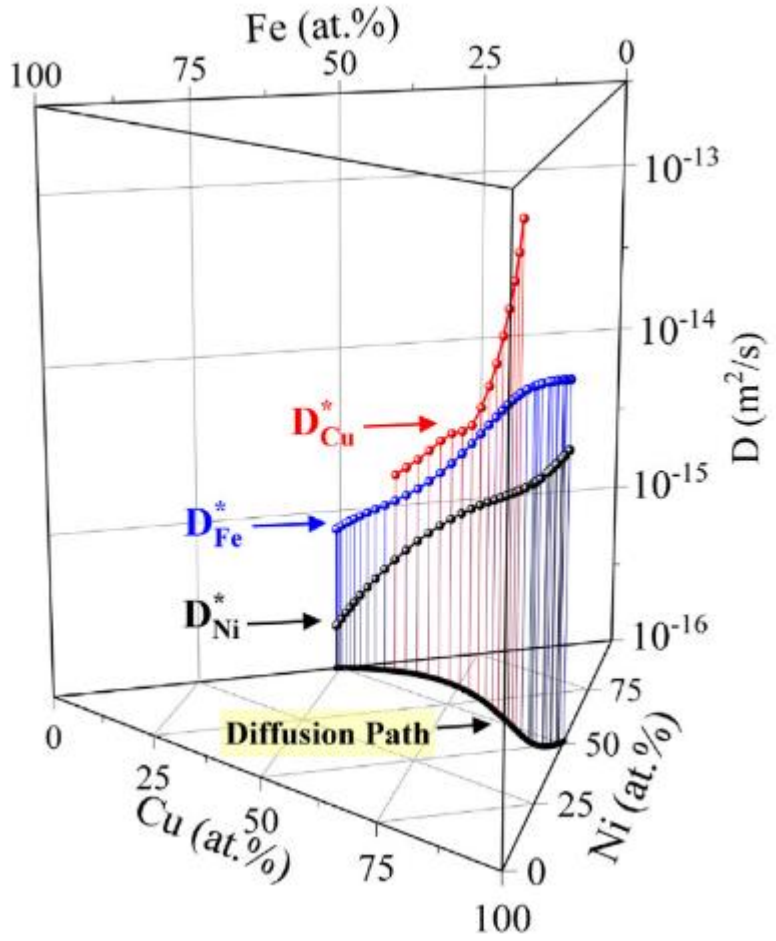






M.G. Muralikrishna et al. Acta Materialia (2025)

Augmented tracer-interdiffusion couple method: CuFeNi



Are the tracer diffusion coefficients measured in concentration gradient (*under chemical potential gradient as driving force*) equal to those determined in homogeneous alloys (*under purely entropic driving force*)?

$$D^{*\prime} = \frac{y_V}{y_V^{eq}} D^*$$

Does the concentration of non-equilibrium vacancies deviate strongly from the equilibrium one?

M.G. Muralikrishna et al. Acta Materialia (2025)

Tracer-interdiffusion couple approach

Vacancy-wind effect in diffusion and deviations from thermodynamic equilibrium conditions

JOHN R. MANNING

Institute for Materials Research, National Bureau of Standards,

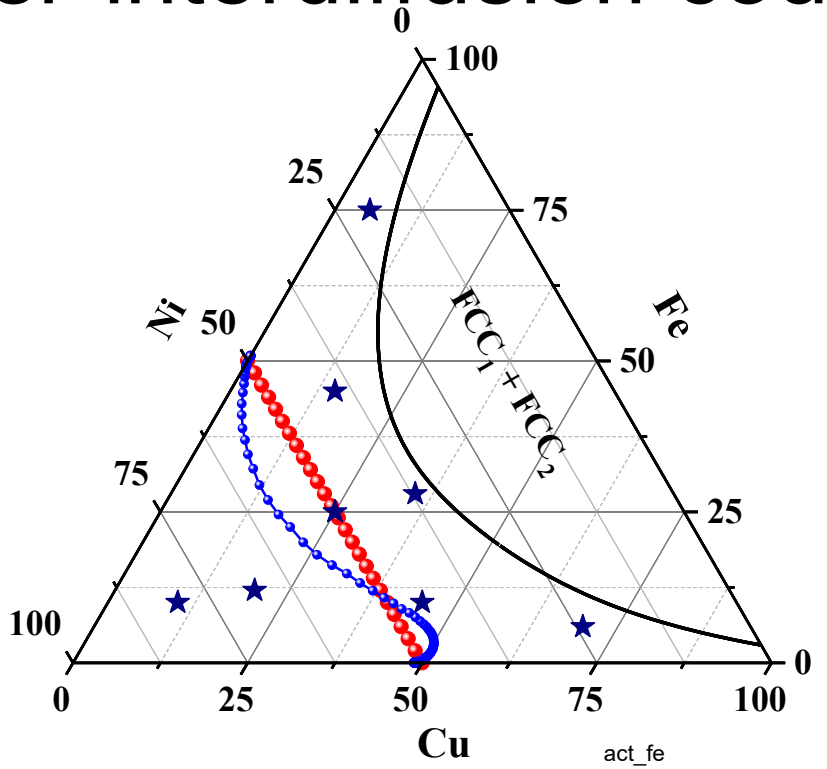
Received November 13, 1967

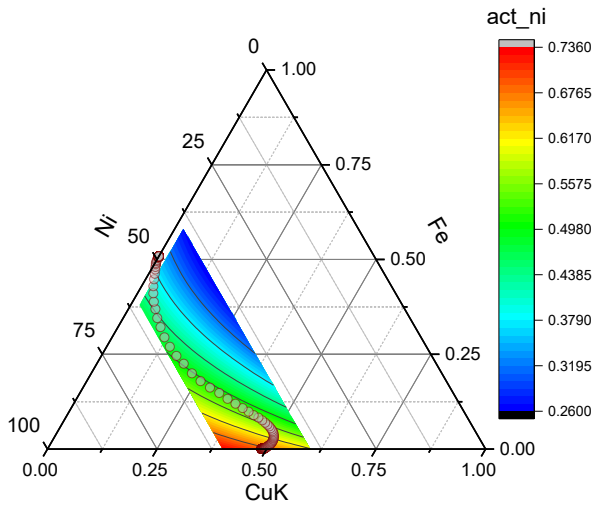
The vacancy-flow (or "wind") term which appears in kinetic treatm
discussed in terms of the vacancy concentrations which appear when
impurity. It is pointed out that this term arises from local distortions in
and not from any overall deviation of the material from equilibrium v
theory of Kirkaldy and Lane, which considers only net deviations fr
entire plane, does not include the vacancy-wind term. Several physic
basic process. The vacancy-wind term can be large and introduces cr
dynamic equations.

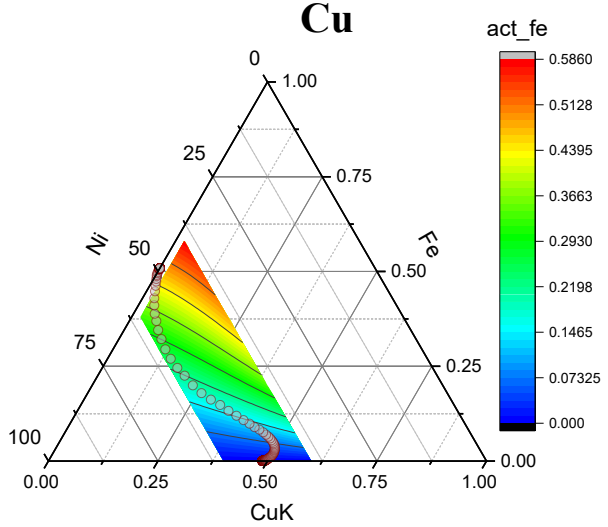
The vacancy-wind effect arises from motion of atoms other than the
accurate kinetic analysis, motion of the diffusing atom itself also must
duces a "mobile-impurity" effect and introduces an additional distortion
Equations including this effect are discussed. The close relationship
and the correlation factor is shown. For self-diffusion, mobile-impurity
cancel in their influence on vacancy distributions.

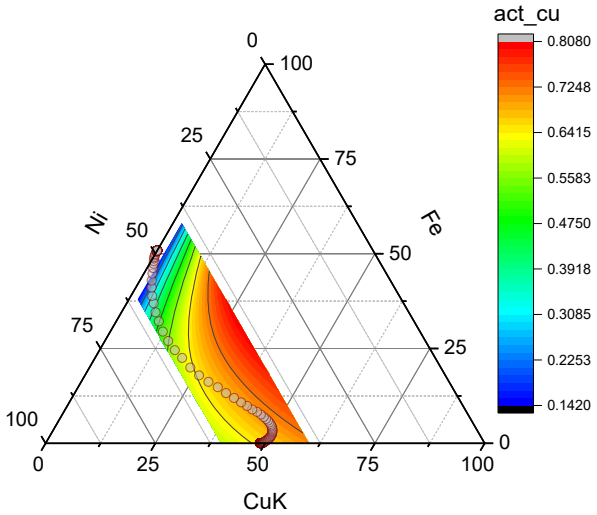
Actually, the apparent conflict between the two analyses arises not because of any error in either analysis, but because two different types of non-equilibrium effects are being considered. The vacancy-wind effect arises because of local deviations from equilibrium, as in Fig. 1. By contrast, the treatment of Kirkaldy and Lane is concerned with deviations over an entire plane, with all sites on planes in the left-hand portion of the crystal having positive values of ΔN_v and in the right-hand portion, negative values. Since the deviations from equilibrium which are treated are very different, it is not surprising that the influence on the Kirkendall shift from these effects is also quite different.

Augmented tracer-interdiffusion couple method: CuFeNi









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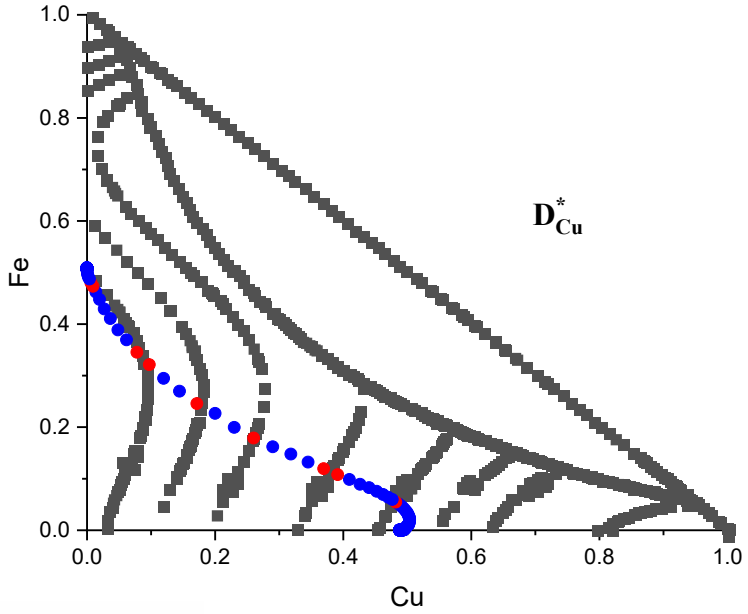
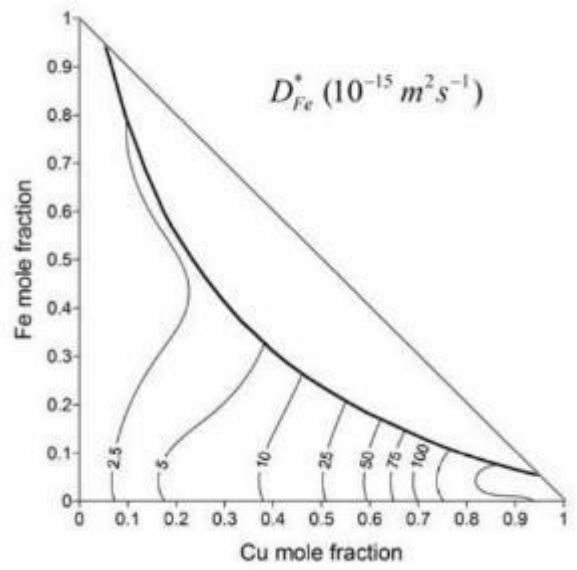
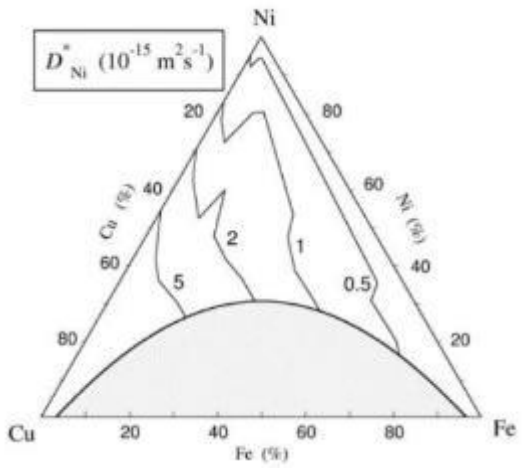
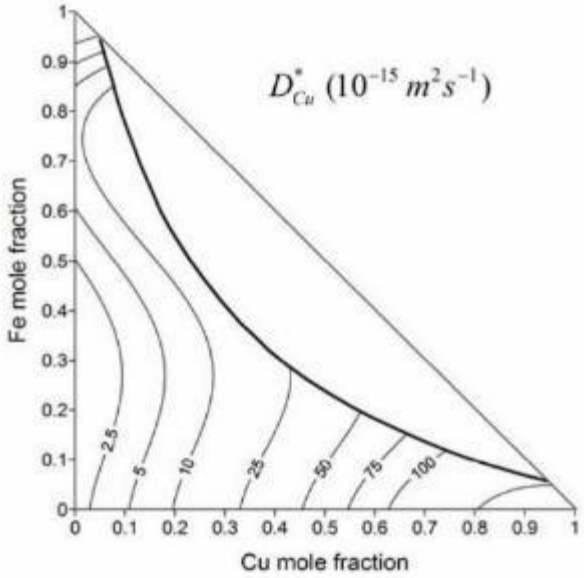
Augmented tracer-interdiffusion couple method: CuFeNi









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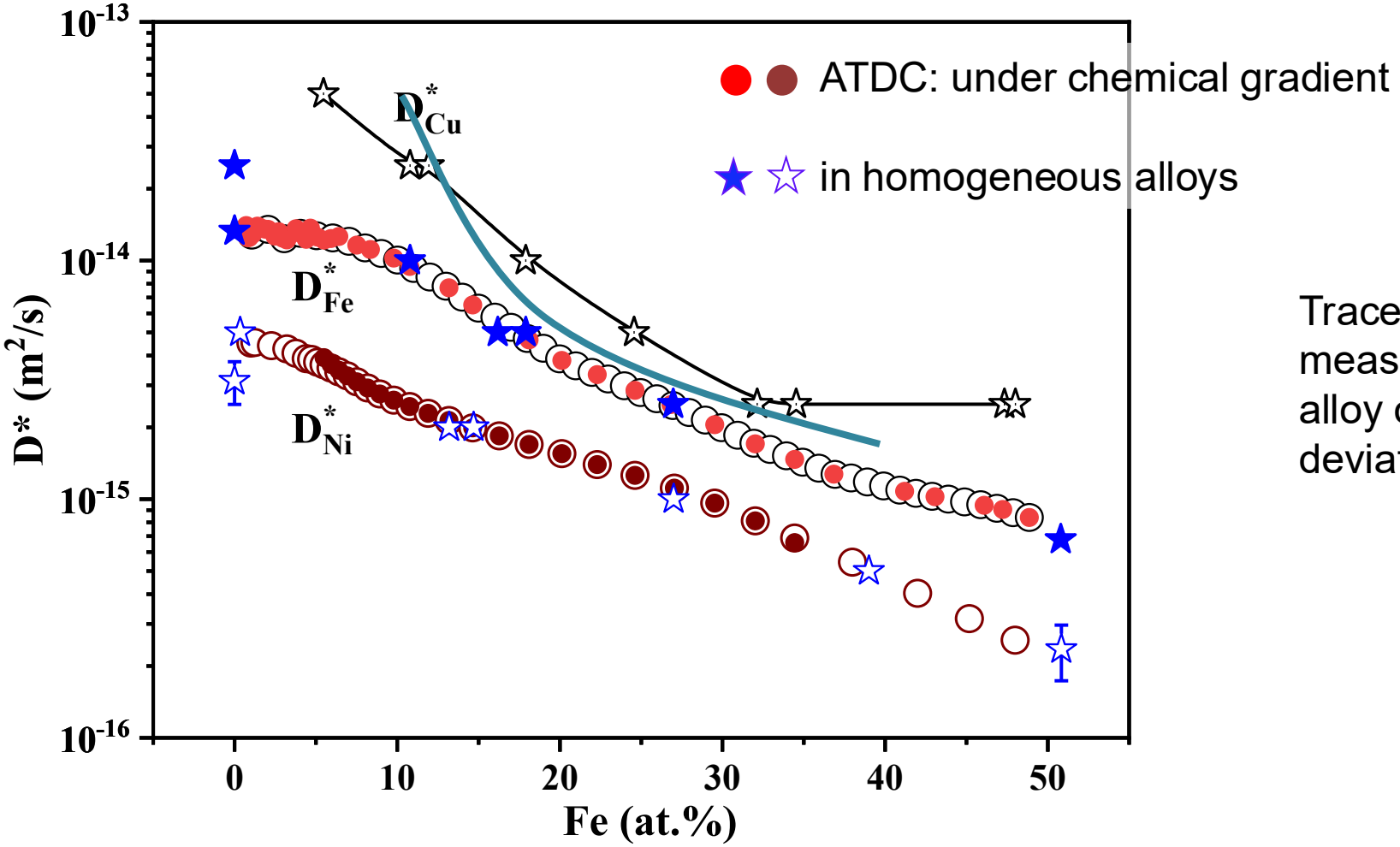

Tracer diffusion coefficients measured in homogeneous alloy or in diffusion couples deviate by less than 20%

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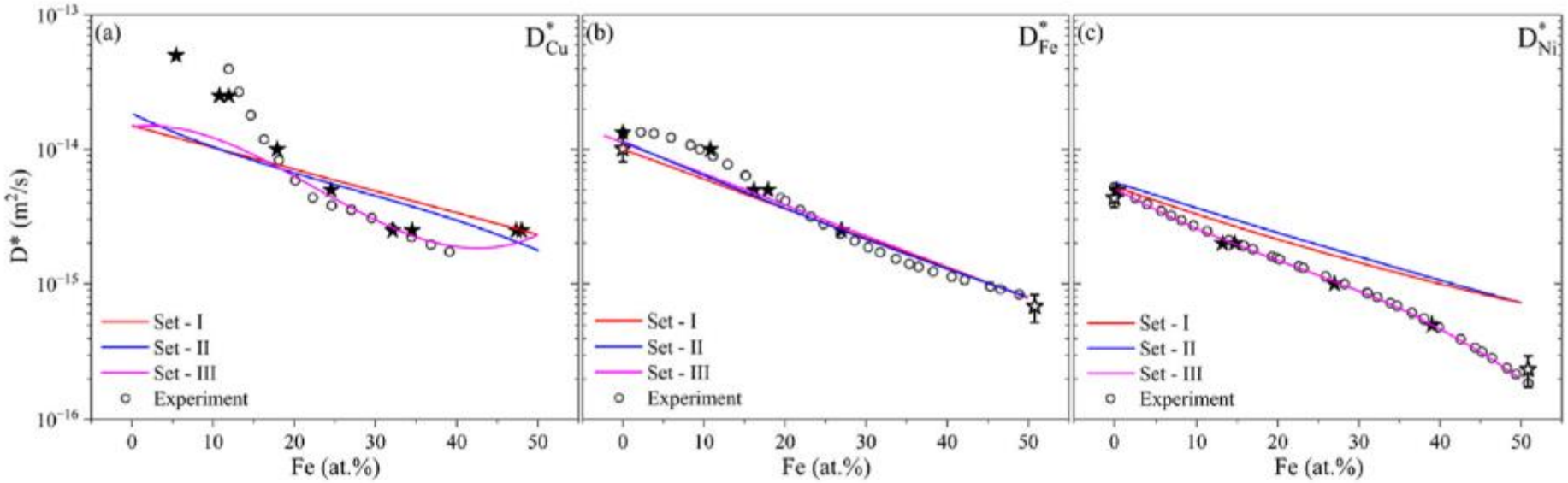
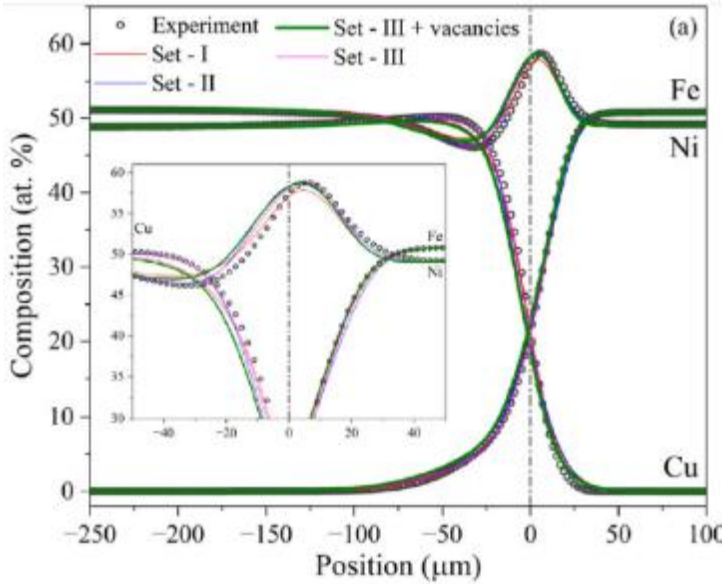
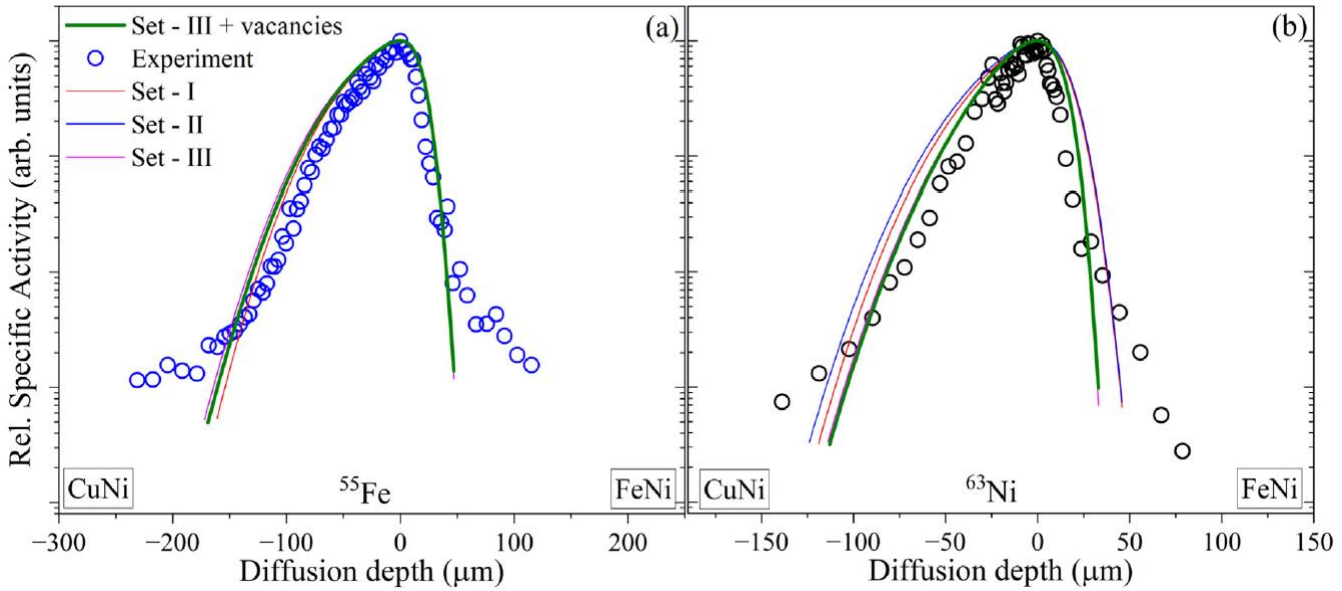
Augmented tracer-interdiffusion couple method: CuFeNi







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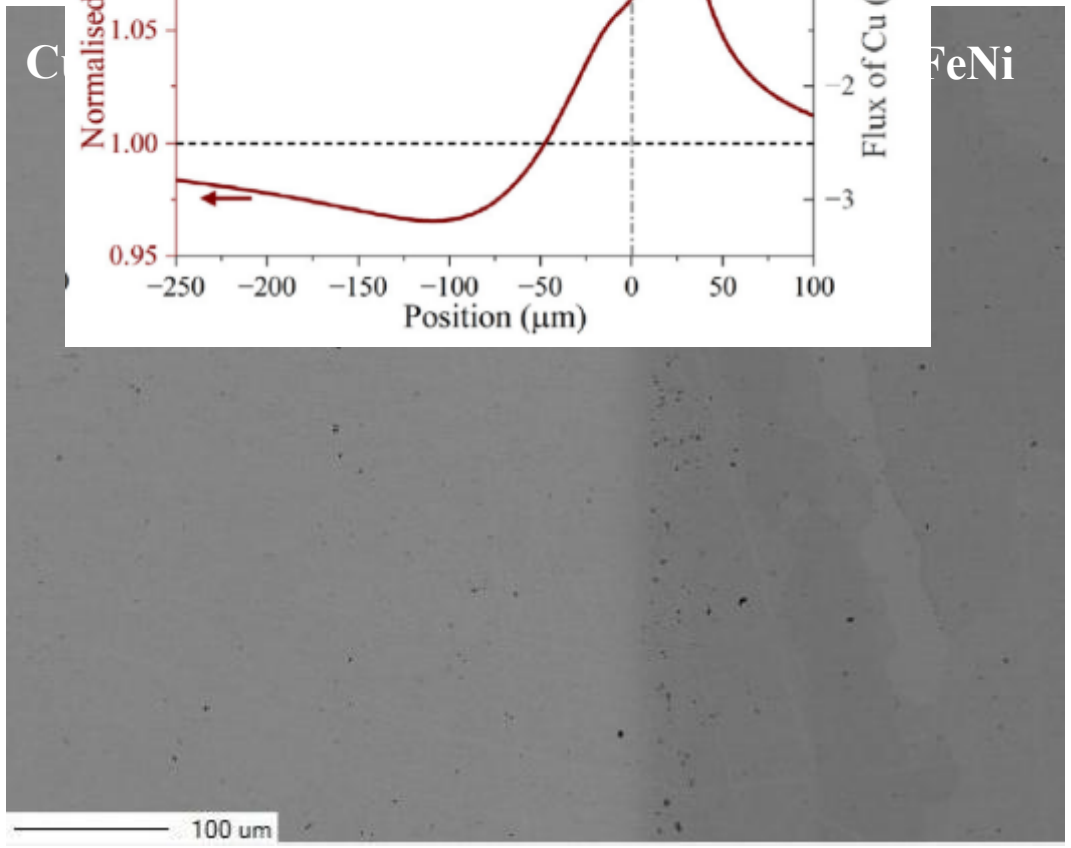
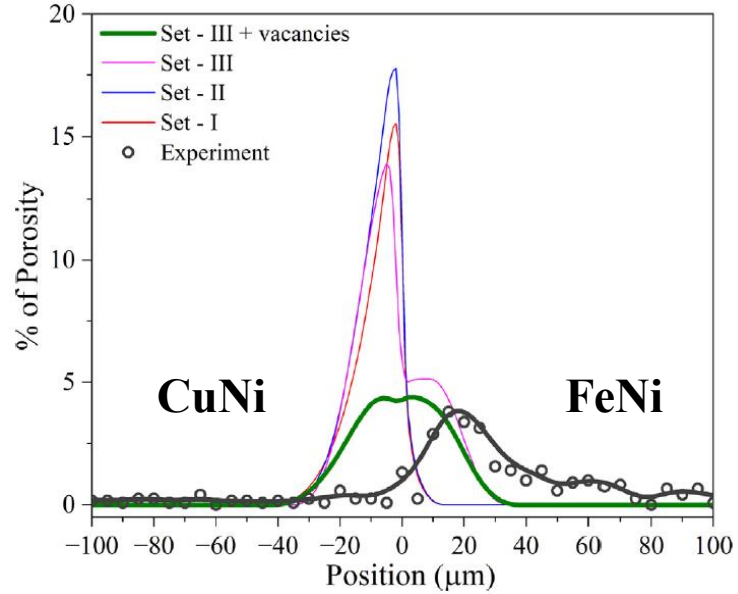
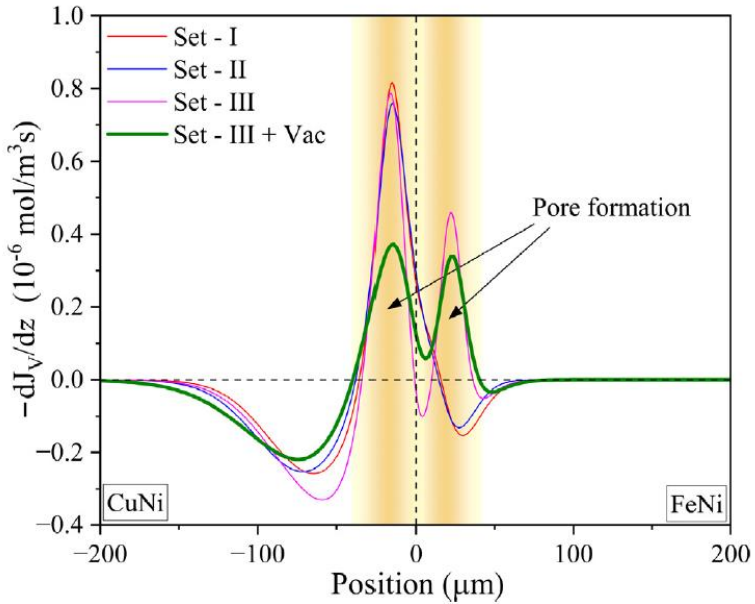
Augmented tracer-interdiffusion couple method: CuFeNi







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Conclusions

- The tracer diffusion coefficients evaluated under chemical gradients agree with those measured on homogeneous alloys
- Impact of non-equilibrium vacancies on atomic migration in the Cu–Fe–Ni system is evaluated, substantiating the general validity of the Darken– Manning scheme
- The predicted pore fraction qualitatively agree with experiment. The maximum pore fraction on the Fe-rich side can be reproduced only by the simulations with explicit accounting for vacancy diffusion.
- The present study demonstrates that chemical diffusion profiles can be fitted even using uncorrected mobility databases, which essentially (by more than a factor of two to three) overestimates the Ni diffusion rates
- **Combination of fluxes, pore fractions, and mobilities is a valid tool for mobility data assessment**

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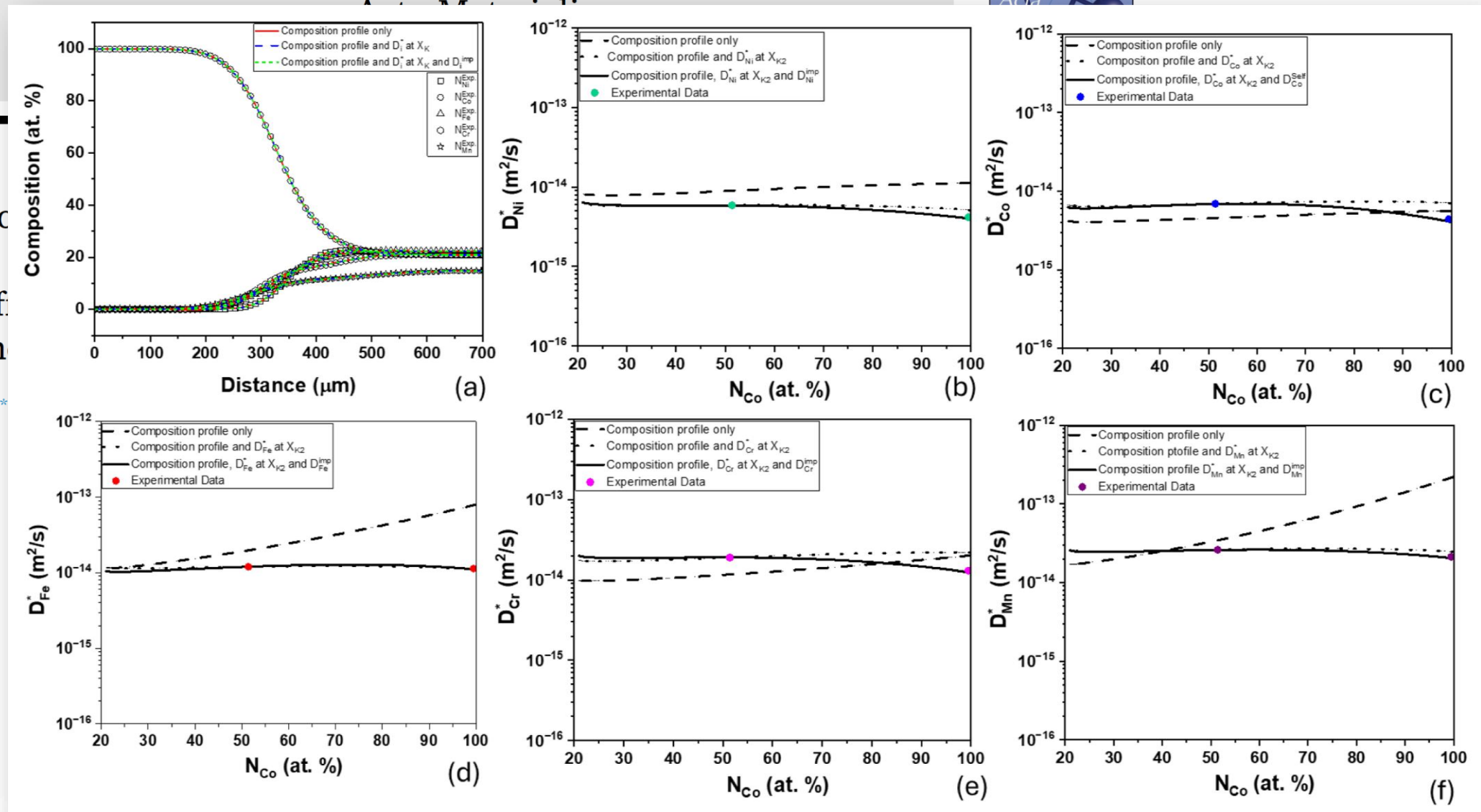

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Suman Sadhu [a,*]

Conclusions

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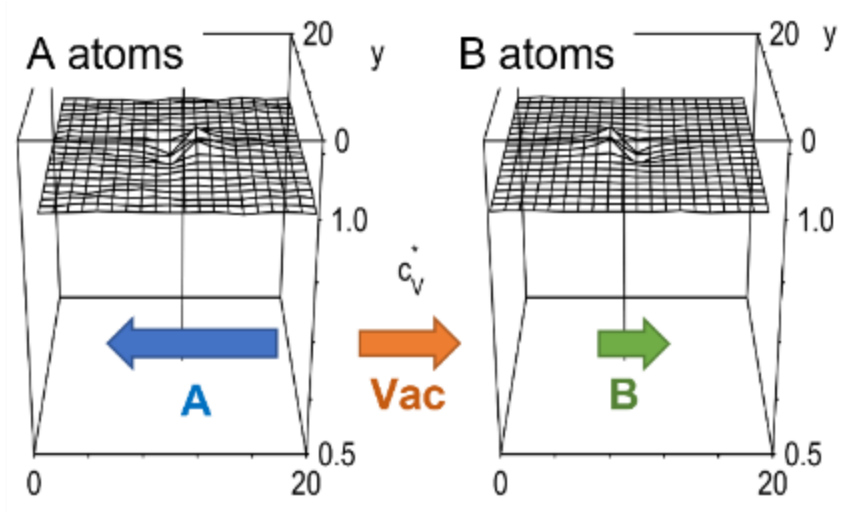
Thank you!

Augmented tracer-interdiffusion couple method: CuFeNi

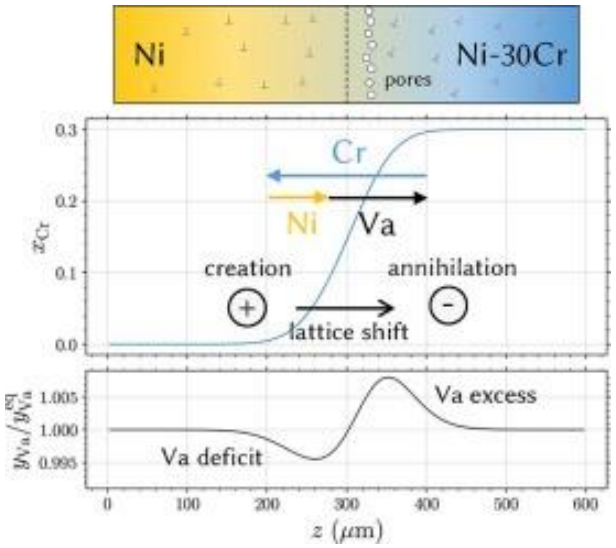
Impact of vacancy flux

vacancy wind effect (cross-terms)



Belova & Murch, *Visualization of the Vacancy-Wind Effect Occurring in Chemical Diffusion and Ionic Conductivity in Solids*. Defect Diffusion Forum 273-276 (2008) 431-444

vacancy production / annihilation



Gheno, Szczepan, Salsi, Desgranges, Monceau, *Simulation of diffusion with non-equilibrium vacancies, Kirkendall shift and porosity in single-phase alloys*, Computational Materials Science 215 (2022) 111785