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Recommendations for simplified yet robust assessments of atomic mobilities and diffusion coefficients of ternary and multicomponent solid solutions

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ABSTRACT

This study extends a 1-parameter Z-Z-Z binary diffusion coefficient model to ternary and multicomponent systems. The cross-binary and ternary interaction parameters in atomic mobility (diffusion coefficient) assessments were systematically tested on 4 ternary solid solutions: fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni, and bcc Nb-Ti-V. A simple combination of the Z-Z-Z binary model parameters without any additional fitting parameters already provides impressive predictions of the ternary diffusion coefficients when the 3 cross-binary parameters are set to be the corresponding binary Z-Z-Z model interaction parameters, leading to a robust *Z-Z-ternary* diffusion model. Employment of 3 independent cross-binary fitting parameters leads to an even better *binary and cross-binary parameters only* (*BCBPO*) model. Recommendations are rendered based upon the amount of available experimental ternary diffusion coefficients. These recommendations will substantially reduce the number of fitting parameters and improve the robustness of the resultant atomic mobility and diffusion coefficient databases for computational materials design.

Diffusion coefficients are essential to model diffusion-controlled processes and properties of materials, and are widely regarded as one of the most important phase-based properties. The general model of diffusion coefficients was elegantly established in terms of atomic mobilities by Andersson and Ågren [1] under the CALPHAD (CALculation of PHAse Diagrams) framework [1–5]. The atomic mobility M_i of element i is defined by Einstein's relation $M_i = D_i^*/RT = D_{0i}^* \exp(-Q_i/RT)/RT$ where D_{0i}^* and Q_i are the pre-factor and activation energy of the tracer diffusion coefficient D_i^*, R is the gas constant, and T is the absolute temperature. M_i is further expressed as:

$$M_i = \frac{D_{0i}^*}{RT}\exp\left(\frac{-Q_i}{RT}\right) = \frac{1}{RT}\exp\left(\frac{RT\ln D_{0i}^* - Q_i}{RT}\right) = \frac{1}{RT}\exp\left(\frac{\Phi_i}{RT}\right) \tag{1}$$

Both D_{0i}^* and Q_i are grouped into a single parameter $\Phi_i = RT\ln D_{0i}^* - Q_i = RT\ln D_i^*$, and this *atomic mobility parameter* Φ_i is further expressed as the summation of the linear combination of the end members in the composition space, the Redlich-Kister polynomial [6] and the Hillert polynomial [7]:

$$\Phi_i = \sum_j x_j \Phi_i^j + \sum_j \sum_{k>j} x_j x_k \left[\sum_{r=0,1,\ldots} {}^r\Phi_i^{j,k}\left(x_j - x_k\right)^r\right] + \sum_j \sum_{k>j} \sum_{l>k} x_j x_k x_l \left[\sum_{s=j,k,l} v_{jkl}^s \cdot {}^s\Phi_i^{j,k,l}\right] \tag{2}$$

Where x_i is the mole fraction of element i, and $v_{jkl}^s = x_s + (1 - x_j - x_k - x_l)/3$. Φ_i^j is the unary atomic mobility parameter of the end member elements, which is essentially the corresponding Φ_i values of the self-diffusion coefficient when $i = j$ or the impurity (dilute) diffusion coefficient when $i \neq j$. ${}^r\Phi_i^{j,k}$ is the *binary mobility interaction parameter* when $i = j$ *or* k and is the *cross-binary mobility interaction parameter* when $i \neq j$ *or* k. Each cross-binary mobility parameter corresponds to the impurity diffusion coefficient of a third element in a binary alloy of the other two elements in a ternary solid solution. The ${}^s\Phi_i^{j,k,l}$ values are the ternary mobility interaction parameters introduced by Hillert [7]. For a ternary A-B-C solid solution, each Φ_i parameter ($i = A,\ B$ *or* C) is:

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$$\Phi_i = x_A\Phi_i^A + x_B\Phi_i^B + x_C\Phi_i^C + x_Ax_B\left[\sum_{r=0,1,\ldots}{}^{r}\Phi_i^{A,B}(x_A-x_B)^r\right] + x_Ax_C\left[\sum_{r=0,1,\ldots}{}^{r}\Phi_i^{A,C}(x_A-x_C)^r\right] + x_Bx_C\left[\sum_{r=0,1,\ldots}{}^{r}\Phi_i^{B,C}(x_B-x_C)^r\right] + x_Ax_Bx_C\left(x_A{}^{\cdot A}\Phi_i^{A,B,C} + x_B{}^{\cdot B}\Phi_i^{A,B,C} + x_C{}^{\cdot C}\Phi_i^{A,B,C}\right) \quad (3)$$

The interaction parameters in the atomic mobility model are optimized from experimental diffusion coefficients, and they are usually assumed to be constants or linear functions of temperature, i.e., $a+bT$ where a and b are constants to be fitted. As demonstrated for 18 diverse binary systems, diffusion coefficients of binary *alloys* can be well modeled without the bT term [8]. The same should hold true for ternary and multicomponent systems even though there are insufficient systematic data for ternary systems to validate this assertion. Considering that most ternary diffusion coefficients are measured over a relatively narrow temperature range, the necessity of introducing the bT term is very slim. *It is thus recommended that no temperature term (i.e., bT) be introduced to any of the cross-binary and ternary mobility interaction parameters during atomic mobility assessments.*

A simple yet general binary diffusion (atomic mobility) model was recently developed from a very systematic assessment of 18 binary systems [8]. It was found that only one fitting interaction parameter (constant) is necessary for each binary solid solution in contrast to 4 or more parameters that are often employed in the literature CALPHAD atomic mobility assessments. This insight motivates us to extend the 1-parameter Z-Z-Z model to ternary and multicomponent solid solutions to reduce the number of fitting parameters while increase the robustness.

Eq. (3) can be converted to Eq. (4) below by: 1) substituting Φ_i with $RT\ln D_i^*$ since these two quantities are equal, 2) dividing both sides of Eq. (3) with RT, 3) setting $r=0$, and 4) setting $\Phi_i^{i,j} = \Phi_j^{i,j} = \Phi^{i,j}$ (a constant for each binary solution) based upon the Z-Z-Z binary diffusion model. Eq. (4) is expressed in diffusion coefficient terms which are more straightforward than the somewhat abstract Φ_i values, especially for those who may not be familiar with the atomic mobility notation and not use CALPHAD software.

$$\ln D_A^* = x_A\ln D_A^A + x_B\ln D_A^B + x_C\ln D_A^C + \left(x_Ax_B\Phi^{A,B} + x_Ax_C\Phi^{A,C} + x_Bx_C\Phi_A^{B,C}\right)/RT + x_Ax_Bx_C\left(x_A{}^{\cdot A}\Phi_A^{A,B,C} + x_B{}^{\cdot B}\Phi_A^{A,B,C} + x_C{}^{\cdot C}\Phi_A^{A,B,C}\right)/RT \quad (4.1)$$

$$\ln D_B^* = x_A\ln D_B^A + x_B\ln D_B^B + x_C\ln D_B^C + \left(x_Ax_B\Phi^{A,B} + x_Bx_C\Phi^{B,C} + x_Ax_C\Phi_B^{A,C}\right)/RT + x_Ax_Bx_C\left(x_A{}^{\cdot A}\Phi_B^{A,B,C} + x_B{}^{\cdot B}\Phi_B^{A,B,C} + x_C{}^{\cdot C}\Phi_B^{A,B,C}\right)/RT \quad (4.2)$$

$$\ln D_C^* = x_A\ln D_C^A + x_B\ln D_C^B + x_C\ln D_C^C + \left(x_Ax_C\Phi^{A,C} + x_Bx_C\Phi^{B,C} + x_Ax_B\Phi_C^{A,B}\right)/RT + x_Ax_Bx_C\left(x_A{}^{\cdot A}\Phi_C^{A,B,C} + x_B{}^{\cdot B}\Phi_C^{A,B,C} + x_C{}^{\cdot C}\Phi_C^{A,B,C}\right)/RT \quad (4.3)$$

Where D_i^j is the self-diffusion coefficient of element i when $i=j$ and denotes impurity diffusion coefficient of i in j when $i\neq j$. $\Phi^{i,j}$ is the binary mobility interaction parameter (a constant, not $a+bT$) between element i and j as defined in the Z-Z-Z model [8], $\Phi_i^{j,k}$ is the cross-binary mobility interaction parameter when $i\neq j$ *or* k, and ${}^{j}\Phi_i^{A,B,C}$ is the ternary interaction parameter. $i, j, k = A, B$ *or* C in the above notations. There are 3 cross-binary and 9 ternary mobility interaction parameters, thus 12 total fitting parameters for each ternary solid solution according to Eq. (4).

The interdiffusion coefficients $\tilde{D}_{ij}^n$ and intrinsic diffusion coefficients ${}^{I}D_{ij}^n$ can then be calculated as [1]:

$$\tilde{D}_{ij}^n = \sum_k(\delta_{ik}-x_i)\frac{x_kD_k^*}{RT}\left(\frac{\partial\mu_k}{\partial x_j} - \frac{\partial\mu_k}{\partial x_n}\right) \quad (5)$$

$${}^{I}D_{ij}^n = \frac{x_iD_i^*}{RT}\left(\frac{\partial\mu_i}{\partial x_j} - \frac{\partial\mu_i}{\partial x_n}\right) \quad (6)$$

Where $\tilde{D}_{ij}^n$ and ${}^{I}D_{ij}^n$ are the interdiffusion and intrinsic diffusion coefficients of element i in the matrix element n driven by the composition (chemical potential) gradient of element j. δ_{ik} is the Kronecker delta. μ_k is the chemical potential of element k, which can be obtained from thermodynamic databases/assessments. The self-diffusion and impurity diffusion coefficients in pure elements and the binary mobility interaction parameters are evaluated in the assessments of the pertinent unary and binary systems. The cross-binary and ternary mobility interaction parameters are optimized from available ternary diffusion coefficients. To investigate the optimal combinations of the 12 fitting parameters for a ternary solution, 11 different combinations were tested in this study as listed in **Table 1**. The objective of the optimization is to find the optimal values of those sets of interaction parameters that minimize the mean squared error (MSE):

$$MSE = \frac{1}{N}\sum_{i=1}^{N}\left(\ln\left|D_i^{exp}\right| - \ln\left|D_i^{pred}\right|\right)^2 \quad (7)$$

Where N is the total number of data points of available ternary diffusion coefficients in a particular ternary solid solution, D_i^{exp} and D_i^{pred} are the experimental diffusion coefficient and predicted diffusion coefficient of the ith data point, respectively. Both D_i^{exp} and D_i^{pred} here include interdiffusion coefficients as well as tracer and intrinsic diffusion coefficients whenever available. A Python program was written to perform the optimization process using the dual-annealing approach [14] to find the global minimum of MSE with the fitting parameters in defined bounds.

After a literature search of ternary diffusion data, the fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni and bcc Nb-Ti-V phases were identified as the testing cases since: 1) ternary interdiffusion coefficients are measured across majority of the composition range of the ternary solid solutions; and 2) the self-diffusion and impurity diffusion coefficients of the pure elements as well as the binary diffusion coefficients are well assessed. It is noted that there is a miscibility gap near the Ag-Cu binary in the Ag-Au-Cu system [9] as well as the Cu-Fe binary in the Cu-Fe-Ni system [15] within which diffusion coefficients could not be measured. The literature experimental ternary diffusion data of these 4 systems are summarized in **Table S1** and their distribution over the composition space is plotted in **Fig. S1** in the Supplementary Information.

The thermodynamic quantities (thermodynamic factors) as required by Eqs. (5) and (6) were obtained using the Thermo-Calc Software [16] and its associated databases TCCU3 [17], TCNI9 [18] and TCTI2 [19]. The pertinent unary and binary systems were already assessed in our previous study [8] and the assessed parameters were directly adopted in this study except for the Ag-Cu and Cu-Fe binaries. The assessed parameters of the impurity diffusion coefficients of Cu in Fe, $D_{Cu}^{Fe} = 2.1\times10^{-5}\exp(-272378/RT)$, and Fe in Cu, $D_{Fe}^{Cu} = 1.0\times$

Table 1
Diffusion models and the corresponding fitting parameters (variables v_i) for each ternary solid solution explored in this study and the number of mobility interaction parameters used in the literature CALPHAD mobility assessments of the fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni and bcc Nb-Ti-V solid solutions in the literature. A, B, C = Ag, Au, Cu or Co, Fe, Ni or Cu, Fe, Ni or Nb, Ti, V, respectively.

Parameter notation		Interaction parameters (v_i) used in this study											Number of interaction parameters used in the literature mobility assessments				
		Model-#											Ag-Au-Cu	Co-Fe-Ni		Cu-Fe-Ni	Nb-Ti-V
		0	0*	1	2	3	4	5	6	7	8	9	Ref. [9]	Ref. [10]	Ref. [11]	Ref. [12]	Ref. [13]
Binary	${}^{\Phi}_{A}{}^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	3	2	2	0	2
	${}^{\Phi}_{B}{}^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	$\Phi^{A,B}$	3	2	2	0	2
	${}^{\Phi}_{A}{}^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	1	1	1	2	0
	${}^{\Phi}_{C}{}^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	$\Phi^{A,C}$	1	1	1	2	5
	${}^{\Phi}_{B}{}^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	2	4	1	4	2
	${}^{\Phi}_{C}{}^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	$\Phi^{B,C}$	2	4	2	4	1
Cross-Binary	${}^{\Phi}_{A}{}^{B,C}$	0	$\Phi^{B,C}$	v_1	0	v_1	v_1	0	v_1	v_1	v_1	v_1	0	0	1	1	0
	${}^{\Phi}_{B}{}^{A,C}$	0	$\Phi^{A,C}$	v_1	0	v_1	v_2	0	v_1	v_2	v_2	v_2	1	0	1	1	0
	${}^{\Phi}_{C}{}^{A,B}$	0	$\Phi^{A,B}$	v_1	0	v_1	v_3	0	v_1	v_3	v_3	v_3	1	0	1	1	0
Ternary	${}^{A}\Phi^{A,B,C}_{A}$	0	0	0	v_4	v_4	0	v_4	v_4	v_4	v_4	v_4	1	1	0	1	1
	${}^{B}\Phi^{A,B,C}_{A}$	0	0	0	v_4	v_4	0	v_4	v_4	v_4	v_4	v_5	0	1	0	1	0
	${}^{C}\Phi^{A,B,C}_{A}$	0	0	0	v_4	v_4	0	v_4	v_4	v_4	v_4	v_6	0	1	0	1	0
	${}^{A}\Phi^{A,B,C}_{B}$	0	0	0	v_4	v_4	0	v_5	v_5	v_4	v_5	v_7	0	1	0	1/3*	1
	${}^{B}\Phi^{A,B,C}_{B}$	0	0	0	v_4	v_4	0	v_5	v_5	v_4	v_5	v_8	0	1	0	1/3*	0
	${}^{C}\Phi^{A,B,C}_{B}$	0	0	0	v_4	v_4	0	v_5	v_5	v_4	v_5	v_9	0	1	0	1/3*	0
	${}^{A}\Phi^{A,B,C}_{C}$	0	0	0	v_4	v_4	0	v_6	v_6	v_4	v_6	v_{10}	1	1	0	1/3*	1
	${}^{B}\Phi^{A,B,C}_{C}$	0	0	0	v_4	v_4	0	v_6	v_6	v_4	v_6	v_{11}	1	1	0	1/3*	0
	${}^{C}\Phi^{A,B,C}_{C}$	0	0	0	v_4	v_4	0	v_6	v_6	v_4	v_6	v_{12}	1	1	0	1/3*	0
Total number of interaction parameters for a ternary system (including binary parameters)		3	3	4	4	5	6	6	7	7	9	15	18	23	12	20	15

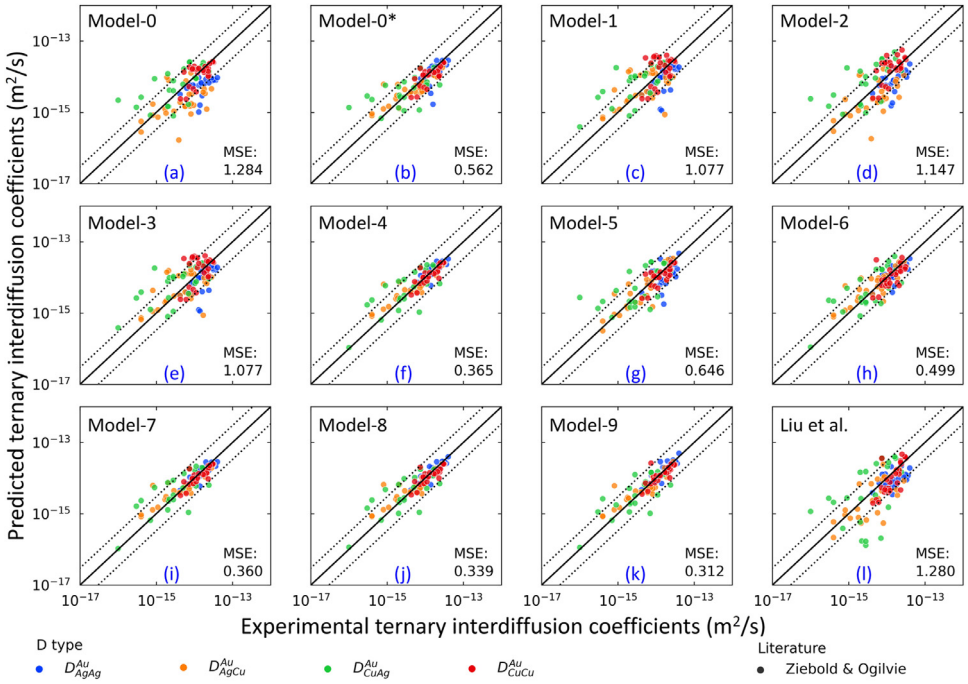

Fig. 1. The performance of different diffusion models for the fcc Ag-Au-Cu solid solution in comparison with the results from the mobility assessment by Liu et al. [9].

$10^{-5}\exp(-197000/RT)$, were taken from Ref. [20], while the parameters of Ag in Cu $D^{Cu}_{Ag} = 4.7 \times 10^{-5}\exp(-191533/RT)$, and Cu in Ag, $D^{Ag}_{Cu} = 2.7 \times 10^{-5}\exp(-179012/RT)$ were accepted from Ref. [9]. The binary mobility interaction parameter between Cu and Fe was determined to be zero ($\Phi^{Cu,Fe} = 0$) according to the assessment by Liu et al. [21] while the binary mobility interaction parameter between Ag and Cu was assessed in the current study as $\Phi^{Ag,Cu} = 71449\,(m^2 \cdot J)/(mol \cdot s)$, as shown in **Fig. S2** in the Supplementary Information.

For the fcc Ag-Au-Cu solid solution, Ziebold and Ogilvie [22] measured the interdiffusion coefficients at 725°C. Liu et al. [9] performed the mobility assessment on this system and reported 12 binary parameters, 2 cross-binary parameters and 4 ternary parameters as summarized in **Table 1**. Eleven models with different combinations of fitting parameters as listed in **Table 1** were tested in this study using the same ternary interdiffusion data, and the model performances are compared with the literature mobility assessment in **Fig. 1**. The solid diagonal line represents a perfect agreement between experimental data and model-predicted data while the two dashed lines denotes a factor of 3 or 1/3 deviation, respectively. It is noted that Model-0 which is a simple combination of the three binary parameters without any ternary related fitting parameters predicts the ternary interdiffusion coefficients as good as that of the mobility assessment of Liu et al. Model-0* *without* the introduction of any ternary-related fitting parameters but simply assuming the cross-binary interaction parameters to be equal to the corresponding Z-Z-Z model binary interaction parameters (i.e., $\Phi^{A,B}_C = \Phi^{A,B}$, $\Phi^{A,C}_B = \Phi^{A,C}$, $\Phi^{B,C}_A = \Phi^{B,C}$, and all 9 ${}^{j}\Phi^{A,B,C}_{i} = 0$) substantially outperforms (has a lower *MSE* than) the assessment of Liu et al.

For the fcc phase of the Co-Fe-Ni system, Cui et al. [10] evaluated the interdiffusion coefficients at 1100°C from the experimental diffusion profiles measured by Ugaste et al. [23], and then assessed the atomic mobility of the ternary system together with the interdiffusion coefficients reported by Sabatier and Vignes at 1136°C [24] and 1315°C [25]. Divya et al. [26] determined the interdiffusion coefficients at 1150°C. Xia et al. [11] measured the interdiffusion coefficients at 900°C and re-assessed the atomic mobilities by combining their own data with the data in Refs. [10,25]. All the ternary interdiffusion coefficients except for the data from Divya et al. [26] were used to optimize the 11 models in this study since their data have much larger variation than the other datasets. The model performances are compared with the 2 literature mobility assessments [10,11] in **Fig. 2**. The number of mobility interaction parameters used in the 2 literature assessments are also summarized in **Table 1**, showing very discrepant choices of parameters for the same system. Cui et al. [10] employed 14 binary interaction parameters and 9 ternary interaction parameters while Xia et al. [11] used 9 binary parameters and 3 cross-binary parameters. Model-0 and Model-0* without any ternary related fitting parameters already predict the ternary interdiffusion coefficients reasonably well. Model-4 with 3 cross-binary parameters has better performance than that of the two literature mobility assessments.

For the fcc Cu-Fe-Ni solid solution, Cserhati et al. [27] and Ugaste et al. [28] reported ternary interdiffusion coefficients at 1000°C. Tracer and interdiffusion coefficients were determined by Danielewski et al. [29] as well as Ronka et al. [30]. Belova et al. [31] evaluated the tracer diffusion coefficients of Cu, Fe and Ni at 998°C. The 11 models were tested in this study using all the above experimental data. The model performances are compared in **Fig. 3** along with the mobility assessment by Liu et al. [12]. Liu's assessment involved 12 binary, 3 cross-binary and 5 ternary interaction parameters as listed in **Table 1**. Model-0 already has good performance. Model-0* without any ternary-related fitting parameters appreciably outperforms the mobility assessment of Liu et al.

For the bcc Nb-Ti-V solid solution, Aitbaev et al. [32] extracted interdiffusion coefficients at both 1000°C and 1200°C via diffusion couples. Wei et al. [13] measured the interdiffusion coefficients at 1000°C, 1100°C and 1200°C, and assessed the atomic mobilities. They used 12 binary parameters and 3 ternary parameters as shown in **Table 1**. The performances of the 11 different models optimized from all the ternary diffusion data are compared in **Fig. 4** along with the mobility assessment of Wei et al. [13]. Model-0

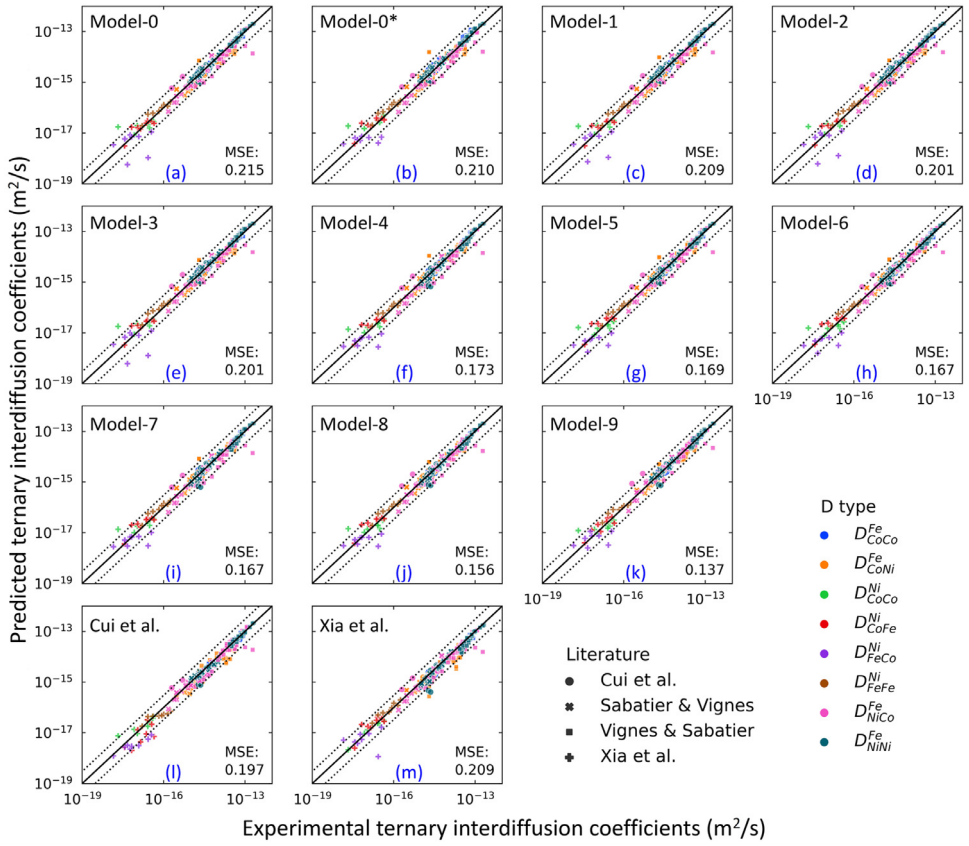

Fig. 2. The performance of different diffusion models for the fcc Co-Fe-Ni solid solution in comparison with the results from the mobility assessments by both Cui et al. [10] and Xia et al. [11]. The analysis with all the datasets, including those from Divya et al. [26], is shown in **Fig. S3** in the Supplementary Information.

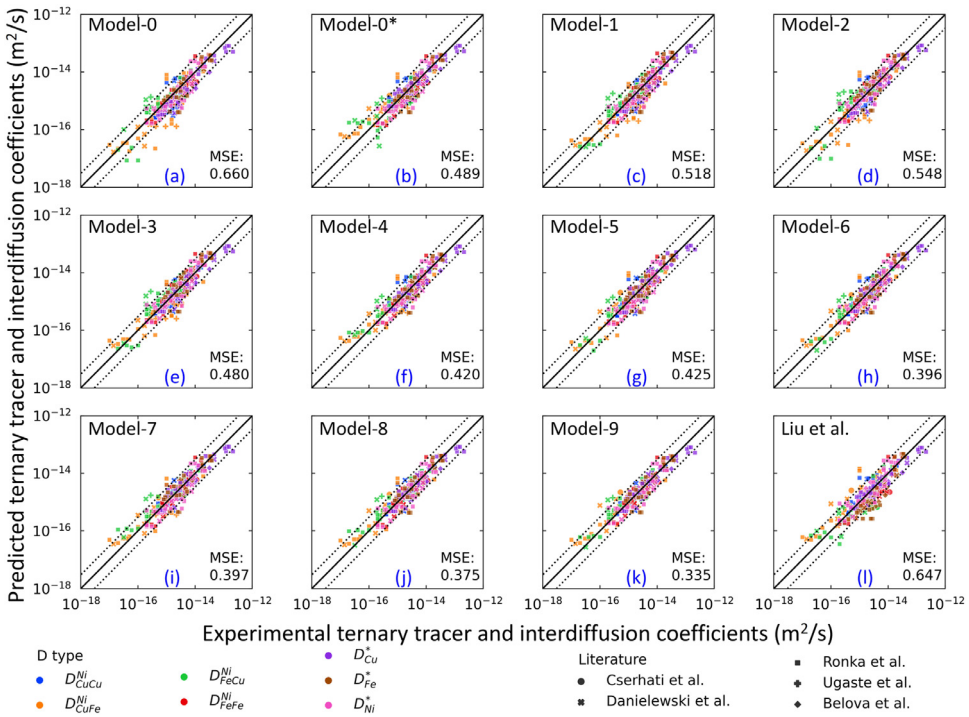

Fig. 3. The performance of different diffusion models for the fcc Cu-Fe-Ni solid solution in comparison with the results from the mobility assessment by Liu et al. [12].

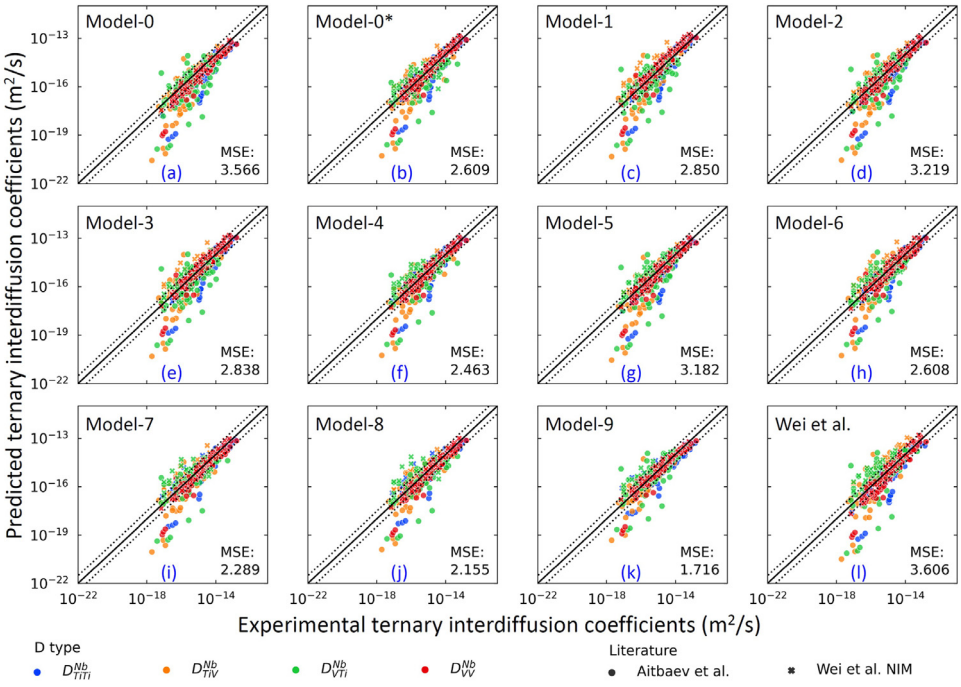

Fig. 4. The performance of different diffusion models for the bcc Nb-Ti-V solid solution in comparison with the results from the mobility assessment by Wei et al. [13].

with only binary interaction parameters without any ternary adjustments already outperforms the literature mobility assessment. Model-0* substantially outperforms Model-0.

The effectiveness of progressive introduction of the cross-binary and ternary interaction parameters on the model performances as measured by the *MSE* value was systematically studied, and the results are shown in **Figs. 1-4** and summarized in **Fig. 5** which shows that Model-0* which sets the cross-binary interaction parameters to be the corresponding Z-Z-Z binary model parameters has surprisingly good performance in comparison with Model-0. The results also clearly show that introduction of 1 cross-binary interaction parameter by setting $\Phi_C^{A,B} = \Phi_B^{A,C} = \Phi_A^{B,C} = constant$ and all 9 ${}^{j}\Phi_i^{A,B,C} = 0$ (Model-1) is usually more effective in improving the model performance (lowering the *MSE* value) than the introduction of 1 ternary interaction parameter by setting all 9 ${}^{j}\Phi_i^{A,B,C} = constant$ and $\Phi_C^{A,B} = \Phi_B^{A,C} = \Phi_A^{B,C} = 0$ (Model-2). Introduction of 2 fitting parameters by setting both $\Phi_C^{A,B} = \Phi_B^{A,C} = \Phi_A^{B,C} = constant$ #1 and all 9 ${}^{j}\Phi_i^{A,B,C} = constant$ #2 (Model-3) leads to minor improvement over Model-1. Introduction of 3 independent cross-binary parameters $\Phi_C^{A,B} \neq \Phi_B^{A,C} \neq \Phi_A^{B,C} = 3$ *constants* and all 9 ${}^{j}\Phi_i^{A,B,C} = 0$ (Model-4) leads to more consistent improvement of performance than Model-5 which introduces 3 ternary mobility interaction parameters by setting ${}^{A}\Phi_A^{A,B,C} = {}^{B}\Phi_A^{A,B,C} = {}^{C}\Phi_A^{A,B,C} = constant$ #1, ${}^{A}\Phi_B^{A,B,C} = {}^{B}\Phi_B^{A,B,C} = {}^{C}\Phi_B^{A,B,C} = constant$ #2, ${}^{A}\Phi_C^{A,B,C} = {}^{B}\Phi_C^{A,B,C} = {}^{C}\Phi_C^{A,B,C} = constant$ #3, and $\Phi_C^{A,B} = \Phi_B^{A,C} = \Phi_A^{B,C} = 0$. Even though Model-5 performs slightly better than Model-4 for Co-Fe-Ni, it is much worse for Nb-Ti-V, even inferior to Model-3, as shown in **Fig. 5(e)**. Thus, the more consistent Model-4 is preferred. Model-7 which is based on Model-4 by introducing a 4th parameter by setting all 9 ${}^{j}\Phi_i^{A,B,C} = constant$ #4 again delivers a more consistent, even though small, improvement of performance over Model-4 than Model-6 which is based on Model-5 by introducing a 4th parameter $\Phi_C^{A,B} = \Phi_B^{A,C} = \Phi_A^{B,C} = constant$ #4. All these results clearly show that *the introduction of cross-binary mobility interaction parameters is more effective and consistent in improving the model performance than the ternary mobility interaction parameters*. Model-8 which is a combination of Model-6 and Model-7 with 3 cross-binary and 3 ternary parameters leads to minor improvements over Model-7. Model-9 includes 3 cross-binary and 9 ternary parameters leads to marginal improvement over Model-7 which only introduces 3 cross-binary and 1 ternary parameters. Considering that experimental ternary diffusion data are usually limited for most ternary systems and often limited to a certain composition space, less plentiful than the 4 systems studied herein, both Model-8 and Model-9 are discouraged since too many fitting parameters are prone to overfitting and less reliable when extrapolating into multicomponent systems.

The above results point to robust diffusion models (Model-0* and Model-4) for ternary solid solutions as represented by Eq. (8) which is simplified from Eq. (4) by eliminating all ternary mobility interaction parameters but still including the 3 cross-binary interaction parameters. It is noted that Model-0* is a special case of Model-4.

$$\ln D_A^* = x_A \ln D_A^A + x_B \ln D_A^B + x_C \ln D_A^C + \left(x_A x_B \Phi^{A,B} + x_A x_C \Phi^{A,C} + x_B x_C \Phi_A^{B,C}\right)/RT \tag{8.1}$$

$$\ln D_B^* = x_A \ln D_B^A + x_B \ln D_B^B + x_C \ln D_B^C + \left(x_A x_B \Phi^{A,B} + x_B x_C \Phi^{B,C} + x_A x_C \Phi_B^{A,C}\right)/RT \tag{8.2}$$

$$\ln D_C^* = x_A \ln D_C^A + x_B \ln D_C^B + x_C \ln D_C^C + \left(x_A x_C \Phi^{A,C} + x_B x_C \Phi^{B,C} + x_A x_B \Phi_C^{A,B}\right)/RT \tag{8.3}$$

The following recommendations are hereby rendered based upon the insights from the current study:

- *When no experimental ternary diffusion data are available, Model-0* should be employed which is entirely based on diffusion data of the unary and binary systems by setting* $\Phi_C^{A,B} = \Phi^{A,B}$, $\Phi_B^{A,C} = \Phi^{A,C}$, *and* $\Phi_A^{B,C} = \Phi^{B,C}$ *in Eq. (8). As a matter of fact, Model-0* yields quite impressive predictions for all 4 systems tested in this study and it is hereby termed "Z-Z-ternary diffusion model" for future referencing convenience.*

Table 2
The assessed mobility interaction parameters of the fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni and bcc Nb-Ti-V solid solutions. A, B, C = Ag, Au, Cu or Co, Fe, Ni or Cu, Fe, Ni or Nb, Ti, V, respectively.

Model Parameters, $(m^2 \cdot J)/(mol \cdot s)$		Ag-Au-Cu (fcc)		Co-Fe-Ni (fcc)		Cu-Fe-Ni (fcc)		Nb-Ti-V (bcc)	
		*Model-0**	*Model-4*	*Model-0**	*Model-4*	*Model-0**	*Model-4*	*Model-0**	*Model-4*
Binary	$\Phi^{A,B}$	-15021	-15021	7120	7120	0	0	77831	77831
	$\Phi^{A,C}$	71449	71449	15096	15096	1083	1083	132825	132825
	$\Phi^{B,C}$	43282	43282	49942	49942	49942	49942	79863	79863
Cross-binary	$\Phi_C^{A,B}$	-15021	-20327	7120	-21426	0	26840	77831	48869
	$\Phi_B^{A,C}$	71449	149619	15096	6438	1083	10038	132825	149667
	$\Phi_A^{B,C}$	43282	43067	49942	18953	49942	35232	79863	74660

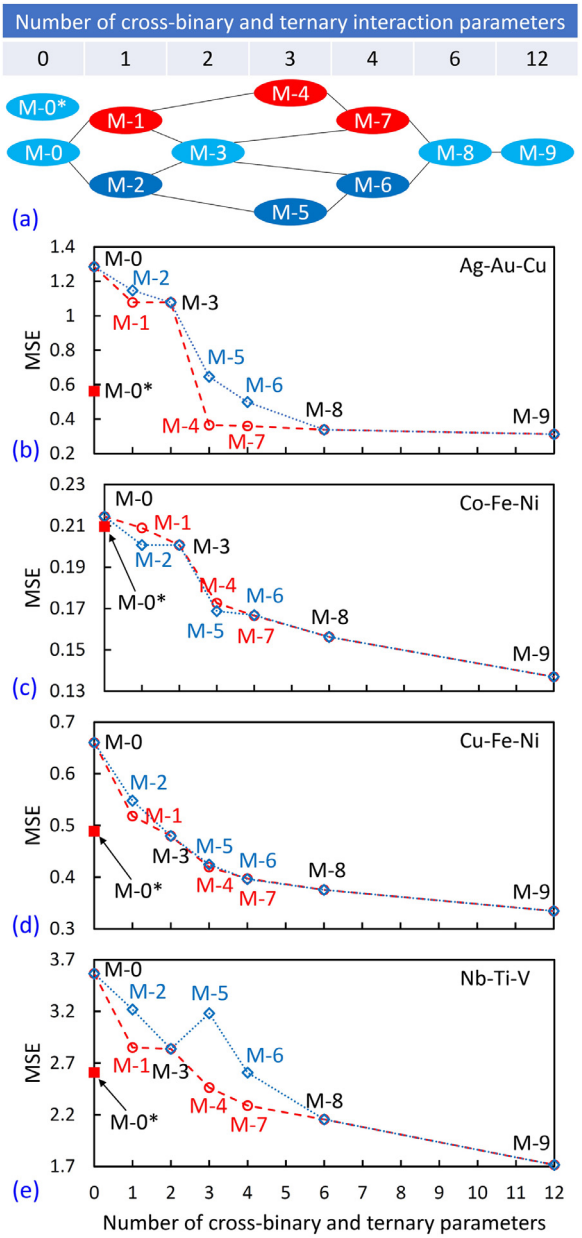

Fig. 5. Model performance (MSE - the lower the better) versus number of cross-binary and ternary mobility interaction parameters: (a) Models (M-i refers to Model-i listed in **Table 1**) and corresponding number of parameters; and (b)(c)(d)(e) Model performance for the fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni, and bcc Nb-Ti-V solid solutions.

- *When some experimental ternary diffusion data are available for a ternary system, Model-4 is recommended where* $\Phi_C^{A,B} \neq \Phi_B^{A,C} \neq \Phi_A^{B,C} = 3$ *fitting constants in Eq. (8). This model is termed "binary and cross-binary parameters only (BCBPO) diffusion model".*
- *When lots of ternary diffusion data are measured for a ternary system, one may try Models 4 to 7 to find the optimal balance of model performance and number of parameters (especially Model-7).*

The second and third recommendations above shall be sound even for those who insist on using 2 interaction parameters (constants $\Phi_i^{i,j} \neq \Phi_j^{i,j}$) for each binary solid solution (More than 2 parameters are discouraged as demonstrated in Ref. [8]). In this case, one simply applies the above recommendations to Eq. (3) during atomic mobility assessments by setting all 9 ternary mobility interaction parameters to zero.

The assessed interaction parameters of both Model-0* and Model-4 of the 4 ternary solid solutions are listed in **Table 2** together with the binary mobility interaction parameters of the pertinent binary systems.

It is straightforward to further extend the robust *Z-Z-ternary* diffusion model (Model-0*) and the *BCBPO* ternary model (Model-4) to multicomponent solid solutions:

$$\ln D_i^* = \sum_j x_j \ln D_i^j + \sum_{j \neq i} x_i x_j \Phi^{i,j}/RT + \sum_{j,k \neq i;\, k>j} x_j x_k \Phi_i^{j,k}/RT \qquad (9)$$

The interdiffusion coefficients ($\tilde{D}_{ij}^n$) and intrinsic diffusion coefficients ($^l D_{ij}^n$) of the multicomponent system, including all the cross-terms, can then be computed from Eqs. (5) and (6) by obtaining the D_i^* values from Eq. (9) and the chemical potential values from the pertinent thermodynamic databases or published CALPHAD assessments. Again one can multiply both sides of Eqs. (8) and (9) with *RT* to convert back into the atomic mobility (Φ_i) notation. Such robust *Z-Z-ternary* and *BCBPO* models will substantially reduce the fitting parameters yet enhance the robustness of future atomic mobility and diffusion databases for reliable modeling of kinetic processes and materials properties.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2021.114227.

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Supplementary Information
for

Recommendations for simplified yet robust assessments of atomic mobilities and diffusion coefficients of ternary and multicomponent solid solutions

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Table S1. *Experimental ternary diffusion data in the literature of the fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni, and bcc Nb-Ti-V solid solutions.* $\widetilde{D}_{ij}^{n}$ *is the interdiffusion coefficient of element* i *in element* n *driven by the composition gradient of element* j.

System	Literature	Temperature, °C	Experimental ternary diffusion data
Ag-Au-Cu (fcc)	Ziebold & Ogilvie [1]	725	$\widetilde{D}_{AgAg}^{Au}$, $\widetilde{D}_{AgCu}^{Au}$, $\widetilde{D}_{CuAg}^{Au}$, $\widetilde{D}_{CuCu}^{Au}$
Co-Fe-Ni (fcc)	Cui et al. [2]	1100	$\widetilde{D}_{CoCo}^{Fe}$, $\widetilde{D}_{CoNi}^{Fe}$, $\widetilde{D}_{NiCo}^{Fe}$, $\widetilde{D}_{NiNi}^{Fe}$
	Sabatier & Vignes [3]	1136	$\widetilde{D}_{CoCo}^{Fe}$, $\widetilde{D}_{CoNi}^{Fe}$, $\widetilde{D}_{NiCo}^{Fe}$, $\widetilde{D}_{NiNi}^{Fe}$
	Vignes & Sabatier [4]	1315	$\widetilde{D}_{CoCo}^{Fe}$, $\widetilde{D}_{CoNi}^{Fe}$, $\widetilde{D}_{NiCo}^{Fe}$, $\widetilde{D}_{NiNi}^{Fe}$
	Divya et al. [5]	1150	$\widetilde{D}_{CoCo}^{Ni}$, $\widetilde{D}_{CoFe}^{Ni}$, $\widetilde{D}_{FeCo}^{Ni}$, $\widetilde{D}_{FeFe}^{Ni}$
	Xia et al. [6]	900	$\widetilde{D}_{CoCo}^{Ni}$, $\widetilde{D}_{CoFe}^{Ni}$, $\widetilde{D}_{FeCo}^{Ni}$, $\widetilde{D}_{FeFe}^{Ni}$
Cu-Fe-Ni (fcc)	Cserhati et al. [7]	1000	$\widetilde{D}_{CuCu}^{Ni}$, $\widetilde{D}_{CuFe}^{Ni}$, $\widetilde{D}_{FeCu}^{Ni}$, $\widetilde{D}_{FeFe}^{Ni}$
	Ugaste et al. [8]	1000	$\widetilde{D}_{CuCu}^{Ni}$, $\widetilde{D}_{CuFe}^{Ni}$, $\widetilde{D}_{FeCu}^{Ni}$, $\widetilde{D}_{FeFe}^{Ni}$
	Danielewski et al. [9]	1000	$\widetilde{D}_{CuCu}^{Ni}$, $\widetilde{D}_{CuFe}^{Ni}$, $\widetilde{D}_{FeCu}^{Ni}$, $\widetilde{D}_{FeFe}^{Ni}$, D_{Cu}^{*}, D_{Fe}^{*}, D_{Ni}^{*}
	Ronka et al. [10]	1000	$\widetilde{D}_{CuCu}^{Ni}$, $\widetilde{D}_{CuFe}^{Ni}$, $\widetilde{D}_{FeCu}^{Ni}$, $\widetilde{D}_{FeFe}^{Ni}$, D_{Cu}^{*}, D_{Fe}^{*}, D_{Ni}^{*}
	Belova et al. [11]	998	D_{Cu}^{*}, D_{Fe}^{*}, D_{Ni}^{*}
Nb-Ti-V (bcc)	Aitbaev et al. [12]	1000, 1200	$\widetilde{D}_{TiTi}^{Nb}$, $\widetilde{D}_{TiV}^{Nb}$, $\widetilde{D}_{VTi}^{Nb}$, $\widetilde{D}_{VV}^{Nb}$
	Wei et al. [13]	1000, 1100, 1200	$\widetilde{D}_{TiTi}^{Nb}$, $\widetilde{D}_{TiV}^{Nb}$, $\widetilde{D}_{VTi}^{Nb}$, $\widetilde{D}_{VV}^{Nb}$

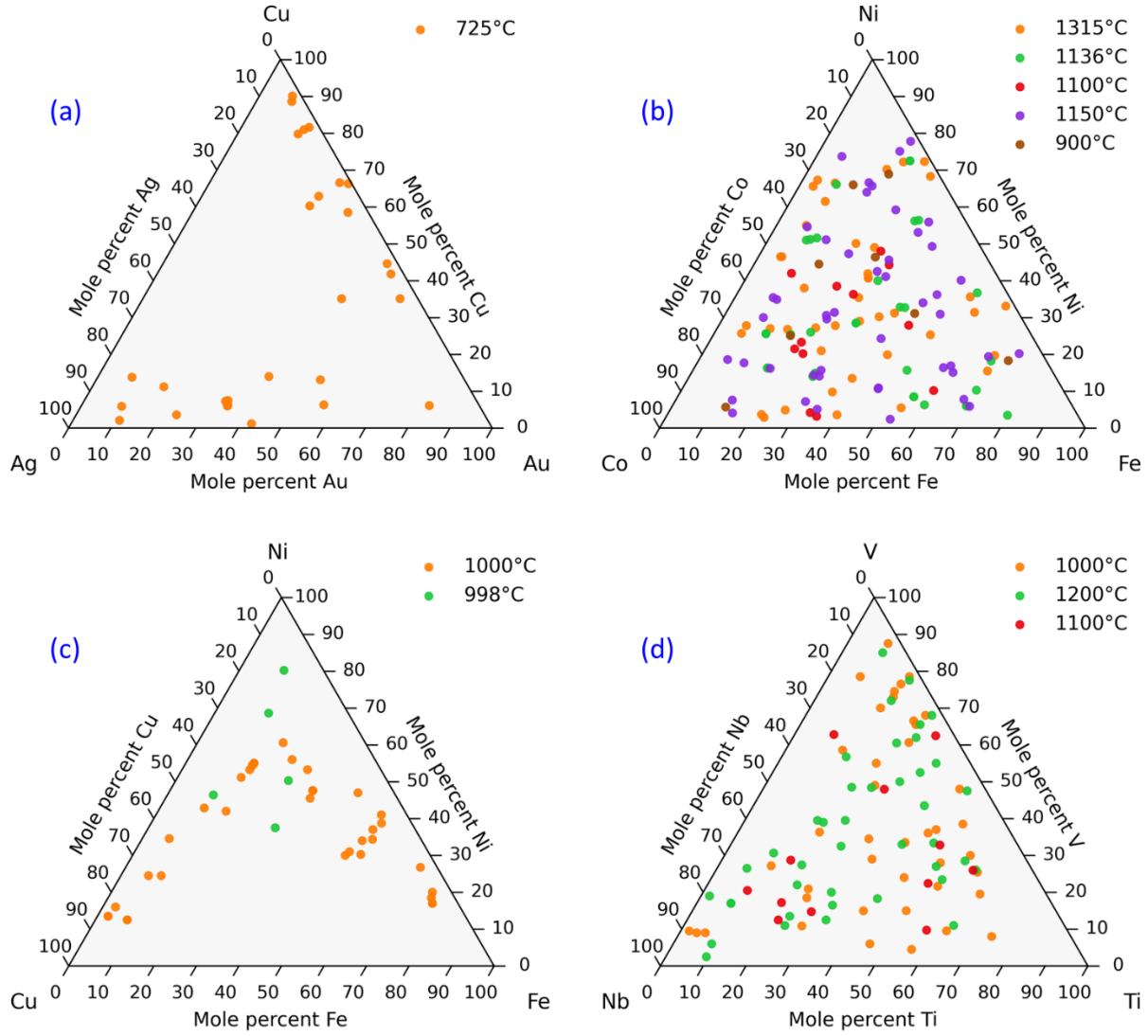

Fig. S1. *Distribution of the experimental ternary diffusion coefficients over the composition space of the 4 ternary systems: (a) the fcc phase of the Ag-Au-Cu system; (b) the fcc phase of the Co-Fe-Ni system; (c) the fcc phase of the Cu-Fe-Ni system; and (d) the bcc phase of the Nb-Ti-V system.*

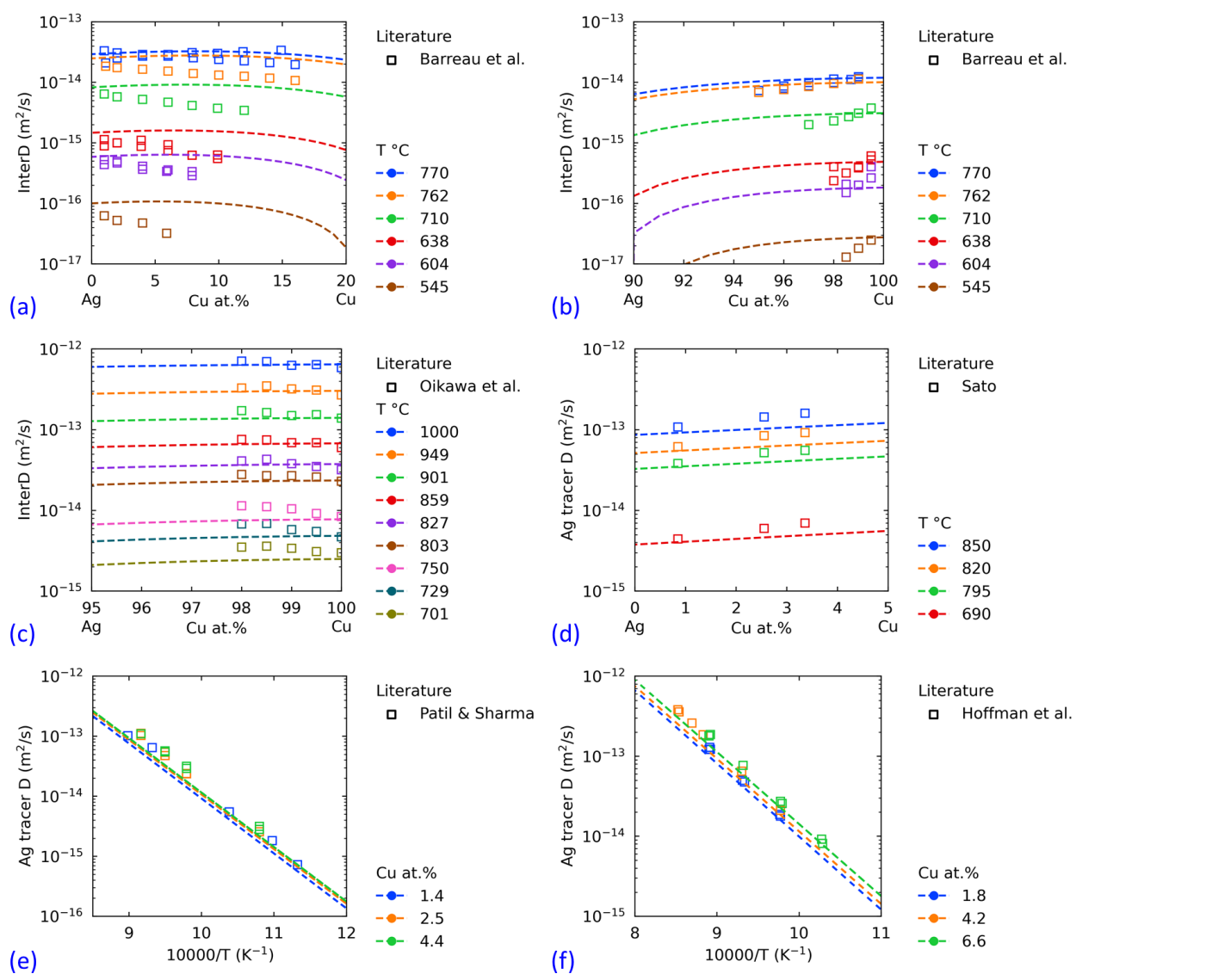

Fig. S2. *The assessment result of the fcc Ag-Cu binary system using the 1-parameter Z-Z-Z model in comparison with the experimental data: (a), (b) and (c) interdiffusion coefficients* [14,15]*; (d), (e) and (f) Ag tracer diffusion coefficients* [16–18].

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