Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2019

Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

# Supplementary Information: A new *ab initio* modeling scheme for ion self-diffusion coefficient applied to $\varepsilon$-$Cu_3Sn$ phase of Cu-Sn alloy

Tom Ichibha,[*a] Genki Prayogo,[b] Kenta Hongo,[cdef] and Ryo Maezono[af]

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

## 1 Equations for coarse-grained network

We will give equations for the vacancy formation rate $C_v$ of rep-site and the jump rates $\eta_{a,\,\tilde{c}}$ of routes $a$, $\tilde{c}$. Rep-site consists of one top site and two base sites, so the vacancy formation rate $C_v$ is given as the sum of their vacancy formation rates:

$$C_{\mathrm{v}}^{(\mathrm{rep})} = C_{\mathrm{v}}^{(\mathrm{top})} + 2C_{\mathrm{v}}^{(\mathrm{base})}. \tag{1}$$

After the vacancy jumps many times inside of a rep-site, the vacancy is found in a top or a base site with a probability

$$\gamma^{(\mathrm{top})} \equiv C_v^{(\mathrm{top})}/C_v^{(\mathrm{rep})} \text{ or } \gamma^{(\mathrm{base})} \equiv C_v^{(\mathrm{base})}/C_v^{(\mathrm{rep})}, \tag{2}$$

respectively. They influence on the tracer jump between two rep-sites, because, for example, for the tracer to jump through route 5 (base $\rightarrow$ base), the vacancy must be at the base site of the destination. Route $a$ consists only of route 5 (base $\rightarrow$ base) and route $\tilde{c}$ does of route 1 (base $\rightarrow$ top), route 1' (top $\rightarrow$ base), and 2 (base$\rightarrow$base), so the jump rate $\eta_{a,\tilde{c}}$ are given as

$$\eta_a = \gamma^{(\mathrm{base})}\eta_5, \;\; \eta_{\tilde{c}} = \gamma^{(\mathrm{top})}\eta_1 + \gamma^{(\mathrm{base})}\left(\eta_{1'} + \eta_2\right). \tag{3}$$

.

* Corresponding author. Tel: +81-8077049258; E-mail: ichibha@icloud.com
[a] *School of Information Science, JAIST, Asahidai 1-1, Nomi, Ishikawa, 923-1292, Japan.*
[b] *School of Materials Science, JAIST, Asahidai 1-1, Nomi, Ishikawa, 923-1292, Japan.*
[c] Research Center for Advanced Computing Infrastructure, JAIST, Asahidai 1-1, Nomi, Ishikawa 923-1292, Japan.
[d] Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba 305-0047, Japan.
[e] PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi-shi, Saitama 322-0012, Japan.
[f] Computational Engineering Applications Unit, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.

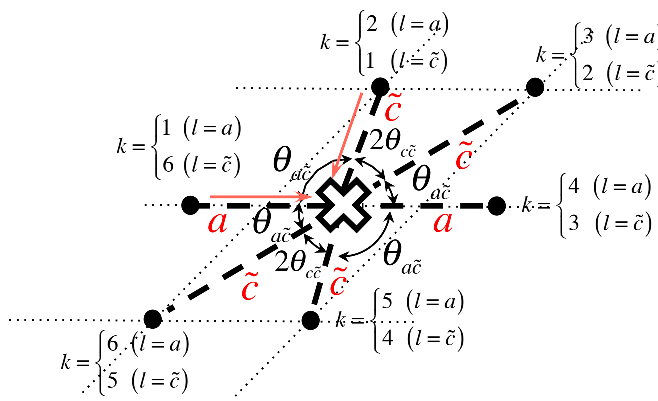


**Fig. 1** The indices of the sites $k$ surrounding the tracer. The tracer has just moved to the central site (open cross) through route $a$ or $\tilde{c}$ along with an arrow. The surrounding 6 sites are indexed with $k = 1 \sim 6$ in a clockwise order beginning from the previous tracer position.

## 2 Evaluation of Correlation Factor

We will deduce probabilities $\left\{P_k^{(l)}\right\}$, with which the tracer exchanges positions with the vacancy at site $k$ after tracer moving through route $l = a$ or $\tilde{c}$. This is necessary to obtain the average cosines $\langle\cos\theta\rangle_{l=a,\,\tilde{c}}^{(n)}$ from eq. 11 in the main paper. Yet before that, we will introduce the correspondance between the site index $k$ and the site positions: It is supposed in Fig. 1 that the tracer (open cross) has just moved through route $l = a$ or $\tilde{c}$ following the arrows towards the tracer. The six sites surrounding the tracer are indexed by $k = 1 \sim 6$ in a clockwise order beginning from the site positioned by the tracer before moving. Thus, the function $L^{(l)}(k)$ introduced in the main paper returns $L^{(a)}(k = 1,4) = a$, $L^{(a)}(k = 2,3,5,6) = \tilde{c}$, $L^{(\tilde{c})}(k = 3,6) = a$, and $L^{(a)}(k = 1,2,4,5) = \tilde{c}$.

$\left\{P_k^{(l)}\right\}$ is given as a sum of the probabilities that vacancy tracks pulling back the tracer from site $k$ realize. Here we suppose that the vacancy selects route $a$ ($\tilde{c}$) with a probability $p_a$ ($p_{\tilde{c}}$) and moves through it. The realization probability of a vacancy track is given as a product of the selection probabilities: For example, in Fig. 2, the vacancy track shown as the blue arrow (red arrows) realizes with $p_a$, ($p_{\tilde{c}}^2$). To obtain $\left\{P_k^{(l)}\right\}$, we have to take into account all of the vacancy tracks which exchange positions with the vacancy from site $k$ and sum up their realization probabilities.

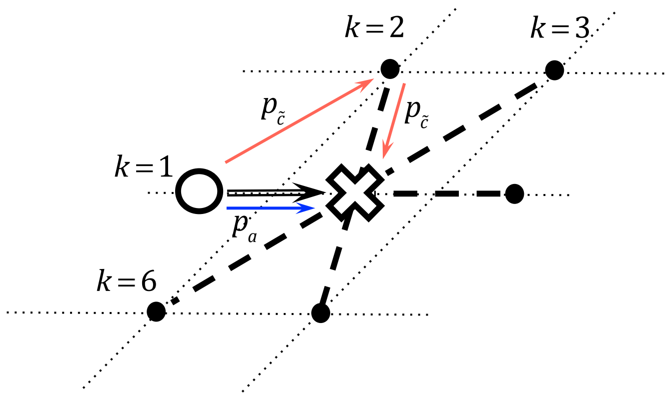


**Fig. 2** Examples of the vacancy tracks for jump $l = a$. The tracer is positioned at the central site (open cross) just after moving along with the double shafted arrow. If limiting the consideration only the vacancy tracks including just one or two routes, there are only two vacancy tracks shown by the red and blue arrows.

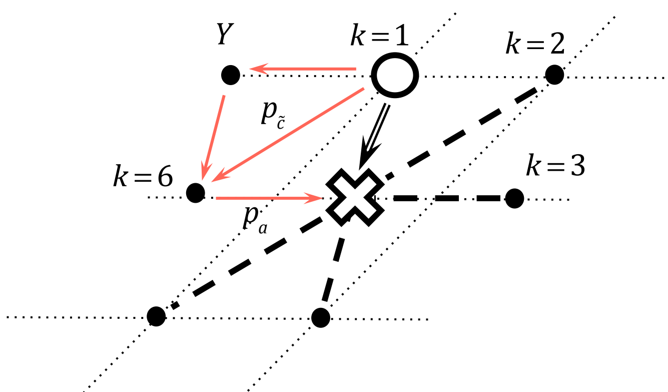


**Fig. 3** Examples of vacancy tracks for jump $l = \tilde{c}$. The tracer is positioned at the central site (open cross) just after moving along with the double shafted arrow. Two vacancy tracks are shown as examples. The site $Y$ is introduced to explain the vacancy tracks taking a path from site $Y$ to site 6.

The selection probability $p_{a,\,\tilde{c}}$ is proportional to $\eta_{a,\,\tilde{c}}(T)$ ($T$: temperature), so they are given as

$$p_{a,\,\tilde{c}}(T) = \frac{\eta_{a,\,\tilde{c}}(T)}{2\eta_a(T) + 4\eta_{\tilde{c}}(T)}. \tag{4}$$

The denominator reflects that a rep-site connects to 2 rep-sites through route $a$ and 4 rep-sites through route $\tilde{c}$. We will approximate $\left\{P_k^{(l)}\right\}$, considering just the vacancy tracks with comparatively high realization probabilities. Since the selection probabilities $p_{a,\,\tilde{c}}(T)$ change according to temperature $T$, such vacancy tracks also change. Thus, we discuss high- and low-temperature cases separately.

First, in high-temperature case, a relationship, $p_a \sim p_{\tilde{c}} \sim 1/6$ (*e.g.*, $p_a/p_{\tilde{c}} = 1.03$ at $T$=1000 K), is obtained from *ab initio* calculations. Hence, $p_l = 17\%$, $p_l^2 = 3.8\%$, and $p_l^3 = 0.46\%$. We ignored vacancy tracks including 3 moves or more. Then, the vacancy cannot pulls back the tracer from site $k = 3 \sim 5$ for a preceding ion move through route $l = a$, and hence $P_{k=3\sim5}^{(a)} = 0$. The other $P_k^{(l=a)}$ are straightforwardly given as $P_{k=1}^{(a)} = p_a$ and $P_{k=2,6}^{(a)} = p_{\tilde{c}} \cdot p_{\tilde{c}}$. Applying the same analogy to $l = \tilde{c}$, $P_{k=3\sim5}^{(\tilde{c})}$ are all zero and the others are $P_{k=1}^{(\tilde{c})} = p_{\tilde{c}}$, $P_{k=2}^{(\tilde{c})} = p_a \cdot p_{\tilde{c}}$, and $P_{k=6}^{(\tilde{c})} = p_{\tilde{c}} \cdot p_a$.

Secondly, in the low temperature case, $p_a$ is much greater than $p_{\tilde{c}}$ (*e.g.*, $p_a/p_{\tilde{c}} = 8.93$ at $T$=300K). Thus, we suppose that, while the number of vacancy moves through route $\tilde{c}$ is limited to 0 or 1, that through route $a$ is not limited. Then, we have to consider infinite patterns of vacancy tracks, which is practically impossible. We introduced three tools to count up vacancy tracks which realize with high probabilities:

- Consider the vacancy tracks as the vacancy finally positioned at the starting site after arbitrary $n$ times of vacancy moves through route $a$. The sum of these probabilities is denoted by $\pi_{\text{even}}$.
- Consider the vacancy tracks as the vacancy finally positioned at the left (right) site of the starting site after arbitrary $n$ times of vacancy moves. The sum of these probabilities is denoted by $\pi_{\text{odd}}$.
- Consider the vacancy tracks as the vacancy finally positioned at the left (right) site of the starting site after arbitrary $n$ times of vacancy moves, with imposing that the vacancy never gets into sites in the right (left) of the starting site. The sum of these probabilities is denoted as $\pi_{\text{oneside}}$.

Here, $\pi_{\text{even}}$ and $\pi_{\text{oneside}}$ must be greater than 1 because the vacancy has to be at the starting site for $n = 0$. It is explained how to deduce $\pi_{\text{even}}$, $\pi_{\text{odd}}$, and $\pi_{\text{oneside}}$ in the next section.

$P_k^{(l)}$ is evaluated for every ($k$, $l$), using the above tools: **(1)** $l = a,\ k = 1$ case; We consider the vacancy tracks that the vacancy roams in the left side from site $k = 1$ (including site $k = 1$) through route $a$ before pulling back the tracer from site $k = 1$. Their probability sum * is exactly $\pi_{\text{oneside}}$, and hence $P_{k=1}^{(a)} = \pi_{\text{oneside}} \cdot p_a$. **(2)** $l = a,\ k = 2 \sim 6$ case; At least two vacancy moves through route $\tilde{c}$ are required to pull back the tracer from these sites. Hence, $P_{k=2\sim6}^{(a)} = 0$. **(3)** $l = \tilde{c},\ k = 1$ case; We consider the vacancy tracks that the vacancy roams through route $a$ before pulling back the tracer from site $k = 1$. Their probability sum is exactly $\pi_{\text{even}}$, and hence $P_{k=1}^{(\tilde{c})} = \pi_{\text{even}} p_c$. **(4)** $l = \tilde{c},\ k = 2$ case; This case is quite similar to case (3). The difference is just that the vacancy pulls back the tracer from site $k = 2$ not $k = 1$, after roaming through route $a$. Their probability sum before pulling back the tracer is exactly $\pi_{\text{odd}}$, and hence $P_{k=2}^{(\tilde{c})} = \pi_{\text{odd}} p_c$. **(5)** $l = \tilde{c},\ k = 3$ case; We consider only vacancy tracks which includes a vacancy move from

* The sum of realization probabilities of a group of vacancy tracks.



This journal is © The Royal Society of Chemistry [year]

site $k=2$ to $k=3$. The probability sum until the vacancy positioned at site $k=3$ is given as $\pi_{\rm odd}p_c$ just like case (4), and that of vacancy tracks from site $k=3$ is given as $\pi_{\rm oneside}p_a$ just like case (1). As a result, $P_{k=2}^{(\tilde{c})}$ is given as a product of them: $P_{k=2}^{(\tilde{c})}=\pi_{\rm odd}p_c\cdot\pi_{\rm oneside}p_a$. **(6)** $l=\tilde{c},\ k=3\sim5$ case; The vacancy tracks have to include at least two moves through route $\tilde{c}$. Hence, $P_{k=3\sim5}^{(\tilde{c})}=0$. **(7)** $l=\tilde{c},\ k=6$ case; We consider two patterns of vacancy tracks before the vacancy moving to site $k=6$: The vacancy moves to $k=6$ from $k=1$ or site $Y$ (shown in Fig. 3). The probability sum before moving to site $k=6$ is given as $(\pi_{\rm even}+\pi_{\rm odd})\,p_{\tilde{c}}$, and that of the rest is equivalent to the one in case (1). As a result, $P_{k=6}^{(\tilde{c})}$ is given as their product: $P_{k=6}^{(\tilde{c})}=(\pi_{\rm even}+\pi_{\rm odd})\,p_{\tilde{c}}\cdot\pi_{\rm oneside}p_a$.

We discussed the high- and low-temperature cases separately above. The sum group of vacancy tracks considered in both cases could cover entire of the temperature range. Thus, we took them to evaluate $P_k^{(l)}$ for any temperature, and they are given as

$$P_k^{(l)}=\begin{cases}\pi_{\rm oneside}\cdot p_a & (l=a,\ k=1)\\ p_{\tilde{c}}^2 & (l=a,\ k=2,6)\\ \pi_{\rm even}\cdot p_{\tilde{c}} & (l=\tilde{c},\ k=1)\\ \pi_{\rm odd}\cdot p_{\tilde{c}} & (l=\tilde{c},\ k=2)\\ \pi_{\rm odd}\pi_{\rm oneside}\cdot p_a p_{\tilde{c}} & (l=\tilde{c},\ k=3)\\ (\pi_{\rm even}+\pi_{\rm odd})\,\pi_{\rm oneside}\cdot p_a p_{\tilde{c}} & (l=\tilde{c},\ k=6)\\ 0 & (otherwise).\end{cases} \tag{5}$$

Then, eq. 11 in the main paper becomes

$$\langle\cos\theta\rangle_a^{(n+1)}=-P_{k=1}^{(a)}\cdot\langle\cos\theta\rangle_a^{(n)}-2\cdot\frac{d_{\tilde{c}}}{d_a}\cdot P_{k=2,6}^{(a)}\cdot\cos\theta_{a\tilde{c}}\cdot\langle\cos\theta\rangle_c^{(n)}, \tag{6}$$

$$\langle\cos\theta\rangle_{\tilde{c}}^{(n+1)}=-\frac{d_a}{d_{\tilde{c}}}\cdot\left\{P_{k=3}^{(\tilde{c})}\cdot\cos(2\theta_{c\tilde{c}}+\theta_{a\tilde{c}})+P_{k=6}^{(c)}\cdot\cos\theta_{a\tilde{c}}\right\}\cdot\langle\cos\theta\rangle_a^{(n)}-\left\{P_{k=1}^{(\tilde{c})}-P_{k=2}^{(\tilde{c})}\cdot\cos 2\theta_{c\tilde{c}}\right\}\cdot\langle\cos\theta\rangle_{\tilde{c}}^{(n)}. \tag{7}$$

The $n$th-order average cosines $\langle\cos\theta\rangle_{a,\,\tilde{c}}^{(n)}$ are obtained from these equations for any order $n$ at last.

## 3 Derivation of $\pi_{\rm even}$, $\pi_{\rm odd}$, and $\pi_{\rm oneside}$

We will derive $\pi_{\rm even}$, $\pi_{\rm odd}$, and $\pi_{\rm oneside}$ here. First, $\pi_{\rm even}$ is a probability sum of the following vacancy tracks: After $2n$ ($n=0,\ 1,\ 2,\ \cdots$) moves, the vacancy is positioned at the starting site. One of the tracks realizes with a probability of $p_a^{2n}\cdot(2n)!\big/(n!)^2$ and $\pi_{\rm even}$ is given by summing up all of the patterns:

$$\pi_{\rm even}=\sum_{n=0}^{\infty}p_a^{2n}\cdot(2n)!\big/(n!)^2. \tag{8}$$

Second, $\pi_{\rm odd}$ is a probability sum of the following vacancy tracks: After $2n+1$ ($n=0,\ 1,\ 2,\ \cdots$) moves, the vacancy is positioned at just one right (left) site of the starting one. One of the tracks realizes with a probability of $p_a^{2n+1}\cdot(2n+1)!/n!\,(n+1)!$ and $\pi_{\rm odd}$ is obtained by summing up all of the patterns:

$$\pi_{\rm odd}=\sum_{n=0}^{\infty}p_a^{2n+1}\cdot(2n+1)!\big/n!\,(n+1)!. \tag{9}$$

Lastly, $\pi_{\rm oneside}$ is a probability sum of the following vacancy track: After $2n+1$ ($n=0,\ 1,\ 2,\ \cdots$) moves, the vacancy is positioned at the starting site yet under the restriction that the vacancy never goes to the right (left) side from the starting site. The number of patterns for arbitrary $n$ is known to be Catalan number:[1]

$$c_n=\frac{1}{n+1}\frac{(2n)!}{(n!)^2} \tag{10}$$

mathematically, and therefore, $\pi_{\rm oneside}$ is given as

$$\pi_{\rm oneside}=\sum_{n=0}^{\infty}c_n p_a^n. \tag{11}$$

## Notes and references


1 R. A. Monte, MIT Undergraduate Journal of Mathematics , 143 (1999).