Non-Gaussian diffusion profiles caused by mobile impurity-vacancy pairs in the five frequency model of diffusion

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Vacancy-mediated diffusion of impurities under strong impurity-vacancy (I-v) attraction has been studied in the framework of the five-frequency model (5FM) for the FCC host. The system of impurities and tightly bound I-v pairs has been treated in the framework of the rate-equations approach of Cowern et al., Phys. Rev. Lett. 65, 2434 (1990), developed for the description of the non-Gaussian diffusion profiles (NGDPs) observed in dopant diffusion in silicon. In the present study this approach has been extended to derive a three-dimensional (3D) integro-differential equation describing the pair-mediated impurity diffusion. The equation predicts the same 1D NGDPs as in Cowern et al. but can also be used for the simulation of 3D profiles of arbitrary geometry in the systems where the diffusion proceeds via a mobile state. The parameters of the theory have been calculated within the 5FM on the basis of available literature data. The database on impurities in aluminum host has been analyzed and promising impurity-host systems for the observation of NGDPs has been identified. The diffusion profiles for an impurity where NGDPs are expected to be easily detectable have been simulated. It has been argued that with the input parameters calculated on the basis of experimental diffusion constants the simulated NGDPs can be accurate enough to serve as a quantitative test of the 5FM.

I. INTRODUCTION

Miniaturization of electronic devices to nanometer sizes has necessitated investigation of peculiarities that technologically important processes may exhibit at this scale. One such process that plays a key role in the doping of semiconductor chips is the diffusion of impurities in elemental crystalline hosts. In experiments of Cowern et al. it was established that some dopants in the silicon host exhibit exponential diffusion profiles instead of the conventional Gaussian ones. This seemingly non-Fickian behavior was attributed to the diffusion mediated by a mobile intermediate state of impurities induced by interaction with point defects, such as vacancies and interstitials. A phenomenological model based on the notion of the mobile state developed by Cowern et al. satisfactorily described the experimental observations with the use of only two adjustable parameters. However, the development of the model into a quantitative theory has been hampered by insufficient understanding of the microscopic mechanisms underlying the mobile state. The main problem poses the presence in semiconductor hosts of several competing mechanisms with their relative importance being impurity-specific and not fully understood.

The analysis of defect-assisted diffusion considerably simplifies when only one mechanism dominates, as was the case in the diffusion in the Cu(001) surface layer where exponential tails in diffusion profiles were also observed. The vacancy mechanism was shown to be dominant and due to its simplicity it was possible not only to reliably fit the values of microscopic parameters to experimental data but also to confirm them in the first-principles calculations. Diffusion in two dimensions (2D), however, is qualitatively different from 3D case and so cannot serve as a model of vacancy-mediated diffusion in 3D systems.

But the vacancy mechanism is also common in 3D solids, even in semiconductors. Arguably, it has been best studied in the FCC metals in the framework of the classic five frequency model (5FM). There exists a wealth of literature on the pertinent host-impurity systems, on approximate solutions of the model, on comparison with experiment as well as large databases containing systematized data on both first-principles calculations of the model parameters and on their empirical values (see, e.g., Refs. 21–32 and references therein).

Furthermore, the mobile state of impurity in the 5FM is also known. It appears in the case of strong impurity-vacancy (I-v) attraction when the I-v pairs that form can exercise long sequences of diffusion jumps because in the bound state the diffusion-mediated vacancy is permanently available. Similarly to the 2D case discussed above, this mechanism was shown to produce non-Gaussian diffusion profiles (NGDPs) also in the FCC systems. The term NGDPs will be used throughout the paper to refer to the profiles that Cowern et al. called exponential, because unlike in the surface layer where truly exponential behavior can be observed due to the specifics of the STM experiment, below we will see that in 3D the tails of the profiles are asymptotically always Gaussian with the exponential behavior being observable only at intermediate distances.

The aim of the present paper is to develop a quantitative theory of impurity diffusion propagated by the bound I-v pairs using the framework of the 5FM for FCC hosts. The theory will be essentially based on the phenomenological approaches of Refs. 4 and 13 with the input parameters calculated within the 5FM from the data available in literature sources.

The paper is organized as follows. In the next section the 5FM is briefly introduced; in Sec. III theory of dif-
fusion of individual tightly-bound I-v pairs is presented; in Sec. IV the diffusion of the ensemble of immobile impurities and mobile pairs is treated within a phenomenological theory based on the approach of Cowern et al.; in Sec. V the integro-differential equation describing 3D diffusion of impurities mediated by the mobile state is derived and illustrated by simulation of 1D NGDPS for lanthanum impurity in aluminum host; in the concluding section VI the results obtained are briefly summarized.

II. THE 5FM

The 5FM for the FCC lattice is a representative of the class of models that describe the vacancy-mediated diffusion as a stochastic process characterized by a set of the transition rates or frequencies of the vacancy jumps between the sites of the host lattice. In Fig. 1 the meaning of the five frequencies \( w_k \), \( k = 0 \rightarrow 4 \), for the FCC host are explained. In the canonical model that will be used in the present paper the vacancy jumps are restricted to only nearest neighbor (NN) sites though generalizations on more complex models with larger sets of parameters are possible. As can be seen from the definition of 5FM in Fig. 1, in the vicinity of impurity only one vacancy is assumed to be present. This, of course, is an approximation but it will be sufficient for our purposes because the NGDPSs we are going to study are the most pronounced at low temperatures where the vacancy concentration is very small. For example, using the experimental vacancy formation enthalpy in aluminum \( E_f = 0.67 \) eV, the vacancy concentration at temperature \( 50^\circ C \) that will be used in our simulations in Sec. V can be estimated to be

\[
c_v \approx e^{-E_f/k_BT} = 3.6 \cdot 10^{-11}. \tag{1}
\]

Here we neglected the entropic contribution (in a rigorous treatment the Gibbs free energy should be used instead of the energy) because the formation entropies \( s_f \) are usually quite small \( s_f \approx 1 \) and the temperature \( 50^\circ C \) in energy units is \( \sim 0.03 \text{ eV} \) while the errors in both experimental and theoretical definitions of \( E_f \) are considerably larger being at least of order of 0.1 eV.40

The frequencies can be calculated from the values of the activation barriers \( E_k \) and the attempt frequencies \( \nu_k \) (see Table I) as

\[
w_k = \nu_k e^{-E_k/k_BT}. \tag{2}
\]

Because the stochastic dynamics in the 5FM is governed by thermal excitations, it satisfies the detailed balance condition which establishes the following relation between the frequencies and the binding energy \( E_b \) of the I-v pair

\[
\frac{w_3}{w_4} \approx \exp\left(-\frac{E_b}{k_BT}\right). \tag{3}
\]

In this definition \( E_b \) is assumed to be positive for I-v attraction. As in Eq. (1), here we also neglected the entropy contribution because of its smallness in comparison with the errors in \( E_f \).

The frequencies \( w_0 \rightarrow w_4 \) together with the vacancy concentration from Eq. (1) and the value of the lattice parameter \( a \) can be used to calculate the diffusion constant of the impurity in the 5FM as

\[
D = c_v w_2 (w_4/w_3)^2, \tag{4}
\]

where the correlation factor

\[
f = \frac{2w_1 + 7F_3(w_4/w_0)w_3}{2w_1 + 2w_2 + 7F_3(w_4/w_0)w_3}. \tag{5}
\]

Accurate expressions for \( F_3 \) were derived in Refs. 41 and 42. For our purposes will be necessary the values of \( f \) in the case of strong I-v binding (large \( E_b \)). According to Eq. (3) this corresponds to cases when \( w_4 \rightarrow 0 \) and/or \( w_4 \rightarrow \infty \). From Eq. (5) it is seen that in the first case \( (w_4 \rightarrow 0) \) the value of \( F_3 \) is irrelevant while in the second case it is known exactly

\[
F_3(w_4/w_0 \rightarrow \infty) = 2/7. \tag{6}
\]

![FIG. 1. Jump frequencies of the vacancy (gray square) in the vicinity of the impurity (black circle) as defined in the 5FM: \( w_1 \)–the jumps in the first coordination shell (CS) of the impurity; \( w_2 \)–frequency of exchange with the impurity atom; \( w_3 \)–frequency of dissociative jumps away from the impurity into higher CS; \( w_4 \)–associative jumps from higher CS into the first one. Not shown in the figure is the frequency \( w_0 \) of exchange with atoms in the host bulk.]

![TABLE I. Parameters entering Eqs. (2) and (9) corresponding to lanthanum impurity (I) in aluminum host (H) taken from the database of Ref. 31]

| \( w_0 \)(eV) | \( \nu_0 \)(THz) |
|---|---|
| 0.5814 | 4.2242 |
| 1.180 | 3.9868 |
| 0.0623 | 2.5182 |
| 0.5637 | 4.1975 |
| 0.092 | 4.0664 |
| Q(eV) | \( D_0 \)(cm²/s) |
| I | 0.7776 | 0.081112 |
| H | 1.2661 | 0.064623 |
Thus, the correlation factor in the limit of infinitely strong binding is
\[ f_\infty = \frac{w_1 + w_3}{w_1 + w_2 + w_3}. \]  
Eq. (5) also accurately reproduces the exactly known value for the case of self-diffusion when all \( w_i \) are equal:
\[ f_0 \approx 0.781. \]  
The most serious obstacle to quantitative predictions based on the 5FM is that the parameters of the model either as fitted to experimental data or as obtained in first-principles calculations may contain quite significant errors.\(^{27,30–32,43}\) The problem aggravates at lower temperatures because of the Arrhenius behavior in Eq. (2). In order to reconcile the measured and calculated values of the host (\( H \)) and the impurity (\( I \), though this subscript will be usually omitted for brevity) diffusion constants
\[ D^{H,I} = D_0^{H,I} \exp \left( -\frac{E^{H,I}}{k_BT} \right), \]  
a correction coefficient was suggested in Ref. 30
\[ C_{\text{shift}} = A_{\text{shift}} \exp \left( -\frac{E_{\text{shift}}}{k_BT} \right). \]  
In the case of aluminum \( A_{\text{shift}} = 12 \) and \( E_{\text{shift}} = 0.2 \) eV, so at 50°C the coefficient \( C_{\text{shift}} \approx 10^{-2} \) which means that the discrepancy between the theory and the experiment amounts to two orders of magnitude at this temperature. Because various quantities in the 5FM may depend on six parameters (five frequencies plus the vacancy formation energy) and their errors combine, we will try to maximally reduce their number in our calculations and whenever possible use instead experimentally measurable quantities.

III. DIFFUSION OF TIGHTLY BOUND I-V PAIRS

According to Eq. (3), strong I-v binding meaning large \( E_b \) value takes place when either \( w_3 \) is very small or \( w_4 \) is very large or both. The case of vanishing escape frequency \( w_3 \) was solved in Ref. 19 so we will consider a more general case of large \( w_4 \gg w_3 \) which comprises also the small \( w_3 \) case.

To begin with, let us find the solution in the limit of the infinitely large of \( w_4 \) and for definiteness let us restrict our consideration only to diffusion along \( Z \) direction because in cubic lattices all \( \{100\} \) directions are equivalent. Similar to Ref. 19, the problem in this case can be reduced to the solution of a set of three equations for the probabilities of three inequivalent mutual I-v orientations. They correspond to the vacancy being in one of three classes 1–3 of the sites in the first coordination sphere (CS) of the impurity (see Fig. 2); inside these classes all positions are equivalent due to our choice of the symmetry direction. In Fig. 2 all sites pertinent to the 5FM are divided into 13 equivalence classes. In the case of infinitely large \( w_4 \) the vacancy will spend all its time on the sites in classes 1–3 because of the following. Classes from 4 to 13 comprise the sites that can be reached from the first CS in one jump with the rate \( w_3 \). If the vacancy jumps at one of these sites, it will have at least one NN site in the first CS (the one it just jumped from) but in general there will be \( l \geq 1 \) such sites. At the next step the vacancy either returns back to the first CS with the rate \( lw_4 \) or diffuses further away from the impurity with the rate \( (12-l)w_0 \). The probability of jumping back to the first CS is given by the ratio\(^{44}\)
\[ p_{\text{back}} = \frac{lw_4}{lw_4 + (12-l)w_0} \]  
which tends to unity when \( w_4 \to \infty \). Moreover, because the residence time \( \Delta t \) of the vacancy at the “outer” site is inversely proportional to the total rate in the numerator of Eq. (11) \( \Delta t \propto 1/[lw_4 + (12-l)w_0] \), as \( w_4 \to \infty \) the time goes to zero. Thus, the vacancy spends all its time in the first CS of impurity with the excursions to sites in classes 4-13 serving only to jumps between classes 1-3 in the first CS.

To formalize this picture let us number the \( (001) \) planes in the direction of the diffusion by integer numbers \( m, n \) ranging from minus to plus infinity. When the impurity is positioned in plane \( n \) the sites of class 1 are in the plane \( m = n + 1 \), sites of class 2 are in the same plane \( n \) and those of class 3 in the plane \( m = n - 1 \) (see Fig. 2). The master equation describing the evolution of the I-v pair can be written with the use of the transition
where the rows and columns are numbered by the class indexes $\alpha, \alpha'$ while subscripts $m$ and $n$ denote the planes. The non-diagonal entries of the matrix correspond to transition rates between the classes. For example, $\tilde{W}_{nm}^{21}$ is the rate of the vacancy jumps from a site in class 1 to a site in class 2 as well as a possible ensuing displacement of the impurity from plane $m$ to plane $n$. The jump can proceed by several routes. The vacancy can reach class 2 directly via NN jumps. This contributes $2w_1$ to the rate because there are exactly two sites in class 2 that are NN to a site from class 1. The indirect way is to first jump out of the first CS on one of two NN sites in class 2 or on the site in class 5 (in total three possibilities). But the return jumps will end up in class 2 only in half of the cases which reduces the contribution to $3w_3/2$. The matrix element is proportional to $\delta_{nn}$ because the vacancy moves do not change the impurity position. In fact, only direct I-v exchanges lead to the impurity diffusion, so the only contributions that change the position of the impurity are those proportional to $w_2$, which is reflected in Eq. (13) (see Fig. 1).

To simplify the task of solving Eq. (12), let us restrict our attention only to macroscopic diffusion that develops at a spatial scale much larger than the lattice constant $a$. At this scale the positions of the impurity and the nearby vacancy are essentially the same so concentrations $C_n^{\alpha}$ need not be distinguished and only evolution of the total pair density

$$C_n = \sum_{\alpha=1}^{3} C_n^{\alpha}$$

(14)

will be detectable experimentally via the impurity profiles. Long diffusion distance means long duration. But solutions of stochastic evolution equations of the kind of Eq. (12) tend toward the equilibrium via exponentially attenuating modes $\propto \exp(zt)$ with all $z_i^p$ being less or equal to zero. So we will be interested only in the longest-lived modes that correspond to the smallest $z_i$.

For a translationally-invariant system with constant coefficients the standard way to find the attenuation rates is to reduce differential equation Eq. (12) to an algebraic equation with the use of integral transforms which we chose to be the Laplace transform in time variable and the Fourier transform in the spatial variables (the LF transform). The 1D Fourier transform of the transition matrix Eq. (13) is

$$\tilde{W}_K = \begin{bmatrix}
-x - y & x & y + \gamma_K \\
x & -2x & x \\
y + \gamma_K^* & x & -x - y
\end{bmatrix},$$

(15)

where

$$x = 2w_1 + \frac{3}{2}w_3$$

(16)

$$y = w_2 + \frac{1}{4}w_3$$

(17)

$$\gamma_K = w_2(e^{iaK/2} - 1)$$

(18)

and $a/2$ is the distance between successive (001) planes. Taking further the Laplace transform over $t$ with the parameter $z$ we obtain the characteristic equation

$$\det(z - \tilde{W}_K) = 0.$$  

(19)

As explained above, we do not need exact expressions for the solutions of this equation but are interested only in the smallest eigenvalue that describes the pair diffusion. At small Fourier momenta $K$ corresponding to large distances in real space the eigenvalue will tend to zero as $\sim K^2$ because the matrix in Eq. (15) is Hermitian. The smallest root (let us denote it $z_1$) can be easily found to this accuracy from Eq. (19) from the linearized equation because as $z_1 \to 0$ the higher orders in $z$ can be dropped:

$$z_1^p(K) \simeq \frac{w_2(w_1 + w_3)}{12(w_1 + w_2 + w_3)} a^2 K^2.$$ 

(20)

Here superscript $p$ reminds us that the solution describes the pair diffusion and the momentum $(0, 0, K)$ describing the diffusion along $Z$ direction is replaced by a general momentum $K = (K_X, K_Y, K_Z)$ because in cubic crystals the diffusion is isotropic to this order in $K$. The remaining two eigenvalues are finite at small $K$ and up to terms $O(K^2)$ are

$$z_2^p(K) = -3x + O(K^2) \simeq -6w_1 - 4.5w_3$$

$$z_3^p(K) = -x - 2y + O(K^2) \simeq -2(w_1 + w_2 + w_3)$$

(21)

as can be easily verified by direct substitution in Eq. (19) at $K = 0$. As is seen, the eigenvalues 2–3 remain finite as $K \to 0$. Therefore, only the term corresponding to
\[ z^p(K) = O(K^2) \] will survive at large times so the Fourier transform of the pair density Eq. (14) will behave as
\[ C_K(t)_{t \to \infty} \propto \exp \left[ -z^p(K)t \right]. \tag{22} \]
Differentiating this by \( t \) and taking the inverse Fourier transform with respect to the spatial variables bring about the conventional diffusion equation
\[ \partial C(R, t)/\partial t \approx D_m \nabla^2 C(R, t), \tag{23} \]
where \( C \) is the continuum approximation to \( C_n \) and according to Eqs. (20), (22), and (7) the diffusion constant of the I-v pairs is
\[ D_m = \frac{w_2(w_1 + w_3)a^2}{12(w_1 + w_2 + w_3)} = \frac{w_2}{12} f_\infty a^2. \tag{24} \]
For \( w_3 = 0 \) this expression coincides with the result of Ref. 19.

The most important property of \( D_m \) is that in contrast to the impurity diffusion constant Eq. (4), it is not proportional to the vacancy concentration and so can be much larger than \( D \). Assuming strong binding in which case one can use \( f_{\infty} \) as \( f \) in Eq. (4) with the use of Eqs. (24), (1), and (3) one gets
\[ \frac{D_m}{D} \approx \frac{w_3}{12c_w w_4} \approx \frac{1}{12} e^{(E_f - E_b)/k_B T}. \tag{25} \]
Simple bond-counting arguments suggest that the vacancy formation energy \( E_f \) should be larger than the binding energy \( E_b \). The latter can be found by comparing the energies of a vacancy surrounded by only host atoms and the vacancy with one neighbor replaced by the impurity which amounts to the difference between energies of a single atomic bond. Creation of a vacancy, on the other hand, costs about six atomic bonds in the FCC lattice. So as \( T \to 0 \) the ratio Eq. (25) normally can take arbitrarily large values. For example, in the case of the LaAl system that will be used in illustrative calculations below, the ratio in Eq. (25) at temperature 50°C may reach according to Eqs. (1)–(3) and Table I the value
\[ (D_m/D)_{T=50^\circ C} \approx 105. \tag{26} \]
It is the presence of two modes of impurity diffusion with very different diffusion constants that underlies the phenomenon of NGDPs.

### A. Decay rate of the I-v pair

Despite large diffusivity, the bound I-v pairs cannot diffuse too far from the place of their association because of their finite lifetime. Irrespective of how strong the I-v binding is, from Eq. (2) it is seen that at finite temperature neither \( w_3 \) can be strictly equal to zero nor \( w_4 \) can be infinitely large. Thus, if the lifetime of the pair is equal to \( \tau_{\text{decay}} \) its decay rate \( r = 1/\tau_{\text{decay}} \) and the characteristic distance \( \lambda \) of the pair diffusion before its decay is equal (up to a numerical constant) to the diffusion length of the pair during its lifetime
\[ \lambda = \sqrt{D_m \tau_{\text{decay}}} = \sqrt{D_m / r}. \tag{27} \]
In Refs. 4 and 5 this quantity is called the mean projected path length.

In the 5FM the decay rate \( r \) can be found as the rate of definite separation of the vacancy from the impurity. It is often approximated by the rate of escape from the first CS into higher coordination shells which is equal to \( 7w_3^{3,34} \) because there is seven NN sites to a site in the first CS that do not belong to the first CS, as can be seen from Figs. 1 or 2. However, as we already saw, this approximation can be completely misleading in the case of large \( w_4/w_0 \) ratio when the vacancy returns into the first CS with probability that almost equals to unity. To account for this \( r \) can be represented as a product of the “bare” escape rate \( 7w_3 \) and the renormalization factor \( p_\infty \) equal to the probability of definite I-v dissociation when the vacancy diffuses infinitely far away from the impurity
\[ r = 7w_3 p_\infty. \tag{28} \]

The problem of calculating the vacancy escape probability \( p_\infty \) is equivalent to finding the return probability into the first CS which is a standard problem of the random walk theory (see, e. g., Ref. 46 and references therein). But to avoid complicated combinatorial calculations we will assess \( p_\infty \) with the help of numerical simulations. The escape of the vacancy from the first CS into the space beyond sufficiently large radius \( R_{\text{max}} \) was simulated for several values of the ratio \( w_4/w_0 \) and for two radii \( R_{\text{max}} = 100(a/2) \) and \( 300(a/2) \) and then interpolated to \( R_{\text{max}} = \infty \). The results are presented in Fig. 3 together with the exactly known two end point values \( p_\infty(w_4/w_0 = 0) = 1 \) and \( p_\infty(w_4/w_0 = \infty) = 0 \) and with the approximating interpolating expression
\[ p_\infty \simeq (1 + bw_4/w_0)^{-1}, \tag{29} \]
where \( b \approx 1.35 \) was found from the largest simulated ratio \( w_4/w_0 = 10 \) because large \( w_4/w_0 \) values are the most interesting to our purposes. However, because of the diminishing number of the decays as \( w_4/w_0 \to \infty \), the statistics are difficult to gather when the ratio is in the range \( O(10^4 \text{--} 10^7) \) that we are interested in (see the next paragraph). It can be calculated in this case within the rigorous approach of Ref. 47, as will be shown in the subsequent publication.\(^{48}\) Therefore, in our calculations below we will use this more accurate value \( b = 1.32 \).

Now substituting Eqs. (28) and (29) into Eq. (27) we can obtain an explicit expression for the phenomenological parameter \( \lambda \) of the theory of Ref. 4 in terms of the frequencies of the 5FM. To calculate \( \lambda \) for 50 impurities listed in the database of Ref. 31 for aluminum host use
Comparing this with Eq. (4) and using Eq. (8) from Eq. (27) one arrives at the expression
\[ \lambda_{w_4 \gg w_0} = Aa \sqrt{D \over D_m}, \]  
(32)
where \[ A = \sqrt{b f_0/84} \approx 0.111 \]  
(33) is a numerical constant. Thus, the parameter \( \lambda \) of the phenomenological theory in the large-\( w_4 \) case can be calculated from only experimentally measurable quantities.

B. Diffusion profiles of unstable I-v pairs

One consequence of the pairs instability is that their diffusion cannot be described by the conventional diffusion equation Eq. (23) because the second Fick’s law expresses the conservation of the diffusing particles which is not the case with the pair diffusion. Being unstable, the I-v pairs obey instead of Eq. (23) the non-Fickian diffusion equation suggested in Ref. 13:
\[ \partial G_p(\mathbf{R}, t) / \partial t = D_m \nabla^2 G_p(\mathbf{R}, t) - r G_p(\mathbf{R}, t), \]  
(34)
where we introduced the pair Green’s function (GF) that satisfies the delta-function initial condition
\[ G_p(\mathbf{R}, t = 0) = \delta(\mathbf{R}) \]  
(35) and describes the probability to find the pair at point \( \mathbf{R} \) at time \( t \). Integrating Eq. (34) over the space variables it is seen that the probability to find the pair at time \( t \) anywhere in the system diminishes as \( e^{-rt} \), as expected. Explicit expressions for the GF of the decaying pair in the space-time variables can be written straightforwardly for any dimension \( d \)
\[ G_p(\mathbf{R}, t) = \frac{1}{(4\pi D_m t)^{d/2}} \exp \left(-{\mathbf{R}^2 \over 4 D_m t} - rt\right). \]  
(36)

Below we will also need the LF-transformed \( G_p \) that is also easily found from Eqs. (34) and (35) as
\[ G_p(\mathbf{K}, z) = \frac{1}{z + r + D_m \mathbf{K}^2}. \]  
(37)
Despite instability of the pairs, the impurity density should conserve irrespective of the diffusion mechanism. This is indeed the case if we take into account the impurities from the decayed pairs that simply immobilize (become stable) and their density grows with time as
\[ G_{sp}(\mathbf{R}, t) = r \int_0^t dt' G_p(\mathbf{R}, t'). \]  
(38)
Integrating this over the spatial variables is easy to check that the normalization of the sum
\[ G_p(\mathbf{R}, t) + G_{sp}(\mathbf{R}, t) \]  
(39)
is equal to unity at all $t$.

We note that the first term in Eq. (39) at large time goes to zero so the impurity distribution is dominated by the second term. Due to the specifics of the STM technique, only the second term was observed experimentally in Refs. 12 and 13 and only at $t = \infty$ in which case the first term vanished and the second acquired the exponential asymptotic behavior in the spatial variables\textsuperscript{12,13}

$$G_{sp}(|\mathbf{R}|, \infty) \propto \exp \left( - \frac{|\mathbf{R}|}{\lambda} \right). \quad (40)$$

It can be shown that this is a universal behavior at $t = \infty$ in all dimensions. To see this we first notice that the Laplace transform of a function at $z = 0$ is just the integral of the function over the time variable from zero to infinity. Thus, using Eqs. (37) and (38) one gets with the use of the inverse Fourier transform

$$G_{sp}(\mathbf{R}, \infty) = \frac{r}{(2\pi)^d} \int d^d \mathbf{K} \frac{e^{i \mathbf{K} \cdot \mathbf{R}}}{r + D_m \mathbf{K}^2} = \frac{1}{(2\pi)^d} \int d^d \mathbf{K} \frac{e^{i \mathbf{K} \cdot \mathbf{R}}}{1 + (\lambda \mathbf{K})^2} \equiv G^P(\mathbf{R}), \quad (41)$$

where on the second line we introduced the kernel of the screened Poisson equation\textsuperscript{49} $G^P$ which is known to have the exponential asymptotic behavior Eq. (40) in all dimensions.

In contrast to the diffusion in surface layers where it is possible to observe individual I-v pairs and ignore the rest of the impurities,\textsuperscript{12,13} in 3D diffusion all impurity atoms contribute so at $t = \infty$ the profile will span the whole crystal and will be seen as just the homogeneous equilibrium distribution. Therefore, NGDPs can be observed only at finite $t < \infty$ in which case their asymptotic will be Gaussian as can be easily illustrated in 1D geometry. Setting in Eqs. (36) and (38) $d = 1$ and $\mathbf{R} = X$ and taking the integral over $t$ one gets

$$G_{sp}(X, t) = r \int_0^t G_p(X, t') dt' = -\frac{1}{4\lambda} \sum_{s=\pm1} s e^{s |X| / \lambda} \text{erfc} \left( \frac{|X|}{2\sqrt{D_m t}} + s \sqrt{rt} \right). \quad (42)$$

Because at $x = -\infty \text{erfc}(x) = 2$, the behavior of this expression at $t = \infty$ is exponential in $|X|$, as expected. At finite $t$, however, the behavior is Gaussian, as can be seen from the behavior of the the $\text{erfc}$ function at large values of its argument\textsuperscript{50}

$$\text{erfc}(x)|_{x \to \infty} \sim e^{-x^2}/(\sqrt{\pi}x).$$

Thus, strictly speaking the exponential tails can never be observed in 3D concentration profiles, only some exponentially-looking transient features, as will be shown in more general case of multiple-encounter diffusion in Sec. V. Still, the profile can be very close to the exponential shape at low temperature and a sufficiently large density of the associated pairs in the initial state. In this case the existing pairs start to diffuse immediately while the immobile impurities need first to enter into association with vacancies. At low temperature the waiting time may be quite long because of the small vacancy concentration so the impurity distribution due to the pair diffusion may advance to the stage where it will only slightly differ from the infinite-time exponential profile.

**IV. IMPURITY DIFFUSION VIA MULTIPLE I-V ENCOUNTERS**

In the previous section we discussed diffusion of individual I-v pairs. In particular, it was noted that Eqs. (38) and (42) that describe the impurity distributions due to the decayed pairs can be studied experimentally in the surface layers by means of the STM microscopy which makes possible investigation of each I-v encounter individually disregarding the diffusion of other impurities.\textsuperscript{12,13} In conventional experiments on diffusion in 3D bulk, however, such separation is not possible. The impurities in the profile are indistinguishable and there is no way to differentiate them according to their evolution history. Therefore, theoretical description should take into account all possible impurities: those belonging to the initial profile, associated impurities in the mobile state, or the impurities that have already undergone one or more I-v encounters. All these contributions should be accounted for in a single diffusion profile with appropriate weights. In Ref. 4 this problem was solved by first finding the solution for zero and one encounter and then iterating the distribution obtained as many times as necessary to describe the profile at a desired stage of the evolution. In the present paper we will essentially follow this route but making it more formally refined.

Namely, we are going to use a technique of the many-body theory usually referred to as the Dyson equation (see, e.g., Ref. 51). In this approach the problem of repeated interactions of a particle is separated into an irreducible and a reducible parts and the repeated iterations of the irreducible part are simply summed up as a geometric series as

$$G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \cdots = \frac{1}{G_0 \Sigma - \Sigma}. \quad (43)$$

Here the products are either convolutions in the space-time variables or the usual algebraic products of the LF-transformed quantities; $G_0$ is the GF of a free particle and $\Sigma$ is the irreducible interaction part that cannot be represented as two interactions separated by the free propagation, as, e.g., in the third term on the left hand side (l.h.s.). The practical observation that makes this approach useful is that the combinatorial problem of finding the sum of all contributions that include the free propagation and a single or multiple I-v encounters as represented in compact form on the r.h.s. of Eq. (43) can be fully recovered from only the first two terms on the l.h.s. with the first term being known exactly. This observation was successfully applied to the problem of...
vacancy-mediated diffusion in Refs. 52 and 53. The authors effectively derived expressions for \( \Sigma \) in Eq. (43) for the cases of the self-diffusion and in a two-frequency model and we are going to apply this approach to the 5FM. We will call the irreducible part \( \Sigma \) the diffusion kernel and express it through another quantity \( D \) that will be called the diffusivity as follows

\[
\Sigma(K, z) = -D(K, z)K^2. \tag{44}
\]

The free GF \( G_0 \) is easily found from the observation that without interaction with the vacancies the impurity is immobile and remains in its initial position: \( G_0(R, t) = G_0(R, t = 0) = \delta(R) \). With the use of the LF transform one easily finds

\[
G_0(z) = \int_0^\infty dt e^{-zt} \int d^dR e^{-iKR} \delta(R) = \frac{1}{z}. \tag{45}
\]

The impurity GF with all I-v encounters being taken into account is obtained by substituting the last two equations Eqs. (44) and (45) into Eq. (43):

\[
G(K, z) = \frac{1}{z + D(K, z)K^2} \approx \frac{1}{z} - \frac{1}{z^2} D(K, z)K^2. \tag{46}
\]

The diffusion constant is found from the diffusivity as

\[
D = D(K = 0, z = 0). \tag{47}
\]

But our main interest is in a nontrivial dependence of \( D \) on its arguments \( K \) and \( z \) because if the diffusivity were independent of \( K \) and \( z \) the GF in Eq. (46) was transformed to the time and space variables would be strictly Gaussian without any traces of the NGDPs we are interested in.

Thus, our goal is to find explicitly the last term in Eq. (46) and with its use to recover the complete impurity GF. To to fulfill this goal we will use Eqs. (3) and (4) from Ref. 4 that in the GF notation read

\[
\begin{align*}
\partial G_m/\partial t &= D_m\nabla^2 G_m - rG_m + gG_s \\
\partial (G_s + G_m)/\partial t &= \partial G/\partial t = D_m\nabla^2 G_m,
\end{align*} \tag{48}
\]

where the total impurity GF \( G = G_m + G_s \) is separated into the mobile \( (G_m) \) and immobile \( (G_s) \) parts with the subscript “s” standing for “static” because in contrast to Refs. 4 and 5 in the 5FM the impurity is always in the substitutional position. Parameter \( g \) in Eq. (48) is the rate of transition of the impurity from the static to the mobile state which in the 5FM is the rate of I-v association. Because in the association participates a vacancy, the rate \( g \) should be proportional to the vacancy concentration and thus is of order \( O(c_v) \). Its calculation will be discussed below.

The LF-transformed set of Eqs. (48) is

\[
\begin{align*}
(z + r + D_mK^2)G_m(K, z, t) - gG_s(K, z) &= 12c_{NN} \\
(z + D_mK^2)G_s(K, z, t) + zG_s(K, z, t) &= 1, \tag{49}
\end{align*}
\]

where we assumed the initial conditions

\[
\begin{align*}
G_m(R, t = 0) &= 12c_{NN}\delta(R) \\
G_s(R, t = 0) &= (1 - 12c_{NN})\delta(R) \\
G(R, t = 0) &= \delta(R). \tag{50}
\end{align*}
\]

Here \( c_{NN} \) is the vacancy concentration at the NN sites of the impurity which can be different from \( c_v \) due to the I-v interaction or because of the way the initial state was prepared, though we will assume that it is of the same order of magnitude as \( c_v \). \( 12c_{NN} \) in Eqs. (50) is the density of associated I-v pairs in the initial state in the FCC lattice which coordination number is 12 which implicitly assumes that all sites around the vacancy are assumed to be equivalent.

It is important to note that in applying the Fourier transform we assume that the crystal is translationally invariant which in particular means that the rate of association \( g \) is a position-independent constant. But because \( g \) depends on the vacancy concentration, this may not be the case in experiments where non-equilibrium vacancy concentration may acquire inhomogeneity because of their influx from the surface or deposited layers.\(^{10,54}\) Such cases cannot be treated by Eqs. (49). It is to be understood that we are considering the dilute systems and \( c_v \) should be constant far from the impurities in the host bulk. In the vicinity of impurity it can be different from its bulk value due to the I-v interaction both at and out of thermal equilibrium. In the latter case in the Smoluchowski picture of the vacancy capture on the impurity NN sites a non-constant vacancy diffusion profile forms near the impurity because the NN sites serve as the sinks.\(^{46}\)

Because, as we pointed out in Sec. II, the 5FM adequately describes the I-v interaction only to first order in the vacancy concentration, we will solve the system Eqs. (49) only to this order by first finding the mobile GF

\[
G_m = \frac{12c_{NN}z + g}{z(z + r + D_mK^2)}. \tag{51}
\]

With known \( G_m \) the total GF \( G = G_s + G_m \) can be found directly from the second of Eqs. (49) as

\[
G = \frac{1}{z} - \frac{1}{z^2} \frac{12c_{NN}z + g}{z + r + D_mK^2}. \tag{52}
\]

As is seen, the approach Ref. 4 turned out to be similar to that of Refs. 52 and 53 by giving only the zeroth and the first order terms of the expansion in Eq. (43) so to obtain the full impurity GF the Dyson equation will have to be used. Comparing Eq. (52) with Eq. (46) we arrive at the expression for the \( K \) and \( z \)-dependent diffusivity

\[
D(K, z) = \frac{12c_{NN}z + g}{z + r + D_mK^2}D_m. \tag{53}
\]

The two contribution to the second term in Eq. (52) describe somewhat different diffusion scenarios so let us discuss them separately. The term proportional to \( c_{NN} \) describes the associated I-v pairs that are present in the
initial profile. Their density $12c_{NN}$ can be arbitrary depending on the way the profile was prepared. From Eqs. (53) and (47) one can see that this term does not contribute to the diffusion constant which is natural because an arbitrary initial condition cannot influence the quantity corresponding to thermal equilibrium. The physical meaning of this term becomes transparent after its rearrangement into three contributions

$$G|_{c_{NN}} = \frac{12c_{NN}D_{m}K^2}{z(z + r + D_{m}K^2)} - \frac{12c_{NN}}{z} + \frac{12c_{NN}}{z + r + D_{m}K^2} + \frac{12c_{NN}r}{z(z + r + D_{m}K^2)}. \quad (54)$$

From Eq. (37) it can be seen that apart from the factor $12c_{NN}$, the first term on the second line in Eq. (54) is the LF transformed $G_p$ Eq. (37) while the second term is Eq. (37) multiplied by $r/z$. But multiplication by $1/z$ of the Laplace transform of a function corresponds to the Laplace transform of the integral of this function over $r$. Thus, the second term on the second line of Eq. (54) corresponds to LF-transformed $G_{sp}$ from Eq. (38), so the sum of the two terms is Eq. (39) multiplied by $12c_{NN}$. Thus, these terms describe the diffusion profile of the pairs of density $12c_{NN}$ that were present in the initial state. The negative term on the first line in Eq. (54) simply accounts for the fact that the associated impurities were taken from the initial delta-function profile (see Eqs. (50) and (45)).

In contrast to the term that describes diffusion of the I-v pairs which already exist in the initial state, the term proportional to $g$ in Eq. (52) describes the diffusion of initially immobile impurities. To enter into the mobile state the impurities need first to be associated with a vacancy. This process is limited by the low vacancy concentration and so the ensuing diffusion is much slower than the pair diffusion. The time scales of the two diffusion modes are defined by the lifetime of the pairs $\tau_{\text{decay}} = 1/r$ and by the characteristic time of the I-v association $\tau_{\text{assn.}} = 1/g$. To compare their relative values we first note that substitution of diffusivity Eq. (53) into Eq. (47) gives

$$D = \frac{g}{r}D_{m} \quad (55)$$

which leads to the relation

$$\frac{\tau_{\text{assn.}}}{\tau_{\text{decay}}} = \frac{D_{m}}{D} \gg 1, \quad (56)$$

where the last inequality follows from Eq. (25) and the discussion that follows it. At low temperatures this ratio can be large. In the LaAl system at 50°C we estimated it in Eq. (26) as amounting to two orders of magnitude. The main reason for this is that while the decay rate $r$ is of zeroth order in the vacancy concentration ($O(c_{v}) = O(1)$), the association rate $g$ is of $O(c_{v})$, as can be seen from the equation

$$g = rD/D_{m} = 84c_{v}w_{4}p_{\infty} \quad (57)$$

obtained from Eqs. (55), (25), and (28).

The expression for the rate of I-v association Eq. (57) was obtained in the framework of the 5FM while in Ref. 4 a Smoluchowski-type formula was used (see their Eq. (12)). To compare the two approaches let us first consider Eq. (57) in the case $w_{4} = w_{0}$ because the Smoluchowski formula describes the flux of vacancies of density $\rho_{0}$ that are being caught by the sphere of radius $R_{c}$ and depends on the vacancy diffusion constant $D_{v}$. The latter is defined in a continuous homogeneous medium where all diffusion steps are equivalent which in the lattice case means that $w_{4}$ cannot be different from $w_{0}$. Thus, substituting $p_{\infty}(w_{4} = w_{0}) = 1/(1 + b)$ from Eq. (29) in Eq. (57) we get

$$g_{5FM}(w_{4} = w_{0}) \approx 35.7c_{v}w_{0}. \quad (59)$$

To find the value from the Smoluchowski formula we note that the per volume vacancy density is $\rho_{0} = 4c_{v}/a^{3}$ because there is four sites in the cubic cell in the FCC lattice, the first CS radius $R_{c} = a/\sqrt{2}$, and $D_{v} = w_{0}a^{2}$. Substituted into Eq. (58) this gives

$$g_{S} \approx 35.5c_{v}w_{0} \quad (60)$$

in excellent agreement with the 5FM value Eq. (59).

As our analysis of the database for aluminum host has revealed, the case of large $w_{4}$, is particularly interesting for experimental purposes. To apply the Smoluchowski equation to this case we remind that as $w_{4} \to \infty$ all vacancies that arrive at the sites belonging to classes 4–13 in Fig. 2 immediately form bound I-v pair (see Sec. III). This means that the capture radius $R_{c}$ is effectively shifted toward a larger value that can be assessed by averaging the distances from the impurity to all sites in these classes. Elementary calculation gives $R_{c} \approx 1.25a$ and from Eq. (58)

$$g_{S}(w_{4} \gg w_{0}) \approx 63c_{v}w_{0}. \quad (61)$$

which is also very close to the 5FM value $\sim 64c_{v}w_{0}$ that can be obtained from Eq. (57) with the use of Eq. (30).

Thus, our Eq. (57) agrees with the formula suggested in Ref. 4 in two cases where the Smoluchowski formula is applicable but in addition covers the cases of arbitrary values of $w_{4}$. But more important to us is that Eq. (57) for large $w_{4}$ can be cast in the form

$$g_{5FM}(w_{4} \gg w_{0}) = \frac{84}{b}f_{0}c_{v}w_{0}f_{0} = D^{ff}/(4\pi a)^{2}, \quad (62)$$

where $A$ is given by Eq. (33). Thus, Eqs. (32) and (62) allow us to express two parameters of the phenomenological theory only in terms of experimentally measurable quantities.
V. DIFFUSION PROFILES

In the GF approach the diffusion profiles are obtained by convolution of the initial profile with the impurity GF. The latter is obtained in our approach by first substituting the diffusivity from Eq. (53) into Eq. (46) and then taking the inverse LF transform to find the GF in the space and time variables. Before proceeding with concrete implementation of this procedure we have to agree on the value of the density of the I-v pairs in the initial profile that was estimated to be equal to \(12c_{NN}\). This estimate presumes that the vacancy can be found at different NN sites of the impurity with equal probability. That may not be the case if the vacancies are introduced in the initial profile by means of a non-equilibrium technique that causes non-isotropic distribution of the vacancies on the NN positions of the impurities.\(^{10,54}\) Such cases are beyond the scope of our approach which is restricted, as we pointed out in Sec. IV, to stationary and homogeneous distributions of I-v pairs, though not necessarily corresponding to thermal equilibrium. The latter, however, is a natural choice, so all estimates will be done for this case. In particular, the equilibrium density of the I-v pairs can be found from the expression

\[
12c_{NN}^{eq} \simeq 12c_v e^{E_b/k_B T}. \tag{63}
\]

With \(E_b \approx 0.47\) (see Table I) the associated impurities will constitute at 50°C about 1% of their total number which is a small but detectable quantity. However, to observe the NGDP behavior which takes place at short distances one needs to keep initial profiles maximally sharp.\(^4,5\) But for establishment of the equilibrium many association-dissociation events must occur accompanied by impurity diffusion with ensuing profile smearing. Therefore, we will assume that the initial distribution was prepared at a temperature so low that corresponding \(c_{NN}^{eq}\) is negligible and that the preparation technique does not introduce excess vacancies. So in our calculations below we for simplicity will neglect the terms proportional to \(c_{NN}^{eq}\) in Eq. (52). In case of necessity they can be taken into account along the lines of derivation presented below. Another reason for omission of these terms is that this reduces the problem to the case studied in Ref. 4, thus facilitating comparison between the two approaches.

Under approximation \(c_{NN} \simeq 0\) the impurity GF is

\[
G(K, z) = \left( z + \frac{gD_m K^2}{z + r + D_m K^2} \right)^{-1}. \tag{64}
\]

This expression can be cast into the form convenient for the inverse Laplace transform and for assessment of the relative magnitude of different contributions:

\[
G(K, z) = \frac{1}{z - z_1} + \frac{z_1 z_2}{z_1 - z_2} \left( \frac{1}{z - z_2} - \frac{1}{z - z_1} \right) \tag{65}
\]

where

\[
z_{1,2} = -\frac{r + D_m K^2}{2} \pm \sqrt{\frac{(r + D_m K^2)^2}{4} - g D_m K^2} \tag{66}
\]

or to the leading order in \(g = O(c_v)\)

\[
z_1 \simeq -\frac{g D_m K^2}{r + D_m K^2} = \Sigma(K, 0) \tag{67}
\]

\[
z_2 \simeq -(r + D_m K^2). \tag{68}
\]

where the diffusion kernel is

\[
\Sigma(K, 0) = -\frac{g D_m K^2}{r + D_m K^2} = g \left( 1 + \frac{1}{1 + (\lambda K)^2} - 1 \right). \tag{69}
\]

Neither the kernel nor the diffusivity now do not depend on \(z\) and in equations below this argument will be dropped.

The Laplace transform in Eq. (65) reduces to the calculation of pole residues:

\[
G(K, t) = e^{t z_1} + \frac{z_1 z_2}{z_1 - z_2} \left( e^{t z_2} - e^{t z_1} \right) \neq e^{t \Sigma(K)} + D(K) K^2 \left( e^{t z_2} - e^{t \Sigma(K)} \right). \tag{70}
\]

As can be seen, in real space the second term on the second line would integrate to zero while the first one to unity because the spacial integration corresponds to the Fourier component \(v\).

\[
e^{-rt} \ll 1 \tag{71}
\]

because \(r = O(1)\) while \(t = O(c_v^{-1})\). Thus, the second term in Eq. (70) is much smaller than the first term and can be neglected if we agree to neglect \(O(c_v)\) contributions.

Thus, the leading \(O(1)\) terms in Eq. (70) can be reduced to the following Fourier-transformed diffusion equation

\[
\frac{\partial C(K, t)}{\partial t} = \Sigma(K) C(K, t), \tag{72}
\]

where \(C\) is the Fourier transform of impurity concentration. In real space the diffusion equation Eq. (72)
turns out to be not a differential equation but an integro-differential one
\[
\frac{\partial C(R, t)}{\partial t} = \int \Sigma(R - R_0)C(R_0, t)dR_0
\] (73)
with the diffusion kernel
\[
\Sigma(R - R_0) = gG^P(R - R_0) - g\delta(R - R_0).
\] (74)
Here \(G^P\) is the GF of the screened Poisson’s equation from Eq. (41) and thus describes the limiting \((t \to \infty)\) profile of the pair diffusion. This makes transparent the physical meaning of Eq. (73). The impurity at point \(R_0\) is picked up by a vacancy with the rate \(g\) (the second term on the r.h.s.) and via the pair diffusion is redistributed with the probability density \(G^P\) (the first term on the r.h.s.). The time dependence of this process is ignored because Eq. (73) describes diffusion on the time scale \(O(c_s^{-1})\) which is much larger than the \(O(r^{-1}) = O(1)\) scale of the pair diffusion. This is exactly the physics studied in Refs. 4 and 5. From Eq. (73) is easy to understand the non-Fickian character of the pair-mediated diffusion discussed in Refs. 4 and 11. Imagine a host with inhomogeneous distribution of impurities in it and a bounded region within that is completely devoid of them. Despite this, the rate of growth of the impurity concentration inside the region will be everywhere positive according to Eq. (73) because of the spatially extended diffusion kernel Eq. (74) that is able to displace impurities at finite distances. This starkly contrasts with the local current picture underlying the Fickian diffusion.

3D diffusion equation Eq. (73) makes possible numerical simulation of the diffusion profiles in any geometry. In large systems the solution should presumably be sought via its direct numerical integration. In 3D the Poisson kernel is singular (it coincides with the screened Coulomb or the Yukawa potential) but efficient techniques of dealing with it were proposed in Ref. 49. In systems of moderate sizes a convenient method provides the Fourier transform. In 1D case the solution reads
\[
C(X, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\Sigma(K)}C_0(K)dK,
\] (75)
where \(C_0\) is the Fourier transform of the initial profile. In this way were calculated NGDPs presented in Fig. 4 where \(C_0\) where chosen to be Gaussian to easier visualize the NGDPs caused by the pair-mediated diffusion (in conventional diffusion an initially Gaussian-shaped profile remain Gaussian at all times). As shown in Appendix A, the 1D profiles calculated within our approach coincide with those of Refs. 4 and 5 so in Fig. 4 one can see the exponential tails in the diffusion profiles similar to those found by Cowern et al. The tails, however, cannot extend on arbitrarily long distances because the diffusion kernel in Eq. (69) at small Fourier momenta behaves as \(\sim K^2\) so from the inverse Fourier transform of the kind of Eq. (75) but for arbitrary dimension it is easy to see that at finite times the large-\(|R|\) asymptotic will be Gaussian, similar to the case of diffusion of individual pair discussed in Sec. III B.

![FIG. 4. 1D profiles for the diffusion of lanthanum impurity in aluminum at temperature 50°C starting from the initial Gaussian distribution of with 0.5 \(\mu m\) (dashed line). Thick solid line: the profile calculated according to Eq. (75) for \(t = 5\) hours; thin solid line: \(t = 50\) hours; dashed-dotted lines: the profiles at 5 and 50 hours as predicted by the conventional diffusion equation; the time intervals were chosen to correspond to \(gt \simeq 1\) and \(\simeq 10\), respectively.](image)

VI. CONCLUSION

In the present paper a theory of the vacancy-mediated diffusion in the case of strong I-v binding has been developed. It has been shown that tightly bound I-v pairs provide the mobile state of impurities that underly the NGDPs similar to those observed in dopant diffusion in semiconductors and in the copper surface layers. By unifying the phenomenological theory of Cowern et al. with the 5FM of the vacancy-mediated diffusion in FCC hosts it has been possible to calculate numerical values of the parameters of the phenomenological theory on the basis of the available data on the parameters of the 5FM. This has made possible identification of the impurity-host systems suitable for the observation of the NGDPs as well as their explicit simulation in LaAl system where the phenomenon is expected to be the most pronounced among the solutes in aluminum host. Because the NGDPs are universal, all impurities listed in Table II should exhibit the same profiles as shown in Fig. 4 but at shorter length scales. The latter can be enlarged by lowering the temperature but the time of the observation will have to be extended correspondingly.

Apart from the calculation of the parameters of the phenomenological model in the framework of the 5FM, the approach of Cowern et al. has been extended in two respects. First, it has been shown that the diffusion
mode studied in Refs. 12 and 13 in 2D can contribute to 3D NGDPs in cases when the initial state already contains associated I-v pairs. Because their diffusion starts immediately, they introduce impurity diffusion on much shorter time scale than that of Ref. 4. For example, in LaAl system at room temperature (20° C) the parameter $\lambda \simeq 2 \mu m$. The conventional diffusion will cover this distance in over a month while the pair diffusion in about three hours. Accounting for this mode of diffusion may be of practical importance in assessment of the longevity of microelectronic devices. Though the concentration of preexisting pairs is usually expected to be small, in some of the projected devices the functional elements will consist of only one atom so the estimates of the longevity that neglect the fast diffusion of the small number of contaminating atoms that are associated with the vacancies introduced during the deposition process may lead to serious errors.

The second extension of the theory of Ref. 4 has been achieved through its blending with the Dyson equation. This resulted in a non-Fickian integro-differential diffusion equation describing the pair-propagated impurity diffusion in arbitrary geometry that can be used in simulations of NGDPs in any elemental hosts.

Special attention in the paper has been devoted to the systems with large $w_4/w_0$ ratio for two reasons. First, the ratio turned out to be large for all impurities in aluminum host with the largest values of $\lambda$, i. e., in the systems that should be the most appropriate for experimental study of NGDPs. Second, and more importantly, this case makes possible accurate quantitative predictions about the phenomenon. A serious problem of the microscopic diffusion theory is that both experimental definitions and first-principle calculations of various activation energies contain errors of order $O(0.1$ eV) in the best case.$^{27,30,31}$ The jump frequencies and diffusion constants depend on the energies via the Arrhenius law and at temperatures in a few hundred Kelvins may be orders of magnitude off from their true values. But it has been shown in the present paper that when $w_4/w_0$ is large the phenomenological parameters $g$ and $\lambda$ can be calculated from only two quantities: the impurity diffusion constant and that of the host self-diffusion. Both can be measured at the experimental temperature independently and the two parameters calculated on their basis can subsequently be used in the profile simulations. The simulated NGDPs should agree with experimental ones quantitatively, provided the 5FM is an adequate model for the system under study. Significant discrepancies will mean that the canonical 5FM is too simplistic for the case under consideration and needs to be improved along the lines suggested by first-principles calculations and physical considerations.$^{20,30,38}$ This conclusion relies on the assumption that the errors in the frequencies $w_4$ and $w_0$ are not too large to reduce our estimates of $w_4/w_0$ ratios for the systems listed in Table I more than 4–6 orders of magnitude. Unfortunately, at present this possibility cannot be completely excluded.

The important question that has not be adequately addressed in the present paper concerns the reliability and the accuracy of the developed theory which has been substantiated mainly by qualitative arguments and phenomenological approaches. This difficult question will be addressed in a separate paper where a rigorous treatment of the 5FM in the general case of the I-v interaction of arbitrary strength will be presented. It will be shown that in the limit of strong I-v attraction the results of the present paper are in excellent agreement with the rigorous solution.$^{47}$

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Appendix A: Comparison with NGDP of Ref. 4

In slightly modified notation, the 1D diffusion profile with initial delta-function distribution was shown to be described by the series given by Eqs. (5)-(10) of Ref. 4 as

$$C(\xi, \theta) = \lambda^{-1} \sum_{n=0}^{\infty} P_n(\theta) \phi_n(\xi, 1),$$

(A1)

where

$$\theta = t, \quad \xi = X/\lambda,$$

(A2)

$$P_n(\theta) = (\theta^n/n!) e^{-\theta},$$

(A3)

$$\phi_n=0(\xi, 1) = \delta(\xi),$$

(A4)

and

$$\phi_{n>0}(\xi, \mu) = \frac{e^{-\sqrt{\mu}|\xi|}}{(2\sqrt{\mu})^{2n-1}} \sum_{k=0}^{n-1} \frac{2^k}{k!} \frac{(2n-2-k)!}{n-1} \left(|\xi|\sqrt{\mu}\right)^k.$$

(A5)

Here we introduced the parameter $\mu$ to facilitate the proof that the profile Eq. (A1) from Ref. 4 coincides with the 1D profile from Eq. (75) with $C_0(K) = 1$ for the delta-function initial profile:

$$C(X, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dK e^{i\lambda K} e^{-\theta t} \exp \left( \frac{gt}{1 + (\lambda K)^2} \right)$$

$$= \frac{1}{\lambda} \sum_{n=0}^{\infty} P_n(\theta) \frac{1}{2^n} \int_{-\infty}^{\infty} \frac{e^{i\mu u} du}{(1 + u^2)^n}.$$  

(A6)

Here the last exponential on the first line has been expanded in the Tailor series so by comparison with Eq. (A1) we conclude that the inverse Fourier transforms on the second line should be equal to $\phi_{n>0}(\xi, 1)$. To show this we first introduce the integrals

$$\phi_n(\xi, \mu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{i\mu u} du}{(\mu + u^2)^n}.$$  

(A7)
and note that if $\phi_{n+1}(\xi, \mu)$ is known, other integrals can be computed recursively as

$$\phi_{n+1}(\xi, \mu) = -\frac{1}{n} \frac{d}{d\mu} \phi_n(\xi, \mu). \quad (A8)$$

Thus, we only need to show that $\phi_{n}(\xi, \mu)$ in Eq. (A5) satisfy the recursion. To this end we first note that with the exponential factor being common to all terms in all functions, the equality in Eq. (A8) will hold if it will be valid for every power of $|\xi|^k$ under the summation sign.

Let us consider one such term in Eq. (A5)

$$\phi_n^{(k)} = \frac{e^{-\sqrt{\mu}|\xi|}}{2^{2n-1}(n-1)!} \frac{(2n-2-k)!}{k!} |\xi|^k \mu^{(k+1)/2-n}. \quad (A9)$$

When substituted in Eq. (A8) it will contribute to $|\xi|^k$ term in $\phi_{n+1}$ through the derivative of its last factor with respect to $\mu$. The only other contribution from $\phi_n$ contributing into $|\xi|^k$ term in $\phi_{n+1}$ is $\phi_n^{(k-1)}$ differentiated with respect to $\mu$ in the exponential function. It is straightforward to check that these two contributions lead to the term $\phi_{n+1}$ as in Eq. (A9) only with $n + 1$ instead of $n$, as required.

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